Hydration-dependent dynamics of confined water

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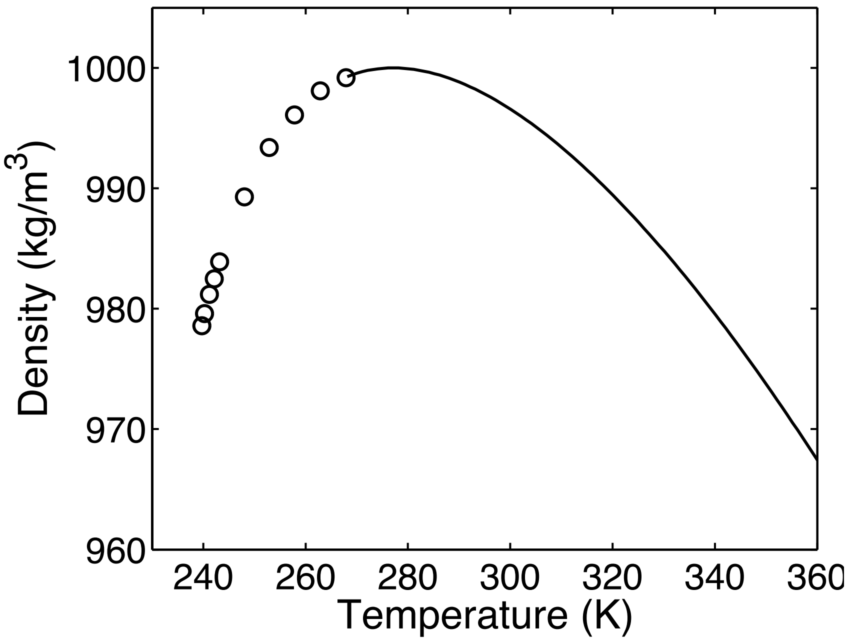
Low-Q Seminar

Overview

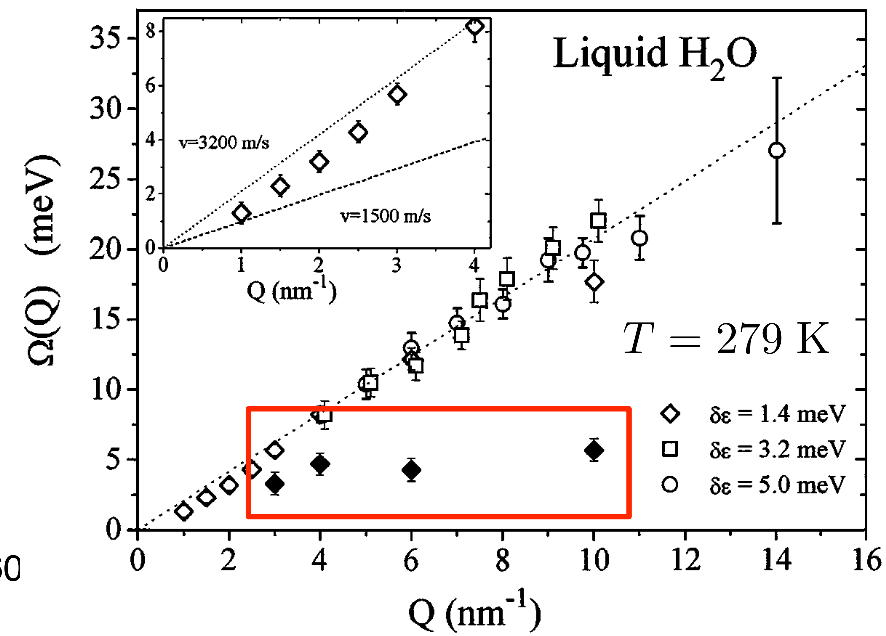
- Properties of water
- Single-particle dynamics of bulk water
- Single-particle dynamics of confined water
- Hydration-dependent dynamics of confined water

Anomalous properties of water

Density maximum



Transverse optical mode



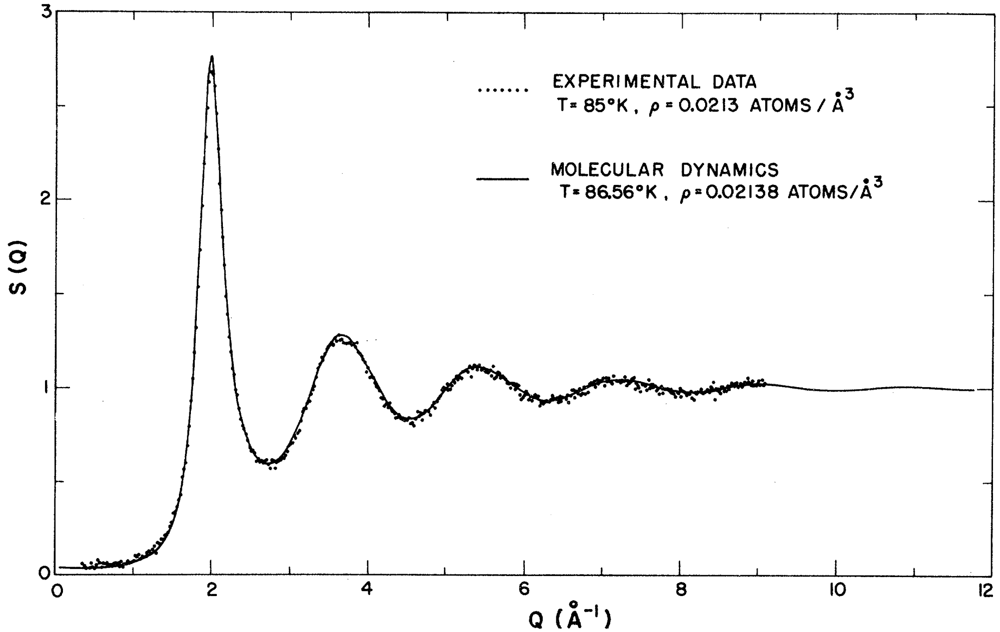
G. S. Kell, *J. Chem. Eng.* **12**, 66 (1967)

D. E. Hare and C. M. Sorensen, *J. Chem. Phys.* **87**, 4840 (1987)

F. Sette et al. , *Phys. Rev. Lett.* **77**, 83 (1996)

Argon: a model simple liquid

Structure factor

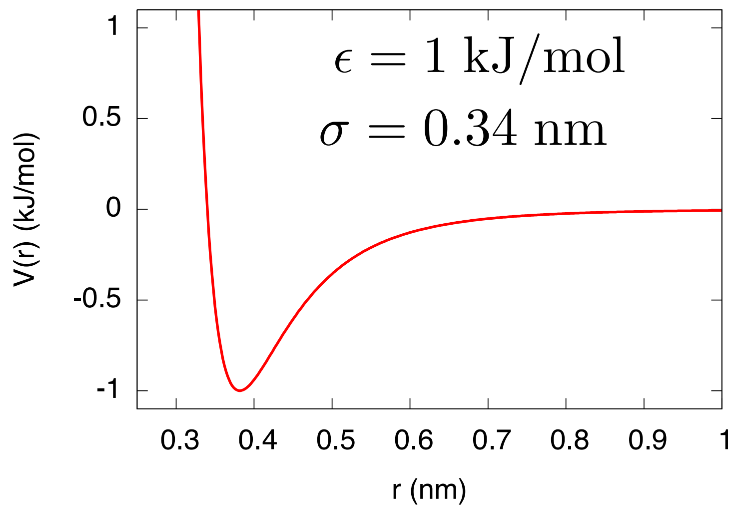


J. L. Yarnell, *Phys. Rev. A* **7**, 2130 (1973)

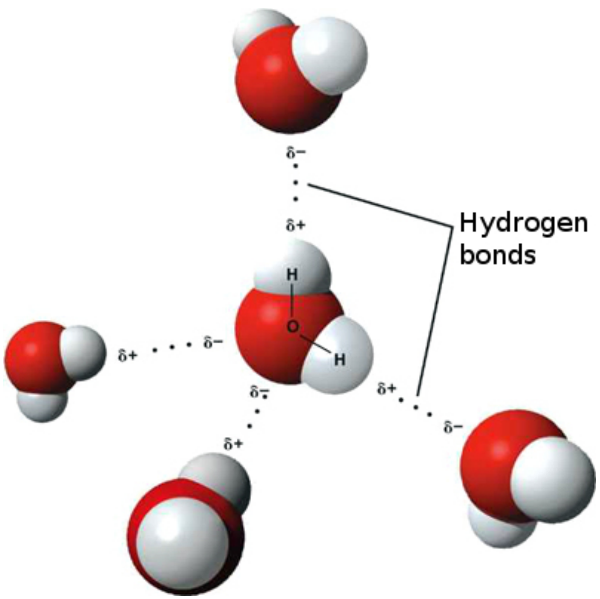
L. Verlet, *Phys. Rev.* **165**, 201 (1968)

Pair potential

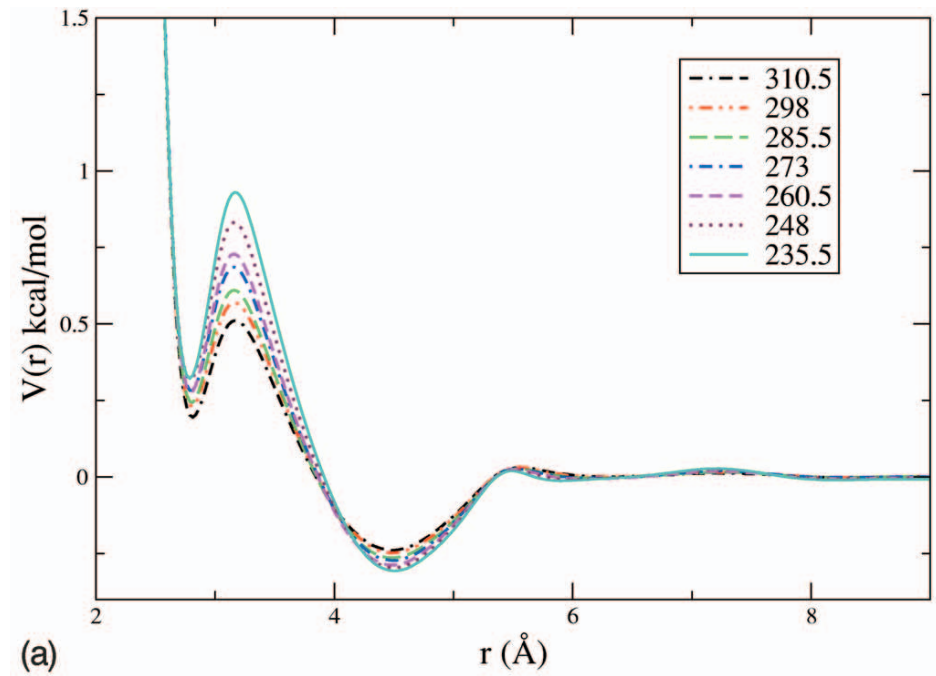
$$V_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Water: an associating liquid



Effective isotropic two-body potential



M. E. Johnson et al., *J. Chem. Phys.* **126**, 144509 (2007)

How do the single-particle dynamics of water and a simple liquid differ?

Collective Dynamics

Full-intermediate scattering function:

Local density

$$F(Q,t) = \frac{1}{N}\int d\mathbf{x}\; e^{i\mathbf{Q}\cdot\mathbf{x}}\;\langle \rho(\mathbf{x},t)\rho(0,0)\rangle$$

Theory: Navier-Stokes Equation

$$m\frac{\partial}{\partial t}\rho(\mathbf{x},t) + \nabla\cdot\mathbf{p}(\mathbf{x},t) = 0$$

$$\frac{\partial}{\partial t}\mathbf{p}(\mathbf{x},t) + \nabla\cdot\mathbf{\Pi}(\mathbf{x},t) = 0$$

$$\frac{\partial}{\partial t}e(\mathbf{x},t) + \nabla\cdot\mathbf{J}^e(\mathbf{x},t) = 0$$

Experiment: Inelastic X-ray Scattering, Dynamic Light Scattering, Neutron Spin-echo

Single-particle dynamics

Self-intermediate scattering function:

Tagged particle position

$$F_\mathrm{s}(Q,t) = \int d\mathbf{x}\, e^{i\mathbf{Q}\cdot\mathbf{x}} \langle \delta(\mathbf{x} - [\mathbf{R}(t) - \mathbf{R}(0)]) \rangle$$

Theory: Langevin equation

$$m\frac{d}{dt}\mathbf{v}(t) = -\xi\mathbf{v}(t) + \delta\mathbf{F}(t)$$

$$\langle \delta F_i(t+t')\delta F_j(t')\rangle = 6\xi k_\mathrm{B} T \delta(t)\delta_{ij}$$

Experiments: Quasielastic neutron scattering, Pulsed gradient spin echo NMR

Quasielastic neutron scattering (QENS) essentially measures the self-intermediate scattering function of hydrogen atoms

The self-intermediate scattering function

Gaussian approximation:

$$F_{\mathrm{s}}(Q,t) \approx \exp\left(-\frac{1}{6}Q^2 \left\langle [R(t) - R(0)]^2 \right\rangle\right)$$

Long-time limit:

$$\lim_{t\to\infty} F_{\mathrm{s}}(Q,t) \approx e^{-\Gamma(q)t}$$

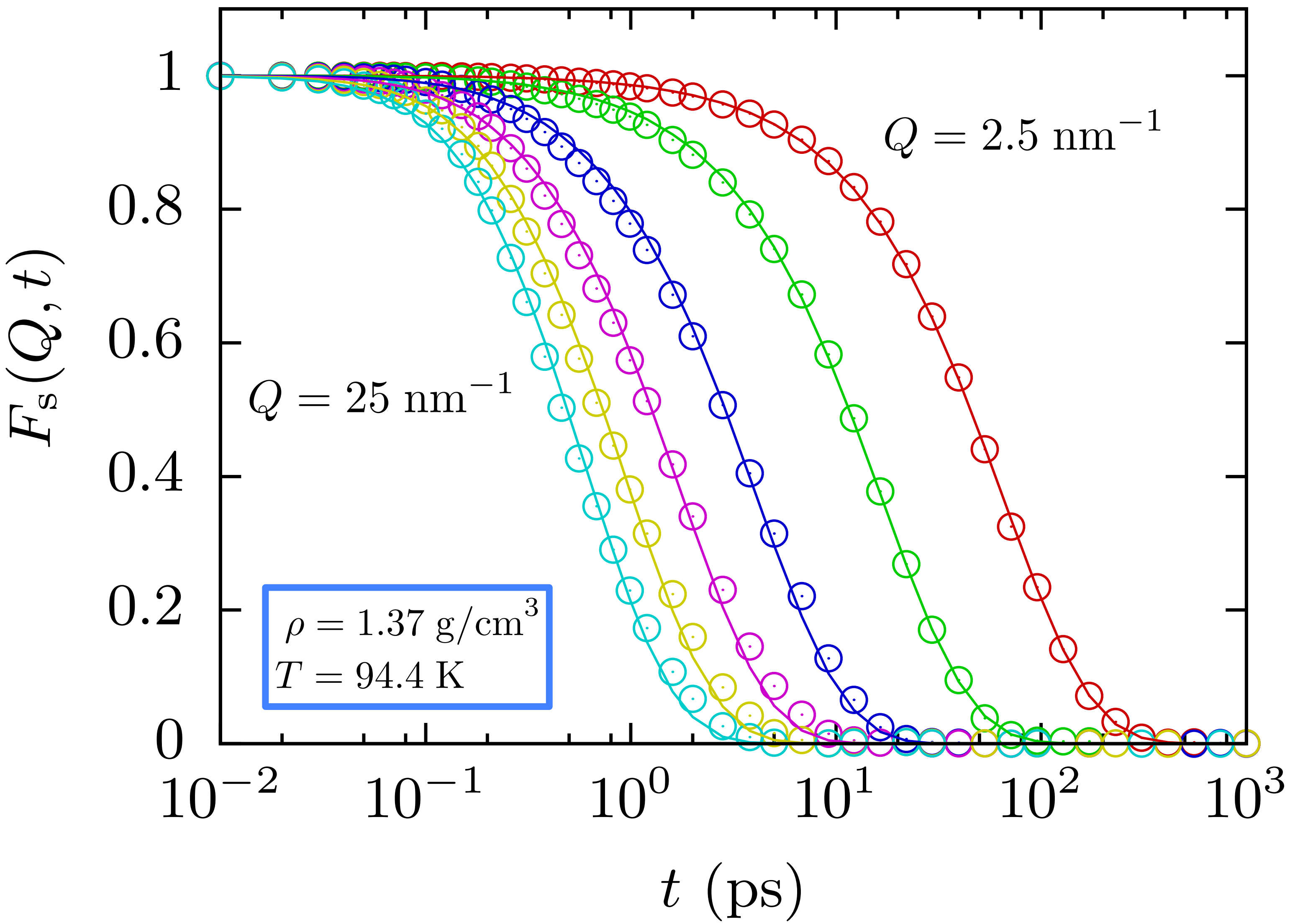
Decay rate

$$\Gamma(Q) = DQ^2$$

Self-diffusion coefficient

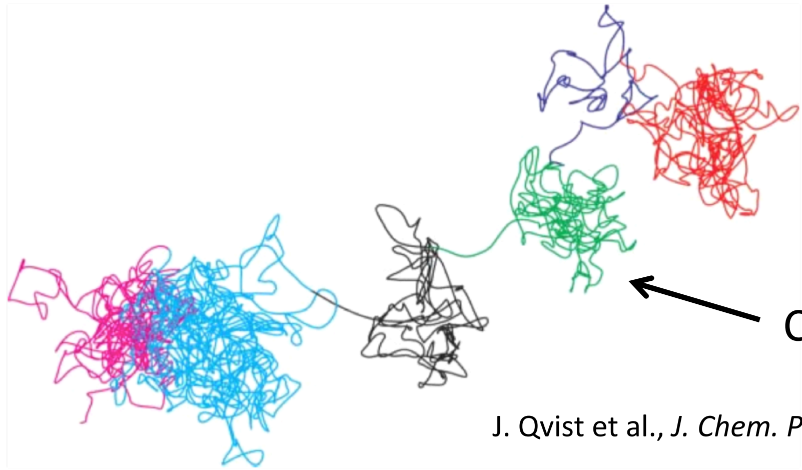
$$D = \frac{k_{\mathrm{B}}T}{\xi}$$

Argon near the triple point



Single particle dynamics of bulk water

MD trajectory:



J. Qvist et al., *J. Chem. Phys.* **134**, 144508 (2011)

Decoupling approximation:

$$F_{\mathrm{s}}(Q,t) = F_{\mathrm{short}}(Q,t) \cdot F_{\mathrm{long}}(Q,t)$$

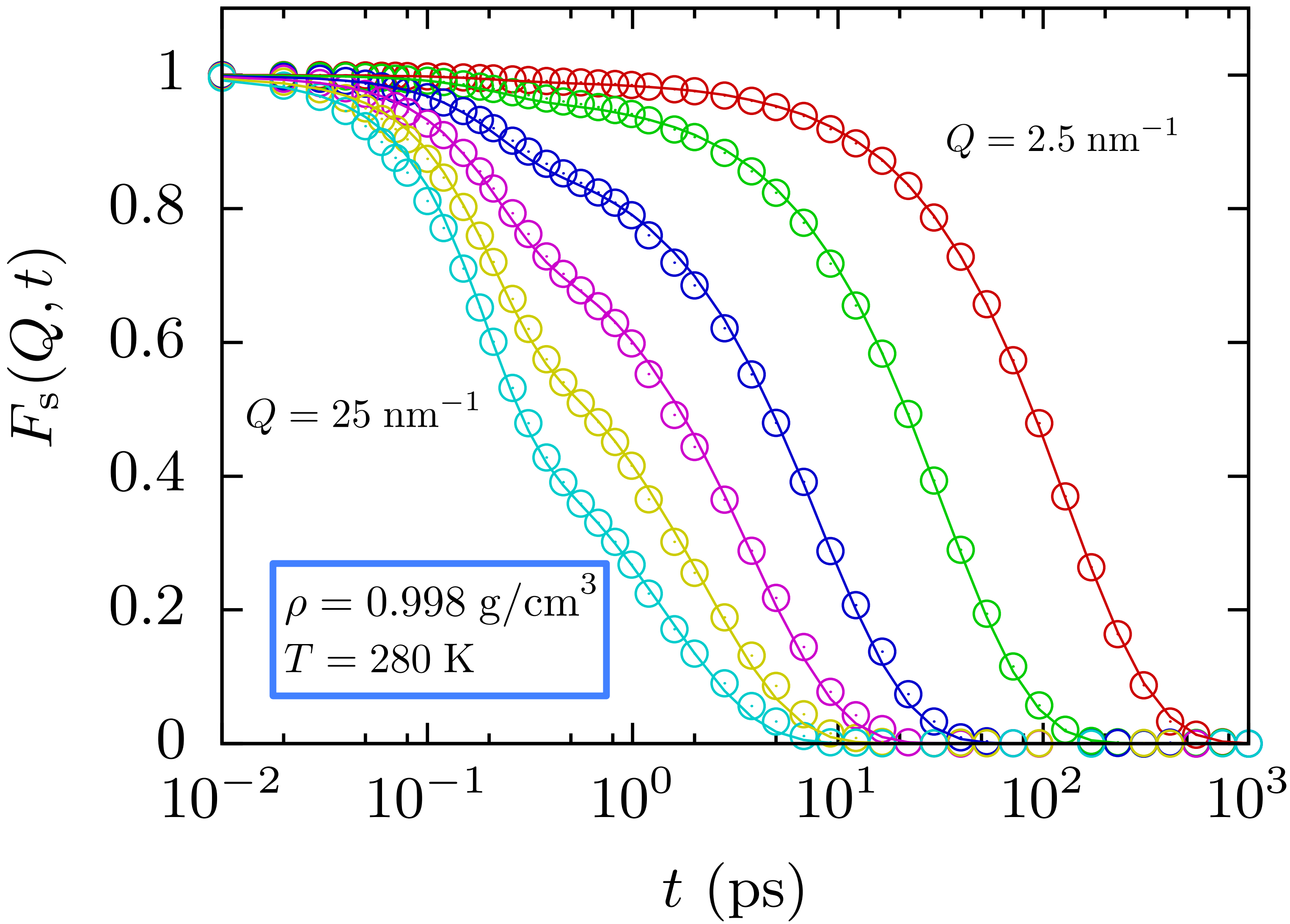
Relaxing-cage model:

$$F_{\mathrm{short}} = \exp\left\{ -v^2 Q^2 \left[\frac{1-C}{\omega_1^2}\left(1 - e^{-\omega_1^2 t^2/2}\right) + \frac{C}{\omega_2^2}\left(1 - e^{-\omega_2^2 t^2/2}\right) \right] \right\}$$

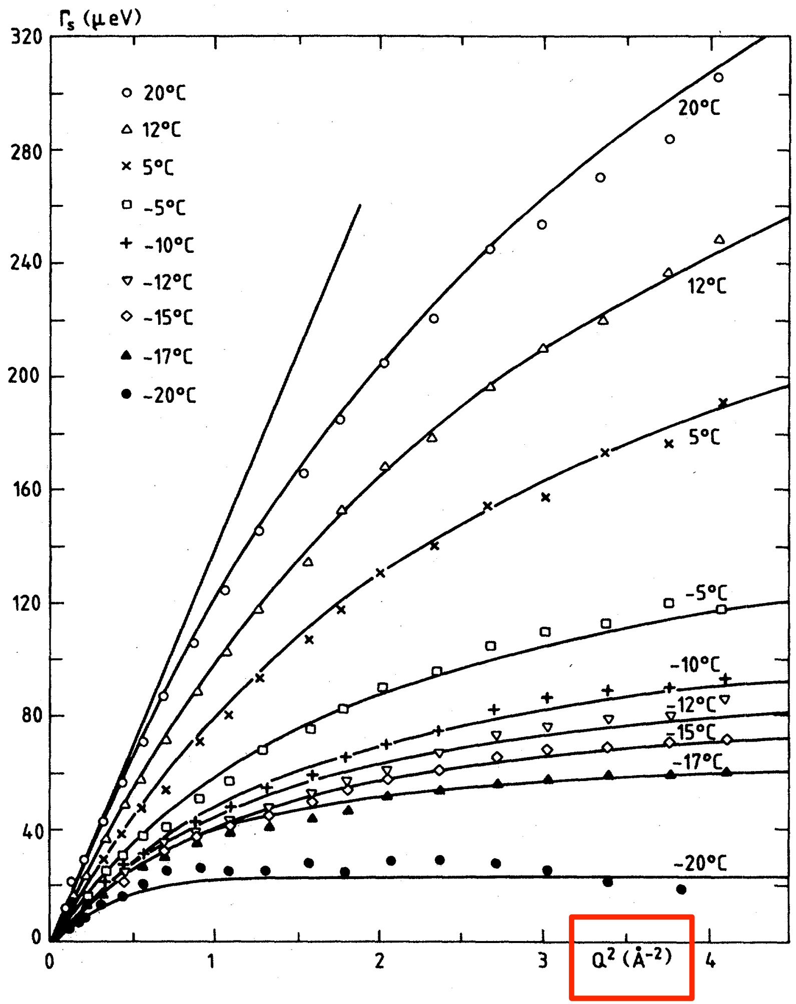
$$\boxed{F_{\mathrm{long}} = e^{-\Gamma(Q)t}}$$

S. H. Chen et al., *Phys. Rev. E* **59**, 6708 (1999)

Water near the triple point



Non-Fickian decay rate



J. Teixeria et al., *Phys. Rev. A* **31**, 1913 (1985)

Jump-diffusion model:

$$\Gamma(Q) = \frac{1}{\tau}\left[\frac{(\ell Q)^2}{1+(\ell Q)^2}\right]$$

$$\lim_{\ell Q \to 0} \Gamma(Q) = \frac{\ell^2}{\tau} Q^2$$

$$\lim_{\ell Q \to \infty} \Gamma(Q) = \frac{1}{\tau}$$

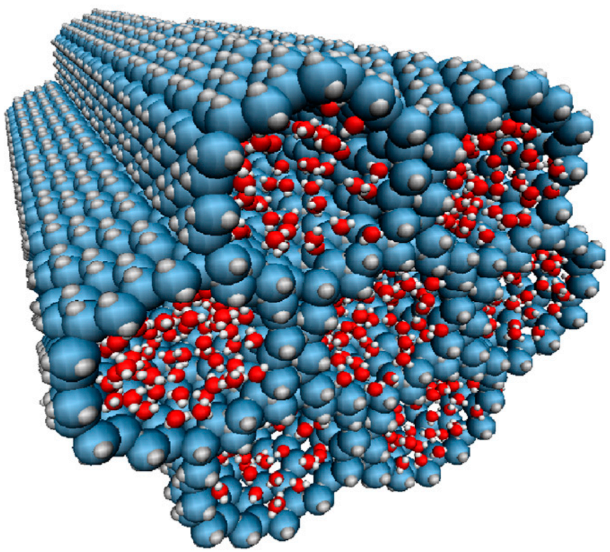
K. S. Singwi and A. Sjolander, *Phys. Rev.* **119**, 863 (1960)

How does confinement affect the single-particle dynamics of water?

Confined water

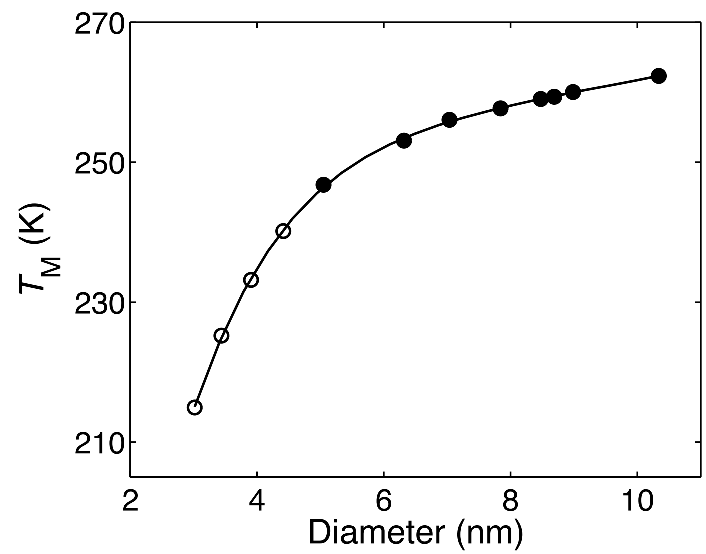
- Confinement introduces finite-size and surface effects

MCM-41 mesoporous silica material



C. E. Bertrand et al., *Phys. Chem. Chem. Phys.* **15**, 721 (2013)

Suppression of freezing

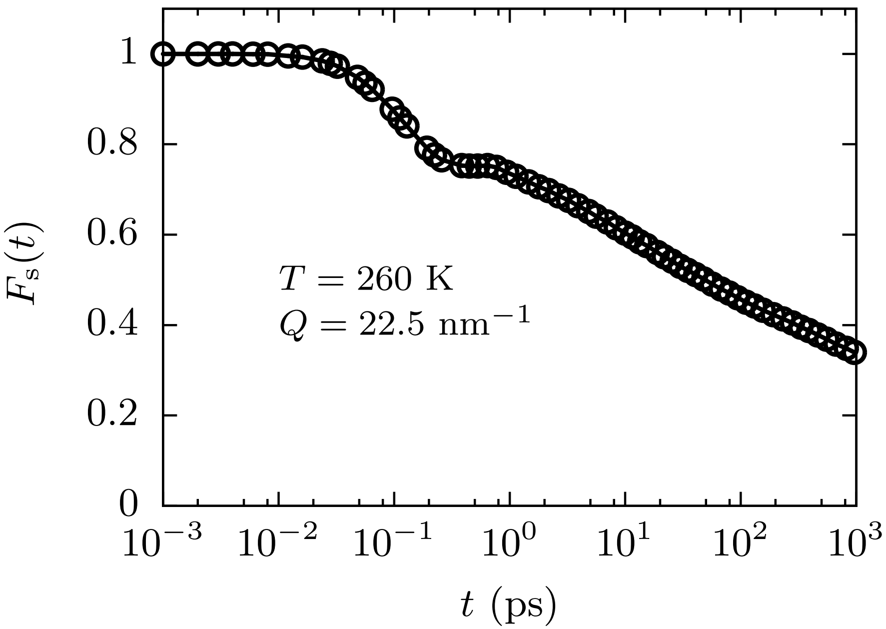


G. H. Findenegg et al., *ChemPhysChem* **9**, 2651 (2008)

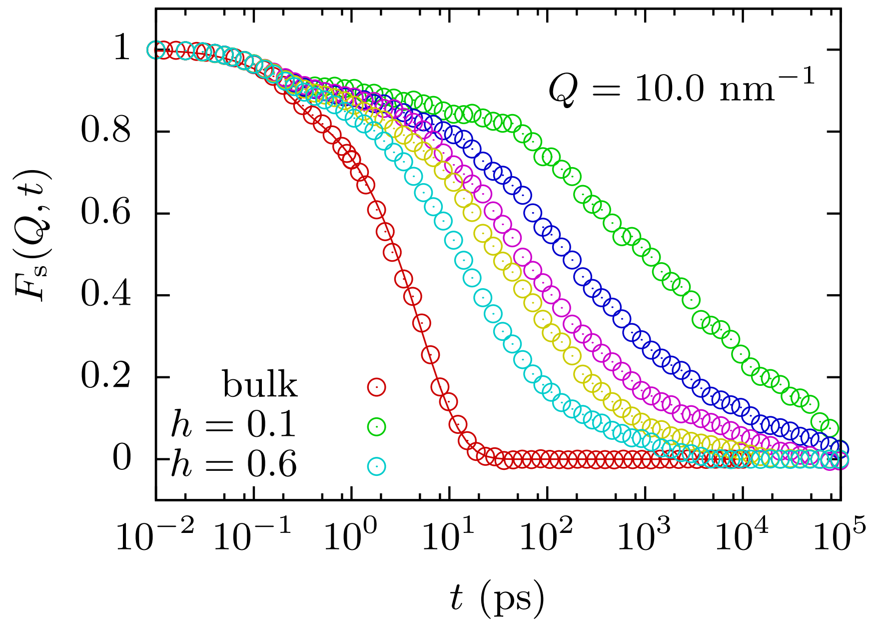
Confined water dynamics

- Confined water dynamics are slow, non-exponential and inhomogeneous

Water in MCM-41

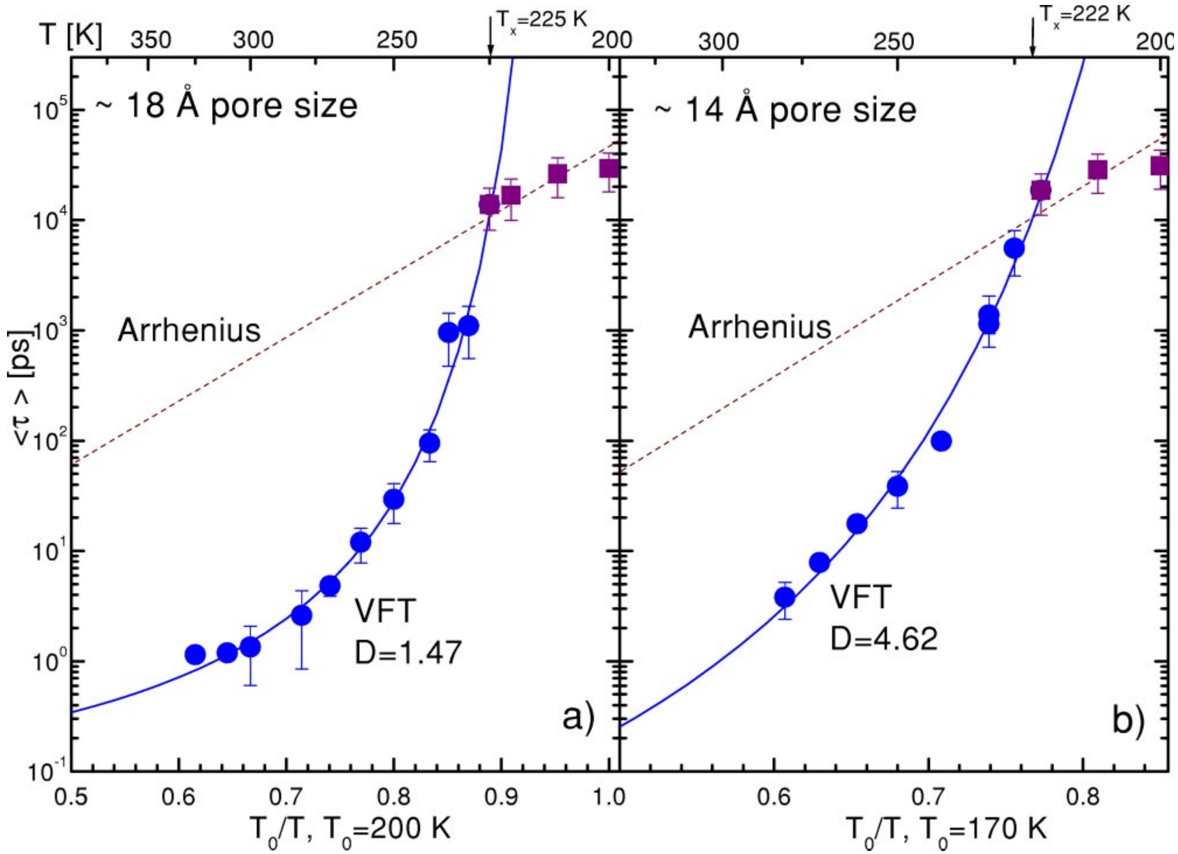


Water in Lysozyme powder



P. Gallo et al., *J. Phys.: Condens. Matt.* **24**, 064109 (2012)

Dynamic crossover



Arrhenius:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_{\mathrm{B}}T}\right)$$

super-Arrhenius:

$$\tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right)$$

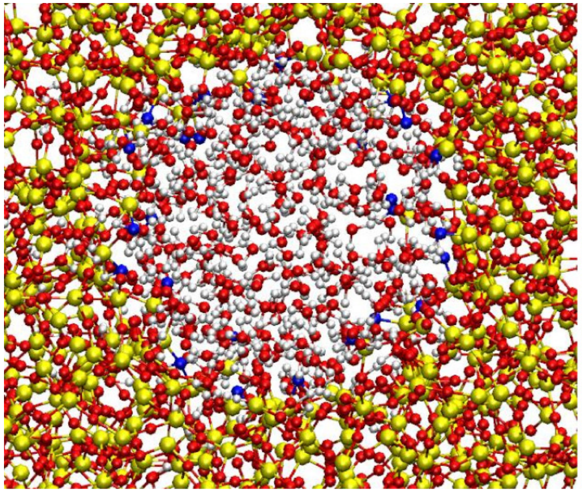
A. Faraone et al., *J. Chem. Phys.* **121**, 10843 (2004)

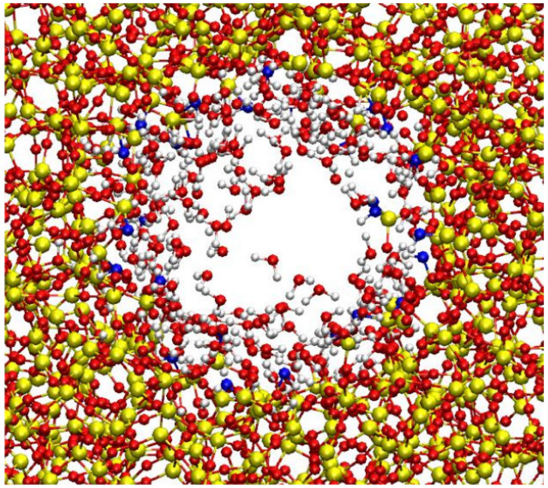
How do the single particle dynamics of confined water depend on the hydration level?

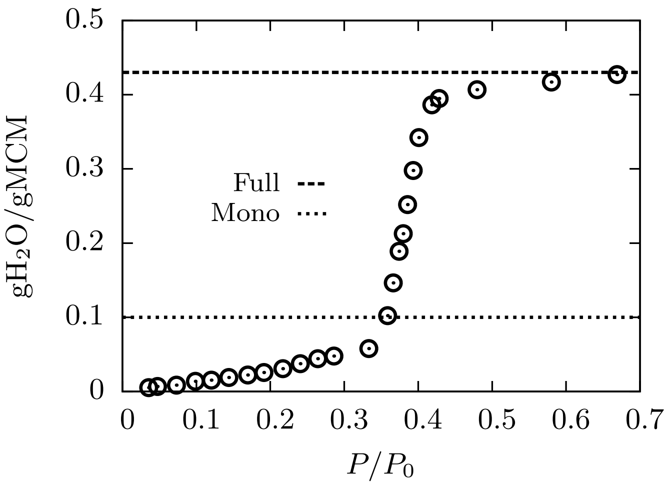
MCM-41 at different hydration levels

Full hydration

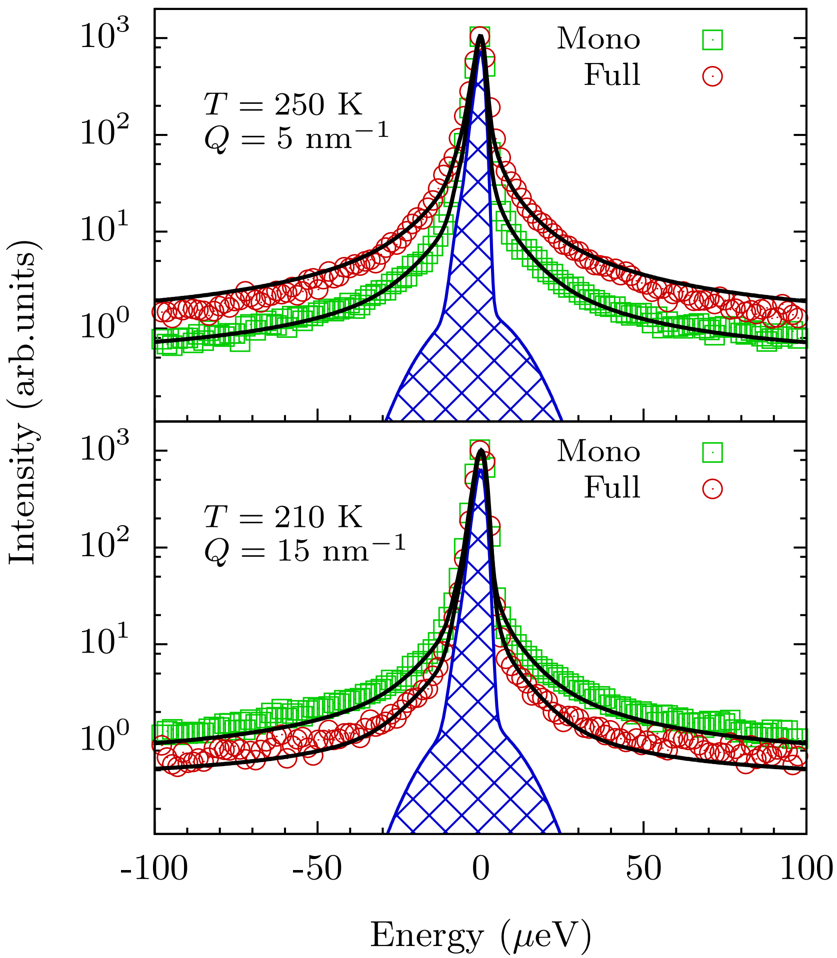
Monolayer hydration







Experimental QENS spectra



Scattering intensity:

$$I(Q,E) \sim \int dt\, e^{iEt/\hbar} F_{\mathrm{s}}(Q,t)$$

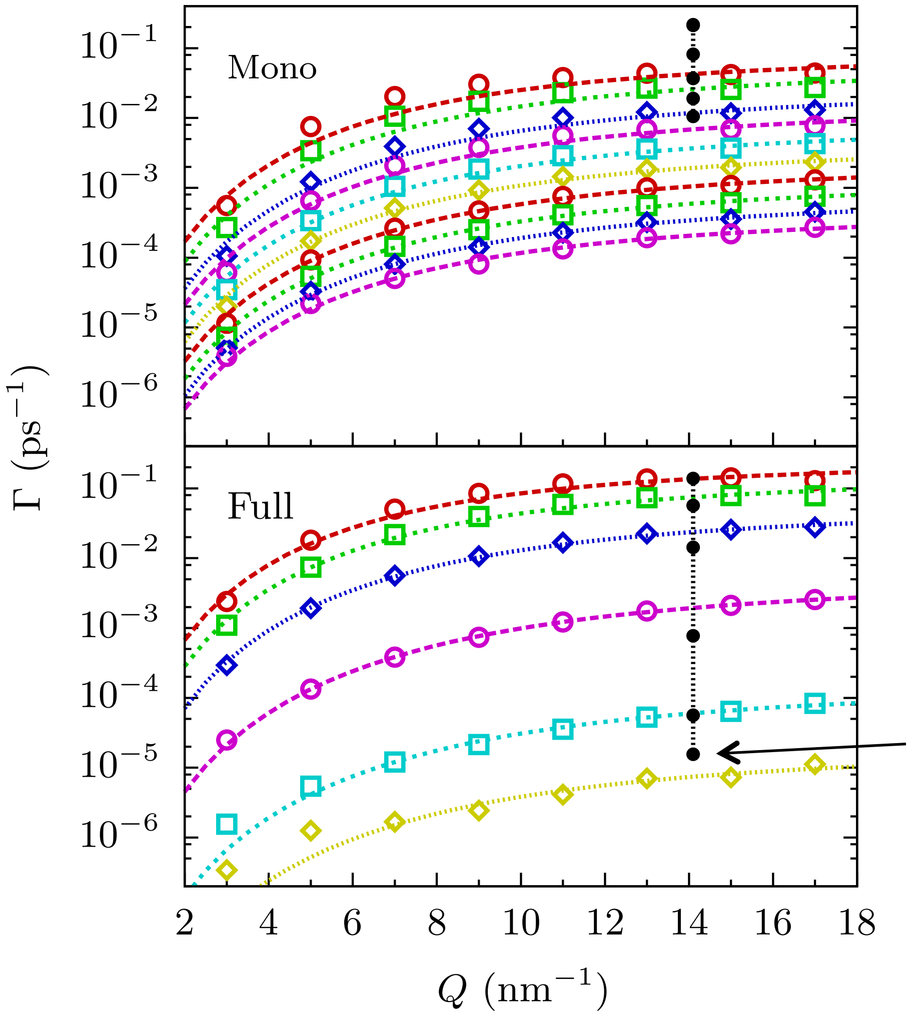
Fit model:

$$F_{\mathrm{s}} \simeq A \exp\left[-(\Gamma t)^{\beta}\right]$$

$$\beta = 0.5$$

C. E. Bertrand, K-H. Liu, E. Mamontov and S.-H. Chen, *Phys. Rev. E* **87**, 042312 (2004)

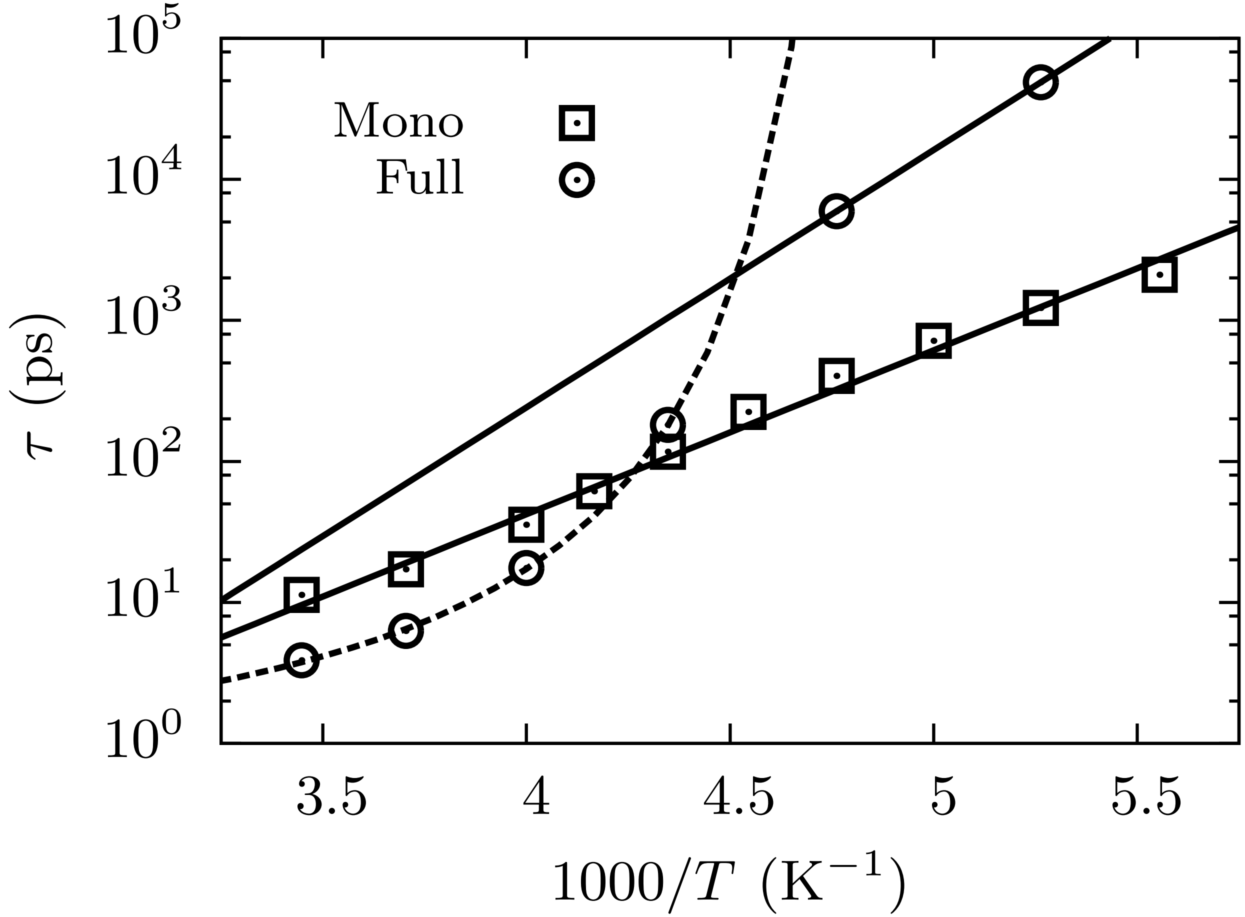
Experimental decay rates



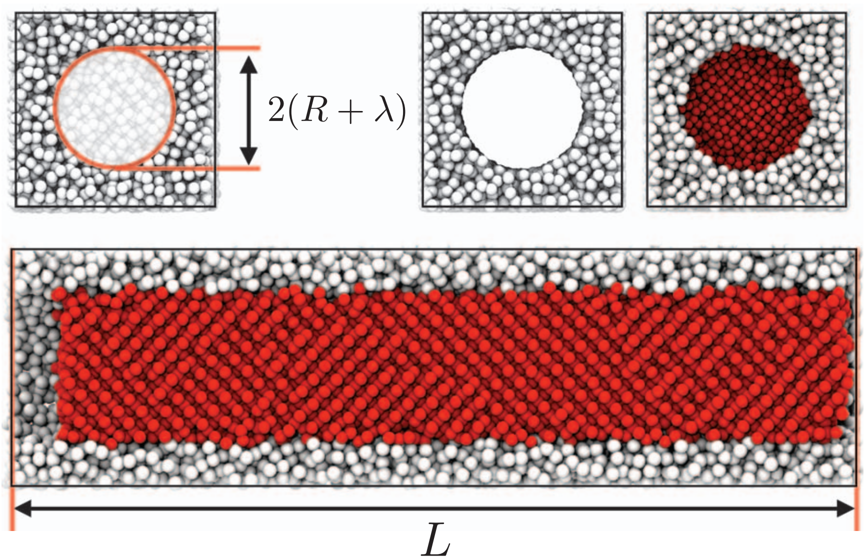
$$\Gamma(Q) = \frac{1}{\tau}\left[\frac{(\ell Q)^2}{1+(\ell Q)^2}\right]^{1/\beta}$$

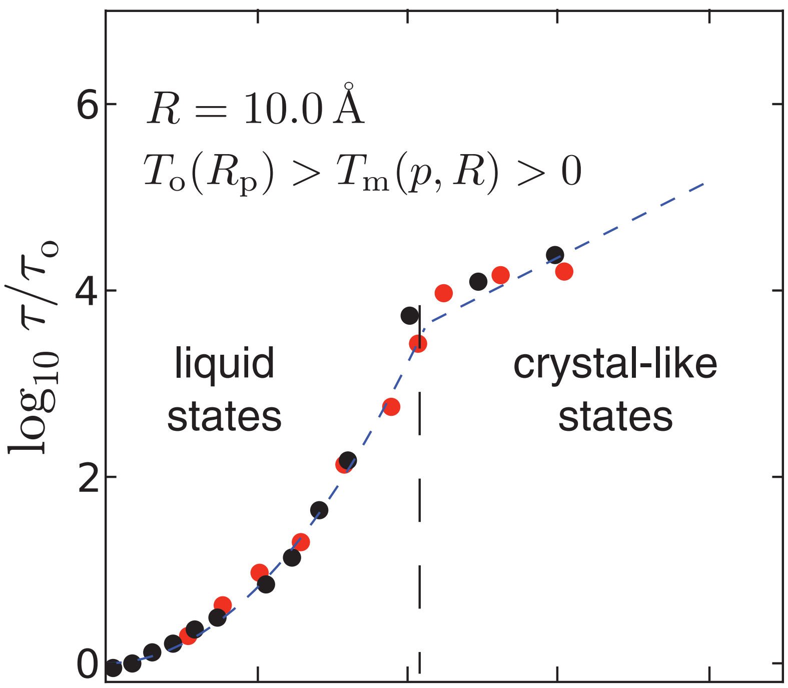
K. Yoshida et al., *J. Phys.: Condens. Matt.* **24**, 064101 (2012)

Relaxation times



Proposed mechanism for dynamic crossover





D. L. Limmer and D. Chandler, *J. Chem. Phys.* **137**, 044509 (2012)

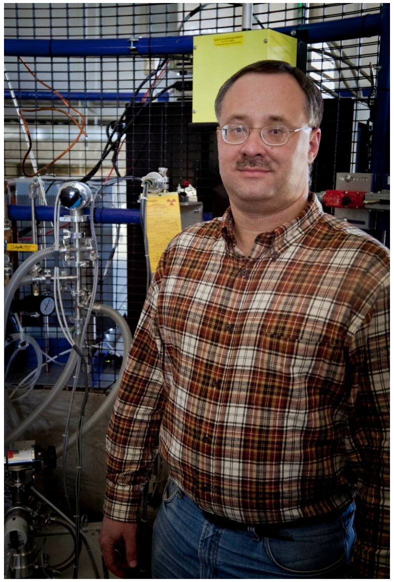
Conclusions

- Measurements of water dynamics at low hydration can be used probe surface-water interactions.
- The single particle dynamics of water remain jump-diffusive in confinement.
- Water does not exhibit a dynamic crossover at monolayer hydration.

Collaborators

Kao-Hsiang Liu, MIT

Sow-Hsin Chen, MIT



Eugene Mamontov, ORNL

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Thank you for your attention