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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.
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

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

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
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 constant”, 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.

$$C = \varepsilon_r C_0$$

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

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_r$</th>
<th>Dielectric strength $(10^6 \text{ V/m})$</th>
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<tbody>
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<td>Air</td>
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<tr>
<td>Paper</td>
<td>3.7</td>
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<td>Glass</td>
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<td>9</td>
</tr>
<tr>
<td>Water</td>
<td>80</td>
<td>–</td>
</tr>
</tbody>
</table>

Orientation of polar molecules:

Charge redistribution within molecules, inducing dipoles:
Static dielectrics

A medium of permanent or induced dipoles has a polarisation density \( \mathbf{P} \), which is the dipole moment per unit volume:

\[
\mathbf{P} = \lim_{\Delta V \to 0} \frac{1}{\Delta V} \sum_{i=1}^{n} \mathbf{p}_i \quad [\text{C} / \text{m}^2]
\]

Without an external electric field \( \mathbf{E} \), the dipoles are oriented randomly and the polarisation density \( \mathbf{P} \) is zero.

The relation between the field \( \mathbf{E} \), and the polarisation density \( \mathbf{P} \), for an isotropic and linear dielectric:

\[
\mathbf{P} = \chi_e \epsilon_0 \mathbf{E}
\]

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

The electric displacement \( \mathbf{D} \) is related to the polarisation density as:

\[
\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 (\chi_e + 1) \mathbf{E} = \epsilon_r \epsilon_0 \mathbf{E}
\]

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

\[
\mathbf{E} = \mathbf{E}_{\text{ext}} + \mathbf{E}_{\text{pot}} = \mathbf{E}_{\text{ext}} - \frac{\mathbf{P}}{\epsilon_0} \quad \Rightarrow \quad \mathbf{E} = \frac{\mathbf{E}_{\text{ext}}}{\epsilon_r}
\]

The field in the material is reduced.

\( \epsilon_0 = \left( \frac{c^2 \mu_0}{1} \right) \)

- in capacitor: \( C = \epsilon_r C_0 \)
Dielectric constant of water

Why is the permittivity temperature dependent?

Static Relative Permittivity of Water at 10 MPa
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)

\[ \varepsilon = \varepsilon' + i \varepsilon'' \]

1. **Ionic motions**
2. **Orientation of dipoles** (microwave)
3. **Atomic motions** ((far-)infrared)
4. **Electronic motions** (UV/Vis)

**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 \( \varepsilon_0 \) remains.

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

\[ P(t) = \varepsilon_0 \int_{-\infty}^{t} \chi_e(t - t') E(t') dt' \]

**Fourier transform of linear system:**

\[ P(\omega) = \varepsilon_0 \chi_e(\omega) E(\omega) \]

Link to causality: polarisation can only depend on \( E \) of previous times.
A material cannot polarise instantaneously in response of an applied field.

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

Treat permittivity as a complex function of frequency:

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

$D_0$ amount of displacement

$E_0$ amplitude of electric field

$i = \sqrt{-1}$

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

High frequency limit: $\epsilon_{\infty}$

$\epsilon'$: energy stored in medium

$\epsilon''$: energy dissipated in medium

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

$\epsilon''/\epsilon' = 0$ : perfect lossless dielectric

$\epsilon''/\epsilon' = \infty$ : perfect conductor
Debye relaxation

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

\[ \varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \]

\[ \varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2 \tau^2} \]

Static limit: \( \varepsilon_s = \lim_{\omega \to 0} \varepsilon(\omega) \)

High frequency limit: \( \varepsilon_\infty \)

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

Peter Debye
1884–1966
Chemistry Nobel prize (1936)

Modifications to Debye model:
- Cole-cole model
- Cole-Davidson model
- Havriilak-Negami relaxation
- …
Water models

Dielectric constant computed:
- Forcefield MD
- NVT ensemble
- 400 molecules
- PBC/Ewald

Dielectric constant from fluctuations:
\[ \epsilon_T = 1 + \frac{4\pi}{3V k_B T} \left( \langle M^2 \rangle - \langle M \rangle^2 \right) \]

- < > : ensemble average
- Total dipole moment: \( M = \sum_i^N p_i \)

Global properties converge slowly:
Solvent at a charged surface

Gouy-Chapman model (1910-1913)

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

$$-\nabla^2 \phi = \frac{\rho_f}{\varepsilon_r \varepsilon_0}$$  \hspace{1cm} \text{Poisson equation}$$

The distribution of the charges is governed by Boltzmann statistics:

$$\rho_i(r) = \rho_i^\infty(r) \exp\left(\frac{-W_i(r)}{k_B T}\right)$$  \hspace{1cm} \text{Boltzmann distribution}$$

Combining these gives the Poisson-Boltzmann equation:

$$\nabla^2 \phi(r) = -\frac{1}{\varepsilon_r \varepsilon_0} \sum_i z_i \rho_i^\infty(r) \exp\left(\frac{-z_i \phi(r)}{k_B T}\right)$$

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

\( z_i \): charge of ion \( i \)  
\( \Phi(r) \): electrostatic potential at \( r \)  
\( \rho(r) \): charge density of the solute  
\( k_B \): Boltzmann’s constant  
\( T \): temperature  
\( \varepsilon \): dielectric constant
Debye-Hückel

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

\[ \exp \left( \frac{-z_i \phi(r)}{k_B T} \right) \approx 1 - \frac{-z_i \phi(r)}{k_B T} \]

giving:

\[ \nabla^2 \phi(r) = -\frac{1}{\varepsilon_r \varepsilon_0} \sum_i \left( \frac{-z_i^2 \rho_i^\infty}{k_B T} \right) \phi(r) - \sum_i -z_i \rho_i^\infty \]

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

The Debye (screening) length: \( \lambda_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{\sum_i -z_i^2 \rho_i^\infty}} \)

The electric potential due to a charge Q is exponential screened by the medium with the characteristic length \( \lambda_D \):

\[ \phi(r) = \frac{Q}{4\pi \varepsilon_r \varepsilon_0 r} e^{-r/\lambda_D} \]
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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:

\[ \Delta G_{\text{sol}} = \Delta G_{\text{elec}} + \Delta G_{\text{VdW}} + \Delta G_{\text{cavity}} \]

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)

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

$q$: charge of the ion

$b$: radius of the ion

bring charge from infinity to $b$:

\[ \Delta U = \frac{1}{\epsilon b} \int_0^{q'} qdq \]

Generalised Born Equation:

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

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 Born radii (i.e. the solvent accessible surface)

GB model neglects:

- cavity energy, solute-solvent VdW
- solvent polarisation by solute
The solvation free energy contains 3 terms:

\[ G_{\text{sol}} = G_{\text{es}} + G_{\text{dr}} + G_{\text{cav}} \]

- **G\text{es}**: electrostatic interaction
- **G\text{dr}**: dispersion + repulsion
- **G\text{cav}**: 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:

\[
v_{\text{pcm}}(\mathbf{r}) = \int_{\Sigma} \frac{\sigma(s)}{|\mathbf{r} - \mathbf{s}|} d\mathbf{s} \approx \sum_{k=1}^{T} \frac{q_k}{|\mathbf{r} - \mathbf{s}_k|}
\]

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:

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

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 Screeening MOdel for Real Solvents

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

$$q = f(\epsilon)q_{\text{solute}}$$

$$f(\epsilon) = \frac{\epsilon - 1}{\epsilon + x}$$

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

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

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

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

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

electrostatic potential at ion $i$:
$$\phi(\mathbf{r}_i) = \sum_{j,n} \frac{q_j}{|\mathbf{r}_{ij} + n\mathbf{L}|}$$

sum over periodic images

neutral box with 2 ions:

unit cell

screened charges

smoothly varying background
Ewald Summation

Choice of Ewald parameters, $\alpha$, $k_{\text{max}}$, $n_{\text{max}}$

- A smaller Gaussian width (i.e. larger $\alpha$) makes the short-range sum converge faster (smaller $n_{\text{max}}$)
- Wider Gaussians (i.e. small $\alpha$) makes the long-range sum converge faster (smaller $k_{\text{max}}$)
- 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: $R_{\text{cuttoff}}=9$ 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)
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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:

\[ U = 3 \times \frac{1}{2} RT + 3 \times \frac{1}{2} RT + (3N - 6) \times RT \]

\[ \text{translation} \quad \text{rotation} \quad \text{vibration} \]

- Quantisation of energy levels is not negligible

\[ q_i^{\text{vib}} = \frac{\exp(-\beta h \nu_i/2)}{1 - \exp(-\beta h \nu_i)} \]

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

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

\[ \kappa = \frac{1}{3V k_B T^2} \lim_{\tau \to \infty} \int_0^\tau \langle J(t) J(0) \rangle dt \]
PT2 method by William Goddard III et al

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: $S$, $H$, $G$, $C_v$, ZPE,..

$$C_v = k\int [DoS(v)_{\text{trans}} W_{\text{trans}}^{C_v}(v) + DoS(v)_{\text{solid}} W_{\text{solid}}^{C_v}(v)] dv$$

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<th></th>
<th>gaff</th>
<th>opls</th>
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<td>$C_p$</td>
<td>30.23</td>
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<tr>
<td>$S$</td>
<td>53.88</td>
<td>45.98</td>
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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)
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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
  \[ V_{ij} = \frac{\mu_i\mu_j}{4\pi\varepsilon_0 r_{ij}^3} \left[ \mathbf{e}_{\mu_i} \cdot \mathbf{e}_{\mu_j} - 3(\mathbf{e}_{\mu_i} \cdot \mathbf{e}_{r_{ij}})(\mathbf{e}_{\mu_j} \cdot \mathbf{e}_{r_{ij}}) \right] \]

- Anisotropy decay
  \[ R(t) = \left\langle \frac{1}{2} (3 \cos^2 \theta - 1) \right\rangle = \sum_i \frac{1}{2} (3 \cos^2 \theta_i - 1) \frac{p_i}{\sum p_i} \]
Orientation dependent decay

(a) Nearest neighbors at large angle

(b) Nearest neighbors approx. parallel

Anisotropy $R$ vs time $t$

$P(\theta)$ vs bond-bond angle $\theta$ (degrees)
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**

- NMA, $x = 0.005$
- EtOH, $x = 0.005$
- NMA, $x = 0.4$
- EtOH, $x = 0.4$
- NMA, $x = 1$
- EtOH, $x = 1$

**Measurement**

- NMA, $x = 1$
- EtOH, $x = 1$
- $x = 0.4$
- $x = 0.05$
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

Fit function: \[ C_2(t) = A_0 \left( \cos \left( \frac{2\pi t}{\tau_{\text{sub}}} \right) \cdot e^{\frac{-t}{\tau_d}} + e^{\frac{-t}{\tau_{\text{fast}}}} \right) + (1 - A_0) e^{\frac{-t}{\tau_{\text{mid}}}} \]
Water partitioning

CMD simulation snapshot

TMU solutes

“bulk” water

“hydrophobic” water

“hydrophilic” water
Water partitioning

![Graphs showing water partitioning with different solvent types: hydrophilic, hydrophobic, bulk-like, and pure water.](image)
<table>
<thead>
<tr>
<th>System method</th>
<th>Fit interval (ps)</th>
<th>( \tau_{\text{fast}} ) (ps)</th>
<th>( \tau_{\text{mid}} ) (ps)</th>
<th>( \tau_{\text{slow}} ) (ps)</th>
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<td>Pure water CMD</td>
<td>0–50</td>
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<td>2.4 (1.9)</td>
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<td>6.1</td>
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<td>TMU CMD</td>
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<td>3.0 (2.2)</td>
<td>9.0 (( \infty ))</td>
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<tr>
<td>All water</td>
<td></td>
<td></td>
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<td>Hydrophilic water</td>
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<td>5.1</td>
<td>&gt;20</td>
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<tr>
<td>Hydrophobic water</td>
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### H-bond life times and breaking mechanism

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<th>Switches (%)</th>
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**Model**

- 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)
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
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• Pyrene-based D–p–A dyes that exhibit solvatochromism and high fluorescence brightness in apolar solvents and water
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• Local orientational ordering in liquids revealed by resonant vibrational energy transfer, M. R. Panman, D. J. Shaw, B, Ensing, and S, Woutersen