PHYSICAL REVIEW A VOLUME 23, NUMBER 1 JANUARY 1981

Critical dynamic viscosities in xenon and in the binary mixture nitrobenzene-*n*-hexane

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(Received 8 February 1980)

Ultrasonic shear data along the critical isochore in xenon and in the binary mixture nitrobenzene-*n*-hexane are interpreted in terms of modified theoretical expressions derived within the framework of the decoupled-mode theory. The new expressions mainly arise from separating the real and imaginary parts from the complex dynamic shear viscosity near a critical point. Numerical analysis of the data shows rather satisfactory agreement between theory and experiments for ultrasonic shear data.

I. INTRODUCTION

In a previous paper,[1] we reported the experimental results of static and dynamic viscosities in the binary mixture nitrobenzene-*n*-hexane near the critical point. The results were compared with the prediction of a generalized form of the Deutch and Zwanzig theory[2] based on the model of a binary van der Waals mixture and the theory gave an excellent qualitative explanation of the dynamic viscosity data. At the same time, however, it has been understood that some conclusions are subject to criticism because of the additional assumptions introduced to perform the calculation. In particular, two important improvements have been required: one is an account of the diverging behavior of the static and dynamic shear viscosities as the critical point is approached and the other is related to an arbitrary parameter introduced to make the data fit to the theory.

The problem of the dynamic shear viscosity near a critical point has recently been reconsidered by Bhattacharjee and Ferrell[3] and independently by two of the present authors[4] on the basis of the decoupled-mode theory.[5] Although the fluctuation-dissipation theorem along the lines indicated by Deutch and Zwanzig has been applied, the calculations have been performed in a different way, and the important improvements previously referred to are included in present formulations. In particular, one of the predictions of the Bhattacharjee and Ferrell theory has been compared successfully with the observed deviations from exponential decay of critical concentration fluctuations in a binary liquid.[6] Furthermore, it has been proposed to analyze the dynamic viscosity data in terms of a reduced frequency ω^*. In this connection, the theories predict that the dynamic viscosity data depend on temperature and frequency through the single reduced variable ω^*, i.e., the data should be described by a dynamic scaling function.

In this paper we wish to report the results of a direct test of the dynamic scaling function based on the decoupled-mode theory by analysis of some recent experimental data for ultrasonic shear viscosity along the critical isochore in xenon[7] and in nitrobenzene-*n*-hexane.[1] In comparing the theories with the experimental data it is necessary to take into account the fact that the real and imaginary parts of the complex dynamic viscosity are not normally measured separately. However, as shown in the following sections, the direct separation is always possible in the viscoelastic method such as the torsional crystal method, which makes possible the more rigorous test of the dynamic scaling function.

II. THEORY

Since the ultrasonic shear wave frequency of interest ω satisfies $\omega/c \ll \kappa$, we have to take into account only the frequency dependence in the shear viscosity, where c is the velocity and κ is the reciprocal correlation length for density (or concentration) fluctuations. To study the problem in more detail, let us consider a binary mixture. The starting point of this calculation is a time correlation function for the complex dynamic shear viscosity $\eta^*(\omega, \kappa)$,[8-12]

$$\eta^*(\omega, \kappa) = \frac{1}{2T} \int d^4 21\, e^{-i\omega|t_{21}|} \langle T_{xy}(2) T_{xy}(1) \rangle , \qquad (1)$$

where the integration is over the entire range of the relative space-time coordinate $(\vec{x}_{21}, t_{21})$, T_{xy} is an off-diagonal component of the stress tensor, and the angular brackets denote the thermal-equilibrium average. The temperature T is measured in natural units so that the Boltzmann's constant is unity.

It is customary to separate the viscosity into a so-called "ideal" background component η_B and a critical component $\Delta\eta^*$. The canonical expression for the stress tensor T_{xy} based on the critical fluctuation has been derived by Perl and Ferrell[5]:

$$T_{xy} = s_x \frac{\partial F}{\partial s_y} = Z^{-1} s_x s_y \,, \tag{2}$$

where the Landau-Ginzburg expression for the free-energy density F depends only upon the partial derivatives of the concentration s_x, s_y through the gradient term $(\nabla s)^2/2Z$ and Z is a constant. In order to study the fluctuations in the stress tensor, we introduce the time-dependent correlation function for the concentration fluctuation,

$$\begin{aligned} G(21) &= \langle s(2) s(1) \rangle \\ &= (2\pi)^{-3} \int d^3q \exp(i\vec{q}\cdot\vec{x}_{21} - \Gamma_q^c |t_{21}|) g(q) \,. \end{aligned} \tag{3}$$

The Fourier transform of the equal-time correlation function is assumed to be of the usual Ornstein-Zernike form for arbitrary values of wave number q and κ,[13]

$$g(q) = \frac{ZT}{q^2 + \kappa^2} \,. \tag{4}$$

The time-dependent correlation function of the stress tensor can be expressed in terms of G by the decoupling approximation,[5]

$$\langle T_{xy}(2) T_{xy}(1) \rangle \simeq Z^{-2} \left[\frac{\partial^2 G(21)}{\partial x_{21}^2} \frac{\partial^2 G(21)}{\partial y_{21}^2} + \left(\frac{\partial^2 G(21)}{\partial x_{21} \partial y_{21}} \right)^2 \right]. \tag{5}$$

From these equations [Eqs. (1)–(5)], by straightforward calculations, one gets

$$\begin{aligned} \Delta\eta^*(\omega, \kappa) &= \frac{2T^{-1}Z^{-1}}{(2\pi)^3} \int d^3q \, q_x^2 q_y^2 \frac{g(q)^2}{2\Gamma_q^c + i\omega} \\ &\equiv \Delta\eta' - i\Delta\eta'' \,, \end{aligned} \tag{6}$$

where $\Delta\eta'$ and $-\Delta\eta''$ are the real and imaginary parts of $\Delta\eta^*$, respectively.

We first choose the following expression for Γ_q^c, which gives a good fit to the experimental data, according to Perl and Ferrell,[5]

$$\Gamma_q^c = \frac{Tq^2(q^2+\kappa^2)^{1/2}}{16\bar{\eta}((q^2+\kappa^2)^{1/2})} , \tag{7}$$

where $\bar{\eta}$ is an adjustable parameter which is determined by fitting Eq. (7) to the linewidth data. Because $\bar{\eta}(q, \kappa)$ depends on q very weakly, when Eq. (7) is substituted into Eq. (6), $\bar{\eta}$ can be taken outside the integral and approximated by setting the argument equal to κ. Final equations for $\Delta\eta'$ and $\Delta\eta''$ are given by

$$\Delta\eta'(\omega, \kappa) = \frac{8}{15\pi^2} \bar{\eta}(\kappa) \int_0^{q_c/\kappa} \frac{dv \, v^8}{(1+v^2)^{3/2} [v^4(1+v^2) + \omega^{*2}]} , \tag{8}$$

$$\Delta\eta''(\omega, \kappa) = \frac{8}{15\pi^2} \bar{\eta}(\kappa) \int_0^{q_c/\kappa} \frac{dv \, v^6 \omega^*}{(1+v^2)^2 [v^4(1+v^2) + \omega^{*2}]} , \tag{9}$$

respectively, where $v = q/\kappa$, the reduced frequency $\omega^* = \omega/\omega_D$, the characteristic frequency $\omega_D = T\kappa^3/8\bar{\eta}(\kappa)$, and the cutoff wave number q_c is a free parameter to be fixed by fitting the shear viscosity data to the following equation (10). In the limit of $\omega \to 0$, Eq. (8) is

$$\begin{aligned} \Delta\eta(\kappa) = \frac{8}{15\pi^2} \bar{\eta}(\kappa) \Bigg(&-\frac{q_c/\kappa}{(q_c^2/\kappa^2+1)^{1/2}} - \frac{(q_c/\kappa)^3}{3(q_c^2/\kappa^2+1)^{3/2}} \\ &+ \ln \left| (q_c/\kappa) + (q_c^2/\kappa^2+1)^{1/2} \right| \Bigg) \,, \end{aligned} \tag{10}$$

which is reduced to the well known logarithmic form when $q_c/\kappa \gg 1$.

Alternatively, one can choose the following refined expression for Γ_q^c proposed by Perl and Ferrell[5,14]:

$$\Gamma_q^c = \frac{T\kappa^3}{6\pi\eta^{\text{eff}}} K_0\left(\frac{q}{\kappa}\right) C\left(\frac{q}{\kappa}\right), \tag{7'}$$

where

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

$$\eta^{\text{eff}} = \eta_B + \frac{8\bar{\eta}}{15\pi^2} \left[\ln \frac{q_D/\kappa}{(1+q^2/\kappa^2)^{1/2}} + \tau\left(\frac{q}{\kappa}\right) \right], \tag{7''}$$

$C(q/\kappa)$ and $\tau(q/\kappa)$ are numerically determined factors,[15] and q_D is a Debye cutoff given by

$$\ln q_D = \ln q_c - \tfrac{4}{3} + \ln 2 \,.$$

When Eq. (7′) is substituted into Eq. (6), the corresponding final equations for $\Delta\eta'$, $\Delta\eta''$, and $\Delta\eta$ are given by,

$$\Delta\eta'(\omega, \kappa) = \frac{1}{5\pi} \int_0^{q_c/\kappa} \frac{dv \, v^6}{(1+v^2)^2} \frac{\eta^{\text{eff}} K_0(v) C(v)}{K_0^2(v) C^2(v) + \omega^{*2}} , \tag{8'}$$

$$\Delta\eta''(\omega, \kappa) = \frac{1}{5\pi} \int_0^{q_c/\kappa} \frac{dv \, v^6}{(1+v^2)^2} \frac{\eta^{\text{eff}} \omega^*}{K_0^2(v) C^2(v) + \omega^{*2}} , \tag{9'}$$

$$\Delta\eta(\kappa) = \frac{1}{5\pi} \int_0^{q_c/\kappa} \frac{dv \, v^6}{(1+v^2)^2} \frac{\eta^{\text{eff}}}{K_0(v) C(v)} , \tag{10'}$$

respectively. It should be noted that the characteristic frequency is given by $\omega_D = T\kappa^3/3\pi\eta^{\text{eff}}$ in this case.

III. TREATMENT OF DATA

The details of torsional crystal methods have been described elsewhere.[1,16] The real and imaginary parts of the complex dynamic shear viscosity η^* are given by

$$\eta' = 2XR/\omega\rho \text{ and } -\eta'' = (X^2 - R^2)/\omega\rho \,, \tag{11}$$

respectively, where R and X are the real and imaginary parts of the shear mechanical impedance, respectively (R and X were determined in the usual manner[17]), and ρ is the density of the solution. Furthermore, η' and η'' are separated into a background component and a critical component

$$\eta' = \eta'_B + \Delta\eta' \quad \text{and} \quad \eta'' = \eta''_B + \Delta\eta'' , \tag{12}$$

respectively, where η'_B is usually estimated by the Arrhenius equation and η''_B equals zero, because simple liquids such as nitrobenzene and n-hexane and, accordingly their mixtures, are not expected to behave elastically with respect to shear until very high frequency is attained, i.e.,

$$\eta' = \eta_B + \Delta\eta' \quad \text{and} \quad \eta'' = \Delta\eta'' . \tag{12$'$}$$

In the static limit,

$$\eta \equiv \lim_{\omega \to 0} \eta' = \eta_B + \Delta\eta . \tag{12$''$}$$

In the present paper, data on xenon[7] as a one-component system and nitrobenzene-n-hexane[1] as a two-component system have been analyzed, because the detailed data of the dynamic viscosity and parameters which are required in a comparison of the results with the theory are available. These parameters are the reciprocal correlation length κ and the decay rate Γ_q obtained by light scattering and Rayleigh linewidth measurements. It should be noted, however, that the theory in its current state cannot discriminate between $\bar{\eta}$ and η.[18] Accordingly, we regard $\bar{\eta}$ as η in the present analysis through Eqs. (8)–(10). This means that the decay rate in the form of Eq. (7) can be evaluated without knowledge of Rayleigh linewidth measurement. In a more rigorous test of the theory, however, it is necessary to deduce $\bar{\eta}$ from linewidth data and then the refined decoupled-mode equations [Eqs. (8′)–(10′)] should be compared with the results of viscosity measurements. The reciprocal correlation length κ is $(10^8/2.0)\epsilon^{0.63}$ cm^{-1} for xenon[19] and $(10^8/2.3)\epsilon^{0.63}$ cm^{-1} for nitrobenzene-n-hexane,[20] where $\epsilon = (T - T_c)/T_c$. By fitting the values of the static shear viscosity and Eq. (10) with the corresponding values of κ, one can determine the cutoff parameter q_c to be 5.38×10^6 cm^{-1} for xenon[15] and 6.89×10^6 cm^{-1} for nitrobenzene-n-hexane.[1]

IV. RESULTS AND DISCUSSION

A comparison of the experimental results with the theory presented in Sec. II is shown in Fig. 1 for xenon and in Fig. 2 for nitrobenzene-n-hexane. From Fig. 1, it can be easily understood that the dynamic viscosity in the one-component system did not show the significant frequency dependence at ultrasonic frequencies: η' is close to η as seen in Fig. 1, although a slight deviation is appeared for the higher values of ω^*. Such a deviation is much more evident in this two-component system as shown in Fig. 2(a). Accordingly, it cannot be ascribed to the breakdown for large ω^* (or small ϵ) of the approximation of the Ornstein-Zernike form for the behavior of the fluctuations,[13] but to the long characteristic relaxation time for the concentration fluctuations as explained by Eq. (8). In this connection, it should be noted that the present comparison between the theory and the experimental data does not contain any arbitrary parameter, while the previous comparison contains an arbitrary parameter; although the present agreement is not apparently superior when comparing with our previous result.[1] The most significant feature is an observation of the imaginary part of the complex viscosity presented in Fig. 2(b). This is quite a new result and may be explained by Eq. (9). Because, in the limit of $\omega^* \to \infty$, Eq. (9) is reduced to a constant,[21] i.e., $4\bar{\eta}/45\pi = 0.028\bar{\eta}$, while our experimental value is 0.023 ± 0.002. Then one gets $\bar{\eta} = (0.82 \pm 0.08) \times 10^{-2}$ (P), which is in excellent agreement with the static value determined by Miyake *et al.*[1] This coincidence is considered a further verification of the correctness of the proposed model.

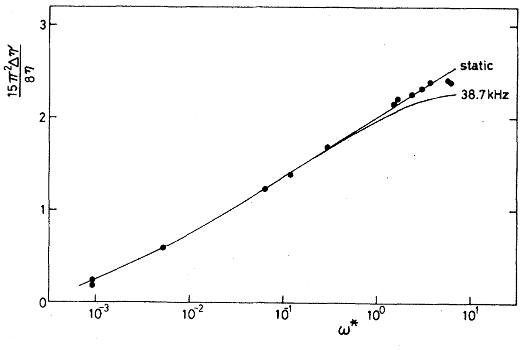

FIG. 1. Anomalous dynamic viscosity in Xe along the critical isochore above T_c as a function of the reduced frequency $\omega^* = \omega/\omega_D$. Ultrasonic shear data are shown at 38.7 kHz. The solid lines show Eqs. (8) and (10).

To study the frequency dependence of the viscosity function, it is convenient to separate out the frequency dependence by subtracting Eq. (8) from Eq. (10) for its static limit $\omega = 0$. The resulting function is independent of q_c/κ and permits us to define a normalized dynamical scaling function $\sigma_{\mathrm{PF}}(\omega^*)$ by

$$\frac{\Delta\eta(\kappa) - \Delta\eta'(\omega,\kappa)}{\bar{\eta}(\kappa)} = \frac{\eta(\kappa) - \eta'(\omega,\kappa)}{\bar{\eta}(\kappa)} = \frac{8}{15\pi^2}\,\sigma_{\mathrm{PF}}(\omega^*) . \tag{13}$$

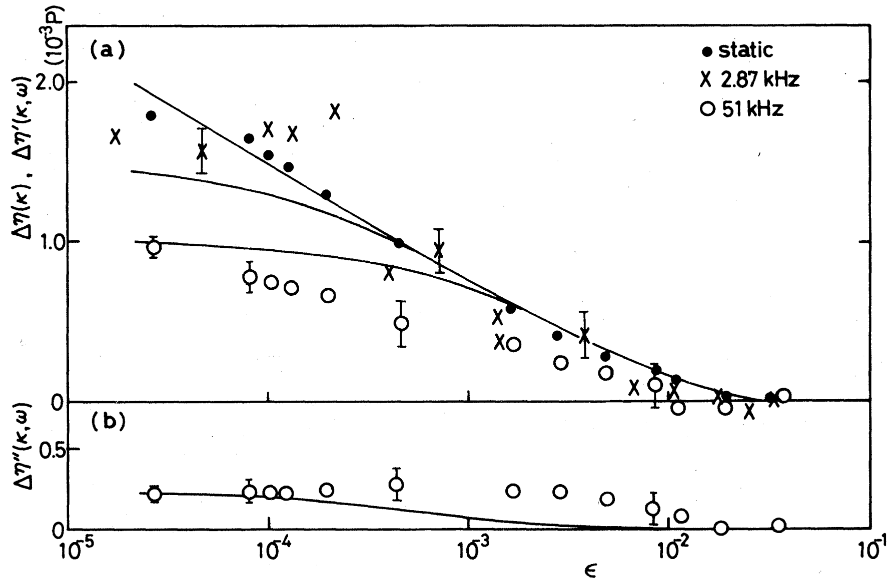

FIG. 2. Real part (a) and imaginary part (b) of the complex viscosity of nitrobenzene-*n*-hexane as a function of the reduced temperature difference $\varepsilon=(T-T_c)/T_c$. (a) The solid lines show Eqs. (8) and (10), (b) the solid line shows Eq. (9) corresponding to 51 kHz.

In taking the difference within the integral sign, we obtain an integral which converges at the upper limit; consequently, the upper limit can be set equal to infinity, $q_c/\kappa\to\infty$. In other words, the cutoff parameter disappears at this point and will no longer occur in the subsequent work. The resulting expression for the dynamical scaling function is a single integral:

$$\sigma_{PF}(\omega^*)=\int_0^\infty \frac{dv\, v^8\omega^{*2}}{(1+v^2)^{5/2}v^4[v^4(1+v^2)+\omega^{*2}]}\,. \tag{14}$$

The normalized dynamic scaling function σ_{PF} is plotted against ω^* in Fig. 3. The most interesting result is that the normalized dynamical scaling function behaves quite similarly in one- and two-component systems and that the dynamical data

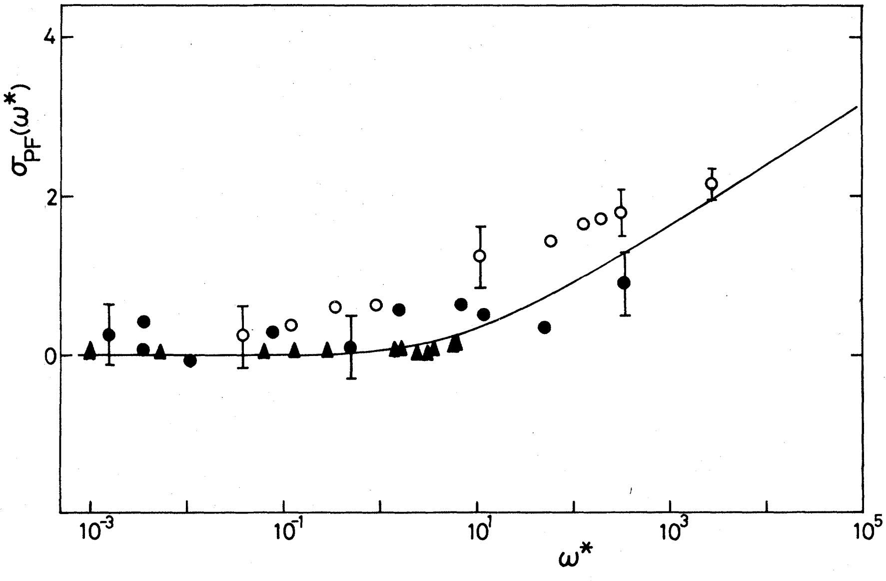

FIG. 3. Viscosity dynamic scaling function $\sigma_{PF}(\omega^*)$ as a function of reduced frequency ω^*. Ultrasonic shear data are shown at 38.7 kHz (Xe, solid angle), 2.87 (solid dot) and 51 kHz (open dot) in nitrobenzene-*n*-hexane. The solid curve represents Eq. (14).

generally follow the prediction of the theory over a wide range of ω^*. Thus the Perl-Ferrell (PF) theory may be successfully applied to the dynamic viscosity. However, we do not claim that these tests are conclusive because of the scattering of our experimental data. It is necessary to improve the ultrasonic shear measurement and investigate the viscosity over a wide range of frequency in various binary systems in order to obtain more conclusive results. Research is in progress along these lines.

ACKNOWLEDGMENTS

We are indebted to Professor M. Kitamura for reading the manuscript. Calculations were carried out on the VOS-3 Computer of the Computer Center of Hokkaido University.

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[21] We wish to express our appreciation to Dr. A. Onuki for this comment and other valuable comments.