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Wetting of gold-plated quartz by liquid ^{4}He

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Experiments with gold-plated quartz-crystal resonators show that uniform and stable films of both superfluid and normal-liquid helium, with thicknesses up to 60 nm, can be formed on a planar substrate. Thick fluid films are also formed in the critical adsorption region above the gas-liquid critical point.

The wetting of solid surfaces by solid and liquid films, due to van der Waals forces, has excited considerable experimental[1] and theoretical[2] interest. Krim *et al.*[1] have shown that many gases completely wet a Au(111) surface only at temperatures above the bulk triple point. In this region a liquid film forms whose thickness d increases continuously (type-I film growth) as the gas pressure P approaches the saturated vapor pressure P_0. Below the triple point a solid film forms whose thickness remains finite at P_0, exhibiting incomplete wetting at coexistence or type-II film growth. The limiting thickness d_0 is temperature dependent and is thought to be due to structural mismatch between the film and the bulk solid phase of the adsorbed gas. Helium, which has no bulk triple point, is a special case as the films adsorbed from the vapor are liquid (apart from the initial atomic monolayer which is tightly bound and localized) at all temperatures below the critical point. However, Bienfait *et al.*[3] have found incomplete wetting on a number of substrates by both superfluid and normal helium films with, for example, $d_0 \simeq 4$ atomic layers for graphite foam, graphite powder and Mylar at $T \simeq 2$ K. Migone *et al.*[4] have reported the incomplete wetting of ^{4}He films on planar Ag and Au(111) surfaces, with d_0 increasing from 10 layers at the λ point to more than 50 layers at higher temperatures with the possibility of a wetting transition within 1 mK of the critical point at 5.1953 K. These results seem to be at variance with numerous other experiments, particularly those of Sabisky and Anderson,[5] Hemming,[6] and Yang and Mason,[7] who found that thick films of He II with d up to 40 nm were stable on various substrates, including Au. Recently, Taborek and Senator[8] have reported a wetting transition in liquid helium at the λ point with the complete wetting of substrates by the superfluid, He II, but only incomplete wetting by He I. We have recently measured the transverse acoustic properties of thick ^{4}He films in both normal[9] and superfluid[10] states and also helium adsorption above the critical point,[11] using quartz-crystal resonators similar to the microbalances used by Migone *et al.*[4] We find that thick films of both superfluid and normal liquid helium can be formed on our gold-plated quartz crystals. The purpose of this paper is to discuss our results and to give theoretical calculations relevant to the experiments by Migone *et al.*, using the theory for the transverse acoustic impedance of inhomogeneous fluids.[12]

We used AT-cut quartz-crystal resonators excited at the third harmonic ($n=3$) at 20.5 MHz to propagate a shear or viscous wave[13] into helium adsorbed on the electrodes of the crystal. The crystal resonator was mounted horizontally a height h above the surface of a reservoir of bulk liquid helium in a copper cell attached to a dilution refrigerator and both its quality factor Q and series resonant frequency f_s were measured. The changes in Q^{-1} and f_s due to the helium are proportional to the real and imaginary parts of the complex transverse acoustic impedance $Z = R - iX$ of the adsorbed helium:

$$\Delta Q^{-1} = 4R/n\pi R_q, \quad \Delta f_s = -2fX/n\pi R_q \ , \tag{1}$$

where R_q ($=8.862\times 10^6$ kg cm^{-2} s^{-1}) is the impedance of the quartz.

The pressure $P'(x)$ and density $\rho(x)$ of the helium a distance x from the crystal are determined by the condition that the chemical potential μ of the ^{4}He atoms must be independent of x. If the thermodynamic properties of the adsorbed helium are identical to those of bulk helium of the same density then we can write[14]

$$m_4 \int_P^{P'} \frac{dP'}{\rho(x)} = -\Phi(x) = \frac{Ak}{x^3} \ , \tag{2}$$

where P is the applied pressure and $\rho(x)$ is related to $P'(x)$ by the equation of state of bulk helium. $\Phi(x)$ is the van der Waals potential[5] which varies as x^{-3} for small x (<5 nm) while for large x (>20 nm) Φ becomes proportional to x^{-4}. Hence the van der Waals parameter A, defined in Eq. (2), depends on x. For our crystals we have taken the empirical value 2.0 K nm^3 [42 K (atomic layers)^3] in the limit $x=0$, decreasing to 0.57 K nm^3 (12 K layers^3) at $x=22.5$ nm. Migone *et al.*[4] found a value of 1.88 K nm^3 (40 K layers^3) for thin films at 2 K. Below the critical point a liquid film forms whose thickness d is given by

$$m_4 \int_P^{P_0} \frac{dP'}{\rho(x)} = -k_B T \ln(P/P_0) = Ak_B/d^3 \ , \tag{3}$$

where $P_0(T)$ is the saturated vapor pressure and the $\ln(P/P_0)$ expression is the result for an ideal gas. In our case P depends on h and on any temperature difference[15] ΔT between the helium film and the liquid reservoir and is given by

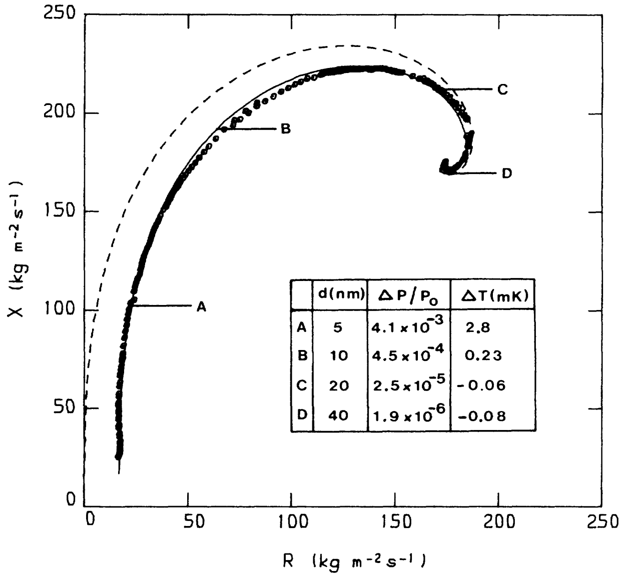
$$P = P_0(T - \Delta T)\exp(-m_4gh/k_BT)$$
$$\simeq P_0(T)\left[1 - \frac{m_4gh}{k_BT}\right] - \left[\frac{\partial P_0}{\partial T}\right]\Delta T \ . \tag{4}$$

Hence

$$\frac{Ak}{d^3} = m_4gh + \frac{k_BT}{P_0}\left[\frac{\partial P_0}{\partial T}\right]\Delta T \ . \tag{5}$$

For an isothermal cell ($\Delta T = 0$), d is determined by h alone and for our crystals varied from 14.5 nm at $h = 7.6$ cm to 22.5 nm at $h = 1.0$ cm. The method for determining d is described below. The effect of ΔT is large. For example, at 3.11 K with $h = 0$ we have $d = 14$ nm for $\Delta T = 0.1$ mK decreasing to 7 nm for $\Delta T = 1$ mK. These equations only apply when the helium film completely wets the substrate. For incomplete wetting the chemical potential and the equation of the state would depend on the film thickness.[2] A variety of different phenomena may then occur.

In our experiments on He I at 3.11 K with $h = 7.6$ cm, we initially observed rapid fluctuations in the Q and f_s of the crystal, and hence in the impedance Z of the helium. These fluctuations were not random but followed a well-defined locus in the impedance plane as shown in the Argand diagram in Fig. 1, and were due to small temperature differentials within the cell produced by the temperature controller which maintained a constant temperature to better than 0.5 mK. We believe that the quartz crystal, the helium film and the surrounding vapor were in good thermal equilibrium but that the bulk helium reservoir, with a relatively large heat capacity, thermally lagged behind the crystal. The effect of this temperature difference is to sweep the vapor pressure on the helium film, as given by Eq. (4). By allowing the temperature to drift slowly, up or down, at different rates round a mean temperature, the impedance locus could be traced out reproducibly and controllably. For large heating rates the film could be almost entirely "burned off" and would then recondense from the vapor.



	d(nm)	$\Delta P/P_0$	ΔT(mK)
A	5	4.1×10^{-3}	2.8
B	10	4.5×10^{-4}	0.23
C	20	2.5×10^{-5}	-0.06
D	40	1.9×10^{-6}	-0.08

FIG. 1. The locus of the measured transverse acoustic impedance of a ^{4}He film at 3.11 K as the film thickness is changed. The curve calculated from transmission-line theory, Eq. (6), is shown for films of bulk impedance 172 $\mathrm{kg\,m^{-2}\,s^{-1}}$ with a vapor impedance of zero (dashed line) and of 16 $\mathrm{kg\,m^{-2}\,s^{-1}}$ (solid line). The crystal was a height 7.6 cm above the surface of bulk helium and the inset table shows the values of $\Delta P/P_0$ and ΔT (see text) required to produce specific film thicknesses for $h = 7.6$ cm.

The transverse acoustic impedance of a homogeneous liquid film[9] (viscosity η_l, density ρ_l) in contact with vapor (viscosity η_v, density ρ_v) is

$$Z = (1-i)(\eta_l\rho_l\omega/2)^{1/2}\tanh[\psi + (1-i)d/\delta] \ , \tag{6}$$

where $\delta = (2\eta_l/\rho_l\omega)^{1/2}$ is the viscous penetration depth of the acoustic wave and $\tanh\psi = \eta_v\rho_v/\eta_l\rho_l$ is the ratio of the vapor to the liquid impedances. For a thick film, $d \gg \delta$, Z tends to the bulk liquid impedance

$$Z_l = (1-i)(\eta_l\rho_l\omega/2)^{1/2} = (1-i)r_l \tag{7}$$

while for thin films, $d \ll \delta$, we find

$$Z = (1-i)(\eta_v\rho_v\omega/2)^{1/2} - i\omega\rho_l d \ , \tag{8}$$

where the first term is the vapor impedance and the second term gives the well-known frequency shift for a microbalance with a mass loading of $\rho_l d$ per unit area. The values of $r_l = 172$ $\mathrm{kg\,m^{-2}\,s^{-1}}$ and $\eta_l = 32$ μP at 3.11 K are known from our previous work[13] and we calculate $\eta_v = 7.9$ μP.[16] The theoretical impedance locus from Eq. (6) as d is varied for a given temperature is shown in Fig. 1, together with the impedance for a liquid film neglecting the effects of the vapor impedance. The locus of Z is a spiral starting at the vapor impedance for $d/\delta \ll 1$ and converging to the bulk liquid impedance for $d/\delta \gg 1$, where $\delta = 19$ nm at 3.11 K.

There will also be an extra mass-loading contribution to Z for a real helium film due to the excess mass per unit area in the high-density atomic layers very close to the crystal. These give a simple frequency shift[13] and to allow for this, the origin of the X axis in Fig. 1 has been chosen so that X equals the known value for the bulk liquid impedance for $d \gg \delta$. The $R = 0$ line corresponds to the temperature independent value of Q^{-1} in He II below 0.6 K.

The agreement between experiment and theory is excellent and shows that the helium films are uniform and stable. Similar results and agreement were also found at 2.33 and 2.78 K. The film thicknesses covered by the data in Fig. 1 range from 1.5 to 60 nm (4 to 170 atomic layers) as shown for selected points and could be swept smoothly over the whole range. For the data in Fig. 1 the crystal was 7.6 cm above the bulk liquid helium reservoir. The inset table in Fig. 1 shows the temperature difference ΔT and the resultant values of $1 - P/P_0 = \Delta P/P_0$ which would produce film thicknesses of 5, 10, 20, and 40 nm, as given by Eqs. (3) and (4) for complete wetting. Unfortunately we were not able to measure ΔP or ΔT directly as these are extremely small, particularly for $d > 10$ nm. Such measurements would constitute a very direct test of Eq. (2) and would conclusively determine the wetting properties of liquid helium on our crystals. However, our measurements show no sign of any limiting film thickness or any discontinuities or instabilities which might be associated with incomplete wetting or a wetting transition.[2] We consider that our results strongly suggest that the conventional idea that liquid helium completely wets solid substrates is correct.

It is worth emphasizing here that the spiral locus of Z in Fig. 1 means that the frequency of a microbalance decreases initially as a liquid film grows but then passes through a minimum for $d \simeq \delta$ and then oscillates weakly about the bulk liquid value. This behavior was described by Yang[17] and Yang and Mason[7] but as R was not measured, the locus of Z could not be plotted. This effect was also seen, though not explained, by Chester, Yang, and Stephens in He II films.[18]

Below the λ point the large heat and mass carrying capability of the superfluid reduces ΔT to a very small value and for He II films we found a stable film thickness determined only by h. Measurements of $Z(T,d)$ were made to below 0.5 K and a full account of this work will be published elsewhere.[10] The value of d for the superfluid film was determined in two independent ways. Figure 2 shows a typical locus of Z as the temperature was increased for a fixed h, in this case 7.6 cm. Below the λ point the film thickness is constant and the loci are almost straight lines on an Argand diagram. Close to T_λ however, the bulk liquid helium, with a large heat capacity, thermally lags behind the crystal and the adsorbed film which rapidly evaporates as it becomes normal and Z then follows the spiral locus as in Fig. 1. By extrapolation of the locus of Z in the superfluid state to the normal spiral, the thickness d of the superfluid film can be estimated. The thickness d below T_λ can also be found by fitting the temperature dependent $Z(T,d)$ to Eq. (6) using the known values[13] for the bulk impedance $Z_l(T)$ at 20.5 MHz which defines η_l and δ, leaving d as the only unknown parameter (below 2 K, the impedance of the vapor can be neglected and $\psi \simeq 0$). The values of d obtained in this way are in good agreement with the λ point extrapolations, and showed no temperature dependence. The van der Waals potential, Eq. (2), was derived from these measurements and was found to be proportional to $x^{-4.0\pm0.4}$ for this range of film thicknesses (14–22 nm) with numerical values close to those found by Hemming[6] for a quartz substrate.

We have also measured[11] the impedance of ^{4}He as a function of pressure at a temperature 49 mK above the gas-liquid critical point as shown in Fig. 3. The frequency shifts were corrected for the linear pressure dependence[13] of the quartz resonator itself. In this region there

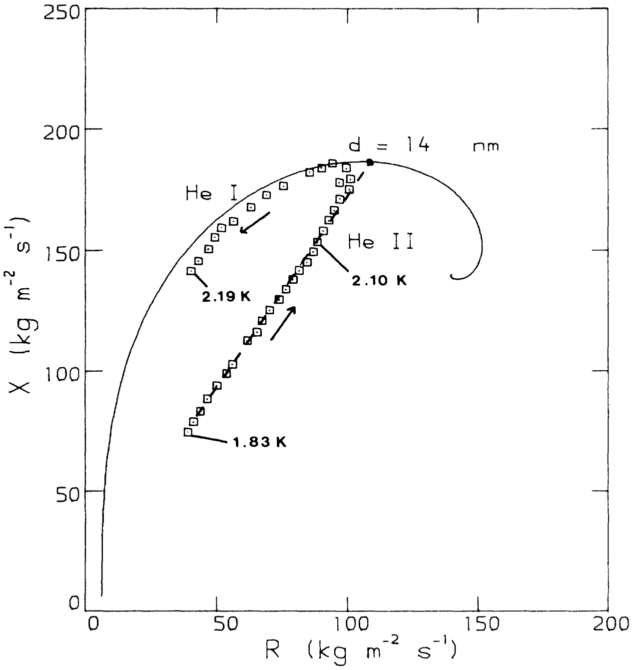


FIG. 2. The locus of the measured transverse acoustic impedance of a ^{4}He film as it warms through the λ transition. The temperatures are shown for selected points. In the superfluid state the film thickness d is constant at 14 nm but the bulk impedance is strongly temperature dependent. The solid line shows the impedance locus for a temperature just above the λ point, as d is varied. The dashed line shows the extrapolation from He II to the λ point to determine d. In the normal state the film thickness decreases as the film evaporates.

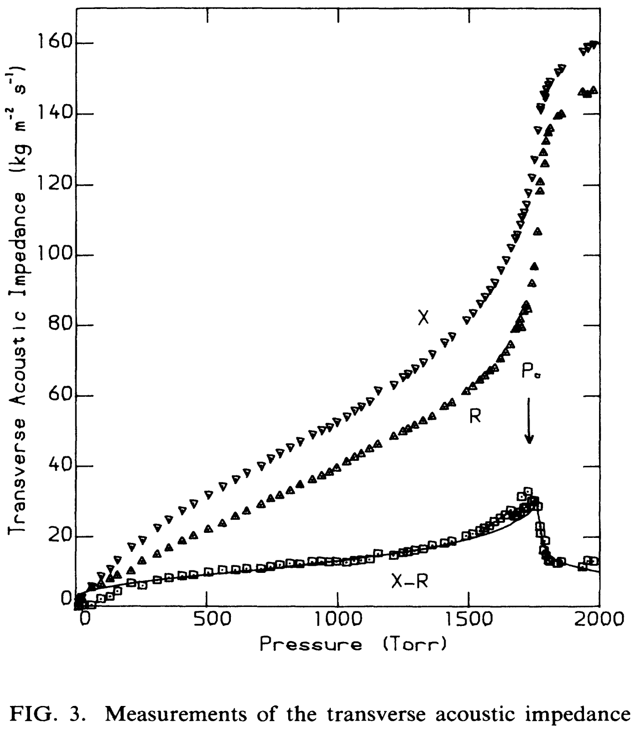


FIG. 3. Measurements of the transverse acoustic impedance $Z = R - iX$ of helium as a function of pressure at a temperature of 5.239 K, 49 mK above the critical temperature. The solid line shows calculations of the excess impedance $X - R$, due to the helium with enhanced density and viscosity close to the crystal surface, as described in the text.

is no liquid-vapor interface and the fluid density $\rho(x)$ varies continuously though it will change rapidly where the local pressure $P'(x)$ is close to the critical pressure P_c(1706 Torr).

The impedance relative to the value at zero pressure is now given by[12]

$$Z=(1-i)(\eta_f\rho_f\omega/2)^{1/2} - i\omega\int_{x_0}^{\infty}\rho(x)\left[1-\frac{\eta_f\rho_f}{\eta(x)\rho(x)}\right]dx\ , \tag{9}$$

where the first term is the impedance of the bulk fluid and the second term is an effective mass loading due to the high density atomic layers near the crystal. This equation can be derived from the differential form of Eq. (6) by integrating the contribution to Z from an incremental layer dx for $x \ll \delta$. The origin for the integration is the fluid boundary at $x=x_0=0.36$ nm since the substrate is coated with a localized monolayer of helium at all pressures.[13] Thus the real part R of the acoustic impedance in Fig. 3 is due to the viscosity of the bulk fluid which gives an equal contribution to X (except at the lowest pressures in the nonhydrodynamic region where $\omega\tau > 1$). The difference $X-R$ is the second term in Eq. (9) due to the excess mass loading, and is shown in Fig. 3. We have calculated the density profile $\rho(x)$ due to the van der Waals forces from Eq. (2) using the equation of state for helium given by McCarty.[19] The viscosity $\eta(x)$ was assumed to depend on the local fluid density as in the bulk,[20] and the van der Waals constant was taken as $A=2.0$ K nm^3, the value for small x. The excellent agreement between the calculations and the data in Fig. 3 show that the adsorption of helium is well described by Eq. (2) with the equation of state of the bulk fluid and that the van der Waals constant is not significantly temperature dependent below 5 K. Any free-energy effects that might lead to incomplete wetting might also be expected to influence the adsorption in the critical region.

The conclusions from our experiments are that both superfluid and normal liquid-helium films of any thickness can be formed on our crystals, and they suggest that complete wetting occurs. Above the critical point, thick fluid films are observed and the adsorption can be calculated from the equation of state of bulk helium and van der Waals forces only. We have previously shown[13] that the growth of solid ^{4}He films on our crystals from the bulk liquid at pressures near the melting curve exhibits incomplete wetting. These conclusions are in line with the work of Krim *et al.*[1]

The results on liquid films, however, differ both qualitatively and quantitatively from those of Migone *et al.*[4] using similar crystals at a fundamental frequency of 8 MHz. They measured the frequency shift of an AT-cut crystal (i.e., the imaginary part X of the impedance) as a function of helium pressure P up to the saturated vapor pressure (SVP), P_0, at temperatures up to the critical point. By extrapolating to P_0 from the thin film regime they concluded that there was a limiting film thickness d_0 and hence incomplete wetting on the coexistence line of vapor and liquid. Although both sets of crystals were gold plated, the surfaces could be significantly different in their wetting characteristics. We used standard commercial crystals, selected for high Q, which were initially cleaned ultrasonically in acetone. The quartz substrate was polished for overtone use and the gold electrodes, 150 nm thick, were smooth down to 10 nm as seen in an electron microscope. The plating was well bonded to the quartz, showing no deterioration after many thermal cycles. In order to compare the two sets of data we have calculated the theoretical impedance, and hence the frequency shift, at 8 MHz as a function of P/P_0 at 4.819 K for complete wetting using Eqs. (3) and (6) with $A=1.88$ K nm^3 (their value at 2 K) as shown in Fig. 4. The dashed line shows the theoretical frequency shift for the helium film alone ($\rho_l=0.106$ g cm^{-3}, $\eta_l=29\mu P$) whose thickness is determined by the van der Waals forces, Eqs. (2) and (3). We used the equation of state given by McCarty[19] to calculate the chemical potential of the nonideal vapor. The solid line shows the total frequency shift for the film and vapor together. The vapor gives the major contribution to Δf at this temperature. Extremely close to P_0 ($\Delta P/P_0 = 3.2\times10^{-5}$), the total frequency shift should pass through a maximum ($\simeq 58.0$ Hz) when the film thickness $d\simeq\delta$ before decreasing to the bulk liquid value of 50.5 Hz at SVP, as shown in the inset in Fig. 4. There will also be

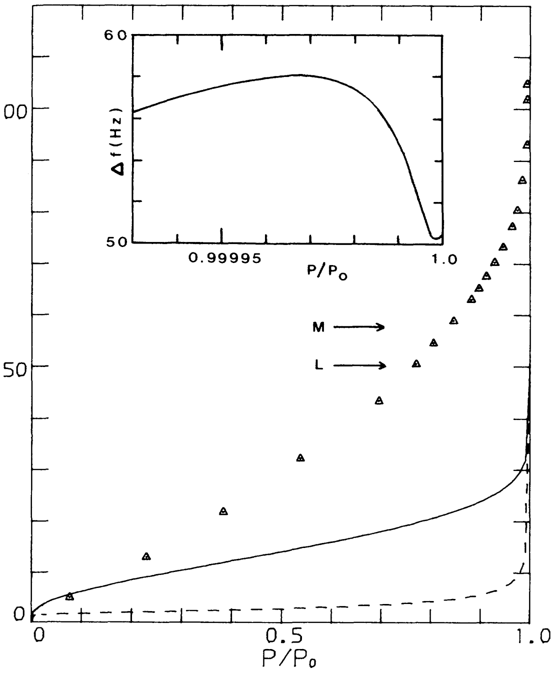


FIG. 4. The calculated frequency shifts for an 8-MHz quartz crystal using Eqs. (2), (3), and (6) for a temperature of 4.819 K. The dashed line shows the contribution from the liquid film only while the solid line shows the total shift from both the film and the vapor. The arrows show the total frequency shift L for the bulk liquid and the maximum M which occurs for $d\simeq\delta$ at $\Delta P/P_0=3.2\times10^{-5}$, as shown in the inset for pressures very close to the SVP. The data points are from Migone *et al.*[4] for the film only.

an additional frequency shift due to the enhancement of the density of the first few atomic layers which should be in place for $P/P_0 > 0.1$ and will be of the order of 7.5 Hz at 8 MHz, though this will depend on the roughness of the gold surface. Also shown in Fig. 4 are the results of Migone *et al.*[4] at 4.819 K which they have corrected for the pressure dependence of the quartz crystal and for the viscosity of the vapor. The observed frequency shift is considerably larger than the theoretical one for the film alone, even for pressures well below the SVP. Migone *et al.*[4] ascribe this to a temperature-dependent van der Waals constant but a value of $A = 4.4 \times 10^3$ K nm^3 is then required, an increase by a factor of 2.4×10^3 from 2 K, which is difficult to justify theoretically. Moreover the observed frequency shift at P_0 is considerably larger than the expected value for bulk liquid. We conclude that the frequency shifts observed at the higher temperatures by Migone *et al.*[4] are not due to the growth of the helium film alone. The effects increase as the critical point is approached and this suggests that they are associated with the increasing vapor pressure. Migone *et al.* also recognized these difficulties in their interpretation and suggested that an impure mode of crystal vibration could couple to longitudinal sound (and hence to sound waves in the vapor) and this might explain their results.

Our observations can also be compared to those of Taborek and Senator.[8] They found that the film thickness on graphite and platinum wires changed dramatically as the film became superfluid even though the temperature differential between the film and the vapor, $\Delta T < 0.1$ mK, and that normal ^{4}He and ^{3}He films had a limiting thickness $d_0 = 13$ layers (4.7 nm). We also observed film thinning when warming through the λ transition as shown by the locus of Z in Fig. 2. This effect was largely due to $\Delta T \sim 0.5$ mK, as it depended strongly on the heating rate, and this would mask, and indeed mimic, the effect seen by Taborek and Senator. As our experiment was mounted on a dilution refrigerator it was not possible to immerse the cell in a bath of superfluid ^{4}He to improve the temperature stability. However our experiments clearly show that thick films ($d \le 60$ nm) of He I can form on a planar substrate. These films are flat and uniform as shown by the agreement between experiment and theory in Fig. 1. The response time of the film thickness was faster than the time constant, 0.3 s, of our measurement system. Since the film thickness could be kept constant for long periods of time, this suggests that these thick films are not metastable but are in dynamic equilibrium with the helium vapor.

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[1] J. Krim, J. G. Dash, and J. Suzanne, Phys. Rev. Lett. **52**, 640 (1984); R. F. Karper, J. W. Schmidt, and M. R. Moldover, Phys. Rev. Lett. **54**, 707 (1985), and references therein.

[2] R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982); D. E. Sullivan and M. M. Telo de Gama, *Fluid Interfacial Phenomena,* edited by C. A. Croxton (Wiley, New York, 1986), pp. 45–134; P. G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985); P. Tarazona and R. Evans, Mol. Phys. **48**, 799 (1983).

[3] M. Bienfait, J. G. Dash, and J. Stoltenberg, Phys. Rev. B **21**, 2765 (1980).

[4] A. D. Migone, J. Krim, J. G. Dash, and J. Suzanne, Phys. Rev. B **31**, 7643 (1985).

[5] E. S. Sabisky and C. H. Anderson, Phys. Rev. A **7**, 790 (1973).

[6] D. Hemming, Can. J. Phys. **49**, 2621 (1971).

[7] L. C. Yang and P. V. Mason, Cryogenics **20**, 91 (1980).

[8] P. Taborek and L. Senator, Phys. Rev. Lett. **57**, 218 (1986).

[9] D. S. Spencer, M. J. Lea, and P. Fozooni, Phys. Lett. **109A**, 295 (1985).

[10] M. J. Lea, D. S. Spencer, and P. Fozooni (unpublished).

[11] M. J. Lea, D. S. Spencer, and P. Fozooni, in *Proceedings of the 17th International Conference on Low Temperature Physics,* edited by V. Eckem, A. Schmid, W. Weber, and H. Wahl (North-Holland, Amsterdam, 1984), Part I, p. 63.

[12] M. J. Lea and P. Fozooni, Ultrasonics **23**, 133 (1985).

[13] M. J. Lea, P. W. Retz, and P. Fozooni, J. Low Temp. Phys. **54**, 303 (1984); M. J. Lea and P. Fozooni *ibid.* **56**, 25 (1984); **62**, 55 (1986).

[14] T. Oestereich and H. Stenschke, Phys. Rev. B **16**, 1966 (1977).

[15] K. R. Atkins, *Progress in Low Temperature Physics,* edited by C. J. Gorter (North-Holland, Amsterdam, 1957), Vol. II, p. 108.

[16] D. S. Betts, Cryogenics **16**, 3 (1976).

[17] L. C. Yang, Ph.D. thesis, University of California at Los Angeles, 1973.

[18] M. Chester, L. C. Yang, and J. B. Stephens, Phys. Rev. Lett. **29**, 211 (1972).

[19] R. D. McCarty, J. Phys. Chem. Ref. Data **2**, 923 (1973).

[20] K. Okbayashi and A. Ikushima, J. Low Temp. Phys. **15**, 33 (1974); J. M. Goodwin, Physica **76**, 177 (1974).