

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/272390623>

# Statistical Thermodynamics of Material Transport in Nonisothermal Suspensions

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · FEBRUARY 2015

Impact Factor: 3.3 · DOI: 10.1021/jp509776b

---

CITATION

1

---

READS

32

2 AUTHORS, INCLUDING:



Semen Semenov

Russian Academy of Sciences

47 PUBLICATIONS 291 CITATIONS

SEE PROFILE

# Statistical Thermodynamics of Material Transport in Nonisothermal Suspensions

Semen Semenov\*,† and Martin Schimpf‡

†Institute of Biochemical Physics RAS, Kosygin St. 4, 119334, Moscow, Russia

‡Boise State University, Boise, Idaho 83725, United States

**ABSTRACT:** An approach to the transport of material in a temperature gradient is outlined using nonequilibrium thermodynamics theory. The model is applicable to the thermophoresis of colloids and nanoparticles in systems with limited miscibility. Component chemical potentials in binary systems are calculated using statistical mechanics. The local pressure distribution is obtained using the condition of local thermodynamic equilibrium around the suspended particle. The Laplace contribution of the local pressure distribution within the layer of liquid surrounding the particle leads to a size dependence that is consistent with empirical data. The contribution of Keezom interaction to the thermodiffusion coefficient is calculated using empirical values of the thermodiffusion coefficient for silica particles in water and acetonitrile. The resulting interaction energies are consistent with those found in the literature.

Thermodiffusion coefficients  $D_T$  of silica particles.

Solvent	Silica $D_T$ $10^7$ (cm <sup>2</sup> s <sup>-1</sup> K <sup>-1</sup> ) Experiment	Silica $D_T$ , $10^7$ (cm <sup>2</sup> s <sup>-1</sup> K <sup>-1</sup> ) Theory (no Keezom)	Keezom Contribution for the Agreement with Experiment (K <sup>-1</sup> )
Water	2.2	0.36	0.3
Acetonitrile	1.6	1.3	0.08

## I. INTRODUCTION AND BACKGROUND

The aim of this paper is to extend our work on the theory of thermophoresis (thermodiffusion) in liquid molecular mixtures based on nonequilibrium thermodynamics<sup>1–4</sup> to suspensions of nano- and colloid particles. As outlined is a recent historical review by Rahman and Saghir,<sup>5</sup> molecular thermodiffusion has typically been described theoretically using a thermodynamic approach. In contrast, theoretical models for thermophoresis of colloids and larger particles in liquids have largely relied on the use of a hydrodynamic approach,<sup>6</sup> although one exception is the recent work of Eslamian, M. Z. Saghir,<sup>7</sup> who extended a thermodynamic approach developed earlier for molecular mixtures. The ability of thermodynamic approaches to predict trends in the empirical data for colloids and larger particles in molecular solvents would be significant because it would mean that thermophoresis (thermodiffusion) in liquids can be considered to arise from the same physical process, regardless of particle size, notwithstanding electrophoretic effects that arise with charged particles.

We begin with a brief review of the two main approaches used in theories of thermophoresis (thermodiffusion).

**Hydrodynamic Approach.** In hydrodynamic models, thermophoresis is based on the flow of liquid established in a layer of liquid at the surface of a wall or suspended particle. Within this surface layer, there is an interaction force acting on molecules of the liquid. The flow is caused by a temperature-induced longitudinal pressure gradient established along the surface. When the solid surface belongs to a movable solid particle, this temperature-induced flow causes particle movement referred to as thermophoresis.

The hydrodynamic approach is based on the Navier–Stokes equation

$$\eta \frac{\partial^2 u_y}{\partial x^2} = -\frac{\partial P}{\partial y} - \frac{1}{v_1} \frac{\partial \Phi_{12}}{\partial y} \quad (1)$$

where  $u_y$  is the longitudinal velocity profile,  $\eta$  is the dynamic viscosity of the liquid,  $x$  is the coordinate normal to the particle surface,  $y$  is the longitudinal coordinate tangent to the surface,  $v_1$  is the partial molecular volume of the liquid, and  $\Phi_{12}(x)$  is the interaction potential between the particle (or wall) surface and molecules of the liquid. The curvature of the surface is ignored in eq 1, which makes it strictly applicable only to particles with a radius significantly larger than the surface layer of liquid surrounding the particle. More specifically, curvature in the particle surface can be ignored when  $(l/R)^2 \ll 1$ , where  $R$  is the particle radius and  $l$  is the characteristic width of the surface layer in which the interaction force is acting.<sup>6</sup> Parameter  $l$  is typically of the same order as the size of the liquid molecules.

Following the method outlined in reference,<sup>8</sup> the transverse pressure distribution  $P(x)$  is obtained using the condition of mechanical equilibrium in the direction normal to the particle surface

$$\frac{\partial P}{\partial x} = \frac{1}{v_1} \frac{\partial \Phi}{\partial x} \quad (2)$$

In liquids, where the molecular volume  $v_1$  is hardly changed with temperature and pressure, eq 1 takes the following form<sup>8</sup>

$$P(x) + P_0 = \frac{\Phi_{12}(x)}{v_1} \quad (3)$$

Received: September 27, 2014

Revised: January 20, 2015

where  $P_0$  is a constant of integration. Physically,  $P_0$  is the macroscopic pressure in the volume far from the surface layer where forces are acting. The boundary conditions for eq 3 are<sup>6</sup>

$$u_y(x=0) = 0; \quad \frac{\partial u_y(x=\infty)}{\partial x} = 0 \quad (4)$$

The dependence of the interaction potential on the longitudinal coordinate  $y$  is canceled by the respective surface pressure gradient if the condition of local equilibrium is fulfilled.<sup>8</sup> Thus, the Navier–Stokes eq 1 that describes the flow profile in the nonisothermal surface layer takes the form

$$\eta \frac{\partial^2 u_y}{\partial x^2} = \frac{\alpha_T \Phi_{12}}{\nu_1} \frac{\partial T}{\partial y} \quad (5)$$

where  $\alpha_T$  is the cubic thermal expansion coefficient and  $T$  is temperature.

Using the boundary conditions defined by eq 4 the solution to eq 5 at distances much greater than the molecular size but much smaller than the transverse size of the particle or typically thin thermodiffusion cell (or channel) yields

$$u_s = u_y(x=\infty) = -\frac{\alpha_T}{\eta \nu_1} \frac{\partial T}{\partial y} \int_0^\infty x \, dx \Phi_{12}(x) \quad (6)$$

Parameter  $u_s$ , which is called the slip velocity, is used as the boundary condition for the “macroscopic” Navier–Stokes equation that describes the flow profile in the channel or around the particle. The interaction potential in molecular liquids is defined as the Hamaker potential<sup>9</sup>

$$\Phi_{12}(\xi) = \frac{1}{\nu_{02}} \int_{\nu_2} \Phi_m(\vec{r}) d^3\vec{r} = -\frac{\varepsilon_{12}}{6} \frac{\sigma_{12}^3}{\nu_{02}} \left( \frac{1}{\xi} + \frac{1}{2+\xi} + \ln \frac{\xi}{2+\xi} \right) \quad (7)$$

where  $\bar{\nu}_2$  is the particle volume,  $\Phi_m = -\varepsilon_{12}(\sigma_{12}/r)^6$  is the London–van der Waals potential of interaction<sup>8</sup> between molecules of liquid and the particle (or channel wall) surface,  $\vec{r}$  is the set of coordinates within the particle,  $r$  is the distance between respective molecules,  $\varepsilon_{12}$  is the energy of the interaction,  $\nu_{02}$  is the partial molecular volume of the particle material,  $\xi = (x/\sigma_{12})$  is the reduced distance from the particle surface to the surface of the nearest solvent molecule, and  $\sigma_{12}$  is the minimal molecular approach distance.

Substituting eq 7 into eq 6 and using the definition<sup>9</sup>  $A_{12} = \varepsilon_{12}(\sigma_{12}^3/\nu_{02})$  for the Hamaker constant we obtain the expression for the slip velocity at the particle surface

$$u_s = \frac{2 - \ln 3}{12} \frac{\alpha_T \sigma_{12}^2 A_{12}}{\eta \nu_{02}} \frac{\partial T}{\partial y} \quad (8)$$

The direction of the particle thermophoresis is opposite to the slip velocity direction. The velocity of thermophoresis related to the slip of liquid is calculated as

$$u_T = \frac{\ln 3 - 2}{12} \frac{\alpha_T \sigma_{12}^2 A_{12}}{\eta \nu_{02}} \left\langle \frac{\partial T}{\partial y} \right\rangle \quad (9)$$

where  $\langle \partial T / \partial y \rangle$  is the lateral temperature gradient averaged on the particle surface. A similar expression was obtained in reference.<sup>10</sup>

Equation 9 indicates that thermophoresis should be directed from the hot to cold region. This result was criticized in ref 6 because it fails to predict negative thermophoresis, that is, movement of the particle toward the hot region, which has

been observed in molecular mixtures.<sup>11</sup> However, eq 9 does not account for the possibility of temperature-induced barodiffusion of the particle related to the secondary pressure gradient  $\nabla P_0$  established in nonisothermal liquids.<sup>1–4,8</sup> Such effects can be significant, resulting in negative molecular thermophoresis. The inability to account for the macroscopic pressure gradient is a shortcoming of the hydrodynamic approach.

When we consider the potential profile described by eq 7 we are also restricted to particles that are compatible with the suspending liquid in the absence of surfactant addition. There are only a few such examples in the literature, which include the thermophoresis of silica particles in water and acetonitrile<sup>12</sup> and in polypropylene glycol.<sup>13</sup> In these examples, the empirical values of the thermodiffusion coefficients were several times larger than those predicted by eq 9.

**Thermodynamic Approach.** Thermodynamic theories of thermophoresis (thermodiffusion) are based on the empirically oriented expression for material flux established in non-equilibrium thermodynamics<sup>14,15</sup>

$$\vec{J}_i^\nu = -\frac{\phi_i}{\bar{\nu}_i} l_{ii} \left( \nabla \frac{\mu_i}{T} + q_i \nabla \frac{1}{T} \right) \quad (10)$$

Here  $l_{ii}$  is the molecular Onsager kinetic coefficient,  $\bar{\nu}_i$  is the partial molecular volume or the physical volume of the particle or molecule depending on the component considered,  $\mu_i$  is the particle or molecular chemical potential, and  $q_i$  is the molecular heat of transport for  $i$ th component. We will consider binary mixtures because they have been studied in detail, both in theory and experimentally. The parameters used in eq 10 are widely used in both equilibrium and nonequilibrium thermodynamics. The parameters are related to a single molecule or particle, while the numerical volume concentration  $n_i$  can be expressed through the relationship between respective volume fraction  $\phi_i$  and specific molecular volume:  $\phi_i = \bar{\nu}_i n_i$ . The component chemical potentials can be expressed through physical parameters as follows<sup>14,15</sup>

$$\nabla \mu_i = \sum_{k=1}^2 \frac{\partial \mu_i}{\partial \phi_k} \nabla \phi_k - \bar{\nu}_i \nabla P + \frac{\partial \mu_i}{\partial T} \nabla T \quad (11)$$

Substituting eq 11 into eq 10, we obtain

$$\vec{J}_i^\nu = -\frac{\phi_i l_{ii}}{\bar{\nu}_i T} \left[ \sum_{k=1}^2 \frac{\partial \mu_i}{\partial \phi_k} \nabla \phi_k - \bar{\nu}_i \nabla P + \left( \frac{\partial \mu_i}{\partial T} - \frac{\mu_i + q_i}{T} \right) \nabla T \right] \quad (12)$$

For closed stationary systems the macroscopic pressure gradient is given by the Gibbs–Duhem equation<sup>14,15</sup>

$$\nabla P = \sum_{k=1}^2 \frac{\phi_k}{\bar{\nu}_k} \left( \frac{\partial \mu_k}{\partial \phi_k} \nabla \phi_k + \frac{\partial \mu_k}{\partial T} \nabla T \right) \quad (13)$$

The material flux of each component is zero

$$\vec{J}_i^\nu = 0 \quad (14)$$

while in the nonstationary systems only the sum of the material fluxes is zero

$$\sum_{i=1}^2 \bar{\nu}_i \vec{J}_i^\nu = 0 \quad (15)$$

**Thermodynamic Approaches that Assume Zero Pressure Gradient.** In the thermodynamic approaches to molecular

thermodiffusion developed in refs 16 and 17, which are based on the results of ref 18, the pressure gradient in eq 22 is assumed to be zero and eq 23 is used for conservation of mass. In this case eq 21, the material fluxes are transformed into the following two equations, one for each component

$$\vec{J}_1^\nu = 0 = -\frac{\phi_1 l_{11}}{\bar{v}_1 T} \left[ \frac{\partial \mu_1}{\partial \phi_1} \nabla \phi_1 + \left( \frac{\partial \mu_1}{\partial T} - \mu_1 - q_1 \right) \frac{\nabla T}{T} \right] \quad (25a)$$

$$\vec{J}_2^\nu = 0 = \frac{\phi_2 l_{22}}{\bar{v}_2 T} \left[ \frac{\partial \mu_2}{\partial \phi_2} \nabla \phi_2 + \left( \frac{\partial \mu_2}{\partial T} - \mu_2 - q_2 \right) \frac{\nabla T}{T} \right] \quad (25b)$$

Equation 25 ignores the cross-coupling kinetic coefficients.

In order to satisfy both eq 25 and the Gibbs–Duhem equation written for an isobaric and isothermal system, that is

$$0 = \sum_{k=1}^2 \frac{\phi_k}{\bar{v}_k} \frac{\partial \mu_k}{\partial \phi_k} \nabla \phi_k \quad (26)$$

the authors assume the following equality<sup>18</sup>

$$\frac{\phi_1}{\bar{v}_1} \left( \frac{\partial \mu_1}{\partial T} - \mu_1 - q_1 \right) + \frac{\phi_2}{\bar{v}_2} \left( \frac{\partial \mu_2}{\partial T} - \mu_2 - q_2 \right) = 0 \quad (27)$$

The parameters in brackets are defined as the net heats of transport of the respective components and designated as  $q_i^*$ . Equation 27 is introduced in an attempt to overcome a problem with the equations for material fluxes, which is that they are overdetermined, that is, the number of unknown parameters is less than the number of equations. In order to solve the problem of an overdetermined system, that is, to ensure that both eq 25a and eq 25b yield the same concentration distribution, some sort of restriction must be imposed on the kinetic coefficients. Equation 27 represents such a restriction. The resulting expression for the Soret coefficient, which characterizes the concentration distribution established in a temperature gradient, is

$$S_T = -\frac{\frac{\partial \phi}{\partial z}}{\phi(1-\phi)\frac{\partial T}{\partial z}} = \frac{q_1^* - q_2^*}{\phi \frac{\partial \mu_2}{\partial \phi} T} \quad (28)$$

Here  $z$  is the coordinate along the direction of the temperature gradient  $\vec{\nabla T}$  and  $\phi = \phi_2$ .

There are several shortcomings in the derivation of eq 28 and its application to specific experimental situations. First, eq 23 is valid only for a stationary closed system, making its use in the derivation of eqs 25–28, which defines a nonstationary system, problematic. Furthermore, when used to calculate the thermodiffusion coefficient  $D_T$  using the relationship  $D_{iT} = S_T D_i$  where  $D_i$  is the mass diffusion coefficient of the respective component,<sup>7</sup> the approach is only valid for highly diluted suspensions. In more concentrated suspensions, the coefficients of mass diffusion and thermodiffusion contain the parameter  $1 - \phi + (D_2 \bar{v}_2 / D_1 \bar{v}_1) \phi$  in the denominator, which is related to the dynamic pressure gradient established due to hydrodynamic friction in a nonstationary system.<sup>1</sup> This hydrodynamic factor can significantly reduce the mass and thermodiffusion coefficients of large particles in a concentrated binary mixture. Formally, it is due to use eq 24 expressing the material conservation instead eq 23.

Second, the Gibbs–Duhem equation for the mentioned isobaric nonisothermal binary system is

$$\sum_{k=1}^2 \frac{\phi_k}{\bar{v}_k} \left( \frac{\partial \mu_k}{\partial \phi_k} \nabla \phi_k + \frac{\partial \mu_k}{\partial T} \nabla T \right) = 0 \quad (29)$$

In order to satisfy both eq 29 and eq 25, eq 27 can be written as

$$\frac{\phi_1}{\bar{v}_1} (\mu_1 + q_1) + \frac{\phi_2}{\bar{v}_2} (\mu_2 + q_2) = 0 \quad (30)$$

with the respective redetermination of the net heats of transport. Note that eq 30 can be satisfied using the assumption

$$q_i = -\mu_i \quad (31)$$

According to eq 31 the heat transferred by a particle is equal to its mean energy in the system expressed as its chemical potential. But in this case, the Soret coefficient in an isobaric system becomes zero.

In fact, there is no reason to consider a nonisothermal and nonhomogeneous system to be isobaric. Although postulated in refs 14–18 the only basis for such an assumption is that the sum of the internal forces acting in the system is zero. This sum is expressed by the right-hand side of eq 22. While such assumption is certainly valid for a system in which there is no energy supply, it is not necessary for a nonisothermal system, where the continual supply of energy produces a constant heat flux. Further argument for the existence of a pressure gradient in nonisothermal mixtures are inherent to the models developed in refs 19–22 where diffusion and thermodiffusion in binary liquids are related to the concentration- and temperature-induced gradients of the excess pressure established in the addition of the solutes in the pure solvent.

In refs 23 and 24, the net heat of transport or the parameter equal to the heat of transport plus a constant value is mentioned as the parameter characterizing the thermophobicity of the pure component, which is independent of concentration. Eq 31 shows that it is impossible and the heat of transport must be a function of concentration. Finally, in a comprehensive set of studies<sup>25</sup> by Piazza and co-workers the Soret coefficient was shown to increase in proportion to particle radius  $R$ , which is inconsistent with eq 28. This inconsistency appears when we consider that the net heat of transport should be proportional to the net energy of interaction of a particle with the surrounding liquid. Because the surrounding molecules are much smaller than the suspended particle, the energy of interaction should be proportional to the surface area of the particle. The proportionality between interaction energy and particle size can be obtained directly from the expressions derived in refs 19–21 resulting in the prediction from eq 28 that  $S_T \approx R^2$ . Because this prediction has not been borne out by experiments, it has been argued that thermodynamics cannot be used to describe phoretic effects in suspensions.<sup>6</sup> Although a linear dependence of the Soret coefficient on particle radius was not observed in experiments with suspended polystyrene particles by Braun and co-workers,<sup>26,27</sup> the authors explain the discrepancy with the work in ref 25 as a consequence of the surface properties of the particles changing with particle size.

**Thermodynamic Approach that Incorporates a Pressure Gradient.** Starting with eq 21 for the heat flux and utilizing the relationship

$$\phi_1 + \phi_2 = 1 \quad (32)$$

for a binary system, along with the standard rule of differentiation of composite functions

$$\sum_{l=1}^2 \frac{\partial \mu_k}{\partial \phi_l} \nabla \phi_l = \frac{\partial \mu_k}{\partial \phi_2} \nabla \phi_2 + \frac{\partial \mu_k}{\partial \phi_1} \frac{\partial \phi_1}{\partial \phi_2} \nabla \phi_2 = 2 \frac{\partial \mu_k}{\partial \phi} \nabla \phi \quad (33)$$

Substituting the Gibbs–Duhem equation in the general form (eq 22) we obtain two equations for the material flux. For a stationary closed system where the fluxes are zero

$$\begin{aligned} 0 &= -\frac{l_{11}}{\bar{v}_1 T} \left[ \phi(1-\phi) \left( 2 \frac{\partial \mu^*}{\partial \phi} \nabla \phi + \frac{\partial \mu^*}{\partial T} \nabla T \right) + (1-\phi) \left( \frac{\mu_1 + q_1}{T} \right) \nabla T \right] \\ 0 &= \frac{l_{22}}{\bar{v}_2 T} \left[ \phi(1-\phi) \left( 2 \frac{\partial \mu^*}{\partial \phi} \nabla \phi + \frac{\partial \mu^*}{\partial T} \nabla T \right) + \phi \left( \frac{\mu_2 + q_2}{T} \right) \nabla T \right] \end{aligned} \quad (34)$$

where

$$\mu^* = \mu_2 - \left( \frac{\bar{v}_2}{\bar{v}_1} \right) \mu_1 \quad (35)$$

is the binary chemical potential of the (binary) mixture. Equation 34 can be made self-consistent if eq 31 is valid. In other words, eq 34 yields the same stationary concentration distribution in the temperature gradient, regardless of which component is assigned to which equation. Thus, the assumption on the equality of the heat of transport and chemical potential with the opposite sign allows a consistent set of transport equations for both the isobaric and nonisobaric nonisothermal system. Note that in this approach, the transport equations yield zero mass flux in pure components, even when the pressure gradient is nonzero, which is consistent with the general thermodynamic expression of the Soret coefficient<sup>19–22</sup>

$$S_T = \frac{\frac{\partial \mu_p^*}{\partial T}}{2\phi(1-\phi) \frac{\partial \mu_p^*}{\partial \phi}} \quad (36)$$

Equation 35 is the chemical potential of the considered particle  $\mu_2$  minus the sum of the chemical potentials of molecules of liquid displaced by the particle  $(\bar{v}_2/\bar{v}_1) \mu_1$ . The latter parameter appears as result of considering the pressure gradient. The displaced volume of liquid can be considered a virtual particle consisting of liquid and having the Hamaker interaction potential of particles interacting with liquid given by eq 7, where  $\varepsilon_{12} \Rightarrow \varepsilon_{11}$ ,  $\sigma_{12} \Rightarrow \sigma_{11}$ , and  $\nu_{02} \Rightarrow \bar{v}_1$ . This concept is used below in microscopic calculations of the chemical potentials. Thus, eqs 34–36 predict that particle thermophoresis is nonzero only if the chemical potentials of the real particle and virtual particle are different. Next, we use statistical mechanics and calculations of local pressure to obtain a microscopic expression for the chemical potential at constant volume and at constant pressure.

**Statistical Mechanical Calculation of the Chemical Potential.** The chemical potential at constant volume is expressed by the following equation<sup>28,29</sup>

$$\mu_{iV} = \mu_{0i} + 4\pi \int_0^1 d\lambda \sum_{j=1}^2 \frac{\phi_j}{\bar{v}_j} \int_{V_{out}^i}^\infty g_{ij}(r, \lambda) \Phi_{ij}(r) r^2 dr \quad (37)$$

where

$$\mu_{0i} = -\frac{3}{2} kT \ln \frac{2\pi m_i kT}{h^2} + kT \ln \frac{\phi_i}{\bar{v}_i} - kT \ln Z_{rot}^i \quad (38)$$

is the chemical potential of the ideal gas of the respective noninteracting molecules or particles,  $h$  is Planck's constant,  $m_i$  is mass, and  $Z_{rot}^i$  is the rotational partition function. Parameter  $V_{out}^i$  is the volume external to the particle or the molecule.

Parameter  $\lambda$  in eq 38 describes the gradual “switching on” of the intermolecular interaction. A detailed description of this representation can be found in refs 28 and 29. Parameter  $r$  is the distance between a molecule of the surrounding liquid and the center of a considered particle,  $g_{ij}(\vec{r}, \lambda)$  is the pair correlation function, and  $\Phi_{ij}$  is the particle-molecular or intermolecular interaction potential. For molecules the London potential is defined as<sup>9</sup>

$$\Phi_{11} = -\varepsilon_{11} \left( \frac{\sigma_{11}}{r} \right)^6 \quad (39)$$

In the integration over  $V_{out}^i$  the lower limit to eq 37 is defined by  $r = \sigma_{11}$ . The Hamaker potential  $\Phi_{12}$  of the particle–molecular interactions is still defined by eq 7.

There is no simple method for calculating the pair correlation function in liquids. However, it should approach unity at infinity, and we could use this extrapolation

$$g_{ij}(r, \lambda) = 1 \quad (40)$$

Using this approximation means ignoring any distortion of the local distribution of solvent molecules by the considered particle, which is widely used in theories of liquids. This approximation assumes that the local distribution of solvent molecules is not disturbed by the considered particle. The approximation of constant local density is used in the statistical mechanical study of liquids as regular solutions.<sup>30</sup> In refs 31 and 32, it is used in combination with a hydrodynamic approach to molecular thermodiffusion. Utilizing this approximation, we obtain

$$\mu_{iV} = \mu_{0i} + \sum_{j=1,2} \frac{\phi_j}{\bar{v}_j} \int_{V_{out}^i}^\infty \Phi_{ij}(r) dv \quad (41)$$

The approximation given by eq 40 ignores decaying oscillations in the pair correlation function when calculating the integrals in eqs 37 and 41. We assume that these decaying oscillations are mutually canceling so that their role is not especially important. Another reason for using eq 40 is that the free volume in liquids is not great, therefore, there is little room for the change of the numeric density of molecules. Finally, in thermodiffusion experiments the components typically have similar properties in order for them to be compatible. Consequently, the energy gain due to enriching or depleting the component around the considered particle is relatively small.

As we noted above, the thermodynamic or “energetic” approach to thermodiffusion is often criticized because these microscopic calculations do not yield the empirically determined size dependence of the Soret coefficient.<sup>33</sup>



However, further refinement of microscopic calculations<sup>2,3</sup> yielded a theoretical expression that explains the size dependence of the Soret coefficient obtained experimentally. The refinement is related to the fact that chemical potential at constant pressure should be used in the calculations. The chemical potentials at constant volume versus constant pressure are related by the following expression

$$\nabla \mu_{iP} = \nabla \mu_{iV} + \int_{V_{out}^i} \nabla \Pi_i dv \quad (42)$$

where  $V_{out}^i$  is the volume external to the molecule or particle of the  $i$ th component, and  $\Pi_i$  is the local pressure distribution around the molecule or particle.

In the following calculations, we consider the term  $(v_2/v_1) \mu_{1V}$  as the free energy of the solvent molecules (component 1) that are displaced by a molecule or particle of component 2, or the chemical potential of a virtual particle consisting of molecules of the first component displaced by a molecule or particle of the second component. In this way, we can extend the results obtained in calculations of the molecular chemical potential  $\mu_{2V}$  of the second component to the calculation of parameter  $(v_2/v_1) \mu_{1V}$ .

Using eqs 7 and 37–41 and the definition of a virtual particle, we write the binary chemical potential at constant volume  $\mu_V^*$  as

$$\begin{aligned} \mu_V^* = & -kT \left( \frac{3}{2} \ln \frac{m_2}{m_2^*} - \ln \frac{\phi}{1-\phi} + \ln \frac{Z_{rot}^2}{Z_{rot}^{2*}} \right) \\ & + \frac{1-\phi}{v_1} \left[ \int_{V_{out}^2} \Phi_{21}(r) dv - \int_{V_{out}^{2*}} \Phi_{11}^*(r) dv \right] \end{aligned} \quad (43)$$

where  $m_2^*$  and  $Z_{rot}^{2*}$  are the mass and rotational partition function of the virtual particle, respectively, and  $\Phi_{12}(r)$ ,  $\Phi_{11}^*(r)$  are the Hamaker interaction potentials for a real and virtual particle in the surrounding liquid, respectively. Interactions between two virtual particles or between two real (nonvirtual) particles in suspension are ignored because the extent of such interactions is minor compared to particle-liquid interactions, even in concentrated suspensions.

To calculate the chemical potential at constant pressure using eq 42 we must calculate the local pressure distribution  $\Pi_i$  following the procedure outlined in refs 2 and 3. The local pressure distribution is usually obtained from the condition of local mechanical equilibrium in the liquid. That condition is defined within a thin spherical layer of thickness  $l$  and area  $S$ , concentric with the considered molecule, where spherical symmetry is maintained when the position is shifted from  $r$  to  $r + dr$ . It is within this layer that the interaction potential  $\Phi_{ij}(r)$  is acting, and the condition of mechanical equilibrium is necessary to the conservation of specific free energy  $F(r) = \Pi_i(r) + \sum_{j=1,2} \phi_j \Phi_{ij}(r)/v_j$  in such a shift. In the thin spherical layer forming the closed surface, the change in the free energy is defined as

$$dF(r) = \nabla \left[ \sum_{j=1,2} \frac{\phi_j \Phi_{ij}(r)}{v_j} + \nabla \Pi_i \right] l S dr + \sum_{j=1,2} \frac{\phi_j \Phi_{ij}(r)}{v_j} l dS = 0 \quad (44)$$

where we consider changes in free energy due to change in the governing parameters within the layer volume ( $dV = S dr$ ), as well as changes in the area  $dS$  of the closed layer. For a spherical layer the changes in volume and surface area are

related by  $dV = 2r dS$ , and we obtain the following modified equation for equilibrium in the closed spherical surface

$$\nabla \left[ \sum_{j=1,2} \frac{\phi_j \Phi_{ij}(r)}{v_j} + \Pi_i \right] + \sum_{j=1,2} \frac{2\phi_j \Phi_{ij}(r)}{v_j r} \vec{r}_0 = 0 \quad (45)$$

where  $\vec{r}_0$  is the unit radial vector. The pressure gradient related to the change in surface area has the same nature as the surface (Laplace) pressure gradient discussed in.<sup>34</sup> Solving eq 45, we obtain

$$\Pi_i = - \sum_{j=1,2} \frac{\phi_j \Phi_{ij}(r)}{v_j} - \int_{\infty}^r \frac{2\phi_j \Phi_{ij}(r')}{v_j r'} dr' \quad (46)$$

Substituting the pressure gradient from eq 46 into eq 42 and using eqs 38 and 40, we obtain the expression for the relevant part of the chemical potential at constant pressure

$$\begin{aligned} \mu_P^* = & -kT \left( \frac{3}{2} \ln \frac{m_2}{m_2^*} - \ln \frac{\phi}{1-\phi} + \ln \frac{Z_{rot}^2}{Z_{rot}^{2*}} \right) \\ & - 2 \frac{1-\phi}{v_1} \int_{V_{out}^2} dr \int_{\infty}^r \frac{\Phi_{21}(r') - \Phi_{11}^*(r')}{r'} dr' \end{aligned} \quad (47)$$

Substituting eq 47 into eq 42 for large particles and integrating we obtain

$$\begin{aligned} \nabla \mu_P^* = & \int_{V_{out}} \frac{(\alpha_T + \alpha_K) dv}{v_1} \nabla_\theta T \int_{\infty}^r \frac{\Phi_{21}(r') - \Phi_{11}^*(r')}{r'} dr' \\ = & 4\pi R(\alpha_T + \alpha_K) \nabla_\theta T \int_0^\infty dx x [\Phi_{21}(x) - \Phi_{11}^*(x)] \end{aligned} \quad (48)$$

The last integral on the right side of eq 47 includes the term  $\alpha_T \int_0^\infty dx x \Phi_{21}(x) \nabla_\theta T$ , which is equivalent to the expression obtained for large particles by the hydrodynamic approach (eq 6 for the slip velocity). Thus, the results of the hydrodynamic approach can be obtained using the thermodynamic approach, which has wider applicability.

Equations 36 and 48 can be combined to obtain the following expression for the Soret coefficient

$$S_T = \frac{(1-\phi)(\alpha_T + \alpha_K)h_2^* - S_T^{\text{kinetic}}}{1 + \phi(1-\phi)h_2^*} \quad (49)$$

where

$$h_2^* = \frac{\pi(2 - \ln 3)RA_{12}}{8kT(n+2)\sigma_{11}} \frac{v_{11}}{v_1} \left( \frac{v_1\sigma_{12}^2}{v_2\sigma_{11}^2} - \frac{A_{11}}{A_{12}} \right) \quad (50)$$

Parameter  $v_{ij} = (4\pi/3)\sigma_{ij}^3$  is the van der Waals volume,  $A_{11}$  is the respective Hamaker constant,  $R$  is the particle radius,  $n$  is the particle–solvent thermal conductivity ratio, and

$$S_T^{\text{kinetic}} = \frac{1}{2T} \left( \frac{3}{2} \ln \frac{m_2}{m_2^*} + \ln \frac{Z_{rot}^2}{Z_{rot}^{2*}} \right) \quad (51)$$

is the contribution of the particle kinetic energy to the Soret coefficient. The last term in the brackets in eq 51 is equal to  $\ln(m_2/m_2^*)$  for uniform particles. The contribution of kinetic energy is small for large particles but can be measurable for nanoparticles like fullerenes where the mass distribution is highly nonuniform.

The denominator of eq 49 can approach zero when the binary differential enthalpy is large and negative, which means

Table 1. Theoretical and Experimental Values of Thermodiffusion Coefficients of Silica Particles in Water and Acetonitrile

solvent	molecular size (nm)	viscosity (cP)	thermal expansion ( $10^{-3} \text{ K}^{-1}$ )	thermal conductivity ( $10^{-4} \text{ W m}^{-1} \text{ K}^{-1}$ )	Hamaker constant ( $10^{-13} \text{ erg}$ )	silica $D_T \times 10^7$ ( $\text{cm}^2 \text{ s}^{-1} \text{ K}^{-1}$ ) experiment	silica $D_T \times 10^7$ ( $\text{cm}^2 \text{ s}^{-1} \text{ K}^{-1}$ ) theory (no Keezom and with $\alpha_K$ from ref 9)	Keezom parameter $\alpha_K$ for agreement with experiment and ref 9 ( $10^{-3} \text{ K}^{-1}$ )
water	0.3	1.0	0.21	0.61	3.7 (4.0)	2.2	0.36 (3.3) <sup>b</sup>	1 (1.67) <sup>a</sup>
acetonitrile	0.5	0.37	1.4	0.15	6.7	1.6	1.3 (2.0) <sup>b</sup>	0.26 (0.67) <sup>a</sup>
silica particle		molecular size (nm)		thermal conductivity ( $10^{-4} \text{ W m}^{-1} \text{ K}^{-1}$ )		Hamaker constant ( $10^{-13} \text{ erg}$ )		
Suspended Particle								
silica		0.15		0.13		6.5		

<sup>a</sup>Keezom parameter calculated using data from ref 9. <sup>b</sup>Silica thermodiffusion coefficient calculated by substituting Keezom parameter from ref 9.

phase layering will occur at a certain critical temperature when  $\phi = (1/2)$ . Below the critical temperature the suspension can exist both as a single-phase and a two-phase system, depending on concentration.

The Keezom thermodiffusion parameter

$$\alpha_K = -\frac{\partial \ln h_2^*}{\partial T} \quad (52)$$

characterizes the contribution of so-called Keezom interactions to thermodiffusion. The interaction potential may contain a temperature-dependent component involving the so-called Keezom or orientation dipole interaction parameter  $\epsilon_{ij}^K$ .<sup>9</sup> This component of the interaction potential is obtained by weight-averaging  $\Phi_{ij}(\vec{r})$  over all orientations between hard dipoles using a Boltzmann factor. The specific expression for the orientation dipole–dipole interaction potential can be found elsewhere.<sup>9</sup> For our calculations the temperature derivative of the Keezom potential can be written as

$$\frac{\partial \epsilon_{ij}^K}{\partial T} = -\frac{\epsilon_{ij}^K}{T} \quad (53)$$

and parameter  $\alpha_K$  can be written as

$$\alpha_K = \frac{h_2^{*K}}{Th_2^*} \quad (54)$$

where  $h_2^{*K}$  is the component of the binary differential enthalpy related to the Keezom interaction potential. When the Keezom interaction prevails in the net van der Waals interaction potential,  $\alpha_K \approx \pm(1/T)$ , which is the upper limit to the value for this parameter.

Equations 49–54 contain the main governing factors for the thermodiffusion of suspended particles. Using well-established relationships for the Hamaker constant in the Stokes–Einstein equation for diffusion, the equation for the thermodiffusion coefficient in dilute suspensions can be written as

$$D_T = \frac{(2 - \ln 3)(\alpha_T + \alpha_K)\sqrt{A_{11}A_{22}}}{6(n+2)\eta\sigma_{11}} \left( \frac{v_1\sigma_{22}}{v_2\sigma_{11}} - \sqrt{\frac{A_{11}}{A_{22}}} \right) \quad (55)$$

According to eq 55 the thermodiffusion coefficient is independent of particle size, which corresponds to empirical data.<sup>25</sup>

## II. RESULTS AND DISCUSSION

We used eq 55 to calculate thermodiffusion coefficients for silica particles in water and acetonitrile and compare them with data in ref 12. There is also data in ref 13 for silica particles in propylene glycol but they are in a form that does not allow for a

direct comparison using eq 55. The results are summarized in Table 1. Thermodiffusion coefficients calculated without the contribution of the Keezom interaction ( $\alpha_K = 0$ ) are summarized in the column labeled “no Keezom”. Neglecting the Keezom interaction yields much better agreement for the moderately polar solvent acetonitrile compared to the highly polar solvent water. To evaluate the theory, we calculate the relative Keezom contribution  $\alpha_K$  necessary for thermodiffusion coefficients calculated from eq 49 to match the empirical values. These values are summarized in the column labeled “Keezom Parameter for Agreement with Experiment”. The comparison of this calculated parameter ( $\alpha_K$ ) with the coefficient of thermal expansion  $\alpha_T$  shows that the Keezom interaction is prevalent in water ( $\alpha_K/\alpha_T \approx 5$ ) and plays a less important although measurable role in acetonitrile ( $\alpha_K/\alpha_T \approx 0.2$ ).

The values of the Keezom parameter also correlate with known properties of the solvents. Direct calculation of the relative contribution of the orientation interaction ( $h_2^{*K}/h_2^* = \alpha_K T$  (eq 48) yields ( $h_2^{*K}/h_2^* \approx 0.3$  for water and ( $h_2^{*K}/h_2^* \approx 0.08$  for acetonitrile, which is qualitatively consistent with reported ratios of 0.5 for water and 0.2 for acetonitrile.<sup>9</sup> However, the value for acetonitrile in ref 9 was approximated as the  $\text{NH}_3\text{--NH}_3$  interaction energy.

The values of the thermodiffusion coefficients calculated using the Keezom parameters given by ref 9 are represent in Table 1 in brackets. The values are about 50% larger than empirical values, however, the Keezom parameters calculated in ref 9 are based on a specific shape of the interaction potential, which may not be valid when the distance between molecules or between molecules and the particle surface is comparable to their sizes. Finally, we are ignoring the contribution of the silica particle dipole moment in this comparison. According to eq 35, the more polar nature of silica would decrease the net Keezom contribution to thermodiffusion.

Finally, in our calculations we have ignored the contribution of the electrostatic interactions to thermodiffusion. According to ref 35 the silica particle zeta potential at pH 7 is about 25 mV. The evaluation of the electrostatics contribution to thermodiffusion based on the approach developed in refs 36 and 37 shows that in pure water, where the numeric concentration of ions is about  $10^{16} \text{ cm}^{-3}$  and the Debye length is about one micron, the relative contribution of the electrostatic mechanism is at most several percent. The evaluations made in ref 13 confirm this conclusion.

## III. CONCLUSION

In conclusion, thermodynamic theory supplemented by microscopic calculations based on statistical mechanics explains many of the characteristic features of particle thermodiffusion in suspensions, including the following: the value of the

thermodiffusion coefficient; the concentration dependence and change of direction in thermophoresis with concentration; and the range of compatibility of the suspensions. The model relates thermophoretic parameters to the physicochemical parameters of the particles and suspending liquid, the Hamaker constants, and the van der Waals parameters. The contribution of the Kezom interaction measured in thermodiffusion experiments may be used in studies of the orientation correlations in liquids. Finally, the approach relates mass and thermodiffusion properties to the critical temperature for phase layering in systems with limited miscibility.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: sem@triniti.ru. Phone: +7(495)939-74-39.

### Notes

The authors declare no competing financial interest.

## REFERENCES

- (1) Semenov, S. N.; Schimpf, M. E. Mass Transport Thermodynamics in Nonisothermal Molecular Liquid Mixtures. *Phys.-Usp.* **2009**, *52*, 1045–1054.
- (2) Semenov, S. N. Statistical Thermodynamic Expression for the Soret Coefficient. *Europhys. Lett.* **2010**, *90*, 56002–56008.
- (3) Semenov, S. N. Statistical Thermodynamics of Material Transport in Non-Isothermal Binary Systems. *Europhys. Lett.* **2012**, *97*, 66003–66009.
- (4) Semenov, S. N.; Schimpf, M. E. Theory of Soret Coefficients in Binary Organic Solvents. *J. Phys. Chem. B* **2014**, *118*, 3115–3121.
- (5) Rahman, M. A.; Saghir, M. Z. Thermodiffusion or Soret effect: Historical review. *Int. J. Heat Mass Transfer* **2014**, *73*, 693–705.
- (6) Anderson, J. L. Colloid Transport by Interfacial Forces. *Annu. Rev. Fluid Mech.* **1989**, *21*, 61–99.
- (7) Eslamian, M.; Saghir, M. Z. On Thermophoresis Modeling in Inert Nanofluids. *Int. J. Thermal Sci.* **2014**, *80*, 58–64.
- (8) Schimpf, M. E.; Semenov, S. N. Mechanism of Polymer Thermophoresis in Nonaqueous Solvents. *J. Phys. Chem. B* **2000**, *104*, 9935–9942.
- (9) Israelashvili, J. N. *Intermolecular and Surface Forces*; Academic Press: New York, 1992.
- (10) Semenov, S. N. Mechanism of Particle Thermophoresis in Pure Solvents. *Philos. Mag.* **2003**, *83*, 2199–2208.
- (11) Wittko, G.; Köhler, W. Universal Isotope Effect in Thermal Diffusion of Mixtures Containing Cyclohexane and Cyclohexane-D<sub>12</sub>. *J. Chem. Phys.* **2005**, *123*, 1–6.
- (12) Regazzetti, A.; Hoyos, M.; Martin, M. Experimental Evidence of Thermophoresis of Non-Brownian Particles in Pure Liquids and Estimation of Their Thermophoretic Mobility. *J. Phys. Chem. B* **2004**, *108*, 15285–15292.
- (13) Schermer, R. T.; Olson, C. C.; Coleman, J. P.; Bucholtz, F. Laser-Induced Thermophoresis of Individual Particles in a Viscous Liquid. *Opt. Express* **2011**, *19*, 1057–1058.
- (14) De Groot, S. R.; Mazur, P. *Non-equilibrium Thermodynamics*; North-Holland: Amsterdam, 1962.
- (15) Kondepudi, K.; Prigogine, I. *Modern Thermodynamics*; Wiley: New York, 1999.
- (16) Eslamian, M.; Saghir, M. Z.; Bou-Ali, M. M. Investigation of the Soret Effect in Binary, Ternary and Quaternary Hydrocarbon Mixtures: New Expressions for Thermodiffusion Factors in Quaternary Mixtures. *Int. J. Therm. Sci.* **2010**, *49*, 2128–2137.
- (17) Eslamian, M.; Saghir, M. Z. Dynamic Thermodiffusion Model for Binary Liquid Mixtures. *Phys. Rev. E* **2009**, *80*, 011201–011210.
- (18) Shukla, K.; Firoozabadi, A. A New Model of Thermal Diffusion Coefficients in Binary Hydrocarbon Mixtures. *Ind. Eng. Chem. Res.* **1998**, *37*, 3331–3339.
- (19) Dhont, J. K. G.; Wiegand, S.; Duhr, S.; Braun, D. Thermodiffusion of Charged Colloids: Single-Particle Diffusion. *Langmuir* **2007**, *23*, 1674–1683.
- (20) Dhont, J. K. G. Thermodiffusion of Interacting Colloids. I. A Statistical Thermodynamics Approach. *J. Chem. Phys.* **2004**, *120*, 1632–1641.
- (21) Dhont, J. K. G. Thermodiffusion of Interacting Colloids. II. A Microscopic Approach. *J. Chem. Phys.* **2004**, *120*, 1642–1653.
- (22) Morozov, K. I. Soret Effect in Molecular Mixtures. *Phys. Rev. E* **2009**, *79*, 031204–1–11.
- (23) Hartmann, S.; Wittko, G.; Koehler, W.; Morozov, K. I. Thermophobicity of Liquids: Heats of Transport in Mixtures as Pure Component Properties. *Phys. Rev. Lett.* **2012**, *109*, 065901–065904.
- (24) Hartmann, S.; Wittko, G.; Schock, F.; Groß, W.; Lindner, F.; Morozov, K. I. Thermophobicity of liquids: Heats of transport in mixtures as pure component properties - The case of arbitrary concentration. *J. Chem. Phys.* **2014**, *141*, 134503–134504.
- (25) Vigolo, D.; Brambilla, G.; Piazza, R. Thermophoresis of Microemulsion Droplets: Size Dependence of the Soret Effect. *Phys. Rev. E* **2007**, *75*, 040401–040403 (R).
- (26) Duhr, S.; Braun, D. Why molecules move along a temperature gradient. *Proc. Nat. Acad. Sci. U.S.A.* **2006**, DOI: 10.1073/pnas.0603873103.
- (27) Duhr, S.; Braun, D. Thermophoretic Depletion Follows Boltzmann Distribution. *Phys. Rev. Lett.* **2006**, *96*, 168301–168304.
- (28) Kirkwood, I.; Boggs, E. The Radial Distribution Function of Liquids. *J. Chem. Phys.* **1942**, *10*, 394–402.
- (29) Fisher, I. Z. *Statistical Theory of Liquids*; Chicago University: Chicago, 1964.
- (30) Kirkwood, J. G. Order and Disorder in Liquid Solutions. *J. Phys. Chem.* **1939**, *43*, 97–107.
- (31) Schimpf, M. E.; Semenov, S. N. Thermophoresis of Dissolved Molecules and Polymers: Consideration of The Temperature-Induced Macroscopic Pressure Gradient. *Phys. Rev. E* **2004**, *69*, 011201–011209.
- (32) Semenov, S. N.; Schimpf, M. E. Molecular Thermodiffusion (Thermophoresis) in Liquid Mixtures. *Phys. Rev. E* **2005**, *72*, 041202–041211.
- (33) Parola, A.; Piazza, R. Particle Thermophoresis in Liquids. *Eur. Phys. J.* **2004**, *15*, 255–263.
- (34) Landau, L. D.; Lifshitz, E. M. *Statistical Physics Part 1*, 3 ed.; Pergamon Press: Elmsford, NY, 1980; Chapter XV, Section 156, eq 156.2.
- (35) Alves, J. A.; Baldo, J. B. The Behavior of Zeta Potential of Silica Suspensions. *New J. Glass Ceram.* **2014**, *4*, 29–37.
- (36) Semenov, S. N.; Schimpf, M. E. Thermodynamics of mass transport in diluted suspensions of charged particles in non-isothermal liquid electrolytes. *C. R. Mec.* **2011**, *339*, 280–286.
- (37) Semenov, S. N.; Schimpf, M. E., Statistical Thermodynamics of Material Transport in Non-Isothermal Mixtures, in *Thermodynamics – Interaction Studies – Solids, Liquids and Gases*; Intech: New York, 2011.