EIGHTH LECTURE

CONTENTS

A. Brownian motion

Robert Brown (1773-1858) studied the dynamics of pollen grains in a fluid, and observed the following properties:

- The motion of the particles is erratic and irregular
- The path of the pollen grains is continuous, but it appears non-differentiable, i.e. it has no tangent at any point.
- Even when particles are close, they appear to move independently to each other.
- The molecular composition and mass density of the pollen grains have no impact on the motion (Robert Brown tested different materials and different solvents)
- As the solvent viscosity is decreased, the motion of the pollen grains becomes more active.
- As the particle radius is decreased, the motion becomes more active.
- As the ambient temperature is increased, the motion becomes more active.
- The motion of the pollen grains never ceases.

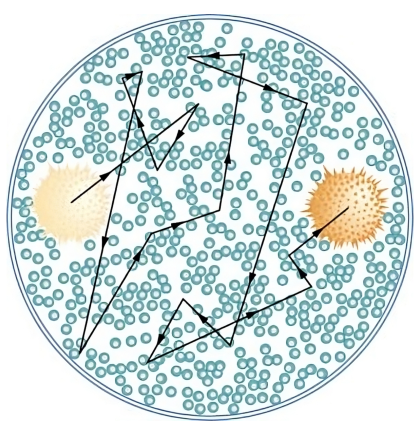

FIG. 1. Pollen particles in water exhibit Brownian motion. Brownian motion is caused by fluctuations in the number of atoms and molecules that collide with a small mass, causing the mass to move along unpredictable trajectories.

B. Einstein's theory

Albert Einstein published a paper in 1905 [1] 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 .

Einstein's argument built upon two key hypotheses:

- The pollen grains move as a result of the incessantly moving solvent molecules striking them frequently.
- The complicated solvent motion can be described only in probabilistic terms.

The Einstein paper answers two questions:

1. How far does a Brownian particle travel in a given period of time?
2. How diffusion is related to other physical quantities?

1. *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 R, where $R \in \mathbb{R}$ is a real random variable that is different for each particle. Under these assumption, Einstein derived the celebrated diffusion equation

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}\,, \tag{1}$$

where we introduced the diffusion constant D and the time-dependent probability density $\rho(x,t)$. The diffusion constant D, with units [nm$^2\, ps^{-1}$], expresses the activity of the Brownian motion, i.e. the greater the value of the diffusion constant, the greater the particle movement will be. The probability density expresses the likelihood that a particle will be located at location x at time t.

Solving this equation, we obtain the solution

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

which is a Gaussian function with mean

$$\mu = x_0\,, \tag{3}$$

and time-dependent standard deviation

$$\sigma(t) = \sqrt{2Dt}\,. \tag{4}$$

Remarks:

- Einstein's derivation is base on a discrete time assumption, then eq. 2 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.

2. *The Stokes-Einstein relation*

The second part of the Einstein's work relates the diffusion constant D to other physical quantities. Applying concepts from statistical and the Stokes' law, one can derive the relation

$$D = \frac{k_B T}{6\pi\nu a}. \tag{5}$$

where k_B is the Boltzmann constant, T is the temperature, a is the radius of the pollen grain and ν denotes the viscosity units

$$[\nu] = \frac{\mathrm{kg}}{\mathrm{m} \cdot \mathrm{s}} = \frac{\mathrm{N}}{\mathrm{m}^2} \cdot \mathrm{s} = \mathrm{Pa} \cdot \mathrm{s}\,. \tag{6}$$

This formula is consistent with the observations made by Robert Brown.

C. Simulation of Brownian motion

The standard deviation $\sigma(t) = \sqrt{2Dt}$ denotes the average displacement that a particle experiences in time t. If we divide the time $[0,\, t]$ in short intervals dt, then we can derive an integration scheme for Brownian particles:

$$x_{k+1} = x_k + \sqrt{2Ddt} \cdot \eta_k\,,$$

where η_k is a random number drawn from a normal distribution.

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