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Critical-Temperature and Coexistence-Curve Measurements in Thick Films[*]

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We report the first observation of a critical-temperature and coexistence-curve dependence on film thickness for a binary fluid mixture (methanol-cyclohexane). The data suggest long-range interactions with mean-field exponent $\beta = \frac{1}{2}$ for film thicknesses, L, in the range $1\ \mu\text{m} \lesssim L \lesssim 6\ \mu\text{m}$.

Theoretical predictions[1,2] have been made on thick-film behavior near a critical point. Exact and Monte Carlo calculations on Ising models[3] for finite systems have corroborated these predictions as, to some extent, have experiments on He films,[4,5] superconductors,[5] and pseudo two-dimensional crystals.[6] A critical-temperature dependence on film thickness has been inferred from data[7] on Ni and shown to be consistent with the theory. However, recent measurements on monomolecular films on water,[8] which should simulate a two-dimensional liquid-gas transition, resulted in mean-field rather than lattice-gas exponents. We report the first measurements of the the critical-temperature shift and the coexistence curve for several thicknesses in the binary fluid mixture methanol-cyclohexane.

The measurement technique employs two fused-silica interferometer flats with high-reflectance coatings[9] tilted slightly so that three or four vertical "equal thickness" fringes are observed. The fluid under study was contained between the coated surfaces of the optical flats (which were flat to $\lambda/100$ but distorted in the process of sealing in the cell to $\lambda/20$ across the 1.5-cm diam). The stainless steel cell containing the fluids and flats was oriented with the flats vertical and illuminated at normal incidence by an expanded and collimated horizontal beam from 0.5-mW He-Ne laser. The flat spacing could be varied continuously by means of differential screws. A reservoir of bulk fluid surrounded the flats and was contained by a bellows that sealed to each cell half. The spacing was determined by measuring the number of coincidences (integral and fractional) for the H red line (6566 Å) and the He-Ne laser line (6328 Å).

The fluid cell containing the flats was mounted inside a 0.5-in.-thick aluminum heat shield and the cell and shield were mounted within a brass vacuum envelope. The cell, shield, and vacuum envelope were mutually isolated from heat conduction and heat was transferred principally through radiation. Corrections for the thermal expansion of the cell were taken into account.

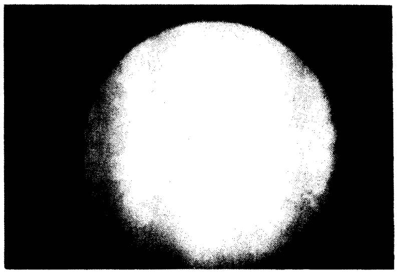
The cell temperature was controlled by a YSI 44004 thermistor in a 33-Hz Kelvin bridge.[10] Temperature measurements were made with other thermistors in an identical bridge circuit. The heat shield was controlled with a dc bridge and power amplifier[11] to ±2 mK over a period of a week. We could consistently measure the cell temperature with a *resolution* of 20 μK and found the cell temperature to hold constant to ±50 μK/day. Since these thermistors were not calibrated, we could only determine our *absolute* temperature to ±0.2 K.

The fluids were Fisher "Spectranalyzed" methanol (99.95% pure) and cyclohexane (99.98% pure) with a composition of (29.08 ± 0.02)% by weight methanol, which is the critical composition.[12,13] Although a small impurity (ours is 0.03% by weight) causes a critical-temperature shift, it does not seem to affect the critical exponents,[12,14] nor is it expected to alter the critical-temperature dependence[15] on spacing.

In order to assure a homogeneous, uniform sample at the critical concentration, the flat separation was increased to 120 μm at 0.7 K above the bulk critical temperature and the entire can, with the cell inside, was shaken. The uniformity of the fringes was used as the guide for a homogeneous sample. The spacing was then reduced to the desired value and the critical temperature was approached. Since the critical behavior of these films was to be measured, particular care was taken to avoid mixing between the film and the surrounding bulk fluid. For films thicker than 12 μm, it typically took 2–3 days for noticeable mixing; for films less than 3 μm thick no mixing was ever observed, and at intermediate spacings some mixing would occur after about a week.

The critical temperature was determined by the appearance of the fringes. For spacings larger than about 12 μm, the fringes became two to three times as broad and took on a "granular" appearance at the transition temperature when approached from above. This transition was sharp to ± 1 mK, whether raising or lowering the temperature, which was done in 1–2-mK steps, taking about a half hour for the system to come to equilibrium, and with a three- to five-hour wait between steps. The "granular" appearance of the fringes was attributed to the many drops which form between the flats on phase separation; however, the spacing was close enough (12–60 μm) that total extinction of the light did not occur. Otherwise, this transition was similar to that observed previously[16] in a bulk (600 μm) system. For spacings 6 μm and smaller, the fringe was seen to split into two parts at the transition temperature, which we attribute to the drops that form on phase separation being large enough to span the space between the flats, creating small regions of each phase with different refractive indices. If an unfiltered Hg lamp was used as a light source, then the broad blue-green bands that were produced (due to the coatings having a low reflectance at these wavelengths) allowed sufficient contrast for the drops to be clearly visible [see Fig. 1(a)]. The results of the critical-temperature determination in the thick films (3 $\mu\text{m} \lesssim L \lesssim 60\ \mu\text{m}$) are shown in Fig. 2.

For those spacings where fringe splitting occurred ($\leq 6\ \mu$m), the coexistence curve could be determined by measuring the fringe splitting, y, fringe spacing, x, and flat separation, L. The difference in refractive index, Δn, between the two phases is given by $y/x = 2L\Delta n/\lambda$, where λ is the vacuum wavelength. The smallest measurable value of Δn depends on the optical resolution, $(y/x)_{\min}$, and ths spacing, L; for our mirrors[9] $(y/x)_{\min} \approx 0.013$. The fringe splitting is thus not observable for small flat separations ($< 3\ \mu$m) until the temperature is well below critical. Critical temperatures for these spacings can be estimated either by extrapolating the $T_c(L)$ data in Fig. 2, or by constraining the data points in Fig. 3 to fit a straight line. We find the values of $T_c(L)$ obtained by extrapolating the logarithmic curve in Fig. 2 to be the values obtained by fitting the data in Fig. 3, within experimental error.


(a)

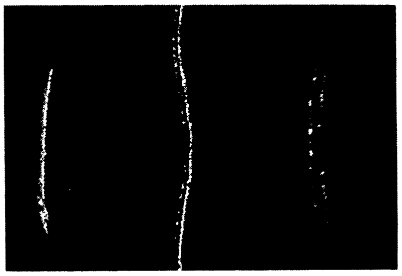

(b)

FIG. 1. (a) "Drops" spanning the flats as seen with an unfiltered Hg light source. The broad light bands are caused by the low reflectivity at these (blue-green) wavelengths. This picture was at $L = 6\ \mu$m and $T_c(L) - T = 0.077$ K. (b) Photograph of fringe splitting almost 2 K below the critical temperature. Flat separation at the center fringes is $0.9 \pm 0.1\ \mu$m and the fringes on the left (right) are at a separation $\lambda/2n$ smaller (larger) than at the center. The fringe splitting is barely detectable at the left but is quite large at the right. This behavior shows the amplitude $A(L)$ and critical-temperature $T_c(L)$ dependence on spacing discussed in the text. These three points are the highest $T_c(L) - T$ points shown in Fig. 3.

The coexistence-curve data in Fig. 3 are presented using the values of $T_c(L)$ from the logarith-

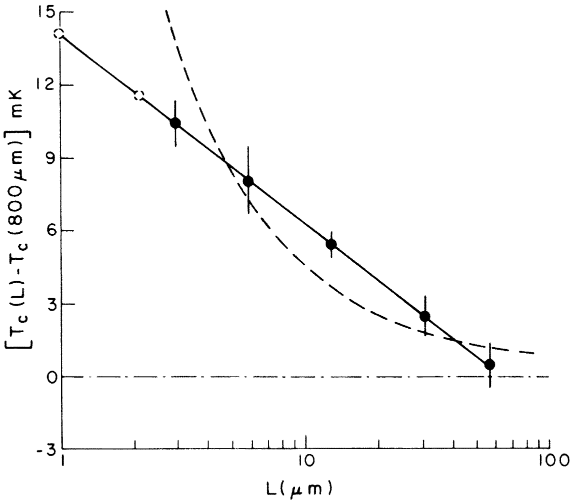


FIG. 2. Shift in critical temperature relative to the bulk (800 μm) value as a function of flat spacing, L. The solid line is the fit to a ln$L$ dependence; the dashed line is the best fit to the data for L^{-1} dependence. The dashed circles are the extrapolated values of $T_c(L)$ used for the coexistence curve. The nature of the curve between 60 and 800 μm is not known. More data are needed to determine this behavior.

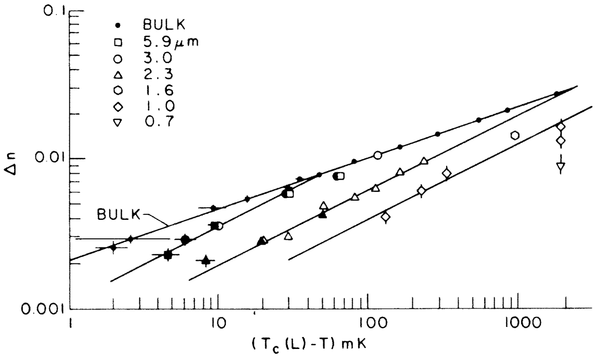


FIG. 3. Coexistence curves for the various spacings. The bulk line and data are from Ref. 13, and have a slope (β_3) of 0.326; lines drawn through the remaining points have a slope (β_2) of 0.5. Open symbols are points taken while lowering (and solid symbols while raising) the temperature.

mic curve in Fig. 2. These data were reproducible whether raising or lowering the temperature as shown in Fig. 3. It is assumed that the dependence of the refractive index difference between the two phases is given by[17] $\Delta n = A(L)\{[T_c(L) - T]/T_c(L)\}^{\beta}$, where $A(L)$ is a constant for a particular thickness L and β is the critical exponent. Thus a plot of $\ln(\Delta n)$ vs $\ln[T_c(L) - T]$ for the various flat spacings should give a set of straight lines. A log-log plot of the data points does indeed appear to give a set of reasonably straight lines, one for each flat spacing (see Fig. 3). Since the most extensive of the coexistence data was obtained for a flat spacing of 2.3 μm (other than the large amount of data for the bulk fluid), a fit was made to determine the slope of a straight line through these data points. This slope is the critical exponent β and the fit gave its value to be very close to 0.5. Straight lines with this slope were also *drawn* through the data points for the spacings 6, 3, and 1 μm. The fact that these data may be fitted by straight lines with a slope of 0.5 also suggests that $\beta \approx 0.5$ for these spacings as well. The data taken at flat spacings of 12 and 125 μm[18] fall on the bulk curve. The bulk curve was determined from 44 data points taken from $T_c - T = 2$ mK to 18 K for a bulk fluid.[13] A *representative* sample of the bulk data is shown in Fig. 3. An apparent "crossover" from bulk to "two-dimensional" behavior occurs in the 3- and 6-μm points. The strong dependence of the coexistence curve (or fringe splitting) on L is vividly shown in Fig. 1(b), where L varies from ~0.7 μm at the left fringe to ~1.2 μm at the right one, but where the fringe splitting is much larger than a factor of 2.

Thus for film thicknesses 1 $\mu\text{m} \lesssim L \lesssim 6$ μm, we infer a value of 0.5 for the critical exponent β. This is the mean-field value and agrees with the experimental results[8] on monomolecular films on water. Our mean-field value for β is consistent with the apparent logarithmic dependence of the critical temperature on spacing (Fig. 2). Scaling arguments[1,2] predict that $T_c(L)$ should behave as $L^{-\lambda}$, with[1] $\lambda = 1$ when the fluid composition is constant for various spacings. However, for long-range interactions,[1] $\lambda \to 0$, which results in either no dependence of $T_c(L)$ upon spacing or the logarithmic dependence, which seems to fit our data best.

Bulk behavior is predicted to "cross over" to "two-dimensional" behavior when $L \sim \xi$. This occurs at a crossover temperature $T^{\times}$ given by[1,2] $\{[T_c(L) - T^{\times}]/T_c(\infty)\} \sim (L/a)^{-\theta}$, where a is the thickness of a monolayer. If one chooses $\theta = 1$ and $a = 6$ Å then the values of $T_c(L) - T^{\times}$ are 0.032, 0.064, 0.083, 0.119, 0.191, and 0.273 K for film thicknesses $L = 5.9$, 3.0, 2.3, 1.6, 1.0, and 0.7 μm, respectively. It is of particular interest that these temperatures are significantly lower than those suggested by the graph of Fig. 3. Strict scaling theory gives $\theta = 1/\nu = 1.56$ which yields much lower crossover temperatures as do larger values for θ (see below). The amplitude

$A(L)$ of the coexistence curve, $\Delta n = A(L)\{[T_c(L) - T]/T_c(\infty)\}^{\beta_2}$, should also scale[1,2] with L: $A(L) \propto L^{(\beta_2-\beta_3)\theta}$, where the subscript on β is the "dimensionality." Our data as plotted in Fig. 3 suggest that the amplitude $A(L)$ varies as L^z with z in the range 0.6 to 0.8. With β_2 taken to be our experimental value of 0.5 and $\beta_3 = 0.326$,[16] then $\theta = 4 \pm 0.5$.

In conclusion, our experimental results on the critical-temperature shift suggest a logarithmic dependence on film thickness for thick films (1 μm $\leq L \leq$ 60 μm). A "mean-field" value of $\beta = 0.5$ was determined from the coexistence curve data taken close to $T_c(L)$ for film thicknesses $\leq$ 6 μm. These results are consistent with each other and suggest that long-range interactions are present, rather than the lattice-gas behavior expected. It is not clear to what extent the walls constraining the fluid mixture affect its critical behavior.

Further experiments are in progress.

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Longitudinal Optical Vibrations in Glasses: GeO_2 and SiO_2

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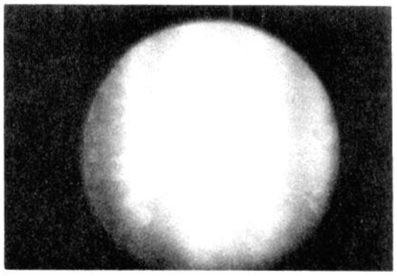
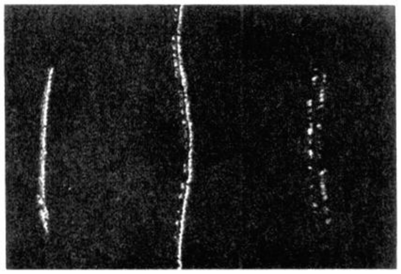
We show that longitudinal optical (LO) vibrational modes account for several previously unexplained peaks in the Raman spectra of vitreous GeO_2 and SiO_2. Identification of LO modes in these and other glasses reduces the complexity of the spectra that must be explained by simple structural models. It also follows that long-range (Coulomb) forces should be included in complete theories of the vibrational properties of many glasses.

The Raman spectra of vitreous germania (v-GeO_2) and vitreous silica (v-SiO_2) have long been puzzling because each contains peaks which have not been explained by vibrational calculations based on the favored structural model. The presently favored model, proposed in 1932 by Zachariasen,[1] asserts that v-SiO_2 is primarily a continuous network of nearly perfect SiO_4 tetrahedra connected to each other in such a way that each corner oxygen atom is shared by a different neighboring tetrahedral unit, thus preserving the chemical formula. The disorder that is characteristic of glasses is accounted for by allowing large variations in the orientation of neighboring tetrahedra. This structure is also thought to be appropriate for v-GeO_2 and for several other glasses, such as v-BeF_2, v-$ZnCl_2$, and v-GeS_2.

The Zachariasen model is especially attractive because it raises the possibility that many properties can be treated by focusing attention on a single representative tetrahedral unit, and by assuming simple statistical laws for the orientation



(a)



(b)

FIG. 1. (a) "Drops" spanning the flats as seen with an unfiltered Hg light source. The broad light bands are caused by the low reflectivity at these (blue-green) wavelengths. This picture was at $L = 6\ \mu\text{m}$ and $T_c(L) - T = 0.077$ K. (b) Photograph of fringe splitting almost 2 K below the critical temperature. Flat separation at the center fringes is $0.9 \pm 0.1\ \mu\text{m}$ and the fringes on the left (right) are at a separation $\lambda/2n$ smaller (larger) than at the center. The fringe splitting is barely detectable at the left but is quite large at the right. This behavior shows the amplitude $A(L)$ and critical-temperature $T_c(L)$ dependence on spacing discussed in the text. These three points are the highest $T_c(L) - T$ points shown in Fig. 3.