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Clustering and percolation transitions in helium and other thin films*

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A theory of the growth of thin films and the evolution of bulk characteristics is developed from a thermodynamic basis. The work has been prompted by recent experiments on ^{3}He, ^{4}He, and N_2 films adsorbed on uniform basal-plane graphite surfaces, which indicate that as coverage increases the characteristics of the films may progress from a monolayer regime to a two-layer regime, and then at coverages which are specific to each system and temperature, to the relatively abrupt appearance of nearly bulklike properties. It is shown that the nature of film growth with increasing adsorption is controlled by three interfacial coefficients and the spreading pressure, which permit three general classes of behavior: (I) uniform deposits at all thicknesses; (II) bulk nucleation after a thin uniform deposit; (III) bulk nucleation with no preadsorption. Metal deposits on inert insulator and semiconductor surfaces typically belong to classes II and III. Van der Waals films are conventionally considered class I, although several class II examples are known. The recent experiments strongly suggest that He and N_2 on graphite are members of class II, and quantitative estimates of the helium-graphite parameters are consistent with this possibility. Further aspects of class-II growth are also considered. On ideal surfaces the clustering transition is guarded by a high nucleation barrier but in real systems the barrier is reduced or entirely removed by substrate heterogeneities. This usually leads to the formation of many isolated clusters which grow into "thick" islands coexisting with ultrathin film. The islands are shown to be markedly flattened by the substrate field, and as more material is deposited they grow principally in the lateral direction. When the coverage is sufficiently high the islands establish connectivity in a percolation transition. Percolation transitions appear to take place in metal films; we propose that they occur also in helium films. In ^{4}He films below T_λ the percolation transition can take place via Josephson tunneling between droplets, at coverages too low for "geometric" connectivity: this causes the superfluid onset temperature to depend on coverage. A number of persistent puzzles associated with onset phenomena are understandable in terms of the theory. It seems likely that models of superfluid onset in uniform slab geometry have little to do with real films.

I. INTRODUCTION

Inelastic neutron scattering has been used recently to measure the energy-momentum dispersion curve of ^{4}He films adsorbed on Grafoil.[1] Carneiro *et al.* discovered a distinct loss peak in films as thin as four layers, corresponding to excitations having the energy and momentum characteristic of rotons in bulk liquid helium. The integrated intensity of the peak increases linearly with quantity absorbed, but energy, momentum, and width remain constant. Linear extrapolation to zero intensity indicates a threshold thickness slightly greater than two layers.

We believe that the results indicate the formation and growth of thin liquid droplets on top of the threshold thickness films, i.e., that the adsorbed helium undergoes a first-order "clustering" transition. Clustering has been proposed to explain recent calorimetric results for liquid ^{3}He films[2] and solid N_2 films[3] adsorbed on Grafoil. Clustering may help to explain several puzzling features of superfluid onset phenomena in thin ^{4}He films adsorbed on various uniform and heterogeneous substrates.

The formation of small liquid or solid clusters on the bare substrate or on top of a thin uniform deposit is typical of strongly cohesive metal films on insulating or semiconducting surfaces.[4] Clustering is also indicated in a variety of physisorbed film systems.[5-9] Evidence in these cases has been obtained primarily through vapor-pressure isotherms, in which the bulk vapor pressure is reached at rather low average coverages.

The theory of clustering and droplet growth is not satisfactory. Although several aspects are understood, considerable areas are poorly understood. For example, although the general condition for the stability of uniform deposits is basic to the phenomena of wetting and adhesion,[10,11] its application to adsorption has not been deeply explored. The critical region of nucleation and early growth is usually treated as a kinetic problem,[12,13] which has been a natural approach for systems involving continuous beam deposition. However, the recent experiments on physisorbed films have emphasized their equilibrium properties, suggesting to us that a thermodynamic treatment might be appropriate. This paper presents the outline of such a theory.

The paper is organized as follows. In Sec. II we examine the stability conditions for the spreading of a uniform thickness film on a solid surface, and develop a criterion for the critical thickness at which it may form droplets instead of a uniform film. In Sec. III small droplets are examined with respect to shape and size effects; they are found to be strongly flattened by substrate field and very thin at first appearance. Section IV discusses questions of nucleation on ideal surfaces, on highly uniform real substrates, and on heterogeneous adsorbents. In Sec. V we consider the growth of droplets as more material is deposited, to a coverage at which droplets merge to form long connected paths. Section V B discusses further growth to thick-film regimes.

II. WETTING CONDITIONS

A. General macroscopic theory

In this section we treat the substrate as an adsorbing surface but neglect the distorting effect of the substrate field on the contact angle. We also assume that the droplets, when they appear, have bulk properties. Size effects as well as effects of the substrate field are treated in Sec. III. The conditions for clustering in a thin film can be developed beginning with the Young-Dupré equation for the contact angle θ of a macroscopic liquid droplet on a solid surface.[10,11,14] For "complete wetting," where the liquid spreads out to cover the surface uniformly, the angle $\theta=0$. This requires that the interfacial tensions

$$\gamma_{sv} > \gamma_{lv} + \gamma_{sl} , \tag{1}$$

where s, l, v stand for solid, liquid, and vapor. The interfacial tension between the solid and the vapor is affected by adsorption, which reduces γ_{sv} by an amount equal to the spreading pressure ϕ of the film. The relationship between γ_{sv} and ϕ follows from the definition of surface tension together with adsorption thermodynamics, but because it is not very familiar a brief outline of the connection will be given here. The surface tension of an interface between two substances or phases in a thermodynamic system is defined as the excess thermodynamic potential per unit area due to the interface,[10,11,14-16] i.e.,

$$\gamma \equiv \Omega_s / A . \tag{2}$$

The thermodynamic potential for all types of systems is the difference between the Helmholtz free energy F and the Gibbs potential G: $\Omega = F - G$. For simple bulk matter $G = F + PV$; in systems having appreciable interfacial area there is an additional contribution, proportional to A. Thus, Ω for the complete system can be decomposed into two parts: a term $\Omega_v = -PV$, which is equal to the proportionate contributions of the bulk components as if entirely unaffected by the presence of the interface, and an excess contribution Ω_s which includes all of the effects of the interface including distortions which may extend over appreciable but limited distances into the bulk phases. If the total thicknesses of the the bulk phases are very great in comparison to the relaxation distances, the effects of the interface will be proportional to A. Changes in γ caused by the adsorption on an interface can be related to film and vapor properties. Suppose that the interface between a bulk substance and vacuum has surface tension coefficient $\gamma_{s0} = \Omega_{s0}/A$. Now if a vapor is introduced to the system, there will be some change in thermodynamic potential of the total system, part of which will be proportional to A. This change is reflected in the surface-tension coefficient: $\delta\gamma = \delta\Omega_s/A$. This change can also be considered an attribute of the film, although it really belongs to the composite interface solid-film-vapor, so that $\Omega_{\mathrm{film}} \equiv \delta\Omega_s$. Ω_f has in principle both a volume and an area term:

$$\Omega_f = -PV_f - \phi A . \tag{3}$$

ϕ is the spreading pressure of the film; Eq. (3) can be considered as the defining equation for ϕ. In most cases of interest the film is so thin that the volume term in (3) is negligible. Then the reduction in γ due to adsorption is just equal to ϕ. If a substrate coefficient is γ_{s0} in vacuum its surface tension γ_{sv} when it is in equilibrium with vapor is, therefore,

$$\gamma_{sv} = \gamma_{s0} - \phi \tag{4}$$

if the adsorbed film thickness $t \ll \phi/P$.

With Eq. (4) we can now write the criterion (1) for complete wetting in terms of ϕ and the coefficients for the bulk phases:

$$\phi < \gamma_{s0} - \gamma_{lv} - \gamma_{sl} . \tag{5}$$

It is important to note here that γ_{sl} is the coefficient of the interface between the solid and the bulk liquid, regardless of what form the transitional region may take, as long as it is relatively thin. There is no need to inspect whether there are any distinct phases or structures in the first few layers of liquid near the solid, because the coefficient γ_{sl} includes all of the change in Ω proportional to the area of the interface. If a liquid drop forms on a film-covered substrate, its thermodynamic properties cannot reveal whether the drop rests on top of the film, or directly on the surface, or whether there are intermediate phases in the transitional region, provided that it is thin ($t \ll \phi/P$).

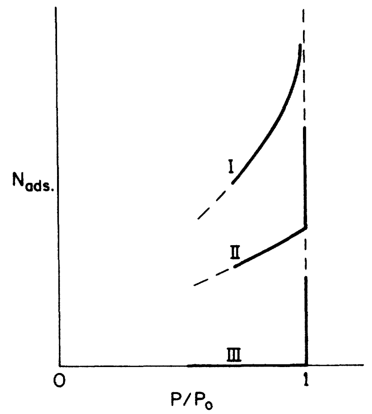

FIG. 1. Schematic vapor-pressure isotherms illustrating the three main classes of film-substrate behavior.

The stability condition (5) leads to three distinct classes of system, depending on the value of ϕ for the saturated film. The maximum spreading pressure that can be attained by a film at temperature T is some ϕ_0 when in equilibrium with saturated vapor at the bulk phase pressure $P_0(T)$. If the inequality (5) is still satisfied for $\phi=\phi_0$, then the film wets the surface completely no matter how thick the film becomes. Such systems will be designated class I. In contrast, some systems have a maximum ϕ_0 which violates the inequality; in these (class II) systems there is a "threshold" coverage at which ϕ is just equal to the right-hand side of (5). Beyond this threshold the contact angle between bulk phase and the substrate is greater than zero: there is no longer "complete wetting," and added material goes to form droplets on the surface. The third class of systems has surface tension coefficients such that the right-hand side of (5) is negative. In these cases there can be no physical solutions for ϕ and hence no adsorption. The substrate is never coated by adsorbate and if bulk phase is formed it does not wet the surface at all, i.e., $\theta=\pi$.

The three classes have distinctive vapor-pressure isotherms. In class-I systems the vapor-pressure isotherm rises gradually (we are not concerned here with steps associated with layer completion); as P approaches P_0 the thickness of deposit increases continuously toward ∞. In class-II systems the vapor pressure reaches P_0 at a finite coverage: then the isotherm rises vertically as bulk material is condensed.[17] Class III isotherms show no adsorption; just a vertical riser at P_0. The three classes of isotherms are shown schematically in Fig. 1. Examples of each type of system are known. Type-I van der Waals films include Kr and Xe on graphite.[18-21] Type II includes Ar on graphite,[20] NO on CdI_2,[8] and SF_6 on Cd,[9] and apparently most metal films.[4] Type III includes Kr on Na and Na_2O,[6] and H_2O on graphite.[7] Experimental isotherms illustrating each class are shown in Figs. 2-4. Of particular interest here are recent calorimetric measurements of $^2He^3$ and $^3N_2$ on Grafoil, indicating that these systems are class II. Clustering in relatively weakly interacting van der Waals films is surprising; especially in He. However, the theory applied to He does indeed predict that clustering is likely. A general approximation for predicting the class of any system is described below: in Sec. II B the method is applied to He.

Quantitative tests of the theoretical stability criterion Eq. (5) are limited by the difficulty in measuring γ_{sl} directly. However, an approximate combining law allows an estimate of γ_{sl} from γ_{s0} and γ_{lv}. If effects of surface excitations and relaxation are neglected, the interfacial tension of dissimilar systems interacting via typical dispersion forces with comparable molecular densities is given by[22]

$$\gamma_{12}=\gamma_1+\gamma_2-2(\gamma_1^d\gamma_2^d)^{1/2}\ , \tag{6}$$

where γ_1^d, γ_2^d are the contributions to γ_1, γ_2 due to the dispersion force interactions across a unit area plane in each medium. Equation (6) provides a consistent and fairly successful quantitative basis for categorizing surfactants and detergents,[23] especially for distinguishing between

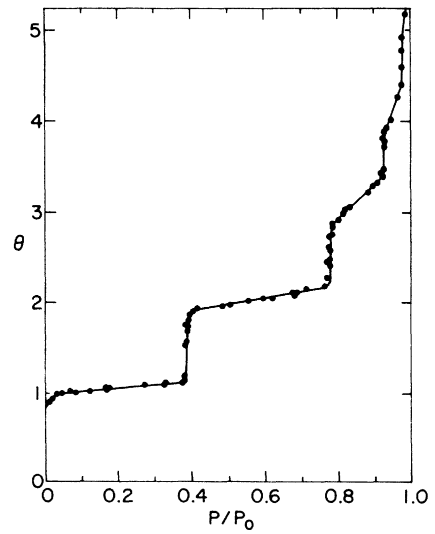

FIG. 2. Experimental class-I isotherm: Kr on exfoliated graphite at 77 K, by A. Thomy, J. Regnier, and X. Duval (Ref. 20). (The ordinate θ is the number of full-coverage layers.)

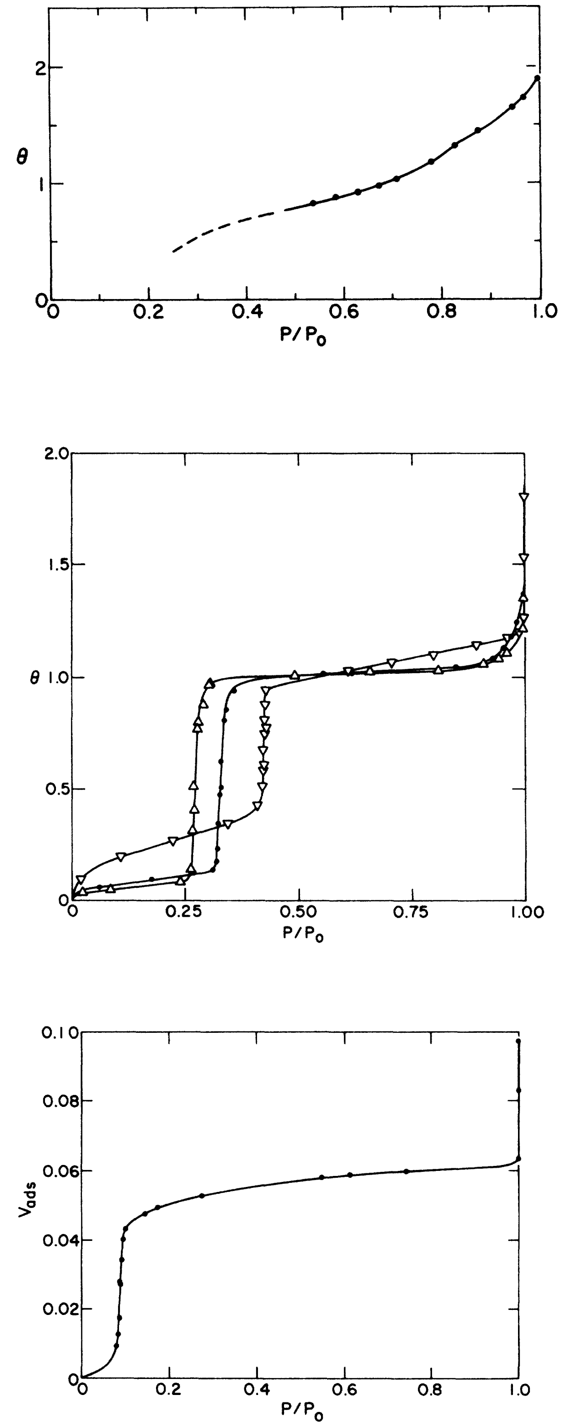

FIG. 3. Examples of class-II isotherms. (a) Ar on Kr-plated graphitized carbon black at 74 K (Ref. 5). (b) NO on lamellar solids (Ref. 8); Δ, $CdBr_2$ at 83 K; ● $CdCl_2$ at 77 K; ∇, CdI_2 at 79 K; (c) CH_3Cl on Cd metal at 144 K (Ref. 9). [The ordinate θ in (a) and (b) is the number of full-coverage layers. In (c) $\theta = 1$ corresponds approximately to $V_{ads} = 0.05$ units.]

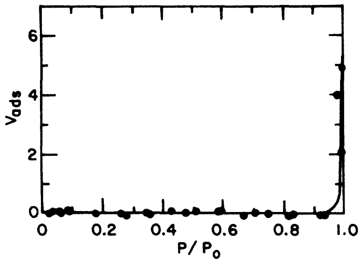

FIG. 4. Experimental class-III isotherm: Kr on Na metal at 75 K (Ref. 6). One full-coverage layer corresponds to $V_{ads} \sim 4$ units on this graph.

classes I and III. If (6) is used to estimate γ_{sl} in (5), one obtains the complete wetting criterion for all classes:

$$\phi < 2[(\gamma^d_{so}\gamma^d_{lv})^{1/2} - \gamma_{lv}] . \tag{7}$$

In addition we can relate ϕ to the equilibrium vapor pressure P by means of the Gibbs isotherm relation and in this way obtain a wetting criterion involving quantities which are either directly measurable or can be approximated from experimental quantities. The Gibbs isotherm for a differential process at constant T for a film and vapor in equilibrium is $d\phi = (v/a)dP$, where a is the area/molecule in the film and v is the volume/molecule in the vapor.[10,11,15,16] If the vapor density is sufficiently low, v can be expressed in terms of P and T by the ideal gas law. Then integrating the Gibbs relation and substituting the result for ϕ in (7) we obtain a condition for complete wetting at pressure P:

$$kT\int_0^P a^{-1}d(\ln P) < 2[(\gamma^d_{so}\gamma^d_{lv})^{1/2} - \gamma_{lv}] . \tag{8}$$

B. Wetting conditions for He films

Application of (8) to the system ^{4}He-graphite requires us to estimate several parameters. The value $\gamma_{lv} \simeq 0.37$ erg/cm^2 for liquid ^{4}He is fairly constant for $T < T_\lambda$, to within the accuracy required for the present considerations. The dispersion coefficient γ^d_{lv} for ^{4}He is considerably larger than γ_{lv}; we estimate it here by a continuum approximation to the surface energy. The attractive potential energy across a unit area plane in a continuum of density n interacting via 6-12 pair potentials can be approximated by the expression

$$u_{att} \simeq \tfrac{1}{3}\pi(\tfrac{4}{3}\pi)^{2/3}\epsilon n^{8/3}\sigma^6 . \tag{9}$$

Since the total interaction energy is strongly weighted by the two layers in contact, the appropriate n in (9) corresponds to a medium with the interatomic spacing of the first adsorbed layer on the substrate in question.

The quantity γ^d_{s0} for graphite has been determined empirically via a series of studies with various liquids and adsorbed gases[24,25]; results vary from about 110 to 150 erg/cm^2. If we take the central value, and identify γ^d_{lv} for ^{4}He with u_{att} calculated above, the right-hand side of Eq. (8) is equal to 26 erg/cm^2.

The spreading pressure can be estimated by combining empirical results with an analytic approximation. The spreading pressure of a completed first layer of ^{4}He on graphite has been determined by analysis of vapor pressure and calorimetric measurements;[25,26] it is found that $\phi_1 = 14.9$ erg/cm^2 independent of T below 3 K. ^{4}He films thicker than a few layers follow a pressure-thickness law

$$P/P_0 = e^{-\alpha/kTt^3}\,, \tag{10}$$

where t is the mean thickness in atomic layers.[27,28] Using (10) we can obtain an analytic expression for the increase of spreading pressure above ϕ_1 for any $t > 1$ by integration of (10) between the limits $t = 1$ and t. We then obtain for the critical thickness t_c at which (8) becomes an equality,

$$\tfrac{3}{2}\,\alpha n_l(1 - t_c^{-2}) = 2(\gamma^d_{s0}\gamma^d_{lv})^{1/2} - \gamma_{lv}] - \phi_1\,, \tag{11}$$

where n_l is the surface density of a single layer (assumed constant for all layers above the first).

The parameter α for ^{4}He-graphite is not definitely established. Measurements using different techniques range from a high value of 1.8×10^{-14} to 4×10^{-15} erg.[27-30] With a value midway between the two extremes and $n_l = 0.08$ Å^{-2},[29] the computed $t_c = 2.8$ layers.

The calculated critical thickness t_c is comparable with the experimental values for the intial appearance of bulklike properties in ^{4}He-graphite films. The extrapolated threshold thickness for the roton loss peak seen in inelastic neutron scattering was found to be between two and four layers. The minimum thickness for the appearance of anomalous mass transport at $T \sim T_\lambda$ ("onset A") was found to be between two and three layers.[27] The minimum thickness for appearance of a specific-heat anomaly at $T \sim T_\lambda$ is between two and three layers.[29] The success of the theoretical estimate may be fortuitous to a certain extent for some of the quantities required for the theoretical estimate are not known to high accuracy. The critical thickness is very sensitive to changes in the parameters, especially for thicknesses greater than ~ 2 layers. Most of the contribution to ϕ in a multilayer film comes from the first few layers: in ^{4}He-graphite ϕ_1 is about half of the maximum exerted by a thick film, and the contributions of higher layers decrease rapidly with increasing distance from the surface. But we can at least conclude that clustering in He films at low temperatures seems likely. The estimated critical thickness for ^{4}He on graphite is somewhat greater than two layers, and this value of t_c is consistent with the indications from several experimental studies.

III. SUBSTRATE FIELD AND SIZE EFFECTS

At thicknesses greater than t_c the stability conditions favor droplet formation and growth in class-II systems. In the early stages of growth the small droplets are markedly distorted from the spherical cap shapes of large drops. The distortions arise from a combination of curvature effect due to small size, together with an effect of the attractive field of the substrate, which tends to flatten the droplets against the surface. The general features can be approximated by combining standard thermodynamic results. We first consider the effect of droplet size alone. Curvature causes an enhancement of the equilibrium vapor pressure above the value P_0 of the bulk phase: for spherical droplets of radius r suspended in the vapor the relative enhancement is[14]

$$\delta P/P_0 = 2\gamma_{lv}v_l/rkT\,, \tag{12}$$

where v_l is the atomic volume of the liquid phase. Equation (12) is valid for relatively large radii, i.e., to the late growth state, but we nevertheless use it to illustrate the trend in shape throughout the droplet regime. In equilibrium the chemical potential of the droplets is equal to that of the vapor: if the vapor is effectively an ideal gas, we can use Eq. (12) to obtain an explicit dependence of the chemical potential μ on r, P_0, and T:

$$\mu(r, P_0, T) = kT \ln\left[\frac{P_0\lambda^3}{kT}\left(1 + \frac{2\gamma_{lv}v_l}{rkT}\right)\right]\,, \tag{13}$$

where $\lambda = h(2\pi mkT)^{-1/2}$ is the thermal de Broglie wavelength. If the substrate field is now introduced, assuming it is a small perturbation on the molecular states of the gas, its effect is a simple shift of μ equal to the single-particle adsorption energy. This makes the chemical potential a local function of the distance to the substrate as well as of r, P_0, and T. If the adsorption potential has the normal t dependence for intermediate range,[14]

$$\mu(t, r, P_0, T) = \mu(r, P_0, T) - \alpha/t^3\,. \tag{14}$$

In the equilibrium system the temperature and chemical potential are uniform but the pressure is not. If P_∞ is the pressure far from the surface, the chemical potential throughout the system can be referred to P_∞ by the ideal gas expression

$$\mu_\infty = kT\ln(P_\infty\lambda^3/kT)\,. \tag{15}$$

Combining (13) and (14), and equating $\mu(t, r, P_0, T)$ to μ_∞, we get radius of curvature as a function of distance from the substrate:

$$r = \frac{2\gamma_{lv}v_l}{kT}\left[\frac{P_\infty}{P_0}\exp\left(\frac{\alpha}{kTt^3}\right) - 1\right]^{-1}. \tag{16}$$

Equation (16) predicts that r increases rapidly with distance. The dependence at large t is approximately as a power law. At large t, and hence large r, the droplets are essentially bulk phase, so that $P_0 \simeq P_\infty$. If $\alpha/kTt^3 \ll 1$, exponential in (16) can be expanded to first order, yielding

$$r = 2\gamma_{lv}v_l t^3/\alpha\,. \tag{17}$$

The cubic dependence on t in Eq. (17), which arises from the third term in (14), holds only over intermediate distances, up to about 100 Å, but beyond this range retardation effects become important and the exponent changes gradually from three to four.

Equations (16) and (17) are derived for nearly spherical, relatively large droplets suspended in the attractive field of a substrate, but not for very small droplets in the strong fields close to the surface. For small droplets resting on realistic surfaces the fields are much stronger than the range of validity of the approximations. In addition, there are two distinct radii of curvature in the distorted droplets, and instead of the factor r^{-1} in Eq. (12) the correct term is the average $(r^{-1})_{\rm av} = \frac{1}{2}(r_1^{-1} + r_2^{-1})$.[14] However in strongly flattened profiles $(r^{-1})_{\rm av}$ is dominated by the smaller of the two radii, which is qualitatively described by Eqs. (16) and (17). Nevertheless we expect that the qualitative behavior we describe here does occur, i.e., the radius of curvature is relatively small close to the surface and increases rapidly with distance. Thus the qualitative shape has a profile like that indicated in Fig. 5. Such shapes have been obtained by Ruckenstein and Lee[31] for very small droplets, from computer calculations for molecules interacting with typical pair potentials at zero temperature.

FIG. 5. Schematic profile of a small droplet of class-II film, showing the flattening due to substrate attraction. The droplet is shown as coexisting with a thin uniform film on the substrate. The transition region at the base of the droplet may have a distinct microscopic structure, but its thermodynamic properties are described by a single interfacial coefficient as long as it is thin ($t \ll \phi/P$).

We can obtain a rough estimate of the aspect ratio of height to width from Eq. (17). The lateral size l of a drop is dictated essentially by its maximum radius r_m (i.e., of its "top cap"), while the mean thickness $\bar{h}$ is somewhat less than the value of $t(r_m)$ corresponding to this radius; we will put $\bar{h} \sim \frac{1}{2}t(r_m)$. Thus, the mean thickness corresponding to lateral dimension $l(\simeq 2r_{\rm max})$ is

$$\bar{h} \sim \tfrac{1}{2}(\alpha l/2\gamma_{lv}v_l)^{1/3}\,. \tag{18}$$

Equation (18) shows that small droplets increase in size primarily by lateral growth, with very modest increases in thickness.

Using Eq. (18) we can estimate the thickness of small droplets of ^{4}He on Grafoil, to compare with the neutron results. Typical domain sizes of monolayers on Grafoil, indicated by calorimetric,[32] neutron scattering,[33] Mössbauer,[34] and strain gauge[35] studies range from 80 Å to a few hundred Å. Although the nature of the domain boundaries on Grafoil has not been determined, it is probable that they are due to localized substrate imperfections such as dislocation lines and growth steps. Features such as these have been observed on single-crystal graphite surfaces by electron microscopy.[36] Such surface imperfections can control the nucleation, size, and lateral width of droplets in thin early growth stages (see Sec. IV). If we take $l = 100$ Å and the remaining parameters appropriate to ^{4}He then according to Eq. (18) $\bar{h} \sim 4$ layers. The droplets are thus predicted to be extremely thin, in qualitative agreement with the scattering results. Moreover, the droplets remain very thin even as they grow considerably in lateral size: for $l = 1000$ Å, $\bar{h}$ is still only about 8 layers. These estimates require that the quantities $2\gamma_{lv}v_l/kT$ and $\alpha/kT(\bar{h})^3$ are small. Both conditions are satisfied for the latter of the two cases above, i.e., for droplets of 1000 Å lateral size. For the smaller droplets one can expect appreciable errors, but nevertheless the same type of strongly flattened profiles.

IV. NUCLEATION AND HETEROGENEITY

The equilibrium properties of very small droplets are different from their bulk phases; of particular relevance here is the fact that their surface tension coefficients are somewhat smaller. This is due to the loss of the long-range part of the attractive energy from atoms far from the droplet surface. For droplet radii comparable with or smaller than such distances the cohesive energy is reduced and the surface tensions γ_{lv} and γ_{sl} are also lowered. These changes modify the conditions governing the clustering transition by *increasing* the threshold value for ϕ given by the right-hand side of Eq. (5), for droplets of small size. Accordingly, if the transition is approached from the low-pressure side, the creation of small clusters is postponed to some point further along the vapor-pressure isotherm, to pressures greater than P_0. Just as for the case of bulk phase condensation in a supersaturated vapor, the pressure may have to be raised to relatively high values before the new phase appears: the onset of droplet growth can be blocked by a high nucleation barrier. This barrier may be overcome, in principle, by thermal fluctuations, but for moderate supersaturation conditions the mean initiation time via fluctuations is extremely long. For the related case of a liquid in a supercooled vapor the probability for the appearance of a droplet of volume V at a slight excess pressure δP above the bulk equilibrium P is[14]

$$W \sim \exp[16\pi\gamma^3 V^2 P^2 / 3(kT)^3(\delta P)^2] \,. \tag{19}$$

The application of Eq. (19) to the nucleation of a droplet resting on a surface requires only minor modifications: the replacement of the single tension coefficient by the difference between the interfacial coefficients before and after nucleation, and a geometrical factor for the nonspherical shape. Typical probabilities according to (19) are extremely small. For example, if $\gamma = 1$ erg/cm^2, $T = 100$ K, $V = (100\ \text{Å})^3$, and $\delta P/P = 0.1$, the probability $W \sim \exp(-6 \times 10^8)$. Therefore the characteristic times for nucleation on an ideal surface are astronomically large. But on real surfaces there are always some imperfections which can reduce or entirely remove the nucleation barrier. At kink sites and concavities the adsorption binding energy is significantly greater than on the uniform flat planes. At these locations the adsorbed film is thicker than on the uniform regions. As the vapor pressure is increased there is a tendency for the local adsorption to "fill up" the concavities and pits, because their concave shapes reduces the equilibrium vapor pressure locally. This preferential thickening can be so pronounced that nucleation occurs at the special sites before the bulk vapor pressure is reached, in which case there is no longer any nucleation barrier for the system as a whole, and droplets can just grow outward continuously from the nucleation sites into the uniform regions. Depending on the extent and nature of the heterogeneity, the onset of clustering may have the nature of a first-order phase change or a more gradual transition. If there are only a few nucleation sites on an otherwise uniform surface the major part of growth takes place at the bulk saturation pressure P_0; indeed, droplet growth on the surface is then the first stage of bulk phase condensation. However, it is distinct from the later stages in that the small droplets coexist with uniform regions of film, so that the properties of uniform thickness film and clusters of bulk are found together on the same surface. [Calorimetric measurements of ^{3}He,[2] and of N_2,[3] adsorbed on Grafoil indicate a range of coverage in which uniform thickness (thin) film coexists with small clusters which have nearly bulk properties (thick films).] The coexistence regime suggests that the thin film-cluster transition is a first-order phase change. It is a true first-order phase change in the limit of a large ideal surface, where there can be at most one equilibrium cluster; the transition is then identical to bulk phase condensation. But on a real substrate, where there are many nucleation sites, the transition is broadened according to the number and range of influence of the sites.

On highly heterogeneous surfaces the distinction between nucleation and droplet growth can become completely blurred, so that there will be a gradual evolution from preferential adsorption on the regions of strongest binding to those of weaker binding, together with growth beginning on the preferential regions. In these cases the vapor-pressure isotherm can approach P_0 asymptotically, resembling class-I systems, even though droplets may be formed on small quasiuniform regions. The distinction between class-I and -II isotherms is therefore quite sensitive to heterogeneity; it is presumably the reason why relatively few class-II isotherms have been reported.

Capillary condensation is a phenomenon somewhat related to the clustering transition. Capillary condensation depends on highly concave surfaces, which help to nucleate adsorbed films into bulk liquid.[37,38] If the structure of the adsorbent is highly tortuous, with long fine pores, the condensed phase tends to fill entire channels rather than distribute evenly on all surfaces. The filled channels are analogous to the droplets of the clustering transition; depending on the sizes of the pores, there may be a regime of overlap between the onset of clustering and capillary condensation.

V. PERCOLATION TRANSITIONS: SUPERFLUID ONSET

A. Establishment of connectivity

After the initiation of clusters, further deposition causes each droplet to grow; as discussed above, this growth is primarily in the lateral direction. The locations of the initial droplets depend on the distribution and types of substrate imperfections. The droplets tend to be of uniform size on very uniform substrates, for the imperfections of uniform surfaces tend themselves to be uniform. As growth proceeds beyond the range of the nucleating imperfections, the droplets still tend to be of uniform size and shape, being governed by contact angle, together with the common dependence of thickness on lateral size. When they spread far enough neighboring droplets coalesce, forming irregularly shaped patches coexisting with regions of thin adsorbed film. With continued growth the average patch length increases, and cross connections multiply. If the connectivity is sufficiently great there will be a continuous path of "thick" film over a macroscopic area of substrate. The statistics of this connection process appear to be describable by two-dimensional percolation theory. Recent measurements[39] of the resistivity of an ultrathin Bi film show that there is an abrupt drop in resistivity when the fractional area covered by the "thick" regions reached 0.67; this value and the critical exponent for the variation of connectivity with average thickness are consistent with the predictions of the two-dimensional continuum percolation model.[40]

The relevance of two-dimensional percolation theory to helium films has been noted previously[41-43] in an attempt to explain experimental observations on heterogeneous films; we now believe that it is relevant to uniform substrates as well. Superfluidity requires a continuous liquid path over macroscopic distances which are characteristic of the experimental detection technique, typically on the order of 1 cm. But for calorimetry and neutron scattering the droplets need not be connected in order to show characteristic properties of He II, hence a λ-point specific-heat anomaly and the roton loss peak can emerge even before there is long-range connectivity. Studies of mass transport[27] and thermal relaxation and specific heat[29] with Grafoil substrates show that for a film of given thickness (greater than about $2\frac{1}{2}$ layers) there are two distinct transitions; anomalies appear at both T_λ and a lower temperature T_0. At T_0 the mass transport coefficient rises by several orders of magnitude and thermal relaxation becomes extremely rapid. The onset temperature T_0 is a function of thickness; T_0 is higher in thicker films, approaching T_λ as t increases toward the thickness of the saturated film, which is on the order of 100 layers at a height of ~1 cm above a bulk liquid reservoir. We have proposed earlier that the anomalies at T_λ are due to clusters; here we associate T_0 with long-range connectivity established in a percolation transition.

The hypothesis of a percolation transition to explain onset has to account for the fact that superfluid onset is a function of temperature as well as thickness. In a purely "geometric" percolation transition there is no temperature dependence to the critical coverage. We believe that the temperature dependence in superfluid onset comes about via quantum phase leakage between clusters. A similar mechanism has been advanced for granular films of superconductors,[44-46] in which the superconductivity of macroscopic samples is a gradual function of temperature. Clusters or grains of superconducting material separated by oxide or normal metal have order parameter phase angles which may be weakly coupled to nearby grains through tunneling or normal conduction. The phases of individual grains undergo thermal fluctuation and are uncorrelated unless the temperature is sufficiently low or the coupling is sufficiently strong. As either T decreases or the separation between grains decreases the phases of adjacent grains become correlated, and when the connections multiply enough, the entire sample establishes a single coherent phase path from one end to the other. It is this general explanation that is proposed for superfluid onset, the principal difference being that here the evidence for clusters is only circumstantial and not yet established by direct observation.

These considerations are not limited to behavior of He^4 on Grafoil but are also relevant to other, less uniform substrates, although their heterogeneity tends to obscure sharp features. The critical thickness for clustering is probably smaller on the other surfaces that have been used for He studies. The binding energy for adsorption on graphite is larger than on all others such as SiO_2 and CaF_2,[28] and this indicates that the surface tension of graphite is larger. Therefore the right-hand side of the clustering criterion Eq. (5) indicates a greater thickness for clustering on graphite. The general trend according to (5) is consistent with wetting phenomena in a more conventional context: more "energetic" surfaces are more readily wetted. Since we conclude that clustering occurs at lower converage thicknesses on other surfaces (e.g., Vycor and glass[47]), we can accordingly expect that percolation occurs earlier. This can come about because of two separate effects: in addition to a lower critical coverage for clustering, there can be on heterogeneous surfaces an extensive network of favorable channels or pathways of stronger binding, which would "fill up" at relatively low coverage. In any event the appearance of superfluid transport can occur at relatively low "thickness" on heterogeneous and weak binding surfaces. Varieties of thermal and transport superfluid onset measurements which have been carried out in many laboratories over several decades have been interpreted recently in terms of percolation theory,[41,42] and an experimental test of the hypothesis was carried out with positive results.[43] The interpretation and experiment now seem to be quite as relevant to relatively uniform films as Grafoil as to more heterogeneous systems.

B. Thick films

In class-II systems as thickness is increased beyond the coverage for "geometric" percolation the area of "thick film" continues to increase at the expense of thin regions. At some coverage the last spot of thin film disappears and the entire sample is covered by a thick film: we will suppose that its thickness is some definite value t_t. It is of both fundamental interest and practical importance to be able to predict t_t for a particular combination of substrate and deposit.

According to the current theory there is no intrinsic value of t_t which is characteristic of just the materials; t_t is also dependent on the size of the sample. Complete coverage of a sample by a thick film is equivalent to its being covered by a single droplet. The thickness-width relation for a droplet is given by Eq. (18). The approximation will serve for a large droplet as well as for a very small one, provided that the thickness is not so great as to require a change in the effective exponent due to retardation. Assuming that retardation is unimportant, we get

$$\bar{t}_t \sim \tfrac{1}{2}\,(\alpha L/2\gamma_{lv} v_l)^{1/3} \tag{20}$$

for a surface of lateral dimension L. We note that $\bar{t}_t$ is the mean thickness; the film is thicker in the center than at the edges. The variation in thickness over the central portion of the sample may be quite slight, especially if the droplet is strongly flattened by the substrate field; this flattening is more pronounced in small and thin droplets, hence in samples of small L. But if L is relatively large, then the profile of a thick covering film approaches a spherical cap shape. The thickness variation of the sample may be very great, depending on the contact angle at the boundaries. Of course these arguments concern equilibrium films only and not to those such as metal evaporated coatings which are typically deposited on cold substrates. But for van der Waals films where there is usually sufficient time and vapor pressure for equilibrium to be attained, these considerations should apply. Helium films are particularly interesting examples of equilibrium deposits: thick superfluid films of ^{4}He have been studied for many years. By the current arguments, such films are not likely to be very uniform over appreciable areas. According to (20) the mean thickness of liquid ^{4}He on a surface of dimension ~1 cm is about 400 layers; if material is removed so as to reduce $\bar{t}_t$ then the edges of the "droplet" would draw away from the boundaries of the substrate, leaving the edges with only a thin coating of thickness t_c. Our estimate of t_t contrasts with typical thicknesses ~100 layers determined in experiments on saturated films in contact with liquid He II. However we have not included gravitational energy in the theory. It is known that the gravitational energy is a significant factor in such situations, and a straightforward treatment of gravity together with substrate attraction yields thicknesses comparable to those observed.[14]

According to the theory, there is no range of finite thickness beyond t_c for which any class-II film can be truly uniform in thickness. Therefore the parameter in Eq. (20) can only be an average effective value beyond the clustering transition, and the local thickness is actually a function of the size and shape of the surface on which the film is adsorbed, as well as on substrate imperfection, gravitational potential, and similar weak influences.

VI. CONCLUSIONS

This paper presents a thermodynamic approach to the problem of clustering behavior in thin adsorbed films. It is clear that the theory is quite incomplete at its present state of development. No attempt has been made to justify or improve upon the simple combining law for interfacial tension.[22] We have not attempted to inspect the detailed dependence of surface tension on the structure of the surface or the droplet phase.[48] The several approximations, for surface tension, spreading pressure, and droplet shape, are quite crude and might be improved considerably although probably with some loss in simplicity. However, within the limitations of the approximations, the analysis seems to work reasonably well. In addition to He, for example, it offers reasonable agreement with measurements on N_2 films,[3] both with respect to the critical thickness and also the typical cluster size at onset.

The theory is not intrinsically limited to weakly bound van der Waals films. Some brief attention has been given to other types of systems including metal coatings on semiconducting and insulating substrates, where clustering at early stages of deposition is a familiar phenomenon.[4] In metal films as well as in ^{3}He and ^{4}He films the dispersion force contribution to the surface tension is significantly different from the total coefficient, and its magnitude is of considerable fundamental and practical interest.[49] According to the theory presented here, systematic measurement of the coefficients of metal films might be carried out by studying clustering on various well characterized substrates.

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[1] K. Carneiro, W. Ellenson, L. Passell, J. P. McTague, and H. Taub, Phys. Rev. Lett. 37, 1695 (1976).

[2] S. W. Van Sciver and O. E. Vilches, Phys. Lett. A 55, 191 (1975).

[3] T. T. Chung and J. G. Dash, J. Chem. Phys. 64, 1855 (1976).

[4] K. L.Chopra, *Thin Film Phenomena* (McGraw-Hill, New York, 1969), Chap. IV; C. A. Neugebauer, in *Handbook of Thin Film Technology*, edited by L. I. Maissel and R. Glang (McGraw-Hill, New York, 1970), Chap. 8.

[5] C. F. Prenzlow and G. D. Halsey, J. Phys. Chem. 61, 1158 (1957).

[6] R. A. Pierotti and G. D. Halsey, Jr., J. Phys. Chem. 63, 680 (1959).

[7] N. N. Avgul, G. I. Berezin, A. V. Kisilev, and I. A. Lygina, Izv. Akad. Nauk SSSR Otd. Khim. Nauk. 2, 205 (1961).

[8] M. Matecki, A. Thomy, and X. Duval, J. Chim. Phys. 71, 1484 (1974).

[9] B. Génot, thesis (University of Nancy I, 1974) (unpublished); J. Chim. Phys. 70, 1565 (1973).

[10] A. W. Adamson, *Physical Chemistry of Surfaces* (Interscience, New York, 1960).

[11] R. Defay, I. Prigogine, A. Bellemans, and D. H. Everett, *Surface Tension and Adsorption* (Longmans, Green, 1966).

[12] J. H. Holomon and D. Turnbull, Prog. Metal Phys. 4, 333 (1953).

[13] D. W. Pashley, Advan. Phys. 14, 361 (1965).

[14] L. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1958), Chap. XV.

[15] J. W. Gibbs, *Scientific Papers* (Longmans, Green, New York, 1906; reprinted by Dover, New York, 1961).

[16] C. Herring, in *Structure and Properties of Solid Surfaces*, edited by R. Gomer (University of Chicago, Chicago, 1952).

[17] The actual pressure at which condensation begins is somewhat lower than P_0 due to the substrate attractive field. This effect is discussed in Sec. V.

[18] A. Thomy and X. Duval, J. Chim. Phys. Physicochim. Biol. 66, 1966 (1969); 67, 286 (1970); 67, 1101 (1970).

[19] G. L. Price and J. A. Venables, Surf. Sci. 49, 264 (1975).

[20] F. A. Putnam and T. Fort, Jr., J. Phys. Chem. 79, 459 (1975); A. Thomy, J. Regnier, and X. Duval, *Thermochimie* (Centre National de la Recherche Scientifique, Paris, 1972), p. 511.

[21] J. H. Singleton and G. D. Halsey, Jr., J. Phys. Chem. 58, 330, 1011 (1954).

[22] L. A. Girifalco and R. J. Good, J. Phys. Chem. 61, 904 (1957).

[23] J. C. Melrose, Adv. Chem. 43, 172 (1964).

[24] F. M. Fowkes, in *Chemistry and Physics of Interfaces*, edited by S. Ross (American Chemical Society, Washington, D.C., 1965).

[25] R. L. Elgin, thesis (Caltech, 1974) (unpublished).

[26] R. L. Elgin and D. L. Goodstein, Phys. Rev. A 9, 2657 (1974).

[27] J. A. Herb and J. G. Dash, Phys. Rev. Lett. 29, 846 (1972).

[28] E. S. Sabisky and C. H. Anderson, Phys. Rev. A 7, 790 (1973); Phys. Rev. Lett. 30, 1120 (1973).

[29] M. Bretz, Phys. Rev. Lett. 31, 1447 (1973).

[30] J. Landau and W. F. Saam, Phys. Rev. Lett. 38, 23 (1977).

[31] E. Ruckenstein and P. S. Lee, Surf. Sci. 52, 298 (1975).

[32] M. Bretz, J. G. Dash, D. C. Hickernell, O. E. McLean, and O. E. Vilches, Phys. Rev. A 8, 1589 (1973).

[33] J. K. Kjems, L. Passell, H. Taub, J. G. Dash, and A. D. Novaco, Phys. Rev. B 13, 1446 (1976).

[34] H. Shechter, J. Suzanne, and J. G. Dash, Phys. Rev. Lett. 37, 706 (1976).

[35] J. G. Dash, J. Suzanne, H. Shechter, and R. E. Peierls, Surf. Sci. 60, 411 (1976).

[36] J. M. Thomas, E. L. Evans, and J. O. Williams, Proc. R. Soc. A 331 417 (1972).

[37] M. W. Cole and W. F. Saam, Phys. Rev. Lett. 32, 985 (1974).

[38] W. F. Saam and M. W. Cole, Phys. Rev. B 11, 1086 (1975).

[39] N. T. Liang, Y. Shan, and S.-Y. Wang, Phys. Rev. Lett. 37, 526 (1976).

[40] S. Kirkpatrick, Rev. Mod. Phys. 45, 574 (1973).

[41] J. G. Dash and J. A. Herb, Phys. Rev. A 7, 1427 (1973).

[42] M. W. Cole, J. G. Dash, and J. A. Herb, Phys. Rev. B 11, 163 (1975).

[43] J. A. Herb and J. G. Dash, Phys. Rev. Lett. 35, 171 (1975).

[44] R. S. Thompson, M. Strongin, O. F. Kammerer, and J. E. Crow, Phys. Lett. A 29, 194 (1969).

[45] J. C. Solinsky and A. M. Goldman, Phys. Lett. A 47, 359 (1974); P. K. Hansma and J. R. Kirtley, J. Appl. Phys. 45, 4016 (1974).

[46] G. Deutscher, Y. Imry, and L. Gunther, Phys. Rev.

B 10, 4598 (1975).

[47] See articles by J. S. Langer and J. D. Reppy, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1970), Vol. VI, p. 1; K. R. Atkins and I. Rudnick, ***ibid***, p. 70.

[48] B. Mutaftschiev, Surf. Sci. (to be published).

[49] H. Jones, Met. Sci. J. 5, 15 (1971).