Shear viscosity relaxation of a critical binary liquid

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Two series of diffusion coefficients D are reported for the triethylamine-water binary critical mixture. One has been obtained from quasielastic light scattering measurements, the other one has been derived from broadband ultrasonic spectra, yielding the relaxation rate of order parameter fluctuations, and shear viscosity data. Using high frequency shear impedance spectrometry in the range 20–130 MHz, relaxations in the background part of the viscosity, resulting in viscoelastic mixture properties, have been found. Both series of D data agree either if a half-attenuation frequency distinctly smaller than the theoretical value $\Omega_{1/2} = 2.1$ is used in the Bhattacharjee-Ferrell scaling function or if the viscosity extrapolated from the shear impedance measurements to low frequencies is applied to the Kawasaki-Ferrell relation. This extrapolated viscosity is smaller than the *static* shear viscosity measured with capillary viscosimeters.

Applied to a binary liquid near its critical demixing point the dynamic scaling hypothesis [1,2] means that, besides a characteristic length scale ξ of local fluctuations in the concentration, there exists also a characteristic time scale

$$\tau_\xi = \frac{\xi^2}{2D}, \tag{1}$$

which may be identified with the lifetime of the fluctuations [3]. The relation between τ_ξ and ξ is controlled by the mutual diffusion coefficient D, which, according to Kawasaki [4] and Ferrell [5],

$$D = \frac{k_B T}{6 \pi \eta_s \xi} \tag{2}$$

depends on the shear viscosity η_s of the liquid. Equivalence of Eq. (2) with the Stokes-Einstein relation suggests the local concentration fluctuations to be transferred in a viscous medium as spherical droplets with radius on the order of ξ. k_B is Boltzmann's constant and T denotes the temperature. Combining Eqs. (1) and (2),

$$\Gamma := \tau_\xi^{-1} = \frac{k_B T}{3 \pi \eta_s \xi^3} \tag{3}$$

follows, indicating that the relaxation rate Γ of concentration fluctuations is inversely proportional to their volume.

In order to experimentally inspect the Kawasaki-Ferrell relation [Eq. (2)], we have determined the diffusion coefficient of the triethylamine-water (TEA-H$_2$O) mixture of critical composition (mass fraction of amine, $Y_c = 0.321$) using two different methods [6]. We measured D directly utilizing a self-beating digital photon-correlation spectrometer to ana-

lyze the light that is quasielastically scattered from the sample. Basically, the diffusion coefficient has been obtained as

$$D(T) = \lim_{q \to 0} \Gamma_{\diagup}(q, T)/q^2 \tag{4}$$

from the decay rate $\Gamma_{\diagup}(q, T)$ of the time autocorrelation function of light scattered at wave vector $\vec{q}$. Crossover corrections in the diffusion coefficient, as proposed recently by Bhattacharjee and Ferrell within the framework of their dynamic scaling theory [7], have been found smaller than 2.5% [6].

Utilizing the relation

$$D = (2\Gamma)^{1/3} [k_B T/(6 \pi \eta_s)]^{2/3}, \tag{5}$$

as following from Eqs. (1) and (3), the diffusion coefficient has been additionally determined from broadband ultrasonic spectrometry. The ultrasonic measurements of the TEA-H$_2$O mixture of critical composition yielded spectra which clearly reveal noncritical background contributions (Fig. 1) and also a critical term $(\alpha/\nu^2)_c$, the amplitude of which increases substantially and the relaxation rate of which decreases dramatically when approaching the critical temperature $T_c = 291.42$ K. We have analyzed the ultrasonic spectra treating the critical part in terms of the dynamic scaling model [8],

$$(\alpha/\nu^2)_c = S \nu^{-1.06} F_{BF}(\Omega), \tag{6}$$

where S denotes an amplitude, ν the frequency, and

$$F_{BF}(\Omega) = [1 + 0.414(\Omega_{1/2}/\Omega)^{1/2}]^{-2} \tag{7}$$

an empirical form of the scaling function. Here $\Omega_{1/2} = 2.1$ [8] is the scaled half-attenuation frequency and $\Omega = 2\pi\nu/\Gamma$ is the reduced frequency. The shear viscosity η_s in Eq. (5) has been obtained from measurements with Ubbelohde viscometers using different capillary diameters and correcting the experimental data for the effect of shear [6].

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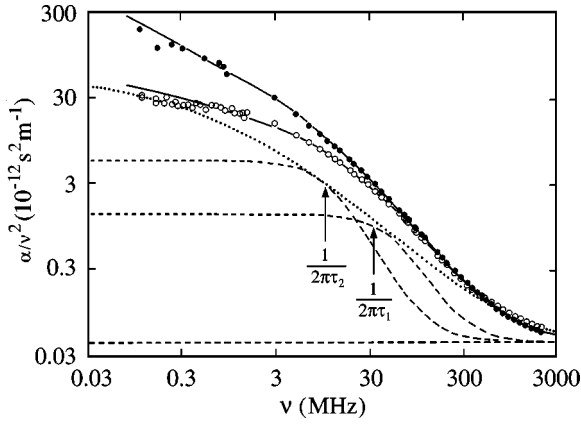
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FIG. 1. Frequency normalized plot of the ultrasonic attenuation spectra of the TEA-H_2O=mixture of critical composition at T=286.15 K ($\bigcirc$) and T=290.15 K ($\bullet$). For the former, the subdivision of the spectrum into a critical part and noncritical background contributions is indicated by dotted and dashed lines, respectively. Full lines are graphs of the complete spectral functions.

In Fig. 2 both series of diffusion coefficients are shown as a function of the reduced temperature $t=|T-T_c|/T_c$. The data display power law behavior,

$$D=D_o t^{\nu^*}, \tag{8}$$

in the crossover region $t \gtrsim 10^{-3}$, the exponents ν^* and amplitudes D_o of the two series of D data, however, are different from one another. Additionally, the ν^* values do not agree with the predictions from dynamic scaling (ν^*=0.671 [13]) and mode-coupling (ν^*=0.664 [4]) theory.
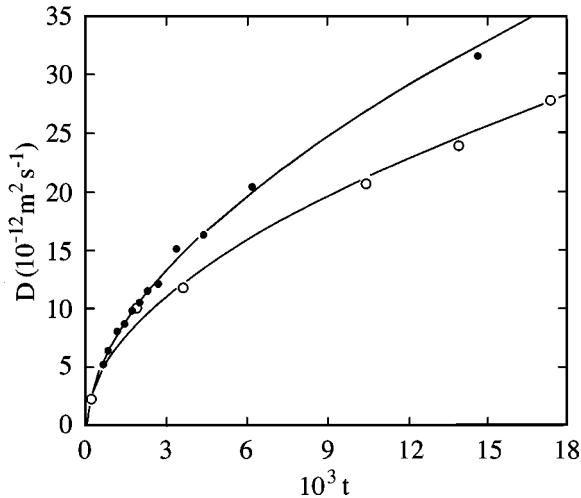

FIG. 2. Diffusion coefficients of the TEA-H_2O mixture of critical composition displayed versus reduced temperature t. Closed symbols show data from dynamic light scattering measurements, and open symbols show those from ultrasonic spectrometry using Eq. (5). It has been shown that crossover corrections for the transition to the hydrodynamical regime [7] are small. Lines are graphs of Eq. (8) with ν^*=0.57, D_o=3.6×10^{-10} m^2 s^{-1}($\bullet$), as well as ν^*=0.53, D_o=2.4×10^{-10} m^2 s^{-1} ($\bigcirc$).

FIG. 3. Complex plane representation of the shear viscosity of the TEA-H_2O mixture at 286.15 K ($\bigcirc$) and 291.15 K ($\bullet$). Semicircles are graphs of the spectral function defined by Eq. (10).

Calculating the D values from the acoustically determined Γ data, the "static" shear viscosities

$$\eta_{so}(t)=\eta_b(t)[Q_o \xi(t)]^{z_\eta} \tag{9}$$

have been used, including the background part $\eta_b(t)$. Here Q_o is a system dependent amplitude and z_η=0.065 [14] the universal critical exponent of viscosity. According to Kawasaki [4] and Ferrell [5], the value of the shear viscosity used in Eq. (5) should lie in the interval between the viscosity if there is no critical anomaly and that with singular part. Aiming, therefore, at a direct determination of the background part η_b, we have measured the shear viscosity of the TEA-H_2O mixture of critical composition at high frequencies. Using a shear impedance spectrometer in the frequency range 20–130 MHz [15], we found the liquid sample to clearly reveal frequency dependent viscoelastic properties. These characteristics may be adequately considered by a frequency dependent complex viscosity $\eta_s(\nu)$ $[=\eta_s'(\nu)-i\eta_s''(\nu)$, where $i^2=-1]$. A complex plane representation of the shear viscosity of the TEA-H_2O mixture is given in Fig. 3. The data exhibit a Debye-type relaxation with discrete relaxation time τ_η. Hence

$$\eta_s(\nu)=\eta_s(\infty)+[\eta_s(0)-\eta_s(\infty)]/[1+i2\pi\nu\tau_\eta]. \tag{10}$$

At 283.15 K$\leq T \leq$291.15 K the shear viscosity relaxation time is independent of temperature ($\tau_\eta \approx 2$ ns) and is also in almost good agreement with the relaxation time τ_1 (≈ 3.5 ns [6]) of the high frequency relaxation in the acoustical spectra (Fig. 1). This acoustical relaxation has been assumed to be due to a protolysis reaction of TEA, associated with a noticeable rearrangement of the voluminous clathrate-like hydration shell. Likely, the shear viscosity relaxation is related to this process. This is particularly true as the contribution to the relaxation amplitude of the ultrasonic spectra,

$$\delta A_1=4\pi[\eta_s(0)-\eta_s(\infty)]/(3\rho c_s^2 \tau_\eta), \tag{11}$$

following from the viscosity relaxation (δA_1=2.3×10^{-3}, 286.15 K) is much smaller than the measured amplitude
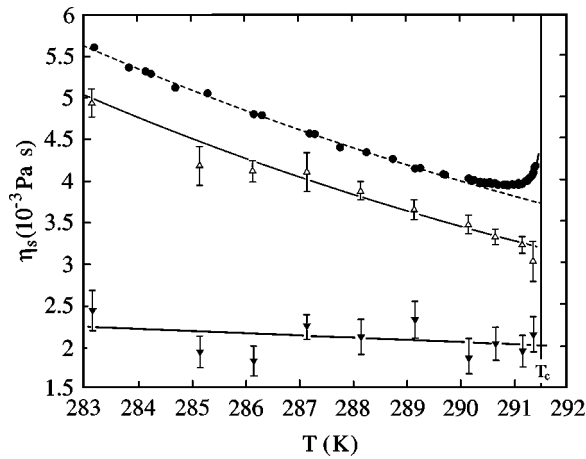
FIG. 4. Static shear viscosity η_{so} (●) as well as extrapolated low frequency [($\eta_s(0)$, △)] and high frequency [$\eta_s(\infty)$, ▼] data from the frequency dependent shear impedance measurements [Eq. (10), Fig. 3]

FIG. 5. Relaxation rates Γ of order parameter fluctuations of the TEA-H_2O mixture of critical composition displayed versus reduced temperature t. The acoustically determined data (○) follow power law behavior $\Gamma = \Gamma_o t^{Z_o \tilde{\nu}}$ with the theoretically predicted critical exponent $Z_o \tilde{\nu} = 1.928$ and $\Gamma_o = 90(4) \times 10^9$ s^{-1} (full line). The other symbols indicate data from diffusion coefficients determined by quasielastic light scattering using $\eta_s(0)$ [□, $\Gamma_o = 93(4) \times 10^9$ s^{-1}] and $\eta_s(\infty)$ [◇, $\Gamma_o = 24(3) \times 10^9$ s^{-1}] in Eq. (5).

($A_1 = 99 \times 10^{-3}$ [6]). In Fig. 4 the $\eta_s(0), \eta_s(\infty)$, and η_{so} data of the TEA-H_2O mixture are plotted versus temperature. The η_{so} and $\eta_s(0)$ data have been corrected for crossover effects because of the transition to the hydrodynamical regime, including the consideration of a small background contribution to the diffusion coefficient as described in Refs. [9–12]. According to our expectations, only the η_{so} data exhibit a critical contribution when T approaches T_c. At all temperatures the extrapolated viscosity $\eta_s(0)$ is smaller than the static η_{so}.

Figure 5 shows the acoustically determined relaxation rate Γ_{ac} along with the relaxation rates Γ_{op} obtained from the optically measured diffusion coefficient and different viscosities. The Γ_{ac} have been corrected to small effects of crossover following the procedure proposed by Bhattacharjee and Ferrell [7]. At $t > 4 \times 10^{-3}$, use of η_{so} leads to Γ_{op} values substantially larger than Γ_{ac} at the same temperature, whereas the use of $\eta_s(\infty)$ data results in Γ_{op} values significantly smaller than Γ_{ac}. $\Gamma_{op} \approx \Gamma_{ac}$ is obtained with $\eta_s(\nu \to 0)$, where no critical contribution is included. The characteristic parameters, such as ξ_o and q_c, are slightly different. Interestingly, agreement of the acoustically and optically measured relaxation rates (Fig. 5) and also be of the two series of diffusion coefficients (Fig. 2) can also be obtained if η_{so} is used in the Kawasaki-Ferrell relation [Eq. (2)], but if the half-attenuation frequency in the scaling function [Eq. (7)] is assumed as $\Omega_{1/2} = 1.0$. This value is considerably smaller than the theoretical value $\Omega_{1/2} = 2.1$ [8]. There are,
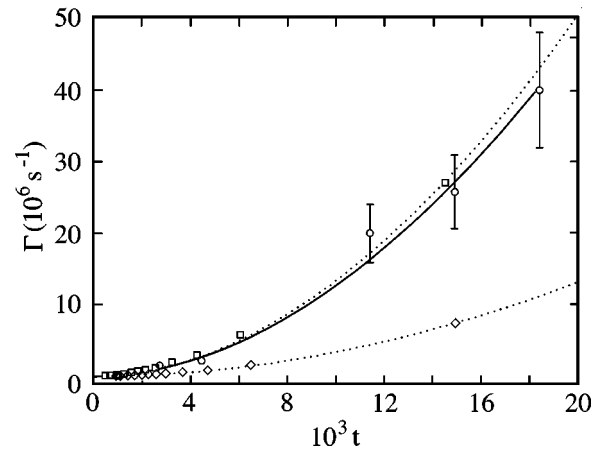
however, also binary critically demixing liquids for which $\Omega_{1/2}$ values larger than 2.1 have been reported [16]. This variance in the experimentally determined $\Omega_{1/2}$ data seems to indicate that some physical effect of real systems may not be included in the theoretical model. It has been suggested recently [17] that a coupling of the critical fluctuations to a chemical mode may act an influence on the relaxation rates derived from acoustical spectrometry, but not those determined optically. This suggestion is based on the idea that the system can relax via two parallel pathways, namely, the diffusion controlled fluctuations in the local concentration and elementary chemical processes such as structural isomerizations, dimerizations, protolysis/hydrolysis, and association as well. Irrespective of our presently incomplete knowledge of the correct value of the half-attenuation frequency in the theoretical model, our high frequency shear relaxation masurements tend to confirm the idea that the diffusion coefficient is controlled by the extrapolated low frequency shear viscosity $\eta_s(0)$ rather than the static shear viscosity $\eta_{s,o}$ that contains the critical contribution.

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