Structure and Dynamics of Water confined in Narrow Carbon Nanotubes

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With Biswaroop Mukherjee, Hemant Kumar, Chandan Dasgupta and Ajay Sood

Outline of the talk

- Introduction and motivation
- Details of simulation
- Structure of confined water
- Results for translational dynamics
- Results for orientational dynamics
- Summary and conclusions

References:

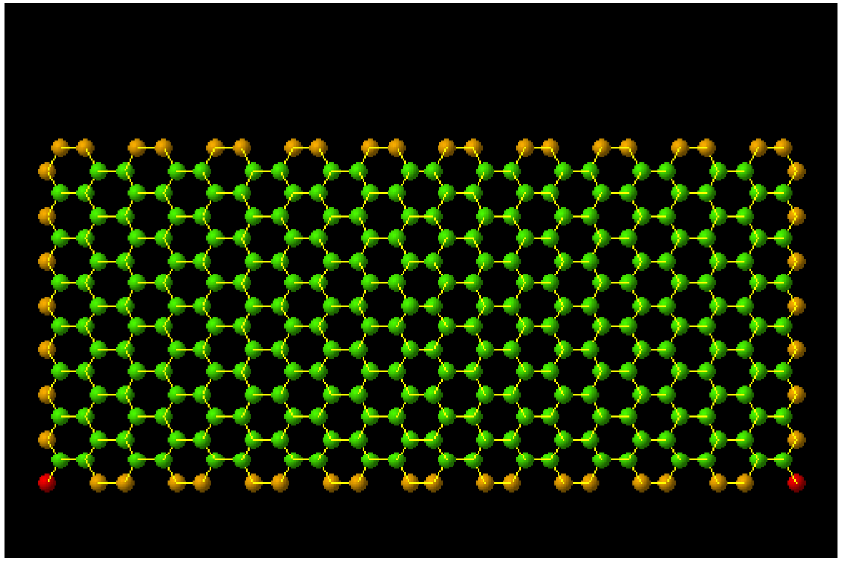
Mukherjee *et al*, J. Chem. Phys. **126**, 124704 (2007);
J. Nanosc. Nanotech. **7**, 1796 (2007);
ACS Nano **2**, 1189 (2008); xxx (2010)
JPCB, 113, 10322 (2009)
J. Nanosc. Nanotech. 9, 5303 (2009)

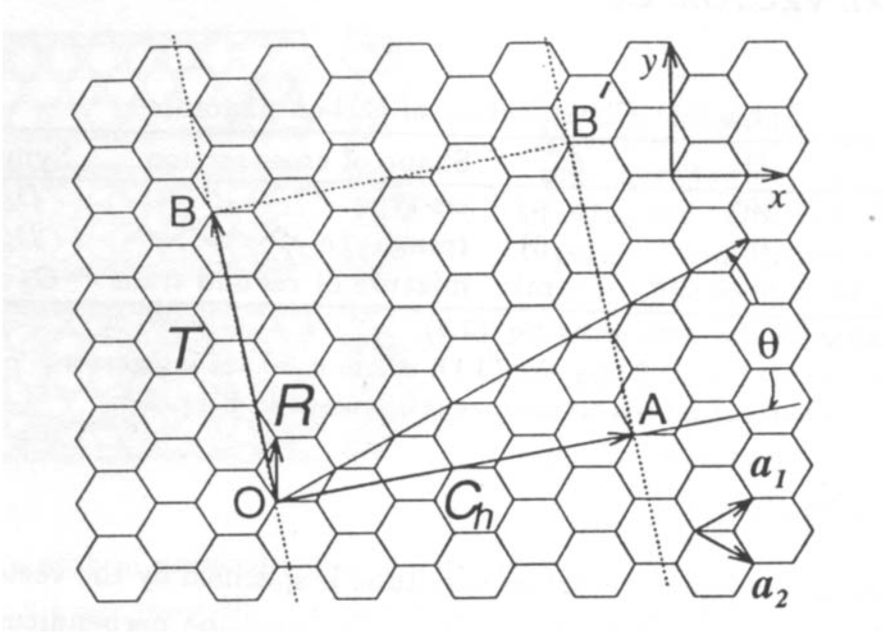
Introduction and Motivation

- Fluids in strongly confined environments exhibit many interesting and unusual structural and dynamic properties
- The diffusion of particles in one-dimensional channels/pores is a basic feature of transport across cell membrane.
- A good testing ground for the various analytical results for 1D systems
- Properties of “biologically confined” water near DNA and protein molecules
- Thermodynamics of water entry: despite a hydrophobic pore water goes inside nanotube

Structure of Carbon nanotube

Visualized as a Rolled Graphene Sheet

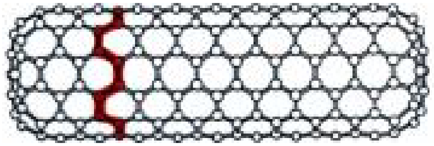




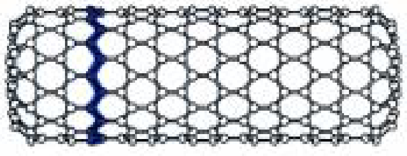
$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m)$$

$$d_t = \frac{|\mathbf{C}_h|}{\pi} = \frac{\sqrt{3}a_{c-c}\sqrt{n^2 + m^2 + nm}}{\pi}$$

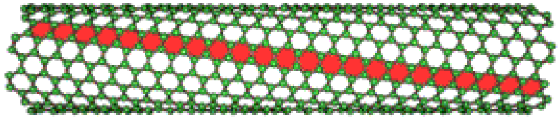
http://www.photon.t.u-tokyo.ac.jp/~maruyama/wrapping3/wrapping.html



Arm Chair (n,n)



Zigzag (n,0)



Chiral (n,m)

Formation of ordered ice nanotubes inside carbon nanotubes

Kenichiro Koga*, G. T. Gao†‡, Hideki Tanaka§ & X. C. Zeng†

Nature, **412**, 802 (2001)

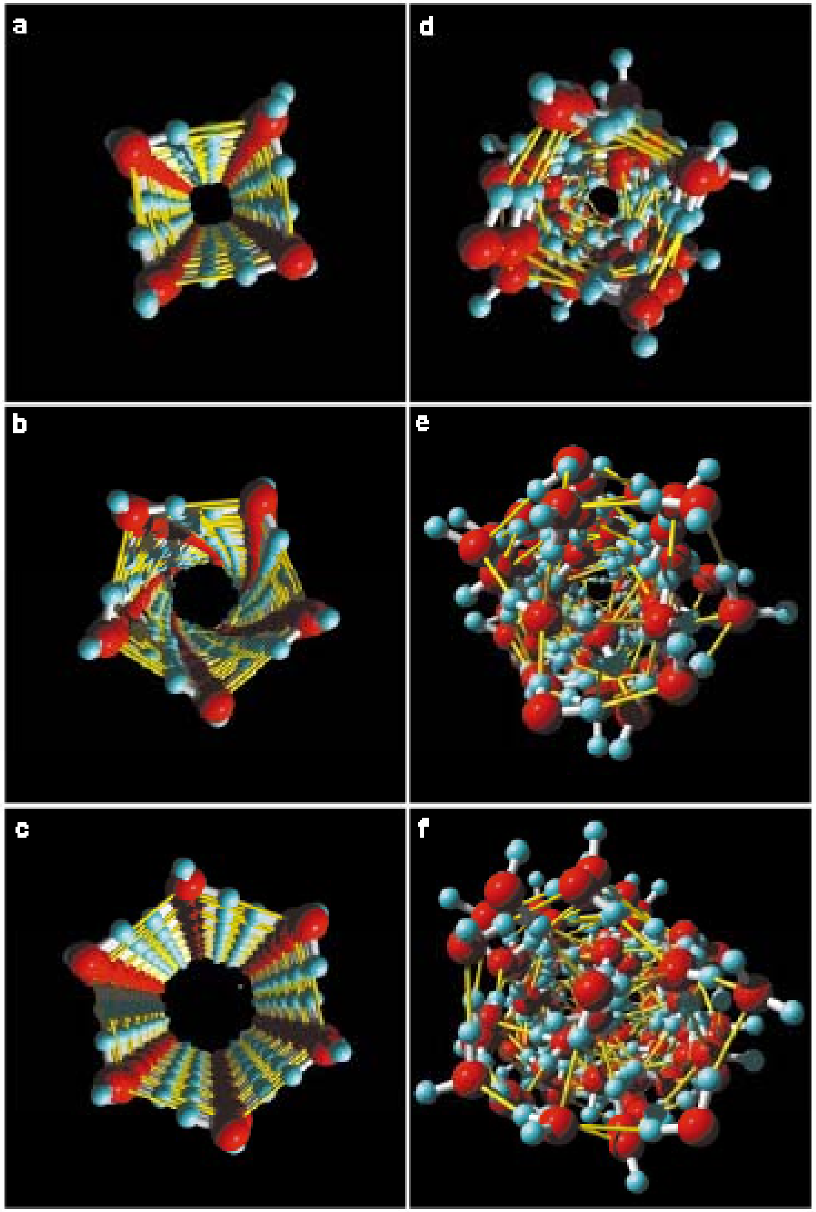


Figure 2 Snapshots of quenched molecular coordinates. **a**, Square; **b**, pentagonal; **c**, hexagonal ice nanotubes in (14,14), (15,15) and (16,16) SWCNs; **d** to **f**, the corresponding liquid phases. The ice nanotubes were formed on cooling under an axial pressure of 50 MPa in molecular dynamics simulations. The nearest-neighbour distances in both ice nanotube and encapsulated liquid water are fairly constant, about 2.7 to 2.8 Å, and this is in part responsible for the novel phase behaviour.

Molecular Dynamics Simulation

VOLUME 93, NUMBER 3 PHYSICAL REVIEW LETTERS week ending 16 JULY 2004

Anomalously Soft Dynamics of Water in a Nanotube: A Revelation of Nanoscale Confinement

Alexander I. Kolesnikov, Jean-Marc Zanotti,* Chun-Keung Loong, and Pappannan Thiyagarajan
Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

Alexander P. Moravsky and Raouf O. Loutfy
MER Corporation, 7960 South Kolb Road, Tucson, Arizona 85706, USA

Christian J. Burnham
University of Utah, Salt Lake City, Utah 84112, USA
(Received 23 December 2003; published 14 July 2004)

Neutron scattering experiment

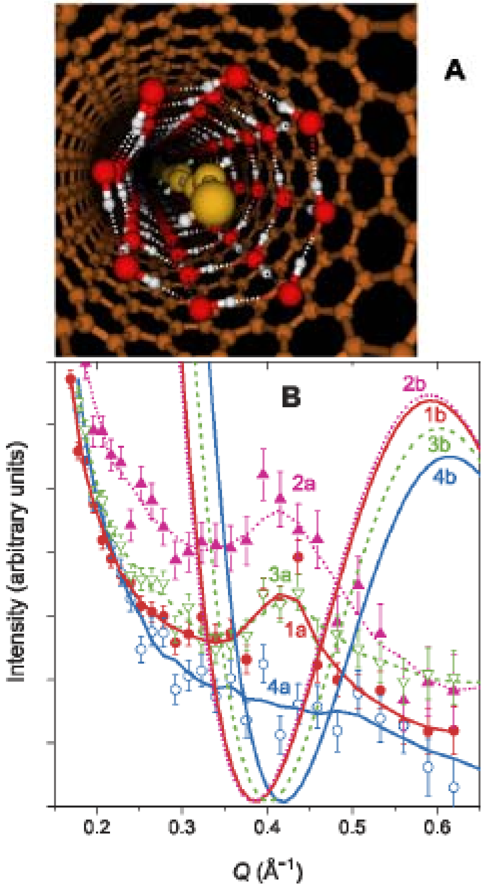
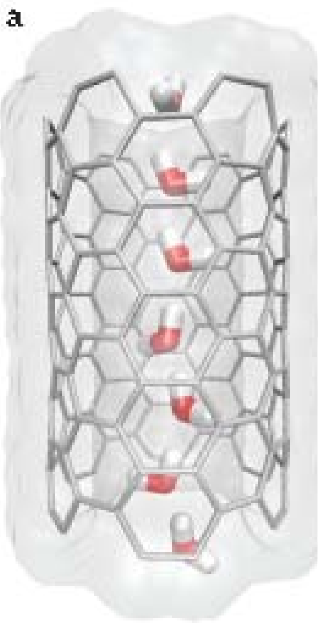


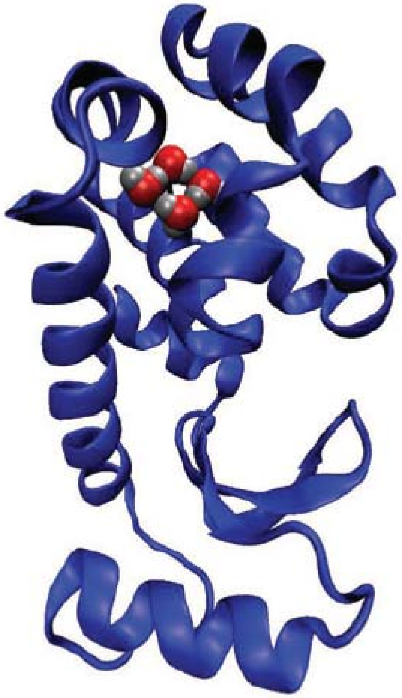
FIG. 1 (color). (a) Proposed structure of nanotube water. The interior "chain" water molecules have been colored yellow to distinguish them from the exterior "shell" water molecules (colored red). (b) Low-Q ND profiles around 0.4 Å^{-1} for the following: $1a$, dry SWNT (red curve with solid circles) and SWNT with the encapsulated water of different isotopic compositions; $2a$, H_2O (pink dotted curve with solid triangles); $3a$, H_2O:D_2O = 1:1 mixture (green short-dashed curve with open triangles); $4a$, D_2O (blue solid curve with open circles). The calculated form factors for $1a$, $2a$, $3a$, and $4a$ are shown by the curves labeled $1b$, $2b$, $3b$, and $4b$, respectively.

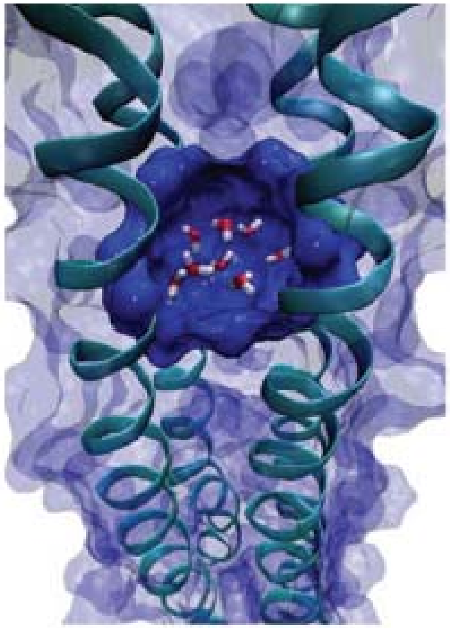
Water in Nonpolar Confinement: From Nanotubes to Proteins and Beyond*

Jayendran C. Rasaiah,[1] Shekhar Garde,[2]
and Gerhard Hummer[3]

Annual Review of Physical Chemistry, **59,** 713 (2008)



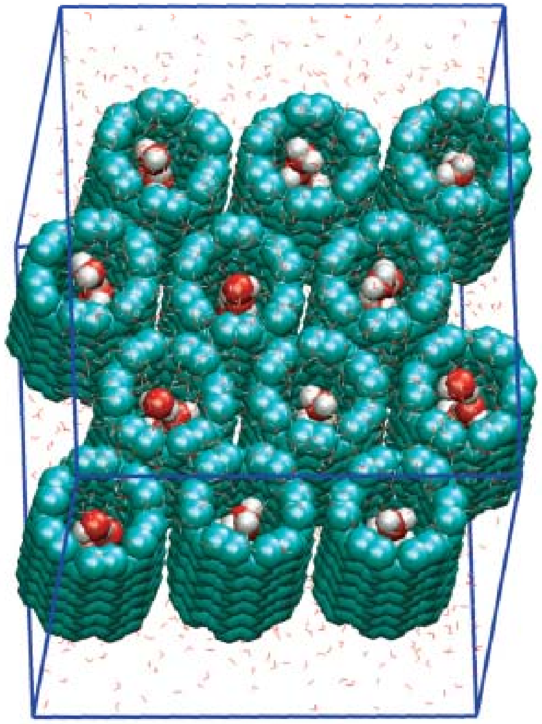




Water and Proton Conduction through Carbon Nanotubes as Models for Biological Channels

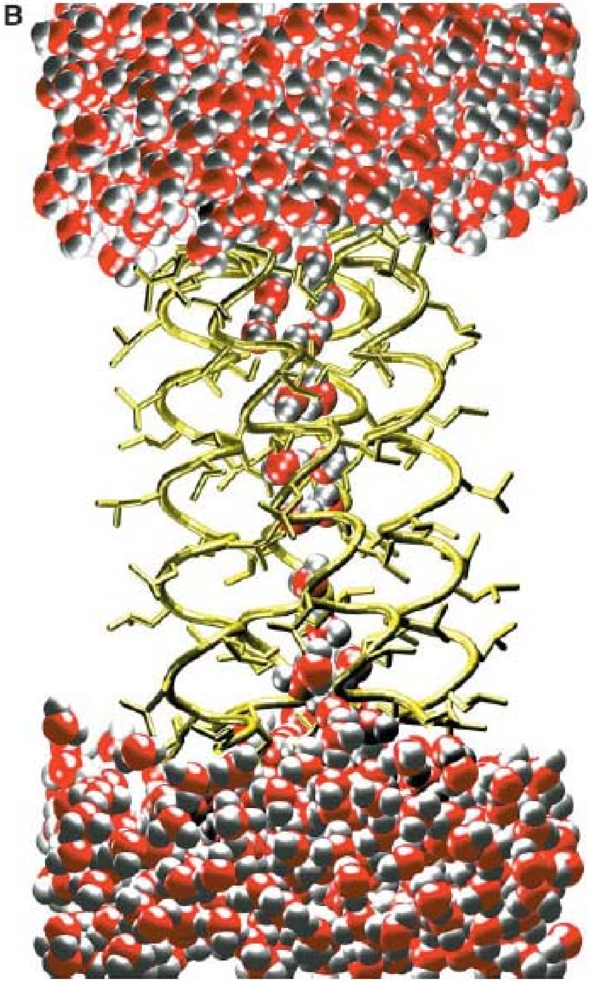
Fangqiang Zhu and Klaus Schulten
Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, Illinois

Biophysical Journal, **85**, 236 (2003)



A Computer Simulation Study of the Hydrated Proton in a Synthetic Proton Channel

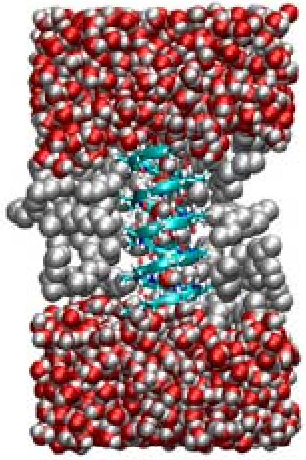
Yujie Wu and Gregory A. Voth
Biophysical Journal **85** (2003) 864–875



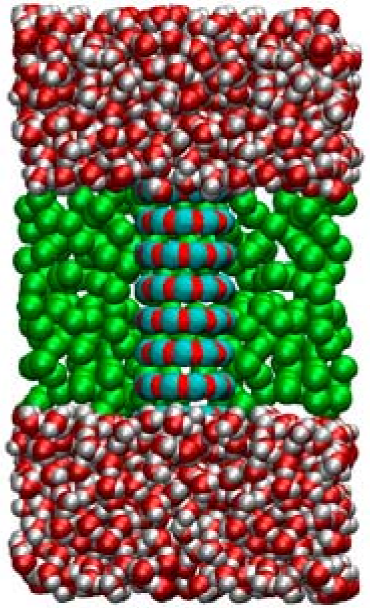
Not Only Enthalpy: Large Entropy Contribution to Ion Permeation Barriers in Single-File Channels

Guillem Portella, Jochen S. Hub, Martin D. Vesper, and Bert L. de Groot

Biophysical Journal Volume **95** September 2008 2275–2282

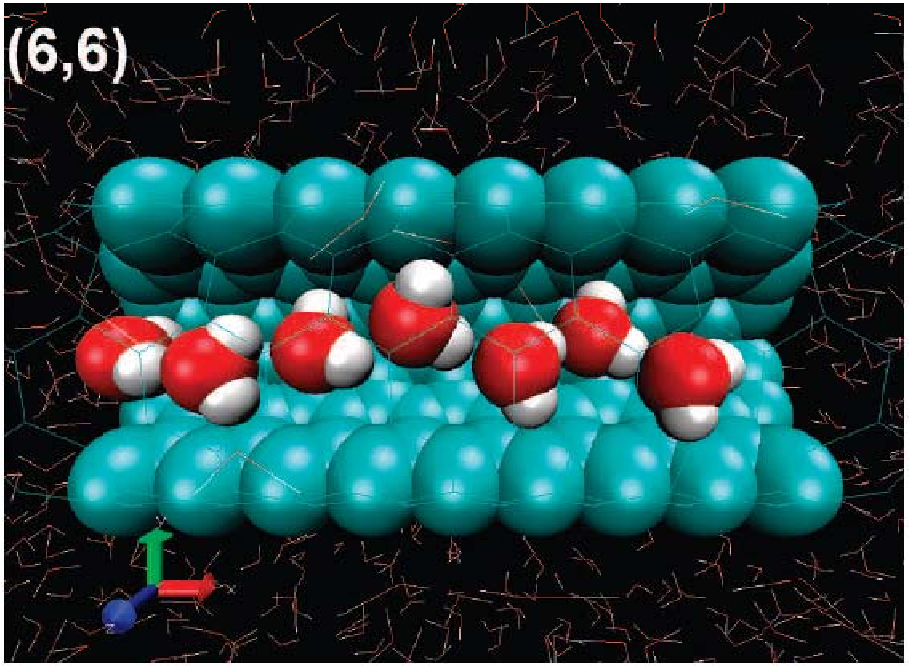


polyalanine pores



ring-structured channels

Molecular Dynamics Simulation of "Single-file" Water in Carbon Nanotubes

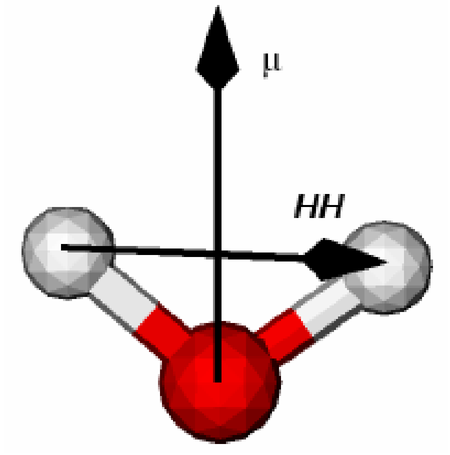


Annual Review of Physical Chemistry, **59,** 713 (2008)

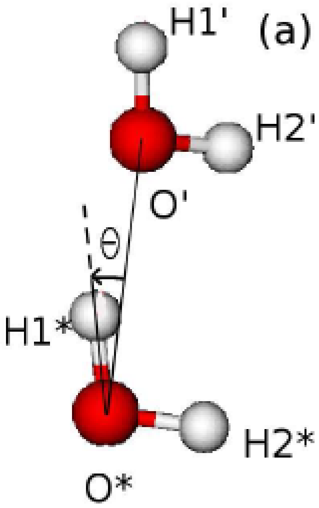
- (6,6) nanotubes immersed in a bath of water at 300K
- TIP3P model for water
- Simulations performed using AMBER 7

Nanotube gets spontaneously filled by a "chain" of water molecules

Details of TIP3P water



- TIP3P : Three point charges, in addition to VDW interactions
- Reproduces the static and dynamic properties of water well
- $Q_H = 0.41$ e, $Q_O =$ -0.82 e
- $\theta_{HOH} = 104.52^o$
- $r_{OH} = 0.957$ Å

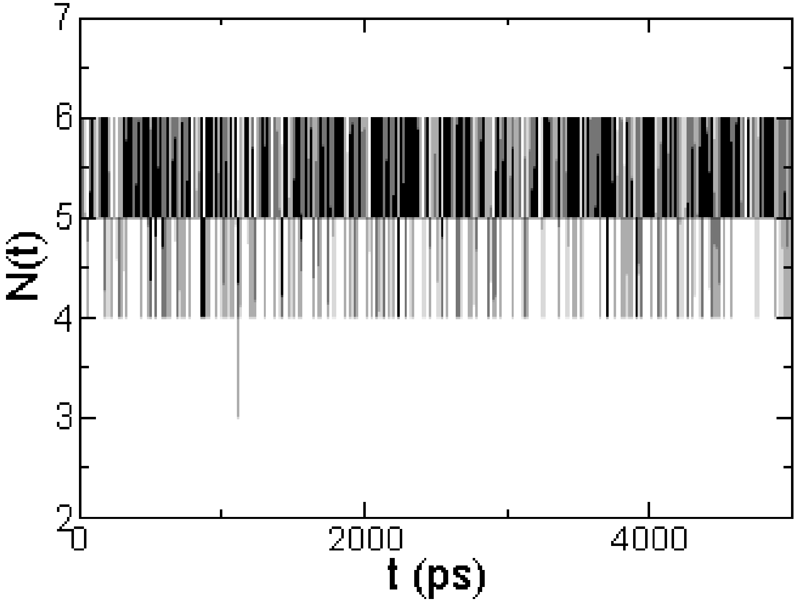


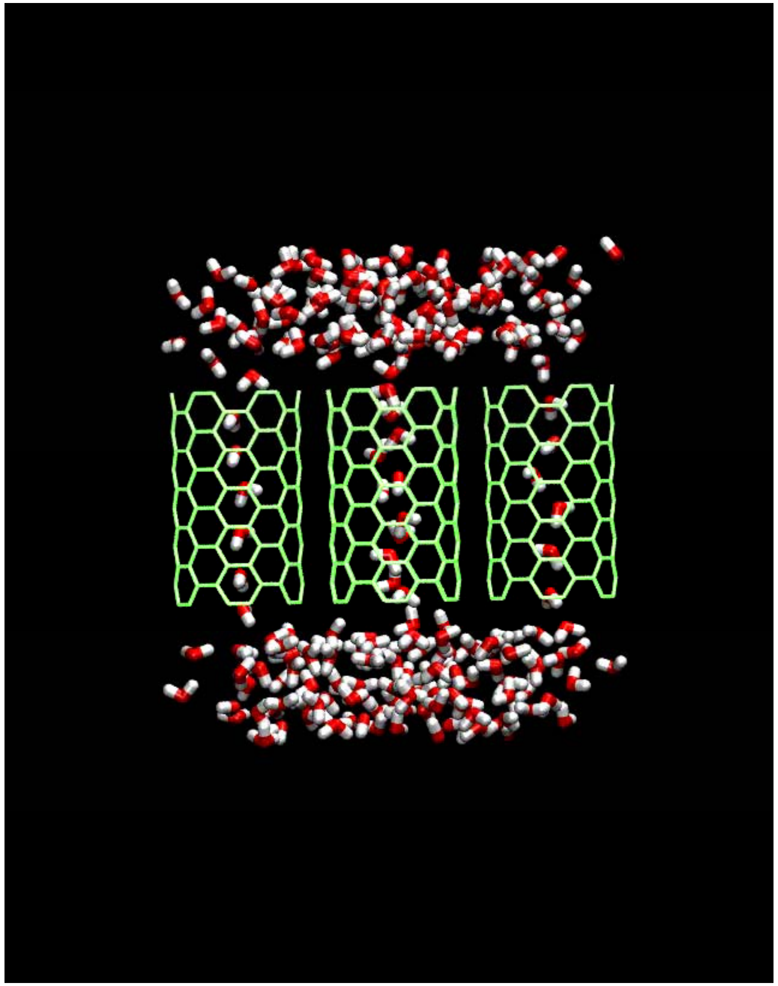
Hydrogen bond definition

- $r_{OO*} < 3.5Å$
- $\theta_{H1*O*O'} < \pi/6$

VdW interaction between oxygen and carbon atoms

Filling transition of hydrophobic nanotube

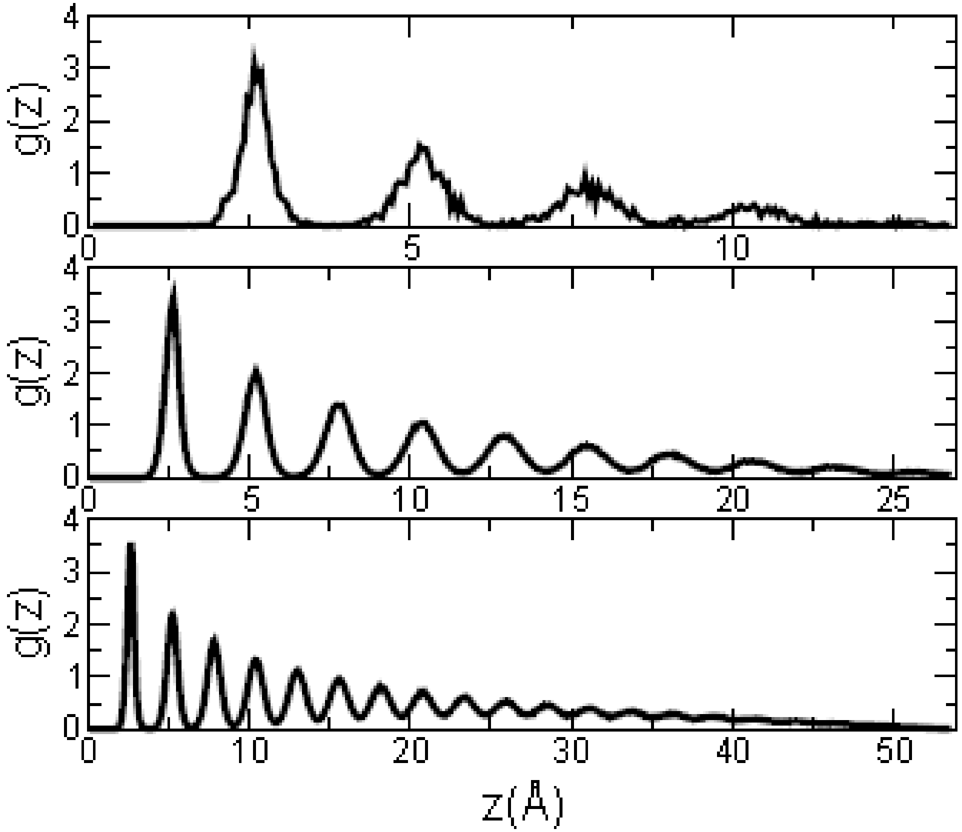




Initially empty nanotubes get spontaneously filled up by water molecules and stays full

Thermodynamics of water entry not fully understood

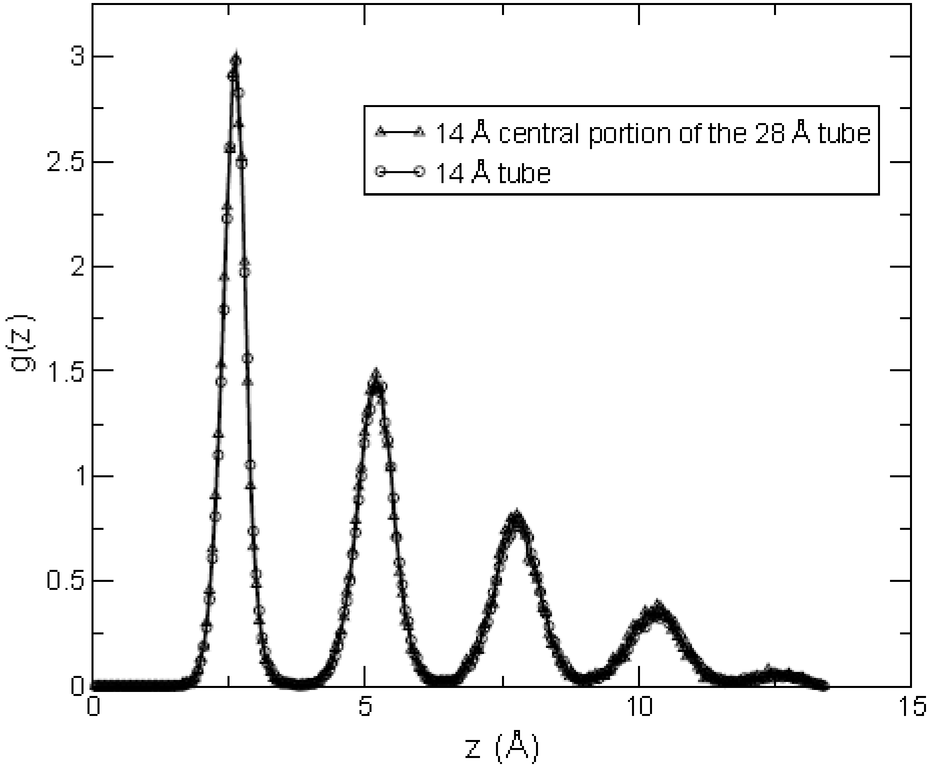
Structural ordering inside nanotube



- “Solid-like” ordering at 300K
- Average spacing between the water molecules 2.6 Å
- Due to finite size effect the height of the peak height is smaller for shorter nanotube

$$g(z) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1, j\neq i}^{N} < \delta(z - z_{ij}) >$$

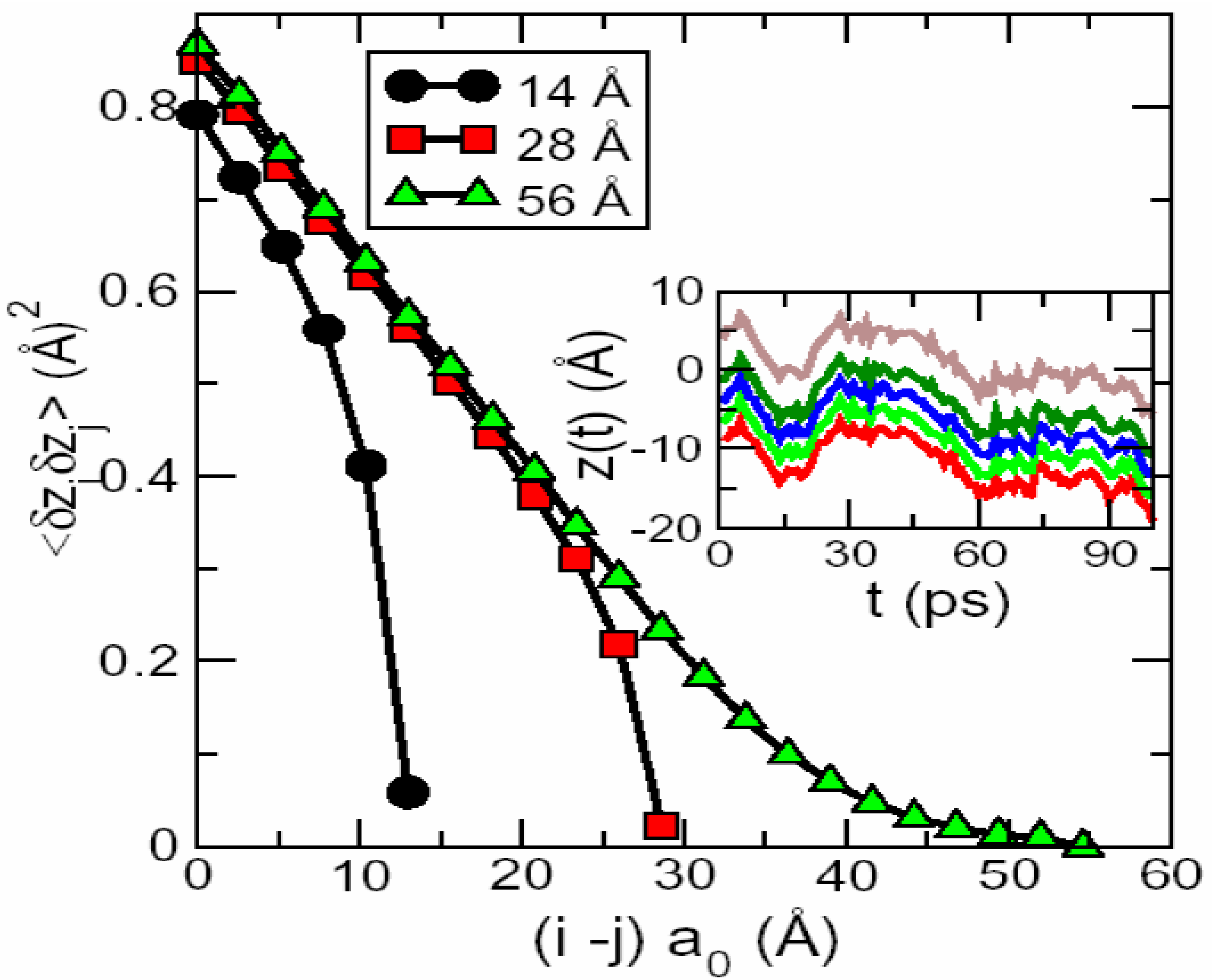
Structural ordering



Comparison of the positional correlation of only the water molecules residing in the central 14°A *within the 28°A nanotube,* with those inside the 14°A *tube.*

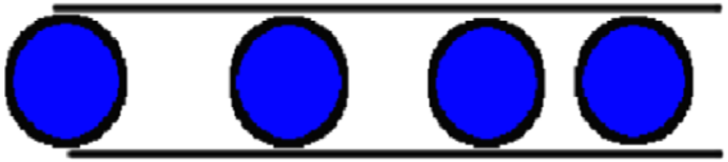
Both the correlation functions are identical confirms that the degree of positional correlations is same in both the nanotubes

Strongly correlated motion of water



← Displacements are strongly correlated

Single-file Diffusion

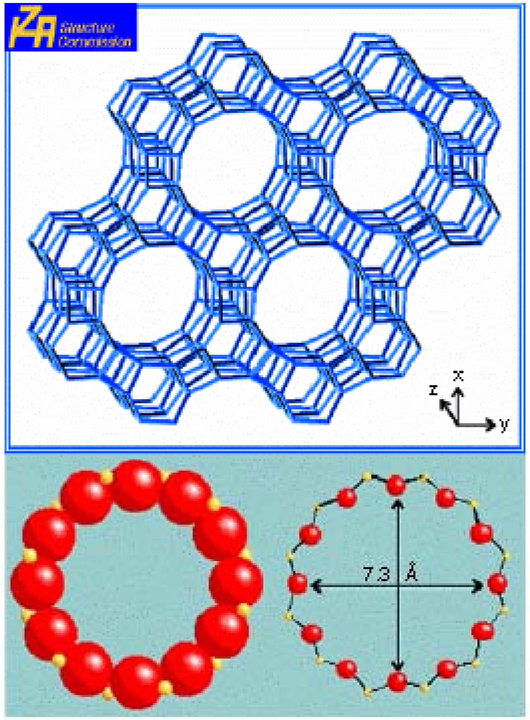


- Displacement of a particle necessciates the motion of other particles in the same direction

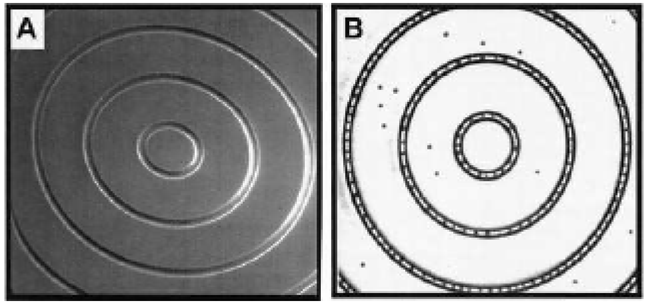
- This introduces additional correlations even at long times, which slows down the dynamics

$$\left\langle \Delta x^2(t) \right\rangle \sim \sqrt{t}$$

Experimentally observed in zeolites and for colloidal particles in narrow channels

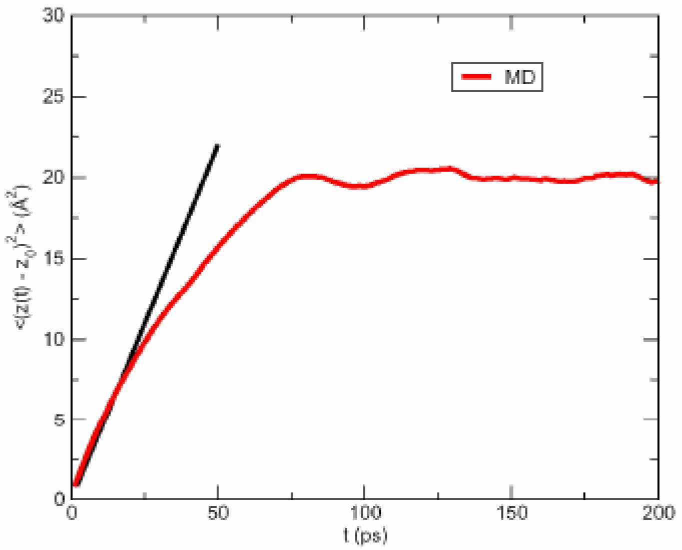


Karger *et al*, NJP (2005)

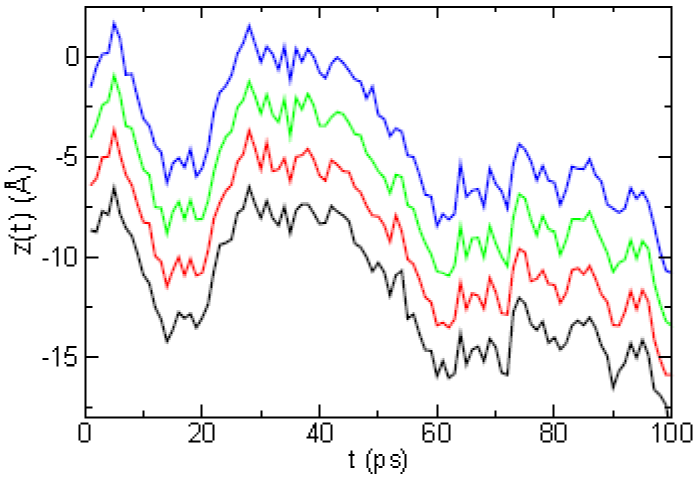


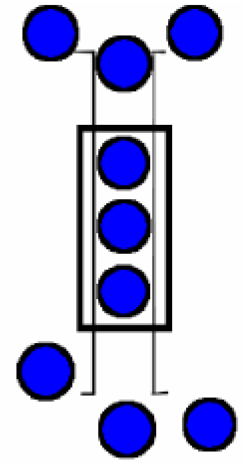
Wei *et al*, Science (2000)

Mean square displacement of water molecules inside the nanotube →



Interpretation of MSD data:





- Particle position and displacements are extremely correlated !!
- Can be thought of the motion of an *effective* single particle
- Single particle moves in the random background of the bath molecules

One-dimensional random walk model:

The probability of finding a particle at position “z” at time “t”, given initial position and time is z_0 at time, t = 0. The probability obeys diffusion equation

$$\frac{\partial P}{\partial t} = D\,\frac{\partial^2 P}{\partial z^2}$$

Boundary conditions :

$$P(0,t\,|\,z_0,0) = P(L,0\,|\,z_0,0) = 0$$

$$P(z,0\,|\,z_0,0) = \delta(z - z_0)$$

Expression for the propagator

$$P(z,t\,|\,z_0,0) = \frac{2}{L}\sum_{n=1}^{\infty}\sin\left(\frac{n\pi z_0}{L}\right)\sin\left(\frac{n\pi z}{L}\right)e^{-D\left(\frac{n\pi}{L}\right)^2 t}$$

Mean-square displacements saturate at long times

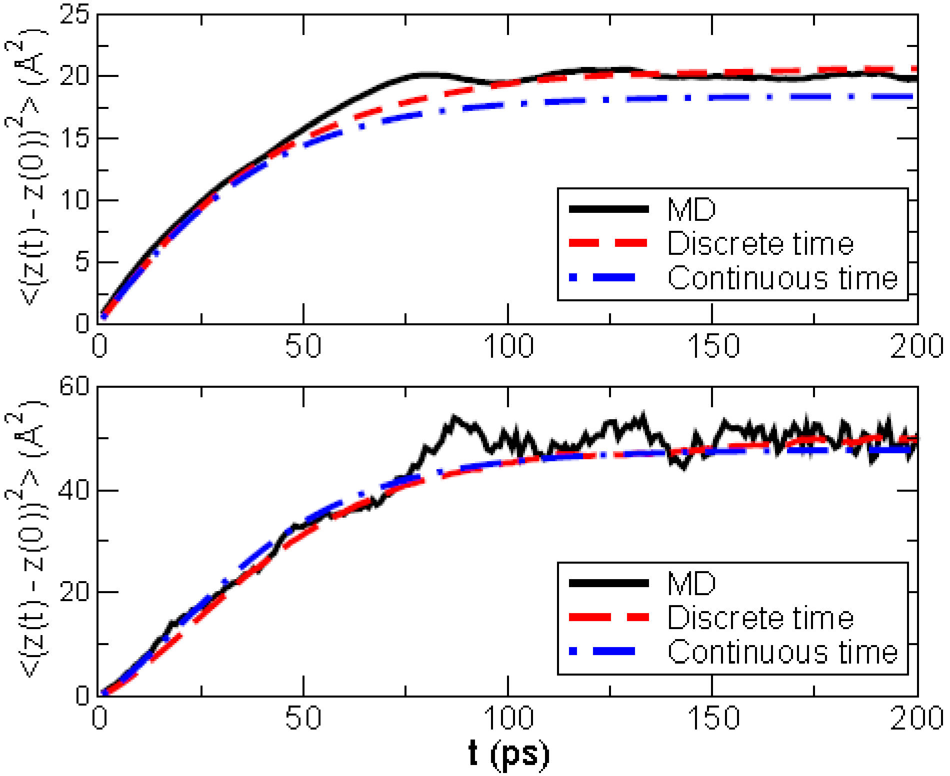
Expression for the time-origin averaged MSD

$$< \Delta z^2(t) >= \frac{\int_0^\infty dt_0 \int_0^L dz_2 \int_0^L dz_1 P(z_2,(t_0+t)\,|\,z_1,t_0)(z_2-z_1)^2 P(z_1,t_0\,|\,z_0,0)}{\int_0^\infty dt_0 \int_0^L dz_2 \int_0^L dz_1 P(z_2,(t_0+t)\,|\,z_1,t_0) P(z_1,t_0\,|\,z_0,0)}$$

The MSD with fixed time origin

$$< \Delta z^2(t) >= \frac{\int_0^L dz\,(z-z_0)^2 P(z,t\,|\,z_0,0)}{\int_0^L dz\, P(z,t\,|\,z_0,0)}$$

Comparison of simulation data with the predictions of 1d random walk model:



← MSD averaged over time origin saturates when

$$\sqrt{\left\langle \Delta z^2(t) \right\rangle} / L \simeq 0.31$$

← MSD measured from time of entry saturates when

$$\sqrt{\left\langle (z(t) - z_0)^2 \right\rangle} / L \simeq 0.52$$

Evidences in favour of normal diffusion

- Good agreement between predictions of Random Walk models and MD data.
- Quadratic scaling of the residence time with confinement length.

Why “normal” diffusion ?

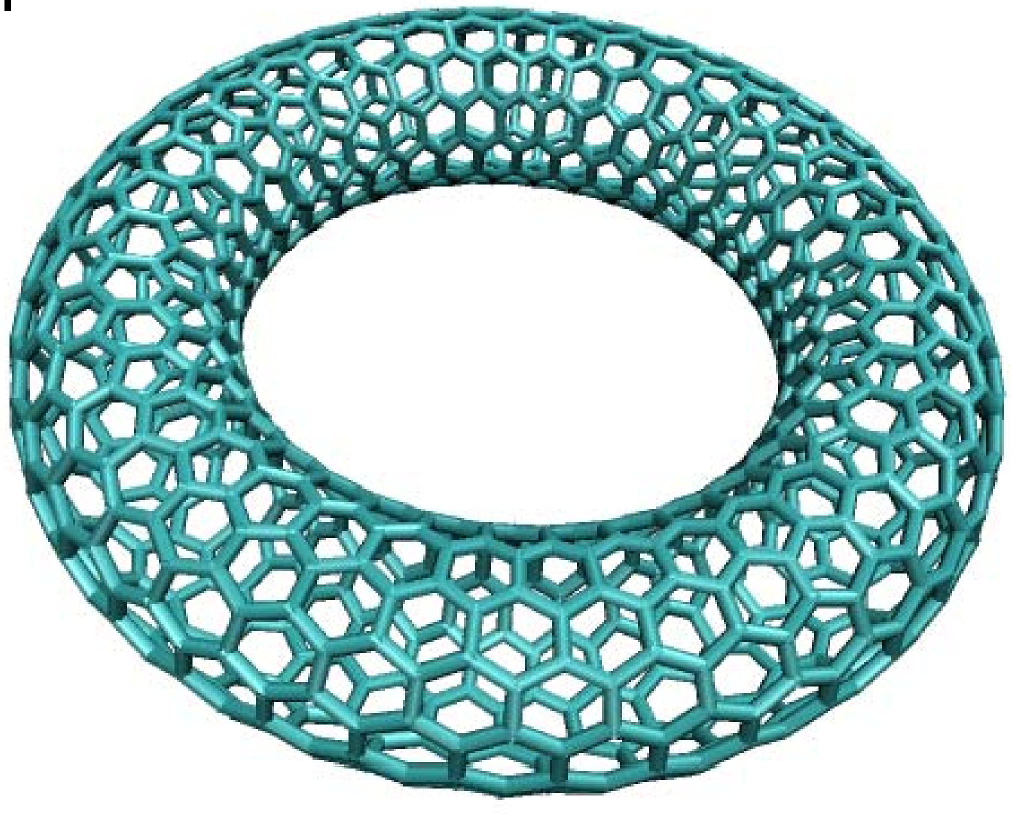
Lengths of tubes considered are not long enough compared to correlation length.

End-effects important for such short confinement lengths.

Water transport in a nanoring: very similar to the colloidal experiment.

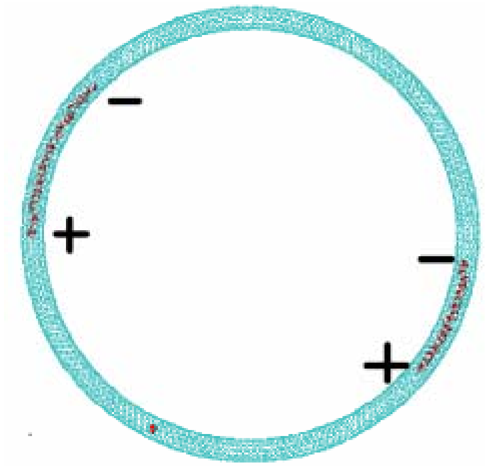
Possibility of interacting water clusters

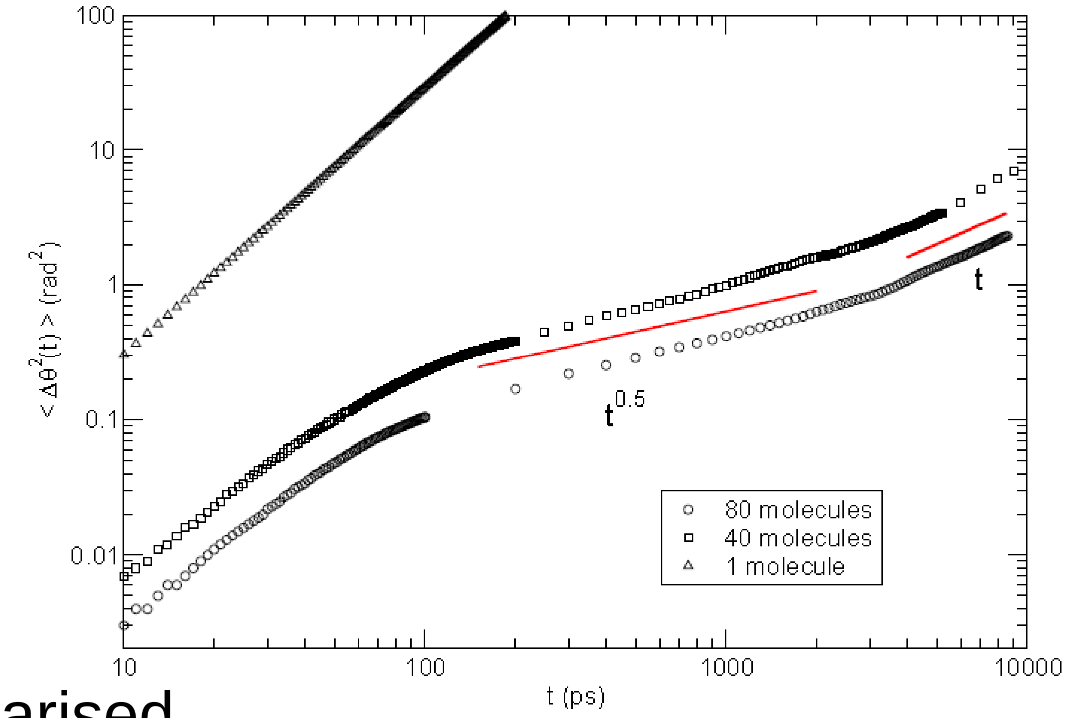
Testing ground for the existence of non-Fickian single file diffusion



Computer generated model of carbon nanoring

Polarized cluster inside nanoring exhibit SFD



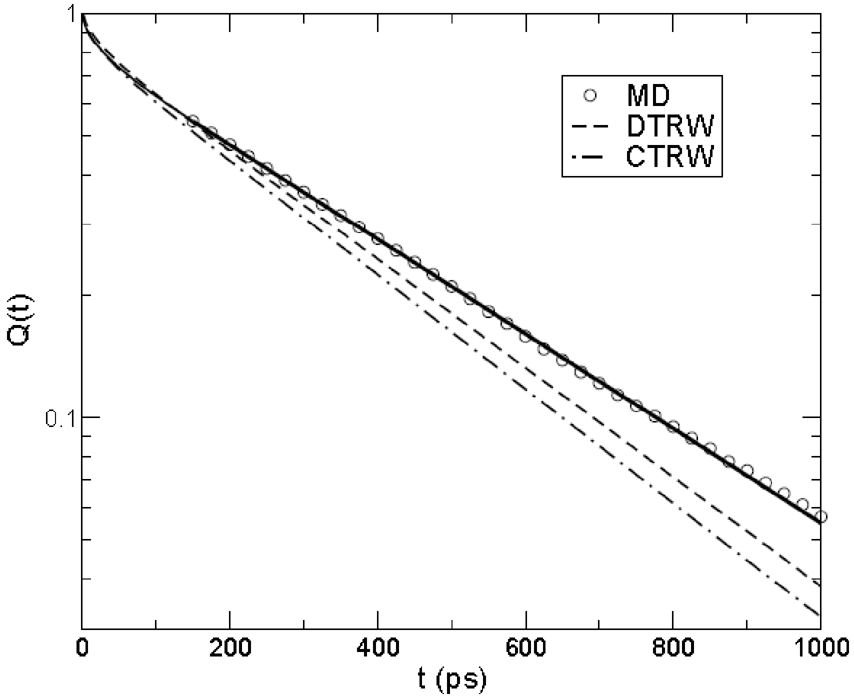


- The water molecules for polarised clusters inside the nanoring
- Bipolar clusters remain till long simulation times (~ 100 ns)
- Eventually the molecules form a single unipolar cluster

Survival probability decays exponentially with time

$$Q(t) = < \prod_{t_k = t_0}^{t_0 + t} P_i(t_k) >$$

$P_i(t)=1$ (if the ith particle is inside CNT at time t)
$P_i(t)=0$ (otherwise)



Exponential decay at long times

$$t_{res} \sim L^2/(\pi^2 D)$$

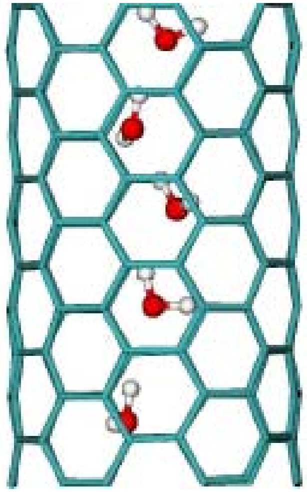
Time scales from survival probability :

The water confined water will have two time-scales :

- **Short time : water exits from the end which it enters the nano-tube.**
- **Long time : water molecules diffuse through the tube and exit from the other end (residence time).**

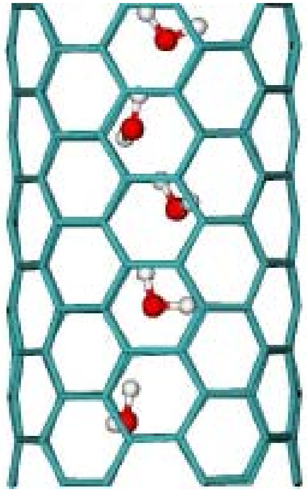
	$\tau_{res}(MD)(ps)$	$\tau_{res}(CTRW)(ps)$
14 Å	73	79.5
28 Å	370	318.6

Orientational Dynamics

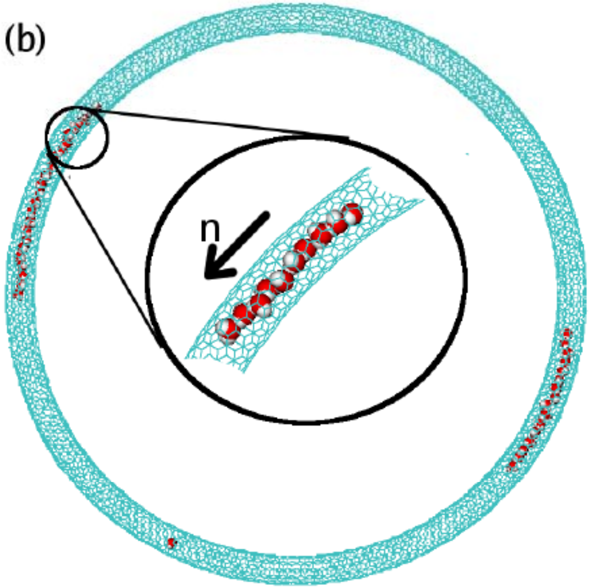


Dipole moments of the water molecules are aligned along the axis of the nanotube

Orientational Dynamics



Dipole moments of the water molecules are aligned along the axis of the nanotube

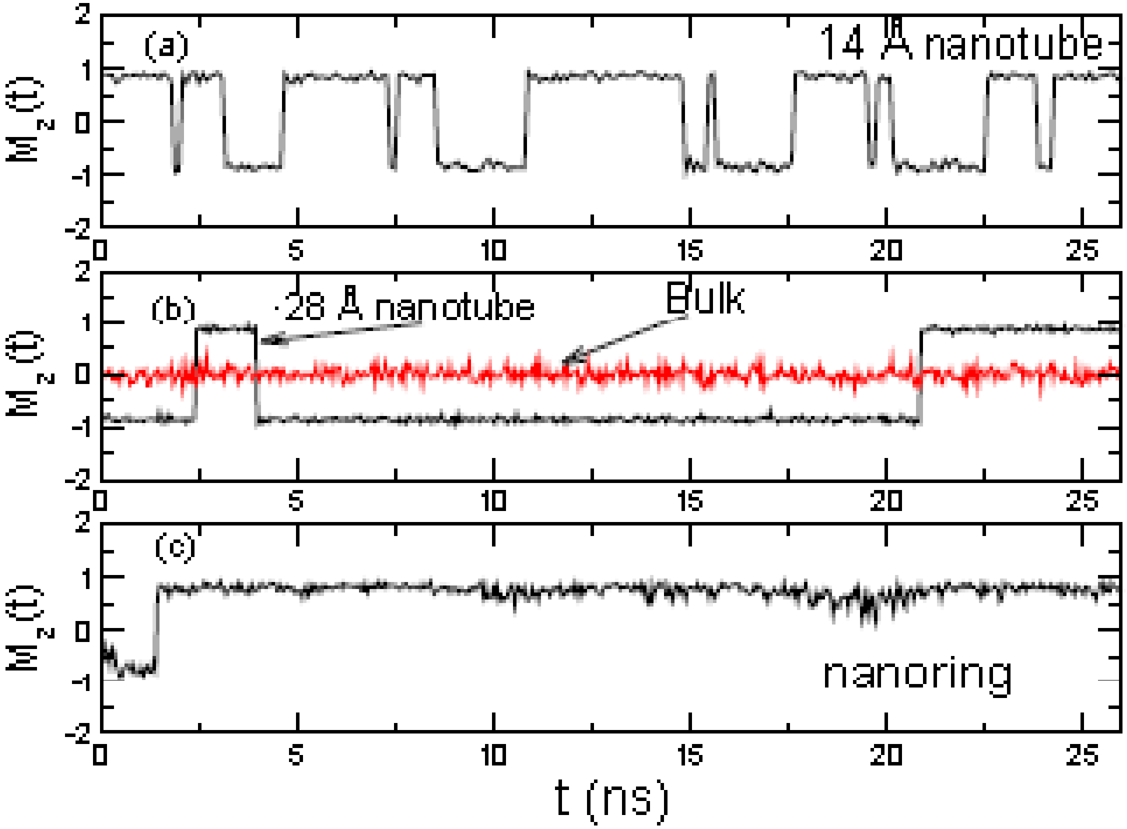


Nanoring at a filling fraction of 0.21 (40 molecules)

Dynamics of the average dipole moment:

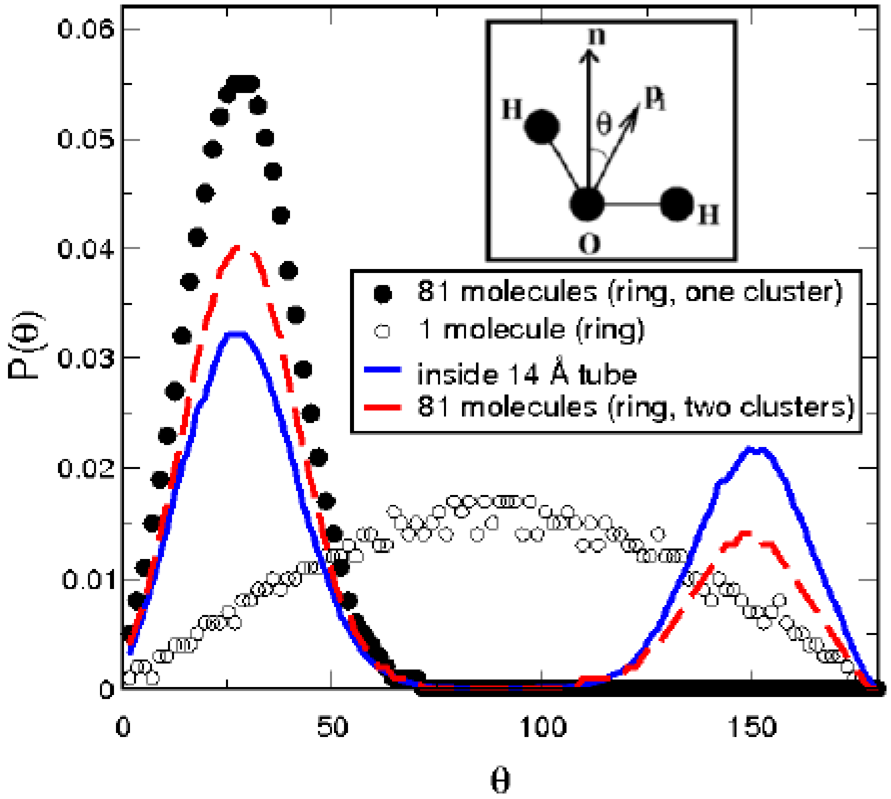
$$M_z(t) = \frac{1}{N(t)} \sum_{i=1}^{N(t)} \mathbf{p_i}(t) \cdot \mathbf{n}$$

Collective flips between the "up" and "down" states

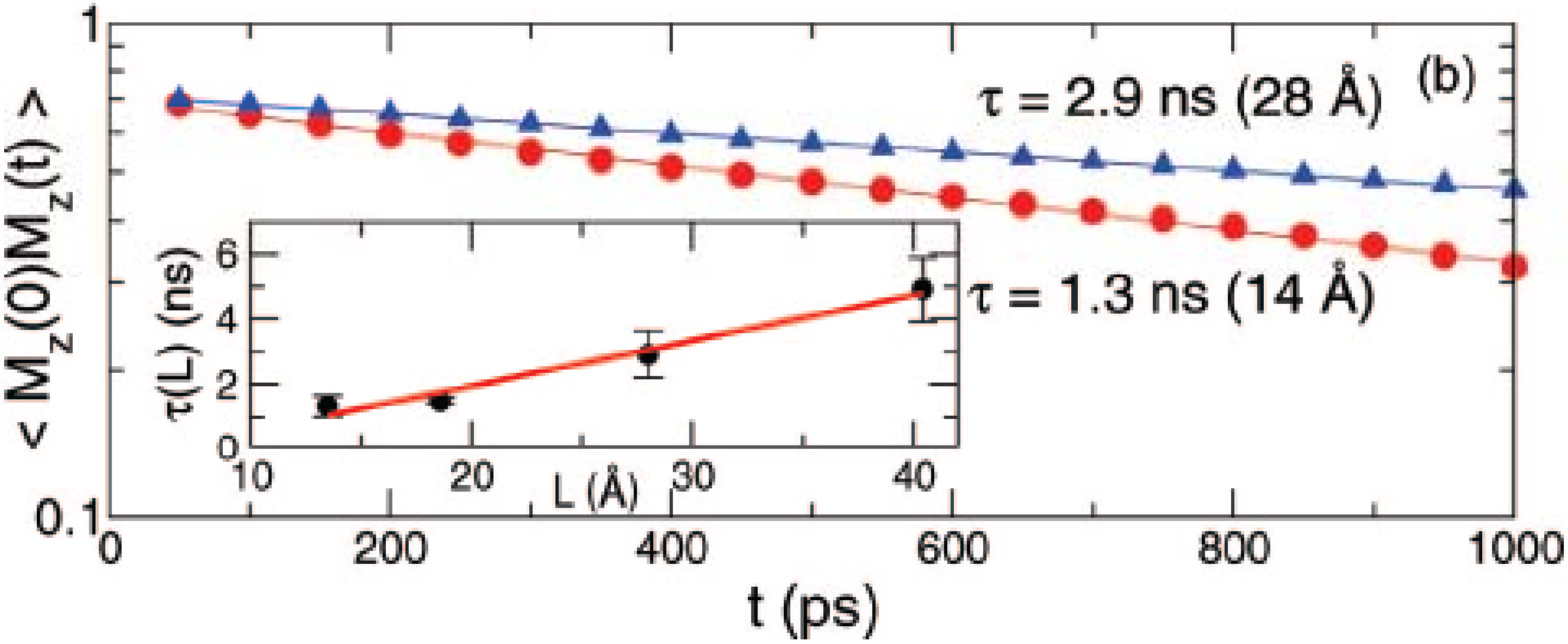


Typical time between successive flips **increases** with the length of the tube

Distribution of angle between dipole and axis



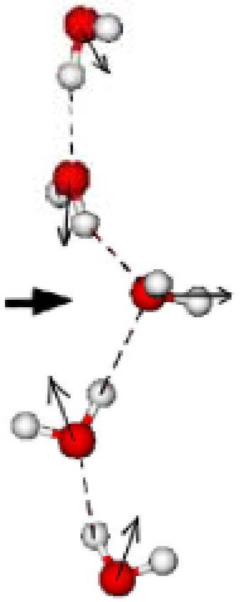
- ☐Bimodal distribution for water molecules inside open CNT
- ☐Unimodal distribution for a single unipolar cluster inside nanoring
- ☐Bimodal distribution for two polarised clusters inside nanoring

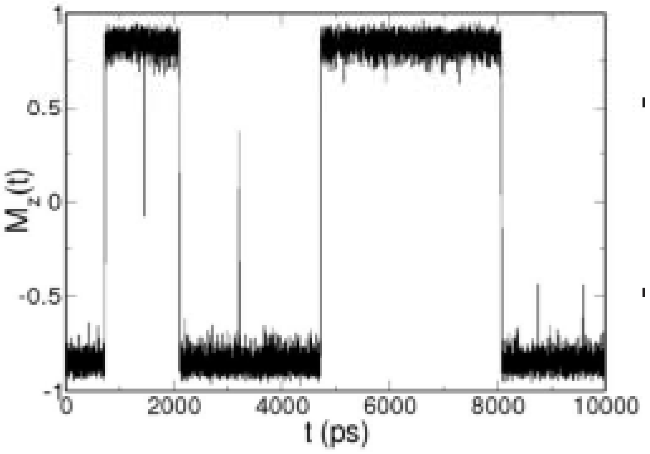


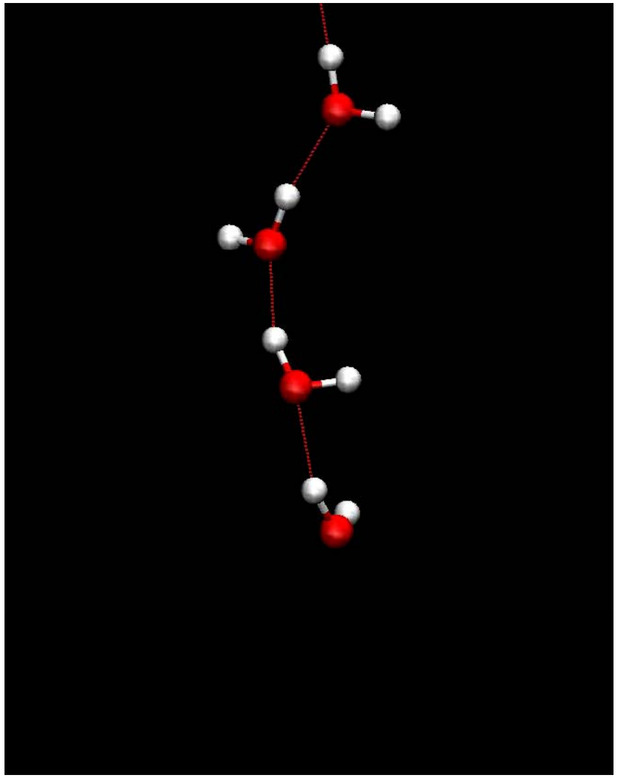
- Dipole moment relaxes very slowly, through collective flips.
- Relaxation time increases with tube length.
- Relaxation times are of the order of nanoseconds (~ 3 orders of magnitude larger than that in bulk water).

Collective flips of the dipole moment are mediated by orientational defects

- Defects are introduced at the free ends of the tube.
- A collective flip occurs when a defect moves across the entire length of the tube.
- Energy to produce a defect increases with tube length.

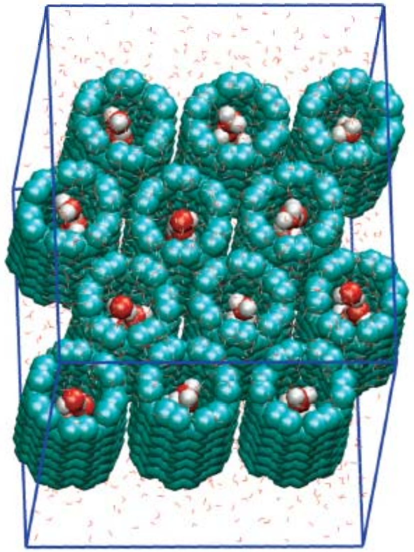






$$E_{defect} \sim pE_{local} \sim 5 \text{ to } 10\, k_B T$$

Why is this interesting?

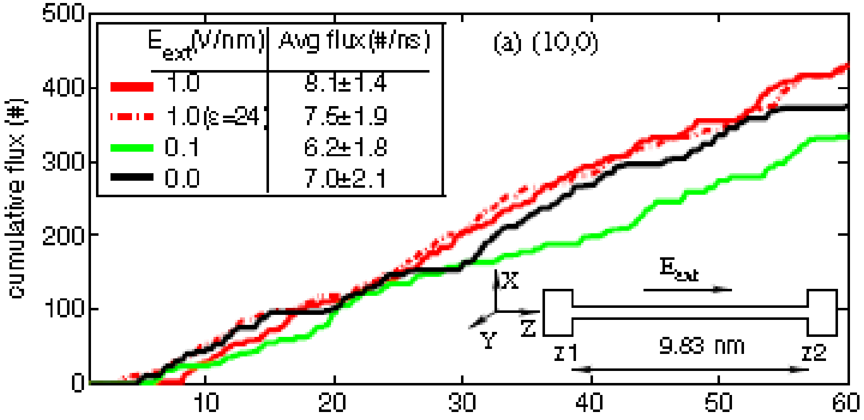


“Giant” dipole moment in each nanotube →
Array of such nanotubes should exhibit interesting collective behaviour.

Pumping of Confined Water in Carbon Nanotubes by Rotation-Translation Coupling

Sony Joseph and N. R. Aluru*
Department of Mechanical Science and Engineering, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

Phys. Rev. Lett. **101**, 064502 (2008)

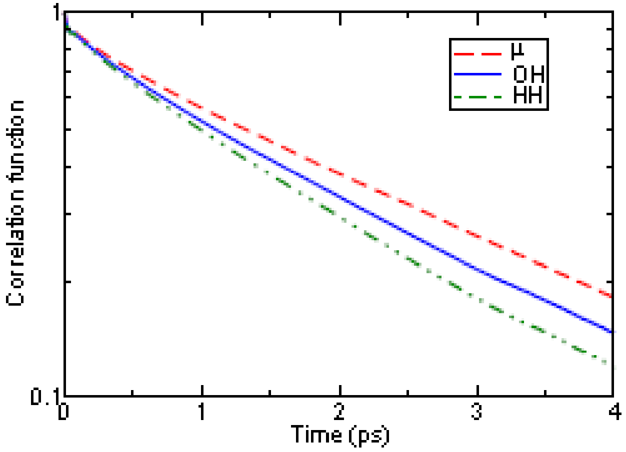


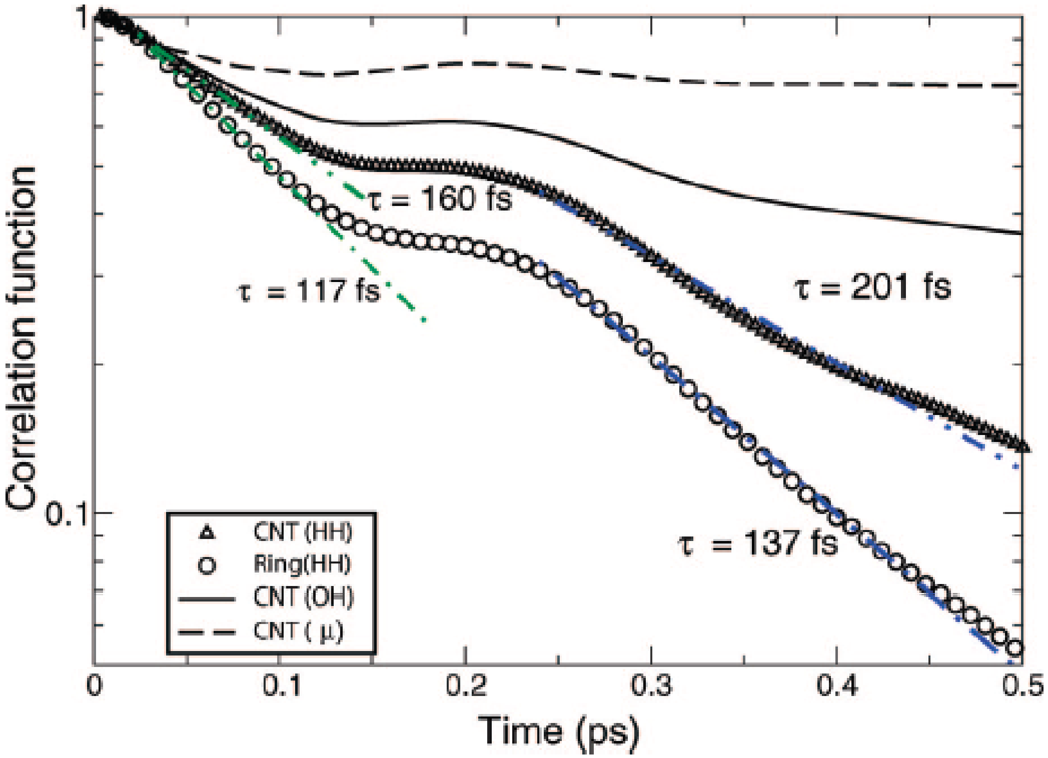
Strong anisotropy in the orientational relaxation:

$$C_{\mu}(t) = \frac{1}{N}\sum_{i=1}^{N}\langle \mu_{\mathrm{i}}(0)\cdot \mu_{\mathrm{i}}(t)\rangle$$

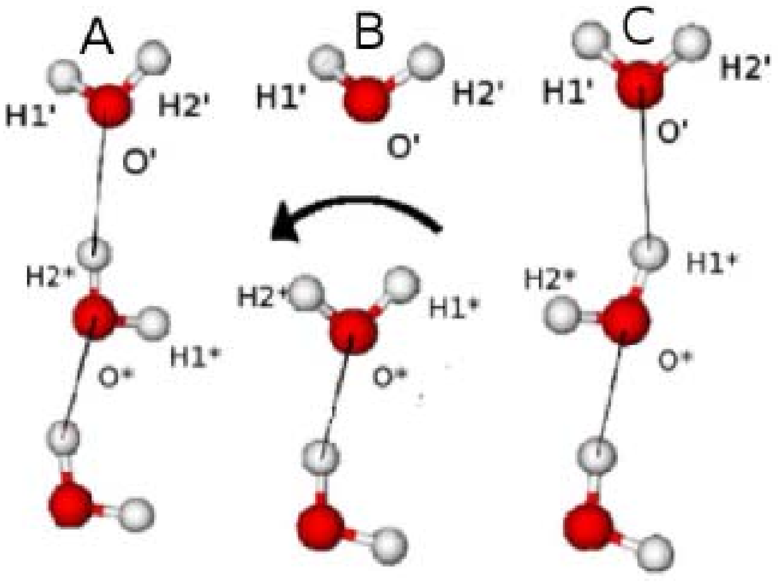
- $C_{OH}(t)$ and $C_{HH}(t)$ are similarly defined
- HH vectors relax fastest ($\sim$ 150 fs), OH intermediate ($\sim$ 30 ps)

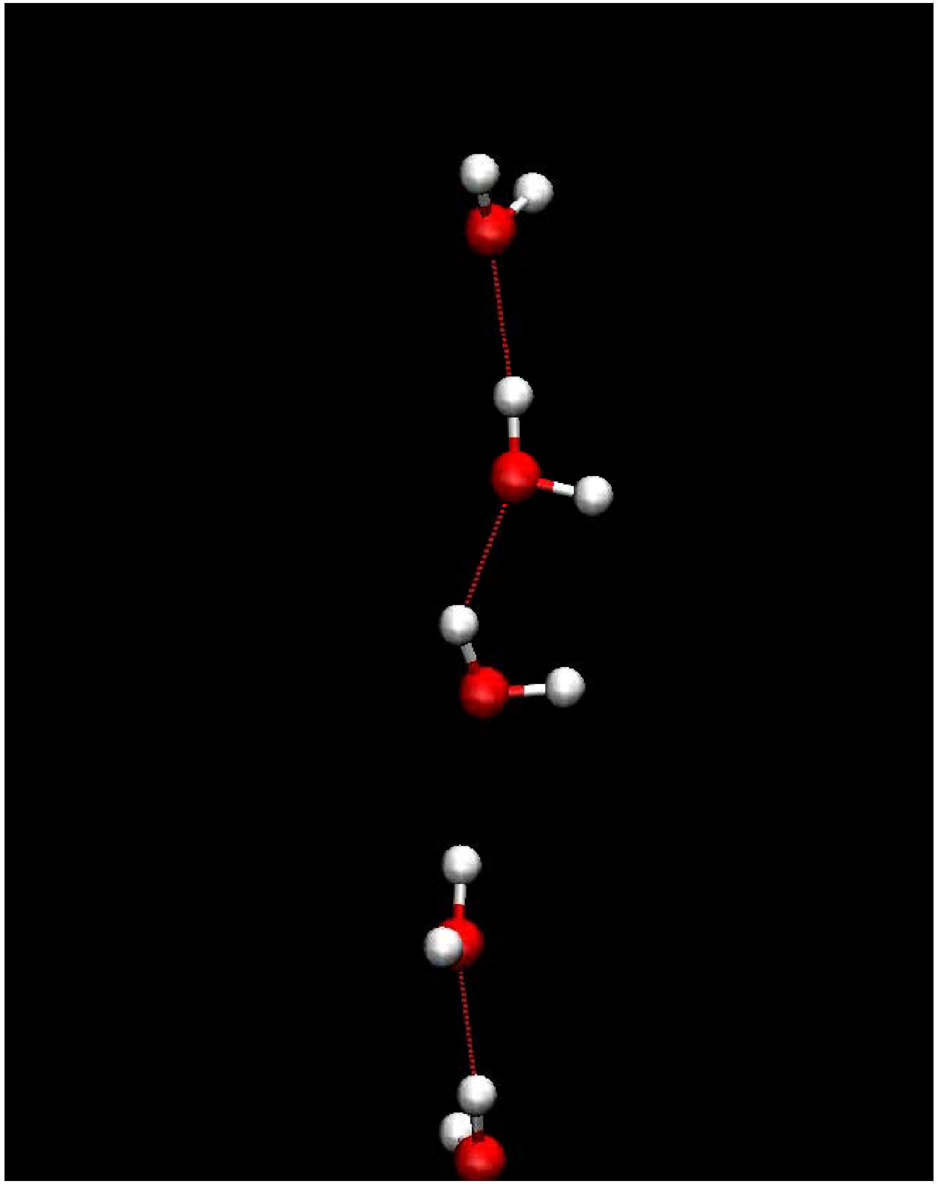
Bulk water





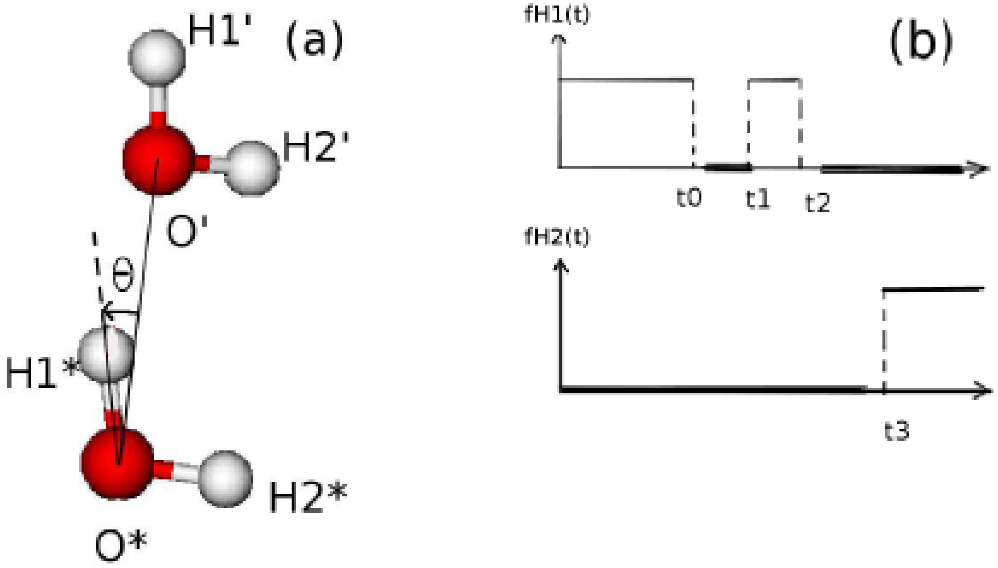
Large-amplitude angular jumps and “bistability”





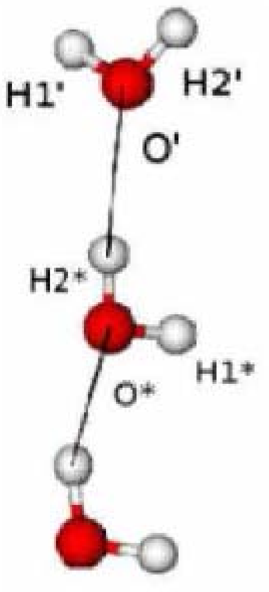
The hydrogen atom participating in the hydrogen bond and the free one exchange positions

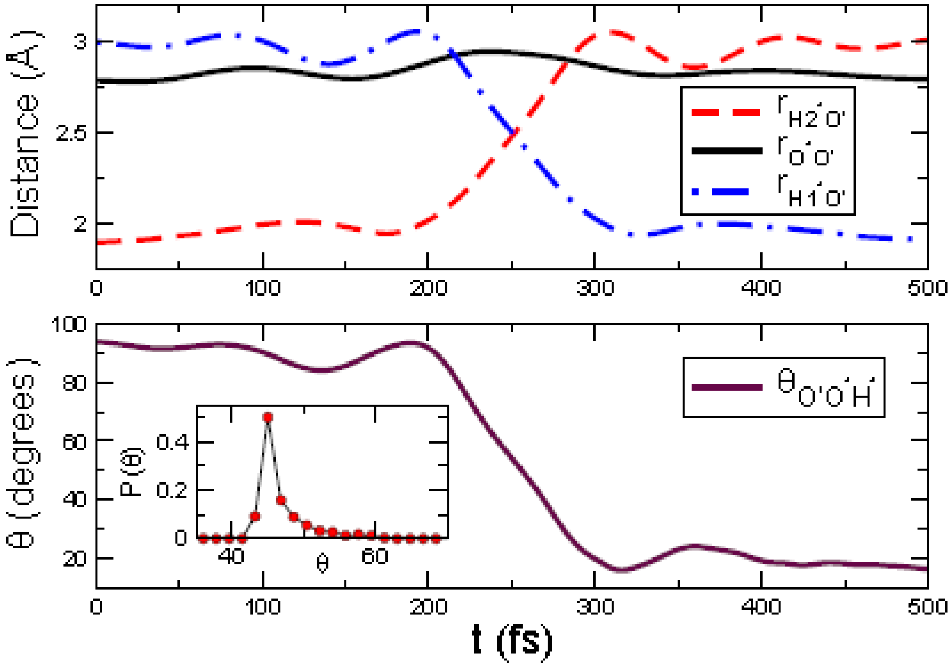
How to detect jumps?



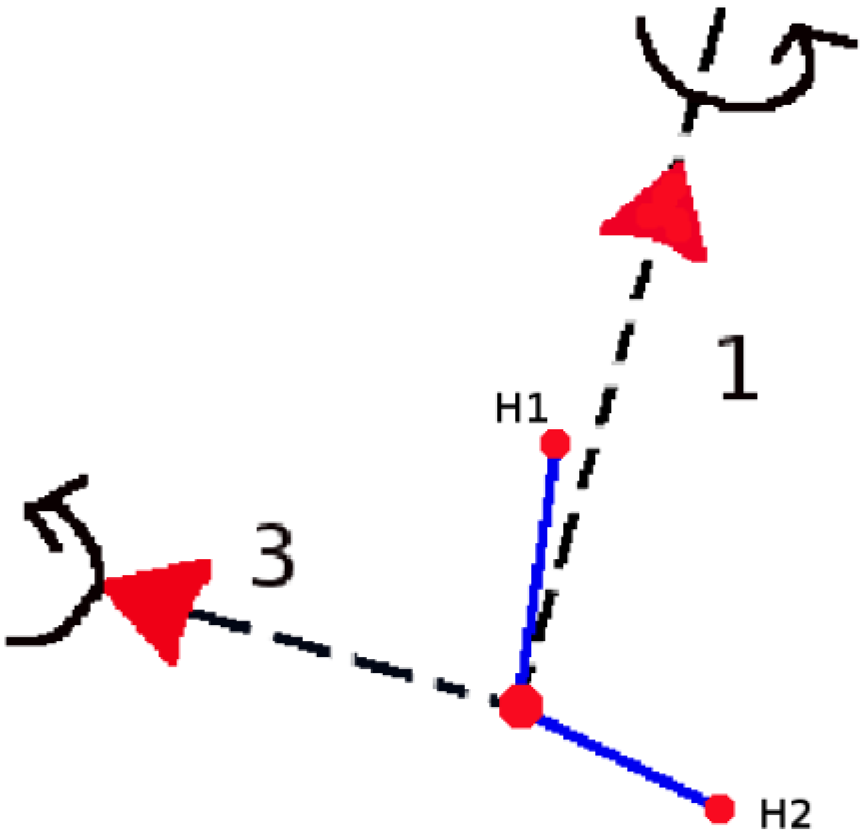
At time t2, fH1 (t) goes from one to zero and at a later instant t3 , fH2 (t) goes from zero to one. This is an example of a successful jump, starting at time t = t2 and ending at t = t3.

Characterization of large-amplitude angular jumps





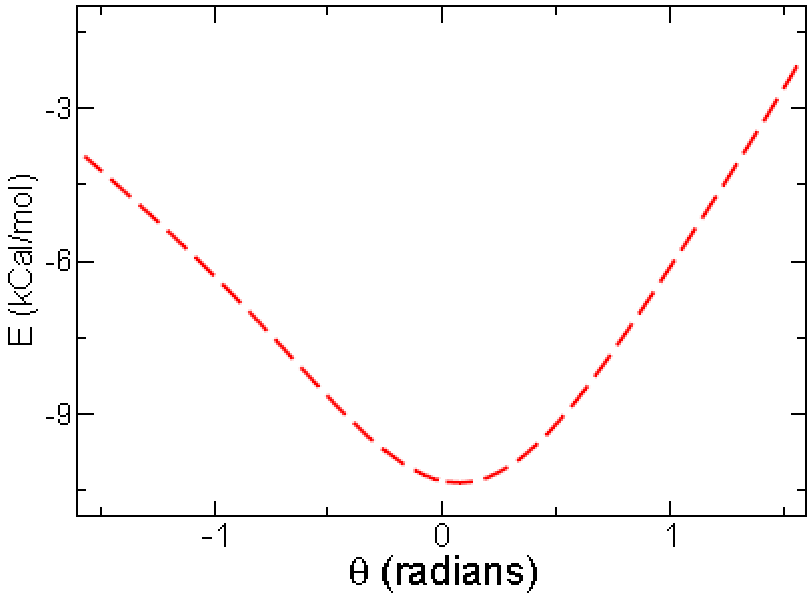
Rotational degrees of freedom



Definition of the three relevant axes of rotation. Axis 1 and 3 are shown, axis 2 is perpendicular to the plane of the paper.

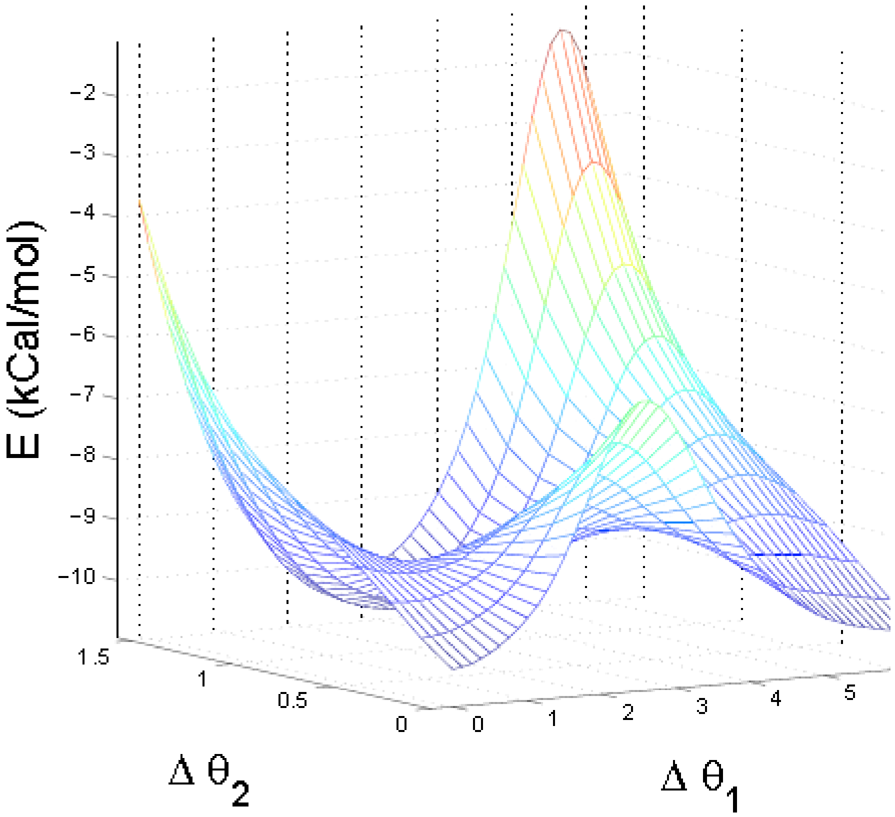
Probing electrostatic energies due to rotation

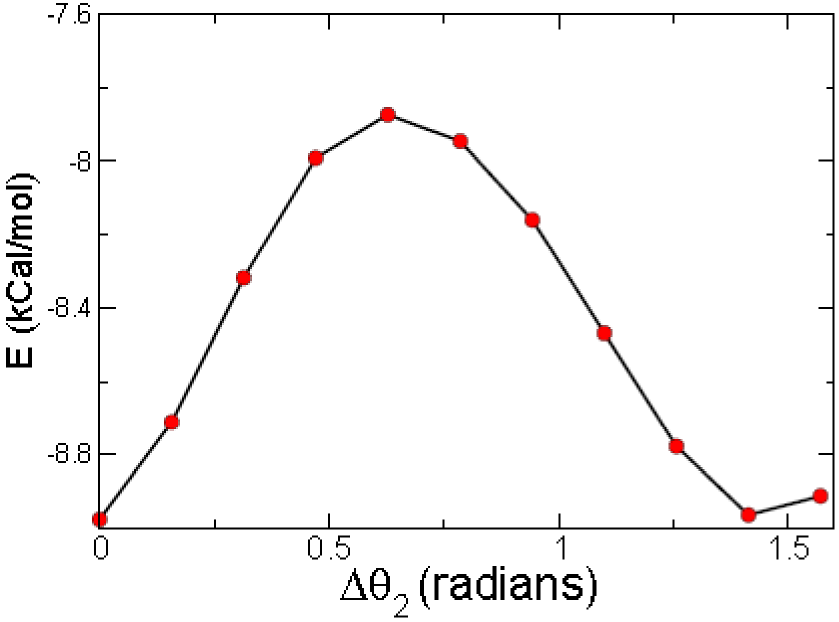
- An NVT simulation of a water cluster inside a nanotube was performed
- A configuration was selected and the inherent structure corresponding to this
- configuration was performed by minimisation
- In the inherent structure, all the water molecules were doubly hydrogen bonded.
- We applied various rotations to such a configuration.



Costly rotation!

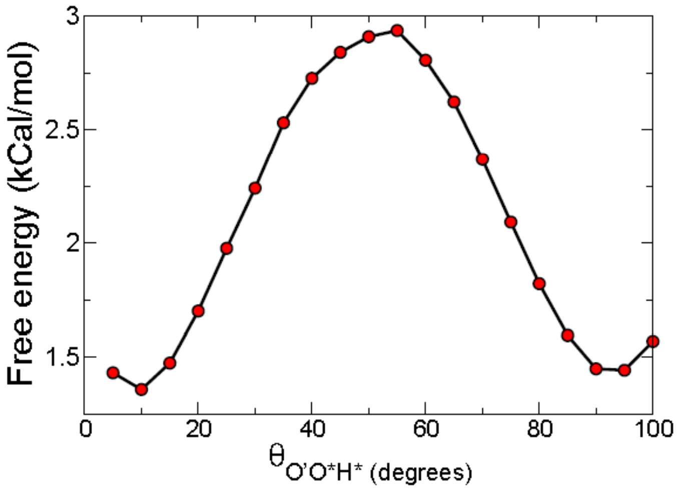
2D energy surface





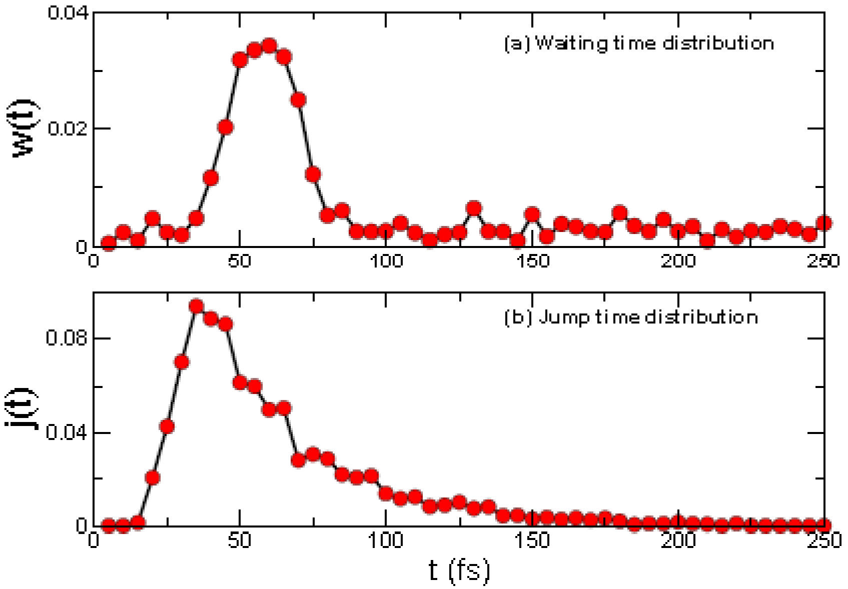
The 2D potential energy surface of a rotating water molecule in the chain as a function of the two rotations about axes 1 and 2. $\Delta\theta_2$ goes from 0 to $\frac{\pi}{2}$ $\Delta\theta_1$ goes from 0 to 2 π

Jump requires crossing an energy barrier of ~ 2kT



- $F = -k_B \text{ T} \ln\left(p(\theta_{O'O*H*})\right)$
- $\Delta F \sim 2.5\, k_B T$

Distribution of waiting time between jumps →



Consistent with calculated height of energy barrier

Rotational dynamics is non-diffusive

Rotational diffusion:

$$\frac{\partial c(\mathbf{u},t)}{\partial t} = D_R \hat{L}^2 c(\mathbf{u},t)$$

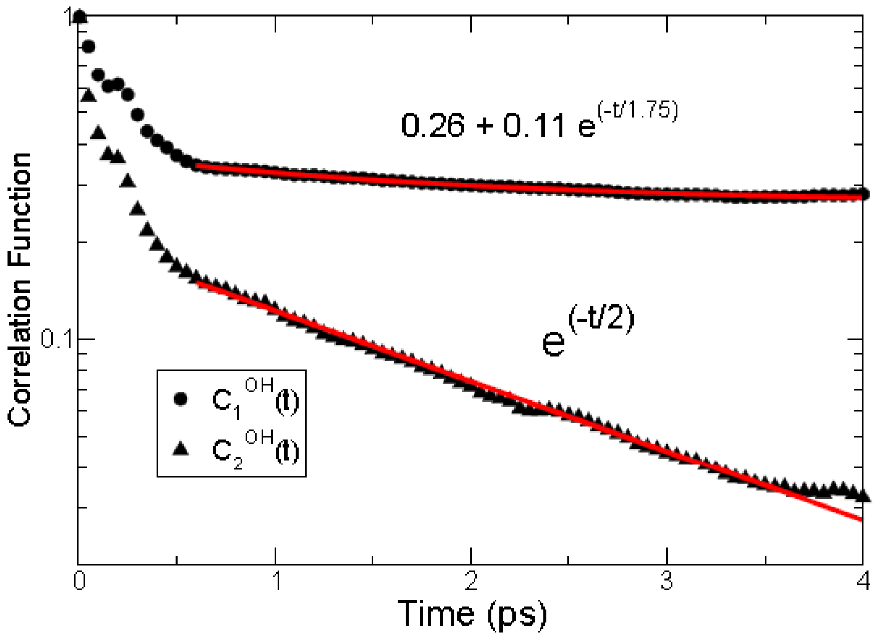
$\hat{L}$ **(angular momentum operator)**

D_R **(rotn. diff. constant)**

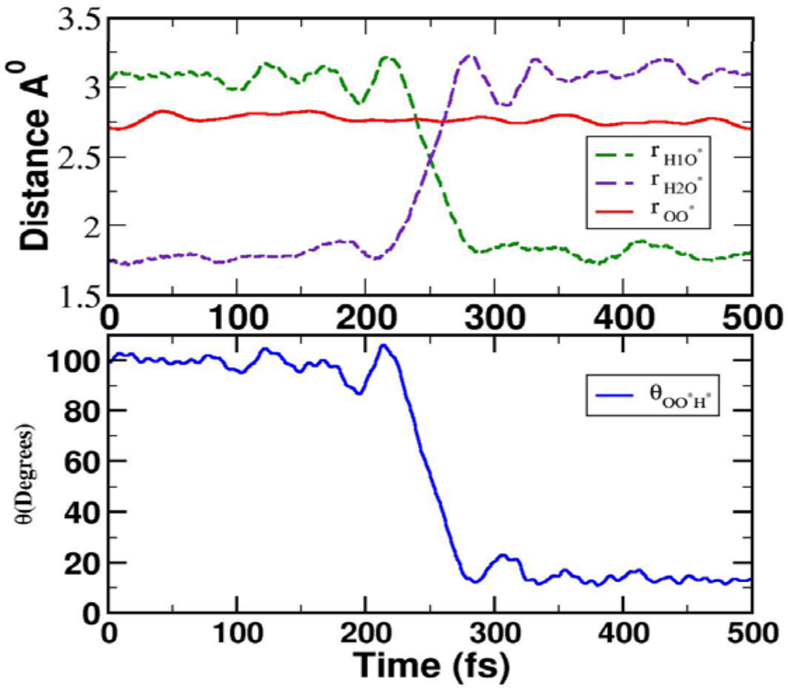
$$c(\mathbf{u},t) = \sum_{lm} exp(-l(l+1)Dt) Y^{\star}_{lm}(\mathbf{u}) Y_{lm}(\mathbf{u_0})$$

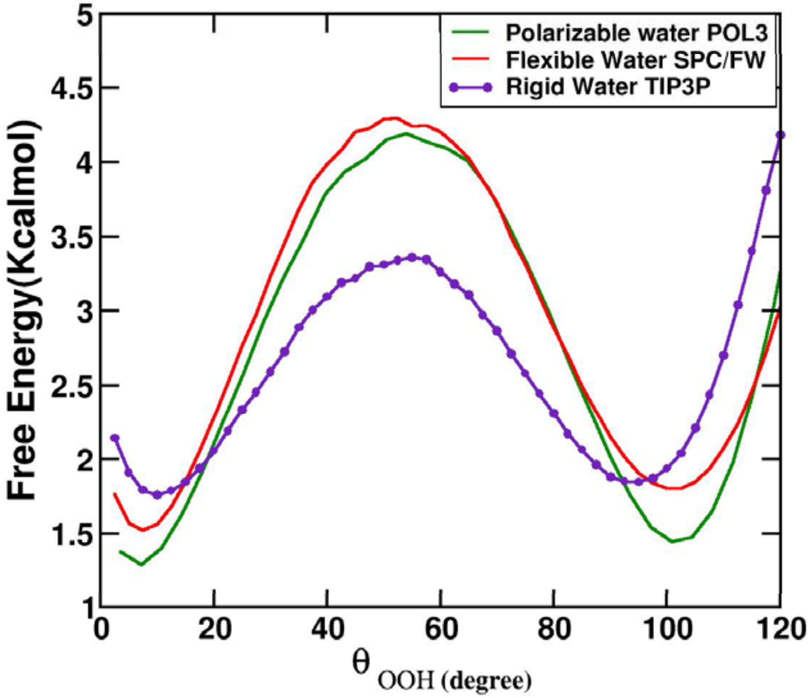
$$\tau_l = \frac{1}{Dl(l+1)} \qquad \frac{\tau_1}{\tau_2} = 3$$

- ➢Deviations from this is a signature of non-diffusive relaxation
- ➢Relaxation involving jumps
- ➢In all bulk molecular liquids relaxing via jumps this ratio is LESS the three !!



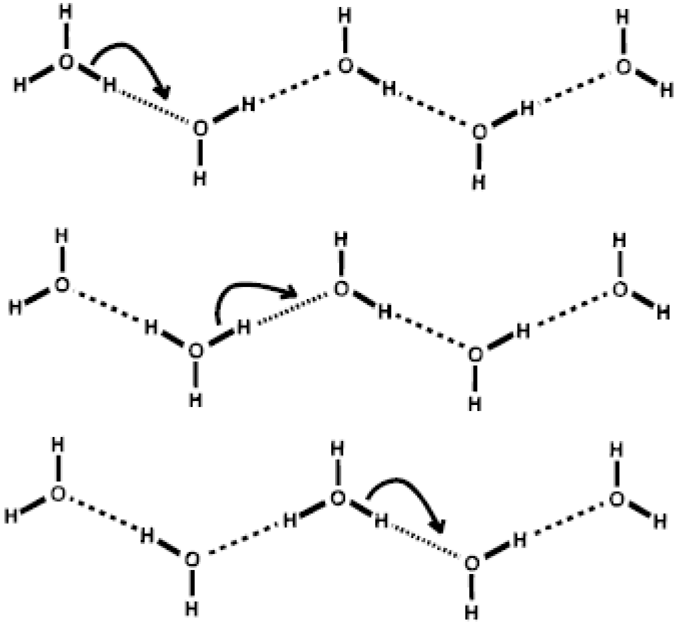
Comparison of various other water models





Essential feature of jump mechanism remains same for all the water model studied
Polarizable and flexible water model gives higher free energy barrier compared to rigid TIP3P model

Why is this important?

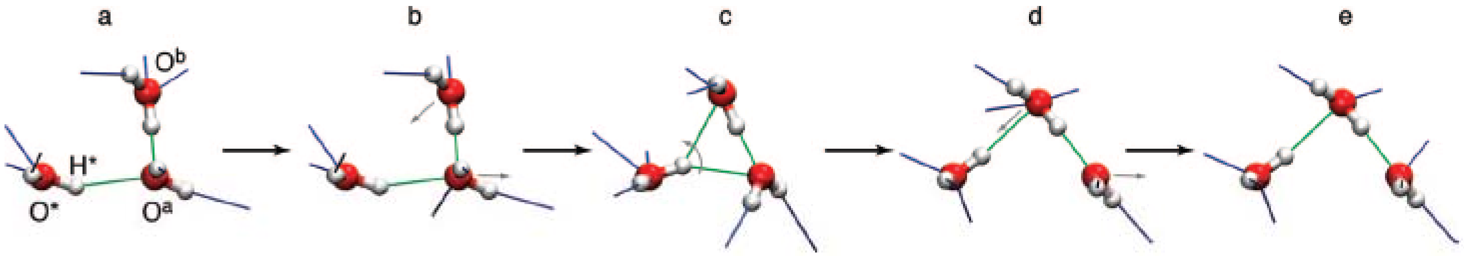


Grotthuss mechanism of proton transport along a “water wire”

Lifetime of hydrogen bonds is important

In bulk water, jump reorientations of water molecules limit the lifetime of hydrogen bonds

Laage, D.; Hynes, J. T. *Science* ***2006,*** *311, 832*



Thermodynamic Properties from DoS

- Thermodynamic Properties

$$E^Q = V_0 + \beta^{-1}\int_0^\infty dv S(v) W_E^Q(v) \qquad W_E^Q(v) = \left[\frac{\beta hv}{2} + \frac{\beta hv}{\exp(\beta hv) - 1}\right]$$

$$S^Q = k_B \int_0^\infty dv S(v) W_S^Q(v) \qquad W_S^Q(v) = \left[\frac{\beta hv}{\exp(\beta hv) - 1} - \ln\left(1 - \exp(-\beta hv)\right)\right]$$

$$A^Q = V_0 + \beta^{-1}\int_0^\infty dv S(v) W_A^Q(v) \qquad W_A^Q(v) = \left[\ln \frac{1 - \exp(-\beta hv)}{\exp(-\beta hv / 2)}\right]$$

$$V_0 = E^{MD} - E^C$$

E^{MD} Total energy from molecular simulation

$$E^C = \beta^{-1}\int_0^\infty dv S(v) W_E^C(v) = \beta^{-1}\int_0^\infty dv S(v)$$

Thermodynamics of water permeation in nanotube

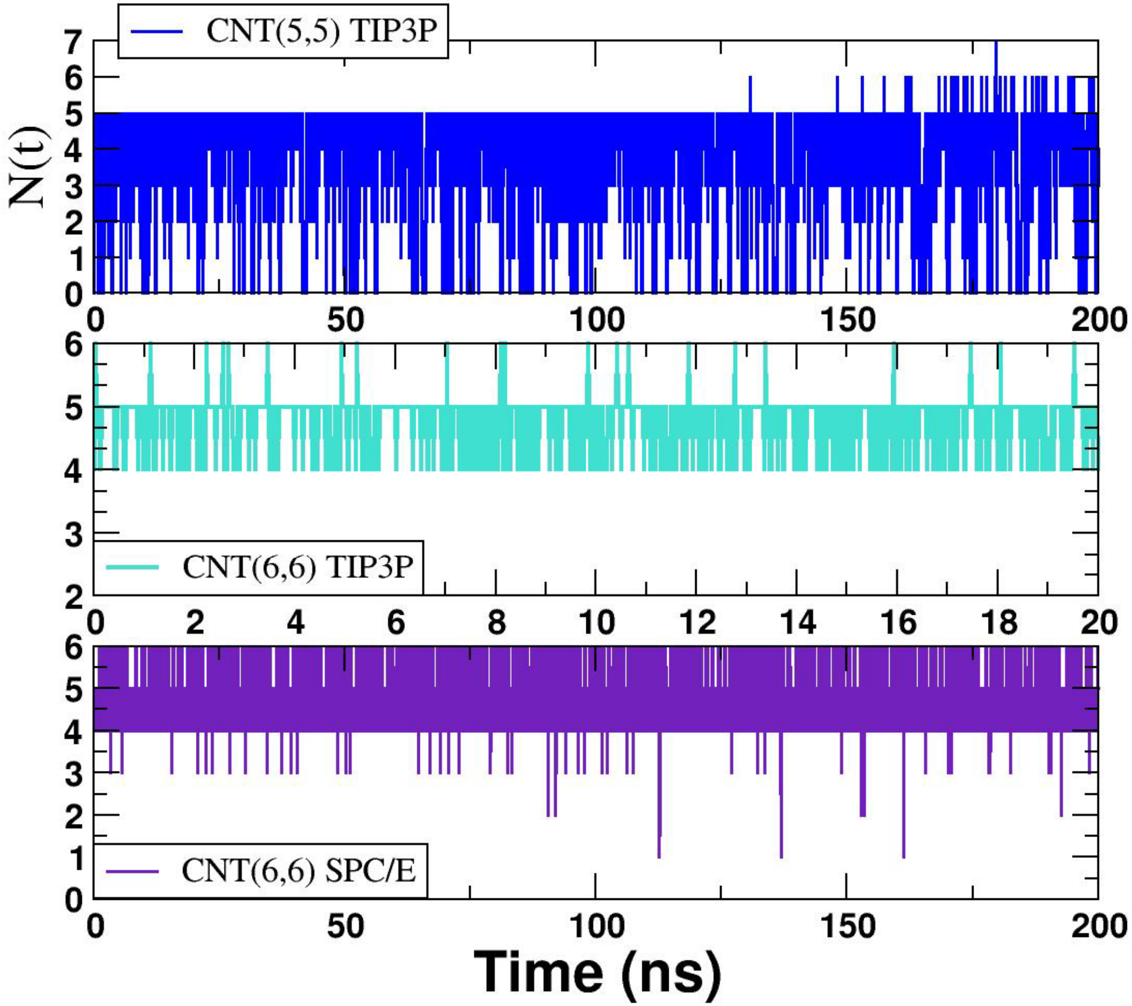
- Two different water models SPC/E ,TIP3P for 2 different pore size of CNT,(5,5)(6.8A) and (6,6)(8.1A) each CNT having length ~57A.
- TIP3P goes inside CNT(5,5) but SPC/E doesn't goes in for same CNT !!!,Free energy lose

	TIP3P	SPC/E
CNT(6,6)	22	21
CNT(5,5)	21	0-3

Free energy

TIP3P	Energy(E) kcal/mol	Entorpy(S)(Trans+ Rot)	F=E-TS (Kcal/mol)
BULK	-9.800±0.02	4.013+0.804±0.04	-14.617±0.06
CNT(6,6)	-9.508±0.3	4.023+1.301±0.25	-14.382±0.55
CNT(5,5)	-8.689±0.3	2.955+1.561±0.25	-13.205±0.55
SPC/E			
BULK	-10.463±0.02	3.547+0.647±0.04	-14.657±0.06
CNT(6,6)	-8.976±0.3	3.612+1.168±0.25	-13.756±0.55
CNT(5,5)(RING)	-7.545±0.2	2.939+1.436±0.20	-11.922±0.40

Free energy dictates the empty-filling transition



- More emptying transition is there if loss in free energy is more.
- Long time behavior was observed for same cases but shorter tube length.

Summary

- Solid-like ordering at room temperature
- Normal diffusion in a single-file system
- Single-file diffusion in a nanoring
- Alignment of dipole moments along tube axis
- Strong anisotropy in orientational relaxation
- Relaxation via large-amplitude angular jumps
- Gain in rotational entropy allow water entry inside hydrophobic pore of the tube