Theory of solvent effects

Han-sur-Lesse, 12-16 December 2016
Bernd Ensing

Contents

1. Intro: what about solvent effects?
2. Fundamentals: Permittivity, dielectric media
3. Implicit solvation: Continuum models, PCM, COSMO,…
4. Explicit solvation: Ewald summation
5. Thermodynamic properties of liquids from the PT2 model
6. Measurements and modelling of anisotropy relaxation

The role of the solvent

Solvent is a medium in which solute molecules can diffuse, interact and undergo molecular transitions

As an innocent bystander (weakly interacting with solutes)

- controlling solute diffusion
- thermostatting solute collisions/interactions

As an interacting medium, affecting relative stabilities of species

- hydrophobic/hydrophilic interaction, surfactant self-assembly, protein folding
- controlling morphology of macromolecules (theta solvent)
- influencing chemical equilibria, (de-)stabilising transition states
- affecting dynamics through friction/viscosity

As an active participant in molecules processes

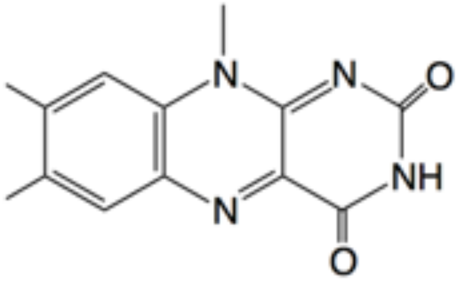
- acid-base chemistry, proton transfer
- redox chemistry, electron transfer
- ligating transition metal complexes/catalysts
- radical chemistry

The influence of solvent on the properties of molecules

Molecular properties are influenced by the molecular environment of a molecule, which is often a solvent. Affected properties include:

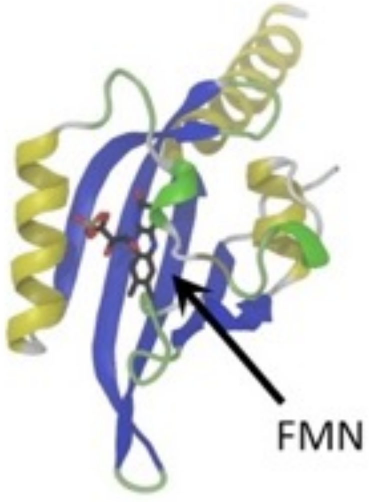
- energy
- geometry
- vibrations
- electronic occupation
- charge distribution
- polarisability
- etc…

Example:
The redox (reduction) potential of a molecule depends strongly on the environment and is very different from the electron affinity.

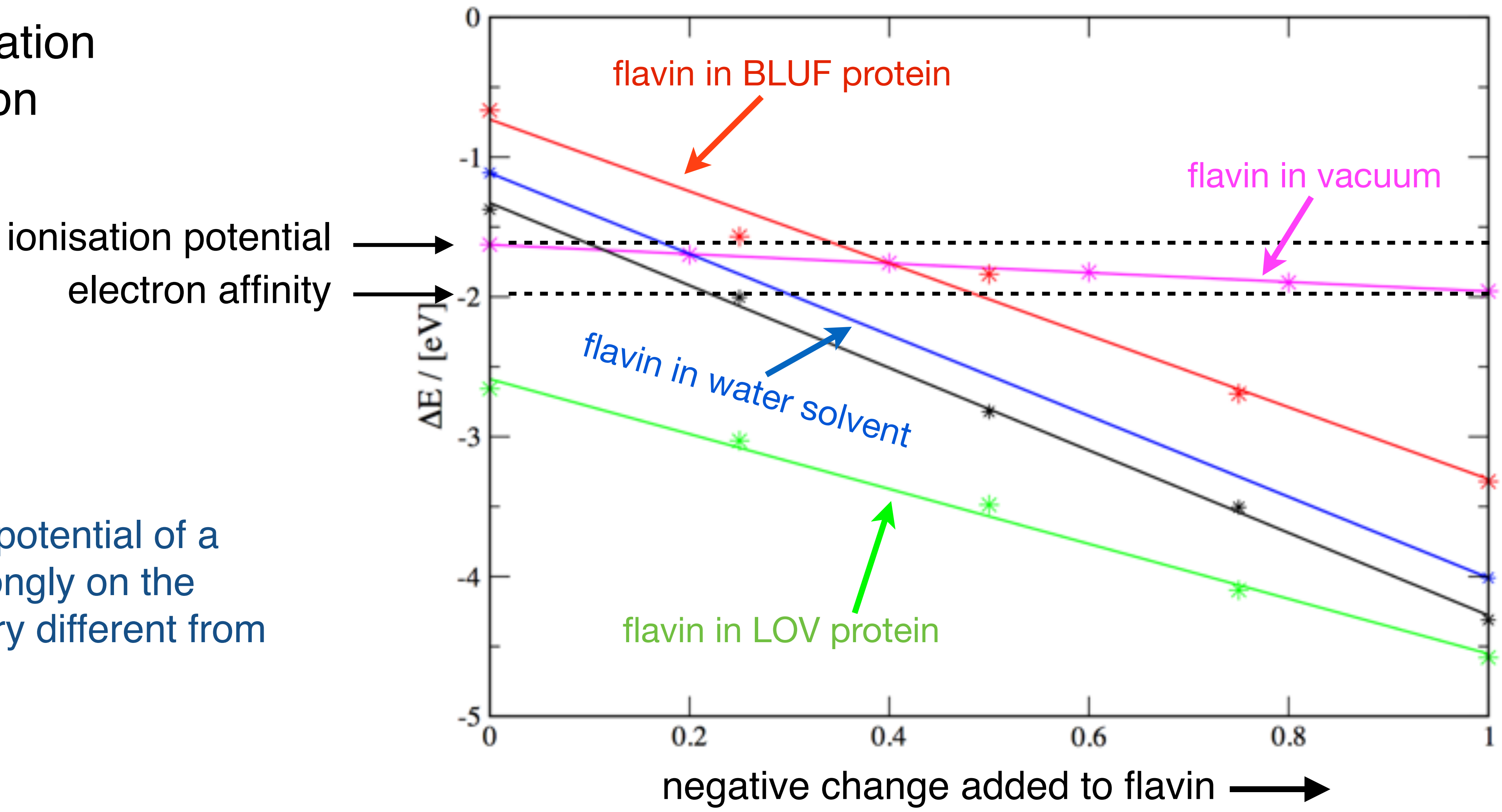


flavin

BLUF protein



LOV protein



The influence of solvent in spectroscopy

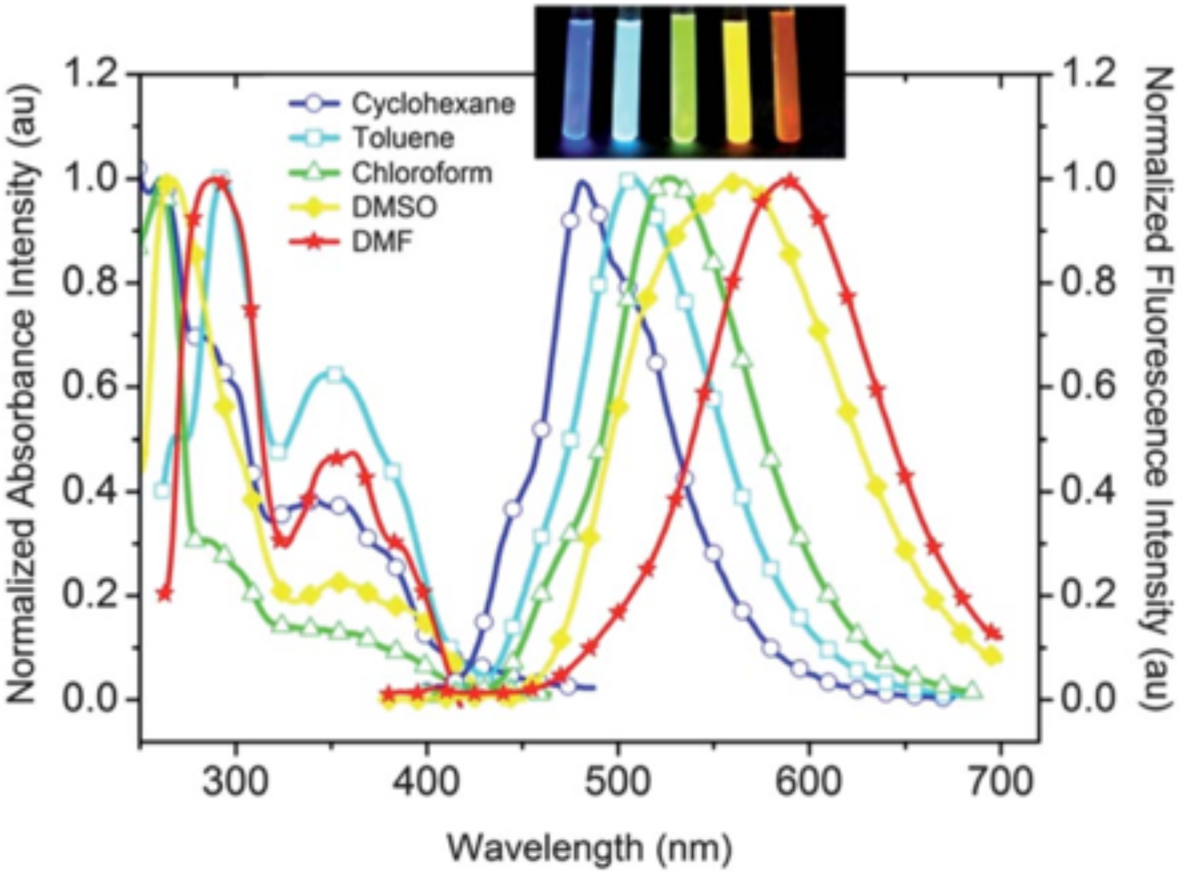
Solvent may affect spectra of IR, Raman, UV/Vis, NMR

Solvatochromism: the ability of a chemical substance to change color due to a change in solvent polarity.

- positive solvatochromism: bathochromic shift (redshift) with increasing solvent polarity
- negative solvatochromism: hypsochromic shift (blue shift) with increasing solvent polarity

9a, $R^1 = R^2 = H$
9b, $R^1 = R^2 = Br$

benzo[a]acridines



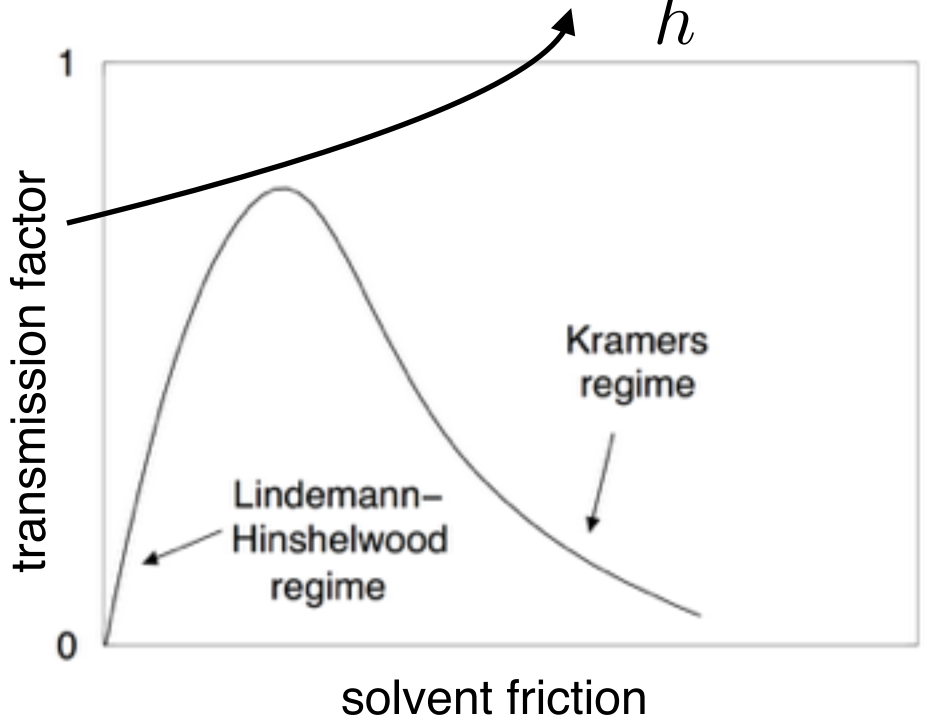
- Non-aggregating solvatochromic bipolar benzo[f]quinolines and benzo[a] acridines for organic electronics
  A Goel, V Kumar, S.P. Singh, A Sharma, S Prakash, C Singhb, R. S. Anand
  J. Mater. Chem. 22, 14880 (2012)
- Pyrene-based D–p–A dyes that exhibit solvatochromism and high fluorescence brightness in apolar solvents and water
  Y. Niko, Y. Cho, S. Kawauchia,G, Konishi
  RSC Adv. 4, 36480 (2014)

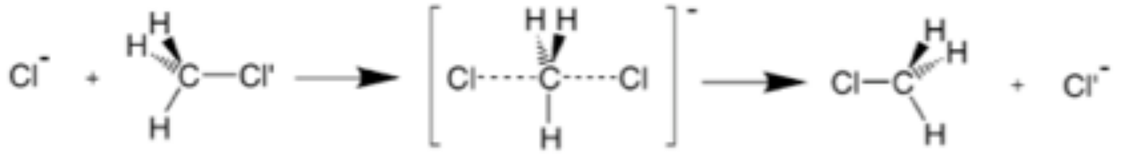
The influence of solvent on chemistry

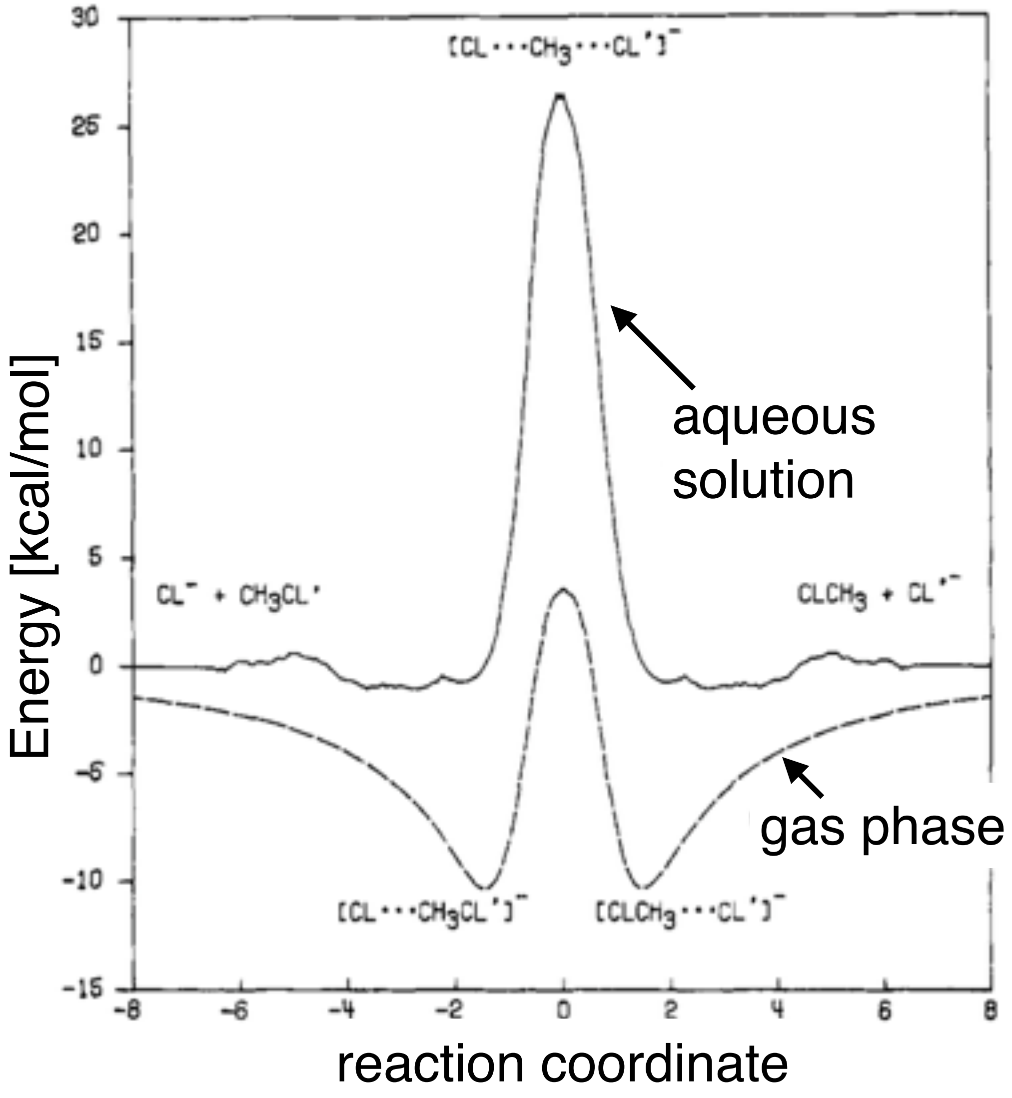
Solvent can have a strong influence on chemical reactions. Solvent interaction affects:

- reaction equilibrium
  different solvation of reactants and products
- reaction rate
  affect stability of the reactant state
  affect the transmission coefficient, barrier crossing probability
- affect the reaction mechanism

Reaction rate: $k = \kappa \frac{k_B T}{h} e^{-\beta \Delta G^{\ddagger}}$







The reaction rate of the S_N2 reaction between chlorine and chloromethane is 13 orders slower in water than in the gas phase.

J. Chandrasekhar, S.F. Smith, W. L. Jorgensen
J. Am. Chem. Soc. 107, 154-163 (1985)

Some terminology

Conductor

- a material through which electric charges can move with little resistance

Insulator

- a material that does not conduct electric charges

Capacitor

- a device that stores electric charge; typically containing two conductors carry opposite charges, separated by a dielectric medium, e.g. vacuum.

Dielectric

- non-conducting material that can store energy by polarisation of molecules; increases capacitor storage.

Polarisability

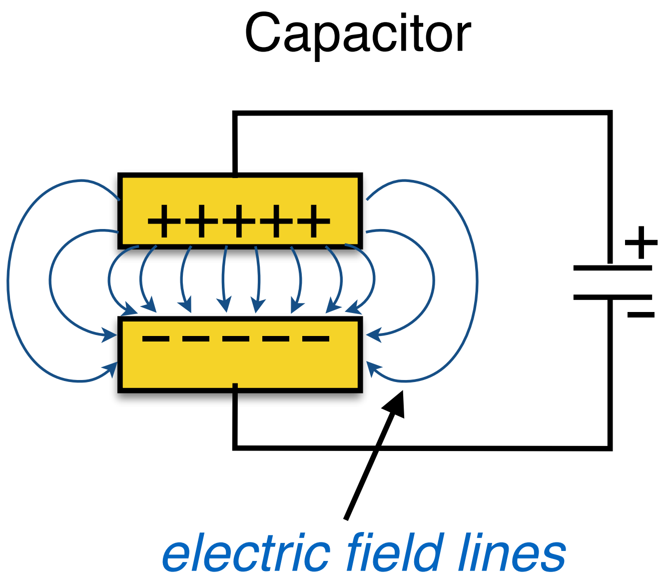
- ability of a molecule to separate positive and negative charge under influence of an electric field

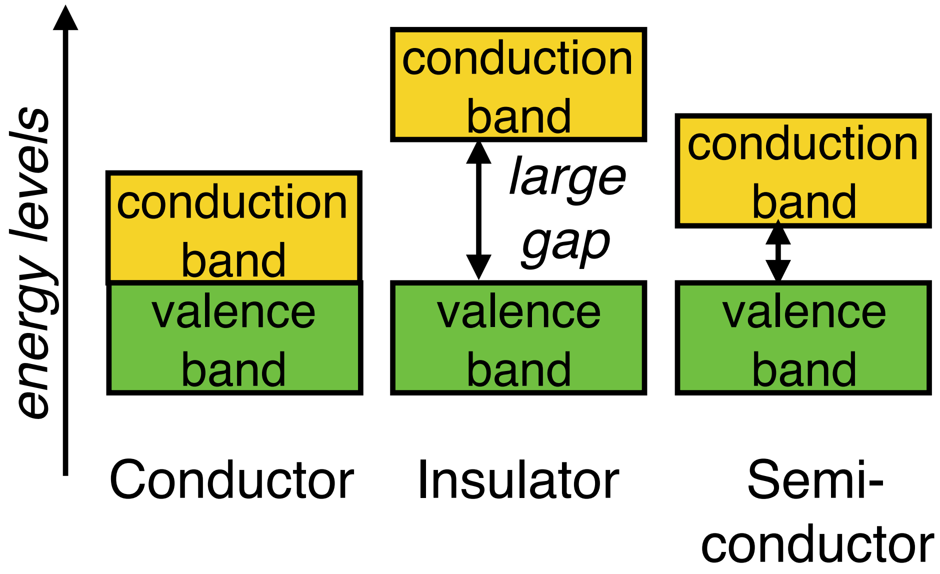
Electric susceptibility

- measure for how easily a material polarises in response of an applied electric field

Relative permittivity

- aka “dielectric contant”, is related to the susceptibility as $\varepsilon_r = \chi_e + 1$. Ability of a material to *resist* an electric field.



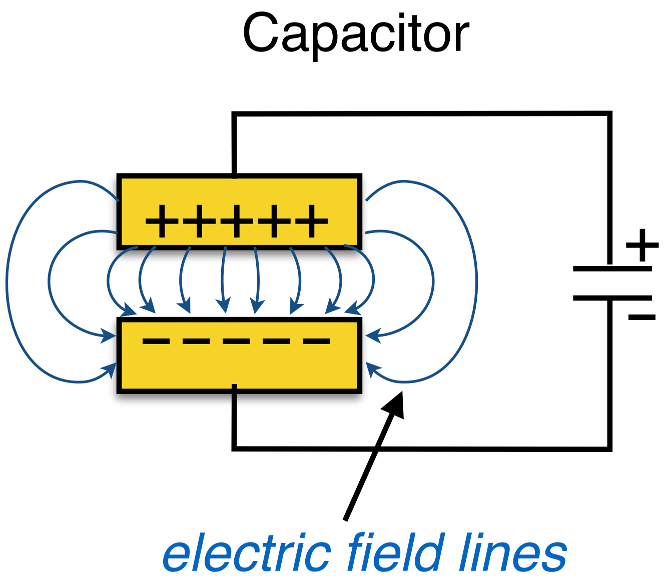


Dielectric materials

The capacitance C increases when a dielectric material is inserted between the charged conductors in a capacitor.

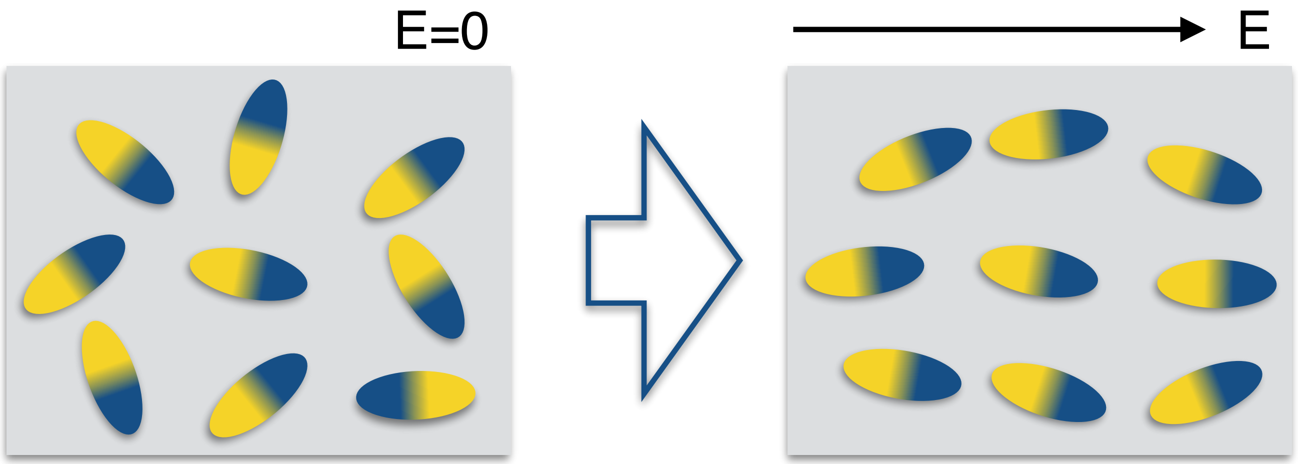
$$C = \epsilon_r C_0$$

- C_0: the capacitance without material between plates
- C: measured capacitance
- ε_r: dielectric constant (>1)

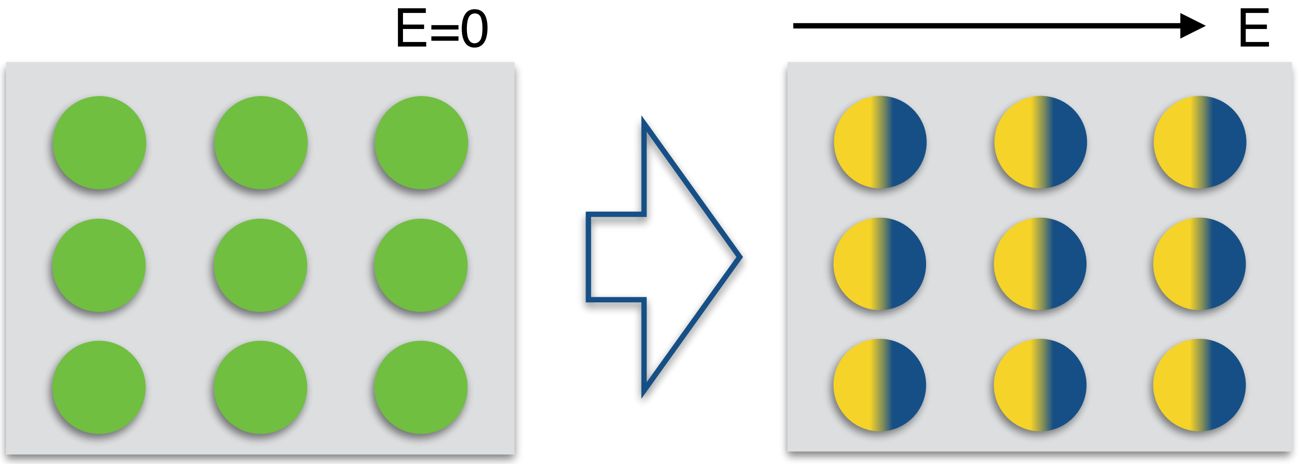


Material	ε_r	Dielectric strength (10^6 V/m)
Air	1.00059	3
Paper	3.7	16
Glass	4–6	9
Water	80	–

Orientation of polar molecules:



Charge redistribution within molecules, inducing dipoles:

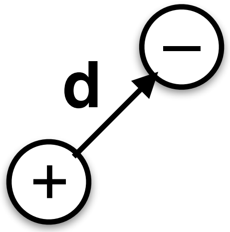


Static dielectrics

A medium of permanent or induced dipoles has a polarisation density **P**, which is the dipole moment per unit volume:

$$\mathbf{P} = \lim_{\Delta V \to 0} \frac{1}{\Delta V} \sum_{i=1}^{n\Delta V} \mathbf{p}_i$$

[C / m^2]



$$\mathbf{p} = q\mathbf{d}$$

dipole moment
[coulomb meter]

$$\mathbf{p} = \alpha \mathbf{E}$$

induced dipole moment

- α is the polarisability

Without an external electric field **E**, the dipoles are oriented randomly and the polarisation density **P** is zero.

The relation between the field **E**, and the polarisation density **P**, for an isotropic and linear dielectric:

$$\mathbf{P} = \chi_e \epsilon_0 \mathbf{E}$$

vacuum permittivity
ε_0=8.8541878176…10^{-12} [F/m]

electric susceptibility [dimensionless]

- linear dielectrics obey this relation
- **P** and **E** not in same direction for anisotropic materials (e.g. crystalline materials)
- ferroelectrics are non-linear and show hysteresis

The electric displacement **D** is related to the polarisation density as:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0(\chi_\mathbf{e} + 1)\mathbf{E} = \epsilon_r \epsilon_0 \mathbf{E}$$

relative permittivity [-]

Connection to speed of light and vacuum permeability:

$$\epsilon_0 = (c^2 \mu_0)^{-1}$$

The aligned dipoles in the material cause a field counteracting the externally applied field:

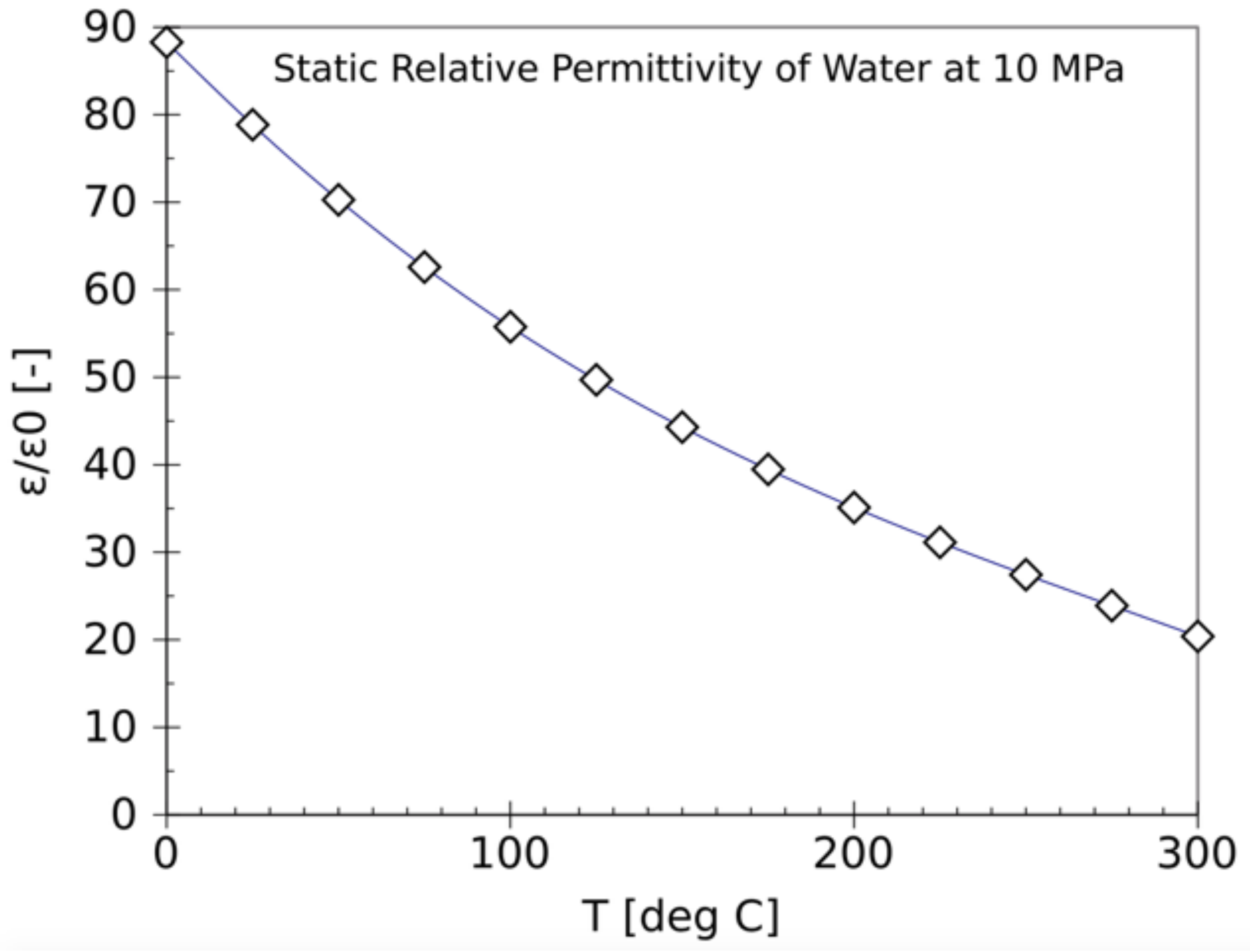
induced field

$$\mathbf{E} = \mathbf{E}_\text{ext} + \mathbf{E}_\text{pot} = \mathbf{E}_\text{ext} - \mathbf{P}/\epsilon_\mathbf{0} \longrightarrow \mathbf{E} = \mathbf{E}_\text{ext}/\epsilon_r$$

The field in the material is reduced.
(e.g. ε = 80 for water)
- in capacitor: $C = \epsilon_r C_0$

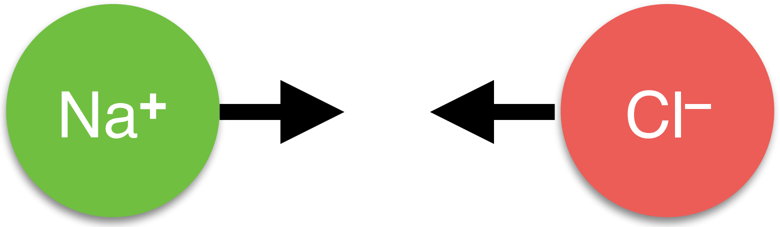
Dielectric constant of water

Why is the permittivity temperature dependent?

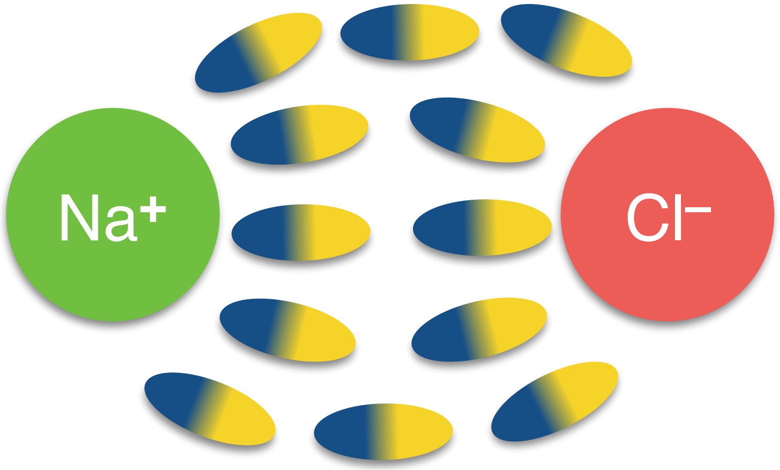


How does solvent screening work?

Two opposite charges in vacuum attract each other.



Polar solvent *in between* the ions are polarised, but do not reduce (screen) the attraction.



Think of the dielectric material in between the capacitor plates, it *enhances* attraction and capacitance!

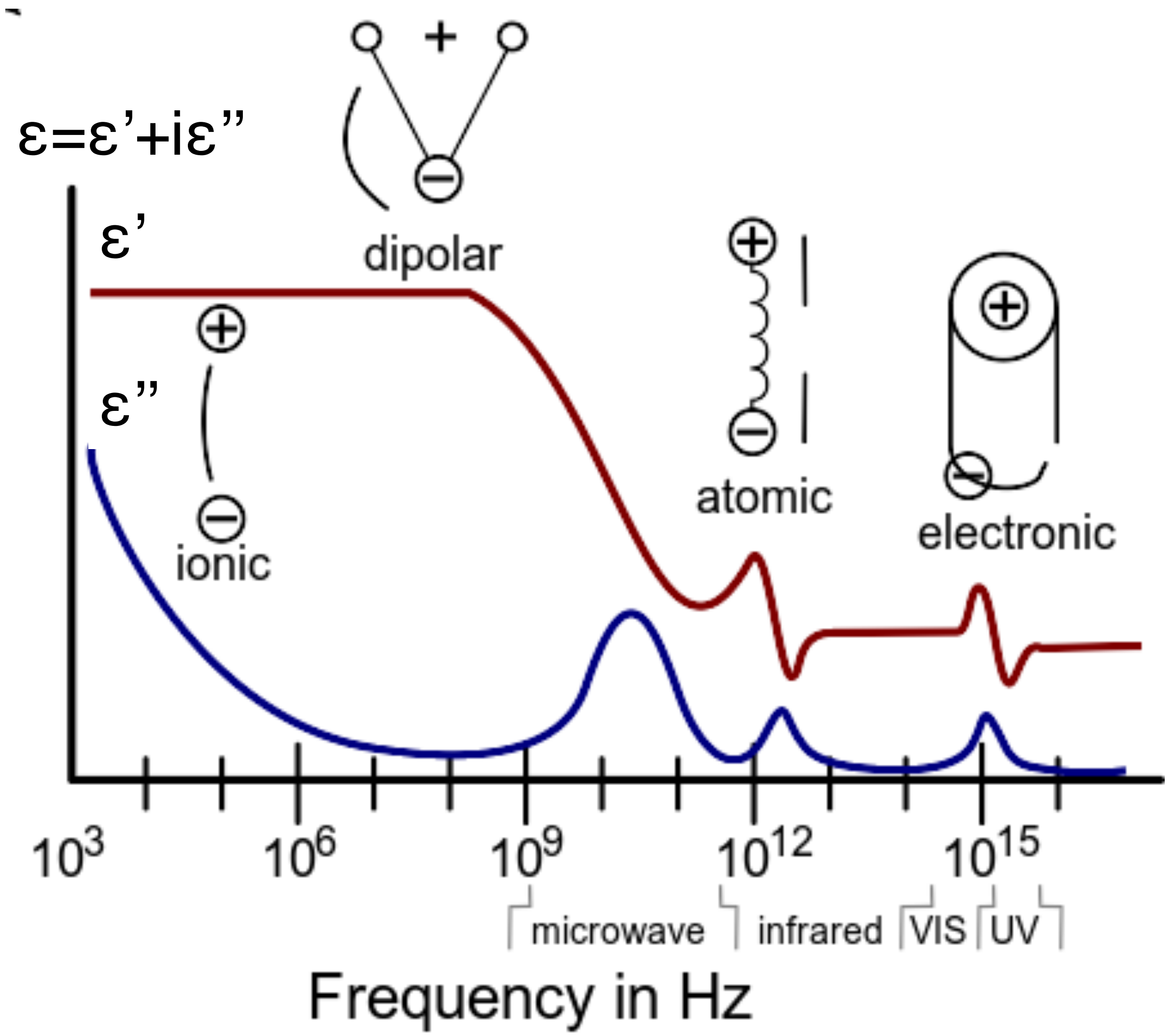
Polar solvent *outside* the ions are polarised, which do reduce (screen) the attraction.

There is more polarised solvent outside the ion pair than in between! This excess explains the screening effect.

Dynamics of dielectrics

A material cannot polarise instantaneously in response of an applied field.

Frequency dependence of dielectric response (figure from Wikipedia)



Dielectric dispersion:

- as the frequency of the applied field increases, polarisation processes stop to follow the oscillations in the order:

  1. ionic motions
  2. orientation of dipoles (microwave)
  3. atomic motions ((far-)infrared)
  4. electronic motions (UV/Vis)

- above ultraviolet, only ε_0 remains.

Polarisation is a convolution of the *past* electric field and the time-dependent susceptibility:

$$\mathbf{P}(t) = \epsilon_0 \int_{-\infty}^{t} \chi_e(t-t')\mathbf{E}(t')dt'$$

Fourier transform of linear system:

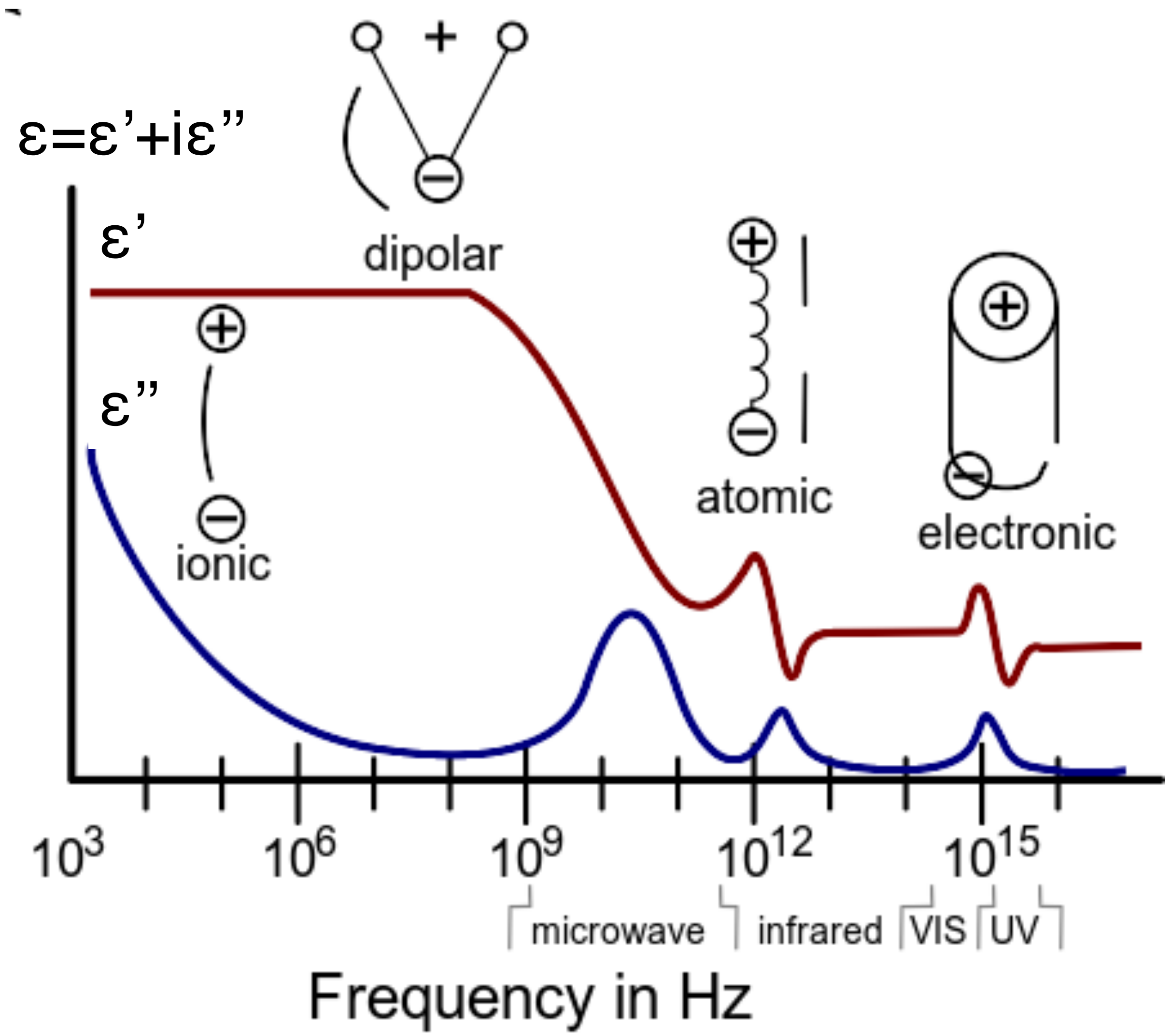
$$\mathbf{P}(\omega) = \epsilon_0 \chi_e(\omega)\mathbf{E}(\omega)$$

Link to causality: polarisation can only depend on **E** of previous times

Dynamics of dielectrics

A material cannot polarise instantaneously in response of an applied field.

Frequency dependence of dielectric response
(figure from Wikipedia)



(microwave oven frequency: 2.45 GHz)

The response *caused* by the field is represented by a phase shift.

Treat permittivity as a complex function of frequency:

$$D_0 e^{-i\omega t} = \hat{\epsilon}(\omega) E_0 e^{-i\omega t}$$

D₀ amount of displacement
E₀ amplitude of electric field
i = √–1

Static limit: $\epsilon_s = \lim_{\omega \to 0} \hat{\epsilon}(\omega)$

High frequency limit: ϵ_∞

ε' : energy stored in medium
ε": energy dissipated in medium

$$\hat{\epsilon}(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = \frac{D_0}{E_0}(\cos\theta + i\sin\theta)$$

ε"/ε' = 0 : perfect lossless dielectric
ε"/ε' = ∞ : perfect conductor

Debye relaxation

The Debye equations describe the dielectric behaviour of (ideal, non-interacting) dipoles as a function of frequency:

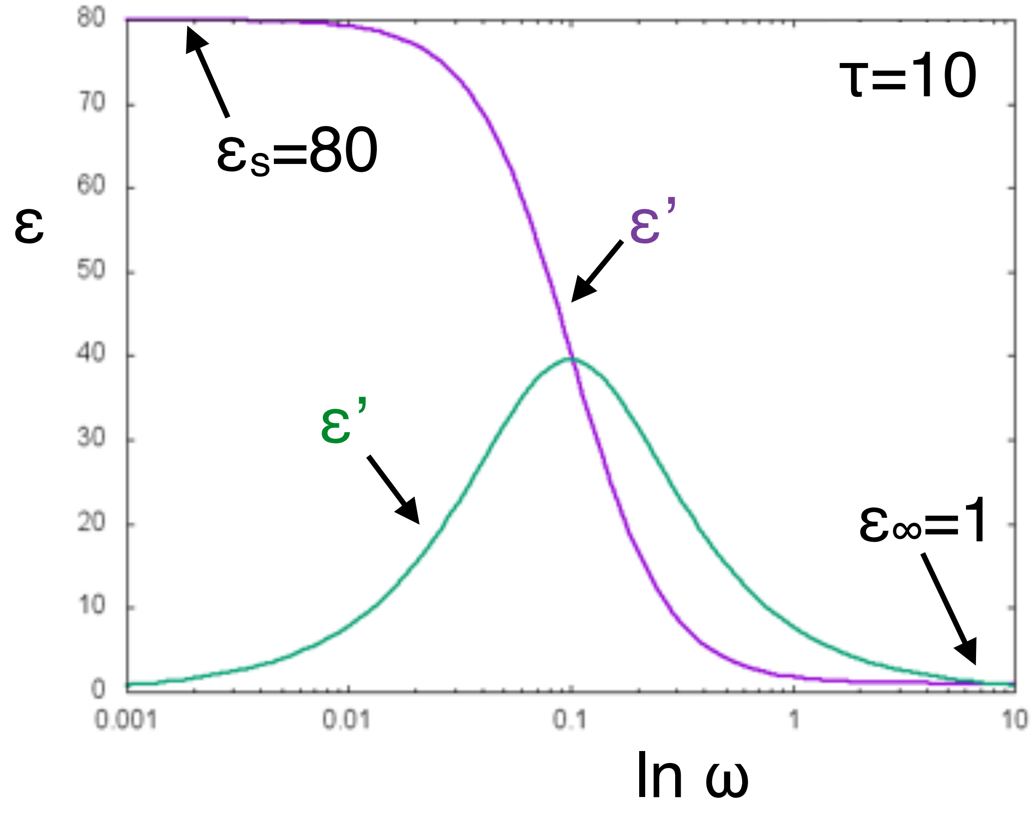
$$\epsilon'(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1+\omega^2\tau^2}$$

$$\epsilon''(\omega) = \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{1+\omega^2\tau^2}$$

Peter Debye
1884–1966
Chemistry Nobel prize (1936)

Static limit: $\epsilon_s = \lim_{\omega \to 0} \hat{\epsilon}(\omega)$

High frequency limit: ϵ_∞



- small $\omega\tau$: $\varepsilon' \longrightarrow \varepsilon_s$
- large $\omega\tau$: $\varepsilon' \longrightarrow \varepsilon_\infty$
- at $\omega\tau=1$: $\varepsilon'=(\varepsilon_s+\varepsilon_\infty)/2$
- ε'' peak at $\omega\tau=1$

Modifications to Debye model:
- Cole-cole model
- Cole-Davidson model
- Havriliak-Negami relaxation
- …

Water models

Dielectric constant computed:

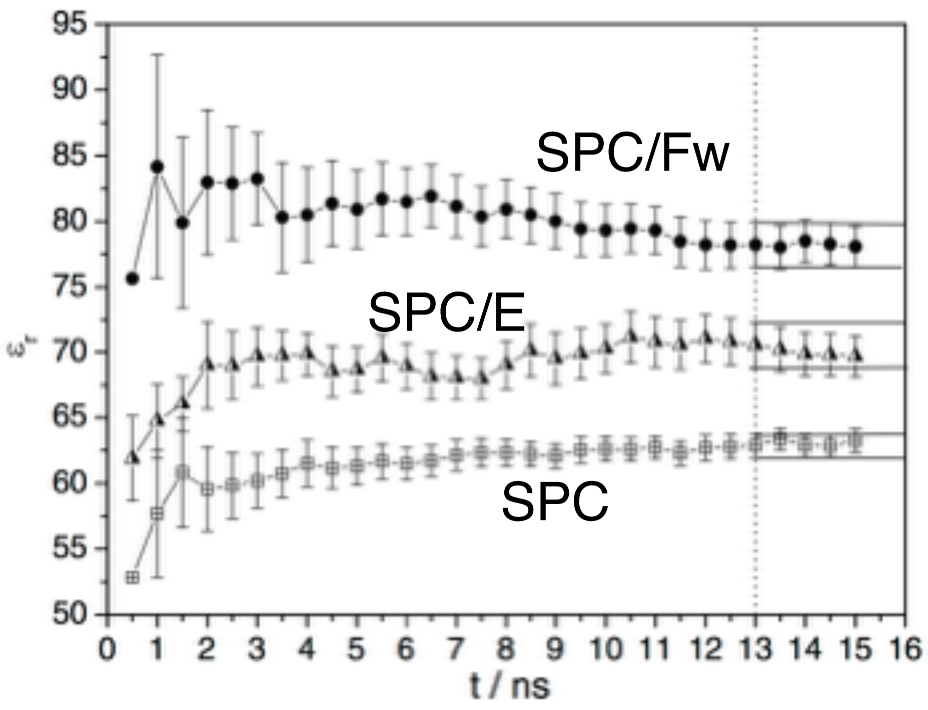
- Forcefield MD
- NVT ensemble
- 400 molecules
- PBC/Ewald

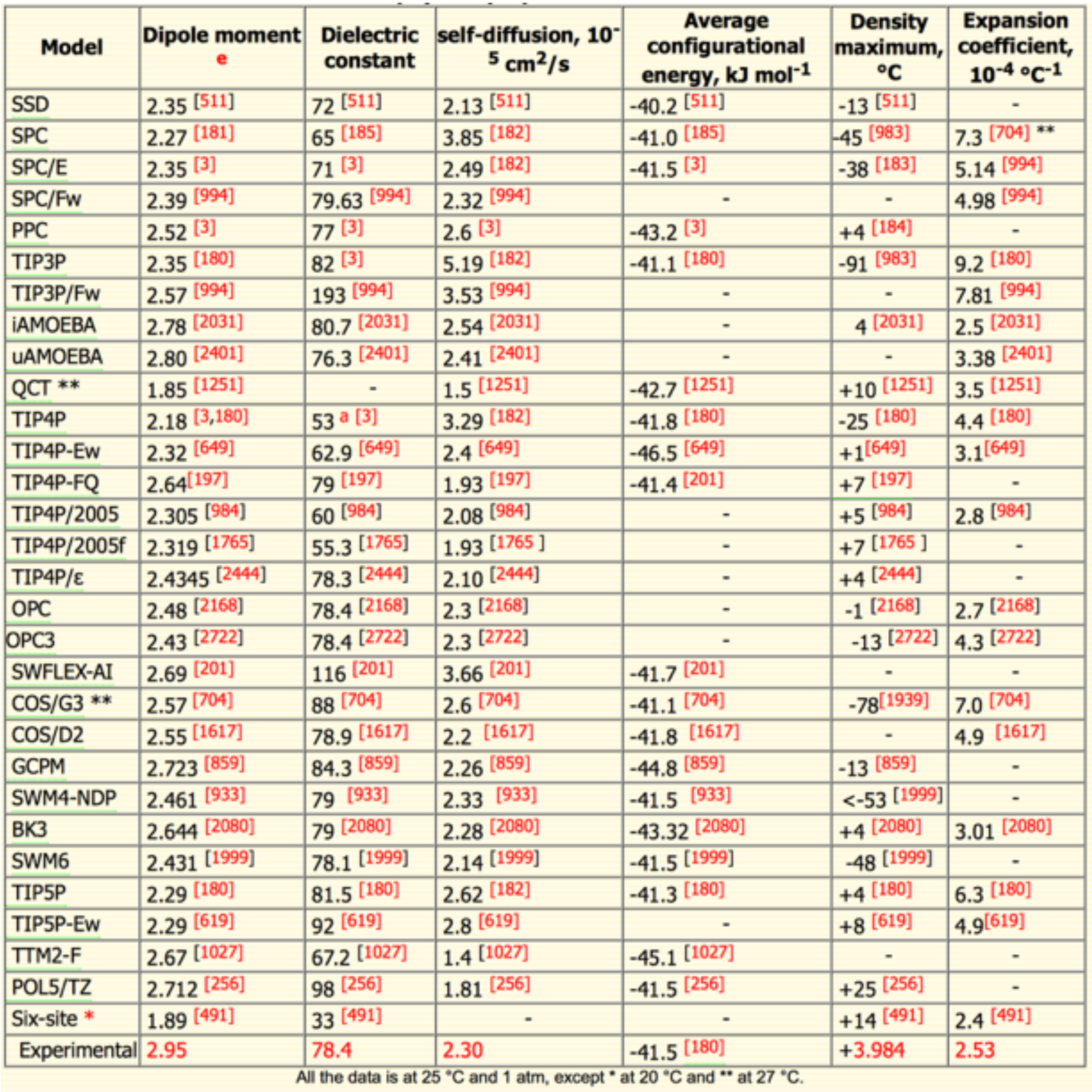
Dielectric constant from fluctuations:

$$\epsilon_\tau = 1 + \frac{4\pi}{3Vk_BT}\left(\langle M^2\rangle - \langle M\rangle^2\right)$$

- < > : ensemble average
- Total dipole moment: $\mathbf{M} = \sum_i^N \mathbf{p}_i$

Global properties converge slowly:





Model	Dipole moment e	Dielectric constant	self-diffusion, 10^{-5} cm^2/s	Average configurational energy, kJ mol^{-1}	Density maximum, °C	Expansion coefficient, 10^{-4} °C^{-1}
SSD	2.35 [511]	72 [511]	2.13 [511]	-40.2 [511]	-13 [511]	-
SPC	2.27 [181]	65 [185]	3.85 [182]	-41.0 [185]	-45 [983]	7.3 [704] **
SPC/E	2.35 [3]	71 [3]	2.49 [182]	-41.5 [3]	-38 [183]	5.14 [994]
SPC/Fw	2.39 [994]	79.63 [994]	2.32 [994]	-	-	4.98 [994]
PPC	2.52 [3]	77 [3]	2.6 [3]	-43.2 [3]	+4 [184]	-
TIP3P	2.35 [180]	82 [3]	5.19 [182]	-41.1 [180]	-91 [983]	9.2 [180]
TIP3P/Fw	2.57 [994]	193 [994]	3.53 [994]	-	-	7.81 [994]
iAMOEBA	2.78 [2031]	80.7 [2031]	2.54 [2031]	-	4 [2031]	2.5 [2031]
uAMOEBA	2.80 [2401]	76.3 [2401]	2.41 [2401]	-	-	3.38 [2401]
QCT **	1.85 [1251]	-	1.5 [1251]	-42.7 [1251]	+10 [1251]	3.5 [1251]
TIP4P	2.18 [3,180]	53 [a] [3]	3.29 [182]	-41.8 [180]	-25 [180]	4.4 [180]
TIP4P-Ew	2.32 [649]	62.9 [649]	2.4 [649]	-46.5 [649]	+1[649]	3.1[649]
TIP4P-FQ	2.64[197]	79 [197]	1.93 [197]	-41.4 [201]	+7 [197]	-
TIP4P/2005	2.305 [984]	60 [984]	2.08 [984]	-	+5 [984]	2.8 [984]
TIP4P/2005f	2.319 [1765]	55.3 [1765]	1.93 [1765]	-	+7 [1765]	-
TIP4P/ε	2.4345 [2444]	78.3 [2444]	2.10 [2444]	-	+4 [2444]	-
OPC	2.48 [2168]	78.4 [2168]	2.3 [2168]	-	-1 [2168]	2.7 [2168]
OPC3	2.43 [2722]	78.4 [2722]	2.3 [2722]	-	-13 [2722]	4.3 [2722]
SWFLEX-AI	2.69 [201]	116 [201]	3.66 [201]	-41.7 [201]	-	-
COS/G3 **	2.57 [704]	88 [704]	2.6 [704]	-41.1 [704]	-78[1939]	7.0 [704]
COS/D2	2.55 [1617]	78.9 [1617]	2.2 [1617]	-41.8 [1617]	-	4.9 [1617]
GCPM	2.723 [859]	84.3 [859]	2.26 [859]	-44.8 [859]	-13 [859]	-
SWM4-NDP	2.461 [933]	79 [933]	2.33 [933]	-41.5 [933]	<-53 [1999]	-
BK3	2.644 [2080]	79 [2080]	2.28 [2080]	-43.32 [2080]	+4 [2080]	3.01 [2080]
SWM6	2.431 [1999]	78.1 [1999]	2.14 [1999]	-41.5 [1999]	-48 [1999]	-
TIP5P	2.29 [180]	81.5 [180]	2.62 [182]	-41.3 [180]	+4 [180]	6.3 [180]
TIP5P-Ew	2.29 [619]	92 [619]	2.8 [619]	-	+8 [619]	4.9[619]
TTM2-F	2.67 [1027]	67.2 [1027]	1.4 [1027]	-45.1 [1027]	-	-
POL5/TZ	2.712 [256]	98 [256]	1.81 [256]	-41.5 [256]	+25 [256]	-
Six-site *	1.89 [491]	33 [491]	-	-	+14 [491]	2.4 [491]
Experimental	2.95	78.4	2.30	-41.5 [180]	+3.984	2.53

All the data is at 25 °C and 1 atm, except * at 20 °C and ** at 27 °C.

Solvent at a charged surface

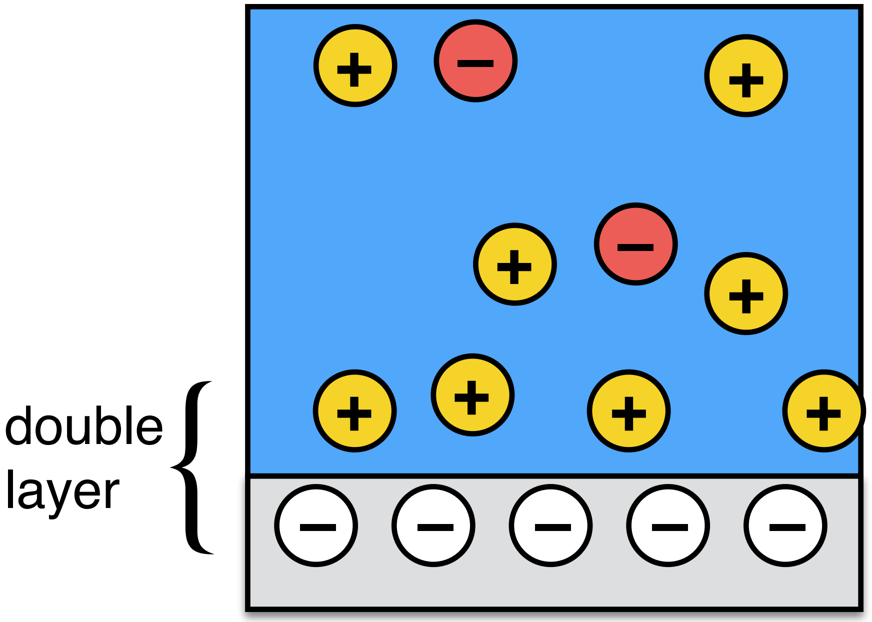
Gouy-Chapman model (1910-1913)

The electric potential in the solution is determined by the charge distribution:

$$-\nabla^2 \phi = \frac{\rho_f}{\epsilon_r \epsilon_0}$$

Poisson equation

electrolyte solution on a surface



The distribution of the charges is governed by Boltzmann statistics:

$$\rho_i(\mathbf{r}) = \rho_i^{\infty}(\mathbf{r}) \exp\left(\frac{-W_i(\mathbf{r})}{k_B T}\right)$$

Boltzmann distribution

W_i: the work to bring an ion from infinity to **r**

Combining these gives the Poisson-Boltzmann equation:

$$\nabla^2 \phi(\mathbf{r}) = -\frac{1}{\epsilon_r \epsilon_0} \sum_i z_i \rho_i^{\infty}(\mathbf{r}) \exp\left(\frac{-z_i \phi(\mathbf{r})}{k_B T}\right)$$

(not so easy to solve this non-linear equation…)

z_i : charge of ion *i*
$\Phi(\mathbf{r})$: electrostatic potential at ***r***
$\rho(\mathbf{r})$: charge density of the solute
kB : Boltzmann's constant
T : temperature
ε : dielectric constant

Debye-Hückel

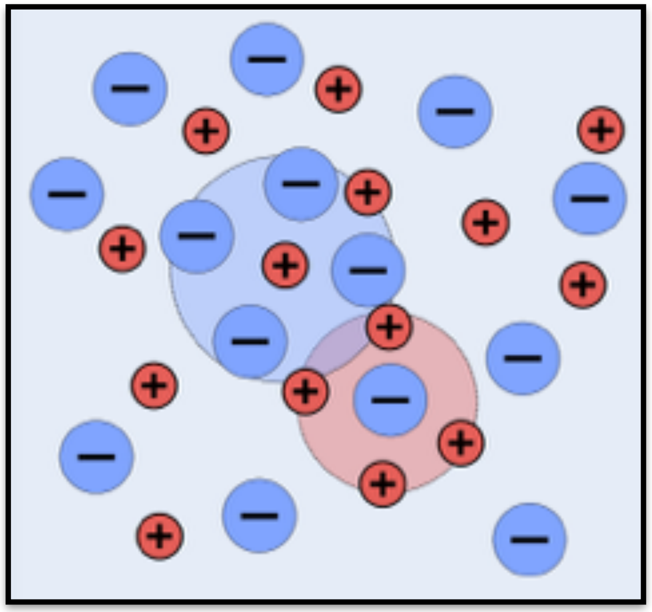
The Poisson-Boltzmann equation can be linearised by making use of a Taylor expansion, and truncating after 1st order

$$\exp\left(\frac{-z_i\phi(\mathbf{r})}{k_BT}\right) \approx 1 - \frac{-z_i\phi(\mathbf{r})}{k_BT}$$

giving: $$\nabla^2\phi(\mathbf{r}) = -\frac{1}{\epsilon_r\epsilon_0}\sum_i\left(\frac{-z_i^2\rho_i^\infty}{k_BT}\right)\phi(\mathbf{r}) - \sum_i -z_i\rho_i^\infty$$

the Debye-Hückel equation (for an electrically neutral system).

electrolyte solution (from Wiki)



The Debye (screening) length: $$\lambda_D = \sqrt{\frac{\epsilon_r\epsilon_0 k_BT}{\sum_i -z_i^2\rho_i^\infty}}$$

The electric potential due to a charge Q is exponential screened by the medium with the characteristic length λ_D:

$$\phi(\mathbf{r}) = \frac{Q}{4\pi\epsilon_r\epsilon_0 r}e^{-r/\lambda_D}$$

Contents

1. Intro: what about solvent effects?
2. Fundamentals: Permittivity, dielectric media
3. **Implicit solvation: Continuum models, PCM, COSMO,…**
4. Explicit solvation: Ewald summation
5. Thermodynamic properties of liquids from the PT2 model
6. Measurements and modelling of anisotropy relaxation

Implicit solvent models

Also known as “continuum” models
in quantum chemistry: perturbation onto the solute Hamiltonian

- combined with DFT, HF, post-HF

in atomistic forcefield and coarse-grain simulations

- e.g. in modeling of protein folding

Homogeneously polarisable medium instead of solvent molecules

The solvation free energy can be partitioned into 3 components:

$$\Delta G_{\mathrm{sol}} = \Delta G_{\mathrm{elec}} + \Delta G_{\mathrm{VdW}} + \Delta G_{\mathrm{cavity}}$$

Some important/popular implicit solvent models:

- (Generalized) Born Model
- Polarisable Continuum Model (PCM)
- COSMO

Generalised Born Model

Born (1920)-Onsager (1936):

solvation energy is the difference in work to charge an ion (Born) in solvent medium versus in vacuum (Onsager introduced dipole of solute)

$$\Delta G_{\mathrm{elec}} = -\frac{1}{2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon}\right)\frac{q^2}{b}$$

q: charge of the ion
b: radius of the ion

bring charge from infinity to b:

$$\Delta U = \frac{1}{\epsilon b}\int_0^{q'} q\,dq$$

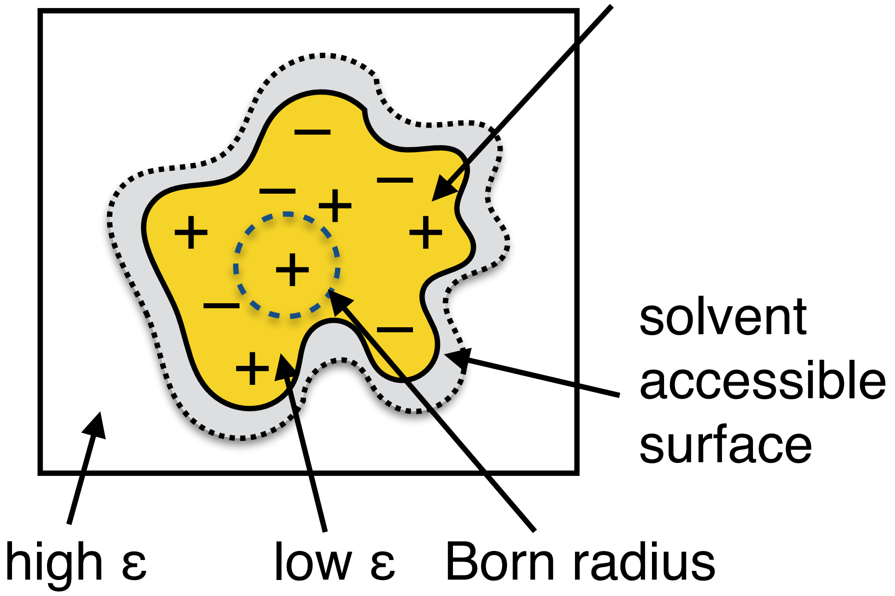
Generalised Born Equation:

$$\Delta G_{\mathrm{elec}} = -\left(1 - \frac{1}{\epsilon}\right)\sum_{i<j}\frac{q_i q_j}{r_{ij}} - \frac{1}{2}\left(1 - \frac{1}{\epsilon}\right)\sum_i \frac{q_i^2}{b_i}$$

Screened Coulomb term

Born-Onsager solvation energy

Molecule as a system of charges



Popular implicit solvent model for forcefield protein simulations

- main limitation: accuracy relies on calculation of Born radii
- variety of more/less accurate/demanding methods to compute the the Born radii (i.e. the solvent accessible surface)

GB model neglects:

- cavity energy, solute-solvent VdW
- solvent polarisation by solute

PCM

The **P**olarizable **C**ontinuum **M**odel

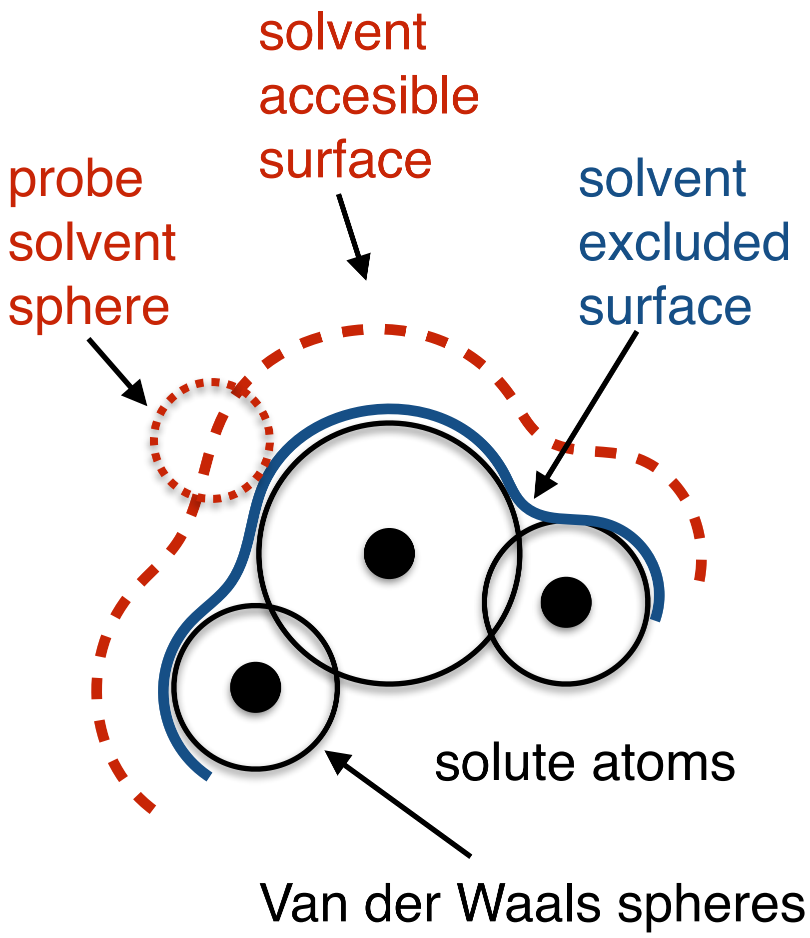
The solvation free energy contains 3 terms:

$$G_{sol} = G_{es} + G_{dr} + G_{cav}$$

electrostatic interaction

dispersion + repulsion

cavitation free energy

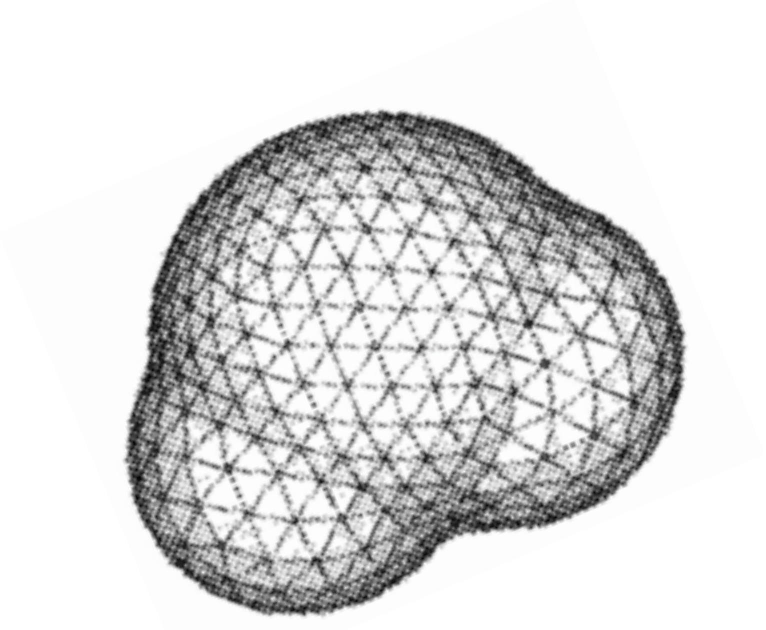


The charge density over the cavity surface is integrated to an effective charge per surface segment, which leads to a potential at the solute:

$$v_{\mathrm{pcm}}(\mathbf{r}) = \int_{\Sigma} \frac{\sigma(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|} d\mathbf{s} \approx \sum_{k=1}^{T} \frac{q_k}{|\mathbf{r}-\mathbf{s_k}|}$$

This adds an external potential to e.g. the Kohn-Sham Hamiltonian due to a contribution from surface charges computed the nuclear and electronic polarisation:

$$v_{\mathrm{KS}}[\rho(\mathbf{r}]) = v_{\mathrm{KS}}^{\mathrm{vac}}[\rho(\mathbf{r})] + \sum_{k=1}^{T} \frac{q_k^e + q_k^n}{|\mathbf{r}-\mathbf{s_k}|}$$



cavity surface tessellation

The PCM method is (also) sensitive to the cavity size and shape.
Leakage of electron density outside the cavity may give problems.
Implemented and extended into several quantum chemistry programs.

COSMO and COSMO-RS

COnductor-like **S**creening **MO**del for **R**eal **S**olvents

Charges of polarisation continuum derived from a scaled-conductor approximation

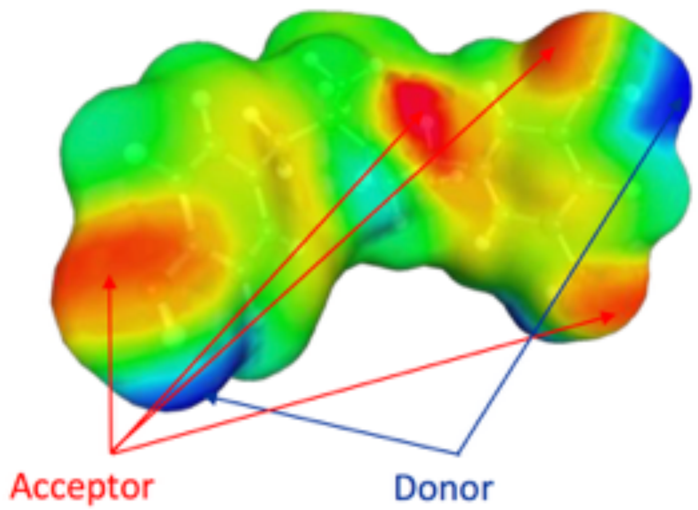
- cavity around solute constructed from segments (e.g. triangles) on atom-centred spheres (VdW radii + 20%)
- obtain the electric potential on the cavity surface due to the solute from a quantum chemical calculation
- Due to the solvent, this potential is lower by a factor f, depending on the dielectric constant of the solvent

$$q = f(\epsilon) q^{\text{solute}} \qquad f(\epsilon) = \frac{\epsilon - 1}{\epsilon + x}$$

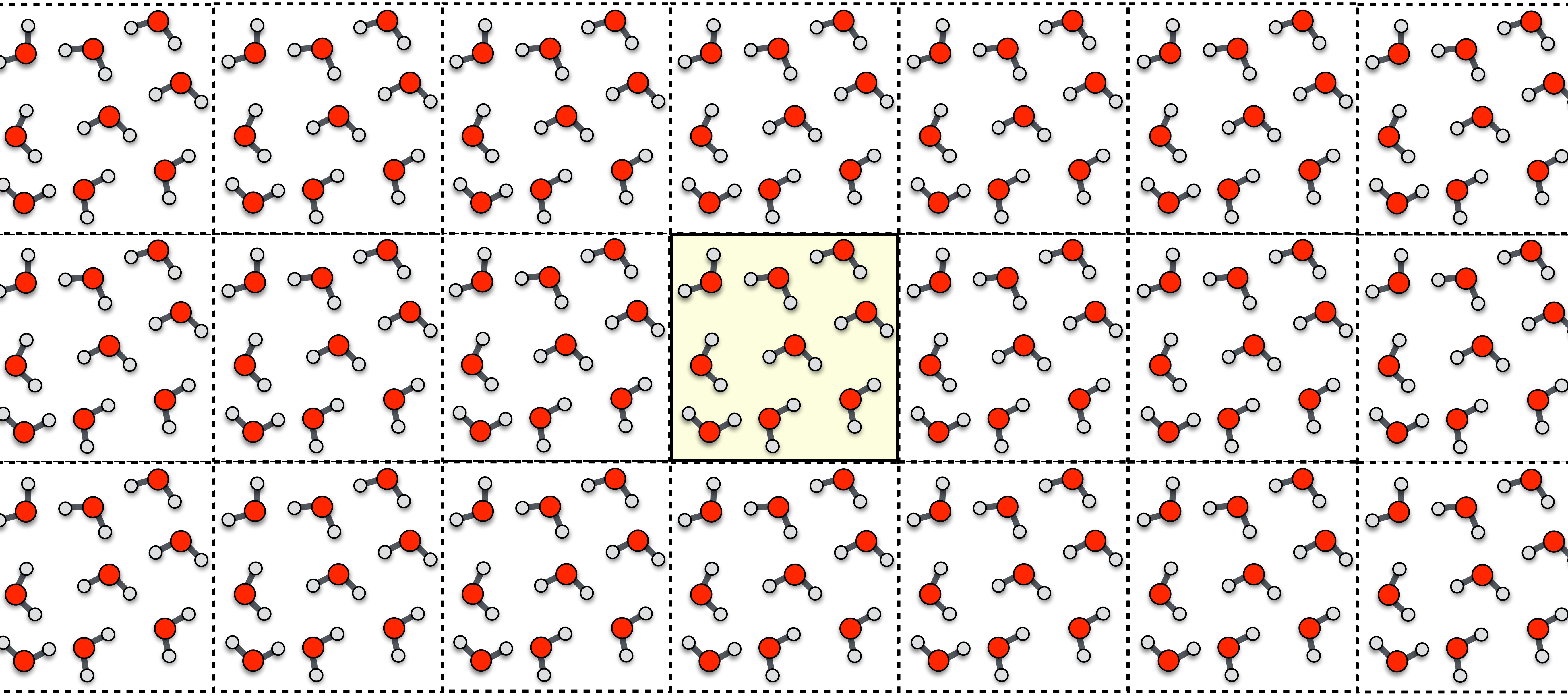
- $x = 0.5$ (or 0.0)
- if solvent were conductor then q would be zero

- Similar to PCM, but simpler math and computationally faster.
- Works very well for high dielectric solvents (water)
- Implemented and extended in various programs.

Fenoterol



Periodic Boundary Conditions



Periodic boundary conditions are used to avoid hard walls in molecular models.

- particle leaving on one side, reappears with same velocity at other side
- minimum image convention: particles interact with closest copy
- implies periodicity onto solvent
- other space filling cells than cubic are possible

Ewald Summation

How to deal with long range interactions?

- electrostatics are long-range, $V \sim r^{-1}$
- Coulomb interaction over infinite array of neutral (!) cells is at best conditionally converging
- truncation at cut-off radius and shifting of potential causes spurious density fluctuations

Solution by Paul Peter Ewald:
Rewrite as a sum of a short-range real-space term and a long-range reciprocal space term and a self-term.

$$U^{\text{Ewald}} = U^{\text{short}} + U^{\text{long}} + U^{\text{self}}$$

real space

$$U^{\text{short}} = \frac{1}{2} \sum_{i \neq j}^{N} q_i q_j \frac{\operatorname{erfc}\left(\sqrt{\alpha} r_{ij}\right)}{r_{ij}}$$

Fourier space

$$U^{\text{long}} = \frac{1}{2V} \sum_{\mathbf{k} \neq 0} \frac{4\pi}{k^2} |\rho(\mathbf{k})|^2 \exp(-k^2/4\alpha)$$

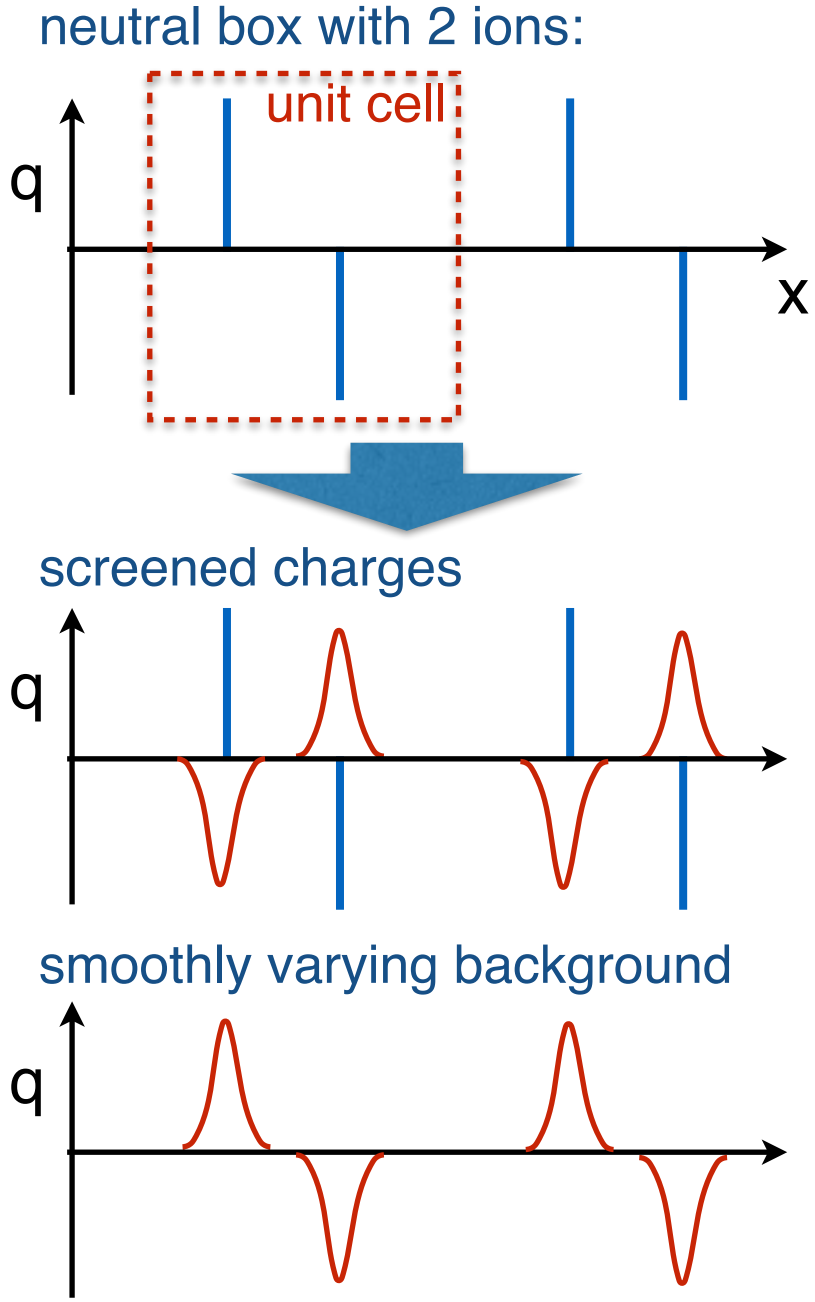
self-interaction

$$U^{\text{self}} = -\sqrt{\frac{\alpha}{\pi}} \sum_{i=1}^{N} q_i^2$$

electrostatic potential at ion i:

$$\phi(\mathbf{r}_i) = \sum_{j,\mathbf{n}} \frac{q_j}{|\mathbf{r}_{ij} + \mathbf{nL}|}$$

sum over periodic images



neutral box with 2 ions:

screened charges

smoothly varying background

Ewald Summation

Choice of Ewald parameters, α, k^{max}, n^{max}

- A smaller Gaussian width (i.e. larger α) makes the short-range sum converge faster (smaller n^{max})
- Wider Gaussians (i.e. small α) makes the long-range sum converge faster (smaller k^{max})
- At $\alpha=\sqrt{\pi}/L$ both sum converged equally fast
- Fast fourier transform libraries are well optimised and parallelized
- Real-space sum is cut-off to L/2 or less (CHARMM: $R_{cuttoff}$=9 Å)

Alternatives to Ewald summation

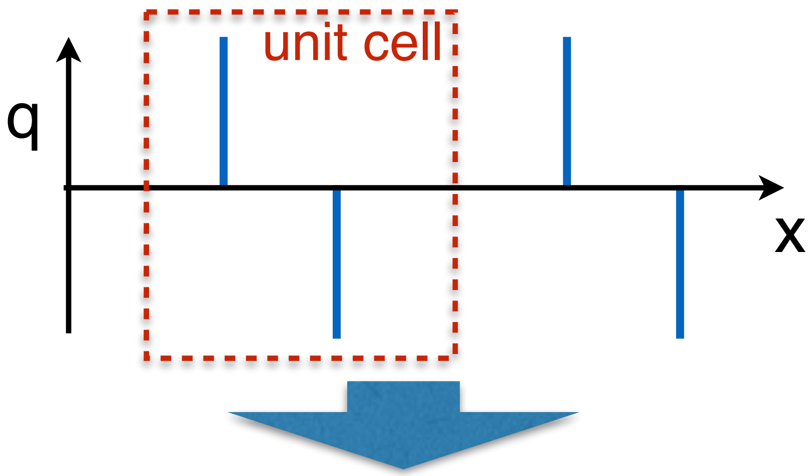
- Ewald sums can be further rearranged and improved
- Particle-particle-particle mesh method (PPPM)
- Particle-Mesh Ewald (PME)
- Fast Multipole Algorithm (FMA) (non-periodic cells)

electrostatic potential at ion i:

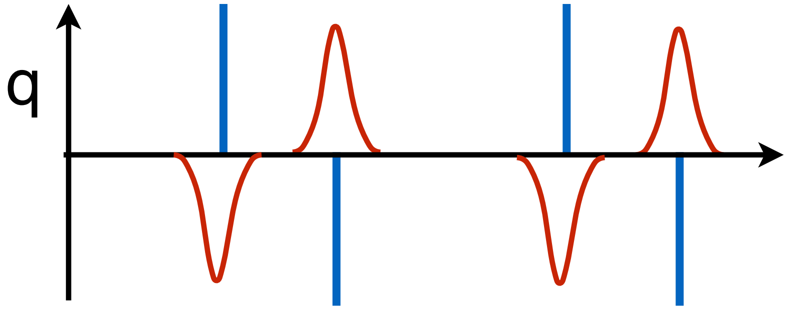
$$\phi(\mathbf{r}_i) = \sum_{j,\mathbf{n}} \frac{q_j}{|\mathbf{r}_{ij} + \mathbf{n}\mathbf{L}|}$$

sum over periodic images

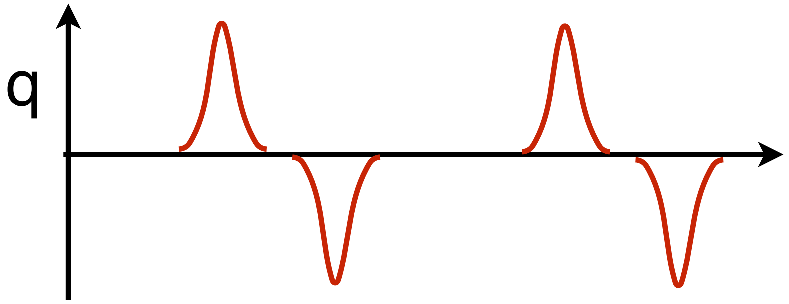
neutral box with 2 ions:



screened charges



smoothly varying background



Contents

1. Intro: what about solvent effects?
2. Fundamentals: Permittivity, dielectric media
3. Implicit solvation: Continuum models, PCM, COSMO,…
4. Explicit solvation: Ewald summation
5. **Thermodynamic properties of liquids from the PT2 model**
6. Measurements and modelling of anisotropy relaxation

Heat capacity

$$C_v = \left(\frac{dU}{dT}\right)_V$$

In materials (liquids)

- Heat stored as kinetic and potential energy
- Translational, rotational, vibrational motion
- Equipartition principle:

$$U = \underbrace{3 \times \tfrac{1}{2}RT}_{\text{translation}} + \underbrace{3 \times \tfrac{1}{2}RT}_{\text{rotation}} + \underbrace{(3N-6) \times RT}_{\text{vibration}}$$

- Quantisation of energy levels is not negligible

$$q_i^{\mathrm{vib}} = \frac{\exp(-\beta h\nu_i/2)}{1-\exp(-\beta h\nu_i)}$$

vibrational partition function

$$\langle E^{\mathrm{vib}}\rangle = -\frac{d\ln q_i}{d\beta} = \frac{1}{2}h\nu_i + \frac{h\nu_i}{\exp[\beta h\nu_i]-1}$$

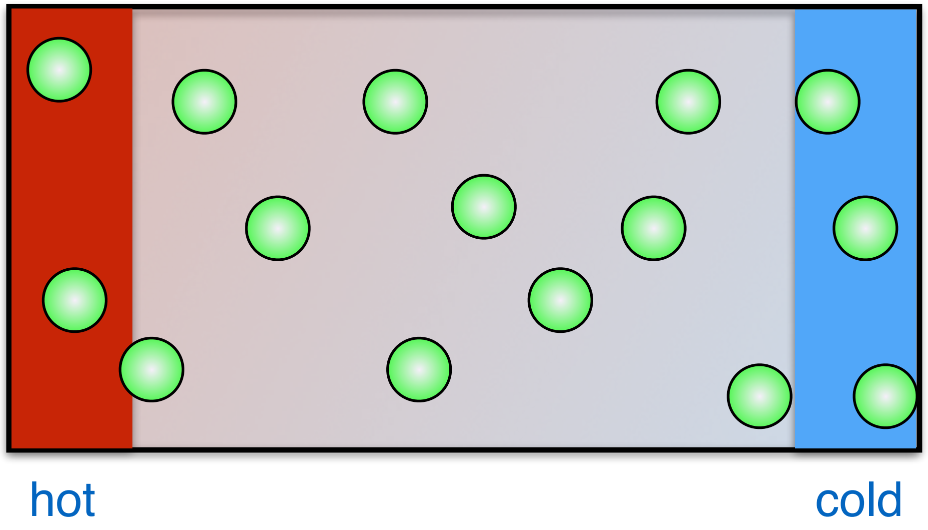
Density of states obtained from frequencies (e.g. DFT calculation)

$$C_v = k\int_0^\infty DoS(\nu)\cdot\frac{(\beta h\nu_i)^2\exp[\beta h\nu_i]}{(\exp[\beta h\nu_i]-1)^2}d\nu$$

Heat conduction

- conduction, convection, radiation
- electronic, photonic, phononic
- no good theory for liquids

A) Non-equilibrium simulation



B) Equilibrium simulation

- Green-Kubo equation

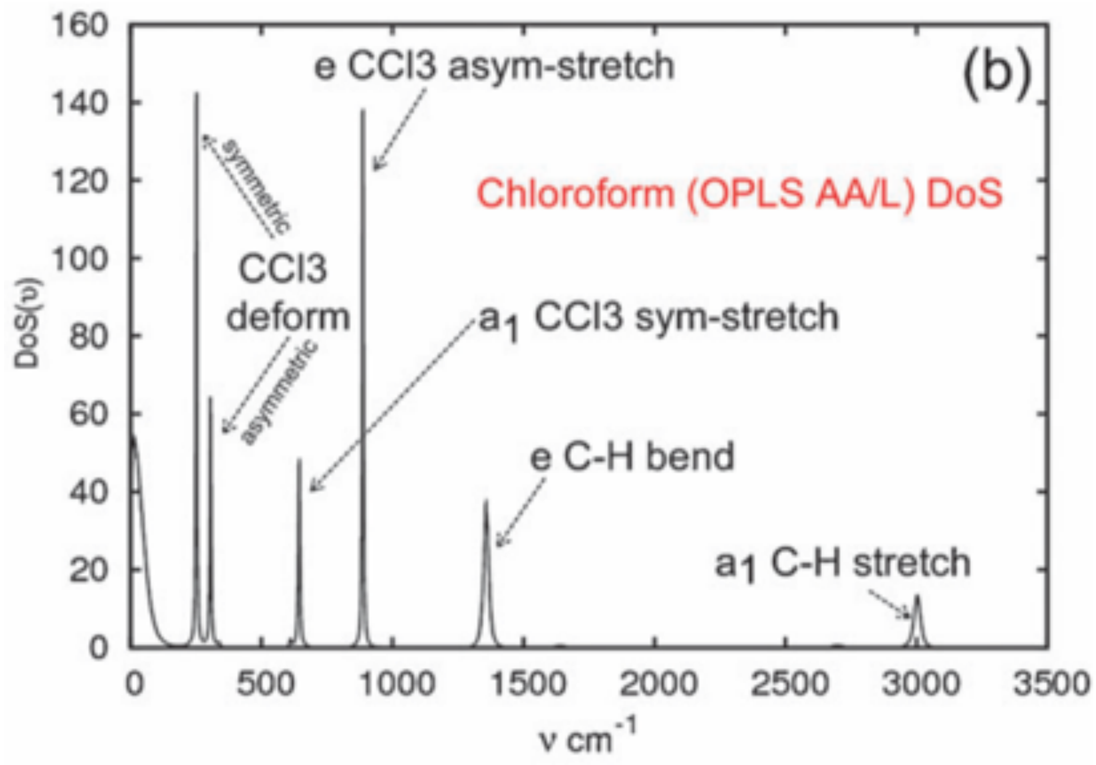
conductivity from auto-correlation of the heat flux, *J*

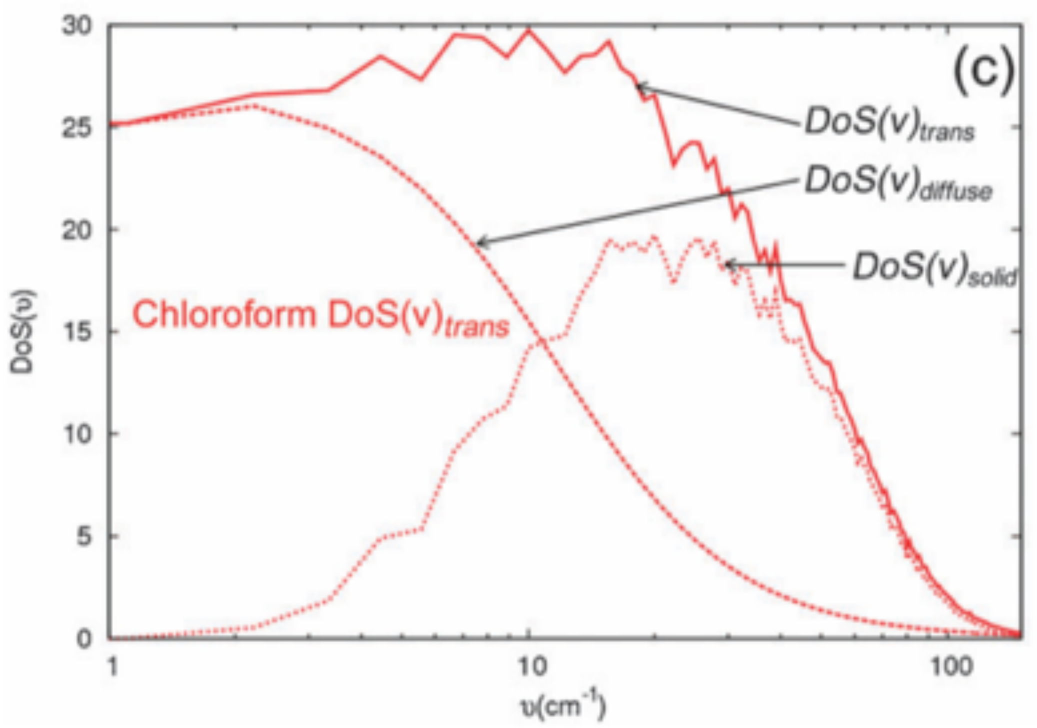
$$\kappa = \frac{1}{3Vk_BT^2}\lim_{\tau\to\infty}\int_0^\tau \langle \mathbf{J}(t)\mathbf{J}(0)dt$$

2PT program

PT2 method by William Goddard III et al
J. Chem. Phys. 119, 11792 (2003)

Example: liquid chloroform at T = 298 K





1. 50 ps MD simulation, NVT
2. separate velocities (trans, rot, vib)
3. compute vacf $\langle v(t)v(0)\rangle$
4. compute density of states
5. separate in “solid” and “gas” part
6. obtain thermodynamic properties

   from integration: S, H, G, Cv, ZPE,..

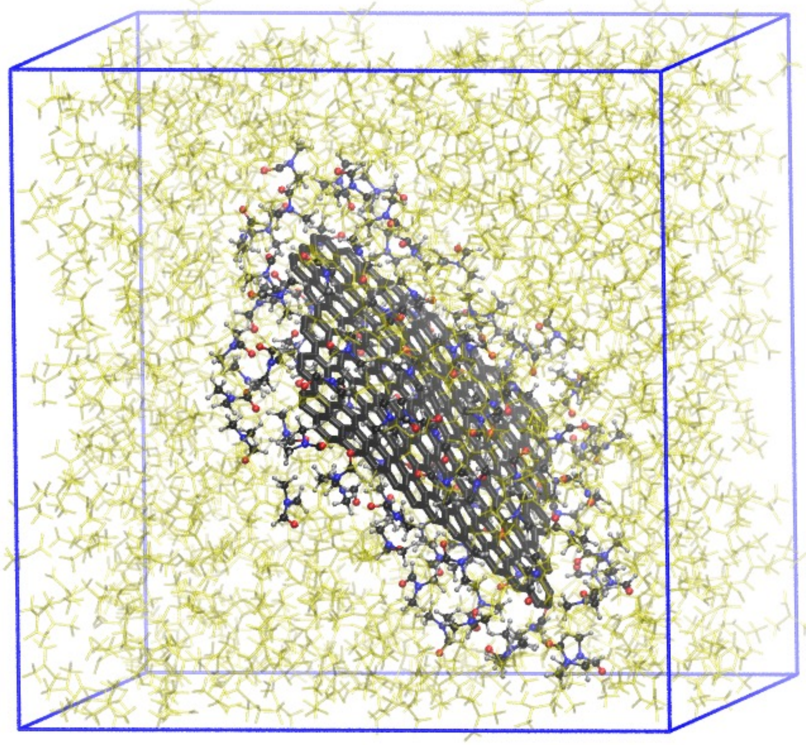
$$C_v = k\int[\mathrm{DoS}(\nu)_{\mathrm{diff}}\, W^{C_v}_{\mathrm{diff}}(\nu) + \mathrm{DoS}(\nu)_{\mathrm{solid}}\, W^{C_v}_{\mathrm{solid}}(\nu)]\mathrm{d}\nu$$

	gaff	opls	exp
Cp	30.23	25.18	27.31
S	53.88	45.98	43.01

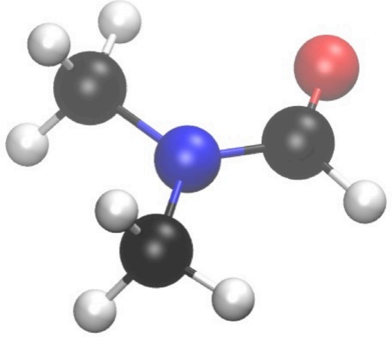
Computational approach

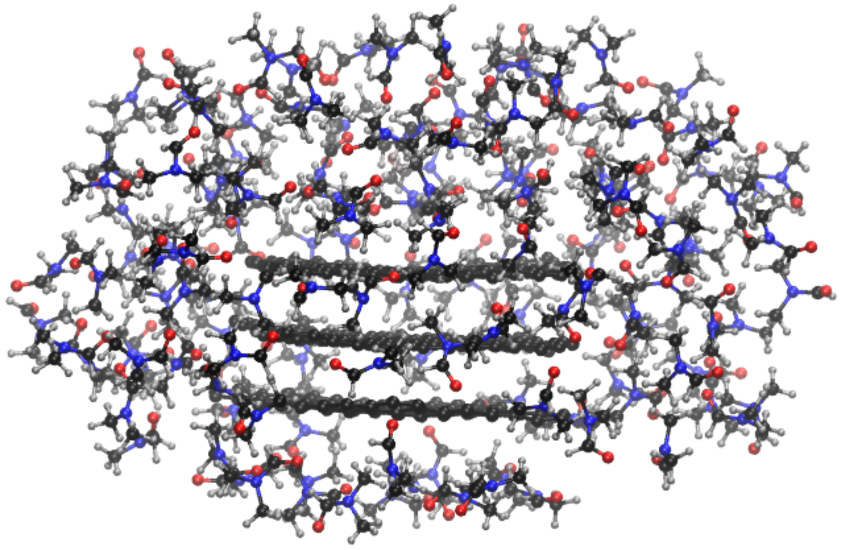
Nanofluid: graphene flakes in DFM

- classical MD simulation
- LAMMPS program, GAFF/OPLS forcefields
- NPT, NVT equilibration

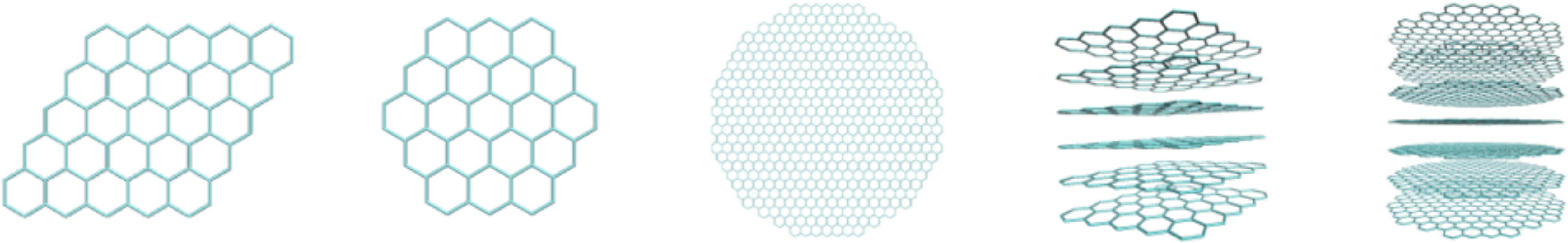


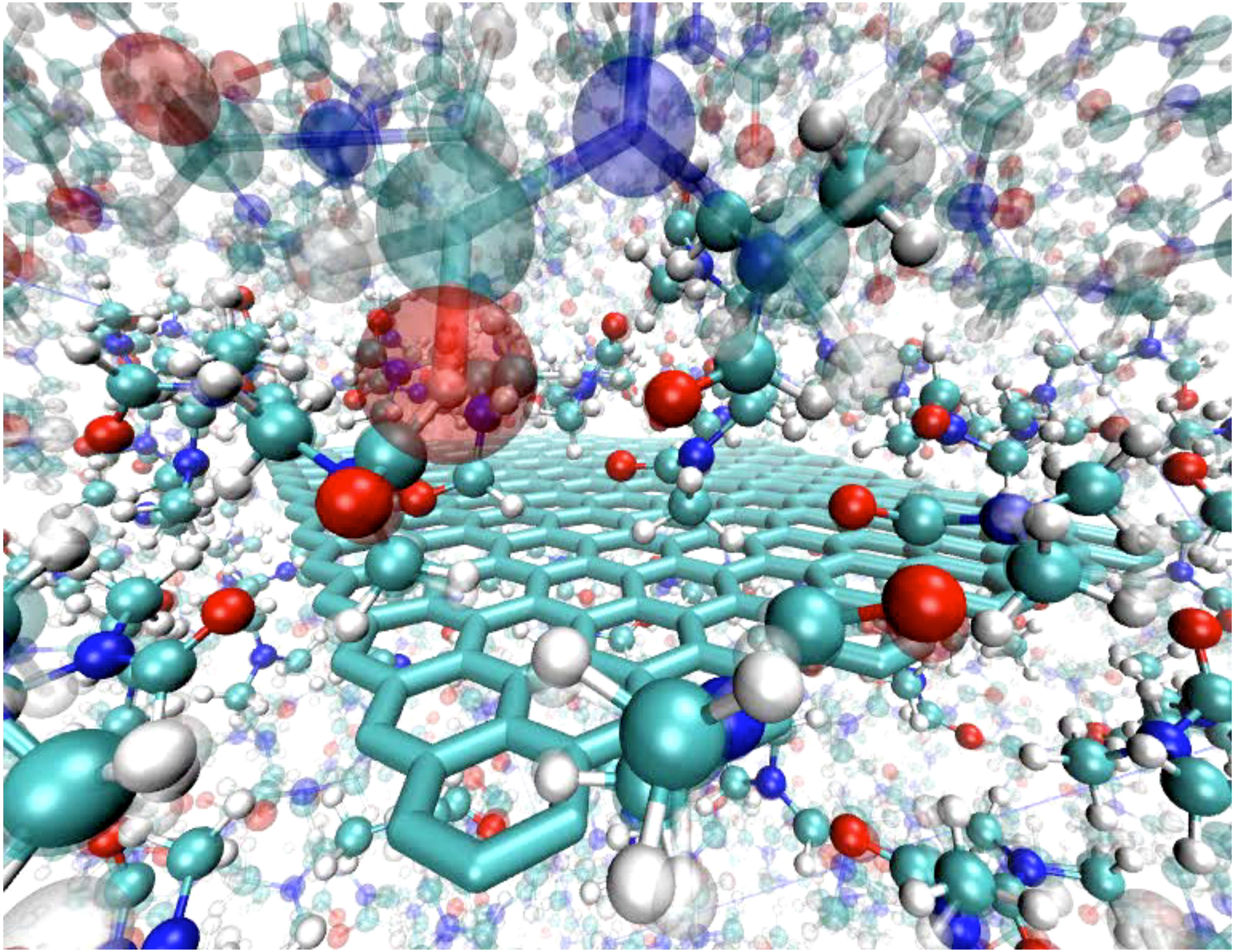
DMF: Dimethylformamide





Graphene nano flakes





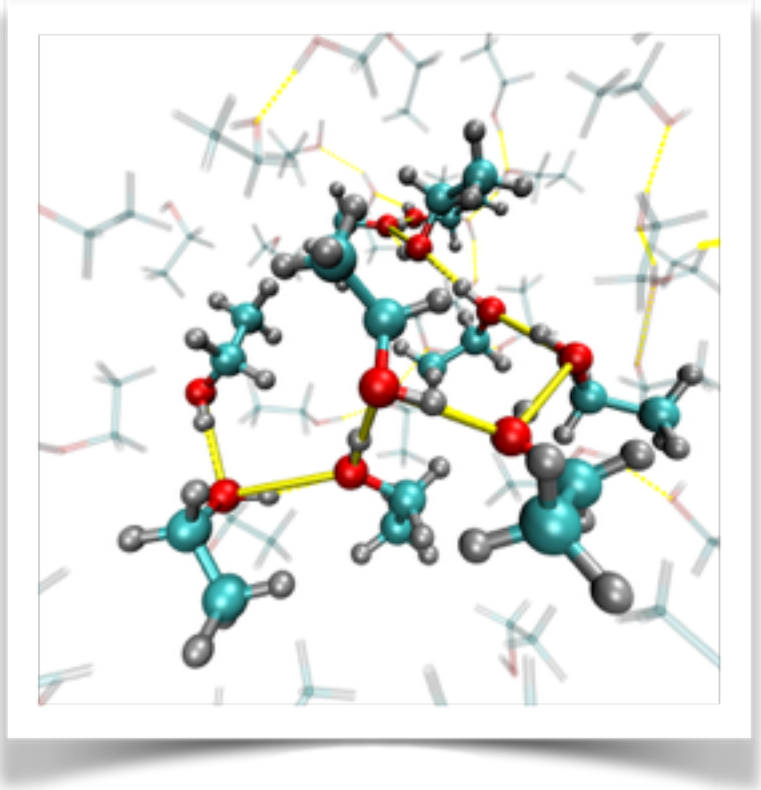
6 ps movie
(out of a 1 ns simulation)

Contents

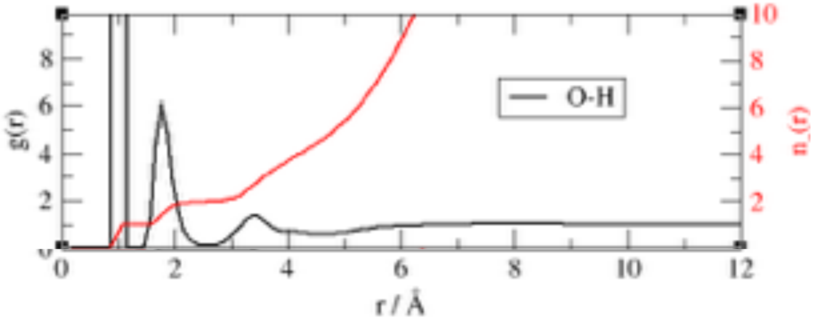
1. Intro: what about solvent effects?
2. Fundamentals: Permittivity, dielectric media
3. Implicit solvation: Continuum models, PCM, COSMO,…
4. Explicit solvation: Ewald summation
5. Thermodynamic properties of liquids from the PT2 model
6. **Measurements and modelling of anisotropy relaxation**

Local orientational ordering in liquids revealed by resonant vibrational energy transfer

Mathijs R. Panman
Daniel J. Shaw,
Sander Woutersen

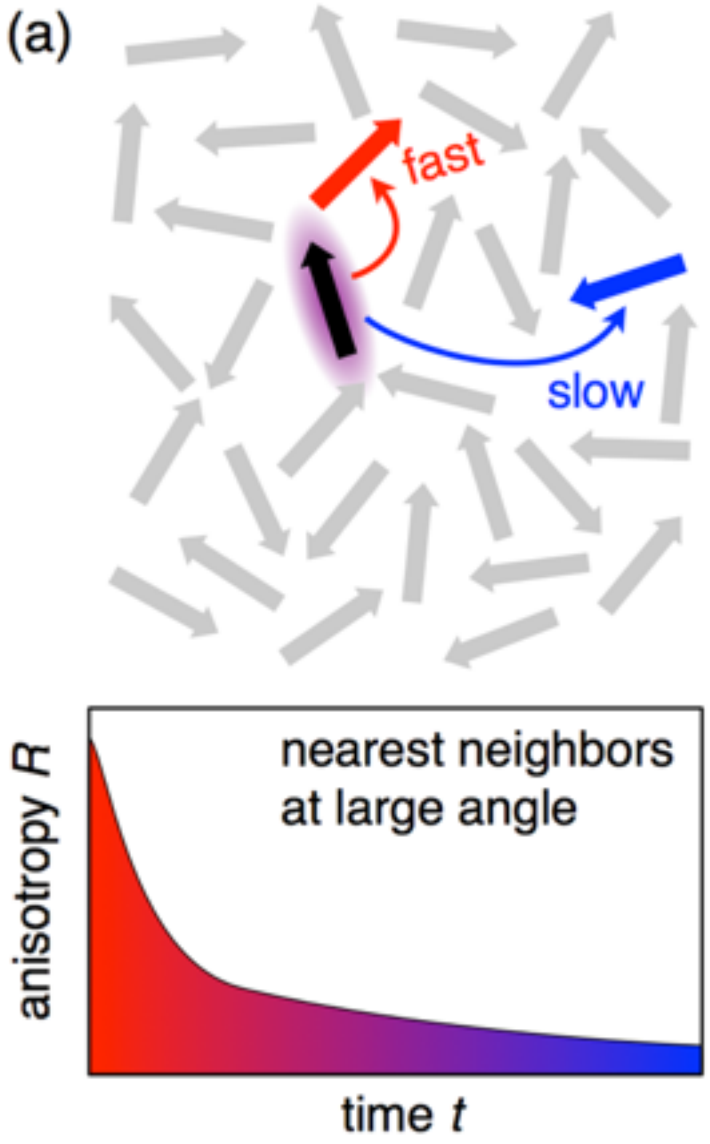


Radial distribution function



What about the orientation?

Infra-red Förster resonance energy transfer



- Energy transfer rate constant (Fermi's golden rule)

$$k_{ij} = \frac{2\pi}{\hbar}|V_{ij}|^2 \int \sigma_i(E)\sigma_j(E)dE$$

- Coupling between transition dipole moments

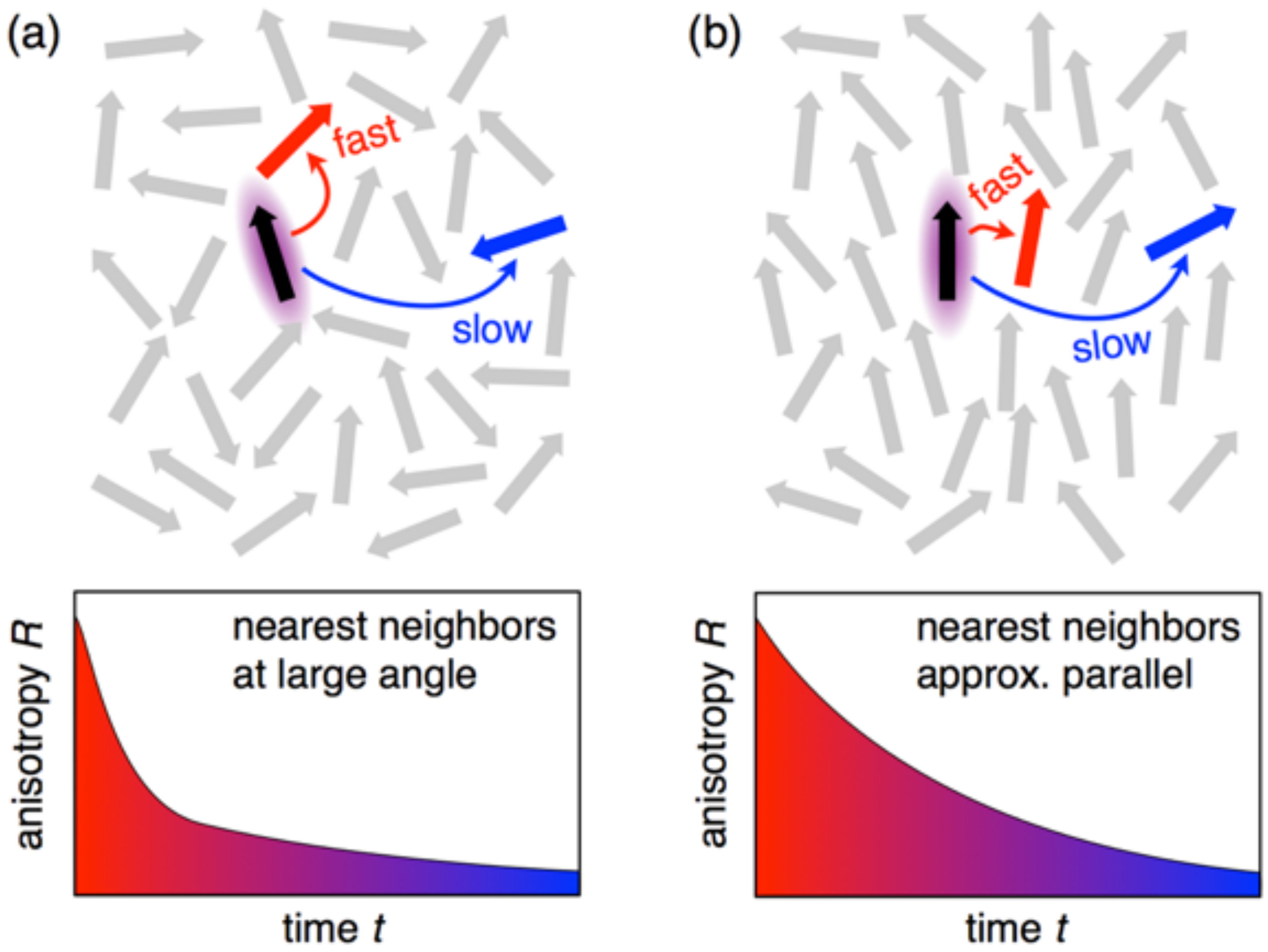
$$V_{ij} = \frac{\mu_i\mu_j}{4\pi\varepsilon_0 r_{ij}^3}\left[\mathbf{e}_{\mu_i}\cdot\mathbf{e}_{\mu_j} - 3(\mathbf{e}_{r_{ij}}\cdot\mathbf{e}_{\mu_i})(\mathbf{e}_{\mu_j}\cdot\mathbf{e}_{r_{ij}})\right]$$

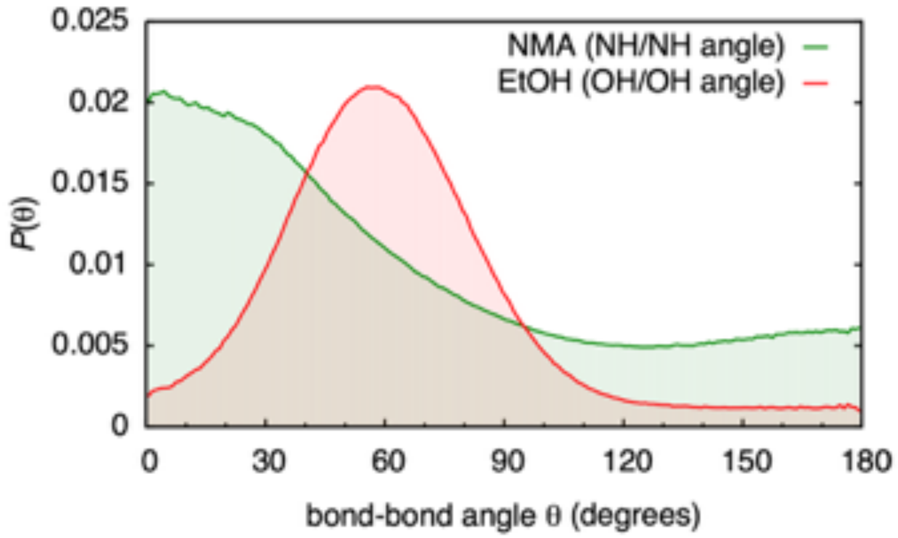
orientation factor

- Anisotropy decay

$$R(t) = \langle \tfrac{1}{2}(3\cos^2\theta - 1)\rangle = \sum_i \tfrac{1}{2}(3\cos^2\theta_i - 1)p_i / \sum_i p_i$$

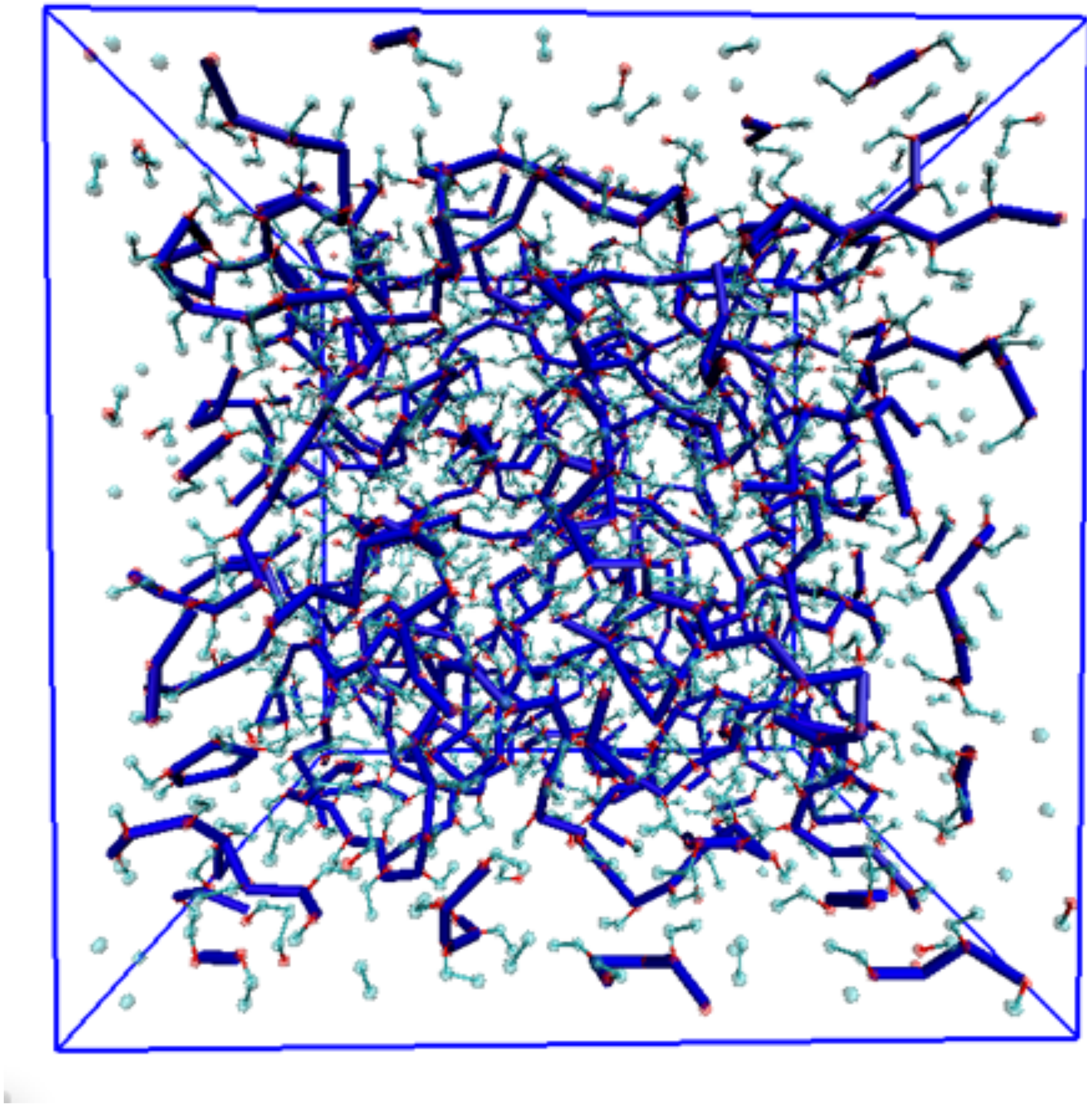
Orientation dependent decay

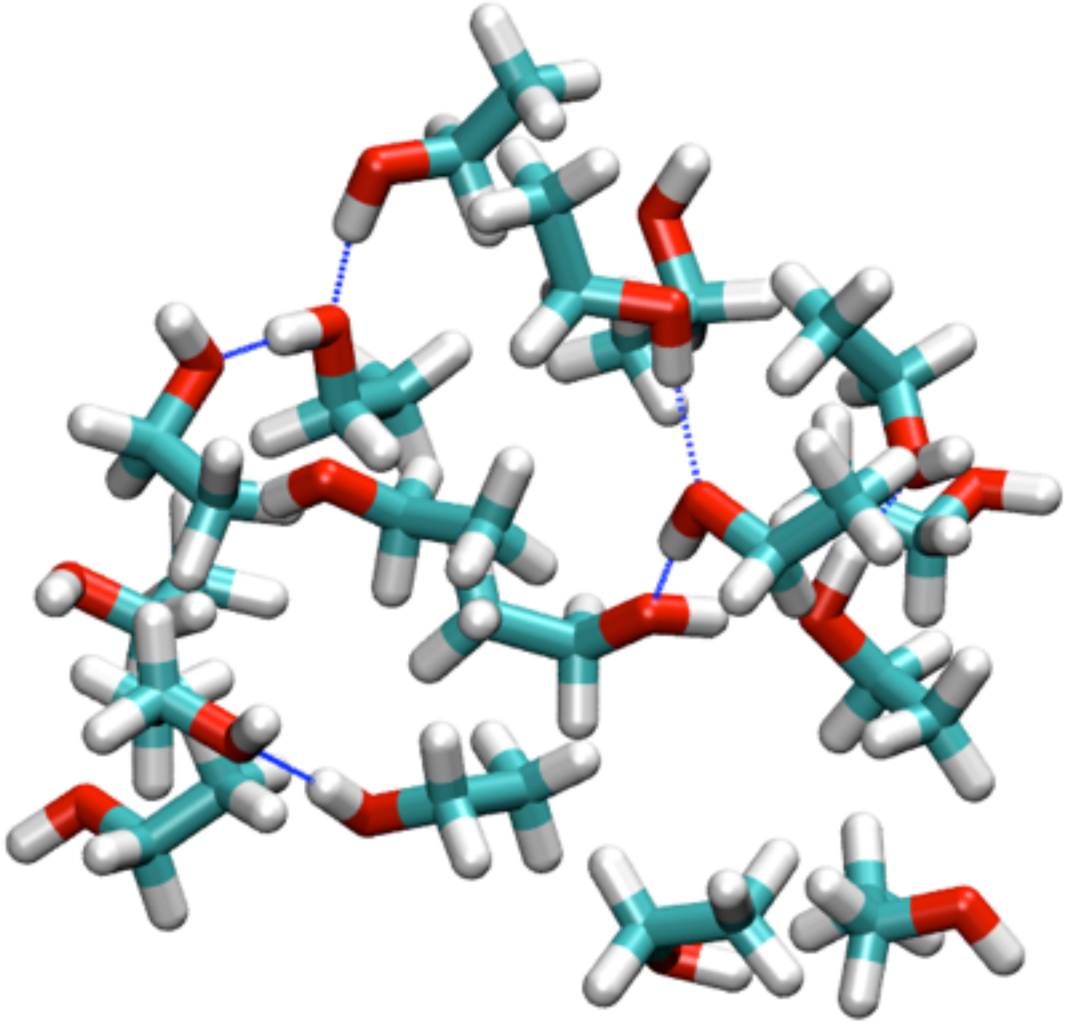




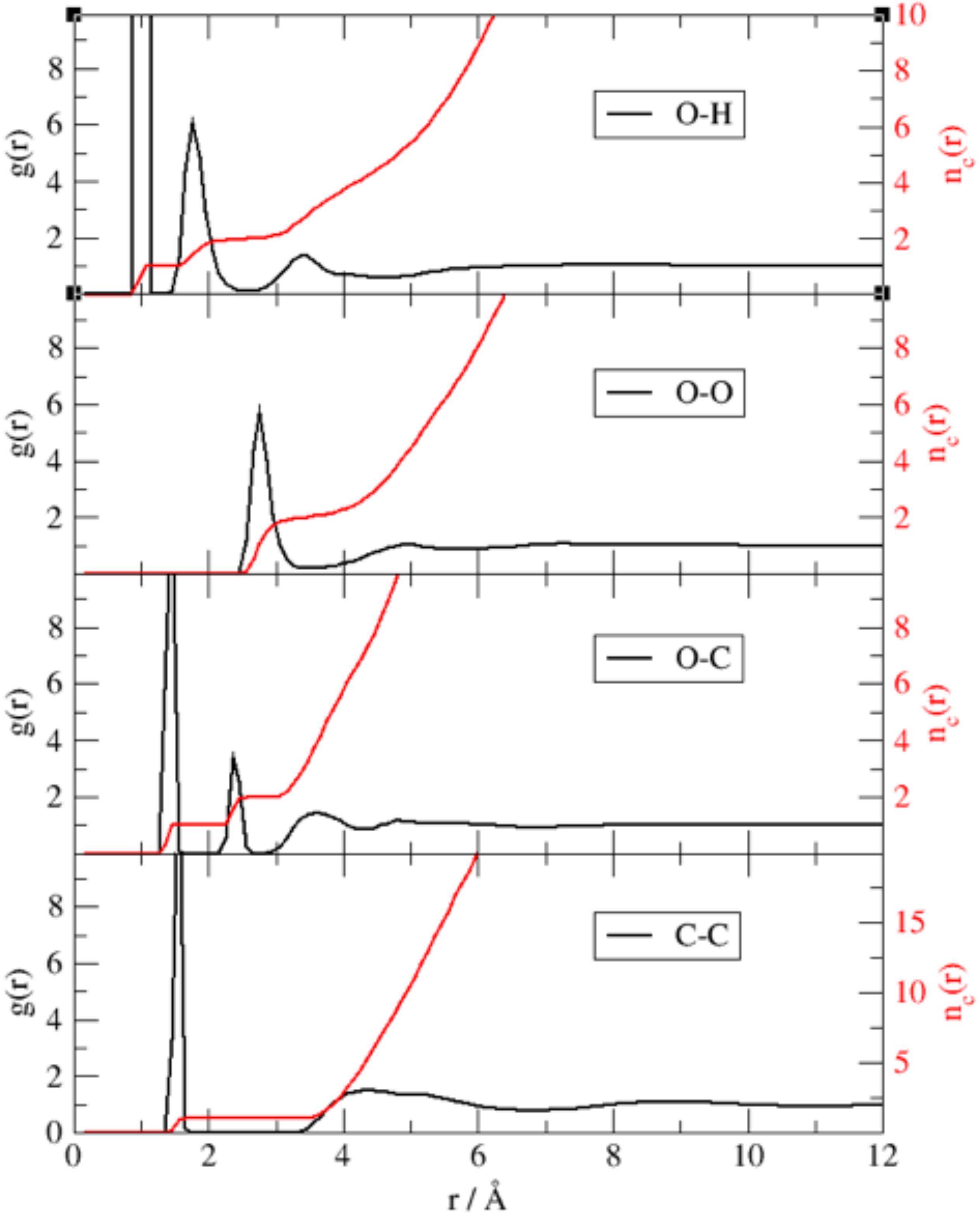
MD of 1000 ethanol molecules at T=300 K

200 ps simulations, NVT ensemble

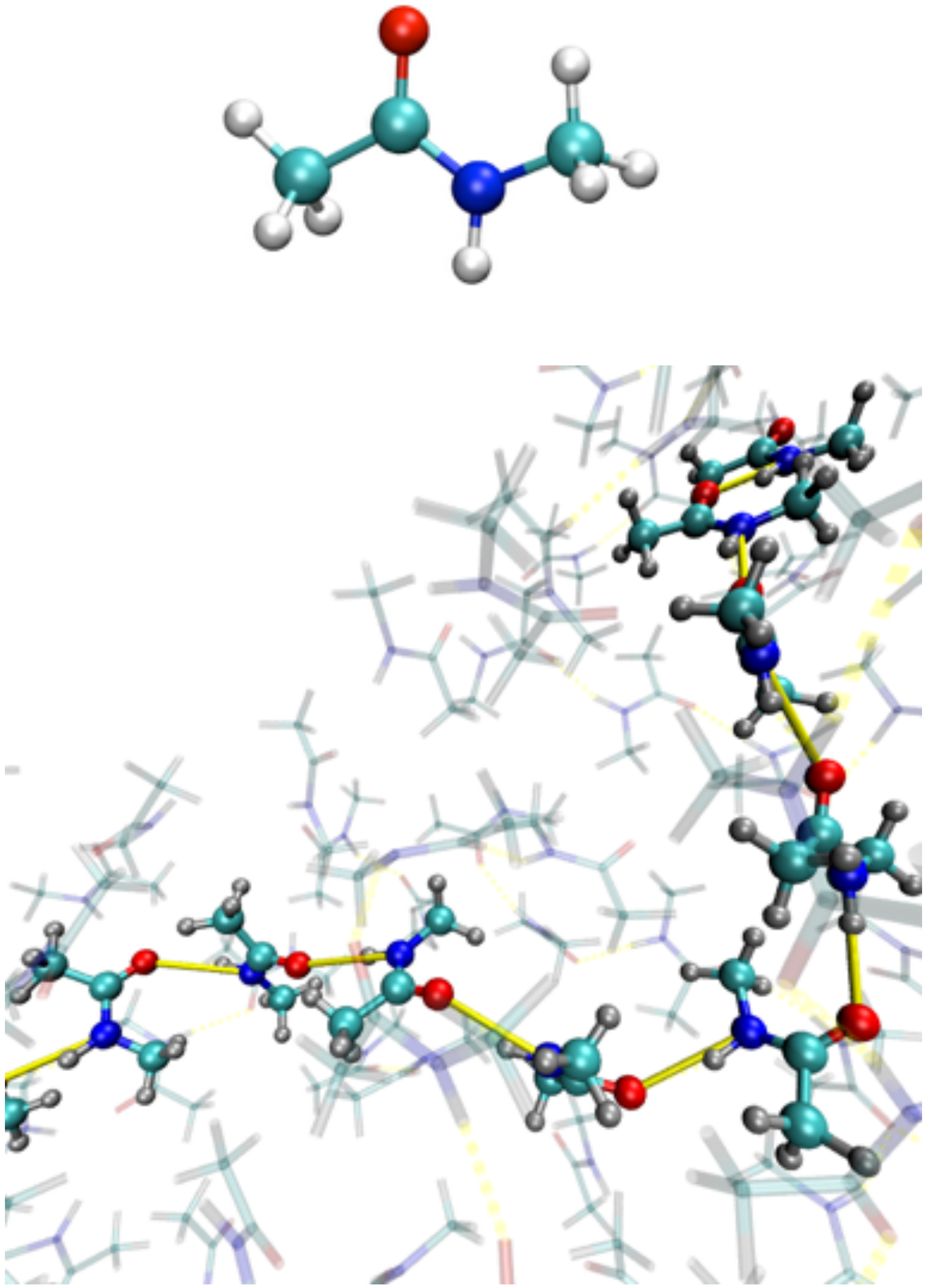




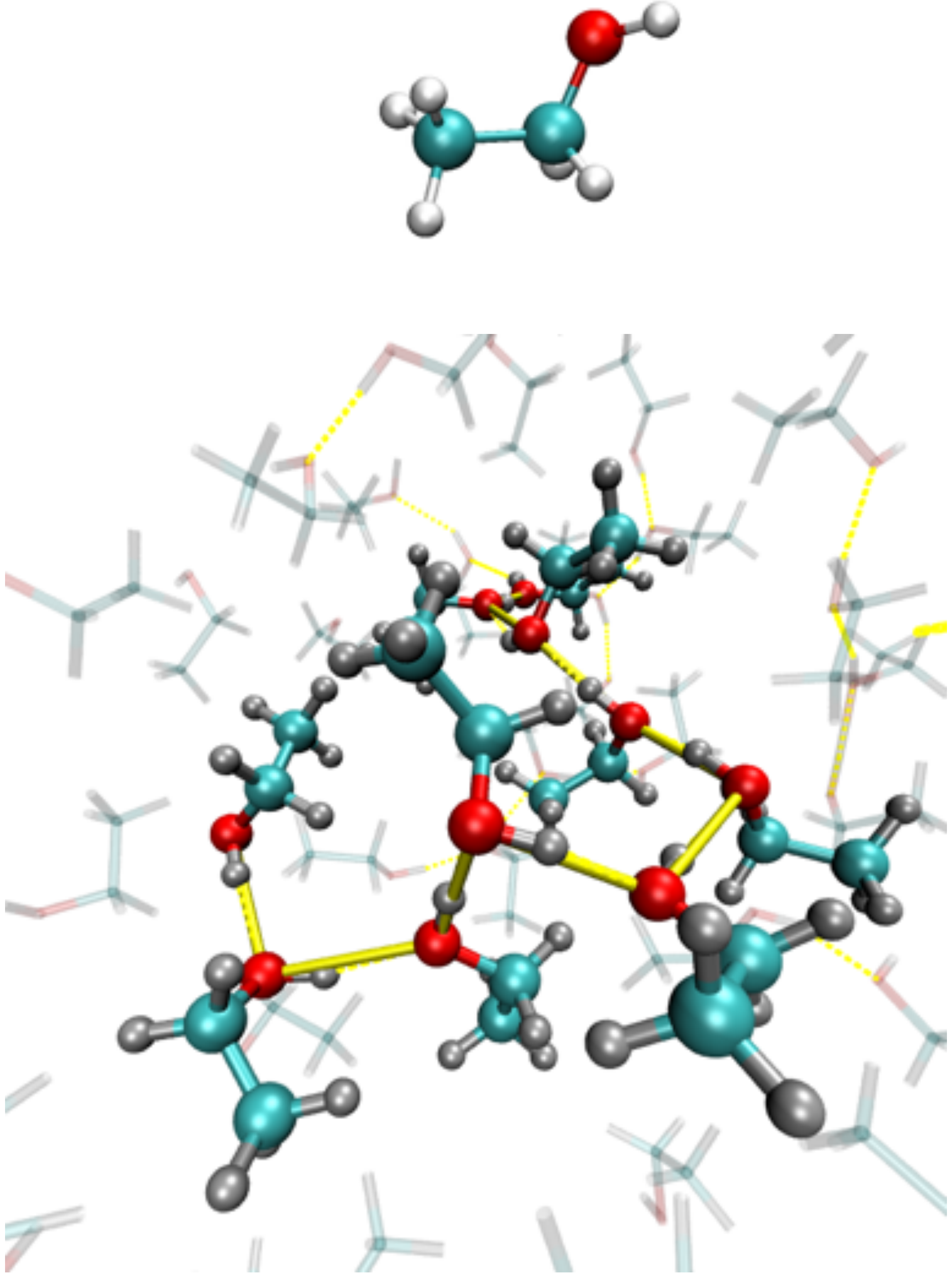
radiele distributie functies



N-methylacetamide (NMA)

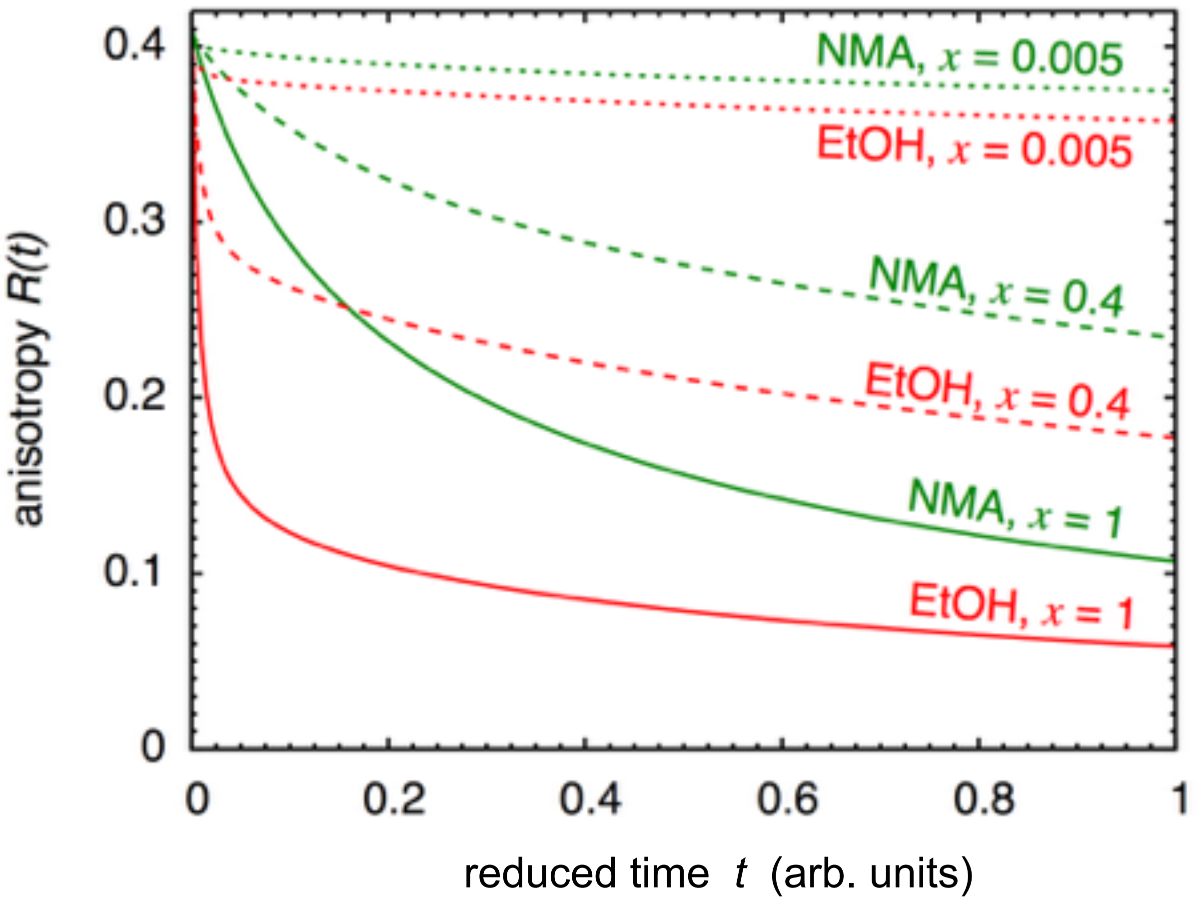


Ethanol

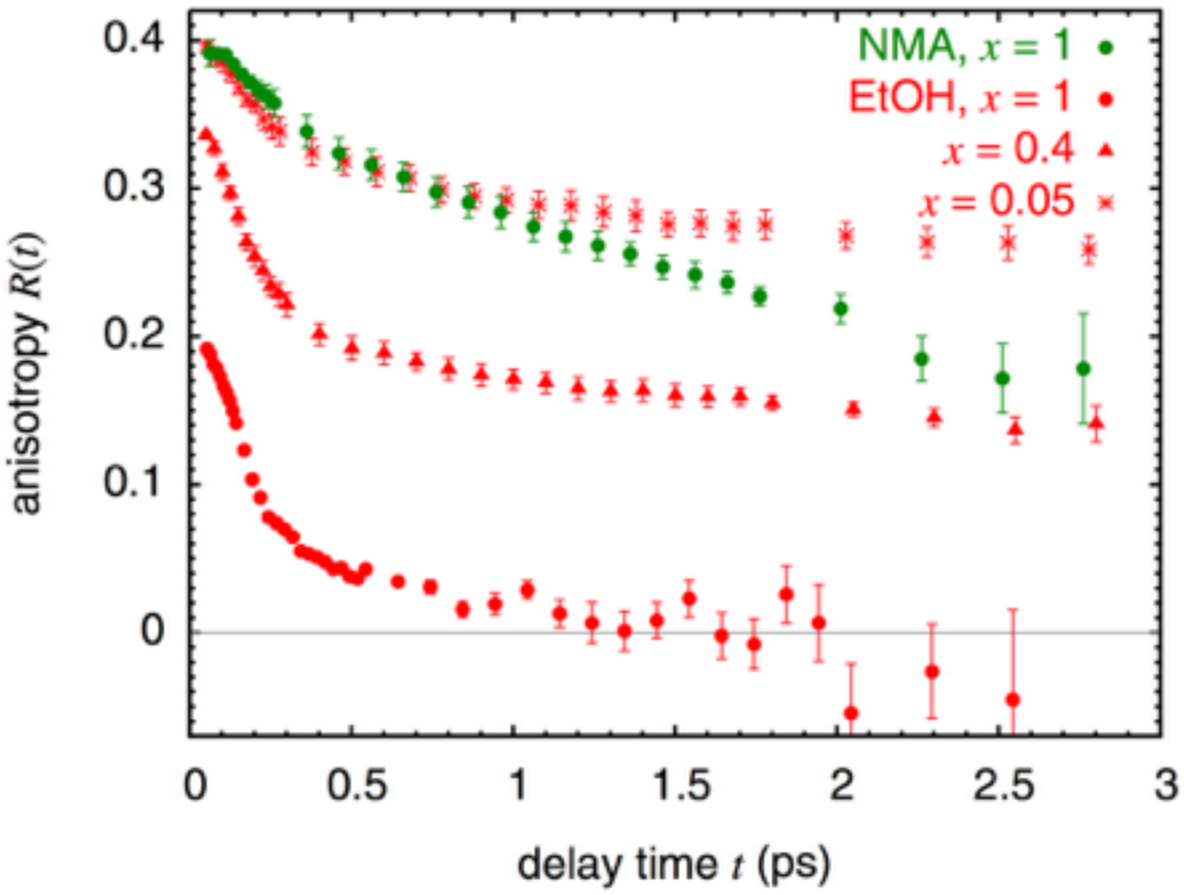


Orientation dependent decay

theory

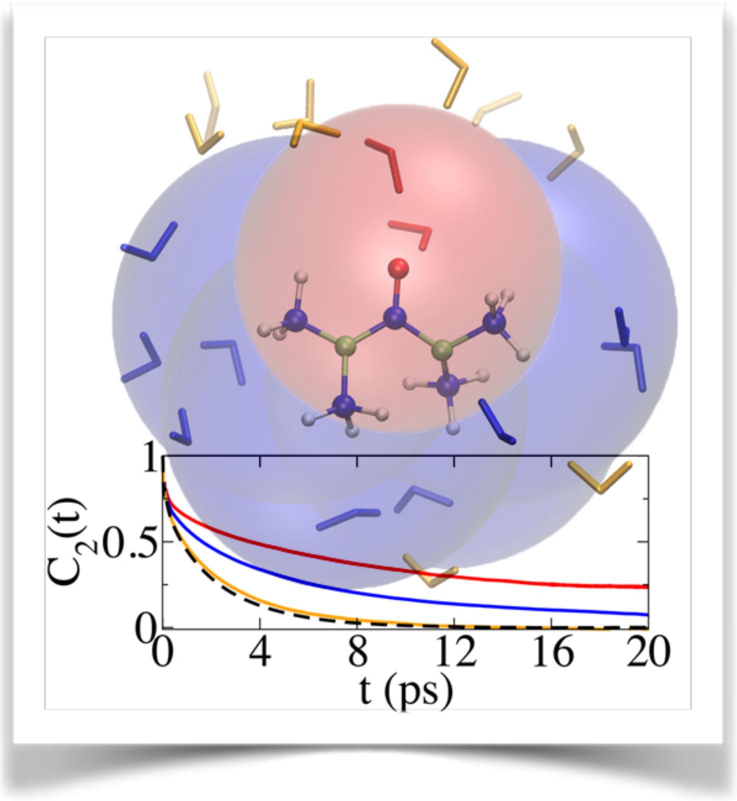


measurement



Phys. Rev. Lett. **113**, 207801 (2014)

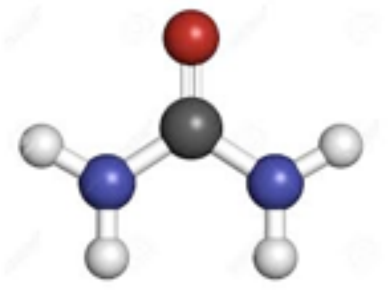
On the slowdown mechanism of water dynamics around small amphiphiles



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

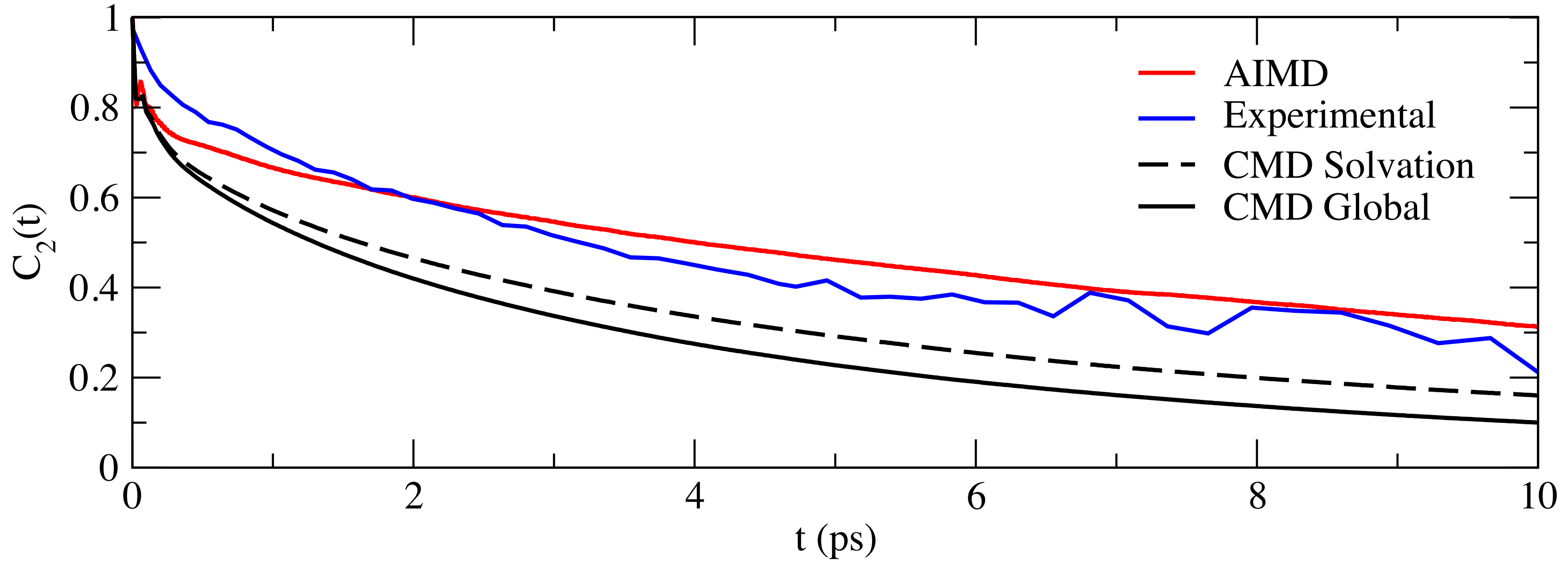
Two amphiphilic molecules in water

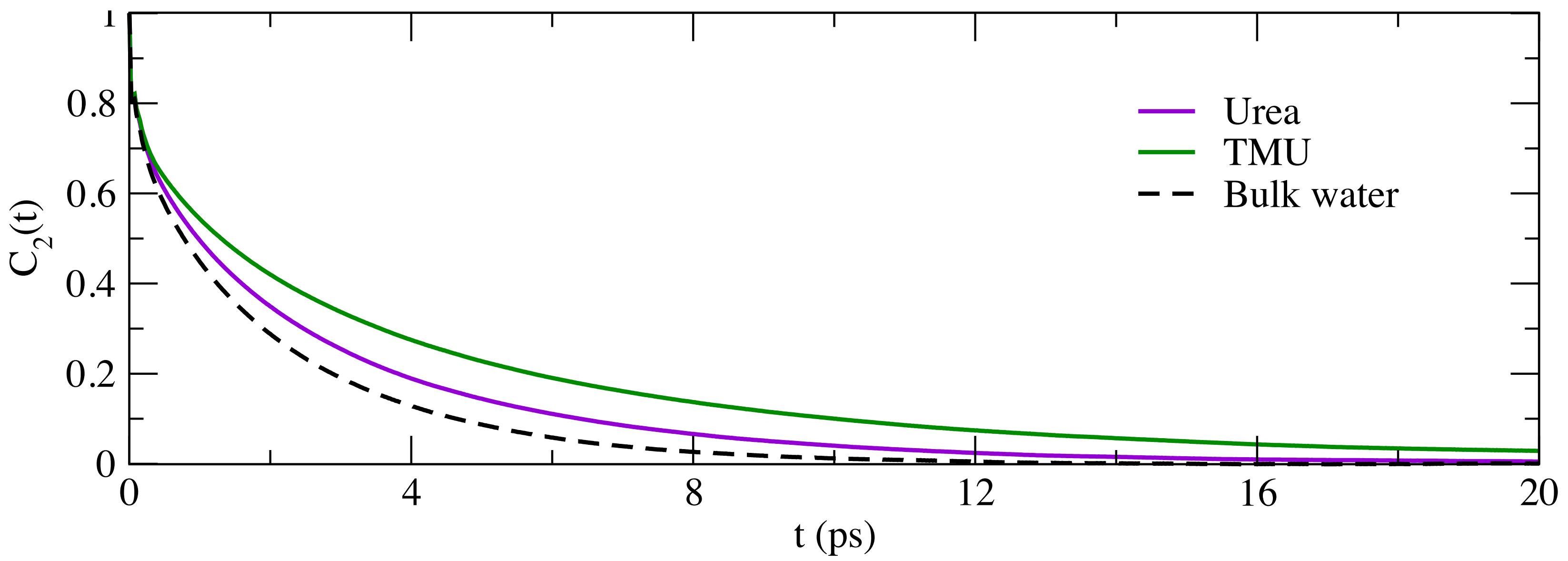
Urea



Tetramethyl urea

Water orientational decay





DFT-MD (AIMD)
- CP2K
- DFT BLYP-D3/TZ2VP
- 4 TMU/40 H_2O
- 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

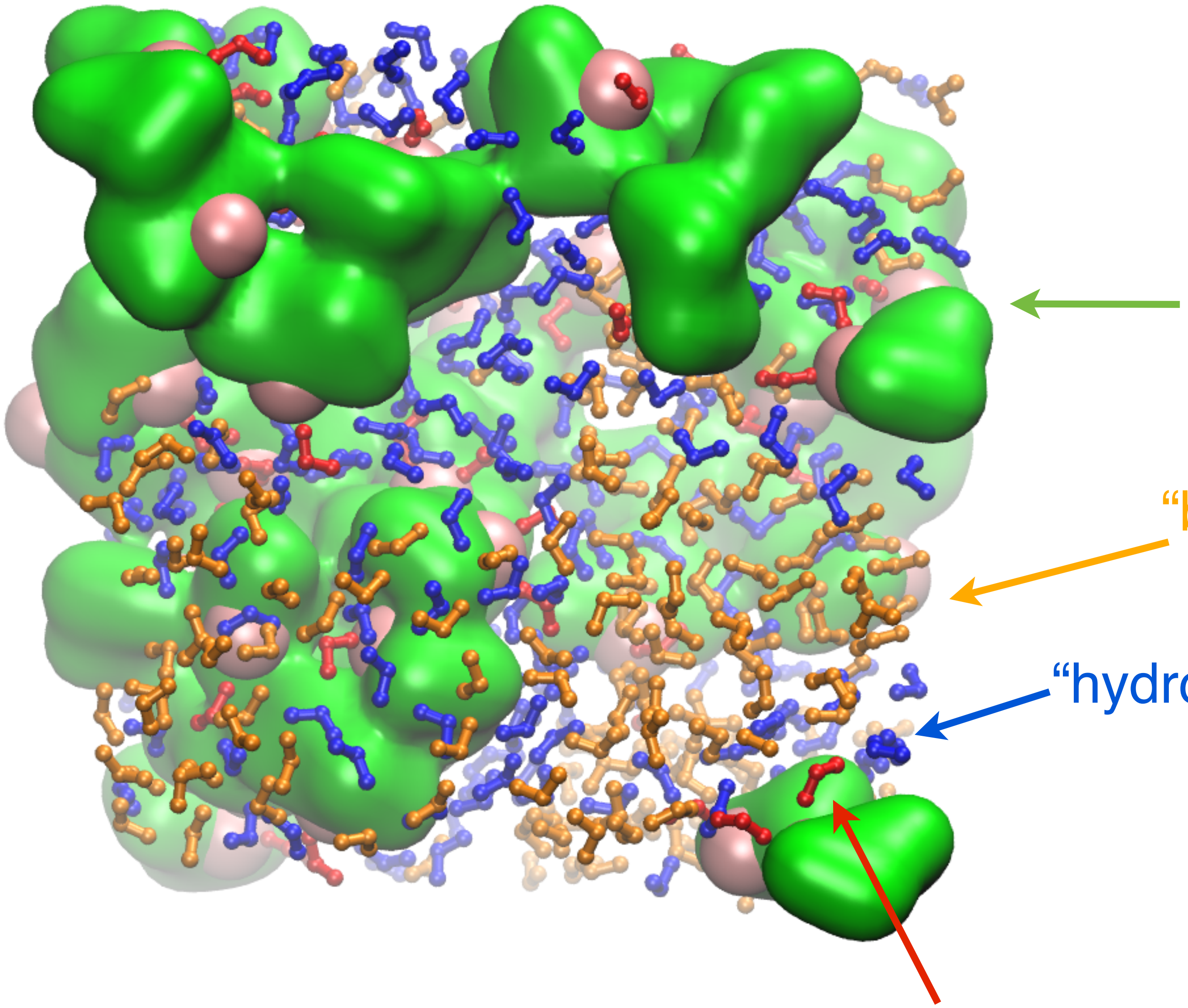
Fit function:

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

Water partitioning

TMU

CMD simulation snapshot



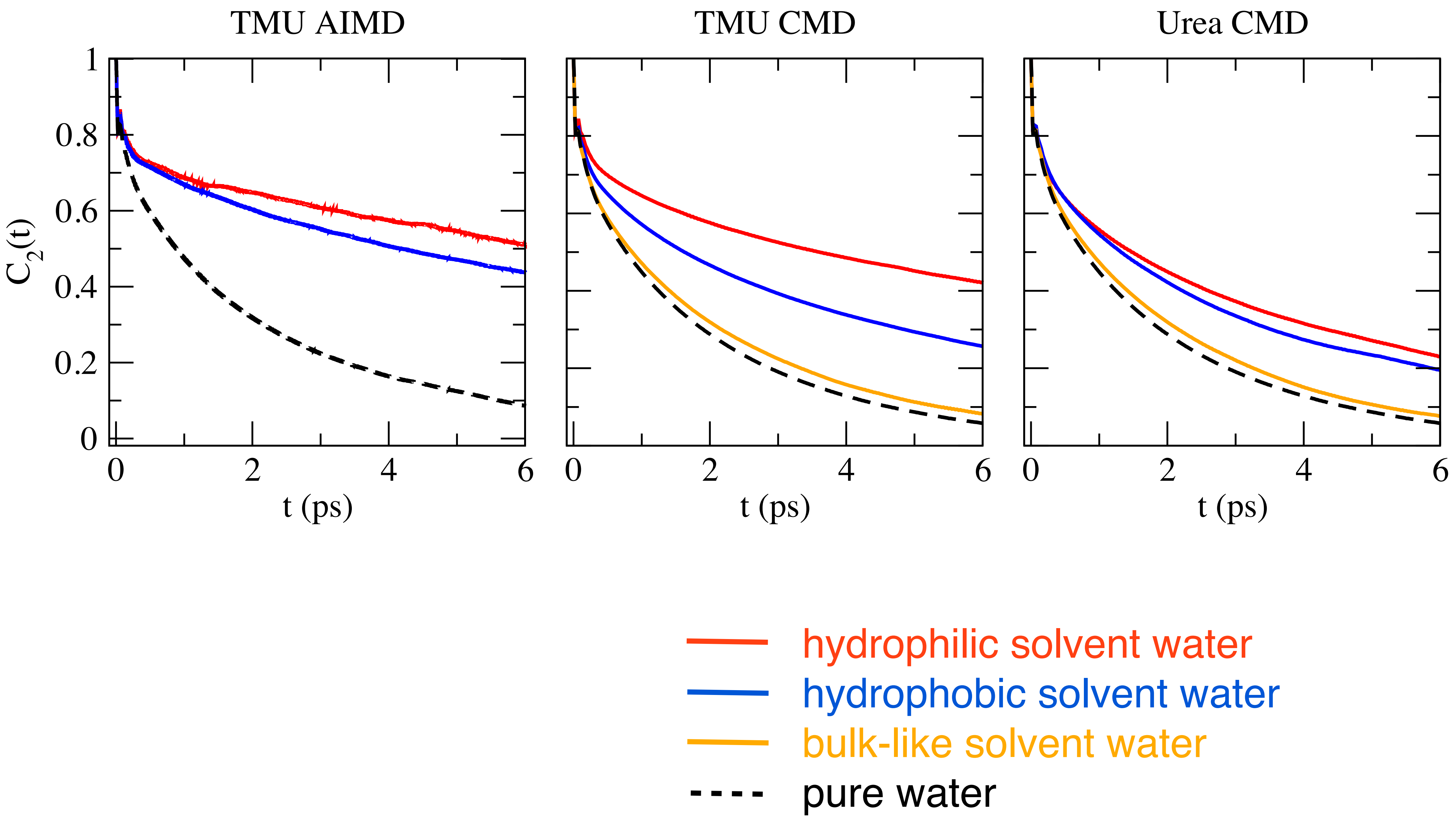
TMU solutes

“bulk” water

“hydrophobic” water

“hydrophilic” water

Water partitioning

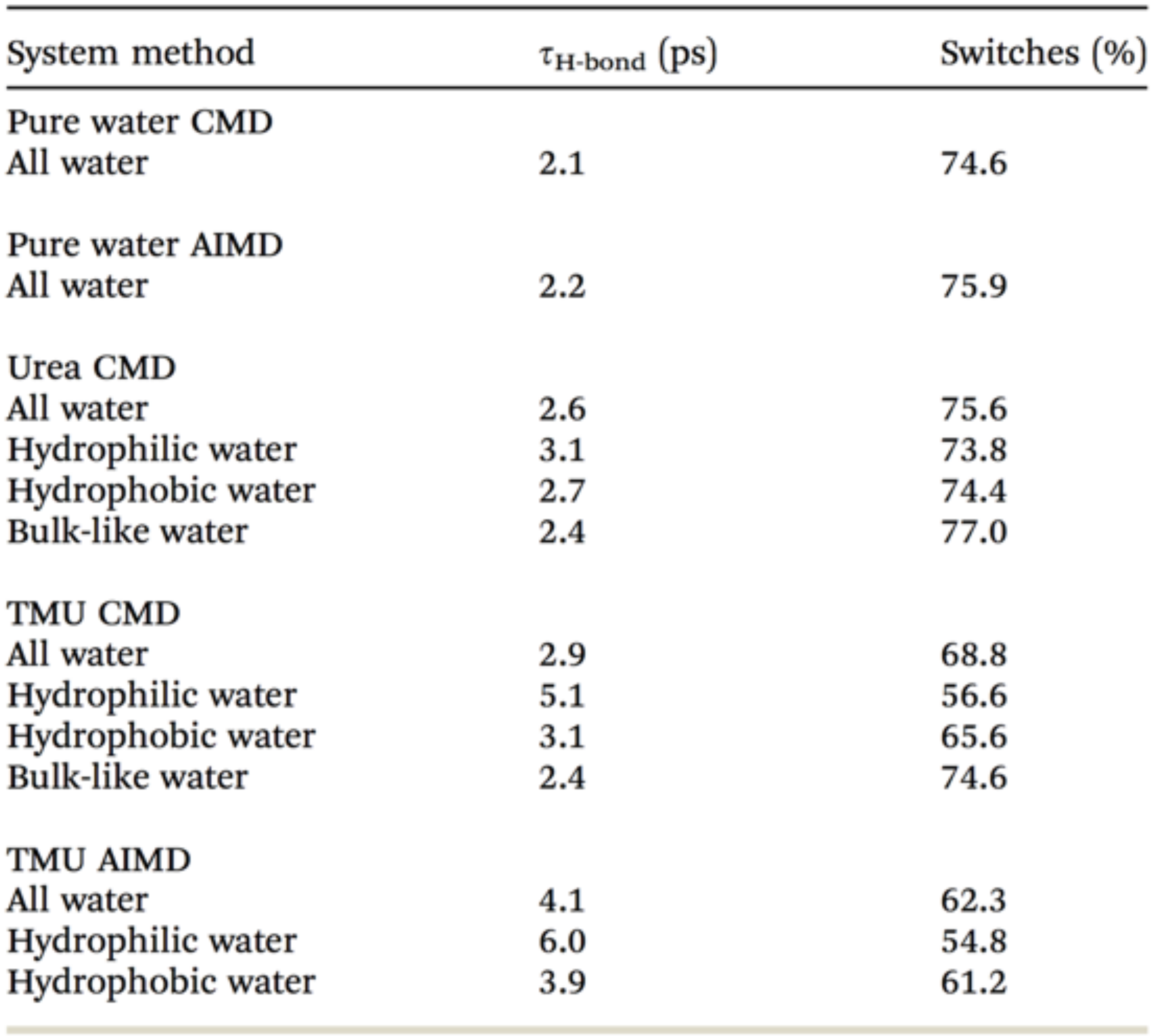


System method	Fit interval (ps)	τ_{fast} (ps)	τ_{mid} (ps)	τ_{slow} (ps)
Pure water CMD	0–50			
All water		0.3	2.4 (1.9)	—
Pure water AIMD	0–15			
All water		0.5	3.1 (2.1)	—
Pure water fs-IR	2–10			
All water		—	— (2.3)	—
Urea CMD	0–12			
All water		0.6	3.6	—
Hydrophilic water		0.5	6.1	—
Hydrophobic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

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)

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

Summary

1. Intro: what about solvent effects?
2. Fundamentals: Permittivity, dielectric media
3. Implicit solvation: Continuum models, PCM, COSMO,…
4. Explicit solvation: Ewald summation
5. Thermodynamic properties of liquids from the PT2 model
6. Measurements and modelling of anisotropy relaxation

Bibliography

- Non-aggregating solvatochromic bipolar benzo[f]quinolines and benzo[a] acridines for organic electronics
  A Goel, V Kumar, S.P. Singh, A Sharma, S Prakash, C Singhb, R. S. Anand
  J. Mater. Chem. 22, 14880 (2012)
- Pyrene-based D–p–A dyes that exhibit solvatochromism and high fluorescence brightness in apolar solvents and water
  Y. Niko, Y. Cho, S. Kawauchia,G, Konishi
  RSC Adv. 4, 36480 (2014)
- J. Chandrasekhar, S.F. Smith, W. L. Jorgensen
  J. Am. Chem. Soc. 107, 154-163 (1985)
- Generalised Born Models of Macromolecular Solvation Effects
  D. Bashford and D.A. Case
  Anna. Rev. Phys. Chem. 51, 129 (2000)
- K.I. Ramachandran, Deepa Gopakumar, and Krishnan Namboori. Computational Chemistry and Molecular Modeling: Principle and Applications. Springer Berlin Heidelberg 2008. Pages 250- 253.
- Mennucci, B., Tomasi, J., Cammi, R., Cheeseman, J.R., et al., Polarizable Continuum Model (PCM) Calculations of Solvent Effects on Optical Rotations of Chiral Molecules. J. Phys. Chem. 2002. 106(25):6102-6113.
- Onsager, L., Electric Moments of Molecules in Liquids.
  J. Am. Chem. Soc. 1936. 58:1486-1493.
- Mennucci, B. and Cammi, R.. Continuum Solvation Models in Chemical Physics: From Theory to Applications. John Wiley & Son 2008. Pages 65-80.
- Marenich, A., Cramer, C.J., and Truhlar, D.G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. J. Phys. Chem. B 2009, 113:6378-6396.
- Cramer, C., Essentials of Computational Chemistry: Theories and Models. John Wiley and Sons 2004. Pages 386-410.
- Foresman, J., and Frisch, A., Exploring Chemisty with Electronic Structure Methods. Gaussian Inc. 1996. Pages 237-248.
- Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena, A. Klamt, J. Phys.Chem. 99,. 2224 (1995)
- Refinement and Parametrization of COSMO-RS, A. Klamt, V. Jonas, T. Bürger, JCW Lohrenz, J. Phys. Chem. A, 102, 5074(1998)
- The COSMO and COSMO-RS solvation models, A. Klamt, Wiley Interdisciplinary Reviews: Computational Molecular Science. WIREs Comput Mol Sci 2011 1 699-709,
- Ewald summation techniques in perspective: a survey
  A.Y. Toukmaji and J.A. Board Jr.
  Comp. Phys. Comm. 95, 73 (1996)
- Understanding Molecular Simulation,
  B. Smit and D. Frenkel 2nd Ed. Academic Press 2002
- The two-phase model for calculating thermodynamic properties of liquids from molecular dynamics: Validation for the phase diagram of Lennard-Jones fluids, S-T. Lin, M. Blanco, and W.A. Goddard III
- J. Chem. Phys 119, 11792 (2003)
- Thermodynamics of liquids: standard molar entropies and heat capacities of common solvents from 2PT molecular dynamicsw, T. A. Pascal,ab ST. Lin and W.A. Goddard III, Phys. Chem. Chem. Phys. 13, 169 (2011)
- Local orientational ordering in liquids revealed by resonant vibrational energy transfer, M. R. Panman, D, J. Shaw, B, Ensing, and S, Woutersen
  Phys. Rev. Lett. 113, 207801 (2014)
- On the slowdown mechanism of water dynamics around small amphiphiles. W.H. Brandeburgo, S.T. van der Post, E.J. Meijer, and B. Ensing, Phys. Chem. Chem. Phys. 17, 24968 (2015)