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Dynamics of Concentration Fluctuations Near the Critical Mixing Point of a Binary Fluid

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The decay rate Γ of the concentration fluctuations near the critical mixing point of 3-methylpentane-nitroethane has been measured as a function of the correlation length ξ and the wave number k in the range $0.1 \leq k\xi \leq 20$. We have confirmed the theoretical prediction that Γ varies as k^3 in the critical regime. An analysis of Γ as a function of $k\xi$ reveals deviations from the theory of Kawasaki, which are discussed.

A system near a critical point exhibits large fluctuations in the order parameter, which decay very slowly in time. A central assumption in the current theoretical descriptions of this phenomenon is that the anomalous behavior of both static and dynamic properties is governed by a single correlation length ξ. It is, therefore, desirable to measure the relaxation time of the fluctuations and the equilibrium correlation length simultaneously. For this purpose we have measured the total intensity and the spectral width of light scattered by concentration fluctuations near the critical mixing point of 3-methylpentane-nitroethane. Details of the experimental arrangement will be published elsewhere.

The scattering angle θ is related to the wave number k of the fluctuations by the Bragg relation $k = 2k_0 \sin\frac{1}{2}\theta$, where k_0 is the wave number of the incident light in the medium. In the hydrodynamic regime ($k\xi \ll 1$), the decay rate Γ of the concentration fluctuations is given by $\Gamma = Dk^2$, where D is the binary diffusion coefficient.[1] The modern theories of dynamical scaling postulate that for all $k\xi$ the decay rate Γ should be a homogeneous function of k and ξ^{-1},[2]

$$\Gamma = \varphi(k, \xi^{-1}) = k^z \varphi(1, 1/k\xi) = k^z \Phi(k\xi), \qquad (1)$$

where $z = 3$ according to the mode-mode coupling theory.[3,4] A specific form for the function $\Phi(k\xi)$ has been derived first by Kawasaki[4] and subsequently by Ferrell[5]:

$$\Gamma/k^3 = A(2/\pi)\{(k\xi)^{-3} + (k\xi)^{-1} + [1 - (k\xi)^{-4}]\arctan k\xi\}, \qquad (2)$$

with $A = k_B T/16\bar{\eta}$, k_B being Boltzmann's constant and $\bar{\eta}$ a shear viscosity which is assumed to be independent of k and ξ in the theory.

We have measured the decay rate Γ from the linewidth of the central component in the spectrum of scattered light by the method of self-beat spectrometry.[6] A total of 88 data points were obtained at the critical concentration in the temperature interval $0.001 \leq T - T_c \leq 0.3$°C for seven different scattering angles. The scaling hypothesis (1) implies that in the critical regime ($k\xi \gg 1$), Γ should vary as k^z. To test this prediction we have plotted the linewidth data obtained at the seven scattering angles at $\Delta T = 0.001$ and 0.003°C as a function of k in Fig. 1. For the exponent z we find 2.99 ± 0.05 at $\Delta T = 0.001$°C

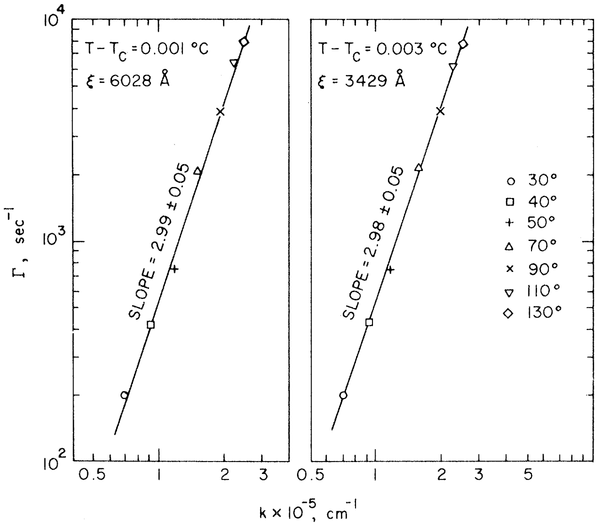

FIG. 1. Log-log plot of the decay rate Γ as a function of k at $\Delta T = 0.001$ and 0.003°C.

and 2.98 ± 0.05 at $\Delta T = 0.003$°C, in excellent agreement with the value 3 predicted by the mode-mode coupling theory.

To test the validity of the Kawasaki function (2) we need to know the correlation length ξ. For that purpose we have measured the intensity of the scattered light $I(k, \xi)$ relative to the intensity of the incident light. The data were obtained as a function of temperature at three scattering angles ($\theta = 40°$, $60°$, and $90°$). In the analysis of the intensity measurements care was taken to correct for background scattering due to density fluctuations, residual dust, etc., as well as a small attenuation of light traveling through the medium.

The correlation length ξ diverges according to a power law $\xi = \xi_0 \epsilon^{-\nu}$, where $\epsilon = (T - T_c)/T_c$. The experimental values of ξ as determined by the slope of $I^{-1}(k, \xi)/I^{-1}(0, \xi)$ as a function of k^2, are shown in Fig. 2. We did not observe any statistically significant deviations from the Ornstein-Zernike theory, and all 82 intensity data points could be represented within their experimental precision by

$$I(k, \xi)^{-1} = I_0^{-1} \epsilon^{\gamma} [1 + k^2 \xi_0^2 \epsilon^{-2\nu}] \tag{3}$$

with

$$\gamma = 1.231 \pm 0.008, \quad \nu = 0.616 \pm 0.003,$$
$$\xi_0 = 2.56 \pm 0.05 \text{ Å}, \tag{4}$$

corresponding to a standard deviation $\sigma_I = 1.6\%$ for the intensity data. The errors quoted represent standard deviations; they are, of course, highly correlated. The standard deviation σ_I stays below 2% when γ is varied by ± 0.04, ν by ± 0.013, and ξ_0 by ± 0.14 Å. The latter errors may be more realistic for an assessment of the absolute accuracy of the parameters. The important point for the present paper is that at each temperature where the decay rate Γ was determined, we also have a reliable knowledge of ξ. Our value for γ is in a good agreement with the value 1.22 ± 0.04 obtained by Wims for the same system.[7]

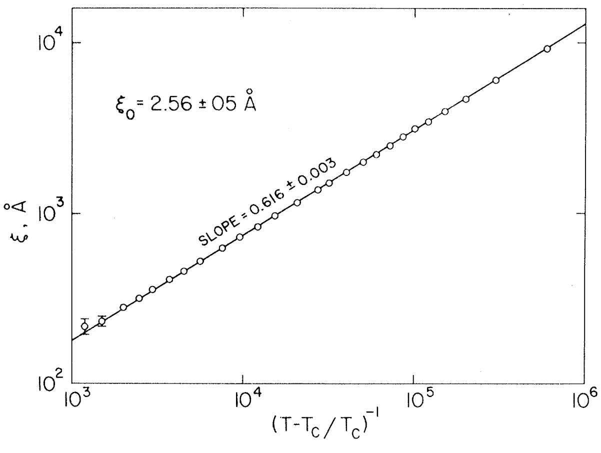

FIG. 2. Log-log plot of the correlation length ξ as a function of inverse reduced temperature.

The experimental data for Γ/k^3 are plotted as a function of $k\xi$ in Fig. 3. The solid curve represents the behavior predicted by Eq. (2). There exists some ambiguity in the meaning of the parameter $\bar{\eta}$ and consequently of A, since the ac-

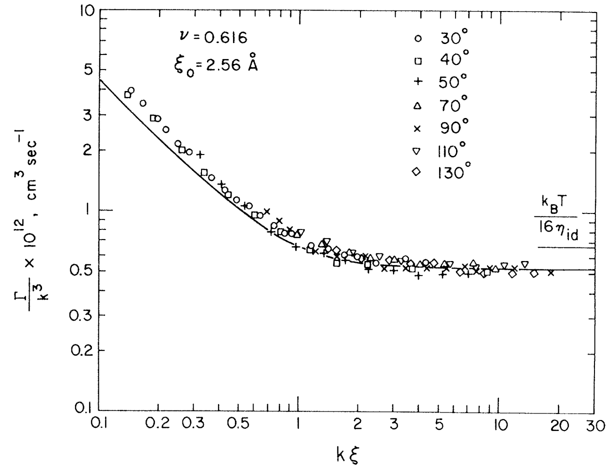

FIG. 3. Γ/k^3 as a function of $k\xi$ with ξ deduced from the intensity measurements. The solid line represents the behavior predicted by the theory of Kawasaki.

tual shear viscosity is not independent of k and ξ. Therefore, we have identified A with the value

$$\lim_{k\xi\to\infty} \Gamma/k^3 = (0.53 \pm 0.03)\times 10^{-12}\ \mathrm{cm^3\ sec^{-1}},$$

observed experimentally. With this identification, however, we note a different between theory and experiment in the hydrodynamic regime which amounts to as much as 20%.

This result is in apparent contradiction with the work of Bergé *et al.* who have concluded that the Kawasaki function describes the decay rate of the concentration fluctuations very well.[8] However, these authors did not calculate the Kawasaki function from an *a priori* knowledge of ξ, but instead fitted the decay rate with the theoretical Eq. (2) using ξ_0 and ν, in addition to A, as adjustable parameters. If we carry out the same procedure for our experimental data, we obtain the results shown in Fig. 4 with the parameters $A = (0.537 \pm 0.001)\times 10^{-12}$ cm³ sec⁻¹, $\xi_0 = 1.47 \pm 0.06$ Å, and $\nu = 0.667 \pm 0.005$. With these values the Kawasaki function represents the linewidth data with a standard deviation of 4.6%. We conclude that this agreement is an apparent one; it is not substantiated when ξ is determined independently from the intensity measurements.

We present some arguments that the disagreement between theory and experiment is due to (a) the presence of a nonsingular background contribution to the Onsager coefficient, and (b) the fact that the shear viscosity $\bar{\eta}$ cannot be treated as a constant.

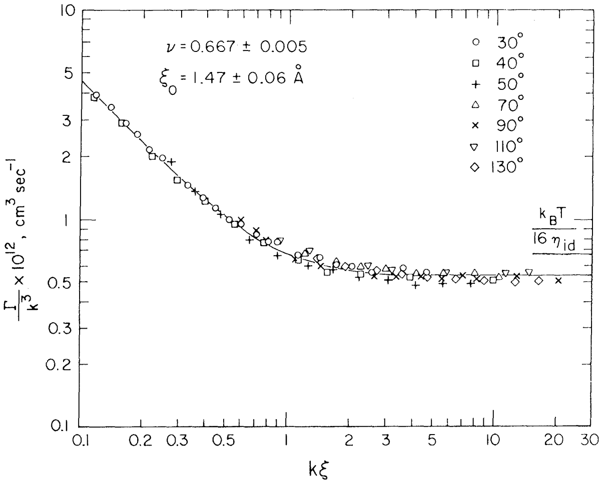

FIG. 4. Comparison of the linewidth data with the theory of Kawasaki using A, ξ_0 and ν as adjustable parameters.

(a) A similar disagreement between theory and experiment was noted by Henry, Swinney, and Cummins for the decay rate of the entropy fluctuations near the gas-liquid critical point.[9] The discrepancy could be resolved by accounting for a nonsingular background contribution to the thermal conductivity.[10] This observation has been confirmed by Swinney, Henry, and Cummins for xenon[11] and by Maccabee and White for carbon dioxide.[12] The diffusion coefficient D is the product of an Onsager kinetic coefficient L and $(\partial\mu/\partial c)_{T,P}$, where μ is the chemical potential and c the concentration of either component.[13] By analogy with the gas-liquid phase transition one would expect the presence of a background term L_0 in the Onsager coefficient. Thus the theory should not be compared with the full experimental decay rate Γ, but only with the asymptotic part,

$$\begin{aligned}\Gamma - \Gamma_0 &= \Gamma - L_0k^2(\partial\mu/\partial c)_{T,P}(1+k^2\xi^2)\\ &= \Gamma - Bk^2\epsilon^{\gamma}(1+k^2\xi^2),\end{aligned}\tag{5}$$

where L_0, and consequently B, can be approximated by a constant in the small temperature range of our measurements. The effect of this background is to reduce the linewidth data at the higher temperatures, i.e., in the hydrodynamic regime ($k\xi \ll 1$) in Fig. 3. The coefficient B in (5) is 6.3×10^{-3} cm² sec⁻¹ for CO$_2$ and 3.3×10^{-3} cm² sec⁻¹ for Xe. For 3-methylpentane-nitroethane we do not have any independent experimental information for the Onsager coefficient. However, if we replace Γ in (2) with (5), evaluate the Kawasaki function on the basis of the equilibrium ξ, but use B as an adjustable parameter, we find $B = (4.1 \pm 0.2)\times 10^{-4}$ cm² sec⁻¹. With this value for B the agreement between theory and experiment is improved substantially and the Kawasaki function does represent the corrected linewidth data to within 4.8%.

(b) Even if the background term were known precisely, one still should not expect a complete agreement between theory and experiment. The viscosity of 3-methylpentane-nitroethane exhibits an anomaly which is close to logarithmic as shown by Stein, Allegra, and Allen[14] and Tsai and McIntyre.[15] In the temperature range of our measurements the viscosity varies from $\eta = 0.458 \times 10^{-2}$ g cm⁻¹ sec⁻¹ at $\Delta T = 0.3$°C to $\eta = 0.540 \times 10^{-2}$ g cm⁻¹ sec⁻¹ at $\Delta T = 0.002$°C. Our experimental value $A = k_BT/16\bar{\eta} = (0.53 \pm 0.03)\times 10^{-12}$ cm³ sec⁻¹ corresponds to $\bar{\eta} = (0.49 \pm 0.03)\times 10^{-2}$ g cm⁻¹ sec⁻¹. This value is 29% larger than the ideal viscosity $\eta_{id}=0.38\times10^{-2}$ g cm^{-1} sec^{-1}, but is of the same order as the experimental viscosity. The assumption that the viscosity is a constant is clearly not justified and one should expect that η should vary both with ξ and k. If we naively neglect the variation of η with k and identify the parameter $\bar{\eta}$ in (2) with the hydrodynamic viscosity $\eta(0,\xi)$ as measured by Stein, Allegra, and Allen,[14] we find a remarkably good agreement without introducing a background term. The Kawasaki function with the equilibrium ξ appears to represent the product $\Gamma\eta/k^3$ to within 4.7%; the coefficient $A\eta$ is only 12.5% larger than its theoretical value $k_BT/16$. A similar observation was recently made by Bergé and Dubois for the decay rate in the hydrodynamic regime.[16] Unfortunately, this procedure is not justified theoretically, since the viscosity in the theory is not the hydrodynamic viscosity $\eta(0,\xi)$ but a viscosity $\eta(k,\xi)$ at large values of k.[4] These results do illustrate, however, that at least part of the disagreement could be caused by the anomalous behavior of the viscosity.

We conclude that the difference between theory and experiment improves significantly (a) if we allow the possibility of a background term in the Onsager coefficient and (b) if the theoretical parameter $\bar{\eta}$ for the viscosity is allowed to vary with temperature. In the absence of independent experimental information concerning the background in the Onsager coefficient and a theoretical understanding of the viscosity anomaly and its effect on the decay rate, it is difficult to separate the two effects.

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