Experimental study of strongly correlated fermion systems under extreme conditions; heavy fermion YbRh$_2$Si$_2$ and $^3$He impurities in a two dimensional $^4$He film

Jan Knapp
A thesis submitted to the degree of
Doctor of Philosophy

Royal Holloway
University of London

March 2022
Declaration of Authorship

I, Jan Knapp, hereby declare that this thesis and the work presented in it is entirely my own. Where I have consulted the work of others, this is always clearly stated.

Sign: ............................................

Date: ............................................
Abstract

This work presents results of two independent experiments performed on a nuclear demagnetisation cryostat in the temperature range from 200 µK to hundreds of mK.

The first experiment is low-frequency NMR measurement on He films, adsorbed on graphite. The graphite substrate was pre-plated with a single pure $^4$He layer, then a second layer was gradually built. The second layer was doped with a small amount of $^3$He, an NMR active isotope. This effectively two-dimensional system has been studied both theoretically and experimentally for some time now. Around coverages where torsion oscillator measurements discovered new phase with coexistence of superfluidity and density wave order, namely a supersolid, and where heat capacity measurements show solidification peaks, some numerical quantum Monte Carlo simulations were suggesting plain superfluid behaviour. The susceptibility of this system, as measured by NMR, supports the formation of solid in the vicinity of the commensurate phases 4/7 and 7/12. This is evident from a power law temperature dependence of the measured susceptibility. Moreover, a sudden increase of the $T_1$ relaxation time at exactly the 7/12 phase was observed. Analyses of the spin–lattice relaxation suggests a distribution of relaxation rates within the sample.

The second experiment is a measurement of the heat capacity of the so-called canonical heavy fermion metal YbRh$_2$Si$_2$. A novel, minimalistic design of experimental cell was developed for this measurement, which allows one to measure very small samples with negligible addendum heat capacity. The cell uses tiny pieces of wire as a noise thermometer, heater and heat switch. The measurements extended to extremely low temperatures to examine the interplay of Yb nuclei with the electronic structure of the strongly correlated metal via the strong hyperfine interaction in this material. A sharp transition was discovered around 1.5 mK, which moves to lower temperatures and broadens when field along the ab-plane of this tetragonal crystal is applied. Measurements at higher magnetic field can be understood within a single ion model with hyperfine interaction between the nuclei and 4f moments and are in agreement with previous measurements of susceptibility. At low fields, below the nuclear transition, a new state with peculiar temperature dependence of the heat capacity is found. The nuclear transition peak is also located very close to the temperature where, according to transport measurements, there is a transition between different superconducting transport regimes.
Acknowledgements

Obtaining experimental results such as those presented in this work is not possible without a group of hard-working people as nature does not give up its secrets easily. I have been so fortunate to be accepted to such group four years ago. Since then I have been able to gain knowledge and live experiences from these people and I was trying my best to reach up to the group’s standards. I would like to take this opportunity to thank these people.

First and foremost I saw in my supervisor Prof. John Saunders fierce passion for physics as craft and an amazing intuition in managing complex scientific experiments. I would like to thank him for the overall supervision of my Ph.D. studies, but also, and above other things for our spontaneous meetings and discussions of physics.

I would then like to thank Dr. Ján Nyéki with whom I have spent countless hours working on the cryostat and measuring and analysing the data. Ján was always willing to go out of his way when splitting the lab duties to make sure I have a valuable free time, or a good night sleep. I always felt I could ask him for help or advice when needing it. His understanding of the technical aspects of the experiment were invaluable.

Among other I personally cherished our discussion with Prof. Brian Cowan. His outstanding pieces of physical theory, he creates specifically to explain our experimental results, always impressed me deeply. His mathematical thinking and insight have always been so well complementary to the sort of technical base of your group.

I would then like to thank Dr. Lev Levitin for great discussions and excellent suggestions. It is only fair to state that without Lev’s vast general knowledge and valuable experience, gained in his career, the measurements of heat capacity could never be performed so well in such extreme conditions. I am also grateful for his friendship and humour.

I would also like to thank Dr. Andrew Casey for his help he provided anytime I asked for it, Dr. Petri Heikkinen for being indulgent when I borrowed tools from ND2 and idled when returning them and lastly Nathan Eng for being an amazing friend and moral support.

I would also like to thank Paul Bamford, Richard Elsom, Ian Higgs and Tom Crane for the everyday reminder of the importance of manual mastery when it comes to building things. The perfection of their products always amazed me, even more so when coming from men of such humble character. Additionally
I would like to thank the remaining technical and administrative staff of the physics department at Royal Holloway.

Last but not least I would like to thank my parents and my grandparents for always supporting me in the pursue of knowledge and finally my amazing wife Petra for being the source of love and support but also my closest science buddy.
Contents

1 Introduction 1

2 Experimental techniques 3
  2.1 Cooling techniques on the nuclear demagnetisation cryostat . . . 3
    2.1.1 Dilution refrigerator ........................................ 4
    2.1.2 Adiabatic demagnetisation technique ......................... 8
  2.2 Low temperature thermometry ................................. 14
    2.2.1 Resistance thermometry .................................... 14
    2.2.2 $^3$He melting curve thermometry ............................ 16
    2.2.3 Carbon and platinum NMR thermometry ...................... 18
    2.2.4 Current sensing noise thermometry .......................... 21
  2.3 Experimental cells ............................................. 29
    2.3.1 Broadband SQUID NMR cell for measuring He films ........ 29
    2.3.2 A new generation heat capacity cell for measuring YbRh$_2$Si$_2$ 38
    2.3.3 A new design of a torsion oscillator cell containing graphene substrate ..................................... 43

3 Helium in two dimensions - Theory and experiments 61
  3.1 Physical adsorption ............................................ 61
    3.1.1 Available Grafoil substrates ................................ 64
    3.1.2 Graphene as the possible adsorption substrate of the future 65
  3.2 Phase transitions in two dimensions .......................... 67
  3.3 Fermi liquid in two dimensions ................................ 68
    3.3.1 Non-interacting fermi gas .................................. 68
    3.3.2 Landau–Fermi liquid ......................................... 70
    3.3.3 Dyugaev Fermi fluid model .................................. 71
  3.4 Phase diagram of second layer of $^4$He on graphite ........... 73
  3.5 Solid helium mixtures in two and three dimensions ............. 78
    3.5.1 Diffusion of defects in quantum crystals .................... 79
    3.5.2 Tunnelling in two dimensions ................................ 80
    3.5.3 Delocalised $^3$He tunneling excitations model ............ 81
3.6 Origin of the spin–lattice and spin–spin relaxation times . . . . . . 85
3.7 Methods of measurement . . . . . . . . . . . . . . . . . . . . . 87
  3.7.1 Data collection and analyses . . . . . . . . . . . . . . . . 87
  3.7.2 Susceptibility normalisation . . . . . . . . . . . . . . . . 88
  3.7.3 Standard methods of $T_1$ measurement . . . . . . . . . . . 90
  3.7.4 Progressive saturation method of $T_1$ measurement . . . . . 91
3.8 Structure of the second layer of $^4$He on graphite . . . . . . . . 99
  3.8.1 Heat capacity, torsional oscillator and susceptibility isotherms 99
  3.8.2 Torsional oscillator measurements . . . . . . . . . . . . . 101
  3.8.3 Heat capacity measurements . . . . . . . . . . . . . . . . 103
  3.8.4 Use of $^3$He diluted in the $^4$He matrix for sensitivity en-
    hancement (NMR and heat capacity) . . . . . . . . . . . . . 107
  3.8.5 Susceptibility results overview . . . . . . . . . . . . . . . 108
  3.8.6 Susceptibility vs. temperature dependence in coverage
    range: 16.5–17.5 nm$^{-2}$ . . . . . . . . . . . . . . . . 109
  3.8.7 Susceptibility vs. temperature dependence in coverage
    range: 18.0–18.5 nm$^{-2}$ . . . . . . . . . . . . . . . . 110
  3.8.8 Power law fitting in the vicinity of the commensurate cov-
    erages . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 111
  3.8.9 Power law fitting at fixed $^3$He coverage . . . . . . . . . 113
  3.8.10 Susceptibility vs. temperature dependence in coverage
    range: 19.0 – 20.0 nm$^{-2}$ . . . . . . . . . . . . . . . . 115
  3.8.11 Promotion to the third layer (sample 20.01 + 0.74 nm$^{-2}$) . 116
  3.8.12 Susceptibility in the high temperature limit . . . . . . . . 118
  3.8.13 Susceptibility in the low temperature limit . . . . . . . . 120
  3.8.14 Susceptibility measurements summary and discussion . . 123
3.9 Spin–lattice and spin–spin relaxation times in the second layer
  of $^4$He on graphite . . . . . . . . . . . . . . . . . . . . . . . . 125
  3.9.1 Measurement of $T_2$ . . . . . . . . . . . . . . . . . . . . 125
  3.9.2 Measurement of $T_1$ . . . . . . . . . . . . . . . . . . . . 126
  3.9.3 Spin–lattice and spin–spin relaxation time isotherms . . . 126
  3.9.4 The spin–lattice relaxation time in the vicinity of the 7/12
    commensurate coverage . . . . . . . . . . . . . . . . . . . 129
  3.9.5 Origins of the anomalous relaxation of $^3$He spins . . . . 132
  3.9.6 Temperature dependence of the relaxation times . . . . . . 143
  3.9.7 Frequency dependence of the relaxation times . . . . . . . 145
  3.9.8 Relaxation times summary and discussions . . . . . . . . . 148
  3.9.9 Further comments and implications of the anomalous $^3$He
    thermalisation; manifestation of many body localisation? 150
3.10 Possibly related system: metal–insulator transition in phosphorus
doped silicon . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 156
4 Low temperature heat capacity of canonical heavy fermion compound YbRh$_2$Si$_2$

4.1 Heavy fermion materials ........................................ 158
  4.1.1 Quantum critical point .................................... 159
  4.1.2 Kondo effect and RKKY interaction as competing effects 160
  4.1.3 Kadowaki–Woods ratio ................................. 162
4.2 YbRh$_2$Si$_2$ compound and results of various measurements on it . 164
  4.2.1 Magnetic properties ..................................... 166
  4.2.2 Resistivity ............................................. 167
  4.2.3 Specific heat ........................................... 169
4.3 Electron-nucleus hyper-fine interaction .......................... 173
4.4 Single ion spin Hamiltonian .................................... 175
4.5 Critical phenomena ........................................... 178
4.6 Heat capacity of YbRh$_2$Si$_2$ as a function of temperature and magnetic field (methods) ........................................ 181
  4.6.1 Adiabatic pulse method of heat capacity measurement 181
  4.6.2 Adiabatic continuous warm-up method of heat capacity measurement ........................................ 183
  4.6.3 Relaxation method of heat capacity measurement ...... 185
  4.6.4 Pseudo adiabatic pulse method of heat capacity measurement ........................................ 187
4.7 Heat capacity of YbRh$_2$Si$_2$ as a function of temperature and magnetic field (Results and analyses) ............................... 189
  4.7.1 Overview of the data .................................... 189
  4.7.2 Discussion of errors of the measured heat capacity points 191
  4.7.3 Evaluation of entropy .................................. 193
4.8 Analyses and interpretation .................................... 196
  4.8.1 Single ion model - Low magnetic field measurements . 196
  4.8.2 Single ion model - High magnetic field measurements . 200
  4.8.3 Dependence of 4f local moment on applied field ...... 204
  4.8.4 Heat capacity below the anomaly: evidence for SDW order 205
  4.8.5 Single ion model fitting summary ........................ 210
  4.8.6 Heat capacity anomaly .................................. 211
  4.8.7 Comparison of the heat capacity data to data from other techniques ........................................ 218
  4.8.8 Final technical remarks on the heat capacity measurements 220
4.9 Interplay of magnetism and superconductivity in YbRh$_2$Si$_2$ .... 224

5 Conclusions ....................................................... 226
Chapter 1

Introduction

This work contains two independent experimental results performed at ultra low temperatures. They are presented in two respective chapters. The first one is the measurement of nuclear magnetic resonance (NMR) on 2D He films adsorbed on graphite. The physical phenomena of adsorption allows helium atoms to become localised in the normal to the surface direction at sufficiently low temperatures. They are however still free to move in the remaining two dimensions. Such adsorbed films are ideal systems to study two dimensional physics. Adsorption of He on the atomically flat surface of graphite takes place through the growth of distinguishable layers. In this work a small amount of the magnetically active isotope of $^3$He was diluted into a second layer of $^4$He. A complete pure solid layer of $^4$He pre-plates the graphite beneath the second layer. These results follow a long-lasting theoretical and experimental endeavour to understand the structure of the second layer of $^4$He on graphite, especially around specific coverages where the amount of He in the first and second layer are commensurate and given by ratios 4/7 and 7/12. The theory and results of this experiment are given in Chapter 3.

The second experimental result is a measurement of heat capacity of the canonical heavy fermion compound YbRh$_2$Si$_2$ (YRS) at previously unachieved temperatures. A completely new experimental cell had to be developed in order to perform this measurement. The design concept of the experimental cell is given in Chapter 2 which also explains other technical aspects of experimental work at ultra low temperatures. Results of the YRS heat capacity are given in Chapter 4. Both experiments were done on the same nuclear–demagnetisation cryostat called ND1, situated at Royal Holloway.

This work also discusses the use of graphene as a possible adsorption substrate of the future in section 3.1. Graphene possesses many advantages to grafoil, but also some disadvantages, including significantly lower specific surface area. The high quality surface is offset to a degree by the presence of the
additional supporting substrate. It was hypothesised that the most straightforward experimental cell to accommodate graphene would be a torsional oscillator cell. While trying to mitigate the problems associated with graphene, and favour its benefits, I have come up with a minimalistic design of such cell, which is presented in section 2.3.3.
Experimental techniques

This chapter describes the experimental equipment used to perform the two main experiments. The ND1 cryostat consists of a commercial dilution unit built by Oxford Instruments [1] in the late 1970s, and upgraded with silver heat exchangers in the early 80s. The next cooling step to ultra-low temperatures is done by a home made copper nuclear demagnetisation stage. Cooling techniques and their realisation on ND1 are described in the first section of this chapter. It is followed by the description of thermometry employed in this work. Lastly the design of the experimental cells is given.

2.1 Cooling techniques on the nuclear demagnetisation cryostat

An ultra-low temperature cryostat lowers the temperature in multiple steps; each using a different cooling method. From the outside the cryostat looks like a big metal cylinder about 2 m high and 1 m in diameter. It is usually suspended from the top where all the structural and maintenance facilities enter and it is hanging in free space. The outer cylinder is a large dewar, filled with liquid $^4$He at a temperature of 4.2 K, isolated from the room temperature by an outer vacuum shield. An inner vacuum can (IVC) is immersed in the liquid $^4$He bath. Natural boil off from the bath is around 1L per hour and the bath needs to be topped up every three days. All parts of the cryostat at colder temperatures than 4.2 K are inside the IVC which isolates them from the warmer bath. The only parasitic heat leak into the colder parts is via conduction through structural parts of the cryostat and via thermal radiation emitted from warmer surfaces. The cryostat is therefore generally built to be low conductive from top to bottom.

Liquid $^4$He from the bath is sucked through a mechanical impedance into a small enclosed volume inside the IVC called the 1 K pot. The 1 K pot is pumped by a rotary pump which creates a large cooling effect. The impedance allows for continuous operation of the pot. $^4$He inside the 1 K pot is superfluid, because
the pumping lowers the temperature below the superfluid transition (λ-point).
The 1 K pot on ND1 cryostat typically operates at 1.8 K (measured by a RuO$_2$
thermometer) which corresponds to about 17 mbar vapour pressure in the pot.
Pressure at the input of the rotary pump is however about 10 mbar. This pres-
sure drop is due to the length and limitations of the pumping line. Figure 2.1
shows the vapour pressure to temperature correspondence for $^4$He and $^3$He.

![Equilibrium vapour pressure of $^4$He and $^3$He above liquid vs. tem-
perature.](image)

Figure 2.1: Equilibrium vapour pressure of $^4$He and $^3$He above liquid vs. tem-
perature.

The 1 K pot cools all structural and maintenance parts of the cryostat which
pass through it to colder stages. It also liquefies incoming $^3$He for the dilution
refrigerator.

### 2.1.1 Dilution refrigerator

Dilution refrigeration is the only continuously working cooling technique that
can reach temperatures below 300 mK and it is therefore currently used almost
exclusively for this purpose instead of single-shot techniques like Pomeranchuk
cooling or demagnetisation of paramagnetic salts [2]. The ND1 dilution unit
(DU) provides stable cooling power in the temperature range from 5 mK to 600
mK. Together with a well tuned PID controller these temperatures can be sta-
bilised to better than 0.1%. The DU requires a mixture of $^3$He and $^4$He isotopes
and a powerful pumping system. The body of the unit consists of three main
parts: still, mixing chamber and heat exchanger. A schematic of the body is
shown in Figure 2.3.

The working principle is the following. The concentrated $^3$He phase is cir-
culated in and out of the refrigerator. Upon returning it is liquefied using the 1 K pot cooling power. When the 1 K pot is present in the refrigerator, the condensing pressure is always less than atmospheric. This is different with dry refrigerators which do not have a 1 K pot, and liquefy the He by passing it through a Joule–Thomson valve.

There are two impedances present on the return line of a DU. The mechanical impedance is an element in a fluid circuit which creates a pressure difference to the mass flow. The role of impedances is therefore to ensure that pressure of returning $^3$He exceeds saturated vapour pressure at temperature of 1 K pot, so that it condenses there. Further pre-cooling of the returning phase is achieved in heat exchangers, where the concentrated phase is cooled by a diluted phase. The two phases exchange heat in two types of heat exchangers. The continuous heat exchanger, consisting essentially of concentric tubes, is effective at high temperatures but the common area becomes too small at lower temperatures for effective heat exchange. At lower temperatures a series of step heat exchangers is used. A step heat exchanger contains blocks of silver sinter of high surface area, which exchange heat with both phases, to reduce the thermal boundary resistance.

The pre-cooled returning $^3$He finally enters the mixing chamber, where cooling takes place. To illustrate the processes in the mixing chamber, the phase diagram of the mixture of the two isotopes is shown in Figure 2.2. The following features of the phase diagram are of extreme importance. First of all, in the vicinity of $T = 0$ there is a broad range of concentrations which is forbidden. This leads to phase separation. While $^3$He remains pure as $T \to 0$; $^4$He allows a maximum concentration of 6.4% of $^3$He to be dissolved in it. The concentrated phase floats on top of the diluted phase in the mixing chamber due to their different densities.

The other side of the DU is filled with the diluted phase from the mixing chamber up to the still. The still on ND1 is usually operated at 610 mK (according to a RuO$_2$ thermometer). It is pumped by either a turbo pump backed by a powerful rotary pump in the case of newer refrigerators or, as in the case of ND1, by an oil diffusion booster pump backed by a sealed rotary pump. $^3$He atoms are preferentially evaporated from the still, compared to their $^4$He counterparts, due to the very large difference in the saturated vapour pressures of the two isotopes shown in Figure 2.1. The diluted phase thus becomes poor in $^3$He. This deficit is felt in the mixing chamber as well. The osmotic pressure gradient drives the $^3$He flow from mixing chamber to still, and hence the flow of $^3$He across phase boundary in mixing chamber.
Figure 2.2: The phase diagram of the mixture of the two He isotopes featuring: The forbidden region, where phase separation occurs. The $\lambda$-transition from normal to superfluid state, which is 2.17 K for pure $^4$He, shifting to lower temperatures with increasing $^3$He concentration. The region below the $\lambda$-point where $^3$He atoms are diluted in a superfluid $^4$He matrix. The $^3$He atoms do not participate in the superfluidity. Picture from [2].

The circulation of the $^3$He is explained, but to explain why the dilution causes cooling requires understanding of the quantum nature of the $^3$He liquid. $^3$He is a fermion and $^3$He liquid behaves approximately as a weakly-interacting Fermi gas regardless whether pure or diluted in superfluid $^4$He. The Fermi temperatures of the two phases are experimentally known [3]. The molar entropy of the Fermi gas is:

$$S = \frac{\pi^2}{2} R \frac{T}{T_F}, \quad (2.1)$$

with Fermi temperature:

$$T_F = 55.2 \frac{m_3}{m^*} \left( \frac{x}{V_m} \right)^{2/3}, \quad (2.2)$$

where $V_m$ is the molar volume and $m^*/m_3$ the enhancement of $^3$He mass. As $T_F$ is smaller for the diluted phase, the entropy is larger and the effect of dilution causes cooling. The cooling power of the dilution process is proportional to the difference of enthalpies of the two phases and the rate of the dilution:

$$\dot{Q} = \dot{n}(H_d - H_c). \quad (2.3)$$
The enthalpy of the diluted phase is larger than enthalpy of the concentrated phase, and this difference scales as [2]:

\[ \Delta H = H_{3,d} - H_{3,c} \approx 95T^2. \]  \hspace{1cm} (2.4)

The constant 95 has units: [J mol\(^{-1}\)K\(^{-2}\)]. Multiplying \(\Delta H\) by the flow rate of \(^3\)He, \(\dot{n}_3\), we get the cooling power at a given temperature. The typical flow rate of \(^3\)He on ND1 is around 100 \(\mu\)mols\(^{-1}\) and the cooling power has indeed been measured to obey the quadratic dependence on temperature.

Figure 2.3: Sketch of a demagnetisation cryostat. Dilution unit using a 1 K pot for condensing the concentrated phase is shown with its pumping system. The nuclear stage can be isolated from the mixing chamber by the heat switch. The demagnetisation magnet is part of the IVC body.

The circulated helium returns into the cryostat via both liquid nitrogen and liquid He cold traps to freeze out any potential contamination either from a leak.
of air into the gas handling system or from an internal sources of contamination like oil reservoirs in the pumps. ND1 however still has a source of contamination which is not caught by the traps in the normal operation of the cryostat. This causes the return line to get blocked somewhere on the way from the room temperature into the IVC. A 30 Ω constantan wire heater was therefore wound around the return line. When the return line becomes blocked too much, as is apparent from the combination of the condensing pressure and the circulation, the heater is switched on and at the same time the return line is pumped by the DU pumps. This cleaning procedure successfully prolongs the experimental time and averts premature warmup.

2.1.2 Adiabatic demagnetisation technique

For cooling various experiments well below 1 mK nuclear adiabatic demagnetisation of copper is the most commonly used technique. The nuclei of copper work as a system of magnetic moments behaving paramagnetically all the way to the lowest temperatures achieved on electronic systems (units of µK). The anti-ferromagnetic nuclear ordering temperature of copper is around 60 nK [4]. Adiabatic nuclear demagnetisation is a single shot cooling technique and its principle of operation is the following. The copper is magnetised by a magnetic field of several T. This is done with a large superconducting magnet located in the main $^4$He bath and surrounds the copper stage. The spin polarisation of the refrigerant (copper) is accompanied by magneto-caloric heat production. The heat is absorbed by the mixing chamber of the dilution refrigerator (DU) and the stage is pre-cooled to the lowest temperature achievable in a reasonable amount of time. The magnetised stage has a heat capacity scaling as $(B/T)^2$, while the cooling power of the DU decreases as $T^2$, which slows down the pre-cool. When the stage is pre-cooled enough, it is isolated from the dilution refrigerator by a superconducting heat switch and the cooling process can begin.

The entropy of a paramagnetic system is a derivative of its partition function $Z$:

$$S = k_B \frac{\partial (T \ln(Z))}{\partial T}. \quad (2.5)$$

The partial function is determined by the Zeeman levels of the nuclei. The splitting of Zeeman levels is given by:

$$\epsilon_m = -m\mu_N g_N B, \quad (2.6)$$

where $\mu_N$ is the nuclear magneton, $g_N$ is the nuclear g-factor and $m$ runs from $-I$ to $I$. The two stable isotopes of copper are: $^{63}$Cu and $^{65}$Cu, both have
nuclear spin \( I = 3/2 \). The partition function for a general spin \( I \) is:

\[
Z = \left( \sum_{m=-I}^{I} e^{\frac{m\mu_{N}g_{N}B}{k_{B}T}} \right)^{N} \equiv \left( \frac{\sinh \left( \frac{(I + \frac{1}{2}) \mu_{N}g_{N}B}{k_{B}T} \right)}{\sinh \left( \frac{\mu_{N}g_{N}B}{2k_{B}T} \right)} \right)^{N}, \tag{2.7}
\]

and the derived entropy is:

\[
\frac{S}{Nk_{B}} = \ln(2I + 1) - \frac{\lambda B^{2}}{2\mu_{0}T^{2}}, \tag{2.8}
\]

where \( \lambda = N_{0}I(I+1)\mu_{0}\mu_{N}^{2}g_{N}^{2}B/3k_{B} \) is the nuclear Curie constant. Formula 2.8 is only valid at small \( B/T \). We can see the entropy depends on the factor \( (B/T)^{2} \).

If the magnetic field is lowered under adiabatic and reversible conditions, the process is isentropic and the final temperature achievable is:

\[
T_{f} = B_{f} \frac{T_{i}}{B_{i}}. \tag{2.9}
\]

The heat capacity of the demagnetisation stage is:

\[
C = \frac{\lambda B^{2}}{\mu_{0}T^{2}}, \tag{2.10}
\]

also depending on \( (B/T)^{2} \). In principle, the process of the stage’s magnetisation could be done isothermally, leading to the lowering of the nuclear entropy. The rate is however limited by the cooling power of the DU at the given temperature. The heat produced in the isothermal process is:

\[
Q_{\text{isot}}(T) = nT[S(0, T) - S(B, T)], \tag{2.11}
\]

where \( n \) is the number of moles of active nuclei. The other option is to magnetise the stage relatively quickly; the limit of this approach would be an adiabatic process in which the entropy does not change. This process warms up the refrigerant to effectively infinite temperature. The heat of the magnetisation is in this case given by the integration of the Schottky law for the heat capacity (equation 2.10) and is:

\[
Q_{\text{adiab}} = 2Q_{\text{isot}}. \tag{2.12}
\]

It may seem like the isothermal magnetisation is the better approach however it is usually not. First of all the heat (even though larger) in the adiabatic approach is removed by the DU at higher temperatures, where it has larger cooling power (equation 2.4). The second reason is technical. When the demagnetisation magnet is powered from the room temperature by a current source, Joule heating is produced in the He bath in the current leads of the magnet. It is therefore desirable to keep the time when current flows between the room temperature and the He bath to a minimum. This favours fast magnetisation.
Demagnetisation magnets are always equipped by a device called the persistent switch. The persistent switch is a link of superconducting wire connected in parallel with the magnet in the He bath. The wire is wrapped around a small heater inside a thermally isolating casing. The heater can drive the wire to its normal state even though it is still immersed in the liquid He. Being made out of 100 µm NbTi alloy, the normal resistance of tens of cm of the wire is hundreds of Ω. When the current in the magnet is to be ramped up the persistence switch is driven normal by the heater. At full field the heater is turned off and the current in the leads can be ramped down.

The magnetisation and pre-cooling can take from 6 hours up to a week on ND1 depending on the target minimum temperature and hold time. Typical starting temperatures for the demagnetisation processes in this work were 12–20 mK. The entropy reductions achieved at these temperatures are however relatively small: 96.7% and 98.8% respectively. It is difficult to find a nuclear Curie paramagnetic system which would allow for larger entropy reduction at temperatures where the DU still performs well. Adiabatic nuclear refrigeration of nuclear Curie paramagnets is therefore often called “brute force” nuclear cooling. Another type of nuclear demagnetisation refrigeration which allows for better time efficiency but has other limitations is the hyperfine enhanced nuclear cooling. The material used almost exclusively is PrNi$_5$. The larger polarisation of the nuclei at the same fields and temperature compared to copper is facilitated by the hyperfine interaction between the nuclei and electronic magnetic moments. An excellent summary of the demagnetisation cooling methods and comparison between the “brute force” and hyperfine enhanced cooling can be found in [5].

The heat switch separating the demagnetisation stage from the DU is another essential component. Superconductors are known to have very small thermal conductivity well below their $T_c$, comparable to insulators, since quasiparticle excitations are gapped out exponentially, leaving only phononic conductivity. The heat switch on ND1 is made out of very pure aluminium which is a type I superconductor with $T_c = 1.18$ K and critical field $B_c = 10.5$ mT.

The switching ratio of a well made heat switch can be of the order of $10^6$ and increases with decreasing temperature as the phononic conductivity follows a $T^3$ law while the electronic conductivity in normal metal is linear. The heat switch is operated by a small magnet surrounding it inside the IVC. An aluminium heat switch of much smaller design and different geometry is also used in the heat capacity cell discussed in section 2.3.2.

Adiabatic demagnetisation follows the thermal separation of the stage and
The principle is shown schematically in Figure 2.4. Being adiabatically isolated, the refrigerant must keep the entropy value achieved by the pre-cool. When the magnetic field is lowered we move from one entropy curve to another at the corresponding magnetic field. The relationship between final field and temperature is given by the formula 2.9

\[ T \text{ [mK]} = \frac{10^{-3}}{10^{-1}} \times S \text{ [J/(mol K)]} \]

Figure 2.4: Entropy and heat capacity curves for the natural Cu in various magnetic fields.

The parasitic heat leak into the stage is always present due to conductance of structural parts, radiation, eddy currents heating due to vibrations, etc. It slowly warms up the stage from any achieved temperature with rate inversely proportional to its heat capacity – specific for the temperature and field. The temperature of the stage eventually exceeds the temperature of the mixing chamber. This is when, generally, the heat switch is closed and the process can be repeated.

The coupling of the copper nuclear spins to the conduction electrons is characterised by the spin–lattice relaxation time, which obeys Körringa law:

\[ T_1 = \frac{\kappa}{T_e}, \]  

(2.13)

where \( T_e \) is the electron temperature and \( \kappa \) is the Körringa constant. The Körringa constant of copper is about 1.2 K·s. \( T_1 \) is the characteristic time for the nuclei to relax to the temperature of electrons held at constant temperature by an outside thermal bath. However, in the present case the nuclear spins dominate the heat capacity and constitute the thermal bath. The electrons thermalise to the nuclear temperature with a modified time constant [2]:

\[ \tau_1' = \frac{T_1 C_e}{C_n + C_e}, \]

(2.14)
which is much shorter at low temperatures. This is why demagnetisation steps can be seen very quickly when using a fast and responsive thermometer.

Typical operation of our ND1 demagnetisation cryostat is the following. The stage is magnetised up to 6 T by a magnet with a field-to-current ratio: 108.4 mT/A. The current step is constant: 15 mA, with usual speed: 1.5 s/step. The magnetisation step generally warms the stage up to approximately 70 mK, if the heat switch is closed. From there it cools down to 15 mK in 2 days. After isolating the stage by the heat switch, the field is lowered with the 15 mA step with a typical speed: 7.51 s/step, later increased to 20.51 s/step at lower temperatures to reduce the heating by eddy currents (proportional to $(\partial B/\partial t)^2$). The cryostat generally achieves temperature around 200 μK on the warmest experimental plate, but parts closest to the nuclear stage get even colder. The stage warms-up to 1 mK in a couple of days.

Photographs of the ND1 nuclear stage and its experimental space are shown in Figure 2.5. The two main experimental plates are shown. The photo from the bottom shows well the colder experimental space, just above the nuclear stage. The He adsorption NMR cell is installed on this plate, together with melting-curve thermometer and Pt NMR thermometer. The higher experimental space is larger, but reaches slightly higher base temperature. It is well seen from the top view. There is the YbRh$_2$Si$_2$ heat capacity cell installed together with a noise thermometer on this upper plate.
Figure 2.5: Photographs of the ND1 cryostat’s ultra low temperature part from top and bottom. The main parts highlighted.
2.2 Low temperature thermometry

Both experiments presented in this work show behaviour of measured quantities as a function of temperature. Accurately knowing the temperature of the studied sample is therefore of the same importance as the accuracy of the measured quantity itself. In both experiments we were able to rely (at least in a limited temperature range) on a thermometer which was directly present inside the experimental cell. This is a great advantage. In many low temperature experiments thermometers outside of the experimental space mounted on experimental plates are used and it is assumed that all links are very well conducting and the experiment and the thermometer are therefore at the same temperature. Figure 2.6 shows what thermometers are available on ND1 and what temperature range they can measure.

![Thermometry options on ND1](image)

Figure 2.6: Thermometry options on ND1. Resistive thermometers are commonly grey, NMR thermometers red and melting-curve and noise thermometers are denoted with their own colour.

In thermometry we distinguish between primary and secondary thermometers. Primary thermometers behave according to a physical law which depends on the thermodynamic temperature in a simple way. Then the measurement of the particular quantity enables extraction of the temperature while all other parameters must be known. Secondary thermometers on the other hand do not depend on the thermodynamic temperature according to a known fundamental law. They have to be calibrated against primary thermometers, or fixed temperature points. On the other hand, secondary thermometers often exceed their primary counterparts in sensitivity, speed or convenience.

2.2.1 Resistance thermometry

Resistance thermometers are a typical example of secondary thermometers as the fundamental formula for the electrical resistivity of a metal or a semiconductor...
is not known. The only primary thermometry based on resistance measurement exploit superconducting fixed points where the resistance suddenly drops to zero at the superconducting transition. Other resistive thermometers typically have their resistance measured by a resistance bridge and their resistance is expected to have a strong temperature dependence. For metal thermometers like Pt100 and RhFe the resistance drops as a function of temperature in almost linear fashion until it experiences a flattening at low temperatures and the thermometers lose sensitivity. Semiconductor thermometers have on the other hand resistivity increasing with decreasing temperature, as the number of carriers decrease according to the thermal activation formula, leading to:

\[ R(T) = \alpha \exp \left( \frac{\Delta E}{2k_B T} \right), \quad (2.15) \]

where \( \Delta E \) is the energy gap and the constant \( \alpha \) is still weakly temperature dependent and includes the temperature dependence of the carrier mobility. The increasing resistivity of the semiconductors at the low temperature increases the precision of the measurement, but can also become too high to make the measurement impossible. Resistance thermometers however remain the most commonly used thermometers in the temperature range from tens of mK to 10 K.

On ND1 the resistance thermometers are used for both rough monitoring of the dilution unit (DU) performance and as a serious temperature standard to assign temperature to measurements. A series of RuO\(_2\) resistors, with 2.4 k\(\Omega\) room temperature resistance, is distributed on all important places of the DU to monitor their temperature. They are only measured in 2-wire configuration as the lead resistance is relatively small. RuO\(_2\) resistors have been calibrated against other thermometers and are found to obey the following formula:

\[ \ln R = \sum_{n=0}^{2} A_n (\ln T)^n, \quad (2.16) \]

where the \( A_n \) constants are given with the calibration curve in Figure 2.7. Temperature is extracted from the measured resistance \( R \) from the appropriate root of the quadratic equation 2.16 relating \( \ln R \) and \( \ln T \). The RuO\(_2\) thermometers are home made from simple and cheap commercial resistors.

There are two calibrated commercial resistance thermometers on ND1: germanium (Ge) \[6\] and carbon–glass, to measure from 50 mK and 1.1 K up respectively. Both are measured in 4-wire configuration and they come with a calibration table from the manufacturer. Both Ge and carbon–glass thermometers are mounted on the mixing chamber. All resistance thermometers on ND1 are measured by the AVS-47 resistance bridge \[1\].
Figure 2.7: Calibration of a RuO$_2$ thermometer, located on ND1 mixing chamber, against germanium thermometer. The measured resistance follows formula 2.16 down to 40 mK with 100 µV excitation. However, when the excitation is lowered the thermometer is still reliable at even lower temperatures.

2.2.2 $^3$He melting curve thermometry

A $^3$He melting curve thermometer (MCT) relies on the variation of the $^3$He melting pressure with temperature. The melting curve is shown in Figure 2.8. The melting pressure was extensively studied by Greywall [3, 7] and one of the commonly used temperature scales based on the melting curve bears his name. $^3$He only solidifies at high pressures, so the MCT is therefore a high pressure cell with an integrated manometer. The pressure is read capacitively and this must be calibrated against an external pressure gauge. In our case it is the high pressure oscillating quartz pressure gauge from Paroscientific [8]. The MCT low temperature sensor is connected to a room temperature high pressure gas handling system (GHS) with a thin fill line. The Paroscientific gauge is connected to the GHS. The sensor capacitance is calibrated as a function of external pressure over the range 29–35 bar. The sensor is then pressurised to about 35 bar and cooled. The initial pressure must be such that the MCT remains on the melting curve to lowest temperatures. A solid plug is formed in the fill line around 800 mK and the MCT sensor becomes isolated from the GHS with coexisting liquid and solid inside. Pressure will start to change upon
cooling and follow the melting curve formula:

\[ p = \sum_{i=-3}^{N} a_i T^i. \] (2.17)

The above formula is empirical and the coefficients \( a_i \) and their number \( N \) vary from temperature scale to temperature scale. Apart from the already mentioned Greywall scale the most commonly used is the so-called PLTS 2000 temperature scale [9]. The Greywall scale is used on ND1 for historic reasons when measuring NMR on adsorbed He. The temperature according to the MCT is assigned to the experiment in the temperature range: 2–200 mK.

The MCT was not used as a serious thermometer standard in the YRS experiment but only as a regular check for the noise thermometers. For that it was running on the PLTS 2000 scale which agrees with our noise thermometers better than the Greywall scale.

The peculiar shape of the \(^3\)He melting curve is caused by the unusual entropy difference of the solid and liquid phase. Normal substances have larger entropy difference of the solid and liquid phase. Normal substances have larger entropy difference of the solid and liquid phase.

Figure 2.8: \(^3\)He melting curve generated using the PLTS 2000 coefficients from [9] with highlighted features and transitions. Inset graphs show the ND1 MTC crossing through the two superfluid transitions. The A-transition is used for calibration while the B-transition is often shifted to lower temperatures (supercooled).
in their liquid state, and so does $^3$He above the minimum at 315 mK. The slope of the melting curve, given by the Clausius–Clapeyron equation, is then positive. The entropy difference is reversed below the minimum and so is the gradient of the curve.

The MCT is used as a transferable standard of temperature due to its intrinsic calibration point: the superfluid A-transition of $^3$He. Any instrumental offset, especially in the Paroscientific gauge, is thus corrected. Figure 2.8 shows typical crossing of the A-transition in the inset. A distinct kink is apparent on the temperature readings in time. The A-transition is a second order phase transition, at which there is a jump in the heat capacity, and therefore does not depend on the speed of the crossing and neither shows any hysteresis. The B-transition on the other hand is a first order phase transition and is often supercooled on the cooldown. It therefore cannot be used as a calibration point.

It is apparent from the look of the melting curve that the MCT looses sensitivity at the lowest temperatures as the pressure varies only weakly with temperature. This is particularly true below the Néel transition at which the nuclear spins order antiferromagnetically (see blue point in Figure 2.8). This is also true around the curve minimum. The pressure resolution should be less than 10 $\mu$bar to be properly sensitive to temperature changes at the low temperatures. This is achieved by using high precision capacitance bridges and using a thin BeCu membrane, a material with excellent mechanical properties, in the low temperature sensor. The machined membrane forms one side of the measurement capacitor. There is also a reference capacitor in the measurement circuit, which is attached to the body of the inner vacuum can (IVC) and rests in the liquid He bath providing good temperature stability. The MCT sensor is mounted next to the NMR cell on the coldest experimental platform on ND1. The capacitance bridge is home made, and operated at 3.3 kHz. It can be balanced automatically using a programmable ratio transformer. The temperature is determined from the bridge ratio and the off-balance deflection voltage, measured by a lock-in, using both the pressure calibration data and melting curve scale, as previously discussed.

2.2.3 Carbon and platinum NMR thermometry

Nuclear magnetic resonance allows, among other quantities, to measure the magnetisation of a selected spin species in a specimen. If the specimen is an ideal Curie paramagnet in the low polarisation limit (low field or high temperature) the measured magnetisation will obey:

$$M = \frac{C}{T},$$  \hspace{1cm} (2.18)
where $C$ is the Curie constant. Ideal paramagnets are difficult to find in systems where the magnetic moments are of electronic nature because of the large influence from the chemical properties of the given compound. Nuclei can however be considered as isolated from the electronic structure in many materials. This is especially true for “simple” mono-atomic materials like pure precious metals. The metal most frequently used for nuclear NMR thermometry is platinum. Our Pt thermometer made out of a bundle of thin Pt wires is present on ND1 as well. Metals typically have very short spin–spin relaxation time ($T_2$) but can have very long spin–lattice relaxation time ($T_1$). In case of Pt the $T_1$ is however significantly lowered due to high RKKY exchange interaction ([10, 11, 12] and section 4.1.2). This exchange interaction also leads to significant increase in $T_2$, for which conduction electrons act as mediators between nuclei, and couple them to the electron sea. The spin–lattice relaxation of magnetically active nuclei $^{195}$Pt in platinum obeys the Korringa law (equation 2.13). The Korringa constant is: $K = 30 \text{ mK} \cdot \text{s}$ for Pt, much smaller than Cu [13]. The NMR field for the Pt thermometer is produced by a magnet wound around the IVC can and cooled by the He bath, similarly to the demag magnet. The Pt wires are positioned horizontally and therefore perpendicularly to the NMR field. A superconducting coil is wound tightly around them on a thin mylar foil and serves as both transmitter and receiver coil. The setup operates at 250 kHz using the PLM4 Pulse NMR System [14].

The other NMR active nuclei, that are used for thermometry purposes on ND1, are $^{13}$C nuclei in the graphite substrate for the He samples. The $^{13}$C nuclei are only 1.11% of the overall number of C nuclei and they precess at roughly three times lower Larmor frequency than $^3$He [15] in the same field. The broadband transmitter pulse, tuned to excite the $^3$He, can however excite the $^{13}$C nuclei as well (see Figure 3.16 in section 3.7.1 for more detail). The small natural abundance of the $^{13}$C nuclei causes their dipole–dipole interaction to be relatively weak and as the result the $T_2$ relaxation time is long. The $^{13}$C FID is characterised by a single exponential decay and the resonance peak can be fitted by a Lorentzian (equation 2.37).

Even though the Curie constant is in principle only dependant on measurable quantities, and the Curie law is a simple function of temperature, NMR thermometers are not primary thermometers. A calibration to another thermometer (most often MCT) is necessary at least at one temperature point. Multiple calibration points can however further support the validity of the Curie law for the given material. An example of the calibration in multiple points done on the $^{13}$C is shown in Figure 2.9. Such a calibration was performed after each demagnetisation procedure.
\(^{13}\)C NMR is the thermometer best suited to determine the temperature of the adsorbed \(^{3}\)He as it is located directly inside the cell. It was found that the \(^{195}\)Pt NMR and noise thermometers reach lower temperature after a demagnetisation, whereas the cell remains at a somewhat elevated temperature due to the parasitic heat leak into it. Typically if the \(^{195}\)Pt thermometer reaches 200\(\mu\)K, the \(^{13}\)C shows 270\(\mu\)K. It was also found out that the \(^{13}\)C has relatively long \(T_1\) and the spin–lattice relaxation shows stretched exponential behaviour. For that reason the \(^{13}\)C temperature usually relaxes more slowly, after the demag, than the adsorbed He sample. One exception to this was a special sample discussed later in this work where \(^{3}\)He doped second layer of \(^{4}\)He on graphite around the so-called 7/12 commensurate phase was measured. In that sample \(T_1\) of \(^{3}\)He clearly exceeded \(T_1\) of \(^{13}\)C. These results are given in section 3.8. The cool down of the \(^{3}\)He and \(^{13}\)C can very nicely be seen when monitoring the magnetisation during and after the demagnetisation routine if the He sample is also showing paramagnetic behaviour.

![Figure 2.9: Calibration of the \(^{13}\)C magnetisation against temperature according to the MCT. The inset shows the resonance peak of the \(^{13}\)C at 8 mK. See Figure 3.16 where a \(^{13}\)C peak taken at 327\(\mu\)K is shown. Its fit yields magnetisation of over 2000.](image)

The magnetisation of \(^{13}\)C is measurable by broadband NMR up to 20 mK. The thermometer is calibrated against the MCT in the temperature range from the base of the dilution unit. The calibration points are shown in Figure 2.9. Due to the long relaxation constants and small signal it is however not used as
the thermometer for the adsorption experiment above 2 mK. This is when the MCT takes over.

2.2.4 Current sensing noise thermometry

It was discovered by Johnson in 1927, that ordinary electric conductors in thermodynamic equilibrium are sources of spontaneous fluctuations of voltage. He attributed this property to the thermal agitation of the electric charges in the material of the conductor [16]. A year later, Nyquist theoretically explained the results and obtained the same formula for voltage fluctuation [17]:

\[ du^2(f) = 4R(f)k_B T df, \]  

(2.19)

where \( du^2 \) is an infinitesimal small voltage square at a certain frequency, \( df \) is the infinitesimal small bandwidth of the frequency, \( T \) is the absolute thermodynamics temperature, and \( k_B \) is the Boltzmann constant. Considering the resistance \( R \) to be frequency independent over a given bandwidth, an integrated version of this formula is commonly written as:

\[ \langle U^2 \rangle = 4Rk_B T \Delta f, \]  

(2.20)

where the averaging is with respect to time and \( \Delta f \) is the frequency bandwidth. The assumption of the independence of resistivity on \( f \) holds for ordinary materials up to very high frequencies, unless the skin effect plays a role. It does not, however, hold for any additional impedance in the sensing circuit. The parasitic capacitance in the sensing circuit is usually negligible, however the inductance is not. It is the current caused by the fluctuating voltage which is measured in our NT. The current is read out by a two stage SQUID amplifier, described in section 2.3.1. It is transformed to magnetic flux in its input coil (see figure 2.10). The input coil has significant inductance and so does the wiring between the sensor and the SQUID (a twisted pair). The formula for the current square fluctuation, taking this inductance into consideration is:

\[ \langle I^2 \rangle = \frac{4k_B T}{R} \frac{1}{1 + \omega^2 \tau^2} \Delta f, \]  

(2.21)

where \( \omega = 2\pi f \) and \( \tau = L/R \), \( L \) is the overall inductance in the circuit.
There are two different types of noise thermometers, shown in Figures 2.10 and 2.11. The first one (2.10) reads the fluctuating current from the resistor $R$ directly, using wires connected to both ends of the resistor. The second one reads fluctuating magnetic flux, caused by the fluctuating current in a resistive block using a coil, wound around the resistive block. In both cases the signal is coupled to the SQUID input coil. The amplified signal is then recorded by a digital oscilloscope (digitiser), the 5922 PXI card from National instruments (NI) [20]. This samples the fluctuating signal in real time with a typical frequency 1 MHz and produces a 24–bit digital output. The resolution decreases to 16–bits at the highest sampling rates. The real time signal of a certain number of points (typically $2^{17}$ or $2^{20}$) is sent to a PC, where it is Fourier transformed to the frequency domain. The current sensing noise thermometer can be operated as a primary thermometer as formula 2.21 strictly relates the fluctuating current to the thermodynamic temperature. The SQUID amplifier brings extra technical parameters into the equation, however in principle they can all be fully characterised. The formula for the mean of the squared fluctuating voltage per unit bandwidth becomes:

\[ P \ [V^2/Hz] = \left( \frac{M_i R_i}{M_f} \right)^2 \frac{4k_B T}{R} \left( \frac{1}{R} \right)^2 + P_{SQUID}, \]  

(2.22)

where all parameters are summarised in table 2.1. The double stage SQUID sensor from PTB has characteristic device noise contributing to the measurement by the additive term $P_{SQUID}$. The exact physical origin of this noise is unknown. The presence of shunt resistors on the chip of the SQUID definitely plays a role but it is not the only source. The SQUID noise is dependant on the temperature of the SQUID platform but, based on our observations, it does not depend linearly on it as the pure Johnson noise of a resistor would. The SQUID noise is white noise with a $1/f$ contribution. In our measurements this becomes noticeable at lowest measured temperatures (see low frequencies at low $T$ in Figure 2.13).

The noise temperature of a device is defined as the temperature at which the noise level in the measured element is the same as in its amplifier (the SQUID).
If the SQUID noise is considered white, the noise temperature of the device is:

$$T_N = \frac{R}{4k_B} \left( \frac{M_i V_{noise}}{M_i R_f} \right)^2, \quad (2.23)$$

Clearly this depends on the choice of sensor resistance, and is about 13 $\mu$K for our large bandwidth NTs introduced next.

**Large bandwidth noise thermometer on ND1 demag stage and inside the YRS heat capacity cell**

A noise thermometer with a large bandwidth is achieved by having a small $L/R$ ratio which determines the roll-off frequency of the noise spectrum, according to formula 2.22. SQUIDs used in our labs have an input inductance around 2 $\mu$H, therefore large bandwidth means increasing the resistance $R$ to sub-1Ω level. This is where the fast sampling ability of the oscilloscope is fully used. The larger bandwidth increases the measurement speed [21, 18]. The precision depends on the measurement time $t_{meas}$ and the bandwidth of the NT in the following way:

$$\frac{\Delta T}{T} \approx \left( \frac{2\tau}{t_{meas}} \right)^{1/2}. \quad (2.24)$$

The two disadvantages of a large bandwidth NT are firstly the smaller overall signal as the signal according to equation 2.22 scales with $R$. The signal can easily get comparable to the SQUID noise at low temperature. The second disadvantage is the thermalisation of the sensor to the measured body. Thermal conductivity ($\kappa$) of many simple resistive materials is related to their resistivity ($\sigma$) by the Wiedemann–Franz (WF) law:

$$\frac{\kappa}{\sigma} = LT, \quad (2.25)$$

where $L = 2.44 \cdot 10^{-8}$ WΩK$^{-2}$ is the so-called Lorenz number. The ability to thermalise at mK temperatures is strongly compromised for resistors close to 1 Ω, for heat leaks into them as small as 1 pW. Special measures have to be made to minimise the heat leak. This involves implementation of silver epoxy filters as a lossy ground, and using very thin superconducting wires as thermal breaks. They are described more in detail in section 2.3.2. From measurements of the heat capacity on the YRS described in chapter 4 we could determine the heat leak into the filtered environment to be around 30 fW. Under the assumption that the noise thermometer leads alone are responsible for the whole heat leak entering the cell, one can take the value 30 fW as an upper limit for the noise thermometer heat leak. Figure 2.12 shows the thermalisation curve calculated as the integral of the WF law for the geometry of the cell NT under two possible heat leaks. The curves can be further assessed from how cold the noise thermometer gets. In our case the lowest temperature measured by the cell NT was
about 175 \( \mu K \). Assuming the 30 fW heat leak; it is the temperature the noise thermometer would reach only if the cryostat was at absolute zero. A more reasonable value for the heat leak is 8 fW from analyses of the YRS calorimetry.

![Figure 2.12: Thermalisation curve of the cell noise thermometer for estimated heat leaks. Curves identifying 10% and 1% error are shown.](image)

Typical noise thermometer spectra in the frequency domain are shown and explained in Figure 2.13 together with the fits according to equation 2.22. Table 2.1 summarises the parameters of our two large bandwidth noise thermometers. The noise temperature is about 10 times smaller than the lowest temperature that was ever measured by our large bandwidth thermometers. The noise temperature can be seen in the low temperature spectrum, shown in Figure 2.13, where the SQUID plateau, apparent at highest frequencies, is clearly an order of magnitude below the sensor’s noise plateau.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Stage NT value</th>
<th>Cell NT value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R ) [m( \Omega )]</td>
<td>resistance of the sensor</td>
<td>247.3</td>
<td>203.0</td>
</tr>
<tr>
<td>( L_i ) [( \mu H )]</td>
<td>input inductance of the SQUID</td>
<td>1.943</td>
<td>1.623</td>
</tr>
<tr>
<td>( M_i ) [H]</td>
<td>input coil mutual inductance</td>
<td>( \Phi/2.4 \times 10^{-7} )</td>
<td>( \Phi/2.932 \times 10^{-7} )</td>
</tr>
<tr>
<td>( M_f ) [H]</td>
<td>feedback coil mutual inductance</td>
<td>( \Phi/41.5 \times 10^{-6} )</td>
<td>( \Phi/41.5 \times 10^{-6} )</td>
</tr>
<tr>
<td>( R_f ) [k( \Omega )]</td>
<td>feedback resistor</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>( V_{SQUID} ) [( \mu V/\sqrt{\text{Hz}} )]</td>
<td>SQUID noise</td>
<td>0.0963</td>
<td>0.083</td>
</tr>
<tr>
<td>( T_N ) [( \mu K )]</td>
<td>noise temperature</td>
<td>14</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 2.1: Parameters of the two noise thermometers on ND1. *Italic* values denote parameters left as free parameters together with \( T \) in standard operation. **Bold** values were determined from a temperature calibration procedure. Normal format means the values are known with various precision from independent measurements.
Figure 2.13: Cell NT spectra at 200 mK and 200 µK. Points from frequency range from 1 kHz to 300 kHz (green colour) were used for fitting with formula 2.22. $T$ and $P_{SQUID}$ were left as the fitting parameters. Black points denote crudely discarded points. Grey points were discarded by an iterative discrimination procedure. Both spectra were recorded by the PXI digitiser in 1MHz frequency as $2^{17}$ points. Fast Fourier transform of the time reading reveals the white character of the noise; the $1/f$ contribution to the SQUID noise is apparent at low $T$ at low frequencies. All was repeated 200 times and averaged.

Figure 2.14 shows the same frequency range as Figure 2.13. It shows distribution of the noise points around the best fit.

**Calibration and fitting procedure of noise thermometers**

If the noise thermometer is not fully characterised as a primary thermometer it is calibrated at a single temperature against either a fixed point or another thermometer. The fitting formula for noise thermometer in secondary mode can be simplified to:

$$ P = G \cdot T \frac{1}{1 + f^2 \tau^2} + P_{SQUID}, $$

(2.26)

where parameters $G$ and $\tau$ are determined during the calibration and fixed in the normal run when $T$ and optionally $P_{SQUID}$ are the free parameters. In our fitting scripts this simplified formula is however not used and the full formula 2.22 is used instead. Table 2.1 specifies which parameters are left to be determined by the calibration and which are known well and fixed. These parameters are different for our two noise thermometers. It potentially matters whether the SQUID noise is left as a free parameter or fixed. The noise spectra acquisition
can be targeted to detect the SQUID noise if a very fast sampling rate is chosen. In the last run the SQUID noise was fixed for the stage noise thermometer and left free for the cell noise thermometer to make a comparison. It was found that recording up to 300 kHz is enough to see the SQUID noise well and leaving it as the free parameter is therefore a valid choice which also increases the precision achieved from a single recorded trace.

As thermometers are not all located on the same experimental plate on the cryostat, the temperature for the calibration is chosen rather high, in our case 200 mK. The fridge was stabilised at this temperature with the Ge resistance thermometer used as the reference. The Ge thermometer also agrees well with the melting curve thermometer at these temperatures. The noise thermometer was recording with the same settings as during the normal measurements. 321 continual points were taken for the calibration and from those the calibration

![Figure 2.14: Residuals distribution about the best fit model of the cell’s NT spectra at 200 mK and 200 µK. Points from frequency range from 1 kHz to 300 kHz (green colour) were used for fitting with formula 2.22. T and PSQUID were left as the fitting parameters. Black points denote crudely discarded points. Grey points were discarded by an iterative discrimination procedure. The 1/f contribution to the SQUID noise is apparent at low T at low frequencies.](image-url)
parameters were determined. The stability of the fitted temperature to additional changes of setting or external parameters was also studied. For example, no changes with magnetic field were found. On the other hand, an interesting dependence on the averaging of the noise thermometer spectra was discovered. The fitting is done by minimising the $\chi^2$ functional of the following form:

$$\chi^2 = \sum_{i=0}^{N} \frac{(n_i - M)^2}{M^2},$$

(2.27)

where $n_i$ are points in the noise spectrum and $M$ is the model according to equation 2.22. The reason to scale the residuals, $n_i - M$, by the model $M$ is the fact that the points in the spectra have a chi–square distribution with a mean value $\bar{n}_i$ and the standard deviation: $\sigma_n = \bar{n}_i / \sqrt{n_{av}}$, where $n_{av}$ is the number of averages. In other words, the scatter appears constant on a logarithmic plot in Figure 2.13 across several orders of magnitude of $P_B$. If the right model agrees with $\bar{n}$ for any $i$, then scaling with the model is the right approach. It was however discovered that the scaling introduces a bias to the estimator ($T$). Bias of estimators are not uncommon [22] in non-linear fitting routines. Typically a scaling factor can be found. We found that the fitting parameter $T'$ which minimises the chi–square functional is related to the real temperature as:

$$T' = T \frac{n_{av} + 1}{n_{av}}.$$  

(2.28)

This was done at the stabilised temperature for calibration, recording spectra using a different number of averages. It can be seen that the scaling factor introduces a larger than 1% error only for spectra taken with less than 100 number of averages. The noise thermometer is set to record $2^{17}$ points with the sampling rate 1 MHz. This means it should take 0.13 s to record a single spectrum. This is usually slowed down a little by the Fourier transform. Nevertheless it is still short enough time that the noise thermometer can record 200 traces or more and average them to determine a single temperature point. This is the setting the cell noise thermometer was most commonly run at.
Figure 2.15: Histogram of the residuals of the cell’s NT spectra at 200 mK and 200 µK. The fit procedure iteratively discards points that are further than 3σ away from the best fit. It thus visibly removes the parasitic peaks from the spectra. The fraction of noise points naturally occurring further than 3σ is much less than 1%.
2.3 Experimental cells

2.3.1 Broadband SQUID NMR cell for measuring He films

Nuclear magnetic resonance (NMR) is a powerful non-invasive technique to probe the local environment of atomic nuclei. This section gives a brief introduction into the technique and introduces the cell used for the experiment, novel and special in many ways.

Principal of nuclear magnetic resonance (NMR)

The magnetic moment of a nucleus is related to its spin $I$ as: $\hat{\mu} = \gamma \hbar \hat{I}$, where $\gamma$ is the gyromagnetic ratio. The gyromagnetic ratio is specific for a given nucleus. Therefore nuclei of different elements will precess at a different frequency, even if they have the same spin and are in the same field. As an example, let’s consider nuclei of $^3\text{He}$ and $^{13}\text{C}$, both having spin $1/2$, but precessing at 32.4 MHz/T and 10.7 MHz/T respectively.

The magnetic moment $\mu$ interacts with an external magnetic field $B_0$ via a Hamiltonian:

$$\hat{H} = -\hat{\mu} \cdot \hat{B}_0.$$  \hspace{1cm} (2.29)

Eigen-energies can be expressed using the quantum number $m$, which for a spin $I$ has $2I + 1$ values:

$$E_m = -\gamma \hbar B_0 m.$$  \hspace{1cm} (2.30)

The energy multiplet is called Zeeman splitting and for $^3\text{He}$ there are only two energies separated by 1.55 mK/T. All measurements on $^3\text{He}$ presented in this thesis were taken on a weakly polarised system, with $k_B T$ well above the Zeeman splitting.

The behaviour of the magnetic moment in the outside magnetic field is, in classical approximation, governed by an equation:

$$\dot{\mu} = \gamma (\mu \times B_0).$$  \hspace{1cm} (2.31)

The solution to this equation in Cartesian coordinates is:

$$\mu^x(t) = \mu \cos(\theta),$$
$$\mu^y(t) = \mu \sin(\theta) \cos(\gamma B t),$$
$$\mu^y(t) = -\mu \sin(\theta) \sin(\gamma B t),$$  \hspace{1cm} (2.32)

where $\theta$ is the angle of $\mu$ with the magnetic field.

The solution describes precession of the vector $\mu$ around the direction $B_0$, which is called Larmor precession. The angular frequency of the precession is:
ω = γB. This solution describes a single magnetic moment in a magnetic field, however a NMR measurement is done on a system of interacting spins. Let’s for simplicity consider a paramagnet, consisting of localised spins. Its magnetisation is given by the excess of population of spins oriented in one direction, over the other: \( M = \mu_N (N_\uparrow - N_\downarrow) \). In the weak polarisation limit, the magnetisation is given by the Curie law [23]:

\[
M = \frac{n\gamma^2 h^2 I(I+1) B}{3k_B T}.
\] (2.33)

The orientation of the magnetic moment is given by the temperature and strength of the magnetic field. If the magnetic moment is perturbed from its equilibrium orientation, it is the equivalent of varying the spin’s temperature [24]. Subsequently, the spin relaxes back to the equilibrium state. Bloch [25] introduced a set of macroscopic, phenomenological equations to describe the return of the magnetisation to equilibrium after disturbance. The equations are equation 2.31 with added terms that govern the relaxation:

\[
\begin{align*}
\dot{M}_x &= \gamma |M \times B|_x - M_x / T_2^*, \\
\dot{M}_y &= \gamma |M \times B|_y - M_y / T_2^*, \\
\dot{M}_z &= \gamma |M \times B|_z + (M_\infty - M_z) / T_1.
\end{align*}
\] (2.34)

The dephasing of the transverse magnetisation is given by the time constant \( T_2^* \) and the relaxation of the longitudinal magnetisation by the constant \( T_1 \). Both of these effects lead to decoherence of the initial spin state. See Figure 2.16 illustrating these effects on the so-called Bloch sphere. The solution to the Bloch equations is:

\[
\begin{align*}
M_x(t) &= M_\infty \sin(\theta) \cos(\gamma B t) \exp \left(-t/T_2^*\right), \\
M_y(t) &= -M_\infty \sin(\theta) \sin(\gamma B t) \exp \left(-t/T_2^*\right), \\
M_z(t) &= M_\infty - M_\infty (1 - \cos(\theta)) \exp \left(-t/T_1\right),
\end{align*}
\] (2.35)

where \( \theta \) is the tipping angle away from \( B_0 \).

Figure 2.16: Graphical illustration of the spin orientation evolution in pulsed NMR. A 90\(^\circ\) pulse tips the spins into the \( xy \)-plane. The spins dephase with the characteristic relaxation time \( T_2^* \) and they relax back to the equilibrium position with the characteristic relaxation time \( T_1 \). Both of these effects lead to decoherence of the initial spin state.
Pulsed NMR

In the pulsed method of NMR a short harmonic magnetic pulse $B_T$ in a direction perpendicular to $B_0$ is applied. It is produced by a transmitter coil and its power spectrum should be strong at the Larmor frequency of the nuclei it is intended to excite. Let’s consider a coordinate system, which rotates together with a magnetisation undergoing Larmor precession. We know a non-zero angle between a magnetisation and magnetic field creates a torque: $\mu_N \times B_0$ acting on the moment. Conversely however no precession means no magnetic field. The moment doesn’t precess in the rotating frame and therefore the effective static magnetic field along $z$ is zero in that frame. On the other hand, the field $B_T$ (let’s say it oscillates in the $x$ direction) is the sum of two circular fields, rotating in the $xy$ plane. One of these will always match the orientation the magnetisation’s precession, while the other will have the opposite orientation. In the rotating frame, the former will appear as static, while the latter will rotate with double the Larmor frequency. Effects of the latter will vanish but the former will again create a torque pulling the moment from the $z$ direction towards the $xy$-plane. The longer the pulse lasts $\tau$, the larger the tipping angle. From equation 2.31:

$$\theta(\tau) = \frac{\gamma B_T}{2} \tau. \quad (2.36)$$

There are two important types of pulses with tipping angles 90° and 180°. The former will last for $\tau_{90^\circ} = \pi/\gamma B_T$ and the latter for $\tau_{180^\circ} = 2\pi/\gamma B_T$. A pick-up (receiver) coil detects magnetic field in the $xy$ plane. The signal detected after a 90° pulse is therefore the largest possible and equals to the full longitudinal magnetisation: $M ||$. Pulses of a smaller tipping angle will generate a signal: $M || \sin(\theta)$. The 180° pulse will generate zero signal, but reverses the orientation of the magnetisation. From there they relax back to the equilibrium according to the Bloch’s equation; namely the solution $M_z(t)$ in 2.35. By monitoring the recovery it is possible to measure the spin–lattice relaxation time $T_1$. More on the measurement of the relaxation times is discussed later in this section.

The signal detected after a tipping pulse is called the free–induction decay (FID) and Bloch’s equation predicts the amplitude to decrease exponentially with time. To extract the information about frequency (frequencies) of the precessing moments, the magnetisation, and other quantities, Fourier analyses of the FID is helpful. Should the FID be a product of a sinusoidal and exponential functions, its Fourier transform will be a convolution of a delta function positioned at the Larmor frequency frequency $\omega_0$ and a Lorentzian profile:

$$L_{abs} = \frac{M}{\pi} \frac{\delta}{\delta^2 + (\omega - \omega_0)^2},$$

$$L_{disp} = \frac{M}{\pi} \frac{\omega - \omega_0}{\delta^2 + (\omega - \omega_0)^2}. \quad (2.37)$$
The two Lorentzian profiles are called absorption and dispersion. The two complex components of the Fourier transform of the FID are always a linear combination of these two profiles, based on the initial phase of the FID $\phi$. The full–width at half–maximum of the Lorentzians is given by $\delta$, which is related to $T_2^*$ as:

$$T_2^* = \frac{1}{\delta}. \quad (2.38)$$

Figure 2.17: Left: Simulated exciting transmitter pulse and its FID. Right: Fourier transforms of both signals. Larmor frequency is $10/T_2^*$ in the simulation.

Figure 2.18: The actual FID measured at 327 $\mu$K on He sample: 18.27 $^4$He + 0.74 $^3$He nm$^{-2}$. The 100 kHz signal from $^3$He is visible and its modulation by $^{13}$C at 33 kHz. $^3$He has about 5 times larger magnetisation than $^{13}$C in the measured units under these conditions. The exponential spin–spin relaxation is apparent as well: $T_2^*$ is 1.0 and 2.3 ms for $^3$He and $^{13}$C respectively. The Fourier transform of this FID is shown in Figure 3.16.

Figure 2.17 shows a simulated FID signal, coming from a single Larmor fre-
frequency and its Fourier transform, manifesting the Lorentzian profile. The transmitter pulse consisting of four periods at the Larmor frequency and its Fourier spectrum is also shown.

Operation of SQUIDs

SQUIDs (superconducting quantum interference devices) are devices extremely sensitive to magnetic flux. They are superconducting loops interrupted by one or two insulating breaks. The sequence: superconductor–insulator–superconductor is called a Josephson junction. Cooper pairs can tunnel between the superconductors through the insulator barrier and this phenomenon gives rise to the ac and dc Josephson effects [26, 27]. The tunneling mechanism can be explained as follows. The wavefunction of the superconducting states on either side of the junction is:

\[ \Psi_{1,2} = \sqrt{n_{1,2}} e^{i\theta_{1,2}}, \]  

where \( n_{1,2} \) is the Cooper pair density and \( \theta_{1,2} \) is the phase. We substitute these into the time dependant Schrödinger equation of the form:

\[ i\hbar \frac{\partial \Psi_{1,2}}{\partial t} = \mu_{1,2} \Psi_{1,2} + K \Psi_{2,1}, \]  

where \( \mu \) is the energy ground state and \( K \) is the barrier-opacity coupling constant across the junction which depends on the width, composition and temperature. It can be shown that:

\[ \hbar \frac{\partial n_1}{\partial t} = -\hbar \frac{\partial n_2}{\partial t} = 2K \sqrt{n_1 n_2} \sin(\theta_2 - \theta_1), \]

\[ -\hbar \frac{\partial}{\partial t}(\theta_2 - \theta_1) = \mu_2 - \mu_1. \]  

(2.41)

The charge transport across the junction is proportional to the Cooper pair density. If there is a voltage \( V \) applied across the junction the grounds states difference is: \( \mu_2 - \mu_1 = 2eV \). We label the difference in the two phases \( \delta = \theta_2 - \theta_1 \) and we obtain for the current across the junction:

\[ I = I_c \sin(\delta), \]  

(2.42)

where \( I_c = 2K \sqrt{n_1 n_2}/\hbar \) is the critical current across the junction, and:

\[ \frac{\partial \delta}{\partial t} = \frac{2eV}{\hbar} \]  

(2.43)

The flow according to equation 2.42 in the absence of any electromagnetic field is called the dc-Josephson effect. If the current exceeds \( I_c \) the junction becomes resistive. The variation of phase difference with applied voltage, which eventually causes alternating current is called the ac-Josephson effect. The junc-
tion can work as a nearly perfect voltage to frequency converter.

The situation is more complicated in real devices as the junctions inherently possess parasitic capacitance. In modern SQUID sensors it is typically around 1 pF [28]. In order to have a non-hysteretic current to voltage characteristic, shunt resistors are added across the junctions.

There are two types of SQUID devices, the rf-SQUID and the dc-SQUID. The former ones are in general simpler and cheaper to make and were used in our department in the past, the latter ones however exceed in sensitivity are therefore mainly used today for NMR measurements and noise thermometry. A dc-SQUID is a flux to voltage transducer. However in both our applications it measures current. The current to be measured generates a magnetic field in the input coil of the SQUID. The dc-SQUID contains two Josephson junctions and is sketched in Figure 2.19.

![Figure 2.19: Schematics of the dc-SQUID field to voltage transducer. Black lines denote superconductor. Two isolating weak-links are connected in parallel and are drawn as red crosses.](image)

For a SQUID of two junctions there will be two phase difference across junction $a$ and $b$ and the total current will be:

$$I_T = I_c (\sin(\delta_a) + \sin(\delta_b)).$$  \hspace{1cm} (2.44)

External flux $\Phi$ is threading the SQUID loop as:

$$2\pi s = \frac{2\pi}{\Phi_0} \Phi + \delta_a + \delta_b,$$  \hspace{1cm} (2.45)

where $s$ is an integer and $\Phi_0 = h/2e$. Combining equations 2.44 and 2.45 we get:

$$I_T = 2I_c \left| \cos \left( \frac{\pi \Phi}{\Phi_0} \right) \right|.$$  \hspace{1cm} (2.46)

The current is periodic with respect to external flux. Figure 2.20 right shows
the current–voltage characteristic of the dc-SQUID for two extreme cases of the flux penetration. A bias current $I_b$ is applied in order to maximally distinguish between the two cases, where variation of flux cause the change in voltage.

![Figure 2.20: Left: Periodic $V - \Phi$ characteristics of the second stage of the PTB two-stage SQUID. The SQUID is operated at the point of maximal slope of $V$ vs $\Phi$ and therefore maximal sensitivity. Right: V-I characteristic of a SQUID for integer and half integer multiples of $\Phi_0$. Bias current $I_b$ is applied to have reasonable sensitivity as variation in voltage with flux.](image)

The SQUID operated in **flux-locked loop (FLL) mode** where feedback stabilises the SQUID at the chosen working point is shown in Figure 2.20. Current through a feedback coil coupled to the SQUID compensates the flux coupled from the SQUID input coil. Measurements of NMR and noise thermometry were always done in the FLL mode. Figure 2.21 shows a sketch of the SQUID amplifier from PTB [29, 28].

![Figure 2.21: Simplified diagram of the two stage dc-SQUID form PTB.](image)
The NMR receiver coil was wound to optimally match to the inductance of the input coil \( L_i \); the noise thermometer produces currently directly. The first stage of the SQUID amplifier is the first SQUID loop, equipped with the input and feedback coils. The output signal from the first stage is fed into the second stage of the SQUID amplifier. It consists of an array of 16 SQUID loops in series. This achieves the required noise matching to the room temperature amplifier. The second stage output signal goes into a room temperature differential amplifier and it is integrated to produce voltage. The output voltage also feeds back into the feedback coil with a feedback resistor \( R_f \) in series. Two bias currents \( I_{B1} \) and \( I_{B2} \) individually control the two stages and maximise the amplitude of the \( V - \Phi \) characteristics shown in Figure 2.20. The use of SQUID for the NMR measurements is discussed in more detail in [30].

**Design of the graphite adsorption cell**

The SQUID NMR cell for measuring adsorbed He samples is that used in previous work [31]. It consists of two major parts. The actual sample container with exfoliated graphite is thermalised to the nuclear stage via a silver post. The container is made out of Stycast 1266, an insulating material. A small coil is wound around the container as the NMR receiver coil. The other part of the cell is a pair of magnets, thermalised to the mixing chamber and suspended from its plate. The main NMR magnet creates static field in the vertical orientation and a saddle type coil inside the main magnet produces transmitter NMR pulses in a direction perpendicular to the main field and to the axis of the receiver coil (to reduce cross-coupling). The magnets surround the cell but the two parts must not touch. A sketch of the setup is shown in Figure 2.22.

The phenomena of adsorption on graphite will be further discussed in the section 3.1. The following summarises the procedure previously used to construct this cell [31]. Exfoliated graphite (grafoil) in the form of 150 \( \mu \)m thick foils was first cleaned by baking in in the furnace at 1000°C for 24 hours. They were then diffusion bonded to silver foils that provide its thermalisation. The diffusion bonding is done under vacuum at 650°C for 8 hours. The foils have squared shape and the full silver–graphite stack needs to fit into the Stycast casing which has internal volume about \( 10 \times 10 \times 10 \) mm. The foils are located horizontally inside the casing, therefore perpendicular to the applied field. The silver foils extend from the part where the grafoil is bonded, they are bent and diffusion bonded to the silver post. The silver post is connected to the nuclear stage experimental plate with a cone joint and provides the final thermal link from the graphite to the cryostat. Along the silver post runs a fill line which enters the casing as well. The fill line brings He from the room temperature gas handling system (GHS). The Stycast casing is closed and sealed with a mixture
of Stycast 1266 and 2580. The receiver coil is wound around the Stycast casing. Its inductance (1.8 $\mu$H) matches the input inductance of the SQUID to which it is connected by a NbTi twisted pair. The coil has 13 turns of a single filament unclad NbTi wire.

Figure 2.22: Schematics of the NMR cell, its magnet system and electronics.

The main requirement for the magnet producing the static magnetic field is its homogeneity. According to equation 3.45 inhomogeneities of the field in the magnet shorten the FID and broaden the spectral lines. The magnet is therefore relatively long: 95 mm and narrow: diameter 32 mm. Second feature enhancing the homogeneity is Hechtfisher shield [32], located inside the magnet core. The Hechtfisher shield is a sheet of niobium, sandwiched between two isolating sheets of fibreglass and wrapped as a roll. The cylindrical roll is however non-continuous, so allows field penetration into its bore. The shield enhances the homogeneity but lowers the current to field ratio. The magnet is wound from four layers of 100 $\mu$m NbTi wire (single superconducting core and CuNi cladded) and it has current to field ratio of 5.24 mT/A with the Hechtfisher shield. This NMR magnet can be persisted. It is operated at a typical current of a 0.6 A giving $^3$He Larmor frequency 100 kHz.
Another advantage of the shield is that it shields transmitter pulses produced by the transmitter coil inside it and transient signals associated with transmitter pulse from the copper body of the main magnet. They would otherwise create serious screening effect. The transmitter coil has a saddle shape depicted in Figure 2.22. It was wound onto a Stycast former out of 105 $\mu$m multi-filament NbTi wire in CuNi clad. Its field to current ratio is: 0.275 mT/A as determined by NMR from the tipping angle dependence and its inductance is 83 $\mu$H.

Transmitter pulses are generated by the NI PXI function generator [33]. Cross diodes prevent leakage of low voltage signals into the line when the pulse is not applied.

2.3.2 A new generation heat capacity cell for measuring YbRh$_2$Si$_2$

A heat capacity cell consists of a few essential components. Apart from the sample itself it requires a heater and a thermometer. Thermal anchoring of the sample to the cryostat is done by either a weak thermal link, or better a heat switch, a device which is able to switch from conducting to non-conducting state. At ultra low temperature physics heat switches are almost exclusively made as superconducting heat switches. An aluminium heat switch for example separates the nuclear stage from the dilution unit and is discussed in section 2.1.2. All the components of the heat capacity cell are mounted on some kind of platform. It is important for the performance of the cell that the heat capacity of the whole setup is dominated by the sample itself, rather than the other components. The addendum heat capacity (which is the heat capacity of the components other than the sample) is measured by simply removing the sample.

When designing the cell for measuring the heat capacity of YbRh$_2$Si$_2$ (YRS) a minimalistic design was chosen. A photography from under a microscope is shown in Figure 2.23. All the components are made out of short lengths of thin wires. They all rest together at the end of a thin plate of alumina which is gaped from the experimental platform. Such design of the heat capacity cell did not allow for a simple measurement of the addendum heat capacity. This measurement would in principle be possible if the sample was cut out from the incoming wires, removed and replaced by a well established material such as silver foil. However, in the first instance this was not done and rather an estimate of the addendum heat capacity compared to the measured data can be seen in section 4.7, Figure 4.54. This approach was motivated by the following reasoning. As we are measuring an extremely heavy fermion material with additional heat capacity coming from nuclear degrees of freedom, other constructional parts should be simple materials with minimum (especially magnetic) impurities, which do not have large nuclear heat capacity. Moreover, the actual physical size of these components should be much smaller compared to the relatively bulky YRS crys-
nal. As can be seen from the photography this was achieved.

Figure 2.23: A photography of the YRS heat capacity cell form under a microscope with the wiring layout sketched. Materials of the components are specified. The blue circle covers the noise thermometer. The red circle covers the heater. The grey arrow points to the superconducting heat switch. Note the arrow specifying the dimension.

The YRS crystal of mass 22.7 mg (52.18 µmol) appears black in the photography and is glued by GE varnish [34] to the alumina support in a shape of a diving board [35]. The sample has relatively flat top. This is because it is a monocrystal. It has a tetragonal structure discussed in section 4.2. The top plane is aligned along the ab-tetragonal plane. As the magnetic field is applied in the vertical direction it is applied in the ab-plane. There also appears to be a corner visible in the left–bottom of the sample. The magnetic field is therefore applied along the tetragonal axes. This might not be important but anisotropy within the ab-plane has not been ruled out yet.

The thermometer measuring sample’s temperature is a noise thermometer (section 2.2.4) and it is the small wire to the left of the sample in the photography. It is made out of Pt₉₂W₈ (shortly PtW) high resistive alloy. The noise thermometer looks flat because the 50 µm PtW wire was squashed in a vice to facilitate spot-welding of wires to it. It is thermalized in the middle to the YRS by a gold wire. The 25 µm gold wire was spot-welded at each end to both materials. The Johnson noise voltage across the PtW wire drives current through the
input coil of a SQUID connected by two Nb wires. These lie side by side inside the cell’s shielded space but outside of the cell are twisted and running inside a thin Nb tube. The resistance of the noise thermometer is 203 mΩ determined by precise measurements at 4 K. This noise thermometer was constructed in a similar way and from the same material as the stage noise thermometer. They also have very similar bandwidth. Their performance is discussed in the noise thermometry section 2.2.4.

The heater is also made out of the PtW alloy and it can be seen above the YRS sample in the photograph. Its resistance is 803 mΩ, dominated by the PtW wire. Heat is produced when current flows across the heater from one side to the other. At one end the PtW wire is spot welded to a Nb lead (I+). At the other end a spot-welded gold link interconnects the PtW and the sample. The current flows across the link and part of the sample and is brought to copper plate at cryostat ground (I-) by an aluminium wire which also serves as the heat switch. Resistances of the gold wire, the sample and the aluminium wire are negligible compared to the PtW and their temperature dependencies therefore unimportant. The heater can be powered by either a current source or a voltage source. For the measurements Keithley 2400 SMU [36] was used as a source of constant current and NI PXI 5441 function generator [33] was used as a source of constant voltage in the form of short pulses. The current line from room temperature includes a cold 100 kΩ resistor mounted on 1K pot to ensure minimal parasitic heating in the cell when the heater is off. The overall resistance of the heater can be measured in-situ by two voltage taps V+ and V-. The wiring scheme of the heat capacity cell can be seen in Figures 2.23 and 2.24.

Thermalization of the YRS to the cryostat is done via aluminium wire ultrasonically wire bonded on both sides. A 50 µm ultra pure Al wire with RRR of about 270 was wedged down with the tip of the wire bonder on the side of the YRS and on the Cu side. The contact resistance Al–Cu was achieved to be negligible but the contact resistance Al–YRS was about 1 mΩ as determined by precise measurement at 4 K and dominated the overall resistance of the link.

The whole cell is mounted inside a magnet which produces field in the ab-plane of the YRS crystal but also goes almost parallel with the Al link. The wire was only mildly bent as suggested by Pobell [2] to avoid flux trapping. By increasing the field above Tc of aluminium (10.5 mT) we drive the heat switch normal and the cell gets thermalized to the cryostat with the time constant given by the YRS heat capacity and conductivity of the normal heat switch, derived using Wiedemann–Franz law (equation 2.25). When the field is lowered below the Tc the aluminium wire goes superconducting and isolates the cell and the cryostat. The slightly larger resistance of the heat switch due to contact resis-
tance turned out to be a happy accident. Thermalisation of the sample took slightly longer but the heat switch still worked as a weak link above $T_c$. That allowed to measure the heat capacity by the relaxation method (section 4.6.3) over a relatively wide temperature range.

![Figure 2.24: A sketch of the heat capacity setup. The sample platform is inserted in a magnet producing field in the ab-plane of the tetragonal YRS crystal. Four wires enter the shielded space on the platform as two twisted pairs, one pair for the noise thermometer, the other for the heater.](image)

The state of adiabatic isolation is best suited for heat capacity measurements, hence alumina was chosen as the material for the mechanical support of the cell. Being made out of grounded sapphire, alumina has very little chance for showing any “glassy”, non-equilibrium behaviour. The size of the Al$_2$O$_3$ grains largely limits the phononic thermal conductivity, which also decays with a relatively large power law at low temperatures. A formula is given in Pobell [2] for temperatures down to 100 mK:

$$\kappa = 0.29 \cdot T^{2.7} \text{[mW/cm K$^{-1}$].}$$

The heat capacity cell rests on a platform which is located inside the magnet. A copper lid can be screwed firmly onto the platform. The setup provides rf-shielding. Moreover the contact groove of the lid and the platform can be painted with epoxy (Stycast 2580 chosen for the first run) that makes the con-
tact leak tight. The lid has a tube sticking from the top which allows the inner space to be pumped out. The rest of the platform was also built to be leak tight.

![Image](image-url)

Figure 2.25: Pictures from the cell build-up. Shown is how the two twisted pairs are wrapped inside the cut thread in the silver epoxy and later on painted over. Apparent is how the small cell is mounted onto the platform and the twisted pairs attached in a type 1 screw terminals. There are type two screw terminals at the bottom of the platform where another two twisted pairs leave for the SQUID and RC filter of the heater.

All four wires needed for the cell pass through a silver epoxy filter, each of length about 82 cm. Both the noise thermometer and the heater leads are twisted forming two twisted pairs which were wrapped about the middle bobbin on the platform. The bobbin had been pre-painted by the silver epoxy and a 0.5 mm pitch double thread had been cut before wrapping the wires and then painting them with the epoxy. The wires are fully covered by the epoxy. The filter provides an extra capacitance to ground, while the ground is resistive (lossy). These filters were measured to have the cut-off frequency of about 100 MHz [37], which corresponds to temperature 1 mK according to Wien’s displacement law:

$$\lambda_{\text{max}} = \frac{2.90 \cdot 10^{-3}}{T} \text{ m} \cdot \text{K}.$$ (2.48)

The noise thermometer wiring is relatively simple, the resistor is connected in parallel with the SQUID receiver coil by all superconducting wires. The heater is grounded via the sample and the heat switch, and this is where the current flows. The aluminium heat switch wire however continues further after making the connection to the ground. It is then spot-welded to a Nb wire, which is the fourth wire entering the shielded space. This serves as the V- probe. The V+ wire detaches the superconducting current line at the mixing chamber level.
The residual parasitic heat leak into the stage was indeed extremely small and close to adiabatic conditions were achieved. The performance of the cell is discussed in section 4.7.

Figure 2.26: Picture of the cell mounted on the cryostat. The magnet is not installed in this image but its posts are visible and so is the RC filter.

2.3.3 A new design of a torsion oscillator cell containing graphene substrate

We discuss a new design of the torsion oscillator, which would incorporate graphene as a substrate for adsorption experiments. Section 3.1 talks about different available substrate materials and emphasises the great potential of graphene for adsorption experiments. The torsion oscillator is thought to be the ideal first attempt to experiment with graphene. In this chapter basic theory of this type of experiment will be given.

A torsion oscillator (TO) works as an extremely sensitive detector of mass and dissipation. It is therefore used for studying quantum phenomena, arising with temperature (superfluidity and supersolidity), in helium in various geometries, accompanied by a decoupling of its mass and changes in its dissipative properties. Torsion oscillators made out of metals (usually alloys) generally have very
high quality factor [38] due to the fact that elastic processes in metals are of low dissipation [39].

An ideal version of a TO consists of a torsion rod, characterised by its torsion constant $k$ and a massive object, attached to one end of the torsion rod, characterised by its moment of inertia $I$ (with respect to the axis given by the torsion rod). The centre of mass of the massive object (from now on called either torsion head or torsion body) generally lies on the torsion axis. The mathematical problem of a mass on a spring fully describes the torsion oscillator as long as the rod has a negligible moment of inertia $I_{\text{rod}}$ compared to $I$ and the elastic constants of the torsion head are characterised by much larger constants $k_{\text{head}}$ than $k$. For TOs discussed here, this condition is always fulfilled due to the major size difference between the head/body and the rods and the high power dependence of the torsion constant and the moment of inertia on radius. A rod with diameter $a$, length $L$, made out of material with shear modulus $G$ has a torsion constant [38]:

$$k = \frac{\pi Ga^4}{32L}. \quad (2.49)$$

The torsion head and body are usually cylindrical. Their moments of inertia are then:

$$I = \frac{mr^2}{2} = \frac{\pi \rho hr^4}{2}, \quad (2.50)$$

where $m$ is their mass, $\rho$ the density and $h$ the height. The oscillator’s resonant frequency is:

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{I}}. \quad (2.51)$$

Both $I$ and $k$ scale to the fourth power of the radial extent of the oscillator (dimensions $a$ and $r$); in other words, the object is radially scalable while maintaining the resonant frequency. The system is not however vertically scalable; an increase of $h$ causes an increase of $f$, while an increase of $L$ causes the decrease of $f$.

TOs used at Royal Holloway in the past have mostly been made out of coin silver. The shear modulus of coin silver has been determined from the behaviour of a torsion oscillator [40] to be $G = 33$ GPa, which is slightly more than 24 GPa for pure Ag and less than 53 GPa for BeCu, another frequently used material. The diameter of standard torsion rods is around 1 mm and their length 1 or 2 mm. That gives: $k \sim 1$-10 Nm.

Both the head and the body of the TO are usually cylindrical shape with both the radius and the height less than 1 cm. The density of coin silver is $10370 \, \text{kg/m}^3$. So their moment of inertia is around $2 \cdot 10^{-7}$ kg m$^2$. 
A common design of the torsion oscillator is the so-called two–stage torsion oscillator (TSTO, figure 2.28). It consists of the torsion head (with moment of inertia $I_2$), interconnected by head’s torsion rod (stiffness $k_2$) with the torsion body. The body has the moment of inertia $I_1$ and is connected by body’s torsion rod (stiffness $k_1$) to the cryostat, or alternatively to another very low natural frequency torsion object called an isolator. An isolator does not influence the resonant frequencies of the two stage oscillator (as we will show), and shields the object from parasitic vibrational noise of the cryostat. The analogy of two masses on two springs in series applies for the TSTO (figure 2.27). We omit dissipation at this stage; thus the system is described by the following two equations of motion:

\[ k_1 x_1 + k_2 (x_1 - x_2) = \Gamma_d - I_1 \ddot{x}_1, \]  
\[ k_2 (x_2 - x_1) = -I_2 \ddot{x}_2. \]  

The drive is assumed to be harmonic, with angular frequency $\omega$:

\[ \Gamma_d = f e^{i\omega t}, \]  
and we therefore seek the solution of the given set of equations in the form:

\[ x_1 = X_1 e^{i\omega t}, \]  
\[ x_2 = X_2 e^{i\omega t}. \]  

The two differential equations now turn into two algebraic equations. In a
matrix form, the natural frequencies of the TSTO can be found as eigenvalues and a displacements ratio \( X_2/X_1 \) as eigenvectors of the matrix. A detailed derivation can be found in [41]. The two eigen-frequencies are:

\[
\omega_{a/s} = \sqrt{\frac{1}{2} \left( \frac{k_1}{I_1} + \frac{k_2}{I_2} \right) \pm \sqrt{\frac{1}{4} \left( \frac{k_1}{I_1} + \frac{k_2}{I_2} \right)^2 - \frac{k_1 k_2}{I_1 I_2}}}.
\]  (2.57)

where the frequency with the plus (minus) sign is called the antisymmetric (symmetric) mode. The antisymmetric mode always oscillates at higher frequency than the symmetric mode. They are thus called, as the eigenvectors corresponding to these eigenvalues are:

\[
\frac{X_2}{X_1}_{a/s} = \frac{1}{2} \left[ \left( 1 + \frac{k_1}{k_2} - \frac{I_1}{I_2} \right) \mp \sqrt{\left( 1 + \frac{k_1}{k_2} + \frac{I_1}{I_2} \right)^2 - 4 \frac{k_1 I_1}{k_2 I_2}} \right].
\]  (2.58)

As the square root term is always greater than the first term, the ratio \( \frac{X_2}{X_1} \) is negative (positive) for the antisymmetric (symmetric) mode, in other words the two stages rotate with opposite phase (in phase).

Let’s define two frequencies: \( \omega_2 \) and \( \omega_1 \). Simply said, they are the characteristic frequencies of the top and bottom stages, should the other stage not be present:

\[
\omega_1 \equiv \sqrt{\frac{k_1}{I_1}},
\]  (2.59)

\[
\omega_2 \equiv \sqrt{\frac{k_2}{I_2}}.
\]  (2.60)

The eigenvectors can be expressed using the frequency \( \omega_2 \):

\[
\frac{X_2}{X_1}_{a/s} = \frac{1}{1 - \omega_{a/s}^2/\omega_2^2}.
\]  (2.61)

Should any of the modes be ever equal to \( \omega_2 \), the amplitude of the top stage’s oscillation would be maximised, while the bottom stage’s amplitude would be zero.

Equations 2.58 only depend on the ratios \( k_1/k_2 \) and \( I_1/I_2 \), while equation 2.57 does not. The ratio \( \omega_a/\omega_s \) can however be proved to be only dependent on the ratios \( k_1/k_2 \) and \( I_1/I_2 \). And additionally, the resulting formula is also symmetric in \( k_1/k_2 \) and \( I_1/I_2 \). That means that interchange of \( k_1/k_2 \) and \( I_1/I_2 \) won’t change \( \omega_a/\omega_s \). The formula and numerical simulations proving the symmetry can be again found in [41].

46
Sensitivity of two-stage torsion oscillator

TSTO usually have the following physical arrangement. The head of the TSTO contains the He sample and therefore $I_2$ consists of the $I_{He}$ from the He sample and $I_{add}$, the addendum moment of inertia. The addendum part arises from the mass of the He substrate (if any) and masses and geometry of all structural parts of the head. If we intend to measure the decoupling of the He mass due to effects like superfluidity and supersolidity, we need to make sure the oscillator is sensitive enough to see the decoupling. We establish $I_{He}/I_2$ from the geometry of the TO. It’s typically $\sim 1 \cdot 10^{-7}$. We also know the ultimate frequency resolution of the TSTO used in the past. It is caused by frequency drifts over time and it is known that it was better than one in a billion ($1 \cdot 10^{-9}$). This is due to experimental electronics, noise, dissipation etc. The value $10^{-7}$ is obviously larger than the value $10^{-9}$. However, the question is how the value $I_{He}/I_2$ will be translated into the resolution of the two torsion modes. One way to approach this question is to simply use equation 2.57 and calculate:

$$\zeta_{a/s} = \frac{\Delta f_{a/s}}{f_{a/s}} = \frac{f_{a/s}(k_1, k_2, I_1, I_{add}) - f_{a/s}(k_1, k_2, I_1, I_2)}{f_{a/s}(k_1, k_2, I_1, I_2)}.$$

(2.62)

The calculated quantity is dimensionless and can be directly compared to the ultimate resolution. In a well designed oscillator, $\zeta_{a/s}$ should be about 100 times the ultimate resolution so that the TO will be able to distinguish decoupling of 1% of the sample.

However to study the mathematical properties of the TSTO’s sensitivity we need to find out a mathematical object that will have the properties of $\zeta_{a/s}$ but will also be derived from equation 2.57 analytically and will be dependent on the same set of variables. It can be shown by numeric comparison with equation 2.62 how the best candidate is a logarithmic derivative of $\omega_{a/s}$ with respect to...
I_2. Precisely speaking it is its negative value, we will call parameter \( \beta \). So from now on define the sensitivity of the antisymmetric mode as:

\[
\beta \equiv -\frac{\partial \ln \omega_a}{\partial \ln I_2} = -\frac{I_2}{\omega_a} \frac{\partial \omega_a}{\partial I_2}.
\]

Similarly we say the sensitivity of the symmetric mode is:

\[
\beta' \equiv -\frac{\partial \ln \omega_s}{\partial \ln I_2} = -\frac{I_2}{\omega_s} \frac{\partial \omega_s}{\partial I_2}.
\]

Document [41] proves the resolutions of the two modes add up to a value 1/2. The resolution of the symmetric mode is then:

\[
\beta' = \frac{1}{2} - \beta.
\]

At this moment we should emphasise the significance of the 1/2 limit. Let’s therefore look at the resolution of a single stage TO:

\[
I \frac{\partial}{\partial I} \left( \frac{\sqrt{k/I}}{\omega} \right) = -\frac{1}{2} \frac{I}{\sqrt{k/I}} \sqrt{\frac{k}{I}} = -\frac{1}{2}.
\]

Note that the resolution of a single stage TO is completely independent of its construction (and its natural frequency). We therefore see the TSTO distributes the maximal sensitivity of 1/2 into its two modes, while none of them ever exceeds it. When one mode reaches the maximal value, the other mode becomes entirely non-sensitive to changes of \( I_2 \).

When the derivative of equation 2.57 with respect to \( I_2 \) is done, we get the \( \beta \) factor explicitly:

\[
\beta = \frac{\left( \omega_a^2 - \omega_s^2 \right)}{2 \left( \omega_n^2 - \omega_s^2 \right)}.
\]

The maximum resolution of the antisymmetric mode is reached should its frequency equal to the characteristic frequency of the top stage (\( \omega_2 \), definition 2.60). Note that the very same condition maximises the \( X_2/X_1 \) ratio (equation 2.61). We will later show when this is the case.

From equation 2.65 the resolution of the symmetric mode is:

\[
\frac{1}{2} - \beta = \frac{\left( \omega_n^2 - \omega_s^2 - \omega_2^2 + \omega_2^2 \right)}{2 \left( \omega_n^2 - \omega_s^2 \right)} = \frac{\left( \omega_n^2 - \omega_s^2 \right)}{2 \left( \omega_n^2 - \omega_s^2 \right)}.
\]

**Dissipation in two-stage torsion oscillator**

Having examined the logarithmic derivatives of \( \omega_a/\omega_s \) with respect to \( I_2 \), one might ask a question what significance would derivatives with respect to \( I_1 \) and also \( k_{1/2} \) have. Unless the parameters change their values during the experiment due
to the studied sample (or for any other reason), these derivatives do not describe
the sensitivity of the device. Yet they are extremely useful to account for losses
from various places of the TO and their contribution to the observed losses on
both torsion modes. We can include the dissipative character of constants \( k_{1/2} \)
and \( I_{1/2} \) by small imaginary addendums to these parameters [41]:

\[
K_1 = k_1 \left( 1 - \frac{i}{Q_{k1}} \right),
\]

\[
K_2 = k_2 \left( 1 - \frac{i}{Q_{k2}} \right),
\]

\[
I_1 = I_1 \left( 1 + \frac{i}{Q_{I1}} \right),
\]

\[
I_2 = I_2 \left( 1 + \frac{i}{Q_{I2}} \right).
\]

Quantities \( Q_{k1/2} \) and \( Q_{I1/2} \) we call the Q factors characterising the given
structural part of the TSTO. They can have various physical origin but we can
as an example give: the shear modulus of a metal is a dynamic modulus and has
a small imaginary part which describes the attenuation of the torsion motion
and becomes significant only at high enough frequency oscillation of the metal.

We would now like to express the dissipation of both torsion modes: \( 1/Q_{a/s} \)
using \( Q_{k1/2} \) and \( Q_{I1/2} \). It is best done again using the logarithmic derivatives.
Following equations present in 8 derivatives, fully describing the problem, with
inner relationships that can be found [41]:

\[
\frac{\partial \ln \omega_a}{\partial \ln I_2} = -\beta,
\]

\[
\frac{\partial \ln \omega_a}{\partial \ln I_1} = \frac{\partial \ln \omega_s}{\partial \ln I_1} = \frac{\partial \ln \omega_s}{\partial \ln I_2} = \beta - \frac{1}{2},
\]

\[
\frac{\partial \ln \omega_a}{\partial \ln k_2} = \frac{\partial \ln \omega_s}{\partial \ln k_1} = \alpha,
\]

\[
\frac{\partial \ln \omega_a}{\partial \ln k_1} = \frac{\partial \ln \omega_s}{\partial \ln k_2} = \frac{1}{2} - \alpha.
\]

The parameter \( \alpha \) is explicitly:

\[
\alpha = \frac{\left( \omega_a^2 - \omega_1^2 \right)}{2 \left( \omega_a^2 - \omega_s^2 \right)}.
\]

The dissipation of the symmetric and antisymmetric modes due to dissipation
in the torsion rods is expressed with the help of parameter $\alpha$:

$$
\frac{1}{Q_a} = (1 - 2\alpha) \frac{1}{Q_{k1}} + 2\alpha \frac{1}{Q_{k2}}, \quad (2.78)
$$

$$
\frac{1}{Q_s} = 2\alpha \frac{1}{Q_{k1}} + (1 - 2\alpha) \frac{1}{Q_{k2}}. \quad (2.79)
$$

The dissipation of the symmetric and antisymmetric modes due to dissipation in the head and body is expressed with the help of parameter $\beta$:

$$
\frac{1}{Q_a} = (1 - 2\beta) \frac{1}{Q_{I1}} + 2\beta \frac{1}{Q_{I2}}, \quad (2.80)
$$

$$
\frac{1}{Q_s} = 2\beta \frac{1}{Q_{I1}} + (1 - 2\beta) \frac{1}{Q_{I2}}. \quad (2.81)
$$

An interesting feature of the parameters $\alpha$ and $\beta$ is, that:

$$
\alpha > \beta. \quad (2.82)
$$

It follows from their definition. Multiplying by their identical denominator (known to be positive from 2.57):

$$
\omega_a^2 - \omega_s^2 > \omega_2^2 - \omega_s^2, \quad (2.83)
$$

$$
\omega_a^2 + \omega_s^2 > \omega_2^2 + \omega_1^2, \quad (2.84)
$$

$$
\frac{k_1}{I_1} + \frac{k_2}{I_1} + \frac{k_2}{I_2} > \frac{k_2}{I_2} + \frac{k_1}{I_1}, \quad (2.85)
$$

$$
\frac{k_2}{I_1} > 0, \quad (2.86)
$$

which is true.

If we again recall the unit of interest $\omega_a = \omega_2$ we see the dissipation of the antisymmetric mode would only be given by the properties of the top stage (the head and its rod). The head is not driven and has no electrodes attached. Therefore, it is geometrically much simpler, so we might think this is the limit for the antisymmetric mode, because its Q factor wouldn’t be spoiled by losses in the torsion body. However, we have yet to show when is this condition fulfilled. It will be done in the next section, with the proposed graphene TSTO in mind.

**Behaviour of TSTO based on their $I_2/I_1$ and $k_2/k_1$ ratios**

We have given the theory describing the properties of a TSTO. We shall now compare a so-called traditional design, which can be seen in Figure 2.29 for instance, to a newly proposed design in which the head of the torsion oscillator is significantly lighter than the body. The dimensions and specifics of the traditional design will be illustrated by TO used at Royal Holloway in the past by to
study thick helium films Antonio Córcoles [43, 40, 44].

Figure 2.30: Numerical simulation of TSTO. Ratio of the two characteristic frequencies against the $I_2/I_1$ ratio. Different lines correspond to different $k_2/k_1$ ratios. Dotted lines are characteristic frequencies of the top stage for a given torsion strength $k$. The two dots denote position of the design by Antonio and the new design proposed here.

It has been shown that the following properties of the TSTO depend only on the $I_2/I_1$ and $k_2/k_1$ ratios. It is the ratio of oscillatory amplitudes $\frac{X_2}{X_1}$ in equation 2.58 and the ratio $\omega_a/\omega_s$ which can in its explicit form be found in [41]. Being dependent merely on these two ratios is quite useful for comparing multiple TSTO differing in all structural parameters. It can so be done in a single graph, where the x-axis is one of the ratios and the multiple plot lines correspond to selected values of the other ratio.

The four following graphs will show the dependency of different quantities on the ratio $I_2/I_1$. The three lines in each graphs (Figures 2.30, 2.31, 2.32, 2.33) correspond to varying values of $k_2/k_1$: the middle one (grey) is $k_2 = k_1$, the small value (green) is a value close to the new design, $k_2 = 0.16k_1$, and finally the large value (red) is a value close to Antonio’s TO, $k_2 = 3.8k_1$. Design of Antonio and the new design are highlighted by points of appropriate colour in all the four figures. The complete numerical set of $k_1$, $k_2$, $I_1$ and $I_2$ for the two designs is given in Table 2.2. Note that they can differ slightly from the values used in the simulation.
Figure 2.31: Numerical simulation of TSTO. Ratio of the amplitudes against the $I_2/I_1$ ratio. Note that the antisymmetric mode amplitude ratio is plotted with inverse sign to be positive.

Figure 2.30 gives values of $f_a/f_s$ corresponding to the $I_2/I_1$ and $k_2/k_1$ ratios. One can see, that $f_a/f_s$ always has a minimum at certain value of $I_2/I_1$. Below the minimum the symmetric mode has constant frequency and the antisymmetric mode rises in frequency. Above the minimum the opposite is happening. This is shown by the use of the dotted line by which the value of $f_2/f_s$ is shown. They are also there to show in what limit $f_a \to f_2$.

It is interesting to see that the $f_a$ and $f_s$ can get arbitrarily close to one another in the following case. The conditions are that we have a small mass on a weak torsion rod on top of a big mass on strong torsion rod (corresponds to $k_2 I_2 \ll k_1 I_1$) and at the same time $\omega_2 = \omega_1$. The frequency difference between the two modes is caused by the factor after the ± sign in equation 2.57. For this case:

$$\sqrt[4]{\frac{1}{4} \left(2\omega_2^2 + 0\right)^2 - \omega_2^4} = 0.$$  \hspace{1cm} (2.87)

We call this case a doubly degenerate TSTO and is of no experimental interest. Let’s also show that a two stage oscillator composed out of two identical rods and two identical mass objects ($\frac{k_2}{I_2} = \frac{k_2}{I_2} = \frac{k_1}{I_1}$) will always have the two
modes separated:
\[ \sqrt[4]{\frac{1}{4} (3\omega_2^2 - \omega_1^2)^2} = \sqrt{\frac{5}{4} \omega_2^2}. \] (2.88)

Figure 2.31 shows the amplitude ratios of the antisymmetric and symmetric mode, where the antisymmetric mode is plotted with opposite sign to be positive. One can see that in case of Antonio’s design, the oscillation of the head was only a couple of times larger amplitude than the oscillation of the body. Compared to that, in the new proposed design, the torsion head should oscillate 1000 times more than the body.

![Figure 2.32](image-url)  
Figure 2.32: Numerical simulation of TSTO. Sensitivity of the two characteristic frequencies (given by parameter \( \beta \) and 1/2-\( \beta \)) against the \( I_2/I_1 \) ratio.

Figure 2.32 shows calculated sensitivity of the two modes from equations 2.67 and 2.68. Dotted is the value 1/2, which corresponds to the sensitivity of a single stage TO. Antonio’s design of the TSTO allows to measure both modes but is compromised by smaller sensitivity. The new design only allows to measure on the antisymmetric mode, but the sensitivity approaches the largest possible value 1/2.

Figure 2.33 shows the parameters \( \alpha \) and \( \beta \) in comparison. It is apparent from this plot that the \( \alpha \) parameter is always larger than the \( \beta \) parameter, as has been proven.
Traditional design of TSTO and its advantages

Table 2.2 shows in its second column the properties of Antonio’s TO in their exact value. In this section we shall illustrate the advantages of this so-called traditional design.

First of all, the oscillator has the two torsion modes, reasonably well separated in frequency (Figure 2.30). Secondly, the resolution of the two modes is comparable (figure 2.32). These features together allow one to measure frequency dependence of the decoupling and dissipation properties of studied He sample. Thirdly, and visible from figure 2.33, the $\alpha$ parameter being very close to $1/2$ means that the dissipation of the antisymmetric mode is mostly given by the head torsion rod and the dissipation of the symmetric mode is mostly given by dissipation in the body rod.
Table 2.2: Summarised parameters of a traditional TSTO and parameters for proposed “light head” torsion oscillator.

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Antonios oscillator</th>
<th>New proposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_2$ [Nm]</td>
<td>13.6</td>
<td>1.6</td>
</tr>
<tr>
<td>$k_1$ [Nm]</td>
<td>3.6</td>
<td>10.3</td>
</tr>
<tr>
<td>$I_2$ [kgm$^2$]</td>
<td>$1.1\times10^{-7}$</td>
<td>$6.5\times10^{-9}$</td>
</tr>
<tr>
<td>$I_1$ [kgm$^2$]</td>
<td>$2.2\times10^{-7}$</td>
<td>$2.6\times10^{-6}$</td>
</tr>
<tr>
<td>$\omega_a^2$ [$(\text{rad/s})^2$]</td>
<td>1.2\times10^8</td>
<td>2.5\times10^8</td>
</tr>
<tr>
<td>$\omega_s^2$ [$(\text{rad/s})^2$]</td>
<td>1.6\times10^7</td>
<td>4.0\times10^6</td>
</tr>
<tr>
<td>$f_2$ [Hz]</td>
<td>1772</td>
<td>2516</td>
</tr>
<tr>
<td>$f_1$ [Hz]</td>
<td>643</td>
<td>318</td>
</tr>
<tr>
<td>$f_a$ [Hz]</td>
<td>2201</td>
<td>2526</td>
</tr>
<tr>
<td>$f_s$ [Hz]</td>
<td>518</td>
<td>316</td>
</tr>
<tr>
<td>$\frac{f_a}{f_s}$</td>
<td>$2.8\times10^{-7}$</td>
<td>$6.2\times10^{-8}$</td>
</tr>
<tr>
<td>$\zeta_a$</td>
<td>$9\times10^{-8}$</td>
<td>$3\times10^{-8}$</td>
</tr>
<tr>
<td>$\zeta_s$</td>
<td>$5\times10^{-8}$</td>
<td>$8\times10^{-11}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.484</td>
<td>0.5000</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.313</td>
<td>0.4987</td>
</tr>
</tbody>
</table>

Version of torsion oscillator with miniaturised head

Highlighted by the green dot in the figures is a different type of TSTO. Even though its two modes have a very similar characteristic frequencies $\omega_a$ and $\omega_s$ to Antonio’s TO, their sensitivity is completely different. The antisymmetric mode has the maximum sensitivity of $1/2$, characteristic for a single stage TO, while the symmetric mode has sensitivity at least 1000 times worse. We see from the graphs that the moment of inertia of the head is only $\sim 100$ times smaller than the body’s moment of inertia. To have a rigorous proof of what happens when the torsion head is much lighter than the body an expansion of $\omega_a/s$ and $X_2/X_1|_{a/s}$ in terms of $I_2/I_1$ has been done [41]:

$$\omega_a^2 = \frac{k_2}{I_2} \left[ 1 + \frac{I_2}{I_1} + \frac{k_1}{k_2} \left( \frac{I_2}{I_1} \right)^2 + \ldots \right], \quad (2.89)$$

$$\omega_s^2 = \frac{k_1}{I_1} \left[ 1 - \frac{I_2}{I_1} - \frac{k_1 - k_2}{k_2} \left( \frac{I_2}{I_1} \right)^2 + \ldots \right]. \quad (2.90)$$

Considering just the absolute and linear term, if the head has 100 times smaller moment of inertia than the body, the antisymmetric mode is at $\omega_2$ and symmetric mode is at $\omega_1$ to better than 1% precision. The displacement ratios are:

$$-\frac{X_2}{X_1} \bigg|_{a/s} = \frac{I_1}{I_2} \left( \frac{k_1}{k_2} + \frac{k_1 I_2}{k_2 I_1} + \frac{k_1 (k_1 - k_2)}{k_2 (k_2 - 1)} \left( \frac{I_2}{I_1} \right)^2 \right) + \ldots, \quad (2.91)$$
$$\frac{X_2}{X_1} = 1 + \frac{k_1 I_2}{k_2 I_1} + \frac{k_1}{k_2} \left( \frac{k_1}{k_2} - 1 \right) \left( \frac{I_2}{I_1} \right)^2 + \ldots \quad (2.92)$$

Considering just the absolute term, the antisymmetric mode diverges in the amplitude ratio, unless the factor $k_1/k_2$ compensates the value of $I_1/I_2$. That would be the case if the light torsion head was on top of a soft torsion rod such that: $\omega_2 = \omega_1$. This is the double degenerate case of TSTO which was already mentioned to have no experimental potential.

Now we can with certainty say that the frequency of the antisymmetric mode of the proposed TO is very close to $\omega_2$ (within 1%). The most important consequences of that are the following: Firstly, as we have seen in equation 2.61 the amplitude of the top stage to the bottom stage is maximised for this mode (figure 2.31). Secondly, parameters $\alpha$ and $\beta$ are both almost exactly equal to 1/2 (see table 2.2) which means, according to equations 2.78 and 2.80 the dissipation of the antisymmetric mode is given purely by the Q factors of the head torsion rod and head itself. And thirdly, $\beta$ being so close to 1/2 also means the derivative: $\frac{\partial \ln \omega_a}{\partial \ln I_1}$, expressing the sensitivity to changes of $I_1$ is zero (equation 2.74), and therefore the antisymmetric mode will not be sensitive to the helium mass (and its dissipative properties) adsorbed on the inner surface of the torsion body.

**Scientific motivation for the small head TSTO**

When approaching the design of a torsion oscillator with a graphene substrate, one might hold on to the design that had already worked in the past and attempt to modify it to accommodate graphene. However, with grafoil there is a contra–argument to this approach. If we indeed use the CVD graphene, grown on 18 $\mu$m Cu foil from Graphenea [45], or a similar commercially available graphene, there is going to be a minimum $I_{He}/I_2$ ratio of $6.7 \times 10^{-7}$ (for a monolayer of $^3$He), just due to the mass of copper. Additionally, any joints between the Cu foil and the rigid body of the head are going to add weight and of course the outer shell of the head is also going to add weight. A realistic design of a torsion oscillator containing many Cu foils (with graphene grown on both sides) inside its torsion head has been done. A minimum of 100 foils have to be carefully stacked into the head, separated by a precise height spacers, and they have to be mechanically and thermally anchored to the oscillators construction. It is also desirable, to have the foils free of any strain and the whole assembly axially symmetric. A major problem can be that the Cu foils in the commercially available graphene probably have not been treated with any extra precaution, to prevent the mechanical strain. The whole problem conspicuously reminds us of the very first torsion oscillator by Andronikashvili, which is known to have been very difficult to manufacture and in which the Q factor was in no way comparable to modern torsion oscillators. Last but not least, the price of the graphene itself would be
around 1200 USD for the 100 foil cell, based on current market prices of graphene.

The question then arises, what would happen if the head consisted of a single Cu foil with graphene on both sides and no outer shell of the head was needed. The answer is that it would be ideal for the $I_2/I_1$ ratio, but the oscillator would lose its ability to measure on two different frequencies, because it would inevitably lead to the “light head” case of TSTO, introduced in this chapter: $I_2 \ll I_1$.

One can however abandon any attempt to measure the frequency dependence with a single instrument within a single run. Although this would be desirable for the study of 2D $^4$He supersolid films, it is not so important for work on putative 2D $^3$He superfluid films. The frequency dependence can for instance be measured by a set of torsion oscillators, with varying torsion rods. Then the idea of a single foil oscillator can be explored.

![Figure 2.34: Sketch of the light head TSTO with the head enclosed inside the body. Cut view and top view in 1:2 ratio to the cut view.](image)

As the experiment relies on adsorption of He onto a substrate, it is obvious that the graphene substrate has to be enclosed in a leak tight container. If the head is a single foil with graphene on it, the only object that can serve as the container is the oscillator’s body. Figure 2.34 shows such design. Shown by blue is the graphene substrate. It is a 250 $\mu$m sapphire wafer (the choice of sapphire will be explained later), with Cu layer deposited on both its sides. The graphene
Graphene substrate design

It is discussed in section 3.1 that most available graphene is compromised by the so-called wrinkling pattern. In recent years a lot of effort has been put into inventing a manufacturing process that would produce wrinkle free graphene. One of the ways to do that is to thermally deposit Cu on the surface on a sapphire (c-cut, direction 0001). The deposited Cu has the preferred (111) orientation naturally, which is ideal for the graphene growth. The graphene grown on this substrate has very fine (wrinkle free) quality [46].

Furthermore as previously discussed, relying on metal foils as the structural part for the TO’s head might not be ideal. The foils can be full of mechanical strain. This can negatively influence the $Q$ factor. This is mitigated by the use of sapphire.

A thin metal foil will have undesired bending modes (sometimes called the drumhead mode) [47]. These modes are solutions to the equilibrium equation:

$$
\rho \frac{\partial^2 \xi}{\partial t^2} + \frac{E h^3}{12(1-\nu^2)} \Delta^2 \xi = 0.
$$

The coefficient $\frac{E h^3}{12(1-\nu^2)}$ is called flexural (cylindrical) rigidity. The dispersion relation is:

$$
f = \frac{k^2}{2\pi} \sqrt{\frac{D}{\rho h}} = \frac{k^2}{2\pi} \sqrt{\frac{E h^2}{12\rho (1-\nu^2)}},
$$

where $E$ is the Young’s modulus, $\nu$ Poisson’s ratio (typically 0.3 for most materials), $\rho$ is the 3D density and $k$ the wave number in units [m$^{-1}$]. Whether the drumhead mode spectrum is discrete or continuous depends on boundary conditions. A circular foil anchored in its centre is going to have a discrete spectrum. The foil’s centre is the node and the perimeter oscillates up and down. One of the boundary conditions is the node at the centre and the other is the perimeter having the stress tensor equal to zero. We will call the fundamental mode a mode with $k = \frac{1}{4\pi}$. The fundamental drumhead mode for the 18 $\mu$m Cu foil is about 8 Hz, which is about 200 time less than the torsion mode. One might imagine an enormous variety of higher harmonic frequencies that could coincide with the torsion mode.
Systems with small dissipation [39] states that the best material to make a resonator out of is sapphire (leucosapphire with minimum amount of metal impurities). The dissipative processes in sapphire are minimised due to low dislocation mobility. This means the natural modes of objects made out of sapphire are of high $Q$ and therefore narrow–band in frequency. It also means, elastic waves, if they get excited, will not dissipate much of their stored energy. So even if the drumhead mode gets excited, it should not deteriorate the torsion motion.

The fundamental drumhead mode for a 430 $\mu$m sapphire wafer (Graphenea product) is about 245 Hz, which is 10 times less than the torsion mode and therefore much safer region.

Another advantage of sapphire, compared to Cu is that is has 2.3 times lower density, 3.3 times bigger shear modulus and 2.9 times bigger Young’s modulus. It is therefore highly advantageous that the sapphire is suitable both for high quality graphene growth and for construction of high quality torsion oscillator.

Conclusion

The proposal is to build a two stage torsional oscillator, effectively working like a single stage oscillator. The presented theory and simulations intend to prove such design possible, and can be done by having much “lighter” torsion head compared to the oscillator’s body. While the body is driven at the frequency $\omega_2 = \omega_a$ the amplitude of its oscillations is very small. The head on the other hand oscillates freely with the oscillations amplitude being maximised. Additionally, dissipation on the antisymmetric mode is only given by the quality factor of the head and its rod.

The following reasons argue for this design:

• It was theoretically proven that a TSTO can actually work like a single stage TO with all its advantages: The characteristic frequency ($\omega_a = \omega_2$) is only given by the moment of inertia of the head and the stiffness of the head’s torsion rod and it is not influenced by the properties of the body. Similarly, neither is the $Q$ factor of this characteristic frequency influenced by elastic properties of the body.

• Unlike in the case of a true single stage TO, in the proposed design there is no need to drive the head into the torsion motion, instead the body is driven at the characteristic frequency and the head resonates.
• On the other hand the oscillations of the head need to be measured as the body remains insensitive to the behavior of the head.

• Two stage oscillators have not always been successful in working well in the symmetric mode.

• The frequency dependence of the possible He mass decoupling and dissipation properties can be measured by having a set of torsion oscillators (or just their parts) with varying $k_2$ and measuring them in different experimental runs, rather than having one with multiple modes.

• Arising from the very essence of the adsorption experiment an outside container surrounding the substrate is needed for having the cell leak tight. Rather than letting the container contribute to the dummy mass of the torsion head (and thus lowering the overall sensitivity) it can serve as the oscillator’s body.

• A torsion oscillator containing a single substrate foil rather than at least 100 of them is much cheaper and easier to make.

• The proposed design is compatible with optimal conditions for a graphene substrate.
3.1 Physical adsorption

The phenomenon of physical adsorption is the tendency of atoms and molecules to become bound on the surface of the substrate due to van der Waals forces. The continuum of adsorbed particles on the surface is sometimes referred to as the adsorbed film. By the nature of the van der Waals forces, the adsorption is fully reversible, temperature dependant and the adsorption potential is given purely by the properties of electron shells of the adsorbed particles and the substrate. The adsorption potential itself is therefore the same for both isotopes of helium. One of the possible numerical forms of the potential for the helium - graphite interaction was proposed by Joly [48]:

$$ V(z) = Ae^{(-\alpha z)} - \frac{C_3}{z^3} - \frac{C_4}{z^4}, $$

(3.1)

with $A = 195.315 \text{ eV}$, $\alpha = 3.715 \text{ Å}^{-1}$, $C_3 = 157.7 \text{ meV Å}^3$ and $C_4 = 888.07 \text{ meV Å}^4$. Even though the adsorption potential is the same for both helium isotopes, the zero point energies are not, due to their different masses. Figure 3.1 shows the adsorption potential and the ground state energies for both isotopes.

The strength of the potential in the z-direction varies laterally due to substrate’s crystal structure (honeycomb for the surface of graphite, which can be thought of as stacked layers of graphene). We call this substrate corrugation. In case of graphite and He the corrugation of the substrate potential is about 40 K. The corrugation can support formation of solid registered phases. It also leads to formation of energy band for a single adsorbed helium atom moving freely over the surface, with a typical width 10 K, and effective mass: $m^*/m \simeq 1.03$ (1.06) for $^3\text{He}$ ($^4\text{He}$) [49].
Adsorbed He atoms interact with each other at higher densities. Noble gases also interact via the van der Waals interaction, but the interaction potential is much weaker than the adsorption potential. Due to short range atomic repulsion, layering occurs. Since $^4\text{He}$ atoms are more strongly bound to the graphite substrate, it is possible to pre-plate the substrate with $^4\text{He}$ and then prepare the further layers with flexible composition of helium isotopes. Pre-plating results effectively in a composite substrate with reduced adsorption potential of graphite and its corrugation. It can also limit the effect of imperfections like edges and steps, present in any substrate.

![Graph showing Adsorption potential](image)

**Figure 3.1:** Adsorption potential of a He atom to a graphite surface, averaged over the corrugation potential. Generated using equation 3.1. Ground state energy levels of $^4\text{He}$ and $^3\text{He}$ atoms -142 K and -136 K respectively are shown too [49].

Growth of the adsorbed film can be relatively easily studied by precise measurements of vapour pressure ($P$) at constant temperature. These measurements are called *adsorption isotherms*. In equilibrium, the chemical potential of the adsorbed phase must equal the chemical potential of the gas:

$$
\mu(T) = k_B T \ln \left[ \frac{P_0(T)}{P} \right],
$$

where $P_0(T)$ is the saturated vapour pressure. By adding atoms in small doses and measuring the pressure as a function of atoms added ($n$) one can either study unknown properties of the adsorbed system, if the surface area is known; or measure the surface area of a well established substrate by looking for a known features in the $P$ vs. $n$ dependence [50]. Al adsorption cells on ND1 cryostat have been characterised by the adsorption isotherm at 4.2 K. Figure 3.3 shows the latest such measurement. The aim is to find the so-called B-point which
marks the completion of the first layer. When the layer is completed the vapour pressure starts to increase much more sharply due to reduction of the binding energy in the second layer [51]. The coverage scale adopted is to define this fiducial point as corresponding to a first layer density 11.4 nm\(^{-2}\), based on neutron scattering results [52, 53]. It has been used consistently across many different sample chambers. Different experimental groups adopt slightly different coverage scales, which must be borne in mind when comparing data from different experiments.

Figure 3.2: A simple schematic of one possible super-lattice of mono-atomic gas, adsorbed on graphite. The black arrows are the lattice vectors of the graphite, the red arrows are lattice vectors of the adsorbed gas. The super-lattice vectors are rotated by 30° and are $\sqrt{3}$ times the length of the graphite lattice vectors. It is a commensurate structure, 1/3 of the graphite honeycombs are covered. This is a well known structure, observed experimentally [54].

The B-point is apparent on the plot of amount of admitted He vs. vapour pressure as a change of behaviour from non-linear below the B-point to linear above the B-point. Correction for the dead volume of the cell must be made. It is quite large even though the fill line of the cell is quite thin. This is of course due to the fact that a big portion of the dead volume is at low temperature. Thus even though the physical volume of the fill line does not change, the gas volume expressed as the volume the particular amount of gas would have at standard pressure and temperature (STP) changes rapidly with temperature. Our dead volume is about 310 cm\(^3\) STP, when the sample is at 4.2 K. The surface area of the cell was determined to be 12.2 ± 0.1 m\(^2\).
Figure 3.3: $^4$He isotherm at 4200 ± 1.5 mK. Dependence of the vapour pressure on the amount of added He. Correction is done with respect to the current level of liquid He in the bath, which influences the dead volume of the fill line.

3.1.1 Available Grafoil substrates

Finding the right substrate for the adsorption experiments is typically a compromise between the total available surface area and the quality of the surface as high quality substrates tend to have small overall surface area. High quality means that areas within the substrate which are ideally atomically flat are as large as possible. In Grafoil these atomically flat areas are hexagonal planes on top and bottom of small chips of the material called platelets. Another consideration is the orientation of these platelets; ideally they are all parallel. This is important if the substrate is used for a NMR cell, where the orientation of the substrate to the magnetic field should be uniform; or in a torsion oscillator experiment, where the interconnectedness of platelets also matters for establishing flow paths.

Graphite is commercially available from various sources, the most suitable options being: Papyex [55], ZXY [56] and Grafoil [57]. Production of Grafoil is described in detail in [58]. Natural flakes of graphite are taken and put into a strongly oxidising medium. The resulting intercalation compound is then rapidly heated and compressed into a foil. Intercalation is the process of inserting a foreign species into the crystal structure of the host. In graphite this can happen, in the form of staging, periodically along the c-axis. Table 3.1 compares the three substrates available. Grafoil was chosen for the NMR cell used for the
measurements presented in this work, due to its large surface area to mass ratio.

<table>
<thead>
<tr>
<th></th>
<th>Crystallite len.</th>
<th>Coherence len.</th>
<th>Angular distrib.</th>
<th>Specific area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[nm]</td>
<td>[nm]</td>
<td>[°]</td>
<td>[m²/g]</td>
</tr>
<tr>
<td>Grafoil</td>
<td>40</td>
<td>10-20</td>
<td>±15</td>
<td>18-30</td>
</tr>
<tr>
<td>Papyex</td>
<td>60</td>
<td>20-30</td>
<td>±15</td>
<td>20</td>
</tr>
<tr>
<td>ZYX</td>
<td>&gt;300</td>
<td>160-220</td>
<td>±5</td>
<td>2-4</td>
</tr>
<tr>
<td>Graphene</td>
<td>&gt;1 000 000</td>
<td>&gt;10 000</td>
<td>substrate dependent</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 3.1: Properties of the available exfoliated graphites. The crystallite length is the length scale of the platelets in the hexagonal plane. The coherence length characterises the length scale on which they are atomically flat. Values are compiled from [59, 60, 61]. CVD grown graphene is added for comparison.

3.1.2 Graphene as the possible adsorption substrate of the future

The carbon based substrate with the best quality surface is graphene. Large area graphene sheets are nowadays produced by chemical vapour deposition (CVD) method on copper. Graphene can be removed from the supporting copper substrate, or left on it. In both cases the application for adsorption experiments differs from the experiments on Grafoil. In the case of suspended graphene sheet, nothing prevents adsorption on both sides of the sheet. The adsorption potential also differs by up to 10% from graphite [62]. Section 3.4 discusses theoretical phase diagrams on both graphite and graphene. In the case of supported graphene, the underlying Cu foil significantly increases the addendum mass and volume of the substrate and will also modify adsorption potential.

On the other hand graphene does provide areas of pristine honeycomb structure with diameter of the order of tens of µm. These areas could host quantum phenomena in the adsorbed films with long coherence lengths which were yet unobserved in 2D, like superfluidity in thin $^3$He films [63, 64]. From experiments in confined geometries we know that superfluidity is suppressed in the given dimension when the slab size becomes comparable with the coherence length [65, 66]. The coherence length of superfluid bulk $^3$He is $\xi_0 = 20$ nm at 35 bar and $\xi_0 = 77$ nm at 0 bar. If this was comparable in 2D more than 10 coherence lengths would easily fit onto the pristine graphene areas.

The CVD grown graphene can either be purchased commercially, or grown in house. One of commercial sources of graphene is the company Graphenea [45]. Figures 3.4 and 3.5 show the commercially available samples from there. Various experimental groups have however succeeded in growing graphene which far exceeds the quality of the commercially available material. Graphene grows
naturally on the surface of Cu, due to the proximity of their lattice parameters. The graphene matches best in the (111) crystallographic orientation. However, since standard Cu foils are polycrystalline, the grown graphene sheet is polycrystalline as well. Boundaries between two grains do not have hexagonal structure. They consist of heptagons and pentagons. The whole sheet also tends to get wrinkled. The wrinkling is further increased if the graphene is transported from one substrate to another [67]. The poly-crystallinity of Cu and the wrinkling pattern of graphene is visible in figure 3.5.

The best quality graphene is achieved when grown on epitaxial copper [68, 46, 69]. In particular interest for one of our potential application, the torsion oscillator cell introduced in section 2.3.3, is the growth of epitaxial copper on the surface of sapphire and subsequently growing the CVD graphene on the top of the copper [70, 71].

Figure 3.4: The CVD graphene grown on Cu foil. Samples from Graphenea [45].

Figure 3.5: CVD grown graphene on Cu foil from Graphenea. Picture from electron microscope. Polycrystallinity of both the substrate and the graphene is apparent. So is the wrinkling pattern.
3.2 Phase transitions in two dimensions

Reducing the number of physical dimensions of a system from three to two or one has vast consequence on the system’s ground state regardless of whether it is fermionic, bosonic or classical in nature. Already in 1935 Peierls has argued that thermal motion of long-wavelength phonons will destroy the long-range order of a two-dimensional (2D) solid in the sense that the mean square deviation of an atom from its equilibrium position increases logarithmically with the size of the system, and the Bragg peaks of the diffraction pattern formed by the system are broad instead of sharp [72]. Using similar arguments it can also be shown that there is no spontaneous magnetization in a 2D magnet with spins with more than one degree of freedom (the Heisenberg model) [73] or that expectation value of the superfluid order parameter in a 2D Bose fluid is zero [74].

Yet there are systems in nature (quasi 2D) that undergo a phase transition at non-zero temperature and do have an ordered ground state. A 2D solid opposing the argument of Peierls is graphene. There are several hypotheses why graphene can exist. One of them for example relies on a strain in the graphene sheet, due to its corrugation in the third dimension, that provides the otherwise missing long range interaction [75].

Another type of system that exhibit a 2D behaviour are gasses adsorbed on a material with atomically flat surface. Spontaneous magnetic ordering in $^3$He adsorbed on graphite [76, 77] is observed; with $T = 0$ order destroyed only at finite temperature by 2D spin-wave excitations, due to the small Zeeman gap, which dominates finite size effects.

We also find 2D superfluids [78]. 2D superfluidity of the $^4$He Bose liquid exists in the absence of long range order; superfluid phase can still be defined and the unbinding of quantum vortices is the key feature of the superfluid transition, described by Kosterlitz–Thouless theory [72]. Being so fundamentally different from the 3D, the physics of 2D systems is a subject of intense theoretical and experimental research.
3.3 Fermi liquid in two dimensions

Fermi liquid theory successfully describes bulk liquid $^3$He in its normal state and is also relevant to understanding electrons in metals, whose band structure introduces further complexities. The statistics of fermions is described by the Fermi–Dirac distribution, which encodes the Pauli exclusion principle:

$$ f(\epsilon) = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) + 1}, $$

where $\mu$ is the chemical potential. At $T = 0$ it defines the Fermi energy, $\epsilon_F = \mu(T = 0)$. The significance of the Fermi energy is the following. At $T = 0$ fermions will fill up all the states below the Fermi energy each state by a single fermion. All states above the Fermi energy will be empty. Adding a new particle would require exactly $\epsilon_F$ hence it equals the chemical potential at $T = 0$. In the following we shall introduce Fermi liquid theory in two dimensions. Specifically we shall derive predicted thermodynamic quantities like susceptibility and specific heat and see if they apply to our NMR measurements on a $^3$He doped $^4$He film.

3.3.1 Non-interacting fermi gas

The Fermi gas model assumes no interaction among the fermions. They are also assumed to be free particles. We will consider them to be confined within a square area $A = L^2$ with a periodic boundary condition. The solution to the time dependent Schrödinger equation are plane waves:

$$ \psi(x, y) = \frac{e^{i\vec{k} \cdot \vec{r}}}{\sqrt{A}}, $$

and the $k$-vectors are quantised with integer numbers $n_x$ and $n_y$:

$$ k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}. $$

Thus defined states occupy an area of $(2\pi/L)^2$ in the $k$-space and the density therefore is:

$$ \rho(\vec{k}) = \frac{A}{4\pi^2}. $$

If we now enclose the states in the $k$-space with a circle of radius $k$ we get number of states:

$$ N(k) = \pi k^2 g \rho(\vec{k}) = \frac{k^2 A}{2\pi}, $$

where $g = 2s + 1 = 2$ is the spin degeneracy of the fermion. The density of states in the $k$-space is acquired by differentiating with respect to $k$:

$$ D(k) = \frac{Ak}{\pi}. $$
The energy of a free particle is simply its kinetic energy:

$$\epsilon = \frac{\hbar^2 k^2}{2m},$$

(3.9)

and energy density of states will therefore be:

$$D(\epsilon) = \frac{dN(k)}{dk} \frac{dk}{d\epsilon} = \frac{Am}{\hbar^2 \pi}.$$  

(3.10)

The energy density of states is independent of energy in two dimensions. The Fermi temperature can be calculated from the density of states by integrating the number of atoms in the system:

$$N = \int_0^\infty D(\epsilon)f(\epsilon)d\epsilon,$$

(3.11)

where \(f(\epsilon)\) is the Fermi–Dirac distribution, equation 3.3. The temperature has to be set to zero and then:

$$N = \int_0^{\epsilon_F} D(\epsilon)d\epsilon.$$  

(3.12)

As the density of states, equation 3.10 is energy independent, the integral is simply:

$$N = \frac{Am}{\pi \hbar^2} \epsilon_F.$$ 

(3.13)

And the Fermi temperature:

$$T_F^0 = \frac{\pi \hbar^2 N}{k_B m A},$$

(3.14)

is therefore dependent on the density. Now we shall derive the thermodynamic quantities heat capacity and susceptibility. For susceptibility we look at the behaviour in the low polarisation limit: \(\mu B \ll \epsilon_F\), \(\mu\) being the magnetic moment. We assume two possible orientation of the magnetic moment in magnetic field: \(N_\uparrow\) and \(N_\downarrow\). Number of the spin up and down states at \(T = 0\) are:

$$N_{\uparrow(\downarrow)} = \frac{1}{2} \int_{\pm \mu B}^{\epsilon_F} D(\epsilon \pm \mu B)d\epsilon = \frac{Am}{2\pi \hbar^2} \int_{\pm \mu B}^{\epsilon_F} d\epsilon = \frac{Am}{2\pi \hbar^2}[\epsilon_F \pm \mu B].$$

(3.15)

From number of spin up and down states we get magnetisation:

$$M = \mu(N_\uparrow - N_\downarrow) = \mu^2 B\frac{Am}{\pi \hbar^2} = \mu^2 BD(\epsilon).$$

(3.16)

The susceptibility therefore is:

$$\chi = \frac{M}{H} = \mu_0 \mu^2 D(\epsilon),$$

(3.17)

where \(\mu_0\) is the permeability of free space. The magnetic susceptibility is thus
proportional to the area $A$. At low temperatures it is also temperature independent. High above $T_F$ we however expect inverse temperature dependence, in accordance with Curie law.

The Heat capacity at constant area:

$$C_A = \left( \frac{\partial U}{\partial T} \right)_A$$

(3.18)

can be calculated from the density of states as well. The internal energy is given by the integral:

$$U = \int_0^\infty D(\epsilon)f(\epsilon)\epsilon d\epsilon.$$  

(3.19)

Well below $T_F$ we get:

$$C_A = \pi k_B A m \frac{3}{\hbar^2} T = \frac{\pi^2}{3} D(\epsilon) k_B T.$$  

(3.20)

The heat capacity is therefore, like the susceptibility, proportional to the area of the Fermi gas. The linear dependence on $T$ can be expressed using the famous Sommerfeld constant $\gamma$: $C_A = \gamma T$, where $\gamma = D(\epsilon_F) k_B^2 (\pi^2 / 3)$.

### 3.3.2 Landau–Fermi liquid

Simple metals and bulk $^3$He are well described already within the framework of Fermi gas but for strongly correlated systems interactions must be taken into account. L.D. Landau attempted to describe interacting Fermi liquid in terms of renormalised Fermi gas in his series of papers [79, 80, 81, 82].

The concept of Landau’s theory is that there are elementary Fermionic excitations within the interacting Fermi system which are weakly interacting. These excitations have defined energy and momentum, with free particle dispersion relation:

$$\epsilon(p) = \frac{p^2}{2m^*},$$

(3.21)

where $m^*$ is the effective mass. The excitations are also called quasi-particles. Following the same procedure as for the Fermi gas, we get density of states of the quasi-particles similar to equation 3.10:

$$D(\epsilon) = \frac{A m^*}{\hbar^2 \pi}.$$  

(3.22)

It is found that only quasi-particles and quasi-holes near the Fermi level play a role. Whereas the particles are strongly interacting, the quasiparticles are only weakly interacting. The interactions between quasiparticles are characterised by Landau–Fermi liquid parameters, which must be determined by experiment. Thermodynamic quantities are renormalised by the Landau pa-
rameters. The spin symmetric Landau parameter $F_0^s$ causes contraction and expansion of the Fermi surface when the chemical potential changes. The spin antisymmetric Landau parameter $F_0^a$ leads to polarisation of the Fermi surface for states with spin up and down. This happens when magnetic field is applied. The last parameter $F_1^s$ causes renormalisation of the particle mass. It creates spin independent distortion of the Fermi surface in the presence of external flow, force or field. Table 3.2 summarises measurable properties within the Fermi gas model and their renormalisation within the Landau–Fermi liquid model.

<table>
<thead>
<tr>
<th>Property</th>
<th>Fermi gas</th>
<th>Landau Fermi liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$m$</td>
<td>$m^* = m(1 + F_1^s)$</td>
</tr>
<tr>
<td>Fermi energy</td>
<td>$\epsilon_F = k_B T_F$</td>
<td>$\epsilon_F^* = k_B T_F^* = \epsilon_F/m^*$</td>
</tr>
<tr>
<td>Density of states</td>
<td>$D(\epsilon_F) = 2m\pi/\hbar^2$</td>
<td>$D^<em>(\epsilon_F) = D(\epsilon_F)(m^</em>/m)$</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>$c_v = \gamma_0 T$</td>
<td>$c_v = \gamma_0(m^*/m)T$</td>
</tr>
<tr>
<td>Susceptibility</td>
<td>$\chi_0 = \mu^2 D(\epsilon_F)$</td>
<td>$\chi = \chi_0(m^*/m)(1 + F_0^a)^{-1}$</td>
</tr>
<tr>
<td>Compressibility</td>
<td>$\kappa_0 = n^2/D(\epsilon_F)$</td>
<td>$\kappa = \kappa_0(1 + F_0^a)(m^*/m)^{-1}$</td>
</tr>
</tbody>
</table>

Table 3.2: Landau Fermi liquid framework renormalisation of Fermi gas properties.

### 3.3.3 Dyugaev Fermi fluid model

Dyugaev created a phenomenological model in 3D in which he described the transition of the susceptibility from the temperature independent behaviour at low temperatures to Curie law above $T_F$ [83, 84]. He made the model to explain bulk $^3\text{He}$ susceptibility data and their fits by Thompson et al. [85, 86]. Dyugaev’s formula for the susceptibility is:

$$\chi(T) = \frac{C}{\sqrt{(\frac{2}{3}T_{F*}^*)^2 + T^2}}, \quad (3.23)$$

where $T_{F*}^*$ is an effective Fermi temperature. The factor $2/3$ disappears in 2D as the $T = 0$ Pauli susceptibility is: $\chi(0) = C/T_F$.

$$\chi(T) = \frac{C}{\sqrt{T_{F*}^* T}}. \quad (3.24)$$

The effective Fermi temperature is related to the Fermi temperature as (see Table 3.2):

$$T_{F*}^* = T_F \left( 1 + \frac{F_0^a}{m^*/m} \right). \quad (3.25)$$

Moreover, Dyugaev also came up with density dependence of $T_{F*}^*$ in 3D:

$$T_{F*}^*(n) = T_{F*}^*(n_0) \left( \frac{n}{n_0} \right)^{\nu}. \quad (3.26)$$
where $T^*_p(n_0) = 239$ mK, $n_0$ corresponds to molar volume $V_0 = 36.84$ cm$^3$mol$^{-1}$ and the index is: $\nu = -1.93$. The success of Dyugaev’s formula in accounting for $\chi(T)$ has been demonstrated both in 3D [87] and 2D [88, 89].
3.4 Phase diagram of second layer of $^4$He on graphite

Our coverage scale is based on $^4$He promotion to the second layer at 11.4 nm$^{-2}$, identified by B-point of a vapour pressure isotherm at 4.2 K (Figure 3.3). We then find the third layer promotion at 20.0 nm$^{-2}$ [42](supplementary),[53]. Coverage scales of others differ slightly from our adopted scale. Crowell and Reppy (C&R) [90] take third layer promotion to be 20.4 nm$^{-2}$; we rescale their coverages by a factor 0.980. Greywall [91] takes third layer promotion to be 21.2 nm$^{-2}$; we rescale his coverages by a factor 0.943. The heat capacity measurements of the Fukuyama group [92], who use ZYX exfoliated graphite, state good agreement with Greywall (who uses Grafoil); we rescale their coverages by the factor 0.943. We also note that the simulations of [93] quote the same third layer promotion as Greywall, so coverages are scaled by the same factor. The simulations by Corboz [94] state promotion to second layer to be 11.4 nm$^{-2}$; no scaling is necessary.

The density of the first layer changes as the second layer is grown, being compressed by the second layer. At the third layer promotion, the first layer coverage is 11.88 nm$^{-2}$, according to neutron scattering measurements by Lauter [52]. It is important to note that the neutron measurements are not able to determine whether the second layer of $^4$He on graphite is solid or liquid.

Both first and second solid layers have triangular lattice structure, as opposed to the underlying graphite. Of particular importance for this work are two special second layer densities, when the amount of He in the second layer is commensurate with the first layer in density ratios: 4/7 and 7/12. A commensurate structure means that the lattice vectors of the superstructure are simple fractional multiples of the lattice vectors of the underlying structure superlattice. The commensurate fraction determines the density of the second layer but there can be several possible relative orientations of the two structures which will differ in their potential energy. This was discussed for example by Elser
and Takagi [95] for the 4/7 commensurate structure of $^3$He on graphite. As example, two possible sites above the first layer are shown in Figure 3.6.

Early measurements of heat capacity of the second $^4$He layer by Polanco et al. indicated coexistence of liquid and gas in the second layer [97] from observation of rounded heat capacity peaks. This is different to solid and gas coexistence in the first layer, where the heat capacity peaks are also observed, and arises from the reduced attraction potential from the graphite. Much sharper heat capacity peaks were also observed in a narrow density range 6.5-7.5 nm$^{-2}$, and were attributed to the formation of commensurate solid. Later heat capacity measurements by Greywall were interpreted to support the coexistence of liquid and gas phase up to the total coverage 19 nm$^{-2}$, above which solid coexists with fluid, and the solid is commensurate [91]. This was also evidenced by heat capacity anomalies (referred to as melting peaks) observed around 1-1.5 K. Later evidence for the formation of a low temperature ordered phase came from heat capacity measurements by Nakamura et al. [92], where they call the phase “quantum hexatic”, instead of commensurate. Their heat capacity peaks are shown in Figure 3.7. The upper bar in the figure is the proposed phase diagram, consisting of liquid, commensurate (quantum hexatic) and incommensurate phases and regions of their coexistence.

Torsional oscillator measurements by Crowell and Reppy [90] followed Greywall’s measurements of heat capacity. They observed a superfluid signal only
in a narrow coverage range 17–19 nm\(^2\), which is where Greywall’s heat capacity measurements suggest gas and liquid phase. However these torsional oscillator measurements were limited by a minimum temperature 20 mK. They were followed by recent torsional oscillator measurements at Royal Holloway [42, 98], which were performed down to 2 mK and also observed very particular temperature dependence of the mass decoupling, different from Kosterlitz–Thouless superfluid transition. The coverage range where the mass decoupling is happening is wider than in case of CkR. Otherwise, the two experiments are consistent with each other. The local torsional oscillator experiment is discussed in more detail in section 3.8.2.

Figure 3.8: The 7/12 commensurate phase according to Corboz [94]. The black dots mark the positions of the first layer particles. Second layer particles are located above the middle of three neighboring first layer particles.

Theoretical work on the He second layer on graphite and graphene was commonly in contradiction with experimental observations. Early theoretical works [99, 100] predicted a stable liquid phase from 16 nm\(^2\) up. Path integral Monte Carlo simulation (PIMS) by Pierce and Manousakis (P&M) [101, 93] predicted the gas-liquid (G+L) coexistence up to a second layer density 4.7 nm\(^2\) (16.7 nm\(^2\) total), followed by a homogeneous fluid, and also identified the 4/7 commensurate phase to be stable against particle/ hole doping over a density range 3%. In disagreement with P&M is the work of Gordillo and Ceperley [102]. Their phase diagram predicts the G+L region in a similar range as P&M, followed by a superfluid region up to 19 nm\(^2\). The superfluid is followed by an incommensurate solid, starting at 7.6 nm\(^2\), up to the third layer promotion. A superfluid region spreading between the G+L and incommensurate solid regions was also claimed by Corboz et al. [94]. Ahn [103] agrees with Corboz that the 4/7 structure is not stable on the top of incommensurate first layer, but predicted that a combination 4/7 structure in the second layer and 7/12 structure in the first layer could be meta-stable. This is on graphite. On a single sheet graphene Gordillo
and Boronat predicted metastable $4/7$ and $7/12$ phases [104], while Kwon [105] discovered melting of the $7/12$ phase due to quantum exchange of $^4$He atoms, but hypothesised that $^3$He doping might stabilise the phase. Simulations by Happacher [106] reject commensurate phases in the second layer on graphene altogether.

To summarise, these simulations often find no solid phase at densities at which both supersolid and melting signatures are observed. By contrast a stable ($7/12$), or at least metastable ($4/7$) commensurate phases are found at these densities in a pure $^3$He second layer [107, 108]. They develop into an incommensurate solid at higher densities, up to the third layer promotion. At much lower densities there is a gas-liquid coexistence phase, also observed in [109].

Only most recently Gordillo and Boronat [110] revisited the phase diagram of the pure $^4$He second layer. They found evidence of a superfluid quantum phase with hexatic correlations, induced by the corrugation of the first He layer, and a quasi-two dimensional supersolid corresponding to the $7/12$ registered phase. The $4/7$ commensurate solid was found to be unstable, while the triangular incommensurate crystals, stable at large densities, were normal (not superfluid).

Figure 3.9: Phase diagram by Choi et al. [111], in reduced coverage, where 1 is the third layer promotion. The top-most line is theoretical phase diagram according to the latest calculations by Gordillo [110] (with regions of phase coexistence regrettably omitted). Shown by cyan points is the superfluid signal onset by the torsion oscillator, and at 1-1.5 K the heat capacity peaks observed by Nakamura et al. [92] are shown.

Recent torsional oscillator measurements by Choi et al. [111] observe mass decoupling in a somewhat similar coverage range to the Royal Holloway measurement. They were unable to measure below 20 mK. Their torsional oscillator works on two well separated frequencies and the observed superfluid signal is frequency independent. This is important for supporting that the effect is gen-
une evidence for superfluidity/supersolidity, and no viscoelasticity. According to their reported phase diagram, shown in Figure 3.9, the superfluid signal is happening in both the fluid and the solid region.

In section 3.8.3 another heat capacity experiment done at Royal Holloway will be summarised. It was performed down to a few mK on $^3$He doped $^4$He second layer. These measurements feature low temperature heat capacity maxima in the vicinity of the commensurate phases. These features can be understood within a model of finite bandwidth impurities in solid $^4$He layer, where the impurities are quasiparticles formed by the $^3$He atoms. The concept of an impurity is introduced in the following section. These measurements are another confirmation of the solidification in the discussed coverage region. Finally, the most recent NMR susceptibility measurements will be presented in the results section 3.8.5, which broadly support these conclusions, and provide significant further insight. They were motivated by the desirability to provide independent thermodynamics evidence for solid order in the region where 2D supersolidity was reported [42, 98].
3.5 Solid helium mixtures in two and three dimensions

A solid is from a classical point of view a periodically ordered set of atoms, where at \( T = 0 \) each atom occupies a given site on the lattice. At higher temperatures atoms thermally vibrate about their equilibrium position. From a quantum point of view however, the atoms vibrate at \( T = 0 \) as well, due to their zero point energy. These oscillations are generally very anharmonic [112]. In quantum crystals the amplitude of the zero point oscillations is so large, that the lattice constant is only a few times larger, than the oscillation amplitude. A dimensionless quantity that describes the importance of the zero point motion in a crystal is the de Boer parameter [113] and has the following form:

\[
\Lambda = \frac{\hbar}{\alpha (mU)^{1/2}},
\]

where \( \alpha \) is the lattice constant, \( m \) the mass of the particle and \( U \) the characteristic energy, or in another words the depth of the lattice potential. The potential depth for both \(^4\)He and \(^3\)He crystals is about 11 K. The de Boer factor comes out then as 0.5 for \(^3\)He, 0.4 for \(^4\)He and 0.1 for Ne. It is vanishingly small for all other crystals.

The small mass of He atoms and relatively weak binding potential allows quantum motion between sites. The motion is directly related to the zero point oscillation which determines the probability of occurrence at a given distance from the equilibrium position. In a perfect crystal, with all lattice sites occupied, the diffusion can only happen as a cyclic permutation of 2, 3 or more atoms, as shown in Fig. 3.10.

Figure 3.10: Cyclic exchange of 2, 3 and 4 atoms in a plane.
The described mechanism can, for example, be observed as magnetic exchange in solid $^3$He [114] and in the diffusion coefficient [115].

### 3.5.1 Diffusion of defects in quantum crystals

So far we have only discussed ideal quantum crystals consisting of single type of atoms and their motion. However, as in classical crystals, we have various type of defects in the quantum crystals too, eg. vacancies. A vacancy in a $^4$He crystal is a boson, a vacancy in a $^3$He crystal a fermion [116].

Another type of crystal defect is an impurity. An atom of different kind can either substitute a constituting atom at a regular position or it can be present in the free space in the crystal lattice, surrounded by the constituting atoms. It is then called an interstitial. A $^4$He interstitial in $^3$He matrix is a boson, a $^3$He interstitial in $^4$He matrix is a fermion. A $^3$He atoms substituting a $^4$He atom in $^4$He matrix is a fermion, however $^4$He atom substituting a $^3$He atom in a $^3$He matrix is also a fermion [116].

These defects and impurities can move through the quantum crystal in a form of elementary excitations. They are commonly called “defectons” and/or “impuritons”. The crystal has a periodic structure and their ballistic motion at low concentrations therefore resembles the motion of electrons in a periodic potential, characterised by the energy bandwidth $\Delta$, velocity $u \sim (\alpha \Delta)/\hbar$ and effective mass $m^* \sim \hbar^2/(\alpha^2 \Delta)$. Of particular interest for our experiment is the tunnelling of $^3$He impurities in a $^4$He crystal.

Diffusion of $^3$He impurities in $^4$He solid has been studied in bulk [117]. It was found that the diffusion coefficient is temperature independent below 1 K, as expected for quantum diffusion. It is limited by the impuriton–impuriton scattering and decreases with $^3$He concentration. This is shown in Figure 3.11. The spin diffusion is governed by the particle diffusion at low concentrations. The diffusion coefficient is also simply the mean free path $l$ multiplied by the mean velocity $u \sim a \tau_c \sim 10^{-1}$ cm/s; $D \sim ul$, where $\tau_c$ is a site-site hoping rate. The mean free path of an impuriton is $l \sim \alpha^3/\sigma x$, where $\sigma$ is the impuriton scattering cross-section. The impuriton–impuriton interaction is elastic in nature, as each impurity deforms the potential of the surrounding, with which another impurity interacts. The mobile impuritons are thus in fact polarons, they carry the deformed lattice with them. The interaction energy takes up the form: $V(r) = V_0(\alpha/r)^3$. The interaction radius $R_0$ can be estimated when the potential is comparable to the bandwidth: $R_0 \sim \alpha(V_0/\Delta)^{1/3}$. The scattering
cross-section is: \( \sigma \sim R_0^2 \). Hence the diffusion coefficient is:

\[
D \sim \frac{\alpha^2 \Delta}{h \xi} \left( \frac{\Delta}{V_0} \right)^{2/3}.
\]  

(3.28)

The inverse proportionality of the diffusion coefficient on \( x \) is apparent from the bulk measurements in Figure 3.11. Let’s estimate the maximum concentration of the impurities where de-localisation is observable. De-localisation of an impurity in the presence of another impurity can take place if: \( \delta V \leq \Delta \), where \( \delta V \sim \alpha(\partial V/\partial r) \). Average separation among impurities is: \( r \sim \alpha/x^{1/3} \). From there we get the concentration limit:

\[
x \leq \left( \frac{\Delta}{V_0} \right)^{3/4},
\]  

(3.29)

which in bulk \( (\Delta \sim 10^{-4} \text{ K}, V_0 \sim 0.1 \text{ K}) \) comes out about 0.5%. This localisation has been observed [118, 117] and is shown in Figure 3.11.

Figure 3.11: Concentration dependence of the diffusion coefficient for \(^3\)He impurities in \(^4\)He crystal with molar volume \( 21 \text{ cm}^3 \) at temperatures below 1.2 K, where the diffusion is temperature independent. Data points by Richards et al. and Grigorev et al. [118, 117].

### 3.5.2 Tunnelling in two dimensions

Tunnelling of \(^3\)He impurities in a \(^4\)He matrix is potentially relevant in two dimensions because the phase diagrams of second layers of pure \(^3\)He and \(^4\)He host solid phases. The tunnelling rate is strongly dependent on the lattice parameter in both three and two dimensions (equation 3.28) [119]. It was hypothesised that the existence of 2D solid \(^4\)He in the second layer could be tested by doping with \(^3\)He impurities and seeking evidence for de-localised impuriton behaviour. This was motivated by the observation of large exchange rates in 2D pure \(^3\)He in the second layer.
Furthermore, previous susceptibility measurements at Royal Holloway on solid helium mixtures in the first layer on graphite found evidence for the impuriton de-localisation, together with phase separation [120]. A degeneracy temperature $T_F \sim 30$ mK was observed. A simple tight-binding model, introduced in section 3.5.3, predicts tunnelling rate: $t \sim 36$ mK, which corresponds to highly re-normalised mass: $m^* \sim 20m_3$. The bandwidth in two dimensions $\sim 0.1$ K far exceeds the typical bulk value. If the bandwidth exceeds interaction energy even at relatively high 2D concentrations the observation of degenerate impuritons might be possible.

3.5.3 Delocalised $^3$He tunneling excitations model

These ideas lead us to model the expected properties of a system of $^3$He impuritons in a 2D $^4$He matrix. We neglect impuriton interactions. As expected we find Fermi gas behaviour, where the fermion effective mass is the band mass, modified at finite temperature by the finite bandwidth. This model is based on the assumption that the $^3$He is delocalised in the $^4$He matrix and it is tunneling through it with a Hamiltonian:

$$\hat{H} = -t \sum_{i,j} a^+_i a_j,$$

(3.30)

where we consider $i$ and $j$ to be nearest neighbours and $t$ is the tunneling amplitude for the nearest neighbour sites. The tunneling amplitude equals the sum of all possible cyclic permutations as depicted in Figure 3.10, $t = J_2 + 2J_3 + 4J_4 + 2J_6...$, where $J$ is the exchange constant for the appropriate particle exchange. In a helium mixture we assume the tunneling rate to be the same for $^3$He–$^4$He and $^4$He–$^4$He pairs [121]. It is possible to construct a simple tight–binding model [122] which will describe the movement of the $^3$He atoms within the crystal, and predict the Fermi temperature of these impuritons:

$$\frac{E_F}{\Delta} = \frac{2\pi}{3\sqrt{3}}x \approx 1.2x,$$

(3.31)

where $x$ is the $^3$He concentration, and the effective mass of the band:

$$m_b = \frac{\hbar^2}{3a^2t},$$

(3.32)

where $a$ is the nearest neighbour distance. Within this model the bandwidth relates to the tunneling amplitude by:

$$\Delta = 9t.$$

(3.33)
The band mass thus depends on the bandwidth by:

\[ m_b = \frac{3\hbar^2}{a^2\Delta}. \] (3.34)

The heat capacity and magnetic susceptibility of an ideal gas of fermions with the band mass was worked out [122]. The internal energy \( U \) of this system is:

\[ U = 2 \int_0^\Delta \frac{g(\epsilon)e}{e^{(\epsilon-\mu)/k_BT} + 1} d\epsilon, \] (3.35)

with a constant density of state:

\[ g = \frac{N_3}{2E_F} \] (3.36)

it becomes:

\[ U = \frac{N_3}{E_F} \int_0^\Delta \frac{\epsilon}{e^{(\epsilon-\mu)/k_BT} + 1} d\epsilon, \] (3.37)

where \( \mu \) is the chemical potential. The chemical potential is found by inverting the formula for number of particles (Fermi–Dirac distribution):

\[ \mu(T) = k_BT \ln \left( \frac{e^{E_F/k_BT} - 1}{1 - e^{(E_F-\Delta)/k_BT}} \right). \] (3.38)

The numerator is the ideal Fermi gas chemical potential while the denominator accounts for the finite bandwidth. The heat capacity \( C = \frac{\partial U}{\partial T} \) is a very complicated expression, but its qualitative description can be given. At low temperatures the bandwidth \( \Delta \) has no influence and the heat capacity is linear in temperature:

\[ C = \frac{\pi^2 k_B^2 N_3}{3 E_F} T. \] (3.39)

At higher temperatures the formula deviates from the linear behaviour and describes a peak. The peak moves to higher temperatures and increases its magnitude with increasing \( E_F/\Delta \) ratio, until \( E_F/\Delta = 0.5 \), then it moves down in temperature again. This behaviour reflects the symmetry of low and high filling, ie. less than a half and more than half fraction of \(^3\text{He}\). Of course we practically only expect the model to work at low concentrations, where interactions are relatively weak. The peak significantly broadens in the \( E_F/\Delta \to 0 \) limit. The high temperature expansion of the heat capacity formula has the leading \( T^{-2} \) temperature dependence, characteristic of a Schottky peak:

\[ \frac{C}{N_3} = \frac{\Delta(\Delta - E_F)}{12k_BT^2} + \frac{\Delta(-\Delta^3 + 2\Delta^2E_F - 2\Delta E_F^2 + E_F^3)}{240k_B^3T^4} + ... \] (3.40)

The overall heat capacity curves are shown in Figure 3.12. When scaled by \( E_F/\Delta \) curves for ratio \( x \) and \( 1 - x \) collapse onto each other. This is the consequence of the particle–hole symmetry of the model.
The magnetic susceptibility is derived from the chemical potential \([122]\) as:

\[
\chi = \frac{k_B C}{N^3 \frac{\partial \mu}{\partial N^3}},
\]

(3.41)

where the Curie constant is:

\[
C = \frac{N^3 m^2}{k_B}.
\]

(3.42)

It is found that:

\[
\chi(T) = \frac{2k_B C}{E_F} \frac{\sinh(E_F/2k_BT)}{\sinh((\Delta - E_F)/2k_BT)} \frac{\sinh(\Delta/2k_BT)}{\sinh(\Delta/2k_BT)},
\]

(3.43)

shown in Figure 3.13 in \(\chi T\) vs. \(T\) coordinates. When scaled by the \(E_F/\Delta\) ratio the particle–hole symmetry is apparent from the graph, similarly to the case of the heat capacity.

Curves from the Finite bandwidth model in Figure 3.13 resemble the Fermi liquid modeled by the Dyugaev formula 3.24. The susceptibility obeys Curie
law at high enough temperatures; and is temperature independent, as Pauli susceptibility at low enough temperatures. Let’s compare the models in more detail; Figure 3.14 serves the purpose. Susceptibility in $\chi/\chi_0$ is modeled using the Dyugaev and finite bandwidth models.

![Figure 3.14: Susceptibility according to the Finite bandwidth and Dyugaev models.](image)

It is apparent that the finite bandwidth lowers the high temperature susceptibility, compared to the non-degenerate Fermi gas. Only the green curves corresponding to $E_F/\Delta = 0.05(0.1)$ get near the Fermi gas susceptibility. High temperature expansion of equation 3.43 actually recovers Curie law: $\chi = \frac{\tilde{C}}{T}$, with $\tilde{C} = (1 - \frac{E_F}{\Delta})C$, the modified Curie constant.

The low temperature asymptote of the finite bandwidth model is: $\chi(T) = \frac{k_B C}{E_F}$, where $C$ is the Curie constant 3.42, same as the Dyugaev model predicts.
3.6 Origin of the spin–lattice and spin–spin relaxation times

The relaxation times $T_1$ and $T_2^*$ are found in the solution of Bloch’s equations (equations 2.34). The constant $T_2^*$ characterises the decay of the FID. When the FID is Fourier transformed the FID $T_2^*$ value determines the width of the resulting Lorentzian (equation 2.37). It is therefore one of the fit parameters, together with frequency, magnetisation and phase. Should all the magnetic moments in the sample experience exactly the same magnetic field there would be no transverse relaxation and the moments would precess coherently until the magnetisation would relax according to $T_1$ back to the vertical direction. Yet, especially in solids, the FID decays (much) faster than the longitudinal magnetisation ($T_2^* < T_1$). The reason is that all individual magnetic moments experience slightly different magnetic field. This is partially due to inhomogeneities in the magnetic field $B_0$ produced by the magnet; we will label these inhomogeneities: $\Delta B_0$; and partially due to dipole–dipole interaction between the moments. The dipole–dipole magnetic field is given by the formula:

$$B_{\text{dip}}(i) = \frac{\mu_0}{4\pi} \sum_j \left[ \frac{\mu}{r_{ij}^3} \left( \frac{\mu \cdot r_{ij}}{r_{ij}^5} - \frac{(\mu \cdot r_{ij}) r_{ij}}{r_{ij}^5} \right) \right],$$  \hspace{1cm} (3.44)

which depends on the geometry of the lattice. The slightly different magnetic field every moment feels leads to a slightly different Larmor frequency for each moment. This inevitably leads to de-phasing, de-coherence and therefore disappearance of the transverse magnetisation. While the one source of magnetic inhomogeneities is purely an instrumental artefact the other carries valuable information about the studied system. We denote the characteristic FID decay time the system would have in an ideally homogeneous magnetic field: $T_2$. $T_2$ is related to $T_2^*$ by the following formula:

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \omega \frac{\Delta B_0}{B_0}. \hspace{1cm} (3.45)$$

Equation 3.45 shows that in a system where $T_2$ is field independent, $T_2$ can be determined by measuring the field dependence of $T_2^*$.

The spin–lattice relaxation time characterises the effectiveness of energy exchange between the nucleus and the “lattice”, how the spins reach thermal equilibrium; whereas $T_2$ is the characteristic time for the spins to equilibrate with each other, and establish a well defined spin temperature. The spin–lattice relaxation can be mediated by unpaired electrons in paramagnetic solids, magnetic impurities [123] or by electric field gradients for nuclei with quadrupolar moment. Neither of these is the case for $^3$He of course. Processes related to the movement of the nuclear spins are of great importance for helium. There are
two fundamentally different mechanisms enabling transport of spin (and spin temperature) [124]:

- self diffusion: transport of mass and therefore spin
- spin diffusion: transport of spin without mass flow.

In order to understand the spin-lattice relaxation the concept of spin temperature of systems described by different Hamiltonians which either commute or do not must be introduced. The full Hamiltonian of the spin system is:

\[ \hat{H} = \hat{H}_Z + \hat{H}_d + \hat{H}_m, \]  

(3.46)

where \(\hat{H}_Z\) is the Zeeman Hamiltonian (equation 2.29) which describes the Larmor precession and adsorption of energy at: \(\omega = \gamma B_0\), \(\hat{H}_d\) is the interaction Hamiltonian of the spins (dipole–dipole interaction for example) and \(\hat{H}_m\) is the Hamiltonian of motion which represents non-spin degrees of freedom. If it was not for the interaction Hamiltonian the other two would not interact:

\[ [\hat{H}_Z, \hat{H}_m] = 0, \]
\[ [\hat{H}_d, \hat{H}_m] \neq 0, \]
\[ [\hat{H}_Z, \hat{H}_d] \neq 0. \]

(3.47)

Figure 3.15 shows the thermalisation path according to Bloembergen and Wang [125] who first realised the importance of spin–spin interaction for the longitudinal relaxation.

![Figure 3.15: The spin–lattice relaxation according to Bloembergen and Wang.](image)

In an NMR experiment power is absorbed by the Zeeman system. If the size of the exchange interaction is large heat contact with the exchange spin system and the lattice is established by dipolar interaction. The direct contact between the magnetic system and the lattice is usually negligible [125].

Further information about the relaxation times can be found for example in [126, 124].
3.7 Methods of measurement

3.7.1 Data collection and analyses

The NMR measurements were made using the cell described in section 2.3.1. The cell contains Grafoil [57] of known surface area. The surface area is regularly checked at the beginning of every new experimental run by performing a $^4\text{He}$ isotherm at 4.2 K. This procedure is discussed in the section 3.1. The doses of He sent into the cell from the room temperature gas handling system (GHS) are accurately known. They are prepared in a manifold of known volume in the GHS, equipped with a high precision Paroscientific oscillating quartz pressure gauge [8]. Helium is only admitted into the cell at temperatures above 3 K, and newly built film is always left to be “annealed” at a vapour pressure of about 1 mbar for at least two hours. It is subsequently cooled down at a rate slower than 1 K per hour to preserve equilibrium. This procedure is validated by the reproducibility of results from many experiments on such films. Adsorbed films of isotopic mixture are grown in defined shots of either He isotope, but in this case reduction of coverage is not possible, unlike in the case of a single isotope film.

![Figure 3.16: Example of recorded NMR spectra for sample 18.27 + 0.74 nm$^{-2}$ ($^4\text{He} + ^3\text{He}$) at 327 $\mu$K according to the $^{13}\text{C}$ thermometer. Shown in green is the Fourier transform of the 4 period long pulse, tuned primarily to tip the $^3\text{He}$ and secondary the $^{13}\text{C}$. Inlets are showing fits according to equations 2.37 to the real and imaginary parts of the spectra for both isotopes.](image)

The sample is typically in a magnetic field of 3.1 mT, created by the main NMR magnet. This makes the nuclei of $^3\text{He}$ in the sample and $^{13}\text{C}$ in the graphite precess at 100 kHz and 33 kHz respectively. Four periods of the transmitter pulse with the frequency 100 kHz tip both the magnetic moments of $^3\text{He}$ and $^{13}\text{C}$ as its spectrum is fairly broad. The spectrum of the four period pulse
can be seen in Figure 3.16, together with the signal peaks from $^{13}\text{C}$ and $^3\text{He}$.
The typical pulse amplitude is 4.5 $V_{\text{pk-pk}}$, which provides tipping angle of 7.2°
for $^3\text{He}$ and 0.38° for $^{13}\text{C}$. Despite this small tipping angle for $^{13}\text{C}$, the Curie law
dependence of its magnetisation generally provides a sufficiently large signal at
low temperatures to precisely determine the temperature. The use of $^{13}\text{C}$ for
thermometry is discussed in section 2.2.3.

The free induction decay (FID) is recorded by the two stage SQUID ampli-
 fier, developed at PTB [29, 28], and discussed in section 2.3.1. The received
FID signal is lost during a dead time of 160 $\mu$s after the pulse due to strong
transient effects in this time period after the pulse. In general the transients
come from magneto-acoustics, decaying eddy currents in structural parts but
in this case are dominated by the operation of the FLL of the SQUID. During
the first 9 $\mu$s of the dead time, and during the pulse itself, the FLL is open
to avoid overload. The FID is numerically extended back to the center of the
pulse when analysing it, to obtain the full magnetisation. The FID after every
pulse is corrected by subtracting a FID recorded on an empty cell at zero field,
and at a field chosen with Larmor frequency at a node of the transmitter pulse
power spectrum, so that $^3\text{He}$ spins are not tipped. The node at 125 kHz was
chosen. These zero and high field backgrounds were recorded using the exact
same pulse as for the rest of the measurements. The purpose of this subtraction
is to remove the majority of the transient background effects in the time domain.
Additionally a 15th order polynomial is fitted in the time domain and subtracted
from the FID. Such cleaned data are fast Fourier transformed (FFT) into the
frequency domain. Frequency, magnetisation and spin–spin relaxation time are
inferred from Lorentzian fits (equation 2.37) of the complex Fourier transform
of the FID. A typical spectrum is shown in Figure 3.16, capturing the peaks of
both $^3\text{He}$ and $^{13}\text{C}$.

### 3.7.2 Susceptibility normalisation

The NMR method provides information about sample magnetisation in arbi-
trary units. The actual measured magnetisation depends on the design of the
experimental cell. It is therefore useful to scale the measured magnetisation by
a measured magnetisation of a simple physical system of known susceptibility,
to present data in dimensionless form, but with a meaningful magnitude. We
make use of the fact that in all cases, at sufficiently high temperatures, the
susceptibility takes the Curie form:

$$\chi (T) = \frac{C}{T} = \frac{C n_3 p_3}{T}, \quad (3.48)$$
where $C_{n3}$ is a Curie constant per unit coverage, which again depends on the design of the experimental cell, and $n_3$ is the coverage per unit area of the $^3$He. To establish the constant $C_{n3}$, isotherms of different $n_3$ are taken at 450 and 550 mK. The measured magnetisation should increase linearly with $n_3$ as it does in Figure 3.17. A deflection from the linear behaviour can be observed at higher coverages ($0.74 \text{ nm}^{-2}$ and higher), where the gas is already partially degenerate at these temperatures. The low temperature ideal Fermi gas susceptibility:

$$\chi_0 = \mu_N^2 \frac{Am}{\pi \hbar},$$  \hspace{1cm} (3.49)

can be extracted from the Curie constant:

$$\chi_0 (T << T_F) = \frac{C_{n3}n_3}{T_F} = \frac{C_{n3}k_Bm}{\pi \hbar^2},$$  \hspace{1cm} (3.50)

where the Fermi temperature of the gas is: $T_F = \frac{\pi \hbar^2}{k_Bm n_3}$.

Figure 3.17: Susceptibility measured at 450 and 550 mK of various $n_3$ coverage samples. Constant $C_{n3}$ is given by the slope. $C_{n3}$ from 550 mK isotherm is used to calculate the $\chi_0$. Colour coding of samples is the same as will be used in the results section 3.8.

It has been observed that the constant $C_{n3}$ does not change very much over the course of years in different runs. Table 3.3 summarises the values of $\chi_0$ from previous, and the most recent runs.
Table 3.3: Low temperature susceptibility of the ideal Fermi gas in local units (l.u.), as determined in our NMR cell in several past runs.

<table>
<thead>
<tr>
<th>Run</th>
<th>Year</th>
<th>$\chi_0$ [l.u.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>2015-16</td>
<td>22.0 ± 0.2</td>
</tr>
<tr>
<td>46</td>
<td>2016</td>
<td>21.7 ± 0.4</td>
</tr>
<tr>
<td>48</td>
<td>2016-17</td>
<td>22.0 ± 0.1</td>
</tr>
<tr>
<td>49</td>
<td>2018-19</td>
<td>22.2 ± 0.1</td>
</tr>
</tbody>
</table>

Susceptibility measurements presented in this work are all scaled by the $\chi_0 = 22.22$ value. We see enhancement of the free Fermi gas susceptibility at low temperature on all samples, sometimes by a several orders of magnitude. This scaling provides physical information to help interpret the enhancement. For example in the case of a Fermi liquid:

$$\frac{\chi}{\chi_0} = \frac{m^*}{m} \left( 1 + F_0^2 \right).$$

(3.51)

### 3.7.3 Standard methods of $T_1$ measurement

It was shown in section 2.3.1 that a 90° NMR pulse applied on the system of magnetic moments tips them to the plane perpendicular to the main field $B_0$ and the magnetisation thus measured is the full longitudinal equilibrium magnetisation. If the 90° pulse was applied on a system of spins which are only relaxing back to their equilibrium orientation, because they had been previously disturbed by a different pulse, the 90° pulse would measure the current value of the longitudinal magnetisation. This is how the spin-lattice relaxation can be measured; a pair of pulses is applied; the first pulse aligns the spins in a certain way, and the second pulse, coming at time $\tau$ after the first pulse, measures the magnetisation. Most popular pulse sequences are: 90° − $\tau$ − 90°, sometimes called saturation recovery, and 180° − $\tau$ − 90°, called inversion recovery. It is called inversion because the 180° pulse orients the spins antiparallel to $B_0$, their equilibrium orientation. A single pair of pulses is of course not sufficient to properly monitor the spin–lattice relaxation. Multiple such pairs must be applied, while varying the delay $\tau$, and they have to be at least time 5$T_1$ apart. This is because a system relaxing according to a pure exponential will recover $1 - e^{-5} \approx 99.3\%$ of the full longitudinal magnetisation. However the 5$T_1$ spacing is only sufficient if the system relaxes according to the pure exponential. Let’s suppose the system should relax according to a stretched exponential function:

$$1 - e^{- (t/T_1)^{0.3}}.$$ 

In this case the spins only recover 80% of their full magnetisation after the 5$T_1$ time. We shall observe exactly this behaviour.

Systems with a very long $T_1$, or showing a non-exponential recovery, should therefore be measured by a different technique. One such technique will be introduced in the next section, and was extensively used in this experiment.
### 3.7.4 Progressive saturation method of $T_1$ measurement

As we have discussed if an arbitrary pulse is applied on a system of magnetic moments while they are still relaxing to equilibrium (according to Bloch’s equations solution 2.35) the magnetisation measured by this pulse will be smaller than the equilibrium magnetisation. This is because the pulse measures the instantaneous magnitude of the longitudinal magnetisation, which is largest in equilibrium. Should the sample be continuously disturbed by pulses of a given strength, $\theta$, in time steps with period, $\tau$, magnetisation measured by these pulses will eventually reach a constant value. The value will depend on both the angle $\theta$, the time period $\tau$, and the system’s $T_1$. We shall call the function $g(\tau, \theta, T_1)$, describing the reduction of the measured magnetisation in the presence of a continuous sequence of tipping pulses, the saturation function and we examine how it can be used to measure $T_1$.

Following a pulse the longitudinal magnetisation $M_{||} \cos \theta$ relaxes to the equilibrium according to the solution to the Bloch’s equation (equation 2.35):

$$M_{||}(t) = M_\infty - (M_\infty - M_{||}(\cos(\theta))) e^{-t/T_1}. \quad (3.52)$$

At the time $\tau$ another $\theta$ pulse is applied. The magnetisation at that point is

$$M_{||}(\tau) = M_\infty - (M_\infty - M_{||}(\cos(\theta))) e^{-\tau/T_1}. \quad (3.53)$$

In the steady state we interpret $M_{||}(\tau)$ as the steady state magnetisation in the presence of the sequence of given pulses, therefore:

$$M_{||}(\tau) = M_\infty - (M_\infty - M_{||}(\tau) \cos(\theta)) e^{-\tau/T_1}. \quad (3.54)$$

Solving equation 3.54 for $M_{||}(\tau)$ we obtain the saturation function:

$$g(\theta, \tau, T_1) = g_\theta(\tau/T_1) = \frac{M_{||}(\tau)}{M_\infty} = \frac{1 - e^{-\tau/T_1}}{1 - \cos(\theta)e^{-\tau/T_1}}. \quad (3.55)$$

Formula 3.55 is derived in the following books [127, 126]. Figure 3.18 (upper) shows the saturation curves for various tipping angles, according to equation 3.55 in solid lines.

It is apparent from the form of the equation that the curves cannot be collapsed onto a single curve by scaling the horizontal axis by a factor depending only on $\theta$ and $T_1$ [128].
It is however of interest to establish a regime for which all data, for different \( \theta \) but a range of repetition rates \( \tau \), can be scaled onto a single curve. Then, from this curve, the universal relaxation characteristics (and their temperature dependence) can be inferred. Another candidate function to express the saturation function \( g(\theta, \tau, T_1) \), and a rival to equation 3.55, is a solution to a modified Bloch equation:

\[
\dot{M}_\| = \frac{(M_\infty - M_\|)}{T_1 - M_\|(1 - \cos(\theta))}/\tau.
\]  

(3.56)

One can understand this equation in terms of the relaxation of the magnetisation, which is repeatedly disturbed by a small tipping pulse \( \theta \), with period \( \tau \). Solution to equation 3.56 is the same as to the bare Bloch equation but with a
modified relaxation time:
\[
\frac{1}{T'_1} = \frac{1}{T_1} + \frac{1}{\hat{\tau}},
\]  
(3.57)

where we define \(\hat{\tau}\) as:
\[
\hat{\tau} = \frac{\tau}{1 - \cos(\theta)},
\]  
(3.58)

and with modified magnetisation \(M'_\infty\):
\[
M'_\infty = \frac{M_\infty}{1 + T_1/\hat{\tau}}.
\]  
(3.59)

The measured transverse magnetisation is again:
\[
M_\perp = \frac{M_\infty}{1 + T_1/\hat{\tau}} \sin(\theta),
\]  
(3.60)

and the saturation function takes the form:
\[
g'(\theta, \tau, T_1) = g'_\theta(\hat{\tau}/T_1) = \frac{M_\infty}{1 + T_1/\hat{\tau}}.
\]  
(3.61)

Seeing that equation 3.60 depends on the angle \(\theta\) and period \(\tau\) let’s examine the possible correspondence to equation 3.55. Analytically equation 3.61 proves to be the first order approximation of equation 3.55, when expanded in powers of \(\theta\):
\[
1 - e^{-\tau/T_1} = \frac{1}{1 + T_1/\hat{\tau}} + \frac{1}{(1 + T_1/\hat{\tau})^2} \frac{\theta^2}{4} + \ldots
\]  
(3.62)

Figure 3.18 (upper) shows the curves generated using equation 3.61 in dashed lines. It is apparent that for small angles the two formulas are interchangeable. For large angles, however, they differ significantly. The ratio of the two formulas is shown in Figure 3.18 (lower). The two formulae differ by less than 2% for angles up to 18°, regardless of the pulsing period \(\tau\). For larger angles the curves agree only at small \(\tau\). Analytically we get a criterion:
\[
\theta^2 \ll 4(1 + T_1/\hat{\tau}).
\]  
(3.63)

We will call the region where this is satisfied the correspondence region.

To re-iterate, the significance of equation 3.61 is that it allows the collapse of saturation curves, taken with a different tipping angle, onto a single curve, in terms of \(\hat{\tau}\), as defined in equation 3.58, on the horizontal axis, instead of \(\tau\).

Equation 3.55 is the saturation curve for a simple exponential relaxation of magnetic moments. Let’s study the case that the relaxation is not described by a single exponential, but rather by an arbitrary function \(f(t)\), which must be independent of the tipping angle. The generalisation is straightforward, equation
3.52 becomes:

\[ M_{\parallel}(t) = M_\infty - (M_\infty - M_{\parallel}\cos(\theta))f(t). \]  \hspace{1cm} (3.64)

And the saturation function will be:

\[ g_\theta(\tau/T_1) = \frac{1 - f(\tau)}{1 - \cos(\theta)f(\tau)}. \]  \hspace{1cm} (3.65)

This correspondence equation directly translates the relaxation function to the saturation function. We can also invert formula 3.65 and we find it is surprisingly symmetric:

\[ f(\tau, T_1) = \frac{1 - g_\theta(\tau)}{1 - \cos(\theta)g_\theta(\tau)}. \]  \hspace{1cm} (3.66)

Physically, the relaxation function must be independent of \( \theta \). This condition puts additional constraint on equation 3.66.

The relaxation function \( f(\tau, T_1) \) can theoretically have variety of possible forms. With respect to the data presented later in this chapter we will limit ourselves to a class of relaxation functions given by the so-called stretched exponential expression:

\[ f(\tau/T_1) = 1 - e^{-(\tau/T_1^n)}, \]  \hspace{1cm} (3.67)

where we replaced \( T_1 \) by \( T_1^\dagger \), but the meaning of this parameter remains that it is the time when recovery reaches \( 1 - e^{-1} \approx 63\% \). The major difference of stretched exponential recoveries with \( n < 1 \) is that after the time \( 5T_1^\dagger \) relaxation reaches more than 99\% for \( n = 1 \), however for \( n = 0.3 \) it is only \( \approx 80\% \).

We now ask the question what the saturation function would look like for the relaxation function given by the stretched exponential. It is given by formula 3.65. When the formula is expanded and simplified for the correspondence region only (condition 3.63), the result is that the data points taken with different tipping angle should be scalable using a factor:

\[ \hat{\tau} = \frac{\tau}{(1 - \cos(\theta))^n}, \]  \hspace{1cm} (3.68)

and follow a universal curve:

\[ \frac{M_\parallel}{M_\infty} = \frac{1}{1 + (T_1^\dagger/\hat{\tau})^n}. \]  \hspace{1cm} (3.69)

We call this model homogeneous, as all moments relax according to a single functional formula with the exact same parameters \( T_1^\dagger \) and \( n \). It will turn out that the data cannot be scaled in this way.

Another possible model we can study is the case that individual moments
relax with a simple exponential relaxation time $T_1$, but there is a distribution of these relaxation times in the specimen. This can also lead to a stretched exponential relaxation, but importantly the scaling is different. We also introduce relaxation rate: $r$, which is the inverse to the relaxation time, and will occasionally be used. If there is a distribution of relaxation rates the overall shape of the relaxation function is:

$$f(r^\dagger t) = \int_0^\infty P(r/r^\dagger) e^{-rt}dr,$$

(3.70)

where $r^\dagger = 1/T_1^\dagger$ is a characteristic rate of relaxation. Equation 3.70 is the Laplace transform of the distribution function $P(r/r^\dagger)$.

A class of distribution functions, one-sided Lévy stable distributions, are of particular interest, as their Laplace transform takes up the stretched exponential form [129]. The one-sided Lévy stable distributions are characterised by the characteristic relaxation rate $r^\dagger$ and an index $n$. A Laplace transform of a Lévy stable distributions with an index $n$ is a stretched exponential whose stretching parameter is the same $n$.

In the case of a general distribution function or relaxation rates, $P(r/r^\dagger)$, the saturation function takes up the following form:

$$g_\theta(r^\dagger \tau) = \int_0^\infty P(r/r^\dagger) \frac{1 - e^{-\tau r}}{1 - \cos \theta e^{-\tau r}} dr.$$

(3.71)

This would be a very non-trivial integral, but it can be much simplified in the correspondence region:

$$g_\theta(r^\dagger \tau) = \int_0^\infty P(r/r^\dagger) \frac{1}{1 + \tau^2} dr.$$

(3.72)

For convenience we shall also define a saturation decay function:

$$G_\theta(\tau) = 1 - g_\theta(\tau).$$

(3.73)

The saturation decay function will have the following form in the case of distribution of relaxation rates, and in the correspondence region:

$$G_\theta(r^\dagger \tau) = \int_0^\infty P(r/r^\dagger) \frac{1}{1 + r^\dagger \tau} dr.$$

(3.74)

This is the so-called Stieltjes transform of $P(r/r^\dagger)$. It is actually a double Laplace transform. The first Laplace transform evaluates the relaxation function from the distribution function of relaxation rates; the second Laplace transform recovers the saturation function from the relaxation function.
There are two questions of interest now. What is the Stieltjes transform of a Lévy stable distribution? This is important for the reason that Lévy stable distribution has an analytical form at least in some particular cases, and can therefore be worked with. The other question is what distribution would give a stretched exponential recovery function.

A numerical simulation was done in attempt to answer these questions. The exact integral of a Lévy stable distribution (equation 3.72) was done. The Lévy stable distribution whose Laplace transform is a stretched exponential with $n = 1/3$ was chosen. This value of $n$ was motivated by the data analyses. This distribution function can be expressed in terms of the Airy Ai function:

$$P(r/r^\dagger) = \frac{1}{3^{1/3}} \left( \frac{r^\dagger}{r} \right)^{4/3} \text{Ai} \left[ \left( \frac{r^\dagger}{r} \right)^{1/3} \right]. \quad (3.75)$$

Figure 3.19, right shows the distribution given by equation 3.75. These distributions are known to be so-called “heavy tailed”. This description comes from the fact that the probability at very high value of $r$ are not vanishingly small, but still large and significant. Very large values of $r$ may be un-physical as no mechanism providing such fast relaxation may be present in a physical system.

Figure 3.19, left shows in green a curve corresponding to one minus the Stieltjes transform of the Lévy stable distribution by equation 3.75, and compares it to a stretched exponential function. It is apparent that the two lines are very difficult to distinguish and their difference can very likely be much smaller than the scatter of experimental data. The stretched exponential is generated using parameters $n = 0.31$ and $r^\dagger = 0.53 r^\dagger_d$, where $r^\dagger_d$ is the rate used in the distribu-
The necessity for horizontal time scaling is peculiar. So let’s have a look into the similarity of the stretched exponential family of curves and the family of Stieltjes transforms of Lévy stable distributions. To demonstrate the significance of the $T_1^\dagger$ Figures 3.20 and 3.21 are constructed. We know of course that every stretched exponential acquires the value $(1 - e^{−1}) \approx 63.2\%$ exactly at $T_1^\dagger$. Let’s therefore see how the Stieltjes transforms behave in that matter. We discover that not only they acquire the value $(1 - e^{−1})$ much later than $T_1^\dagger$, but also that the point is not universal among the curves specified by different indexes. They do not intercept at one particular point at all when the Figure is zoomed in. From distance however, it almost looks like there might be a point like that. It was found, that the horizontal value of $\hat{\tau}/T_1^\dagger$, where the Stieltjes transforms acquire the magnitude $(1 - e^{−1})$ is approximately the needed horizontal scaling factor for collapsing them onto stretched exponentials.

Summary

The implications of the theoretical analyses done in this section are the following. A system in which the spin–lattice relaxation is governed by a simple exponential, but not uniform within the specimen (inhomogeneous), and characterised by a Lévy stable distribution of relaxation rates with the index $n = 1/3$ (equation 3.75), will have the saturation function almost indistinguishable from a stretched exponential. The stretching parameter $n'$ will however not be equal to $1/3$ and an additional horizontal scaling has to be applied. This will nevertheless provide the parameter $T_1^\dagger$, which uniquely characterises the spin–lattice relaxation, and shall thus be called characteristic relaxation time.

Fitting the saturation curve data to a stretched exponential is one approach. Another would be to attempt to directly transform the data from the recovery...
domain to the relaxation domain by an inverse Stieltjes transform. The difference of these two approaches can be found in a work on liquid $^3$He in porous media by Gazizulin [130]. They measured the spin–lattice relaxation time by the spin echo method. Their data show a non-exponential recovery, and can be well fitted with the stretched exponential function. The data and the fit are shown in Figure 3.22, left, and the agreement is excellent. Strikingly, when they do an inverse Laplace transform of the fit function, in order to determine the distribution of relaxation times within the specimen, they get a completely different result to what is obtained when they do the transform on the raw data. The inverse Laplace transform of the data is shown in Figure 3.22, right. The distribution obtained from the raw data is actually the one correctly characterising the experiment, as determined from its special geometry. In the distribution function, there is a plateau apparent, which comes from $^3$He in the porous clay. At higher relaxation times, there is a peak apparent, which comes from $^3$He in a central hole of their experimental cell.

![Figure 3.22: $T_1$ measurements and analyses by Gazizulin. Left: The recovery of liquid $^3$He nuclei spin echo signal in clay sample on frequency 12 MHz and temperature 1.5 K. Right: Distribution of liquid $^3$He $T_1$ relaxation times for a clay sample obtained by regularized inverse Laplace transform UPEN algorithm. From [130]. Added is the red curve in the right figure, showing the inverse Laplace transform of the stretched exponential fit (A Lévy stable distribution).](image)

This experiment well illustrates a very important phenomenon. The stretched exponential is a very robust form, that can often describe observed relaxation. However, large changes in the distribution of relaxation times might result to minor changes in the observed stretched exponential. And vice versa, a small deviation from the stretched exponential functional can represent a massive difference in the distribution function. This is valid both for the Gazizulin experiment, where the Laplace transform connects the physical relaxation and the spin-echo recovery; and our experiment, where the Stieltjes transform connects the physical relaxation and the saturation function.
3.8 Structure of the second layer of $^4$He on graphite

The current knowledge of the structure of the second layer of $^4$He on graphite was summarised in section 3.4, including all disputes among different experimental techniques and theoretical calculations. In this chapter, results of two previous experiments performed at Royal Holloway will be reviewed in more detail, and compared to the most recent measurements of NMR susceptibility. The two earlier experiments are: torsion oscillator measurement on pure $^4$He samples [42, 98], and measurements of heat capacity, where small amount of $^3$He was added into the $^4$He matrix [131]. The results of NMR measurements of magnetic susceptibility on $^3$He doped samples, which form part of this thesis, are described subsequently.

3.8.1 Heat capacity, torsional oscillator and susceptibility isotherms

Figure 3.23 presents isotherms of the measured susceptibility NMR data in the bottom-most figure. Isotherms of heat capacity data of samples with 0.7 nm$^{-2}$ of $^3$He in it are presented in the middle figure. Finally, the data from the torsion oscillator measurement on pure $^4$He samples are present in the top-most figure. The 4/7 and 7/12 registered phases are shown as vertical lines.

Figure 3.23 basically shows enhancement of all the measured quantities at particular temperatures, approximately in the middle of the displayed coverage range. In case of the torsional oscillator, the inferred superfluid fraction at $T = 0$ is plotted. The fraction is most pronounced around 18 nm$^2$, where it reaches 80%, has a strong onset at lower coverages, much slower decrease at higher coverages, and eventually flattens out at approximately 18% all the way to the second layer completion.

The heat capacity isotherms show an enhancement in an intermediate temperature region (30–60 mK), which arises from the maximum around these temperatures. The full temperature dependencies are shown later in Figure 3.27. The occurrence of a peak has an onset at coverage 18 nm$^2$, and vanishes around the third layer completion. Outside of this region the heat capacity has an approximately linear dependence on temperature.

The magnetisation (susceptibility) by NMR show enhancement at the lowest temperatures. This is a consequence of a power law temperature dependence of the measured susceptibility, which is not far from the Curie law, in the coverage range 18–19 nm$^2$. Outside of this range the temperature dependence of the susceptibility is different and has a very particular form.
Figure 3.23: Isotherms as a function of total coverage: TOP torsional oscillator “superfluid” fraction at $T = 0$ (pure $^4$He) Different density regimes labeled as A, B and I, II are discussed in section 3.8.2. MIDDLE heat capacity ($^3$He coverage fixed at 0.7 nm$^{-2}$). BOTTOM $^3$He nuclear susceptibility ($^3$He coverage fixed at 0.51 nm$^{-2}$ below 18.8 nm$^{-2}$, and 0.74 nm$^{-2}$ above). The colored stars at the very top respect the sample’s color coding which shall be used later in the chapter to identify individual NMR samples.
3.8.2 Torsional oscillator measurements

The torsional oscillator measurements performed at Royal Holloway (in the torsional oscillator shown in Figure 2.29), reported here [42, 98], were motivated by the earlier torsional oscillator experiments on this system by Crowell and Reppy [90], which found an anomalous mass decoupling over a narrow coverage range. In that work, the destruction of superfluidity with increasing coverage was attributed to solidification of the film. This torsional oscillator experiment was performed over a finer grid of coverages, and down to much lower temperatures, and observed mass decoupling over a wider coverage range. A novel state of intertwined superfluidity and density wave order was proposed to explain the observations, in which the two seemingly incompatible orders are entangled. The model successfully explains the large superfluid fractions observed. The temperature onset of the mass decoupling was inconsistent with the Kosterlitz–Thouless transition. The anomalous temperature dependence observed was explained at the lowest temperatures in terms of a spectrum of elementary excitations with a set of softening roton minima. The inferred density wave order follows from the fact that the structure factor is strongly peaked at the momenta of these minima.

There are four distinct coverage ranges apparent on the isotherm of superfluid fraction at \( T = 0 \), shown in Figure 3.23, which differ in how the temperature dependence of the superfluid signal can be scaled and collapsed onto a universal curve. Division into these regions provides further evidence of the interplay between film structure and superfluid response.

![Figure 3.24](image)

Figure 3.24: Left: Collapse of temperature dependence of the superfluid signal onto two mother curves in regions I and II. Collapse achieved by horizontal scaling by energy parameter \( \Delta \) (shown right), and vertical scaling by \( \rho_s(T = 0) \). Figures from [42].

The coverage range labeling stands for the following. Regions I and II allow collapse of the temperature dependencies of the superfluid signal using a single “energy scale” parameter \( \Delta \), which scales the horizontal temperature axis. The value of \( \Delta \) is found manually and has different density dependence in re-
regions I and II. It is shown in Figure 3.24, right. Additionally, vertical scaling by $\rho_s(T = 0)$ is done; this value is determined by projecting the temperature dependence to $T = 0$. The collapse onto the two different mother curves in the regions I and II is shown in Figure 3.24, left.

Regions A and B require two parameter scaling to achieve collapse onto the mother curve. The energy scale parameter, $\alpha_T$, scaling the temperature axis, works in the same way as in regions I and II. An additional superfluid response parameter $\alpha_\rho$ is needed to provide vertical scaling. Values of these parameters which enable the collapse shown in Figures 3.25 and 3.26, left, are shown in the same figures, right.

Figure 3.25: Left: Collapse of temperature dependence of the superfluid signal onto two mother curves in region A. Collapse achieved by horizontal scaling by energy parameter $\alpha_T$ and vertical scaling by parameter $\alpha_\rho$. Right: The two scaling parameters vs. density. Figures from [98].

Figure 3.26: Left: Collapse of temperature dependence of the superfluid signal onto two mother curves in region B. Collapse achieved by horizontal scaling by energy parameter $\alpha_T$ and vertical scaling by parameter $\alpha_\rho$. Right: The two scaling parameters vs. density. Figures from [98].

Figures 3.25 and 3.26 show interesting development of the scaling parameters with coverage, which clearly differs in region A and B. In region A the energy
factor varies very mildly, while the superfluid response parameter decreases dramatically with coverage. The superfluid signal is multiplied by $\alpha \rho$, hence the decrease of the parameter stands for decrease of the decoupling superfluid fraction. The opposite is however happening in region B: the superfluid response parameter is remaining almost constant, while the energy scale parameter of the superfluid is increasing. The increase reflects the decrease of the temperature where the superfluid signal is observed. This explain why different experimental groups [90, 111], limited by lowest temperatures tens of mK, cannot see any superfluid signal at these coverages.

The behaviour of the two scaling parameters in regions A and B can be understood within a phase coexistence model. In region A the phase experiencing superfluidity expands with coverage at the expense of the “normal” phase, hence the superfluid signal increases. The characteristic temperature scale of the superfluid does not however change. In region B the amount of the superfluid phase remains constant, but its nature is changing.

We believe the region A to be the region of solid–liquid coexistence, in accordance with the phase diagram constructed by Nakamura et al. [92], shown in Figure 3.7 (keeping in mind their coverage needs to be scaled by the factor 0.943). Unusually, in this solid–liquid coexistence region the solid experiences the “superfluidity”, while the liquid is normal. It is worth noting that the suppression of superfluidity in a fluid mono-layer, subject to a periodic potential, was previously observed on a graphite substrate with various HD (hydrogen-deuterium) pre-platings [132].

On our scale 19.9 nm$^{-2}$ corresponds to the formation of incommensurate solid. The structure of the second layer in the narrow coverage range immediately preceding may feature coexistence of the commensurate and incommensurate solids. The formation of the incommensurate solid could influence the energy scale of the supersolid.

### 3.8.3 Heat capacity measurements

The heat capacity was measured by Fanoula Ziouzia [131, 133] at temperatures of tens of mK, therefore much smaller than the previous heat capacity measurements observing peaks around 1-1.5 K [91, 92]. At these temperatures a pure $^4$He film has heat capacity of unobservable magnitude. $^3$He doping of the $^4$He matrix significantly increases the sample’s heat capacity. The objective of this experiment was to study the $^4$He second layer in the coverage range from uniform 2D liquid to the third layer promotion. The heat capacity measurements predate the torsional oscillator measurements; but are retrospectively of partic-
ular interest, given the four distinct scaling regions discovered by the torsional oscillator experiment. And of course the region around the 4/7 and 7/12 commensurate phases, where the stability of the solid order was in dispute, is also of great interest.

Measurements were made with a fixed $^3$He coverages of 0.7 and 1.0 nm$^{-2}$, varying the $^4$He coverages. This is shown in Figure 3.27. Additionally, several samples with much higher concentration of $^3$He were measured with a total coverage in the region around the commensurate phases (Figures 3.30 and 3.29).

Figure 3.27 shows how linear temperature dependence changes to a maximum in the vicinity of the commensurate phases and later gradually changes back to linear, near the third layer promotion. This evidence from the heat capacity maximum is in agreement with prediction of the $^3$He impuriton Fermi gas model, where the peak arises from the finite bandwidth (see section section 3.5.3). Clearly the heat capacity in the low temperature limit is not linear, as would be expected in this model; but we attribute this to the effects of localisation by interactions between $^3$He impurities. Further evidence for such localisation will emerge from the new NMR results, reported here.

Figure 3.27: Heat capacity measurements on the second layer of $^4$He on graphite doped with 0.70 nm$^{-2}$ of $^3$He. The values specify the total coverage. Data by Fanoula Ziouzia [133].
Nevertheless the location of the heat capacity maximum in temperature allows us to estimate the bandwidth. The location of the heat capacity maximum according to the finite bandwidth model is shown in Figure 3.28. Since $E_F/\Delta$ is determined by $x_3$, according to equation 3.31 (assuming the effective mass is the band mass, and neglecting interactions), we obtain $\Delta$ from the temperature of the heat capacity maximum. Then we calculate $E_F$ and estimate band mass.

Figure 3.28: Position and magnitude of the heat capacity peak according to the finite bandwidth model. See Figure 3.12, where the modelled heat capacity peaks are shown.

Figure 3.29: Heat capacity measurements near the vicinity of the commensurate phases with varying concentration of $^3$He. Data by Fanoula Ziouzia [133]. Lines predicted by the finite bandwidth model for a given $\Delta$ and $E_F$ are shown.

Results of two samples with 0.70 and 1.00 nm$^{-2}$ of $^3$He are given in Table 3.4, and the heat capacity peaks are shown in Figure 3.29 together with the finite bandwidth model predictions for a given $^3$He concentration. Note that in the Fermi gas model, an increase in $x_3$ should lead to an increase in $E_F/\Delta$ and hence $T_p$ for fixed bandwidth. This is not observed: $T_p$ decreases. This may arise from
increase in effective mass due to interactions. Nevertheless we can estimate a bandwidth of order 400 mK. This high level of quantum motion is understandable since $\Delta = 9t$, where $t = J_2 + 2J_3 + 4J_4$... and the bandwidth is compatible with the exchange coefficients inferred from analysis of the magnetism of the second pure $^3\text{He}$ layer, at comparable total densities, using atomic ring exchange model, and calculated ab initio by path integral Monte Carlo [134]. The hopping rate values of $J_2$, $J_3$ and $J_4$ are 10.9, 8.3, and 5.6 mK respectively. Together they give $t = 50.7$ mK and hence $\Delta = 450$ mK.

<table>
<thead>
<tr>
<th>sample</th>
<th>$x_3$</th>
<th>$T_p$ [mK]</th>
<th>$a$ [nm]</th>
<th>$k_B T_p/\Delta$</th>
<th>$\Delta$ [mK]</th>
<th>$E_F$ [mK]</th>
<th>$m_b/m_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.07 + 0.70</td>
<td>0.103</td>
<td>50</td>
<td>0.413</td>
<td>0.104</td>
<td>467.0</td>
<td>69.1</td>
<td>5</td>
</tr>
<tr>
<td>17.86 + 1.00</td>
<td>0.146</td>
<td>50</td>
<td>0.410</td>
<td>0.112</td>
<td>434.6</td>
<td>92.1</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Table 3.4: Parameters of heat capacity peaks of two measured samples and implications within the finite bandwidth model.

There is no evidence of isotopic phase separation as observed in bulk isotopic mixtures. This is qualitatively understandable in terms of the far higher bandwidth of impuritons in 2D, which is much larger than the strain interaction at low densities. Hence, in the simplest picture, the reduction in zero point energy associated with delocalisation of $^3\text{He}$ impurities (and consequent band formation) dominates the potential energy gain from phase separation. In this way delocalised impuritons exist at sufficiently high densities to observe degeneracy.

In order to test these ideas the heat capacity at much larger $^3\text{He}$ concentration of 38% was studied. It is shown in Figures 3.30 and 3.29. These results show a broad heat capacity maximum at 28 mK, and a distinct maximum at a few mK. The latter is attributed to magnetic exchange in clusters of phase separated pure $^3\text{He}$. Comparison with measurements on a pure $^3\text{He}$ second layer on a first $^4\text{He}$ layer shows that only around 50% of the $^3\text{He}$ sample has phase separated. It coexists with a homogeneous solution of $^3\text{He}$ in solid $^4\text{He}$, with concentration of 20%. This indicates finite solubility of $^3\text{He}$ in 2D solid $^4\text{He}$ at this concentration, analogous with the properties of dilute liquid solutions. Furthermore, this result is consistent with the absence of phase separation at the lower concentrations we have discussed.

Shown in Figure 3.29 is a quantitative comparison of the Fermi gas model. The curve for the 38% concentration sample (where the low temperature exchange maximum has been subtracted from the data) uses a finite solubility $x_3 = 24\%$. It uses a bandwidth of $\Delta = 66$ mK, inferred from $T_p$. 

106
Figure 3.30: Heat capacity measurements near the vicinity of the commensurate phases with varying concentration of $^3\text{He}$. Data by Fanoula Ziouzia [133].

In relation to the torsional oscillator experiment the main conclusion of this work was that in the regime where the supersolid response is observed there the heat capacity measurements support solid order. This is preceded at lower coverages by a region of heat capacity with linear temperature dependence, corresponding to mobile $^3\text{He}$ in or on a uniform $^4\text{He}$ film. A subtlety is that in this quantum solid $^3\text{He}$ impurities are sufficiently mobile to exhibit quantum degeneracy.

This motivated the complementary study of the magnetism of the $^3\text{He}$ impurities in this system, where in contrast to the heat capacity, localised $^3\text{He}$ atoms have a strong contribution.

3.8.4 Use of $^3\text{He}$ diluted in the $^4\text{He}$ matrix for sensitivity enhancement (NMR and heat capacity)

The $^4\text{He}$ isotope is not magnetically active due to its zero nuclear spin. In order to study the second layer of $^4\text{He}$ by the NMR method the $^4\text{He}$ layer has to be doped with a small amount of $^3\text{He}$ atoms. Throughout the NMR experiment the amount of $^3\text{He}$ was kept constant at two values ($0.51 \text{ nm}^{-2}$ and $0.74 \text{ nm}^{-2}$), while the amount of $^4\text{He}$ was progressively increased. In the previous heat capacity experiment the $^3\text{He}$ coverage was kept constant at the value $0.70 \text{ nm}^{-2}$.

The second layer of $^4\text{He}$ on graphite starts at the coverage $11.4 \text{ nm}^{-2}$. The NMR measurement was done from the total coverage of $16.74 \text{ nm}^{-2}$ ($5.34 \text{ nm}^{-2}$ in the second layer) up to $20.75 \text{ nm}^{-2}$. The first sample consisted of $16.23 \text{ nm}^{-2}$ of $^4\text{He}$ and $0.51 \text{ nm}^{-2}$ of $^3\text{He}$. Figure 3.31 shows how the measurements pro-
gressed. It shows the total coverage, $^3$He coverage and $^3$He concentration in the mixture of the studied samples. $^4$He was gradually added up to the sample $18.27 + 0.51 \text{ nm}^{-2}$. Then $^3$He was added in a single step, so its coverage was increased to $0.74 \text{ nm}^{-2}$. After that $^4$He coverage was gradually increased again. The two samples with $^3$He coverages 0.1 and 0.3 nm$^{-2}$ were measured in earlier experimental runs.

![Figure 3.31: Summary map of NMR experiment studied samples' $^3$He overall atomic concentration (star symbol), and concentration in the 2nd layer (diamond symbol) vs. the total coverage (bottom axis) and 2nd layer density (top axis).](image)

### 3.8.5 Susceptibility results overview

The temperature dependencies of the measured susceptibility are divided into four sections based on their visual appearance, in which they clearly differ. Data are presented in normalised susceptibility $\chi/\chi_0$ vs. temperature coordinates on log-log plots (graphs a). Concurrently $\chi T$ vs. $T$ data are plotted in linear axes (graphs b). The $\chi T$ vs. $T$ coordinates have the power to clearly capture the true Curie law: $\chi = C/T$, manifesting itself as a horizontal line; and deviations from it. For degenerate Fermi liquid, described by temperature independent Pauli susceptibility, $\chi T \to 0$ linearly as $T \to 0$. This limit is true both for the Fermi liquid in the Dyugaev model (see Figure 3.39), and the Finite bandwidth tunneling model (Figure 3.13).

Nevertheless, Fermi liquids are not the only systems that go to $\chi T = 0$ at
$T = 0$, a power law of the form: $\chi = \frac{C}{T^\alpha}$, where $0 \leq \alpha \leq 1$ will have the same limit. Such power law behaviour will however manifest itself as a straight line on the $\chi$ vs. $T$ graph in log-log plot, and as such is clearly distinguishable from the Fermi liquid. The combination of these two plots should therefore capture most possible scenarios.

### 3.8.6 Susceptibility vs. temperature dependence in coverage range: 16.5 – 17.5 nm$^{-2}$

The first three samples were taken at the homogeneous liquid region (purple stars), and solid-liquid coexistence (blue, grey stars) region of the commonly accepted phase diagram in Figure 3.7. The heat capacity measurements show clear linear temperature dependence in this region. The torsional oscillator detected no mass decoupling at the coverage of the first sample, and only small mass decoupling at the other two samples’ coverages.

These samples have a particular temperature dependence of the magnetic susceptibility. They are described by the simple Fermi gas model, characterised by the $^3$He coverage 0.51 nm$^{-2}$, at the highest temperatures. As the temperature is decreased there is a tendency for $\chi/\chi_0$ to flatten, resembling Pauli susceptibility, only to start rising again at even lower temperatures. Even though the susceptibility below 1 mK is significantly enhanced from the $\chi_0$ value, the $\chi T$ limit at $T \to 0$ is very small and surprisingly similar for all three samples; it is around 10 mK. We shall interpret this seeming intercept in terms of a “solid fraction” later in section 3.8.13. For that a high temperature asymptote of the $\chi T$ vs. $T$ plot will be needed, which is discussed in section 3.8.12.

Figure 3.32: Measured susceptibility of the first three samples. The inset in Figure b shows the limit: $T \to 0$. 

These samples have a particular temperature dependence of the magnetic susceptibility. They are described by the simple Fermi gas model, characterised by the $^3$He coverage 0.51 nm$^{-2}$, at the highest temperatures. As the temperature is decreased there is a tendency for $\chi/\chi_0$ to flatten, resembling Pauli susceptibility, only to start rising again at even lower temperatures. Even though the susceptibility below 1 mK is significantly enhanced from the $\chi_0$ value, the $\chi T$ limit at $T \to 0$ is very small and surprisingly similar for all three samples; it is around 10 mK. We shall interpret this seeming intercept in terms of a “solid fraction” later in section 3.8.13. For that a high temperature asymptote of the $\chi T$ vs. $T$ plot will be needed, which is discussed in section 3.8.12.
This particular shape of the susceptibility temperature dependence markedly resembles what is observed in phosphorus doped silicon in the vicinity of the metal–insulator transition, on the metallic side. This possibly related system is introduced at the end of this chapter (section 3.10, see Figure 3.68).

3.8.7 Susceptibility vs. temperature dependence in coverage range: 18.0 – 18.5 nm$^{-2}$

Increasing the coverage from 17.6 to 18.0 nm$^{-2}$ significantly changes the temperature dependence of the susceptibility. The overall shape $\chi$ vs. $T$ resembles the Curie law. In reality the straight line on the log-log plot corresponds to a slightly lower value of the index than 1. The power law fitting is done in the next two sections. The first two samples of the four (black and red stars) correspond to coverages where the torsion oscillator detects largest mass decoupling of the pure $^4$He film, while the first sample is in the two parameter scaling region, A, and the second sample in the single parameter region, I. The following two samples (green and blue stars) were measured very close to the commensurate coverages ($4/7$ and $7/12$ respectively), which are located in the single parameter scaling, II, TO region. These commensurate phases are in the pure $^4$He film expected at coverages 18.58 and 18.77 nm$^{-2}$ according to our scale.

![Figure 3.33: Measured susceptibility of four samples in the coverage region where the TO detects largest mass decoupling, and slightly larger, close to the commensurate phases.](image)

These samples behave as a Fermi gas at the highest temperatures, as evidenced from the susceptibility normalisation procedure, same as the first three samples. This implies the high temperature limit of the susceptibility is Curie law. The susceptibility however goes over to the smaller $\alpha$ value power law incredibly smoothly. To address this issue residual plots were generated when
doing the power law fitting routine.

Later in section 3.9, which presents results of the relaxation times measurements, we will observe a very sudden increase of the spin–lattice relaxation time in the sample $18.27 + 0.51 \text{ nm}^{-2}$. It is interesting to see that the sample does not differ substantially from its nearest coverage neighbours in terms of the measured susceptibility, yet it behaves so differently in terms of the spin–lattice relaxation. Here it is important to note, that due to the larger $T_1$, this sample was measured down to slightly higher minimum temperature, than the others. The susceptibility results are however not influenced by the large $T_1$, as appropriate pulsing rates were established across the whole temperature range.

### 3.8.8 Power law fitting in the vicinity of the commensurate coverages

The samples closest to the commensurate coverages with varying $^3\text{He}$ concentration were fitted with a power law. The fitting formula is:

$$
\frac{\chi T}{\chi_0} = C T^{1-\alpha}.
$$

This was done in the $\chi T$ vs. $T$ coordinates. No known errors are assumed for the data points, constant uncertainty is therefore assumed by the $\chi^2$-fitting routine by default. This is why the $\chi$ vs. $T$ coordinates are not appropriate, as the susceptibility spreads across several orders of magnitude. The unequal temperature spacing of the experimental points, apparent in both linear and log temperature, can also be a source of issues for the fit, in the case the fit is not perfect across the whole temperature range. Averaging of the data points ensuring the points are spaced at least 10% apart in temperature was therefore done. This routine is described in details in the YbRh$_2$Si$_2$ chapter (section 4.7.2).

The results of the fitting are shown in Figure 3.34. The samples have varying amount of $^3\text{He}$ from 0.10 to 0.74 nm$^{-2}$. The two datasets of samples with 0.10 and 0.30 nm$^{-2}$ were measured in earlier experimental runs than the rest of the samples presented here. Table 3.5 gives the fit parameters and fit quality results. The values of the index $\alpha$ are also shown in Figure 3.35, against the $^3\text{He}$ density in the second layer. The uncertainty of the fit parameters could not be reliably established because the fit quality is not sufficient and the uncertainty of the experimental points is not established. A goodness of the fit parameter $\chi^2$ (not to be mistaken with the susceptibility $\chi$) was calculated in the following way:

$$
\chi^2 = \sum_{i=1}^{n_p}\frac{(x_i - M)^2}{M^2},
$$

111
where \( x_i \) are the experimental points and \( M_i \) the values of the model. The quality of the fit is presented as \( \chi^2/n_p \), i.e divided by the number of experimental points. If all experimental points were exactly \( \pm 1\% \) away from the model, the value of \( \chi^2/n_p \) would be \( 1 \cdot 10^{-4} \).

\[
\chi^2/n_p = \sum \frac{(x_i - M_i)^2}{\sigma_i^2}
\]

\[
C = \sum \frac{x_i}{\sigma_i}
\]

\[
\alpha = \sum \frac{2}{\sigma_i}
\]

\[
\frac{(\chi^2/n_p)'}{n_p'} = \frac{\chi^2}{n_p} + \sum \frac{2}{\sigma_i'}
\]

\[
C' = \sum \frac{x_i}{\sigma_i'}
\]

\[
\alpha' = \sum \frac{2}{\sigma_i'}
\]

Table 3.5: Results of the power law fitting in \( \chi T \) vs. \( T \) and \( 1/(\chi T) \) vs. \( 1/T \) coordinates (bare and primed letters). Sum of residuals, scaled by the model-\( \chi^2 \) divided by the number of data points and the two fit parameters are given.

<table>
<thead>
<tr>
<th>sample</th>
<th>( \chi^2/n_p )</th>
<th>( C )</th>
<th>( \alpha )</th>
<th>( (\chi^2/n_p)' )</th>
<th>( C' )</th>
<th>( \alpha' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.65 + 0.10 nm(^{-2})</td>
<td>248 \cdot 10^-4</td>
<td>6.6</td>
<td>0.69</td>
<td>244 \cdot 10^-4</td>
<td>7.8</td>
<td>0.78</td>
</tr>
<tr>
<td>18.31 + 0.30 nm(^{-2})</td>
<td>6.5 \cdot 10^-4</td>
<td>60.0</td>
<td>0.86</td>
<td>9.3 \cdot 10^-4</td>
<td>59.7</td>
<td>0.86</td>
</tr>
<tr>
<td>18.27 + 0.51 nm(^{-2})</td>
<td>9.2 \cdot 10^-4</td>
<td>125</td>
<td>0.89</td>
<td>6.8 \cdot 10^-4</td>
<td>128</td>
<td>0.90</td>
</tr>
<tr>
<td>18.04 + 0.51 nm(^{-2})</td>
<td>4.2 \cdot 10^-4</td>
<td>144</td>
<td>0.91</td>
<td>3.2 \cdot 10^-4</td>
<td>146</td>
<td>0.92</td>
</tr>
<tr>
<td>18.27 + 0.74 nm(^{-2})</td>
<td>11.6 \cdot 10^-4</td>
<td>185</td>
<td>0.90</td>
<td>12.0 \cdot 10^-4</td>
<td>192</td>
<td>0.91</td>
</tr>
</tbody>
</table>

The power law fitting routine was also done in different coordinates: \( 1/(\chi T) \)
vs. $1/T$, which will be discussed later in the section 3.8.13. These coordinates are helpful as they emphasize the lowest temperature behaviour. No averaging of the data points was done in those coordinates. The fit results will be shown in Figure 3.42, but the fit parameters and quality is presented already here, in Table 3.5, for comparison with the fit results in $\chi T$ vs. $T$ coordinates.

Fitting in $\chi T$ vs. $T$ and $1/(\chi T)$ vs. $1/T$ coordinates yields very similar results. The sample with the smallest $^3$He coverage (0.1 nm$^{-2}$) agrees most poorly with the power law fit; this is also reflected by the small disagreement of the two fitting results. It is however important to stress that the experimental challenges associated with the measurement of samples with such little $^3$He were substantial, and these data points certainly come with the largest uncertainty.

The index $\alpha$ seem to saturate at a value of about 0.9. In the phosphorus doped silicon experiments (section 3.10) saturation of the index was observed as well, but at a lower value $\alpha \approx 0.65$ [135].

![Figure 3.35: Dependence of the index on the $^3$He concentration in the second layer.](image)

**3.8.9 Power law fitting at fixed $^3$He coverage**

The power law fitting was also done on selected samples with 0.51 nm$^{-2}$ $^3$He coverage. This concerns the four samples shown together in section 3.8.7, where the first two correspond to the region where the torsional oscillator detects the largest superfluid signal, and the other two correspond to the two commensurate densities of interest.

The data treatment and fitting routine was the same. The fit results are
shown in Figure 3.36 and given in Table 3.6. Figure 3.37 shows the development of the index $\alpha$ with coverage.

The value of the index $\alpha$ peaks slightly below the commensurate phases coverages. Even though the overall quality of the power law fit is good, there is an apparent disagreement at the highest temperatures. This is nonetheless expected, as we know the samples are Fermi gases at 550 mK and as such should follow a power law with $\alpha = 1$; the Curie law.

The agreement of these four samples with the power law model is very good, except for the discussed high temperature end, described by the Curie law. The agreement with the power law at the lowest temperatures indicates that we should not seek the seeming intercept with the $\chi T$ axis at $T = 0$, as it should be zero. And indeed the samples do show this type of behaviour, when zoomed in the $\chi T$ vs. $T$ coordinates. See Figures 3.33 and 3.43.

![Figure 3.36: Power law fits of four samples with $^3$He coverage 0.51 nm$^{-2}$.](image)


<table>
<thead>
<tr>
<th>sample</th>
<th>$\chi^2/n_p$</th>
<th>$C$</th>
<th>$\alpha$</th>
<th>$(\chi'^2/n'_p)$</th>
<th>$C'$</th>
<th>$\alpha'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$17.45 + 0.51 \text{ nm}^{-2}$</td>
<td>$5.5 \cdot 10^{-4}$</td>
<td>126</td>
<td>0.88</td>
<td>$4.4 \cdot 10^{-4}$</td>
<td>123</td>
<td>0.87</td>
</tr>
<tr>
<td>$17.69 + 0.51 \text{ nm}^{-2}$</td>
<td>$4.1 \cdot 10^{-4}$</td>
<td>146</td>
<td>0.91</td>
<td>$5.1 \cdot 10^{-4}$</td>
<td>143</td>
<td>0.90</td>
</tr>
<tr>
<td>$18.04 + 0.51 \text{ nm}^{-2}$</td>
<td>$4.2 \cdot 10^{-4}$</td>
<td>144</td>
<td>0.91</td>
<td>$3.2 \cdot 10^{-4}$</td>
<td>146</td>
<td>0.92</td>
</tr>
<tr>
<td>$18.27 + 0.51 \text{ nm}^{-2}$</td>
<td>$9.2 \cdot 10^{-4}$</td>
<td>125</td>
<td>0.89</td>
<td>$6.8 \cdot 10^{-4}$</td>
<td>128</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Table 3.6: Results of the power law fitting in $\chi T$ vs. $T$ and $1/(\chi T)$ vs. $1/T$ coordinates (bare and primed letters). Sum of residuals, scaled by the model-$\chi^2$ divided by the number of data points and the two fit parameters are given. Results for samples $18.04 + 0.51 \text{ nm}^{-2}$ and $18.27 + 0.51 \text{ nm}^{-2}$ are of course identical to Table 3.5.

Figure 3.37: Dependence of the power magnitude on the total coverage of samples with $0.51 \text{ nm}^{-2}$ of $^3\text{He}$.

### 3.8.10 Susceptibility vs. temperature dependence in coverage range: 19.0 – 20.0 nm$^{-2}$

The samples presented in this section had an increased amount of $^3\text{He}$ to $0.74 \text{ nm}^{-2}$ from the previous $0.51 \text{ nm}^{-2}$. From the susceptibility normalisation we know the isotherm of these samples does not lie on the established line of $\chi$ vs. amount of $^3\text{He}$, see Figure 3.17, not even at the highest temperature $550 \text{ mK}$. This implies that there is already a partial degeneracy of the $^3\text{He}$ atoms at $550 \text{ mK}$. These samples, which is even more pronounced at $450 \text{ mK}$. Figure 3.38 shows an interesting development of the temperature dependence of susceptibility with increasing coverage. The lowest coverage, sample: $18.27 + 0.74 \text{ nm}^{-2}$, is successfully fitted by the power law. Any higher coverage sample cannot be fitted by the power law formula as the curves are clearly not straight lines on the $\chi$ vs. $T$ log-log plot. Neither can these samples be fitted by a simple sum of a solid and liquid fraction. Nevertheless, these samples do seem to have a significant
“solid portion” at the lowest temperatures, determined by the seeming intercept of $\chi T$ at $T = 0$. This is going to be discussed in Section 3.8.13 about the low temperature behaviour of the susceptibility. Observed spin–spin relaxation time $T_2^*$ also suggest possible structural changes below 100 mK, from the presence of pronounced “dips” in the temperature dependence of the $T_2^*$. This is shown in Figure 3.63 in section 3.9 about relaxation times.

It is important to relate this set of measurements to the torsion oscillator experiment. Three of these samples (dark grey, dark red and dark green) lie in the coverage region in which collapse using two scaling parameters is achieved [98], as opposed to one parameter scaling which is sufficient at lower coverages, where the other two samples (magenta and cyan) are located. The exact range of the two parameter scaling $B$ is $19.36 - 19.96 \text{ nm}^{-2}$.

![Figure 3.38: Measured susceptibility of five samples with 0.74 nm$^{-2}$ $^3$He coverage above the region of commensurate phases. The inset in Figure b shows the limit: $T \to 0$.](image)

3.8.11 Promotion to the third layer (sample 20.01 + 0.74 nm$^{-2}$)

The region just below the third layer promotion is slightly uncertain for the $^3$He doped samples. It was established that 20.0 nm$^{-2}$ is the promotion coverage for pure $^4$He film. The $^3$He dopants could however potentially leave the second layer and occur in the third layer already below 20.0 nm$^{-2}$.

The last measured sample was prepared such that the $^4$He coverage was at the assumed promotion to the third layer, and then there was the excess of the 0.74 nm$^{-2}$ of $^3$He. Due to the larger zero-point motion of the $^3$He atoms we assume they are all in the third layer, while the two layers underneath are complete. Such a system should behave as a Fermi liquid. The temperature dependence of the susceptibility is shown in Figure 3.39, where it is fitted by a
sum of the Dyugaev formula and Curie law. The fitting is done in the $\chi$ vs. $T$ coordinates, and the fitting formula is:

$$\frac{\chi}{\chi_0} = \frac{C_C}{T} + \frac{C_D}{\sqrt{T^2 + T_F^{**2}}}$$

(3.78)

where $C_C$ is Curie constant of a small assumed solid fraction and $C_D$ is the Curie constant of the liquid fraction. The data points were averaged not to be spaced closer than $\Delta T/T_{\text{mean}} < 10\%$. The fitting parameters are given in Table 3.7. The Curie paramagnetic contribution is assumed generated by atoms trapped by inhomogeneities in the graphite, such as edges and steps.

![Graph](image)

Figure 3.39: Measured susceptibility of the first sample after the third layer promotion. Fit with a two component model is done. The inset in Figure b shows the limit: $T \to 0$. The ratio of $\chi T$ at $T = 0$ and $\infty$ determines a solid fraction of the sample.

<table>
<thead>
<tr>
<th>parameters</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^2/n_{df}$</td>
<td>$3.3 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$C_C$</td>
<td>2.3</td>
</tr>
<tr>
<td>$C_D$</td>
<td>365</td>
</tr>
<tr>
<td>$T_F^{**}$</td>
<td>231</td>
</tr>
</tbody>
</table>

Table 3.7: Fit parameters of the two components and quality of the fit as normalised $\chi^2$.

The value of $\chi T$ as $T \to \infty$ is $C_C + C_D = 367.3 \text{ mK}$. This is in reasonable agreement with the asymptote obtained in the next section (3.8.12) for samples with smaller total coverages. As $C_C = 2.3$, the solid fraction is only 0.61%. The effect that such little solid fraction has on the susceptibility at low temperatures is however enormous.
3.8.12 Susceptibility in the high temperature limit

The 550 mK susceptibility isotherm, done in section 3.7.2, suggested that measured samples with 0.51 nm$^{-2}$ of $^3$He, and less, behave as Fermi gas at these temperatures, with the susceptibility only dependent on the amount of $^3$He. The isotherm points of samples with 0.74 nm$^{-2}$ of $^3$He lay slightly below the established linear dependence of $\chi$ vs. $n$ of $^3$He, suggesting partial degeneracy at 550 mK. This isotherm procedure did not however discover any systematic development of $\chi$ at 550 mK with coverage (and thus also the $^3$He concentration).

In summary, these observation did not agree with the predictions of the finite bandwidth model, namely the suppression of the Curie constant, given by the $^3$He concentration, $x$. The heat capacity measurements suggested the bandwidth to be of the order of 400 mK. We however hypothesize existence of excited states, in which the $^3$He can exist at such high temperatures. In a system with multiple bands the finite bandwidth effect will be suppressed and $^3$He will behave as a free Fermi gas. Hence the susceptibility will be:

$$\chi_0 = \frac{C}{T_f^0}, \quad (3.79)$$

with the Curie constant:

$$C = \frac{\mu_0\mu^2}{k_B}N, \quad (3.80)$$

and the Fermi temperature given by equation 3.14, here simplified to: $T_f^0 = 505.4 \text{ mK} \cdot n_3$. The Fermi temperature is thus 258 (374) mK for the 0.51 (0.74) nm$^{-2}$ coverages respectively; and this is the value the data should be asymptotically approaching in the $\chi T/\chi_0$ vs. $T$ coordinates.

Figure 3.40: Susceptibility in the $\chi T$ vs. $1/T$ coordinates of two subset of samples with 0.51 and 0.74 nm$^{-2}$ of $^3$He, left and right, respectively. The value of the scaling constant used is $\chi_0 = 22.22$, as determined from the 550 mK isotherm.
Figure 3.40 shows the data in $\chi T/\chi_0$ vs. $1/T$ coordinates. It is of interest to study how the data approach the asymptote $T_F^0$, as different models predict different behavior in the limit, and these coordinates are ideal to demonstrate which model is favoured by the data. In the Free Fermi gas model the leading correction to the Curie law is linear:

$$\frac{\chi T}{C} = 1 - \frac{T_F}{2T} + \ldots,$$

in comparison, in Dyugaev model the leading correction is quadratic:

$$\frac{\chi T}{C} = 1 - \frac{1}{2} \left( \frac{T_{F*}}{2T} \right)^2 + \ldots$$

The linear fits in Figure 3.40 clearly demonstrate that the data favour the Free Fermi gas model, over Dyugaev model, at high temperature. Simultaneously however we make an interesting observation. The asymptote 374 mK, calculated using 505.4 mK nm$^{-2}$ multiplied by the $^3$He density 0.74 nm$^{-2}$, does agree with the data and the linear fit. However the asymptote 258 mK does not work with the data and the linear fit. If the linear fit of the data is done, it approaches a different asymptote, 265 mK. This discrepancy of a few percent does not significantly alter the conclusions drawn from the measurements. All data was analysed with $\chi_0 = 22.22$.

Figure 3.41: Fermi temperature according to the Free Fermi gas model (equation 3.81) at high temperatures for samples in the range of total coverage 18.0-19.5 nm$^{-2}$. Fermi temperature $T_{F*}$, according to the Dyugaev model, of the last sample (fit in Figure 3.39) shown for comparison.

Fermi temperatures determined from the slope of the linear fits are shown in Figure 3.41. They show a regular increase with total coverage, with no perceiv-
able feature between samples with 0.51 and 0.74 nm$^2$; this is in striking contrast with the observation that the 0.51 and 0.74 nm$^2$ samples predict different asymptote. The Fermi temperature $T_F^*$, according to the Dyugaev model, of the third layer sample, 20.01 + 0.74 nm$^2$ (fit in Figure 3.39) is shown for comparison in Figure 3.41. It is much larger than Fermi energies from the Free Fermi model. A Fermi temperature of the order of 80 mK is consistent with the Fermi temperature determined from the analyses of the heat capacity data, shown in Table 3.4.

3.8.13 Susceptibility in the low temperature limit

So far we have used the coordinates $\chi$ vs. $T$ and $\chi T$ vs. $T$ and vs. $1/T$, but we have not properly looked into the low temperature limit of the measured susceptibility. Coordinates $1/(\chi T)$ vs. $1/T$ best serve this purpose. A true Curie law manifests itself as a horizontal line. A power law with $0 \leq \alpha \leq 1$ will look fundamentally different, however, $\frac{1}{\chi T} = \frac{1}{C} (\frac{1}{T})^{1-\alpha}$. So if $\alpha \sim 0.9$ the curve is going to have a sharp increase from $1/(\chi T) = 0$, followed by flattening into a line. Such fundamental difference between the index $\alpha = 1$ and indices $\alpha \to 1$ has already been seen using the $\chi T$ vs. $T$ coordinates. The last model to check is the degenerate Fermi liquid, well below $T_F$, with temperature independent Pauli susceptibility $\chi_P$, $\frac{1}{\chi T} = \frac{1}{\chi_P} \frac{1}{T}$. This is a linear dependence.

We shall also address here the issue of the “solid fraction”, mentioned several times, calculated as the ratio of $\chi T$ at $T = 0$, established from the seeming intercept with the axis, and $\chi T$ at $T = \infty$. The reason for this definition is that the most simple solid, where all $^3$He atoms are fully localised and do not exchange energy, will behave as a simple Curie paramagnet, and will remain non-degenerate all the way to $T = 0$. In all the other models we see degeneracy of the fermions, and thus deviation from the Curie law. So if the measured sample leaves the high temperature isotherm upon cooling, and reaches a non-zero value of $\chi T$ at $T = 0$, we shall interpret this as a formation of a non-degenerate component, and simply call it the “solid fraction”.

Let’s explore one more model with respect to the $1/(\chi T)$ vs. $1/T$ coordinates. If the data points show a decrease of $1/(\chi T)$ with increasing $1/T$, it can only be explained by a rapid increase of the “solid fraction”, or ferromagnetism. This is because none of the models presented here have stronger dependence on temperature than the Curie law; only ferromagnetism shows an additional upturn in $\chi$ vs. $T$, upon cooling below $T_c$. Similarly, if we have phase coexistence of a degenerate liquid and non-degenerate solid, and upon cooling atoms from the liquid would rapidly solidify, we might observe the same behaviour.
Figure 3.42: Susceptibility in the \(1/(\chi T)\) vs. \(T\) coordinates of two different subsets of samples. On the left samples fitted with the power law are shown and the power law fit line is shown as well, with one exception, the sample 18.65 + 0.10 nm\(^{-2}\), which is shown on the right plot due to its small susceptibility. On the right samples below and above the power law fit region are shown. No averaging of the data executed.

Figure 3.42 shows the \(1/(\chi T)\) vs. \(1/T\) plots of all measured samples. Samples which have been fitted by the power law are shown together with their fits. The power law fit has always been done in both \(1/(\chi T)\) vs. \(1/T\) coordinates and \(\chi T\) vs. \(T\) coordinates, and it was shown that the difference is marginal, and the power law is therefore an appropriate model. Figure 3.42 indeed shows that very nicely in the low temperature limit. Sample 18.65 + 0.10 nm\(^{-2}\), in which the power law fit shows largest deflections from the data, is shown in the right panel of the figure. Generally, samples shown in the right panel manifest a very broad range of low temperature behaviours. At least two samples, 16.23 + 0.51 nm\(^{-2}\) and 16.82 + 0.51 nm\(^{-2}\) show clear decrease of \(1/(\chi T)\) with increasing \(1/T\). As argued previously this must be the consequence of a temperature activated solidification, or possibly ferromagnetism of a certain fraction of \(^3\)He atoms. This is consistent with the fact that these samples could never be fitted by a simple model based on Fermi liquids, the Finite bandwidth model and Curie law.
Figure 3.43: Susceptibility in the $\chi T$ vs. $T$ coordinates of two different subsets of samples. On the left samples fitted with the power law are shown and the power law fit line is shown as well. No averaging of the data executed.

Figure 3.44: “Solid fraction” of samples which have a putative intercept of $\chi T$ axis at $T = 0$, calculated as the intercept divided by high temperature asymptote of the $\chi T$ vs. $T$ plots.

Figure 3.43 addresses the question about the “solid fraction” of the studied samples. The data are shown once again in $\chi T$ vs. $T$ coordinates, but zoomed in at the lowest temperatures. It is remarkable that the majority of the samples
seems likely to intercept the $\chi T$ axis at a non-zero value at $T = 0$, all except the ones which most resemble the Curie law in $\chi$ vs. $T$ coordinates, and are successfully fitted with the power law. These samples, with 0.51 nm$^{-2}$ of $^3$He, actually remain true to the power law all the way to the lowest temperatures, as demonstrated in Figure 3.42, and should therefore reach $\chi T = 0$ at $T = 0$. The sample $18.27 + 0.74$ nm$^{-2}$, which was also fitted with the power law, however shows slight deflection from its fit curve, and inclination to the Curie law. For this sample, and for the rest of the samples, the putative intercept at a non-zero value of $\chi T$ at $T = 0$ was found. This was scaled by the high temperature asymptote of the $\chi T$ vs. $T$; values 258 and 374 mK were used, more on this was discussed in section 3.8.12. This is how the “solid fraction” was established, and it is shown in Figure 3.44.

3.8.14 Susceptibility measurements summary and discussion

The NMR susceptibility results give yet another insight into the structure of the pure $^4$He second layer on graphite. Nevertheless, it is important to note, that the observed behaviour might not only be determined by the physics of the second layer structure, but also by the interactions amongst Fermions, introduced by the $^3$He doping. We also add that the coverage scale of $^3$He doped film might differ slightly from the coverage scale of the pure film. Nevertheless, we believe this approach still gives us an invaluable insight into the second layer structure, which could otherwise be not studied by NMR. Our experimental observations can be summarised as follows:

- Susceptibility of all samples at the highest measured temperature, 550 mK, is determined by the amount of $^3$He. A degeneracy is observed for the samples with 0.74 nm$^{-2}$ of $^3$He.

- First three samples, measured in coverage range 16.7 - 17.7 nm$^{-2}$, show varying temperature dependence of $\chi$, but almost seem to reach the same low temperature limit of $\chi T$. In this coverage range the heat capacity measurements show linear temperature dependence and the TO measurements detect none, or small mass decoupling, characterised by the two-parameter scaling, where the energy scale parameter changes mildly, and the signal scale parameter changes substantially.

- Temperature dependence of susceptibility of samples in coverage range 17.9 - 19.1 nm$^{-2}$ can be very well fitted with a power law of the form $\chi \sim 1/T^\alpha$, where $\alpha$ varies with $^3$He coverage (concentration) between 0.65 and 0.9. For a given $^3$He coverage no large variation of $\alpha$ with total coverage was observed.

- Interestingly, these samples belong to several distinct regions according to
the TO and heat capacity. At the lowest coverage (black sample) we are still at TO region A, and heat capacity temperature dependence shows a pronounced dip. At higher coverages a pronounced maximum around 50 mK is observed in the heat capacity. We get to this region with the next sample (red), while we also move to TO region I, where largest superfluid signals are observed. The next two samples (green and blue) are in the near vicinity of the two commensurate phases, which are found in TO region II. The last sample fitted with the power law (magenta sample), has increased coverage of $^3$He, compared to its predecessors. The groups of samples with 0.74 nm$^{-2}$ were found to behave slightly differently compared to the samples with 0.51 nm$^{-2}$, at the highest temperatures (as evidenced by the infinite $T_0^F$ asymptote), and the lowest temperatures (as evidenced by the seeming intercept of $\chi T$ at $T = 0$).

- With the samples following in the coverage range 19.2 - 20.0 nm$^{-2}$, we are moving into the TO region B, characterised by two parameter scaling, with large variations of the energy scale parameter and minor variations of the superfluid signal scale parameter. The “solid fraction” of these samples varies very rapidly (see Figure 3.44); this is in interesting contrast with the samples from the lowest coverage range 16.7 - 17.7 nm$^{-2}$, where only very mild variation of the “solid fraction” is observed.

- A question thus naturally arises, whether the “solid fraction” is somehow related to the energy scale parameter observed by the TO experiment.

- Another question arises, whether the power law temperature dependence of $\chi$ is characteristic for the single parameter scaling region.

- The next section, 3.9, shows results of spin–lattice and spin–spin relaxation times measured on these samples. We shall experience a striking increase of the spin–lattice relaxation time in the vicinity of the $(7/12)$ commensurate phase. We shall also identify a coverage region in which the $T_2^*$ relaxation time shows a saturation below 10 mK. This coverage region is very similar to the region of the power law fitting, and contains the whole single parameter scaling region by TO.
3.9 Spin–lattice and spin–spin relaxation times in the second layer of $^4\text{He}$ on graphite

The method of measuring spin–lattice and spin–spin relaxation times are explained in section 3.7.4. Measurements of the relaxation times are not always part of an NMR experiment. For instance, the chosen way to study the second layer of $^4\text{He}$ on graphite by NMR was to measure the susceptibility of the $^3\text{He}$ dopants, which clearly distinguish the solid and liquid behaviour. The relaxation times do however influence the NMR measurements and thus the susceptibility, and it is therefore necessary to at least estimate them while performing the experiment.

3.9.1 Measurement of $T_2$

The spin–spin relaxation time ($T_2$) was never measured directly in this experiment. However, the time $T_2^*$, which determines the width of the resonance peak (equation 2.38), comes out automatically from every measured susceptibility point. The field-independent $T_2$ can be determined from $T_2^*$ according to equation 3.45. The field dependence of $T_2^*$ must be measured for that. The sample $18.27 + 0.51$ nm$^{-2}$ (denoted in the susceptibility result section by the dark blue star) was measured in three different fields, corresponding to Larmor frequencies 52, 100 and 153 kHz. An attempt to determine the field inhomogeneity $\Delta B/B_0$ and thus $T_2$ at the temperature 50 mK was made and it is shown in Figure 3.45. The resulting value: $\Delta B/B_0 = 540$ ppm roughly agrees with Frank Arnold’s measurements of the same magnet using the field dependence of $^{13}\text{C}$. His result was: $\Delta B/B_0 = (490 \pm 20)$ ppm [31].

It is also interesting to compare the inferred values of $T_2$ to an estimate of what the $T_2$ relaxation time should be, due to dipole–dipole interaction, in a homogeneous, rigid lattice, sample. The order of magnitude of the dipolar field at the distance $r$ from a magnetic moment $\mu$ is approximately [126]:

$$b \approx \frac{\mu_0 \mu}{4\pi r^3}. \quad (3.83)$$

For an inter-atomic spacing 1 nm, which corresponds to coverage 1.15 nm$^{-2}$, we get the dipolar field $b \approx 2.1 \mu\text{T}$. $T_2$ relates to it by:

$$\frac{1}{T_2} = \gamma \langle b^2 \rangle^{1/2}, \quad (3.84)$$

and comes out 2.3 ms. $^3\text{He}$ coverages studied in this work were all less than 1 nm$^{-2}$. Their dipole–dipole limited $T_2$ value is 89.8, 17.3, 7.8 ms and 4.46 for 0.10, 0.30, 0.51 and 0.74 nm$^{-2}$ respectively. Please also see a more accurate cal-
culation done in section 3.9.9, added after the viva.

Figure 3.45: Left: Field dependence of $T_2^*$ for the experimental sample: $18.27 + 0.51 \text{ nm}^2$. The data suggest $T_2$ is field independent and its value at 50 mK is $T_2 = 3.9 \text{ ms}$. The magnet inhomogeneity comes out: $\frac{\Delta B}{B_0} = 5.4 \cdot 10^{-4}$. Right: Calculated $T_2$ to $T_2^*$ correspondence according to equation 3.45 for different fields using the determined magnet inhomogeneity value.

### 3.9.2 Measurement of $T_1$

It was not originally intended to systematically measure $T_1$ in this experiment. One reason is that $T_1$ measurements are usually time consuming and another is that the spin–lattice relaxation time is often fairly short, and the measurements would be challenging the abilities of the NI PXI waveform generator [33] used for pulsing. Occasional pulse rate checks (PRC) are however always carried out during normal susceptibility measurements, to ensure that the magnetisation saturation effect, described in section 3.6, is not affecting the measured data. When studying the second layer of $^4\text{He}$ on graphite, a large increase of the spin–lattice relaxation time only started to occur when approaching the registered phases 4/7 and 7/12. While measuring the sample $18.27 + 0.51 \text{ nm}^2$ the effect became so pronounced, we decided to look into the spin–lattice relaxation in detail. The progressive saturation method seemed like a suitable way of measuring $T_1$ because of its similarity to the already well established pulse rate checks. The method is in fact best suited for samples with short $T_2$ compared to $T_1$ [127], which turned out to be precisely our case.

### 3.9.3 Spin-lattice and spin-spin relaxation time isotherms

The spin–lattice relaxation time was quite extensively studied for the sample $18.27 + 0.51 \text{ nm}^2$ for multiple reasons. Its sudden increase with coverage was very striking and seemed to have confirmed the significance of the commensurate
phases. Furthermore, its temperature dependence was very interesting. And finally, the relaxation was also found not to be described by a single exponential. Saturation functions obtained were found to be at least approximately described by stretched exponentials (equation 3.85), which are characterised by two parameters: $T_1^\ddagger$ and $n$. The $T_1^\ddagger$ isotherm across the region of the coverage, where it was measurable, is shown in Figure 3.46.

When increasing the coverage further to $18.27 + 0.74 \text{ nm}^{-2}$ by adding $^3\text{He}$, $T_1^\ddagger$ dropped very drastically. For coverages starting with $18.27 + 0.74 \text{ nm}^{-2}$ and higher, a proper measurement using a dense saturation curve was always performed at at least two temperatures. The relaxation time however never increased back to the very large values measured in the sample $18.27 + 0.51 \text{ nm}^{-2}$.

![Figure 3.46: $T_1^\ddagger$ isotherms as a function of coverage at 13 mK in the left graph and 4.6 mK in the right graph showing the enormous increase of $T_1^\ddagger$ in the vicinity of the commensurate phases. $T_1^\ddagger$ was properly measured by the saturation method at coverages $18.27 + 0.51$ and higher, and approximated for lower coverages.](image)

For samples with lower coverage than $18.27 + 0.51 \text{ nm}^{-2}$ we only had limited data from the PRCs and from calibration of the $^{13}\text{C}$ thermometer. The $^{13}\text{C}$ calibration was found to be the most reliable source. It was always done at 13 mK, with pulsing rate 2 s, and the standard tipping angle 7.2°. $T_1$ of $^{13}\text{C}$ is shorter than 2 s at these temperatures, but $^3\text{He}$ spins were getting saturated. $T_1^\ddagger$ is extracted from the magnetisation saturation assuming the approximative
functional formula 3.85 (a stretched exponential function), describing the sample 18.27 + 0.51 nm$^2$, with $n = 0.3$. The actual shape of the saturation curve remains of course unknown, hence large error bars were assigned to these data, assuming the stretching factor in the range: $0.2 \leq n \leq 0.8$. The samples closest to the commensurate densities 4/7 and 7/12 have by far the longest spin–lattice relaxation time. This can only be explained by localisation of the $^3$He impurities.

$T_2^*$ isotherms at 1, 10 and 100 mK are shown in Figure 3.47. The 100 mK isotherm shows regular decrease of $T_2^*$ up to coverage 19.3 nm$^2$, followed by an increase. Surprisingly, there is no pronounced step in $T_2^*$ when moving with $^3$He coverage from 0.51 to 0.74 nm$^2$, even though the sample is becoming significantly more concentrated; in the single step from approximately 7% to 11% in the second layer. This is true across the whole temperature range. There is a coverage range in which the 10 and 1 mK isotherms are almost identical. This range includes all samples that can be fitted by the power law, i.e. 18 – 19 nm$^2$; plus two additional samples with higher coverages. Samples outside this range show temperature development of $T_2^*$ all the way to the lowest temperatures.

![Figure 3.47: $T_2^*$ isotherms as a function of coverage at three different temperatures. A temperature independence of $T_2^*$ is apparent below 10 mK in the middle coverage range.](image-url)
3.9.4 The spin–lattice relaxation time in the vicinity of the 7/12 commensurate coverage

An example of the progressive saturation method measurement is shown in Figure 3.48 taken at 14.7 mK with a pulse strength $\theta = 7.2^\circ$. One can clearly see how individual plateaus are established when the pulsing time constant $\tau$ is changed, and the saturation curve thus progresses. Averaging of multiple FIDs used to obtain an individual measurement point is increased significantly when varying $\tau$, this is why the points have much smaller uncertainty at smaller $\tau$, than close to $M_\infty$. The reason is that making $\tau$ 12 times smaller allows for 12 times more averages to be taken, which results in factor $\sim 3.5$ decrease of uncertainty. However, the increase of uncertainty due to the measured magnetisation being smaller is only 1.1 times larger according to equation 3.60, which gives the saturation value of regularly relaxing system (and it is about 1.5 larger, estimating from the actual measurement in Figure 3.48). To obtain the saturation curve, points in each plateau were averaged together and scaled by the $M_\infty$ value, taken at the smallest pulsing rate which was found to be sufficiently long. Transition points between the plateaus were discarded.

Figure 3.48: An example of the progressive saturation method measurement, taken at 14.7 mK and with a pulse strength $\theta = 7.2^\circ$.

The saturation curves from a variety of temperatures and tipping angles are shown in Figure 3.49. The were found not to obey equation 3.55. Unexpectedly, saturation curves taken at a given temperature but with a different tipping angle
could be collapsed, scaling the \( \tau \) axis by \( 1 - \cos(\theta) \); and scaled as such they are shown in Figure 3.49. The arising factor is the known factor \( \hat{\tau} \) from equation 3.58. After being scaled by the angle factor, the saturation curves can be fitted by a stretched exponential function:

\[
\frac{M(t)}{M_{\infty}} = 1 - \exp \left( - \left( \frac{\hat{\tau}}{T_1^*} \right)^n \right). \tag{3.85}
\]

It was shown in section 3.7.4 that if the data are scalable, using the factor \( \hat{\tau} \), and the fit function is the stretched exponential, this is consistent with the sample having spatially inhomogeneous relaxation, with a distribution of relaxation times \( T_1 \) within the sample. The parameter labeled as \( T_1^* \), in the stretched exponential formula, denotes the pulsing for which the saturation function reaches the saturation level of \( (1 - e^{-1})M_{\infty} \). The stretched exponential fit of the saturation curves in Figure 3.49 was done for each combination of temperature and tipping angle, even though as explained, saturation curves from different tipping angles are actually collapsed together, and the resulting collapsed curves could be fitted as well. The first approach, however, gives us additional information about the reliability and uncertainty of the fit. Fit parameter results from all the saturation curves are given in Table 3.8, and their temperature dependence is shown in Figure 3.50.

Figure 3.49: Fits of the saturation curves with formula 3.85, taken at different temperature and with a different tipping angle.
Table 3.8: Fitting parameters of the saturation curves shown in Figure 3.49, according to equation 3.85, taken at different temperatures and using a different tipping angles.

<table>
<thead>
<tr>
<th>T [mK]</th>
<th>$\theta$ [°]</th>
<th>$T_1^\parallel$ [s]</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>2.6</td>
<td>2572</td>
<td>0.33</td>
</tr>
<tr>
<td>1.6</td>
<td>7.2</td>
<td>2889</td>
<td>0.39</td>
</tr>
<tr>
<td>4.7</td>
<td>2.6</td>
<td>1177</td>
<td>0.34</td>
</tr>
<tr>
<td>4.7</td>
<td>7.2</td>
<td>1334</td>
<td>0.34</td>
</tr>
<tr>
<td>4.7</td>
<td>27.1</td>
<td>1059</td>
<td>0.34</td>
</tr>
<tr>
<td>14.7</td>
<td>7.2</td>
<td>267</td>
<td>0.28</td>
</tr>
<tr>
<td>14.7</td>
<td>14.4</td>
<td>322</td>
<td>0.24</td>
</tr>
<tr>
<td>14.7</td>
<td>27.1</td>
<td>244</td>
<td>0.28</td>
</tr>
<tr>
<td>20.0</td>
<td>7.2</td>
<td>60</td>
<td>0.28</td>
</tr>
<tr>
<td>20.0</td>
<td>14.4</td>
<td>49</td>
<td>0.28</td>
</tr>
<tr>
<td>25.0</td>
<td>7.2</td>
<td>10.1</td>
<td>0.28</td>
</tr>
<tr>
<td>25.0</td>
<td>14.4</td>
<td>8.2</td>
<td>0.30</td>
</tr>
<tr>
<td>30.0</td>
<td>7.2</td>
<td>1.53</td>
<td>0.24</td>
</tr>
<tr>
<td>30.0</td>
<td>14.4</td>
<td>1.96</td>
<td>0.29</td>
</tr>
<tr>
<td>50.0</td>
<td>7.2</td>
<td>0.15</td>
<td>0.29</td>
</tr>
<tr>
<td>50.0</td>
<td>14.4</td>
<td>0.11</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Figure 3.50: Temperature dependence of the two saturation curves fit parameters. Legend same as in Figure 3.49.

It can be seen in the semi-logarithmic plot in Figure 3.50, left that there is very strong temperature dependence of the characteristic relaxation time $T_1^\parallel$; in comparison, there is a very weak, if any, temperature dependence of the stretching parameter $n$. If we assume the stretching to be indeed constant, we can achieve a further collapse of the saturation curves to a universal curve. This can be done in two different ways. Either the $\tilde{\tau}$-axis of saturation curves is simply
divided by $T_1^\dagger$ values from the best fit, Table 3.8; another possibility is to do another set of fits in which the stretching parameter is fixed on the mean value of $n$. Collapse accomplished by using both of these approaches is shown in Figure 3.51, where the stretching factor was fixed at a value $n = 0.3$; and in Figure 3.53, where the stretching is done by using $T_1^\dagger$ values from the two parameter fit. The collapse however has very similar quality in both cases.

The universal curve shown in Figure 3.51 can of course be fitted by the stretched exponential functional formula as well as the individual measurements. The fit line is shown in Figure 3.51. The saturation curve spreads across five orders of magnitude of $\hat{\tau}/T_1^\dagger$ and it is very different from a single exponential saturation function shown in dashed line. In the next section we shall investigate the origins of this anomalous relaxation and the implications of this observation.

## 3.9.5 Origins of the anomalous relaxation of $^3$He spins

Before going into the detail analyses we shall remind the notation of the mathematical functions and transformations we use. Figure 3.52 serves this purpose.
A Distribution function of relaxation times describes how many spins in the sample relax with a particular value of $T_1$. A Laplace transform of the distribution function gives the Relaxation function, which describes how the sample magnetisation is changing after a pulse. It is measurable by the inversion recovery method for instance (see section 3.7.3). Another Laplace transform of the relaxation function gives the Saturation function, which is measured by the progressive saturation method. The double Laplace transform equals the Stieltjes transform, which directly relates the distribution function and the saturation function.

Figure 3.52: Mutual relations of different discussed functions by Laplace and Stieltjes transform.

According to the analyses done in section 3.7.4 the significance of the stretched exponential is that, even though it is not the true Stieltjes transform of a Lévy stable distribution, the Stieltjes transform of a particular Lévy stable distribution is almost indistinguishable from the stretched exponential. For that the horizontal axis is scaled by a factor, and also the index of the Lévy stable distribution and the stretching factor are not equal. This was shown in Figure 3.19 for the $n = 1/3$ index Lévy stable distribution and $n = 0.31$ stretched exponential. The origins of the necessary horizontal (time) scaling were shown in Figures 3.21 and 3.20; where it was identified that the two families of curves reach the particular value of $(1 - e^{-1})M_\infty$ at a different value of $\hat{\tau}/T_1^\dagger$.

It was observed that the data are actually in a very good agreement with the Stieltjes transform of the $n = 1/3$ Lévy stable distribution. This is shown in Figure 3.53. The data points were collapsed using the first method; division by $T_1^\dagger$ from the two parameter stretched exponential fit; as opposed to the collapse in Figure 3.51. This was to illustrate how marginal the difference is. Additionally, the data has to be horizontally re-scaled by a factor of 1.7123. The value of
this factor was found numerically to minimise the $\chi^2$ of the model and the data, using formula 3.87. Scaling by the factor only results in a horizontal shift in the semi-logarithmic axes. This is how the Stieltjes transforms of the Lévy stable distributions are made to agree with stretched exponentials; it is therefore how the Stieltjes transform of the Lévy stable distribution curve is made to agree with the data, which are pre-processed using the stretched exponential.

![Collapsed saturation curves](image)

Figure 3.53: Collapsed saturation curves taken at different temperatures and with a different tipping angle. A stretched exponential fit (not shown) with two free parameters, $T^*_1$ and $n$, used for the collapse. A line obtained as one minus the Stieltjes transform of the Lévy stable distribution with index $n = 1/3$ (equation 3.75) shown as the dashed line.

The distribution of relaxation times for the $n = 1/3$ Lévy stable distribution is shown in Figure 3.54; this can be compared to the distribution of relaxation rates in Figure 3.19. There is of course no guarantee that the Lévy stable distribution with this particular index is the best description of the data. Furthermore, there is no guarantee that the physical distribution of relaxation times can be modelled by Lévy stable distributions in the first place. This family of distributions is however a good starting point, as within the Central limit theorem they can describe a broad range of physical systems with non-negative variable. We could search among the Lévy stable distributions for a distribution with even better agreement with the data, than the index $n = 1/3$. We chose not to do that at this point and instead we moved to a direct method of determination of the distribution function.
Direct method of the relaxation time distribution determination

The agreement of the Stieltjes transform of the \( n = 1/3 \) Lévy stable distribution model function and the data is fairly good, but not perfect, especially at low values of \( \hat{\tau}/T_1^* \). Furthermore, the data on the universal curve in this region seem to split into two sub-curves themselves. This is also supported by the step in the stretching parameter, \( n \), resulting from individual stretched exponential fits, in between curves taken at temperature higher than 10 mK and lower than 10 mK, shown in Figure 3.50. Due to limited number of experimental points it is not possible to examine saturation curves from individual temperatures by anything more complicated than the stretched exponential fit. We are therefore reliant on their collapse onto the universal curve. Nevertheless, it is still possible to divide the whole data set into two subsets, 10 mK being the limiting temperature.

![Figure 3.54: Lévy stable distribution according to formula 3.75 as relaxation times, rather than rates, which are shown in Figure 3.19. The semi-logarithmic plot requires the vertical axes to be in \( p(T_1)/T_1 \). The heavy tail is apparent at very small relaxation times.](image)

The most correct, and direct, mean of analysing the saturation curve is to do the true inverse Stieltjes transform of the curve. It was however found out that the Stieltjes-Perron formula [136] for calculating the inverse Stieltjes transform, which works with complex numbers, is not applicable to our data, real in nature.
Another approach, commonly used when trying to do an inverse transform of experimental data, is the so-called Uniform PENalty inversion algorithm (UPEN). This algorithm tries to minimize squared error of a fit plus a penalty term. It was for example utilised by Villiam Bortolotti et al., in the University of Bologna [137, 138]. This algorithm was also used by Gazizulin et al. [130] when analysing the measurements of $T_1$ of $^3$He in clay (Figure 3.22). In Bologna, they developed a whole software suite for finding the inverse Laplace transform. It has turned out that their software suite can be adapted to find the inverse Stieltjes transform as well. These algorithms find the solution by having an initial assumption about the distribution function, and then iteratively improving it by checking the agreement with the data. Bortolotti et al. claim that their UPEN algorithm is able to “avoid more maxima and minima in the distribution, than demanded by the data, minimizing the appearance of separate populations in
the computed distributions to the extent permitted by the data. Usually some smoothing is implemented in the distributions by means of the penalty function in order to avoid excess variation” [137].

The possible existence of peaks and similar structure in the distribution function is in fact very fundamental. It was shown that a continuous and smooth function, like the Lévy stable distribution, can be a very good starting point for the distribution function search; its Stieltjes transform model the data almost perfectly. Thus the question arises, whether the true distribution function does or does not feature peaks, which would perhaps explain the data even better. Moreover, it is fair to ask the question whether the data actually are not described by discrete relaxation mechanisms only. We shall examine the discrete component model first, before introducing preliminary results by the UPEN algorithm.

Figure 3.56: Temperature divided universal curve. Fit according to formula 3.86 with \( n = 3 \), and 6 fitting parameters. Graphs feature thin lines, showing the contributions of independent components. Bottom graphs show the position and significance of the relaxation mechanism with error bars determined from the uncertainty of the fits.
The discrete relaxation mechanism conception is in fact very straightforward to examine. A discrete relaxation mechanism implies a Dirac delta function in the distribution function. Stieltjes transform of the delta function is the bare Stieltjes kernel: \( \frac{1}{1 + \frac{\tau}{T_i}} \), or in our notation recognised as the function 3.61. The hypotheses of a distribution function consisting of \( n \) delta functions is therefore equivalent to doing a fit of the universal curve by the following functional formula:

\[
\frac{M_\tau}{M_\infty} = \sum_{i=1}^{n} \frac{x_i}{1 + (\tau/T_i)/(\hat{\tau}/T_i^\dagger)},
\]

(3.86)

where \( x_i \) denotes the fraction relaxing according to \( T_i \), and technically are the integrals under the particular delta function; and \( \hat{\tau}/T_i^\dagger \) are positions of the delta functions on the \( \hat{\tau}/T_i^\dagger \) axis. The sum of \( x_i \) must be equal to one; this condition can be imposed on the fitting routine to lower the number of fit parameters from \( 2n \) to \( 2n - 1 \).

Figure 3.57: Full data set universal curve. Fit according to formula 3.86 with \( n = 3 \), and 6 fitting parameters shown in solid black curve. The graph features thin lines, showing the contributions of independent components. Shown in dashed red curve is the \( n = 1/3 \) Lévy stable distribution, and shown in dotted blue is the stretched exponential. Inset graph shows the position and significance of the relaxation mechanism, within the three mechanism model, with error bars determined from the uncertainty of the fit, and the Lévy stable distribution in green.
The fitting of the universal curve, divided into the low and high temperature subsets, according to formula 3.86, was done. The data do not obviously support a single mechanism relaxation model. A two component model works well with the low temperature data, while being slightly insufficient for the high temperature data. Three components fit the high temperature data very well and still remains a good fit for the low temperature data, but become unstable, as evidenced by the error bars which come out of the fitting routine. The high temperature data become unstable with a four component model. The best fits of the two (three) component model are shown in Figure 3.55 (3.56), featuring both data subsets.

The most important outcome of this two subsystem division analyses was to find out how significant is the disagreement of the two temperature ranges, on the universal curve, in the lowest values of $\tilde{\tau}/T_1^\dagger$. Figures 3.55 and 3.56 show that there is always a mechanism in the vicinity of $T_1^\dagger$ in both temperature regimes, and the only difference between the two regimes is in mechanisms with $T_1^\dagger \ll T_1^\dagger$. While there is a significant fast relaxation mechanism present at high temperatures, it is less pronounced at lower temperatures. The observation that there is a relaxation mechanism in the near vicinity of $T_1^\dagger$ is also crucial, because we shall later investigate the temperature dependence of $T_1^\dagger$ and this increases its importance from mere 'characteristic relaxation time' to spin–lattice relaxation time of an actual relaxation mechanism.

Figure 3.56 suggests that the three discrete relaxation mechanism model fits the universal curve just as well, or even slightly better, than the Stieltjes transform of the $n = 1/3$ Lévy stable distribution. It especially helps in the region of the smallest $\tilde{\tau}/T_1^\dagger$, where the high temperature data peel off from the transformed Lévy stable distribution function. We can numerically calculate the goodness of the proposed models using the $\chi^2$ value:

$$\chi^2 = \sum_{i=1}^{n_p} \frac{(x_i - M)^2}{M^2},$$

where $n_p$ is the number of points. This definition is the same as used in the susceptibility measurements analyses. Using the $\chi^2$ value we shall compare the three component model on the full, undivided data set, to the best fit by the transformed Lévy stable distribution. The two models and the data are shown in Figure 3.57. We are still using the Stieltjes transformed Lévy stable distribution with index $n = 1/3$, which is scaled by the horizontal factor 1.7123 (same as in Figure 3.53).

The values of $\chi^2/n_p$, where $n_p$ is the number of experimental points was calculated for the two models in the whole range of $\tilde{\tau}/T_1^\dagger$. The results then are:
Three component model: $\chi^2/n_p = 6.59 \cdot 10^{-4}$.

- Transformed Lévy stable distribution with $n = 1/3$: $\chi^2/n_p = 76.9 \cdot 10^{-4}$.
- Stretched exponential: $34.3 \cdot 10^{-4}$.

It was also calculated over a limited range $0.1 < \chi^2/n_p$. The results then are:

- Three component model: $\chi^2/n_p = 4.62 \cdot 10^{-4}$.
- Transformed Lévy stable distribution with $n = 1/3$: $\chi^2/n_p = 5.64 \cdot 10^{-4}$.
- Stretched exponential: $7.0 \cdot 10^{-4}$.

The fitting and the $\chi^2$ analyses support the discrete three mechanism model against the continuous Lévy distribution model. The difference in the goodness of the fit is however not too big. This illustrates a very important property of transformed distributions. In accordance with the Central limit theorem relatively large changes to the distribution function result to only minor changes in the transformed function; in our case the saturation function.

**Preliminary results by the UPEN algorithm and their testing using the Monte Carlo approach**

Distribution functions found by the UPEN algorithm developed by Bortolotti et al. are shown in Figures 3.59 and 3.61 for the temperature divided and undivided universal curve. Preliminary results suggest that these distribution functions have superior agreement with the data, given by the $\chi^2$ value, than the three component model and the transformed Lévy stable distribution. The question however arises whether the distribution found by the UPEN algorithm is the best and unique one. A very simple, yet powerful method to test a reliability of an algorithm which searches for a solution, is to use Monte Carlo approach and search for a solution completely randomly. If the Monte Carlo routine finds a better solution than the tested algorithm, the tested algorithm is not working properly; if it finds distributions with equally good agreement with the data, it means the tested algorithm did not find a unique solution. In that case, it is possible that the data do not enable that. If the Monte Carlo approach does not find a better solution than the tested algorithm, it speaks in favour of the algorithm.
In case of the UPEN algorithm, which searches for a distribution of relaxation times, the proposed Monte Carlo test simulation will work in the following way. A homogeneous logarithmic spacing of certain number of bins \((N_b)\) is created in a range between two values of \(T_1^i\) (it could be \(10^{-3} - 10^{3}\) of \(T_1^\dagger\)). \(N_b\) of random numbers are generated, while requiring their sum to be equal to one. These numbers are also randomly distributed into the prepared bins. A completely random distribution is thus constructed. Equation 3.86 is used, where \(n = N_b\), to calculate the saturation function. The saturation function is compared with the data using the \(\chi^2\) value. This is repeated until a distribution function is found, which gives an agreement with the data better than a value required.

Figure 3.58: Saturation functions, and their agreement with the data, according to distribution functions found by the Monte Carlo approach.

Figure 3.59: Comparison of distribution functions obtained by different approaches for the low and high temperature universal curve.
The Monte Carlo search was applied for the low and high temperature subsets of the universal curve. Distributions which have an agreement with the data better than the three component fit were relative easily found by this random approach, this is shown in Figure 3.58. So far however, no distribution was found which would exceed the quality of the distribution found by the UPEN algorithm. This analysis is currently a work in progress.

Figure 3.60: Saturation function corresponding to the UPEN found distribution function, shown in Figure 3.61. Figure by Villiam Bortolotti.

Figure 3.61: Comparison of distribution functions obtained by different approaches for the global universal curve.
Figure 3.61 shows the UPEN distribution found for the undivided universal curve. It is plotted together with the Lévy stable distribution with index $n = 1/3$ and the three peaks from the three component fit. A broad agreement is apparent especially around $T_1^{\dagger}$. The results have a slight disagreement at low values of $T_1^{\dagger}$. This is the result of small point density on the universal curve there and possibly additional constrains within the UPEN algorithm. The saturation curve corresponding to the UPEN distribution in Figure 3.61 is shown in Figure 3.60.

To summarise, by comparing the distribution function results obtained by several approaches we were able to spot the following common features:

- There is always a relaxation mechanism in the near vicinity of $T_1^{\dagger}$.
- There are relaxation mechanisms at times up to 50 times longer than $T_1^{\dagger}$.
- There are relaxation mechanisms significantly shorter than $T_1^{\dagger}$. Due to the smaller density of the data points at low values of $\tau/T_1^{\dagger}$ precise determination of these mechanisms does not seem possible.

In the next sections we shall investigate the temperature dependence of the characteristic relaxation time $T_1^{\dagger}$. Results obtained in this section tell us that this dependence will accurately describe the long relaxation mechanisms, as those were observed to be temperature independent. It will however not describe the fast relaxation mechanisms, as those were observed to become less pronounced below 10 mK already from the look of the saturation functions. A work in progress is establishing a microscopic model of the system, to explain why do we have the distribution of relaxation times in the first place.

### 3.9.6 Temperature dependence of the relaxation times

**Temperature dependence of the characteristic spin–lattice relaxation time $T_1^{\dagger}$**

$T_1^{\dagger}$ extracted from the stretched exponential fits of the individual saturation curves was found to have a particular temperature dependence. It is shown in Figures 3.50 and 3.62. The strong increase below 30 mK can be well understood within the picture of a thermally activated process. This process on its own would however predict $T_1$ at 1 mK to be of the order of $10^{88}$ sec. Another relaxation process must be present to ensure thermalisation of the sample. The low temperature end was found to be consistent with a Korringa type of behaviour, in which the relaxation time and the temperature are inversely proportional. These two effects are added together and give the value of relaxation rate, which is the inverse of the relaxation time:

$$
\frac{1}{T_1^{\dagger}} = r^{\dagger} = a \exp\left(-\frac{\Delta}{T}\right) + \frac{T}{\kappa}.
$$

(3.88)
The temperature dependence of $T_1^\dagger$ was fitted by this formula and the result is shown in Figure 3.62. The fit parameters are summarised in Table 3.9.

<table>
<thead>
<tr>
<th>parameter</th>
<th>fitted value</th>
<th>uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ [s$^{-1}$]</td>
<td>529</td>
<td>±96</td>
</tr>
<tr>
<td>$\Delta$ [mK]</td>
<td>210</td>
<td>±6</td>
</tr>
<tr>
<td>$\kappa$ [mKs]</td>
<td>4900</td>
<td>±360</td>
</tr>
</tbody>
</table>

Table 3.9: Results of the thermal activation process and Korringa type of relaxation fit (equation 3.88).

![Figure 3.62](image)

Figure 3.62: The temperature dependence of $T_1^\dagger$, the inset shows temperature dependence of relaxation rates in log-log plot. Fit by formula 3.88 was done to relaxation rates. Uncertainty of the data points was taken as the standard deviation of the points at a given temperature.

The temperature dependence of $T_1^\dagger$ seems to be well described by formula 3.88, even though the uncertainty of the fit parameters is substantial. Normalised $\chi^2/n_{df}$ value is calculated as:

$$\chi^2 = \sum_{i=1}^{n_p} \left( \frac{r_i^\dagger - M_i}{\sigma_i} \right)^2,$$

(3.89)

where $n_p$ is the number of data points and $M_i$ the model. The number of degrees of freedom is $n_{df} = n_p - n_{par}$, where $n_{par}$ is the number of parameters;
here three. Calculated in that way, normalised $\chi^2$ is $\chi^2/n_{df} = 2.75$, meaning that the disagreement of the data points and the fit line is of the same order as the standard deviation of the data points.

**Temperature dependence of the spin–spin relaxation time**

The temperature dependence of $T_2^*$ for all recently measured samples can be seen in Figure 3.63, top. $T_2$, recalculated from $T_2^*$ using equation 3.45 and the magnet inhomogeneity: $\frac{\Delta B}{B_0} = 5.4 \cdot 10^{-4}$, is shown for selected samples in Figure 3.63, bottom. The recalculated $T_2$ inherits, of course, uncertainty coming from the uncertainty of the magnet inhomogeneity value. Assuming that to be 50 ppm (taken as the difference of measurements on $^3$C by Frank Arnold [31], and current measurements on $^3$He), this uncertainty is represented by error bars of size increasing with the value of $T_2$. The low temperature values of $T_2$ are fairly reliable, whereas the high temperature values are very imprecise. Nevertheless, the overall trend of increasing $T_2^*$ with temperature of course remains. Samples $16.23 + 0.51 \text{ nm}^{-2}$ and $20.01 + 0.74 \text{ nm}^{-2}$ (corresponding to the lowest and the highest coverage) differ in their $T_2^*$ value at 550 mK from the rest of the samples. This observation contrasts with the susceptibility isotherm at 550 mK, where simple dependence on the amount of $^3$He in the sample is observed.

### 3.9.7 Frequency dependence of the relaxation times

The frequency dependence of $T_2^*$ was discussed in section 3.9.1, where we determined the magnet inhomogeneity. In order to do that, $T_2$ was in fact assumed frequency independent. This was supported by the data, as the measured points lay on a straight line.

As opposed to that, $T_1^\dagger$ characteristic relaxation time does have a frequency dependence, which was measured by the progressive saturation method. The frequency dependence is shown in Figure 3.65. The shape of the saturation curves does not seem to be changing with field. This is shown in Figure 3.64, where the saturation curves are fitted with stretched exponentials and the three component model. The stretched exponential yields the two parameters, $T_1^\dagger$ and $n$, which are given in Table 3.10. Knowing the respective values of $T_1^\dagger$ from the stretched exponential fit, the data are scaled by $T_1^\dagger$, and the three component model fit is done (Figure 3.64, middle row). The three component model produces three peaks which are shown in the bottom-most line of Figure 3.64. The position and significance of the three peaks actually seems very similar for the 52 and 153 kHz fits, with slight disagreement with the 100 kHz peaks. We must however bear in mind that the single temperature universal curve lacks the proper point density for precise observations.
Figure 3.63: TOP: Temperature dependence of $T_2^*$ as determined from the Lorentzian fits to FIDs. The vertical upper limit 3 ms corresponds to the maximum value of $T_2^*$ we are able to measure, due to the magnet inhomogeneity limitation. BOTTOM: Temperature dependence of $T_2$ calculated form $T_2^*$ using formula 3.45 and the magnet inhomogeneity 540 ppm. Dashed horizontal lines denote $T_2$ values approximated from dipole–dipole interaction of the particular $^3$He coverage (equation 3.84).
Figure 3.64: Frequency dependence of the saturation curves taken at 14.1, 14.7 and 14.1 mK at 52, 100 and 153 kHz respectively, fitted by stretched exponential (top row), and the three component model (equation 3.86, middle row). The bottom row shows the three found components.

<table>
<thead>
<tr>
<th>$f$ [kHz]</th>
<th>$T$ [mK]</th>
<th>$\theta$ [°]</th>
<th>$T_1^f$ [s]</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>14.1</td>
<td>4.0°</td>
<td>167</td>
<td>0.33</td>
</tr>
<tr>
<td>52</td>
<td>14.1</td>
<td>7.2°</td>
<td>158</td>
<td>0.31</td>
</tr>
<tr>
<td>100</td>
<td>14.7</td>
<td>7.2°</td>
<td>267</td>
<td>0.28</td>
</tr>
<tr>
<td>100</td>
<td>14.7</td>
<td>14.4°</td>
<td>332</td>
<td>0.24</td>
</tr>
<tr>
<td>100</td>
<td>14.7</td>
<td>27.1°</td>
<td>244</td>
<td>0.28</td>
</tr>
<tr>
<td>153</td>
<td>14.1</td>
<td>4.1°</td>
<td>432</td>
<td>0.28</td>
</tr>
<tr>
<td>153</td>
<td>14.1</td>
<td>7.2°</td>
<td>402</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 3.10: Fitting parameters results. Fit of the saturation curves shown in Figure 3.64, obtained at different frequencies, according to equation 3.85.
The measurement temperature was slightly different at 100 kHz, compared to the other two fields. The 100 kHz points were corrected using the discovered temperature dependence of $T^\ast_1$ (see Figure 3.62). The observed field dependence shown in Figure 3.65 appears approximately linear. The linear fits through the points in Figure 3.65 yield: $T^\ast_1 [s] = (2.8 \pm 0.1)f_L [kHz]$ and $T^\ast_1 [s] = (2.5 \pm 0.2)f_L [kHz] + (40 \pm 26)$. This linear dependence is further discussed in section 3.9.9.

![Figure 3.65: Field (Larmor frequency) dependence of $T^\ast_1$. 100 kHz corrected value taken from the established temperature dependence, equation 3.88. Linear fits with free and fixed origin done through the (corrected) data points.](image)

3.9.8 Relaxation times summary and discussions

A summary of the measurements and analyses done on the relaxation times is the following:

- The spin–lattice relaxation is significantly slowed down in the near vicinity of the commensurate phases, particularly the 7/12 phase. This is shown in Figure 3.46.

- The spin–lattice relaxation was studied by the so-called progressive saturation method. Within this method, we remained in the so-called correspondence region, in which the functional form of the saturation curve is given by equation 3.72 (in the general case of distribution of relaxation times). One minus the saturation function is recognised as the Stieltjes transform of the relaxation time distribution.

- We have indeed seen that the saturation curve does not support a single component relaxation time. We have tried to model the distribution of
relaxation times to be continuous and discrete, and tried to determine if the saturation function prefers one of the cases.

- A software suite for finding the inverse Stieltjes transform of the saturation curve using the UPEN algorithm [137] provided us with a distribution function featuring three slightly broadened peaks (Figures 3.59 and 3.61). This is consistent with the overall good agreement of the discrete three peaks model and the universal curve.

- The distribution function found by the UPEN algorithm has the best value of $\chi^2$ of all the studied models. Nevertheless the appearance of this distribution function, and especially presence of the three peaks, creates broad consistency across the done analyses. It is desirable that a microscopic model is constructed, which will explain these observations.

- The appearance of the saturation function slightly changes between temperature ranges above and below 10 mK. There seems to be an additional fast relaxation mechanism playing a role above 10 mK; this fast relaxation mechanism is less pronounced below 10 mK. This is shown in Figure 3.56.

- Temperature dependence of the characteristic relaxation time $T_1^\ddagger$ was established and successfully fitted by a model consisting of a thermally activated process and a Korringa type of relaxation. These two respective mechanisms actually govern the relaxation above and below 10 mK, as can be seen in Figure 3.62, so the observation of the changes to the distribution function around this temperature is consistent.

- The spin–spin relaxation time $T_2^*$ was extracted from $T_2^\ast$ by subtracting the effect of magnet inhomogeneity. These calculated $T_2$ values are reliable below 10 ms, but their uncertainty increases substantially above 10 ms.

- $T_2^*$ increases with increasing temperature for all measured samples above 10 mK. Samples from a relatively broad coverage range, 18.0 - 19.5 nm$^{-2}$, however show a saturation of $T_2^*$ below 10 mK.

- $T_2^*$ does not show any striking dependence on the amount of $^3$He in the sample.

- Susceptibility isotherm at 550 mK of the samples with 0.51 nm$^{-2}$ of $^3$He reveals non-degenerate Fermi gas behaviour. $T_2^*$ however differs at this temperature even among samples with the same amount of $^3$He.

- Characteristic $T_2$ relaxation time calculated for direct dipole–dipole interaction among immobile homogeneously distributed spins with a given $^3$He coverage was calculated. Surprisingly, obtained $T_2$ seems to be below the dipole–dipole value at low temperatures, and above it at high temperatures.
3.9.9 Further comments and implications of the anomalous $^3$He thermalisation; manifestation of many body localisation?

This section was added to the original helium experiment chapter after the viva. Its purpose is to react to comments and suggestions received in the viva in a concise way. The examiners requested some further explanations about the measurements and analyses of the two relaxation times. Furthermore, they pointed out that the anomalous thermalisation of the $^3$He spins in the commensurate 7/12 sample is likely a manifestation of the so-called many body localisation, a phenomenon in statistical physics describing an alternative time evolution of a quantum many body system to thermalisation.

Rigid lattice behaviour

Our observation of very long $T_1$, yet fairly short $T_2$ is a typical behaviour of a rigid lattice (solid), as can be seen in Figure 3.66, which describes a typical behaviour of 3D systems. The figure features the following regimes: If the characteristic motion of spin carrying particles is fast compared to the Larmor frequency, $\tau_c \ll \omega_0^{-1}$, the two relaxation times equal each other. This is the case in most liquids. When $\tau_c = \omega_0^{-1}$, we observe a minimum in $T_1$ and the two relaxation times stop being equal. If the characteristic motion is much slower than the Larmor frequency, $\tau_c \gg \omega_0^{-1}$, $T_1$ rises with $\tau_c$, while $T_2$ flattens out and remains constant. The increase of $T_1$ with $\tau_c$ changes form system to system. It is however important to note, that in most systems $T_1$ increases slowly (like a power law for instance), while a strong divergence, as observe in this work, is very rare. As an example, $T_1$ in normal liquid $^3$He is believed to obey the power law dependence [139, 140], $T_1 = K \frac{m^*}{\hbar} (\frac{m^*}{k_B T})^3$. For thermally activated systems, the correlation time is typically a simple monotonous function of inverse temperature [141]. 2D systems differ from 3D systems by having a very broad $T_1$ minimum. In the vicinity of this minimum, the field dependence of $T_1$ was found to be linear [142]. This is consistent with our observation of the field dependence, nevertheless it is unlikely that our system would actually be close the the $T_1$ minimum, as $T_1$ is clearly diverging. The observation of simultaneous field independence of $T_2$ and linear field dependence of $T_1$, while $T_1$ approaches divergence, is therefore striking. Nevertheless, the dependence of the relaxation times on field is still an unresolved problem in NMR [143].

Let’s examine closely the “solid” limit of $T_2$, where is becomes independent of $\tau_c$. A more accurate formula to formula 3.84, describing the spin–spin relaxation in a rigid triangular lattice, taking more nearest neighbours into account [144,
\[ T_2 \approx 0.56 \frac{a^3}{\hbar \gamma^2} \frac{4\pi}{\mu_0}, \]  

(3.90)

where \( \gamma \) is the gyromagnetic ratio and \( a \) the lattice parameter. If we consider the known coverage of \( ^3\text{He} \) in the sample with the diverging \( T_1 \), 0.51 nm\(^{-2} \), to be forming a triangular lattice, hence \( a = 1.5 \text{ nm} \), we obtain \( T_2 \approx 4.3 \text{ ms} \), which is about a half of the result of formula 3.84. The observed \( T_2 \) is still about a factor of 2 smaller than this value. We must however keep in mind, that formula 3.90 is still only approximative and does not consider for example displacement due to zero point motion. The calculated and observed values of \( T_2 \) can therefore be considered to be in fair agreement. This comparison provides a proof that the \( ^3\text{He} \) atoms are, to an extent, immobile with respect to each other. We do not however know if they occupy fixed or random positions in the second layer lattice, and how do they contribute to the supersolidity of the second layer. For this coverage it is observed by the torsional oscillator experiment (see Figure 3.23), that only about half of the mass would eventually decouple in the \( T = 0 \) limit.

![Figure 3.66: Variation of \( T_1 \) and \( T_2 \) with motion in a typical 3D system, featuring a “liquid” region where the relaxation times are equal, a minimum of \( T_1 \) at the inverse of Larmor frequency, and a “solid” region where the relaxation times behave very differently. For thermally activated systems, the correlation time \( \tau_c \) is typically a simple monotonous function of inverse temperature [141]. Figure from [126].](image)

Another piece of experimental observation is that the FID in the sample with 0.51 nm\(^{-2} \) of \( ^3\text{He} \) is exponential and hence the NMR lines are Lorentzians. A true rigid lattices would typically have a Gaussian line shape, while the Lorentzian line shape is common to liquids. However, the exponential FID can also be explained by having a distribution of Gaussian \( T_2 \) relaxation times [141]. This is of course natural to observe, considering there is also the distribution of \( T_1 \) relaxation times.
Let’s now examine what happens for the samples in the vicinity of the commensurate phases when the concentration of $^3\text{He}$ is lowered. This considers the orange and green samples in Figure 3.63 with 0.30 and 0.10 nm$^{-2}$ of $^3\text{He}$ respectively. Most strikingly, in neither of these two samples the low temperature divergence of the spin–lattice relaxation time was observed. This implies that an existence of rigid lattice is not sufficient for occurrence of the divergence; interactions among $^3\text{He}$ atoms must play a role too. The observations suggest that a minimum amount of $^3\text{He}$ dopants is required to induce the divergence.

The behaviour of $T_2$ in the samples with lesser content of $^3\text{He}$ is also very interesting. In case of the sample with 0.30 nm$^{-2}$ of $^3\text{He}$ coverage, $T_2$ is very similar to the sample with 0.50 nm$^{-2}$ of $^3\text{He}$ coverage. Further lowering the $^3\text{He}$ coverage to 0.10 nm$^{-2}$ even causes $T_2$ to decrease in the lowest temperature limit, compared to the previous two samples. If in all samples the $^3\text{He}$ was forming a rigid triangular lattice (or be located in a rigid triangular lattice), $T_2$ should be significantly longer in the lower coverage, yet we observe the exact opposite behaviour. These measurements certainly have the potential to tell us a lot about the $^3\text{He}$ interactions, nevertheless at this stage this behaviour is not understood.

It is however clear from these observations, that we cannot increase $T_2$ by decreasing concentration in this particular system, thus creating a system which would feature both relaxation times to be long.

Figure 3.67: A boundary between ergodic and MBL systems featuring a quantum critical point (QCP) according to Abanin [146]. The coupling strength to an external bath $\gamma$ is to an extend equivalent to temperature in standard systems with quantum criticality (like heavy Fermions). The potential $\Delta$ captures the disorder of the environment.

**Anderson many body localisation**

The phenomenon of many body localisation (MBL) dates back to a paper by P. Anderson [147], in which he had shown that an impurity system in low concentrations, where the motion is realised via quantum jumps with a characteristic energy $J$, and where medium is to an extend random, the impurities will fail
to thermalise and will reach a state of localisation, as a consequence of the absence of diffusion. The ratio of $\Delta/J$ plays a fundamental role here. Methods of statistical mechanics cannot be applied for systems in MBL, as they are not in equilibrium with their surrounding [146]. The system can arrive into the state of MBL by non-thermodynamic transition via a local critical point [148] (see Figure 3.67). This phenomenon has been observed in ultra cold gasses [149]; let’s mention for example a 2D lattice of fermions with a variable disorder potential [150], a system which resembles our own. MBL was also proposed for the system of $^3$He impuritons in bulk solid $^4$He [151, 152], which is discussed in section 3.5 as a very closely related system to ours.

Our system features $^3$He impuritons, diluted in the second layer of $^4$He, adsorbed on graphite. The whole of second layer is in the 7/12 commensurate coverage with respect to the first layer (see section 3.4). This commensurate coverage features lattice sides with inequivalent adsorption potential, above the lattice of the first layer. The $^3$He impuritons hence move in a potential which is to an extent random, at least on short length scales. The impuritons interact via strain interactions; these are however weak. The system can be prepared by increasing the second layer coverage, which is of course a parameter other than temperature. These are all characteristics which make our system a good candidate for the realization of MBL. We observe a thermally activated divergence (see Figure 3.62), which on its own would give the spin–lattice relaxation time at 1 mK of the order of $10^{88}$ sec, which is 71 orders of magnitude longer time than the age of the universe! This striking divergence is compromised by the presence of another relaxation process, in which $T_1^\dagger$ diverges as $1/T$, and resembles the Korringa type of relaxation. The origins of this low temperature relaxation mechanism are unknown. Another important fact is that our system is observed to be very inhomogeneous, as evidenced by the very broad distribution of relaxation times. The distribution is, to a first approximation, temperature independent. What distinguishes the slow and the fast fraction of the spins and how they influence each other is a conundrum. Of crucial importance might be the fact, that in this coverage, the torsional oscillator detects only about 50% mass decoupling. The natural question is, whether the $^3$He impuritons contribute exclusively to the supersolid or normal fraction, or into both.

The lack of thermal relaxation in MBL systems reduces the decoherence. In ideal case, both $T_1$ and $T_2$ are long. Such systems attract much attention as potential candidates for quantum memories, see for instance [153, 154, 155]. Our system does not however fall into this category, as the spin–spin relaxation time was found to be impossible to prolong by dilution of $^3$He, and thus it is inevitably too short.
The effect of $^{13}$C impurities on the relaxation times

The effect of $^{13}$C nuclei in the graphite on the spin–spins relaxation is estimated to be small. Their abundance in natural graphite is only 1.11%. Assuming the hexagonal lattice parameter of graphite, $a = 1.42\text{Å}$, the coverage of these impurities in a single layer of graphite is $0.04\text{nm}^2$, more than ten times smaller than the $^3\text{He}$ coverage. The exact distance of the second He layer from the graphite is not known, but a rough estimate would be a couple of Angstroms. This gives the magnitude of the dipolar field produced by the $^{13}$C impurity in the second layer of the order of $1\mu\text{T}$. This is comparable to the typical magnet inhomogeneity for the experimental field corresponding to $^3\text{He}$ Larmor frequency 100 kHz (see section 3.9.1). This field inhomogeneity coming from the $^{13}$C impurities is of course immobile, like the true magnet inhomogeneity, but has a much shorter characteristic length scale. The $^{13}$C dipolar field is of the same order of magnitude, but slightly smaller, as the rigid lattice dipolar fields coming from $^3\text{He}^3\text{He}$ interaction. From these estimates it is clear that this effect the spin–spin relaxation only marginally.

Another question is the influence of the $^{13}$C impurities on the spin–lattice relaxation. This phenomenon of the “relaxation by unlike spins” is discussed for example in [143]. To estimate this effect it is important to know the spectral density of the auto-correlation functions of the $^3\text{He}$ atoms, at frequency corresponding to the difference of the Larmor frequencies of both isotopes ($^3\text{He}$ and $^{13}$C). This is a very complicated issue, nevertheless it could potentially be very important. Spin–lattice relaxation in $^{13}$C, and its temperature dependence, is described in section 2.2.3. It was also previously measured at Royal Holloway [31]. $T_1$ of $^{13}$C flattens as a function of increasing temperature at around 20 mK at a value of about 300 sec. Below 20 mK it increases with decreasing temperature approximately as $T^{-1/2}$. This behaviour was found to be the generalised Korringa type of behaviour for semiconductors [156]. We see noting of this temperature dependence in our the measurements on $^3\text{He}$. Above 15 mK, $T_1$ of $^3\text{He}$ is in fact shorter than that of $^{13}$C. It is only below 10 mK where the $^{13}$C might play a role. If this was the case it would somehow likely be responsible for the unexplained Korringa type of behaviour observed.

Measurements of the spin–spin relaxation by spin echo

The spin echo measurement is able to eliminate the instrumental effect of the magnet inhomogeneity and measure the pure spin-spin relaxation time $T_2$. The principle of the echo is the following. A 90° pulse tips the spins into the $xy$-plane. The spins dephase due to the mutual dipolar fields and due to the magnet inhomogeneities. After a time period $t$, which is short or comparable to $T_2$, a 180° pulse is applied. This kind of pulse reverses the orientation of the spins. If
the spin–lattice relaxation time is long compared to $T_2$, this spin reversal still happens in the $xy$-plane; if not, the partially relaxed spins are reversed in the $z$-direction as well. In any case, after another time period $t$, the spins produced a spontaneous transverse signal ($E(2t)$), which is observed and measured by the pick-up coil. The magnet inhomogeneity effect on the dephasing is suppressed in the spin echo sequence, because, neglecting time motion in the inhomogeneous field, a single spin experience exactly the same field before and after the 180° pulse and therefore all the spins catch up with each other after the second time period $t$. On the other hand, dephasing as a consequence of the spin’s dipolar fields is irreversible and the true $T_2$ can thus be obtained from the height of the spin echo:

$$E(2t) = \exp(-2t/T_2).$$  \hspace{1cm} (3.91)

This spin echo is a very powerful technique, nevertheless somewhat excessive for our purposes. The geometry of the static NMR magnet, and the use of external and internal Nb shield, makes the magnet inhomogeneity very small. Moreover, the “solid” nature of the studied samples, at least in the most interesting temperature region, causes $T_2$ to be quite short. In that case it is most efficient to calculate $T_2$ from $T_2^*$, which is naturally obtained from the FID fits. The correction to the magnet inhomogeneity is fairly negligible, as evidenced by the size of the errorbar in Figure 3.63. The spins echo measurement cannot be implemented withing the progressive saturation method, because the method was limited the small pulses (remaining in the so-called correspondence region), where the collapse of the saturation curves could be achieved, using the parameter $\hat{\tau}$. The spin echo technique becomes invaluable when measuring liquid samples, where $T_2$ can become quite large due to the effect of “motional narrowing” [126].
3.10 Possibly related system: metal–insulator transition in phosphorus doped silicon

Doped semiconductors have been widely studied to probe the nature of the metal–insulator transition (MIT) in disordered systems. Si:P is a well characterized, homogeneous system, where P donors sit substitutionally, and randomly, in a dislocation-free Si lattice. It is our belief that the solidification of the second layer of $^4$He on graphite in the vicinity of the commensurate phases can be related to the MIT in phosphorus doped silicon.

The most striking similarity of our experiment on helium and experiments on Si:P system is the emergence of the power law dependence of magnetic susceptibility on the insulating side of the MIT. There is also no magnetic ordering due to the exchange coupling of donor electrons down to lowest temperatures in Si:P. In this system the power has an upper bound of the index, $\alpha \approx 0.65$ [135], whereas we observed power law index up to $\alpha \approx 0.9$.

In the Si:P system the power law behaviour was theoretically understood by studying highly disordered antiferromagnetic systems [157]. The model considers itinerant quasiparticles which provide charge transport and at the same time local electron moments [158, 159].

![Figure 3.68: Susceptibility of P doped Si on the metallic side, close to the MIT. Deflection from Pauli susceptibility apparent. From [160].](image)

The measurements of electron-spin resonance (ESR) have also showed an interesting behaviour of the susceptibility on the metal site of the MIT. Instead of a Pauli temperature independent susceptibility at the lowest temperature, the susceptibility continues to rise [160]. This is shown in Figure 3.68 and resembles our own observation of in the samples on either side of the commensurate coverages. This behaviour in Si:P can be qualitatively explained by the theory of
Further magnetisation measurements support the power law dependence on the insulating side of the MIT [162]. A power law dependence is observed in measurements of heat capacity as well [163, 162].

Measurements of spin–lattice relaxation time on Si:P with very low phosphorus concentrations have discovered the thermally activated process, dominating the relaxation at high temperatures. This is shown in Figure 3.69. This was our observation on the samples closest to the 7/12 commensurate phase as well. In our case, however, the low temperature spin–lattice relaxation is governed by a Korringa type of behaviour, while in Si:P we have other mechanisms denoted as direct and Raman, which describe different ways of scattering on phonons [164]. The direct mechanism is a single phonon relaxation process, during which emitted and absorbed phonons have energy equal to the Zeeman splitting of the spin. This mechanism does not depend on temperature but does of course depend on the magnetic field. The Raman process has a $T^{-9}$ temperature dependence and arises from two-phonon scattering via a continuum of excited states. The Orbach process requires excitation of the donor state. The excited state is separated by $\Delta$ from the ground state.

![Figure 3.69: Temperature dependence of electron spin relaxation time $T_1$ in $^{28}$Si:P at $B \sim 0.34$ T. Solid line is fit to the experimental data, made up of contributions (dashed lines) from different relaxation mechanisms. Measurements by Castner [165, 166]. Figure from [164].](image)
Chapter 4

Low temperature heat capacity of canonical heavy fermion compound YbRh$_2$Si$_2$

4.1 Heavy fermion materials

Several inter-metallic compounds consisting of atoms with unfilled 4 and 5 f shells were found to have two or three orders of magnitude larger electronic heat capacity at low temperatures than expected (from mean field theory approaches). The first such compound was CeAl$_3$, discovered in 1975 [167]. It was proposed that although the f electrons are de-localised, the f-shell’s wave functions overlap is small, therefore the electron’s bandwidth is small and their effective mass is large [23].

The first heavy fermion found, which showed superconductivity, was CeCu$_2$Si$_2$, discovered in 1979 [168]. That proved that these two effects are not contradictory to each other. CeCu$_2$Si$_2$ is also the first unconventional superconductor (impossible to be described by the BCS theory) ever discovered. Another important experimental breakthrough were measurements on ultra pure CeIn$_3$ and CePd$_2$Si$_2$ which proved that superconductivity can arise because of magnetic order and not in spite of it. The authors even called the magnetic interaction between charge carriers the “magnetic glue” of the superconductivity [169].

All heavy fermion compounds belong to a wider group of materials called strongly correlated electron systems. Strongly correlated electron systems are materials with unfilled f and d shells where the argument of small wave function overlap of these orbitals, and therefore small bandwidth for the electrons, still holds. In comparison to the heavy fermion materials, some materials with unfilled d shells are in certain conditions insulating.
The f-electrons of heavy fermion materials give rise to the phenomenon the heavy fermion materials are mostly studied for: the realisation of the quantum critical point.

### 4.1.1 Quantum critical point

The quantum critical point is a point on the phase diagram of a material at $T=0$, where continuous (second order) phase transition takes place. Because it happens at $T = 0$, the cause of the transition are random collective fluctuations of quantum rather than thermal nature. To experimentally reach quantum critical point the condition $T = 0$ does not have to be achieved in full. Even at non-zero temperature (but low enough) the quantum fluctuations can be dominant to the thermal ones. Quantum phase transition of the studied material from one phase to another is achieved by tuning external parameters other than temperature, like pressure, magnetic field, or concentration of a dopant.

![Phase diagram of CePd$_2$Si$_2$, where superconductivity emerges around the quantum critical point. It is achieved by cooling just below 1 K and increasing pressure. Figure from [169].](image)

From the theoretical point of view, the central issue of heavy fermion physics is, whether or not the f-electrons are included in the volume of the Fermi surface. Ordinarily, two scenarios are considered regarding that question. In the first scenario f-electrons and f-holes are included in the Fermi volume. That leads to large-type Fermi surface. In the other scenario they are not included and generate what is commonly called a small-type Fermi surface [170, 171].
4.1.2 Kondo effect and RKKY interaction as competing effects

The Kondo effect describes the scattering of conduction electrons on magnetic impurities. The heavy fermion materials are sometimes referred to as Kondo lattices because the f electrons often have localised character at high temperatures. The Kondo scattering on a single impurity has one energy scale, the Kondo temperature:

\[ k_B T_K = k_B D e^{-\frac{1}{N_0 J}}, \]  

(4.1)

where \( D, N_0 \) and \( J \) are the bandwidth of conduction electrons, the density of states in the conduction band and the exchange energy of the conduction electron and the impurity respectively. At temperatures and fields large compared to the \( T_K \), the magnetic moment of the impurity is unscreened and follows Curie susceptibility. At temperatures and field small compared to \( T_K \), the magnetic moment is screened because it forms an elastic scattering centre inside the Landau Fermi liquid of the conduction electrons with Pauli susceptibility: \( \chi_P \sim \frac{1}{T_K} \).

The Kondo effect has a characteristic signature in temperature dependence of resistivity at \( T \sim T_K \), where it predicts logarithmic divergence of the resistivity. The predicted resistivity with typical additional terms can be written as:

\[ \rho = \rho_0 + AT^2 + C \ln \left( \frac{\mu}{T} \right) + BT^5, \]  

(4.2)

where \( \rho_0 \) is the residual resistivity, the term \( AT^2 \) is Fermi liquid behaviour [172], the term \( BT^5 \) comes from electron scattering on phonons and \( C \) and \( \mu \) are Kondo parameters.

![Figure 4.2: Characteristic signatures of Kondo effect in resistivity, magnetic susceptibility, and specific heat. Resistivity is generated using formula 4.2. Susceptibility qualitatively shows transition from Curie to Pauli susceptibility. Specific heat shows enhancement at low temperatures. The shaded area is the full spin entropy \( R \ln 2 \).](image-url)
The RKKY (Rudermann–Kittel–Kasuya–Yoshida) interaction is an indirect exchange interaction among localised magnetic moments (both nuclear and electronic) via conduction electrons. It was first formulated for nuclear moments by Ruderman and Kittel [10] in 1954. The formalism was later used by Zener to explain ferro-magnetism in transition metals [173] and extended by Kasuya [11] and Yosida [12] to the indirect coupling between localized electronic moments in metals.

The RKKY interaction has binding energy dependent on the electron–impurity (magnetic moment) exchange energy and the density of states like the Kondo effect:

\[
k_B T_{RKKY} \sim J^2 N_0.
\]  
(4.3)

The two effects are therefore competing. The size of the exchange interaction can be expressed as:

\[
J_{RKKY}(i, j) = \frac{J^2 \hbar^6}{\epsilon_F} \frac{\hbar^2 v^2}{N^2 (2\pi)^3} F(2k_F R_{ij}),
\]  
(4.4)

with the following spacial dependence:

\[
F(x) = \frac{\sin(x) - x \cos(x)}{x^4}.
\]  
(4.5)

This spacial dependence and its consequence on the kind of the interaction: ferro vs. antiferromagnetic, is illustrated in Figure 4.3.

![Figure 4.3: The RKKY interaction oscillating from ferromagnetic to antiferromagnetic action as we move away from the magnetic moment (orange arrow), according to formula 4.4.](image_url)

As the Kondo and RKKY interactions depend on the same parameters, but
in different functional formula, a plot illustrating their competition can be con-structed. It was first realised by Doniah [174] and the plot, shown in Figure 4.4, bears his name. In the Doniah’s picture the quantum critical point is realised when the two effects have comparable strengths. If the RKKY interaction dom-inates the system prefers magnetic ordering; if the Kondo effect dominates the system behave as a Fermi liquid. More on this phenomena can be found in [175].

\[ R_{KW} = \frac{A}{\gamma^2}. \]  

(4.6)

Figure 4.4: Doniah [174] model illustrating the competition between the Kondo effect and the RKKY interaction. From [176].

4.1.3 Kadowaki–Woods ratio

The Kadowaki–Woods ratio is the ratio of the quadratic resistivity term coefficient, $A$, and the heat capacity coefficient $\gamma$ squared:

\[ R_{KW} = \frac{A}{\gamma^2}. \]  

The significance of this formula is that the resistivity coefficient describes the electron–electron scattering while the Sommerfeld constant reflects renormalisa-tion of the electron’s mass. When the electron–electron scattering dominates over the electron–phonon scattering, the Fermi liquid quadratic term in the re-sistivity is observed. Many heavy fermion compounds possess a very uniform value of $R_{KW} \sim 10 \mu\Omega\text{cm}\text{mol}^2K^2J^{-2}$ [177]. This can be seen in Figure 4.5. YRS is found in this figure at the very right, top corner. Hence it is sometimes called the 'canonical heavy fermion'. Calculation of the $R_{KW}$ for YRS is in details described in [178], as YRS is a very rich compound and obtaining the values of $A$ and $\gamma$ is not straightforward.
Figure 4.5: Kadowaki–Woods ratio for heavy fermions. From [179].
4.2 YbRh$_2$Si$_2$ compound and results of various measurements on it

YbRh$_2$Si$_2$ (YRS) is sometimes called the canonical heavy fermion compound because of its very high $\gamma$ coefficient (see Figure 4.5). This nickname was further empathised by Erwin Schuberth when his low temperature measurements of the specific heat of the YRS were published [180]. The large advantage of YRS to other heavy fermions is that the compound is already close to its quantum critical point (QCP) at ambient pressure and strong non-Fermi liquid behaviour has been observed while tuning the compound with magnetic field. Changing magnetic field is of course experimentally easier than changing pressure. External pressure actually only strengthens antiferromagnetic order in Yb based compounds. This is contrary to Ce based compounds where the pressure is necessary for the realisation of the QCP. One of the current understandings of the QCP is that it is of unconventional type with a Kondo breakdown. This means that the size of the Fermi surface changes by tuning of the Kondo effect. This type of QCP cannot be explained by the standard Spin-fluctuation theory [181].

YRS crystallises in tetragonal ThCr$_2$Si$_2$-type of crystal structure. The space group is $I4/mmm$. Many heavy fermion compounds were synthesised having this crystal structure. It is called the “RM$_2$X$_2$” series, where R is an element with unfilled f-shell: Ce, Yb, U...; M is a transition metal and X is Si or Ge. Sometimes a little amount of Ge is added to otherwise Si matrix (and vice versa) to introduce strain or disorder [182]. The crystal structure is shown in Figure 4.6. The lattice constants are $a = 4.007 \pm 0.005$ Å and $c = 9.858 \pm 0.005$ Å.

![Figure 4.6: Crystal structure of YbRh$_2$Si$_2$. Cyan circles are Yb, green circles are Rh and purple circles are Si atoms. Picture from [183].](image-url)
YbRh$_2$Si$_2$ consists of atoms of Yb, Rh and Si. While Rh only has one stable isotope, both Si and Yb have several stable isotopes with significant natural abundances. The properties of the isotopes are summarised in Table 4.1.

Pure metallic Yb is only weakly paramagnetic and has the lowest magnetic susceptibility of all the rare-earth metals. The electronic configuration of the Yb atom in YRS is the trivalent configuration (2 electrons removed from the 6s orbital and one from 4f). The hole in the 4f shell is the origin of several interesting phenomena. There is a discussion on its similarity to the one electron in the 4f shell of the Ce based heavy fermion compounds [184]. The Kondo effect gives rise to the formation of quasiparticles made by the combination of the 4f hole with the conduction electrons near the Fermi energy. The quasiparticles possess highly renormalized properties such as the enhancement of their effective mass. The 4f$^{13}$ configuration has a magnetic moment that usually gives rise to a long range magnetic order [181]. In some compounds on the other hand stabilises the Yb ion the 4f$^{14}$ configuration that is Yb$^{2+}$. Small deviations from the 4f$^{13}$ configuration can give rise to the heavy fermion behaviour.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$I$</th>
<th>$\gamma$ [MHz/T]</th>
<th>$Q$ [$10^{-28}$m$^2$]</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{174}$Yb</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>31.8</td>
</tr>
<tr>
<td>$^{172}$Yb</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>21.8</td>
</tr>
<tr>
<td>$^{173}$Yb</td>
<td>5/2</td>
<td>-2.073</td>
<td>2.8</td>
<td>16.1</td>
</tr>
<tr>
<td>$^{171}$Yb</td>
<td>1/2</td>
<td>7.52</td>
<td>-</td>
<td>14.3</td>
</tr>
<tr>
<td>$^{176}$Yb</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>12.8</td>
</tr>
<tr>
<td>$^{170}$Yb</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>3.0</td>
</tr>
<tr>
<td>$^{168}$Yb</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>$^{103}$Rh</td>
<td>1/2</td>
<td>-1.35</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>$^{28}$Si</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>92.2</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>1/2</td>
<td>-8.465</td>
<td>-</td>
<td>4.7</td>
</tr>
<tr>
<td>$^{30}$Si</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 4.1: Isotopes of Yb, Rh and Si, their nuclear spin $I$, gyromagnetic ratio, electric quadrupole $Q$ (from optical spectroscopy [15]) and natural abundance.
4.2.1 Magnetic properties

The high temperature magnetic susceptibility ($> 200$ K) of YRS follows the Curie–Weiss law. The effective magnetic moment is close to free Yb$^{3+}$ ion, which is: $\mu_{Yb^{3+}} = 4.5 \mu_B$ [185]. The Weiss temperatures differ for the crystallographic directions: in–plane and along c axis: $\Theta_W^a = -9$ K and $\Theta_W^c = -180$ K. The ratio of the two susceptibilities at $T = 0$ should be 20 however it increases to about 100 [186]. The tetragonal ab-plane is therefore often called the 'easy magnetisation' plane.

In zero magnetic field a small peak in susceptibility is observed at $T = 65$ mK. The peak shifts to lower temperatures with increasing field. The transition lacks hysteresis. From these facts it was identified as an antiferromagnetic ordering transition. The position of the Néel temperature peak can be followed up in fields [187]. Above 50 mT the susceptibility remains constant with temperature, indicating Pauli susceptibility. A strange possible underlying ferromagnetic behaviour was observed between 40 and 50 mT [188]. Below the AF transition is the ordered magnetic moment only $\mu \sim 0.002 \mu_B$ [189].

![Figure 4.7: a: Magnetic susceptibility of YRS in the ab-plane for various fields. b: Isothermal magnetisation in the ab-plane and along the c-axis, proving the ab-plane is the 'easy magnetisation' plane. Inset: Derivative of the magnetisation curve in the ab-plane agreeing with the susceptibility measurement. Taken from [188].](image)

Low temperature measurements of susceptibility (see section 4.8.7) and magnetisation show a Curie-Weiss upturn which they explain by enhanced polarisation of the 4f moments due to hyperfine coupling. The DC magnetisation measurements, shown in Figure 4.8, C, clearly show the Meissner effect below 2 mK [180].

166
Figure 4.8: A: Field-cooled DC magnetization curve of YRS taken at \( B = 0.09 \text{ mT} \) applied in the ab-plane. Three main features are clearly visible: the AF phase transition at 70 mK, a shoulder in magnetization at \( T_B \approx 10 \text{ mK} \), and a sharp peak at \( T_A = 2 \text{ mK} \). C: Zero field cooled and field cooled DC magnetisation at very small fields. Arbitrary offset. From [180].

4.2.2 Resistivity

The resistivity of YRS is anisotropic even at room temperature. For \( j \parallel c \) is \( \rho_{300K} = 40 \pm 5 \mu\Omega cm \), while for \( j \perp c \) is \( \rho_{300K} = 75 \pm 5 \mu\Omega cm \). The resistivity increases upon cooling below 100 K, which is a typical behaviour of dilute Kondo alloys. The Kondo temperature of YRS is around 25 K.

YRS shows quasi-linear dependency on temperature from 80 mK to 10 K. The anti-ferromagnetic transition below 80 mK is only apparent with samples with residual resistivity ratio (RRR) larger than 20 [188]. In this context we define the ratio as \( RRR = \rho_{300K}/\rho_0 \), where \( \rho_0 \) has to be determined from a fit because the resistivity does not flatten, even at lowest temperatures. The resistivity below \( T_N \) can be fitted with the following expression:

\[
\rho(T) = \rho_0 + DT \left[ 1 + \frac{2T}{\Delta} \right] e^{-\frac{T}{T_N}} + AT^2,
\]

where the second term is due to scattering on magnons and the third term is the Fermi liquid behaviour. Data from [188] are shown in Figure 4.9 and the fit below \( T_N \) is done, however results suggest that the spin gap is either not present, or negligible. The numeric results are: \( \rho_0 = 1 \mu\Omega cm, D = 0.04 \mu\Omega cmK^{-1}, A = 13.66 \mu\Omega cmK^{-2} \) and \( \Delta = 0.008 \text{ K} \).

The linear temperature dependence of \( \rho \) at \( T > T_N \) is attributed to quantum
criticality. In YbRh$_2$Si$_2$ there is a quantum critical point tuned by magnetic field (60 mT in the ab-plane). See the phase diagram in Figure 4.14. A perspective on this QCP is extensively described in several reviews. This should however be regarded as a matter of controversy and is not discussed further in this thesis.

![Figure 4.9](image)

**Figure 4.9:** Zero field resistivity of YRS measured by Custers [188]. (a) Low temperature data show the anti-ferromagnetic transition at $T_N$. (b) High temperature data show the resistivity anisotropy and Kondo effect. (c) Fit of the low temperature data according to formula 4.7.

The onsets of superconductivity at zero magnetic field, as seen in transport measurements by Lev Levitin at Royal Holloway, are typically found around 10 mK, but they vary from sample to sample. This onset of superconductivity is a place where the resistivity starts to drop. We call this transition $T_B$ and it moves to lower temperatures with field. $T_B$ transition is followed by $T_S$ transition at about 6 mK in zero field, which is also field dependent. $T_S$ denotes large drop in resistance. At the region where measured resistance is effectively zero we find a state where persistent currents are observed, limited by transition temperature $T_P$. At 1.7 mK we see a big drop in the imaginary part of the measured sample impedance. We call this transition $T_A$. This transition point is very weakly, if at all, field dependent up to 10 mT applied in the ab-plane. For non-zero applied fields in the ab-plane and along the c-axis we see a re-entrance of the normal state at temperature below $T_A$. This re-entrance considers both the real and imaginary part of the sample’s impedance. All discussed transition, and the transport regimes they define, are shown in the phase diagram in Figure 4.10. Temperature dependencies of the measured real and imaginary parts at two applied fields are shown in Figures 4.50, where they are compared to the new heat capacity data. Details of the impedance measurements can be found.
These transport measurements at Royal Holloway provided the motivation for the heat capacity study reported here. In particular $T_A$ is close to the temperature at which a distinct signature of Meissner screening is seen in [180] at fields below 0.4 mT. Furthermore, a heat capacity anomaly was also reported in [180], but measurements were only made at 2.4 mT. This defined the requirement for heat capacity measurements as a function of magnetic field. In the next section we review prior heat capacity measurements on this system.

![Transport phase diagram of YRS for fields in the ab-plane and along the c-axis. Measurements by Lev Levitin.](image)

**Figure 4.10:** Transport phase diagram of YRS for fields in the ab-plane and along the c-axis. Measurements by Lev Levitin.

### 4.2.3 Specific heat

Heat capacity measurements from other groups typically go down to about 40 mK, a higher temperature than other experimental techniques. One exception are measurements from Schuberth [180] done by a relaxation technique in a temperature range 1-10 mK. The high temperature measurements confirm the antiferromagnetic phase transition seen in susceptibility measurements, however report slightly higher temperature: 72 mK [191, 192, 193]. The authors attempt to extract the plain electronic specific heat from the raw heat capacity data by subtracting phononic and nuclear quadrupolar contributions. The quadrupolar contribution can be approximated by: $C_Q(T) = \alpha_Q/T^2$ at high temperatures, where $\alpha_Q = 5.68 \cdot 10^{-6}$ J/(mol K) is determined from Mössbauer spectroscopy measurements [194]. The phononic heat capacity is obtained from measurements on non-magnetic compound LuRh$_2$Si$_2$. Both contributions are however about 1% of the measured heat capacity at 70 mK [193]. Specific heat measurements
from 20 K down to 40 mK, with magnetic field along the c-axis, are shown in Figure 4.11.

Figure 4.11: Electronic specific heat of YRS in fields up to 1 T applied along the c-axis. Inset: specific heat at zero field up to 20 K showing the logarithmic divergence.

Figure 4.12: Electronic specific heat of YRS in fields up to 60 mT applied perpendicular to the c-axis [192].

In agreement with the linear dependence of the resistivity on temperature (strange metal behaviour), the electronic specific heat divided by temperature shows logarithmic divergence at the temperature range 300 mK - 10 K. This behaviour can be described by a formula: \( C_e(T)/T = a \ln(T_0/T) \), with \( a = 0.15 \text{J/mol K}^2 \) and \( T_0 \) of the order of the Kondo temperature. An additional upturn is present below 300 mK. It can be described by \( C/T \sim T^{-0.34} \). The AF peak at 72 mK supports a second order phase transition. Entropy gain of this transition is approximately \( 0.03R \ln 2 \) (calculated as integral of the AF peak). Increasing magnetic field lowers the phase transition temperature \( T_N \), reduces the magnitude of the AF peak, and also lowers the value of the heavy fermionic heat capacity. The small upturn at lowest temperatures on the dataset taken at
1 T originates from the hyperfine contribution [188]. Figure 4.12 shows specific heat of YRS in fields applied in the ab-plane. As observed by the susceptibility measurements too, we can again see that much smaller fields are required to suppress the AF transition in the ab-plane, than along the c-axis.

Krellner et al. [193] attempted to fit the critical behaviour at the vicinity of the Néel transition peak. Their critical exponent (\(\alpha = 0.38\)) is ratio of critical amplitudes (\(A^+/A^- = 0.58\), +(-) being above(below \(T_N\))) however does not agree with any known theory (Heisenberg, Ising, etc. models). See section 4.5 for the theory of critical phenomena. Our attempt of fitting the antiferromagnetic peak is shown in section 4.8.6.

Interplay with nuclei at low temperatures

Figure 4.13: A: Low temperature heat capacity measurements as C/T vs. T of YRS. Data are from two magnetic fields applied in the ab-plane. Solid lines are theoretical predictions [195] due to the quadrupole and Zeeman moments, considering four field-induced Yb-derived ordered magnetic moments. B: Heat capacity data taken at 2.4 mT after subtracting the calculated nuclear quadrupole contribution. C: nuclear entropy determined from plot B [180].

This is a description by Schuberth [180] based on his recent measurements. Below 10 mK nuclear heat capacity of Yb atoms starts to play role. That includes heat capacity due to quadrupole moment and due to magnetic moment. Table 4.1 summarises Yb isotopes and gives their nuclear spin. Naturally, 30.4% of Yb atoms have nuclear magnetic moment and only 16.1% have electric quadrupole moment (which is only present by nuclei wit \(I > 1/2\)). At zero magnetic field only the quadrupole moment plays role as the ordered AF moments are small. Using only the high temperature tail of a Schottky peak and \(\alpha_Q\) value from the Mössbauer measurement [194] we get at 1mK: \(C_Q/T = 5.68 \times 10^{-6}/1.1 \times 10^{-9} = 914\) Jmol\(^{-1}\)K\(^{-2}\). This is a huge increase from the already quite high Sommerfeld heavy fermion coefficient \(\gamma_0 = 1.7\) Jmol\(^{-1}\)K\(^{-2}\) holding below the AF transition.
Such high heat capacity was indeed measured, using the sample magnetisation as a thermometer. Only a limited number of magnetic fields were studied. The results are shown in Figure 4.13.

Figure 4.14: Low temperature and applied field (in the ab-plane) phase diagram of YRS, obtained from ac-magnetisation and ac-susceptibility measurements [180]. It shows following phases: paramagnetic phase $P$ above $T_N$, electronic anti-ferromagnetic phase $AF$ and nuclear anti-ferromagnetic, concurrent with heavy fermion superconductivity $A+SC$. Inset: The SC phase boundary showing relatively large slope $dB_C/dB_T \sim -25 \ T/K$. 

![Figure 4.14](image-url)
4.3 Electron-nucleus hyper-fine interaction

In atomic physics the magnetic coupling of a nucleus with the electrons has been proposed as early as 1924 to explain the hyperfine structure observed in optical spectra \[143\]. It was later in 1935 proposed that some nuclei have a non-zero quadrupole moment (resulting from a non-spherical charge distribution) which also interacts with electric field gradients, present in a crystal. The magnetic interaction of an electron’s angular momentum \( J \) with a nuclear spin \( I \) is described by the Hamiltonian:

\[
\hat{H} = A_{hf} \vec{J} \cdot \vec{I} - \vec{\mu}_J \cdot \vec{B} - \vec{\mu}_I \cdot \vec{B}.
\] (4.8)

Its solution for a simple case of \( J = 1/2 \) is the famous Breit–Rabi formula \[196\]. Equation 4.8 describes collective behaviour of electrons and nuclei. The hyperfine interaction constant \( A_{hf} \) typically has the units of energy. Occasionally a different version of the hyperfine constant is of use. It expresses the magnetic field created on the nucleus by the unit of electronic moment, the Bohr magneton, i.e. \( T/\mu_B \).

In the “slow relaxation regime” the coupling between the 4f angular momentum, \( J \) and the nuclear spin \( I \) dominates the coupling between the 4f electrons and the conduction electrons. This gives rise to quantum entanglement state in which \( F = J + I \) is a good quantum number. This studies of dilute (42 ppm) \(^{171}\)Yb in Au \[197\] demonstrate an \( F = 0 \) electro-nuclear spin singlet state due to hyperfine coupling dominating Kondo screening. Crystal-field ground state of Yb is a doublet with pseudo-spin \( \frac{1}{2} \).

However \( \text{YbRh}_2\text{Si}_2 \) is in the opposite “fast relaxation regime”. Coupling between the 4f moments and conduction electrons is much larger than hyperfine coupling between 4f moments and nuclear moments. This was experimentally confirmed by Mössbauer spectroscopy \[198\]. In this limit the Yb nuclei experience the hyperfine field of the static component of the (screened) 4f moment.

In rare earth metals the field generated on the nucleus is mostly from the angular momenta of 4f electrons. Other less important effects are: Polarisation of inner atomic shells by the spin moments of 4f electrons. And polarisation of conduction electrons by the s-f interaction on the ion. \( A_{hf} \) was calculated by Jun Kondo for the first, most important effect \[199\]. He gives values: \( 300 \cdot 10^{-4} \text{ cm}^{-1} \) (43.14 mK) and \( -85 \cdot 10^{-4} \text{ cm}^{-1} \) (12.22 mK) for \(^{171}\)Yb and \(^{173}\)Yb respectively. This translates to a hyperfine constant in \( [T/\mu_B] \):

\[
A_{hf} [T/\mu_B] = 43.14 \text{ mK}/(2\pi\gamma_{171}\hbar/k_B) = 120,
\] (4.9)
where $\gamma$ is the gyromagnetic ratio. Experiments on Yb give slightly lower value of $A_{hf}$. Bonville [200, 201] gives a value of 102 T/$\mu_B$. This is the value we will be using in this experiment. It is important to note that the hyperfine constant is ferromagnetic for both Yb isotopes. The quadrupolar hyperfine interaction of nuclei and electrons is addressed in the next section.
4.4 Single ion spin Hamiltonian

The heat capacity of paramagnetic system of nuclei is typically described by the so-called Schottky peak. More generally a Schottky peak describes the heat capacity of any quantum multi-level system. For our purposes let’s write down the functional formula for a nucleus with a spin \( I > 3/2 \). Such nucleus will experience Zeeman splitting if it is in the magnetic field (equation 2.29). It will also experience quadrupolar splitting if the following two conditions are met:

- The nucleus has a non-zero quadrupolar moment \( Q \) which expresses the non-sphericity of the charge distribution in the nucleus. This is only possible for nuclei with \( I > 1 \).
- The nucleus is in an environment with lower than cubic symmetry and there are gradients of electric field present (second spatial derivatives of the electric potential).

If the electric field gradient is only in a principal z-axis the quadrupolar Hamiltonian will have the form:

\[
\hat{H}_Q = \frac{e^2 qQ}{4I(2I-1)}(3I_z^2 - I(I+1)),
\]

where \( e \) is the elementary charge and the electric field gradient is usually given by \( eQ \) in the units of \([\text{Vm}^{-2}]\). When either the Zeeman or the quadrupolar splitting is small with respect to the other the full nuclear Hamiltonian is a sum of equation 2.29 and 4.10. If the splittings happen along different crystallographic axes the formula incorporates an angle \( \theta \). These two special cases of the Hamiltonian can be found for example in [202] (small quadrupole) and [203] (small Zeeman).

When the two splitting mechanisms are of comparable strength, the Hamiltonian is given by a square matrix of size \( 2I+1 \). Let’s suppose the quadrupolar splitting is happening in the Cartesian direction \( z \) due to the electric field gradient being oriented like that; and the Zeeman splitting is happening along the \( x \) coordinate due to the magnetic field being applied like that. The Hamiltonian will have the form according to equation 4.11. The energy levels \( E_i \) are the eigenvalues of the matrix.

\[
\hat{H}_{\text{combined}} = \begin{pmatrix}
\frac{e^2 qQ}{4} & \frac{\sqrt{5}}{2} \mu_n gB & 0 & 0 & 0 & 0 \\
\frac{\sqrt{5}}{2} \mu_n gB & -\frac{e^2 qQ}{20} & \sqrt{2} \mu_n gB & 0 & 0 & 0 \\
0 & \sqrt{2} \mu_n gB & -\frac{e^2 qQ}{3} & \frac{3}{2} \mu_n gB & 0 & 0 \\
0 & 0 & \frac{3}{2} \mu_n gB & -\frac{e^2 qQ}{3} & \sqrt{2} \mu_n gB & 0 \\
0 & 0 & 0 & \sqrt{2} \mu_n gB & -\frac{e^2 qQ}{20} & \frac{\sqrt{5}}{2} \mu_n gB \\
0 & 0 & 0 & 0 & \frac{\sqrt{5}}{2} \mu_n gB & -\frac{e^2 qQ}{4}
\end{pmatrix}
\]

The specific heat is derived from the partition function as follows. First we
express the partition function:

\[ Z = \sum_{i=-I}^{I} e^{-E_i/k_B T}, \] (4.12)

where \( E_i \) are the energy eigenvalues. The mean value of energy is derived from the partition function as:

\[ \langle E \rangle = -\frac{d \ln(Z)}{d 1/\beta} = \frac{\sum_{i=-I}^{I} E_i \exp([-E_i/\beta])}{Z}. \] (4.13)

The entropy is:

\[ S = \frac{\langle E \rangle}{T} + k_B \ln(Z), \] (4.14)

and the specific heat is:

\[ C = N \frac{d\langle E \rangle}{dT} = \frac{R}{(k_B T)^2} \frac{\sum_{i=-I}^{I} \sum_{j=-I}^{I} (E_i^2 - E_i E_j) \exp[-(E_i + E_j)/k_B T]}{\sum_{i=-I}^{I} \sum_{j=-I}^{I} \exp[-(E_i + E_j)/k_B T]} \] (4.15)

If magnetic field has two components, along \( z \) and along \( x \), the Hamiltonian matrix 4.11 takes the Zeeman splitting along \( z \) into its diagonal and becomes:

\[ \tilde{H}_{dual B} = \tilde{H}_{combined} + \begin{pmatrix} \frac{5}{2} \mu_n g B_z & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{3}{2} \mu_n g B_z & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} \mu_n g B_z & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} \mu_n g B_z & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{3}{2} \mu_n g B_z & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{5}{2} \mu_n g B_z \end{pmatrix} \] (4.16)

Hamiltonian according to 4.16 was modeled to see how the energy levels develop. The quadrupolar splitting was fixed for that and only the magnetic field was varied in the two distinct directions. This is shown in Figure 4.15.
In YbRh$_2$Si$_2$ we are in the limit that the nuclear spins experience a hyperfine field due to the static part of the f-shell moment. For the magnetic fields used in our experiment the hyperfine field is dominant. However, we will find that the f-shell moment depends strongly on applied magnetic field. We will also see that there are circumstances where this moment is temperature dependent. The origin of these effects will be discussed. Here the point to emphasize is that it is not possible to write the nuclear heat capacity of the $^{173}$Yb isotope as hyperfine (Zeeman) plus quadrupole contributions. Exact diagonalisation of the Hamiltonian is essential.
4.5 Critical phenomena

Critical phenomena is the behaviour of a system in the close vicinity of a continuous phase transition happening at $T_c$. This could typically be the Curie point in a ferromagnetic system in zero magnetic field. Thermodynamic variables like the specific heat ($C$), susceptibility ($\chi$) or order parameter ($M$; which is the measure of the system’s symmetry) often have singularities at $T_c$. Their behaviour near $T_c$ is described in terms of a reduced temperature:

$$|t| = \left| \frac{T - T_c}{T_c} \right|$$ \hspace{1cm} (4.17)

The variables are found (theoretically and experimentally) to obey the following laws:

$$C \sim |t|^{-\alpha},$$
$$M \sim |t|^\beta,$$
$$\chi \sim |t|^{-\gamma}. \hspace{1cm} (4.18)$$

The coefficients $\alpha$, $\beta$ and $\gamma$ are called the critical exponents.

Different models predict different values for the critical exponents however together they are universally bound by the so-called scaling laws which can be found for example in [204]. The most common theoretical models related to a general 3D spin system are the mean field theory, Ising model, and Heisenberg model; they predict 0, 0.12 and -0.14 respectively for the specific heat coefficient $\alpha$. It may look like the Ising model is the only one which predicts diverging specific heat at $T_c$ but the case $\alpha = 0$ also allows for a divergence. The three types of behaviour for the $\alpha = 0$ case are:

- no singular behaviour,
- a discontinuity at $T_c$,
- a logarithmic divergence. This is because for any positive power $\alpha$, $|t|^{-\alpha}$ diverges faster than $\log |t|$.

The logarithmic divergence gives the famous lambda-type curve known from the superfluid transition of $^4$He at 2.17 K. The Heisenberg model predicts the negative $\alpha$, which gives a finite value at $T_c$. The overall look of the feature is called a “cusp”. However, formula 4.18 actually predicts the value 0 at $T_c$ and the cusp is down facing. The formula has to be therefore multiplied by $A/\alpha$, where $A$ is positive. The formula also has a provision for offset, $B$. The overall formula is therefore:

$$C = \frac{A}{\alpha} |t|^{-\alpha} + B \hspace{1cm} (4.19)$$

The same formula describes the Ising model but there the offset $B$ is not of such fundamental importance. The formula describing the logarithmic diver-
gence is:

\[ C = A \log |t| + B. \]  \hspace{1cm} (4.20)

The three models are shown in Figure 4.18. First, the peaks in C vs. T coordinates are shown. It is clear that the models are difficult to distinguish to a human eye. Better coordinates are shown in the middle figure. The Ising model appears as a convex function while the Heisenberg model appears as a concave function (and also converging as \( T \to -\infty \)), and the logarithmic divergence as a line. The curves were generated with the same parameter \( A \) above and below \( T_c \). This is however not the real case. The mentioned models often predict a certain (rather small) ratio of \( A/A' \) and measurements support that. This difference makes the curves from data above and below \( T_c \) split on this type of graph.

![Figure 4.16: Heat capacity at saturated vapour pressure of liquid \( ^4\)He near the lambda point. The upper data set is for \( T < T_\lambda \) and the lower data set for \( T > T_\lambda \). From [205].](image1)

![Figure 4.17: Specific heat vs. the reduced temperature of nearly Heisenberg ferromagnet \( \text{Eu}_{0.95}\text{Sr}_{0.05}\text{S} \). The fit is according to equation 4.19 with added term \( E \cdot t \). From [206].](image2)

Measuring critical behaviour of a material is extremely demanding experimental task. To get to the level of \( 10^{-6} \) near the critical point at 1 K one must have a thermometer with \( \mu \text{K} \) resolution. Additionally, to measure the heat capacity precisely, the heat leak into the cell must be small with respect to the measured heat capacity and acquisition speed of the thermometer. Finally, the critical behaviour must not be disrupted by inhomogeneity effects within the sample. In the case of \(^4\)He, even a weak gravitational effect played a role, which eventually lead to measurement of the critical behaviour on Earth’s orbit [207]. Even when the measurement is successfully performed, it still seems difficult to distinguish a logarithmic singularity from a small positive value of \( \alpha \) [208].

Figure 4.16 shows the behaviour of \(^4\)He lambda point and Heisenberg ferromagnet \( \text{EuS} \). The lambda point was long thought to be an example of the logarithmic divergence but was later found to be described by a small negative critical exponent -0.026. The ration \( A/A' \) is found to be about 1.112 for the lambda point [205]. Figure 4.17 shows the critical behaviour of doped \( \text{EuS} \)
which, when pure, very well agrees with the Heisenberg model; when doped by Sr the coefficient $\alpha$ goes down from the initial value -0.14 [206].

Figure 4.18: Modelling of the critical phenomena for various models. The left-most graph shows the look of the peaks themselves. The middle graph shows the peaks in coordinates which best distinguish the value of the critical exponent. The right-most graph shows warm-up curves across the peak.
4.6 Heat capacity of YbRh$_2$Si$_2$ as a function of temperature and magnetic field (methods)

The objective of this work was primarily to see signatures of superconductivity which happen below 10 mK. Another objective was to see what happens to electronic heat capacity below the Néel point. Lastly, the effect of magnetically active nuclei was of interest and their possible interplay with superconductivity.

Design of the experimental cell is described in detail in section 2.3.2. The so-called minimalist design of the cell allowed the addendum heat capacity to be ignored. This is further discussed in section 4.8.8. It is worth noting that the negligible mass of the noise thermometer plays a crucial role.

We managed to measure the heat capacity of YRS by the adiabatic method in the temperature range from 187 $\mu$K to above 90 mK and in the field range 0 to 10 mT, which is the critical field of the aluminium heat switch. Due to advantageous ratio of the measured heat capacity, and the conductivity of the heat switch in its normal state, we were also able to measure the heat capacity above 10 mT, up 70 mT, at sufficiently low temperatures. The temperature–field map in Figure 4.19 explains which method is suitable for a given temperature–field combination and the following sections explain the used methods.

![Temperature–Field Map of Used Methods](image)

Figure 4.19: A temperature–field map of used methods to measure the heat capacity.

4.6.1 Adiabatic pulse method of heat capacity measurement

The heat capacity is an external property of a sample describing how much heat is needed to warm it up by a unit of temperature. If the heat is produced by a calibrated external heater, it is naturally desirable not to experience any heat
losses. The best situation is therefore if the cell is adiabatically isolated from its surroundings (the nuclear stage of the cryostat). In our case the aluminium superconducting heat switch and alumina support served this purpose. The Al heat switch is superconducting below 10.5 mT and the switching ratio (ratio of thermal conductivities in both states) is very large for ultra pure, high RRR Al. The heat conductivity of alumina has relatively high power law dependence on temperature (equation 2.47). Experimentally the cell was found to start visibly leaking at around 20 mK. The measurements below this temperature and the field 10.5 mT are done by the fully adiabatic method.

Even without direct thermal link to the cryostat in the adiabatic regime, the cell is still subject to photonic parasitic heat leak, which is mostly independent on the temperature of the nuclear stage. This heat leak causes an inevitable background warm up of the cell even when no heat is produced in the heater. The cell incorporates local know-how on minimising this external heat leak (more on this can be found in section 2.3.2). Typically the heat leak into the cell was about 30 fW. It can be accurately measured from observed warm-up drifts in between heat capacity measuring pulses. Figure 4.20 shows typical time development of temperature when measuring the heat capacity in the adiabatic regime. The warm-up drifts are standardly fitted with a linear function. That relies on two assumptions: constant heat leak; and weakly temperature dependent heat capacity of the sample throughout the drift between heat pulses.

After having fitted the drifts with the linear functions, the fit functions are evaluated in time corresponding to the middle of the heat pulse. $T_{\text{high}}$ is the temperature according to n-th fit function in the middle of pulse number n-1. $T_{\text{low}}$ is the temperature according to (n-1)-th fit function in the middle of pulse number n-1. We define $\Delta T = T_{\text{high}} - T_{\text{low}}$ as the temperature increase due to the applied pulse of magnitude $Q$. The heat capacity is then simply calculated as:

$$C = \frac{Q}{\Delta T}. \quad (4.21)$$

Figure 4.20 shows an extremely cold measurement; yet a pulse magnitude $\Delta T/T = 2.2\%$ could be performed. At higher temperatures, when the heat capacity was larger, it was possible to apply even smaller pulses with percentage increase less than 1%. The parameters governing the choice of heat pulse are the time dependence of sample temperature following a pulse, the magnitude of sample heat capacity and the parasitic heat leak. The performance of our noise thermometer (NT) was described in section 2.2.4. It measures with 1% precision in approximately 45 s. If it is left to obtain about 100 points in a temperature drift (usually it was about 1 hour), the precision improves by a factor of 10 and heat pulses can have $\Delta T/T < 1\%$. It is however necessary that the temperature drift within that 1 hour does not clearly deviate from linearity. Still as the heat
leak was about 30 fW and the heat capacity ranged from 2 \(\mu\)J/K to 500 \(\mu\)J/K, the temperature increase in an hour was in units of \(\mu\)K.

![Figure 4.20: Typical heat pulses and temperature drifts at the lowest achieved temperature of 175 \(\mu\)K. Points containing a cross are used for fitting, empty points are transition points and not used for fitting.](image)

### 4.6.2 Adiabatic continuous warm-up method of heat capacity measurement

Another method to determine the heat capacity of a sample is to apply a constant power into the heater and simply follow the resulting warmup. The time derivative of the temperature is inversely proportional to the heat capacity as:

\[
\Delta T = \frac{Q}{C},
\]

and therefore

\[
\frac{\partial T}{\partial t} = \frac{\dot{Q}}{C},
\]  

(4.22)

where \(\dot{Q}\) consists of both the applied power and also the parasitic heat leak. It is desirable for the applied power to be much larger than the parasitic heat leak, if there is uncertainty about the time stability or magnitude of the parasitic heat leak. Figure 4.21 shows how the temperature readings are processed to extract the heat capacity. Data were processed in python. First a numerical derivative is done using the `numpy.gradient` function. Second the ratio of the power over the gradient is calculated to determine the heat capacity. A larger applied power results in less scattered heat capacity points, but also smaller temperature resolution. Heat capacity obtained using 3 different powers and its comparison to
heat capacity point obtained from the pulse method will be shown in Figure 4.48 later on.

Figure 4.21: Extraction of the heat capacity from a continuous warmup measurement. The applied current in the heater was 2 µA which results in 803 fW.
4.6.3 Relaxation method of heat capacity measurement

Fast thermal equilibration within the YRS sample itself allowed us to measure the heat capacity even above the critical field of aluminium, 10.5 mT, by a relaxation method. The heat spreads within the sample in less than 100 seconds, even at the lowest temperatures. The fast thermalisation within the sample is apparent from the zero field data. When the pulse is applied, only two or three temperature points are influenced before the stationary state is reached. Also, no overheating is happening. This means that the relaxation time which governs the thermalisation of the heated electrons to the nuclei has to be shorter than the diffusion time from the heater to the thermometer across the sample. To see if this time was measurable, following test was performed at zero field. Powerful heat pulses lasting only 1 second were applied and the noise thermometer was set to short acquisition time of about 5 seconds. This is shown in Figure 4.22. We could clearly observe overheating at temperatures where nuclear heat capacity of YRS dominates. This is below 10 mK and will be discussed in the main result body. The relaxation of electrons to the nuclear degrees of freedom is loosely fitted by an exponential decay yielding a time constant $\tau \sim 3.5$ sec.

![Figure 4.22: Relaxation of overheated electrons to nuclear degrees of freedom. Acquisition time of the noise thermometer in this check was only 5 sec.](image)

For the validity of the relaxation method it is essential that the internal relaxation time of the sample is short compared to the time constant given by the sample’s typical heat capacity $\sim 100 \mu$J/K and the conductivity of the heat switch in the normal state. The normal state conductivity is described by the Wiedemann–Franz law, and comes out about: $\sim 5 \cdot 10^{-8}$ W/K. It was very fortunate that the resistance of the heat switch ended up to be about 0.5 mΩ. These parameters give the time constant of the relaxation $\sim 2000$ s. This is
sufficiently long to precisely follow the relaxation of the sample to the cryostat’s
temperature. At higher temperatures the relaxation becomes too fast and the
method loses reliability. Fitting the relaxation to the stage temperature by
an exponential and evaluating it at time immediately after the pulse, the tem-
perature rise $\Delta T$ for the heat capacity calculation is obtained similarly to the
adiabatic method. The relaxation method works from the lowest temperatures
up to roughly 7 mK, depending on the actual magnitude of heat capacity at the
given field.

When warm-up of the nuclear stage became too fast, the relaxations of the
cell were fitted by a sum of an exponential and a linear function describing the
drift of the stage. The stage drifts were fitted first and the resulting values were
fed as initial guesses to the cell relaxation fitting routine. This ensured reliability
of the fits. Figure 4.23 shows the fitting routine in the relaxation regime. The
pulse size can be made larger than in the case of the adiabatic method as the
cell naturally cools back down after the pulse.

![Figure 4.23: Typical heat pulses and temperature relaxation in the relaxation
regime, in magnetic field 60.1 mT. Black circles are temperature of the stage.
A simple exponential plus a linear temperature drift extracted from the stage
readings was found to fit the cell temperature readings well.](image)
4.6.4 Pseudo adiabatic pulse method of heat capacity measurement

Figure 4.24: Typical heat pulses and temperature drifts in the pseudo-adiabatic regime. Black circles are temperature of the cryostat, which is stabilised by a PID controller. The cell still works very well at temperatures above 80 mK. One can also note the excellent agreement of the stage noise thermometer and the cell noise thermometer at these temperatures.

Above roughly 20 mK the structural parts of the cell start to thermally leak. It is most likely first the alumina table which starts leaking and only at higher temperatures does the heat switch start leaking too. The measurement method above 20 mK is pseudo-adiabatic, meaning the typical linear temperature drifts from the adiabatic method turn into exponential relaxations. The exponential relaxations are however typically longer than in the case of the leaking normal state heat switch in the relaxation method. The pseudo-adiabatic method is therefore still very precise. Fortunately also, temperatures above 20 mK can easily be stabilised by the dilution unit, thus a protocol was adopted to limit the temperature difference between the sample and the thermal bath. The mixing chamber was kept at a stabilised temperature, while several pulses were applied into the cell. The time after pulses was much shorter than what it would take for the cell to thermalised back to the stabilised temperature. The cell thus ends up at a temperature about 5 mK higher than the stabilised temperature. The next stabilised temperature is that temperature then and so on. The method still worked very well to about 90 mK, where current measurements overlap the
older heat capacity measurements by Oeschler [192] and Krellner [193]. A measurement by the pseudo-adiabatic method is shown in Figure 4.24.
4.7 Heat capacity of YbRh$_2$Si$_2$ as a function of temperature and magnetic field (Results and analyses)

4.7.1 Overview of the data

The heat capacity was measured for external fields applied perpendicular to the c-axis of 0.0, 8.4, 10.5, 14.7, 21.1, 35.9, 42.2, 60.0, 69.7 mT. The temperature range of the measurements and the method adopted was determined by practical considerations discussed in section 4.6. In the best case, at 0.0 mT, the temperature range extended from 175 $\mu$K to 90 mK.

The measured heat capacity data sets can be divided into two groups. Results at magnetic field in the ab-plane up to 25 mT present a relatively sharp peak around 1.5 mK which we shall call the low temperature heat capacity anomaly $T_A$, in correspondence with the former measurements of susceptibility and magnetization which discovered features around this temperature [180]. The measurements done above 25 mT do not display any such feature and their overall shape resembles a Schottky peak. All measurements in the second group were done by the relaxation method and they are therefore limited to low enough temperatures. Measurements in the first group were done by the adiabatic method up to the field 10.5 mT above which they were done by the relaxation method. Figures 4.27 and 4.28 show these two distinct groups of measurement in the full temperature range. The majority of the data presented come from the pulse method. Only in case of the measurement at 8.4 mT a data set from continuous warm-up method was included as well, because the pulse method measurements taken did not cover lowest temperatures.

Checks were made to establish agreement between data taken by different methods (pulse adiabatic, pulse relaxation, continuous warmup). The results are shown in Figures 4.48 and 4.52. The pulse method however enables in-situ background heat leak extraction while the warmup method does not. The pulse method results are therefore taken as more reliable. The warmup method results however possess very valuable information about the dynamics of transients, as shown in Figure 4.47.
Figure 4.25: Heat capacity data taken at zero applied magnetic field, showing the known Néel anomaly at 71 mK and another very sharp transition at 1.5 mK.

Figure 4.26: Heat capacity data taken at 14.7 mT. The inset shows the double structured anomaly amplified in linear coordinates.
Figure 4.27: Heat capacity data taken at magnetic field up to 25 mT. These data sets display the low temperature anomaly at temperature $T_A$. C vs. T and C/T vs. T coordinates.

Figure 4.28: Heat capacity data taken at higher magnetic field which do not display any anomaly. C vs. T and C/T vs. T coordinates.

4.7.2 Discussion of errors of the measured heat capacity points

The data-sets presented in the overview section 4.7.1 are shown with errorbars both in the heat capacity and temperature. Errors of the data points come from two sources. First they were established from uncertainties of individual fittings according to appropriate formula done to extract the heat capacity. These are the linear functions describing the temperature drifts in the adiabatic method and the exponential relaxations in the relaxation and pseudo-adiabatic methods. The temperature point measured by the noise thermometer are not passed into the fitting routine with any errors assumed. It is in spite of the fact that uncertainty of temperature measured by the noise thermometer was measured. However the plateaus in between measurement pulses were sufficiently long for the fitting routine to follow the scatter of the temperature points and thus ex-
tract the uncertainty on its own. The Python fitting routine `curve_fit` from the `scipy.optimize` library is able to do that. This approach ensures that if the errors of the measured temperature was changing, the fitting routine will take this into account.

The number of measured heat capacity points was relatively large and it was therefore possible to see if the errorbars reflect the scatter of the points. It can be seen from the presented graphs that the errorbars seem appropriate. It will later be seen, that the estimated errors are, to a degree, supported by analyses of the temperature dependence of the heat capacity, and the ability to account for the data with a reasonable model.

![Graph showing heat capacity data](image)

**Figure 4.29:** Low field heat capacity data as C/T vs. T below 2 mK and in lin-lin coordinates. It is apparent that field applied in the ab-plane moves the anomaly to lower temperatures and the peak decreases in magnitude. Particularly interesting is the split of the anomaly into a double peak at 14.7 mT.

The temperature errorbars are also determined by the fitting routine. After all, both $\Delta T$ used for the heat capacity calculation and the effective temperature of the point, taken as the mean of $T_l$ and $T_h$, have the uncertainty: $\sqrt{\sigma T_l^2 + \sigma T_h^2}$, where in the case of the effective temperature it is divided by 2. This is the full size of the right hand side facing temperature errorbars. The left hand side errorbars are however visibly longer, especially at the lowest temperatures. The source of this extra uncertainty is a possible heat leak into the noise thermometer, which would make the 0.2 Ω resistor not fully thermalised to the sample at
low temperatures. In the worst case scenario the full heat leak of about 30 fW, detected by the adiabatic method, would go into the noise thermometer only. This would however prevent the noise thermometer to reach the lowest temperatures altogether. From careful assessment on how cold the noise thermometer could have possibly gotten by the demagnetisation steps we arrived to a reasonable upper limit of the heat leak into the thermometer of 8 fW. The contribution to the magnitude of the left hand sided errorbars is calculated under the assumption of this heat leak by the Wiedemann–Franz law for the geometry of the noise thermometer. More on this matter can be found in the section about noise thermometry 2.2.4.

The heat capacity data were averaged to improve visual appearance and to ensure the fitting of the data would not be biased by the distribution of clusters of points over temperature. The averaging was done in the following way. A single pair of points in the data set is found such that its temperature spacing calculated as: $\Delta T/T_{\text{mean}}$ is the smallest of all pairs. If this factor is less than a given limit, the points are averaged as arithmetic mean in terms of their temperature and heat capacity and errors of the temperature and the heat capacity. The spacing criterion used was $\Delta T/T_{\text{mean}} = 3\%$ in the regular regions and $\Delta T/T_{\text{mean}} = 0.5\%$ in anomalies. In some cases no averaging of the points was done. These are typically plots where we look for possible hidden features. Graphs, where fitting of the anomalies by the critical phenomena models is shown, feature no averaging as well.

4.7.3 Evaluation of entropy

Our hypothesis is that we should be measuring the release of the total nuclear spin entropy. Even with the combination of quadrupole energy with initially unknown hyperfine interaction, the upper bound for each species is clearly $R \ln(2I + 1)$. This section will show how the data are indeed in excellent agreement with these bounds.

The entropy at temperature $T$ can be calculated from the measured heat capacity as a rolling integral:

$$S_M(T) = \int_0^T \frac{C_M}{T'} dT'.$$

(4.23)

The problem is that the measurements do not extend to $T = 0$. Nevertheless the entropy is additive; in other words $S_M(T)$ is also:

$$S_M(T) = \int_{T_{\text{min}}}^T \frac{C_M}{T'} dT' + S_M(T_{\text{min}}),$$

(4.24)
where $T_{\text{min}}$ is the lowest measurement temperature. $S_M(T_{\text{min}})$ is of course generally unknown. We can however determine it when we are dealing with a simple system of known total entropy and if we measure the heat capacity to effectively infinite temperature. To illustrate this a simple example is one mole of magnetic moments with spin $I$, which has maximum entropy: $S = R \ln(2I + 1)$. Let’s assume a Zeeman splitting by an external magnetic field. If the heat capacity is measured to high enough temperature, where it becomes negligible as $T^{-2}$, the integral 4.24 can be subtracted from the value $R \ln(2I + 1)$ and the offset $S_M(T_{\text{min}})$ thus determined.

Such procedure was performed on our heat capacity data. It is clear from the overview plots that the nuclear entropy becomes important below 20 mK as above we only see electronic heat capacity, linear in $T$. The electronic contribution can be subtracted from the data and the remaining should be purely nuclear. The rolling integral was calculated using the `integrate.cumtrapz` function in Python library SciPy. For data sets which have not been measured to at least 30 mK the heat capacity above maximum measured temperature was predicted from single ion fitting, discussed in the next section 4.8. The resulting entropy curves are shown in Figure 4.30. Horizontal lines on the graph show the maximum entropy values for all magnetic nuclei in the YRS compound in their respective amounts. The graph also features dashed lines, which are only apparent in lowest temperatures, where they deflect from the solid lines. They are generated considering the hypothesis of not fully thermalised thermometer. Under this assumption, the values of $C/T$ should increase and their $T$ value should decrease. This would of course influence the calculated entropy. The dashed lines are generated for data points corrected assuming 8 fW heat leak.

The entropy curves give us following information about YbRh$_2$Si$_2$. The heat capacity measurements from the lowest temperature of 174 µK seem to recover exactly the nuclear entropy of the both magnetically active Yb species. We do not seem to be detecting the nuclear entropy of $^{103}$Rh, nor $^{29}$Si. Measurements of Knight shift and $T_1$ relaxation time by Ishida [209] yield hyperfine constant of the $^{29}$Si to be: $A_{hf}(^{29}\text{Si}) = -72.7$ mT/$\mu_B$, where the electronic moment is the 4f electronic moment of the Yb atoms. For a 0.1 $\mu_B$ state 4f moment, this hyperfine constant gives the splitting of the Zeeman doublet only 3 µK, therefore consistent with our observations.
Figure 4.30: Entropy curves determined from the heat capacity measurements as a rolling integral, subtracted from the full entropy of $^{171}\text{Yb}$ and $^{173}\text{Yb}$ nuclei. The horizontal line denoting $^{103}\text{Rh}$ entropy is not visible as the rhodium entropy is 11.53 J/(mol K), much larger than the measured entropy. Lines separated by a gap from the maximum entropy value line could not have been measured up to 30 mK and the gap had to be estimated from single ion fitting. Inset shows the behaviour in the anomalies amplified.

Our observations however reject a proposed hyperfine constant of $^{103}\text{Rh} - 62.88 \, \text{T/µB}$ quoted in Steppke et al. [195]. It would give the splitting of the Zeeman doublet for 0.1 µB state 4f moment 407 µK and we would definitely observe its heat capacity, especially considering the magnitude of rhodium’s entropy.

The heat capacity anomalies $T_A$ translate to relatively sudden drops on the entropy lines. They are however not strictly vertical, as expected for a first order phase transition scenario.
4.8 Analyses and interpretation

The most striking result is the heat capacity anomaly observed at magnetic fields in the range 0 - 21 mT. This is very sharp at 0 mT and with increasing field shifts to lower temperatures and broadens. A splitting into a double peak is resolved at 14.7 mT. This anomaly sits on a pronounced highly temperature dependent heat capacity. Our initial approach is to attempt to explain as much as possible by the single ion Hamiltonian, introduced in section 4.4. Quadrupolar splitting of the $^{173}$Yb nuclei and Zeeman splitting of both Yb isotopes were considered. The other two elements were not considered in the model.

The effective magnetic field producing the Zeeman splitting is dominated by the hyperfine interaction. It became clear that the data could not be explained by the historically accepted value of the quadrupole interaction, for which no experimental determination at ambient pressure exists. But the quadrupolar interaction can be determined by the zero field data. Then the nuclear heat capacity becomes a method to determine the static part of the 4f moment.

Attempts to fit the two peaks in the zero field heat capacity data within the known theories of the critical phenomena were also made and are discussed in sections 4.8.6 and 4.8.6.

4.8.1 Single ion model - Low magnetic field measurements

We shall start with the zero field measurement. Measurements of muon spin resonance by Ishida et al.[189] have shown that the size of the static 4f local moments in zero magnetic field is only about 0.002 $\mu_B$. The f-moments are obviously the only source of magnetic field for the nuclei via the hyperfine interaction, as the external field is zero. As for the quadrupolar interaction of the $^{173}$Yb species we have a value of the electric field gradient, determined from Mössbauer spectroscopy [195, 210]. We also have the value of nuclear quadrupole of the $^{173}$Yb nucleus (table 4.1), which is determined from optical spectroscopy [15].

The characteristic temperature of the quadrupolar interaction is: $\frac{e^2 q Q}{k_B} \sim 4.7$ mK. Compared to that, the characteristic temperature of the Zeeman interaction due to hyperfine interaction is: $0.002 \mu_B \mu_{N} g_{Yb} / k_B \sim 20(74)$ $\mu$K for $^{173}$Yb ($^{171}$Yb), where we are using the value $\mu_{hf} = 102 T/\mu_B$ as discussed in section 4.3.

We can see that the temperature scales are very different. The Zeeman splitting seems to be negligible while the quadrupolar splitting is almost too large to
describe the zero field data.

We can however attempt to fit the zero field data with a Schottky peak coming from purely quadrupolar splitting and treating the electric field gradient as a free parameter. This was done and the result is shown in Figure 4.31. The range of fitting was above the anomaly: 1.85–30 mK and the fitting formula is:

\[ C_M(T) = n a_{173} \cdot C_{Sch}(eq) + \gamma T, \]  

(4.25)

where \( n a_{173} \) is the natural abundance of the \(^{173}\)Yb species and the \( C_{Sch} \) is given by formula 4.15, where the energy levels are eigenvalues from Hamiltonian 4.10. \( \gamma \) is the Sommerfeld constant of the heavy fermions. Its value is clearly apparent on the C/T vs. T plot in the temperature range 20–40 mK but it was also left as a free parameter in the fit.

![Figure 4.31: Zero applied field heat capacity data. Fitting done in the temperature range 1.8–20 mK by a pure quadrupole plus heavy fermion formula.](image)

It is apparent that the model describes the data very well from the sharp heat capacity anomaly up to temperatures where the Néel ordering starts to play role. The resulting values are given in table 4.2:

<table>
<thead>
<tr>
<th>parameter</th>
<th>received value</th>
<th>fitted value</th>
<th>uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>( eq ) [Vm(^{-2})]</td>
<td>5.76 ( \cdot ) 10(^{21} ) [195]</td>
<td>2.062 ( \cdot ) 10(^{21} )</td>
<td>±0.007 ( \cdot ) 10(^{21} )</td>
</tr>
<tr>
<td>( \gamma ) [J/(mol K(^2))]</td>
<td>1.7 [193]</td>
<td>1.650</td>
<td>±0.009</td>
</tr>
</tbody>
</table>

Table 4.2: Zero field fit parameters results, their uncertainty and comparison to received values from literature.
The normalised $\chi^2$ value of the fit is: 0.8 and the p-value is: 0.88. This suggest the individual measurements errors might be overestimated slightly. Deviations of experimental points from the fit across the fitted temperature range is shown in Figure 4.32. No averaging has been done on the points in order to see any potential spikes or anomalies since the transport measurements indicate superconductivity onset at around 10 mK.

Figure 4.32: Deviations from the fit show in Figure 4.31 expressed as measurements minus the model, scaled by the model.

The high temperature tail of the Schottky peak which is so well fitted by the pure quadrupole model at zero field moves to slightly higher temperatures for measurements in small applied field. This suggest the Zeeman splitting starts to play a role. These measurements were fitted in the temperature range from the heat capacity anomaly $T_A$ up to 30 mK, or up to the temperature they could be measured at. In this case the fitting formula had to incorporate both the quadrupolar splitting on the $^{173}$Yb and the Zeeman splitting on both isotopes. Such model requires the full Hamiltonian 4.11. When looking for the minima of the $\chi^2$ during the fitting routine, exact numerical diagonalization of the Hamiltonian is done in each iteration. The eigenvalues of energy are fed to the equation for specific heat, equation 4.15. The value of electric field gradient was first left free to see if there is any systematic development of it with field. It was observed that there in none. The higher field measurements do not however possess the quality of the zero field measurements and this additional free parameter brought uncertainty to all fit parameters. The quadrupolar parameter was therefore fixed at the value from the zero field measurement for all other fittings.

The same was done with the heavy fermion Sommerfeld constant. We first looked for potential development with field. It cannot be ruled out, nevertheless
the higher field measurements do not typically extend to high enough temperatures and they therefore cannot determine the constant accurately, nor precisely. The Sommerfeld constant was therefore also fixed on the zero field value. The only remaining free parameter is the magnetic field on the nuclei $B_{nuclear}$, while $eq = 2.062 \cdot 10^{21} \text{V/m}^2$ and $\gamma = 1.65 \text{J/(mol K}^2\text{)}$ are fixed. The fitting formula is:

$$C_M(T) = na_{173} \cdot C_{Sch}(eq, B_{nuclear}) + na_{171} \cdot C_{Sch}(B_{nuclear}) + \gamma T, \quad (4.26)$$

where $na_{171/173}$ are the natural abundances. It is clear that the origin of the field splitting must be the effective hyperfine field. However, as is apparent from Table 4.3, the hyperfine field, and hence the state 4f moment depends strongly on the relatively weak external field applied in the ab-plane, as the applied field is far too small to produce sufficient Zeeman splitting. The results are summarised in table 4.3 and in Figure 4.39.

Figure 4.33: Heat capacity of low field measurements presenting the sharp peak. Fitting done in the temperature range from the anomaly (1.4–1.8 mK) up to 30 mK.
Table 4.3: Low field measurements only fit parameter: the magnetic field on the nuclei, and its uncertainty.

<table>
<thead>
<tr>
<th>experimental magnetic field [mT]</th>
<th>$B_{\text{nuclear}}$ [T]</th>
<th>uncertainty [T]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.4 mT</td>
<td>1.55</td>
<td>±0.02</td>
</tr>
<tr>
<td>10.5 mT</td>
<td>1.53</td>
<td>±0.03</td>
</tr>
<tr>
<td>14.7 mT</td>
<td>2.33</td>
<td>±0.03</td>
</tr>
<tr>
<td>21.1 mT</td>
<td>3.68</td>
<td>±0.02</td>
</tr>
</tbody>
</table>

It is also striking that the parameters inferred from these fits above the anomaly completely fail to account for the data at lower temperatures. This is an indication of a reconfiguration of the electronic magnetisation below the anomaly.

4.8.2 Single ion model - High magnetic field measurements

The higher external field measurements, 35.9 - 69.7 mT, which do not display any anomaly have the overall shape resembling a Schottky peak. They were therefore fitted in the whole temperature range by the single ion model. The fits are shown in Figure 4.37. These data sets however contain more experimental points than the low field data, where only the region above the anomaly can be used. We could have therefore study them more systematically in terms of the respective strengths of the quadrupole and Zeeman splittings. It was observed that the Schottky peak fit is occasionally susceptible to the initial guesses of the
fit parameters ($B_{\text{nuclear}}$ and $eq$). This is because both effects produce energy level splitting which can to some extend be complimentary to each other. In other words, larger assumed quadrupolar splitting causes smaller Zeeman splitting to still achieve overall agreement with the data, and vice versa. To properly study this, contour plots were made to illustrate goodness of fit over the 2D parameter space. These plots cover the full parameter space of the field on the nuclei and the quadrupolar parameter $eq$. The results are shown in Figure 4.35. The model formula was:

$$C_M(T) = na_{173} \cdot C_{\text{Sch}}(eq, B_{\text{nuclear}}) + na_{171} \cdot C_{\text{Sch}}(B_{\text{nuclear}}) + \gamma T,$$

(4.27)

and the $\chi^2$ value was calculated as:

$$\chi^2 = \sum_{i=1}^{N} \left( \frac{C_M^i - \text{model}}{\sigma C_M^i} \right)^2,$$

(4.28)

where $N$ is the number of experimental points and $\sigma C_M^i$ are errors of the individual data points. Errors in temperature are not considered in the results presented here; nevertheless regular checks were made to see if the fits favour the non-thermalised hypothesis, which shifts points at lowest temperatures to even lower. No such observation was made.

Figure 4.35: Inverse of the $\chi^2$ value (multiplied by 100) for a fit according to formula 4.27 with a given pair of parameters $eq$ and $B_{\text{nuclear}}$. 

201
The contour plots prove that the low value of the electric field gradient from the zero field measurements is a stable one. It is true that for the highest field measurements, taken at 60.0 mT and 69.7 mT, allow for a wider combination of $eq$ and $B_{\text{nuclear}}$ as evidenced by the long valley of low values of $\chi^2$ in Figure 4.35. These data sets allow a combination of the two parameters where the electric field gradient is larger than the value from the zero field fit and $B_{\text{nuclear}}$ is accordingly smaller; $eq$ can almost reach the received value from [195]. However, this variant does not prevail to low fields and it is therefore most likely not physical. The fact that the data sets can support wider range of fit parameters is closely related to the fact that the model formula never fits the data perfectly, as can be seen in Figure 4.37. This is unlikely a fault of the data. Though not perfect, we believe they were measured accurately and precisely enough. Most likely it is that the true physical description of the system is more complicated than the single ion model. There is possibly a development of the static electronic f-moment with temperature, or an evolution of the electronic contribution approaching the QCP and associated with ‘strange metal’ behaviour. The latter could be studied in future using $^{174}\text{Yb}$ isotopically enriched samples.

![Figure 4.36](image)

Figure 4.36: High field measurements with their fits on a common graph in logarithmic axes. Fits according to the single ion (Schottky) model shown as lines.

With an incomplete model the fits can never be perfect and they can allow for more possible outcomes which have to be critically judged. Based on this analyses it was considered justified to fix the electronic field gradient (and hence quadrupolar interaction) and the Sommerfeld coefficient. The fits are shown in Figures 4.37 and 4.36. They also show an increase in hyperfine field with exter-
nal field, which we discuss in the next section.

Figure 4.37: Heat capacity measurements at high fields not showing any heat capacity anomaly in the form of a sharp peak. Fitting done in the whole temperature range.

<table>
<thead>
<tr>
<th>experimental magnetic field [mT]</th>
<th>$B_{nuclear}$ [T]</th>
<th>uncertainty [T]</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.9 mT</td>
<td>6.73</td>
<td>±0.03</td>
</tr>
<tr>
<td>42.2 mT</td>
<td>7.83</td>
<td>±0.03</td>
</tr>
<tr>
<td>60.0 mT</td>
<td>11.12</td>
<td>±0.04</td>
</tr>
<tr>
<td>69.7 mT</td>
<td>11.36</td>
<td>±0.04</td>
</tr>
</tbody>
</table>

Table 4.4: High field measurements fit parameter: the magnetic field on the nuclei and its uncertainty.
Figure 4.38: Energy levels by Hamiltonian 4.11 for $^{173}$Yb (bottom) and simple Zeeman splitting for $^{171}$Yb (top) for magnetic fields $B_{nuclear}$ determined by the fits vs. applied magnetic field.

4.8.3 Dependence of 4f local moment on applied field

The high field fits and the low field fits both give the magnetic field on the nuclei given in tables 4.3 and 4.4. Together they are shown in Figure 4.39. As discussed, given the hyperfine constant, this determines the evolution of the 4f local moment. Our results are complimentary to direct measurements of the electronic magnetic moment by susceptibility by Brando et al. [211]. They measured the magnetic moment at 20 mK and 50 mK and got qualitatively and quantitatively the same results. Results at 20 mK are shown in Figure 4.39. Our magnetic moment comes out about 30% larger. The fact is that $B_{nuclear}$ is extracted from heat capacity data measured at temperatures lower than 20 mK. This would point in the direction of the temperature development of the electronic moment. Another explanation for the disagreement could be an uncertainty in susceptometer calibration by Brando et al. or a different value of the hyperfine constant $A_{hf}$. The reason for this slight disagreement is currently under investigation. Our results also tentatively identify a break field dependence at QCP (60 mT) consistent with [211].

We take this qualitative agreement as support for the single ion model in the region so far discussed. Independent of the nature of the electronic magnetic order, the nuclear spins are used to determine the magnitude of the electronic local moment.
Figure 4.39: Applied magnetic field in the ab-plane and resulting magnetic field on the nuclei (left axis) and magnetic moment of the 4f moments (right axis) as directly measured by susceptibility measurements in [211] and obtained by fitting our heat capacity data to the single ion model. $A_{hf} = 102 \, T/\mu_B$.

### 4.8.4 Heat capacity below the anomaly: evidence for SDW order

So far we have a consistent description of the data at all magnetic fields and at temperatures above the anomaly, which is seen in fields below 21.1 mT. This is within the single ion picture. The heat capacity anomaly is a signature of a collective ordering transition. In the following discussion we look at the temperature dependence at low temperatures in an attempt to infer the ground state of the system.

The zero field heat capacity data below the $T_A$ anomaly have a very distinct shape which rules out ordering in a single effective field, which is happening in large fields. The “best fit” of the zero field data according to the single ion model can be seen in Figure 4.40. The parameter $B_{\text{nuclear}}$ comes out 5.7 T. It can clearly be seen that the model does not describe the data. Furthermore, the low temperature tail below the anomaly is too long; the nuclei keep their entropy to much lower temperature than a single Schottky peak arising from a particular hyperfine field suggests. Inspection of Figure 4.33 also suggests that within the single ion picture there is a significant difference between the hyperfine field at low temperatures and above the anomaly.
However the special shape of the low temperature data could be explained by a distribution of magnetic fields within the sample. In that case some nuclei would have energy levels split much less than other nuclei and thus keeping their entropy to lower temperatures. This could physically be realised if the f-moments were forming an incommensurate spin-density wave (SDW). Archetypal SDW order material is Chromium [212]. The electronic moment has spatial periodicity in the SDW state.

The following model was examined. The magnitude of electronic magnetic moment varies periodically as a sine wave with a period incommensurate with the lattice constant. Active nuclei $^{171}\text{Yb}$ (14.3%) and $^{173}\text{Yb}$ (16.1%) are distributed randomly in the lattice. They experience a hyperfine magnetic field given by the size of the electronic moment times the hyperfine constant. Their individual splitting and heat capacity is calculated simply by the single ion model used previously. This is depicted in the inset in Figure 4.41. In another words, we distribute the number of active Yb isotopes into $n$ groups, where $n$ is sufficiently large (100 was used). The hyperfine magnetic field each of these $n$ groups experience is between 0 and $B_{\text{max}}$, and varies as a sine function. The single ion model is used to calculate the heat capacity for each of these groups and their resulting heat capacities summed up together. The maximum magnetic field $B_{\text{max}}$, or alternatively $\mu_{\text{max}}$ as the maximum electronic moment is the only free parameter within this model. We have no information on the wavelength of the
SDW, which does not enter the model. The fitting formula can be written as:

\[
C_M(T) = \sum_{i=1}^{100} na_{173}/100 \cdot C_{Sch}(eq, B_{nuclear}) + \frac{na_{171}}{100} \cdot C_{Sch}(B_{nuclear}) + \gamma T,
\]

where \(B_{nuclear}\) varies as:

\[
B_{nuclear} = B_{max} \sin\left(\frac{i}{100}(\pi/2)\right),
\]

Figure 4.41 shows the fit according to the SDW model. The full line is the fit of the experimental points up to 0.8 mK, dashed line is the fit of the points, again up to 0.8 mK, but when shifted to lower temperatures by the non-fully thermalised thermometer hypothesis correction. The inset depicts how the magnetic moment of the f-states varies within the 1D model. We assume the magnetic moments to be in the ab-plane of YRS. This is reasonable as the resulting \(\mu_{max}\) parameter comes out too large to be oriented along the c-axis. The results of the SDW fitting is: \(\mu_{max} = 0.090 \mu_B\) for the raw data points fit and \(\mu_{max} = 0.075 \mu_B\) for the corrected data points fit.

The result is striking for a number of reasons:

- The moment much larger than the accepted value of around 0.002\(\mu_B\), which is also consistent with our heat capacity data above the anomaly.
- It points to a re-orientation of the moments from along the c-axis, above the anomaly, into the ab-plane below the anomaly.

The SDW model does not describe the anomaly, or behaviour just below the anomaly. By examining the excess heat capacity to the SDW model (Figure 4.44) it was observed that it could be well described by a step jump and an exponential decay. So phenomenologically a term of the following form:

\[
C_M = a \exp\left(-\frac{\Delta}{T}\right)
\]

is added to the SDW model 4.29 and applied on the raw data. The agreement of the model and the data is striking and shown in Figure 4.41 as red dotted line. The fit yields following results:

<table>
<thead>
<tr>
<th>parameter</th>
<th>fitted value</th>
<th>uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) [J/(mol K)]</td>
<td>1.7</td>
<td>(\pm 0.2)</td>
</tr>
<tr>
<td>(\Delta) [mK]</td>
<td>1.75</td>
<td>(\pm 0.14)</td>
</tr>
<tr>
<td>(\mu_{max}) [(\mu_B)]</td>
<td>0.093</td>
<td>(\pm 0.001)</td>
</tr>
</tbody>
</table>

Table 4.5: Results of the SDW + gap model.
The normalised $\chi^2$ of this model is 0.28 and the p-value is 1 within 7 decimal places. The fit also does not support the hypothesis of non-fully thermalised thermometer. It agrees excellently with the raw data and more poorly with the corrected data. Entropy in the gap formula of the heat capacity by equation 4.31 is 0.28 J/(mol K), therefore relatively significant. Nevertheless, the majority of the nuclear entropy is within the bare SDW model.

![Graph](image)

Figure 4.41: SDW based fits at temperatures below the $T_A$ anomaly. C vs. T coordinates. The inset depicts our simple model. Green arrows are f-moments without an active nucleus underneath them, red arrows are f-moments with active nuclei, which are randomly distributed in the lattice.

**Development of the SDW order with applied field**

It can be seen from the overview graphs (Figure 4.27) that the data points below the $T_A$ anomaly differ only very slightly from each other when magnetic field is applied. Nevertheless there is a slight deflection from the zero field data and also the $T_A$ peaks lie at different temperatures and have different shapes. The shape of the data below $T_A$ in applied field actually suggests that the magnetic ordering is not happening as in the pure SDW scenario, the data tend to zero at higher temperatures than the zero field data. This suggests that there is a minimum magnetic field the nuclei experience, unlike in the pure SDW scenario, where the moments on the nodes of the sine wave have effectively zero magnetic
field and keep their entropy to the lowest temperatures. The model function is:

\[ C_M(T) = \sum_{i=1}^{100} n_{a173}/100 \cdot C_{Sch}(eq, B_{nuclear}) + \]
\[ n_{a171}/100 \cdot C_{Sch}(B_{nuclear}) + a \exp\left(\frac{-\Delta}{T}\right) + \gamma T, \]  

\[ (4.32) \]
where \( B_{nuclear} \) varies as:

\[ B_{nuclear} = B'_{max} \sin\left(\frac{i}{100}\right) (\pi/2) + B_{min}, \]  

\[ (4.33) \]
where \( B'_{max}, a \) and \( \Delta \) are the free parameters, \( B_{min} \) was fixed at the value determined from the single ion fits above the anomaly for the appropriate data set (values from table 4.3). The results of this fitting approach for the two highest fields which still display the \( T_A \) anomaly: 14.7 mT and 21.1 mT are shown in Figure 4.42 and the fit parameters summarised in table 4.6.

<table>
<thead>
<tr>
<th>14.7 mT</th>
<th>parameter</th>
<th>fitted value</th>
<th>uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) [J/(mol K)]</td>
<td>0.66</td>
<td>±0.30</td>
<td></td>
</tr>
<tr>
<td>( \Delta ) [mK]</td>
<td>0.9</td>
<td>± 0.5</td>
<td></td>
</tr>
<tr>
<td>( \mu'_{max} ) [( \mu_B )]</td>
<td>0.075</td>
<td>±0.007</td>
<td></td>
</tr>
<tr>
<td>( \mu_{min} ) [( \mu_B )]</td>
<td>0.0228</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>21.1 mT</td>
<td>parameter</td>
<td>fitted value</td>
<td>uncertainty</td>
</tr>
<tr>
<td>( a ) [J/(mol K)]</td>
<td>1</td>
<td>± 2</td>
<td></td>
</tr>
<tr>
<td>( \Delta ) [mK]</td>
<td>1</td>
<td>± 2</td>
<td></td>
</tr>
<tr>
<td>( \mu'_{max} ) [( \mu_B )]</td>
<td>0.055</td>
<td>±0.018</td>
<td></td>
</tr>
<tr>
<td>( \mu_{min} ) [( \mu_B )]</td>
<td>0.036</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6: Results of the field modified SDW + gap model at two applied fields. Values of \( \mu_{min} \) were fixed for the fits from the obtained values above the anomaly (Table 4.3).

The actual maximum value of the electronic moment is \( \mu_{max} = \mu'_{max} + \mu_{min} \), which comes out 0.097 and 0.091 \( \mu_B \) for the 14.7 and 21.1 mT case respectively, and agrees with the zero field fitting. Due to the small number of experimental points in the in-field data, the fit parameter results have large uncertainty. Nevertheless, the normalised \( \chi^2 \) value comes out 0.32 and 0.66 for the 14.7 and 21.1 mT fit respectively. The numerical formula therefore describes the data well, even though the accurate physical description might be slightly more complicated.
Figure 4.42: Modified SDW + gap model fit at temperatures below the $T_A$ anomaly for two applied fields. The zero field data fit line drawn for comparison. Linear coordinates, unlike in Figure 4.41.

4.8.5 Single ion model fitting summary

Three chosen fields with their respective fits are shown in Figure 4.43. This is to summarise which models describe the data in which field and what temperature range. High field data do not display any heat capacity anomaly and they overall resemble a Schottky peak. They were fitted in the whole temperature range with a single ion model with a fixed quadrupole value determined from the zero field fit. Zero field data are fitted by a pure quadrupole plus heavy fermion models above the heat capacity anomaly $T_A$. Below the anomaly they are fitted with a model describing a SDW order in the electronic system, plus a gap formula. The SDW model is based on the single ion model but considers a distribution of magnetic fields felt by the nuclei, due to the SDW order of electrons and the hyperfine interaction. The gap formula describes well the middle region between the lowest temperature and the anomaly. It is an excess to the SDW scenario and might be coming from dynamical formation of the SDW order. The 14.7 mT data set shown in Figure 4.43 is the one which shows a double peak feature on the anomaly. Above the anomaly it is fitted by the single ion model with a fixed quadrupole strength and the Sommerfeld constant. Below the anomaly it is fitted with a SDW scenario with a minimum value of the felt field, due to the applied field, plus the gap formula. This model visibly deflects from the pure SDW model, used for zero field fitting, at the lowest temperatures.
It is worthy of note that there is limited knowledge of the nature of the electronic order that develops in YbRh$_2$Si$_2$ below $T_N$. So far, neutron scattering above $T_N$ infers incommensurate spin fluctuations [213]. An examination of the Fermi surface to identify potential nesting vectors, driving SDW order, would be of interest. Here we are able to use the nuclear spins to interrogate the SDW through detection of a spatially modulated hyperfine field.

4.8.6 Heat capacity anomaly

**Comparison of the $T_A$ and $T_N$ peaks**

It is worth noting that the 1.5 mK anomaly peak $T_A$ to some extend resembles the Néel peak $T_N$ at 70 mK. Both peaks are not symmetric; they have a significant tail at the low temperature side while being much sharper at the high temperature side. The gap formula in equation 4.31 can very well describe these low temperature tails of both peaks. This is shown if Figure 4.44 for both peaks. The SDW model without the exponential term was subtracted from the data below the anomaly and the quadrupolar plus heavy fermion model was subtracted above the anomaly. As for the behaviour above $T_N$, Krellner et al. [193] give a temperature dependence:

$$C/T \sim T^{-0.34},$$

(4.34)

They do not unfortunately give the proportionality constant but it can be roughly estimated from our data assuming this exponent. The formula for the
background heat capacity used above $T_N$ is:

$$C_M = 0.502 T^{0.66}.$$  \hspace{1cm} (4.35)

Figure 4.44: Excess to the heat capacity models above and below the anomaly $T_A$ given by the quadrupolar plus heavy fermion model and the pure SDW model respectively. Both peaks show a tail at the low temperature side which was fitted by the formula 4.31.

For completeness the fit parameters below $T_N$ by formula 4.31 shown in Figure 4.44 are: $a = 0.905 \text{ J/(mol K)}$ and $\Delta = 196 \text{ mK}$.

Néel transition $T_N$

Even though the Néel transition has been found to move in temperature according to sample’s quality; our data show the heat capacity peak at the Néel point at 70 mK in fair agreement with the earlier work ([192, 193]) in terms of position and magnitude. Our sample, and the ones used in works cited here, have very high quality, characterised by a resistivity residual ratio larger than 80. The heat capacity peak measured in this work in zero field is shown in Figure 4.45.
Figure 4.45: The Néel point heat capacity peak at 70 mK in zero magnetic field. Models describing the data below and above the anomaly are shown.

An attempt to fit the peak according to the critical exponents models introduced in section 4.5 was made but the data are not dense enough to support one model over the others. The heat capacity above and below the transition temperature was subtracted according to known models, as was introduced in the previous section. The model below $T_N$ consists of the heavy fermion contribution, pure quadrupolar contribution (however fairly negligible) and the gap function, formula 4.31. The model above $T_N$ is the formula 4.35. The fit equation to the singular part below $T_N$ is then:

$$C = A' |t|^{-\alpha} + B',$$

where $t$ is the reduced temperature. And the fit equation above $T_N$ was:

$$C = A |t|^{-\alpha} + B.$$  \hspace{1cm} (4.37)

In case of the logarithmic divergence the factor $|t|^{-\alpha}$ was replaced with $\log |t|$. The resulting parameters of the fits are given in Table 4.7 and the fits are shown in Figure 4.46.

The entropy of the cleaned peak shown in Figure 4.46 comes out 0.014 J/(mol K) (about 0.0024$R\ln(2)$) by numerical integration of $C/T$ points. The development of the entropy through the anomaly is shown in Figure 4.46 inset. This
The value of entropy is about 10 times smaller than the value previously quoted [214]. This discrepancy probably arises from the careful subtraction of the models from both sides of the peak done in this work, to better reveal the singular part. The smallness of $\Delta S$ is likely related to smallness of the ordered moment below $T_N$.

![Graph showing heat capacity and entropy changes across the Neel transition]

**Figure 4.46:** Measured heat capacity at the Néel point at 70 mK in zero magnetic field with subtracted appropriate models below and above $T_N$. Data are fitted with three models described in section 4.5. Inset shows the development of entropy across the transition.

<table>
<thead>
<tr>
<th>Model</th>
<th>$T_c$ [mK]</th>
<th>$A/A'$</th>
<th>$B/B'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ising</td>
<td>70.59</td>
<td>1.02</td>
<td>1.10</td>
</tr>
<tr>
<td>Heisenberg</td>
<td>70.53</td>
<td>1.16</td>
<td>1.10</td>
</tr>
<tr>
<td>Log div</td>
<td>70.58</td>
<td>1.05</td>
<td>1.25</td>
</tr>
</tbody>
</table>

**Table 4.7:** Fittings of the Néel transition at 70 mK shown in Figure 4.46 according to the Ising and Heisenberg model and logarithmic divergence.

Precise measurements of the $T_N$ anomaly were also done by Krellner et al. [193]. Their measuring heat pulses were as small as 0.1% and they observed the amplitude of the peak to be increasing with decreasing pulse size. The peak amplitude for pulse magnitude 0.1% is even slightly higher than our observed amplitude. They fitted the peak by the critical behaviour formulae 4.36 and 4.37, with added linear term, and allowed the critical exponent $\alpha$ to be free. Their results do not agree with any of the established models (Heisenberg, Ising). The
α coefficient came out positive and α ∼ 0.38.

We were not able to confirm if our data of the $T_N$ anomaly agree with any of the established models, or are described by a different critical coefficient, like the one observed by Krellner. A question of what are the critical exponents of a SDW also arises. Improved measurements should be possible using our heat capacity method but will require high quality samples, as critical exponents are very sensitive to disorder. This was observed for example in Sr doped EuS [206]. EuS behaves as almost ideal Heisenberg ferromagnet (shown in Figure 4.17), however with increasing Sr content the critical exponent decreases. In the limit of strong disorder it reaches a value −0.9, which is consistent with theory [215].

![Figure 4.47: Continuous warm-up crossings of the anomaly in YRS (field 0.1 mT) in different speeds realized by different power applied in the heater. The legend specifies the overall power for the given warm-up curve which consists of the applied part and parasitic heat leak contribution: 80 fW. It is important to note that the collapse of the curves is slightly compromised when the parasitic heat leak value is varied. The value 80 fW however ensures agreement even in the non-singular temperature ranges of the measurement. The absence of a time spanned temperature plateau and hysteresis speaks against a first order phase transition.](image)

The low temperature heat capacity anomaly $T_A$

To distinguish between a first and second order phase transition from an observed apparent heat capacity anomaly, a continuous warmup measurement is
of great help. If there is a latent heat associated with the transition it will show as a plateau in the temperature vs. time plot. The time span of the plateau times the power to the sample will equal the latent heat. Hysteretic behaviour, like overheating or super-cooling, are not uncommon with first order phase transition. In order to study the observed heat capacity anomaly in YbRh$_2$Si$_2$ in zero magnetic field, the continuous warmup measurement was performed in three different continuous heater powers. The result can be seen in Figure 4.47. The result does not support a first order phase transition, even though the slow down of the warm up rate is very pronounced. The three warm-up curves also lie perfectly on top of each other, which rules out overheating. The parasitic heat leak value used, 80 fW, is slightly larger than the heat leak observed by the pulse method. Different instruments providing current/voltage are however used in the two methods, so such observation is not surprising. In the continuous warm-up method, the parasitic heat leak is an adjustable parameter which is either determined from multiple warm-ups, and their comparison in a non-singular temperature range, or by requiring agreement with the pulse method measurements.

![Figure 4.48: Comparison of measurements at 0.1 mT by continuous warm-up and pulse method at 0.0 mT. Different applied current causes different density and precision of heat capacity points.](image)

Figure 4.48 shows a comparison of the extracted heat capacity from the continuous warm-up measurements under the three continuous powers to the pulse method data points. The two methods agree extremely well even though the
continuous warm-up data were taken at slightly higher field 0.1 mT.

![Graph showing critical phenomena fits (section 4.5) to the low temperature anomaly $T_A$. The peak is cleaned by subtracting appropriate models below and above 1.482 mK. Inset shoes the development of entropy across the anomaly.](image)

Figure 4.49: Critical phenomena fits (section 4.5) to the low temperature anomaly $T_A$. The peak is cleaned by subtracting appropriate models below and above 1.482 mK. Inset shoes the development of entropy across the anomaly.

Given the evidence that the $T_A$ transition is a second order, the same approach was taken as in the case of the $T_N$ transition to explore critical behaviour. Appropriate models were first subtracted from the left and right tail of the peak. Below the peak it is the SDW scenario with added gap (equation 4.32), above the peak it is the pure quadrupole plus heavy fermion model (equation 4.25). The transition between the two models at $T_A$ is easily visible in Figure 4.43. The two models were subtracted from the data below and above the peak and the excess was fitted with the Heisenberg, Ising and logarithmic divergence formulas (section 4.5). The result of the fits is shown in Figure 4.49 and the fit parameters are given in Table 4.8. The peak seems to be slightly broader near its summit than the formulae suggest. It is possible that the transition peak is artificially broadened by inhomogeneities or strain within the sample. Alternatively we do see a double peak at the $T_A$ transition at 14.7 mT, so it is possible that grounds for this phenomena are already present at zero field.
Table 4.8: Fittings of the low temperature anomaly at 1.48 mK shown in Figure 4.49 according to the Ising and Heisenberg model and logarithmic divergence.

<table>
<thead>
<tr>
<th>Model</th>
<th>$T_c$ [mK]</th>
<th>$A/A'$</th>
<th>$B/B'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ising</td>
<td>1.484</td>
<td>0.95</td>
<td>0.90</td>
</tr>
<tr>
<td>Heisenberg</td>
<td>1.485</td>
<td>0.91</td>
<td>0.96</td>
</tr>
<tr>
<td>Log div</td>
<td>1.485</td>
<td>0.89</td>
<td>0.78</td>
</tr>
</tbody>
</table>

The entropy of the cleaned peak shown in Figure 4.49 comes out 0.24 J/(mol K) (about 0.04 $R \ln(2)$) by numerical integration of $C/T$. The development of the entropy through the anomaly is shown in Figure 4.49 inset. We can compare this value to the value of entropy under the Néel transition and we can see it is 17 times larger.

4.8.7 Comparison of the heat capacity data to data from other techniques

Comparison to transport measurements

Measurements of complex impedance on YbRh$_2$Si$_2$ were done at RHUL by Dr. Lev Levitin on ND3 cryostat. Figure 4.50 shows comparison of the heat capacity and transport data for two fields near fields 0 and 8.4 mT. The data do not exactly match their magnetic fields so two closest field in transport were plotted with a single heat capacity data set. The transport data present these following features:

- The real part ($\Re$) of the measured impedance drops to effective zero at 5mK, 6 mK in 8.4 mT, 0 mT respectively. In the higher field there appears to be a re-entrance of the normal state below 1 mK which is not apparent on the zero field data.

- The imaginary part ($\Im$) has a distinct drop in the very vicinity of the heat capacity anomaly. This has been called the $T_A$ transition. In zero field the imaginary part simply drops to a constant value and stays there to the lowest temperatures. This is preceded in both fields by a sharp decay from 6 mK down to 2 mK. Only in the higher field there is a subsequent increase of the imaginary part below $T_A$, which is probably related to the re-entrant behaviour seen on the real part.
Figure 4.50: Heat capacity measurements at zero magnetic field and 8.4 mT compared to transport measurements at 0, 8.2 and 8.6 mT. Real and imaginary part of the impedance are shown.

**Comparison to susceptibility**

It was discussed in section 4.2.1 what other groups observed when measuring the YbRh$_2$Si$_2$ susceptibility and magnetisation. The static magnetic moment of the f-states and its development with field in the ab-plane determined from susceptibility and heat capacity is shown in Figure 4.39. Another feature seen by both techniques is a peak around 2 mK. Comparison of the position of the peak in the two techniques is shown in Figure 4.51. It can be seen that there is a disagreement of the two methods in low fields up to 10 mT; above this field there is a reasonable agreement. Even though the thermometry used in [216] does not inspire confidence, we propose a different scenario to explain this. In the low magnetic fields the susceptibility peaks are well below the superconduc-
tivity onset temperature. From transport measurements we know that YbRh$_2$Si$_2$ enters gradually into the superconducting region. The Meissner screening effect influences the susceptibility measurements and works against the susceptibility peak coming from a magnetic ordering. At some temperature the Meissner effect overpowers the magnetic ordering signatures and the susceptibility peak thus summits at higher temperature than it would have, without the Meissner screening. Compared to that, at higher fields the superconductivity is at least partially suppressed and the susceptibility peak can therefore manifests itself in its whole.

![Figure 4.51: Low temperature heat capacity anomaly $T_A$ position with comparison to susceptibility peak position from [216]. Dotted line is a possible continuation of the heat capacity peak position. We intend to properly measure the field region 21 - 36 mT with a new experimental setup.](image)

**4.8.8 Final technical remarks on the heat capacity measurements**

**Reliability of the relaxation method**

The aluminium heat switch was found being slightly hysteretic. When the field is lowered just below the $T_C$ of aluminium, 10.5 mT, it still remains conductive at least down to 8 mT and its conductivity is not significantly lowered from the normal state. To ensure proper opening of the heat switch, the field was always lowered all the way to zero before ramping it up again, if needed. The hysteresis however allowed us to compare the adiabatic and relaxation method on the exact same field. Figure 4.52 shows a comparison of the two methods and is meant to demonstrate the reliability of the relaxation method. We can see that the agreement of the two methods is perfect below 2 mK, even though the scatter of the measured points is larger in the relaxation method. Above 2
mK the relaxation method can deflect and we see that the scatter of the points in not properly described by the errorbar size. The reason for this is that the exponential relaxation become too short and their fitting breaks down. It is however also fair to say that the relaxation measurements at 10.5 mT have the lowest quality of all the relaxation measurements, because with the larger applied field the heat capacity goes up at a given temperature and that prolongs the exponential relaxation and increases the reliability.

Figure 4.52: Comparison of the adiabatic and relaxation methods on the same experimental field.

Another way to check the reliability of the relaxation method at high temperatures was to measure isotherms. Multiple pulses were applied while the temperature of the nuclear stage was not changing. As the noise thermometer acquisition is not commensurate with the array of heat pulses, recovery after each pulse will be have slightly different position of temperature points. In a scenario that the method was largely dependent on the positioning, the points would not form a cloud on a C vs. T plot. A signature that the method is reliable is whether or not the points form a small cloud and individual errorbars have the size of the cloud spread. Such isotherms were performed and the heat capacity points are shown in Figure 4.53. The errorbar size is typically a bit smaller than the cloud size. We can also notice a particular tilt elliptical shape the clouds have. This is the result of the negative correlation between the extracted $\Delta T$, which translates into the temperature of the point, and the derived
heat capacity.

Figure 4.53: Heat capacity measurements at a given field when temperature is stable. Lines according to the single ion model are added even though the disagreement from the model can be significant at these temperatures.

The addendum heat capacity

Figure 4.54 shows comparison of the measured data in zero field together with an estimate of the addendum heat capacity of other constructional parts of the cell. This namely comes from platinum in the PtW wire, gold wire and also alumina support. The two points labelled as Au from 2DEG is a heat capacity which was measured by our group on gold submerged in liquid He in the past [37]. The relatively large value does not correspond to known electronic and nuclear properties of gold. It was hypothesised it could come from nuclear quadrupolar effects of gold atoms which do not experience cubic symmetry, like on grain boundaries or dislocations. Still it is clear the heat capacity of the Au and PtW wires are nowhere comparable to the YRS crystal. The alumina support could on the other hand compete with the YRS heat capacity due to the large nuclear heat capacity of aluminium in magnetic field. However, alumina is a non-conductive material with the phononic thermal conductivity quickly vanishing at low temperatures (formula 2.47). Even without knowing the spin–lattice relaxation time of Al nuclei in alumina an upper bound on thermal diffusivity can be made for our design of the support table from the conductivity 2.47 and the heat capacity. Figure 4.54 also gives the time constant as the inverse of the
thermal diffusivity and proves that even though the heat capacity of the alumina table is large this thermal bath is very much disconnected from our cell.

Figure 4.54: The zero field heat capacity data of YRS compared to the estimated heat capacity of other constructional parts in the cell (left). And the lower limit on the time constant with which Al nuclei in the alumina thermalize to the cryostat or the cell (right).

**Heat switch of the future**

The most pronounced imperfection of the heat capacity cell was that it did not allow for the adiabatic measurements at higher fields. The relaxation method had to be used which does not extend to high enough temperatures and looses reliability at higher temperatures. We could not properly measure the heavy fermion behaviour below $T_N$, and look for the QCP.

The solution to that is using a different material for the heat switch. The highest critical field type I superconductor is lead with, $H_C = 80.3$ mT. This is enough for valuable measurements in the ab-plane. We did not observe any release of energy associated with the operation of the aluminium heat switch in the last run. It is possible it was simply not visible among cooling effects taking place while the magnetic field is lowered. It is a question whether lead heat switch with much higher condensation energy: $\Delta G = 1/2\mu_0H_c^2V_m$ will cause problems or not [217]. Nevertheless we believe that lead is the next material to go with and a new version of the heat capacity cell is currently under construction.
4.9 Interplay of magnetism and superconductivity in YbRh$_2$Si$_2$

The phase diagram shown in Figure 4.55 is constructed from transport measurements by Lev Levitin and also features positions of the $T_A$ anomalies, as detected by the heat capacity experiment. Another comparison of both the real and imaginary part of sample’s impedance and the heat capacity was shown in Figure 4.50. That was done in relatively small fields, 0 and 8 mT, on a sample where the real part of the sample’s impedance drops to zero at approximately 6 mK, and only deep in the superconducting region, at 1.5 mK, we observe the sharp drop in the sample’s imaginary impedance, accompanying the magnetic transition called $T_A$. In comparison, the transport measurements shown on the phase diagram in Figure 4.55 were taken on a different sample, which only reached the fully superconducting state just above the drop in the imaginary impedance. The phase diagram only displays the real part of the impedance, so the concurrence of the magnetic transition and the imaginary impedance drop in small fields is not captured there. We can summarise the transport measurements as follows:

- The samples are only “properly superconducting” in low enough temperatures and fields. We mean by this the situation when the real part of the impedance is zero and persistence currents can be observed.

- In moderate fields, approximately 8 - 40 mT, and low temperatures, we observe a normal state resistance re-entrance. This state borders the “properly superconducting” state found at lower fields, and a partially superconducting state found at higher temperatures.

- Surprisingly, above 40 mT the sample is again, to an extend, superconducting down to the lowest temperatures. The resistance does not however drop all the way to zero.

- To vaguely relate the transport observation to the thermodynamic ones, we can say that the SDW state below $T_A$ hosts a genuine superconductivity with a relatively small critical field. The AFM state with very small magnetic moments above $T_A$ hosts a weaker superconductivity, which can however extend to much larger fields. This weak superconductivity is, to an extend, even supported by magnetic field, because the transition to the superconducting state happens at higher temperature around the quantum critical field, 55 mT, than around 30 mT.

- It is therefore important to realise, that that the thermodynamic transition $T_A$ is not always into a superconducting, or “more superconducting” state, like in the zero field. At moderates fields, the transition seems to border the normal resistance state from the weakly superconducting state at higher
temperature. The leading phenomenon in YbRh$_2$Si$_2$ therefore must be the magnetism, while the superconductivity seems to only follow it.

- We must also be open to the possibility that only small fraction of the material’s volume is superconducting. This is in fact the only way to explain the resistance not dropping all the way to zero at certain parts of the phase diagram.

- The “weaker” type superconductivity above $T_A$ extends beyond Pauli limit. This opens up the possibility for a spin triplet superconductivity.

Figure 4.55: Low temperature, and field applied in the ab-plane, phase diagram of YbRh$_2$Si$_2$. The colour contours come from the real part of the sample’s impedance, as measured by transport. Positions of the $T_A$ peaks from the heat capacity experiment are shown as purple stars.
Conclusions

This thesis consists of two independent experiments, both concerning strongly correlated fermionic systems, and thus very important for the Condensed matter research.

Our NMR measurements on the $^3$He doped second layer on graphite give evidence that the second layer is indeed solid in the coverage range where the putative “supersolid” behaviour was reported [42, 98]. This is evidenced by the behaviour of magnetic susceptibility and heat capacity. Furthermore, our observation of the spin–lattice relaxation time divergence shows beyond any doubt the significance of the $7/12$ commensurate phase, after decades of uncertainty, as the effect was observed only at that particular coverage. It seems that the observed localisation of the $^3$He impuritons is partially allowed by the special properties of the commensurate structure and partially by the physics of the impuritons themselves, mainly a long range interaction coming from a different zero point motion compared to the host $^4$He. A minimum concentration of impuritons is needed for the $T_1$ divergence to take place, this is in accordance with the localisation observed in bulk [152, 118, 117]. We believe this might be the manifestation of many-body localisation (MBL) [147, 146, 149, 150]. This system features both pseudo-random potential, coming from inequivalent sites in the $7/12$ structure, and interaction among the impuritons. With regards to the $T_1$ divergence observation, two issues should be addressed. Primarily, the heterogeneity of the system, captured in the existence of very differently relaxing components, should be explained. Secondarily, we believe the MBL phenomenon is manifested in the thermally activated divergence, while the Korringa type relaxation mechanism (which is active only at the lowest temperatures) is most likely less fundamental and might even originate from the graphite substrate. Thus of interest would be to study the system on a different substrate, supposing the $7/12$ commensurate structure still forms.

Two papers presenting the observations on the He film are currently be-
ing written. The first one gives the evidences that the coverage region, where
the torsional oscillator detects large mass decoupling, is solid. The second one
presents the observation of the $T_1$ divergence within the framework of possible
many body localisation.

YbRh$_2$Si$_2$ heat capacity results, and conclusions drawn from them, provide
a lot of new information about an already highly studied system, mostly due to
unprecedentedly low achieved temperatures and highly accurate thermometry.
To summarise, the Néel order established at 70 mK is not the true zero field
ground state of the system, a new state establishes below $T_A \approx 1.5$ mK. The
state features spatial modulation of the magnetic order parameter and the most
straightforward conclusion is that it is a spin density wave (SDW). We do not
rule out the possibility that the magnetic orders $T_N$ and $T_A$ coexist. Potentially
very interesting possibility would be if both orders were spatially modulated
with the same $q$-vector. The SDW state below $T_A$ is very likely superconducting
in small magnetic fields. Spatially modulated orders, like charge density waves
(CDW), pair density waves (PDW), and SDW, are a subject of high scientific
interest, among other reasons, due to their discovery in high temperature super-
conductors. It is possible that superconductivity and magnetism are intertwined;
if the superconducting order parameter is odd-parity it opens up a potential for
a p-wave PDW state [218, 219]. However, the suppression of the SDW with field
does not track the suppression of superconductivity, as apparent in Figure 4.55.

This work can also have a vast influence on the understanding of quantum
criticality in YbRh$_2$Si$_2$, which is believed to be induced by magnetic field as the
tuning parameter [220, 221]. A natural question arises whether it even makes
sense that the suppression of the AFM order, establishing at 70 mK, could in-
duce quantum criticality, if there is another state arising at lower temperatures.
Additionally, we observe that the energy associated with estimated critical field
of the SDW state (36 mT) is consistent with the transition temperature $T_A$ in
zero field. This is not valid for the AFM state below $T_N$, where the character-
istic energy scale of the order destruction is much smaller than the transition
temperature $T_N$.

Our measurements dispute the conjecture made in [180, 222], that the low
temperature superconductivity can be accounted for by nuclear order induced
quantum criticality in which a hybrid electro-nuclear order suppresses the elec-
tronic AFM and allows superconductivity to emerge. The release of majority of
the Yb nuclear entropy in temperatures above 0.2 mK can only be explained by
significantly strong source of Zeeman splitting for the nuclei, hence the magnetic
moment must grow. Nothing about our observations suggest that the $T_A$ transi-
tion would primarily be a nuclear magnetic transition, induced by an exchange
interaction amongst the nuclei. The conjecture is then that it is a nuclear as-
isted electronic transition.

The calorimetry measurements are currently being summarised and a paper written. The publication of the transport measurements should closely follow closely. How the suppression of the SMO with field tracks the suppression of superconductivity is the subject of future work. Our heat capacity method should also be applied to the investigation of isotopically enriched samples. This includes potential nuclear spin ordering in $^{171}\text{Yb}$ and $^{173}\text{Yb}$, as well as investigations of heavy fermion quantum criticality in $^{174}\text{Yb}$, in the absence of nuclear magnetism. Although YbRh$_2$Si$_2$ is an important and highly studied canonical heavy fermion system, it is apparent that extending its study into the microkelvin regime through the development of new experimental techniques offers significant new insights into the role played by the nuclear magnetism, and through that into the interplay of magnetism and superconductivity.
List of Figures

2.1 Equilibrium vapour pressure of $^4$He and $^3$He above liquid vs. temperature. ........................................... 4
2.2 The phase diagram of the mixture of the two He isotopes. ....... 6
2.3 Sketch of a demagnetisation cryostat. .............................. 7
2.4 Entropy and heat capacity curves for the natural Cu in various magnetic fields. ............................................. 11
2.5 Photographs of the ND1 cryostat’s ultra low temperature part from top and bottom. ............................. 13
2.6 Thermometry options on ND1. ................................. 14
2.7 Calibration of a RuO$_2$ thermometer. .............................. 16
2.8 $^3$He melting curve. .............................................. 17
2.9 Calibration of the $^{13}$C thermometer. .......................... 20
2.10 Sketch of a current sensing noise thermometer (CSNT). ...... 22
2.11 Sketch of a magnetic flux noise thermometer (MFNT). ..... 22
2.12 Thermalisation curve of the cell noise thermometer for estimated heat leaks. ........................................... 24
2.13 Cell noise thermometer spectra at 200 mK and 200 $\mu$K. .... 25
2.14 Residuals distribution about the best fit model of the cell’s noise thermometer spectra at 200 mK and 200 $\mu$K. ................ 26
2.15 Histogram of the residuals of the cell’s noise thermometer spectra at 200 mK and 200 $\mu$K. ........................... 28
2.16 Graphical illustration of the spin orientation evolution in pulsed NMR. ......................................................... 30
2.17 Simulated exciting transmitter pulse and its FID. Fourier transforms of both signals. .............................. 32
2.18 The actual FID measured at 327 $\mu$K on He sample: 18.27 $^4$He + 0.74 $^3$He nm$^2$. .................................................. 32
2.19 Schematics of the dc-SQUID field to voltage transducer. ...... 34
2.20 Periodic $V - \Phi$ characteristics of the second stage of the PTB two-stage SQUID. $V$-$I$ characteristic of a SQUID for integer and half integer multiples of $\Phi_0$. ................................. 35
3.18 Saturation curves modelling. 92
3.19 Numerical integral of the Lévy stable distribution and the Lévy stable distribution. 96
3.20 Stretched exponentials with different stretching parameter $n$. 97
3.21 One minus Stieltjes transforms of Lévy stable distributions and the search for a universal point. 97
3.22 $T_1$ measurements and analyses by Gazizulin. 98
3.23 Isotherms of torsional oscillator, heat capacity and susceptibility as a function of total coverage. 100
3.24 Collapse of temperature dependence of the superfluid signal in torsional oscillator regions I and II. 101
3.25 Collapse of temperature dependence of the superfluid signal in torsional oscillator region A. 102
3.26 Collapse of temperature dependence of the superfluid signal in torsional oscillator region B. 102
3.27 Heat capacity measurements on the second layer of $^4$He on graphite. 104
3.28 Position and magnitude of the heat capacity peak according to the finite bandwidth model. 105
3.29 Heat capacity measurements near the vicinity of the commensurate phases with varying concentration of $^3$He. 105
3.30 Heat capacity measurements near the vicinity of the commensurate phases with varying concentration of $^3$He. 107
3.31 Summary map of NMR experiment studied samples. 108
3.32 Measured susceptibility of the first three samples. 109
3.33 Measured susceptibility of four samples in the coverage region where the TO detects largest mass decoupling, and slightly larger, close to the commensurate phases. 110
3.34 Power law fit of four samples close to the commensurate phases coverage with varying $^3$He coverage. 112
3.35 Dependence of the index on the $^3$He concentration in the second layer. 113
3.36 Power law fits of four samples with $^3$He coverage 0.51 nm$^{-2}$. 114
3.37 Dependence of the power magnitude on the total coverage of samples with 0.51 nm$^{-2}$ of $^3$He. 115
3.38 Measured susceptibility of five samples with 0.74 nm$^{-2}$ $^3$He coverage above the region of commensurate phases. 116
3.39 Measured susceptibility of the first sample after the third layer promotion. 117
3.40 Susceptibility in the $\chi T$ vs. $1/T$ coordinates of two subset of samples with 0.51 and 0.74 nm$^{-2}$ of $^3$He. 118
3.41 Fermi temperature according to the Free Fermi gas model at high temperatures. 119
3.42 Susceptibility in the $1/(\chi T)$ vs. $T$ coordinates of two different subsets of samples. 121
3.43 Susceptibility in the $1\chi T$ vs. $T$ coordinates of two different subsets of samples. 122
3.44 Solid fraction of samples which have a putative intercept of $\chi T$ axis at $T = 0$, calculated as the intercept divided by high temperature asymptote of the $\chi T$ vs. $T$ plots. 122
3.45 Field dependence of $T_2^*$ and calculated $T_2$ to $T_2^*$ correspondence. 126
3.46 $T_1^\dagger$ isotherms as a function of coverage. 127
3.47 $T_2^*$ isotherms as a function of coverage. 128
3.48 An example of the progressive saturation method measurement. 129
3.49 Fits of the saturation curves. 130
3.50 Temperature dependence of the two saturation curves fit parameters. 131
3.51 Collapsed saturation curves taken at different temperatures and with a different tipping angle. 132
3.52 Mutual relations of different discussed functions by Laplace and Stieltjes transform. 133
3.53 Collapsed saturation curves taken at different temperatures and with a different tipping angle and a line obtained as one minus the Stieltjes transform of the Lévy stable distribution. 134
3.54 Lévy stable distribution. 135
3.55 Temperature divided universal curve. Two component fit. 136
3.56 Temperature divided universal curve. Three component fit. 137
3.57 Full data set universal curve. Three component fit. 138
3.58 Saturation functions, and their agreement with the data, according to distribution functions found by the Monte Carlo approach. 141
3.59 Comparison of distribution functions obtained by different approaches for the low and high temperature universal curve. 141
3.60 Saturation function corresponding to the UPEN found distribution function. 142
3.61 Comparison of distribution functions obtained by different approaches for the global universal curve. 142
3.62 The temperature dependence of $T_1^\dagger$. 144
3.63 Temperature dependence of $T_2^*$ and $T_2$. 146
3.64 Frequency dependence of the saturation curves. 147
3.65 Field (Larmor frequency) dependence of $T_1^\dagger$. 148
3.66 Variation of $T_1$ and $T_2$ with motion in a typical 3D system. 151
3.67 A boundary between ergodic and MBL systems featuring a quantum critical point (QCP) according to Abanin. 152
3.68 Susceptibility of phosphorus doped silicon. 156
3.69 Temperature dependence of electron spin relaxation time $T_1$ in $^{28}$Si:P. .......................................................... 157

4.1 Phase diagram of CePd$_2$Si$_2$, where superconductivity emerges around the quantum critical point. ................................. 159

4.2 Characteristic signatures of Kondo effect in resistivity, magnetic susceptibility, and specific heat. .................................................. 160

4.3 The RKKY interaction oscillating from ferromagnetic to antiferromagnetic action as we move away from the magnetic moment. 161

4.4 Doniach model illustrating the competition between the Kondo effect and the RKKY interaction. ............................................. 162

4.5 Kadowaki–Woods ratio for heavy fermions. ................................ 163

4.6 Crystal structure of YbRh$_2$Si$_2$. ........................................... 164

4.7 Magnetic susceptibility and magnetisation of YbRh$_2$Si$_2$ in the ab-plane. ................................................................. 166

4.8 Magnetisation of YbRh$_2$Si$_2$ in low fields. ................................ 167

4.9 Zero field resistivity of YbRh$_2$Si$_2$ measured by Custers. .......... 168

4.10 Transport phase diagram of YbRh$_2$Si$_2$ for fields in the ab-plane and along the c-axis. ....................................................... 169

4.11 Electronic specific heat of YbRh$_2$Si$_2$ in fields up to 1 T applied along the c-axis. ........................................................... 170

4.12 Electronic specific heat of YbRh$_2$Si$_2$ in fields up to 60 mT applied perpendicular to the c-axis. ............................................. 170

4.13 Low temperature heat capacity of YbRh$_2$Si$_2$ by Schuberth. ... 171

4.14 Low temperature and applied field (in the ab-plane) phase diagram of YbRh$_2$Si$_2$. ............................................................ 172

4.15 Single ion energy levels. .......................................................... 177

4.16 Heat capacity at saturated vapour pressure of liquid $^4$He near the lambda point. .............................................................. 179

4.17 Specific heat vs. the reduced temperature of nearly Heisenberg ferromagnet Eu$_{0.95}$Sr$_{0.05}$S. .............................................. 179

4.18 Modelling of the critical phenomena for various models. ......... 180

4.19 A temperature–field map of used methods to measure the heat capacity. ................................................................. 181

4.20 Typical heat pulses and temperature drifts at the lowest achieved temperature of 175 $\mu$K. .............................................. 183

4.21 Extraction of the heat capacity from a continuous warmup measurement. ................................................................. 184

4.22 Relaxation of overheated electrons to nuclear degrees of freedom. 185

4.23 Typical heat pulses and temperature relaxation in the relaxation regime. ................................................................. 186

4.24 Typical heat pulses and temperature drifts in the pseudo-adiabatic regime. ................................................................. 187
4.25 Heat capacity data taken at zero magnetic field. 190
4.26 Heat capacity data taken at 14.7 mT. 190
4.27 Heat capacity data taken at magnetic field up to 25 mT. 191
4.28 Heat capacity data taken at higher magnetic field which do not display any anomaly. 191
4.29 Low field heat capacity data as C/T vs. T below 2 mK and in lin-lin coordinates. 192
4.30 Entropy curves determined from the heat capacity measurements as a rolling integral, subtracted from the full entropy of $^{171}$Yb and $^{173}$Yb nuclei. 195
4.31 Zero applied field heat capacity data. Fitting done in the temperature range 1.8–20 mK by a pure quadrupole plus heavy fermion formula. 197
4.32 Deviations from the fit show in Figure 4.31 expressed as measurements minus the model, scaled by the model. 198
4.33 Heat capacity of low field measurements presenting the sharp peak. 199
4.34 Low field measurements with their fits on a common graph in logarithmic axes. 200
4.35 Colour maps studying the stability of the single ion model with measurements at high fields. 201
4.36 High field measurements with their fits on a common graph in logarithmic axes. 202
4.37 Heat capacity measurements at high fields not showing any heat capacity anomaly in the form of a sharp peak. 203
4.38 Energy levels changes with applied field. 204
4.39 Applied magnetic field in the ab-plane and resulting magnetic field on the nuclei. 205
4.40 Single ion fit below the anomaly (0-1.4 mK) with a uniform magnetic field. 206
4.41 Spin density wave based fits at temperatures below the $T_A$ anomaly. 208
4.42 Modified spin density wave + gap model fit at temperatures below the $T_A$ anomaly for two applied fields. 210
4.43 Measurements at three chosen fields with their best fits in C/T vs. T coordinates. 211
4.44 Excess to the heat capacity models above and below the anomaly $T_A$ given by the quadrupolar plus heavy fermion model and the pure spin density wave model respectively. 212
4.45 The Néel point heat capacity peak at 70 mK in zero magnetic field. 213
4.46 Measured heat capacity at the Néel point at 70 mK in zero magnetic field with subtracted appropriate models below and above $T_N$. Data are fitted with three theoretical models. 214
4.47 Continuous warm-up crossings of the anomaly in YbRh$_2$Si$_2$ (field 0.1 mT) in different speeds realized by different power applied in the heater. 215

4.48 Comparison of measurements at 0.1 mT by continuous warm-up and pulse method at 0.0 mT. 216

4.49 Critical phenomena fits to the low temperature anomaly $T_A$. 217

4.50 Heat capacity measurements at zero magnetic field and 8.4 mT compared to transport measurements at 0, 8.2 and 8.6 mT. 219

4.51 Low temperature heat capacity anomaly $T_A$ position with comparison to susceptibility peak position. 220

4.52 Comparison of the adiabatic and relaxation methods on the same experimental field. 221

4.53 Heat capacity measurements at a given field when temperature is stable. 222

4.54 The zero field heat capacity data of YRS compared to the estimated heat capacity of other constructional parts in the cell. 223

4.55 Low temperature, and field applied in the ab-plane, phase diagram of YbRh$_2$Si$_2$. 225
List of Tables

2.1

Parameters of the two noise thermometers on ND1. . . . . . . . .

2.2

Summarised parameters of a traditional TSTO and parameters

24

for proposed “light head” torsion oscillator. . . . . . . . . . . . .

55

3.1

Properties of the available expholiated graphites. . . . . . . . . .

65

3.2

Landau Fermi liquid framework renormalisation of Fermi gas properties. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .

3.3

Low temperature susceptibility of the ideal Fermi gas, as determined in our NMR cell in several past runs. . . . . . . . . . . . .

3.4

71
90

Parameters of heat capacity peaks of two measured samples and
implications within the finite bandwidth model. . . . . . . . . . . 106

3.5

Results of the power law fitting in χT vs. T and 1/(χT ) vs. 1/T
coordinates. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 112

3.6

Results of the power law fitting in χT vs. T and 1/(χT ) vs. 1/T
coordinates. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 115

3.7

Fit parameters of the two components and quality of the fit as
normalised χ2 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 117

3.8

Fitting parameters of the saturation curves. . . . . . . . . . . . . 131

3.9

Results of the thermal activation process and Korringa type of
relaxation fit. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 144

3.10 Frequency dependence, fitting parameters results. . . . . . . . . . 147
4.1

Isotopes of Yb, Rh and Si. . . . . . . . . . . . . . . . . . . . . . . 165

4.2

Zero field fit parameters results, their uncertainty and comparison
to received values from literature. . . . . . . . . . . . . . . . . . . 197

4.3

Low field measurements only fit parameter: the magnetic field on
the nuclei, and its uncertainty. . . . . . . . . . . . . . . . . . . . 200

4.4

High field measurements fit parameter: the magnetic field on the
nuclei and its uncertainty. . . . . . . . . . . . . . . . . . . . . . . 203

4.5

Results of the SDW + gap model. . . . . . . . . . . . . . . . . . 207

4.6

Results of the field modified spin density wave + gap model at
two applied fields.

. . . . . . . . . . . . . . . . . . . . . . . . . . 209
236


4.7 Fittings of the Néel transition at 70 mK according to the Ising 
and Heisenberg model and logarithmic divergence. . . . . 214
4.8 Fittings of the low temperature anomaly at 1.48 mK according to 
the Ising and Heisenberg model and logarithmic divergence. . . 218
Bibliography


[56] ZXY, A product of GrafTech International Advanced Electronics Technology, 11709 Madison Ave. Lakewood, OH 44107 USA, formerly UCAR.

[57] Grafoil, A product of GrafTech International Advanced Electronics Technology, 11709 Madison Ave. Lakewood, OH 44107 USA, formerly UCAR.


[130] R. R. Gazizulin, A. V. Klochkov, V. V. Kuzmin, K. R. Safiullin, M. S. Tagirov, and A. N. Yudin. $^3$He NMR in porous media: Inverse Laplace transformation. 2010.


B. Cowan. Private communication.


251


[190] L. V. Levitin et al. Multiple superconducting transport regimes in heavy fermion metal YbRh$_2$Si$_2$. in preparation.


255


