

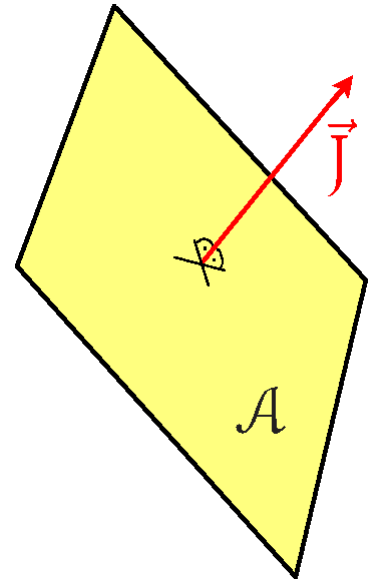
Transport (kinetic) phenomena: diffusion, electric conductivity, viscosity, heat conduction ... **not convection, turbulence, radiation...**

- Flux* of mass, charge, momentum, heat,
- \vec{J} = amount (of quantity) transported per unit area (perpendicular to the vector of flux) within time unit
Units: energy/heat flux: $\text{J m}^{-2} \text{s}^{-1} = \text{W m}^{-2}$,
current density: A m^{-2}

- Cause = (generalized, thermodynamic) force
 $\vec{F} = -$ gradient of a potential
(chemical potential/concentration, electric potential, temperature)

- Small forces—linearity

$$\vec{J} = \text{const} \cdot \vec{F}$$



In gases we use the **kinetic theory**: molecules (simplest: hard spheres) fly through space and sometimes collide

* also *flux intensity* or *flux density*; then, the total flux is just *flux*

First Fick Law: Flux \vec{J}_i of compound i (units: $\text{mol m}^{-2} \text{s}^{-1}$)

$$\vec{J}_i = -D_i \vec{\nabla} c_i$$

is proportional to the **concentration gradient**

$$\vec{\nabla} c_i = \text{grad } c_i = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) c_i = \left(\frac{\partial c_i}{\partial x}, \frac{\partial c_i}{\partial y}, \frac{\partial c_i}{\partial z} \right)$$

D_i = diffusion coefficient (diffusivity) of molecules i , unit: $\text{m}^2 \text{s}^{-1}$

For mass concentration in kg m^{-3} , the flux is in $\text{kg m}^{-2} \text{s}^{-1}$

Flux is given by the mean velocity of molecules \vec{v}_i :

$$\vec{J}_i = \vec{v}_i c_i$$

Thermodynamic force = $-\text{grad}$
of the chemical potential:

$$\vec{\mathcal{F}}_i = -\vec{\nabla} \left(\frac{\mu_i}{N_A} \right) = -\frac{k_B T}{c_i} \vec{\nabla} c_i$$

Difference of chemical potentials = reversible work needed to move a particle (mole) from one state to another

where formula $\mu_i = \mu_i^\ominus + RT \ln(c_i/c^{\text{st}})$ for infinity dilution was used.

Friction force acting against molecule moving by velocity \vec{v}_i through a medium is:

$$\vec{\mathcal{F}}_i^{\text{fr}} = -f_i \vec{v}_i$$

where f_i is the friction coefficient. Both forces are in equilibrium:

$$\vec{\mathcal{F}}_i^{\text{fr}} + \mathcal{F}_i = 0 \quad \text{i.e.} \quad -\vec{\mathcal{F}}_i^{\text{fr}} = f_i \vec{v}_i = f_i \frac{\vec{J}_i}{c_i} = \mathcal{F}_i = -\frac{k_B T}{c_i} \vec{\nabla} c_i$$

On comparing with $\vec{J}_i = -D_i \vec{\nabla} c_i$ we get the **Einstein equation**: $D_i = \frac{k_B T}{f_i}$

(also Einstein–Smoluchowski equation, example of a more general fluctuation-dissipation theorem)

Non-stationary phenomenon (c changes with time).
The amount of substance increases within
time dt in volume $dV = dx dy dz$:

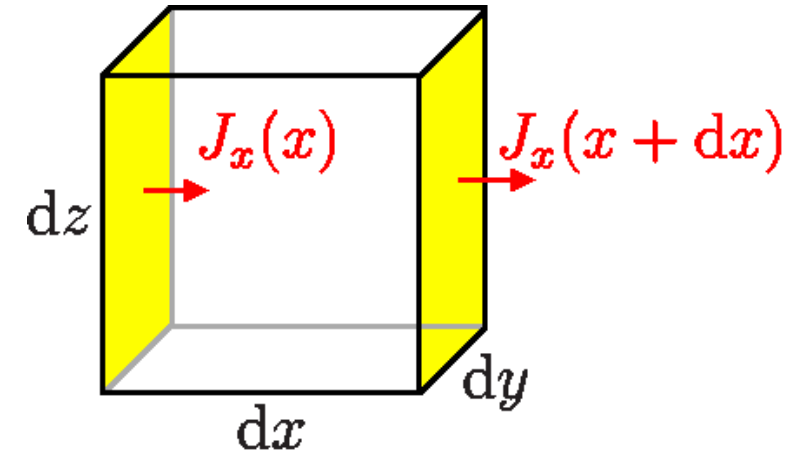
$$\sum_{x,y,z} [J_x(x) - J_x(x + dx)] dy dz$$

$$= \sum_{x,y,z} [J_x(x) - \{J_x(x) + \frac{\partial J_x}{\partial x} dx\}] dy dz$$

$$= - \sum_{x,y,z} \frac{\partial J_x}{\partial x} dx dy dz = -\vec{\nabla} \cdot \vec{J} dV = -\vec{\nabla} \cdot (-D\vec{\nabla}c) dV$$

$$= D\vec{\nabla}^2 c dV = D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) c dV$$

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i$$



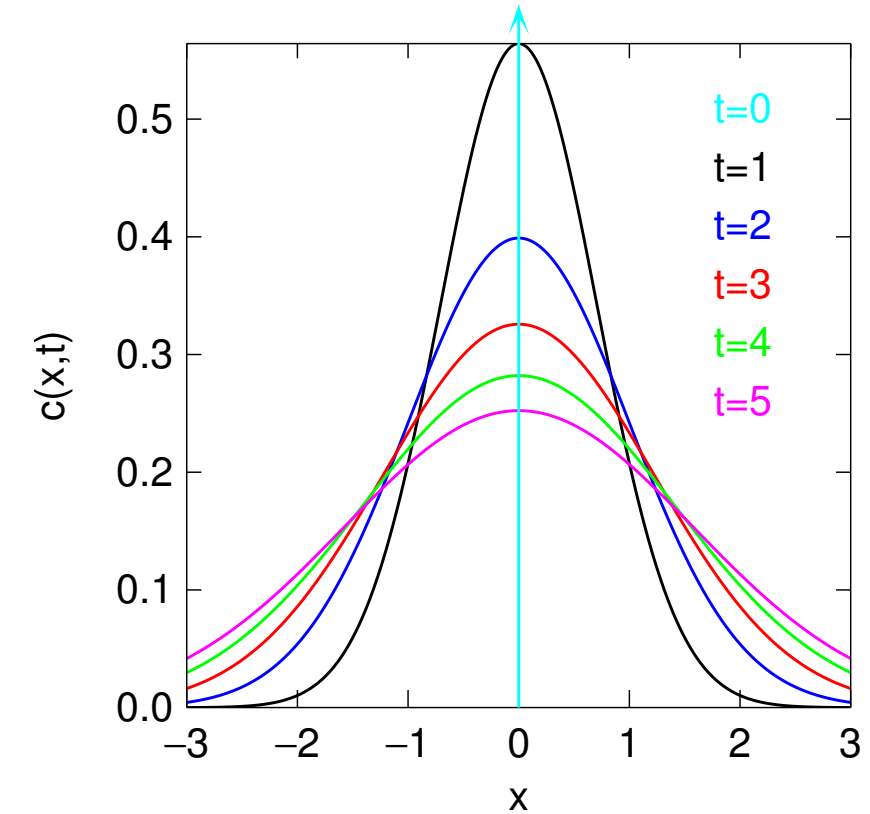
This type of equation is called “equation of heat conduction”. It is a parabolic partial differential equation

Diffusion and the Brownian motion

Instead of for $c(\vec{r}, t)$, let us solve the 2nd Fick law for the probability of finding a particle, starting from origin at $t = 0$. We get the **Gaussian distribution** with half-width \propto

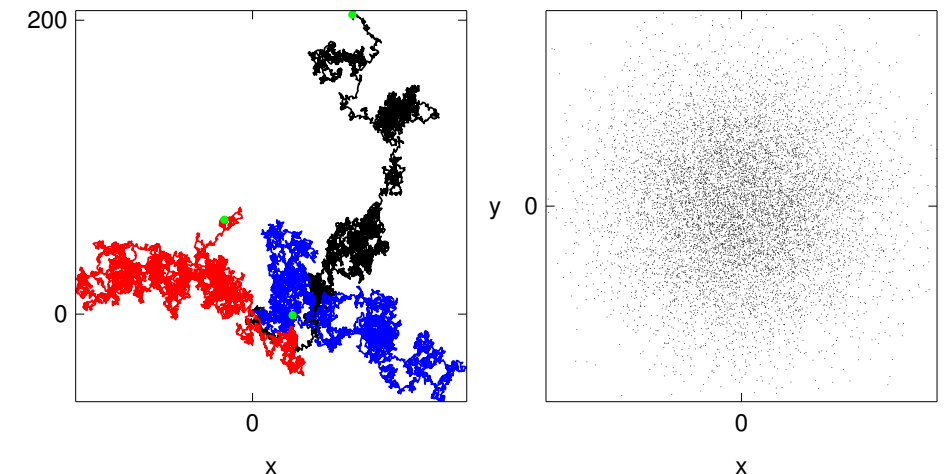
$$1\text{D: } c(x, t) = (4\pi Dt)^{-1/2} \exp\left(-\frac{x^2}{4Dt}\right)$$

$$3\text{D: } c(\vec{r}, t) = (4\pi Dt)^{-3/2} \exp\left(-\frac{r^2}{4Dt}\right)$$



● 1D: $\langle x^2 \rangle = 2Dt$

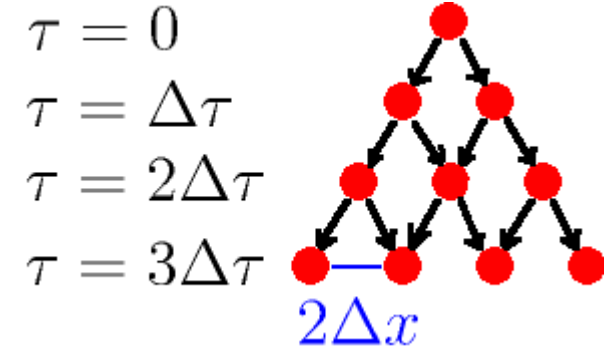
● 3D: $\langle r^2 \rangle = 6Dt$



Brownian motion as a random walk

(Smoluchowski, Einstein)

- within time Δt , a particle moves randomly
 - by Δx with probability 1/2
 - by $-\Delta x$ with probability 1/2



Using the central limit theorem:

- in one step: $\text{Var } x = \langle x^2 \rangle = \Delta x^2$
- in n steps (in time $t = n\Delta t$): $\text{Var } x = n\Delta x^2$
 ⇒ Gaussian normal distribution with $\sigma = \sqrt{n\Delta x^2} = \sqrt{t/\Delta t}\Delta x$:

$$\frac{1}{\sqrt{2\pi}\sigma} e^{-x^2/2\sigma^2} = \frac{1}{\sqrt{2\pi t}} \frac{\sqrt{\Delta t}}{\Delta x} \exp\left[-\frac{x^2}{2t} \frac{\Delta t}{\Delta x^2}\right]$$

which is for $2D = \Delta x^2/\Delta t$ the same as $c(x, t)$

NB: $\text{Var } x \stackrel{\text{def.}}{=} \langle (x - \langle x \rangle)^2 \rangle$, for $\langle x \rangle = 0$, then $\text{Var } x = \langle x^2 \rangle$

Example. Calculate $\text{Var } u$, where u is a random number from interval $(-1, 1)$

You do not know the central limit theorem?

- during time $2\Delta\tau$ a walker moves
 - by $2\Delta x$ with probability $1/4$
 - by $-2\Delta x$ with probability $1/4$
 - by 0 with probability $1/2$

- during time $2n\Delta\tau$ a walker moves by $2k\Delta x$ with probability

$$\pi(n, k) = \binom{2n}{n-k} 4^{-n}$$

Let us start from $\pi(n, 0)$. Since

$$\binom{2n}{n+1} = \frac{(2n)!}{(n-1)!(n+1)!} = \frac{(2n)!}{n!/n \cdot n!(n+1)} = \binom{2n}{n} \times \frac{n}{n+1}$$

we can write, neglecting second-order terms ($\propto 1/n^2$)

$$\begin{aligned} \ln \pi(n, 1) &= \ln \pi(n, 0) + \ln \frac{n}{n+1} \\ &= \ln \pi(n, 0) + \ln \left(1 - \frac{1}{n+1} \right) \approx \ln \pi(n, 0) + \ln \left(1 - \frac{1}{n} \right) \approx \ln \pi(n, 0) - \frac{1}{n} \end{aligned}$$

Analogously: $\ln \pi(n, 2) = \ln \pi(n, 1) + \ln \left(1 - \frac{3}{n+2}\right) \approx \ln \pi(n, 1) - \frac{3}{n} \approx \ln \pi(n, 0) - \frac{1}{n} - \frac{3}{n}$

and generally: $\ln \pi(n, k) \approx \ln \pi(n, 0) - \sum_{j=1}^k \frac{2j-1}{n}$

Now let us replace the sum by an integral:

$$\sum_{j=1}^k (2j-1) \approx \int_0^k (2k-1) dk = k(k-1) \stackrel{k \text{ is large}}{\approx} k^2$$

And similarly for negative k . In the limit of large k , n :

$$\pi(n, k) \approx \pi(n, 0) \exp\left(-\frac{k^2}{n}\right)$$

Again $\Delta x = (2D\Delta\tau)^{1/2}$, $k = x/\Delta x = x/(2D\Delta\tau)^{1/2}$, $n = t/(2\Delta\tau)$:

$$\pi(n, k) = c(x, \tau) \approx c(x, 0) \exp\left(-\frac{x^2}{4D\tau}\right)$$

After normalization (condition $\int \pi(x, \tau) dx = 1$), we get $c(x, \tau)$.

Random walk in one variable:

$\phi(\delta x)$ = probability density of a particle traveling by δx in time δt

$$\int_{-\infty}^{+\infty} \phi(\delta x) d\delta x = 1, \quad \phi(-\delta x) = \phi(+\delta x)$$

The development of the density (of probability) $\rho(x, t)$ within time δt :

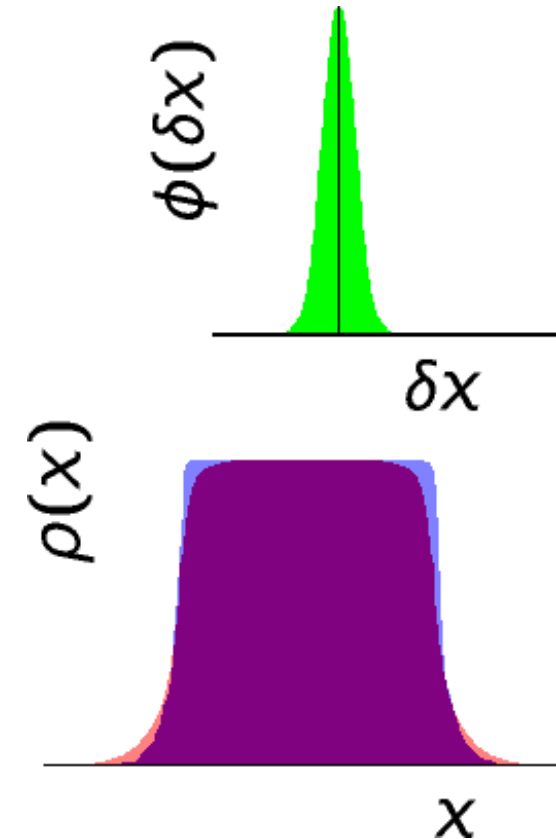
$$\rho(x, t + \delta t) = \int_{-\infty}^{+\infty} \rho(x + \delta x, t) \phi(\delta x) d\delta x$$

$$\rho(x + \delta x, t) = \rho(x, t) + \delta x \frac{\partial \rho}{\partial x} + \frac{\delta x^2}{2} \frac{\partial^2 \rho}{\partial x^2} + \dots$$

On integration (odd terms cancel out, higher-order can be neglected):

$$\rho(x, t + \delta t) \approx \rho(x, t) + \delta t \frac{\partial \rho}{\partial t} = \rho(x, t) + \frac{\partial^2 \rho}{\partial x^2} \int_{-\infty}^{+\infty} \frac{\delta x^2}{2} \phi(\delta x) d\delta x$$

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}, \quad D = \frac{1}{\delta t} \int_{-\infty}^{+\infty} \frac{\delta x^2}{2} \phi(\delta x) d\delta x$$



A (colloid) particle in a viscous environment + random hits:

$$\dot{x} \equiv dx/dt$$

$$m\ddot{x} = f - f\dot{x} + X(t)$$

● f = “normal” (conservative) force – for now $f = 0$

● f = friction coefficient; spheres: $f = n\pi\eta R$ (Stokes), $n = 4|6$ for ideally smooth|rough sphere

● X is **random force**: does not depend on t, x , $\langle X(t) \rangle = 0$, $\langle X(t)X(t') \rangle = A \delta(t - t')$

Multiply by x and rearrange:

$$d^2(\frac{1}{2}x^2)/dt^2 = d(\dot{x}x)/dt$$

$$m\ddot{x}x = -f\dot{x}x + Xx$$

$$\frac{m}{2} \frac{d^2}{dt^2}(x^2) - m\dot{x}^2 = -\frac{f}{2} \frac{d}{dt}(x^2) + Xx$$

Apply the canonical expectation value and $\langle X(t)x \rangle = 0$:

$$\frac{m}{2} \frac{d^2}{dt^2} \langle x^2 \rangle - k_B T = -\frac{f}{2} \frac{d}{dt} \langle x^2 \rangle$$

$$\frac{m}{2} \frac{d^2}{dt^2} \langle x^2 \rangle - k_B T = -\frac{f}{2} \frac{d}{dt} \langle x^2 \rangle$$

This is a linear differential equation for $\frac{d}{dt} \langle x^2 \rangle$, solvable by the separation of variables

$$\frac{d}{dt} \langle x^2 \rangle = \frac{2k_B T}{f} + C e^{-ft/m} \xrightarrow{t \rightarrow \infty} 2 \frac{k_B T}{f}$$

after integration

$$\langle x^2 \rangle = \frac{2k_B T}{f} t + \frac{Cm}{f} [1 - e^{-ft/m}]$$

At long t (neglecting the **initial transient**)

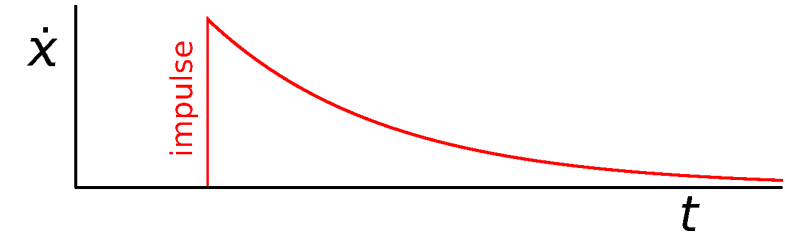
$$\langle x^2 \rangle = 2Dt, \quad \text{where } D = \frac{k_B T}{f}$$

This is the Einstein–Smoluchowski equation to predict D from f at given T

However, in MD (for a stochastic thermostat) we rather need a formula for $X(t)$.

Langevin equation for $f = 0$:

$$\ddot{x} = -\frac{f}{m}\dot{x} + \frac{1}{m}X(t)$$



where $X(t)$ is the (Gaussian) random force: $\langle X(t) \rangle = 0$, $\langle X(t)X(t') \rangle = A \delta(t - t')$, $A = ?$

Explicit solution for velocity – initial problem $\dot{x}(0)$ is relaxing exponentially to 0, more impulses $X(t)$ are integrated:

$$\dot{x}(t) = \dot{x}(0)e^{-\frac{f}{m}t} + \frac{1}{m} \int_0^t X(t')e^{-\frac{f}{m}(t-t')} dt' \quad t \rightarrow \infty, \text{history} \Rightarrow \dot{x}(0) = \frac{1}{m} \int_0^\infty X(-t)e^{-\frac{f}{m}t} dt$$

We want T ! The expected kinetic energy:

$$\begin{aligned} \langle m\dot{x}^2 \rangle &= m \left\langle \frac{1}{m} \int_0^\infty X(-t)e^{-\frac{f}{m}t} dt \cdot \frac{1}{m} \int_0^\infty X(-t')e^{-\frac{f}{m}t'} dt' \right\rangle \\ &= \frac{1}{m} \int_0^\infty dt' \int_0^\infty dt A \delta(t - t') e^{-\frac{f}{m}(t+t')} = \frac{1}{m} \int_0^\infty dt A e^{-\frac{f}{m}2t} = \frac{A}{2f} \end{aligned}$$

$$\langle m\dot{x}^2 \rangle = k_B T \Rightarrow A = 2fk_B T = \frac{2(k_B T)^2}{D}$$

Langevin thermostat and Brownian dynamics

In the simulation, $X(t)$ is replaced by an impulse $A\xi/\sqrt{h}$ every timestep h , where ξ is a random number with the normalized normal distribution.

- As a thermostat: All degrees of freedom are sampled (also the momentum in the periodic b.c.)
- Momentum and center of mass not conserved
- As Brownian dynamics: kinetic model of implicit solvent

Dissipative particle dynamics (DPD)

Good for coarse-grained models:

- Groups of atoms (e.g., 4 H₂O, bead in a polymer) are replaced by a superparticle. Its properties are adjusted (empirically, by a comparison with a full-atom simulation).
- Internal motion is approximated by random forces so that (for $t \rightarrow \infty$), both the **Brownian motion** and **hydrodynamic behavior** is correct; particularly, the momentum is conserved.

Equations of motion

$$m\ddot{\mathbf{r}}_i = \sum_{j \neq i} (\vec{f}_{ij}^{\text{C}} + \vec{f}_{ij}^{\text{D}} + \vec{f}_{ij}^{\text{R}})$$

where \vec{f}_{ij}^{C} is a **C**onservative pair force.

Dissipation of velocity in the direction of \hat{r}_{ij} (\Rightarrow CoM conserved):

$$\vec{f}_{ij}^{\text{D}} = -f\omega^{\text{D}}(r_{ij})(\vec{v}_{ij} \cdot \hat{r}_{ij})\hat{r}_{ij}, \quad \hat{r}_{ij} = \frac{\vec{r}_{ij}}{r_{ij}}$$

Random force also acts in the direction of \hat{r}_{ij} :

$$\vec{f}_{ij}^{\text{R}} = \sigma\omega^{\text{R}}(r_{ij})\xi\hat{r}_{ij}$$

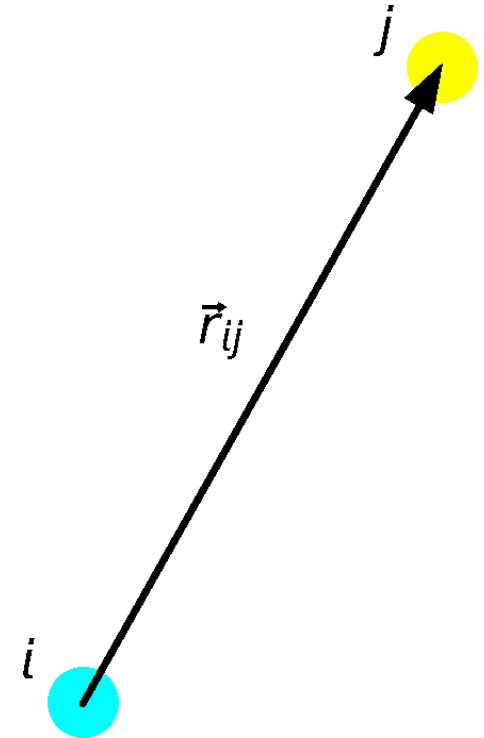
The “fluctuation-dissipation theorem” is:

$$\omega^{\text{D}} = [\omega^{\text{R}}]^2, \quad \sigma = 2k_{\text{B}}Tf$$

● $\xi = \xi(t)$ = normalized Gaussian force, $\langle \xi(0)\xi(t) \rangle = \delta(t)$

● ω (or ω_{ij}) = short-ranged, e.g., $\omega^{\text{R}}(r) = 1 - r/r_{\text{cutoff}}$

● $r_{\text{cutoff}} \approx$ the typical size of coarse-graining



$$[\xi] = s^{-1/2}$$

We are interested in coefficients of (linear) response to a (small) perturbation:

$$\vec{J}_{\text{compound A}} = -D\vec{\nabla}c_A$$

$$\vec{J}_{\text{heat}} = -f\vec{\nabla}T$$

$$\eta \frac{\partial v_x}{\partial y} = P_{xy}$$

Methods:

- EMD (*equilibrium molecular dynamics*), simulation in equilibrium
e.g., $D_i = \lim_{t \rightarrow \infty} \langle [r_i(t) - r_i(0)]^2 \rangle / 6t$
- NEMD (*non-equilibrium molecular dynamics*), simulation under an external force or perturbation

- a perturbation with energy $\Delta\mathcal{H}$, $\mathcal{H}' = \mathcal{H} + \Delta\mathcal{H}$ added
- we measure quantity B in the canonical ensemble (with perturbation)

$$\beta = \frac{1}{k_B T}$$

$$\begin{aligned}\langle B \rangle' &= \frac{\int B \exp(-\beta\mathcal{H}') dpdq}{\int \exp(-\beta\mathcal{H}') dpdq} \approx \frac{\int B(t) \exp(-\beta\mathcal{H})(1 - \beta\Delta\mathcal{H}) dpdq}{\int \exp(-\beta\mathcal{H})(1 - \beta\Delta\mathcal{H}) dpdq} \\ &= \frac{\langle B \rangle - \beta\langle B\Delta\mathcal{H} \rangle}{1 - \beta\langle \Delta\mathcal{H} \rangle} \approx (\langle B \rangle - \beta\langle B\Delta\mathcal{H} \rangle)(1 + \beta\langle \Delta\mathcal{H} \rangle) \approx \langle B \rangle - \beta(\langle \Delta\mathcal{H}B \rangle - \langle \Delta\mathcal{H} \rangle\langle B \rangle) \\ &= \langle B \rangle - \beta\text{Cov}(B, \Delta\mathcal{H}) \stackrel{\langle B \rangle=0}{=} -\beta\langle B \Delta\mathcal{H} \rangle\end{aligned}$$

Example. Classical harmonic oscillator $\mathcal{H} = \frac{K}{2}x^2$, perturbation $\Delta\mathcal{H} = gx$, we measure $B = x$:

$$\langle x \rangle = -\beta\langle \Delta\mathcal{H}x \rangle = -\beta\langle gx^2 \rangle = -\beta g \frac{\int x^2 \exp(-\beta\frac{K}{2}x^2) dx}{\int \exp(-\beta\frac{K}{2}x^2) dx} = -\frac{g}{K}$$

which is correct, because the potential minimum was actually only shifted:

$$\mathcal{H}' = \frac{K}{2}x^2 + gx = \frac{K}{2}\left(x + \frac{g}{K}\right)^2 + \text{const}$$

Diffusivity from MSD in 1D (Einstein):

$$\langle x^2 \rangle = 2Dt \quad (t \rightarrow \infty)$$

$$D(t) = \frac{1}{2} \frac{d}{dt} \langle [x(t) - x(0)]^2 \rangle = \langle [x(t) - x(0)] \dot{x}(t) \rangle$$

$$= \left\langle \left[\int_0^t \dot{x}(t') dt' \right] \dot{x}(t) \right\rangle = \left\langle \int_0^t \dot{x}(t') \dot{x}(t) dt' \right\rangle \quad (\text{subst. } t' = t - t'')$$

$$= - \int_t^0 \langle \dot{x}(t - t'') \dot{x}(t) \rangle dt'' = \int_0^t \langle \dot{x}(0) \dot{x}(t'') \rangle dt'' = \left\langle \int_0^t \dot{x}(0) \dot{x}(t') dt' \right\rangle$$

We are interested in the limit $t \rightarrow \infty$:

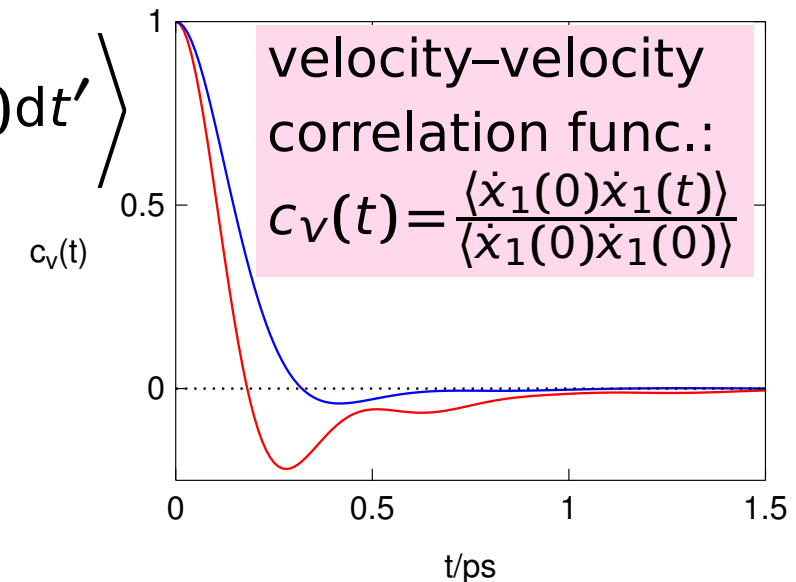
$$D = \int_0^{\infty} \langle \dot{x}(0) \dot{x}(t) \rangle dt$$

This is a simple example of the **Green-Kubo formula**

Interpretation: The longer a velocity at time t is (positively) correlated with the velocity at time 0, the further the particle travels, and the diffusivity is higher.

MSD = mean squared deviation/displacement

$$\langle a(t_1)b(t_2) \rangle = \langle a(t_1 + \Delta t)b(t_2 + \Delta t) \rangle$$



- We work in the Hamiltonian formalism (positions and momenta), using distribution functions (in q, p).
- At time $t = 0$ an impuls changes the value of the Hamiltonian by $\Delta\mathcal{H} = \mathcal{H}_{t>0} - \mathcal{H}_{t<0}$.
- In case of a time-dependent perturbation, we integrate over time.

Example of a result for diffusion (Green–Kubova formula in 3D):

$$D = \frac{1}{3} \int_0^{\infty} \langle \dot{\vec{r}}_i(t) \cdot \dot{\vec{r}}_i(0) \rangle dt$$

Another example – viscosity:

$$\eta = \frac{V}{k_{\text{BT}}} \int_0^{\infty} \langle P_{xy}(0) P_{xy}(t) \rangle dt$$

where P_{xy} are components of the pressure tensor. No corresponding Einstein relation exists!

Hamilton's equations:

$$\dot{q} = \frac{\partial \mathcal{H}}{\partial p} \equiv \frac{p}{m}, \quad \dot{p} = -\frac{\partial \mathcal{H}}{\partial q} \equiv f$$

Perturbation (impuls) at time $t = 0$:

$$\dot{q} = \frac{p}{m} - A_p \delta(t), \quad \dot{p} = f + A_q \delta(t)$$

where $A_p = \frac{\partial A}{\partial p}$ and $A_q = \frac{\partial A}{\partial q}$ for some $A = A(q, p)$.

Example: $A = \mathcal{F}_1 x_1$ or $A_{x_1} = \mathcal{F}_1$, $A_q = 0$ for $q \neq x_1$ and $A_p = 0$.

$$\dot{p}_{1,x} = f_{1,x} + \mathcal{F}_1 \delta(t)$$

A has unit energy \times time
($\dot{A}(0)$ is energy jump),
 \mathcal{F}_1 has unit force \times time
= momentum.

Stepwise change of the total energy by:

$$\begin{aligned} \mathcal{H}_{t>0} - \mathcal{H}_{t<0} &= \mathcal{H}(q - A_p, p + A_q) - \mathcal{H}(q, p) \\ &= \sum \left(-\frac{\partial \mathcal{H}}{\partial q} A_p + \frac{\partial \mathcal{H}}{\partial p} A_q \right) = \sum (\dot{p} \cdot A_p + \dot{q} \cdot A_q) \equiv \dot{A}(0) \end{aligned}$$

Example: $\mathcal{H}_{t>0} - \mathcal{H}_{t<0} = \mathcal{F}_1 \dot{x}_1(0) \begin{cases} > 0 & \text{for a hit in the direction of particle flight,} \\ < 0 & \text{for a hit against the direction of particle flight} \end{cases}$

A perturbation (leading to a jump in \mathcal{H}) will be **turned off** (using a δ -impuls) at $t = 0$. The system is canonical for $t < 0$, but I will measure (run simulation) using a non-perturbed state $\mathcal{H} = \mathcal{H}_{t>0}$.

Let us measure quantity B , $\langle B \rangle = 0$. The response:

$$\langle B(t) \rangle_{A\delta(t)} = \frac{\int B(t) \exp[-\beta\mathcal{H}_{t>0} + \beta\dot{A}(0)] dpdq}{\int \exp[-\beta\mathcal{H}_{t>0} + \beta\dot{A}(0)] dpdq}$$

By expanding for small $\beta\dot{A}(0)$ we get

$$\langle B(t) \rangle_{A\delta(t)} = \beta \langle \dot{A}(0) B(t) \rangle_{t>0}$$

where the expectation value right is measured for $t > 0$
the energy $\mathcal{H}_{t>0}$ changed, but the distribution did not

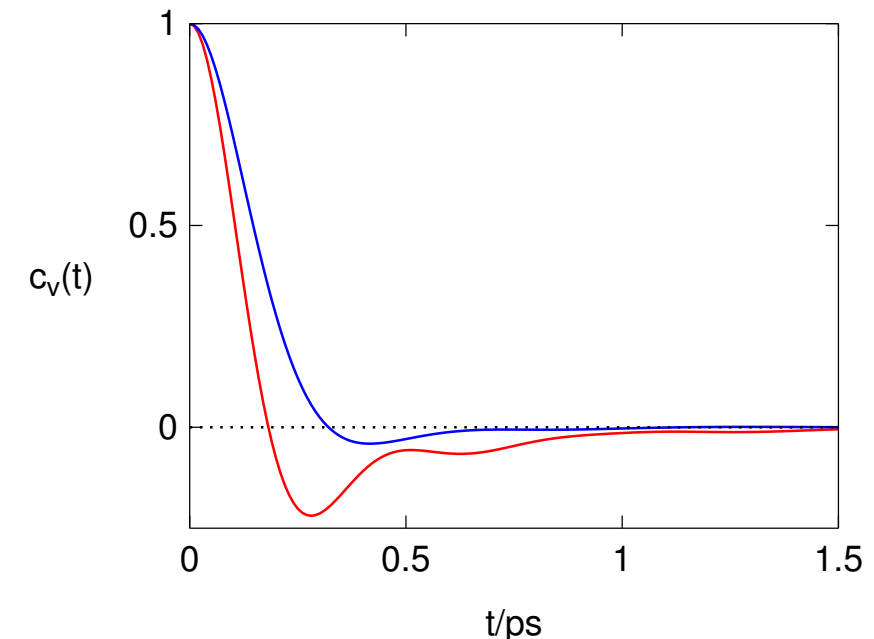
Example: $B = \dot{x}_1$ ($S \mathcal{H}_{t>0} - \mathcal{H}_{t<0} = \mathcal{F}_1 \dot{x}_1(0)$):

$$\langle \dot{x}_1(t) \rangle_{A\delta(t)} = \mathcal{F}_1 \beta \langle \dot{x}_1(0) \dot{x}_1(t) \rangle$$

velocity relaxation following a hit

\propto

time correlation function velocity-velocity



Long-time perturbation: $A(t) = \text{constant}$ for $t > 0$. Limit $t \rightarrow \infty$:

$$\langle B \rangle_A = \beta \int_0^\infty \langle \dot{A}(0) B(t) \rangle dt$$

E.g., system in an electric field: dipolar relaxation/electric conductivity (heats up!)

Example:

$$\dot{p}_{1,x} = f_{1,x} + \mathcal{F}_1 \Rightarrow \langle \dot{x}_1 \rangle_A = \mathcal{F}_1 \beta \int_0^\infty \langle \dot{x}_1(0) \dot{x}_1(t) \rangle dt$$

$$\text{Einstein–Smoluchowski: } \beta D_i = \frac{v_i}{\mathcal{F}_i} \Rightarrow D_1 = \int_0^\infty \langle \dot{x}_1(0) \dot{x}_1(t) \rangle dt$$

For $\mathcal{F}_1 = E_x q_1$ we get the ionic mobility

$$u_1 = \frac{\langle \dot{x}_1 \rangle}{E_x} = \frac{q_1 D_1}{k_B T}$$

and after multiplying by the charge per mole we get the Nernst–Einstein equation for the limiting molar conductivity

$$\Lambda_1^\infty = \frac{\langle \dot{x} q_1 N_A \rangle}{E_x} = \frac{q_1^2 D_1}{RT}$$

● Einstein:

$$\kappa = \int_0^{\infty} \langle \dot{X}(0)\dot{X}(t) \rangle dt$$

$$\int_0^t \langle \dot{X}(0)\dot{X}(t') \rangle dt' = [\langle \dot{X}(0)X(t') \rangle]_0^t$$

interchange $t \rightarrow -t$ (NB: $\dot{X}(0) \rightarrow -\dot{X}(0)$) and shift by $t \Rightarrow$

$$\int_0^t \langle \dot{X}(0)\dot{X}(t') \rangle dt' = \frac{1}{2} \frac{d}{dt} \langle [X(t) - X(0)]^2 \rangle$$

In the limit $t \rightarrow \infty$ then

$$2t\kappa = \langle [X(t) - X(0)]^2 \rangle$$

E.g., for the diffusion:

● Green-Kubo $D = \frac{1}{3} \int_0^{\infty} \langle \dot{\vec{r}}_i(t) \cdot \dot{\vec{r}}_i(0) \rangle dt$

● Einstein $2tD = \frac{1}{3} \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle$

cf. NEMD: apply force to a particle while cooling, $D_i = k_B T \langle v_i \rangle / \mathcal{F}_i$, calculate limit $\mathcal{F}_i \rightarrow 0$

- NEMD (non-equilibrium molecular dynamics), electric field E is turned on (in periodic b.c.). The current density is measured:

$$\vec{j} = \kappa \vec{E}$$

Cooling is needed (thermostat). Extrapolation $\vec{E} \rightarrow 0$.

- Green-Kubo:

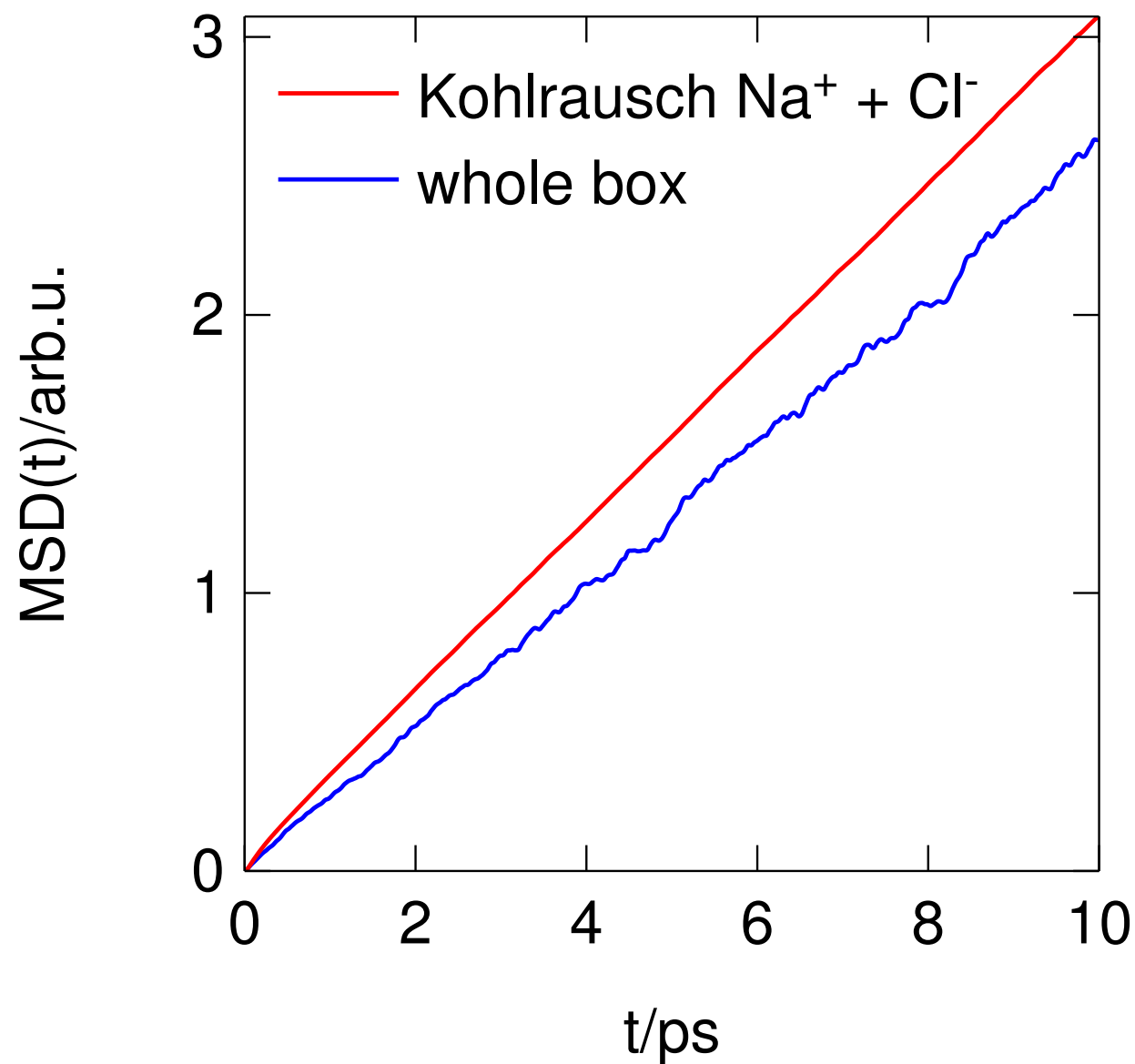
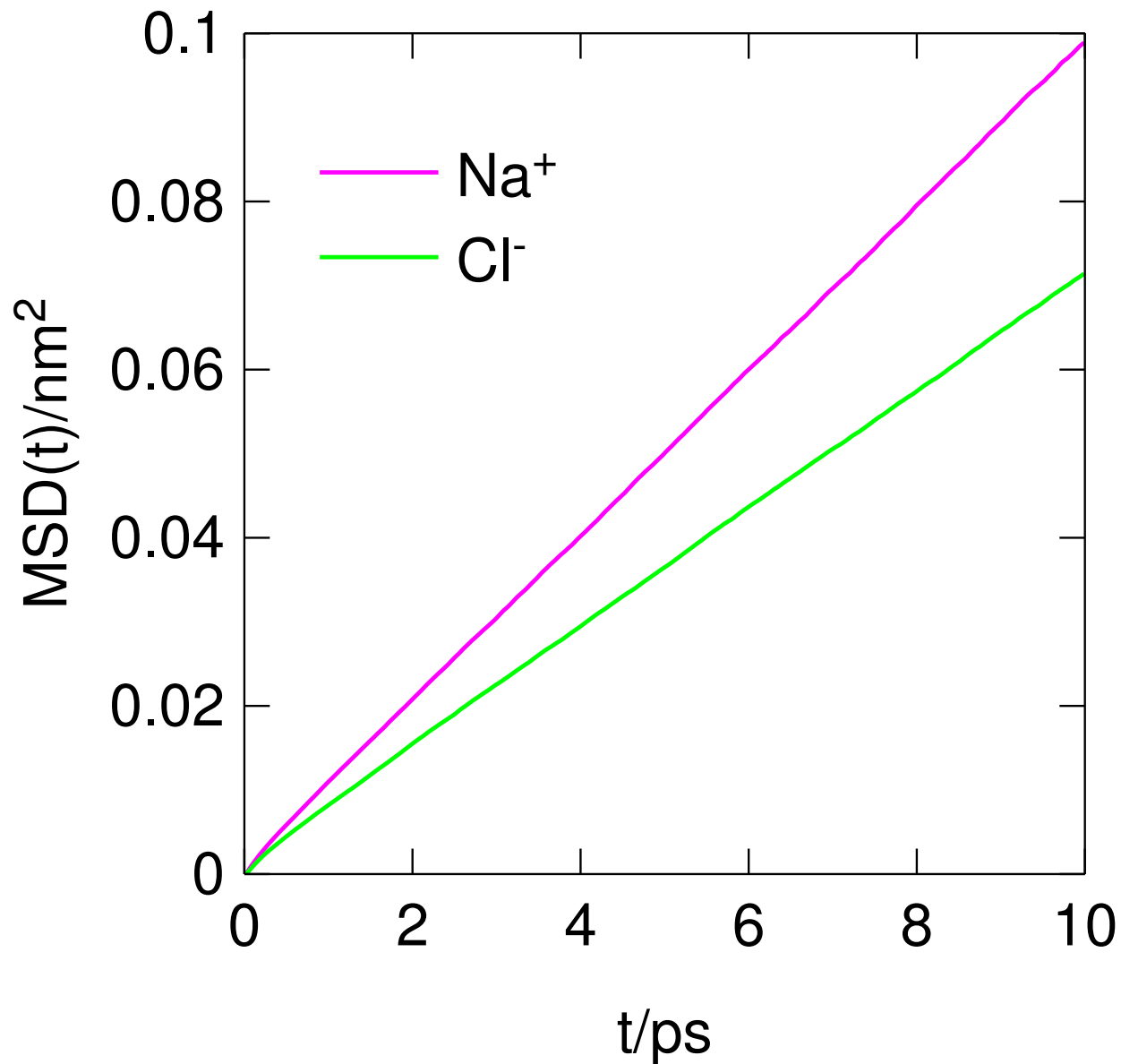
$$\kappa = \frac{V}{k_B T} \int_0^\infty \langle \vec{j}(t) \cdot \vec{j}(0) \rangle$$

- Einstein

$$\kappa = \lim_{t \rightarrow \infty} \frac{d}{dt} \frac{1}{6k_B T V} \left\langle \left\{ \sum_i q_i [\vec{r}_i(t) - \vec{r}_i(0)] \right\}^2 \right\rangle$$

NB: No Einstein relation for viscosity is known

Conductivity of molten NaCl using EMD:



The periodic image of a particle is L far away and diffusing always in the same direction!

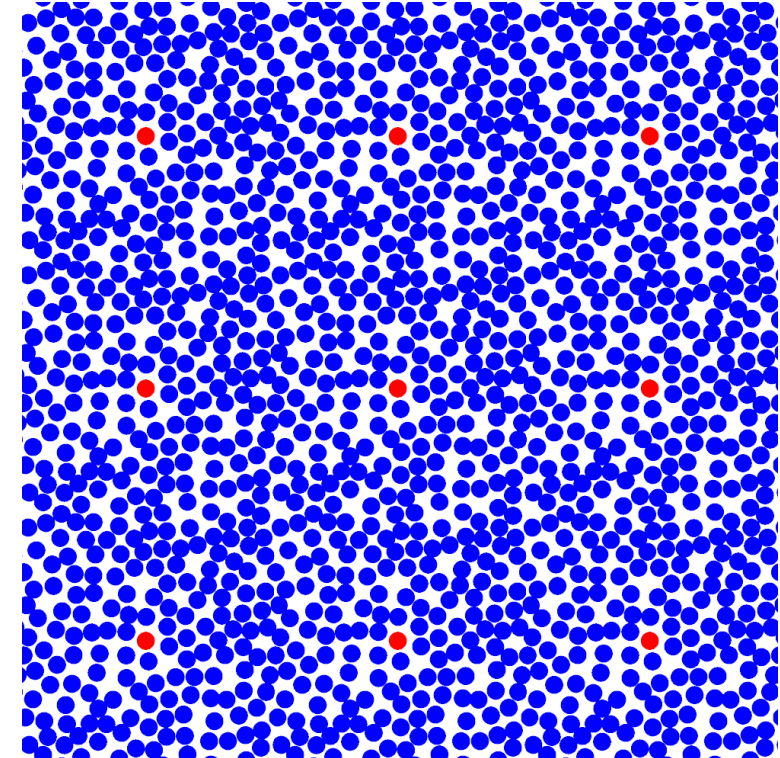
Pure liquid in 3D:

$$D = D_{\text{PBC}} + \frac{2.873k_{\text{B}}T}{6\pi\eta L}$$

$$\frac{D_{\text{PBC}} - D}{D} = -\frac{2.873R}{L} \propto \mathcal{O}(N^{-1/3})$$

where $R = k_{\text{B}}T/6\pi\eta D$

- pure fluid: determine viscosity and include corrections
- generally: calculate for several L and extrapolate



B. Dünweg and K. Kremer, J. Chem. Phys., 1993, 99, 6093–6997;

I.-C. Yeh and G. Hummer, J. Phys. Chem. B, 2004, 108, 15873–15879.

Not so easy: corrections

Ar
^^
EvdW=-0.2380684 kcal/mol, RvdW=1.910992 AA
T=143.76 (T*=1.2)
rho=1344.2582 kg/m3 (rho*=0.8)

viscosity (Green-Kubo): eta=0.00017543 Pa.s
D is in 1e-9 m^2/s
Dcorr = Dsim + 2.837*k*T / (6*pi*eta*L)

```
=====
N method tau/ps  Dsim  stderr Dcorr
-----
250   B   0.2     4.217 0.019 4.954
250   B   1       4.229 0.022 4.966
250   N   0.2     4.210 0.021 4.947
250   N   1       4.220 0.022 4.957
2000  B   0.2     4.560 0.012 4.928
2000  B   1       4.567 0.011 4.935
2000  N   0.2     4.568 0.013 4.936
2000  N   1       4.578 0.010 4.947
=====
```

2000: L=46.21296 AA
250: L=23.10648 AA
N=Nose+Gear
B=Berendsen(+Shake)

SPCE water
^^^^^^^^^^
T=298.15 K

```
=====
N method tau/ps  Dsim  stderr Dcorr
-----
250   B   1       2.30 0.06 2.84
250   B   1       2.26 0.07 2.80
2000  B   1       2.49 0.10 2.76
2000  B   1       2.56 0.09 2.83
=====
```

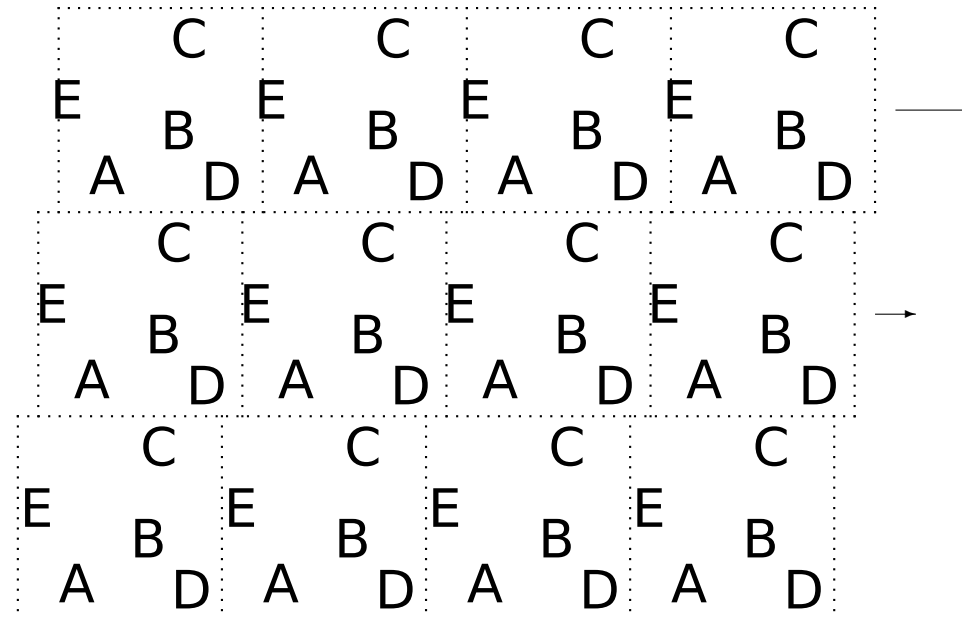
viscosity (N=250): 0.00058(6) Pa.s
L=19.575161 AA (N=250)

NB: later results, N=300
viscosity=0.00073(4) Pa.s
Dsim=2.390(8), D=2.80(2) [1e-9 m^2/s]

[J. Malohlava (University of Ostrava) and J. Kolafa (2010), unpublished results.]

NEMD = Non-equilibrium molecular dynamics

- as a real experiment (turn on a field, gradient of temperature, ...)
- problem: linearity (extrapolation to zero perturbation)
- problem: cooling needed
- viscosity:
 - SLODD (Lees-Edwards)
 - transfer of momentum
 - cos-modulated force



Green–Kubo:

$$\eta_{ab} = \frac{V}{kT} \int_0^\infty \langle P_{ab}(t)P_{ab}(0) \rangle dt, \quad a \neq b$$

$$\eta_{ab} = \eta_{ba}$$

Curiously, also diagonal elements can be used*:

$$\eta_{aa} = \frac{3}{4} \frac{V}{kT} \int_0^\infty \langle P'_{aa}(t)P'_{aa}(0) \rangle dt, \quad P'_{aa} = P_{aa} - \frac{1}{3} \sum_{b=x,y,z} P_{bb}$$

It is not so accurate. Recommended mixing:

$$\eta = \frac{3}{5} \eta_{\text{off}} + \frac{2}{5} \eta_{\text{trless}}, \quad \eta_{\text{off}} = \frac{1}{3} \sum_{ab=xy,yz,zx} \eta_{ab}, \quad \eta_{\text{trless}} = \frac{1}{3} \sum_a \eta_{aa}.$$

⊕ : more accurate than NEMD

⊖ : P_{ab} needed (sometimes problematic or not available)

*Daivis P.J., Evans D.J.: Comparison of constant pressure and constant volume nonequilibrium simulations of sheared model decane, *J. Chem. Phys.* **100**, 541 (1993)

- elongated box (e.g., $L_x : L_y : L_z = 1 : 1 : 3$)
- modulated force

laminar flow:
pressure-induced in a pipe: Poiseuille
drag-induced: Couette

$$\vec{f}_i = m_i C_f \cos\left(\frac{2\pi z_i}{L_z}\right) \vec{n}, \quad \vec{n} = (1, 0, 0) \text{ nebo } \frac{(1, 1, 0)}{\sqrt{2}}$$

- correction so that total force = 0

Navier–Stokes equations for the Poiseuille flow of incompressible fluid:

$$\eta \nabla^2 \vec{v} + \vec{f} = 0, \tag{1}$$

$$\vec{f} = \rho C_f \left(\cos \frac{2\pi z}{L_z} \right) \vec{n}$$

where $\rho = \sum_i m_i / V$. Solution:

$$\vec{v} = \frac{C_f \rho L_z^2}{4\pi^2 \eta} \cos\left(\frac{2\pi z}{L_z}\right) \vec{n}$$

Thus, η is calculated from the velocity profile, $\int_0^{L_z} \vec{v}(z) \cdot \vec{n} \cos\left(\frac{2\pi z}{L_z}\right) dz$

NEMD viscosity

Dissipation of energy:

$$\frac{dE}{dt} = \frac{1}{2} \int \eta (\nabla v)^2 dV = \frac{V}{\eta} \left(\frac{C_f \rho L_z}{4\pi} \right)^2.$$

- one can also determine η from the dissipation (less accurate)
- one can estimate how the cooling constant of a thermostat (e.g., Berendsen)
- extrapolation $C_f \rightarrow 0$ needed
- ⊖ less accurate than Green-Kubo
- ⊕ pressure tensor not needed

