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Simple ideas about thermodiffusion in a binary liquid mixture

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ABSTRACT

The simplest system where the microscopic physical nature of thermodiffusion can be understood theoretically is a binary mixture. The case of a liquid mixture is considered here, starting from the equilibrium state such as described by thermodynamics. Under a uniform temperature, gradients of composition and/or pressure bring about a non-equilibrium state where local enthalpy is not minimum and/or local entropy is not maximum. The gradients of enthalpy and entropy define a thermodynamic force which is shown to drive composition and pressure diffusions. The thermodynamic force considered in this paper has the physical dimension of a force, it is defined per particle, it is invariant under gauge transformations of enthalpy and entropy and lastly it obeys Newton's third law. Under a non-uniform temperature, it is shown that such a thermodynamic force does not account for thermodiffusion. The thermodiffusive force is of a non-thermodynamic essence. The kinetic-theory account of the transport coefficients is examined in mixtures of long macromolecules with small solvent molecules.

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1. Introduction

Thermodiffusion was discovered more than 150 years ago [1,2], but the frequent meetings held on thermodiffusion show that a simple explanation is still lacking in the liquid state. In the gaseous state, thermodiffusion is accounted for by the Chapman–Enskog solution to the Boltzmann kinetic equation [3–5], yet the case of polyatomic molecules is still under study [6]. This contribution focuses on the simplest physical system – a binary liquid mixture – in order to bring out simple theoretical ideas. A suspension of colloidal particles in a unary liquid is not a binary mixture in the thermodynamic sense because a suspension consists of two phases (liquid and solid) instead of one, so that different thermodynamic tools are called for [7]. Therefore, suspensions are not considered herein but they are referred to in Section 5 where very asymmetric binary mixtures are envisaged.

The paper has been organised as follows. Section 2 recalls how the interdiffusion current density in a binary mixture arises in describing the kinetics of mixing or unmixing. Section 3 deals with interdiffusion caused by a gradient of composition (“ordinary diffusion”) or of pressure (“barodiffusion”). Both phenomena can be accounted for by means of a *thermodynamic* driving force (derived from the thermodynamic functions of the mixture) and the account given in Section 3 is equivalent to the one of Landau and Lifshitz [8]. The nexus of the paper is Section 4 where it is argued that interdiffusion caused by a temperature gradient cannot be accounted for by a thermodynamic force because the two sides of the force, energetic and entropic, cancel each other exactly as a consequence of double gauge invariance, previously noticed in a study of thermoelectric effects [9]. The thermodiffusive driving force thereby calls for a kinetic coefficient, while the response to the total force requires another kinetic coefficient, namely mobility. The kinetic theory of the coefficients is the subject of Section 5, where the issue is: may we ignore correlations between two-body molecular encounters (i.e. assume

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the Stoßzahlansatz to hold) or not? We proceed inductively from the available experimental evidence; dilute solutions of long polymer chains provide a clue. Section 6 summarizes the main points.

2. Absolute transport and relative transport

The continuity equations $(\partial n_{A,B}/\partial t) + \text{div} \mathbf{j}_{A,B} = 0$ expressing local conservation of particles involve the number density n_A (n_B) and number-current density \mathbf{j}_A (\mathbf{j}_B) of species A (B). Transport velocities \mathbf{u}_A and \mathbf{u}_B are associated to those current densities through $\mathbf{j}_{A,B} = n_{A,B} \mathbf{u}_{A,B}$; they are mesoscopic ensemble averages. From the transport velocities of A and B, one can define an overall velocity of particle (\mathbf{u}) or mass (\mathbf{v}) transport,

$$\mathbf{u} = x_A \mathbf{u}_A + x_B \mathbf{u}_B \quad \text{or} \quad \mathbf{v} = \omega_A \mathbf{u}_A + \omega_B \mathbf{u}_B \quad (1)$$

where $x_A = n_A/(n_A + n_B)$ is the particle fraction, $\omega_A = m_A n_A/(m_A n_A + m_B n_B)$ is the mass fraction, m_A is the mass of A, and likewise for B. The velocity \mathbf{u} or \mathbf{v} is an absolute velocity in the kinematic sense. The other combination of the transport velocities is the relative velocity $\mathbf{u}_B - \mathbf{u}_A$ of component B with respect to component A.

The evolution of composition $(\partial x_B/\partial t) = (n_A + n_B)^{-1} [x_A (\partial n_B/\partial t) - x_B (\partial n_A/\partial t)]$ is obtained from the continuity equations where $\mathbf{j}_{A,B} = n_{A,B} \mathbf{u}_{A,B}$ and $n = n_A + n_B$. A similar calculation yields $(\partial \omega_B/\partial t)$. It is found that

$$n \left(\frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \right) x_B + \text{div} \mathbf{J}_B = 0 \quad \text{or} \quad \rho \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \omega_B + \text{div} \vartheta_B = 0 \quad (2)$$

where $\rho = m_A n_A + m_B n_B$ is the mass density, $\nabla = \partial/\partial \mathbf{r}$ is the gradient operator and

$$\mathbf{J}_B = n x_A x_B (\mathbf{u}_B - \mathbf{u}_A) \quad \text{or} \quad \vartheta_B = \rho \omega_A \omega_B (\mathbf{u}_B - \mathbf{u}_A) \quad (3)$$

is the particle or mass interdiffusion current density. The mixing/unmixing of A and B only involves the relative velocity through \mathbf{J}_B or ϑ_B . That velocity is intrinsic, i.e. observer-independent. The absolute transport velocity \mathbf{u} or \mathbf{v} , which depends on the observer through the choice of a frame of reference (rigid coordinate system), is unrelated to the mixing or unmixing. Accordingly, the absolute current density $n \mathbf{u} = \mathbf{j}_A + \mathbf{j}_B$ or $\rho \mathbf{v} = m_A \mathbf{j}_A + m_B \mathbf{j}_B$ cannot play any role in the kinetics of mixing. The mass-transport velocity \mathbf{v} is governed by the Navier–Stokes equation [8,10].

It is worth remarking that the interdiffusion current density cannot serve to express conservation of either B or A, for $(\partial n_B/\partial t) + \text{div} \mathbf{J}_B = -n \text{div}(x_B \mathbf{u})$ does not vanish. In like manner [10,11], introducing the advective derivative $D/Dt = \partial/\partial t + \mathbf{u} \cdot \nabla$, there is a “source” term in:

$$\frac{Dn_B}{Dt} + \text{div} \mathbf{J}_B = -n_B \text{div} \mathbf{u} \quad (4)$$

The “source” term in Eq. (4) is fake since B is conserved. Therefore $\mathbf{J}_B/n_B = \mathbf{u}_B - \mathbf{u}$ cannot be thought of as the ensemble average of the peculiar velocity of species B defined as the velocity of the molecule with respect to coordinates moving with the number-average velocity \mathbf{u} (formula 7.2-5 in [12]). This comes about because the non-vanishing divergence of \mathbf{u} forbids considering a coordinate system of local velocity \mathbf{u} (with respect to the laboratory) as a frame of reference in the sense of kinematics. The divergence of the velocity field $\mathbf{u}(\mathbf{r}, t)$ or $\mathbf{v}(\mathbf{r}, t)$ embodies the deformable nature of the medium [10,11].

3. Interdiffusion as the kinetics of mixing: isothermal case

3.1. Interdiffusion driven by composition and pressure gradients

In non-equilibrium thermodynamics, the interdiffusion current density is written as a linear combination of the gradients of the independent intensive state variables, namely pressure p , temperature T and composition x_B (for \mathbf{J}_B) or ω_B (for ϑ_B) [8]. Interdiffusion due to ∇x_B is often called ordinary diffusion while interdiffusion due to ∇p is called pressure diffusion or barodiffusion. In Section 3 temperature is taken to be uniform ($\nabla T = 0$).

Consider first pressure diffusion. It drives each component toward places of lower pressure through the buoyancy force $-v_A \nabla p$ or $-v_B \nabla p$, where $v_{A,B} = (\partial g_{A,B}/\partial p)$ is the partial volume of A or B (per molecule) and $g_{A,B}$ is the partial Gibbs energy (chemical potential) of A or B (per molecule). The relative transport of B with respect to A is driven by the differential force $-(v_B - v_A) \nabla p = -(\partial^2 g/\partial p \partial x_B) \nabla p$, where $g = x_A g_A + x_B g_B$ is the Gibbs energy per molecule. The component of larger partial volume will concentrate in the places of lower pressure.

The upshot of ∇p is to filter out (partially unmix) components A and B according to their partial volumes: a composition gradient ∇x_B grows up. This in turn affects interdiffusion since g_A and g_B depend on x_B . Ordinary diffusion drives components A and B through the forces $-(\partial g_A/\partial x_B) \nabla x_B$ and $-(\partial g_B/\partial x_B) \nabla x_B$. The relevant force driving relative transport of B with respect to A is the differential force $-[(\partial g_B/\partial x_B) - (\partial g_A/\partial x_B)] \nabla x_B = -(\partial^2 g/\partial x_B^2) \nabla x_B$. As the thermodynamic stability of the mixture requires $(\partial^2 g/\partial x_B^2) > 0$, the differential force opposes the growth of ∇x_B . Whereas pressure diffusion causes unmixing, ordinary diffusion causes mixing. In a steady state involving both pressure and ordinary diffusions, $-(\partial^2 g/\partial p \partial x_B) \nabla p - (\partial^2 g/\partial x_B^2) \nabla x_B = 0$, i.e. $-\nabla g_{BA} = 0$, where the subscript BA henceforth denotes the difference (here $g_B - g_A$) between the partial thermodynamic functions of B and A.

No external force field such as gravity \mathbf{g} has been included in this picture. That field adds up the forces $m_A \mathbf{g}$ and $m_B \mathbf{g}$ and entails a sedimentation kinetics where the component i of smaller partial specific volume v_i/m_i tends to concentrate at lower locations [13].

3.2. Thermodynamic driving force

It is possible to write $g = h - Ts$ where $s = -(\partial g/\partial T)$ is the entropy per molecule. The tendency to minimizing the Gibbs energy g stems from the universal competition of energy h and entropy s [14] occurring under constant (here, spatially constant) temperature. (Since we are not considering that the volume of the container has a given value, enthalpy h is used instead of internal energy.) The driving force $-\nabla g$ is a thermodynamic force in that it has two sides: one is mechanical (derived from energy h), whereas the other is unmechanical (derived from entropy). Statistical-thermodynamically speaking, the latter side of the force is formally proportional to Boltzmann’s constant k [14]. In the binary case considered herein, a molecule A is apportioned an enthalpy h_A and an entropy s_A , and likewise for B, so that $h = x_A h_A + x_B h_B$ and $s = x_A s_A + x_B s_B$. The corresponding thermodynamic forces acting upon A and B obey Newton’s third law since the force per unit volume, whether enthalpic or entropic, vanishes as the result of the Euler identity linking the partial thermodynamic functions, namely:

$$n_A(-\nabla h_A) + n_B(-\nabla h_B) = 0 \tag{5}$$

$$n_A(T\nabla s_A) + n_B(T\nabla s_B) = 0 \tag{6}$$

As remarked by de Groot [15], when the Gibbs energy per particle and other functions of thermodynamics are allowed to depend on position, (non-equilibrium) thermodynamics becomes a *field theory*. Enthalpy and entropy give rise to force fields driving the particles. In the next section, we remark that enthalpy and entropy actually are *gauge fields*, and gauge invariances have to be ensured in order to ensure the meaningfulness of the thermodynamic force. We only consider global gauge transformations whereby the enthalpy or entropy per particle is shifted by the same amount at all locations.

4. Thermodiffusion and the “third side of the force”

It is henceforth considered that a temperature gradient is present. A problem arises if the response \mathbf{J}_B is written as a linear combination of the “driving forces” $-\nabla g_{BA}$ and ∇T , namely:

$$\mathbf{J}_B = \alpha(-\nabla g_{BA}) + \beta \nabla T \tag{7}$$

The problem is that $-\nabla g_{BA}$ has no physical meaning, because it is not invariant under a change of the entropy gauge $s \rightarrow s + s_0$: as entropy is gauged differently, $\beta \rightarrow \beta + \alpha s_0$ is modified. Note that s_0 is independent of position so that the gauge transformation is global, not local; but s_0 may be chosen arbitrarily large. Therefore, calling α and β phenomenological coefficients is misleading. Because it is reliant on the choice of a gauge for entropy, the coefficient β is not the reflection of a *phenomenon*.

Likewise, the “driving force” $-\nabla(g_{BA}/T)$ is unphysical because it is not invariant under a change of the energy gauge $h \rightarrow h + h_0$ (h_0 is independent of position \mathbf{r} and time t and can be arbitrarily large). If \mathbf{J}_B is written as a combination of $-\nabla(g_{BA}/T)$ and $\nabla(1/T)$, namely:

$$\mathbf{J}_B = a \left[-\nabla \left(\frac{g_{BA}}{T} \right) \right] + b \nabla \left(\frac{1}{T} \right) \tag{8}$$

the coefficient b depends on the choice of a gauge for energy: $h \rightarrow h + h_0$ entails $b \rightarrow b + ah_0$. Thus, the coefficient b is not genuinely phenomenological.

The only gauge-invariant thermodynamic force is $-\nabla h_{BA} + T\nabla s_{BA} = -\nabla g_{BA} + s_{BA}\nabla T$ [9,16]. Expressing that force as a linear combination of the gradients ∇x_B , ∇p and ∇T yields no ∇T term as a result of the identity:

$$-\left(\frac{\partial h}{\partial T} \right) + T \left(\frac{\partial s}{\partial T} \right) = 0 \quad \text{or} \quad dh|_{p,x_B} = T ds|_{p,x_B} \tag{9}$$

The identity embodies the ambivalent (energetic and entropic) status of heat. The absence of a ∇T term in $-\nabla h + T\nabla s$ means that no force built from thermostatic quantities (i.e. quantities derived from g) can drive thermodiffusion, it being understood that a thermodynamic force must be gauge-invariant with respect to both energy and entropy gauges. To ensure gauge invariances, one must write, instead of (7) or (8):

$$\mathbf{J}_B = \alpha(-\nabla h_{BA} + T\nabla s_{BA}) + \beta \nabla T \tag{10}$$

Many works on thermodiffusion refer to de Groot and Mazur’s book [17]. The authors make use of an isothermal gradient of the chemical potential, e.g. $\nabla_T g_A$, where ∇_T is defined as $\nabla - \nabla T(\partial/\partial T)$, see also Eq. (5.5) of [18]. Obviously, for mathematical reasons, $\nabla_T g_A = (\partial g_A/\partial x_B)\nabla x_B + (\partial g_A/\partial p)\nabla p$ has no contribution from ∇T , and $\nabla_T g_A = \nabla_T h_A - T\nabla_T s_A$ is

invariant under both energy and entropy gauge transformations. Our point in this paper is one of physics: we have shown that $\nabla h_A - T \nabla s_A$ is a linear combination of ∇x_B and ∇p without ∇T . This is a physical result inferred from relation (9). Because the thermodynamic force $-\nabla h_A + T \nabla s_A$ has no component along ∇T , it can be replaced by $-\nabla_T h_A + T \nabla_T s_A = -\nabla_T g_A$ such as used in [17].

Given that $\mathbf{J}_B = n x_A x_B (\mathbf{u}_B - \mathbf{u}_A)$, Eq. (10) is tantamount to stating that $\mathbf{u}_B - \mathbf{u}_A$ is driven by a three-sided force:

$$\mathbf{u}_B - \mathbf{u}_A = \mu \left[-\nabla h_{BA} + T \nabla s_{BA} - h^* \left(\frac{\nabla T}{T} \right) \right] \tag{11}$$

where $\mu = \alpha / n x_A x_B$ and $\mu h^* / T = -\beta / n x_A x_B$. In (11), μ is a mobility coefficient (velocity response to a negative energy gradient) and thermodiffusion is accounted for by a “third side of the force” involving a non-thermodynamic energy h^* (heat of transport). Just as any force, the thermodiffusive force $-h^*(\nabla T/T)$ is a time-rate of momentum transfer. That force stems from the imbalance in molecular transfers of momentum between A and B caused by the anisotropy of the relative-momentum distribution function [16]. The anisotropy is due to the temperature gradient. Onsager’s reciprocity theorem shows that h^* is related to a covariance of enthalpy and velocity [16], but that feature does not make the calculation of h^* significantly easier. As Wannier [19] remarked, even though a transport coefficient can be related to a time-dependent feature of the equilibrium state (for instance, in a dilute regime, μ is related to the autocorrelation of velocity), the computation of the coefficient is not facilitated thereby as much as might have been expected.

Before dealing with the coefficients μ and h^* in the next section, we rewrite (11) as:

$$0 = -\left(\frac{\mathbf{u}_B - \mathbf{u}_A}{\mu} \right) + \left[-\nabla h_{BA} + T \nabla s_{BA} - h^* \left(\frac{\nabla T}{T} \right) \right] \tag{12}$$

Eq. (12) can be envisioned as the subtraction of two force-balance equations, namely

$$0 = -x_A \left(\frac{\mathbf{u}_B - \mathbf{u}_A}{\mu} \right) + \left[-\nabla h_B + T \nabla s_B - x_A h^* \left(\frac{\nabla T}{T} \right) \right] \tag{13}$$

$$0 = -x_B \left(\frac{\mathbf{u}_A - \mathbf{u}_B}{\mu} \right) + \left[-\nabla h_A + T \nabla s_A + x_B h^* \left(\frac{\nabla T}{T} \right) \right] \tag{14}$$

Eq. (13) expresses the view that a three-sided (energetic, entropic and thermodiffusive) driving force acting on B is balanced by a friction force linear in the relative transport velocity and in the particle fraction of the other component A. Similarly, Eq. (14) is the force-balance equation for A which undergoes a friction force linear in x_B so that the two frictions satisfy Newton’s third law. This is the Maxwell–Stefan picture of interdiffusion where $1/\mu$ is the so-called coefficient of resistance (Widerstandskoeffizient) and the motion is overdamped (accelerationless) [11,16,20].

At this juncture, we remember that the original description of Maxwell and Stefan (devised before Gibbs invented the chemical potential) involved the partial pressures p_A and p_B such that $\nabla p_A = n_A \nabla g_A$ and $\nabla p_B = n_B \nabla g_B$ in an isothermal ideal gaseous mixture [20]. Morozov’s approach to thermodiffusion [21] introduces “partial pressures” p_A and p_B in a binary liquid after the theory of Bearman and Kirkwood [18]. The p_A in Eq. (5.3) of [18] is defined from the isotropic part of the partial stress tensor of component A, and likewise for B. Therefore, in [18,21], p_A and p_B are defined as hydrodynamic, not thermodynamic, quantities (although the partial stress tensors do not exist in the conventional hydrodynamics of Navier and Stokes [8]). p_A and p_B would be thermodynamic quantities if they were derived from the partition function (or a Legendre transform thereof) of equilibrium statistical mechanics. But Eq. (5.3) of [18] shows that this is not so in Kirkwood’s statistical mechanics of transport processes. The thermodynamic definition of partial pressures from the chemical potentials is given by Eqs. (7-155)–(7-156) of Kirkwood’s textbook [22]. It is seen in [22] that $p_A + p_B$ is equal to p only in an ideal mixture, whereas $p_A + p_B$ is always equal to p in [18]. Accordingly, nowhere in the paper by Bearman and Kirkwood does the phrase “partial pressure” ever appear. Their theory is clearly hydrodynamic in essence, unlike the modern Maxwell–Stefan approach based upon gradients of thermodynamic quantities supplemented with a non-thermodynamic thermodiffusion term [20]. There is no simple link between Morozov’s hydrodynamic approach and the present one.

5. Obtaining the kinetic coefficients

The coefficients μ and h^* in Eq. (12) cannot be obtained from classical or statistical thermodynamics. They have to be calculated from kinetic theory. Consider first μ . It can be expressed in two ways, either as a bare (“Boltzmann”) or a renormalized (“Stokes”) coefficient, according to whether uncorrelated or correlated two-body encounters (A–A, A–B or B–B) are taken into account. Taking A and B to be similar in size and mass, rough expressions of the bare (μ_b) and renormalized (μ_r) coefficients are:

$$\mu_b \approx [n^1 n^{-2/3} m (kT/m)^{1/2}]^{-1} \quad \text{and} \quad \mu_r \approx (4\pi \eta n^{-1/3})^{-1} \tag{15}$$

where the typical size of a molecule in the liquid state is taken as $\approx n^{-1/3}$, the momentum transfer scattering cross section in a two-body encounter is taken as $\approx n^{-2/3}$, the typical mass is m , and η is the shear viscosity of the mixture. Taking values relevant to a water–ethanol mixture at $\omega_B \approx 0.5$ under standard conditions, we compute:

$$\mu_b \approx 3 \times 10^{13} \text{ s/kg} \quad \text{and} \quad \mu_r \approx 10^{10} \text{ s/kg} \quad (16)$$

Based on these estimates, the correlation of two-body scattering events renormalizes mobility by a factor of ≈ 3000 . The experimental value deduced from the mutual diffusion coefficient $D_{AB} = \mu \chi_A \chi_B (\partial^2 g / \partial x_B^2)$ is found to be $\mu \approx 10^{11} \text{ s/kg}$ [23]. As μ is closer to μ_r , the correlation of two-body scattering events renormalizes mobility by a factor of ~ 300 . (As far as nomenclature is concerned, some authors [24] label μ_b as “kinetic” and μ_r as “hydrodynamic” because viscosity is involved in μ_r .)

What about h^* ? A theoretical expression of h^* obtained from bare kinetic theory [16] predicts that, for structureless A and B particles, $|h^*|$ is roughly equal to kT , which is consistent with experimental data [25]. In case that B is a long macromolecule in a solvent A, the dissimilarity in size and mass is reflected in a large dimensionless parameter, e.g. the number N of rigid (Kuhn) segments of B. Assuming them to be slender (Kuhn length $l \gg$ radius a), B has $2N$ internal degrees of freedom besides the three external ones. The rough result $|h^*| \approx kT$, pertinent to no internal degree of freedom, is not expected to hold. In case that A is a good solvent of B, experiments performed in the dilute regime show that (i) $\mu \approx (4\pi\eta l N^{0.6})^{-1}$ and (ii) $h^* \approx \pm N^{0.6} kT$ in the limit $2N \gg 1$ [26,27]. (We disregard a non-dimensional system-dependent factor of order l/a .) To interpret those experimental facts, we rewrite the force-balance equation (12) as:

$$0 = -\frac{1}{\mu}(\mathbf{u}_B - \mathbf{u}_A) + (m_B - m_A)\mathbf{g} - h^* \frac{\nabla T}{T} \quad (17)$$

where an external force (gravity) has been included for later comparison purposes. Neither kinetic coefficient in Eq. (17) is equal to its bare value. Consider first the friction coefficient $1/\mu$. The friction force undergone by the chain moving with respect to the solvent is *not* the sum of the friction forces undergone by the segments, as the latter sum is N times $\approx -4\pi\eta l(\mathbf{u}_B - \mathbf{u}_A)$. So the actual $1/\mu$ is $N^{-0.4}$ times the bare friction coefficient $\approx 4\pi\eta l N$ (“bare” is meant here with respect to the Kuhn segment). Because the friction exerted on the chain is not the uncorrelated superposition of the frictions exerted on the segments, the friction force (or coefficient) is renormalized by the hydrodynamic coupling between segments. That coupling means the breakdown of the Stoßzahlansatz: the approximation of molecular chaos (statistically independent binary encounters) is inappropriate here.

Consider now the thermodiffusive force coefficient h^* of the chain. The actual $h^* \approx \pm N^{0.6} kT$ is $N^{-0.4}$ times the bare coefficient $\approx \pm N kT$ obtained by adding up the thermodiffusive forces $\approx \mp kT(\nabla T/T)$ undergone by each segment. Therefore, also the thermodiffusive force is renormalized by the correlation of two-body collisions. The assumption of molecular chaos, predicting the mere superposition of N forces $\approx \mp kT(\nabla T/T)$ each, is wrong. In contradistinction, in the limit $N \gg 1$, the external force in Eq. (17) is the mere superposition of N contributions $m_B \mathbf{g}/N$ from each Kuhn segment. The same is true (in the dilute-chain limit $N \chi_B \ll 1$) of the barodiffusive force $-(v_B - v_A)\nabla p$ but not of the diffusive force $-(\partial^2 g / \partial x_B^2)\nabla \chi_B = -(kT/\chi_A \chi_B)\nabla \chi_B$.

The friction and thermodiffusive forces originate in momentum transfers during molecular encounters. The statistical correlation of the encounters causes the non-superposition of the momentum transfer rates. As experiments show that $1/\mu$ and h^* scale in the same way with respect to N , the mechanisms of momentum transfer underlying friction and thermodiffusion are governed by the same correlations. The ratio $h^* \mu$, which is T times the thermodiffusion coefficient of the polymer/solvent mixture, is not affected by the correlations. Consequently $h^* \mu$, which can be viewed as either $(N^{0.6} \mu)(h^*/N^{0.6})$ or $(N\mu)(h^*/N)$, behaves as a bare coefficient. This was used in [27] to calculate $h^* \mu$ as a function of the physical parameters of the mixture, from the bare quantities of the Kuhn segment. This amounts to effectively ignoring the correlations (hydrodynamic coupling) between different Kuhn segments. (Note that, like Brochard [28] and unlike Yang and Ripoll [29], I use the phrase “hydrodynamic coupling” rather than “hydrodynamic interaction”. We have to do with a statistical correlation, not a physical interaction. Physical interactions are short-ranged whereas statistical correlations typical of the liquid state – where the Stoßzahlansatz breaks down – can be long-ranged.)

Can one theoretically justify the property (inferred from experiment) that $1/\mu$ and h^* are renormalized in the same way as $N \gg 1$? We mention the earliest and latest attempts. Brochard and de Gennes [30] invoked the reciprocity between the transports of matter and heat to show that $h^* \mu$ is unaffected by the correlations. But they did not check that their choice of gradients was consistent with Onsager’s theorem. Yang and Ripoll [29] state that the thermodiffusive force undergone by a monomer (in the case $l = a$) is hydrodynamically renormalized by the forces undergone by the other monomers. But the fact that the forces are generated by a temperature gradient seems to play no role in their reasoning.

The thermodiffusive behaviour of a long macromolecule in a good solvent, such as pictured here, is similar to the behaviour of a large solid sphere suspended in a thermally inhomogeneous unary fluid, such as theoretically investigated by Goldhirsch and Ronis [24]. They found that:

- (i) diffusivity (or μ) and the thermophoretic force are renormalized by correlated collisions;
- (ii) the thermophoretic velocity (proportional to the thermodiffusion coefficient in the large-sphere or long-chain limit [31]) is not renormalized, i.e. it is given by bare kinetic theory.

The authors reached their conclusions by showing that the same diagrams (of ring and repeated-ring correlated collisions) were dominating the field-theoretic expansions of μ and h^* .

The foregoing view of bare and renormalized quantities is not restricted to a long macromolecule in a good solvent. In a theta solvent, one expects $\mu \sim N^{-0.5}$ and $h^* \sim N^{0.5}$ so that $\mu h^* \sim N^0$ is the bare quantity at the scale of the Kuhn length. Again, the facts that $1/\mu$ and h^* do not scale as N are evidences of correlation. While $\mu \sim N^{-0.5}$ has been predicted and observed long ago [32,33], recent observations of Rauch and Köhler [34] show that $\mu h^* \sim N^{0.00-0.07}$ as $N \gg 1$ for polystyrene in theta solvent conditions. This supports our expectation $\mu h^* \sim N^0$.

6. Summary

In a gaseous binary mixture, thermodiffusion had not been observed before its theoretical prediction. The prediction did not come from thermodynamics, but from kinetic theory in a model of light spheres dilute among heavy spheres [35,36]. Subsequently, the effect could be described only by means of the complicated Chapman–Enskog machinery [3–6] because no thermodynamic explanation is possible. In this contribution, we argued that this is not only true in the gaseous state but in the liquid state as well. The nexus of our argument is that, when the inhomogeneity of a mixture is due to a temperature gradient, the energetic side of the thermodynamic force (tending to decrease h) is exactly cancelled by the entropic side of the thermodynamic force (tending to increase s). Therefore, if the interdiffusion current density is thought of as a linear response to the difference of forces on the A and B components, with a friction coefficient, and if the force difference is taken as a linear combination of ∇x_B , ∇p and ∇T , then the coefficients of ∇x_B and ∇p are thermodynamic quantities whereas the coefficient of ∇T is not.

Once the kinetic essence of the thermodiffusive force is recognized, the next question is: can one use bare kinetic theory involving uncorrelated binary scatterings only, or should correlation between binary scatterings be considered? The first answer is correct in a dilute gas, i.e. the Stoßzahlansatz holds. In a liquid, it is incorrect for μ , but it seems that h^* is calculable within bare kinetic theory for monatomic molecules. Long macromolecules with a large number of degrees of freedom show that the thermodiffusive force coefficient h^* , just like the friction force coefficient $1/\mu$, is renormalized by the correlation of binary collisions. Yet the ratio of the two force coefficients, and thence the thermodiffusion coefficient, is accountable for within bare kinetic theory.

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