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Critical adsorption in the undersaturated regime

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The interaction between a near-critical binary liquid and a solid substrate can be modeled by an effective surface field h_1. Critical adsorption experiments to date have been done in the limit of strong field, but we have been able to produce intermediate-strength fields by chemically modifying a surface. We present here an experimental demonstration of critical adsorption in this undersaturated regime. Our reflectivity data indicate that critical adsorption can remain undersaturated even within 3 mK of T_c — a surprising result difficult to reconcile with current expectations of the behavior of the critical scaling function.

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I. INTRODUCTION

The phenomenon of critical adsorption [1] occurs, for example, when a binary liquid mixture approaches its critical temperature from above in the presence of a solid surface. If one component of the mixture is preferentially attracted to the surface, then it may become partially adsorbed, and the structure of the liquid near the substrate will be perturbed over a distance on the order of the bulk correlation length ξ. The liquid-solid interaction can be modeled by an effective surface field of strength h_1 [2], which corresponds to the chemical potential difference between having one or the other liquid species near the wall. It has been assumed that experiments to date have been done in the limit of strong surface field [3–6] — a "saturated" regime in which increasing the value of $|h_1|$ does not affect the variation with distance z from the substrate of the order parameter $m(z)$, given here by the difference between the local chemical concentration and the bulk concentration [7]. As we shall discuss later, this is a natural assumption given the scaling hypothesis for $m(z)$ offered by Fisher and de Gennes [1]. But limiting study of critical adsorption to the saturated regime causes us to miss out on much of the interesting physics of this phenomenon. An instructive, if imperfect, analogy is studying ferromagnetism always in the presence of a strong applied magnetic field; the results are not likely to be as interesting as they would be if one could vary the field strength. Similarly, exploring critical adsorption of intermediate and weak surface fields [5,8,9] — undersaturated regimes in which h_1 is an important parameter — is a crucial goal.

In a step towards meeting this goal, we present here an experimental demonstration of critical adsorption outside of the strong-field limit. We will even call into question whether all systems other than the one discussed can be said to be in the strong-field limit, as has been repeatedly supposed. The system we study is one that has been used in previous critical adsorption experiments [10,11]: a binary liquid mixture of carbon disulfide and nitromethane in contact with a borosilicate glass surface. When the glass is cleaned so that it is fully hydroxylated, it very strongly prefers nitromethane — presumably because polar nitromethane molecules can hydrogen bond to the surface — and a substantial nitromethane adsorption layer builds up as T_c, the critical temperature, is approached from above with the mixture at the critical concentration. Schlossman and co-workers [10,12] measured moments of the order parameter in this case and found consistency with the Fisher–de Gennes scaling hypothesis in the limit of large h_1 [13]. When the glass is chemically modified so that it is fully silylated (i.e., surface hydroxyl groups replaced to a considerable extent by methyl groups), carbon disulfide is favored, and a substantial carbon disulfide adsorption layer can be detected in the critical region. Dixon *et al.* [11] found that for a particular preparation the silylation's effect was to switch the sign of the effective surface field h_1.

These results suggest that a way of producing substrates with reduced values of $|h_1|$ is to silylate to an intermediate degree — to produce surfaces in which the coverage of methyl groups is less than complete. A way of doing this was employed by Durian and Franck [14] in capillary-rise experiments on this binary liquid. They reacted clean hydroxylated glass capillary tubes with the vapor of hexamethyldisilazane (HMDS) [15]. They then made capillary-rise measurements on these tubes as a function of temperature in the phase-separated region ($T < T_c$). While hydroxylated capillaries were always completely wetted by the nitromethane-rich phase, lightly silylated capillaries were less attractive to nitromethane and exhibited transitions from incomplete to complete wetting as the temperature was raised toward T_c; the temperature location of these wetting transitions could be varied by varying the HMDS reaction time. Heavily silylated capillaries were attractive to carbon disulfide, though none were completely wetted by the carbon disulfide-rich phase. The wetting transition data could be collapsed in a way suggested by a scaling relation [16] for the contact angle θ that assumes short-range interactions given by h_1:

$$\cos\theta \approx F(h_1/t^{\Delta_1}). \qquad (1)$$

Above, $t = |(T - T_c)/T_c|$ is the reduced temperature,

$F(x)$ is a scaling function, and Δ_1 is the surface "gap" exponent. In the completely wet regime, $F(x) = 1$; in the incompletely wet regime, one expects it should be proportional to x $(= h_1/t^{\Delta_1})$ assuming x is small. This is indeed what Durian and Franck found; not only could the data be collapsed as expected, but they resulted in an experimental measurement for Δ_1 of 0.44 ± 0.06, which agreed well with the theoretical prediction of 0.44 [17]. It should be emphasized that these were measurements of the macroscopic effects of bulk criticality relatively far ($|T - T_c| \geq 100$ mK) from the bulk critical point, in contrast to the microscopic adsorption measurements that we present here whose most dramatic consequences are much closer to bulk criticality ($|T - T_c| \leq 10$ mK).

One problem encountered in the capillary-rise experiments was that the silylation was unstable. Over time surfaces originally very attractive to carbon disulfide became less and less so; eventually they became indistinguishable from hydroxylated surfaces, strongly preferring nitromethane. This may have been because the binary liquid attacked the chemical preparation or because trace amounts of water in the sample cell became physically adsorbed on the surface [18]. In the present experiment, we used this aging problem to our advantage by preparing a surface which was heavily silylated and then making critical adsorption measurements on it from day to day as the surface changed. On the first day of the run presented here, we found that the surface very much preferred carbon disulfide; on the second day, it did so to a lesser extent; by the eleventh day, it very much preferred nitromethane. In this way we were able to examine, in a single sample cell, surfaces with a wide variety of preferences for one or the other liquid species — with a wide variety of values of h_1.

II. EXPERIMENTAL DETAILS

The experimental method used was frustrated total internal reflection. Light from a He-Ne laser (633 nm, < 0.8 mW) was reflected off the liquid-solid interface in an s-polarized manner at an angle ($77.1° \pm 0.1°$) just below that of total internal reflection, and the intensity of the reflected light was measured. The details of the apparatus are similar to those of Ref. [10]. The one significant difference was in how the sample cell was prepared. The glass parts of the cell were first cleaned so as to have fully hydroxylated surfaces. After the cell was assembled and vacuum baked, HMDS vapor at ≈ 2.4 mm Hg was introduced into its interior and allowed to react with the glass for 10 d. This produced heavily silylated surfaces. The cell was then filled in air with a critical composition of carbon disulfide and nitromethane [19,20], sealed, and placed in the thermostat. Each day thereafter we measured the reflectivity as a function of temperature from $T \approx T_c$ up to $T \approx T_c + 7$ K. At each temperature setting, we mixed the sample thoroughly and took two to four intensity measurements; these measurements generally differed from each other by no more than 1–2 %. We were able to probe the critical region [$(T - T_c) \leq 80$ mK] in less than 2 h; repeated measurements indicated no detectable aging effects in this short a time frame. The critical temperature itself drifted at an average rate of +4 mK/day. On the twelfth day after the cell was filled, it apparently sprang a leak and data collection for the run presented here stopped.

Reflectivity R measures the deviation of the index of refraction of the liquid mixture from that of the substrate and the deviation of the dielectric profile near the liquid-solid interface from that of a sharp Fresnel interface. The index of the bulk liquid is less than that of glass, so one expects a nonzero background reflectivity R_b even in the absence of a critical adsorption layer. But the build-up of the adsorption profile near T_c alters the dielectric profile near the surface, and causes R to deviate from R_b. It is by measuring this deviation, $\Delta R \equiv R - R_b$, that we measure critical adsorption in this experiment. When nitromethane is preferentially adsorbed, R sharply increases as T_c is approached from above; when carbon disulfide is preferred, it sharply decreases. This can be understood qualitatively as follows: The lowest index is that of nitromethane; its adsorption increases the index mismatch between liquid and substrate; this in turn increases the reflectivity. The adsorption of carbon disulfide, on the other hand, brings us closer to a state of index matching; this decreases the reflectivity. A deeper understanding of how to relate ΔR to the profile $m(z)$ is provided by a moments analysis [10,11], which we employ below. To perform quantitative tests it can prove necessary to resort to model profiles to obtain $m(z)$ itself [4,10]. A weakness of this reflectivity technique is that the quantitative results are sensitive to the measurement of the background reflectivity R_b and the accuracy of the solution to Maxwell's equations employed [4]. Fortunately, for the main purposes of this paper, a qualitative understanding of the meaning of ΔR will suffice.

III. RESULTS AND DISCUSSION

Figure 1 shows how R varied with T over the full temperature range studied; different symbol types indicate data taken on different days. The variation in each data set for $(T - T_c) > 0.5$ K is a bulk effect, which is believed to be due to the drop that thermal expansion causes in the liquid's refractive index as T is increased [10]. Above $T \approx T_c + 6.4$ K, the index was such that the incident light was totally internally reflected; measurements at these temperatures allowed us to put the reflectivity on an absolute scale. Because only the surface, and not the liquid, is expected to change from day to day, one expects that data taken on different days should agree fairly well for temperatures well above T_c, where R equals R_b. This is indeed the case: Only data taken on the first day after the sample cell was filled differ noticeably from the others. (We do not know why the first data set is at all different.) These background reflectivity measurements can be extrapolated to provide an estimate of R_b in the critical region.

It is the behavior of R in the critical region which is

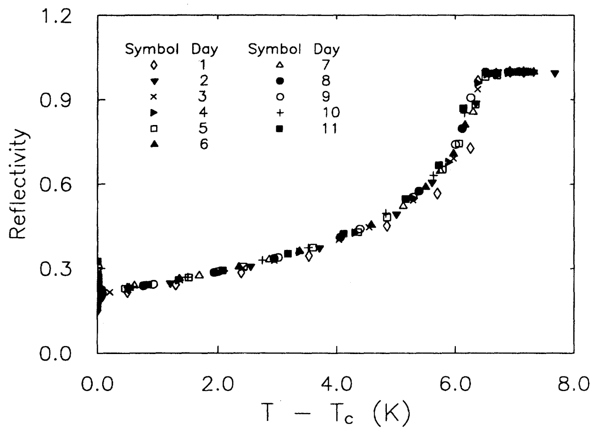

FIG. 1. Reflectivity R versus temperature $T - T_c$ over the full temperature range. Different symbol types refer to data taken on different days. The sample cell was filled on day 0. Variation in R for $(T - T_c) > 0.5$ K is due to thermal expansion of the bulk liquid. Above $T \approx T_c + 6.4$ K, light is totally internally reflected. Near T_c, adsorption effects are visible (see Fig. 2 for details of this region).

of interest to us (Fig. 2). Here the effect of the surface is pronounced because of the divergence of ξ. Here we expect the change in surface field from day to day to manifest itself. And indeed the differences between the data sets are striking. On day 1, R drops sharply as T_c is approached, corresponding to a surface preference for carbon disulfide. But over the next few days, the drop becomes smaller. On day 5, neither component of the mixture is strongly preferred. On day 6, a small increase in R near T_c is definitely visible. By day 11, the surface strongly prefers nitromethane, and a large increase in the reflectivity is observed. The accumulation of curves at late days indicates a return to the saturated adsorption regime. It is remarkable how clearly these data reveal the change in surface preference with time. To some extent the differences between data sets are visible 30 mK above T_c; this is not particularly surprising since critical adsorption effects have been seen in reflectivity data even 200 mK above T_c [21]. But the differences are especially apparent very close $[(T - T_c) \leq 10 \text{ mK}]$ to the critical temperature. Indeed the reflectivity measurements for different days are distinguishable less than 3 mK from T_c — even making conservative estimates that allow for an uncertainty in T_c of ±1 mK and in T of ±0.5 mK. We see in these data a sweep of intermediate- and weak-field behavior that fills in the extremes of strong-field response.

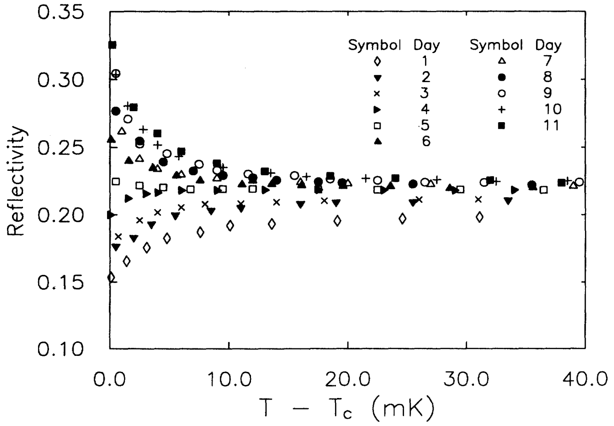

FIG. 2. Reflectivity R versus temperature $T - T_c$ in the critical region. The depression in R near T_c on day 1 corresponds to carbon disulfide adsorption on the substrate. The increase in R on day 11 corresponds to nitromethane adsorption.

This observation really is rather surprising because until now there has been a presumption that critical adsorption can only be measured in the saturated limit. Consider the scaling hypothesis for critical adsorption offered by Fisher and de Gennes [1]:

$$m(z) \approx m_0 t^{\beta} P(z/\xi, h_1/t^{\Delta_1}), \tag{2}$$

where m_0 is a constant amplitude, β is the order parameter exponent, and $P(x,y)$ is a scaling function. Because $\Delta_1 > 0$, the scaled field h_1/t^{Δ_1} diverges as $t \to 0$. In this "strong-field limit," the scaling function $P_{\text{sat}}(x) \equiv P(x,\infty)$ applies, and the adsorption profile loses its dependence on h_1. Since critical adsorption is a phenomenon which occurs rather close to T_c, it has become the conventional wisdom of the field to assume that experiments to date have been done in this saturated regime [3–6]. This assumption makes a certain physical sense: One does expect that the substrate eventually will be covered by a monolayer or more of the preferred liquid species, and that this will be the real surface for the remainder of the liquid. Peliti and Leibler [3] went further: They justified the strong-field approximation by arguing that, in its absence, critical adsorption effects should not be observable. But, in some of our data sets (days 4–6 especially), adsorption effects certainly are observable even though the system is clearly not saturated. It is important to emphasize again that this is true even within 3 mK of T_c. While it is possible that the strong-field limit is achieved for temperatures closer to T_c, this would still leave the range of applicability of the approximation disappointingly limited. One is led to wonder about the correctness of using the saturated scaling function, $P_{\text{sat}}(x)$, to describe earlier adsorption experiments, with the exception of the system discussed here when it is fully hydroxylated [10].

We can test the compatibility of our data with the scaling hypothesis embodied in Eq. (2) by invoking results from a moments analysis. First we note from Refs. [10] and [12] that the primary contribution to ΔR comes from the first moment of the order parameter profile. The appropriate scaling description derived from Eq. (2) is

$$\Delta R \sim t^{\beta} \xi^2 Q(h_1/t^{\Delta_1}), \tag{3}$$

where the scaling functions are related by $Q(y) \equiv \int_0^{\infty} xP(x,y)dx$. Now, considering only the $t = 0$ limit, we can invoke a weak form of the strong-field hypothesis (that is to say for $t = 0$ only) to argue that Q loses its

h_1 dependence as its argument diverges. Reference [12] explicitly shows this for classical scaling theory. This prediction is in direct contradiction to our observation that as t approaches 0, ΔR remains h_1 dependent over the range of observed behavior as h_1 swings between the strong-adsorption limits.

Our failure to see the expected limiting behavior of the scaling function raises questions about the validity of Eq. (2) itself. Answering these questions is difficult because we do not have an independent measure of h_1 for our data. However, one thing we can do is see if any values of surface field will allow our reflectivity data to be fitted to the form suggested by Eq. (3). According to that equation, the scaling function $Q(h_1/t^{\Delta_1})$ is proportional to $\Delta R/t^{\beta-2\nu}$. So a plot of this latter quantity should have the same temperature dependence as Q. For large values of scaled surface field, one expects Q to be a constant. For small values, Q must be a decreasing function of t; a reasonable guess is that it will be proportional to its argument and hence go as $t^{-\Delta_1}$. Figure 3 is a log-log plot of $|\Delta R|/t^{\beta-2\nu}$ versus t for our data sets. The points in each set closer than 1 mK to T_c have been eliminated because, on a logarithmic scale, their temperature uncertainty is much too large for them to be of use; also gone are points farther than 10 mK from T_c because, for these temperatures, moments of $m(z)$ other than the first become important and Eq. (3) becomes suspect [10]. The background reflectivity R_b was computed, as in Ref. [10], by extrapolating the bulk thermal expansion part ($T - T_c > 0.5$ K) of each reflectivity curve into the critical region; this was done by fitting the liquid's bulk index of refraction n_b to the form

$$n_b = n_0 + at, \tag{4}$$

where n_0 and a are constants. Note that we have ignored a possible $t^{1-\alpha}$ singularity in the refractive index (see the discussion in Ref. [10]). Individual data sets in Fig. 3 have been shifted horizontally by various amounts to make the graph easier to read; if $Q(h_1/t^{\Delta_1})$ were proportional to its argument, these shifts would be equivalent to making a specific choice of h_1 for each data set. The error bars indicate uncertainty in t and R, but not in R_b. Uncertainty in the background reflectivity affects data points in each set as a group, rather than individually, and is difficult to show on a graph such as Fig. 3. What we can say easily is that this uncertainty in R_b does not affect the qualitative features of the figure. Two features stand out: (i) curves from the last days appear to be rather flat, as one would expect in the strong-field limit; (ii) curves from most other days appear to be either flat at a lower level or increasing functions of t. This last feature goes against what one expects from Eq. (3) — and by extension Eq. (2) — which indicates Q should be a decreasing function of t in intermediate-field regimes, regardless of the actual value of h_1. This conclusion raises further doubts about current expectations of the scaling behavior, though these doubts are necessarily tentative because of the paucity of data points and their rather large uncertainties. One fact worth mentioning is that this same analysis carried out on data from two other sample cells produced the same two qualitative features, though data from one of the cells were noisier than those presented here.

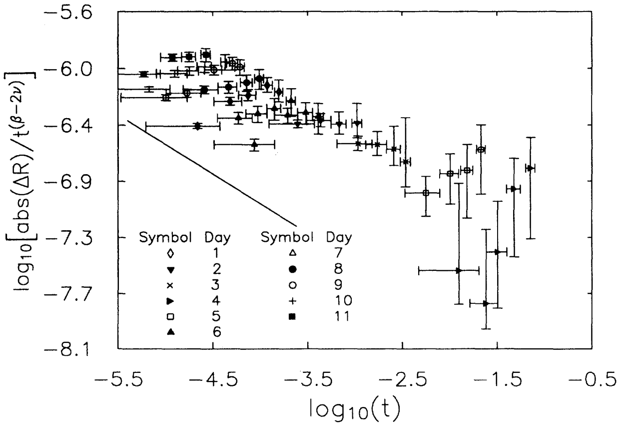

FIG. 3. Dependence of the scaling function Q ($\sim \Delta R/t^{\beta-2\nu}$) upon reduced temperature t. The straight line at left has a slope equal to $-\Delta_1 = -0.44$, which is the behavior expected for very weak surface fields. Note that data from days 4 and 5 show unexpected behavior. Data from different days have been shifted horizontally by varying amounts to make them easier to distinguish.

It is appropriate at this point to discuss two factors which might complicate the interpretation of the data. First, there is the question of whether surface heterogeneity plays any role. We are inclined to think the answer is no because the sharp wetting transitions that Durian and Franck [14] measured in this system were consistent with a description that included only a homogeneous surface field h_1. Also, we expect the initial silylation to be sufficiently uniform since the kinetics of the process [15] by which HMDS bonds to the glass are rather simple. There is no particular reason to believe that the surfaces are heterogeneous over length scales long enough (presumably of order ξ) to matter. But without a direct measure of the surface chemistry (which we lack) and a better understanding of what effect surface heterogeneity might be expected to have, we cannot rule out this possibility. Second, Eq. (2) is the simplest and most common way to describe how the nature of the surface affects critical adsorption, but it is not the only way. In particular, one might ask whether the surface chemistry affects g [2,8], the coupling parameter that describes how the presence of the wall modifies the interaction between molecules near the wall. Also, it is possible that long-range interactions (e.g., electrostatic forces) may be important.

IV. CONCLUSIONS

We are hopeful that the results of our experiment will open up new opportunities for the study of critical adsorption. Certainly there is a need to explain theoretically why the reflectivity data remain undersaturated even within a few mK of T_c. Such an explanation might involve clarifying the nature of the scaling function's dependence on the scaled field h_1/t^{Δ_1} in Eq. (2), or including a more complicated description of surface effects than h_1 alone. It would also be helpful to have a better understanding of how to relate theoretical parameters, like h_1 and g, to real physical surfaces. Experimentally, many possibilities exist. While we have not attempted here to characterize our data sets with values of h_1, it may be possible to do so through the use of a modified Landau-Ginzburg theory as was done in Ref. [10]; one could also attempt, in this sort of experiment, to measure wetting transitions as well as adsorption, and so obtain an estimate of h_1 in the manner of Durian and Franck [14]. At the least, quantification of h_1 would possibly lead to a quantitative test of Fisher–de Gennes scaling in order to go beyond the qualitative one we have provided. Recently, Law and Smith [22] have discussed new critical amplitude ratios in the strong h_1 limit at the liquid-vapor interfaces of several binary liquids; it would be interesting to see if tuning the surface field affects such ratios. One can also imagine many experiments that could benefit from a tunable surface. For example, experiments that search for the effects of geometry and dimensional crossover in thin films [23] and porous systems would benefit from the simplification of using surfaces of neutral preference. Finally, the undersaturated boundary field critical adsorption phenomena presented here should have analogs in various systems (e.g., single component fluids, magnets, superconductors, and binary alloys) near bulk criticality.

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