Wetting Layers and Dispersion Forces for a Fluid in Contact with a Vertical Wall

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When a liquid wets a vertical wall, wetting layers form on the wall high above the liquid-vapor meniscus. These layers are stabilized against gravity by dispersion forces. For SF_6 in contact with fused silica, we find layers between 20 and 40 nm thick in a range of temperatures below critical. Our results support the predictions of Dzyaloshinskii, Lifshitz, and Pitaevskii, in contrast to recent experiments which are much harder to reconcile with theory.

In the usual hydrostatic picture[1] of a liquid that wets a vertical wall, the long-ranged dispersion, or van der Waals, forces[2] between the wall, the liquid, and the vapor are neglected. The liquid then rises up to the wall a distance equal to the capillary length, $a = (2\sigma/g\Delta\rho)^{1/2}$, at which point the liquid-vapor surface is tangent to the wall [see Fig. 1(a)]. The rise and shape of this meniscus can be understood in terms of the pressure drop across the meniscus (which is the product of the meniscus curvature and the liquid-vapor surface tension σ), and the buoyant force per unit volume of fluid, $\Delta\rho g$ ($\Delta\rho$ is the mass density difference between the liquid and the vapor and g is the gravitational acceleration). When dispersion forces are considered, the meniscus shape is slightly altered and a thin liquid-like adsorbed film is predicted to form between the vapor and the wall at heights h greater than the capillary length.[2] It is this film, or wetting layer, which is the subject of the present study [Fig. 1(b)].

The Dzyaloshinskii-Lifshitz-Pitaevskii[2] (DLP) theory of dispersion forces enables one to calculate the thickness of the wetting layer as a function of height from the expression

$$F(L) + \Delta\rho g h = 0, \tag{1}$$

where $F(L)$ is an integral over the frequency-dependent dielectric functions of the wall, the wetting liquid, and the vapor, evaluated at imaginary frequencies. The equation is valid when the curvature of the interference is negligible, i.e., for heights h slightly larger than one capillary length.[3] The DLP theory of the film has been quantitatively confirmed by Sabisky and Anderson[4] only for the unique case of superfluid helium films adsorbed on a strontium fluoride surface. In the present work we report new measurements, obtained by ellipsometry, of the thickness of the wetting layer of sulfur hexafluoride (SF_6) that forms on a fused silica surface partially immersed in liquid SF_6. In agreement with the DLP theory, we find that the layer's thickness decreases from 40 to 20 nm as the height of the measurement is increased from 0.7 to 3 mm above the liquid-vapor interface. Within the resolution of our measurements, the layer's thickness is independent of temperature in the range 10 to 0.1 K below the critical temperature ($T_c = 319$ K). The DLP theory predicts a very weak temperature dependence which we could not have detected.

Our present measurements were stimulated by two recent studies of wetting layers which yielded thicknesses which are much harder to reconcile with theoretical ideas. Moldover and Gammon[5] studied wetting layers of SF_6 very close to T_c on two closely spaced multilayer dielectric mirrors (1–4-μm separations) acting as an interferometer. They reported layer thicknesses on the order of hundreds of nanometers, an order of magnitude larger than the DLP prediction discussed below! Kwon *et al.*[6] studied wetting layers adsorbed on the liquid-vapor interface above two very different binary solutions: The coexisting phases for one solution differed in density by 800 mg/cm^3, while the coexisting phases of the other solution differed in density by about 2 mg/cm^3. They found thicknesses in the range 7–40 nm for both solutions. This result is difficult to understand because it implies that the dispersion forces for one solution are several hundred times larger than for the other. In contrast with these earlier measurements, the present measurements demonstrate that in the case of a simple geometry (a single vertical wall), and a well-characterized substrate (fused silica), the thickness of wetting layers can be understood quantitatively.
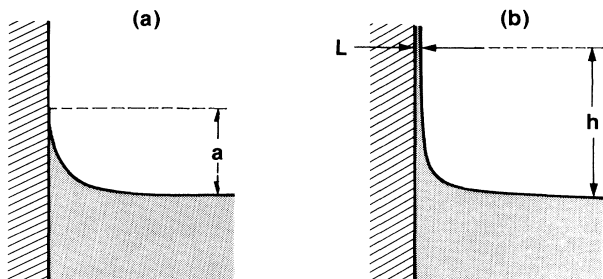

FIG. 1. (a) Macroscopic hydrostatic picture of a liquid wetting a vertical wall. The quantity a is the capillary length. (b) Modified picture obtained by including dispersion forces. The thickness L of the liquidlike layer decreases as the height h increases.

Results for the wetting layer thickness as a function of height are presented in Fig. 2 for temperatures 10 K and 3 K below T_c. At these temperatures the capillary lengths are[7] 0.38 and 0.23 mm, respectively. The shaded regions bound several sets of data obtained under different experimental conditions, e.g., different strains in the optical-cell window, as described below. The solid curve and dashed line are the predictions of the DLP theory with and without retardation effects. (Details of the calculations are presented below.) The dashed line becomes valid for thin films ($L < 5$ nm), for which $L \propto h^{-1/3}$. For the thicker films that we studied, the theoretical value of L varies approximately as $h^{-0.30}$. In contrast with the experiments cited above, the present experimental results are in agreement with the DLP theory (including retardation). The slight temperature dependence of the DLP thicknesses is not visible on the scale of the figure. Our results are independent of temperature within experimental error (± 7.5 nm).

Results obtained closer to the critical temperature [at $t = (T - T_c)/T_c = -0.003$ and -0.0005] are similar to those in Fig. 2, but the scatter is larger. This is expected because the index of refraction of the wetting layer approaches that of the vapor near T_c, and ellip-

sometry becomes less sensitive to the thickness of the layer. Nevertheless, our layers close to T_c remain on the order of 20 nm thick and are much thinner than those found by Moldover and Gammon[5] at similar temperatures. The multilayer dielectric mirrors that they used might be responsible for the discrepancy: A poorly known phase shift enters into the interpretation of the interference pattern used to measure the spacing between the mirrors.

Our measurements were obtained by ellipsometry, i.e., by reflecting light from the fused-silica–SF$_6$ interface and measuring the change in polarization. The most difficult problems we encountered were caused by strain-induced birefringence in the fused silica and by spurious changes in the thickness of the wetting layers resulting from temperature gradients. Thus we shall discuss the optical and thermal aspects of the apparatus in more detail than any other.

The optical components in the ellipsometer were arranged in a standard configuration described by Muller[8]: He-Ne laser ($\lambda_0 = 0.6328$ μm), polarizer, quarter-wave plate with 45° azimuth, optical cell, analyzer, and photomultiplier tube. The instrument operated in a horizontal plane with the angle of incidence fixed at 35°. This particular angle was chosen from sensitivity studies; it is slightly smaller than Brewster's angle for a fused-silica–SF$_6$ vapor interface throughout the temperature range studied.

An optical-grade fused-silica prism fabricated to reflect light at 35° formed one boundary [see Fig. 3(a)] of the high-pressure optical cell ($P_c = 3.8$ MPa). The prism was polished flat to $\lambda/20$ and thoroughly cleaned before being clamped to the stainless steel cell body. We used a standard indium O-ring seal. Both the prism and the clamp were designed to minimize strain-induced birefringence caused by the clamping forces and by the pressure difference across the prism. The 1.9-cm^3 cell was filled to an overall density sufficiently close to the critical density ($\rho_c = 0.74$ g/cm^3) that the liquid-vapor meniscus stayed in the center of
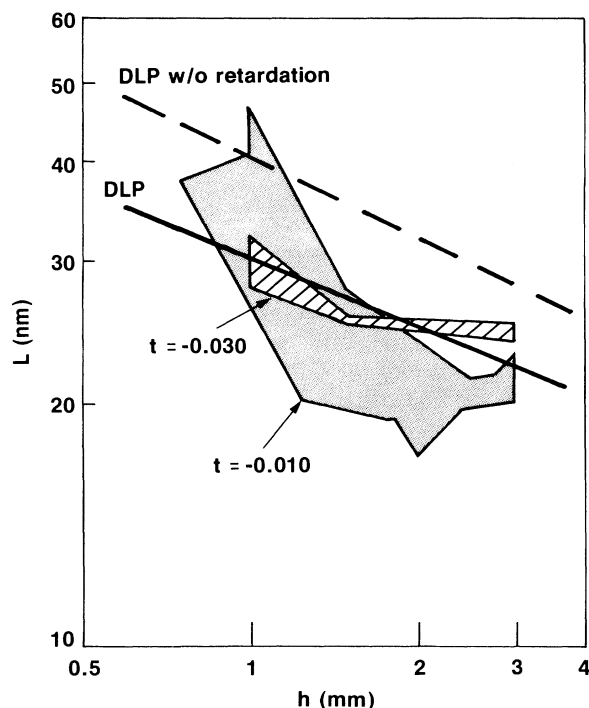
FIG. 2. Measured wetting layer thicknesses L as a function of height h for two reduced temperatures $t = (T - T_c)/T_c$. The shaded regions bound data obtained under a variety of experimental conditions. The solid and dashed lines are predictions of the DLP theory with and without retardation effects.
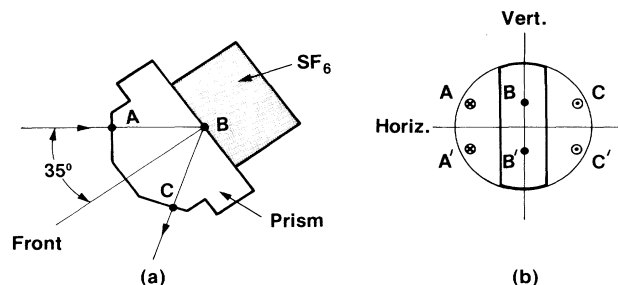
FIG. 3. (a) A top view of our optical cell illustrating the geometry of the reflection from the fused-silica–SF$_6$ interface. (b) A front view of the prism illustrating the two ellipsometric measurements used to model strain-induced birefringence in the prism.

the cell near the critical temperature.

After assembly and filling, the optical cell was inserted into a four-stage concentric-shell thermostat. The outer two stages were actively controlled, while the inner two were passive. The thermostat was capable of regulating the temperature of the cell to a precision of 50 μK for periods of hours. The thermostat was also designed to minimize temperature gradients across the optical cell. We were unable to measure any temperature difference between cell top and bottom; a gradient of 50 μK/cm could have been detected.

To demonstrate the importance of isothermal conditions we deliberately induced a temperature gradient across the cell by reducing the temperature of the outermost thermostat stage. This caused a thick film of liquid SF_6 to condense on the prism. The film achieved a steady state through a competition between condensation and draining. These draining films had thicknesses of several micrometers and were visible as horizontal interference fringes extending several millimeters above the liquid-vapor meniscus. We were able to predict the fringe positions as a function of height with a model due to Nusselt.[9] The draining film extends to a height $h = (dP/dT)_{coex}(-\Delta T)/\rho_v g$, where ΔT is the temperature difference between the prism surface and the SF_6 far away. The thickness of the film draining in Poiseuille flow increases as $z^{1/2}$, where z is distance measured downward from the top of the film. For SF_6 near its critical point, a ΔT of 0.1 mK will cause a draining film on the order of 1 mm high and hundreds of nanometers thick. Modulation of the draining film at $t = -0.01$ showed that the ellipsometer signal-to-noise ratio was about 40-to-1, which corresponds to a thickness resolution of 5 nm.

A second thermal consideration was laser heating. The unfocused laser was attenuated with neutral-density filters (before the polarizer) until we found a range of light levels that did not affect the wetting layer. Most of the data were taken with 1 μW incident on the film. Periods of several days were allowed for equilibration at each temperature, and the ellipsometric measurements remained stable for 24 h periods.

We turn now to the problem of translating the ellipsometric data into wetting layer thicknesses. For this one must model the dielectric constant profile from the fused silica through the wetting layer and into the vapor. We first established that we would not be able to distinguish, within the accuracy of our data, between the predictions of a simple slab model and more sophisticated models. In the slab model one assumes a discontinuous profile in which the dielectric constant is constant within each phase and attains the bulk liquid value within the wetting layer. This is an excellent approximation far from T_c where the bulk correlation length is much smaller than the equilibrium layer thickness. The more sophisticated models

that we considered took into account compression of the liquid SF_6 close to the fused silica surface, the nonabrupt transition from liquid to vapor at the edge of the wetting layer, and effects due to averaging over the 1-mm width of the laser beam.

By far our biggest problem was to account for strain-induced birefringence in the fused silica prism. The strain depended on temperature and was capable of changing the polarization of the light as much as the wetting layer itself. Given this, we exploited the symmetry of the strain with respect to vertical and horizontal planes perpendicular to the fused-silica–SF_6 interface [see Fig. 3(b)]. With symmetry, the optical effects of the prism along paths BC, $A'B'$, and $B'C'$ are simply related to that along AB. Our procedure was to find pairs of ellipsometer nulls at each temperature: one for reflection from the liquid-silica interface below the center of the cell, and one for reflection from the wetting layer at an equal height above the center of the cell. This procedure yields pairs of polarizer and analyzer angles that are related to the optical properties of the prism and the thickness of the wetting layer by nonlinear equations that must be solved numerically. (The birefringence of the prism along AB is equivalent to a partial-wave plate followed by a rotator.[10]) Measurements made above the critical temperature confirmed that the strain was symmetric with respect to the horizontal plane. We were unable to test the symmetry with respect to the vertical plane, but measurements made with different vertical planes indicated that this was not an important factor. Measurements were also made in which the clamping of the prism was changed, and these too gave similar wetting-layer thicknesses.

An alternative procedure for taking strain into account involves making two measurements at a single height above the liquid-vapor meniscus: one with the wetting layer present and in thermal equilibrium, and one with the wetting layer burned off by greatly increasing the laser power. The prism that we used was not designed to exploit this possibility.

The theoretical curves in Fig. 2 were obtained by evaluation of the function $F(L)$ in Eq. (1) with the slab model. For the solid curve $F(L)$ is given by Eq. (4.14) in Ref. 2, while for the dashed curve it is given by Eq. (4.18) in the same reference. For the dielectric constants of fused silica and liquid and vapor SF_6 evaluated at imaginary frequencies, we adopted a Ninham-Parseghian representation[11,12]:

$$\epsilon(i\omega) = 1 + (n^2 - 1)/(1 + \omega^2/\omega_0^2),$$

with n the index of refraction in the visible region and ω_0 the most important absorption frequency in the ultraviolet. For fused silica we took[13] $n = 1.457$ and[12] $\omega_0 = 2 \times 10^{16}$ rad/s. For SF_6 we took indices of refraction from Rathgen and Straub[7] and $\omega_0 = 2 \times 10^{16}$ rad/s

for both liquid and vapor.[14] The solid theoretical curve changed by less than 5% as we varied ω_0 for SF_6 from 1×10^{16} to 4×10^{16} rad/s. This insensitivity to the fluid properties is expected from the DLP theory whenever the substrate (fused silica here) has a polarizability per unit volume which is much higher than that of the adsorbed liquid film.

In conclusion, we have found that wetting layers on a vertical surface are extremely sensitive to temperature gradients; however, if one is careful to eliminate these, one finds equilibrium thicknesses in agreement with the DLP theory of dispersion forces.

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