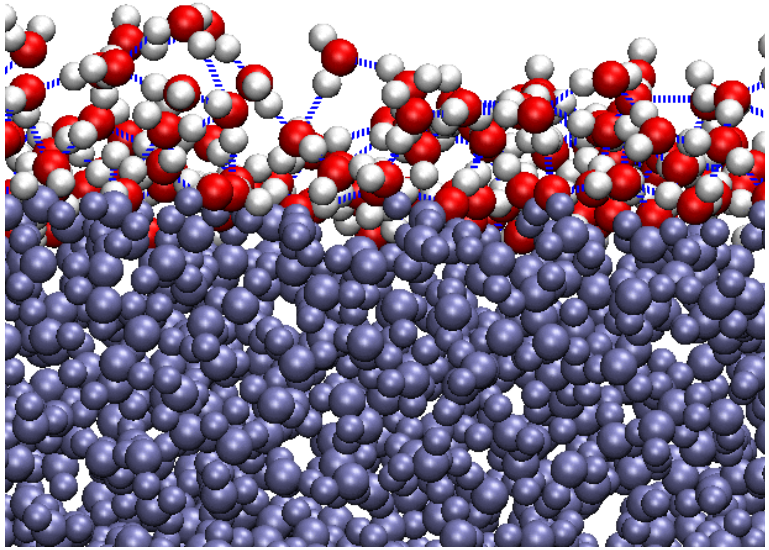
When water molecules meet air



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• Dr. Nils Becker
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• SARA Computing and Networking Services (www.sara.nl)

Why study structural dynamics at the air/water interface?

Atmospheric and ocean chemistry (e.g. dissolution of CO_2 in water)

https://pangea.stanford.edu/research/atmosphere/

Water/air interface is a good model hydrophobic interface

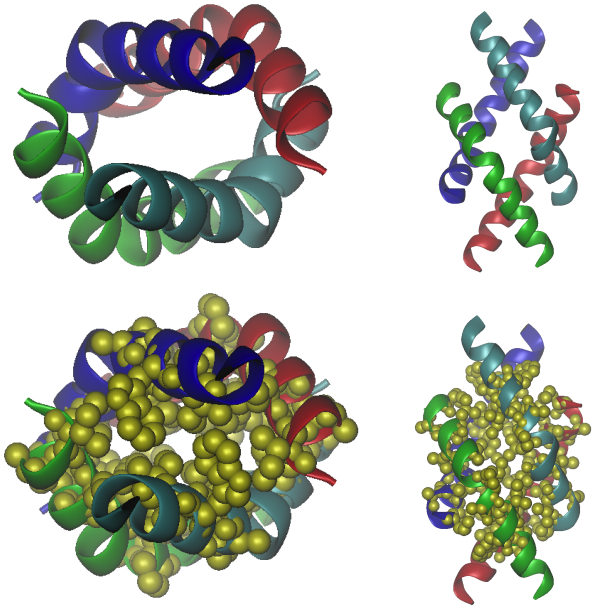
- Protein folding or ligand binding involve **dewetting**

dewetting kinetics

↕

structure/kinetics of interfacial water

Melittin tetramer



How to study structural dynamics at the air/water interface?

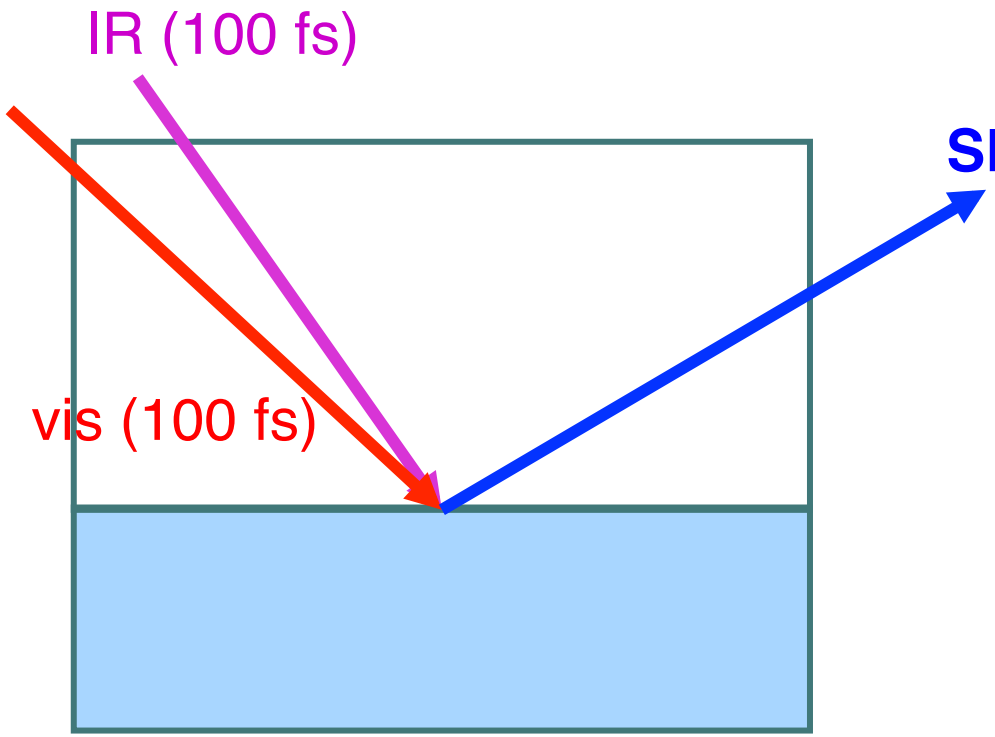
Understanding water structural dynamics at interfaces is tool-limited.

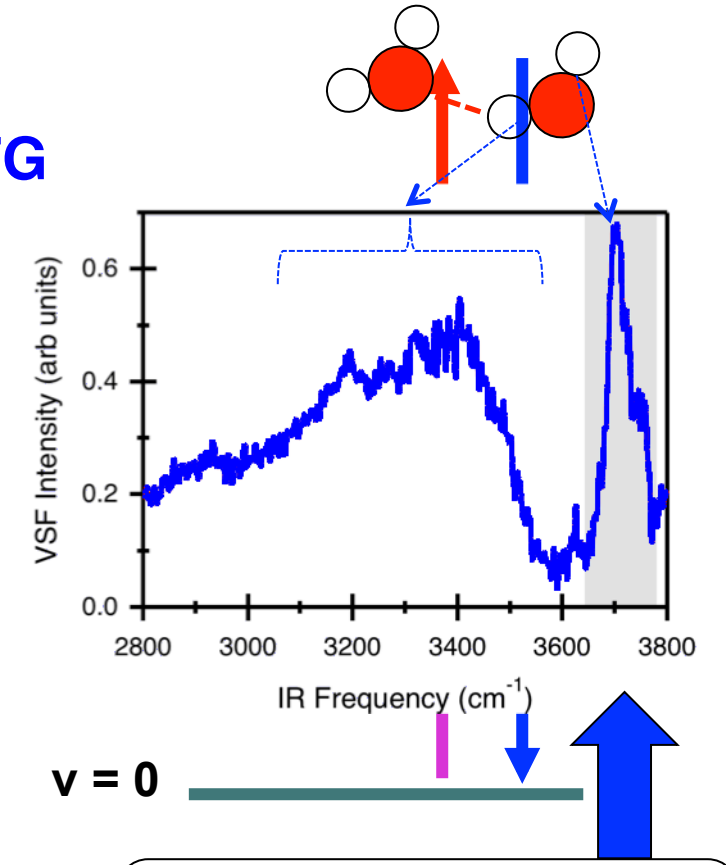
Interface-specific vibrational spectroscopy

+

Molecular dynamics simulations

IR pump+VSFG probe detects the vibrational relaxation and reorientation of *surface* free OH

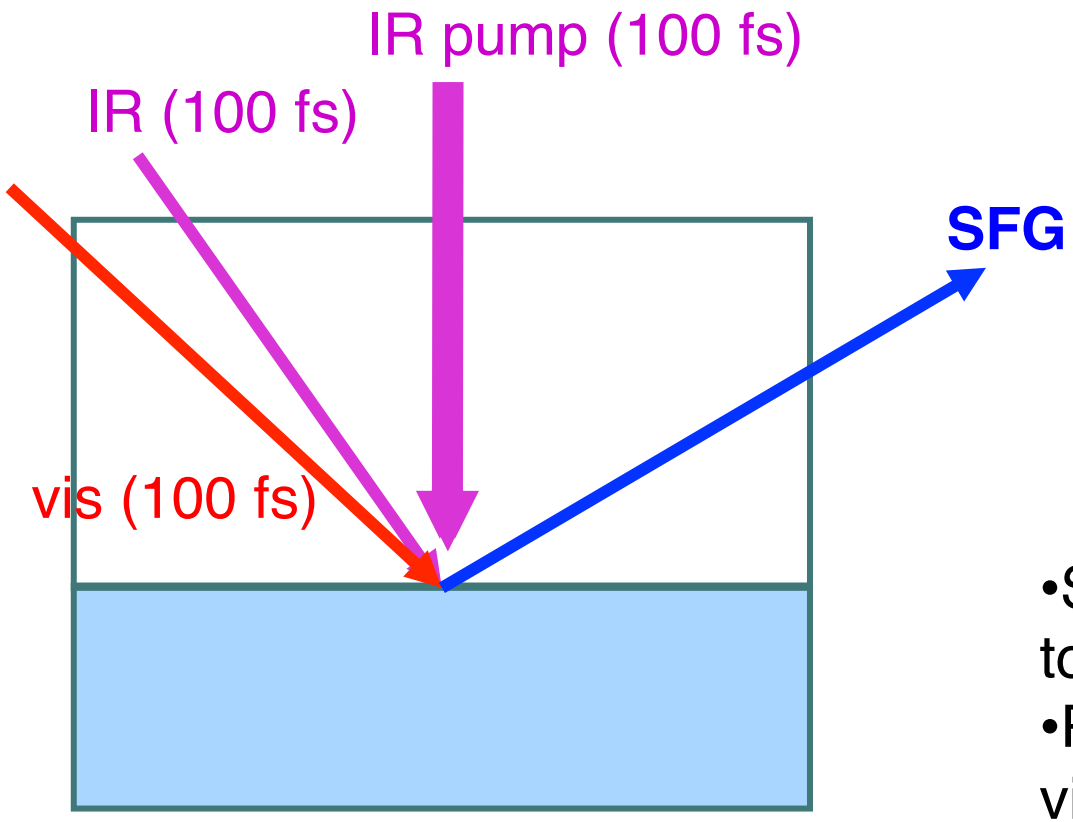


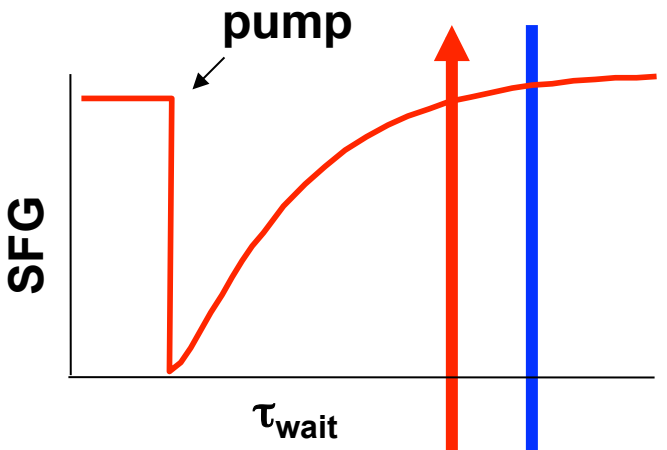


VSFG = vibrational sum frequency generation

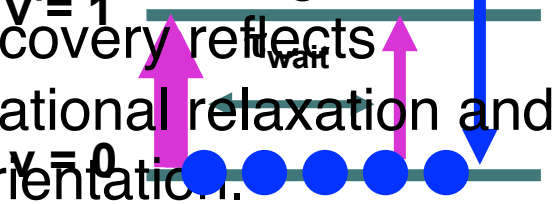
Free OH
-NOT hydrogen bonded
-NOT present in the bulk

IR pump+VSFG probe detects the vibrational relaxation and reorientation of *surface* free OH



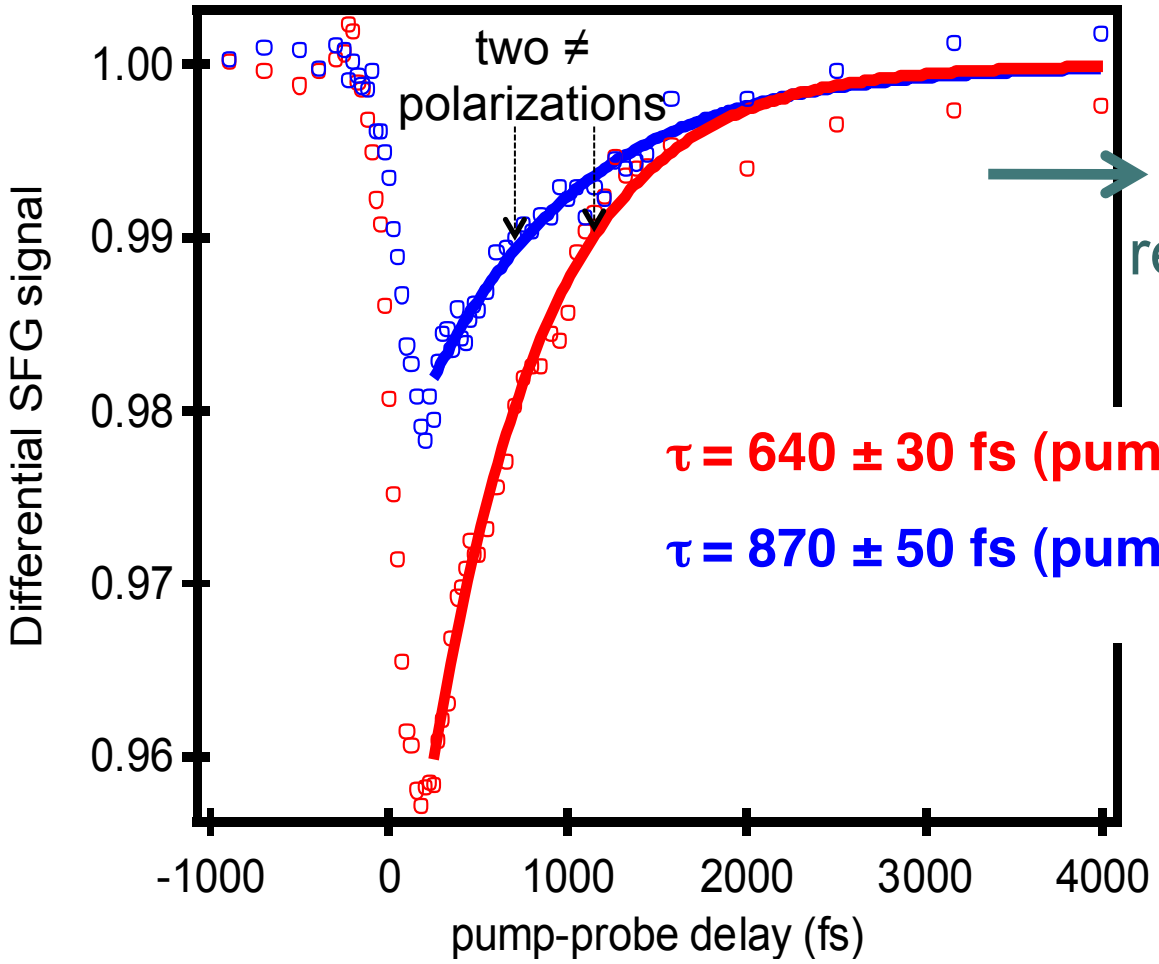


- SFG signal decreases due to depletion of ground state.
- Recovery reflects vibrational relaxation and reorientation.



VSFG = vibrational sum frequency generation

Free OH shows very fast dynamics: anisotropy decays in ~1 ps



Fast, subpicosecond reorientation of free OH

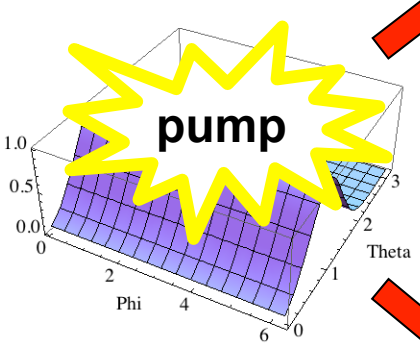
How fast?

$\tau = 640 \pm 30$ fs (pump // probe)

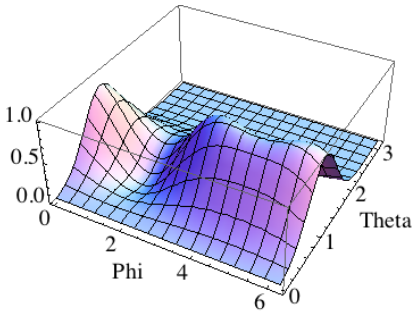
$\tau = 870 \pm 50$ fs (pump $\perp$ probe)

Numerical model is necessary to interpret VSFG signal

Initial population of free OH

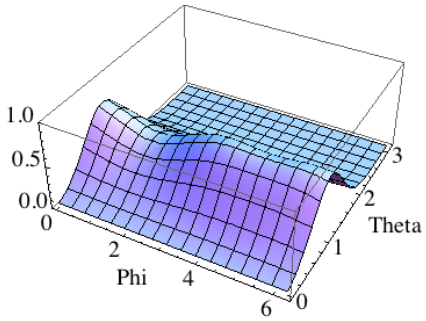


SFG-emitting population t=0

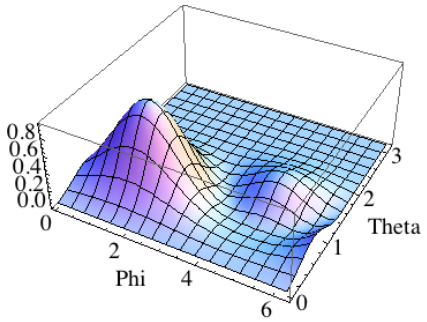


reorientation

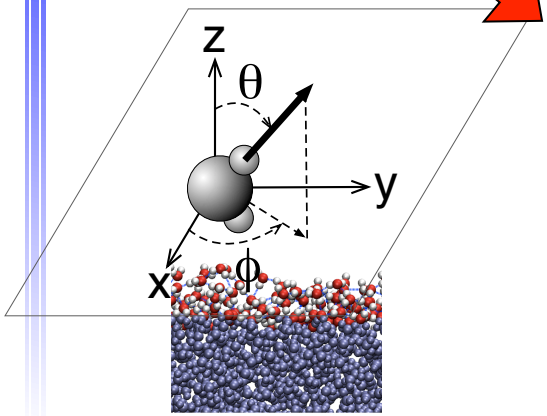
SFG-emitting population, t>0



Bleached (pumped) population t=0



Vibrational relaxation + reorientation

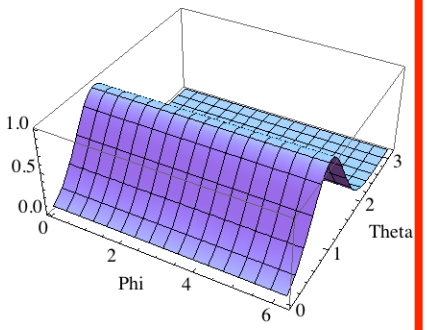


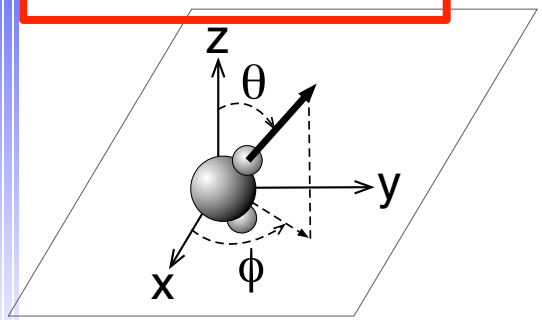
Calculate VSFG signal!

Nienhuys, H.-K. & Bonn, M., J Physl Chem B, 2009, 113, 7564-7573

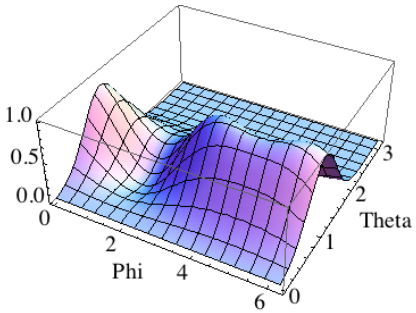
Assumptions for numerical model are investigated with molecular dynamics simulations

Initial population of free OH

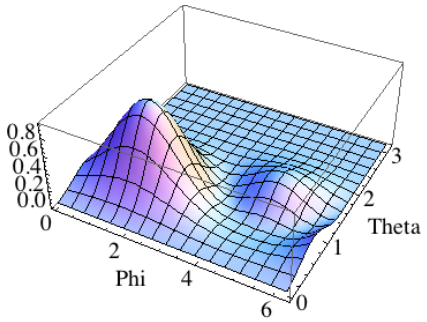




SFG-emitting population t=0



Bleached (pumped) population t=0



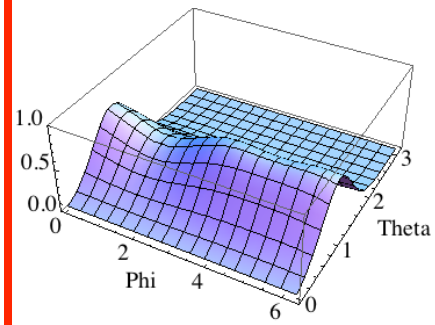
reorientation + hydrogen bonding

Vibrational relaxation + hydrogen bonding + reorientation

Reorientation motion
- **Diffusive or not?**
- **Diffusion constants (D_ϕ and D_θ)**

Lifetime of free OH

SFG-emitting population, t>0



Calculate VSFG signal!

Nienhuys, H.-K. & Bonn, M., J Physl Chem B, 2009, 113, 7564-7573

The principles of classical molecular dynamics simulations

Molecular dynamics →

Solving Newton's equations of motion

Force = mass*acceleration (F = m*a)

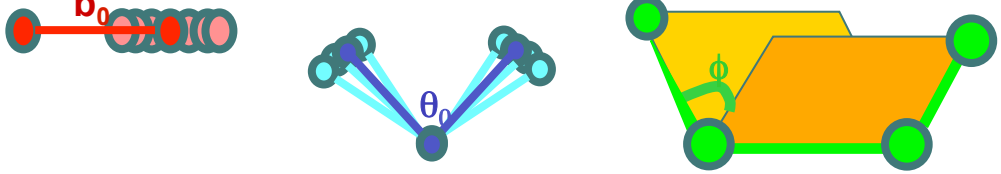
$v = v_i + a*t$

$x = x_i + v_i*t + 0.5*a*t^2$

How do we do this in practice?

1 – Calculate F from the potential energy of the system: $F_{i,x} = -\frac{dU_{total}}{dx_i}$

$$U_{total} = \underbrace{U_{bond} + U_{angle} + U_{dihedral}}_{\text{Bonded Interactions}} + \underbrace{U_{VdW} + U_{electrostatic}}_{\text{Non-Bonded Interactions}}$$

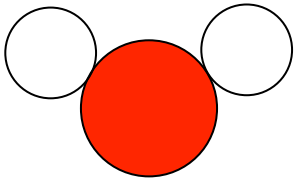


repeat

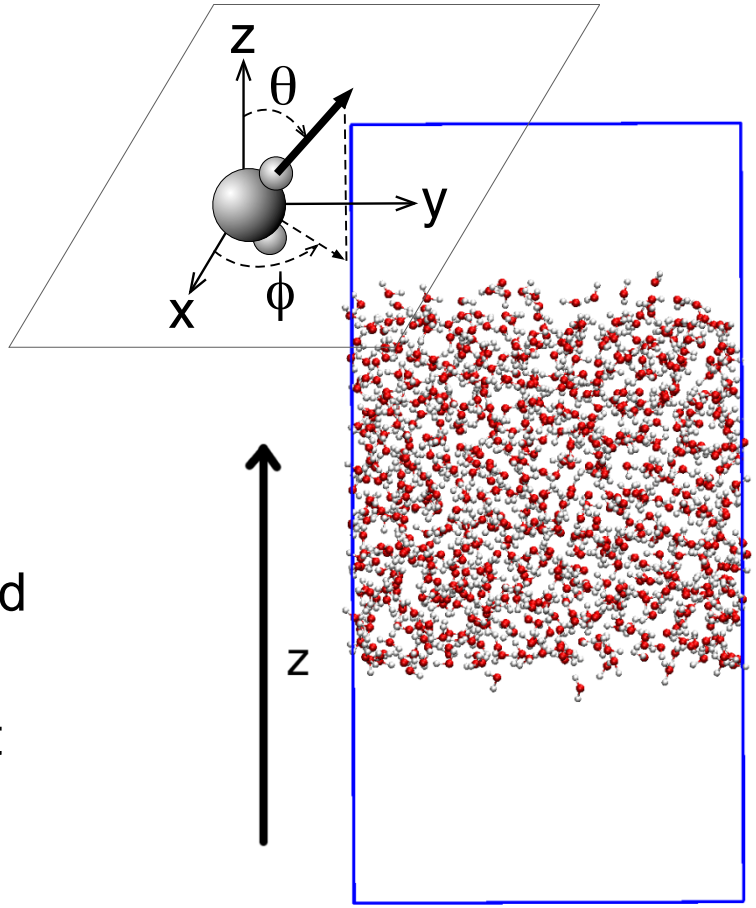
2 – Allow particles to move for a short time, Δt

Connecting VSFG results to molecular motion requires molecular simulations

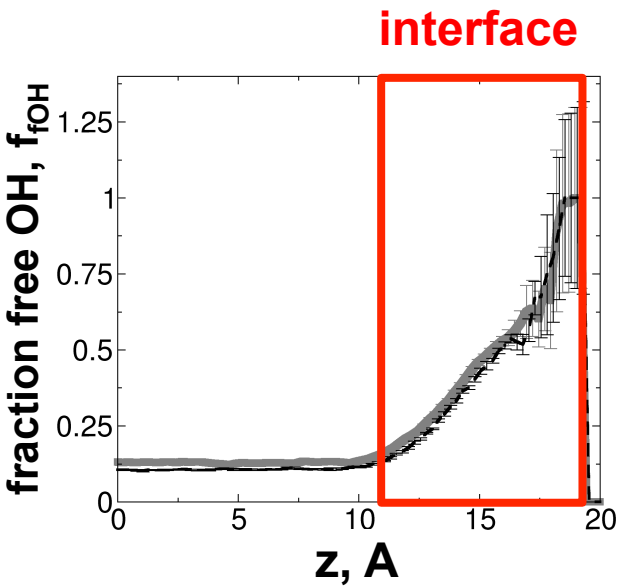
- SPC/E water model.
  - Partial charges at H and O
  - Lennard-Jones potential for O

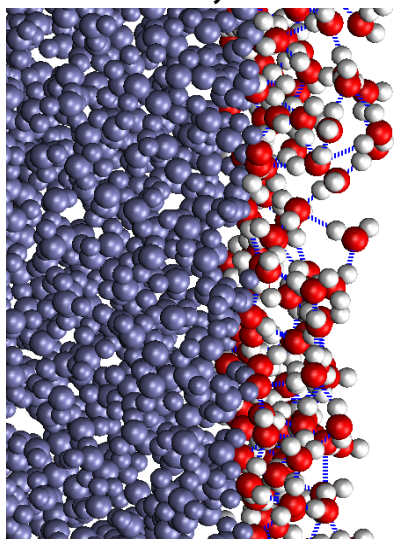


  - Reproduces (±20%) many structural and dynamic properties of water
- Molecular dynamics simulations at constant number of particles, volume, energy (NVE)
- Simulation box is 30*30*60 Å.
- Periodic boundary conditions.
- Simulation run for 2 ns (step duration = 1 fs).



Interface is defined using time- and space-averages





$$f_{fOH}(z) = \frac{\langle n_{fOH}(z) \rangle}{\langle n_{OH}(z) \rangle}$$

Criteria for hydrogen-bonded state:
O…O distance < 3.5 Å
O-H…O angle >140º

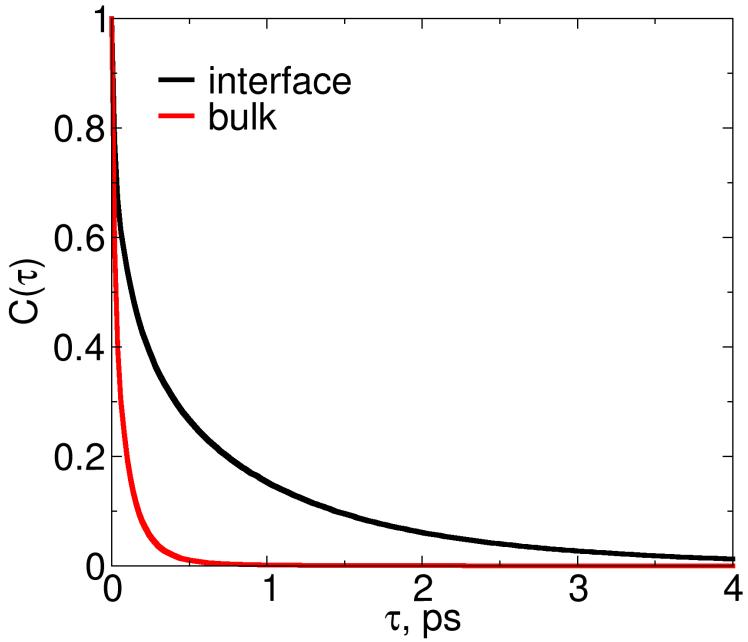
Lifetime of free OH state is of order 800 fs

Decay of free OH state is calculated from

$$C_{free}(t) = \langle n_{free}(0)\, n_{free}(\tau) \rangle$$

$n_{free}(\tau) = 1$ if OH is free at time t

Absorbing boundary conditions are used

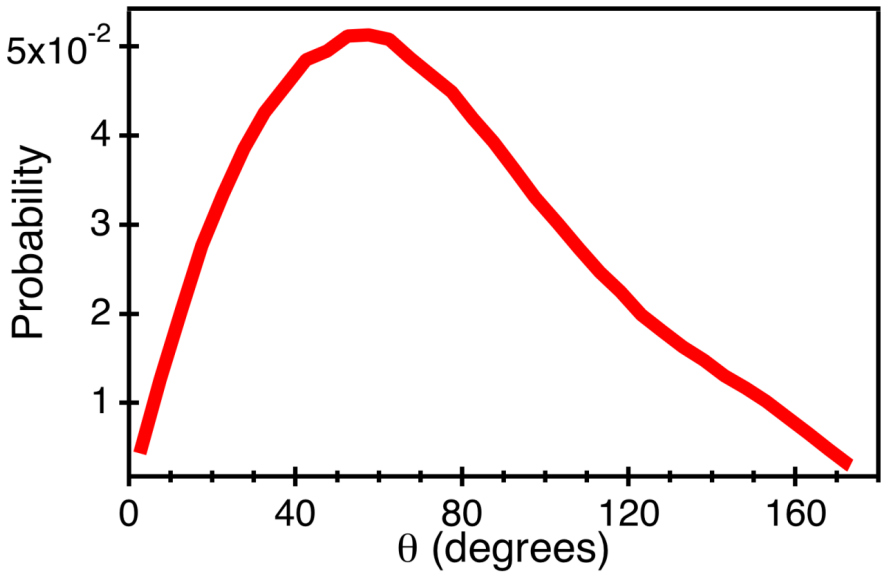


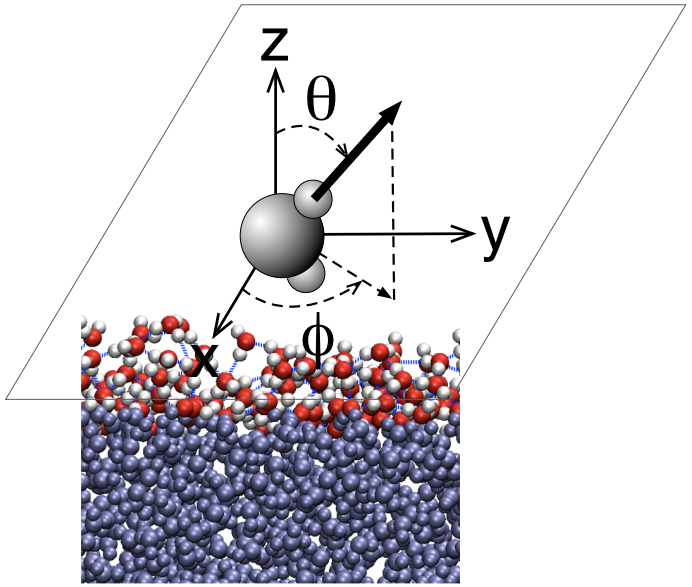
The decay time for the free OH is

$$\tau_\nu = 800 \pm 100\, fs$$

(residence time of waters at the interface is ≈10 ps)

Free OH groups point preferentially to the air





Movement of free OH groups in θ occurs **in a potential V(θ):**

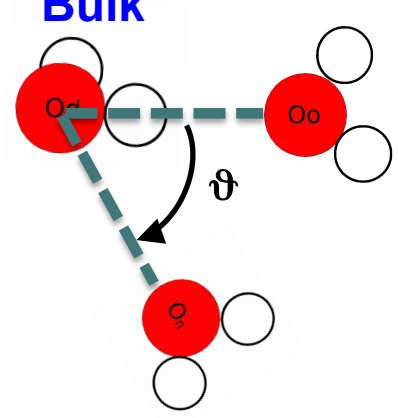
$$V(\theta) = -k_B T \log\left(P(\theta)\right)$$

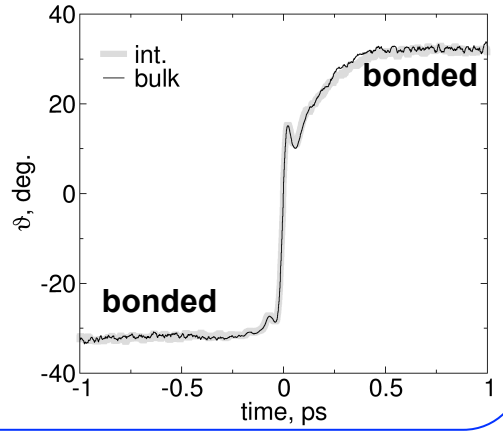
$$V(\theta) = \frac{k_B T}{2\left(\Delta\theta\right)^2}\left(\theta - \theta_0\right)^2$$

$$\theta_0 = 59^\circ \qquad \Delta\theta = 26^\circ$$

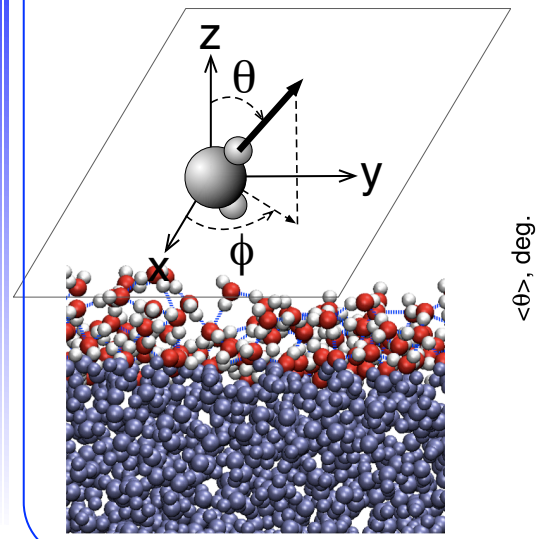
Rotational motion of free OH is well-approximated as diffusive over 0.2-1 ps

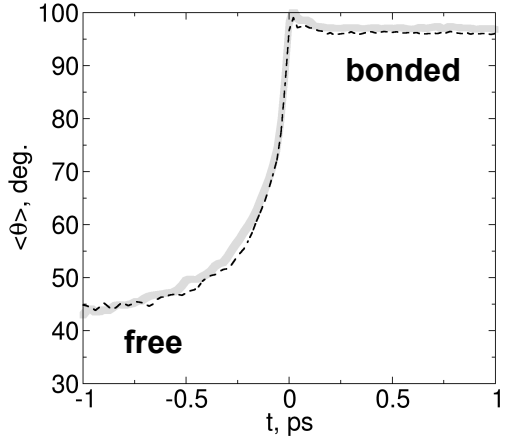
Bulk

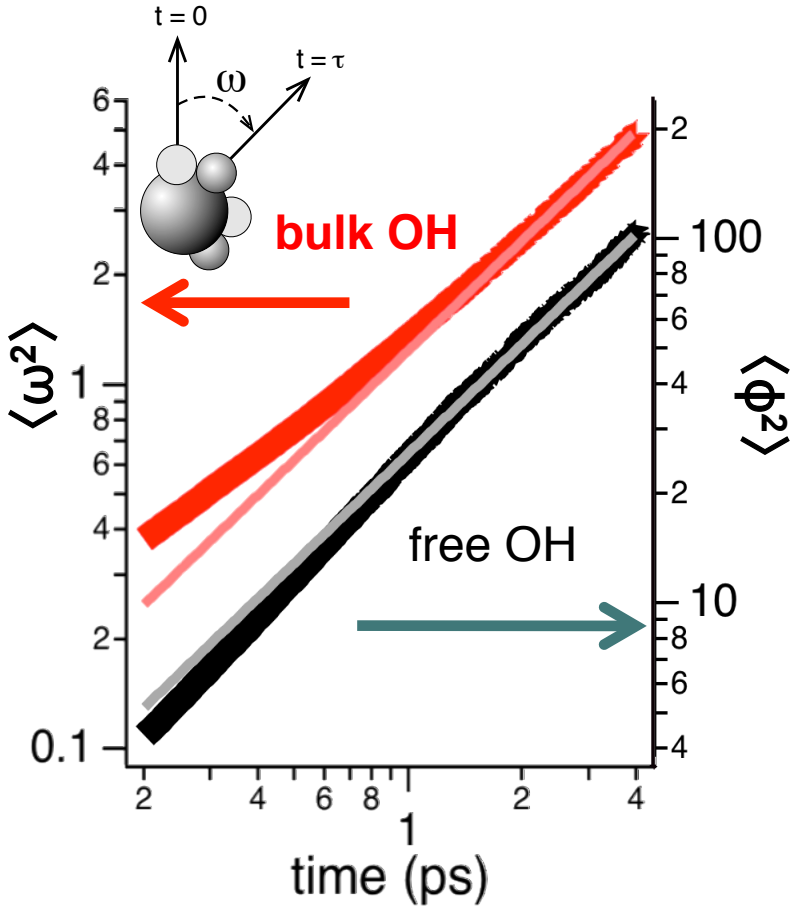




Interface, free OH





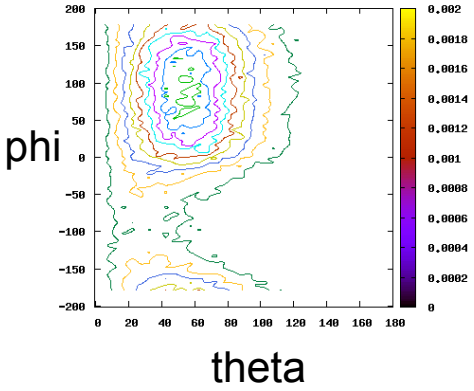


<ω²> Mean square angular displaceme
<ϕ²> In-plane mean square angular displacement

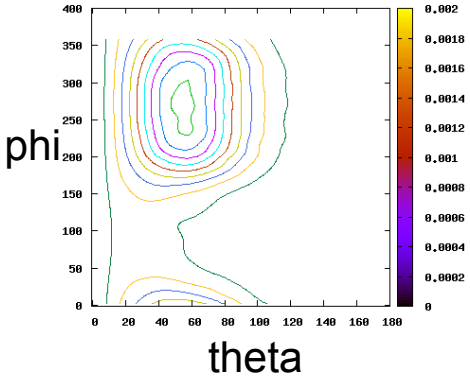
Free, interfacial, OH groups rotate 3× faster than bulk water

Effective D_ϕ and D_θ are obtained by fitting the numerical solution of the diffusion equation to simulation data

Simulation, time *t*



Numerical solution of diffusion equation, time *t*



$$\frac{\partial \rho}{\partial t} = \frac{D_\phi}{\sin^2\theta}\frac{\partial^2 \rho}{\partial \phi^2} + \frac{D_\theta}{\sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial \rho}{\partial \theta} + \frac{D_\theta}{k_B T}\frac{\partial \rho}{\partial \theta}\frac{\partial V}{\partial \theta} + \frac{\rho D_\theta}{k_B T \sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial V}{\partial \theta}$$

Bulk (hydrogen bonded) OH

D_ϕ = 0.1 rad^2/ps

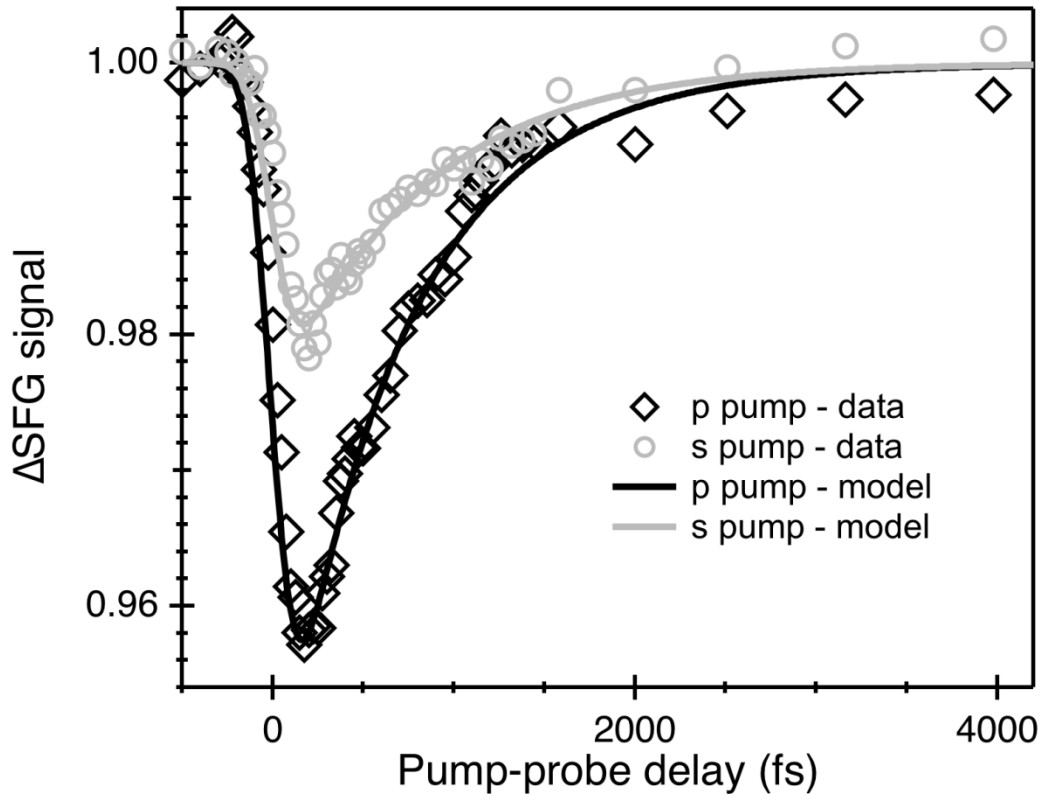
D_θ = 0.1 rad^2/ps

Free OH at interface

D_ϕ = 0.32 rad^2/ps

D_θ = 0.36 rad^2/ps

Model using parameters from MD reproduces VSFG signal of free, interfacial OH groups

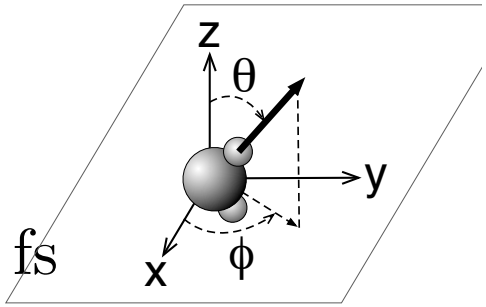


Parameters from simulation

$\theta_0 = 59°$

$\Delta\theta = 26°$

$\tau_v = 800$ fs



$$D_\theta = 0.36 \frac{rad^2}{ps}$$

$$D_\phi = 0.32 \frac{rad^2}{ps}$$

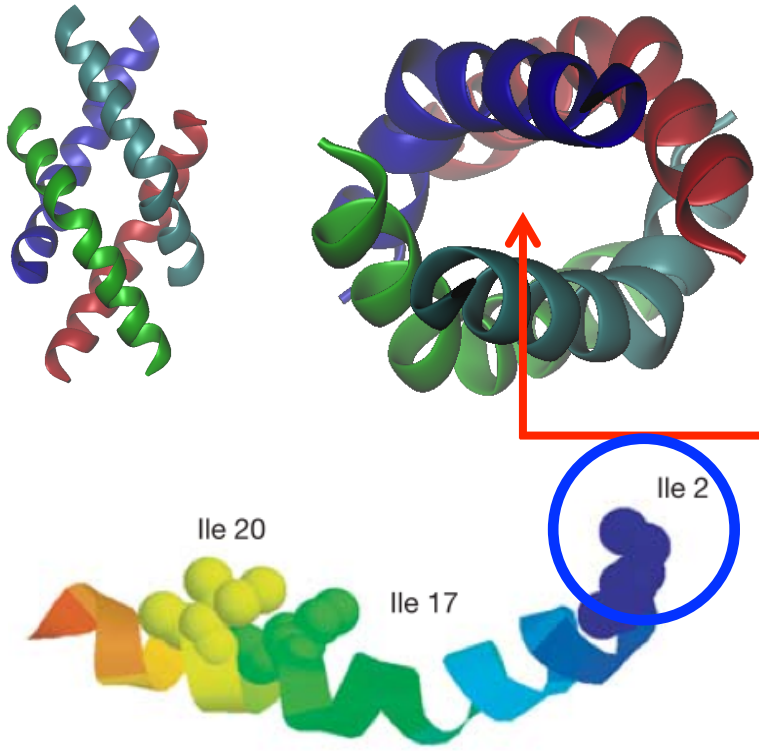
To take home…

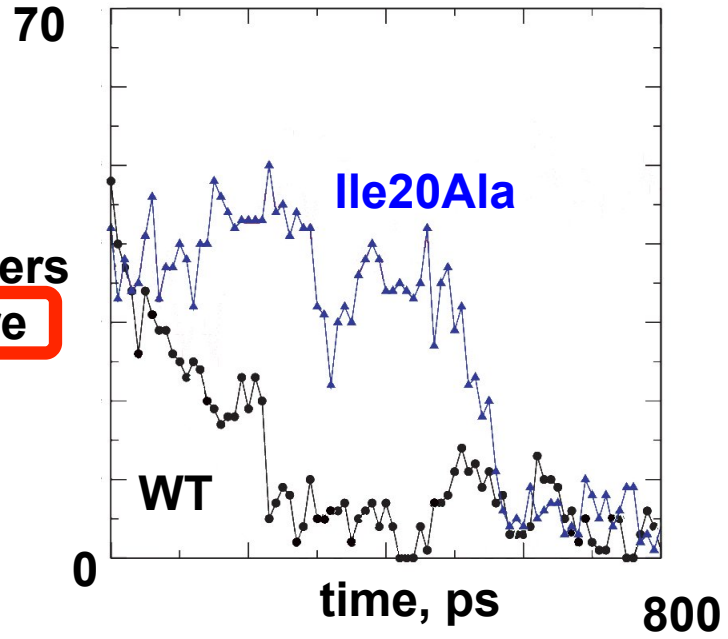
- Classical water model SPC/E describes structure and dynamics at the air/water interface (room temperature)
- Free OH at air/water interface reorients ≈ 3 x faster than bulk OH groups

How does this influence de-wetting in proteins?

Changes in the population of the free OH groups affect kinetics of dewetting of melittin tetramer

Melittin tetramer





Liu et al (2005), Nature 437, 159

Connection between density fluctuations near interfaces and the dynamics of free OH groups needs to be further investigated…