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Excitation Spectrum and Thermodynamic Properties of Liquid Films in Cylindrical Pores*

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We examine the dynamic and thermodynamic properties of adsorbed liquid films in cylindrical cavities. We find a dynamical stability limit for the thickness of films adsorbed uniformly on the walls. This limit is shown to coincide with a thermodynamic stability limit which depends on both substrate and capillary forces. The Kelvin equation describing capillary condensation is generalized to include the substrate interaction. The low-temperature properties of the films are calculated.

Considerable attention has been directed recently toward understanding the excitation spectrum and thermal properties of multilayer He⁴ films.¹⁻⁶ The film differs from the bulk liquid for several reasons, including explicit size effects associated with the boundary conditions for the velocity and superfluid order parameter, and exchange of particles, energy, and momentum with both vapor and substrate. As one or more dimensions of the film becomes comparable to or smaller than the thermal wavelength of the excitations in bulk He⁴, the excitation spectrum begins to take on discrete character, leading to pronounced modification of the thermal behavior.

In this paper we report studies of volume and surface excitations of liquid films in partially and completely filled cylindrical cavities, an idealization of the geometry in a porous material. Anomalous behavior of the calculated spectrum leads us to consider the thermodynamics of adsorption. We then generalize the Kelvin equation to include the substrate potential, obtaining results applicable to the adsorption of He⁴ and those normal liquids which wet the substrate walls.

We take the liquid to be compressible, inviscid, and irrotational with velocity $\vec{V} = \nabla\varphi$. We consider motion of a single component (superfluid) alone, neglecting effects of the normal fluid in the boundary healing region. This is plausible for a relatively thick film of He⁴ at low temperature. By linearizing the continuity and Euler equations,

we find for motion at frequency ω

$$\nabla^2\varphi + (\omega/s)^2\varphi = 0, \quad (1)$$

where we take the speed of sound s to be constant. The modes of the system are determined by solving (1) subject to appropriate boundary conditions.⁷ The solutions are of the form

$$\varphi = f_{km}(r) \exp[i(kz + m\theta)]$$

in terms of variables r , θ , and z appropriate to the cylindrical symmetry. In all cases f_{km} is expressed in terms of Bessel functions.

The most interesting case is that of partially filled pores [illustrated in Fig. 1(a)]. The eigenfrequencies, when $l^2 \equiv k^2 - \omega^2/s^2 > 0$, are given by

$$\omega_{km}^2 = [-g(a) + (\sigma/\rho_0 a^2)(1 - m^2 - k^2 a^2)] \\ \times l(d \ln f_{km}/dr)_{r=a}. \quad (2)$$

Here $Mg(a) = -(dU/dr)_{r=a}$, where M is the atomic mass and $U(r)$ is the Van der Waals potential due to the substrate; σ is the surface tension.⁸ We identify these modes as ripplons in the sense that such surface oscillatory modes occur in the limit of an incompressible fluid, in which case l is replaced by k .

The case $m=0$, $lR \ll 1$ is of particular interest. Using the small-argument limit of the Bessel

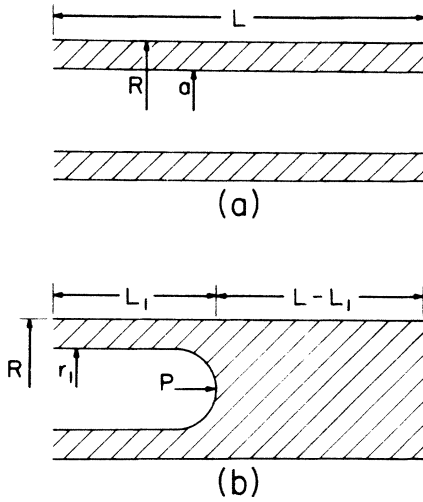


FIG. 1. Liquid (hatched area) adsorbed in cylindrical pores of radius R and length L , viewed in longitudinal section. (a) Film adsorbed uniformly and symmetrically on walls. (b) Partially filled and partially empty pore geometry, occurring when number of atoms present exceeds the critical number.

functions to evaluate f_{km} leads to

$$\omega = c_0 k [(1 + k^2/k_0^2)^{-1} + c_0^2/s^2]^{-1/2}, \quad (3a)$$

$$c_0^2 = [ag(a) - \sigma/\rho_0 a] [(R/a)^2 - 1]/2. \quad (3b)$$

Here $k_0^2 = \rho_0 g(a)/\sigma - a^{-2}$. For sufficiently small a , the right-hand side of (3b) becomes negative and the frequency imaginary. This dynamic instability occurs for thick films because the system tends to eliminate the surface. The modes soften as a approaches the critical value a_c , defined by

$$\sigma = \rho_0 a_c^2 g(a_c). \quad (4)$$

We show below that a_c coincides with a radius of instability derived from thermodynamic considerations alone, and calculate its numerical value as a function of film and substrate parameters.

Films thinner than critical (i.e., $a > a_c$) have $\omega \cong c_0 k$ for long wavelengths ($k \ll k_0 \approx 10^6 \text{ cm}^{-1}$). Below $T = 0.1 \text{ K}$ the term linear in k in (3a) suffices to calculate the contribution of the $m=0$ mode to the energy, and the contribution of all other modes is exponentially small. We find that the energy E and the ratio of the specific heat c to that of bulk He^4 , c_{bulk} , are

$$E = \frac{\pi L}{6\hbar c_0 \beta^2}, \quad \frac{c}{c_{\text{bulk}}} = \frac{5}{2\pi^2} \left(\frac{\hbar \beta s}{R} \right)^2 \frac{s}{c_0}. \quad (5)$$

Here $\beta = 1/k_B T$. Note that c is linear in T be-

cause of the one-dimensional character of those modes which are excited.

The result for the case of full pores is identical to (5) apart from a substitution of s for c_0 . Since $c \approx 0.1 s$, the full pore energy is much smaller than that given in (5). In a subsequent publication we discuss in greater detail the thermodynamic properties of He^4 in this geometry.

Several recent experiments have determined low-temperature behavior of He in porous materials.^{2,3,5} The superfluid density ρ_s in tightly packed lampblack powder was found³ to depend linearly on T . This result differs from a T^2 dependence expected in the present one-dimensional limit, probably because⁴ the powder possesses no dimension L long compared to the characteristic phonon wavelength $\hbar s \beta$. A partially filled porous material, in contrast, has a size criterion for the one-dimensional limit $L \geq \hbar c_0 \beta$, which is less stringent because $c_0 \ll s$. Thus one might expect to see such behavior even in relatively nonuniform materials. Preliminary experimental results² on He in porous Vycor indicate that the free surface contributes to the heat capacity a term $\sim T^{3/2}$, which disagrees with both the present calculations and similar ones for spherical geometry, for which case the modes possess an energy gap. Before drawing definitive conclusions, however, it is necessary to have measurements for more closely spaced coverages. Especially valuable will be data for large-radius pores where superfluid onset and solid boundary-layer effects are less important.

We now examine the thermodynamics of the instability. At the liquid-vapor interface, the equilibrium pressures p_l and p_v , respectively, satisfy in the geometry of Fig. 1(a)

$$p_v = p_l + \sigma/a. \quad (6)$$

The equations of state for the two phases can be integrated (we assume the vapor to be ideal) to determine the chemical potential μ in terms of μ_0 and p_0 of the saturated liquid and the potential at the interface, $U(a)$,

$$\mu_v = \mu_0(p_0) + \beta^{-1} \ln(p_v/p_0) + U(a), \quad (7a)$$

$$\mu_l = \mu_0(p_0) + v_l(p_l - p_0) + U(a), \quad (7b)$$

where we neglect the small variation of $v_l = M/\rho_0$ with pressure. Equating (7a) to (7b) and using (6) along with $p_0 - p_v \ll \sigma/a$ yields $\ln(p_v/p_0) = -\beta v_l \sigma/a$. Expressing the pressure $p(\infty)$ of the vapor outside the capillaries in terms of p_v , one finds

$$p(\infty) = p_0 \exp\{\beta[U(a) - v_l \sigma/a]\}. \quad (8)$$

Thus the chemical potential of the film is $\mu = \mu_0 + U(a) - v_1\sigma/a$. Differentiating with respect to a yields $\mu'(a) = -Mg(a) + v_1\sigma/a^2$. A thermodynamic criterion for stability of an adsorbed film is that $\partial\mu/\partial N$ be positive definite.⁹ If the film is to be stable, therefore, $\sigma \leq \rho_0 g(a)a^2$, which is identical to the dynamical stability limit (4). Since $g(0) = 0$ by symmetry, the instability limit will eventually be reached for a sufficiently thick film. We show below that the instability arises because it is energetically favorable to fill the pore partially, as in Fig. 1(b), in order to reduce the surface area.

We have calculated the critical radius a_c by assuming that U is given by a sum of pair interactions $-c/r^6$ with the substrate atoms, of density n_s . While not precise, this will provide correct qualitative trends. We choose $n_s c$ such as to reproduce the known result of Dzyaloshinskii, Lifshitz, and Pitaevskii⁹ a distance D above a flat surface, $U = -\alpha D^{-3}$. Then integrating

$$U(\vec{r}) = -n_s c \iint d^3r' |\vec{r} - \vec{r}'|^{-6}$$

over the substrate, one finds

$$U(a) = -(n_s c \pi^2 / 4R^3) F(\frac{3}{2}, \frac{5}{2}; 1; y^2),$$

where $y \equiv a/R$ and F is a hypergeometric function. Using this, the instability criterion (4) can be written in terms of a scaling parameter $R_0 = (3\pi\alpha/\sigma v_1)^{1/2}$ as

$$\left(\frac{R}{R_0}\right)^2 = y_c^2 (1 - y_c^2)^{-5/2} P_{3/2}^1 \frac{1 + y_c^2}{1 - y_c^2}. \tag{9}$$

Here $y_c \equiv a_c/R$ and $P_{3/2}^1$ is an associated Legendre function. The universal curve generated by this equation has been calculated numerically and is displayed in Fig. 2. As a specific illustration, one axis of Fig. 2 shows the scaling for He in MgO, for which $R_0 \approx 31 \text{ \AA}$ has been obtained from the calculated value^{9,10} of α . For example, if $R = 60 \text{ \AA}$, the critical radius $a_c = 36 \text{ \AA}$, so the instability occurs at about 64% pore filling.

There exists a regime of film thickness $a < a_m$ for which the symmetric configuration of Fig. 1(a) is metastable relative to the partially filled configuration of Fig. 1(b). We determine a_m as follows. The parameters r_1 and L_1 of that geometry are found by minimizing the total free energy for given $N = \pi L(R^2 - a^2)/v_1$. We neglect the role of the curved-surface transition region in determining a_m , an approximation valid if the cylinder is long. For any $a < a_m$, we have $L_1/L = (a/r_1)^2$. The result of minimizing the free ener-

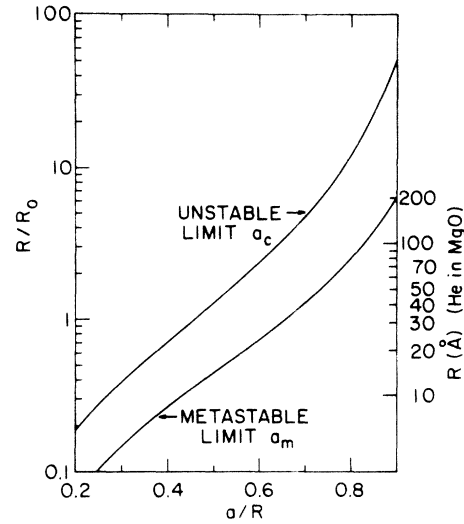


FIG. 2. Critical values of inner radii, a_m and a_c , divided by pore radius R , expressed as universal functions of the dimensionless variable R/R_0 . An example, the scaling appropriate to liquid helium on an MgO substrate, $R_0 = 31.4 \text{ \AA}$, is shown on the right-hand ordinate. The film is stable if $a > a_m$, metastable if $a_c < a < a_m$, unstable if $a < a_c$.

gy is¹¹

$$2r_1^{-2} \int_0^{r_1} dr r U(r) = U(r_1) + \sigma v_1 / r_1, \tag{10}$$

a result independent of N . We conclude that the metastable radius $a_m = r_1$, in that if sufficiently many particles are present ($a < r_1$), it is energetically favorable for the system to assume the configuration of Fig. 1(b). Figure 2 shows the universal curve for the metastable radius derived from Eq. (10).

L_1 changes as particles are added to the system shown in Fig. 1(b), but the chemical potential does not, as expected for this essentially two-phase system. Thus we predict a vertical adsorption isotherm— N independent of P . However, when the pores are being filled, the system will tend to remain in the metastable geometry until the radius of instability is approached. On emptying, the vertical isotherm will occur at the radius of metastability. Such hysteresis has been seen for many materials and is usually attributed¹² to nonuniform pore shapes for which the film radius of curvature depends on whether the liquid is being added or removed. While we cannot rule out this explanation, we can examine the behavior expected from our alternative model.¹³ Specifically, Fig. 2 shows the radii a_m and a_c at which vertical isotherms should appear. Furthermore, we make an unambiguous predic-

tion for liquid helium of a constant *negative* differential specific heat $(\partial C/\partial N)_T$ on starting to empty. Since on emptying, the free surface area increases, so should the heat capacity, which depends at low T on excitation of the ripplon modes (3) with $a = a_m$, the metastable radius. This increase more than compensates for the decreasing filled-pore term, since $c_0(a_m) \ll s$.

Finally, we note that if r_p is one of the two equal radii of curvature at the point P of Fig. 1(b), it follows from (8) and the assumption of equilibrium that

$$\ln[p(\infty)/p_0] = \beta[U(0) - 2v_l\sigma/r_p].$$

This and Eq. (8) are generalizations of the Kelvin equation of capillary condensation¹² to include substrate forces.

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Pressure Shifts and Quenching of Atomic and Molecular States Produced in Electron-Bombarded Liquid Helium*

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The optical absorption and emission spectra of electron-bombarded liquid helium has been studied as a function of pressure between the saturated vapor pressure and 25 atm. The transitions of He* and He₂* in the liquid shift toward the blue with increasing pressure. The observed line profile and pressure shift of the He(2³P) ← He(2³S) atomic absorption line are in good agreement with recent static line broadening calculations. We also report a strong pressure-dependent quenching of the excited atomic and molecular states in the liquid.

The optical fluorescence of liquid systems has been a subject of long-standing scientific interest. However, the excited states of most liquids are difficult to study because the surrounding fluid

usually causes rapid nonradiative de-excitation of the excited states.¹ In contrast to the usual situation, recent spectroscopic studies of electron-beam-bombarded superfluid helium have