Concentration Fluctuations and Crossover Effects of Critical Binary Liquids Near Their Consolute Point

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Summary

Various scaling functions for the critical acoustic absorption of demixing binary liquids have been predicted theoretically. In this article measurements are reported to experimentally determine the scaling function without adjustable parameter, taking into account the effects of the crossover from critical to mean-field behaviour. It is found that the empirical Bhattacharjee-Ferrell scaling function nicely fits to the experimental findings, particularly if a possible temperature dependence in the sound velocity and in the amplitude of the critical absorption term is considered accordingly.

Introduction

Much interest is directed towards systems near a critical point because of their feature to display order parameter fluctuations over multiple scales of length. These fluctuations tend to mask the individual characteristics, thus resulting in a striking similarity of systems which are otherwise quite different. The similarity is expressed by universal power laws which describe the thermodynamic and transport properties close to a critical point. A fascinating aspect is the interactions, promoting correlations between the molecules so extensively throughout a macroscopic system that universal behaviour results. Other points of lively scientific debates are the crossover region near the critical point where the transition from critical to mean-field behaviour occurs and also crossover effects between the critical dynamics and other elementary molecular processes, like conformational changes, dimerisations, and micelle formations. Acoustical spectrometry is a powerful tool to study the molecular dynamics and fast chemical kinetics of such liquids since the critical fluctuations in the local concentration and the elementary processes as well couple to the sonic field. Various theoretical expressions have been proposed for the frequency dependence of the critical part α_λ^c [1-3] in the total absorption coefficient per wavelenght, $\alpha_\lambda = \alpha\lambda$. Therefore, more complicated spectra cannot be unambiguously evaluated without additional information on the correct shape of the α_λ^c term. For this reason this shape has been determined by measurements of critically demixing binary liquids without additional relaxation terms [4-7]. In order to reduce the number of unknown parameters, ultrasonic spectrometry has been complemented by dynamic light scattering and shear viscosity measurements.

1 Results and discussion

In Figure 1 an ultrasonic absorption spectrum of the n-pentanol-nitromethane mixture (n-PE-NE) of critical composition is shown in the homogeneous phase at temperature T about 7.5 K above the (upper) critical temperature T_c of the system.
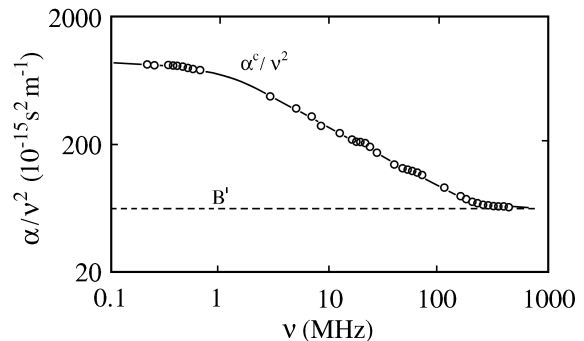

Figure 1. UItrasonic absorption spectrum in the frequency normalized format for the n-pentanol-nitromethane mixture of critical composition (mole fraction of alcohol $X_c = 0.385$) at 34.8°C (upper critical temperature $T_c = 27.30$°C) [6]. The dashed line indicates the noncritical background contribution. The full line is the graph of the spectral function (3) with $F(\Omega) = F_{BF}(\Omega)$ as defined by (11).

In order to accentuate the low frequency part of the spectrum the data are shown in the frequency normalized format

$$\alpha/\nu^2 = \alpha_\lambda/(c_s\nu). \tag{1}$$

In this format the data approach asymptotically the frequency independent value

$$\lim_{\nu \to \infty} (\alpha/\nu^2) = B' = B/c_s \tag{2}$$

which, for this binary system, represents the noncritical background part. The critical part of the spectrum can be well represented by the Bhattacharjee-Ferrell dynamic scaling model [1]

$$\alpha_\lambda^c(\nu, T) = \alpha_\lambda - B\nu = c_s(T)A(T)F(\Omega) \qquad (3)$$

with an amplitude factor that, according to

$$A(T) = S(T)\nu^{-\delta}, \qquad (4)$$

is only weakly dependent upon ν, because $\delta = \alpha_0/(Z_0\tilde{\nu})$ follows from the universal critical exponents α_0, Z_0, and $\tilde{\nu}$ as small as 0.06. $S(T)$ can be calculated from thermodynamic quantities of the critical mixture [1]. In (3) $F(\Omega)$ is the scaling function. It depends upon the reduced frequency

$$\Omega = 2\pi\nu/\Gamma(\epsilon) \qquad (5)$$

where Γ denotes the relaxation rate of order parameter fluctuations, assumed to follow power law behaviour

$$\Gamma(\epsilon) = \Gamma_0\epsilon^{Z_0\tilde{\nu}}. \qquad (6)$$

Here Γ_0 is an amplitude and

$$\epsilon = |T - T_c|/T_c \qquad (7)$$

is the reduced temperature.

According to the dynamic scaling hypothesis

$$\Gamma = 2D/\xi^2 \qquad (8)$$

the relaxation rate Γ can be calculated if the mutual diffusion coefficient D and the fluctuation correlation length ξ of the system are available. Taking crossover effects into account D and ξ can be derived from a combined evaluation of shear viscosity and dynamic light scattering data as [8]

$$\eta_s(\epsilon) = \eta_b(\epsilon)exp\left(Z_\eta H\right) \qquad (9)$$

with the background viscosity η_b, the critical exponent $Z_\eta = 0.065$ of the viscosity and with a crossover function $H(\xi, q_D, q_c)$ that, besides on ξ, depends on two cut-off wavenumbers, q_D and q_c. The analytical form of H is given elsewhere [8]. The mutual diffusion coefficient, also consisting of a singular part and a background part, may be written in the form [8]

$$D = \frac{k_B T}{6\pi\eta_s\xi}G(\xi, q_D, q_c, \eta_s, \eta_b). \qquad (10)$$

Hence it depends likewise on parameters ξ, q_D, and q_c, as well as on η_s and η_b.
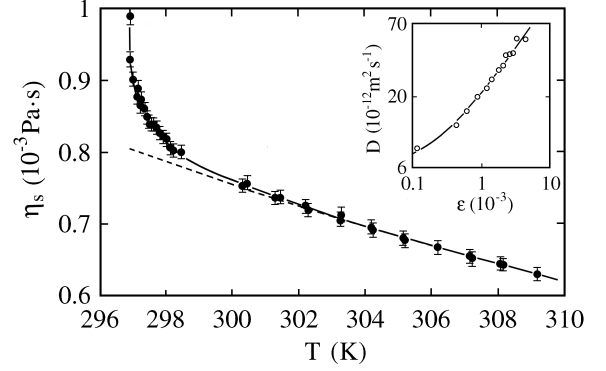

Figure 2. Shear viscosity η_s and mutual difusion coefficient D of the nitro-ethane-cyclohexane mixture of critical composition (mole fraction $X_c = 0.452$ of NE, $T_c = 296.46$ K [7] as a function of temperature T and reduced temperature ϵ, respectively. The full lines represent the theoretical descriptions as resulting from the combined evaluation of (9) and (10). The dashed line shows the background part η_b of the viscosity.

In Figure 2, as an example, the shear viscosity and the diffusion coefficient of the nitroethane-cyclohexane (NE-CH) mixture of critical composition are plotted versus temperature and reduced temperatue, respectively. The full lines show functions (9) and (10), respectively, as following from the combined evaluation of shear viscosity and dynamic light scattering measurements [7]. The resulting relaxation rates of the NE-CH and also of the n-PE-NE follow the power law (6) with the theoretical exponent $Z_0\tilde{\nu} = 1.93$ and with the amplitudes $\Gamma_0 = 156 \cdot 10^9 \text{s}^{-1}$ (NE-CH) and $187 \cdot 10^9 \text{s}^{-1}(n-\text{PE-NE})$.
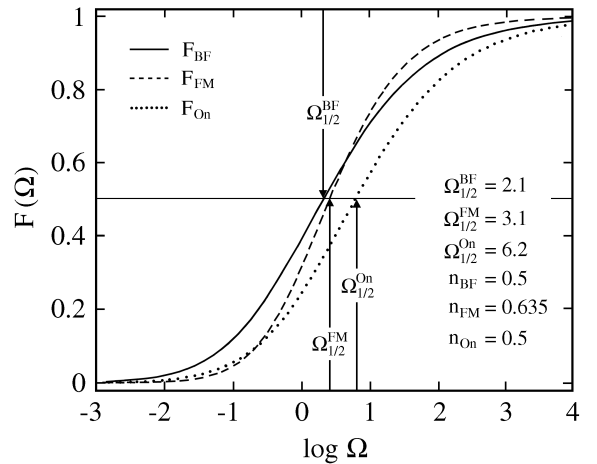

Figure 3. Graphs of the Bhattacharjee-Ferrell (full line [1]), the Folk-Moser (dashed line [2]), and the Onuki (dotted line [3]) scaling functions and parameters for their analytical representation according to (11).

Various theoretical expressions have been proposed for the the scaling function $F(\Omega)$ of critically demixing binary liquids. The most prominent functions

can be analytically expressed [9] by the relation ($x = BF, FM, On$)

$$F_x(\Omega) = [1 + 0.414(\Omega^x_{1/2}/\Omega)^{n_x}]^{-2} \tag{11}$$

where BF refers to the Bhattacharjee-Ferrell dynamic scaling model [1], FM to the Folk-Moser mode coupling theory [2], and On to Onuki's intuitive description of the bulk viscosity [3].

The half-attenuation frequencies $\Omega^x_{1/2}$, defined by $F_x(\Omega^x_{1/2}) = 0.5$, and the exponents n_x are given in Figure 3. The scaling function of various binary liquids has been determined recently [4-7], mostly by utilizing the relaxation rates from dynamic light scattering and shear viscosity measurements and calculating $F(\Omega)$ from ultrasonic spectra without any adjustable parameter [6,7]. Absorption coefficient data at low frequencies, where the critical part dominates over the background contribution have been used to obtain the scaling function as the ratio [7]

$$F(\Omega) = F^* \alpha^c_\lambda(\nu, T)/\alpha^c_\lambda(\nu, T_c). \tag{12}$$

Herein factor

$$F^* = A(T_c)c_s(T_c)/[A(T)c_s(T)] \tag{13}$$

normalizes for the temperature effect in the sound velocity and amplitude if measurements were extended over a wide temperature range. Normally $F^* = 1$.
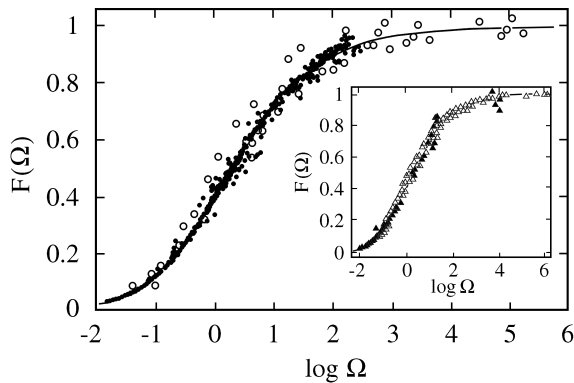

Figure 4. Scaling function data for the nitroethane-cyclohexane system ($\bullet$ [7], $\circ$ [10]) as well as the n-pentanol-nitromethane ($\blacktriangle$ [6]) and the 3-methylpentane-nitroethane ($\triangle$ [11]) system. The lines are graphs of the Bhattacharjee-Ferrell scaling function $F_{BF}(\Omega)$.

In Figure 4 scaling function data for the NE-CE system [7], including literature data [10], are given and also data for the systems n-PE-NE [6] and 3-methylpentane-nitroethane [11]. The experimental

scaling function data nicely fit to the empirical scaling function of the Bhattacharjee-Ferrell model, the graph of which is also given in the figures.

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