Molecular-weight dependent thermal diffusion in dilute polymer solutions

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Thermal diffusion of high polymers in a continous medium is independent of the molecular weight M_w. Accounting for the solvent molecular structure and the Brownian motion of the solute, we derive an additional contribution of opposite sign which is significant for short chains but vanishes as $M_w \to \infty$. Our findings explain the dependence on M_w observed recently for polystyrene, and its inverse Soret effect at very small M_w. Moreover, they bridge the gap between the macroscopic hydrodynamics description for large solutes and the enthalpy-of-transport picture for small molecules.

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Introduction. Diffusion in dilute polymer solutions depends strongly on the molecular weight [1]. The Brownian motion of each monomer results in a finite velocity of the surrounding fluid. Summing these single-bead contributions, one finds that the polymer chain drags a fluid volume of the size of its gyration radius R. Since the latter increases with the molecular weight, the Einstein coefficient $D \sim 1/R$ decreases as the chain becomes longer; thus a polymer of 10^5 units diffuses about thousand times more slowly than a single mer.

Thermal diffusion, on the contrary, is insensitive to a variation of the molecular weight M_w. The drift velocity of high polymers in a temperature gradient,

$$\mathbf{u} = -D_T \boldsymbol{\nabla} T, \tag{1}$$

does not depend on the chain length. Experimental studies on polystyrene, polymethylmethacrylate, and polyisoprene in various organic solvents, found the transport coefficient D_T to be constant in the range $M_w = 20...600$ kg/Mol [2–7], with typical values $D_T \sim 10^{-11}$ m^2/sK. Thus thermally driven transport is faster than diffusion; the large ratio D_T/D makes a thermal gradient an efficient trap in a microchannel with ambient flow [8]. An explanation for the molecular-weight independent coefficient D_T was given by Brochard and de Gennes [9]: In contrast to the long-range flow due to body forces like gravity, the velocity field created by the thermal forces decays rapidly with distance; as a consequence, hydrodynamic interactions between different parts of the polymer are negligible, and D_T is independent of the chain length.

Recent experiments show, however, that the thermophoretic mobility D_T of short chains does depend on the molecular weight; for polystyrene in toluene, a significant variation with M_w occurs in the range below 10 kg/Mol, corresponding to less than hundred molecular units [10]. Even more surprisingly, a very recent study [11] reports inverse Soret motion ($D_T < 0$) for effective monomers in different solvents. Adding more styrene units results in a change of sign to normal thermal diffusion ($D_T > 0$); then D_T increases with the number of units n and saturates at $n \sim 100$ [11].

Before treating thermally driven transport of polymers, we briefly recall the underlying principle. The stationary state of a non-equilibrium system corresponds to a minimum of the entropy production rate σ per unit volume [12],

$$\sigma = \mathbf{J}_Q \cdot \boldsymbol{\nabla} \frac{1}{T} - \sum_i \mathbf{J}_i \cdot \boldsymbol{\nabla} \frac{\mu_i}{T}, \tag{2}$$

which is a bilinear form of the fluxes of heat $\mathbf{J}_Q$ and particles $\mathbf{J}_i$, and the corresponding generalized forces; the latter are given by the gradients of temperature and the chemical potentials μ_i. Onsager's "phenomenological equations" establish linear relations between fluxes and forces, yet do not provide an explicit scheme for calculating transport coefficients like D_T. This is achieved by evaluating the thermally driven motion in terms of diffusion models [13–17], molecular dynamics simulations [18–21], or hydrodynamics.

Theoretical work on the Soret effect of complex fluids mainly dealt with viscous effects in the framework of low-Reynolds number hydrodynamics, where the solute velocity $\mathbf{u}_1$ is derived from Stokes' equation $\eta \boldsymbol{\nabla}^2 \mathbf{v} = \boldsymbol{\nabla} P - \mathbf{f}$, with the force density $\mathbf{f}(\mathbf{r})$ exerted by the solute on a unit volume of the surrounding fluid of viscosity η, pressure P, and velocity $\mathbf{v}$. Ruckenstein thus obtained D_T for weakly charged particles [22]. Later on, this was formalized and generalized to high valencies and non-uniform electrolytes [23–27]. This hydrodynamic approach treats the solvent as a continuous medium; it neglects both the solvent molecular diffusivity [28] and fluctuations [29].

In the present work we show that the solvent molecular structure and the solute Brownian motion give rise to a second contribution $\mathbf{u}_2$ of opposite sign. Since $\mathbf{u}_2$ depends on the size of the solute, the overall velocity

$$\mathbf{u} = \mathbf{u}_1 + \mathbf{u}_2 \tag{3}$$

and the transport coefficient D_T vary with M_w and may take both signs. We consider a dilute solution of polymers of n beads; their radius a is equal to that of a solvent molecule. For the sake of simplicity, both are described as "atoms" that interact through a van der Waals attractive potential $v_{ps} = -C_{ps}/r^6$. Then the energy of a solute atom p in the solvent s of density c reads $-\varepsilon_p = -C_{ps} \int dV\, c/r^6$, and similarly $-\varepsilon_s$ with C_{ss} for the solvent. Since the parameters $\varepsilon_i > 0$ are much larger

than the thermal energy, we may identify the chemical potential per bead with the single-atom energy, $\mu_i = -\varepsilon_i$. The number density c of solvent molecules varies with temperature according to

$$c = \bar{c}(1 - \beta\ \mathbf{r}\cdot\boldsymbol{\nabla}T), \tag{4}$$

where $\bar{c}$ is a reference value and $\beta = -(1/\bar{c})dc/dT$ the thermal expansivity.

Diffusion of a single bead. We briefly discuss the case of a single bead $n = 1$ in dilute solution. Balancing the generalized forces and Stokes friction with coefficient $6\pi\eta a$, and imposing zero net mass flow $\mathbf{J}_p + \mathbf{J}_s = 0$, we have $\mathbf{u} = (T/6\pi\eta a)\boldsymbol{\nabla}(\mu_s/T - \mu_p/T)$; with the derivative $\boldsymbol{\nabla}\mu_i = \varepsilon_i\beta\boldsymbol{\nabla}T$ this leads to

$$D_T = \left(\frac{1}{T} + \beta\right)\frac{\varepsilon_p - \varepsilon_s}{6\pi\eta a}. \tag{5}$$

When taking $-(1+\beta T)\varepsilon_i$ as the enthalpy of transport h_i, we recover the standard thermodiffusion model for solute and solvent molecules of equal size [13–15]. Eq. (5) relies on the crucial assumption that the response to the generalized forces in (2) is given by a single friction coefficient $6\pi\eta a$. Clearly, this ceases to be valid if solute and solvent differ in molecular volume, since diffusive motion in general depends on size.

Polymer-solvent interactions. We evaluate the velocity contribution driven by solute-solvent forces, $\mathbf{u}_1$, from Stokes' equation. Taking v_{ps} to be constant with respect to temperature, we find the force on the solvent to be proportional to the density gradient, $\mathbf{f} = v_{ps}\boldsymbol{\nabla}c$. Following standard arguments [30] and neglecting a geometrical factor of the order of unity, one obtains the transport velocity

$$\mathbf{u}_1 = -\frac{\beta\varepsilon_p}{6\pi\eta a}\boldsymbol{\nabla}T. \tag{6}$$

In physical terms this means the solute particle migrates to regions of higher solvent density, where its potential energy is lower. Note that $\mathbf{u}_1$ corresponds to the term proportional to $\beta\varepsilon_p$ in (5) and to the force $\boldsymbol{\nabla}\mu_p$ in (2).

We emphasize that $\mathbf{u}_1$ is independent of the size of the solute, as is well known for transport driven by forces at sticky surfaces [30, 31]. When considering a large sphere of radius a_n, consisting of n atoms, one has to sum their interaction potentials, resulting in the modified form $v_{ps} = -nC_{ps}/(r^2 - a_n^2)^3$ [32]. Yet the transport velocity $\mathbf{u}_1$ turns out to be independent of n and a_n, and is entirely determined by the single-atom energy ε_p and radius a.

For the present case of polymer thermophoresis, Eq. (6) describes a monomer as well as a chain of n repeat units [33]. This is easily understood in terms of the short-ranged velocity field $\mathbf{v}(\mathbf{r})$ of the surrounding fluid; contrary to external forces that result in $\mathbf{v} \sim 1/r$, the flow induced by surface forces decays with the third power of the inverse distance, $\mathbf{v} \sim 1/r^3$ [34]. Thus hydrodynamic interactions between distant beads are weak, and Eq. (6) is valid independently of the chain length.

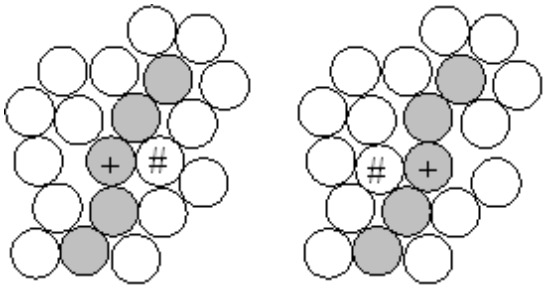

FIG. 1: Schematic view of a random move $\hat{x}(t)$ of a solute molecule (+), accompanied by an opposite solvent flow (#). The coherent current of both solute and solvent correspond to the volume of a single bead. In a uniform system, the left and right states occur with equal probability. A temperature gradient gives rise to thermal forces that favor one of the positions, thus resulting in a net solute velocity u_2.

Brownian motion. Now we turn to the second contribution $\mathbf{u}_2$ to the transport velocity, which arises from the Brownian motion of the solute and relies on the molecular structure of the solvent. The equation of motion of a particle of mass M along the x-axis,

$$M\partial_t\hat{u} = -\xi\hat{u} + \hat{f}, \tag{7}$$

involves Stokes drag with the friction coefficient ξ and a random force $\hat{f}$; the hat indicates fluctuating quantities. The random force satisfies [35]

$$\left\langle \hat{f}(t)\hat{f}(t')\right\rangle = 2\xi k_B T\delta(t - t'), \tag{8}$$

and the formal integral of (7) reads

$$\hat{u}(t) = \frac{1}{M}\int_0^t dt' e^{-(t-t')/\tau}\hat{f}(t'), \tag{9}$$

with the relaxation time $\tau = M/\xi$. Integrating once more, $\hat{x}(t) = \int_0^t dt'\hat{u}(t')$, and using (8), one readily finds the mean square displacement $\left\langle \hat{x}(t)^2\right\rangle = 2Dt$, with the diffusion coefficient $D = k_B T/\xi$. The fluctuating force vanishes in the average, and so does the mean velocity of the Brownian particle $\langle\hat{u}(t)\rangle = 0$.

In a non-uniform system, however, the fluctuating force may result in directed motion. As illustrated in Fig. 1, a solute moving by a small distance $\hat{x}(t)$, creates an opposite flow in the surrounding fluid. According to the generalized forces in (2), the molecules prefer regions of lower temperature and lower chemical potential, resulting in mean fluxes $\mathbf{J}_i$.

This directed motion is quantified in terms of the Fluctuation theorem, which relates the work done on the system to the free energy change [36], or alternatively, the probability of forward and backward trajectories to their entropy production [37]. In order to obtain a statistical

weight for non-equilibrium states, it turns out convenient to use the total entropy change $k_B\psi$, as expressed by the dimensionless quantity

$$\psi(t) = \frac{1}{k_B}\int_0^t dt'' \int dV \sigma(t''). \tag{10}$$

As a consequence of the second law of thermodynamics, a trajectory with positive ψ is more likely to occur than the backward trajectory with $-\psi$ [37]; their probability distributions satisfy $\mathcal{P}_+(\psi)/\mathcal{P}_-(-\psi) = e^{\psi}$. The corresponding average results in the mean solute velocity $\langle \hat{u} e^{\psi} \rangle$. Linearizing in ψ and noting $\langle \hat{u} \rangle = 0$, one has

$$u_2 = \langle \hat{u}(t)\psi(t) \rangle . \tag{11}$$

Inserting (9) and (10), we find that the velocity u_2 is determined by the two-time correlation function $\langle \hat{f}(t')\sigma(t'') \rangle$.

A perfectly rigid polymer in a homogeneous fluid, would induce the solvent flow $\int dV \hat{J}_s = -n\hat{u}$, which is n times larger than that of a monomer. Yet real polymers are flexible, and the molecular structure of the solvent results in retarded hydrodynamic interactions. As a consequence, the solvent flow $\hat{J}_s$ around a moving polymer is to a large extent out of phase with respect to the random force acting on a given bead.

In order to evaluate the correlation function in Eq. (11), we write the random force as a sum of independent one-atom contributions,

$$\hat{f}(t) = \sum_k \hat{f}_k(t), \tag{12}$$

and $\hat{u} = \sum_k \hat{u}_k$, accordingly. As shown schematically in Fig. 1, we assume that solvent motion correlated with $\hat{f}_k$ is limited to the direct vicinity of bead k; then the coherent part of $\hat{J}_s$ corresponds to a single bead moving at velocity $-\hat{u}_k$. Thus we have

$$\int dV \left\langle \hat{f}_k(t')\hat{J}_{p/s}(t'') \right\rangle = \pm \left\langle \hat{f}_k(t')\hat{u}_k(t'') \right\rangle , \tag{13}$$

where the plus and minus signs corresponds to p and s, respectively. Since the gradient of the solute chemical potential $\boldsymbol{\nabla}\mu_p$ is already accounted for in (6), the remaining entropy production rate reads

$$\sigma = -\hat{J}_p \mu_p \nabla(1/T) - \hat{J}_s \nabla(\mu_s/T).$$

Inserting these relations in (11), summing over k, using (8), and performing the time integrals for $t \gg \tau$, we find

$$\mathbf{u}_2 = \frac{\boldsymbol{\nabla}\mu_s}{\xi} + \frac{(\mu_p - \mu_s)}{\xi}\frac{\boldsymbol{\nabla}T}{T}. \tag{14}$$

As in Eq. (6) above, we identify the single-bead chemical potential μ_i with the van der Waals attractive energy $-\varepsilon_i$ and the derivative $\boldsymbol{\nabla}\mu_s = \beta\varepsilon_s\boldsymbol{\nabla}T$. The friction coefficient of a polymer reads $\xi = \kappa\eta R$, where the gyration radius of long chains is given by the scaling law $R = \ell n^{\nu}$ [1] and κ is a numerical constant.

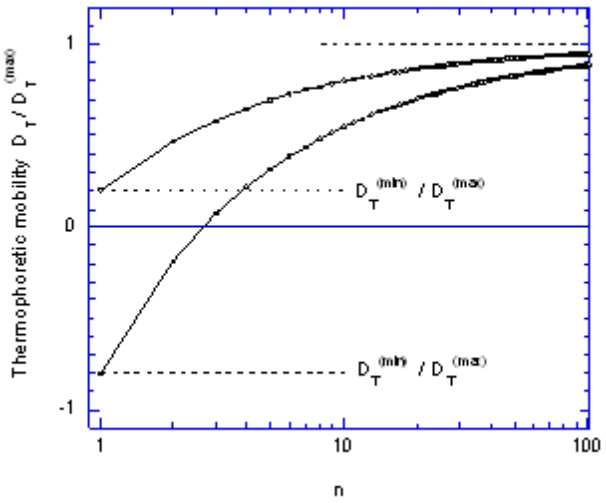

FIG. 2: Reduced thermophoretic mobility as a function of the chain length n. The points are calculated from Eq. (15) with $\nu = 0.6$. The dashed lines indicate the maximum and minimum values where $D_T^{(\max)} = \beta\varepsilon_p/(6\pi\eta a)$ and $D_T^{(\min)} = D_T^{(\max)} - \beta\varepsilon_s/(\kappa\eta\ell)$; the latter may be positive or negative, depending on the relative magnitude of the two terms.

As an essential result of this paper, the two velocity contributions of Eq. (3) differ with respect to the friction coefficient; the gradient of the solute chemical potential gives rise to $\mathbf{u}_1 = -\boldsymbol{\nabla}\mu_p/(6\pi\eta a)$ with the single-bead coefficient $6\pi\eta a$, whereas $\mathbf{u}_2$ depends on ξ. Thus we obtain the thermophoretic mobility of a polymer chain

$$D_T = \frac{\beta\varepsilon_p}{6\pi\eta a} - \frac{\beta\varepsilon_s + (\varepsilon_s - \varepsilon_p)/T}{\kappa\eta R}. \tag{15}$$

Putting $\kappa R = 6\pi a$ for a single bead ($n = 1$) one recovers Eq. (5). Increasing the chain length leaves the first term $\beta\varepsilon_p/(6\pi\eta a)$ unchanged, whereas the remainder is reduced by the ratio a/R. For $n \to \infty$ the second term vanishes, i.e., thermal transport of high polymers is entirely determined by the contribution from solute-solvent interactions, $\beta\varepsilon_p/(6\pi\eta a)$. Thus Eq. (15) bridges the gap between the thermodiffusion model Eq. (5) and the result from macroscopic hydrodynamics Eq. (6).

With typical values for $\varepsilon_p, \varepsilon_s, \beta$, the coefficient D_T is an increasing function of the number of beads; in the limit $n \to \infty$ it takes the positive value $\beta\varepsilon_p/(6\pi\eta a)$, whereas for short chains both signs may occur, as shown in Fig. 2. We discuss these aspects in view of the experimental findings on polystyrene (PS) reported in [10, 11]. Evaluating the mobility of long chains $D_T = \beta\varepsilon_p/(6\pi\eta a)$ with the Berthelot relation $\varepsilon_p \sim \sqrt{A_p A_s}$, the Hamaker constant $A_p \sim 7\times10^{-20}$ J of PS, the atomic size $a \sim 0.3$ nm, and the parameters β, η, A_s gathered in Table I of Ref.

[38], one finds a quantitative agreement with experiment. Both the absolute values and the dependencies on β and η for eight different solvents are well described by (15).

An inverse Soret effect is expected to occur for a single bead if $\varepsilon_p < \varepsilon_s$. A negative D_T has indeed been observed for effective monomers in the solvents cyclohexane, cyclooctane, and tetrahydrofuran [11], whereas in ethyl-acetate, toluene and methyl-ethyl-ketone, the coefficient D_T is strongly reduced but does not change its sign. These experimental data suggest that the relative value of the second term in (15) depends on additional parameters such as polarity and the molecular size and mass, which are not accounted for in the present work. Moreover, a refined analysis would replace $\beta\varepsilon_p$ with $\beta_p\varepsilon_p$, where β_p is determined by the anharmonicity of the solute-solvent potential.

Though derived here for polymers in organic solvents, the molecular-weight dependence applies equally well to aqueous solutions, and could indeed be relevant for experimental findings on polyoxyethylene in water [6]. A very complex behavior has been reported for charged proteins in an electrolyte solution, where the sign of D_T depends on temperature and salinity [39].

Regarding the influence of the persistence length, simple rescaling $\ell_\zeta = \zeta\ell$ leads to the gyration radius $R_\zeta = \zeta^{1-\nu}R$. This affects the second velocity contribution u_2 only, whereas the first one u_1 remains unchanged. Thus for a stiff polymer ($\zeta > 1$) the second term in Eq. (15) is reduced, and D_T is shifted to more positive values. This enhancement agrees with molecular dynamics simulations [18] for $\zeta = 4.2$ and 7.9, whereas the data for $\zeta = 2.9$ rather indicate an opposite tendency.

We conclude with a remark on whether dynamical aspects cancel in the ratio of thermal diffusion and Einstein coefficients, that is, whether the Soret coefficient $S_T = D_T/D$ can be obtained from static quantities. As pointed out by de Groot in his doctoral thesis [40], thermostatics does not account for the entropy flow and cannot provide a general description for the Soret effect. This is illustrated by Eq. (15); because of the different friction coefficients $6\pi\eta a$ and $\kappa\eta R$, the two terms cannot be derived from a heat-of-transport picture.

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