Measurement of Epitaxial Adsorption of Solid ^{4}He on Graphite

S. Ramesh and J. D. Maynard
Department of Physics and the Applied Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

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Solid adsorption isotherms and crystal growth rates for ^{4}He epitaxially adsorbed on graphite have been determined from measurements of fourth sound in Grafoil. The results suggest first-order transitions in each layer below a critical temperature and continuous growth with a decreasing nucleation barrier above the critical temperature.

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The idea of two-dimensional cooperative phenomena occurring at the interface between a crystal and its liquid or gas phase was first considered by Burton, Cabrera, and Frank.[1] Studies of such phenomena, in particular the surface roughening transition,[2] have continued with more sophisticated models and computer simulations. Recently the roughening transition has been related to the universality class of Kosterlitz-Thouless transitions,[3] and the first experimental evidence indicating such a transition has been reported.[4,5] Another system involving the crystal interface, which may have novel properties, occurs in the epitaxial growth (solid adsorption) of one crystal onto the surface of another. In this system the surface cooperative phenomena are modified by the presence of the substrate's attractive field. When the crystal-liquid interface is close to the substrate and the substrate field is strong, the interface width near roughening is severly restricted, and the interface transition should approach a two-dimensional Ising-like transition (with critical temperature $T_{c,2D}$). When the interface is far from the substrate, the behavior approaches that of bulk roughening, for which the interface width diverges at the bulk roughening transition temperature, T_R. At intermediate positions of the interface, critical behavior should occur at a temperature between $T_{c,2D}$ and T_R, and progressively more layers should become involved in density fluctuations as the interface recedes from the substrate. Quantitative theories of this surface behavior in epitaxial growth are currently under development and some interesting results should be forthcoming.[6] Here we report the analysis of an experiment which provides significant information about such behavior for solid ^{4}He adsorbed from the superfluid phase onto graphite. The measurements indicate that epitaxial growth does occur, and the data are analyzed so as to yield solid adsorption isotherms and a kinetic growth coefficient for the ^{4}He crystal surface. The results reported here show evidence of critical behavior near T_R and possibly other novel, theoretically predicted behavior.[6]

The experiment involves the measurement of the superfluid fourth-sound velocity C_4 in an exfoliated graphite (Grafoil) superleak as a function of temperature and pressure. The fourth sound probes the solid surface via a coupling between the sound pressure wave and a recently studied freezing-melting wave[5,7] unique to the solid-He II interface; this will be discussed subsequently. The sound velocity was determined with an annular resonator of square cross section with an i.d. of 1.91 cm, and o.d. of 3.18 cm, and a height of 0.64 cm. The superleak consisted of a single, commercially available Grafoil ring (shaft seal) which was press-fitted into an annular groove milled into a brass plate. The annulus was sealed with a cover plate containing two diametrically opposite electret transducers which were used to drive and detect the fourth-sound resonances. Measurements of the pressure dependence of the resonance frequencies from 5 bars to the solidification curve were made along eight isotherms from 1.0 to 1.7 K.

In plotting and analyzing the pressure dependence of the data, it is convenient to convert the measured pressure P to an average coverage θ_F (layers) with a Franchetti[8] relation:

$$\theta_F = [6.7 \text{ layers bar}^{1/3}](P_s - P)^{-1/3}. \quad (1)$$

Here P_s is the bulk solidification pressure and the numerical factor is calculated on the assumption of a van der Waals force constant of 2.8×10^{-37} erg cm^3 and a monolayer thickness $h_0 = 2.96$ Å.[9]

A plot of the measured fourth-sound resonance frequencies versus θ_F for the various isotherms is shown in Fig. 1. Superimposed on the ordinary fourth-sound pressure dependence are oscilla-

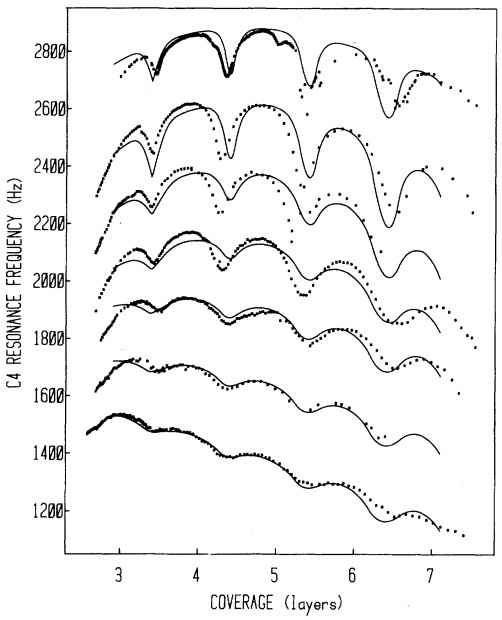

FIG. 1. Fourth-sound resonance frequencies vs Franchetti coverage θ_F. Points are experimental data; solid lines are theory. Temperatures for the isotherms are 1.0 K (upper curve) to 1.6 K (lower curve) in 0.1 K steps.

tions with minima occurring at odd half-integral layer coverages. (The isotherm $T = 1.7$ K also showed some oscillations, but they were very weak.) The first minima occur at about 15 bars and this effect repeats until the pressure approaches P_s to within about 1 bar. The periodic nature of the minima is certainly due to layer-by-layer solid nucleation; one may infer that solid ^{4}He does grow epitaxially on a graphite basal-plane substrate, which is in agreement with a number of recent experiments[9,10] concerned with the role of substrate symmetry in the nucleation of solid ^{4}He. In accord with current theories of epitaxy, one or two layers may nucleate on any substrate, and if the misfit is not large, subsequent layers may continue nucleating as in bulk growth (this occurs for hcp ^{4}He on graphite and bcc ^{3}He on MgO). However, if the misfit is sufficiently large, then subsequent layers can either continue nucleating with dense arrays of defects, or the solid must nucleate homogeneously[2] in the bulk liquid (as for bcc ^{4}He and hcp ^{3}He on graphite).

For further analysis of the data, the fourth sound is modeled as a plane pressure wave in the superfluid propagating between graphite platelets which have a mean separation $w \approx 500$ Å. The oscillation of the pressure in the sound wave about the equilibrium superfluid pressure causes the solid adsorbed onto the graphite surfaces to grow and melt alternately. The flux of mass between the liquid phase and the higher-density solid phase gives the superleak an effective compressibility which modifies the sound propagation velocity. A detailed analysis[11] of the sound propagation includes the effect of the latent heat involved in the freezing and melting and introduces a relaxation time τ which represents the finite rate at which the adsorbed solid may grow or melt. The resulting expressions for the sound propagation speed C and attenuation coefficient κ (nepers/wavelength) at a frequency ω (rad/sec) are

$$C = C_4[1 - \Gamma/(1+\omega^2\tau^2)] \quad (2)$$

and

$$\kappa = \Gamma\omega\tau/(1+\omega^2\tau^2), \quad (3)$$

where

$$\Gamma = [(\rho_2 - \rho_1)C_1^2 h_0/w](\partial\theta/\partial P). \quad (4)$$

ρ_1 and ρ_2 are the He II and solid-phase mass densities, C_1 is the He II first-sound velocity, h_0 and w are as previously defined, and $\theta(P)$ is the actual equilibrium coverage (in layers) of adsorbed solid, which may differ from θ_F. In the derivation of C and κ the thermal effects in the sound wave are found to be negligible and are omitted in Eqs. (2) and (3); $\partial\theta/\partial P$ is taken as the isothemal derivative, i.e., the slope of the adsorption isotherm. From Eqs. (2) and (3) it can be seen that measurements of the sound velocity and attenuation can uniquely determine Γ and τ; systematic measurements of their temperature and pressure dependence yield the solid adsorption isotherm $\theta(P)$ and the crystal growth rate for small driving forces.

The sound propagation is sensitive to the solid-liquid interface because freezing and melting can follow the pressure oscillations in the liquid. In ordinary solid-liquid systems the freezing and melting rates are limited by the transport processes required for the removal of the latent heat of solidification. For these systems the growth rate coefficient $1/\tau$ is much smaller than a typical acoustic frequency, so that $\omega\tau \gg 1$, $C \approx C_4$, and the attenuation κ is determined by other effects. However, the solid-He II system is unique in that the latent heat can be rapidly diluted with the appearance of the superfluid component. The possibility of high growth rates for ^{4}He was

pointed out by Andreev and Parshin,[7] who further predicted the existence of surface freezing-melting waves which could propagate at bulk sound frequencies. Such waves have been experimentally observed[5] at frequencies as high as 2 kHz, sufficiently high to permit coupling between the fourth sound and the freezing-melting wave.

For the fourth-sound data analysis, the effects of the complicated superleak preclude the use of the attenuation measurement to determine τ precisely. It is worth noting that the resonance peak amplitudes show oscillatory behavior with sharp minima (similar to the velocity data of Fig. 1) as one would expect from Eq. (3). In our analysis of the fourth-sound data, we have related τ to θ and used a parametric fit to the data. If the crystal surface is predominantly sharp, then the growth rate is assumed to be proportional to the density of kink sites on the surface,[2] which is in turn proportional to the fractional coverage in excess of (or deficiency from) an integral number of layers. If the crystal surface is rough, then the growth rate is assumed to be independent of coverage. Since the growth rate is proportional to $1/\tau$, we use for the parametric fit

$$1/\tau = 2\pi(R_S|\theta - n|/\sigma + R), \quad (5)$$

where n is the integer closest to θ, R_S and R are sharp and rough surface growth rates, and σ is a measure of the surface sharpness, with $\sigma \to \infty$ corresponding to a rough surface. Classical theories of crystal growth[12] indicate that the growth rates should have pressure and temperature dependences given by factors of the form exp[(activation energy)/kT]. We have found[11] that the simple assumption $R_S = R\exp(U/kT)$, with R constant, is sufficient for fitting the data.

In parametrizing an expression for $\theta(P)$, we assume that for a sharp surface the adsorption is controlled by the nucleation of two-dimensional critical clusters containing i atoms. The coverage is then derived from the Walton equation[12] normalized to θ_F at integral numbers of half layers. For a rough surface the adsorption is continuous and $\theta = \theta_F$. In the parametric fit we use

$$\theta = n + 2^{i-1}(1-\gamma)(\theta_F - n)^i + \gamma(\theta_F - n) \quad (6)$$

for $n \leq \theta_F < n + \frac{1}{2}$ and a corresponding expression for $n - \frac{1}{2} \leq \theta_F < n$. The parameters γ and i are related to the surface sharpness and the nucleation barrier, respectively, and are manifested in the fourth-sound data in the width and depth of the minima. By restricting i and γ to be simple functions of only U/kT, a minimum number of fitting parameters are (within reasonable limits) uniquely determined by the data. In this way the sound velocity data yield both the adsorption isotherms and the growth-rate coefficient.

With the procedure outlined above, all of the fourth-sound data can be fitted to good precision, with the exception of the $T = 1.0$ K isotherm. This isotherm cannot be fitted with parameters smoothly extrapolated from the higher-temperature data, but it can be accommodated by placing discontinuities in its adsorption isotherm (see Fig. 2). By analogy with a low-temperature system of Ising spins in an external field, the occurrence of first-order layering transitions in low-temperature isotherms, as the external pressure is varied, can be expected; such transitions have been observed in computer simulations[13] and are predicted in Weeks's model.[6] The necessity of introducing the discontinuities in the 1.0-K isotherm and not in the higher isotherms is consistent with the presence of a critical temperature near the bulk roughening temperature [$T_R = 1.08$ K (Ref. 4)] as predicted by the theoretical models.[13]

We have found that the parametric fit to the data produces adsorption isotherms which are in good agreement with those calculated by Weeks.[6] When

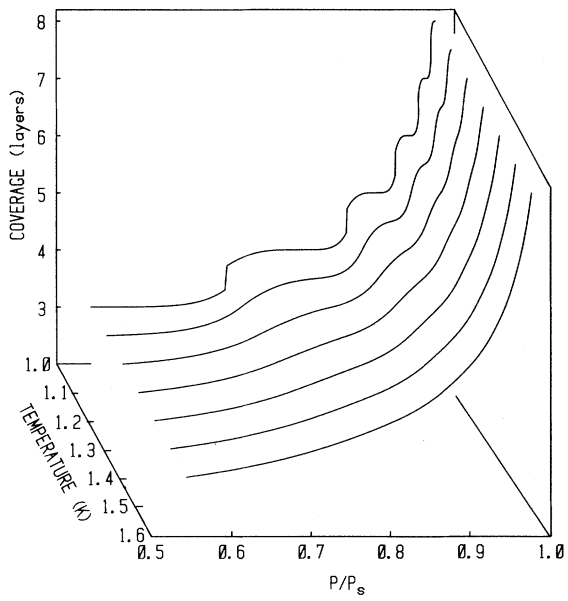

FIG. 2. Solid adsorption isotherms for ^{4}He adsorbed epitaxially on graphite. Pressure is normalized with the bulk solidification pressure P_s.

applied to coverages of an integral number of half layers, Weeks's analysis yields a tractable formula which can be used to determine the temperature and pressure dependence of our fitting parameters. If we use Weeks's theory to obtain i, γ, and σ, then the required adjustable parameters reduce to only the constant R and the size of the discontinuities in the 1.0 K isotherm. Taking $R = 1$ kHz, which is in good agreement with the measured surface-wave frequencies,[5] we obtain the fit to the data indicated by the solid lines in Fig. 1. The solid adsorption isotherms which correspond to the fit are presented in Fig. 2. The upper curve (1.0 K) contains the first-order transitions and shows flat regions around integral coverages which result from the nucleation barrier. The lower curves (1.1 to 1.6 K) indicate the decrease of the nucleation barrier and the tendency toward continuous adsorption as represented by the Franchetti formula [Eq. (1)].

Weeks's theory predicts that below T_R there may be other first-order transitions to metastable regions of fractional coverages; the presence of small satellite minima in the 1.0 K fourth-sound data may be evidence for this effect. To confirm this and other interesting predictions more isotherms in the vicinity of T_R will be examined. As improved models and computer simulations of epitaxial growth are developed, more valuable information may be extracted from fourth-sound measurements.

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