Course 05/1

Dynamic property: diffusion coefficient – Einstein's relation

- Macroscopic definition of diffusion coefficient
- Einstein's relation
- Mean square displacement of Lennard-Jones liquid
- Mean square displacement: average over initial times

Diffusion coefficient

The diffusion coefficient is defined through Fick's law, which is a macroscopic law describing diffusion:

$$\vec{j} = -D\,\vec{\nabla}\,c$$

where $\vec{j}$ is the current of the diffusing material

c the concentration

D the diffusion coefficient.

The conservation of the diffusing material is described by the continuity relation:

$$\frac{\partial c}{\partial t}(\vec{r}, t) + \vec{\nabla} \cdot \vec{j}(\vec{r}, t) = 0$$

Diffusion equation

By combining Fick's law with the continuity equation, we obtain the diffusion equation:

$$\frac{\partial c}{\partial t}(\vec{r}, t) - D\,\nabla^2 c(\vec{r}, t) = 0$$

Example:

Initial condition:

$$c(\vec{r}, t = 0) = \delta(\vec{r})$$

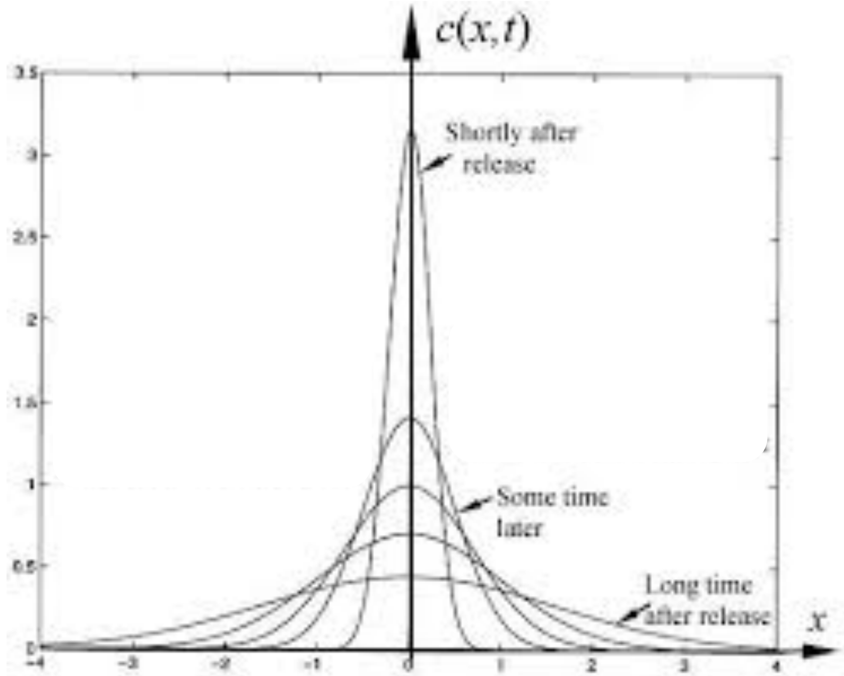
Analytical solution:

$$c(\vec{r}, t) = \frac{1}{(4\pi D t)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

Evolution with time

$$c(\vec{r}, t=0) = \delta(\vec{r})$$

$$c(\vec{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$



NB the number of particles is conserved:

$$\int c(\vec{r}, t=0)\, d\vec{r} = 1$$

$$\int c(\vec{r}, t)\, d\vec{r} = 1$$

Relation between mean square displacement and diffusion coefficient

$$c(\vec{r}, t=0) = \delta(\vec{r}) \qquad\qquad c(\vec{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

Mean square displacement (MSD):

$$\begin{aligned} \langle r^2(t) \rangle &= \int c(\vec{r}, t)\, r^2\, d\vec{r} \\ &= \int c(\vec{r}, t)\,(x^2 + y^2 + z^2)\, d\vec{r} \\ &= 3 \cdot (2Dt) = 6\,Dt \end{aligned}$$

Note: depends on dimension!

Einstein's relation

We assume a localized initial distribution of a labeled species: $c\,(\vec{r}, t = 0\,)$

We only use 1. the diffusion equation: $$\frac{\partial c}{\partial t}(\,\vec{r}, t\,) - D\,\nabla^2 c\,(\,\vec{r}, t\,) = 0$$

2. the conservation of mass: $$\int c\,(\,\vec{r}, t\,)\, d\vec{r} = 1$$

$$\frac{\partial}{\partial t}\langle\, r^2(\,t\,)\,\rangle = \frac{\partial}{\partial t}\int r^2\, c\,(\,\vec{r}, t\,)\, d\vec{r} \underset{\text{Diff. eq.}}{=} D\int r^2\,\nabla^2 c\; d\vec{r}$$

Using $\vec{\nabla}(\,r^2\,\vec{\nabla}\,c\,) = (\,\vec{\nabla}\,r^2\,)\cdot(\,\vec{\nabla}\,c\,) + r^2\,\nabla^2 c$ we have

$$= D\int \vec{\nabla}\cdot(\,r^2\,\vec{\nabla}\,c\,)\, d\vec{r} - D\int (\,\vec{\nabla}\,r^2\,)\cdot(\,\vec{\nabla}\,c\,)\, d\vec{r}$$

$$= \underbrace{D\int (\,r^2\,\vec{\nabla}\,c\,)\cdot d\vec{S}} - 2D\int \vec{r}\cdot(\,\vec{\nabla}\,c\,)\, d\vec{r}$$

= 0 (the concentration of a labeled species is vanishing on a distant surface)

Einstein's relation

$$\frac{\partial}{\partial t}\langle r^2(t)\rangle = -2D\int \vec{r}\cdot(\vec{\nabla} c)\, dr$$

We now use $\vec{\nabla}(\vec{r}\cdot c) = (\vec{\nabla}\cdot\vec{r})\,c + \vec{r}\cdot\vec{\nabla} c$ and obtain

$$= -2D\int \vec{\nabla}(\vec{r}\cdot c)\, d\vec{r} + 2D\int \underbrace{(\vec{\nabla}\cdot\vec{r})}_{=\,3\text{ (depends on dimension!)}}\, c\, d\vec{r}$$

$$= \underbrace{-2D\int (r\,c)\cdot d\vec{S}}_{\text{vanishes on distant surface}} + 6D\underbrace{\int c\; d\vec{r}}_{=1\text{ (mass conservation)}}$$

Result: $$\boxed{\frac{\partial}{\partial t}\langle r^2\rangle = 6D}$$ Einstein's relation

Mean square displacement

Einstein's relation $$\frac{\partial}{\partial t}\langle r^2 \rangle = 6D$$

range of validity:
macroscopic regime

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle \| \Delta\vec{r}(t) \|^2 \rangle$$

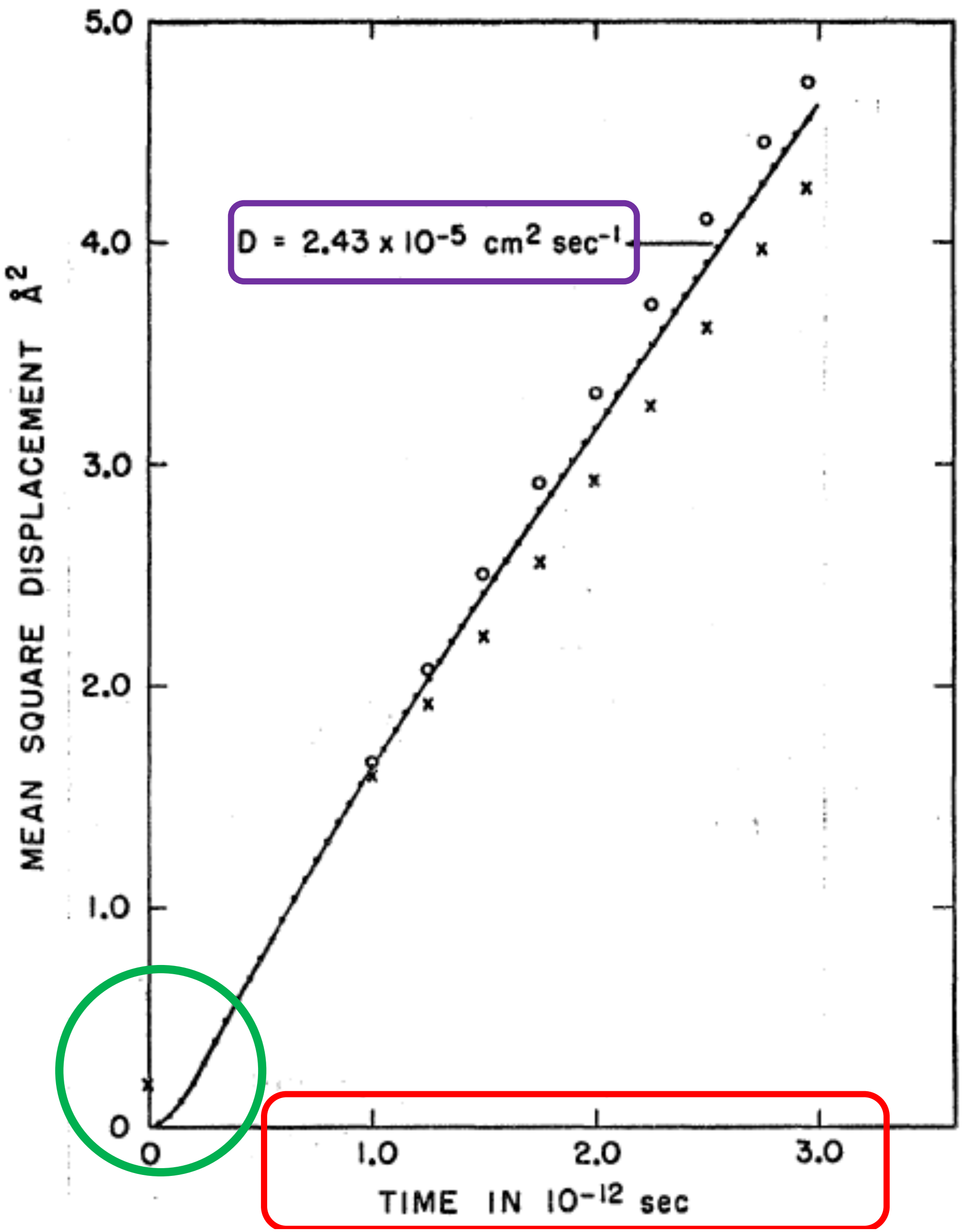
where $\langle \| \Delta\vec{r}(t) \|^2 \rangle$ is the mean square displacement (MSD):

$$\langle \| \Delta\vec{r}(t) \|^2 \rangle = \langle \underbrace{\frac{1}{N} \sum_{l=1}^{N}}_{\text{average over particles}} \| \Delta\vec{r}_l(t) \|^2 \rangle = \langle \frac{1}{N} \sum_{l=1}^{N} \| \vec{r}_l(t) - \vec{r}_l(0) \|^2 \rangle$$

$\langle \ldots \rangle$ average over configurations

Einstein's relation establishes a link between a macroscopic quantity like the diffusion coefficient D and the atomistic evolution of the particle positions.

Mean square displacement of Lennard-Jones liquid

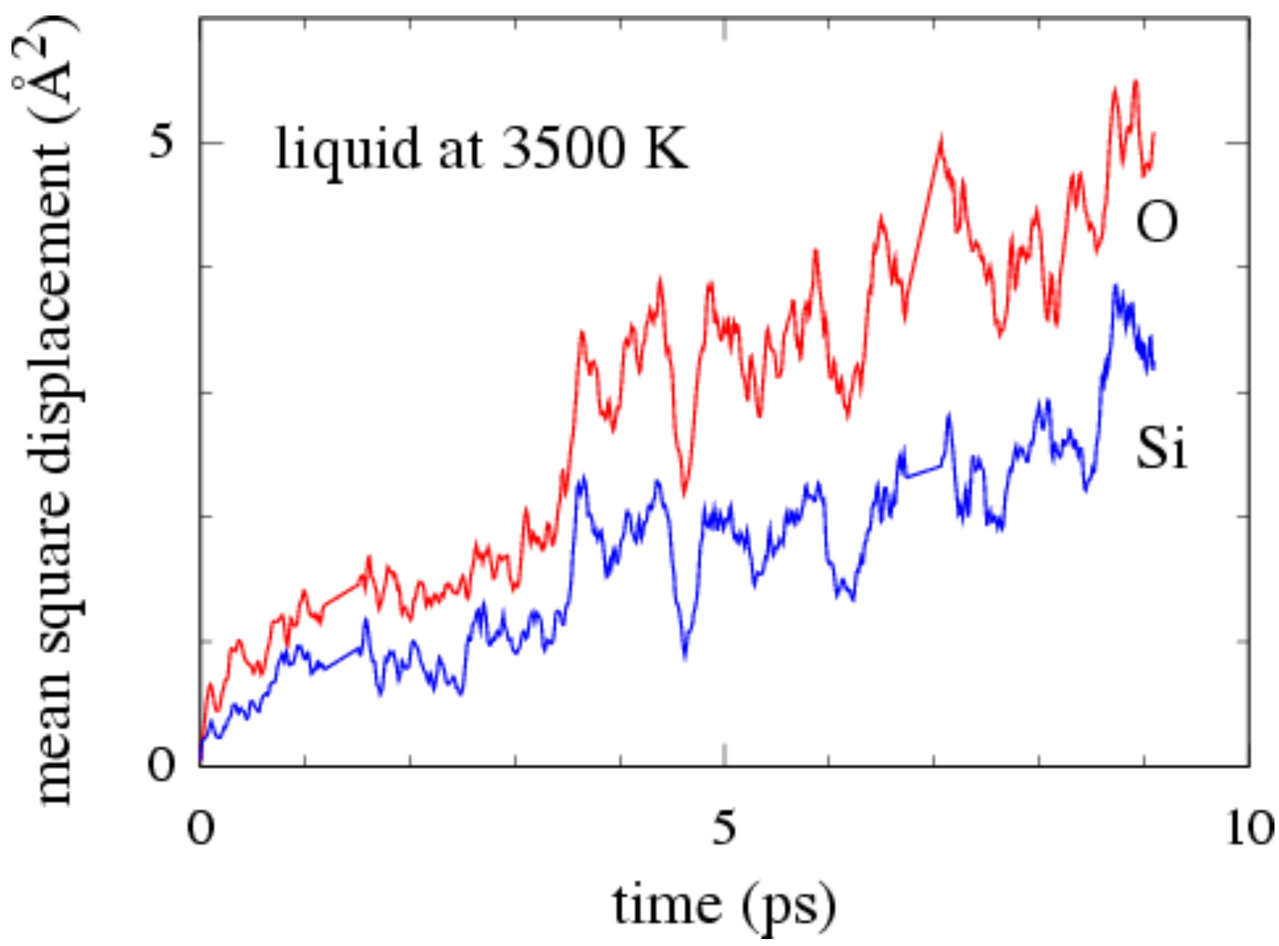


Average over 64 curves

Atomistic regime: ballistic

3 ps

Mean square displacement of liquid silica

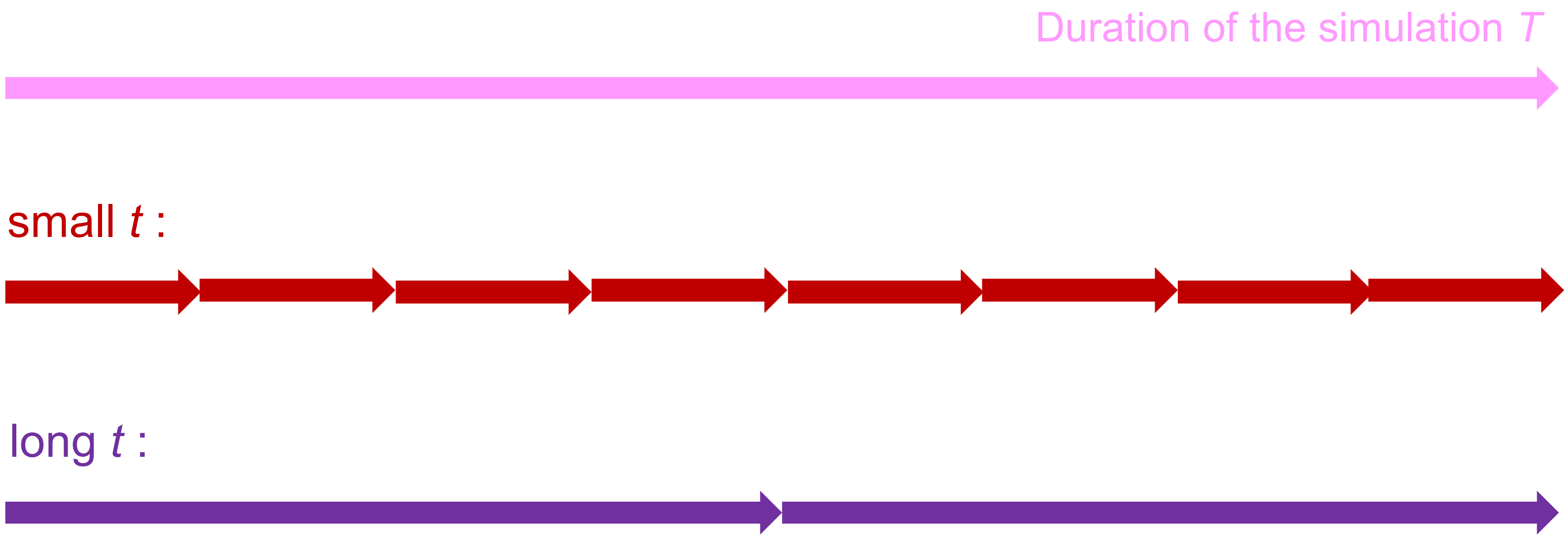


MSD: average over initial times

$$\langle \| \Delta\vec{r}(t) \|^2 \rangle = \langle \frac{1}{N} \sum_{l=1}^{N} \| \vec{r}_l(t) - \vec{r}_l(0) \|^2 \rangle$$

$t_0 + t$ $\quad$ t_0

Average over t_0



Hence, the error for long t is larger than for small t !

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