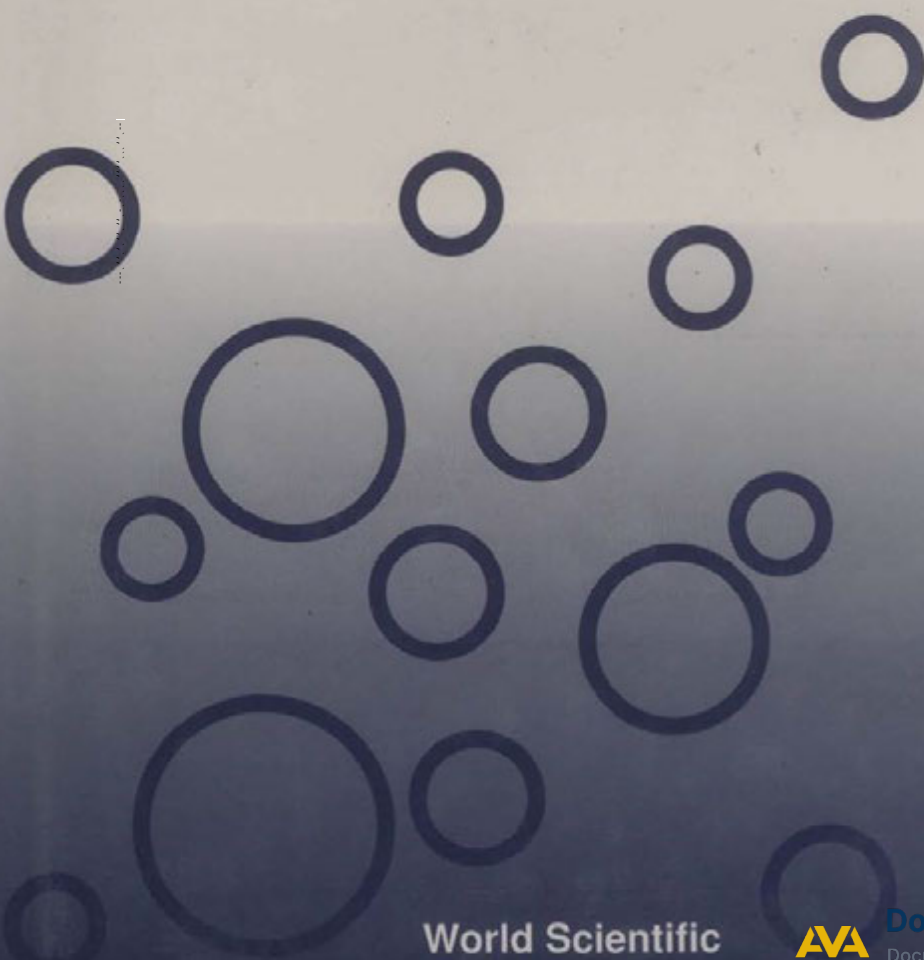


Topics on Diffusion in Emulsions

M Nichelatti



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Topics on Diffusion in Emulsions

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TOPICS ON DIFFUSION IN EMULSIONS

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My interest in emulsions began some years ago in a pharmaceutical Company for professional reasons, but I suddenly was captured by this fascinating topic also from a scientific point of view, and this book is the result of some cross-studies, attempting to better understand some problems often encountered in pharmaceutical literature.

Among people contributing in various ways to increase my interest in the field, I must cite at least my friends Michael Barnett (University of Wales) and Alexander "Sasha" Samsonov (Russian Academy of Sciences): some discussions I had with them were crucial to focalize some arguments.

Indeed, I'm also greatly indebted to my colleague, Regina Saottini, who has very kindly revised the English version of the whole manuscript, and to Ms. Sook-Cheng Lim, Scientific Editor of WS Publishing House, for her constant and patient help during the manuscript preparation.

The Author

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PREFACE

This booklet is intended to be a very simple collection (at an introductory level) of topics bridging diffusion phenomena (in a wider sense) and emulsion behaviour. It is the result of some years of experience in the field of oil-in-water emulsions, carried out in some pharmaceutical Companies.

In general, the only mathematical tool necessary to the reader is nothing but a basic knowledge in differential and integral calculus, because the book is intended as a preliminary guide for Pharmacists dealing with emulsion, both as beginners and at research level. The main task was the reduction and standardisation of mathematical formalism whenever possible, and many arguments have been introduced recalling their more familiar macroscopic background.

Indeed, some topics are not very simple and sometimes the mathematical formalism was unavoidable, but - in most cases - development and calculus have been actually reported step by step, to let the reader easier understand the conceptual meanings. Moreover, whenever a "new" concept is used, it is also introduced or followed by a short explicative note. In general, all Chapters are quite readable by every pharmacist with an almost good mathematical background (except, maybe, Chapter 2 and few Sections devoted to particular topics, which could be postponed), and some more advanced topics have been placed in Appendices.

In general, arguments, discussions and examples arise from pharmaceutical literature about oil-in-water emulsions: indeed, the pharmaceutical use of emulsions (as carriers for drugs, or in intravenous nutrition) is increasing day by day, and many Pharmacists are now dealing with emulsion stability and compatibility problems, even if their knowledge is often limited to practical observations, and hence, this booklet could be useful also to recall the meanings and basis of their observations, also in order to stimulate their interest in this fascinating topic.

In each chapter, some textual references are mentioned: nevertheless, the book has been written using some "fixed" general references, as main guidance and help through the development of main and specific arguments: these references should be used for a more advanced study, a more detailed understanding and a more comprehensive bibliography.

The general references are both textbooks and original papers, as follows:

1. Textbooks

i) the **A.W. Adamson's** "bible" in the field of surface physics: "*Physical Chemistry of Surfaces*" (5th. edition, Wiley Interscience, 1990); ii) two top-level books by **R.J.**

Hunter: "*Foundations of Colloid Science*" (Vol. I and II, Clarendon Press, 1990) and "*Zeta Potential in Colloid Science. Principles and Applications*" (Academic Press, 1988);
 iii) the classic text written by N.S. Goel and N. Richter-Dyn "*Stochastic Models in Biology*" (Academic Press, 1974).

2. Original papers

i) the masterpiece article by S. Chandrasekhar "*Stochastic Problems in Physics and Astronomy*" (Rev. Mod. Phys., vol. 15, pp. 1-89, 1943); ii) three fundamental papers written by M. von Smoluchowski: "*Über Brownsche Molekularbewegung unter Einwirkung äußerer Kräfte und deren Zusammenhang mit der verallgemeinerten Diffusionsgleichung*" (Ann. d. Physik, vol 48, pp. 1103-1112, 1915), "*Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Lösungen*" (Zeitschrift f. physik. Chemie, vol. 92, pp. 129-168, 1916) and "*Drei Vorträge über Diffusion, Brownsche Molekularbewegung und Koagulation von Kolloidteilchen*" (Physik. Zeitschr., vol. 17, pp. 557-571 and 585-599, 1916).

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1. DIFFUSION

Diffusion is a phenomenon deriving from a non uniform distribution of one or more system properties: this fact could be determined by a gradient of temperature, velocity, concentration, and so on. The particles sited in the regions in which the parameters have higher value, transfer the parameters by means of their movement and collisions with other particles, such that the parameter will be more uniformly distributed among all particles of the system. Since the particles travel an average path equal to their mean free path before a collision, one may generally agree that they actually carry the given parameters, and this renders the thermal conduction (heat transfer), the viscosity (momentum transfer), the molecular diffusion (density transfer), and, in general, all the irreversible processes called transport phenomena.

1.1 Particles in a box

Consider a set of N particles, or gas molecules, located in some adjacent boxes in series (see figure 1.1), such that i -th box contains n_i molecules, and $N = \sum_i n_i$. Assuming that molecules may jump with equal probability to adjacent boxes, i.e., from i -th to $(i+1)$ -th and $(i-1)$ -th, with a constant transition frequency ϕ (we may also assume that ϕ does not depend on the i -th box position), per unit time we shall have $\phi n_i/2$ particles jumping from i to $i+1$ and $\phi n_i/2$ jumping to $i-1$: in the meanwhile, $\phi n_{i+1}/2$ molecules initially sited in the $(i+1)$ -th box and $\phi n_{i-1}/2$ initially in the $(i-1)$ -th box will reach the i -th box. From the above assumptions, one obtains the rate equation for the molecule population in the i -th box as the sum of all contributions to n_i , so as to have:

$$\frac{dn_i(t)}{dt} = \frac{1}{2} \phi n_{i+1} + \frac{1}{2} \phi n_{i-1} - \frac{1}{2} \phi n_i - \frac{1}{2} \phi n_i,$$

hence:

$$\frac{dn_i(t)}{dt} = \frac{1}{2} \phi (n_{i+1} + n_{i-1} - 2n_i), \quad (1.1)$$

and the particle fluxes J between adjacent boxes may be written:

$$J_{i \leftrightarrow i+1} = \frac{1}{2} \phi (n_i - n_{i+1}), \quad (1.2)$$

and

$$J_{i \leftrightarrow i-1} = -\frac{1}{2} \phi (n_i - n_{i-1}). \quad (1.3)$$

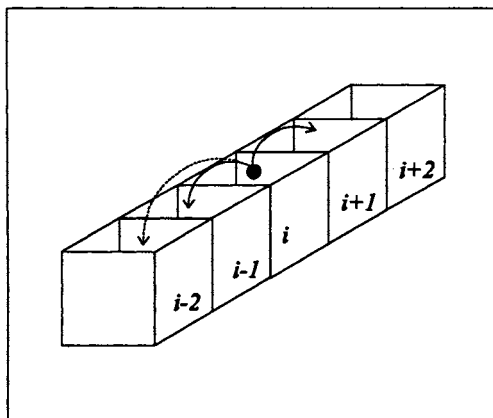


Figure 1.1. The considered model is shown: molecules may jump from their box to an adjacent one. We must assume that jumps between non adjacent boxes (see dotted arrow) are not allowed.

One easily observes that the net fluxes depend on the n_i , n_{i+1} and n_{i-1} values, and obviously become equal to zero when $n_i = n_{i+1} = n_{i-1}$, thus, the rate equation, i.e., the conservation equation for our system is:

$$\frac{dn_i(t)}{dt} = J_{i \leftrightarrow i+1} - J_{i \leftrightarrow i-1}. \quad (1.4)$$

Now, following the method outlined by Ghez [1] to obtain continuum equations, we will assume that boxes are sited in sequence along the x axis, and that each box has length Λ , such that $x_i = \Lambda i$ represents the coordinate of the i -th box (of course, also $x_{i \pm 1} = \Lambda(i \pm 1)$), thus we may introduce a function $f(x, t)$, defined by the formula:

$$f(x, t)|_{x=x_i} = n_i(t). \quad (1.5)$$

Since the Taylor's formula for a function $f(x, \xi)$ derivable $k + 1$ times, tells us that:

$$f(b, \zeta) \equiv f(a, \zeta) + \sum_{i=1}^k \left(\frac{(b-a)^i}{i!} \frac{\partial^i f(x, \zeta)}{\partial x^i} \right)_{x=a}; \quad a \leq x \leq b,$$

then, expanding $f(x, t)$ up to second order terms, we obtain:

$$f(x, t)|_{x=x_{i+1}} = f(x, t)|_{x=x_i} + \Lambda \frac{\partial f(x, t)}{\partial x} \Big|_{x=x_i} + \frac{1}{2} \Lambda^2 \frac{\partial^2 f(x, t)}{\partial x^2} \Big|_{x=x_i},$$

and

$$f(x, t)|_{x=x_{i-1}} = f(x, t)|_{x=x_i} - \Lambda \frac{\partial f(x, t)}{\partial x} \Big|_{x=x_i} + \frac{1}{2} \Lambda^2 \frac{\partial^2 f(x, t)}{\partial x^2} \Big|_{x=x_i},$$

hence, using definition (1.5), we get the expressions for n_{i+1} and n_{i-1} :

$$n_{i+1}(t) = n_i(t) + \Lambda \frac{\partial f(x, t)}{\partial x} \Big|_{x=x_i} + \frac{1}{2} \Lambda^2 \frac{\partial^2 f(x, t)}{\partial x^2} \Big|_{x=x_i},$$

and

$$n_{i-1}(t) = n_i(t) - \Lambda \frac{\partial f(x, t)}{\partial x} \Big|_{x=x_i} + \frac{1}{2} \Lambda^2 \frac{\partial^2 f(x, t)}{\partial x^2} \Big|_{x=x_i},$$

hence, invoking equation (1.1) for the balance of n_i , we obtain a partial differential equation describing the diffusion process in terms of the concentration $c(x, t) = f(x, t)/\Lambda$ as follows:

$$\frac{\partial c(x, t)}{\partial t} = \frac{1}{2} \phi \Lambda^2 \frac{\partial^2 c(x, t)}{\partial x^2}. \quad (1.6)$$

Now, to balance the continuous flux we must combine the fluxes as given in equations (1.2-3), hence using the values for n_{i+1} and n_{i-1} previously obtained:

$$J_{i \leftrightarrow i+1} = -\frac{1}{2} \phi \Lambda \frac{\partial f(x, t)}{\partial x} \Big|_{x=x_i} - \frac{1}{4} \phi \Lambda^2 \frac{\partial^2 f(x, t)}{\partial x^2} \Big|_{x=x_i}, \quad (1.7)$$

and:

$$J_{i \leftrightarrow i-1} = -\frac{1}{2} \phi \Lambda \frac{\partial f(x, t)}{\partial x} \Big|_{x=x_i} + \frac{1}{4} \phi \Lambda^2 \frac{\partial^2 f(x, t)}{\partial x^2} \Big|_{x=x_i}, \quad (1.8)$$

We see that in equations (1.7-8), the fluxes differ for the second term on the r.h.s., thus eliminating these divergent terms, and again using the concentration, we may assume that an equation for continuous flux in each box has the form:

$$J(x, t) = -\frac{1}{2} \phi \Lambda^2 \frac{\partial c(x, t)}{\partial x}, \quad (1.9)$$

and comparing r.h.s. factors in equations (1.6) and (1.9), we easily get (see Appendix 1):

$$\frac{\partial c(x, t)}{\partial t} = -\frac{\partial J(x, t)}{\partial x}, \quad (1.10)$$

from which, defining the diffusion coefficient:

$$D = \frac{1}{2} \phi \Lambda^2, \quad (1.11)$$

the half-product of transition frequency times the squared one-step length (thus, D is measured in $\text{cm}^2 \text{s}^{-1}$), and using definition (1.11) in equations (1.10), (1.9) and (1.6), we obtain, starting from a discrete one-step model, three equations respectively corresponding to the well-known phenomenological equations for macroscopic diffusion and for all other transport phenomena, like Ohm's law. More precisely:

i) from equation (1.10) we have:

$$\frac{\partial c(x,t)}{\partial t} = - \frac{\partial J(x,t)}{\partial x}, \quad (1.12a)$$

which is the continuity equation, and indicates that the system obeys the mass conservation law;

ii) from equation (1.9) we get:

$$J(x,t) = -D \frac{\partial c(x,t)}{\partial x}, \quad (1.12b)$$

which corresponds to the first Fick's law, where the minus sign in front of r.h.s. is put to render the fact that particles must flow in the direction of regions with lower concentration;

iii) from equation (1.6) we have:

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}. \quad (1.12c)$$

which corresponds to second Fick's law, arising as a consequence of previous one, and is called the diffusion (or the heat) equation, describing for any initial density distribution a monotone and irreversible evolution towards the equilibrium state [2].

According to first Fick's law, when the system reaches its steady-state, the amount of mass leaving a region in the unit time is equal to mass entering the same region, and the mass changes in each region is the sum of in and out contribution. For example, in a region limited between a and b (with $a \leq x \leq b$), the total mass will be:

$$m(t) = \int_a^b c(x,t) dx,$$

thus:

$$\frac{dm(t)}{dt} = \int_a^b \frac{\partial c(x,t)}{\partial t} dx,$$

and, by virtue of Fick's law:

$$\frac{dm(t)}{dt} = - \int_a^b \frac{\partial J(x,t)}{\partial x} dx = J(x_a, t) - J(x_b, t).$$

In our previous assumptions, we set both ϕ and Λ constants, thus D is a constant, too. In the more general case in which, for example, transition frequency ϕ is a function of position along x , or of n , then D becomes also a function, and equation (1.12c) must account for this fact. Hence, as general form for the Fick's second law, we should have written (1.12c) as follows:

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial c(x,t)}{\partial x} \right], \quad (1.13)$$

thus:

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial D}{\partial x} \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2}.$$

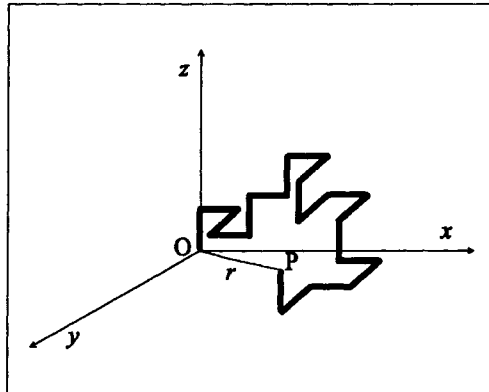


Figure 1.2. Simple model of a three-dimensional random walk. A particle moves from origin O , jumping in one of the three possible directions x , y or z , reaching its final position in the point $P(x,y,z)$, ranging r from origin; each jump has unitary length and has the same probability to be oriented in each direction x , y or z . The distance r of P from origin is given by the relation $r^2 = x^2 + y^2 + z^2$.

The random walk in three dimensions (see an example in figure 1.2) requires three parameters i , j , and k to locate each box in the Cartesian three-dimensional space, whereas $n_{i,j,k}$ is the number of particles in the box. If we take into account three constant

transition frequencies ϕ_i , ϕ_j and ϕ_k for the three possible directions of jumps, we obtain the flux vector $J(r, t)$ in three dimensions as:

$$J = -D \text{grad } c(x, y, z, t), \quad (1.14)$$

whereas

$$\frac{\partial c(x, y, z, t)}{\partial t} = -\text{div } J, \quad (1.15)$$

hence, inserting equation (1.14) into (1.15), we have the general equation:

$$\frac{\partial c(x, y, z, t)}{\partial t} = \text{div}(D \text{grad } c), \quad (1.16)$$

which, if D is constant, may be written as:

$$\frac{\partial c(x, y, z, t)}{\partial t} = D \nabla^2 c,$$

where

$$\nabla^2(\cdot) = \text{div grad}(\cdot) = \nabla \cdot [\nabla(\cdot)] = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)(\cdot)$$

is the Laplacian operator in Cartesian coordinates.

1.2 Solution of the diffusion equation

Let us rewrite Equation (1.12c):

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2}; \quad (1.17)$$

there are some methods to find the general solution of equation (1.17). For example, we may find a solution by assuming that at initial time $c(x, 0) = \delta(x)$, being $\delta(x)$ the Dirac delta. Now, using the Fourier transform:

$$\hat{c}(k, t) = \int_{-\infty}^{+\infty} c(x, t) e^{ikx} dx,$$

we may rewrite equation (1.17) in the simpler form:

$$\frac{\partial \hat{c}(k, t)}{\partial t} = -Dk^2 \hat{c}(k, t),$$

with solution:

$$\hat{c}(k, t) = C e^{-Dkt},$$

from which, being $\hat{c}(k, 0) = 1$, we obtain $C = 1$.

Using the inverse transform, we have:

$$c(x, t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-ikx} e^{-Dk^2 t} dk$$

thus, we obtain the solution for the diffusion equation in the form:

$$c(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left\{-\frac{x^2}{4Dt}\right\}. \quad (1.18)$$

1.3 Mean free path

We may define the mean free path λ as the average distance travelled by particle between two consecutive collisions with other particles; collisions occur randomly, and this is the reason why we are dealing with a "mean" free path. This last is generally written using equation:

$$\lambda = \frac{\langle v \rangle}{Z},$$

being $\langle v \rangle$ the average velocity of particles during an unitary displacement, and Z the number of collisions. The mean free path could be also expressed in probabilistic terms as follows:

$$\lambda = \int_0^\infty \frac{x}{\lambda} q(x) dx,$$

where $q(x)$ is the probability that no collisions occurred while particle has travelled a distance x .

Assuming that a particle has the same probability of a collision in any interval $[x, x + dx]$, and since the average number of collisions per unit length is given by $1/\lambda$, then the probability to have a collision in the interval dx is:

$$p(dx) = \frac{dx}{\lambda},$$

whereas the probability that no collisions occur is, of course,

$$q(dx) = 1 - \frac{dx}{\lambda}.$$

Now, if we define with $q(x)$ the probability that no collisions occur in x , then, for the whole interval $[x+dx]$, we have:

$$q(x+dx) = q(x)q(dx) = \left(1 - \frac{dx}{\lambda}\right)q(x).$$

Thus, expanding in series l.h.s. of (1.19):

$$\frac{dq(x)}{dx} = -\frac{1}{\lambda}q(x),$$

hence the solution of equation (1.20) represents a Poisson distribution [3]:

$$q(x) = e^{-x/\lambda},$$

from which we obtain the probability to have a collision:

$$p(x) = 1 - e^{-x/\lambda}.$$

1.4 Diffusion and Fokker-Planck equations

The equations of the form of (1.2) are useful to describe time evolution of a given process $q(t)$ involving a series of ordered states i ; in a general way, for a process $q(t)$ we may write:

$$\frac{\partial q(x,t)}{\partial t} = \sum_y \varphi(y|x)q(y,t) - \varphi(x|y)q(x,t), \quad (1.19)$$

where $\varphi(y|x)$ is the transition frequency between x and y . Equations like (1.19) are generally called master equations (see also Appendix 2).

The master equation could be used to study the position $x(t)$ of a given set of particles undergoing monodimensional diffusion along x . Let us define $P(x,t)dx$ the probability that an arbitrary particle is sited in the interval $[x, x+dx]$ at time t . Now, defining $Q(y,x)dydt$ as the probability for a particle initially sited in x to undergo after a time interval dt a transition to a position in the interval $[y, y+dy]$, then the master equation for the total probability flux is:

$$\frac{\partial P(x,t)}{\partial t} = \int_{-\infty}^{+\infty} [P(y,t)Q(x,y) - P(x,t)Q(y,x)]dy. \quad (1.20)$$

Assuming that transitions are allowed only between adjacent sites, then $Q(y,x)$ must show a sharp peak around x , and otherwise must rapidly decrease to zero.

On the basis of this assumption, putting $\xi = y-x$, such that $Q(y,x) = Q(x|\xi)$, we have the peak around the value $\xi = 0$. Thus, we are allowed to expand (1.20) in Taylor's series around $\xi = 0$, which, truncating at second term and omitting negligible values, gives a Fokker-Planck equation [4,5] (see Appendix 3), written as:

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}[a_1(x)P(x,t)] + \frac{1}{2}\frac{\partial^2}{\partial x^2}[a_2(x)P(x,t)], \quad (1.21)$$

where

$$a_1(x) = \int_{-\infty}^{+\infty} \xi P(x|\xi) d\xi = \frac{\langle dx \rangle}{dt} = \langle v_x \rangle, \quad (1.22a)$$

and

$$a_2(x) = \int_{-\infty}^{+\infty} \xi^2 P(x|\xi) d\xi = \frac{\langle (dx)^2 \rangle}{dt}. \quad (1.22b)$$

It is important to note the analogy between the microscopic equation (1.21) and the macroscopic equation (1.12c). As above written, this last describes an irreversible monotone evolution towards an equilibrium state, whereas, the term containing the first derivative in equation (1.21) accounts for a systematic slowing down effect. Thus, Fokker-Planck equation describes the overposition of a viscous force and the diffusion driving force. If, for example, at initial time we have the velocity distribution centred in $v = v_0$, after a time t , the maximum of velocity distribution will be centred on a lower velocity (due to systematic friction), whereas the peak will broaden due to diffusion in the velocity.

As we already saw, if no external forces are acting on the particles, (1.28) reduces to same form of (1.12c), with solution:

$$f(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left\{-\frac{(x-x_0)^2}{4Dt}\right\}. \quad (1.23)$$

From (1.23) we have

$$\langle x \rangle = x_0, \quad (1.24)$$

and

$$\langle x^2 \rangle = x_0^2 + 2Dt, \quad (1.25)$$

which, in a three-dimensional space, is to be written as:

$$\langle r^2 \rangle = r_0^2 + 6Dt.$$

Thus, in the case of absence of external forces acting on the system, the Gaussian broadens, remaining centred on x_0 (see also figure 1.3).

To analyse the situation arising if external forces act on the system, let us assume that particles are subject to a force $F = -fx$, and let us define a parameter A (i.e., the drift of particles), such that for a spherical particle of radius R moving in a fluid with viscosity η ,

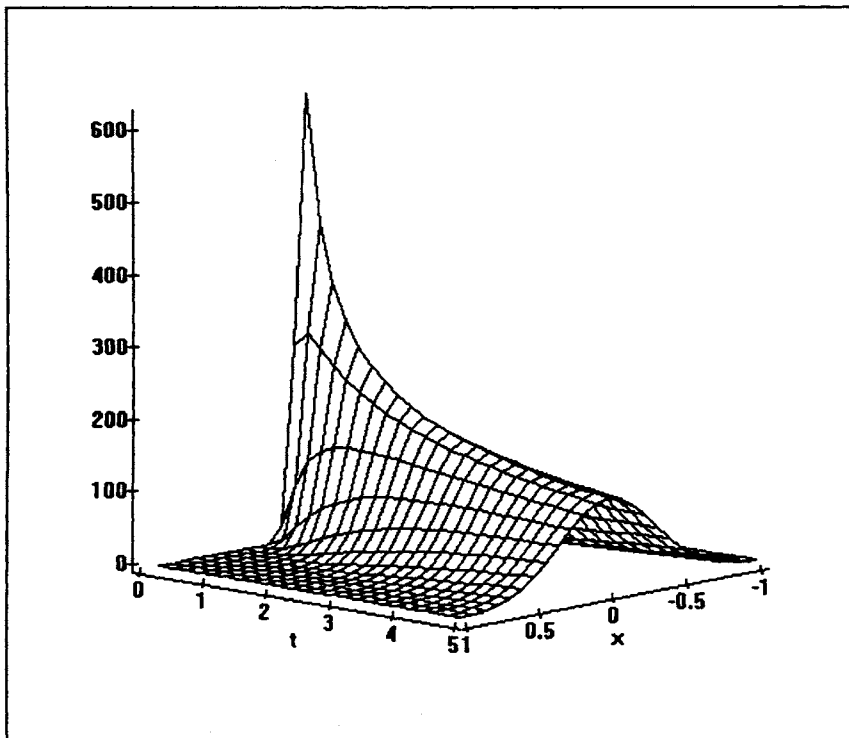


Figure 1.3. Computer simulation showing evolution after $t = 5$ s of particle distribution around their initial position in $x = 0$. The value attributed to D was $10^{-2} \text{ cm}^2 \text{ s}^{-1}$.

and according to Stoke's law, it must be $A = 1/(6\pi\eta R) = B^{-1}$ (where B is the frictional parameter). At steady-state state the average viscous force must balance external force, so as to have:

$$-\frac{\langle v_x \rangle}{A} + F = 0,$$

hence, given (1.22a):

$$\langle v_x \rangle = a_1(x) = -fAx.$$

Now, assuming $x_0 = 0$ in equations (1.24-25), from equation (1.22b) we have $a_2(x) = 2D$. But, since $D = AKT = KT/6\pi\eta R$, we obtain:

$$a_2(x) = 2AKT,$$

and (1.21) becomes:

$$\frac{\partial P(x,t)}{\partial t} = fA \frac{\partial}{\partial x}(xP) + AKT \frac{\partial^2 P}{\partial x^2}. \quad (1.26)$$

If we use (1.26) for a set of particles initially centred in x_0 , the general solution will be:

$$P(x,t) = \sqrt{\frac{f}{2\pi KT(1 - \exp\{-2fAt\})}} \exp\left\{-\frac{f(x - x_0 \exp\{-fAt\})^2}{2KT(1 - \exp\{-2fAt\})}\right\}, \quad (1.27)$$

and therefore we have:

$$\langle x \rangle = x_0 e^{-kAt}, \quad (1.28)$$

and:

$$\langle x^2 \rangle = \frac{KT}{f}(1 - \exp\{-2fAt\}) + x_0^2 \exp\{-2fAt\}. \quad (1.29)$$

Thus, when $t \rightarrow \infty$, one obtains:

$$\langle x \rangle = 0,$$

and:

$$\langle x^2 \rangle = \frac{KT}{f}.$$

Equations (1.27-29) correspond to the situation of an Ornstein-Uhlenbeck process satisfying initial condition $P(x, t|x_0, t_0) = \delta(x - x_0)$, and in which the Fokker-Planck equation reads:

$$\frac{\partial P(x, t|x_0, t_0)}{\partial t} = k \frac{\partial}{\partial x}[xP(x, t|x_0, t_0)] + \frac{D}{2} \frac{\partial^2 P(x, t|x_0, t_0)}{\partial x^2}, \quad (1.30)$$

with $k > 0$ and $D(x, t) \geq 0$. The analogy of equations (1.30) and (1.26) is evident if one finds the solution $P(x, t|x_0, t_0)$, which assumes the form:

$$P(x, t|x_0, t_0) = \sqrt{\frac{k}{\pi D[1 - \exp\{-2k(t - t_0)\}]}} \exp\left\{-\frac{k[x - x_0 \exp\{-k(t - t_0)\}]^2}{2D[1 - \exp\{-2k(t - t_0)\}]}\right\}, \quad (1.31)$$

and becomes:

$$P(x, \infty|x_0, t_0) = \sqrt{\frac{k}{\pi D}} \exp\left\{-\frac{kx^2}{D}\right\}, \quad (1.32)$$

as $t \rightarrow \infty$.

1.5 Moments of the process

Equations (1.22a-b and (1.24-25) represent respectively the first and the second moment of the process. The n -th moment may be obtained with equation (see Chapter 4):

$$\langle x(t)^n \rangle = \int_{-\infty}^{+\infty} x^n c(x, t) dx,$$

i.e, for the first moment:

$$\langle x(t) \rangle = \int_{-\infty}^{+\infty} x c(x, t) dx,$$

thus, after integration over x we get:

$$\frac{d\langle x(t) \rangle}{dt} = 0,$$

which gives the same result of equations (1.22a) and (1.24), showing that average position of particles does not change in time.

To evaluate the second moment, we have to multiply both sides of diffusion equation by x^2 , and then to integrate again, so as to have:

$$\frac{d\langle x^2(t) \rangle}{dt} = 2D,$$

and hence:

$$\langle x^2(t) \rangle = 2Dt,$$

exactly corresponding to equations (1.22b) and (1.25).

1.6 Remarks about rotational diffusion

We have considered the behaviour of physically isotropic particles. Indeed, non-spherical (ellipsoidal) particles may be subject to overposition of translational and rotational motion, this last being determined by the non-spherical symmetry in the collisions with the surrounding fluid (or by the imposition of an electric field if particles are dipoles), and ellipsoidal particles become rotors, characterised by a rotational axis, hence there must be an orientation distribution with respect to a given direction in the space.

Assuming that $c(\vartheta)d\vartheta$ the number of particles oriented within an angle included in the interval $[\vartheta, \vartheta + d\vartheta]$ with respect to a given axis x (see figure 1.4), after a time t , some particles will change their orientation by virtue of a rotation imposed by asymmetric collisions (for example, determined by thermal motion in the fluid), and in analogy with Fick's first law we have a resulting angular flux:

$$\frac{dc}{dt} = -R \frac{\partial \rho}{\partial \vartheta},$$

where R is the rotational diffusion coefficient (measured in s^{-1}), and

$$\rho = \frac{dc}{d\vartheta}$$

is the orientation density.

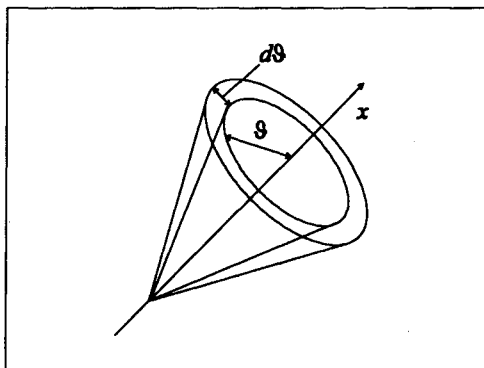


Figure 1.4. Representation of $\vartheta + d\vartheta$ angle with respect to a fixed axis x .

At steady-state, the rotation with angular velocity ω is balanced by a rotational friction force M , depending on ω :

$$M = -B_r \omega,$$

and in analogy with linear diffusion, one has:

$$R = \frac{KT}{B_r},$$

being B_r the rotational friction parameter, describing the force necessary for rotation with unitary angular velocity. For spherical particles of radius R , one may see from fluid dynamics that:

$$B_r = 8\pi\eta R^3.$$

Hence, ellipsoidal particles undergoing Brownian motion are subject to rotational diffusion R , and this movement may be treated as the translational diffusion. In particular, if $\langle \vartheta \rangle$ is the average change in particle orientation after a time t , then we must have:

$$\langle \vartheta^2(t) \rangle = 4Rt.$$

The diffusion equations for particles subject to an electric field E and with dipolar moment p have been reported by de Groot and Mazur [6] in the form:

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial \vartheta} \left\{ \sin \vartheta \left[R \frac{\partial}{\partial \vartheta} (\rho \arcsin \vartheta) + \rho B_r p E \right] \right\},$$

and

$$\frac{\partial n}{\partial t} = \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left\{ \sin \vartheta \left[R \frac{\partial n}{\partial \vartheta} + n B_r p E \sin \vartheta \right] \right\},$$

where:

$$n(\vartheta) = \frac{\rho(\vartheta)}{\sin \vartheta}.$$

In the previous equations, the distribution function ρ of particle orientation is given in terms of polar coordinates (see Appendix 4) instead of normal Cartesian ones. After opportune manipulations of the diffusion equation, it is possible to show that for a set of particles initially oriented at $\vartheta = 0$:

$$\langle \cos \vartheta \rangle = e^{-2Rt},$$

hence, the time required to obtain an isotropic distribution with $\langle \cos \vartheta \rangle = 0$ will be $t \equiv R^{-1}$ (Hunter [7]).

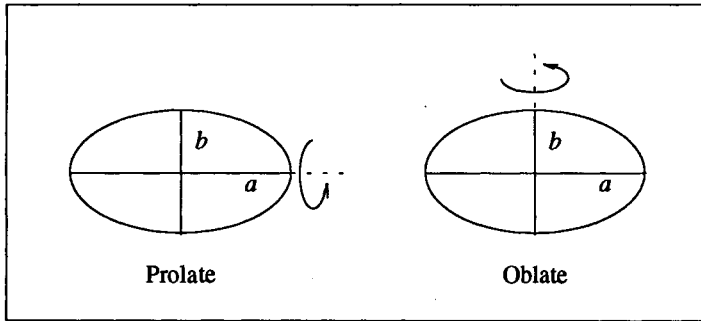


Figure 1.5. Prolate and oblate ellipsoids.

By solving the Stokes equation, it is possible to obtain, for a prolate ellipsoid (see figure 1.5), the following expression for rotational diffusion (see Perrin [8]):

$$R = \frac{KT}{16\pi\eta a^2 q^2 (1-q^4)} \left\{ 3 \left[\ln(1+\sqrt{1-q^2}) - \ln q \right] q^2 (2-q^2) \sqrt{1-q^2} - 3q^2 \right\},$$

a and b respectively being the major and minor axis of ellipsoid, whereas $q = b/a$. The equivalent form for oblate ellipsoid is:

$$R = \frac{3KT}{16\pi\eta ab^2 (1-q^4)} \left[q^2 (2-q^2) (\sqrt{q^2-1})^{-1} \arctan(\sqrt{q^2-1}) + 1 \right].$$

1.7 Diffusion equation from a mathematical point of view

The diffusion equation (also called the heat or the Fourier equation), should be written in the form:

$$\frac{\partial f(x, y, z, t)}{\partial t} = a^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) f(x, y, z, t),$$

but is normally given in the monodimensional form:

$$\frac{\partial f(x, t)}{\partial t} = a^2 \frac{\partial^2 f(x, t)}{\partial x^2}, \quad (1.33)$$

which corresponds to one of the most important second order partial differential equation (PDE), together with the wave equation:

$$\frac{\partial^2 f(x, t)}{\partial t^2} = a^2 \frac{\partial^2 f(x, t)}{\partial x^2},$$

and the Laplace equation:

$$\frac{\partial^2 f(x, y)}{\partial x^2} + \frac{\partial^2 f(x, y)}{\partial y^2} = 0.$$

Equation (1.33) is classified as a parabolic differential equation, since, given the general form for second order PDE

$$A(x, y) \frac{\partial^2 f}{\partial x^2} + B(x, y) \frac{\partial^2 f}{\partial x \partial y} + C(x, y) \frac{\partial^2 f}{\partial y^2} = W \left(f, \frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, x, y \right),$$

the relation $B^2 - 4AC = 0$ is true at least over some points of (x, y) .

A solution of diffusion equation has been already obtained in Section 1.2 by using the Fourier transform. Nevertheless, it could be interesting to solve the diffusion equation using the method of separation of variables, which leads to formal solution on the basis

of the specific boundary conditions: moreover, this approach will be useful as a basic example of solution of a differential equation.

The first task is the separation of variables in equation (1.33): this is done by assuming that:

$$f(x, t) = X(x)T(t), \quad (1.34)$$

where $X(x)$ is a function of position only and $T(t)$ is a function of time only. In this case, we have:

$$\frac{\partial f(x, t)}{\partial t} = XT',$$

and:

$$\frac{\partial^2 f(x, t)}{\partial x^2} = X''T,$$

thus, equation (1.33) reads now:

$$XT' = a^2 X''T,$$

and separating the variables:

$$\frac{X''}{X} = \frac{T'}{a^2 T}.$$

Since each side of above equation depends only on a variable, then we may assume that both members are equal to a constant, here called $-\psi^2$, hence:

$$\frac{X''}{X} = -\psi^2; \quad \frac{T'}{a^2 T} = -\psi^2,$$

from which we have:

$$X'' + \psi^2 X = 0; \quad (1.35)$$

$$T' + a^2 \psi^2 T = 0. \quad (1.36)$$

Equation (1.35) has general solution:

$$X(x) = A \sin \psi x + B \cos \psi x, \quad (1.37)$$

A and B being two arbitrary constants, whereas equation (1.36) may be easily solved to get:

$$T(t) = C \exp\{-a^2 \psi^2 t\}, \quad (1.38)$$

where C is also an arbitrary constant.

Thus, invoking equation (3.34) we have the solution:

$$f(x, t) = (A \sin \psi x + B \cos \psi x) \exp\{-a^2 \psi^2 t\}, \quad (1.39)$$

where we put $C = 1$.

Equation (1.39) satisfies diffusion equation: on the other hand, it must satisfy also boundary conditions, which depend on the problem we must analyse.

For example, assume that we are dealing with a diffusion along the x axis between the limits $x_0 = 0$ and $x_1 = 1$. Let us set initial conditions as:

$$f(x, 0) = \varphi(x); \quad 0 \leq x \leq 1,$$

and boundary conditions as:

$$f(0, t) = 0; \quad f(1, t) = 0; \quad \forall t \geq 0.$$

For $x = 0$, we have:

$$f(0, t) = 0 = B \exp\{-a^2 \psi^2 t\},$$

thus, $B = 0$ and:

$$f(x, t) = A \exp\{-a^2 \psi^2 t\} \sin \psi x. \quad (1.40)$$

For $x = 1$, we have:

$$f(1, t) = 0 = A \exp\{-a^2 \psi^2 t\} \sin \psi,$$

and a nontrivial solution is found for $\sin \psi = 0$, hence:

$$\psi = n\pi; \quad n = 0, \pm 1, \pm 2, \dots, \quad (1.41)$$

and inserting equation (1.41) into (1.40) we get the solutions of the diffusion equation:

$$f_n(x, t) = A_n \exp\{-\mu n^2 t\} \sin n\pi x, \quad (1.42)$$

where we put $\mu = a^2 \pi^2$, taking only positive n values. But, since equation (1.42) gives all the independent solutions, and since equation (1.33) is linear and homogeneous, then the sum of all $f_n(x, t)$ will be a solution of diffusion equation, and therefore we may write:

$$f(x, t) = \sum_{n=1}^{\infty} A_n \exp\{-\mu n^2 t\} \sin n\pi x \quad (1.43)$$

as a general form of the solution of diffusion equation according to boundary conditions.

1.8 Examples of diffusion-like equations

One encounters differential equations of the same form of (1.12c) in other physical processes involving continuity and transport. Bearing in mind the first Fick's law:

$$J = -D \frac{\partial c}{\partial x},$$

we could find some other equations describing fluxes, and having the equivalent form. For example, we recall the heat flow equation (Fourier's law):

$$J = -\kappa \frac{\partial T}{\partial x},$$

the Poiseuille's law:

$$J = -C \frac{\partial P}{\partial x},$$

and the equation for electrical current (Ohm's law):

$$J = -\varphi \frac{\partial V}{\partial x}.$$

The analogy of diffusion equation with equations of heat transfer is evident because the continuity equation takes the form:

$$C\rho \frac{\partial T}{\partial t} = -\frac{\partial J}{\partial x},$$

C being the thermal capacity for the unitary mass, ρ the density, and T the temperature. Using the flux as written in the Fourier equation, in which κ stands for the thermal conductivity coefficient, we obtain:

$$\frac{\partial T}{\partial t} = \Theta \frac{\partial^2 T}{\partial x^2},$$

where $\Theta = \kappa/\rho C$, is the thermal diffusivity. It is to note that Θ has the same dimensions ($\text{cm}^2 \text{s}^{-1}$) of the diffusion coefficient D .

An analogous set of equations is necessary to describe the momentum transfer in a fluid: in this case the fluid velocity obeys the continuity equation:

$$\rho \frac{\partial v}{\partial t} = -\frac{\partial T}{\partial x},$$

where T is the shear stress, which, according to Newton's law, is related to velocity and position by means of equation:

$$\tau = -\eta \frac{\partial v}{\partial x},$$

where η stands for the dynamic viscosity of the fluid. Combining the two last equation, and defining the kinematic viscosity $\mu = \eta/\rho$, we have the diffusion relation:

$$\frac{\partial v}{\partial t} = \mu \frac{\partial^2 v}{\partial x^2},$$

where μ also has the same dimensions of D .

1.9 Diffusion as a stochastic process

Diffusion in physics may be treated using the stochastic processes theory (see also Appendix 1), where the diffusion processes are special cases of Markov ones [9]. More precisely, Arnold [10] has shown that a diffusion process is a Markov process having small probability to suffer large amplitude variations over small time ranges, and having the transition probability $P(s, x, t, B)$ completely determined by the drift vector f and diffusion matrix $B = \{b_{ij}\}$.

The first property may be written in the form:

$$\Pr\{|M(t) - M(s)| \leq \epsilon | M(s) = x\} = 1 - o(t - s),$$

whereas the second property may be demonstrated observing that each diffusion process in the n -dimensional space R^n is characterised by a differential operator L such that:

$$L = \sum_{i=1}^n f(s, x) \frac{\partial}{\partial x_i} + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n b_{ij}(s, x) \frac{\partial^2}{\partial x_i \partial x_j},$$

which must correspond to the infinitesimal operator A (also called generator) of the process, defined by equation:

$$A[g(x)] = \lim_{t \downarrow 0} \frac{\theta_t g(x) - g(x)}{t}; \quad g \in B(R^n),$$

for $t_0 \leq t \leq \theta$. According to Arnold, the correspondence between generator and differential operator may be seen by rewriting the generator in the integral form:

$$A[g(s, t)] = \lim_{t \downarrow 0} \frac{1}{t} \int_{R^n} [g(s+t, y) - g(s, x)] P(s, x, t+s, dy),$$

then, using the conditions for a diffusion process for the drift $f(s, x)$:

$$\lim_{t \downarrow 0} \frac{1}{t-s} \int_{\|y-x\| \geq \epsilon} (y-x) P(s, x, t, dy) = f(s, x);$$

and for the $n \times n$ diffusion matrix $B(s, x)$:

$$\lim_{t \downarrow s} \frac{1}{t-s} \int_{\epsilon \geq |y-x|} (y-x)(x-y)' P(s, x, t, dy) = B(s, x),$$

one evolves that it must be:

$$A = \frac{\partial}{\partial s} + L,$$

hence, for time independent functions:

$$A \equiv L = \sum_{i=1}^n f(s, x) \frac{\partial}{\partial x_i} + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n b_{ij}(s, x) \frac{\partial^2}{\partial x_i \partial x_j}.$$

2. BROWNIAN MOTION

The stochastic approach to Brownian motion studies the effects exerted by the fluid on the Brownian particles. Thus, this approach describes the whole process in a phenomenological way, and does not matter about the nature of interactions between fluid and particles. Using the stochastic theory, one is dealing with a process which can be divided in two parts: *i*) a frictional effect exerted by fluid on the particles, which are slowed down; *ii*) the random movement of the particles, assumed to be caused by a fluctuating force exerted by the medium. Since one cannot exactly know the value of the fluctuating force, then one should attempt to understand its statistical properties; the further step will be to know the probability of a given change in position and velocity of the particle after a given time range. There are several references available in scientific literature about Brownian motion (both as physical event and as stochastic process) but, possibly, one of the most clear and interesting is the paper written by Chandrasekhar [1], which will be used as guide and general reference in this Chapter.

2.1 General introduction

Brownian motion (or Brownian movement) is observed when particle immersed in a fluid interacts with fluid molecules, which transfer energy to particles by means of random collisions occurring during very short time ranges, of the order of 10^{-21} s [1].

The collisions with fluid molecules give a series of successive displacements of the particle, which undergoes a random movement through the liquid, done by the sum of different trajectories assumed by the particle after successive collisions (see figure 2.1): each trajectory, indeed, is given by the sum of all the momenta transferred from fluid molecules to the particle during each collision.

On the basis of equipartition principle, and considering particles as big molecules, one may estimate the mean quadratic velocity of a particle with mass m , by using the formula relating kinetic energy and thermal energy:

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} K T,$$

from which:

$$\sqrt{\bar{v}^2} = \frac{\sqrt{3KT}}{m},$$

being K the Boltzmann constant and T the absolute temperature.

The Brownian movement is generally observed in all the cases in which a body is immersed in a fluid, if dimensions of the body are of the order of the mean free path of the fluid molecules: a common example is given by the galvanometer, in which

Brownian movements resulting by collisions with gas molecules constitute a limitation for this instrument.

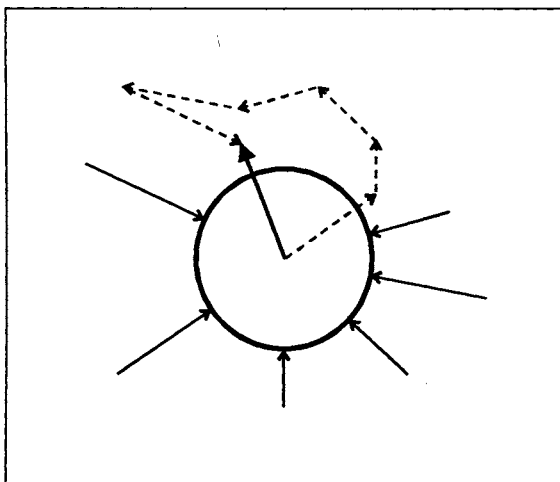


Figure 2.1. Simplified picture showing the net displacement suffered by a spherical Brownian particle after six simultaneous collisions with surrounding fluid. See text for more details.

An useful approach to analyse Brownian motion is given by Langevin equation (see next Section), where the velocity changes of particles are taken into account by means of the overposition of an inertial term (depending on both fluid viscosity and particle size and shape) and a rapidly fluctuating force (called also white force or stochastic force), characterised by the fact that its mean value is zero, thus this force is negligible over large time scale, but it is fundamental for the mathematical treatment of time scales of order of a collision.

2.2 Langevin equation

When a Brownian particle moves in a surrounding fluid, the motion is slowed down by the dissipative action of fluid itself; one assumes that the frictional coefficient β for the particle is independent of the velocity of the particle. Assuming that we are dealing with a spherical particle with mass m and radius R moving in a fluid having a viscosity η , the frictional coefficient will be:

$$\beta = \frac{6\pi\eta R}{m}.$$

One must also assume that the medium exerts a fluctuating force on the particle, and that this force depends only on elapsed time. If we assume also that effects of frictional and fluctuating forces are additive, and that no other external forces are acting on the system, then the motion of the particle will be described by the Langevin equation [2,3]:

$$\frac{du}{dt} = -\beta \frac{dr}{dt} + S(t), \quad (2.1a)$$

where r and u respectively are the position and velocity of the particle, and $S(t)$ is the term due to fluctuating force. If also external forces are acting on the system, a third term $F(r,t)$ should be added to (2.1a), so as to have:

$$\frac{du}{dt} = -\beta \frac{dr}{dt} + S(t) + F(r,t). \quad (2.1b)$$

As one easily sees in (2.1a) and (2.1b), the motion of particle at time t does not depend on the motion at preceding time $t - dt$, and does not determine the motion at a successive time $t+dt$, and this is due to assumption that collisions with external fluid molecules are instantaneous.

From what written above, and assuming that time required for variation of macroscopic quantities is much greater than time elapsed between two successive fluid-particle collisions, we may define a small time interval Δt , in which all the macroscopic variables undergo very small changes, so as to have:

$$\langle u(t) \rangle \gg \langle u(t + \Delta t) \rangle - \langle u(t) \rangle. \quad (2.2)$$

In this time interval, indeed, we also must assume that $S(t)$ was subject to a great number of fluctuations, and therefore $S(t + \Delta t)$ and $S(t)$ are quite uncorrelated: this set of assumptions allow us to describe the very small velocity changes of the Brownian particle during collisions with fluid molecules [1].

More precisely, in time interval Δt the particle undergoes a net acceleration $B(\Delta t)$ given by:

$$B(\Delta t) = \int_t^{t+\Delta t} S(\xi) d\xi,$$

as the total contribution of all the microscopic random accelerations suffered during time Δt .

Consider a series of simple steps r_i , whose magnitude and direction do not depend on the previous ones r_{i-1} : we take into account a distribution function $\vartheta_i(r_i)$ giving the probability distribution that a step r_i is in the interval $[r_i, r_i + dr_i]$. Thus, the problem is to find the probability $P(\Delta r, \Delta t)$ that, after a time interval Δt , the particle is sited at a distance Δr from its original position.

This problem is similar to random flights problem [4,5]: in the monodimensional case, in which all steps have the same length, if the particle is sited at the origin at $t = 0$, the probability that the particle lies at m after N steps (with $-N \leq m \leq N$) will be:

$$P(m, N) = \frac{1}{2} P(m-1, N-1) + \frac{1}{2} P(m+1, N-1), \quad (2.3a)$$

with

$$P(1, 1) = P(-1, 1) = \frac{1}{2}. \quad (2.3b)$$

We may see that equations (2.3a-b) refer the same situation one encounters by tossing a coin N times; in this case, m represents the net difference between heads and tails. Again, we observe that m is even or odd only if N is respectively even or odd. The probability of each sequence of N steps leading to position m is therefore $(1/2)^N$, and the probability $P(m, N)$ will be the number of series of steps leading to m multiplied times $(1/2)^N$. Using the Fourier transform

$$\hat{P}_N(l) = \sum_{m=-\infty}^{+\infty} P(m, N) \exp\{-ilm\}, \quad (2.4)$$

equations (2.3a-b) reduce to:

$$\hat{P}_N(l) = \cos l \hat{P}_{N-1}(l) \quad (2.5a)$$

and:

$$\hat{P}_1(l) = \cos l, \quad (2.5b)$$

from which:

$$\hat{P}_N(l) = (\cos l)^N.$$

Thus, inverting transformation (2.4):

$$P(m, N) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} (\cos l)^N \exp\{ilm\} dl.$$

Now, using the relation:

$$(\cos l)^N = \frac{1}{2^N} \sum_{n=0}^N \frac{N!}{n!(N-n)!} \exp\{-(N-2n)il\},$$

we can obtain:

$$P(m, N) = \frac{1}{2^N} \sum_{n=0}^N \frac{N!}{n!(N-n)!} \frac{\sin \pi(N-2n-m)}{\pi(N-2n-m)},$$

in which the last term on the r.h.s. vanishes for $N-m-2n \neq 0$. Hence we have:

$$P(m, N) = 0,$$

for m even and N odd, or vice versa, and

$$P(m, N) = \frac{N!}{2^N \left(\frac{N-m}{2}\right)! \left(\frac{N+m}{2}\right)!},$$

for both m and N even or odd.

Now, for $N \rightarrow \infty$ and $m \ll N$, we may use the Stirling's formula:

$$\ln n! = \left(n + \frac{1}{2}\right) \ln n - n + \frac{1}{2} \ln 2\pi + O(n^{-1}); \quad n \rightarrow \infty,$$

where, with notation $O(a)$ in the r.h.s. we indicate terms the order of a . Hence:

$$\begin{aligned} \ln[P(m, N)] &\approx \left(N + \frac{1}{2}\right) \ln N - \frac{N+m+1}{2} \ln \left[\frac{N}{2} \left(1 + \frac{m}{N}\right)\right] \\ &\quad - \frac{N-m+1}{2} \ln \left[\frac{N}{2} \left(1 - \frac{m}{N}\right)\right] - \frac{\ln[2\pi]}{2} - N \ln 2. \end{aligned}$$

Thus, by means of the series expansion

$$\ln \left(1 \pm \frac{m}{N}\right) = \pm \frac{m}{N} - \frac{m^2}{2N^2} + O\left(\frac{m^3}{N^3}\right),$$

we obtain:

$$\ln[P(m, N)] \cong \ln \left[\sqrt{\frac{2}{\pi N}} \right] - \frac{m^2}{2N}.$$

Hence, we get the asymptotic relation:

$$P(m, N) \approx \sqrt{\frac{2}{\pi N}} \exp \left\{ -\frac{m^2}{2N} \right\}.$$

Now, given the step length l , with a time ϑ between two successive steps, we are allowed to define the new variables

$$x = ml; \quad \Delta t = N\vartheta,$$

thus, the probability that the particle lies in the interval $[x, x + \Delta x]$ after a time Δt becomes:

$$P(x, \Delta t) \Delta x = \sum P(m, N) \\ = \frac{1}{2l} P\left(\frac{x}{l}, \frac{t}{\vartheta}\right),$$

where the factor $1/2$ in the r.h.s. of above equation accounts for the fact that for each N (even or odd) the contribution becomes only from one half of the m values (even or odd). Hence, we have:

$$P(x, \Delta t) = \frac{1}{\sqrt{4\pi\Delta t} l^2 / 2\vartheta} \exp\left\{-\frac{x^2}{4\Delta t l^2 / 2\vartheta}\right\},$$

and, putting $l^2 / (2\vartheta) = D$:

$$P(x, \Delta t) = \frac{1}{\sqrt{4\pi D \Delta t}} \exp\left\{-\frac{x^2}{4D \Delta t}\right\}. \quad (2.6)$$

Now, if the positions of the particle are subject to the spherically symmetric probability distribution $\vartheta(lr^2)$, then equation (2.6) reads:

$$P(\Delta r, \Delta t) = \frac{1}{\sqrt{(4\pi D \Delta t)^3}} \exp\left\{-\frac{|\Delta r|^2}{4D \Delta t}\right\}. \quad (2.7)$$

By analogy with this problem, we shall assume that the probability distribution of $B(\Delta t)$ will have the same form of (2.7), i.e.:

$$P[B(\Delta t)] = \frac{1}{\sqrt{(4\pi q \Delta t)^3}} \exp\left\{-\frac{[B(\Delta t)]^2}{4q \Delta t}\right\}, \quad (2.8)$$

where q is a constant, and represents a fluctuation-dissipation theorem. To better specify the nature of q , we must take into account some opportune assumptions (see next Section) about equilibrium of velocity distribution function.

2.3 Diffusion coefficient in velocity space

The solution of the Langevin equation (2.1) is:

$$u - u_0 \exp\{-\beta t\} = \exp\{-\beta t\} \int_0^t \exp\{\beta \xi\} S(\xi) d\xi, \quad (2.9)$$

and since the statistical properties of both sides of (2.9) must be the same, one may define the quantity:

$$\lambda = \exp\{-\beta t\} \int_0^t \exp\{\beta \xi\} S(\xi) d\xi,$$

hence, dividing the interval $[0, t]$ in N intervals Δt , and assuming that Δt obeys equation (2.1), then we can write:

$$\lambda = \sum_i \exp\{-\beta(t - i \Delta t)\} B(\Delta t) = \sum_i \lambda_i.$$

Again, we are dealing with a problem similar to random flights one, as seen above: using a similar mathematical treatment we have:

$$P(\lambda) = \left[4\pi q \int_0^t \exp\{2(\xi - t)\} d\xi \right]^{-3/2} \exp\left\{-|\lambda|^2 \left[4 \int_0^t \exp\{2\beta(\xi - t)\} d\xi \right]^{-1}\right\}.$$

Thus, the velocity distribution function in the velocity space is:

$$P(u, t | u_0) = \left[\frac{2\pi q(1 - \exp\{-2\beta t\})}{\beta} \right]^{-3/2} \exp\left\{-\frac{\beta |u - u_0 \exp\{-\beta t\}|^2}{2q(1 - \exp\{-2\beta t\})}\right\}, \quad (2.10)$$

and for long time ranges we have the asymptotic expression:

$$P(u, \infty | u_0) = \left(\frac{2\pi q}{\beta} \right)^{-3/2} \exp\left\{-\frac{\beta u^2}{2q}\right\}. \quad (2.11)$$

From equation (2.11), we note that the system has an irreversible evolution up to a Gaussian distribution, which is the Maxwell-Boltzmann equilibrium distribution, and that this evolution does not depend on u_0 . According to this statement, the constant q , representing the diffusion constant in the velocity space, must be appointed in such a manner that:

$$q = \frac{\beta K T}{m},$$

where m is the mass of the particle.

To completely evaluate the distribution function for the Brownian particle in the velocity space, it is therefore necessary to consider that fluctuations are accounted in the Langevin equation, and that time scale for $S(t)$ changes is much smaller than time scale for macroscopic variable changes; moreover, the net accelerations suffered by particles in the intervals $[t, t + \Delta t]$ depends only on Δt , and the distribution function for acceleration is

Gaussian, while the velocity is asymptotically distributed according to a Maxwell-Boltzmann statistics.

2.4 Fokker-Planck equation in velocity space and phase space

The problem of finding the probability distribution function may be simplified and reduced to finding the solutions of the Fokker-Planck equation. In this case, we will deal with less restrictive assumptions about fluctuating forces, and further restrictions may be considered as boundary conditions to be imposed in the solution.

One must assume that the Brownian motion of the particle is a Markov process, thus the probability distribution $P(u, t + \Delta t)$ obeys equation:

$$P(u, t + \Delta t) = \int P(u - \Delta u, t) \psi(u - \Delta u; \Delta u) d(\Delta u), \quad (2.12)$$

where $\psi(u; \Delta u)$ is the transition probability for an increase Δu in the velocity after a given time Δt . Expanding (2.12) in power series respectively of Δt and Δu , we obtain the Fokker-Planck equation:

$$\begin{aligned} P(u, t) + \frac{\partial P}{\partial t} \Delta t + O(\Delta t^2) = & \\ = \iiint \left\{ \left[P - \sum_i \frac{\partial P}{\partial u_i} \Delta u_i + \frac{1}{2} \sum_i \frac{\partial^2 P}{\partial u_i^2} \Delta u_i^2 + \sum_{i < j} \frac{\partial^2 P}{\partial u_i \partial u_j} \Delta u_i \Delta u_j + \dots \right] \right. & \\ \times \left[\psi(u, \Delta u) - \sum_i \frac{\partial \psi}{\partial u_i} \Delta u_i + \frac{1}{2} \sum_i \frac{\partial^2 \psi}{\partial u_i^2} \Delta u_i^2 + \sum_{i < j} \frac{\partial^2 \psi}{\partial u_i \partial u_j} \Delta u_i \Delta u_j + \dots \right] & \\ \left. \times d(\Delta u_1) d(\Delta u_2) d(\Delta u_3), \right\} & \end{aligned}$$

and using the expressions:

$$\begin{aligned} \langle \Delta u_i \rangle &= \int_{-\infty}^{+\infty} \Delta u_i \psi(u, \Delta u) d(\Delta u); \\ \langle \Delta u_i^2 \rangle &= \int_{-\infty}^{+\infty} \Delta u_i^2 \psi(u, \Delta u) d(\Delta u); \\ \langle \Delta u_i \Delta u_j \rangle &= \int_{-\infty}^{+\infty} \Delta u_i \Delta u_j \psi(u, \Delta u) d(\Delta u), \end{aligned}$$

the Fokker-Planck equation becomes:

$$P(u, t) + \frac{\partial P}{\partial t} \Delta t + O(\Delta t^2) = -\frac{\partial}{\partial u_i} (\langle \Delta u_i \rangle P) + \frac{1}{2} \frac{\partial^2}{\partial u_i \partial u_j} (\langle \Delta u_i \Delta u_j \rangle P) + O(\langle \Delta u_i \Delta u_j \Delta u_k \rangle), \quad (2.13)$$

In the Langevin equation the frictional coefficient contains all the continuous effects, whereas the stochastic force behaves randomly; thus, passing to the limit $\Delta t \rightarrow 0$ in equation (2.13), we obtain the general form of the Fokker-Planck equation in velocity space as follows:

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial u_i} \left(\frac{\langle u_i \rangle}{\Delta t} P \right) + \frac{1}{2} \frac{\partial^2}{\partial u_i \partial u_j} \left(\frac{\langle u_i u_j \rangle}{\Delta t} P \right). \quad (2.14)$$

But, the Langevin equation (2.1) tells us that:

$$\Delta u = -\beta u \Delta t + B(\Delta t),$$

then, taking into account equation (2.8), and bearing in mind that the asymptotic distribution is a Maxwell-Boltzmann, we get:

$$\psi(u, \Delta u) = \left(4\pi \frac{\beta K T}{m} \Delta t \right)^{-3/2} \exp \left\{ -\frac{m |\Delta u + \beta u \Delta t|^2}{4\beta K T \Delta t} \right\}. \quad (2.15)$$

Moreover, since:

$$\langle \Delta u_i \rangle = -\beta u_i \Delta t,$$

and:

$$\langle \Delta u_i \Delta u_j \rangle = \frac{2\beta K T}{m} \delta_{i,j} + O(\Delta t)^2,$$

then, we obtain the special case of (2.14):

$$\frac{\partial P}{\partial t} = \beta \frac{\partial}{\partial u_i} (u_i P) + \frac{\beta K T}{m} \frac{\partial^2 P}{\partial u_i^2}, \quad (2.16)$$

and its fundamental solution, for which:

$$P(u, 0 | u_0) = \delta(u - u_0),$$

is given by equation (2.10).

In the phase space, the distribution function in equation (2.12) becomes:

$$P(r, u, t + \Delta t) = \iint P(r - \Delta r, u - \Delta u, t) \Psi(r - \Delta r, u - \Delta u; \Delta r, \Delta u) d(\Delta r) d(\Delta u), \quad (2.17)$$

thus, again invoking the Langevin equation we get:

$$\Delta r = u \Delta t,$$

and considering an external force $F(r, t)$ acting on the system:

$$\Delta u = -(\beta u - F) \Delta t + B(\Delta t),$$

hence:

$$\Psi(r, u; \Delta r, \Delta u) = \Psi(u; \Delta u) \delta(\Delta r - u \Delta t).$$

Thus, and inserting the external force term $-F\Delta t$ in the exponential of equation (2.15), we may evolve:

$$\begin{aligned} \left(\frac{\partial P}{\partial t} + u_i \frac{\partial P}{\partial r_i} \right) \Delta t + O(\Delta t)^2 = & - \frac{\partial}{\partial u_i} (\langle \Delta u_i \rangle P) + \frac{1}{2} \frac{\partial^2}{\partial u_i \partial u_j} (\langle \Delta u_i \Delta u_j \rangle P) \\ & + O(\langle \Delta u_i \Delta u_j \Delta u_k \rangle), \end{aligned}$$

hence, passing to the limit $\Delta t \rightarrow 0$, one obtains the Fokker-Planck equation in the phase space as follows:

$$\frac{\partial P}{\partial t} + u_i \frac{\partial P}{\partial r_i} + F_i \frac{\partial P}{\partial u_i} = \beta \frac{\partial}{\partial u_i} (u_i P) + \frac{\beta K T}{m} \frac{\partial^2 P}{\partial u_i^2}. \quad (2.18)$$

2.5 Diffusion equation and diffusion coefficient

We will consider a system given by a fluid having n Brownian particles not uniformly distributed (thus there is a concentration gradient), and we will assume that mutual interactions between particles can be neglected. The distribution function $P(r, u, t)$ in the phase space will be the product of the distribution functions of each particle, so as to have:

$$P(r, u, t) = \prod_{i=1}^n P_i(r_i, u_i, t),$$

where all P_i obey the Fokker-Planck equation.

In the system, we will observe the overposition of Brownian movement and diffusion of Brownian particles, by virtue of the concentration gradient. Since the first process occurs in a time scale of the magnitude of β^{-1} , then one may assume that over a greater time scale, the distribution function of particles has the form:

$$P_i(r_i, u_i, t) = n_i(r_i, t) \left(\frac{m_i}{2\pi KT} \right)^{-3/2} \exp \left\{ -\frac{m_i u_i^2}{2KT} \right\} + \delta P_i(r_i, u_i, t), \quad (2.19)$$

where the second terms accounts for a small additive effect due to diffusion, and depends on the order of magnitude of the concentration gradient.

The integration over u of the Fokker-Planck equation (2.18) after opportune manipulations, leads to equation:

$$\frac{\partial}{\partial t} \left[\int P_i du_i - \frac{1}{\beta} \frac{\partial}{\partial r_i} \int u_i P_i du_i \right] = -\frac{1}{\beta} \frac{\partial^2}{\partial r_i^2} \int u_i^2 P_i du_i, \quad (2.20)$$

from which, using equation (2.19) and taking into account only small order terms, we evolve the diffusion equation:

$$\frac{\partial n_i(r_i, t)}{\partial t} = D \nabla_{r_i}^2 n_i(r_i, t), \quad (2.21)$$

where we put:

$$D = \frac{KT}{\beta m} = \frac{KT}{B} = \frac{KT}{6\pi\eta R}, \quad (2.22)$$

D being the "classical" diffusion coefficient and B a mobility factor: this relation represents the fluctuation-dissipation relation in the configuration space.

Since the particle density in a point x of the space is:

$$c(x, t) = \sum_{i=1}^n \int \delta(x - r_i) P(r, u, t) dr_i du_i,$$

and taking into account only small order terms, such that:

$$c(x, t) = \sum_{i=1}^n n_i(x, t),$$

we may show that the spatial distribution obeys the diffusion equation:

$$\frac{\partial c(x, t)}{\partial t} = D \nabla^2 c(x, t).$$

2.6 Uncertainty in Brownian motion and physical meaning of β

Remarkably, the information we have about the motion of Brownian particles is given by diffusion coefficient, which allows us to obtain a probability distribution for the particle position, and not the exact position. Diffusion coefficient, indeed, is a macroscopic

parameter, and Brownian motion is affected by some uncertainty, which could be formally similar to quantum mechanical one. For a complete discussion of this relationship, one may refer to Furth [6], who made a comparison between Brownian motion and quantum mechanics; a very clear presentation of this topic is also in the paper written by Galluzzi [7], whose approach will be used as main reference in the following discussion.

We will see that the Brownian uncertainty could be found to be formally similar to the well known Heisenberg uncertainty principle of the quantum mechanics, i.e.,

$$\Delta x \Delta p = \frac{1}{2} \hbar$$

(here p stands for the momentum mv), even if this formal analogy does not correspond to a genuine physical equivalence of the uncertainties. In quantum mechanics indeed, the Heisenberg equation arises from experimental observation and measures, which introduce perturbations in the system, whereas Brownian uncertainty mainly depends on random interactions with the medium.

Given a particle subject to monodimensional Brownian motion, there exists a probability density $q(x, t)$ such that $q(x, t) dx$ accounts for the probability that at time t the particle lies in the interval $[x, x + dx]$. Since the total number of particles remains unchanged, the probability density obeys the well-known continuity equation:

$$\frac{\partial q(x, t)}{\partial t} = - \frac{\partial J(x, t)}{\partial x}, \quad (2.23)$$

in which $J(x, t)$ represents the probability flux. The starting point is the assumption that last term is generally given by two distinct contributions: the first corresponding to forces exerted on the Brownian particles, and the second is due to diffusion caused by collisions with fluid molecules. These relations could be written for analogy:

$$J_F = qv_F, \quad (2.24a)$$

and:

$$J_D = qv_D, \quad (2.24b)$$

even if we know that the contribution due to diffusion must obey the well known Fick's law:

$$J_D = -D \frac{\partial q(x, t)}{\partial x}, \quad (2.25)$$

and hence we must assume that in equation (2.24b) the diffusion velocity is:

$$v_D = -D \frac{\partial}{\partial x} (\ln q). \quad (2.26)$$

The explicit form for v_D must be obtained using the new continuity equation, arising from insertion of equations (2.24) and (2.25) into (2.23):

$$\frac{\partial q}{\partial t} = D \frac{\partial^2 q}{\partial x^2} - q \frac{\partial v_F}{\partial x} - \left(v_F - \frac{\partial D}{\partial x} \right) \frac{\partial q}{\partial x}, \quad (2.27)$$

which, if v_F and D are constants, reduces to:

$$\frac{\partial q}{\partial t} = D \frac{\partial^2 q}{\partial x^2} - v_F \frac{\partial q}{\partial x},$$

and the normalised solution has the familiar form:

$$q(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp \left\{ -\frac{(x - v_F t)^2}{4Dt} \right\}, \quad (2.28)$$

representing the Gaussian probability distribution.

In this equation, the average value, initially set to be zero (i.e., we assumed that the particles are at the origin of the coordinate system at initial time), changes in time by virtue of the external driving forces, so as to have:

$$\langle x \rangle = v_F t,$$

whereas the second moment of the process is subject to contribution of the diffusion coefficient, and its value increases in time according to equation (see also equations (1.24-25) in Section 1.4):

$$\langle x^2 \rangle = 2Dt. \quad (2.29)$$

and on the basis of equations (2.26) and (2.27), one may obtain the explicit form for v_D by writing:

$$\begin{aligned} v_D &= \frac{x - v_F t}{2t} \\ &= \frac{x - \langle x \rangle}{2t}, \end{aligned}$$

thus,

$$\langle v_D \rangle = 0,$$

while: