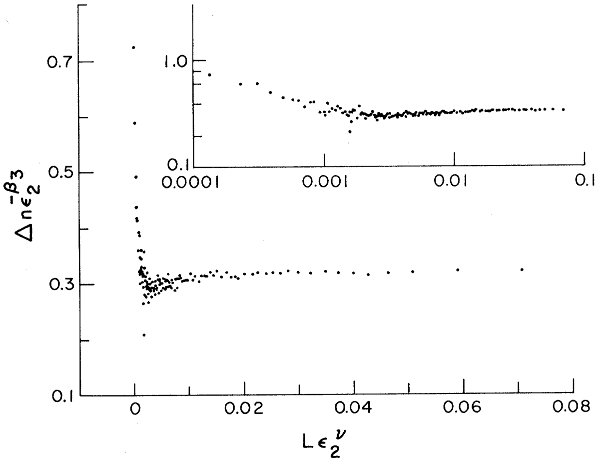

FIG. 2. Smoothed plot of $\epsilon_2^{-\beta_3}\Delta n(T,L)$ vs $L\epsilon_2^{\nu}$, and (inset) log-log plot of same quantities. Each plotted point is the average of 10 of our 1300 data points for 23 distinct film thicknesses. Although averaging reduces the apparent scatter of the data, the residuals of the individual data from the mean behavior are not systematically dependent on film thickness.

in the scatter of our data.

In conclusion, coexistence curves have been determined for films of 2,6-lutidine + water near its lower critical point. We find that for $L \leqslant 6$ μm the films crossover from a 3D to a 2D regime. The β_3 result is in excellent agreement with experimental values found for bulk binary fluid systems and with latest renormalization-group estimates.[10] β_2 agrees with the value $\frac{1}{8}$ for the 2D Ising model. This represents the first evidence of interdimensional crossover and of 2D scaling in Ising fluids. Finally, the scaling-theory requirement that a *law of corresponding states* exist for films is verified for our system.

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Critical Phenomena in Fluid Films: Critical-Temperature-Shift, Crossover-Temperature, and Coexistence-Curve-Amplitude Exponents, and a Fluid-Boundary Interaction

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Refractive-index coexistence curves for films of the binary fluid mixture 2,6-lutidine + water are analyzed. The critical-temperature–shift exponent and the crossover-temperature exponent agree well with scaling-theory predictions. The two-dimensional coexistence-curve amplitudes are largely consistent with the scaling prediction. The predicted behavior is superimposed on systematically displaced coexistence curves. We argue that the displacement arises from interaction between the fluid and the plane mirrors which confine it.

It has been shown[1] that coexistence curves for films of the critical binary mixture 2,6-lutidine + water exhibit a crossover from one universality class to another. The crossover, between three-dimensional (3D) and two-dimensional (2D) Ising-model scaling, occurs when the 3D correlation length ξ becomes comparable to the film thickness L. The result is in accord with the scaling theory treatment of such films. The scaling theory also provides several predictions which describe how the critical temperature, crossover temperature, and coexistence-curve amplitude depend on film thickness. The purpose of this Letter is to show that these predictions are verified by the experimental coexistence curves presented in Ref. 1. We will also introduce new data in evidence of an effect due to the presence of the interferometer mirrors bounding the fluid films. This effect amounts to a displacement in temperature of each film's coexistence curve by an amount dependent on its thickness. We conclude that the experimental curves can be understood as follows. Their internal structures confirm scaling theory predictions for fluid films, while the displacement is the result of film/boundary interaction.

To accomplish our first purpose, we will treat the numerical results of Ref. 1 as data. Specifically, the data for each of the films are the film thickness L, the coexistence-curve parameters for the 3D domain $[T_{c3}(L),\ \beta_3,\ A_3]$, and the analogous parameters for the 2D domain $[T_{c2}(L),\ \beta_3,\ A_2(L)]$.[2] The 3D and 2D parameters were determined from the coexistence-curve data by the analysis procedures detailed in Ref. 1.

The data are to be compared to scaling-theory predictions which are power laws in the film thickness. These arise because each film's finite thickness bounds the growth of the correlation length in one dimension. This constraint is predicted to result in a shift or change of the critical temperature given by

$$T_{c2}(L)-T_{c3}(L)=KL^{-1/\nu},\quad K\ \text{const.} \tag{1}$$

The amplitude of the coexistence curve for the 2D domain should depend on the film thickness:

$$A_2(L)=EL^{(\beta_2-\beta_3)/\nu},\quad E\ \text{const.} \tag{2}$$

We locate the crossover by defining the crossover temperature $T_\times(L)$ as the temperature of intersection of the 2D and 3D portions of a coexistence curve [Eqs. (1) and (2) of Ref. 1]. Then the width in temperature of the 2D domain is predicted to be

$$T_\times(L)-T_{c2}(L)=JL^{-1/\nu},\quad J\ \text{const,} \tag{3}$$

while the equation

$$T_\times(L)-T_{c3}(L)=ML^{-1/\nu},\quad M\ \text{const,} \tag{4}$$

embodies our expectation that crossover should occur when ξ becomes comparable to L. The derivation of Eqs. (1)–(4) also provides the relation among the coefficients,

$$E=A_3(J+K)^{\beta_3}/J^{\beta_2}. \tag{5}$$

The numbered equations define what we call the internal structure of the coexistence curves. Aside from the fact that they allow for possibly different extrapolated 3D critical temperatures, where ξ diverges, they are the same as the free-film equations of Fisher.[3] The internal structure they predict is identical to the free-film predictions. In accord with the foregoing definition of the crossover temperature, we generated the experimental $T_\times(L)$ datum for each film as the intersection of the fitted coexistence curves of the 2D and 3D domains.

We performed weighted least-squares analyses of the data for each of Eqs. (1), (3), and (4). The results are shown in Table I. Most significantly, the critical-temperature–shift exponent [Eq. (1)] and the crossover-temperature exponents [Eqs. (3) and (4)] are nearly equal and agree quite closely with the renormalization-group value[4] 0.630

TABLE I. Best least-squares fits with power laws in film thickness L, in micrometers.

Temperature difference (k)	Number of data points	Coefficient	(Exponent)$^{-1}$	Reduced χ^2
$T_{c2}(1)-T_{c3}(L)$ [Eq. (1)]	28	-0.0129 ± 0.0012	0.64 ± 0.09	2.05
$T_\times(L)-T_{c2}(L)$ [Eq. (3)]	28	0.0264 ± 0.0016	0.61 ± 0.06	5.30
$T_\times(L)-T_{c3}(L)$ [Eq. (4)]	28	0.0127 ± 0.0010	0.66 ± 0.06	1.68
$T_{c3}(L)-T_c(\infty)$ (Ag)	43	0.047 ± 0.002	$(0.80\pm0.08)^{-1}$	6.76
$T_{c3}(L)-T_c(\infty)$ (dielectric mirrors)	32	-0.24 ± 0.08	$(0.81\pm0.09)^{-1}$	8.59

for ν. We conclude that our experiments support these scaling-theory predictions. As to the coefficients of the same equations, we find that $|K| = M$ and $J/M = 2$ within our precision. Both results indicate that $T_{c3}(L)$ is quite near the middle of the 2D domain. The crossover is expected to occur when ξ becomes comparable to L. If we express this as $L = m\xi$ and use Eq. (4) to eliminate L we find that $m = M^{\nu}/\xi_0 T_{c3}{}^{\nu}(L)$, where ξ_0 is the correlation-length amplitude. Using the experimental determination[5] $\xi_0 = 2.9$ Å for 2,6-lutidine + water we find that $m = 4^{+3}_{-2}$. We should, of course, use the two-phase correlation-length amplitude ξ_0', but no experimental determination has been made. Tarko and Fisher[6] have calculated that $\xi_0/\xi_0' \approx 1.96$ for the second-moment correlation length, while Fisher[7] has argued that $\xi_0/\xi_0' \approx 1.5$ for the true range of correlation. The use of either of these would produce values for m larger by the factors cited. The large scatter in our data near crossover prevents us from reaching conclusions regarding the sharpness of crossover.

We are unable to confirm the 2D amplitude prediction of Eq. (2). We can determine a value for E from experimental quantities via Eq. (5). Use of this result and predicted exponents in Eq. (2) enables us to "predict" $A_2(L)$. All ten films for $L < 2.2$ μm are randomly but rather widely scattered about the predicted line. Seven films of greater thickness also cluster about the line, but eleven films for $L > 2.2$ μm show $A_2(L)$ values which are larger than the prediction by 25–60%. The majority of the data are consistent with the scaling prediction, but we are unable to account for the large values of the remainder. Thus we cannot confirm the prediction, despite our belief that it is very likely correct.

We can also examine the behavior of $T_{c3}(L)$. For a free film we would expect $T_{c3}(L) = T_c(\infty)$ for all L, where $T_c(\infty)$ is the critical temperature of a bulk ($L \rightarrow \infty$) sample of the critical binary mixture. Our experimental films, on the contrary, are bounded by the interferometer mirrors and can interact with them. Since such an interaction could conceivably displace the 3D critical temperature, there is no *a priori* reason why $T_{c3}(T)$ should be constant. In fact, the experimental $T_{c3}(L)$ do vary with the film thickness.

All 32 films show a displacement $|T_{c3}(L) - T_c(\infty)|$. The three thicker films ($L \simeq 14$ μm) show the displacement but no crossover. To determine the scope of the displacement phenomena, we made eleven more determinations of $T_{c3}(L)$ for $6 < L < 182$ μm. These determinations amounted to beginning in a film's one-phase region and raising its temperature in 1- or 2-mK steps. When phase separation was visually observed, the phase-separation temperature (PST) was known to ± 1 mK. We take these PST as 3D critical temperatures, $T_{c3}(L)$, since (1) $T_{c3}(L)$ and $T_{c2}(L)$ are experimentally unresolvable for these thicker films, and (2) PST determined for the original 32 films showed very good agreement with the critical temperatures determined by numerical analysis.

All eleven PST show the thickness-dependent displacement. We combined these with the other 32 $T_{c3}(L)$ and performed least-squares analysis of the 43 total data. This showed that the displacement is reasonably well described by a power law in film thickness:

$$T_{c3}(L) - T_c(\infty) = (0.047 \pm 0.002)L^{-(0.81 \pm 0.08)}.$$

The fact that the displacement exists independently of crossover suggests the hypothesis that it arises from a film/mirror interaction.

We found further evidence for the hypothesis by changing the mirrors. The data so far discussed were collected from films bounded by silvered mirrors. We also determined 32 PST's for films bounded by dielectric material. These mirrors consisted of multilayer dielectric mirrors overcoated with SiO_2. The films had thicknesses between 8 and 272 μm. Their critical temperatures were also displaced from $T_c(\infty)$ in an L-dependent manner. Least-squares analysis establishes that

$$T_{c3}(L) - T_c(\infty) = -(0.24 \pm 0.08)L^{-(0.80 \pm 0.09)},$$

for these films. Comparing this result to that for the Ag mirrors we see the following. The power-law exponents appear to be equal for the two kinds of mirrors, but *changing the mirror material changes both the direction and size of the 3D critical-temperature displacement.* These results are depicted in Fig. 1.

The foregoing is clear evidence for the role of a film/mirror interaction underlying the coexistence-curve displacements. However, the effects arising from the constraint on ξ are evidently independent of the interaction. This is true insofar as β_2, β_3, and A_3 have the expected values which are independent of L, and to the rather extensive degree to which the coexistence curves' internal structures verify the scaling-theory predictions.

A previous study of binary-fluid-film critical behavior was reported by Jacobs, Mockler, and O'Sullivan.[8] They examined the mixture methanol

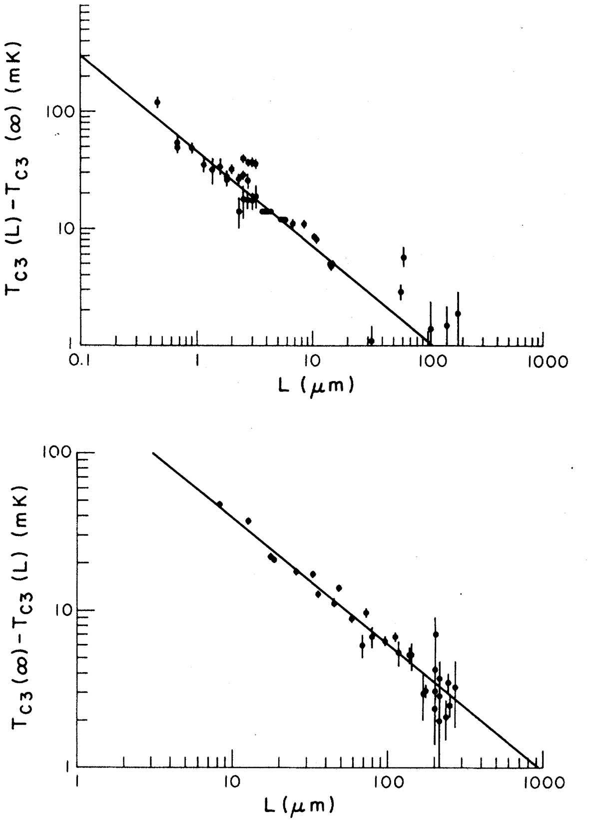

FIG. 1. Plot of $\ln[T_{c3}(L) - T_{c3}(\infty)]$ vs $\ln L$ for Ag mirrors (upper panel); plot of $\ln[T_{c3}(\infty) - T_{c3}(L)]$ vs $\ln L$ for SiO_2-overcoated dielectric mirrors (lower panel).

+ cyclohexane and developed a forerunner of the apparatus and experimental technique employed in the present work. In light of our experience and results with 2,6-lutidine + water we are unable to reach the same conclusions they reported regarding their data. There are not enough data on methanol + cyclohexane to resolve several issues. For example, the film-sample preparation procedure they described was inadequate for our experiments, because it yielded irreproducible critical temperatures. Its adequacy for methanol + cyclohexane was not demonstrated, since no reproducibility checks were run. Thus the logarithmic critical-temperature shift which they reported is of uncertain validity. The balance of their analysis is also open to question, since it relies on the reported critical-temperature–shift relation. We believe that more extensive studies are needed to fully elucidate the critical behavior of methanol + cyclohexane films.

The film-preparation techniques used in the present experiments led to considerably reduced scatter and much greater reproducibility of critical temperatures. We believe, however, that small variations in film composition from sample to sample are still the most important source of experimental error and are probably the major source of the large reduced χ^2 values shown in the table.

In summary, we have studied finite-size effects in films of the critical binary fluid mixture 2,6-lutidine + water. Our data can be understood as the superposition of two effects. The first arises as the result of a film/mirror interaction. It amounts to a simple displacement or translation in temperature of entire coexistence curves. The second effect has its origin in the fact that the films' finite thicknesses constrain the growth of the correlation length. Our results provide the first verification in an Ising fluid system of the scaling-theory predictions for the critical-temperature–shift and crossover-temperature exponents arising from the constraint. The prediction regarding the 2D amplitude exponent receives tentative support.

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