Capillary-Wave and Intrinsic Thicknesses of the Surface of a Simple Liquid

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Ellipsometric measurements of the thickness of the liquid-vapor interface of carbon tetrachloride between room temperature and near the critical temperature are shown to indicate that the surface thickness is determined by capillary-wave excitations at large $t=(T_c-T)/T_c$, but by an intrinsic interfacial thickness at small t, the crossover occurring when δ/d lies in the range between 1 and 2, where δ is a measure of the thickness and d is the molecular diameter.

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As the surface of a liquid is traversed the density varies from the liquid value to the vapor value. There are two models for this interface. The first, originally due to Van der Waals (discussed fully by Rowlinson and Widom[1]), assumes that a free-energy functional exists for the densities in the interface region lying between the values of the coexisting homogeneous liquid and vapor phases; this model leads to an "intrinsic" interfacial density profile, where the density approaches that of the homogeneous phases exponentially with a characteristic length which is identified as the bulk correlation length ξ. The alternative model (Buff, Lovett, and Stillinger[2]) is based upon thermal excitation of capillary waves at the sharp interface between the two phases. This thermal activation leads to a mean square thickness

$$\langle \xi_{\mathrm{cw}}^2 \rangle = (k_B T/4\pi\sigma)\ln(k_m^2 l^2+1),$$

where σ is the interface surface tension, $l^2=\sigma/(\Delta\rho g)$ is the capillary length, and k_m is an upper cutoff wave vector for the capillary waves. This thickness depends, albeit weakly, upon properties external to the liquid, with a divergence in $\langle \xi_{\mathrm{cw}}^2 \rangle$ as $g \to 0$, and there is no identifiable intrinsic thickness. This paradox has been reviewed in the literature, for instance by Rowlinson and Widom[1] and by Percus and Williams[3]; one suggestion (Weeks) is to identify the capillary modes whose wave vectors are greater than $1/\xi$ with the intrinsic thickness, and another is to superimpose the capillary waves upon an intrinsic profile.

In this paper a measurement of the thickness of the liquid-vapor interface of carbon tetrachloride using ellipsometric techniques is reported, in the range from room temperature to near the critical temperature. Neither of the above models satisfactorily predicts the observed temperature dependence, although the capillary-wave model is clearly preferred. An alternative interpretation is proposed, based upon the need for a consistent interface thickness throughout the temperature range. Far from the critical point the thickness follows the capillary-wave model; closer to the critical temperature a crossover to intrinsic behavior occurs. It is believed that the results show that large-amplitude, short-wavelength excitations are not sustained by the surface, nature thus avoiding the theoretical paradox described above.

Carbon tetrachloride has been chosen for its convenient critical temperature (283.15 °C) and because both the surface tension and the coexisting densities follow the scaling-law variation throughout the temperature range. Young's data[4] for $\Delta\rho=\rho_l-\rho_v$ and $\rho_l+\rho_v$ are shown in Fig. 1, along with data for σ.[5] There is a slight curvature in the $\Delta\rho$ data; for $t>0.24$ we find $\Delta\rho=\Delta\rho_0 t^\beta$ with $\Delta\rho_0=2.022$ g/cm^3, $\beta=0.316$, and $\rho_l+\rho_v=1.1145+1.012t$ g/cm^3; for $t<0.24$, $\Delta\rho_0=2.103$ g/cm^3, $\beta=0.335$, and $\rho_l+\rho_v=1.1136+1.000t$ g/cm^3. For $\sigma=\sigma_0 t^\mu$ we find $\sigma_0=67.7$ erg/cm^2, and $\mu=1.230$. Here $t=(T_c-T)/T_c$. Since both σ and $\Delta\rho$ follow the scaling-law variation, the same is to be expected for the surface thickness.

A quantity η which characterizes the interface is obtained from ellipsometric measurements.[6] Traditionally this has been interpreted in terms of the intrinsic profile with the density varying continuously between liquid and

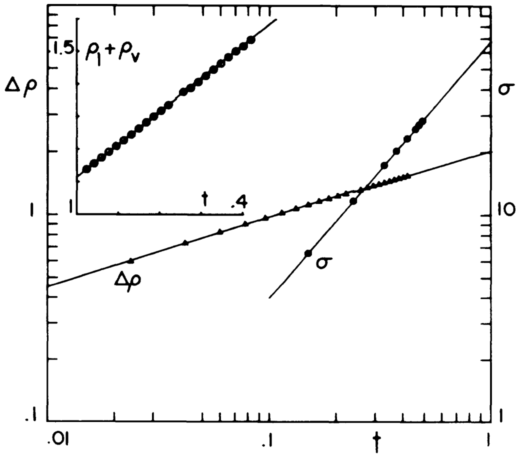

FIG. 1. The densities of the coexisting phases (grams per cubic centimeter) and the surface tension (ergs per square centimeter) as a function of t. The straight lines show the scaling-law fits used in analyzing the ellipsometric data.

vapor values, and

$$\eta_i = \int dz(\varepsilon-\varepsilon_1)(\varepsilon-\varepsilon_2)/\varepsilon = (\varepsilon_1-\varepsilon_2)\ln(\varepsilon_1/\varepsilon_2)\delta,$$

where the integral has been evaluated with the use of a $\tanh(z/2\delta)$ profile. Here ε is the optical dielectric constant, which through its dependence upon density becomes a function of z, the coordinate normal to the plane of the surface. ε_1 and ε_2 characterize the coexisting phases. An alternative interpretation of η was proposed by the present author and based upon the surface roughened by thermally activated capillary waves. It was shown in Ref. 6 that waves whose wave vectors are greater than that of light in the media determine the ellipsometric response, with η given by

$$\eta_{\mathrm{cw}} = -k_B T(\varepsilon_1-\varepsilon_2)^2 k_m/\pi\sigma(\varepsilon_1+\varepsilon_2).$$

Note that the dominant temperature dependence of η_i is given by $\Delta\varepsilon^2\xi$ or $\Delta T^{2\beta-\nu}$, while for η_{cw} it is given by $T\Delta\varepsilon^2 k_m/\sigma$ or $T(\Delta T^{2\beta+\nu-\mu})$. Since both $2\beta-\nu$ and $2\beta+\nu-\mu$ are small, η_{cw} through the T prefactor varies more rapidly at large t.

The high vapor pressure of the liquid in the critical region (45 atm for CCl_4) caused the major experimental difficulty in this measurement. Tests indicated that small, almost spherical glass cells (about 3 cm in diameter) could withstand these pressures. The CCl_4 charge was sealed into the cell under vacuum, and the cell then placed in a thick-walled copper enclosure, which had two small (3-mm) apertures to allow the incident and reflected light beams to pass. The copper enclosure was mounted in a temperature-controlled furnace. Ellipticity and temperature were monitored continuously throughout the experiment, and values were recorded only under equilibrium conditions. Values for ε_1 and ε_2 were needed to derive η from the coefficient of ellipticity. These were calculated from the density data with the Clausius-Mossotti relation, with use of the room-temperature value to determine the molecular polarizability. While small systematic errors may enter in this procedure, the scaling variations will be reliable in the small-t region.

Figure 2 shows the experimental data for η from room temperature to 275°C (t in the range 0.47 to 0.013). For t smaller than 0.08, η is almost constant, varying as $t^{-0.017}$. For larger values of t a strong temperature dependence is observed. The two surface models have been used to analyze these data. Figure 3 shows both δ and L as functions of t, where k_m derived from the capillary-wave model has been set equal to π/L.

The intrinsic model gives δ varying with exponent $\nu \approx 0.7$ at small t, but becoming steeper at large t; the capillary-wave model gives L varying with about the same exponent at large t, but becoming less steep at small t. A single straight line passes remarkably through both the small-t intrinsic data and the large-t capillary data as shown in Fig. 3, strongly suggesting that each model has its separate region of applicability, and that the factor relating k_m to $1/\delta$ is π. The line shown has $\delta_0/d = 0.442$ and $\nu = 0.683$, where d is the molecular diameter (5.16 Å).

The failure of each model outside its region of applicability is emphasized in Fig. 2, where both the intrinsic prediction at large t and the capillary-wave prediction at small t fall well away from the experimental data. A fit for the capillary-wave model at small t is also shown which is unsatisfactory at large t.

An effort has been made to fit a mixed model[6] with both intrinsic and capillary-wave contributions to the experimental η. This has been unsuccessful, because subtracting an almost temperature-independent η_i leads to a

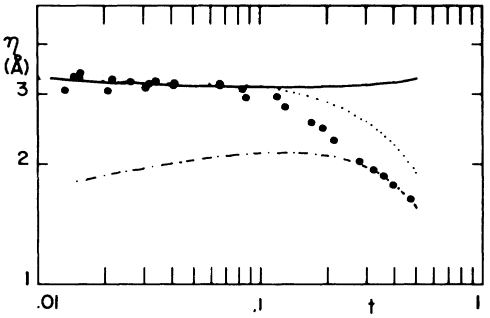

FIG. 2. Experimental η as a function of t. The full line shows the prediction of the intrinsic model at large t. The predictions of the capillary-wave model are shown by the broken lines, where the parameters have been adjusted to match the data in the appropriate regions. For the full line $\delta_0 = 2.15$ Å, $\nu = 0.70$; for the dotted line $L_0 = 2.09$ Å, $\nu = 0.58$; for the dot-dashed line $L_0 = 2.38$ Å, $\nu = 0.69$.

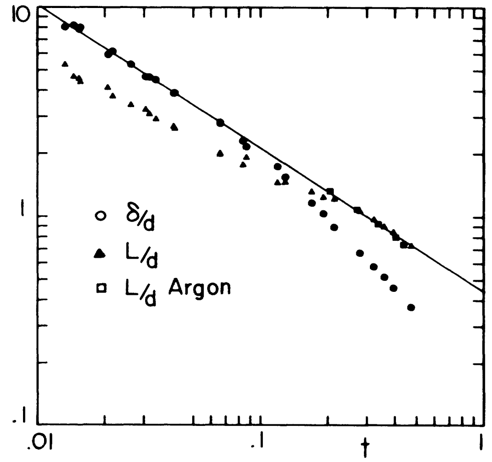

FIG. 3. δ/d and L/d as functions of t derived by use of the intrinsic and capillary-wave models (with $k_m = \pi/L$). The straight line has the parameters $\delta_0 = 2.28$ Å and $\nu = 0.683$. The figure also shows L/d for argon from Ref. 6.

stronger temperature dependence in η_{cw} at large t and a corresponding weaker temperature variation for k_m. It seems essential to apply each model separately in each region.

The remarkable continuity of the fit shown in Fig. 3 is probably fortuitous. In the intrinsic region theoretical analysis prefers the Fisk-Widom profile to the tanh profile used in the present analysis. No analytic relation between η and δ is available for that profile, but numerical integration indicates that values of δ about 15% smaller over the whole range of t are obtained. In the capillary region the bare surface tension σ_0 should perhaps be used in the expression for η_{cw}, related to the experimental surface tension by $\sigma_0 = \sigma + 3kTk_m^2/16\pi$. This correction decreases the derived values for L/d by about a factor of 1.5. While the details of the analysis remain to be clarified, both the failure of each model to predict the full temperature variation and the matching of the exponents in the two regions appear quite certain.

In summary, the data strongly suggest (i) that the surface is characterized by an intrinsic thickness throughout the temperature range, with $\delta/d = 0.44t^{-0.68}$; (ii) the surface ellipsometric response is that of an intrinsic interface at small t, and of a capillary-wave interface at large t with $k_m = \pi/\delta$; and (iii) the crossover from one region to the other occurs in the region where δ/d lies between 1 and 2.

Support for this interpretation of the data comes from the universal scaling relation between σ and ξ. Moldover[7] shows that the ratio $R = \sigma_0(\xi_0^+)^2/k_B T_c$ has a value between 0.35 and 0.45 for a variety of critical liquid systems. ξ_0^+ in this expression is the prefactor for the bulk correlation length in the one-phase region. If δ is identified[8] with ξ^+, the present data give $R = 0.46$. Egelstaff and Widom[9] have suggested an alternative estimate for the thickness near the triple point, namely $0.07L = \sigma\chi$, where χ is the isothermal compressibility. With $\sigma = 26$ erg/cm^2 and $\chi = 107 \times 10^{-12}$ cm^2/dyn at room temperature[10] this relation predicts $L/d = 0.72$, in comparison with 0.73 with the present data if L is identified with δ.

The temperature dependence of the surface of other pure liquids has been studied only by Wu and Webb[11] and the present author.[6] Wu and Webb measured the reflectivity of the surface of SF_6 near the critical temperature for $t < 5 \times 10^{-2}$. They analyzed the data in terms of an intrinsic interface, and found that both the Fisk-Widom and the error-function profiles (which latter results from the space average of the capillary-wave excitation) gave reasonable predictions for the temperature dependence, with a slight preference for the latter profile. I studied liquid argon in the range $t = 0.45$ to 0.2. Those data analyzed with the capillary-wave model are also shown in Fig. 3. The exponent for L of 0.7 also suggests that the argon surface is characterized by capillary-wave excitations in this region.

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