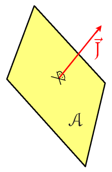
Transport phenomena

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

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

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

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

Diffusion—microscopic view

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

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

Thermodynamic force = −grad of the chemical potential:

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

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

where formula $\mu_i = \mu_i^\ominus + RT\ln(c_i/c^\mathrm{st})$ 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:

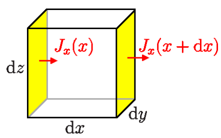
$$\vec{\mathcal{F}}_i^\mathrm{fr} + \vec{\mathcal{F}}_i = 0 \quad \text{i.e.} \quad -\vec{\mathcal{F}}_i^\mathrm{fr} = f_i \vec{v}_i = f_i \frac{\vec{J}_i}{c_i} = \vec{\mathcal{F}}_i = -\frac{k_\mathrm{B}T}{c_i}\vec{\nabla} c_i$$

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



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

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

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

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

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

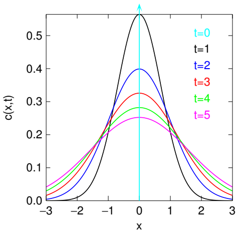
This type of equation is called "equation of heat conduction". It is a parabolic partial differential equation

Diffusion and the Brownian motion

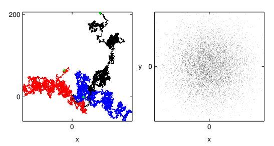
Instead of for $c(\vec{r},t)$, let us solve the 2nd Fick law for the probability of finding a particle, starting from origin at $t=0$. We get the **Gaussian distribution** with half-width ∝

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

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

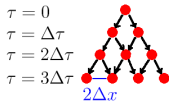


- 1D: $\langle x^2\rangle = 2Dt$
- 3D: $\langle r^2\rangle = 6Dt$



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 $\sigma = \sqrt{n\Delta x^2} = \sqrt{t/\Delta t}\,\Delta x$:

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

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 $(-1,1)$

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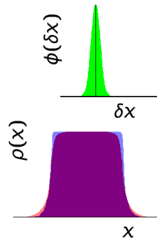
Einstein derivation

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 can be neglected):

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

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

Langevin equation

A (colloid) particle in a viscous environment + random hits: $\dot{x} \equiv \mathrm{d}x/\mathrm{d}t$

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

- f = "normal" (conservative) force – for now $f = 0$
- $\mathfrak{f}$ = friction coefficient; spheres: $\mathfrak{f} = n\pi\eta R$ (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: $\mathrm{d}^2(\frac{1}{2}x^2)/\mathrm{d}t^2 = \mathrm{d}(\dot{x}x)/\mathrm{d}t$

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

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

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

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

Langevin equation

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

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

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

after integration

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

At long t (neglecting the initial transient)

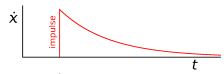
$$\langle x^2\rangle = 2Dt, \quad \text{where } D = \frac{k_\mathrm{B}T}{\mathfrak{f}}$$

This is the Einstein–Smoluchowski equation to predict D from $\mathfrak{f}$ at given T

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

Fluctuation-dissipation theorem

Langevin equation for $f = 0$:



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

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:

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

We want T! The expected kinetic energy:

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

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

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

Langevin thermostat and Brownian dynamics

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

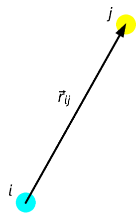
Good for coarse-grained models:

- Groups of atoms (e.g., $4\,H_2O$, 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):

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

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, $\langle\xi(0)\xi(t)\rangle = \delta(t)$ — $[\xi] = s^{-1/2}$
- 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) — $\beta = \dfrac{1}{k_BT}$

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

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

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

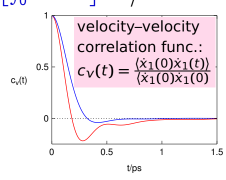
which is correct, because the potential minimum was actually only shifted:

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

Linear response theory: motivation (Green–Kubo)

Diffusivity from MSD in 1D (Einstein): — MSD = mean squared deviation/displacement

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



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), 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):

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

Another example – viscosity:

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

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: $A = \mathcal{F}_1x_1$ čili $A_{x_1} = \mathcal{F}_1$, $A_q = 0$ 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

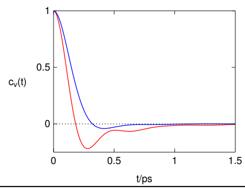
$$\langle B(t)\rangle_{A\delta(t)} = \beta\langle\dot A(0)B(t)\rangle_{t>0}$$

where the expectation value right is over the final system with energy $\mathcal{H}_{t>0}$ (canonical unperturbed):

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 folowing a hit
∝
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 $\mathcal{F}_1 = E_xq_1$ we get the ionic mobility

$$u_1 = \frac{\langle\dot x_1\rangle}{E_x} = \frac{q_1D_1}{k_BT}$$

and after multiplicating by a 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 ⇒

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

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, $D_i = k_BT\langle v_i\rangle/\mathcal{F}_i$, 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 os measured:

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

Cooling is needed (thermostat) and extrapolation $\vec{E} \to 0$

- Green–Kubo:

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

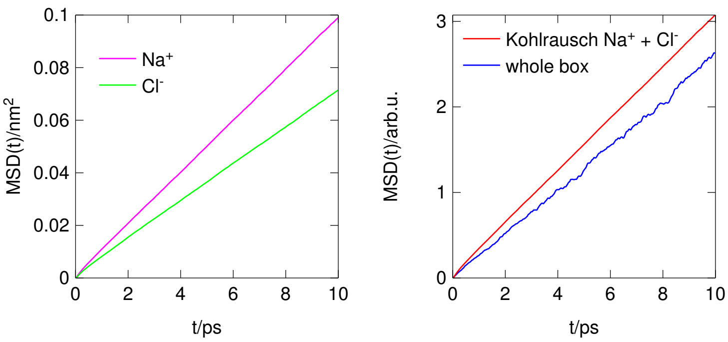
- Einstein

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

NB: No Einstein relation for viscosity is known

Using the Einstein formula

Conductivity of molten NaCl using EMD:



Not so easy: corrections

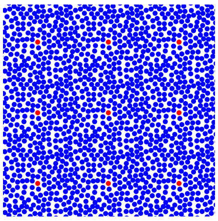
Pure liquid in 3D:

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

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

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

- 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)
```

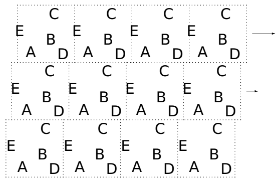
```
SPCE water
^^^^^^^^^^
T=298.15 K

==================================
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

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



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 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:

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

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

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