Fundamentals of diffusion for optimized applications

This paper outlines some basic concepts on diffusion phenomena occurring in an isolated thermodynamic system initially out of equilibrium. The physical link between definition of mass flow and concentration gradient law is evidenced by exploiting the uncertainty equations of statistical quantum mechanics. The statistical expression of entropy is also inferred as a corollary. The approach has a general character and applies to diffusion systems in solid, liquid and gas phases

Sebastiano Tosto

I fondamenti della diffusione per applicazioni ottimizzate

Il lavoro ha lo scopo di delineare alcuni concetti fondamentali sui fenomeni di diffusione che si verificano in un sistema termodinamico isolato in condizioni di non-equilibrio. Viene evidenziata la connessione fisica fra definizione di flusso di massa e legge del gradiente di concentrazione utilizzando la formulazione statistica della indeterminazione quantistica. È derivata come corollario l'espressione statistica dell'entropia. L'approccio ha carattere generale e vale per la diffusione in fase solida, liquida e gassosa

Introduction

Diffusion brings intuitively to mind the transport of matter, whatever the actual activation and transfer mechanisms might be. Despite its plain meaning, however, the diffusion is a complex and multifaceted physicochemical process that controls a broad variety of microscopic phenomena with or without permanent phase changes; think for instance to diffusion in solid phase, whose end effects are local composition changes possibly corresponding to new microstructures, or in gas mixtures, which activates chemical reactions and irreversible formation of new compounds. Despite the high complexity of the phenomena involved, however, the theoretical background of the diffusion basically relies on an intuitive definition and a simple physical hypothesis about the driving force governing the mass transfer: the former concerns the concept of mass flow $\mathbf{J} = c\nu$ with reference to the rate ν, with which an arbitrary amount of matter per unit volume c displaces through the diffusing medium; the latter has to do with the initial condition of non-equilibrium, necessary for the mass transfer to occur. Another general requirement is that the net mass transfer is a leading mechanism through which any thermodynamic system, initially in a non-equilibrium state, approaches the equilibrium state. In particular, whatever the diffusion medium might be, e.g., simply the vacuum or a gas/liquid/solid phase, a general principle is that any system initially inhomogeneous tends to eliminate concentration gradients; this is substantially the meaning of the Fick laws describing the evolution of a thermodynamic system.

The generality of such expectation is so evident to skip a more profound consideration about its actual

Sebastiano Tosto
ENEA

physical meaning. It is however sensible to expect that just this generality, and that of the related concentration gradient driving force itself, should be in fact consequence of some fundamental principle of nature. This consideration reasonably recalls the second law of thermodynamics, as concerns in particular the probabilistic character of the entropy. Consider a large number of particles of a species **a** diffusing within a medium **b**; whatever the former might be, e.g., particles, ions, atoms, molecules and so on, in the following the system formed by **a** and **b** will be shortly referred to as *diffusion system*. One expects that after a proper time range, the system attains the most probable configuration, i.e., a uniform distribution of **a** into **b** regardless of the particular initial configuration. This means that before reaching this limit situation a net mass flow was necessarily occurring, after which no net mass flow is allowed to take place. The entropy is a thermodynamic function closely related to the possible system configurations. One expects therefore that the dimensionless entropy definition $-\Sigma_i \, w_i \log(w_i)$, where the index i numbers the thermodynamic states allowed in the system, tends to the simpler form $-\log(w_{eq})$when the equilibrium configuration is effectively attained by consequence of the diffusion process; also, the net mass flow **J** is different from zero only during the diffusion transient and tends to zero at the asymptotic equilibrium. Both concepts share the same principle and should be therefore involved since the beginning into the concentration/activity gradient formulation of any diffusion problem. Since, in effect, we exploit on the one side a phenomenological hypothesis – the concentration gradient law – and, on the other side, a general property of nature, the entropy, it would be significant to infer both concepts as a natural consequence of a unique, more general principle of nature without the need of specific assumptions. Of course, a general approach cannot leave out the quantum aspect of any problem, in particular that of describing the dynamics of particles on microscopic scale. Justifying from the quantum point of view the concentration gradient driven diffusion law would therefore provide a sound physical basis to the general problem of mass transport. It is certainly significant to demonstrate the quantum origin of the macroscopic equations describing how the configuration of the diffusion system evolves as a function of time because of the mass transfer; besides, this task appears to be further noteworthy if carried out within the same theoretical frame that allows describing the quantum properties of matter. The purpose of the present paper is to introduce the basic classical and quantum concepts hidden into the gradient law, i.e., to demonstrate that the quantum uncertainty is the basic quantum principle leading to the first Fick law as a corollary. Moreover the theoretical model proposed here also confirms through a simple and straightforward approach that the entropy of the diffusion system is the other key concept underlying the mechanisms of mass transport.

The importance of the diffusion in science and technology is evident if we think of how many technological processes require the transport of matter, e.g., ions in solid or liquid electrolytes of fuel cells and batteries, or chemical reactions in the gas phase.

In the literature, there are several excellent textbooks on the diffusion phenomena, e.g. [1]; some of them are focused on the microscopic aspects of the problem, e.g. [2], other ones on the macroscopic thermodynamic models, e.g. [3]. Other papers mostly concern the applications, e.g. [4,5]. A further paper, merely aimed at proposing these concepts once again, would be necessarily incomplete and unexciting. The purpose of the present paper is instead to emphasize in a self-contained way some basic concepts underlying the diffusion in connection with the expectations of the quantum theory, which, because of its probabilistic character due to the uncertainty principle, offers a new perspective on both thermodynamic and microscopic concepts, usually inferred from the classical physics; for this reason some opening considerations on the classical concepts are introduced in sections 2 and 3. Section 4 exploits the contribution of the quantum mechanics to summarize some results fully described in [6]. This work has been carried out in the framework of a SSA European Project on advanced ITSOFCs, aimed at optimizing the ion conductivity of solid-oxide electrolytes at low *T*; the contribution of ENEA to the program concerned a theoretical investigation on the ion diffusion mechanisms under an applied electro-chemical potential gradient.

The previous considerations regard any species diffusing in any multi-element material; for sake of simplicity, however, the index *i* referred to the *i*-th element contributing to the global chemical composition of the diffusion medium, e.g., its concentration c_i or activity a_i, will be omitted in the present paper to simplify the notation.

Thermodynamic approach

The present paragraph introduces some general concepts underlying the mass transport, which do not need explicit reference to the atomistic nature of matter. Consider for simplicity an isolated thermodynamic system formed by an isotropic body of matter in non-equilibrium condition, where mass flow is allowed to occur; the usual way to define the flow as amount of mass crossing a unit surface per unit time reads

$$\mathbf{J} = c\mathbf{v} \qquad c = c(x,y,z,t) \qquad 2,1$$

where *c* is the concentration or more in general the activity of the diffusing species and **v** its diffusion velocity. Introduce now also a physical hypothesis about the thermodynamic force **F** that governs the flow: the following equation, postulated and known as first Fick law,

$$\mathbf{J} = -D\nabla c \qquad D = D(c) \qquad 2,2$$

combined with eq 2,1 yields

$$\mathbf{v} = -\frac{D}{k_B T}\nabla[k_B T \log(c / c_0)] \qquad c_0 = c_0\,(t) \qquad 2,3$$

being c_0 an arbitrary reference concentration. Here *D* is a proportionality factor called diffusion coefficient. Define now also the mobility β of the diffusing species as follows

$$\mathbf{v} = \beta\mathbf{F} \qquad 2,4$$

then one finds

$$\mathrm{D} = \beta k_B \mathrm{T} \qquad \mathbf{F} = -\nabla\mu \qquad \mu = k_B \mathrm{T} \log\,(c / c_0) \qquad 2,5$$

The concept of mobility yields therefore the well known Einstein equation linking β to *D* and a reasonable expression of the sought force **F** through the gradient of the potential energy $\mu = k_B\mathrm{T} \log\,(c / c_0)$. Both β and *D* are macroscopic quantities that, like temperature itself, statistically summarize a variety of microscopic situations that control the diffusion mechanism; their physical meaning has thus statistical average valence that surrogates the lack of a detailed knowledge on the microscopic phenomena. If the diffusing species is uniformly distributed everywhere in the diffusion system, then *c* is a constant; so, whatever c_0 might be, at constant temperature one finds $\mathbf{F} = 0$ and thus $\mathbf{v} = 0$ everywhere. For this reason c_0 is often taken as a constant equal to the limit value of uniform concentration corresponding to the equilibrium condition and thus to the end of the diffusion process. According to the IUPAC, the self-diffusion is the process occurring with chemical potential gradient equal to zero, i.e., it describes the displacement of an atom through a crystal lattice of the same species; instead $\mathbf{F} \neq 0$ governs the net mass flow in the diffusion system. The chemical potential μ of the diffusing species appears at the right hand side of eq 2,5, while *D* is related to temperature and to the thermodynamic driving force $\nabla\mu$ that triggers the diffusion. So the most general way of defining the mass flow is

$$\mathbf{J} = -L\nabla\mu \qquad L = \beta\boldsymbol{c} \qquad 2,6$$

where L is a new proportionality factor having physical dimensions of mobility times concentration. The last way to define the mass flow explicitly introduces the thermodynamic force controlling the mass transport. Note that the eqs 2,1 and 2,2 should be more appropriately expressed as a function of the activity, defined as $a = \gamma c$ through a coefficient $\gamma = \gamma(c)$ accounting for the non-ideal behavior of the species in the diffusion medium; then also eqs 2,3 and 2,5 would result functions of the activity *a*. Since the first eq 2,6 yields $\mathbf{J} = -L(\alpha\mu / \alpha c)\nabla c$, if μ has the form $kT \log(a / a_0)$, where a_0 is a constant reference activity, then

$$D^* = L\frac{\partial\mu}{\partial c} = \frac{k_B T L}{c}\left(1 + \frac{\partial\log(\gamma)}{\partial\log(c)}\right) \qquad 2,7$$

This equation holds for a homogeneous body of matter, for instance in the case of self-diffusion of an isotope in a matrix of the same element. Once regarding *L* according to eq 2,6, one infers from eq 2,7

$$\frac{D^*}{D} = 1 + \frac{\partial\log(\gamma)}{\partial\log(c)} \qquad \mathrm{D} = k_B T\,\beta \qquad 2,8$$

This is the Darken equation; the second equation agrees with the first eq 2,5. Extend this equation to the case of charged particles replacing the general value of β with that $\beta_{ch} = \beta / ze$ referred to the amount of charge *ze* carried by the particle; since the physical dimensions of β are $mass^{-1}$ x*time*, the right hand side introduces the amount of charge *mze* corresponding to the mass *m* proportional to the number of ion carriers.

Eq 2,5 reads

$$D = \frac{k_B T \beta_{ch}}{ze} \qquad 2,9$$

Once having shown that the diffusion law can be effectively related to a thermodynamic function that describes the driving force responsible for the transport of matter, a step forward exploits again eq 2,1 to emphasize how arbitrary changes of both c and $\mathbf{v}$ affect $\mathbf{J}$. Let $\mathbf{J}$ be allowed to change by $\delta\mathbf{J}$ during the time range $\delta t = t - t_o$, being t_o the beginning of the diffusion process and t the current diffusion time; then, considering again the concentration for simplicity,

$$\delta\mathbf{J} = \mathbf{v}\delta c + \delta\mathbf{J}' \qquad \delta\mathbf{J}' = c\delta\mathbf{v} \qquad 2,10$$

In general one expects $\delta(cv) / \delta t < 0$ because at increasing time the diffusion tends to the equilibrium condition of uniform c, which also entails $\mathbf{v} \rightarrow 0$ according to eq 2,3. Hence, in agreement with the second law, $\delta\mathbf{J}$ and $\delta\mathbf{v}$ are negative quantities when defined with reference to a positive δt. Consider, for simplicity, the space range along the x-direction where the particles are allowed to diffuse during this time interval; being $\delta x = -v_x\ \delta t$, the x-component of eq 2,10 reads $-\ \delta J_x / \delta x = \delta c / \delta t - c\delta v_x / \delta x$. To link this result with eq 2,2, read $\delta J_x / \delta x$ as $\partial J_x / \partial x$ for infinitesimal changes of the process parameters c and $\mathbf{v}$ and dynamical variables t and x, so in general the first eq 2,10 yields $-\nabla \cdot \mathbf{J} = \partial c / \partial t - c\nabla \cdot \mathbf{v}$, i.e.

$$\nabla \cdot \left(D\nabla c\right) = \frac{\partial\left(c - C\right)}{\partial t} \qquad C = \int_{t_o}^{t} c'\nabla \cdot \mathbf{v}'dt' \qquad C=C(x,y,z,t) \qquad 2,11$$

The integral is calculated between t_0 and t. To calculate the integral the local perturbation must be purposely specified case by case depending on the physical features of the diffusion system. In the particular case, for the second addend the condition $\nabla \cdot \mathbf{v} = 0$, then $\nabla \cdot (D\nabla c) = \partial c / \partial t$ describes a particular diffusion process where the change rate of concentration is equal to the change of related mass flow, which necessarily means lack of sinks or sources of matter within the volume element V where is defined c: indeed the divergence of a vector measures the strength of a source or sink in a given point, so the Stokes theorem $\nabla \cdot \mathbf{v} = \lim_{V \to 0} \int\int_S |V|^{-1} \mathbf{n} \cdot \mathbf{v} dS = 0$ shows that the integral of inwards and outwards diffusion velocity at the surface S of an infinitesimal volume V is null, i.e., the net mass transfer at the boundary of V is zero.

Since $c\nabla \cdot \mathbf{v}$ results because of the term $\delta\mathbf{J}'$ additional to $\delta\mathbf{J}$, the well known second Fick equation appears as a particular case of eq 2,10 for $\delta\mathbf{J}'=0$. It is usually acknowledged that the time enters into the diffusion equation thanks to the continuity condition that leads to the second Fick law. Actually the time evolution of the system is controlled by the concentration gradient law only, although the latter does not contain itself any reference to time, through $\mathbf{v}$ simply admitting that the range δt is also required to justify $\delta\mathbf{J}'$; no process occurs instantaneously in nature. The continuity condition appears to be itself a corollary of eqs 2,1 and 2,2 rather than an additional boundary condition. Even from a merely classical point of view, therefore, the time evolution of the system appears as a necessary ingredient together with the space displacement accounting for the mass transfer of any diffusion problem. To better highlight this point, consider an arbitrary function $f=f(x,y,z,t)$ with x and t diffusion coordinate and time. The change δf of f between x,y,z,t and an arbitrary $x + \delta x,\ y,z,t + \delta t$ is calculated at the first order differentiating f with respect to x and t, which yields $\delta f = (\partial f / \partial x)\delta x + (\partial f / \partial t)\delta t$; by definition δx is an arbitrary length not dependent on the local coordinate x. Let f represent a quantity conserved in the given range of variables, for instance a fixed amount of a given species simply redistributed within δx during the time range δt without changing its initial value of total mass per total length. Then $\delta f = 0$ yields in general $\nabla \cdot \mathbf{G} - f\nabla \cdot \mathbf{v} = -\partial f / \partial t$ with $\mathbf{G} = \mathbf{v}f$. In the specific case of present interest, putting $f \equiv c$ and so $\mathbf{G} \equiv \mathbf{J}$, the condition $\delta c = 0$ yields again $\nabla \cdot \mathbf{J} - c\nabla \cdot \mathbf{v} = -\partial c / \partial t$. This result shows that the second Fick equation with $\nabla \cdot \mathbf{v} = 0$ is actually just the continuity equation of mass transport as a consequence of eq 2,2, which is valid if in particular the diffusion process occurs without sources or sinks of matter; indeed from $c=m/V$ one infers of course $\delta c=0=\delta m/V$ and thus $\delta m=0$, having implicitly assumed that V does not depend on c. Note, however, that is also reasonable to suppose $\delta c = V^{-1} (\delta m - mV^{-1}\delta V)$, i.e., $\delta m = mV^{-1}\delta V = c\delta V$ with V somehow related to c; this is in principle possible when δm causes a change of the whole volume of the diffusion medium, e.g. when a chemical reaction is allowed to occur in a diffusing mixture of gas phases. If so, the condition $\delta c =$

0 on c is still compatible with the continuity and admits in general $\delta m \neq 0$ provided that the consequent δV is constrained by $\delta V = \delta m/c$. Indeed this relationship is verified for an ideal gas of molecular weight M reacting at constant pressure P and temperature; defining $P\delta V = (\delta m/M)RT$ and replacing M into $PV=(m/M)RT$ one finds just $\delta V=(V/m)\delta m$, i.e., c^{-1} appears at right hand side. In any case the condition $\nabla \bullet v=0$ does not represent a hypothesis *ad hoc*; in general it is simply a particular case of $\nabla \bullet \mathbf{v}$ required by a finite time range necessary for any $\delta \mathbf{J}$ to occur. Eq 2,10 emphasizes that $\delta \mathbf{J}' \neq 0$ is not only due to a possible chemical reaction perturbing the local concentrations of the diffusion system but, more in general, also to any local force field attracting or repelling the diffusing particles and perturbing their motion. Indeed $\delta \mathbf{J}' = ca\delta t = \mathbf{F}_V \delta t$ yields

$$\frac{\delta \mathbf{J}'}{\delta t} = \mathbf{F}_V = \frac{\mathbf{F}'}{V}$$

i.e., $\delta \mathbf{J}' \neq 0$ also entails a force per unit volume that affects $\mathbf{v}$ and causes $\nabla \bullet \mathbf{v} \neq 0$. This is particularly significant to introduce, for instance, the case of charged particles in an ionic medium where polarized impurities are active. Clearly in general $\mathbf{F} \neq \mathbf{F}'$: the driving force of the diffusion is $\mathbf{F}$ of eq 2,5, $\mathbf{F}'$ is the additional force related to the term $\delta \mathbf{J}'$ appearing in eq 2,10 as a perturbation of $\mathbf{J}$. Indeed the component of $\delta \mathbf{J}'$ along δv

$$\delta E_V = \delta \mathbf{v} \cdot \delta \mathbf{J}' = \frac{m\delta \mathrm{v}^2/2}{V}$$

represents the change of kinetic energy of the mass m per unit volume. Relevant interest has the relationship that links the diffusion coefficient to the electrical conductivity σ. An elementary way to show the link between σ and D exploits the eq 2,4. Let us specify the additional force as that due to an electric field $\mathbf{E}$ acting on the charge ze of the diffusing species; so, eqs 2,4 and 2,5 yield $\mathbf{v}=(k_BT)^{-1} D\mathbf{E}$ i.e., $\mathbf{v}=-(k_BT)^{-1} zeD\nabla\phi$, being ϕ the electric potential. Multiply now both sides by zec and note that we obtain at left hand side a charge flow $\mathbf{J}_{ch}=zec\mathbf{v}$; since $\mathbf{J}_{ch}=-\sigma\nabla\phi$, which is nothing else but the Ohm law, the result is

$$\sigma = \frac{D(ze)^2 c}{k_B T} \qquad 2,12$$

Moreover the drift velocity of the charge carriers results from both concentration gradient, eq 2,3, and electric potential

$$\mathbf{v} = -\frac{D}{k_B T}(ze\nabla\phi + \nabla\mu)$$

whereas eq 2,1 yields the corresponding flow, often expressed through the so called electrochemical potential Φ

$$\mathbf{J} = -\frac{cD}{k_B T}\nabla\Phi \qquad \Phi = ze\phi + \mu$$

These relationships have fundamental importance in modelling the conductivity in electrolyte of solid oxide fuel cells in the case of a multi-ion conduction mechanism[7]; the aim of the quoted paper was to solve the 3D transport equation for each diffusing species

$$\nabla \cdot \left[D\left(\nabla c + \alpha \frac{zec}{k_B T}\nabla\phi - \frac{c\mathbf{F}}{k_B T} \right) \right] - \frac{\partial c}{\partial t} = 0$$

being $\mathbf{F}$ the stress field of the dislocations and α a correlation coefficient relating ionic conduction and self-diffusion, and to simulate the electric performances of the cell as a function of D. A significant result of the computer simulation concerned the concept of *ion highways*, heavily involving the interaction between stress field of the dislocations and drift speed of the charge carriers. An interesting link exists also between D and the mean squared displacement $\sqrt{<\delta x^2>}$ travelled by any number of non-interacting particles in the absence of a net driving force. An elementary derivation of this link in the 1D case is carried out here, considering an ideal reference plane crossed by any particles randomly moving in the presence of a concentration gradient δc along the x-axis; this assumption reduces for simplicity the problem to the one dimensional motion perpendicularly to an arbitrary cross section of the plane. Consider $\partial c/\partial x$ on the reference plane and the concentration difference $\delta c=c_2-c_1$ between two arbitrary points δx apart at the opposite sides of the plane with $c_2>c_1$. Write $\delta c = (\partial c/\partial x)\delta x$ and multiply both sides of the equation by the diffusion rate v_x defined as $\delta x/\delta t$; i.e., δx is the distance travelled by the particles diffusing during the time range δt, both arbitrary and fixed once for all so that v_x is constant. One finds for the net flux δJ_x of matter crossing the plane $\delta J_x = \mathrm{v}_x \delta c = (\partial c/\partial x)\delta x^2/\delta t$. Averaging both sides of the equation that define δJ_x to calculate the average concentration $<c>$ on the plane, one finds at right hand side $<\delta x^2>/\delta t$, at left hand side

$<\delta J_x>$. Regard the latter as the average net flux of matter $J_{eff} = -(c_2 - <c>)v_x$ crossing the plane and define $<c>$ in agreement with the conservation of mass flow $(c_2 - <c>)v_x = (<c> - c_1)v_x$ on the plane; thus $<\delta c>v_x$ is twice $-J_{eff}$, i.e., $2J_{eff} = -(\partial c/\partial x) < \delta x^2 > / \delta t$. So, comparing with eq 2,2, one finds the well known result

$$D = \frac{< \delta x^2 >}{2\delta t} \qquad 2,13$$

The extension of this result to the 3D case is trivial in an isotropic diffusion medium, where by symmetry $< \delta x^2 > = < \delta y^2 > = < \delta z^2 >$, so that $< \delta r^2 > = < \delta x^2 > + < \delta y^2 > + < \delta z^2 > = 3 < \delta x^2 >$; thus eq 2,13 reads

$$D = \frac{< \delta r^2 >}{6\delta t}$$

These results show that the diffusion coefficient, early introduced as a mere proportionality factor between thermodynamic force and displacement rate, actually enters into a large variety of phenomena of physical and technological interest. Actually this is not an accident, since several physical laws, in fact, present a formal analogy between flux and gradient with the Fick law: for example the amounts concerned by the Fourier heat diffusion law are heat and temperature gradients, whereas the Ohm law concerns instead current and voltage gradients. The former reads $\mathbf{J}_Q = -K\nabla T$, where K is the heat conductivity and $\mathbf{J}_Q$ the heat flow; the latter $\mathbf{J}_{ch} = \sigma\mathbf{E}$, where σ is the electrical conductivity and $\mathbf{J}_{ch}$ the charge flow, is in fact analogous simply recalling the definition $\mathbf{E} = -\nabla\phi$. Both share a similar form to describe the displacement of heat or charges per unit time and cross section of diffusing medium. Even the Poiseuille law $\mathbf{J} = -(R^2/8\eta)\nabla p$ describes the motion of a fluid of viscosity η through a cylindrical pipe of radius R in the presence of a pressure gradient ∇p; in the cases where it is possible to assume a dependence of p upon c, e.g., through the related partial pressure in gas phase, writing $\nabla p = -(\partial p/\partial c)\nabla c$ one finds formally

$$D = \frac{R^2}{8\eta}\frac{\partial p}{\partial c} \qquad 2,14$$

A further relationship linking the viscosity to the diffusion coefficient is the so called Einstein-Stokes equation that exploits the Stokes law $\beta^{-1} = 6\pi\eta r$, valid at low Reynolds number; at left hand side appears the drag coefficient, inversely proportional to the mobility of a spherical particle of radius r moving in a fluid of viscosity η; so eq 11 yields

$$D = \frac{kT}{6\pi\eta r} \qquad 2,15$$

This result is of interest to describe the diffusion of large molecules possibly having non-spherical geometry; for a spherical geometry of the diffusing molecule $r = (3MV/4\pi N)^{1/3}$, being V the partial specific volume and M the molecular weight. Hence the ratio

$$\frac{D_{sph}}{D_{non-sph}} = \left(\frac{M_{sph}}{M_{non-sph}}\right)^{1/3}$$

Hence, measurements of diffusivity provide information about the deviation from this law and thus about the geometry of such molecules by comparison with that of a reference molecule whose geometry and M are known. Thus a common gradient law describes different forms of kinetic energy, due to the oscillation frequency of atoms/ions/molecules within the heat diffusion thermodynamic system and the velocity of electrons propagating within a conductor, respectively.

To guess the form of D, note that β/D has the physical dimensions of a reciprocal energy. Therefore it is certainly possible to write the following dimensional equation

$$\frac{\partial\beta}{\partial D} = \frac{1}{E} = q\frac{\beta}{D} \qquad 2,16$$

where E denotes an arbitrary energy and q is an arbitrary proportionality factor; accordingly, the first eq 2,5 requires $E = k_BT/q$. Write now β as $\beta = \beta_0 + \beta_1(x - x_0) + \beta_2(x - x_0)^2 + \ldots$, where x is an appropriate parameter as a function of which is the series expansion and x_0 a reference value of this parameter corresponding to β_0; for instance x could be the local chemical composition or the temperature. Hence β_0 can be regarded as a constant, whereas the convergence of the series requires $\beta_1(x - x_0) << \beta_0$ and thus $\beta_2(x - x_0)^2 << \beta_1(x - x_0)$ as well. So eq 2,16 reads, with good approximation,

$$\frac{\partial\left(\beta_1(x - x_o)\right)}{\partial D} = \frac{k_BT}{E}\frac{\beta_o}{D}$$

having neglected the higher order terms for simplicity. This equation is immediately integrated; the result is $\log(D/D_0) = (E/k_BT\beta_0)\int d(\beta_1(x - x_0))$, being D_0 an arbitrary integration constant. Owing to the fact that E is arbitrary, it is possible to write $\varepsilon = -E\beta_0^{-1}\int d(\beta_1(x - x_0)$ whatever the result of the integral might be. The minus sign is easily justified in several ways. First of all, this is possible because indeed one can chose the arbitrary value of D_0 such that $D_0 > D$. Second for T→0 one reasonably expects that the diffusion process is quenched, likewise the thermal activation of the lattice vibrations; so the right hand side tending to minus infinity requires T→0, which is actually reasonable. Third, without the minus sign $\beta_0 \to 0$ would mean vanishing mobility and thus $\mathbf{v} \to 0$ with divergent D at any finite T, which is clearly unphysical. Hence, one finds

$$D = D_0 \exp(-\varepsilon / k_B T) \qquad 2,17$$

Indeed this form of D is typical of Arrhenius-like processes that occur via an appropriate activation energy and is very well known; for brevity further comments on eq 2,17 are omitted.

From a mathematical point of view, the second Fick law is often solved approximately regarding D as a constant to simplify the calculations. This approximation is easily removed, as actually the diffusion coefficient changes depending on T and on the local chemical composition of the diffusion medium. Suppose for instance $D=D(c,T)$, whose dependence upon c and T is assumed to be known; defining $\varphi = \int (D(c',T)/D_0)\,dc'$, which can be calculated, then $\partial\varphi / \partial x = (D / D_o)\partial c / \partial x$. In an analogous way $\partial\varphi / \partial t = (D / D_o)\partial c / \partial t$. So the second Fick equation reads $D\partial^2\varphi / \partial x^2 = \partial\varphi / \partial t$, which can be solved more easily with respect to $\varphi=\varphi(x,t)$ with D taken out of the derivative; the latter in turn yields the functional dependence of D on c. Let us mention very shortly that the form of the solution of the Fick equation strongly depends on the boundary conditions of the specific problem; typically one can assume an infinite source of diffusing species, e.g. two sheets of different metals in contact having finite thicknesses, or a finite source of diffusing species, e.g. the case of a very thin sheet of a metal that diffuses into a thick substrate of different material. The solutions are, respectively:

$\varphi(x,t) = \varphi_o \, erf(x / \sqrt{4Dt})$, where

$erf(y) = 2\pi^{-1/2} \int_0^y \exp(-\zeta^2)\,d\zeta$ is the error function and φ_0 the integration constant;

$$\varphi(x,t) = \frac{Nm}{\sqrt{4\pi Dt}} \exp(-x^2 / 4Dt)$$

, where N is the number of source atoms of mass m per unit surface area.

In any case the Fick laws provide a continuum description of diffusion, regardless of any correlation between diffusion coefficient and microstructure of the medium; any information on the latter is hidden in the value of D, so far merely regarded as a macroscopic thermodynamic parameter that summarizes statistically the local microscopic details of the transport mechanism.

Microscopic approach

All of the previous considerations are true, however, in isotropic media only, where the diffusion coefficient is uniquely defined. In anisotropic media the diffusion coefficient must be replaced by a tensor, i.e.,

$$\mathrm{J} = -\begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zx} & D_{zz} \end{pmatrix} \begin{pmatrix} \partial c/\partial x \\ \partial c/\partial y \\ \partial c/\partial z \end{pmatrix}$$

Owing to Onsanger's reciprocity theorem, the diffusivity tensor is symmetric; since any such tensor can be transformed to its three principal axes, the D matrix reduces to the form

$$\begin{pmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{pmatrix}$$

This matrix defines therefore three diffusion principal coefficients, the unique eq 2,1 splits into three equations having the forms $J_i = D_i \partial c / \partial x_i$ with i=1,2,3. Strictly speaking the cubic crystal symmetry only is isotropic, so that i=1, i.e., $D_i = D$; instead the hexagonal, tetragonal and rhombohedral symmetries have, for instance, i=2, i.e., $D_1 = D_2 \neq D_3$, with the principal axis parallel to their crystal axis. From an experimental point of view, therefore, the diffusion coefficient should be evaluated in principle with one-dimensional measurements in single crystals oriented along well defined crystallographic directions; if one of these directions is parallel to one of the principal axes, then they are measured directly D_1 or D_2 or D_3. Of course on could take into account the anisotropic effect merely from the macroscopic point of view; yet these considerations compel paying a greater attention to the crystal structure of the diffusion medium and to the atomistic character of matter. To shortly explain purposes and methods of the microscopic approach let us start just from the diffusion coefficient. Consider two neighbour planes with the same index of a crystal lattice; let n_1 and n_2 the respective atom densities, i.e., numbers of atoms of mass m per unit surface, and a their spacing. If for instance $n_2>n_1$, one expects a net excess of jumps from plane 2 to plane 1, that tends to cancel their different densities. The net flux J_n of atom jumps between the crystal planes is thus calculated by introducing a further quantity, the jump frequency ν_n; then J_n is given by $(n_2-n_1)m\nu_n$ in agreement with the dimension mass per unit surface and time already introduced. Rewrite this result as

$$J_n=[(c_2-c_1)a^{-1}]a^2\nu_n \qquad 3,1$$

noting that $c_i=n_im/a$ is the usual definition of concentration; also, $a^2\nu_n$ has dimension $lenght^2$ x $time^{-1}$ and is calculated through the length that defines the direction of the jumps. So it is reasonable to write $J_n=[(c_2-c_1)a^{-1}]D_n$. Eventually, if c_1 and c_2 are close to each other and the lattice spacing is small, then the amount in parenthesis tends to $-\partial c/\partial a$; hence, one finds again the equation $J_n=-D_n\partial c/\partial a$ formally similar to eq 2,2. Now however a simple reasoning, based on the microscopic features of the crystal, i.e., the excess of atoms in either plane and the jump rate, explains the driving force of the diffusion process. Of course there is no reason to expect that ν_n is the same for all planes, e.g. because of their different spacing and atom densities; even without theoretical considerations, therefore, it is immediately evident why D is in general different for various crystal planes. The mechanisms controlling D are directly related to the microstructure, which prospects further chances of theoretical analysis about the diffusion coefficient. The random walk theory, based on the modelling of atomic jumps, allows a broad understanding of the microscopic details that govern the diffusion process. In solids the atom displacement involves lattice defects, in particular the vacancies[8]; the distance travelled by the diffusing species results from the sum of multiple jump events, each of length λ. From the kinetic point of view the jump frequency is of the order of the Debye frequency, 10^{12} to 10^{13} s^{-1}, whereas the residence time on a lattice site is much longer than the reciprocal jump frequency. Without going into the mathematical details of the theory, it is evident the fundamental role of the activation energy, upon which the resulting jump rate depends. Elementary considerations show that $D=Z^{-1}\nu\lambda^2$, where the coefficient Z is the number of nearest interstices available for the jump, i.e., the coordination number; for instance, in a cubic lattice Z=6. The residence time is instead $\tau=(Z\nu)^{-1}$. The thermal energy of atoms in a lattice is of the order of kT, i.e., 10^{-2} eV at room temperature, whereas the activation energy ΔG_a is much higher, of the order of some eV[9], so the Boltzmann distribution law shows that the atoms mostly vibrate around their equilibrium lattice sites or interstitial positions. Calculations of molecular dynamics show that large oscillations allow displacements by a single step λ, after which the atom is deactivated because of the energy spent to overcome the energy barrier of a successful jump. Further oscillations on the new position allow performing again another jump, and so on. The free energy gap between saddle point and equilibrium energy describes the energy balance of each jump as a function of the migration enthalpy and entropy. Two kinds of jumps are possible depending on whether each one of them has or not memory of the previous history. An example of the former kind regards atom and vacancy exchanging their places in the lattice: one atom fills the site where was previously located a vacancy, which therefore annihilates, whereas a new vacancy forms in the lattice site previously occupied by the atom. If so, then there is a significant probability that after the first jump the atom returns back to the previous position; this circumstance decreases the net displacement probability. Without memory of the previous event, instead, we speak about a Markov sequence or uncorrelated random walk; a typical example of this kind of process is the diffusion in a lattice via an interstitial mechanism, e.g. a tracer atom randomly moving via successive jumps through various interstitial positions. Although also in this case the atom has the chance of returning back in the initial position, the probability of reversed path is now less significant than before, but the interstitial diffusion mechanism is less efficient than that activated by vacancies. It is easy to briefly exemplify the non-Markov mechanism through the so called correlation coefficient, whose meaning is sketched as follows thinking to a tracer atom. The total path $X=\sum_n x_n$ of this atom after an arbitrary number *n* of jumps defines the scalar $<X^2>=\sum_n<x^2_n>+2\sum_i\sum_j<x_ix_j>$; the first sum averages single jumps, the second two different jumps, e.g. the *i*-th one followed by the *j*-th one. The Markov sequence of events requires $<X^2_{rnd}>=\sum_n<x^2_n>$; the subscript *rnd* stands for random. Indeed, to every pair of jumps x_ix_j correspond possible sequences of jumps x_ix_j, equal and of opposite sign, so that the global contribution of the second sum to the random path $<X^2>$ is statistically null. It is not so, however, if each jump has some memory of the previous ones. Thus, it is possible to introduce the non-Markovian correlation factor defined as follows

$$f=\lim_{n\to\infty}\frac{<X^2>}{<X^2_{rnd}>}=1+2f_0 \qquad f_0=\frac{\sum_i\sum_j<x_ix_j>}{\sum_n<x^2_n>}$$

Formally *f* consists of a Markovian jump sequence plus a correction factor f_0 controlled by the sums of jumps. To guess the sign of the non-Markovian term consider again the atom diffusion in solids, activated by vacancies taking also into account the non-null chance of jumps that follow the direction of motion of the vacancy. This occurrence expectedly reverses the diffusion path, thus providing a negative contribution to the terms *ij* of the sum, i.e., f_0 is negative. Hence, the conclusion is that $f_0\leq 1$: the equality sign stands in Markovian processes like that of interstitial diffusion. The idea of describing the diffusion path as the sum of atomic jumps is validated both by its reasonable consequences and by its agreement with the results previously found in a macroscopic way. Let us sketch this point briefly, considering the 1D diffusion of particles along the *x*-axis first. Let $c(x,t)$ the number of particles on a plane perpendicular to the *x*-axis located at the point at the time and imagine that this number results from the number of particles $c(x-\delta x,t-\delta t)$ that have travelled a distance δx during the time range δt. The displacement is described introducing the probability distribution function $w(\delta x,\delta t)$ and supposed to depend on δt only; this means that the diffusivity does not depend on the particular choice of *x* and *t*. Therefore it is possible to write $c(x,t)=\Sigma_{\delta x}c(x-\delta x,t-\delta t)w(\delta x,\delta t)$, i.e., in general the current position *x* is reached after a certain number of jumps, each one of length δx. Expanding the right and left sides of this equation in series of powers respectively around $\delta x=0$ and $\delta t=0$ yields in principle, with an arbitrary number of terms,

$$c(x,t-\delta t)+\frac{\partial c}{\partial t}\delta t=\sum_{\delta x}w(\delta x,\delta t)\left(c(x,t-\delta t)-\frac{\partial c}{\partial x}\delta x+\frac{1}{2}\frac{\partial^2 c}{\partial x^2}\delta x^2+\cdots\right)$$

Normalizing to 1 the probability function, one finds by definition $\Sigma_{\delta x}w(\delta x,\delta t)=1$. The derivatives $\partial^i c/\partial x^i$ have fixed values because they are calculated at $x-\delta x$ and $t-\delta t$; so one finds

$$\frac{\partial c}{\partial t}=-\frac{<\delta x>}{\delta t}\frac{\partial c}{\partial x}+\frac{1}{2}\frac{<\delta x^2>}{\delta t}\frac{\partial^2 c}{\partial x^2}+\cdots$$

$$<\delta x>=\Sigma_{\delta x}w(\delta x,\delta t)\delta x$$

$$<\delta x^2>=\Sigma_{\delta x}w(\delta x,\delta t)\delta x^2$$

If in particular $<\delta x>=0$ in the absence of a drift force and the higher order terms are neglected, then by comparison with eq 2,1 one finds

$$D=\frac{1}{2}\frac{<\delta x^2>}{\delta t}$$

as previously found in eq 2,13.

In principle it is reasonable to assume that the total energy balance of the diffusion process is given by $\delta\varepsilon=\varepsilon_{end}-\varepsilon_{init}$, i.e., by the energy difference between the final and initial configuration of the diffusion system; this configuration change is in turn related to the statistical formulation of the entropy describing the transition from the initial non-equilibrium state to the final equilibrium state of the diffusion system. The conceptual basis to be further implemented in the next section through quantum considerations thus concerns three items summarized as follows: (i) physical root of the intuitive definition of mass flow, eq 2,1; (ii) physical root of the gradient concentration law, eq 2,2; (iii) connection between diffusion driven mass flow and entropy evolution $-\sum\pi_i\log\pi_i\rightarrow-\log\pi^{eq}$.

Quantum approach

This section introduces the basic ideas to describe the diffusion system according to the statistical formulation of quantum uncertainty, i.e., by exploiting the relationships

$$\Delta x\Delta p_x=n\hbar=\Delta t\Delta\varepsilon \qquad 4,1$$

where *n* is an arbitrary number of quantum states allowed to any particle moving in the space range Δx with conjugate momentum falling in the momentum range Δp_x. The second equality is formally obtained from the first one defining $\Delta t=\Delta x/v_x$ and $\Delta\varepsilon=\Delta p_x/v_x$ linked by the same n, i.e., v_x is the average velocity with which a delocalized particle travels through Δx during the time range Δt. No hypothesis is necessary about the ranges that quantify the concepts of space and time uncertainty; they are positive by definition, their sizes are arbitrary, unknown and unknowable. Moreover nothing is known about their analytical form, e.g., any local functional relationship like $p_x=p_x(x)$ within Δx is physically meaningless because both local values p_x and x are assumed random, unknown and unpredictable. Yet, despite such an agnostic point of view that disregards since the beginning and conceptually any local value, relevant information can be obtained through eqs 4,1, which indeed have a very general valence; they allow successful describing complex quantum systems like many-electron atoms and diatomic molecules[9,10]. To exploit the concept of uncertainty in the present case, divide both sides of $\Delta\varepsilon=\Delta p_x v_x$ by an arbitrary volume V and an arbitrary velocity of modulus v; then $\Delta\varepsilon/(vV)$ takes the physical dimensions $ml^{-2}t^{-1}$, i.e., it reads ΔJ_x, while $v_x\Delta p_x/(vV)$ is dimensionally a concentration times a velocity, i.e., it reads $\Delta(cv_x)$. Both notations are reasonable because Δp_x and v_x are arbitrary along with $\Delta\varepsilon$ too, so that no proportionality constants are necessary. So the statistical formulation of the quantum uncertainty yields $\Delta J_x = \Delta(cv_x)$ that corresponds in 3D to the vector equation $\Delta\mathbf{J} = \Delta(c\mathbf{v})$, whence the form

$$J = cv \qquad 4,2$$

is to be expected for the random local values within the respective uncertainty ranges. Since the range sizes are arbitrary, this last result is compatible in particular with ranges $\delta J = \delta(cv)$, small enough to be rewritten as $\delta J = v\delta c + c\delta v$. We already know this equation, previously inferred in a mere classical way from the intuitive definition $\mathbf{J} = cv$; however in eq 2,10 both $\mathbf{J}$ and cv could be exactly defined in principle, here these quantities are unknowable values within their uncertainty ranges. Now let us show that even the first Fick equation can be obtained with the help of eqs 4,1. The topic has been fully described in [6], here only the main points of the paper are highlighted. Consider $\Delta J_x = \Delta\varepsilon/Vv=\Delta p_x/V$ with $v=v_x$ and put $V=\Delta x^3$; there is no need to define V as $\Delta x\Delta y\Delta z$ because, being Δx arbitrary like Δy and Δz, any value allowed to their product is identically allowed to Δx^3 too. Being $\Delta x^{-3}=-(1/2)\partial\Delta x^{-2}/\partial\Delta x$, then, by consequence of eqs 4,1

$$\Delta J_x=-(n^2\hbar^2)^{-1}\Delta p_x^2\partial\Delta p_x/\partial\Delta x \qquad \Delta x = x - x_0 \qquad 4,3$$

Here the coordinate x_0 denotes the position of V with respect to the origin of an arbitrary system of coordinates, x is the current variable denoting the size of Δx and thus of V. Moreover, one also finds $\Delta J_x=-(3n^2\hbar^2)^{-1}\partial\Delta p_x^3/\partial\Delta x$ i.e., $\Delta J_x=-(n\hbar/3)\partial(1/\Delta x^3)/\partial\Delta x$. If m remains constant within Δx^3, which means a simple redistribution of diffusing species without sinks or sources inside this volume, then

$$\Delta J_x=-\frac{n\hbar}{3m}\frac{\partial(m/\Delta x^3)}{\partial\Delta x};$$

this is, in principle, possible because Δx^3 is arbitrary and thus can be accordingly regarded. Note that this position establishes a constrain on m, which in fact is regarded as a constant; indeed $m/\Delta x^3$ has physical dimensions of constant mass per unit volume, i.e., that simply redistributed within V. Therefore c changes as a function of Δx because V, early introduced as an arbitrary volume for dimensional purposes, does so; indeed it is expressed as $\partial\Delta x^{-3}/\partial x$. Of course, another x-coordinate defines another m' constant in its own volume $\Delta x'^3$ and so on. This means distributing a given total mass of diffusing species in several elementary masses m_i constant in the respective elementary volumes Δx_i^3; yet, m_i can be regarded as average values function of time. This distribution does not need being calculated in detail, i.e., m_i and Δx_i^3 have conceptual worth and are, in principle, arbitrary. Moreover, note that $\hbar/m$ has physical dimensions lenght²time⁻¹. Thus, putting $c=m/\Delta x^3$ and $n\hbar/m=D$, one finds $\Delta J_x=-D\partial c/\partial\Delta x$; note that it results $D=D(x,t)$ with m defined in this way. If x_0 is a constant uniquely defined for each elementary volume, while x is the current variable defining the size change $d\Delta x$, then $d\Delta x=dx$; hence, the form of the random J_x included within ΔJ_x must be

$$J_x=-D\frac{\partial c}{\partial x} \qquad 4,4$$

The key point to infer eq 4,4 is the quantity $\Delta p_x^2\partial\Delta p_x/\partial x$ inherent the eq 4,3. Indeed, a trivial numerical factor apart, $\Delta p^2_x d\Delta p_x$ is proportional to the number of particles, the momentum of which was, at a given time, included in a sphere of radius Δp_x and after an arbitrary time range δt takes values falling in the section of sphere between Δp_x and $\Delta p_x + d\Delta p_x$. It means that J_x is defined by the concentration change due to an outwards/inwards flow of matter that links $d\Delta p_x$ to $d\Delta x$ and thus to the elementary volume change; indeed $d\Delta p_x$ requires $-\Delta x^{-2}\, d\Delta x$. From eq 4,4, also the second Fick equation follows, as already shown in section 2. Note that now the diffusion volume is regarded as a delocalization volume, for which of course the statistical considerations carried out in section 3 are true. Hence both the definition eq 2,1 of mass flow and the physical hypothesis of eq 2,2 appear to be corollaries of the quantum equations 4,1; all of the considerations of section 2 have therefore quantum basis themselves. A further step forwards is possible identically rewriting eq 4,4 as follows

$$J_x = -Dc_o f \frac{\partial \log(f)}{\partial x} \qquad f = \frac{c}{c_o} \qquad c_o = \frac{m}{V_o} \qquad c_0 = c_0(t) \qquad 4{,}5$$

For sake of brevity let us sketch here only the principal steps of the mathematical approach explained in detail in [6]. Calculate eq 4,5 in an arbitrary point x_a; one finds, with obvious notation,

$$J_a = -D_a c_o f_a \left.\frac{\partial \log(f)}{\partial x}\right|_{f_a} = -D_a \left.\frac{\partial c}{\partial x}\right|_{x=x_a} \qquad f_a = \frac{c_a}{c_o}$$

$$D_a = D(x_a, t) \qquad 4{,}6$$

Note that expanding $\log(x)$ in series of powers around an arbitrary point x_a, one finds

$$\log(x) = \log(x_a) + \left.\frac{\partial \log(x)}{\partial x}\right|_{x=x_a}(x - x_a) + \frac{1}{2}\left.\frac{\partial^2 \log(x)}{\partial x^2}\right|_{x=x_a}(x - x_a)^2 + \cdots$$

which yields at the second order

$$\left.\frac{\partial \log(x)}{\partial x}\right|_{x=x_a} = \frac{\log(x) - \log(x_a)}{x - x_a} - \frac{1}{2}\left.\frac{\partial^2 \log(x)}{\partial x^2}\right|_{x=x_a}(x - x_a)$$

Expand now in series the function $\log(f)$ around x_a and calculate the resulting expression in another arbitrary point x_b; one finds

$$\left.\frac{\partial \log(f)}{\partial x}\right|_{f_a} = \frac{\log(f_b) - \log(f_a)}{x_b - x_a} - \frac{1}{2}\left.\frac{\partial^2 \log(f)}{\partial x^2}\right|_{f_a}(x_b - x_a) - \cdots$$

$$f_b = \frac{c_b}{c_o} \qquad 4{,}7$$

Replacing this result into eq 4,6 one finds

$$\frac{J_a}{J_o} = -f_a \log(f_a) + \left(f_a \log(f_b) - \frac{f_a (x_b - x_a)^2}{2} \left.\frac{\partial^2 \log(f)}{\partial x^2}\right|_{f_a} + \cdots \right)$$

$$J_o = -\frac{D_a c_o}{x_b - x_a} \qquad 4{,}8$$

The ratio J_a/J_o describes by definition the local chance of net mass flow between two arbitrary points x_a and of x_b the diffusion system. Define c_o, whose form has been not yet specified, as $c_o = (c_b - c_a)/\gamma$; here γ is a dimensionless proportionality factor not dependent on x, yet it can depend upon time. Hence, one finds

$$J_o = -\frac{D_a}{\gamma}\frac{c_b - c_a}{x_b - x_a} \qquad f_a = \gamma \frac{c_a}{c_b - c_a} \qquad f_b = \gamma \frac{c_b}{c_b - c_a}$$

$$\gamma = \gamma(t) \qquad 4{,}9$$

The physical meaning of J_o is still the modulus of a mass flow conceptually analogous to J_a; the former has, however, diffusion coefficient $\gamma^{-1} D_a$. Indeed for $x_b \rightarrow x_a$, which requires $c_b \rightarrow c_a$, one finds the expected differential form $J_o = -(D_a \gamma^{-1})\partial c / \partial x$. In this limit, $J_o \rightarrow J_a$ would require $\gamma \rightarrow 1$, whereas instead in general $\gamma \neq 1$ as shown below; this fact suggests that J_o has physical meaning consistent with J_a but differs numerically from the latter. Since the second and third eqs 4,9 require $f_b = \gamma + f_a$, eq 4,8 reads at the second order of series expansion

$$\frac{J_a}{J_o} = -f_a \log(f_a) + \left(f_a \log\left(f_a + \gamma\right) - d_{ab}^2 \left.\frac{\partial^2 \log(f)}{\partial x^2}\right|_{f_a} \right)$$

$$d_{ab}^2 = f_a \frac{(x_b - x_a)^2}{2} \qquad 4{,}10$$

Therefore the time parameter γ controls the evolution of the ratio J_a/J_o. Two chances allow $c_b \rightarrow c_a$. The first chance is for $t \rightarrow 0$, i.e., at the beginning of the diffusion process, when starting coordinate and end coordinate are very close to each other. Omitting the full discussion of this equation, the first result is

$$\lim_{c_a \to c_b} \gamma / (c_b - c_a) = \gamma_{ab} \qquad t \rightarrow 0 \qquad \gamma \rightarrow 0 \qquad 4{,}11$$

i.e., J_a tends to zero for $t \rightarrow 0$, whereas J_o does not. As expected, in agreement with an obvious boundary condition about the beginning of the diffusion process, at $t=0$ the ratio $J_a \rightarrow J_o$ does not describe any net mass flow yet. The second chance allowing $c_b \rightarrow c_a$ is instead for $t \rightarrow \infty$, i.e., when the diffusion system tends to a uniform concentration everywhere. Since in this limit $c_b \rightarrow c_a$ even though $x_a \neq x_b$ requires again $\gamma \rightarrow 0$, one finds

$$\lim_{\substack{c_b \to c_a \\ x_b \neq x_a}} \frac{J_a}{J_o^{eq}} = \frac{D_a}{J_o^{eq}} \left.\frac{\partial c}{\partial x}\right|_{x=x_a} = \gamma - d_{ab}^2 \left.\frac{\partial^2 \log(f)}{\partial x^2}\right|_{f^{eq}}$$

$$t \rightarrow \infty \qquad \gamma \rightarrow 0 \qquad 4{,}12$$

As expected, also in this limit J_a/J_o does not describe any net mass flow because f tends to the constant value f^{eq}. Putting by definition

$$\lim_{c_a \to c_b} \gamma / (c_b - c_a) = \gamma_{ab} \qquad \gamma_{ab} \neq 0 \qquad 4{,}13$$

the left hand side of eq 4,12 reads $(x_b - x_a)\gamma(c_b - c_a)^{-1}(\partial c / \partial x)_{x=x_a}$, whereas the right hand side vanishes for $\gamma \to 0$ if $c_a = c_b = const$ everywhere, whence the notation J_0^{eq} for $f_a \to f^{eq}$. As expected, the uniform concentration entails on microscopic scale the asymptotic thermodynamic equilibrium without net mass transfer. It is possible to demonstrate indeed [6] that summing all terms of eq 4,12 over the indexes *a* and *b* the resulting condition is

$$\sum_{b,a} \lim_{\substack{c_b \to c_a \\ x_b \neq x_a}} \frac{J_a}{J_o^{eq}} = 0 \qquad t = \infty \tag{4,14}$$

At any intermediate times between these limits, instead,

$$\sum_{b,a} \frac{J_a}{J_o} \neq 0 \qquad t > 0 \tag{4,15}$$

The sums are extended to all paths of particles from the respective starting points x_b to their end points x_a; being both coordinates arbitrary, the sums represent, in fact, any path between any points in the diffusion system. An interesting consequence follows summing the expression 4,9

$$\sum_{a,b} \frac{J_a}{J_o} = -\sum_{a,b} f_a \log(f_a) + \sum_{a,b} \left(f_a \log(f_a + \gamma) - d_{ab}^2 \left. \frac{\partial^2 \log(f)}{\partial x^2} \right|_{f_a} \right) \tag{4,16}$$

The sum over all probabilities of diffusion paths yields the resulting configuration change of the diffusion system at any time. Omitting for brevity the discussion of eq 4,16 as a function of time, which exploits the previous considerations about the parameter γ, note that the first addend at right hand side is clearly an entropic term; defining f^{eq} in order that $\sum_{a,b}(f^{eq}) = 1$, whatever the number of terms of the sum might be, then f_a takes the significance of thermodynamic state probability related to the current configuration of the diffusion system. If so, the first sum of eq 4,16 is such that when the system evolves towards the equilibrium, then $-\sum_{a,b} f_a \log(f_a) \to -\sum_{a,b} \log(f^{eq})$. Rewrite now eq 4,16 as follows

$$\sum_{a,b} \frac{J_a}{J_o} = \frac{S_t}{k_B} - \frac{S_o}{k_B} \tag{4,17}$$

being

$$\frac{S_t}{k_B} = -\sum_{a,b} f_a \log(f_a)$$

$$\frac{S_o}{k_B} = -\sum_{a,b} \left(f_a \log(f_a + \gamma) - d_{ab}^2 \left. \frac{\partial^2 \log(f)}{\partial x^2} \right|_{f_a} \right)$$

According to the physical meaning of the ratio J_a/J_o previously emphasized – local chance of net mass flow between two arbitrary points of the diffusion system – the first sum is therefore the flow efficiency throughout the whole diffusion system, i.e., $\Pi_{netflow} = \sum_{a,b} J_a / J_o$. It is therefore possible to introduce the total chance of mass transfer $\prod_{transfer}$ with and without net mass flow, being of course

$$\prod\nolimits_{transfer} = \prod\nolimits_{netflow} + \prod\nolimits_{noneflow} \tag{4,18}$$

This kind of definition is suggested by the possibility of normalizing $\prod_{transfer}$ to 1, which means the total path of the diffusing species prospects the probabilities of effective net displacement or return to the initial position. Comparing with eqs 4,17 and 4,18, one infers

$$\Pi_{transfer} = \frac{S_t}{k_B} \qquad \Pi_{nonetflow} = \frac{S_o}{k_B}$$

In fact S_t, the most general statistical definition of entropy, is also here the most general way to describe the configuration of *N* diffusing particles, the previous elementary masses m_i, in the N_v volumes available in the diffusion medium, the previous Δx_i^3; this is true regardless of whether the current configuration changes or not when the diffusion system approaches the equilibrium condition. Hence $\prod_{netflow}$ describes the probability of configuration change; instead S_0 does not refer to net transfer of atoms, its value reflects the number of ways to realize the current distribution of particles and thus the thermodynamic probability of the current configuration. Hence, the entropic terms surrogate the two different kinds of diffusion mechanisms allowed to occur as a function of time, i.e., they are the quantum equivalent of the Markovian and non-Markovian jumps. The probabilistic character of the quantum information agrees with the statistical definition of entropy inferred through the statistical uncertainty equations 4,1. It is noteworthy to remark that the well known definition of statistical entropy, usually regarded as a postulate, is here obtained as a corollary of eqs 4,1.

Discussion

The distinctive tasks of the present paper were: (i) to show that the definition **J**=*c***v** and the classical postulate **J**=–*D*∇*c* introduce the basic features of any diffusion process in gas, liquid and solid phases; (ii) to show that these equations can be inferred from a general quantum principle, the statistical formulation of uncertainty, which also allows to describe the quantum systems; (iii) to show how the entropy is related to the concept of non-equilibrium state of the diffusion system inherent the definition of flux of matter. These targets were indeed obtained in eqs 4,2 and 4,4, leading to eq 4,17. A more direct evidence of the connection between **J** and entropy is now provided examining just the quantum nature of the mass flow, evidenced replacing v_x of eq 2,3 into the x-component of eq 2,1, which yields with the help of eqs 2,5 and 4,1

$$J_x = -\frac{k_B T}{n\hbar}\Delta x^2 c\frac{\partial \log(c/c_o)}{\partial x} \qquad 5,1$$

Also now an expression appears having the form $c\partial\log(c)/\partial x$, which can be handled in a way completely analogous to that followed in section 4 to infer entropic terms like $c\log(c/c_0)$ of eqs 4,8 and 4,17. Calculating J_x in an arbitrary point x_a around which $\log(x)$ is expanded in series of powers, one easily finds at the first order

$$J_{x_a} = -Qk_B\frac{c}{c_a}\log\left(\frac{c}{c_a}\right) \qquad Q=\frac{T}{n\hbar}\Delta x_a c_a \qquad \Delta x_a = x - x_a \qquad 5,2$$

Here Δx is specified with reference to the arbitrary coordinate x_a. Apart from the factor Q, one recognizes, also in this result, the entropic term to be summed over all the elementary volumes Δx_a^3 that form the whole volume of the diffusion medium. There are two ways to regard the ratio c/c_a, i.e.: as m/m_a if different masses are regarded in a given volume of the diffusion system at different times, or as V_a/V, i.e., regarding equal masses delocalized in different volumes. Both cases fit the statistical definition of entropy, in that they concern in how many ways the arbitrary numbers n_a of particles of the diffusing species, to which the various m_a are proportional, can be arranged in the available volumes, e.g., interstitial sites or vacancies, of the diffusion medium. If V, arbitrary and not yet defined, is regarded as the total diffusion volume, then the thermodynamic character of the ratios of allowed microstates of the whole system becomes evident; if so, then the sum of all J_{x_a} corresponds to the entropic terms previously introduced. Recalling that in eqs 4,1 n is a number of states, $J_x \rightarrow 0$ for $n \rightarrow \infty$ agrees in fact with the eq 2,3: an increase in entropy due to the increase in states accessible to the diffusion system corresponds to the reaching of asymptotic equilibrium where the net mass flow vanishes. As expected, the result here obtained via the time coordinate defining v_x agrees with that previously obtained through the space coordinate only. Verify the validity of eq 5,1 comparing it with eq 4,4, which yields $D=(k_B T/n\hbar)\Delta x^2$. Note that $k_B T/n\hbar$ has physical dimensions of *time*$^{-1}$; this ratio defines therefore τ calculating n times $\hbar/k_B T$. Average this equation of D between the time t=0 where $\Delta x^2 \rightarrow 0$ and the time τ where the total diffusion spread is $\Delta x^2 = \Delta x^2_\tau$, which thus yields $\overline{\Delta x^2} = \Delta x_\tau^2/2$; one finds immediately the known Einstein's one-dimensional result previously found

$$D = \frac{1}{2}\frac{\Delta x_\tau^2}{\tau}$$

Moreover note that multiplying and dividing Q of eq 5,2 by an arbitrary frequency ν_*, one finds

$$Q = \frac{J_*}{S_*} \qquad S_* = \frac{n\hbar\nu_*}{T} \qquad J_* = c_a\nu_*\Delta x_a$$

where, by dimensional reasons, S_* and J_* are to be regarded as an entropy and a related matter flux; in particular, the latter is formally analogous to eq 3,1, in which case ν_* has the physical meaning of jump rate between lattice sites here identified by x_a and any x. Hence, replacing these positions in eq 5,2, one finds

$$\frac{J_{x_a}}{J_*} = -S_*^{-1}\left[k_B\frac{c}{c_a}\log\left(\frac{c}{c_a}\right)\right]$$

Defining ν_* as an average jump rate, then shared by all the possible x_a, the S_* does not depend on the particular coordinate x_a; so it can be taken out the summation on all the coordinates allowed to the diffusing species. Thus, once again

$$\sum_{a,x}\frac{J_{x_a}}{J_*} = \frac{S}{S_*} \qquad S = -k_B\sum_{a,x}\frac{c}{c_a}\log\left(\frac{c}{c_a}\right)$$

This confirms the entropic physical meaning of the right hand side of the first eq 5,2, linked to the local mass flow J_{x_a} via a proportionality term S_* constant at a given temperature. Clearly this result is formally similar to the eqs 4,17. Then eqs 4,1 explain the link between concentration gradient law and entropy of diffusion system through elementary algebraic manipulations of formulae, without need of hypotheses *ad hoc* about the physical features of the diffusion system and its driving mechanisms; in principle, the present conclusions are true for diffusion processes in solid or liquid or gas phases. No assumption was made indeed about the coordinates of the points x_a and x_b, falling within the respective elementary volumes Δx_a^3 and Δx_b^3, whose size and position as a function of time have been indeed never specified in section 4; for this reason, eqs 4,14 to 4,17 are never calculated in practice, actually they have mere conceptual meaning. In fact, such kind of local information is irrelevant to calculate the entropy; it is enough to compute how the number of particles corresponding to a given mass can be distributed in various volume elements, regardless of where these latter might actually be in the diffusion medium. It is not surprising that the model describes the time evolution of the system without knowing in detail how the local configuration of particles and volumes is progressively modified as a function of time. Nothing is known about the motion of these particle within their own Δx^3, because it would require some sort of information about x and p_x within their uncertainty ranges. The impossibility of establishing if within this arbitrary volume the motion is, for instance, Markovian or non-Markovian compels admitting that both chances are in fact allowed, whence the probabilistic character of eq 4,18; this also justifies why the diffusing species *must* be involved in a mass transfer process both with and without net displacement of particles. Indeed, as previously emphasized, the entropic terms S_t and S_0 account in a probabilistic way for the chances that the path of the diffusion species entails a real displacement or not. This conclusion does not conflict with the fact that by definition J_x represents a net mass flow explicitly related to an effective concentration gradient; eq 4,4 simply concerns the link between the existence of a local concentration gradient and the tendency of the system to annul the non-equilibrium gradient in agreement with the second law of thermodynamics; yet J_x appears in eq 4,17 as the ratio J_x/J_o, which converts the deterministic definition of mass flow into a time dependent probabilistic event through the time parameter γ; indeed, the latter itself controls the net displacements at $t=0$, at $t=\infty$ and at intermediate times.

Conclusion

The present paper was essentially focused on the basic aspects underlying the concept of mass flow only. The classical treatment of the problem starts from reasonable assumptions, which in effect are proven enough to outline a coherent picture of driving force and essential phenomenology of diffusion in the frame of a thermodynamic approach. A deeper level of knowledge is allowed by the microscopic approach, at the cost however of a much more complicated mathematical formalism and further hypotheses about the local mechanisms governing rate and features of the lattice jumps; only a short sketch on these aspects was possible in this paper, because in general these mechanisms are based on phenomenological assumptions, e.g., via molecular dynamics or functional density approaches. Yet in general these computational methods lack the universal character of the laws of thermodynamics and need mathematical approximations that deserve a dedicated discussion out of the purposes of the present paper. Instead, the previous results show that an essential contribution in this respect is provided by the quantum approach. Even without *ad hoc* hypotheses, e.g., without specifically specifying the gas, or liquid, or solid nature of the diffusion medium, the quantum principles reveal the order → disorder transition inherent the diffusion process. This is not surprising: only a very general principle, formulated through eqs 4,1, can infer another general concept like the entropy as a straightforward corollary. ●

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