

Heterogeneous surfaces and superfluid onset*

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(Received 1 July 1974)

Nonuniformity of substrate properties can be detected in the physical adsorption of common molecular gases including helium. Effects due to binding-energy variation extend beyond the first adsorbed layer, usually to thicknesses of many layers. We qualitatively describe reasons for this persistence and show how its form and range are related to the spatial variation of the binding energy. Heterogeneity can play an important role in the appearance of superfluidity in thin films of He^4 . It is argued that heterogeneity has been a more serious perturbation in superfluid-onset experiments than is generally recognized; that heterogeneity can account for the lack of agreement between experiments which use different techniques and/or substrates; that the experimental disagreements have hindered development of a satisfactory theory of superfluidity in thin films. We derive a thermodynamic formula relating the shifts of onset temperature with thickness to the lateral scale of the thickness variations caused by substrate heterogeneity, and illustrate its application in simple examples. The sensitivity of superfluid onset to heterogeneity might be exploited for surface characterization, yielding important information that is not presently obtainable by other methods. As a separate benefit, it can lead to a clearer understanding of superfluidity. Specific experimental tests are suggested.

I. INTRODUCTION

A wide variety of experimental techniques have been applied to the study of superfluid onset in thin films of He^4 .¹⁻⁷ Although the results are in qualitative agreement on the principal aspects of the phenomenon, i.e., the monotonic decrease of superfluid-onset temperature with decreasing film thickness, there are disturbingly large quantitative discrepancies. A serious obstacle in the way of their explanation is the unsatisfactory state of the theory of superfluidity in thin films. But the theory is unsettled largely because the experimental results are not consistent; if measurements were more reproducible they would at least provide sharper tests of theoretical predictions.

We believe that a major reason for the persistence of the puzzle has been the neglect of heterogeneity as a perturbing influence in all real films. Dash and Herb⁸ have recently suggested a mechanism by which surface heterogeneity, in the form of spatial variations of binding energy, could affect the experimental manifestations of superfluid onset. In this paper we explore the mechanism in some detail with a view toward separating its influence from the "intrinsic" nature of superfluid onset in an ideal uniform film. We also explore the form and the nature of superfluid onset on a heterogeneous surface, and show that it may become useful as a particularly sensitive probe of surface character. In preparation we first summarize the current state of understanding of heterogeneity in physisorption, presented in the Sec. II.

II. SUBSTRATE HETEROGENEITY IN PHYSICAL ADSORPTION

The most extensive evidence for effects of heterogeneity in physisorption has been obtained in

vapor-pressure studies. Whereas with most adsorbents the vapor pressure isotherms of van der Waals gases have smooth sigmoid shapes, experimental isotherms taken with a small number of special substrates exhibit distinct steps corresponding to the completion of individual layers. Two examples of such behavior are shown in Fig. 1. Substrates which have yielded such "staircase

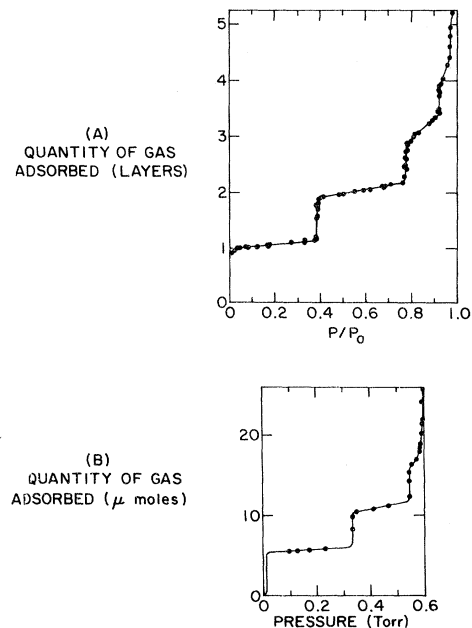


FIG. 1. Examples of stepwise vapor-pressure isotherms characteristic of physical adsorption on relatively uniform surfaces at low temperatures. (A) Kr on exfoliated graphite at 77.3 K (Ref. 12); (B) Kr on cleavage faces of CdBr_2 at 73.1 K (Ref. 13).

isotherms" include alkali halides,^{9,10} graphitized carbon black,¹¹ exfoliated graphite,¹² and divalent metal halides.¹³ The essential difference between these substrates and common surfaces is a greater uniformity of binding energy, which requires that there be mainly one type of crystal plane exposed to the gas. The necessity for single-facet exposure in homogeneous adsorption was demonstrated by Rhodin¹⁴ with a copper surface and then by Polley, Schaeffer, and Smith¹⁵ on a series of progressively graphitized carbon blacks. More directly, Ehrlich and Hudda¹⁶ and Engel and Gomer¹⁷ have shown by field-emission microscopy that adjacent facets of a single tungsten crystal have markedly different binding energies for adsorption of rare gases; the differences can be as much as a factor 2. Such differences are readily demonstrated theoretically by pairwise summation of dispersion forces,¹⁸ which might be appropriate for molecular gases on rare-gas crystals. For the more general theory of adsorption on dielectric and metallic substrates,^{19,20} there will be an obvious dependence on crystal facet if the dielectric properties are anisotropic.^{21,22} Thus, on a substrate which presents several types of crystal face for adsorption, adsorbed layers will have different thicknesses in equilibrium, and on each type of face the steps for each layer will occur at different pressures. Such a superposition, together with thermal excitation (with or without chemical contamination, dislocations, defects, and strains), is responsible for the smooth character of typical isotherms,²³ as exemplified in Fig. 2. Sigmoid isotherms of this type are conveniently described by a formula due to Brunauer, Emmett, and Teller²⁴ (BET). The success of the BET equa-

tion in fitting major portions of many experimental isotherms has led some people to conclude that such systems are in some sense "ideal," and that, since the BET theory does not invoke heterogeneity, smooth sigmoid isotherms are evidence of uniformity.^{25,26} But the assumptions of the BET model are so unphysical that the vapor-pressure equation can only be taken as a convenient basis for characterizing surfaces in terms of two or three empirical constants. The BET model assumes that the atoms of the first layer are adsorbed on surface sites with some characteristic binding energy, and that successive layers adsorb with the binding energy of liquid. The assumption that the substrate field is no longer felt at layers beyond the first is incorrect, but it is not the most serious defect. Much more unrealistic is the assumption that higher layers can be formed statistically by deposition on single adatoms, i. e., with no lateral interactions.^{23,27,28} The model thus removes any significance of liquidlike properties while at the same time assuming that the liquid represents the state of all higher layers. But the correct explanation for the BET isotherm is that it is a superposition of stepwise isotherms from different portions of a heterogeneous surface, the steps occurring at different pressures on different facets or otherwise distinctive regions of the substrate. An additional factor tending to obscure steps, even on a uniform surface, is thermal excitation between layers, for the distinction between one layer and the next becomes lost when kT becomes comparable to or larger than the difference in their binding energies to the substrate.²⁹ Since the difference in binding of adjacent layers falls off rapidly as the distance increase, it is the higher-layer steps that become blurred first, whether because of heterogeneity or because of thermal excitation. Thus, the most uniform films are those which display the greatest number of steps, provided the temperature is sufficiently low. By the same token, it is most unusual for the heterogeneity to be so great as to remove any evidence of first-layer completion, particularly in the noble gases (where adatom-adatom interactions are generally weaker than adatom-substrate interactions), and it is this remnant that causes the "knee" of the BET isotherm.

Nevertheless, the similarity of most isotherms and their apparent independence of the material of the substrate (barring the "anomalous" substrates which yield stepwise isotherms) is sometimes taken as evidence that effects of heterogeneity are progressively healed out in thicker films, but the following argument shows that this is not necessarily true. Suppose that the vapor pressure-thickness relation $P(D)$ is given by the "Frenkel-Halsey-Hill" formula²³

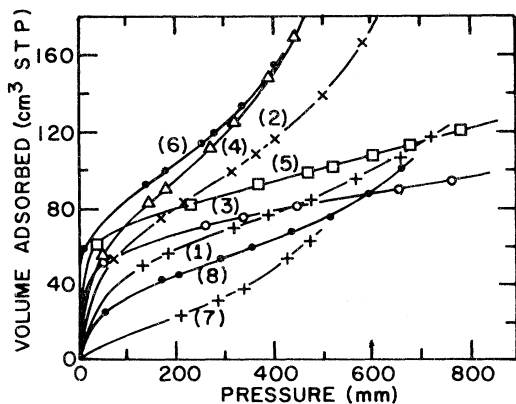


FIG. 2. Vapor-pressure isotherms of the BET type, indicative of heterogeneity of the substrate and/or relatively high temperature. Various gases on silica gel²⁴: (1) CO₂ at 195 K; (2) Ar at 90 K; (3) N₂ at 90 K; (4) O₂ at 90 K; (5) CO at 90 K; (6) N₂ at 77.4 K; (7) C₄H₁₀ at 273 K; (8) SO₂ at 273 K.

$$P(D) = P_0(T) e^{-\alpha/\kappa T D^n}, \quad (1)$$

where $P_0(T)$ is the vapor pressure of the bulk phase, α is a constant related to the binding energy of the specific gas and substrate, and the exponent $n \approx 3$. On a nonuniform adsorbate the constant α varies from place to place and yet the vapor pressure in equilibrium is constant throughout. Obviously, D must therefore vary so as to keep the exponent constant, which leads immediately to a coupling between the variations of thickness and of binding. Thus, setting the total differential of the exponent to 0:

$$\delta D/D \approx (1/n) (\delta \alpha/\alpha). \quad (2)$$

The relation is curious and seems at first sight to violate one's physical intuition. It predicts, for example, that a film which has a thickness variation of 1 layer when the mean thickness is 5 layers will have a variation of 10 layers when the mean thickness is 50 layers. That is, rather than the effects of heterogeneity becoming healed out with increasing thickness, they are amplified in proportion to the thickness. As a film gets thicker it becomes "softer" and more responsive to perturbations, whether they be the binding-energy variations specifically considered, temperature gradients, or any other influencing field. But our considerations up to this point have implicitly assumed that the film thickness is small compared to the typical lateral distances of the variations in α . As long as this condition holds the thickness variations continue to grow with thickness, but when D becomes comparable with the lateral scale of heterogeneity of the substrate, an averaging process becomes important; the topmost layers of the film "see" a wider field of view of the surface encompassing a broader range of binding energies. When the film thickness is much larger than the lateral scale of heterogeneity, the averaging will become quite effective and the film thickness tends to a uniform value.

The preceding paragraph involves an important characteristic of all real substrates, the spatial correlations between regions of different binding energy. In most treatments of heterogeneity it is assumed that the surface is composed of uniform patches of various types, each type having a characteristic binding energy, and each patch being large enough to permit the neglect of edge effects. The heterogeneity is then characterized by listing the fraction of the total surface area (or adsorption sites) with their characteristic binding energies, usually in terms of a density-of-states function

$$\rho(\epsilon_b) \equiv \frac{dN_s}{d\epsilon_b}, \quad (3)$$

where N_s is the total number of sites having binding energy greater than ϵ_b . An adsorbed film in equilibrium on such a surface acts as a superposition of

individually uniform films, each with proper binding energy; the properties of the composite can then be formally described as an integral over ϵ_b of the uniform function multiplied by $\rho(\epsilon_b)$.³⁰

Although patchwise uniformity is evidently a reasonable approximation for thin films on relatively large crystal facets, it is not universally applicable. Relatively smooth and long-range variations in binding energy can be caused by short-range crystalline disorder, strains, dislocation fields, and chemical impurities. Long-range variations in binding energy create effective lateral fields aligned parallel to the surface. Lateral fields acting on adsorbed films can cause their properties to be qualitatively different from uniform films, as demonstrated by various theoretical models. Roy and Halsey³¹ proposed that strong lateral fields could account for the persistence of T^2 heat capacities in He films at low coverages on copper substrates. Campbell, Dash, and Schick³² showed that an ideal two-dimensional Bose gas is extremely sensitive to lateral fields, exhibiting a pronounced heat-capacity anomaly associated with a combined momentum-spatial condensation; the two-dimensional Fermi gas, on the other hand, is quite insensitive to lateral fields. These examples draw attention to the importance of determining the spatial variations of binding energy as well as the magnitude of the variations, i.e., the "topography" of ϵ_b as a function of the surface coordinate \vec{r} . The topography can be described by a local density-of-states function $\rho(\epsilon_b, \vec{r})$. The local density is related to the ordinary density of states $\rho(\epsilon_b)$ by the sum rule

$$\int \rho(\epsilon_b, \vec{r}) d^2r = \rho(\epsilon_b). \quad (4)$$

In the following sections we discuss the connections between the topography of ϵ_b and the appearance of superfluidity in thin films of He⁴.

III. RELEVANCE TO HELIUM FILMS

Current understanding of nonuniformity of multilayer films is based primarily on evidence obtained from vapor-pressure measurements on van der Waals gases such as Ar, Kr, and Xe, but the general conclusions regarding heterogeneity are also applicable to He. So far there have been no reports of sharply stepped vapor pressure isotherms of He on uniform surfaces, but very abrupt first-layer corners have been observed by Lerner and Daunt³³ for He⁴ on exfoliated graphite at low temperature. He⁴ multilayer films exhibit step structure in heat capacities. A sharp distinction between the first and second layers on exfoliated graphite persists to temperatures well above 4 K.^{34,35} At very low temperatures on Vycor³⁶ and sintered copper³⁷ there is some evidence of completion of the first and second layers. Sabisky and Anderson³⁸ have provided di-

rect evidence for thickness uniformity of He^4 films on cleaved surfaces of alkaline-earth fluoride single crystals and for the blurring of detail caused by surface damage. The Sabisky and Anderson technique uses interferometry of ultrasonic monochromatic phonons generated within the substrate and partially transmitted to an adsorbed film. With a cleaved crystal of MgF_2 they were able to observe sharp resonances in progressively thicker He^4 films at low temperature, up to fifth order, corresponding to a thickness of about 200 Å. But with a polished MgF_2 crystal, only two resonances were observed. This loss of detail is consistent with the damage that is known to be caused by polishing, i. e., the production of an amorphous surface region of some tens to hundreds of atomic layers deep.³⁹ Such a layer is characteristically marked by microscopic striations and variations in thickness and profile which cause the surface to be less uniform in binding energy than the original cleaved crystal.

Several other measurements reveal dramatic differences between He films adsorbed on graphite and those on less uniform surfaces. Bretz's⁶ heat-capacity study of thick He^4 films on graphite at temperatures near T_λ shows qualitatively different behavior from previous work on jeweler's rouge⁴⁰ and on Vycor,³ with remarkably sharp detail persisting to at least 11 layers' thickness. Similarly, the mass-transport measurements of helium films on graphite by Herb and Dash⁴ found the onset of superflow to occur at a significantly higher temperature for a given thickness than had been seen previously. In addition, the latter experiment revealed qualitatively different behavior in other respects, including a distinct change in flow rate near the λ temperature of bulk liquid. It is plausible to relate the distinctive character of these results to the relatively high degree of surface uniformity of the graphite substrates.

IV. ONSET BEHAVIOR

As mentioned in the Introduction, Dash and Herb⁸ have suggested that the properties of a He film near the temperature and coverage at which superfluidity appears are rather sensitive to substrate heterogeneity. The fundamental reason for this is the collective nature of the ordered state, involving correlation over distances large compared to a substrate lattice constant. Substrate heterogeneity will modify this relationship through its effect on the helium. Any experiment capable of detecting the existence of superfluid over an extended region of the surface will be sensitive to such modification. The onset of superfluidity is particularly susceptible because it relies on criteria involving both the size of superfluid domains and how these coalesce to form connected paths. Different experiments will present

different criteria for apparent superfluid onset. In the following we illustrate the influence of heterogeneity on superfluid-onset behavior with the specific example of the quartz microbalance experiment of Chester, Yang, and Stephens.⁵

This experiment measures the change Δf in resonant frequency of the shear-mode oscillation of a quartz crystal as He is adsorbed, where Δf is proportional to the total adsorbed mass that oscillates with the crystal. At "onset" some of the film appears to become superfluid and so does not follow the crystal's motion. Thus the frequency shift for a given mass loading at temperatures below the onset temperature T_0 is smaller than for $T > T_0$.

In the presence of substrate heterogeneity, the film will vary in both thickness and density. Thus superfluidity will not appear uniformly, but rather in certain, presumably thicker, areas first.^{41,42} However, a very small region of superfluid will continue to move with the substrate at low oscillation frequency because of the boundary conditions with contiguous normal fluid. At sufficiently high frequency it would be free to move laterally with respect to the substrate. This would be revealed experimentally as a decreased inertial-mass loading, i. e., an increased resonant frequency. Conversely, at fixed frequency, there is a minimum size for regions to appear to be superfluid, which is of the order of the third-sound wavelength $\lambda_3 = c_3/f$ at the given frequency.⁸ This criterion determines an apparent onset coverage σ_0 , the threshold for experimental appearance of superfluid. Units for σ are taken to be mass/area.

Consider a particular coverage for which only certain regions of the film are superfluid at temperature T . Figures 3 and 4 illustrate the growth of

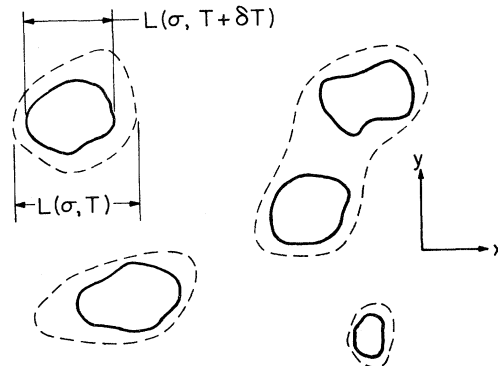


FIG. 3. Schematic depiction of superfluid-domain growth on the surface for fixed film coverage σ (\vec{z} is the surface normal). As the temperature is lowered from $T + \delta T$ to T , regions of superfluid grow in lateral size from those bounded by the solid lines to the larger regions indicated by the dashed curve. Alternatively such a picture could describe domain growth as film coverage is increased.

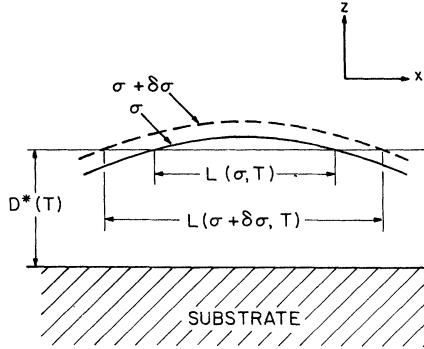


FIG. 4. Growth of one particular superfluid domain as film coverage increases from σ to $\sigma + \delta\sigma$. $D^*(T)$ is the intrinsic superfluid-onset thickness at the given temperature T .

superfluid domains, of characteristic lateral size $L(\sigma, T)$, as coverage σ is increased or as T is lowered. A region of the film thicker than an intrinsic onset thickness $D^*(T)$ is taken to be superfluid. As mentioned above, the criterion for such a region to *appear* as superfluid in an oscillating crystal experiment is $L(\sigma, T) \geq \lambda_3(\sigma, T)$. Thus the critical condition for onset is $L(\sigma_0, T) = \lambda_3(\sigma_0, T)$. By comparing with the corresponding criterion at infinitesimally higher temperature $T + \delta T$, $L(\sigma_0 + \delta\sigma, T + \delta T) = \lambda_3(\sigma_0 + \delta\sigma, T + \delta T)$, we may differentiate to determine the change in experimental onset coverage with temperature, or conversely, the change in onset temperature T_0 with coverage:

$$\frac{dT_0}{d\sigma} = \left[\left(\frac{\partial L}{\partial T} \right)_\sigma - \left(\frac{\partial \lambda_3}{\partial T} \right)_\sigma \right]^{-1} \left[\left(\frac{\partial \lambda_3}{\partial \sigma} \right)_T - \left(\frac{\partial L}{\partial \sigma} \right)_T \right]. \quad (5)$$

This differs from an erroneous result of Chester and Yang,⁴³ which omits the important dependence of L on T and λ_3 on σ . The conclusion of these authors that the connectivity model⁸ disagrees with their data⁵ is thus unwarranted.

Estimation of the individual terms in Eq. (5) requires knowledge of the dependence of third-sound speed near onset, which is experimentally controversial,⁴⁴ as well as a description of the film thickness variation along the surface. Alternatively, one may view Eq. (5) as a tool for characterizing this variation via a systematic determination of the other parameters which enter. In particular, measurement of the frequency dependence of onset will be useful because of the dependence of the gauge λ_3 on frequency. An oscillating crystal experiment in progress in this laboratory has indeed found such a dependence, with results to be reported elsewhere.⁴⁵

In general, the behavior predicted by Eq. (5) is rather complicated. However, we can show how the model simplifies in certain regimes of surface con-

dition and experimental frequency. Consider first the ideal case of a film adsorbed on a uniform surface. Then L either is zero or equals the surface lateral dimension, $A^{1/2}$, depending on whether the coverage is less than or greater than the critical value $\sigma_0(T)$. That is,

$$L = A^{1/2} H(\sigma - \rho D^*(T)), \quad (6)$$

where $H(x)$ is the unit step function at $x = 0$ and ρ is the liquid mass density. Since $dH/dx = \delta(x)$, Eqs. (5) and (6) give the proper uniform surface result in this limit:

$$\frac{d\sigma}{dT_0} = \rho \frac{dD^*}{dT} \quad (\text{uniform surface}). \quad (7)$$

Another limiting case is that of a high-frequency experiment. Assume that the thickness varies relatively slowly over the surface, with characteristic gradient $g \equiv \langle |\nabla D(x, y)| \rangle_{av}$. Then $(\partial L/\partial T)_\sigma \approx -g^{-1} (dD^*/dT)$ and $(\partial L/\partial \sigma)_T \approx (\rho g)^{-1}$ are estimates based on shrinking (growth) of superfluid regions with increasing $T(\sigma)$. At high frequency the terms in (5) involving λ become relatively unimportant, yielding

$$\lim_{f \rightarrow \infty} \frac{d\sigma}{dT_0} \approx \rho \frac{dD^*}{dT} \left\{ 1 + \frac{g}{f} \left[\frac{dT}{dD^*} \left(\frac{\partial c_3}{\partial T} \right)_\sigma + \rho \left(\frac{\partial c_3}{\partial \sigma} \right)_T \right] \right\}. \quad (8)$$

Note that the right-hand side prefactor is the desired intrinsic onset curve, and the bracketed expression provides the leading frequency-dependent correction. Equation (8) is valid for frequency sufficiently high that this correction is $\ll 1$. This limiting form obtains because the third-sound wavelength is small at high frequency, so that even a minute region of superfluid will be manifested experimentally.

Our theoretical understanding of superfluid onset in films is unsatisfactory, in part because of the unsettled experimental situation. This impedes detailed application of Eqs. (5) and (8) to onset studies at present. However recent developments in the field of critical phenomena and extensions of the Landau model to the film encourage optimism in this regard.^{42,46-49} It is plausible that systematic investigation of the effects of heterogeneity will facilitate progress considerably.

V. APPLICATIONS

The preceding arguments lead us to suggest that superfluidity can provide the basis for new methods of characterizing solid surfaces. The sensitivity of superfluid onset to thickness variations induced by substrate heterogeneity can be used to provide information on the spatial variations of binding energy, i.e., on the local density of binding-energy states $\rho(\epsilon_b, \vec{r})$. The initial applications of the method need not depend on an understanding of

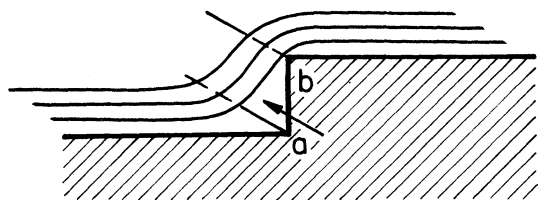


FIG. 5. Film thickness in the region of a cleavage step. Since the film is thicker in the region of the lower corner a and thinner at the upper corner b , the onset temperature is higher for superflow in the direction of the arrow than at right angles to it.

superfluidity in thin films per se, but only on the universal property that onset temperature T_0 is depressed as the thickness is decreased, all other experimental conditions being constant.

The specific experiments involve the connectivity of superfluidity in a variable-thickness film under controlled conditions. To discuss these we imagine the variations of binding energy with position on a realistic surface, plotted in the form of a three-dimensional model, in which the vertical axis is the atom-substrate potential energy ($-\epsilon_s$). The topography of real surfaces will then resemble particular features of ordinary landscapes, and we can describe them by the familiar names; plains, craters, mountains, and so forth. The most uniform surfaces resemble smooth plains; the most heterogeneous will be very rugged. But now we can distinguish two general classes of heterogeneous landscapes; those which are dominated by craters and pits, and others which are primarily

channeled. On the first class of surface, superfluidity will begin first in isolated domains in the craters and pits, and superfluid connectivity will be postponed until the regions separating the domains are sufficiently thick or cold to become superfluid. But on a channeled surface connectivity is obtained much more readily, when there is enough thickness of film in the channels.⁵⁰ Therefore it is not possible to gauge whether a surface is more or less uniform by how easy it is to detect superfluidity of its film, i.e., whether the onset pressure is higher or lower than on some other surface. In the absence of a theory of the film it is not possible to use other quantitative or qualitative features as a firm guide. However, it should be possible to test some of these ideas by some specially prepared surfaces which resemble one or the other model. We can suggest two examples of a channeled surface on which superfluid onset ought to exhibit anisotropy. One is a polished surface having a definite polishing direction; another is a cleaved single crystal. The polished surface will have striations of binding energy running parallel to the direction of rubbing, and superfluid connectivity ought to appear along this direction earlier than transverse to it. A cleaved crystal has cleavage steps tending to be oriented at right angles to the cleavage direction. These steps have both larger and smaller binding energies than on the flat planes; larger at the inside corners and smaller at the outside corners. Therefore the steps tend to reduce the connectivity in the cleavage direction, and superfluidity will occur earlier in the direction parallel to the steps: This is illustrated in Fig. 5.

*Research supported by The National Science Foundation.

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- ⁵⁰These considerations bear directly on the interpretation of recent experiments detecting superfluid onset at very low temperatures. J. H. Scholtz, E. O. McLean, and I. Rudnick [Phys. Rev. Lett. 32, 147 (1974)] detected third-sound signals in films at partial pressures which were estimated to correspond to thicknesses as low as 2.1 layers. Assuming a solid first layer they concluded that the experiments demonstrated superfluidity in a liquid film of slightly more than 1 layer, i.e., effectively “two-dimensional” liquid. However since their substrate of polished CaF_2 was almost certainly heterogeneous (see Ref. 38) the film thickness was not uniform, and the detected signals at onset must have been transmitted through a network of thicker than average regions. In the persistent current experiments of M. H. W. Chan, A. W. Yanof, and J. D. Reppy [Phys. Rev. Lett. 32, 1347 (1974)] the partial pressures at onset corresponded to greater thicknesses, ~ 2.4 layers. The discrepancy between these results (which were obtained with porous Vycor glass substrate) and the third-sound data can be ascribed to differences between the two types of surface together with specific requirements for superfluid connectivity at the limits of detection. In neither study was the substrate sufficiently well characterized to permit a quantitative estimate of intrinsic onset thickness, and neither has provided a qualitative test of two-dimensional superfluidity.