We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

5,000 Open access books available
125,000 International authors and editors
140M Downloads

154 Countries delivered to
TOP 1% Our authors are among the most cited scientists
12.2% Contributors from top 500 universities

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
1. Introduction

This chapter outlines a theoretical framework for the microscopic approach to material transport in liquid mixtures, and applies that framework to binary one-phase systems. The material transport in this approach includes no hydrodynamic processes related to the macroscopic transfer of momenta. In analyzing the current state of thermodynamic theory, we indicate critically important refinements necessary to use non-equilibrium thermodynamics and statistical mechanics in the application to material transport in non-isothermal mixtures.

2. Thermodynamic theory of material transport in liquid mixtures: Role of the Gibbs-Duhem equation

The aim of this section is to outline the thermodynamic approach to material transport in mixtures of different components. The approach is based on the principle of local equilibrium, which assumes that thermodynamic principles hold in a small volume within a non-equilibrium system. Consequently, a small volume containing a macroscopic number of particles within a non-equilibrium system can be treated as an equilibrium system. A detailed discussion on this topic and references to earlier work are given by Gyarmati (1970). The conditions required for the validity of such a system are that both the temperature and molecular velocity of the particles change little over the scale of molecular length or mean free path (the latter change being small relative to the speed of sound). For a gas, these conditions are met with a temperature gradient below $10^4$ K cm$^{-1}$; for a liquid, where the heat conductivity is greater, the speed of sound higher and the mean free path is small, this condition for local equilibrium is more than fulfilled, provided the experimental temperature gradient is below $10^4$ K cm$^{-1}$.

Thermodynamic expressions for material transport in liquids have been established based on equilibrium thermodynamics (Gibbs and Gibbs-Duhem equations), as well as on the principles of non-equilibrium thermodynamics (thermodynamic forces and fluxes). For a review of these models, see (De Groot, 1952; De Groot, Mazur, 1962; Kondepudi, Prigogine, 1999; Haase, 1969).
Non-equilibrium thermodynamics is based on the entropy production expression

\[ \Sigma = \sum_{i=1}^{N} (\dot{J}_i \cdot \nabla \left( \frac{1}{T} \right)) - \sum_{i=1}^{N} \dot{J}_i \cdot \nabla \left( \frac{\mu_i}{T} \right) \]  

(1)

where \( \dot{J}_i \) is the energy flux, \( \dot{J}_i \) are the component material fluxes, \( N \) is the number of the components, \( \mu_i \) are the chemical potentials of components, and \( T \) is the temperature. The energy flux and the temperature distribution in the liquid are assumed to be known, whereas the material concentrations are determined by the continuity equations

\[ \frac{\partial n_i}{\partial t} = -\nabla \dot{J}_i \]  

(2)

Here \( n_i \) is the numerical volume concentration of component \( i \) and \( t \) is time. Non-equilibrium thermodynamics defines the material flux as

\[ \dot{J}_i = -n_i L_i \nabla \left( \frac{\mu_i}{T} \right) - n_i L_{iq} \nabla \left( \frac{1}{T} \right) \]  

(3)

where \( L_i \) and \( L_{iq} \) are individual molecular kinetic coefficients. The second term on the right-hand side of Eq. (3) represents the cross effect between material flux and heat flux.

The chemical potentials are expressed through component concentrations and other physical parameters (De Groot, 1952; De Groot, Mazur, 1962; Kondepudi, Prigogine, 1999):

\[ \nabla \mu_k = \sum_{k=1}^{N} \frac{\partial \mu_k}{\partial n_l} \nabla n_l - \nabla P + \frac{\partial \mu_k}{\partial T} \nabla T \]  

(4)

Here \( P \) is the internal macroscopic pressure of the system and \( \bar{v}_k = -\frac{\partial \mu_k}{\partial P} \) is the partial molecular volume, which is nearly equivalent to the specific molecular volume \( v_k \).

Substituting Eq. (4) into Eq. (3), and using parameter \( q_i = L_{iq}/L_i \), termed the molecular heat of transport, we obtain the equation for component material flux:

\[ \dot{J}_i = -\frac{n_i L_i}{T} \left[ \sum_{k=1}^{N} \frac{\partial \mu_k}{\partial n_k} \nabla n_k - \nabla P + \frac{\partial \mu_k}{\partial T} \left( \frac{\mu_k + q_i}{T} \right) \nabla T \right] \]  

(5)

Defining the relation between the heat of transport and thermodynamic parameters is a key problem because the Soret coefficient, which is the parameter that characterizes the distribution of components concentrations in a temperature gradient, is expressed through the heat of transport (De Groot, 1952; De Groot, Mazur, 1962). A number of studies that offer approaches to calculating the heat of transport are cited in (Pan S et al., 2007).

Eq. (5) must be augmented by an equation for the macroscopic pressure gradient in the system. The simplest possible approach is to consider the pressure to be constant (De Groot, 1952; De Groot, Mazur, 1962; Kondepudi, Prigogine, 1999; Haase, 1969; Landau, Lifshitz, 1959), but pressure cannot be constant in a system with a non-uniform temperature and concentration. This issue is addressed with a well-known expression referred to as the

\[ \nabla P = \sum_{i=1}^{N} n_i \left( \sum_{k=1}^{N} \frac{\partial \mu_k}{\partial n_k} \nabla n_k + \frac{\partial \mu_k}{\partial T} \nabla T \right) \]  

(6)

The Gibbs-Duhem equation defines the macroscopic pressure gradient in a thermodynamic system. In equilibrium thermodynamics the equation defines the potentiality of the thermodynamic functions (Kondepudi, Prigogine, 1999). In equilibrium thermodynamics the change in the thermodynamic function is determined only by the initial and final states of the systems, without consideration of the transition process itself. In non-equilibrium thermodynamics, Eq. (5) plays the role of expressing mechanical equilibrium in the system. According to the Prigogine theorem (De Groot, 1952; De Groot, Mazur, 1962; Kondepudi, Prigogine, 1999; Haase, 1969), pressure gradient cancels the volume forces expressed as the gradients of the chemical potentials and provides mechanical equilibrium in a thermodynamically stable system. However, in a non-isothermal system, the same authors considered a constant pressure and the left- and right-hand side of Eq. (6) were assumed to be zero simultaneously, which is both physically and mathematically invalid.

Substituting Eq. (6) into Eq. (5) we obtain the following equation for material flux:

\[ \vec{j}_i = \frac{\phi_i L_{1i}}{v_i T} \left( (1 - \phi_i) \sum_{k=1}^{N} \frac{\partial \mu_k}{\partial \phi_i} \nabla \phi_i + \frac{\partial \mu_k}{\partial T} \nabla T \right) - \sum_{k=1}^{N} v_i \phi_i \sum_{l=1}^{N} \frac{\partial \mu_k}{\partial \phi_l} \nabla \phi_l + \frac{\partial \mu_k}{\partial T} \nabla T - (\mu_i + q_i) \frac{\nabla T}{T} \]  

(7)

In Eq. (7), the numeric volume concentrations of the components are replaced by their volume fractions \( \phi_i = n_i/v_i \), which obey the equation

\[ \sum_{i=1}^{N} \phi_i = 1 \]  

(8)

Using Eq. (8) and the standard rule of differentiation of a composite function

\[ \frac{\partial \mu_k}{\partial \phi_i} \phi_i (\ldots \phi_l \ldots) \nabla \phi_i = \frac{\partial \mu_k}{\partial \phi_i} \nabla \phi_i + \frac{\partial \mu_k}{\partial \phi_l} \frac{\partial \phi_l}{\partial \phi_i} \nabla \phi_i = 2 \frac{\partial \mu_k}{\partial \phi_i} \nabla \phi_i \]  

(9)

we can eliminate \( \phi_i \) and obtain Eq. (7) in a more compact form:

\[ \vec{j}_i = -\frac{L_{1i}}{T} \sum_{k=1}^{N} \phi_i \left[ 2 \sum_{l=1}^{N} \frac{\partial \mu_k}{\partial \phi_l} \nabla \phi_l + \frac{\partial \mu_k}{\partial T} \nabla T \right] - (\mu_i + q_i) \frac{\nabla T}{T} \]  

(10)

Here \( \phi_i \) is expressed through the other volume fractions using Eq. (8), and the following combined chemical potential is introduced:

\[ \mu^*_k = \mu_i - \frac{q_i}{v_i} \mu_k \]  

(11)

We note that the volume fraction selected for elimination is arbitrary (any other volume fraction can be eliminated in the same manner), and that in subsequent mathematical
expressions, we express the volume fraction of the first component through that of the others using Eq. (8).

Equations for the material fluxes are usually augmented by the following equation, which relates the material fluxes of components (De Groot, 1952; De Groot, Mazur, 1962; Kondepudi, Prigogine, 1999; Haase, 1969; Ghorayeb, Firoozabadi, 2000; Pan S et al., 2007):

$$\sum_{i=1}^{N} v_i \bar{j}_i = 0 \quad (12)$$

Eq. (12) expresses the conservation mass in the considered system and the absence of any hydrodynamic mass transfer. Also, Eq. (12) is used to eliminate one of the components from the series of component fluxes expressed by Eq. (10). That material flux that is replaced in this way is arbitrary, and the resulting concentration distribution will depend on which flux is selected. The result is not significant in a dilute system, but in non-dilute systems this practice renders an ambiguous description of the material transport processes.

In addition to being mathematically inconsistent with Eq. (12) because there are \(N+1\) equations [i.e., \(N\) Eq. (10) plus Eq. (12)] for \(N-1\) independent component concentrations, Eq. (10) predicts a drift in a pure liquid subjected to a temperature gradient. Thus, at \(\phi = 1\) Eq. (10) predicts

$$\dot{j}_i = -\frac{L_i}{T} \frac{(\mu_i + q_i)}{v_i} \nabla T \quad (13)$$

This result contradicts the basic principle of local equilibrium, and the notion of thermodiffusion as an effect that takes place in mixtures only. Moreover, Eq. (13) indicates that the achievement of a stationary state in a closed system is impossible, since material transport will occur even in a pure liquid.

The contradiction that a system cannot reach a stationary state, as expressed in Eq. (13), can be eliminated if we assume

$$q_i = -\mu_i \quad (14)$$

With such an assumption Eq. (10) can be cast in the following form:

$$\bar{j}_i = -\frac{L_i}{T} \sum_{k=1}^{N} \phi_k \mu_{ik} \left( \frac{\partial}{\partial \phi_k} \frac{\partial}{\partial T} \phi_k + \frac{\partial}{\partial T} \phi_k \right) \quad (15)$$

Because the kinetic coefficients are usually calculated independently from thermodynamics, the material fluxes expressed by Eq. (15) cannot satisfy Eq. (12) for the general case. But in a closed and stationary system, where \(\bar{j}_i = 0\), Eqs. (12) and (15) become consistent. In this case, any component flux can be expressed by Eq. (15) through summation of the other equations. The condition of mechanical equilibrium for an isothermal homogeneous system, as well as the use of Eqs. (1) – (6) for non-isothermal systems, are closely related to the principle of local equilibrium (De Groot, 1952; De Groot, Mazur, 1962; Kondepudi, Prigogine, 1999; Haase, 1969). As argued in (Duhr, Braun, 2006; Weinert, Braun; 2008), thermodiffusion violates local equilibrium because the change in free energy across a particle is typically comparable to the thermal energy of the particle. However, their calculations predict that
even for large (micron size) particles, the energy difference is no more than a few percent of $kT$. But the local equilibrium is determined by processes at molecular level, as will be discussed below, and this argumentation cannot be accepted.

3. Dynamic pressure gradient in open and non-stationary systems:

Thermodynamic equations of material transport with the Soret coefficient as a thermodynamic parameter

Expressing the heats of transport by Eq. (14), we derived a set of consistent equations for material transport in a stationary closed system. However, expression for the heat of transport itself cannot yield consistent equations for material transport in a non-stationary and open system.

In an open system, the flux of a component may be nonzero because of transport across the system boundaries. Also, in a closed system that is non-stationary, the component material fluxes $\dot{j}_i$ can be nonzero even though the total material flux in the system, $\dot{j} = \sum_{i=1}^{N} v_i \dot{j}_i$, is zero. In both these cases, the Gibbs-Duhem equation can no longer be used to determine the pressure in the system, and an alternate approach is necessary.

In previous works (Schimpf, Semenov, 2004; Semenov, Schimpf, 2005), we combined hydrodynamic calculations of the kinetic coefficients with the Fokker-Planck equations to obtain material transfer equations that contain dynamic parameters such as the cross-diffusion and thermal diffusion coefficients. In that approach, the macroscopic gradient of pressure in a binary system was calculated from equations of continuity of the same type as expressed by Eqs. (2) and (8). This same approach may be used for solving the material transport equations obtained by non-equilibrium thermodynamics.

In this approach, the continuity equations [Eq. (2)] are first expressed in the form

$$\frac{\partial \phi_i}{\partial t} = \nabla \cdot \left( \frac{\phi_i L_i}{T} \left( 2 \sum_{k=1}^{N} \frac{\partial \phi_k}{\partial \phi_i} \nabla \phi_k - \nabla \Pi + \frac{\partial \mu_i}{\partial T} \nabla T \right) \right)$$

(16)

Summing Eq. (16) for each component and utilizing Eq. (8) we obtain the following equation for the dynamic pressure gradient in an open non-stationary system:

$$\nabla \Pi = \left[ \dot{\Pi} + \sum_{i=1}^{N} \phi_i L_i \left( 2 \sum_{k=1}^{N} \frac{\partial \mu_i}{\partial \phi_k} \nabla \phi_k + \frac{\partial \mu_i}{\partial T} \nabla T \right) \right] / \sum_{i=1}^{N} \phi_i L_i$$

(17)

Substituting Eq. (17) into Eq. (16) we obtain the material transport equations:

$$\frac{\partial \phi_i}{\partial t} = \nabla \cdot \left( \frac{\phi_i L_i}{T} \left[ \dot{\Pi} + \sum_{j=1}^{N} \phi_j v_j L_j \left( 2 \sum_{k=1}^{N} \frac{\partial \mu_i}{\partial \phi_k} \nabla \phi_k + \frac{\partial \mu_i}{\partial T} \nabla T \right) \right] \right) / \sum_{j=1}^{N} \phi_j v_j L_j$$

(18)

Comparing Eq. (18) with Eq. (15) for a stationary mixture shows that former contains an additional drift term $-\frac{\phi_i v_j L_j \dot{j}}{\sum_{k=1}^{N} \phi_k v_k L_k}$ proportional to the total material flux through the open
system. The term \( \frac{\dot{f}T}{N} \sum_{k=1}^{N} \phi_k v_k L_k \) in Eq. (17) describes the contribution of that drift to the pressure gradient. This additional component of the total material flux is attributed to barodiffusion, which is driven by the dynamic pressure gradient defined by Eq. (17). This dynamic pressure gradient is associated with viscous dissipation in the system. Parameter \( \dot{f} \) is independent of position in the system but is determined by material transfer across the system boundaries, which may vary over time.

If the 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 the existence of a temperature or pressure gradient. This drift is determined by conditions at the boundaries and is independent of any force applied to the system. For example, the system may have a component source at one boundary and a sink of the same component at opposite boundary. As molecules of a given species move between the two boundaries, they experience viscous friction, which creates a dynamic pressure gradient that induces barodiffusion in all molecular species. The pressure gradient that is induced by viscous friction in such a system is not considered in the Gibbs-Duhem equation.

Equations (6), (7), and (15) describe a system in hydrostatic equilibrium, without viscous friction caused by material flux due to material exchange through the system boundaries. Unlike the Gibbs-Duhem equation, Eq. (17) accounts for viscous friction forces and the resulting dynamic pressure gradient. For a closed stationary system, in which \( \dot{f} = 0 \) and \( \frac{\partial \phi}{\partial t} = 0 \), Eq. (18) is transformed into

\[
\sum_{i=1}^{N} \left( 2 \sum_{j=1}^{N} \frac{\partial \mu_i^*}{\partial \phi_j} \right) \nabla \phi_i + \left( \sum_{j=1}^{N} \frac{\partial \mu_i^*}{\partial T} \right) \nabla T = 0
\]

There are thermal diffusion experiments in which the system experiences periodic temperature changes. An example is the method used described by (Wiegand, Kohler, 2002), where thermodiffusion in liquids is observed within a dynamic temperature grating produced using a pulsed infrared laser. Because this technique involves changing the wall temperature, which changes the equilibrium adsorption constant, material fluxes vary with time, creating a periodicity in the inflow and outflow of material. A preliminary analysis shows that material fluxes to and from the walls have relaxation times on the order of a few microseconds until equilibrium is attained, and that such non-stationary material fluxes can be observed using dynamic temperature gratings.

The Soret coefficient is a common parameter used to characterize material transport in temperature gradients. For binary systems, Eq. (19) can be used to define the Soret coefficient as

\[
S_T = -\frac{\partial \mu_{21P}^*}{\partial T} \frac{2\phi_2 (1-\phi_2) \frac{\partial \mu_{21P}}{\partial \phi_2}}{\partial \phi_2}
\]

www.intechopen.com
where subscript $P$ is used to indicate that the derivatives are taken at constant pressure, as is the case in Eqs. (4) and (6). We can solve Eqs. (19) to express the “partial” Soret coefficient $S_T^k$ for the $k$'th component through a factor of proportionality between $\nabla \phi_k$ and $\nabla T$.

4. Statistical mechanics of material transport: Chemical potentials at constant volume and pressure and the Laplace component of pressure in a molecular force field

The chemical potential at constant volume can be calculated using a modification of an expression derived in (Kirkwood, Boggs, 1942; Fisher, 1964):

$$
\mu_{ij} = \mu_{bi} + \frac{1}{\rho} \sum_{j=1}^{N} \phi_j \int g_{ij}(\vec{r}, \lambda) \Phi_{ij}(r) dv 
$$

(21)

Here

$$
\mu_{bi} = -\frac{3}{2} kT \ln \frac{(2\pi m_i kT)^{3/2}}{h^3} + kT \ln \frac{\phi_i}{v_i} - kT \ln Z_{i1}^{\text{rot}} - kT \ln Z_{i1}^{\text{vib}}
$$

(22)

is the chemical potential of an ideal gas of the respective non-interacting molecules (related to their kinetic energy), $h$ is Planck’s constant, $m_i$ is the mass of the molecule, $Z_{i1}^{\text{rot}}$ and $Z_{i1}^{\text{vib}}$ are its rotational and vibrational statistical sums, respectively, and $V_{i1}^{\text{ext}}$ is the volume external to a molecule of the $i$’th component. The molecular vibrations make no significant contribution to the thermodynamic parameters except in special situations, which will not be discussed here. The rotational statistical sum for polyatomic molecules is written as (Landau, Lifshitz, 1980)

$$
Z_{\text{rot}} = \sqrt{\frac{\pi}{\gamma}} \sqrt{\left(8\pi^2 kT\right)^3 I_1 I_2 I_3}
$$

(23)

where $\gamma$ is the symmetry value, which is the number of possible rotations about the symmetry axes carrying the molecule into itself. For H$_2$O and C$_2$H$_5$OH, $\gamma = 2$; for NH$_3$, $\gamma = 3$; for CH$_4$ and C$_6$H$_6$, $\gamma = 12$. $I_1, I_2,$ and $I_3$ are the principal values of the tensor of the moment of inertia.

In Eq. (21), parameter $\lambda$ describes the gradual “switching on” of the intermolecular interaction. A detailed description of this representation can be found in (Kirkwood, Boggs, 1942; Fisher, 1964). Parameter $r$ is the distance between the molecule of the surrounding liquid and the center of the considered molecule; $g_{ij}(\vec{r}, \lambda)$ is the pair correlative function, which expresses the probability of finding a molecule of the surrounding liquid at $\vec{r}$ ($r = |\vec{r}|$) if the considered molecule is placed at $r = 0$; and $\Phi_{ij}$ is the molecular interaction potential, known as the London potential (Ross, Morrison, 1988):

$$
\Phi_{ij} = -\phi_{ij} \left(\frac{\sigma_{ij}}{r}\right)^6
$$

(24)
Here $\varepsilon_{ij}$ is the energy of interaction and $\sigma_{ij}$ is the minimal molecular approach distance. In the integration over $V_{\text{out}}$, the lower limit is $r = \sigma_{ij}$.

There is no satisfactory simple method for calculating the pair correlation function in liquids, although it should approach unity at infinity. We will approximate it as

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

(25)

With this approximation we assume that the local distribution of solvent molecules is not disturbed by the particle under consideration. The approximation is used widely in the theory of liquids and its effectiveness has been shown. For example, in (Bringuier, Bourdon, 2003, 2007), it was used in a kinetic approach to define the thermodiffusion of colloidal particles. In (Schimpf, Semenov, 2004; Semenov, Schimpf, 2000, 2005) the approximation was used in a hydrodynamic theory to define thermodiffusion in polymer solutions. The approximation of constant local density is also used in the theory of regular solutions (Kirkwood, 1939). With this approximation we obtain

$$\mu_{iV} = \mu_{0i} + \sum_{j=1}^{N} \phi_{ij} \int_{V_{\text{out}}} \Phi_{ij}(r) dv$$

(26)

The terms under the summation sign are a simple modification of the expression obtained in (Bringuier, Bourdon, 2003, 2007).

In our calculations, we will use the fact that there is certain symmetry between the chemical potentials contained in Eq. (11). The term $\frac{\nu_{i}}{\nu_{k}} \mu_{k}$ can be written as $N_{ik} \mu_{k}$, where $N_{ik} = \frac{\nu_{i}}{\nu_{k}}$ is the number of the molecules of the $k$th component that can be placed within the volume $\nu_{i}$ but are displaced by a molecule of $i$th component. Using the known result that free energy is the sum of the chemical potentials we can say that $N_{ik} \mu_{k}$ is the free energy or chemical potential of a virtual molecular particle consisting of molecules of the $k$th component displaced by a molecule of the $i$th component. For this reason we can extend the results obtained in the calculations of molecular chemical potential $\mu_{iV}$ of the second component to calculations of parameter $N_{ik} \mu_{iV}$ by a simple change in the respective designations $i \to k$. Regarding the concentration of these virtual particles, there are at least two approaches allowed:

a. we can assume that the volume fraction of the virtual particles is equal to the volume fraction of the real particles that displace molecules of the $k$th component, i.e., their numeric concentration is $\frac{\phi_{ik}}{\nu_{i}}$. This approach means that only the actually displaced molecules are taken into account, and that they are each distinguishable from molecules of the $k$th component in the surrounding liquid.

b. we can take into account the indistinguishability of the virtual particles. In this approach any group of the $N_{ik}$ molecules of the $k$th component can be considered as a virtual particle. In this case, the numeric volume concentration of these virtual molecules is $\frac{\phi_{ik}}{\nu_{i}}$.

We have chosen to use the more general assumption b).
Using Eqs. (21) and (22), along with the definition of a virtual particle outlined above, we can define the combined chemical potential at constant volume \( \mu_{ikV}^* \) as

\[
\mu_{ikV}^* = kT \left( \frac{3}{2} \ln \frac{m_{ikN_k}}{m_{ikN_k}} + \ln \phi_k + \ln \frac{Z_{ikN_k}^i}{Z_{ikN_k}^j} \right) + \sum_{j=1}^{N_k} \int_{v_{int}}^\infty \Phi_{ij}(r) dv - \sum_{j=1}^{N_k} \int_{v_{int}}^\infty \Phi_{ij}^{N_k}(r) dv
\]

where \( m_{ikN_k} = m_iN_k \) and \( Z_{ikN_k}^i \) are the mass and the rotational statistical sum of the virtual particle, respectively. In Eq. (27), the total interaction potential \( N_k\Phi_{ij} \) of the molecules included in the virtual particle is written as \( \Phi_{ij}^{N_k} \). We will use the approximation

\[
\Phi_{ij}^{N_k} = N_k\Phi_{ij} = -\epsilon_iN_k\left(\frac{\sigma_{ij}}{r}\right)^6
\]

This approximation corresponds to the virtual particle having the size of a molecule of the i'th component and the energetic parameter of the k'th component.

In further development of the microscopic calculations it is important that the chemical potential be defined at constant pressure. Chemical potentials at constant pressure are related to those at constant volume \( \mu_{iV} \) by the expression

\[
\nabla \mu_{ip} = \nabla \mu_{iV} + \int_{v_{int}} \nabla \Pi_i dv
\]

Here \( \Pi_i \) is the local pressure distribution around the molecule. Eq. (29) expresses the relation between the forces acting on a molecular particle at constant versus changing local pressure. This equation is a simple generalization of a known equation (Haase, 1969) in which the pressure gradient is assumed to be constant along a length about the particle size.

Next we calculate the local pressure distribution \( \Pi_i \), which is widely used in hydrodynamic models of kinetic effects in liquids (Ruckenstein, 1981; Anderson, 1989; Schimpf, Semenov, 2004; Semenov, Schimpf, 2000, 2005). The local pressure distribution is usually obtained from the condition of the local mechanical equilibrium in the liquid around i'th molecular particle, a condition that is written as:

\[
\nabla \left( \Pi_i + \sum_{j=1}^N \frac{\phi_j}{v_j} \Phi_{ij}(r) \right) = 0.
\]

In (Semenov, Schimpf, 2009; Semenov, 2010) the local pressure distribution is used in a thermodynamic approach, where it is obtained by formulating the condition for establishing local equilibrium in a thin layer of thickness \( l \) and area \( S \) when the layer shifts from position \( r \) to position \( r+dr \). In this case, local equilibrium expresses the local conservation of specific free energy

\[
F_i(r) = \Pi_i(r) + \sum_{j=1}^N \frac{\phi_j}{v_j} \Phi_{ij}(r)
\]

in such a shift when the isothermal system is placed in a force field of the i'th molecule.

In the layer forming a closed surface, the change in the free energy is written as:
\[ dF(r) = \sqrt{\sum_{j=1}^{N} \frac{\phi_j}{v_j}} \Phi_j(r) + \nabla \Pi \int Sdr + \sum_{j=1}^{N} \left[ \frac{\phi_j}{v_j} \Phi_j(r) \right] dS = 0 \]  

where we consider changes in free energy due to both a change in the parameters of the layer volume \( dV = Sdr \) and a change \( dS \) in the area of the closed layer. For a spherical layer, the changes in volume and surface area are related as \( dV = 2\pi S r dr \), and we obtain the following modified equation of equilibrium for a closed spherical surface:

\[ \nabla \left[ \sum_{j=1}^{N} \frac{\phi_j}{v_j} \Phi_j(r) \right] + \frac{2}{r} \sum_{j=1}^{N} \frac{\phi_j}{v_j} \Phi_j(r) - \bar{r}_0 = 0 \]  

where \( \bar{r}_0 \) is the unit radial vector. The pressure gradient related to the change in surface area has the same nature as the Laplace pressure gradient discussed in (Landau, Lifshitz, 1980). Solving Eq. (31), we obtain

\[ \Pi_j = \sum_{j=1}^{N} \frac{\phi_j}{v_j} \Phi_j(r) + \int_{\infty}^{r} \frac{2}{r'} \Phi_j(r') dr' \]  

Substituting the pressure gradient from Eq. (32) into Eq. (29), and using Eqs. (24), (27), and (28), we obtain a general expression for the gradient in chemical potential at constant pressure in a non-isothermal and non-homogeneous system. We will not write the general expression here, rather we will derive the expression for binary systems.

### 5. The Soret coefficient in diluted binary molecular mixtures: The kinetic term in thermodiffusion is related to the difference in the mass and symmetry of molecules

In this section we present the results obtained in (Semenov, 2010, Semenov, Schimpf, 2011a). In diluted systems, the concentration dependence of the chemical potentials for the solute and solvent is well-known [e.g., see (Landau, Lifshitz, 1980)]: \( \mu_s(\phi) = kT \ln \phi \), and \( \mu_i \) is practically independent of solute concentration \( \phi = \phi_2 \). Thus, Eq. (20) for the Soret coefficient takes the form:

\[ S_T = -\frac{\partial \mu^*_P}{\partial T} \]  

where \( \mu^*_P \) is \( \mu^*_{21P} \).

The equation for combined chemical potential at constant volume [Eq. (28)] using assumption b) in Section 3 takes the form

\[ \mu^*_r = -kT \left( \frac{3}{2} \ln \frac{m_2}{m_1} - \ln \frac{\phi}{1 - \phi} + \ln \frac{Z_1}{Z_1^N} + 4\pi \int_{\bar{r}}^{r} \frac{\Phi_{21}(r) - \Phi_{11}^N(r)}{v_1} r^2 dr \right) \]  

www.intechopen.com
where \( N_1 = N_{21} \) is the number of solvent molecules displaced by molecule of the solute, \( \Phi_{11}^{N_1} \) is the potential of interaction between the virtual particle and a molecule of the solvent. The relation \( \phi = 1 - \phi \) is also used in deriving Eq. (34). Because \( \ln \left[ \phi/(1 - \phi) \right] \to -\infty \) at \( \phi \to 0 \), we expect the use of assumption a) in Section 3 for the concentration of virtual particles will yield a reasonable physical result.

In a dilute binary mixture, the equation for local pressure [Eq. (32)] takes the form

\[
\Pi_i = -\sum_{j=1}^{N} \frac{\Phi_{ij}(r)}{v_1} + \int_\infty^{r_i} \frac{2\Phi_{ii}(r)}{v_1 r'} dr' \quad (35)
\]

where index \( i \) is related to the virtual particle or solute.

Using Eqs. (29), (34), we obtain the following expression for the temperature-induced gradient of the combined chemical potential of the diluted molecular mixture:

\[
\nabla \mu_\phi = -k T \left[ \frac{3}{2} \ln \frac{m_2}{m_{N_1}} + \ln \frac{Z_{ii}}{Z_{ii}^0} \right] + \int \frac{\alpha_i d\theta}{v_1} \nabla T \frac{\Phi_{21}(r) - \Phi_{11}^{N_1}(r)}{r} dr' \quad (36)
\]

Here \( \alpha_i \) is the thermal expansion coefficient for the solvent and \( \nabla T \) is the tangential component of the bulk temperature gradient. After substituting the expressions for the interaction potentials defined by Eqs. (23), (24), and (28) into Eq. (36), we obtain the following expression for the Soret coefficient in the diluted binary system:

\[
S_T = \frac{1}{2T} \left[ \frac{3}{2} \ln \left( \frac{m_2}{m_{N_1}} \right) + \ln \left( \frac{\gamma_{N_1} \sqrt{l_1 l_2 l_3}}{\gamma_2 \sqrt{l_1 l_2 l_3}} \right) \right] + \frac{\pi^2 \alpha_3 \sigma_{ij}^3}{18 \nu_1 k T} \left( \frac{\epsilon_{11}}{\epsilon_{12}} - 1 \right) \quad (37)
\]

In Eq. (37), the subscripts 2 and \( N_1 \) are used again to denote the real and virtual particle, respectively.

The Soret coefficient expressed by Eq. (37) contains two main terms. The first term corresponds to the temperature derivative of the part of the chemical potential related to the solute kinetic energy. In turn, this kinetic term contains the contributions related to the translational and rotational movements of the solute in the solvent. The second term is related to the potential interaction of solute with solvent molecules. This potential term has the same structure as those obtained by the hydrodynamic approach in (Schimpf, Semenov, 2004; Semenov, Schimpf, 2005).

According to Eq. (37), both positive (from hot to cold wall) and negative (from cold to hot wall) thermdiffusion is possible. The molecules with larger mass \( (m_2 > m_{N_1}) \) and with a stronger interactions between solvent molecules \( (\epsilon_{11} > \epsilon_{12}) \) should demonstrate positive thermodiffusion. Thus, dilute aqueous solutions are expected to demonstrate positive thermophoresis. In (Ning, Wieand, 2006), dilute aqueous solutions of acetone and dimethyl sulfoxide were shown to undergo positive thermophoresis. In that paper, a very high value of the Hildebrand parameter is given as an indication of the strong intermolecular interaction for water. More specifically, the value of the Hildebrand parameter exceeds by two-fold the respective parameters for other components.
Since the kinetic term in the Soret coefficient contains solute and solvent symmetry numbers, Eq. (37) predicts thermodiffusion in mixtures where the components are distinct only in symmetry, while being identical in respect to all other parameters. In (Wittko, Köhler, 2005) it was shown that the Soret coefficient in the binary mixtures containing the isotopically substituted cyclohexane can be in general approximated as the linear function

$$S_T = S_{iT} + a_m \Delta M + b_i \Delta I$$

(38)

where $S_{iT}$ is the contribution of the intermolecular interactions, $a_m$ and $b_i$ are coefficients, while $\Delta M$ and $\Delta I$ are differences in the mass and moment of inertia, respectively, for the molecules constituting the binary mixture. According to Eq. (37), the coefficients are defined by

$$a_m = \frac{3}{4Tm_{N_i}}$$

(39)

$$b_i = \frac{(\gamma_{N_i})^2}{4T(\gamma_2)^2 \sqrt{(I_1I_2I_3)_{N_i}}}$$

(40)

In (Wittko, Köhler, 2005) the first coefficient was empirically determined for cyclohexane isomers to be $a_m = 0.99 \cdot 10^{-3} \text{K}^{-1}$ at room temperature ($T=300 \text{ K}$), while Eq. (39) yields $a_m = 0.03 \cdot 10^{-3} \text{K}^{-1}$ ($M_1 = 84$). There are several possible reasons for this discrepancy. The first term on the right side of Eq. (38) is not the only term with a mass dependence, as the second term also depends on mass. The empirical parameter $a_m$ also has an implicit dependence on mass that is not in the theoretical expression given by Eq. (39). The mass dependence of the second term in Eq. (37) will be much stronger when a change in mass occurs at the periphery of the molecule.

A sharp change in molecular symmetry upon isotopic substitution could also lead to a discrepancy between theory and experiment. Cyclohexane studied in (Wittko, Köhler, 2005) has high symmetry, as it can be carried into itself by six rotations about the axis perpendicular to the plane of the carbon ring and by two rotations around the axes placed in the plane of the ring and perpendicular to each other. Thus, cyclohexane has $\gamma_{N_i} = 24$. The partial isotopic substitution breaks this symmetry. We can start from the assumption that for the substituted molecules, $\gamma_2 = 1$. When the molecular geometry is not changed in the substitution and only the momentum of inertia related to the axis perpendicular to the ring plane is changed, the relative change in parameter $b_i$ can be written as

$$\frac{(\gamma_{N_i})^2}{4T(\gamma_2)^2 \sqrt{(I_1I_2I_3)_{N_i}}} = \frac{(\gamma_{N_i})^2}{4T(\gamma_2)^2 m_{N_i}} \cdot \frac{(\gamma_{N_i})^2 - (\gamma_2)^2}{4T(\gamma_2)^2}$$

(41)

Eq. (41) yields

$$a_m = \frac{1}{4Tm_{N_i}} \left[ 3 + \left( \frac{\gamma_{N_i}}{\gamma_2} \right)^2 \right]$$

(42)
Using the above parameters and Eq. (42), we obtain $a_m \approx 5.7 \cdot 10^{-3} K^{-1}$, which is still about six-times greater than the empirical value from (Wittko, Köhler, 2005). The remaining discrepancy could be due to our overestimation of the degree of symmetry violation upon isotopic substitution. The true value of this parameter can be obtained with $\gamma_2 \approx 2 - 3$. One should understand that the value of parameter $\gamma_2$ is to some extent conditional because the isotopic substitutions occur at random positions. Thus, it may be more relevant to use Eq. (42) to evaluate the characteristic degree of symmetry from an experimental measurement of $a_m$ rather than trying to use theoretical values to predict thermodiffusion.

6. The Soret coefficient in diluted colloidal suspensions: Size dependence of the Soret coefficient and the applicability of thermodynamics

While thermodynamic approaches yield simple and clear expressions for the Soret coefficient, such approaches are the subject of rigorous debate. The thermodynamic or “energetic” approach has been criticized in the literature. Parola and Piazza (2004) note that the Soret coefficient obtained by thermodynamics should be proportional to a linear combination of the surface area and the volume of the particle, since it contains the parameter $\mu_0$ given by Eq. (11). They argue that empirical evidence indicates the Soret coefficient is directly proportional to particle size for colloidal particles [see numerous references in (Parola, Piazza, 2004)], and is practically independent of particle size for molecular species. By contrast, Duhr and Braun (2006) show the proportionality between the Soret coefficient and particle surface area, and use thermodynamics to explain their empirical data. Dhont et al (2007) also reports a Soret coefficient proportional to the square of the particle radius, as calculated by a quasi-thermodynamic method.

Let us consider the situation in which a thermodynamic calculation for a large particle as said contradicts the empirical data. For large particles, the total interaction potential is assumed to be the sum of the individual potentials for the atoms or molecules which are contained in the particle

$$\Phi_{ii} (r) = \int \frac{dV_{ir}}{v_i} \Phi_{ii} \left( \rho_i \bar{r} \right)$$

(43)

Here $V_{ir}$ is the internal volume of the real or virtual particle and $\Phi_{ii} \left( \rho_i \bar{r} \right)$ is the respective intermolecular potential given by Eq. (24) or (28) for the interaction between a molecule of a liquid placed at $\bar{r} \left( r = \rho_i \bar{r} \right)$ and an internal molecule or atom placed at $\rho_i \bar{r}$. Such potentials are referred to as Hamaker potential, and are used in studies of interactions between colloidal particles (Hunter, 1992; Ross, Morrison, 1988). In this and the following sections, $v_i$ is the specific molecular volume of the atom or molecule in a real or virtual particle, respectively. For a colloidal particle with radius $R >> \sigma_{ij}$, the temperature distribution at the particle surface can be used instead of the bulk temperature gradient (Giddings et al, 1995), and the curvature of the particle surface can be ignored in calculating the respective integrals. This corresponds to the assumption that $r' \approx R$ and $d\rho \approx 4\pi R^2 dr$ in Eq. (36). To calculate the Hamaker potential, the expression calculated in (Ross, Morrison, 1988), which is based on the London potential, can be used:
Here $y = \frac{x}{\sigma_{21}}$, and $x$ is the distance from the particle surface to the closest solvent molecule surface. Using Eqs. (36) and (44) we can obtain the following expression for the Soret coefficient of a colloidal particle:

$$S_T = \frac{\pi^2 \alpha_i R \sigma_{21}^2 \nu_{21} \sigma_{21} \left( \frac{\epsilon_{11}}{\epsilon_{21}} - 1 \right)}{2(n+2)\nu_2 kT \nu_1 \left( \frac{\epsilon_{11}}{\epsilon_{21}} - 1 \right)}$$  \hspace{1cm} \text{(45)}$$

Here $n$ is ratio of particle to solvent thermal conductivity. The Soret coefficient for the colloidal particle is proportional to $\frac{R \sigma_{21}^2}{\nu_1 \nu_2}$. In practice, this means that $S_T$ is proportional to $\frac{R}{\sigma_{21}}$, since the ratio $\frac{\sigma_{21}^2}{\nu_1 \nu_2}$ is practically independent of molecular size. This proportionality is consistent with hydrodynamic theory [e.g., see (Anderson, 1989)], as well as with empirical data. The present theory explains also why the contribution of the kinetic term and the isotope effect has been observed only in molecular systems. In colloidal systems the potential related to intermolecular interactions is the prevailing factor due to the large value of $\frac{R \sigma_{21}^2}{\nu_1}$. Thus, the colloidal Soret coefficient is $R \frac{\sigma_{21}}{\nu_1}$ times larger than its molecular counterpart. This result is also consistent with numerous experimental data and with hydrodynamic theory.

### 7. The Soret coefficient in diluted suspensions of charged particles: Contribution of electrostatic and non-electrostatic interactions to thermodiffusion

In this section we present the results obtained in (Semenov, Schimpf, 2011b). The colloidal particles discussed in the previous section are usually stabilized in suspensions by electrostatic interactions. Salt added to the suspension becomes dissociated into ions of opposite electric charge. These ions are adsorbed onto the particle surface and lead to the establishment of an electrostatic charge, giving the particle an electric potential. A diffuse layer of charge is established around the particle, in which counter-ions are accumulated. This diffuse layer is the electric double layer. The electric double layer, where an additional pressure is present, can contribute to thermodiffusion. It was shown in experiments that particle thermodiffusion is enhanced several times by the addition of salt [see citations in (Dhont, 2004)].

For a system of charged colloidal particles and molecular ions, the thermodynamic equations should be modified to include the respective electrostatic parameters. The basic thermodynamic equations, Eqs. (4) and (6), can be written as

$$\nabla \mu_k = \sum_{k=1}^{N} \frac{\partial \mu_k}{\partial \mu_k} \nabla \eta_k - \nabla \mu_k \nabla P + \frac{\partial \mu_k}{\partial T} \nabla T + \epsilon_k \tilde{E}$$  \hspace{1cm} \text{(46)}$$
\[ \nabla P = \sum_{i=1}^{N} n_i \left( \sum_{k=1}^{N} \frac{\partial \mu_k}{\partial \phi_i} \nabla n_k + \frac{\partial \mu_i}{\partial T} \nabla T + e_i \hat{E} \right) \]  

(47)

where \( e_i = -\frac{\partial \mu_i}{\partial \Phi} \) is the electric charge of the respective ion, \( \Phi \) is the macroscopic electrical potential, and \( \hat{E} = -\nabla \Phi \) is the electric field strength. Substituting Eq. (47) into Eq. (46) we obtain the following material transport equations for a closed and stationary system:

\[ \bar{J}_i = 0 = -\frac{L}{T} \sum_{k} \frac{\phi_k \phi_i}{v_i} \sum_{i=1}^{N} \frac{\partial \mu_{ik}^*}{\partial \phi_i} \nabla \phi_i + \frac{\partial \mu_{ik}^*}{\partial T} \nabla T - \frac{\partial \mu_{ik}^*}{\partial \Phi} \hat{E} \]  

(48)

where

\[ \frac{\partial \mu_{ik}^*}{\partial \Phi} = e_i - N_{ik} e_k \]  

(49)

We will consider a quaternary diluted system that contains a background neutral solvent with concentration \( \phi_1 \), an electrolyte salt dissociated into ions with concentrations \( \phi_k = n_i v_\pm \), and charged particles with concentration \( \phi_2 \) that is so small that it makes no contribution to the physicochemical parameters of the system. In other words, we consider the thermophoresis of an isolated charged colloidal particle stabilized by an ionic surfactant. With a symmetric electrolyte, the ion concentrations are equal to maintain electric neutrality

\[ v_+ \phi_2 = v_- \phi_2 \]  

(50)

In this case we can introduce the volume concentration of salt as

\[ \phi_{s} = \phi_1 \left( 1 + \frac{v_-}{v_+} \right) = \phi_1 \left( 1 + \frac{v_+}{v_-} \right) \]  

and formulate an approximate relationship in place of the exact form expressed by Eq. (8):

\[ \phi_1 + \phi_i \approx 1 \]  

(51)

Here the volume contribution of charged particles is ignored since their concentration is very low, i.e. \( \phi_2 \ll \phi_1 \ll \phi_i \). Due to electric neutrality, the ion concentrations will be equal at any salt concentration and temperature, that is, the chemical potentials of the ions should be equal: \( \mu_+ = \mu_- \) (Landau, Lifshitz, 1980).

Using Eqs. (48) – (51) we obtain equations for the material fluxes, which are set to zero:

\[ \bar{J}_L = 0 = -\frac{\phi_L}{v_- T} \left[ 3 \frac{\partial \mu_{1L}^*}{\partial \phi_L} \nabla \phi_2 + 3 \frac{\partial \mu_{2L}^*}{\partial \phi_2} \nabla \phi_L + \frac{\partial \mu_{L}^*}{\partial T} \nabla T + e_L \hat{E} \right] \]  

(52)

\[ \bar{J}_s = 0 = -\frac{\phi_s}{v_+ T} \left[ 3 \frac{\partial \mu_{1s}^*}{\partial \phi_s} \nabla \phi_1 + \frac{\partial \mu_{s}^*}{\partial T} \nabla T - e_s \hat{E} \right] \]  

(53)
\[ \bar{j}_1 = 0 = -\frac{\phi_1 L}{v_1 T} \left( 3 \frac{\partial \mu_{1s}^*}{\partial \phi_1} \nabla \phi_1 + \frac{\partial \mu_{1s}^*}{\partial T} \nabla T + e \bar{E} \right) \]  
(54)

where \( e_s = -e_c = e \) (symmetric electrolyte). We will not write the equation for the flux of background solvent \( \bar{j}_1 \) because it yields no new information in comparison with Eqs. (52) - (54), as shown above. Solving Eqs. (52) – (54), we obtain

\[ \nabla \phi_s = -\nabla T \left( \frac{\partial (\mu_{1s}^* + \mu_{2s}^*)}{\partial T} \right) \]
\[ = \frac{2e}{3} \left( \frac{\partial (\mu_{1s}^* - \mu_{2s}^*)}{\partial \phi_s} \right) \nabla \phi_s + \frac{\partial (\mu_{1s}^* - \mu_{2s}^*)}{\partial T} \nabla T \]
(55)

Eq. (55) allows us to numerically evaluate the concentration gradient as

\[ \nabla \phi_s \approx \phi S_{ST}^s \nabla T \]
(57)

where \( S_{ST}^s \approx 10^{-3} \) is the characteristic Soret coefficient for the salts. Salt concentrations are typically around \( 10^{2-10} \) mol/L, that is \( \phi_s \approx 10^{-4} \) or lower. A typical maximum temperature gradient is \( \nabla T \approx 10^4 K \text{ / cm} \). These values substituted into Eq. (57) yield \( \nabla \phi_s \approx 10^{-4} - 10^{-3} \text{ cm}^{-1} \). The same evaluation applied to parameters in Eq. (56) shows that the first term on the right side of this equation is negligible, and the equation for thermoelectric power can be written as

\[ \bar{E} \approx \frac{\partial (\mu_{1s}^* - \mu_{2s}^*)}{\partial T} \nabla T \]
\[ = \frac{v_s - v_c \frac{\partial \mu}{\partial T}}{2e} \]
(58)

For a non-electrolyte background solvent, parameter \( \frac{\partial \mu}{\partial T} \) can be evaluated as \( \frac{\partial \mu}{\partial T} = \alpha T \), where \( \alpha \) is the thermal expansion coefficient of the solvent (Semenov, Schimpf, 2009; Semenov, 2010). Usually, in liquids the thermal expansion coefficient is low enough (\( \alpha \approx 10^{-3} \text{ K}^{-1} \)) that the thermoelectric field strength does not exceed \( 1 \text{ V/cm} \). This electric field strength corresponds to the maximum temperature gradient discussed above. The electrophoretic velocity in such a field will be about \( 10^{-5} - 10^{-4} \text{ cm/s} \). The thermophoretic velocities in such temperature gradients are usually at least one or two orders of magnitude higher.

These evaluations show that temperature-induced diffusion and electrophoresis of charged colloidal particle in a temperature gradient can be ignored, so that the expression for the Soret coefficient of a diluted suspension of such particles can be written as

\[ S_{ST}^s = -\frac{\phi_2}{\phi_2 \nabla T} \frac{\partial \mu_{2sP}}{\partial T} = -\frac{1}{kT} \frac{\partial \mu_{2sP}}{\partial \phi_2} \]
(59)

Eq. (59) can also be used for microscopic calculations.
For an isolated particle placed in a liquid, the chemical potential at constant volume can be calculated using a modified procedure mentioned in the preceding section. In these calculations, we use both the Hamaker potential and the electrostatic potential of the electric double layer to account for the two types of the interactions in these systems. The chemical potential of the non-interacting molecules plays no role for colloid particles, as was shown above.

In a salt solution, the suspended particle interacts with both solvent molecules and dissolved ions. The two interactions can be described separately, as the salt concentration is usually very low and does not significantly change the solvent density. The first type of interaction uses Eqs. (25) and the Hamaker potential [Eq. (44)]. For the electrostatic interactions, the properties of diluted systems may be used, in which the pair correlative function has a Boltzmann form (Fisher, 1964; Hunter, 1992). Since there are two kinds of ions, Eq. (21) for the “electrostatic” part of the chemical potential at constant volume can be written as

\[ \mu_2 = -4\pi n_s \int_0^R dr \left( \frac{\phi_s}{r} - e^{\frac{\phi_s}{kT}} \right) \Phi_e(r) r^2 dr = -4\pi n_s kT \int_0^R \left( e^{\frac{\phi_s}{kT}} + e^{-\frac{\phi_s}{kT}} - 2 \right) r^2 dr \]

where \( n_s = \frac{\phi_s}{v_s + v_-} \) is the numeric volume concentration of salt, and \( \Phi_e = e\Phi \) is the electrostatic interaction energy.

Eq. (32) expressing the equilibrium condition for electrostatic interactions is written as

\[ \nabla \left[ (n_s - n_-) \Phi_e(r) + \Pi \right] + 2(n_s - n_-) \Phi_e(r) \frac{\vec{r}}{R} = 0 \]

where \( \vec{r}_0 \) is the unit radial vector. In Eq. (61) it is assumed that the particle radius is much larger than the characteristic thickness of the electric double layer. Solving Eq. (62) assuming a Boltzmann distribution for the ion concentration, as in (Ruckenstein, 1981; Anderson, 1989), we obtain

\[ \Pi_e = n_s kT \left( e^{\frac{\phi_s}{kT}} + e^{-\frac{\phi_s}{kT}} - 2 \right) - \frac{2n_s}{R} \int_0^R \left( e^{\frac{\phi_s}{kT}} + e^{-\frac{\phi_s}{kT}} \right) \Phi_e(r) dr' \]

Substituting the pressure gradient calculated from Eq. (62) into Eq. (29), utilizing Eq. (60), and considering the temperature-induced gradients related to the temperature dependence of the Boltzmann exponents, we obtain the temperature derivative in the gradient of the chemical potential for a charged colloidal particle, which is related to the electrostatic interactions in its electric double layer:

\[ \frac{\partial \mu_2}{\partial T} = \frac{4\pi n_s kR}{(n + 2)} \int_0^R \left( e^{\frac{\phi_s}{kT}} + e^{-\frac{\phi_s}{kT}} \right) \Phi_e^2(r') \frac{dr'}{(kT)^2} \]

Here \( n \) is again the ratio of particle to solvent thermal conductivity. For low potentials \( (\Phi_e < kT) \), where the Debye-Hückel theory should work, Eq. (63) takes the form
Using an exponential distribution for the electric double layer potential, which is characteristic for low electrokinetic potentials $\zeta$, we obtain from Eq. (64)

$$
\frac{\partial \mu_p}{\partial T} = \frac{8\pi n_0 k R^2 \zeta}{(n+2)} \int \frac{\Phi^2(r')}{R} dr' 
$$

(64)

where $\lambda_D$ is the Debye length [for a definition of Debye length, see (Landau, Lifshitz, 1980; Hunter, 1992)].

Calculation of the non-electrostatic (Hamaker) term in the thermodynamic expression for the Soret coefficient is carried out in the preceding section [Eq. (45)]. Combining this expression with Eq. (65), we obtain the Soret coefficient of an isolated charged colloidal particle in an electrolyte solution:

$$
S_T = \frac{8\pi n_0 R \lambda_D^2}{T(n+2)} \left( \frac{\epsilon \epsilon_a}{kT} \right)^2 + \frac{\pi^2 \alpha_1 R \sigma_2 v_1 (\epsilon \epsilon_a)}{2(n+2) v_2 kT v_1^2 (\epsilon_{21} - \epsilon_1)} 
$$

(66)

This thermodynamic expression for the Soret coefficient contains terms related to the electrostatic and Hamaker interactions of the suspended colloidal particle. The electrostatic term has the same structure as the respective expressions for the Soret coefficient obtained by other methods (Ruckenstein, 1981; Anderson, 1989; Parola, Piazza, 2004; Dhont, 2004). In the Hamaker term, the last term in the brackets reflects the effects related to displacing the solvent by particle. It is this effect that can cause a change in the direction of thermophoresis when the solvent is changed. However, such a reverse in the direction of thermophoresis can only occur when the electrostatic interactions are relatively weak. When electrostatic interactions prevail, only positive thermophoresis can be observed, as the displaced solvent molecules are not charged, therefore, the respective electrostatic term is zero. The numerous theoretical results on electrostatic contributions leading to a change in the direction of thermophoresis are wrong due to an incorrect use of the principle of local equilibrium in the hydrodynamic approach [see discussion in (Semenov, Schimpf, 2005)].

The relative role of the electrostatic mechanism can be evaluated by the following ratio:

$$
\frac{8 n_0 \sigma_2^2 \epsilon_{21} (\epsilon \epsilon_a^2)}{\pi \alpha_1 T \sigma_2^2 \sigma_2^1 (\epsilon_{21} - \epsilon_1)} 
$$

(67)

The physicochemical parameters contained in Eq. (67) are separated into several groups and are collected in the respective coefficients. Coefficient $\frac{n_0 \sigma_2^2}{\pi \alpha_1 T}$ contains the parameters related to concentration and its change with temperature, $\frac{\lambda_D^2}{\sigma_2^2}$ is the coefficient reflecting the respective lengths of the interaction, $\frac{\sigma_1}{\sigma_2}$ reflects the geometry of the solvent molecules, and
\[
\frac{(\varepsilon_2^r)^2}{(\varepsilon_{11} - \varepsilon_{21})kT}
\]

is the ratio of energetic parameters for the respective interactions. Only the first two of these four terms are always significantly distinct from unity. The characteristic length of the interaction is much higher for electrostatic interactions. Also, the characteristic density of ions or molecules in a liquid, which are involved in their electrostatic interaction with the colloidal particle, is much lower than the density of the solvent molecules. The values of these respective coefficients are \( \frac{\lambda_0^2}{\sigma_{21}^2} \geq 10^3 \) and \( \frac{n_1v_2}{\varepsilon T} \approx 10^{-3} \) for typical ion concentrations in water at room temperature. The energetic parameter may be small, (~0.1) when the colloidal particles are compatible with the solvent. Characteristic values of the energetic coefficient range from 0.1-10. Combining these numeric values, one can see that the ratio given by Eq. (67) lies in a range of 0.1-10 and is governed primarily by the value of the electrokinetic potential \( \zeta \) and the difference in the energetic parameters of the Hamaker interaction \( \varepsilon_{11} - \varepsilon_{21} \). Thus, calculation of the ratio given by Eq. (67) shows that either the electrostatic or the Hamaker contribution to particle thermophoresis may prevail, depending on the value of the particle’s energetic parameters. In the region of high Soret coefficients, particle thermophoresis is determined by electrostatic interactions and is positive. In the region of low Soret coefficients, thermophoresis is related to Hamaker interactions and can have different directions in different solvents.

8. Material transport equation in binary molecular mixtures: Concentration dependence of the Soret coefficient

In this section we present the results obtained in (Semenov, 2011). In a binary system in which the component concentrations are comparable, the material transport equations defined by Eq. (18) have the form

\[
\frac{\partial \phi}{\partial t} = \nabla \left[ L_2 \phi (1 - \phi) \left( 2 \frac{\partial \mu^r}{\partial \phi} \nabla \phi + \frac{\partial \mu^r}{\partial T} \nabla T \right) \right] \frac{1}{T} \left( 1 - \phi + \frac{L_3 v_2}{L_1 v_1} \phi \right) \tag{68}
\]

Eq. (68) can be used in the thermodynamical definition of the Soret coefficient [Eq. (59)]. The mass and thermodiffusion coefficients can be calculated in the same way as the Soret coefficient. The microscopic models used to calculate the Soret Coefficient in (Ghorayeb, Firoozabadi, 2000; Pan et al., 2007) ignore the requirement expressed by Eq. (10) and cannot yield a description of thermodiffusion that is unambiguous. Although the material transport equations based on non-equilibrium thermodynamics were used, the fact that the chemical potential at constant pressure must be used was not taken into account. In these articles there is also the problem that in the transition to a dilute system the entropy of mixing does not become zero, yielding unacceptably large Soret coefficients even for pure components. An expression for the Soret coefficient was obtained in (Dhont et al, 2007; Dhont, 2004) by a quasi-thermodynamic method. However, the expressions for the thermodiffusion coefficient in those works become zero at high dilution, where the standard expression for osmotic pressure is used. These results contradict empirical observation.

Using Eq. (27) with the notion of a virtual particle outlined above, and substituting the expression for interaction potential [Eqs. (24, 28)], we can write the combined chemical potential at constant volume \( \mu^r \) as
\[ \mu_v^* = -kT \left( \frac{3}{2} \ln \frac{m_{z}}{m_{N_i}} - \ln \frac{\phi}{1 - \phi} + \ln \frac{Z^2_{\text{rot}}}{Z^2_{\text{rot}}_{\text{int}}} \right) + \]

\[ + \frac{\phi}{v_2} \int \frac{q}{V_{\text{rot}}_{\text{int}}} \Phi_{22}(r) \, dv - \frac{q}{V_{\text{rot}}_{\text{int}}} \Phi_{12}(r) \, dv \right] + \frac{1 - \phi}{v_1} \int \frac{q}{V_{\text{rot}}_{\text{int}}} \Phi_{21}(r) \, dv - \frac{q}{V_{\text{rot}}_{\text{int}}} \Phi_{11}(r) \, dv \right] \]

(69)

In order to proceed to the calculation of chemical potentials at constant pressure using Eq. (29), we must calculate the local pressure distribution \( \Pi_i \) using Eq. (32). We can subsequently use Eqs. (29) and (33) to obtain an expression for the gradient of the combined chemical potential at constant pressure in a non-isothermal and non-homogeneous system:

\[ \nabla \mu_r^* = \left[ \frac{kT}{\phi(1 - \phi)} + a \left( \frac{\epsilon_{11} + \beta \epsilon_{22}}{\epsilon_{12}} - 1 - \beta \right) \right] \nabla \phi + \]

\[ + a \left[ \alpha_3 \beta \phi \left( 1 - \frac{\epsilon_{22}}{\epsilon_{12}} \right) - \alpha_1 \left( 1 - \phi \right) \left( 1 - \frac{\epsilon_{11}}{\epsilon_{12}} \right) \right] \nabla T - \]

\[ - k \left( \frac{3}{2} \ln \frac{m_{z}}{m_{N_i}} - \ln \frac{\phi}{1 - \phi} + \ln \frac{Z^2_{\text{rot}}}{Z^2_{\text{rot}}_{\text{int}}} \right) \nabla T \]

(70)

Here \( \alpha_i \) is the thermal expansion coefficient for the respective component, \( \beta = \frac{v_2 \sigma_{12}^2}{v_1 \sigma_{12}} \) is the parameter characterizing the geometrical relationship between the different component molecules, and \( a = \frac{\pi^2 \sigma_{12} \sigma_{12}}{9 v_1} \) is the energetic parameter similar to the respective parameter in the van der Waals equation (Landau, Lifshitz, 1980) but characterizing the interaction between the different kinds of molecules. Then, using Eqs. (20), (70), we can write:

\[ S_T = \frac{r}{T} (1 - \phi) S_{1T} - \phi S_{2T} + S_{2}^{\text{int}} \]

\[ \frac{4(\phi - 1/2)^2 + \tau - 1}{(\phi - 1/2)^2 + \tau - 1} \]

(71)

where \( r = T/T_c \) is the ratio of the temperature at the point of measurement to the critical temperature \( T_c = a \left( \frac{\epsilon_{11} + \beta \epsilon_{22}}{\epsilon_{12}} - 1 - \beta \right) \), where phase layering in the system begins.

Assuming that \( \beta \approx 1 \), the condition for parameter \( T_c \) to be positive is as \( \epsilon_{11} + \epsilon_{22} > 2 \epsilon_{12} \). This means that phase layering is possible when interactions between the identical molecules are stronger than those between different molecules. When \( \epsilon_{11} + \epsilon_{22} < 2 \epsilon_{12} \), the present theory predicts absolute miscibility in the system.

At temperatures lower than some positive \( T_c \), when \( \tau < 1 \) only solutions in a limited concentration range can exist. It this temperature range, only mixtures with \( \phi \leq \phi_1 = \phi_0 \) can exist, where \( \phi_1 = \left( 1 + \sqrt{1 - \tau} \right)/2 \), which is equivalent to the equation that defines the boundary for phase layering in phase diagrams for regular solutions, as discussed in...
Statistical Thermodynamics of Material Transport in Non-Isothermal Mixtures

(Kondepudi, Prigogine, 1999). $S_{IT} = \alpha_0 a \left( \varepsilon_{ii} / \varepsilon_{12} \right) - 1 \right) / 2kT$ is the “potential” Soret coefficient related to intermolecular interactions in dilute systems. These parameters can be both positive and negative depending on the relationship between parameters $\varepsilon_{ii}$ and $\varepsilon_{12}$. When the intermolecular interaction is stronger between identical solutes, thermodiffusion is positive, and vice versa. This corresponds to the experimental data of Ning and Wiegand (2006).

When simplifications are taken into account, the equations expressed by the non-equilibrium thermodynamic approach are equivalent to expressions obtained in our hydrodynamic approach (Schimpf, Semenov, 2004; Semenov, Schimpf, 2005). Parameter $S_{kin}^{(i)}$ in Eq. (71) is the kinetic contribution to the Soret coefficient, and has the same form as the term in square brackets in Eq. (37). In deriving this “kinetic” Soret coefficient, we have made different assumptions regarding the properties and concentration of the virtual particles for different terms in Eq. (70).

In deriving the temperature derivative of the combined chemical potential at constant pressure in Eq. (70) we used assumption a) in Section 4, which corresponds to zero entropy of mixing. Without such an assumption a pure liquid would be predicted to drift when subjected to a temperature gradient. Furthermore, the term that corresponds to the entropy of mixing $-k \ln \phi / (1 - \phi)$ will approach infinity at low volume fractions, yielding unacceptably high negative values of the Soret coefficient. However, in deriving the concentration derivative we must accept assumption b) because without this assumption the term related to entropy of mixing in Eq. (70) is lost. Consequently, the concentration derivative becomes zero in dilute mixtures and the Soret coefficient approaches infinity.

Thus, we are required to use different assumptions regarding the properties of the virtual particles in the two expressions for diffusion and thermodiffusion flux. This situation reflects a general problem with statistical mechanics, which does not allow for the entropy of mixing for approaching the proper limit of zero at infinite dilution or as the difference in particle properties approaches zero. This situation is known as the Gibbs paradox.

In a diluted system, at $\phi \ll 1$, Eq. (71) is transformed into Eq. (37) at any temperature, provided $\phi < \phi'$. At $|r| > 1$, when the system is miscible at all concentrations, $S_T$ is a linear function of the concentration

$$S_T = (1 - \phi)S_{T1} - \phi S_{T2} + S_{kin}^{(i)} \quad (72)$$

Eq. (72) yields the main features for thermodiffusion of molecules in a one-phase system. It describes the situation where the Soret coefficient changes its sign at some volume fraction. Thus a change in sign with concentration is possible when the interaction between molecules of one component is strong enough, the interaction between molecules of the second component is weak, and the interaction between the different components has an intermediate value. Ignoring again the kinetic contribution, the condition for changing the sign change can be written as $(\varepsilon_{22} + \varepsilon_{11}) / 2 > \varepsilon_{12} > \varepsilon_{11}$ or $(\varepsilon_{22} + \varepsilon_{11}) / 2 < \varepsilon_{12} < \varepsilon_{11}$. A good example of such a system is the binary mixture of water with certain alcohols, where a change of sign was observed (Ning, Wiegand, 2006).

9. Conclusion

Upon refinement, a model for thermodiffusion in liquids based on non-equilibrium thermodynamics yields a system of consistent equations for providing an unambiguous
description of material transport in closed stationary systems. The macroscopic pressure gradient in such systems is determined by the Gibbs-Duhem equation. The only assumption used is that the heat of transport is equivalent to the negative of the chemical potential. In open and non-stationary systems, the macroscopic pressure gradient is calculated using modified material transport equations obtained by non-equilibrium thermodynamics, where the macroscopic pressure gradient is the unknown parameter. In that case, the Soret coefficient is expressed through combined chemical potentials at constant pressure. The resulting thermodynamic expressions allow for the use of statistical mechanics to relate the gradient in chemical potential to macroscopic parameters of the system.

This refined thermodynamic theory can be supplemented by microscopic calculations to explain the characteristic features of thermodiffusion in binary molecular solutions and suspensions. The approach yields the correct size dependence in the Soret coefficient and the correct relationship between the roles of electrostatic and Hamaker interactions in the thermodiffusion of colloidal particles. The theory illuminates the role of translational and rotational kinetic energy and the consequent dependence of thermodiffusion on molecular symmetry, as well as the isotopic effect. For non-dilute molecular mixtures, the refined thermodynamic theory explains the change in the direction of thermophoresis with concentration in certain mixtures, and the possibility of phase layering in the system. The concept of a Laplace-like pressure established in the force field of the particle under consideration plays an important role in microscopic calculations. Finally, the refinements make the thermodynamic theory consistent with hydrodynamic theories and with empirical data.

10. List of symbols

\begin{align*}
a & \quad \text{Energetic parameter characterizing the interaction between the different kinds of molecules} \\
a_m & \quad \text{Empiric coefficient in Eq. (38)} \\
b_i & \quad \text{Empiric coefficient in Eq. (38)} \\
\dot{E} & \quad \text{Electric field strength} \\
e_i & \quad \text{Electric charge of the respective ion} \\
g_{ij} & \quad \text{Pair correlation function for respective components} \\
h & \quad \text{Planck constant} \\
I_1, I_2, I_3 & \quad \text{and Principal values of the tensor of the moment of inertia} \\
\vec{J} & \quad \text{Total material flux in the system} \\
\dot{J}_e & \quad \text{Energy flux} \\
\vec{J}_i & \quad \text{Component material fluxes} \\
k & \quad \text{Boltzmann constant} \\
L_i & \quad \text{and } L_{ij} \text{ Individual molecular kinetic coefficients} \\
l & \quad \text{Thickness of a spherical layer around the particle} \\
m_i & \quad \text{Molecular mass of the respective component} \\
m_{N_i} & \quad \text{Mass of the virtual particle} \\
N & \quad \text{Number of components in the mixture}
\end{align*}
$N_{ik}$ Number of the molecules of the $k$’th component that are displaced by a molecule of $i$’th component

$N_1 = N_{21}$ Number of solvent molecules displaced by the solute in binary systems

$n$ Ratio of particle to solvent thermal conductivity

$n_s$ Numeric volume concentration of salt

$n_i$ Numeric volume concentration of the respective component

$P$ Internal macroscopic pressure of the system

$q_i$ Molecular heat of transport

$r$ Coordinate of the correlated molecule when the considered particle is placed at $r = 0$

$r_0$ Unit radial vector

$r_i$ Coordinate of internal molecule or atom in the particle

$R$ Radius of a colloidal particle

$S$ Surface area of a spherical layer around the particle

$S_T$ Soret coefficient in binary systems

$S_{i,T}$ Contribution of the intermolecular interactions in Eq. (38) and in the Soret coefficient for diluted systems.

$S_T^* \approx 10^{-3}$ Characteristic Soret coefficient for the salts

$S_{kin}^*$ Contribution of kinetic energy to the Soret coefficient

$T$ Temperature

$T_c$ Critical temperature, where phase layering in binary systems begins

$t$ Time

$V_{i,ext}$ Volume external to a molecule of the $i$’th component

$V_{i,in}$ Internal volume of a molecule or atom of the $i$’th component

$\sigma_k$ Partial molecular volume of respective component

$\nu_k$ Its specific molecular volume

$x$ Distance from the colloid particle surface to the closest solvent molecule surface

$y$ Dimensionless distance from the colloid particle surface to the closest solvent molecule surface

$Z_{rot}$ Rotational statistical sum for polyatomic molecules

$Z'_{rot}$ Rotational statistical sum for the respective component

$Z_{vib}'$ Vibrational statistical sum for the respective component

$Z_{N,k}$ Rotational statistical sum for the virtual particle of the molecules $k$’th component displaced by the molecule of $i$’th component

$\alpha_i$ Thermal expansion coefficient for the respective component

$\beta$ Parameter characterizing the geometrical relationship between the different component molecules
ΔI  Difference in the moment of inertia for the molecules constituting the binary mixture
ΔM  Difference in the mass for the molecules constituting the binary mixture
ε_{ij}  Energy of interaction between the molecules of the respective components
Φ_{ij}(r)  Interaction potential for the respective molecules
Φ_{N_{e}}  Total interaction potential of the atoms or molecules included in the respective virtual particle
Φ_{1}^{*}(r)  Hamaker potential of isolated colloid particle
Φ  Macroscopic electrical potential
Φ_{e} = e\Phi  Electrostatic interaction energy
φ = φ_{2}  Volume fraction of the second component in binary mixtures
φ_{i}  Volume fraction of the respective component
φ_{1,2}^{*}  Boundary values of stable volume fractions in binary systems below the critical temperature
γ_{i}  Molecular symmetry number for the respective component
γ_{N_{i}}  Molecular symmetry number for the virtual particle in binary mixture
λ  Parameter which describes the gradual “switching on” of the intermolecular interaction
λ_{D}  Debye length
μ_{i}  Chemical potential of the respective component
μ_{0i}  Chemical potential of the ideal gas of the molecules or atoms of the respective component
μ_{k}^{*} = μ_{i} - \frac{\nu_{i}}{\nu_{k}}\mu_{k}  Combined chemical potential for the respective components
μ_{p} = \mu^{*} = \mu_{21P}  Combined chemical potential at the constant pressure for the binary systems
μ_{p}, ν_{i}, μ_{iV}  Chemical potentials of the respective component at the constant pressure and volume, respectively
μ_{2}^{e}  Electrostatic contribution to the chemical potential at the constant volume for the charged colloid particle
μ_{2P}^{e}  Electrostatic contribution to the chemical potential at the constant pressure for the charged colloid particle
Π_{i}  Local pressure distribution around the respective molecule or particle
Π_{e}  Electrostatic contribution to the local pressure distribution around the charged colloid particle
σ_{ij}  Minimal molecular approach distance
ζ  Electrokinetic potential
τ = T/T_{c}  Ratio of the temperature at the point of measurement to the critical temperature
11. References


www.intechopen.com


Thermodynamics is one of the most exciting branches of physical chemistry which has greatly contributed to the modern science. Being concentrated on a wide range of applications of thermodynamics, this book gathers a series of contributions by the finest scientists in the world, gathered in an orderly manner. It can be used in post-graduate courses for students and as a reference book, as it is written in a language pleasing to the reader. It can also serve as a reference material for researchers to whom the thermodynamics is one of the area of interest.

In order to correctly reference this scholarly work, feel free to copy and paste the following:
