RMP Colloquia

This section, offered as an experiment beginning in January 1992, contains short articles intended to describe recent research of interest to a broad audience of physicsts. It will concentrate on research at the frontiers of physics, especially on concepts able to link many different subfields of physics. Responsibility for its contents and readability rests with the Advisory Committee on Colloquia, U. Fano, chair, Robert Cahn, S. Freedman, P. Parker, C. J. Pethick, and D. L. Stein. Prospective authors are encouraged to communicate with Professor Fano or one of the members of this committee.

Novel wetting behavior in quantum films

E. Cheng

Department of Physics, The Ohio State University, Columbus, Ohio 43210
and Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802

M. W. Cole

Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802

J. Dupont-Roc

Laboratoire de Spectroscopie Hertzienne, Département de Physique de l'Ecole Normale Supérieure,
24 rue Lhomond, 75231 Paris CEDEX 05, France

W. F. Saam

Department of Physics, The Ohio State University, Columbus, Ohio 43210

J. Treiner

Division de Physique Théorique, Institut de Physique Nucléaire, F-91406 Orsay CEDEX, France

Theory and experiment have revealed that novel behavior occurs when a Cs surface is exposed to ^{4}He vapor. For temperature T below the wetting temperature ($T_w \simeq 2$ K), ^{4}He forms only a microscopically thin film as the vapor pressure P increases from zero to its saturated value. For intermediate values of T ($T_w \leq T \leq T_c \simeq 2.5$ K), the film thickness jumps discontinuously at a prewetting transition pressure $P_{pw}(T)$. For $P > P_{pw}$, and for all P if $T > T_c$, the film grows continuously to infinite thickness as saturation is approached. Microscopic theories of these phenomena are discussed in terms of the basic physics of electrons and atomic interactions. Initial experimental observations are summarized. Related phenomena of interest are described, including observation of prewetting with adsorbates other than He and substrates other than Cs.

CONTENTS

I. INTRODUCTION

Helium has proven to be an extraordinarily fascinating subject of study, not only for its own unique properties, such as superfluidity, but also for properties that transcend its niche in low-temperature physics, proving of broad interest in condensed matter physics and materials science. Among the latter are the critical phenomena associated with the λ-point, tricritical phenomena in ^{3}He-^{4}He mixtures, topological long-range order in films, and the roughening transition of the ^{4}He solid interface. Indeed, ^{4}He remains the only system in which the vanishing of crystalline facets and associated dynamical phenomena can be studied with precision and detail. Very recently another intriguing example has been added to this list, that of a *wetting* transition with its associated line of *prewetting* transitions, where the film thickness undergoes finite jumps. Our colloquium focuses on this latter paradigm.

It has come as a major surprise to the low-temperature physics community that superfluid ^{4}He, long thought to be the "universal wetting agent" (Goodstein, 1975, p. 327), does *not* wet all substances. In a classic experiment (Wilks, 1967), a generic beaker is observed to empty itself of ^{4}He via a superfluid film flow up and over its walls; the surprise is that a Cs beaker will not. The subtle reason is that though *all* materials have stronger long-range (van der Waals) attractions for ^{4}He atoms than ^{4}He atoms have for themselves, this is not the sole criterion determining wetting. The repulsive cores of interparticle potentials have to be sufficiently small to allow the potential well to become sufficiently deep. This is illustrated in Fig. 1, which compares the potential acting on a ^{4}He atom above a Cs substrate to that for the same atom above a liquid ^{4}He "substrate." The outer electrons of Cs are very weakly bound, giving rise to an unusually-long-range repulsion for the He atom. The key physical point needed to understand the recent discoveries is the *difference* between the curves of Fig. 1. A single He *atom* would rather "sit" near a He surface than a Cs surface. As we shall see below, however, at sufficiently high temperature, a *thick film* of He can exist. Indeed a kind of phase-transition behavior can occur which had not been seen previously for *any* adsorption system. Why and how this happens is the subject of our discussion.

Wetting and nonwetting[1] are most commonly visualized in terms of a liquid droplet on a substrate under conditions of bulk liquid/vapor coexistence. Let σ_{ab} be the interfacial tension of an *a*-*b* interface and the subscripts *s*, *l*, and *v* refer to substrate, liquid, and vapor, respectively. Then the force balance shown in Fig. 2 leads to Young's equation,

$$\sigma_{sv}=\sigma_{lv}\cos\theta+\sigma_{sl} \ , \tag{1.1}$$

relating the contact angle θ to the interfacial tensions. Wetting, sometimes called "complete wetting," occurs when $\theta=0$, resulting in a coverage of the substrate by a macroscopically thick film. Nonwetting ($\theta\neq 0$), sometimes called "partial wetting," means that only a finite film, often microscopic, covers the surface, possibly coexisting with a drop of bulk liquid; see Fig. 2. Now consider a surface that is exposed to a gas at pressure P. If the gas is ideal, its chemical potential is (Landau and Lifshitz, 1969)

$$\mu=k_BT\ln(P/P_0)+\mu_0(T) \ , \tag{1.2}$$

where μ_0 and P_0 are those values at which bulk liquid and vapor coexist at the temperature T. An important property that the coexisting film must have in equilibrium is that its chemical potential be equal to that of the vapor. Then the question we consider is: how does the film's thickness vary as P is increased between zero and P_0? A convenient framework for the discussion makes use of the surface grand free energy σ_s (Landau and Lifshitz, 1969). We define σ_s in terms of the corresponding Helmholtz free energy per unit area $f_s(T,n_s)$ of the film as the minimum of

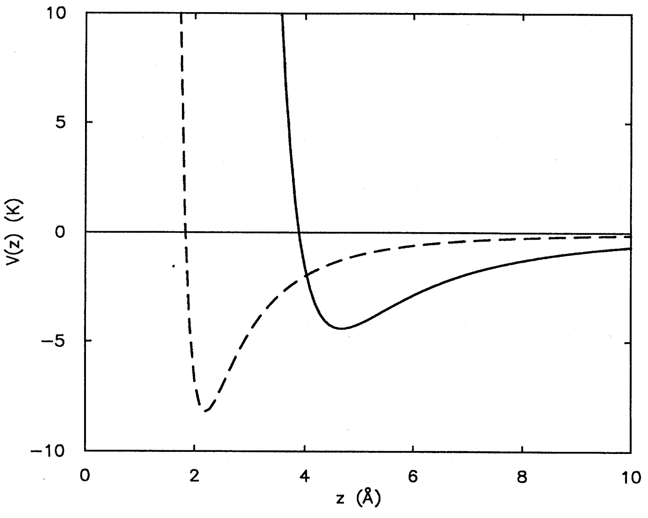


FIG. 1. Interaction potentials for a ^{4}He atom above a Cs substrate (solid curve) and above a liquid ^{4}He "substrate" (dashed curve).

$$\sigma_s(T,\mu,n_s)=f_s(T,n_s)-\mu n_s \tag{1.3}$$

over the coverage n_s (number of particles per unit area). Let us consider the specific case $\mu=\mu_0(T)$. There is always a local minimum at $n_s=\infty$ due to the van der Waals attraction of the substrate. If this is the global minimum of σ_s, one has wetting (infinite coverage). Otherwise one has nonwetting (finite coverage). Figure 3 shows typical wetting and nonwetting cases. A *wetting transition* would occur if, upon varying T, the minimum of σ_s jumped from a finite value of n_s to $n_s=\infty$. In other terms,

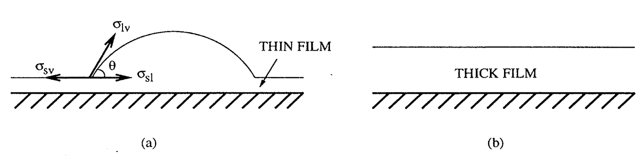
$$\sigma_s(T,\mu_0,\infty)=\sigma_{sl}+\sigma_{lv} \ , \tag{1.4}$$

while σ_s at the small n_s minimum is just σ_{sv}. The condition for nonwetting is then

$$\sigma_{sl}+\sigma_{lv}>\sigma_{sv} \ , \tag{1.5}$$

in agreement with Eq. (1.1). At the wetting transition there is an infinite jump in n_s.

When attractive long-range forces, such as van der Waals forces, are dominant, the wetting transition is expected to be first order and accompanied by a line of *prewetting transitions* (Ebner and Saam, 1977, 1987; Cahn, 1977). A prewetting transition is simply a wetting



(a) (b)

FIG. 2. Droplet on a substrate showing the surface tension forces, in the cases of (a) nonwetting and (b) wetting. The pressure is at its saturated value P_0.

---

[1] Recent reviews are those of Dietrich (1988) and Schick (1990).

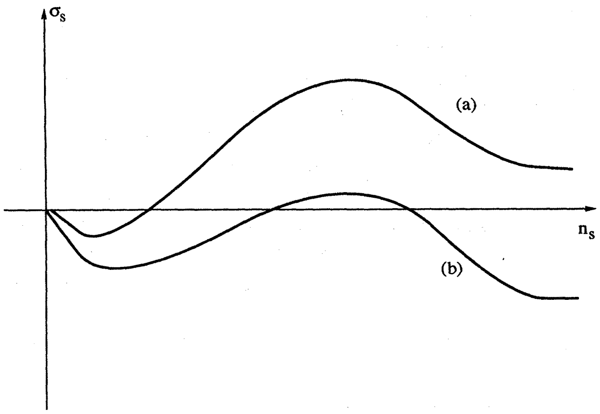


FIG. 3. Typical curves showing $\sigma_s(T,\mu_0,n_s)$ vs n_s at coexistence ($\mu=\mu_0$). Curves (a) and (b) are for nonwetting and wetting, respectively. A wetting transition occurs if variation in T causes curve (a) to evolve into curve (b) so that the minimum jumps from a finite to an infinite value of n_s.

transition continued off of coexistence ($P<P_0$). To see this, write Eq. (1.3) as

$$\sigma_s(T,\mu,n_s)=\sigma_s(T,\mu_0,n_s)-n_s\Delta\mu\ , \tag{1.6}$$

where $\Delta\mu=\mu-\mu_0$. Off of coexistence $\Delta\mu<0$ [from Eq. (1.2)], and the minimum at $n_s=\infty$ in curve (b) of Fig. 3 is shifted to finite n_s, as illustrated in Fig. 4. Sufficiently negative $\Delta\mu$ will lift the large-n_s minimum above that at small n_s, and there will be a discontinuous jump in n_s, signaling a prewetting transition, when the minima cross at a value of $\Delta\mu=\Delta\mu(T)$ depending on T. At sufficiently large T, the size of the jump in n_s will vanish, at a prewetting critical point. The recent excitement in this field is associated with the fact that the wetting transition and the first evidence of prewetting have now been observed in ^{4}He films (Ketola, Wang, and Hallock, 1992; Taborek and Rutledge, 1992; Rutledge and Taborek, 1992).

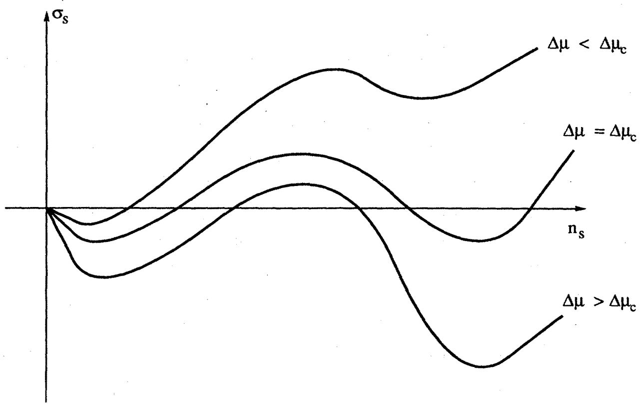


FIG. 4. Curves of σ_s, defined in Eq. (1.4), vs coverage n_s at fixed T and variable $\Delta\mu=\mu-\mu_0$. The top curve (low vapor pressure) possesses a minimum at small n_s, while the bottom curve (high P) has its minimum at large n_s. The middle curve corresponds to the value of μ at which the prewetting jump in coverage occurs.

This paper is organized as follows. Section II discusses why the alkali metals are (surprisingly) *inert* surfaces for He adsorption. Section III presents a "back of the envelope" calculation, along with a more accurate calculation, of the energetics of the energetics of He adsorption; the new transitions were predicted by these methods (Cheng *et al.*, 1991, 1992; Saam *et al.*, 1992). Section IV discusses the experimental situation. Section V describes a variety of other explorations, which are either in progress or worth pursuing.

II. INTERACTION POTENTIALS

Predictions of wetting phenomena require a knowledge of the relevant interaction potentials. This includes both the gas-surface and gas-gas interactions. While the latter are known rather well (Aziz, 1984), in the case of the inert gases pertinent to physical adsorption the adsorption potential is not adequately known in many cases (Bruch, 1983; Vidali *et al.*, 1991). Although He provides the most studied and best understood adsorption interactions, we are still lacking information about potentials on weak-binding surfaces, which is the domain of greatest relevance to the present paper. We emphasize one point: He binding to *most* surfaces is characterized by a well depth D of order 5 to 10 meV (60 to 120 K), which sounds "small." The phenomena discussed here involve values of D that are *even smaller,* by a factor of 10! This means that D is comparable to $-\mu_0=7.2$ K$=0.62$ meV, the cohesive energy per atom of liquid ^{4}He. It is the similarity of the values of D, $|\mu_0|$, and k_BT that gives rise to the special behavior we are describing.

We restrict our discussion to potentials that depend only on the z coordinate normal to the surface. This leaves out the possibility of epitaxial effects, which we believe to be unimportant in the cases described here.[2] Our potential is assumed to take the simple two-parameter form

$$V(z)=\frac{4C_3^3}{27D^2z^9}-\frac{C_3}{z^3}\ , \tag{2.1}$$

which involves the coefficient C_3 of the long-range (van der Waals) gas-surface interaction, the value of which is known to within about 15%.

This leaves as a principal difficulty the calculation or measurement of the well depth D. The traditional means of this determination is an adsorption isotherm, i.e., measuring $n_s(P)$ at fixed T. For the case of He, H_2, and sometimes Ne, molecular-beam scattering provides par-

---

[2] In the present case, the adatom's equilibrium distance is so far from the top layer of the solid that the atom feels only weak corrugation effects.

ticularly detailed information about the potential (Celli, 1992). On the theoretical side, there exists a huge literature, including both *ab initio* and semiempirical methods. We address the theory of $V(z)$ below, after first describing the general trends observed in the cumulative database.

Perhaps the most interesting fact is that there exists a simple empirical relation between a few quantities (Ihm *et al.*, 1987):

$$D = bC_3/z_{\rm eq}^3 \ . \tag{2.2}$$

Here the constant b is about 1.7 and $z_{\rm eq}$ is the equilibrium distance in the adsorption potential, measured from the image plane of the substrate. This universal relation can be understood in terms of a corresponding states "law" associated with adsorption potentials. Of course, knowing this relation does not help us to compute D unless we know $z_{\rm eq}$! Nevertheless, we will find that it is helpful in understanding why some D values are very small.

It has long been realized that there exists a basically repulsive short-range interaction between a He (or other closed-shell) atom and an incident electron (Rama Krishna and Whaley, 1988). This is due to the Pauli principle, which requires orthogonalization of the wave functions of the external electron and the valence orbitals of the He atom. A rapidly varying electronic wave function ensues; this is equivalent to a high kinetic energy and a repulsive interaction.

This repulsion has interesting consequences for electrons near or inside liquid He. Above the free surface, for example, an electron feels an attractive "image" force pulling it toward the surface. When it arrives at the liquid-vapor interface, it encounters instead a very high barrier, due to the short-ranged repulsion provided by each of the atoms. The net potential has a minimum just outside the interface, resulting in a hydrogenic spectrum of bound states (Leiderer, 1992). Suppose instead that a high-energy electron is injected into the liquid (or is created within it by a radioactive decay process). Not realizing that its absolute minimum in potential energy lies just outside the liquid, the electron ingeniously makes its own surface by repelling the atoms from a spherical cavity around it. The large size (20 Å) of this bubble is dramatic evidence of the electron-He repulsion (Hernandez, 1991).

Returning to our original problem, the He-surface interaction, we encounter an analogous fact: electrons sticking out of a solid surface repel any He atom located there. Indeed, the lowest-order approximation to the potential energy of the atom immersed at position $\mathbf{r}$ among these electrons,

$$V_{\rm rep}(\mathbf{r}) = 2\pi n(\mathbf{r}) a\hbar^2/m = 4\pi[n(\mathbf{r})a^3][\hbar^2/(2ma^2)] \ , \tag{2.3}$$

is precisely the same expression used to characterize the energy of an electron injected into a gas of atoms (Fermi, 1934); in either case, $n(\mathbf{r})$ represents the local density of the medium in which the particle resides. When Eq. (2.3) is evaluated in terms of an effective electron-He scattering length ($a = 0.7$ Å, from Cole and Toigo, 1985), we find that the atom experiences a repulsive energy of order 1 meV when the electron density provided by the surface is of order $10^{-4}/\text{Å}^3$. This is a very low density, present typically at distances of order 3–4 Å above the top ionic layer. It is therefore at such distances that the repulsion becomes comparable to the attraction, so that equilibrium occurs.

This brings us to an explanation of why the alkali-metal surface provides a small binding energy for He atoms: the alkali surface has a particularly small work function. Thus the conduction electrons' wave functions extend far out into the vacuum region. Because of the associated repulsion, the He atom is unable to approach close to the metal's surface in order to exploit the z^{-3} attraction. The resulting equilibrium distances are large, typically greater than 5 Å. The simple relation (2.2) then tells us that the well depth D is small (Ihm *et al.* 1990); see Fig. 5.[3]

A variety of theoretical methods has been applied to the problem of calculating He-surface potentials. The most reliable use a convenient relation (Zaremba and Kohn, 1977),

$$V_{\rm rep} = \sum_k \delta E_k \ , \tag{2.4}$$

between the energy shift of individual substrate electrons (δE_k) and the net repulsive potential $V_{\rm rep}$ felt by the He atom. This repulsion is supplemented by a van der Waals attraction, the second term in Eq. (2.1). Such a separation of the two parts of the potential may not be rigorously justified, but is virtually always used. There are further complications: it is important to know where to put the "image plane," i.e., the origin for distance in the attractive potential. This is known only for the case of the jellium model of the surface, an abruptly terminated continuum of uniform charge, designed to mimic the ions. This model is also used to calculate $V_{\rm rep}$ (with unknown uncertainty!). Finally, there is some controversy about how to handle "damping" and higher-order dispersion terms. Damping is an attempt, usually semiempirical, to modify the asymptotic expression (z^{-3}) for the dispersion energy so that it can be applied at close approach. The higher-order dispersion terms can be rigorously derived at large distance, but they too are not known reliably at the equilibrium position.

These uncertainties in the theory must be borne in mind when predictions are made which incorporate these potentials in the statistical mechanics of adsorption. The uncertainty, especially in D, is particularly acute when

---

[3] A similar argument applies to the He two-body interaction with alkali atoms for which the well depth is also very small (Scoles, 1990).

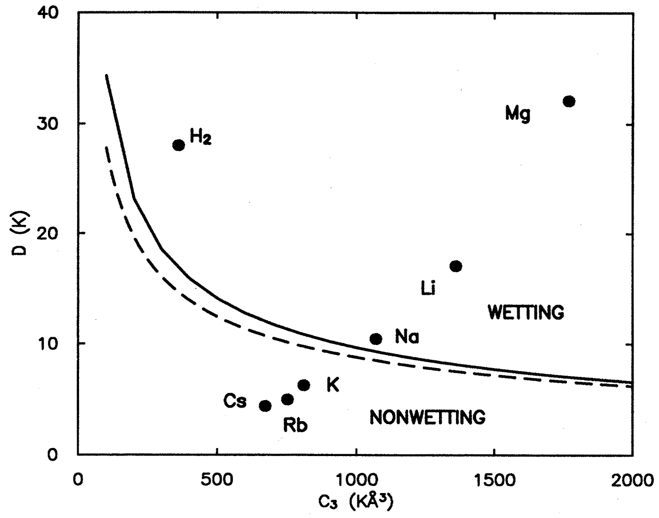


FIG. 5. Phase diagram for ^{4}He adsorption on weak-binding substrates. Each point corresponds to a substrate potential characterized by a well depth D and van der Waals coefficient C_3; numerical values are given by Cheng, Cole, Saam, and Treiner (1992). Estimated uncertainties are 30% and 10%, respectively. The solid curve is the wetting-nonwetting boundary predicted by the nonlocal density-functional theory, while the dot-dashed curve uses the simple estimate of Eq. (3.4).

dealing with the alkali surface case, which until recently had received little attention experimentally. Indeed, it is perhaps amusing that such a complex phenomenon as wetting can provide the first experimental information about the single atom's adsorption potential.

III. ADSORPTION THEORY

A. Zero temperature

We begin our discussion of the theory of He adsorption at temperature $T=0$ (Cheng *et al.*, 1991, 1992). We first present a *simple* model designed to predict which surfaces will be wet by He. Then we address the more general problem of film structure using a more realistic, albeit complicated, model. The simple model begins with the approximation

$$\sigma_{sl} \simeq \sigma_{sv} + \tilde{\sigma}_{sl} + \rho_0 \int_{z_{\rm eq}}^{\infty} V(z)dz \ , \tag{3.1}$$

where σ_{sv} is the cost of creating the substrate-vacuum interface, $\tilde{\sigma}_{sl}$ is the cost of forcing the liquid density to vanish at the substrate, and the last term on the right is the gain provided by the substrate attraction to the liquid. The latter is estimated by assuming that the liquid density has its bulk value ρ_0 for distance z greater than $z_{\rm eq}$, the potential-energy minimum.

Then the approximate wetting criterion based on Eq. (1.5) is

$$\tilde{\sigma}_{sl} + \sigma_{lv} + \rho_0 \int_{z_{\rm eq}}^{\infty} V(z)dz \le 0 \ . \tag{3.2}$$

We make one further approximation; that is to estimate $\tilde{\sigma}_{sl} \simeq \sigma_{lv}$. This means that the energy cost of the liquid's nonuniform density near the substrate is similar to that of the bulk liquid/vapor interface. This estimate is good for weakly attractive substrates. Then using the model potential (2.1), we see that the wetting condition becomes

$$(C_3 D^2)^{1/3} \ge 3.33 \sigma_{lv}/\rho_0 \ . \tag{3.3}$$

This result divides the domain of interaction parameters into two distinct regions, shown in Fig. 5. Substrates having parameter values above the dot-dashed curve are predicted by our simple model to be wet by ^{4}He at $T=0$. Note[4] that the heavy alkali metals are unique in being predicted to be nonwetting surfaces for He.

Equation (3.3) is based on a plausible, but approximate, description of the energetics. To improve upon this, as well as to predict other film properties, is a nontrivial task. Alternative strategies can be pursued. One strategy is to obtain "exact" results. The possibility of an exact solution to the problem is realized by the Green's function Monte Carlo method, but this has proved feasible thus far only for systems consisting of small numbers of particles, periodically reproduced (Whitlock *et al.*, 1988). Similar numerical limitations pertain to the path-integral Monte Carlo method (Pollock and Ceperley, 1987; Wagner and Ceperley, 1992). Film structures have been computed within the "hypernetted chain" approximation by Krotscheck (1985a, 1985b). The variational method has also been applied to this problem, yielding a rigorous upper bound to the domain of parameter space such that *no* adsorption occurs (Carraro and Cole, 1992a, 1992b).

Another approach to predicting film structure is to use a phenomenological density functional.[5] The method sacrifices much of the detailed information embodied in the exact wave function. Instead it focuses on the most important physical variables and is designed to be consistent with the pertinent properties of helium.

Our group used a density-functional method (Dupont-Roc *et al.*, 1990), which properly describes (a) the bulk fluid equation of state, (b) the liquid-vapor interfacial structure, and (c) the function describing the fluid's response to short-wavelength perturbations. The energy

---

[4] Interestingly (and perhaps surprisingly) ^{3}He films are predicted to wet *all* surfaces, even though an individual ^{3}He atom is less strongly bound than a ^{4}He atom is to any surface (because of zero-point motion). See Carraro and Cole (1992a) and Cheng *et al.* (1992).

[5] The general derivation of the density-functional method appears in Hohenberg and Kohn (1964). The present authors used the method of Dupont-Roc *et al.* (1990). Other models have been proposed by Ji and Wortis (1986) and by Ebner and Saam (1975).

is taken to be a functional of the density $\rho(\mathbf{r})$ above the surface:

$$\begin{aligned} E[\rho]=&\frac{\hbar^2}{2m}\int[\nabla\rho^{1/2}(\mathbf{r})]^2 d\mathbf{r}\\ &+\frac{1}{2}\int\rho(\mathbf{r})\rho(\mathbf{r}')V_l(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}\,d\mathbf{r}'\\ &+\frac{c}{2}\int\rho(\mathbf{r})\bar{\rho}(\mathbf{r})^{1+\gamma}d\mathbf{r}+\int\rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}\ . \end{aligned} \tag{3.4}$$

The first term on the right hand side is a quantum-kinetic energy; m is the atomic mass. The next two terms represent the He-He potential energy, involving a screened pair potential V_l and a spatially averaged density $\bar{\rho}(\mathbf{r})$. The last term is the interaction with the substrate. This functional contains three parameters, fit to the experimental energy, density, and compressibility of bulk helium at equilibrium at $T=0$.

The procedure used is now conceptually straightforward. At $T=0$ and fixed μ, we minimize the function σ_s of Eq. (1.3) with respect to variations in $\rho(\mathbf{r})$. If A is the surface area and $n_s=\int\rho(r)d\mathbf{r}$,

$$\sigma_s=E[\rho]/A-\mu n_s\ . \tag{3.5}$$

From the minimization one gets n_s as a function of μ. This relation can be inverted and allows one to express σ_s as

$$\sigma_s=\int_0^{n_s}[\mu(n)-\mu(n_s)]dn\ . \tag{3.6}$$

We include no dependence on the surface-parallel variables x and y, since none is present in the substrate potential and we do not expect two-dimensional crystallization of the helium in the weak-binding cases considered here. Such crystallization occurs only when helium is highly compressed, i.e., on strongly attractive substrates.[6]

Some results for the density profiles and chemical potential are shown in Figs. 6 and 7. Note the dramatic difference in compression of the films on graphite, an ultra-attractive substrate ($D\sim190$ K) on which solid layers exist (Lauter *et al.*, 1987), and Na, a relatively inert substrate ($D\sim10$ K) on which He is expected to remain liquid (Cheng, Ihm, and Cole, 1989; Cheng, Cole, *et al.*, 1992). The layered structure is reflected in the shape of the curves $\mu(n_s)$ of Fig. 7. On graphite, two well-defined plateaus indicate that the first two layers are formed, each at almost constant μ. The variations get smoother for subsequent layers, as for Mg and Na: the layers tend to lose their individuality, but the liquid is still inhomogeneous. This has consequences for the velocity of third sound c_3, given by $mc_3^2=n_s\,d\mu/dn$. Third sound is a surface wave (ripplon) of a He film. Because of the layering, c_3 exhibits oscillations with a one-layer periodicity (see Cheng, Cole, Saam, and Treiner, 1993).

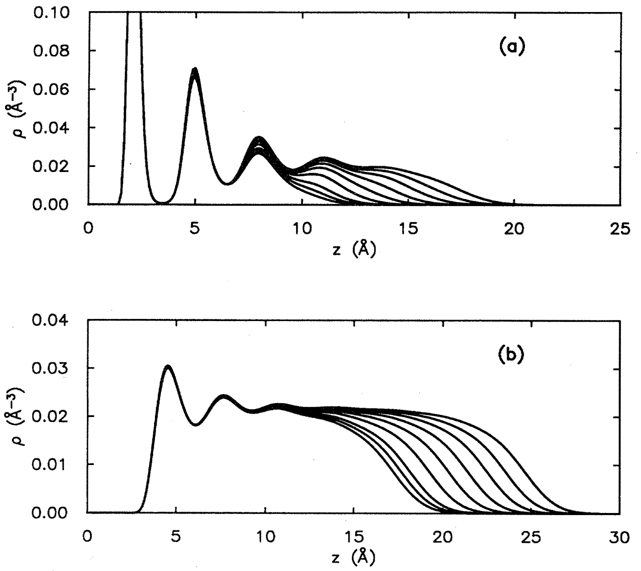


FIG. 6. Density profiles computed for helium on (a) graphite and (b) Na. The various film coverages shown are 0.294, 0.305, 0.329, 0.353, 0.377, 0.401, 0.424, and 0.448 Å^{-2}. From Cheng *et al.* (1992).

Another remarkable feature of the curves $\mu(n_s)$ is that all start with a negative slope near $n_s=0$. This implies, from Eq. (3.6), that σ_s is positive for small coverage and that thin films are thermodynamically unstable. For each substrate, through a Maxwell construction, one can determine the thickness of the smallest stable film, which is also the value for which the free energy of the film σ_s crosses zero. In the case of a strongly attractive substrate, this smallest film will be a submonolayer film, i.e., a quasi-two-dimensional system. As 2D helium at $T=0$ is a liquid, the minimum coverage will be close to the 2D

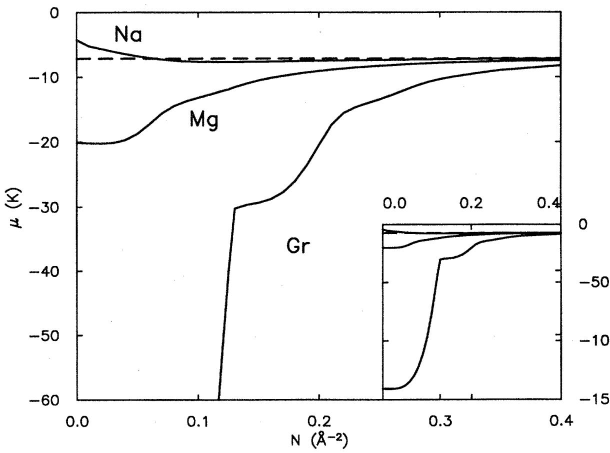


FIG. 7. The chemical potential μ as a function of film coverage for ^{4}He on graphite (Gr), Na, and Mg.

---

[6] "Strongly" here means well depth $D\gtrsim30$ K. See Cheng, Ihm, and Cole (1989), Cheng, Cole, Saam, and Treiner (1992), and Lauter *et al.* (1987).

equilibrium density.[7] That is, even a few He atoms on a graphite surface will automatically condense to this density at $T=0$. More novel, and at first sight surprising, is the existence of a very broad minimum in Fig. 7 for μ of Na at much higher coverage. This means that the smallest film on Na will be a multilayer film—about five layers. Indeed, this jump from zero thickness to a finite value is the form taken by the prewetting transition for helium at $T=0$, as discussed in more detail below. The physical origin of this large jump can be understood in simple terms. In the case of a weak substrate, the film must be thick enough so that the potential energy of attraction provided by the substrate is sufficient to justify paying the price in surface tension at two interfaces; see Eq. (3.2).

B. The wetting transition and prewetting at $T>0$

Consider a case, e.g., Cs, in which there is no wetting at $T=0$, and define the spreading coefficient

$$S(T)=\sigma_{sv}(T)-\sigma_{sl}(T)-\sigma_{lv}(T)\ . \tag{3.7}$$

Nonwetting persists at finite temperature as long as $S(T)<0$. A wetting transition occurs at T_w if thermal excitations lower the film's free energy to the point where $S(T_w)=0$. The modes with the most important T dependence are excitations at the liquid-vapor free surface, so that neglecting the temperature dependence of $\sigma_{sl}(T)$ and $\sigma_{sv}(T)$ gives the condition (Cheng, Cole, *et al.*, 1992)

$$\sigma_{lv}(T_w)-\sigma_{lv}(0)\simeq S(0) \tag{3.8}$$

determining T_w. Experimental values of $\sigma_{lv}(T)$ (Ikushima, Jino, and Suzuki, 1986) and the calculated $S(0)$ within the simple approximation of Eq. (3.1) yield an approximate value for T_w which depends upon D and C_3. Agreement (Saam *et al.*, 1992) with the experimental value $T_w=1.95$ K is found for a value $D=8.6$ K for Cs, about twice as large as theoretical estimates (Zaremba and Kohn, 1977; Chizmeshya, and Zaremba, 1989). From the wetting point at coexistence emerges a prewetting line, whose form, near T_w, can be determined using the appropriate Clausius-Clapeyron equation. The result is shown in Fig. 8(a), where the prewetting critical-point temperature $T_c=2.5$ K has been taken from experiment (Rutledge and Taborek, 1992). As noted earlier, when there is $T=0$ wetting, there is a thin-to-thick film transition as coexistence is approached. We expect a line of such transitions to extend for $T>0$ up to a critical point C, as shown in Fig. 8(b), which refers to ^{4}He on a solid H_2 substrate (Saam *et al.*, 1992).

The line PW-C of Fig. 8(b) is not the conventional line of thin-to-thick film transition terminating in a thermally driven first-order wetting transition such as that of Fig. 8(a). However, since the point PW is on a line of $T=0$ thin-thick transitions terminating in a first-order wetting transition traced out by varying D, it seems natural to generalize conventional terminology slightly and call PW-C (a segment of) a prewetting line; see Fig. 9. The $T=0$ segment of this line could be explored with experiments on alloys of Cs with other alkali metals, e.g., Rb, which are wet by ^{4}He

IV. EXPERIMENTS

The possibility of finding substrates that are not wetted by liquid helium has attracted much interest among ex-

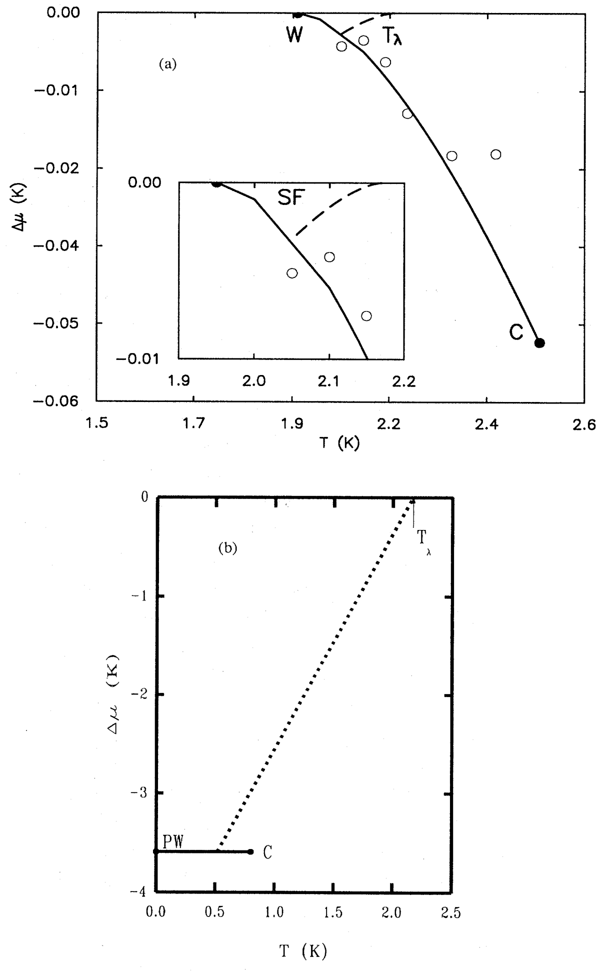


FIG. 8. Prewetting transition lines for ^{4}He on Cs and on H_2: (a) Phase diagram of ^{4}He on Cs, showing the prewetting transition line (solid) connecting the wetting transition W with the prewetting critical point C, and the superfluid transition line (dashed). The open circles are the data of Rutledge and Taborek (1992). (b) Phase diagram for ^{4}He on H_2 showing the prewetting transition line (solid) connecting $T=0$ prewetting transition PW with the prewetting critical point C, and the superfluid transition line (dashed).

---

[7] See Whitlock *et al.* (1988) concerning the 2D liquid. In the strong-binding case, $|\mu|$ is the sum of a binding energy to the substrate plus a 2D cohesive energy ($\simeq 0.8$ K/atom).

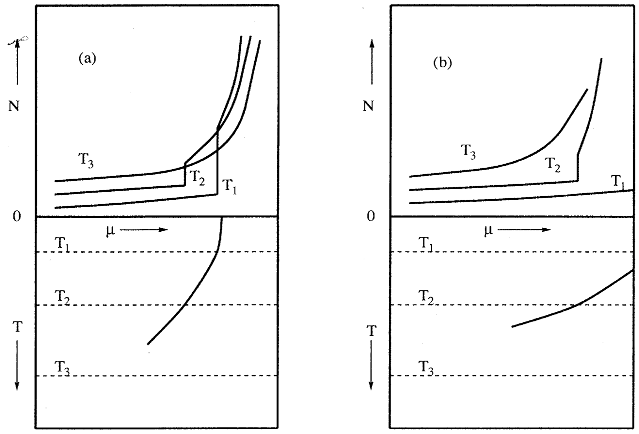


FIG. 9. Chemical potential, coverage, and temperature schematically shown in the cases of wetting temperature (a) $T_w=0$ and (b) $T_w \neq 0$. These are exemplified by He on Rb and Cs, respectively.

perimentalists. Several experiments have been set up to test the predictions (Cheng *et al.*, 1991) of unusual wetting properties of alkali-metal substrates, with the hope of observing first-order wetting transitions and the prewetting diagram for helium on those surfaces. Uncertainties have remained, however. Difficulties were anticipated and found in producing clean and smooth alkali-metal surfaces. The high reactivity of alkali metals with oxygen and water can easily result in oxidized surfaces. In that case, the surface would be much more binding for helium and could become wetted. Also the ability to produce flat or at least smooth surfaces with alkali metals has not yet been established, and it has been noted that rough substrates favor wetting (Robbins *et al.*, 1991). Hence experimental biases exist which could produce a wetted surface from an ideally nonwetted material.

One standard method of measuring the coverage of a surface with adsorbed material is the quartz microbalance. A thin disc of a quartz crystal is made to oscillate in a shear mode by applying an rf voltage across it at a frequency corresponding to one of its eigenfrequencies. For carefully designed crystals, these frequencies are well defined, with very high Q (more than 10^5). The loading of the disc by a fraction of an atomic layer may be detected by a change in the frequency.[8] For detecting helium films at low temperatures, one can also take advantage of the superfluidity of liquid ^{4}He. Superfluidity ensures very efficient transport mechanisms, which originate from the frictionless motion of the superfluid component of the film. This gives rise to phenomena that do not exist for nonsuperfluid films. For example, temperature waves, called third sound, can be propagated along such a film. Significant heat flux can also be transferred by a film without a significant temperature gradient. For most situations studied up to now, nonwetting substrates are expected to be covered by films too thin to be superfluid. Thus a change from a nonsuperfluid film to a superfluid one is expected to accompany the wetting or prewetting transitions on weak-binding substrates. Hence third sound or heat transport can be used to reveal the existence or the absence of thick wetting or prewetting films. Finally, adsorption isotherm measurements by standard thermodynamic methods are feasible probes of film wetting behavior.

Among alkali metals, cesium is predicted to be the least binding for helium and thus the most likely to be nonwetting. Figure 10 shows experimental evidence for nonwetting obtained by the heat transport method (Nacher and Dupont-Roc, 1991; Bigelow *et al.*, 1992). A pyrex tube containing a sufficient amount of helium has been cooled down to 1.18 K, below the saturation temperature (about 1.75 K for that sample). A small puddle of liquid lies at the bottom of the cell. Above the surface of the liquid, a thick saturated film covers all wetted surfaces. Its thickness is determined by equilibrium involving the gravitational energy with respect to the puddle's surface and the negative potential energy due to the van der Waals attraction by the wall. At 10 cm above the liquid surface, a typical thickness is 30 layers of helium, much larger than the 2 or 3 layers required to have a superfluid film at 1.18 K. The inner surface of the middle of the tube is covered with cesium metal. To determine whether its surface is covered by a thick wetting film of helium, heat is made to flow along the tube. In the re-

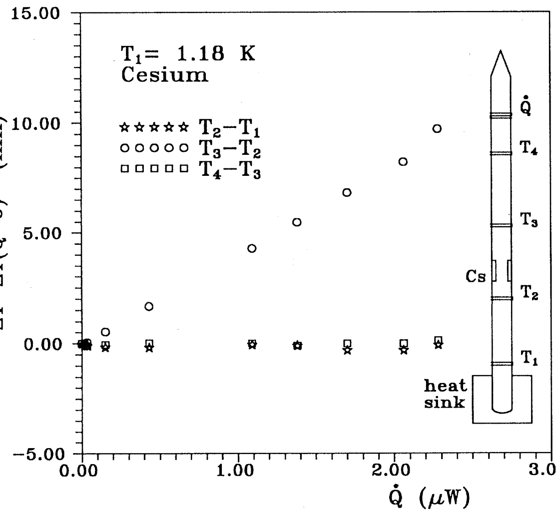


FIG. 10. Evidence for resistive heat transport along a Cs surface revealing the absence of a wetting superfluid film, as discussed in the text. In contrast, adjacent glass surfaces are covered with thick He films, insuring superfluid heat transport with negligible thermal gradients. Thermometer offsets at heat flux $Q=0$ are subtracted out.

---

[8] In fact, the loading is not complete for a liquid, and corrections are needed to derive the coverage from the measured loading. See Fozoni (1985).

gions where a superfluid film exists, it transports heat very efficiently. No temperature gradients show up in these regions, monitored by thermometer pairs (1, 2) and (3, 4). In contrast, a temperature difference arises across the central region (between thermometers 2 and 3), where the cesium ring is located. This shows the absence of a thick superfluid film on the cesium surface and reveals a nonwetted situation. Similar characteristics were found in the entire temperature range below 1.73 K, suggesting that the wetting temperature for helium on cesium is higher than this temperature.

Adsorption isotherm data were found to be consistent with this result (Mukherjee *et al.*, 1992). The experiment consisted of measuring film coverage on a porous graphite medium, which had been preplated with Cs. The results were indicative of little or no He adsorption at low temperature.

While nonwetted at low temperature, the cesium surface is expected to become wetted at some higher temperature, bounded by the critical temperature of helium; see Eq. (3.8). Using the quartz microbalance method, Taborek and Rutledge (1992) indeed found at 2.7 K film thicknesses comparable to those on gold. Thus the cesium surface appears wetted at that temperature. In their more recent work, they located the wetting temperature around 1.95 K. They observed the wetting transition as a rapid increase in the coverage of the surface when the temperature is swept through 1.95 K, starting with a nonwetted surface at low temperature under saturated conditions; see Fig. 11. This is the first time that a wetting transition has been observed with helium.

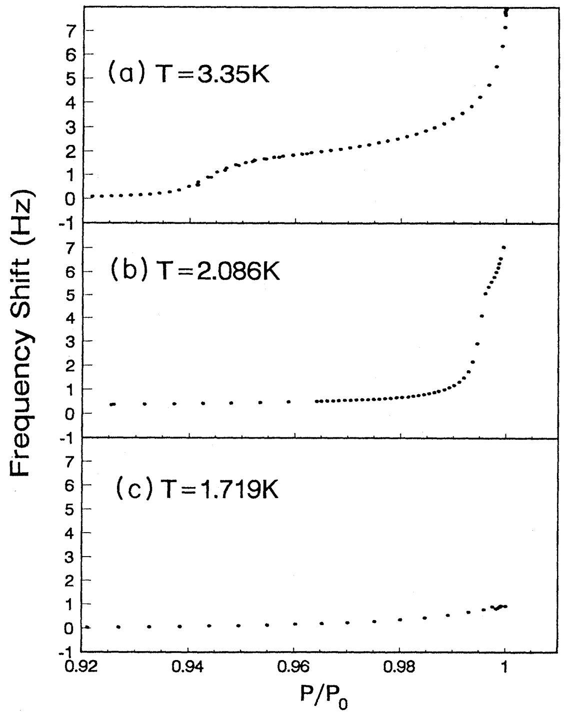


FIG. 11. Frequency shift measured for helium adsorbed on a cesium surface. The shift, which is proportional to the mass loading by the helium, is shown as a function of pressure relative to the saturation pressure $P_0(T)$ for three different temperatures. At (a) high T, the film wets the surface, i.e., the coverage increases smoothly to infinity. The shoulder at $P/P_0=0.945$ is a precursor to prewetting, which happens at lower T. At (b), intermediate T, a prewetting transition occurs at $P/P_0=0.995$, i.e., the film thickens discontinuously at a particular value of the pressure. At (c), low T, the film does not wet the surface. From Rutledge and Taborek (1992), with permission.

Detailed study of the prewetting transition on cesium has been reported by Rutledge and Taborek (1992). They observed a step in the adsorption isotherms for temperatures ranging from 1.95 K up to 2.5 K. The step is somewhat smeared, as shown in Fig. 11, presumably due to substrate inhomogeneity. The smearing increases substantially above 2.5 K, which is tentatively identified as the prewetting critical point. Figure 8 displays the phase diagram deduced from these data.

Other indications of prewetting transitions have also been found (Shirron and Mochel, 1991; Ketola *et al.*, 1992). While their cesium surface is wetted by a helium film at saturation, Ketola *et al.*,[9] found that third-sound pulses do not propagate over the cesium surface far from coexistence. Propagation reappears suddenly when the chemical potential approaches saturation within 15 mK, presumably because of a transition from a thin nonsuperfluid film to a thick superfluid film. Adsorption isotherm measurements of He on H_2 substrates, reported by Shirron and Mochel (1991), show sharp rises at low pressure which could be consistent with prewetting predictions at $T=0$.

Up to now cesium is the only substance whose surface has been demonstrated to be nonwetted by liquid helium. Rubidium has been found (Bigelow *et al.*, 1992; Mistura and Chan, 1993) to be wetted down to 0.8 K and transitions to thin coverages have been observed only off saturation, as prewetting transitions. Extrapolation of the prewetting line at $T=0$ could give indication of the wetting situation at zero temperature. Study of this transition is evidently of current interest.

We may summarize the experimental situation as follows. The Cs data are qualitatively, but not quantitatively, consistent with the theory of Cheng, Cole, *et al.* (1991, 1992). The wetting temperature is much lower than expected on the basis of Eq. (3.8). Hypothetical explanations of the discrepancy have included the possibility (Saam *et al.*, 1992) that D is substantially (4 K) greater than theory predicts or (Cole, Swift, and Toigo, 1992) that the adsorption process leads to a reduced substrate phonon zero-point energy, which was left out of the original theory. Either or both of these hypotheses may explain the Rb data. It is premature to draw a conclusion.

---

[9] At their temperature, 1.38 K, this wetting is at variance with others' findings of nonwetting. The difference is tentatively attributed to substrate roughness.

Further data for other alkali metals will help to clarify these issues.

V. FUTURE PROSPECTS

This paper has reviewed progress to date; what remains to be explored and explained? The answer can be divided into two categories of study:

1. New systems to be explored.
2. Improved experiment and theory for He on the alkalis.

As to the first of these, it ought to be noted that weak or negligible inert-gas adsorption on the alkalis was first reported long ago by Pierotti and Halsey (1959). Similar results have been seen quite recently for these classical systems and H_2.[10] There remain to be addressed many questions concerning the theory of these phenomena. As for He, good potentials are crucial for quantitative prediction, and these are lacking at present. We would expect to see prewetting phenomena for classical systems also.

Concerning the helium case, no measurement has been done with ^{3}He or helium isotopic mixtures. Since ^{3}He is predicted to be a better wetting agent than ^{4}He—as can be checked by feeding the appropriate values into Eq. (3.3)—it may induce the wetting of ^{4}He (Pettersen and Saam, 1993). For relatively strong substrates, we anticipate that ^{3}He will not exhibit a prewetting transition (because ^{3}He possesses no 2D liquid-gas transition). As the well depth D is decreased, there will be a wetting transition and associated $T=0$ prewetting. Study of the crossover between these two regimes would be of considerable interest. Among the intriguing possibilities, we predict that "sandwichlike" structures of a ^{4}He film with one layer of ^{3}He near the substrate and one layer at the film-vapor interface can be formed on weak-binding surfaces. High-temperature ^{3}He superfluidity may ensue as a result of the coupling between the layers (Ginzburg, 1964). It should be emphasized that "exact" ground-state and finite-T calculations are needed for both ^{3}He and ^{4}He.

On the experimental side, the alkali-metal surfaces used in the experiments have to be characterized more precisely. Alloys of alkali metals should be considered as well as alkali metal films. The properties of these surfaces with respect to helium atoms (surface bound-state energy, van der Waals coefficient) remain to be measured. Concerning wetting, the contact angle of liquid helium with nonwetted cesium and the way this angle goes to zero as the wetting temperature is approached from below are still to be studied.

The existence of nonwetted substrates opens a new field for experimental helium physics, namely, the study of film borders. The edge of a superfluid helium film at thermal equilibrium has never been available before. The value of the tension of these lines and their dynamics (wetting dynamics, motion of superfluid drops) are some of the questions that must be addressed; see Schick and Taborek, 1992.

Among applications, the possibility of burning superfluid films with very small heating power is certainly the most obvious one. Practical use of cesium film "burners" is, however, limited to sealed cells. Such a device has already been operated in a polarized ^{3}He-^{4}He mixture experiment (Cornut and Nacher, 1993). Another potential application is to bolometers (Torii *et al.*, 1992); if there is no He film present, the sensitivity of this device is increased (because the film has a high heat capacity).

As is always true, we expect intriguing new phenomena when new interaction domains are explored. It is fair to say that until now we have barely "scratched the surface" of this field. Nevertheless, exciting discoveries have already been made, whetting our appetite for further exploration.

ACKNOWLEDGMENTS

We are very grateful to our collaborators and colleagues who have helped to stimulate and enhance this research. These include Carlo Carraro, Moses Chan, Robert Hallock, Pierre-Jean Nacher, Nicholas Bigelow, Nicholas Pavloff, Jack Mochel, Peter Taborek, Jack Rutledge, Giacinto Scoles, Flavio Toigo, Genevieve Tastevin, Michael Schick, and Oscar Vilches. We are grateful to Daniel Stein and Ugo Fano for their comments and suggestions concerning this paper. Support by the National Science Foundation Grants DMR-9022681 and DMR-9014679, by a Petroleum Research Fund Grant, and by an Ohio Supercomputer Center grant has also been necessary and is appreciated.

REFERENCES

Aziz, R. A., 1984, in *Inert Gases,* edited by M. L. Klein (Springer, Berlin).

Bigelow, N., P. J. Nacher, and J. Dupont-Roc., 1992, J. Low Temp. Phys. **89**, 135.

Bruch, L. W., 1983, Surf.Sci. **125**, 194.

Cahn, J. W., 1977, J. Chem. Phys. **66**, 3667.

Carraro, C., and M. W. Cole, 1992a, Phys. Rev. B **46**, 10 947.

Carraro, C., and M. W. Cole, 1992b, J. Low Temp. Phys. **89**, 597.

Celli, V., 1992, in *Helium Atom Scattering from Surfaces,* edited by E. Hulpke (Springer, Berlin).

Cheng, E., G. Mistura, H. C. Lee, M. H. W. Chan, M. W. Cole, C. Carraro, W. F. Saam, and F. Toigo, 1993, Phys. Rev. Lett.

---

[10] See the data of Mullins, White, and Luftman (1986), as reinterpreted by Onellion and Erskine (1986), Lerner *et al.* (1993), and Friess *et al.* (1993). Theory and experiment for H_2 on the alkalis are indicative of similar wetting and prewetting behavior (Cheng *et al.*, 1993).

70, 1854.

Cheng, E., M. W. Cole, W. F. Saam, and J. Treiner, 1991, Phys. Rev. Lett. **67**, 1007.

Cheng, E., M. W. Cole, W. F. Saam, and J. Treiner, 1992, Phys. Rev. B **46**, 13967.

Cheng, E., M. W. Cole, W. F. Saam, and J. Treiner, 1993, unpublished.

Cheng, E., G. Ihm, and M. W. Cole, 1989, J. Low Temp. Phys. **74**, 519.

Chizmeshya, A., and E. Zaremba,1989, Surf. Sci. **220**, 443.

Cole, M. W., M. R. Swift, and F.Toigo, 1992, Phys. Rev. Lett. **69**, 2682.

Cole, M. W., and F. Toigo, 1985, Phys. Rev. B **31**, 727.

Cornut, M., and P. J. Nacher, 1992, J. Low Temp. Phys. **89**, 731.

Dietrich, S., 1988, in *Phase Transitions and Critical Phenomena,* Vol. 12, edited by C. Domb and J.L. Lebowitz (Academic, San Diego).

Dupont-Roc, J., M. Himbert, N. Pavloff, and J. Treiner, 1990, J. Low Temp. Phys. **81**, 31.

Ebner, C., and W. F. Saam, 1975, Phys. Rev. B **12**, 923.

Ebner, C., and W. F. Saam, 1977, Phys. Rev. Lett. **38**, 1486.

Ebner, C., and W. F. Saam, 1987, Phys. Rev. B **35**, 1822.

Fermi, E., 1934, Nuovo Cimento **11**, 157.

Fozoni, L., 1985, Phys. Lett. A **109**, 295.

Friess, W., E. Steinacker, T. Brunner, and D. Menzel, 1993, submitted to Phys. Rev. Lett.

Ginzburg, V. L., 1964, Phys. Lett. **13**, 101.

Goodstein, D. L., 1975, *States of Matter* (Prentice-Hall, Englewood Cliffs, NJ).

Hernandez, J. P., 1991, Rev. Mod. Phys. **63**, 675.

Hohenberg, P. C., and W. Kohn, 1964, Phys. Rev. **126**, 8864.

Ihm, G., M. W. Cole, F. Toigo, and J. R. Klein, 1990, Phys. Rev. A **42**, 5244.

Ihm, G., M. W. Cole, F. Toigo, and G. Scoles, 1987, J. Chem. Phys. **87**, 3995.

Ikushima, A. J., M. Jino, and M. Suzuki, 1986, Can. J. Phys. **65**, 1505.

Ji, G., and M. Wortis, 1986, Phys. Rev. B **34**, 7704.

Ketola, K. S., S. Wang, and R. B. Hallock, 1992, Phys. Rev. Lett. **68**, 201.

Krotscheck, E., 1985a, Phys. Rev. B **31**, 4258.

Krotscheck, E., 1985b, Phys. Rev. B **32**, 5713.

Landau, L. D., and E. M. Lifshitz, 1969, *Statistical Physics,* 2nd ed. (Addison-Wesley, Reading, MA), Chap. XV.

Lauter, H. J., H. P. Schildberg, H. Godfrin, H. Wiechert, and R. Haensel, 1987, Can. J. Phys. **65**, 1435.

Leiderer, P., 1992, J. Low Temp. Phys. **87**, 235.

Lerner, E., R. Morley, and O. E. Vilches, 1992, J. Low Temp. Phys. **89**, 593.

Menzel, D., 1993, private communication.

Mistura, G., and M. H. W. Chan, 1993, unpublished.

Mullins, D. R., J. M.White, and H. S. Luftman, 1986, Surf. Sci. **167**, 39.

Mukherjee, S. K., D. P. Druist, and M. H. W. Chan, 1992, J. Low Temp. Phys. **87**, 113.

Nacher, P. J., and J. Dupont-Roc, 1991, Phys. Rev. Lett. **67**, 2966.

Onellion, M., and J. L. Erskine, 1986, Surf. Sci. **177**, L983.

Pettersen, M. S., and W. F. Saam, 1993, J. Low Temp. Phys. (in press).

Pierotti, R. A., and G. D. Halsey, Jr., 1959, J. Phys. Chem. **63**, 680.

Pollock, L., and D. M. Ceperley, 1987, Phys. Rev. B **36**, 8343.

Rama Krishna, M. W., and K. B. Whaley, 1988, Phys. Rev. B **38**, 11839.

Robbins, M. O., D. Andelman, and J. F. Joanny, 1991, Phys. Rev. A **43**, 4344.

Rutledge, J. E., and P. Taborek, 1992, Phys. Rev. Lett. **69**, 937.

Saam, W. F., J. Treiner, E. Cheng, and M. W. Cole, 1992, J. Low Temp. Phys. **89**, 637.

Schick, M., 1990, in *Liquids at Interfaces,* edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (Elsevier, Amsterdam), p. 415.

Schick, M., and P. Taborek, 1992, Phys. Rev. B **46**, 7312.

Scoles, G., 1990, Int. J. Quantum Chem. **24**, 275.

Shirron, P. J., and J. M. Mochel, 1991, Phys. Rev. Lett. **67**, 1118.

Taborek, P., and J. E. Rutledge, 1992, Phys. Rev. Lett. **68**, 2184.

Torrii, R., S. R. Bandler, T. More, F. S. Porter, R. E. Lanou, H. J. Maris, and G. M. Seidel, 1992, Rev. Sci. Instrum. **63**, 230.

Vidali, G., G. Ihm, H. Y. Kim, and M. W. Cole, 1991, Surf. Sci. Rep. **12**, 133.

Wagner, M., and D. M. Ceperley, 1992, J. Low Temp. Phys. **89**.

Whitlock, A., G. V. Chester, and M. H. Kalos, 1988, Phys. Rev. B **38**, 2418.

Wilks, J., 1967, *The Properties of Liquid and Solid Helium* (Clarendon, Oxford), Chap. 24.

Zaremba, E., and W. Kohn, 1976, Phys. Rev. B **13**, 2270.

Zaremba, E., and W. Kohn, 1977, Phys. Rev. B **15**, 1769.