Observation of a Correlation-Length Finite-Size Effect in Rayleigh Scattering from Thin Critical Fluid Films

Yeke Tang, Paul D. Beale, R. C. Mockler, and W. J. O'Sullivan
Department of Physics, University of Colorado, Boulder, Colorado 80309
(Received 30 September 1985)

Rayleigh linewidth data gathered at small scattering angles on critical-mixture films of thickness $2L$ are found to collapse about a single universal curve, $\Gamma^*(K\xi^{\rm eff})$, where $\Gamma^*(x)$ is the 3D reduced Rayleigh linewidth function, and $\xi^{\rm eff}$ is an effective correlation length obeying a general finite-size scaling relation, $\xi^{\rm eff}/L = F(\xi/L)$. The latter reveals that $\xi^{\rm eff}$ grows with ξ until $\xi \approx L$, when its growth terminates, implying the existence of surface layers of thickness ξ formed by preferential wall–fluid interactions.

PACS numbers: 68.10.Cr, 64.60.Ht, 64.70.Ja, 66.10.Cb

The excellent agreement between precise Rayleigh linewidth data collected on binary-liquid critical mixtures and the predictions of mode-mode coupling and dynamic renormalization (RG) theories has left little doubt that these models provide a correct representation of liquid critical dynamics in three dimensions (3D). This success encouraged us to consider whether Rayleigh scattering measurements made on binary-fluid films might reveal the effects size restrictions have on critical fluid dynamics, including possible crossovers from 3D to 2D response near film critical points.

In our experiments, finite-size conditions are achieved by filling the space between two fused-silica optical flats with a binary liquid mixed at the bulk critical composition. For such films, naive dynamic scaling arguments predict that the Rayleigh linewidth dependence upon $k\xi$ should be indistinguishable from that for otherwise identical large-volume samples, until conditions defined by $\xi \approx L$ and $\Lambda \approx 2L$ are satisfied. Here, $2L$ is the film thickness, ξ the correlation length, and $\Lambda = 2\pi k^{-1}$ the sampling length probed by the scattering process at wave number k. When both finite-size conditions have been met, the same arguments suggest that a dynamic universality-class crossover from 3D to 2D should occur. In fact, such primitive arguments are unlikely to apply to our class of films, as suggested especially by the theoretical studies of Fisher and Nakanishi[1] and the results of recent mode calculations by Calvo and Ferrell.[2,3] To begin with, the solid surfaces are not idealized boundaries, but will interact selectively with the two components comprising the mixture. Consequently, surface layers rich in one component and deficient in the second will form and thicken as the film is brought toward its nominal critical temperature. In a sealed film having a fixed global composition, the preference shown by the surfaces for one component ensures that the fluid composition varies symmetrically about its midplane, where the deficiency in surface-rich component is balanced by an excess concentration of surface-poor component. If the surface-force–induced gradients are sufficiently large across the film, then locally the film will be pulled away from the critical composition and it will not display critical behavior.

The first Rayleigh-scattering measurements on thin critical fluid films were carried out by Casalnuovo and co-workers[4,5] on closed films of 2,6-lutidine + water formed at the large-volume critical composition; films ranging in thickness from 13.1 to 0.5 μm were studied at a fixed scattering angle of 60°. The data were in excellent agreement with mode-mode and RG predictions for the Rayleigh linewidth dependence upon $k\xi$ in 3D, although both finite-size scaling conditions were apparently satisfied in the 0.5-μm film. There was no evidence of preferential wetting.

Subsequently, Calvo and Ferrell[2] and Calvo[3] applied mode-mode theory to determine the expected critical diffusion coefficient for binary-fluid film under conditions specified by two key conditions: First, the walls are neutral, ensuring the absence of preferential adsorption; second, the fluid in direct contact with the walls is stationary. The calculations cover both the asymptotic limit ($k\xi >> 1$ and $kL >> 1$) and the region away from the critical point for arbitrary $k\xi$. They predict that no crossover between 3D and 2D dynamic regimes should occur in critical fluids confined between two parallel walls; rather, the order-parameter relaxation rate should be suppressed continuously as a function of ξ, L, and k, relative to the large-volume rate. In the asymptotic regime where the effect is greatest, one expects a reduction of $\sim 36\%$ in the Rayleigh linewidth for $kL = 3$, the effect falling off appreciably at larger values of kL. Consequently, even were asymptotic limit conditions satisfied in our experiment on the 0.5-μm film, and they were not, the predicted correction is smaller than was our experimental uncertainty.

In this Letter we report the first results of Rayleigh linewidth studies, carried out at scattering angles of $19.5 \pm 0.1°$ and $8.1 \pm 0.1°$ on 2-μm-thick films of a critical mixture of 2,6-lutidine + water. We find that the film Rayleigh linewidths increase at forward scattering angles in contrast to the predictions of Calvo and Ferrell,[2,3] and argue that our results imply an "effective" correlation-length finite-size effect, consistent with the existence of composition gradients induced by a discriminatory wall–fluid interaction.

The experiments consisted of heterodyne photon autocorrelation measurements of the Rayleigh linewidth in the homogeneous phase, made from about 50 mK to within 0.1 mK of the observed film phase-separation temperatures. Several films were studied, all with $2L = 2.0 \pm 0.1$ μm, this value being set by a 2-μm-thick SiO spacer annulus deposited on one of the fused-silica flats. Aside from modifications necessary to allow heterodyne detection at forward angles, the experimental apparatus used is identical to that reported earlier,[4,5] as is the scattering configuration which ensures that the scattered wave vector lies in the plane of the film. Measurements at each scattering angle were made at laser wavelengths of 514.5, 488.0, and 457.9 nm, corresponding to a 12% spread in k.

The data are displayed in Figs. 1(a) and 1(b) in terms of the reduced Rayleigh linewidth, $6\pi\eta\Gamma/Rk_BTk^3$, plotted as a function of $k\xi$. We use the value of the shear viscosity for 2,6-lutidine + water measured near the critical point by Gulari *et al.*[6], and the value for R of 1.020 ± 0.028 reported by Burstyn and Sengers.[7] The sampling length is nearly equal to the film thickness ($\Lambda \approx 1.5$ μm) and roughly twice the film thickness ($\Lambda \approx 3.6$ μm) for scattering angles of 19.5° and 8.1°, respectively. The 19.5° data set includes eight points with $\xi > 1$ μm and 24 with $k\xi > 1$; the 8.1° set includes three points with $\xi > 1$ μm and six with $k\xi > 1$. Each datum point is the value of Γ^* corresponding to the mean Rayleigh linewidth determined by an average of the fitted results of ten measurements of the intensity autocorrelation function. At 19.5°, typical decay-time relative standard deviations were $\sigma_\tau/\bar{\tau} \approx \pm 0.05$, and the autocorrelation function nonexponentiality factor, Q ($Q = K_2/K_1^2$, where K_i is the ith cumulant), was typically 0.1. The corresponding 8.1° results were ± 0.1 and ~ 0.2 to 0.3, respectively. The increased "noise" in the 8.1° results is consistent with the much smaller k value and the concomitant increase in $\Delta k/k$, where Δk is fixed by the detection optics.

Two theoretical curves are included for comparison with each data set: The reduced Rayleigh linewidth behavior in 3D is represented by the lowest-order Kawasaki function[8] multiplied by a factor[7] which accounts for the effects of a weak critical viscosity, i.e.,

$$\Gamma^*(k\xi) = [\Omega(k\xi)/k\xi][1 + 0.25(k\xi)^2]^{x_\eta/2}, \qquad (1)$$

where

$$\Omega(x) = \tfrac{3}{4}x^{-2}[1 + x^2 + (x^3 - x^{-1})\tan^{-1}(x)]$$

and $x_\eta \approx 8/15\pi^2$. The corresponding functions Γ_C^* for a 2-μm film with neutral boundaries are given by this expression multiplied by the complete two-wall correction factor derived by Calvo[3] [Eq. (4.13) in Ref. 3]; i.e.,

$$\Gamma_C^*(k,\xi,L) = \Gamma^*(k\xi)G_C(k,\xi,L).$$

In all cases, the correlation length is estimated from $\xi = \xi_0|(T - T_C)/T_C|^{-\nu}$ with[9] $\nu = 0.63$ and[6] $\xi_0 = 2.0 \pm 0.2$ Å.

The 19.5° results agree rather well with the predictions for 3D behavior, as was the case in our earlier studies.[4,5] However, the Calvo two-wall corrections

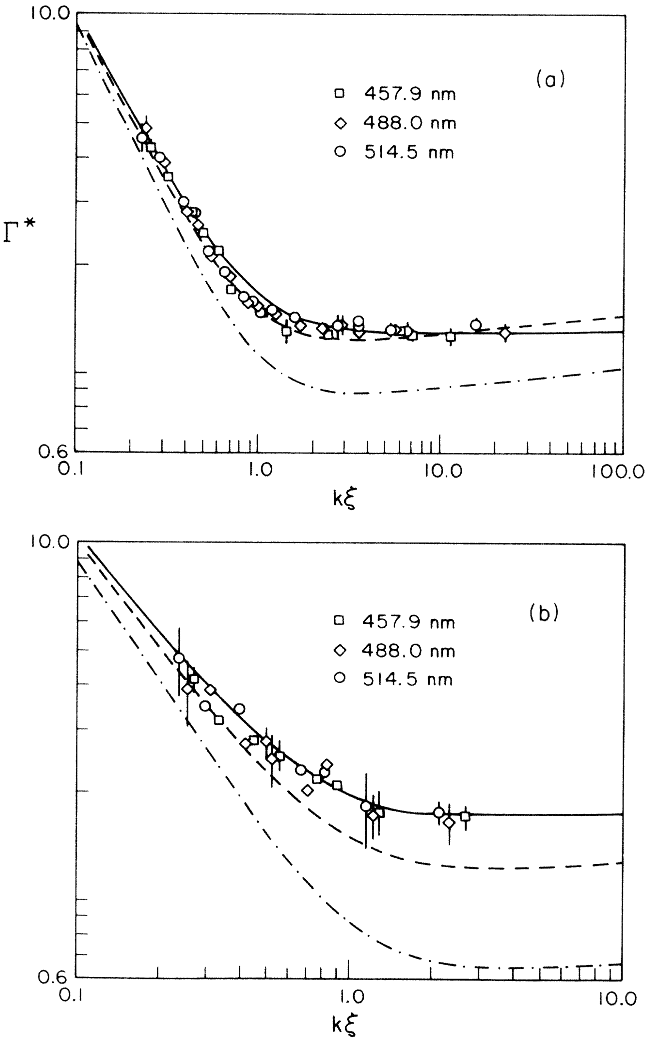

FIG. 1. (a) Reduced Rayleigh linewidth data from a 2-μm film with 19.5° scattering angle; (b) the same for a scattering angle of 8.12°. The dashed curves are the 3D theoretical predictions [Eq. (1)]; the dot-dashed curves are the Calvo predictions for the film-reduced Rayleigh linewidths for $\lambda = 457.9$ nm; and the solid curves are Eq. (1) with $\xi^{\rm eff}$ substituted for ξ. In the latter case, C [Eq. (2)] was set equal to 1.0 and 0.9 to generate the 19.5° and 8.12° curves, respectively.

are clearly inappropriate. Of greater interest are the 8.1° data which reveal a significant shift toward higher relaxation rates away from the predicted large-volume behavior, and a still greater departure from two-neutral-wall predictions.[2,3] This result is indirect evidence that a preferential wall–fluid interaction does exist.

We observe that the 8.1° reduced Rayleigh linewidth data still collapse on a single universal curve, dependent on $k\xi$. In view of this, we make the *Ansatz* that the functional form of $\Gamma^*(k\xi)$ remains *unchanged* in the switch from a large-volume sample to one consisting of a critical-mixture film confined by walls which interact selectively with it; in which case it should simply be replaced by $\Gamma^*(k\xi^{\rm eff})$, the effective correlation length, $\xi^{\rm eff}$, corresponding to an average across the film with weighting determined by the light-scattering process. We assume further that $\xi^{\rm eff}$ is a manifestation of finite-size effects on the film and should depend on both L and the infinite-volume correlation length, ξ, consistent with the general finite-size scaling form, $\xi^{\rm eff}/L = F(\xi/L)$.

Since we used three probe wavelengths and two scattering angles, Γ^* was measured for six independent wave numbers at each value of $\xi((T-T_C)/T_C)$. Consequently, we can use the 3D scaling form for the reduced Rayleigh linewidth,

$$\Gamma^*(k\xi^{\rm eff}) = \left[\frac{\Omega(k\xi^{\rm eff})}{k\xi^{\rm eff}}\right][1+0.25(k\xi^{\rm eff})^2]^{x_\eta/2}$$

and, by requiring that it fit our complete data set, determine $F(\xi/L) = \xi^{\rm eff}/L$.

Figures 2(a) and 2(b) are semilog and linear plots, respectively, of the derived values of $\xi^{\rm eff}/\xi$ vs ξ/L. From Fig. 2(a) it appears that the $\xi^{\rm eff}/\xi$ values for $\xi \lesssim L$ form a band that seems to collapse about a straight line, while from Fig. 2(b) the data for $\xi \gtrsim L$ behave like $\xi^{\rm eff}/\xi \sim 1/\xi$; i.e., $\xi^{\rm eff} \approx$ constant. We infer

$$F(\xi/L) = \xi^{\rm eff}/L = \begin{cases} (\xi/L)\, e^{-C\xi/L}, & \xi \lesssim L, \\ \text{const} \sim e^{-C}, & \xi \gtrsim L, \end{cases} \qquad (2)$$

where C is a constant which should roughly equal unity. The solid curves in Figs. 2(a) and 2(b) were generated from Eq. (2) with $C=1$. The agreement apparent in Fig. 2(b) is particularly impressive, seemingly justifying the *Ansatz* that the scaling function form for the reduced Rayleigh linewidth is invariant under the switch from large-volume sample to film, as well as the inference that the effective correlation length becomes constant when ξ approximates L.

The solid curves appearing in Figs. 1(a) and 1(b) are plots of $\Gamma^*(k\xi^{\rm eff})$ vs $k\xi$, with $C=1$ and $C=0.9$, respectively, for an incident-light wavelength of 488.0 nm. The agreement with experiment is excellent.

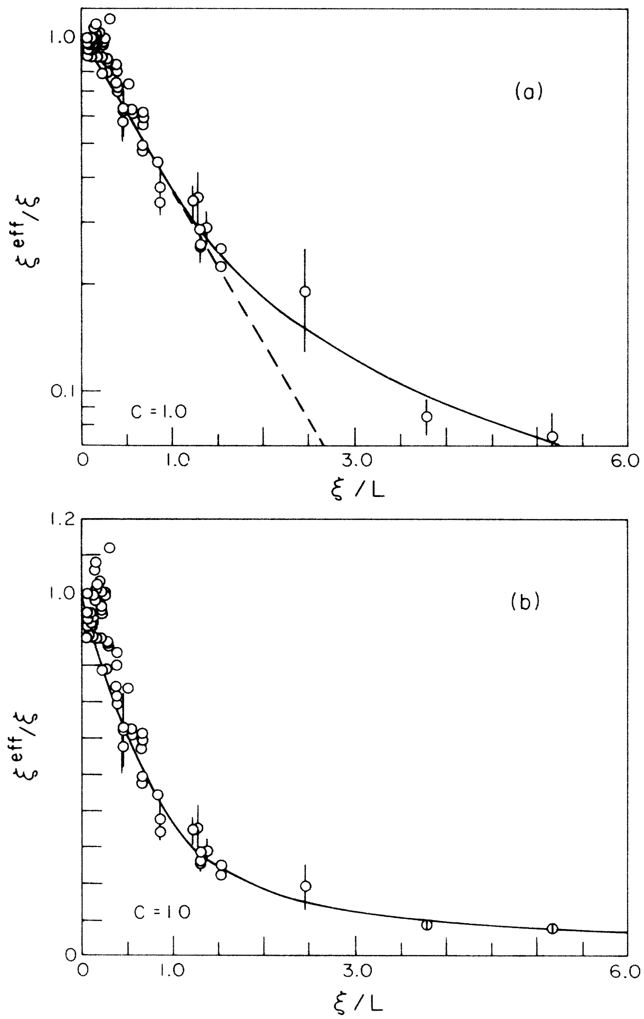

FIG. 2. (a) Semilog plot of $\xi^{\rm eff}/\xi$ vs ξ/L; (b) linear plot of $\xi^{\rm eff}/\xi$ vs ξ/L. In each case the solid curve corresponds to the choice [Eq. (2)] $C=1.0$, while the dashed line in (a) is an extrapolation beyond $\xi/L=1$ of the $\xi/L<1$ portion of Eq. (2).

Although the evidence is indirect, the effects we observe probably signal the existence of composition variations which expand to span the film as phase separation is approached and whose origin can be traced to preferential wall–fluid forces.[10,11] Far from the phase-separation temperature, in the homogeneous phase of a closed binary-fluid film whose composition is globally critical, the composition of the film interior will be nearly critical, with severe offloading limited to thin layers of thickness ξ in contact with the walls. Under these conditions, the results of a Rayleigh linewidth study, carried out at a small scattering angle so as to interrogate both the interior and surface regions of a film, will agree with equivalent data from a large-volume sample. As the phase-separation temperature is approached the layer thickness increases as

ξ until $\xi \approx L$ and the entire film becomes an effective boundary layer, largely offloaded, while globally fixed at the critical composition. In this case, the linewidths should be enhanced relative to the large-volume example since the total sample appears locally noncritical. As the temperature is moved closer to phase separation, the progress in local offloading should saturate as a result of the competition between interior and surface free-energy changes and the Rayleigh linewidth excess should remain fairly constant.

These observations are in general agreement with the results of our experiments. The fact that the earlier film Rayleigh linewidth measurements showed no evidence of surface layers is understandable. Even the new 19.5° data reveal only a subtle influence, reflected in the flat Γ^* vs $k\xi$ dependence for $\xi \gtrsim L$ and the significant discrepancy between them and the Calvo-Ferrell–model predictions.

We have presented results of small-angle-scattering Rayleigh linewidth measurements on critical binary-liquid films. These demonstrate conclusively that the reduced Rayleigh linewidth dependence on $k\xi$ in such films requires the replacement of $\Gamma^*(k\xi)$ by $\Gamma^*(k\xi^{\text{eff}})$, where the temperature dependence of ξ^{eff} is governed by a general finite-size scaling function. We use our data to infer the structure of the scaling function which appears divided into two regimes: (1) For $\xi/L \lesssim 1$, ξ^{eff} grows as $\xi \exp(-C\xi/L)$ as the phase transition is approached; (2) for $\xi/L \gtrsim 1$ (i.e., ξ becomes roughly half the film thickness), a crossover to zero-growth behavior occurs until the phase-separation temperature is reached. This remarkably simple picture provides a very good description of our Rayleigh linewidth data with the constant C constrained to be about 1.

The likely source of the finite-size behavior that we observe is the "anomalous" surface adsorption due to preferential wall–fluid forces which has been observed in a single wall–critical-fluid interfaces by Beysens and Leibler,[10] and by Franck and Schnatterly.[11]

This research was supported by U.S. Department of Energy Grant No. DE-AC02-82ER13004.

[1] M. E. Fisher and H. Nakanishi, J. Chem. Phys. **75**, 5857 (1981); H. Nakanishi and M. E. Fisher, J. Chem. Phys. **78**, 3279 (1983).

[2] M. Calvo and R. A. Ferrell, Phys. Rev. A **31**, 2570 (1985).

[3] M. Calvo, Phys. Rev. A **31**, 2588 (1985).

[4] S. A. Casalnuovo, Ph.D. thesis, University of Colorado, Boulder, 1982 (unpublished).

[5] S. A. Casalnuovo, R. C. Mockler, and W. J. O'Sullivan, Phys. Rev. Lett. **48**, 939 (1932), and Phys. Rev. A **29**, 257 (1984).

[6] E. Gulari, A. F. Collings, R. L. Schmidt, and C. J. Pings, J. Chem Phys. **56**, 6169 (1972).

[7] H. C. Burstyn and J. V. Sengers, Phys. Rev. A **25**, 448 (1982).

[8] K. Kawasaki, Ann. Phys. (N.Y.) **61**, 1 (1970).

[9] J. C. Le Guillou and J. Zinn-Justin, Phys. Rev. Lett. **39**, 95 (1977).

[10] D. Beysens and S. Leibler, J. Phys. (Paris), Lett. **43**, L133 (1982).

[11] C. Franck and S. E. Schnatterly, Phys. Rev. Lett. **48**, 763 (1982).