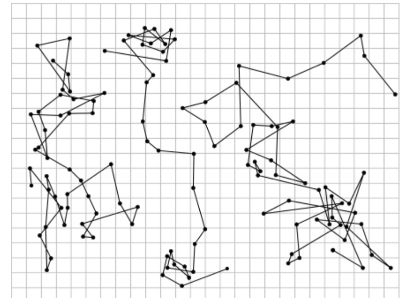
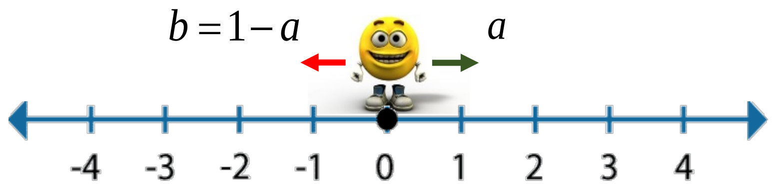
Recall what we did last time

probabilistic

Connection ?

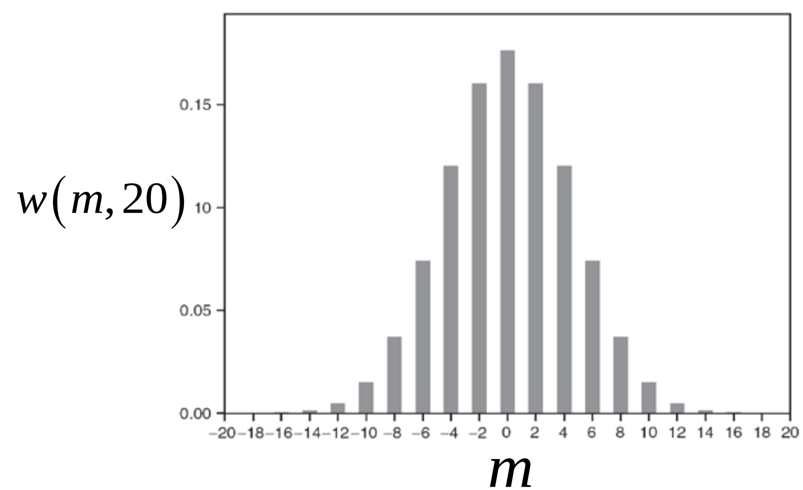
deterministic





random walk: 1-D lattice model

$$w(m, N) = \frac{C_p^N}{2^N}$$



Characteristic function

$$\lambda(\theta) = ae^{i\theta} + be^{-i\theta}$$

$$P_N(m) = \frac{1}{2\pi}\int_{-\pi}^{\pi} \lambda^N(\theta)e^{-i\theta m}d\theta$$

$$= w(m,N) = \frac{C_p^N}{2^N}$$

General characteristic function

$$\lambda(k) = \int_{-\infty}^{\infty} p(x)e^{ikx}dx$$

$$P_N(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \lambda^N(k)e^{-ikx}dx$$

3.1.3 Mean, Variance, and the Generating function

The expected value of function f is defined by

$$\langle f \rangle = \sum_{m=-N}^{N} f(m) w(m,N)$$

e.g. $$\langle p \rangle = \sum_{m=-N}^{N} p(m) w(m,N) = \sum_{p=0}^{N} p C_p^N 2^{-N}$$

$$\langle m^n \rangle = \sum_{m=-N}^{N} m^n w(m,N)$$ n-th moment

$\langle m \rangle$ mean displacement

$\langle m^2 \rangle$ mean square displacement or variance

3.1.3 Mean, Variance, and the Generating function

In order to evaluate various moments, we introduce generating function

$$G(u) = \sum_{p=0}^{N} u^p w(m, N)$$

or

$$G(u) = \sum_{p=0}^{N} u^p C_p^N \left(\frac{1}{2}\right)^N = \sum_{p=0}^{N} C_p^N u^p \left(\frac{1}{2}\right)^{N-p} \left(\frac{1}{2}\right)^p$$

$$= (1+u)^N \left(\frac{1}{2}\right)^N$$

Their derivatives are related to *n*-th moments

Example 1: $\langle m \rangle = ?$

$$G'(u) = \sum_{p=0}^{N} p u^{p-1} w(m,N) \Rightarrow G'(1) = \sum_{p=0}^{N} p w(m,N) = \langle p \rangle$$

$$G'(u) = N(1+u)^{N-1}\left(\frac{1}{2}\right)^{N} \Rightarrow G'(1) = N/2$$

$$\boxed{\langle p \rangle = N/2}$$

$$\langle p \rangle = \frac{1}{2}\sum_{p=0}^{N}(N+m)w(m,N)$$

$p = (N+m)/2$

$$= \frac{1}{2}\sum_{p=0}^{N} N w(m,N) + \frac{1}{2}\sum_{p=0}^{N} m w(m,N) = \frac{N}{2} + \frac{\langle m \rangle}{2}$$

$$\boxed{\langle m \rangle = 0}$$

Example 2: $\langle m^2 \rangle = ?$

$$G'(u) = \sum_{p=0}^{N} p u^{p-1} w(m,N) \qquad G''(u) = \sum_{p=0}^{N} p(p-1) u^{p-2} w(m,N)$$

$$G''(1) = \sum_{p=0}^{N} p(p-1) w(m,N) = \langle p(p-1) \rangle = \langle p^2 \rangle - \langle p \rangle$$

$$G(u) = (1+u)^N \left(\frac{1}{2}\right)^N \Rightarrow G''(u) = N(N-1)(1+u)^{N-2} \left(\frac{1}{2}\right)^N$$

$$\Downarrow$$

$$G''(1) = \frac{N(N-1)}{4}$$

3.1.3 Mean, Variance, and the Generating function

$$\langle p \rangle = N/2$$

$$G''(1) = \langle p^2 \rangle - \langle p \rangle$$

$$G''(1) = \frac{N(N-1)}{4}$$

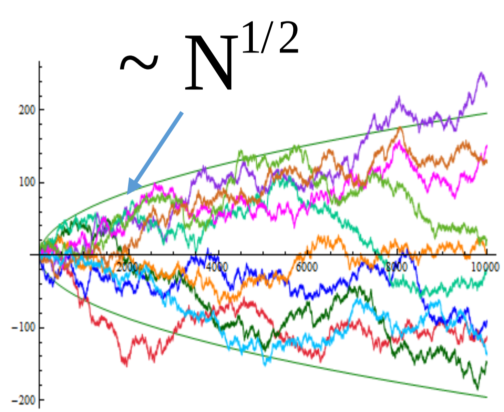
$$\langle p^2 \rangle = \langle p \rangle + \frac{N(N-1)}{4} = \frac{N^2}{4} + \frac{N}{4}$$

$$m = 2p - N$$

$$\langle m^2 \rangle = \langle (2p-N)^2 \rangle = 4\langle p^2 \rangle + N^2 - 4N\langle p \rangle$$

$$= N^2 + N + N^2 - 4N\frac{N}{2} = N$$

$$\langle m^2 \rangle^{1/2} = N^{1/2}$$



3.1.3 Mean, Variance, and the Generating function

Generally the nth- moment $\langle x^n \rangle = \int_{-\infty}^{\infty} p(x) x^n dx$

Its characteristic function

$$\lambda(k) = \langle e^{ikx} \rangle = \int_{-\infty}^{\infty} p(x) e^{ikx} dx = \int_{-\infty}^{\infty} p(x) \sum_{m=0}^{\infty} \frac{(ikx)^m}{m!} dx$$

$$= \sum_{m=0}^{\infty} \frac{i^m k^m}{m!} \int_{-\infty}^{\infty} p(x) x^m dx = \sum_{m=0}^{\infty} \frac{i^m k^m}{m!} \langle x^m \rangle$$

n-th moments represented by characteristic function

$$\left. \frac{d^n \lambda}{dk^n} \right|_{k=0} = \sum_{m=0}^{\infty} i^m \langle x^m \rangle \frac{m(m-1)\cdots(m-n+1)}{m!} k^{m-n} \Bigg|_{k=0} = i^n \langle x^n \rangle$$

$$\Rightarrow \quad \boxed{\langle x^n \rangle = -i^n \left. \frac{d^n \lambda(k)}{dk^n} \right|_{k=0}}$$

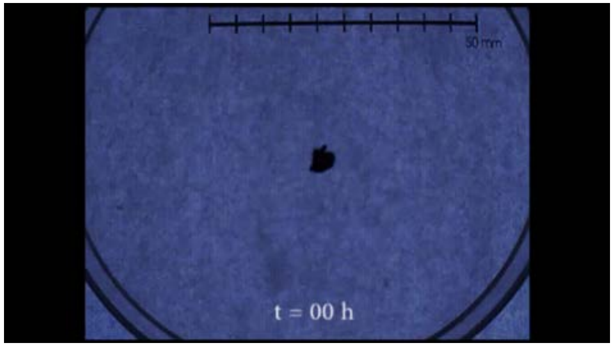
3.1.4 To determine Boltzmann's constant from Brownian Motion

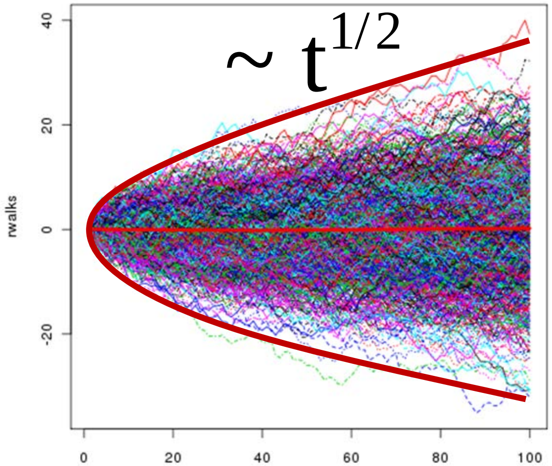
Einstein (1905)

- assume that the macroscopic resistance on the particle is proportional to the velocity - using classical hydrodynamics
- predicated diffusion follows the statistical law

$$\langle x^2 \rangle = \frac{1}{3}\left[\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle\right] = \frac{1}{3}\langle r^2 \rangle = 2Dt$$

$$\langle m^2 \rangle^{1/2} = N^{1/2}$$





Perrin:
experiment in 1908.
Nobel Prize in 1926

3.1.4 To determine Boltzmann's constant from Brownian Motion

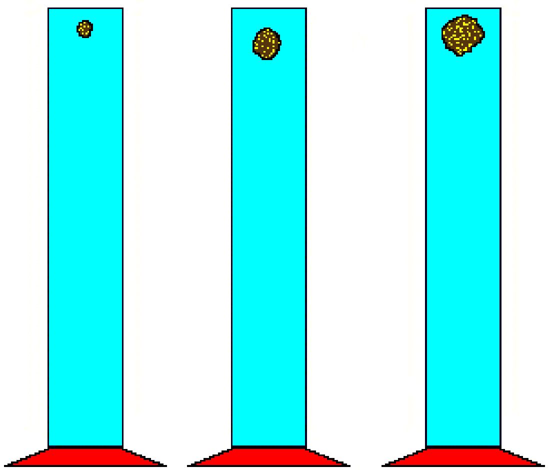
diffusion coefficient D

$$D = kT / f$$

T : absolute temperature;

K : Boltzmann's constant

f : the coefficient of resistance



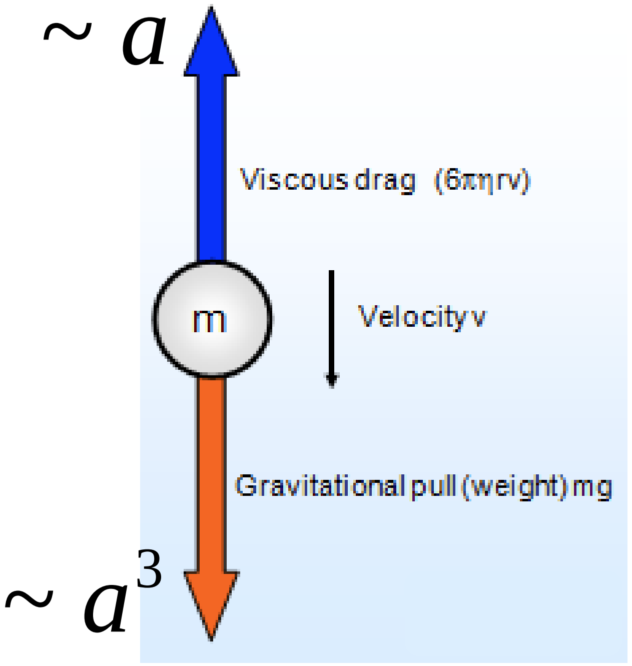
Stokes' law: the drag force F

$$F = f V = 6\pi\eta a V$$

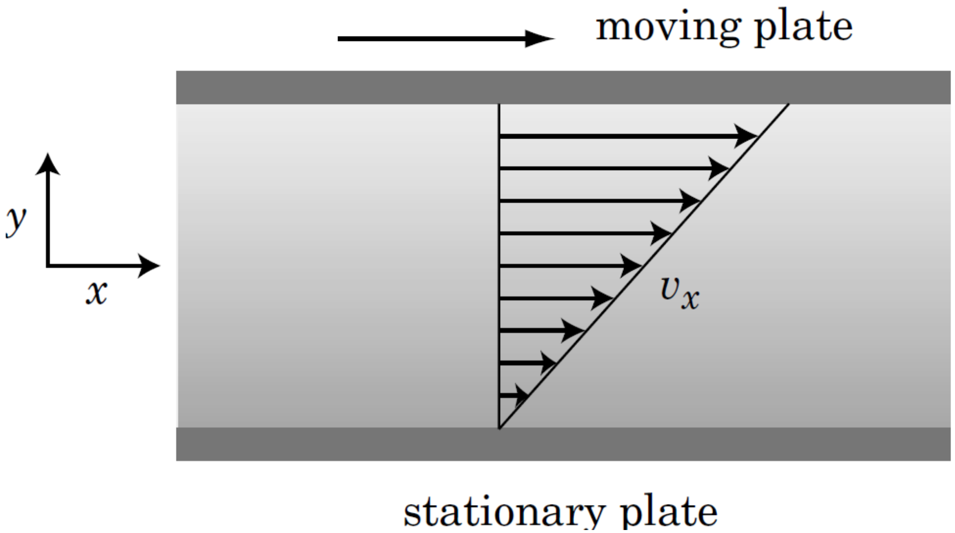
η : viscosity coefficient

a : particle size

V: velocity



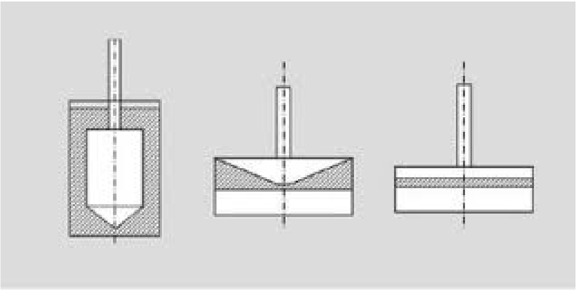
Viscosity of Solutions



$$\eta \frac{\partial v_x}{\partial y} = \sigma_{yx}$$

the unit of η is $N \cdot s/m^2$

Viscosity



Anton Paar Germany Inc

The modern theory of the Brownian motion

Langevin's equation $$m\frac{d\mathbf{v}}{dt} = -f\mathbf{v} + \mathbf{F}(t)$$

- ***v*** the velocity of the particle and *m* mass.
- The random force follows Fluctuation-dissipation relation

$$\langle \mathbf{F}_i(t)\cdot\mathbf{F}_i(t')\rangle = 6fk_BT\delta(t-t')$$

3.1.4 To determine Boltzmann's constant from Brownian Motion

To solve $$m\frac{d\mathbf{v}}{dt} = -f\mathbf{v} + \mathbf{F}(t)$$

multiply both sides with **x**, and take the average

$$m\left\langle \mathbf{x}\cdot\frac{d\mathbf{v}}{dt}\right\rangle = -f\left\langle \mathbf{x}\cdot\mathbf{v}\right\rangle + \left\langle \mathbf{x}\cdot\mathbf{F}(t)\right\rangle$$

$$m\left(\frac{d\left\langle \mathbf{x}\cdot\mathbf{v}\right\rangle}{dt} - \left\langle v^2\right\rangle\right) = -f\left\langle \mathbf{x}\cdot\mathbf{v}\right\rangle + \left\langle \mathbf{x}\cdot\mathbf{F}(t)\right\rangle$$

$$\left\langle \mathbf{x}\cdot\mathbf{F}(t)\right\rangle = 0$$

Not correlated

$$\frac{d\left\langle \mathbf{x}\cdot\mathbf{v}\right\rangle}{dt} + \frac{f}{m}\left\langle \mathbf{x}\cdot\mathbf{v}\right\rangle - \left\langle v^2\right\rangle = 0$$

$$\frac{d\langle \mathbf{x}\cdot\mathbf{v}\rangle}{dt}+\frac{f}{m}\langle \mathbf{x}\cdot\mathbf{v}\rangle-\langle v^2\rangle=0$$

⇩

$$\langle \mathbf{x}\cdot\mathbf{v}\rangle = c\exp[-\frac{f}{m}t]+\frac{m}{f}\langle v^2\rangle$$

$$\rightarrow \frac{m}{f}\langle v^2\rangle \text{ stationary solution}$$

3.1.4 To determine Boltzmann's constant from Brownian Motion

$$\langle \mathbf{x}\cdot\mathbf{v}\rangle = \frac{1}{2}\frac{d\langle \mathbf{x}\cdot\mathbf{x}\rangle}{dt} = \frac{1}{2}\frac{d\langle r^2\rangle}{dt} = \frac{1}{2}\frac{d(6Dt)}{dt} = 3D$$

When in equilibrium

$$\langle \mathbf{x}\cdot\mathbf{v}\rangle = \frac{m}{f}\langle v^2\rangle$$

$$\langle x^2\rangle = \frac{1}{3}\langle r^2\rangle = 2Dt$$

$$\frac{1}{2}m\langle v^2\rangle = \frac{1}{2}f\langle \mathbf{x}\cdot\mathbf{v}\rangle = \frac{3}{2}fD$$

$$\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}kT$$

energy equipartition principle

Boltzmann constant

$$k = D\frac{f}{T} = D\frac{6\pi\eta a}{T}$$