Thickness of the Liquid-Vapor Wetting Layer

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(Received 3 November 1981)

In certain binary solutions the lower of the two liquid phases forms a layer which intrudes between the upper liquid phase and the vapor. The intruding layer's thickness (measured by ellipsometry) was between 70 and 400 Å. It varied approximately as $L^{-1/3}$ where L is the height spanned by the upper liquid phase. This behavior was predicted by de Gennes using the idea that the long-ranged part of the intermolecular potential governs the layer's thickness. Deviations from $L^{-1/3}$ behavior occur near consolute points.

PACS numbers: 68.10.Cr, 68.10.Gw, 64.70.Ja, 78.65.Jd

Heady and Cahn[1] observed the striking phenomenon of a layer of a more dense liquid phase in equilibrium above a less dense liquid phase. Strong surface forces maintained this density inversion. Here, we report ellipsometric measurements of the thickness of this layer and we compare the data to the theory of de Gennes.[2]

In Fig. 1 we have sketched two binary liquid mixtures below their critical solution temperatures, T_c. In each container the upper liquid phase, the lower liquid phase, and the vapor are denoted by u, l, and v, respectively. Cahn[3] has argued that sufficiently near T_c, one of the liquid phases must completely wet the interface between the other liquid phase and the vapor. It often happens that this wetting phase is the denser of the two liquid phases as illustrated in Fig. 1. Then the l phase forms the intruding layer between the u and v phases. Moldover and Cahn demonstrated that it can be made to form abruptly as a parameter related to the distance from T_c is varied.[4] Its formation suggests a description in terms of a phase transition in the structure of the u-v interface.

In the absence of external fields that tend to separate the u and l phases, the intruding layer would be of macroscopic thickness. In the gravitational field the layer thins until the sum of the gravitational potential energy per unit area $\Delta\rho gLh$ (where $\Delta\rho$ is the difference of the densities of the l and u phases, g the gravitational acceleration, L the height spanned by the u phase, and h the thickness of the wetting layer) and the free energy per unit area due to the finiteness of the layer's thickness is minimized. De Gennes[2] suggests that the contribution to the latter arising from the long-range van der Waals forces is W/h^2 (neglecting retardation), where W depends on the polarizabilities α of the phases through $W \propto -(\alpha_v - \alpha_l)(\alpha_u - \alpha_l)$. When $W > 0$, de Gennes finds W/h^2 to be the most important of the terms that together balance $\Delta\rho gLh$. Thus he estimates the thickness of the wetting layer by minimizing $\Delta\rho gLh + W/h^2$ to obtain

$$h = (2W/\Delta\rho gL)^{1/3}. \tag{1}$$

In contrast with Eq. (1), theories such as that of Cahn[3] which ignore long-ranged interactions would predict that h is proportional to $\ln L$. In

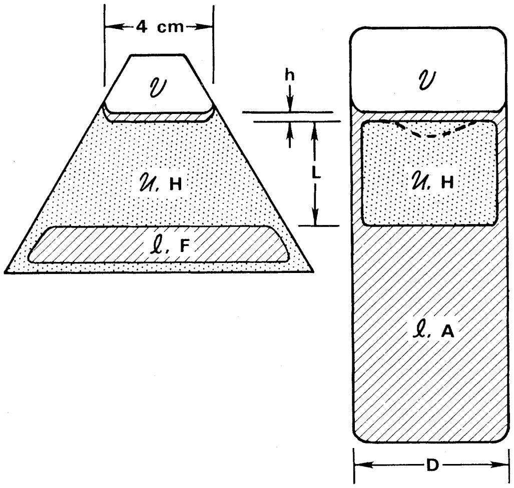

FIG. 1. Configuration of the hydrocarbon-fluorocarbon mixture (left) and alcohol-hydrocarbon mixture (right) used to measure the dependence of the thickness of the intruding layer (h) upon the height of the upper liquid phase (L). The fluid phases are v, vapor; u, upper liquid phase; and l, lower liquid phase. The predominant components are H, hydrocarbon; F, fluorocarbon; and A, alcohol.

the experiments to be described below we find that far below T_c, h is indeed proportional to $L^{-1/3}$ in agreement with Eq. (1).

With W proportional to $\alpha_u - \alpha_l$, both W and $\Delta\rho$ would vary as $(\Delta T)^\beta$ with $\beta \simeq \frac{1}{3}$ and with ΔT the temperature interval from the u-l consolute point. It follows that the ratio $W/\Delta\rho$ should then be constant; i.e., h should be nearly independent of ΔT. Far from T_c we confirm this; however, close to T_c our data are inconsistent with both the T and L dependence implied by Eq. (1). This may not be surprising because near T_c the correlation length in the u and l phases exceeds the thickness that the intruding layer would have had if h were independent of ΔT.

Preliminary experiments have been carried out on two different mixtures by using somewhat different techniques. We now describe them.

The mixture methylcyclohexane-perfluoromethylcyclohexane was studied at the U. S. National Bureau of Standards. Many properties of this hydrocarbon-fluorocarbon (H-F) system are well known.[1] The fluorocarbon-rich phase is the lower liquid phase; however, this phase does not wet the quartz container (see the sketch on the left-hand side of Fig. 1). Thickness equilibration must then occur by diffusion through the u phase. Our H-F samples were studied in a two-stage thermostat designed to facilitate *in situ* stirring with a glass-encapsulated magnet. To obtain more reproducible data we waited many hours (typically 12) after stirring the H-F samples at the temperatures of interest. The remaining scatter in the data is not from instrumental noise. It may result from residual thermal gradients or vibrations.

An ellipsometer was constructed to measure both the real and the imaginary parts of the ratio r_p/r_s of the liquid-vapor interface above the H-F system. (r_p is the amplitude reflectance for p-polarized light; r_s is the amplitude reflectance for s-polarized light.) The measurements were made with 6328-Å light incident at 59.5° in the vapor phase. Data were taken at three temperatures: 23, 43.13, and 45.27 °C. The corresponding values of $t = (T_c - T_c)/T_c$ are -0.07, -0.009, and -0.002, respectively. At each temperature L was varied by changing the overall composition of the mixture. The H-F data are plotted in Fig. 2. The three solid curves in Fig. 2 are calculated using the following assumptions: (1) The intruding layer has the same index of refraction as that of the l phase, (2) the layer's boundaries are sharp, and (3) the layer is less than $\frac{1}{2}$ wavelength of light thick. Some evidence supporting this picture comes from the fact that the data for various values of the height of the upper phase, L, at $t = -0.07$ all fall near the calculated curve. The same assumptions have been used to interpret the data of Fig. 2 to yield the layer's thickness (h) vs L (see solid squares in Fig. 3).

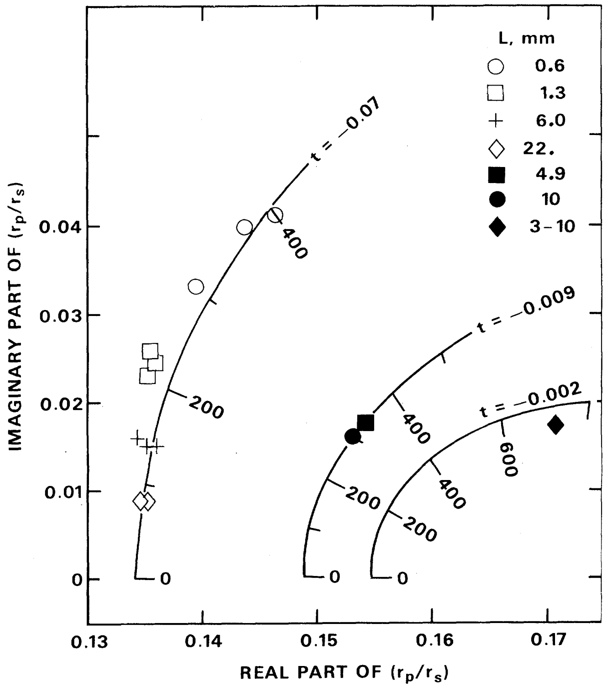

FIG. 2. Measured and calculated complex reflectance ratio for the H-F mixtures. Many measurements of r_p/r_s at the smaller values of t overlap and are plotted as a single symbol. The thickness of the intruding layer in angstroms is indicated.

In contrast with the data at $t = -0.07$, it was not possible to detect any dependence of h upon L at $t = -0.002$. This is in conflict with Eq. (1).

The mixture methanol-cyclohexane was studied at Cornell University. Many properties of this alcohol-hydrocarbon (A-H) system are well known.[5,6] The alcohol-rich phase is the lower liquid phase. It completely wets glass containers, giving a continuous l phase (see the sketch on the right-hand side of Fig. 1). Two different samples were used. The first A-H sample had a T_c of 50.8 °C, suggesting[6] the presence of 0.4 wt.% water impurity. This water concentration is low enough that the system falls well within the wetting range as found by Moldover and Cahn.[4] The second A-H sample had a T_c of 45.27 ± 0.05 °C, close to 45.14 °C reported for pure components.[5]

The A-H system was studied with an ellipsom-

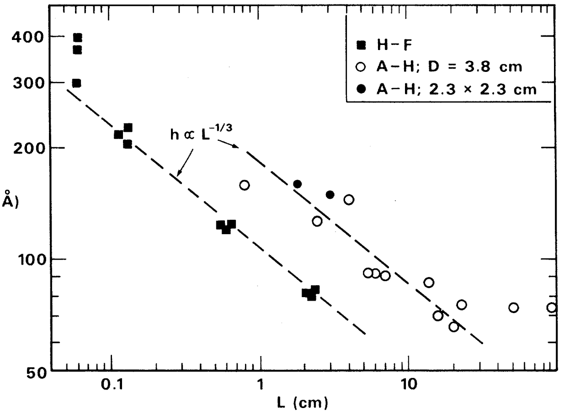

FIG. 3. Thickness of the intruding layer (h) as a function of the height spanned by the upper liquid phase (L).

eter operating at the temperature-dependent Brewster's angle for the hydrocarbon-rich upper phase. Under these conditions, the quantity that is measured is the coefficient of ellipticity,[7] $\bar{\rho} \equiv \mathrm{Im}(r_p/r_s)$. For consistency with the known refractive indices of the liquid phases and with the picture of the vapor-liquid interface as consisting of a thin layer of the methanol-rich phase $\bar{\rho}$ must be positive. Measurements did confirm that $\bar{\rho}$ is greater than zero.

The A-H mixture was held in vertical glass tubes of varying diameter (D) and height. In this configuration, equilibration of the intruding layer with the bulk of lower liquid phase is probably facilitated by the presence of the wetting layer between the glass and the upper phase. If the liquids were allowed to stand for some time the wetting layer at the liquid-vapor interface was often observed to develop into a drop with zero contact angle shown by the dashed line in Fig. 1. This appears to be due to vapor condensing on the glass walls and draining into the central surface area and is not an equilibrium phenomenon. When L was small this drop formation occurred more readily and $\bar{\rho}$ showed considerable fluctuation. The smallest values of $\bar{\rho}$ have been taken to indicate the intrinsic equilibrium thickness. Under the assumption that the intruding layer has the same index of refraction as the lower phase, these smallest values of $\bar{\rho}$ are interpreted as measurements of h for the A-H system and are also shown in Fig. 3. [The A-H data plotted are for the first sample ($T_c = 50.8\,^\circ\mathrm{C}$) at room temperature with $D = 3.8$ cm.] As indicated in Fig. 3, these A-H data are also consistent with de Genne's prediction that $h \propto L^{-1/3}$.

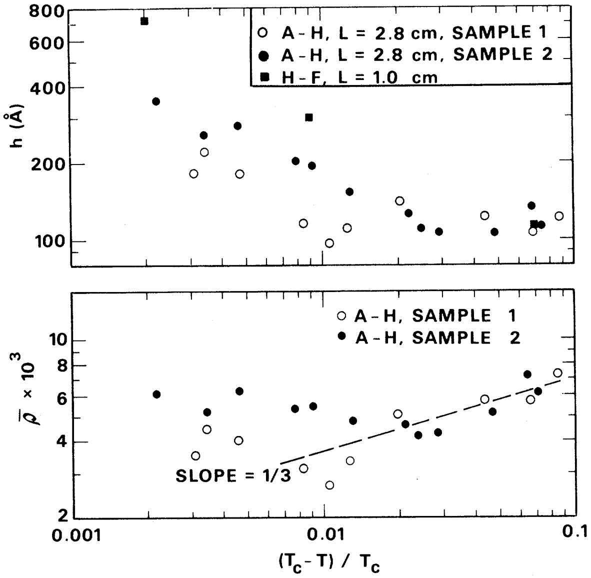

FIG. 4. Top: Thickness of the intruding layer as a function of the reduced temperature, assuming that the layer is identical in composition with the lower liquid phase. Bottom: The imaginary part of r_p/r_s as a function of the reduced temperature.

We remarked above that the h from Eq. (1) would be independent of ΔT. Because $\bar{\rho}$ is proportional to h and to the difference in indices of refraction of the two liquid phases, this implies $\bar{\rho} \sim (\Delta T)^{1/3}$. It is seen in Fig. 4 that below T_c the A-H data are consistent with this for $|t| \gtrsim 0.01$ but at smaller $|t|$, $\bar{\rho}$ is nearly constant or perhaps increases slightly as $|t| \to 0$.

Above T_c, $\bar{\rho}$ slowly declines with increasing $|t|$. The slowness of this decline suggests that when $T > T_c$, the remnant of the intruding layer in the cyclohexane-methanol system resembles the multilayer adsorption found by Beaglehole[8] above the consolute temperature of cyclohexane-aniline mixtures.

We have described two experiments carried out with quite different chemical systems in different laboratories using somewhat different techniques. Both experiments yield values for h between 50 and 400 Å at room temperature. Both experiments result in $h \propto L^{-1/3}$ for small heights of the u phase near room temperature as suggested by de Gennes on the assumption that the wetting layer is stabilized by a van der Waals interaction term W/h^2. The approximate fitting of Eq. (1) represented by the dashed lines in Fig. 3 is consistent with $W = 50 \times 10^{-17}$ erg for the H-F system and $W \sim 0.4 \times 10^{-17}$ erg for the A-H system. These values of W are much smaller than de

Gennes's estimate: $W = 5 \times 10^{-14}$ erg. We have no explanation for this discrepancy.

The data for the A-H system suggest that there may be departures from $L^{-1/3}$ at large heights at room temperature (although there could be some doubt about equilibrium in the tallest samples). The data for the H-F system are inconsistent with $L^{-1/3}$ at $t = -0.002$ (no L dependence could be detected). Furthermore, the temperature dependence of h, as displayed in Fig. 4, is not fully consistent with Eq. (1). We could suppose that the intruding layer was stabilized not only by the free energy per unit area W/h^2 with $W > 0$ but also by an additional term of the form $\gamma \exp(-h/\xi)$ reflecting the effects of short-ranged forces.[2] Even with such a term we were not able to obtain a fully consistent account of the data at all L and ΔT, especially if the parameter γ were required to have the magnitude of a typical interfacial tension and ξ the magnitude and temperature dependence of a near-critical correlation length.

Near the critical point the picture of the wetting layer as a uniform film of l phase with sharp interfaces is undoubtedly oversimplified, and both the theory and the interpretation of the ellipsometric data might require a more realistic picture of the interfacial structure.

In summary, we find that near ambient temperature the L dependence of the thickness of the intruding layer is reasonably consistent with the theoretical picture of de Gennes.[2] Near the critical point there are inconsistencies that may require an altered picture.

This work was supported in part by the Cornell University Materials Science Center and in part by NASA under Contract No. C-62861-C.

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Separation of the D_{4h} and O_h Phases near the Surface of $SrTiO_3$

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(Received 10 November 1981)

Elastic compliance data are reported for thin plates of $SrTiO_3$. An analysis is presented in terms of two spatially separated phases, the one of low symmetry residing near the surface. From the thickness of the surface layers, a static correlation length $\xi = \xi_0(T/T_c - 1)^\nu$, with $\xi_0 = (0.35 \pm 0.02)$ μm and $\nu = -0.68 \pm 0.03$, is deduced.

PACS numbers: 62.20.Dc, 64.70.Kb, 68.25.+j

Recently, several reports have appeared on the separation of phases of different stoichiometric composition near the surface of alloys.[1-3] The conclusion was that a surface favored the presence of one component with respect to the other. This also held for the case of liquid ^{3}He-^{4}He mixtures investigated by third-sound propagation.[4] Coexistence of two phases of D_{4h} and O_h symmetry in crystalline $SrTiO_3$ has also been reported on the basis of x-ray depth profiling.[5] Neutron-scattering experiments[6] failed, however, to confirm these results. Stabilization of a low-symmetry phase by a surface is a fundamental lattice-dynamical problem for which as yet there is little experimental insight. In the present Letter, we analyze data on elasticity and deduce from