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THE SOLUBILITY OF $^4$HE IN LIQUID $^3$HE IN THE FERMI LIQUID REGION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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* * * * *

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1998

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ABSTRACT

We have measured the solubility of $^4$He in liquid $^3$He down to about 40 mK and pressures from $P = 0$ up to $\sim 24$ atm. Two parallel plate capacitors, identical in construction but with different gaps, measured the thickness of the superfluid $^4$He film in contact with unsaturated dilute mixtures of $^4$He in $^3$He. The cell was closed by a hydraulically operated cold valve, so that, for each mixture, the total amount of $^4$He and $^3$He in the cell was conserved. By measuring the film thickness, hence the amount of $^4$He in the film, we deduced the $^4$He concentration in the bulk $X^b_t$. From $X^b_t$, Henry's law was used to find the solubility $X^s_t$.

By fitting the solubility to Fermi liquid theory, we obtained the parameters $m^*_t$ and $\Delta$ as a function of pressure. Here, $m^*_t$ is the effective mass and $\Delta$ the difference in binding energy of $^4$He in $^3$He and in $^3$He. The difference in binding energy has a minimum at around 10 atm. The average of the results for $m^*_t$ at different pressures, is $(1.29 \pm 0.21)m_4$. The partial volume of $^4$He in $^3$He, $v^*_t$, was obtained by taking the derivative of $\Delta$ with respect to pressure. With $m^*_t$, it was used to predict the diffusion coefficient $D$. Measurements of $D$ at 50 to 100 mK using the same apparatus, the subject of Todd Culman's thesis, agree well with the theory.

A pre-wetting transition, in the $^4$He film in contact with the $^3$He, was observed at 24 atm.
Dedicated to grandmother
ACKNOWLEDGMENTS

I find myself fortunate in being able to work in the Ultra Low Temperature Lab under the guidance of Prof. David Edwards. Through his extraordinary ability in reducing a complex matter into simple terms, for example, Prof. Edwards demonstrated to me, daily, how a real physicist thinks. Indeed, I am very thankful.

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Dr. Todd Culman came to the lab with me the same time, and we have been working hand in hand for the past years. I learned a lot from his hardworking attitude, his persistence and disciplineness. Dr. Hannan Baddar inspired me with her enthusiasm in physics, and, in life. Her countless helps and advice really helped the progress of our project. I will always remember her. May she be blessed. I also like to thank Mr. Hans Hjort for all the works done together and helps he gave during all phases of the project, including helping me writing up my thesis. Dr. Siddartha Mukherjee is a constant source for solving computer related problems. Many interesting discussions about the project is also very beneficial.

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CHAPTER 1

INTRODUCTION

1.1 Historical background

The phenomena of mixing and phase separation is one of the most fascinating subject of physics and of most fundamental importance. The mixing of liquid $^3$He and $^4$He at low temperatures is even more interesting, for the following reasons: 1) The isotopes of $^3$He and $^4$He are two substances that represent the two most fundamental behaviors of quantum statistics, Fermi statistics and Bose statistics. The $^3$He is a fermion with a spin of one-half, and the $^4$He is a boson with spin zero. Both liquids, in their pure forms, manifest macroscopic quantum effects through superfluid transition at very low temperatures. The mixing of these two liquids promises an even richer system for studying quantum phenomena. 2) Because of their closed electron s-shell structure, the minimum in the interatomic potential is very shallow (about 9 K). At large distances, the interaction is the van der Waals force. Overall, the interaction has a simple spherical symmetry and is one of the most accurately known intermolecular potentials[20]. 3) Helium is the only element that remains liquid at $T = 0$. This is due to the large zero point energy which is comparable to the minimum in the interatomic potential. Because other substances freeze out of liquid helium at very low temperatures, liquid helium samples are naturally pure of impurities.

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Fig. 1.1 shows the phase diagram of liquid $^3$He-$^4$He mixture at the saturated vapor pressure. The two isotopes mix completely at high temperatures. At low temperatures, they separate into a lower $^4$He-rich phase and an upper $^3$He-rich phase. Up to 6.4% of $^3$He can dissolve in the lower phase at $T = 0$\cite{21}. This is because $^3$He is more strongly bounded to pure $^4$He than to pure $^3$He. There are extensive studies of dilute $^3$He-$^4$He mixtures. Please refer to reference\cite{22} for a review about the thermodynamic properties of dilute $^3$He-$^4$He mixtures.
Figure 1.2: Early $^4$He solubility measurements before 1973, down to $\sim 0.2$ K.
For the $^3$He-rich side of the phase diagram, various experiments indicate that the solubility of $^4$He goes to zero exponentially as $T$ goes to zero\cite{23,16,17,15}. Fig.1.2 shows their results. The solubility vanishes because the difference in binding energy of $^4$He in $^4$He and in $^3$He, $\Delta = L_4 - E_4$, is positive. Here $L_4$ is the binding energy of pure $^4$He (at $P = 0$, the latent heat at $T = 0$), and $E_4$ is the binding energy of $^4$He in $^3$He. The value of $\Delta$ was found to be 0.71 K by Edwards and Daunt, with $m_4^*$, the effective mass of $^4$He in liquid $^3$He, equal to 5.3 times of the bare mass $m_4$\cite{4}. Later, Saam and Laheurte, by fitting more recent solubility measurements made at lower temperatures, found $\Delta = 0.56$ K and $m_4^*/m_4 = 4.5$\cite{3}. The underlying theory the above authors used to analyze the data was first proposed by Zharkov and Silin\cite{24} based on Landau's Fermi liquid theory. However, Fermi liquid theory is only valid for liquid $^3$He at temperatures less than 0.1 K. The lowest temperature of the data shown in Fig.1.2 is $\sim 0.2$ K. Because of the exceedingly small solubility, measurements at lower temperatures are very difficult.

Nakamura, Fujii, Shigi, and Nagao were the first group to measure the $^4$He solubility in the Fermi liquid region, below 0.1 K\cite{1}. Their data, which were measured at the saturated vapor pressure, were analyzed by Edwards et al.\cite{12}. They found $\Delta = (0.21 + 0.03/ - 0.01)$ K and $m_4^*/m_4 = (1.1 + 0.4/ - 0.1)$.

In studying the properties of the mixture, we published a paper\cite{25} which shows that the diffusion coefficient, $D$, of $^4$He in $^3$He can be predicted from Fermi liquid theory. The predicted $D$ is inversely proportion to $T$ and the value of $DT$ depends only on the thermodynamic data, namely the effective mass $m_4^*$ and the partial volume $\nu_4^*$. These can be found by measuring the solubility at different pressures\cite{25}. Since
Figure 1.3: Log-log plot of the first solubility measurement in the Fermi liquid region. The • and ■ are data by Nakamura et al[1]. The ▽ are data by Laheurte[2] at higher temperatures, included for comparison. The full curve is the fit by Saam and Laheurte[3]. The broken curve is the fit by Edwards and Daunt[4]. The shaded area is the Fermi liquid region where Fermi liquid theory can be successfully applied to pure liquid $^3$He.

The prediction is exact in the $T \to 0$ limit, a measurement of $D$, $m_i^*$, and $v_i^*$ allows a strict test of Fermi liquid theory.

We have constructed a cell to measure both the diffusion coefficient and $X_{i}^{\text{sat}}$, the solubility of $^4$He in liquid $^3$He. The measurements agree very well with the prediction of the theory. The measurements of $D$ are described in detail in Culman’s thesis [11]: here we concentrate on the solubility measurements which give $m_i^*$ and $\Delta$. 
1.2 Fermi liquid theory

Fermi liquid theory was originally developed by Landau to predict the properties of pure liquid $^3$He at low temperatures. In his theory, the liquid is composed of quasiparticles which have an energy spectrum resembling a Fermi gas. There is a one-to-one correspondence between particle and quasiparticle energy states. Just like $^3$He atoms, the quasiparticles obey Fermi statistics. The total number of quasiparticles is the same as the total number of the $^3$He atoms in the liquid. The energy of a quasiparticle is now a functional of the quasiparticle distribution function, due to the interaction between the particles,

$$\epsilon(\vec{p}_3) = -L_3 + \frac{p_3^2}{2m_3^*} + \int f(\vec{p}_3, \vec{p}_3') \delta n_{3\vec{p}} d\vec{p}_3'$$  \hspace{1cm} (1.1)

Here $L_3$ is the binding energy, equal to the latent heat at $T = 0$, $m_3^*$ is the effective mass of the $^3$He quasiparticles, $f(\vec{p}_3, \vec{p}_3')$ is the Landau $f$-function which describes the interaction between quasiparticles with momenta $\vec{p}_3$ and $\vec{p}_3'$, $\delta n_{3\vec{p}} = n_{3\vec{p}} - n_{3\vec{p}}^0$ is the difference between the $^3$He quasiparticle distribution function and the equilibrium distribution at $T = 0$.

Landau's Fermi liquid theory successfully predicted the thermodynamic properties of pure liquid $^3$He (in its normal state). For example, below 0.1 K the specific heat is linear in $T$ with a coefficient determined by $m_3^*$. Fermi liquid theory also finds extensive applications in many other systems, e.g., electrons in metals.

Zharkov and Silin developed a theory [24] for a dilute solution of $^4$He in liquid $^3$He based on Fermi liquid theory. In addition to the $^3$He quasiparticles in the mixture, the $^4$He are treated as quasiparticles that obey Bose statistics. Like the $^3$He quasiparticle
energy in Eq.\( (1.1) \), the energy spectrum of a \(^4\text{He} \) quasiparticle is,
\[
\epsilon(\vec{p}_4) = -E_4 + \frac{\vec{p}_4^2}{2m_4^*} + \int f^{34}(\vec{p}_4, \vec{p}_3)\delta n_{3\vec{p}}d\vec{p}_3 + \int f^{44}(\vec{p}_4, \vec{p}_4')n_{4\vec{p}}d\vec{p}_4' \tag{1.2}
\]
where \( E_4 \) is the binding energy of \(^4\text{He} \) in \(^3\text{He} \), \( f^{34} \) and \( f^{44} \) are the Landau \( f \) functions describing the \(^3\text{He}^-^-^4\text{He} \) and \(^4\text{He}^-^-^4\text{He} \) quasiparticle interactions, \( n_{4\vec{p}} \) is the \(^4\text{He} \) distribution function. Because of the \(^3\text{He} \) background, \(^4\text{He} \) quasiparticle has an effective mass of \( m_4^* \), which, according Leggett[26], can not be smaller than its bare mass.

The quantities \( E_4 \) and \( m_4^* \) and the Landau \( f \)-functions \( f^{34} \) and \( f^{44} \) depend on the \(^3\text{He} \) number density \( n_3 \) in the mixture. For a dilute solution of \(^4\text{He} \) in \(^3\text{He} \) at low temperatures, \( n_3 \) is determined by the pressure. For a more detailed account of the Fermi liquid theory of dilute \(^4\text{He} \) in \(^3\text{He} \), please refer to the references by Saam[27], Saam and Laheurte[3], and Edwards et al[12].

Based on Zharkov and Silin’s Fermi liquid theory, we can write the \(^4\text{He} \) chemical potential as approximately
\[
\mu_4 = -E_4 + k_BT\ln\left[ X_4 \left( \frac{T^*}{T} \right)^{3/2} \right] \tag{1.3}
\]
where \( T^* = \frac{2\pi\hbar}{\sqrt{3/m_4^*k_B}} \)[12]. In Eq.\( (1.3) \), we have neglected term due to the interaction with the \(^3\text{He} \) quasiparticles which is proportional to \( (T/T_F)^2 \)[12]. Here \( T_F = (3\pi n_3)^{2/3}\hbar^2/2m_3^* \approx 1.77 \) K is the Fermi temperature for pure liquid \(^3\text{He} \) with a density of \( n_3 \). Since the solubility of \(^4\text{He} \) in \(^3\text{He} \) is exceedingly small at low temperatures, we have also neglected the interactions between \(^4\text{He} \) themselves and treated \(^4\text{He} \) as a non-degenerate Boltzmann gas.

In the saturated, lower \(^4\text{He} \)-rich phase in contact with the upper \(^3\text{He} \)-rich phase, the chemical potential of \(^4\text{He} \) is[22],
\[
\mu_4^* = -L_4 - \pi_f v_4 - \pi_3^* v_4 \tag{1.4}
\]
Here \( \pi_f \) is the fountain pressure, \( \pi_3^s \) is the osmotic pressure of the saturated solution, and \( \upsilon_4 \) is the atomic volume of pure \(^4\)He. In our temperature range, we can neglect \( \pi_f \upsilon_4 \) completely, since it is due to phonon excitations with a temperature dependence of \( T^4 \).

When the upper and lower phase are in contact and in equilibrium, the \(^4\)He chemical potential is uniform throughout. By equating Eqs.(1.3) and (1.4), we find,

\[
X_i^{sat} = \left( \frac{T}{T^*} \right)^{3/2} \exp \left( -\frac{\Delta - \pi_3^s \upsilon_4}{k_B T} \right)
\]  

(1.5)

Eq.(1.5) is based on Fermi liquid theory. The validity of this equation also depends on the approximations that we made previously. The saturated concentration of \(^4\)He in \(^3\)He, \(X_i^{sat}\), from Eq.(1.5), is a function of temperature and the liquid \(^3\)He density, \(n_3\), where \(n_3\) itself is a function of \(T\) and \(P\). Based on Eq.(1.5), the pressure and temperature dependence of \(X_i^{sat}\) is determined by the two parameters, \(T^*\) (or \(m_i^*\)), and \(\Delta\), which are functions of \(n_3\). In order to find \(m_i^*\) and \(\Delta\), we measure \(X_i^{sat}(P,T)\) and fit it to Eq.(1.5) below 0.1 K.

1.3 The superfluid \(^4\)He-rich film and \(X_i^{sat}\)

The conventional way of measuring the solubility, by detecting the onset temperature of a bulk phase separation of \(^4\)He-rich phase, becomes exceedingly difficult as the temperature is lowered. This is because \(X_i^{sat}\) decreases exponentially with temperature. For example, at \(T = 50\) mK and \(P = 0\), \(X_i^{sat}\) is only \(\sim 2\) ppm. Since \(^4\)He occupies a smaller volume than \(^3\)He, it is preferentially attracted to the walls by the van der Waals force and a superfluid film forms at low temperatures, well above the bulk phase separation temperature (see the following subsection). In a closed cell,
depending on the surface to volume ratio, there might not be enough \(^4\)He to form a bulk \(^4\)He-rich phase even at \(T = 0\). All the \(^4\)He will form an unsaturated film.

In this section, we will discuss a way to determine \(X_{4}^{\text{sat}}\) by measuring the temperature dependence of the \(^4\)He-rich superfluid film.

### 1.3.1 The superfluid \(^4\)He-rich film

The existence of a \(^4\)He-rich superfluid film, covering the walls of a container of dilute \(^4\)He-\(^3\)He mixture at low temperatures, was first demonstrated at the Second International Conference on the Peaceful Uses of Atomic Energy in Geneva in 1958\[28\]. More systematic subsequent studies showed that the film exists even for unsaturated mixtures and its superfluid transition temperature is much higher than the bulk phase separation temperature\[23\][29].

Because of the van der Waals potential, the concentration \(X_4\) and the pressure \(P\) increase towards the walls. At the interface of the film, \(X_4 = X_{4}^{\text{sat}}(P^*)\). Here we assume that our film is thick enough that it has the same thermodynamic properties as the bulk phase, but under the local pressure and potential. Note that the local pressure at the interface, \(P^*\), is always larger than the applied pressure, \(P\). This is due to the van der Waals attraction from the walls to the \(^3\)He liquid on top of the \(^4\)He film. The attraction applies additional force to the film.

Below a certain critical thickness, the film is not superfluid. The film becomes superfluid only after additional \(^4\)He is added. The change in the two dimensional superfluid density is then found to be proportional to the additional amount of \(^4\)He added\[30\]. The non-superfluid layer is usually referred to as the inert layer. Since we need to know the amount of \(^4\)He in the film for our analysis, as explained in chapter
3. we need to know the properties of this inert layer. Culman's thesis contains a nice summary on this subject[11].

The saturated $^4\text{He}$ concentration $X_4^{sat}(P^s)$ at the interface can be related to $X_4^b$, the concentration in the bulk liquid, by using Henry's Law. The relationship depends on the van der Waals potential $V(D^s)$ at the top of the film of thickness $D^s$ and the thermodynamic properties of the liquid, which are known functions of $P$ and $T$. The potential $V(D^s)$ was determined in a separate experiment where $^3\text{He}$ films, in equilibrium with their vapor, were measured.

1.3.2 Henry's Law and $X_4^{sat}/X_4^b$

Henry's law states that the partial vapor pressure of a dilute solute is proportional to the concentration, $X$. This is because, when $X \rightarrow 0$, the solute atoms are moving independently without interacting or "seeing" each other. Each atom stays a fixed proportion of time in the vapor and in the liquid solvent. Consequently, the number density, $1/v_X$, or the partial vapor pressure, $P_X = RT/v_X$, is proportional to $X$ in the liquid. Here, $R$ is the gas constant. When the liquid is in equilibrium with the vapor, the chemical potential of the solute in the liquid, $\mu_L$, is equal to that in the vapor, $\mu_V$. At constant $T$ and $P$, with $P > P_X$, for a given change of $\delta X$,

$$\delta \mu_V = v_X \delta P_X$$
$$= \frac{k_B T}{P_X} \delta P_X$$

(1.6)

Here we are treating the solute atoms in the vapor as ideal gas.
Because $\delta \mu_V = \delta \mu_L$, from Eq.(1.6) we get,

$$
\left( \frac{\partial \mu_L}{\partial X} \right)_{P,T} = \frac{k_B T}{X}
$$

(1.7)

This is the Henry's Law, which is valid in the limit of $X \to 0$.

In our system, a dilute $^4$He-$^3$He liquid mixture, the pressure and $^4$He concentration $X_4$ are not uniform due to the van der Waals field. However, in equilibrium, the temperature and chemical potential $\mu_3$ and $\mu_4$ are uniform. Therefore, the difference in $\mu_4$ between two adjacent positions in the van der Waals field, is zero.

$$
d\mu_4 = \frac{k_B T}{X_4} dX_4 + v'_4 dP + dV(D) = 0
$$

(1.8)

where $v'_4$ is the partial atomic volume of $^4$He in the mixture, and $D$ is the distance from the substrate.

Because of mechanical balance in the mixture, we have,

$$
vdP + dV(D) = 0
$$

(1.9)

This can also be derived from the uniformity of $\mu_3$ and $\mu_4$.

By integrating Eq.(1.9) with respect to $P$, from inside the bulk to the top of the film, we get:

$$
\int_P^{P^s} v dP = -V(D^s)
$$

(1.10)

Eq.(1.10) determines the pressure at the film interface, $P^s$, when the applied pressure is $P$ and the film thickness is $D^s$.

By substituting $V(D)$ in Eq.(1.8) with Eq.(1.9) and integrating it from $P$ to $P^s$, $X_4^{sat}(P^s)$ is related to the $^4$He concentration in the bulk $X_4^b$.

$$
k_B T \ln \frac{X_4^{sat}(P^s)}{X_4^b} = \int_P^{P^s} (\mu_3 - v'_4) dP
$$

(1.11)
Here, we approximate the atomic volume of the $^3\text{He}$-rich mixture by $v_3$, the atomic volume of pure $^3\text{He}$, because the $^4\text{He}$ concentration is exceedingly small.

![Graph](image)

Figure 1.4: The fractional excess volume vs the pressure, reproduced from reference [5] (except the • point). The O are the data points measured at higher temperatures. The • is a value of $\alpha_4$ based on a measurement by Sato and Suzuki[6]. The solid curve is a fit to the data. The broken curve is $\alpha_4$ at $T = 0$, calculated by Laheurte from his phase separation data.

In order to find $X_4^{sat}$ from Eq.(1.11), we have to know $v_4^*$. Sato and Suzuki, in their $^4\text{He}$-$^3\text{He}$ interfacial tension experiment[6], have measured the density of $^4\text{He}$-$^3\text{He}$ mixtures with $^4\text{He}$ concentration of 2.5% and 5.2%. Their mixtures were under saturated vapor pressure and the temperature range was from about 3 K to 0.3 K.
An extrapolation to \( T = 0 \) of their data gives \( \alpha_4 = -0.300 \pm 0.015 \). Here \( \alpha_4(P) \) is defined by,

\[
\alpha_4 = \frac{v_4^* (P)}{v_3 (P)} - 1
\]  

Laheurte determined \( \alpha_4 \) as a function of pressure, up to 15 atm. by measuring the density variation in the same cell for both \(^3\)He and a mixture with \( \chi_4 = 14.8\% \) at \( T = 1.2 \) \( \text{K} \)[5]. His results for \( \alpha_4 \) at 1.2 K are shown as circles in Fig.1.4. Laheurte also calculated \( \alpha_4 \) at \( T = 0 \) from his measurements for \( T > 0.25 \) K. This is shown as the dashed line.

If \( P^s \) is close enough to \( P \), so that \( v_3 \) can be treated as a constant, Eq.(1.10) can be approximated as,

\[
-V(D^s) = \int_{P^s}^{P} v_3 dP \\
\approx (P^s - P) v_3
\]

Similarly, with Eq.(1.12) we can approximate Eq.(1.11) as,

\[
\ln \left( \frac{X_4^{\text{sat}}(P^s)}{X_4^p} \right) = \int_{P}^{P^s} \frac{(v_3 - v_4^*) dP}{k_B T} \\
\approx -\frac{(P^s - P) v_3 \alpha_4}{k_B T} \\
= -\frac{\alpha_4 V(D^s)}{k_B T}
\]

For an example, based on measurements from our No.1 sample, the film thickness is \( \sim 60 \) Å (from the gold surface) at 50 mK and \( P = 0 \). This corresponds to a van der Waals potential of \( -V(D^s)/k_B \approx 0.014 \) K and \( P^s \approx 0.03 \) atm. If we use
\[ \alpha_4 = -0.300 \text{ at } P = 0, \] we get \( X_4^{sat}/X_4^b \simeq 1.09, \) a very small correction compared to the experimental errors in determining \( X_4^b. \)

The corrections at higher temperature with thinner films are much larger. In fact, based on the measurement by Nakamura et al [1], the solubility is about 500 ppm at \( T = 0.1 \) K. For our No.1 sample, which has a bulk concentration of \( \sim 16 \) ppm, assuming most of the \(^4\text{He}\) has dissolved in the bulk at 0.1 K, this corresponds to a correction ratio \( X_4^{sat}/X_4^b \) of \( \sim 30. \) Thus our method has large errors at higher temperatures.

The errors in \( X_4^{sat} \) are also large at very low temperatures. For example, \( X_4^{sat} \) is predicted to be \( \sim 0.01 \) ppm at 30 mK, based on our data analysis. This requires a corresponding capacitance ratio signal change of about \( 0.001 \) ppm, clearly beyond the resolution of our setup.

### 1.3.3 Finding \( X_4^{sat}/X_4^b \) based on Fermi liquid theory

In the previous section, we derived the ratio \( X_4^{sat}(P^s)/X_4^b \) based on Henry's Law. The result is model independent and is valid as long as the concentration is low. However, it does require knowledge of \( \alpha_4. \) We also need to correct for the difference between \( P \) and \( P^s. \)

In this section, we are going to derive a relationship between \( X_4^b \) and \( X_4^{sat}(P) \) by using Fermi liquid theory. As a result, we do not need \( \alpha_4 \) for the analysis. The correction from \( P^s \) to \( P \) is also avoided. However, using this relationship means that our solubility results depend on the validity of Fermi liquid theory. However, this does not reduce the rigor of our claim of a strict test of Fermi liquid theory below 0.1 K. Instead of first measuring \( X_4^{sat} \) and then trying to fit the data with Eq.(1.5) to
find $\Delta(P)$ and $m_4^*(P)$, we use the Fermi liquid theory directly in the data analysis. Above 0.1 K, outside the Fermi liquid region, our method of correcting $X_4^{sat}$ is only approximate. However, as we already demonstrated, the corrections have already very large errors at high temperatures, due to the large corrections ratio of $X_4^{sat}/X_4^b$.

We start with equating the chemical potentials of $^4$He in the mixture and in the film. Based on Eqs.(1.3, 1.4), with $X_4 = X_4^b$ and including the Van der Waals potential, we get,

$$-E_4(P) + k_B T \ln \left( \frac{T^*(P)}{T} \right)^{\frac{3}{2}} X_4^b = V(D^*) - L_4(P^*) - \pi^{sat} v_4(P^*)$$  \hspace{1cm} (1.15)

Also

$$L_4(P^*) = L_4(P) - \int_P^{P^*} v_4 dP$$  \hspace{1cm} (1.16)

Therefore

$$X_4^b = \left( \frac{T}{T^*(P)} \right)^{3/2} \exp \left[ - \frac{L_4(P) - E_{43}(P) + \pi^{sat} v_4(P^*)}{k_B T} \right] \exp \left( - \int_P^{P^*} \frac{v_3 - v_4}{k_B T} dP \right)$$  \hspace{1cm} (1.17)

With Eq.(1.5),

$$X_4^{sat}(P) = X_4^b \exp \left( \int_P^{P^*} \frac{v_3 - v_4}{k_B T} dP \right) \exp \left( \frac{\pi^{sat} v_1(P^*) - \pi^{sat} v_1(P)}{k_B T} \right)$$  \hspace{1cm} (1.18)

### 1.4 Outline of the thesis

Section 1.5 is a transcript of a paper that gives a general description of the setup and the methods of our experiment. Some brief theoretical background is also presented.

Chapter 2 explains the construction of the capacitors, the structure of the cell, the layout of the experiments. Also explained is the calibration of the thermometers and the pressure gage.
Chapter 3 describes how the film thickness is obtained by measuring the capacitance ratio. We discuss the problem of capillary condensation in tiny cracks inside the cell. We construct a model to account for the $^4\text{He}$ in the cracks. We show that the effect of the capillary condensation is almost negligible for the sample with lowest overall concentration.

The van der Waals potential plays a very important role in our data analysis, especially for thin films at higher temperatures. We describe measurements of two $^3\text{He}-^4\text{He}$ films in contact with their vapor. The analysis of these experiments gives us the van der Waals potential and the surface area of the cell.

The last part of Chapter 3 explains how we fitted the solubility data to Fermi liquid theory.

Chapter 4 presents all the capacitance ratio data, for four samples with different concentrations at various pressures. The two higher concentration samples were used to find information about capillary condensation. The first two samples with lower concentrations were fitted to Fermi liquid theory to find $m^*$ and $\Delta$. In the process, we also found the solubility as a function of pressure. Our results indicate that the solubility of $^4\text{He}$ in liquid $^3\text{He}$ is zero at $T = 0$ for any pressure.

The last chapter, Chapter 5, gives a conclusion to our experiments on the solubility of $^4\text{He}$ in $^3\text{He}$. The chapter also includes a transcript of a paper that has been accepted for publication by \textit{Physical Review Letters}. The paper gives an overall summary of the project which also includes the measurement of diffusion coefficient.
An Experiment to Measure the Diffusion of $^4$He in $^3$He in the Fermi Liquid Region (J. Low Temp. Phys. 101, 167 (1995))

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The diffusion coefficient $D$ and the thermal diffusion factor $\gamma_T$, for $^4$He in liquid $^3$He at low temperatures $T$, have recently been calculated by solving the Boltzmann equation derived from Fermi-liquid theory. As $T \rightarrow 0$, $\gamma_T$ approaches a constant and $D$ varies as $1/T$. Both transport coefficients are determined solely by $q^3_0$, the $\ell = 0$ forward scattering amplitude. Because $q^3_0$ can be found from thermodynamic data, e.g. the solubility of $^3$He in liquid $^3$He, $X^{sat}_4$, a strict test of the theory is possible. We have built an apparatus to measure $D$ and $X^{sat}_4$ as functions of pressure and temperature. The ratio of the capacitances of two parallel plate capacitors measures the number of $^4$He atoms diffusing out of the liquid into the superfluid film. A bellows initiates the diffusion by changing the pressure in the liquid and thus the equilibrium concentration. A change of $\sim 10^{-8}$ in the $^4$He concentration can be detected.

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1.5.1 Introduction

Extensive experimental efforts have shown that Landau's Fermi liquid theory gives an accurate picture of normal liquid $^3$He below 0.1 K[31]. By adding a small amount of $^4$He to liquid $^3$He, we have a probe to extract additional information. Zharkov and Silin [24] first applied Fermi liquid theory to this system. In their picture, the $^4$He impurity acts as a gas of quasiparticles which interact with the $^3$He quasiparticles. However, since the binding of a $^4$He atom in $^4$He is stronger than that of a $^4$He in $^3$He, the solubility of $^4$He in liquid $^3$He at zero pressure tends to zero exponentially with decreasing temperature [4, 23, 3, 5, 1]. At 0.1 K, above which the Fermi liquid
theory is not valid, the saturated concentration is only \( \sim 300 \text{ ppm} \). At 50 mK it is predicted to be \( \sim 17 \text{ ppm} \). This creates a certain challenge for experimentalists.

Measurements of the solubility of \(^4\text{He}\) in liquid \(^3\text{He}\) provide information about the thermodynamic properties of the system. The binding energy of \(^4\text{He}\) in \(^3\text{He}\), \(E_{43}\), and the \(^4\text{He}\) quasiparticle mass, \(m_4^*\), can be determined from the solubility curve. The appropriate formulas are given in Refs. 3, 5 and 8. At low temperatures the theoretical form of the saturated concentration \(X_4^{\text{sat}}\) simplifies to[12]:

\[
X_4^{\text{sat}} = \left( \frac{T}{T^*} \right)^{3/2} \exp \left( \frac{E_{43} - E_{44} - \pi_3^4 v_4}{k_B T} \right),
\]

where \(T^*\) is defined by \(k_B T^* = 2\pi \hbar^2/(m_4^* v_3^2)^{2/3}\). \(E_{44}\) is the binding energy of \(^4\text{He}\) in pure \(^4\text{He}\). \(v_4\) and \(v_3\) are the atomic volumes of the liquid \(^4\text{He}\) and \(^3\text{He}\) at \(T = 0\), and \(\pi_3^4\) is the osmotic pressure of a saturated solution of \(^3\text{He}\) in liquid \(^4\text{He}\). The value of \(\pi_3^4 v_4/k_B\) is small: \(\sim 7.5 \text{ mK at } P = 0\).[32]

By fitting the recent measurements of the solubility by Nakamura et al.[1] at 0.13 K and below, Edwards et al.[12] find

\[
m_4^*/m_4 = 1.1^{+0.4}_{-0.1}
\]

and

\[
(E_{44} - E_{43})/k_B = 0.21^{+0.03}_{-0.01} \text{ K}.
\]

These values at \(P = 0\) agree with recent microscopic calculations[14, 13], which give \(m_4^*/m_4 \approx 1.21\) and \((E_{44} - E_{43})/k_B \approx 0.19 \text{ K}\).

The diffusion coefficient \(D\) and the thermal diffusion factor \(\gamma_T\) for a dilute solution of \(^4\text{He}\) in \(^3\text{He}\) are defined by the equation for the impurity mass current in terms of the gradients of the \(^4\text{He}\) mass concentration, \(c = X_4 m_4/(X_4 m_4 + X_3 m_3)\), and of the
temperature[33]:

\[ i = -\rho c D \left[ \frac{\nabla c}{c} + \gamma T \frac{\nabla T}{T} \right]. \]  

(1.20)

Here \( \rho \) is the mass density of the mixture. When the total mass current \( \rho v \) is zero, \( i \) is simply the \(^4\text{He} \) mass current; otherwise the \(^4\text{He} \) current is \( \rho c v + i \) and the \(^3\text{He} \) current is \( (1 - c)\rho v - i \).

The theoretical study of the diffusion of \(^4\text{He} \) in liquid \(^3\text{He} \) originated with Zharkov and Silin[24]. They wrote the Boltzmann transport equations for the \(^3\text{He} \) and \(^4\text{He} \) quasiparticles, but found \( D \) independent of \( T \) due to an incorrect approximation in the collision integral. This was pointed out by Leggett and ter Haar [26] who showed that, as \( T \rightarrow 0 \), \( D \) should vary as \( 1/T \). Calculations of the product \( DT \) were made by Dandache et al. [34] and Geilikman and Chechetkin [35], again with simplifying assumptions about the collision integral. An exact solution to the Boltzmann transport equation as \( T \rightarrow 0 \) was found recently by Culman et al.[25]. Their results may be expressed as

\[ D = 0.4661 \frac{\hbar}{m_4} \frac{T_F}{m_3} \frac{m_4^*}{(1 + \alpha_4^0)^2} \]  

(1.21)

\[ \gamma T = 0.3823 \ldots, \]  

(1.22)

where \( m_3^* \) is the \(^3\text{He} \) quasiparticle effective mass. The \(^3\text{He} \) Fermi temperature is given by \( k_B T_F = p_F^2/2m_3^* \) and \( (1 + \alpha_4^0) v_3 \) is the partial volume at \( T = 0 \) of a \(^4\text{He} \) atom in liquid \(^3\text{He} \) of atomic volume \( v_3 \).

Equation (3) shows that \( D \) at low temperatures can be predicted from purely thermodynamic data. This is true because \( D \) is determined by \( a_{34}^{31} \), the \( l = 0 \) \(^3\text{He}^{-4}\text{He} \)
forward scattering amplitude. It was shown by Saam and Laheurte [36, 37] that:

\[ a_0^{34} = \left( 1 + \alpha_4^0 \right)/\nu(0), \]  

(1.23)

where \( \nu(0) = 3/(2 v_3 k_B T_F) \) is the density of states of pure \(^3\)He. From \( E_{43} \) we can derive \( \alpha_4^0 \):

\[ 1 + \alpha_4^0 = -\frac{1}{v_3} \frac{\partial E_{43}}{\partial P}. \]  

(1.24)

Thus a measurement of \( \gamma_T \), or \( DT \) and \( X_{4}^{\text{sat}} \), permits a strict quantitative test of the underlying Fermi-liquid theory. From this point of view, \(^4\)He in \(^3\)He is unique among applications of Fermi-liquid theory. For example, in pure \(^3\)He or in \(^3\)He in liquid \(^4\)He, assumptions about the dependence of the scattering amplitude on the momentum transfer are needed to relate the kinetic coefficients to the thermodynamic properties [31]. In contrast[25], for \(^4\)He in \(^3\)He, the momentum dependence appears only in terms of order \( T/T_F \), with \( T_F \approx 1.77 \) K at zero pressure.

The diffusion coefficient \( D \) at the freezing pressure of \(^4\)He-\(^3\)He mixtures was measured by Vvedenskii and Peshkov [19], between 0.5 K and 1.0 K, with mass concentrations between 10% and 40%. Since Fermi liquid theory only works at temperatures below 0.1 K, new experiments to measure \( D \) and \( \gamma_T \) below 0.1 K are needed. We have designed an experiment to measure the solubility \( X_{4}^{\text{sat}} \) and the diffusion coefficient \( D \) at low temperatures and various pressures. We intend to determine the thermodynamic properties \( E_{43}, \alpha_4^0, \) and \( m_4^* \) from the measurements of \( X_{4}^{\text{sat}} \). The theory embodied in Eqs. (3) and (5) can then be tested.

Data from the density measurements of Ref. 6 show that the partial volume of \(^4\)He in \(^3\)He, \( (1 + \alpha_4^0) v_3 \), is less than the atomic volume in pure \(^4\)He at pressures below about 11 atm. The data indicate that the difference in the \(^4\)He binding energy to \(^4\)He
and $^3$He, $E_{44} - E_{43}$, has a minimum at around this pressure[38]. Thus we expect to see enhanced solubility in this region.

In Ref. 8, it was pointed out that at least one experiment[39] (see also Kim et al.[40]) has been performed near $\approx 11$ atm, where the presence of a $^4$He film enhanced the superfluidity of a thin layer of $^3$He. However it is still possible that $^4$He is soluble in liquid $^3$He at $T = 0$ near this pressure. Geilikman and Chechetkin[35] have asserted that the equation for the effect of impurity scattering on the superfluid-B transition in Balian and Werthamer[41] may not apply to $^4$He quasiparticles. They suggest that the effect of $^4$He impurities is reduced by an additional factor of $(T/T_F)^2$.

1.5.2 Experimental

It is difficult to keep track of the $^4$He dissolved in the $^3$He because the solubility is so small. However, because of the van der Waals field, even in an unsaturated $^4$He-$^3$He mixture, a superfluid $^4$He-rich film coats the walls[42, 2]. In a mixture of low initial concentration all the $^4$He will reside in the film at $T = 0$. Following the method of Nakamura et al.[1], we use parallel plate capacitors to observe the thickness of the film. As the temperature or pressure rises, the amount of $^4$He dissolved in the $^3$He changes. This decreases the film thickness, enabling us to calculate the solubility. The analysis of this kind of data is described in Ref.[12]. When the pressure is suddenly changed, observing film thickness with time allows us to determine the diffusion coefficient.

To relate the film thickness to the solubility, the volume to area ratio, $\Omega$, must be known. If a solution of known concentration is in the cell, by observing the change in film thickness from $\approx 1$ K to very low temperatures, we could determine $\Omega$. However, for dilute solutions, we cannot be certain that the concentration of the mixture that
Figure 1.5: Schematic of experimental apparatus.
condenses in the cell is the same as the concentration at room temperature. We can, before filling the cell, however, measure $Q$ by admitting a small amount of pure $^3$He or $^4$He to the cell and closing the cold valve described below. Some of the helium adsorbs on the walls while the remainder is in the vapor phase. From observations of the helium film thickness as a function of temperature, we can determine $Q$.

Two capacitors were fabricated from optically flat sapphire disks 0.75 inches in diameter by 0.10 inches thick. Both capacitors are identical except for the size of the gaps, which are 6.7 $\mu$m and 16.8 $\mu$m. For each capacitor, circular active areas 0.55 inches in diameter were formed by evaporating a 2000 Å gold film onto the surfaces of two disks. Three small $\text{Al}_2\text{O}_3$ spacers were sputtered onto the outer edge of one of the disks. Silver epoxy was used to glue the two plates together and also to glue the leads to the electrodes.

The experimental cell, shown schematically in Fig. 1.5, and in a cut-away view in Fig. 1.6, is made of OFHC copper. It consists of two volumes separated by a BeCu bellows: the inner volume contains the dilute mixture of $^3$He in $^3$He and the outer volume contains liquid $^4$He to compress the mixture. All the surfaces inside the cell are gold plated. The capacitors are installed vertically in the cell with the wide gap capacitor sitting below the one with the narrow gap so that capillary condensation occurs in both capacitors at about the same degree of saturation. This may be useful in measuring the interfacial tension, as discussed at the end of the paper. A cap is placed on top of the capacitors to simplify the space inside the bellows where most of the diffusion takes place.

The cell is connected to a dilution refrigerator through a superconducting indium heat switch. Applying a pressure step to the mixture causes the equilibrium film
Figure 1.6: Simplified cut-away view of the cell.
thickness to change; this causes diffusion. The pressure step also causes the temperature of the liquid to change. By opening the heat switch, the cell is thermally isolated from the refrigerator and, apart from the small effect due to the heat capacity of the walls, we avoid causing temperature gradients in the sample. Thus we measure the effect of $D$ in Eq. (2). Alternatively, we can close the heat switch to study the effect of $\gamma_T$, the thermal diffusion factor. In this case, however, the thermal relaxation of the liquid will complicate the observations. A graph comparing the predicted diffusion coefficient, $D = (5.0 \times 10^{-4} \text{ K cm}^2/\text{s}) / T$ at $P = 0$, with the thermal diffusivity of liquid $^3\text{He}$, is included in Ref. 16.

A RuO$_2$ resistance thermometer[43] measures the temperature of the cell. The resistance ratio of the RuO$_2$ resistor to a reference metal film resistor is recorded using a ratio transformer bridge. The resistance thermometer is calibrated against a $^3\text{He}$ melting curve thermometer mounted on the mixing chamber plate.

A liquid $^4\text{He}$ activated hydraulic cold valve confines the mixture in the pressurized cell. It is similar to the valve of Roach et al. [44] but has a kel-F tip and stainless steel seat. The cell pressure is measured with a Straty-Adams strain gauge.

In principle, from one of the capacitances $C$, we can determine the thickness of the $^4\text{He}$-rich film, $D^s$,

$$C = C_0 / (1 - 2 \Delta \epsilon D^s / \epsilon^s d), \quad \text{(1.25)}$$

where $d$ is the capacitor gap, $C_0$ is the capacitance with no $^4\text{He}$ film but full of the liquid mixture, and $\Delta \epsilon = \epsilon^s - \epsilon \approx 0.015$ is the difference in the dielectric constants of the film and liquid. The second term in the parentheses is small compared to one, less than $\sim 5 \times 10^{-6}$. Since $\epsilon$ is a function of $T$, $P$ and $X_4$, $C_0$ also changes with $T$, $P$ and $X_4$. To avoid this complication, the ratio of two capacitances is measured using
Figure 1.7: Stability of the capacitance ratio reading overnight. The noise in the ratio transformer is about 10 parts per billion while the drift is about 4 ppb over 10 hours. The axis on the right shows the equivalent change in \(^4\)He film thickness. The noise corresponds to a change in the \(^4\)He concentration of about \(10^{-8}\).

A General Radio 1493 ratio transformer. To first order in the small parameter, the change in film thickness is given by

\[
\delta D^* = \frac{\varepsilon^*}{2 \Delta \varepsilon} \left( \frac{d_1^2}{d_2 - d_1} \right) \delta \left( \frac{C_1}{C_2} \right) \approx (7.5 \times 10^5 \text{ Å}) \delta \left( \frac{C_1}{C_2} \right). \tag{1.26}
\]

where \(d_1\), \(d_2\), \(C_1\) and \(C_2\) are the gaps and capacitances of the two capacitors, and \(\delta (C_1/C_2)\) is the change in the ratio of the narrow to the wide gap capacitance. The temperature of the ratio transformer is regulated to improve its stability. The bridge circuit measuring the ratio is very sensitive; the noise is equivalent to \(\delta (C_1/C_2) \approx 20\) ppb, which corresponds to a change in film thickness of \(\delta D^* \approx 0.15\) Å, as shown in Fig. 1.7. This is equivalent to a change in the \(^4\)He concentration of \(\delta X_4 = 10^{-8}\).
If the film is too thin, the diffusion coefficient is difficult to measure. The van der Waals potential between a helium atom and a wall at a distance $z$, varies as $z^{-3}$. When the pressure is suddenly increased, the amount of $^4$He in the bulk liquid starts increasing causing the film thickness to decrease. As the van der Waals potential at the film surface gets stronger, the amount of $^4$He that can dissolve in the bulk becomes smaller, decreasing the diffusion time. The effect is very large for thin films, but it is negligible for thick films.

When the film becomes very thick, a bulk phase forms in the capacitors due to capillary condensation. In this case, the capacitors can measure the total amount of $^4$He rich phase condensed in them. The diffusion coefficient is then found by measuring the amount of bulk $^4$He in the capacitors as a function of time after a pressure step. This method is more sensitive than measuring the film thickness because most of the $^4$He not dissolved in the $^3$He is in the capacitors.

In addition to studying the diffusion coefficient and solubility, when the $^4$He-rich phase is condensed in the capacitors, we intend to measure the interfacial tension between the $^3$He-rich and $^4$He-rich phases more precisely than in previous work at low temperatures[45]. The interfacial tension is proportional to the difference in the heights of the interfaces in the two capacitors. Errors due to spatial variations in the capacitor gaps may be eliminated by controlling the positions of the interfaces by applying electric fields, as was done in experiments on the $^4$He liquid-vapor interface.[46]

ACKNOWLEDGMENTS

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Mark Meisel for some RuO$_2$ thermometers, and Prof. Sebastion Balibar for sharing his design of the low temperature valve. Discussions with Profs. Will Saam, Michael Pettersen and Moses Chan have been very helpful.
2.1 Capacitors

There are two parallel plate capacitors used in our experiment, with almost identical construction but with different gaps. Each plate is a sapphire crystal disc of 0.750 inch in diameter and 0.100 inch in thickness. One side of the disc is polished flat to 1 wave length per cm and the other side is grounded flat but unpolished. We had previously tried to use silicon wafers for the capacitor plates. But after many trials, it was found out that the thin wafer was too flexible that was almost impossible to prevent the two plates from touching each other. On the other hand, sapphire is known for its hardness and with a thickness of 0.100 inch the stiffness is more than enough for our application.

The polished side, chosen to be the active area of the capacitor, is covered with a gold film. The film, which formed circular electrodes, was deposited by evaporating gold through a stack of stainless steel sheet masks. They were pressed tightly on to the sapphire disc and secured on a holder. The gold film is about 1500 to 2000 Å in thickness. Before the gold was deposited, we evaporated a layer of chromium about 10 Å thick, in order to improve the adhesion between the gold film and the sapphire
disc. The diameter of the circular electrode of 0.550 ± 0.005 inch is determined by the opening in the masks. There was a cut in the masks so that a strip of gold film with a width of 0.200 inch extends from the electrode, continuously over the edge, to the side of the sapphire disc. Here a wire was glued to serve as a lead to the outside electronic circuit. The undercut or penetration of the gold film under the masks is negligible. Under a 3 × 10 sample preparation microscope, the undercut is not observable. This corresponds to less than 20μm in width.

The evaporation source was put in a small tungsten “boat”, the size of about 1/2 inch. The heat was provided by a current source of about 100 amps. The target was put about 15 inches above the source. The deposition rate varies approximately as 1/s², where s is the distance between the source and target. The thicknesses of chrome and gold films were monitored with a crystal, placed above the source, whose frequency changes with the mass evaporated onto its surface. The thickness of the film deposited on the crystal was previously calibrated by the frequency shift. By comparing the distances of the source to the target and the thickness monitor, we determined the film thickness on our substrate.

Fig. 2.1 shows a photo of an assembled capacitor, and a disassembled capacitor. The five cent coin serves as a scale.

We originally chose alumina for the spacers in the capacitors. Three evenly spaced dots with a diameter of about 0.02 inch were formed by depositing alumina with a sputter machine. This was done before the gold film was formed. The spacers are arranged on a circle of about 0.65 inch in diameter. However, the success rate of sputtering was low, especially for spacers of large thickness. The alumina spacers do not always stick to the surface of the sapphire. A successful deposition depends on
Figure 2.1: Photos of an assembled capacitor, two discs from a breakdown capacitor, and a five cents coin for the scale.
many parameters in the sputter machine setup and also the choice of the filling gas in the chamber of the sputter machine during the process. After a few trials, we made one good deposition, with a thickness of about 6.7μm.

The spacers for the other capacitor, with a thickness of 16.8μm, were made from photoresist material by following the standard photolithography procedure. We choose photoresist material over alumina because it is much easier to work with and its thickness was close to the desired thickness.

The disc with the spacers was carefully placed on the other one to form a capacitor. Extreme care was taken to reduce the chance of dust particles falling onto the surfaces of the discs after they were taken out of the evaporation chamber. Once the discs were pushed against each other, silver epoxy was used at three spots around the edges to secure the two disks in place. Two of the silver epoxy spots are at the places where the extensions of the electrodes reach the edge so that wires can be glued in place to form leads.

A General Radio (GR) type 1615 capacitance bridge and a GR type 1316 oscillator were used to measure the capacitances of the two capacitors. It was done using a three-terminal configuration, where only direct capacitance, is measured. The direct capacitance does not include any capacitance to the third terminal which is ground. Thus only field lines crossing directly from one electrode to the other one are included. The capacitors were measured after they were installed in the cell where, due to an oversight, each capacitor was NOT shielded from the other. Fig. 2.2 shows a schematic drawing of the two capacitors installed in the cell with their leads labeled. We measured the capacitances of all the combinations of two out of the four leads, while the other two were grounded. Table 2.1 lists the results of the measurements.
Figure 2.2: Schematic drawing of the wide and narrow gap capacitors with the leads labels.
Notice that most of the conductances are negative. There are two possibilities: 1) the existence of a ground problem in the measuring circuit; 2) the residual resistance inside the capacitance bridge is larger than the dissipation of the capacitors.

<table>
<thead>
<tr>
<th></th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>82.6298 (0.000002)</td>
<td>0.1405 (-0.000046)</td>
<td>0.06612 (-0.000027)</td>
</tr>
<tr>
<td>b</td>
<td>1.044 (-0.000030)</td>
<td>0.08720 (-0.000029)</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td></td>
<td>207.020 (-0.000029)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: The capacitances and conductances of the capacitor leads, measured in liquid $^3$He and extrapolated to $T = 0$. Fig. 2.2 shows the labeling of the leads. The excitation voltage and frequency are $V_x = 1.0$ V and $f = 1.0$ kHz. The unit for the capacitances is pf. The conductances are in the parentheses, in $\mu\Omega$.

The correction for the stray capacitance to $c_{ab} \equiv c_N$, the narrow gap capacitance, is $(1/c_{ac} + 1/c_{cd} + 1/c_{da})^{-1} = 0.0450$ pf. Similarly, the correction for the wide gap capacitance is $\sim 0.0376$ pf. However, the capacitances of the two capacitors will not be affected by the stray capacitances, as long as they are measured with the other two leads grounded.

The frequency dependence of the capacitance and conductance of the two capacitors were measured at the room temperature in vacuum, from $f = 0.1$ to $\sim 10$ kHz. The results are shown in Fig. 2.3. The $f^2$ dependence of $G$ for the wide gap capacitor is due to a series resistance of about $485\Omega$ in the circuit. However, the cause for the approximately $f^{3/2}$ dependence of $G$ for the narrow gap capacitors was not fully investigated. The dissipation of the narrow gap capacitor became larger and
Figure 2.3: The capacitances, $c_N$ and $c_W$, and conductances, $G$ of the narrow and wide gap capacitors vs the excitation frequency $f$. The $\bullet$ and $\blacksquare$ are for the narrow and wide gap gap capacitor, respectively.
Figure 2.4: The conductance of the narrow gap capacitor vs the excitation voltage. The ○ was measured before the zapping and the ● was measured after.

larger over the time, after repeated subjugation to high excitation voltages of about 30 $V_{p-p}$. This prompted us to "zap" it in order to improve its performance. The zapping was done with a 0.56 $\mu$F capacitor, charged up to 70 V which corresponds to 1.4$\mu$J of energy stored. This large capacitor was then connected to the narrow gap capacitor, now in liquid $^3$He at $T = 4$K, and discharged. Our goal was to burn away any objects that might have been causing the large dissipation, especially at higher $V_x$. The zapping proved to be very successful. The conductance as a function of $V_x$ before and after the zapping is plotted in Fig. 2.4. There was negligible capacitance change from the procedure.
The gaps of the two capacitors were derived from the capacitance measurements in vacuum at 4 K. The formula we used is based on a model of two parallel plates, with the fringe effects neglected,

\[ c = \frac{\varepsilon_0 a}{d} \]

where \( \varepsilon_0 = 8.85 \times 10^{-12} \) (F/m) is the permittivity constant, \( a = \pi \sigma^2/4 \) is the area of the electrode, and \( d \) is the gap. The formula is in MKS units. The frequency and excitation voltage was set at \( f = 2 \) kHz and \( V_x = 10 \) V. We summarize the results as the following:

<table>
<thead>
<tr>
<th></th>
<th>Narrow Gap</th>
<th>Wide gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) (cm^2)</td>
<td>1.53</td>
<td>1.53</td>
</tr>
<tr>
<td>( c ) (pf)</td>
<td>196.911</td>
<td>77.8282</td>
</tr>
<tr>
<td>( G ) (( \mu )( \Omega ))</td>
<td>0.000155</td>
<td>0.00056</td>
</tr>
<tr>
<td>( d ) (( \mu )m)</td>
<td>6.7</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Table 2.2: The capacitances and conductances of the wide and narrow gap capacitors, measured in vacuum at \( T = 4 \) K. The gaps were derived with Eq.(2.1).

### 2.2 Capacitance ratio bridge

We used a ratio transformer bridge to measure the ratio of the two capacitors in the cell. The schematic diagram of the circuit is shown in Fig. 2.5. The ratio transformer is a GR Type 1493 Precision Decade Transformer. A GR Type 1316 oscillator provided the excitation voltage, \( V_x \), through a general purpose shielded step-down transformer. A transformer was used to "float" the output of the oscillator.
whose output is grounded. It has a primary to secondary ratio of about 6:1. We set the oscillator output to \( \sim 10 \text{ V} \) so that we had a voltage of \( V_z \sim 1.6 \text{ V} \) across the two capacitors. The output voltage and the frequency of the oscillator were monitored. We put in a Balun filter\cite{47} in order to reduce any ground loop problems that might arise from the grounding of the frequency counter and voltmeter. The Balun was easily made by winding a coax cable around a ferrite ring as many times as possible. This results in a filter that suppresses common mode currents while having no effect on the differential mode signals.

A variable resistance was put in series in one arm of the ratio bridge in order to balance the conductance of the capacitors and the resistances in the wires. The balance of the bridge is monitored with a Princeton Applied Research model 124 lock-in amplifier, with a model 119 plug-in preamplifier. This analog lock-in is revered for its low noise which is essential for low temperature experiments.

The noise in the ratio measurements is about \( 10 \text{ppb}/\sqrt{\text{Hz}} \). The long term stability is about 10 ppb. We used a time constant of \( \tau = 30 \text{ sec} \) in the lock-in amplifier, which corresponds to a bandwidth of \( \Delta f = 1/8\tau = 4.2 \text{ mHz} \). So we have a noise of about 0.6 ppb. But the non-reproducibility is about 20 ppb for the latest sample and 40 ppb for the earlier ones.

The output of the lock-in was sent out of the screen room through a specially designed feedthrough to computer controlled digital voltmeters. The feedthrough is isolated from the screen room walls. This is to prevent introducing an additional ground to the ratio bridge circuit. However, a coaxial cable going through the wall of a screen room, "floating", will dramatically reduce the effectiveness of radio frequency shielding. The problem was solved by using a 10 \( \times \) 10 inch metal plate tightly clamped
Figure 2.5: Schematic diagram of the capacitance ratio measuring circuit.
to the screen room wall with a sheet of 0.005 inch mylar in between to provide electric isolation. The coaxial cables were connected this plate, which is coupled capacitively to the screen room wall. This way, all the feedthroughs were “DC” isolated to the walls, but all radio signals will be redirected by the capacitive plate, to the screen room wall and so that they will not travel down the cables into the room.

2.3 Pressure Measurement and the Strain Gage

The pressure is measured with a capacitive strain gage following the design by Straty and Adams[48]. The advantages of a capacitive strain gage are its ultra high sensitivity, small dissipation, high repeatability, and quick response.

Fig. 2.6 shows a cut-away drawing of the pressure gage. It consists of the top lid, the middle membrane, the body, and a pair of round electrodes to form a parallel plate capacitor. The lid and the membrane was first bolted together with indium seal to form the chamber for the gage. The membrane was machined from BeCu with a thickness of 0.037 inch. We chose BeCu for its excellent elasticity and large yield stress. The membrane deflects under pressure. A small post at the middle of the membrane moves the top electrode relative to the bottom one. Both electrodes were glued to the membrane and the body with a very small amount of Stycast 2850FT epoxy to avoid spill over. This is to prevent the electric field from “seeing” the epoxy which has a temperature dependent dielectric constant at low temperatures. Both electrodes were electrically isolated from the other part of the pressure gage. The movement of the two plates relative to each other changes the capacitance which was monitored by a GR capacitance bridge in the 3 terminal mode. The excitation frequency was 5 kHz and the voltage was 10 Vrms. After machining, The two electrode
Figure 2.6: Scaled drawing of the capacitive strain gage assembly.
plates were polished and lapped against each other with 1.0µm alumina polishing compound to ensure a flat surface. All the parts of the pressure gage were made of BeCu for the purpose of a uniform thermal expansion coefficient at low temperatures.

It is critical for the two electrodes to be as close to each other as possible, without ever touching, in order to maximize the capacitance and the sensitivity. This was achieved by letting the epoxy cure with the two electrodes pressed together by the membrane under a pressure slightly larger than the maximum working pressure. In
our case, the maximum pressure at low temperatures is limited by the $^4$He solidification pressure and is about 25 atm, because the mixture in the bellows is compressed by $^4$He. However, the Young's module is different at room temperature and low temperature. At low temperature, $E \approx 2.7 \times 10^{12}$ dynes/cm$^2$, is about 1.5 times the one at room temperature, $E \approx 1.2 \times 10^{12}$ dynes/cm$^2$. This resulted in a maximum pressure of about 20 atm at room temperature.

The strain gage was calibrated against a Texas Instrument Precision Pressure Gage (TI gage). The TI gage was previously calibrated against a dead weight tester. The TI gage is accurate to ±0.2 psi. Fig. 2.7 shows the pressure calibration and its residual of the fit. There was some hysteresis in the strain gage or the TI gage, of about ±0.1 psi.

2.4 Thermometry

2.4.1 Melting curve thermometer

We used a $^3$He melting curve thermometer, mounted on the mixing chamber plate, as a standard thermometer in our experiments. This is possible because of the very well defined property of the $^3$He melting curve. It has a high resolution because the pressure can be measured capacitively to better than $10^{-6}$ atm, corresponding to temperature resolution a fraction of one $\mu$K. Repeatability is also very good because the hysteresis in the pressure gage is low, if care is taken in material selection and gage construction. It has almost no dissipation and is not very susceptible to magnetic fields or RF noises. However, it does require a $^3$He gas handling system.
Figure 2.8: The pressure measured on a Heise gage vs the capacitance of the melting curve thermometer. The + is the data. The curve is a fit. The o is the residual of the fit, and the thin lines connecting the points are used to indicate the sequence of measurement.
The first step in setting up the melting curve thermometer at low temperatures was to cycle it up and down the whole pressure range that was to measure later, in order to further reduce hysteresis. It was then calibrated against an external pressure gage. Fig. 2.8 shows one of the pressure calibrations. This was done when the fridge was at 1 K and the melting pressure gage was filled with liquid \(^{3}\text{He}\). The calibration is good to about \(\pm 0.1\) psi. This corresponds to an uncertainty of \(\sim 0.2\) mK near \(T = 10\) mK and \(\sim 0.9\) mK near \(T = 200\) mK in the temperature.

The blocked-capillary method was the standard way that is used to seal the \(^{3}\text{He}\) sample inside the gage in order to have a constant average density. After the pressure calibration and before the fridge was started, we compressed the \(^{3}\text{He}\) sample to about 530 psi or 36 atm at \(\sim 1\) K, under which pressure and temperature the \(^{3}\text{He}\) is still liquid. Then we started the circulation and the fridge began to cool, with the still the coolest part of the fridge and the mixing chamber the warmest before the \(^{3}\text{He}-^{4}\text{He}\) interface of the dilution refrigerator mixture entered it. This caused \(^{3}\text{He}\) to solidify as soon as the \(T\) dropped to the freezing temperature at 36 atm. near the still. This solid plugged the fill line to the melting pressure gage. As the fridge continued to cool, the solid-liquid interface followed the temperature change. The melting pressure gage would always be filled with both solid and liquid if the starting pressure was chosen correctly.

As the temperature of the mixing chamber passes through 0.32 K, there is a minimum in the pressure. This is shown in Fig. 2.9. Our pressure minimum was measured to be 28.9956 atm. The accepted pressure minimum of the \(^{3}\text{He}\) melting curve is 28.940 \(\pm 0.003\) atm[50][53]. This resulted in applying a correction of 0.0556 atm to our pressure calibration.
Figure 2.9: The pressure on the melting pressure gage vs the time, when passing through the minimum.
Greywall and Busch have fitted the $^3$He melting curve with an expression [51] for the temperature in the range from $\sim 2.75$ mK to the temperature at the pressure minimum, $T_{min} = 318$ mK,

$$P - P_A = \sum_{i=-2}^{5} a_i T^i$$

where $P_A$ and $a_i$ are the coefficients determined from the fit. In order to find $T$ in terms of $P$, we fitted their $P(T)$ equation brute forcefully with a 12th order polynomial, the highest possible in our plotting software. Fig. 2.10 shows the residual of the fit. Even though it oscillates, an error of $\sim 40 \mu K$ is sufficiently good for our purpose.

![Figure 2.10: The residual of a 12th order polynomial fit to the $P(T)$ formula by Greywall and Busch.](image)
2.4.2 Thick chip $RuO_2$ resistance thermometer

We used the recently developed thick-film chip resistors based on $RuO_2$ [54][55] to measure the temperature of the cell. The advantages of this type of thermometer are its simplicity, reproducibility, and reliability. It also has a very quick response time due to its very small size.

We chose the resistors manufactured by Dale Electronics of Norfolk, Nebraska, USA. They had a room temperature nominal resistance of 500 $\Omega$. Their size is very small, about $2 \times 2 \times 1$ mm. We glue two copper leads to it with silver epoxy. It was mounted on the cell body with GE vanish. The copper leads were heat sunk to the cell body.

We built a resistance ratio bridge[56] to measure the resistance ratio of the $RuO_2$ thermometer and a reference resistor. The reference resistor is a metal film resistor with a nominal value of 1 K$\Omega$ at room temperature. The reference resistor was also mounted on the cell. The thermometer is calibrated against the melting curve thermometer mounted on the mixing chamber. During the period of the experiment, one of the thermometer leads started to come loose due to a bad solder joint and the repeated thermal cycling due to the daily liquid He transfer. So we had to do two calibrations. It is reassuring to see that they agree well with each other. At lower temperatures, the thermometer starts to loose sensitivity due to selfheating. See Fig. 2.11.
Figure 2.11: The ratio of the resistance of the $RuO_2$ thermometer to that of a standard resistor vs the melting curve thermometer temperature
3.1 Data interpretation

3.1.1 The capacitance ratio

We follow the pioneering work of Nakamura et al.[1] who used parallel plate capacitors to measure the superfluid $^4\text{He}$-rich film thickness. This is possible because the film has a larger dielectric constant than the bulk liquid. Instead of one capacitor, as used by Nakamura et al., we use two capacitors with almost exactly the same construction but with different gaps. By measuring the ratio of the capacitances, we almost cancel out the effects due to bulk $^3\text{He}$ density change when $P$ and $T$ changes.

When immersed in the dilute $^4\text{He}$-$^3\text{He}$ mixture and covered with $^4\text{He}$-rich film, the capacitance of a parallel plate capacitor, based on a simple layer model which neglects edge effects, is,

$$c = a \left( \int_0^d \frac{dz}{\epsilon(z)} \right)^{-1}$$

(3.1)

where $a$ is the active area of the electrode, $d$ is the separation of the plates, $\epsilon$ is the dielectric constant of the liquid in between. For convenience, we can simplify Eq.(3.1) into two parts which are related to the bulk and the film respectively,

$$\frac{1}{c} = \frac{1}{\epsilon_0 a} \left[ d - \int_0^d \left( 1 - \frac{\epsilon_3}{\epsilon(z)} \right) dz \right] = \frac{1}{\epsilon_0} \left( 1 - \frac{2}{d} \delta \right)$$

(3.2)
where we use the pure $^3\text{He}$ dielectric constant $\varepsilon_3$ as that of the $^3\text{He}$-rich upper phase, which is essentially pure $^3\text{He}$ in our experiments, $c_0$ is approximately the capacitance without the $^4\text{He}$ film, and

$$\delta = \int_0^{d/2} \left(1 - \frac{\varepsilon_3}{\varepsilon(z)}\right) dz$$  \hspace{1cm} (3.3)

is the small correction accounting for the presence of the $^4\text{He}$-rich film due to van der Waals field. Is is of the order of $(\varepsilon_4 - \varepsilon_3) D^s$. In order to calculate $\delta$, a detailed model was used to calculate the density and the $^3\text{He}$ concentration profiles in the $^4\text{He}$-rich film. This was done by Hjort and will be presented in his thesis[57]. Here we will examine the asymptotic relationship of the film thickness and coverage with the capacitance ratio for thick films.

When the film is thick compared to the range where van der Waals potential is effective, but still very thin compared with the capacitor plates separation $d$, we can treat the film as a layer of the $^4\text{He}$-rich lower phase, with uniform density and $^3\text{He}$ concentration under the external pressure. Under this assumption, $\delta$ is related to the film thickness $D^s$ by the equation,

$$\delta = \left(1 - \frac{\varepsilon_3}{\varepsilon_l}\right) D^s$$  \hspace{1cm} (3.4)

From Eqs.(3.2, 3.4), we find,

$$\frac{c_N}{c_W} = \frac{c_{N0}}{c_{W0}} \left[ 1 - \frac{2D^s}{d_N} \right]$$  \hspace{1cm} (3.5)

Because $d \gg D^s$, we can expand Eq.(3.5) to the first order of $D^s/d$.

$$\frac{c_N}{c_W} \approx \frac{c_{N0}}{c_{W0}} \left[ 1 + \frac{2D^s}{d_N} \left(\frac{1}{d_N} - \frac{1}{d_W}\right) \right]$$  \hspace{1cm} (3.6)
The capacitance ratio bridge measures the capacitance ratio $R$, which is defined as,

$$R = \frac{C_N}{C_N + C_W}$$  \hspace{1cm} (3.7)

Since it is not possible to determine $D^s$ directly from $R$, due to the systematic error in the $R$ measurement, we need to find the change of the film thickness $\delta D^s$, from the change of the ratio, $\delta R$. From Eqs. (3.7, 3.6), we find.

$$\delta R = R_{00} (1 - R_{00}) \left( \frac{\epsilon_3}{\epsilon_l} - 1 \right) \left( \frac{1}{d_N} - \frac{1}{d_W} \right) 2 \delta D^s$$  \hspace{1cm} (3.8)

where $R_{00} \sim 0.7149$ is a constant defined as $d_W/(d_N + d_W)$.

The dielectric constant is determined from the Clausius-Mossotti relation.

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi a_p}{v}$$  \hspace{1cm} (3.9)

where $\epsilon$ is the atomic volume of the liquid and $a_p \sim 0.1231 \text{ cm}^3$ [58] is the atomic polarizibility for helium. For example, at $P = 0$ and $T = 0$, $\delta R/\delta D^s$ asymptotes to $46.34 \text{ ppb} / \text{Å}$, as the $^4\text{He}$ film thickness increases. Because our bridge setup is stable to about 5 ppb, this corresponds to a resolution of about 0.1 Å in film thickness.

**Background Capacitance Ratio**

Now we know the coefficient of $\delta D^s/\delta R$, we need to define a reference capacitance ratio, in order to determine the film thickness from $R$. This was achieved by measuring $R$ after draining away the superfluid film. This measured ratio is called the background ratio $R_0$.

The superfluid film was drained away through the cold valve, which became a superleak when partially opened. The superfluid film flows to the hot part of the fridge, possibly the heat sink on the cell fill line at the still of about 0.7 K. As the
remaining film in the cell became thinner, it underwent a KT transition\textsuperscript{[59, 60, 30, 61]} and became nonsuperfluid. This normal film is the same as the inert layer. Its thickness changes very slightly with the cell temperature (see P. 72 of Culman's thesis\textsuperscript{[11]}), negligible in our experiments.

With no film in the capacitors, we expect $R$ to be independent of $P$ and $T$, because the change of the dielectric constant of the bulk liquid $\epsilon_3(P,T)$ does not affect the ratio of the two capacitors. However, the measurements of $R_0$ indicate it changes linearly with $P$ and $\epsilon_3(P,T)$,

$$R_0(P,T) - R_0(0,0) \approx A (\epsilon(P,T) - \epsilon_0) - B P$$ \hspace{0.5cm} (3.10)

where $A \approx 9.083 \times 10^{-8}$ and $B \approx 1.90894 \times 10^{-3}$. From $P = 0$ to $\sim 7$ atm, the first term in Eq.\textsuperscript{(3.10)} dominates, resulting in a increase in $R_0$ of about 5 ppm. See Fig. 3.1, reproduced from Culman's thesis\textsuperscript{[11]}. At higher pressures, the second term (in $P$) dominates, causing a maximum in $R_0$ at about 7 atm, from which it starts to decrease, for another 5 ppm when the $P$ is increased to $\sim 24$ atm. The first term in Eq.\textsuperscript{(3.10)} is explained with the fringe effect that causes some of the electric field to go through the sapphire. We do not have a quantitative model, but we had made calculations that shows that the size of $A$ is very plausible. The second term in Eq.\textsuperscript{(3.10)} is due to mechanical stress. The pressure caused the wide gap capacitance to increase more than the narrow gap, because the wide gap capacitor uses photoresist while the narrow gap capacitor uses very hard alumina. The effects on $R_0$ as a function of $P$ and $T$ from the immobile layer and the gradient in the $^3$He density are negligible.

The intrinsic temperature dependence of $R_0$ was also measured, after the cell was depleted of helium liquid and film at low temperatures. (We do not have a reliable measurement of the ratio right after the cryostat was cool down and the cell still
Figure 3.1: $R_0$ vs $P$ at various temperatures.
The intrinsic temperature dependence is small at low temperatures and is approximately \(-0.23 \times 10^{-6} T^2\) below 0.2 K.

We measured \(R_0\) as a function of \(P\) and \(T\), and fitted the data with an equation similar to Eq.(3.10) but with additional terms of \(P^2\) and \((\epsilon_3(P,T) - \epsilon_{30})^2\) and \(P(\epsilon_3 - \epsilon_{30})\). Fig.3.1 shows the \(R_0\) measurement as a function \(P\) at various temperatures. Notice the hysteresis and ratio jumps in the measurement. See Culman’s in his thesis for a more detailed account of the \(R_0\) data and the fit\([11]\).

**3.1.2 \(^4\text{He}-\text{rich film thickness and coverage}\)**

In the previous section, we made an estimate of \(\delta D^s/\delta R\) for a very thick film when the density and \(X_3\) gradients in the \(^4\text{He}\) film can be neglected. The whole effect is due to van der Waals potential. When the film is thin, we have to take these into account.

Hjort has made a detailed model, which calculates the the \(^3\text{He}\) concentration and pressure profile in the liquid and in the film\([57]\). With the known bulk properties of liquid \(^3\text{He}\) and dilute \(^3\text{He}-\text{\textsuperscript{4}He}\) mixtures, the number density profile is evaluated. For a given \(^4\text{He}\) film thickness \(D^s\), it is then straightforward to calculate the dielectric constant profile, from which the length \(\delta\) in Eq.(3.3) is evaluated. From \(\delta\) the capacitance ratio \(R\) is determined. Also, from the density and \(^3\text{He}\) concentration profile in the \(^4\text{He}\) film, the \(^4\text{He}\) film coverage \(N_i^4\) can be calculated. The same process was repeated to calculate the ratio and \(^4\text{He}\) coverage without a superfluid film. This ratio corresponds to the measurement of \(R_0\). More details will be given in Hjort’s thesis\([57]\).
Figure 3.2: The difference between the calculated and the asymptotic values of $N_i^s$ vs the film thickness $D^s$, at $P = 0$. The • and ■ are for $T = 0$ and 0.12 K respectively. The curves are generated from interpolations of the residuals of the fit.

Hjort calculated $R - R_0$ and $N^s$, the difference of the $^4$He coverage with and without the superfluid $^4$He-rich film, for a set of values of $D^s$. The range of $D^s$ is from 0 Å to 150 Å. The pressures were 0, 4, 10, and 24 atm. The temperature were 0, 0.04, 0.08, 0.12, 0.2, and 0.35 K. The results of the calculation of $R - R_0$ and $N_i^s$ vs $P$ and $T$ were each fitted with a simple quadratic form,

$$f_0 + \left[1 + g(T)P + hP^2\right]c(T)D^s$$  \hspace{1cm} (3.11)

where $f_0$ and $h$ are constants, and $g(T)$ and $c(T)$ are quadratic functions of temper-
Figure 3.3: The difference between the calculated and the asymptotic values of $R$ vs the film thickness $D^s$, at $P = 0$. The $\bullet$ and $\blacksquare$ are for $T = 0$ and $0.12$ K respectively. The curves are generated from interpolations of the residuals of the fit.

The $g_i$ and $c_i$ are constants determined from the fits. We then interpolated the residual from the fits in order to find the values of $R - R_0$ and $N_i^s$ for arbitrary $D^s$, $P$ and $T$. Figs. 3.2, 3.3 show some of Hjort’s calculations at $P = 0$ and $T = 0, 0.12$K. They are plotted as the difference from $N_{asym}^s$ and $R_{asym}$, the asymptotic values of
$N^s_i$ and $R$. We have shown, in the previous section, that $R_{asym}/D^s$ is 46.34 ppb/A at $T = 0$ and $P = 0$. Values for it at other temperatures and $N_{asym}/D^s$ can be calculated similarly.

### 3.1.3 Overall bulk $^4$He concentration, $X_{40}$, and conservation of $^4$He

Because the total mole number of $^4$He atoms in the closed cell is fixed, we have the $^4$He conservation equation.

$$A_N^s + X_{40}^b n_0 = X_{40} n_0$$  \hspace{1cm} (3.14)

where $A$ is the total surface area of the cell. $N^s_i$ is the adsorption of $^4$He film, $n_0$ is the total mole numbers of the liquid mixture, $X_{40}$ is the bulk $^4$He concentration at high temperatures when the superfluid film vanishes and dissolves in the mixture. It is also called the overall $^4$He concentration in the mixture. The coverage of the inert layer is not included in $X_{40}$. The total amount of $^4$He in the cell is the sum of $X_{40} n_0$ and the amount of $^4$He in the inert layer. We also assumed that the thickness or coverage of the inert layer remains constant under the superfluid film in the temperature range of our measurement. However, $X_{40}$ may depend on pressure even for the same sample and with the cold valve closed. This is because the inert layer coverage increases with the pressure. This is indicated by our data analysis and with the result of the experiments. (see also a summary by Culman[11]).

The number of moles $n_0$ was measured to be $(0.55 \pm 0.02)$ mole, when the cell was filled at 1 K. We metered the $^3$He gaseous sample at room temperature and released it through the fill line to the cell. The gas was first cooled by the cryostat then
condensed into liquid. Only a small amount of the sample gas was released to the cell at a time, in order to avoid overloading the fridge.

The parameter $X_{10}$ can be only deduced from the fit to the data for a given sample and pressure.

The effective area $A$ is different from the geometric area $A_g$. From the drawings of the cell and parts inside, the area $A_g$ was calculated to be 201 cm$^2$. The effective area, also referred to as "true surface" or "physical surface" in adsorption phenomena[62], was determined in the $^3$He vapor adsorption measurement. It is about three times the geometric area due to roughness and microscopic cracks and crevices. Todd Culman measured the surface roughness of part of the cell and the capacitor plates with an atomic force microscope[11].

3.2 Data analysis

3.2.1 Numerical calculation of $\int_P^P' (v_3 - v_1) dP$

The pressure dependence of the molar volumes of the pure isotopes $v_1$ and $v_3$ can be obtained from speed of sound measurements in liquid helium. This is because

$$c_T^2 = \left( \frac{\partial P}{\partial \rho} \right)_T \quad (3.15)$$

where $c$ is the isothermal sound velocity, $\rho = m/v$ is the mass density. By integrating Eq.(3.15) at constant $T$, we get,

$$\rho - \rho_0 = \int_{P_0}^{P} \frac{dP}{c^2} \quad (3.16)$$

Maris[63] argues that the cube of the sound speed in liquid $^4$He or $^3$He, near the critical pressure of the liquid, $P_c$, should be linear in $P - P_c$.

$$c^3 \propto P - P_c \quad (3.17)$$
Here $P_c$ is the critical pressure when the sound velocity goes to zero and the compressibility of the liquid is infinite. The critical pressure is negative and it represents the limit of the stability of a metastable state.

There are no measurements of speed of sound at negative pressures in helium yet. However, the existing measurements of the pressure dependence of the speed of sound for $P \geq 0$, by Abraham and Osborne[8] and Abraham et al[64, 7] fit Eq.(3.17) very well. While their measurements are for the adiabatic speed of sound, $c_s$, at very low temperatures, the difference is negligible. This is because,

$$\frac{c_s^2}{c_T^2} = \gamma = \frac{c_p}{c_v} \approx 1$$  \hspace{1cm} (3.18)

where $c_p$ and $c_v$ are the specific heat at constant $P$ and $V$. This can be shown by using thermodynamic relations to express $\gamma$ as,

$$\gamma = 1 + \frac{\nu T \alpha_P^2}{c_v \kappa_T}$$  \hspace{1cm} (3.19)

where $\alpha_P$ is the thermal expansion coefficient at constant $P$, $\kappa_T$ is the isothermal compressibility. At $T = 0.1$ K, $(\gamma - 1) = 8.1 \times 10^{-4}$.

In Fig.(3.4), the cube of the speed of sound in liquid $^4$He and liquid $^3$He is plotted against the pressure. The fit for the $^4$He data is extremely good. For $^3$He, there are small systematic deviations. The critical pressures for $^4$He and $^3$He, $P_{4c}$ and $P_{3c}$ respectively, are obtained from the intercept, where $P_{4c} = -9.494$ atm and $P_{3c} = -2.790$ atm.

If we try to fit the exponent of the sound velocity $n$, instead of a fixed value of $n = 3$, we find a very good fit to the $^3$He data with $n = 2.859$, which we later approximated with 20/7. Fig.3.5 plots the residuals of the fits to $c_3$ for $n = 3$ and $n = 2.859$. The critical pressure for $n = 2.859$, is $P_{c3} = -3.319$ atm.
Figure 3.4: The cube of the speed of sound for $^4$He and $^3$He. The o are the data taken from Ref.[7]. The o are data points generated from a polynomial fit equation by Ref.[8]. The straight lines are best fits to the data points in the whole pressure range.
Figure 3.5: Residual of the fits to $^3$He speed of sound data, for $n = 3$ and $n = 2.859$, vs pressure.
However, as can be shown later, the algorithm in evaluating the integral \( \int v dP \), can be greatly simplified if \( n = 3 \) is used. The integral cannot be carried out analytically with \( n = 2.859 \). But if we approximate \( n \) with \( 20/7 \), it can be done. Fig.3.5 shows the discrepancy between using \( n = 3 \) and \( n = 2.859 \). The difference is only about 0.7% at \( P = 100 \) atm. It is not known why \( n \) is so close to 3 for \(^4\)He while is a 2.859 for \(^3\)He.

If \( c^3 \propto P - P_c \), we can write,

\[
\left( \frac{c}{c_0} \right)^3 = \frac{P - P_c}{-P_c}
\]

(3.20)

where \( c_0 \) is the speed of sound at \( P = 0 \). Using Eq.(3.20), we integrate Eq.(3.15)

\[
\left( \frac{P - P_c}{-P_c} \right)^{1/3} = \frac{\rho - \rho_c}{\rho_0 - \rho_c}
\]

(3.21)

here \( \rho_0 \) and \( \rho_c \) is the density at \( P = 0 \) and \( P = P_c \), respectively. We can get a relationship between \( \rho_c, \rho_0, \) and \( P_c \), by taking the derivative of Eq.(3.21) with respect of \( \rho \). Using Eq.(3.20), we have,

\[
\rho_c = \rho_0 + \frac{3P_c}{c_0^2}
\]

(3.22)

By equating Eqs.(3.20, 3.21), we find \( c \) is actually linear in \( \rho \) for \( n = 3 \),

\[
\frac{c}{c_0} = \frac{\rho - \rho_c}{\rho_0 - \rho_c}
\]

(3.23)

With Eqs.(3.15, 3.23),

\[
\int_P^{P_s} v dP = \int_\rho^{\rho_s} v \left( \frac{\partial P}{\partial \rho} \right)_T d\rho
\]

\[
= \int_\rho^{\rho_s} v c^2 d\rho
\]

\[
= \int_\rho^{\rho_s} \frac{m}{\rho} c_0^2 \left( \frac{\rho - \rho_c}{\rho_0 - \rho_c} \right)^2 d\rho
\]

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With the introduction of a new variable, \( x \equiv \rho/\rho_c \).

\[
\int_P^{P_0} \nu dP = K f(x)|_{x}^{\frac{1}{2}}
\]  

(3.24)

where,

\[
K = \frac{mc_0^2}{(\rho_0/\rho_c - 1)^2}
\]  

(3.25)

and

\[
f(x) = \int \frac{(x - 1)^2}{x} dx = \frac{x^2}{2} - 2x + \ln x
\]

For the case of \( n = 20/\pi \), \( K' \), corresponding to \( K \), is

\[
K' = \frac{mc_0^2}{(\rho/\rho_0 - 1)^{7/3}}
\]  

(3.26)

and for \( f(x) \), \( f'(x) \) is,

\[
f'(y) = 3 \left( \frac{y^7}{7} - \frac{y^4}{4} + \frac{y}{1} \right) - \frac{1}{2} \ln \frac{y - 1}{y + 1} - \sqrt{3} \tan^{-1} \left( \frac{2y - 1}{\sqrt{3}} \right)
\]  

(3.27)

where \( y \equiv x^{1/3} \).

### 3.2.2 The Osmotic pressure

Due to the \(^3\)He dissolved in the \(^4\)He-rich film, the \(^4\)He chemical potential is lower than the pure liquid value, by \( \pi_3^s v_1 \). This causes the small correction term \( \pi_3^s v_1 \) in the formula for \( X_3^{sat} \) in Eq.(1.5). For example, at \( P = 0 \) and \( T = 0 \), \( \pi_3^s v_1/k_B \) is about 7.5 mK.

The osmotic pressure \( \pi_3 \) for a dilute \(^3\)He-\(^4\)He solution is caused by the gas of \(^3\)He quasi-particles in the \(^4\)He superfluid background. It is defined as the pressure difference across a superleak between the solution and pure superfluid \(^4\)He at the
<table>
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<td>-</td>
<td>49.76</td>
</tr>
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</table>

Table 3.1: List of the parameters used in calculating the integral of \(\int_P^P' (v_3 - v_1) dP\).

same temperature. The pressure is \(P\) in the solution and \(P - \pi_3\) in the pure \(^4\text{He}\). The \(^4\text{He}\) chemical potential is the same in the pure liquid and in the solution.

\[
\mu_4(P, T, X_3) = \mu_4(P - \pi_3, T, 0) \tag{3.28}
\]

here \(X_3\) is the concentration of \(^3\text{He}\) in \(^4\text{He}\). By expanding the right hand side of Eq.(3.28) to first order in \(\pi_3\), we get,

\[
\mu_1(P, T, X_3) = \mu_4(P, T, 0) - \pi_3 v_4 \tag{3.29}
\]

where we have used the relation,

\[
v_4 = \left( \frac{\partial \mu_4(P, T, 0)}{\partial P} \right)_{T, X_3} \tag{3.30}
\]

We have obtained the osmotic pressure of dilute \(^3\text{He}-^4\text{He}\) mixtures from the measurements by Landau et al\[65\]. Hjort has fitted \(\pi_3\) as a function of \(P\) and \(T\) with the
following function,
\[
\pi_3(X_3) = \left[ c_1 X_3^{5/3} + c_2 X_3^2 + c_3 X_3^3 + \left( d_1 X_3 + d_2 X_3^2 \right) \frac{T^2}{T + e} \right] \left( 1 + fP \right) \tag{3.31}
\]
Here \( c_i, d_i, e \) and \( f \) are adjustable parameters determined from the fit. The result of the fit is shown in Fig.3.6. Please refer to Hjort's thesis[57] for more details.

In order to get \( \pi_3^{\text{sat}} \), we need to find \( X_3^{\text{sat}} \). This was also fitted by Hjort to the data of Watson et al [9] and Edwards et al[10], with the result.
\[
X_3^{\text{sat}}(P, T) = X_3^{\text{sat}}(0, 0.05) \left( \sum_{i=0}^{4} a_i P^i \right) \left( 1 + 3T^2 + \gamma T^3 \right) \tag{3.32}
\]

As well as the \(^3\text{He} \) excitations in liquid \(^4\text{He} \), there are also phonons and rotons. At low temperatures, their densities are so low that they can be completely neglected.

### 3.2.3 The van der Waals potential

We use the retarded van der Waals potential in the form proposed by Cheng and Cole [66]:
\[
V(z) = -\frac{\alpha}{z^3} \left[ 1 + 1.64 \left( \frac{z}{D_{1/2}} \right)^{1.4} \right]^{-\frac{1}{1.4}} \tag{3.33}
\]
where \( \alpha \) is the van der Waals coefficient between the helium atoms and a flat substrate, with a distance of \( D; D_{1/2} \) is a length scale at which the retardation starts to become important.

In our model of the potential, we start with the gold substrate with which all of the surfaces inside the cell have been coated. The van der Waals coefficient for gold is \( \alpha_g = 3113.1 \text{ KÅ}^3\text{[67]} \) and \( D_{1/2} = 160 \text{ Å}\text{[66]} \). The contribution from the gold is called \( V_g(D^g) \), where the subscript \( g \) denotes gold.
Figure 3.6: The data and fit of the osmotic pressures at various pressures and $\chi^2$. From Reference 9, 10.
After the cell and everything else were installed in place, it was flushed several times with \( N_2 \). After the last flush, it was pumped for about nineteen hours with a mechanical pump. We estimated the time constant for pumping a volume through a long tube, at the Knudson region, is about 1.3 hours. However, it is not surprising to still have a few layers of \( N_2 \) or air stuck to the walls. We assume a uniform thin layer of air, with a thickness of \( D_a \), coats the walls on top of the gold. Even though solid \( N_2 \) does not wet gold\([68, 69]\), it is reasonable to assume the first few layers are uniform in thickness\([69]\). The van der Waals coefficient for \( N_2 \) is \( \alpha_a = 802.9 \text{KÅ}^3\)[67]. The contribution of the air to the total van der Waals potential is \( V_a(D^a - D_a) - V_a(D^a) \). Here the subscript \( a \) denotes air, \( D^a \) is measured from the gold surface (will change to the inert layer later on). We express this thin layer as a combination of one infinite thick layer minus another infinite layer, offset by the thickness of the air layer. We also assume \( D_{1/2} \) is the same for gold and \( N_2 \), since we could not find a value for \( N_2 \) and because the effect of retardation in our experiment is relatively unimportant.

Above the air layer and beneath the \( ^4\text{He} \)-rich superfluid film is the inert layer. Even though the density of the inert layer is higher than that of the film or the bulk liquid, the van der Waals attraction from this denser inert layer to the other helium atoms is assumed to be negligible. Fig.3.7 shows a schematic drawing of the structure of layers on the gold surface.

The resulting van der Waals potential, for one \( ^4\text{He} \) atom in the superfluid film or in liquid \( ^3\text{He} \), is

\[
V(D^a) = V_g(D^s + D_i + D_a) - V_a(D^s + D_i + D_a) + V_a(D^a) = V_a(D^a + D_a) \tag{3.34}
\]
here we changed the reference point of $D_s$ from the gold surface to the surface of the inert layer. With this new definition, $D_s$ is only the thickness of the superfluid film.

3.2.4 Capillary condensation

Based on the data, we have evidence that there is capillary condensation inside the cell when the $^4$He-rich film is thick, see section (4.1.2). Because of the capillary condensation, the conservation equation, Eq.(3.14), needs to be modified. This is because the amount of $^4$He condensed in the cracks changes with the film thickness.
The modified $^4$He conservation equation is:

$$A \cdot N_l + X^b P_0 + n^{cap} X^l_1 = X_{40} n_0$$

(3.35)

where $n^{cap}$ is the number of moles in the lower upper phase occupying the cracks, and $X^l_1$ is the $^4$He concentration.

**The basics of capillary condensation:**

The general equation for the shape of an interface between $^4$He-rich(lower phase) and $^3$He-rich(upper phase) is,

$$V(D^3) \left( \frac{1}{v_l} - \frac{1}{v_u} \right) + \left( \frac{m_l}{v_l} - \frac{m_u}{v_u} \right) gz = \sigma \Gamma$$

(3.36)

where $v_u$ is the molar volume for the upper phase, $m_l$ and $m_u$ are the average molar masses for the lower and upper phase, $g$ the acceleration due to gravity, $z$ is the height above the base line, $\sigma$ is the interfacial tension, and $\Gamma$ is the curvature of the interface. Note that the flat interface of the bulk phase separation ($V = 0$ and $\Gamma = 0$) corresponds to $z = 0$. This equation comes from the uniformity of $\mu_3$ and $\mu_4$, and the pressure drop across the interface, $\Delta P = \sigma \Gamma$. If the interface is spherical, then the curvature is just $\Gamma = 2/R$, where $R$ is the radius of the sphere.

Let's examine the minimum film thickness, $D_r$, above which $^4$He-rich phase will bridge across two infinite half planes parallel to each other and separated by a distance of $2h$. First, we can simplify Eq.(3.36) into a dimensionless form by using a simple non-retarded form of the van der Waals potential for an infinite plane substrate.

$$V(D) = -\frac{\alpha g}{D^3}$$

(3.37)

With the variation of the height in $z$ neglected, Eq.(3.36) becomes,

$$\Gamma = -\sum_{i=1}^{2} \frac{1}{D_i^3} + \frac{1}{D_c^3}$$

(3.38)
Figure 3.8: Schematic drawing of a capillary condensation inside a channel of width 2h. The curvature of the interface is approximately spherical when the gap is large and has a radius of $R$. The critical film thickness, above which the channel can be bridged by $^4\text{He}$-rich liquid, is $D_c$.

$D_i$ is the distance from the point on the interface to each of the two walls (i=1,2).

All lengths are in units of $\lambda$, the “capillary length”, where $\lambda$ is defined by,

$$\lambda^2 = \frac{\alpha_g}{\sigma} \left( \frac{1}{v^i} - \frac{1}{v^u} \right)$$

(3.39)

For the interface of $^4\text{He}$ and $^3\text{He}$, $\sigma = 0.022$ (dyne/cm)[45]. With $\alpha_g = 3113.1 \text{KÅ}$, we get $\lambda = 31.6 \text{Å}$. When the opening of the channel is large, and we are far from the wall, the contributions from $1/D_i$ are small and $\Gamma$ is more or less constant. We can approximate $\Gamma$ as $1/R$, where $R \approx h - D^s$ and $D^s$ is the film thickness inside the
channel (see Fig.3.8). If we approximate $D^s$ with $D_c$, from Eq.(3.38) we get,

$$\frac{1}{h - D_c} \approx \frac{1}{D_c^2}$$  \hspace{1cm} (3.40)

This gives the relation between the half width $h$ and critical film thickness $D_c$,

$$h \approx D_c(1 + D_c^2)$$  \hspace{1cm} (3.41)

Eq.(3.41) is only the asymptotic function of $h(D_c)$ at large $D_c$. For small $D_c$ and the realistic van der Waals potential that also includes contributions from the air layer, we solved the differential equation of Eq.(3.38) numerically. The result for $h$ as a function of $D_c$ was fitted with the following form,

$$h = a_1 D_c + a_2 D_c^2 + D_c^3$$  \hspace{1cm} (3.42)

where $a_1$ and $a_2$ are coefficients determined from the fit. They are $a_1 = 1.439$ and $a_2 = 0.772$ for a air layer of $D_a = 10$ Å and inert layer of $D_i = 5$ Å. Notice that $h$ is zero when $D_c = 0$ and when $D_c$ is large $h \approx D_c^3$ as expected. Both $h$ and $D_c$ are measured from the air layer.

The wedge model:

We have made a model of capillary condensation in the cell, which assumes that the effective shape of the crack is a wedge. The contribution to this might come from two indium seals in the cell, the screw holes, and the contacts between the capacitors and mylar sheets. We model the length of the crack to be twice the circumference of the cell $2L$. The angle of the crack is determined by fitting the data.

The wedge is illustrated in Fig.3.9. We assume the angle of the wedge to be small so that we can use the relationship between $h$ and $D_c$ that is based on a parallel channel. For any given film thickness $D^s$, the capillary condensation fills up the
wedge to the opening \( h \) that satisfies the relationship \( h = h(D^s) \). The total volume of the capillary condensation \( \Omega_{\text{cap}} \) is thus,

\[
\Omega_{\text{cap}}(D^s) = \Omega_{\text{max}} \left( \frac{h(D^s)}{h_{\text{max}}} \right)^2
\]

(3.43)

where \( \Omega_{\text{max}} = 2Lh_{\text{max}}^2/\theta \), the maximum volume, corresponds to \( h = h_{\text{max}} \). The capillary volume \( \Omega_{\text{cap}}(D^s) \) is related to \( n_{\text{cap}} \) through,

\[
n_{\text{cap}} \chi_i = N_i^s \frac{\Omega_{\text{cap}}}{D_s}
\]

(3.44)

In Eq.(3.43), the only unknown of \( \Omega_{\text{max}} \) is determined by fitting the data.

### 3.3 Helium vapor experiments

Our solubility experiment alone can not determine the solubility, because only the film thickness or coverage were measured. Without knowing the area, we don't know
the total amount of $^4\text{He}$ moving in or out of the film. The total cell area $A$ needs to be known. The van der Waals potential is also undetermined, because $D_a$ and $D_i$ are both unknown. This section will describe how we can measure $A$ and $V(D^a)$ through helium vapor experiments.

The solution of $^4\text{He}$ into liquid $^3\text{He}$ is analogous to the evaporation of helium into vacuum. In the solubility experiments, liquid $^3\text{He}$ acts like a vacuum background for the $^4\text{He}$. When the $^4\text{He}$ dissolves into liquid $^3\text{He}$, it behaves like a gas of quasiparticles. The only difference, when compared with $^4\text{He}$ vapor, is the effective mass $m^*_4$, due to the interaction with $^3\text{He}$, instead of the bare mass $m_4$.

At low concentration or low densities, they can all be treated as a classical gas, obeying Boltzmann statistics. Their chemical potentials are:

for $^4\text{He}$ in $^3\text{He}$:

$$\mu_4^\text{sol} + E_4 = k_B T \ln \left( \frac{2 \pi \hbar^2}{m^*_4 k_B T} \frac{n_4^\text{sol}}{2} \right)$$

(3.45)

for $^4\text{He}$ in vapor:

$$\mu_4^v = k_B T \ln \left( \frac{2 \pi \hbar^2}{m_4 k_B T} \frac{n_4^v}{2} \right)$$

(3.46)

for $^3\text{He}$ in vapor:

$$\mu_3^v = k_B T \ln \left( \frac{2 \pi \hbar^2}{m_3 k_B T} \frac{n_3^v}{2} \right)$$

(3.47)

where $n_4^\text{sol}$ is $N_4/\nu_3$, the $^4\text{He}$ number density in $^3\text{He}$. $n_4^v$ and $n_3^v$ are the number density of $^4\text{He}$ and $^3\text{He}$ in their vapors, respectively. Note that in Eq.(3.47), there is an additional factor of $1/2$ for $n_3^v$. This is due to the fact that $^3\text{He}$ is a Fermion with spin 1/2.

Correspondingly, the chemical potential in the condensed phase is approximately,

$$\mu_4^l \sim -L_4$$

(3.48)
\[
\begin{align*}
\mu_3^I & \sim -L_3 \\
& = -2.473 (K) \\
& = -7.17 (K)
\end{align*}
\]

Here, \( L_4 \) and \( L_3 \) are the latent heat of pure liquid \( ^4\text{He} \) and \( ^3\text{He} \), their values are from Ebner and Edwards[22].

Because helium atoms are strongly bonded to themselves in the condensed phase, as shown in Eqs.(3.49, 3.50), the saturated pressure \( P_{sat} \) decreases exponentially with temperature. This is also true for \( ^4\text{He} \) in liquid \( ^3\text{He} \) where the difference in binding energy between the \( ^4\text{He} \) in liquid \( ^4\text{He} \) and in liquid \( ^3\text{He} \) is positive, \( \Delta = L_4 - E_4 > 0 \). When the temperature decreases, \( ^4\text{He} \) phase separates out of the liquid \( ^3\text{He} \) and the saturated concentration \( X_{4}^{sat} \) decreases exponentially.

In contrast, the binding energy of \( ^3\text{He} \) in \( ^4\text{He} \), \( E_3 \), is about 2.785 K[22]. It is larger than \( L_3 \), so that \( ^3\text{He} \) can always stay dissolved in liquid \( ^4\text{He} \), even at \( T = 0 \).

The experimental procedures are also similar between the solubility and vapor experiments. We measured the temperature dependence of the unsaturated film thickness or coverage in contact with the vapor. Unlike the solubility experiments where \( X_{4}^{sat} \) is unknown, \( P_{sat} \) is known experimentally.

The vapor experiments had to be carried out at much higher temperatures than the solubility measurements. This is because the differences in binding are much larger for helium in vapor and in liquid than for \( ^4\text{He} \) in \( ^3\text{He} \). This is especially true for \( ^4\text{He} \) vapor, whose vapor pressure is almost non-measurable below 0.5 K, due to the large value of \( L_4 = 7.17 K \).
3.3.1 Pure $^3$He vapor

We have two samples in the vapor experiments: the vapor/film of a $^4$He-$^3$He mixture and the vapor/film of pure $^3$He. Let us first consider the simpler case of pure $^3$He vapor.

The pressure in the vapor $P$ is always smaller than the $^3$He saturated vapor pressure $P_{3\text{sat}}$ for the unsaturated film. However they are related by the equation.

$$\frac{P}{P_{3\text{sat}}} = \exp\left(\frac{V(Ds)}{k_BT}\right) \quad (3.50)$$

This is because the chemical potential is uniform when the vapor is in equilibrium with the film.

$$d\mu = -sdT + vdP + dV = 0 \quad (3.51)$$

Using the ideal gas law, $Pv = k_BT$, and integrating Eq.(3.52).

$$-V = \int_P^{P_{3\text{sat}}} vdP = k_BT \ln \frac{P_{3\text{sat}}}{P}$$

This result is analogous to Eq.(1.15), where $X_{4\text{sat}}$ is related to $X_4$ through $V(Ds)$. The only difference is that $P_{3\text{sat}}$ is known experimentally, while $X_{4\text{sat}}$ is unknown and need to be measured.

Just like the conservation of $^4$He in the solubility measurements, the total number of helium atoms inside the cell is also conserved. The cold valve was kept closed during the vapor experiments. As in Eq.(3.35), the conservation equation for $^3$He is.

$$AN_{3\text{sat}} + n_{3\text{cap}} + \Omega_{\text{cap}}/\nu_3 = n_{3\text{0}} \quad (3.52)$$
By using the ideal gas law again for the $^3$He in the vapor, from Eq.(3.52) we get,

\[ P = k_B T n_3^v = k_B T (n_{30} - A N^s) \]

So the equations for analyzing pure $^3$He vapor data are:

\[ \frac{P}{P_{sat}} = AN_3^v + n_3^v + \frac{\Omega_{cap}}{v_3} \]

\[ P = RT (n_{30} - A N^s) \]  \hspace{1cm} (3.52)

\[ \hspace{1cm} (3.53) \]

here, $A$ and $n_{30}$ are two unknown constant. They can be determined along with $V(D^s)$ by fitting the data.

### 3.3.2 Vapor of the $^3$He and $^4$He mixture

At high temperature, most of the helium atoms left the film and went into the homogeneous $^3$He-$^4$He vapor. When it was cooled down, $^4$He first started to condense into the film and the film thickness grew. The $^3$He condensed at a lower temperature because its saturated vapor pressure is higher. When the temperature was decreased further, a phase separation in the film occurred. There were two films, with the denser $^4$He-rich film against the walls and the lighter $^3$He-rich film on top.

In order to find out the relationship between the film thickness and vapor pressure, we need to again find out the chemical potentials of $^3$He and $^4$He. We treated $^3$He and $^4$He in the vapor as ideal gases. Their chemical potentials are already described in Eqs.(3.47, 3.46). The chemical of $^3$He in $^4$He is similar to Eq.(3.45), as long as their concentration $X_3$ is low so that they can be treated as a gas of quasiparticles.

\[ \mu_3 + E_3 = k_B T \ln \left[ \left( \frac{2\pi \hbar^2}{m_3 k_B T} \right)^{3/2} \frac{X_3}{2v_l} \right] + V(D) \]  \hspace{1cm} (3.53)

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Here, similarly, there is a factor of 2 in the equation, due to the fact that $^3$He is a Fermion. We also included the van der Waals potential in the formula.

We derive the chemical potential of $^4$He in the film from the Gibbs-Duhem relationship, at constant $T$ and $P$,

$$X_3d\mu_3 + X_4d\mu_4 = 0 \quad (3.54)$$

Since from Eq.(3.53), $d\mu_3 = k_BTdX_3/X_3$, by including the van der Waals potential, we get,

$$\mu_4^0 = \mu_4^0(P_4, T) + k_BT\ln(1 - X_3) + V(D) \quad (3.55)$$

Here $\mu_4^0$ is the chemical potential for pure liquid $^4$He, $P_4$ is the partial $^4$He pressure in the vapor. Since $d\mu = vdp$ and $Pv = k_BT$, we get,

$$\mu_4^0(P, T) = \mu_4^0(P_{4sat}) + k_BT\ln\frac{P_4}{P_{4sat}} \quad (3.56)$$

Here $P_{4sat}$ is the saturated vapor pressure for liquid $^4$He. This gives the $^4$He vapor density $n_4^v$ as,

$$n_4^v = \frac{P_4}{k_BT} = \frac{P_{4sat}}{k_BT}(1 - X_3)e^{\frac{V}{k_BT}}$$

By equating the $\mu_3$ in Eqs.(3.47, 3.53), we get the $^3$He vapor density $n_3^v$,

$$\frac{n_3^v}{n_3^i} = \frac{m_3^{3/2}}{m_3^i} \exp\left(\frac{V - E_3}{k_BT}\right) \quad (3.57)$$

The corresponding conservation equations for $^3$He and $^4$He are,

$$\frac{A}{\Omega}(n_{30} - N_3^i) = n_3^v \quad (3.58)$$

$$\frac{A}{\Omega}(n_{40} - N_4^i) = n_4^v$$

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The above equations of 3.57, 3.57, 3.59 are enough to analyze the mixture vapor data to determine \(A\) and \(V(D^\text{H})\).

The formulas derived above correspond to the simplest model for the mixture, the so called "ideal mixture" model. In this model, the total Gibbs function is the sum of the Gibbs functions of the two unmixed isotopes plus an additional term originating from the entropy of mixing,

\[
g(P, T, X_3) = X_3 g_{30}(P, T) + (1 - X_3) g_{40}(P, T) + g_m \quad (3.59)
\]

where \(g_{30}\) and \(g_{40}\) are the Gibbs free energy for pure \(^3\text{He}\) and \(^4\text{He}\). and \(g_m\) is due to mixing,

\[
g_m = k_B T \left[ X_3 \ln X_3 + (1 - X_3) \ln(1 - X_3) \right] \quad (3.60)
\]

Since there is no interaction between the two components in the ideal mixture model, liquid \(^3\text{He}\) and \(^4\text{He}\) will remain mixed even at \(T = 0\). This contradicts the experimental facts. In order to model phase separation, an additional term in the Gibbs function is needed, such as,

\[
g_I = A_I X_3 (1 - X_3) \quad (3.61)
\]

Here, in the regular solution model, \(A_I\) is a positive constant accounting for the interaction between \(^3\text{He}\) and \(^4\text{He}\). It depends on pressure only and is of the order of \(T_{\text{trc}} \approx 0.78\) K at \(P = 0\), the tri-critical temperature.

The regular solution model correctly predicts a phase separation at. However, it is still a crude model. In order to avoid an overly complicated model, we decided not to analyze the low temperature part of the vapor mixture data when \(^3\text{He}\) starts to condense into film and then phase separates. For the part of the data at higher temperature, the ideal mixture model is sufficient, since most of the \(^3\text{He}\) stay in the

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vapor and the solubility of $^3$He in $^4$He film is low. This condition could be self-consistently checked once the data was fitted and $X_3$ calculated.

3.4 Data fitting algorithm

We used a FORTRAN program CURFIT, developed by Philip Bevington [70], to find the parameters of $m_1^*$ and $\Delta$ by fitting the capacitance ratio data. It is based on the Marquardt method, a combination of linearized least square and steepest decent, to minimize $\chi^2$ in the parameter space. Here $\chi^2$ is defined as

$$\chi^2 = \sum_i (y(x_i) - y_i)^2$$  \hspace{1cm} (3.62)

where $x_i$ is the independent variable, $y(x_i)$ is the function based on the theory, and $y_i$ is the data for $x_i$. In our case, the independent variable is $T$ and the dependent variable is $R$.

The parameters are sets of $m_1^*/m_4$ and $\Delta$, for each pressure that $R$ was measured at; $X_{10}$, for each data file for different pressures and samples: the maximum capillary condensation volume $\Omega_{cap}$ at a maximum film thickness $D_{max}$; and $\Delta R$, the corrections for ratio jumps for each data file. The jumps occurred between each measurements due to circuit changes and very long term drifts. We assumed that there is no change in $R_0$ during each set of measurements at a given pressure, which usually lasted a few days to a week.

There is no indication that the total number of $^4$He atoms in the cell change over the periods when the the cold valve was kept closed. However, due to the uncertainty in the $^4$He coverage interpretation of the ratio which is based on a model calculation, we allow $X_{10}$ to have different values for measurements at individual pressure even
for the same sample. Another reason is that the areal density of the immobile non-superfluid $^4$He increases with pressure. However, there is no accurate information on its dependence on pressure[11].

The equations used to calculate $R(T_i)$ are Eqs.(3.14, 1.18, 1.5, 1.10, 3.34). The relevant functions are Eqs.(3.31, 3.32, 3.34, 3.33). The following is a brief summary of the formula:

**Equations:**

\[
X_4^b = X_{40} - \frac{A}{n_0} N^s 
\]  
(3.14)

\[
X_4^{sat} = X_4^b \exp \left( \int_P^{P_s} \frac{v_3 - v_4}{k_B T} dP \right) \exp \left( \frac{\pi^{sat} v_4(P_s) - \pi^{sat} v_4(P)}{k_B T} \right) 
\]  
(1.18)

\[
X_4^{sat} = \left( \frac{T}{T^*} \right)^{3/2} \exp \left( \frac{-\Delta - \pi_3^s v_4}{k_B T} \right) 
\]  
(1.5)

\[
\int_P^{P_s} v dP = -V 
\]  
(1.10)

**Numerical Functions:**

\[
V(D^s) = V_g(D^s + D_i + D_a) - V_a(D^s + D_i + D_a) + V_a(D^s + D_a) 
\]  
(3.34)

\[
V_x(D) = -\frac{\alpha_x}{D^3} \left[ 1 + 1.64 \left( \frac{D}{D_{1/2}} \right)^{1.4} \right]^{-\frac{1}{1.4}} 
\]  
(3.33)

\[
\pi_3^s(X_3) = \left[ c_1 X_3^{5/3} + c_2 X_3^2 + c_3 X_3^3 + \left( d_1 X_3 + d_2 X_3^2 \right) \frac{T^2}{T + e} \right] (1 + fP) 
\]  
(3.31)

\[
X_3^{sat}(P, T) = X_3^{sat}(0, 0.05) \left( \sum_{i=0}^{4} a_i P^i \right) (1 + \beta T^2 + \gamma T^3) 
\]  
(3.32)
The Knowns:
\( n_0, v_3, v_4, A, D_a, D_i \)

The Unknowns:

\( P^s, D^s, X^b_4, V \)

Parameters:

\( m^*_4, \Delta X^b_4, \Delta R_0 \)

By eliminating \( P^s, X^b_4, i \), and \( V \), in the set of the four equations, we can get one complicated equation where \( D^s \) is the only unknown. We used a root finder routine. \textit{DZBREN}, in a FORTRAN Math lab. \textit{IMSLIB}, to solve \( D^s \) as a function of \( T_i \). We then use the function \( R(D^s) \) to find \( R - R_0 \) and add the correction of \( \Delta R_0 \). It is now possible to evaluate \( \chi^2 \) using Eq.(3.62). The parameters are varied to get a minimum \( \chi^2 \).
4.1 Overall concentration and capillary condensation

4.1.1 Changing the overall $^4\text{He}$ concentration

We change the overall concentration by reducing the pressure on the cold valve actuator at low temperatures slowly, so that the superfluid $^4\text{He}$ leak out to the warmer part of cryostat. The mixture inside the cell is under pressure. The fill line outside the cold valve leads to a 4 K valve that can be operated at room temperature. Both the capacitance ratio and the pressure inside the cell are monitored. The ratio will start to decrease when the cold valve actuating pressure reaches below a certain value. We had planned to close the cold valve immediately once the ratio drops to a prescribed value, Unfortunately, the film had always leaked out more than we wanted and we had to warm up the cell all the way to 1 K. With the cold valve completely opened again, the mixture had to be pushed in and out the cell so that it can mix with the $^4\text{He}$-rich liquid.

Fig. 4.1 shows one example of the process to leak out the $^4\text{He}$-rich superfluid film. During this period, the cell pressure was monitored closely to make sure it does not plummet as the result of a fully opened cold valve. Notice that the pressure
Figure 4.1: The capacitance ratio and the cell pressure vs the time during a super leak, when superfluid $^4$He-rich film leaked out of the cold valve. The cell was at $T = 27.3$ K and the pressure was very steady.

Of the cell is at about 260 psi, much higher than the pressure outside of the cold valve. It is pretty steady while the capacitance ratio was dropping over a time of about 15 minutes. The drift up and down in the pressure is probably due to the room temperature variation caused by people getting in and out the screen room and opening and closing of the doors. This shows that it is indeed a superleak and it is also the first direct observation of superfluid film moving to warmer part of the fridge.
4.1.2 Evidence for capillary condensation

At $T = 0$, all the $^4$He atoms are in the film. As $T$ increases, the film thickness decreases slowly at first, because the solubility is low at low temperatures. However, as $T$ continues to increase, the solubility starts to increase exponentially and the film thickness decreases accordingly. When the film thickness is becoming thinner and thinner, the van der Waals potential starts to become stronger. The amount of film thickness change will slow down because of the stronger van der Waals attraction. For the same amount of small increase in temperature, the change in film thickness is always more for a thick film than that of a thinner film. Here, we assume that everything coming out of the film will go into the bulk, or vice versa. This may not be true if there is an additional source of $^4$He.

In Fig.4.2, we plot the capacitance ratio data of two measurements, and their difference. Both of them are at the same pressure of $P \sim 0.4$psi, but at different overall concentrations. The sample No.1 has a smaller overall concentration of $X_{40} \sim 16$ ppm and that of sample No.2 is larger, with $X_{40} \sim 30$ ppm. Instead of monotonically decreasing, the difference of in the two ratios shows a peak. This peak indicates that the film thickness for the larger sample decreases slower than that of the smaller sample at low temperatures. It could only be explained as that there are other sources that releases $^4$He in liquid $^3$He. We believe this source is a capillary condensation.

We don't have any other independent verification of this assumption, except that a simple capillary model fits the data very well. See section 3.2.4 for more details about the model. The parameter out of the fit is also roughly consistent with our setup.
Figure 4.2: The • and o are the $P \sim 0.4$ psi capacitance ratio data of sample No.2 and No.1, respectively. The curves are fits to the data and the difference of the two fits. The curve of difference has a peak indicating the presence of capillary condensation. See text for more details.

4.1.3 Capillary volume

The wedge model works well for the less concentrated samples of No.1 and No.2. But the model breaks down for the more concentrated samples of No.3 and No.4, because there is a lot of $^4$He is in the cracks and it is an oversimplification to assume that the cracks behave like a simple wedge. However, since we successfully fitted the data of sample No.1 and 2 with Fermi liquid theory and a simple wedge model, we can also use Fermi liquid theory to deduce a profile of the effective crack in the cell.
Figure 4.3: The capillary condensation volume $\Omega$ vs the square of the half width of the crack, $h^2$. The $\circ$ and $\bullet$ are data from sample No.1. The $\triangledown$, $\Delta$, and $\circ$ are for sample No.2, 3, and 4, respectively. The curve is the fit through the points.

From the conservation equation of Eq.3.14, we find:

$$\Omega_{cap} = \left( (X_{i0} - X_i) + n_0 - N^s A \right) v_1$$

(4.1)

In order to find $N^s$ for No.3 and No.4 samples we need to know their $R_0$. This is done by fitting all the samples together (No.1, 2, 3, and 4), but with the No.3 and 4 samples’ low temperature data cut off. A simple wedge model is then used. This way the capillary condensation is limited even for the high concentrated samples because the film thickness will not be thick enough to throw off the simple model.
Fig. 4.3 shows the capillary volumes as a function of the opening of the effective crack. Notice that a simple wedge corresponds to a straight line. The plot shows that the cracks start with a simple wedge shape, but deviate away when the opening $h$ becomes large.

4.2 Helium vapor experiment

After we finished the solubility and diffusion experiments, we started the helium vapor experiments, where helium films in contact with their vapors were measured against temperature. Before the experiments, all the liquid had to be emptied from the cell. We started with release the pressure on the cold valve compressor so that the cold valve would open completely. The cell was then heated up to a temperature slightly above 3 K. in order to have a high enough vapor pressure for the gas to be pumped away, through very small filling tubes to the room temperature storage tanks. When most of the liquid was emptied, the cell temperature was warmed up to about 4 K to speed up the pumping of the remaining liquid. However, we were careful to not let the cell temperature getting much warmer than 4 K. because we wanted to keep the surface condition inside the cell the same as before. This way, it is reasonable to believe that the cell area $A$ and the van der Waals potential $V(D^*)$, that derived from the vapor experiments, are exactly the same as in the solubility and diffusion experiments. Because we planned to measure the temperature dependence of the film, similar to the solubility experiments, we made sure that there is only a thin film left in the cell, when all the vapor are condensed at low temperatures. If the film was too thick, the capillary condensation would dominate. We tried to make the film at least $\sim 20 \, \text{Å}$ but less than $100 \, \text{Å}$ at $T = 0$. Based on our back-of-the-envelop
calculation, the cell was pumped at liquid helium temperature with a diffusion pump for about 10 days, then it was sealed with the cold valve closed.

4.2.1 Data of $^3$He-$^4$He mixture vapor

We found there were two rises in the capacitance ratio when the cell was cooled down. The first one was at higher temperatures, close to 0.9 K, and the other one at lower temperatures, around 0.3 to 0.4 K. This was puzzling first. The mystery was solved once we realized that some $^4$He had left behind with $^3$He. The two rises correspond to the condensation of $^3$He and, later, $^4$He from a mixture of $^4$He and $^3$He vapor, as the temperature was lowered.

Fig. 4.4 shows the capacitance ratio vs the temperature. The background ratio $R_0$, or intrinsic temperature dependence of the ratio, had been subtracted from $R$. The rise due to $^4$He is about 1.3 ppm, and the rise due to $^3$He is about 5.2 ppm. A quick calculation indicates that there was about 30% of $^4$He in the cell in terms of total molar numbers.

The circles in Fig. 4.4 are measured with the bellows compressed, hence a smaller cell volume, while the triangles are with the bellows almost free. The reduction in the cell volume shifted the formation of the film to at a higher temperature. The final film thickness remained the same because the area did not change due to the compression of the bellows. The fractional volume $f$ gives an additional variation to the experiments so that $A$ and $V(D^4)$ can be measured and checked to be independent of $f$. We define $f$ as the ratio of the cell volume $\Omega$ to the free volume $\Omega_0$. $f = \Omega/\Omega_0$. The volume of the cell is changed by applying pressure from outside the bellows with liquid $^4$He.
Figure 4.4: The capacitance ratio, minus the background ratio, vs $T$. The $\bigcirc$ are measured with the cell compressed, with a fractional volume $f = 0.73$. The $\square$ are for $f = 0.98$. The curves are fit to part of the data, the ranges of which are indicated with the arrows.
The curves in Fig. 4.4 are fit to the data, with the formula developed in section 3.3. Due to the complexity, only data within part of the temperature range were analyzed. The temperature range is from 0.55 to 0.80 K, as indicated with the arrows in the figure. At this high temperature range, most of the $^3$He stay in the vapor. The concentration of $^3$He in the $^4$He-rich film $X_3^{lf}$ was very low, less than 1%. This was calculated based on the result from the fit. See Fig. 4.5. This shows that it is valid, in section 3.3, to assume $X_3^{lf}$ is low that we can treat the $^3$He dissolved in the $^4$He film as a gas of quasiparticles.

The runaway of the fit at the highest temperature in Fig. 4.4 is due to that $R_0$ was not accurately known above 0.8 K.

4.2.2 Data of pure $^3$He vapor

At low temperatures, all $^4$He and $^3$He of the previous mixture sample, condensed out and phase separated into two layers of films, with the lighter upper phase on top of the heavier lower phase, which was superfluid. We used the same method in the solubility measurements to completely drain out the superfluid $^4$He film by making the cold valve temporarily a superleak. The superfluid film flew out of the cell to the hot part of the fridge. Since the solubility of $^4$He in $^3$He is close to zero at very low temperatures, almost all the $^4$He were drained away, except the non-superfluid $^4$He inert layer was left with the $^3$He film.

Fig. 4.6 shows the data after the drainage. The disappearance of the first ratio rise confirmed our previous judgment of the presence of $^4$He and the successful draining of the superfluid film. Again, we measured the temperature dependence of the film.
Figure 4.5: The partial vapor densities of $^3$He and $^4$He and the $^3$He concentration in the film, $X_3^f$, as a function of $T$. They were calculated based on the fitting of the data in Fig.4.4.
Figure 4.3

He partial vapor density

N$_3^{\text{vapor}}$ and N$_4^{\text{vapor}}$ (n mol / cm$^3$)
at different cell volumes. The data were fitted to the formula developed in section 3.3.

4.2.3 The cell area and van der Waals potential

We fit the vapor data to the formula, established in section 3.3, that calculate $R$ as a function of $T$. The calculation depends on the parameters of the area $A$ and van der Waals potential $V(D^*)$, and the total molar number of the atoms inside the cell for each measurement. We fitted all the data of the pure $^3$He sample with the $^3$He and $^4$He vapor mixture, which all share the same $A$ and $V(D^*)$. Each run of the measurement has its own total number of $^3$He or $^4$He as an adjustable parameter. This is to account for any small losses of $^4$He or $^3$He to, for example, the pressure gauge. The pressure gauge, mounted at the mixing chamber and always colder than the cell, might cryo-pump the cell, if the cell is much hotter than the pressure gauge.

The van der Waals potential, is determined by tow adjustable parameters. $D_i$ and $D_a$, the thicknesses of inert layer and air layer respectively.

As we mentioned in the earlier section, only part of the data of the mixture sample, the first rise in the capacitance ratio due to $^4$He evaporation (condensation), were fitted. The amount of $^3$He in the mixture is not an independent parameter to be fitted. It was chosen to be the same as the total $^3$He inside the cell for the immediate run after $^4$He was removed. It can be seen from Fig.4.4 that the curve agrees well with the data at the lowest temperatures, indicating that the amount of $^3$He did not change indeed. From the same figure, it is clear that the curves do not fit the part of the data at the temperature range outside the arrows at all. This is because our simple ideal mixture model break down at lower temperature when more
Figure 4.6: Capacitance ratio, minus the background ratio, vs temperature at different cell volumes. The ● (cool down) and ○ (warm up) are for $f = 0.98$. The ■ are for $f = 0.73$. The curves are fits to the data.
Figure 4.6
Table 4.1: Result of the fit to the helium vapor data.

<table>
<thead>
<tr>
<th>$A$ (cm$^2$)</th>
<th>549.7 $\pm$ 22.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_a$ (Å)</td>
<td>8.8 $\pm$ 0.6</td>
</tr>
<tr>
<td>$D_i$ (Å)</td>
<td>5.4 $\pm$ 0.4</td>
</tr>
</tbody>
</table>

and more $^3$He goes into the film and the high concentration making the interaction the interaction non-negligible.

The effect of capillary condensation was also included in the fitting. However, since the maximum value of $D^a/\lambda$ (see section 3.2.4) is relatively small for the vapor experiment, its parameter $\Omega_{cap}$ was given, based on the results of solubility data fitting.

The summary of the fitting results is given in Table 4.1.

4.3 Solubility experiments

4.3.1 The capacitance ratio data

The capacitance ratio data of the temperature dependence of the superfluid film thickness were taken at various pressures for five different samples. Sample No.1 has the lowest overall concentration of $^4$He, and each consecutive sample has higher concentration, with sample No.5 the highest. On the other hand, sample No.1 is the most recent made sample, and sample No.5 is the earliest sample. See Table 4.3.1. The concentration of sample No.5 was estimated to be about 100 ppm, and is not listed in Table 4.3.1. The cold valve had been kept closed during the measurements at different pressures for each sample to ensures that the total amount of $^4$He and
Table 4.2: List of the four samples with their overall $^4$He concentrations and the pressures under which the film experiments were carried out.

$^3$He inside the cell was constant. The cold valve was opened slightly only when the concentration of the mixture needed to be changed, as is discussed in the previous section.

The pressure in the cell was controlled by the liquid $^4$He outside the bellows. The liquid $^4$He is connected to the room temperature plumbing system through a narrow fill line, so that the bellows could be compressed from room temperature. Since both $\Delta$ and $m_\text{th}$ are functions of the $^3$He density $n_3$, rather than the pressure $P$, (see section 1.2), we need to check the change of $n_3$ during the capacitance ratio measurement. The compressibility of $^4$He and $^3$He are comparable, $\sim 1.4 \times 10^{-2}$ and $2.7 \times 10^{-2}$ atm$^{-1}$ at $P = 0$[71, 72], respectively. The thermal expansion coefficient of $^4$He is totally negligible below 0.5 K and $^3$He expands $\sim 0.35\%$ from 0.3 to 0 K at $P = 0$[8]. From these values, we estimated the change of $n_3$ from 0 to 0.3 K to be about 0.3% at $P = 0$. The corresponding pressure changes is $\sim 0.02$ psi at $P = 0$, when the capacitance ratio were measured from 0.020 to 0.3 K. This change of $\Delta$ due to the density change is about 3 mK.

<table>
<thead>
<tr>
<th>samples</th>
<th>No.1</th>
<th>No.2</th>
<th>No.3</th>
<th>No.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{10}$ (ppm)</td>
<td>$\sim 16$</td>
<td>$\sim 30$</td>
<td>$\sim 40$</td>
<td>$\sim 60$</td>
</tr>
<tr>
<td>pressures (psi)</td>
<td>0.4(2), 74.3, 150.0</td>
<td>0.5, 155.1</td>
<td>3.8, 49.8, 117.9</td>
<td>1.2, 169.8, 258.9</td>
</tr>
<tr>
<td></td>
<td>217.8, 291.5(3), 353.9</td>
<td>259.3</td>
<td></td>
<td>337.6</td>
</tr>
</tbody>
</table>
Figure 4.7: A typical set of data of capacitance ratio, temperature, and pressure vs time. This one is for sample No.1. The cell was first given a heat pulse. It was then left to relax into equilibrium. The solid line is the temperature, the broken line is the pressure, the dots are the capacitance ratio. The overshoot of the temperature indicates that the cell body, where the thermometer was mounted, was at a higher temperature than that of the bulk mixture. The ratio went down when the power was first applied. It then went back up after the heating was stopped. See text for explanation.

We increased the cell temperature by applying power to a resistive heater mounted on the cell for from 1 ~ 10 minutes. We could also cool the cell by closing the heat switch. The cooling usually took much longer time than heating. It ranges from half an hour to as long as a whole day, depending on the temperature of the cell. We changed the temperature of about a few hundredth of a Kelvin, in either directions, each time. Fig.4.7 and 4.8 shows two typical runs of measuring the ratio, temperature
and pressure. During the heating, the capacitance ratio had a dip. This is due to the temperature difference between the two capacitors. The wide gap capacitor, which was mounted closer to the cell body, was warmer than the narrow gap capacitor when the cell was heated. This caused the film in the wide gap capacitor to be thicker and its capacitance to be higher than that of the narrow gap, and hence a smaller ratio. It is the similar reason that caused the ratio to have a peak during the cooling.

The heat switch had always been kept open so that the cell is thermally isolated with the mixing chamber. We also kept the mixing chamber as cold as possible, which was usually at around 10 mK if the cell was not at too high a temperature. This way, the pressure gauge was always at a lower temperature than the cell and the $^4$He film would not flow to it. This is opposite to the case in the vapor experiment where we tried to keep the heat switch closed all the time, so that the cell was at the same temperature as the mixing chamber. Otherwise, the pressure gage, which was mounted on the mixing chamber and connected to the cell, would be at much lower temperature than the cell and would cryopump on the cell, causing the total number of helium inside the cell to change with time.

There was no noticeable hysteresis in the data. However, small jumps in the values of the capacitance ratio occurred from time to time. The main cause is probably due to the electronics. Since the signal we were trying to measure was so small, its measurements were susceptible to some sudden changes in ground current. It was difficult to get rid of ground loop problem complete. However, the circuit had been improved gradually as the experiments were carried out. Because of this, the quality of the data taken later were improved over the earlier ones.
Figure 4.8: A typical set of data of capacitance ratio, temperature, and pressure vs time. This one is for sample No.1. The cell was cooled first by closing the heat switch. After about an hour, the heat switch was opened and the cell was let to reach equilibrium. The designations of the lines are the same as Fig.4.7. The over cooling of the temperature indicates that the cell body was at a lower temperature of the bulk mixture, similar to the case of heating. The overshoot of the ratio was due to the temperature difference between the two capacitors. See text for explanation.

Fig.4.9 shows the capacitance ratio, minus the background ratio, \( R - R_0 \), as a function of temperature at different pressures for sample No.1. Based on the fit, the overall \(^4\)He concentration for this sample is about 17 ppm at \( P = 0 \), which is the lowest among all the samples. The curves going through the data are fits using Fermi liquid theory.

Fig.4.10 shows the data for sample No.2, which has only two measurements at 0 and 10 atm. Based on the fit, \( X_{40} \sim 30 \) ppm at \( P = 0 \).
Figure 4.9: The ratio difference $R - R_0$ vs $T$ for sample No.1. The $\bullet$ is at $P = 0$, and the next ones are at 5, 10, 15, 20, and 24 atm. The curves are fits to the data.
Figure 4.10: The ratio difference $R - R_0$ vs $T$ for sample No.2. The • is at $P = 0$. The ○ is at $P = 10$ atm. The curves are fit to the data.
Figure 4.10

$R - R_0$ (ppm)

$T$ (mK)

20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300

0 1 2 3 4

107
Fig. 4.11 shows the zero pressure measurements of the No.3 and No.4 samples. Because of capillary condensation, we did not use them to get $\Delta$ and $m^*$. These data were only used to extract information about the capillary condensation, i.e., the profile of the effective wedge, see section 4.1.3.

We do not have good quality data for sample No.5, which is the first sample that we had attempted to do solubility and diffusion experiments. The problems for this sample are the lacking of room temperature stabilization for the ratio bridge, the ground loop problem for the circuit, the large concentration that caused large effect of capillary condensation. All these problems resulted in too much drifts and jumps in the capacitance ratio data.

4.3.2 Prewetting at $P = 24$ atm

During the measurement of the capacitance ratio for sample No.1 at $P = 24$ atm, we found a surprising jump in the ratio at $T \sim 80$ mK. See Fig. 4.9. The data, excluding those in the region of transition, can be fitted very nicely with the same formula used for measurements at lower pressures where no transition was observed. This indicates that a superfluid film forms, similar to the ones at lower pressure, below the transition temperature of about 78 mK. Above the transition temperature the appearance of the superfluid film is suppressed. No freezing occurs even though 24 atm is very close to the freezing pressure of liquid $^4$He and that the pressure near the wall could very well be even higher. This is possible because the surface free energy of the $^4$He solid, which only partially wet the walls, prevents the solidification of a solid.
Figure 4.11: The ratio difference $R - R_0$ vs $T$ for sample No.3 and No.4, at $P = 0$. The ● is for sample No.3 and ○ is for sample No.4.
The sudden appearance of the superfluid film might be an indication of the so-called “pre-wetting transition”[73]. Tholen and Parpia[74] observe a similar transition at around the same pressure and film thickness. They interpreted it as the solidification of superfluid 4He film as the pressure was increased. One difference of their data with ours is the association of hysteresis, which we lack in our data. This might be due to the pores in the sinter used in their cell.

4.3.3 Data fitting with Fermi liquid theory

We fit the data of samples No.1 and 2 at various pressures to the formula listed in section3.2 based on Fermi liquid theory. Samples with higher concentrations, i.e. sample No.3, No.4, and No.5, were not used in the fit because of the large amount of capillary condensation. All the data were fitted simultaneously with one set of parameters, so that the same values or functions of $\Delta(P)$, $m_1^*(P)$, and the parameters for capillary condensation are fitted. The value and function of area and van der Waals potential are also the same for all the data. They were obtained from fitting the vapor data.

ratio jumps

We first subtracted the capacitance ratio with the background ratio $R_0$, which is a function of $P$ and $T$. But since $R(P,T)$ and $R_0(P,T)$ were measured over the span of about two years, jumps and drifts in the ratio measurement occurred sometimes due to changes of circuit and relocation of cables, or without any explicable reasons at all. The jumps are difficult to trace back accurately due to the changing conditions. During the period of measurement at each pressure, which usually lasted one to two weeks, there were very few jumps because of the very short period of time. Even if
Figure 4.12: The ratio difference $R - R_0$ data at $P = 24$ atm for sample No.1. The insert shows an enlargement of the data at $T \sim 80$ mK, where an interesting jump occurred.
there were jumps, it was relatively easy for us to correct. Thus every set of data at each pressure has an adjustable parameter, $\Delta R_0$, to account for the jumps. Their values were determined during the fit.

**overall $^4$He concentration $X_{40}$**

Even though the total number of $^4$He atoms in the mixture for each sample is fixed at different pressure, the overall concentration $X_{40}$ was not constant. This is because some $^4$He go into the inert $^4$He layer as the pressure was increased. There are various measurements indicating that the inert layer coverage does increase with pressure. This has been very nicely summed up by Culman[11]. See Fig.4.14 which plots out the pressure dependence of the coverage of the $^4$He inert layer for various substrates. As shown in Fig.4.14, the change of the coverage as a function of pressure is not known quantitatively and it depends on the specimen of substrates. To account for this unknown factor, and also consideration that the calculation relating $D^s$, $V^s$, and $R$ has uncertainties due to the dependence on measured values and possible small systematic errors in the model, each data file at different pressures and samples is allowed to have its own $X_{40}$ which was determined from the fitting.

We plotted out the values of $X_{40}$ for sample No.1 and No.2 against pressure in Fig.4.13. The values for each samples are relatively constant, which indicates that the model calculation for $N^s$ and $D^s$ is correct and the cold valve was not leaky. The straight lines are linear fits to the data points of the two samples. Both lines have the same slope but different intercepts. From this result, it indicates that there is a decrease of the overall concentration of about 1 ppm, as the pressure was increased from zero to 24 atm. We think this is due to the increase of about 1 nmol/cm$^2$ in the $^4$He inert layer coverage, consistent with data shown in Fig.4.14.
Figure 4.13: The overall concentrations, deduced from the fit, as a function of pressures, for sample No.1 and No.2. The $\bullet$ is for sample No.1 and the $\bigcirc$ is for sample No.2. The solid line is a fit to the points.
Figure 4.13
thickness of inert layer

From the fit to the vapor data, we found the thickness of the inert layer $D_i$ is $5.4 \pm 0.6 \text{Å}$ at zero pressure. In order to find the pressure dependence, we need to know either the direct measurement, or the pressure dependence of the coverage and density profile of the inert layer. Since none of the above mentioned are available, we assumed it to be independent of pressure.

The pressure independence assumption about the inert layer of $5.4 \text{ Å}$, indicate a molar volume of about 21.6 cc. correspond to the value under $P = 45 \text{ atm}$. if we extrapolate the formula based on the speed of sound measurements. Here we assumed a coverage of about 2.5 nmol/cm$^2$, consistent with the available experiments. Also from Fig.4.13. and the re-confirmed by the result of the fit, it is plausible that the inert layer coverage increase about 1 nmol/cm$^2$ from 0 to 25 atm. Our assumption of the constant value of the inert layer thickness corresponds to a molar volume of.

We had also assumed a linear pressure dependence for the inert layer coverage. The thickness increase from $D_i = 5 \text{ Å}$ at $P = 0$ to $D_i = 7.5 \text{ Å}$ at $P = 25$. The results from the fit do not change significantly. We will take this as part of the systematic error in our results.

Capillary condensation

From the fit to the data, the capillary condensation, which is modeled with a straight wedge, consume about 5% and 30% of the total amount of $^4\text{He}$ at $T = 0$ for sample No.1 and 2 respectively.
Figure 4.14: Measurements and upper and lower limits for the coverage of the $^4$He inert layer as a function of pressure and substrate. From Culman's thesis[11].
Figure 4.14

Solid Layer Coverage vs Pressure

- Si, TO, Tholen & Parpia
- 70 nm Ag powder, TO, Tholen & Parpia
- Stycast 1266, TO, Richie et al.
- Mylar, TO, McQueeney et al.
- Mylar, TO & NMR, Freeman & Richardson
- Cu, s. f. flow, Steel et al.
- Al₂O₃, 4th sound, Kim et al.
- Mylar, NMR, Kawae et al.
4.3.4 Fermi liquid parameters for the dilute $^4\text{He}-^3\text{He}$ mixture

From the fit to the capacitance ratio we find the difference in binding energy $\Delta$ and the effective mass $m_4^*$. Their values at different are plotted in Fig.4.15.

We find the ratio of $m_4^*/m_4$ is close to one. There is no trend of it going up or down with pressure. The best guess is an almost constant $m_4^*/m_4$ with a very weak dependence on pressure. A fit gives a mean of $m_4^* = 1.29$ with a scatter around the mean of 0.21.

Since there is no theoretical prediction of the pressure dependence of $\Delta$ available, in order to make a fit for the $\Delta$ vs $P$ data, we made an assumption about $\alpha_4$. This is because $\nu_4^*$ is related to $\Delta(P)$ by the equation.

$$\frac{\Delta}{P} = \nu_4^* - \nu_4$$  \hspace{1cm} (4.2)

We find that fractional excess volume of $^4\text{He}$ in $^3\text{He}$ changes almost linearly with the molar volume based on the extrapolation of Laheurte's measurements of $X_1^{sat}$ at higher temperature and concentrations. See Fig.4.16. So we made a very simple assumption of the functional form for $\alpha_4$.

$$\alpha_4 = \alpha_{40} + \beta \left( \frac{v_3(P)}{v_3(0)} - 1 \right)$$  \hspace{1cm} (4.3)

where $\alpha_{40}$ is fractional excess volume at $P = 0$, $\beta$ is a coefficient need to be determined, $v_3(P)$ is the pressure dependence of the molar volume of liquid $^3\text{He}$.

The results of $\Delta$'s at different pressures, except the one at $P = 24$ atm, were fitted with Eq.4.3 with the assumption of Eq.4.4. The point of $\Delta$ at $P = 24$ atm is not a legitimate point, because of the presence of the so called pre-wetting transition.
Figure 4.15: Results of $\Delta$ and $m_4^*/m_4$ as a function of pressure. The $\bullet$ are our measurements. The $\triangledown$ is a fit of the Nakamura et al.'s data[1] by Edwards et al[12]. The solid curve going through the $\bullet$ is a fit based on the assumption that $\alpha_4$ is linear in the molar volume of $^3$He $v_3$. See text and Fig.4.16. The horizontal straight line going through our measurement of $m_4^*/m_4$ is a weighted fit. The value is 1.29 with a standard deviation of 0.21 about the mean. The broken curves are microscopic calculations from Refs.[13, 14].
Figure 4.15
Figure 4.16: The fractional excess volume of $^4$He in liquid $^3$He $\alpha_4$ vs $P$. The solid line is linear in $v_3$. Its slope and intercept were determined from the fit to our measurement of $\Delta$ as a function of pressure. The broken line is Laheurte's calculation based on his solubility measurements at higher temperatures and concentrations[5]. The □ is a measurement by Sato and Suzuki[6].
Figure 4.16
The fact that all $\Delta > 0$ means that the solubility of $^4$He in liquid $^3$He is zero at $T = 0$ for all pressures. The minimum at $P \sim 12$ atm shows that there is a maximum solubility at that pressure range. It also indicates that $v_4^* = v_4$.

### 4.3.5 Solubility as a function $T$ and $P$

We deduce the solubility $X_4^{sat}$ from the $R - R_0$ data as a function of $T$ and $P$. We first calculated $N^*$ and $D^*$ from $R - R_0$. The bulk concentration $X_4^b$ is then found by using Eq.refeq-he4consv,

$$X_4^b = X_{40} - \frac{AX^s}{n_0} - \frac{\Omega}{n_0} \quad (4.4)$$

where $\Omega$ is the volume filled by capillary condensation. The van der Waals potential for a film thickness of $D^*$ is calculated with Eq.3.34 and $X_{40}$'s are obtained from the fit.

We then solve the Eq.1.10 to find $P^*$. By integrating $\int P^* PvdP$, and with corrections from $\pi^* v_4$, we find the saturated concentration using Eq.1.18

$$X_4^{sat} = X_4^b \exp\left(\frac{\int P^* (v_3 - v_4) dP}{k_BT}\right) \exp\left(\frac{\pi^* v_4}{k_BT} - \frac{\pi^* (P^*) v_4}{k_BT}\right) \quad (4.5)$$

This is different from the exact equation

$$X_4^{sat}(P^*) = X_4^b(P) \exp\left(\frac{\int P^* (v_3 - v_4) dP}{k_BT}\right) \quad (4.6)$$

However, if we use this equation, we still need to know $v_4^*$ which can only be obtained from the fit, $v_4^* = v_4 - \partial E_4/\partial P$, if we don’t use results from other groups. We also need to correct $P$ from $P^*$.

Since our fit using fermi liquid theory is very good, and the prediction of the diffusion coefficient is also very good[11], it is safe to use Eq.1.18 to find $X_4^{sat}$.

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Figure 4.17: The solubility $X_{i}^{\text{sat}}$ as a function of $T$ and $P$. The results are derived from sample No.1 and No.2. The bottom data points and fit are at $P = 0.03$ atm. The display of data and fits of $P = 5.06, 10.6, 14.8, 19.85, 24.0$ atm are offseted one decade, in value of $X_{i}^{\text{sat}}$, of the previous pressure.
Figure 1.7

$X_{\text{sat}}$ vs $T$ (mK)

- $x10^1$
- $x10^2$
- $x10^3$
- $x10^4$
- $x10^5$
CHAPTER 5

CONCLUSION

5.1 Conclusion

We have measured the solubility of \(^4\)He in liquid \(^3\)He down to about 40 mK and pressures from \(P = 0\) up to \(\sim 24\) atm. The solubility was determined from the superfluid film thickness data on two samples of dilute \(^4\)He-\(^3\)He mixtures, with overall \(^4\)He concentrations \(X_{_{40}}\) of 16 and 30 ppm. We had a total of five samples. The overall \(^4\)He concentrations for the rest of the samples were 40, 60, and \(\sim 100\) ppm. There was too much capillary condensation for samples No.3, 4, and 5, for them to be used to derive the solubility. We only used these data to derive some information about the capillary condensation. The capillary condensation for the sample No.1 and No.2 was relatively small and could be accounted for with a simple wedge model.

By fitting the solubility to Fermi liquid theory, we obtained the parameters \(m_4^*\) and \(\Delta\) as a function of pressure. The difference in binding energy has a minimum at around 10 atm. The average of the results for \(m_4^*\) at different pressures, is \((1.29 \pm 0.21)m_4\). The partial volume of \(^4\)He in \(^3\)He, \(v_4^*\), was obtained by taking the derivative of \(\Delta\) with respect to pressure. With \(m_4^*\), it was used to predict the diffusion coefficient \(D\).
Measurements of $D$ at 50 to 100 mK using the same apparatus, agree well with the theory.

A pre-wetting transition, in the $^4$He film in contact with the $^3$He, was observed at 24 atm.

Finally, we fitted the logarithm of the solubility at the saturated vapor pressure, measured at higher temperatures by various groups[1. 2. 5. 15. 16. 17] and by our group at lower temperatures, with a third order polynomial in $\log_{10} T$. Because of the disagreement of our data with Nakamura et al.'s[1], we reduced the weight of their data by about a factor of 10 in the fit. The data and fit are shown in Fig.5.1. The formula for the fit, valid between $T = 0.04$ to about 0.85 K, is.

$$\log_{10} \chi_{i}^{\text{sat}} = -0.36 + 1.92 \log_{10} T - 0.85(\log_{10} T)^2 + 0.59(\log_{10} T)^3 \quad (5.1)$$
Figure 5.1: The solubility of $^4\text{He}$ in liquid $^3\text{He}$ at $P \sim 0$ or saturated vapor pressure. The $\bullet$ and $\bigcirc$ are our measurements based on sample No.1 and No.2. The rest of the points are from various groups[1, 2, 5, 15, 16, 17]. The solid curve is a 3rd order polynomial fit to all the data, with the weight on the data by Nakamura et al[1] an order of magnitude smaller than the rest of the points.
Figure 5.1
5.2 Measurements of the Solubility and Diffusion Coefficient of $^4\text{He}$ in Liquid $^3\text{He}$ in the Fermi Liquid Region, (accepted for publication by *Phys. Rev. Lett.)*

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The solubility of $^4\text{He}$ in $^3\text{He}$ has been measured down to 40 mK at various pressures. The resulting values of $m_1^*$ and $v_1^*$, the effective mass and partial volume, are used to predict the diffusion coefficient $D$ from Fermi liquid theory. Measurements of $D$ at 50 to 100 mK agree well with the theory. At 24 atm, a pre-wetting transition is observed in the $^4\text{He}$ film in contact with the $^3\text{He}$. PACS numbers: 67.60.Dm, 67.55.Lf, 67.55.Hc, 68.45.Gd
Below 0.1 K, where liquid $^3$He obeys Fermi liquid theory, dissolved $^4$He impurities are predicted[25] to have a unique characteristic: their transport properties, such as the diffusion coefficient $D$, can be calculated from their thermodynamic properties. In this Letter we describe an experimental test of this prediction. To obtain the thermodynamic data, we measured $X_1^{\text{sat}}$, the solubility of $^4$He in $^3$He, as a function of temperature and pressure. We also measured the diffusion coefficient $D$ below 0.1 K. The solubility gives $E_4$, the $^4$He binding energy, and $m_4^*$, the effective mass. These are used to predict $D$, but they are also intrinsically interesting since they can be compared with microscopic theory[13, 14].

The scattering between the $^4$He and $^3$He quasiparticles at low temperatures is “forward scattering” where the particles are deflected very little in the center of mass frame. Forward scattering dominates because the $^4$He, which obey Bose statistics, have energies of the order of $k_B T$, much less than the Fermi energy $k_B T_F$. With the Pauli principle, this restricts the energy transfer to $\sim k_B T$, so that the momentum transfer is small compared to the $^3$He Fermi momentum $p_F$.

In Fermi liquid theory, the forward scattering amplitude is related to the Landau function $f^{34}$, the functional derivative of the energy with respect to the $^4$He and $^3$He distributions. In turn, $f^{34}$ is related[75, 18] to the thermal properties.

At low $T$, the $^4$He-$^3$He forward scattering amplitude is given by the formula derived by Saam and Laheurte[75]

$$a_0^{34} = \frac{f_0^{34}}{1 + F_0^3} = \frac{2}{3} v_4^* k_B T_F$$

(5.2)

Here $T_F = p_F^2/(2m_3^* k_B)$ is the Fermi temperature, $F_0^3$ the Fermi liquid parameter and $m_3^*$ the effective mass of liquid $^3$He. The $^4$He partial volume $v_4^*$ is the pressure derivative of the binding energy, $v_4^* = -dE_4/dP$. 133
From the Boltzmann equation in the $T \to 0$ limit, using the scattering amplitude in (5.2), Culman et al.\[25\] obtained the diffusion coefficient

$$ D = 0.4461 \left( \frac{\hbar}{m_4} \right) \left( \frac{m_3}{m_4} \right) \left( \frac{v_3}{v_4} \right)^2 \left( \frac{T_F}{T} \right) \tag{5.3} $$

where $v_3$ is the $^3\text{He}$ atomic volume. The finite temperature corrections to the product $DT$ have recently been estimated\[76\]. Compared to Eq. (5.3), they are smaller by a factor of order $T/T_F$. Since $T_F$ is 1.77 K at zero pressure\[77\], the corrections are probably small below 0.1 K.

By equating the $^4\text{He}$ chemical potentials in the $^3\text{He}$-rich upper phase and the $^4\text{He}$-rich lower phase, one finds for the solubility at low $T$,

$$ X_4^{\text{sat}} = \left( \frac{T}{T^*} \right)^{3/2} \exp \left[ -\left( \Delta + \pi_3^{\text{sat}} v_4 \right)/k_B T \right] \tag{5.4} $$

Here $T^* = 2\pi \hbar^2/(m_4 v_3^{2/3} k_B)$ is about 4 K. The energy $\Delta = L_4 - E_4$, which is about 0.3 K, is the difference in binding for $^4\text{He}$ in pure $^4\text{He}$ and in $^3\text{He}$. The term in $\pi_3^{\text{sat}}$, the osmotic pressure of a saturated solution of $^3\text{He}$ in liquid $^4\text{He}$ is small, and corrects for the lower chemical potential in the $^4\text{He}$-rich phase compared to pure $^4\text{He}$. It varies from 7 to about 20 mK, depending on the temperature and pressure\[65, 32\].

The principal difficulty in studying $^4\text{He}$ in $^3\text{He}$ below 0.1 K is its very small solubility. At 50 mK and zero pressure, $X_4^{\text{sat}}$ is about 2 ppm. This is so small, that it is difficult to measure the concentration directly. Instead, we measure it indirectly by monitoring the thickness $D^s$ of the superfluid $^4\text{He}$ film\[42, 1, 18\] on the walls of the container. Although the bulk liquid remains unsaturated, its concentration $X_4^{\text{b}}$ is related to the concentration at the surface of the film $X_4^{\text{sat}}$. By equating the $^4\text{He}$ chemical potentials in the bulk and above the film, we find

$$ k_B T \ln \left[ \frac{X_4^{\text{sat}}(P^s)}{X_4^{\text{b}}} \right] = \int_P^{P^s} (v_3 - v_4^*) dP' \tag{5.5} $$
Here $V(D^s)$ is the van der Waals potential at the surface of the film. Since the $^3$He-rich liquid is very nearly pure, we have approximated its atomic volume by $v_3$. Eq. (5.5) makes use of Henry’s law, $(\partial \mu_4 / \partial \ln X_4)_T = k_B T$, which depends only on the condition $X_4 \ll 1$.

The value of $X_4^{\text{sat}}$ in (5.5) is for the pressure $P^s$ at the surface of the film rather than the applied pressure $P$ in the bulk. In analyzing the data we correct for this effect which is important only at high $T$ when $D^s$ is small. For convenience, the correction is made self-consistently using Eq. (5.4). Apart from the small difference between $\pi_3^{\text{sat}} v_4$ at $P^s$ and $P$, the result is to simplify Eq. (5.5): $X_4^{\text{sat}}(P)$ is replaced by $X_4^{\text{sat}}(P^s)$, and $v_4^*$ is replaced by $v_4$, the atomic volume of pure $^4$He. Hence, we do not need $v_4^*$ to obtain $X_4^{\text{sat}}(P)$ from the data.

To find the bulk concentration $X_4^b$, we use the $^4$He conservation equation

$$X_4^b = X_4^0 - \mathcal{N}_4^s A/n$$

where $X_4^0$ is the overall concentration of the sample, $n = 0.55 \pm 0.02$ mol is the total number of moles in the container and $A$ is the area of the walls. The adsorption $\mathcal{N}_4^s$ is the amount of $^4$He per unit area in the film.

The film thickness $D^s$ and the related $\mathcal{N}_4^s$ are monitored using two parallel plate capacitors with gaps $d_N = 6.7$ and $d_W = 16.8 \ \mu\text{m}$ [78] (see Fig. 5.2). A ratio transformer bridge enclosed in a thermostat measures $R = C_N/(C_N + C_W)$, where $C_N$ and $C_W$ are the capacitances. Except for small edge and strain effects, changes in the dielectric constant and pressure of the bulk liquid do not affect $R$. However $R$ is sensitive to the thickness of the film. At $P = 0$, a change in $R$ of 1 ppm is equivalent
Figure 5.2: The solubility $X^{\text{sat}}_4$ near 0.03 atm as a function of $T$, and a section through the cell. The • and ○ are from our 17 and 30 ppm samples; the ◊ and □ from Ref.[1]. The pressure is controlled by compressing the bellows with liquid $^4\text{He}$. The capacitors $C_N$ and $C_W$ under the bellows monitor the thickness of the superfluid $^4\text{He}$ film.

to about 21 Å of film which is equivalent to about 8 ppm in $X^{b}_4$. At 24 atm, it equals 35 Å of film and 17 ppm in $X^{b}_4$. The noise in the circuit is 0.02 ppm/$\sqrt{\text{Hz}}$.

To obtain the potential $V(D^s)$ and the area $A = 550 \pm 22 \text{ cm}^2$, we emptied the cell of liquid and, without warming above 4 K, measured two samples of the remaining $^3\text{He}$-rich film in contact with the vapor. At $T = 0$, the first sample separated into $\sim 35$ Å of $^3\text{He}$ above $\sim 17$ Å of $^4\text{He}$. The second had the superfluid $^4\text{He}$ removed, reducing the thickness by 12 Å at $T = 0$. As $T$ was increased, $^3\text{He}$ and $^4\text{He}$ evaporated and, from the film thickness $D^s$, we obtained the amount of $^3\text{He}$ or $^4\text{He}$ in the vapor. The formulas $V(D^s)/k_B T = \ln(P_3/P_3^{\text{sat}}) = \ln(P_4/P_4^{\text{sat}})$, where $P_3^{\text{sat}}$ and $P_4^{\text{sat}}$ are the known vapor pressures over a bulk mixture with the same concentration, gave $V(D^s)$ and the area $A$. The potential agrees well with the retarded potential of a gold surface (the walls of the cell were gold-plated), covered with a thin layer of air (9 Å) and the
usual inert layer of strongly-bound, non-superfluid helium about 5 Å thick[79, 30]. The thickness of the air layer is consistent with the amount of air left in the cell before it was cooled.

To calculate $N_4^1$ and $D^s$ from measurements of $R$, we constructed a detailed model of the pressure and concentration distribution in the film. This is based on the measured $V(D^s)$, known properties of liquid $^3$He-$^4$He mixtures, and the Clausius-Mosotti equation.

The sample cell[78] is cooled by a dilution refrigerator through a superconducting heat switch, and sealed by a valve at the temperature of the mixing chamber. The $^4$He-$^3$He sample is enclosed in a BeCu bellows compressed by $^4$He to control the pressure. To measure the diffusion coefficient $D$, the sample is compressed adiabatically while measuring $R$ as a function of time. This monitors the diffusion of the $^4$He in the cylindrical space enclosed by the bellows[78]. Some of our preliminary measurements of $D$ appeared in Ref.[80].

To find $N_4^{sat}$, equilibrium values of $R$ are compared with $R_0$, measured at the same $P$ and $T$, but with the superfluid $^4$He film drained away. The valve is opened slightly to form a superleak, allowing the superfluid part of the $^4$He film to escape to higher temperatures. This is an effective way to purify the sample or to change its concentration[1]. The $^4$He is stopped by another valve at 4 K and it can be re-admitted to the cell by warming to 1 K. At constant $P$, the measured temperature dependence of $R_0$ is roughly $T^2$ and approximately $-50$ ppb between 0 and 0.3 K.

Fig. 5.3 shows $R - R_0$ vs $T$ at various pressures for the lowest concentration sample, $X_4^0 \approx 17$ ppm (excluding the inert layer). Since $R_0(P, T)$ was sometimes measured months after the measurements of $R$, some corrections, independent of

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Figure 5.3: Change of capacitance ratio $R - R_0$ versus $T$ for the 17 ppm sample at various pressures. From top to bottom the pressures are: 0.03, 5.06, 10.6, 14.8, 19.85, and 24.0 atm. The inset is an enlargement of some of the data at 24 atm.

$T$ and $P$, have been made for long term shifts in the ratio-transformer. Data for all but the lowest concentration sample were affected by capillary condensation at low temperatures. A fit to the four lowest concentration samples (17, 30, 40, and 60 ppm) as well as the vapor-film samples, using the known interfacial tension[6], gives the volume condensed as a function of $D^*$. There was little or no hysteresis, indicating very few bottle-shaped voids. The fit to the volume condensed is consistent with the roughness of the gold-plated machined surfaces in the cell, as measured by an atomic force microscope. Because the capillary condensation has a large effect on the solubility data for the more concentrated samples, we used only the 17 and 30 ppm samples to obtain values of $\Delta$ and $m^*_1$. The diffusion measurements were made on the 60 and 100 ppm samples to get greater changes of the film thickness with pressure. For diffusion, only a minor correction is needed for capillary condensation. Further details will be given in a longer paper.
The data in Fig. 5.3 at 24.0 atm, just below the freezing pressure of $^4$He, have an interesting jump at $\sim 80$ mK (shown in the inset), with no hysteresis. Normally, the surface free energy of the solid (which only partially wets the walls[81]) prevents freezing, even though the local pressure near the wall is above freezing.

Our data at 24 atm do not seem to indicate freezing. Instead, it seems that there is a "pre-wetting transition"[82] as the $^4$He-rich film becomes superfluid. As $T$ is lowered through 80 mK, a surface free energy barrier is overcome and the superfluid film appears with a thickness of about 3.5 Å (1.5 nmol/cm$^2$) above the $\sim 5$ Å of the non-superfluid film. Below 80 mK the data agree with the curve in Fig. 5.3. This corresponds to values of $X_i^0$, $m_i^*$ and $\Delta$ that are consistent with those at lower pressures, indicating that the film below 80 mK is superfluid with no solid phase. A similar transition (differently interpreted) was observed by Tholen and Parpia[74] at about the same film thickness and pressure. Their experiments, in a silver sinter at much lower temperatures, showed hysteresis, perhaps associated with the pores in the sinter.

The curves in Fig. 5.3 represent a fit below 0.1 K to the theory embodied in (5.4) to (5.7). From the fit, we find that $X_i^0$ is nearly the same at each pressure for a given sample. This confirms the accuracy of our model which relates $D^s$, $X_i^s$ and $R - R_0$ for the film. However, within the experimental error, including the uncertainty in $V(D^s)$, there is a small decrease of 0.5 to 1 ppm in $X_i^0$ with pressure, corresponding to an increase in the $^4$He in the non-superfluid inert layer. This is consistent with other experiments on various substrates[30, 74]. We have assumed the thickness of the inert layer, as opposed to the amount of $^4$He in it, to be constant at 5 Å.
Figure 5.4: The difference in binding energy, $\Delta = L_4 - E_4$, and the effective mass ratio $m_4^*/m_4$ as a function of pressure. The $\bullet$ are from our 17 and 30 ppm samples. The $\triangledown$ were estimated in Ref.[18] from the data in Ref.[1]. The dashed curves are the microscopic theory from Refs.[13] and [14].

From $R - R_0$, using (5.5) to (5.7) we obtain the solubility $X_4^{\text{sat}}(P,T)$. The values at 0.03 atm are shown in Fig. 5.2. The curve is the fit and its extrapolation above 0.1 K. Data at high $T$ where $X_4^{\text{sat}}/X_4^{\text{b}}$ is larger than $\sim 10$ have large uncertainty, and they are not used in the fit. Our solubility agrees well with the pioneering measurements of Nakamura et al.[1] down to 90 mK, but is slightly smaller at lower temperatures.

Fig. 5.4 shows the fitted values of $\Delta = L_4 - E_4$ and the effective mass ratio as a function of pressure. Since $\Delta$ has a positive minimum at $\sim 11$ atm, $^4$He is insoluble in $^3$He at $T = 0$ at all pressures. The full curve was fitted to $\Delta$ (excluding the point at 24 atm) and used to determine $v_4^*$. Based on the integration of $v_4^* - v_4 = d\Delta/dP$, the curve assumes that the "Bardeen-Baym-Pines parameter"[5], $\alpha_4 \equiv v_4^*/v_3 - 1$, is
linear in the $^3\text{He}$ atomic volume $v_3$. The fit is $\alpha_4 = -0.31 + 0.80(1 - v_3(P)/v_3(0))$.

This agrees with the extrapolation from high temperature and high concentration made by Laheurte[5]. Density measurements by Sato and Suzuki[6], on 2.5% and 5% samples, extrapolate to $-0.30 \pm 0.02$ at $P = 0$, which agrees well with our equation.

It is quite surprising that, below the minimum in $\Delta$ at $\sim 11$ atm, $v_4^*$ is smaller than $v_4$. Also, $v_4^*$ is quite weakly dependent on $P$. Both of these features were predicted by the microscopic theory[13], shown as the dashed curve for $\Delta$ in Fig. 5.4.

The effective mass ratio $m_4^*/m_4$, shown in the lower part of Fig. 5.4, has standard deviations which are highly correlated with those in $\Delta$. The usable range of $T$ is not quite large enough to separate the exponential and $3/2$ power-law $T$-dependences in (5.4) decisively. The horizontal line at $m_4^*/m_4 = 1.29$ is a weighted fit to the data. The standard deviation about the mean is 0.21. Although some of the data and error bars extend below 1, Leggett[83] has shown that an impurity cannot have less than its bare mass in a Fermi liquid.

The dashed curve for $m_4^*/m_4$ in Fig. 5.4 is the microscopic theory[14]. The mass enhancement $m_4^* - m_4$ is small compared to the enhancement of the $^3\text{He}$ mass in liquid $^4\text{He}$. According to the theory[14], the backflow around $^4\text{He}$ in liquid $^3\text{He}$ has a small effect mainly because the $^3\text{He}$ liquid density is smaller than that of $^4\text{He}$. In fact, the classical Stokes formula $(1 + \alpha_4)m_3/2$, half of the mass of the displaced liquid, gives $m_4^*/m_4 = 1.26$ at $P = 0$ and 1.33 at 20 atm, agreeing with both theory and experiment.

The product of the diffusion coefficient $D$ and the temperature $T$ predicted from Eq. (5.3), using $m_4^*/m_4 = 1.29 \pm 0.21$, is shown in Fig. 5.5. The width of the band is due to the uncertainty in $m_4^*$.
Figure 5.5: The product of the diffusion coefficient and temperature $DT$ versus pressure. Our results are: 60 ppm, $\Delta$ 65 mK; 100 ppm, ■ 51 mK, • 83-93 mK. The ◇ were measured by Vvedenskii and Peshkov, Ref.[19], at freezing from 0.55 to 1.0 K. The band is the prediction from Eq. (5.3).

Within the errors, the agreement between theory and experiment in Fig. 5.5 is remarkable, since there are no adjustable constants. We conclude that Eqs. (5.2) and (5.3) are correct, but greater accuracy in determining both $D$ and $m_4^*/m_4$ would be desirable.

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A.1 R-FT-INT-SMPL21-2W.FOR

implicit real*8 (a-h,o-z)
character fn*12, dtnlst(30)*8, today*12, now*12, filename*(*)
parameter (filename='r-ft-int-smpl21-2w.for')

This program will fit the data of four different samples: #9, #0, #1, and #2. There are 4 files or pressures for #9 and #0 each, and 2 files or pressures for #1, and 9 files of 6 pressures for #2.
The fitted parameters are:

X40 for the 4 samples: the overall He4 concentration when all the He4 are in the bulk.
dE & m4*/m4 for 11 Ps: I made it 11 pressures, but it could be some other numbers.
D_solid for the 11 Ps:
R0 for all the 19 fits:
D_air and A and W: A is the total area, and W is the depth of a wedge needed for the capillary condensation model.

Subroutine:
Open Dsnsfile in "r-opn-dsns-int.for" : open and read "drdnsdtpt.dat"
Into arrays ddt(nd), tdt(nt), drdt(nd,nt,np), and dmsdt(nd,nt,np), for interpolation.
Curfit etc. in "curfit.for": it's been modified so that
1) it can skip up to five parameters and leave them constant by specifying ja1,...,ja5.
2) it can calculate the individual chisquare or chisquare per points for each data file.

Curfit in "curfit.for"
Function in "r-fnc-int-1lp.for": here "-int-" stands for interpolation.
V3 in "r-v3.for": calculates the molar volume of He3.
Addr in "r-dsns-int-1lp.for": calculates R as a function of Ds at T and P, which are passed through some common blocks. The original interpolation is for 14 different pressures. So now a few P
will share the same pressure coefficients for the conversion from R to Ds and Ns
Ans in "r-dsns-int-1lp.for":
c f ds in "r-ds.for-int":
c jan 1997, July 1997, Aug 1997 to include area,
c
dimension ai(500),r(500),yfit(500),sigmay(500)
dimension a(100),sigmma(100),deltaa(100)
dimension v3p(6),v4p(6),pp(6),delte(6),sigmea(6)
dimension a4coef(100),sigmma4(3),da4coef(3),a4(6),v4str(6)
dimension ip(500),ir0(500),ttbl(500),iplst(30),islst(30),is(500)
dimension nptsf(30),chisqr(30),npptsold(30),achisqr(2),nptsaf(2)
dimension t1(30),t2(30),t3(30),syserr(30)
dimension covar(100,100),covara(100,100),ja(10)
real*8 v3,v4
c to pass the table of temperature to r-fnc-glb.for
common /temptable/tbl

c to pass the index of samples and pressures to r-fnc-glb.for
common /paraindex/ip,ir0,is
common /switch/switch

data sigmay /500*0.045/
data sigmaa /100*0.0/
data a4coef /100*0.0/
data pp /0.4,74.3,150.0,217.7,291.6,353.3/
data ja /10*10000/
nolst=11
nop=6
dtfnlst(1)='200s616'
dtfnlst(2)='200e614'
dtfnlst(3)='205d613'
dtfnlst(4)='210e613'
dtfnlst(5)='215n613'
dtfnlst(6)='220e613'
dtfnlst(7)='220d623'
dtfnlst(8)='220j713'
dtfnlst(9)='224j713'
dtfnlst(10)='220e613'
dtfnlst(11)='101612'

iplst(1)=1
iplst(2)=1
iplst(3)=2
iplst(4)=3
iplst(5)=4
iplst(6)=5
iplst(7)=5
iplst(8)=5
iplst(9)=6
iplst(10)=1
iplst(11)=3
islst(1)=1
islst(2)=1
islst(3)=1
islst(4)=1
islst(5)=1
islst(6)=1
islst(7)=1
islst(8)=1
islst(9)=1
islst(10)=7
islist(11)=6

write('Please type tmin1-6')
read(tmin1,tmin2,tmin3,tmin4,tmin5,tmin6)

max=300.
tmax=300.
tmin(1)=0.
tmin(2)=100.
tmin(3)=200.
tmin(4)=0.
tmin(5)=90.
tmin(6)=100.
tmin(7)=200.
tmin(8)=0.
tmin(9)=90.
tmin(10)=100.
tmin(11)=160.
serr(1)=0.035
serr(2)=0.033
serr(3)=0.033
serr(4)=0.033
serr(5)=0.033
serr(6)=0.033
serr(7)=0.033
serr(8)=0.033
serr(9)=0.033
serr(10)=0.053
serr(11)=0.045
c a(1) to a(6) is -dtE
do 50 i=1,6
50 a(i)=0.25
a(1)=0.34197
a(2)=0.25915
a(3)=0.23480
a(4)=0.24369
a(5)=0.27662
a(6)=0.31841
c a(7) is are U
a(7)=600.
c a(8) to a(15) is x40 ppm
do 65 i=1,nop
65 a(i+7)=20
do 66 i=1,2
66 a(i+13)=33

c a(16) and a(21) is (m4*/m4)
do 60 i=1,nop
60 a(i+15)=1.0
do 61 i=1,2
61 a(i+20)=1.0

c a(22) and a(32) is RO
i=-10
a(32+i)=-0.46
a(33+i)=1.15
a(34+i)=0.79
a(35+i)=1.43
a(36+i)=0.88
a(37+i)=1.4
a(38+i)=0.78
a(39+i)=0.15
a(40+i)=0.04
a(41+i)=-0.7
a(42+i)=0.3

c a(33) is capillary volume/2L for sample#1, in "ang*cm":
c a(34) is capillary volume/2L for sample#2, in "ang*cm":
a(33)=100.
a(34)=0

c write(*,*).'Please input errsign for air and solid(+/-1):'
c read(*,*) errsign_air, errsign_solid

c a(35) Dair:
a(35)=10
zero=0.
a(36)=5
nterms=36-1
ntera=36

c Delta a will be about 1e-5 of the estimated value
do 110 i=1,ntera
110 deltaa(i)=dabs(a(i))*1e-5
i=1
ntpsold(i)=1
do 400 j=1,nofls
   fn=dtfnlst(j)//.prn'
   write(*,*)'Openin',fn
      open(unit=10,file=fn,status='old',err=911)
100 read(10,*,end=200)tt,dtt,rr,dr,pp,dp

c t1 < T < tmax:
   if(tt.lt.t1(j)).or.(tt.gt.tmax).or.
   & ((tt.gt.t2(j)).and.(tt.lt.t3(j))))goto 100

c get rid of that particular point of "200s615.prn" at T=172 mK
if(rr.lt.-0.49)goto 100

tbl(i)=tt/1000.
ri=rr
sigmay(i)=sqrt(dr**2+syserr(j)**2)
     ip(i)=iplst(j)
     ir0(i)=j
     is(i)=islst(j)
     ai(i)=i
\begin{verbatim}
C area with area/volume ratio of 27.52+/-0.37 from adsorption fit
C n0=0.55+/-0.02 => volume=0.55*36.86=20.27+/-3.67:
C 0.37/27.52*100%=1.34%
C => total relative error : 3.8%
ai(i)=-10
C area/vol = 27.5196 for wvl=100
C r(i)=20.27*27.5196
C r(i)=515.44
C r(i)=549.72
C sigmay(i)=22.4
i=i+1
ai(i)=-20
C Dair=8.9209 for wvl=100
C r(i)=8.9209
C r(i)=7.78
C r(i)=8.703
C sigmay(i)=0.58
i=i+1
ai(i)=-30
C Dsolid=4.5931 for wvl=100
C r(i)=4.5931
C r(i)=4.7417
C r(i)=4.612
C sigmay(i)=0.69
C w of the wedge
C capillary volume/2L for sample#1, a data point from fit, in "ang*cm":
C ai(i)=-20
C r(i)=15
C sigmay(i)=300
npts=i
write(*,*)'Total # of points:',npts
C open the ds/ns vs r,t fitting file to get the fit parameters
C call opndsnsfile
mode=1
delt_chisqr=1e-5
C for delt E fit:
C zero=0
C nterms=3
C initial value for dacof and sigma:
v30=v3(zero,zero)
do 230 i=1,nop
v3p(i)=v3(pp(i),zero)
do 230 v4p(i)=v4(pp(i))
nptsaf(1)=nop
noflsa=1
de0=0.25547452
a40=-0.3044003
a41=-0.7045687
a4coef(1)=de0
\end{verbatim}
a4coef(2)=a40-a41+1.
a4coef(3)=a41
do 290 i=1,3
290 da4coef(i)=a4coef(i)*1e-5
delta(nop+1)=-0.300
sigmae(nop+1)=0.015

c switch : 1 for quadratic fit for deltE(v3p);
c:-1 for fit of Ds(T).
switch=-1
flamda=10
old_chisqr=1e10

c ja is index which a(ja) is fixed!
ja(1)=34
c ja(2)=2
c ja(3)=3
c ja(4)=4
c ja(5)=5
c ja(6)=6
c ja(7)=7
c ja(8)=21
c ja(9)=22
do 20 i=1,100

call curfit(ai,r,sigmay,npts,nterms,mode,a,deltaa,sigmaa,
& flamda,yfit,chisqr,nptsf,nofls,covar,ja)
chis=chisqr(nofls+1)
write(*,3)'Compl',i,'Lamda',flamda,'dlch',
& old_chisqr-chi,'Ch/fr',chi,'Chi',chi*(npts-nterms)
3 format(1x,a4,13,a6,e8.1,a7,e9.2,a6,f16.12,a4,f16.10)
write(*,17)'Chi/pnt',(chisqr(j),j=1,10)
17 format(1x,a7,10f8.3)
write(*,6)'a7:','a(7)',
write(*,14)'
6 format(1x,a8,f9.3,3(a9,f10.2))
write(*,17)'
4 format(1x,a8,8f7.2)
write(*,8)'dltE:',(a(j),j=1,6)
8 format(1x,a8,6f7.2)
write(*,9)'m4*s:',(a(j),j=16,21)
9 format(1x,a8,6f7.2)
write(*,11)'msolid:',(a(j),j=36,40)
11 format(1x,a8,5f7.2)
if((old_chisqr-chisqr(nofls+1)).lt.delt_chisqrgoto 21
write(*,*)old_chisqr-chisqr(nofls+1)
old_chisqr=chisqr(nofls+1)
20 continue

21 continue

c rearrange the error bars:
ja2=500
do 23 j=nterms,1,-1
ja1=j
do 25 k=1,10
25 if(ja2.le.ja(k))goto 28
26 ja1=ja1+1
27 sigmaa(ja1)=sigmaa(j)
ja2=ja1-1
do 26 k=10,1,-1
26 if(j.eq.ja(k))sigmaa(j)=0
23 continue
switch=1
flamdal=1e-4
old_chisqr=1e10
do 270 j=1,nop
sigmae(j)=sigmaa(j)
if(sigmas(j).lt.1e-6) sigmas(j)=1e-6
270 delte(j)=a(j)
do 70 j=1,10
70 ja(j)=1000
do 220 j=1,100
  call curfit(pp,delte,sigmas,nop,naterms,mode,a4coef,da4coef,
&   sigmaa4,flamdal,yfit,achisqr,nptsa1,noflsa,covar,a)
write(*,*),'flamdal,achisqr : ',flamdal,achisqr(2)
if ((old_chisqr-achisqr(2)).lt.delt_chisqr) goto 221
220 old_chisqr=achisqr(2)
221 a40=a4coef(2)+a4coef(3)-1.
a41=a4coef(3)
de0=a4coef(1)
write(*,*)'deltE0 alpha40 alpha41'
write(*,243)de0,a40,a41
write(*,242) 'p','v3','v4','v4*','a4','de','a','sigmas'
243 format(ix,3f13.9)
242 format(ix,8a9)
do 240 k=1,nop
a4(k)=a40+a41*(v3p(k)/v30-1.)
v4str(k)=(1.+a4(k))*v3p(k)
write(*,241)pp(k),v3p(k),v4p(k),v4str(k),a4(k),
&   yfit(k),a(k),sigmaa(k)
241 format(ix,f9.2,3f9.3,3f9.5,f10.4)
240 continue
260 continue
open(10,file='glbfitsmpl21.out',status='unknown',err=911)
call date(today)
call time(now)
write(10,*),today,now,' glbfitsmpl21.out for ','filename,
&   'chisqr = ' ,chisqr(nofls+1)
write(10,*)
do 85 i=1,nop+2
  ix=i+7
85 write(10,246) 'X40_','i','(ppm): ',a(ix),'+/-',sigmaa(ix)
246 format(ix,a6,i2,a6,f10.3,a4,f10.4)
write(10,*)
write(10,5) , A (cm^-2) : ',a(7),'+/-',sigmaa(7)
write(10,5) Dair (ang) : ',a(35),'+/-',sigmaa(35)
write(10,5) Dsold (ang) : ',a(36),'+/-',sigmaa(36)
write(10,5) wv1 (ang*cm) : ',a(33),'+/-',sigmaa(33)
write(10,5) wv2 (ang*cm) : ',a(34),'+/-',sigmaa(34)
write(10,*)
do 80 i=1,nop
  i8=i
80 write(10,12) '-deltE_','i','(K) : ','a(i8),'+/-',sigmaa(i8)
12 format(ix,a12,i2,a10,f12.4,a4,e10.3)
write(10,*)
do 81 i=1,nop
  im=i+15
81 write(10,12) 'm4*/m4_','i',' : ','a(im),'+/-',sigmaa(im)
write(10,*)
c do 82 i=1,nop
  c id=i+35
  c82 write(10,12)'Dsolid_ ',i,'(angstrom) :' ,a(id),' +/- ',sigmma(id)
c write(10,*)
  write(10,242)'p', 'v3', 'v4', 'v4*', 'a4', 'de', 'a', 'sigma'
do 84,k=1,nop
  84 write(10,241)pp(k),v3p(k),v4p(k),v4str(k),a4(k),
         & yfit(k),a(k),sigmma(k)
write(10,245)'Chisqr of fit of dE vs P: ',old_chisqra
245 format(1x,a30,f15.7)
write(10,*)
  write(10,15)'file & P #', 'npts', 'press(psi)', 'chisqr/pnpts',
     & ' T1 : T2 : T3 : Tmax (mK)', 'add err (ppm)'
15 format(1x,a12,a6,a11,a14,a25,a14)
do 120 i=1,nofl5s
  jp=iplst(i)
120 write(10,13)i,jp,nptsf(i),pp(jp),chisqr(i),
     & t1(i),t2(i),t3(i),tmax,syserr(i)
13 format(1x,3i6,f11.2,f10.5,f5.0,f6.0,f7.3)
write(10,*)'Total points : ',npts
do 83 i=1,nofl5s
  ir=i+21
83 write(10,12)' R0_ ',i,'(ppm) :' ,a(ir),' +/- ',sigmma(ir)
write(10,*)
  write(10,*)'alpha_4 parameter : '
write(10,243)de0,a40,a41
close(10)
open(10,file='m4dile.out',status='new',err=911)
write(10,1002)'-dlt_E', 'err_dE', 'm4*/m4', 'err_m4*', 'X40',
     & 'err_X40', '-dE_fit', 'alpha_4'
1002 format(1x,4a8,a4,3a8)
do 1000 i=1,nop
  1000 write(10,1001)a(i),sigmma(i),a(15+i),sigmma(15+i),
     & a(7+i),sigmma(7+i),yfit(i),a4(i)
1001 format(1x,f8.5,f8.5,f8.4,f7.3,f7.3,f6.3,f8.5,f8.4)
write(10,*)'P(psi) v3 v4 delte(K) alpha_4 v4*
1200 d=0,p=0.350
  v3pt=v3(p,zero)
v4pt=v4(p)
pp1(p)=p
dep=functn(pp,1,a4cof)
a4p=(a4cof(2)+a4cof(3)-1.)*a4cof(3)*(v3pt/v30-1.)
v4strp=(1.+a4p)*v3pt
1200 write(10,1201)p,v3pt,v4pt,dep,a4p,v4strp
1201 format(1x,f8.2,2f10.3,2f10.5,f10.3)
close(10)
write(*,*)'chisqr = ',chisqr(nofl5s+1)
write(*,*)
do 96 i=1,nop+2
ix=i+7
96 write(*,246)' X40_ ',i,'(ppm) :',a(ix),'+/- ',sigmma(ix)
write(*,5)' A (cm^2) :',a(7),' +/- ',sigmma(7)
write(*,5)' Dair (ang) :',a(35),' +/- ',sigmma(35)
write(*,5)' Radius (cm) :',a(33),' +/- ',sigmma(33)
write(*,5)' W (1/16") :',a(34),' +/- ',sigmma(34)
write(*,*)
do 90 i=1,nop
ie=i+0
90 write(*,12) ' -deltE',i,' (K) : ','a(ie)','+/-',sigmaa(ie)
write(*,*)
do 91 i=1,nop+2
im=i+16
91 write(*,12) ' m4*/m4 ',i,' : ','a(im)','+/-',sigmaa(im)
write(*,*)
c do 92 i=1,nop
    c_id=i+35
c92 write(*,12) 'Dsolid',i,'(angstrom) : ','a(id)','+/-',sigmaa(id)
c write(*,*)
c do 93 i=1,nofls
c iy=i+22
c93 write(*,12) ' D solid',i,'(angstrom) : ','a(id)','+/-',sigmaa(id)
c write(*,*)
do 94,k=1,nop
    c_pp(k),v3p(k),v4p(k),v4str(k),a4(k),
    & yfit(k),a(k),sigmaa(k)
write(*,245) 'Chisqr of fit of dE vs P : ',old_chlsqra
write(*,*)
write(10,15)'file & P #','npts','press(ksi) ','chisqr/pnpts',
   & 'T1 : T2 : T3 : Tmax (mK)' ,'add err (ppm)'
do 130 i=1,nofls
    jp=iplst(i)
130 write(*,13)i,jp,nptsf(i),pp(jp),chisqr(i),
   & t1(i),t2(i),t3(i),tmax(syserr(i)
write(*,*)
write(*,*)'Total points : '+npts
write(*,*)
f c fit results saved into "glbfitxmpl21.para"
open(10, file='glbfitxmpl21.para',status='unknown',err=911)
write(10,*)nofls
write(10,*)npar
write(10,*)nters
write(10,*)npara
do 30 i=1,npara
30 write(10,*)a(i)
do 34 i=1,nofls
34 write(10,*)syserr(i)
do 35 i=1,nters
35 write(10,*)covar(i,j)
close(10)
stop
911 write(*,*)'I/O error'
end
A.2 R-FNC-INT-SMPL21-2W.FOR

c r-fnc-all-int-smpl21-2w.for

c Using parameter set based on "ns0, x40, and alpha4

to find the root of fds(r), which gives "r" as

c a function of "t=tt".

c main program:

c r-ft.for

c Subroutine:

c v3(t,p) in r-v3.for

c fds(r) in r-ds.for

c ads(r) and ans(r) in r-dsns.for

c Jan 1997, July 1997

c

function functn(tt,i,aa)

implicit real*8 (a-h,o-z)

parameter (am3=3.016,am4=4.0026,v30=36.821,v40=27.579)

parameter (c30=1.7844e4,c40=2.3823e4,atmcgs=1.01325e6)

parameter (gasconst=8.314e7)

c values of rhoc and Pc could be found in P.19 of book "thesis"

parameter (rhoc=0.05528,rhoc=0.09426)

parameter (pc3=-2.7902*atmcgs,pc4=-9.4944*atmcgs)

c K=m*c0^2/(rho_0/rhoc-1)^2/R (K), see P.19 of "thesis":

parameter (ak3=am3*c30**2/(am3/v30/rhoc-1)**2/gasconst)

parameter (ak4=am4*c40**2/(am4/v40/rhoc-1)**2/gasconst)

dimension ip(500),ir0(500),is(500),ttbl(500)

dimension aa(1),tt(1)

real*8 functn,fds,adr

external fds

common xs0,x40,area0,area,dsolid,dair,ww1,ww2,v,xb,xs,am4str

c pass t to fds(r) in r-ds.for

common /temp/t

common /temptable/ttbl

common /paraindex/ip,ir0,is

common /pressindex/jp

common /switch/switch

c f1=int(v,dP); f2=int(v^2/v30,dP)

f1(x)=x*x/2.-2.*x+dlog(x)

f2(x)=x**2.*dlog(x)-1./x

c coef=m/v0/rhoc-1:

rhobar(p=pc,p,coef)=1.+coef*(1-p/p)**(1./3.)

explnt=40.

era=0.0

err=1e-14

c coef3=am3/v30/rhoc-1

c coef4=am4/v40/rhoc-4-1

coef3=am3/v30/rhoc-1

c checking:

c previous calculation shows that:

K3=49.76; K4=93.90; K33 is about 73

-cp3/coef3^3=24.38; -pc4/coef4^3=60.46

write(*,*)'Checking parameters: '

write(*,*)'K3=49.76,k4=93.90,k3=73,-pc3/coef3^3=24.38'

write(*,*)'-pc4/coef4^3=60.46',ak3,ak4,am3/v30/rhoc*ak3,

c & -pc3/atmcgs/coef3^3,-pc4/atmcgs/coef4^3

pause

if (switch.gt.0.5) then

p=tt(i)/14.69*atmcgs

152
if (p.lt.0) then
    functn = aa(2) + aa(3) - 1
    return
endif
rho3bar = rho3bar (pc3, p, coef3)
rho4bar = rho4bar (pc4, p, coef4)
rho30bar = am3/v30/rho3c
rho40bar = am4/v40/rho4c
delte = aa(1) + aa(2) * ak3 * (f1(rho3bar) - f1(rho30bar)) +
        & aa(3) * ak3 * am3/v30/rho3c * (f2(rho3bar) - f2(rho30bar)) -
        & ak4 * (f1(rho4bar) - f1(rho40bar))
    functn = delte
    return
endif
if (switch.gt.-0.5) then
    write('**','*something is wrong!')
    stop
endif
j = tt(i) + err
tstr0 = 4.91
area0 = aa(7)
daair = aa(35)
dsolid = aa(36)
wv1 = aa(33)
wv2 = aa(34)
if (j.lt.1) then
    functn = area0
    if (j lt. 11) functn = daair
    if (j lt. 21) functn = dsolid
    return
endif
j = tt(i) + err
t = ttbl(j)
rrt = t * 1e3
jp = ip(j)
jl0 = ir0(j)
js = is(j)
if (jp eq. 6) dsolid = 9
x40 = aa(6+jp+js)/1e6
c de4t = -aa(jp+js-1)/t
c am4str = aa(14+jp+js)
de4t = -aa(jp)/t
am4str = aa(15+jp)
ro = aa(21+jl0)
c if (de4t gt. explmt) de4t = explmt
xs0 = (t/tstr0)**1.5*exp(de4t)
da = -20
db = 5e3
nitr = 100
call dzbren(fds, era, err, da, db, nitr)
if (db .le. 0) db = 0.
   dr = adr(db)
   functn = dr + r0
   return
end
A.3 R-DS-2W.FOR

C r-ds-2w.for
C Calculate the difference of Xb (calculated from the conservation
C of He4) and Xt (calculated from solubility equation) with "t" and
C "r", the temperature and the ratio. The parameters of "ns0, xs(the
C saturated concentration in the x0 unit), and a4, he4 excess volume
C Subroutines:
C ads(r) and ans(r) in r-dsns.for
C
C function fds(ddss)
implicit real*8 (a-h,o-z)
real*8 fds,ans,v3,opsat
parameter (hal=1.43916487,ha2=0.7721781297)
dimension pp(5)
data pp/0.4,74.3,150.0,217.7,291.6/
common /temp/t
common xsO,x4,darea,area,dsolid,dair,wb1,wb2,v,xs,am4str
common /pressindex/jp
common /ps/ps
C from MAPLE program of "capill4" Dec.15.97
hf(x)=x*(hal+x*(ha2+x))
p=pp(jp)/14.69
vlmt=alog(10e10)
epsd=0.001
gamaO=3113.1
gama=835.6
dhlf=160.
an0=0.55
annss=ans(ddss)/1e6
if (((ddss+dsolid).lt.epsd).or.((ddss+dsolid+dair).lt.epsd))then
  xbxs=0
ds=dsolid+dair
else
  ds=ddss+dsolid+dair
  v=-((gamaO-gama)/ds**3/(1+1.64*(ds/dhlf)**1.4)**(1./1.4)
ds=ds+dair
  v=v-gama/ds**3/(1+1.64*(ds/dhlf)**1.4)**(1./1.4)
ds=ds+dair
  xbxs=dexp(xsxbv(v,p)/t)
endif
p=pp(jp)
ppss=ps*14.69
v3p=v3(p,t)
v30=v3(zero,zero)
p3v4=opsat(ppss,t)
xs=xso*am4str**1.5*v3p/v30*dexp(-p3v4/t)
x=x*xbxs
C lamda=31.6 for He3/He4, 21.6 (?) for He3, 15.75 for He4:
almda=31.6
cir=14.
d0=dsolid+dair
area=area0
h1=340.
h2=800.
an1=2.

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an2=2.
c hds=h(ds/alamda)*alamda-d0
hds=dair+hf((ds-dair)/alamda)*alamda-ds
if(hds.le.1e-4)goto 100
wv=wvl*(hds/h1)**an1
c if(hds.gt.h1)wv=wvl+wv2*(hds**an2-h1**an2)/(h2**an2-h1**an2)
if(ds.gt.d0)area=area0+2.*cir*wv/(ds-d0)
100 fds=(an0*x40-annss*area)-xb*an0
return
end
This program is to calculate $D_s$ and $N_s$, the film thickness and coverage in the units of angstroms and micro mol/cm$^2$, from the ratio, which is the argument of $ads(r)$ and $ans(r)$. Note that all of them are real*8 type data. The formulae are based on Hans’ calculation, which are represented as coeff(10). Coeff(10) are passed from parameter files, DS-VS-RT.PAR and NS-VS-RT.PAR, which are opened in the main program.

Also, whichever program to call ads and ans, it need to pass "t" in common block "/temp/" and "p" in common block "/pressure/".

Implicit real*8 (a-h,o-z)
Real*8 ads,v3,v4
Parameter (nd=53,nt=20,np=14)
Parameter (a=-0.54585485,b=0.04411686,b2=-0.02941486)
Parameter (c=-0.002186902,c2=-0.0003465146,d=3.728163e-6)
Dimension ddrdata(nd,nt,np),dnsndata(nd,nt,np),ddata(nd),tdata(nt)
Dimension p(6),ipp(6)
Common /temp/t
Common /drnsvsdtp/ddrdata,dnsndata,ddata,tdata
Common /pressindex/ipp
Data p/0.4,74.5,150.0,217.7,291.5,353.3/
Data ipp/1,5,7,10,12,14/
C Bilinear formula:

$$f_{blin}(x,x1,x2,y1,y2) = \frac{(y1-y2)}{(x1-x2)}(x-x1)+y1$$

$$f0(ds,t,p) = a+(c+c2*t*t)*p+d*p*p*(b+b2*t*t)*ds$$

Ipp=ipp(ipp)

D solid0=5 dair0=10 are the thickness of the inert and air layers used by Hans’ calculation:

D solid0=5
dair0=10.
x1=ds+dsolid0+dair0
x2=t

C find i and j:
do 100,i=0,nd-1
c ddata is strictly increasing
100 if (x1.le.ddata(i+1)) goto 101
c ds is > ddata(nd)=16
i=nd-1
101 continue
if(i.eq.0)i=1
xli=ddata(i)
xlipi=ddata(i+1)
do 110,j=0,nt-1
c tdata is strictly increasing
110 if(t.le.tdata(j+1)) goto 111
c T is > tdata(nd)=350
j=nt-1
111 continue
if(j.eq.0)j=1
x2j=tdata(j)
x2jp1=tdata(j+1)
c write(*,'i,j,ip',i,j,ip)
yij=ddrdata(i,1,j,ip)
yip1j=ddrdata(i+1,1,j,ip)


\[ y_{ij1} = d\text{rdata}(i, j+1, ip) \]
\[ y_{ip lj1} = d\text{rdata}(i+1, j+1, ip) \]
\[ fbj = fblin(x_1, x_1, x_{lip1}, y_{ij}, y_{ip1j}) \]
\[ fbj1 = fblin(x_1, x_1, x_{lip1}, y_{ip1j}, y_{ip1j1}) \]
\[ adr = fblin(x_2, x_2, x_{2jp1}, fbj, fbj1) \]
\[ *1 + f0(x_1, x_2, p(iipp)) \]

if (iipp lt. 1000) return

pp = p(iipp)
\[ \text{v3t} = v3(t, pp) \]
\[ \text{v4p} = v4(pp) \]
\[ r0 = 0.7143 \]
\[ dw = 5.8 \]
\[ \text{dn} = 6.8 \]
\[ \text{const3} = 4.3.14159/3.*0.12341/v3tp \]
\[ \text{eps3} = (2.*\text{const3} + 1.)/(1.-\text{const3}) \]
\[ \text{const4} = 4.3.14159/3.*0.12341/v4p \]
\[ \text{eps4} = (2.*\text{const4} + 1.)/(1.-\text{const4}) \]
\[ \text{drdds} = r0*(1.-r0)*(1.-\text{eps3}/\text{eps4})*(1./\text{dn}-1./\text{dw}*2.*1e2 \]
\[ \text{adr} = \text{drdds}*(ds-15.) \]

write(*,*) 'p, ds, v4, v3, drdds, dr', pp, ds, v4p, v3tp, drdds, adr

return

end

function ans(ds)

implicit real*8 (a-h,o-z)
real*8 ads, v3, v4
parameter (nd=53, nt=20, np=14)
parameter (a=-0.00488692, b=0.0003389258, b2=-0.00024588056)
parameter (c=0.000207003, c2=-0.0003105293, d=3.848525e-7)
dimension drrdata(nd, nt, np), dndata(nd, nt, np), ddata(nd), tdata(nt)
dimension p(6), iipp(6)
common /temp/t
common /drnsvstdp/drrdata, dndata, ddata, tdata
data p/0.4, 74.5, 150.0, 217.7, 291.5, 353.3/
data iipp/1, 5, 7, 10, 12, 14/
c b linear formula:
\[ fblin(x, x_1, x_2, y_1, y_2) = (y_1-y_2)/(x_1-x_2) * (x-x_1) + y_1 \]
\[ f0(ds, t, p) = a+((1+(c+c2*t*t)*p+d*p*p)*(b+b2*t*t)*ds \]

ip = iipp(ds)

c dsolid0=5 dair0=10 are the thickness of c the inert and air layers used by Hans' calulation:
dsolid0=5
dair0=10.
x = ds+dsolid0+dair0
x2=t

c find i and j:
do 100, i=0, nd-1
c ddata is strictly increasing
100 if (x1.1e.ddata(i+1)) goto 101
c ds is > ddata(nd)=16
i = nd-1
101 continue
if (i.eq.0) i=1
x1 = ddata(i)
x1ip1 = ddata(i+1)
do 110, j=0, nt-1
c tdata is strictly increasing
110 if (t1.e.tdata(j+1)) goto 111
c T is > tdata(nd)=350

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j = nt - 1
ll1 continue
if (j.eq.0) j = 1
x2j = tdata(j)
x2jp1 = tdata(j + 1)
c write(*,*)'i , j : ', i, j, ip
yij = dnsdata(i, j, ip)
yijp1 = dnsdata(i + 1, j, ip)
yijp1p1 = dnsdata(i + 1, j + 1, ip)
fbj = fblin(x1, x1i, x1ip1, yij, yijp1)
fbjp1 = fblin(x1, x1i, x1ip1, yijp1, yijp1p1)
ans = fblin(x2, x2j, x2jp1, fbj, fbp1) + f0(x1, x2, p(iipp))
c ans = f0(ds, t, p(ip))
if (iipp.lt.1000) return

pp = p(iipp)
v4p = v4(pp)
ans = (ds - 15.)* 1e-2/v4p
c write(*,*)'p, ds, v4p, ns', pp, ds, v4p, ans
return
end
A.5  R-OSMO.FOR

c  r-osmo.for
c  pp in " psi " unit and p in " atm " unit:
function opsat(pp,t)
implicit real*8 (a-h,o-z)
parameter (atm = 1.013e6, pi = 3.1415927)
c  Molar volume of 4He at zero pressure.
c  Molar mass of 4He
parameter (VL = 27.58, MM4 = 4.00260, AVOGADRO = 6.02205e23)
c  Boltzmann's constant erg/K
parameter (akb = 1.3807e-16, Rgas = AVOGADRO*akb)
c  The molar volume of 4He as function of pressure in atm.
c  # Old formula based on the speed of sound data
v_4old(p) = 1.0/(3*((1.4057E6*p*atm+23823**3)**(1./3.))
  & -23823)/(1.4057E6*MM4) + (1./VL))
c  A fit for the saturated 3He concentration in the lower phase,
c  [A.E. Watson, J.D. Reppy, and R.C. Richardson, Phys Rev. 188, 384
c (1969)]
X31s(p,t) = .97226*(0.0669596 + 0.006495939*p
  & -0.000453332232*p**2 +8.77926e-6*p**3)
  & *(1+11.603*t**t*(1-0.33155*t))
c  The osmotic pressure (dyne/cm^2) as a function of X (1=pure) and T in K
opr1(x) = (1.6949*(x*100.)**(5./3.) - 0.6216*(x*100.)**2 +
  & 0.012365*(x*100.)**3)/7.501e-4
opr2(x,t) = ((26.343*(x*100.)**2)*t**2/(t+0.094472))/7.501e-4
   & 1.0963*(x*100.)**2*(t+0.094472))/7.501e-4
   & write(*,'(opsat: p,t,v4,x31,rgas',p,t,v_4old(p),x31s(p,t),rgas
   & write(*,'opsat: opr1, opr2',opr1(x31s(p,t)),opr2(x31s(p,t),t)
   & write(*,'atm,mm4,avogadro',atm,mm4,avogadro
p=pp/14.69
c  opsat, p in atm
opsat = (opr1(X31s(p,t))+opr2(X31s(p,t),t))
  & *(1+0.0073935*p)*v_4old(p)/Rgas
return
end
BIBLIOGRAPHY


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[69] From a private communication with Prof. Moses Chan.


