On the Brownian motion according to Einstein

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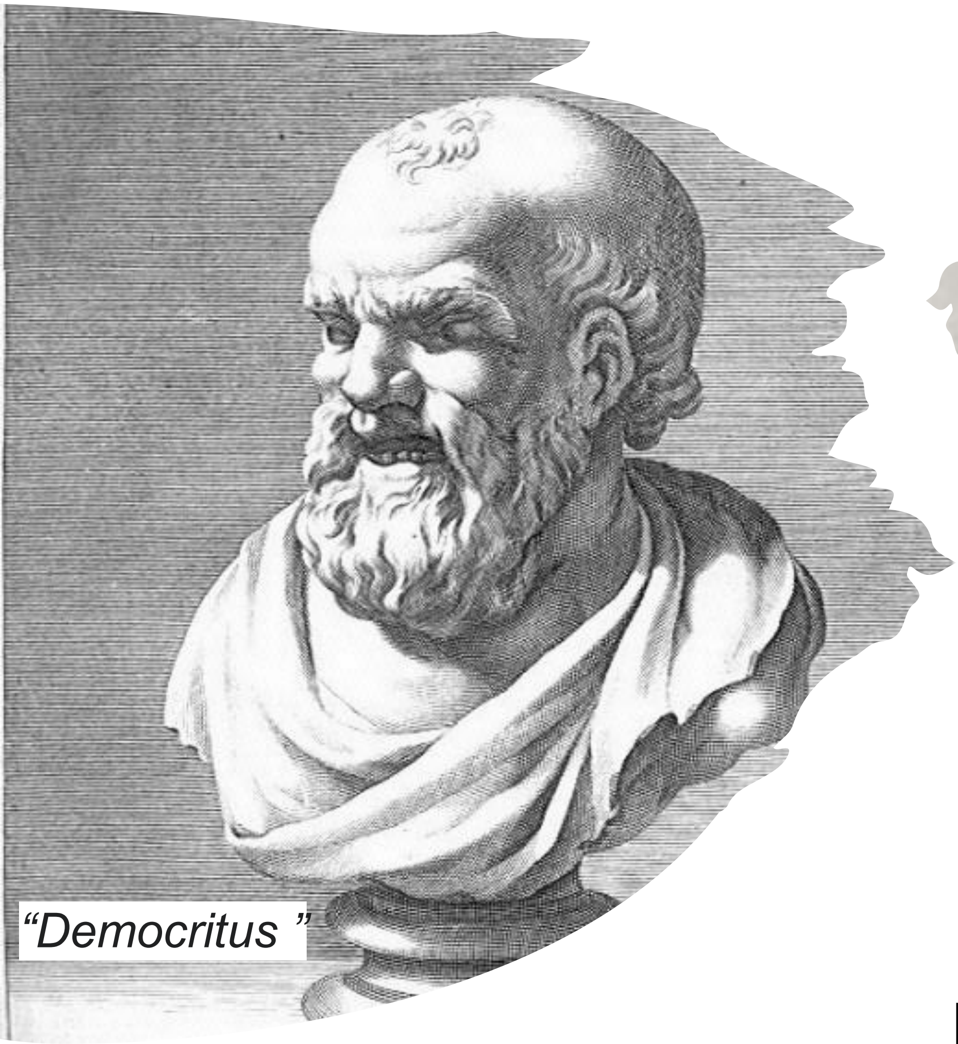
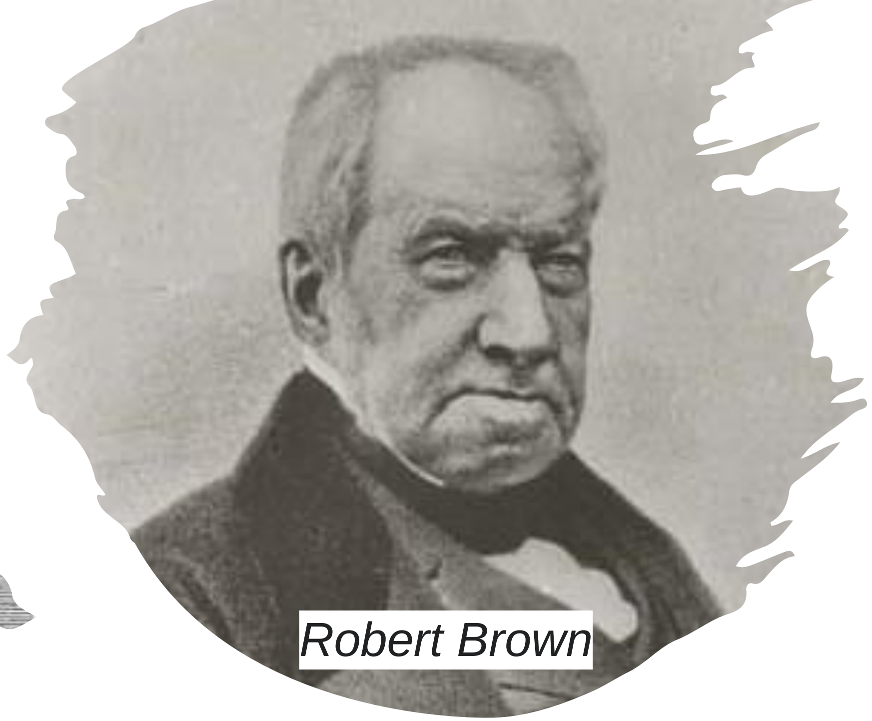
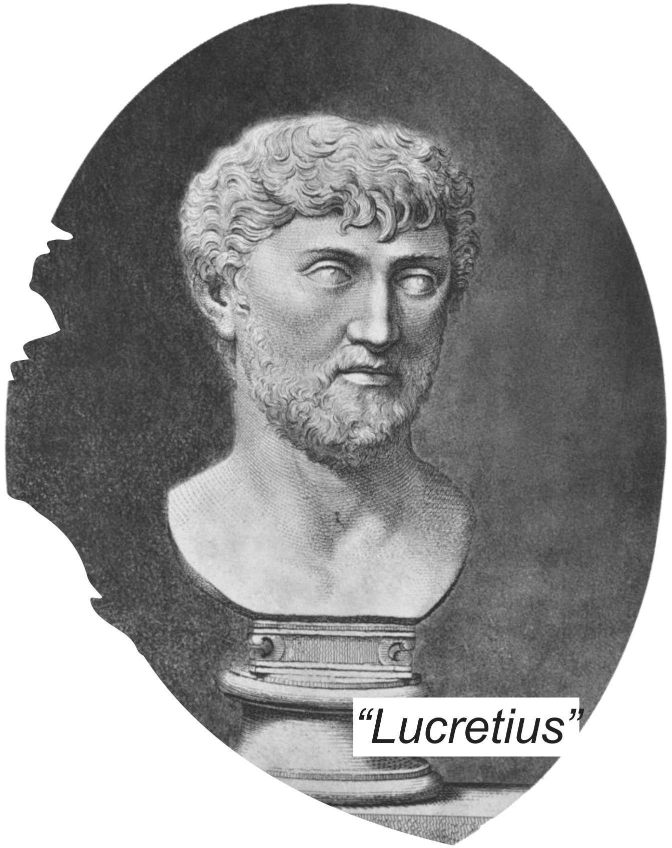


“Democritus ”



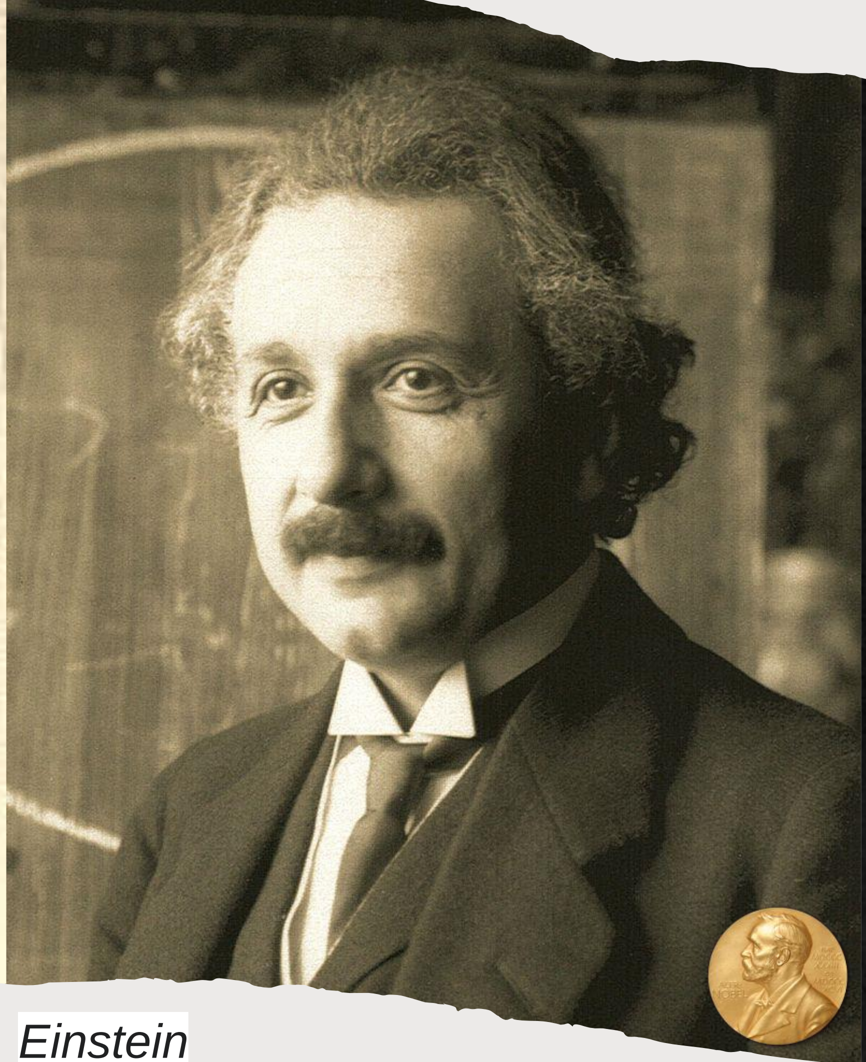
Robert Brown



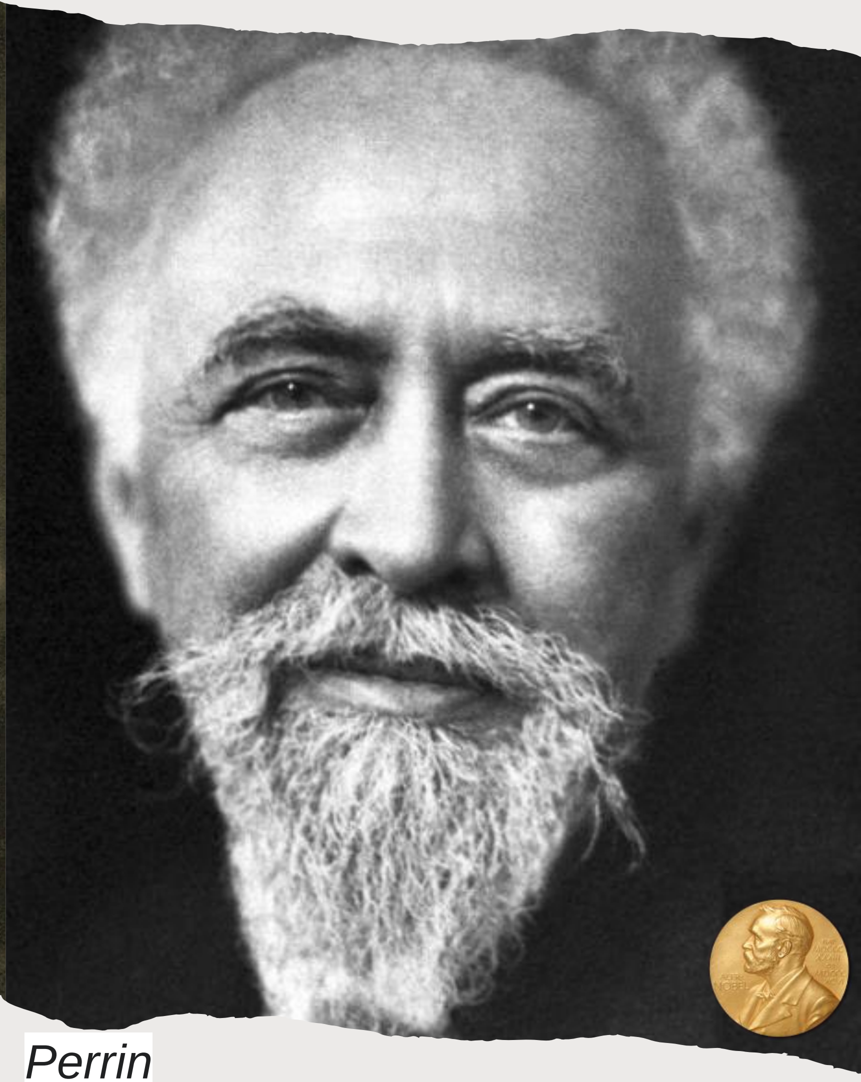
“Lucretius”

From the ancient Greece to Robert Brown

Boltzmann

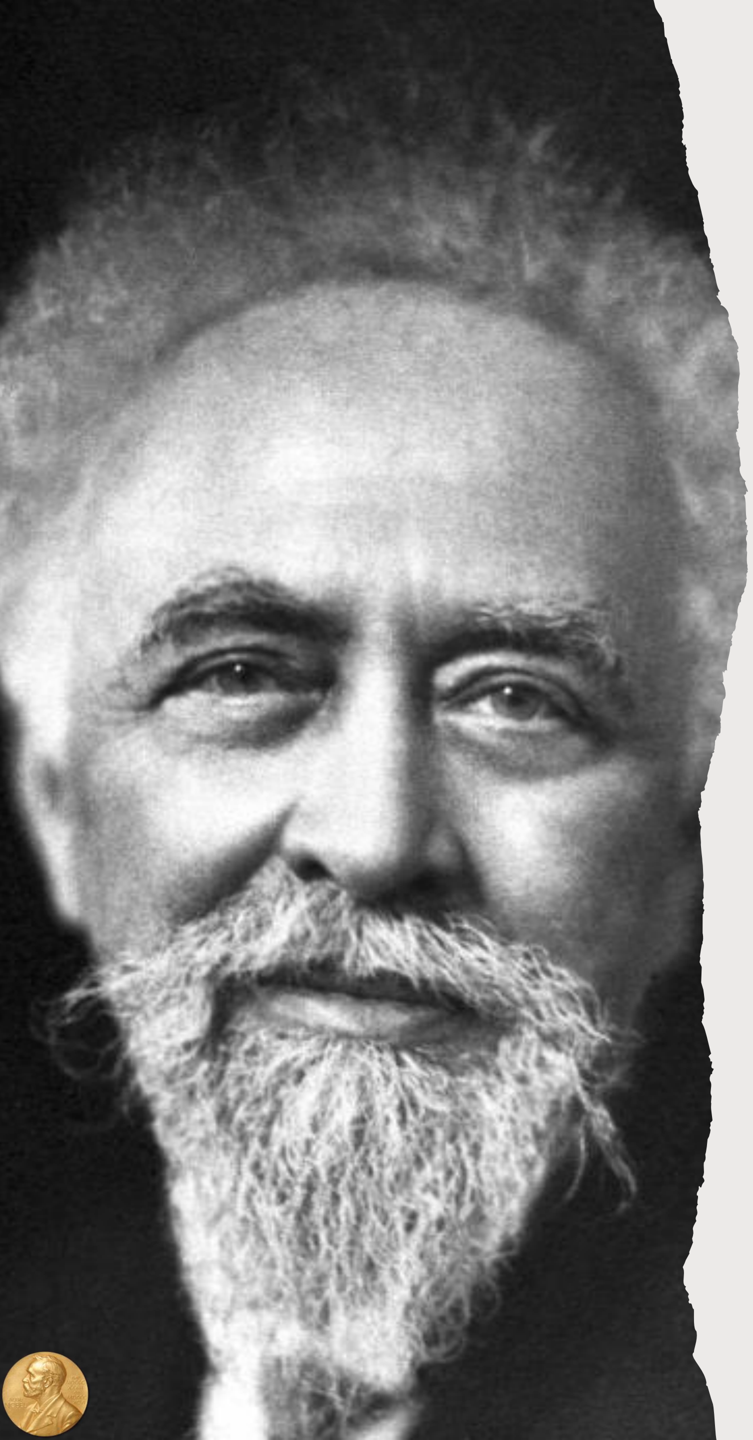


Einstein



Perrin

From Boltzmann to the Nobel Prize of 1926



Brownian motion

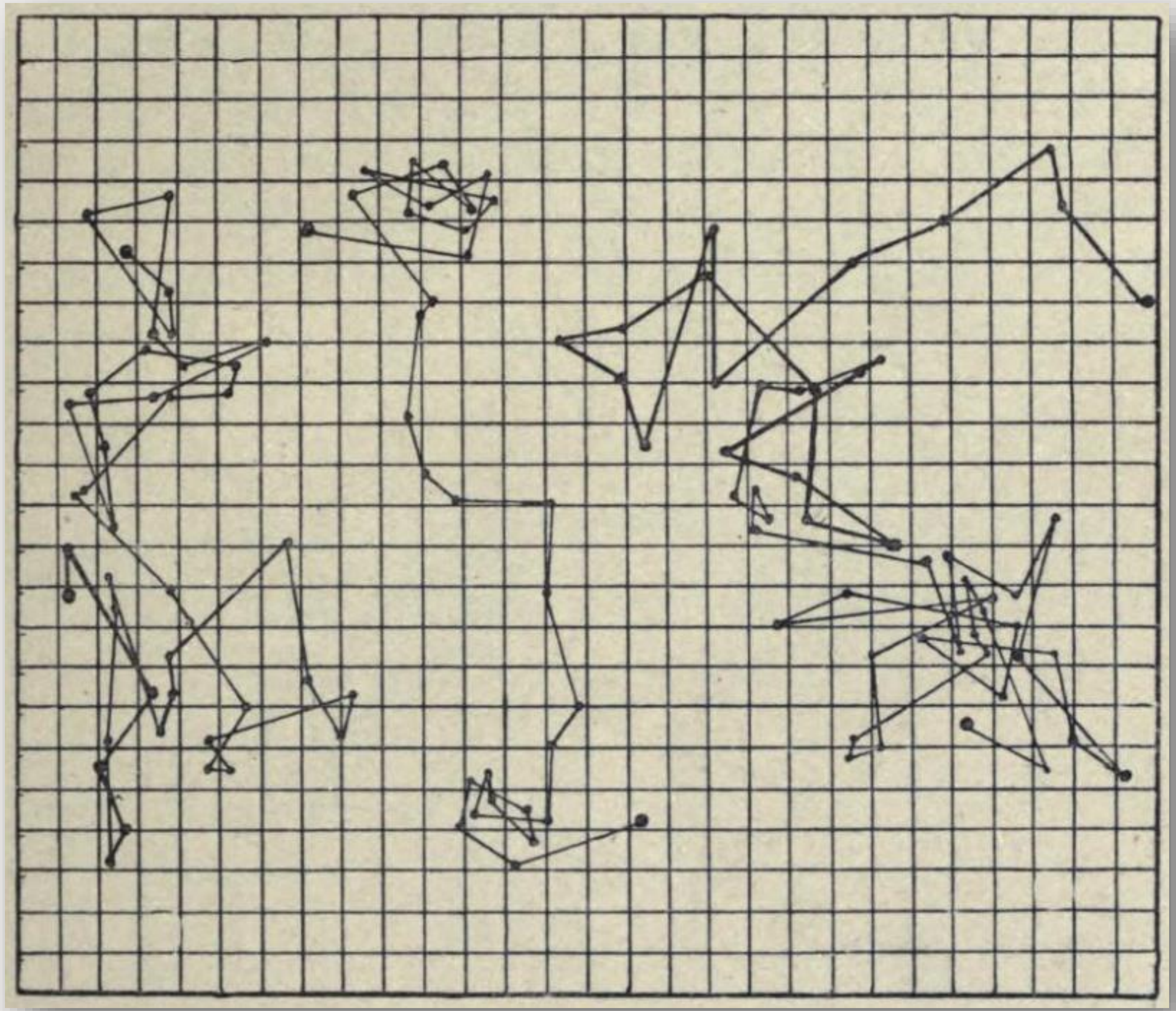


Diagrama feito por J. Perrin in his work *Les Atoms.*

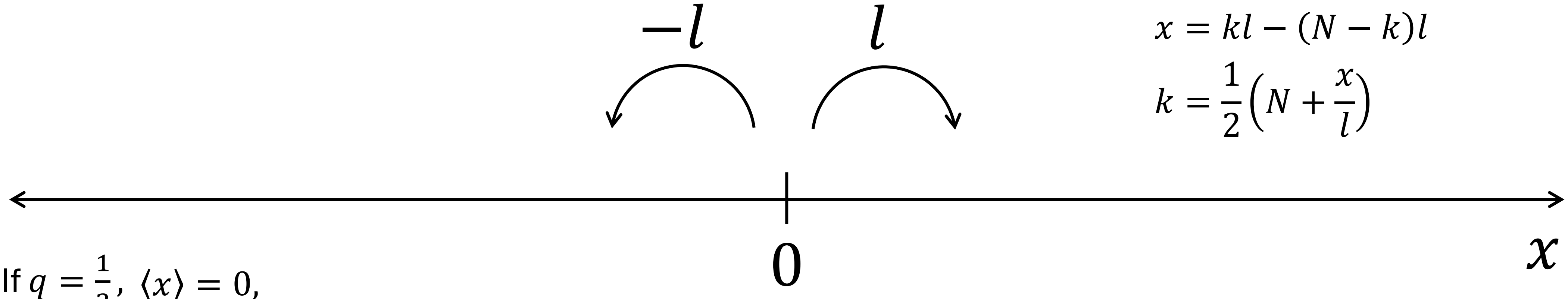
A simple approach to the one-dimensional Brownian motion

k: steps to the right
$N - k$: steps to left

$$\phi(k, N) = \binom{N}{k} q^{N-k} (1-q)^k$$

$$x = kl - (N-k)l$$

$$k = \frac{1}{2}\left(N + \frac{x}{l}\right)$$



If $q = \frac{1}{2}$, $\langle x \rangle = 0$,

$$\langle x^2 \rangle = Nl^2 \Rightarrow \lambda = \sqrt{\langle x^2 \rangle} = \sqrt{N}l$$

$$N \to \infty, \quad \phi(x, N) \approx \frac{1}{\sqrt{4\pi D}} \exp\left(-\frac{x^2}{4\pi D}\right)$$

$N \propto t$ because $t = N\tau$ so we *ad-hoc* write

$$\boxed{\lambda = \sqrt{2Dt}}$$

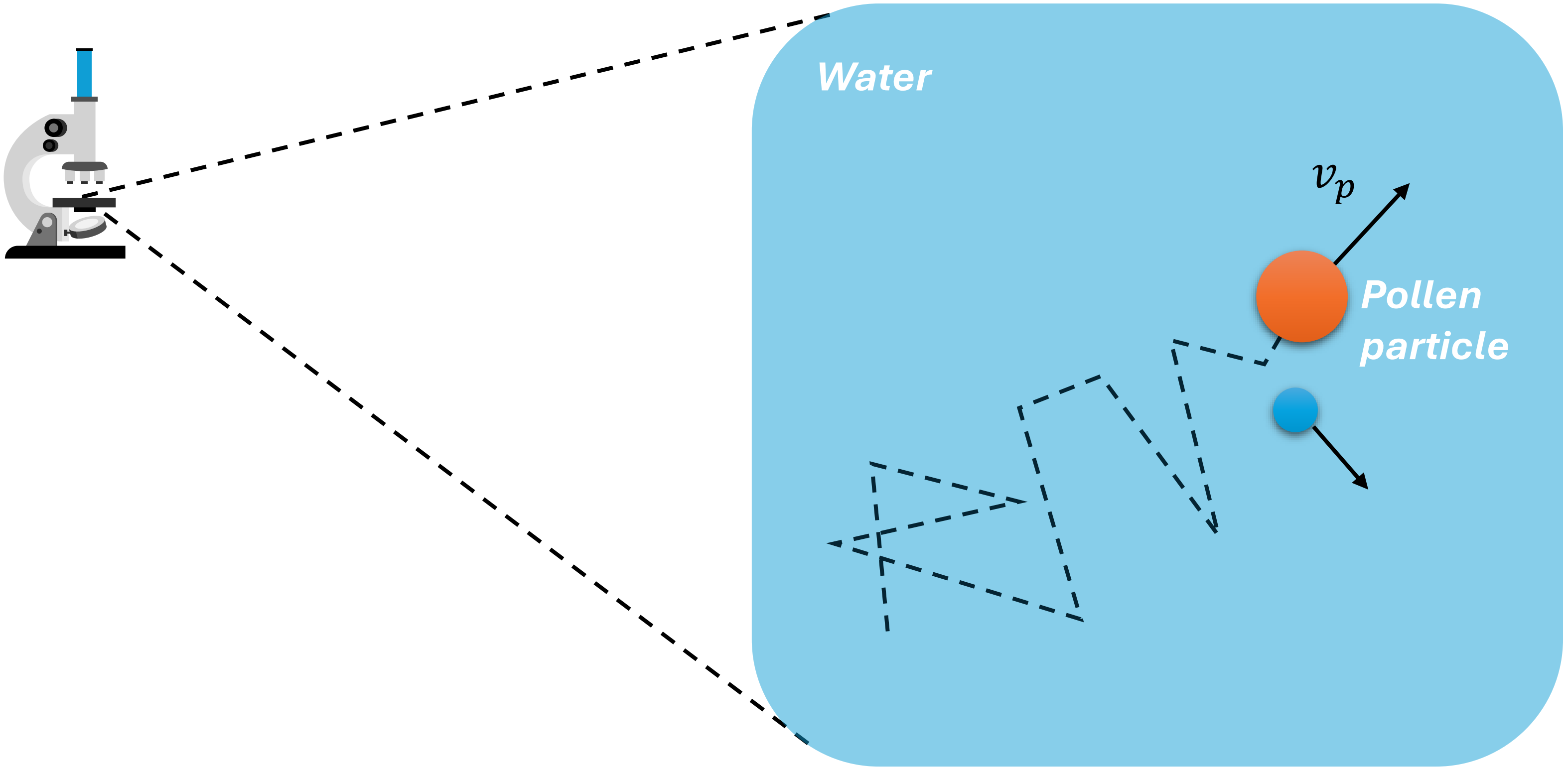
D is just a proportionality constant here.

$^*\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = 2Nl^2$

Experiment

Observational data

$v_q \sim 0.1$ mm/**min**



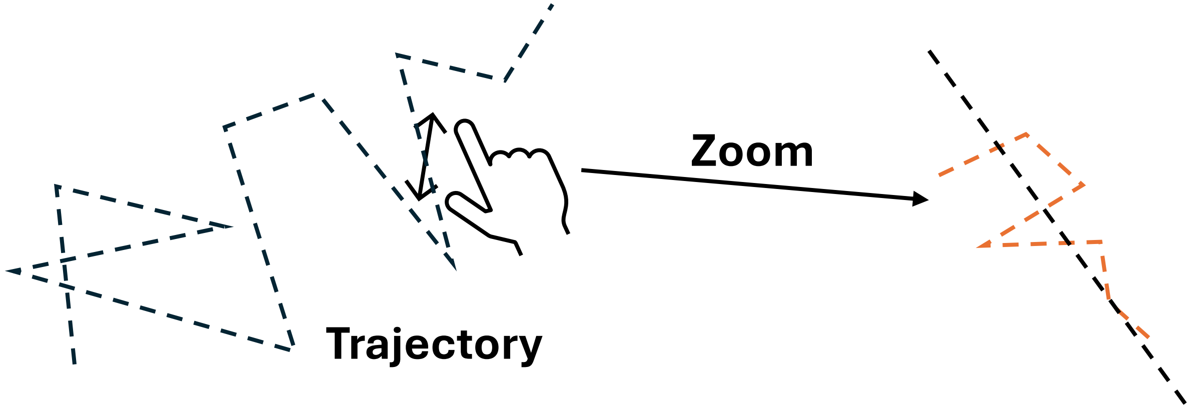
Prediction?!

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

$v_q \sim 0.1$ mm/**s**

As a matter of fact diagrams of this sort [...] in which a large number of displacements are traced on an arbitrary scale, gives only a very meagre idea of the extraordinary discontinuity of the actual trajectory. For if positions were to be marked at intervals of time 100 times shorter, each segment would be replaced by a polygonal contour relatively just as complicated as the whole figure, and so on.

-Perrin.



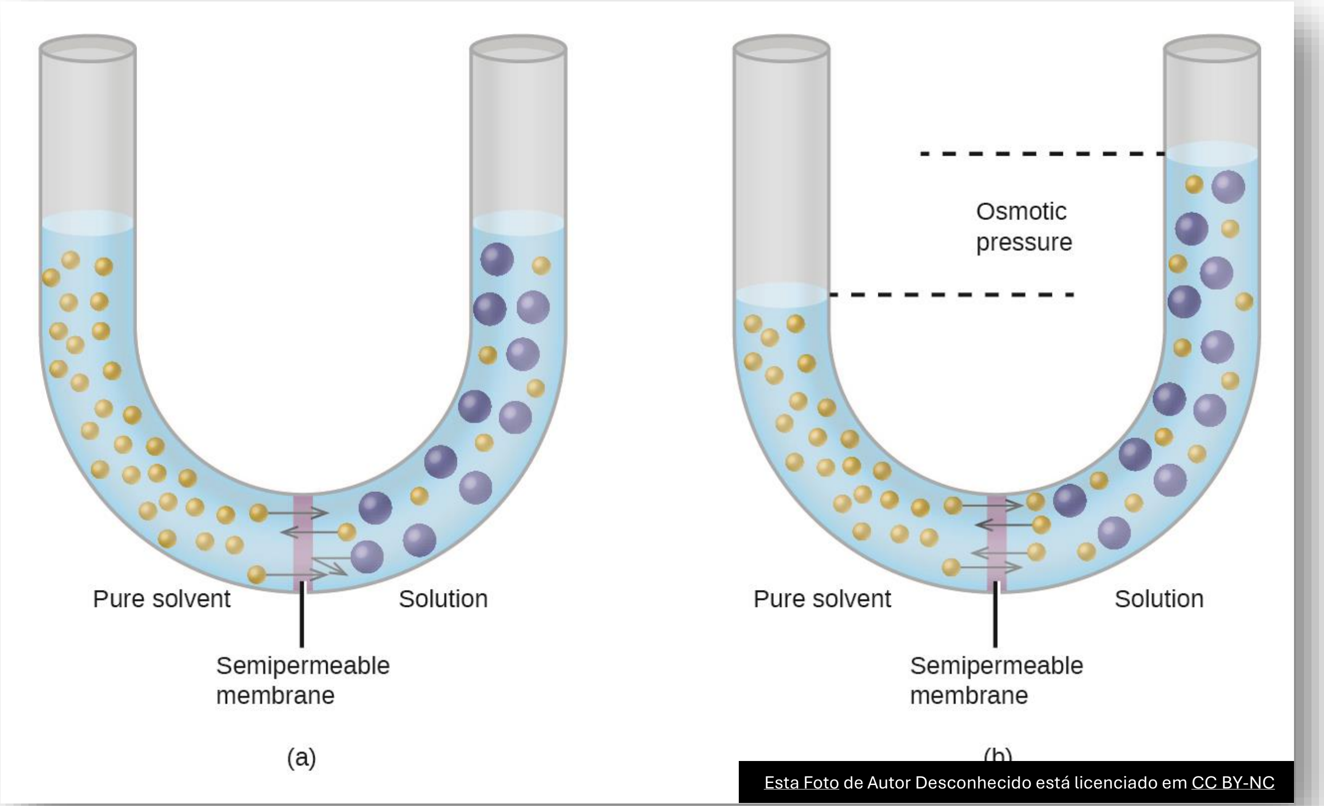
Prerequisites

Osmosis

Low *concentration* —*Solvent*→ *High* *concentration*

Osmotic pressure

Difference in pressure caused by osmosis



Osmotic pressure overview

Gibbs' free energy

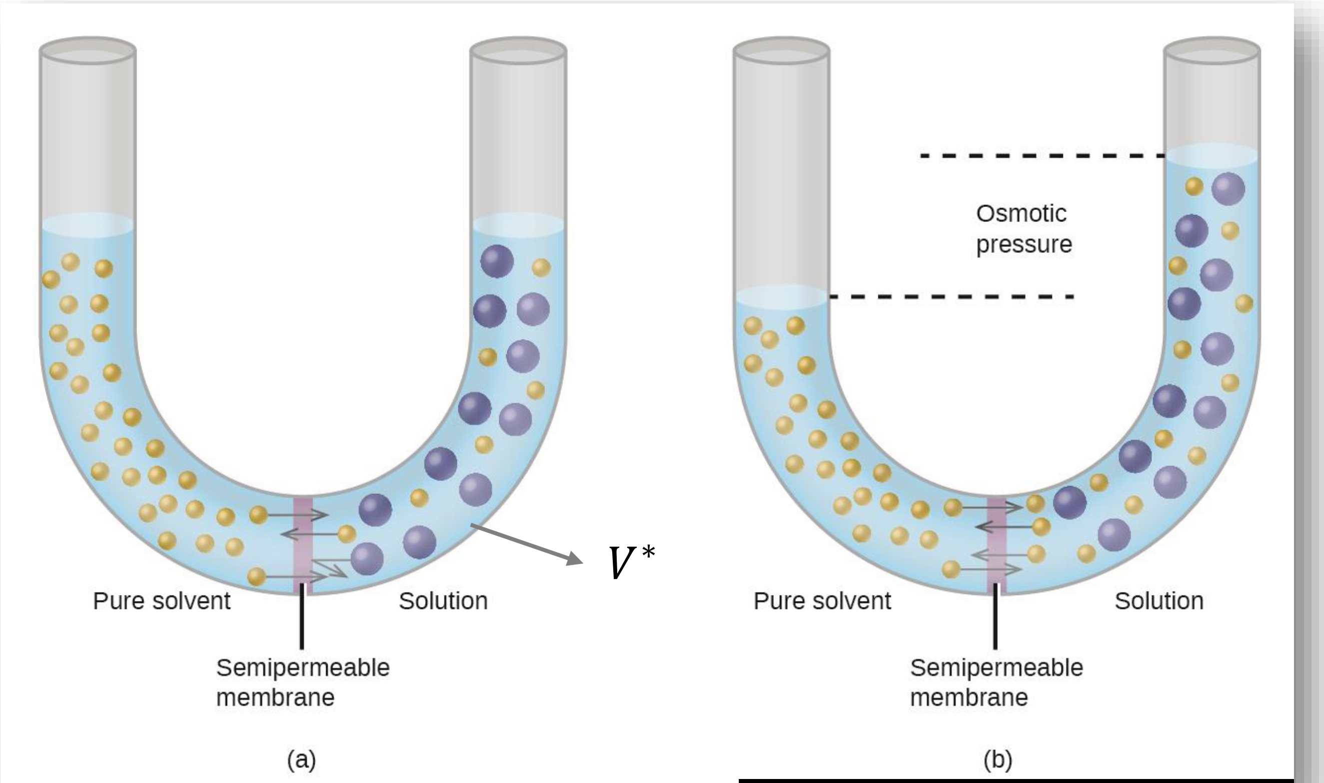
$$\mu^{(2)} - \mu^{(1)} = \bar{V}_i(p_2 - p_1) + RT\ln\frac{X^{(2)}}{X^{(1)}}$$

Osmotic pressure

$$\bar{V}\Pi = -RT\ln(1 - X_s)$$

$$\bar{V}\Pi = -RT\ln(1 - X_s) \approx RTX_s \longrightarrow X_s \approx \frac{n_s}{n_l}$$

$$n_l\bar{V} \approx V^*$$



$$\boxed{\Pi = \frac{n_s RT}{V^*}}$$

$$d\mu_i = \bar{S}_i\, dT + \bar{V}_i dp + \textstyle\sum_k \partial_{n_k}\mu_i dn_k$$

Einstein's approach

Does the kinetic theory of heat lead to osmotic pressure?

$$F = -k_B T \ln \mathfrak{B}$$

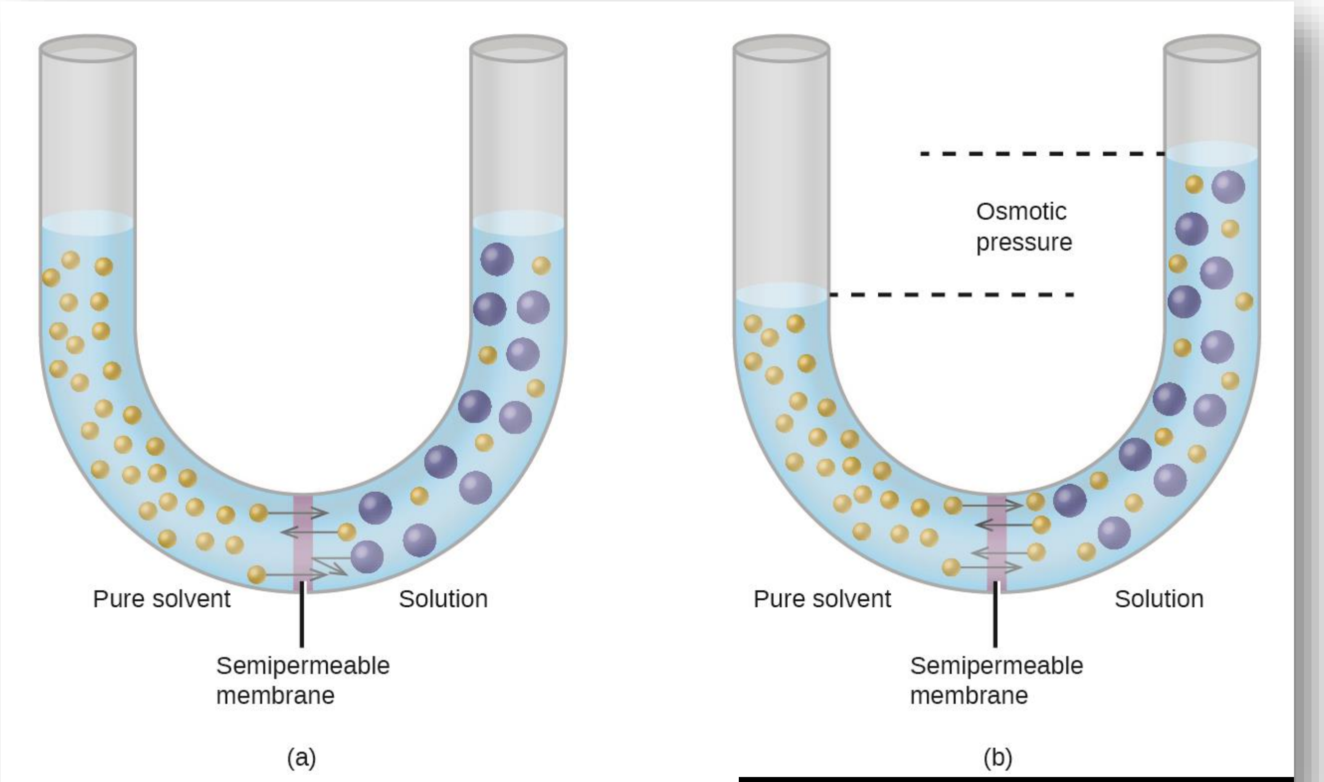
$$\mathfrak{B} = \int e^{-\beta\varepsilon} d^3\vec{r}\ d^3\vec{p} = (V^*)^N \left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

$$F = -n_s RT \left[\ln V^* + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta}\right)\right]$$

Because, $P = -\dfrac{\partial F}{\partial V^*}$

$$\boxed{P = \frac{n_s RT}{V^*}}$$

Yes!*



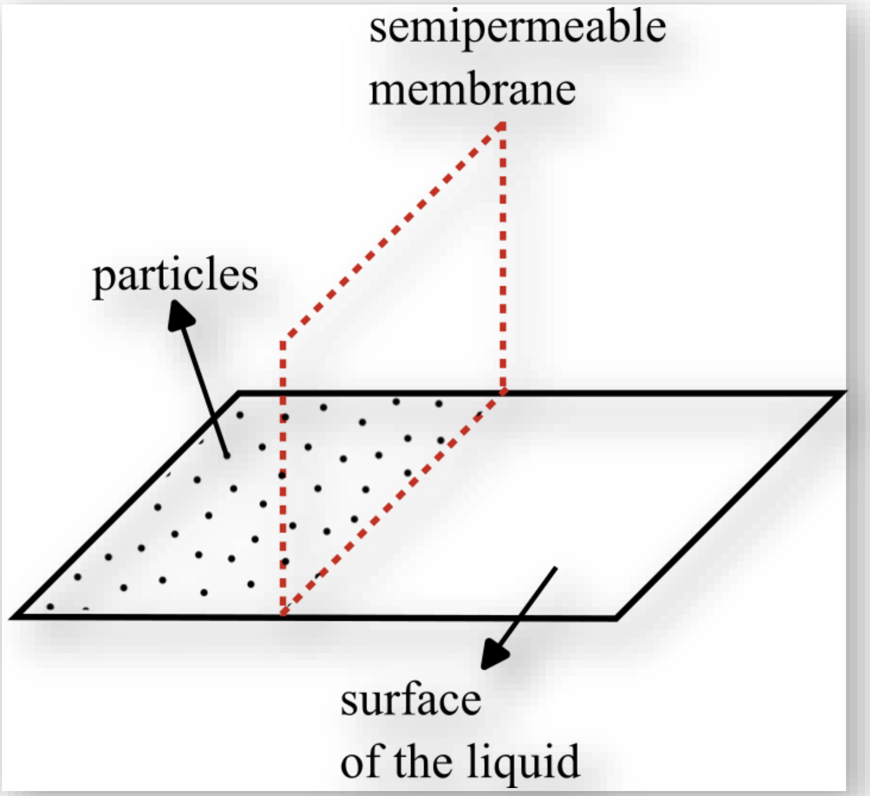
*for spaced noninteracting particles

Equilibrium

According to the kinetic theory the particles suspended in fluid should exert a pressure on a semipermeable membrane much like the osmotic pressure.

Classical thermodynamics $\delta F = 0$

The system is in equilibrium should NOT depend the position of the particles or the membrane, so why there is a force?



Calculations

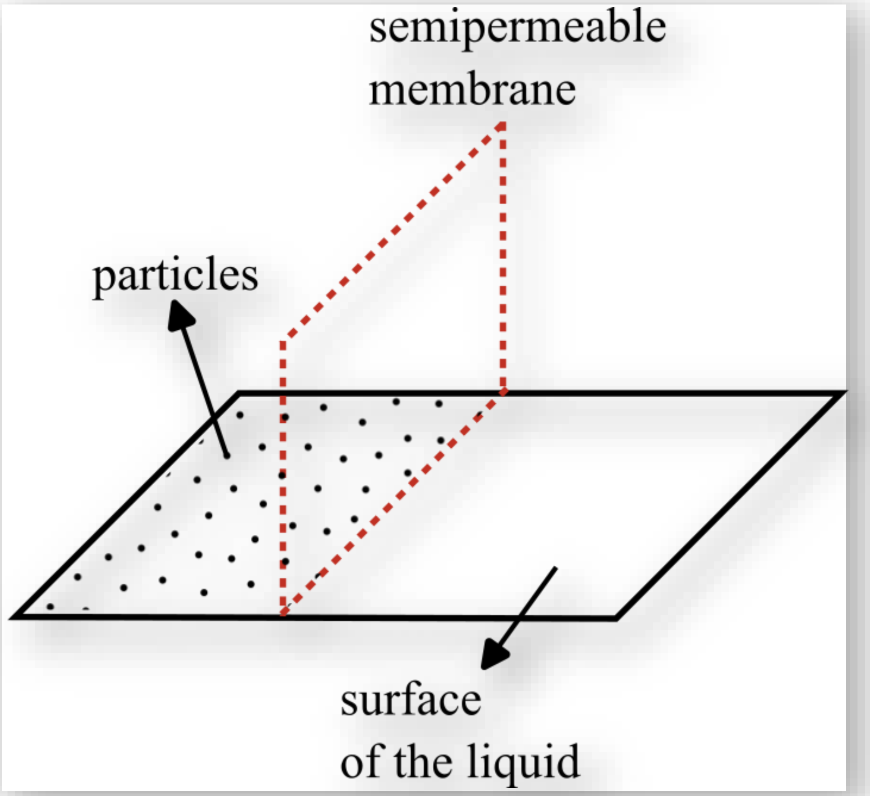
$$F = E - TS$$

For a virtual displacement δx we a have a volume variation of $\delta V = A\delta x$, then

$$\delta F = \delta E - T\delta S$$

Introducing the a force field $f(\vec{r})\hat{x}$ in the x direction extending through the surface.

$$\delta E = \delta W = -\int_0^L \frac{N}{V^*} f\,\delta x\,dx$$



$$\delta F = \delta E - T\delta S$$

Calculations

$$\frac{\eta}{N_A} \equiv \frac{n_P}{V^*}$$

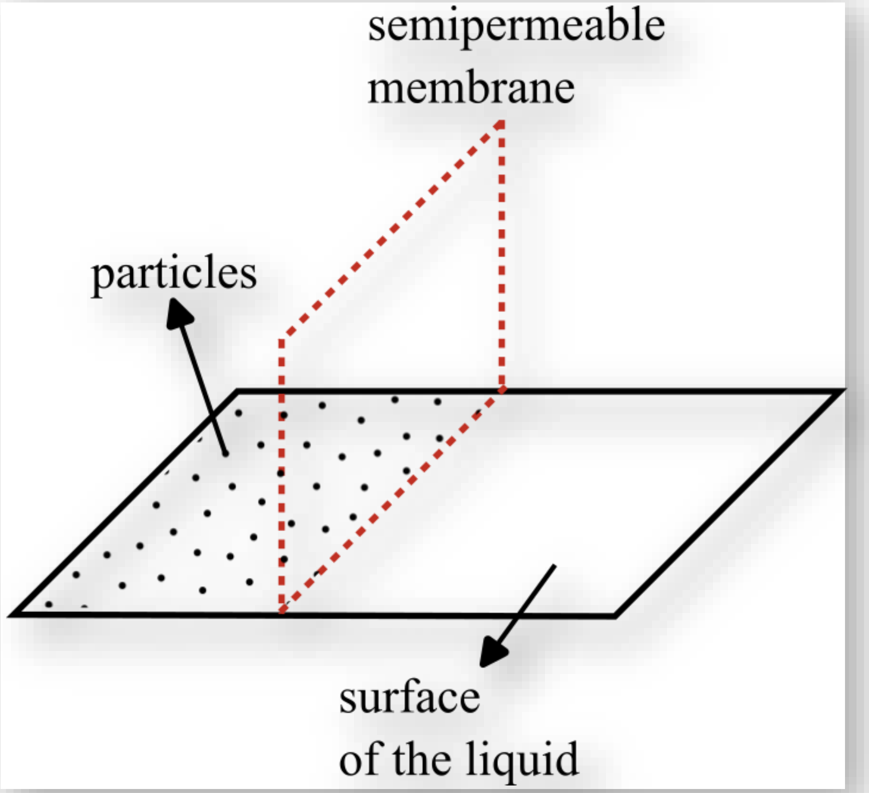
Nº particles per unit volume

$$dS = \frac{n_p R}{V^*} dV^*$$

$$S = \int \frac{n_p R}{V^*} dV = \int_0^L \frac{n_p R}{V^*} (1 \cdot dx)$$

$$\delta S = \int_0^L \frac{R}{N_A} \eta \delta dx = -\frac{R}{N_A} \int_0^L \eta \frac{\partial \delta x}{\partial x} dx =$$

$$\delta S = -\frac{R}{N_A} \int_0^L \frac{\partial \eta}{\partial x} \delta x \, dx$$



$$\delta F = \delta E - T\delta S$$

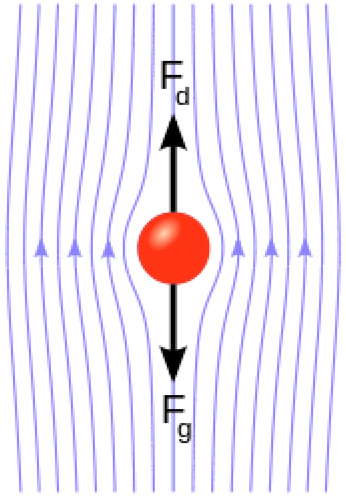
Calculations

$$\eta f - \frac{RT}{N_A}\frac{\partial \eta}{\partial x} = 0$$

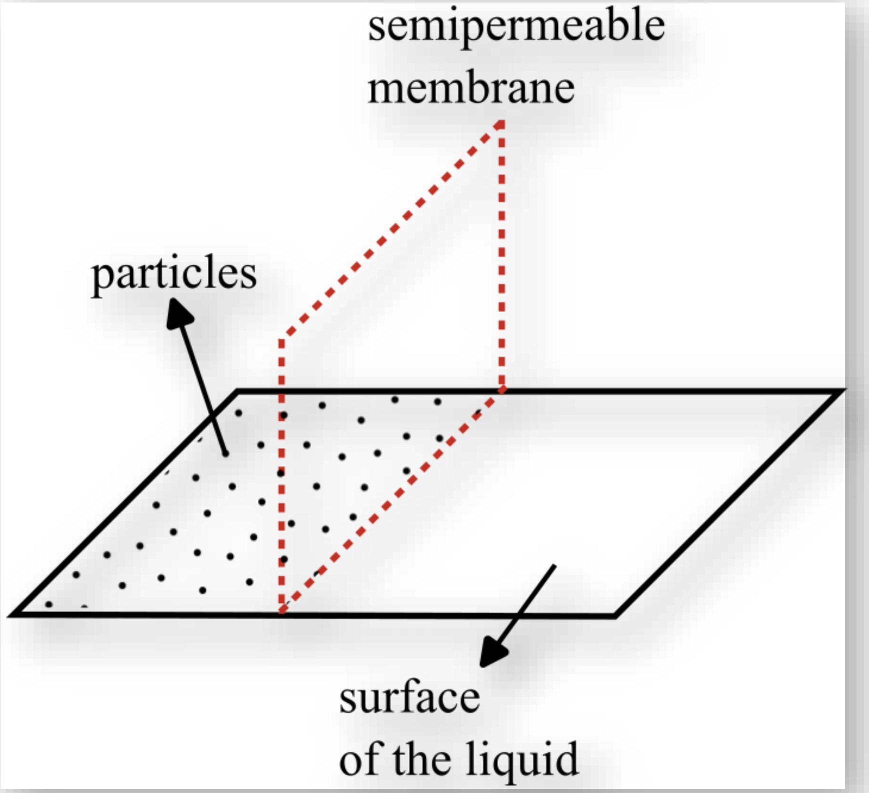
$$\frac{\eta f}{6\pi k r v} - D\frac{\partial \eta}{\partial x} = 0$$

$$D \equiv \frac{RT}{N_A}\frac{\eta f}{6\pi k r}$$

Stokes' law



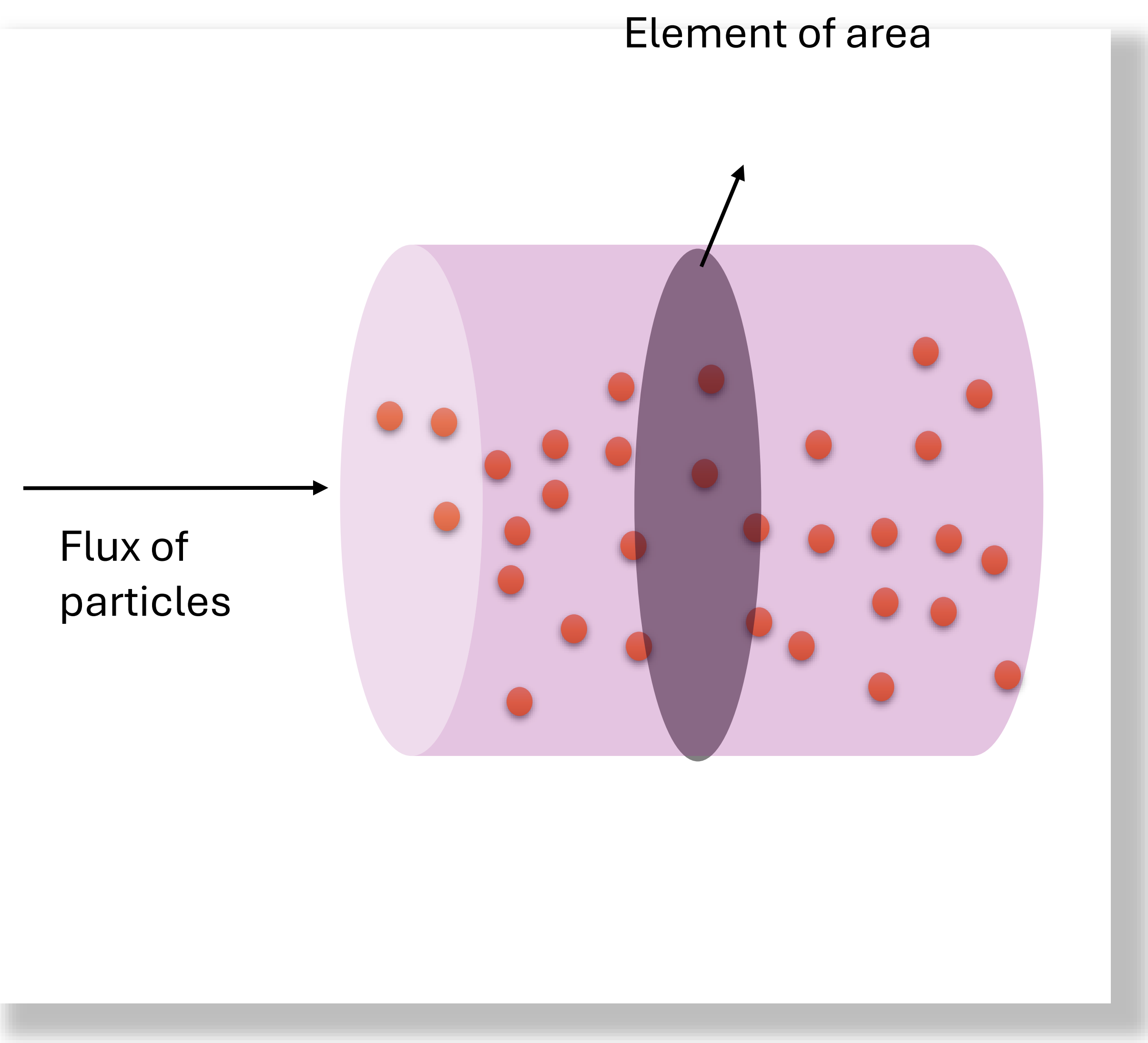
$$f = 6\pi k r v$$



Einstein results (pt.1)

$$D\frac{\partial \eta}{\partial x} = \frac{\eta f}{6\pi k r v} \qquad \frac{[mols]}{[area][time]}$$

Diffusion!



Probability distribution

Probability distribuition of the displacements of the particles:

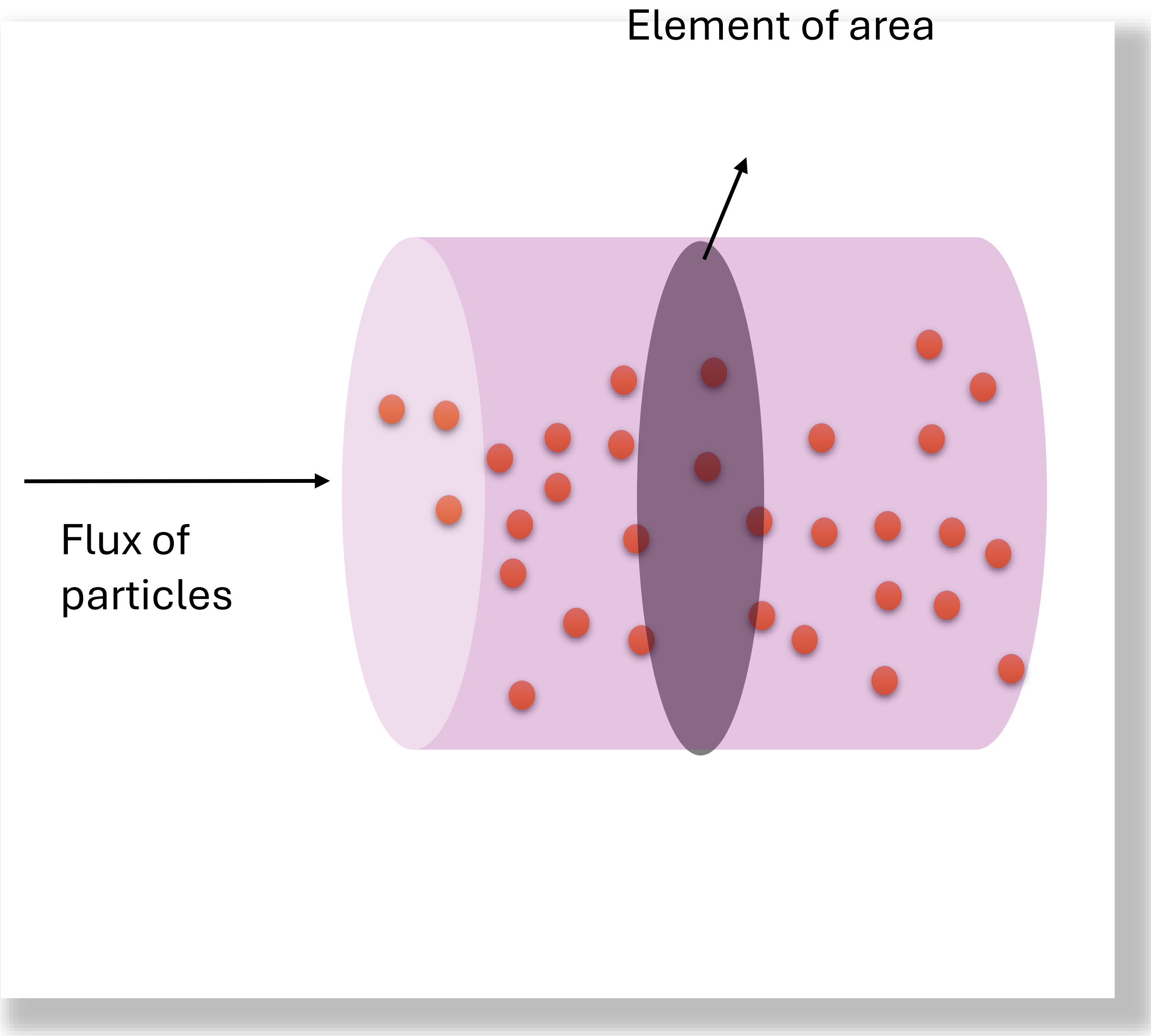
$$\int_{-\infty}^{\infty} \phi(\Delta)\ d\Delta = 1$$

Isotropy:

$$\phi(\Delta) = \phi(-\Delta)$$

Number of particles with displacement between Δ e $\Delta + d\Delta$:

$$dN = N\phi(\Delta)d\Delta$$

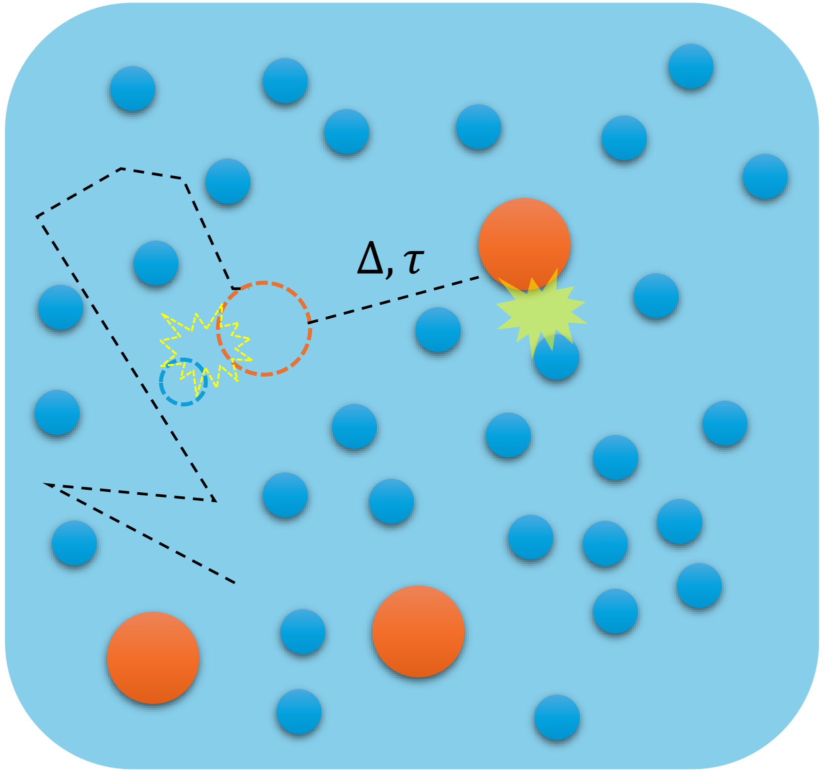


$$D\frac{\partial \eta}{\partial x} = \frac{\eta f}{6\pi k r v}$$

Diffusion equation

Hypothesis:

- η depends only on x and t;
- The collisions are independent of each other;
- Two consecutive collision of the same particle are independent.



$$\eta(x, t+\tau) \approx \eta(x,t) + \tau\frac{\partial \eta}{\partial t}$$

$$\eta(x+\Delta, t) \approx \eta(x,t) + \Delta\frac{\partial \eta}{\partial x} + \frac{\Delta^2}{2!}\frac{\partial \eta^2}{\partial x^2} + \cdots$$

$$\frac{\Delta^2}{2!}\frac{\partial \eta^2}{\partial x^2} = \tau\frac{\partial \eta}{\partial t}$$

$$\frac{\partial \eta}{\partial t} = D\frac{\partial \eta^2}{\partial x^2}$$

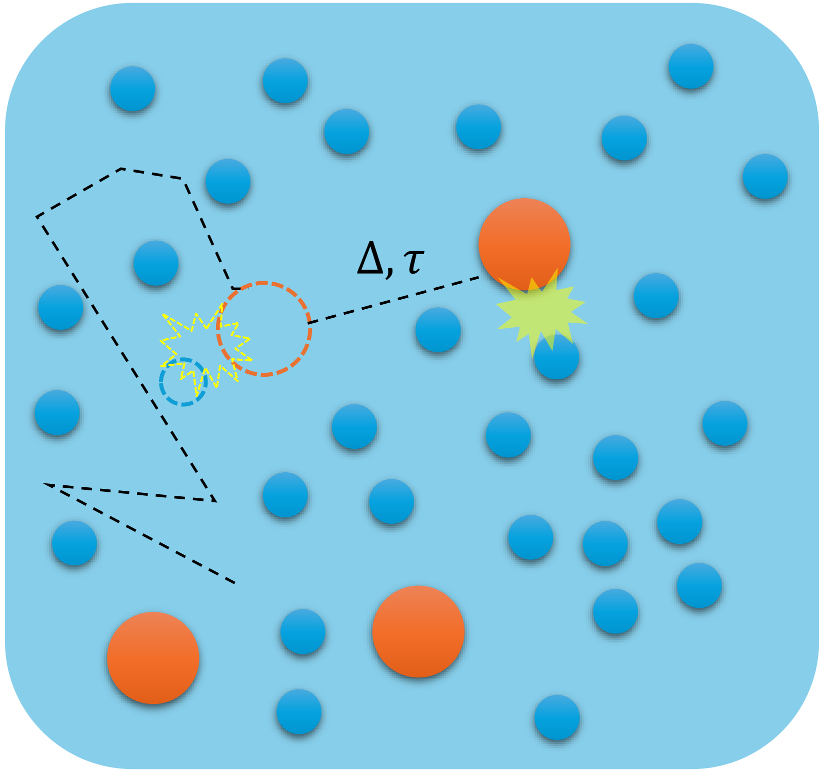
Diffusion equation

$$\frac{\partial^2 \eta}{\partial x^2}\int_{-\infty}^{\infty}\frac{\Delta^2}{2!}\phi(\Delta)d\Delta = \tau\frac{\partial \eta}{\partial t}\int_{-\infty}^{\infty}\phi(\Delta)d\Delta$$

$$\boxed{\frac{\partial \eta}{\partial t} = D\frac{\partial \eta^2}{\partial x^2}}$$

$$\eta(x,t) = \frac{1}{\sqrt{4\pi D t}}\exp\left(-\frac{x^2}{4Dt}\right)$$

$$\langle x^2\rangle = 2Dt$$



$$\boxed{\lambda_x = \sqrt{2Dt}}$$

Free quadratic mean path

Avogadro's number

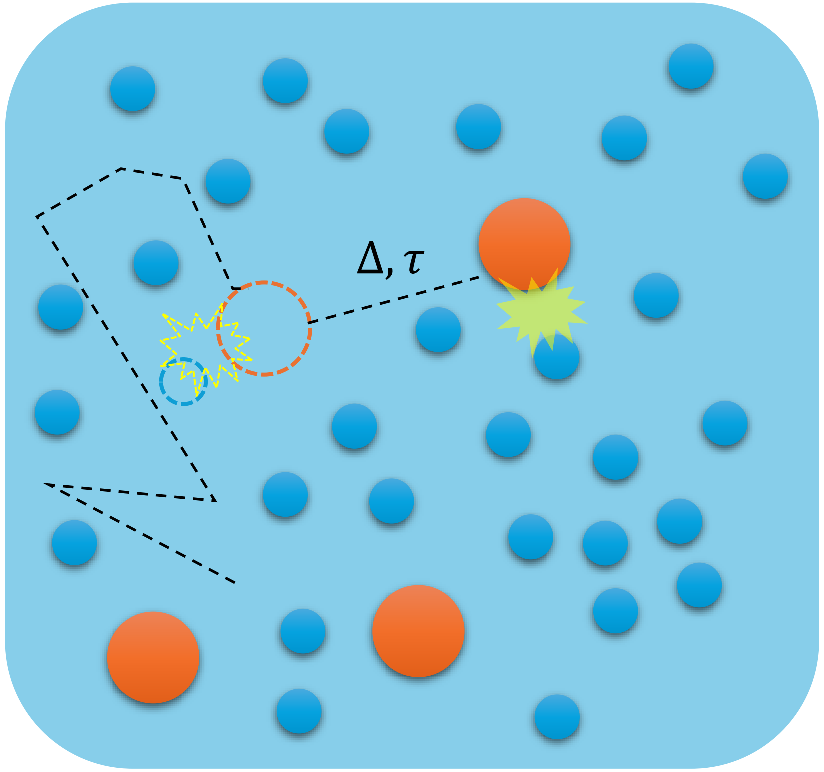
$$\lambda_x = \sqrt{2Dt}$$

Remembering:

$$D = \frac{RT}{N_A}\frac{\eta f}{6\pi k r}$$

$$\boxed{N_A = \frac{RT}{3\pi k r \lambda_x^2}}$$

So, Einstein also found a way of measuring the Avogadro's number knowing λ_x.



Conclusion

[…] What then is the result of these researches? How many molecules are there in two grams of hydrogen? The three methods have given the following answers to this question: 68.2 x 10^{22}; 68.8 x 10^{22}; 65 x 10^{22}.[…]

- Presentation Speech by Professor C.W. Oseen, member of the Nobel Committee for Physics of the Royal Swedish Academy of Sciences, on December 10, 1926

Muito obrigado

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