8-3-1987

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Abstract

We report measurements of the state of wetting of two liquid mixtures at coexistence near their respective critical consolute temperatures. Borosilicate glass capillary tubes were reacted with hexamethyldisilazane to produce substrates of uniform and controlled silylation. Surfaces of low coverage exhibit a series of first-order partial to complete wetting transitions and obey a short-range force scaling relation. Surfaces of high coverage yield surprising results which may be understood as a consequence of long-range forces.

Disciplines

Physical Sciences and Mathematics | Physics

Comments

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(Received 17 March 1987)

We report measurements of the state of wetting of two liquid mixtures at coexistence near their respective critical consolute temperatures. Borosilicate glass capillary tubes were reacted with hexamethyldisilazane to produce substrates of uniform and controlled silylation. Surfaces of low coverage exhibit a series of first-order partial to complete wetting transitions and obey a short-range force scaling relation. Surfaces of high coverage yield surprising results which may be understood as a consequence of long-range forces.

Close to a bulk critical point, the structure of a liquid is especially sensitive to the presence of a physical boundary through solid-liquid interactions and altered liquid-liquid coupling. Long-range, power-law forces of sufficiently large exponent are irrelevant to bulk as well as certain surface critical phenomena.[1] Therefore, in their investigation of wetting near a bulk critical point, Nakanishi and Fisher[2] make the natural approximation of short-range, contact interactions only. Later workers argue that wetting is not necessarily by bulk criticality and that long-range forces cannot be neglected in real systems. Most recently, Ebner and Saam[3] (ES) provide examples of wetting phenomena in systems near bulk criticality with both contact and power-law substrate-adsorbate potentials. Their wetting phase diagrams share many features with those of Nakanishi and Fisher, but only for the case of weak long-range forces.

In this Letter we present experimental results consistent with theoretical predictions for the case of short-range plus weak long-range forces. In another liquid mixture, previously unpredicted behavior is observed which we propose may be a consequence of strong long-range forces. Our method is capillary rise in which we continuously tune the solid-liquid interaction via surface chemistry.

The method and sample cells used are described by Abeysuriya, Wu, and Franck[4] (AWF). Fluids are at liquid-vapor as well as liquid-liquid coexistence.[5] Borosilicate capillary tubes of radii 0.134 and 0.188 mm are cleaned by sonocation with acetone, methanol, ethylenediamine tetra-acetic acid, distilled H_2O, nitric acid, and distilled H_2O followed by vacuum baking at 120 °C. The tubes are then transferred to an Ar atmosphere and subsequently handled such that they are never exposed to air. This procedure is intended to yield clean, maximally hydroxylated surfaces, free of physically adsorbed water; i.e., with polar silanol groups, Si_sOH, on the surface (subscript s).

The variation of the surface field,[2] h_1, is accomplished by our partially reacting the clean hydroxylated surface with the vapor of hexamethyldisilazane (HMDS),

$NH[Si(CH_3)_3]_2$, according to[6]

$$2[Si_sOH] + HMDS \rightarrow 2[Si_sOSi(CH_3)_3] + NH_3.$$
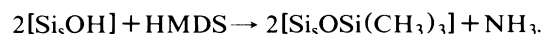
The coverage, or degree of silylation, can be controlled by the pressure of HMDS vapor or time of reaction. Presumably the heavier the silylation, the less attractive to polar fluids is the surface. A useful property of HMDS is that it scavenges physically adsorbed water. So the above reaction goes forward, albeit more slowly, in the presence of water. We find it most convenient to clean many tubes together and react them individually at 2.4 mm Hg from 1 to 500 h. Zettlemoyer and Hsing[6] show that this is slightly below the pressure which yields monolayer coverage. Our procedure gives monotonically increasing coverage with reaction time for tubes with otherwise identical histories. Thus, our substrates are improved on those of AWF in several ways: The silylation of each capillary is uniform over its length, is well defined chemically (no polymerization, coverage less than monolayer), and can be widely varied. However, we have not measured the actual silyl coverage resulting from our reactions. Furthermore we do not have an understanding of the solid-liquid forces necessary to predict h_1 as a function of this coverage. Rather, we characterize our substrates by their wetting properties.

Each sample cell contains one or two hydroxylated tubes of different radii and up to four silylated tubes of identical radii. Capillary parameter, $a^2 = rise \times radius$, should be constant for identical substrates if there is no systematic error in locating the bulk meniscus. Such an error does exist on account of curvature of the bulk meniscus at the sample-cell wall and around the individual tubes. A correction requiring that hydroxylated-tube capillary parameters be identical is not used because it increases the systematic error without altering the power-law fits to be discussed.

Carbon disulfide + nitromethane (CS₂ + NMe). — The four sample cells had bulk critical temperatures in the range $T_c = 63.052 \pm 0.011$ °C (determined visually). Receding-meniscus[7] capillary parameters are plotted

versus temperature in Fig. 1 after being averaged over different positions of the tubes through the bulk meniscus. The hydroxylated tubes are completely wetted by the upper, nitromethane-rich (N^*) phase. They exhibit capillary depression with predicted temperature dependence $a^2 = -a_0^2 |t|^{\mu-\beta}$; a_0 is the capillary constant and $t = (T - T_c)/T_c$ is the reduced temperature with T and T_c in kelvins. This is based on the well-known capillary-rise formula[8]

$$a^2 = (2\sigma_{\alpha\beta}/\Delta\rho g)\cos\theta,$$

where $\sigma_{\alpha\beta} \approx \sigma_0 |t|^\mu$ is the liquid-liquid interfacial surface tension, $\Delta\rho \sim |t|^\beta$ is the liquid-liquid mass-density difference, g is gravitational acceleration, and θ is the contact angle. Note the sign convention, $\cos\theta = -1$ for complete wetting by N^*. We find $a_0^2 = 48.3 \pm 0.5$ mm^2 and $\mu - \beta = 0.94 \pm 0.01$ (cf. theoretical value[9] of 0.935 ± 0.015). This fit is shown in Fig. 1 for complete wetting by either phase; between these extremes lie states of partial wetting.

Lightly silylated tubes exhibit capillary depression and a transition between partial and complete wetting by N^* at a particular T_w ($< T_c$) for each capillary. Since the hydroxylated tubes are completely wetted, we use the capillary rise formula to compute $\cos\theta = a^2_{\text{silylated}}/a^2_{\text{hydroxylated}}$ for each silylated substrate. The predicted temperature dependence is $\cos\theta \sim |t|^{\beta_1-\mu}$ far below T_w. This follows from the short-range force (SRF) scaling relation[10]

$$\sigma_{\alpha\beta}\cos\theta \approx \sigma_0 |t|^{2-\alpha_s} F\left[\frac{h_1}{|t|^{\Delta_1}}\right] \rightarrow \sigma_0 h_1 |T|^{\beta_1}, \quad (1)$$

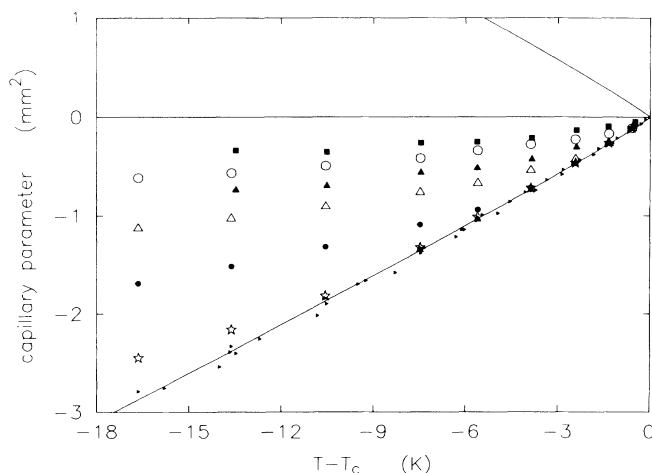with $\beta_1 = 2 - \alpha_s - \Delta_1$ being the surface order-parameter

exponent. We adopt a scale for h_1 such that the argument of F is 1 at the transition point. The small-x limit in Eq. (1) is $F(x) = x$ because F must be both analytic around $x = 0$ and odd by symmetry. To test this prediction, the wetting transition temperatures were estimated, then used in the making of Fig. 2. Most data fall within the plotted lines giving the result $\beta_1 - \mu = -0.44 \pm 0.06$. This agrees with the recent experimental[11] and theoretical[12] values of -0.34 ± 0.05 and -0.44, respectively. Note that tubes with a wide range of wetting transition temperatures, $|T_w - T_c| = 0.1 - 10$ K, are described by one function. In retrospect we argue that because[2] $t_w \approx h_1^{1/\Delta_1}$ and $2 - \alpha_s = \mu$, Fig. 2 is actually a scaling plot of $\cos\theta$ vs $|t|/h_1^{1/\Delta_1}$. Therefore we have experimentally measured the scaling function to be $F(x) = x$ for $x \leq 1$ and 1 for $x \geq 1$. The data show no systematic deviation from this form even near the wetting transition, $x = 1$, where the linear expansion of Eq. (1) might fail. In particular, we emphasize that the transition appears to be first order because of the discontinuity in slope[13] at $x = 1$. Since our method directly compares partially wetted with completely wetted tubes, we have a much clearer view of the transition than do other capillary-rise experiments.[11,14]

Heavily silylated tubes exhibit capillary rise and no clear transition from partial to complete wetting by C^* below T_c; these data are not shown. AWF report this behavior and argue that short-range forces favorable to C^* and long-range forces favorable to N^* cause partial wetting by C^* but forbid complete wetting at all $T < T_c$. If this is true, then SRF scaling, Eq. (1), can no longer hold. Quantitative predictions are difficult to check experimentally because mislocation of the bulk meniscus and breakdown of the capillary rise formula near T_c lead to unacceptably large systematic errors in the computation of $\cos\theta$.

FIG. 1. Capillary parameters vs temperature, relative to the bulk critical temperature, for CS$_2$+NMe on glass. Large symbols are for different surface silylations; small triangles are for fully hydroxylated surfaces. Data falling on the curves (described in text) represent states of complete wetting; between these extremes are states of partial wetting.
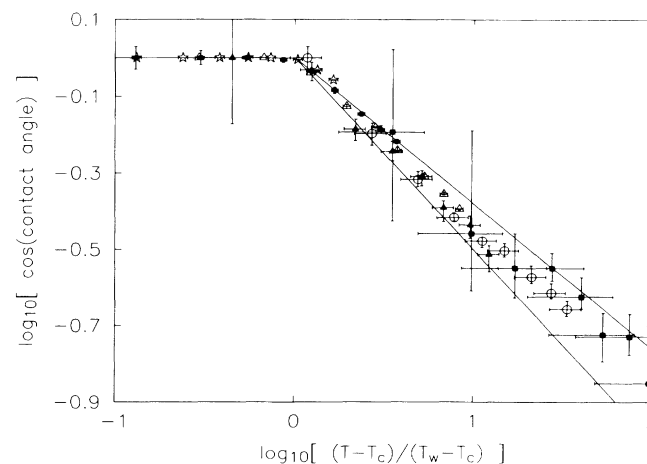

FIG. 2. Contact angles for Fig. 1 data, plotted to show universal temperature dependence of substrates which become completely wetted by N^*. The slope is $\beta_1 - \mu = -0.44 \pm 0.06$.
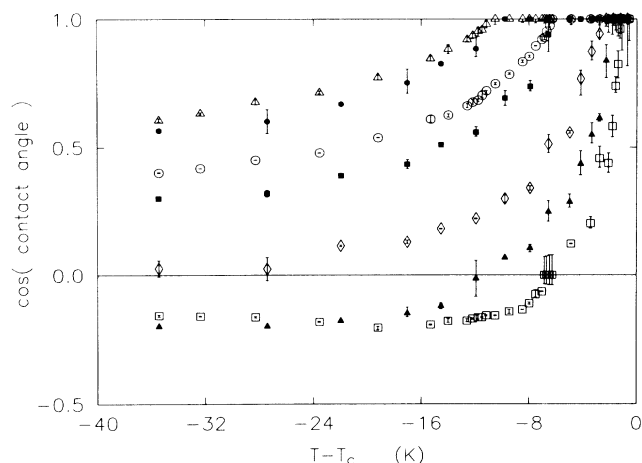
FIG. 3. Contact angles for CY+AA on glass. Note the surprising reversal in capillary rise with temperature observed in two samples. Symbols refer to different surface silylations.

FIG. 4. Partial wetting exponent, ϕ, vs wetting transition temperature: $\cos\theta \sim |t|^{\phi}$ as $\cos\theta \rightarrow 1$. Observe that $\phi \rightarrow \beta_1 - \mu$ ($= -0.44 \pm 0.06$ from Fig. 2) at large $|T_w - T_c|$. The symbols indicate capillaries in different sample cells.

It should be noted that these silylated surfaces are prone to attack by $CS_2 + NMe$. After 30 h the systematic change in capillary rise due to aging is comparable to the observed scatter. Eventually the silylated tubes become indistinguishable by capillary rise from hydroxylated tubes. Data discussed above were taken over a 15–20-h period. Aging may be partially responsible for the observed drift in critical temperature of, typically, +5 mK/d.

Cyclohexane + acetic anhydride (CY + AA).— The two sample cells studied had critical temperatures of 52.408 and 52.305 °C which drift on the order of −3 mK/d. Hydroxylated surfaces are completely wetted by the lower, acetic anhydride-rich (A^*) phase. Experimentally, there is no time restriction because this mixture does not attack our silylated surfaces. Detailed contact-angle data, presented in Fig. 3, show that all silylated capillaries have first-order transitions to complete wetting by A^* below T_c. Using the arguments of Nightingale and Indekeu,[15] as in AWF, we immediately conclude that long-range forces, if present, favor A^*.

The temperature dependence of the partially wetted states exhibits several new features. The three most heavily silylated capillaries have rises which reach a maximum and then decrease as $|T - T_c|$ is increased; two of these show a dramatic change in preference by actually decreasing through zero. A less obvious, but related, feature is that $\cos\theta$ obeys a power law on approach to complete wetting but with an exponent which changes systematically with surface preparation. This variation is plotted in Fig. 4 and suggests that the universal value, $\beta_1 - \mu$, is approached in the limit of large $|T_w - T_c|$, or equivalently, large h_1. We may be observing the breakdown of SRF scaling as long-range forces begin to dominate over increasingly weaker short-range forces. Compare this situation to that of $CS_2 + NMe$: SRF scaling

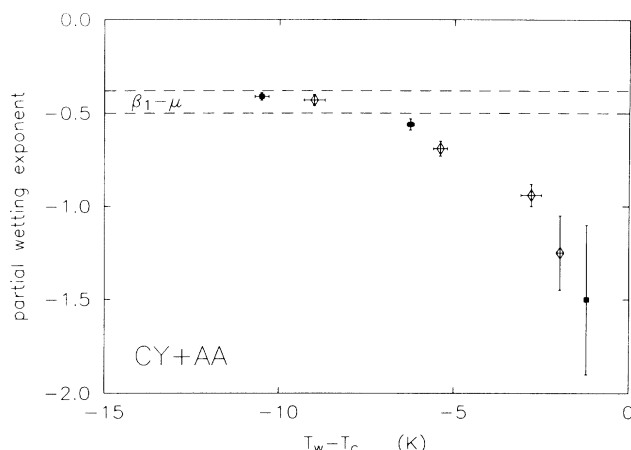seems to work for all h_1 which favor N^*, but fails when h_1 has crossed over to favor C^*. It may be possible for one to observe the breakdown of SRF scaling by studying surfaces with $|T_w - T_c|$ smaller than we have produced so far. In both systems, SRF scaling works only when one phase is strongly preferred, presumably by a
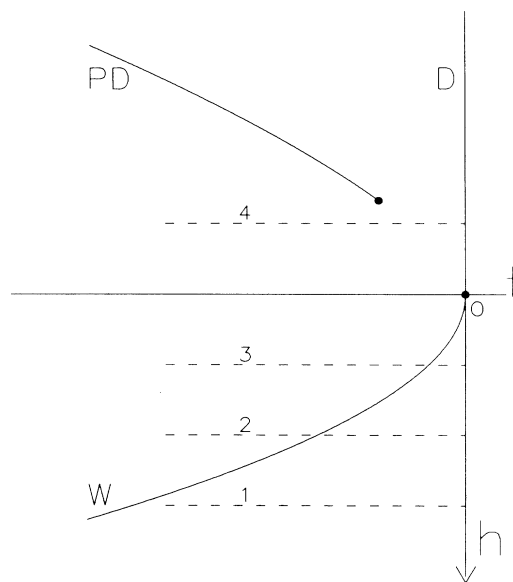

FIG. 5. Wetting phase diagram from ES. W is the locus of first-order transitions to complete wetting (by "liquid"; e.g., N^*), D is a line of continuous drying transitions (i.e., to complete wetting by "vapor"; e.g., C^*). They meet at the so-called ordinary point, O. PD is the locus of first-order partial drying transitions. Trajectories represent substrates with different surface preparation. This is for the case of negative surface enhancement and a weak long-range force which favors the wetting phase, N^*, independent of h_1.

short-range force, over the other.

All data on the $CS_2 + NMe$ system, AWF included, can be summarized by the wetting phase diagram of ES Fig. 1(a), reproduced here in Fig. 5, which shows the state of wetting in the surface field versus temperature plane. Trajectory 1 represents hydroxylated tubes, which are always completely wetted in the temperature range studied. Trajectories 2 and 3 are for lightly silylated tubes, which undergo first-order transitions between partial and complete wetting by N^* when crossing W. Trajectory 4 is for a heavily silylated tube which remains partially wetted by C^* below T_c. Like AWF, we have not established that $\cos\theta \to 1$ at T_c for this case. A wetting phase diagram similar to Fig. 5 cannot explain our $CY + AA$ data unless the solid-liquid interaction can be described by a temperature-dependent h_1^{eff}. Alternatively, it may be possible to understand our data with the diagrams of ES Fig. 3 for the case of strong long-range forces. This second possibility is more appealing since we already suspect that strong long-range forces are present and responsible for the breakdown of SRF scaling as $T_w \to T_c$. For further progress, quantitative understanding of the solid-liquid forces is required.

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