

# Mass transport thermodynamics in nonisothermal molecular liquid mixtures

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**Abstract.** Mass transport in a nonisothermal binary molecular mixture is systematically discussed in terms of nonequilibrium thermodynamics, which for the first time allows a consistent and unambiguous description of the process. The thermodynamic and hydrodynamic approaches are compared, revealing that nonequilibrium thermodynamics and physicochemical hydrodynamics yield essentially the same results for molecular systems. The applicability limits for the proposed version of the thermodynamic approach are determined for large particles.

## 1. Introduction

The aim of this paper is to more accurately define and to extend the thermodynamic approach to mass transport in liquid mixtures, and to compare its results with those obtained in the hydrodynamic approach. For simplicity, we consider a simple binary mixture of molecular size nonionic particles, and then, whenever possible, extend our results to multicomponent and polymer systems. We then calculate equilibrium thermodynamic parameters using methods of statistical physics and compare the results with those obtained with the hydrodynamic approach for diluted systems.

Thermodynamic equations for mass transport in liquids are well known [1–3] and are based both on equilibrium thermodynamic considerations (Gibbs and Gibbs–Duhem equations) and on those of nonequilibrium thermodynamics (equations for thermodynamic forces and fluxes). Underlying

the nonequilibrium thermodynamic approach is the entropy production expression

$$\sigma = \mathbf{J}_e \nabla \left( \frac{1}{T} \right) - \mathbf{J}_1 \nabla \left( \frac{\mu_1}{T} \right) - \mathbf{J}_2 \nabla \left( \frac{\mu_2}{T} \right), \quad (1)$$

where  $\mathbf{J}_e$  is the energy flux,  $\mathbf{J}_1$  and  $\mathbf{J}_2$  are the component mass fluxes,  $\mu_1$  and  $\mu_2$  are the component chemical potentials, and  $T$  is the temperature. The energy flux and the temperature distribution in the liquid are assumed to be known, whereas the mass fluxes are determined by the continuity equations [3, Ch. 16]

$$\frac{\partial n_i}{\partial t} = -\nabla \mathbf{J}_i, \quad (2)$$

where  $n_i$  is the numerical concentration of the  $i$ th component and  $t$  is time. Nonequilibrium thermodynamics defines the mass flux as [1–3]

$$\mathbf{J}_i = -n_i L_i \nabla \frac{\mu_i}{T} - n_i L_{iQ} \nabla \frac{1}{T}, \quad (3)$$

where  $L_i$  and  $L_{iQ}$  are kinetic coefficients of individual molecules.

The second term in the right-hand side of Eqn (3) represents the cross effects between the mass and thermal energy fluxes.

The chemical potentials in Eqn (3) are usually expressed in terms of component concentrations and other measurable parameters of the system ([3, Ch. 16], [4, Ch. 6]):

$$\nabla \mu_k = \sum_{l=1}^2 \frac{\partial \mu_k}{\partial n_l} \nabla n_l - \bar{v}_k \nabla P + \frac{\partial \mu_k}{\partial T} \nabla T, \quad (4)$$

where  $P$  is the internal macroscopic pressure of the system and  $\bar{v}_k = \partial \mu_k / \partial P$  is the partial molecular volume.<sup>1</sup> Substitut-

<sup>1</sup> We note that in the latest edition of Landau and Lifshitz's *Hydrodynamics* (Moscow: Fizmatlit, 2006, Ch. 6), the pressure gradient is defined by the Gibbs–Duhem equation.

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ing Eqn (4) in Eqn (3) results in

$$\mathbf{J}_i = \frac{n_i L_i}{T} \left\{ - \sum_{k=1}^2 \frac{\partial \mu_i}{\partial n_k} \nabla n_k + \bar{v}_i \nabla P + \left[ \left( \frac{\mu_i}{T} - \frac{\partial \mu_i}{\partial T} \right) - \frac{L_i Q}{T L_i} \right] \nabla T \right\}. \quad (5)$$

The expression in square brackets in the right-hand side of (5) can be written in a quasithermodynamic form using the parameters  $h_i = \mu_i - T \partial \mu_i / \partial T$  and  $q_i = L_i Q / L_i$ , which are respectively defined as the molecular enthalpy and molecular heat of transport [1–3]. Whereas the molecular enthalpy  $h_i$  is a thermodynamic parameter proper, the heat of transport  $q_i$  is simply a ratio of two kinetic coefficients (dynamic parameters). To our knowledge, no general proof has yet been given of the purely thermodynamic nature of the heat of transport (although in the particular case of an ideal gas mixture, it is shown [2] that the heat of transport is a purely thermodynamic parameter). Finding the relation between the heat of transport and thermodynamic parameters is no doubt of interest because the so-called Soret coefficient, the key parameter characterizing the concentration distribution of components in a nonuniform temperature field, is expressed in terms of the heat of transport [1, 2, 5, 6]. A large number of studies that offer different approaches to calculating the heat of transport are cited in [6]. In Section 2 of this paper, we discuss the relation between the heat of transport and thermodynamic parameters in more detail.

Equations (2) and (5) must be complemented by an equation for the macroscopic pressure gradient in the system. The simplest possible approach, which is to consider the pressure constant [1–4], is inadequate if the temperature and concentration are nonuniform over the system. For diluted systems, this follows from the thermodynamic equation  $\Pi_i = k T n_i$  for the partial osmotic pressure of the mixture component. Another argument favoring the establishment of a pressure gradient in the system is the Gibbs–Duhem equation [1–6]

$$\nabla P = \sum_{i=1}^2 n_i \left( \sum_{k=1}^2 \frac{\partial \mu_i}{\partial n_k} \nabla n_k + \frac{\partial \mu_i}{\partial T} \nabla T \right). \quad (6)$$

Equation (6) ensures that the system is in mechanical equilibrium and guarantees the potentiality of its thermodynamic functions, whose values therefore depend only on the initial and final values of the parameters of a reversible process. In Ref. [6], the pressure gradient is taken to be zero. An equation equivalent to Eqn (6) was derived in [7] and used to calculate kinetic coefficients—ignoring, however, the mass flux equations in doing so. In Ref. [8], in which a mass flux expression obtained from the Kramers equation is used to calculate kinetic coefficients, the authors disregard the pressure gradient, whose presence is necessary for a system to be in mechanical equilibrium. Papers [8–10] also consider the so-called thermophoretic force, which is due to the gradient in the kinetic energy of an isolated particle in a liquid under a temperature gradient. (We note that no consideration is given to whether the molecules of the suspending liquid experience this force and what the implications of this are.)

Gibbs–Duhem equation (6) is the condition of mechanical equilibrium in the system. Bulk forces of different origins are expressed in (6) in terms of the corresponding chemical potential gradients [1–3] and can be related to the tempera-

ture, pressure, component concentrations, etc.—the determining parameters of the chemical potential. Equation (4), similarly, is for the total force acting on the particle. The bulk forces are balanced by the pressure gradient that is established in the system, and this mechanical equilibrium must establish both in the system as a whole and at the local molecular level, when all the bulk forces around a chosen particle must add up to zero for the particle to be in a stationary state. The last condition must be satisfied at least in an isothermal equilibrium system, in which all the particles are at rest on average.

The mechanical equilibrium condition for an isothermal homogeneous system, as well as the use of Eqns (1)–(6) in general, is closely related to the principle of local equilibrium applied to nonequilibrium and inhomogeneous systems. As argued in Refs [11, 12], local equilibrium is violated in thermophoresis because the free energy change across a particle is typically comparable to the thermal energy of the particle. Calculations in Refs [11, 12] show that even for large (micron size) particles, the change in question is no more than a few percent of  $kT$ . The authors provide no arguments to support this statement, which is questionable because (if for no other reason), given the same temperature gradient, local equilibrium should be first violated for large rather than small particles, because the temperature drop across the former is larger. It is not easy to assume that with the conditions being equal, local equilibrium can be fulfilled, for example, for molecules but not for colloidal particles.

The conditions for the local equilibrium principle to hold are in fact a well-researched subject and relate to the case where physical properties change little over the molecular length and the mean free path scale. A detailed discussion on this topic and references to earlier works are given in [13]. In summary, for the local equilibrium principle to hold, both the relative change in temperature and the change in molecular velocity must be small over the mean free path (in comparison to the speed of sound). For a gas, this corresponds to the temperature gradient about  $10^5 \text{ K cm}^{-1}$  according to Ref. [13], and for a liquid, with its heat conductivity and speed of sound higher and mean free path shorter, this condition should be more than fulfilled, noting that the experimental temperature gradient does not exceed  $10^4 \text{ K cm}^{-1}$ . We therefore assume that the local equilibrium condition is satisfied in the nonisothermal systems considered here.

Equations (2)–(6) are complemented by equations relating the fluxes or concentrations of the components,

$$v_1 \mathbf{J}_1 + v_2 \mathbf{J}_2 = \mathbf{J}, \quad (7)$$

where  $\mathbf{J}$  is the total mass flux through the system. In a closed system, which cannot exchange particles with its environment,  $\mathbf{J} = 0$ . Equation (7) can also be written as

$$\phi_1 + \phi_2 = 1, \quad (8)$$

where  $\phi_1$  and  $\phi_2$  are the volume fractions of the corresponding components. Because of Eqn (8), the component concentrations cannot be considered independent variables. The term  $\sum_{i=1}^2 \partial \mu_k / \partial n_i \nabla n_i$  in Eqns (4)–(6) can be represented as the gradient of the composition function  $\mu_k = \mu_k[n_2, n_1(n_2)]$ . Passing to more convenient volume fraction variables  $\phi_2 = \phi$  and  $\phi_1 = 1 - \phi$  [see Eqn (8)], we find that

$$\sum_{i=1}^2 \frac{\partial \mu_k}{\partial n_i} \nabla n_i = \frac{\partial \mu_k}{\partial \phi_2} \nabla \phi_2 + \frac{\partial \mu_k}{\partial \phi_1} \frac{\partial \phi_1}{\partial \phi_2} \nabla \phi_2 = 2 \frac{\partial \mu_k}{\partial \phi} \nabla \phi, \quad (9)$$

where we note that  $\partial\mu_k/\partial\phi_2 = -\partial\mu_k/\partial\phi_1$  and  $\partial\phi_1/\partial\phi_2 = -1$ , as Eqn (8) suggests.

## 2. Thermodynamic expressions for heats of transport. Closed stationary systems

Substituting Eqns (6) and (9) in the mass flux in Eqn (5), we obtain the following two equations for the component mass fluxes expressed in terms of the volume fraction of the second component  $\phi$ :

$$\mathbf{J}_1 = \frac{L_1}{Tv_1} \left[ \phi(1-\phi) \left( 2 \frac{\partial\mu^*}{\partial\phi} \nabla\phi + \frac{\partial\mu^*}{\partial T} \nabla T \right) + (1-\phi)(\mu_1 - q_1) \frac{\nabla T}{T} \right], \quad (10)$$

$$\mathbf{J}_2 = \frac{L_2}{Tv_1} \left[ -\phi(1-\phi) \left( 2 \frac{\partial\mu^*}{\partial\phi} \nabla\phi + \frac{\partial\mu^*}{\partial T} \nabla T \right) + \frac{v_1}{v_2} \phi(\mu_2 - q_2) \frac{\nabla T}{T} \right]. \quad (11)$$

In deriving Eqns (10) and (11), it was assumed that the partial molecular volumes  $\bar{v}_k$  are equal to the specific molecular volumes  $v_k$ ; this assumption introduces an error of no more than a few tenths of a percent for a wide variety of substances. Another important feature of the derivation is the introduction of the so-called combined chemical potential, defined as

$$\mu^* = \mu_2 - \frac{v_2}{v_1} \mu_1. \quad (12)$$

The concept of the combined chemical potential  $\mu^*$  as a characteristic parameter of a binary mixture was introduced many years ago (Refs [1, 2]) and is in wide use today (see, e.g., Refs [5–7]). The authors of Ref. [4] introduce a similar parameter but assume that one single kinetic parameter is sufficient to characterize an isothermal binary mixture. However, such a kinetic coefficient should take the form of the well-known Stokes–Einstein expressions in both diluted systems, which is impossible to achieve with only one kinetic coefficient, and therefore it is preferable to retain different and a priori unequal kinetic coefficients in Eqns (10) and (11). We note that, as is to be shown in Section 3, the diffusion coefficient can be calculated for any concentration if the viscosity and hydrodynamic radii of the component are known.

It is clearly seen from Eqn (12) that the chemical potential of the solvent becomes the prevailing factor for large molecules, for which  $v_2/v_1 \gg 1$ . The mass diffusion and thermal diffusion of such particles are at first sight independent of the particle properties (except its volume) and depend only on the properties of the solvent, which leads to the conclusion (see review [14]) that expressions involving combined chemical potential (12) produce results that are not physical in nature. However, it is shown in Refs [7, 15] that the combined chemical potential is in any case simply a parameter proportional to the osmotic pressure in the system. We show in Section 4 that a more detailed microscopic treatment using statistical perturbation theory gives a different picture, and that the proposed approach is obviously valid if the interacting molecules or their interacting fragments are of a size comparable to the scale of change of their interaction potential. The case of larger particles, for which the interaction potential varies on a definitely smaller scale than their size, needs a separate study.

In Ref. [15], the mass transport problem for colloidal particles is approached using equilibrium thermodynamics and ignoring the production of entropy and the associated fluxes.

Having discussed dynamic arguments, we next consider the purely thermodynamic aspects of describing a system, which is the most important topic at this point because it is probably in order to overcome the difficulties arising here that the integrated diffusion coefficient was introduced in Ref. [4].

Equations (8), (10), and (11) determine mass fluxes in a binary system. Formally, the problem with these equations is that their number is larger than that of the unknowns: there are two equations for fluxes and there is one unknown, the volume fraction of the second component. For an isothermal mixture, this problem is overcome by using the  $L_1 = L_2$  assumption in Ref. [4] (see above), thus making Eqns (10) and (11) equivalent. This approach, however, does not work for a system with a temperature gradient. Of greater use is the approach in [1–3, 5, 6], in which one of the components is considered the solvent and the other the solute, their respective concentration distributions being described by Eqns (7), (8) and by one of Eqns (10), (11) (that is, one of the mass flux equations is simply ignored). Both flux equations (and hence the production of entropy in a nonequilibrium system) were ignored in [7], where the corresponding form of the Gibbs–Duhem equation was used to calculate the concentration distribution (or chemical potential) in the solvent. All the other studies known to us use one of Eqns (10), (11) for the solute and then use Eqn (7) to calculate the flux of the solvent.

Admittedly, such approaches are intuitively applicable to diluted solutions, with their clear distinction between the solvent and the solute. But in high-concentration solutions, with components comparable in concentration, it is a totally arbitrary choice as to which of them is the solvent and which the solute. As a result, we have equally valid approaches to describe a mixture: two for a binary system, three for a ternary, etc. From our standpoint, this means that we need a different solution to this problem, one that would make flux equations (10) and (11) compatible with Eqn (7).

A closer look at Eqns (10) and (11) reveals a further problem. The flux terms proportional to  $\nabla T/T$  in Eqns (10) and (11) describe the mass transport of pure components in a nonisothermal system, the process having no relation whatsoever to the corresponding thermal osmosis or to whether the system have walls. The present authors are not aware of any reason for this phenomenon, nor has it ever been observed experimentally, which naturally suggests the elimination of these terms from the mass flux equations. This is most easily done by assuming the following general relations between the heat of transport and the corresponding chemical potential of a component:

$$\mu_1 = q_1, \quad (13)$$

$$\mu_2 = q_2. \quad (14)$$

Equations (13) and (14) define heats of transport as thermodynamic parameters, with the consequence that the mass flux caused by the temperature gradient and producing a concentration gradient in a homogeneous mixture can be expressed as a quantity proportional to  $(\partial\mu^*/\partial T)\nabla T$ . Recalling that the specific molecular entropy of a component is defined as  $s_{1,2} = \partial\mu_{1,2}/\partial T$ , such mass transport (traditionally

associated with thermal diffusion) can be assumed to have a purely entropic origin. Thus, eliminating ‘extra’ terms from the mass transport equations allows the heat of transport to be defined in thermodynamic terms and the thermal diffusion to be defined as a purely entropic process.

Equations (13) and (14) alone do not guarantee that Eqns (10) and (11) are compatible in all cases, and should be complemented by the conditions

$$\mathbf{J}_1 = \mathbf{J}_2 = 0 \quad (15)$$

which express the stationary and closed nature of the system.

It is only under these conditions that Eqns (7), (10), and (11) become compatible, and hence only a closed stationary system allows an unambiguous thermodynamic description of mass transport in a binary mixture with a temperature gradient. Nonequilibrium thermodynamics, as it is currently formulated, fails to unambiguously predict the behavior of open and/or nonstationary systems (for more on this, see Section 3).

We now use one of equations (7) and (8) (which are now compatible) to obtain the following expression for the Soret coefficient  $S_T$ , the key physical parameter that characterizes the stationary nonuniform concentration distribution resulting from the balance between the thermal diffusion flux and the diffusion flux:

$$S_T = -\frac{\nabla\phi}{\phi(1-\phi)\nabla T} = -\frac{\partial\mu^*/\partial T}{2\phi(1-\phi)\partial\mu^*/\partial\phi}. \quad (16)$$

Using Eqn (16) allows calculating the Soret coefficient for systems in which component chemical potentials vary with concentration and temperature in a known way. Traditionally, the Soret coefficient is considered positive if the colder region of a mixture is enriched with the component under consideration. For the highly diluted systems ( $\phi \ll 1$ ) studied in the experiments in Ref. [16], expression (16) becomes

$$S_T = -\frac{\partial\mu_2^0/\partial T - (v_2/v_1)(\partial\mu_1^0/\partial T)}{2kT}, \quad (17)$$

where  $\mu_1^0$  is the chemical potential of the pure solvent and  $\mu_2^0$  is that of an isolated particle in the solvent. The derivation of Eqn (17) assumes that the ratio  $v_2/v_1$  is essentially unchanged with temperature because both molecular volumes in a diluted system have their temperature dependence determined by processes in the solvent that are due to the thermal motion of the solvent molecules.

### 3. Open and nonstationary systems and the dynamic pressure gradient

In an open system, the mass flux of a component may be nonzero because there is a flux of mass across the system boundary. In a nonstationary closed system, the component mass fluxes  $\mathbf{J}_1$  and  $\mathbf{J}_2$  are nonzero even though the total mass flux in the system,  $\mathbf{J}$ , is zero. As a result, the Gibbs–Duhem equation can no longer determine the pressure in the system; hence, some other approach should be found for the purpose.

In previous works [17, 18], we combined the purely kinetic approach with the Fokker–Planck equations to obtain mass transport equations in which dynamic parameters, cross-diffusion coefficients, and thermal diffusion coefficients were calculated using the equations of hydrodynamics. The

macroscopic pressure gradient was calculated from continuity equations of type (2) and from Eqn (8). The same approach can be used to solve the flux equations of non-equilibrium thermodynamics.

In this case, the continuity equations become

$$\frac{\partial\phi}{\partial t} = \nabla \left[ \frac{L_1(1-\phi)}{T} \left( 2 \frac{\partial\mu_1}{\partial\phi} \nabla\phi - v_1 \nabla P + \frac{\partial\mu_1}{\partial T} \nabla T \right) \right], \quad (18)$$

$$-\frac{\partial\phi}{\partial t} = \nabla \left[ \frac{L_2\phi}{T} \left( 2 \frac{\partial\mu_2}{\partial\phi} \nabla\phi - v_2 \nabla P + \frac{\partial\mu_2}{\partial T} \nabla T \right) \right]. \quad (19)$$

In Eqns (18) and (19), the heat of transport is taken to be defined in accordance with Eqns (13) and (14). Solving the set of equations (18) and (19) for  $\phi$  and  $\nabla P$  using Eqn (8) yields

$$\begin{aligned} \nabla P = & \frac{1}{v_2[(v_1/v_2)(1-\phi) + (L_2/L_1)\phi]} \\ & \times \left\{ -\frac{\mathbf{J}}{L_1} + 2 \left[ (1-\phi) \frac{\partial\mu_1}{\partial\phi} + \frac{L_2}{L_1} \phi \frac{\partial\mu_2}{\partial\phi} \right] \nabla\phi \right. \\ & \left. + \left[ (1-\phi) \frac{\partial\mu_1}{\partial T} + \frac{L_2}{L_1} \phi \frac{\partial\mu_2}{\partial T} \right] \nabla T \right\}, \quad (20) \end{aligned}$$

$$\begin{aligned} \frac{\partial\phi}{\partial t} = & \frac{L_2}{T} \\ & \times \nabla \left[ \frac{\phi(1-\phi)(2(\partial\mu^*/\partial\phi)\nabla\phi + (\partial\mu^*/\partial T)\nabla T) - \phi\mathbf{J}/L_1}{1-\phi + L_2v_2/(L_1v_1)\phi} \right]. \quad (21) \end{aligned}$$

A comparison of Eqn (21) with Eqn (14) for a stationary mixture shows that Eqn (21) contains an additional drift term  $\phi\mathbf{J}/L_1$  proportional to the mass flux through the open system. The term  $-\mathbf{J}/L_1$  in Eqn (20) describes the corresponding pressure gradient component. The additional mass flux component is due to barodiffusion driven by the dynamic pressure gradient associated with viscous dissipation in the system. The parameter  $\mathbf{J}$  is independent of position in the system but is determined by mass transport across the system boundaries and may vary with time. Mathematically, the parameter  $\mathbf{J}$  is determined by the boundary conditions for Eqn (19).

If a system is open but stationary, molecules entering it through one of its boundary surfaces can leave it through another, thus creating a molecular drift that is independent of whether the temperature or pressure have a gradient. This drift is determined by the conditions at the boundaries and is independent of any force applied to the system. For example, the system may have a source of some molecular species at one boundary and a sink at another. As molecules of a given species move between the two, they experience viscous friction, which creates a dynamic pressure gradient, with the result that both this and the other molecular species are involved in barodiffusion. This additional pressure gradient, due to viscous friction, is not taken into account in the Gibbs–Duhem force balance equation.

Equations (6) and (10), (11) describe a system in hydrostatic equilibrium without viscous friction caused by the material flux due to material exchange with the environment. Unlike the Gibbs–Duhem equation, Eqn (20), which is also a force balance type equation, accounts for viscous friction forces and their compensating dynamic pressure

gradient in closed and nonstationary systems. For a closed stationary system, in which  $\mathbf{J} = 0$ ,  $\partial\phi/\partial t = 0$ , Eqn (21) transforms into

$$\phi(1 - \phi) \left( 2 \frac{\partial\mu^*}{\partial\phi} \nabla\phi + \frac{\partial\mu^*}{\partial T} \nabla T \right) = 0, \quad (22)$$

to which Eqns (10), (11) also reduce if the proposed heat of transport expressions (13) and (14) are taken into account.

The interaction of system components with the walls also develops a dynamic pressure gradient in the system. Adsorption on the walls causes the molecules to leave the system, whereas their desorption causes their influx: the two fluxes of course disappear when the adsorption–desorption process reaches equilibrium.

There are thermal diffusion experiments, however, in which the system experiences periodic temperature changes, as is the case, for example, with the method in [19], where thermal diffusion was observed by recording a dynamic temperature lattice in a liquid using a pulsed infrared laser. Because this involves changing the wall temperature and thereby changing the equilibrium adsorption constant, material fluxes vary with time, resulting in an influx/outflux periodicity. Preliminary analysis shows that material fluxes to and from the walls have relaxation times about a few microseconds until equilibrium is attained, and such nonstationary material fluxes, due to changes in the wall temperature, can be observed using dynamic temperature lattices.

For a diluted isothermal system, Eqn (21) should reduce to the standard diffusion equation. We must therefore define the kinetic coefficients as  $L_i = D_i(\phi)/(2k)$ , where  $D_i$  is the Stokes–Einstein diffusion coefficient corresponding to the real hydrodynamic radius of the molecule under consideration and to the value of viscosity of a real liquid mixture at the given concentration. We note that the ratio  $L_2v_2/(L_1v_1)$  is independent of the concentration if the hydrodynamic radii of the components do not change. In experiments using optical methods to study the dynamics of fluctuations, the effective diffusion coefficient is determined from the fluctuation decay rate. According to Eqn (21), the effective diffusion coefficient depends on the concentration as

$$D_{\text{eff}} = \frac{D_2(\phi)}{kT} \frac{\phi(1 - \phi) \partial\mu^*/\partial\phi}{1 - \phi + D_2v_2/(D_1v_1)\phi}. \quad (23)$$

The diffusion coefficient thus defined can be calculated for a system of miscible solvents using solubility parameters [20, 21].

At temperatures well above the critical separation temperature, solutions can be considered ideal, which allows using the well-known expressions

$$\mu_1(\phi) = \mu_1^0 + kT \ln(1 - \phi), \quad (24)$$

$$\mu_2(\phi) = \mu_2^0 + kT \ln\phi. \quad (25)$$

For such systems, the effective diffusion coefficient takes the form

$$D_{\text{eff}} = D_2(\phi) \frac{1 + (v_2/v_1 - 1)\phi}{1 - \phi + D_2v_2/(D_1v_1)\phi}. \quad (26)$$

The diffusion coefficient given by Eqn (26) is valid for all concentrations if the solution can be considered ideal. For diluted systems, the dynamic barodiffusion factor

$(1 - \phi + D_2v_2/(D_1v_1)\phi)^{-1}$  becomes unity, and the diffusion coefficient in (23) transforms into the well-known Stokes–Einstein expression for an isolated molecule in the corresponding component in pure form. If there is no such factor, as in the model in Ref. [7] or in Ref. [4], the limiting process is possible only for one diluted solution of the two possible, even in ideal solutions.

In semidiluted solutions, the second virial coefficient is typically used to describe the concentration dependence of the effective diffusion coefficient [22]. This approach is based on representing the combined chemical potential in terms of the osmotic pressure  $\Pi$  (see, e.g., Refs [7, 9]). In this approximation, the isothermal diffusion coefficient is usually written as

$$D_{\text{eff}} = D_2(\phi = 0) \frac{v_2}{kT} \frac{\partial\Pi/\partial\phi}{1 + (5/2)\phi}, \quad (27)$$

where the osmotic pressure is expressed in terms of the second virial coefficient  $B$  as [22]

$$\Pi = kT \frac{\phi}{v_2} \left( 1 + B \frac{\phi}{v_2} \right). \quad (28)$$

Equation (27) contains the well-known expression for the viscosity of a diluted liquid mixture

$$\eta(\phi) = \eta_0 \left( 1 + \frac{5}{2} \phi \right),$$

where  $\eta_0$  is the viscosity of an infinitely diluted liquid [4]. Equation (23) then becomes

$$D_{\text{eff}} = \frac{D_2}{kT} \frac{\phi(1 - \phi) \partial\mu^*/\partial\phi}{(1 - \phi + D_2v_2/(D_1v_1)\phi)(1 + (5/2)\phi)} \approx D_2(\phi = 0) \left[ 1 - \left( \frac{2B}{v_2} - \frac{D_2v_2}{D_1v_1} - \frac{3}{2} \right) \phi \right]. \quad (29)$$

With the effects of the dynamic pressure gradient and of its associated barodiffusion neglected, the concentration dependence of the effective diffusion coefficient becomes [22]

$$D_{\text{eff}} = D_2(\phi = 0) \left[ 1 - \left( \frac{2B}{v_2} - \frac{5}{2} \right) \phi \right]. \quad (30)$$

Using Eqn (30) to calculate the second virial coefficient is a standard practice, for example, in polymer physics [22]. The second virial coefficient is used as an intermolecular interaction parameter. For noninteracting particles, the second virial coefficient  $B$  takes the value  $8v_2$ , where  $8v_2$  is the volume that the molecule under consideration makes inaccessible to other particles. Using this parameter, the relative contribution of dynamic barodiffusion to the second virial coefficient is estimated as  $(2/27)|D_2v_2/(D_1v_1) - 1|$ . For a mixture of methanol and ethanol with the respective molar volumes  $41 \text{ cm}^3$  and  $58 \text{ cm}^3$  and with essentially equal radii, the contribution of dynamic barodiffusion is about 3%. For a mixture of methanol/*n* and propanol with  $v_1/v_2 \approx 41/75$ , the contribution is about 6%.

We note that the second virial coefficients themselves for such mixtures should, if expressed in terms of  $B/v_2$ , be virtually identical because such systems differ very little in terms of molecular interaction. Such effects in the concentration dependence of the effective diffusion coefficient are quite measurable using standard optical methods. For macromol-

ecules, these effects should be even more pronounced. Thus, dynamic barodiffusion should necessarily be taken into account when measuring the second virial coefficient derived from the concentration dependence of the effective diffusion coefficient.

For processes involving macromolecules, dynamic barodiffusion should be even more important because the parameter  $D_2v_2/(D_1v_1)$  that determines its contribution is much larger than that for low-molecular compounds. The thermal diffusion of DNA molecules, which are 50 to 50,000 base pairs in length, was observed in [16] at concentrations 1 pM to 1  $\mu$ M; a decrease in the DNA diffusion coefficient with increasing the chain length was reported. The theoretical explanation of this result is still lacking. According to the currently accepted theory, the thermal diffusion coefficient (also known as the thermophoretic mobility or the velocity of motion under a unit temperature gradient) of macromolecules and colloidal particles is independent of their ‘macroscopic’ size and is determined solely by the size of ‘microscopic’ monomer-type inhomogeneities (see, e.g., review [14] or the original work by de Gennes [25]). For a polymer, this is about the size of a monomer unit. The data in Ref. [16] can at least qualitatively be explained based on the results in the present paper.

It follows from Eqn (21) that the expression for the thermal diffusion coefficient is

$$D_T = \frac{D_2}{2kT} \frac{(1-\phi)\partial\mu^*/\partial T}{1-\phi + D_2v_2/(D_1v_1)\phi}. \quad (31)$$

According to Eqn (31), the thermal diffusion coefficient vanishes for  $\phi \approx 1$ . For a diluted solution, with  $\phi \ll 1$ , the numerator in Eqn (31) takes a form consistent with Eqn (17). Unfortunately, the temperature derivative of the combined chemical potential is unknown for an isolated molecule. As far as the calculation of this derivative is concerned, the methods of statistical physics (see Section 4) compare well with the hydrodynamic approach, allowing the use of the latter for estimates [17, 18]. According to hydrodynamic calculations (and in agreement with a much earlier estimate in [25]),  $D_2\partial\mu^*/\partial T$  is proportional to the square of the size of a ‘dissolved’ molecule (monomer). But this is only true for  $D_2v_2/(D_1v_1)\phi \ll 1$ . For large molecules or monomers, this condition can even fail for thermodynamically dilute ( $\phi \ll 1$ ) mixtures. For  $D_2v_2/(D_1v_1)\phi \ll 1$ , the thermal diffusion coefficient of a dilute solution is

$$D_T = \frac{D_1}{2kT} \frac{v_1\partial\mu^*/\partial T}{v_2\phi}. \quad (32)$$

It follows from Eqn (32) that the thermal diffusion coefficient is inversely proportional to the molecular volume of the particle if the concentration of these particles is sufficiently high. We thus see that in the theory under discussion, the decrease in the thermal diffusion coefficient with the DNA molecular mass is qualitatively explained as a barodiffusion-induced concentration effect. It has been estimated that the condition  $D_2v_2/(D_1v_1)\phi \geq 1$  is satisfied for at least some of the concentrations and DNA sizes from the ranges investigated in Ref. [16]. Importantly, the conclusions above can only hold for molecules in a compact conformation. For random-coil molecules, there is much experimental evidence that the volume of a monomer unit serves as a molecular volume  $v_2$ .

Thus, in addition to the standard thermodynamic definition of a dilute solution ( $\phi \ll 1$ ), the theory under discussion provides the dynamic dilution criterion

$$\frac{D_2v_2}{D_1v_1}\phi \ll 1.$$

This criterion implies that the contribution of the dynamic barodiffusion is small and allows a thermodynamic description based on the Gibbs–Duhem equation.

#### 4. Calculating $\partial\mu^*/\partial T$ : a microscopic approach

In this section, we calculate the parameter  $\partial\mu^*/\partial T$  and compare our results with those obtained previously using the hydrodynamic approach. In the hydrodynamic approach, the local pressure distribution around a particle is calculated and the Navier–Stokes equations are solved, yielding the liquid flux velocity profile and the hydrodynamic stress field around the particle [14, 17, 18]. This is followed by calculating either the velocity of the particle in the presence of a temperature gradient or the thermal diffusion coefficient. Comparing the thermodynamic and hydrodynamic approaches to the theory of thermophoresis is important as a means to check the results of the proposed approach and to discuss a number of problems that arise in the hydrodynamic approach. No less important, this comparison also yields the range of applicability of the proposed method.

The parameter  $\partial\mu^*/\partial T$  is most conveniently calculated using a microscopic treatment. We confine ourselves here to the case of limiting dilution, in which the property to be calculated is the temperature derivative of the chemical potential of an isolated particle. In this case, we can use the thermodynamic perturbation theory [26, 27] and write the chemical potential of an isolated ‘dissolved’ particle as

$$\mu_2^0(\mathbf{r}) = \left\langle \sum_i \Phi_{12}(\mathbf{r} - \mathbf{r}_{1i}) + \frac{\mathbf{p}^2}{2m_2} + \delta \left[ \frac{1}{2} \sum_{i,j} \Phi_{11}(\mathbf{r}_{1j} - \mathbf{r}_{1i}) \right] \right\rangle, \quad (33)$$

in agreement with its basic definition as the change in the free energy of the system due to the addition of this particle. Here,  $\Phi_{11}$  and  $\Phi_{12}$  are the respective intermolecular interaction potentials of the particle–solvent and solvent–solvent systems and  $\mathbf{p}^2/(2m_2)$  is the kinetic energy of a particle of momentum  $\mathbf{p}$  and mass  $m_2$ . The last term in the right-hand side is the change in the interaction energy between solvent molecules due to the presence of the particle. The angular brackets denote averaging in the usual sense of statistical thermodynamics, assuming the Hamiltonian of the system to be unperturbed by the particle under consideration.

Averaging the kinetic energy yields  $\langle \mathbf{p}^2/(2m_2) \rangle = 3kT/2$  for both an isolated ‘dissolved’ particle and all solvent molecules, and therefore, in the presence of a temperature gradient, a corresponding (uniform) force should act on all particles in the system. This force cannot impart thermophoretic motion to the particle under study and can only lead to the motion of the liquid as a whole or to the appearance of a pressure gradient in the system, which compensates the force according to the Gibbs–Duhem equation. The logical choice is the second option, and this casts doubt on the approach in Refs [8–10] using a similar force related to the change in the particle kinetic energy as the driving force of thermophoresis. The change in the intermolecular interaction

in the solvent due to the presence of the molecule under discussion can also be described as a pressure gradient  $\nabla P$  around the particle. Below, we discuss a way to calculate this change.

Under all the assumptions above, the chemical potential corresponding to Eqn (33) has the gradient

$$\frac{\partial \mu_2^0(\mathbf{r})}{\partial \mathbf{r}} = - \int_V \frac{\partial \Phi_{12}(\mathbf{r} - \mathbf{r}_1)}{\partial T} \nabla T(\mathbf{r}_1) n_1(\mathbf{r}_1) dV_1 + \int_V \frac{\partial \Pi(\mathbf{r}_1)}{\partial T} \nabla T(\mathbf{r}_1) dV_1, \quad (34)$$

where  $n_1(\mathbf{r}_1)$  is the local numerical concentration distribution of solvent molecules,  $\mathbf{r}$  and  $\mathbf{r}_1$  are the corresponding radius vectors,  $V$  is the volume of the system (except for the volume of the isolated particle itself), and  $\nabla = \partial/\partial \mathbf{r}_1$ . Expression (34) takes into account that according to Newton's third law,  $\partial \Phi_{12}(\mathbf{r} - \mathbf{r}_1)/\partial \mathbf{r} = -\nabla \Phi_{12}(\mathbf{r} - \mathbf{r}_1)$  and that the total force the solvent molecules exert on the 'dissolved' molecule is zero in an isothermal system,

$$\int_V [-\nabla \Phi_{12}(\mathbf{r} - \mathbf{r}_1) n_1(\mathbf{r}_1) + \nabla \Pi(\mathbf{r}_1)] dV_1 = 0. \quad (35)$$

Equation (35) can be interpreted as expressing the local mechanical balance in the surroundings of a 'dissolved' particle:

$$\nabla \Phi_{12}(\mathbf{r} - \mathbf{r}_1) n_1(\mathbf{r}_1) = \nabla \Pi(\mathbf{r}_1), \quad (36)$$

where the bulk force  $\nabla \Phi_{12}(\mathbf{r} - \mathbf{r}_1) n_1(\mathbf{r}_1)$  is compensated by the pressure gradient  $\nabla \Pi(\mathbf{r}_1)$ . We note that except for a difference in notation, the first term in square brackets in Eqn (35) is identical to the expression obtained in Ref. [8]. The difference, however, is that the study in Ref. [8] neglects the conditions for an isothermal system given by Eqns (35) and (36) and ignores the changes caused by the presence of an isolated molecule in the solvent.

Equation (36) can be interpreted as a local Gibbs–Duhem relation and used to calculate the pressure distribution in the system. According to the local equilibrium principle, the temperature–pressure–particle distribution relation given by Eqn (36) should also hold for a nonisothermal nonequilibrium system. Although the local distribution  $n_1(\mathbf{r}_1)$  is often expressed in the literature in terms of the pair correlation function [28], the extreme difficulties encountered in calculating liquid-state correlation functions make this approach unsuitable for our purpose. Instead, we adopt some simple assumptions on the concentration distribution that can ensure good agreement with experiment. If the particle under study interacts not with solvent molecules but only with the molecules of a low-concentration surface-active substance it dissolves, then

$$n_1(\mathbf{r}_1) \approx n_0 \exp\left(-\frac{\Phi_{12}(\mathbf{r}_1)}{kT}\right), \quad (37)$$

where  $n_0$  is the concentration of surface-active molecules far from the particle under study (located at  $\mathbf{r} = 0$ ). We note that according to Eqn (36), the local pressure distribution takes the form

$$\Pi(\mathbf{r}_1) - \Pi_0 = n_0 kT \left[ \exp\left(-\frac{\Phi_{12}(\mathbf{r}_1)}{kT}\right) - 1 \right]. \quad (38)$$

Expression (38), which is widely used in treating the diffusiophoresis and thermophoresis of colloidal particles [29], is just a usual distribution of osmotic pressure in the potential field around an isolated particle.

Another extreme case occurs when the particle interacts with all the solvent molecules but the concentration distribution cannot change to any noticeable extent simply because there is no free volume for this around the particle. In this case, a good approximation is given by

$$n_1(\mathbf{r}_1) \approx \frac{1}{v_1}, \quad (39)$$

yielding the local pressure

$$\Pi(\mathbf{r}_1) - \Pi_0 = \frac{\Phi_{12}(\mathbf{r}_1)}{v_1}. \quad (40)$$

The quantity  $\Pi_0$  in Eqns (38) and (40) is the macroscopic pressure, which does not vary significantly on a molecular scale, but is not necessarily uniform on a macroscopic scale.

Using Eqns (38) and (40), we can calculate the pressure gradient in Eqn (34) and the force acting on the particle.

From Eqn (38), the pressure gradient is

$$\begin{aligned} \nabla \Pi(\mathbf{r}_1) &= \\ &= \nabla \Pi_0 + n_0 k \left\{ \exp\left(-\frac{\Phi_{12}(\mathbf{r}_1)}{kT}\right) \left[ 1 + \frac{\Phi_{12}(\mathbf{r}_1)}{kT} \right] - 1 \right\} \nabla T(\mathbf{r}_1) \\ &\quad - n_0 \exp\left(-\frac{\Phi_{12}(\mathbf{r}_1)}{kT}\right) \frac{\partial \Phi_{12}(\mathbf{r}_1)}{\partial T} \nabla T(\mathbf{r}_1), \end{aligned} \quad (41)$$

and from Eqn (40), for the other extreme, the pressure gradient is

$$\nabla \Pi(\mathbf{r}_1) = \nabla \Pi_0 - \alpha_T \frac{\Phi_{12}(\mathbf{r}_1)}{v_1} \nabla T(\mathbf{r}_1) + \frac{\partial \Phi_{12}(\mathbf{r}_1)/\partial T}{v_1} \nabla T(\mathbf{r}_1). \quad (42)$$

Expressions (41) and (42) correspond to the last term in the right-hand side of Eqn (34). Substituting them in Eqn (34) yields expressions for the chemical potential gradient of an isolated particle,

$$\begin{aligned} \frac{\partial \mu_2^0(\mathbf{r})}{\partial \mathbf{r}} &= v_2 \nabla \Pi_0 + \int_V n_0 k \left\{ \exp\left(-\frac{\Phi_{12}(\mathbf{r}_1)}{kT}\right) \right. \\ &\quad \times \left. \left[ 1 + \frac{\Phi_{12}(\mathbf{r}_1)}{kT} \right] - 1 \right\} \nabla T(\mathbf{r}_1) dV_1, \end{aligned} \quad (43)$$

$$\frac{\partial \mu_2^0(\mathbf{r})}{\partial \mathbf{r}} = v_2 \nabla \Pi_0 - \frac{\alpha_T}{v_1} \int_V \Phi_{12}(\mathbf{r}_1) \nabla T(\mathbf{r}_1) dV_1. \quad (44)$$

That Eqns (43) and (44) do not contain terms with the temperature derivatives of the intermolecular interaction potential is a direct consequence of the local equilibrium principle used in calculating the local pressure gradient in a nonisothermal system. As shown in Ref. [18], the above arguments are also valid for the concentration dependence of the interaction potential. Expression (43) is readily extended to the case of more than one species of molecular or ionic surfactants, and Eqn (44) can also be extended to molecular liquid mixtures.

Thus, for a system in local equilibrium, the temperature and concentration dependence of the intermolecular interac-

tion potential cannot be regarded as the driving force of thermophoresis (thermodiffusion) processes. This fact is ignored in numerous original and review papers on thermophoresis (see, e.g., Refs [7–9, 15, 30, 31]). The most common approach in dealing with charged particles is to calculate the thermodiffusion coefficient due to the temperature dependence of the dielectric constant. In some studies, effects due to the temperature dependence of the Debye length are considered. These dependences are indeed strong enough to cause a particle to move in the presence of a temperature gradient, but their influence is compensated due to the corresponding local pressure gradient, as shown above.

We cannot here consider the thermophoresis of ions (this would require a somewhat different formulation of the thermodynamic aspects of the problem) and limit ourselves to considering uncharged molecules and polymers. As shown, for a small particle with a size of the order of the change scale of the intermolecular interaction potential, the particle thermodiffusion is essentially independent of the detailed charge distribution around it [32], and it therefore follows from Eqn (44) that

$$\frac{\partial \mu_2^0(\mathbf{r})}{\partial \mathbf{r}} = v_2 \nabla \Pi_0 - \frac{\alpha_T \nabla T_\infty}{v_1} \int_V \Phi_{12}(\mathbf{r}_1) dV_1, \quad (45)$$

where  $\nabla T_\infty$  is the ‘macroscopic’ temperature gradient far away from the particle. For nonionic molecules, the interaction potential can be written as [17, 18, 33]

$$\Phi_{12} = -\varepsilon_{12} \left( \frac{\sigma_{12}}{r_1} \right)^6, \quad (46)$$

where  $\varepsilon_{12}$  is the characteristic interaction energy and  $\sigma_{12}$  is the characteristic molecular size defined by the minimum separation between molecules in the liquid. Using Eqns (45) and (46), we obtain

$$\frac{\partial \mu_2^0(\mathbf{r})}{\partial \mathbf{r}} = v_2 \nabla \Pi_0 + \frac{\alpha_T \varepsilon_{12} v_{12}}{v_1} \nabla T_\infty, \quad (47)$$

where  $v_{12} = 4\pi\sigma_{12}^3/3$ .

The same calculations can be performed for a solvent molecule, giving

$$\frac{\partial \mu_1^0(\mathbf{r})}{\partial \mathbf{r}} = v_1 \nabla \Pi_0 + \frac{\alpha_T \varepsilon_{11} v_{11}}{v_1} \nabla T_\infty. \quad (48)$$

The notation in Eqn (48) is obviously derived from that in expression (47). Because the mass transport of the solvent itself is impossible in our picture of the thermophoresis of an isolated particle, we must set  $\partial \mu_1^0(\mathbf{r})/\partial \mathbf{r} = 0$ . Physically, this means that the bulk forces in a nonisothermal solvent are compensated due to the macroscopic pressure gradient that arises in it. With the corresponding expression for the macroscopic pressure gradient, Eqn (47) assumes the closed form

$$\frac{\partial \mu_2^0(\mathbf{r})}{\partial \mathbf{r}} = \alpha_T \varepsilon_{12} \frac{v_{12}}{v_1} \left( 1 - \frac{v_{11} v_2 \varepsilon_{11}}{v_{12} v_1 \varepsilon_{12}} \right) \nabla T_\infty. \quad (49)$$

From Eqns (17) and (49), the Soret coefficient for a diluted mixture can be written as

$$S_T = -\alpha_T \frac{\pi \varepsilon_{12}}{8kT} \frac{v_{12}}{v_1} \left( 1 - \frac{v_{11} v_2 \varepsilon_{11}}{v_{12} v_1 \varepsilon_{12}} \right). \quad (50)$$

Expression (50) becomes identical to its hydrodynamic analog obtained in Ref. [32] if we set  $\varepsilon_{12} = \sqrt{\varepsilon_{11} \varepsilon_{22}}$  (as was done there) and introduce the corresponding hydrodynamic volumes  $v_{1,2}^H = (4\pi/3)R_{1,2}^3$  expressed in terms of the hydrodynamic radii  $R_1$  and  $R_2$  (rather than  $v_{11}$  and  $v_{12}$ ). The relation between the hydrodynamic and molecular volumes must be  $v_{1,2}^H = (3\pi/32)v_{1,12}$ . This seems to be quite a natural difference remembering that the hydrodynamic radii of the molecules should be smaller than the corresponding minimum separation, which (according to a model at least) is simply the sum of the hydrodynamic radii of the interacting particles. Expression (50) contains only microscopic parameters characterizing the equilibrium state of the system and is therefore preferable to its hydrodynamic counterpart (see Refs [17, 18, 32]). Using the Lennard-Jones model potential

$$\Phi_{12} = 4\varepsilon_{12} \left[ \left( \frac{\sigma_{12}}{r_1} \right)^{12} - \left( \frac{\sigma_{12}}{r_1} \right)^6 \right]^6, \quad (51)$$

which is widely used in simulating the equilibrium and kinetic properties of liquids, we express the Soret coefficient as

$$S_T = -\alpha_T \frac{\pi \varepsilon_{12}}{9kT} \frac{v_{12}}{v_1} \left( 1 - \frac{v_{11} v_2 \varepsilon_{11}}{v_{12} v_1 \varepsilon_{12}} \right) \quad (52)$$

where we can further substitute the parameters obtained by numerical simulation.

We note that expressions (50) and (52) differ only by a factor of 8/9, which means that our result for thermophoretic parameters is not oversensitive to the form of the repulsion core of potential (51).

The interaction potentials in (46) and (51) do not describe cooperative effects due to the interaction between solvent molecules. In [34], these effects were taken into account by considering how the interaction of solvent molecules affects the effective pair potential for an isolated particle and a solvent molecule.

The effective pair potential is calculated using the simplest possible form of the standard chain of equations for correlation functions. It was believed—and calculations confirmed—that the cooperative interaction contributes little to the effective pair interaction potential. The only case where cooperative effects in the above sense contribute significantly to the effects we consider is for the molecules of surface-active substances, for which the original pair interaction potential for an isolated particle and a solvent molecule is an order of magnitude weaker than for surface-inactive molecules in solutions. In these systems, such cooperative effects are indeed very important and lead to a number of interesting phenomena. For most systems used in experiments, such an analysis leads to insignificantly small corrections.

The thermodynamic approach and the hydrodynamic approach predict qualitatively the same dynamic behavior for an isolated molecule (or a polymer chain), and any differences that may occur are attributed to the approximations adopted in calculations. For example, the direction of thermophoretic motions is always determined by the inequalities  $v_{11} v_2 \varepsilon_{11}/(v_{12} v_1 \varepsilon_{12}) > 1$  and  $v_{11} v_2 \varepsilon_{11}/(v_{12} v_1 \varepsilon_{12}) < 1$ , the parameter  $v_{11} v_2 \varepsilon_{11}/(v_{12} v_1 \varepsilon_{12})$  being determined not by the size but by the geometry and physical properties of the molecules.

The Soret coefficient is proportional to the ratio  $v_{12}/v_1$ , fully consistent with the scaling estimates obtained by de

Gennes [25] using the hydrodynamic approach. It is shown in Ref. [25] that the velocity  $U_T$  of thermophoretic motion of a polymer chain is proportional to the squared size of the smallest hydrodynamic inhomogeneity in the system. In our case, the velocity  $U_T$  is calculated by equating the thermophoretic force acting on a molecule or a monomer in accordance with Eqns (47) and (48) to the hydrodynamic resistance force  $-6\pi\eta R_2 U_T$  ( $\eta$  is the viscosity of the liquid) acting on the molecule or the monomer. We then obtain

$$U_T = -\alpha_T \frac{2\varepsilon_{12}\sigma_{12}^3}{9\eta v_1 R_2} \left( 1 - \frac{v_{11}v_2\varepsilon_{11}}{v_{12}v_1\varepsilon_{12}} \right) \nabla T_\infty. \quad (53)$$

For molecules having a simple shape, whose remainders do not differ much in their physical and chemical properties, the ratio  $\sigma_{12}/R_2$  of the ‘energy’ or van der Waals size to the hydrodynamic size should depend very weakly on the particle size, and hence, in full agreement with the results in Ref. [25],  $U_T \sim \sigma_{12}^2$ . We note that  $\sigma_{12}$  is the characteristic change length of the interaction potential and that (unlike the size of the isolated particle itself) it is on a molecular scale. For molecules larger than the molecular size, the thermophoretic velocity ceases to be proportional to the particle size (it is, as before, proportional to a certain, usually second, power of the molecular-scale change length of the interaction potential) and is virtually independent of the particle size. This is in qualitative agreement both with the experimental data in [29] and with theoretical results on the phoresis of colloidal particles.

In general, the results obtained for molecules and polymers cannot be directly translated to colloidal particles. This is not only because of the difference between the physical size of the particles and the change length of the interaction potential, noted above, but also because of the existence of a surface layer whose physical properties differ from those of the liquid itself. This layer should be considered separately when treating mass transport thermodynamically, but this is a topic for another study. An attempt at such a theory was made in Ref. [15], but that analysis neglected a number of important factors and should be improved to include corrections of the kind made above.

The results obtained for molecules and polymers compare well both qualitatively and quantitatively with other theoretical results and experimental data. In addition to the fact (mentioned above) that  $U_T \sim \sigma_{12}^2$ , the Soret coefficient in Eqns (50) and (52) is proportional to the thermal expansion coefficient of the solvent  $\alpha_T$ . Such a dependence was observed for a number of solvent–particle pairs in Ref. [35].

The behavior  $U_T \sim \alpha_T$  obtained from theories using the hydrodynamic and thermodynamic approaches is also predicted by the theory developed in Ref. [36] (see also numerous self-citations in this work). Unfortunately, because of our insufficient understanding of this theory, we are not in a position to outline it here and instead confine ourselves to discussing its conclusions. One of these—that the velocity of thermophoresis is independent of both the size and the physicochemical properties of the particle—is incompatible with the bulk of experimental data. According to Ref. [36], thermophoresis can occur in the liquid in any region that can be regarded as a kind of a solid particle located in the liquid. But because the theory does not distinguish between the physical properties of the particle and those of its surrounding liquid, it immediately follows that any molecule of the liquid itself is in fact such a solid particle. The theory in

Ref. [36] therefore describes not only the thermophoresis of isolated particles but also a certain motion of the liquid under a temperature gradient, both processes occurring via the same mechanism. With thermo-osmosis neglected, the ‘thermophoretic’ motion of a pure liquid is impossible according to the laws of formal logic. However, eliminating this motion also requires eliminating the thermophoresis of isolated particles. Therefore, our results can be considered the only explanation for the experimental  $U_T \sim \alpha_T$  dependence.

A hydrodynamic expression for the Soret coefficient—an analog of Eqns (50) and (52)—was compared with experimental results more than once. For example, the hydrodynamic approach was used in [32] to calculate the thermal diffusion parameter of polystyrene in cyclohexane, benzol, toluene, methyl ethyl ketone, and ethyl acetate. In all cases, it was found that average values correlate well with the measured parameters, even though there exists a wide spread due to the necessity of calculating the unknown hydrodynamic radius of a monomer. The correspondence we obtained here between the thermodynamic and hydrodynamic results will allow avoiding this uncertainty. That diffusion parameters are proportional to the thermal expansion coefficient—a fact that follows from our theory—has been confirmed experimentally for lysozyme, poly L-lysine, and  $\beta$ -dodecylmaltoside in water [35]. Therefore, the approximation we use indirectly agrees quite well with experiment.

The results presented in this section suggest good qualitative correspondence between the thermodynamic approach and the hydrodynamic approach in the theory of thermal diffusion of molecules and polymers. Also, both theories fully account for the basic qualitative features of thermophoresis for such objects.

## 5. Conclusions

Our analysis of the standard thermodynamic approach to mass transport in nonisothermal binary liquid mixtures revealed that the equations for mass fluxes are inconsistent and that they predict a certain kind of mass transport in nonisothermal pure liquid, unless it is assumed that the heat of transport is equal to the chemical potential of the corresponding component.

As a consequence, it is also confirmed that thermal diffusion is entirely of an entropic nature.

Our analysis also shows that the standard approach using the Gibbs–Duhem equation for the pressure gradient cannot be applied to mass transport in open and nonstationary systems. If the dynamic pressure gradient is calculated based on the mass transport equations themselves using our expressions for the heat of transport of the components, then the resulting equations for the diffusion and thermal diffusion coefficients demonstrate reasonable physical behavior and exhibit good agreement with experiment over the entire range of concentrations. This distinguishes them favorably from their counterparts in previous thermodynamic theories.

The difference between the statistical (Gibbs–Duhem) and dynamic pressure gradients in a system is due to two factors: the viscous friction and the corresponding energy dissipation in the system. Even in an isothermal system, if at least one of its components exchanges matter with the environment, all the components of the mixture can undergo transfer in the form of barodiffusion driven by the dynamic pressure gradient. Owing to this dynamic barodiffusion, some

mixtures can even be not diluted when analyzed in terms of diffusion and barodiffusion, even though they are diluted in a purely thermodynamic sense. This may be the reason for the observation that the thermal diffusion coefficient of DNA depends on its molecular mass. Using the proposed model to find the second virial coefficient in semidiluted solutions shows that barodiffusion should be taken into account in interpreting experimental data.

Calculating the chemical potential of an isolated particle microscopically allows using the obtained thermodynamic results to describe thermophoresis in diluted systems. Results obtained with this approach essentially coincide with those obtained previously using the hydrodynamic approach.

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