New Critical Anomaly Induced in a Binary Liquid Mixture by a Selectively Adsorbing Wall

Carl Franck and S. E. Schnatterly

Department of Physics, University of Virginia, Charlottesville, Virginia 22901

(Received 29 October 1981)

The upper demixing critical point in carbon disulfide + nitromethane bounded by a crown glass surface which is expected to preferentially adsorb nitromethane has been studied. The σ-polarized reflectivity of the liquid/glass interface rises sharply with decreasing temperature above the bulk critical temperature. This effect cannot be explained as a purely bulk phenomenon, but agrees well with an approximate version of the critical wall-layer theory of de Gennes and Fisher.

What is the effect of a selectively adsorbing boundary on the critical demixing transition of a binary fluid system? De Gennes and Fisher answered this question from a perturbative viewpoint by claiming that the chemical concentration of the bulk liquid can be modified over distances on the order of a correlation length from the boundary.[1] Such a situation is analogous to the proximity effect of superconductivity. We set out to detect the Fisher-de Gennes critical wall layer by measuring the reflectivity of a binary liquid/solid interface as a function of temperature.

Our sample cell is pictured in Fig. 1. The top face of the crown glass prism is the surface of interest. We watch bulk critical behavior through the glass side wall. The cell is partially filled with 2.51 ml of reagent grade carbon disulfide and nitromethane. The liquid volume fraction of carbon disulfide, 0.602 ± 0.007, is consistent with the published critical value,[2] 0.6010 ± 0.0004. A stainless-steel thermistor probe and a glass encapsulated floating magnetic mixer are immersed in the liquid. We studied the upper demixing point (above T_c, one phase; below T_c, two phases). It has a published temperature[2] of $T_c = 61.98$ °C.

The sample cell is immersed in a stirred water bath, which is surrounded by styrofoam insulation. The bath temperature can be proportionally controlled by immersion heaters and a dc thermistor. The sample thermistor is used in a 150-Hz bridge with a lock-in null detector. The sample thermometer has a sensitivity of better than 1 mdeg C. It was calibrated to ± 0.5 °C.

The light reflected from the liquid/glass interface is provided by a He-Ne laser (0.633 μm, $\lesssim 7$ mW, divergence $< 0.09°$ and horizontal polarization). The incident beam is monitored through a beam splitter by a photodiode. The light is reflected from the sample in a σ-polarized manner at an angle of incidence equal to $77.1 \pm 1.0°$ from

normal. An exit aperture excludes reflections due to the liquid/liquid meniscus from the output beam. The output intensity is measured by a second photodiode. In order to reduce the importance of source fluctuations, the output voltage is electronically divided by the input monitor voltage.

There are two primary reasons why we selected the carbon disulfide (CS_2) + nitromethane ($MeNO_2$) binary liquid system. The first is that adsorption studies of $MeNO_2$ + carbon tetrachloride (like CS_2, a molecule with zero permanent electric dipole moment) indicate that $MeNO_2$, a polar molecule, is preferentially adsorbed onto silica gel.[3] Presumably, surface polar groups on silica attract polar more than nonpolar molecules.[4] By use of numbers derived from this study, the $MeNO_2$ volume fraction of material adsorbed at the liquid/glass interface is expected to be 0.81, while the volume fraction in the bulk liquid just above T_c is only 0.40.

A second reason for selecting CS_2 + $MeNO_2$ was that it was expected to have an index of refraction (hereafter we abbreviate "index of refraction" by "index") nearly equal to that of crown glass. We use an angle of incidence that is beyond the
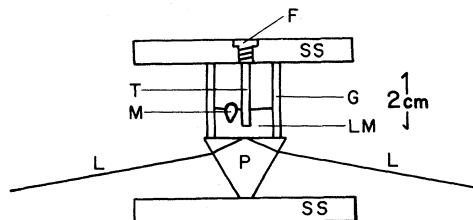

FIG. 1. Horizontal view of sample cell. LM: liquid mixture; P: prism; L: light beam; T: thermistor probe; M: magnetic mixer buoy; SS: stainless-steel disk; G: glass cylinder (Teflon gaskets on ends); F: fill hole (uses screw plug and Teflon gasket).

expected critical angle for the glass/wall layer interface. A preliminary calculation showed this to be a favorable arrangement for detecting a $MeNO_2$-rich surface layer of subwavelength thickness. As the temperature decreases to T_c, we expect a $MeNO_2$-rich wall layer with an index smaller than that of the glass to grow in thickness, producing a significant increase in surface reflectivity.

Figure 2 shows measurements of σ reflectivity (R^σ) versus temperature (T) outside the critical point. We heated $(ABCDE)$, then cooled $(A'B'C' D'E')$ the sample at an average rate of $=1.4 \times 10^{-3}$ °C sec^{-1} with the mixer on. Below T_c (bulk), warming the sample produces a CS_2-rich phase on the bottom of the cell, with the lighter $MeNO_2$-rich phase floating above. Cooling the sample while below T_c(bulk) condenses $MeNO_2$-rich droplets on glass surfaces. This effect allows us to observe both branches of the coexistence curve below T_c. Upon heating, bulk heterogeneity was seen to disappear by the time $T=T_1$ was reached leaving a homogeneous opalescent liquid. While cooling, bulk phase separation was first noticed at T_2. Therefore, $T_2 \lesssim T_c$(bulk) $\lesssim T_1$.

The solid lines in Fig. 2 for $T < T_c$ are due to a two-region model consisting of liquid with index n_l over glass with index $n_g = 1.518 \pm 0.002$. n_l is based on the coexistence curve of Gopal et $al.$[2,5,6]
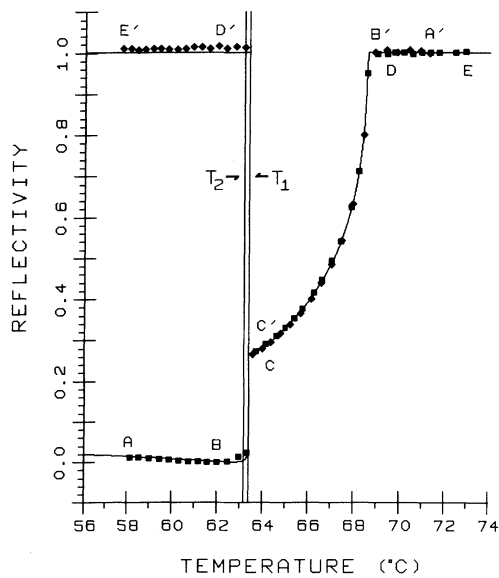
For $T > T_c$, we use the model discussed below in connection with the critical measurements. Over the noncritical temperature range studied here, the dominant effect is thermal expansion. Returning to the two-region model, this means $n_l \approx n_0 + at$ where n_0 and a are constants and $t \equiv (T - T_c)/ T_c$ is the reduced temperature (T and T_c in kelvins). We find $a = -0.15$, a typical rate of thermal expansion.[7] In summary, we can qualitatively explain the noncritical measurement.

In Fig. 3, we present an $R^\sigma(t)$ measurement in the critical region above T_c(bulk). The reduced temperature scale is based on $T_c = 62.7445$ °C. There is a striking departure from the thermal expansion trend. In order to perform the measurement the temperature was swept up, then down, using our electronic controller. At each controller setting, three groups of reflectivity measurements were taken. The first was five minutes after a new controller setting was made and with the sample mixer on. The second and third measurements were made three and five minutes later, with the mixer off. After the third measurement, the bulk was observed. We estimate that the standard deviation in R^σ is 0.001. We found that $62.733 (= T_2) \lesssim T_c$(bulk) $\lesssim 62.751$ °C$(= T_1)$. The bulk transition and the maximum value of the reflectivity anomaly occur within 0.02 °C of each other. Except near the

FIG. 2. Reflectivity (R^σ) over a broad temperature (T) range. The measurements are *outside* the critical region. Diamonds (squares) and (un)primed labels indicate cooling (heating). T_1 and T_2 are limits to T_c (bulk). Model curves described in text.
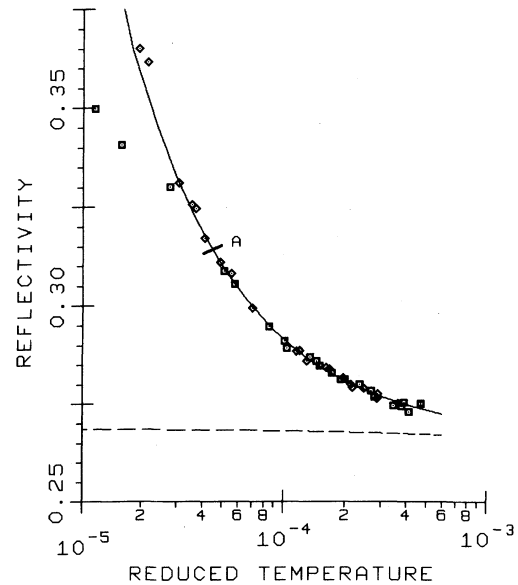
FIG. 3. Reflectivity (R^σ) vs reduced temperature (t) in critical region showing anomaly. Diamonds (squares) indicate cooling (heating). Data below A were used in fit. Solid curve is fit to de Gennes–Fisher critical wall-layer theory. Broken line is bulk background.

maximum in R^a, the results did not significantly depend on whether the mixer was on or off, or whether the sample was cooling or heating.

A difficulty in the measurement was an apparent drift in the bulk and reflectivity transition temperature of about $+7 \times 10^{-3}$ °C day^{-1}. However, a 125-day-old sample produced an anomaly with the same size and shape as one that was 8 days old. Also, both samples had the same transition temperature within 0.15 °C on the day they were loaded into the cell. Finally, the magnitude of the anomaly within a few hours of loading the sample was consistent with all other measurements.

What is the nature of the anomalous change in reflectivity which we have discovered above T_c(bulk)? If we treat it as a purely bulk effect, we require a change in bulk index from the background value of at least $\Delta n/n = -4 \times 10^{-4}$. This is at least a factor of 50 larger than the "large" bulk anomaly index observed by Beysens and Bourgou in the single-phase region of a binary liquid mixture.[8] Both Beysens' analysis and a recent theoretical review[9] claim that the most significant part of the bulk critical index anomaly is given by the third term in the following expression for the bulk index (n_b):

$$n_b = n_0 + at + bt^{1-\alpha}, \tag{1}$$

where, n_0, a, b, and α are constants; α is the specific-heat exponent, 0.11.[8] Thermal expansion is represented by the second term. An attempt to fit our data with Eq. (1) gives an unacceptably large χ^2 of 891 for 33 degrees of freedom. We conclude that a purely bulk description is inadequate.

An alternative possibility is that the reflectivity anomaly is an interface phenomenon. The recent discovery of a reflected-light anomaly in the ellipsometric work of Beaglehole at a binary-liquid/vapor interface supports this idea.[10] Cahn et al. have also suggested and demonstrated related critical wetting phenomena at binary-liquid interfaces.[11] Beysens and Leibler have detected anomalous adsorption at a binary-liquid/solid interface in a fluorescence experiment which uses evanescent-wave excitation.[12] And the thin-film experiments of Meadows et al. demonstrated surface dependence of T_c.[13] In summary, there is considerable evidence for the modification of binary-liquid critical behavior by interfaces.

In order to test the de Gennes–Fisher critical wall-layer (CWL) idea,[1] we apply the following simplified version of their model: We assume

that above T_c, the system is composed of three parts: a macroscopic bulk liquid with index n_b; a CWL of thickness equal to a bulk correlation length, ξ, and index n_w; and glass with index n_g. Following de Gennes and Fisher, we use bulk values for the critical exponents. We make a considerable simplification in their model by assuming the following expression for the order parameter perturbation: $n_w - n_b(t = 0) = ct^\beta$, where c is a constant. For β we use the measured bulk exponent value, 0.315.[2] For the correlation length we take $\xi = \xi_0 t^{-\nu}$, where the bulk amplitude ($\xi_0 = 0.3$ nm, typical) and bulk exponent ($\nu = 0.63$) are taken from light scattering experiments.[14] Finally, for the bulk index we use Eq. (1), which includes thermal expansion and the leading bulk-index critical anomaly. The data set for the critical analysis consists of the indicated points in Fig. 3 ($T \geq 62.76$ °C). Using the expression for the reflectivity of a three-layer system,[15] we fit for T_c, n_0, b, and c. We find a by fitting our noncritical data with T_c, n_0, b, and a as free parameters, while using the critical-data value for c. From the critical data set, we find a minimum χ^2 of 20 for 31 degrees of freedom and the following parameters: $T_c = 62.744 + 0.002$ °C, $n_0 = 1.48333 + 0.00008$, $b = 0.09 \pm 0.06$, and $c = -0.28 \pm 0.05$. The best fit is plotted in Fig. 3. The fitted value of T_c determines the reduced temperature scale. The same model with $c = 0$ (no CWL) gives the bulk background curve.

If we include data with $t < 5 \times 10^{-5}$ ($T < 62.76$ °C), the residuals appear to be nonrandom, and χ^2 becomes unacceptably large. Such points may be out of equilibrium, especially since the heating and cooling curves diverge. Nevertheless, we see that our critical measurement for $t \geq 5 \times 10^{-5}$ ($\xi/\lambda \leq 0.25$) is consistent with a simplified version of the de Gennes–Fisher CWL theory. We note that as expected by de Gennes and Fisher, the interface value of T_c measured from reflectivity agrees with the bulk value that was measured visually and quoted above. From the adsorption work discussed earlier, the difference between the indices of adsorbed and bulk fluid can be estimated.[3,6] The shift (-0.1) has the same sign and order of magnitude as the wall layer's critical amplitude, c.

There is a possible inconsistency in our background analysis. The value found for the bulk-index critical amplitude, $b = -0.08$, from the noncritical data of Fig. 2 appears to disagree with the fitted value from our critical data. This problem may be due to a failure of our model, or

765

a real discrepancy between the data sets. In any case, this background uncertainty is not large enough to change our interpretation of the reflectivity anomaly.

In conclusion, we have discovered a critical reflectivity anomaly in the single-phase region of a binary fluid mixture. The effect cannot be explained as a completely bulk phenomenon. It agrees with the de Gennes–Fisher picture of a bulk fluid perturbed by a selectively adsorbing wall. This effect may require the reinterpretation of the Meadows film experiment.[13] We plan to further test the critical wall-layer theory.

[1]Michael E. Fisher and Pierre-Gilles de Gennes, C. R. Acad. Sci., Ser. B 287, 207 (1978); Helen Au-Yang and Michael E. Fisher, Phys. Rev. B 21, 3956 (1980); Michael E. Fisher and Helen Au-Yang, Physica (Utrecht) 101A, 255 (1980); Pierre-Gilles de Gennes, C. R. Acad. Sci. 292, 701 (1981).

[2]E. S. R. Gopal, R. Ramachandra, P. Chandra Sekhar, K. Govindarajan, and S. V. Subramanyam, Phys. Rev. Lett. 32, 284 (1974).

[3]J. J. Kipling, Adsorption from Solutions and Non-Electrolytes (Academic, New York, 1965), p. 177.

[4]Kipling, Ref. 3, F. E. Bartell, G. H. Scheffler, and C. K. Sloan, J. Am. Chem. Soc. 53, 2501 (1931).

[5]For this and subsequently discussed fits, we used CURFIT from Philip R. Bevington, Data Reduction and Error Analysis for the Physical Sciences (McGraw-Hill, New York, 1969), p. 237.

[6]Samuel H. Maron and Carl F. Prutton, Principles of Physical Chemistry (Macmillan, New York, 1968), 4th ed., p. 693; we use the indices for 20 °C from CRC Handbook of Chemistry and Physics, edited by Robert C. Weast (Chemical Rubber, Boca Raton, Florida, 1980), 60th ed.; J. R. Partington, An Advanced Treatise on Physical Chemistry (Longmans, London, 1953), Vol. 4.

[7]The Lorentz-Lorenz relation gives $(1/\rho)(d\rho/dT)$ where ρ is the fluid density. Compare with n-octane, hexane, and toluene in N. B. Vargaftik, Tables on the Thermophysical Properties of Liquids and Gases (Hemisphere Publishing Corp., Washington D.C., 1975), 2nd ed.

[8]D. Beysens and A. Bourgou, Phys. Rev. A 19, 2407 (1979).

[9]J. V. Sengers, D. Bedeaux, P. Mazur, and S. C. Greer, Physica (Utrecht) 104A, 573 (1980), and references therein.

[10]D. Beaglehole, J. Chem. Phys. 73, 3366 (1980).

[11]John W. Cahn, J. Chem. Phys. 66, 3667 (1977); M. R. Moldover and John W. Cahn, Science 207, 1073 (1980); O'D. Kwon, D. Beaglehole, W. W. Webb, B. Widom, J. W. Schmidt, J. W. Cahn, M. R. Moldover, and B. Stephenson, Phys. Rev. Lett. 48, 185 (1982).

[12]D. Beysens and S. Leibler, to be published.

[13]M. R. Meadows, B. A. Scheibner, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. 43, 592 (1979).

[14]M. A. Anisimov, Usp. Fiz. Nauk 114, 249 (1974) [Sov. Phys. Usp. 17, 722 (1975)].

[15]Miles V. Klein, Optics (Wiley, New York, 1970), p. 582.