An Analysis of States in the Phase Space: Uncertainty, Entropy and Diffusion

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The paper aims to show the physical link between Fick's laws and entropy increase in an isolated diffusion system, initially inhomogeneous and out of the thermodynamic equilibrium, within which transport of matter is allowed to occur. Both the concentration gradient law and the entropic terms characterizing the diffusion process are inferred from the uncertainty equations of statistical quantum mechanics. The approach is very general and holds for diffusion systems in solid, liquid and gas phases.

1 Introduction

Diffusion concerns the transport of matter activated by thermal motion of atoms and molecules. Theoretical and experimental reviews on the mechanisms of mass transfer in solid, liquid and gas phases are widely reported in literature, e.g. [1, 2]. The importance of diffusion is well recognized in the kinetics of microstructural changes, nucleation of new phases, phase transformations, homogeneization and recrystallization of alloys and so on [3]; for instance electric conduction includes phenomena closely related to the transport mechanisms of ions and electrons.The theoretical background of the diffusion is based on an intuitive hypothesis: the driving energy that governs the mass transfer is related to the concentration gradient of molecules or atoms or ions in a diffusion medium, which can be simply the vacuum or a gas/liquid/solid phase. Such an assumption is so simple and reasonable to skip a more profound consideration just about the physical meaning of its general character. It is sensible to expect that this generality, and that of the related concentration gradient driving force itself, should be in fact consequence of some general principle of nature. This consideration recalls in effect the second law of thermodynamics, as concerns in particular the probabilistic character of the entropy. Consider an arbitrary number of particles "a" diffusing within a medium "b"; whatever the former might be, e.g. ions, atoms, molecules and so on, in the following they will be shortly referred to as particles, whereas the system formed by "a" and "b" will be 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 assumed in general in a non-equilibrium state. So a net mass flow was necessarily occurring before reaching this limit situation, after which it is no longer allowed to occur. The entropy seems to be the thermodynamic concept most closely related to describe the transient and final configurations. This means that: (i) the dimensionless entropy formula $-\sum_i w_i \log(w_i)$, where the index i numbers the thermodynamic states allowed to the diffusing particles, should be involved since the beginning into the concentration gradient formulation of any diffusion problem; (ii) this formula should reduce to the simpler Boltzmann form $-\log(w_{eq})$ when the equilibrium configuration is effectively attained; (iii) the mass flow $\mathbf{J}$ is by consequence different from zero only during the time step (i), whereas it reduces to zero at the asymptotic time step (ii). Our knowledge on the diffusion process is thus based on a phenomenological hypothesis, the concentration gradient law, and on a general principle of nature, the entropy. It would be significant to regard both concepts as a natural consequence of a unique and more general principle of nature, without the need of phenomenological assumptions. Of course a general approach to this problem cannot leave out the quantum aspect of any problem inherent the dynamics of particles on microscopic scale. Justifying from the quantum point of view the concentration gradient driven diffusion law would provide a sound physical basis to the general problem of mass transport, whereas the continuity equation, if applicable, would also appear itself as a corollary identified by well-defined physical requirements about the diffusion system. On the one side it is certainly significant to demonstrate by means of a unique general principle 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. On the other side this task seems 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 investigate the quantum basis hidden into the gradient law, i.e. to demonstrate that the 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.

2 Classical background

For simplicity, let us regard the diffusion system as an isolated thermodynamic system formed by an isotropic body of matter and introduce the mass flow as follows:

$$\mathbf{J} = c\mathbf{v}, \tag{2,1}$$

where c is the concentration or more in general the activity of the diffusing particle and $\mathbf{v}$ its displacement velocity. Eq.

2,1 is simply a definition. A further equation appears necessary to introduce a physical hypothesis about the thermodynamic force **F** that triggers the flow. Expressing this hypothesis through the following equation, known as first Fick law

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

and combining these equations, one finds indeed

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

where c_0 is an arbitrary reference concentration not dependent upon x but possibly dependent on time. The definition of mobility β of the diffusing particle

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

entails therefore as a consequence at constant T

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

One finds therefore through the definition of mobility both the sought force, which reasonably results equal to the gradient of the potential energy $\mu = k_B T \log(c/c_0)$, and the well known Einstein equation linking β to D. The form of **F** provides a partial answer to the aforesaid point (iii): if c is equal everywhere in the diffusion system, then it does not longer depend upon x; so, defining c_0 equal or proportional to this uniform limit value of c, one finds $\mathbf{F} = 0$ and thus $\mathbf{v} = 0$ everywhere. This shows that **F** accounts for the net mass flow in the diffusion system until $c \to c_0$. These preliminary considerations highlight that the diffusion law can be effectively related to a thermodynamic function, the chemical potential, that describes the driving force allowing the transport of matter. Exploit now again the basic definition eq. 2,1 to evidence how arbitrary changes of both c and **v** affect **J**. Consider then

$$\delta\mathbf{J} = \mathbf{v}\delta c + \delta\mathbf{J}', \qquad \delta\mathbf{J}' = c\delta\mathbf{v} \qquad (2,6)$$

in the time range δt during which $\delta\mathbf{J}$ is allowed to occur. Note that δc can be due: (i) to the change δm of m within the reference volume V defining c or (ii) to the change δV of V for fixed m or (iii) to both reasons. In any case, defining the space range $\delta x = v_x \delta t$ where the particles are allowed to diffuse along the x-direction during δt, the x-component of eq. 2,6 reads $\delta J_x/\delta x = \delta c/\delta t + c\delta v_x/\delta x$. So, for infinitesimal changes dc and $d\mathbf{v}$ of the process parameters and of the dynamical variables dt and dx, the last equation reads $\nabla\cdot\mathbf{J} = \partial c/\partial t + c\nabla\cdot\mathbf{v}$, i.e. in general

$$\nabla\cdot\mathbf{J} = \frac{\partial(c + C)}{\partial t}, \qquad C = \int_{t_o}^{t} c'\nabla\cdot\mathbf{v}'dt', \qquad C = C(x, t) \quad (2,7)$$

with the integral calculated between the fixed time t_o, e.g. the beginning of the diffusion process, and the current time t. If holds the condition $\nabla\cdot\mathbf{v} = 0$, then $\nabla\cdot\mathbf{J} = \partial c/\partial t$ describes a particular diffusion process where the rate of concentration change is equal to the gradient of related mass flow, which necessarily means lack of sinks or sources of matter within the volume element where is defined c. Since $c\nabla\cdot\mathbf{v}$ results because of the term $\delta\mathbf{J}'$ additional to $\delta\mathbf{J}$, it appears that the well known second Fick equation is a particular case of eq. 2,6 for $\delta\mathbf{J}' = 0$. Actually $\delta\mathbf{J}' \neq 0$ is due not only to a possible chemical reaction that involves the diffusing particle and modifies the local concentration of the diffusion system but, more in general, also to any local force field that attracts or repels the diffusing particles and perturbs their motion. Note indeed that $\delta\mathbf{J}' = c\mathbf{a}\delta t = \mathbf{F}'_V\delta t$ yields

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

being in general $\mathbf{F} \neq \mathbf{F}'$. The force per unit volume $\mathbf{F}'_V$ that controls the perturbation term $\delta\mathbf{J}'$, appearing in eq. 2,6 as a perturbation of **J** is particularly interesting for charged particles diffusing in an ionic medium where polarized impurities are active. Note indeed that $\mathbf{v}\cdot\mathbf{J}$ has physical dimensions of energy per unit volume; then $\mathbf{v}\cdot\delta\mathbf{J}' = (m\delta \mathrm{v}^2/2)V^{-1}$, i.e. the effect of $\mathbf{F}'_V$ is that of perturbing the kinetic energy of the particle in the interaction volume V. It is usually acknowledged that the time enters into the diffusion equation thanks to the continuity condition that leads to the second Fick law. Yet the mere definition of eq. 2,1 entails an interesting conclusion: regardless of the aforesaid effects related to δm that possibly alter the plain diffusion process, the time evolution of the system is actually consequence of the concentration gradient law; although the Fick hypothesis does not contain explicit reference to the time, this latter enters indeed into the problem through **v**. The present considerations show therefore that the ancillary condition of continuity is not necessary to infer the second Fick law; rather, simply taking into account the finite range δt required to justify $\delta\mathbf{J}$, as nothing changes instantaneously in nature, the continuity condition appears to be itself a corollary of the definition of mass flow and not an additional boundary condition. Otherwise stated, even from a merely classical point of view the time coordinate appears a necessary ingredient together with the space displacement to account for the mass transfer in any diffusion problem; consequently the position $\nabla\cdot\mathbf{v} = 0$ does not represent a supplementary hypothesis "ad hoc" but simply a possible chance allowed for $\delta\mathbf{J}$. This conceptual basis, to be further implemented by quantum considerations reasons in the next section, is characterized by three physical features summarized as follows: (i) the definition of mass flow, eq. 2,1; (ii) the gradient concentration law; (iii) the necessity of introducing diffusion driven displacement $\delta\mathbf{r}$ and time range δt linked by $\delta\mathbf{r} = \mathbf{v}\delta t$, which also introduces the energy range $\delta\varepsilon = (\mathbf{v}\cdot\delta\mathbf{J})V$ corresponding to $\mathbf{F}\cdot\delta\mathbf{r}$ within the reference volume V defining c.

3 Preliminary quantum considerations

This section introduces the basic ideas to describe the diffusion system according to the uncertainty relationships

$$\Delta x \Delta p_x = n\hbar = \Delta t \Delta \varepsilon, \qquad (3,1)$$

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 ranges are taken positive by definition. As already shown in [4], the second equality is obtained from the first one defining formally $\Delta t = \Delta x / v_x$ and $\Delta\varepsilon = \Delta p_x v_x$ linked by the same n; v_x is the velocity with which the particle travels within Δx. No hypothesis is required about the ranges that quantify the concepts of space and time uncertainty. Their sizes, in principle arbitrary, can vary from zero to infinity; 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 p_x and x are assumed random, unknown and unpredictable. Yet, despite such an agnostic point of view, relevant features of the ranges are apparent. First, v_x must be upper bounded. Consider a free particle in finite sized Δx and Δp_x with n finite as well: if $v_x \to \infty$ then $\Delta t \to 0$ would require $\Delta\varepsilon \to \infty$, which in turn would allow in principle an infinite energy ε; but this is impossible once having merged both uncertainties via a unique n, as $\varepsilon \to \infty$ is inconsistent with any p_x falling within the finite range Δp_x and thus necessarily finite itself. Hence the simple fact of having regarded together space and time uncertainties, i.e. admitting that both dynamical variable concur to describe any physical system, requires $v_x \le v_x^{\max}$; eqs. 3,1 entail as a corollary the well acknowledged existence of an upper limit for the propagation rate of any signal. Moreover put $\Delta x = x - x_o$ and consider that the coordinate x_o, whatever it might be, is defined in an appropriate reference system that defines position and size of Δx and v_x as well; yet, being x_o indeterminate and indeterminable, the present approach based on Δx only does not specify in fact any particular reference system. The same holds for course also for the other ranges of eqs. 3,1, in particular for the time frame. Also, in lack of constrains or hypotheses the reference system could be in principle Cartesian or curvilinear or inertial or non-inertial or anything else. This means that any physical problem discarding "a priori" the local dynamical variables and exploiting eqs. 3,1 only, i.e. replacing

$$x \to \Delta x, \qquad p_x \to \Delta p_x, \qquad t \to \Delta t \qquad (3,2)$$

holds by definition in any space-time reference system R. Hence eqs. 3,1 entail that all reference systems are indistinguishable and thus equivalent in describing the properties of quantum particles. If so, it eventually follows that the upper value allowed to v_x, whatever it might be, must be invariant in any R. Indeed v_x is defined by its own reference system; being the former arbitrary, the latter is arbitrary as well. Consider instead a well specified value of v_x, e.g. just its maximum value $v_x^{\max}$; this latter must be uniquely defined in R and in any other R' otherwise R and R' could be identified depending on their own $v_x^{\max}$, e.g. because of a greater velocity allowed in either of them, thus contradicting their indistinguishability. It appears therefore that equivalence of all reference systems and invariance of $v_x^{\max}$ are strictly linked. The time coordinate, previously introduced to account for the finite rate with which occurs the mass flow change $\delta\mathbf{J}$, still appears here as a consequence of the finite velocity v_x with which any particle moves within Δx and entails a finite time range to change the configuration of the diffusion system. Yet now Δt takes a more general physical meaning, as it appears from the previous considerations and it will be shown in the next sections. The uncertainty inherent eqs. 3,1 requires innately a time range for particles delocalized in Δx, i.e.: any physical process characterized by an energy spread $\Delta\varepsilon$ requires a time range Δt during which is to be expected a momentum change falling within Δp_x too. Previous papers [5, 6] have shown that this way of regarding eqs. 3,1 is enough to calculate the energy levels of hydrogenlike and many electron atoms/ions and diatomic molecules without solving any wave equation; then is attracting the idea that even the diffusion model can be formulated in terms of particles randomly spreading within their own delocalization space ranges conceptually arbitrary, unknown and unknowable themselves. As in the quoted papers, the statistical formulation of the quantum uncertainty is the only assumption necessary also in the context of the present problem. Suppose of having N particles in N_V elementary volumes Δx^3 of diffusion medium at a fixed time of the diffusion process. Regardless of the equilibrium or non-equilibrium situation at the given time, let

$$W_{cl} = \binom{N}{N_V}, \quad N = N(t), \quad N_V = N_V(t), \quad V = \Delta x^3 \qquad (3,3)$$

be the number of ways to distribute N classical particles in N_V available sites of the diffusion medium. From a quantum point of view the combinatorial calculus still holds in principle also in the case of identical particles, as it is done in the Fermi-Dirac and Bose-Einstein statistics; one must simply replace W_{cl} with the pertinent expressions of numbers of states taking into account the indistinguishability of identical particles. Note in this respect the characteristic way of working of eqs. 3,1: once accepting the replacements 3,2, the physical interest about the system moves from the constituent particles to their phase space. On the one side just this feature of eqs. 3,1 entails the corollary of quantum indistinguishability of identical particles when considering uniquely ranges of dynamical variables where *any* particle could be found, rather than the actual dynamical variables of the particle itself; indeed this latter is never specified "a priori". On the other side this explains the general worth of the eqs. 3,1 regardless of the specific system concerned: the present model holds in principle for diffusion processes in solid or liquid or gas phase, since no hypothesis is formulated about N and N_V of W_{FD} or W_{BE}. Further information on the process, e.g. the role of lattice defects on the effectiveness of mass transport, are to be introduced "a posteriori" through specific values of the coefficient D only, see eq. 2,2, whose quantum root will be indeed highlighted in the next section. It is important however that regardless of the kind of diffusion system, the computation of the number of allowed states accessible to the particles requires calculating the ways of distributing N objects into N_V volume elements of sizes $\Delta x^3_{1\leq i\leq N_V}$; this is possible even in the present approach because the combinatorial computation of allowed states does not require knowing where exactly are located these volumes in the diffusion system, which indeed would be prevented by eqs. 3,1. Just this computation yields the corresponding entropy of the diffusion system. At the very beginning of the diffusion process one can imagine an isolated ordered system S_0 where all particles are confined in some arbitrary volume of the system; as the particles are allowed to walkover randomly to occupy a greater volume, the number of allowed thermodynamic states progressively increases as a function of time. For $t \to \infty$ the system reaches an asymptotic state S_∞ to which corresponds a net mass flow $\mathbf{J} = 0$. The driving force of the diffusion process is thus certainly correlated to the tendency of the system towards its state of thermodynamic equilibrium and maximum entropy. Thus eqs. 3,3 simply tell that in non-equilibrium conditions the system $S(t)$ at the time t is such that $S_0 \leq S(t) < S_\infty$, until the distribution of particles corresponds to the maximum number of quantum states inherent $S_\infty \neq 0$; correspondingly $\mathbf{J} \neq 0$ describes net mass flow in the system tending the maximum entropy, until when $\mathbf{J} \to 0$. The next section aims to show that this intuitive picture of diffusion process will be inferred together with the concentration gradient law through eqs. 3,1 only, without need of any phenomenological hint.

4 Diffusion quantum model

By definition the uncertainty ranges of eqs. 3,1 include any position and momentum of the particles during the diffusion process, despite both dynamical variables are expected to change as a function of time by effect of an appropriate driving force $\mathbf{F}$. In principle one could think Δx and Δp_x large enough to include any possible change of x and p_x from the initial stage of the diffusion process to the final state of thermodynamic equilibrium; indeed the eqs. 3,1 admit possible interactions of these particles with the surrounding medium along the diffusion path $\delta\Delta x = v_x\delta t$ from $\delta t = 0$ to $\delta t \to \infty$, e.g. by elastic and anelastic collisions, through an appropriate size of the energy range $\Delta\varepsilon$. Owing to the complete arbitrariness of the ranges, however, this approach although sensible does not appear far reaching to get relevant information about the process. Yet it is also possible, and more heuristic, to require that Δx and Δp_x are allowed to change themselves as a function of time without contradicting their arbitrariness and without requiring any information on the local values x and p_x; in effect eqs. 3,1 can be differentiated with respect to t and x whatever the current time and space coordinates of particles might be. Consider thus $\delta\Delta x$ and $\delta\Delta p_x$, rather than δx and δp_x, regardless of whether the displacement of matter from two different points of the diffusing medium occurs with or without net mass flow; $\delta\Delta x$ describes the change of delocalization range to which is related the assumed change of momentum $\delta\Delta p_x$ by effect of $\mathbf{F}$. The force is here easily justified by eqs. 3,1 themselves, regardless of other specific motivations: $\Delta\dot{x}$ defining $\delta\Delta x = \Delta\dot{x}\delta t$ requires $\Delta\dot{p}_x$, which therefore affects the range of values allowed to any p_x; in turn the change of p_x, allowed to occur and thus in fact occurring, entails $F_x = m\partial v_x/\partial t$. Since it is possible to write $\delta\Delta p_x = (\partial\Delta p_x/\partial t)\delta t$, then

$$\frac{\partial\Delta p_x}{\partial t} = -n\hbar\Delta x^{-2}v_x = F_x = m\frac{\partial v_x}{\partial t}, \qquad v_x = \frac{\partial\Delta x}{\partial t}. \quad (4,1)$$

Note that here v_x is not the diffusion velocity of the particle but the rate with which changes Δx, so F_x is defined in the phase space of the particle. Yet this information is enough as concerns the diffusion problem: by effect of F_x the particle is allowed to move faster, being however still delocalized within the larger range $\Delta x' = \Delta x + \delta\Delta x$. This is why the momentum of the particle is allowed to change along with $\delta\Delta x$. The notation of velocity is unique to emphasize that v_x of eq. 4,1 and v_x of the particle defining eqs. 3,1 are both arbitrary and thus assumed coincident. On the one side this representation is consistent with well known ideas of the diffusion process, e.g. particle jumps through different sites in a crystal lattice or particle collisions randomly occurring in gas phase; on the other side it suggests that the local concentration change is described by a constant amount of mass m allowed to move slower or faster in a decreasing or increasing phase space delocalization range depending on the sign of the velocity component v_x. In this way the force component F_x introduced via the deformation of the momentum range is conceptually consistent with that of eq. 2,5: to the momentum change rate that defines the classical force corresponds now, from the point of view of eqs. 3,1, the existence of a force field $\Delta\dot{p}_x$ necessary to account for any possible $\dot{p}_x$ during the diffusion process. Let us differentiate now eqs. 3,1 with respect to x to link the change of size of the delocalization range $\delta\Delta x$ and that of the momentum range $\delta\Delta p_x$ when the particle displaces by δx; this yields

$$\frac{\partial\Delta p_x}{\partial x} = -n\hbar\Delta x^{-2}\frac{\partial\Delta x}{\partial x}. \quad (4,2)$$

Eqs. 4,1 and 4,2 describe the dynamics of the diffusing particle as a function of time in agreement with eqs. 3,1. The classical eqs. 2,6 and 2,7 have introduced $\mathbf{v}$ as macroscopic average velocity describing the net mass flow due to the displacement rate of the particle; now the quantum approach shows how the uncertainty compels regarding a random mass flow in the phase space of the particle: the deterministic force of eq. 2,5, exactly defined at any point of the diffusion system, is now replaced by the random force of eq. 4,1 controlled by arbitrary values of n and Δx. Let us show now that this agnostic point of view, far from being elusive of the problem, is actually source of relevant physical information. The fact that the diffusion is allowed in a given volume $V = (n\hbar)^3\Delta p_x^{-3}$ suggests exploiting an approach conceptually identical but formally different from that introduced in section 2. If the motion of the particle is random, the orientation of its momentum **p** is defined in general within a sphere of radius $|\Delta\mathbf{p}|$ whose volume is thus $\propto \Delta p_x^3$ once taking $\Delta p_x \equiv |\Delta\mathbf{p}|$; since the medium is isotropic and the uncertainty ranges are arbitrary and unknown, there is no necessity to introduce explicitly separate ranges Δp_x, Δp_y and Δp_z. So, instead of starting from $\partial\Delta p_x/\partial x$, it is more convenient considering $a'''\Delta p_x^2\partial\Delta p_x/\partial x$, where a''' is a proper proportionality factor; indeed $\hbar^{-3}\Delta p_x^2 d\Delta p_x$ is proportional to the number of particles whose momentum was initially included in a sphere of radius Δp_x and takes after the time range δt values falling in the section of sphere between Δp_x and $\Delta p_x + d\Delta p_x$. So introducing the quantity $a''\partial\Delta p_x^3/\partial x$ means considering a volume element in the momentum space of the particle, which yields in turn with the help of the eq. 3,1 $a'\partial\Delta x^{-3}/\partial x$; here a'' and a' are trivial numerical factors. In conclusion, although starting from a 1D equation, we have introduced a volume element $V = \Delta x^3$ that represents an elementary volume of the diffusion medium where is located a given amount of diffusing mass m corresponding to the concentration c. This defines the equation

$$-\frac{a'}{V^2}\frac{\partial V}{\partial x} = \frac{a'}{V}\frac{\partial \log(V_o/V)}{\partial x}, \qquad (4,3)$$

$$V = V(x,t), \qquad V_o = V_o(t),$$

where the arbitrary constant V_o is a reference volume by definition not dependent on x but possibly dependent on t. Consider first the left hand side of this identity, which reads

$$-\frac{a'}{V^2}\frac{\partial V}{\partial x} = -\frac{a'm}{V^2}\frac{\partial c^{-1}}{\partial x} = \frac{a'm}{c^2V^2}\frac{\partial c}{\partial x} = \frac{a'}{m}\frac{\partial c}{\partial x},$$

$$c = \frac{m}{V}, \qquad c = c(x,t),$$

where c has here the same physical meaning introduced in the early eq. 2,1, although the equation concerns now the phase space rather than a selected volume of matter. This result regards m as a constant with respect to x, i.e. c depends on x through the volume Δx^3 around m only. This point of view, extended to various volumes Δx_i^3 in which the diffusion medium can be ideally divided, entails that the deformation extents $(\Delta x_i + \delta\Delta x_i)^3$ change as a function of x in order that the respective δc_i represent by consequence these changes; this holds when a total amount of matter $\sum_i m_i$ is simply redistributed along x, thus changing the reference volumes that physically define the respective c_i only, or when $\sum_i m_i$ is subjected to change itself because of sinks or sources of matter in the diffusion medium; this is why the time has been explicitly introduced in eqs. 3,3. The right hand side of the first eq. 4,3 depends certainly upon time through V_o; the same holds therefore for the left hand side, i.e. $a' = a'(t)$. Moreover a' depends in general on x as well; indeed it accounts for how $\partial\Delta x^{-3}/\partial x$ changes in general as a function of x, so $a' = a'(x,t)$. Eventually a' must be consistent with the idea of a mass m crossing the momentum space surface proportional to Δp_x^2 during the time range δt, i.e. the physical dimensions of a' must be $\mathrm{mp^2t} = \mathrm{ml^2t^{-1}}$ like that of $\hbar$; this point will be better emphasized in section 5. Specifying thus purposely the proportionality factor a' in order that also the right hand side of eq. 4,3 depends on c, one finds

$$J_x = -D\frac{\partial c}{\partial x}, \qquad a' = -Dm, \qquad D = D(x,t). \qquad (4,4)$$

The physical dimensions of D are therefore $\mathrm{l^2t^{-1}}$. This result represents the first task of the present paper: to infer the concentration gradient law governing any diffusion process as a consequence of the fundamental eq. 3,1, thus showing the quantum origin of the first Fick law. To proceed further, consider now the right hand side of eq. 4,3 rewritten with the help of the second eq. 4,4 as

$$J_x = -Dc_of\frac{\partial \log(f)}{\partial x}, \qquad f = \frac{c}{c_o}, \qquad c_o = \frac{m}{V_o}, \qquad c_o = c_o(t).$$

The first expression calculated in an arbitrary point $x = x_a$ defines $f = f_a$ through the local concentration c_a and reads, with obvious meaning of symbols,

$$J_a = -D_ac_of_a\left.\frac{\partial \log(f)}{\partial x}\right|_{f_a} = -D_a\left.\frac{\partial c}{\partial x}\right|_{x=x_a}, \qquad (4,5)$$

$$f_a = \frac{c_a}{c_o}, \qquad D_a = D(x_a,t).$$

Let us expand in series the function $\log(f)$ around x_a

$$\log(f) = \log(f_a) +$$

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

and calculate this expression in another point x_b, arbitrary as well; this yields

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

$$f_b = \frac{c_b}{c_o}.$$

Replacing in eq. 4,5 and putting $J_o = -D_a c_o/(x_b - x_a)$ one finds

$$\begin{aligned}\frac{J_a}{J_o} &= -f_a \log(f_a) + \\ &+ \left(f_a \log(f_b) - \frac{f_a (x_b - x_a)^2}{2} \left. \frac{\partial^2 \log(f)}{\partial x^2} \right|_{f_a} + \cdots \right).\end{aligned} \qquad (4,7)$$

Rewrite now c_o not yet defined as $c_o = (c_b - c_a)/\gamma$, being γ a dimensionless proportionality factor; this position entails

$$J_o = -\frac{D_a}{\gamma} \frac{c_b - c_a}{x_b - x_a}, \qquad (4,8)$$

$$f_a = \gamma \frac{c_a}{c_b - c_a}, \qquad f_b = \gamma \frac{c_b}{c_b - c_a}, \qquad \gamma = \gamma(t).$$

The last position agrees with the dependence of c_o upon time through V_o. In this way J_o agrees conceptually with J_a and thus with the definition of concentration gradient driven mass flow yet with a different diffusion coefficient $D_o = \gamma^{-1} D_a$; it reduces indeed to the usual differential form $J_o = -D_o \partial c/\partial x$ in the limit $x_b \to x_a$ that necessarily entails $c_b \to c_a$. One would expect that in this limit $J_o \to J_a$, which should require $\gamma \to 1$; however the fact that in general $\gamma \neq 1$, as it is shown below, suggests that J_o is physically consistent with but numerically different from J_a. Before concerning this point, note that the second and third eqs. 4,8 require $f_b = \gamma + f_a$; so eq. 4,7 reads

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

$$d_{ab}^2 = f_a \frac{(x_b - x_a)^2}{2}, \qquad (4,9)$$

having neglected for simplicity the higher order terms of series development of $\log(f)$. The time function γ is therefore a parameter controlling the evolution of the ratio J_a/J_o, which results to be also a function of $x_a - x_b$ and $c_a - c_b$ via f_a. To explain this result, let x_b be the coordinate of a particle at the beginning of the diffusion process and x_a that of the particle at a later time, while c_b and c_a are the respective concentrations. In general $f_a \neq f_b$ for $x_a \neq x_b$ since $c_a \neq c_b$. Consider however in this respect the particular limit condition $c_b \to c_a$ to be expected in two relevant cases: (i) at the very beginning of the diffusion process, when the particle has traveled an infinitesimal path so that x_a is very close to its initial position x_b; (ii) at the end of the diffusion process, when the particle has traveled a finite path with x_a arbitrarily far from x_b but the concentration is uniform throughout the diffusion system. In both cases it is convenient to define $\gamma \to 0$ in order that the undetermined form $\gamma/(c_b - c_a) \to 0/0$ does not necessarily cause divergent values of f_a and f_b. If $c_b \to c_a$ simply because $x_b \to x_a$, case (i), elementary manipulations of eq. 4,9 show that both sides tend to γ provided that $\gamma/f_a \to 0$; in effect this is verified because by definition $\gamma/f_a = (c_b - c_a)/c_a$, see eq. 4,8. The result is thus

$$\lim_{\substack{c_b \to c_a \\ x_b \to x_a}} \frac{J_a}{J_o} = \gamma, \qquad t \to 0, \qquad \gamma \to 0. \qquad (4,10)$$

This simply means that at $t = 0$ there is no net flow of matter as $J_a = 0$. This is reasonable, because after a very short path the particle has high probability to return to its initial position. The second chance for $c_b \to c_a$ even though $x_a \neq x_b$ yields, putting again $\gamma \to 0$,

$$\lim_{\substack{c_b \to c_a \\ x_b \neq x_a}} \frac{J_a}{J_o^{eq}} = \frac{D_a}{J_o^{eq}} \left. \frac{\partial c}{\partial x} \right|_{x = x_a} = \gamma - d_{ab}^2 \left. \frac{\partial^2 \log(f)}{\partial x^2} \right|_{f^{eq}}, \qquad (4,11)$$

$$t \to \infty, \qquad \gamma \to 0.$$

Note that γ can fulfill both conditions if its form is, for instance, like $t/(t^2 + t_o)$. Also note that in fact the behavior of γ can be consistent with any $c_b - c_a$, i.e. whatever this limit might be depending on the kind of diffusion system; being γ defined here by its limit condition only, one could hypothesize any stronger/weaker time dependence, e.g. like $t^k/(t^{k+1} + t_o)$, with k ensuring a finite value of $\gamma(c_b - c_a)^{-1}$ no matter how rapidly $c_a \to c_b$ case by case. Put therefore by definition

$$\lim_{c_a \to c_b} \gamma/(c_b - c_a) = \gamma_{ab}, \qquad \gamma_{ab} \neq 0. \qquad (4,12)$$

The left hand side of eq. 4,11 has now the form

$$(x_b - x_a)\gamma(c_b - c_a)^{-1}(\partial c/\partial x)_{x = x_a}.$$

The right hand side vanishes for $\gamma \to 0$ if $c_a = c_b = const$ everywhere in the diffusion system because f is now a constant defined by the limit $f_a \to f^{eq}$, whence the notation J_o^{eq}. Hence $x_a \neq x_b$ and γ such that γ_{ab} remains finite require $\partial c/\partial x$ vanishing at x_a. As expected, the situation of uniform concentration entails on microscopic scale the asymptotic condition of thermodynamic equilibrium without net mass transfer. Hence the maximum chance of displacement is expected at times intermediate between 0 and infinity. If c_a is the same everywhere because x_a is arbitrary, then actually neither side of eq. 4,11 depends on x; so must hold also on a macroscopic statistical scale the conclusion that a uniform distribution of particles in the diffusion system makes the ratio J_a/J_o^{eq} of eq. 4,9 inconsistent with a net flow of particles. In fact this requires verifying that also the sum of all terms of eq. 4,9 over the indexes a and b fulfills the condition

$$\sum_{b,a} \lim_{\substack{c_b \to c_a \\ x_b \neq x_a}} \frac{J_a}{J_o^{eq}} = 0, \qquad t = \infty, \qquad (4,13)$$

whereas in general, since f_a never diverges,

$$\sum_{b,a} \frac{J_a}{J_o} \neq 0, \qquad t > 0. \qquad (4,14)$$

Actually the sums are extended to all paths of particles from the respective starting points x_b to their end points x_a, which also means summing over all elementary volumes $V_a = \Delta x_a^3$ and $V_b = \Delta x_b^3$ of the diffusing medium in which the particles are found with corresponding concentrations c_a and c_b; since both coordinates are arbitrary, this picture represents in fact any path between any points in the diffusion system. Before demonstrating eq. 4,13, note that the sum has conceptual meaning because in fact it does not require computing anything; it is introduced in principle because neither x_a nor x_b are known but are merely referred to their own V_a and V_b only, wherever their position in the diffusion system might be. Also note that the ratio J_a/J_o entails two harmonized but different definitions of mass flow: at numerator appears a local term, characterized by a concentration difference between two coordinates infinitely close each other, at denominator a macroscopic term characterized by coordinates arbitrarily apart. The flow described by J_a is thus a net flow of matter only controlled by D_a, since by definition an effective concentration gradient corresponds to it. The fact that the sum of ratios is finite in eq. 4,14 and equal to 0 in eq. 4,13 suggests that J_o must concern a macroscopic diffusion term controlled by $D_o = D_a\gamma^{-1}$, describing total displacement of matter that consists in principle of both vanishing and non-vanishing net mass flows because $J_o \neq 0$ even though $J_a = 0$; both flows are in fact allowed to occur in a macroscopic volume of diffusion system, so that neither of them can be excluded. Hence the ratio J_a/J_o in eq. 2,3 represents a sort of "displacement efficiency" corresponding to the thermodynamic force F_x of eq. 4,1, i.e. the chance that the random motion of particles produces an effective flow of matter between two arbitrary volumes within the diffusion system. Eq. 4,13 is then easily justified noting that J_o^{eq} changes sign by exchanging x_a and x_b if $c_a = c_b$, whereas J_a does not for the simple reason that its definition has nothing to do with x_b. In effect just the presence of a concentration gradient makes the environment around the coordinates x_a and x_b physically different; if the coordinates belong to different volumes V_a and V_b that define the respective non-equilibrium concentrations, the displacement of a particle between two points out of the equilibrium is distinguishable from that obtained keeping fixed c_a and c_b with reversed path. Instead the sums $\sum_{a,b}$ and $\sum_{b,a}$ at the equilibrium must be in principle identical, because a uniform distribution of particles within the diffusion system makes indistinguishable starting points and end points; if the diffusion system is perfectly homogeneous, then all volumes $V_i = \Delta x_i^3$ where $c \neq 0$ are identical. This is consequence of having defined c as due to a unique value of m into different volumes of phase space that define V_a and V_b of the diffusing medium. Thus the only chance for a sum to coincide with its own value of opposite sign is that the sum is null. Eq. 4,13 is in fact possible from a mathematical point of view because

$$\partial^2 \log(f)/\partial x^2 = -f^{-2}(\partial f/\partial x)^2 + f^{-1}\partial^2 f/\partial x^2, \qquad (4,15)$$

i.e. the former addend is certainly negative whereas the second can take in principle both signs; hence in principle the sum of terms at right hand side of eq. 4,11 can vanish for an appropriate value of $f_a = f_b = f^{eq}$. Let us return now to eq. 4,9 and note with the help of eq. 4,8 that for $f_a = 0$, i.e. $c_a = 0$, the ratio J_a/J_o is identically null in agreement with its probabilistic meaning. Then, since each coordinate x_a belongs to its own volume V_a that defines c_a, summing over all the possible indexes a means summing over states really accessible to the particles; empty volumes V_a with $c_a = 0$ do not contribute to the sum. It is clear therefore that each f_a represents a possible state allowed for the diffusion system: the values f_a, $f_{a'}$, $f_{a''}$, ... in various points labeled by a, a', a'', ... quantify the ways of distributing the total mass M into various elementary volumes reached by the diffusing species during the diffusion process. Summing both sides of eq. 4,9 over the indexes a and b as done before, means therefore estimating the total probability of mass transport within the diffusion system; then let us introduce, even without carrying out any explicit calculation,

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

Summing over all probabilities of diffusion paths, one finds the resulting configuration change of the diffusion system at any time. A few remarks are enough to guess what to expect from this equation. At $t \to 0$ one finds a sum of terms $f_a \log(1 + \gamma/f_a)$, which for $\gamma \to 0$ tend to γ, plus terms that contain the factor d_{ab}; since in this limit $x_a - x_b \to 0$, neither of them contributes to the sum. At $t > 0$ both addends contribute to the sum. At the equilibrium asymptotic time where again $\gamma = 0$ the sum vanishes according to eq. 4,15 because $f_a \to f^{eq}$ everywhere; this result agrees with the statistical limit $\sum_{a,b} J_a/J_o = 0$ previously inferred, which actually is the macroscopic result revealed by the experience. The first addend at right hand side is clearly an entropic term, whereas f_a defined in eq. 4,5 must have the probabilistic significance of thermodynamic state related to the current configuration of the diffusion system. In effect it is possible to define the limit value f^{eq} such that $\sum_{a,b}(f^{eq}) = 1$ whatever the number of terms of the sum might be; indeed according to eq. 4,12 the finite limit γ_{ab} for $c_b \to c_a$ and $\gamma \to 0$ has been defined finite but not specified; the value of γ_{ab} can be therefore taken as that fulfilling the required property of f^{eq}. If so the first sum of eq. 4,16 is such that when the system evolves towards the equilibrium then

$$-\sum_{a,b} f_a \log(f_a) \to -\sum_{a,b} \log(f^{eq}).$$

The possibility of relating f_a to the thermodynamic probability of states allowed to the diffusing particles defines the physical meaning of the time parameter γ: depending on the value of this latter the totality of possible values of x_a and x_b, whatever they might be, corresponds to a possible arrangement of diffusing particles at the current time starting from an arbitrary initial configuration in the diffusing medium. According to eq. 4,10 it appears that $\gamma = 0$ at $t = 0$ defines the initial configuration. So, through the totality of possible paths from any x_b to any x_a, the parameter $\gamma > 0$ provides an indication of the order→disorder evolution of the configuration of the diffusion system as a function of time. Rewrite now eq. 4,16 as follows

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

where

$$\frac{S_t}{k_B} = -\sum_{a,b} f_a \log(f_a), \qquad (4,18)$$

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

The ratio J_a/J_o has been previously identified as the local chance of net mass flow between two arbitrary points of the diffusion system; the sum at left hand side is therefore the flow efficiency throughout the whole diffusion system, i.e. $\Pi_{netflow} = \sum_{a,b} J_a/J_o$. It is possible therefore to introduce the total chance of mass transfer, Π_{tr}, with and without net mass flow such that of course $\Pi_{tr} = \Pi_{netflow} + \Pi_{nonetflow}$ with obvious notation. This kind of definition is suggested by the possibility of normalizing Π_{tr} to 1. Hence comparing with eqs. 4,17 and 4,18 one infers

$$\Pi_{tr} = \frac{S_t}{k_B}, \qquad \Pi_{nonetflow} = \frac{S_o}{k_B}.$$

Of course S_t, the most general statistical definition of entropy, is also the most general way to describe the configuration of N diffusing particles in the N_V volumes available in the diffusion system, regardless of whether or not the configuration entails a net displacement of matter; instead S_o, which does not refer to net transfer of atoms, counts simply the number of ways to arrange any prefixed distribution of particles and thus the thermodynamic probability of any configuration. Hence the entropic terms concern two different kinds of diffusion mechanisms allowed to occur as a function of time. In effect the possibility that $x_b \to x_a$ is not excluded in the present model even at times t_1, t_2,..; it would be enough to define γ for instance as $t(t-t_1)(t-t_2)/(t+t_o)^4$ in agreement with the previous considerations at $t \to 0$ and $t \to \infty$ and at any time where $x_b \to x_a$ entails $c_b \to c_a$ too. Further considerations are possible about the results hitherto obtained.

5 Discussion

The eqs. 3,1 only have been exploited to highlight the link between concentration gradient law and entropy of diffusion system through elementary considerations. Both concepts have been extracted through elementary algebraic manipulations of the left and right hand sides of the unique eq. 4,3. No hypotheses "ad hoc" have been introduced about the physical features of the diffusion system and its driving mechanisms, leading for instance to Markovian jumps or not, interstitial or defect activated jumps, collisions in gas phase and so on. This is due to the general worth of eqs. 3,1 regardless of the specific system concerned: the present conclusions hold in principle for diffusion processes in solid or liquid or gas phase.

Regarding the statistical formulation of the uncertainty as fundamental principle of nature, the diffusion particles result randomly delocalized within elementary volumes $V = \Delta x^3$ into which can be ideally subdivided the whole system, whose size is however inessential to infer the entropic terms $-f \log f$; these volumes control the concentrations c, which in turn define the thermodynamic states allowed to the diffusing particles in relation to their occupation probability. No assumption was made about the coordinates of the points x_a and x_b falling within the respective elementary volumes, whose number, size and position indeed have been never specified in section 4. In fact such a kind of local information is irrelevant to calculate the entropy; it is enough to compute how N particles can be distributed in N_V volume elements, regardless of how many and where these latter might actually be in the diffusion medium. For this reason the model describes the time evolution of the whole system even without knowing in detail how is progressively modified the configuration of particles and volumes as a function of time. Actually eqs. 4,17 admit also empty elementary volumes that however do not contribute to the total entropy of the system, in fact determined by the distribution of particles only. So S_o in eq. 4,17 corresponds in general to the ways of distributing particles into available microstates described by Δx^3, possibly taking into account the indistinguishability of identical particles, through a dynamical pattern of particles exchanging their occupation volumes even without net mass flow. In effect, also this kind of information does not require a detailed knowledge on the local motion of particles. Nothing is known about this motion within their own Δx^3, because it would require some sort of local information about x and p_x. Being impossible to establish if within this arbitrary volume the motion is for instance Markovian or not, one must admit that both chances are in fact allowed; this also justifies why the diffusing species is involved in mass transfer process with and without net displacement of particles.

This conclusion does not conflict with the fact that J_x entails explicitly an effective concentration gradient; eq. 4,4 is simply the differential formulation of a physical law related to the driving force that triggers the displacement, see eqs. 4,1 and 2,3 and 2,5 as well. The quantum approach behind this step accounts for the physical basis of eq. 2,2, whereas the definition 2,1 has now the rank of a corollary of eq. 4,4 rather than a mere definition: now the physical dimensions of eq. 2,1 are required by quantum motivations, rather than being suggested by a reasonable assumption. Indeed the available information about the diffusion system is inferred in the typical way of quantum mechanics, i.e. without requiring an exact local knowledge about position and momentum of the particles, as follows:

(i) from a macroscopic point of view, through J_o of eq. 4,8 and the entropic terms of eq. 4,17;

(ii) through the probabilistic meaning of the ratio J_a/J_o, which indeed represents the probability of effective mass transport as concerns the chances of Marcovian or non-Marcovian displacements.

Non-trivial consequence of these constrains about our degree of information is the heuristic achievement resulting from the quantum approach with respect to that provided by the classical physics where, from the point of view of the continuity equation, the general character of both Fick's laws is merely due to the lack of sinks/sources perturbing the diffusion process. This fact appeared already in the classical section 2 when it was found that in general $\mathbf{F} \neq \mathbf{F}'$, i.e. the driving force controlling the mass transport is in principle different from that due to local perturbations; the former was uniquely inferred from general hypotheses, eqs. 2,1 and 2,2, the latter remained instead unspecified and does so still now. This is not incompleteness of the present model, but rather the statement that the local perturbations must be purposely specified case by case depending on the physical features of the diffusion system. The worth of any theoretical approach depends on its ability to be generalized beyond the specific problem for which it was formerly conceived. In the case of diffusion the generalization is evident: several important physical laws are expressed through the gradient of a well defined function.

One example is the Fourier equation, $\mathbf{J}_Q = K\nabla T$, where K is the heat conductivity and $\mathbf{J}_Q$ the heat flow; also the Ohm law, $\mathbf{I} = R^{-1}\nabla V$, exhibits a similar form involving the electrical resistance R and the electric potential V to describe the displacement of charges per unit time. Although a common gradient law describes in the former case the transport of heat and in the latter that of electrons, both equations involve forms of kinetic energy, respectively due to the oscillation frequency of atoms/ions/molecules within the heat diffusion thermodynamic system and to the velocity of electrons propagating within a conductor. The entropic aspects in these systems are clear. In the former case they were already evidenced by the crucial Boltzmann intuition, although in lack of any quantum reference; it is not surprising that indeed the statistical definition of entropy inferred here goes back to the early times when the thermodynamics was essentially the science of heat exchanges. The entropy difference in the absence and presence of an electric field is also evident in the latter case: without electric field the motion of the electrons is random, in the **k** space it is represented by a sphere; the presence of the field instead orients the motion of the electrons along a preferential direction. The applied field triggers thus a more ordered motion of electrons, which suggests in turn a loss of total entropy. The analogy with the case discussed in section 4 is clear, although the respective entropy changes have opposite sign. This is not surprising: in an isolated system the entropy always increases, in a system interacting with an external field this is not necessarily true. In all cases however the gradient-like laws, mass diffusion, heat diffusion and Ohm law, are similarly consistent with entropic terms describing the actual numbers of accessible states during the displacement of matter or energy. Another consequence of the generality of the present model concerns the driving force of the diffusion process. In section 2, eq. 2,5 was inferred from eqs. 2,1 and 2,2, the only equations available. Of course the same can be done identically here, though on a more profound quantum basis. Yet the approach carried out in section 4 allowed inferring eq. 4,1, which introduces the concept of force directly as a consequence of eqs. 3,1 and deserves thus further considerations.

First of all, the quantum nature of the mass flow can be evidenced replacing v_x of eq. 4,1 into the x-component of eq 2,1, which yields thanks to eq. 2,5

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

So, simply identifying F_x of eq. 2,5 with that of eq. 4,1 appear again terms of J_x having the form $c\partial\log(c)/\partial x$, which can be handled in a completely analogous way as in section 4 to infer entropic terms like $c\log(c/c_o)$ of eq. 4,5. Moreover $J_x \to 0$ for $n \to \infty$ agrees with eq. 4,16; an increase of entropy due to the increase of states accessible to the diffusion system corresponds to the reaching of asymptotic equilibrium where the net mass flow vanishes. As expected, the result obtained via the time coordinate defining v_x agrees with that previously obtained through the space coordinate only. Yet it is worth remarking that the combined information of the first eq. 4,18 plus eq. 5,1 regards this time behavior of any isolated diffusion system as a spontaneous evolution process: indeed $t \to \infty$ requires $J_x \to 0$ that in turn requires a maximum number of allowed states $n \to \infty$. Two fundamental statements of thermodynamics appear here as corollaries of eqs. 3,1: the statistical formula of entropy and the entropy increase in an isolated system.

Let us exploit eq. 5,1 noting that $k_BT/n\hbar$ has physical dimensions of time. So compute this equation at the time τ where the total diffusion spread lies within an average value of Δx^2 computed starting from $\Delta x^2 \to 0$ at $t = 0$ up to the value $\Delta x^2 = \Delta x_\tau^2$ at the time τ; this means assigning to Δx^2 the particular mean value $\overline{\Delta x^2} = \Delta x_\tau^2/2$ averaged between zero and Δx_τ^2. Comparing with eq. 4,4, one finds immediately the known Einstein's one-dimensional result

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

6 Heuristic aspects of the quantum uncertainty

The present section, based on wide-ranging considerations about v_x, extends somewhat the preliminary remarks introduced in section 3 and has prospective worth. The aim is to emphasize that F_x of eq. 4,1 has actually a physical meaning much more general and contains much more information than the mere eq. 2,5. The byproduct of eqs. 3,1 proposed here is so short, straightforward and relevant to deserve being sketched although, strictly speaking, beyond the mere purposes of the present model; accordingly, however, the results hitherto inferred appear as a particular kind of selected physical information extracted from a broader context able to link topics apparently dissimilar.

Key tools of the following considerations are the replacements 3,2 that compel changing the way to formulate any physical property P from the usual form $P(x, p_x, t)$ to $P(\Delta x, \Delta p_x, \Delta t)$ and thus to $P(\Delta x, n, \Delta\varepsilon)$. In effect the paper [4] has shown that the number n of states coincides with the quantum number appearing in the eigenvalues of the harmonic oscillator, while the papers [5, 6] show that this is true in general; e.g. the number l of states calculated for the angular momentum coincides with the orbital quantum number. The first remark concerns the two ways of expressing F_x in eqs. 4,1:

(i) F_x follows from the definition of momentum itself, $\Delta\dot{p}_x = m\dot{v}_x$, and involves directly the mass m, previously introduced with mere reference to the concentration of diffusion particles and now regarded in general as the mass of any particle accelerated in Δx;

(ii) $F_x = -n\hbar\Delta x^{-2}v_x$ does not involve directly any mass but the deformation rate, $\Delta\dot{x} = v_x$, of Δx only.

Why in (ii) the mere time deformation of Δx in the phase space surrogates the presence of an accelerated mass? The answer rests on the same considerations already introduced in section 4: if a growing/shrinking range is accessible to a particle, then this latter can move faster/slower while being still therein delocalized; the fact that the particle can accelerate/decelerate simply reaffirms once more that nothing in known about how any dynamical variables change within the respective delocalization ranges.

However, in lack of constraining hypotheses, there is no reason to exclude that this idea holds regardless of whether the range sizes are stationary or not. Otherwise stated: slow motion in a short range or faster motion in a larger range are two indistinguishable chances, both allowed to occur for a particle by the lack of local information inherent the eqs. 3,1 and in fact both occurring. This rationalizes why just the uncertainty of x, p_x, ε and t links the deformation rate of time dependent range sizes of the phase space to the acceleration of any particle, possible and thus actual. The size and position of any range require a reference system to be defined in principle, although never quantifiable.

Consider for instance $\Delta x = x_t - x_o$ and $\Delta p_x = p_t - p_o$: the coordinate x_o, whatever it might be, is defined with respect to the origin O of an arbitrary reference system R, while the same also holds for the momentum p_o of the range Δp_x conjugate to Δx. So a free particle is described in R by its own Δx and Δp_x; indeed eqs. 4,1 have been inferred in R keeping constant x_o and regarding x_t as a time function. Yet, if neither of these boundaries is specifiable, one could also think x_t fixed and x_o time function. The difference is apparent: the displacement of x_o means that now Δx deforms while contextually moving in R, as O displaces at rate $-\partial x_o/\partial t$ with respect to x_t. Thus it is possible to introduce another reference system R_o solidal with x_o such that a particle accelerated in R is at rest in R_o, which moves with the same acceleration in R. Clearly still acts on the particle a force that justifies the acceleration of R_o in R, although however the particle is in fact at rest in R_o.

The conclusion of this reasoning is well known: a particle at rest in an accelerated reference frame is subjected to a force F_x indistinguishable from that due to the presence of mass. Of course with large sized Δx one can speak about average force F_x, whereas in a small sized range F_x takes a value better and better defined. This statement is nothing else but the equivalence principle, here inferred as a corollary of eqs. 3,1. After having introduced in eqs. 4,1 $F_x = m\dot{v}_x$, can be inferred also the link between F_x and Newton's law after these preliminary remarks? Of course let us start again from eqs. 4,1 with v_x and $\dot{v}_x$ defined in any R.

First of all, the fact that the mass in eq. 4,1 is unique and that the equivalence principle has been obtained elaborating independently both sides of $m\dot{v}_x = F_x = -n\hbar\Delta x^{-2}v_x$ shows the identity of inertial and gravitational mass. Moreover just the fact the unique mass m must somehow appear also in the second equality compels putting $v_x = \zeta' m$ via an appropriate dimensional factor ζ'; hence $F_x = -n\hbar\zeta' m\Delta x^{-2}$ with the acceleration no longer appearing explicitly in this expression, which rather has the form of an interaction force $F_x^{m,\zeta'}$ between m and another entity that can be nothing else but ζ'.

This result suggests a more interesting form of F_x putting $\zeta' = n\sum_k \zeta_k m'^k$, being ζ_k coefficients of the power series development of ζ' and m' a further arbitrary mass that interacts with m. The series truncated at the first order only yields approximately $\zeta' \simeq n\zeta m'$, with ζ unique proportionality factor; here n is inessential and does not play any role because, being m' arbitrary, $m'n$ is another value arbitrary as well. In this way one finds $F_x^{m,m'} \approx -\hbar\zeta(m/\Delta x)(m'/\Delta x)$ at the first order of approximation, i.e. an attractive force is originated between the linear densities $m/\Delta x$ and $m'/\Delta x$ of masses by definition delocalized within Δx. This sensible result appears better understandable thinking to particle waves that propagate through Δx rather than to point particles moving randomly within Δx.

Moreover the proportionality factor ζ can be regarded as a constant since the arbitrary masses m and m' account for the arbitrariness of v_x. With the notation $\zeta = G/\hbar$ one recognizes the approximate Newton law; the classical distance $x_{m,m'}$ between local coordinates exactly known of particles is replaced by any random distance falling within the uncertainty range including them.

Obviously Δx^{-2} shows that the functional dependence of $F_x^{m,m'}$ on all possible distances between the masses is like $x_{m'm}^{-2}$. This confirms that effectively the diffusion particles are acted by the force F_x, whose physical meaning can be extended even to the gravitational interaction. Note however that actually both signs are allowed for the velocity component v_x along x, which correspond to the signs of $\partial\Delta x/\partial t$ depending on whether Δx shrinks or expands as a function of time.

In agreement with the idea of phase space-time deformation in the presence of mass, one would expect thus $v_x = \pm\zeta' m$, i.e. even a negative value of m. This conclusion emphasizes nothing else but the existence of antimatter. After this instance about how eqs. 3,1 can be purposely exploited, let us proceed with another example short enough to be mentioned here, i.e. the Coulomb law. It is not a chance that even this latter has a form similar to that of the Newton law, with the charges playing the role of the masses. To emphasize the reason of this similarity, let us introduce in eq. 4,1 the fine structure constant $\alpha = e^2/\hbar c$. Eliminating $\hbar$ eq. 4,1 reads $F_x = e'e/\Delta x^2 = m_e a_x$, where now m_e is the electron mass and $e' = n v_x (c\alpha)^{-1} e$. This latter reads more expressively $e' = \pm n\,|v_x|\,(c\alpha)^{-1} e$. Again, the charges interact through their linear densities $e/\Delta x$ and $e'/\Delta x$ for the reasons previously explained. Also the electron charges appear therefore because of the phase space-time deformation in the presence of the mass m_e. Once more is crucial the characteristic value of v_x of charged particles; for instance $v_x = 0$ would describe a neutral particle, whereas it also appears that a massless particle would be chargeless as well. A boundary condition of the problem is that for an appropriate value n^* of the integer n one must find $e' = e$, as nothing hinders indeed just such a possibility. So $e' = \pm(n/n^*)e$; e.g. for a couple of electrons one must take $n = n^*$ i.e. $|v_x| = c\alpha$, whose value seems therefore to be a combined constant of nature. It is reasonable to assume $n^* = 3$ since actually one should consider v_x, v_y and v_z for the respective components replacing the early F_x, for simplicity the only one hitherto considered, whereas the number n of states should be counted as $n = n_x + n_y + n_z$. Take the ground values $n_x = n_y = n_z = 1$ and consider the three chances $v_x \neq 0, v_y \neq 0, v_z \neq 0$ and $v_x \neq 0, v_y \neq 0$ and $v_x \neq 0$ only. This means considering the charges of particles resulting from $n = 1, 2, 3$ with $n^* = 3$. As inferred before, $n = n^*$ holds for protons and electrons. Yet, in addition to $e' = \pm e$, possible values of e' result respectively to be $e' = \pm e/3$ or $e' = \pm(2/3)e$ as well, i.e. particles with fractional charges should also exist in nature. But, being n arbitrary, what about hypothetical charges described by $n > n^*$?

A full discussion on this question is clearly far beyond the purpose of the present paper; further work is in progress on this specific topic. As concerns the results hitherto introduced, it is enough to conclude that the formal analogy between the Fourier law and the mass/charge transport laws is due to their common quantum basis, discussed here with reference to the entropic aspects too, that goes back to the intimate quantum nature of the entropy and Newton and Coulomb forces themselves.

7 Conclusion

The quantum origin of the diffusion law has been described with the help of eqs. 3,1 only. The assumption of uncertainty that allowed to calculate the energy levels of many-electron atoms and diatomic molecules, enables even the basic law controlling the transport of matter to be inferred in a very simple way. It is also remarkable that elementary considerations on eqs. 3,1 open the way to further results much more general than the specific task to which they were initially addressed in the present diffusion model. This emphasizes the heuristic character of eqs. 3,1: the uncertainty, regarded itself as a fundamental principle of nature rather than as mere corollary of commutation rules of operators, appears a key tool to infer a conceptual background unifying seemingly different physical phenomena. As concerns the present model, the level of comprehension provided by the approach based on the phase space-time uncertainty opens the way to more specific considerations on the possible mechanisms of transport in solid, liquid and gas phases.

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