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Thickness of the Surface of Liquid Argon near the Triple Point

D. Beaglehole
Victoria University of Wellington, Wellington, New Zealand

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The coefficient of ellipticity of the liquid-vapor interface of liquid argon has been measured to be $\bar{\rho}\times 10^4 = 5.7 \pm 0.4$ at 90°K, rising to 8.8 ± 0.6 at 120°K. Assuming a Fermi density profile and isotropy of the dielectric constant in the interface region, this yields a 10%-90% interface thickness $t(90\text{°K}) = 7.9 \pm 0.5$ Å and $t(120\text{°K}) = 15.2 \pm 1.0$ Å, averaged over a surface dimension of the wavelength of light. The measurement is compared with predictions, and theoretical uncertainties are emphasised.

Liquid argon is the classic simple liquid for testing theoretical descriptions of the fundamental properties of liquids. Interest has recently turned to the surfaces of simple liquids. One theoretical approach has been to study the thermal excitations of surface waves,[1,2] another to study the statistical mechanics of the interface,[3-8] and a third to carry out computer simulations of the interface.[9-11] The predictions of theory have been summarized by Lekner and Henderson[7]; the predictions show considerable variation, for instance, estimates of the 10%-90% thickness t of the interface density profile near the triple point for liquid argon range between $1.0d$ and $3.8d$, where d is the atomic diameter, 3.4 Å for argon. A direct experimental measurement is thus important. An ellipsometric determination of the thickness is reported here, for temperatures between 85 and 120 °K. While the surfaces of many other liquids have been studied by ellipsometry,[12] none are simple and cannot reasonably be compared with theory.

The ellipsometer is based upon that of Jasperson and Schnatterly[13] and measures the real and imaginary parts of the complex reflectivity ratio $r = r_p/r_s = \rho e^{i\Delta}$, where r_p and r_s are the amplitude reflectivities for p- and s-polarized light, respectively. At the Brewster angle of incidence $\Delta = 90°$ and $\mathrm{Im}r = \bar{\rho}$, the coefficient of ellipticity, while $\mathrm{Re}r = 0$, a condition which is used to accurately position the ellipsometer at this angle. For interfaces which are thin compared with the wavelength of the light,

$$\bar{\rho} = \frac{\pi}{\lambda}\frac{(\epsilon_1+\epsilon_2)^{1/2}}{\epsilon_1-\epsilon_2}\int\frac{(\epsilon-\epsilon_1)(\epsilon-\epsilon_2)}{\epsilon}\,dz\,, \qquad (1)$$

where $\epsilon = \epsilon(z)$ is the variation of the dielectric constant through the interface and the light beam is incident onto the surface of a medium with dielectric constant ϵ_2 from a medium with dielectric constant ϵ_1. The Expression (1) was first derived by Drude[14] and holds for a transition region which is homogeneous, i.e., $\epsilon(z)$ is uniform at a depth z, and isotropic. For simple liquids the Clausius-Mossotti relation between ϵ and density is followed, and the measurement of $\bar{\rho}$ leads to an estimate of the interface thickness once a functional form for the density profile is assumed.

The liquid argon was contained in a well-annealed Pyrex sphere of 3 cm diam, and the light beam from a He-Ne laser, $\lambda = 6328$ Å, entered the cell normal to the glass wall, reflecting off the interface from the liquid side, thus avoiding any condensation on the upper half of the sphere. The sphere showed little strain birefringence even at 120 °K when the pressure in the cell was 12 atm, and this small birefringence had negligible effect on the determination of $\mathrm{Im}r$ exactly at the Brewster angle. The area of surface illuminated by the beam was approximately 1 mm^2. The Brewster angle itself provides a determination of the bulk dielectric constant: Within the precision of the angle measurement, the value at

85 °K agreed with the value of Sinnock and Smith.[15]

The value of $\bar{\rho}$ at 90 °K was found to be $-(5.7 \pm 0.9)\times 10^{-4}$. The temperature dependence is shown in Fig. 1, where the data points are the values taken during three slow warming cycles to 120 °K. The random scatter is partly due to fluctuations in the liquid and partly due to off-Brewster-angle conditions—the Brewster angle varied with temperature, and hence time. (The experimental uncertainty is smaller than that achieved by other workers[12].)

If the density at the interface is taken to follow the Fermi profile, then $\bar{\rho}$ at 90°K implies, with use of Eq. (1), a 10%-90% thickness $t(\mathrm{F}) = 7.9 \pm 0.5$ Å, while if the error-function profile is assumed, $t(\mathrm{erf}) = 8.2 \pm 0.5$ Å. At 120 °K the corresponding thicknesses are $t(\mathrm{F}) = 15.2 \pm 1.0$ Å and $t(\mathrm{erf}) = 15.8 \pm 1.0$ Å.

A word of caution must be inserted here. Application of Eq. (1) to the liquid-vapor interface is itself subject to some uncertainty. There are two points to note. Firstly, anisotropy of $\epsilon(z)$ in the interface region modifies the Drude relation between $\bar{\rho}$ and t (see Abelès[16]). There are indications (Castle and Lekner[17]) that indeed a small anisotropy will be present in the surface of a simple liquid, which depends upon the interface thickness, which would lead to an underestimate of t by about 10% at 90 °K and 3% at 120 °K. Secondly, some uncertainty arises from the assumption of uniformity in the interface region used to derive Eq. (1), since there are indications (see below) that wave excitations lead to a rough rather than uniform transition region.

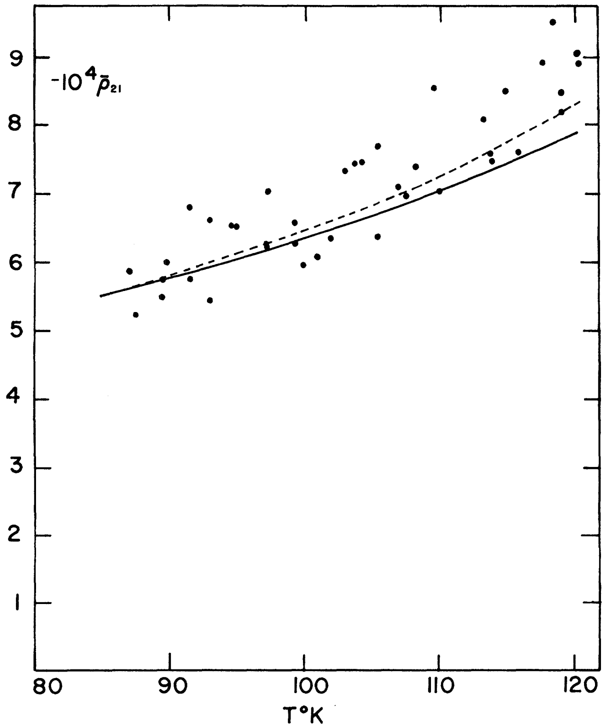

FIG. 1. The variation of $\bar{\rho}$ with temperature. Dots indicate experimental values taken during three slow warmings from 85 to 120 °K. The full curve shows the variation predicted by Eq. 1 with use of the experimental surface tension and $k_{\mathrm{max}} = 2\pi/t$, while for the dotted curve k_{max} is held constant.

Surface-wave theory[1,2] uses the surface-tension wave dispersion relation to predict a mean square surface displacement:

$$\xi_w^2 = (k_B T/2\pi\sigma)\ln(k_{\mathrm{max}}/k_{\mathrm{min}}). \tag{2}$$

Here T is the temperature, σ the interface surface tension (which varies with temperature), and k_{max} and k_{min} are upper and lower cutoffs for the wave modes. k_{max}^{-1} is assumed to be determined by the surface thickness itself, while k_{min}^{-1}, determined by the longest-wavelength mode excited clearly depends upon the dimension of the surface studied. In a light-reflection experiment, long-wavelength oscillations of the surface only modulate the angle of reflection and, since both Rer and Imr are linear with this angle around the Brewster angle, these oscillations do not affect the coefficient of ellipticity. In these experiments then, only contributions to ξ_w^2 from excitations with wavelengths shorter than λ, the wavelength of light, will be observed. The density profile associated with the surface waves is of the error-function form.[10] If one sets k_{max} equal to $2\pi/t$ and k_{min} equal to $2\pi/\lambda$ and uses the experimental value for the surface tension[18] $\sigma = 11.86$ erg/cm^2, this theory predicts $t_w(\mathrm{erf}) = 2.563\xi_w(\mathrm{rms} = 8.22$ Å at 90 °K, a value which is perhaps fortuitously close to the experimental value, given the theoretical uncertainties in deriving t from $\bar{\rho}$. The predicted temperature dependence of $\bar{\rho}$ is shown in Fig. 1. It is slower than observed experimentally. If k_{max} is held constant, the variation is closer to that observed. If the estimates of anisotropy are borne out by further theory, the predicted temperature dependence will be close to experiment.

Theoretical work has in some cases[1,4-6] separated a wave contribution to the thickness from an "intrinsic" thickness, in writing

$$\xi^2 = \xi_w^2 + \xi_1^2. \tag{3}$$

Instead of the experimental surface tension, a "bare" surface tension σ_0 is used in Eq. (2), with

$$\sigma_0 = \sigma + (3/16\pi) k_B T k_{\max}^2. \tag{4}$$

In this case, theory predicts (with $k_{\max} = 2\pi/t_w$) $\sigma_0 = 18.8$ erg/cm^2 and $t_w(\text{erf}) = 6.67$ Å at 90 °K, which when subtracted from the experimental value leaves an intrinsic component $t_i(\text{erf}) = 4.8 + 0.6$ Å, increasing to 11.3 Å at 120 °K.

Computer simulation[9-11] can handle only a small number of atoms, with, consequently, a small surface dimension. With a surface dimension of $5d$, Ref. 9 finds $t = 1.7d$, while Ref. 10 with a surface dimension of $4d$ finds $t = 1.3d$. Simulations which vary the area of the surface[9] find a slow increase in the thickness as the surface dimension increases, and give support to the suggestion of an intrinsic plus a wave contribution. Kalos, Percus, and Rao[11] have found transverse correlations in their simulated interface, which appears rough rather than uniform.

In summary, the ellipsometry study reported here provides for the first time a measurement on a simple liquid to compare with theory, and it is evident that further theoretical work is needed to clarify the nature of, and the interaction of light with, the liquid-vapor interface.

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Positional and Orientational Correlations in the Graphite Intercalate $C_{24}Cs$

Roy Clarke,[a] N. Caswell,[b] S. A. Solin,[c] and P. M. Horn[d]
James Franck Institute and Department of Physics, University of Chicago, Chicago, Illinois 60637

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An x-ray study of the Cs layers in $C_{24}Cs$ is presented. The Cs layer has a uniform 2-d liquidlike structure at 300 K not in registry with the graphite layers. A crossover to 3-d interlayer correlation is observed at 165 K. Single-crystal measurements show that the Cs layers rotate relative to the graphite ⟨100⟩ directions. An orientational ordering between two positionally disordered phases occurs at 228 K and a new transition to a mixed registered phase at 50 K is reported.

There have been several recent studies[1-5] of alkali-metal graphite intercalates showing an interesting variety of ordering phenomena associated with the intercalant atoms. These systems provide a unique arena for studying the melting of layers of metal atoms under varying degrees of interlayer coupling as the intercalation "stage," n, is varied (n = number of carbon layers between intercalant layers). This Letter describes a detailed x-ray study of the structure and temperature dependence of such intercalant layers in a higher-stage ($n = 2$) compound, $C_{24}Cs$. We will show that *orientational* correlations of the intercalant interatomic bonds, which have been ignored in previous studies, are very important for a complete description of the physical properties of some of the higher-stage cesium intercalates.

X-ray diffuse scattering experiments were