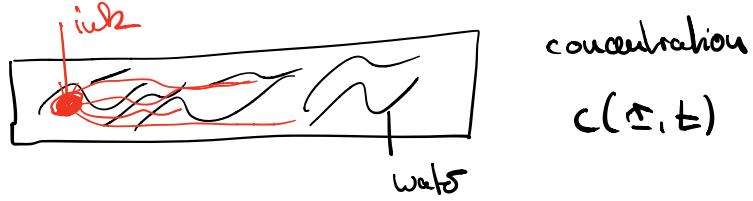


§ 10 Analyzing Molecular Dynamics Simulations

In a few examples of MD simulations we have seen so far, we have seen glimpses of macromolecular structures and their conformations. However, conformational analysis and its relation to function is specific for biomolecular questions and by far not the only type of structure/properties to analyze. In particular for liquids, some additional analysis can be performed and actually be compared to experimental characterizations.

Atomistic Model of Diffusion

Example: particle movement from a region with high concentration to one with low concentration



can be modeled as (isotropic medium)

$$\frac{\partial c(\underline{\sigma}, t)}{\partial t} = \nabla \left[D(c, \underline{\sigma}) \nabla c(\underline{\sigma}, t) \right]$$

$D(c, \underline{\sigma})$: diffusion coefficient of concentration c at $\underline{\sigma}$

If D is constant, this turns into a linear DE

$$\boxed{\frac{\partial c(\underline{\sigma}, t)}{\partial t} = D \nabla^2 c(\underline{\sigma}, t)}$$

Macroscopically: diffusion $\hat{=}$ change in concentration

Microscopically: " $\hat{=}$ net movement of particles

$\Rightarrow MD$

MD can be used to predict / model the diffusion constant.

But how?

1D example



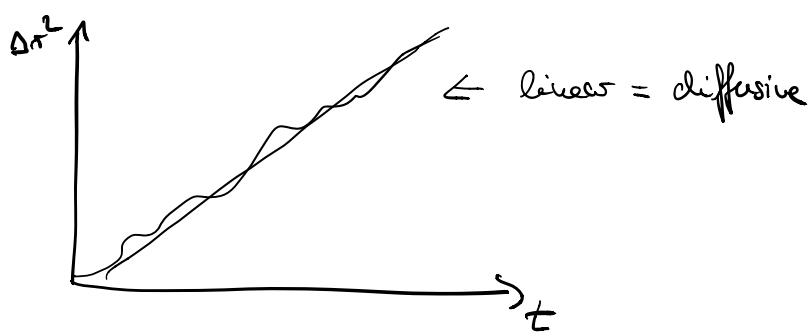
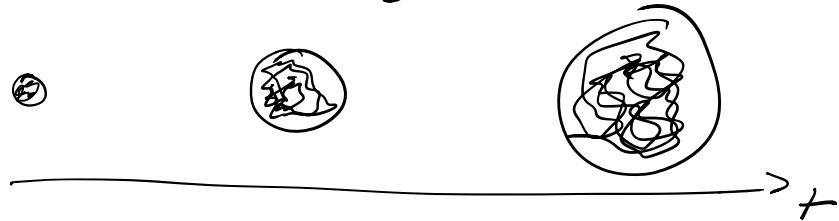
Diffusion constant

= ability of a particle to move Δx^2 over a time Δt

$$D = \rho \frac{\Delta x^2}{\Delta t}$$

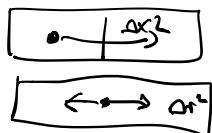
Idea: measure in MD the square displacement of a particle from its initial position

$$\langle \Delta r^2(t) \rangle = \frac{1}{N} \sum_i (\vec{r}_i(t) - \vec{r}_i(0))^2$$



However: Δr^2 is not the same as Δx^2 in the "definition" of D (from left to right)

1D

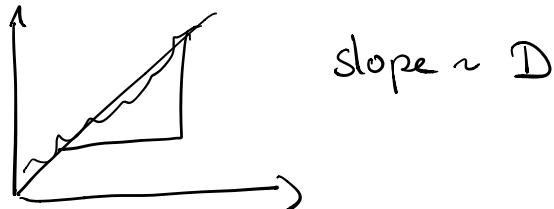


$$D_{1D} = \frac{1}{2} \frac{\Delta r^2}{\Delta t}$$

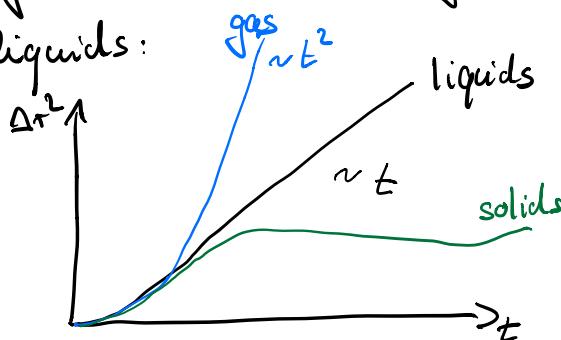
For general d dimensions:

$$D = \frac{1}{2} \frac{1}{d} \frac{\Delta r^2}{\Delta t}$$

$$\sim 2dD\Delta t \sim \Delta r^2 \Rightarrow \text{Diffusion} \rightarrow \text{linear}$$



Of course, this analysis only applies to isothermal liquids:



In an MD simulation:

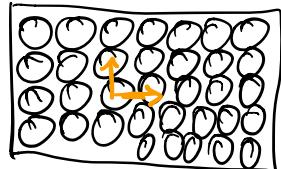
- check value of D vs. literature
- check if the system you are simulating is a gas, liquid, or solid.

10.2 The radial distribution function

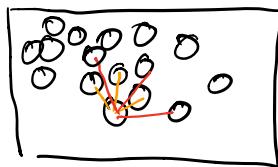
In order to analyze the diffusion constant ($\sim \Delta r^2$) obviously requires the full trajectory information over time.

- \sim
 - a lot of data
 - depending on the method, dynamics may not be physical \sim thermokinetic

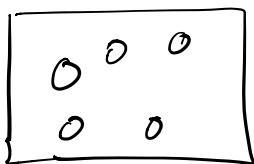
What else can we do? → How do we characterize a material state?



Solid
regular spacing
characteristic distances



Liquid
neighbors at
"approximate
distances"

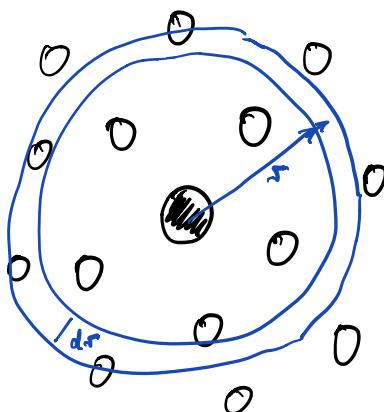


Gas
"random
positions"

- Idea:
- measure distances of particles to their neighbors
 - average over a "large" number particle
 - average over time

Formally: Radial distribution function

Describes a relative density of atoms as a function of radius



$$g(r) = \frac{s(r)}{s}$$

$s(r)$ local density

s overall density $\frac{N}{V}$

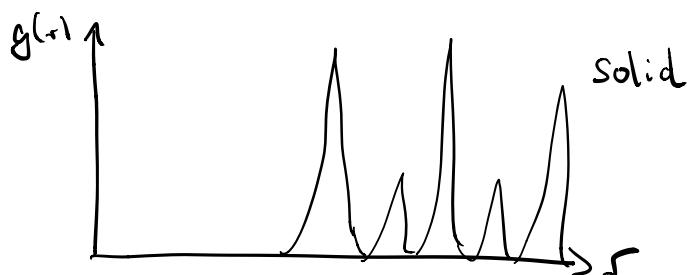
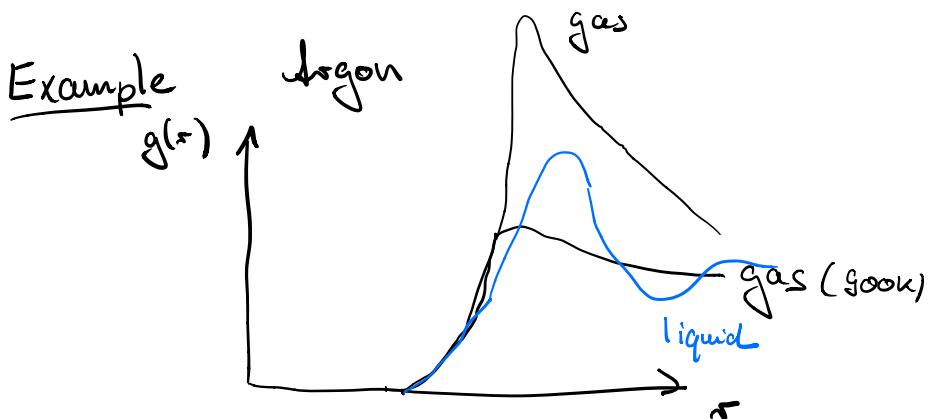
In a discrete version

$$g(r) = \frac{\langle N(r \pm \frac{\Delta r}{2}) \rangle}{2(r \pm \frac{\Delta r}{2})} \cdot \frac{1}{s}$$

average # of atoms in shell
volume of the shell

Alternatively:

$g(r) 2\pi r^2 dr$ $\hat{=}$ Number of particles in a spherical shell of radius r and thickness dr



10.3 Scattering Experiments

Structural information about materials is often found via scattering experiments, where a sample is irradiated by x-rays, neutrons, light, etc. The sample produces a scattering amplitude:

$$F(\underline{k}) = \int B(\underline{\sigma}) \exp(i\underline{k} \cdot \underline{\sigma}) d^3\sigma$$

$B(\underline{\sigma})$: scattering power at $\underline{\sigma}$,

\underline{k} : $= \underline{k}_{\text{out}} - \underline{k}_{\text{in}}$ is the difference of

incoming and outgoing wave

The intensity registered at a detector

$$\langle |F(\underline{k})|^2 \rangle = \iint B(\underline{\varepsilon}) B(\underline{\varepsilon}') \exp(i \underline{k}(\underline{r} - \underline{r}')) d^3 r d^3 r'$$

and we write the scattering power as atomic contribution

$$B(\underline{\varepsilon}) = \sum_j b(\underline{\varepsilon} - \underline{\varepsilon}_j)$$

With this one finds [...]

$$\langle |F(\underline{k})|^2 \rangle = N |\mathbf{f}(\underline{k})|^2 \left\langle \frac{1}{N} \sum_i \sum_j \exp(i \underline{k}(\underline{r}_i - \underline{r}_j)) \right\rangle$$

and $\mathbf{f}(\underline{k}) = \int b(\underline{\varepsilon}) \exp(i \underline{k} \cdot \underline{\varepsilon}) d^3 r$

$$= 1 + \frac{1}{N} \left\langle \sum_i \sum_{j \neq i} \exp(i \underline{k}(\underline{r}_i - \underline{r}_j)) \right\rangle$$

$$= 1 + \int g(r) \exp(i \underline{k} \cdot \underline{r}) d^3 r \quad g(r) = \frac{s(r)}{s}$$

$$= 1 + \int s(g(r)-1) \exp(i \underline{k} \cdot \underline{r}) d^3 r + (2\pi)^3 s \delta(\underline{k})$$

Except for the $\delta(\underline{k})$ term (forward scattering $\underline{k}=0$), one measures the so called scattering factor:

$$S(\underline{k}) = 1 + \int (g(r)-1) \exp(i \underline{k} \cdot \underline{r}) d^3 r$$

- which is the Fourier transform of $g(r)$.

One can also calculate several quantities from $g(r)$, if one knows the total interaction potential of particles $\phi(r)$.

$$U = E = \frac{3}{2} NkT + \frac{1}{2} N \int g(r) \phi(r) d^3r$$

$$P = \frac{NkT}{V} - \frac{1}{6} s^2 \int g(r) r \frac{d\phi}{dr} d^3r$$

or the compressibility:

$$\frac{S kT}{P} = 1 + s \int (g(r) - 1) d^3r = S(\underline{k=0})$$

For an ideal gas $\phi(r) = 0$

$$U = \frac{3}{2} NkT , \quad PV = NkT \quad \text{well-known.}$$