DIFFUSE INTERFACE IN A CRITICAL FLUID MIXTURE*

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We have measured the reflectivity of the interface between the two phases in equilibrium just below the critical consolute temperature of a binary fluid mixture. By comparison with the Fresnel reflectivity calculated for a sharp boundary using measured values of the indices of refraction, we find that the interface is diffuse with an effective thickness ~1000 Å at 0.38°C below the critical temperature. The temperature dependence of the effective thickness is near that predicted by lattice-gas models for the range of correlations in critical fluids.

Recent theoretical discussions of critical phenomena[1,2] in liquid mixtures, fluids, and ferromagnets, based on numerical solutions of the Ising lattice or lattice-gas models,[3] provide satisfying agreement with available experimental data on critical phenomena that was unattainable with the classical models homologous with van der Waals or Bragg-Williams theories. As $T \rightarrow T_C$, physical properties can be represented by powers of $|T - T_C|$. For example, the composition miscibility gap ΔC in a mixture of fluids, and the spontaneous magnetization M of a nonconducting ferromagnet, are supposed to vary as $(T_C - T)^\beta$ where the theoretical and experimental values of β are ~$\frac{1}{3}$.[3-5] An "effective" range of correlations Λ that diverges as $(T_C - T)^{-\nu}$ is a feature of the theory. But the parameter ν is only approximately specified by the theory, and is moreover rather sensitive to experimental errors. Best values seem to be $\nu \sim 0.6$ to 0.7. Classical theory yields $\nu = 0.50$. Our results provide a new measure of quantities related to ν and β.

However, we have measured an interface property, not a bulk property of a critical mixture. A thorough thermodynamic treatment of the interface in classical critical fluids has been given by Cahn and Hilliard,[6-8] and it has been slightly extended.[9] Landau and Lifshitz[10] point out that the law by which the interface of separation disappears in a critical fluid "has not yet been discovered." However, we conjecture that the effective interface thickness is related to the effective range of correlations.

We studied the binary system cyclohexane plus methanol which displays a miscibility gap with a critical temperature of $T_C = 45.14°C$ at about 50 at.% cyclohexane.[11] We consistently attained this value of T_C only within 0.1°C after purification. Temperatures were measured with a Beckmann-type thermometer to ±0.01°C and controlled to ±0.01°C during measurements taken only after equilibration by vigorous mixing and protracted settling. The indices of refraction of the two phases in equilibrium and n_2 were measured at 5790 Å to ±0.000 05 and at other wavelengths to ±0.0002 with a Bausch and Lomb dipping refractometer modified to reduce contamination and permit immersion in a water bath with temperatures regulated to ±0.005°C.

The reflectivity of the interface was measured relative to a glass reflectance standard at five wavelengths. The filtered light from a high-intensity mercury discharge tube was reflected from the interface in nearly normal incidence, measured with a photomultiplier, and compared with the attenuated source intensity monitored by another photomultiplier. Relative to a glass reflectivity standard the interface reflectivity values were reproducible to ±4% in any series of measurements, but absolute values for all experiments are accurate to only ±15% over a range of 10^4. The interface reflection of the highly collimated incident beam always formed a sharp reflection although the reflectivity was as small as 10^{-6}. Background scattering due to critical opalescence gradually increased with temperature to about half of the reflected power at $T_C - T = 0.38°C$. Correction for background scattering was made by subtracting the detected power with the photomultiplier moved just off the reflected beam. Losses due to scattering in the fluids were negligible, but corrections for window losses were essential. Minute disturbances of the interface could be detected as distortion of the reflected light beam. To avoid bending of the interface by surface tension a large cell diameter (8 cm) was selected, and to avoid radiative cooling through the windows the cell was immersed deep in a constant-temperature bath and the
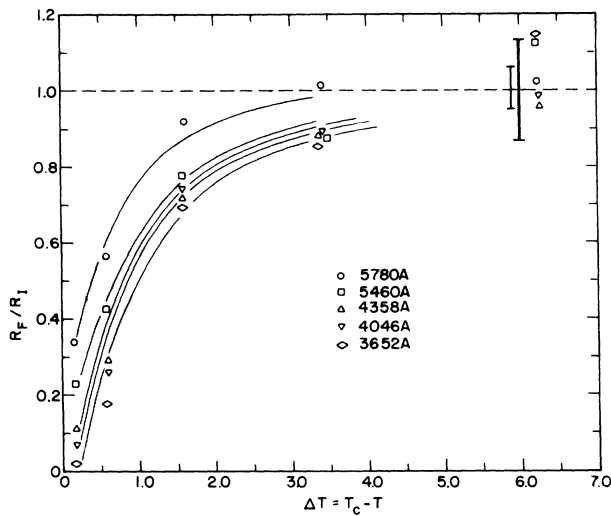
FIG. 1. Temperature dependence of the ratio of the measured absolute interface reflectivity R_I to the calculated reflectivity of a sharp interface R_{Fr}.

light beam transmitted through a long evacuated tube with a shutter.

Absolute reflectivity results are presented as a function of $T_c - T$ in Fig. 1 as the ratio of R_I, the interface reflectivity, to $R_{Fr} = [(n_2 - n_1)/(n_2 + n_1)]^2$, the reflectivity of a sharp interface given by the Fresnel formulas. Each point represents the average of several readings in several different runs. The small error bars represent the reproducibility, and the heavy error bar the absolute error. It is clear that as the temperature approaches T_c,

the observed reflectivities R_I fall far below the Fresnel values expected of corresponding sharp interfaces, with greater attenuation of shorter wavelengths. Precisely these properties would be expected of a diffuse interface.

In order to calculate the interface thickness from its reflectivity, it is assumed that the interface region can be regarded as optically uniform in any plane parallel to the interface. Our observation that the interface reflection is always sharp supports this approach, which neglects diffuse scattering by the fluctuations that are expected in the interface as in both bulk phases. Cahn and Hilliard[6] have shown that the concentration profile of the interface in a classical mixture should be $[C(y) - C_c]/ \Delta C = \tanh(2y/L)$, where y is distance perpendicular to the interface, C_c is the critical composition, and ΔC is the miscibility gap in composition. Assuming that the dielectric constant is proportional to the concentration, the normal reflectivity of this profile is[12]

$$R_I = \frac{\cosh[\pi^2(n_2 - n_1)L/\lambda] - 1}{\cosh[\pi^2(n_2 + n_1)L/\lambda] - 1}. \tag{1}$$

In the limit $\pi^2(n_2 - n_1)L/\lambda \ll 1$, the ratio R_I/R_{Fr} is

$$\frac{R_I}{R_{Fr}} = \frac{[\pi^2(n_2 + n_1)L/2\lambda]^2}{\sinh^2[\pi^2(n_2 + n_1)L/2\lambda]}. \tag{2}$$

Application of Eq. (2) to the data of Fig. 1 yields values of the effective interface thickness L plotted as open symbols in Fig. 2. Ef-
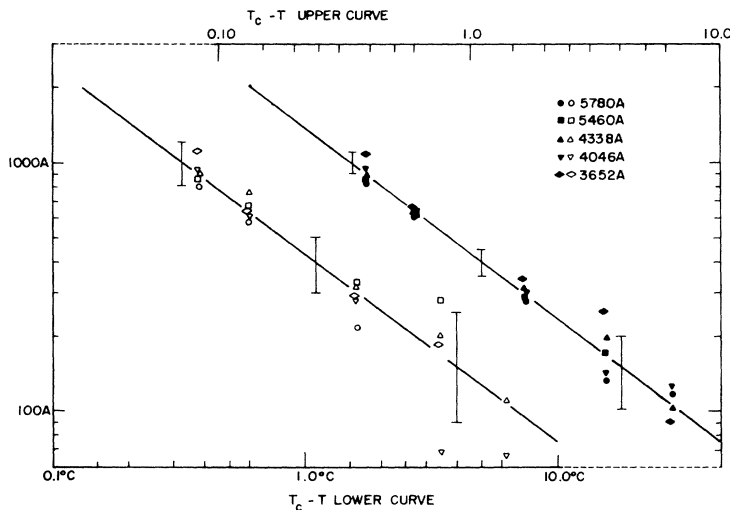

FIG. 2. Temperature dependence of effective interface thickness. Open symbols indicate absolute calibration; closed symbols indicate relative optimized data. Wavelength designations are as follows: circles, 5780 Å; squares, 5460 Å; triangles, 4358 Å; inverted triangles, 4046 Å; diamonds, 3652 Å.

fective interface thicknesses up to ~1000 Å at $T_C-T=0.38°C$ decreasing to ~100 Å at T_C-T $=6.25°C$ were found. The uncertainties are ~200 Å, but the scatter is reduced to ~50 Å by eliminating the factors for absolute calibration that are the largest source of error and recalculating relative values optimized at low temperatures as indicated by the solid points in Fig. 2.

All wavelengths gave coincident results within experimental error, thus suggesting the applicability of the assumed interface contour. However, the details of the interface contour cannot be deduced from our results at this stage.[13] With the assumed contour the temperature dependence of the effective thickness takes the form $L \propto (T_C-T)^{-\mu}$, where $\mu = 0.76$ ± 0.1 for both absolute and relative data treatments in Fig. 2. Since the value of μ depends somewhat on interface contour, it is subject to correction as the contour is better established either by theory or by experiment.

We may compare the experimental quantity μ with various predictions. The value $\mu = \frac{1}{2}$ derived for an interface in a classical fluid by Cahn and Hilliard is outside the experimental uncertainty. Application of thermodynamic fluctuation arguments[14] connects the volume and magnitude of a composition fluctuation. If we assume[15] that the effective interface thickness is the cube root of the most probable volume for a composition fluctuation ΔC, where

ΔC is the equilibrium miscibility gap, and that gradient energy contributions proportional to $(\nabla C)^2$ predominate in the critical region, we obtain $\mu = \frac{2}{3}$. A corresponding argument[15] without gradient terms yields $\mu = 23/36 = 0.64$. Implicitly assumed are $\beta = \frac{1}{3}$ and the usual thermodynamics.[16]

For comparison, lattice-gas calculations of the temperature dependence of the effective range of correlations yields $\nu = 0.64$. However, we are unable to connect rigorously μ and ν.

Finally, we can estimate β using the index of refraction data along the coexistence curve. In Fig. 3, n_2-n_1 fits an equation of the form $n_2-n_1 \propto (T_C-T)\beta'$, where $\beta' = 0.347 \pm 0.008$. Lattice-gas calculations yield $\beta = 0.3125$ for the composition gap. The measured composition miscibility gap parameter[17] $\beta \cong 0.33 \pm 0.01$ is very close to β' because of the weak and symmetric dependence of n on C and T. However, the precise experimental values of β and β' are subject to strong effects of impurities[11] that may limit the absolute accuracy of β and β' to ±0.02. Various samples yielded slightly different β' values, although each one had high precision. This source of error may be the cause of larger values of β and "flat tops" occasionally reported for miscibility gaps in critical mixtures.[18]

These results establish the existence in critical mixtures of diffuse interfaces ~1000 Å thick. The temperature dependence of the ef-
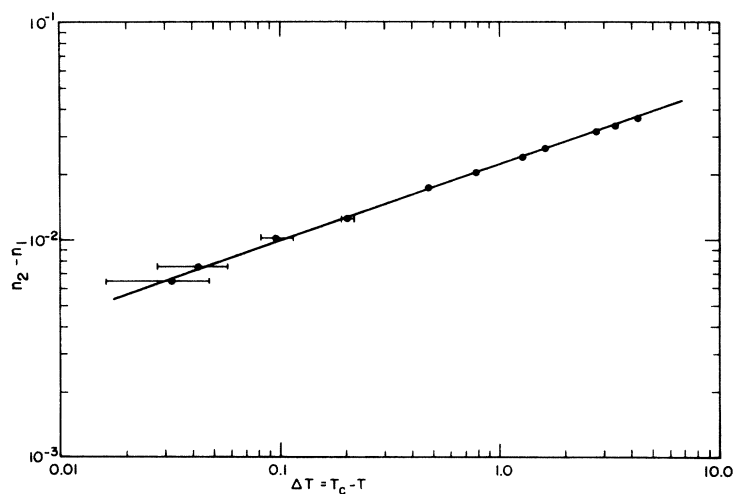

FIG. 3. Temperature dependence of the miscibility gap represented by the coexisting indices of refraction for the cyclohexane-methanol system. The error bars indicate the error possible due to impurity effects on critical temperature. Errors of measurement are ± 0.005°C and ± 0.000 05 index units. For this sample $\beta' = 0.347 \pm 0.008$ and $T_C = 45.222 \pm 0.01°C$.

fective interface thickness is near that expected
of the range of correlations in a lattice-gas
model for a critical mixture and should pro-
vide a useful measure of the range of correla-
tions. We hope that these measurements will
stimulate theoretical development of lattice-
gas models for the interface. More detailed
experiments are underway.

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[13](a) That the occurrence of the diffuse interface is
common in critical mixtures is suggested by prelimi-
nary observations on the one other system studied,
carbon disulfide—acetic anhydride, where similar dif-
fuse interfaces were found near the critical tempera-
ture. (b) The possibility of impurity effects in the dif-
fuse interfaces cannot be entirely excluded since there
are nearly enough total impurities present to supply
impurity for layers of the observed thickness. How-
ever, there was nothing in our results to suggest per-
turbations due to soluble impurities at the level at-
tained.
[14]Reference 10, page 367 {for $[(n-\bar{n})/b]^2$ read $[(n-\bar{n})/l]^2$ in second footnote}.
[15]B. Widom, private communication.
[16]See reference 3. We assumed $\gamma = 5/4$.
[17]Deduced from data of reference 11.
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EXCITON ABSORPTION IN THE PRESENCE OF EXCITED F CENTERS*

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Since Swank and Brown[1] observed an unexpect-
edly long lifetime of the relaxed F excited state,
the peculiarities of this state in alkali halides
have given rise to a number of experimental[2]
and theoretical[3] investigations. This Letter
describes an experiment to measure the opti-
cal absorption of crystals containing defects
in excited states which will in particular add
a new method of studying the excited F center
in alkali halides.

This experiment in KI has shown an optical
absorption band which exists only during the
lifetime of the excited electronic state of the
F center. The position and strength of the ab-
sorption band suggest that it is due to an exci-
ton state formed in the vicinity of the relaxed
excited F center. The reported absorption will
then depend on the crystal field surrounding
the center and thus give direct evidence of its
symmetry properties.

The experimental setup, best described as
a pulse-transmission experiment (Fig. 1), is
similar in its layout to the two-photon-absorp-
tion experiment reported by Hopfield, Worlock,
and Park.[4] Light from a xenon flash tube FX-
38A is focused on the sample and then imaged
on the entrance slit of a Jarrell-Ash Model-82
monochromator. During the duration of the
flash pulse the signal from a Dumont 7664 pho-
tomultiplier is simultaneously used to deter-
mine the transmitted flash-tube intensity $I_0(\lambda)$
and, by means of a high-pass filter, to deter-
mine fast changes $\Delta I(\lambda)$ of the transmitted light
intensity. Changes of transmission, both posi-