Diffusion and Thermal Diffusion of Semidilute to Concentrated Solutions of Polystyrene in Toluene in the Vicinity of the Glass Transition

J. Rauch and W. Köhler*
Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany

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The approaching glass transition in polystyrene/toluene solutions leads to a sharp decay of both the collective diffusion coefficient D and the thermal diffusion coefficient D_{T} at concentrations above 0.2 g/cm^3. The Soret coefficient $S_{\mathrm{T}} = D_{\mathrm{T}}/D$ follows power-law scaling from semidilute to concentrated and is not influenced by the slowing down of the dynamics associated with the glass transition. Both D and D_{T} are governed by the same friction coefficient. The scaling behavior of S_{T} with concentration on approach of the glass transition is compared to the divergence of S_{T} near a consolute critical point.

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In an isotropic binary fluid mixture with nonuniform concentration and temperature, the mass flow $\vec{J}_{\mathrm{m}}$ of component 1 contains both a contribution stemming from the concentration and one from the temperature gradient [1]:

$$\vec{J}_{\mathrm{m}} = -\rho D \,\mathrm{grad} c - \rho c(1 - c) D_{\mathrm{T}} \,\mathrm{grad} T\,, \qquad (1)$$

where D is the collective diffusion coefficient, D_{T} the thermal diffusion coefficient, ρ the mass density, and c the concentration of component 1 in weight fractions. $C = \rho c$ is the corresponding concentration measured in mass per unit volume. In a stationary state, where the diffusion flow $\vec{J}_{\mathrm{m}}$ vanishes, the Soret coefficient S_{T} is given by

$$S_{\mathrm{T}} \equiv \frac{D_{\mathrm{T}}}{D} = -\frac{1}{c(1 - c)} \frac{|\mathrm{grad} c|}{|\mathrm{grad} T|}\,. \qquad (2)$$

The occurrence of a mass flow which is driven by a temperature gradient is termed thermal diffusion or Ludwig Soret effect.

While abundant data on mass diffusion are available in the literature, the experimental database on thermal diffusion and Soret coefficients is scarce. Some reliable results exist for mixtures of simple liquids and dilute polymer solutions, but nothing is known about thermal diffusion at the glass transition and only a little in the vicinity of phase transitions [2–5], where dramatic dynamic and structural changes occur within a narrow temperature interval. It has been found that concentration and temperature gradient induced diffusion currents behave quite differently at a consolute critical point, resulting in a diverging Soret coefficient [3–5]. Similar to the critical slowing down on the approach of a second order phase transition, a dramatic slowing down of mass diffusion is observed at a glass transition. The question of whether glass and phase transition would lead to a comparable behavior of S_{T} was the main motivation for the present work. To our knowledge, no predictions exist for S_{T} and D_{T} at the glass transition.

One of the few binary fluids where thermal diffusion has been investigated by a number of authors with different experimental techniques are solutions of polystyrene (PS) in toluene [6–12]. Most of these experiments have been carried out within the dilute regime, where a constant, concentration and molar mass independent, thermal diffusion coefficient of $D_{\mathrm{T}} \approx 1.1 \times 10^{-7}$ cm^2(sK)$^{-1}$ has been found [6,9–11].

So far, only Zhang *et al.* have extended the concentration range into the semidilute regime well above the overlap concentration C^* by utilizing a Soret cell with an optical beam deflection technique [10]. Up to their highest concentration of $C = 0.543$ g/cm^3, D_{T} remains molar mass independent and almost constant, with a slight 30% decay above $C \approx 0.1$ g/cm^3. The collective diffusion coefficient D at infinite dilution shows the well known power-law dependence $D \propto M^{-\nu_{\mathrm{D}}}$ with $\nu_{\mathrm{D}} = 0.53 \pm 0.02$. D becomes molar mass independent within the semidilute regime, and its concentration dependence approaches the asymptotic power law $D \propto (C/C^*)^{x_{\mathrm{D}}}$. Scaling theory predicts $x_{\mathrm{D}} = 0.77$, whereas the experimental value is $x_{\mathrm{D}} = 0.65 \pm 0.02$. Since D_{T} varies only weakly, the concentration dependence of the Soret coefficient $S_{\mathrm{T}} = D_{\mathrm{T}} D^{-1}$ is mainly determined by the concentration dependence of D^{-1}. S_{T} depends on molar mass for low concentrations, and it approaches a molar mass independent scaling relation $S_{\mathrm{T}} \propto (C/C^*)^{-x_{\mathrm{T}}}$ with $x_{\mathrm{T}} = 0.73 \pm 0.03$ within the semidilute regime. The authors attribute the small difference between x_{D} and x_{T} to the slight concentration dependence of D_{T}.

Mass diffusion in semidilute solutions of polystyrene in toluene has also been investigated by Brown *et al.* [13] and Rehage *et al.* [14]. These authors observed the characteristic speeding up of collective diffusion with increasing concentration, which is characteristic for polymers in good solvents. At higher concentrations above $C \approx 0.2$ g/cm^3, however, D passes through a maximum and then decays. This decay is an indication of the approaching glass transition, whose transition temperature T_{g} rapidly increases with increasing polymer concentration from $T_{\mathrm{g}}^{\mathrm{s}} = 117$ K of pure toluene [15] to $T_{\mathrm{g}}^{\mathrm{p}} \approx 363$ K of polystyrene ($M = 10$ kg/mol). The precise value of $T_{\mathrm{g}}^{\mathrm{p}}$ depends weakly on molar mass [16]. T_{g} of the solution can be estimated from the Fox equation [17]:

$$\frac{1}{T_g} = \frac{c}{T_g^p} + \frac{1-c}{T_g^s}. \tag{3}$$

In this contribution, we extend the investigations of Zhang *et al.* into the vicinity of the glass transition at polymer concentrations up to $C = 0.9$ g/cm^3 and temperatures between 285 and 342 K for three different molar masses M_w of 4.75 kg/mol ($C^* = 0.15$ g/cm^3), 10.3 kg/mol ($C^* = 0.056$ g/cm^3), and 101 kg/mol ($C^* = 0.021$ g/cm^3). The overlap concentration is estimated from $C^* = [\eta]^{-1}$, $[\eta]$ being the intrinsic viscosity [18], for $T = 25$°C.

Collective and thermal diffusion coefficients and Soret coefficients have been measured with the transient holographic grating technique of thermal diffusion forced Rayleigh scattering (TDFRS) [19,20]:

A holographic interference grating is written into the slightly absorbing sample by means of an argon ion laser (488 nm) and induces a temperature grating. A small amount of an inert dye (quinizarin) is added for sufficient absorption. The temperature gradients within this temperature grating trigger thermal diffusion, causing the buildup of a concentration grating. Both temperature and composition changes lead to a spatially periodic modulation of the refractive index. The diffraction efficiency of this phase grating is read in a heterodyne experiment by a third laser beam, operating at a wavelength where the sample is transparent (633 nm). The time-dependent diffraction efficiency yields D, D_T, S_T, and the thermal diffusivity D_{th}. Temperature and concentration contributions in the diffraction efficiency can easily be separated, since their respective diffusion time constants $\tau_{th} = (D_{th} q^2)^{-1}$ and $\tau = (Dq^2)^{-1}$ differ by typically 3 orders of magnitude in case of polymer solutions. $q = 2\pi/d$ is the grating wave vector. The fringe spacing d of the grating is typically 10 μm.

Photon correlation spectroscopy (PCS) has additionally been employed for the measurement of the diffusion coefficient at selected concentrations and temperatures. Anionically polymerized PS samples with $M_w/M_n \approx 1.03$ were obtained from PSS (Mainz, Germany) and toluene (pro analysi) from Merck. Concentrations above 0.8 g/cm^3 were prepared by starting from a lower concentrated sample and evaporating solvent at 60–70 °C. Enough time for equilibration of the ready samples was given. Equilibrium was confirmed by constant values for the transport coefficients over many days. The contrast factors $(\partial n/\partial T)_{p,c}$ and $(\partial n/\partial c)_{p,T}$ have been measured interferometrically and with an Abbe refractometer, respectively [20].

Figure 1 shows the decay of the heterodyne diffraction efficiency in a TDFRS experiment at a concentration of $C = 0.868$ g/cm^3. At short times (10^{-2} ms), there is the relaxation of the imprinted temperature grating and at long times (10^2 ms) the relaxation of the induced concentration grating. At such a high concentration, the α relaxation starts to enter the experimental time window (10^{-6}–10^2 s) and just becomes visible in the tail of the temperature signal. A unique separation between temperature signal and α relaxation is difficult, but time scale separation of the mass diffusion mode is still possible with a high accuracy. The total signal has been normalized such that temperature signal and α relaxation together have an amplitude of unity. This normalization has been chosen, since the sample is in the fluid state with a fully relaxed density at times longer than the α relaxation, and both contrast factors $(\partial n/\partial c)_{p,T}$ and $(\partial n/\partial T)_{p,c}$ have been determined on such a slow time scale. Also shown in Fig. 1 is the diffraction efficiency of a sample of lower concentration, normalized to the amplitude of the temperature signal, where the dynamic glass transition is still outside the experimental time window.

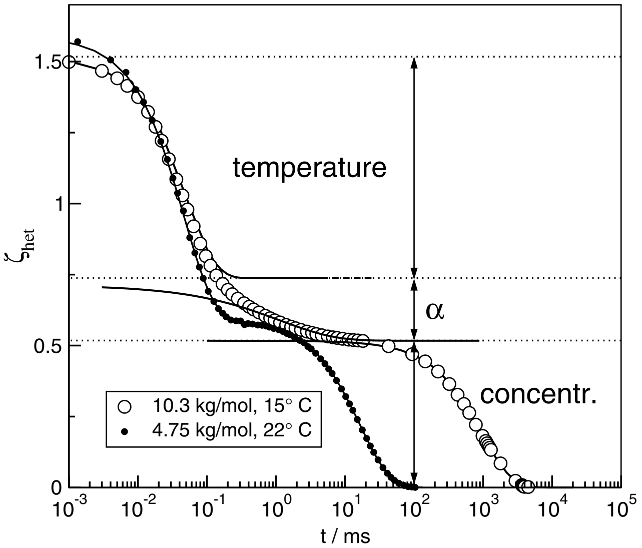

FIG. 1. Decay of heterodyne diffraction efficiency after step excitation in a TDFRS experiment on PS in toluene ($M_w = 10.3$ kg/mol, $C = 0.868$ g/cm^3, $T = 15$ °C). The α relaxation is fitted by a Kohlrausch-Williams-Watts function with $\beta = 0.3$. Temperature and concentration mode are single exponential. For comparison a lower concentration ($M_w = 4.75$ kg/mol, $C = 0.079$ g/cm^3, $T = 22$ °C), where the α relaxation is still outside the time window (biexponential fit).

Mass diffusion coefficient.—Figure 2 shows the diffusion coefficient D as a function of polymer concentration. In the dilute regime, D shows the well known molar mass dependence cited in the introduction, which vanishes approximately above the overlap concentration C^*.

D first increases slightly up to $C \approx 0.2$ g/cm^3, passes through a maximum, and then drops over more than three decades at higher concentrations. This observation is in qualitative agreement with results of Brown *et al.* [13], Rehage *et al.* [14], and, for concentrations $C < 0.2$ g/cm^3, with the data of Zhang *et al.* [10]. A similar behavior has also been reported by Nicolai and Brown for PS in DOP [21] and by Koch *et al.* for PS in dioxane [22]. The solid line in Fig. 2 shows the asymptotic power law $D \propto C^{0.65}$ from Ref. [10]. Our data at concentrations above 0.2 g/cm^3 are in contradiction to the results of Zhang *et al.,* who did not observe any slowing down of mass diffusion caused by a nearby glass transition up to $C = 0.543$ g/cm^3.

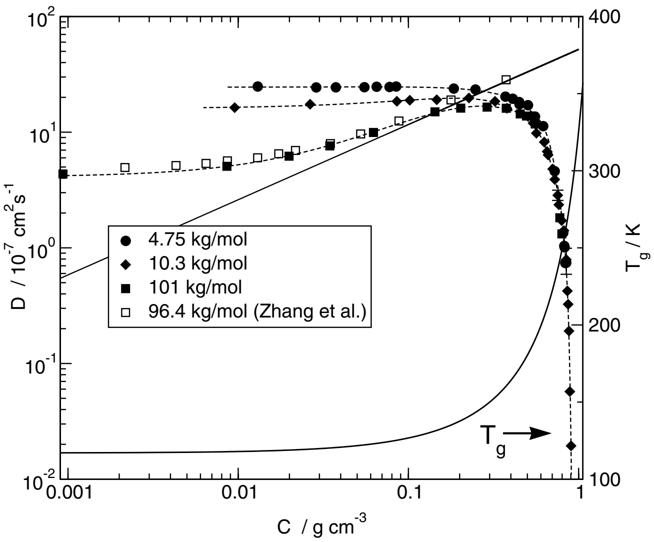

FIG. 2. Diffusion coefficient as a function of concentration for PS in toluene. The legends refer to the molar mass M_w of PS. The straight line represents the asymptote $D \propto C^{0.65}$. Temperature 22 °C. Also plotted is the glass transition temperature T_g according to Eq. (3).

Generally, D contains a thermodynamic and a frictional contribution [21]:

$$D = (1 - \varphi)^2 \frac{K_{os}}{f}, \tag{4}$$

where φ is the polymer volume fraction, $K_{os} = C(\partial\pi/\partial C)$ the osmotic modulus, and f the friction coefficient. Alternatively, Eq. (4) can be written in a Stokes-Einstein-like form:

$$D = (1 - \varphi)^2 \frac{kT}{6\pi \eta_{eff} R_h^a}, \tag{5}$$

where η_{eff} is an effective viscosity and R_h^a an apparent hydrodynamic radius which depends on the osmotic modulus.

For systems far above the glass transition, the polymer solvent friction coefficient remains constant throughout the semidilute regime, and the effective viscosity is that of the solvent: $\eta_{eff} \approx \eta_s$. The concentration dependence is determined by the osmotic modulus, leading to the scaling behavior cited in the introduction.

The picture changes completely in the vicinity of the glass transition. The viscosity, and hence the friction coefficient, increases by many orders of magnitude within a narrow temperature window, leading to a dramatic slowing down of mass diffusion. Since an increase in polymer concentration is, according to Eq. (3), accompanied by a rise of T_g, an increase of concentration is, with respect to the frictional contribution, equivalent to a decrease of temperature, as it brings the system closer to its glass transition. The sharp decay of D above $C \approx 0.2$ g/cm^3 reflects this increase of η_{eff}, whereas friction is almost constant at lower concentrations where the thermodynamic factor dominates. PCS and TDFRS yield identical diffusion coefficients for all concentrations investigated.

Thermal diffusion coefficient.—Figure 3 shows the thermal diffusion coefficient D_T as a function of polymer concentration. In agreement with literature, D_T is independent of molar mass and almost constant below $C \approx 0.2$ g/cm^3, with $D_T \approx 1.1 \times 10^{-7}$ cm^2(sK)$^{-1}$ as limiting value for infinite dilution [6,9–11].

At higher concentrations, D_T shows a similar decay as D, which is apparently caused by the approaching glass transition. As already in the case of D, Zhang *et al.* observed a weaker decrease of D_T at the highest concentration ($C = 0.543$ g/cm^3) accessible in their experiments. Below $C = 0.1$ g/cm^3, their data agree almost perfectly with our results [10].

Soret coefficient.—Interestingly, the Soret coefficient $S_T = D_T/D$ seems to be insensitive to the glass transition. In Fig. 4, it can be seen that S_T varies merely by a factor of 3 above $C = 0.2$ g/cm^3, while both D and D_T drop over more than three decades within the same concentration range. The solid line in Fig. 4 is the scaling relation $S_T \propto C^{-0.73}$ from Ref. [10]. Since D_T does not depend on molar mass, the molar mass dependence of S_T is determined by the molar mass dependence of D^{-1}: S_T increases with M within the dilute regime below C^*, and it becomes molar mass independent above C^*.

Obviously, S_T behaves above C^* as if D followed the scaling law $D \propto C^{x_D}$ and as if D_T were almost constant over the entire concentration range. The approach to the glass transition has a pronounced effect on D and D_T, but not on S_T. The scaling relation in Fig. 4 gives a reasonable description up to the highest concentration of $C = 0.9$ g/cm^3, which is already beyond the semidilute regime, despite the fact that it has been derived from measurements at lower concentrations and without taking the slowing down of the diffusion dynamics caused by the glass transition into account.

The dashed line in Fig. 4 gives an even better description of S_T. It corresponds to the assumption of a constant D_T

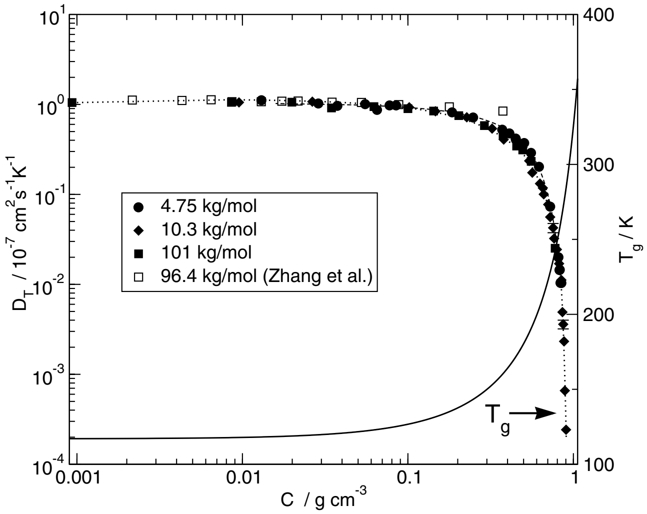

FIG. 3. Thermal diffusion coefficient as a function of concentration for PS in toluene. The legends refer to the molar mass M_w of PS. Temperature 22 °C, T_g according to Eq. (3).

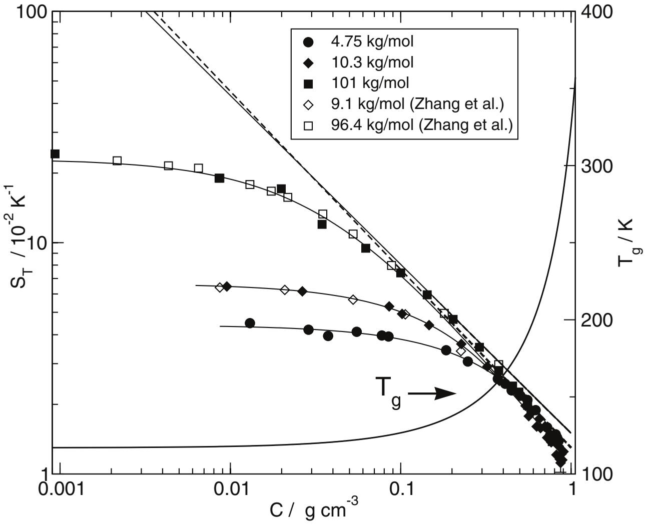

FIG. 4. Soret coefficient as a function of concentration for PS in toluene. The legends refer to the molar mass M_w of PS. Temperature 22 °C, T_g according to Eq. (3).

and the theoretical scaling exponent $x_D = 0.77$; hence, $S_T \propto C^{-0.77}$.

This is a remarkable result, since it tells us that both diffusion coefficients D and D_T are affected by the glass transition in the same way. The same friction constant must be responsible for the slowing down of collective and thermal diffusion, and we can write

$$D_T = \frac{\Delta_T}{f}. \tag{6}$$

f is the same friction coefficient as the one for D in Eq. (4). Δ_T contains all dependencies of D_T other than the friction coefficient. So far, no generally accepted theory is available for D_T, and hence for Δ_T. In our picture, the glass transition affects neither $(1 - \phi)^2 K_{os}$ nor Δ_T but only the friction coefficient f, which cancels out in the Soret coefficient S_T. We attribute the slight decrease of S_T along the line predicted by the scaling law to the concentration dependence of K_{os}.

There is no rigorous proof of this assumption, since Δ_T is not accessible by independent measurements. It is, however, very plausible, if we keep in mind that both D and D_T change over many decades, while S_T still follows the scaling law as if there were no glass transition at all.

At this point, it is of interest to compare binary liquids near a glass transition to critical mixtures, where collective diffusion slows down on approach of a consolute critical point. Contrary to the glass transition, critical slowing down is accompanied by a diverging correlation length ξ. D vanishes approximately like ξ^{-1}, whereas $D_T \propto \xi^0$. Hence, S_T diverges approximately like the correlation length: $S_T = D_T D^{-1} \propto \xi$ [2]. This divergence of S_T has been nicely demonstrated utilizing holographic grating [3,4] and optical beam deflection [5] techniques.

In summary, we have investigated collective and thermal diffusion in dilute, semidilute, and concentrated polystyrene/toluene solutions. Collective diffusion approaches scaling behavior above C^*, but then slows down with increasing concentration due to the approaching glass transition. The thermal diffusion coefficient D_T slows down with the same effective friction coefficient as D. As a consequence, the Soret coefficient $S_T = D_T/D$ is insensitive to the glass transition and follows a scaling law in the semidilute to concentrated concentration regime, as expected for polymer solutions without glass transition. This is in sharp contrast to binary mixtures close to a critical point, where S_T diverges due to critical slowing down of translational diffusion.

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*To whom correspondence should be addressed.
Email address: werner.koehler@uni-bayreuth.de

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