

# BROWNIAN MOTION

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## 1 Introduction

**Brown** Brownian motion is the random motion of particles suspended in a fluid (a liquid or a gas). This phenomenon is named after the botanist Robert Brown. In 1827, while looking through a microscope at particles found in pollen grains of size  $10^{-3}$  cm in water, he noted that

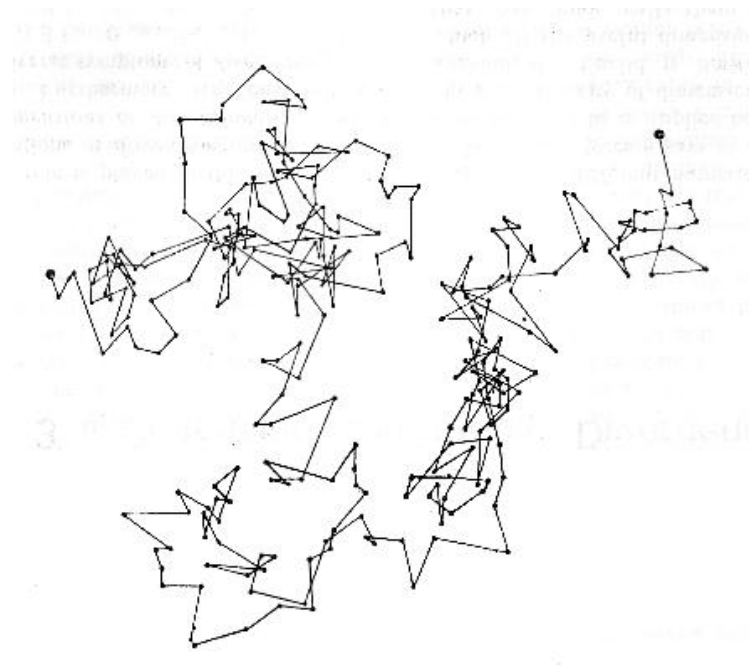
the particles moved through the water but was not able to determine the mechanisms that caused their motion.

**Einstein** Albert Einstein published a paper in 1905 that explained in precise detail how the motion that Brown had observed was a result of the pollen being moved by individual water molecules. This explanation of Brownian motion served as definitive confirmation that atoms and molecules actually exist, and was further verified experimentally by Jean Perrin in 1908. Perrin was awarded the Nobel Prize in Physics in 1926 *for his work on the discontinuous structure of matter.*

**Present** The theory of Brownian motion is perhaps the simplest approximate way to treat the dynamics of nonequilibrium systems. At its heart there is a relation between frictional forces and random forces. The ***fluctuation-dissipation theorem*** relates these forces to each other. The theory of Brownian motion has been extended to situations where the fluctuating object is not a real particle at all, but instead some collective property of a macroscopic system. This has led to the present

theory of *hydrodynamic fluctuations*.

## 2 Einstein's theory



**Brownian motion = macroscopic manifestation of the microscopic** The chaotic perpetual motion of a Brownian particle is the result of its colli-

sions with the molecules of the surrounding fluid. The Brownian particle is much bigger and heavier than the colliding molecules of the fluid. The radius  $a$  of the Brownian particle is typically

$$10^{-9} \text{ m} < a < 5 \times 10^{-7} \text{ m} .$$

Therefore each collision has a negligible effect, but the superposition of many small interactions produces an observable effect. The molecular collisions of a Brownian particle occur in very rapid succession and their number is tremendous. Thus a Brownian particle (e.g., colloidal gold particles of radius  $50 \mu$ ) will suffer about  $10^{20}$  collisions per second if immersed in liquid under normal conditions containing a number of molecule  $N$  of the order of the Avogadro number. This frequency is so high that the small changes in the particle's path caused by each single impact are too fine to be discerned experimentally. However, in one hundredth of a second the average imbalance,  $\sqrt{N}$ , will be of order  $10^9$ , enough to make a change in the velocity of Brownian particle. In other words, the agitated motion of Brownian particle—much slower than that of the atoms —***is the result of random and rapid collisions due to density fluctuations in the fluid*** and thus it is a macroscopic mani-

festation of the microscopic structure of matter.

**Time scales** There are in general three vastly different time scales

$$\tau_s \approx 10^{-20} \text{ s} \ll \tau_B \approx 10^{-3} \div 10^{-7} \text{ s} \ll \tau_r$$

Here  $\tau_s$  is the short atomic scale,  $\tau_B$  is the Brownian timescale for the relaxation of the particle velocity and  $\tau_r$  is the relaxation time for the Brownian particle. In dense colloidal suspensions  $\tau_r$  can become very long of the order of minutes or hours.

## First part of Einstein's argument

There are two parts to Einstein's argument. The first is mathematical and will be discussed later. It is aimed at determining ***how far a Brownian particle travels in a given time interval.***

The result is the following: Let  $f = f(\mathbf{r}, t)$  be the probability density that a Brownian particle is at  $\mathbf{r}$  at time  $t$ . Then, making certain probabilistic assumptions (some of them implicit), Einstein derived the diffusion

equation

$$\frac{\partial f}{\partial t} = D\Delta f \quad (1)$$

where  $D$  is a positive constant, called the coefficient of diffusion. If the particle is at  $\mathbf{0}$  at time  $0$ , so that  $f(\mathbf{0}, 0) = \delta(\mathbf{r})$ , then

$$f(\mathbf{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-\frac{|\mathbf{r}|^2}{4Dt}} \quad (2)$$

(in three-dimensional space, where  $|\mathbf{r}|$  is the Euclidean distance of  $\mathbf{r}$  from the origin). Thus the average value (over many trajectories)  $\langle \mathbf{r}^2(t) \rangle$  of the squared displacement of a Brownian particle in a time interval  $t$  is eq. (2)

$$\begin{aligned} \langle \mathbf{r}^2(t) \rangle &= \frac{1}{(4\pi Dt)^{3/2}} \int |\mathbf{r}|^2 e^{-\frac{|\mathbf{r}|^2}{4Dt}} d^3\mathbf{r} \\ &= 3 \times \frac{1}{(4\pi Dt)^{1/2}} \int x^2 e^{-\frac{x^2}{4Dt}} dx \\ &= 6Dt. \end{aligned} \quad (3)$$

## Second part of Einstein's argument

**The revolutionary hypothesis** The second part of the argument, which relates  $D$  to other physical quantities, is physical. Einstein starts with the remark that the Brownian particles, although of huge size, can still be considered as large molecules and, hence, one can apply statistical mechanics to them. So, if one would consider a large assembly of Brownian particles suspended in water, one could treat them as an ideal gas exercising a partial pressure (osmotic pressure)

$$p = k_B n T \quad (4)$$

where  $k_B$  is Boltzmann's constant,  $n$  is density of the Brownian particles and  $T$  is the temperature of water (Raoult's law for ideal solutions). The idea was **revolutionary** because in contrast with classical thermodynamics, but not with statistical mechanics and the atomic hypothesis. Einstein's task was how to find observable macroscopic consequences from this hypothesis.

**Stokes' law** Since the particle under consideration is much larger than the particles of the surrounding fluid, the collective effect of the interaction between the Brownian particle and the fluid may be considered to be of hydrodynamical character. More precisely, we may take one force acting on the Brownian particle to be the force of dynamical friction. The frictional force exerted by a fluid on a small sphere immersed in it can be determined from Stokes' law, which states that the drag force acting on a spherical particle of radius  $a$  is given by

$$F_d = M \frac{dv}{dt} = -\gamma v, \quad \gamma = 6\pi\eta a \quad (5)$$

where  $M$  is the mass of the particle and  $\eta$  is the fluid viscosity coefficient of water. Thus, the characteristic time scale for the loss of the velocity acquired in a single collision is

$$\tau_B = \frac{M}{\gamma} = \frac{M}{6\pi\eta a} \quad (6)$$

**When the transport of matter is diffusive**  $\tau_B$  is a very short time, but much larger than the microscopic time  $\tau_s \approx 10^{20}$ . For instance, assuming



the density of the material of a Brownian particle to be the same as that of water, and given that  $\eta_{\text{water}} \approx 10^{-3}$  cgs units, for a Brownian particle of radius  $1\mu$ , one finds  $\tau_B \approx 10^{-7}$  sec. Then the motion of the Brownian particles appears random when observed for times  $t > \tau_B$ , that is on a time scale large compared to the time necessary to dissipate the velocity  $v$  acquired by an unbalance in the density of water. On the time scale  $t \gg \tau_B$  motion will be diffusive. In such motions ***there is transport of matter only when there is a density gradient.***

**micro**  $\Leftrightarrow$  **macro**, Einstein now links microscopic quantities to macroscopic ones. The background water fixes the temperature and the time scale over which a particle undergoes a diffusive motion. To find the diffusion coefficient  $D$  for a single particle one considers a gas of particles of arbitrary density  $n$ , but so small that the ideal gas law (4) holds. ***This is done in spite of the fact that in the classical experiments the Brownian particles are so few that they can be considered isolated from each other.***

Then one imagines that some external force  $F$  acts only on the gas of Brownian particles. This force generates, in a stationary state, a gradi-

ent of pressure  $F n = \nabla p$ . Given the ideal gas law (4), we have

$$F n = k_B T \nabla n .$$

The force might be gravity<sup>1</sup>, as in the figure below, but the beauty of the argument is that  $F$  is entirely virtual.

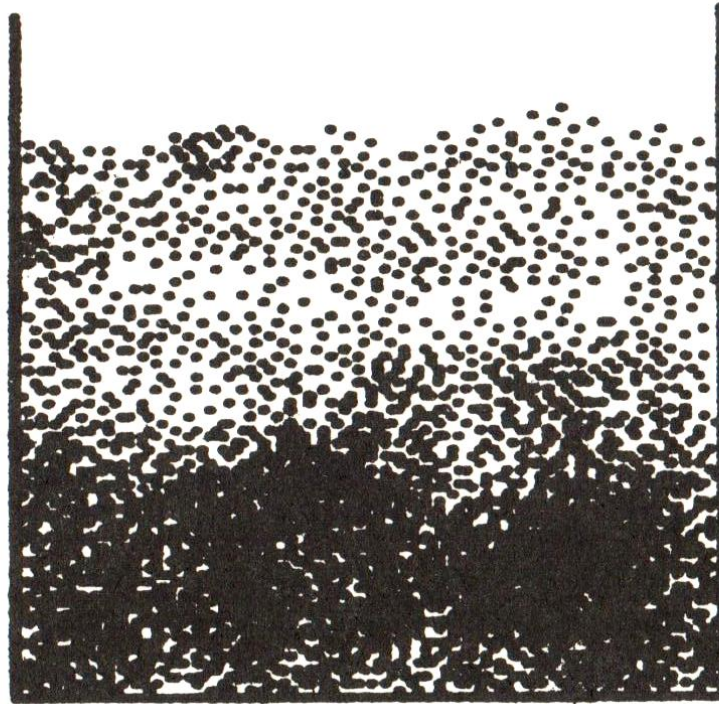
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<sup>1</sup>For particles in a gravitational field (in the vertical direction  $z$ ) pressure and density are (barometric law)

$$p = p_0 e^{-\frac{Mgz}{k_B T}} , \quad n = n_0 e^{-\frac{Mgz}{k_B T}}$$

and thus for  $F = -Mg$ :

$$\nabla p = \frac{-Mgz}{k_B T} p = F n = k_B T \nabla n .$$



Let us now treat the Brownian particle as macroscopic and assume that Stokes law holds. Then in presence of an external force  $F$  we have

$$M \frac{dv}{dt} = -\gamma v + F \quad (7)$$

with steady solution

$$v = \frac{F}{\gamma} = \mu F \quad (8)$$

where  $\mu = 1/\gamma$  is the so-called **mobility**. Then the steady density of flux of particles generated by the force is

$$J_{\text{force}} = nv = n\mu F = \mu k_B T \nabla n \quad (9)$$

The assumption that the individual particles undergo a diffusive motion implies that a density of flux of particles

$$J_n = -D \nabla n \quad (10)$$

where the proportionality constant  $D$  is the diffusion coefficient. At (dynamical) equilibrium the two fluxes compensates each others:

$$J_{\text{force}} + J_n = 0, \quad (11)$$

whence (recalling the explicit formula for the mobility  $\mu = 1/\gamma$  given by Stokes law (5))

$$D = \mu k_B T \quad (12)$$

**The Einstein relation** Eq. (12) is the famous Einstein relation (also known as Einstein-Smoluchowski relation) revealing an unexpected connection between the mean square displacement of the particle ( $D$ ), the mobility  $\mu$ , (that is the ratio of the particle's terminal drift velocity  $v$  to an applied force,  $\mu = v/F$ ) and the mean equilibrium energy ( $k_B T$ ).

By substituting the explicit formula for the mobility, we obtain

$$D = \mu k_B T = \frac{k_B T}{6\pi\eta a} = \frac{RT}{6\pi\eta a N_A} \quad (13)$$

where  $R$  is the universal gas constant and  $N_A$  the Avogadro number. As a consequence of eq. (1),  $D$  is also directly related to the average value (over many trajectories)  $\langle r^2(t) \rangle$  of the squared displacement of a Brownian particle in a time interval  $t$ . We have in fact from eq. (3) that  $\langle r^2(t) \rangle = 6Dt$ , whence

$$\frac{\langle r^2(t) \rangle}{t} = \frac{RT}{6\pi\eta a N_A}. \quad (14)$$

Since the value of  $\langle r^2(t) \rangle$  is directly measurable in a microscope, this relation that can be checked experimentally. The first one to do this was

Jean Perrin thereby settling the century-long dispute about the atomic hypothesis.

**A lesson in philosophy of science** As an application Einstein deduced (1906) the value of Boltzmann's constant  $k_B$ , hence of Avogadro's number  $N_A$ . On the basis of accurate experiments, by using the theory of Einstein, Perrin and collaborators obtained a value essentially equal to the recently accepted value of  $N_A$ ,

Brownian motion theory was derived by Einstein ***without him being really familiar with the details of the experiments that had been performed for about 80 years***. He proceeded ***deductively***, relying on ideal experiments, starting from the remark that particles, even if of macroscopic size, had to obey the laws of statistical mechanics. In particular they had to show energy equipartition and their osmotic pressure had to obey the perfect gas law.

### 3 From random walks to diffusions

**Random walk** Let a particle be subject, at times  $k\tau$ ,  $k = 1, 2, \dots$ , to independent random impacts as a result of which it is displaced each time to the right by an amount  $h$  with probability  $p$  and to the left by an amount  $h$  with probability  $q = 1 - p$ . Denote by  $f(x, t)$  the probability that the moving particle, after starting from the point  $x = 0$  at time  $t = 0$ , will, as a result of  $N$  impacts, reach the position  $x$  at time  $t = N\tau$ . Then  $f(x, t)$  satisfies the following difference equation:

$$f(x, t + \tau) = pf(x - h, t) + qf(x + h, t) \quad (15)$$

This is the evolution equation of the transition probabilities of a **random walk** in one dimension. Such a random walk is called **symmetric** if  $p = q = 1/2$ , otherwise is called **asymmetric**.

Let us see how the difference equation changes if we let both  $h$  and  $\tau$  tend to zero, that is, when we take the **continuum limit**. The physical nature of the problem will compel us to impose certain restrictions on  $h$  and  $\tau$ . By the same reasoning, the quantities  $p$  and  $q$  cannot be taken arbitrarily. Nonobservance of certain conditions discussed below can

result in the particle, within a finite interval of time, going off to infinity with probability one.

Subtracting  $f(x, t)$  from both sides of eq. (20), we get

$$f(x, t + \tau) - f(x, t) = p [f(x - h, t) - f(x, t)] + q [f(x + h, t) - f(x, t)] \quad (16)$$

Suppose that  $f(x, t)$  is differentiable with respect to  $t$  and twice differentiable with respect to  $x$ . Then

$$\begin{aligned} f(x, t + \tau) - f(x, t) &= \tau \frac{\partial f}{\partial t} + o(\tau) \\ f(x - h, t) - f(x, t) &= -h \frac{\partial f}{\partial x} + \frac{1}{2} h^2 \frac{\partial^2 f}{\partial x^2} + o(h^2) \\ f(x + h, t) - f(x, t) &= +h \frac{\partial f}{\partial x} + \frac{1}{2} h^2 \frac{\partial^2 f}{\partial x^2} + o(h^2) \end{aligned}$$

Substituting these equation into eq. (16) we obtain

$$\tau \frac{\partial f}{\partial t} + o(\tau) = -(p - q)h \frac{\partial f}{\partial x} + \frac{1}{2} h^2 \frac{\partial^2 f}{\partial x^2} + o(h^2) \quad (17)$$



To obtain a finite limit, we impose the following requirements: when  $N$  tends to infinity,  $x$  and  $t = N\tau$  are kept of order 1 and

$$\frac{h^2}{\tau} \rightarrow 2D, \quad \text{and} \quad (p - q)\frac{h}{\tau} \rightarrow v \quad (18)$$

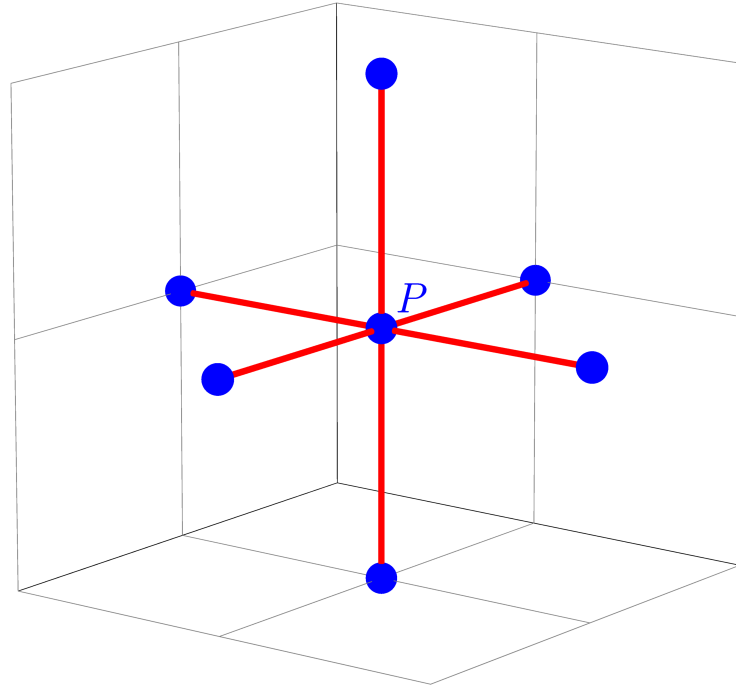
where  $v$  and  $D$  are certain constants, the former called the **drift** the latter, the **diffusion coefficient**. And from this, we find that in the limit eq. (17) becomes

$$\frac{\partial f}{\partial t} = -v\frac{\partial f}{\partial x} + D\frac{\partial^2 f}{\partial x^2} \quad (19)$$

with initial condition  $f(x, 0) = \delta(x)$ .

It is interesting to note that this rather artificial statement of the problem has yielded a physically meaningful result which reflects quite well the essential feature of diffusion in physical space.

Let us consider a symmetric random walk in 3 dimensions. Then at times  $k\tau$ ,  $k = 1, 2, \dots$  the particle at the point  $P$  of coordinates  $\mathbf{r} = (x, y, z)$  is displaced each time with probability  $1/6$  in one of 6 nearest neighborhoods of the point as shown in the picture below:



Then the probability  $f(\mathbf{r}, t)$  that the moving particle, after starting from the point  $\mathbf{r} = 0$  at time  $t = 0$ , will, as a result of  $N$  impacts, reach the position  $\mathbf{r} = (N_1h, N_2h, n_3h)$  at time  $t = N\tau$ .  $f(\mathbf{r}, t)$  satisfies the following difference equation

$$f(\mathbf{r}, t + \tau) = \frac{1}{6} \sum_{i=1}^3 f(\mathbf{r} - h\mathbf{e}_i, t) + f(\mathbf{r} + h\mathbf{e}_i, t) \quad (20)$$

where  $e_i$  are the 3 unit vectors of the Cartesian coordinate system. Then, proceeding as before one finds that

$$\tau \frac{\partial f(\mathbf{r}, t)}{\partial t} + o(\tau) = \frac{1}{6} h^2 \Delta f(\mathbf{r}, t) + o(h^2). \quad (21)$$

If we now let  $N$  tends to infinity, while keeping  $x$  and  $t = N\tau$  of order 1 and

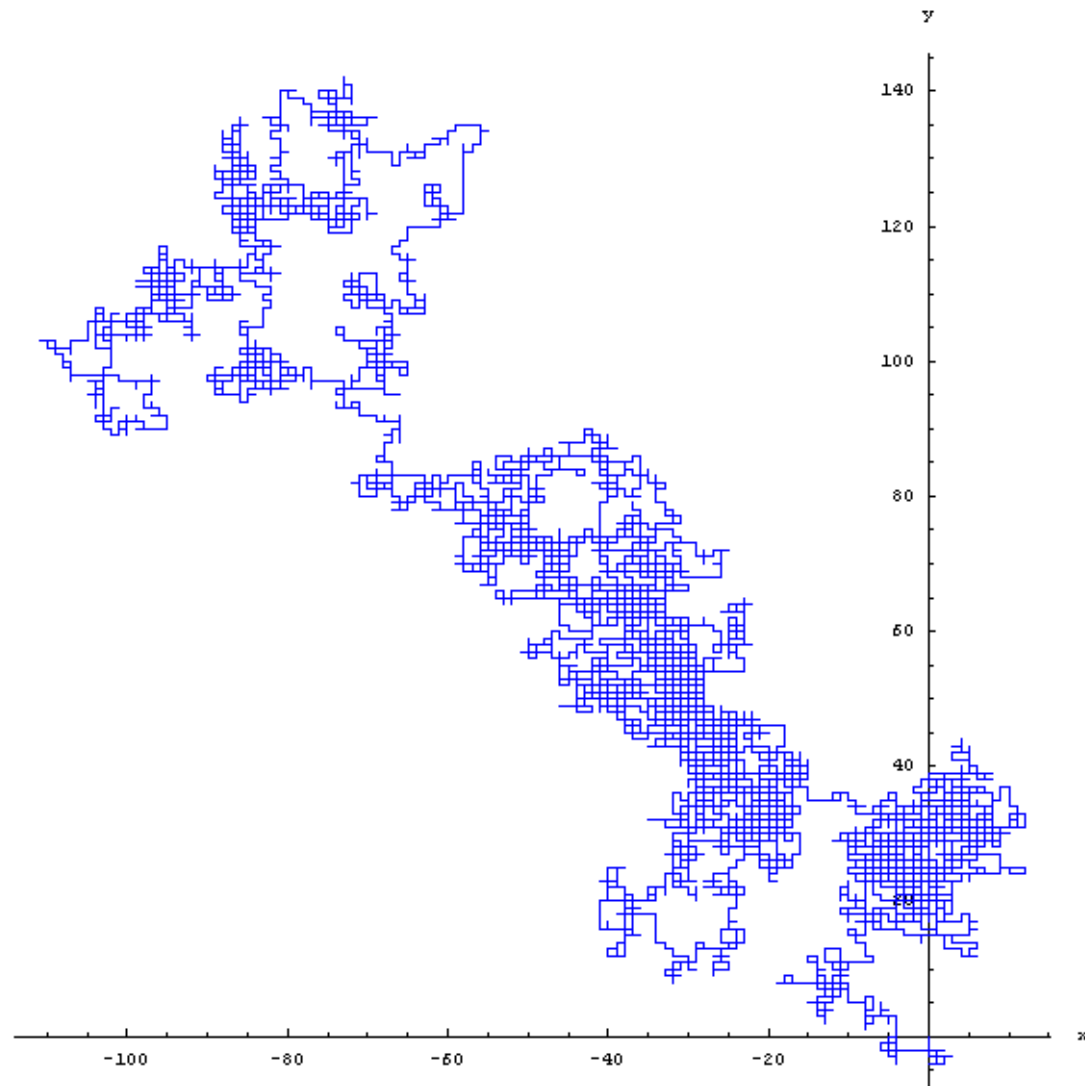
$$\frac{h^2}{\tau} \rightarrow 6D \quad (22)$$

we arrive at

$$\frac{\partial f(\mathbf{r}, t)}{\partial t} = D \Delta f(\mathbf{r}, t),$$

that is, the diffusion equation (1). So, we have made plausible, through a very idealized probabilistic model, the mathematical part of Einstein's argument.

Sample path of a symmetric random walk in the plane:



**The Fokker-Planck equation** Let us now go back to the asymmetric random walk and assume that it has been extended to 3 dimensions. It is useful to change notation and to write  $f(\mathbf{r}, t | \mathbf{0}, 0)$  instead of  $f(\mathbf{r}, t)$  to emphasize that it represents the conditional probability density that the particle is at position  $\mathbf{r}$  at time  $t$  given that it was at the origin at time 0. Since the transition probabilities at each step are invariant under space and time translations, the probability  $f = f(\mathbf{r}, t | \mathbf{q}, s)$  that the particle is at  $\mathbf{r}$  at time  $t$  given that it was at  $\mathbf{q}$  at time  $s < t$  is equal to  $f(\mathbf{r} - \mathbf{q}, t - s | \mathbf{0}, 0)$ . The probability so defined satisfies the initial value problem

$$\frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} \cdot (\mathbf{v}f) = D\Delta_{\mathbf{r}}f \quad (23a)$$

$$\lim_{t \downarrow s} f(\mathbf{r}, t | \mathbf{q}, s) = \delta(\mathbf{r} - \mathbf{q}) \quad (23b)$$

We have written eq. (23) in this form (we could have put the constant  $v$  outside of the nabla symbol), because in this way also the case of a non uniform  $\mathbf{v} = \mathbf{v}(\mathbf{r})$  is covered. Note that the LHS is just the usual form of the free transport of a density. For  $D = 0$  we have just the continuity

equation, so that we may regard  $D$  as a measure of the effect of the random impacts (collisions).

In the physics literature eq. (23) is called ***Fokker-Planck equation*** (1913). Since it was rediscovered by Kolomogorov in 1931, in the probabilistic litterature is known as ***(forward) Kolmogorov equation***.

## 4 The continuum limit as a central limit

Let us consider the result we have obtained from a deeper probabilistic perspective. For simplicity, let us discuss first the case of a symmetric random walk in one dimension.

Before taking the limit (22),  $f(x, t)$  is the probability distribution of the random variable

$$X_N = \sum_{k=0}^N \Delta X_k \quad (24)$$

where  $\Delta X_i$  are i.i.i.d. random variables with mean equal to 0 and variance

given by

$$\text{Var}(\Delta X) = h^2 \left(\frac{1}{2}\right) + h^2 \left(\frac{1}{2}\right) = h^2 \quad (25)$$

In the limit  $N \rightarrow \infty$  we are taking,  $t = N/\tau$  (the macroscopic time) is kept  $O(1)$  and since also  $h^2/\tau$  is kept  $O(1)$ ,  $h^2 = O(\tau) = O(1/N)$ . So  $X_N$  is the sum of  $N$  mean zero random variables with variance  $O(1/N)$ . Thus the **CLT** applies and for  $\tau \rightarrow 0$  we have

$$X^{(\tau)}(t) \equiv \sum_{k=0}^{t/\tau} \Delta X_k \rightarrow X(t) \quad (26)$$

where  $X(t)$  is a mean zero **gaussian** random variable with variance  $Dt$ , that is with density

$$f(x, t) = \frac{1}{(4\pi Dt)^{1/2}} e^{-\frac{x^2}{4Dt}} \quad (27)$$

The power of the **CLT** is its universality: no matter what is the distribution of the the variables  $\Delta X_k$  the limit (26) holds, so we can abandon the

unrealistic assumption that the particle moves by steps all of the same amount. All that matters is independence and finite variance of the  $\Delta X_k$ . (Even the assumption of identical distribution can be relaxed, provided that Lyapunov or Lindeberg conditions are satisfied; see lecture on the limit theorems).

Finally, we can also do away with the assumption that the impacts occur only regularly, every  $\tau$  seconds. With a little bit of more work (but not so much) we can also consider  $\tau$  to be a random variable, say with an exponential distribution

$$\rho(\tau) = \frac{1}{\langle \tau \rangle} e^{-\tau/\langle \tau \rangle}, \quad (28)$$

familiar from elementary kinetic theory. Then in the continuum limit we shall take  $\langle \tau \rangle \rightarrow 0$ .

The probabilistic model so described is more realistic than the random walk we started with. Let us make some rough estimates (forgetting numerical prefactors) for a brownian particle in a fluid at temperature  $T$



with mass  $m$  and  $\langle \tau \rangle \sim \tau_B$ , with  $\tau_B = \mu m$  (as given by eq. (6)).

$$D \sim \frac{(\Delta X)^2}{\langle \tau \rangle} \sim \langle v^2 \rangle \langle \tau \rangle \sim \frac{k_B T}{m} \mu m \sim \mu k_B T \quad (29)$$

in agreement with Einstein relation (12).

The probabilistic model can be used to describe the **self-diffusion** of each atom in a gas. In this case  $\langle \tau \rangle$  is of the order of the mean time between two successive collisions and  $\Delta X$  is of the order of the mean free path. Thus

$$D \sim \frac{(\Delta X)^2}{\langle \tau \rangle} \sim \frac{1}{n^2 \sigma^2} \times n v \sigma \sim \frac{v}{n \sigma} \quad (30)$$

where  $\sigma$  is the area of the base of the collision cylinder,  $v$  the mean speed and  $n$  the density of the gas.