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Evidence of Mode-Mode Coupling and Nonlocal Shear Viscosity in a Binary Mixture near the Consolute Point*

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Linewidths of Rayleigh scattering from a binary liquid system of *n*-hexane plus nitrobenzene have been measured at two fixed scattering angles over a temperature range such that $\epsilon \equiv (T-T_c)/T_c$ extends from 10^{-2} to 10^{-6}. The ratio of the linewidths at two angles as a function of the correlation length ξ have been compared with recent self-consistent mode-mode coupling calculations of Kawasaki and Lo. The theory takes into account the nonlocality of shear viscosity near the critical point, and the data clearly establish the predicted effect in the critical region.

It has been well established both theoretically[1] and experimentally[2] that the decay rate Γ_k of the concentration fluctuation C_k deviates appreciably from the hydrodynamic expression K^2D as one approaches the critical region, as defined by $K\xi \geqslant 1$. In fact, an explicit $K\xi$ dependence of the diffusion coefficient $D(K\xi)$ has been given by Kawasaki[1] as

$$\Gamma_k \equiv K^2 D(K\xi) = (k_B T/6\pi\eta^*)\xi^{-3}K_0(K\xi), \qquad (1)$$

where

$$K_0(x) = \tfrac{3}{4}[1+x^2+(x^3-x^{-1})\tan^{-1}x] \qquad (2)$$

and η^* is loosely called the "high-frequency" shear viscosity. Experimental work of Berge *et al.*[3] indicated that with reasonable choices of ξ_0 and ν in the defining equation $\xi=\xi_0\epsilon^{-\nu}$, η^* could be taken as a constant in fitting the Rayleigh linewidth data over the entire temperature range covered. Since then there have been new measurements[4] indicating that far away from the critical point η^* approaches $\eta(T)$, the hydrodynamic shear viscosity, and near the critical point it deviates from $\eta(T)$ but not entirely temperature independently. Based on these observations, Kawasaki and Lo[5] recently made an attempt to clarify the meaning of η^* by solving self-consistently the coupled equations of C_k and V_q, the transverse local velocity fluctuation.

Far away from the critical point, the time dependence of these two fluctuating modes assumes the hydrodynamic expression $C_k(t) \sim \exp(-K^2Dt)$

and $V_q(t) \sim \exp(-q^2\eta t/\rho)$ and both transport coefficients D and η are local quantities. As one approaches the critical region the increased order-parameter fluctuations cause appreciable nonlinear coupling between C_k and V_q. Since the fluctuation of V_q is always much faster than C_k because of the finiteness of the shear viscosity and the critical slowing down of the order-parameter fluctuation, the stochastic variable $C_k(t)$ can be taken to be Markovian in the time scale of observation by light scattering. Thus the exponential decay of $C_k(t)$ is valid even when the coupling is taken into account except now $D \rightarrow D(K\xi)$, i.e., the diffusion coefficient becomes nonlocal. In the self-consistent treatment, this latter statement is also true for the shear viscosity.

The Kawasaki-Lo[5] treatment gave the following essential results:

$$\eta_q = \eta(t)[1 - F(q\xi)], \qquad (3)$$

$$\eta^* = \eta(T)K_0(K\xi)/K(K\xi), \qquad (4)$$

$$\Gamma_k = [k_B T/6\pi\eta(T)]\,\xi^{-3}K(K\xi), \qquad (5)$$

where functions $F(x)$ and $K(x)$ are related through Eq. (8) of Ref. 5 and numerical values of both are given there. Two essential points are to be re-

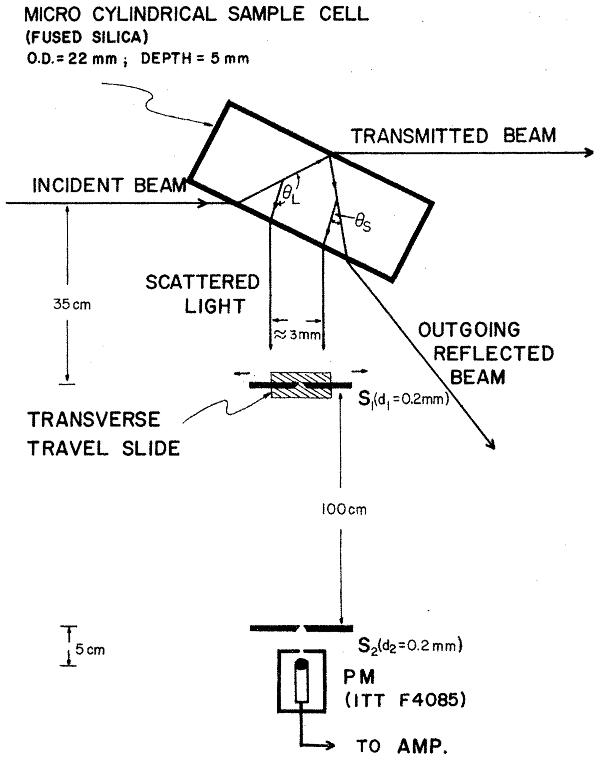

FIG. 1. Scattering geometry for measurement at two fixed scattering angles.

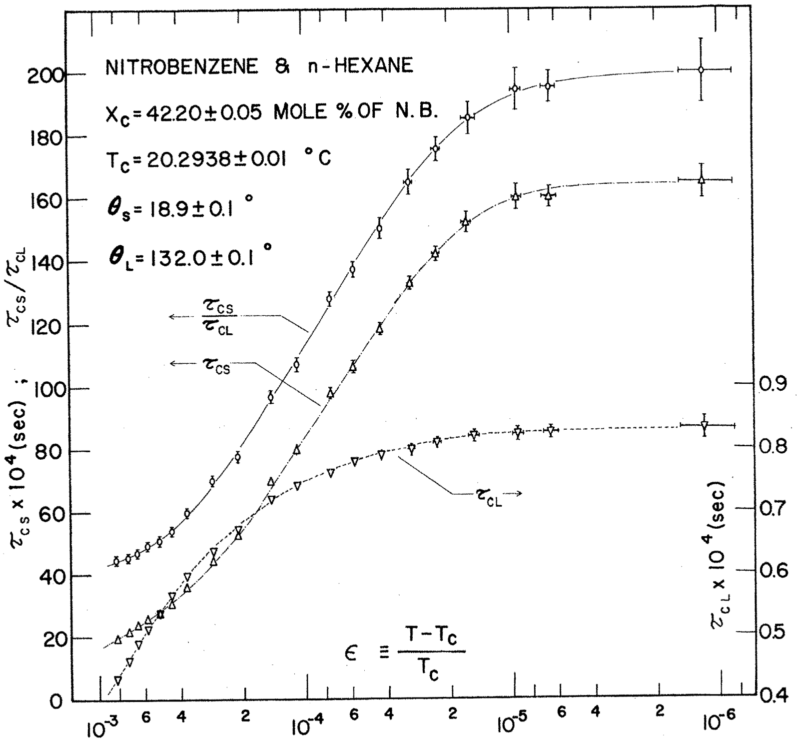

FIG. 2. Fluctuation decay constants and their ratio at small and large scattering angles as a function of reduced temperature.

marked here. Both the nonlocal and the high-frequency viscosities are smaller than $\eta(T)$ and the nonlocal shear viscosity reduces to $\eta(T)$ in the limit $K\xi \to 0$. In this limit $K(0)=1.055K_0(0)$ which agrees with the observation[4] that $\eta^* \to \eta(T)$. However, the real test of accuracy of the theory comes from the critical region $K\xi \geqslant 10$, where $K(x)$ can be 20% or more larger than $K_0(x)$. The obvious check of the theory is to use the experimental values of $\eta(T)$ and to plot the product $\Gamma_k \eta(T)$ as a function of $\xi(T)$ at a fixed K. Since in the system of n-hexane plus nitrobenzene an accurate measurement of $\eta(T)$ is not yet available,[6] we choose to test the theory in the following way.

We perform the linewidth measurement at two fixed K values as a function of temperature, taking advantage of the fact that the correlation length depends only on temperature along the critical isoconcentration line. Thus according to Eq. (5)

$$\frac{\Gamma_{kL}}{\Gamma_{kS}} \equiv \frac{\tau_{cS}}{\tau_{cL}} = \frac{K(K_L\xi)}{K(K_S\xi)}. \tag{6}$$

Note that if η_q were local, i.e., $F(x)=0$, $\eta^* \simeq \eta(T)$, then Eq. (1) would have predicted

$$\frac{\Gamma_{kL}}{\Gamma_{kS}} = \frac{\tau_{cS}}{\tau_{cL}} = \frac{K_0(K_L\xi)}{K_0(K_S\xi)}. \tag{7}$$

The purpose of this experiment is therefore to distinguish between two possibilities, (6) and (7).

The linewidth Γ_k is measured by the technique of intensity correlation spectroscopy.[7] The scattered photons are detected by a photomultiplier and the resulting pulses fed into a 128-channel digital autocorrelator.[8] The output of the correlator, except for a known dc background, is proportional to $|\langle C_{-k}(0)C_k(t)\rangle|^2 \sim \exp(-2\Gamma_k t)$. The line

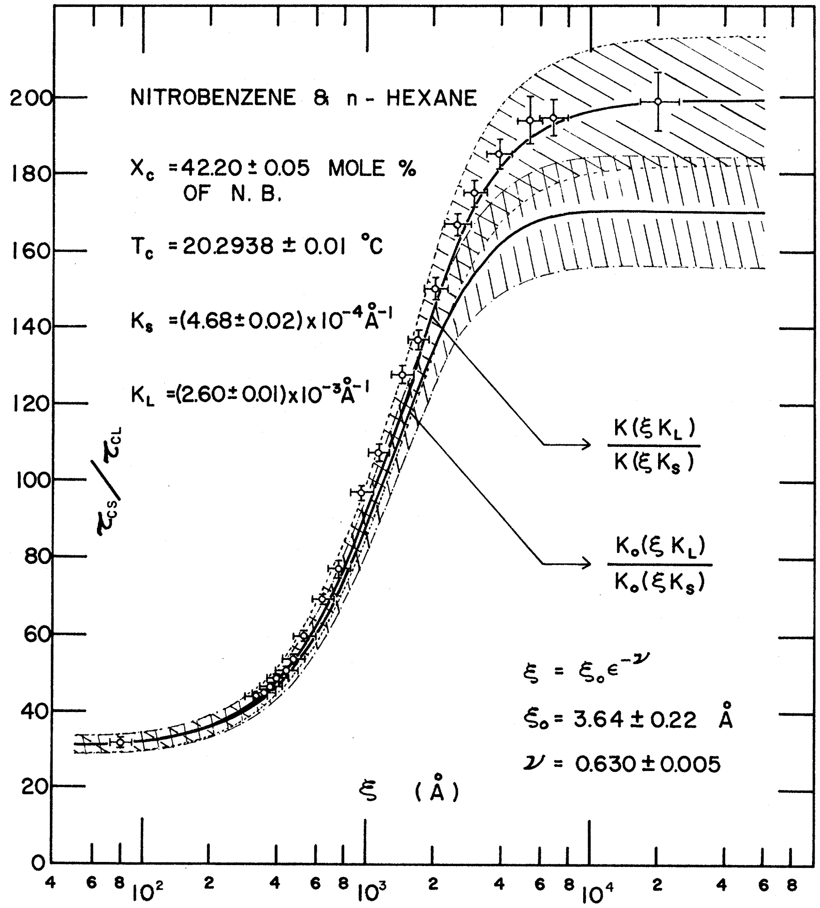

FIG. 3. Comparison of measured decay time constant ratio as a function of correlation length with theories of Kawasaki and Lo (Ref. 5) and Kawasaki (Ref. 1) The shaded areas around the theoretical curves take into account the indicated uncertainties in K values.

width thus determined is accurate to better than a percent. The schematic arrangement of the scattering geometry is given in Fig. 1. This particular geometry is chosen because it is extremely important to maintain a constant temperature for the measurement at both K_L and K_S. Two consecutive measurements at each temperature were made with only slight displacement of slit S_1. This allows us to measure scatterings from two angles with a minimal disturbance to the system. For example, we do not have to shift the laser beam during the whole measurement. The temperatures of the cell are constantly monitored by a thermistor and are maintained to about 0.1 mdeg stability. The part of the linewidth data which is relevant to the present article is given in Fig. 2. Figure 3 gives the comparison between the ratio of the linewidths measured and the two theoretical expressions (6) and (7).

In plotting Fig. 3 the crucial points are the conversion of measured temperature T to the correlation length ξ and the accurate determination of K_L and K_S. First, the T_c is located by observation of transmitted light and also by the linewidth data above and below the phase separation. The error of T_c given in Fig. 3 reflects only the calibration accuracy of the thermister, but the relative value of $\Delta T \equiv T - T_c$ is believed to be accurate to ± 0.1 mdeg. K_L and K_S are determined by both an optical method and the linewidth measurement in the hydrodynamic limit where one knows $\Gamma_k = K^2 D$.

The values of ξ_0 and ν are determined by a separate intensity measurement[9] which gives $\xi_0 = 3.64 \pm 0.22$, $\nu = 0.63 \pm 0.005$. These values are consistent with values reported in literature and also agree with the earlier measurement of Chen and Polonsky[7] on the same system.

In conclusion we have shown that accurate linewidth data decisively prefer expression (6) over (7) in the critical region. The change of values of ξ_0 and ν within a reasonable range would not change substantially this conclusion. This method of comparison with the theory has the advantage that one can avoid the uncertainty in values of $\eta(T)$ extremely close to the critical point due to the fact that the viscosity measurement is seldom reliable when ΔT is less than 1 mdeg.

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