

Thermophoresis of dissolved molecules and polymers: Consideration of the temperature-induced macroscopic pressure gradient

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The movement of molecules and homopolymer chains dissolved in a nonelectrolyte solvent in response to a temperature gradient is considered a consequence of temperature-induced pressure gradients in the solvent layer surrounding the solute molecules. Local pressure gradients are produced by nonuniform London–van der Waals interactions, established by gradients in the concentration (density) of solvent molecules. The density gradient is produced by variations in solvent thermal expansion within the nonuniform temperature field. The resulting expression for the velocity of the solute contains the Hamaker constants for solute-solvent and solute-solute interactions, the radius of the solute molecule, and the viscosity and cubic coefficient of thermal expansion of the solvent. In this paper we consider an additional force that arises from directional asymmetry in the interaction between solvent molecules. In a closed cell, the resulting macroscopic pressure gradient gives rise to a volume force that affects the motion of dissolved solutes. An expression for this macroscopic pressure gradient is derived and the resulting force is incorporated into the expression for the solute velocity. The expression is used to calculate thermodiffusion coefficients for polystyrene in several organic solvents. When these values are compared to those measured in the laboratory, the consistency is better than that found in previous reports, which did not consider the macroscopic pressure gradient that arises in a closed thermodiffusion cell. The model also allows for the movement of solute in either direction, depending on the relative values of the solvent and solute Hamaker constants.

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I. BACKGROUND

In 1856 Ludwig reported on the migration of molecules in response to a temperature gradient [1]. Nearly a century later this transport process was used by Debye and Bueche to fractionate polymers [2]. Since then a great number of studies have been reported, both theoretical and empirical in nature, aimed at understanding this complex phenomenon which is referred to by a variety of names, including thermal diffusion, thermodiffusion, thermophoresis, and the Soret effect. As outlined below, our model considers the movement of mass in a temperature gradient to be a surface driven effect, therefore, we prefer the term thermophoresis.

The system designed by Debye and Bueche relied on the use of convection currents established by thermophoresis in a vertical column to separate polymers with low resolution. Since then, a variety of systems have been designed to measure and quantify thermophoresis in the absence of convection. An early method developed for studying thermophoresis is based on the deflection of a laser beam [3–6] to monitor mass movement in a temperature gradient. Thermophoresis has also been studied in a thermal lens [7,8], where laser beams are used to not only monitor the mass migration, but to heat the surrounding fluid. In the technique of forced Raleigh scattering, two laser beams are used to produce a spatially modulated concentration gradient of solute with properties governed by thermophoresis [9–15]. In our laboratories we have studied polymer and colloid thermophoresis using thermal field-flow fractionation (ThFFF). In this technique, a temperature gradient applied across the thin dimension of a ribbon-shaped (Thomaes) cell is used to retard the migration of dissolved or suspended material though the cell in a quantifiable manner related to the material's thermo-

phoresis [16]. ThFFF is used primarily to separate and characterize polymers on an analytical scale [17], but its ability to measure thermophoresis with high accuracy and precision has been known since 1970 [18].

In the first of several systematic studies, we demonstrated the independence of polymer thermophoresis on chain length and branching [19], as predicted by Brochard and de Gennes [20]. In a subsequent study, the thermophoretic properties of polystyrene, poly(α -methyl)styrene, polymethylmethacrylate, and polyisoprene in several organic solvents was used to systematically examine the myriad of existing theories in the literature [21]. That work clearly demonstrated that polymer-solvent interactions play an important role in thermophoresis.

The independence of polymer thermophoresis on chain length and branching means that a homopolymer chain moves in a temperature gradient with the same velocity as each individual monomer unit (mer). As a result, one can model polymer thermophoresis using the same approach as that used for particles, where the mers are initially considered to be spherical particles for the sake of simplicity. Several models of particle thermophoresis have been presented over the past few decades. The approach of modeling thermophoresis as a surface driven phenomenon was first considered by Ruckenstein [22]. Piazza and Guarino [23] found the Ruckenstein model to yield qualitative prediction of the electrostatic contribution to the thermophoresis of charged micelles. In a model presented by Morozov [24,25], particle thermophoresis is a result of stresses induced by the redistribution of solutes around a suspended colloid. Bringuier and Bourdon [26] use a purely kinetic approach, beginning with Brownian motion and incorporating a temperature-dependent internal energy, which is governed by the interaction of par-

ticles with their surroundings. The model is in qualitative agreement with measured thermophoretic behavior of colloids, including the potential for thermophoresis in both directions. As with other models, however, it cannot be used for quantitative predictions of particle thermophoresis.

Our approach considers the flow of liquid caused by the gradient in osmotic pressure within the surface layer of the particle [27], ignoring (for now) any interaction between mers. Although the thermophoresis of any dissolved solute can be considered with this approach, we use measurements of polymer thermophoresis to check the theory because of the greater availability of such data. In the following discussion, the term solute will be used to indicate anything dissolved in a liquid, including the mers in a polymer as well as other low-molecular weight molecules.

In the case of colloids and microscopic particles suspended in a liquid, the excess osmotic pressure Π in the surface layer due to the accumulation of solutes (e.g., salts and surfactant molecules) is often written as

$$\Pi = kTc_0[e^{-\Phi(x)/kT} - 1], \quad (1)$$

where k is Boltzmann's constant, T is the temperature, c_0 is the solute concentration in the bulk liquid, Φ is the surface potential responsible for solute accumulation, and x is the coordinate normal to the particle surface. Combined with the local temperature-induced pressure gradient in the particle surface layer, this expression also describes the macroscopic pressure gradient $kc_0\nabla T$ established in the solvent, even when suspended particles are absent. The aim of this paper is to consider such a macroscopic pressure gradient in calculations of solute thermophoretic mobility.

Equation (1) assumes that the concentration of solute in the surface layer is low enough that its volume is negligible compared to the volume of surrounding solvent molecules. This assumption holds for suspensions in which the surfactant or ion concentration does not exceed (10^{-3} – 10^{-2}) M . In the absence of ions and surfactants, only solvent molecules can take part in the accumulation process, in the form of variations in solvent density around the solute. In such cases, the only volume available for solvent accumulation is the free volume of the solvent, which is 10–20% of the entire volume occupied by the body of the molecules [28], as indicated by volume changes associated with melting. Thus, the concentration of solvent molecules in the surface layer is quite high, and the use of a Boltzmann distribution, as expressed in Eq. (1), is inappropriate. Nevertheless, the local excess pressure gradient around the solute molecule can act as a driving force in solute thermophoresis, and we described a method for overcoming the limitation of Eq. (1) in a previous paper [29]. The method is too complex to reiterate here, and only the resulting equations are summarized below.

In most papers on particle phoresis, the thickness of the surface layer is assumed to be much smaller than the radius of the particle. Such an assumption is not valid for solutes, which have a size that exceeds that of the solvent molecules by several times at most. For particle electrophoresis, Teubner [30] presented a more general approach, in which particles having an arbitrary surface layer thickness were exam-

ined. We have modified the model developed by Teubner, in order to evaluate the hydrodynamic situation of solvent molecules moving in the vicinity of solutes during thermophoresis.

Most ThFFF experiments on polymers have been carried out in solvents with low electrical conductivities, where ions are not present in appreciable quantities. In such solvents, only dipole-dipole interactions play a role [31]. These include interactions between permanent dipoles (Keesom interactions), those between permanent and induced dipoles (Debye induction interactions), and those induced spontaneously (London dispersion interactions). According to the Fowkes approach [31], these dipole-dipole interactions have a common dependence on the distance between dipoles, and may be written in the following simple form

$$\Phi(r) = -\frac{16A(r_m r_0)^3}{9r^6}. \quad (2)$$

Here, A is the Hamaker constant used in colloid chemistry to characterize the potential energy of dipole-dipole interactions between a solute of radius r_m and a solvent molecule of radius r_0 , or between two solvent molecules ($r_m = r_0$). The closest approach distance (r_{\min}) between interacting mers and solvent molecules in the Fowkes model is approximated by $r_{\min} = \sqrt{r_m r_0}$. This approximation compensates for a discrepancy that occurs at short distances when Eq. (2) is used in place of the exact form of the interaction potential. The Hamaker constant is governed by the permanent dipole moments of the monomer and solvent molecules, and on the low and high frequency electric susceptibilities, which govern London dispersion forces [31].

The derivation of thermophoretic mobility can be divided into five stages. (1) Calculation of the local temperature distribution around the solute. (2) Derivation of the local excess pressure distribution around the solute or the selected solvent molecule due to solute-solvent or solvent-solvent interactions, respectively. (3) Derivation of the expressions for the solvent velocity profile around the solute or solvent molecule due to the local pressure gradient, and the resulting thermophoretic velocity of the molecule. (4) Derivation of the macroscopic pressure gradient established in the solvent as a compensation of the thermophoretic force acting on the solvent molecules in the temperature gradient. (5) Derivation of the general expression for the net velocity of the solute.

II. THEORY

A. Temperature distribution around the solute

Calculation of the temperature distribution around the solute is outlined in many papers on particle thermophoresis (e.g., see Ref. [27]). We discuss the formulation of the problem and the final results only, considering the molecule to be a spherical particle.

It is assumed that the temperature distributions inside and outside the particle (T_i and T_e , respectively), as obtained from the temperature conduction equation, have the following dipole forms:

$$T_i = \nabla T r \cos \vartheta, \quad (3)$$

$$T_e = T_0 + \nabla_i T r \cos \vartheta + \frac{M_T}{r^2} \cos \vartheta. \quad (4)$$

Here, T_0 is the temperature at the center of the particle, r is the distance from its center, ϑ is the angle between the radius vector \vec{r} and the outer temperature gradient ∇T , M_T is the temperature dipole moment of the particle, and $\nabla_i T$ is the internal temperature gradient in the particle. On the molecule surface ($r = r_m$), we have the following boundary conditions:

$$T_i = T_e, \quad (5)$$

$$\theta_i \frac{\partial T_i}{\partial r} = \theta_e \frac{\partial T_e}{\partial r}, \quad (6)$$

where θ_i and θ_e are the thermal conductivities of the particle and external liquid, respectively. Equations (3)–(6) give the complete picture of the temperature distribution around the mer or other solute molecule. Using the definition $M_T = \nabla T [(1-n)/(n+2)] r_m^3$ obtained in calculations, Eq. (4) can also be expressed in the form

$$T_e = T_0 + \nabla T r_m \cos \vartheta \left(\frac{r}{r_m} + \frac{1-n}{n+2} \frac{r_m^2}{r^2} \right), \quad (7)$$

where $n = \theta_i / \theta_e$. For further calculations, it is convenient to write the following expressions for the tangential and radial components of the temperature gradient, respectively:

$$\nabla T_{\vartheta} = -\nabla_{\vartheta} T \sin \vartheta \left(1 + \frac{1-n}{n+2} \frac{r_m^3}{r^3} \right), \quad (8a)$$

$$\nabla_r T = \nabla T \cos \vartheta \left(1 - 2 \frac{1-n}{n+2} \frac{r_m^3}{r^3} \right). \quad (8b)$$

These expressions are easily converted to the corresponding expressions for the solvent molecule by the obvious substitutions $r_m \rightarrow r_0$, $n = 1$.

B. Local pressure distribution around the solute

The concentration of solvent molecules in a force field obeys the convection-diffusion equation, which takes the following form for concentrated systems [32]:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \left\{ \frac{K(\phi)}{6\pi\eta r_0} \left[\frac{d\Pi}{d\phi} \nabla \phi + \frac{\phi}{v_0} \nabla \Phi \right] \right\}. \quad (9)$$

Here t is time, η is solvent viscosity, $K(\phi)$ is the coefficient describing the concentration dependence of the hydrodynamic friction (its concrete form does not require further consideration), v_0 is the specific volume occupied by one solvent molecule, Φ is the interaction potential given by Eq. (2), and ϕ is the volume fraction of solvent, which is related to the numeric concentration c_0 by

$$\phi = v_0 c_0. \quad (10)$$

Under steady-state conditions, Eq. (9) is transformed into the following equation [32], which defines the local excess pressure around the solute based on the condition of local hydrostatic equilibrium across the solute surface layer in the direction perpendicular to the surface

$$\frac{d\Pi}{dx} + \frac{\phi}{v_0} \frac{d\Phi}{dx} = 0. \quad (11)$$

In order to define the local pressure resulting from solute-solvent or solvent-solvent interactions, we assume that changes in the solvent concentration around the solute due to solvent-solute interactions are low enough to use the unperturbed solvent molecule concentration in solving Eq. (11):

$$\Pi = - \frac{\Phi(r)}{v_0}. \quad (12)$$

Equation (12) defines the local excess pressure in the solvent mixture due to the presence of the selected molecule and its interaction with other solvent molecules; solute-solute interactions are neglected. Using Eq. (12) we calculate the local temperature-induced pressure gradient in the solvent around the solute as

$$\nabla \Pi = \frac{\alpha_T \Phi}{v_0} \nabla T, \quad (13)$$

where α_T is the cubic thermal expansion coefficient of the solvent, defined as

$$\alpha_T = \frac{\partial \ln v_0}{\partial T}. \quad (14)$$

In principle, the temperature dependence of any parameter contained in Eq. (12) could lead to the establishment of a local pressure gradient around the solute. However, terms associated with the temperature dependence of the interaction potential are compensated by the respective volume force arising in the solvent due to spatial changes of the interaction potential. Therefore, only the temperature dependence of the solvent parameters is considered in Eq. (13).

Equation (13) represents the expression for the local temperature induced pressure gradient, which will be used to solve the hydrodynamic problem of solvent flow around the solute. This expression is not related to any model equation of state for the solvent; it contains solvent parameters that can be independently obtained.

C. Flow velocity profile around the solute and solute thermophoretic velocity

The flow velocity profile in the solute surface layer is defined by the Navier-Stokes equation

$$\eta \Delta \vec{u} = -\nabla \Pi, \quad (15)$$

where \vec{u} is velocity of the liquid. In solving Eq. (15) for a spherical particle, we use the approach taken by Teubner [30], which utilizes the generalized reciprocal theorem on the invariance of the following integral:

$$\eta \int_S \vec{u}' \cdot \hat{\sigma} \cdot d\vec{S} + \eta \int_V \vec{u}' \cdot \vec{f} dV = \eta' \int_S \vec{u} \hat{\sigma}' \cdot d\vec{S} + \eta' \int_V \vec{u} \cdot \vec{f}' dV. \quad (16)$$

Here, S is the outer surface of a moving body, V is the outer volume surrounding this surface, and $\hat{\sigma}$ is the hydrodynamic stress tensor expressed by the components of the flow velocity gradient [33]. The primed and unprimed parameters in Eq. (16) are interrelated in two separate problems on the movement of a given body. The theorem was proven by Teubner [30] for the case in which only a volume force is acting in a liquid, and the osmotic pressure gradient is absent. However, the Navier-Stokes equation allows the external volume force in a liquid to be interchanged with a predetermined “external” pressure gradient. Thus, the reciprocal theorem can be generalized to situations where only the predetermined pressure gradient is present in a liquid. We use this generalization and the results in reference [30], which relates particle phoresis to the volume force and fluid velocity distribution in the space around a particle moving with constant unit velocity $\vec{U}_1(\vec{r})$, where \vec{r} is the radius vector directed from the particle center to the observation point, analogous to the temperature distribution problem. The velocity distribution $\vec{U}_1(\vec{r})$ that corresponds to the boundary conditions $\vec{U}_1(r=r_m)=\vec{u}_0$ and $\vec{U}_1(r=\infty)=0$, is defined as [33]

$$\vec{U}_1(\vec{r}) = \frac{3}{4} \frac{r_m}{r} [\vec{u}_0 + \vec{n}_0(\vec{u}_0 \cdot \vec{n}_0)] + \frac{1}{4} \left(\frac{r_m}{r} \right)^3 \times [\vec{u}_0 - 3\vec{n}_0(\vec{u}_0 \cdot \vec{n}_0)], \quad (17)$$

where \vec{u}_0 is the unit vector directed along the \vec{U}_1 vector and \vec{n}_0 is the unit vector directed along the radius vector. Instead of the volume force considered in Ref. [30], we combine the local excess pressure gradient defined in Eq. (13) with the temperature gradient distribution defined in Eq. (8). Using the steady-state condition that the sum of the hydrodynamic friction force and the thermophoretic force acting on the particle is equal to zero, we obtain the following general expression for the thermophoretic velocity U_T^{loc} related to the local pressure gradient:

$$U_T^{\text{loc}} = \frac{1}{6\pi\eta r_m} \int_0^\pi \sin \vartheta d\vartheta \int_{r_H}^\infty 2\pi r^2 dr \frac{d\Pi}{dT} [\vec{U}_1 \cdot (\nabla \vec{T})]. \quad (18)$$

Next, we substitute expressions for the temperature gradient and the temperature derivative of the local excess pressure into Eq. (18). By substituting Eqs. (2), (8), (13), and (17) into Eq. (18) and carrying out some simple but cumbersome integral calculations, we obtain the following expression for the thermophoretic velocity of the solute:

$$U_T^{\text{loc}} = -\frac{16}{27} \frac{\alpha_T A r_m^2}{v_0 \eta} \left(\frac{1}{2} + \frac{2}{63} \frac{n-1}{n+2} \right) \nabla T. \quad (19)$$

Parameter $(n-1)/(n+2)$ changes from a value of $-1/2$ at $n=0$ to 1 as $n \rightarrow \infty$. Therefore, the terms in Eq. (19) that

contain this parameter cannot exceed about 6% and can be neglected. Thus, the difference in thermal conductivities of the solute and solvent is not a significant factor in solute thermophoresis.

Ignoring the negligible terms, the solute thermophoretic mobility (thermodiffusion coefficient) b_T^{loc} arising from the local pressure gradient, which is defined as the thermophoretic velocity per unit temperature gradient, is expressed as

$$b_T^{\text{loc}} = -\frac{8}{27} \frac{\alpha_T A r_m^2}{v_0 \eta}. \quad (20)$$

Equation (20) contains two parameters that characterize the solute, namely, its radius (r_m) and the Hamaker constant that defines its interaction with the solvent (A). The equation also contains parameters that characterize the solvent: the cubic thermal expansion coefficient (α_T), the specific volume (v_0), and the solvent viscosity (η). The solvent parameters can be measured independently, and many are tabulated (e.g., see Refs. [34,35]).

D. Macroscopic pressure gradient and its contribution to thermophoretic velocity

Repeating the considerations leading to Eq. (20), one can obtain a similar equation for the thermophoretic mobility of solvent molecules

$$b_T^0 = -\frac{8}{27} \frac{\alpha_T A_s r_0^2}{v_0 \eta}, \quad (21)$$

where A_s is the Hamaker constant for the solvent molecules. Unlike the thermophoretic mobility of polymers or other solute molecules, the thermophoretic mobility of the solvent cannot be observed directly. Nevertheless, it is related to a situation in which solvent molecules placed on the hot side of the selected solute molecule are at a larger distance than solvent molecules placed on the cold side (in the case of a positive thermal expansion coefficient). Because the interaction with hot-hand and cold-hand molecules is distinct, the resulting spatial asymmetry leads to a net force acting on the solute.

The specific force acting on unit volume of the solvent, in which $1/v_0$ solvent molecules is contained, can be written as

$$f = \frac{6\pi\eta r_0}{v_0} b_T^0 \nabla T. \quad (22)$$

In a closed cell, as in the FFF channel, the solvent cannot move *in total*, therefore, this specific force must be compensated by a macroscopic pressure gradient. The result of this process is described by an equation of hydrostatic balance similar to Eq. (11), which gives the following temperature-induced macroscopic pressure gradient:

$$\nabla \Pi_{\text{macro}} = \frac{6\pi\eta r_0}{v_0} b_T^0 \nabla T. \quad (23)$$

Equation (23) is true only for a closed cell, whereas the specific volume force given by Eq. (22) has the more general application to any system with a temperature gradient. For example, in open channels with a longitudinal temperature gradient this force can cause various liquid flows, such as those observed in experiments with thermocapillary motion. This force can also contribute to thermoconvection in a closed cell placed in a gravity field.

The particle placed in the pressure gradient experiences the force expressed as the integral of the pressure on the particle surface [33]. Using this rule in relation to Eq. (23), we obtain the following expression for the force acting on a particle placed in a macroscopic temperature gradient:

$$F_{\text{macro}} = -6\pi\eta r_0 \frac{v_m}{v_0} b_T^0 \nabla T, \quad (24)$$

where v_m is the partial specific volume of the solute. Dividing this expression by the hydrodynamic friction coefficient $f = 6\pi\eta r_m$ for the solute, we obtain the contribution of the macroscopic pressure gradient to the thermophoretic velocity of the solute

$$U_T^{\text{macro}} = -\frac{v_m r_0}{v_0 r_m} b_T^0 \nabla T. \quad (25)$$

By combining Eqs. (25) and (18), we obtain the net velocity resulting from the local and macroscopic pressure gradients

$$U_T = U_T^{\text{loc}} - U_T^{\text{macro}} = \left(b_T^{\text{loc}} - \frac{v_m r_0}{v_0 r_m} b_T^0 \right) \nabla T. \quad (26)$$

III. MAIN OUTCOMES AND RESULTS

The polymer thermophoretic mobility b_T is the velocity per unit temperature gradient, which is obtained by the rearrangement of Eq. (26):

$$b_T = b_T^{\text{loc}} - \frac{v_m r_0}{v_0 r_m} b_T^0. \quad (27)$$

Substituting Eqs. (20) and (21) into Eq. (27) we obtain a general expression for the thermophoretic mobility of solute in a closed cell:

$$b_T = -\frac{8}{27} \frac{\alpha_T \sqrt{A_p A_s} r_m^2}{v_0 \eta} \left(1 - \frac{v_m r_0^3}{v_0 r_m^3} \sqrt{\frac{A_s}{A_p}} \right), \quad (28)$$

where the following Fowkes approximation [31] is used for the Hamaker constant that characterizes mer-solvent interactions:

$$A = \sqrt{A_p A_s}. \quad (29)$$

Here, A_p and A_s are the Hamaker constants for the polymer and solvent, respectively.

Equation (28) contains the specific volume rationed to the third power of the radius for both solute and solvent molecules. This ratio, subsequently referred to as the character-

TABLE I. Estimation of monomer and solvent radii.

Solvent or monomer	Radius (Å)	
	Eq. (33)	Eq. (34)
Cyclohexane	7.0	2.8
Benzene	6.5	2.6
Toluene	6.9	2.8
Ethylbenzene	7.3	2.9
Methylethyl ketone	6.6	2.6
Tetrahydrofuran	6.4	2.5
Ethyl acetate	6.8	2.7
Styrene	7.2	2.9

istic ratio, is dimensionless and varies with the geometry of the molecule. For spherically symmetric molecules, the characteristic ratio is

$$\frac{v_0}{r_0^3} = \frac{v_m}{r_m^3} = \frac{4\pi}{3}. \quad (30)$$

The physical volume of the solute v_m is typically considered to be equal to the partial specific volume, which corresponds to an increase in the liquid volume when a single solute molecule is hypothetically added to this liquid. This approach is used successfully in the theory of sedimentation methods [16]. For the solvent, the specific volume occupied by the molecule and the partial specific volume are equivalent.

Determination of solute hydrodynamic volume, which is equal to $(4\pi/3)r_m^3$ becomes more complicated with increasing asymmetry in molecular shape. Most molecules are not, in fact, spherical. However, many can be approximated by an ellipse, or by cylinders with an aspect ratio close to unity. In such cases, the hydrodynamic radius can be approximated as half the molecule's maximal dimension, if we consider the molecule to be freely rotating in its Brownian (diffusional) motion. Consequently, its hydrodynamic volume can be approximated by a sphere with that radius, and the characteristic ratio can be approximated by Eq. (30). For molecules with more extreme asymmetry, such as disks or elongated ellipsoids, estimates of their hydrodynamic volume based on the volume swept out by a rotating molecule are likely to be high.

For solutes without a large degree of shape asymmetry, substitution of Eqs. (29) and (30) into Eq. (28) yields

$$b_T = -\frac{8}{27} \frac{\alpha_T \sqrt{A_p A_s} r_m^2}{v_0 \eta} \left(1 - \sqrt{\frac{A_s}{A_p}} \right). \quad (31)$$

By comparing Eq. (31) to Eq. (20), which considers only the local pressure gradient as the driving force [29], it is apparent that our consideration of the macroscopic pressure gradient in this work is accounted for by a simple correction term $1 - \sqrt{A_s/A_p}$. Next, we consider the impact of this correction term on the agreement between values of b_T calculated from the model and those measured by ThFFF.

TABLE II. Hamaker constants used to calculate thermophoretic mobilities.

Polymer or solvent	Average A_p (ergs) {range} [38]	Average A_s (ergs) {range} [39]	$A = \sqrt{A_s A_p}$ (ergs) [Eq. (29)]
Styrene	8.1×10^{-13} {6.37–9.8 × 10 ⁻¹³ }		
Cyclohexane		5.2×10^{-13} {4.64–5.9 × 10 ⁻¹³ }	6.5×10^{-13}
Benzene		5.0×10^{-13}	6.3×10^{-13}
Toluene		5.7×10^{-13} {5.3–6.1 × 10 ⁻¹³ }	6.5×10^{-13}
Methylethyl ketone		4.6×10^{-13} {4.53–4.7 × 10 ⁻¹³ }	6.1×10^{-13}
Ethyl acetate		4.17×10^{-13}	5.8×10^{-13}

The greatest uncertainty in evaluating our proposed model lies in the value assigned to the mer radius r_m , because empirical values are not available. In this work we calculate r_m by first estimating the specific volume of the solute as

$$v_m = \frac{M_m}{d_m N_a}, \quad (32)$$

where M_m and d_m are the molecular mass and density of the mer and N_a is Avagadro's number. We approximate the density of the mer by the density of liquid monomer. Next the radius r_m is calculated using a model that relates the specific volume occupied by one molecule to its radius. In Ref. [29], we used the state equation for a hexagonal crystal consisting of closely packed spheres

$$v_m = \frac{\pi r_m^3}{6}. \quad (33)$$

Equation (33) corresponds to the closest possible sphere packing of solvent molecules. When this equation was used in Eq. (20) (i.e., without considering the temperature induced macroscopic pressure gradient), it led to an overestimation of the thermophoretic mobilities. In fact, values calculated by this approach have exceeded measured values by as much as tenfold [36]. This discrepancy was eliminated by using a state equation that corresponds to a cubic crystal of spheres [37]:

$$v_m = 8r_m^3. \quad (34)$$

Table I compares the values calculated for the radius of a styrene mer, as well as the radii for several solvents, using Eq. (33) versus Eq. (34). The lower values obtained with Eq. (34) translate into a sixfold decrease in the values of the calculated thermophoretic mobilities.

Table II summarizes the Hamaker constants used in calculating thermophoretic mobilities. Individual values are reported for styrene (A_p) and each of several solvents (A_s) in which the thermophoretic mobility of polystyrene was measured in the laboratory. Also reported in Table II are the Hamaker constants (A) for each styrene-solvent pair, as calculated from Eq. (29). A range of A_p and A_s values are reported in the literature. We used a common source for all

of the solvent (A_s) values, so that the evaluation of solvent trends in b_T are not complicated by variance associated with the use of different methodologies for obtaining A_s values.

The other solvent parameters required to calculate values of b_T were also taken from a common source [34]; these are summarized in Table III. The specific volume occupied by a solvent molecule was calculated by

$$v_0 = \frac{M_0}{d_0 N_a}, \quad (35)$$

where M_0 and v_0 are the molecular weight and density of the solvent, respectively. Using the data from Tables I–III and Eq. (31), values of the thermophoretic mobilities for polystyrene in the various solvents were calculated; these are summarized in Table IV. Thermophoretic mobilities calculated using mer radii estimated by Eqs. (33) and (34) are labeled in Table IV as b_T^{\max} and b_T^{\min} , respectively. For comparison, Table IV also contains thermophoretic mobilities calculated using Eq. (21), i.e., without considering the macroscopic pressure gradient. Values calculated by Eq. (21) are labeled $b_T^{\text{loc,max}}$ if Eq. (33) was used to estimate r_m , and $b_T^{\text{loc,min}}$ if Eq. (34) was used for r_m . Finally, Table IV includes the values of b_T measured by ThFFF [5]. Values of b_T calculated using Eq. (33) for r_m are about six times larger than those calculated using Eq. (34). This range in values demonstrates the importance of an accurate mer radius in the calculation of thermophoretic mobilities.

Note that each of the values measured by ThFFF lies within the range of calculated values, provide the macro-

TABLE III. Solvent parameters used to calculate thermophoretic mobilities.

Solvent	α_T (K ⁻¹)	η (cP)	M_0 (g/mol)	d_0 (g cm ⁻³)	$v_0 \times 10^{22}$ (cm ³)
Cyclohexane	0.0012	0.98	84	0.78	1.79
Benzene	0.0012	0.65	78	0.89	1.45
Toluene	0.0011	0.55	92	0.87	1.75
Methylethyl ketone	0.0012	0.40	72	0.80	1.49
Ethyl acetate	0.0014	0.40	88	0.90	1.62

TABLE IV. Summary of calculated and measured values of the thermophoretic mobilities for polystyrene in several solvents.

Solvent	Thermophoretic mobility $b_T \times 10^8$ (cm ² s ⁻¹ K ⁻¹)				
	ThFFF	Calculated values			
		$b_T^{\text{loc,min}}$	$b_T^{\text{loc,max}}$	b_T^{min}	b_T^{max}
Cyclohexane	6.6			2.2	13.5
		10.8	67.5		
Benzene	8.9			4.1	25.6
		19.4	121.8		
Toluene	10.3			3.4	21.2
		21.1	132.8		
Methylethyl ketone	13.5			7.2	44.8
		29.9	186.6		
Ethyl acetate	11.6			8.5	53.3
		30.4	190.3		

scopic pressure gradient is taken into account [i.e., Eq. (31) is used]. By contrast, all values of b_T^{loc} , which consider only the local excess pressure gradient, are 2–3 times larger than the measured values. In principle, the correct mer radius can be calculated from values of b_T measured by ThFFF data, since all other parameters are independently obtained. Unfortunately, the uncertainty in the Hamaker constants makes such an approach impractical. On the other hand, one could measure mer radii by light scattering from the monomer solution, thermophoretic mobility by ThFFF, and use the information to calculate Hamaker constants in a new way.

Equation (31) predicts a change in the sign of the thermophoretic mobility (thermodiffusion coefficient) when a molecule is placed in a solvent with a high Hamaker constant, such that $A_s > A_m$. For polystyrene, where the Hamaker constant is high, this possibility is rather exotic, but for polypropylene oxide with a Hamaker constant of 3.95×10^{-13} erg [31], a negative thermophoresis (movement toward the hot wall) is possible in several organic solvents. Note that in our model, negative thermophoresis arises from a competition between the local temperature-induced pressure gradient due to solute-solvent interactions, and a macroscopic pressure gradient due to solvent-solvent interactions. When the latter interactions are stronger, negative thermophoresis is observed.

Finally, we consider an interesting situation with solute molecules that have more extreme shapes, such as that of a disk or elongated ellipsoid. For these molecules, the specific volume v_m will be significantly smaller than the volume of solvent swept out by the freely rotating molecule. In a prolate ellipsoid, for example, with transverse radius r_t , the ratio v_m/r_m^3 can be written as $\pi(r_t/r_m)^2$. From Eq. (28), the general equation for the thermophoretic mobility of such solutes is

$$b_T = -\frac{8}{27} \frac{\alpha_T A_s r_m^2}{v_0 \eta} \left[1 - \frac{3}{4} \left(\frac{r_t}{r_m} \right)^2 \sqrt{\frac{A_s}{A_p}} \right] \quad (\text{prolate ellipsoid}). \quad (36)$$

Thus, nonspherical molecules will undergo thermophoresis even in solvents that have Hamaker constants that are

equivalent to that of the solute. Consider, for example, solvent molecules that form clusters (oligomers). If we represent the solvent oligomers as rigid rods suspended in a liquid consisting of monomers with $v_m \ll v_0$, then Eq. (28) yields the following value for the thermophoretic mobility:

$$b_T = -\frac{8}{27} \frac{\alpha_T A_s r_0^2}{v_0 \eta} \quad (\text{rod-shaped solvent oligomers}). \quad (37)$$

IV. CONCLUSIONS

The model developed here for polymer and molecule thermophoresis takes the hydrodynamic approach similar to that recently proposed for suspended particles and polymers [27,29]. These models are based on the slip flow of liquid around the surface of a dilute component either dissolved or suspended in the liquid. The slip flow is induced by a pressure gradient, which is established by the temperature dependence of the solvent parameters. The difference between dissolved polymers and suspended particles lies in the source of the local pressure gradient. With suspended particles, the osmotic pressure gradient is produced by a gradient in the concentration of dissolved solutes near the comparatively large particle surface. In polymer or molecular solutions, the pressure gradient is produced solely by a temperature-related gradient in the concentration of solvent molecules. The resulting slip flow is strong enough to induce thermophoresis of the mers or molecules in pure solvents.

The resulting expression for the thermophoretic mobility of the solute is based on a mathematical procedure developed previously for modeling electrophoresis. By applying the same procedure to calculations of the solvent thermophoretic mobility in a closed cell with no convection, a volume force that is compensated by a macroscopic pressure gradient is derived. The thermophoretic movement of the solute molecule is a net force from the combined action of the local pressure gradient around the molecule and the force caused by the macroscopic pressure gradient.

Compared to values measured by ThFFF, thermophoretic mobilities calculated by the model are 2–10 times larger when only the local pressure gradient is considered. By contrast, the range of predicted values bracket the experimental values when both the local and macroscopic pressure gradients are considered. Variations within the range are due to uncertainties in the estimations of molecular radii. When radii are chosen so that calculated values of the thermophoretic mobilities match those measured in the laboratory, the radii are similar for the different solvents examined.

The “thermophoretic” force responsible for the macroscopic pressure gradient may introduce significant corrections in the general understanding of thermoconvection and thermocapillary motion. Finally, the competition between local and macroscopic gradients can result in negative molecular thermophoresis in solvents whose Hamaker constants are higher than that of the solute.

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- [1] C. Ludwig, *Sitzungsber. Akad. Wiss. Wein* **20**, 539 (1856).
- [2] P. Debye and A. M. Bueche, *High Polymer Physics*, edited by H. A. Robinson (Chemical Publishing, New York, 1948).
- [3] M. Giglio and A. Vendramini, *Phys. Rev. Lett.* **34**, 561 (1975).
- [4] M. Giglio and A. Vendramini, *Phys. Rev. Lett.* **38**, 26 (1976).
- [5] P. Kolodner, H. Williams, and C. Moe, *J. Chem. Phys.* **88**, 6512 (1988).
- [6] K. J. Zhang, M. E. Briggs, R. W. Gammon, and J. V. Sengers, *J. Chem. Phys.* **104**, 6881 (1996).
- [7] N. V. Tabiryan and W. L. Luo, *Phys. Rev. E* **57**, 4431 (1998).
- [8] T. Du and W. Luo, *Phys. Lett.* **72**, 272 (1998).
- [9] K. Thyagarajan and P. Lallemand, *Opt. Commun.* **26**, 54 (1978).
- [10] D. W. Pohl, *Phys. Rev. A* **77**, 53 (1980).
- [11] J.-C. Bacri, A. Cebers, A. Boudon, G. Demouchy, B. M. Heegard, and R. Perzynski, *Phys. Rev. Lett.* **74**, 5032 (1995).
- [12] W. Köhler and B. Müller, *J. Chem. Phys.* **103**, 4367 (1995).
- [13] R. Spill, W. Köhler, G. Lindenblatt, and W. Schaertl, *Phys. Rev. E* **62**, 8361 (2000).
- [14] J. Lenglet, A. Bourdon, J. C. Bacri, and G. Demouchy, *Phys. Rev. E* **65**, 031408 (2002).
- [15] *Thermal Nonequilibrium Phenomena in Fluid Mixtures*, edited by S. Wiegand and W. Köhler (Springer, Berlin, 2002), p. 189.
- [16] M. E. Schimpf, *Entropie* **217**, 67 (1999).
- [17] M. E. Schimpf, *Trends Polym. Sci.* **4**, 114 (1996).
- [18] J. C. Giddings, M. E. Hovingh, and G. H. Thompson, *J. Phys. Chem.* **74**, 4291 (1970).
- [19] M. E. Schimpf and J. C. Giddings, *Macromolecules* **20**, 1561 (1987).
- [20] F. Brochard and P.-G. de Gennes, *C. R. Hebd. Seances Acad. Sci.* **293**, 1025 (1981).
- [21] M. E. Schimpf and J. C. Giddings, *J. Polym. Sci., Part B: Polym. Phys.* **27**, 1317 (1989).
- [22] E. Ruckenstein, *J. Colloid Interface Sci.* **83**, 77 (1981).
- [23] R. Piazza and A. Guarino, *Phys. Rev. Lett.* **88**, 208302 (2002).
- [24] D. I. Morozov, *Thermal Nonequilibrium Phenomena in Fluid Mixtures* (Ref. [15]), p. 38.
- [25] K. I. Morozov, *Phys. Rev. E* **53**, 3841 (1996).
- [26] E. Bringuier and A. Bourdon, *Phys. Rev. E* **67**, 011404 (2003).
- [27] J. C. Giddings, P. M. Shiundu, and S. N. Semenov, *J. Colloid Interface Sci.* **176**, 454 (1995).
- [28] R. J. Hunter, *Foundations of Colloid Science* (Clarendon, London, 1992), Vol. 2.
- [29] M. E. Schimpf and S. N. Semenov, *J. Phys. Chem. B* **104**, 9935 (2000).
- [30] M. Teubner, *J. Chem. Phys.* **76**, 5564 (1982).
- [31] S. Ross and I. D. Morrison, *Colloidal Systems and Interfaces* (Wiley, New York, 1986).
- [32] R. J. Hunter, *Foundations of Colloid Science* (Clarendon, London, 1989), Vol. 1.
- [33] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959).
- [34] *Organic Solvents. Physical Properties and Methods of Purifications*, 4th ed., edited by J. A. Riddik, W. B. Bunger, and T. K. Sakano (Wiley, New York, 1986).
- [35] D. Freifelder, *Physical Biochemistry* (Freeman, San Francisco, 1976).
- [36] S. Wiegand (private communication).
- [37] M. E. Schimpf and S. N. Semenov, *Philos. Mag. B* (to be published).
- [38] J. van Oss, *Interfacial Forces in Aqueous Media* (Dekker, New York, 1994).
- [39] A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces* (Wiley, New York, 1997), p. 239.