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Abstract

The paper analyses particle diffusion from a thermodynamic standpoint. The
main goal of the paper is to highlight the conceptual connection between particle
diffusion, which belongs to non-equilibrium statistical physics, and mechanics,
which deals with particle motion, at the level of third-year university courses.
We start out from the fact that, near equilibrium, particle transport should occur
down the gradient of the chemical potential. This yields Fick's law with two
additional advantages. First, splitting the chemical potential into 'mechanical'
and 'chemical' contributions shows how transport and mechanics are linked
through the diffusivity–mobility relationship. Second, splitting the chemical
potential into entropic and energetic contributions discloses the respective roles
of entropy maximization and energy minimization in driving diffusion. The
paper addresses first unary diffusion, where there is only one mobile species
in an immobile medium, and next turns to binary diffusion, where two species
are mobile with respect to each other in a fluid medium. The interrelationship
between unary and binary diffusivities is brought out and it is shown how
binary diffusion reduces to unary diffusion in the limit of high dilution of
one species amidst the other one. Self- and mutual diffusion are considered
and contrasted within the thermodynamic framework; self-diffusion is a time-
dependent manifestation of the Gibbs paradox of mixing.

(Some figures in this article are in colour only in the electronic version)

1. Motivation

Diffusion of particles is taught both in physics and chemistry courses, and the subject-matter
has roots in biology if we think of Adolf Fick or Robert Brown. For the teacher, the matter
is challenging in that diffusion somehow looks like particle motion in mechanics, but the
statistical nature of diffusion does not allow an understanding in mechanical (deterministic)
terms. Because statistical physics, at the atomic–molecular level, is the counterpart of
thermodynamics at the macroscopic level, thermodynamics is expected to be involved in

understanding diffusion. Another reason why thermodynamics should be relevant is that diffusion is observed at a given temperature imposed by some thermostat and often shows a dependence on temperature. But equilibrium thermodynamics is not sufficient as diffusion is the upshot of a departure from equilibrium, even when diffusion occurs in a steady state. Thus, diffusion is not only a subject-matter of concern to physics and chemistry, including engineering applications, but it is also at the crossroads of several areas of physics.

At the graduate level of researchers, diffusion continues to be a challenging matter. It is striking that in 1995 the *Journal of Membrane Science* republished a set of pioneering papers by Graham [1], Fick [2] and others. The launching of the journal *Diffusion Fundamentals* in 2005 reveals that even among researchers there is a need to question and revisit the basics of particle diffusion [3]. In view of this, it is appropriate to throw light upon the basics at the undergraduate level. This is the goal of the present paper, which is concerned with establishing ties between diffusion and the usual background expected from sophomores in mechanics and thermodynamics. In a previous paper [4], we had followed a pathway leading from the notion of motion (in mechanics) to that of particle transport (in statistical physics), with thermodynamics lying in between. In this one, we shall specifically develop the thermodynamic foundations of diffusion.

The phenomenology of particle diffusion in a gaseous, liquid or solid medium involves the particle-current density $\mathbf{j}(\mathbf{r}, t)$ (in $\text{m}^{-2} \text{ s}^{-1}$ in SI units) such that $\mathbf{j} \cdot \mathbf{dA}$ is the number of particles crossing, per unit time, the oriented surface $\mathbf{dA}$ at location $\mathbf{r}$ and at time t. A straightforward mathematical consequence of that definition of $\mathbf{j}$ is the so-called equation of continuity giving the evolution of the particle number density $n(\mathbf{r}, t)$ (in m^{-3}),

$$\frac{\partial n}{\partial t} + \text{div}\,\mathbf{j} = 0, \tag{1.1}$$

which expresses the local conservation of particles. The phenomenological law of diffusion, first enunciated as a local law by Fick [2], relates $\mathbf{j}(\mathbf{r}, t)$ to the particle density in the neighbourhood of $\mathbf{r}$ at the same time t:

$$\mathbf{j} = -D\nabla n. \tag{1.2}$$

In that law, D (in $\text{m}^2 \text{ s}^{-1}$) is the particle diffusivity, or diffusion constant as it is taken to be independent of n, $\mathbf{r}$ and t in elementary accounts, and ∇ denotes the gradient $\partial/\partial\mathbf{r}$. Particles travel, on average, from places of higher density to places of lower density; equilibrium is reached ($\mathbf{j} = 0$) when density has become uniform. The equilibrium state being that of maximum uniformity, the student is usually told that the final state maximizes entropy under the existing constraints. In the parlance of statistical physics [5], it is the most likely macrostate, i.e. the one having the largest statistical multiplicity (the largest number of microstates). This link-up between diffusion and thermodynamics (entropy maximization) or statistical physics (microstate counting) looks satisfactory to most sophomores.

In this paper, we shall show that the link is made too hastily and that much more can be said while staying at the level of undergraduate thermodynamics. To this end, we shall first distinguish unary and binary diffusions. In the former phenomenon, there is only one mobile species in an immobile medium; this makes the phenomenon easier to conceptualize to newcomers. Only after unary diffusion is understood in section 2 do we deal in section 3 with binary diffusion, where two species move with respect to each other. In section 4, the concepts devised in section 3 are specialized to the two kinds of binary diffusion, namely self- and mutual diffusions. Section 5 concludes the paper by pointing to the historical deconstruction taken in our approach.

The required prior knowledge is the equilibrium thermodynamics of a single-component substance in section 2. In that section, statistical–thermodynamic expressions

of thermodynamic quantities usually taught during the third university year have been used because their physical meaning is more apparent than in classical thermodynamics. Yet we do not aim at a microscopic expression of diffusivity although the notion of a mean free path is mentioned once. Sections 3 and 4 dealing with binary diffusion make use of the equilibrium thermodynamics of a two-component fluid[1]. Because the thermodynamic features specific to a two-component fluid are not known to all third-year university students, they will be sketched in section 3.1 for the sake of self-containedness. Readers already familiar with those features are invited to skip section 3.1 and directly go to section 3.2.

2. Unary diffusion

2.1. From equilibrium thermodynamics to Fick's law

In unary diffusion, one considers that mobile particles move in a background medium which scatters the particles but is not affected by their passage. A good example of unary diffusion is provided by neutron diffusion in a solid material where absorption and generation of neutrons can be neglected [7]. Another example is the transport of electrons in a metallic or semiconducting solid, in the absence of a macroscopic electric field [8]. The aim of this subsection is to recover Fick's law (1.2) in such examples by means of a reasoning based upon notions of mechanics and thermodynamics known to third-year university students. Of course, we do not purport to demonstrate that law (which is rooted in experiments) from mechanics and thermodynamics; rather, we want to point out the connections between the physics already understood by the students and the new realm opened by Fick's law, namely non-equilibrium statistical physics.

Out of equilibrium, thermodynamics tells us [9] that, at fixed temperature T and pressure p or volume V, transfer of particles occurs between subsystems having different chemical potentials, so as to minimize the Gibbs energy (free enthalpy) of the whole system under fixed T and p, or to minimize the (Helmholtz) free energy of the whole system under fixed T and V. The latter formulation is suited to a solid medium where V is invariable and no energy can be exchanged in the form of work against pressure forces. This is why that formulation is used in the present section whereas section 3 will consider a fluid medium of which volume V can vary under fixed T and p, allowing energy to be exchanged in the form of work against pressure forces. Denoting by $\tilde{\mu}$ the chemical potential per particle[2] (instead of per mole), transfer occurs to the subsystem of lower $\tilde{\mu}$ so as to minimize the free energy of the whole system. Where $\tilde{\mu}$ is a smooth function of position, the current density is expected to be caused by the local value of the gradient $\nabla\tilde{\mu}$. More specifically, $\mathbf{j}$ is expected to be directed along, and proportional to, $-\nabla\tilde{\mu}$, in the limit of a weak gradient associated with a small departure from equilibrium. Such a proportional relationship is called the linear response to the disequilibrium. Besides, the current is expected to be proportional to the density of particles available locally. Therefore, it is expected that

$$\mathbf{j} = \mu n(-\nabla\tilde{\mu}),\tag{2.1}$$

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[1] We are speaking about a fluid medium for definiteness, but much of the description in sections 3 and 4 is also suited to diffusion in a solid medium. For specific aspects of solid-state diffusion at the undergraduate level, see Philibert's book [6].
[2] This notation is used for consistency with [4].

where the coefficient μ is positive. We note that the chemical potential $\tilde{\mu}$ of the assembly of particles is a function of the independent intensive variables T and n defining the macrostate of the assembly. Since T is held fixed, from (2.1) we recover Fick's law (1.2) by letting

$$D = \mu n \left(\frac{\partial \tilde{\mu}}{\partial n} \right)_T . \tag{2.2}$$

For the experimentalist, Fick's form (1.2) is obviously better than (2.1) as the former involves the directly measurable parameter n (Fick [2] related n to the local mass density of the solution), while (2.1) involves thermodynamical knowledge. But the coefficient μ in (2.1) has a simple mechanical meaning that will be commented on in section 2.2.

To illustrate expression (2.2), the simplest example is that of non-interacting classical point particles, such that [10–12]

$$\tilde{\mu}(T, n) = kT \ln \left(n \lambda_{dB}^3 \right), \tag{2.3}$$

where $\lambda_{dB} = \hbar (2\pi / mkT)^{1/2}$ is the thermal de Broglie wavelength, $\hbar$ is the reduced Planck constant and m is the mass of the particles (taken to be without spin). In classical, rather than statistical, thermodynamics, the chemical potential is written as $\tilde{\mu}^0(T) + kT \ln n$. The link with (2.3) is $\tilde{\mu}^0(T) = kT \ln \lambda_{dB}^3$. Putting (2.3) into relation (2.2), we get

$$D = kT\mu. \tag{2.4}$$

Relation (2.4) was theoretically obtained by Maxwell[3] in a mixture of gases [13], by Nernst for ions in an aqueous solution [14], by Townsend for ions in a gas [15] and later used by Einstein in his theory of Brownian motion [16]. It holds for electrons in semiconductors [17].

Consider now non-interacting fermions modelling conduction electrons in a metal at room temperature. Their chemical potential is given by [10, 18]

$$\tilde{\mu}(T, n) = E_F(n) \left(1 - \frac{\pi^2}{12} \left[\frac{kT}{E_F(n)} \right]^2 \right) \tag{2.5}$$

where $E_F(n) = \hbar^2 (3\pi^2 n)^{2/3} / 2m^*$ is the zero-temperature Fermi energy reckoned from the bottom of the conduction band. For simplicity[4] we have taken particles characterized by an effective mass m^*. Expression (2.5) holds in the so-called degeneracy limit where the occupancy of the low-lying quantum states is close to unity and the Pauli exclusion effect changes the Maxwell–Boltzmann into the Fermi–Dirac occupancy. In that limit, $E_F(n)$ is much larger than the room-temperature thermal energy kT (in Cu, $E_F(n) \approx 7$ eV $\gg kT \approx 2.5 \times 10^{-2}$ eV). To the lowest order in $kT/E_F(n)$, expression (2.2) of the diffusivity reads

$$D = \tfrac{2}{3} E_F(n)\mu, \tag{2.6}$$

in stark contrast with Nernst's relation (2.4).

We are now in a position to examine the frequent, but loose, statement that diffusion tends to maximize entropy. The chemical potential $\tilde{\mu}$ may be split up into energetic (h) and entropic ($-Ts$) contributions,

$$\tilde{\mu} = h - Ts, \tag{2.7}$$

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[3] Maxwell (Stefan) introduced a 'coefficient of resistance' ('Widerstandscoëfficient') instead of the mobility μ, and similarly Nernst's discussion was cast in terms of a friction force.

[4] A calculation of $\tilde{\mu}$ going beyond that approximation can be found in [10, 18, 19]. Because the effective-mass approximation is poor for metallic conduction electrons, we may only say that $D \approx E_F(n)\mu$.

which are written down further. Minimizing $\tilde{\mu}$ can be achieved both by maximizing s (corresponding to a more likely macrostate) and by minimizing h (corresponding to a state of lower energy). The latter tendency generalizes the mechanical propensity to minimizing energy, as can be seen by introducing an external potential energy $U(\mathbf{r})$. For, then, $\tilde{\mu}$ is replaced by $\tilde{\mu} + U$ [9, 10, 12, 20], $h \to h + U$ (see appendix A) and the minimization of $h + U$ is the thermodynamical generalization of the mechanical principle of minimization of U. In (2.1), the current density $\mathbf{j}$ is driven by

$$-\nabla\tilde{\mu} = -\nabla h + T\nabla s, \tag{2.8}$$

which is the sum of a 'mechanical force' (or 'energetic force') $-\nabla h$ and of an 'entropic force' $T\nabla s$. Which force prevails depends on the temperature: if low temperatures can be reached, the system will look more mechanical as the entropic contribution can be neglected together with thermal agitation.

For non-interacting classical point particles, $\tilde{\mu}$ is given by (2.3) and it is shown in appendix A that

$$h = \tfrac{5}{2}kT \qquad \text{and} \qquad s = k\left[\tfrac{5}{2} - \ln\left(n\lambda_{dB}^3\right)\right]. \tag{2.9}$$

There is no driving force associated with h and diffusion is entirely driven by the entropic force $T\nabla s = -kT\nabla n/n$. It is because most elementary presentations consider classical non-interacting particles that we are used to viewing diffusion as an entropic trend.

For non-interacting fermions in the degeneracy limit, $\tilde{\mu}$ is given by (2.5) and it is shown in appendix A that

$$h = E_F(n) + \frac{5\pi^2(kT)^2}{12\,E_F(n)} \qquad \text{and} \qquad Ts = \frac{\pi^2(kT)^2}{2\,E_F(n)}. \tag{2.10}$$

To the lowest order in $kT/E_F(n)$, the driving force associated with h is $-(\mathrm{d}E_F/\mathrm{d}n)\nabla n$ while the entropic force is $-(\pi kT/E_F)^2(\mathrm{d}E_F/\mathrm{d}n)\nabla n$. Therefore,

$$T\nabla s = \pi^2\frac{kT}{E_F(n)}(-\nabla h). \tag{2.11}$$

In the degeneracy limit, the entropic contribution to $-\nabla\tilde{\mu}$ is negligible compared to the energetic contribution. Diffusion of degenerate fermions is essentially driven by the latter contribution $-\nabla h$, where $h \propto n^{2/3}$ is an increasing function of density n. Conduction electrons in a metal diffuse to places of lower density in order to minimize energy, with maximization of entropy playing only a negligible role. The fact that degenerate fermions are an essentially mechanical system[5] stems from the weak temperature dependence of the free energy which entails $s \approx 0$, so that $\tilde{\mu} \approx h$.

2.2. Fick's law and dynamics

Let us attempt a mechanical anatomy of Fick's law by relating the current density $\mathbf{j}(\mathbf{r}, t)$ to the average particle velocity $\mathbf{u}(\mathbf{r}, t)$ through

$$\mathbf{j} = n\mathbf{u}. \tag{2.12}$$

[5] This is consistent with the earlier statement that the system becomes more mechanical as thermal agitation becomes negligible. At room temperature the agitation of metallic conduction electrons is essentially quantal, not thermal, as it is due to the indeterminacy and exclusion principles. We briefly sketch the argument in the case of free particles. As each fermion is allocated a volume $\Delta x^3 = 1/n$ by the exclusion principle (omitting the spin-degeneracy factor), the standard deviation in momentum is $\Delta p \approx \hbar n^{1/3}$ according to the indeterminacy principle. Ehrenfest's relation $\langle p\rangle/m = \mathrm{d}\langle x\rangle/\mathrm{d}t$ and the steady localization of each fermion in the volume Δx^3 entail $\langle p\rangle = 0$, whence $\langle p^2\rangle = \Delta p^2 \approx \hbar^2 n^{2/3}$ and thus $\langle p^2\rangle/2m \approx \hbar^2 n^{2/3}/2m \approx E_F(n)$. Q.E.D. The condition $E_F(n) \gg kT$ is alternatively written $n\lambda_{dB}^3 \gg 1$, which is just the condition of degeneracy of the fermion gas.

From the definition of $\mathbf{j}$ in section 1, $\mathbf{u}(\mathbf{r}, t)$ is the ensemble average of the individual velocities, at a given time t, of the particles contained in a macroscopically small, but microscopically large, volume element located at position $\mathbf{r}$. We shall call $\mathbf{u}$ the transport velocity. Expressed with $\mathbf{u}$, the diffusion law (2.1) becomes

$$\mathbf{u} = \mu(-\nabla\tilde{\mu}). \tag{2.13}$$

In (2.13), $-\nabla\tilde{\mu}$ appears as a force undergone by the average mobile particle and driving it towards places of lower chemical potential, and μ has the meaning of a mechanical mobility. That meaning is best seen when the particles are acted upon by an external conservative force $\mathbf{F} = -\nabla U$ such as gravity. Then, we know from thermodynamics [9, 10, 12, 20] that $\tilde{\mu}$ should include the external potential energy $U(\mathbf{r})$ in addition to $\tilde{\mu}_c$, the chemical potential in the absence of $\mathbf{F}$ (called by Gibbs intrinsic potential of the substance, here the assembly of mobile particles). The ensuing expression of the transport velocity,

$$\mathbf{u} = \mu(-\nabla U - \nabla\tilde{\mu}_c), \tag{2.14}$$

shows that μ^{-1} is the coefficient of friction due to the motion, at a steady velocity $\mathbf{u}$, in the material medium.

The friction is modelled here as a linear one, but it is not always so. This can be seen from the example of conduction electrons in a semiconducting medium. When a conduction electron is subjected to the force $-\nabla U$ due to the potential energy U of an external electric field, the response $\mathbf{u}$ to the force is linear in the so-called Ohmic range of fields, i.e. less than about 10^5 V m^{-1} in Ge [21] and Si. In higher fields, departure from Ohm's local law is observed and accounted for [21–23]. We can estimate the range of applicability of the linear response (2.14) by writing $|\nabla\tilde{\mu}_c|$ as kT/L, where kT is the typical electron energy and $L = |\nabla n/n|^{-1}$ is the characteristic length over which $\tilde{\mu}_c$ varies with n, see (2.3). Taking 10^5 eV m^{-1} as the upper limit of kT/L in Ge or Si requires $L > 250$ nm at 300 K. That condition is often satisfied in practice. In this paper, we assume linearity of the response throughout.

The mechanically minded student will think that the response to a force is not a velocity, but an acceleration, and so will tend to write

$$m\dot{\mathbf{u}} = \mathbf{F} - \mu^{-1}\mathbf{u}, \tag{2.15}$$

where m is the particle's mass. Let us introduce the typical variation time T such that $\dot{\mathbf{u}} \approx \mathbf{u}/T$. Then, $\mathbf{u} \approx \mu\mathbf{F}(1 + \mu m/T)$ reduces to $\mu\mathbf{F}$ if T largely exceeds the characteristic time scale μm. In other words, (2.13) is valid in a quasi-steady regime excluding high-frequency variations of $\mathbf{u}$ or $\mathbf{F}$. In the high-frequency regime $\omega \gg 1/\mu m$, the steady response (2.13) is unlikely to hold. Consider first Na$^+$ in water as an illustrative example. Using an electric force to drive Na$^+$, its mechanical mobility at a high dilution in water is measured to be $\mu = 3.24 \times 10^{11}$ s kg^{-1} under standard conditions [24]. As the time $\mu m \approx 10^{-14}$ s is very short, from (2.15) the steady regime is expected to hold up to high frequencies. Consider now neutron diffusion. It is known [7] that Fick's law is not accurate when the neutrons scatter infrequently with the medium. Spatially speaking, a low scattering frequency is associated with a long neutron mean free path. Fick's law is no longer accurate on spatial scales smaller than or equal to the mean free path [7]. The latter can exceed 1 cm in the case of neutrons. A long mean free path (>1 cm) or a low scattering frequency ($<10^5$ s^{-1}) is tantamount to a low friction.

In the parlance of mechanics, the motion has to be overdamped in order for Fick's law to be accurate[6].

While $-\nabla\tilde{\mu}$ expresses the departure from equilibrium, mobility expresses the rate at which equilibrium tends to be restored by the transport of matter along $-\nabla\tilde{\mu}$. For the teacher, the law (2.13) provides an opportunity of pointing out the distinction between equilibrium and kinetic parameters. Relation (2.2) shows that diffusivity depends both on a kinetic parameter (mobility, i.e. the time rate of response to a force) and on an equilibrium parameter (the characteristic energy $n(\partial\tilde{\mu}/\partial n)_T$). To check the kinetic nature of μ, consider again Na$^+$ in water as an illustrative example. Although Navier–Stokes fluid dynamics is not expected to hold on the atomic scale, $\mu = 3.24 \times 10^{11}$ s kg^{-1} can be equated to $1/6\pi\eta R$, where $\eta = 0.89 \times 10^{-3}$ Pa s is the dynamical viscosity of water under standard conditions, if we take $R = 0.18$ nm as the ion radius. This is not far from the truth, even though the ion radius is an ill-defined parameter. Consider now the temperature dependence of μ. It is measured to be d $\ln\mu/\mathrm{d}T = 0.022$ K^{-1} [24]. Without assigning a definite value to R, that dependence is close to the one expected from the Stokes formula, since d $\ln\eta/\mathrm{d}T = -0.024$ K^{-1} [24]. Thus, owing to the value and temperature dependence of μ, it makes sense to break up D into a kinetic factor μ and an equilibrium factor $n(\partial\tilde{\mu}/\partial n)_T$.

In (2.14), $-\nabla\tilde{\mu}_c$ drives current in the same way as the mechanical force $-\nabla U$. There is one major difference, however. The effect of the mechanical force $-\nabla U$ is to shift the particle distribution $n(\mathbf{r}, t)$ without altering its shape, whereas the properly thermodynamical driving force $-\nabla\tilde{\mu}_c$ smears out the shape. To see it, note that the density response $n(\mathbf{r}, t)$ to the total force is given by the equation of continuity (1.1). That equation of first order in time rules the evolution of $n(\mathbf{r}, t)$ from the initial distribution $n(\mathbf{r}, t = 0)$. Taking for $n(\mathbf{r}, t = 0)$ the sharp distribution $\delta(\mathbf{r} - \mathbf{r}_0)$ and a constant[7] D, the solution at time t in boundless space is the Gaussian function

$$n(\mathbf{r}, t) = (4\pi Dt)^{-3/2} \exp\left(-\frac{[\mathbf{r} - \mathbf{r}_0 - \mu(-\nabla U)t]^2}{4Dt}\right), \tag{2.16}$$

if the force field $-\nabla U$ is uniform. In (2.16), the density $n(\mathbf{r}, t)$ exhibits a typical spatial extension $(2Dt)^{1/2}$ per component, showing that $-\nabla\tilde{\mu}_c$ acts as an indeterministic force (*Zitterkraft*), also called noise [4]. Correspondingly, the transport velocity $\mathbf{u} = \mu(-\nabla U) - (D\nabla n)/n$ is calculated from (2.16) to be

$$\mathbf{u}(\mathbf{r}, t) = \frac{\mathrm{d}\langle\mathbf{r}\rangle}{\mathrm{d}t} + \frac{\mathbf{r} - \langle\mathbf{r}\rangle}{2t}, \tag{2.17}$$

where $\langle\mathbf{r}\rangle$ denotes the average position $\mathbf{r}_0 + \mu(-\nabla U)t$ reached at time t. Thus, $\mathbf{u}$ does not have one single value: the transport velocity is not a velocity in the usual mechanical (deterministic)

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[6] While we shall throughout restrict our attention to slow phenomena, we point out that fast diffusion processes, where Fick's law is no longer sufficient, are an area of lively research [25–27]. It is found that a simple equation such as (2.15) does not hold generally. For example, rather than $\partial\mathbf{u}/\partial t + \mathbf{u}/\mu m = -m^{-1}(\partial\tilde{\mu}/\partial n)\nabla n$, the simple kinetic model of section 2 of [28] arrives at $\partial\mathbf{j}/\partial t + \mathbf{j}/\tau = -(D/\tau)\nabla n$, where τ is the the momentum-relaxation time. More complex models use a range of relaxation times rather than a single value τ. Students may prefer a reasoning in the frequency domain. Then, if $\tilde{\mu}$ only consists of the potential energy U, (2.15) implies $\mu(\omega) = \mu/(1 + i\omega/\omega_0)$, where $\omega_0 = 1/\mu m$. In actual systems, the frequency dependence of $\mu(\omega)$ often involves several characteristic frequencies instead of a single one, namely ω_0. Correspondingly, $D(\omega)$ is not given by the simple first-order low-pass function $D/(1 + i\omega/\omega_0)$. Often the description of transport at high frequencies involves more detail than is contained in the instantaneous gradient $\nabla\tilde{\mu}$ and a closed-form equation such as (2.15) does not hold [27].

[7] For fermions in the degeneracy limit, D depends on density n. A small localized departure $n_1(\mathbf{r}, t = 0) \propto \exp[-(\mathbf{r} - \mathbf{r}_0)^2/2\sigma_0^2]$ from a uniform background $n_0 \gg n_1$ evolves as a Gaussian function with a position variance per component $\sigma^2(t) = \sigma_0^2 + 2D(n_0)t$ at time $t > 0$.

sense [4]. The general relationship between the drift (macroscopic) and transport velocities is [4]

$$\frac{d\langle \mathbf{r} \rangle}{dt} = \frac{\iiint n\mathbf{u} \, d^3\mathbf{r}}{\iiint n \, d^3\mathbf{r}}. \tag{2.18}$$

Before turning to binary diffusion in a fluid medium in section 3, we collect the main points made in this section:

(i) diffusion is pictured as the transport of mobile particles down their chemical potential gradient, with a mobility coefficient relating the transport velocity to the negative gradient (driving force);

(ii) since the chemical potential includes any kind of potential energy reflecting work done in displacing particles, the mobility is an inverse friction coefficient in the mechanical sense;

(iii) deterministic particle motion (in the inertial regime) arises from the explicit position dependence of $\tilde{\mu}$ whereas implicit dependence (through the particle density) smears out that motion;

(iv) breaking up the chemical potential into energetic and entropic contributions shows that diffusion is not necessarily due to entropy maximization.

3. Binary diffusion

3.1. Equilibrium thermodynamics of a binary mixture

From now on, we consider a mixture of two substances A and B. Thermodynamics provides answers to long-puzzling questions [29] about the nature of mixing in the equilibrium state. In short, thermodynamics does not view a binary mixture as a mechanical aggregate, where the molecules of the two substances are situated side by side without loss of individual identity, but rather as a chemical combination, even in the absence of a genuine chemical reaction between the two substances. In the blending of the ingredients, the original properties, such as the volume or the Gibbs energy (free enthalpy), do not just add up [24, 30–32]. The corresponding properties of the mixture, denoted by v and g (per particle), represent an averaging of the properties of the ingredients,

$$v = x_A v_A + x_B v_B, \tag{3.1}$$

$$g = x_A \tilde{\mu}_A + x_B \tilde{\mu}_B, \tag{3.2}$$

where x_A and $x_B = 1 - x_A$ are the particle fractions (or mole fractions), $\tilde{\mu}_A$ and $\tilde{\mu}_B$ are the chemical potentials and $v_A = (\partial \tilde{\mu}_A / \partial p)_{T,x_A}$ and $v_B = (\partial \tilde{\mu}_B / \partial p)_{T,x_B}$ are the partial molecular volumes of A and B respectively. But v_A and v_B in the mixture differ from the molecular volumes $v_A(x_B = 0) = v_A^0$ and $v_B(x_B = 1) = v_B^0$ of pure A and pure B, respectively. Likewise, $\tilde{\mu}_A$ and $\tilde{\mu}_B$ in the mixture differ from the chemical potentials of the pure substances $g(x_B = 0) = \tilde{\mu}_A^0$ and $g(x_B = 1) = \tilde{\mu}_B^0$. Relations (3.1) and (3.2) are shown graphically in figures 1 and 2.

The non-additivity of the molecular volumes of the pure substances v_A^0 and v_B^0 (i.e. the fact that v departs from $x_A v_A^0 + x_B v_B^0$) is a manifestation of the interaction between A and B. More precisely, it is a manifestation of the differential interaction due to the microscopic (chemical) dissimilarity of A and B molecules. Figure 3, after [33, 34], shows the volume change on mixing $v - (x_A v_A^0 + x_B v_B^0)$ in the water–ethanol binary mixture.[8]

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[8] From $v(x_B)$ it is found that v_A and v_B in the water–ethanol mixture are not monotonic functions of x_B [30].
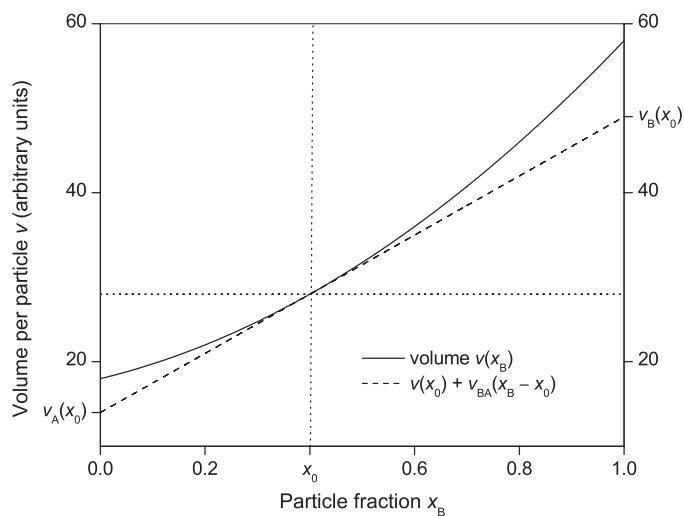
Figure 1. Volume per particle v in a binary mixture A–B as a function of the particle fraction x_B under constant p and T. The tangent to $v(x_B)$ is shown at $x_B = x_0$. It crosses the vertical straight line $x_B = 0$ $(x_B = 1)$ at $v = v_A (v = v_B)$ and has a slope $v_{BA} \equiv v_B - v_A$. The partial volumes per particle in the mixture, v_A and v_B, are functions of x_0 and differ from the volumes per particle in the pure substances $v_A^0 = v(x_B = 0)$ and $v_B^0 = v(x_B = 1)$.
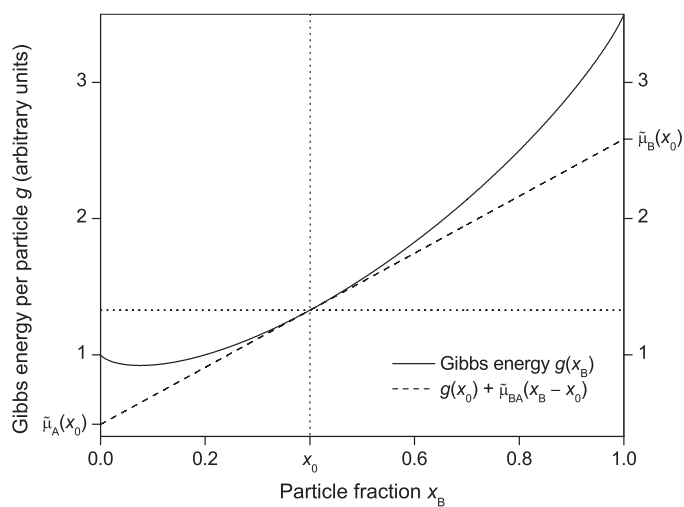

Figure 2. Gibbs energy (free enthalpy) per particle g in a binary mixture A–B as a function of particle fraction x_B under constant p and T. The tangent to $g(x_B)$ is shown at $x_B = x_0$. It crosses the vertical straight line $x_B = 0$ $(x_B = 1)$ at $g = \tilde{\mu}_A$ $(g = \tilde{\mu}_B)$ and has a slope $\tilde{\mu}_{BA} \equiv \tilde{\mu}_B - \tilde{\mu}_A$. The chemical potentials in the mixture, $\tilde{\mu}_A$ and $\tilde{\mu}_B$, are functions of x_0 and differ from the chemical potentials in the pure substances $\tilde{\mu}_A^0 = g(x_B = 0)$ and $\tilde{\mu}_B^0 = g(x_B = 1)$.

Figure 4, after [35, 36], shows the Gibbs-energy change on mixing $g - \left(x_A\tilde{\mu}_A^0 + x_B\tilde{\mu}_B^0\right)$ in the same mixture. It is customary to express that change as the sum of two contributions.
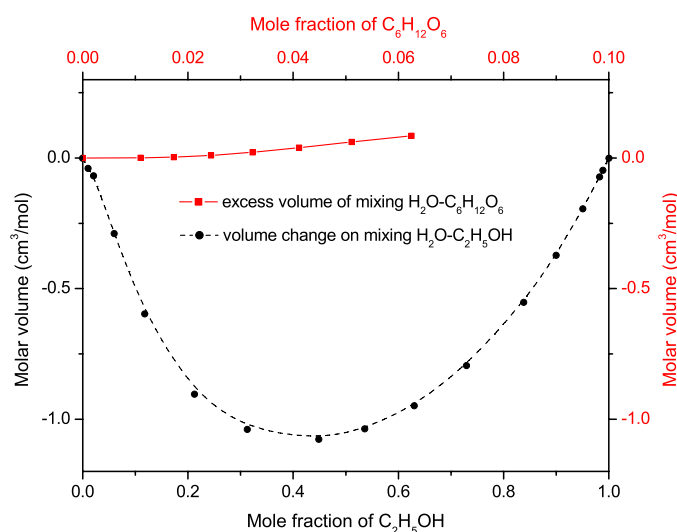
Figure 3. Volume change on mixing $v - (x_A v_A^0 + x_B v_B^0)$ against composition x_B in the water–ethanol binary mixture under standard pressure and temperature conditions ($v_A^0 = 18.07$ cm^3 mol^{-1} and $v_B^0 = 58.37$ cm^3 mol^{-1}), after [33]. For the solution of glucose in water under the same conditions, $v - (x_A v_A^0 + x_B v_B^0)$ is the excess volume of mixing ($v_B^0 = 111.88$ cm^3 mol^{-1}), after [34]. The plot of the glucose solution ends at $x_B = 0.06$. Note the different scale used for the ethanol (on the bottom axis) and the glucose (on the top axis) mole fraction. The volumes shown on this figure are relative to 6.02×10^{23} particles (one mole).

One is independent of the chemical nature of A and B and is called the *ideal* Gibbs-energy of mixing, whereas the other one is the *excess* Gibbs-energy of mixing g^E,

$$g - \left(x_A \tilde{\mu}_A^0 + x_B \tilde{\mu}_B^0\right) = kT(x_A \ln x_A + x_B \ln x_B) + g^E. \tag{3.3}$$

Since Lewis, it is usual in chemical thermodynamics to introduce the activity[9] a_B of B, varying between zero (no B, $x_B = 0$) and unity (pure B, $x_B = 1$), as

$$\tilde{\mu}_B(p, T, x_B) = \tilde{\mu}_B^0(p, T) + kT \ln a_B, \tag{3.4}$$

while $\tilde{\mu}_B^0(p, T)$ is the standard chemical potential of B and does not vary with the composition x_B of the mixture. Activity a_A of A is introduced similarly. Mixing is ideal if $a_{A,B} = x_{A,B}$, in which case $v_{A,B} = v_{A,B}^0$ regardless of x_B. The relative activity γ_B, also termed activity correction, is defined through $a_B = \gamma_B x_B$. Then, from (3.2)–(3.4), the excess Gibbs-energy of mixing is

$$g^E = kT(x_A \ln \gamma_A + x_B \ln \gamma_B). \tag{3.5}$$

The limit $x_B = 1$ (or $a_B = 1$) does not exist under standard conditions if $A = $ H$_2$O and $B = $ C$_6$H$_{12}$O$_6$ (glucose) because pure B is solid. As solid glucose dissolves into water, $\tilde{\mu}_B$ in the liquid phase increases with x_B, starting from infinitely negative values [9, 24]. When $\tilde{\mu}_B$ reaches the value of the chemical potential of B in the solid phase, further dissolution is not possible since it would increase the overall free enthalpy. Then, the solution of glucose in water is saturated and x_B is called the solubility. In a solution of B in A, expression (3.4)

[9] The definitions of the activity and of the standard chemical potential depend on the scale used for defining the composition of the mixture. In this paper, the mole-fraction scale is used throughout because it gives simpler formulae. See [31, 32] for other scales.
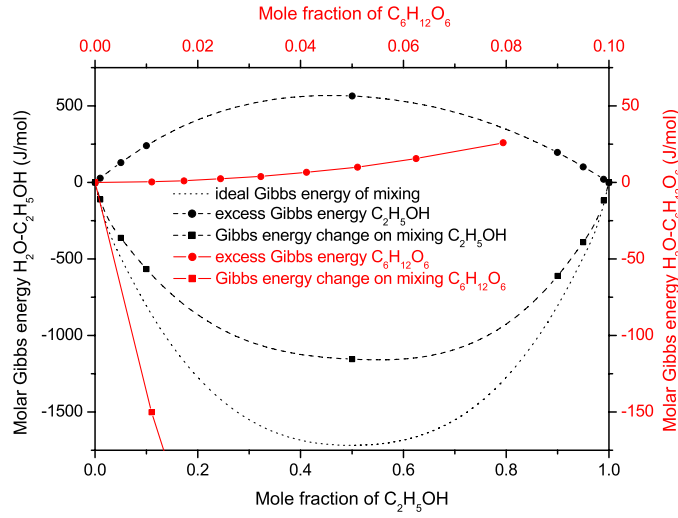
Figure 4. Gibbs-energy change on mixing $g - (x_A \tilde{\mu}_A^0 + x_B \tilde{\mu}_B^0)$ against composition x_B in the water–ethanol binary mixture, under standard pressure and temperature conditions, after [35]. The Gibbs-energy change on mixing has been resolved into its ideal and excess (g^E) contributions. For the solution of glucose in water under the same conditions, g^E has been plotted after [36]. The plot of the glucose solution ends at the glucose solubility $x_B = 0.08$. Note the different scales used for ethanol (on the bottom and left axes) and glucose (on the top and right axes). On this figure, the Gibbs energies are molar (6.02×10^{23} particles) instead of molecular.

is used for the chemical potential of B, but now $\tilde{\mu}_B^0(p, T)$ does not have the meaning of the chemical potential of pure B. In

$$v_B = v_B^0(p, T) + kT \left(\frac{\partial \ln \gamma_B}{\partial p} \right)_{T, x_B}, \tag{3.6}$$

v_B^0 is the molecular volume of B at infinite dilution ($\gamma_B \to 1$ as $x_B \to 0$) and the second term on the right-hand side expresses the composition dependence of v_B. We calculate $v - (x_A v_A^0 + x_B v_B^0) = (\partial g^E/\partial p)_{T, x_B}$, which is sometimes called the excess volume, and plot it in figure 3. Figure 4 shows g^E in the same solution of glucose in water.

The Euler identity [31, 32] for an extensive observable per particle such as v or g relates the variations of the partial observables of both ingredients as the composition x_B of the mixture is varied under fixed p and T. Those relations,

$$0 = x_A \, dv_A + x_B \, dv_B, \tag{3.7}$$

$$0 = x_A \, d\tilde{\mu}_A + x_B \, d\tilde{\mu}_B, \tag{3.8}$$

are named after Gibbs and Duhem. The more often used is the latter one and for that reason is often referred to as 'the' Gibbs–Duhem relation. Application of (3.7) and (3.8) to (3.1) and (3.2) entails $(\partial v/\partial x_B)_{p,T} = v_B - v_A$ and $(\partial g/\partial x_B)_{p,T} = \tilde{\mu}_B - \tilde{\mu}_A$. This is pictured in figures 1 and 2 where the local slopes $v_B - v_A$ and $\tilde{\mu}_B - \tilde{\mu}_A$ are denoted as v_{BA} and $\tilde{\mu}_{BA}$.

Letting $n = 1/v$ (the over-all particle density), $n_A = nx_A$ and $n_B = nx_B$, from (3.1) partial molecular volumes are such that $n_A v_A + n_B v_B = 1$; $n_A v_A$ is called the volume fraction of A and denoted by ϕ_A, and similarly $\phi_B = n_B v_B$. From (3.7) it follows that

$$v_A \, dn_A + v_B \, dn_B = 0 \tag{3.9}$$

under fixed p and T. Relation (3.9) means that an increase in n_A is accompanied by a decrease in n_B according to the ratio v_B/v_A of the partial molecular volumes[10]. The fact that n_A and n_B do not vary independently under fixed p and T stems from the relation of state of the fluid. That relation is usually written $v = v(p, T, x_B)$ and its isobaric isothermal plot is just figure 1, but it can be rewritten as $(n_A + n_B)v(p, T, n_B/(n_A + n_B)) = 1$.

Consider now an inhomogeneous A–B mixture at fixed p and T and assume that thermodynamic relationships hold locally although the inhomogeneity entails a departure from equilibrium. From (3.9) and (3.8), we infer

$$0 = v_A \nabla n_A + v_B \nabla n_B, \tag{3.10}$$

$$0 = x_A \nabla \tilde{\mu}_A + x_B \nabla \tilde{\mu}_B. \tag{3.11}$$

The local-equilibrium approximation that is being used is found to hold in the limit of vanishing gradients.

3.2. From equilibrium thermodynamics to the law of diffusion

Having summed up some basic thermodynamic tools for dealing with a mixture of two substances, we turn to transport of A and B. Instead of considering mobile particles B in a rigid medium of particles A as had been done in section 2, we now consider that both A and B particles can move. The motivation for studying binary, instead of unary, diffusion, is obvious. When sugar (e.g. glucose $C_6H_{12}O_6$) molecules in water (H_2O) diffuse towards sugar-free places, water molecules take the place of sugar molecules which deplete sugar-rich places. Therefore, transport of H_2O has to be considered together with that of $C_6H_{12}O_6$. Thermodynamically speaking, transport of B at fixed p and T changes the density n_B and the particle fraction $x_B = n_B/n$ and therefore modifies the local chemical potential $\tilde{\mu}_B$ of B. We expect a consequent change in the chemical potential $\tilde{\mu}_A$ of A as a result of the Gibbs–Duhem relationship. So there is a driving force $-\nabla \tilde{\mu}_A$ on A together with $-\nabla \tilde{\mu}_B$ acting on B. Mechanically speaking, the Gibbs–Duhem relation (3.11), rewritten as

$$n_A(-\nabla \tilde{\mu}_A) + n_B(-\nabla \tilde{\mu}_B) = 0, \tag{3.12}$$

expresses the force balance per unit volume; it is the thermodynamic extension of Newton's third law. Just as in section 2, we may break up $\tilde{\mu}_A$ into energetic (h_A) and entropic ($-Ts_A$) contributions, and similarly for B. Under a fixed pressure, this is achieved through the second Gibbs–Helmholtz relationship for a mixture [31], namely

$$h_{A,B} = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{\tilde{\mu}_{A,B}}{T} \right) \right]_{p, x_B}. \tag{3.13}$$

The Euler identity yields Gibbs–Duhem relations on the partial molecular enthalpies $h_{A,B}$ and entropies $s_{A,B}$, which in turn entail separate balance of energetic and entropic forces,

$$n_A(-\nabla h_A) + n_B(-\nabla h_B) = 0, \tag{3.14}$$

$$n_A(T \nabla s_A) + n_B(T \nabla s_B) = 0. \tag{3.15}$$

Just as in section 2, we shall only consider here quasi-steady transport where inertial effects can be ignored. In a steady regime, the driving force acting on B is offset by a friction force. Friction is due to the fact that B particles release momentum to A particles in moving amidst the latter.

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[10] Actually a partial molecular volume may be negative, as happens with $B = MgSO_4$ in $A = H_2O$ at high dilution $x_B \to 0$ [30]: $v_B = -1.4$ cm^3 mol^{-1} and $v_A = 18$ cm^3 mol^{-1}. In this case, n_A decreases together with n_B.

The exchange of momentum between B particles does not affect the ensemble-average velocity $\mathbf{u}_B = \mathbf{j}_B/n_B$ of B. In keeping with the mechanically minded line of reasoning of section 2, we take friction to be linear in the relative velocity $\mathbf{u}_B - \mathbf{u}_A$ with a friction coefficient f_B:

$$-\nabla\tilde{\mu}_B - f_B(\mathbf{u}_B - \mathbf{u}_A) = 0, \tag{3.16}$$

and similarly for A. Application of the Gibbs–Duhem relation (3.11) demands that $x_A f_A = x_B f_B$. Letting $f_A = x_B f$ and $f_B = x_A f$ in order to satisfy that condition, we find that the friction undergone by B is proportional to the particle fraction of A. This is understandable since B particles release less momentum to A particles in moving amidst them as $x_A \to 0$. Yet f may in general be a function of composition x_A. The 'mechanical' line of reasoning above was devised by Maxwell [37] and retooled by Stefan [38] dealing with multinary (multi-component) gaseous mixtures. It holds in liquid mixtures as well [39] provided that chemical potentials be used instead of partial pressures which are relevant only in the gaseous state.

Each component moves down its chemical potential gradient and the gradients are directed contrariwise. Letting $\mu = 1/f$ and using again the Gibbs–Duhem relation (3.11) to transform equation (3.16) gives the law of relative motion as a simple generalization of equation (2.13) of unary diffusion, namely

$$\mathbf{u}_B - \mathbf{u}_A = -\mu\nabla(\tilde{\mu}_B - \tilde{\mu}_A). \tag{3.17}$$

Mobility μ retains its meaning of the coefficient of response to a mechanical force: would $U(\mathbf{r})$ affect B without affecting A particles, $\tilde{\mu}_B$ would become $\tilde{\mu}_B + U$ and $\mathbf{u}_B - \mathbf{u}_A$ would increase by $-\mu\nabla U$. From (3.17), the force driving the relative motion is seen to be $-\nabla\tilde{\mu}_{BA}$.

The absolute transport velocities $\mathbf{u}_A$ and $\mathbf{u}_B$ depend on the choice of a reference frame. Unlike unary diffusion, binary diffusion has no naturally defined reference frame, and this is why the latter topic is hardly touched upon at the undergraduate level. For a mechanically minded student, it is natural to consider the centre-of-mass frame where the total momentum per unit volume $m_A n_A \mathbf{u}_A + m_B n_B \mathbf{u}_B$ is zero (m_A and m_B are the masses of A and B particles). In that frame, transport of A and B particles across a fixed plane entails no net transport of mass across that plane. In practice, however, although the centre-of-mass frame is the one of which the velocity appears in the momentum-balance equation of fluid dynamics, it is usually not the most convenient one. As diffusion is often studied in a vessel which can exchange momentum with the enclosed particles, the latter are not mechanically isolated. The centre-of-volume frame, where $v_A n_A \mathbf{u}_A + v_B n_B \mathbf{u}_B$ is zero, is often preferred because it coincides with that of the vessel in the limit of an almost homogeneous mixture [40]. Once a reference frame is chosen, well-defined values of $\mathbf{u}_A$ and $\mathbf{u}_B$ are obtained from (3.17). They may be written as

$$\mathbf{u}_A = -\mu_A\nabla\tilde{\mu}_A \qquad \text{and} \qquad \mathbf{u}_B = -\mu_B\nabla\tilde{\mu}_B, \tag{3.18}$$

where μ_A and μ_B are proportional to μ. Reference [4] gives μ_A and μ_B in the centre-of-mass frame, where $\mu_A/\mu_B = m_B/m_A$. In the centre-of-volume frame, we would have $\mu_A/\mu_B = v_B/v_A$.

The transports of A and B can now be envisaged as two unary diffusions. Considering $\tilde{\mu}_B$ as a function of (p, T, n_B) rather than (p, T, x_B), we have

$$\mathbf{j}_B = -D'_B\nabla n_B, \tag{3.19}$$

where[11]

$$D'_B = kT\mu_B\left(\frac{\partial\ln a_B}{\partial\ln n_B}\right)_{p,T} \tag{3.20}$$

[11] We put a prime on this diffusivity because D_B in [4] was defined slightly differently, using x_B instead of n_B, so that $D_B = nv_A D'_B$, see the derivation of (3.34).

and a_B is the activity of B such as defined in section 3.1. Given the current equation (3.19) for B and its analogue for A, it is possible to describe the diffusions of A and B particles in space through continuity equations similar to (1.1),

$$\frac{\partial n_{A,B}}{\partial t} + \operatorname{div} \mathbf{j}_{A,B} = 0, \tag{3.21}$$

ruling the evolutions of $n_A(\mathbf{r}, t)$ and $n_B(\mathbf{r}, t)$ from the initial densities $n_A(\mathbf{r}, t = 0)$ and $n_B(\mathbf{r}, t = 0)$. Just as in section 2.2, an infinitely sharp $n_B(\mathbf{r}, t = 0)$ evolves into a Gaussian cloud with a typical spatial extension $(2D'_B t)^{1/2}$ per component. Note that the diffusions of A and B are coupled through the relation of state of the fluid, of which a differential form under fixed p and T is (3.9)[12].

3.3. Interdiffusion

In actual practice, it is often more interesting, and more directly observable, to consider the interdiffusion of B with respect to A, or *vice versa*. We are then concerned with the particle fraction x_B rather than the density n_B. To this end, we have to change variables, $(n_A, n_B) \rightarrow (n, x_B)$, where $n = n_A + n_B$ and $x_B = n_B/n$. The evolutions of $n(\mathbf{r}, t)$ and $x_B(\mathbf{r}, t)$ follow from the evolutions (3.21) of n_A and n_B:

$$\frac{\partial n}{\partial t} + \operatorname{div} \mathbf{j} = 0, \tag{3.22}$$

$$n \left(\frac{\partial x_B}{\partial t} \right) + \mathbf{j} \cdot \nabla x_B + \operatorname{div}(\mathbf{j}_B - x_B \mathbf{j}) = 0, \tag{3.23}$$

where $\mathbf{j}$ denotes the total particle-current density $\mathbf{j}_A + \mathbf{j}_B$. The physical meaning of (3.22) is obvious, while equation (3.23) is better understood after it is rewritten as

$$n \left(\frac{\mathrm{D} x_B}{\mathrm{D} t} \right) + \operatorname{div} \mathbf{J}_B = 0, \tag{3.24}$$

where

$$\mathbf{J}_B = \mathbf{j}_B - x_B \mathbf{j} = n_B(\mathbf{u}_B - \mathbf{u}). \tag{3.25}$$

In equation (3.24), $\mathrm{D}/\mathrm{D}t = \partial/\partial t + \mathbf{u} \cdot \nabla$ is the advective, or Lagrange, derivative of fluid dynamics, and

$$\mathbf{u} = \mathbf{j}/n = x_A \mathbf{u}_A + x_B \mathbf{u}_B \tag{3.26}$$

is the average transport velocity of particles. Equation (3.24) means that, in an elemental fluid volume moving at velocity $\mathbf{u}$, the rate of change of composition x_B is due to the divergence of $\mathbf{J}_B$. The latter current density is proportional to the departure of $\mathbf{u}_B$ from the average particle velocity $\mathbf{u}$ and is called the interdiffusion current density of B. Because $\mathbf{u}_B - \mathbf{u}$ is a velocity difference, $\mathbf{J}_B$ does not depend on the choice of a reference frame. This is a major interest of the interdiffusion current density. Similarly, $\mathbf{J}_A$ is defined as $n_A(\mathbf{u}_A - \mathbf{u})$ and it is seen that $\mathbf{J}_A = -\mathbf{J}_B$.

Because of the mathematical difference between equations (3.22) and (3.24), the inward flux of $\mathbf{J}_B$ through a closed surface moving at velocity $\mathbf{u}$ is *not* the rate of change of the number of B particles contained in the volume enclosed by the surface, unless $\mathrm{D}n/\mathrm{D}t$ vanishes, i.e. unless n be independent of x_B at fixed p and T. The discrepancy lies in $x_B(\mathrm{D}n/\mathrm{D}t)$ which

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[12] Using (3.9) and the definition (3.20) of D'_B and D'_A, one further arrives at $D'_A/\mu_A v_A = D'_B/\mu_B v_B$. Thus, in the centre-of-volume frame, $D'_A = D'_B$. That value coincides with D_{BA} according to (3.35).

according to (3.22) is $-n_B \operatorname{div} \mathbf{u}$. While div $\mathbf{u}$ would vanish in a rigid medium such that $\mathbf{u}(\mathbf{r}, t) = \mathbf{u}_0(t) + \boldsymbol{\omega}(t)\mathbf{x}\mathbf{r}$ in the laboratory frame is the superposition of a translation (at a linear velocity $\mathbf{u}_0$) and a rotation (at an angular velocity $\boldsymbol{\omega}$), in contrast div $\mathbf{u}$ generally does not vanish in a fluid medium. The velocity field $\mathbf{u}(\mathbf{r}, t)$ is apt to define a transformation between rigid reference frames only insofar as it is not divergent. If it is, there does not exist any reference frame (in the sense of mechanics) where $\mathbf{J}_B$ can be thought of as the particle-current density of B. So students should be warned that an interdiffusion current is not a particle current in the sense used in section 1. Although the rightmost term of (3.25) seems to be cast on the pattern (2.12), $\mathbf{u}_B - \mathbf{u}$ cannot be thought of as the transport velocity of B in any actual reference frame. Likewise, if (3.25) is rewritten as

$$\mathbf{j}_B = n_B \mathbf{u} + \mathbf{J}_B, \tag{3.27}$$

it is customary to say that the current of B is the sum of an advection (or convection) current $n_B \mathbf{u}$ and an interdiffusion current $\mathbf{J}_B$. It is a mathematical way of speaking as the advection current, just as $\mathbf{J}_B$, is not a particle current in the usual sense if $\mathbf{u}$ is a divergent field.

From the definition (3.26) of $\mathbf{u}$, we get $\mathbf{u}_B - \mathbf{u} = x_A(\mathbf{u}_B - \mathbf{u}_A)$. Then, $\mathbf{J}_B = nx_Bx_A(\mathbf{u}_B - \mathbf{u}_A)$ is seen to vanish in the limits $x_B \to 0$ and $x_A \to 0$. From the law of relative motion (3.17), we arrive at

$$\mathbf{J}_B = -n_B \mu \boldsymbol{\nabla} \tilde{\mu}_B. \tag{3.28}$$

It is formally a generalization of the law of unary diffusion (2.1), with $\mathbf{J}_B$ replacing $\mathbf{j}_B$. Replacing the chemical potential with the activity yields

$$\mathbf{J}_B = -D_{BA} n \boldsymbol{\nabla} x_B, \tag{3.29}$$

where

$$D_{BA} = kT\mu \left(\frac{\partial \ln a_B}{\partial \ln x_B} \right)_{p, T} \tag{3.30}$$

is called the coefficient of interdiffusion, or interdiffusivity, of B in A. Expression (3.29) is the law of binary diffusion found in textbooks [39, 41–43]. The reader is warned, however, about the variety of composition variables (e.g. mass fraction instead of particle fraction) and interdiffusion currents (e.g. volume current instead of particle current) used by various authors.

Three remarks on (3.29) are in order. First, since $\mathbf{J}_A + \mathbf{J}_B = 0$ and $\boldsymbol{\nabla}(x_A + x_B) = 0$, $D_{AB} = D_{BA}$, there is only one interdiffusivity, just as there is only one mobility μ or friction coefficient f. Secondly, the identity of D_{AB} and D_{BA} is consistent with

$$\left(\frac{\partial \ln a_A}{\partial \ln x_A} \right)_{p, T} = \left(\frac{\partial \ln a_B}{\partial \ln x_B} \right)_{p, T}, \tag{3.31}$$

which can be derived from the Gibbs–Duhem relation (3.8) between the chemical potentials of A and B at fixed p and T. This is not surprising, given that we had relied on that relation in obtaining the law of relative motion (3.17). The common value (3.31) is termed the thermodynamic non-ideality factor of the mixture. That factor is equal to unity if the mixture of A and B is ideal, in which case $a_A = x_A$ and $a_B = x_B$. Strong departure from ideality occurs when the thermodynamic factor tends to change sign at a particular value of x_B. Then, the mixture can decrease its Gibbs energy by unmixing [32, 39]. Here, this is manifested in a negative D_{BA} meaning a tendency to segregation instead of interdiffusion (a $\mathbf{J}_B$ oriented along $\boldsymbol{\nabla} x_B$ strengthens that gradient). Just as in unary diffusion, writing down D_{BA} as the product of a kinetic quantity μ and an equilibrium quantity $x_B(\partial \tilde{\mu}_B / \partial x_B)_{p, T}$ allows one to sort out the different factors at work in interdiffusion [39].

Table 1. Unary versus binary diffusion.

	Unary diffusion	Binary diffusion
Driving force	$-\boldsymbol{\nabla}\tilde{\mu}$	$-\boldsymbol{\nabla}\tilde{\mu}_{BA}$
Transport velocity	$\mathbf{u} = \mu(-\boldsymbol{\nabla}\tilde{\mu})$	$\mathbf{u}_B - \mathbf{u}_A = \mu(-\boldsymbol{\nabla}\tilde{\mu}_{BA})$
Current density	$\mathbf{j} = n\mathbf{u}$	$\mathbf{J}_B = nx_B x_A(\mathbf{u}_B - \mathbf{u}_A)$
Diffusion law	$\mathbf{j} = -D\boldsymbol{\nabla}n$	$\mathbf{J}_B = -D_{BA}n\boldsymbol{\nabla}x_B$
Diffusivity	$D = \mu\left(\frac{\partial\tilde{\mu}}{\partial\ln n}\right)_T$	$D_{BA} = \mu\left(\frac{\partial\tilde{\mu}_B}{\partial\ln x_B}\right)_{p,T}$

Thirdly, it is possible to relate D_{BA} to the unary diffusivities D'_A and D'_B describing the diffusions of A and B in space. To this end, we identify $\mathbf{J}_B = -D_{BA}n\boldsymbol{\nabla}x_B$ with $\mathbf{J}_B = nx_B x_A(\mathbf{u}_B - \mathbf{u}_A)$, where

$$\mathbf{u}_B = -D'_B\boldsymbol{\nabla}\ln n_B = -D'_B\left(\frac{\partial\ln n_B}{\partial\ln x_B}\right)_{p,T}\boldsymbol{\nabla}\ln x_B \tag{3.32}$$

involves the unary diffusivity D'_B, and similarly for $\mathbf{u}_A$. We then factor out $\boldsymbol{\nabla}x_B = -\boldsymbol{\nabla}x_A$ in $\mathbf{u}_B - \mathbf{u}_A$. From $x_B = n_B/(n_A + n_B)$, we evaluate

$$\left(\frac{\partial\ln x_B}{\partial\ln n_B}\right)_{p,T} = \frac{1}{n_A + n_B}\left[n_A - n_B\left(\frac{\partial n_A}{\partial n_B}\right)_{p,T}\right]. \tag{3.33}$$

The link between n_A and n_B at fixed p and T is relation (3.9), so that

$$\left(\frac{\partial\ln x_B}{\partial\ln n_B}\right)_{p,T} = \frac{1}{nv_A}. \tag{3.34}$$

Using the volume fractions $\phi_A = nx_A v_A$ of component A and $\phi_B = nx_B v_B$ of B, we obtain

$$D_{BA} = \phi_A D'_B + \phi_B D'_A, \tag{3.35}$$

consistent with [44]. The physical meaning of (3.35) is clear: the richer the mixture in A, the closer D_{BA} to D'_B. We recover unary diffusion of B as the limiting case of binary diffusion in a mixture where A is abundant. In that limit, the indefinition of D'_B due to the indefiniteness of the reference frame loses its relevance because D_{BA} then refers to diffusion of B with respect to a medium essentially made up of A molecules (this is referred to as the solvent-based frame, with B being termed the solute). The specification of a reference frame is relevant when neither the volume fraction ϕ_B nor ϕ_A is vanishingly small.

Before applying the formalism of interdiffusion to specific binary mixtures in section 4, we list the main points made in this section (see also table 1):

(i) in binary diffusion, the relevant velocity is the difference between the ensemble-average velocities of B and A, namely $\mathbf{u}_B - \mathbf{u}_A$;

(ii) the thermodynamic force driving the relative motion $\mathbf{u}_B - \mathbf{u}_A$ is $-\boldsymbol{\nabla}\tilde{\mu}_{BA}$ where $\tilde{\mu}_{BA}$ is the rate of change of the molecular Gibbs energy g with composition x_B;

(iii) in the local frame moving at the average particle velocity $\mathbf{u} = x_A\mathbf{u}_A + x_B\mathbf{u}_B$, the evolution of x_B (but not of n_B) is ruled by the divergence of the interdiffusion current density $\mathbf{J}_B = n_B(\mathbf{u}_B - \mathbf{u})$;

(iv) if div $\mathbf{u} \neq 0$, there exists no global frame of which the local velocity with respect to the laboratory frame is $\mathbf{u}$;

(v) the law of interdiffusion is $\mathbf{J}_B = -nD_{BA}\boldsymbol{\nabla}x_B$ with an interdiffusivity D_{BA} given by (3.30).

4. Self- versus mutual diffusion

4.1. Self-diffusion

Given a chemical species A, its self-diffusion is defined as the diffusion of labelled A^* molecules moving amidst unlabelled, but otherwise identical, A molecules. It is the simplest example of binary diffusion, for which

(i) because of the chemical identity of A^* and A, the mixture of A^* and A is thermodynamically ideal;

(ii) because of the physical identity of A^* and A, the average transport velocity $\mathbf{u} = x_A \mathbf{u}_A + x_{A^*} \mathbf{u}_{A^*}$ coincides with the centre-of-mass and centre-of-volume velocities; therefore, if the reference frame where diffusion is described is the vessel containing the mixture, self-diffusion is such that $\mathbf{u} = 0$.

The above definition of self-diffusion appeals to a *Gedankenexperiment* which can be approximately turned into a real-world experiment by using for A^* a radioactive isotope of A with a small mass difference, for example heavy water D_2O in ordinary water H_2O ($D = {}^2H$ is the deuterium). Then, condition (i) is fulfilled as the chemical reactivities are the same while condition (ii) is approximately satisfied with a typical expected relative error $(20-18)/18 \approx 10\%$ in this example.

As a result of (i), $\tilde{\mu}_A = \tilde{\mu}_A^0(p, T) + kT \ln x_A$ and $\tilde{\mu}_{A^*} = \tilde{\mu}_A^0(p, T) + kT \ln x_{A^*}$. The same standard chemical potential[13] is used because of the identity of A and A^*. The self-diffusivity of species A is then defined as the interdiffusivity D_{A^*A}. From (3.30) we find that

$$D_{A^*A} = kT \mu_{A^*A}, \tag{4.1}$$

where the friction coefficient $1/\mu_{A^*A}$ expresses the drag force undergone by A^* in moving amidst A molecules. Note that the coefficient is independent of x_{A^*} because of the physico-chemical identity of A^* and A.

Writing $\tilde{\mu}_{A^*A} = kT \ln(x_{A^*}/x_A)$ as $h_{A^*A} - T s_{A^*A}$ by means of the second Gibbs–Helmholtz relation (3.13) shows that $h_{A^*A} = 0$ does not contribute to the driving force $-\nabla \tilde{\mu}_{A^*A}$. The driving force reduces to

$$T\nabla s_{A^*A} = -\frac{kT \nabla x_{A^*}}{x_A \, x_{A^*}}. \tag{4.2}$$

It is purely entropic and drags A^* towards the locations of lower x_{A^*}. The equilibrium state is the one of uniform composition: it maximizes the entropy of the mixture without involving any change in enthalpy (or internal energy). Here, we recover the well-known Gibbs paradox of mixing: there would be no increase in entropy if the intermixing particles were strictly identical, because then diffusion would not change the macrostate of the mixture [12, 20, 45]. The entropy increase occurs because labelled, distinguishable particles A^* confined in a subvolume of the vessel, where x_{A^*} is larger, are lost throughout the whole volume in the process of diffusion. The entropy increase appears as a loss of information; *a contrario*, no information is lost if the particles are indistinguishable [12]. Thus, self-diffusion provides a time-dependent illustration of the Gibbs paradox.

The equation of evolution of composition (3.24), namely

$$n \left(\frac{Dx_{A^*}}{Dt} \right) + \text{div} \left(-n D_{A^*A} \nabla x_{A^*} \right) = 0, \tag{4.3}$$

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[13] In the real-world experiment involving isotopes, there is a slight difference between the standard chemical potentials, see section 96 of [20].

simplifies into

$$\frac{\partial n_{A^*}}{\partial t} + \mathrm{div}\,(-D_{A^*A}\nabla n_{A^*}) = 0, \tag{4.4}$$

because $(\partial n/\partial x_{A^*})_{p,T} = 0$ and $\mathbf{u} = 0$. The latter equation just describes the spreading of A^* in space with a root-mean-square deviation $(2D_{A^*A}t)^{1/2}$ per component, starting from a sharp distribution at zero time. Interdiffusion reduces here to diffusion.

4.2. Mutual diffusion

When the two species A and B are chemically different, their interdiffusion is called mutual diffusion. The interdiffusion current density $\mathbf{J}_B$ is driven by $-\nabla\tilde{\mu}_{BA}$ which can be written in two ways. It can be related to the slope of the Gibbs-energy change on mixing,

$$-\nabla\tilde{\mu}_{BA} = -\nabla\frac{\partial}{\partial x_B}\left[g - \left(x_A\tilde{\mu}_A^0 + x_B\tilde{\mu}_B^0\right)\right], \tag{4.5}$$

or it can be written in terms of the activities a_A and a_B, see (3.4), as

$$-\nabla\tilde{\mu}_{BA} = -kT\nabla\ln(a_B/a_A). \tag{4.6}$$

Writing a_A (a_B) as $\gamma_A x_A$ ($\gamma_B x_B$), where γ_A (γ_B) is the relative activity of A (B), changes (4.6) into

$$-\nabla\tilde{\mu}_{BA} = -\frac{kT\nabla x_B}{x_A\,x_B} - \nabla\left(\frac{\partial g^E}{\partial x_B}\right)_{p,T}, \tag{4.7}$$

where $g^E = kT\,(x_A\ln\gamma_A + x_B\ln\gamma_B)$ is the excess Gibbs energy.

The Gibbs–Duhem relation (3.8) links the relative activities through $x_A\,\mathrm{d}\ln\gamma_A + x_B\,\mathrm{d}\ln\gamma_B = 0$ as composition is varied while p and T are kept fixed. Writing $\tilde{\mu}_{BA}$ as $h_{BA} - Ts_{BA}$ by means of the second Gibbs–Helmholtz relation, it is easily found that

$$-\nabla h_{BA} = \frac{kT}{x_A}\left(T\frac{\partial^2\ln\gamma_B}{\partial T\,\partial x_B}\right)\nabla x_B \tag{4.8}$$

$$T\nabla s_{BA} = -\frac{kT}{x_A}\left[1 + x_B\frac{\partial^2(T\ln\gamma_B)}{\partial T\,\partial x_B}\right]\frac{\nabla x_B}{x_B}. \tag{4.9}$$

In the interdiffusion current density $\mathbf{J}_B = nx_Bx_A\mu_{BA}(-\nabla h_{BA} + T\nabla s_{BA})$ of section 3.3, the energetic contribution, driven by $-\nabla h_{BA}$, is entirely due to the activity correction γ_B. The entropic contribution to $\mathbf{J}_B$, driven by $T\nabla s_{BA}$, is affected by the non-ideality $\gamma_B \neq 1$, but would exist anyway in case of ideal mixing of A and B.

The interdiffusion current density $\mathbf{J}_B$ is written $-D_{BA}n\nabla x_B$, see (3.29), where

$$D_{BA} = \mu_{BA}\left[kT + x_Ax_B\left(\frac{\partial^2 g^E}{\partial x_B^2}\right)_{p,T}\right] \tag{4.10}$$

and μ_{BA} is the mobility appearing in the law of relative motion (3.17). Obviously, the mutual diffusivity D_{BA} differs from the self-diffusivity D_{A^*A} and from D_{B^*B} as well if pure B can exist as a fluid at p and T. Besides, whereas the self-diffusivity D_{A^*A} can be viewed as the time derivative of the half variance of any component of $\mathbf{r}_{A^*}$, the mutual diffusivity D_{BA} should be viewed only as the coefficient of linear response of $\mathbf{J}_B$ with respect to $-n\nabla x_B$ [46]. The spreading of B in space (in a specified reference frame) is described by the unary diffusivity D_B' which is approximately equal to D_{BA} only in the limiting case of high dilution of B in the A-based reference frame ($\phi_B \to 0$ in (3.35)).

5. Concluding remarks

This paper has set up a thermodynamic framework to describe particle diffusion in various media. The basic idea is that the transport of particles from one place to another, whether by diffusion or under the effect of a mechanical force, is ruled by the inhomogeneity of the chemical potential. The negative gradient of the chemical potential is the effective force driving diffusion. The description has been applied to unary diffusion, where there is only one kind of mobile particle (e.g. neutrons or electrons) in an immobile, solid medium. Unary diffusion has been discovered later than binary diffusion in gases or liquids, but its description is simpler as

  (i) only one chemical potential is needed;
 (ii) there is a natural reference frame, namely the immobile background medium.

Because of that greater simplicity, students and teachers concerned in either the phenomenology or the modelling of diffusion have interest in starting from unary diffusion before tackling binary diffusion.

The thermodynamic force driving diffusion is a generalization of the mechanical force. That generalization allows us to distinguish two 'causes' for diffusion. One is the tendency to maximizing entropy which is frequently, but loosely, invoked in elementary accounts of diffusion. The other factor is the mechanical tendency to minimizing energy, which in some systems is the main 'cause' of diffusion. We have shown that the thermodynamic driving force can be separated out into entropic and energetic contributions. Under fixed temperature and pressure conditions, the separation is performed by means of the second Gibbs–Helmholtz relationship.

Next, the response to the force involves an inverse friction coefficient (mobility) which is kinetic in nature, i.e. beyond reach of thermodynamics. The diffusivity is split up into an equilibrium parameter, related to the chemical potential, and a kinetic parameter[14]. Such linear instantaneous response is valid in a quasi-steady state which holds until high frequencies provided that friction be strong enough; dynamically speaking, the motion is overdamped.

Binary diffusion, where two species A and B are mobile with respect to each other, has been described in this paper by means of the Maxwell–Stefan scheme where the link-up with mechanics is apparent. Binary diffusion can be thought of as the superposition of two unary diffusions, but the arbitrariness in the reference frame makes it more convenient to consider interdiffusion of one species through the other. The description of interdiffusion is then closely related to the thermodynamics of mixing; interdiffusion is just the kinetics of mixing. For example, we have seen that self-diffusion provides a time-dependent illustration of the Gibbs paradox of mixing. Whereas the unary diffusivity quantifies the spreading in space of an initially sharp particle distribution, the binary interdiffusivity quantifies the rate at which mixing occurs. When one species is abundant, it makes up the natural reference frame and interdiffusion reduces to unary diffusion of the other species in that frame. Another difference between unary and binary diffusion is that in the latter phenomenon allowance is made for the non-rigid nature of the medium, i.e. the dependence of the volume per particle upon composition under fixed T and p.

In this paper, we have overturned the historical sequence of the discoveries in order to base our account of diffusion upon unary diffusion, in which the role of equilibrium-thermodynamic features has been pointed out in a simple way. It is worthy of remark that, as far as equilibrium

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[14] Postgraduate readers will note that, far away from equilibrium where the notion of temperature loses relevance, a link-up between diffusivity and mobility continues to hold and to be due to the entropyless nature of a mechanical force field [47, 48].

thermodynamics is concerned, we have also upset the historical order. The notion of a chemical potential was unknown to Graham and Fick although nowadays it looks natural in describing the transfer of particles from one place to another [9]. Likewise, van't Hoff [49], Nernst [14] and Einstein [16] used the notion of an osmotic pressure where today we use the notion of a thermodynamic activity difference. Yet the former notion is still invoked in some lectures and papers and appendix B shows how that notion is related to the present framework. Our final remark will be that Fick [2] devised his law after Fourier's law of heat transfer. That analogy is still used in many popular textbooks on heat and mass transfer although it is also acknowledged [42] that mass transfer is often significantly more complex than heat transfer.

Appendix A. Energy and entropy contributions to the chemical potential of a perfect gas in a rigid box

The statistical thermodynamics of an assembly of non-interacting particles (or 'perfect gas') in a constant-volume container is dealt with in many textbooks [12, 20]. For convenience, this appendix picks up a few useful relations. The free energy F of the assembly of particles confined in a rigid box of invariable volume V is such that $dF = -S\,dT + \tilde{\mu}\,dN$, where S is the entropy and N is the number of particles. Therefore,

$$S = -(\partial F/\partial T)_{N,V} \qquad \text{and} \qquad \tilde{\mu} = (\partial F/\partial N)_{T,V}. \qquad (A.1)$$

Introducing the free energy per particle $f = F/N$ and the entropy per particle $s = S/N$, equalities (A.1) become

$$s = -(\partial f/\partial T)_n \qquad \text{and} \qquad \tilde{\mu} = f + N(\partial f/\partial N)_{T,V}. \qquad (A.2)$$

In the first equality (A.2), use has been made of the fact that f is a function of the intensive variables $n = N/V$ and T. By the same token, the second equality (A.2) becomes

$$\tilde{\mu} = f + n(\partial f/\partial n)_T. \qquad (A.3)$$

The chemical potential $\tilde{\mu}$ of an assembly of classical point particles is given by (2.3). It is easily checked that the solution of (A.3) is

$$f = kT \ln\left(n\lambda_{dB}^3\right) - kT. \qquad (A.4)$$

The chemical potential $\tilde{\mu}$ of an assembly of degenerate fermions is given by (2.5). It is easily checked that the solution of (A.3) is

$$f = \tfrac{3}{5} E_F(n) - \frac{\pi^2(kT)^2}{4\,E_F(n)}. \qquad (A.5)$$

Calculation of the entropy per particle s from (A.4) and (A.5) through the first equality (A.2) yields expressions (2.9) and (2.10). The energetic contribution h to $\tilde{\mu}$ is obtained as $\tilde{\mu} + Ts$.

In section 2, it is stated that addition of an external potential energy $U(\mathbf{r})$ changes h into $h + U$. Indeed, starting from $\tilde{\mu} \to \tilde{\mu} + U$ [9, 10, 12, 20, 32], (A.3) yields $f \to f + U$, whence s is unchanged as a result of the first equality (A.2) (the external potential energy U is independent of T inasmuch as it is a mechanical quantity).

The model of a rigid box is used at the undergraduate level to describe conduction electrons or neutrons in a solid. Actually, the volume of the box may slightly change with temperature, but the ensuing corrections to thermodynamic relations are very weak [19].

Appendix B. Osmotic pressure and diffusion

The concept of osmotic pressure has played an important role in early developments of chemical thermodynamics and near-equilibrium transport processes. The phenomenon of osmotic pressure had been studied by van't Hoff [49] before Gibbs's work on the chemical potential and before Lewis defined the activity. Since the present description of diffusion is based upon the latter concepts, it is instructive to rephrase the description in terms of the osmotic pressure. We first consider unary diffusion such as studied in section 2.2, before turning to binary diffusion such as studied in section 4.2.

Unary diffusion is the transport of one mobile species in a medium of immobile scatterers at temperature T. The steady-state momentum balance (2.15) between the thermodynamical and frictional forces acting upon a mobile particle can be written slightly differently, as

$$-v\nabla\Pi - \frac{\mathbf{u}}{\mu} = 0, \tag{B.1}$$

where $v = 1/n$ is the volume per mobile particle and

$$\Pi = \int_0^n n'\left(\frac{\partial\tilde{\mu}}{\partial n'}\right)_T dn'. \tag{B.2}$$

From (B.1), the force driving diffusion formally looks like a buoyancy force if Π is identified to a local pressure pushing particles of effective volume v towards places of lower Π. It is easy to obtain Π for non-interacting classical particles from expression (2.3) of $\tilde{\mu}$,

$$\Pi = kTn. \tag{B.3}$$

To illustrate (B.3), instead of taking conduction electrons in a semiconducting solid as we had in section 2, we shall consider NaCl in water under standard conditions. We may do so because we have seen in section 3 that, in the limit of high dilution of NaCl in H_2O, binary diffusion of NaCl in H_2O reduces to unary diffusion of NaCl in a stagnant medium. For n corresponding to 0.6 mol L^{-1} NaCl, which is roughly the salt concentration of sea water, (B.3) yields $\Pi \approx$ 30 bar. As we shall see shortly, Π is the so-called osmotic pressure of the solution. Clearly, Π is not the hydrostatic pressure acting upon a body immersed in the solution: a swimmer does not feel a significantly different buoyancy force in sea water compared to pure water where $\Pi \approx 10^{-6}$ bar (the only solutes are HO^- and H_3O^+ at concentrations 10^{-7} mol L^{-1} under standard conditions) [50]. The difference in buoyancy is due to the fact that sea water (mass density ≈ 1030 kg m^{-3} under standard conditions) is slightly denser than pure water (mass density 997 kg m^{-3}). The idea that the ions present in water would exert on immersed bodies a gas-like pressure Π given by (B.3) in the dilute limit cannot be taken literally.

Likewise, considering the degenerate gas of non-interacting fermions, equations (B.2) and (2.5) yield

$$\Pi = \tfrac{2}{5}nE_F(n) \tag{B.4}$$

at zero temperature. In Cu where $n = 0.84 \times 10^{29}$ m^{-3} and $E_F \approx 7$ eV, we compute $\Pi = 5 \times 10^{10}$ Pa or 5×10^5 bar, which is unrelated to the actual pressure felt by the lattice.

We now turn to binary diffusion of B in A. Owing to the Gibbs–Duhem relation (3.12), the interdiffusion current density (3.28) can be alternatively written as

$$\mathbf{J}_B = \mu n_A \nabla\tilde{\mu}_A. \tag{B.5}$$

Now $\tilde{\mu}_A = \tilde{\mu}_A^0(p, T) + kT \ln a_A$ may be expressed differently by introducing the so-called osmotic pressure Π of the solution. By definition, Π is the difference of pressure between two vessels, one with pure A and the other with solvent A and solute B, if the membrane

between the vessels allows transfer of A but not of B. Equilibrium of A entails the equality of its chemical potential on both sides,

$$\tilde{\mu}_A^0(p, T) = \tilde{\mu}_A^0(p + \Pi, T) + kT \ln a_A. \tag{B.6}$$

The right-hand side may be expanded as $\tilde{\mu}_A^0(p, T) + v_A^0 \Pi + kT \ln a_A$ if the dependence of $v_A^0 = \left(\partial \tilde{\mu}_A^0 / \partial p\right)_T$ on p can be neglected. Then,

$$\Pi = -(kT \ln a_A)\big/ v_A^0. \tag{B.7}$$

Therefore, the osmotic pressure appears basically as a surrogate for the activity of the solvent in the solution.

Since v_A^0 is independent of x_B, the interdiffusion current (B.5) can be rewritten as

$$\mathbf{J}_B = -\mu n_A v_A^0 \boldsymbol{\nabla} \Pi. \tag{B.8}$$

Let us obtain Π to the lowest order in n_B. For high dilution of B, $a_A \approx x_A = 1 - x_B$, whence $kT \ln a_A \approx -kT x_B$ and $\Pi \approx kT x_B / v_A^0 = kT n_B / n v_A^0$. Again in the limit of high dilution, $n v_A^0 \approx 1$, so that

$$\Pi \approx kT n_B. \tag{B.9}$$

In the same limit, $n_A v_A^0 \approx 1$ and $\mathbf{j}_B \approx \mathbf{J}_B$, so that (B.8) reduces to

$$\mathbf{j}_B \approx -\mu \boldsymbol{\nabla}(kT n_B), \tag{B.10}$$

which is just Fick's law.

From (B.8), the interdiffusion current of B formally looks as though it were due to a pressure gradient. From (B.9), in the dilute limit that pressure Π is given by the classical perfect-gas law. However, as was shown above, this is merely a formal mathematical analogy, as Π is not an actual pressure. Correspondingly, we can transform (B.10) into a 'mechanical' balance equation similar to (B.1),

$$\frac{1}{n_B v_B}(-v_B \boldsymbol{\nabla} \Pi) - \frac{\mathbf{u}_B}{\mu} = 0. \tag{B.11}$$

We can see that the pseudo-buoyancy force $-v_B \boldsymbol{\nabla} \Pi$ on B associated with the osmotic-pressure gradient is multiplied by a dimensionless factor $1/n_B v_B$ much larger than unity in the limit $n_B \to 0$ (remember that $1 = n_A v_A + n_B v_B$). This makes the pressure analogy physically irrelevant in accounting quantitatively for diffusion. Moreover, in case that several solutes $B, C \dots$ are hosted in the solvent A, the interdiffusion currents $\mathbf{J}_B, \mathbf{J}_C \dots$ are driven by $\boldsymbol{\nabla} \tilde{\mu}_B, \boldsymbol{\nabla} \tilde{\mu}_C \dots$ [4, 39] which are not reducible to $\boldsymbol{\nabla} \Pi$, even in the limit of high dilution of $B, C \dots$.

Although the concept of osmotic pressure has played an important heuristic role in early studies [14, 16, 49] and could be tempting as a didactic tool at the undergraduate level in view of the simplicity of (B.8) and (B.9), it is necessary to warn students as does Böddeker [51]:

> As to van't Hoff's lasting contribution to solution theory, such is the beauty of the apparent analogy between gas pressure and osmotic pressure of dilute solutions that it persists although proven wrong a long time ago. [. . .] Indeed, the numerical correspondence of the osmotic pressure of an aqueous sugar solution with the ideal gas pressure on an equimolar footing must be regarded as one of nature's profound jokes.

Similarly, Hooge [52] has shown that wherever appeal is made to the concept of osmotic pressure in Einstein's paper on Brownian motion [16], that concept is actually unnecessary.

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