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Connection between thermophoresis and thermodiffusion in a liquid binary mixture

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Connection between thermophoresis and thermodiffusion in a liquid binary mixture

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In a liquid suspension, thermophoresis is the motion of a suspended particle under a temperature gradient. In a liquid binary mixture, thermodiffusion is the generation of a composition gradient upon application of a temperature gradient. In this paper, a quantitative connection is established between the two phenomena without making assumptions about their mechanisms. It is shown that Galilean invariance and the choice of a Galilean reference frame play a key role in that connection. Our results are not restricted to very dilute suspensions or mixtures.

Keywords: thermophoresis; suspension; thermodiffusion; binary mixture; Galilean invariance

PACS: 66.10.C-, 47.57.E-, 05.70.Ln

1. Statement of the issue

The physics of liquid suspensions and that of binary mixtures are known to overlap. The classic works of Einstein [1], Smoluchowski [2] and Perrin [3], on Brownian motion and the atomic-molecular reality of matter, are about liquid suspensions but they borrow concepts from the thermodynamics of binary mixtures, or solutions. Those works dealt with isothermal suspensions, and the connection with isothermal mixtures continues to be fruitful much later [4,5]. In case that the temperature is not homogeneous, the physics of suspensions is concerned with the thermophoresis of suspended particles, i.e. their motion under the temperature gradient [6,7], whereas the physics of mixtures envisages the thermodiffusion,

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4 also called thermal diffusion [8–10], of the two components; it is a partial demixtion induced
5 by the temperature gradient, which is opposed by the remixing effect of ordinary diffusion. In
6 the viewpoint of thermophoresis, the particles move through a quiescent medium unperturbed
7 by the guest particles. In the viewpoint of thermodiffusion, the molecules of the suspending
8 medium are treated on the same footing as the suspended particles.
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11 It appears that the connection between thermophoresis and thermodiffusion has been
12 much less investigated than the one between the isothermal phenomena, and is subject to
13 confusions due to the disparate concepts involved in the two areas [11]. The purpose of the
14 present paper is to dispel those confusions. We shall stay at the phenomenological level
15 throughout, with no attempt at investigating the underlying transport mechanism(s) or making
16 any assumption thereabout. The paper is structured as follows. Section 2 expounds the
17 statistical tools needed to describe the transport of particles in a medium which is not
18 necessarily homogeneous. Section 3 reviews two experiments measuring the so-called
19 thermophoretic velocity acquired by a suspended particle under the applied temperature
20 gradient. Special attention is paid to the conditions under which that velocity is measured as
21 they are an integral part of the notion of thermophoretic velocity. Next, section 4 applies the
22 statistical tools of section 2 to the measurements reviewed in section 3. The observables used
23 in the thermophoresis and thermodiffusion viewpoints are then related to each other. It
24 appears that the often unspoken specification of a Galilean reference frame is crucial in
25 establishing the link between both viewpoints. Section 5 gathers the conclusions.
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38 **2. Constructing a Galilean-invariant equation of matter transport**

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40 This section describes the statistical framework needed to handle particle *transport*, which is
41 often not deterministic in contrast to particle *motion* in mechanics. This comes about because
42 the particle interacts with the infinitely many thermally fluctuating degrees of freedom of the
43 medium. The latter will be allowed to be inhomogeneous; that feature is mandatory if
44 temperature T varies with position, since many relevant physico-chemical parameters (such as
45 the mass density or the viscosity of the medium) are functions of T .
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50 The laboratory frame where transport is observed is taken to be Galilean. Considering
51 only one coordinate x for simplicity and denoting time by t , the simplest description of the
52 non-deterministic motion $x(t)$ of a particle suspended in the medium involves the average
53 position $\langle x \rangle$ and the variance $\langle (x - \langle x \rangle)^2 \rangle$. The notation $\langle \rangle$ means the averaging over a
54 statistical ensemble of particles in which each particle has a distinct trajectory $x(t)$.
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58 Consider first a homogeneous medium. Starting from an ensemble of N particles
59 sharply localized at position x_0 at zero time, i.e. a particle number density $n(x, t=0) = N\delta(x -$
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x_0) where δ is the Dirac distribution, it is expected that, at time $t > 0$, $n(x, t)$ be a Gaussian distribution,

$$n(x, t) = \frac{N}{[2\pi\langle(x - \langle x \rangle)^2\rangle]^{3/2}} \exp\left(-\frac{(x - \langle x \rangle)^2}{2\langle(x - \langle x \rangle)^2\rangle}\right), \quad (1)$$

where the mean and variance are linear in time:

$$\langle x \rangle = x_0 + v_d t, \quad (2)$$

$$\langle (x - \langle x \rangle)^2 \rangle = 2Dt. \quad (3)$$

The reasons for (1)-(3) are threefold [12,13]:

(i) because of homogeneity, the rates ($d\langle x \rangle/dt$) and ($d\langle (x - \langle x \rangle)^2 \rangle/dt$) are independent of x_0 ; v_d in (2) is called the drift (or migration) velocity and D in (3) is called the diffusivity;

(ii) it is also assumed that the process is stationary, i.e. the rates are independent of the origin of time;

(iii) because the random increments of the particle's position are independent but obey the same probability law owing to (i) and (ii), the central limit theorem of probabilities entails a Gaussian distribution of x after a sufficiently long time t .

We notice that (1)-(3) are equivalent to

$$\frac{\partial n}{\partial t} + \frac{\partial j}{\partial x} = 0, \quad (4)$$

$$j(x, t) = v_d n - \frac{\partial(Dn)}{\partial x}. \quad (5)$$

Equation (4) expresses the local conservation of particles and j is the conserving particle-current density.

In actuality, statement (iii) and expression (5) do not hold over a short time t and $n(x, t)$ is not Gaussian. This is well known in neutron transport when the scattering events are infrequent, i.e. when the neutron's mean free path approaches the container's size [14]. In electron transport in a solid medium, scattering events are so frequent that the deviation from the Gaussian shape can only be 'observed' in a numerical simulation of transport performed over a very short duration or very small length. It is then found that expression (5) of the current density has to be supplemented with paradiffusion terms such as $\partial^2(Pn)/\partial x^2$ and higher-order spatial derivatives [15], skewing $n(x, t)$ with respect to the Gaussian shape. This provides the most complete description of the non-deterministic motion, which includes moments or cumulants of $x(t)$ of all orders [16]. However, if only one paradiffusion term is used in j , namely $\partial^2(Pn)/\partial x^2$, then negative values of $n(x, t)$ are found at some positions [15]. Marcinkiewicz [17] has shown that it is necessary to include all high-order derivatives in order that positivity of $n(x, t)$ be preserved. That is the reason why, although the inclusion of one paradiffusion term improves the description of transport over short durations [15], in practice the expansion of j is truncated after the first two terms, corresponding to the central limit theorem. We follow that practice in the following.

If the medium is not homogeneous, v_d and D are functions of position. Accordingly, the formulae (2) and (3) are not valid any longer. The definitions of v_d and D should now be local, i.e.

$$v_d(x_0) = \left(\frac{d\langle x \rangle}{dt} \right), \quad (6)$$

$$D(x_0) = \frac{1}{2} \left(\frac{d\langle (x - \langle x \rangle)^2 \rangle}{dt} \right), \quad (7)$$

depend on the initial position x_0 of the sharp group of particles. Local particle conservation (4) is ensured with the current density j given again by expression (5) provided that v_d and D be considered as functions of position. Those functions should be smooth, i.e. vary little over the mean free path, defined as the length needed for decorrelation of the instantaneous velocity due to the random changes of that velocity in scattering events.

We stress that, for the coefficient of n in (5) to mean the local drift velocity of a sharply localized ensemble of particles (the velocity of their centroid according to (6)), the other contributions to j should be *total spatial derivatives*. If $j = v_d(x)n + (\partial f / \partial x)$ with f vanishing on the container's borders, then an integration by parts of (4)-(5) (the Ostrogradsky-Gauss theorem in three dimensions) proves that $(d\langle x \rangle / dt) = v_d(x_0)$ for $n(x, t=0) = N\delta(x - x_0)$ [11,18,19]. This has been checked experimentally on Brownian particles in an inhomogeneous (albeit isothermal) medium [20,21]. If in addition $f = 0$, it is easily verified that $n(x, t=0) = N\delta(x - x_0)$ evolves into $n(x, t) = N\delta(x - X(t))$ where $X(t)$ satisfies the following differential equation:

$$\frac{dX}{dt} = v_d(X(t)), \quad X(t=0) = x_0. \quad (8)$$

Then, position evolves as a deterministic function $X(t)$ of time. The contributions to j other than $v_d(x)n$, namely $(\partial f / \partial x)$ with $f = -Dn + \partial(Pn) / \partial x + \dots$, are the diffusion and paradiffusion current densities [15]. Once paradiffusion is dropped, we are left with a non-homogeneous drift-diffusion equation, often labelled 'Fokker-Planck equation' [18]. It is a continuous-time self-repeating application of the central limit theorem of probabilities making allowance for a smooth change of v_d and D with x and possibly with t [16]¹.

Whether in the homogeneous or inhomogeneous case, the particle transport equation (4)-(5) exhibits manifest Galilean invariance. We can see it by observing transport in a different Galilean frame, such that $x \rightarrow x - Vt$, with V denoting the translation velocity of the new frame with respect to the first one. Then, from (6) and (7), $v_d \rightarrow v_d - V$ transforms as a vector while $D \rightarrow D$ is a Galilean scalar². If the current density (5) be written as

¹ Ryskin [16] remarks that the label 'Fokker-Planck equation' has often been given to an equation having the same pattern but with a wrong definition of $D(x_0)$, not consistent with Galilean invariance.

² If the medium were anisotropic, D would actually be a second-order tensor D^{ij} instead of $D\delta^{ij}$ in the isotropic case (δ^{ij} is the Kronecker symbol).

$$j(x, t) = \left(v_d - \frac{\partial D}{\partial x} \right) n - D \left(\frac{\partial n}{\partial x} \right), \quad (9)$$

then the coefficient of n in (9) cannot be interpreted as the local rate of change of $\langle x \rangle$ in any frame.

3. Observation of a thermophoretic velocity

The first observation of the thermophoresis of particles in a liquid was reported by McNab and Meisen [6]. They were studying spherical polystyrene latex particles, of diameter ranging between 0.8 and 1.0 μm , dilute in an aqueous medium. The liquid suspension was subjected to a vertical gradient of temperature. The vertical drift, or migration, velocity was computed from the transit time, i.e. the time needed by a particle to move over a given distance in the medium. The actions of gravity and of the temperature gradient were assumed to be additive. As the particle Reynolds number never exceeded 0.1, the terminal gravitational velocity (corrected for buoyancy) was obtained from the Stokes law and it was subtracted from the observed velocity in order to isolate the effect of the temperature gradient alone.

In the more recent experiment of Regazzetti and co-workers [7], the temperature gradient is horizontal, so that no gravitational/buoyant correction to the horizontal velocity is needed. The time t required for the drift of the particle across the horizontal thickness w of the channel is measured in three experiments, and $\langle t \rangle$ denotes the mean value. The thermophoretic velocity is operationally defined³ by equation (1) of [7] as $w/\langle t \rangle$, i.e.

$$v_d = \left(\frac{dx}{d\langle t \rangle} \right), \quad (10)$$

instead of $v_d = (d\langle x \rangle/dt)$ of section 2. Both definitions of v_d are consistent with each other insofar as the uncertainty $[\langle (t - \langle t \rangle)^2 \rangle]^{1/2}$ is much less than the mean $\langle t \rangle$. Since $x - x_0 \approx v_d t$ to zero order in the uncertainties, the condition $[\langle (t - \langle t \rangle)^2 \rangle]^{1/2} \ll \langle t \rangle$ amounts to $[\langle (x - \langle x \rangle)^2 \rangle]^{1/2} \ll v_d \langle t \rangle$, i.e.

$$2D \ll v_d^2 \langle t \rangle \approx v_d (x - x_0). \quad (11)$$

The left-hand side is computed by means of the Stokes-Einstein formula to be about 10^{-12} m^2/s while the right-hand side is about 10^{-9} m^2/s [6].

In [6], the liquid is enclosed in a rigid container. Since the volume is constant, the pressure is not controlled by the experimentalist. It is determined by the system itself through the relation of state of the suspension, as discussed in the appendix. Although the value of pressure is not known, we show in section 4.1 that its horizontal gradient vanishes very

³ Actually in their equation (1) w is replaced by $w - d$, where d is the diameter of a particle as it can be a significant fraction of w .

quickly while its vertical gradient offsets gravity. In [7], the control of the flow rate demands a vertical pressure gradient associated with the viscous resistance of the channel; that gradient adds up to the gravitational pressure gradient. As for the horizontal pressure gradient, it is shown in section 4.1 to vanish very quickly. Therefore the thermophoretic velocity is either measured in the absence of a pressure gradient [7] or corrected for the effect of that gradient [6].

In both experiments, the temperature gradient over the particle's path $x - x_0$ is established after a typical time $\tau = (x - x_0)^2/\Delta$ where Δ is the thermal diffusivity of the suspension. As the time needed to cross $(x - x_0)$ is $\langle t \rangle = (x - x_0)/v_d$, we have

$$\tau/\langle t \rangle = v_d(x - x_0)/\Delta. \quad (12)$$

In water under standard conditions, $\Delta \approx 10^{-7} \text{ m}^2/\text{s}$. The typical measured thermophoretic velocities [6] were about $5 \times 10^{-6} \text{ m/s}$ and $(x - x_0) \approx 2 \times 10^{-4} \text{ m}$, so that $\tau/\langle t \rangle \approx 10^{-2} \ll 1$. Therefore, the temperature gradient, just as the pressure gradient, may be regarded as static during thermophoresis.

4. Connection with thermodiffusion

4.1. Unary versus binary transport

From the previous section, the phenomenology of thermophoresis calls for the transport description of section 2 in which diffusion is neglected. The evolution of the liquid medium where particles are suspended is not considered. Basically, thermophoresis is regarded as a phenomenon of unary transport, i.e. there is one mobile species B in a quiescent medium of A molecules. The transport of B obeys a local equation of conservation (in three dimensions)

$$\frac{\partial n_B}{\partial t} + \text{div } \mathbf{j}_B = 0, \quad (13)$$

where n_B is the number density of B and the vector field $\mathbf{j}_B(\mathbf{r}, t)$ is the conserving particle-current density of B at position \mathbf{r} . It is $n_B \mathbf{u}_B(\mathbf{r}, t)$, where the transport velocity \mathbf{u}_B is the average velocity of the ensemble of particles contained in a macroscopically small, but microscopically large, volume element located about \mathbf{r} . From section 2, a first approximation to \mathbf{j}_B is $v_d n_B$ and a second approximation, including the spreading about the centroid, is $v_d n_B - \nabla(Dn_B)$, where ∇ denotes the gradient operator.

In the viewpoint of thermodiffusion [8–10], one is considering a binary mixture of the species A and B where they play symmetrical roles. Just as B, A is locally conserved, so that (13) is supplemented with

$$\frac{\partial n_A}{\partial t} + \text{div } \mathbf{j}_A = 0, \quad (14)$$

where n_A is the number density of A, $\mathbf{j}_A = n_A \mathbf{u}_A$ is the conserving current density of A and \mathbf{u}_A is the transport velocity of A. The evolution of the mixture composition, defined as the particle fraction $x_B = n_B/n$ where $n = n_A + n_B$ is the total particle-number density, is obtained [22] by combining the equations of continuity (13) and (14):

$$n \left(\frac{Dx_B}{Dt} \right) + \text{div} \mathbf{J}_B = 0, \quad (15)$$

where

$$\mathbf{J}_B = x_A \mathbf{j}_B - x_B \mathbf{j}_A \quad (16)$$

is the particle interdiffusion current density and $x_A = n_A/n$. In (15), the advective derivative D/Dt is $\partial/\partial t + \mathbf{u} \cdot \nabla$ where $\mathbf{u} = x_A \mathbf{u}_A + x_B \mathbf{u}_B$ is the number-averaged transport velocity (ensemble average velocity of particles in a mesoscopic volume). Equation (15) describes the interdiffusion, or mixing, of A and B. The physical meaning of \mathbf{J}_B is more straightforward if it is rewritten as

$$\mathbf{J}_B = n x_A x_B (\mathbf{u}_B - \mathbf{u}_A), \quad (17)$$

so that mixing stops when A and B are transported at the same velocity.

It is equally possible to describe the evolution by considering the *mass* fraction and current densities instead of the *particle* fraction x_B and current densities \mathbf{j}_B and \mathbf{J}_B , and we shall do so in the appendix. The mass and particle fractions are homographic functions of each other, involving the ratio of masses m_A of A and m_B of B, and the mass and particle densities are related likewise.

The main concern of this paper is the unary limit of guest particles B being very dilute in a host medium of molecules A. Then, one intuitively expects the medium to be hardly perturbed by the transport of a few guest particles B. In (14), n_A is expected to be independent of time and \mathbf{u}_A to vanish in the laboratory frame. But is that actually possible? In equilibrium n_A is a function of the local thermodynamic state (p, T, x_B) of the mixture. The equilibrium relation $n_A = n_A(p, T, x_B)$ retains its validity when the change in x_B is slow; that is one usual assumption, or rather approximation, of non-equilibrium thermodynamics, which is borne out in experiments and in numerical studies of the molecular dynamics [23]. Since p and T do not vary with time, we have

$$\frac{\partial n_A}{\partial t} = \left(\frac{\partial n_A}{\partial x_B} \right)_{p, T} \left(\frac{\partial x_B}{\partial t} \right). \quad (18)$$

The upshot is that interdiffusion, i.e. $(\partial x_B / \partial t) \neq 0$, prevents us from taking $\text{div} \mathbf{j}_A = 0$ in (14) and thereby from considering that $\mathbf{u}_A = 0$. Therefore the medium of molecules A may not be regarded as being at rest. More precisely, relation (18) tells us that the medium of molecules A is locally expanded or contracted because of its change in composition x_B . The medium may not be taken as a reference frame (in the sense of mechanics) *because it is a non-rigid fluid instead of a solid*. The condition of rigidity is $\text{div} \mathbf{u}_A = 0$ while the actual velocity field is such that $\text{div} \mathbf{u}_A = -(\partial/\partial t + \mathbf{u}_A \cdot \nabla) \ln n_A$ which does not vanish in general. As a result, the equations

of unary transport (4)-(5) pertinent in thermophoresis cannot be straightforwardly recovered from the equations of binary transport (15)-(16) used in thermodiffusion.

That conclusion is further supported by the fact that \mathbf{J}_B is a Galilean-invariant vector field, whereas $\mathbf{j}_B \rightarrow \mathbf{j}_B - n_B \mathbf{V}$ in a Galilean frame moving at velocity \mathbf{V} with respect to the laboratory frame. Because of those distinct behaviours with respect to Galilean invariance, \mathbf{J}_B cannot be carelessly identified with \mathbf{j}_B , as one would like in letting $x_A \rightarrow 1$ and $\mathbf{u}_A = 0$ in (17).

Consider now the mass transport velocity

$$\mathbf{v} = (m_A n_A \mathbf{u}_A + m_B n_B \mathbf{u}_B) / \rho \quad (19)$$

where $\rho = m_A n_A + m_B n_B$ is the mass density. That velocity appears in the local conservation of mass in fluid dynamics [24],

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho \mathbf{v}) = 0, \quad (20)$$

and it is the solution of the Navier-Stokes equation [24],

$$\rho \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \mathbf{v} = -\nabla p + \rho \mathbf{g} + \eta \Delta \mathbf{v}, \quad (21)$$

where \mathbf{g} is the Earth's gravity field and η is the shear viscosity (we ignore the volume viscosity and the position dependence of η for simplicity). In mechanical equilibrium,

(i) there is no horizontal pressure gradient and a vertical pressure gradient offsets gravity;

(ii) the solution $\mathbf{v}(\mathbf{r}, t)$ of equation (21) is constant and uniform.

Its value \mathbf{v} in the laboratory frame is determined by the breaking of Galilean invariance due to the rigid container. The latter exerts a viscous braking force on the liquid and makes \mathbf{v} vanish with respect to the container, which may be taken as a Galilean reference frame and usually is at rest in the laboratory. From the dimensional analysis of (21), it is seen that mechanical equilibration ($\mathbf{v} = 0$) is achieved over a typical transient time L^2/ν , where L is a typical length of the container and $\nu = \eta/\rho$ is the momentum diffusivity of the liquid [24] ($\nu \approx 10^{-6}$ m²/s in water under standard conditions). That time is much shorter than the typical time for interdiffusion, namely L^2/D_{BA} , where D_{BA} is the mutual diffusivity appearing in the phenomenological equation written in section 4.2: $D_{BA} \approx 10^{-12}$ m²/s for suspended spheres [6,7] and $\approx 10^{-9}$ m²/s for ethanol dilute in water [25]. Because the momentum density $\rho \mathbf{v}$ and the composition x_B evolve over disparate time scales, it is possible to consider that \mathbf{v} approximately vanishes everywhere in the container's frame while $\mathbf{u}_A - \mathbf{u}_B$ does not. In other words, because of its faster time scale, mechanical equilibration adjusts to the slower 'chemical equilibration', i.e. interdiffusion [26,27]. The relative error incurred in approximating \mathbf{v} to zero is of the order of $D_{BA}/\nu \approx 10^{-3}$ or less in the examples considered. From $\mathbf{v} \approx 0$ in the container's frame and from definitions (16) and (19), we are now in a position to connect \mathbf{j}_B in that frame with \mathbf{J}_B , as

$$\mathbf{J}_B \approx \left[x_A + \left(\frac{m_B}{m_A} \right) x_B \right] \mathbf{j}_B. \quad (22)$$

It is emphasized that the connection (22) is specific to liquid media where $D_{BA}/v \ll 1$. In gaseous media where $D_{BA}/v \approx 1$ [28,29], it would not hold. Indeed it is not found in the literature on thermodiffusion in gases [8,9].

The mathematical relation between the rates of change of $n_B = n(p, T, x_B)x_B$ and of x_B is

$$\frac{\partial n_B}{\partial t} = \left[n + x_B \left(\frac{\partial n}{\partial x_B} \right)_{p, T} \right] \left(\frac{\partial x_B}{\partial t} \right). \quad (23)$$

Furthermore, the vanishing of the mass transport velocity yields the advective derivative

$$\frac{Dx_B}{Dt} = \frac{\partial x_B}{\partial t} + \left(1 - \frac{m_B}{m_A} \right) x_B \mathbf{u}_B \cdot \nabla x_B. \quad (24)$$

It is found after some algebra that the evolutions (13) of n_B and (15) of x_B are compatible provided that

$$\frac{\partial}{\partial t} (m_A n_A + m_B n_B) = 0. \quad (25)$$

This is just the local conservation of mass (20) as we have considered that $\mathbf{v} = 0$ after the typical transient time L^2/v of mechanical equilibration.

4.2. Relation between thermophoretic velocity and thermodiffusion coefficient

The first step in the phenomenology of thermodiffusion was to write an equation of evolution (15) of the mixture composition involving an interdiffusion current. The second step is to assume that the latter current responds to the local departures from thermodynamic equilibrium in a linear fashion. Since the independent intensive thermodynamic state variables are p , T and x_B , and the experiment is performed under uniform pressure (in case of horizontal transport), those departures are ∇x_B and ∇T . The linear response to those departures is written as [26,30]

$$\mathbf{J}_B = -n(D_{BA} \nabla x_B + D_{T,BA} x_A x_B \nabla T), \quad (26)$$

where D_{BA} is called the mutual diffusivity and $D_{T,BA}$ the thermodiffusion coefficient. Other, equivalent definitions of linear-response coefficients exist but they are not of interest to our concern.

Section 4.1 has related \mathbf{J}_B to the unary current density \mathbf{j}_B in the laboratory frame where the container is at rest. Writing \mathbf{j}_B as $\mathbf{v}_d n_B - \nabla(Dn_B)$ and expressing it as a linear combination of ∇x_B and ∇T , we have to equate the coefficients of the latter two gradients on both sides of relation (22). The calculation is elementary but somewhat lengthy. It involves

$$\nabla D = \frac{\partial D}{\partial T} \nabla T + \left(\frac{\partial D}{\partial x_B} \right) \nabla x_B, \quad (27)$$

$$\nabla n = n\beta \nabla T + \left(\frac{\partial n}{\partial x_B} \right) \nabla x_B, \quad (28)$$

where $\beta = (\partial \ln n / \partial T)_{p, x_B}$ denotes the coefficient of thermal expansion of the liquid mixture. The outcome of the calculation is

$$D_{BA} = D \left[1 + x_B \left(\frac{\partial \ln(nD)}{\partial x_B} \right) \right] \left[x_A + \left(\frac{m_B}{m_A} \right) x_B \right], \quad (29)$$

$$-x_A D_{T,BA} \nabla T = \left[\mathbf{v}_d - \left(\frac{\partial D}{\partial T} + \beta D \right) \nabla T \right] \left[x_A + \left(\frac{m_B}{m_A} \right) x_B \right]. \quad (30)$$

In most cases, one is interested in guest particles B dilute in a host medium of molecules A, so that x_B is close to zero. To the lowest order in x_B , the previous relations simplify to

$$D \approx D_{BA}, \quad (31)$$

$$\mathbf{v}_d \approx \left(-D_{T,BA} + \frac{\partial D}{\partial T} + \beta D \right) \nabla T. \quad (32)$$

In (31) we have regained a known result of the literature on isothermal diffusion [1–3,22]: the unary diffusivity D is approximately equal to the binary (mutual) diffusivity D_{BA} . In contrast, the thermophoretic velocity (32) is *not* proportional to the thermodiffusion coefficient $D_{T,BA}$. As was shown earlier [11], the main departure from proportionality stems from the dependence of the diffusivity $D \approx D_{BA}$ on temperature.

5. Conclusions

The purpose of this paper was to establish a connection between thermophoresis (the motion of a suspended particle under a temperature gradient) and thermodiffusion (the partial demixtion of a binary mixture under a temperature gradient). The phenomenology of thermodiffusion involves an interdiffusion current which is Galilean invariant whereas the phenomenology of thermophoresis involves a velocity which depends on the choice of a reference frame. Connecting the two phenomenologies demands the specification of a frame. We have shown that the apparently natural frame, namely the suspending liquid, is not at rest with respect to the laboratory frame as soon as suspended particles move and, more importantly, the suspending liquid may not be considered as a Galilean reference frame because it is not rigid.

We have examined the time scales underlying the measurement of the thermophoretic velocity. The temperature and pressure gradients may be regarded as static during thermophoresis; the latter gradient should vanish, otherwise its contribution has to be subtracted from the measured velocity. In the thermodiffusion viewpoint, the composition gradient evolves over a 'chemical equilibration' time scale much longer than the thermal and mechanical equilibration time scales. Because the latter equilibration entails a (horizontally) uniform pressure, the mass transport velocity of the mixture approximately vanishes everywhere in the container's frame with a relative error D_{BA}/v . That equilibration provides a

link between the transport velocities of A and B in that frame, which in turn connects the unary quantities (\mathbf{v}_d , D) used in thermophoresis with the binary quantities ($D_{T,BA}$, D_{BA}) used in thermodiffusion. The ladder of time scales for mechanical, thermal and 'chemical' equilibrations is specific to the liquid state; it does not arise in the gaseous state where v , Δ and D_{BA} have similar orders of magnitude. Thereby, besides providing a more rigorous derivation than our previous work [11], the present paper has generalised the connection between \mathbf{v}_d and $D_{T,BA}$ to arbitrary particle fractions.

Appendix

This appendix examines the behaviour of pressure in a constant-volume experiment [6]. First, we acknowledge the existence of a relation of state of the mixture (or suspension) between the volume per particle or its inverse, pressure p , temperature T and composition. Taking quantities per unit mass, instead of per particle, that relation takes the form

$$\rho = \rho(p, T, \omega_B), \quad (\text{A.1})$$

where ρ is the mass density and $\omega_B = m_B x_B / (m_A x_A + m_B x_B)$ is the mass fraction of B. Relation (A.1) states that the specific volume $1/\rho$ is a dependent state variable if p , T and ω_B are taken as the independent intensive state variables. That equilibrium relation holds to a good approximation when variations occur slowly so that no dynamical equation is needed.

Secondly, the conservation of mass in a rigid box of horizontal length L and lateral area A is expressed by

$$\frac{d}{dt} \left[\int_0^L \rho(p(t), T(\xi), \omega_B(\xi, t)) A d\xi \right] = 0. \quad (\text{A.2})$$

For ease of reasoning, we have considered that transport occurs horizontally, along ξ varying between 0 and L , instead of vertically, in the presence of a time-independent temperature field $T(\xi)$. The composition ω_B varies with time t over the time scale L^2/D_{BA} . As argued in section 4.1, the horizontal pressure gradient $\partial p/\partial \xi$ vanishes very quickly over the time scale L^2/v as the momentum diffusivity v is much larger than the particle mutual diffusivity D_{BA} . That is why the position dependence of p is ignored. In (A.2) the time dependence of p compensates for that of ω_B so that the total mass keeps constant.

Once the mass transport velocity \mathbf{v} has vanished after the fast transient of mechanical equilibration, (A.2) is replaced by (20),

$$\frac{\partial}{\partial t} \rho(p(t), T(\xi), \omega_B(\xi, t)) \approx 0. \quad (\text{A.3})$$

Equation (A.3) is inaccurate by a term of relative order D_{BA}/v . It can be rewritten as

$$\left(\frac{\partial \rho}{\partial p} \right) \frac{dp}{dt} + \left(\frac{\partial \rho}{\partial \omega_B} \right) \frac{\partial \omega_B}{\partial t} = 0. \quad (\text{A.4})$$

The mass fraction evolves according to an equation similar to (15), namely

$$\rho \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \omega_B + \text{div}(\omega_A \mathbf{j}_B - \omega_B \mathbf{j}_A) = 0, \quad (\text{A.5})$$

where the argument of the divergence operator is the mass interdiffusion current density. Since $\mathbf{v} = 0$ owing to local mechanical equilibration, from (A.4) and (A.5) we get

$$\frac{dp}{dt} = \frac{1}{\rho} \frac{(\partial \rho / \partial \omega_B)}{(\partial \rho / \partial p)} \text{div}(\omega_A \mathbf{j}_B - \omega_B \mathbf{j}_A). \quad (\text{A.6})$$

In the framework of linear response [26,30], $\omega_A \mathbf{j}_B - \omega_B \mathbf{j}_A$ is a linear combination of $\nabla \omega_B$ and ∇T on the same pattern as equation (26). Consequently $\text{div}(\omega_A \mathbf{j}_B - \omega_B \mathbf{j}_A)$ is of *second order* in the gradients (it contains second-order spatial derivatives and products of first-order derivatives). The time variation of pressure accompanying the transport of particles is thus negligible in the linear-response framework. The latter may be used only for weak composition gradients, i.e. a nearly homogeneous liquid. As a counter-example, the mixing of pure water with pure ethanol gives rise to a noticeable contraction of volume under constant pressure (up to 3.5 % under standard conditions) or equivalently a change in pressure under constant volume. In case of very large $\nabla \omega_A$ and $\nabla \omega_B$ such as occurs at the border between pure A and pure B, a linear-response ('small-signal') analysis is not appropriate [31].

References

- [1] A. Einstein, Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen, *Ann. Phys. (Leipzig)* **322** (1905) p. 549.
- [2] M. Smoluchowski, Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen, *Ann. Phys. (Leipzig)* **326** (1906) p. 756.
- [3] J. Perrin, *La Structure discontinue de la matière*, P. A. Norstedt & Söner, Stockholm, 1927; English translation in *Nobel Lectures in Physics 1922-1941*, World Scientific, Singapore, 1998.
- [4] G. K. Batchelor, Brownian diffusion of particles with hydrodynamic interaction, *J. Fluid Mech.* **74** (1976) p. 1.
- [5] E. Bringuier, From mechanical motion to Brownian motion, thermodynamics and particle transport theory, *Eur. J. Phys.* **29** (2008) p. 1243; corrigendum **30** (2009) p. 435.
- [6] G. S. McNab and A. Meisen, Thermophoresis in liquids, *J. Coll. Interf. Sci.* **44** (1973) p. 339.
- [7] A. Regazzetti, M. Hoyos and M. Martin, Experimental evidence of thermophoresis of non-Brownian particles in pure liquids and estimation of their thermophoretic velocity, *J. Phys. Chem. B* **108** (2004) p. 15285.

- 1
2
3
4 [8] S. Chapman and F. W. Dootson, A note on thermal diffusion, *Phil. Mag.* **33** (1917) p. 248.
5 [9] E. A. Mason, R. J. Munn and F. J. Smith, Thermal diffusion in gases, *Advances in Atomic*
6 *and Molecular Physics*, Vol. 2, D. R. Bates and I. Estermann, eds., Academic Press, New
7 York, 1966, pp. 33-91.
8
9 [10] S. Wiegand, Thermal diffusion in liquid mixtures and polymer solutions, *J. Phys.:*
10 *Condens. Matter* **16** (2004) p. R357.
11
12 [11] E. Bringuier, On the notion of thermophoretic velocity, *Phil. Mag.* **87** (2007) p. 873.
13 [12] P. Beckmann, *Elements of Applied Probability Theory*, Harcourt, Brace & World, New
14 York, 1968, chapter 3.
15
16 [13] J. Mathews and R. L. Walker, *Mathematical Methods of Physics*, 2nd ed.,
17 Benjamin/Cummings, Menlo Park, CA, 1970, section 14-5.
18 [14] A. M. Weinberg and E. P. Wigner, *The Physical Theory of Neutron Chain Reactors*, The
19 University of Chicago Press, Chicago, IL, 1958, chapter IX.
20
21 [15] E. Bringuier, The current equation in strong electric fields, *Phil. Mag. B* **79** (1999) p.
22 1659.
23
24 [16] G. Ryskin, Simple procedure for correcting equations of evolution: Application to
25 Markov processes, *Phys. Rev. E* **56** (1997) p. 5123.
26
27 [17] J. Marcinkiewicz, Sur une propriété de la loi de Gauß, *Math. Z.* **44** (1939) p. 612.
28
29 [18] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, 2nd ed., North-
30 Holland, Amsterdam, 1992, pp. 279-282.
31
32 [19] E. Bringuier, Kinetic theory of inhomogeneous diffusion, *Physica A* **388** (2009) p. 2588.
33
34 [20] P. Lançon, G. Batrouni, L. Lobry and N. Ostrowsky, Drift without flux: Brownian walker
35 with a space-dependent diffusion coefficient, *Europhys. Lett.* **54** (2001) p. 28.
36
37 [21] J. Bławdziewicz and S. Bhattacharya, Comment on 'Drift without flux: Brownian
38 walker with a space-dependent diffusion coefficient', *Europhys. Lett.* **63** (2003) p. 789.
39
40 [22] E. Bringuier, Anatomy of particle diffusion, *Eur. J. Phys.* **50** (2009) p. 1447.
41
42 [23] S. Kjelstrup, D. Bedeaux, I. Inzoli and J.-M. Simon, Criteria for validity of
43 thermodynamic equations from non-equilibrium molecular dynamics simulations, *Energy* **33**
44 (2008) p. 1185.
45
46 [24] G. K. Batchelor, *An Introduction to Fluid Dynamics*, Cambridge University Press,
47 Cambridge, 1967, pp. 74 and 147, 36-37 and 175.
48
49 [25] M. T. Tyn and W. F. Calus, Temperature and concentration dependence of some binary
50 liquid systems, *J. Chem. Eng. Data* **20** (1975) p. 310.
51
52 [26] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland,
53 Amsterdam, 1962, pp. 30-31 and 43-44.
54
55 [27] G. H. Wannier, *Statistical Physics*, Wiley, New York, 1966, p. 396.
56
57 [28] W. M. Deen, *Analysis of Transport Phenomena*, Oxford University Press, New York,
58 1998, pp. 13 and 18.
59
60

1
2
3
4 [29] R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport phenomena*, 2nd ed., Wiley,
5 New York, 2002, p. 516.

6
7 [30] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, Pergamon Press, Oxford, 1959
8 (original Russian edition, Mir, Moscow, 1954), chapter 6.

9
10 [31] J. G. Kirkwood, R. L. Baldwin, P. J. Dunlop, L. J. Gosting and G. Kegeles, Flow
11 equations and frames of reference for isothermal diffusion in liquids, *J. Chem. Phys.* **33**
12 (1960) p. 1505.
13
14
15
16
17
18
19
20
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