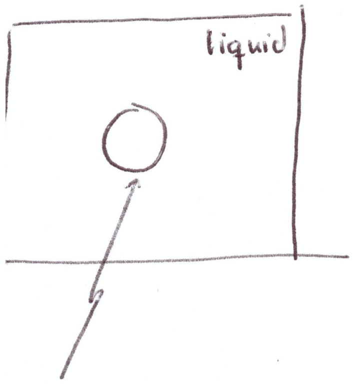
Brownian dynamics

Brown, 1827 "Description of pollen of the plant Clarkia pulchella inmersed in water, when looking through the microscope"

Explanation

Einstein, 1905.
Smoluchowski, 1906
Langevin, 190_
...



macroscopic particle immersed in a liquid. $\longrightarrow$ due to the thermal "kicks" of the solvent molecules, it describes a random motion, today called "Brownian" motion. (see animation).

How do we describe the Brownian motion of this particle?

- One possibility: MD. $\longrightarrow$ However, it is too computationally expensive:
- We are often not so interested in the solvent molecules, so
- How about trying to consider all the thermal fluctuations as "mean" forces on the macroscopic particle?

For simplicity in one dimensión:

$$m \frac{\partial^2 x}{\partial t^2} = F(t) + F_{ext}(t) \qquad (1)$$

Effective force by the solvent.

Other external forces acting on the particle (e.g. electrostatic, ...)

Force ~~with~~ by the solvent:

$$F(t) = \underbrace{-m\gamma V}_{\substack{\text{Viscous} \\ \text{Force} \\ \text{Prop. to } V}} + \underset{\substack{\uparrow \\ \text{Noise}}}{\xi}$$

γ: Friction coefficient

$V = \frac{\partial x}{\partial t}$ velocity.

so (1) becomes:

$$m\frac{\partial^2 x}{\partial t^2} = -m\gamma\frac{\partial x}{\partial t} + f_{ext}(t) + \xi \qquad (2)$$

Langevin equation:

- to solve it one needs Stochastic calculus due to the noise term ξ
- Under some circumstances it can be solved analitically (F. Reif, Fundamentals of Stat. & Thermal Phys, p. 560)
- It can also be solved numerically.

Numerical "Euler-like" solutions at discrete times Δt

~~$x(t+\Delta t) = x(t) +$~~

- Diffusive regime → Friction force is strong such that velocities relax within Δt:

$$\gamma^{-1} \ll \Delta t:$$

$$x(t+\Delta t) = x(t) + \frac{1}{m\gamma} f_{ext}(t)\,\Delta t + \underbrace{X(\Delta t)}_{\text{Random term}} \qquad (3)$$

Random term:
- Obtained from a Gaussian distribution:

Average : $\langle X(\Delta t)\rangle = 0$

Widht - $\langle \Delta X^2(\Delta t)\rangle = \frac{2k_BT}{m\gamma}\Delta t$

How do we get the friction coefficient: $m\gamma$?

<u>Einstein relation:</u> (no time to demonstrate it. Look at Reif Book for it).

$$D = \frac{k_B T}{m\gamma}$$

Diffusion coefficient

Related with a fundamental theorem in statistical physics: Fluctuation - Dissipation theorem.

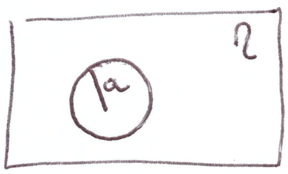
Replacing D in (3):

$$x(t+\Delta t) = x(t) + \frac{D}{k_B T} f_{ext}(t)\,\Delta t + \underbrace{X(\Delta t)}$$

$$\mu = \langle X(\Delta t) \rangle = 0$$

$$\sigma^2 = \langle \Delta X^2(\Delta t) \rangle = 2D\Delta t.$$

<u>Particular case; a sphere immersed in a viscous medium:</u>



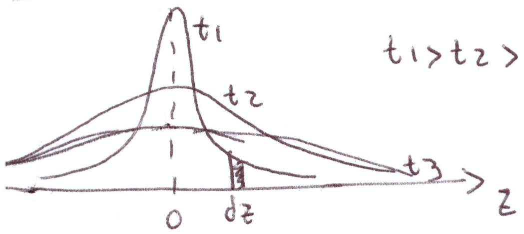
Friction force: $= -6\pi\eta a v$ Stokes law

Dynamic Viscosity: Property of the medium
e.g. water at ~~300 K~~ 20 °C
$\eta = 1.002$ mPa · s

Geometric property of the diffusing particle.

$$m\gamma = 6\pi\eta a \Rightarrow \boxed{D = \frac{k_B T}{6\pi\eta a}}$$

Example : 1D - Diffusion



$t_1 > t_2 > t_3$

$$P(z,t)\,dz = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-(z-\mu)^2/2\sigma^2}\,dz$$

Gaussian which is spreading over time:

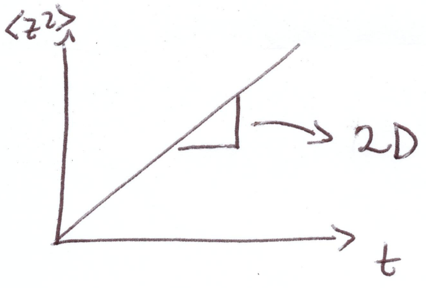
average position : $\mu = \langle z \rangle = 0$

sigma : $\sigma = \langle z^2 \rangle = 2Dt$

Note the difference:

Diffusion : $\langle z^2 \rangle = 2Dt$ Mean Square displacement $\propto t$

Ballistic : $\langle z^2 \rangle \propto t^2$



How to get to this result from Langevin eq. explained in Reif. F. P. 560

Example 2: constant force and no inertial term

$f_{ext} = f \Rightarrow$ constant force.

$$m\frac{\partial^2 x}{\partial t^2} = 0 \Rightarrow$$ Velocities relax very fast due to strong friction

$$m\gamma \frac{\partial x}{\partial t} = f + \xi$$

Taking averages :

$$m\gamma \langle v \rangle = f + \langle \xi \rangle$$

$\langle \xi \rangle \to 0$: if it is white noise

$$\boxed{\langle v \rangle = \frac{f}{m\gamma} = \frac{Df}{K_BT}}$$