Growth Instability in Helium Films

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We study the growth of liquid ^{4}He films on weakly attractive substrates. Close to the substrate the film grows by formation of well defined liquid layers. Above a minimum stable coverage, a liquid monolayer uniformly covers the surface. Upon increasing the coverage a second liquid layer begins to grow by the formation of two-dimensional liquid "clusters." Above a certain coverage, the second layer leaves vacuum-cluster coexistence, and the system regains the full planar symmetry. The scenario is repeated for a third liquid layer. The results are interpreted in terms of recent experiments of helium on graphite.

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In the low-temperature liquid phase, helium atoms adsorbed to a substrate form a layerlike structure with layers parallel to the substrate surface. The cause of this layering is the hard-core-like repulsion between the individual atoms. The precise mechanism for the formation of such a structure depends on the detailed geometry of the substrate. If the substrate is smooth or, as in the case to be studied below, consists of one or more layers of solid helium, the growth scenario can be described on the basis of relatively simple principles.

At very low densities, the first liquid layer (we will refer to this layer as the "first" layer, independently of whether the substrate itself consists of solid layers of ^{4}He) will form a low-density two-dimensional liquid. The saturation density of this liquid ρ_{2D} is known [1] to be approximately 0.042 Å^{-2}. Below a certain minimum density the compressibility vanishes and the two-dimensional system moves into a state of spinodal decomposition, i.e., ^{4}He clusters coexisting with the vacuum. A good estimate of $\rho_{2D_{\min}}$ is 0.037 Å^{-2} [2]. It is important to note that ρ_{2D} is considerably below the saturation density ρ_{3D} of three-dimensional ^{4}He, which would translate into a surface density of $\rho_{3D}^{2/3} \approx 0.077$ Å^{-2}. Therefore, by adding further atoms to the liquid, the two-dimensional system must become highly compressed in order to approach the bulk equilibrium density. While a weakly attractive adsorbate-substrate interaction would naturally favor a compressed layer, a density will inevitably be reached at which point it becomes energetically favorable to elevate particles to a second (or even a third) layer, before the first layer can be further compressed. An important point is that for a highly layered liquid there will once again exist a minimum coverage below which the *second* liquid layer is unstable to spinodal decomposition. In this Letter we provide convincing evidence that a zero-temperature liquid ^{4}He film is a striking example of such a highly layered liquid.

The present Letter is devoted to a microscopic description of film growth. Our theoretical tool is the hypernetted-chain (HNC) theory for inhomogeneous systems [3], which we have recently generalized [4,5] to include triplet correlations and elementary diagrams. The level of implementation of the theory used here is identical to our theory for the bulk liquid [6], which reproduces the equation of state over a wide density regime within better than 0.02 K, and is, when compared with the Monte Carlo calculations of Ref. [1], similarly successful in two dimensions [7]. Calculations on similar systems have also been carried out within a phenomenological density-functional approach [8]. The applicability of that theory in the two-dimensional limit has not been examined.

The HNC theory is based on a variational ansatz for the ground-state wave function of the many-body system of the form

$$\Psi_0(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \exp\frac{1}{2}\Bigg[\sum_i u_1(\mathbf{r}_i) + \sum_{i<j} u_2(\mathbf{r}_i,\mathbf{r}_j) + \sum_{i<j<k} u_3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k)\Bigg]. \quad (1)$$

Phenomenological input to the theory is the microscopic Hamiltonian which we assume to be of the form

$$H = \sum_i \left[-\frac{\hbar^2}{2m}\nabla_i^2 + U_{\rm sub}(\mathbf{r}_i)\right] + \sum_{i<j} V(|\mathbf{r}_i - \mathbf{r}_j|), \quad (2)$$

where $V(|\mathbf{r}_i - \mathbf{r}_j|)$ is the liquid ^{4}He-^{4}He interaction, and $U_{\rm sub}(\mathbf{r})$ is the substrate-adsorbate potential. Other "adjustable parameters" are in a sense only the restriction to triplet correlations in the wave function (1) and the effort one is willing to spend in the computation of the relevant "elementary" diagrams. From the experience with bulk quantum liquids and quantum liquid mixtures in two and three dimensions, we expect that the uncertainty caused by the phenomenological Hamiltonian (2) is larger than the uncertainty caused by the approximations implicit to the HNC theory.

An important part for the variational approach is the optimization of the many-body correlations by solving the Euler equations

$$\frac{\delta E}{\delta u_n(\mathbf{r}_1,\ldots,\mathbf{r}_n)} = 0, \quad (3)$$

where E is the energy expectation value of the Hamiltonian (2) with respect to the wave function (1).

Besides the practical advantage of providing the best possible wave function in the given function space, one can show generally that *the Euler equations do not give (unphysical) solutions if the assumed geometry of the system under consideration is unstable against infinitesimal density fluctuations.* For example, Euler equations will cease to have solutions if one makes the incorrect assumption that the liquid will be in a uniform state, and then attempts to lower the density below the thermodynamic *spinodal line* where the compressibility becomes negative [9]. The Euler equations will have solutions only if they are defined in a general enough space that includes the broken-symmetry phase; in this example, the liquid-droplet–gas coexistence. Consequently, one has confidence that the theory is describing the correct physics, in particular, in the vicinity of such structural phase transitions.

This feature of the Euler equations is particularly relevant in the scenario we are describing here: the growth of helium films on a substrate. As discussed above, it may become energetically favorable for a second (third...) layer to form on the substrate *before* the first (second...) layer has been compressed to, or above, its bulk equilibrium density. In this situation "patches" of ^{4}He can form on the second layer, and the translational symmetry parallel to the helium surface is spontaneously broken. Formally, the effect is described by the fact that the chemical potential is no longer a monotonic function of the surface coverage, or, equivalently, that the third sound velocity becomes imaginary.

In order to describe our procedure and our results, we must briefly review the basic ingredients of the theory. A complete description of the basic theory is found in Ref. [3]; technical details on the three-body equations are discussed in Refs. [4,5].

First, the energy expectation value is rewritten as a functional of the physically observable one-body density $\rho_1(\mathbf{r})$ and the pair distribution function $g(\mathbf{r},\mathbf{r}')$. A natural representation is

$$E = \int d^3r \left[\frac{\hbar^2}{2m}\left|\nabla\sqrt{\rho_1(\mathbf{r})}\right|^2 + \rho_1(\mathbf{r})U_{\rm sub}(\mathbf{r})\right] + E_c\left[g(\mathbf{r},\mathbf{r}'),\rho_1(\mathbf{r})\right], \qquad (4)$$

where E_c is the "correlation energy." Its precise functional form is irrelevant for the purpose of our present discussion. The energy is then minimized with respect to the one-body density, which gives a generalized Hartree equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U_{\rm sub}(\mathbf{r}) + V_H(\mathbf{r})\right]\sqrt{\rho_1(\mathbf{r})} = \mu\sqrt{\rho_1(\mathbf{r})}\ , \qquad (5)$$

where $V_H(\mathbf{r}) \equiv \delta E_c/\delta\rho(\mathbf{r})$, and μ is the chemical potential.

The Euler equation for the pair distribution function can be formulated in various ways depending on whether the short- or the long-range structure of the system is under consideration. Since we are interested here in long-wavelength, low-lying excitations, a formulation that emphasizes these features is, of course, preferable. The excited states of the system in a generalized Feynman approximation are obtained from the eigenvalue equation

$$\int d^3r'\left[\delta(\mathbf{r}-\mathbf{r}')H_1(\mathbf{r}) + 2\hat{V}_{p\text{-}h}(\mathbf{r},\mathbf{r}')\right]H_1(\mathbf{r}')\psi_\omega(\mathbf{r}') = \hbar^2\omega^2\psi_\omega(\mathbf{r}) \qquad (6)$$

where

$$H_1(\mathbf{r}) \equiv -\frac{\hbar^2}{2m}\frac{1}{\sqrt{\rho_1(\mathbf{r})}}\nabla\rho_1(\mathbf{r})\cdot\nabla\frac{1}{\sqrt{\rho_1(\mathbf{r})}} = -\frac{\hbar^2}{2m}\nabla^2 + U_{\rm sub}(\mathbf{r}) + V_H(\mathbf{r}) - \mu\ , \qquad (7)$$

and $\hat{V}_{p\text{-}h}(\mathbf{r},\mathbf{r}')$ is the so-called "particle-hole interaction," which is defined diagrammatically through the HNC equations. In principle, $\hat{V}_{p\text{-}h}(\mathbf{r},\mathbf{r}')$ can also be defined as the second variational derivative of the correlation energy with respect to the one-body density,

$$\hat{V}_{p\text{-}h}(\mathbf{r},\mathbf{r}') = \sqrt{\rho_1(\mathbf{r})}\frac{\delta^2 E_c}{\delta\rho_1(\mathbf{r})\delta\rho_1(\mathbf{r}')}\sqrt{\rho_1(\mathbf{r}')}. \qquad (8)$$

In practice, the relationship (8) is true *only in an exact theory;* the comparison between the diagrammatically and variationally defined $V_{p\text{-}h}(\mathbf{r},\mathbf{r}')$, or derived quantities, provides in any approximate theory a useful consistency check. The eigenfrequencies $\hbar\omega$ are the frequencies of the collective excitations in the system.

In the geometry to be considered here, we assume that $U_{\rm sub}$ depends only on the distance z from the substrate, and that the system is translationally invariant in the x-y plane. In that geometry, the eigenvalue equation (6) can be decoupled in momentum space as a function of the momentum $q_\parallel$ parallel to the surface. The long-wavelength limit of the lowest-lying mode, which we identify with the third sound, can be calculated and is found to be

$$\hbar\omega_3(q_\parallel) = \hbar c_3 q_\parallel \qquad (9)$$

with

$$mc_3^2 = \frac{\hbar^2}{2m}\frac{n}{\left(\sqrt{\rho}\left|\left[H_1(0) + 2\hat{V}_{p\text{-}h}(0)\right]^{-1}\right|\sqrt{\rho}\right)}\ , \qquad (10)$$

where $n = \int dz\,\rho_1(z)$ is surface coverage, and $H_1(0)$ and $\hat{V}_{p\text{-}h}(0)$ are the long-wavelength limits of the corresponding quantities defined above. The relationship (10) may also be derived from Eq. (5); one finds the well-known hydrodynamic relationship

$$mc_3^2 = n\frac{d\mu}{dn}. \qquad (11)$$

The same precautions as mentioned above apply: The velocity of third sound calculated by the hydrodynamic derivative (11) and the long-wavelength limit of the collective excitations, Eq. (10), will normally agree only for an exact theory. In general, one expects that the expres-

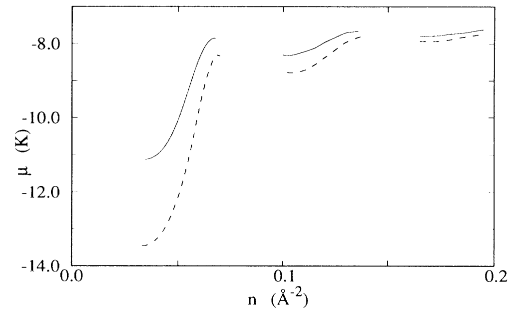

FIG. 1. The coverage dependence of the chemical potential of the ^{4}He film. The coverage scale is adjusted to include the *liquid* layers only. The full (dashed) line corresponds to $S = 1$ ($S = 1.1$) in Eq. (14).

sion (10) is less accurate than the hydrodynamic derivative (11) since the diagrams included in Eq. (10) are a proper subset of those included in Eq. (11). In particular for thick films, where the third-sound velocity goes to zero, one must expect large-scale numerical cancellations in the evaluation of expression (10).

In this investigation, we have studied the behavior of liquid helium adsorbed to two layers of solid helium on graphite. The substrate potential consists of three terms,

$$U_{\rm sub}(z) = U_0(z + z_0) + \sum_{i=1}^{2} U_i(z + z_i) \qquad (12)$$

with

$$U_0(z) = e\left[\frac{1}{15}\left(\frac{\sigma}{z}\right)^9 - \frac{1}{2}\left(\frac{\sigma}{z}\right)^3\right] , \qquad (13)$$

where the strength e has been chosen to match the asymptotic strength of the graphite-helium interaction [10], $e\sigma^2/2 = 186$ meV. The two solid helium planes were modeled by averaging Lennard-Jones potentials over a plane,

$$U_i(z) = 4\pi\epsilon n_i\sigma^2\left[\frac{1}{5}\left(\frac{\sigma}{z}\right)^{10} - \frac{S}{2}\left(\frac{\sigma}{z}\right)^4\right] , \qquad (14)$$

with $\epsilon = 10.22$ K and $\sigma = 2.556$ Å. The surface densities n_i ($i = 1, 2$) were taken to be the experimental values [11] $n_1 = 0.115$ Å^{-2} and $n_2 = 0.093$ Å^{-2}. The offsets z_i are such that the distance between individual solid layers and between the first solid layer and the substrate is about 3.3 Å. The adjustable parameter S, which has a direct effect on the well depth, was initially set equal to 1. We have chosen here the Lennard-Jones potential since its simple form allows one to carry out the plane-averaging analytically. This choice is perhaps slightly inconsistent with the choice of the Aziz potential [12] used for $V(|\mathbf{r}_i - \mathbf{r}_j|)$, but other uncertainties, arising from ignoring the corrugations in the underlying graphite substrate, and from omitting zero-point motion caused by the assumption that the solid helium layers are completely rigid, make this inconsistency irrelevant.

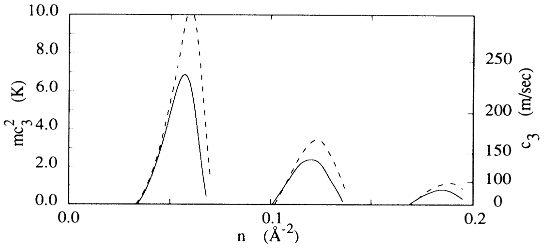

FIG. 2. Same as Fig. 1 but for the compressibility (left scale) and the sound velocity (right scale).

We have calculated the ground-state structure of the liquid film for surface coverages between $n = 0.035$ Å^{-2} and $n = 0.20$ Å^{-2}. Plots of the chemical potentials and mc_3^2 are shown in Figs. 1 and 2. The most important observation is that Euler equations *do not* have solutions for all coverages. As was alluded to in the above discussion, this observation is consistent with the feature of the HNC theory that the Euler equations have solutions only if the geometry under consideration is stable against infinitesimal perturbations, in other words, when $mc_3^2 = n\, d\mu/dn > 0$.

The first instability is encountered for coverages below $n_{\rm min} = 0.035$ Å^{-2}. Below this value, which is in close agreement with $\rho_{\rm 2D_{min}}$ obtained from Green function Monte Carlo [2], the *two-dimensional* liquid is unstable against density fluctuations — the liquid exits in patches, above the solid layers, in coexistence with the vacuum. As the coverage is increased above $n_{\rm min}$, the film uniformly covers the surface; the ^{4}He film has the full planar symmetry forced on it by the substrate. Initially the film becomes more stable, but beyond a surface coverage of 0.055 Å^{-2} the compressibility drops rapidly. The cause of the rapid drop is a pronounced thickening of the film (Fig. 3) which had been highly two dimensional up to that point.

The quasi-two-dimensional phase becomes unstable between surface coverages of 0.068 Å^{-2} and 0.069 Å^{-2}: The film consists of a cluster-vacuum coexistence above

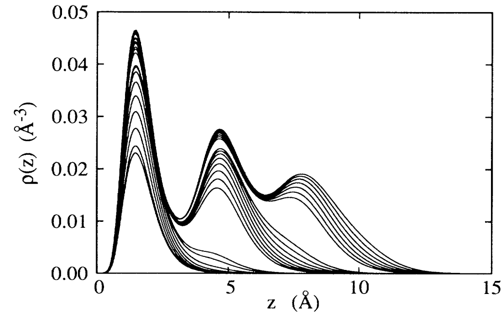

FIG. 3. The density profile for various values of coverage. The profiles correspond to surface coverages of 0.035, 0.040, ..., 0.065, and 0.068 Å^{-2} for the monolayer, 0.10, 0.105, ..., 0.13 Å^{-2} for the double layer, and 0.165, 0.17, ..., 0.195 Å^{-2} for the triple layer.

the first liquid layer. The feature that makes ^{4}He films highly layered emerges from the realization that the instability region of the *second* layer once again has a width in coverages of 0.035 Å^{-2}. Beyond a coverage of 0.1 Å^{-2} the second layer uniformly covers the surface. The same pattern is repeated for the third layer: An instability region of width 0.035 Å^{-2} exists between coverages of 0.13 Å^{-2} and 0.165 Å^{-2} [13].

If the conjecture that proposed growth scenario ^{4}He is correct, then the value of width of the instability region, $\Delta n = 0.035$ Å^{-2}, should be reflected mainly in the adsorbate-adsorbate interaction and not the substrate-adsorbate potential. Indeed when the well depth of the latter was increased by 10%, by altering S in Eq. (14) (cf. Figs. 1 and 2), we find (A) an expected overall increase in the maximum of the compressibility, in the stable regions, indicating an increased local density per layer, (B) a slight uniform shift in the coverage, and (C) the value $\Delta n = 0.035$ Å^{-2} persisted.

As mentioned above, our largest uncertainty comes from choosing a substrate potential. Comparison of our results with recent high-resolution adsorption isotherm data [14] indicates that Eq. (14) is a realistic potential. The coexistence regions will obviously be strongly influenced by finite-temperature effects. Nevertheless, at 0.65 K, clearly distinguishable ^{4}He layers are observed. Vapor pressure measurements show regions of slowed rates of adsorption for coverages in regions corresponding to coexistence. The experiments also reveal well defined oscillations in the c_3, with periodicities coinciding with the formation of layers. In our calculations, inner layers continue to grow during the growth process of outer layers. Our first layer saturates at a density near 0.07 Å^{-2} by the time the third layer is a partial way through its growth. This value is once again in good agreement with the corresponding experimental value.

After this work was completed, we learned of recent measurements of fourth-sound velocities of helium on graphite [15]. While these measurements are carried out under pressure and correspond to a liquid-solid transition, the reported growth scenario is completely analogous to the one reported in this work: Depending on the coverage, the solid layer either grows continuously or by the growth of small clusters coexisting with the liquid. This behavior persists through the growth of eight solid layers.

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