Lecture 1

Overview of Brownian motion, Einstein's and Langevin's theories

CONTENTS

I. INTRODUCTION

Stochastic and diffusive processes are mathematical models that describe physical phenomena that appear to be dominated by randomness. There are several examples in nature, e.g. the movement of molecules in a gas, the molecular dynamics of biomolecules (e.g. proteins), molecular binding/unbinding processes. On larger scales, we can mention the growth of populations of viruses and bacteria, the dynamics driving the spread of a disease, the dynamics of the atmosphere, geophysical motions, stock market prices, etc. But the most famous example, which later gave rise to the theory of stochastic models, is the motion of pollen grains in water.

II.   BROWNIAN MOTION

Robert Brown (1773-1858), Scottish botanist, observed under the microscope the movement of pollen grains in water and reported the following conclusions in 1827 [1]:

- The motion of the particles is erratic and irregular.

- The path of the pollen grains is <u>continuous</u>, but it appears <u>non-differentiable</u>, i.e. it has no tangent at any point.

- Even when particles are close, they appear to move independently of each other. The interaction between pollen grains appears to be purely elastic.

- The molecular composition and mass density of the pollen grains have no impact on the motion (Robert Brown tested different materials and different liquids).

- As the liquid <u>viscosity</u> (i.e. the resistance of a fluid to deformation) is decreased, the motion of the pollen grains becomes more active.

- As the particle <u>radius</u> is decreased, the motion becomes more active.

- As the ambient <u>temperature</u> is increased, the motion becomes more active.

- The motion of the pollen grains never ceases.

Robert Brown studied the motion of pollen grains, later called Brownian motion, only from a qualitative point of view. For a theoretical treatment of the phenomenon, we will have to wait until the beginning of the 20th century when Albert Einstein and Paul Langevin proposed two theories, from two different points of view.

III.   EINSTEIN'S THEORY

Albert Einstein, in 1905 [2], provided a theory of Brownian motion based on the following points key hypotheses

- Pollen grains move as a result of constantly moving solvent molecules colliding with them repeatedly.

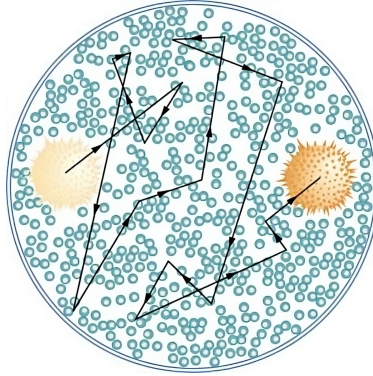- It is possible to describe Brownian motion using a probabilistic model.

FIG. 1. Pollen particles in water exhibit Brownian motion. Brownian motion is caused by fluctuations in the number of atoms and molecules that collide with a small mass, causing the mass to move along unpredictable trajectories.

Based on these assumptions, Einstein's article answers the following questions:

1. How far does a Brownian particle travel in a given period of time?

2. How Brownian motion is related to other physical quantities?

A. The diffusion equation

We assume that there are n particles (i.e. pollen grains) suspended in a liquid. In an interval of time τ, suppose that the x-coordinate of each of these particles changes by Δ, where $\Delta \in \mathbb{R}$ is a real <u>random variable</u> that is different for each particle. The number dn of particles experiencing a displacement between Δ and $\Delta + d\Delta$ is

$$dn = n\varphi(\Delta)d\Delta \,, \tag{1}$$

where φ is a probability density which satisfies

$$\int_{-\infty}^{+\infty} \varphi(\Delta)\, d\Delta = 1 \,, \tag{2}$$

and

$$\varphi(-\Delta) = \varphi(\Delta) \,. \tag{3}$$

Let $f(x,t)$ be the number of particles per unit volume, i.e. the probability density that expresses the likelihood that a particle will be located at location x at time t. Then $f(x, t+\tau)$,

with τ small timestep, is determined by the ensemble average of all possible distributions obtained by shifting the particles by a random displacement Δ:

$$\begin{aligned} f(x, t + \tau) &= \langle f(x + \Delta, t) \rangle_\varphi \\ &= \int_{-\infty}^{+\infty} f(x + \Delta, t) \, \varphi(\Delta) d\Delta \,. \end{aligned} \tag{4}$$

Note that eq. 4 assumes Markovianity, i.e. $f(x, t + \tau)$ depends only on $f(x, t)$ at time t, not at time $s < t$. Under these assumption, applying the Taylor expansion to $f(x, t)$ in both space and time, Albert Einstein derived the celebrated diffusion equation

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2} \,, \tag{5}$$

where we introduced the diffusion constant D with units $[\mathrm{m^2 \, s^{-1}}]$. The diffusion constant expresses the activity of the Brownian motion, i.e. the greater the value of the diffusion constant, the greater the Brownian motion activity will be.

The solution of the equation depends on the initial and boundary conditions. In his work, Albert Einstein assumes the initial condition

$$f(x, 0) = \delta(x - x_0) \,, \tag{6}$$

where δ is the Dirac delta function, and the boundary condition

$$\lim_{x \to \pm\infty} f(x, t) = 0 \,. \tag{7}$$

Under these conditions, the solution of the diffusion equation is

$$f(x, t) = \frac{1}{\sqrt{2\pi\sigma^2(t)}} \exp\left(-\frac{(x - \mu)^2}{2\sigma^2(t)}\right) \,, \tag{8}$$

which is a Gaussian function with mean

$$\mu = x_0 \,, \tag{9}$$

and time-dependent standard deviation

$$\sigma(t) = \sqrt{2Dt} \,. \tag{10}$$

Remarks:

- Einstein's derivation is base on a discrete time assumption, then eq. 8 must be regarded as an approximation which holds only for small τ, i.e. considering the time t.

- Einstein's argument does not give a dynamical theory of Brownian motion; it only determines the nature of the motion and the value of the diffusion coefficient on the basis of some assumptions.

1. The Fick's laws

The diffusion equation defined in eq. 5 is also known as <u>second Fick's law</u>, and it can be written as continuity equation

$$\frac{\partial f}{\partial t} = -\frac{\partial J_d}{\partial x}, \tag{11}$$

where we introduced the diffusion flux

$$J_d = -D\frac{\partial f}{\partial x}, \tag{12}$$

that represents the amount of particles that cross a surface orthogonal to the direction of motion in the unit time. Eq. 12 is also known as <u>first Fick's law</u>. The flux is opposite to the derivative of the probability density function f, then the direction of motion is given by minus the particle concentration derivative (or gradient in high-dimensional systems):

- If $\partial f/\partial x|_{x^*} > 0$, then the particles in x^* will move to x values such that $x < x^*$.

- If $\partial f/\partial x|_{x^*} < 0$, then the particles in x^* will move to x values such that $x > x^*$.

B. The Stokes-Einstein relation

The second part of Einstein's work relates the diffusion constant D to other physical quantities, applying concepts from statistical thermodynamics.

Consider a vessel of water separated by a semi-permeable membrane of area A (fig. 2). By inserting Brownian particles into either half of the vessel (e.g. in the left half), we observe a shift of the membrane to the right because the pressure p_L of the left half is greater than the pressure p_R of the right half of the vessel. To return the membrane to its initial position, it is necessary to exert on the membrane an external force equal to

$$F_e = (p_L - p_R)A, \tag{13}$$

where the difference $p_L - p_R$ is the osmotic pressure. Let us now assume that the membrane is removed, and consider a volume of water $V = A\Delta x$, with Δx the depth of the volume, located where the membrane was previously placed. n Brownian particles in the volume V are now subject to an average force
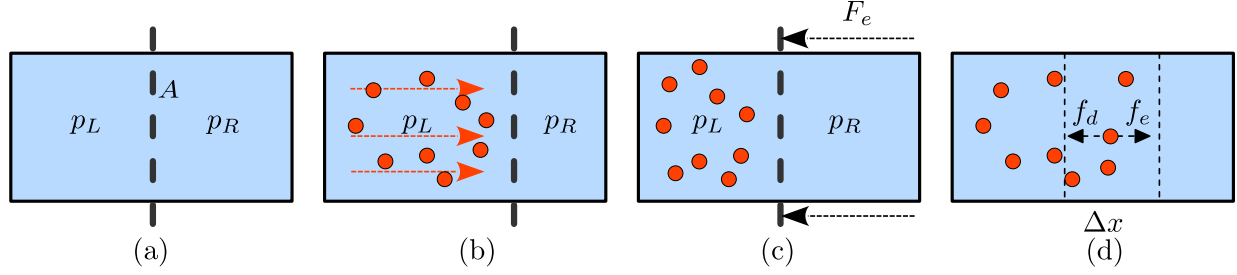
$$f_e = \frac{1}{n}(p_L - p_R)A$$

FIG. 2. (a) The vessel is separated by a semi-permeable membrane. (b) Brownian particles are inserted in the left half of the vessel. (c) An external force is applied to the membrane. (d) The membrane is removed.

$$\begin{aligned} &= \frac{1}{fV}(p_L - p_R)A \\ &= \frac{1}{f\Delta x}(p_L - P_R) \end{aligned} \tag{14}$$

where $f = n/V$ is the density. In the limit $\Delta x \to 0$:

$$f_e = \frac{1}{f(x)}\frac{dp}{dx}. \tag{15}$$

In this way, we have defined the force acting on the particles due to a change in pressure. Now let us rewrite this force in terms of thermodynamic variables Assuming that the Brownian particles do not interact, we can apply the ideal gas law

$$pV = nk_BT, \tag{16}$$

where k_B and T are respectively the Boltzmann constant and the temperature, and derive the expression

$$f_e = \frac{k_BT}{f(x)}\frac{df}{dx}. \tag{17}$$

However, the force f_e due to the change in pressure is not the only force acting on the particles. It is known (Stokes law), that a particle moving in a fluid with velocity dx/dt, is subject to a resistance drag in the opposite direction to the velocity, due to the viscosity of the fluid:

$$f_d(t) = -\gamma\frac{dx}{dt} \tag{18}$$

where γ, with units $[s^{-1}]$, is the friction constant. For spherical particles it is written as

$$\gamma = 6\pi\nu a, \tag{19}$$

where a is the radius of the particles, ν is the viscosity, i.e. the resistance of the fluid to deformation, with units $[\mathrm{kg\,m^{-1}s^{-1}}]$.

We can now write the equation of motion of the particles:

$$m\frac{d^2x}{dt^2} = f_d(t) + f_e(t)\,. \tag{20}$$

At equilibrium, the acceleration is zero, then (from eq. 18)

$$f_e = \gamma\frac{dx}{dt}\,. \tag{21}$$

Then, the velocity is written as

$$\frac{dx}{dt} = \frac{f_e}{\gamma}\,, \tag{22}$$

The two forces generate two fluxes,:

$$
\begin{aligned}
J_e &= f(x)\frac{dx}{dt}\\
&= f(x)\frac{f_e}{\gamma}\\
&= \frac{k_B T}{\gamma}\frac{df}{dx}\,,
\end{aligned}
\tag{23}
$$

and the diffusion flux due to the concentration gradient (eq. 12)

$$J_d = -D\frac{df}{dx}\,. \tag{24}$$

At equilibrium $J_e + J_d = 0$, from which we derive

$$
\begin{aligned}
D &= \frac{k_B T}{\gamma}\\
&= \frac{k_B T}{6\pi\nu a}\,.
\end{aligned}
\tag{25}
$$

This formula, known as Stokes-Einstein relation, is consistent with the observations made by Robert Brown.

IV.   LANGEVIN'S THEORY

Paul Langevin, in 1908 [3], provided a dynamical model that describes the motion of individual Brownian particles. We assume that a particle suspended in a fluid is subject to two forces:

$$m\frac{d^2x}{dt^2} = f_d(t) + f_r(t) \tag{26}$$

where $f_d(t) = -\gamma \frac{dx}{dt}$ is again the viscous drag, and $f_r(t)$ is a random force that can assume both positive and negative values such that the motion of the particle is never stopped.

Afterward, we multiply both sides of eq. 26 by x, and after a few algebraic steps, we derive the equation

$$\frac{m}{2} \frac{d^2 x^2}{dt^2} - m \left(\frac{dx}{dt} \right)^2 = -\frac{\gamma}{2} \frac{dx^2}{dt} + x f_r(t) \tag{27}$$

Given a large number of particles, the equation for the average position $\langle x \rangle$ is written as

$$\frac{m}{2} \frac{d^2 \langle x^2 \rangle}{dt^2} - m \left\langle \left(\frac{dx}{dt} \right)^2 \right\rangle = -\frac{\gamma}{2} \frac{d\langle x^2 \rangle}{dt} + \langle x f_r(t) \rangle . \tag{28}$$

At this point we make two assumptions:

1. According to the equipartition theorem, at high temperature, any quadratic term in the classical Hamiltonian function with respect to position x or momentum p, contributes as $k_B T / 2$ to the average energy of the system. For example, given the Hamiltonian of the harmonic oscillator $H(x, p) = p^2/2m + x^2/2$, the average energy is $\langle E \rangle = k_B T$. Then, the second term on the left side of eq. 28 is written as

$$m \left\langle \left(\frac{dx}{dt} \right)^2 \right\rangle = k_B T . \tag{29}$$

2. The position x is uncorrelated with the random force f_r, then

$$\langle x f_r(t) \rangle = 0 . \tag{30}$$

Inserting eqs. 29, 30 into eq. 28 yields

$$\frac{m}{2} \frac{d^2 \langle x^2 \rangle}{dt^2} - m k_B T = -\frac{\gamma}{2} \frac{d\langle x^2 \rangle}{dt} . \tag{31}$$

Eq. 31 is a first-order differential equation with solution

$$\frac{d\langle x^2 \rangle}{dt} = \frac{2k_B T}{\gamma} - C \frac{m}{\gamma} e^{-\frac{\gamma}{m} t} , \tag{32}$$

where C is an arbitrary constant. In accordance with experimental results, the relaxation time is $m/\gamma \approx 10^8$ s, then the second term can be dropped and

$$\frac{d\langle x^2 \rangle}{dt} = \frac{2k_B T}{\gamma} . \tag{33}$$

Integrating over time, one finds that the average square distance grows linearly with time

$$\langle x^2 \rangle = 2\frac{k_B T}{\gamma}t = 2Dt\,. \tag{34}$$

The average square distance is the variance of the Gaussian function, defined in eq. 10, and solution of the diffusion equation with infinity boundary condition. The standard deviation $\sqrt{2Dt}$ is the average displacement of a particle. Then, given a Brownian particle at position x_0, the position x_t is estimated as

$$x_t = x_0 + \eta\sqrt{2Dt}\,, \tag{35}$$

where η is a random number drawn from the standard normal distribution: $\eta \in \mathcal{N}(0,1)$.

A.   Limits of Langevin's theory and differences with Einstein's theory

1. In Langevin's theory, the presence of water is fully replaced by a single random force. However, the force f_r is not well defined.

2. In Einstein's theory, the stochastic term Δ is a shift in position, while in Langevin's theory, the stochastic term is a force.

3. Einstein derives a Partial Differential Equation (PDE) which describes the time evolution of a probability density function, while Langevin derives a Stochastic Differential Equation (SDE) which describes the trajectory of a single Brownian particle. However, a strong mathematical theory of SDEs is still missing.

4. Einstein explicitly assumes Markovianity, while in Langevin's theory, Markovianity is implicitly assumed in eq. 30.

5. What happens at timescales smaller than 10^8 s?

6. How do Einstein's and Langevin's theories change in the presence of an external force?

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[1] R. Brown, A brief account of microscopical observations made in the months of june, july and august 1827, on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies, Philos. Mag. **4**, 161 (1828).

[2] A. Einstein, Über die von der molekularkinetischen theorie der wärme geforderte bewegung von in ruhenden flüssigkeiten suspendierten teilchen, Ann. Phys. **322**, 549 (1905).

[3] P. Langevin, Sur la theorie du mouvement brownien, C. R. Acad. Sci. **146**, 530–533 (1908).