

Introduction to correlation, Kirkwood-Buff theory, Onsagers regression theory, and Green's functions

Winter School for Theoretical Chemistry and Spectroscopy
Han-sur-Lesse, 10-14 December 2018

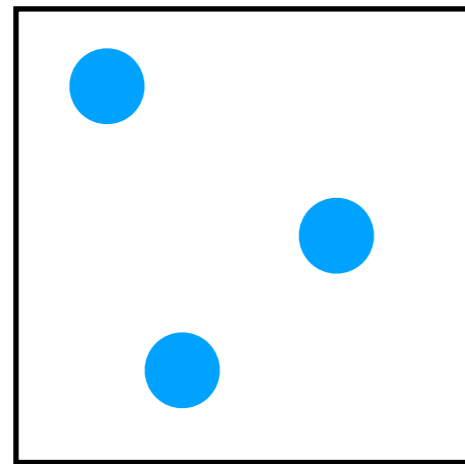
by
Bernd Ensing

Content

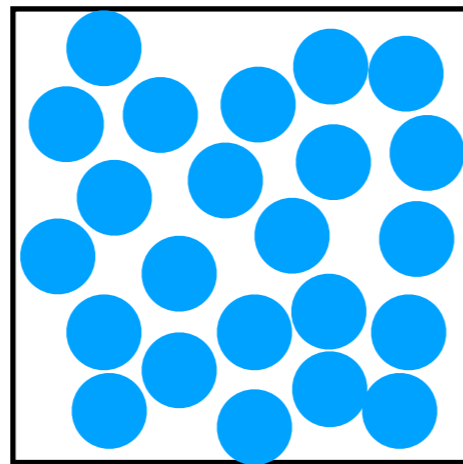
- Spatial correlation
- Time correlation
- Application: Anisotropy decay in water
- Reaction rate theory, reactive-flux method (Bennet-Chandler)

The radial distribution function

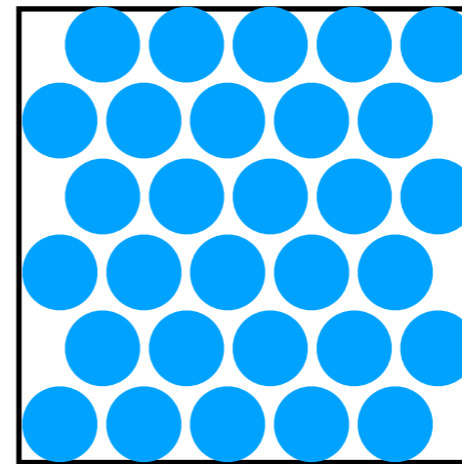
The structure of materials is governed interaction between the particles (atoms, molecules,...) and the external conditions (T, p,...).



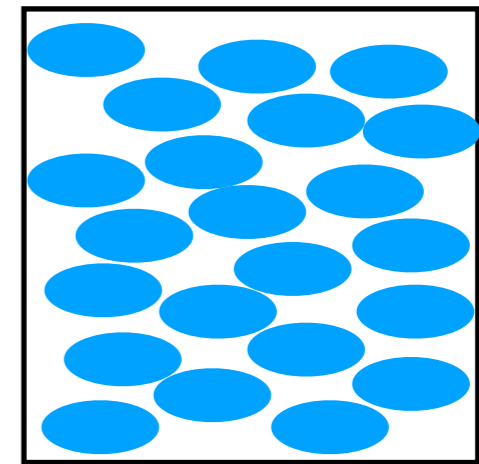
gas



liquid



solid



liquid crystal

The radial distribution function (RDF), aka the pair-correlation function, measures the (excess) probability to find a particle j at a distance, r , from a reference particle i , relative to the average density of particles j .

average density:

$$\rho_j = \frac{n_j}{V}$$

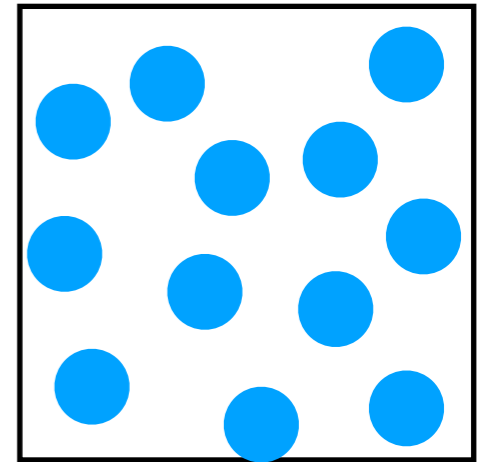
The radial distribution function

The probability to find a certain configuration of particle positions is given by Boltzmann's distribution:

$$P(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{Z} e^{-\beta V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)} \quad \beta = 1/k_B T$$

$$Z = \int \dots \int e^{-\beta V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)} d\mathbf{r}_1 \dots d\mathbf{r}_N$$

$$\rho = \frac{N}{V}$$

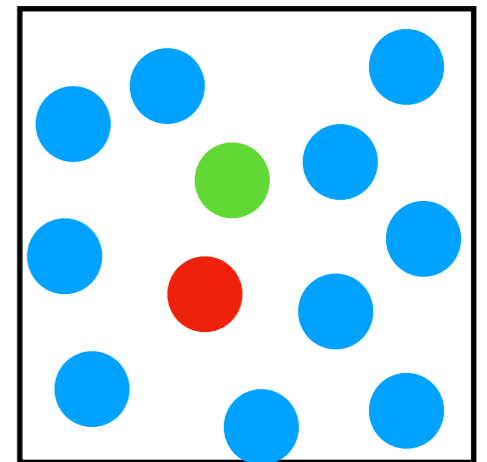


The probability to find particles 1 and 2 at a certain position:

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{Z} \int \dots \int e^{-\beta V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)} d\mathbf{r}_3 \dots d\mathbf{r}_N$$

The probability that any of the particles is at those positions is given by the 2-particle density:

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{N!}{(N-2)!} P(\mathbf{r}_1, \mathbf{r}_2)$$



Define the correlation function $g(\mathbf{r}_1, \mathbf{r}_2)$

$$g(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho(\mathbf{r}_1, \mathbf{r}_2)}{\rho^2} = \frac{V^2 N!}{N^2 (N-2)!} \frac{1}{Z} \int \dots \int e^{-\beta V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)} d\mathbf{r}_3 \dots d\mathbf{r}_N$$

is equal to one if there is no correlation (= no interaction)

$N(N-1)$

The radial distribution function

The radial distribution function (RDF), $g(r)$, considers the correlation of particles “2” at a distance r from particles “1”

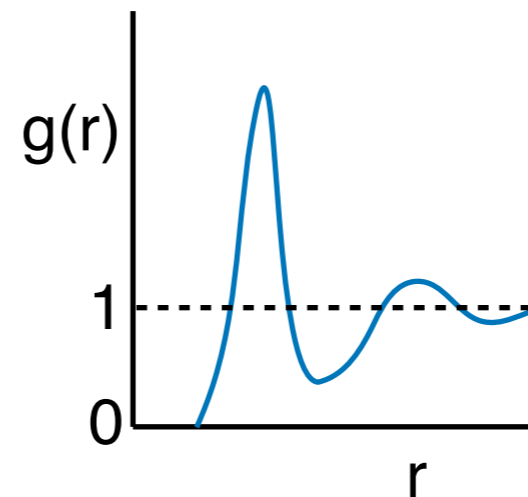
The number of particles at a distance between r and $r+dr$ from any central particle:

$$4\pi r^2 \rho g(r) dr$$

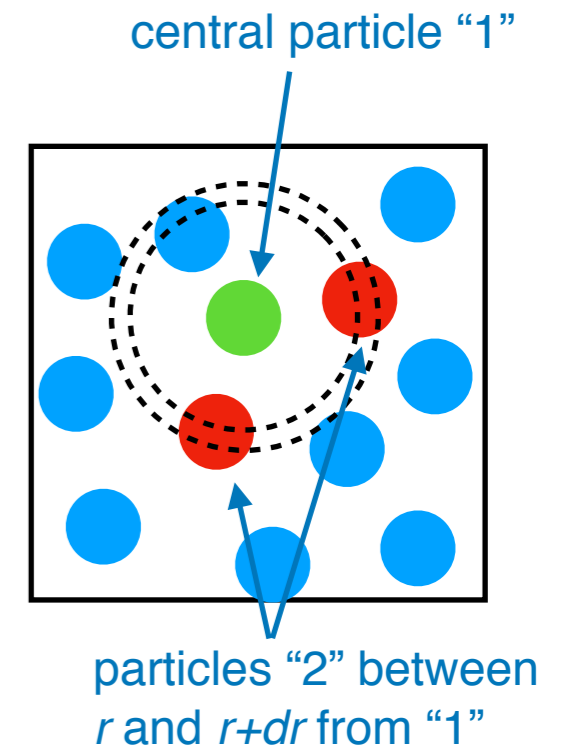
- at very small distances: $g(0) = 0$
- at very large distances: $g(\infty) = 1$

The RDF can be obtained from:

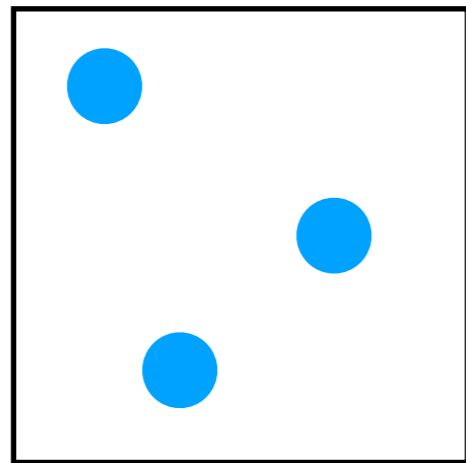
- MD or MC simulation
- neutron or X-ray diffraction (structure factor)
- microscopy (for colloids and other large particles)



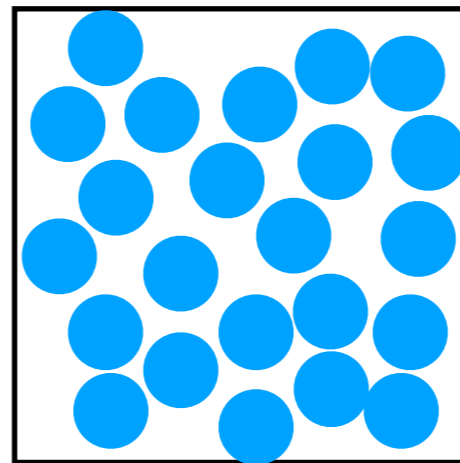
distance $r = |r_2 - r_1|$



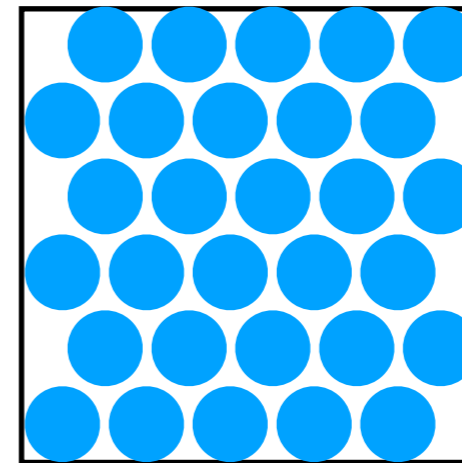
The radial distribution function



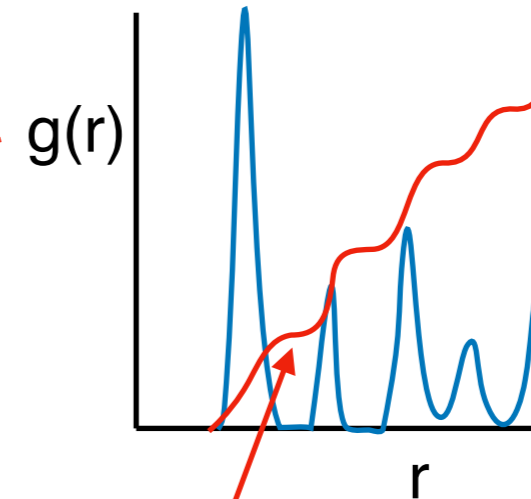
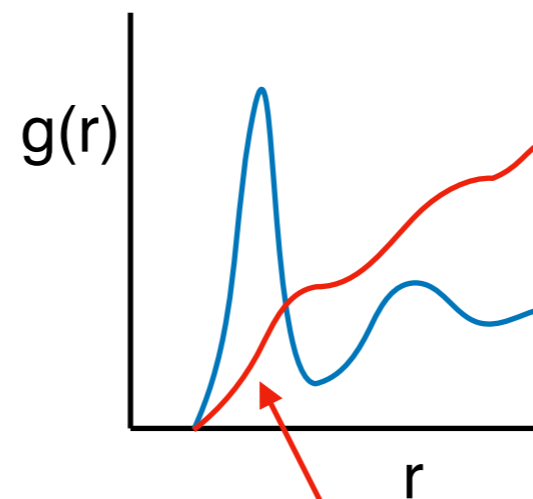
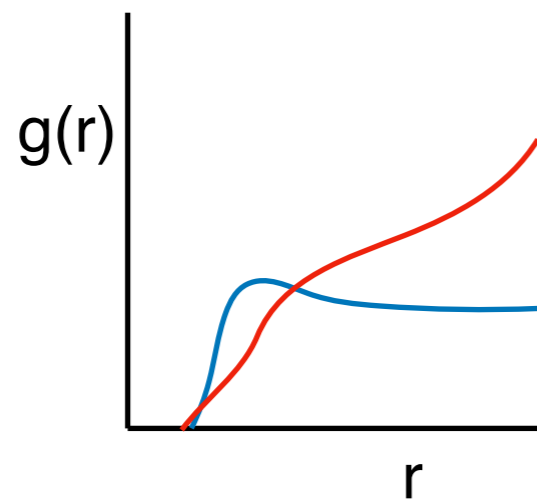
gas



liquid



solid

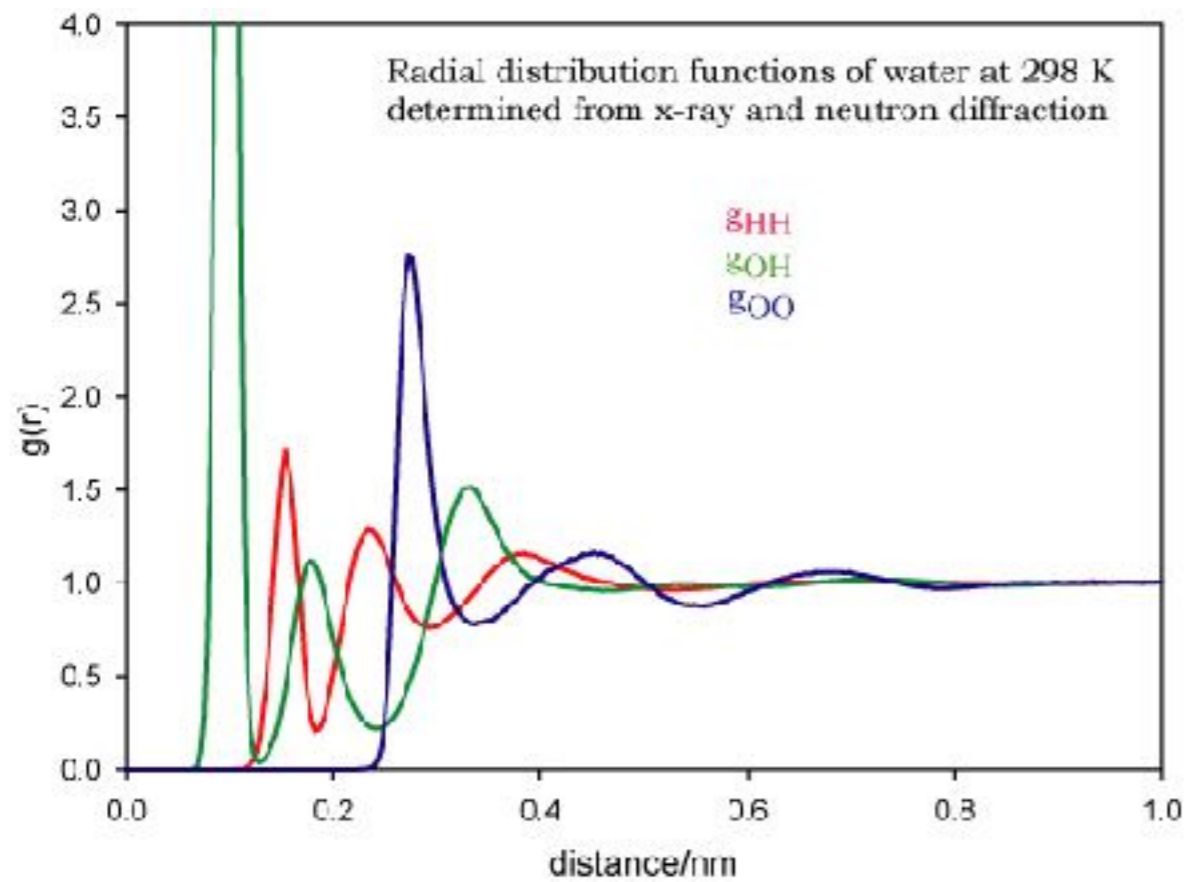


Integration provides information on the coordination number

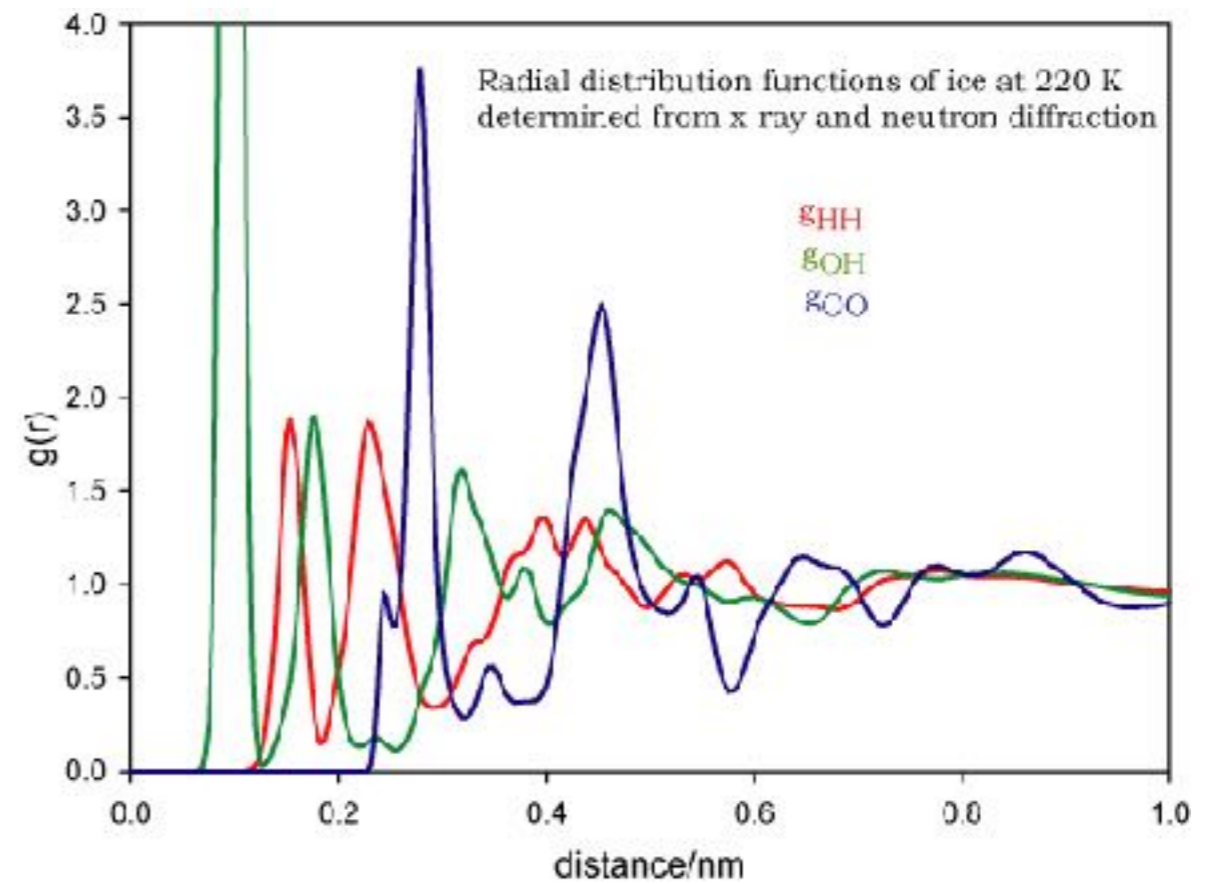
$$n_c = \rho \int_0^R 4\pi r^2 g(r) dr$$

The radial distribution function

liquid water



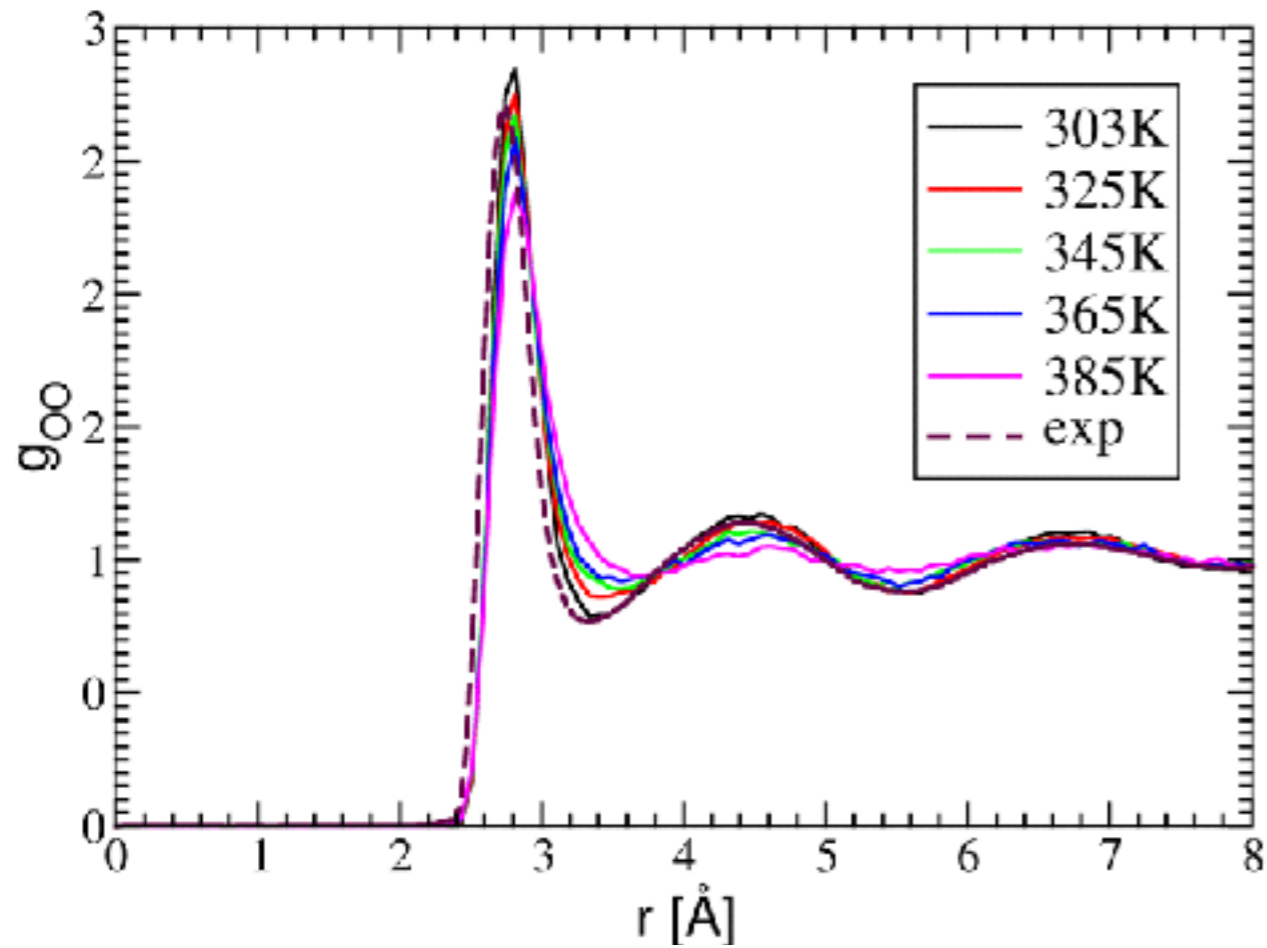
ice



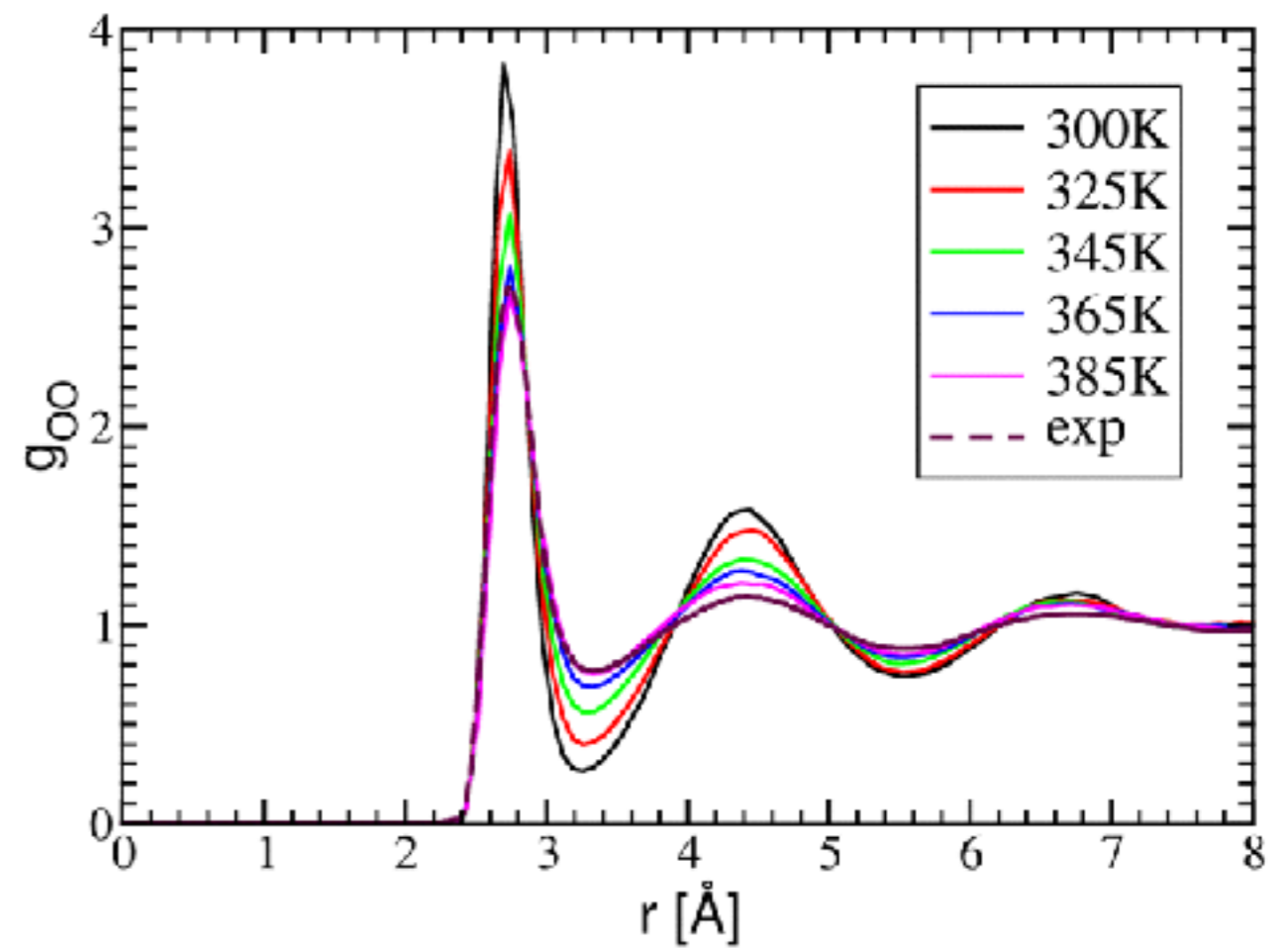
The radial distribution function

Liquid water, DFT-MD simulation

BLYP+D3/TZV2P



PBE+D3/TZV2P



The radial distribution function

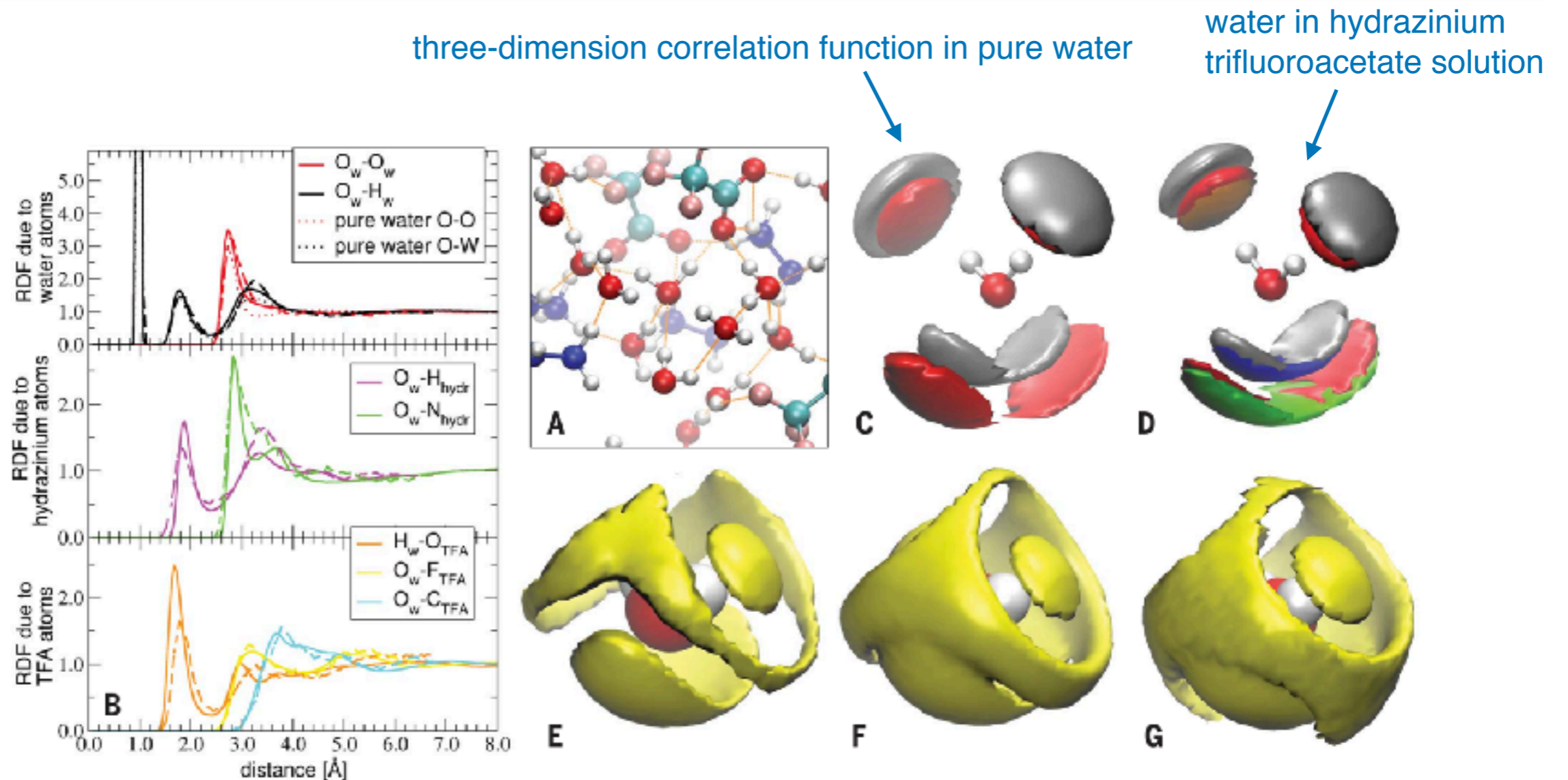


Fig. 3. MD simulations of the investigated solution. (A) Snapshot of the classical MD simulation. (B) Radial distribution functions (RDFs) of different H-bond donor and acceptor atoms in the solution around water atoms, obtained from the classical (solid lines) and DFT (dashed lines) MD simulations. In the top panel, radial distributions of the water O and H atoms are compared to these functions in bulk water (dotted lines). (C and D) Three-dimensional structural density plots of the first coordination shell of a water

molecule, in neat water (C) and in N₂H₅TFA solution (D), showing the distribution of different H-bond donor and acceptor atoms. Color code for isosurfaces: red, water O atom; gray, water H atom; orange, TFA O atom; blue, hydrazinium H atom; green, hydrazinium N atom. (E to G) Three-dimensional structural density plots of the H-bond acceptor atoms (water O, TFA O, and hydrazinium N) in the first and second coordination shells of a water molecule (in the center) in neat water at 1 bar (E), in neat water at 6 kbar (F), and in N₂H₅TFA solution at 1 bar (G).

Thermodynamic properties

The RDF can be used to compute various thermodynamic properties, such as:

- potential energy
- pressure
- compressibility

total energy:

$$U = U^{\text{kin}} + U^{\text{intra}} + \frac{1}{2} N \rho \int_0^{\infty} dr 4\pi r^2 g(r) u(r)$$

translation energy
 $U^{\text{kin}} = \frac{3}{2} N k_B T$

avoid double counting

potential energy of a particle

Pressure

The pressure in the canonical ensemble is computed for a system with pairwise interactions from the virial equation:

$$P = \rho k_B T + \frac{1}{3V} \left\langle \sum_{i < j} \mathbf{f}(\mathbf{r}_{ij}) \cdot \mathbf{r}_{ij} \right\rangle$$

using instead the radial distribution function:

$$P = \rho k_B T - \frac{2}{3} \pi \rho^2 \int_0^\infty dr \frac{du(r)}{dr} r^3 g(r) dr$$

avoid double
counting

force

Isothermal compressibility

The isothermal compressibility is: $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}$

which is linked to the fluctuations in the number of particles in an open system

$$\langle N \rangle \rho k_B T \kappa_T = \langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2$$

integration of the RDF over all particle 1 and 2 positions gives something similar:

$$\int_V d^3 r_1 \int_V d^3 r_2 \rho^2 g(r_{12}) = \langle N(N-1) \rangle = \langle N^2 \rangle - \langle N \rangle$$

add $\langle N \rangle$ and subtract $\langle N \rangle^2$:

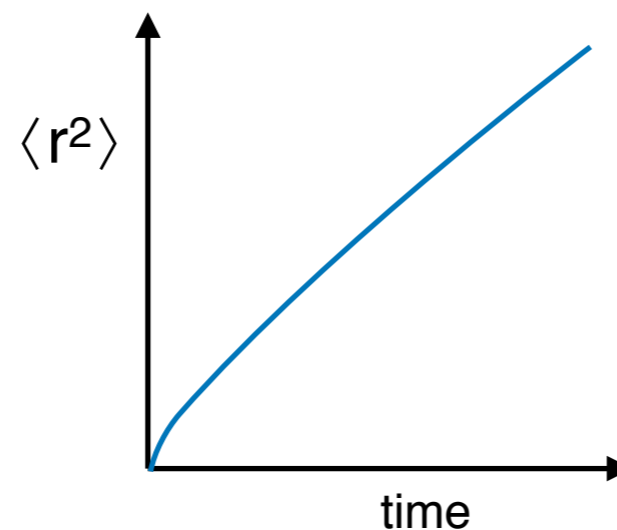
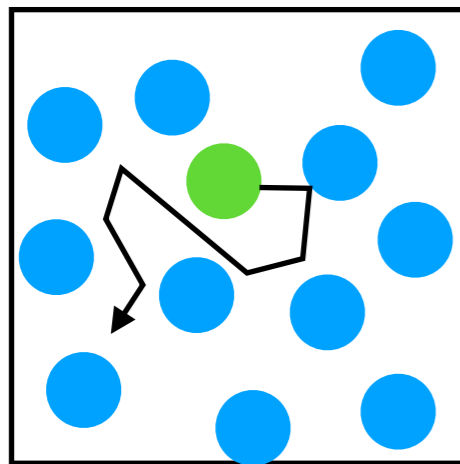
$$\begin{aligned} \langle N \rangle \rho k_B T \kappa_T &= \rho \int_V d^3 r_1 \rho \int_V d^3 r_2 g(r_{12}) + \langle N \rangle - \rho \int_V d^3 r_1 \rho \int_V d^3 r_2 \\ &= \rho \int_V d^3 r_1 \rho \int_V d^3 r_2 (g(r_{12}) - 1) + \langle N \rangle \end{aligned}$$

compressibility: $\kappa_T = (k_B T)^{-1} \int_{\mathbb{R}^3} d^3 r (g(r) - 1) + (\rho k_B T)^{-1}$

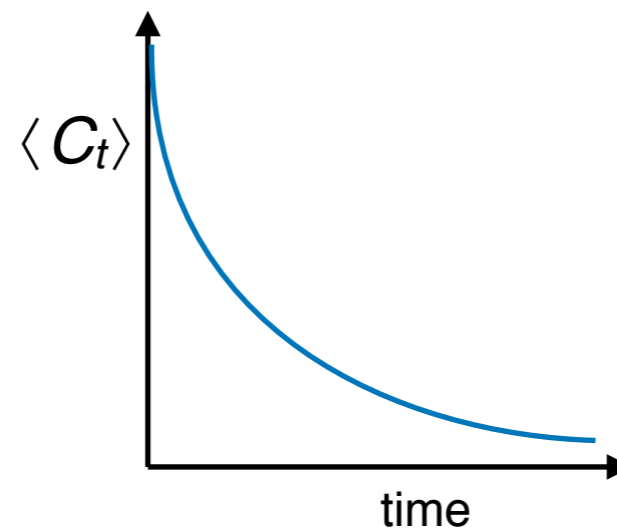
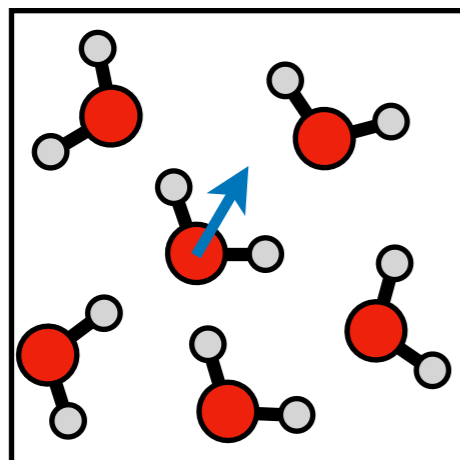
Dynamical properties

Thus far: spatial correlations between particles.

A material or liquid in equilibrium has also an underlying dynamics of the particles. Particle positions and velocities continuously change. Most quantities fluctuate in time.



self-diffusion of
a molecule in a
liquid



anisotropy decay
due to rotation of
dipoles

Time correlation functions

The dynamics of microscopic processes can be captured by time-correlation functions

$$\langle A(0)B(t) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T d\tau A(\tau)B(\tau + t)$$

$$\langle A(0)A(t) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T d\tau A(\tau)A(\tau + t)$$

time auto-correlation function
(correlate with itself)

At very short time intervals, the correlation is maximal

- $\langle A(0)A(0) \rangle = \langle A^2 \rangle$

At very long times, the correlation has decayed to zero

- $\langle A(0)A(\infty) \rangle = \langle A \rangle \langle A \rangle$

- $\langle A(0)B(\infty) \rangle = \langle A \rangle \langle B \rangle$

Often, the correlation function is normalized by dividing it by $\langle A(0)A(0) \rangle$

Time correlation functions

In equilibrium, any time can be taken as the $t=0$ moment, so, $\langle A(t)A(t + \Delta t) \rangle$ is independent of t . Therefore:

$$\frac{d}{dt} \langle A(t)A(t + \Delta t) \rangle = \langle \dot{A}(t)A(t + \Delta t) \rangle + \langle A(t)\dot{A}(t + \Delta t) \rangle = 0$$

product rule

time derivative

and

$$\langle \dot{A}(t)A(t + \Delta t) \rangle = -\langle A(t)\dot{A}(t + \Delta t) \rangle$$

but note that $A(t)$ and $A(t+\Delta t)$ are permutable:

$$\langle A(t)A(t + \Delta t) \rangle = \langle A(t + \Delta t)A(t) \rangle$$

$$\left. \frac{d}{dt} \langle A(0)A(t) \rangle \right|_{t=0} = 0$$

every correlation function starts with a horizontal slope

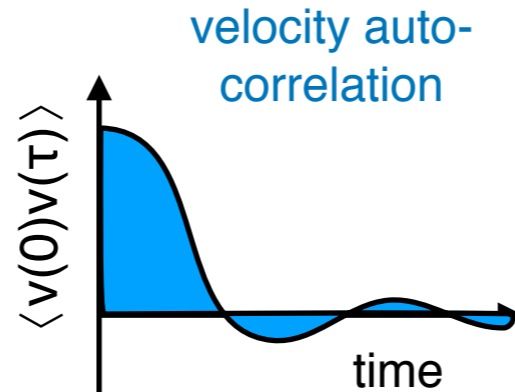
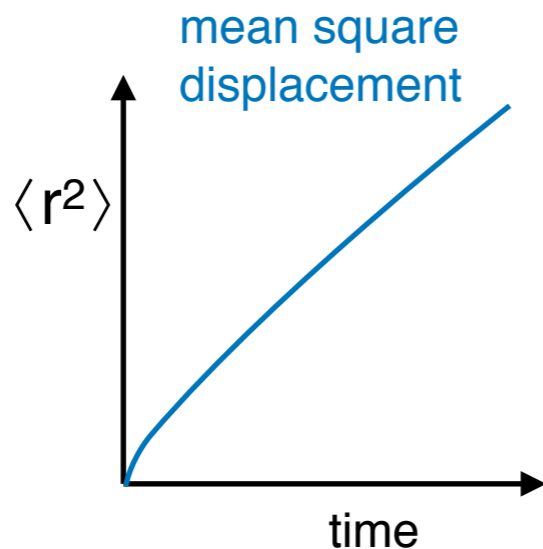
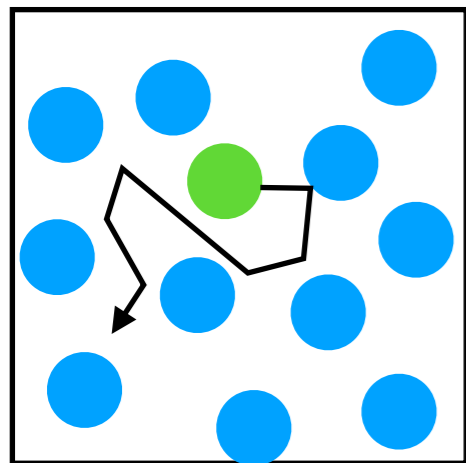
We can also derive:

$$\frac{d^2}{dt^2} \langle A(t)A(t + \Delta t) \rangle = -\langle \dot{A}(t)\dot{A}(t + \Delta t) \rangle$$

$$\left. \frac{d^2}{dt^2} \langle A(0)A(t) \rangle \right|_{t=0} = -\langle \dot{A}^2(t) \rangle < 0$$

every correlation function starts with a negative curvature

Example: self-diffusion



Fick's law:

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = D \nabla^2 P(\mathbf{r}, t)$$

diffusion coefficient
(units of m²/s)

Diffusive dynamics is characterised by a mean square displacement that is proportional to time.

in one dimension, for large enough t :

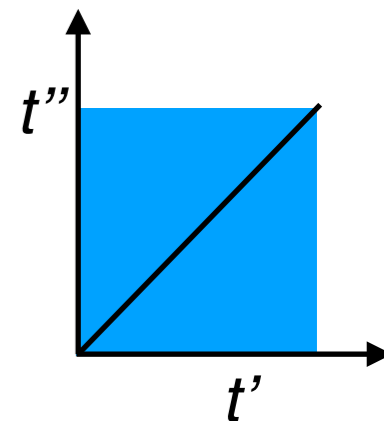
$$\langle (x(t) - x(0))^2 \rangle = 2Dt$$

(Einstein equation)

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

$$D = \frac{1}{2} \frac{d\langle x^2(t) \rangle}{dt} = \int_0^t dt' \langle v_x(0) v_x(t' - t') \rangle$$

- take the derivative to t
- shift the time origin by t'
- $\tau = t'' - t'$
- take limit to infinite time



in 3D:

$$D = \frac{1}{3} \int_0^\infty d\tau \langle v(0) v(\tau) \rangle$$

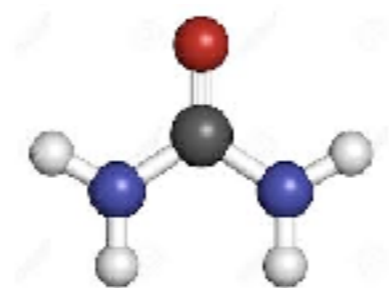
Green-Kubo relation (relates a transport property, here D , to a time correlation function)

Application: anisotropy decay

On the slowdown mechanism of water dynamics around small amphiphiles

Two amphiphilic molecules in water

Urea



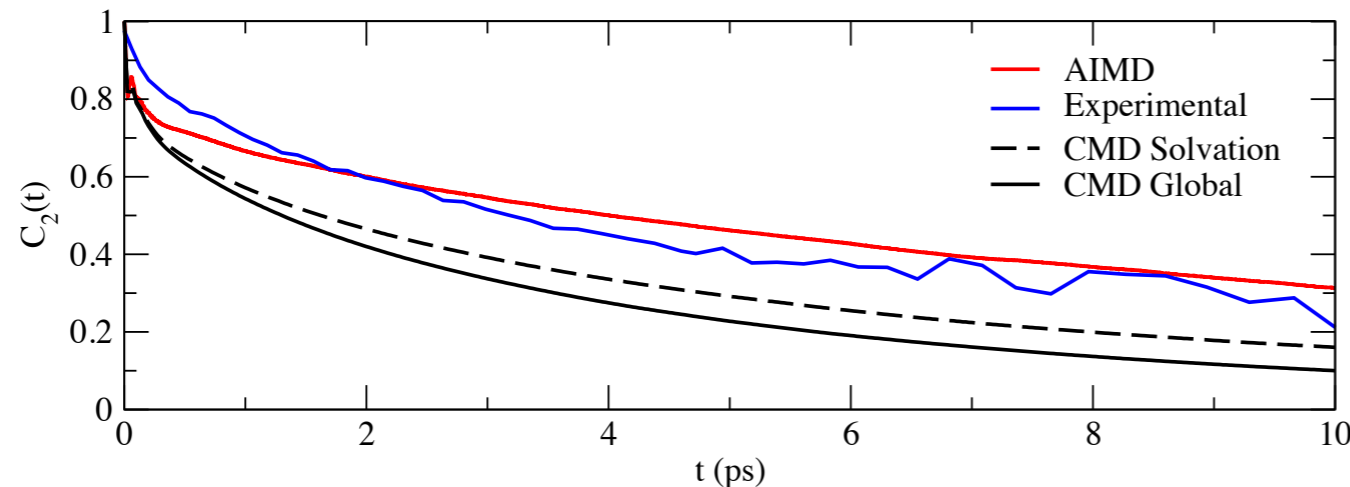
Tetramethyl urea



Wagner H. Brandeburgo
Evert Jan Meijer
Sietse T. van der Post

Application: anisotropy decay

Water orientational decay



DFT-MD (AIMD)

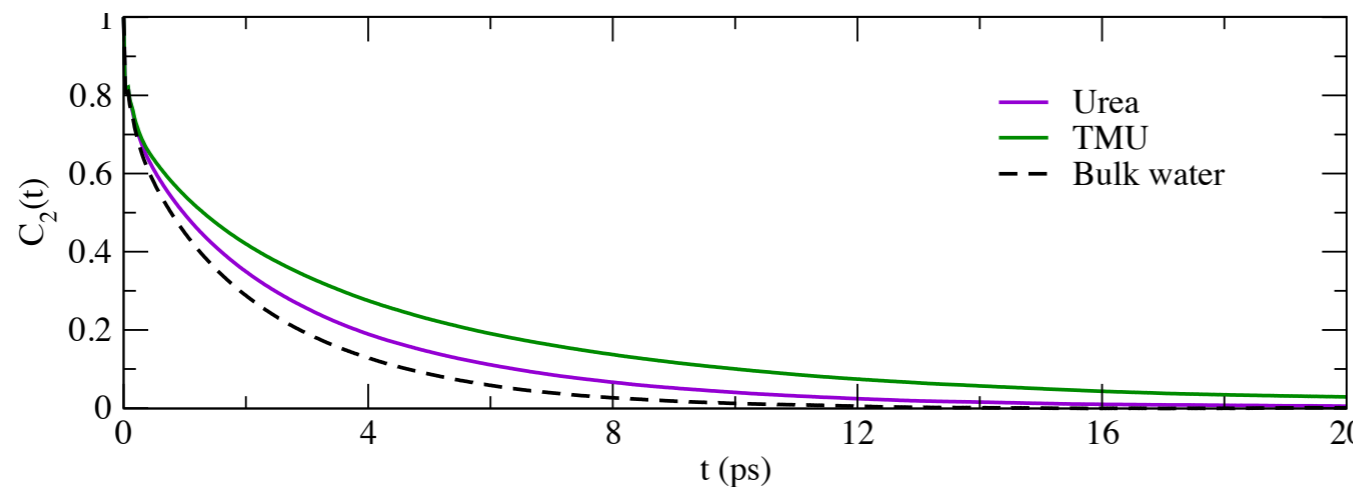
- CP2K
- DFT BLYP-D3/TZ2VP
- 4 TMU/40 H₂O
- t ~ 20 + 50ps (NVT)

forcefield MD (CMD)

- LAMMPS
- SPC-E / rigid TMU / KBFF urea
- N ~ 500 molecules
- t ~ 200 ps (NPT+NVT)

Experiment

- fs-IR



dipole auto-correlation:

$$C_l(t) = \left\langle P_l(\mu(0)\mu(\tau)) \right\rangle$$

first and second order Legendre polynomials:

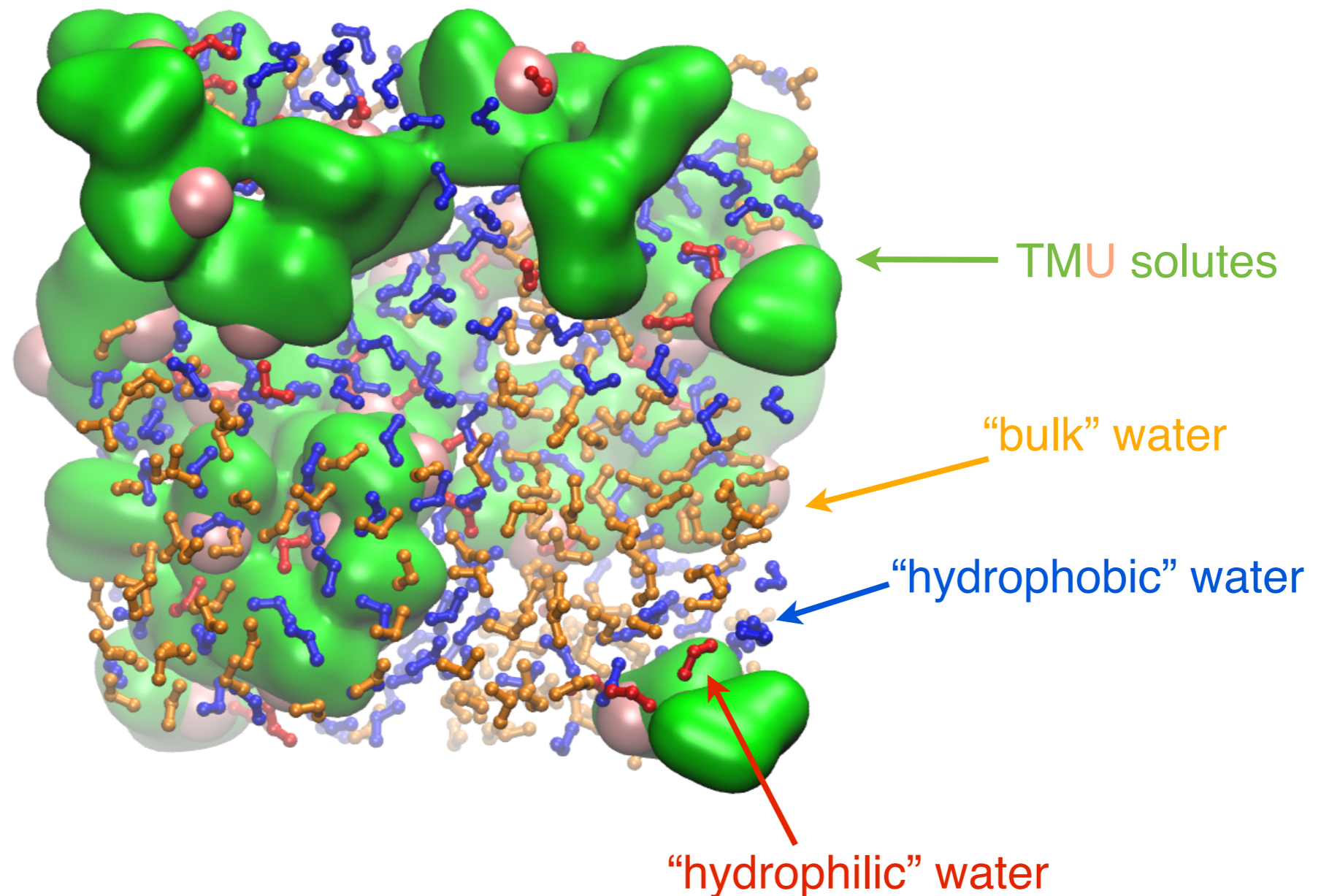
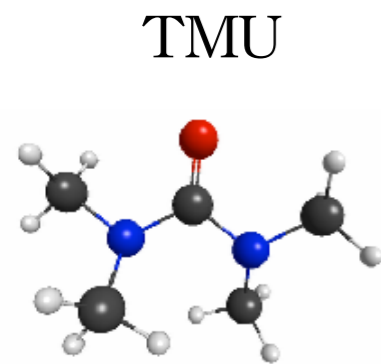
$$P_1(x) = x \quad P_2(x) = \frac{1}{2}(3x^2 - 1)$$

Fit function:

$$C_2(t) = A_0 \left(\cos\left(\frac{2\pi t}{\tau_{\text{sub}}}\right) \cdot e^{\frac{-t}{\tau_{\text{d}}}} + e^{\frac{-t}{\tau_{\text{fast}}}} \right) + (1 - A_0)e^{\frac{-t}{\tau_{\text{mid}}}}$$

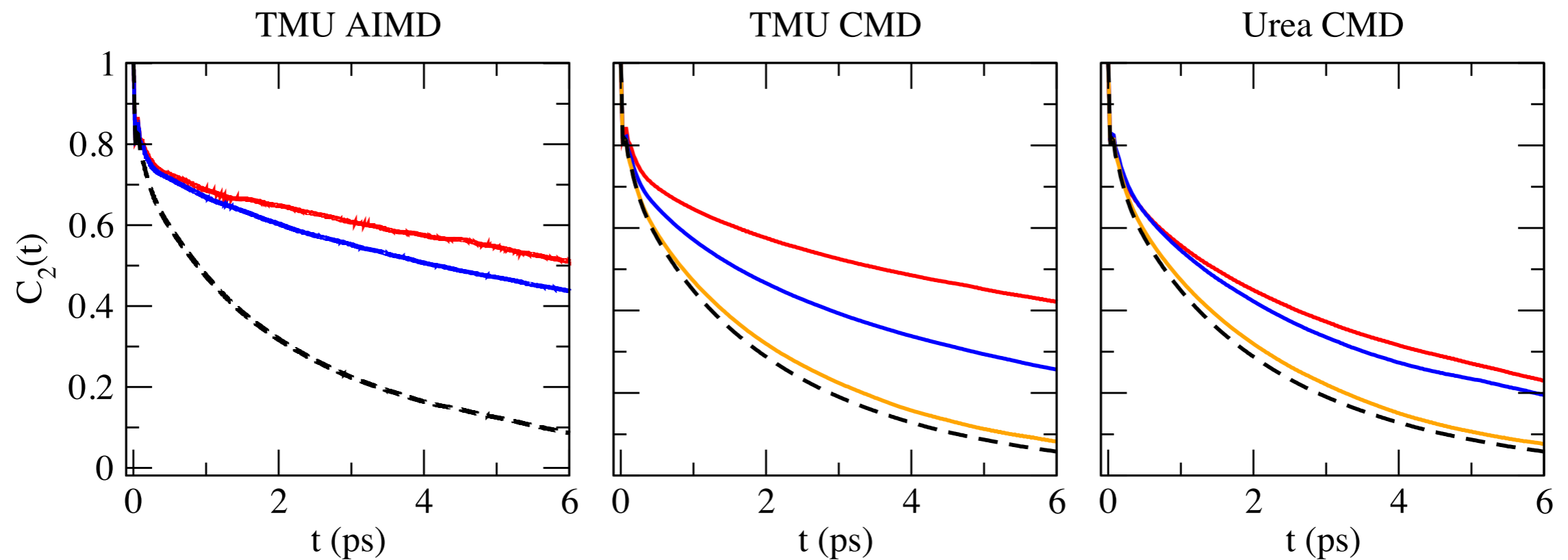
Application: anisotropy decay

Water partitioning



Application: anisotropy decay

Water partitioning



- hydrophilic solvent water
- hydrophobic solvent water
- bulk-like solvent water
- - - pure water

Application: anisotropy decay

System method	Fit interval (ps)	τ_{fast} (ps)	τ_{mid} (ps)	τ_{slow} (ps)
Pure water CMD All water	0–50	0.3	2.4 (1.9)	—
Pure water AIMD All water	0–15	0.5	3.1 (2.1)	—
Pure water fs-IR All water	2–10	—	— (2.3)	—
Urea CMD All water	0–12	0.6	3.6	—
Hydrophilic water		0.5	6.1	—
Hydrophobic water		0.6	5.3	—
Bulk-like water		0.3	2.7	—
TMU CMD All water	0–20	0.3	3.0 (2.2)	9.0 (∞)
Hydrophilic water		0.3	5.1	> 20
Hydrophobic water		0.3	3.3	15.5
Bulk-like water		0.3	2.9	—
TMU AIMD All water	0–12	0.2	2.0 (2.8)	> 12 (∞)
Hydrophilic water		0.2	3.9	> 12
Hydrophobic water		0.1	2.3	> 12
TMU fs-IR All water	2–10	—	— (2.6)	— (∞)

Application: anisotropy decay

H-bond life times and breaking mechanism

System method	$\tau_{\text{H-bond}}$ (ps)	Switches (%)
Pure water CMD All water	2.1	74.6
Pure water AIMD All water	2.2	75.9
Urea CMD All water	2.6	75.6
Hydrophilic water	3.1	73.8
Hydrophobic water	2.7	74.4
Bulk-like water	2.4	77.0
TMU CMD All water	2.9	68.8
Hydrophilic water	5.1	56.6
Hydrophobic water	3.1	65.6
Bulk-like water	2.4	74.6
TMU AIMD All water	4.1	62.3
Hydrophilic water	6.0	54.8
Hydrophobic water	3.9	61.2

Model

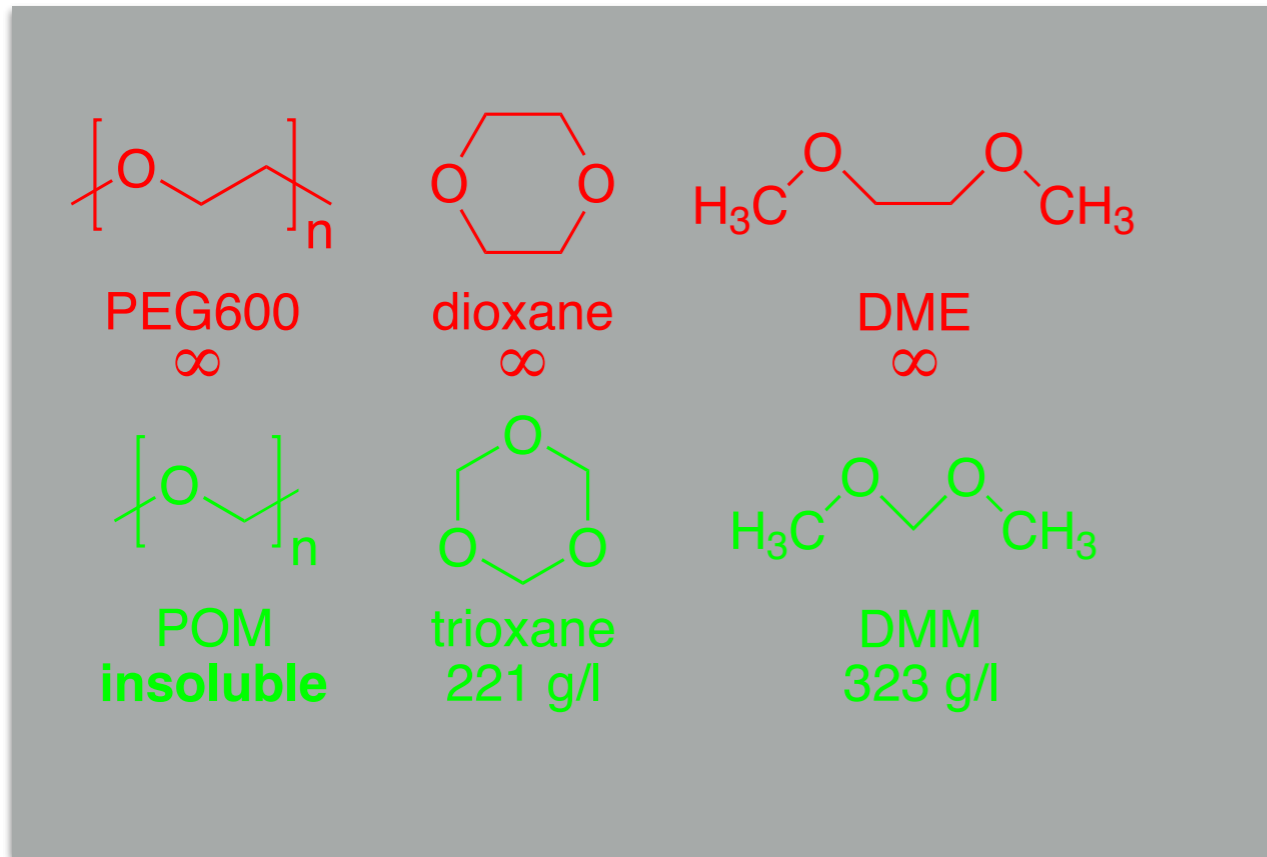
- Jump model by Laage and Hynes, *J. Phys. Chem. B* 112,14230–14242 (2008)
- Hydrogen bond life times
- **Associative / dissociative** H-bond breaking
- Close to hydrophobic surface: dissociative mechanism becomes important (excluded volume effect)
- After dissociative breaking, bond often restores, resetting the timer (new life time)

PEG and POM

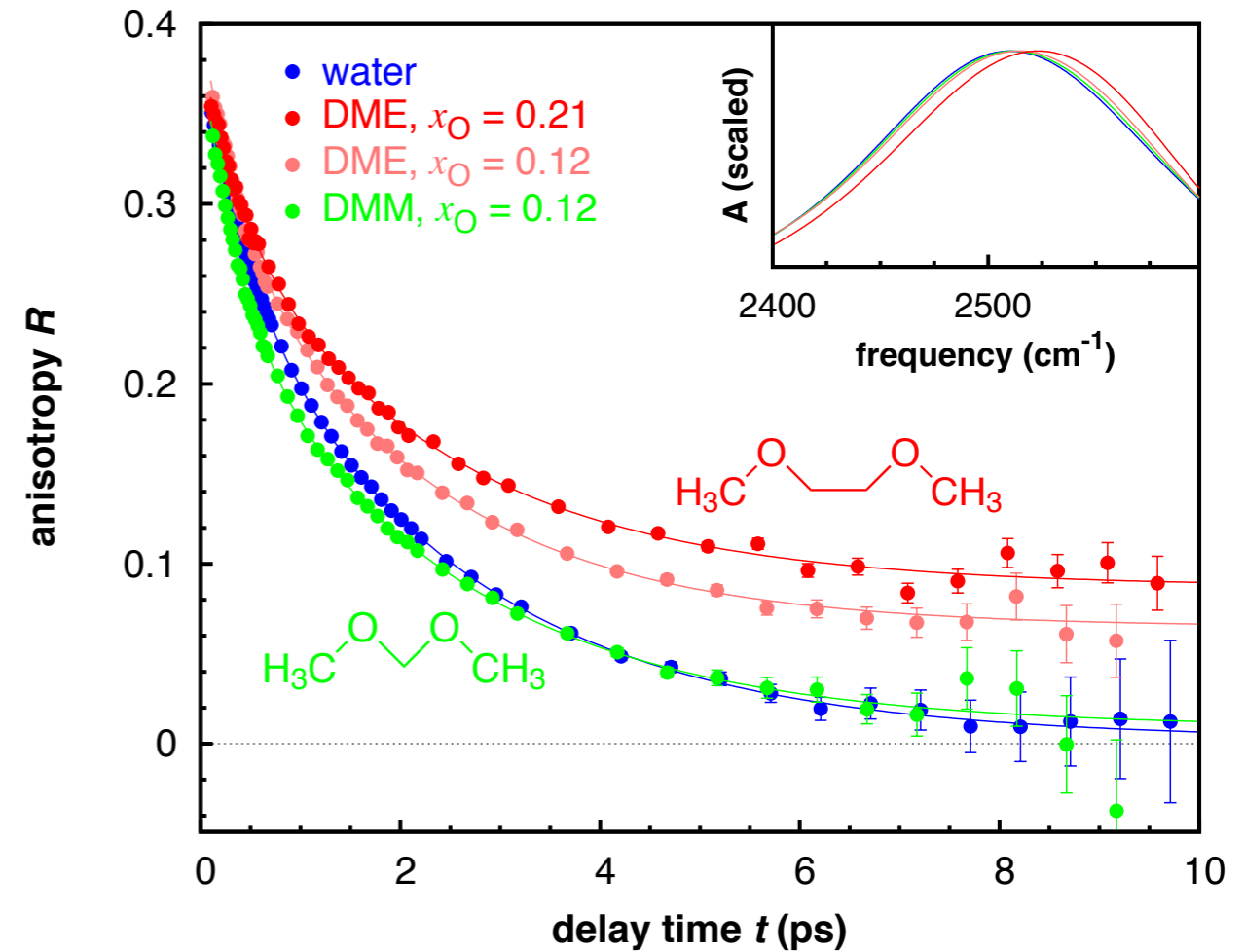
The solvation mystery unraveled from the solvent dynamics

- polyethylene glycol, $[-\text{CH}_2-\text{CH}_2-\text{O}-]_n$
- polyoxymethylene, $[-\text{CH}_2-\text{O}-]_n$

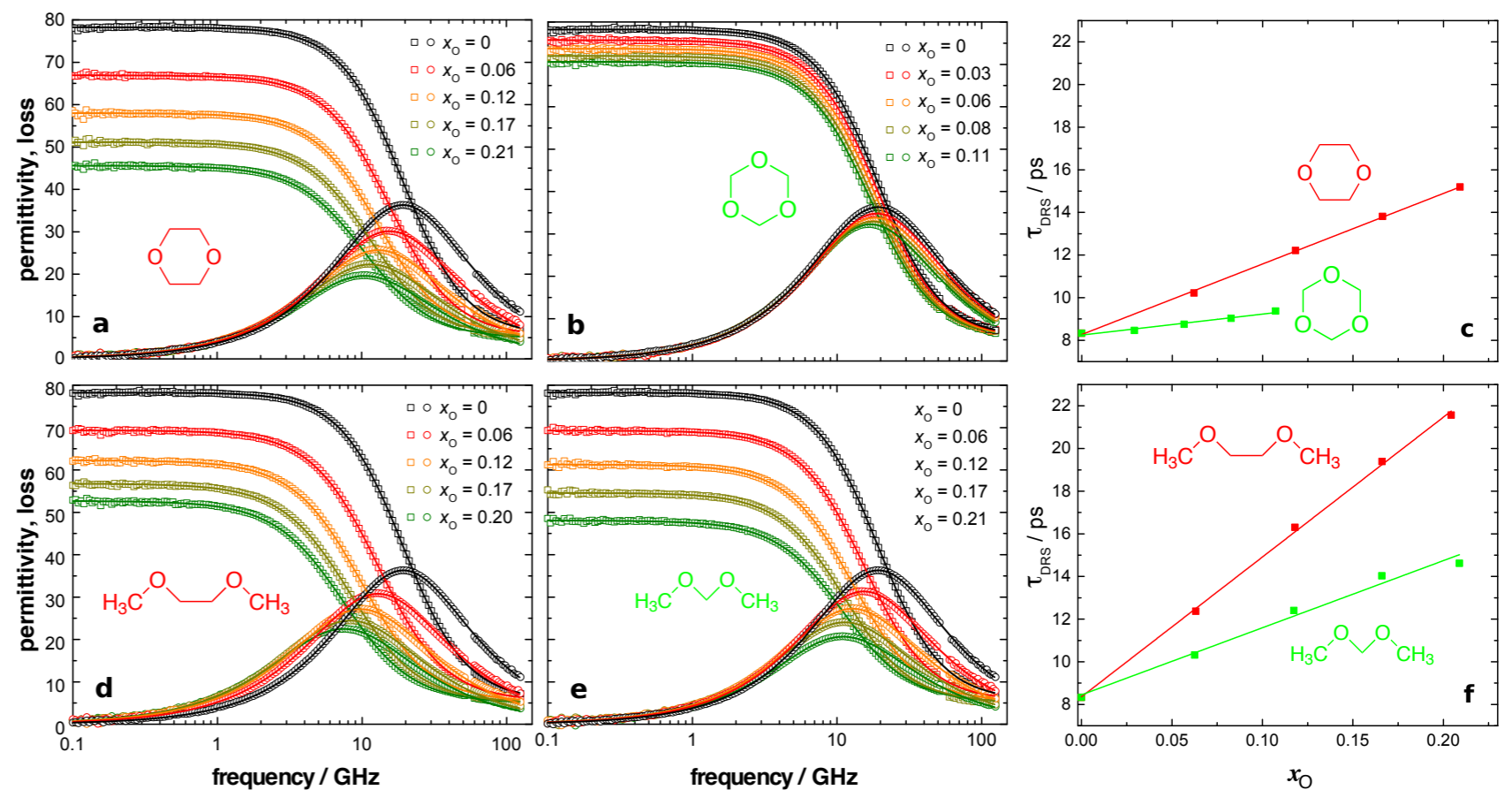
Solubilities of PEG and POM

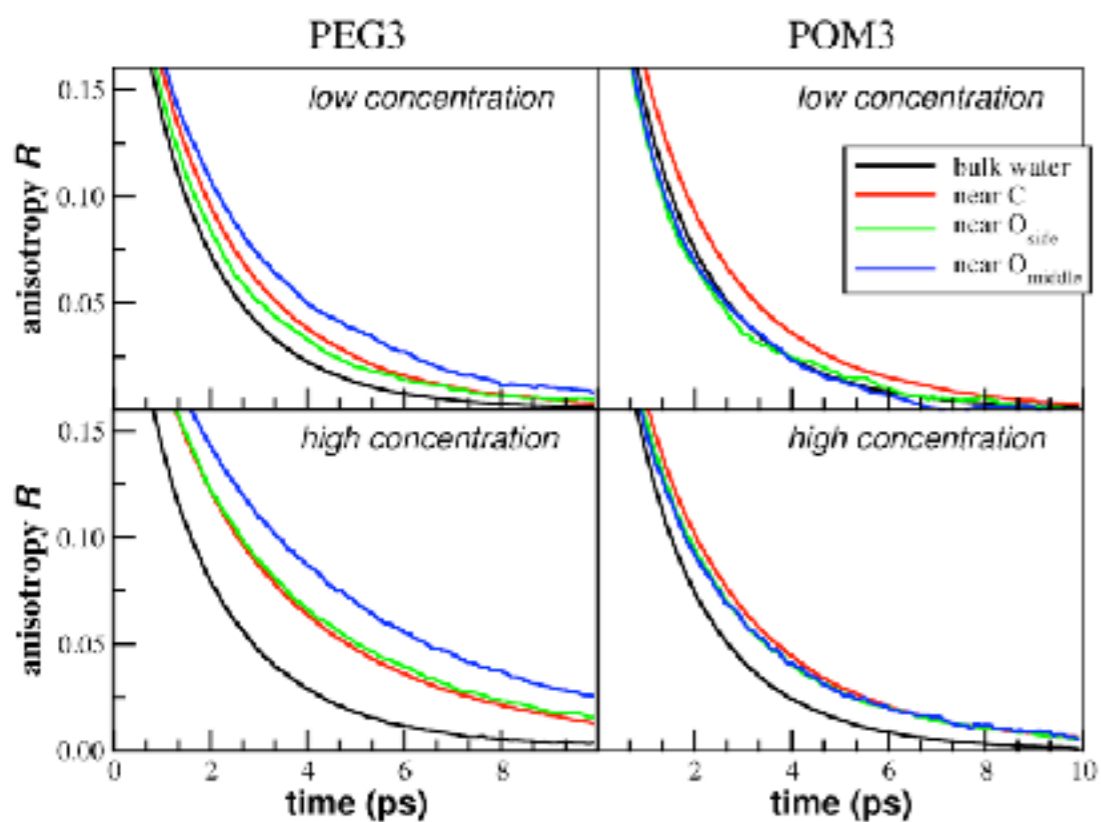
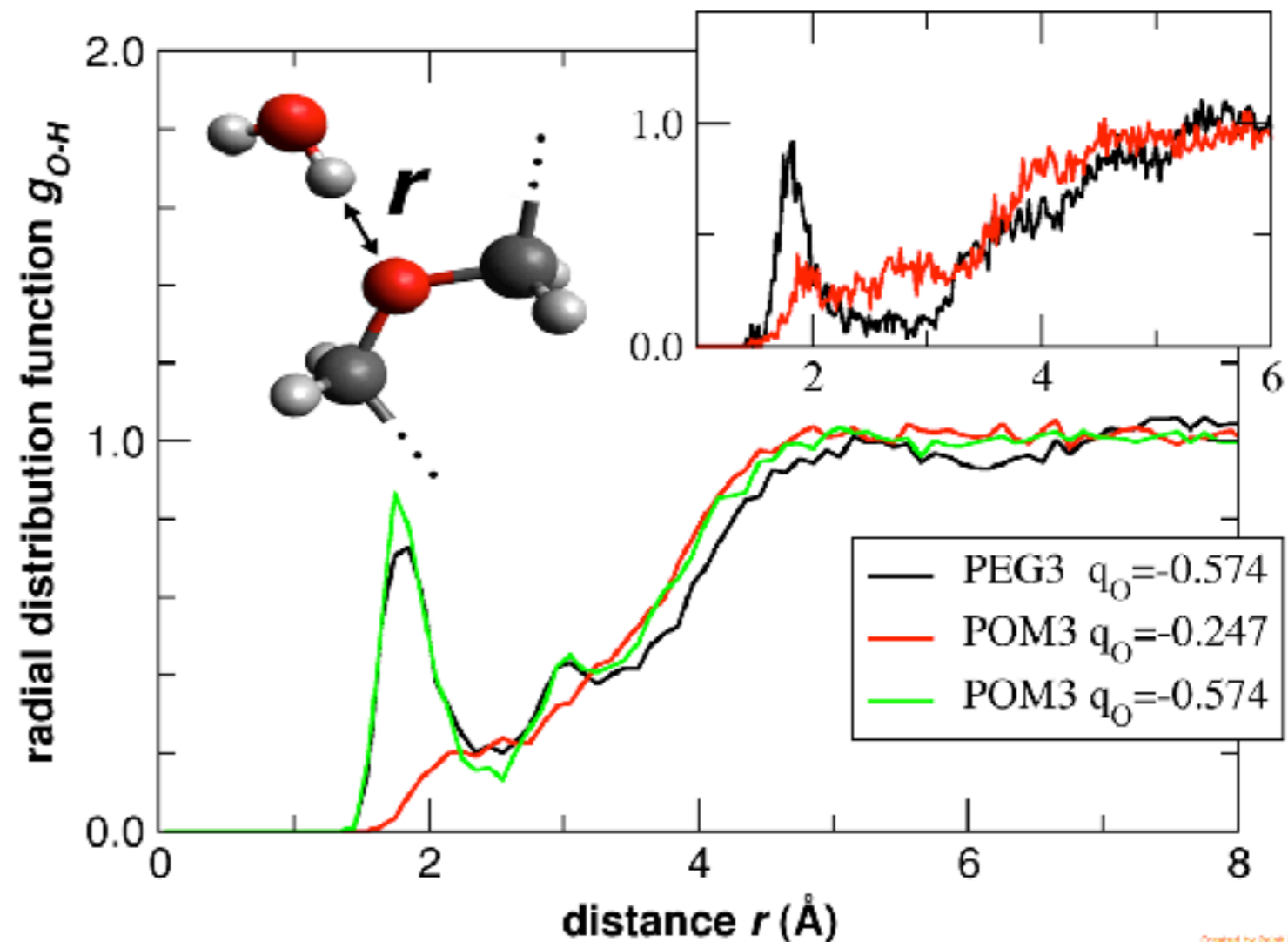
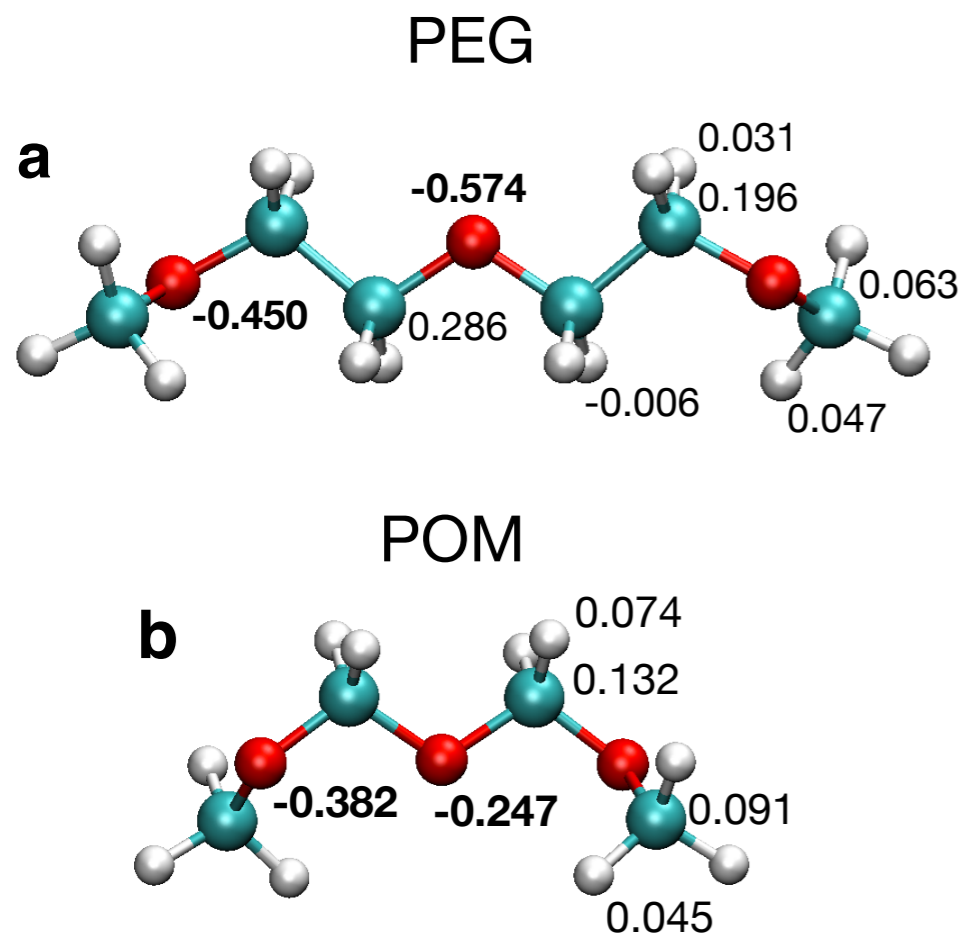


O-D stretch anisotropy decay

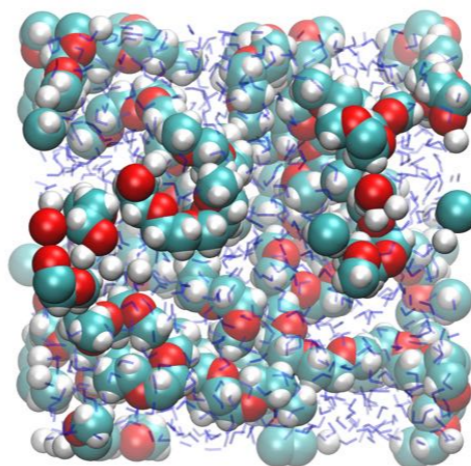


Dielectric permittivity/loss and orientational relaxation times of the water molecules

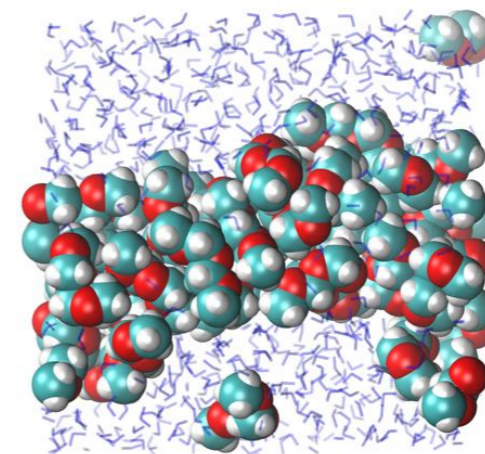




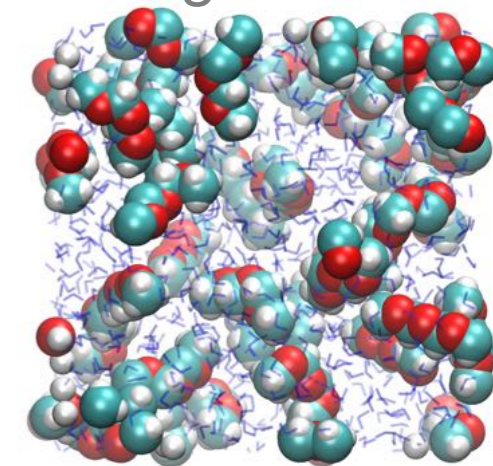
PEG in H_2O :
infinitely
soluble



POM:
completely
insoluble



POM with
PEG's partial
charges

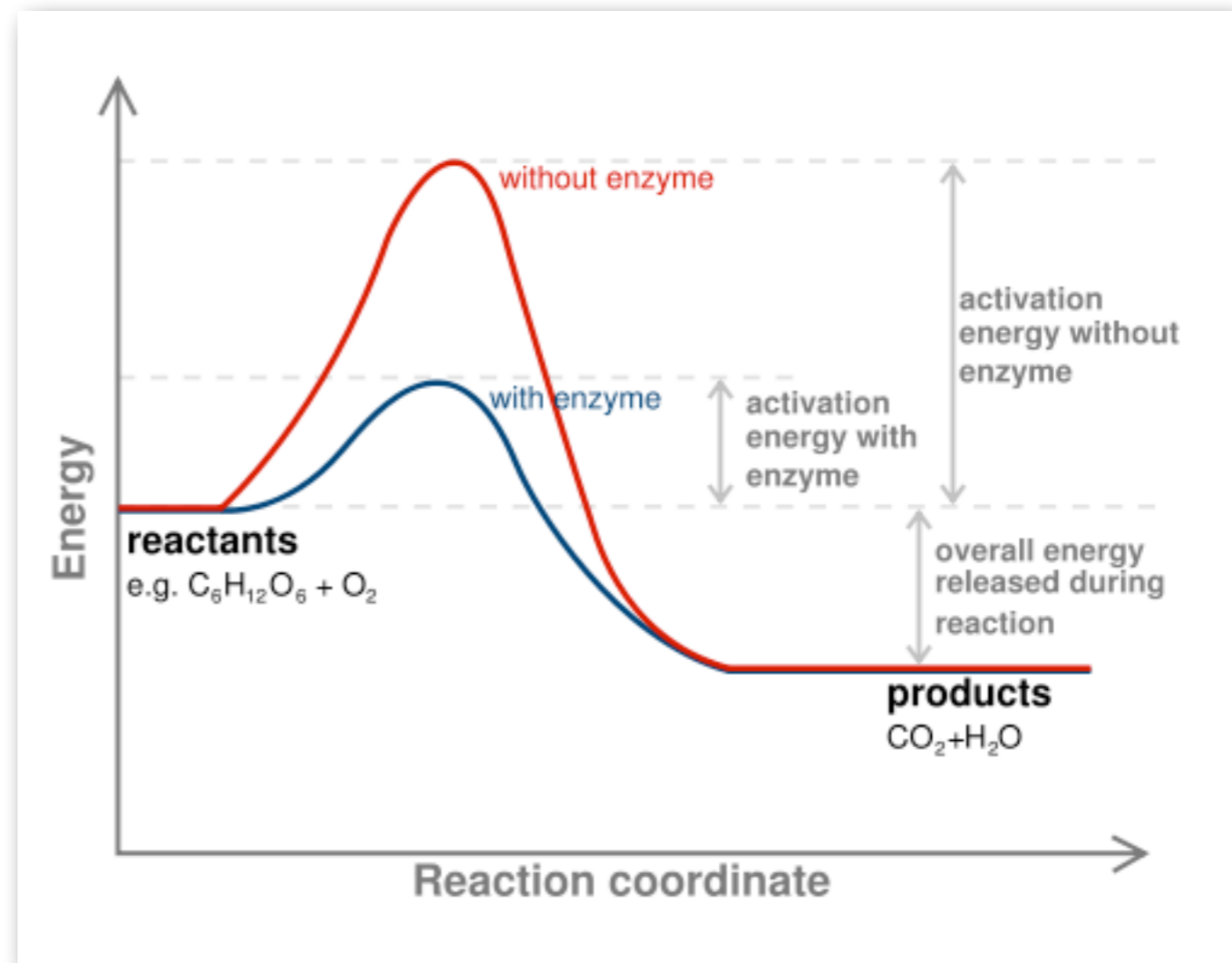


Rare events

In real life (experiment)

- no direct access to free energy
- reaction rate measurement

$$k = k_0 e^{-\Delta G/kT}$$



Rare event simulation

Macroscopic phenomenological theory

Chemical reaction: $A \leftrightarrow B$

$$\frac{dc_A(t)}{dt} = -k_{A \rightarrow B}c_A(t) + k_{B \rightarrow A}c_B(t)$$

$$\frac{dc_B(t)}{dt} = +k_{A \rightarrow B}c_A(t) - k_{B \rightarrow A}c_B(t)$$

Total number of molecules:

$$\frac{d[c_A(t) + c_B(t)]}{dt} = 0$$

Equilibrium:

$$\frac{dc_A(t)}{dt} = \frac{dc_B(t)}{dt} = 0 \quad \frac{\langle c_A \rangle}{\langle c_B \rangle} = \frac{k_{B \rightarrow A}}{k_{A \rightarrow B}}$$

Rare event simulation

Macroscopic phenomenological theory

Make a small perturbation:

$$c_A(t) = \langle c_A \rangle + \Delta c_A(t) \quad c_B(t) = \langle c_B \rangle + \Delta c_B(t)$$

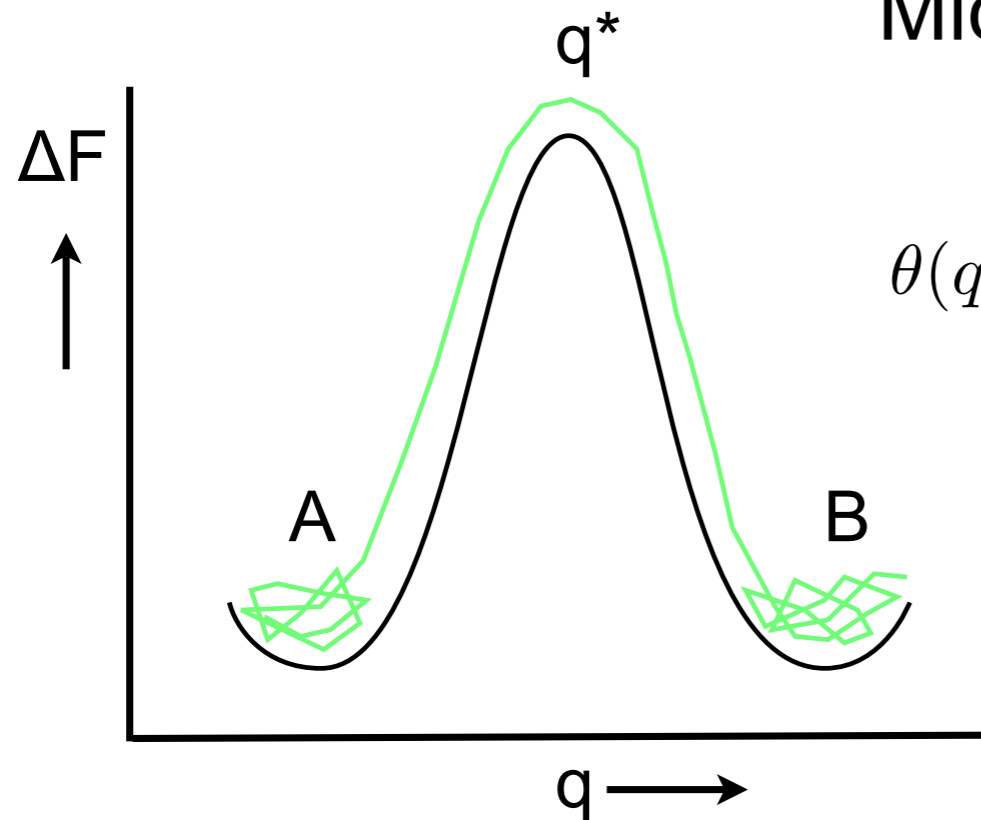
$$\frac{d\Delta c_A(t)}{dt} = -k_{A \rightarrow B} \Delta c_A(t) - k_{B \rightarrow A} \Delta c_A(t)$$

$$\begin{aligned} \Delta c_A(t) &= \Delta c_A(0) \exp[-(k_{A \rightarrow B} + k_{B \rightarrow A})t] \\ &= \Delta c_A(0) \exp[-t/\tau] \end{aligned}$$

$$\begin{aligned} \tau &= (k_{A \rightarrow B} + k_{B \rightarrow A})^{-1} \\ &= k_{A \rightarrow B}^{-1} \left(1 + \langle c_A \rangle / \langle c_B \rangle\right)^{-1} = \frac{\langle c_B \rangle}{k_{A \rightarrow B}} \end{aligned}$$

Rare event simulation

Microscopic linear response theory



$$\theta(q - q^*) = \begin{cases} 0 & \text{if } q - q^* < 0 \quad (\text{Reactant A}) \\ 1 & \text{if } q - q^* > 0 \quad (\text{Product B}) \end{cases}$$

Perturbation

add bias to increase concentration c_A

$$H = H_0 - \epsilon g_A(q - q^*)$$

$$g_A(q - q^*) = 1 - \theta(q - q^*) = \theta(q^* - q)$$

$$\Delta c_A = \langle c_A \rangle_\epsilon - \langle c_A \rangle_0$$

$$\Delta c_A = \langle g_A \rangle_\epsilon - \langle g_A \rangle_0$$

$\langle g_A \rangle \rightarrow$ probability to be in state A

Linear response theory: static

$$\langle \Delta A \rangle = \langle A \rangle - \langle A \rangle_0 \quad H = H_0 - \epsilon B$$

$$\langle A \rangle_0 = \frac{\int d\Gamma A \exp[-\beta(H_0)]}{\int d\Gamma \exp[-\beta(H_0)]} \quad \langle A \rangle = \frac{\int d\Gamma A \exp[-\beta(H_0 - \epsilon B)]}{\int d\Gamma \exp[-\beta(H_0 - \epsilon B)]}$$

$$\begin{aligned} \left\langle \frac{\partial \Delta A}{\partial \epsilon} \right\rangle &= \frac{\int d\Gamma \beta AB \exp[-\beta(H_0 - \epsilon B)] \int d\Gamma \exp[-\beta(H_0 - \epsilon B)]}{\left\{ \int d\Gamma \exp[-\beta(H_0 - \epsilon B)] \right\}^2} \\ &- \frac{\int d\Gamma A \exp[-\beta(H_0 - \epsilon B)] \int d\Gamma \beta B \exp[-\beta(H_0 - \epsilon B)]}{\left\{ \int d\Gamma \exp[-\beta(H_0 - \epsilon B)] \right\}^2} \\ &= \beta \{ \langle AB \rangle_0 - \langle A \rangle_0 \langle B \rangle_0 \} \end{aligned}$$

Very small perturbation: linear response theory

$$\Delta c_A = \langle g_A \rangle_\epsilon - \langle g_A \rangle_0 \quad H = H_0 - \epsilon g_A(q - q^*)$$

How does the response (Δc) depend on the perturbation ($\Delta \epsilon$)?

$$\begin{aligned} \frac{d\Delta c_A}{d\epsilon} &= \beta \left(\langle (g_A)^2 \rangle_0 - \langle g_A \rangle_0^2 \right) \\ &= \beta \left(\langle g_A \rangle_0 \left(1 - \langle g_A \rangle_0 \right) \right) \\ &= \beta \left(\langle c_A \rangle_0 \left(1 - \langle c_A \rangle_0 \right) \right) = \beta \langle c_A \rangle_0 \langle c_B \rangle_0 \end{aligned}$$

Outside the barrier

$$g_A = 0 \text{ or } 1$$

$$g_A(x)g_A(x) = g_A(x)$$

Switch of the perturbation: dynamic linear response

$$\begin{aligned} \Delta c_A(t) &= \Delta c_A(0) \frac{\Delta g_A(0) \Delta g_A(t)}{\langle c_A \rangle \langle c_B \rangle} \\ &= \Delta c_A(0) \exp[-t/\tau] \end{aligned}$$

holds for sufficiently long times

$$\exp[-t/\tau] = \frac{\langle \Delta g_A(0) \Delta g_A(t) \rangle}{\langle c_A \rangle \langle c_B \rangle}$$

Derivative

$$-\frac{1}{\tau} \exp[-t/\tau] = \frac{\langle g_A(0) \dot{g}_A(t) \rangle}{\langle c_A \rangle \langle c_B \rangle} = \frac{\langle \dot{g}_A(0) g_A(t) \rangle}{\langle c_A \rangle \langle c_B \rangle}$$

Δ has disappeared
because of derivative

For sufficiently short t

$$k_{A \rightarrow B}(t) = \frac{\langle \dot{g}_A(0) g_A(t) \rangle}{\langle c_A \rangle}$$

$$\dot{g}_A(q - q^*) = \dot{q} \frac{\partial g_A(q - q^*)}{\partial q} = -\dot{q} \frac{\partial g_B(q - q^*)}{\partial q}$$

$$k_{a \rightarrow B}(t) = \frac{\left\langle \dot{q}(0) \frac{\partial g_B(q(0) - q^*)}{\partial q} g_B(t) \right\rangle}{\langle c_A \rangle}$$

Stationary

$$\frac{d}{dt} \langle A(t)B(t+t') \rangle = 0$$

$$\langle A(t)\dot{B}(t+t') \rangle + \langle \dot{A}(t)B(t+t') \rangle = 0$$

$$\langle A(t)\dot{B}(t+t') \rangle = -\langle \dot{A}(t)B(t+t') \rangle$$

Eyring's transition state theory

$$\begin{aligned}
 k_{a \rightarrow B}(t) &= \frac{\left\langle \dot{q}(0) \frac{\partial g_B(q(0) - q^*)}{\partial q} g_B(t) \right\rangle}{\langle c_A \rangle} \\
 &= \frac{\langle \dot{q}(0) \delta(q(0) - q^*) \theta(q(t) - q^*) \rangle}{\langle \theta(q^* - q) \rangle}
 \end{aligned}$$

Correlation between velocity of states that are at the top of the barrier at $t=0$ and in the product state B some time t later.

Let us consider the limit $t \rightarrow 0^+$:

$$\begin{aligned}
 \lim_{t \rightarrow 0^+} &= \theta(q(t) - q^*) = \theta(\dot{q}(t)) \\
 k_{a \rightarrow B}^{\text{TST}}(t) &= \frac{\langle \dot{q}(0) \delta(q(0) - q^*) \theta(\dot{q}) \rangle}{\langle \theta(q^* - q) \rangle}
 \end{aligned}$$

Bennett-Chandler approach

(or Reactive flux method)

$$k_{a \rightarrow B}(t) = \frac{\langle \dot{q}(0) \delta(q(0) - q^*) \theta(q(t) - q^*) \rangle}{\langle \theta(q^* - q) \rangle}$$

$$k_{a \rightarrow B}(t) = \frac{\langle \dot{q}(0) \delta(q(0) - q^*) \theta(q(t) - q^*) \rangle}{\langle \delta(q(0) - q^*) \rangle} \times \frac{\delta(q(0) - q^*)}{\theta(q^* - q)}$$

Conditional average: $\dot{q}(0) \theta(q(t) - q^*)$
given that we start on top of barrier

Probability to find q
on barrier top

Computational scheme:

- Determine the probability with free energy calculation
- Compute conditional average from “shooting” trajectories from barrier top

Summary

- The structure of matter and fluids is governed by interactions between particles, which causes **spatial correlations**.
- The best known is the pair-correlation function, or **radial distribution function**, which can be obtained from MD or MC simulation, neutron or X-ray diffraction, or microscopy.
- Dynamics can be probed by **time-correlation functions**.
- **Green-Kubo relations** connect macroscopic transport properties to microscopic time correlation functions.
- The orientational dynamics of water molecules in solutions can be captured by the decay of the dipole auto-correlation function.
- The Bennett-Chandler approach, or **reactive flux method**, allows for accurate estimation of reaction rates, by combining a **free energy calculation** (giving the transition state theory estimate of the rate) with a correction using the **transmission coefficient**.