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Abstract
A temperature gradient induces different driving forces on the components of a mixture which translates into their segregation. We show that these driving forces constitute the physical picture behind the thermodiffusion effect, and provide an alternative expression of the Soret coefficient which can be applied to both colloidal suspensions and molecular mixtures. To verify the validity of the formalism, we quantify the related forces in an Eulerian reference frame by non-equilibrium molecular simulations. Furthermore, we present an analytical argument to show that the hydrodynamic interactions need to be accounted for to obtain the proper scaling of the thermophoretic force. This result combined with the presented expression satisfactorily explains the experimentally known size dependence of the thermodiffusion coefficient in dilute polymer solutions.

(Some figures may appear in colour only in the online journal)

1. Introduction

Thermodiffusion or the Soret effect refers to the transport of mass induced in a fluid mixture by a temperature gradient. This effect was first observed more than one and a half centuries ago [1, 2], and has already found many applications like isotope separation [3], or fractionation of colloid/polymer dispersions [4]. In the last two decades, new and precise experimental techniques have stimulated much interest in investigating this effect in various systems [5, 6], and precise techniques to control the temperature at the microscale are allowing the development of microfluidic applications [7, 8]. In a recent study [9], the interaction of proteins in biological liquids was analyzed in terms of their thermophoretic behavior.

Despite its relevance and long history, the theoretical basis of the Soret effect is still under debate. In liquids there are two families of approaches. The first is related to the study of molecular mixtures where the components have similar sizes and masses. The theories are based on the concepts of transport-heat, transport-enthalpy or activation energy [10–15], such that the transport of mass is related to these quantities by the differences between the two components. The second family of approaches is related to the study of complex systems like colloidal suspensions in which the relevant length and time scales of solute and solvent are separated by orders of magnitude. The mass transport properties are then determined by balancing the mechanical-level driving force and viscous drag on the solute with a Smoluchowski-type equation [16–19, 6, 20, 21]. The driving force is calculated from an approach that is either thermodynamic [16–19], or hydrodynamic [6, 20, 21].

In this work, we propose a new theoretical expression for the Soret coefficient S_T, one of the main transport properties in thermodiffusion, which applies equally well to molecular mixtures and colloidal suspensions. Its validity is nicely verified by means of computer simulations. The main contribution with respect to existing theories is the explicit consideration of the forces applied to each component of the system. Based on the new expression of S_T, an effective method to measure the Soret coefficient in dilute solutions is discussed. Moreover, we estimate the scaling behavior of the thermophoretic driving force on a long polymer in dilute solution where, in contrast to previous works [21–23], the effect of hydrodynamic interactions is shown to be relevant. The size-independent thermophoretic velocity results from the cancelation of size dependence between the thermophoretic force and the friction force, without the requirement of an additional friction mechanism. By combining the obtained result with the new expression for S_T, we can justify the

crossover from long to short polymer behavior which has been experimentally observed [24, 5, 25–27].

2. The phenomenological thermodiffusion equation

The total diffusive particle flux of one component in a binary mixture is not only given by Fick's law and determined by the concentration gradient, but an additional contribution proportional to the temperature gradient has to be considered. It is characterized as [28]

$$\mathbf{J}(\mathbf{r}) = -\tilde{n} D_{\mathrm{m}} \nabla x - \tilde{n} x (1-x) D_{\mathrm{T}} \nabla T, \tag{1}$$

with D_{m} the mutual diffusion coefficient and D_{T} the thermal diffusion coefficient. Here, $\tilde{n} = n + n'$ denotes the total number density of solution particles, n and n' being the number densities of the two components. The mole fraction of species 1 is $x = n/\tilde{n}$. The competition between the particle flux due to the temperature gradient and that due to the mole fraction gradient can establish a separation between the two components, which is quantified by S_T,

$$S_T \equiv \frac{D_{\mathrm{T}}}{D_{\mathrm{m}}}. \tag{2}$$

In the absence of mass flux, S_T can be written as

$$S_T = -\frac{1}{x(1-x)} \frac{\nabla x}{\nabla T}. \tag{3}$$

These steady-state profiles of concentration and temperature are easily measured in many experiments [5], and by non-equilibrium simulations [29–33], such that equation (3) provides the standard way to quantify S_T. Nevertheless, it does not reveal any physical origin of the separation between the two components.

3. The van Kampen equation

Based on the extended Kramers equation, van Kampen proposed in 1988 [34] an equation that governs the particle flow of an inhomogeneous system,

$$\mathbf{J}(\mathbf{r}) = n(\mathbf{r})\mu(\mathbf{r})\mathbf{f} - \mu(\mathbf{r})\nabla[n(\mathbf{r})k_{\mathrm{B}}T(\mathbf{r})], \tag{4}$$

with $\mathbf{f}$ the mechanical driving force and $\mu(\mathbf{r})$ the particle mobility, which in general is not proportional to the collective or mutual diffusion coefficient in equation (1). An expression similar to equation (4) has been derived by Dhont [17] from force balance arguments. The so-called *Brownian force* is the gradient of the ideal gas osmotic pressure, $n(\mathbf{r})k_{\mathrm{B}}T(\mathbf{r})$. This is a macroscopic force arising from the momentum change in a volume element due to particles entering into or departing from the volume element, such that direct interactions do not contribute to it. We refer to direct interactions as those that apply directly to each individual particle. This is the case of inter-particle interactions and external forces, like gravity.

The force $\mathbf{f}$ was originally understood by van Kampen only as the externally applied force, but Widder and Titulaer [35] have already extended this concept to consider also the mechanical driving forces exerted on single particles by an inhomogeneous surrounding fluid. As a consequence,

the temperature gradient will generally contribute to both the Brownian and the mechanical driving forces. Note also that the driving forces include both equilibrium and non-equilibrium contributions. Another relevant aspect is that van Kampen derived equation (4) for a dilute Brownian particle suspension where μ referred to the mobility of a single particle in a background random solvent. However, when considering a tagged particle in a concentrated solution, the environment can be regarded as an effective solvent. Equation (4) is then correct by understanding all quantities referred to those of a tagged particle, and in particular μ as an effective mobility that includes both solute–solvent and solute–solute contributions.

Equation (4) can be understood as an extension of the uniform-temperature Smoluchowski flux equation. It has been widely applied to colloidal suspensions [35, 16, 19], although its validity has not yet been really proved for these systems. Molecular mixtures are a different type of system where the dynamics of the particles can be described by a Markov random walk on a coarse grained time scale. In spite of the differences, it is reasonable to assume that the Markov master equation reduces to the Smoluchowski equation [36] in the case that only small jumps occur during the random walk, or when the jump moment and position distributions vary linearly in space. In such cases, equation (4) is valid for large particles like colloids, for small particles like solvent molecules, and for each of the components of a binary liquid. The verification of this equation can provide then a unified framework to describe thermodiffusion. In [37] equation (4) is employed to investigate the relation of drift velocity and driving forces in inhomogeneous systems.

4. New expression for the Soret coefficient

In the absence of a particle flow equation (4) can be written as

$$\frac{\nabla n(\mathbf{r})}{n} = [\mathbf{f} - k_{\mathrm{B}} \nabla T(\mathbf{r})] \frac{1}{k_{\mathrm{B}} T}. \tag{5}$$

With the relation $x = n/(n + n')$ for the molar fraction, equation (3) can be written in terms of the gradients of concentration of the two components as

$$S_T = \left(\frac{\nabla n'}{n'} - \frac{\nabla n}{n} \right) \frac{1}{\nabla T}. \tag{6}$$

Since we expect equation (5) to be valid for both components, it can be substituted into equation (6), such that

$$S_T = (\mathbf{f}' - \mathbf{f}) \frac{1}{k_{\mathrm{B}} T \nabla T}, \tag{7}$$

where $\mathbf{f}$ and $\mathbf{f}'$ are the steady-state mechanical driving forces suffered by a single particle of each component. These will be the solute and solvent in the case of a colloidal or polymeric suspension or each component of a molecular mixture. In contrast to the traditional expression of the Soret coefficient in equation (3), the proposed equation (7) brings a clear physical picture. The separation between two components characterized by S_T is simply related to the difference of the driving forces acting on the two components.

In dilute conditions $n \ll n'$, the calculation of **f** and **f**′ is greatly simplified since they only depend on the steady-state density distribution $n'(\mathbf{r})$. In an early work, Bearman and Kirkwood [38] referred to the gradient of equilibrium partial pressures exerted on each component of the mixture as the 'thermodiffusional driving force'. Based on that work, Morozov [39] employed the equilibrium pair correlation function to approximately calculate S_T for infinitely dilute molecular mixtures. It can be found that **f** − **f**′ in equation (7) corresponds to the 'thermodiffusional driving force' in [39], when the non-equilibrium parts of **f** and **f**′ are ignored.

An additional approximation valid only in dilute conditions is that $D_{\mathrm{m}} \simeq D_{\mathrm{s}}$, with D_{s} the solute self-diffusion coefficient. The thermal diffusion coefficient is then

$$D_{\mathrm{T}} = (\mathbf{f}' - \mathbf{f})\frac{D_{\mathrm{s}}}{k_{\mathrm{B}}T\nabla T}. \qquad (8)$$

This indicates that the forces exerted on both components, **f** and **f**′, contribute to D_{T}. This differs from the general consideration of D_{T} as being proportional to the thermophoretic force applied on just one component [40]. Nevertheless, when $|\mathbf{f}'| \ll |\mathbf{f}|$, as it is for most complex fluids [8, 41–43], equation (8) reduces to the widely used expression

$$D_{\mathrm{T}} \simeq -\mathbf{f}\frac{D_{\mathrm{s}}}{k_{\mathrm{B}}T\nabla T}. \qquad (9)$$

This expression also results from directly balancing the driving force **f** with the friction created by the thermophoretic velocity $\mathbf{f}_{\zeta} \simeq -\zeta \mathbf{v}_{\mathrm{T}}$, considering that the friction coefficient is related to the self-diffusion coefficient by the Einstein relation $D_{\mathrm{s}} = k_{\mathrm{B}}T/\zeta$, and that the thermophoretic velocity is defined as $\mathbf{v}_{\mathrm{T}} = -D_{\mathrm{T}}\nabla T$ [44, 37]. Otherwise, when **f**′ is comparable to **f**, for instance in molecular mixtures, in colloidal suspensions with low S_T, or in low-weight polymer solutions, both contributions **f** and **f**′ are important. Consequently, **f**′ can be interpreted as the quantity that bridges the gap of thermodiffusion between complex fluids and molecular mixtures.

5. Validation with computer simulations

Non-equilibrium molecular dynamics simulations are performed to test equation (7) by comparing with the standard method in equation (3). We consider a molecular mixture modeled by a binary mixture of Lennard-Jones (LJ) particles. This system has been so far the most popular system employed to understand by means of computer simulations the mechanisms of thermodiffusion [29–32]. Two particles i and j at a distance r_{ij} interact via the potential

$$U_{\mathrm{LJ}}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]. \qquad (10)$$

Here ϵ_{ij} is the potential depth and σ_{ij} is the particle diameter. The interaction parameters between unlike particles are determined through the Lorentz–Berthelot mixing rules, $\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{22}}$ and $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$. The potential is truncated with a cutoff distance $r_{\mathrm{c}} = 2.5\sigma_{11}$. The equations

Table 1. Summary of the parameters employed in the simulations and comparison of the Soret coefficients obtained with both methods. The symbol n refers to the new method in equation (7), and t to the traditional method in equation (3). The units of S_T are 10^{-3} K^{-1}.

m_{11}/m_{22}	σ_{11}/σ_{22}	$\epsilon_{11}/\epsilon_{22}$	$\overline{T^*}$	$\overline{\rho^*}$	S_T^n	S_T^t
4	1	1	2.0	0.4	4.0(2)	3.7(2)
1	1.5	1	2.0	0.4	−1.2(3)	−1.1(2)
1	2.2	1	2.0	0.4	−2.7(4)	−2.8(2)
1	1	2	2.0	0.4	2.6(5)	2.6(3)
4	1	1	0.85	0.81	19.4(8)	19.1(9)
1	1	2	0.85	0.81	18.6(5)	18.8(6)

of motion are integrated by the velocity-Verlet algorithm with a time step $\Delta t \simeq 0.002$. To simulate a steady-state system with a constant temperature gradient, we employ the heat exchange algorithm [29, 45], where the average temperature $\bar{T}$ is fixed by the Berendsen thermostat [46]. Periodic boundary conditions are employed in all directions. All quantities are expressed in reduced units, i.e. m_{22}, σ_{22} and ϵ_{22} are set to 1, with temperature $T^* = k_{\mathrm{B}}T/\epsilon_{12}$ and density $\rho^* = \rho\sigma_{12}^3$. In order to express S_T in physical units, we consider species 2 as an argon-like fluid: $\sigma_{22} = 0.341$ nm and $\epsilon_{22} = 996$ J mol^{-1}. In order to validate our framework in different thermodynamic states, two different parameter ranges have been chosen: an equimolar gas mixture with mean temperature $\overline{T^*} \equiv k_{\mathrm{B}}\bar{T}/\epsilon_{12} = 2.0$ and mean density $\overline{\rho^*} \equiv N\sigma_{12}^3/V = 0.4$, and an equimolar dense liquid mixture with $\overline{T^*} = 0.85$ and $\overline{\rho^*} = 0.81$. A typical system size is $30\sigma_{22}$ in the ∇T direction and $12\sigma_{22}$ in the perpendicular one. The parameters employed are summarized in table 1.

The forces coming from direct interactions between neighboring particles are straightforward to quantify in computer simulations, since they are anyway computed to update the particle positions. Nevertheless, the driving force will be mostly accompanied by other forces which generally impede its independent measurement. The first naive procedure could be to measure the forces acting on a single particle over a relatively long time, that is, in a Lagrangian reference frame. The result in this case is the sum of two contributions, the driving force and the single particle or Lagrangian friction, since the stochastic force will vanish on average. This means that in the stationary state the total measured force will vanish. An adequate approach to compute the driving forces is to consider an Eulerian reference frame. This is to measure the average force acting on particles, as long as they remain in a small, arbitrary and fixed volume element (figure 1). This can be understood since the mass flux in a volume element is described by equation (4), and this equation can be translated into a force balance equation by dividing each term by the mobility $\mu(r)$. A non-vanishing mass flux will produce an Eulerian friction force J/μ, that is balanced by the corresponding driving and Brownian forces. As already explained, the Brownian force does not contribute to the force measurement when only measuring inter-particle direct interactions. Therefore, in the absence of a particle flux, the average force evaluated from direct interactions in a volume element corresponds directly to the driving force.
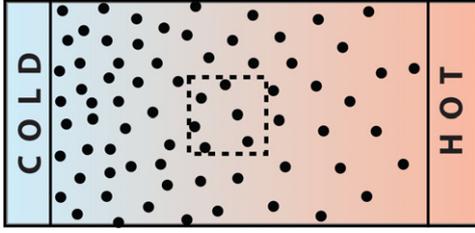
Figure 1. Schematic picture depicting a Brownian particle suspension with temperature gradient. The middle square represents a volume element in which the driving forces are evaluated. In our simulations, a slab can be employed to improve the statistics.

Since the forces are an average particle quantity, the actual size of the volume element is not relevant. The considered dimensions should only be large enough to facilitate the gathering of statistics, small enough such that the local equilibrium assumption is still valid, and placed such that boundary effects can be neglected. In the presented example, we have typically used a slab perpendicular to the temperature gradient of thickness $2.5\sigma_{22}$ and placed equidistant from both thermal baths. The evaluated forces characterize the S_T at the averaged slab temperature. Consequently, if different slabs with different averaged temperatures are employed, they will characterize different points of $S_T(T)$. Nevertheless, when considering small temperature gradients, the variations will most likely be within the errors of the measurements.

To compute the Soret coefficient S_T of a binary mixture by means of equation (7), the forces on both components have to be separately quantified. Figure 2(a) displays one example. The instantaneously measured forces fluctuate significantly. In order to give an estimation of the average value, here we show the forces as time integrals, and averaged over 16 independent runs. The initial fluctuations then become smaller due to the larger averaging with increasing times. For comparison, we also measure S_T in the same systems by following the standard procedure in equation (3), by quantifying the temperature and the density profiles of both components in the steady state, as plotted in figure 2(b), such that the gradients of temperature and molar fraction are determined. Our results are summarized in table 1, where the values of S_T obtained with both methods agree very well within the statistical uncertainty

for the whole range of explored parameters. Therefore, we can conclude that equation (7) is very convincingly verified. Note that both types of value for S_T in table 1 are actually computed in the same simulations, such that the statistical errors of the two methods are obtained from the same computational cost. The values of S_T in table 1 are also similar to those obtained by other groups [30, 31].

6. Dilute solutions

One of the most obvious advantages of the method we suggest in equation (7) is that it can be used to determine the Soret coefficients of dilute solutions. It becomes unfeasible to measure the concentration profile when the number of particles is very small due to the poor statistics [47], such that the standard method is then difficult or impossible to apply. Regardless of the concentration, the driving force applied on a particle can be directly measured by disturbing the particle in such a way that its frictional force vanishes.

In a recent simulation study Galliero and Volz [40] proposed a related scheme to quantify the S_T of a single nanoparticle in suspension denoted as the single particle thermodiffusion algorithm (SPTA). Their idea was to attach the nanoparticle to a spring and to directly relate the elongation produced by the temperature gradient with the thermophoretic force. This constitutes a good approximation, although it disregards the contribution of the driving force on the solvent particles. The thermal diffusion factor $\alpha_T = TS_T$ obtained from the SPTA is compared with an extrapolation to low concentration of finite-concentration values of α_T standardly computed by determining concentration profiles. The SPTA results slightly underestimate the extrapolated ones. The underestimation of the dimensionless factor α_T is about 1–1.5 for different nanoparticles. Here, we attribute the underestimation to the solvent contribution. In order to provide an estimation for this contribution, the employed dense liquid solvent can be considered incompressible, $\nabla n' \simeq 0$, which together with equation (4) and the fact that the solute is very diluted implies that $\mathbf{f}' \simeq k_B \nabla T$. Thus, from equation (7) the solvent contribution of α_T results as $T\mathbf{f}'/k_B T \nabla T = 1$. The previous approximation for the solvent contribution already explains very well the underestimation
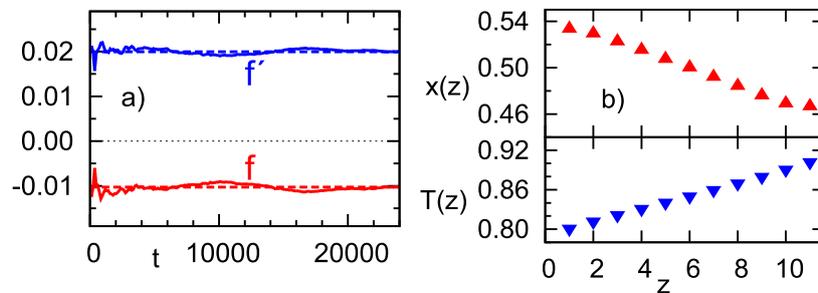
Figure 2. Determination of S_T for a binary mixture of LJ particles. (a) The driving forces corresponding to equation (7). The continuous lines are time integrals versus time for each of the two components. The dashed lines are the final averaged values. (b) Temperature profile and molar fraction profile of species 1, corresponding to equation (3). Physical quantities are expressed in reduced units and simulation parameters are specified in the last entry of table 1.

observed in the SPTA simulation results [40], although a more precise measurement of $\mathbf{f}'$ could also be performed. These results also constitute a further check of the validity of equation (7) and an additional theoretical justification of the SPTA. The deviation originated by disregarding the driving force exerted on the solvent is expected to be more significant as the solute size decreases. Therefore, we can infer that the SPTA will be a good approximation when the size/mass difference between the two components is large. The method can find further applications in the determination of the Soret coefficient in dilute solutions of colloids, polymers, or other complex structures, and this is not only by means of computer simulations, but also with appropriate experimental techniques, like laser tweezers.

7. Polymer solutions

Experimental results for dilute high-weight polymer solutions have shown that D_T is independent of polymer length [24, 5]. Recent experiments [25–27] have, however, shown that D_T becomes polymer length dependent in the limit of short polymers. With a hydrodynamic argument we evaluate the scaling properties of the thermophoretic force where hydrodynamic interactions are shown to be relevant. The combination of this argument with the new expression of the Soret coefficient provides a satisfactory explanation of the crossover behavior between high and low polymer weight polymers.

7.1. Long polymers

Two limits apply in the high-weight polymer case. One is that the driving force suffered by a solvent particle due to the temperature gradient, $\mathbf{f}'$, is negligible in comparison with the driving force suffered by the whole polymer chain, $\mathbf{f}$. The thermodiffusion coefficient is then given by equation (9).

The second limit is that scaling arguments can be applied for the calculation of both D_s and $\mathbf{f}$. The self-diffusion coefficient of a polymer chain in a hydrodynamic solvent is well known to scale with the number of monomers $D_s \sim N^{-\nu}$ ($\nu \simeq 0.6$ for good solutions or 0.5 for Θ solutions). In order to estimate the driving force behavior, we consider the situation where the center of mass of the polymer is averagely fixed by a soft spring, thus the friction vanishes and $\mathbf{f}$ is balanced by the external force exerted by the soft spring. This nonzero net force between the polymer and the surrounding fluid results in a fluid flow. The force exerted on a polymer will be equally shared by each of the constituent monomers, $\mathbf{f} = \mathbf{f}_m N$, and the force on each monomer, $\mathbf{f}_m$, can be calculated as the sum of two contributions,

$$\mathbf{f}_m = \mathbf{f}_m^0 + \mathbf{f}_h. \tag{11}$$

The isolated monomer force, $\mathbf{f}_m^0$, is the driving force undergone by a single monomer due to the interaction with the temperature-dependent solvent. This force coincides with the force that a polymer with only one monomer would have, and it is then size independent. The hydrodynamic monomer force, $\mathbf{f}_h$, is the force exerted on each monomer i by the

hydrodynamic drag produced by all the other monomers j. It can be expressed as

$$\mathbf{f}_h = 6\pi\eta a \left\langle \sum_{j \neq i} \mathbf{u}_j(\mathbf{r}_{ij}) \right\rangle. \tag{12}$$

Here η is the solvent viscosity, a is the monomer radius, $\mathbf{u}_j$ is the flow field around monomer j, and $\langle \cdot \rangle$ is the average over polymer configurations. The problem now is reduced to calculating the average velocity field produced by $\mathbf{f}_m$ applied on each monomer.

The flow field around each monomer can be calculated by solving the Stokes equation for an incompressible liquid with the following boundary conditions: (i) vanishing velocity field at infinity, (ii) vanishing normal component of flow field at the monomer surface, and (iii) the integral of the stress tensor over the surface of the monomer corresponding to $\mathbf{f}_m$. The result is

$$\mathbf{u}(\mathbf{r}) = -\frac{1}{8\pi\eta r}(\hat{\mathbf{r}}\hat{\mathbf{r}} + \mathbf{I}) \cdot \mathbf{f}_m + \frac{a^2}{8\pi\eta r^3}(3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \mathbf{f}_m, \tag{13}$$

with r the distance from the monomer, $\hat{\mathbf{r}} = \mathbf{r}/|\mathbf{r}|$ the related unit vector, and $\mathbf{I}$ the unit tensor. This expression was also employed by Di Leonardo *et al* [48] to investigate colloids in the proximity of a wall. To calculate the average velocity from equation (13) the faster decaying term $(1/|\mathbf{r}_{ij}|)^3$ can be neglected, such that

$$\left\langle \sum_{j \neq i} \mathbf{u}_j(\mathbf{r}_{ij}) \right\rangle = -\frac{N}{6\pi\eta} \frac{1}{R_h} \mathbf{f}_m, \tag{14}$$

with R_h the hydrodynamic radius of the polymer,

$$\frac{1}{R_h} = \frac{1}{N^2} \left\langle \sum_i^N \sum_{j \neq i}^N \frac{1}{|\mathbf{r}_{ij}|} \right\rangle. \tag{15}$$

Considering now that $R_h \sim aN^\nu$, and $\mathbf{f}_m^0$ is independent of polymer length, and substituting equation (14) in equation (12) and then in equation (11), we have that $\mathbf{f}_m \sim N^{\nu-1}$ and finally

$$\mathbf{f} \sim N^\nu. \tag{16}$$

This means that the dependence on the length of the thermophoretic force and the self-diffusion coefficient of the polymer cancel each other such that D_T becomes polymer length independent in agreement with the experimental results.

7.2. Short polymers

For low-weight polymer, $\mathbf{f}'$ is important and cannot be ignored, and furthermore the scaling arguments cannot really be applied. In any case, it is reasonable to assume that D_s will have a strong dependence on the polymer size. Since $\mathbf{f}'$ is independent of the polymer size, the term $\mathbf{f}'D_s$ in equation (8) will be responsible for the polymer length dependence of D_T.

7.3. Discussion

In contrast to our argument, previous related studies of polymer thermophoresis [49, 21–23] regard hydrodynamic

interactions as negligible. The flow field around a freely moving monomer in a temperature gradient is shown to decay with $1/r^3$ [50, 21]. This flow field can be understood as the one produced by a fixed object (in equation (13)) superimposed with the flow field of a moving particle under external forces, for which the term proportional to $1/r$ exactly cancels the first term on the right hand side of equation (13). Therefore, we agree that the thermophoretic velocity is not strongly affected by hydrodynamic interactions, and consequently D_T shows no dependence on the polymer length. Nonetheless, a separate inference is whether hydrodynamic interactions are or are not negligible in the thermophoretic force and friction. In the case that they are disregarded [21, 23], the scaling would be $\mathbf{f} = N\mathbf{f}_m^0 \sim N$, and the friction coefficient would behave following the Rouse behavior $\zeta \sim N$, which would coexist with the well-known friction coefficient of the normal diffusion with scaling law $\sim N^\nu$. In our argument, the scaling law of the thermophoretic force is explicitly evaluated in the absence of the opposing friction; this is when the polymer is averagely fixed, which proves the relevance of hydrodynamic interactions. The size-independent D_T can then be understood as the cancelation of size dependence between the thermophoretic force and the friction coefficient, without introducing any additional friction coefficient.

8. Conclusions

We propose a new expression for the Soret coefficient in terms of the difference in the mechanical driving forces induced by the presence of temperature inhomogeneities on the constituent particles of the mixture. In principle, the Soret coefficient is then not simply proportional to the force exerted on only one component but on all of them. The formalism is based on the van Kampen equation for the mass flux in inhomogeneous systems, and it is valid for systems as fundamentally different as colloidal dispersions and molecular mixtures. The new expression is validated by means of computer simulations and results to be especially suitable for studying the thermal diffusion of dilute solutions, providing, for example, the theoretical basis for a method denoted as SPTA. For dilute polymer solutions, we present a hydrodynamic argument that shows that the thermodiffusion coefficient D_T of large polymers is size independent. For short polymer chains the combination of this argument with the validated expression can nicely explain the existence of a size-dependent D_T, in agreement with experimental observations.

Acknowledgment

References

[1] Ludwig C 1856 *Sitzber., Preuss. Akad. Wiss., Phys. Math. Kl.* **20** 539
[2] Soret C 1879 *Arch. Sci. Phys. Nat.* **3** 48
[3] Jones R C and Furry F H 1946 *Rev. Mod. Phys.* **18** 151
[4] Giddings J 1993 *Science* **260** 1456–65
[5] Wiegand S 2004 *J. Phys.: Condens. Matter* **16** R357–79
[6] Piazza R and Parola A 2008 *J. Phys.: Condens. Matter* **20** 153102
[7] Jiang H R, Wada H, Yoshinaga N and Sano M 2009 *Phys. Rev. Lett.* **102** 208301
[8] Duhr S and Braun D 2006 *Proc. Natl Acad. Sci.* **103** 19678–82
[9] Wienken C J, Baaske P, Rothbauer U, Braun D and Duhr S 2010 *Nature Commun.* **1** 1093
[10] Haase R 1949 *Z. Phys.* **127** 1
[11] Prigogine I, deBrouckere L and Amand R 1950 *Physica* **16** 577
[12] Tichacek L, Kmack W and Drickamer H 1956 *J. Phys. Chem.* **60** 660
[13] Shukla K and Firoozabadi A 1998 *Ind. Eng. Chem. Res.* **37** 3331
[14] Kempers L 2001 *J. Chem. Phys.* **115** 6330
[15] Artola P A, Rousseau B and Galliero G 2008 *J. Am. Chem. Soc.* **130** 10963–9
[16] Bringuier E and Bourdon A 2003 *Phys. Rev. E* **67** 011404
[17] Dhont J K G 2004 *J. Chem. Phys.* **120** 1642–53
[18] Dhont J K G, Wiegand S, Duhr S and Braun D 2007 *Langmuir* **23** 1674
[19] Fayolle S, Bickel T, Le Boiteux S and Würger A 2005 *Phys. Rev. Lett.* **95** 208301
[20] Schimpf M E and Semenov S N 2000 *J. Phys. Chem.* B **104** 9935–42
[21] Würger A 2007 *Phys. Rev. Lett.* **98** 138301
[22] Würger A 2009 *Phys. Rev. Lett.* **102** 078302
[23] Bringuier E 2010 *Physica* A **389** 4545–51
[24] Schimpf M E and Giddings J C 1989 *J. Polym. Sci.* B **27** 1317
[25] Rauch J and Köhler W 2005 *Macromolecules* **38** 3571–3
[26] Stadelmaier D and Köhler W 2008 *Macromolecules* **41** 6205–9
[27] Stadelmaier D and Köhler W 2009 *Macromolecules* **42** 9147
[28] de Groot S R and Mazur P 1984 *Nonequilibrium Thermodynamics* (New York: Dover)
[29] Hafskjold B, Ikeshoji T and Ratkje S K 1993 *Mol. Phys.* **80** 1389–412
[30] Reith D and Müller-Plathe F 2000 *J. Chem. Phys.* **112** 2436–43
[31] Galliéro G, Duguay B, Caltagirone J P and Montel F 2003 *Fluid Phase Equilib.* **208** 171–88
[32] Artola P A and Rousseau B 2007 *Phys. Rev. Lett.* **98** 125901
[33] Leonardi E, D'Aguanno B and Angeli C 2010 *J. Chem. Phys.* **132** 124512
[34] van Kampen N 1988 *J. Phys. Chem. Solids* **49** 673
[35] Widder M and Titulaer U M 1989 *Physica* A **154** 452
[36] van Kampen N 1992 *Stochastic Processes in Physics and Chemistry* (Amsterdam: North-Holland)
[37] Yang M and Ripoll M 2011 *J. Chem. Phys.* submitted
[38] Bearman R and Kirkwood J 1958 *J. Chem. Phys.* **28** 136
[39] Morozov K I 2009 *Phys. Rev. E* **79** 031204
[40] Galliéro G and Volz S 2008 *J. Chem. Phys.* **128** 064505
[41] Hartung M, Rauch J and Köhler W 2006 *J. Chem. Phys.* **125** 214904
[42] Ning H, Dhont J K G and Wiegand S 2008 *Langmuir* **24** 2426–32
[43] Braibanti M, Vigolo D and Piazza R 2008 *Phys. Rev. Lett.* **100** 108303
[44] Bringuier E 2007 *Phil. Mag.* **87** 873–83
[45] Müller-Plathe F 1997 *J. Chem. Phys.* **106** 6082–5
[46] Allen M P and Tildesley D J 1987 *Computer Simulations in Liquids* (Oxford: Clarendon)
[47] Zhang M and Müller-Plathe F 2006 *J. Chem. Phys.* **125** 124903
[48] Di Leonardo R, Ianni F and Ruocco G 2009 *Langmuir* **25** 4247
[49] Brochard F and de Gennes P G 1981 *C.R. Acad. Sci., Paris* II **293** 1025
[50] Anderson J L 1989 *Annu. Rev. Fluid Mech.* **21** 61