Computational Spectroscopy of Reverse Micelles

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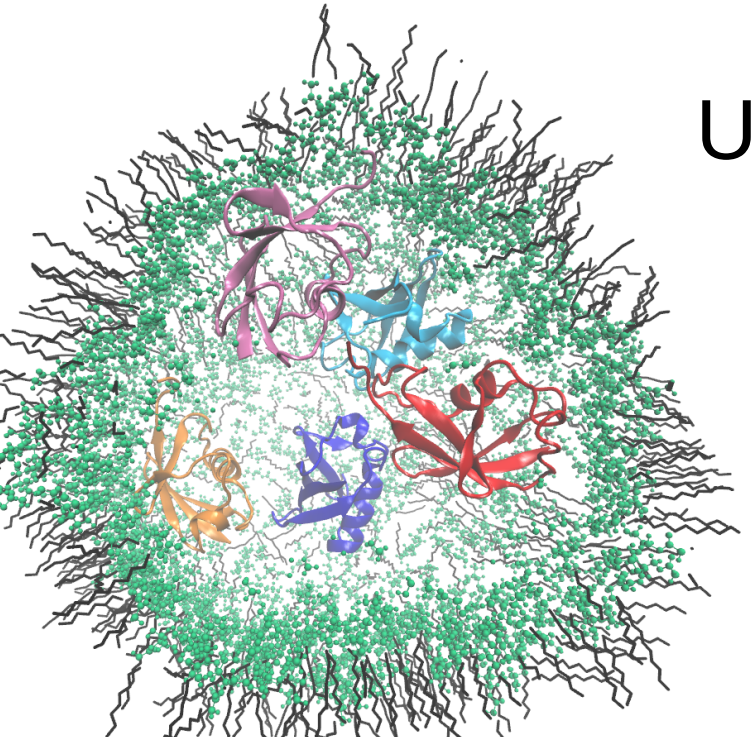
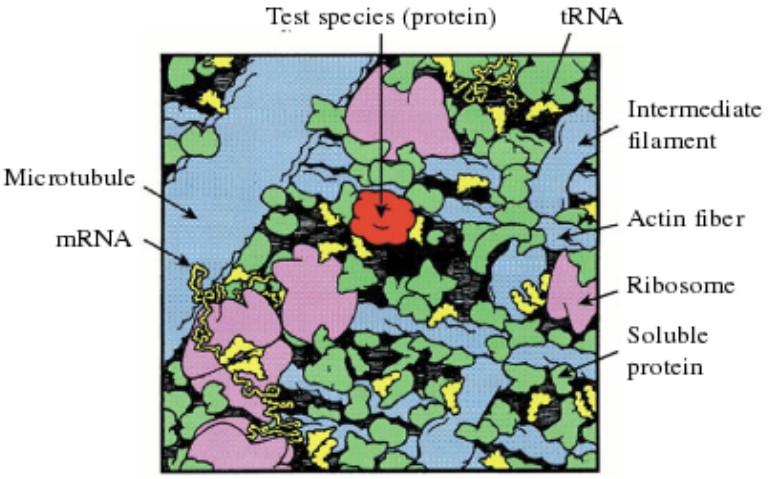


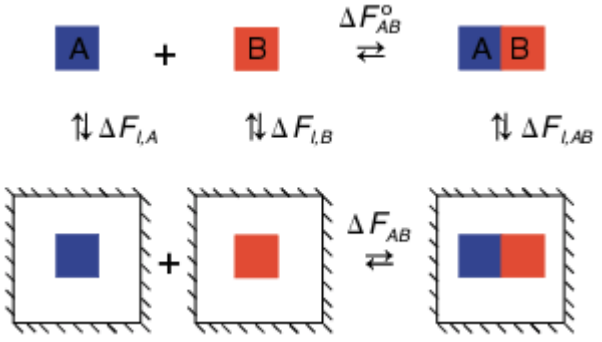
universität wien

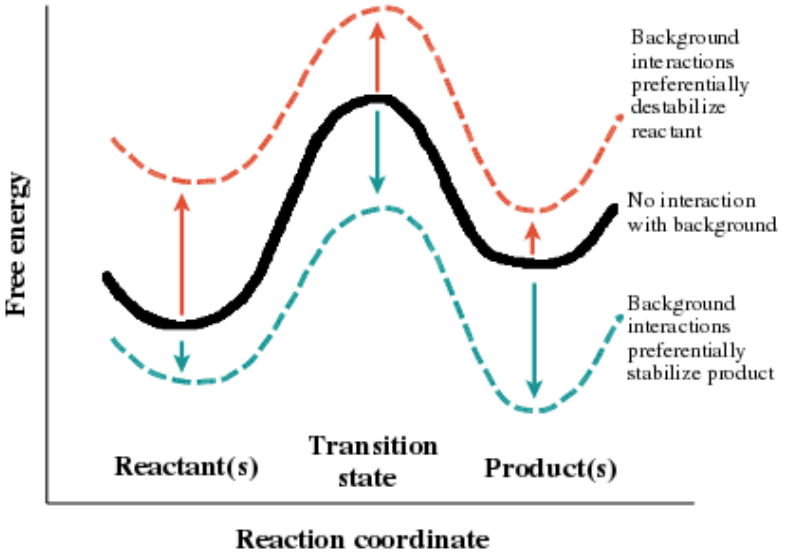
Crowding and encapsulation

- Chemical environment of an actual cell differs from that of a diluted buffer



- Impacts both thermodynamic equilibria and kinetic reaction rates





Images taken from A. P. Minton, *J. Cell Sci.* **2006** *119*, 2863-2869

Macromolecular confinement

- Impact on:
  - Molecular mobility
  - Folding rates
  - Aggregation behaviour
  - Biomolecular equilibria
  - Reaction rates
  - ...

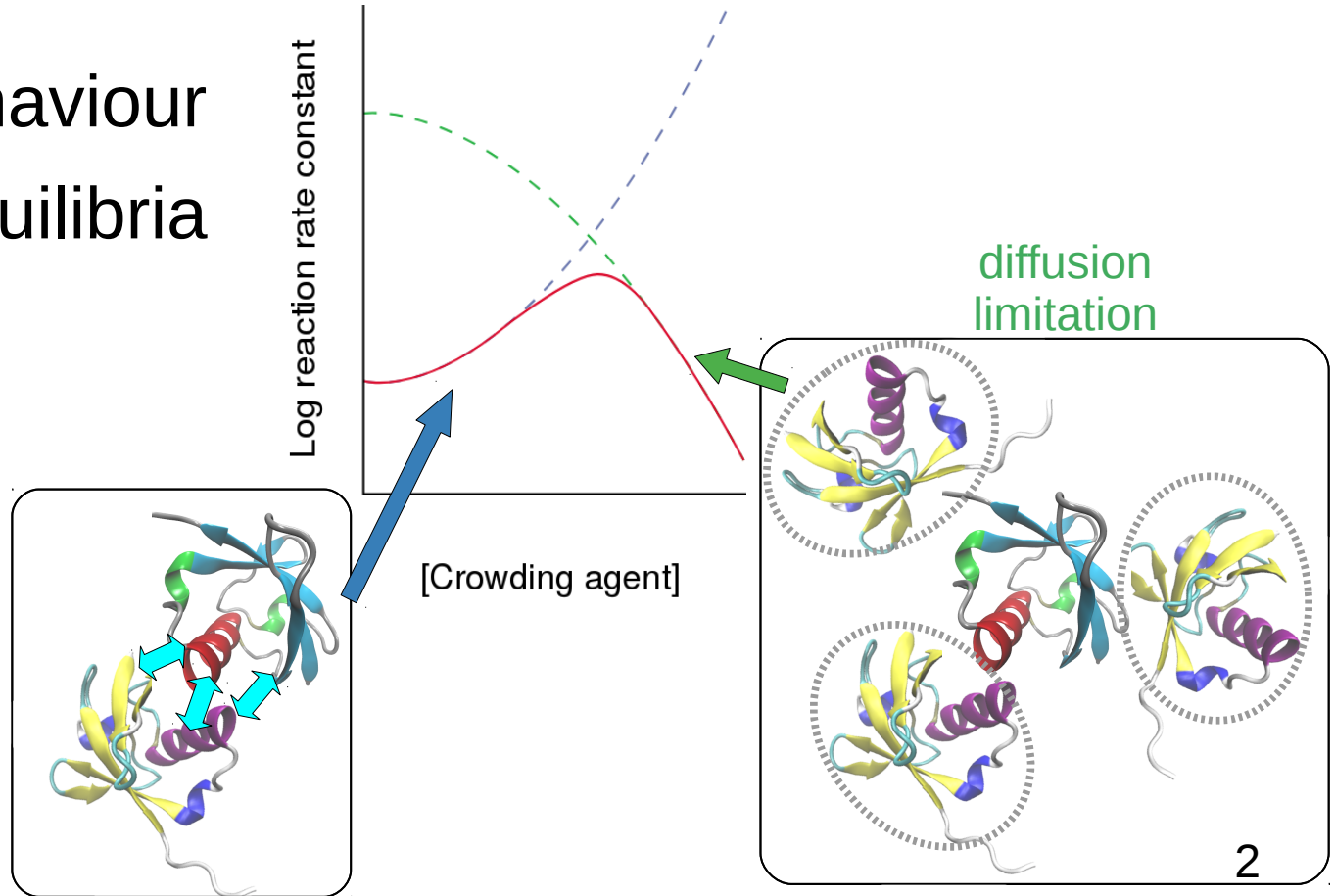
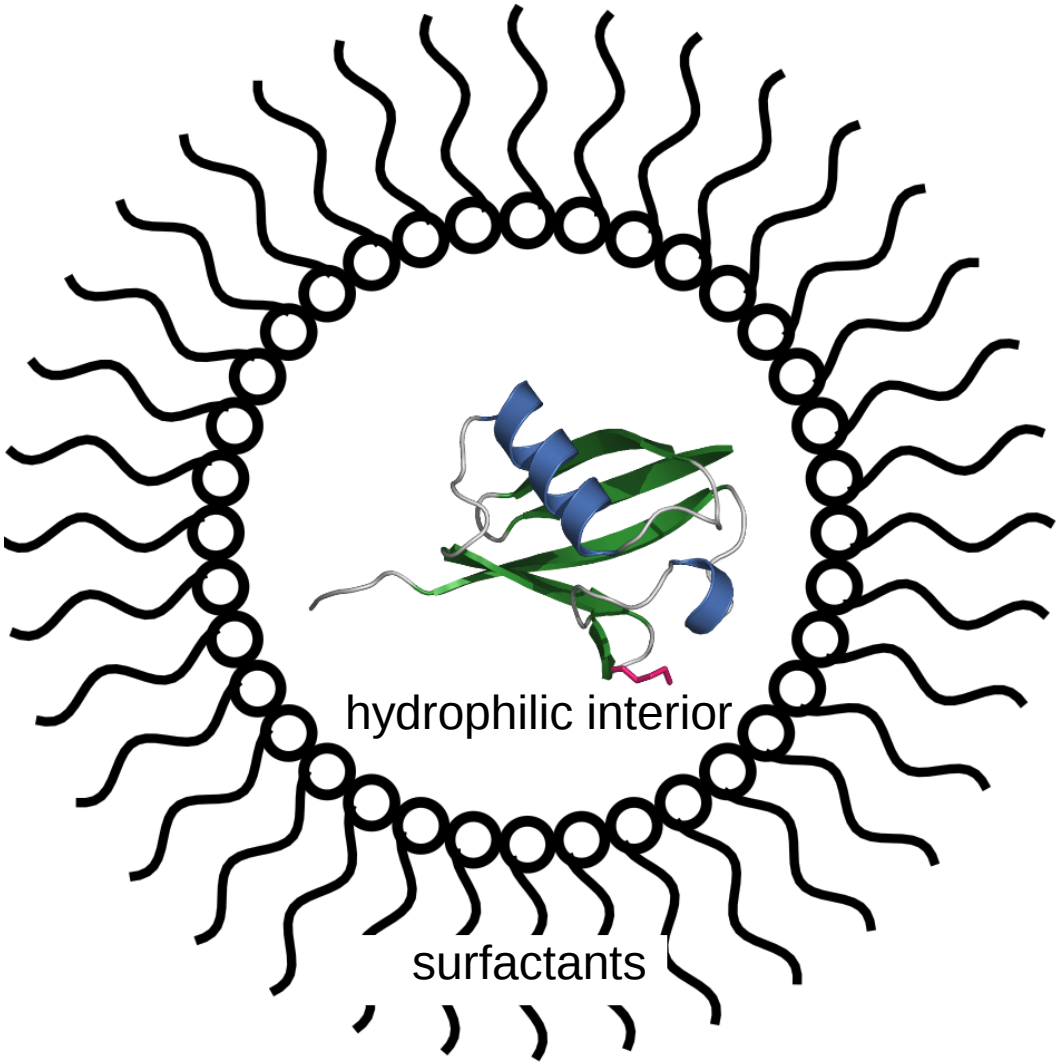
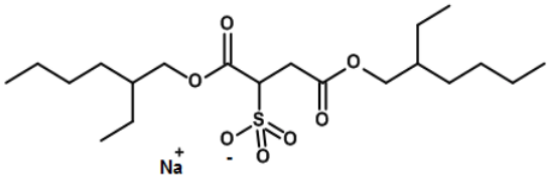


Diagram taken from R. John Ellis, *Trends Biochem. Sci.* 2001, *26*, 2863-2869

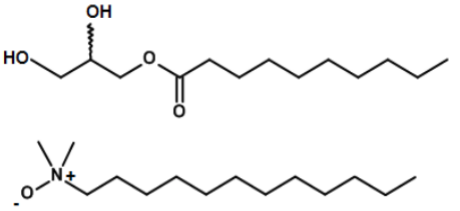
Reverse micelles as cell mimics



Example surfactant molecules:



bis(2-ethylhexyl)-sulfosuccinate
(aerosol-OT, AOT)



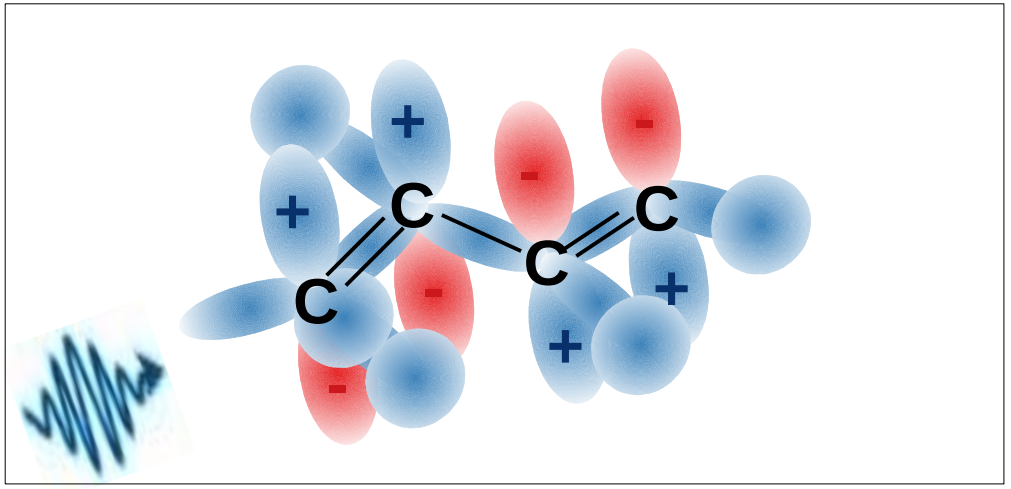
65 1-decanoyl-rac-glycerol (DMAG) / 35
lauryldimethylamine-N-oxide (LDAO)

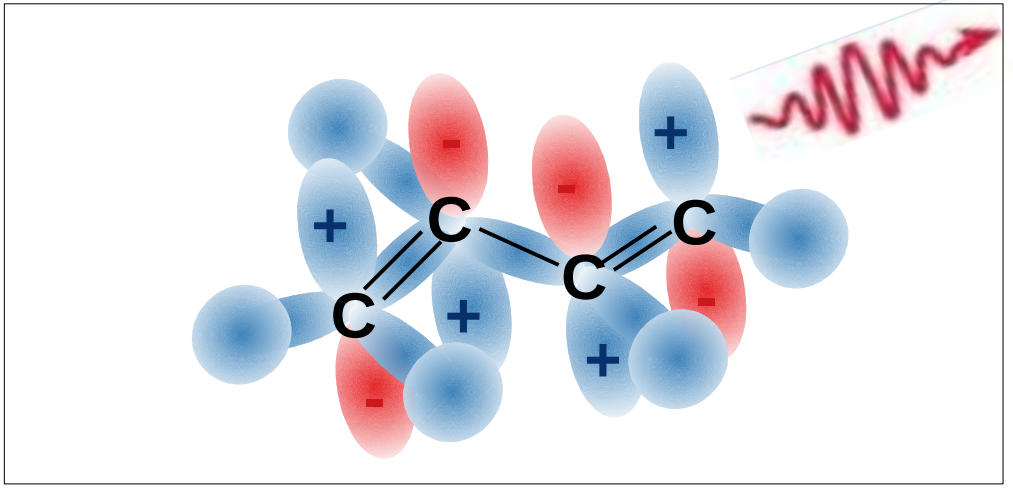
Spectroscopy:
A molecule-level microscope

The umbrella term spectroscopy encompasses various kinds of measurements of the interaction between matter and electromagnetic waves.

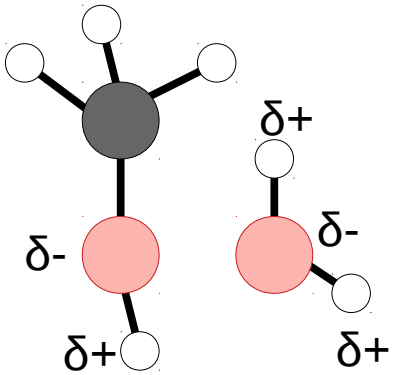
Depending on the latter's frequency, different constituents of physical matter will resonate with the incoming radiation.

M. Schmollngruber





Molecular Dynamics (MD) Simulations

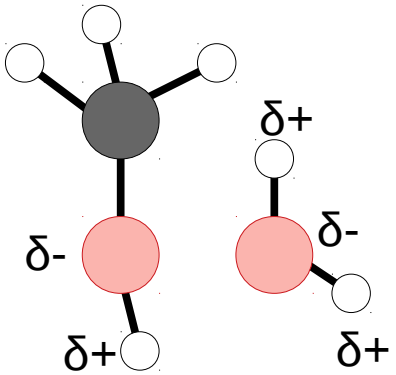


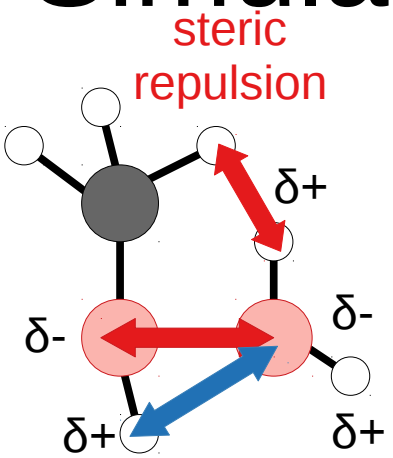
time step *t*

Atom count n
Atom positions **r**(n,x,y,z,t)
Atomic masses m(n)
Atomic charges q(n)
Nonbonded parameters
Bonds, Angles, Dihedrals

→ **evaluate potentials**

Molecular Dynamics (MD) Simulations





time step *t*	potential function V(n)
Atom count n Atom positions **r**(n,x,y,z,t) Atomic masses m(n) Atomic charges q(n) Nonbonded parameters Bonds, Angles, Dihedrals → **evaluate potentials**	Calculate the atomic forces as the negative gradient of the potential → **calculate forces**

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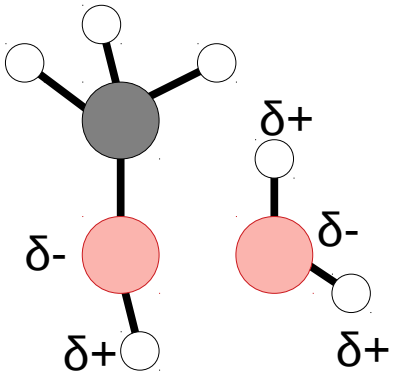

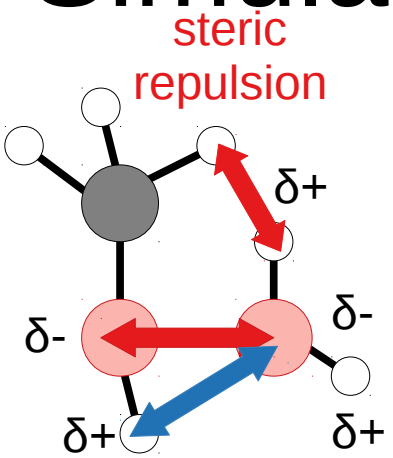

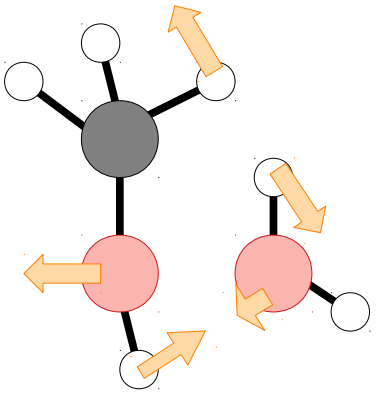

time step *t*	potential function V(n)	forces f(n,x,y,z,t)
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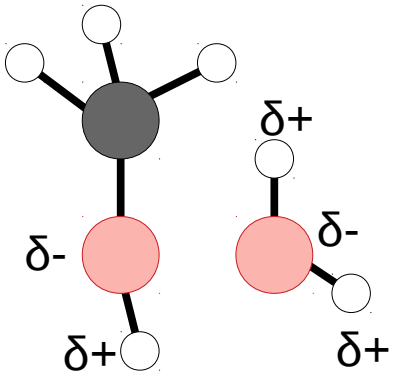
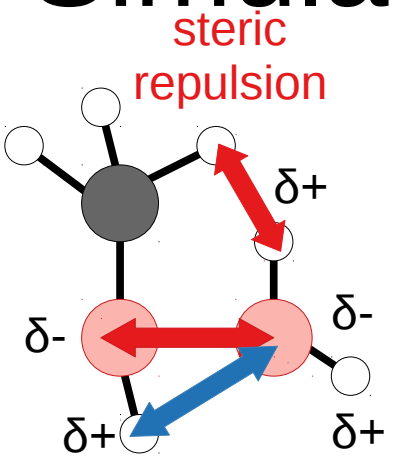
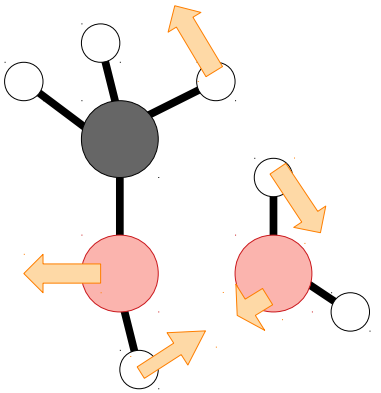
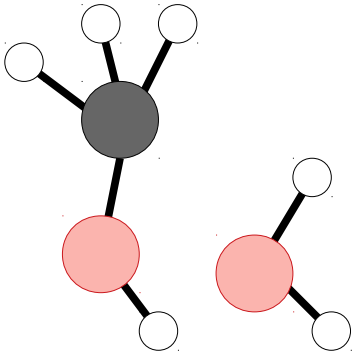
Molecular Dynamics (MD) Simulations









time step *t*	potential function V(n)	forces f(n,x,y,z,t)	time step *t*+1
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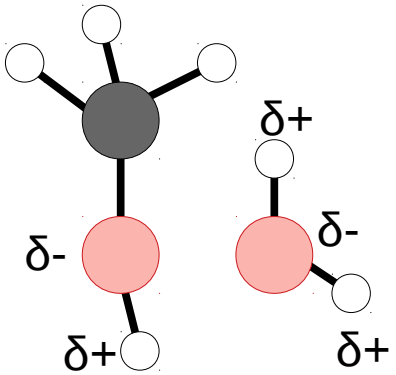
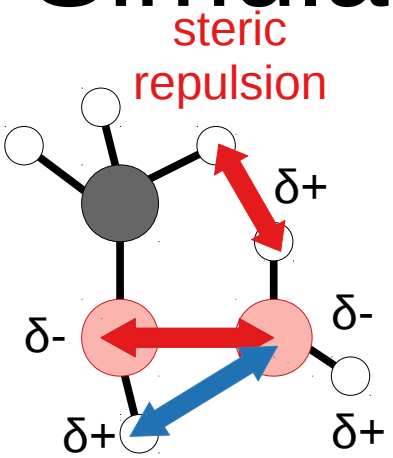
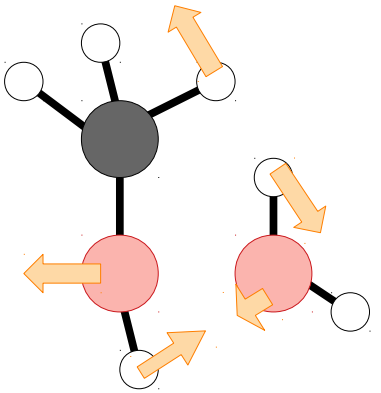
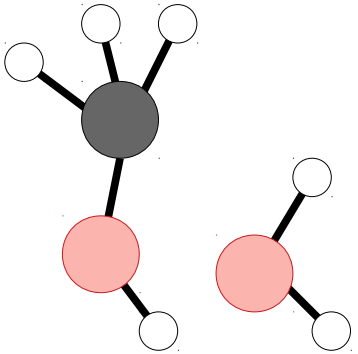
Molecular Dynamics (MD) Simulations





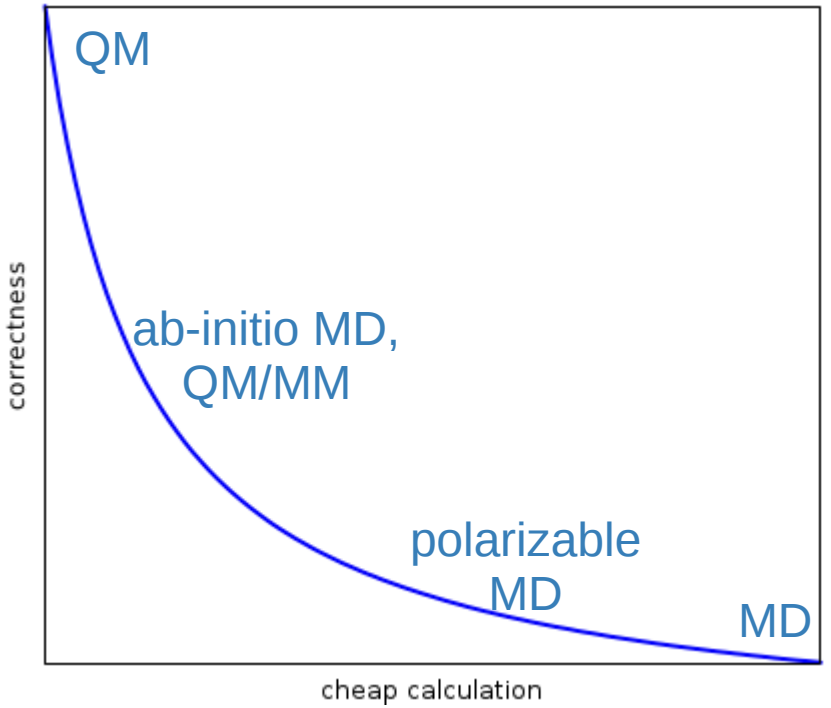




time step *t*	potential function V(n)	forces f(n,x,y,z,t)	time step *t*+1
Atom count n Atom positions **r**(n,x,y,z,t) Atomic masses m(n) Atomic charges q(n) Nonbonded parameters Bonds, Angles, Dihedrals → **evaluate potentials**	Calculate the atomic forces as the negative gradient of the potential → **calculate forces**	Integrate the equations of motion to get the new atomic positions → **calculate r(**n,x,y,z,t+1**)**	Iterate this t_{max} times to obtain the trajectory: r(n,x,y,z,t) v(n,x,y,z,t)

Why MD simulations?

… and not Quantum Mechanics (QM)?



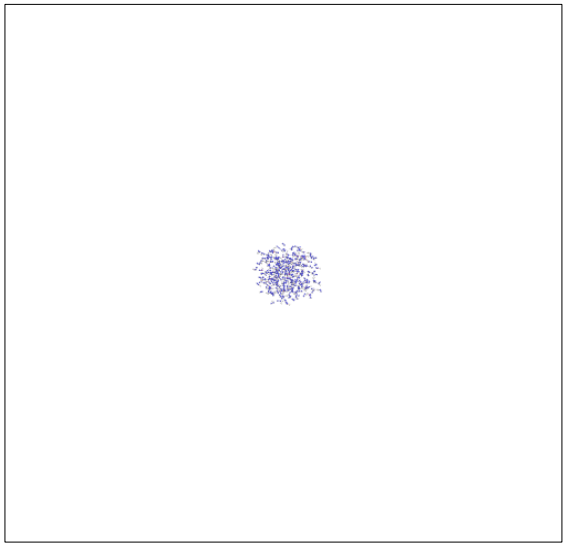
"*The only way to calculate spectroscopic observables correctly is to use QM*"

Why Molecular Dynamics Simulations?

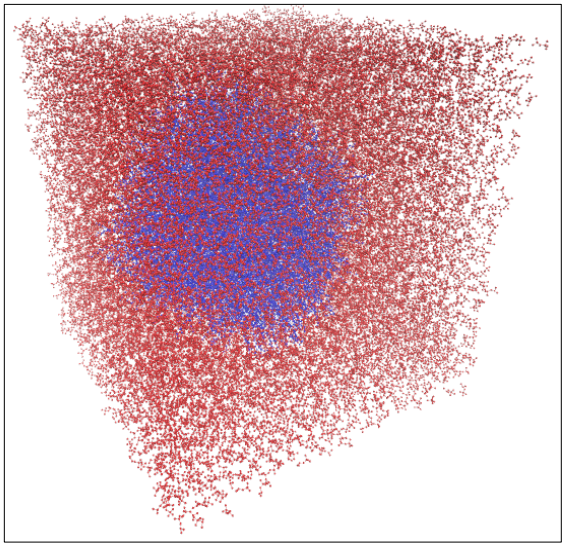
- QM is size-limited, hence limited to some classes of matter.

  Soft matter systems:

  - Condensed like solids
  - Dynamics like fluids
  - Complicated dynamics with manifold processes



Manageable with QM:
~768 atoms



Our system size:
~119,655 atoms

Why Molecular Dynamics Simulations?

- QM is size-limited, hence not always applicable

  Soft matter systems:

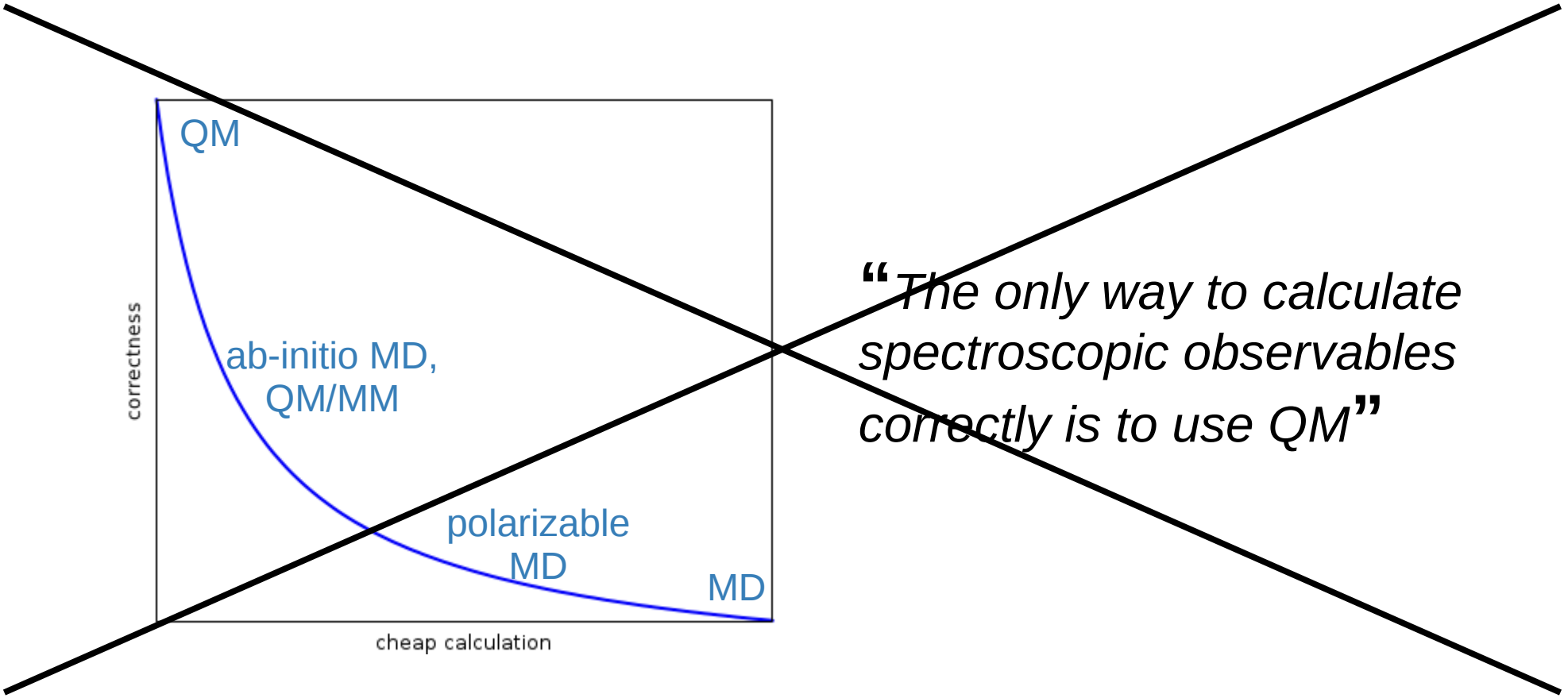
  - Condensed like solids
  - Dynamics like fluids
  - Complicated dynamics with manifold processes

- QM not always better at reproducing observables than MD!

  QM bound to fail if the statistic stability of an observable

  - Requires many time frames
  - Requires many particles
  - Requires large spatial extension (boundary conditions)

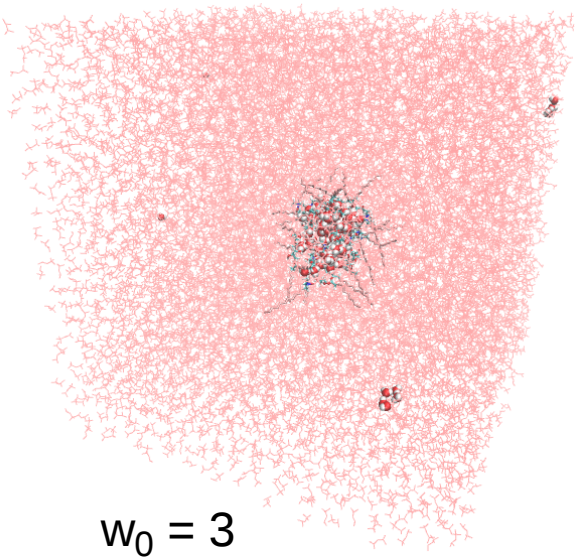
Why MD simulations?



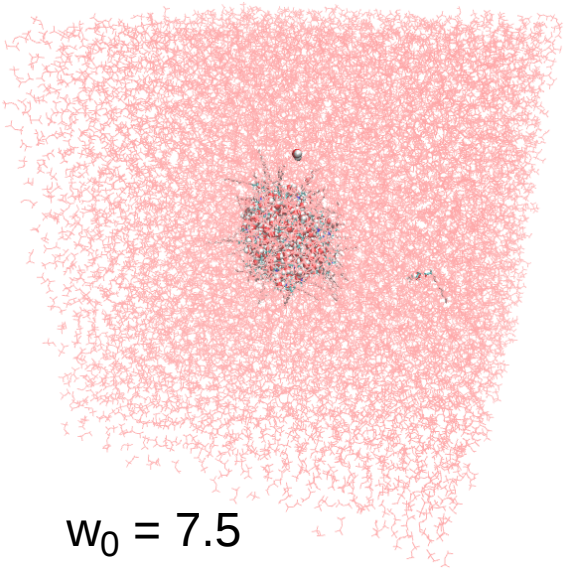
"The only way to calculate spectroscopic observables correctly is to use QM"

→ **Use the right tool for the right job!**

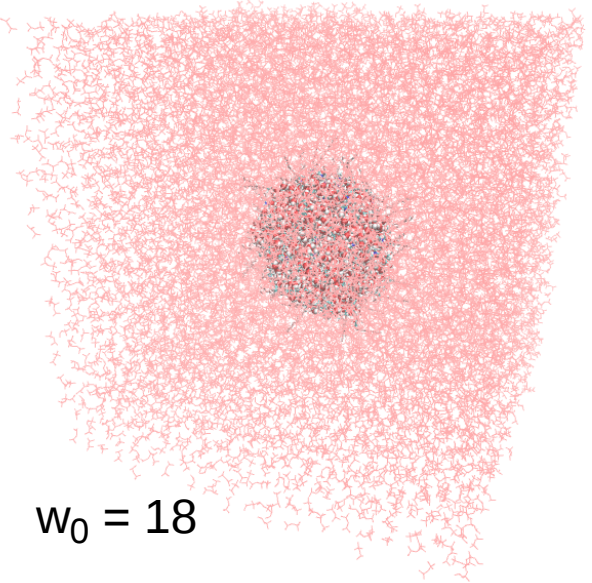
MD simulations of reverse micelles



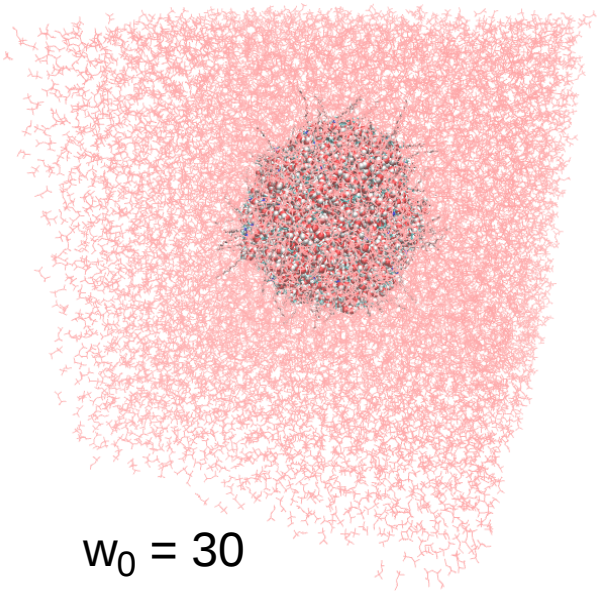
$w_0 = 3$



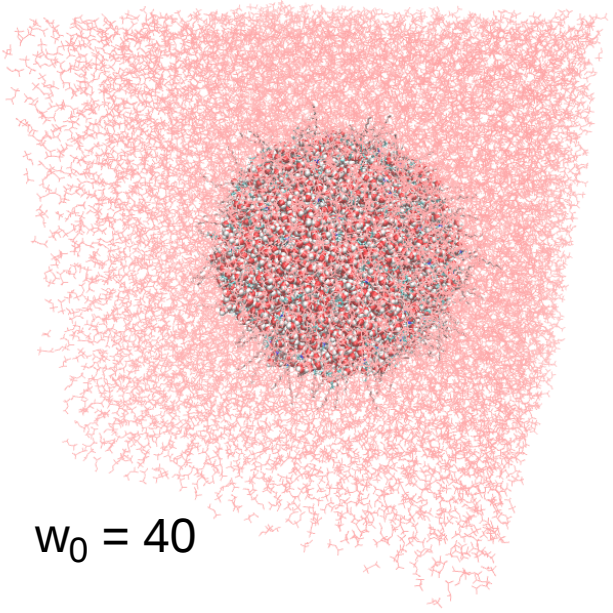
$w_0 = 7.5$



$w_0 = 18$



$w_0 = 30$

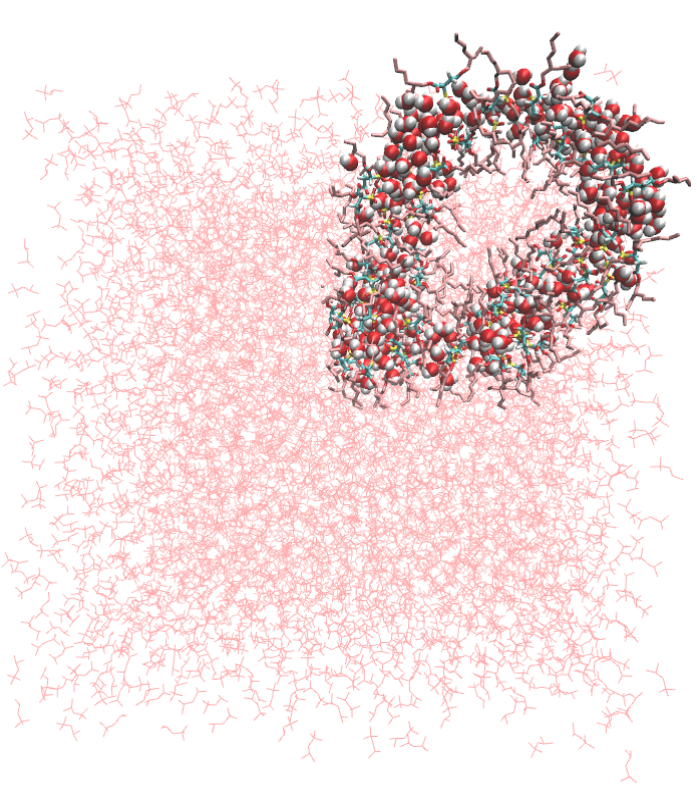


$w_0 = 40$

$w_0 = [H_2O]/[surfactant]$

$= N(H_2O)/N(surfactant)$

MD simulations of reverse micelles



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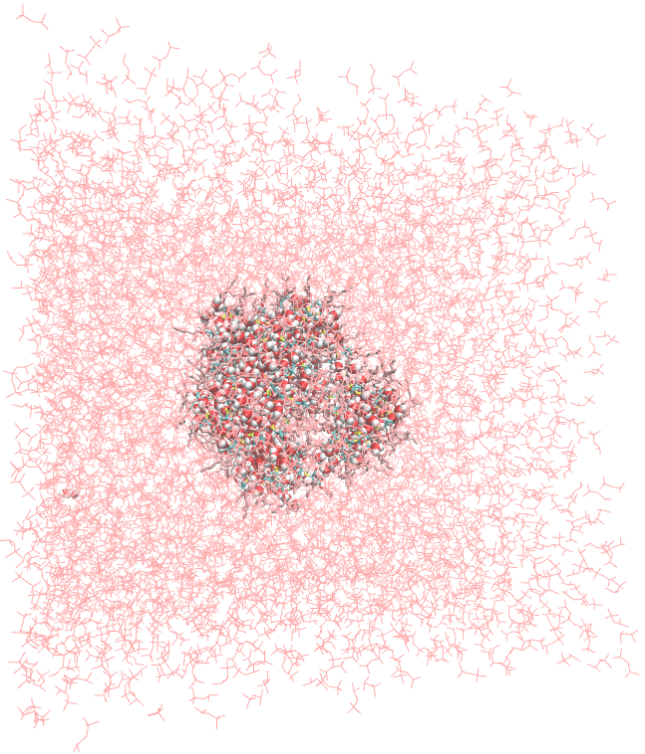

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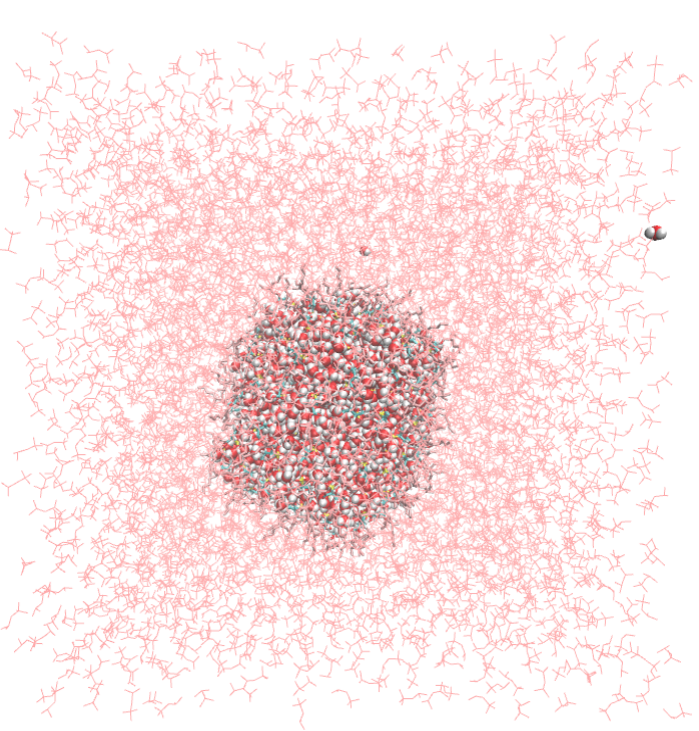
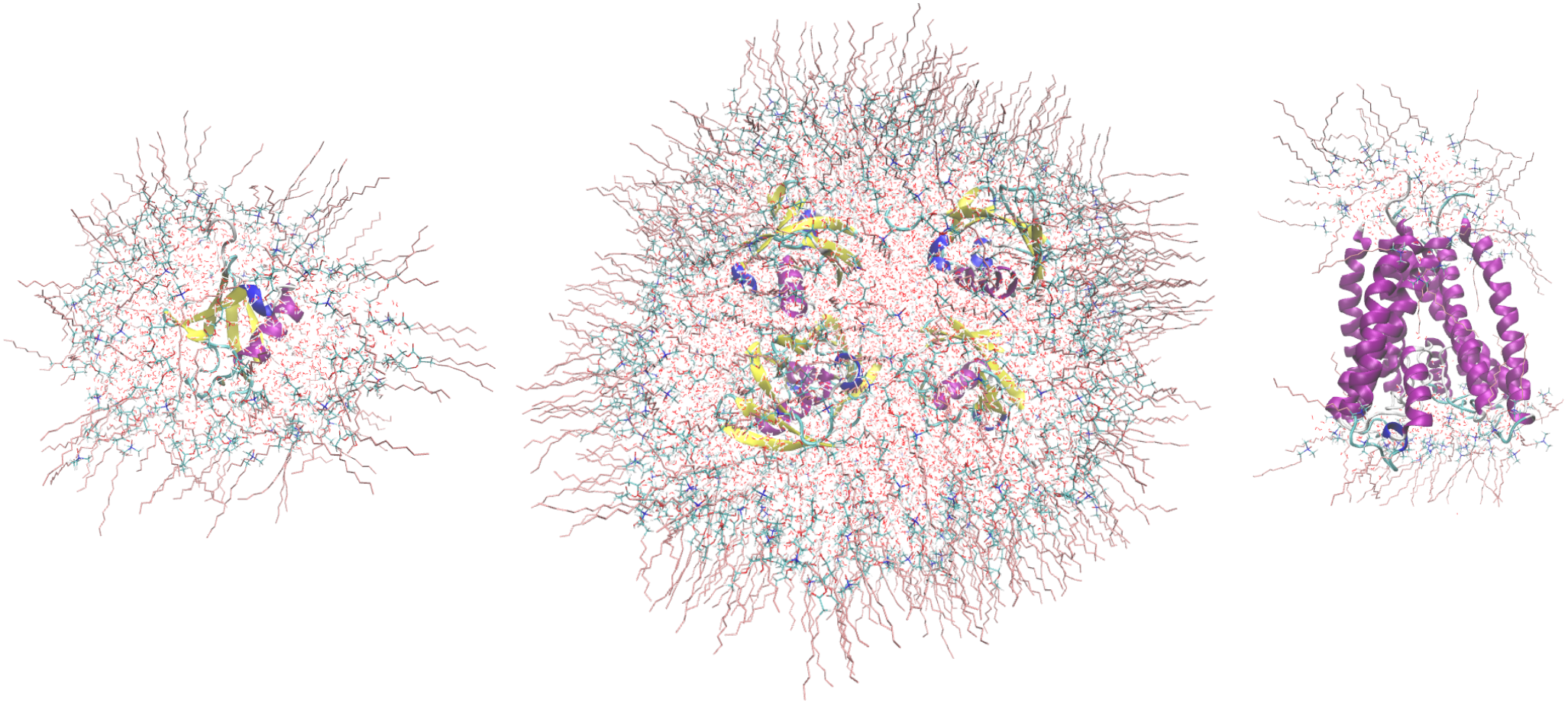


$w_0 = 18$

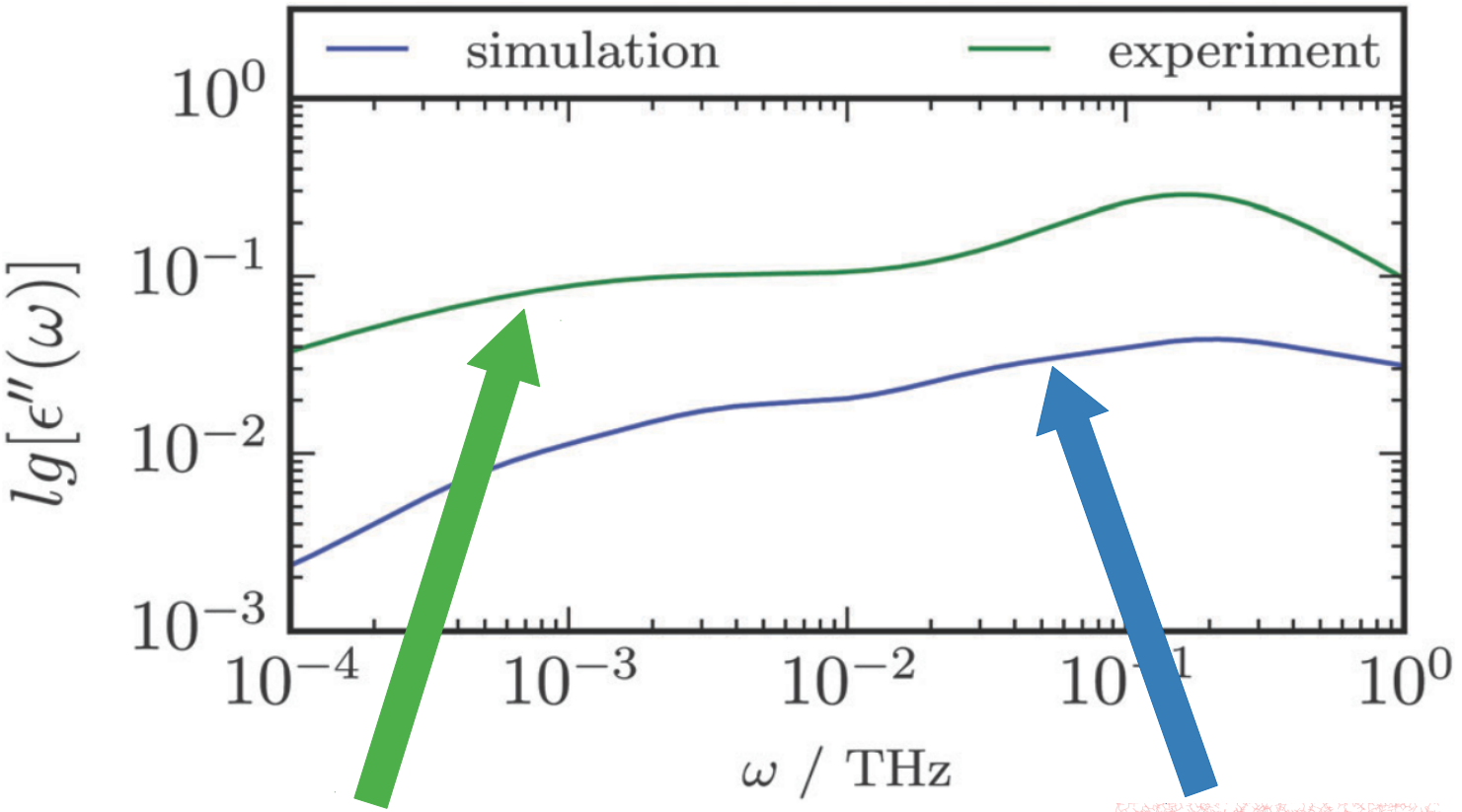
MD simulations of reverse micelles

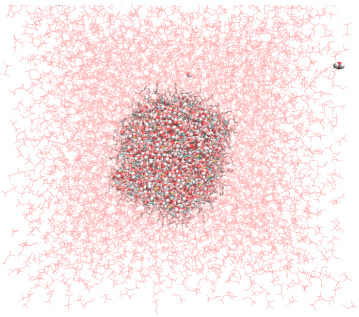


Computational spectroscopy –

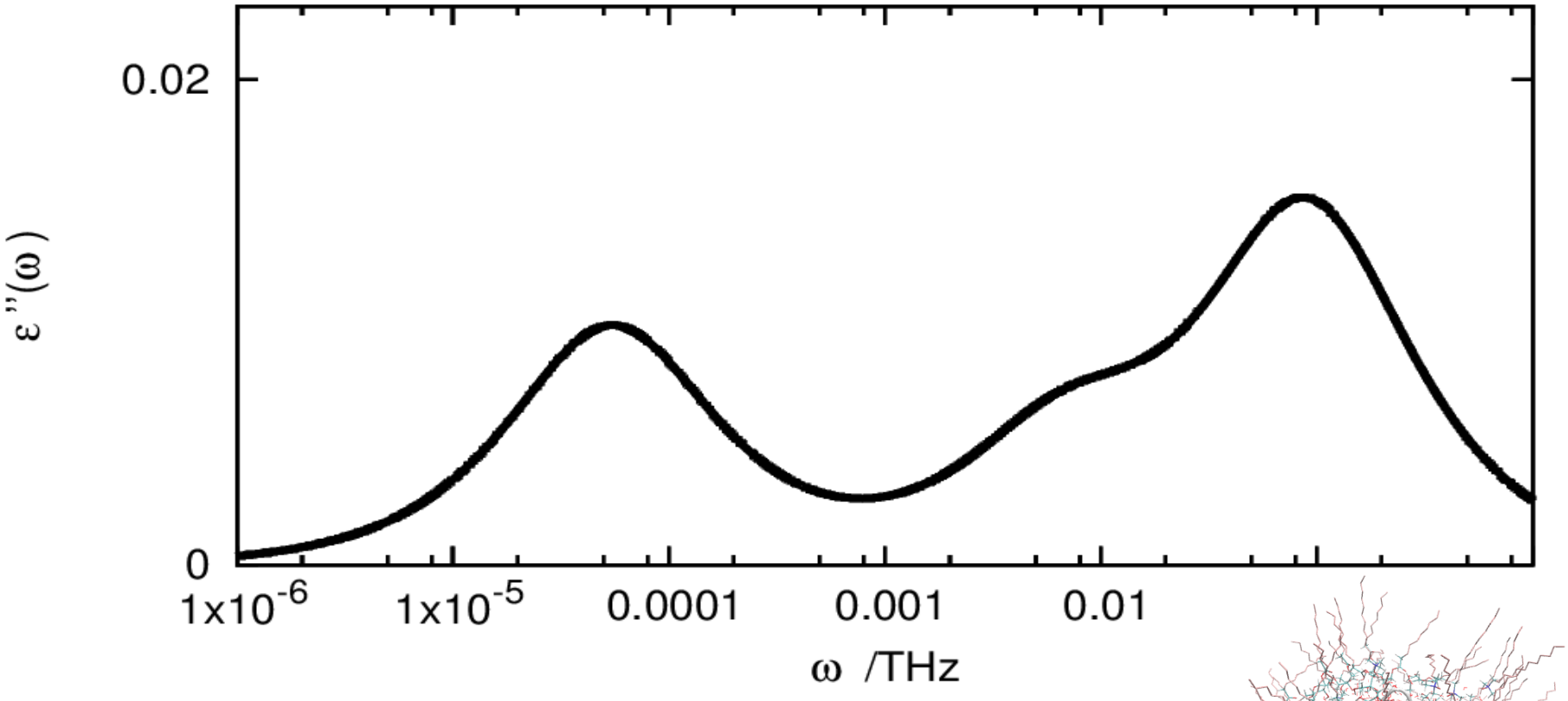
Link between experiment and simulation!

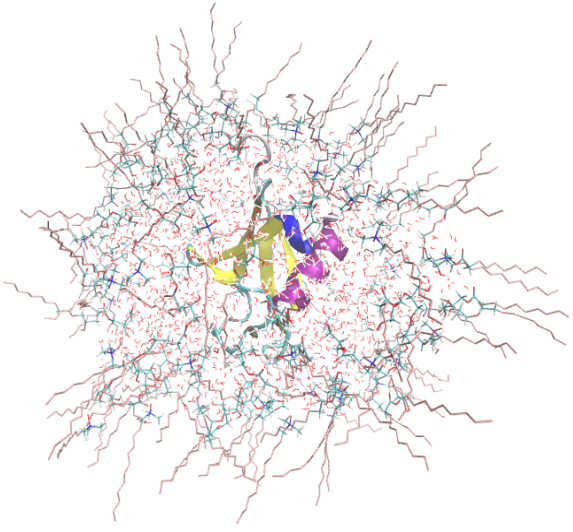
Why computational spectroscopy?





Why computational spectroscopy?





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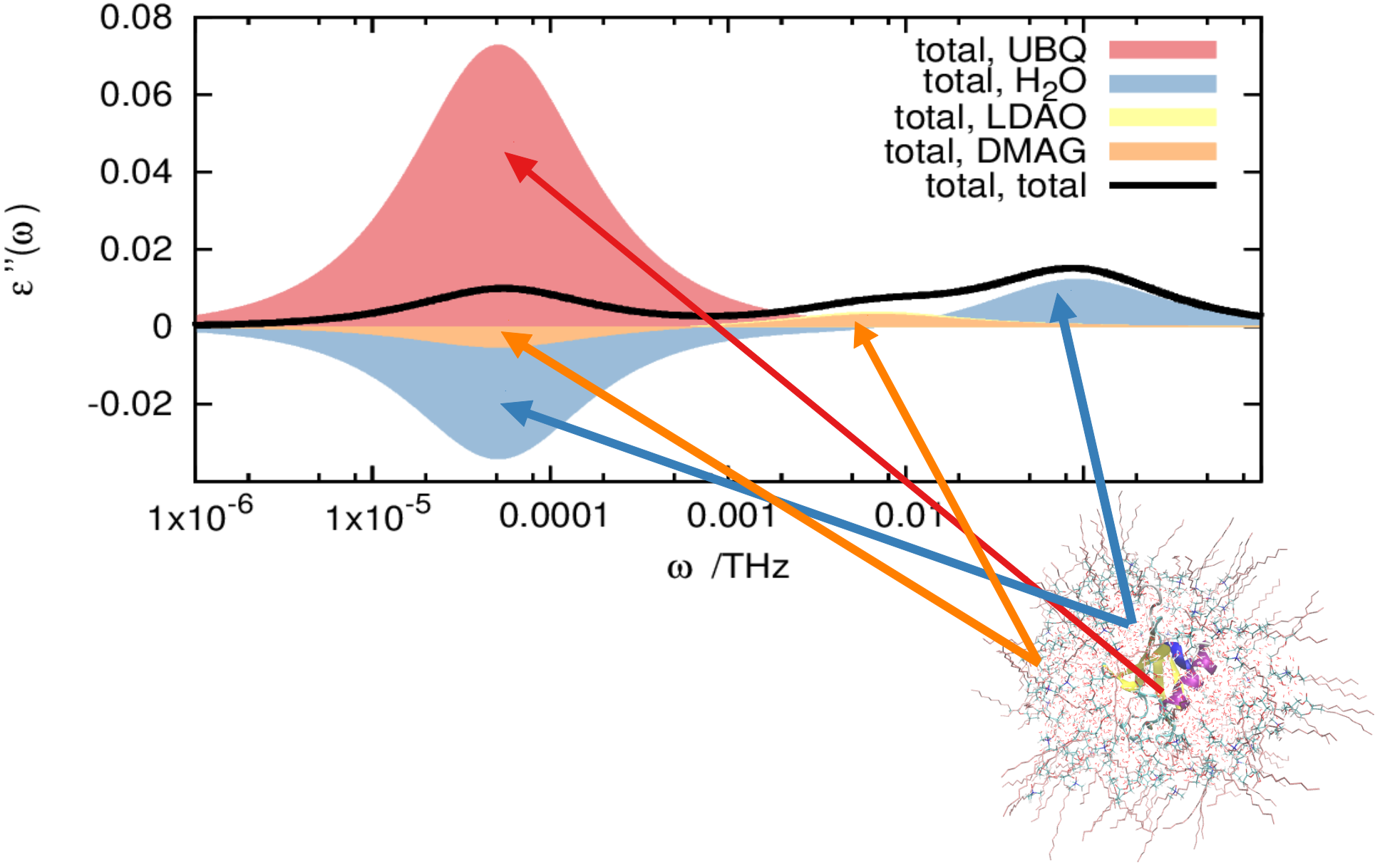

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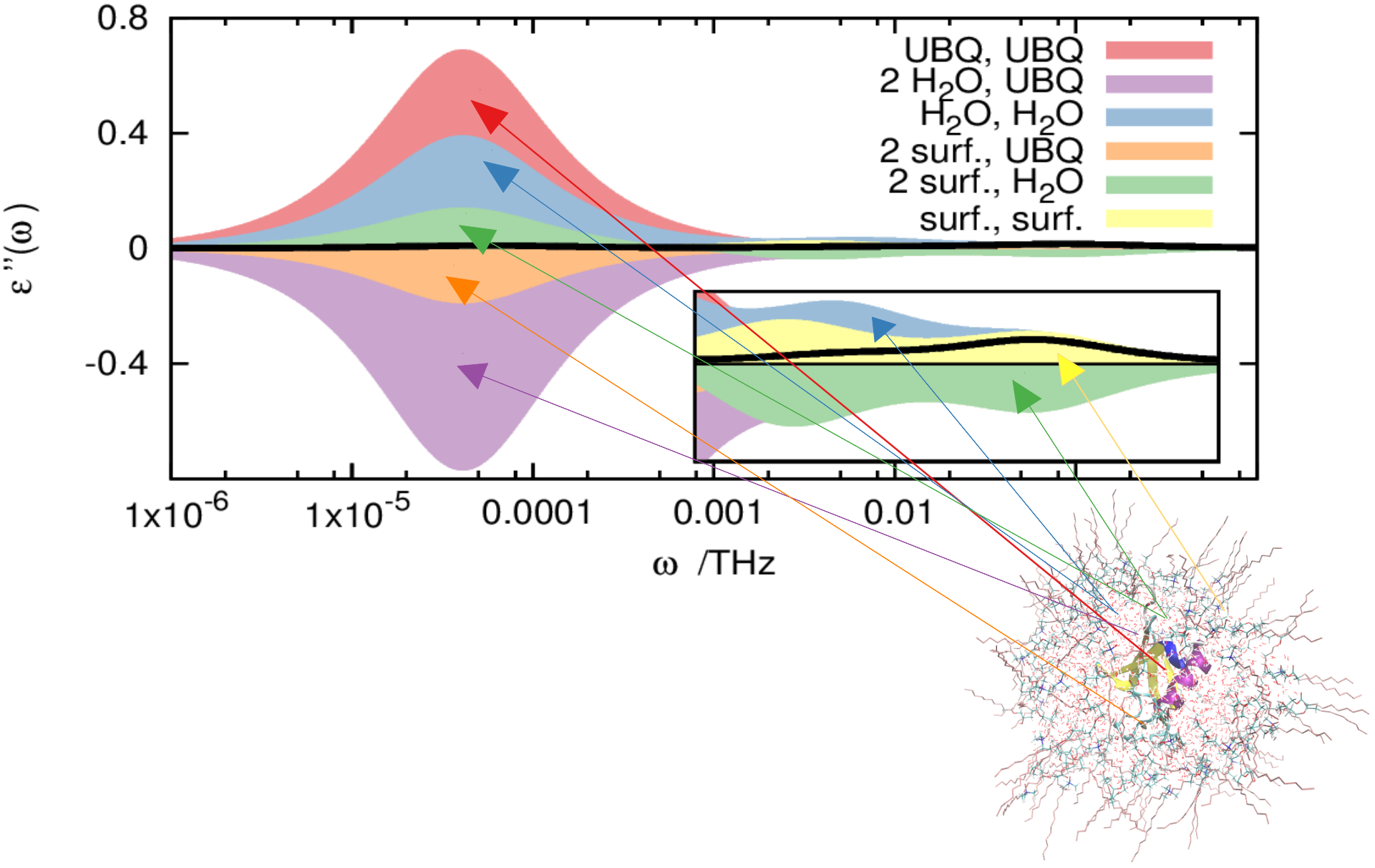
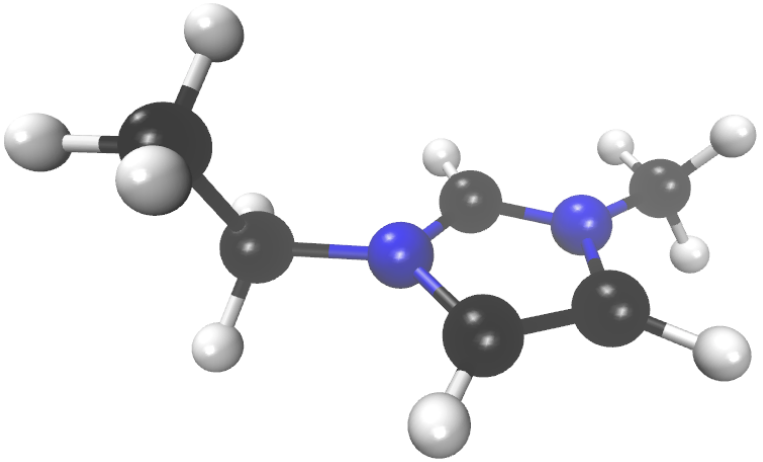


Computational spectroscopy

In theory, any spectral function can be calculated as the Fourier transform of the correlation function of the corresponding molecular property.

A wide range of such properties are accessible from molecular dynamics simulations.

M. Schmollngruber



some process A(t)

Forward Fourier Transformation

some observable spectral feature $\tilde{A}(\omega)$

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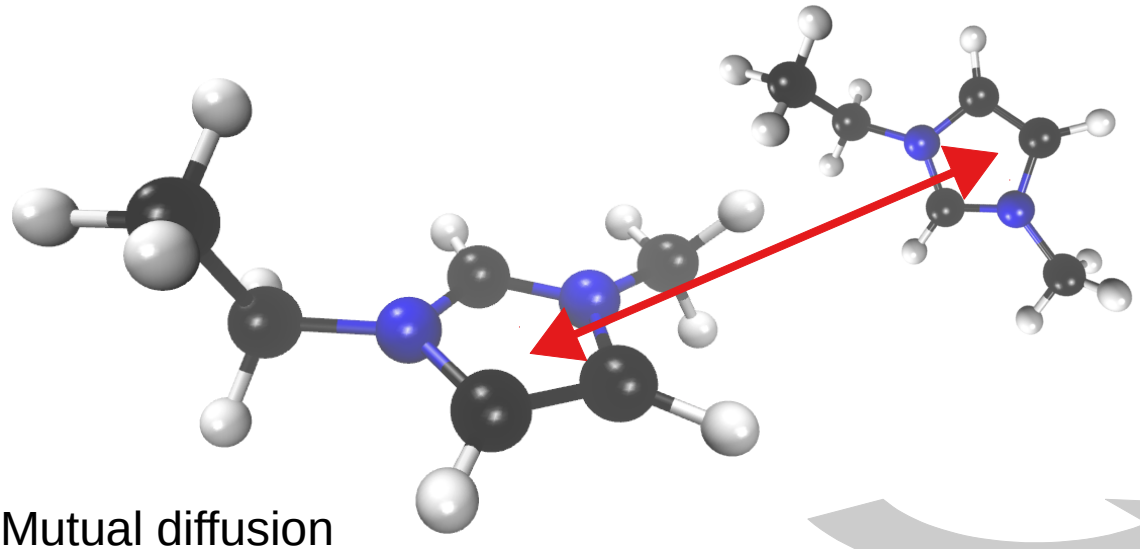
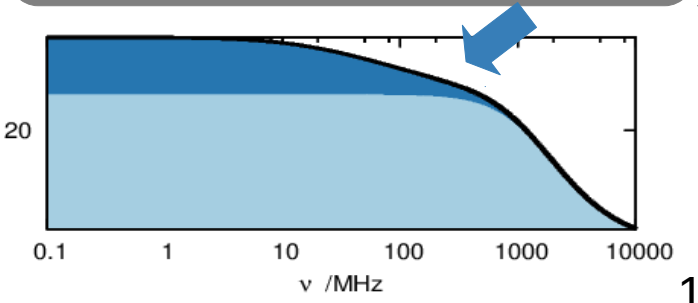
M. Schmollngruber



Mutual diffusion

Forward Fourier Transformation

Fast Field Cycling NMR dispersion R(ω)



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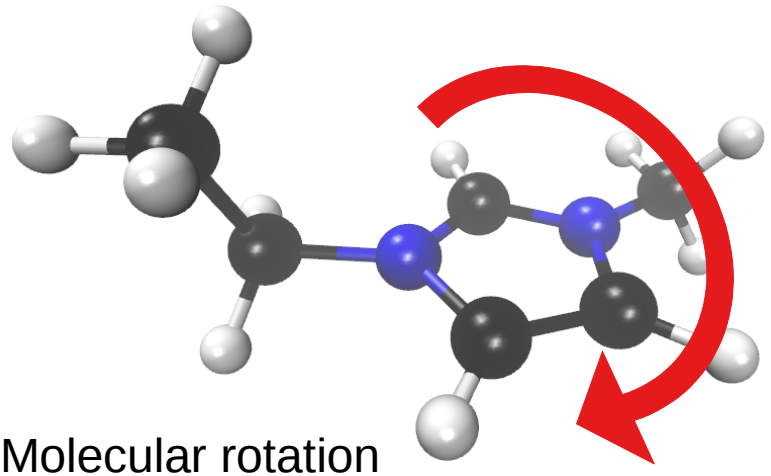
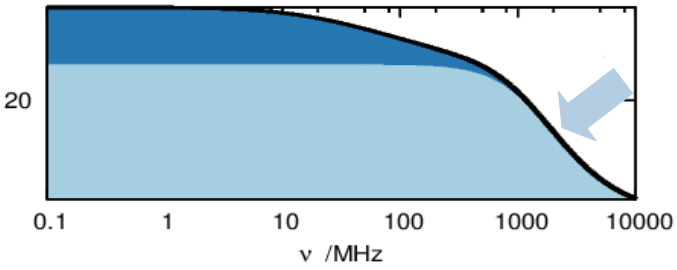
M. Schmollngruber



Molecular rotation

Forward Fourier Transformation

Fast Field Cycling NMR dispersion R(ω)



Computational spectroscopy

In theory, any spectral function can be calculated as the Fourier transform of the correlation function of the corresponding molecular property.

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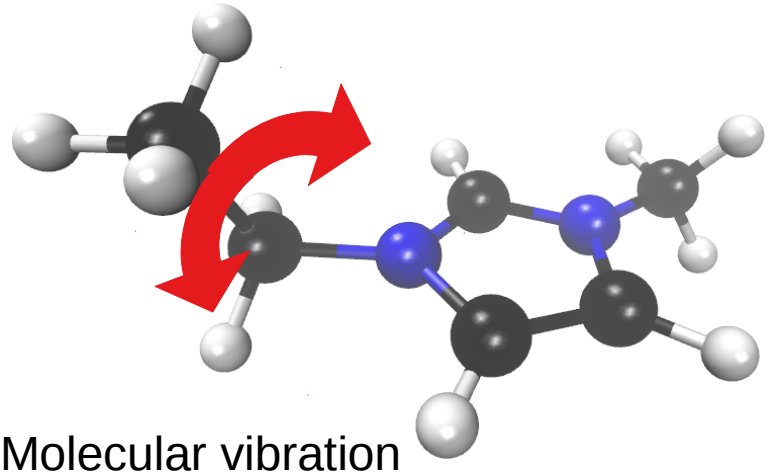
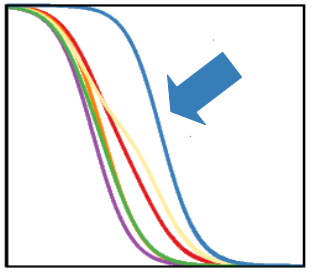
M. Schmollngruber



Molecular vibration

Forward Fourier Transformation

Fast Field Cycling NMR dispersion R(ω)



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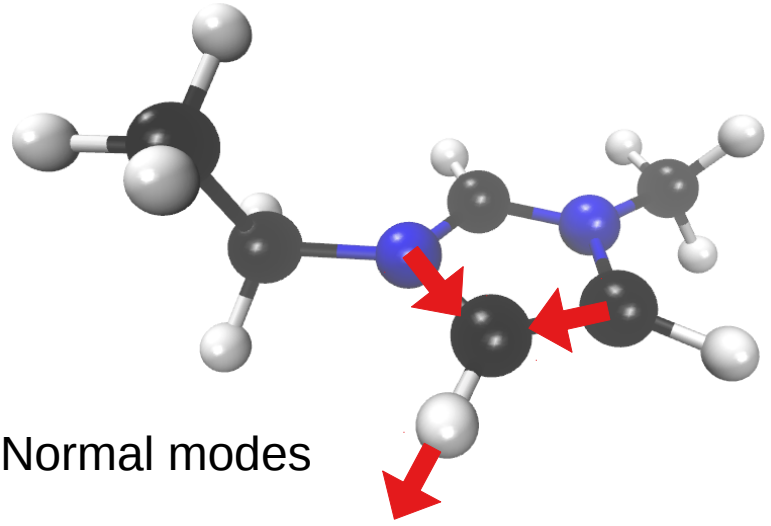
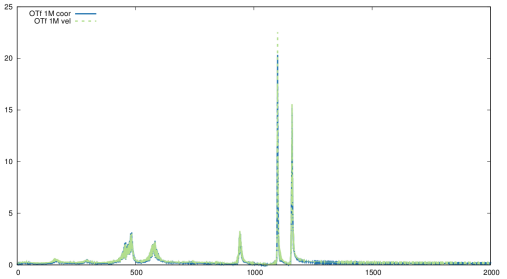


Normal modes

Forward Fourier Transformation

Infrared spectroscopy
T(ú)



Computational spectroscopy

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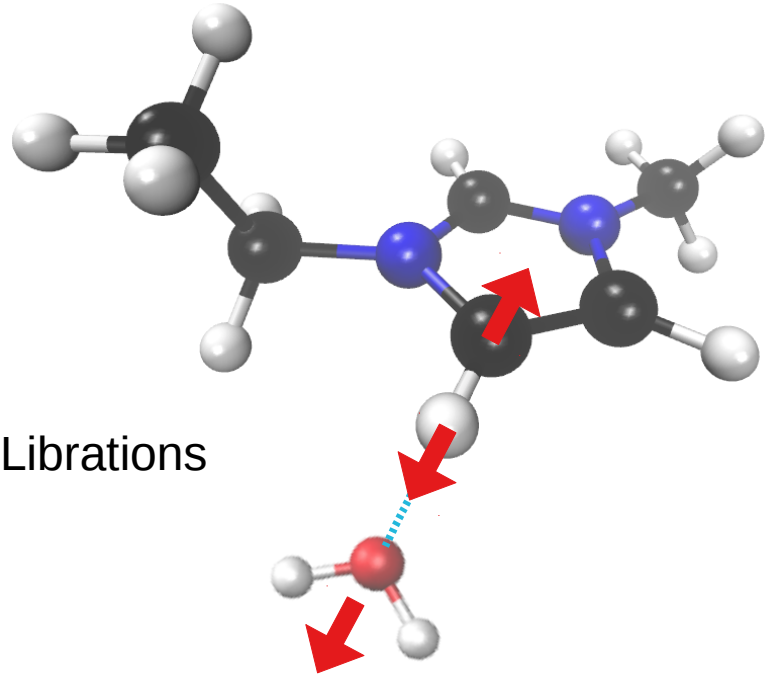
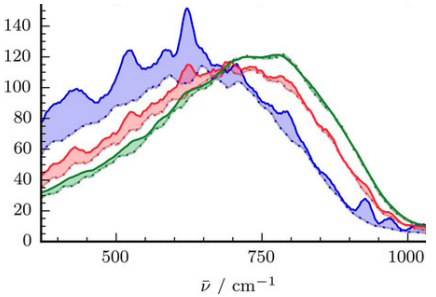
M. Schmollngruber



Librations

Forward Fourier Transformation

Terahertz spectroscopy T(ú)



Computational spectroscopy

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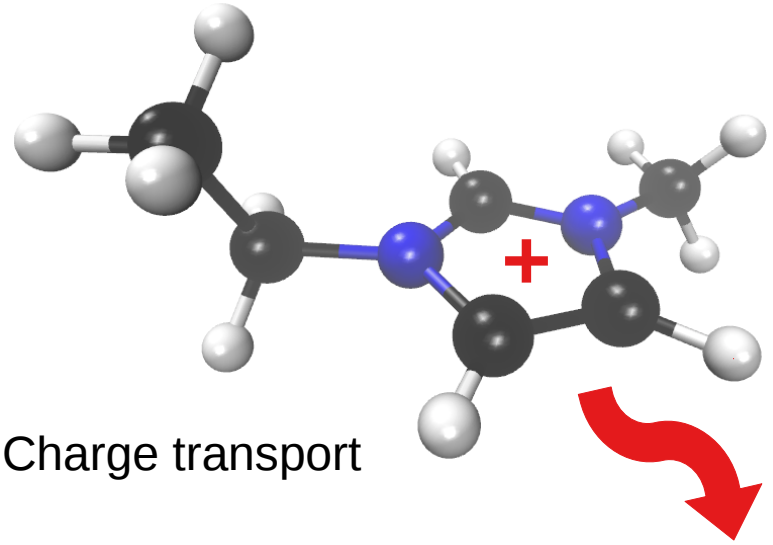
A wide range of such properties are accessible from molecular dynamics simulations.

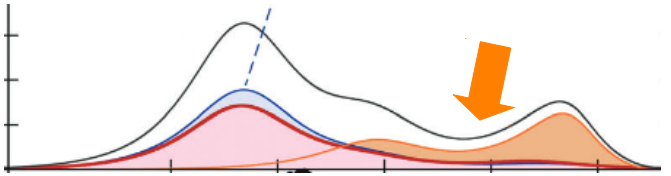
M. Schmollngruber



Charge transport

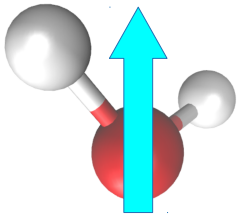
Forward Fourier Transformation

Ionic conductivity
$\Sigma(\omega)$



Computational spectroscopy

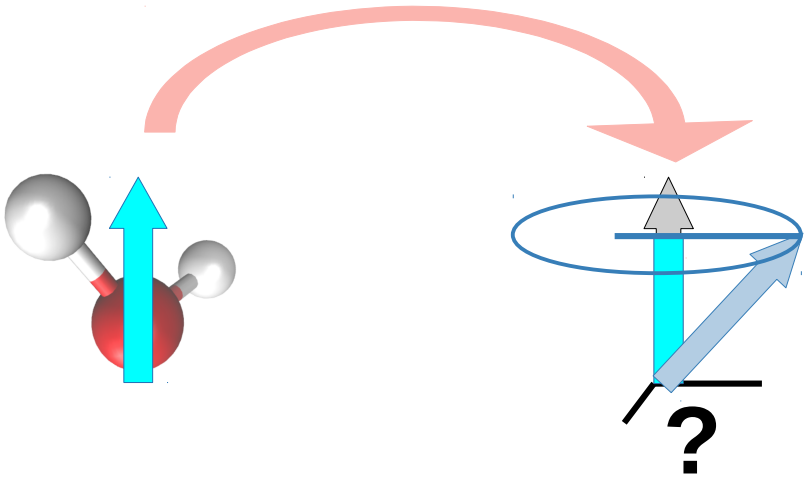
t = 0



$\langle \mathrm{A}(0) \bullet \mathrm{A}(0) \rangle$

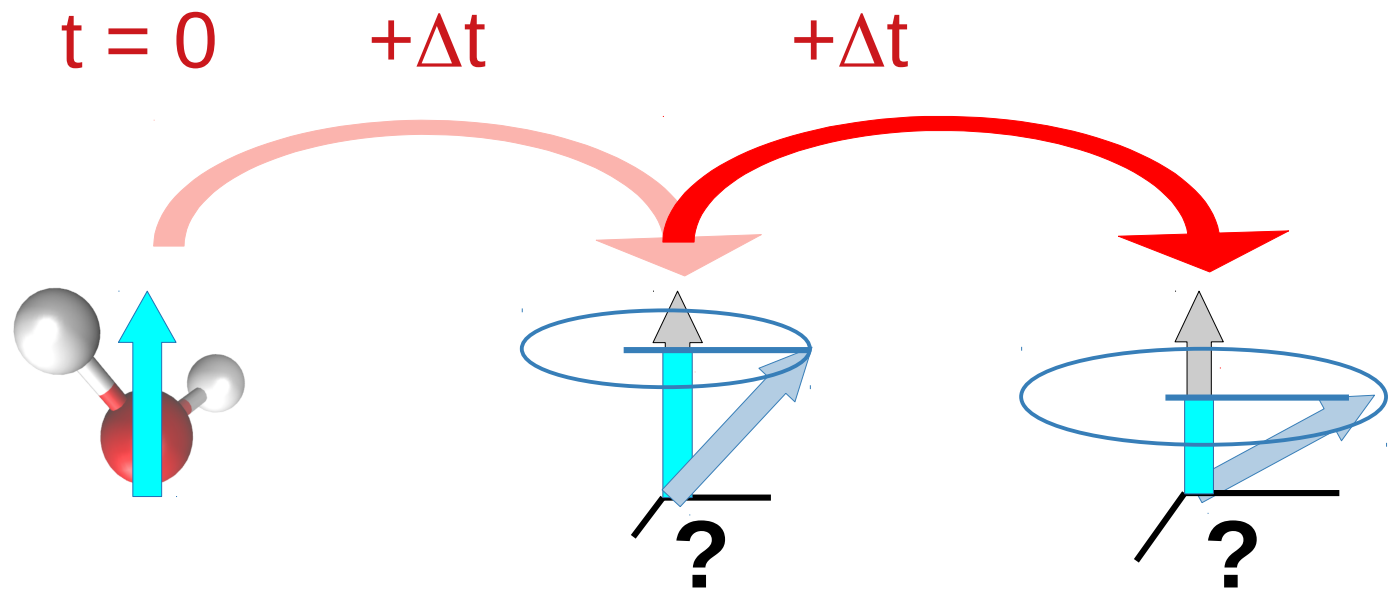
Computational spectroscopy

t = 0 $+\Delta t$

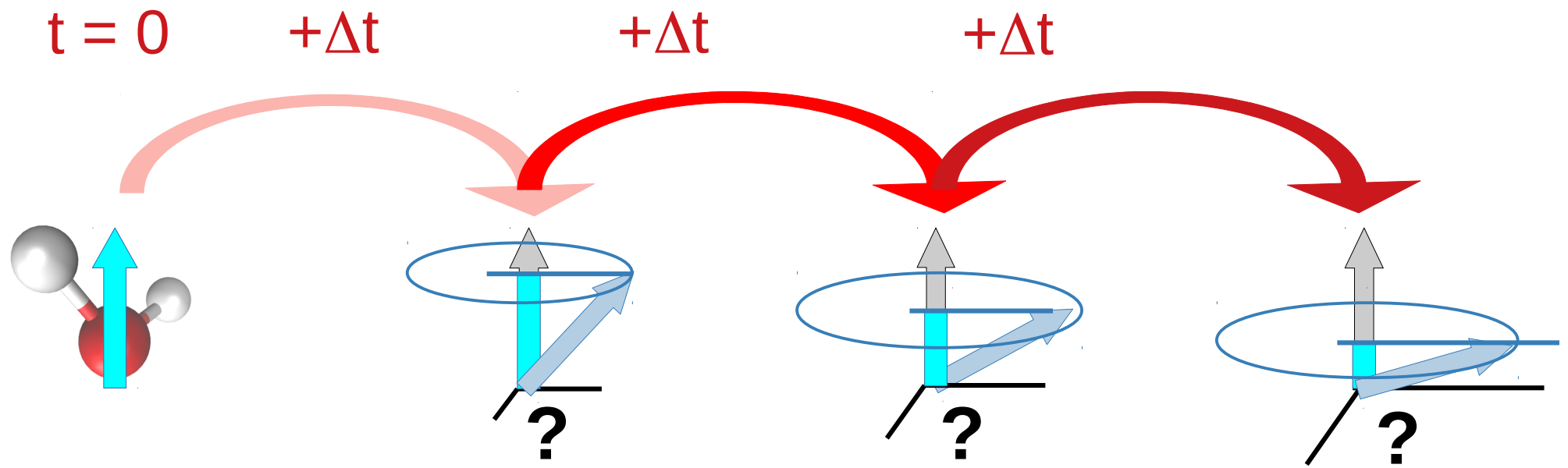


$\langle A(0) \bullet A(0) \rangle$ $\langle A(0) \bullet A(\Delta t) \rangle$

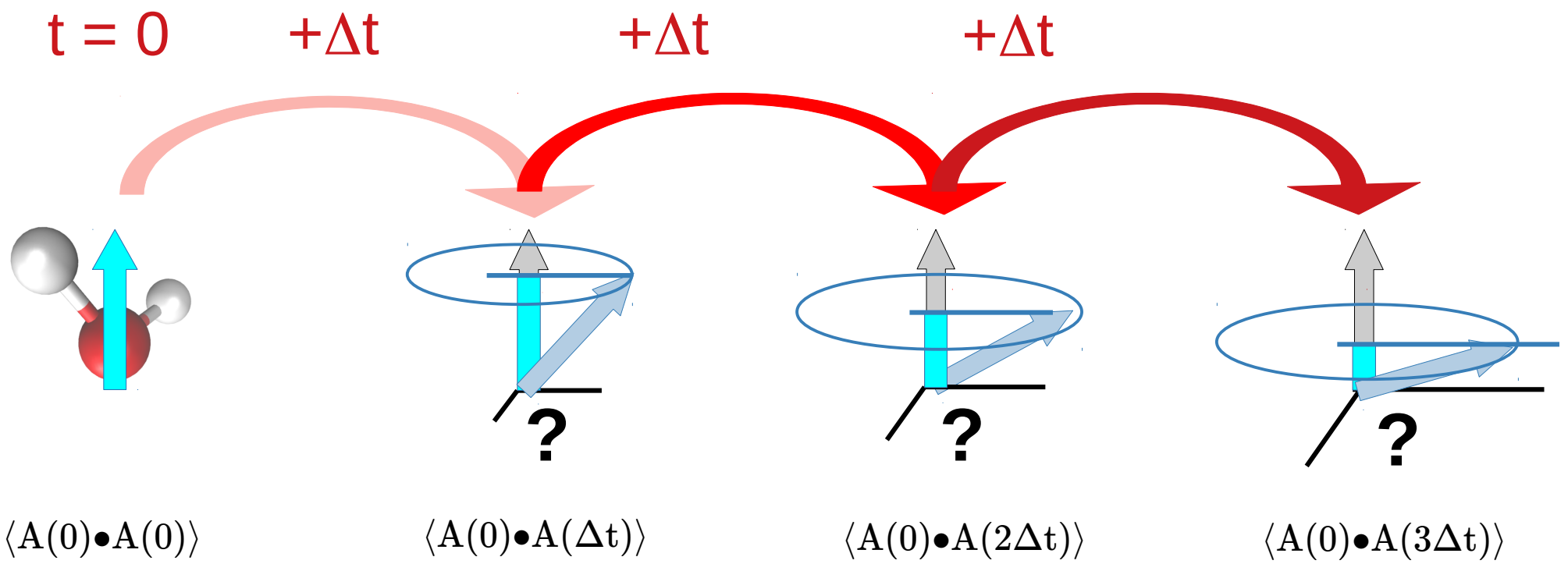
Computational spectroscopy

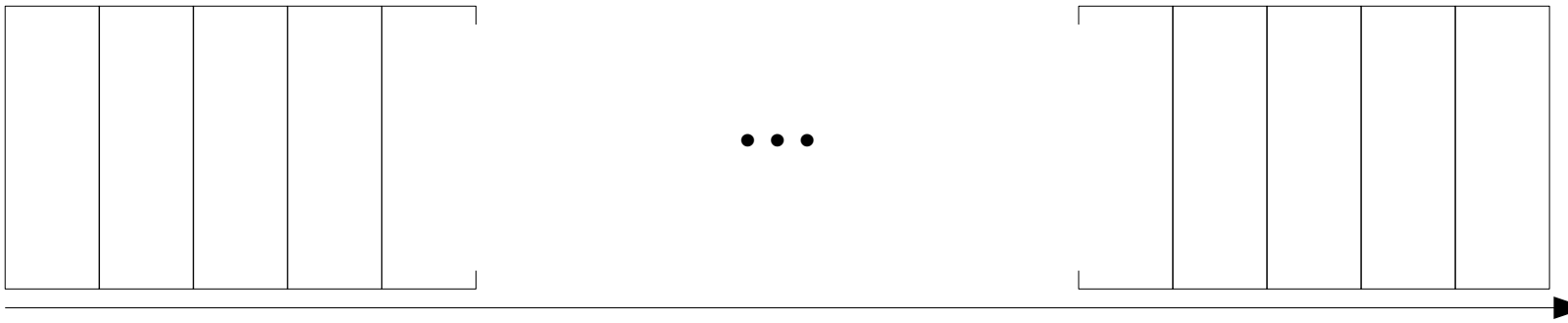


Computational spectroscopy



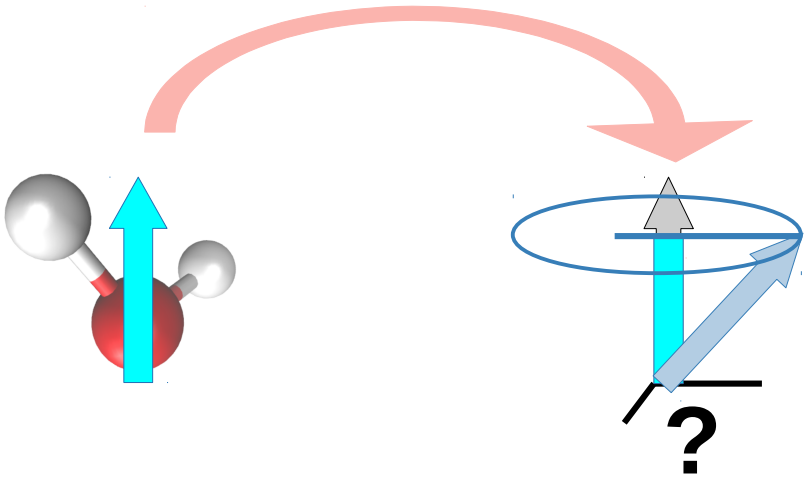
Computational spectroscopy



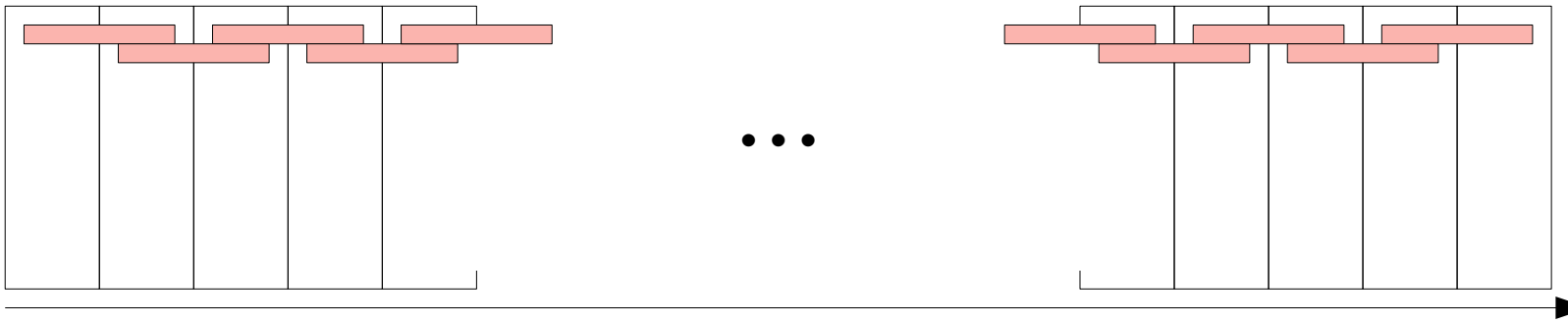


Computational spectroscopy

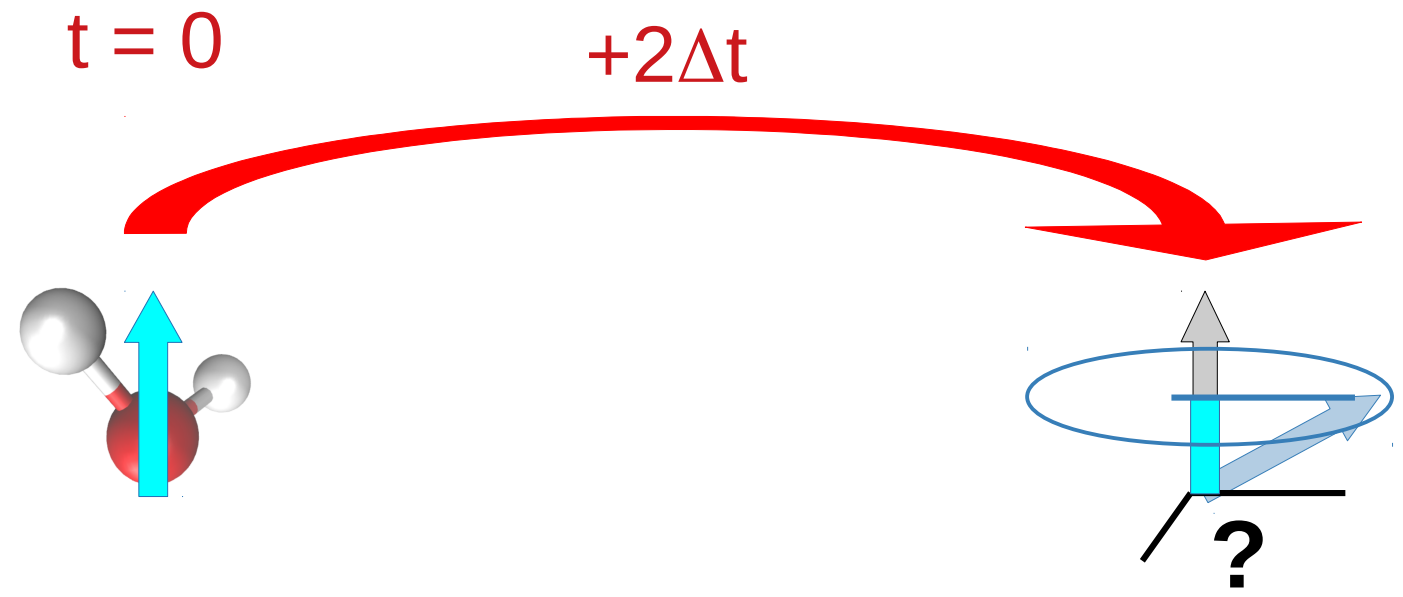
t = 0 $+\Delta t$



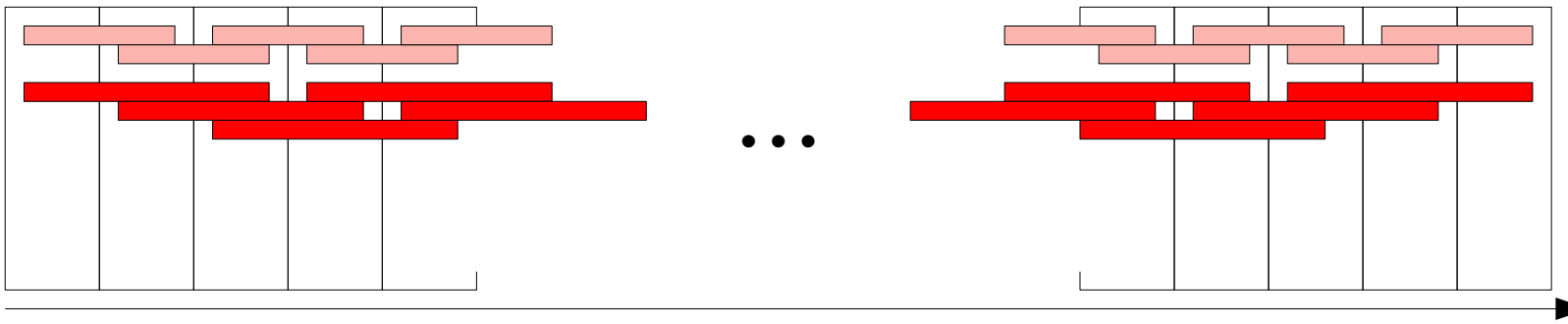
$\langle A(0) \bullet A(0) \rangle$ $\langle A(0) \bullet A(\Delta t) \rangle$



Computational spectroscopy



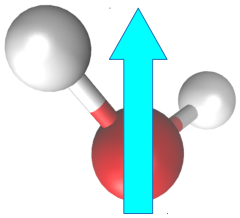
$\langle A(0) \bullet A(0) \rangle$ $\langle A(0) \bullet A(2\Delta t) \rangle$

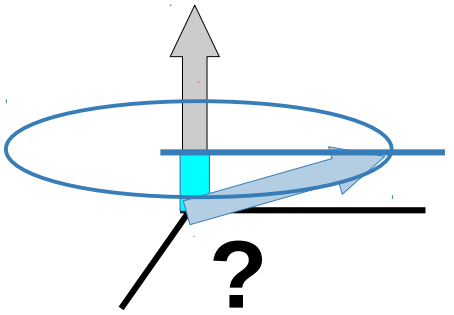


Computational spectroscopy

t = 0

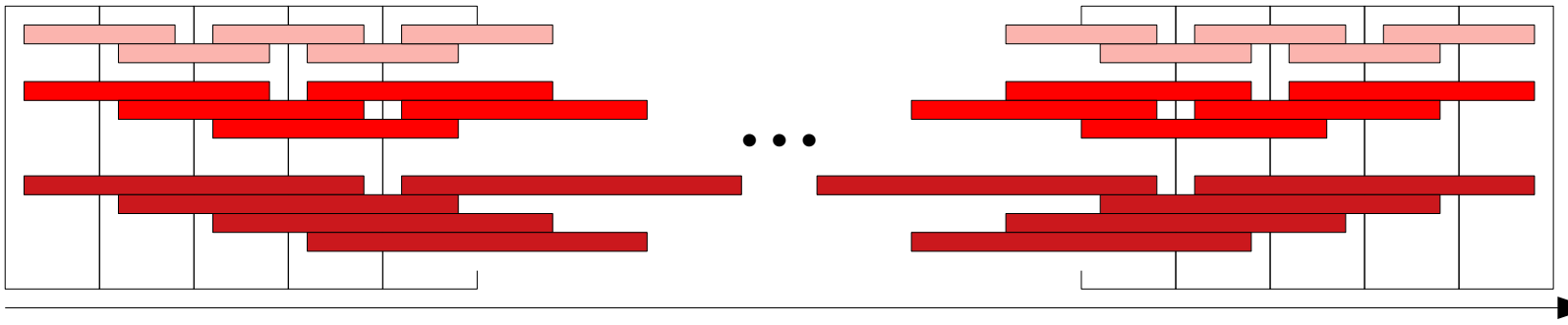
+3Δt



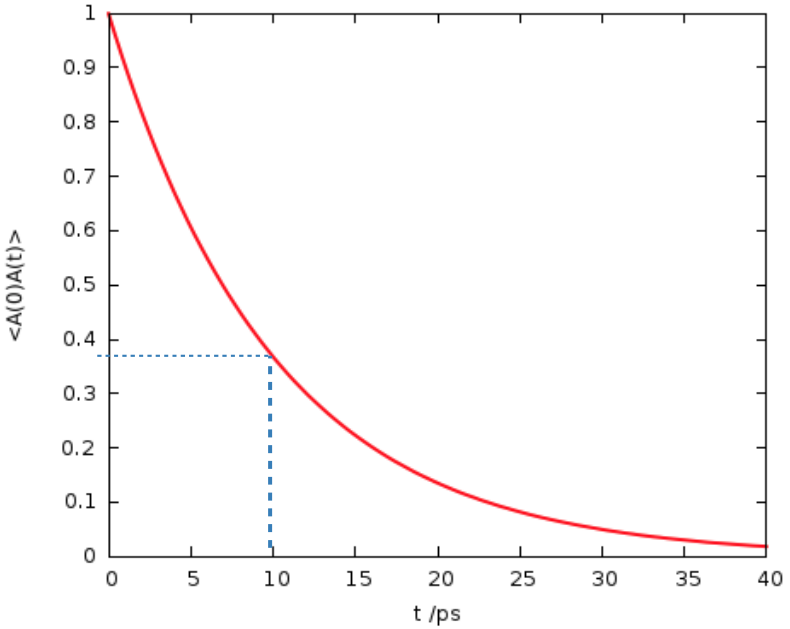


$\langle A(0) \bullet A(0) \rangle$

$\langle A(0) \bullet A(3\Delta t) \rangle$

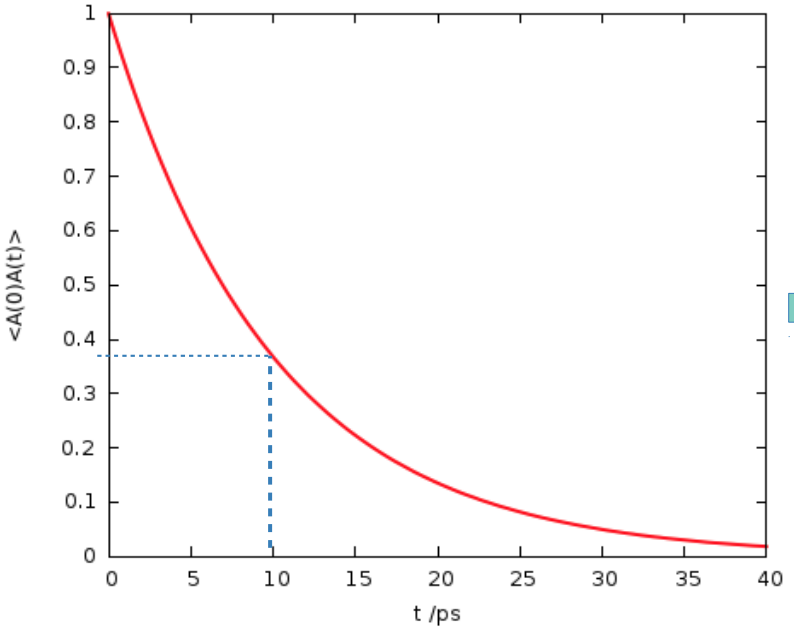


Computational spectroscopy



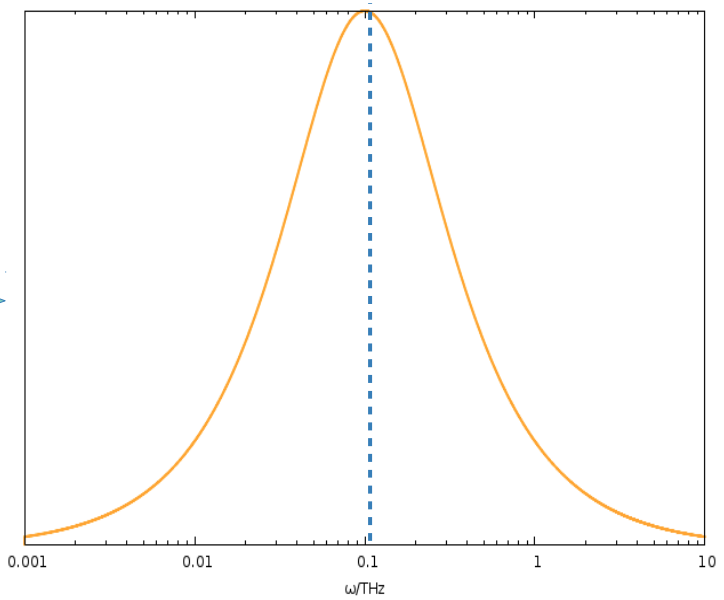
$\langle A(0) \bullet A(t) \rangle$

Computational spectroscopy



$\langle A(0) \bullet A(t) \rangle$

Fourier-Transform

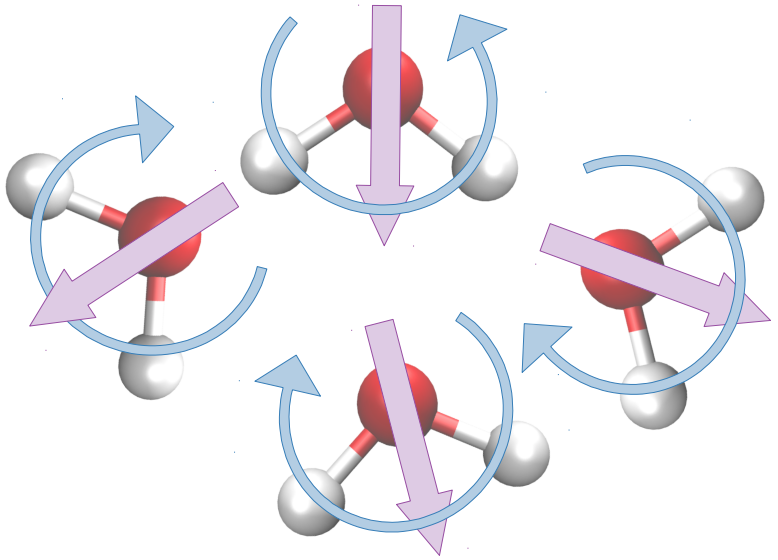


$\tilde{A}(\omega)$

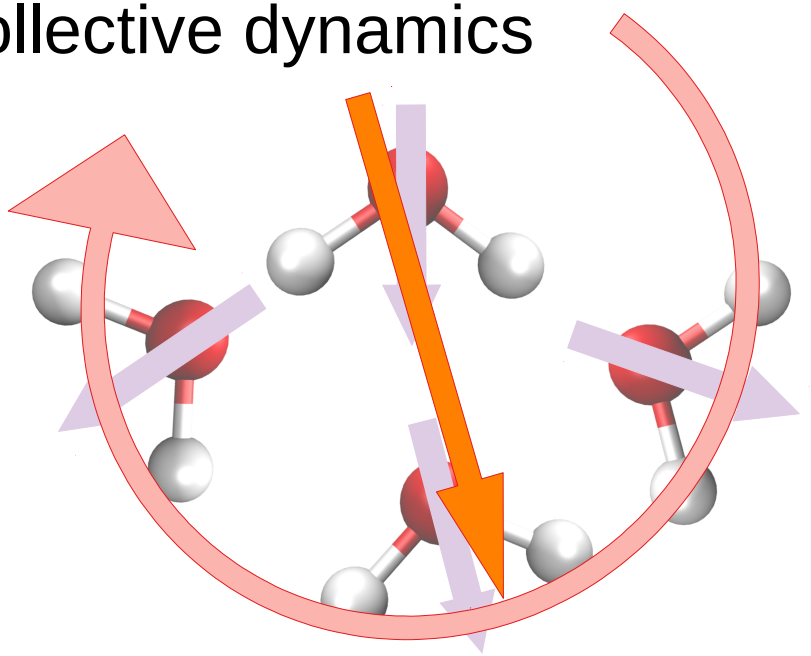
$$\tilde{A}(\omega) = \int_{-\infty}^{+\infty} \langle A(0)A(t) \rangle e^{-i\omega t} dt$$

Water under confinement

Difference single-particle vs. collective dynamics



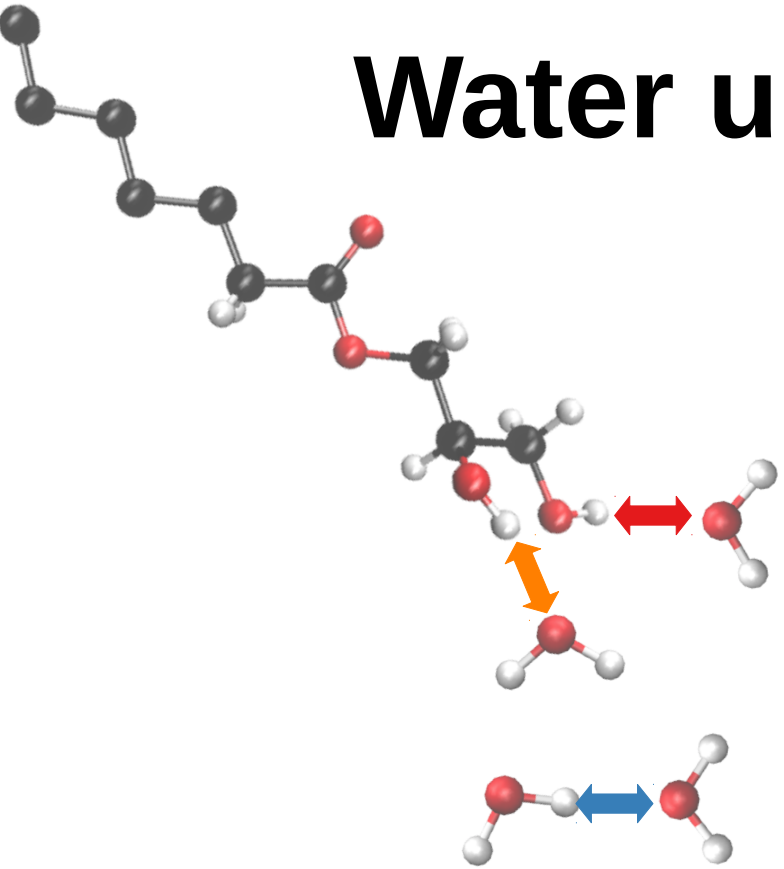
- Motion of single molecular dipoles
- Average

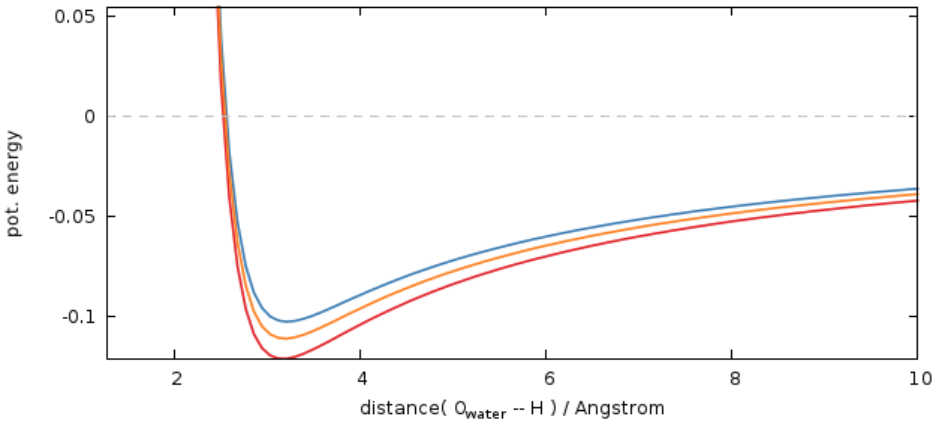


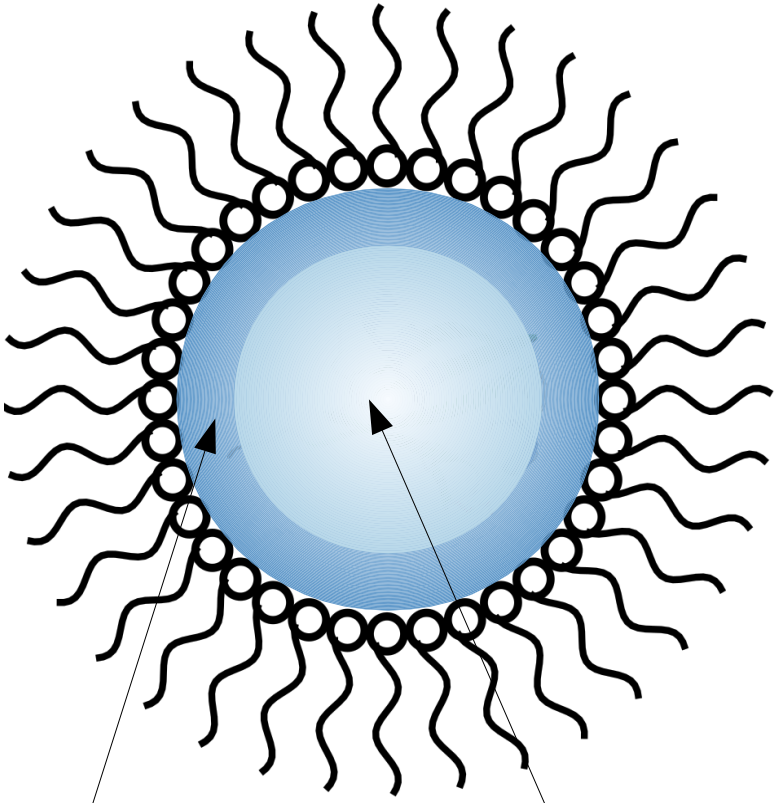
- Motion of sample sum dipole
- Sum
- Contains cross correlations

Connected via mutual orientational structure (?)

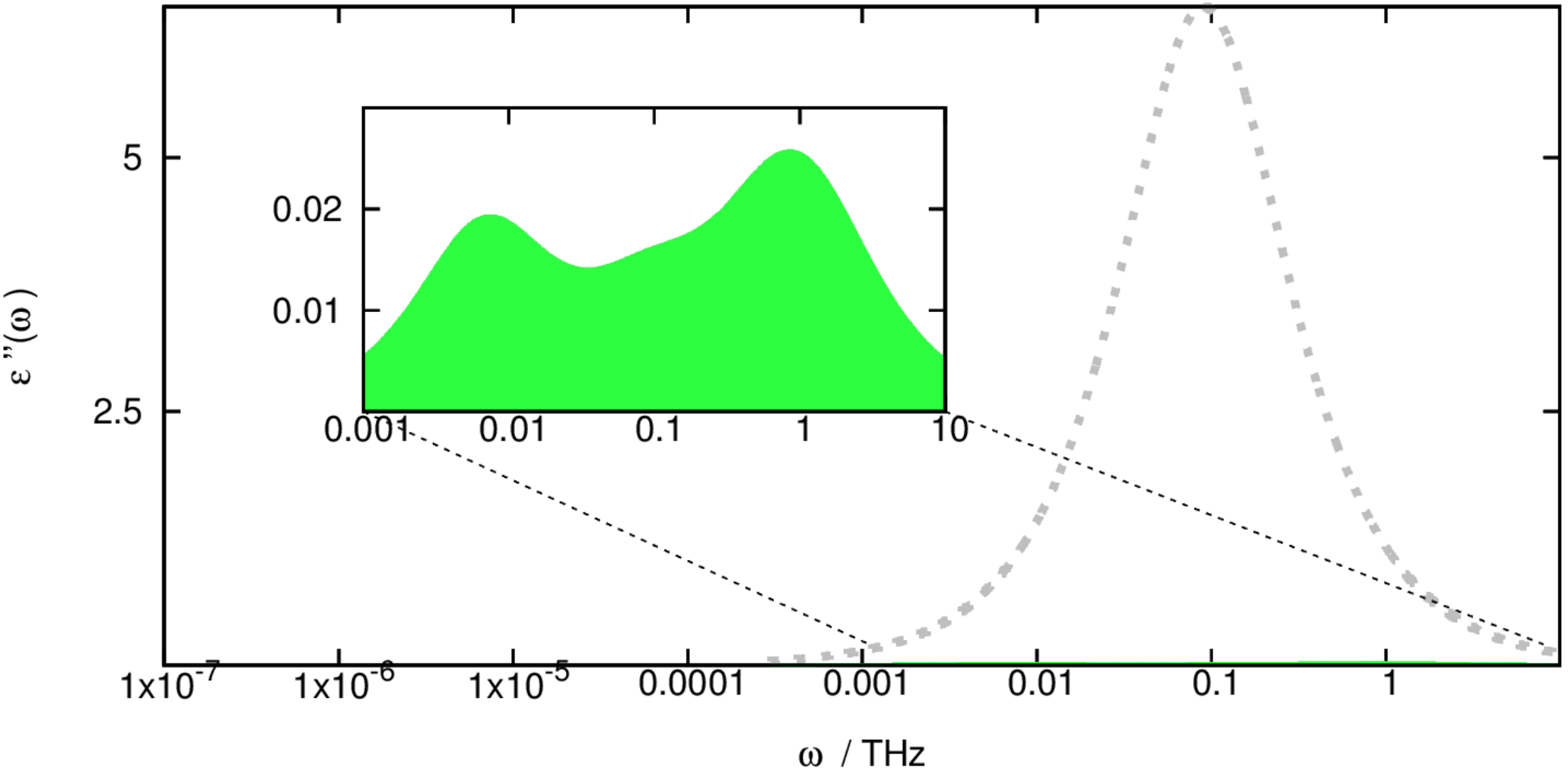
Water under confinement



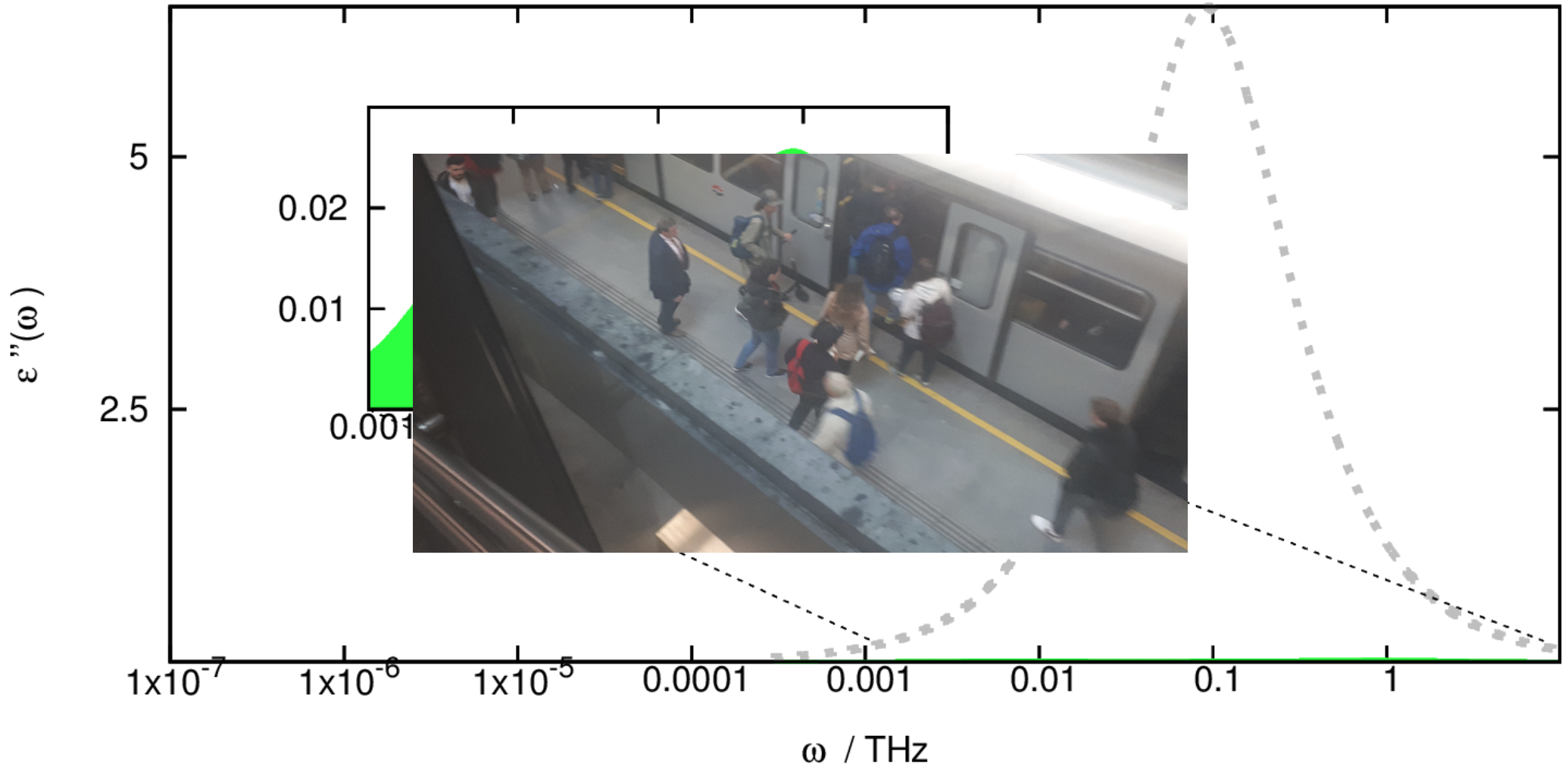




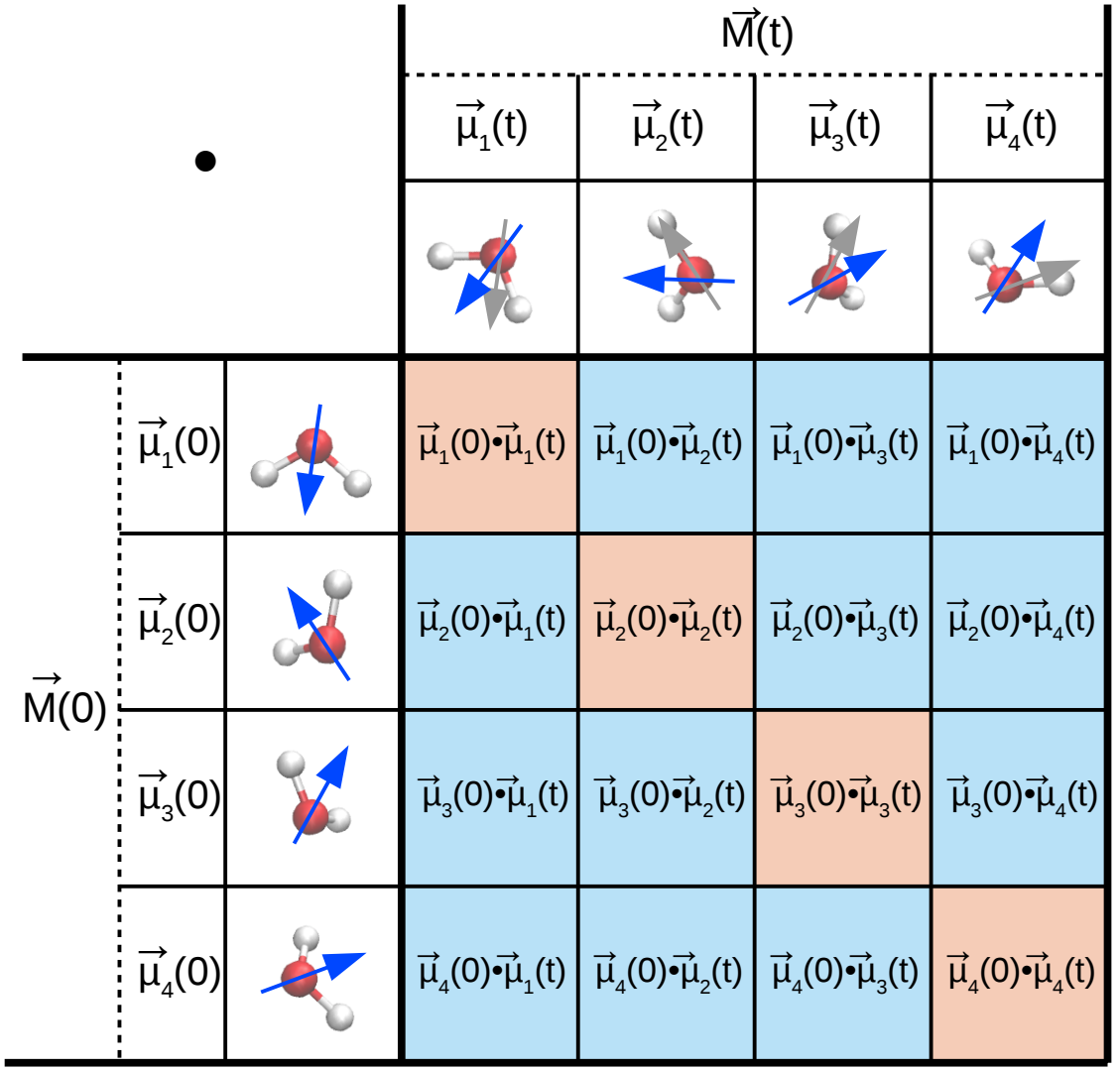
DRS absorption spectra of aqueous reverse micelles



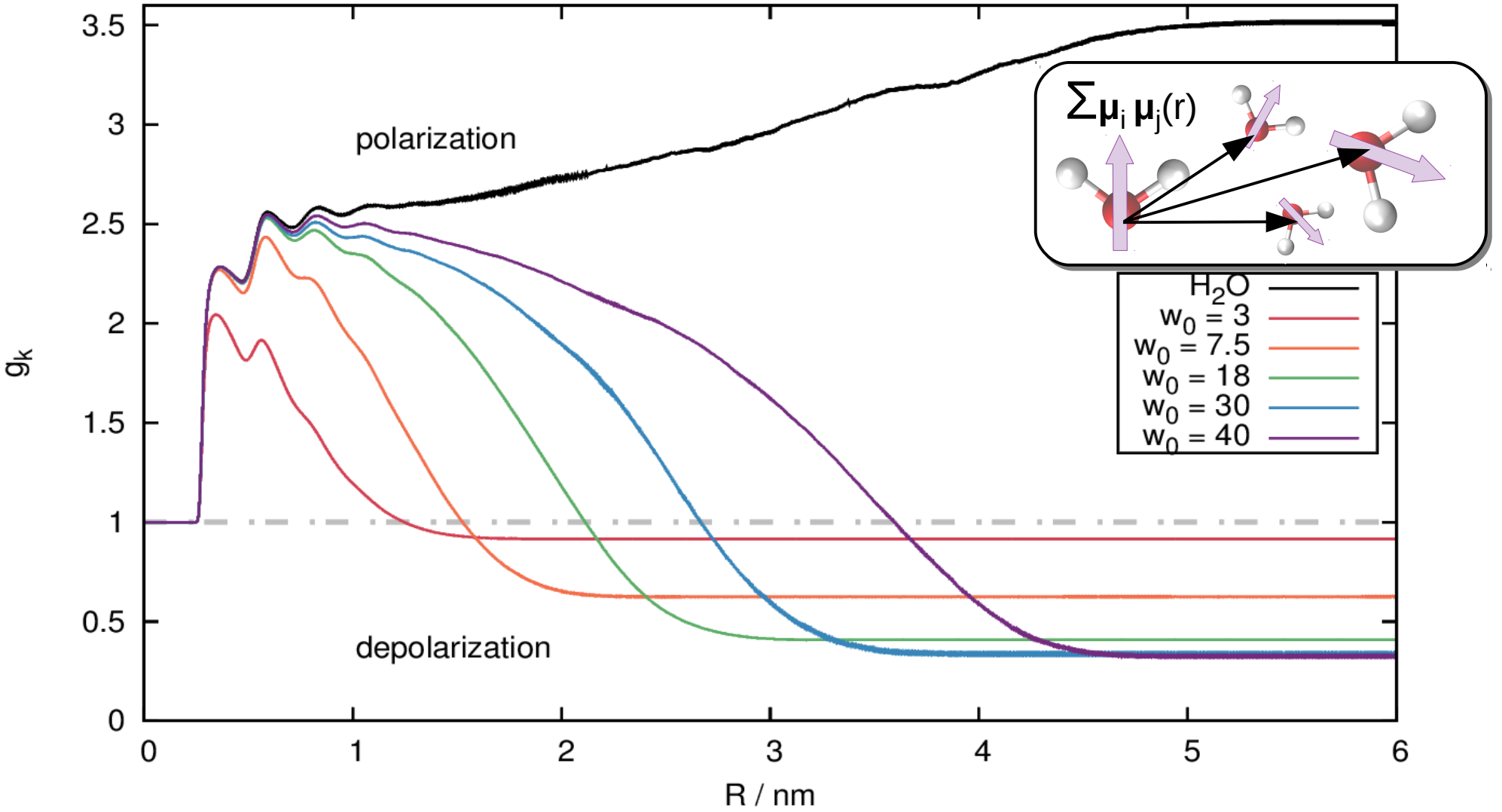
DRS absorption spectra of aqueous reverse micelles



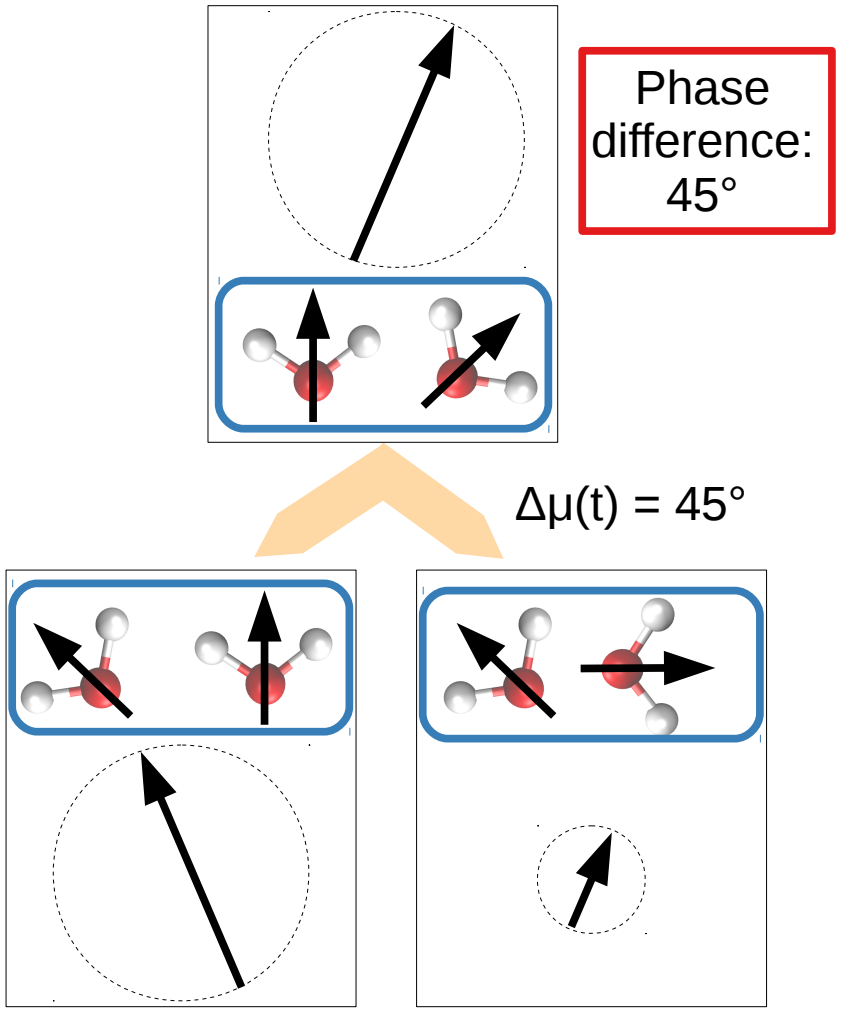
Collective dynamics include cross-correlations!

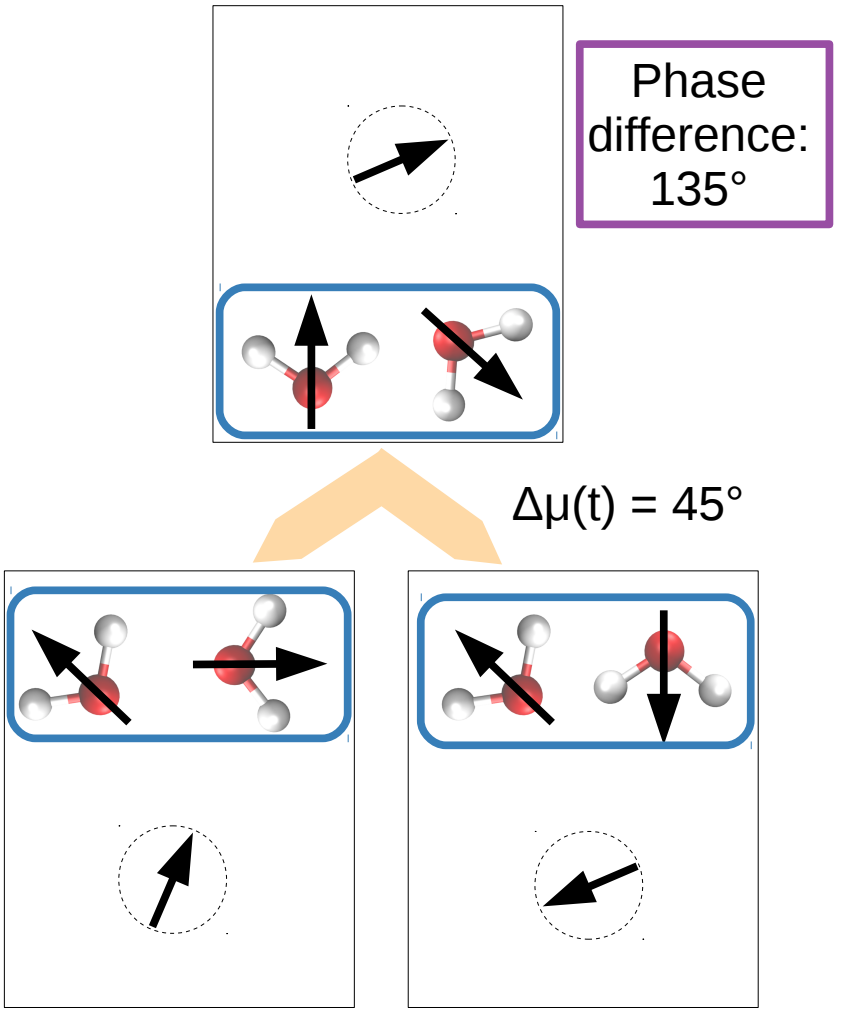


Mutual dipole orientation: Kirkwood g-factor



Why does structure modulate dynamics? A thought experiment

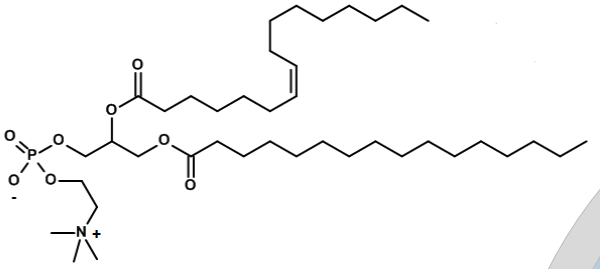


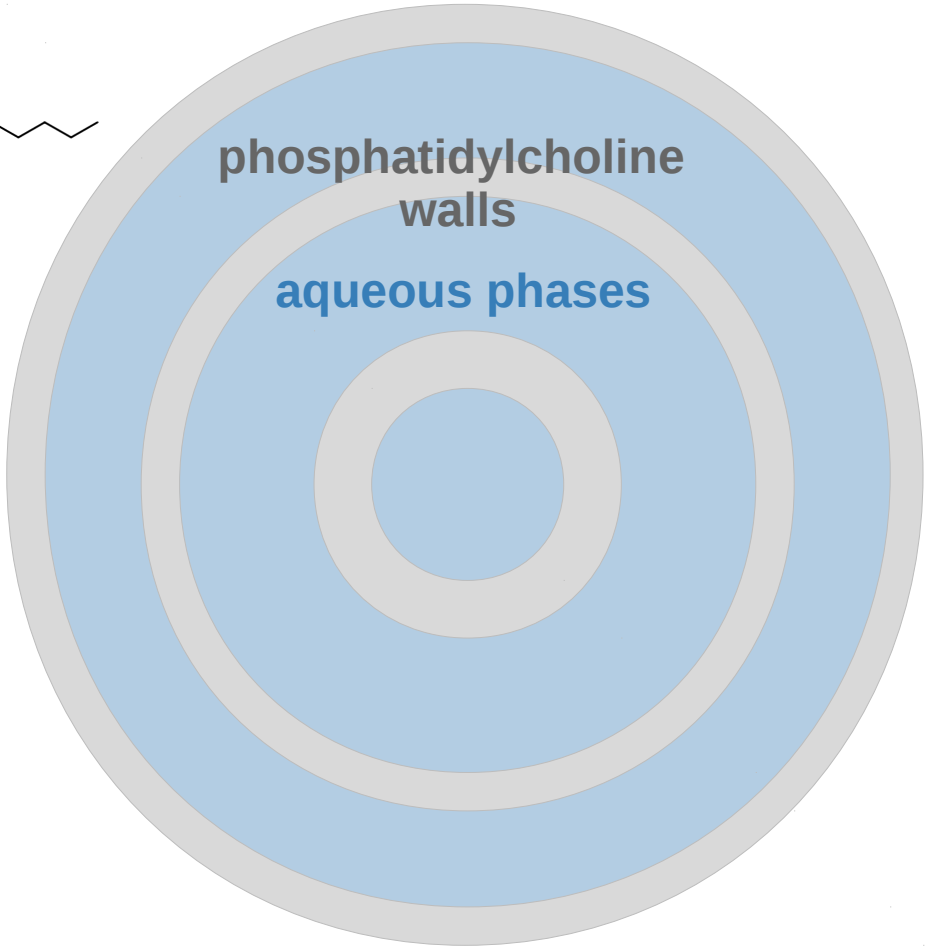


… but is this a real thing?

Experimental setup: Phosphatidylcholines as surfactants, onion-like vesicles, dielectric spectroscopy

Gun-Sik Park,
Seoul National University





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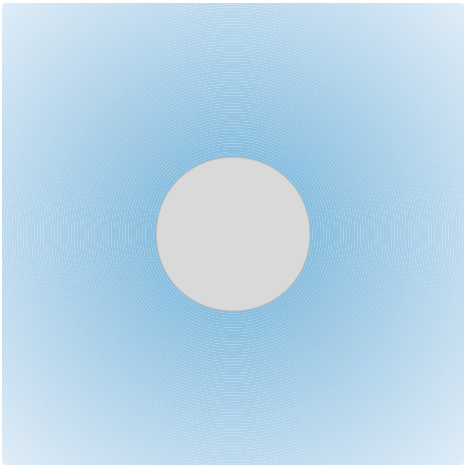
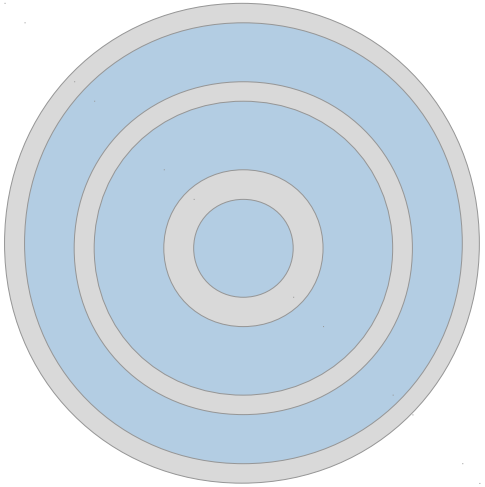
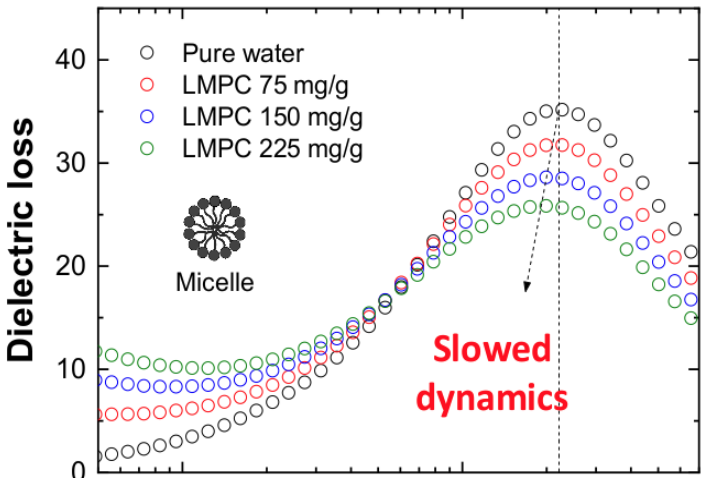
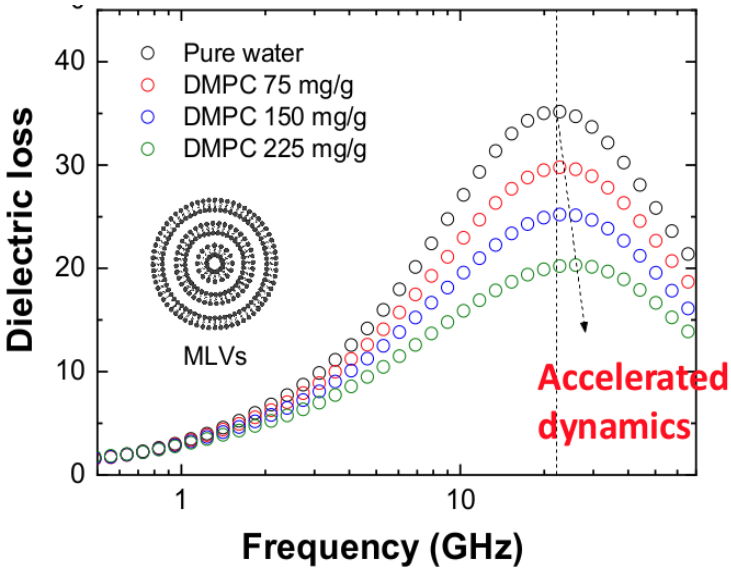


Micelle, unconfined water



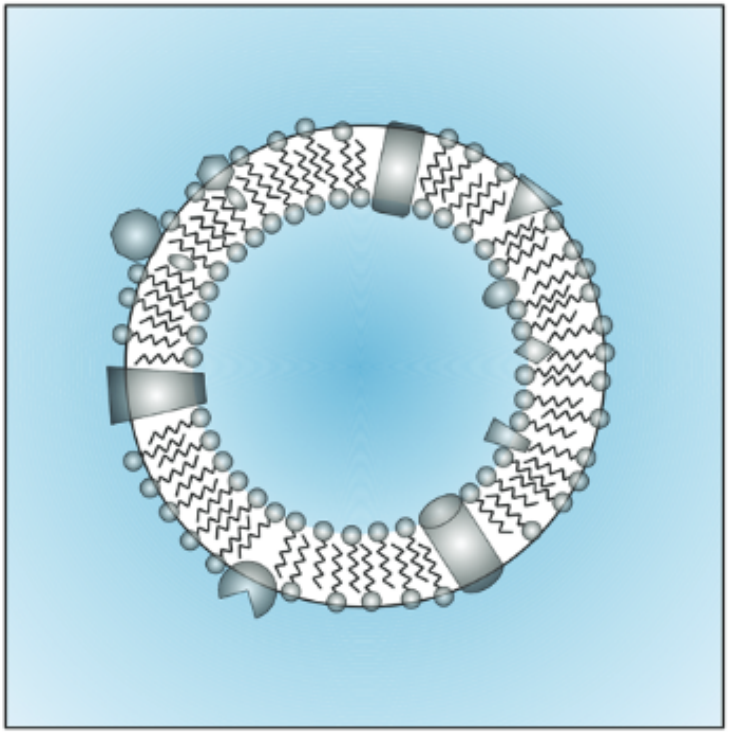
Reverse micelle, confined water

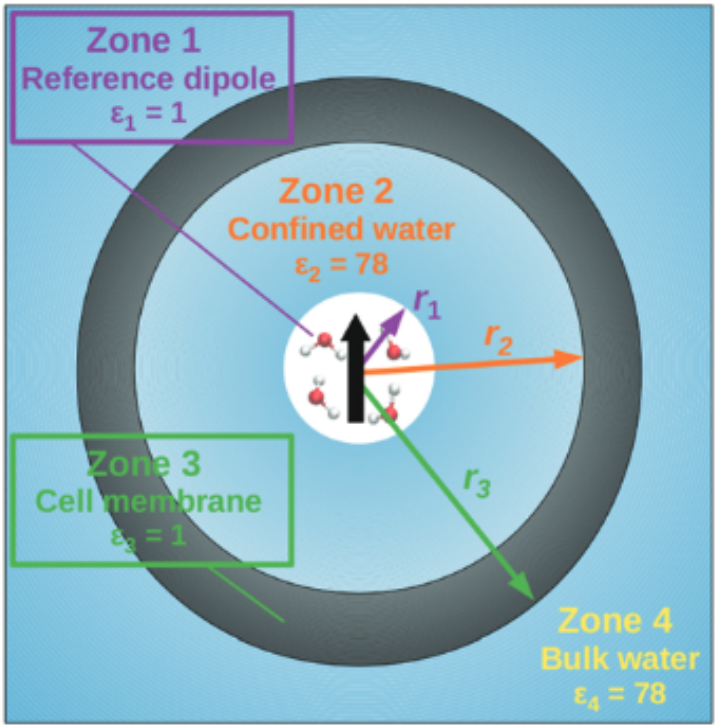




Can this be generalized to biological cells?

- Size beyond fully atomistic MD simulation
- Idea: Solve dielectric equations directly using a concentric spherical model





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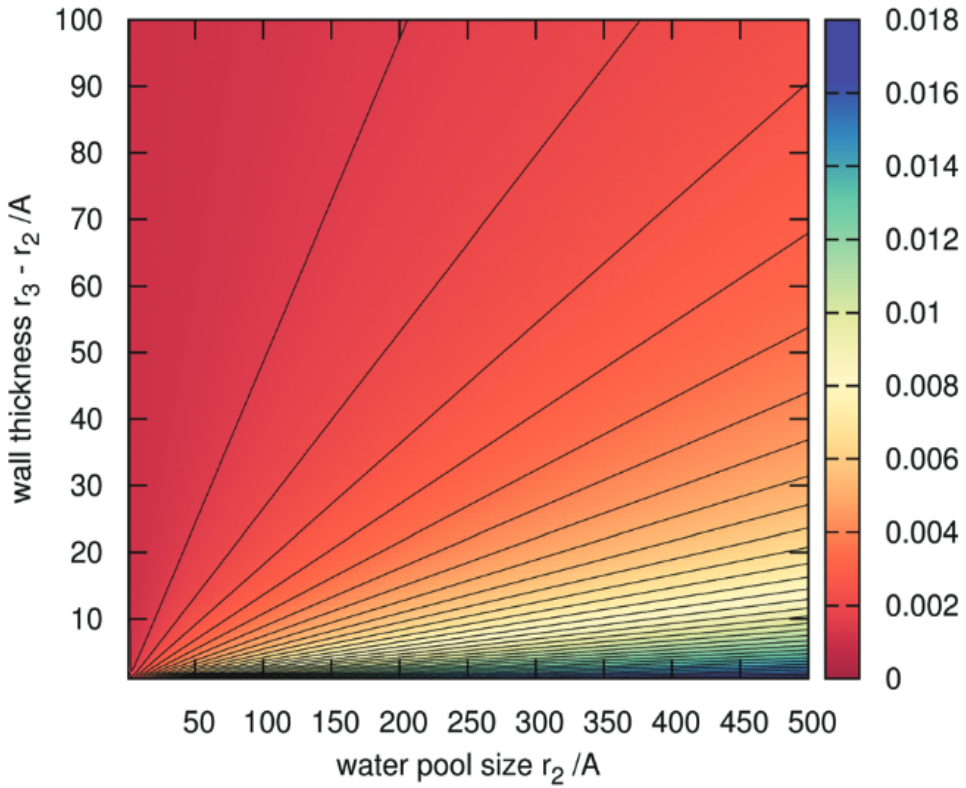
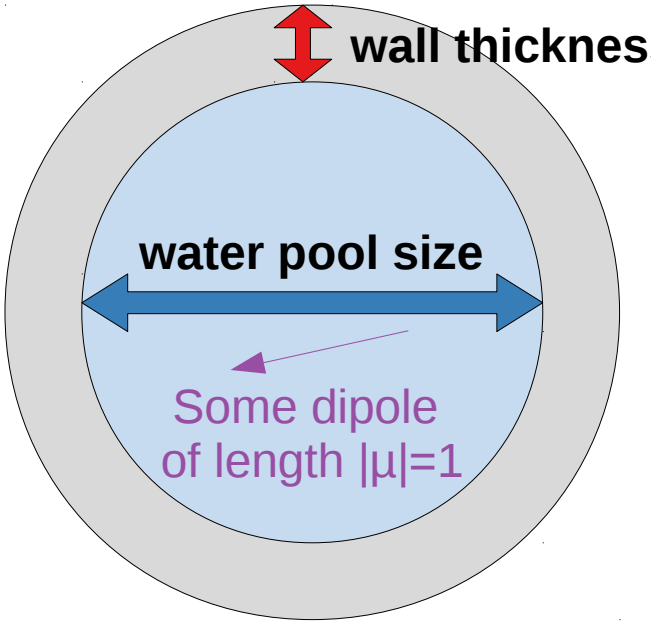
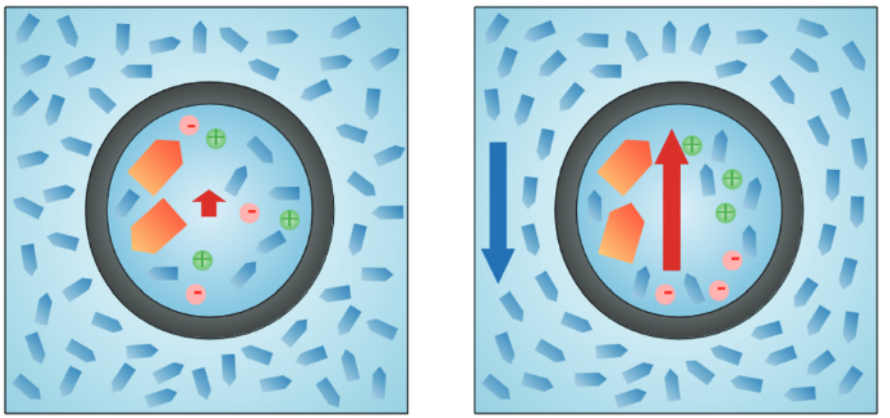




→ **Embedding mechanisms**



Thank you for your attention!