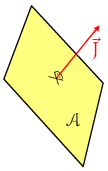
Transport phenomena

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

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

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: $\mathrm{mol\,m^{-2}\,s^{-1}}$)

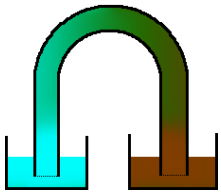
$$\vec{J}_i = -D_i \vec{\nabla} c_i$$

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:

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

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

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

Einstein–Stokes equation

Colloid particles or large spherical molecules of radius R_i in a solvent of viscosity η it holds (Stokes formula)

f_i

$$\vec{f}_i = 6\pi\eta R_i \vec{v}_i$$

Arrhenius law for viscosity (decreases with increasing T), diffusivity (increases with increasing T

⇒ Einstein–Stokes equation:

$$D_i = \frac{k_\mathrm{B}T}{f_i} \quad \Rightarrow \quad D_i = \frac{k_\mathrm{B}T}{6\pi\eta R_i}$$

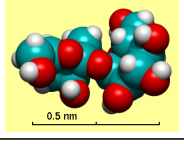
Opposite reasoning—hydrodynamic (Stokes) radius defined as:

$$R_i = \frac{k_\mathrm{B}T}{6\pi\eta D_i}$$

≈ effective molecule size (incl. solvation shell)

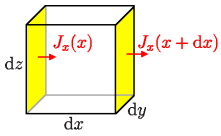
Example. Estimate the size of the sucrose molecule. Water viscosity is $0.891 \cdot 10^{-3}$ $\mathrm{m^{-1}\,kg\,s^{-1}}$ at 25 °C.

$R = 0.47$ nm



Second Fick Law

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



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

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

$$= -\sum_{x,y,z} \frac{\partial J_x}{\partial x}\mathrm{d}x\mathrm{d}y\mathrm{d}z = -\vec{\nabla}\cdot\vec{J}\,\mathrm{d}V = -\vec{\nabla}\cdot(-D\vec{\nabla}c)\,\mathrm{d}V$$

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

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

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

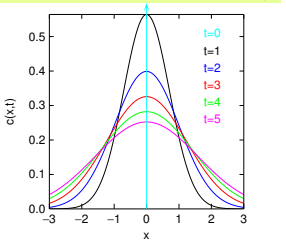
Diffusion and the Brownian motion

Let's solve the the 2nd Fick equation for the amount of matter n at time $t = 0$ at surface $x = 0$ of area $\mathcal{A}$ / in the origin.
We get the Gaussian distribution (see Maple):

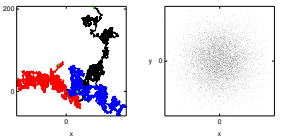
$$\text{1D:} \quad c(x,t) = \frac{n}{\mathcal{A}}(4\pi Dt)^{-1/2} \exp\left(-\frac{x^2}{4Dt}\right)$$

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

Reinterpretation: ∝ probability of finding a particle provided that at $t = 0$ at surface $x = 0$ / in point $\vec{r} = (0,0,0)$



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



Calculations in v Maple


```
> restart;
> assume(DD>0,t>0);
> c:=exp(-x^2/(4*DD*t))/sqrt(4*Pi*DD*t);
```

$$c := \frac{1}{2}\,\frac{e^{-\frac{1}{4}\frac{x^2}{DD\sim t\sim}}}{\sqrt{\pi\, DD\sim t\sim}}$$

normalization

```
> int(c,x=-infinity..infinity);
```

$$1$$

insert to the equation of heat conduction

```
> diff(c,t)-DD*diff(c,x,x);
```

$$\frac{1}{8}\,\frac{x^2 e^{-\frac{1}{4}\frac{x^2}{DD\sim t\sim}}}{DD\sim t\sim^2 \sqrt{\pi\, DD\sim t\sim}} - \frac{1}{4}\,\frac{e^{-\frac{1}{4}\frac{x^2}{DD\sim t\sim}}}{(\pi\, DD\sim t\sim)^{3/2}}\,\pi\, DD\sim - DD\sim\left(-\frac{1}{4}\,\frac{e^{-\frac{1}{4}\frac{x^2}{DD\sim t\sim}}}{DD\sim t\sim \sqrt{\pi\, DD\sim t\sim}} + \frac{1}{8}\,\frac{x^2 e^{-\frac{1}{4}\frac{x^2}{DD\sim t\sim}}}{DD\sim^2 t\sim^2 \sqrt{\pi\, DD\sim t\sim}}\right)$$

simplification ⇒ is valid

```
> simplify(%);
```

$$0$$

mean displacement $\langle x \rangle$ is zero

```
> int(c*x,x=-infinity..infinity);
```

$$0$$

mean squared displacement $\langle x^2 \rangle$

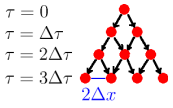
```
> int(c*x^2,x=-infinity..infinity);
```

$$2\, t\sim\, DD\sim$$

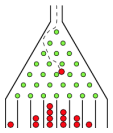
```
>
```

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: $\mathrm{Var}\, x = \langle x^2 \rangle = \Delta x^2$
- in n steps (in time $t = n\Delta t$): $\mathrm{Var}\, x = n\Delta x^2$
  ⇒ 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: $\mathrm{Var}\, x \overset{\mathrm{def.}}{=} \langle (x - \langle x \rangle)^2 \rangle$, 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 $(-1, 1)$

9/1

Central limit theorem

Derivation using the **Central limit theorem**:

- in one step: $\mathrm{Var}\, x \overset{\langle x \rangle = 0}{=} \langle x^2 \rangle = \Delta x^2$
- in n steps (in time $t = n\Delta t$): $\mathrm{Var}\, x = n\Delta x^2$
  ⇒ Gauss normal distribution with $\sigma = \sqrt{n\Delta x^2} = \sqrt{t/\Delta t}\Delta x$, i.e.

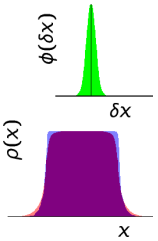
$$\frac{1}{\sqrt{2\pi}\sigma} e^{-x^2/2\sigma^2} = \frac{1}{\sqrt{2\pi t}}\frac{\sqrt{\Delta t}}{\Delta x} \exp\left[-\frac{-x^2}{2t}\frac{\Delta t}{\Delta x^2}\right]$$

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

Einstein derivation

Random walk in one variable:
$\phi(\delta x)$ = probability density of a particle traveling by δx in time δt

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



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

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

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

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

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

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

Langevin equation

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

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

$$m\ddot{x} = f - \not{f}\dot{x} + X(t)$$

- f = "normal" (conservative) force – for now $f = 0$
- $\not{f}$ = friction coefficient; spheres: $\not{f} = n\pi\eta R$ (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:

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

$$\begin{aligned} m\ddot{x}x &= -\not{f}\dot{x}x + Xx \\ \frac{m}{2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}(x^2) - m\dot{x}^2 &= -\frac{\not{f}}{2}\frac{\mathrm{d}}{\mathrm{d}t}(x^2) + Xx \end{aligned}$$

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

$$\frac{m}{2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle x^2\rangle - k_\mathrm{B}T = -\frac{\not{f}}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle$$

Langevin equation

$$\frac{m}{2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle x^2\rangle - k_\mathrm{B}T = -\frac{\not{f}}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle$$

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

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle = \frac{2k_\mathrm{B}T}{\not{f}} + C\,\mathrm{e}^{-\not{f}t/m} \overset{t\to\infty}{=} 2\frac{k_\mathrm{B}T}{\not{f}}$$

after integration

$$\not{f}t\langle x^2\rangle = \frac{2k_\mathrm{B}T}{\not{f}}t + \frac{Cm}{\not{f}}[1 - \mathrm{e}^{-\not{f}t/m}]$$

At long t (neglecting the initial transient)

$$\langle x^2\rangle = 2Dt, \quad \text{where } D = \frac{k_\mathrm{B}T}{\not{f}}$$

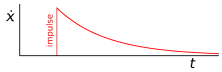
This is the Einstein–Smoluchowski equation to predict D from $\not{f}$ at given T

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

Fluctuation-dissipation theorem

Langevin equation for $f = 0$:

$$\ddot{x} = -\frac{\not{f}}{m}\dot{x} + \frac{1}{m}X(t)$$



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:

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

We want T! The expected kinetic energy:

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

$$\langle m\dot{x}^2\rangle = k_\mathrm{B}T \quad \Rightarrow \quad A = 2\not{f}k_\mathrm{B}T = \frac{2(k_\mathrm{B}T)^2}{D}$$

Langevin thermostat and Brownian dynamics

simolant -N20 -Ptau=1,rho=0.01

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)

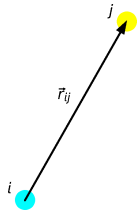
Good for coarse-grained models:

- Groups of atoms (e.g., 4 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 are correct; particularly, the momentum is conserved.

Dissipative particle dynamics (DPD)

Equations of motion

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



where $\vec{f}_{ij}^\mathrm{C}$ is a **C**onservative pair force.
Dissipation of velocity in the direction of $\hat{r}_{ij}$ ($\Rightarrow$ CoM conserved):

$$\vec{f}_{ij}^\mathrm{D} = -\not{f}\omega^\mathrm{D}(r_{ij})(\vec{v}_{ij}\cdot\hat{r}_{ij})\hat{r}_{ij}, \quad \hat{r}_{ij} = \frac{\vec{r}_{ij}}{r_{ij}}$$

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

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

The "fluctuation-dissipation theorem" is:

$$\omega^\mathrm{D} = [\omega^\mathrm{R}]^2, \quad \sigma = 2k_\mathrm{B}T\not{f}$$

- $\xi = \xi(t)$ = normalized Gaussian force, $\langle\xi(0)\xi(t)\rangle = \delta(t)$ $\quad [\xi] = \mathrm{s}^{-1/2}$
- ω (or ω_{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:

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

$$\vec{J}_\text{heat} = -\not{f}\vec{\nabla}T$$

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

Methods:

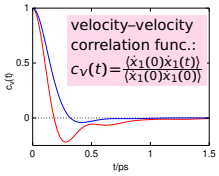
- EMD (*equilibrium molecular dynamics*), simulation in equilibrium
  e.g., $D_i = \lim_{t\to\infty}\langle[r_i(t) - r_i(0)]^2\rangle/6t$
- NEMD (*non-equilibrium molecular dynamics*), simulation under an external force or perturbation

Linear response theory: motivation (Green–Kubo)

Diffusivity from MSD in 1D (Einstein):

MSD = mean squared deviation/displacement
$\langle a(t_1)b(t_2)\rangle = \langle a(t_1+\Delta t)b(t_2+\Delta t)\rangle$

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



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: static perturbation

- 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)

$\beta = \frac{1}{k_\mathrm{B}T}$

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

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:

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

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:

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

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

Linear response theory

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:

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

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

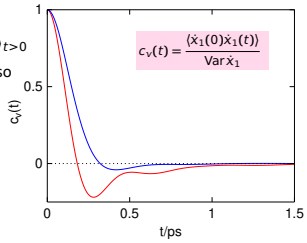
$$\langle B(t)\rangle_{A\delta(t)} = \beta\langle\dot{A}(0)\,B(t)\rangle_{t>0}$$

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: $A(t) =$ 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:

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

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

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

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

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

$$\Lambda_1^\infty = \frac{\langle\dot{x}q_1N_A\rangle}{E_x} = \frac{q_1^2D_1}{RT}$$

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 $D = \frac{1}{3}\int_0^\infty\langle\vec{r}_i(t)\cdot\vec{r}_i(0)\rangle\mathrm{d}t$
- 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, $D_i = k_\mathrm{B}T\langle v_i\rangle/\mathcal{F}_i$, 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:

$$\kappa = \frac{V}{3k_\mathrm{B}T}\int_0^\infty\langle\vec{j}(t)\cdot\vec{j}(0)\rangle$$

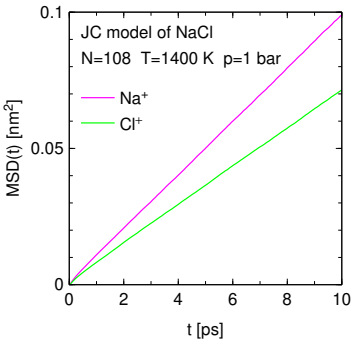
- EMD – Einstein

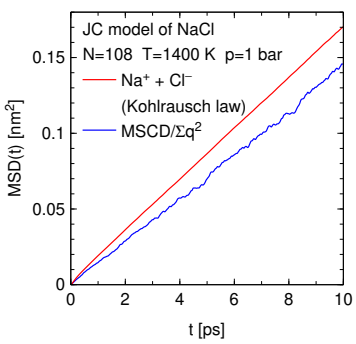
$$\kappa = \lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{6k_\mathrm{B}TV}\left\langle\left\{\sum_i q_i[\vec{r}_i(t)-\vec{r}_i(0)]\right\}^2\right\rangle$$

NB: No Einstein relation for viscosity is known

Using the Einstein formula

Conductivity of molten NaCl using EMD, trajectory 1 ns, overlapping blocks 10 ps long:





Not so easy: corrections

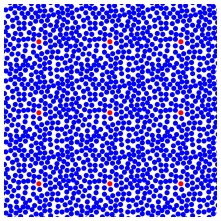
The periodic image of a particle is L far away and diffusing always in the same direction!

Pure liquid in 3D:

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

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

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*:

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

It is not so accurate. Recommended mixing:

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

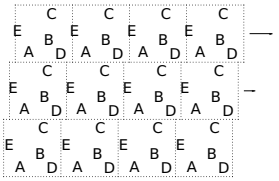
⊕ : more accurate than NEMD
⊖ : P_{ab} needed (sometimes problematic or not available)

*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:
  - SLLOD (Lees-Edwards)
  - transfer of momentum
  - cos-modulated force



NEMD viscosity

- 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

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

- correction so that total force = 0

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

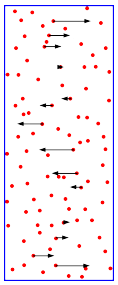
$$\eta\nabla^2\vec{v} + \vec{f} = 0, \qquad (1)$$

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

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

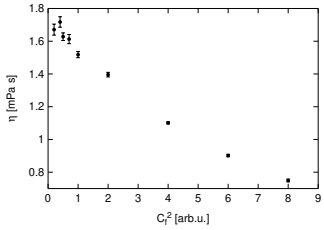
$$\vec{v} = \frac{C_f\rho L_z^2}{4\pi^2\eta}\cos\left(\frac{2\pi z}{L_z}\right)\vec{n}$$

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



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 η from the dissipation (less accurate)
- one can estimate how the cooling constant of a thermostat
- extrapolation $C_f \to 0$ needed
- less accurate than Green–Kubo
- pressure tensor not needed