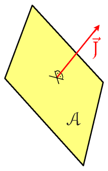
Transport phenomena

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

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

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**

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

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:

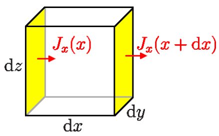
$$\vec{\mathcal{F}}_i^\mathrm{fr} + \vec{\mathcal{F}}_i = 0 \quad \text{i.e.} \quad -\vec{\mathcal{F}}_i^\mathrm{fr} = f_i\vec{v}_i = f_i\frac{\vec{J}_i}{c_i} = \vec{\mathcal{F}}_i = -\frac{k_\mathrm{B}T}{c_i}\vec{\nabla}c_i$$

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

(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 $\mathrm{d}V = \mathrm{d}x\mathrm{d}y\mathrm{d}z$:



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

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

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

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

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

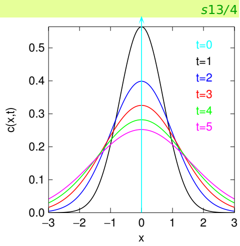
This type of equation is called "equation of heat conduction". It is a parabolic partial differential equation

Diffusion and the Brownian motion

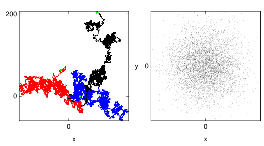
Instead of for $c(\vec{r},t)$, let us solve the 2nd Fick law for the probability of finding a particle, starting from origin at $t=0$. We get the **Gaussian distribution** with half-width ∝

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

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

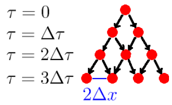


- 1D: $\langle x^2\rangle = 2Dt$
- 3D: $\langle r^2\rangle = 6Dt$

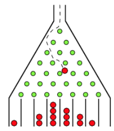


Brownian motion as a random walk

(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: $\mathrm{Var}\,x = \langle x^2\rangle = \Delta x^2$
- 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: $\mathrm{Var}\,x \overset{\text{def.}}{=} \langle(x-\langle x\rangle)^2\rangle$, 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 $(-1,1)$

9/τ

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

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

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:

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

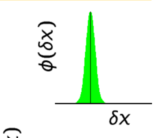
Again $\Delta x = (2D\Delta\tau)^{1/2}$, $k = x/\Delta x = x/(2D\Delta\tau)^{1/2}$, $n = t/(2\Delta\tau)$:

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

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

Einstein derivation

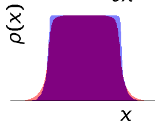
Random walk in one variable:
$\phi(\delta x)$ = probability density of a particle traveling by δx in time δt



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

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

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

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

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

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

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

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

Langevin equation

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

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

$$\frac{d}{dt}\langle x^2\rangle = \frac{2k_BT}{f} + C\,e^{-ft/m} \stackrel{t\to\infty}{=} 2\frac{k_BT}{f}$$

after integration

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

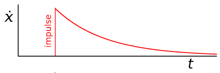
At long t (neglecting the initial transient)

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

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:

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

We want T! The expected kinetic energy:

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

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

$$\langle m\dot{x}^2\rangle = k_BT \quad\Rightarrow\quad A = 2fk_BT = \frac{2(k_BT)^2}{D}$$

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.

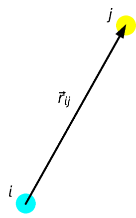
- As a thermostat: All degrees of freedom are sampled (also the momentum in the periodic b.c.)
- Momentum and center of mass not conserved
- As Brownian dynamics: kinetic model of implicit solvent

Dissipative particle dynamics (DPD)

Good for coarse-grained models:

- Groups of atoms (e.g., 4 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

$$m\ddot{\vec{r}}_i = \sum_{j\neq i}\left(\vec{f}^C_{ij} + \vec{f}^D_{ij} + \vec{f}^R_{ij}\right)$$

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

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

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

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

The "fluctuation-dissipation theorem" is:

$$\omega^D = [\omega^R]^2,\quad \sigma = 2k_BTf$$

- $\xi = \xi(t)$ = normalized Gaussian force, $\langle\xi(0)\xi(t)\rangle = \delta(t)$ $\qquad [\xi] = s^{-1/2}$
- ω (or ω_{ij}) = short-ranged, e.g., $\omega^R(r) = 1 - r/r_{cutoff}$
- $r_{cutoff} \approx$ the typical size of coarse-graining

Kinetic quantities

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

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

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

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

Methods:

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

Linear response theory: static perturbation

- 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) $\qquad \beta = \frac{1}{k_BT}$

$$\langle B\rangle' = \frac{\int B\exp(-\beta\mathcal{H}')dpdq}{\int\exp(-\beta\mathcal{H}')dpdq} \approx \frac{\int B(t)\exp(-\beta\mathcal{H})(1-\beta\Delta\mathcal{H})dpdq}{\int\exp(-\beta\mathcal{H})(1-\beta\Delta\mathcal{H})dpdq}$$

$$= \frac{\langle B\rangle - \beta\langle B\Delta\mathcal{H}\rangle}{1-\beta\langle\Delta\mathcal{H}\rangle} \approx (\langle B\rangle - \beta\langle B\Delta\mathcal{H}\rangle)(1+\beta\langle\Delta\mathcal{H}\rangle) \approx \langle B\rangle - \beta(\langle\Delta\mathcal{H}B\rangle - \langle\Delta\mathcal{H}\rangle\langle B\rangle)$$

$$= \langle B\rangle - \beta\,\mathrm{Cov}(B,\Delta\mathcal{H}) \stackrel{\langle B\rangle=0}{=} -\beta\langle B\,\Delta\mathcal{H}\rangle$$

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:

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

Linear response theory: motivation (Green–Kubo)

MSD = mean squared deviation/displacement

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

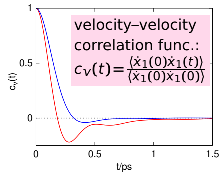
Diffusivity from MSD in 1D (Einstein):

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

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

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

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



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

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

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.

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):

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

Another example – viscosity:

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

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

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: $A = \mathcal{F}_1x_1$ 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:

$$\mathcal{H}_{t>0} - \mathcal{H}_{t<0} = \mathcal{H}(q-A_p, p+A_q) - \mathcal{H}(q,p)$$

$$= \sum\left(-\frac{\partial\mathcal{H}}{\partial q}A_p + \frac{\partial\mathcal{H}}{\partial p}A_q\right) = \sum(\dot{p}\cdot A_p + \dot{q}\cdot A_q) \equiv \dot{A}(0)$$

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:

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

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

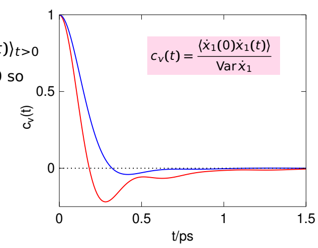
$$\langle B(t)\rangle_{A\delta(t)} = \beta\langle\dot{A}(0)B(t)\rangle_{t>0}$$

where the expectation value right is measured for $t>0$ 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
∝ time correlation function velocity–velocity



Linear response theory: Green–Kubo

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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

$$u_1 = \frac{\langle \dot x_1\rangle}{E_x} = \frac{q_1 D_1}{k_B T}$$

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

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

Green–Kubo → Einstein

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- 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, $D_i = k_B T \langle v_i\rangle/\mathcal{F}_i$, calculate limit $\mathcal{F}_i \to 0$

Conductivity

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- 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

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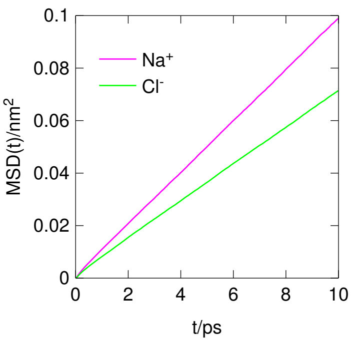
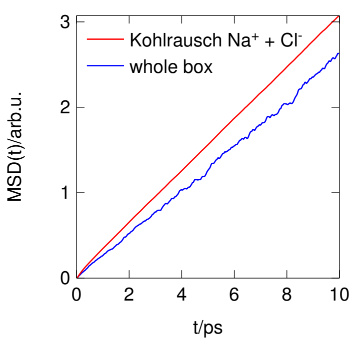
Conductivity of molten NaCl using EMD:





Not so easy: corrections

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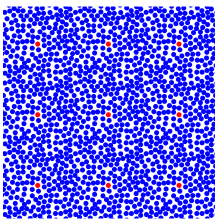
The periodic image of a particle is L far away and diffusing always in the same direction!

Pure liquid in 3D:

$$D = D_{\rm PBC} + \frac{2.873 k_B T}{6\pi\eta L}$$

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

where $R = k_B T/6\pi\eta D$



- 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

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```
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

pol4d/Ptxy.sh 27/30 s13/4

Green–Kubo:

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

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

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

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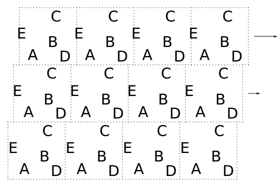
NEMD = Non-equilibrium molecular dynamics

- 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

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- 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:

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

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

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

pol4d/shear.sh 30/30 s13/4

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 (e.g., Berendsen)
- extrapolation $C_f \to 0$ needed
- (−) less accurate than Green–Kubo
- (+) pressure tensor not needed