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Triple-point wetting of neon films

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High-resolution quartz microbalance measurements of Ne films on Ag show a continuous transition from incomplete to complete wetting. The wetting temperature is identical to the triple point T_t to within a few millikelvins. The frequency shift Δf_0 corresponding to the maximum thickness at $T < T_t$ follows a power law $\Delta f_0 \sim t^{-1/n'}$, with $n' = 2.39$, at reduced temperatures $0.001 < t < 0.03$. Frequency-pressure isotherms above T_t indicate higher-order terms in the thermodynamic potential. These terms can be quantitatively explained by a model of substrate-field-induced solidification. Similar isotherm shapes below T_t suggest that stratification occurs on both sides of the triple point.

I. INTRODUCTION

Wetting transitions[1] near the triple point of the bulk material have been observed in many adsorbed films.[2–9] Krim *et al.*[3] have shown that the "triple-point wetting transition" is a continuous change from incomplete to complete wetting, and have described the temperature dependence of the maximum film thickness d_0 below the transition as a power law

$$d_0 = AT^{-1/n}, \quad t \equiv (T_w - T)/T_w, \quad T_w = T_t \;, \tag{1}$$

where T_t is the temperature of the bulk triple point. They related the exponent in Eq. (1) to the range dependence of the film-substrate potential by a phenomenological theory, such that the empirical $n = 3$ corresponds to the exponent of the atom-substrate potential $u(z) = \alpha z^{-3}$ of simple van der Waals systems. This result follows from the assumptions that the growth of the film is primarily due to the addition of adsorbate in the liquid phase, and that the thickness of the liquid portion is much greater than that of the solid. Further, the liquid is assumed to wet the substrate at the triple point and above. Corrections to the right-hand side of Eq. (1) can arise from several sources: additional terms in the interaction[10] possibly due to many-body effects, substrate structure and foreign adsorbed layers,[11] or structure within the film itself.[12] Provided the thickness is not so large as to incur retardation effects in $u(z)$,[13] these corrections would not be expected to change the asymptotic form of the divergence. It must also be noted that the assumption that $T_w = T_t$, while reasonable, is not the only possible scenario.[14]

The importance of some of these effects can be addressed by high-resolution measurements of the transition. We chose neon for such a study for its convenience and because it wets graphite incompletely at low temperature,[15] although its behavior on other substrates and at temperatures near T_t was unknown.

II. EXPERIMENTAL PROCEDURE

The measurements used a quartz-crystal high-frequency microbalance, which provides a direct measure of the mass adsorbed on the crystal electrodes by a shift Δf of its resonant frequency. Except for minor changes the apparatus was the same as that used for recent wetting studies in this laboratory.[3,16] The resonant crystal was a commercial AT-cut, 8-MHz crystal with evaporated Ag electrodes, and its frequency was compared with a similar crystal maintained at room temperature. Stability during an isotherm was approximately ±0.1 Hz, equivalent to a coverage change of less than 0.01 layer. Cell temperature was stabilized to within 1 mK by controllers on the outer bath and the cell. Temperature calibration was obtained from the saturation pressure P_0 and the Ne vapor pressure scale,[17] which places the triple point at $T_t = 24.562$ K and $P_0(T_t) = 325.0$ Torr.

III. RESULTS

A. Behavior above the triple point

Isotherms were obtained by introducing gas to the cell in small increments. The frequency shifted quickly upon each addition and then remained constant for as long as the conditions were unchanged. The results, plotted as $\log_{10}(P_0/P)$ vs $(\Delta f)^{-3}$, are shown in Fig. 1. This type of graph is suggested by a simple model of adsorption. If $u(z) = -\alpha z^{-3}$ and the interaction is not appreciably modified by intervening film,[13] then the thickness d of wetting film obeys the Frenkel-Halsey-Hill[18] (FHH) isotherm:

$$kT \ln(P_0/P) = \alpha d^{-3} \;. \tag{2}$$

Figure 1 would seem to indicate that Eq. (2) does not hold, but linearity also requires that Δf is proportional to d. Several effects can destroy proportionality.

Nonlinearity can arise from shear motion in the film. Shear becomes appreciable in thick liquid layers, but is negligible when d is less than half of the hydrodynamic penetration depth.[16] Calculations indicate that shear was negligible in the thickness range of these measurements.

More generally, nonlinearity can arise from the same sources, noted earlier, that can contribute corrections to Eq. (1). One of these is density gradients due to the combination of finite compressibility of the film and the

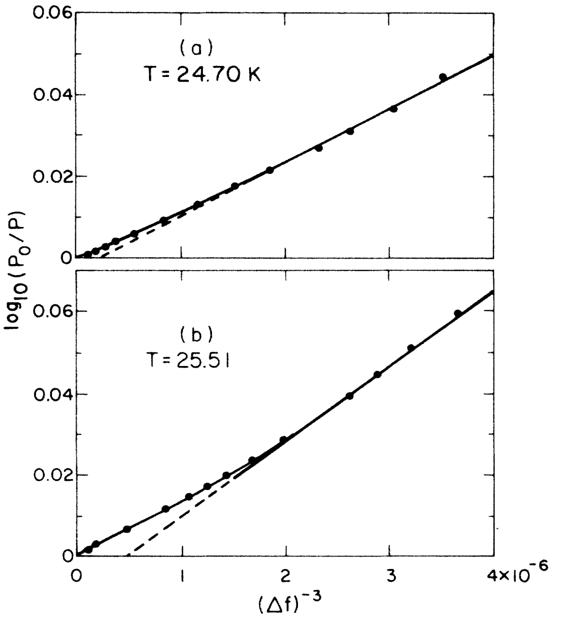

FIG. 1. Frequency-pressure isotherms above the triple point, $T_t=24.562$ K, $P_0=325.0$ Torr. The solid lines are calculated from the two-phase solid model, with bulk neon and Ne-Ag parameters.

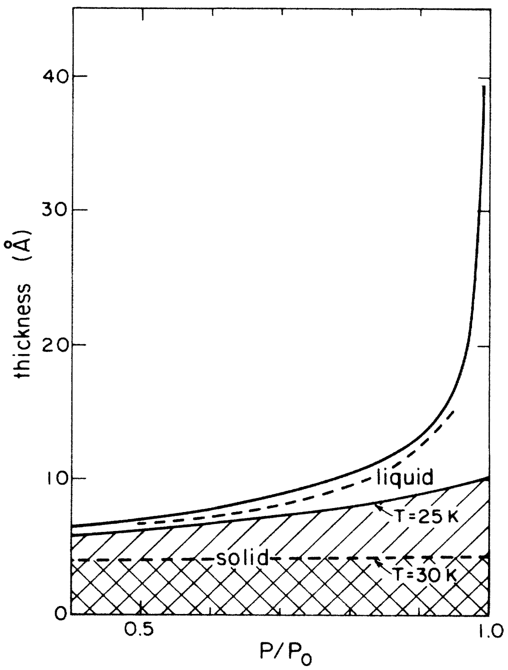

FIG. 2. Liquid and solid layer thicknesses as functions of reduced pressure, calculated according to the slab model. The double-hatched region marks the solid layer thickness at $T=30$ K, and the single-hatched region marks the solid thickness at 25 K. The solid and dashed lines correspond to the total thicknesses at 25 and 30 K, respectively.

strong adsorption potential next to the substrate. Density variation is particularly important when the field is sufficiently strong to cause solidification. Substrate-field-induced solidification has been observed in bulk liquid helium,[19] and should occur in other strong-adsorber systems where the solid phase wets the substrate. Furthermore, this source of nonlinearity lends itself to explicit calculation. In a stratified film the frequency response of a microbalance is a composite of the thicknesses and densities of the liquid and solid laminae:

$$\Delta f=\Gamma[\rho_l d+(\rho_s-\rho_l)d_s] \ , \tag{3}$$

where Γ is the mass sensitivity of the microbalance.

A recent theory allows quantitative calculation of the solid layer thickness. Krim and Dash[12] treat the effect in a continuum model film on a smooth substrate, finding that for a potential varying as z^{-3} the solid layer thickness is

$$d_s=[(\alpha\kappa\rho)^{-1}(1-\rho_{lv}/\rho_{ls})+d^{-3}]^{-1/3} \ , \tag{4}$$

where κ and ρ are the mean compressibility and density of bulk liquid, and ρ_{lv} and ρ_{ls} are the densities of the liquid in equilibrium with vapor and solid. We calculated d_s as a function of d for the temperatures of the two isotherms above T_t according to Eq. (4), using the parameters for bulk Ne (Ref. 20) and the semi-empirical attractive interaction for Ne-Ag.[21] As illustration of the effect, the computed thicknesses for two temperatures above T_t are shown in Fig. 2. Calculations for the actual isotherms were then fitted to the data according to Eq. (3) by varying the crystal sensitivity Γ as the only adjustable parameter. The fitted curves, shown as the solid lines in Fig. 1, agree with the data over the entire range of the experiment. The empirical Γ's are different for the two isotherms; in units of Hz Å^2/Ne molecule, $\Gamma=116$ at 24.704 K, while $\Gamma=129$ gives a marginally better fit for 25.514 K. These values average 25 percent higher than the theoretical value 97.7 for 8 MHz crystals at room temperature.[22] The change in sensitivity is reasonable in view of the temperature dependence of the elastic constants of quartz and of the resonant frequency of AT-cut crystals,[22] but we are not aware of any measurements of the temperature dependence of Γ.

B. Measurements below the triple point

We measured 16 isotherms at temperatures ranging from 2.5 K to 70 mK below T_t. A typical curve, shown in Fig. 3, resembles the nonlinear isotherms seen above T_t, but with the additional feature of a finite frequency intercept Δf_0 at P_0, clear indication of incomplete wetting. After reaching P_0, the further addition of gas to the cell temporarily increased the pressure and frequency, but then P fell very rapidly and Δf more slowly, to their original values. We believe that the frequency changes were due to the initial nucleation of bulk Ne on the crystal at $P>P_0$, followed by distillation of the excess material from the crystal to the bottom of the cell. (The difference in height between the crystal faces and the bottom of the cell was about 2 cm, producing a gravitational potential

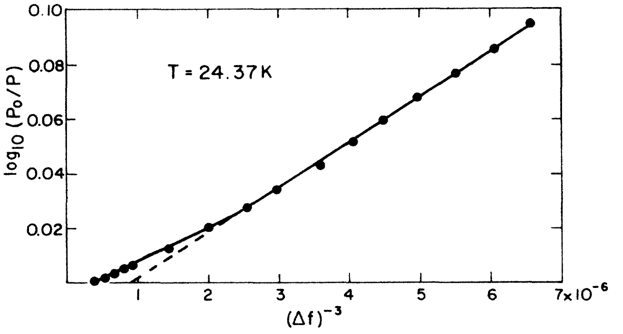

FIG. 3. Typical isotherm below T_t showing finite intercept and nonlinearity.

difference equivalent to a pressure variation of 6 mTorr at the triple point.) Repeated additions of gas produced the same result. The stability and reproducibility of Δf_0 permitted us to survey its temperature dependence more efficiently than by isotherms. We introduced an excess of gas to the cell above the triple point, insuring that a small amount of bulk Ne was present at all $T<T_t$. We then measured Δf as T was decreased in small steps. With adequate time for equilibrium after each step, the shifts were reproducible, and they agreed with the Δf_0 intercepts of the isotherms.

The results, shown in Fig. 4, are described quite well by a power law

$$\Delta f_0 = \text{const}\times t^{-1/n'} . \tag{5}$$

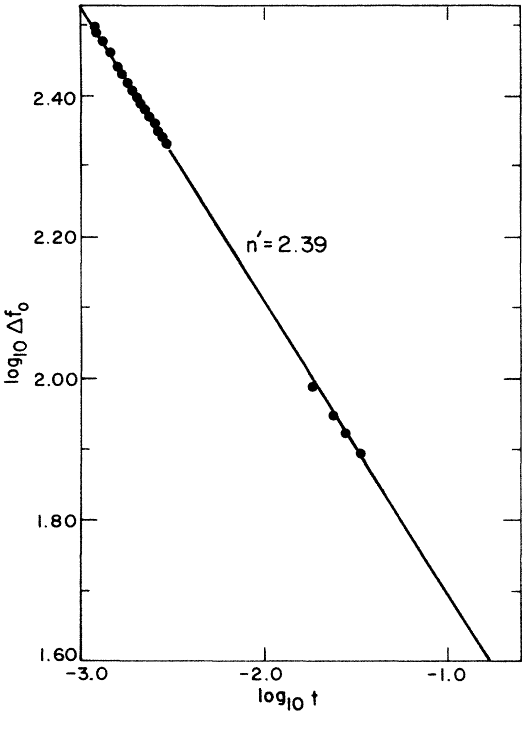

FIG. 4. Frequency shift Δf_0 at saturation versus reduced temperature $t=(T_t-T)/T_t$.

Least-squares fitting yields $n'=2.39\pm0.06$ over the full range, $0.001<t=(T_t-T)/T_t<0.03$. On omission of the group of four measurements at the low T end, the range is considerably narrowed to $0.001<t<0.003$, but the empirical exponent is the same to within statistical error: $n'=2.43\pm0.04$. These results are calculated with T_t equal to the published value.[16] A variation $\delta T_t=\pm5$ mK, which is about five times our estimated uncertainty, contributes a variation in n' of ±0.11.

IV. DISCUSSION

The shapes of the frequency isotherms above the triple point appear to provide an indication of liquid-solid stratification. Where stratification occurs, nonlinearities will not be limited to microbalance measurements. Relations similar to Eq. (3) should govern many types of adsorption experiments: the "coverage" Θ or some other extensive property is proportional to adsorbed mass, but the total thickness depends on the separate thicknesses and densities of solid and liquid layers. This is the case in conventional isotherms, where Θ is determined by volumetric measurements of a supply gas, and it should also hold in ellipsometry, since for thin films the signal amplitude is proportional to the total optical path length in the film.[23]

Equation (1) was proposed by Krim *et al.*[3] on the basis of microbalance measurements such as those reported here. They fitted their frequency shifts to Eq. (5) and obtained the empirical exponent $n'=3$. This result is expected for a predominantly liquidlike film undergoing triple-point wetting, in the asymptotic limit of very thick films. However, we find an exponent n' for Ne/Ag substantially lower than 3. The data of the earlier study, of somewhat lower resolution and more limited range of t than the present work, are also consistent with our value of n'.

We consider a few possible causes for our result. Retardation effects[13] can be ruled out since they would increase the exponent above 3 rather than reduce it. The most obvious cause is that the data are not in the asymptotic region. But we note that the data in Fig. 4, although ranging over not much more than a decade $(0.001<t<0.03)$, show no sign of turning upward toward a larger value of n' at smaller t. Another possibility is a slight shift between T_w and T_t: if $T_w>T_t$, the calculated n' will be reduced, especially as T comes very close to the triple point. Thus, this effect also would be seen as a change of n' with t. The possibility of a wetting transition slightly above[8] or below[9] T_t impelled us to examine our data with particular care. (We note, however, that the system methane on graphite studied by Lysek *et al.*[9] forms very thick or completely wet films at low temperature,[24] and therefore is in a class different from the typical incomplete wetting type such as Ne/Ag.) Our results show only a single transition, with T_w indistinguishable from T_t: the effective intercept of Eq. (5) does not shift more than a few millikelvins over the experimental range, a relative difference $(T_w-T_t)/T_t<8\times10^{-5}$. However, the questions of a possible shift between T_w and T_t and whether the data have reached the asymptotic region are closely linked. A finite difference (T_w-T_t) or an error in the location of

T_t would change the empirical n' and cause it to be temperature dependent. A downward shift of T_t would raise n', particularly near the transition. If this decrease in T_t were as much as 5 mK, n' would become ≥ 3 at $t < 1.5 \times 10^{-3}$. The appearance of the data at larger t would then suggest that this was the beginning of the true asymptotic region. The argument could be tested if there were extensive data at smaller t or if theory could provide an estimate of the range of the asymptotic region. Unfortunately, neither test is possible at present.

Another explanation involves film stratification. The frequency shift, Eq. (3), contains a contribution due to the solid layer: if d_s remains constant or relatively small as d increases, the asymptotic limit of n' will be equal to n. Since n' is not converging toward n as t becomes very small, it is possible that d_s increases with d. Further experiments which can detect layering and measure the thicknesses of solid and liquid layers would be extremely useful.

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