Broadband ultrasonic spectrometry of polystyrene-cyclohexane critical mixtures

Sirojiddin Z. Mirzaev^{1,2} and Udo Kaatze¹

¹Drittes Physikalisches Institut, Georg-August-Universität, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany ²Institute of Ion-Plasma and Laser Technologies, Uzbek Academy of Sciences, Dormon Yuli Street 33, 100125 Taschkent, Uzbekistan (Received 20 August 2013; published 31 October 2013)

Mutual diffusion coefficients, shear viscosities, and broadband ultrasonic attenuation spectra in the frequency range 100 kHz to 300 MHz have been measured for solutions of polystyrene in cyclohexane at two degrees of polymerization N and various temperatures near the critical. The exponent y_{η} in the power law representation of the critical part in the viscosity deviates substantially from the universal value $y_{\eta} = 0.0435$: $y_{\eta} = 0.028$ (N = 288) and $y_{\eta} = 0.014$ (N = 6242). Also, the adiabatic coupling constant g and the amplitudes ξ_0 and Γ_0 in the power laws of the correlation length and the relaxation rate of fluctuations, respectively, depend on N. This is especially obvious with the relaxation rates, for which $\Gamma_0 = 5.8 \times 10^9$ at N = 288 and $\Gamma_0 = 6.1 \times 10^7$ with the larger polymer results. A noteworthy feature is the difference between the relaxation rates from the diffusion coefficients and shear viscosities on the one hand and from the ultrasonic spectra on the other. Near the critical temperatures the latter Γ values deviate from power law behavior, indicating a coupling between the concentration fluctuations and structural isomerizations of the polymers.

DOI: 10.1103/PhysRevE.88.042316

PACS number(s): 64.70.Ja, 61.20.Ja, 64.60.Ht, 43.35.+d

I. INTRODUCTION

Asymptotically close to a critical demixing point of binary liquids, long-wavelength fluctuations in the local concentrations develop, which cover a vast range of sizes. These fluctuations effectively mask the individual interactions and lead to striking similarities in the properties of systems that are otherwise quite different [1–6]. These similarities have provoked universality conceptions and classifications of critical systems. As to their thermodynamic properties, binary liquids near their consolute point belong to the same universality class as fluids near their van der Waals critical point and uniaxial magnets near their Curie point. Within the scope of the Ising lattice gas model [7,8] the correlation length ξ of fluctuations increases following the power law

$$\xi = \xi_0 \varepsilon^{-\tilde{\nu}} \tag{1}$$

on approaching the critical temperature T_c . In this relation ξ_0 is an individual amplitude, $\varepsilon = |T - T_c|/T_c$ is the reduced temperature, and \tilde{v} (=0.63 [9]) is a universal critical exponent. The dynamics of fluctuations is controlled by a relaxation time τ_{ξ} , which, according to the dynamic scaling hypothesis [9–12]

$$\tau_{\xi} = \xi^2 / 2D, \qquad (2)$$

is given by correlation length and the mutual diffusion coefficient D. The relaxation time likewise follows the power law

$$\tau_{\xi} = \tau_0 \varepsilon^{-Z\tilde{\nu}},\tag{3}$$

with individual amplitude τ_0 and the dynamics critical exponent

$$Z_0 = d + x_\eta. \tag{4}$$

Here *d* denotes the dimensionality of space, i.e., d = 3 for critically demixing liquids, and x_{η} is the exponent for the divergence of the shear viscosity. Space shuttle microgravity experiments have yielded $x_{\eta} = 0.069$ [13], in nice agreement with three-loop mode coupling calculations from which $x_{\eta} = 0.0679$ [14] was obtained.

In measurements the range of true asymptotic behavior often is small since, on departure from the critical temperature, a crossover from Ising-type to mean-field criticality occurs, involving changes in the values of critical exponents. In this way the microscopic structure of the liquid still exerts an impact on the liquid features because the range of crossover depends on the molecular interaction forces and on a molecular size cutoff. In mixtures of low-molecular-weight fluids, called simple mixtures below, crossover to mean-field criticality is never completed due to a too short cutoff length on the order of molecular sizes [15,16]. In this context critically demixing polymer solutions can provide useful information as their cutoff length, without noticeable changes of the interaction forces, can be tuned by the degree of polymerization. Hence, in such more complex mixtures a competition between two mesoscopic length scales exists, namely, the fluctuation correlation length ξ and the structural cutoff length, which, in dilute solutions, is assumed proportional to the radius of gyration R_{g} of the polymer [16]. Because of the strong temperature dependence of the correlation length near T_c [Eq. (1)] a temperature exists at which ξ becomes equal to the structural length, i.e., equal to R_g . At temperatures closer to T_c the system is governed by the critical fluctuations and is thus expected to reveal Ising-like critical behavior, whereas at temperatures further away from T_c the mesoscopic molecular structure will be dominant in determining the system properties.

Interference of critical fluctuations in the local concentration with a structural length scale has promoted interest in the properties of polymer systems near their consolute point. Experimental investigations of the polystyrene-cyclohexane system, as well as endeavors to model its properties theoretically, date back to Debye *et al.* [17–20]. In a more recent series of papers [16,21–24] Anisimov and co-workers have reported on the competition of mesoscales in polystyrene-cyclohexane mixtures as appearing in dynamic light scattering experiments using polymer molecular weights between 0.2×10^6 and 11.4×10^6 g/mol. Only at the lowest polymer molecular weight the dynamic correlation function was found to obey a single exponential as in Ising-like critical systems. At higher polymer molecular weights two dynamic modes were observed, which originate from a coupling of the fluctuations in the local concentration and conformational variations of the polymer chains [24]. This finding made us interested in performing a broadband ultrasonic attenuation, dynamic light scattering, and shear viscosity study of polystyrene-cyclohexane mixtures with polymer molecular weights below and above 2×10^5 g/mol in order to study the interaction between the relaxations due to critical fluctuations and due to conformational variations.

By disclosing fluctuations in the local concentration as well as structural relaxations, ultrasonic attenuation spectrometry applies favorably to the investigation of interactions between both molecular mechanisms [25]. The ultrasonic spectra of critically demixing liquids according to

$$\alpha_{\lambda}(\nu, T) = \alpha_{\lambda}^{c}(\nu, T) + \alpha_{\lambda}^{b}(\nu, T)$$
(5)

can be expressed as a sum of a critical *c* part and a background *b* part. Here $\alpha_{\lambda} = \alpha \lambda$ with sonic attenuation coefficient α and wavelength $\lambda = c_s/\nu$, ν is the frequency of the sonic field, and c_s is the sound velocity of the liquid. Within the framework of the Bhattacharjee-Ferrell dynamic scaling theory [25–27] the critical contribution may be expressed as a product

$$\alpha_{\lambda}^{c}(\nu,T) = c_{s}A(T)F(\Omega) \tag{6}$$

of c_s , an amplitude A(T) weakly depending on frequency, and an empirical scaling function

$$F(\Omega) = [1 + 0.414 (\Omega_{1/2}/\Omega)^{1/2}]^{-2} = (1 + 0.6 \,\Omega^{-1/2})^{-2}$$
(7)

of the reduced frequency $\Omega = 2\pi \nu \tau_{\xi} = 2\pi \nu / \Gamma$. In these relations, $\Omega_{1/2}$ (=2.1 [25]) denotes the half-attenuation frequency [$F(\Omega_{1/2}) = 0.5$] and $\Gamma = 1/\tau_{\xi}$ is the relaxation rate of concentration fluctuations. Here Γ can be calculated from the shear viscosity and the mutual diffusion coefficient. Combining in a simple approach, for example, Eq. (2) with the suggestive Stokes-Einstein-Kawasaki-Ferrell relation [12,28–30]

$$D(T) = k_B T / 6\pi \eta_s(T) \xi(T), \tag{8}$$

the relaxation rate can be calculated as

$$\Gamma = 72\pi^2 \eta_s^2 D^3 / (k_B T)^2 \tag{9}$$

from the shear viscosity and diffusion coefficient data. The latter derive directly from the dynamic light scattering experiments. The amplitude A(T) of the critical contribution to the sonic attenuation can be calculated from thermodynamic quantities so that, within the framework of the Bhattacharjee-Ferrell model, the critical contributions α_{λ}^c to the sonic attenuation spectra are known. Knowledge of the critical contributions, of course, greatly facilitates the proper extraction of the noncritical background contributions to the spectra and thus the evaluation of structural relaxations.

Various ultrasonic attenuation studies of polystyrenes in cyclohexane or other solvents have been performed in the past [31-37]. Unfortunately, in those studies the frequency range of measurements was too small to properly account for broadband critical contributions to the spectra. In addition, most studies aimed at the conformational changes of the polymer chains.

Only one paper [36] refers also to critical fluctuations. Since measurements had been done not closer than 1 K to the critical point, however, slowing down in the observed relaxation was assigned to polymer segregation fluctuations rather than critical fluctuations in the local concentrations.

II. EXPERIMENT

A. Critical mixtures

Polystyrenes with molar masses 3×10^4 g/mol (PS1) $(M_W/M_N < 1.03)$ and 6.5×10^5 g/mol (PS2) $(M_W/M_N < 1.06)$ have been supplied by Pressure Chemical (Pittsburgh, PA), cyclohexane (CH) ($\geq 99.9\%$) was obtained from Sigma-Aldrich (Munich, Germany). All chemicals were used without further purification. Solutions were prepared by weighing appropriate amounts of the chemicals into suitable flasks and were always kept in a dry nitrogen atmosphere in order to avoid water uptake from the air. The critical mass fractions Y_c of polymers and the corresponding critical temperatures were determined according to the equal-volume criterion. Virtually the same data as from previous heat capacity measurements [38] were found: $Y_c = 0.186 \pm 0.001$ and $T_c = (283.10 \pm 0.02)$ K for PS1 and $Y_c = 0.061 \pm 0.001$ and $T_c = (300.90 \pm 0.02)$ K for PS2.

The critical temperatures agree well with the transition temperatures in the densities of the samples (Fig. 1). Densities have been measured with a high-precision vibrating tube densitometer (Physica DMA 5000, Anton Paar, Graz, Austria) with built-in reference oscillator and sensitive Peltier temperature control. The repeatability of the density measurements was 10^{-6} and temperature fluctuations were smaller than 0.001 K. The critical temperatures also fit nicely to the literature data shown in a Flory representation [39] in the inset of Fig. 1.

B. Ultrasonic spectrometry

Using spot frequency methods, the ultrasonic attenuation coefficient α of the liquid samples has been measured as a function of frequency ν between about 0.1 and 300 MHz.



FIG. 1. Detail of a temperature scan of the density of the PS1-CH mixture of critical composition. The arrow marks the visually determined critical temperature T_c (=9.95 °C). The inset shows the reciprocal $1/T_c$ as a function of $N^{-1/2} + 0.5N^{-1}$, where N denotes the degree of polymerization of polystyrenes. Closed circles represent the data for the PS1 and PS2 samples, respectively, and open circles indicate data from the literature [16,19,20,40–45].

Because of the Stokes damping of the sonic wave within the fluid, the background part $\alpha_{\lambda}^{b}(v,T)$ in the attenuation per wavelength contains a contribution $B(T)\nu$, proportional to frequency. The strong frequency dependence thereby imposed upon the attenuation coefficient necessitates the use of two different methods. At frequencies below 12 MHz, at which α is small, a cavity resonator method has been used in which the path length of interaction between the sonic wave and the sample is virtually increased by multiple reflections. Two different cylindrically shaped resonator cells were used. With both cells the faces were formed by piezoelectric quartz disks of which one was used as transmitter, the other one as receiver transducer. The cell operated at lowest frequencies (100 kHz $\leq v \leq 2.7$ MHz, where d = 70 mm, with d equal to the diameter of the sample volume) was provided with one concavely cut transducer in order to reduce diffraction losses within the frequency range of measurements [46]. The other cell (800 kHz $\leq v \leq 12$ MHz, d = 16.8 mm) was made from two plane transducers [47]. Both cells were equipped with precisely tunable screws for parallel adjustment of the transducers.

Due to the finite lateral dimensions of the cells, higherorder (satellite) resonance peaks result at frequencies above a principal resonance. In order to take the effects of the satellites on the principal resonances carefully into account, the complex transfer function in the frequency range around a principal resonance peak has been always recorded and suitable theoretical functions have been used to obtain the resonance frequency v_r and the half-power bandwidth $\delta v = v_r/Q_{\text{total}}$ of the peak. Here Q_{total} is the experimental total quality factor of the resonance. Using the common relation

$$1/Q_{\text{liquid}} = 1/Q_{\text{total}} - 1/Q_{\text{cell}},\tag{10}$$

which is based on energy arguments, the quality factor Q_{liquid} to be used in the evaluation of the liquid attenuation coefficient has been obtained. In Eq. (10) Q_{cell} represents the intrinsic cell losses that have been obtained from reference measurements with liquids of well-known sonic attenuation coefficient and matched sound velocity and density.

At frequencies above 3 MHz attenuation coefficient measurements have been performed by transmitting ultrasonic waves through specimen cells of variable distance. At each frequency of measurement the transfer function of the cell has been recorded as a function of sample length, i.e., of the distance between the piezoelectric transmitter and receiver units. The coefficient α has been obtained from a regression analysis of the transfer function data in terms of the corresponding analytical forms [48,49]. In order to avoid interferences from electrical cross talk, the different transition times of electromagnetic and acoustic waves have been utilized by using pulse-modulated signals. The stability of the electronic setup was regularly checked with the aid of suitable high-precision below-cutoff piston attenuators. Again two cells have been used that were operated at odd overtones of the fundamental frequencies v_a of their transducers thickness vibrations. The cells mainly differed from another by their dimensions and by their transducer material. At 3 MHz $\leq v \leq$ 60 MHz the cell was equipped with X-cut quartz disks with $v_q = 1 \text{ MHz}$ [42]. At 30 MHz $\leq v \leq$ 300 MHz rotated Y-cut

lithium niobate transducers were used that stuck on the back face of cylindrical delay lines made of fused quartz.

The temperature of the cells was controlled to within ± 0.03 K by circulating thermostat fluid through suitable channels in the cell and also through pipes in an additional thermostatic guard. The experimental errors in α data from such temperature fluctuations were negligibly small. The uncertainties in the attenuation coefficients, as resulting from repeated measurements including cell cleaning and refilling procedures in between, are $\Delta \alpha / \alpha = 0.1, 0.1-3$ MHz; $\Delta \alpha / \alpha = 0.02, 3-25$ MHz; and $\Delta \alpha / \alpha = 0.01, 25-300$ MHz. Errors due to fluctuations in the measurement frequency ($\Delta \nu / \nu < 0.0001$) were negligibly small throughout.

C. Quasielastic light scattering

The mutual diffusion coefficient D(T) of the liquids, according to the relation

$$D(T) = q^{-2} \Gamma_{\ell}(q, T), \qquad (11)$$

has been determined from the decay rate Γ_ℓ of the normalized autocorrelation function

$$S_{\ell}(q,t) = \exp[-t\Gamma_{\ell}(q,T)]$$
(12)

of the light scattered from the sample. Here

$$q = |\vec{q}| = \frac{4\pi n}{\lambda_0} \sin(\Theta/2) \tag{13}$$

is the modulus of the wave vector selected by the scattering geometry, Θ is the scattering angle, *n* is the refractive index of the liquid, and λ_0 is the wavelength of the incident light. The self-beating digital photon correlation spectrometer applied in the measurements was operated at fixed scattering geometry $(\Theta = \pi/2)$ using light ($\lambda_0 = 532$ nm) that was provided by a frequency-doubled Nd:YAG laser (Coherent, Santa Clara, CA). The sample was contained in a circular cell equipped with planar windows in order to avoid diffraction of the incident and the unscattered light. A microscope objective focused the scattered light onto the cathode of a photomultiplier (Hamamatsu R647P, Hamamatsu, Japan). High spatial resolution was reached by a system of slits and lenses as well as an aperture and a pinhole in front of the photomultiplier. An interference filter excluded fluorescent light from the detector and a pair of adjusted polarization filters avoided contributions from orientation correlations within the samples. The time sequence of photons detected by the photomultiplier was analyzed by a real-time digital correlation board (ALV-5000/E, Laser, Langen, Germany) to determine the autocorrelation function S_{ℓ} at times between 2×10^{-7} and 3.4×10^3 s [50]. With the low-polymer-molecular-weight sample (PS1) indeed a singleexponential autocorrelation function (12) has been found. With the higher-polymer-molecular-weight sample (PS2) indications of a second dynamic mode have been observed. Such deviations from single-exponential behavior had been reported already for polystyrene-cyclohexane mixtures with polymer molecular weights larger than 1.1×10^6 g mol⁻¹ and had been assigned to a coupling between critical fluctuations with viscoelastic relaxations of polymer chains [24].

The sample cell was provided with chambers for circulating thermostat fluid. The optical part of the spectrometer was

placed on a vibration-damped table and was completely shielded by a thermostatic guard again equipped with pipes for circulating thermostat fluid. Temperature fluctuations and temperature gradients within the small scattering volume were smaller than 0.01 K. Close to the scattering volume the sample temperature was measured to within ± 0.01 K with the aid of a Pt-100 thermometer, which had been calibrated against high-precision mercury-in-glass thermometers with 0.01-K graduation. The uncertainty in the diffusion coefficients was $\Delta D/D = 0.05$.

D. Shear viscosity

The kinematic viscosity ν_{η} of the samples has been determined as a function of temperature using a set of Ubbelohdetype capillary viscometers (Schott, Mainz, Germany). For appropriate temperature control the viscometers were immersed in a glass container through which thermostat water flowed. The container was placed in a thermostatic box, the temperature of which in turn was controlled by circulating water from a second laboratory thermostat. The kinematic viscosities were converted into dynamic viscosity $\eta_s = v_n \rho$ values using the densities ρ from the vibrating tube densitometer measurements mentioned before. In order to ensure that the viscosity data of the samples were not affected by preferential evaporation of cyclohexane, a falling ball viscometer (Haake, Karlsruhe, Germany) was also employed. Its downpipe was concentrically set into a larger glass drum through which thermostat water was circulated. With both types of viscosity measurements the sample temperature was controlled to within ± 0.02 K. It was measured with Pt-100 and negative temperature coefficient thermometers, which had been also calibrated against high-precision mercury thermometers. Effects due to finite shear rates in the viscosity data were substantially smaller than the experimental uncertainty $\Delta \eta_s / \eta_s = 0.02$.

E. Sound velocity

At $\nu < 12$ MHz the sound velocities $c_s(T)$ of the sample liquids have been calculated from series [46]

$$\nu_n = \frac{c_s}{d} \left[\frac{n}{2} + \frac{1}{\pi} \arctan\left\{ \frac{Z}{Z_t} \cot\left(\pi \frac{\nu_n}{\nu_t}\right) \right\} \right], \quad n = 1, 2, \dots,$$
(14)

of resonance frequencies of the ultrasonic resonator cells (Sec. II B), taking into account the nonequidistant distribution of the v_n data. In Eq. (14) *d* is the distance between the transducers, i.e., the length of the liquid column, *Z* and Z_t are the acoustic impedances of the liquid and the transducers, respectively, and v_t is the fundamental frequency of transducer thickness vibrations. The experimental uncertainty in the sound velocity data was $\Delta c_s/c_s < 0.005$.

III. RESULTS AND DISCUSSION

A. Noncritical ultrasonic relaxations

In order to get an idea of potential contributions of noncritical relaxations to the ultrasonic spectra attenuation coefficient measurements of a solution of polystyrene in cyclohexane have been performed at small polymer content.



FIG. 2. Ultrasonic attenuation spectra in the frequencynormalized format for a noncritical PS1-CH mixture (mass fraction of polystyrene Y = 0.0189) at two temperatures: 10 °C (**I**) and 30 °C (**\blacklozenge**). The inset shows the excess attenuation per wavelength (15) for the same mixture at 40 °C (**\bullet**). The solid lines represent the respective relaxation spectral functions with parameter values from nonlinear least-squares regression analyses, the dashed lines display the subdivision of the excess attenuation spectrum in two Debye terms, and the dotted line indicates the asymptotic high-frequency contribution $B' = \lim_{v \to \infty} (\alpha/v^2)$ to the frequency-normalized attenuation coefficient data at 10 °C.

At two temperatures the frequency-normalized attenuation coefficients α/ν^2 of a PS1-CH mixture with mass fraction of polymer Y = 0.0189 ($\approx 0.1 Y_c$) are displayed versus frequency ν in Fig. 2. In each series of data the α/ν^2 values monotonically decrease with frequency, revealing two relaxation regions $[d(\alpha/\nu^2)/d\nu < 0]$, and approach asymptotically a limiting high-frequency value B'. Two relaxations appear also as peaks in the excess attenuation spectrum, which, for the same sample, is displayed in the inset of Fig. 2. Excess attenuation per wavelength

$$(\alpha\lambda)_{\rm exc} = \alpha_{\lambda} - B\nu = \left(\frac{\alpha}{\nu^2} - B'\right)c_s\nu$$
 (15)

is the contribution to α_{λ} that exceeds the asymptotic highfrequency term $B\nu$. A careful analysis of the excess spectra showed that they can be well represented by two Debye-type relaxation terms [51], i.e., the total attenuation per wavelength of the sample of noncritical composition has been fitted to the relaxation spectral function

$$\alpha_{\lambda}(\nu,T) = \frac{A_1(T)\omega\tau_1(T)}{1 + [\omega\tau_1(T)]^2} + \frac{A_2(T)\omega\tau_2(T)}{1 + [\omega\tau_2(T)]^2} + B(T)\nu,$$
(16)

where $\omega = 2\pi v$. The values of the relaxation amplitudes A_i and relaxation times τ_i , i = 1,2, as well as of parameter *B* are given in Table I.

Though the Debye-type frequency dependences in the spectra definitely reflect conformational changes in the polymer molecules, evidence from our secondary data is insufficient to clearly relate the relaxation terms to theoretical models

TABLE I. Sound velocity c_s and parameters of Eq. (16) for a solution of PS1, with mass fraction Y = 0.0189, in CH.

| <i>T</i> (°C) | $c_s \pm 0.5\%$ (m/s) | $A_1 \pm 10\%$ (10 ⁻³) | $	au_1 \pm 20\%$ (ns) | $A_2 \pm 10\%$ (10 ⁻³) | $	au_2 \pm 20\%$ (ns) | $B \pm 2\%$ (ps) |
|------------------|-----------------------|---------------------------------------|-----------------------|---------------------------------------|-----------------------|------------------|
| 10.0 | 1332.8 | 0.51 | 231 | 2.4 | 3.0 | 228 |
| 20.0 | 1280.0 | 0.33 | 190 | 3.7 | 2.1 | 230 |
| 30.0 | 1230.0 | 0.25 | 133 | 3.2 | 1.9 | 232 |
| 40.0 | 1183.3 | 0.39 | 47 | 4.9 | 1.1 | 232 |

of polymer chain motions [52–58] such as coupled damped torsional oscillations. We thus consider the relaxation terms assuming a three-state conformational mechanism. As the relaxation times differ by more than a factor of 40 (Table I) the mechanisms may be considered decoupled from one another. Hence the relaxations are simply assigned to two thermally activated unimolecular equilibria for which the relaxation rates τ_i^{-1} , i = 1,2, are given by the relation [59,60]

$$\tau_i^{-1} = \frac{k_B T}{\hbar} (1 + K_i) \exp\left(\frac{\Delta S_i^{\#}}{R}\right) \exp\left(\frac{-\Delta H_i^{\#}}{RT}\right), \quad (17)$$

where \hbar denotes Planck's constant divided by 2π ; *R* is the gas constant; and K_i , $\Delta H_i^{\#}$, and $\Delta S_i^{\#}$ are the equilibrium constants, the molar activation enthalpies, and the molar activation entropies, respectively. The van't Hoff equation

$$d\ln K_i/dT^{-1} = -\Delta H_i/R \tag{18}$$

yields

$$K_i = \exp(-\Delta H_i/RT) \exp(\Delta S_i/R)$$
(19)

with (molar) reaction enthalpies and entropies ΔH_i and ΔS_i , respectively. Assuming, as is the rule, the activation enthalpies and entropies $\Delta H_i^{\#}$ and $\Delta S_i^{\#}$ to be independent of *T*, the slopes

$$d\ln\left(\frac{\hbar\tau_i^{-1}}{k_BT}\right) \middle/ dT^{-1} = -\frac{\Delta H_i^{\#}}{R} - \frac{K_i}{1+K_i}\frac{\Delta H_i}{R},$$

$$i = 1, 2,$$
 (20)

follow from the above relations. These slopes are independent of *T* only if $\Delta H_i = 0$ so that the second term on the right-hand side of Eq. (20) vanishes. For both relaxation terms in the ultrasonic spectra the logarithms of $\hbar \tau_i^{-1}/k_B T$ are plotted versus 1/T in Fig. 3. Evidently, only the high-frequency term follows ordinary Eyring behavior [61] with $\Delta H_2 = 0$, corresponding to $K_2 = 1$ and thus with equipartition of both conformers involved. The slope yields an activation enthalpy $\Delta H_i^{\#} = 22$ kJ/mol on the order of the hydrogen bond energy (23 kJ/mol [62]) of liquid water. Polystyrene does not form hydrogen bonds. Nevertheless, steric hindrance of its rather voluminous aromatic side groups and possibly interactions between the delocalized π electron systems of those groups may provoke the comparatively large activation enthalpy of the conformational equilibrium.

For the slow relaxation (i = 1) the Eyring plot reveals a curvature, indicating that it involves a finite reaction enthalpy. A potential scheme of the underlying chemical equilibria is displayed as an inset to Fig. 3.

Another noteworthy feature of the data in Table I is the almost independence of the B values from temperature. Since



FIG. 3. Eyring plot of relaxation rates τ_i^{-1} of the low-frequency $[i = 1 \ (\bullet)]$ and high-frequency $[i = 2 \ (\blacksquare)]$ relaxation terms in the ultrasonic spectra of a noncritical solution of PS1 (Y = 0.0189) in CH. The inset shows a scheme of two coupled relaxation processes in reaction coordinates.

the (static) shear viscosity η_s decreases substantially with *T* the Stokes contribution [63]

$$B_{\text{stokes}}(T) = \frac{4\pi \eta_s(T)}{\rho(T)c_s^2(T)} = 4\pi \eta_s(T)\kappa_s(T)$$
(21)

should also decrease for increasing temperature. Here κ_s is the isentropic compressibility. The constancy of *B* values (Table I) may thus point at a frequency dependence in the shear viscosity or at a contribution contained in *B* in addition to B_{Stokes} . This contribution could be a relaxation term with amplitude in which, depending upon temperature, the reaction enthalpy term and the isothermal reaction volume term partly cancel each other.

B. Shear viscosity and diffusion coefficient of critical mixtures

The viscosities of the mixtures of critical composition are shown for both polystyrene samples as a function of reduced temperatures. As characteristic for systems with upper critical point, the critical contributions can hardly be identified in the temperature dependences of the η_s data. For that reason, in the inset, η_s/η_b ratios are additionally given in a log-log plot. This delineation is based on the viscosity representation [64]

$$\eta_s(\varepsilon) = \eta_b(\varepsilon)(Q_0\xi)^{x_\eta} = \eta_b(\varepsilon)(Q_0\xi_0)^{x_\eta}\varepsilon^{y_\eta}, \qquad (22)$$

where

$$\eta_b = A_n \exp[B_n/(T - T_n)], \qquad (23)$$

with A_{η} and B_{η} independent of T, denotes the noncritical background viscosity and where Q_0 is a system-dependent individual parameter and $y_{\eta} = x_{\eta}\tilde{v}$ a critical exponent. The parameters of the background viscosity (Table II) have been obtained from the viscosity data more than 10 K above T_c and

TABLE II. Parameters of the viscosity relations (22) and (23) and critical temperatures visually determined in the viscometers for PS1 and PS2 mixtures of the critical composition in CH.

| Polymer | $A_{\eta} \pm 20\%$ (10 ⁻⁶ Pa s) | $B_{\eta} \pm 20\%$ (K) | $\begin{array}{c} T_{\eta} \pm 3\% \\ (\mathrm{K}) \end{array}$ | $y_{\eta} \pm 10\%$ | $T_{\rm c} \pm 0.015 \text{ K}$ (K) |
|---------|--|-------------------------|---|---------------------|-------------------------------------|
| PS1 | 0.95 | 174 | 227 | 0.028 | 283.05 |
| PS2 | 7.35 | 37 | 267 | 0.014 | 301.29 |

also from fitting Eq. (22) to the complete series of η_s data. The negative slopes of the $\ln(\eta_s/\eta_b)$ -versus- $\ln(\varepsilon)$ curves are significantly smaller than predicted by the theoretical exponent $y_{\eta} = 0.0435$ (Fig. 4). Furthermore, in both series of data the η_s/η_b values do not further increase when approaching the critical temperature closer than roughly 0.1 K. At first glance the bending in the viscosity curves might be assumed to be due to the use of inappropriate values for the critical temperature. However, since the viscometers were made of glass, the effective T_c has been directly determined visually during the viscosity measurements. With the PS1 sample that temperature agreed to within 0.05 K with the one determined initially. With the PS2 sample the deviation was indeed larger. We shall discuss these deviations of the viscosity ratio data from power law behavior below, combined with special features in the diffusion coefficients of the critical mixtures. At first it is interesting to compare the y_{η} values (Table II) derived from the slopes in the curves of Fig. 4 with literature data for polystyrene-cyclohexane critical mixtures. Figure 5 clearly demonstrates the finding that the exponents are distinctly smaller than the universal value $y_{\eta} = x_{\eta}\tilde{\nu}$ for low-weight critical mixtures. The more recent data in Fig. 5 also reveal a substantial dependence of the y_{η} values upon the molar weight of the polymer.

In Fig. 6 the diffusion coefficients of both polystyrenecyclohexane mixtures of critical composition are displayed versus reduced temperature. At $\varepsilon > 10^{-3}$, corresponding to $T - T_c \approx 0.3$ K, the data reveal clearly critical slowing. Closer



FIG. 4. Shear viscosity η_s versus reduced temperature ε and loglog plot of the viscosity ratio η_s/η_b as a function of ε (inset) for polystyrene-cyclohexane mixtures of critical composition [PS1 (•) and PS2 (\blacksquare)]. The shaded area indicates the slope following from the universal exponent $y_s = x_n \tilde{v}$ (=0.0435).



FIG. 5. Exponent y_{η} in the power law representation of the shear viscosity (22) as a function of molar weight M_W of polymer for the mixtures of PS1 and PS2 in CH (•). Also shown are the literature data for the polystyrene-cyclohexane system (\blacksquare , [65]; \triangle , [66]; and \Diamond , [67]). The shaded area accentuates the trends in the more recent data.

to T_c , however, the $\ln(D)$ -versus- $\ln(\varepsilon)$ relations show deviations from linearity to adopt a significantly smaller slope close to T_c . In this respect the diffusion coefficients show behavior similar to the viscosity ratios η_s/η_b (Fig. 4, inset), including the almost identical temperature of transition between the linear characteristics and the flattening of the curves. The bending of the diffusion coefficient at small reduced temperatures has been occasionally found with low-molecular-weight critical systems, such as 2,6-dimethylpyridine–water [68] and triethylene glycol monoheptyl ether–water [69] systems. With those systems, the assumption of this effect to be due to the crossover to the hydrodynamic regime and application of appropriate analytical expressions for the mutual diffusion coefficient had resulted in close agreement of the theoretical predictions with the experimental results.

Since we were interested in finding out whether the diffusion coefficients of the polymer solutions follow likewise the theoretical predictions for the crossover behavior, we



FIG. 6. A log-log plot of the diffusion coefficient D as a function of reduced temperature ε for polystyrene mixtures of critical composition [PS1 (•) and PS2 (\blacksquare)] in cyclohexane. The dashed lines accentuate the linear parts in the data from which the critical exponents have been calculated. The inset shows the fluctuation correlation length ξ of the PS1 mixture over ε .



FIG. 7. A log-log representation of the correlation length amplitudes ξ_0 as a function of the polymer molar weight M_W for polystyrene-cyclohexane mixtures of critical composition: PS1 and PS2 (•) and literature data [24] (\blacksquare).

performed a combined evaluation of the shear viscosity and diffusion coefficient data, using the shear viscosity model [64,70,71] with a more elaborate crossover function. In this model the shear viscosity is expressed as

$$\eta_s(\varepsilon) = \eta_b(\varepsilon) \exp(Z_\eta H), \qquad (24)$$

where η_s is again given by Eq. (23). The crossover function *H* depends on the fluctuation correlation length ξ as well as on two cutoff wave numbers q_D and q_c [64,70,71]. The mutual diffusion coefficient

$$D = D_b + \Delta D \tag{25}$$

is likewise considered to be composed of a background part

$$D_b = D_{\text{SEKF}} \frac{3\pi \eta_s}{16\eta_b} (1 + x^2) \big[q_D^{-1} + (\tilde{q}_c)^{-1} \big]$$
(26)

and a critical part

$$\Delta D = D_{\text{SEKF}} R \Omega_K(x) [1 + b^2 x]^{Z_\eta/2}.$$
 (27)

In these relations D_{SEKF} is the Stokes-Einstein-Kawasaki-Ferrell diffusion coefficient (8), R = 1.03, b = 0.55, $x = q\xi$, \tilde{q}_c is given by

$$\tilde{q}_c^{-1} = q_c^{-1} + (2q_D)^{-1}, \tag{28}$$

and Ω_K is the Kawasaki function, defined as

$$\Omega_K(x) = 0.75x^{-2}[1 + x^2 + (x^3 - x^{-1})\arctan(x)].$$
 (29)

It was found that the shear viscosity and diffusion coefficient data of the polystyrene-cyclohexane mixtures of critical composition can be conjointly represented in terms of the *H* function (Fig. 6) if power law behavior of the fluctuation correlation length (1) with universal critical exponent $\tilde{\nu}$ is assumed (Fig. 6, inset).

The amplitude of the correlation length reveals a substantial dependence upon polymer molar weight ($\xi_0 = 0.17$ nm for PS1 and $\xi_0 = 0.63$ nm for PS2). The former value complies with the amplitudes typically found with low-molecular-weight critical mixtures (e.g., $\xi_0 = 0.11$ nm for the triethylamine-water mixture [72] and $\xi_0 = 0.37$ nm for the ethanol-dodecane mixture [73]). The value for the PS2



FIG. 8. Frequency-normalized ultrasonic attenuation spectra for the PS1 mixture of critical composition in CH at $T - T_c = 27.06$ K [T = 310.16 K (•)] and $T - T_c = 0.032$ K [T = 283.13 K (•)]. Also shown for comparison is the spectrum for the mixture at noncritical composition (Y = 0.0189) at 40 °C [T = 313.15 K (•)]. The inset shows low-frequency parts of the PS1 spectra at critical composition and at five temperatures close to the critical one: $\varepsilon = 0.1$ (•), $\varepsilon =$ 0.088 (□), $\varepsilon = 0.025$ (•), $\varepsilon = 0.0012$ (•), and $\varepsilon = 0.000$ 85 (•).

solution, however, exceeds the amplitudes that so far have been reported even for micellar systems ($\xi_0 = 0.41$ nm for triethylene glycol monoheptyl ether–water systems [69]), ionic liquid mixtures ($\xi_0 = 0.47$ nm for ethyl ammonium nitrate–*n*-octanol mixtures [74]), and polymer blends ($\xi_0 =$ 0.60 nm for polypropylene-polyethylene blends [75]). A similar trend had been discovered [24] within a series of polystyrene-cyclohexane critical mixtures with polymer molar weights ranging from 0.196 to 11.4×10^6 g mol⁻¹ (Fig. 7).

C. Relaxation rate of fluctuations and scaling function

In Fig. 8 ultrasonic attenuation spectra of the PS1-CH mixture of critical composition are presented at two temperatures in the frequency normalized format

$$a/v^2 = a_\lambda/c_s v. \tag{30}$$

Also shown is a spectrum for a mixture of noncritical composition in order to point to the significantly larger α/ν^2 values of the critical mixture at low frequencies. The added ultrasonic attenuation clearly reflects the fluctuations in the local concentration of the mixture of critical composition. The dominating role of the fluctuations in the low-frequency part of the spectra is also demonstrated by the substantial increase in the α/ν^2 data on approaching the critical temperature, i.e., at decreasing ε .

Since we are mainly interested in the contribution from the critical fluctuations we performed a series of low-frequency attenuation coefficient measurements of the mixture of critical composition. The data were recorded at several temperatures close to T_c , keeping the sample within the same (plano-concave) resonator cell. They were subsequently used to calculate the scaling function $F(\Omega)$ of the Bhattacharjee-Ferrell dynamic scaling theory (6). If the weak temperature dependences of the sound velocity c_s and the amplitude A are neglected, theory predicts $F(\Omega)$ to be given by the ratio of the



FIG. 9. Scaling function data for the polystyrene mixtures with cyclohexane [PS1 (\bullet) and PS2 (\blacksquare)]. The lines are graphs of the scaling function predicted by the Bhattacharjee-Ferrell dynamic scaling theory [Eq. (7)].

critical attenuation at T to that at T_c , viz.,

$$F(\Omega) = \frac{\alpha_{\lambda}^{c}(\nu, T)}{\alpha_{\lambda}^{c}(\nu, T_{c})} = \frac{\alpha_{\lambda}(\nu, T) - \alpha_{\lambda}^{b}(\nu, T)}{\alpha_{\lambda}(\nu, T_{c}) - \alpha_{\lambda}^{b}(\nu, T_{c})}.$$
 (31)

According to the results for the mixture of noncritical composition discussed in Sec. III A, the background attenuation, in addition to the asymptotic high-frequency term $B\nu$, likely contains contributions from two relaxations. Since, however, the relaxation frequency $(2\pi\tau_2)^{-1}$ of one term is much larger than the upper frequency limit of the resonator data under consideration, it is sufficient to consider the low-frequency part $2\pi A_2 \tau_2 \nu$, proportional to frequency, only. Hence the background contribution has been taken as

$$\alpha_{\lambda}^{b}(\nu,T) = \frac{A_{1}(T)\omega\tau_{1}(T)}{1 + [\omega\tau_{1}(T)]^{2}} + \hat{B}(T)\nu, \qquad (32)$$

where $\hat{B} = B + 2\pi A_2 \tau_2$. The experimental $\alpha_{\lambda}^c(v,T)/\alpha_{\lambda}^c(v,T_c)$ data have been fitted to the theoretical form of the scaling function using the relaxation rate $\Gamma(T)$ as an adjustable parameter. For both polystyrene samples the scaling functions resulting from the nonlinear least-squares regression analysis are given in Fig. 9. The scatter in the data reflects the enhanced uncertainties due to the subtraction of the noncritical contributions. The fact that no data at $\Omega < 1$ have been achieved points at small amplitudes in the relaxation rates Γ of the polymer solutions, as will be discussed below.

For the PS1-CH mixture of critical composition the Γ values obtained from the analysis of ultrasonic attenuation data in terms of the Bhattacharjee-Ferrell scaling function are displayed versus reduced temperature ε in Fig. 10. At $\varepsilon > 2 \times 10^{-2}$ the relaxation rate follows the power law

$$\Gamma = \tau_{\xi}^{-1} = \Gamma_0 \varepsilon^{Z\tilde{\nu}},\tag{33}$$

with universal exponent $Z\tilde{\nu} = 1.93$ and amplitude $\Gamma_0 = 5.8 \times 10^9 \text{ s}^{-1}$. This comparatively small amplitude [25] compares to $\Gamma_0 = 26 \times 10^9 \text{ s}^{-1}$ for the methanol-cyclohexane [76] and $\Gamma_0 = 156 \times 10^9 \text{ s}^{-1}$ for the nitroethane-cyclohexane [77] critical systems. As a result of the smaller diffusion coefficient (Fig. 6) and the distinctly larger correlation length (Fig. 7) at the same reduced temperature, the amplitude $\Gamma_0 = 6.1 \times 10^7 \text{ s}^{-1}$ for the PS2-CH critical mixture is even markedly smaller than for the low-polymer-molecular-weight sample.



FIG. 10. Relaxation rate Γ of fluctuations as resulting from the ultrasonic attenuation spectra of the PS1 sample versus reduced temperature ε . The gray line indicates the slope following from the universal critical exponent $Z\tilde{v} = 1.93$ [Eq. (3) with $\Gamma = \tau_{\xi}^{-1}$]. The inset shows the same data (•) along with the data from η_s and *D* measurements (dotted line) using Eq. (9).

Closer to the critical point the relaxation rates deviate from power law to approach an almost-temperature-independent value slightly below 10^6 s^{-1} , corresponding to a relaxation time $\tau_{\xi} = 1.1 \,\mu$ s. In contrast, the Γ values calculated according to Eq. (9) from the experimental shear viscosity and diffusion coefficient data follow a power law down to $\varepsilon = 10^{-3}$ (Fig. 10, inset) and only slightly bend close to the critical temperature due to the crossover effects discussed before. Such difference between the relaxation rates from ultrasonic spectra and from mutual diffusion coefficients appears also with the binary isobutoxyethanol-water system (Fig. 11), which, in addition to critical demixing, is capable of forming micelles [78,79]. Obviously the deviations of the Γ values



FIG. 11. Relaxation rate Γ of the isobutoxyethanol-water mixture of critical composition versus reduced temperature ε . Closed symbols show data from ultrasonic spectroscopy [78] and open symbols indicate Γ values from static and dynamic light scattering measurements [79]. The dotted line represents the power law (33) with a universal critical exponent.

from the ultrasonic spectra originate from a coupling between relaxations due to the concentration fluctuations and other modes. Close to the critical point, where the fluctuations in the local concentrations are considerably slowed down, both systems follow ultrasonic field changes via a parallel pathway rather than a readjustment of the fluctuation pattern. With the polystyrene- cyclohexane mixtures (Fig. 10) the second pathway is likely provided by the structural isomerization of the polymer chains. With the surfactant system (Fig. 11) the micelle formation and disintegration kinetics evidently dominates the microdynamics.

D. Critical amplitude and coupling constant

As mentioned in the Introduction, the amplitude A(T) of the critical contribution to the ultrasonic attenuation per wavelength (6) is weekly depending on frequency [25–27]:

$$A(T) = v^{-\delta} S(T), \tag{34}$$

with critical exponent $\delta = \alpha_0/(Z_0\tilde{\nu}) = 0.06$, where $\alpha_0 = 0.11$ [80,81] denotes the specific heat critical exponent. According to

$$S = \frac{\pi^2 \delta A^+ c_s(T_c)}{2T_c C_{pb}} \left[\frac{\Omega_{1/2} \Gamma_0}{2\pi} \right]^{\delta} g^2, \qquad (35)$$

the frequency-independent amplitude parameter *S* is predominantly controlled by the adiabatic coupling constant *g*, which can thus be derived from the ultrasonic spectra. The half-attenuation frequency $\Omega_{1/2}$ [=2.1, Eq. (7)] and the sound velocity c_s (T_c) at the critical temperature are known from the ultrasonic measurements. The parameters A^+ and C_{pb} ($\approx C_p$) are related to the critical part and the background part of the heat capacity at constant pressure:

$$C_p(\varepsilon) = \frac{A^+}{\alpha_0} \varepsilon^{-\alpha_0} + E\varepsilon + B.$$
(36)

Using $A^+/\alpha_0 = 1.91 \times 10^{-2}$ J cm⁻³K⁻¹ and $C_{pb} = 1.42$ J cm⁻³K⁻¹ [38], |g| = 0.26 follows from the amplitude parameter $S = 2.9 \times 10^{-7}$ s^{0.94} m⁻¹ of the PS1 critical mixture. This value nicely agrees with g = -0.26 as obtained from the thermodynamic relation

$$g = C_p dT_c / dp - Ta_p, \tag{37}$$

with the slope dT_c/dp in the pressure dependence of the critical temperature along the critical line and with the thermal expansion coefficient

$$\alpha_p = \rho(T_c) [\partial \rho^{-1} / \partial T]_p \tag{38}$$

at constant pressure. In calculating the g value for the PS1-CH mixture of critical composition, $dT_c/dp = 3.2 \times 10^{-8}$ K/Pa [82] has been used and $\alpha_p = 1.1 \times 10^{-3}$ K⁻¹ has been derived from our density measurements.

With the PS2-CH critical mixture the agreement between the coupling constants from the ultrasonic amplitude parameter [|g| = 0.35, Eq. (35)] and from the thermodynamic relation [g = -0.42, Eq. (37)] is less perfect. In any case, however, the absolute value of the coupling constant is significantly larger than for the PS1 system. The g data for the PS2 sample have been obtained using the following parameter values: $S = 2.9 \times 10^{-7} \text{ s}^{0.94} \text{ m}^{-1}$, $A^+/\alpha_0 = 0.74 \times 10^{-2} \text{ J cm}^{-3} \text{K}^{-1}$,



FIG. 12. Slope in the pressure dependence of the critical temperature along the critical line for PS-CH samples at different polymer molar weights [82].

 $C_{pb} = 1.46 \text{ J cm}^{-3}\text{K}^{-1}, dT_c/dp = -4.1 \times 10^{-8} \text{ K/Pa [82]},$ and $\alpha_p = 1.2 \times 10^{-3} \text{ K}^{-1}$. Hence, with increasing polymer molecular weight, the effect from the larger g^2 in Eq. (35) is overcompensated by a significantly smaller critical part in the heat capacity so that a smaller *S* value results.

The negative sign in the pressure dependence of the critical temperature of the PS2 sample attracts attention. As illustrated by Fig. 12, the dT_c/dp data switch their sign roughly at $M_W = 10^5$ g/mol. Nearly up to that polymer molar weight the correlation function of the light quasielastically scattered from polystyrene-cyclohexane mixtures appears to decay exponentially, whereas it becomes bimodal at higher weights [24].

IV. CONCLUSION

Polystyrene-cyclohexane mixtures of critical composition differ from simple (low-molecular-weight) critical systems by the competition between two mesoscopic parameters, the fluctuation correlation length and the polymer-chain length. Such mixtures have been shown previously [16] to display fluctuation-controlled three-dimensional Ising-type behavior near the critical point where the correlation length is large. They change to mean-field tricritical behavior near the θ point where both mesoscales diverge. In conformity with evidence reported in the literature [24], the sample with lower molecular weight $M_W = 3 \times 10^4$ g/mol (PS1), corresponding to the degree of polymerization N = 288, showed a singleexponential autocorrelation function of the quasielastically scattered light. At larger polymer molecular weight (M_W = 6.5×10^5 , N = 6242, PS2) indications of a second exponential exist.

The parameters of the polymer solutions evaluated from shear viscosity, dynamic light scattering, and broadband ultrasonic measurements vary monotonically with molar weight. The critical exponent $y_{\eta} = x_{\eta}\tilde{v}$ in the *Q* model representation of the shear viscosity (22) decreases from its universal value $y_{\eta} = 0.0435$ for simple systems to $y_{\eta} = 0.028$ and 0.014 for the PS1 and PS2 mixtures of critical composition, respectively. Similarly, the amplitude in the fluctuation correlation length increases from a quite common value $\xi_0 = 0.17$ nm (PS1) to $\xi_0 = 0.63$ nm (PS2) and $\xi_0 = 1.40$ nm at $M_W = 1.1 \times 10^7$ (N = 110 000 [24]).

Broadband ultrasonic attenuation spectra, when treated as a linear superposition of critical contributions due to the concentration fluctuations and of noncritical relaxations due to the polymer conformational changes, reveal the scaling function of the Bhattacharjee-Ferrell dynamic scaling model with the relaxation rate Γ of fluctuations as the only adjustable parameter. At reduced temperature $\varepsilon > 2 \times 10^{-2}$, i.e., $T - T_c >$ 5.7 K, the Γ values from such analysis of the ultrasonic spectra follow indeed a power law with universal critical exponent. Closer to T_c , however, the Γ -versus- ε relations deviate to approach an almost constant value near the critical temperature. This finding is a strong indication of a coupling between the local fluctuations in concentrations and the polymer conformational changes. When the system slows down near T_c the relaxation rate Γ of fluctuations follows indeed power law behavior with a universal critical exponent, as revealed by the Γ data from dynamic light scattering and shear viscosity data. Due to the coupling between the fluctuations and the conformational variations of the polymer

molecules, however, the relaxation rates from the ultrasonic spectra feature significant deviations from the power law. Close to T_c the system is evidently capable of following the pressure variations of the sound field by changes of molecular conformations faster than by rearrangement of the local concentration pattern. This view still needs a theoretical model, similar to the theory of noncritical concentration fluctuations when bypassed by a specific rate process [83].

The coupling between the fluctuations and the conformational variations also appears to be insufficiently described by the existing shear viscosity theories. As indicated by the molecular-weight-dependent viscosity exponents, existing theories fail to represent the subdivision of η_s in a background part and a critical part correctly if both parts are linked. Again, continuing theoretical developments are required to better understand the experimental results.

ACKNOWLEDGMENT

Financial assistance from the Alexander von Humboldt foundation, Bonn, Germany, is gratefully acknowledged.

- [1] M. E. Fisher, Rev. Mod. Phys. **70**, 653 (1998).
- [2] H. E. Stanley, Rev. Mod. Phys. 71, S358 (1999).
- [3] M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach, Philadelphia, 1991).
- [4] J. Binney, N. J. Dowrick, A. J. Fisher, and M. E. J. Newman, *The Theory of Critical Phenomena* (Clarendon, Oxford, 1992).
- [5] C. Domb, The Critical Point: A Historical Introduction to the Modern Theory of Critical Phenomena (Taylor and Francis, London, 1996).
- [6] A. Onuki, *Phase Transition Dynamics* (Cambridge University Press, Cambridge, 2002).
- [7] L. Onsager, Phys. Rev. 65, 117 (1944).
- [8] K. Binder, in *Encyclopedia of Mathematics*, edited by M. Hazewinkel (Springer, Berlin, 2001).
- [9] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. 49, 435 (1977).
- [10] L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968).
- [11] B. I. Halperin and P. C. Hohenberg, Phys. Rev. 177, 952 (1969).
- [12] R. A. Ferrell, Phys. Rev. Lett. 24, 1169 (1970).
- [13] R. F. Berg, M. R. Moldover, and G. A. Zimmerli, Phys. Rev. Lett. 82, 920 (1999).
- [14] H. Hao, R. A. Ferrell, and J. K. Bhattacharjee, Phys. Rev. E 71, 021201 (2005).
- [15] Y. C. Kim, M. A. Anisimov, J. V. Sengers, and E. Luijten, J. Stat. Phys. **110**, 591 (2003).
- [16] M. A. Anisimov, A. F. Kostko, J. V. Sengers, and I. K. Yudin, J. Chem. Phys. **123**, 164901 (2005).
- [17] P. Debye, H. Coll, and D. Woermann, J. Chem. Phys. 33, 1746 (1960).
- [18] P. Debye, D. Woermann, and B. Chu, J. Chem. Phys. 36, 851 (1962).
- [19] P. Debye, B. Chu, and D. Woermann, J. Chem. Phys. 36, 1803 (1962).
- [20] P. Debye and R. T. Jacobsen, J. Phys. Chem. 48, 203 (1968).

- [21] J. Jacob, M. A. Anisimov, J. V. Sengers, V. Dechabo, I. K. Yudin, and R. W. Gammon, Appl. Opt. 40, 4160 (2001).
- [22] M. A. Anisimov, A. F. Kostko, and J. V. Sengers, Phys. Rev. E 65, 051805 (2002).
- [23] A. F. Kostko, M. A. Anisimov, and J. V. Sengers, Phys. Rev. E 66, 020803(R) (2002).
- [24] A. F. Kostko, M. A. Anisimov, and J. V. Sengers, Phys. Rev. E 76, 021804 (2007).
- [25] J. K. Bhattacharjee, U. Kaatze, and S. Z. Mirzaev, Rep. Prog. Phys. 73, 066601 (2010).
- [26] J. K. Bhattacharjee and R. A. Ferrell, Phys. Rev. A 24, 1643 (1981).
- [27] R. A. Ferrell and J. K. Bhattacharjee, Phys. Rev. A 31, 1788 (1985).
- [28] G. G. Stokes, Trans. Cambridge Philos. Soc. 8, 287 (1845).
- [29] A. Einstein, Ann. Phys. (Leipzig) 17, 549 (1905).
- [30] K. Kawasaki, Ann. Phys. (NY) 1, 61 (1970).
- [31] H.-J. Bauer, H. Hässler, and M. Immendörfer, Disc. Faraday Soc. 49, 238 (1970).
- [32] O. Fünfschilling, P. Lemaréchal, and R. Cerf, Chem. Phys. Lett. 12, 365 (1971).
- [33] W. Ludlow, E. Wyn-Jones, and J. Rassing, Chem. Phys. Lett. 13, 477 (1972).
- [34] P. Lemaréchal, Chem. Phys. Lett. 16, 495 (1972).
- [35] J. I. Dunbar, A. M. North, R. A. Pethrick, and D. B. Steinhauer, J. Polym. Sci. Polym. Phys. Ed. 15, 263 (1977).
- [36] D. B. Fenner, J. Chem. Phys. 81, 5179 (1984).
- [37] S. K. Hassun, K. H. Hussain, and N. A. Hassan, Acta Polym. 41, 438 (1990).
- [38] S. Z. Mirzaev, T. Heimburg, and U. Kaatze, Phys. Rev. E 82, 061502 (2010).
- [39] A. R. Shultz and P. J. Flory, J. Am. Chem. Soc. 74, 4760 (1952).
- [40] S. C. Greer and D. T. Jacobs, J. Phys. Chem. 84, 2888 (1980).
- [41] R. Kita, K. Kubota, and T. Dobashi, Phys. Rev. E 58, 793 (1998).

- [42] A. Ritzl, L. Belkoura, and D. Woermann, Phys. Chem. Chem. Phys. 1, 1947 (1999).
- [43] J.-M. Schröder, S. Wiegand, L. B. Aberle, M. Kleemeier, and W. Schröer, Phys. Chem. Chem. Phys. 1, 3287 (1999).
- [44] J.-M. Schröder, A. Becker, and S. Wiegand, J. Chem. Phys. 118, 11307 (2003).
- [45] A. Siporska, J. Sydlowski, and L. P. N. Rebelo, Phys. Chem. Chem. Phys. 5, 2996 (2003).
- [46] F. Eggers, U. Kaatze, K. H. Richmann, and T. Telgmann, Meas. Sci. Technol. 5, 1131 (1994).
- [47] U. Kaatze, B. Wehrmann, and R. Pottel, J. Phys. E Sci. Instrum. 20, 1025 (1987).
- [48] U. Kaatze, K. Lautscham, and M. Brai, J. Phys. E Sci. Instrum. 21, 98 (1988).
- [49] U. Kaatze, V. Kühnel, K. Menzel, and S. Schwerdtfeger, Meas. Sci. Technol. 4, 1257 (1993).
- [50] K. Schätzel, M. Drewel, and M. Stimiac, Mod. Opt. 35, 711 (1988).
- [51] P. Debye, Polar Molecules (Chemical Catalog, New York, 1929).
- [52] B. H. Zimm, J. Chem. Phys. 24, 269 (1956).
- [53] P. E. Rouse, J. Chem. Phys. 108, 4628 (1998).
- [54] P. E. Rouse, J. Chem. Phys. 21, 1272 (1953).
- [55] A. V. Tobolsky and J. J. Aklonis, J. Phys. Chem. 68, 1970 (1964).
- [56] A. V. Tobolsky, J. Polym. Sci. A 6, 1177 (1968).
- [57] A. V. Tobolsky and D. B. DuPré, Adv. Polym. Sci. 6, 103 (1969).
- [58] G. Strobel, The Physics of Polymers (Springer, Berlin, 1997).
- [59] H. Strehlow, *Rapid Reactions in Solution* (VCH, Weinheim, 1992).
- [60] R. Behrends and U. Kaatze, J. Mol. Liq. 107, 1 (2003).
- [61] H. Eyring, J. Chem. Phys. 3, 107 (1935).
- [62] S. J. Suresh and V. M. Naik, J. Chem. Phys. 113, 9727 (2000).
- [63] A. J. Matheson, *Molecular Acoustics* (Wiley, London, 1971).
- [64] H. C. Burstyn, J. V. Sengers, J. K. Bhattacharjee, and R. A. Ferrell, Phys. Rev. A 28, 1567 (1983).

- [65] H. Tanaka, Y. Nakanishi, and N. Takubo, Phys. Rev. E 65, 021802 (2002).
- [66] Y. Izumi, H. Sawano, and Y. Miyake, Phys. Rev. A 29, 826 (1984).
- [67] W. A. Goedel, A. Zielesny, L. Belkoura, T. Engels, and D. Woermann, Ber. Bunsenges. Phys. Chem. 94, 17 (1990).
- [68] S. Z. Mirzaev, R. Behrends, T. Heimburg, J. Haller, and U. Kaatze, J. Chem. Phys. **124**, 144517 (2006).
- [69] J. Haller, R. Behrends, and U. Kaatze, J. Chem. Phys. **124**, 124910 (2006).
- [70] J. K. Bhattacharjee, R. A. Ferrell, R. S. Basu, and J. V. Sengers, Phys. Rev. A 24, 1469 (1981).
- [71] R. F. Berg and M. R. Moldover, J. Chem. Phys. 89, 3694 (1988).
- [72] R. Behrens, T. Telgmann, and U. Kaatze, J. Chem. Phys. 117, 9828 (2002).
- [73] S. Z. Mirzaev, I. Iwanowski, and U. Kaatze, Chem. Phys. Lett. 435, 263 (2007).
- [74] S. Z. Mirzaev and U. Kaatze, Phys. Rev. E 65, 021509 (2002).
- [75] W. Mayer, S. Hoffmann, G. Meier, and I. Alig, Phys. Rev. E 55, 3102 (1997).
- [76] R. Behrends, U. Kaatze, and M. Schach, J. Chem. Phys. 119, 7957 (2003).
- [77] R. Behrends, I. Iwanowski, M. Kosmowska, A. Szala, and U. Kaatze, J. Chem. Phys. 121, 5929 (2004).
- [78] K. Menzel, S. Z. Mirzaev, and U. Kaatze, Phys. Rev. E 68, 011501 (2003).
- [79] F. Höhn, Ph.D. thesis, Universität zu Köln, 1992.
- [80] A. C. Flewelling, R. J. DeFonseka, N. Khaleeli, J. Parkee, and D. T. Jacobs, J. Chem. Phys. **104**, 8048 (1996).
- [81] P. F. Rebillot and D. T. Jacobs, J. Chem. Phys. 109, 4009 (1998).
- [82] S. Saeki, N. Kuwahara, N. Nakata, and M. Kaneko, Polymer 16, 445 (1975).
- [83] A. Rupprecht and U. Kaatze, J. Phys. Chem. A 103, 6485 (1999).