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Comparative Examination of Nonequilibrium Thermodynamic Models of Thermodiffusion in Liquids

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Abstract: We analyze existing models for material transport in non-isothermal non-electrolyte liquid mixtures that utilize non-equilibrium thermodynamics. Many different sets of equations for material have been derived that, while based on the same fundamental expression of entropy production, utilize different terms of the temperature- and concentration-induced gradients in the chemical potential to express the material flux. We reason that only by establishing a system of transport equations that satisfies the following three requirements can we obtain a valid thermodynamic model of thermodiffusion based on entropy production and understand the underlying physical mechanism: (1) maintenance of mechanical equilibrium in a closed steady-state system, expressed by a form of the Gibbs-Duhem equation that accounts for all the relevant gradients in concentration, temperature, and pressure and respective thermodynamic forces; (2) thermodiffusion (thermophoresis) is zero in pure unbounded liquids (i.e., in the absence of wall effects); (3) invariance in the derived concentrations of components in a mixture, regardless of which concentration or material flux is considered to be the dependent versus independent variable in an overdetermined system of material transport equations. The analysis shows that thermodiffusion in liquids is based on the entropic mechanism.

1. Introduction

The aim of this work is to discuss a variety of proposed non-equilibrium thermodynamic material transport equations for non-isothermal non-electrolyte liquid mixtures, in order to select a self-consistent and physically reasonable approach that adequately describes the empirical data.

The fundamentals of non-equilibrium thermodynamics are well-established and widely used to model relatively slow transport processes in liquids and dense gases [1–7]. Results based on non-equilibrium thermodynamics generally agree with those that utilize the Boltzmann kinetic equation for small deviations from equilibrium [2], confirming the validity of this semi-empirical approach.

The advantage of employing non-equilibrium thermodynamics for theoreticians is the ability to combine equilibrium physical parameters such as chemical potential with kinetic coefficients derived from kinetic and hydrodynamic theory. Experimentalists can then use thermodynamic parameters from the literature and principles of non-equilibrium thermodynamics to explain empirical data on mass- and thermodiffusion.

Approaches based on non-equilibrium thermodynamics can be applied to a broad range of materials. Our work here is restricted to the study of non-electrolyte binary molecular solutions and colloidal suspensions placed in a temperature gradient. In our study of these seemingly simple systems over the past couple of decades we have been surprised at the pronounced contrast in the results obtained by different researchers. Although non-equilibrium thermodynamics assumes only that the system is close to thermodynamic equilibrium with maximal entropy, there are numerous

interpretations of the fundamental principles used to derive the material transport equations and associated physical parameters. In this work we review the various approaches and define the issues and inconsistencies from our perspective, in an effort to gain insight into the current state of the problem. We then present and explain a set of basic principles that we believe can be used to select a unique but consistent system of material transport equations and discuss the compatibility of existing theories with these principles.

These principles formulated above could be accepted as the trivial repetition of the well-known concepts, unless there is the controversy in the interpretation of these basic criteria in monographs, research articles and reviews.

2. Equilibrium Thermodynamics and the Condition of Mechanical Equilibrium

2.1. The Gibbs Equation

The use of non-equilibrium thermodynamics starts with the Gibbs equation, which is applicable to a small unit of volume within a macroscopic system of molecules and particles:

$$Tds = du - \sum_k \mu_k dn_k \quad (1)$$

Here T is the local temperature, s is the local entropy, u is the internal energy of a small unit volume, and μ_k and n_k are the chemical potential and numeric volume concentration of components in a mixture, respectively. Note that Equation (1) holds for both constant and changing pressure p , since it is written for a unit volume [1], i.e., the term $p dv$ corresponding to the change in entropy during a change in system volume is always zero. The Gibbs equation is used to derive the entropy production in the non-equilibrium systems.

In [2], an equation from [3] similar to Equation (1) is used to define a system with changing volume. In [4] an equation analogous to Equation (1) is written for a volume containing unit mass of a binary mixture (i.e., the specific volume), which utilizes the equality $n_1^* m_1 + n_2^* m_2 = 1$. In the latter case, the Gibbs equation can be written in the form

$$du^* = T ds^* - p dv^* + \mu dc \quad (2)$$

where v^* is the specific volume, and

$$\mu = \frac{\mu_1}{m_1} - \frac{\mu_2}{m_2} \quad (3)$$

$$c = n_1^* m_1 \quad (4)$$

Here, n_1^* and n_2^* are the numbers of particles or molecules per unit mass, while m_1 and m_2 are the respective masses. Here and below, values with an asterisk are normalized to unit mass, while thermodynamic terms without an asterisk are parameters per unit volume.

The approach used in [4] is restricted to the *relative* transport of two components, i.e., the kinetic properties of the individual components are not considered. Consequently, predications based on the approach are inconsistent with the growing body of empirical data on individual diffusion coefficients and component mobilities. In order to accurately predict absolute (versus relative) values for mobilities, equilibrium thermodynamic behavior must be described separately using individual chemical potentials of components before being inserted into kinetic formulations. Next, we outline the use of Equation (1) in non-equilibrium thermodynamics to calculate entropy production and the associated flux of mass.

2.2. Mechanical Equilibrium and the Gibbs-Duhem Equation

In local thermodynamic equilibrium, Equation (1) should be supplemented by the Gibbs-Duhem equation, which expresses mechanical equilibrium in the system [1–3]:

$$\sum_{i,k} n_k \left(\frac{\partial \mu_k}{\partial p} dp + \frac{\partial \mu_k}{\partial T} dT + \frac{\partial \mu_k}{\partial n_i} dn_i \right) = 0 \quad (5)$$

The partial derivative $\frac{\partial \mu_k}{\partial p}$ in Equation (5) can be related to molecular (or particle) partial volume $\frac{\partial \mu_k}{\partial p} = -\bar{v}_k$. In liquids, which can be considered incompressible in most situations, the molecular partial volume can be considered as the volume occupied by one molecule in a space filling solution. In this case, we can use the equality

$$\sum_k n_k \bar{v}_k = 1 \quad (6)$$

and the general form of the Gibbs-Duhem equation can be accurately expressed as

$$\sum_{i,k} n_k \left(\frac{\partial \mu_k}{\partial T} \nabla T + \frac{\partial \mu_k}{\partial n_i} \nabla n_i \right) = \nabla p \quad (7)$$

According to Equations (5)–(7) the pressure gradient can be cancelled by temperature- and pressure-induced gradients in the chemical potentials established in the system by either internal or external factors, thus providing for mechanical (hydrodynamic) equilibrium. This is in contrast to the approaches used in [1–7], which assume the pressure gradient is non-zero only when there is an *external* force acting on the system. By contrast, we argue that a force field responsible for establishing the pressure gradient does not necessarily have to be applied from outside the system; rather, it can be established within the system under factors such as a temperature or concentration gradient, which is caused by the input or output of energy or mass. One well-known example of such an “internal” field is the electric field established in electrolyte solutions that are either non-homogeneous or non-isothermal [1,2]. An example of the establishment of a pressure gradient from a temperature or concentration gradient can be obtained from the well-known expression for osmotic pressure in diluted solution [1]

$$p = kT \sum_k^n n_k \quad (8)$$

where k is the Boltzmann constant, leading to an osmotic pressure gradient defined by

$$\nabla p = kT \sum_k^n \nabla n_k + k \nabla T \sum_k^n n_k \quad (9)$$

For the isothermal systems, Equation (9) yields the expression derived by Einstein in the work [8] where the Brownian motion was proved to be the non-equilibrium thermodynamic effect caused by the internal pressure gradient in the system. In [8] it is shown also that the concentration-induced pressure gradient can be established in the absence of the external forces. Other examples of internally-derived pressure gradients include radiation and chemical reactions. Likewise, internal pressure gradients can also be caused by the input or output of heat, as in a non-equilibrium system that experiences *continuous* non-uniform heating. Thus, the assumption of constant pressure in non-isothermal mixtures cannot be accepted axiomatically; pressure and concentration gradients can be established in mechanically stable steady-state systems through the action of internal factors, without

the application of an external force field. We note, however, that in non-steady state systems the pressure gradient cannot be adequately defined by the Gibbs-Duhem equation because such systems are not, strictly speaking, mechanically stable since the molecules or particles are moving in a directed fashion.

A more robust approach is to calculate the pressure gradient from an additional condition placed on the system, as is done in [9,10]. Since the Gibbs-Duhem equation is valid for describing mechanical equilibrium within a local thermodynamic equilibrium, it should also be valid for a closed steady-state system. The equation that expresses the condition of mechanical equilibrium should include all the relevant thermodynamic variables: temperature, pressure and the component concentrations. If any of these variables are omitted, the Gibbs-Duhem equation will not correctly define the condition of mechanical equilibrium, a truth that is disregarded in many works. For example, in [1–3,5–7] Equation (2) is written in the form

$$\sum_{i,k} n_k d_{p,T} \mu_k = 0 \quad (10)$$

where the dependence of chemical potential on temperature is omitted and the pressure gradient is assumed to be zero. Consequently, the condition of mechanical stability is ignored. Non-isothermal systems described by Equation (10) make allowance for hydrodynamic flows or other collective movements.

In [4] the Gibbs-Duhem equation is not utilized but the pressure in a non-isothermal system is still assumed to be constant, as in [1–3], because it is argued that there is no external driving force. We repeat, however, that the general Gibbs-Duhem equation [Equation (7)] allows for a pressure gradient to be established when there are concentration- or temperature-induced gradients in the chemical potentials.

In an ingenious application of the Gibbs-Duhem Equation (9) a two-chamber model is considered, with particles exchanged between two isothermal chambers maintained at different temperatures and pressures. Separate Gibbs-Duhem equations for isothermal and isobaric systems are written for each chamber. In this system, the reversible work in particle exchange is calculated through the difference in the relevant chemical potentials between the two chambers, with the changes in entropy assumed to be zero. The thermodiffusion parameters are expressed through the difference in the excess pressure between chambers using Equations (6) and (7), where the entropic term $\frac{\partial \mu_k}{\partial T} \nabla T$ is omitted. Using the respective “isoentropic” Gibbs-Duhem equation, the excess pressure difference between the chambers $\Delta \Pi$ can be calculated as the difference in the binary chemical potential $\mu_2 - \frac{\bar{v}_2}{\bar{v}_1} \mu_1$ between chambers

$$\Delta \left(\mu_2 - \frac{\bar{v}_2}{\bar{v}_1} \mu_1 \right) = \bar{v}_1 \Delta \Pi \quad (11)$$

and the mass- and thermodiffusion parameters are expressed through concentration- and temperature-induced excess pressure gradients.

In a space filling model of liquid mixtures, the combination of chemical potentials relevant to various thermodynamic theories of mass- and thermodiffusion may be defined as

$$\tilde{\mu} = \mu_2 - \frac{\bar{v}_2}{\bar{v}_1} \mu_1 \quad (12)$$

regardless of the validity of Equation (11). The temperature-induced change in excess pressure expressed by Equation (11) is defined in [10] as the driving force of thermodiffusion. However, this

works for thermodiffusion only if the entropy is unchanged (see the term $\sum_k \frac{\partial \mu_k}{\partial T} \Delta T$ in Equation (7) above and Equation (56) in [10] that expresses mechanical equilibrium, where the analogous partial entropic term, while written expressly, is subsequently ignored in defining non-isothermal material transport). This assumption of constant entropy is a significant flaw, since particles that move from the cold to hot chamber must become warmer, just as particles moving in the opposite direction become colder.

According to the Clausius inequality [1], the respective minimal change in entropy can be defined as

$$\Delta S = \frac{\Delta N_2 c_{2V} - \Delta N_1 c_{1V}}{T} \Delta T \quad (13)$$

where ΔN_1 and ΔN_2 are the numbers of the respective particles exchanged between chambers and c_{1V} and c_{2V} are the corresponding thermal capacities. The entropy can remain unchanged in such a particle exchange only under very exotic conditions. Thus, while this approach works well for isothermal mass diffusion [11] where the entropic term $\frac{\partial \mu_k}{\partial T} \nabla T$ is absent, it can lead to serious

mistakes in thermodiffusion, where entropy is changing. The critical difference is that the chemical potential and its temperature derivative are functions of particle mass, even if the pressure is not. Specifically, in statistical mechanics the chemical potential is proportional to the derivative of the partition function with respect to the corresponding particle number and includes mass dependence in the term related to the kinetic energy of thermal motion. By contrast, the pressure is proportional to the derivative with respect to the volume of the system and has no mass dependence.

The use of an excess pressure gradient as the driving force in thermodiffusion based on the principles formulated in [9,10] resulted in the conclusion that only quantum effects lead to differences in isotope thermodiffusion behavior [12], although the contribution of quantum effects is several orders of magnitude smaller than those arising from classical terms used in the theory of isotope effects, both in isothermal and non-isothermal systems [13,14]. In [9] the absence of any isotope effect in liquids is related to rapid dissipation of energy in liquids. We note again that Equation (12) in [9], which relates the transport parameter to component chemical potentials, is a simple consequence of Equations (6) and (7) and does not require an assumption of isoentropy.

In [7] a set of two Gibbs-Duhem equations is considered. These include Equation (10) for the isothermal isobaric system, despite the system being non-isothermal, and the equation

$$n_1 \left(\frac{\partial \mu_1}{\partial T} - \mu_1 - q_1 \right) + n_2 \left(\frac{\partial \mu_2}{\partial T} - \mu_2 - q_2 \right) = 0 \quad (14)$$

where q is the heat of transport [1,2] utilized in non-equilibrium thermodynamics. The heat of transport is equal to the ratio of Onsager kinetic coefficients, which we discuss further in the next section. It characterizes the heat transported by the particle in the isothermal the system or the heat directly carried out by the specific particle in its directed movement. As it will be shown further, Equation (14) is necessary for providing the invariance in the independent material fluxes.

The authors of [7] make no attempt to justify this equality or explain its physical meaning, nor do they indicate how this set of equations is transformed in moving the system to equilibrium. As a result, a hybrid set of Gibbs-Duhem equations of mixed origin (equilibrium–nonequilibrium) is derived axiomatically, while the condition of mechanical equilibrium is left unaddressed.

We re-emphasize that the establishment of mechanical equilibrium is necessary only for closed steady-state systems. If the system is open and/or non-steady state, it is out of mechanical equilibrium, leading to directed motion of particles through the system. In [15], the pressure gradient given by the Gibbs-Duhem equation [Equation (7)] is used in the right-hand side of the Navier-Stokes

equation in calculations of the surface flow profile in a hydrodynamic approach to thermophoresis, but use of the Gibbs-Duhem equation necessitates the complete absence of hydrodynamic flows in the system.

3. Entropy Production, Thermodynamic Forces and Fluxes

In non-equilibrium thermodynamic theory, the derivation of entropy production expressed through thermodynamic forces and fluxes is based on the time derivative of Equation (1):

$$\frac{ds}{dt} = \frac{1}{T} \frac{du}{dt} - \sum_k^N \frac{\mu_k}{T} \frac{dn_k}{dt} \quad (15)$$

The function $\frac{ds}{dt}$ is defined as entropy production in the uniform system, it is the important parameter in non-equilibrium thermodynamics. The significance of entropy as a basic parameter is emphasized in Einstein's expression for the probability of fluctuations in a system [1], which contains the exponent $e^{\frac{\Delta S}{k}}$, where ΔS is the change of system entropy in the transition from equilibrium to the state under consideration. Thus, entropy change is necessary to describe the transition to a given non-equilibrium state. In the approach taken in [1], the time derivatives $\frac{ds}{dt}$, $\frac{du}{dt}$, and $\frac{dn_k}{dt}$ in Equation (15) are substituted with partial derivatives in the respective equations of conservation:

$$\frac{\partial n_k}{\partial t} = -\nabla \vec{J}_k \quad (16)$$

and

$$\frac{\partial u}{\partial t} = -\nabla \vec{J}_u \quad (17)$$

The total derivatives $\frac{ds}{dt}$, $\frac{du}{dt}$, and $\frac{dn_k}{dt}$ can be substituted for their respective partial derivatives from Equations (16) and (17) in closed systems without any hydrodynamic flows because the partial and total time derivatives are identical (see the explanations above Equation (2.8) in [3]).

Substituting Equations (16) and (17) into Equation (15), and using the rule of differentiation for the product of scalar (thermodynamic force) and vector (thermodynamic flux), we obtain:

$$\frac{\partial s}{\partial t} + \nabla \left(\frac{\vec{J}_u}{T} - \sum_k \frac{\vec{J}_k \mu_k}{T} \right) = \vec{J}_u \nabla \frac{1}{T} - \sum_k \vec{J}_k \nabla \frac{\mu_k}{T} \quad (18)$$

Comparing Equation (18) to the standard equation for conservation of entropy [1]

$$\frac{\partial s}{\partial t} + \nabla \vec{J}_s = \sigma \quad (19)$$

the right-hand side of the former is the expression for entropy production σ arising from thermodynamic fluxes \vec{J}_u and \vec{J}_k conjugated with the respective thermodynamic forces $\nabla \frac{1}{T}$ and $\nabla \frac{\mu_k}{T}$, i.e.,

$$\sigma = \vec{J}_u \nabla \frac{1}{T} - \sum_k \vec{J}_k \nabla \frac{\mu_k}{T} \quad (20)$$

In principle, the term expressing entropy production from viscous friction should be included in Equation (20), as stated by the authors of [15], since viscous dissipation heats the medium. However, substituting appropriate numeric values into the thermal conductivity equation shows that such heating is negligible (see Equation (50.2) in [4]).

The flux of internal energy and material corresponds to transport of internal energy and mass, respectively. These fluxes can be written as phenomenological linear combinations of the relevant thermodynamic forces, where the matrix of kinetic coefficients is symmetric according to the Onsager reciprocity principle:

$$\vec{J}_u = n_k \left(L_{uu} \nabla \frac{1}{T} + \sum_k L_{uk} \nabla \frac{\mu_k}{T} \right) \quad (21)$$

$$\vec{J}_k = n_k \left(L_{ku} \nabla \frac{1}{T} + \sum_k L_{ki} \nabla \frac{\mu_i}{T} \right) \quad (22)$$

In Equations (21) and (22) and below, the Onsager kinetic coefficients are molecular parameters related to single molecules. The expression for material flux given by Equation (22) is the key equation in non-equilibrium thermodynamic theories of mass- and thermodiffusion in liquids, while the energy flux can be considered as preset and defined by boundary conditions associated with an experimental design.

In [2] the derivation of Equations (21) and (22) is modified to consider the change in volume. The author of [3] follows those in [1] to derive thermodynamic fluxes for unit volume, while in [4] the chemical potential and specific volume of the mixture, rather than those of individual components, is used in deriving the time derivative of the Gibbs equation. Subsequently, the conservation equations for mass concentration c and complete specific energy (potential plus kinetic energy of the unit mass) are derived and substituted into the time derivative of the specific dissipative function Tds^* . The resulting flux equations are:

$$\vec{i} = -\alpha \nabla \mu - \beta \nabla T \quad (23)$$

$$\vec{q} - \mu \vec{i} = -\delta \nabla \mu - \gamma \nabla T \quad (24)$$

Here \vec{i} and \vec{q} are the relative mass and heat flux, respectively, and parameters α , β , δ , and γ are kinetic coefficients. We note that kinetic coefficients in this approach are not Onsager coefficients in the strict sense, but allow the equations to be written in a more common form. Equations (23) and (24) differ from Equations (21) and (22) in their absence of temperature in the denominator and in defining only the *relative* flux of two materials in a binary mixture.

4. Transformations of Thermodynamic Fluxes and Conservation of Mass

The non-equilibrium thermodynamic approach should yield unambiguous equations for the thermodynamic fluxes [Equations (21) and (22)]. However, some approaches shift certain terms from the expression for material flux [Equation (22)] to that for internal energy flux [Equation (21)]. We will focus our attention on the expressions derived for material flux, since they are substituted into the continuity equations [Equation (16)] to calculate component concentration distributions. By contrast, expressions for heat or internal energy flux are preset by boundary conditions and/or the distribution of heat sources.

In approaches used in [1–3,5–7] certain terms in the material flux [Equation (22)], such as the terms including temperature gradient in the chemical potential, are shifted from the equation for material flux to that for heat flux. Below, we will discuss these transformations for a binary system. We begin with the general expression for material flux, which includes explicit differentiations for the pressure, temperature, and concentration dependencies of the chemical potential.

Differentiating Equation (22) we obtain the following general equation for material flux for non-electrolyte systems in the absence of chemical reactions:

$$\vec{J}_k = -n_k L_{ku} \frac{\nabla T}{T^2} + n_k \sum_{k,i=1,2} \frac{L_{ki}}{T} \left[\left(T \frac{\partial \mu_i}{\partial T} - \mu_i \right) \frac{\nabla T}{T^2} + \left(\frac{\partial \mu_i}{\partial p} \nabla p + \frac{\partial \mu_i}{\partial n_k} \nabla n_k \right) \right] \quad (25)$$

Equation (25) is transformed in various ways in the literature. The off-diagonal kinetic coefficients L_{ki} are usually ignored. In [1–3,5], for example, all the terms that contain a temperature gradient are shifted to the equation for heat flux. Furthermore, the pressure gradient is assumed to be zero and the dependence of a given component flux on the chemical potentials of other components is ignored. The resulting expression for the material flux is

$$\vec{J}_k = -n_k L_{ku} \frac{\nabla T}{T^2} + n_k \frac{L_{kk}}{T} \sum_i \frac{\partial \mu_{kP,T}}{\partial n_i} \nabla n_i \quad (26)$$

In these approaches that ignore the off-diagonal kinetic coefficients L_{ki} , thermodiffusion is related to the presence of the cross-coupling between the heat and material fluxes through the term $L_{ku} \nabla \frac{1}{T}$, which is a kinetic effect.

In [4], the term $\frac{\partial \mu}{\partial T}$ is contained in the following derived expression for *relative* material flux:

$$\vec{J}_1 = n_k \left(-\frac{L_{ku}}{T^2} + L_{kk} \frac{\partial \mu_{P,c}}{\partial T} \right) \nabla T + n_k L_{kk} \frac{\partial \mu_{P,T}}{\partial c} \nabla c \quad (27)$$

Here μ and c are determined by Equations (3) and (4). According to [4] and Equation (27) thermodiffusion (determined by the terms in brackets) is related to both the above cross-coupling and the molecular entropy of the mixture, as determined by the term $\frac{\partial \mu_{P,c}}{\partial T}$. Thus, in this theory the nature of thermodiffusion is a mixed kinetic-entropic nature. In [6,7] Equation (22) is used to derive the *absolute* material flux for single and multi-component mixtures in non-isothermal systems assuming $\nabla p = 0$, although in [7] the other terms in Equation (25) are retained:

$$\vec{J}_k = -n_k L_{ku} \frac{\nabla T}{T^2} + n_k \frac{L_{kk}}{T} \left[\left(T \frac{\partial \mu_k}{\partial T} - \mu_k \right) \frac{\nabla T}{T} + \sum_i \frac{\partial \mu_k}{\partial n_i} \nabla n_i \right] \quad (28)$$

Finally, Equation (25) with zero off-diagonal kinetic coefficients is used to derive an expression for material flux in [16], where the pressure gradient is determined by the general Gibbs-Duhem equation [Equation (7)]:

$$\vec{J}_k = -n_k L_{ku} \frac{\nabla T}{T^2} + n_k \frac{L_{kk}}{T} \left[\left(T \frac{\partial \mu_k}{\partial T} - \mu_k \right) \frac{\nabla T}{T} - \bar{v}_k \sum_i n_i \left(\frac{\partial \mu_i}{\partial T} \nabla T + \sum_{i,j} \frac{\partial \mu_i}{\partial n_j} \nabla n_j \right) + \sum_i \frac{\partial \mu_k}{\partial n_i} \nabla n_i \right] \quad (29)$$

Thus, at least four different approaches are used in the literature to distribute terms from the general non-equilibrium thermodynamic theory into expressions for heat and material flux. All of these arrangements begin with the same expression for entropy production but yield different expressions for the component concentration distributions in a temperature gradient. Each of these expressions except [16] assume constant pressure and could, therefore, be improved by using the general form of the Gibbs-Duhem equation for the pressure gradient [Equation (7)]. Nevertheless, not all approaches can be valid, since they produce significantly different results.

There is also the issue of equivalence or invariance in the expressions for material flux related to the frame of reference used in solving the transport equations. All material fluxes must be expressed in a consistent way using one of the four Equations (25)–(29) and supplemented by the expression for conservation of matter

$$\sum_k \bar{v}_k \vec{J}_k = \vec{I} \quad (30)$$

Here, \vec{I} is the net volumetric flux of various kinds of particles passing through the system, which is determined in different ways in the literature. Equation (30) is obtained by summing the component volume fractions of particles, which should be conserved according to Equation (6). Most works incorrectly assume that Equation (30) is satisfied automatically.

In [1–3,5] the net flux \vec{I} is defined as the flux corresponding to the mass-averaged velocity of particles contained in the system. In cases where the thermodynamic mass- and thermodiffusion fluxes are derived in a barycentric system, the thermodynamic material fluxes are considered to be the only fluxes that provide for a constant position of the center of mass; other fluxes corresponding to motion of the mass center are assumed to be convective and ignored in the context of mass or thermodiffusive flux. However, any kind of mass- or thermodiffusion transport in a system where components are distinct in their mass density will change the center of mass position. The simplest example is isotope mass- and thermodiffusion, where a change in the center of mass is unavoidable even in absence of convection. Moreover, in deriving Equation (20) for entropy production, Equations (16) and (17) for the convection-free system are substituted into Equation (15), expressing the time derivative of the Gibbs equation. Such an approach is valid only for a hydrodynamically stable and closed system, where net material flux is zero.

In [1,2,5], the non-equilibrium thermodynamic expression for material flux [Equation (22)] in a binary system is written for one component only, defined as the independent component; the flux of the second component is considered dependent and eliminated using Equation (30). In [3,5] the need to place restrictions on the Onsager kinetic coefficients, in order to provide for material conservation [Equation (30)], is noted but not discussed in detail. In [4] the requirement of material conservation is omitted. Finally, in [7] Equation (22) for material flux is combined with the expression [Equation (30)] for material conservation.

5. Principles of Zero Thermodiffusion in Pure Liquids and Invariance of Component Fluxes in an Overdetermined System

In this section we derive an unambiguous set of non-equilibrium thermodynamic equations for material flux in non-isothermal systems. We begin with an explanation of the principle of zero thermodiffusive flux in a pure liquid.

5.1. Non-Isothermal Material Transport as an Effect that Occurs Only in Mixtures

Although non-isothermal material transport is observed in liquid solutions, colloidal suspensions, and even pure liquids, it is a mixture or two-phase effect. In pure liquids, however, thermoosmosis is often conjugated with thermodiffusion. Thermoosmosis is related to the interaction between moveable molecules of liquid and a steady-state solid wall that has physical properties distinct from those of the liquid. A derivation of thermoosmotic flux using hydrodynamic theory can be found in [17]. To summarize, a surface liquid-solid potential established at the walls will lead to a temperature-induced pressure gradient within a thin interfacial layer at the liquid-wall boundary. That pressure gradient causes what is commonly referred to as thermoosmotic “slip” flow. An interfacial potential is established because molecules in the wall have different physical parameters than those in the liquid, leading the latter to become distinctly arranged. Thus, thermoosmosis is inherently a two-phase phenomenon.

Thermodiffusion can be considered as thermoosmosis in a reference framework in which the liquid is steady-state and the solid wall representing a solid particle or molecule is moving. Thermoosmosis ceases to exist when molecules of the wall have identical physical parameters to molecules of the pure liquid, just as thermodiffusion ceases to exist when two different molecules have the same physical properties or when there is only one type of molecules in the system. Consider an imaginary system in which a plane divides a pure liquid into two parts. In such a system, the interfacial potential causing slip flow will be absent because the forces acting on molecule of liquid from either side of the plane are equal. Now consider a colloidal particle or molecule surrounded by liquid. The only difference from the former system is that a pressure distribution around the curved surface of the particle can be calculated using thermodynamic methods for small systems [18]. Likewise, for molecular mixtures, thermodynamic methods for small systems can be applied to a single solute particle [19]. While in principle, material flux can occur even in pure liquids due to the entropic mechanism expressed by $\frac{\partial \mu_k}{\partial T} \nabla T$, in space-filling liquids this flux is cancelled by an equal flux of particles moving in the opposite direction, which move to fill the cavities arising from entropic motion. According to Equations (12) and (13) both the complete change in entropy and the respective material flux due to entropy in pure liquids must equal zero. Thus, non-isothermal material transport in mechanically stable and *unbounded* pure liquids must equal zero. Mathematically, this means that material fluxes must be expressed through component physical parameters, which become zero when physical differences between the components approach zero, e.g., in a single-phase pure liquid.

5.2. Invariance with Changes in the Component Concentration and Component Fluxes Defined as Dependent Versus Independent

In a closed steady-state system the condition of mechanical equilibrium is strictly expressed by the Gibbs-Duhem equation. Instead of expressing material conservation by Equation (30), we can use the softer condition

$$\vec{J}_k = 0 \quad (31)$$

In such a system having two components, there exists three equations to characterize the behavior of the system:

$$\vec{J}_1(\phi_1, \phi_2) = 0 \quad (32)$$

$$\vec{J}_2(\phi_1, \phi_2) = 0 \quad (33)$$

$$\phi_1 + \phi_2 = 1 \quad (34)$$

Equation (34) is equivalent to Equation (6) with component concentrations defined in terms of the volume fraction $\phi_k = n_k \bar{v}_k$. Using volume fractions the material flux can be expressed in one of two ways, that is, by using either ϕ_1 or ϕ_2 as the independent variable. As a result, we have four equations to be met in expressing the component concentration distribution:

$$\vec{J}_1[\phi_1, \phi_2(\phi_1)] = 0 \quad (35)$$

$$\vec{J}_2[\phi_1, \phi_2(\phi_1)] = 0 \quad (36)$$

and

$$\vec{J}_1[\phi_2, \phi_1(\phi_2)] = 0 \quad (37)$$

$$\bar{J}_2[\phi_2, \phi_1(\phi_2)] = 0 \quad (38)$$

In Equations (35)–(38) one of the component concentrations can be excluded as a dependent variable through the use of Equation (34), while the other is defined as the independent concentration variable. All possible forms of Equations (35)–(38) must yield the same concentration distribution of components in the system. This requirement forms the foundation for the following principle of concentration invariance:

the same component concentration distribution must be obtained from material transport equations regardless of which concentration is considered to be independent and which expression for the component material flux is used in calculations.

This simple and obvious principle will be used to select a set of expressions for material flux that is consistent with a physically meaningful description of non-isothermal mixtures. In this way, we identify a unique system of equations (or multiple equivalent systems of equations) for material transport.

Note, that the principle of concentration invariance has two components that are similar but different. First is the invariance regarding the selected independent concentration; second is the invariance of the selected independent material flux regardless of the steady-state material transport equation selected among Equations (35)–(38).

6. Evaluation of Non-equilibrium Thermodynamic Expressions for Material Flux in the Literature for Compliance with Three Criteria

In this section we examine all the possible combinations of expressions for material fluxes and Gibbs-Duhem equations for their compliance with the following three criteria: (1) maintenance of mechanical equilibrium in a closed steady-state system, as expressed through a form of the Gibbs-Duhem equation that accounts for gradients in concentration, temperature, and pressure; (2) thermodiffusion being absent in pure unbounded liquids (i.e., in the absence of wall effects); (3) invariance in the derived component concentrations regardless of which concentration is considered to be the dependent versus independent variable and which component material flux is used in an overdetermined system. In performing this evaluation, we will invoke the Soret coefficient, which is commonly used to quantify thermodiffusion:

$$S_T = -\frac{\nabla\phi_2}{\phi_2(1-\phi_2)\nabla T} = \frac{\nabla\phi_1}{\phi_1(1-\phi_1)\nabla T}; \quad S_T \rightarrow 0 \text{ at } \bar{v}_2 - \bar{v}_1, \mu_2 - \mu_1 \rightarrow 0 \quad (39)$$

6.1. Thermodiffusion as a Kinetic Effect Caused by the Cross-Coupling of Heat and Material Transport [1–3,5,6]

We begin our analysis of the most common thermodynamic models that contain a kinetic component within the expression for material flux given by Equation (26). Utilizing Equation (34) and the standard rule of differentiation of composite functions on terms containing the concentration gradients, we obtain

$$\sum_{i=1}^2 \frac{\partial\mu_k}{\partial\phi_i} \nabla\phi_i = \frac{\partial\mu_k}{\partial\phi_2} \nabla\phi_2 + \frac{\partial\mu_k}{\partial\phi_1} \frac{\partial\phi_1}{\partial\phi_2} \nabla\phi_2 = 2 \frac{\partial\mu_k}{\partial\phi_2} \nabla\phi_2 \quad (40)$$

When the volume fraction of either the first or second component is eliminated from equations for material flux as outlined above, the resulting expression is identical in either case except that ϕ is replaced with ϕ_2 . Thus, expressions including Equation (40) satisfy the first component of the principle of concentration invariance.

Using the approach in [1–3,5–7] to define material flux, with ϕ_2 as the independent concentration in a closed steady-state system, we obtain

$$\begin{aligned} 0 &= -2 \frac{\partial \mu_1}{\partial \phi_2} \nabla \phi_2 + \frac{q_1}{T} \nabla T \\ 0 &= 2 \frac{\partial \mu_2}{\partial \phi_2} \nabla \phi_2 + \frac{q_2}{T} \nabla T \end{aligned} \quad (41)$$

where

$$q_i = \frac{L_{iu}}{L_{ii}} \quad (42)$$

is the heat of transport mentioned above, defined as the energy transferred by particle movement in the absence of a temperature gradient [1–3].

Substituting the Gibbs-Duhem equation defined in [1–3,5–7] and Equation (7) above in the form

$$\frac{1-\phi_2}{\bar{v}_1} \frac{\partial \mu_1}{\partial \phi_2} \nabla \phi_2 + \frac{\phi_2}{\bar{v}_2} \frac{\partial \mu_2}{\partial \phi_2} \nabla \phi_2 = 0 \quad (43)$$

into Equation (41) we obtain two equivalent steady-state material transport equations, provided the following condition for the heats of transport is fulfilled:

$$\frac{1-\phi_2}{\bar{v}_1} q_1 + \frac{\phi_2}{\bar{v}_2} q_2 = 0 \quad (44)$$

Equation (44) is the restriction put on the kinetic coefficients to yield the invariance in the material fluxes. According to Equation 44, the heat of transport becomes zero in pure liquids. This conclusion seems not be true since the heat should be transferred by moving particles even in the pure liquids.

Using Equations (26), (31), (41), (43), (44), the Soret coefficient can be written as

$$\begin{aligned} S_T &= - \frac{q_2 - q_1}{4T \frac{\partial \mu_1}{\partial \phi_2} (1-\phi_2) \left[\frac{\bar{v}_2}{\bar{v}_1} (1-\phi_2) + \phi_2 \right]} = \\ &= \frac{q_2}{2\phi_2 (1-\phi_2) \frac{\partial \mu_2}{\partial \phi_2} T} = - \frac{q_1}{2\phi_2 (1-\phi_2) \frac{\partial \mu_1}{\partial \phi_2} T} \end{aligned} \quad (45)$$

Equation (45) indicates that the approach of [1–3,5–7] provides for both the principle of concentration invariance [using Equation (44) which was not considered in these works] and the absence of thermodiffusion in pure liquids but cannot provide for mechanical equilibrium in a non-isothermal system, since the utilized Gibbs-Duhem equation includes no entropic terms $\frac{\partial \mu_k}{\partial T} \nabla T$.

Furthermore, because thermodiffusion is considered a kinetic effect caused by the cross-coupling of heat and material transport, the expression for material flux [Equation (41)] does not allow for the insertion of a distinct form of the Gibbs-Duhem equation to account for temperature-induced gradients in the pressure or molecular entropy.

6.2. *Thermodiffusion as a Mixed Kinetic-Thermodynamic Effect According to the Modified Approach Used in [4]*

In [4] thermodiffusion is modeled as a mixed kinetic-thermodynamic effect, defined by the *relative* motion of components caused by molecular entropy and a cross-coupling between heat and material transport. In such an approach the principle of concentration invariance plays no role. However, the approach does provide the compliance the principle of zero thermodiffusion in pure liquids. We modify the approach used in [4] to obtain the thermodiffusion characteristics of individual components.

A similar method to that used above can be applied to this evaluation, using chemical potentials of the individual components instead of the chemical potential of the mixture. In this case, the expressions for zero material flux analogous to Equation (23) can be written as

$$\begin{aligned} 0 &= -2 \frac{\partial \mu_1}{\partial \phi_2} \nabla \phi_2 + \left(\frac{\partial \mu_1}{\partial T} + \frac{q_1}{T} \right) \nabla T \\ 0 &= 2 \frac{\partial \mu_2}{\partial \phi_2} \nabla \phi_2 + \left(\frac{\partial \mu_2}{\partial T} + \frac{q_2}{T} \right) \nabla T \end{aligned} \quad (46)$$

We note the obvious relation of coefficient $\nabla \phi_2$ with its respective counterpart in Equation (23).

When we write the “isothermal” Gibbs-Duhem equation in the form of Equation (43), according to the approach used in [1–3,5–7] where pressure and temperature gradients are ignored, the principle of concentration invariance can be satisfied by defining the following equality:

$$(1 - \phi_2) \left(T \frac{\partial \mu_1}{\partial T} + q_1 \right) + \phi_2 \left(T \frac{\partial \mu_2}{\partial T} + q_2 \right) = 0 \quad (47)$$

The expressions in brackets are subsequently designated q_i^* . In this approach parameter q_i^* plays the same role as parameter q_i in the previous section. Thus, expressions similar to Equations (43)–(45) can be written where q_i is replaced with q_i^* . Likewise, the Soret coefficient can be expressed by an equation similar to Equation (45) with parameter q_i replaced by q_i^* . Thus, the approach also satisfies the principle of concentration invariance, as well as the absence of thermodiffusion in pure liquids. However, the nature of thermodiffusion becomes mixed because the temperature-induced concentration gradient is determined by both the kinetic factor q_i and the molecular entropy $\frac{\partial \mu_i}{\partial T}$. Furthermore, the approach does not provide for mechanical equilibrium in a non-isothermal system because the Gibbs-Duhem equation that is used in the derivation lacks the entropic term $\frac{\partial \mu_i}{\partial T} \nabla T$.

6.3. Thermodiffusion as a Mixed Entropic-Kinetic effect With Cross-Coupling Between Heat and Material Transport according to the Approach Used in [7]

The selection of adequate material transport equations depends on the form of the Gibbs-Duhem equation that is used to describe the steady-state system, as well as on the specific form of the expression used for material flux. In [7] the material fluxes in a steady-state system are written as

$$\begin{aligned} 0 &= 2 \frac{\partial \mu_1}{\partial \phi_2} \nabla \phi_2 + \frac{\partial \mu_1}{\partial T} \nabla T + \frac{q_1 - \mu_1}{T} \nabla T \\ 0 &= 2 \frac{\partial \mu_2}{\partial \phi_2} \nabla \phi_2 + \frac{\partial \mu_2}{\partial T} \nabla T + \frac{q_2 - \mu_2}{T} \nabla T \end{aligned} \quad (48)$$

which corresponds with the material flux determined by Equation (10). The Gibbs-Duhem equation has the same “isothermal” form as Equation (43), and the equation providing the principle of concentration invariance can be expressed as

$$\frac{1-\phi_2}{\bar{v}_1} \left(\frac{\partial \mu_1}{\partial T} + \frac{q_1 - \mu_1}{T} \right) + \frac{\phi_2}{\bar{v}_2} \left(\frac{\partial \mu_2}{\partial T} + \frac{q_2 - \mu_2}{T} \right) = 0 \quad (49)$$

Each expression in brackets can be designated by $\frac{q_i^{**}}{T}$. Calculations similar to those made in the derivation of Equation (45) yield similar expressions for the Soret coefficient, where parameter $\frac{q_i^{**}}{T}$ replaces $\frac{q_i}{T}$ in Equation (45). Thus, this approach provides for both the principle of concentration invariance and the absence of thermodiffusion in pure liquids but does not provide for mechanical equilibrium in a non-isothermal system.

In summary, the theoretical approaches analyzed in this section can yield the absence of thermodiffusion in pure liquids only with the assumption that $\frac{\partial \mu_i}{\partial T} = 0$ in the Gibbs-Duhem equation. Since the temperature derivative of the molecular chemical potential is molecular entropy, in a non-isothermal system this means that molecular entropy is assumed to be zero, which is unacceptable.

Although the models including zero pressure gradient cannot provide for mechanical equilibrium in non-isothermal systems, the obtained results can be used to analyze some theoretical ideas in literature. One such idea using the concepts of thermophilicity-thermophobicity of components is discussed in Appendix.

6.4. Thermodiffusion as an effect caused by molecular entropy derived from the pressure gradient calculated from the complete Gibbs-Duhem equation according to the Approach Used in [19]

Substituting the pressure gradient ∇p expressed by the general form of the Gibbs-Duhem equation [Equation (7)] into Equation (25) for material flux we obtain two equations [Equation (29)] for the material fluxes, where the volume fractions ϕ_1 and ϕ_2 are dependent and independent concentrations, respectively. For a steady-state closed system where the fluxes are zero:

$$\begin{aligned} 0 &= -\frac{L_{11}}{\bar{v}_1 T} \left[\phi_2 (1 - \phi_2) \left(2 \frac{\partial \tilde{\mu}}{\partial \phi_2} \nabla \phi_2 + \frac{\partial \tilde{\mu}}{\partial T} \nabla T \right) + (1 - \phi_2) \left(\frac{\mu_1 + q_1}{T} \right) \nabla T \right] \\ 0 &= \frac{L_{22}}{\bar{v}_2 T} \left[\phi_2 (1 - \phi_2) \left(2 \frac{\partial \tilde{\mu}}{\partial \phi_2} \nabla \phi_2 + \frac{\partial \tilde{\mu}}{\partial T} \nabla T \right) + \phi_2 \left(\frac{\mu_2 + q_2}{T} \right) \nabla T \right] \end{aligned} \quad (50)$$

Here, $\tilde{\mu}$ is the chemical potential of the mixture defined by Equation (12).

Both expressions given by Equation (50) yield the same equation determining concentration distribution:

$$2 \frac{\partial \tilde{\mu}}{\partial \phi_2} \nabla \phi_2 + \frac{\partial \tilde{\mu}}{\partial T} \nabla T = 0 \quad (51)$$

provided the heats of transports satisfy the following equality:

$$q_i = -\mu_i \quad (52)$$

According to Equation (52) the heat transferred by a particle is equal to its mean energy in the system, as expressed by the chemical potential. Such a restriction placed on the Onsager coefficients is consistent with the ideas proposed in [3].

As outlined in [19] incorporation of the requirement established by Equation (52) provides for at least one model of material transport that is compliant with all three criteria necessary to obtain a valid thermodynamic model of thermodiffusion based on entropy production. It is easy to see that combined with Equation (52), Equation (50) for material flux satisfies the principles of invariance. The resulting stationary material transport equations obtained by the model can be written as:

$$\phi_2 (1 - \phi_2) \left(2 \frac{\partial \tilde{\mu}}{\partial \phi_2} \nabla \phi_2 + \frac{\partial \tilde{\mu}}{\partial T} \nabla T \right) = 0 \quad (53)$$

The model also provides for mechanical equilibrium in a non-isothermal steady-state liquid mixture in a closed system, and shows that to achieve such equilibrium a non-zero pressure gradient must be established. Furthermore, the transport equations in this model yield zero mass flux in pure liquids, which is consistent with the general thermodynamic expression of the Soret coefficient:

$$S_T = \frac{\frac{\partial \tilde{\mu}_p}{\partial T}}{2\phi_2 (1 - \phi_2) \frac{\partial \tilde{\mu}_p}{\partial \phi_2}} \quad (54)$$

Note that Equation (12) which determines the chemical potential of mixture $\tilde{\mu}_p$ at constant pressure is the chemical potential of a considered particle μ_2 minus the sum of the chemical potentials of all molecules of liquid displaced by the particle $\frac{\bar{v}_2}{v_1} \mu_1$. This parameter appears as a result of considering the pressure gradient in the space-filling mixture. The displaced volume of liquid can be considered as a virtual particle consisting of the non-displaced component. Thus, Equation (54) predicts that thermodiffusion is non-zero only if the chemical potentials of the real particle and virtual particle are different.

6.5. Non-Steady State Systems

Discuss briefly nonstationary systems. In non-steady-state closed non-isothermal systems, where mechanical equilibrium is absent, the pressure gradient should be determined by substituting the expressions for material flux given by Equation (25) into Equation (30) and utilizing the equality expressed by Equation (56) for a closed system (with $I = 0$). A detailed description of this approach can be found in [20,21]. For the sake of brevity, we present only one of two non-steady-state material transport equations:

$$\frac{\partial \phi_2}{\partial t} = \frac{L_{22}}{T} \nabla \frac{\phi_2 (1 - \phi_2) \left(2 \frac{\partial \tilde{\mu}}{\partial \phi_2} \nabla \phi_2 + \frac{\partial \tilde{\mu}}{\partial T} \nabla T \right)}{1 - \phi_2 + \frac{\bar{v}_1}{\bar{v}_2} \frac{L_{22}}{L_{11}} \phi_2} \quad (55)$$

This expression is transformed into Equation (53) for steady-state systems but the coefficients of mass diffusion and thermodiffusion, which are expressed by the separate terms in brackets in the numerator, are modified by parameter $1 - \phi_2 + \frac{\bar{v}_1}{\bar{v}_2} \frac{L_{22}}{L_{11}} \phi_2$ in the denominator. This modifying parameter is related to the dynamic pressure gradient established by hydrodynamic friction in a non-

steady-state system and arises from the expression of material conservation in non-steady-state systems described by Equation (30) rather than Equation (32). This hydrodynamic factor can significantly reduce both the mass and thermodiffusion coefficients of large particles, even in a moderately concentrated binary mixture. Note that the hydrodynamic factor approaches unity at $\frac{\bar{v}_1 L_{22}}{\bar{v}_2 L_{11}} = 1$ that is, when the Stokes-Einstein diffusion coefficients or hydrodynamic radii of the components are equal. In this case, the pressure gradient is expressed by the Gibbs-Duhem equation, even for non-steady state systems.

7. Conclusions

To obtain adequate material transport equations for non-isothermal systems, it is necessary to consider the temperature-induced pressure gradient formulated by the Gibbs-Duhem equation, in order to satisfy three criteria: (1) mechanical equilibrium in steady-state closed system; (2) invariance of material transport equations under any choice for the independent material flux and concentration; and (3) the absence of thermodiffusion in a pure liquid. Material transport equations that assume a zero pressure gradient cannot satisfy all three principles. Satisfying the three criteria also requires the heat of transport to be equal to the respective chemical potential with the opposite sign.

Appendix

Equations (44), (47), (53) provide for the principle of concentration invariance. Similar equation is used in [7] [see the discussion around Equation (14)]. Here, we consider the notion of using thermophobicity or thermophilicity of pure components as a parameter that can predict the properties of liquid mixtures in a temperature gradient [22]. The concept is based on an equation for the Soret coefficient similar to Equation (45) derived in [7], where the Soret coefficient is proportional to the difference in the net heats of transport of pure components or other similar parameters.

For example, consider the heats of transport used in Equation (45), although the same conclusion is reached with the use of other similar parameters that include terms responsible for the individual thermophobicity or thermophilicity of components q_{i0} and a term b corresponding to the interaction between components. Consider an equimolar mixture, where $n_1 = n_2$, and Equation (44) can be written as

$$q_1 + q_2 = 0 \quad (\text{A1})$$

In this case, according to [22], the Soret coefficient is proportional to the difference $q_{20} - q_{10}$ of the pure components. Accounting for Equations (44) and (A1) this expression can be written as

$$q_2 - q_1 = q_{20} - q_{10} = 2q_2 = 2q_1 = 2(q_{20} + b) = 2(q_{10} + b) \quad (\text{A2})$$

The value of the interaction parameter b depends on the properties of both components. Thus, the idea that one can rely solely on some pre-defined measure of component thermophobicity or thermophilicity to predict thermodiffusion of mixture is impossible; any predictive model must include component interaction parameter(s), in order to comply with the basic principles used to derive the Soret coefficient of a mixture.

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