

## Diffusivity - Einstein Relationship

Fick's law of diffusion (macroscopic)

$$\vec{j} = -D \nabla c \quad (1)$$

flux                  Diffusion coefficient                  Concentration ( $\nabla$  should be  $\nabla \mu$ )

Particularly simple version of Fick's Law for self-diffusion of a "tagged" molecule:  $\nabla c \propto \nabla \mu$

Conservation of mass: 
$$\frac{\partial c(r,t)}{\partial t} + \nabla \cdot \vec{j}(r,t) = 0 \quad (2)$$

Combining (1) + (2): 
$$\frac{\partial c(r,t)}{\partial t} - D \nabla^2 c(r,t) = 0 \quad (3)$$

Let's assume initial condition  $c(r,0) = \delta(r)$

"Spike" at origin

Solving (3) gives:

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

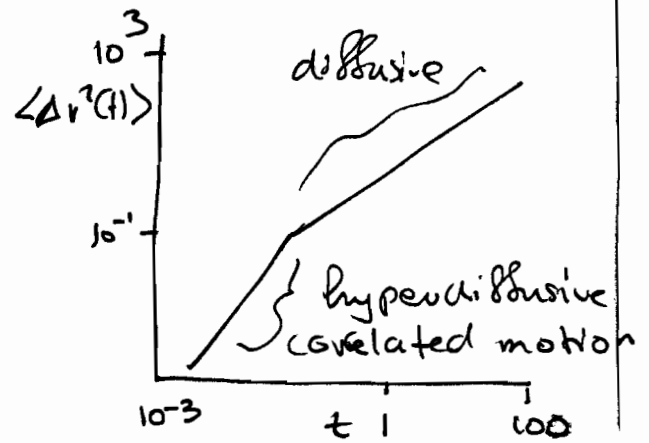
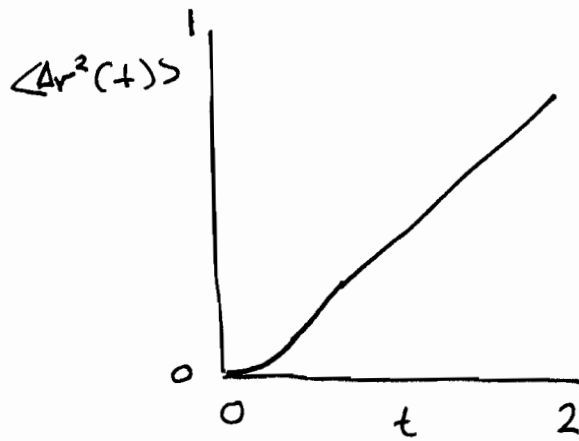
$d$ : dimensionality of space

The mean-square displacement can be obtained from (3):

$$\frac{\partial}{\partial t} \int d\vec{r} r^2 c(r,t) = D \int d\vec{v} r^2 \nabla^2 c(r,t)$$

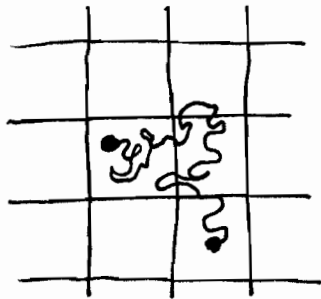
$$\frac{\partial \langle r^2(t) \rangle}{\partial t} = 2dD, \text{ see FTS p. 88}$$

Einstein relationship



$$(LJ, T=1.50, \rho=0.844)$$

Note that in order to perform this calculation properly, we need to keep track of the actual position of particles in the periodic images of the central box:



The particle is very near its starting position in the central box, but has travelled  $\pm L$  distance in both  $x$ - and  $y$ -directions

### Green-Kubo relations

Instead of following the displacement as a function of time, we can express the diffusion coefficient in terms of a "time correlation function":

$$\vec{r}(t) = \int_0^t dt' \vec{v}(t') \quad \text{or - along } x \text{ coordinate} \quad x(t) = \int_0^t dt' v_x(t')$$

$$\begin{aligned} \langle X^2(t) \rangle &= \left\langle \left[ \int_0^t dt' v_x(t') \right]^2 \right\rangle = \\ &= \int_0^t \int_0^t dt' dt'' \langle v_x(t') v_x(t'') \rangle = \end{aligned}$$

$$= \int_0^t \int_0^{t'} dt' dt'' \langle v_x(t') v_x(t'') \rangle + \int_0^t \int_0^t dt' dt'' \langle v_x(t') v_x(t'') \rangle$$

$$= 2 \int_0^t \int_0^{t'} dt' dt'' \langle v_x(t') v_x(t'') \rangle$$

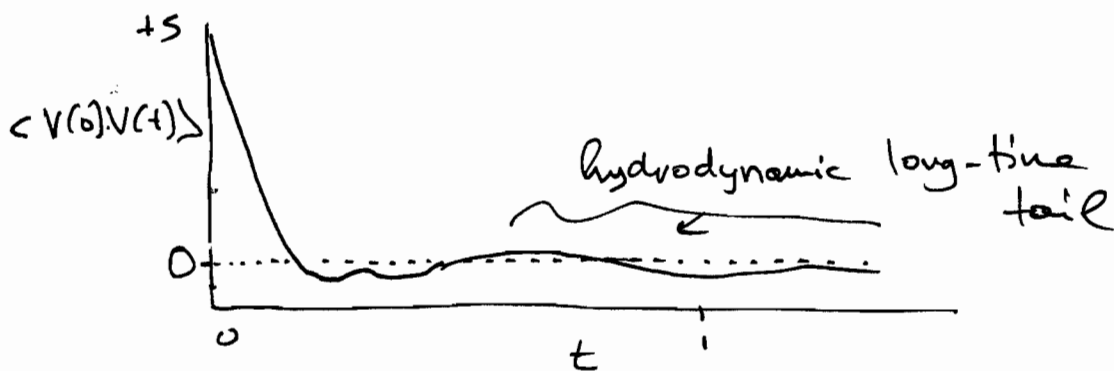
At equilibrium, only time differences are relevant - origin of  $t$  is not:

$$\langle v_x(t') v_x(t'') \rangle = \langle v_x(t' - t'') v_x(0) \rangle$$

$$\therefore 2D = \lim_{t \rightarrow \infty} \frac{\partial \langle x^2(t) \rangle}{\partial t} = \lim_{t' \rightarrow \infty} 2 \int_0^{t'} dt'' \langle v_x(t' - t'') v_x(0) \rangle$$

$$\Rightarrow D = \int_0^{\infty} dz \langle v_x(z) v_x(0) \rangle$$

Green-Kubo relationship: diffusion coefficient as integral of a time correlation function



Other Green-Kubo relationships:

Viscosity  $\eta = \frac{1}{VKT} \int_0^{\infty} dz \langle \sigma^{xy}(0) \sigma^{xy}(z) \rangle$

$$\sigma^{xy} = \sum_{i=1}^N (m_i v_i^x v_i^y + \frac{1}{2} \sum_{j \neq i} x_{ij} f_y(r_{ij}))$$

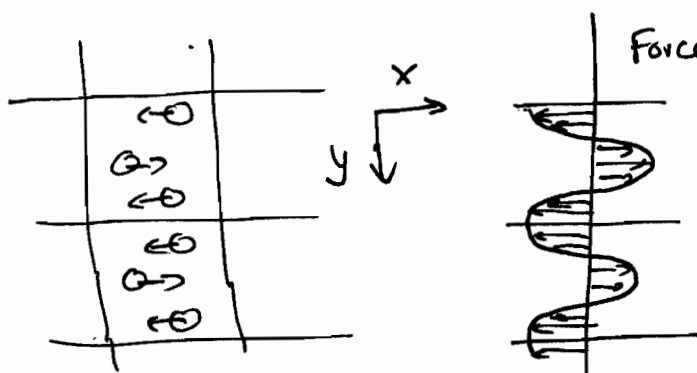
Thermal Co-conductivity  $\lambda_z = \frac{1}{VKT} \int_0^{\infty} dz \langle \dot{j}_z^e(0) \dot{j}_z^e(z) \rangle$

$$\dot{j}_z^e = \frac{d}{dt} \sum_{i=1}^N z_i \frac{1}{2} (m_i v_i^2 + \sum_{j \neq i} u(r_{ij}))$$

Non-Equilibrium MD

Green-Kubo relations become hard to use for systems with long relaxation times. Even for simpler systems, statistical noise can be a problem. One way to measure transport coefficients is non-equilibrium simulations in the presence of external forces or shear.

E.g. viscosity calculation (A) impose external force



Force

$$F_{ix}^{ext} = F \cos\left(\frac{2\pi n r_{iy}}{L}\right)$$

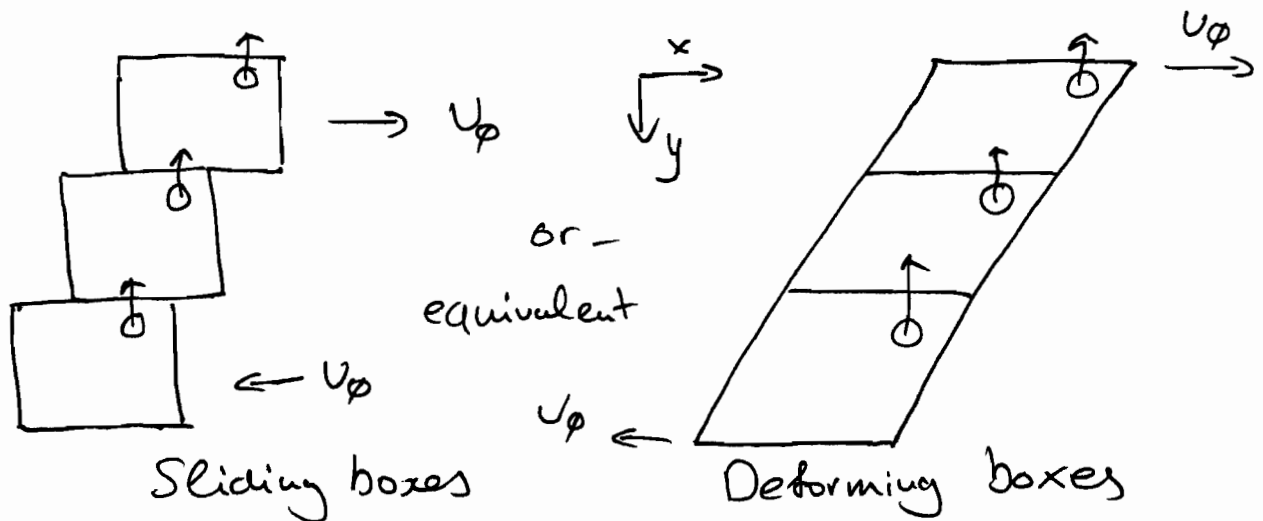
$$= F \cos(k r_{iy})$$

$$\langle U_x(r_y) \rangle \approx \left(\frac{\rho F}{k^2 n}\right) \cos(k r_y)$$

(Gosling et al., Mol. Phys. 26: 1495, 1973)

This computes a force- and wave vector-dependent viscosity that needs to be extrapolated to  $f \rightarrow 0$ ,  $k \rightarrow 0$

(B) Impose shear rate, measure stress:  
(Hees + Edwards, J. Phys C 5: 1921-9, 1972)



or - equivalent

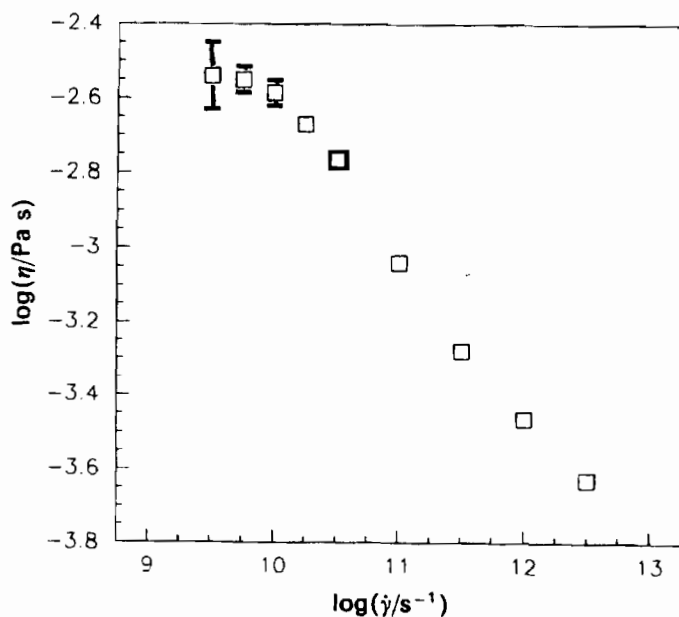
Sliding boxes

Deforming boxes

In both cases, when a particle crosses the  $y$  boundary, its  $x$  position is shifted by a time-dependent amount and the  $x$  velocity changed by  $\pm U_0$ . The viscosity is given by

$$\underbrace{\langle P_{yx}(t \rightarrow \infty) \rangle}_{\text{yx-component of pressure tensor}} = -\eta \underbrace{\frac{du_x}{dy}}_{\text{velocity gradient}}$$

Example: Viscosity of  $n$ -hexadecane - Berker et al.,  
J. Chem. Soc. Faraday Trans. 88: 1719 (1992)



\* huge  $\dot{\gamma}$  rates  
(because of small box size)

\* Need extrapolations to  $\dot{\gamma} \rightarrow 0$

\* Shear thinning behavior generally seen.

For both approaches, energy is input into the system, so temperature control is essential (see next sections); also, internal  $T$ -gradients may develop.