PHYSICAL REVIEW B VOLUME 31, NUMBER 12 15 JUNE 1985

Incomplete wetting of ^{4}He films on Ag and Au(111) surfaces

A. D. Migone, J. Krim,* and J. G. Dash
Physics Department, University of Washington, Seattle, Washington 98195

J. Suzanne
Département de Physique, Faculté des Sciences de Luminy, Université d'Aix-Marseille II,
Case Postale 901, F-13288 Marseille (Cédex) 9, France

(Received 24 January 1985)

The wetting behavior of ^{4}He adsorbed on planar Ag and Au(111) surfaces has been studied by means of a quartz, high-frequency microbalance. Incomplete wetting was observed over the entire experimental temperature (T) range from below 1.4 K to 1 mK below the critical point. The limiting film thickness d_0 at coexistence with bulk liquid increases from about 10 layers at the λ point to more than 50 layers at the highest temperature. Over a considerable interval the T dependence of d_0 is consistent with the power law $d_0 \propto (T_w - T)^{-1}$ proposed by Dietrich and Schick for critical wetting. Below the λ point the frequency isotherms develop pronounced dips at pressures well below saturated vapor pressures P_0. The dips are associated with superfluid onset, and the clear separation between the dips and the abrupt increases in frequency at P_0 show that superfluid onset and bulk fluid condensation are independent phenomena.

I. INTRODUCTION

Thin adsorbed films of helium have been studied for many years as model systems for adatom-substrate potential calculations and in the context of superfluidity onset.[1-4] Central to these studies is the uniformity and mode of growth of the helium film. Several experiments have given indirect evidence for incomplete wetting, i.e., uniform layer deposition only up to some critical thickness before condensation of the bulk, of ^{3}He and ^{4}He adsorbed on graphite and other substrates.[5-8] Nonetheless, the mode of growth of helium on these substrates has been a matter of disagreement, due to ambiguities in the interpretation of experimental results. The mode of growth of He films is an important question for the understanding of wetting phenomena in physisorption. This paper presents conclusive evidence for incomplete wetting of ^{4}He on Ag and Au(111) over the entire experimental temperature range, from 1.4 K to 10 mK (see *Note added in proof.*) below the critical point.

Traditional belief has held that at $T=0$, physisorbed films on smooth, strongly attractive substrates can coexist with the bulk phase only in the limit of infinite film thickness, while on less attractive substrates a film of finite thickness coexists with the bulk. The former behavior is termed "type-1," or Frank—van der Merwe growth, and corresponds to a completely wet film at coexistence. The latter behavior is termed "type-2," or Stranski-Krastanov growth, the film being incompletely wet at coexistence.[9] It was recently discovered that type-1 growth of solid films at low T is limited to a narrow range of relative substrate attraction, type-2 growth being observed for systems characterized by both stronger and weaker relative substrate attraction.[10-12] The occurrence of reentrant type-2 growth at large relative substrate attraction was quickly explained as a result of structural mismatch between the layers close to the substrate and close-packed planes of the bulk.[13-16] The first few adsorbed layers are compressed by strong substrate forces, to densities greater than the bulk planes, preventing continued epitaxial growth to greater thicknesses. This mechanism explains why the only thick films observed at low temperature have relative substrate strengths falling within a narrow range of values. It also explains "triple-point wetting,"[12] in that the transition to complete wetting is generally at the triple point, where bulk phase crystallinity disappears.

In view of the foregoing explanation, the wetting behavior of helium films is paradoxical, for they are extreme cases of "strong substrate" systems, yet their surface layers and coexisting bulk phases are liquid. Thus, incomplete wetting of these films can neither be explained by structural mismatch nor by weak substrate forces. The strength of the substrate-atom interaction is illustrated in Table I, which compares atom-atom and atom-substrate interactions of rare-gas—graphite films and ^{4}He/Au(111), together with their observed growth habits at low temperature. Two different gauges are given. One is the ratio u_1/h_0, which was proposed by Bienfait *et al.*:[11] u_1 is the low-coverage atom binding energy, and h_0 is the 0-K cohesive energy of the bulk adsorbate. Also tabulated are the values of C_3/h_0, where C_3 is the coefficient of the coefficient of the long-range atom-substrate interaction. This alternative ratio is more appropriate to the wetting behavior of thicker films, e.g., of He on graphite and gold. We see that, employing either criterion, both ^{4}He/graphite and ^{4}He/Au(111) are characterized by much stronger relative substrate strength than those films which display type-1 growth. The interaction parameters for Ag are comparable to those for Au.[18] Thus, the motivation for this experiment was a definitive test of the wetting characteristics of ^{4}He on open and well-characterized

TABLE I. Comparison of atom-atom and atom-substrate interaction strengths.

Gas	Substrate	h_0/k (K)[a]	u_1/h_0[b]	C_3/h_0 (Å)[c]	Growth type
H_2O	graphite	5720	0.33		2
C_2H_4 (ethylene)	graphite	2309	0.4—0.7		2[d]
Xe	graphite	1908	1.18	23.1	1[a]
Kr	graphite	1353	1.15	22.0	1[a]
Ar	graphite	930	1.28	22.9	1[a]
Ne	graphite	226	1.55	29.7	2[a]
^{4}He	graphite	7.22	20.0	296.0	2[e]
^{4}He	Au(111)	7.22	6.0	477.0	2[f]

[a] Reference 11.
[b] Reference 17.
[c] References 18 and 19.
[d] References 20—22.
[e] References 3 and 6—8.
[f] This work.

"strong" substrates, where the results could not be confused by effects of capillarity.

II. EXPERIMENTAL DETAILS

We determined the growth characteristics of ^{4}He on polycrystalline Ag and Au(111) surfaces from vapor pressure isotherms. The film thicknesses were measured directly by the frequency shift of a high-frequency quartz microbalance. Descriptions of the apparatus and technique are given elsewhere,[12,23,24] and are summarized here. The microbalance crystals were 8-MHz *AT*-cut quartz, and the adsorption substrates were the metal film electrodes deposited on the plane faces of the crystal. Isotherms were obtained with the polycrystalline Ag electrode surfaces of the commercial crystals,[25] and with specially prepared Au surfaces. We produced the Au films by UHV evaporation of 99.999%-purity Au on the faces of quartz-crystal blanks. The deposits were examined by x-ray diffraction, low-energy electron diffraction, and Auger electron spectroscopy. These showed the films to be polycrystalline, with (111) surfaces parallel to the surface plane. Substrate perfection, determined from the verticality of Krypton vapor pressure isotherm steps, indicated that the effective size of uniform surface domains was at least 200 Å.

Most of the isotherm measurements were taken from the Ag-plated crystals, which were found to be somewhat more stable and robust. The Au-plated crystals usually became inoperative after several cycles to room temperature, perhaps because of some defects in design of the crystal mounts. The Ag substrates were evidently less uniform as measured by vapor pressure isotherms, but we found no essential differences in the wetting behavior on the two types of surface.

The oscillator frequency is compared with a similar oscillator whose crystal is maintained in an insulated chamber at room temperature. The difference frequency Δf was monitored to 0.01 Hz in continuous recording, and to 0.1 Hz in point-by-point isotherms. The shift was stable to within 0.1 Hz over a period of one hour, a typical experimental run lasting fifteen minutes to somewhat over one hour. The isotherms were recorded by plotting pressure, as recorded by a capacitance manometer, versus Δf, either by continuous chart recording during the slow admission of He gas to the system, or by discrete measurements after small increments of He. The latter method was used for the most careful work near P_0, especially at high temperature. During each isotherm the temperature was held constant within 10^{-3} K. Temperatures were determined from vapor pressures on the 1958 scale[26] (see *Note added in proof.*).

III. EXPERIMENTAL RESULTS; QUALITATIVE BEHAVIOR

Figure 1 displays three typical frequency-vapor pressure isotherms. The principal features are, after a very rapid frequency shift at low pressure, a gradual rise up to $P/P_0 \simeq 0.8$ and then an accelerated increase to saturated vapor pressure, where the frequency rises abruptly. The finite-frequency intercept Δf_0 at $P/P_0=1$ is a signature of incomplete wetting, indicating a finite film thickness d_0 at coexistence with bulk. The reversal in the $T=1.555$ K isotherm is due to superfluid onset, discussed later.

In conventional uses of microbalances, as for thickness gauges of solid films, frequency shift is proportional to the thickness of deposited film. The relation becomes nonlinear for thick liquid films such as we encountered at relatively high temperatures; nevertheless, a finite-frequency intercept at P_0 remains a clear indication of incomplete wetting. A detailed analysis of thick liquid film behavior is postponed to the next section.

The frequency intercepts can be estimated directly from the Δf-versus-P isotherms, or with somewhat greater precision, from graphs of $\ln(P/P_0)$ versus $(\Delta f)^{-3}$. We found that all isotherms at $T>T_\lambda$ near $P=P_0$ are linear when plotted in this way. This empirical behavior is similar to the findings of Krim *et al.*[12] in the incomplete wetting regimes of classical films above and just below their wetting transitions. As those authors observed, the relation stems from the range dependence of the van der Waals interaction between adsorbate and substrate. Although the exact relation becomes nonlinear in thick liquid films, as we show later, linearity continues to be a

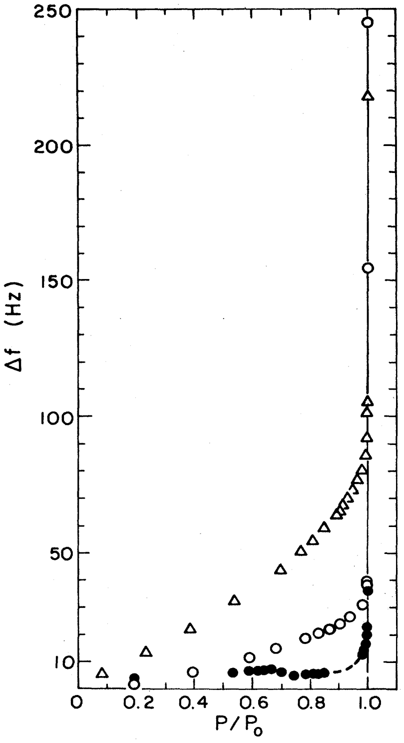

FIG. 1. Examples of frequency-vapor pressure isotherms. ●, 1.555 K; ○, 3.917 K; △, 4.819 K. The reversal in the $T=1.555$ K isotherm is attributed to superfluid onset, discussed in the text; and shown with greater clarity in Fig. 3.

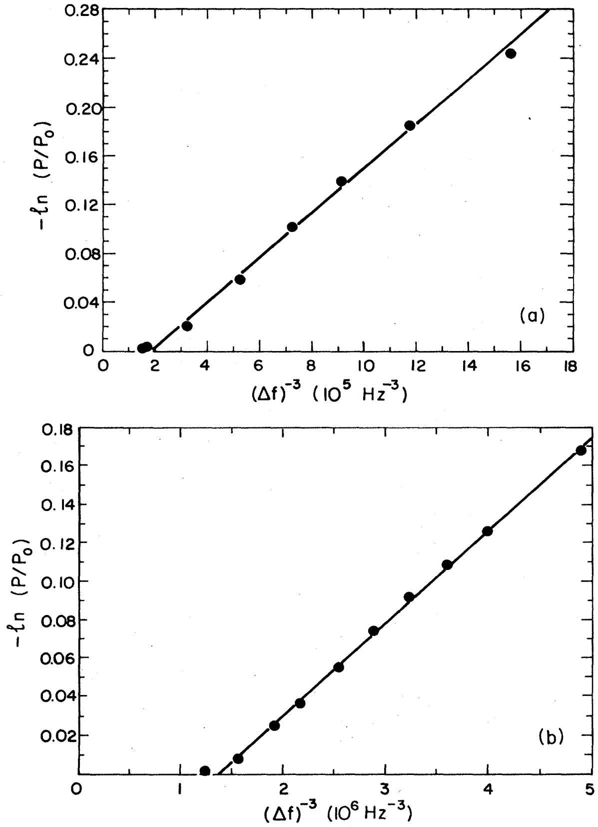

FIG. 2. Isotherm data for (a) 3.817 K and (b) 4.819 K, illustrating the linearity of $\ln P$ versus $(\Delta f)^{-3}$.

useful approximation over a limited range near $P=P_0$. Figure 2 illustrates this linearity with the same data as shown in Fig. 1: it allows our estimate of Δf_0 to within a few percent.

Several years ago, Chester, Wang, and Stephens[27] conducted such measurements of He adsorption, in a study of superfluid onset is unsaturated films. Herb and Dash[28] subsequently studied effects of heterogeneity on the transitions. However, neither of these experiments examined the nature of the isotherms near P_0. Chester *et al.* reported anomalous frequency shifts near P_0, which they were unable to explain. We found similar shifts in some of our early work with certain crystals and crystal mounts, which we believe were due to mode instabilities at high mass loading. Other crystals and mounts were found to be more suitable, enabling us to obtain stable and reproducible shifts at all film thicknesses.

At temperatures below the λ point, $T_\lambda=2.172$ K, the frequency isotherms develop distinctive dips. Δf reverses direction rather suddenly, and then gradually returns to its original trend, as seen in the lowest-temperature isotherm of Fig. 1, and in greater detail in Fig. 3. Such dips were observed in the earlier microbalance studies of He films and attributed to superfluid onset. We find good agreement with the previous measurements of the pressures $P(T)$ of the sudden reversals. It has been argued that the superfluidity of thin films is a consequence of bulk droplet condensation at pressures below P_0.[3] However, this appears not to be the case: the abrupt rises of

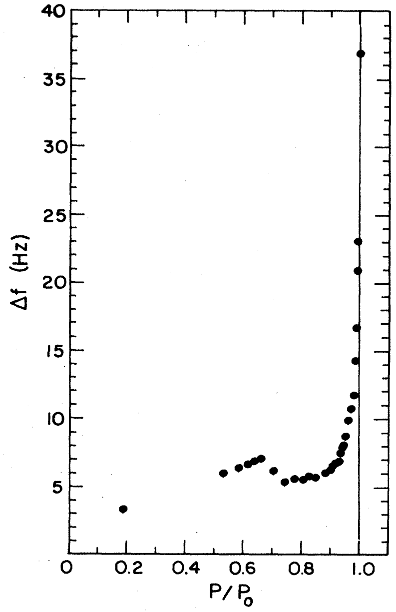

FIG. 3. Frequency-pressure isotherm for $T=1.555$ K, showing the characteristic dip due to superfluid onset in low-temperature films at $P<P_0$, and the abrupt condensation of bulk fluid at P_0.

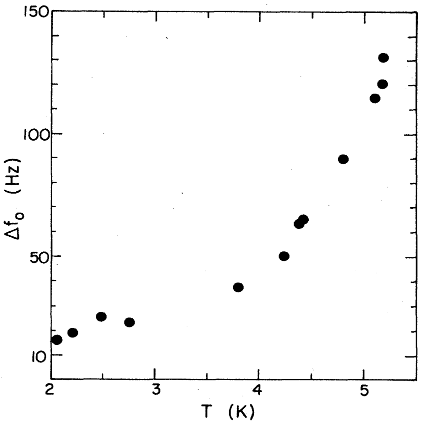

FIG. 4. Frequency intercepts Δf_0 at $P/P_0=1$, versus T.

frequency at P_0 which signal bulk condensation are seen to be quite distinct from the dips. The two features are well separated in both the Ag-plated and Au-plated crystals, showing that neither superfluid onset nor bulk condensation are seriously perturbed by substrate heterogeneity on these relatively uniform surfaces. The implications of these results, as related to superfluid onset in thin films, are discussed further in Sec. V. In Fig. 4 we present a graph of the frequency intercepts over the temperature range above T_λ. The general trend is a smooth monotonic increase of Δf_0 with T, from about 16 Hz at 2.1 K to 132 Hz at 5.189 K, which is only 10 mK (see *Note added in proof.*) below T_c. There may be a weak local maximum near Δf_0 at 2.5 K, but we find no dramatic changes near T_λ.

IV. ANALYSIS: FILM THICKNESS

The frequency-mass dependence in our study is more complicated than the simple proportionality which holds for thin films. (The simplest corrections are vapor effects: a frequency shift due to hydrostatic pressure on the crystal, strictly proportional to P, and a mass shift due to viscous drag of the vapor.[23,24] Both types of correction were routinely applied to the directly measured shifts before any analysis for film thickness. In the following, all discussion of Δf refers to the corrected shifts.)

The mass sensitivity of the crystal frequency can be estimated theoretically from the resonant frequency and the elastic constants and density of quartz.[23] For mass σ per unit area deposited uniformly on each plane face, the sensitivity of our 8-MHz crystals is $K=df/d\sigma=2.89\times10^8$ Hz cm^2/g. We also measured K directly, from N_2 adsorption at 67.3 K, above the bulk N_2 triple point.

Krim *et al.*[12] found that all of the adsorbates they studied, including N_2, completely wet Au(111) above their triple points. Our results for N_2/Ag are consistent with theirs, in that the calibration isotherm showed a similar dependence of frequency shift with pressure over a substantial range, with no indication of a finite-frequency intercept at P_0. We computed film thickness according to the van der Waals relation

$$kT\ln(P_0/P)=C_3/d^3 \tag{1}$$

with interaction constant $C_3=1.81$ eV Å^3 given by Rauber *et al.*[18] for N_2/Ag. A small correction was applied to C_3 to account for the reduction of effective interaction due to the adsorbed film.[29] The calibrated sensitivity is $K=3.32\times10^8$ Hz cm^2/g, 15% larger than the theoretical factor. Thicknesses were computed using the calibration value.

In a typical application of a high-frequency microbalance the film deposited on the crystal faces is relatively thin. In this case the added mass is only a small fractional change, and the film moves rigidly with transverse motion of the surface. Thus, the frequency shift is simply proportional to the added mass, as given by the sensitivity factor K. The simple proportionality holds for liquid films provided the film thickness is much less than the "penetration depth" δ of viscous shear waves at the operating frequency ω:

$$\delta=(2\eta/\rho\omega)^{1/2}\ , \tag{2}$$

where η is the viscosity and ρ the mass density of the fluid. The thin-film condition $d\ll\delta$ was satisfied in the recent study of triple-point wetting,[12] but in the present study the film thickness varies from relatively small to large values. Since these conditions are not normally treated in discussions of the microbalance method,[30] we outline the analysis here.

The shear motion in a viscous medium in the small velocity limit satisfies the simplified Navier-Stokes equation for small velocities:[31]

$$\rho\, d\mathbf{v}/dt-\eta\nabla^2\mathbf{v}=0\ . \tag{3}$$

For a flat solid boundary at $z=0$ moving in a transverse direction, Eq. (3) simplifies to a scalar equation in z and the time t. The general solution for the velocity field in the fluid is

$$v_x=\exp(\pm\gamma z+\gamma^2\eta t/\rho)\ . \tag{4}$$

For harmonic motion of the surface, the integration constant γ is given by

$$\gamma=(1\pm i)(\omega\rho/2\eta)^{1/2}\ . \tag{5}$$

The viscous interaction in the fluid exerts a tangential force on the solid surface. The inertial (real) component of the force is proportional to the effective mass of the fluid. For a semi-infinite fluid the effective mass per unit area is

$$\sigma(\infty)=\rho\delta/2\ , \tag{6}$$

where δ is the penetration depth as given in Eq. (2). In the case of a finite thickness d of fluid, the shear force vanishes at $z=d$. The appropriate special solution can be constructed from the general form given in Eq. (4). The effective mass is then found to be $\sigma(d)=\sigma(\infty)F(2d/\delta)$, where

$$F(\xi)=\frac{\tanh(\xi)+\sin(\xi)/\cosh(\xi)}{1+\cos(\xi)/\cosh(\xi)}\ . \tag{7}$$

Equation (7) indicates that the microbalance responds linearly to changes in film thickness as $\sigma(d)=\rho d$ when $d\ll\delta$, but becomes progressively less sensitive as d in-

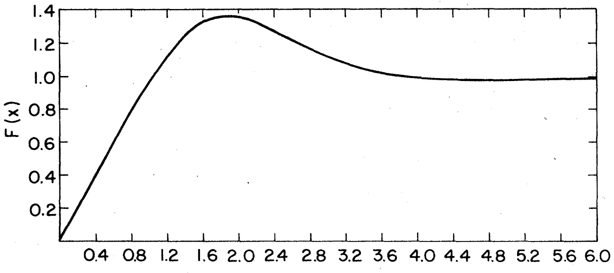

FIG. 5. The effective-mass function of viscous films on a plane substrate in transverse oscillation (see text).

creases, and approaches Eq. (6) as d/δ becomes large. Figure 5 presents a graph of the function $F(\xi)$, showing its strongly damped wave character. The dependence is approximately linear over a substantial range below $\xi=1$, and after a broad maximum and a very weak minimum the function asymptotically approaches unity.

As noted earlier, the variation of frequency with pressure near P_0 for all $T > T_\lambda$ is well described by

$$\ln(P/P_0)=J[(\Delta f_0)^{-3}-(\Delta f)^{-3}] . \quad (8)$$

The empirical constant J increases monotonically with T. The frequency term in Eq. (8) has the form of a truncated variation of P with thickness, as observed by Krim *et al.*[12,24] below the wetting temperature:

$$kT\ln(P/P_0)=C_3(d_0^{-3}-d^{-3}) . \quad (9)$$

In the range 2.2—2.5 K the empirical J on the Ag electrodes implies a van der Waals constant $C_3=162$ meV Å^3. Rauber *et al.*[18] have calculated theoretical expressions for one-body dispersion energies on metal substrates. Their result for He/Ag is $C_3=305$ meV Å^3, is nearly twice our result. The discrepancy may be due to oxide or impurity layers on the Ag surfaces, although the close agreement between the N$_2$ calibration and C_3 calculated by Rauber *et al.* for He/Ag indicates otherwise.

We find a substantial increase of the empirical C_3 with temperature, which we ascribe to nonideality of the vapor at high pressure. At high vapor density the chemical potential contains corrections due to molecular interactions. For slight imperfection the correction is adequately described by means of a second virial coefficient $B(T)$. Its effect is to introduce a correction to the slope of $\ln(P/P_0)$ versus $(d)^{-3}$, so that C_3 is replaced by an effective coefficient C_3^*:

$$C_3^* = C_3(1+BP/kT)^{-1} . \quad (10)$$

Thus, where $B<1$ as in the present study, $C_3^* > C_3$. At moderate pressures the enhancement of C_3 is in reasonable agreement with Eq. (10), using empirical values of B.[32] At higher temperatures and pressures the empirical coefficient rises more rapidly, qualitatively consistent with the limitations of the virial expansion, although we find a larger increase than appears to be indicated by gas imperfection alone.

TABLE II. Frequency shifts.

T (K)	(T_c-T) (K)[a]	Δf_0 (Hz)
2.212	2.9874	19.3
2.493	2.7064	25.1
2.758	2.4414	23.5
3.817	1.3824	37.8
4.245	0.9544	50.9
4.390	0.8094	63.6
4.423	0.7764	65.0
4.819	0.3804	89.9
5.114	0.0854	115.0
5.173	0.0264	120.9
5.189	0.0104	132.0

[a] $T=5.1994$ K; Ref. 26. (See *Note added in proof.*)

The measured frequency shifts Δf_0 are listed in Table II. Figure 6 presents these values (which in the small thickness approximation are proportional to d_0) as a logarithmic function of T_c-T. The general trend over much of the range above T_λ can be described by a power law with exponent (-1) as

$$d_0 \propto (T_w-T)^{-1} , \quad (11)$$

where T_c equal to the wetting temperature T_w. Equation (11) is particularly interesting, since it has the form predicted by Dietrich and Schick[33] on rather general grounds, for van der Waals systems undergoing critical wetting (see Sec. V). In Fig. 6 we see appreciable deviation beginning $\sim$0.5 K below T_c. We think it likely that the principal cause for this divergence is actually due to a failure of the linear frequency-mass relation at large thickness as discussed below. The linear dependence holds for thicknesses lower than $d \simeq \delta/2$, which corresponds to $T \simeq 3.8$ K.[34,35] The proportionality may continue down to low temperatures; however, since the frequency shift depends only on the viscous component of the film, the onset of superfluidity allows only a lower estimate of thickness at $T < T_{\text{onset}}$. Extrapolation of the

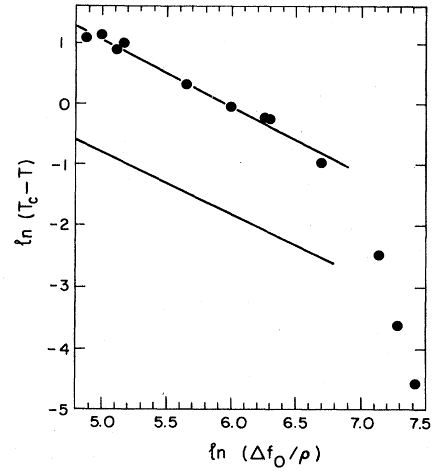

FIG. 6. Logarithmic dependence of frequency shift on the temperature difference (T_c-T). The ratio $(\Delta f_0/\rho)$, where ρ is the density of bulk liquid, is proportional to limiting film thickness d at $T<3.8$ K, but at higher temperature Δf_0 is increased by instrumental effects. The solid line has a slope of -1.

power law yields $d_0 \cong 6$ layers at $T=0$.

For temperatures above ~ 4 K, the measured frequency shifts exceed the maximum predicted from Eq. (7) and the calibrated sensitivity factor K. We speculate on two possible mechanisms for the excess.

The theoretical effective mass in Eq. (7) presumes perfect shear mode oscillation of the crystal. In real crystals, however, there are admixtures of longitudinal and/or flexural vibration.[36] These modes can couple the crystal with film thicknesses up to $d \sim \lambda/2$, where λ is the wavelength of first sound in the fluid. Since λ(8 MHz, 4K)$=2.4\times10^{-3}$ cm,[37] while $\delta=8.5\times10^{-6}$ cm, the effective mass excited by other modes can well exceed the shear wave limit. In solid or thin liquid films the longitudinal modes cause no difficulty since the total effective mass remains proportional to the thickness, but for thick liquid layers the frequency shift involves a nonlinear dependence due to shear; hence the relation between shift and thickness then depends on the relative amplitudes of the two types of vibration. The proportions of mode mixing in our crystals have not been measured.

The theory presumes a planar film-vapor surface, but the crystal motion must also excite surface waves, coupled through lateral variations of the films' binding to the substrate. The surface waves absorb energy and contribute to the total effective mass. For thin films the relatively large van der Waals attraction of the substrate tends to suppress surface waves, hence their effect is small, but as thickness increases the wave amplitudes increase. A quantitative estimate of the effect requires detailed knowledge of the surface irregularities, but such characterization is well beyond the scope of the study.

The two effects prevent us from obtaining a quantitative estimate of the thickness at high temperature. Nevertheless, the monotonic trend of Δf_0 indicates that d_0 continues to increase up to the highest temperatures of the experiment.

V. DISCUSSION

This study has yielded clear proof of nonwetting of ^{4}He adsorbed on uniform planar surfaces from T_λ to 10 mK (see *Note added in proof.*) below T_c. Several earlier experiments on porous and heterogeneous adsorbents have indicated nonwetting below 2.5 K, but their evidence is less conclusive, especially due to the effects of capillary condensation near saturation pressure. From the results of the present and earlier studies, it now appears that the nonwetting regime may extend over the entire domain of liquid-vapor coexistence. An explanation of nonwetting of He films at *any* temperature requires a serious modification or extension of current theory. According to present understanding, nonwetting has two possible causes: weak substrate attraction, or mismatch between the lateral crystal structures of the film and its bulk phase. Neither of these can apply to He films: Virtually all solid substrates are relatively strongly attractive to He, and both the bulk phase and the top layers of the film at coexistence are fluid. On graphite, which has a stronger first-layer attraction but a weaker long-range interaction than Ag and Au (see Table I), the first two layers of adsorbed He at coexistence are solid.[38] On the Ag and Au substrates the first two or perhaps three layers are probably solid, and the remaining layers liquid. Since the solid layers must be covered by liquid at coexistence and the bulk phase is liquid, there can be no structural mismatch at the film-bulk interface.

Apart from its underlying cause, the nature of the wetting transition in the He films is extremely intriguing. Our results strongly suggest that the He/Ag system undergoes a continuous transition, i.e., that the limiting thickness d_0 diverges continuously to infinity as T increases toward the wetting temperature T_w. Although the data do not extend to T_w, the trend of d_0 at lower temperature shows no sign of a finite thickness limit at any $T < T_w$. We have not determined T_w, but it is closely bracketed in the interval $T_c - 10$ mK (see *Note added in proof.*) $\lesssim T_w \lesssim T_c$, since the maximum possible wetting temperature (if wetting occurs at all) is T_c.

The order of wetting transitions is of considerable current interest. In first-order wetting d_0 remains finite as T rises, and then jumps discontinuously to infinity at T_w, where bulk condensation begins. Two types of continuous wetting transitions are possible: triple-point wetting, which involves the intervention of a third bulk phase extending into the unsaturated film region, and critical wetting which involves only two bulk phases. One example of first-order wetting has been reported, CF_4 on graphite.[39] Many examples of triple-point wetting have been observed.[12,20–22] The present results provide the first evidence for critical wetting in any adsorption system.

Theoretical studies have examined the dependence of the order of the transition on the nature of the forces in the system. Several calculations have predicted that first-order wetting can occur for systems with either short-range or long-range forces, but that critical wetting requires short-range forces. Since the van der Waals forces between atoms and between atoms and a substrate are long ranged, it appeared that the wetting transitions of physisorbed films could only be first order. Recently, Dietrich and Schick[33] have explored simple Ising models with long-range interactions which do undergo critical wetting. Their calculation shows that the continuous transition depends crucially on higher-order terms d^{-n}, $n \gtrsim 4$, in the range dependence of the atom-substrate interaction. Dietrich and Schnick predict that, if critical wetting does occur, the variation of thickness with temperature will be described by the power law Eq. (11). Figure 6 shows that our measurements agree with the prediction over a considerable range of T, with $T_w = T_c$. The data show a more rapid increase of thickness close to the critical point, but as we discussed earlier, there are important corrections to the data near T_c which will bring the results into closer agreement with the simpler power law. Furthermore, one might expect the dependence to fail near T_c due to the effects of bulk phase fluctuations. The power law is predicted to hold down to low temperature, provided that d_0 remains much larger than one layer.[40] This condition is satisfied down to T_λ, where $d_0 \simeq 10$ layers, and it may continue to still lower temperature; however, since the microbalance is only sensitive to the viscous component of the film we cannot test the law below the superfluid transition. As for the source of the higher-order terms in the theory, Dietrich and Schick point out that such corrections can originate from many-body forces in the film and the nature and structure of the substrate. Ebner, Saam, and Sen[41] suggest a specific source: a layer of foreign atoms close to the substrate. It is possible that such layers exist on the Ag electrodes in our study, but appreciable contamination is unlikely on the Au electrodes. Moreover, the close agreement between the theoretical sensitivity of the crystal and the value obtained by N_2 adsorption with the theoretical C_3 for N_2/Ag indicates that the Ag is relatively clean. A common feature in the Ag and Au experiments does possibly fit the theoretical requirement: the layer of solid helium next to the substrate. Since the solid has a distinctly different density it certainly introduces higher-order terms in the long-range potential. All known absorption substrates are sufficiently strong to solidify at least one layer of helium, hence critical wetting of helium films may be universal.

Although the principal focus of this study is on wetting, the results have considerable relevance to thin-film superfluidity. Our measurements show that the two phenomena are largely independent. This is not to say that the experiments rule out all forms of coupling between superfluidity and wetting. For example, since both phenomena depend on the equilibrium properties of film and bulk phases, one might expect that $d_0(T)$ will show some evidence of the existence of the bulk transition.[42] However, our measurements are evidently too coarse to show such features. We confirm the dips in frequency below 2 K which were first reported by Chester, *et al.*[27] and attributed by them to the onset of superfluidity in the unsaturated film. Dash and Herb[43] offered a different explanation: They accepted the dips as evidence of the onset of superflow but attributed the superfluidity to bulk droplets coexisting with a nonsuperfluid, uniform thickness film. This interpretation was stimulated by indirect evidence from earlier experiments which indicated droplet formation, i.e., type-2 growth, in thin films on graphite.[3] They proposed an experimental test of the idea, which was carried out successfully.[26] These positive results appeared to prove that thin-film superfluidity is (always) associated with type-2 growth, thereby making questionable many apparent experimental proofs of two-dimensional superfluidity. One essential part of the Herb-Dash argument was implied, but not explicitly stated: that droplet formation occurred at markedly reduced pressures, i.e., lower than the saturation P_0, possibly caused by capillary condensation on the heterogeneous substrate. Our present results show that this is not the case, at least to the degree necessary to explain superfluid onset at pressures markedly below P_0: We find that the frequency dips are quite distinct from the strong, nearly discontinuous increases at saturation. Moreover, we find similar behavior on the Ag and on the more uniform Au surfaces. Krim *et al.*[12] likewise found that wetting in classical molecular films is insensitive to substrate heterogeneity. Therefore the present study gives direct and convincing proof that the evident superfluid onset below saturated vapor pressure is an attribute of the unsaturated film, not of bulk droplets.

Note added in proof. Temperatures quoted in the text were obtained from the measured vapor pressures on the 1958 Temperature Scale,[26] according to which $P_c = 1718$ Torr and $T_c = 5.1994$ K. More recent measurements indicate that the 1958 values are overestimates of both quantities. According to the EPT-76 Scale (Echelle Provisoire de Température de 1976 entre 0.5 K et 30 K),[44] our highest temperature (vapor pressure 1705.3 Torr) is in fact 1 mK below T_c (5.1953 K). We are grateful to M. R. Moldover for drawing our attention to this correction.

ACKNOWLEDGMENTS

We thank M. Schick for continuing discussions, advice, and encouragement in these studies, and R. Puff for a discussion of hydrodynamics. We are grateful for research support from National Science Foundation under Grant No. DMR-81-16421. The participation of J.S. was assisted by Centre National de la Recherche Scientifique (CNRS), France under Grant No. ATP06931-0418, and by North Atlantic Treaty Organization (NATO), under collaborative Research Grant No. 420/83. Partial support for J.K. by NATO is also gratefully acknowledged.

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[*] Present address: Département de Physique, Faculté des Sciences de Luminy, Université d'Aix-Marseille II, Case Postale 901, F-13288 Marseille (Cédex) 9, France.

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