

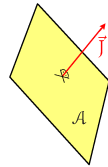
## Transport phenomena

1/30  
s13/4

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

● Flux\* of mass, charge, momentum, heat, ...

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



● Cause = (generalized, thermodynamic) force

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

● Small forces—linearity

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

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

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

## Diffusion—macroscopic view

2/30  
s13/4

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

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

is proportional to the **concentration gradient**

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

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

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

## Diffusion—microscopic view

3/30  
s13/4

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

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

Thermodynamic force =  $-$ grad of the chemical potential:

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

where formula  $\mu_i = \mu_i^\circ + RT \ln(c_i/c^\circ)$  for infinity dilution was used.

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

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

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

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

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

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

## Second Fick Law

4/30  
s13/4

Non-stationary phenomenon ( $c$  changes with time).

The amount of substance increases within time  $dt$  in volume  $dV = dx dy dz$ :

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

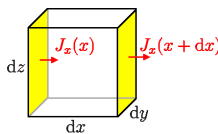
$$= \sum_{x,y,z} [J_x(x) - J_x(x) + \frac{\partial J_x}{\partial x} dx] dy dz$$

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

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

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

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



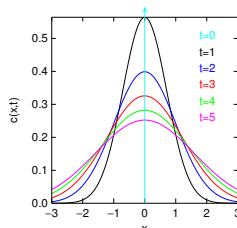
## Diffusion and the Brownian motion

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s13/4

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  $\propto$

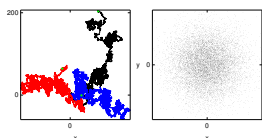
$$1D: c(x, t) = (4\pi Dt)^{-1/2} \exp\left(-\frac{x^2}{4Dt}\right)$$

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



● 1D:  $\langle x^2 \rangle = 2Dt$

● 3D:  $\langle r^2 \rangle = 6Dt$

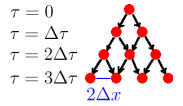


## Brownian motion as a random walk

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s13/4

(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:  $\text{Var } x = \langle x^2 \rangle = \Delta x^2$

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

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

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

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

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

9/1

## You do not know the central limit theorem?

+ 7/30  
s13/4

● during time  $2\Delta\tau$  a walker moves

- by  $2\Delta x$  with probability  $1/4$
- by  $-2\Delta x$  with probability  $1/4$
- by  $0$  with probability  $1/2$

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

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

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

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

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

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

## Brownian motion as random walk III

+ 8/30  
s13/4

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

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

Now let us replace the sum by an integral:

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

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

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

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

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

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

## Einstein derivation

+ 9/30  
s13/4

Random walk in one variable:

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

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

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

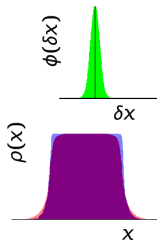
$$\rho(x, t + \delta t) = \int_{-\infty}^{+\infty} \rho(x + \delta x, t) \phi(\delta x) d\delta x$$

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

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

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

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



## Langevin equation

10/30  
s13/4

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

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

●  $f$  = "normal" (conservative) force - for now  $f = 0$

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

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

Multiply by  $x$  and rearrange:

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

$$\begin{aligned} m\ddot{x}x &= -f\dot{x}x + Xx \\ \frac{m}{2} \frac{d^2}{dt^2}(x^2) - m\dot{x}^2 &= -\frac{f}{2} \frac{d}{dt}(x^2) + Xx \end{aligned}$$

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

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

### Langevin equation

11/30 s13/4

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

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

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

after integration

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

At long  $t$  (neglecting the initial transient)

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

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

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

### Linear response theory: static perturbation

16/30 s13/4

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

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

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

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

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

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

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

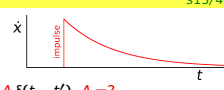
which is correct, because the potential minimum was actually only shifted:

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

### Fluctuation-dissipation theorem

12/30 s13/4

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:

$$\dot{x}(t) = \dot{x}(0) e^{-\frac{f}{m}t} + \frac{1}{m} \int_0^t X(t') e^{-\frac{f}{m}(t-t')} dt'$$

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

We want  $T$ ! The expected kinetic energy:

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

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

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

### Linear response theory: motivation (Green-Kubo)

17/30 s13/4

Diffusivity from MSD in 1D (Einstein):

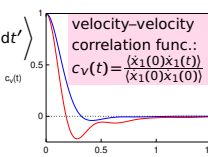
$$\langle x^2 \rangle = 2Dt \quad (t \rightarrow \infty)$$

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

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

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

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

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


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

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

### Langevin thermostat and Brownian dynamics

13/30 s13/4

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<sub>2</sub>O, bead in a polymer) are replaced by a superparticle. Its properties are adjusted (empirically, by a comparison with a full-atom simulation).
- Internal motion is approximated by random forces so that (for  $t \rightarrow \infty$ ), both the **Brownian motion** and **hydrodynamic behavior** is correct; particularly, the momentum is conserved.

### Linear response theory: principles

18/30 s13/4

- 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):

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

Another example – viscosity:

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

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

### Dissipative particle dynamics (DPD)

14/30 s13/4

Equations of motion

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

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

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

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

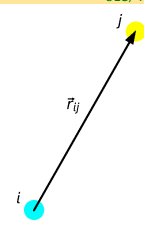
Random force also acts in the direction of  $\hat{r}_{ij}$ :

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

The “fluctuation-dissipation theorem” is:

$$\omega^D = [\omega^R]^2, \quad \sigma = 2k_B T f$$

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



### Linear response theory: time-dependent perturbation

19/30 s13/4

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  $A_p = 0$ .

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

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

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

### Kinetic quantities

15/30 s13/4

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

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

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

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

**Methods:**

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

### Linear response theory

20/30 s13/4

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:

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

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

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

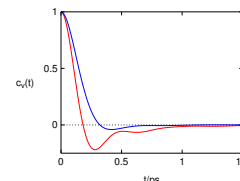
where the expectation value right is measured for  $t > 0$  the energy  $\mathcal{H}_{t>0}$  changed, but the distribution did not

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

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

velocity relaxation following a hit

$\propto$  time correlation function velocity-velocity



### Linear response theory: Green-Kubo

21/30  
s13/4

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

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

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

**Example:**

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

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

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

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

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

$$\Lambda_1^\infty = \frac{\langle \dot{x}_1 q_1 N_A \rangle}{E_x} = \frac{q_1^2 D_1}{RT}$$

### Not so easy: corrections

+ 26/30  
s13/4

Ar

EvdW=0.2380684 kcal/mol, RvdW=1.91992 AA  
T=143.76 (T=1.2)  
rho=1344.2582 kg/m3 (rho=0.8)

SPE water  
T=298.15 K

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

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)

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.]

### Green-Kubo → Einstein

22/30  
s13/4

● Einstein:

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

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

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

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

In the limit  $t \rightarrow \infty$  then

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

E.g., for the diffusion:

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

● Einstein  $2tD = \langle [r_i(t) - r_i(0)]^2 \rangle$

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

### NEMD

27/30  
s13/4

NEMD = Non-equilibrium molecular dynamics

● as a real experiment (turn on a field, gradient of temperature, ...)

● problem: linearity (extrapolation to zero perturbation)

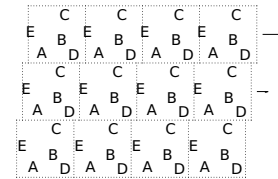
● problem: cooling needed

● viscosity:

- SLODD (Lees-Edwards)

- transfer of momentum

- cos-modulated force



### Conductivity

23/30  
s13/4

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

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

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

● Green-Kubo:

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

● Einstein

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

NB: No Einstein relation for viscosity is known

### EMD viscosity

[pol4d/Ptxy.sh] 28/30  
s13/4

Green-Kubo:

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

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

Curiously, also diagonal elements can be used\*:

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

It is not so accurate. Recommended mixing:

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

⊕ : more accurate than NEMD

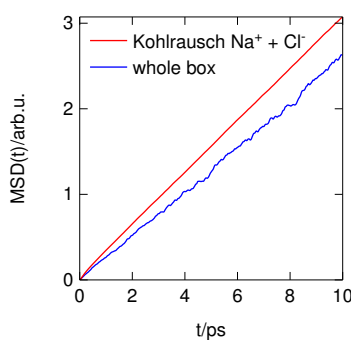
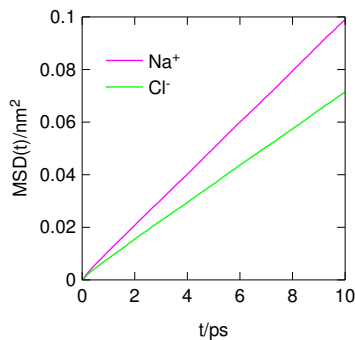
⊖ :  $P_{ab}$  needed (sometimes problematic or not available)

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

### Using the Einstein formula

24/30  
s13/4

Conductivity of molten NaCl using EMD:



### NEMD viscosity

29/30  
s13/4

● 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:

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

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

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

### Not so easy: corrections

25/30  
s13/4

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

Pure liquid in 3D:

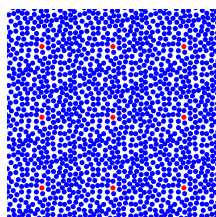
$$D = D_{\text{PBC}} + \frac{2.873 k_B T}{6\pi \eta L}$$

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

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.

### NEMD viscosity

[pol4d/shear.sh] 30/30  
s13/4

Dissipation of energy:

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

● one can also determine  $\eta$  from the dissipation (less accurate)

● one can estimate how the cooling constant of a thermostat (e.g., Berendsen)

● extrapolation  $C_f \rightarrow 0$  needed

● less accurate than Green-Kubo

⊕ pressure tensor not needed

