Helium Prewetting and Nonwetting on Weak-Binding Substrates

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New wetting and nonwetting phenomena for ^{4}He adsorbed on weak-binding substrates such as the alkali metals are predicted. With a nonlocal density-functional model, we calculate the density profile of ^{4}He films adsorbed on surfaces characterized by an attractive van der Waals potential tail of strength C_3 and a well depth D. As a function of C_3 and D, ^{4}He films exhibit both nonwetting and wetting, the latter being accompanied by a prewetting transition. Specifically, we find that ^{4}He will *not* wet all the alkali metals; only on Li and Na is wetting behavior, with prewetting, expected.

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While our understanding of wetting transitions has grown rapidly since their prediction [1,2] more than a decade ago, a key aspect of the simplest transitions, the existence of prewetting, has yet to be unambiguously observed [3]. There is a general consensus [4,5] that in classical systems prewetting transition lines lie exceedingly close to coexistence, rendering their observation very difficult. In this Letter we predict prewetting transitions as well as the existence of nonwetting in a new regime, that of low temperatures in a quantum fluid. Specifically, we predict that ^{4}He adsorbed on weak-binding substrates such as the alkali metals will exhibit, as a function of substrate potential parameters, either nonwetting or wetting accompanied by prewetting at low temperatures. From our estimates, prewetting should be accessible experimentally. This is the first work to provide theoretical evidence that superfluid ^{4}He will fail to wet all substrates.

The key physical point in this work is the observation that adsorbate-substrate interactions $V(z)$ are characterized both by a long-ranged van der Waals tail $-C_3/z^3$, where z is the distance from the substrate to an adsorbate atom, and by a well depth D, and that C_3 and D can be varied independently. The relation between D and C_3 has been explicitly discussed in Ref. [6]. The short-range repulsive potential is predominantly due to the exchange energy from the overlap of the charges of the adatoms and substrate. For those substrates whose electrons are weakly bound, the electrons extend far outward from the surface, resulting in a large substrate-adatom equilibrium distance ξ. In this case, D is reduced by a factor of ξ^{-3}. Indeed, metal surfaces generally have smaller well depths than insulators having the same C_3 value [6]. The extreme case is the alkali metals, which have quite small well depths.

In earlier work it has been shown that monolayer ^{4}He films do not solidify on such weak-binding surfaces [7]. Furthermore, the relatively large z motion perpendicular to the surface causes the adatoms to be less strongly bonded laterally. A quasi-two-dimensional Bose gas may occur on such surfaces [8,9]. The present work shows that an even more dramatic consequence can occur for appropriate parameters. If the well depth is extremely small, then the adatom's binding energy may be less than the 7-K binding energy of 3D helium (this occurs for Cs, K, Na, and Rb substrates), suggesting that no monolayer will form since the lateral interactions give very weak (0.6 K) [10] binding. As an example we remark that the He-Li interatomic well depth of about 5 K is one-half that of He-He, and a similarly small relative result occurs for the other noble-gas–alkali-metal interactions [11]. There can ensue two possible kinds of behavior: nonwetting or prewetting. To understand the different scenarios, we first make a simple estimate of the energy balance and then present results of a more reliable determination.

Qualitatively, the gain in energy per unit area of a thick film due to the attractive well is of the order of the integral of $\rho(z)V(z)$, where $V(z)$ is the external potential due to the substrate, which occupies the half space $z \leq 0$, and where $\rho(z)$ is the film density. The loss is that due to the creation of two interfaces in the film and is of order a few times the liquid-gas surface tension σ_{lg}. Thus, an approximate criterion for nonwetting takes the form

$$\sigma_{lg} \gtrsim -\tfrac{1}{2}\rho_0 \int_{z_{\min}}^{\infty} V(z)\,dz\,, \tag{1}$$

where we have approximated $\rho(z)$ by the bulk ^{4}He value ρ_0, and $z_{\min}$ is the position of the minimum of $V(z)$.

For quantitative analysis we use a nonlocal density-functional model developed by Dupont-Roc *et al.* [12] and used in a study of helium-mixture films [13]. Our treatment is restricted to $T=0$, so that any ^{4}He film is presumed to be completely superfluid, containing no normal component. In this model, the energy of liquid ^{4}He at zero temperature is written as a functional of the ^{4}He density ρ:

$$E=\int d\mathbf{r}\left[\frac{\hbar^2}{2m}|\nabla\phi|^2+\rho V(z)\right]+H_{\rm nl}\,, \tag{2}$$

$$H_{\rm nl}=\tfrac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')V_l(|\mathbf{r}-\mathbf{r}'|)+\tfrac{1}{2}c\int d\mathbf{r}\,\rho(\mathbf{r})[\bar{\rho}(\mathbf{r})]^{1+\gamma}\,, \tag{3}$$

where m is the mass of a ^{4}He atom, $\phi(\mathbf{r}) = [\rho(\mathbf{r})]^{1/2}$, and $H_{\rm nl}$ is the nonlocal Hamiltonian introduced by Dupont-Roc *et al.* [12] to account for interactions and correlations between ^{4}He atoms. For V_l we take the standard Lennard-Jones form with $\epsilon = 10.22$ K and $\sigma = 2.556$ Å, screened at distances shorter than a characteristic distance h_4. Specifically, with $x \equiv |\mathbf{r} - \mathbf{r}'|/\sigma$,

$$V_l = \begin{cases} 4\epsilon(x^{-12} - x^{-6}) & \text{for } |\mathbf{r} - \mathbf{r}'| \geq h_4, \\ V_l(h_4)(\sigma x/h_4)^4 & \text{for } |\mathbf{r} - \mathbf{r}'| < h_4. \end{cases} \tag{4}$$

In Eq. (3), $\bar{\rho}(\mathbf{r})$ is the local density averaged over a sphere of radius h_4 centered at $\mathbf{r}$. We adopt the common (9-3) potential form

$$V(z) = \frac{4C_3^3/27D^2}{z^9} - \frac{C_3}{z^3}. \tag{5}$$

With $V=0$ and the parameters $h_4 = 2.377$ Å, $c = 1.04554 \times 10^7$ K Å$^{3(1+\gamma)}$, and $\gamma = 2.8$ of Ref. [12], this model correctly reproduces the equation of state, surface tension, and the static density-density response function of bulk liquid ^{4}He [14]. The film density profile is determined by the Euler equation:

$$\mu = \delta E/\delta\rho(z). \tag{6}$$

This equation can be integrated numerically to obtain the film profile at any chemical potential μ for any surface characterized by C_3 and D. A set of calculated film profiles is shown in Fig. 1. A further integration gives the film coverage N (or a corresponding nominal film thickness d) and the surface free energy α (per unit area):

$$d \equiv \frac{N}{\rho_0 A} = \frac{1}{\rho_0}\int_0^\infty dz\, \rho(z), \tag{7}$$

$$\alpha = E - \mu N, \tag{8}$$

where A is the surface area. In the low-coverage limit $H_{\rm nl}$ is negligible so that Eq. (6) becomes the Schrödinger equation for a single particle in $V(z)$ and the density profile is proportional to the square of the ground-state wave function of this equation.

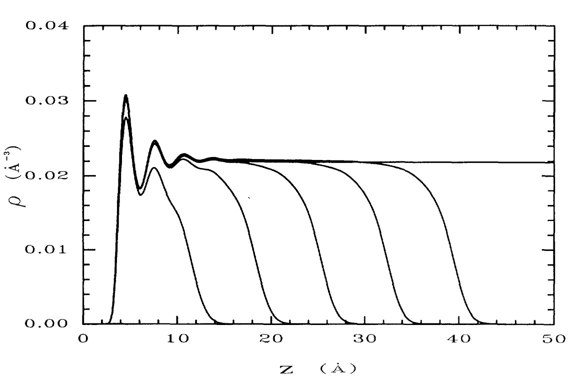

FIG. 1. Typical film profiles calculated from Eq. (6) on a surface with $C_3 = 1000$ K Å^3 and $D = 10$ K.

A film is said to wet a surface when d grows continuously to ∞ as $\mu \to \mu_0$, the chemical potential at bulk liquid-vapor coexistence, from below. This can be done by increasing the vapor pressure P to its saturation value P_0. On the other hand, nonwetting occurs when the film thickness remains bounded as $P \to P_0$, at which point bulk droplets appear. In most cases, a unique minimum-energy solution to Eq. (6) can be found for a given chemical potential μ ($\leq \mu_0$). More remarkably, there are cases where two such solutions to Eq. (6) can be found, one corresponding to a film having zero thickness and the other to a film with $d > 0$. This coexistence of two states characterizes the first-order prewetting transition. It occurs when the free energies α associated with the two states become equal. In the corresponding adsorption isotherm, there is a finite jump in the coverage, Δd, at a vapor pressure P ($< P_0$).

In Fig. 2, we present a phase diagram of the substrates characterized by C_3 and D. Regions of different wetting behavior are marked as wetting or nonwetting, respectively. In the wetting region we always find a prewetting jump, though the size of this jump, infinite on the nonwetting-wetting boundary, decreases with increasing D. Also indicated is the boundary above which the first adsorbate layer has been estimated to solidify [7]. Detailed predictions of our theory for the region above this boundary are of course suspect, but substances falling in this region are clearly expected to be wet by ^{4}He [15]. The approximate criterion of Eq. (1) becomes, for the potential of Eq. (5), $42.6 \geq (C_3 D^2)^{1/3}$. The boundary determined by this criterion is also plotted in Fig. 2, and the qualitative agreement with the full nonlocal theory is quite pleasing.

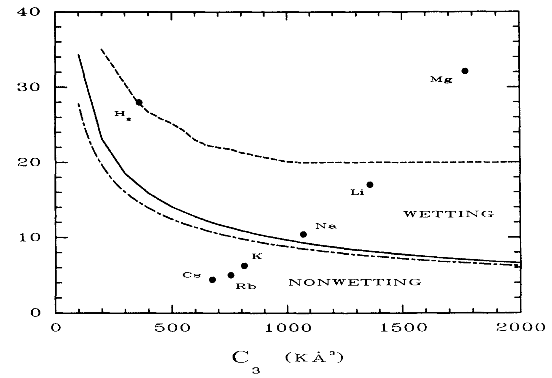

FIG. 2. The phase diagram of ^{4}He adsorption on weak-binding substrates. Values of C_3 and D for the indicated elements were taken from Refs. [6] and [7]. The solid line is the wetting-nonwetting boundary predicted by the full nonlocal theory. The dot-dashed line is the same boundary as predicted by the qualitative criterion of Eq. (1). Above the dashed line, the first layer of ^{4}He is expected to be solid, while below it the films are expected to be liquid (see Ref. [7]).

TABLE I. Contact angles θ in degrees, prewetting film-thickness jumps (in layers), where relevant, and values of the potential parameters C_3 and D for the alkali metals and H_2 appearing in Fig. 2.

Element	θ	Δd	C_3 (K Å^3)	D (K)
Li	0°	0.80	1360	17.1
Na	0°	5.25	1070	10.4
K	73°	···	812	6.26
Rb	87°	···	754	4.99
Cs	95°	···	673	4.41
H_2	0°	0.42	360	28

The contact angles of ^{4}He droplets on the substrates shown in Fig. 2 are found from Young's equation

$$\cos(\theta) = (\alpha_{sv} - \alpha_{sl})/\alpha_{lv} , \tag{9}$$

where α_{sv}, α_{sl}, and α_{lv} are the substrate-vapor, substrate-liquid, and liquid-vapor interfacial tensions, respectively. The right-hand side of Eq. (9) is readily computed from Eq. (8) at coexistence. The results are given in Table I. Note that the contact angle varies from slightly more than 90° to 0° (wetting).

One may more clearly understand Fig. 2 by noting that the nonwetting-wetting boundary is a line of first-order wetting transitions in $\Delta\mu$-C_3-D space at $\Delta\mu \equiv \mu - \mu_0 = 0$. A prewetting sheet emerges from this line.

It is important to assess the observability of prewetting within our theory, given that prewetting transitions have proven so notoriously difficult to observe in classical systems [3-5]. We find that prewetting typically occurs at $\Delta\mu \sim -1$ K. While our calculations are strictly applicable only at $T=0$, we can assume that at low temperatures the phase diagram will be similar to that at $T=0$, so that prewetting would occur at a ^{4}He vapor pressure P given by the ideal gas result $P = P_0 \exp(\Delta\mu/T) \leq P_0/2.7$ for $T \leq 1$ K. Thus, P is expected to be substantially separated from P_0 and should be readily observable. A plot of the magnitude of the prewetting jump Δd (in layers) is given in Fig. 3 as a function of D for fixed $C_3 = 1000$ K Å^3. Note that Δd is infinite at the wetting-nonwetting boundary (at $D = D_0 = 9.6$ K) and appears to saturate at a value of about 0.4 layer for large D. We expect that the thin films at prewetting transitions, which have zero thickness at $T=0$, will have increasing nonzero thicknesses as a function of T.

Substrates such as H_2, Ne, and Ar, which are less weak binding than the alkali metals, have received recent experimental interest [16-19]. The case of a H_2 substrate, quite near the wetting-nonwetting borderline, but falling on the wetting side, is of particular interest. Recent experiments show that ^{4}He in fact wets H_2 [18,19].

Note that the profiles of Fig. 1, in spite of the weakness of the substrate, possess considerable structure. We anticipate that this structure will be visible in third-sound measurements such as those of Maynard and Chan [20] and Shirron and Mochel [19].

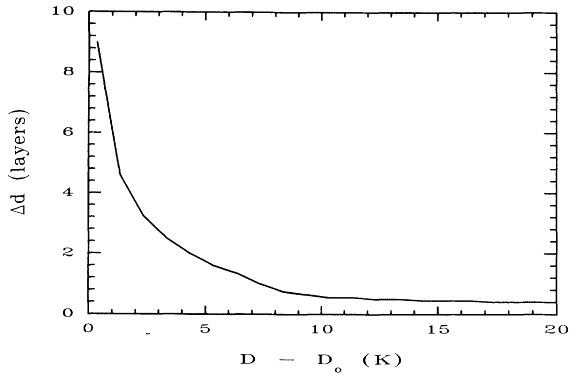

FIG. 3. The film-thickness jump Δd as a function of $D - D_0$ for $C_3 = 1000$, where $D_0 = 9.6$ K is the value of D at the wetting-nonwetting boundary.

In summary, with a density-functional model we have demonstrated new and interesting phenomena in the wetting behavior of liquid-^{4}He films on weak-binding substrates. Our phase diagram distinguishes two different phase regions: wetting (with prewetting) and nonwetting. ^{4}He films are predicted to be nonwetting on the alkali metals Cs, Rb, and K. Wetting with prewetting behavior is predicted on Li, Na, and solid H_2 surfaces. Note that the predicted prewetting jump of 5.25 layers on Na is rather large and should be readily observable. It must be borne in mind, however, that the detailed predictions for specific elements are subject to uncertainties in the values of the potential parameters (see Table I) used. These are in fact theoretical values, as there exist no experimental data pertinent to He adsorption on the alkali metals. Published theoretical values for D differ by as much as 50%, while those for C_3 differ by up to 10% [6]. Under these circumstances, our quantitative predictions for specific substrates, but not the qualitative trends, are somewhat uncertain. Indeed, interest in the adsorption potentials for He-alkali-metal systems provides motivation for further experimental study.

Behavior qualitatively similar to that of ^{4}He is expected for the heavier noble gases, but the interaction parameters are not well known. Indeed, there are experimental data [21] which have been interpreted [22] as implying that Xe and Ar do not wet potassium-coated Ni(100) but do wet the bare surface. Further, recent work [23] indicates that none of the heavier rare gases, Ne through Xe, wets Li, Na, or K-plated Ru(001), although they do wet bare Ru.

Results for nonzero temperatures would clearly be of interest, allowing, among other things, calculations of prewetting critical temperatures.

The results presented here are of great potential importance. If realized experimentally, they open a new and fascinating field involving not only wetting and prewetting transitions in ^{4}He films, but also the interplay of these transitions with superfluid onset [24]. Third sound would appear to be an ideal tool to probe this physics, especially that of prewetting transitions to films which undergo superfluid-onset transitions as a function of temperature.

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