Lecture 20
CH-4114
Molecular Simulation

"Everything that living things do can be understood in terms of the jigglings and wigglings of atoms."

- Richard P. Feynman

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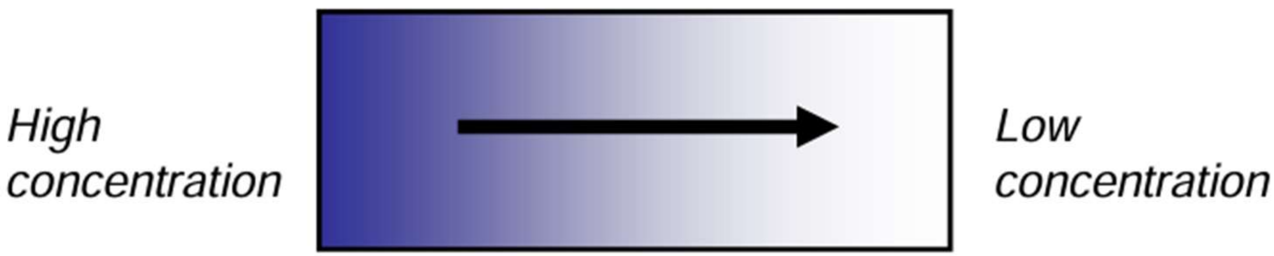
More Towards Time-dependent MD analysis: Diffusion Coefficient

Introduction: Diffusion

- Particles move from a domain with **high concentration** to an area of **low concentration**
- **Macroscopically**, diffusion measured by change in concentration
- **Microscopically**, diffusion is process of spontaneous net movement of particles

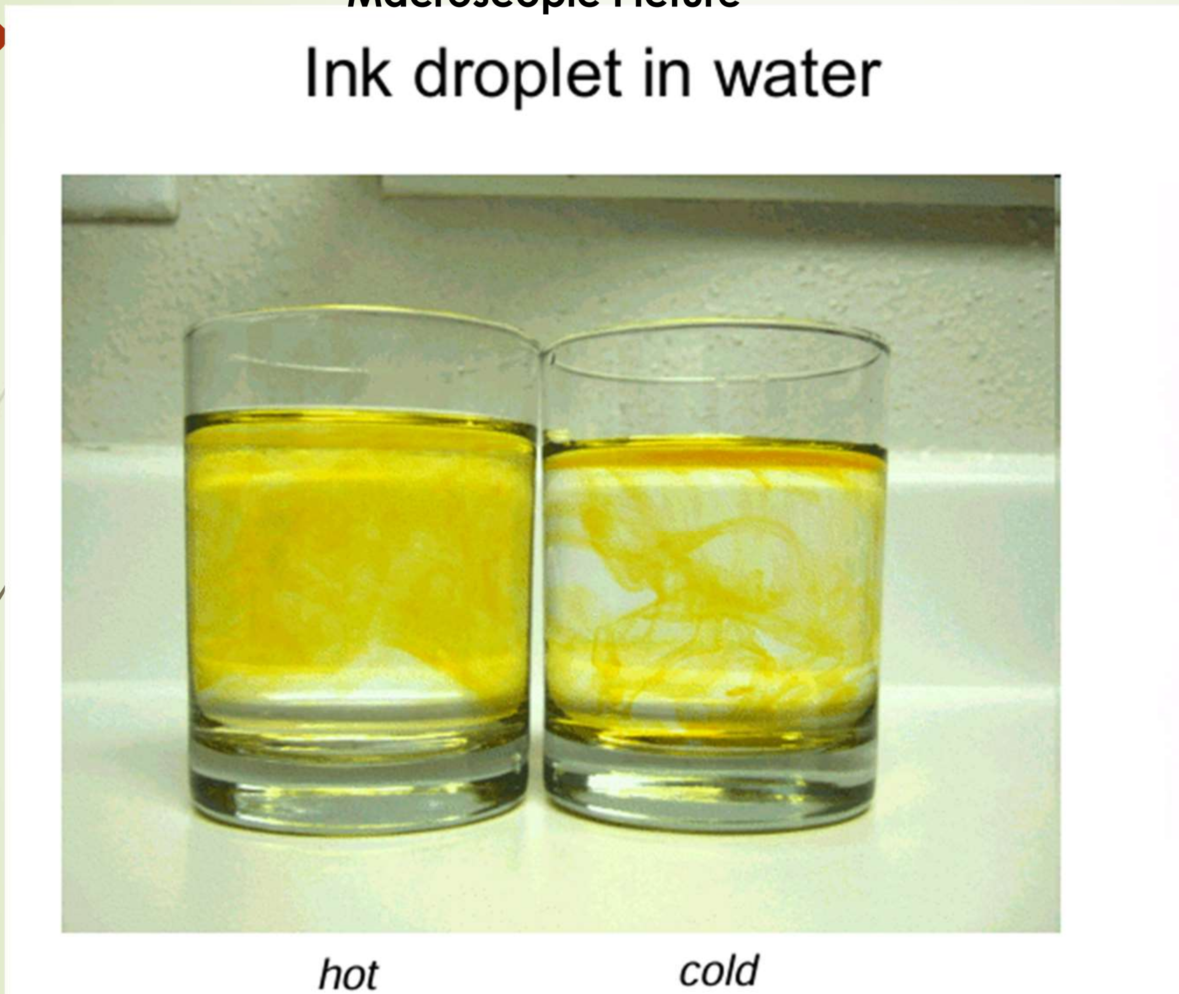
  Result of random motion of particles (“Brownian motion”)



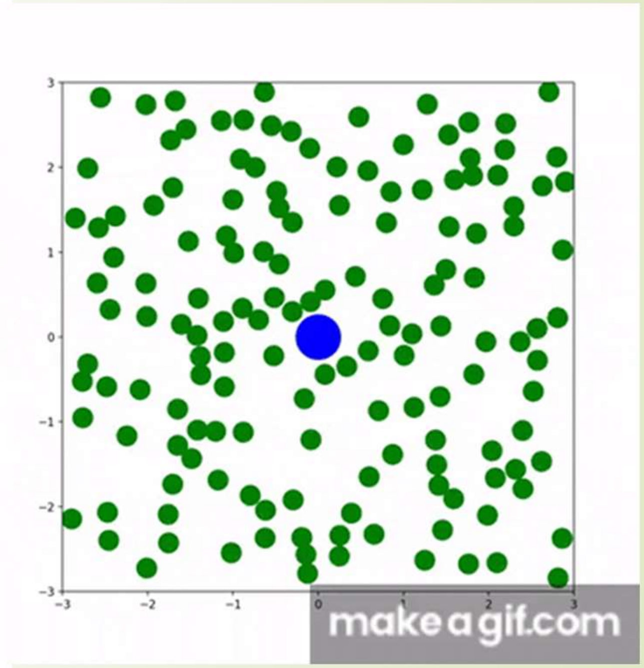
$$c = m/V = c(\vec{x}, t)$$

Diffusion is sensitive to environmental stimuli, like temperature

Macroscopic Picture

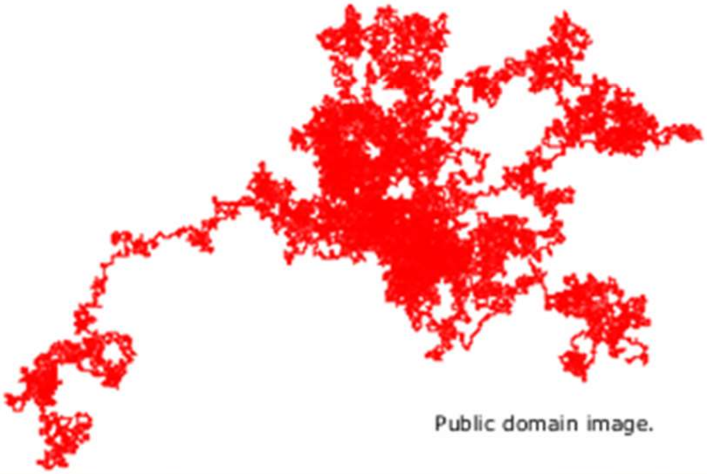


Microscopic Picture



Microscopic mechanism: "Random walk" – or Brownian motion

- Brownian motion was first observed (1827) by the British botanist Robert Brown (1773-1858) when studying pollen grains in water
- Initially thought to be sign of life, but later confirmed to be also present in inorganic particles
- The effect was finally explained in 1905 by Albert Einstein, who realized it was caused by water molecules randomly smacking into the particles.



Public domain image.

Robert Brown's Microscope 1827

Instrument with which Robert Brown studied **Brownian motion** and which he used in his work on identifying the nucleus of the living cell

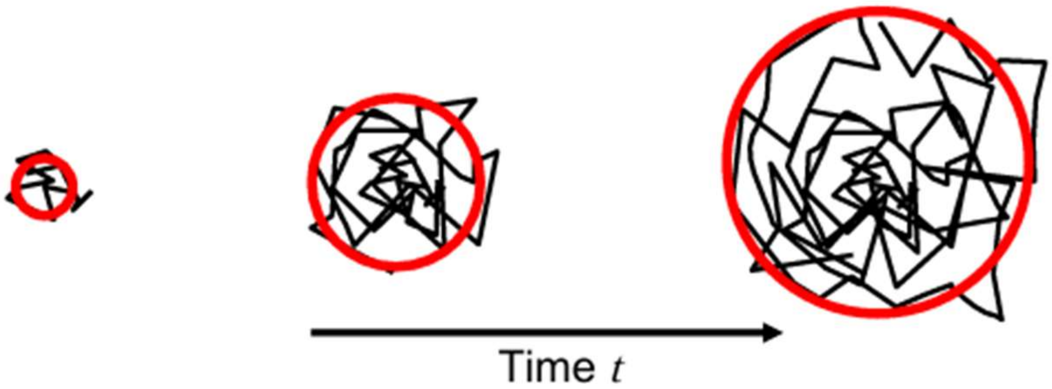
Instrument is preserved at the Linnean Society in London

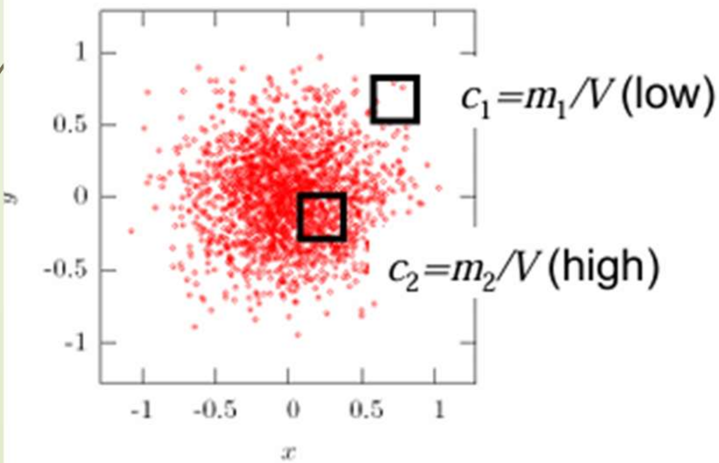
It is made of brass and is mounted onto the lid of the box in which it can be stored

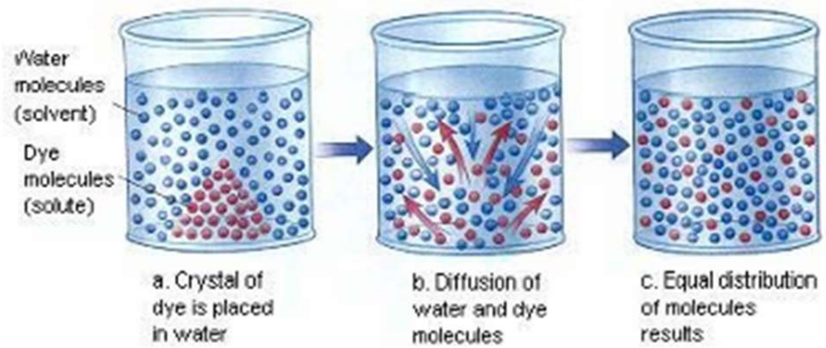
http://www.brianjford.com/pbrownmica.jpg

This portable Ellis-type microscope is a simple and portable device. Made according to the model described in 1755 by John Ellis (1707-1776). With this microscope **Robert Brown** described Brownian motion and the characteristics of the cell nucleus and it was used by **Charles Darwin** on his voyage on the Beagle in 1830.

Brownian motion leads to net particle movement





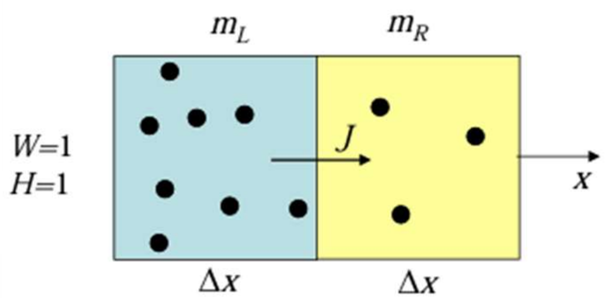


Two approaches to investigate “Diffusion”

- **Continuum description (top-down approach), partial differential equation**
- **Atomistic description (bottom-up approach), based on dynamics of molecules, obtained via numerical simulation of the molecular dynamics**

Approach 1: Continuum model

- Develop differential equation based on differential element

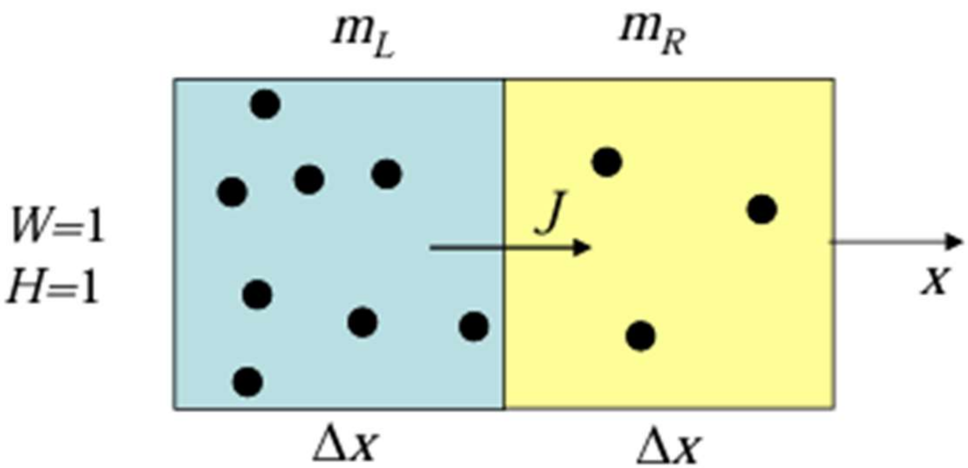


J: Mass flux (mass per unit time per unit area)

Concept: Balance mass [here], force etc. in a differential volume element; much greater in dimension than inhomogeneities

Approach 1: Continuum model

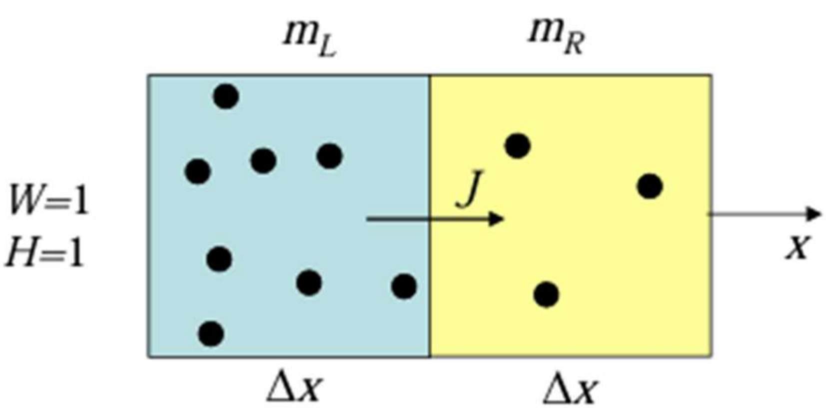
- Develop differential equation based on differential element



Probability of mass m crossing the central boundary during a period Δt is equal to p

Approach 1: Continuum model

- Develop differential equation based on differential element



Probability of mass m crossing the central boundary during a period Δt is equal to p

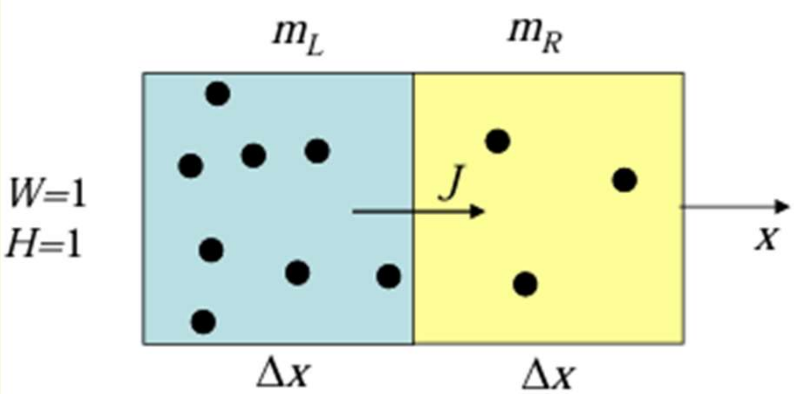
$$J_L = \frac{1}{1\times 1}\frac{p}{\Delta t} m_L$$ Mass flux from left to right

$$J_R = \frac{1}{1\times 1}\frac{p}{\Delta t} m_R$$ Mass flux from right to left

[J] = mass per unit time per unit area

Approach 1: Continuum model

- Develop differential equation based on differential element



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Effective mass flux

$$J = \frac{1}{1\times 1}\frac{p}{\Delta t}\left(m_L - m_R\right)$$

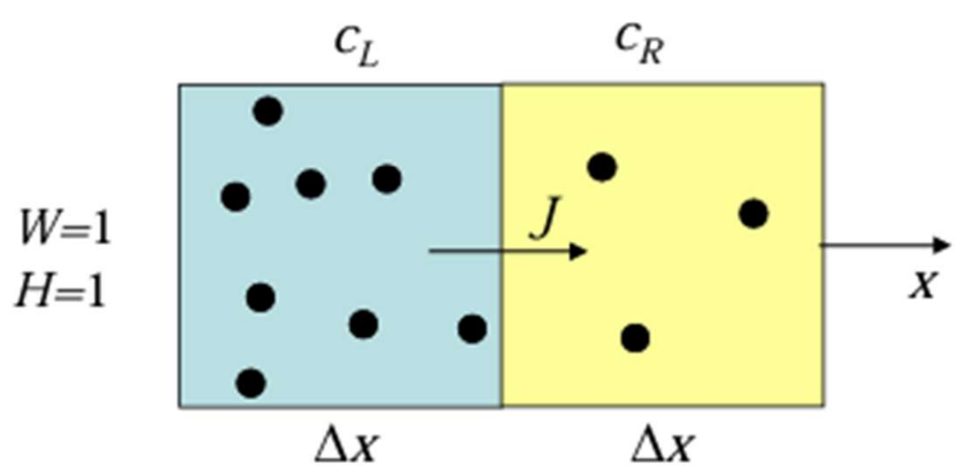
More mass, more flux (m_L is ~ to number of particles)

Continuum model of diffusion

Express in terms of mass concentrations

$$c = \frac{m}{V} \qquad m = cV \qquad J = \frac{p}{\Delta t}\left(m_L - m_R\right)$$

$$J = \frac{1}{1\times 1}\frac{p}{\Delta t}\underbrace{\left(c_L - c_R\right)}_{= -\Delta c}\cdot \underbrace{\Delta x \times 1 \times 1}_{= V}$$



Continuum model of diffusion

Express in terms of mass concentrations

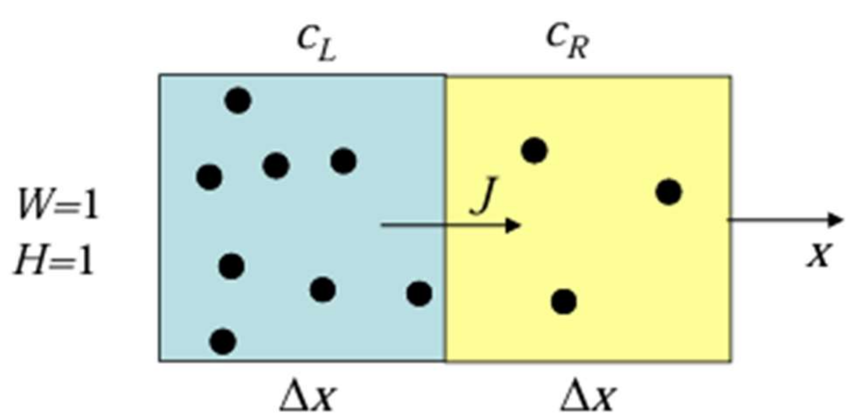
$$c = \frac{m}{V}$$

$$J = \frac{1}{\cancel{1\times 1}}\frac{p}{\Delta t}\underbrace{\left(c_L - c_R\right)}_{=-\Delta c}\cdot \underbrace{\Delta x \times \cancel{1\times 1}}_{=V}$$

Concentration gradient

$$J = -\frac{p}{\Delta t}\Delta c \Delta x = -\frac{p}{\Delta t}\Delta x^2 \frac{\Delta c}{\Delta x}$$

expand Δx



Continuum model of diffusion

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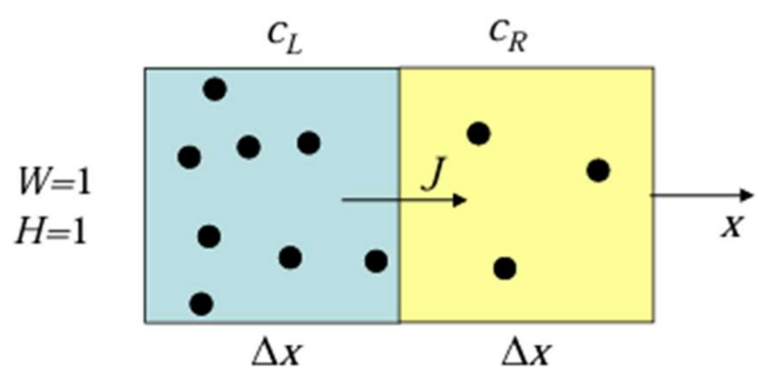
$$J = -\frac{p}{\Delta t}\Delta c\Delta x = -\frac{p}{\Delta t}\Delta x^2\frac{\Delta c}{\Delta x}$$

Concentration gradient

$$\boxed{J = -\frac{p}{\Delta t}\Delta x^2\frac{dc}{dx} = -D\frac{dc}{dx}}$$

$$D = p\frac{\Delta x^2}{\Delta t}$$ Parameter that measures how "fast" mass moves (in square of distance per unit time)



Diffusion constant & 1st Fick law

Reiterate: Diffusion constant D describes the how much mass moves per unit time

Movement of mass characterized by square of displacement from initial position

Flux

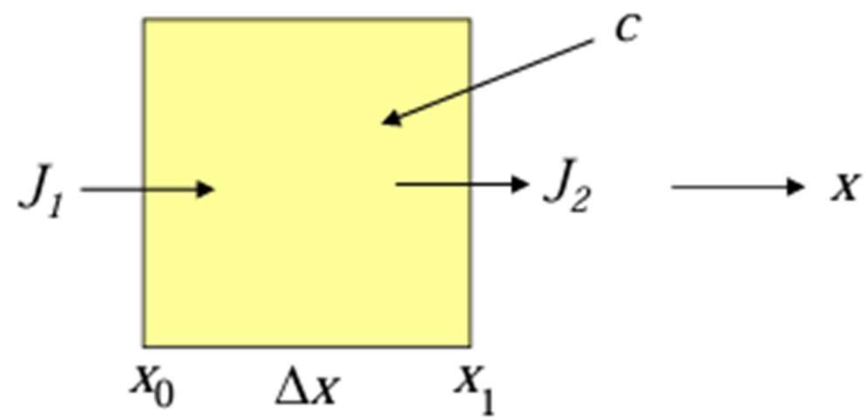
$$J = -\frac{p}{\Delta t}\Delta x^2 \frac{dc}{dx} = -D\frac{dc}{dx}$$

1st Fick law
(Adolph Fick, 1829-1901)

$$\boxed{D = p\frac{\Delta x^2}{\Delta t}}$$

2nd Fick law (time dependence)

$$J = -D\frac{dc}{dx}$$ 1st Fick law

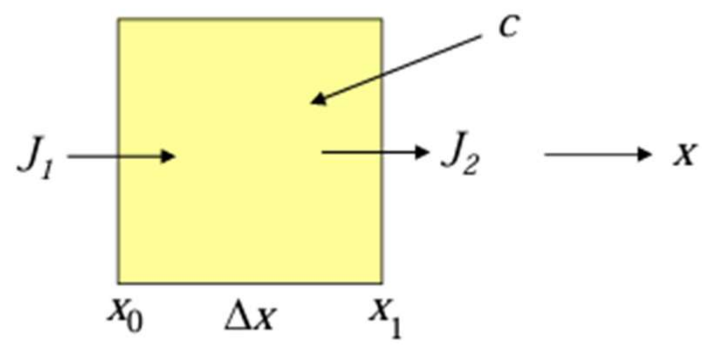


$$\frac{\Delta c}{\Delta t} = \frac{(J_1 - J_2)\cancel{\times 1 \times 1}}{\Delta x \cancel{\times 1 \times 1}}$$

J: Mass flux (mass per unit time per unit area)

2^{nd} Fick law (time dependence)

$$J = -D\frac{dc}{dx}$$ 1st Fick law

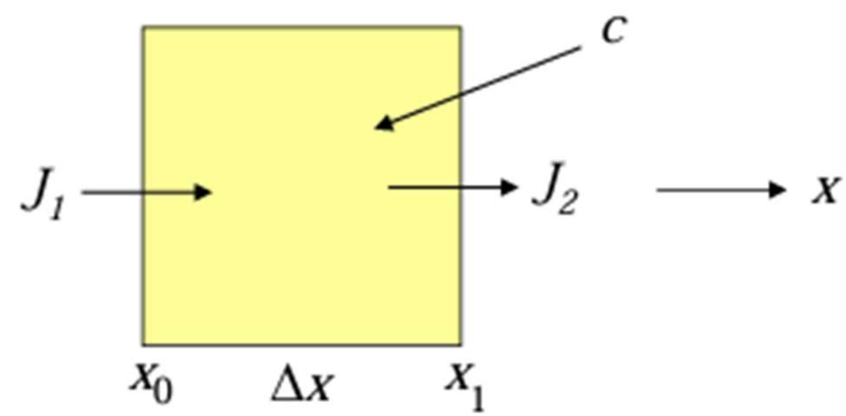


$$\frac{\Delta c}{\Delta t} = \frac{J_1 - J_2}{\Delta x} = \frac{1}{\Delta x}\left(-D\frac{dc}{dx}\Big|_{x=x_0} - \left[-D\frac{dc}{dx}\Big|_{x=x_1}\right]\right)$$

$$J_1 = J(x = x_0) = -D\frac{dc}{dx}\Big|_{x=x_0}$$

2^{nd} Fick law (time dependence)

$$J = -D\frac{dc}{dx}$$ 1st Fick law



$$\frac{\Delta c}{\Delta t} = \frac{1}{\Delta x}\left(\overbrace{-D\frac{dc}{dx}\bigg|_{x=x_0} + D\frac{dc}{dx}\bigg|_{x=x_1}}^{\Delta J}\right)$$

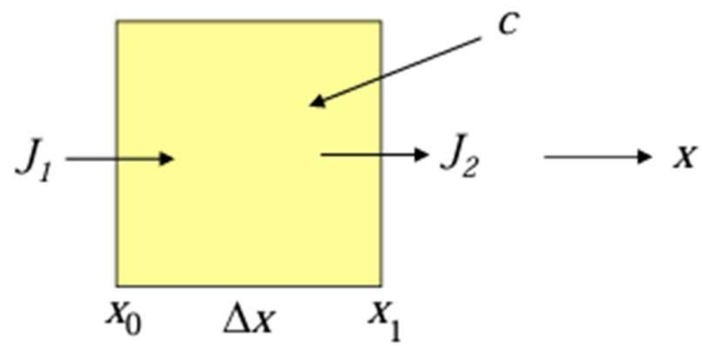
$$\downarrow$$

$$\frac{\partial c}{\partial t} = -\frac{d}{dx}(J) = -\frac{d}{dx}\left(-D\frac{dc}{dx}\right)$$

Change of concentration in time equals change of flux with x (mass balance)

2^{nd} Fick law (time dependence)

$$J = -D\frac{dc}{dx}$$ 1st Fick law



$$\frac{\Delta c}{\Delta t} = \frac{1}{\Delta x}\left(\overbrace{-D\frac{dc}{dx}\bigg|_{x=x_0} + D\frac{dc}{dx}\bigg|_{x=x_1}}^{\Delta J}\right)$$

$$\frac{\partial c}{\partial t} = -\frac{d}{dx}(J) = -\frac{d}{dx}\left(-D\frac{dc}{dx}\right)$$

Change of concentration in time equals change of flux with x (mass balance)

$$\boxed{\frac{\partial c}{\partial t} = D\frac{d^2 c}{dx^2} \qquad 2^{nd} \text{ Fick law}}$$

PDE

Solve by applying ICs and BCs…

Recall: $$\boxed{D = p\frac{\Delta x^2}{\Delta t}}$$

In **Einstein relation,** D represents **how quickly the mean-square displacement grows with time**.
The proportionality and it is derived from Fick's law

$$D = \frac{1}{2}\frac{d\langle x^2\rangle}{dt}$$

Substitute the random-walk result:

$$D = \frac{1}{2}\cdot\frac{(\Delta x)^2}{\Delta t}$$

For 1D random walk, this is famous Einstein relation of diffusion→

$$\boxed{\langle(\Delta x)^2\rangle = 2Dt}$$

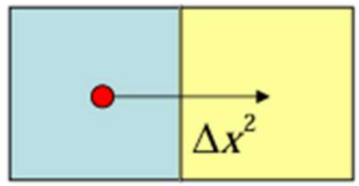
is the **Einstein diffusion relation**, bridging:

- **Fick's law** (continuum flux equation), and
- **Random molecular motion** (microscopic Brownian motion).

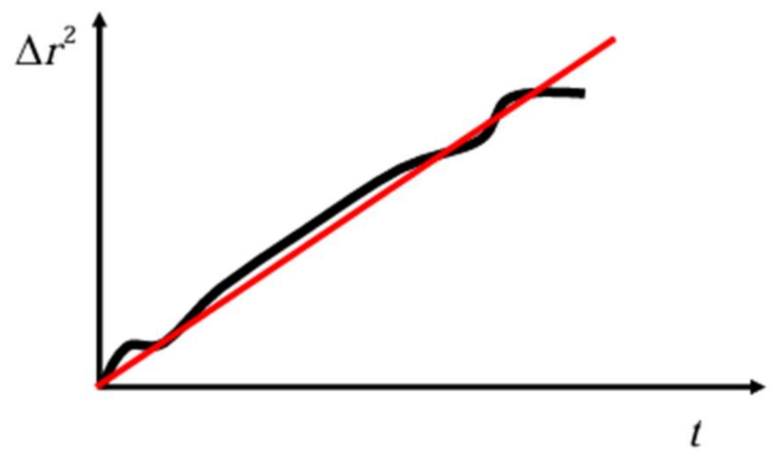
Link atomistic trajectory with diffusion constant (1D)

Diffusion constant relates to the "ability" of a particle to move a distance Δx^2 (from left to right) over a time Δt

$$D = p\frac{\Delta x^2}{\Delta t}$$

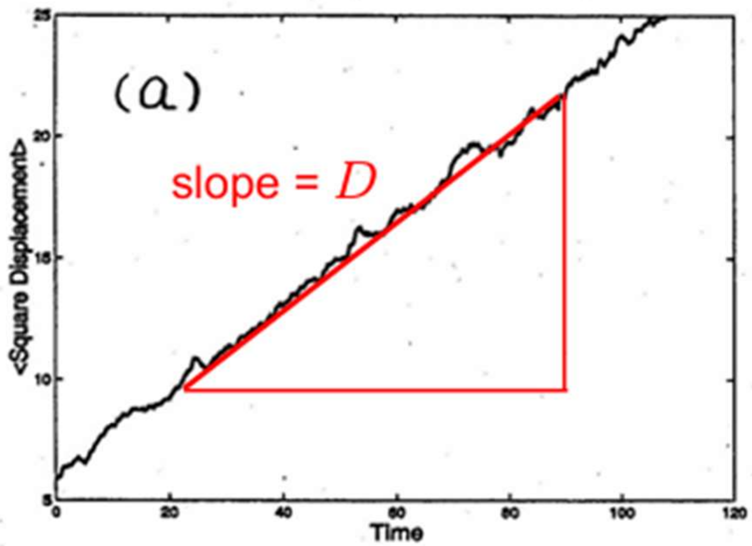


MD simulation: Measure square of displacement from initial position of particles, $\Delta r^2(t)$:



Example: MD simulation

Δr^2



source: S. Yip, lecture notes

$$D = \frac{1}{2d} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}\,t} \left(\Delta r^2 \right)$$

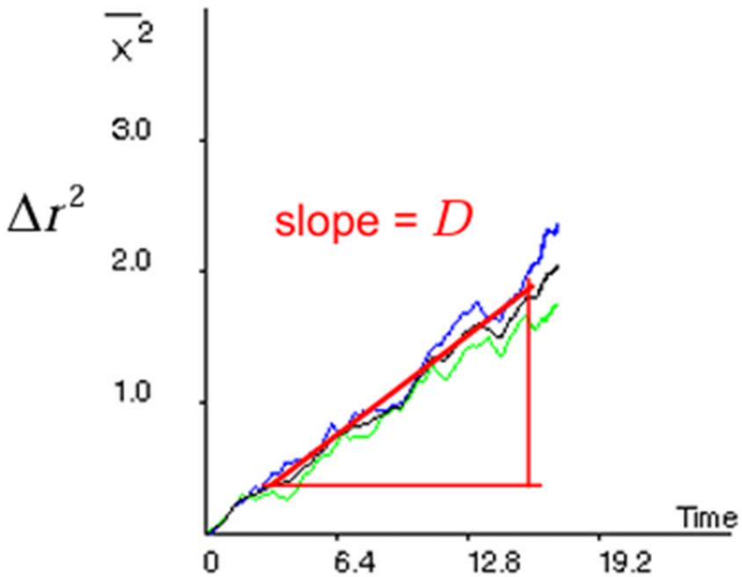
1D=1, 2D=2, 3D=3

$$D = \frac{1}{2d} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}\,t} \left\langle \Delta r^2 \right\rangle$$

$\langle .. \rangle$ = average over all particles

Example calculation of diffusion coefficient

$$\left\langle \Delta r^2(t) \right\rangle = \frac{1}{N} \sum_i \big(\underbrace{r_i(t)}_{\text{Position of atom } i \text{ at time t}} - \underbrace{r_i(t=0)}_{\text{Position of atom } i \text{ at time t=0}} \big)^2$$



$$\boxed{D = \frac{1}{2d} \lim_{t\to\infty} \frac{\mathrm{d}}{\mathrm{d}\,t} \left\langle \Delta r^2 \right\rangle}$$

1D=1, 2D=2, 3D=3

We start from the Einstein relation (MSD definition of diffusion):

$$D = \lim_{t\to\infty} \frac{1}{2d} \frac{d}{dt} \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle.$$

Express MSD in terms of velocities

Write the displacement as time integral of velocity:

$$\mathbf{r}(t) - \mathbf{r}(0) = \int_0^t \mathbf{v}(t')\, dt'.$$

Then the mean-squared displacement (MSD) is

$$\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle = \left\langle \left(\int_0^t \mathbf{v}(t') dt' \right) \cdot \left(\int_0^t \mathbf{v}(t'') dt'' \right) \right\rangle = \int_0^t \int_0^t \langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle\, dt'\, dt''.$$

Because the process is stationary $\langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle = C_v(|t' - t''|)$. Change variables to $\tau = |t' - t''|$ and perform the double integral

$$\boxed{\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle = 2 \int_0^t (t - \tau)\, C_v(\tau)\, d\tau}.$$

Differentiate MSD with respect to t

Differentiate both sides w.r.t. t:

$$\frac{d}{dt}\langle[\mathbf{r}(t)-\mathbf{r}(0)]^2\rangle = 2\int_0^t C_v(\tau)\,d\tau$$

(using Leibniz rule; derivative of $(t-\tau)$ gives 1 and the upper limit contributes nothing beyond the integral).

Take long-time limit and get Green–Kubo

Plug into Einstein relation and take $t\to\infty$:

$$D = \lim_{t\to\infty}\frac{1}{2d}\frac{d}{dt}\langle[\mathbf{r}(t)-\mathbf{r}(0)]^2\rangle = \frac{1}{d}\int_0^\infty C_v(\tau)\,d\tau.$$

Since $C_v(\tau)=\langle\mathbf{v}(0)\cdot\mathbf{v}(\tau)\rangle$, we often write the vector form. For isotropic systems, component form gives the common scalar expression in d dimensions. In particular for $d=3$:

$$\boxed{D = \frac{1}{3}\int_0^\infty \langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle\,dt}.$$

Equivalently, per single Cartesian component (if components are identical and independent):

$$D = \int_0^\infty \langle v_x(0)\,v_x(t)\rangle\,dt.$$