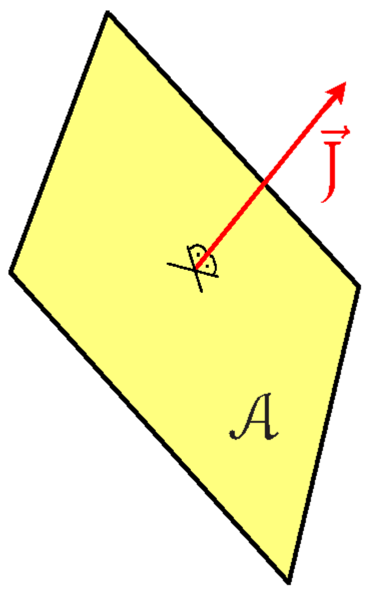
# Transport phenomena

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: $\mathrm{J\,m^{-2}\,s^{-1}} = \mathrm{W\,m^{-2}}$,
  current density: $\mathrm{A\,m^{-2}}$




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

$$\vec{J} = \mathrm{const} \cdot \vec{\mathcal{F}}$$

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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*

# Diffusion—macroscopic view



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

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

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

is proportional to the **concentration gradient**

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

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

# Diffusion—microscopic view



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

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

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

Thermodynamic force = −grad of the chemical potential:

$$\vec{\mathcal{F}}_i = -\vec{\nabla}\left(\frac{\mu_i}{N_\mathrm{A}}\right) = -\frac{k_\mathrm{B}T}{c_i}\vec{\nabla}c_i$$

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

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

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

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

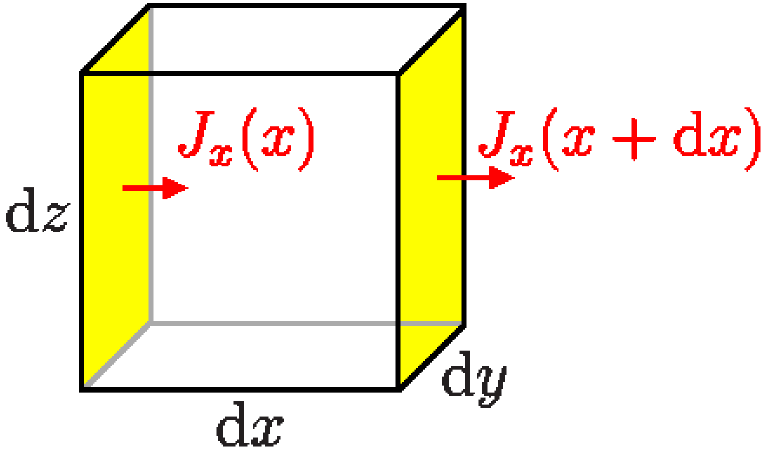
$$\vec{\mathcal{F}}_i^{\mathrm{fr}} + \vec{\mathcal{F}}_i = 0 \quad \text{i.e.} \quad -\vec{\mathcal{F}}_i^{\mathrm{fr}} = f_i\vec{v}_i = f_i\frac{\vec{J}_i}{c_i} = \vec{\mathcal{F}}_i = -\frac{k_\mathrm{B}T}{c_i}\vec{\nabla}c_i$$

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

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

# Second Fick Law

Non-stationary phenomenon ($c$ changes with time).
The amount of substance increases within time $\mathrm{d}t$ in volume $\mathrm{d}V = \mathrm{d}x\mathrm{d}y\mathrm{d}z$:




$$\sum_{x,y,z} [J_x(x) - J_x(x+\mathrm{d}x)]\,\mathrm{d}y\mathrm{d}z$$

$$\begin{aligned}
&= \sum_{x,y,z} [J_x(x) - \{J_x(x) + \frac{\partial J_x}{\partial x}\mathrm{d}x\})]\,\mathrm{d}y\mathrm{d}z \\
&= -\sum_{x,y,z} \frac{\partial J_x}{\partial x}\mathrm{d}x\mathrm{d}y\mathrm{d}z = -\vec{\nabla}\cdot\vec{J}\,\mathrm{d}V = -\vec{\nabla}\cdot(-D\vec{\nabla}c)\,\mathrm{d}V \\
&= D\vec{\nabla}^2 c\,\mathrm{d}V = D\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) c\,\mathrm{d}V
\end{aligned}$$

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

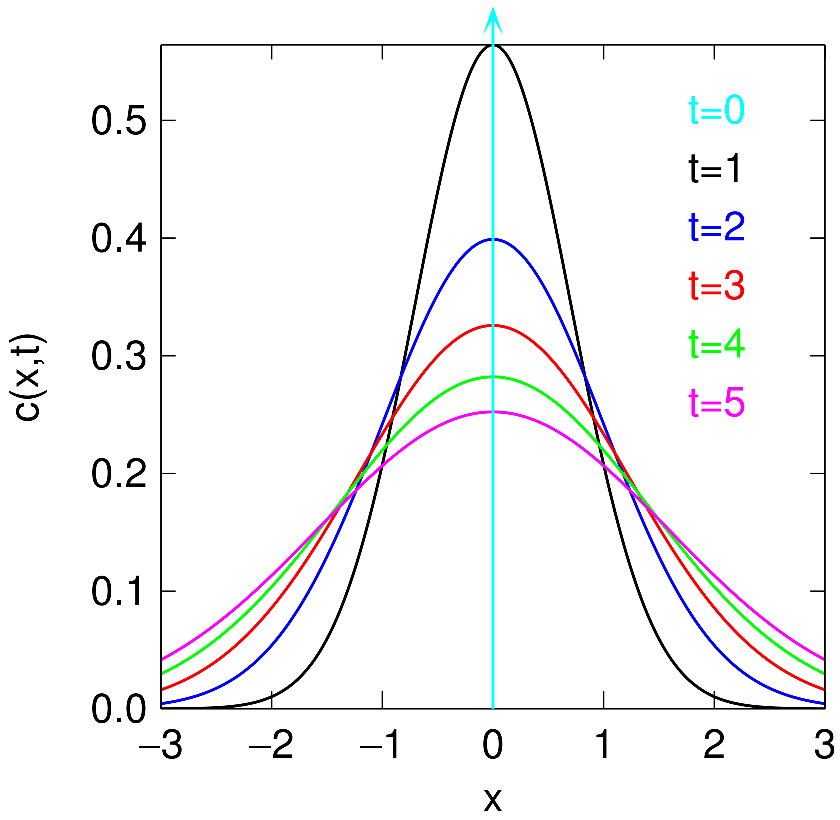
This type of equation is called "equation of heat conduction".
It is a parabolic partial differential equation

# Diffusion and the Brownian motion

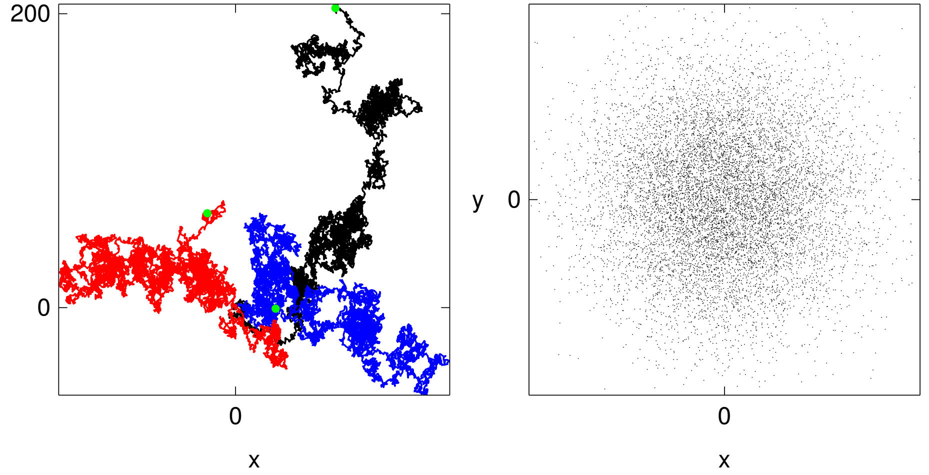
Instead of for $c(\vec{r},t)$, let us solve the 2nd Fick law for the probability of finding a particle, starting from origin at $t = 0$. We get the **Gaussian distribution** with half-width $\propto$

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

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

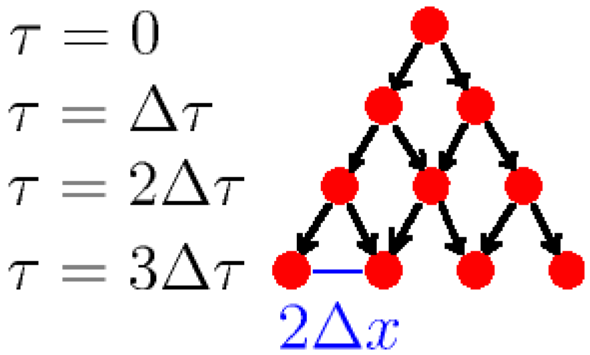



- 1D: $\boxed{\langle x^2\rangle = 2Dt}$
- 3D: $\boxed{\langle r^2\rangle = 6Dt}$



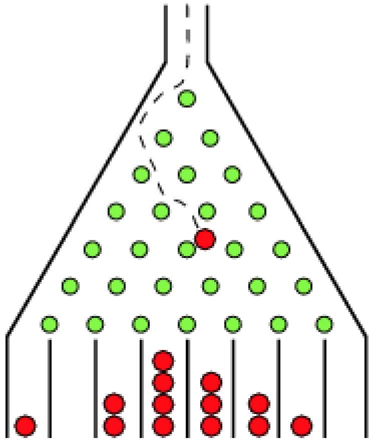
# Brownian motion as a random walk

(Smoluchowski, Einstein)




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

Using the central limit theorem:



- in one step: $\mathrm{Var}\, x = \langle x^2 \rangle = \Delta x^2$
- in $n$ steps (in time $t = n\Delta t$): $\mathrm{Var}\, x = n\Delta x^2$
  $\Rightarrow$ 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: $\mathrm{Var}\, x \stackrel{\text{def.}}{=} \langle (x - \langle x \rangle)^2 \rangle$, for $\langle x \rangle = 0$, then $\mathrm{Var}\, x = \langle x^2 \rangle$

**Example.** Calculate $\mathrm{Var}\, u$, 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

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

Let us start from $\boldsymbol{\pi}(n,0)$. 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 ($\propto 1/n^2$)

$$\ln \boldsymbol{\pi}(n,1) = \ln \boldsymbol{\pi}(n,0) + \ln \frac{n}{n+1}$$

$$= \ln \boldsymbol{\pi}(n,0) + \ln\left(1 - \frac{1}{n+1}\right) \approx \ln \boldsymbol{\pi}(n,0) + \ln\left(1 - \frac{1}{n}\right) \approx \ln \boldsymbol{\pi}(n,0) - \frac{1}{n}$$

# Brownian motion as random walk III



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

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

Now let us replace the sum by an integral:

$$\sum_{j=1}^{k}(2k-1) \approx \int_0^k (2k-1)\mathrm{d}k = k(k-1) \overset{k \text{ is large}}{\approx} k^2$$

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

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

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

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

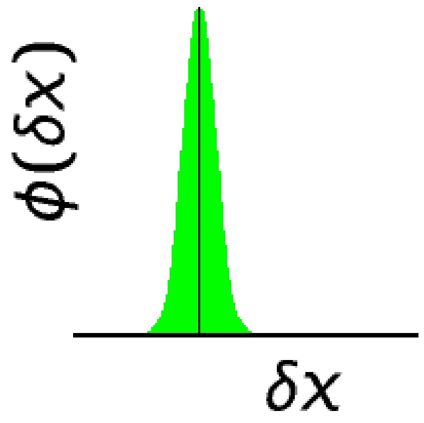
After normalization (condition $\int \boldsymbol{\pi}(x,\tau)\mathrm{d}x = 1$), we get $c(x,\tau)$.

# Einstein derivation



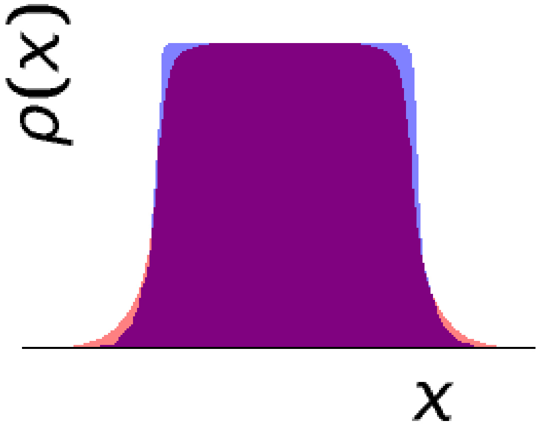
Random walk in one variable:

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




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

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




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

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

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

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

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

# Langevin equation



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

$\dot{x} \equiv \mathrm{d}x/\mathrm{d}t$

$$m\ddot{x} = f - ƒ\dot{x} + X(t)$$

- $f$ = "normal" (conservative) force – for now $f = 0$
- $ƒ$ = friction coefficient; spheres: $ƒ = n\pi\eta R$ (Stokes), $n = 4|6$ for ideally smooth|rough sphere
- $X$ is **random force**: the distribution function does not depend on $t$,
$$\langle X(t)\rangle = 0,\ \langle X(t)X(t')\rangle = A\,\delta(t-t')$$

Multiply by $x$ and rearrange:

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

$$\begin{aligned} m\ddot{x}x &= -ƒ\dot{x}x + X\,x \\ \frac{m}{2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}(x^2) - m\dot{x}^2 &= -\frac{ƒ}{2}\frac{\mathrm{d}}{\mathrm{d}t}(x^2) + Xx \end{aligned}$$

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

$$\frac{m}{2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle x^2\rangle - k_\mathrm{B}T = -\frac{ƒ}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle$$

# Langevin equation



$$\frac{m}{2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle x^2\rangle - k_\mathrm{B}T = -\frac{f}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle$$

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

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle = \frac{2k_\mathrm{B}T}{f} + C\,\mathrm{e}^{-ft/m} \overset{t\to\infty}{=} 2\frac{k_\mathrm{B}T}{f}$$

after integration

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

At long $t$ (neglecting the initial transient)

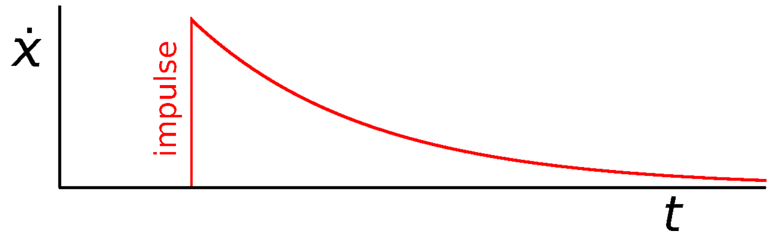
$$\langle x^2\rangle = 2Dt, \quad \text{where } D = \frac{k_\mathrm{B}T}{f}$$

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 $X(t)$.

# Fluctuation-dissipation theorem

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:

$$\dot{x}(t) = \dot{x}(0)\mathrm{e}^{-\frac{f}{m}t} + \frac{1}{m}\int_0^t X(t')\mathrm{e}^{-\frac{f}{m}(t-t')}\mathrm{d}t' \quad \overset{\substack{t\to\infty \\ \text{history}}}{\Rightarrow} \quad \dot{x}(0) = \frac{1}{m}\int_{-\infty}^0 X(t)\mathrm{e}^{\frac{f}{m}t}\mathrm{d}t = \frac{1}{m}\int_0^\infty X(-t)\mathrm{e}^{-\frac{f}{m}t}\mathrm{d}t$$

We want $T$! The expected kinetic energy:

$$\langle m\dot{x}^2\rangle = m\left\langle \frac{1}{m}\int_0^\infty X(-t)\mathrm{e}^{-\frac{f}{m}t}\mathrm{d}t \cdot \frac{1}{m}\int_0^\infty X(-t')\mathrm{e}^{-\frac{f}{m}t'}\mathrm{d}t' \right\rangle$$

$$= \frac{1}{m}\int_0^\infty \mathrm{d}t' \int_0^\infty \mathrm{d}t\, A\delta(t-t')\mathrm{e}^{-\frac{f}{m}(t+t')} = \frac{1}{m}\int_0^\infty \mathrm{d}t\, A\mathrm{e}^{-\frac{f}{m}2t} = \frac{A}{2f}$$

$$\langle m\dot{x}^2\rangle = k_\mathrm{B}T \quad \Rightarrow \quad \boxed{A = 2fk_\mathrm{B}T = \frac{2(k_\mathrm{B}T)^2}{D}}$$

## Langevin thermostat and Brownian dynamics

In the simulation, $X(t)$ is replaced by an impulse $A\xi/\sqrt{h}$ every timestep $h$, where $\xi$ 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:

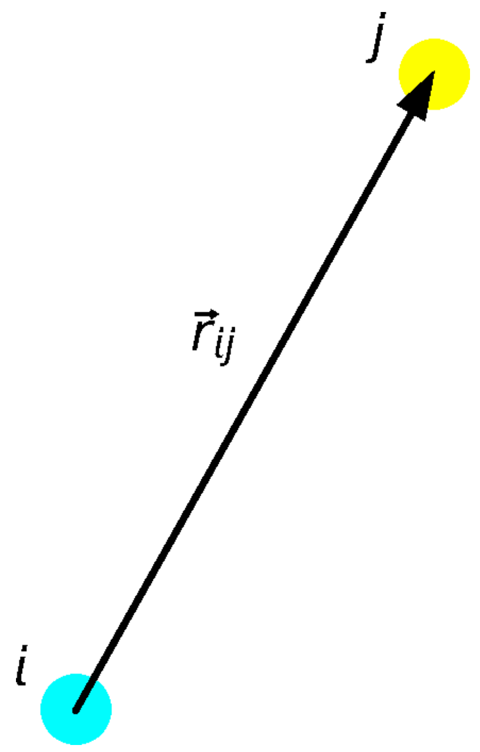
- Groups of atoms (e.g., $4\,H_2O$ in the MARTINI force field, bead in a polymer) are replaced by a superparticle. Its properties are adjusted (empirically, by a comparison with a full-atom simulation).
- Internal motion is approximated by random forces so that (for $t \to \infty$), both the **Brownian motion** and **hydrodynamic behavior** is correct; particularly, the momentum is conserved.

# Dissipative particle dynamics (DPD)



Equations of motion

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




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

**D**issipation of velocity in the direction of $\hat{r}_{ij}$ ($\Rightarrow$ CoM conserved):

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

**R**andom force also acts in the direction of $\hat{r}_{ij}$:

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

The “fluctuation-dissipation theorem” is:

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

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

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

- $\omega$ (or $\omega_{ij}$) = short-ranged, e.g., $\omega^{\mathrm{R}}(r) = 1 - r/r_{\mathrm{cutoff}}$
- $r_{\mathrm{cutoff}} \approx$ the typical size of coarse-graining

# Kinetic quantities



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

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

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

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

**Methods:**

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

# Linear response theory: static perturbation



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

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

$$\begin{aligned}
\langle B\rangle' &= \frac{\int B \exp(-\beta\mathcal{H}')\mathrm{d}p\mathrm{d}q}{\int \exp(-\beta\mathcal{H}')\mathrm{d}p\mathrm{d}q} \approx \frac{\int B(t)\exp(-\beta\mathcal{H})(1-\beta\Delta\mathcal{H})\mathrm{d}p\mathrm{d}q}{\int \exp(-\beta\mathcal{H})(1-\beta\Delta\mathcal{H})\mathrm{d}p\mathrm{d}q} \\
&= \frac{\langle B\rangle - \beta\langle B\Delta\mathcal{H}\rangle}{1-\beta\langle\Delta\mathcal{H}\rangle} \approx (\langle B\rangle - \beta\langle B\Delta\mathcal{H}\rangle)(1+\beta\langle\Delta\mathcal{H}\rangle) \approx \langle B\rangle - \beta(\langle\Delta\mathcal{H}B\rangle - \langle\Delta\mathcal{H}\rangle\langle B\rangle) \\
&= \langle B\rangle - \beta\mathrm{Cov}(B,\Delta\mathcal{H}) \overset{\langle B\rangle=0}{=} -\beta\langle B\,\Delta\mathcal{H}\rangle
\end{aligned}$$

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

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

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

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

# Linear response theory: motivation (Green–Kubo)

MSD = mean squared deviation/displacement

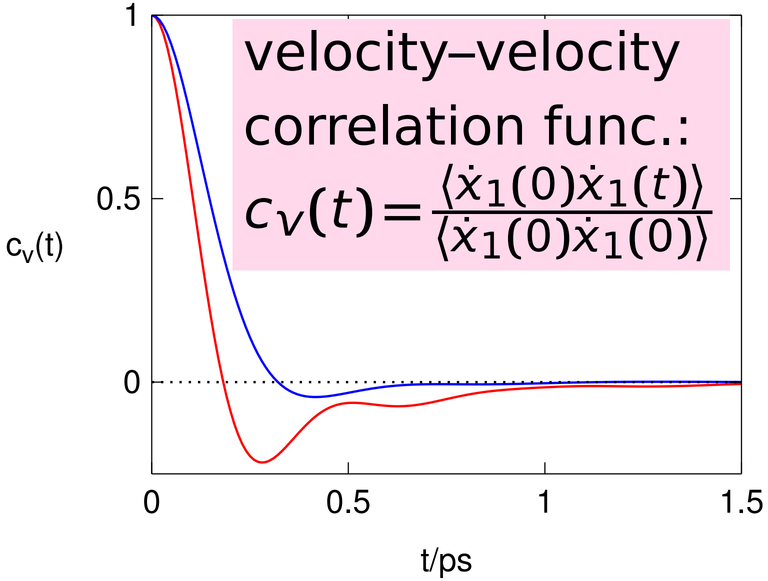
$$\langle a(t_1)b(t_2)\rangle = \langle a(t_1+\Delta t)b(t_2+\Delta t)\rangle$$

Diffusivity from MSD in 1D (Einstein):

$$\begin{aligned}
\langle x^2\rangle &= 2Dt \quad (t\to\infty)\\
D(t) &= \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\left\langle [x(t)-x(0)]^2\right\rangle = \langle [x(t)-x(0)]\dot x(t)\rangle\\
&= \left\langle \left[\int_0^t \dot x(t')\mathrm{d}t'\right]\dot x(t)\right\rangle = \left\langle \int_0^t \dot x(t')\dot x(t)\mathrm{d}t'\right\rangle \quad (\text{subst. } t'=t-t'')\\
&= -\int_t^0 \langle \dot x(t-t'')\dot x(t)\rangle \mathrm{d}t'' = \int_0^t \langle \dot x(0)\dot x(t'')\rangle \mathrm{d}t''
\end{aligned}$$

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

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




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.

# Linear response theory: principles



- We work in the Hamiltonian formalism (positions and momenta)
  preferably 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–Kubo formula in 3D):

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

Another example – viscosity:

$$\eta = \frac{V}{k_\mathrm{B}T}\int_0^\infty \langle P_{xy}(0) P_{xy}(t) \rangle \mathrm{d}t$$

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

# Linear response theory: time-dependent perturbation

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 $q \neq x_1$ a $A_p = 0$.

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

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

Stepwise change of the total energy by:

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

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

# Linear response theory

A perturbation (leading to a jump in $\mathcal{H}$) will be **turned off** (using a $\delta$-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:

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

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

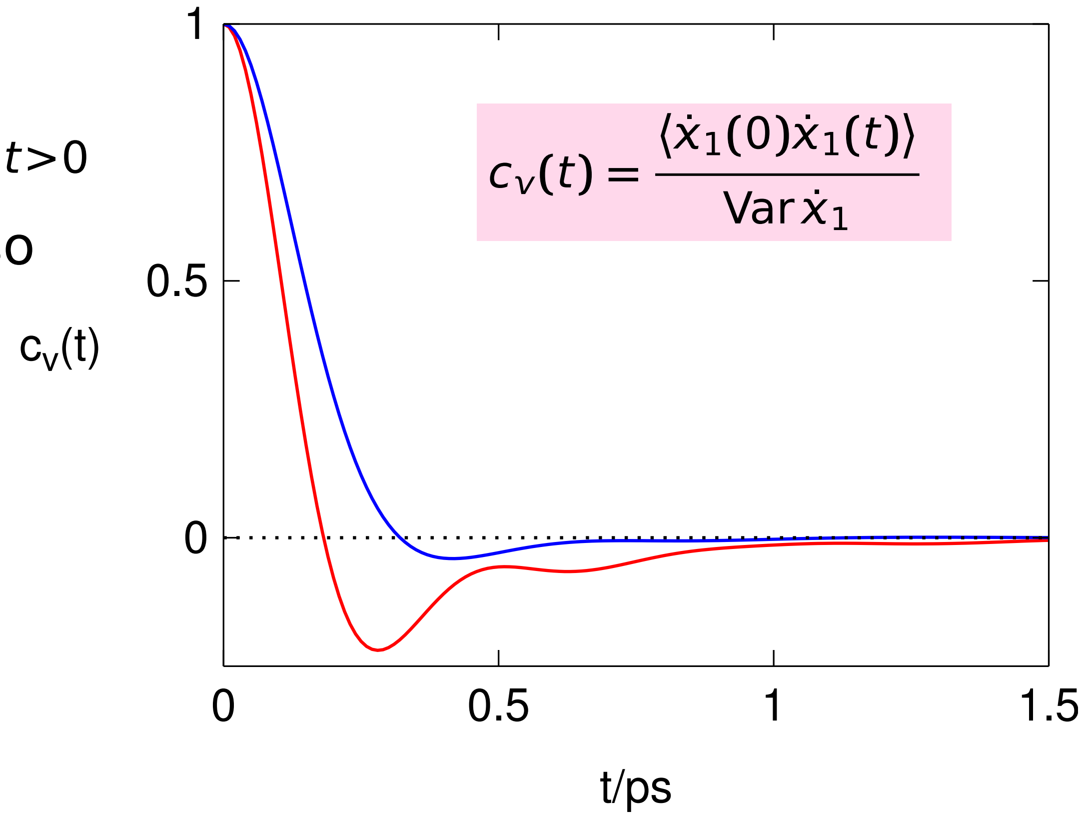
$$\langle B(t) \rangle_{A\delta(t)} = \beta \langle \dot{A}(0) B(t) \rangle_{t>0}$$

where the expectation value right is measured for $t > 0$ so that $\mathcal{H}_{t>0}$ has changed, but the distribution has not.

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

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

velocity relaxation folowing a hit
$\propto$ time correlation function velocity–velocity



# Linear response theory: Green–Kubo



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

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

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

**Example:**

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

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

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

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

# Green–Kubo → Einstein



- Einstein:

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

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

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

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

In the limit $t \to \infty$ then

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

E.g., for the diffusion:

- Green–Kubo $D = \dfrac{1}{3}\displaystyle\int_0^\infty \langle \dot{\vec r}_i(t)\cdot\dot{\vec r}_i(0)\rangle \mathrm{d}t$
- Einstein $2tD = \dfrac{1}{3}\langle|\vec r_i(t)-\vec r_i(0)|^2\rangle$

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

# Conductivity



- 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 $\vec{E} \to 0$.

- EMD – Green–Kubo:

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

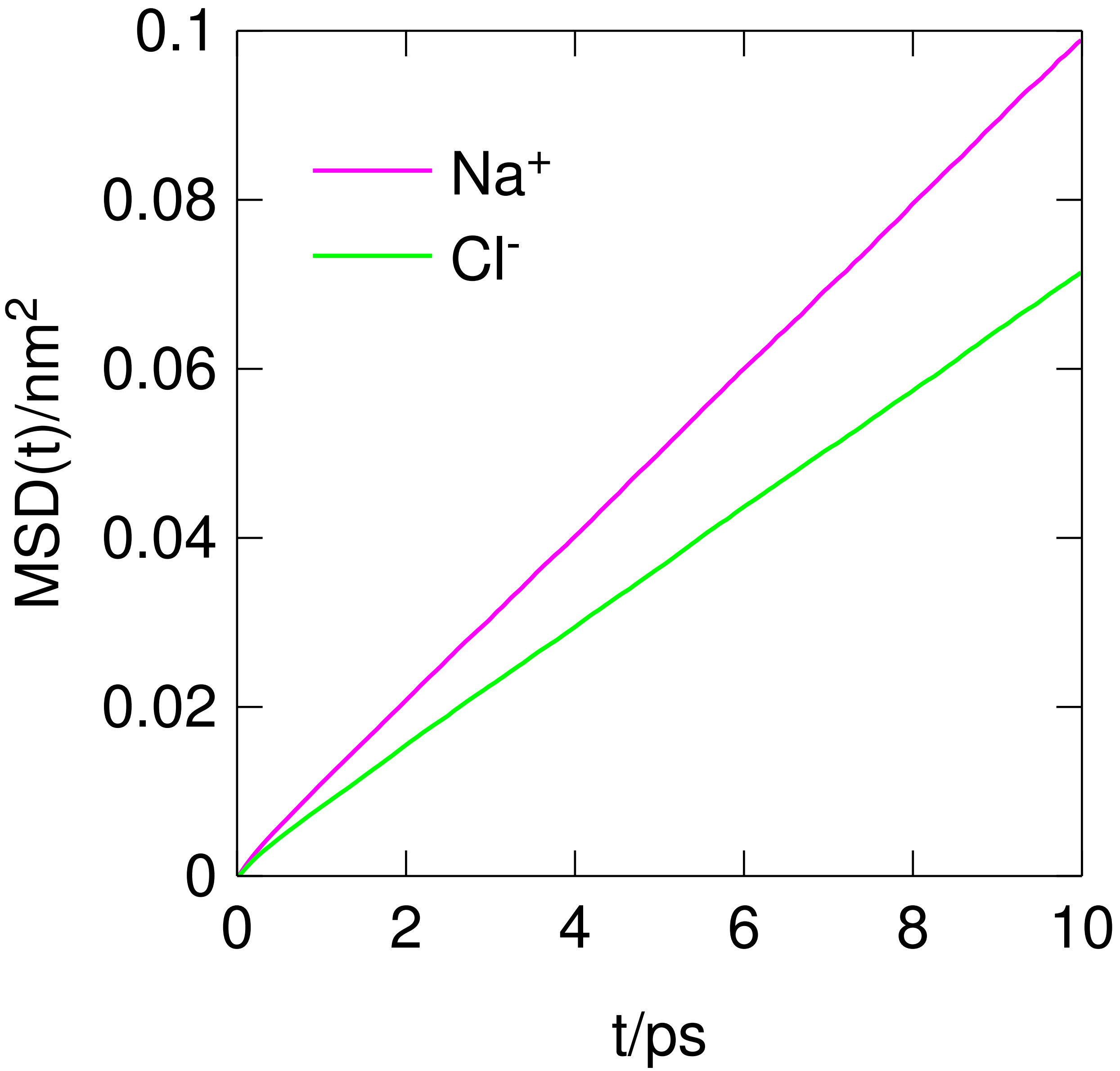
- EMD – Einstein

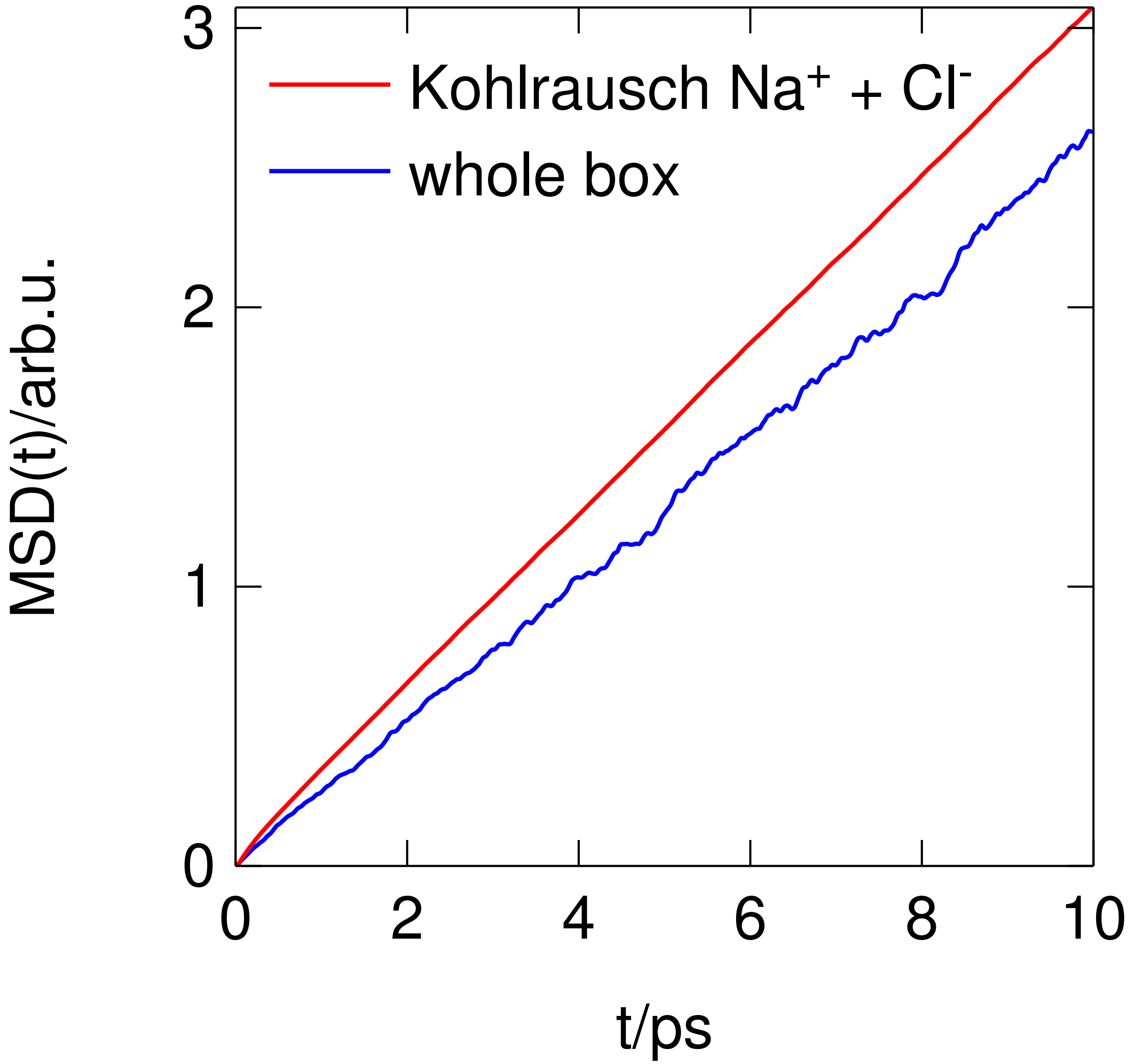
$$\kappa = \lim_{t\to\infty} \frac{\mathrm{d}}{\mathrm{d}t} \frac{1}{6 k_B T V} \left\langle \left\{ \sum_i q_i [\vec{r}_i(t) - \vec{r}_i(0)] \right\}^2 \right\rangle$$

NB: No Einstein relation for viscosity is known

# Using the Einstein formula

Conductivity of molten NaCl using EMD:



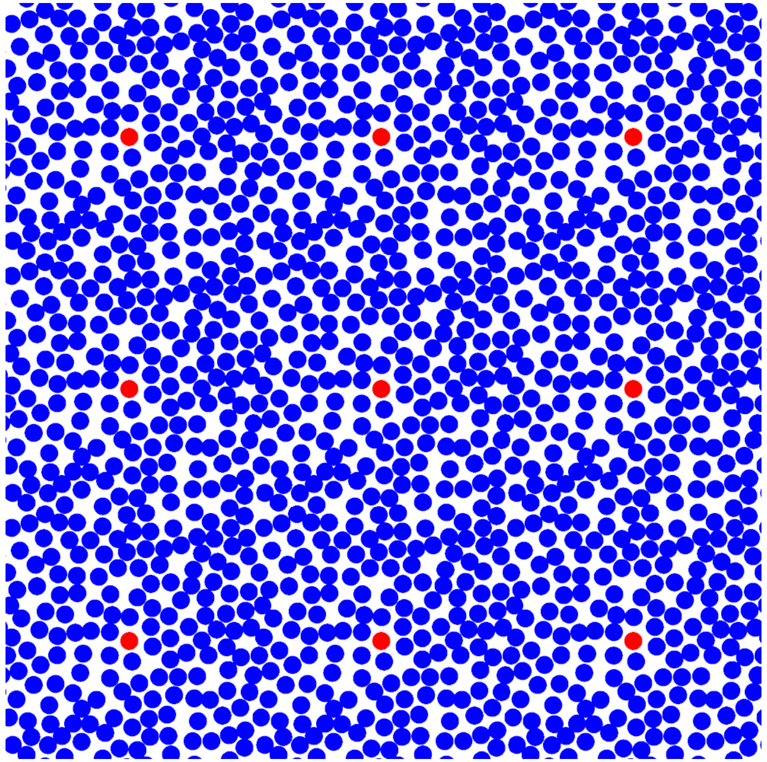



# Not so easy: corrections



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

Pure liquid in 3D:



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

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

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

- 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

Both viscosity and diffusivity can be obtained without extrapolation from one simulation in an orthorhombic box with $L_z/L_x = L_z/L_y = 2.79336$:

J. Busch and D. Paschek, J. Phys. Chem. B 2023, 127, 7983–7987

# 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.]

# EMD viscosity

Green–Kubo:

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

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

Curiously, also diagonal elements can be used*:

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

It is not so accurate. Recommended mixing:

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

⊕ : more accurate than NEMD

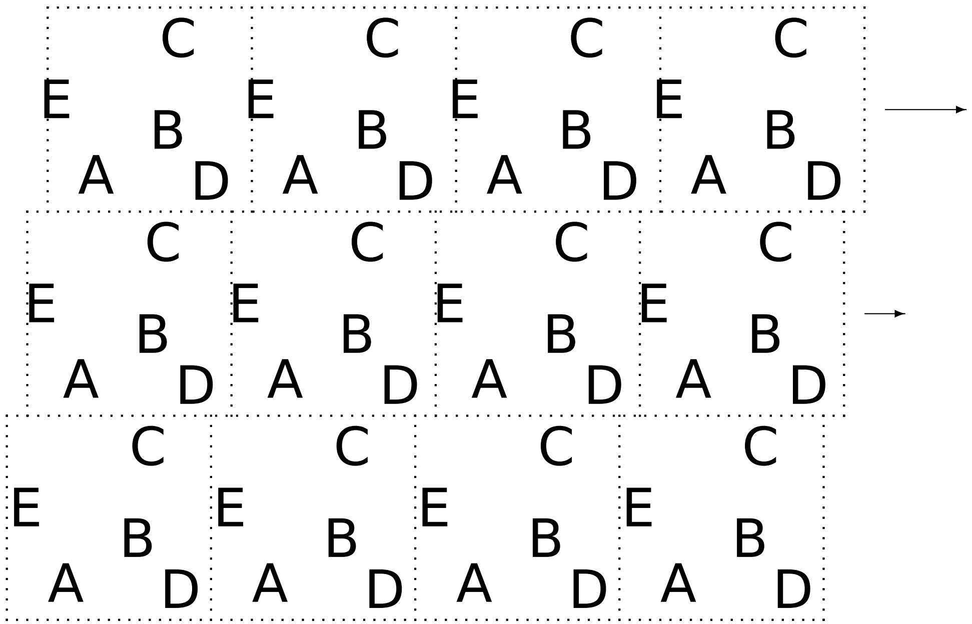
⊖ : $P_{ab}$ needed (sometimes problematic or not available)

*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)

# NEMD

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



# NEMD viscosity

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

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

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

- 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, $\eta$ is calculated from the velocity profile, $\int_0^{L_z} \vec{v}(z)\cdot\vec{n}\cos\left(\frac{2\pi z}{L_z}\right)\mathrm{d}z$

# NEMD viscosity

Dissipation of energy:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{1}{2}\int \eta(\nabla v)^2 \mathrm{d}V = \frac{V}{\eta}\left(\frac{C_f \rho L_z}{4\pi}\right)^2 .$$

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