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Third sound of helium on a hydrogen substrate

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Measurements of third sound of thin helium films on molecular-hydrogen substrates have been made as a function of the measured helium film thickness, both by a time-of-flight technique and in a third-sound resonator. Great care has been devoted to making uniform films of hydrogen, to determine reliable values of the helium-hydrogen van der Waals constant α and the thickness of the helium dead layer, Δ. Areal and gas-loading parameters have been measured to allow an absolute determination. We find a value of 21.3 K layer^3 for α and 2.0 for Δ. Comparisons are made to other values in the literature. Our value of the van der Waals constant is in good agreement with a complementary determination by Paalanen and Iye and by Cieslikowski *et al.*, using electron mobility, but is much larger than a value reported by Mochel and a value calculated by Cheng *et al.* We also determine values for helium on copper; however, this determination depends on the literature value for the van der Waals parameter for helium on glass.

I. INTRODUCTION

The behavior of superfluid helium films has been of interest for several decades. The probes have included third sound,[1,2] adsorption isotherms,[3,4] critical flow experiments,[5,6] electron mobility,[7,8] quartz microbalance,[9] torsional oscillators,[10] and neutron diffraction.[11] The helium film is known to solidify on a strongly binding substrate such as graphite,[11] but it has been recently suggested that the first monolayer of a helium film would not solidify on a weakly binding substrate such as H_2, Li, K, Na, Rb, and Cs.[12] These weakly binding surfaces may allow the helium to exhibit submonolayer superfluidity. The metallic substrates are difficult to handle due to their reactivity; on the other hand, clean, pure hydrogen surfaces can be prepared, *in situ,* by condensation of H_2 at low temperature. In this work we use third sound to directly measure the He-H_2 van der Waals constant and the thickness of the nonsuperfluid layers in a helium film adsorbed on a molecular H_2 substrate.

There is further motivation for studying a helium film adsorbed onto a H_2 substrate. Third sound can be used as a probe for the Kosterlitz-Thouless transition in an atomic hydrogen film. Such hydrogen films can only be produced on a helium film; the helium film lies on a substrate, which develops into H_2 as the atomic hydrogen recombines.[13] Thus, in steady-state third-sound experiments that study the atomic hydrogen, the helium film will be on an H_2 substrate. These third-sound measurements of helium on hydrogen surfaces pave the way to future atomic hydrogen experiments.

II. THIRD SOUND

A. Theory

Third sound is both a thickness and temperature oscillation in a thin superfluid film.[14] Its dispersion relation is[1,2]

$$C_3^2 = \frac{\rho_s}{\rho_{\text{tot}}} f d \ , \tag{1}$$

where C_3 is the velocity of the third-sound wave, ρ_s is the superfluid density of the film, ρ_{tot} is the total density of the superfluid film, f is the restoring force per unit mass on the surface of the superfluid, and d is the thickness of the superfluid film. The restoring force is due to the van der Waals attraction between the atoms of the substrate and the atoms in the film. For thin films, it is of the form

$$f(z) = 3\alpha / z^4 \ , \tag{2}$$

where α is the van der Waals constant and z is the distance of the atom from the substrate. In this potential, the velocity of third sound can be written as

$$C_3^2 = (\rho_s / \rho_{\text{tot}})_{\text{film}} 3\alpha / d^3 \ . \tag{3}$$

The subscript "film" denotes that the film average of the density ratio must be taken. In general, the first one to two layers of the helium film will solidify and not contribute to the flow in the film. If we denote the thickness of this solid layer as Δ and assume that the rest of the film has a total density and superfluid density of bulk helium liquid[15] then,

$$C_3^2 = (\rho_s / \rho_{\text{tot}})_{\text{bulk}} (1 - \Delta / d) 3\alpha / d^3 \ . \tag{4}$$

B. Review of earlier third-sound and surface work

This section is intended to sample some of the work done in helium films using third sound as a probe. It is not intended as a comprehensive review of third-sound work but is aimed at reviewing the knowledge of the van der Waals constant between helium and various substrates. Although there is extensive literature, in most reported measurements using third sound, the van der Waals constant was irrelevant or assumed.

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Third sound was predicted in 1957 by Atkins,[14] although its effect was seen by Knudsen (and not understood) in an experiment conducted to measure the thickness of a He-II film at large heights above a helium bath in 1954.[16] Experiments on third-sound standing waves, done in 1962,[17] showed that the third-sound velocity had no frequency dependence and was of a magnitude consistent with Atkins' predictions. These first two measurements used light to drive the third-sound excitation and ellipsometry to detect it. In each case the measurements were done on saturated helium films.

A very elegant technique to both drive and detect third sound, which allowed measurements of undersaturated helium films, was developed in 1968 by Rudnick *et al.*[18] Their technique used thin superconducting bolometers to detect the thermal component of the third-sound wave. Their data was plotted against the pressure of the gas above the film, eliminating the need to know the van der Waals constant of the substrate. They did, however, calculate film thicknesses using a van der Waals constant of 87 K layer^3 for an argon substrate, which was determined from an adsorption isotherm of helium on argon plated copper, measured by McCormick, Goodstein, and Dash.[19]

This technique generated a great deal of data that did not completely agree with Atkins' original paper. This deficiency in the theory was answered by Bergman's extensive analysis of third sound,[20,21] although there are still some discrepancies between Bergman's more complete analysis and experiment, such as the attenuation of the wave.

Third-sound resonators were developed in 1970 by Ratnam and Mochel.[22] In these cells, quartz plates were hermetically sealed around the edges in an atmosphere of argon and helium. Subsequently, the cell was cooled and measurements were made using carbon strip bolometers mounted on the resonator. Their technique allowed the measurement of third sound as a function of temperature for a known amount of He on an argon substrate. Their data fit best with an assumed van der Waals constant of 79 K layer^3; however, Ratnam and Mochel's final analysis used the McCormick, Goodstein, and Dash value for the van der Waals constant of 87 K layer^3 for an argon substrate. This experiment is one of the very few third-sound experiments that required a knowledge of the van der Waals constant in order to analyze the data.

In 1972, Sabisky and Anderson[23] did their landmark experiment confirming the Lifshitz theory for the van der Waals interaction. They measured the thickness of an adsorbed helium film by setting up a high-frequency first sound standing wave in the helium film on ionic crystals. With the confirmed Lifshitz theory, they calculated a table of van der Waals constants, among them 14.5 K layer^3 for argon, although they did not measure this.

In 1975, Washburn, Rutledge, and Mochel,[24] using an improved technique over that of Ratnam and Mochel, continued the study of ^{4}He films on argon substrates. They sealed argon gas into a quartz resonator and then diffused known amounts of helium into the sealed resonator at room temperature, in which the internal gas pressure could be measured. Although they had the capability to determine the van der Waals constant for their surface of argon, they used the Sabisky and Anderson value of 14.5 K layer^3, to analyze their data.

A circular resonator, which could be filled at low temperature, was developed by Ellis and Hallock in 1982.[25] They used their resonantor to confirm the layered nature of ^{3}He-^{4}He films.[26] They measured a shift from the pure ^{4}He velocity that did not explicitly depend on the value of the van der Waals constant.

Smith and Hallock[27] examined the effect of surface roughness on the velocity of third sound by placing smooth and rough silicon wafers in a chamber and measuring the third-sound velocities on each of them. They found that the third-sound velocity was slower on the roughened sample by as much as a factor of 6.

Mochel and co-workers[28–30] used a modified Brunauer-Emmett-Teller (BET) isotherm technique and third-sound measurements to determine the van der Waals constant for several different substrates. We shall discuss this work in a subsequent section.

Most third-sound measurements to date consist of relative measurements, so that knowledge of the absolute values of the van der Waals constant was unnecessary. The more recent third-sound experiments that have required a knowledge of the van der Waals constant have used the calculated values of Sabisky and Anderson. However, the third-sound velocity is also a function of the surface roughness and not just the van der Waals constant and the thickness of the ^{4}He film. The van der Waals constants determined by gas isotherms are consistently higher than the Lifshitz theory value.[31] This has been attributed to the effect of the roughened surfaces. Sabisky and Anderson measured on cleaved, smooth surfaces and, consequently, got the Lifshitz theory value. Thus, it is important to consider the physical structure of the substrate in determining effective van der Waals constant for a surface.

III. EXPERIMENTAL

A. Methods for measuring third sound

Third sound is generally studied either by measuring the time of flight of a third sound wave, or by determining the frequencies of resonant modes in a cavity; we have used both of these techniques. The time-of-flight cell (TOFC)[32] used in this work is shown in Fig. 1(a). This was made from a glass microscope slide that has a sputtered gold film on one end to act as a heater-driver of a third-sound pulse. Sputtered gold capacitor plates on the other end of the TOFC act as a receiver-detector of the third-sound wave. The third-sound velocity is determined in the TOFC by electrically pulsing the heater to launch a third-sound wave by locally modulating the temperature and hence the thickness of the helium film. The thickness variation of the passing wave is detected by a change in the capacitance of the receiver-detector. The time between the heater pulse and the capacitive detection is the propagation time.

The third-sound resonator cell (TSC)[33,34] shown in Fig. 1(b), was made by epoxying two microscope slides togeth-

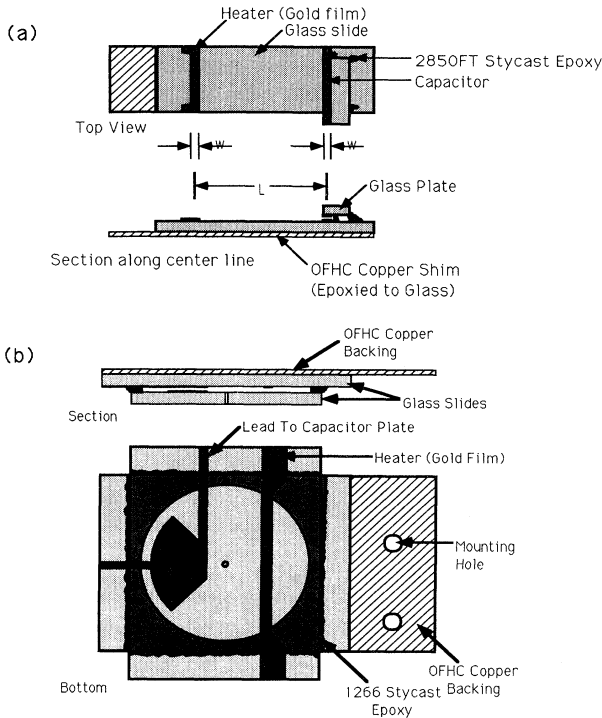

FIG. 1. (a) The time-of-flight cell (TOFC). (b) The third-sound resonator cell (TSC). OFHC copper is oxygen-free high-conductivity copper.

er to form a pancake-shaped cavity. This cell also uses a heater to drive the wave and a capacitor to detect the wave. The heater is driven with a sinusoidal current source whose frequency is slowly swept, while the detector's capacitance is monitored for a response. The quality factor of these resonators is very high ($\sim 10^3 - 10^5$), which allows a precise determination of the resonant frequency.

In general, the resonant frequency obeys

$$f_n = \chi_n C_3 , \tag{5}$$

where f_n is the nth resonant frequency, C_3 is the third-sound velocity, and χ_n is a geometry dependent coefficient for the nth resonant mode. The χ's for the circular resonator shown Fig. 1(b) are

$$\chi_n = x_n / 2\pi R , \tag{6}$$

where R is the radius of the resonator, C_3 is the third-sound velocity, and x_n is a zero of a Bessel function (for example $x_1 = 1.841$, $x_2 = 3.054$, $x_3 = 4.201, \ldots$). Using Eqs. (4) and (5) yields

$$f_n^2 d^4 = 3\alpha \chi_n^2 (\rho_s / \rho_{\text{tot}})_{\text{bulk}} (d - \Delta) . \tag{7}$$

The only unknowns in Eq. (7) are α and Δ, so that if $f^2 d^4$ vs d is plotted, then the points should fall on a straight line, determining both α and Δ. The thickness d can be determined by depositing a measured amount of helium onto a surface of known area. The values of f_n and χ_n are measured directly from the resonator and $(\rho_s / \rho_{\text{tot}})_{\text{bulk}}$ is a well-documented[35] function of temperature.

B. Cryogenic apparatus

Figure 2 shows the cell chamber used in this experiment. It contains both a TSC and a TOFC. The TSC is generally more sensitive to third-sound variations in thin films than the TOFC. We used the TOFC to check the values of χ_n for our TSC. The chamber also contains two stacks of glass cover slips, separated by 70-μm-diam wire, to give a large surface area to stabilize the helium film thickness.

The tunnel diode oscillators[36,37] (TDO's) are used to detect the capacitance changes in the TOFC and TSC due to the third-sound waves. The capacitive detector is part of an LC tank circuit in the TDO. The passage of the third-sound wave between the capacitor plates modulated the frequency of the oscillator. The signal from the TDO was demodulated using the electronics shown in Fig. 3. Figure 3(a) is a block diagram of the equipment used to determine the third-sound time of flight. A pulse signal from a pulse generator was applied to the heater through an attenuator; this also triggered a Nicolet signal averager. The third-sound wave propagated across the TOFC and modulated the TDO frequency as it passed between the detection capacitor plates. The TDO signal was amplified, filtered, demodulated, and filtered again before it was recorded by the signal averager. The third-sound velocity was calculated as

$$C_3 = L / t_f , \tag{8}$$

where L is the distance between the heater and the detection capacitor, and t_f is the propagation time.

The detection-drive electronics for the TSC, shown in Fig. 3(b), used an HP 3325A frequency synthesizer to generate a sinusoidal drive signal for the TSC heater. The drive signal was also applied to the reference input of a two phase lock-in amplifier. The TDO signal was amplified, filtered, and frequency shifted to a 10.7-MHz carrier frequency for the demodulator. The demodulated signal was fed to the signal input of a two-phase lock-in

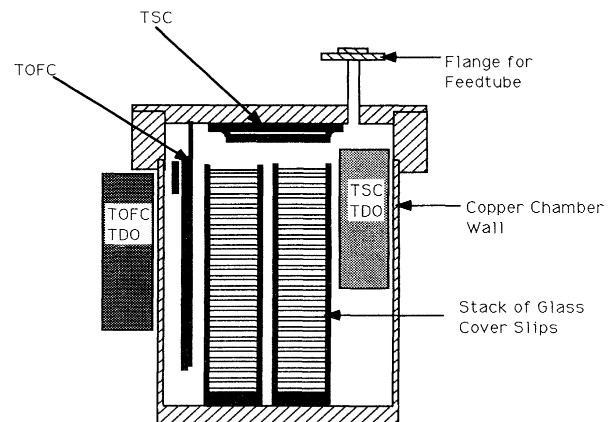

FIG. 2. The cell chamber.

amplifier. The lock-in amplifier detected at twice the reference frequency, since the heater "rectified" the electrical input into a temperature oscillation, and drove the resonator at twice the drive frequency. The drive frequency was slowly swept, while the response of the resonator was monitored by the lock-in amplifier.

C. Error analysis

We shall express our determined values in the form $\alpha=[x(A)]^{+B}_{-C}$ so that we may separate various sources of error, and so that we can compare our results with others. Here x is the value we determine, A is the statistical error determined from the fits of our data, and B and C represent the total error in our values including systematic error. In interpreting results from other work it is not always possible to separate the errors. In those cases we have placed a question mark in the appropriate space. The major source of error in our determination of the van der Waals constant is the uncertainty in the area of our cell chamber and will be reflected in the difference between the error A and the errors B and C.

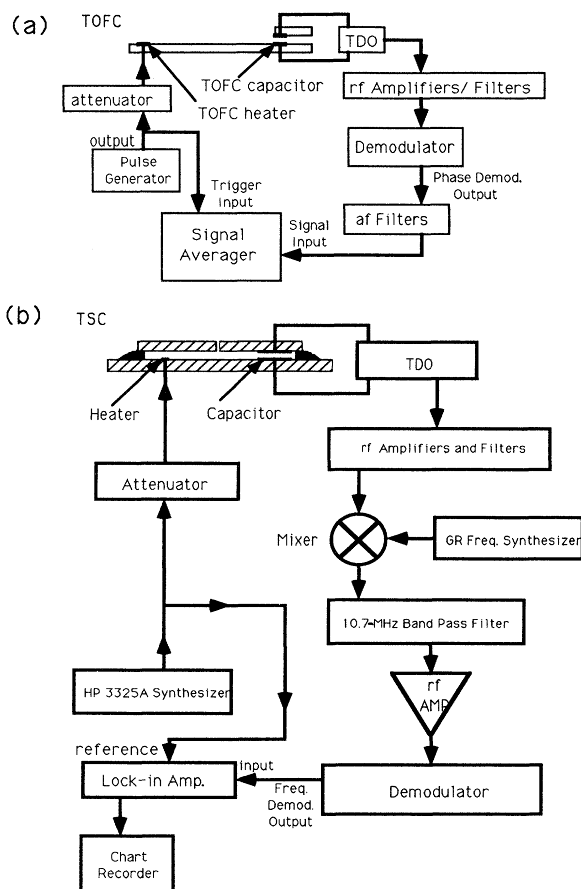

FIG. 3. (a) Demodulation electronics of the TOFC. (b) Demodulation electronics for the TSC.

D. Experimental procedure

1. Areal determination

The area of the third-sound chamber was determined using the standard BET isotherm technique.[38–40] Our measurement consisted of loading known amounts of krypton gas into the cell chamber, at 77 K, and recording the pressure of gas in the chamber. This data was fit to the standard BET equation that yielded the number of atoms in a monolayer of atoms on the surface of the cell chamber. The area of a krypton atom[39] (19.2 ± 3.5 Å^2) multiplied by the number of these atoms on the surface of the cell yielded the total area of the cell of 0.52 ± 0.09 m^2 to be compared to 0.41 ± 0.02 m^2 for the geometric area. It is not unusual for the BET area to be significantly larger than that calculated using measurements with a ruler. Since the BET isotherm accounts for the roughness of the cell surfaces, we shall use this value for the area of our cell.

2. Procedure of determining the average van der Waals constant of the cell chamber

The evacuated cell chamber was cooled to 450 mK and measured amounts of helium were added into the uncoated cell chamber. A frequency sweep for resonances of the TSC was made after each new introduction of helium film. A plot of the first resonance mode (f^2d^4) vs the calculated film thickness is shown in Fig. 4(a).

3. Calibration of the TSC

As mentioned earlier, the TSC is more sensitive than the TOFC and can detect third sound in thinner films.

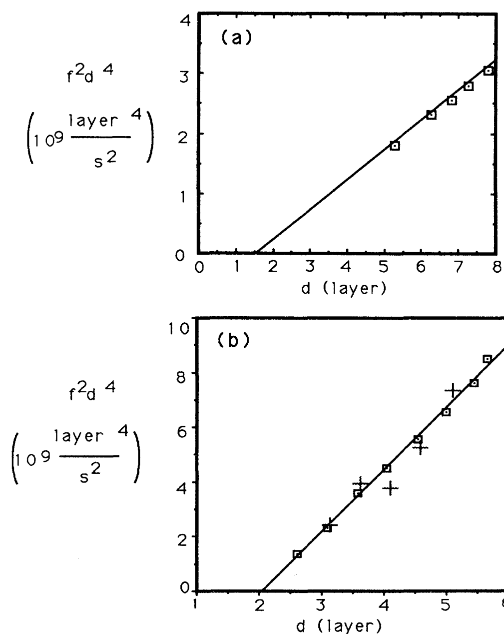

FIG. 4. (a) Plot of bare cell data. (b) Plot of hydrogen substrate data. The different symbols indicate separate data runs.

Therefore, in order to measure third-sound velocities in the thin-film limit, where Eq. (7) is valid, the TSC was used.

The initial tests of the TSC showed that the resonances (χ's) were not described by the series given by Eq. (6). This means that the resonator geometry was not circular and that the actual value of χ was unknown for a given resonance. In order to determine χ, we filled the cell with a 72-Å-thick helium film and simultaneously measured the time of flight of the TOFC and the resonant frequency of the TSC. These measurements coupled with Eqs. (5) and (8) determined χ.

4. *Procedure for determining the van der Waals constant of H_2*

a. Coating of a cell. It was necessary to create a uniform hydrogen coating in the cell chamber. The chamber was coated by cooling it with H_2 gas inside so that the gas would freeze onto the chamber's surfaces. A nonuniform layer would be formed if there were temperature gradients present, since the hydrogen would preferentially freeze onto the coldest surfaces. To estimate how large a temperature gradient can be tolerated while plating the H_2, we used the simple model outlined in Appendix B.

Table I shows the effect of a temperature gradient according to Eq. (B3). The table shows equilibrium thickness distributions of a H_2 film on two surfaces, 1 and 2, for several temperature differences, $T_1 - T_2$, between those surfaces. We see that a 5-mK gradient at 4.2 K can thin a 20-layer-thick film by a factor of 2. Clearly, small gradients of the temperature of the cell can significantly alter the thickness of the hydrogen film at 4.2 K. This effect will be significant only if the hydrogen film is mobile at 4.2 K. Here mobility refers to the ability of the solid layer of hydrogen to redistribute itself by evaporation, recondensation, or diffusion.

In order to develop a procedure for forming hydrogen films, we formulated a simple model to estimate an upper bound on the mobility of the H_2 film. This model is described in Appendix C, and relevant results are given in Table II. This table shows maximum desorption rates of a thick solid H_2 film for several temperatures near 4.2 K according to Eq. (C3). Since the actual film mobility may be a factor of 10 less than the values given in Table II, we can conclude that the time for the redistribution of a monolayer may be several minutes, and for tens of layers, several hours at 4.2 K. However, the film will remain in place for any changes that occur over the time scale of seconds at 4.2 K and below.

TABLE I. The calculated values of d_1, the thermal gradient thinned film thickness in Eq. (B3) for various values of T_2.

T_1 (K)	d_2 (layer)	T_2 (K)	d_1 (layer)
4.2	20	4.200	20.0
4.2	20	4.195	10.0
4.2	20	4.190	8.1
4.2	20	4.185	7.1
4.2	20	4.150	4.8

TABLE II. Desorption rates δl of a thick hydrogen film according to Eq. (C3) in Appendix C.

T (K)	δl (layer/s)	$1/\delta l$ (s/layer)
4.3	0.305	3.28
4.2	0.173	5.78
4.1	0.099	10.4
4.0	0.051	19.4
3.9	0.027	37.3
3.7	0.007	153.0
3.0	0.000 01	98 000.0

b. Coatings of hydrogen. The measured value of α_{H_2} will be affected by the uniformity of the hydrogen coating in the cell chamber. For example, if the hydrogen admitted into the cell chamber were to deposit entirely in one small area, then the α determined with Eq. (7) would reflect not the α of the He-H_2 interaction but the average interaction between the helium and the exposed surfaces of the cell chamber (see Appendix A). We have developed a technique to ensure the deposition of a uniform molecular hydrogen film on the surfaces of the cell chamber.

The cell chamber was mounted in a ^{3}He refrigerator as shown in Fig. 5. The feedpipe to the cell chamber was

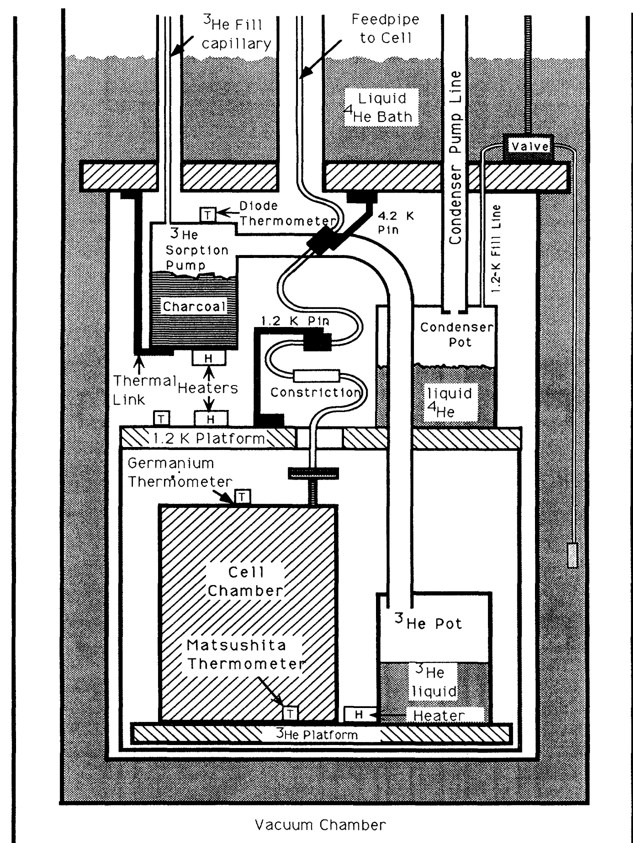

FIG. 5. The cryogenic part of the apparatus. Note that both the 1.2- and 4.2-K thermal anchors are equipped with a heater and a thermometer, which are not shown.

wrapped with a manganin heater wire and the thermal pinnings at 4.2 and 1.2 K were each equipped with a heater and thermometer. A 300-μm-diam constriction was placed in the feedpipe to minimize the heat load to the ^{3}He refrigerator due to superfluid helium film flow. We loaded a premeasured amount of hydrogen into the cell chamber at 77 K and cooled the system to 4.2 K ensuring that the cell chamber was the coldest point in the system at all times. This was done by filling the vacuum chamber around the cell chamber with ^{4}He exchange gas at a pressure of several torr. Each of the heaters (the feedpipe, 1.2-K pinning, and the 4.2-K pinning) were turned on as cold ^{4}He was slowly flowed into the liquid-^{4}He reservoir. The temperatures of the cell chamber, 1.2-K pinning, and 4.2-K pinning were all monitored to confirm that the cell chamber was the coldest region exposed to the H_2 gas. The molecular hydrogen presumably initially plated out nonuniformly. The cell chamber was then allowed to sit at 4.2 K for at least 12 h to achieve a uniform coating on the isothermal walls of the cell chamber.

We then cooled the cell chamber as rapidly as possible (in about 45 s) from 4.2 to 1.2 K, at which temperature the hydrogen film is immobile. Computer simulations of this procedure,[41] confirm that the H_2 film cannot significantly redistribute itself in the cell chamber during this cooldown. This method hinges on the low, but nonzero, mobility of hydrogen at 4.2 K shown in Table II. For a lower vapor pressure gas such as deuterium, the temperature for redistribution must be increased.

We have also tried several other programs of coating our cells with hydrogen using a technique of slowly cooling down from 4.2 to 1.2 K. In each case, we found that the small temperature gradients that inevitably appeared in our cell, were enough to allow significant nonuniformities in our hydrogen film to develop. The criterion for this was the determination of a larger value of the van der Waals constant, more characteristic of the bare cell walls. Our technique of allowing the hydrogen to redistribute at 4.2 K does not suffer from large temperature gradients, since the cell is enveloped in a ^{4}He bath of uniform temperature.

From 1.2 K, the cell chamber was cooled down to 450 mK and measured amounts of helium were admitted into the cell. A frequency sweep of the resonator's response was made after each introduction of helium. A plot of the lowest resonant frequency (f^2d^4) vs the film thickness (d) is shown in Fig. 4(b). The points shown in Fig. 4(b) are from two separate cooldowns. The scatter of the points in Fig. 4(b) we attribute to small temperature gradients in our ^{3}He refrigerator. In our error analysis of the data in Fig. 4, each value of f^2d^4 has an uncertainty of 5×10^7 s^{-2} layers^4 due to this effect.

E. Results: Determination of α_{H_2} and α_{Cu}

The bare cell chamber, shown in Fig. 2, has surfaces of glass and copper. As a result, the third-sound measurements give an average of these surfaces' van der Waals constants (see Appendix A). The fit shown in Fig. 4(a) results in a determination of the average α of the cell surface of $[46.8(2.4)]^{+38}_{-18}$ K layer^3 and a nonsuperfluid (dead) layer thickness of $[1.55(0.26)]^{+38}_{-38}$ layers (3.6 Å = 1 layer). The large systematic error results from the inherent uncertainty in the BET determination of the area of the cell.

An estimate of the van der Waals constant for copper can be made from this measurement. If the area of the glass in the cell is accurately calculated from geometric considerations (0.35 m^2) and the literature value of 27 K layer^3 (Refs. 27 and 42) is assumed for the van der Waals constant of glass, then the van der Waals constant for copper is $[59.2(4.2)]^{+46}_{-28}$ K layer^3 (see Appendix A).

For measurements on H_2, all the surfaces are covered with hydrogen, so we determine the "pure" values for α and Δ. The fit shown in Fig. 4(b) gives values of α_{H_2} of $[21.3(1.41)]^{+16.9}_{-8.5}$ K layer^3 and Δ_{H_2} of $[2.0(0.1)]^{+0.41}_{-0.41}$ layers. Table III contains our values and those of several other groups' values of the van der Waals constants.

F. Discussion

The error bars in our determined van der Waals constants and the nonsuperfluid layer thickness are due primarily to the uncertainty in the area ascribed to the krypton atom in the BET isotherm. There would be some improvement in the errors if another gas, such as nitrogen, which has a better known area per molecule, were used to determine the area. Although the BET technique has become a standard method for determining surface area, it

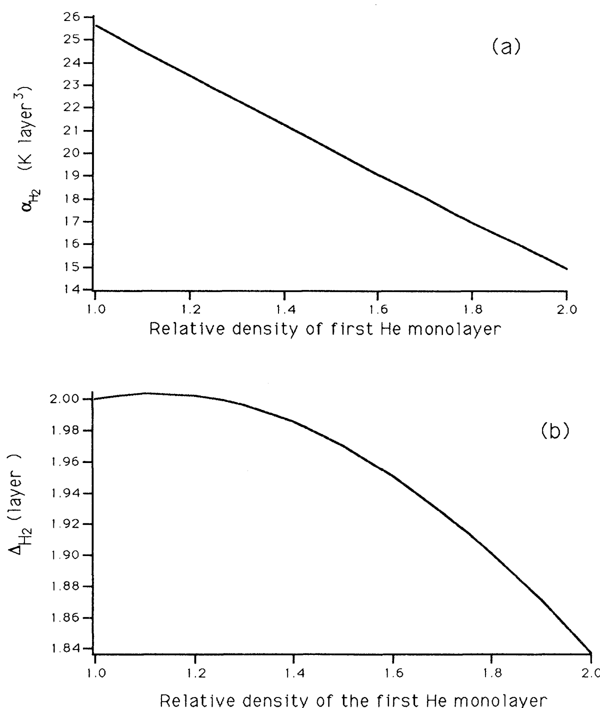

FIG. 6. Plot of our calculated value of the van der Waals constant (a) and the nonsuperfluid layer thickness (b) for ^{4}He on a hydrogen substrate as a function of the assumed density of the first He monolayer relative to that of the bulk liquid. A density of 1 corresponds to the bulk density value.

TABLE III. van der Waals constants for the interaction of ^{4}He film and the specified substrate. Units are in K layer^3.

Substrate	This work	Shirron, Gillis, and Mochel (Refs. 28–30)	Cheng *et al.* (Ref. 12)	Paalanen and Iye (Ref. 7)	Cieslikowski *et al.* (Ref. 8)
Cu	$[59.2(4.2)]^{+46}_{-28}$	$[30.9(4.4)]^{+?}_{-?}$	55.9		
H_2	$[21.3(1.41)]^{+16.9}_{-8.5}$	$[4.5(0.4)]^{+?}_{-?}$	7.7	$[20(?)]^{+7}_{-7}$	$[20(?)]^{+7}_{-7}$

has been found to be no more accurate than about 10% for the determination of area.[39] The fits shown in Fig. 4 are capable of determining both α and Δ much more accurately if the surface area of the cell is better known.

Cheng, Ihm, and Cole[12] suggested that hydrogen is on the borderline of the weakly interacting substrates that do not solidify the first monolayer of a helium film and the strongly interacting substrates that do. However, they used 7.7 K layer^3 for the van der Waals constant of the H_2-^{4}He, nearly a factor of 3 weaker than what we have measured. For a van der Waals constant (for hydrogen) of 22 K layer^3, the first layer of a helium film should be solid according to Cheng, Ihm, and Cole. This is in general agreement with our measurement of a nonsuperfluid layer of helium.

The density of the solid layer of helium is believed to be compressed relative to that of the bulk liquid.[31] The α_{H_2} and Δ_{H_2} values we calculate are dependent on the density of this layer, as it affects our determination of the thickness of the superfluid helium film. In Fig. 6, we show the value of α_{H_2} and Δ_{H_2} as determined from our data, as a function of the assumed density in the first helium layer. Early BET isotherms[39] and some quartz microbalance experiments[9] suggest that the density of the first monolayer of ^{4}He on a substrate is twice the density of bulk helium. We have assumed, in the analysis for the Cu-glass data, that the first layer density is double the bulk density. Although the density enhancement may be quite high for strongly binding substrates,[11] a relatively weakly binding substrate, such as hydrogen, would not be expected to have a density enhancement factor of 2. Using values given by Cheng, Ihm, and Cole[12] and scaling their assumed value of α_{H_2} to 20 K layer^3, we estimate the enhancement of the first helium layer to be 1.35, which has been used in our analysis. Shirron, Gillis, and Mochel[28] have developed a modified BET isotherm technique of helium on several substrates and have found that the first monolayer has an enhanced density which ranges from 1.29 to 1.45 for substrates with van der Waals constants in the range of 17–31 K layer^3.

There is also a dependence of the measured α_{H_2} on the thickness of the hydrogen film. If the hydrogen is too thin, then the substrate below the hydrogen, glass and copper in our case, will contribute to the van der Waals interaction and distort our measured value of α_{H_2}. Figure 7 is the result of a calculation[41] to estimate the possible error contributed by this effect in our cell for two possible values of α_{H_2}. Since we believe our H_2 films to be at least 15 layers thick, this effect should not significantly distort our results.

If our films have significant surface roughness, the third-sound velocities we measure will be slower than that of a smooth surface; consequently, our determined van der Waals constant will be smaller than the actual van der Waals constant. Our value should be viewed as a lower boundary, although we believe our films to be smooth.

Electron mobility measurements[7,8] of an electron film on a helium film over a hydrogen substrate have been used to determine α_{H_2} to be $[20(?)]^{+7}_{-7}$ K layer^3, which agrees with our determined value.

Recently, a value of the van der Waals constant for a hydrogen substrate using a modified BET isotherm technique was reported by Mochel,[30] who gives a value for α_{H_2} of $[4.5(0.4)]^{+?}_{-?}$ K layer^3. The measurement is discussed in Shirron's doctoral thesis[29] and the technique is outlined in Shirron, Gillis, and Mochel.[28] Since there is a large discrepancy between their value and ours, it is useful to consider the analyses in more detail. In our BET analysis, the large error was due to the uncertainty in the area of the krypton atom. Mochel *et al.*, measured an adsorption isotherm using helium gas and analyzed this with a modified BET. Although they find excellent fits to their data, they do not consider the possible systematic error that can arise from the analysis. Their modified BET analysis still suffers from the basic assumptions of all BET isotherms, namely the following.[3]

(1) Adsorption takes place on fixed sites. Adsorption in higher layers is on top of atoms already adsorbed and not on "in between positions."

(2) There is no lateral interaction between adsorbed

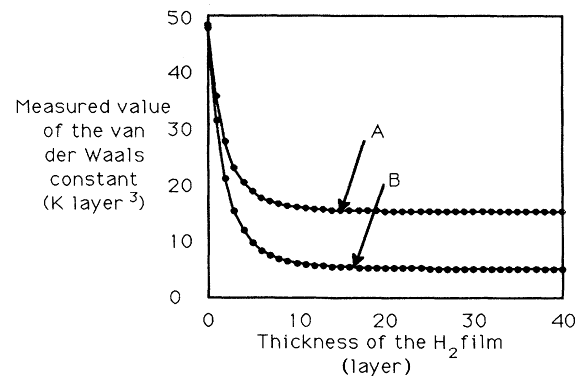

FIG. 7. (a) The dependence of the measured van der Waals constant vs the thickness of the hydrogen film. This is calculated assuming the underlayer has a van der Waals constant of 48 K layer^3. Curve A: α-H_2 assumed to be 15 K layer^3; curve B: α-H_2 assumed to be 5 K layer^3.

atoms.

(3) The first and second layer are the only layers that interact with the substrate. All subsequent layers have the interparticle interaction of bulk liquid and involve only the interaction in the vertical stack of atoms adsorbed at each site. We should note here that a standard BET isotherm assumes that only the first layer interacts with the substrate and that Mochel *et al.*, have modified Steele's bilayer BET model, which assumes both the first and second layers interact with the substrate.[4]

(4) Classical statistics are assumed to apply. This may not be the appropriate for a quantum liquid such as ^{4}He.

(5) There are regions where the BET isotherm is inappropriate to apply, such as in the region of very low vapor pressures ($P/P_{sat} < 0.05$) where small local inhomogeneities in the substrate will preferentially adsorb gases (this is contrary to the assumption of a set of uniformly adsorbing sites) and in regions of high vapor pressure ($P/P_{sat} > 0.40$), where surface tension effects begin to modify the isotherm.[40]

It is for these reasons that BET isotherms have an inherently large error in the number of atoms in the first monolayer, which is reflected in our nonparenthetic error declarations. Mochel and co-workers[28–30] consider only the error in their fits to the data (corresponding to our parenthetic errors) and not the inherent BET error (our nonparenthetic errors). Unfortunately, their modified BET isotherms do not lend themselves to finding their "inherent error" as the model has only been used for ^{4}He. Consequently, we feel that their error bars are overly optimistic.

We also believe that their technique for coating their cell with a uniform H_2 substrate film may be flawed. They lowered their H_2 filled cell, already precooled to 77 K, down into a 4.2-K helium bath in a period of 5 min. They then cooled their helium bath down to 1.72 K (Ref. 29). Our analysis, outlined previously, and our experience suggest that this method will not result in a uniform H_2 coating of the cell unless the cell is allowed to remain at 4.2 K for many hours.

We cannot reconcile our value with theirs. We note, however, that the periodic variation of the third-sound velocity that they observe is $[0.60(0.04)]^{+?}_{-?}$ layers, whereas one might expect a variation with integral change in layering. If we assume that their area determination, and hence film thickness determination, is off by a factor of 1.6, then we find that their value of α_{H_2} is 18.9 K layer^3. This is an appealing assumption because it brings their van der Waals value into agreement with three other independent measurements and because their oscillations in the third-sound velocity would then correspond to layer completions in the helium film, just as do the variations in the mobility of electrons adsorbed on helium.[7,8]

In conclusion, we have determined the van der Waals constant for the He-H_2 interaction to be $[21.3(1.41)]^{+16.9}_{-8.5}$ K layer^3, which agrees with the value determined by electron mobility measurements. We have used a simple model of a thin helium film, where the first layer is assumed to be 1.35 times as dense as bulk helium. The thickness of the nonsuperfluid part of the film is determined to be $[7.2(0.36)]^{+1.48}_{-1.48}$ Å.

Note added in proof. Subsequent to preparation of this article, the work in Ref. 30 was published by Shirron and Mochel.[46]

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APPENDIX A: AVERAGING THE van der WAALS CONSTANTS

It will be shown in this appendix that a TSC in a chamber containing two different types of surfaces results in a van der Waals constant, which is an "average" van der Waals constant for the two surfaces. Consider a chamber with two types of surfaces with areas A_1 and A_2 and van der Waals constants α_1 and α_2. In equilibrium, the chemical potential of a helium atom on top of the helium film above surface 1 is the same as that above surface 2, or

$$\frac{\alpha_1}{d_1^3}=\frac{\alpha_2}{d_2^3}\ , \tag{A1}$$

where d_1 and d_2 is the thickness of the He film above substrate 1 and 2, respectively. As a result

$$d_2=\left[\frac{\alpha_1}{\alpha_2}\right]^{1/3} d_1 \equiv \gamma d_1\ . \tag{A2}$$

We can relate this to the total volume of the helium film,

$$V_{\mathrm{He}}=A_1 d_1 + A_2 d_2\ . \tag{A3}$$

Substituting Eq. (A2) into Eq. (A3) yields

$$d_1=\frac{V_{\mathrm{He}}}{A_1+A_2}\left[1+\frac{(\gamma-1)A_2}{A_1+A_2}\right]^{-1}\ . \tag{A4}$$

Noting that $V_{\mathrm{He}}/(A_1+A_2)$ is just d_0, the average thickness of the helium film, we rewrite Eq. (A4) and define ξ:

$$d_1=d_0\left[1+\frac{(\gamma-1)A_2}{A_1+A_2}\right]^{-1}\equiv d_0\xi^{-1}\ . \tag{A5}$$

If the TSC is part of surface 1, then the third-sound velocity will be

$$C_3^2=\left[\frac{\rho_s}{\rho_{\mathrm{tot}}}\right]_{\mathrm{surf}}\frac{3\alpha_1}{d_1^3}=\left[\frac{\rho_s}{\rho_{\mathrm{tot}}}\right]_{\mathrm{bulk}}\left[1-\frac{\Delta}{d_1}\right]\frac{3\alpha_1}{d_1^3}\ . \tag{A6}$$

Substituting Eq. (A5) into Eq. (A6) and using Eq. (5) ($f=\chi C_3$) for the resonant frequency of the TSC gives

$$f^2 d_0^4=3\alpha_1\chi^2\left[\frac{\rho_s}{\rho_{\mathrm{tot}}}\right]_{\mathrm{bulk}}\xi^3(d_0-\Delta\xi)\ . \tag{A7}$$

A plot of $f^2 d_0^4$ vs d_0 yields a line with a slope, m, which will be given by

$$m = 3\alpha_1 \chi^2 \left[\frac{\rho_s}{\rho_{\rm tot}} \right]_{\rm bulk} \xi^3$$
$$\equiv 3\alpha_{\rm meas} \chi^2 \left[\frac{\rho_s}{\rho_{\rm tot}} \right]_{\rm bulk} . \quad \text{(A8)}$$

$\alpha_{\rm meas}$ is the van der Waals constant we would measure from the fit, assuming only one type of surface was in the cell chamber; we then find

$$\alpha_{\rm meas} = \alpha_1 \xi^3 = \frac{\alpha_1}{\alpha_2} \left[\frac{\alpha_2^{1/3} A_1 + \alpha_1^{1/3} A_2}{A_1 + A_2} \right]^3 . \quad \text{(A9)}$$

We see from this expression that the measured van der Waals constant is an average of the van der Waals constants of the materials present in the cell chamber. It is straightforward to show that

$$\alpha_2 = \alpha_1 \left\{ 1 + \left[\frac{A_1 + A_2}{A_1} \right] \left[\left[\frac{\alpha_{\rm meas}}{\alpha_1} \right]^{1/3} - 1 \right] \right\}^3 . \quad \text{(A10)}$$

This is the expression used to calculate the value of $\alpha_{\rm copper}$, given $\alpha_{\rm glass}$ and the respective areas of glass and copper.

APPENDIX B: THE EFFECT OF TEMPERATURE GRADIENTS ON THE HYDROGEN FILM

Here we use a simple model to estimate the effect of temperature gradients on the thickness variation of a hydrogen film in the vicinity of 4.2 K. The local pressure above a hydrogen film of thickness d and temperature T can be modeled using the Frenkel-Halsey-Hill isotherm[39]

$$P = P_{\rm sat}(T) \exp \left[-\frac{\alpha_{\rm H_2-sub}}{T d^3} \right] , \quad \text{(B1)}$$

where $P_{\rm sat}(T)$ is the saturated vapor pressure for the adsorbing gas, hydrogen in this case, and $\alpha_{\rm H_2-sub}$ is the van der Waals constant for the interaction between the substrate and the hydrogen film. We assume here that the substrate is copper and that $\alpha_{\rm H_2-sub} = 142$ K layer^3 (Ref. 43).

The measurement by Borovik, Grishin, and Grishina[44] of the vapor pressure of H_2 around 4.2 K can be fit to an exponential, resulting in

$$P_{\rm sat}(T) = A \exp \left[-\frac{B}{T} \right] , \quad \text{(B2)}$$

where $A = 19\,898$ torr and $B = 104.02$ K for hydrogen.

Consider now the case where two surfaces are at two different temperatures, T_1 and T_2. In steady state the thicknesses of the films will adjust so that the pressures over the films will equalize. Using Eqs. (B1) and (B2) we can solve for one film thickness in terms of the other:

$$d_1^3 = \frac{T_2}{(B/\alpha_{\rm H_2-sub})(T_1 - T_2) + (T_1/d_2^3)} . \quad \text{(B3)}$$

Table I shows the effect of a temperature gradient according to Eq. (B3). We see that a 5-mK gradient at 4.2 K can thin a 20-layer-thick film by a factor of 2. Clearly small gradients of the temperature of the cell can significantly alter the thickness of the hydrogen film at 4.2 K.

APPENDIX C: AN ESTIMATE OF THE MOBILITY OF A HYDROGEN FILM

In order to establish an estimate of the mobility of hydrogen at 4.2 K, consider that in equilibrium the hydrogen atoms desorb from the surface at the same rate as the atoms strike and stick to the surface. From kinetic gas theory the flux of atoms onto the surface is[45]

$$\nu = \tfrac{1}{4} n v_a , \quad \text{(C1)}$$

where n is the number of molecules per unit volume in the gas, and v_a is the mean velocity of a molecule in the vapor given by

$$v_a = [8kT/(\pi m)]^{1/2} . \quad \text{(C2)}$$

If we assume that each molecule that strikes the surface sticks (sticking coefficient of 1) then ν in Eq. (C1) is the rate at which molecules desorb from the surface per unit area. The number of layers that desorb from the surface is obtained by dividing ν by the areal number density of the hydrogen solid n_a. Combining Eqs. (B1), (B2), (C1), and (C2) and using $n = P/kT$ for the vapor, we find

$$\delta l = \frac{A}{n_a (2\pi m k T)^{1/2}} \exp \left[-\frac{B}{T} \right] \exp \left[-\frac{\alpha_{\rm H_2-sub}}{T d^3} \right] . \quad \text{(C3)}$$

δl is the number of layers of the surface lost per unit time if there is no replenishment by incident atoms from the gas. Hence, Eq. (C3) is an upper boundary to the rate at which a hydrogen surface can desorb. Table II shows the maximum desorption rate, according to Eq. (C3) of a thick solid H_2 film for several temperatures near 4.2 K.

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