

# *Anomalous Soft Dynamics in Nanotube-Water: A Revelation of Nanoscale Confinement*

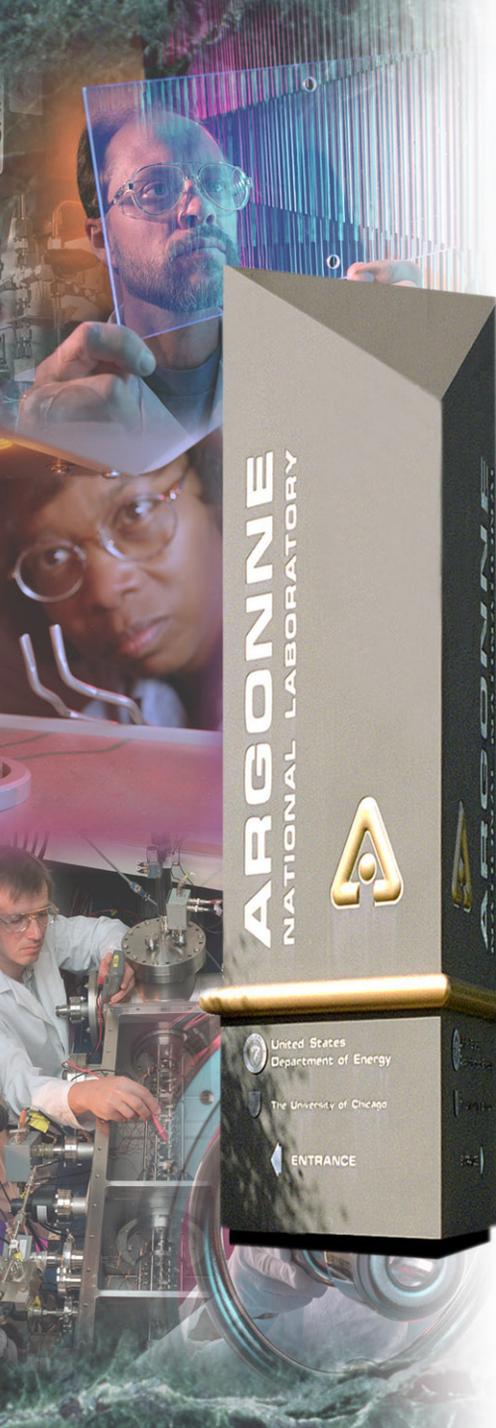
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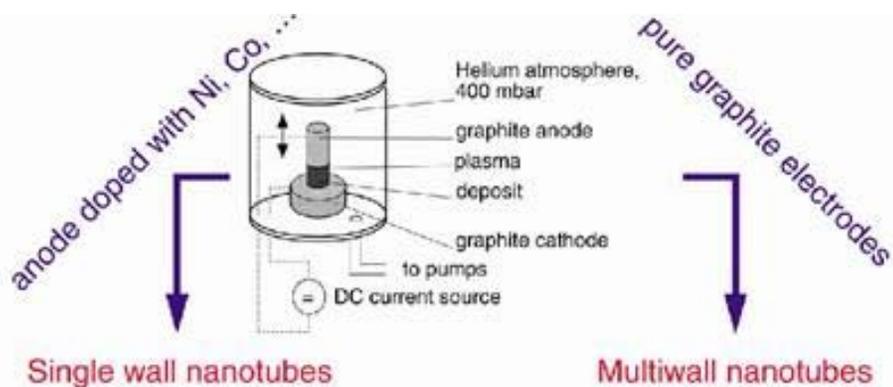
Office of Science  
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WEB SHOTS

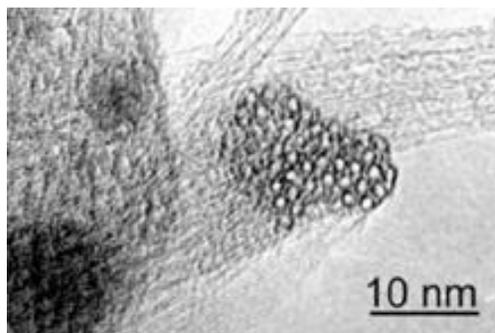
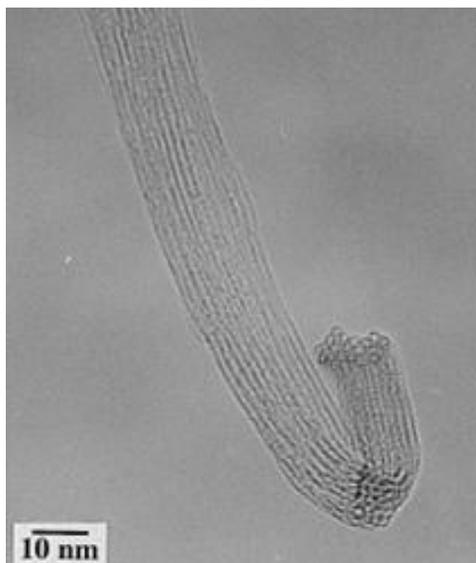
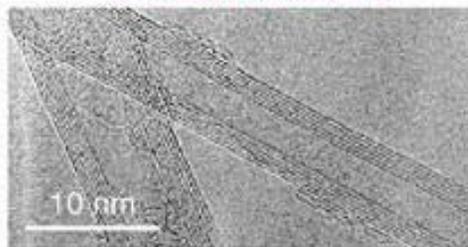
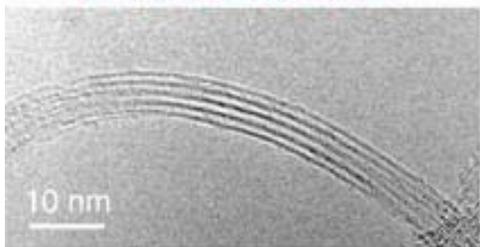
- 1. Can water enter the SWNT (inner diameter 14 Å)?**
- 2. What are the effects of nanotube confinement on the dynamics of water?**
- 3. MD simulations and proposed nanotube-water structure.**



Raw material was produced by direct current arc vaporization of graphite/metal composite rods. Co/Ni catalyst in a 3:1 mixture. Purification with hydrochloric acid followed by oxidation of non-tube carbon components by air at 300-600°C.

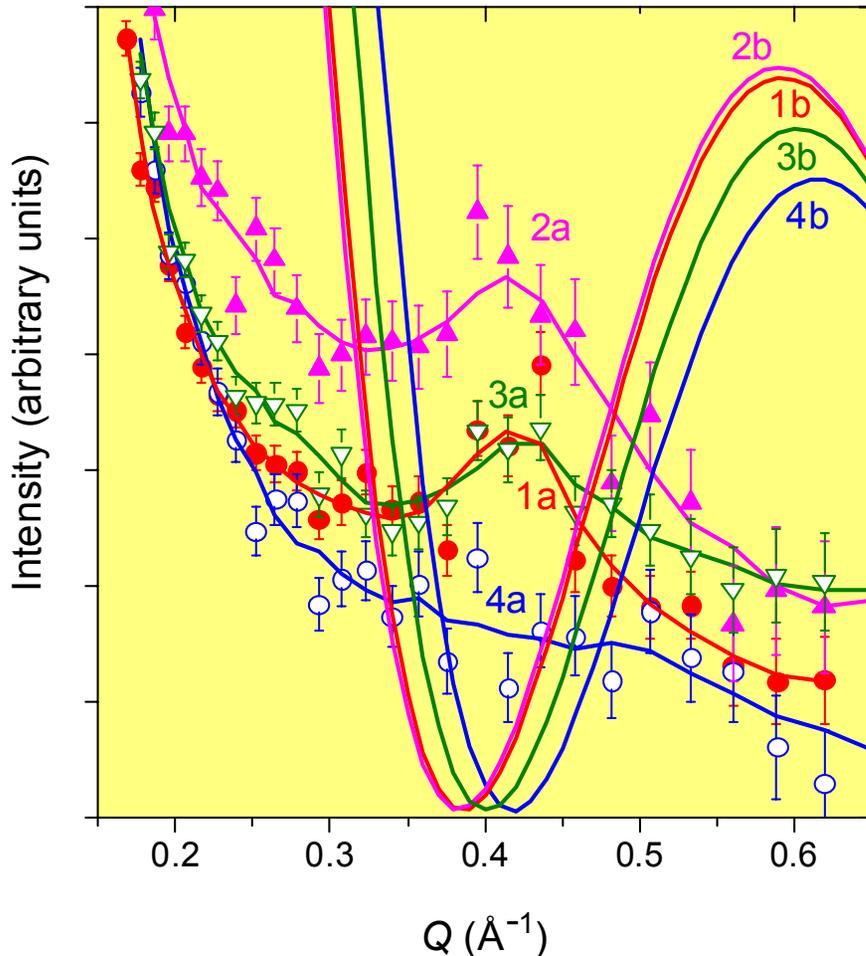
Pure **SWNT** sample ( $m=3.8$  g) with  $D \approx 14 \pm 1$  Å,  $l \sim 10$  μm as revealed by HRTEM, TEM, SEM and Raman measurements.

To fill the SWNT with water, the dry SWNT sample was first exposed to saturated vapor from a water bath (1:1 weight ratio) at 110°C for 2 hours in an enclosed environment. The excess water adsorbed in the exterior of the nanotubes was then evaporated at 45°C. An optimal filling, in terms of H<sub>2</sub>O/SWNT mass ratio was found to be 11.3%.

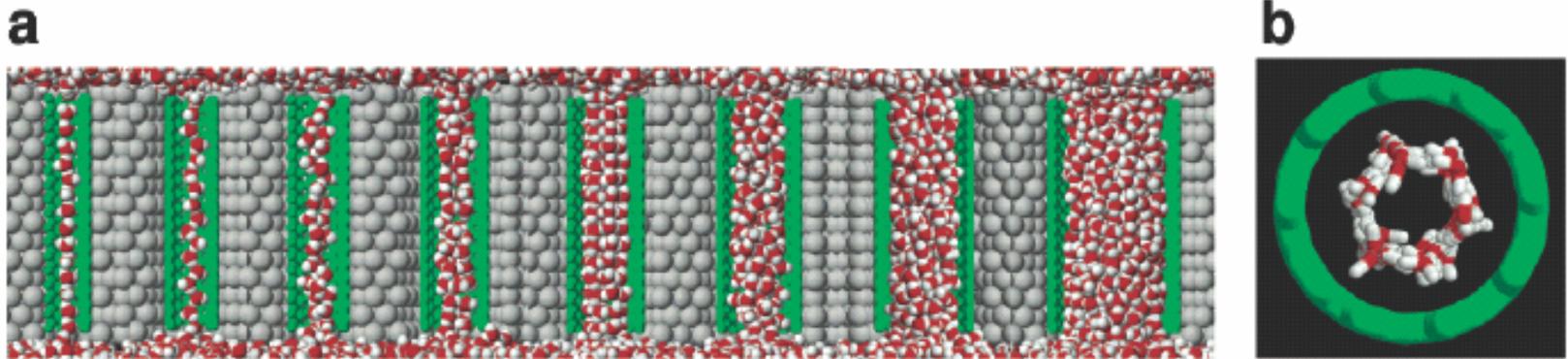


## Water Enters the Nanotubes by Exposing SWNT to Water Vapor at $\sim 110^\circ\text{C}$

Low-angle neutron diffraction:  $I(Q) \sim S(Q) \cdot F(Q)$ . Here,  $S(Q)$  consists of a Bragg reflection at  $0.41 \text{ \AA}^{-1}$  from the (01) planes of the 2D hexagonal lattice of SWNT crystalline bundles.



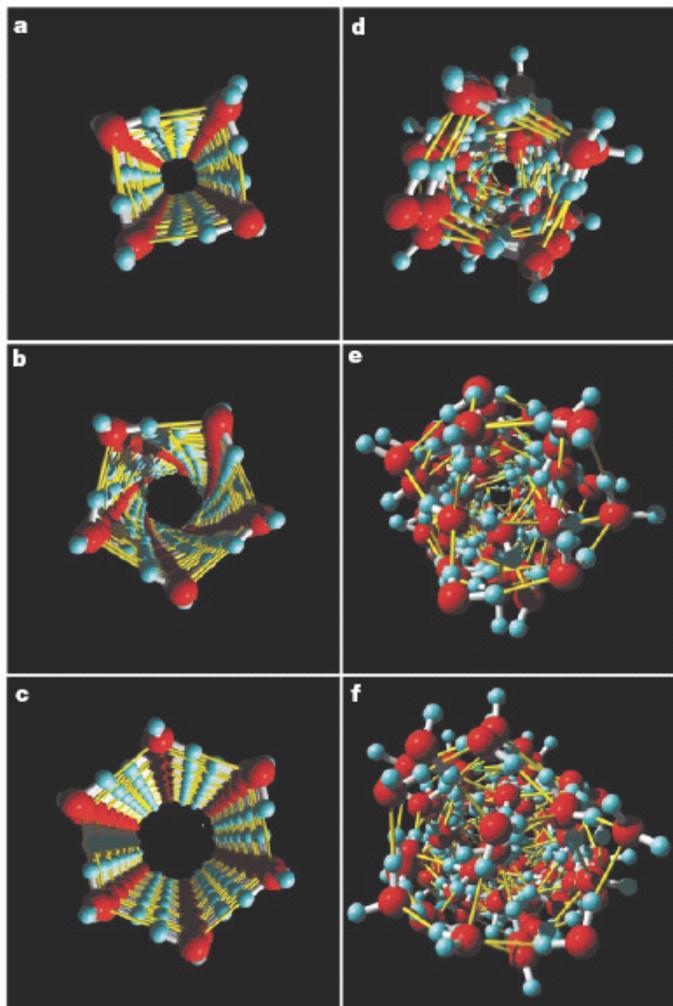
The calculated form factors  $F(Q)$  for the nanotubes with water *inside* show a shift of minimum from  $0.385$  to  $0.41 \text{ \AA}^{-1}$  for  $\text{H}_2\text{O}$  to  $(\text{H}_2\text{O})_{50}(\text{D}_2\text{O})_{50}$  to  $\text{D}_2\text{O}$ . This implies the peak intensity at  $0.41 \text{ \AA}^{-1}$  will decrease with increasing deuteration, which was observed experimentally. If water were outside of the nanotubes,  $F(Q)$  minimum would always be at  $Q \leq 3.85 \text{ \AA}^{-1}$ , therefore no strong intensity change.



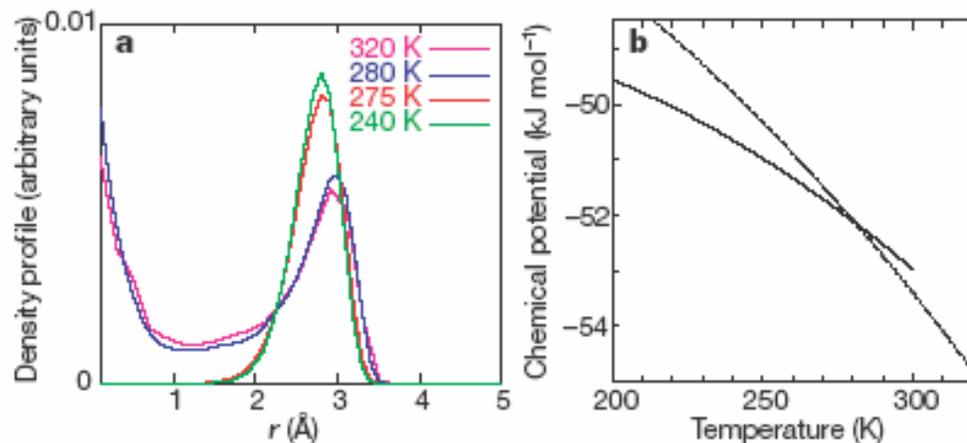
**Figure 1.** Snapshots from molecular dynamics simulations at 300 K. (a) Composite image of all systems (see Table) with nanotube size increasing from left to right. In narrow nanotubes, the water adopts a single-file arrangement but becomes more disordered in a fashion similar to that of bulk water in wider nanotubes. Confined within a nanotube of a “critical” diameter (fifth from left), the water spontaneously orders into a regular array. (b) Cross-sectional view of water inside the critical-sized 8.6-Å-diameter nanotube showing a multicolumnar water structure. Colors: nanotube (green), wafer (gray), water oxygens (red), water hydrogens (white). Images were derived from visualizations using RasMol.

“... the water generally shows **slowed dynamics compared to that of the bulk**, in nanotubes of a critical diameter it forms a structure resembling a stack of cyclic water hexamers exhibiting properties characteristic of both hexagonal ice and liquid water.”

R.J. Mashl et al., *Nano Lett.* **3** (2003) 589



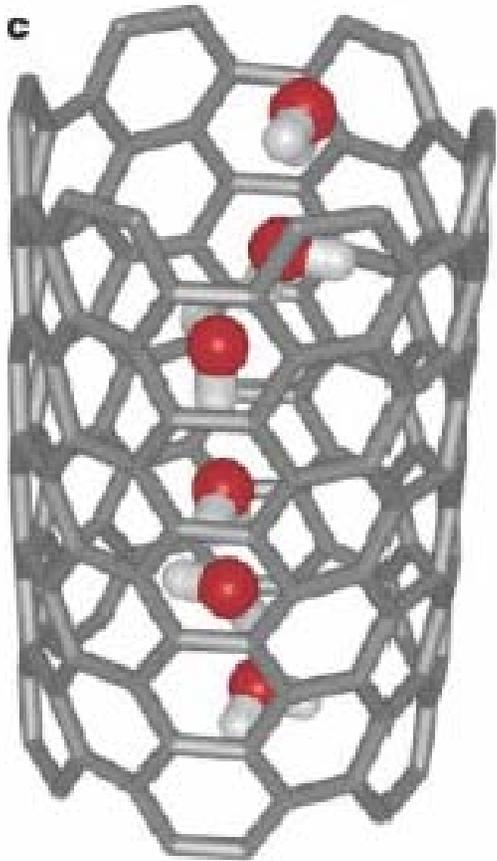
**Figure 2** Snapshots of quenched molecular coordinates. **a**, Square; **b**, pentagonal; **c**, hexagonal ice nanotubes in (14,14), (15,15) and (16,16) SWCNs; **d** to **f**, the corresponding liquid phases. The ice nanotubes were formed on cooling under an axial pressure of 50 MPa in molecular dynamics 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.



**Figure 3** Properties associated with the first-order phase transition in the (16,16) SWCN at a fixed pressure of 50 MPa. **a**, Radial density profile of confined water at various temperatures. **b**, Chemical potential of liquid water (filled circles and dashed line) and the hexagonal ice nanotube (solid line) against temperature.

“... we found that water can exhibit a first-order freezing transition to hexagonal and heptagonal ice nanotubes, and a continuous phase transformation into solid-like square or pentagonal ice nanotubes.”

K. Koga et al., *NATURE* **412** (2001) 802



Structure of the hydrogen-bonded water chain inside the nanotube.

“... we observe pulse-like transmission of water through the nanotube.”

G. Hummer et al., NATURE **414** (2001) 188

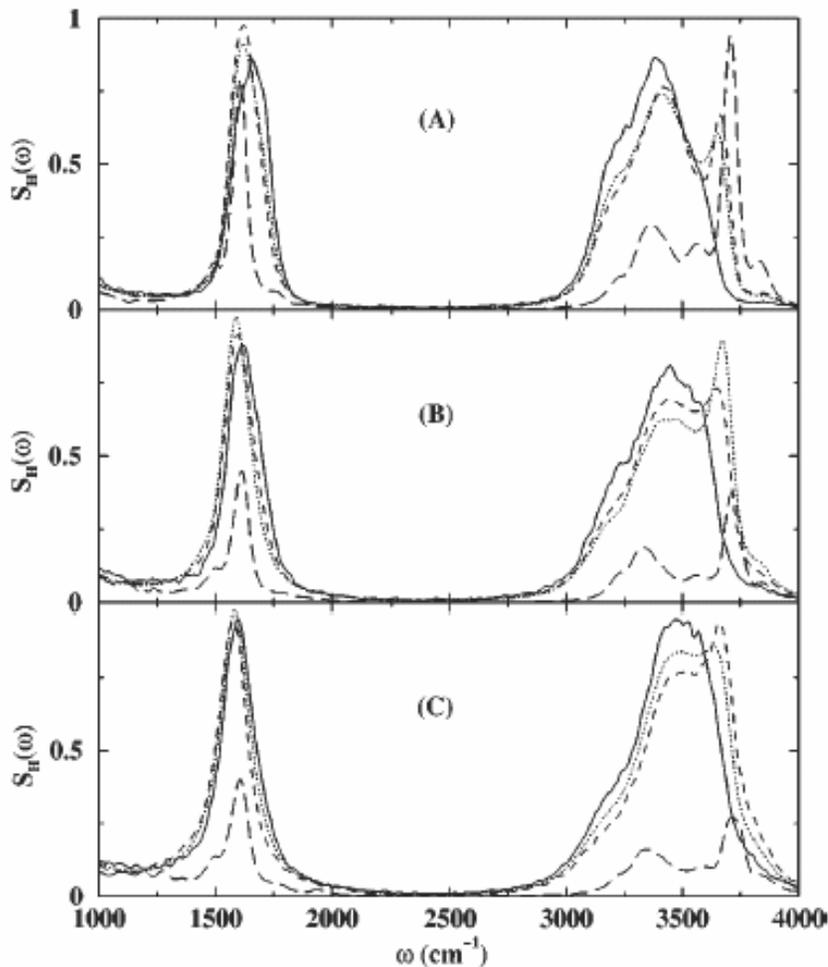
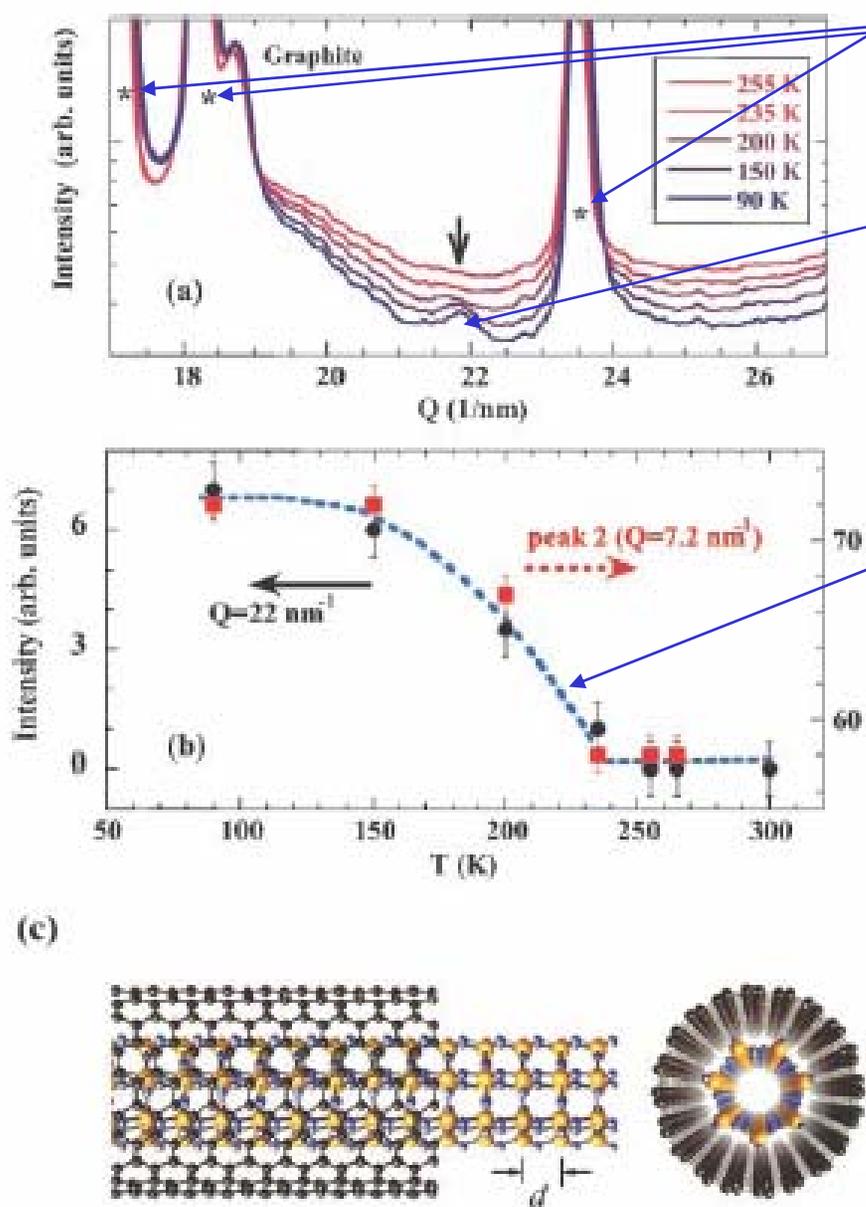


FIG. 5. Hydrogen spectral densities for CN at different temperatures. High frequency range (1000–4000  $\text{cm}^{-1}$ ). (A) 298 K, (B) 400 K, (C) 500 K. Bulk is represented by full lines at ambient conditions, (6,6) CN are represented by longdashed lines, (8,8) CN are represented by dashed lines, and (10,10) CN are represented by dotted lines. Bulk has been computed at 298, 403, and 523 K.

“The hydrogen-bond network of constrained water has been revealed to be weaker than the one of bulk water at all simulated temperatures. ... We observed that narrow tubes do not allow complex H-bonded structures and, in many cases, the adsorbed water molecules inside are forming long linear chains. ... We have found that diffusion in the  $z$  direction is clearly faster than the bulk value in all cases.

... One relevant fact is the detection of a high vibrational frequency in the stretching spectral region of all constrained water samples which is absent in the bulk.”

J. Martí and M.C. Gordillo, Phys. Rev. E 64 (2001) 021504



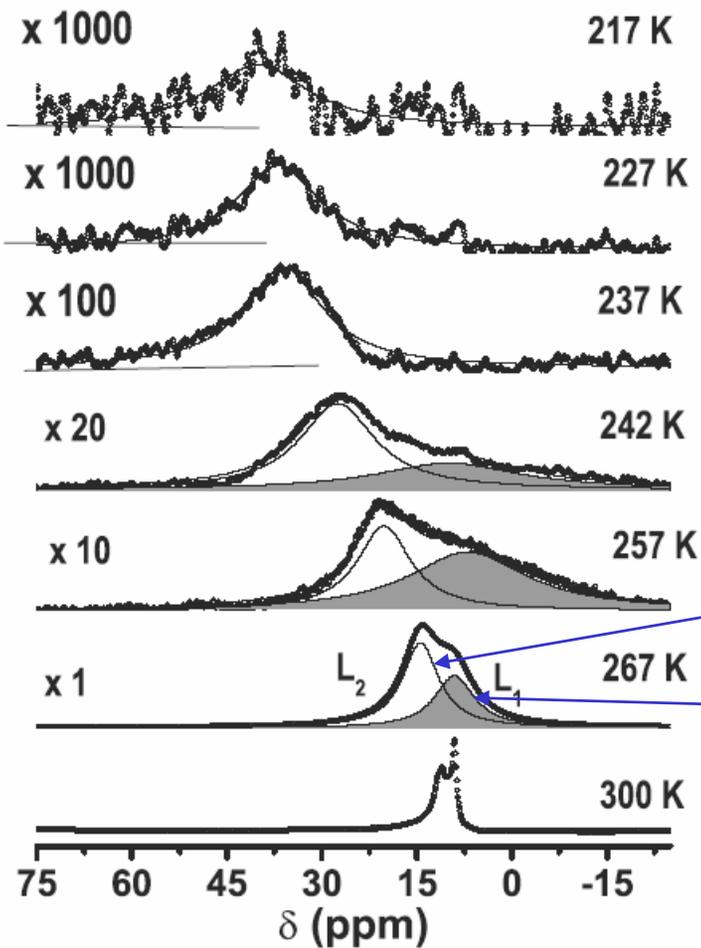
Bulk ice external to the SWNT

Nanotube-ice peak

“Liquid-like water transforms into a new solid form” in nanotube

Fig. 4. (a) Temperature dependence of XRD profiles in water-exposed SWNT bundles. Stars (\*) denote peaks due to bulk ice. (b) Temperature dependence of the intensity of the peak around  $Q = 22 \text{ nm}^{-1}$  shown by the arrow in (a), along with that of peak 2 at around  $Q = 7.2 \text{ nm}^{-1}$ . The background intensity due to the presence of a quartz capillary was subtracted. (c) The proposed structure of the ice nanotube inside a SWNT. The estimated  $d$ -spacing is  $0.287 \text{ nm}$  at  $90 \text{ K}$ .

Y. MANIWA et al.,  
 J. Phys. Soc. Japan **71** ( 2002) 2863



$L_2$  Lorentzian attributed to water near the nanotube wall

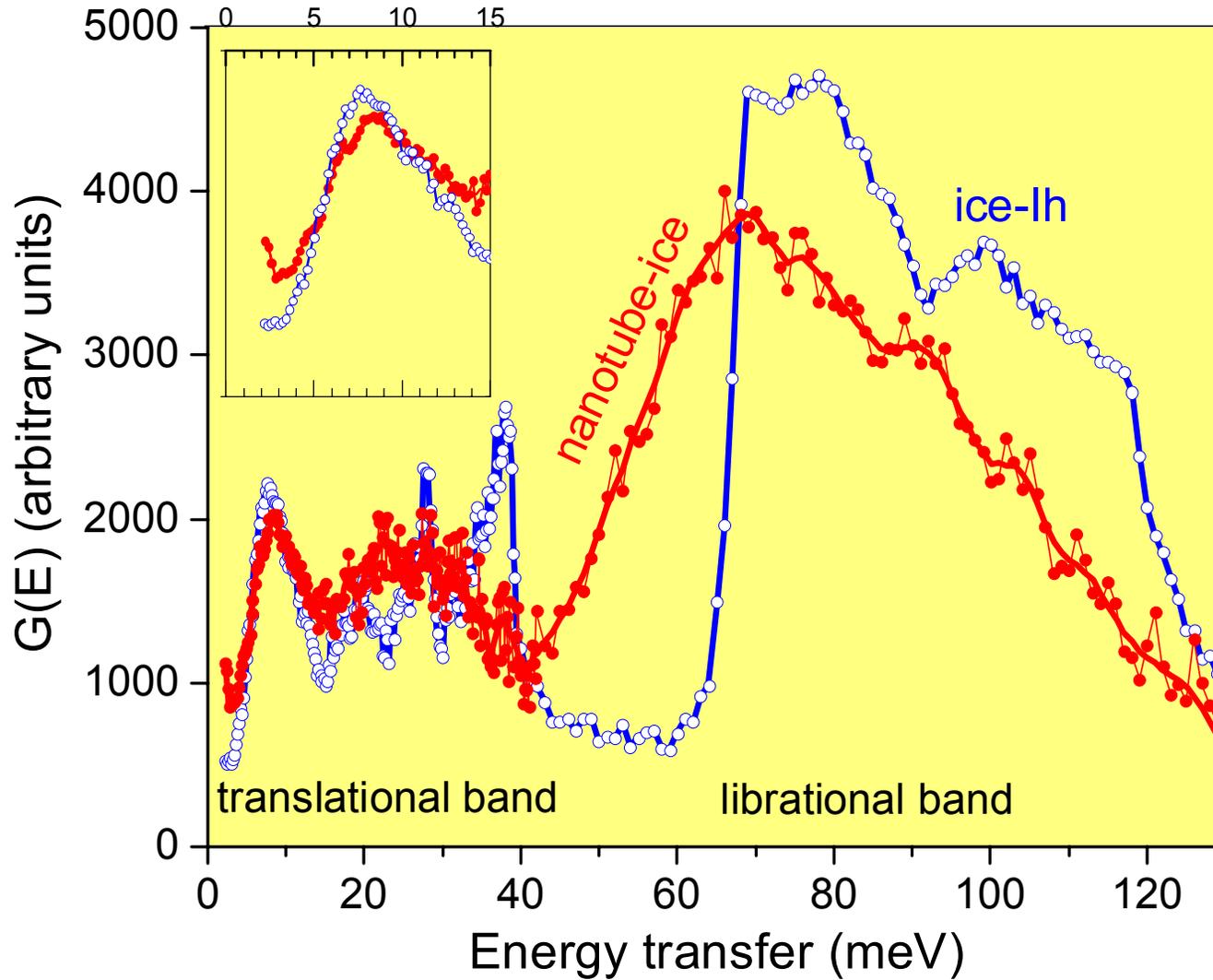
$L_1$  Lorentzian attributed to the central water

The disappearance of  $L_1$  below  $\sim 237$  K was interpreted as the transfer of the central water to the water-tube ( $L_2$ ) which subsequently freezes at  $\sim 212$  K.

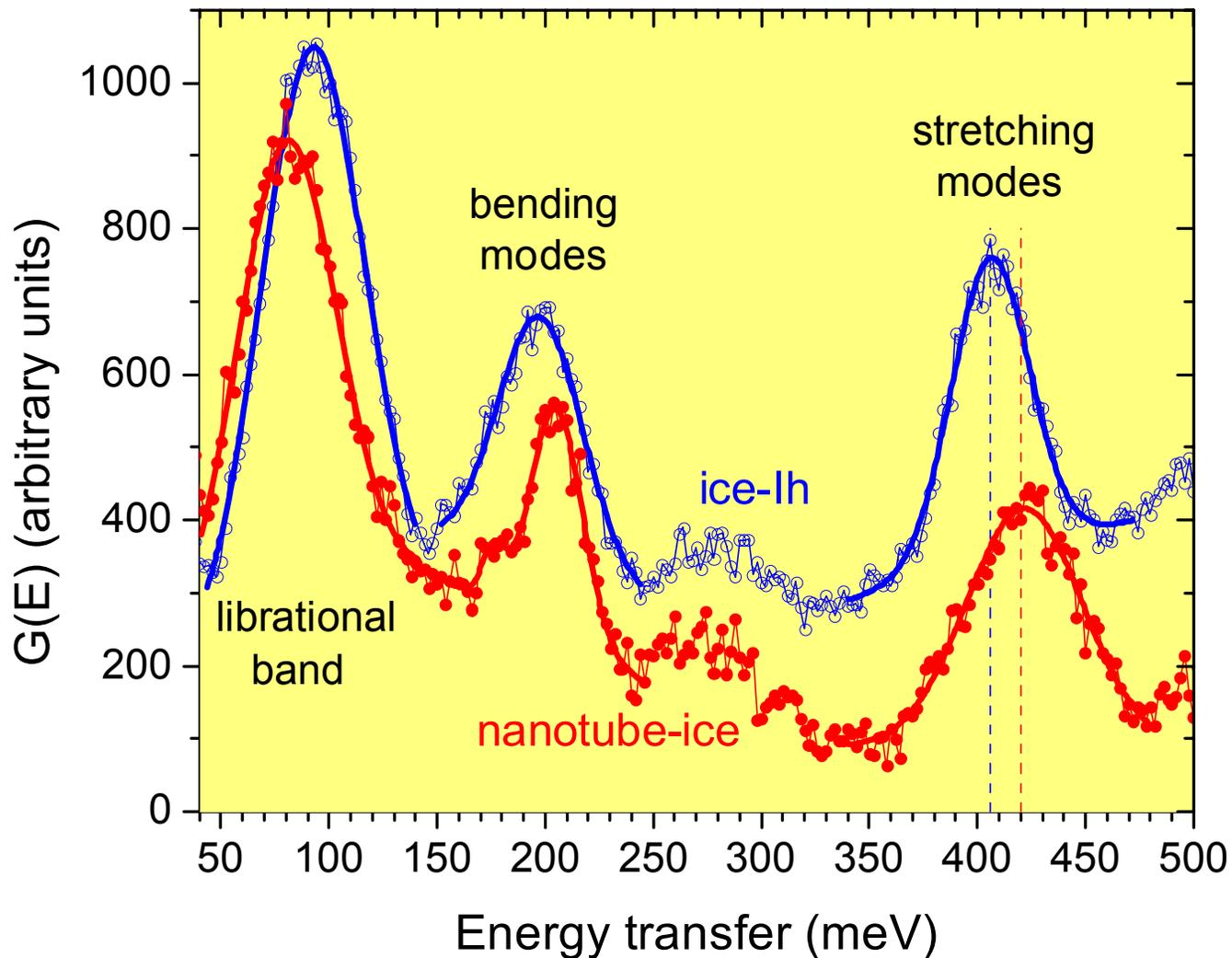
Water at nanoscale confined in single-walled carbon nanotubes studied by NMR.

S. Ghosh et al., *Europhys. Lett.* **65** (2004) 678

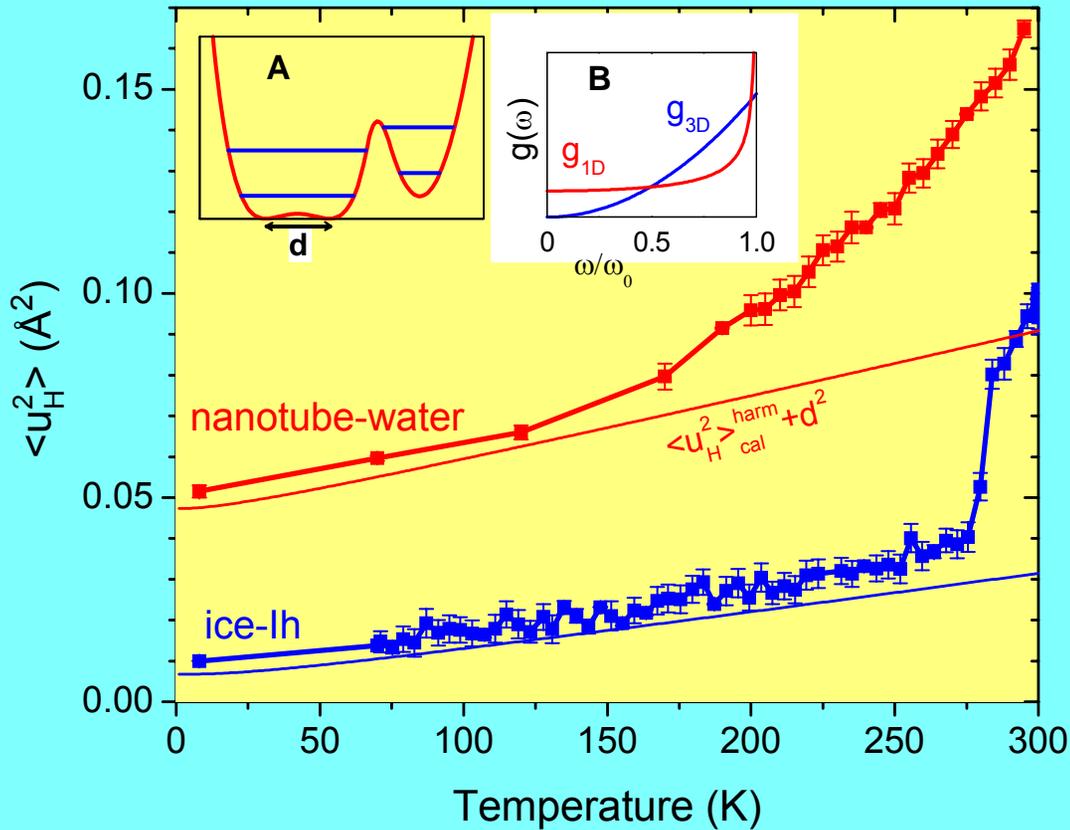
# Strong Renormalization of the Low-Energy Intermolecular Vibrational Density of States



# *A Significantly Weakened Hydrogen-Bond Network in Nanotube-Water*

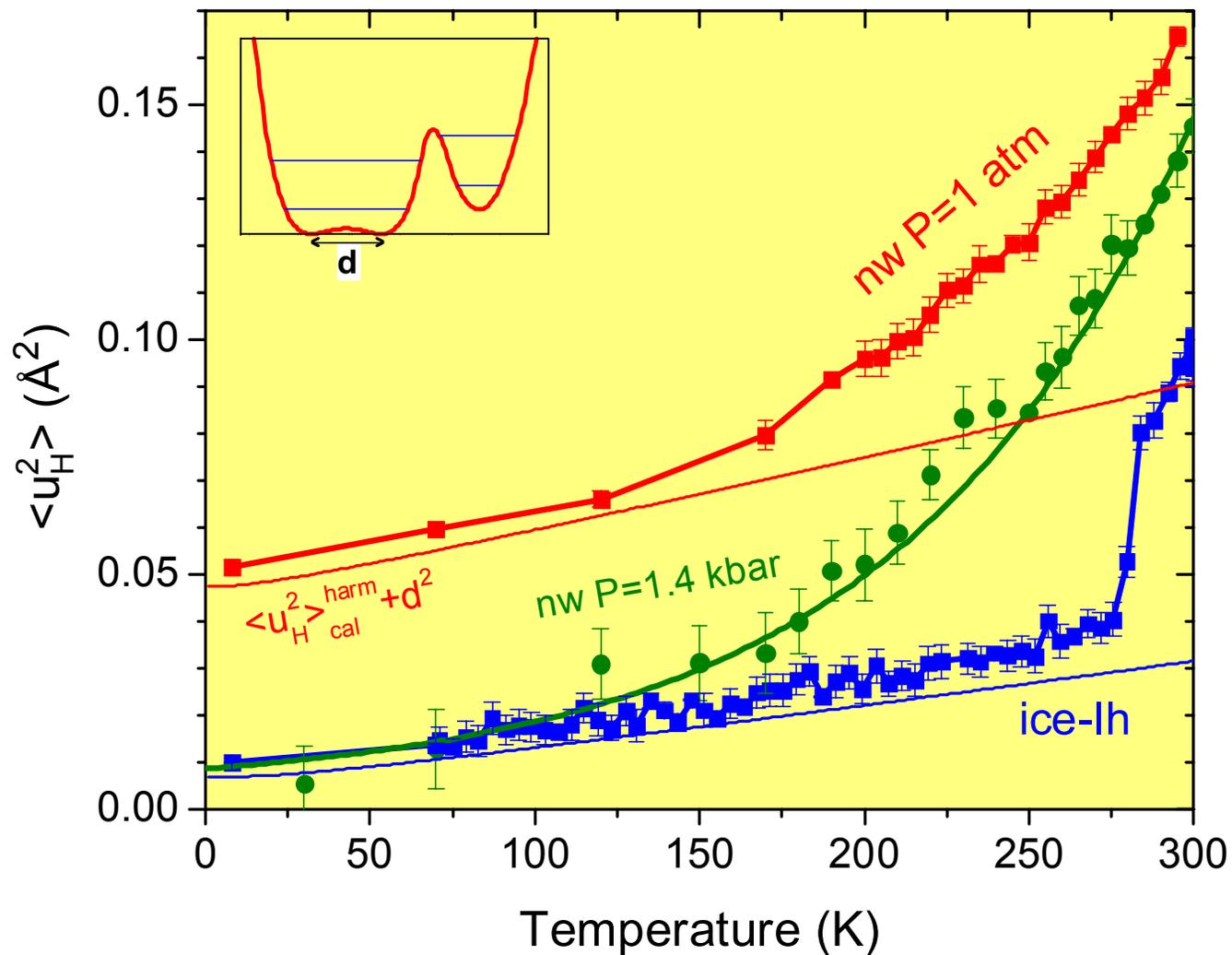


The observed stretching mode frequency of nanotube-ice (**422 meV**) is higher than that of ice-*Ih* (**406 meV**). The higher O-H stretching frequency arises from the shorter O-H covalent bonds,  $R_{\text{O-H}}$ , and a longer intermolecular O-O distance,  $R_{\text{O-O}}$ . Based on the observed O-H stretching frequency and a phenomenological model [Klug & Whalley, 1984] **the estimated  $R_{\text{O-O}}$  distance for nanotube-ice at 9 K is 2.916 Å**. Comparing with the  $R_{\text{O-O}}$  (**2.76 Å**) of ice-*Ih*, the structure of nanotube-ice supports a weaker hydrogen-bonded network.



The employment of high-resolution ( $\Delta E = 80 \mu\text{eV}$ ) spectrometer allowed an accurate measurement of  $\langle u_H^2 \rangle$  according to the elastic incoherent scattering from hydrogen,  $\sim \exp(-\langle u_H^2 \rangle Q^2)$ . The measured  $\langle u_H^2 \rangle \approx 0.05 \text{ \AA}^2$  in nanotube-ice at 8 K is about 4 times the displacement in ice-1h, and upon heating to 300 K it monotonically increases to  $\sim 0.17 \text{ \AA}^2$ . The latter value definitely implies a liquid-state of nanotube-water at 300 K; therefore, *the nanotube-ice exhibits a continuous transition from solid to liquid state upon heating.*

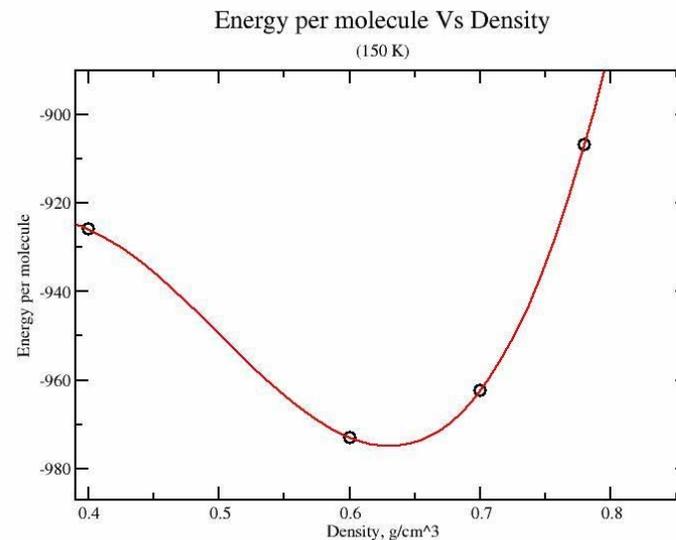
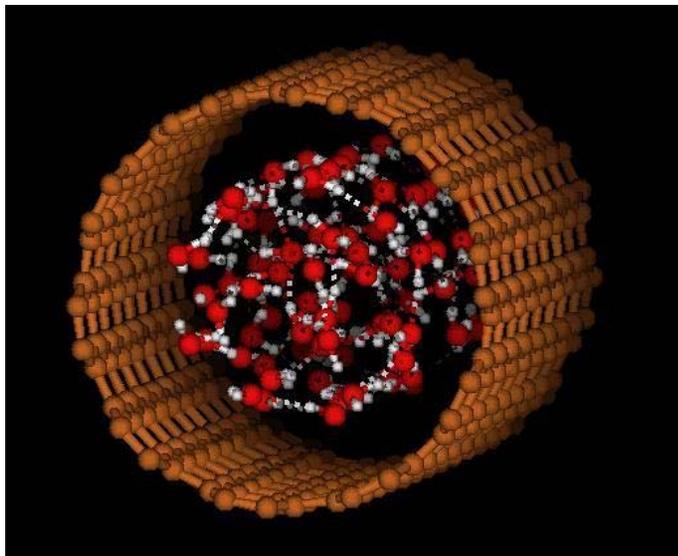
Red and blue solid lines show the  $\langle u_H^2 \rangle$  dependences calculated in harmonic approximation using one phonon part of the measured generalized vibrational densities of states for the studied samples. To describe the measured  $\langle u_H^2 \rangle$  for nanotubes-water the calculated curve was vertically shifted by supposed delocalization,  $d \sim 0.2 \text{ \AA}$ , of the hydrogen atoms in water molecules due to the flattened bottom of its potential (insert A). Insert B shows another possible scenario, when the large  $\langle u_H^2 \rangle$  in quasi one-dimensional nanotube-water can be originated from finite value of the density of phonon states at low frequencies in one-dimensional chain,  $g(\omega) \sim (\omega_0^2 - \omega^2)^{-1/2}$ , compared to  $g(\omega) \sim \omega^2$  behavior for the bulk three-dimensional case.



$\langle u_H^2 \rangle$  for nanotube-water under pressure  $P=1.4$  kbar below 100 K is reduced drastically to values comparable to those in ice-Ih. At higher temperatures it rises very rapidly above the ice-Ih value. Data show no abrupt transition near 273 K.

## *Summary: Experimental Observation*

- **Water vapor enters the single-walled open-ended nanotubes at ambient condition, likewise in many biological counterparts such as aquaporin, gramicidin and bacteriorhodopsin.**
- **The hydrogen-bond energetics of water confined within nanotubes is significantly modified. The blue shift of intramolecular vibrations and red-shift of intermolecular bands indicate more pliable hydrogen bonds. The broadening of the bands and excess density at low-energies suggest a more disordered structure.**
- **Nanotube-water is extraordinary “soft” - hydrogen atoms may be considered as situated in a strongly anharmonic potential well, implying a higher diffusion rate of protons. An applied pressure (1.4 kbar) first suppresses the soft dynamics below ~150 K but gives way to thermal excitations at higher temperatures.**



MD calculations for water in SWNT have been performed using the **TTM2-F polarizable flexible water model** of Burnham and Xantheas (uses smeared charges and dipoles to model short range electrostatics) [1]. This model has been shown to be in excellent agreement with high-level electronic structure data for small water clusters and can also reproduce bulk behavior of ice and ambient liquid water.

Our MD simulations consist of a rigid carbon nanotube of length 40 Å in periodic boundary conditions that interacts with waters through the Lennard-Jones potential (from Ref. 2). An Ewald sum was used for the long-range Coulomb interactions.

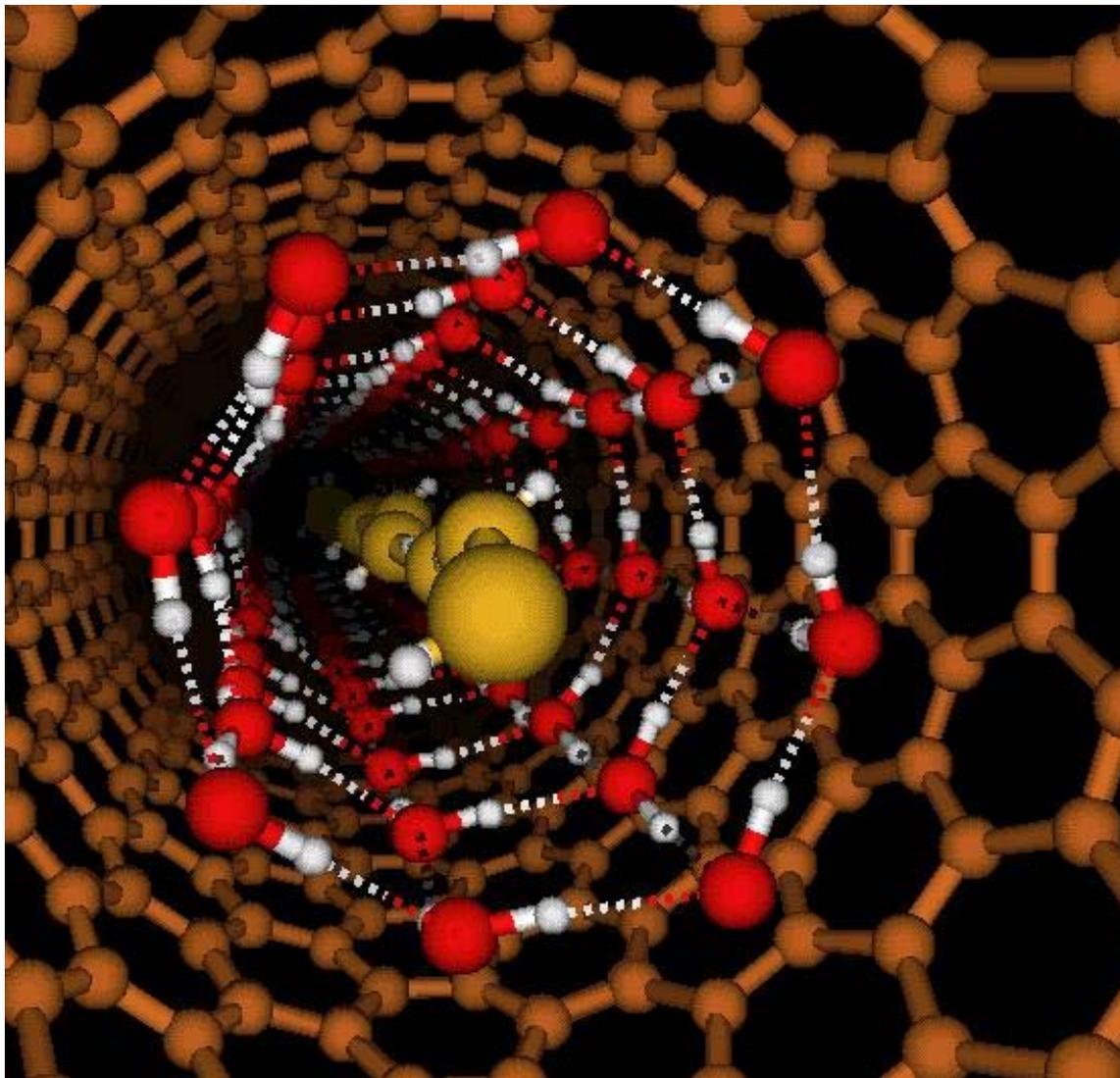
We initially attempted slow simulated annealings at a range of different water densities in order to find candidate structures with the lowest energy per water-molecule.

1. C.J. Burnham and S.S. Xantheas, J. Chem. Phys. **116** (2002) 1500, 5115
2. J.H. Walther et al., J. Phys. Chem. B **105** (2001) 9980

**MOLDEN**

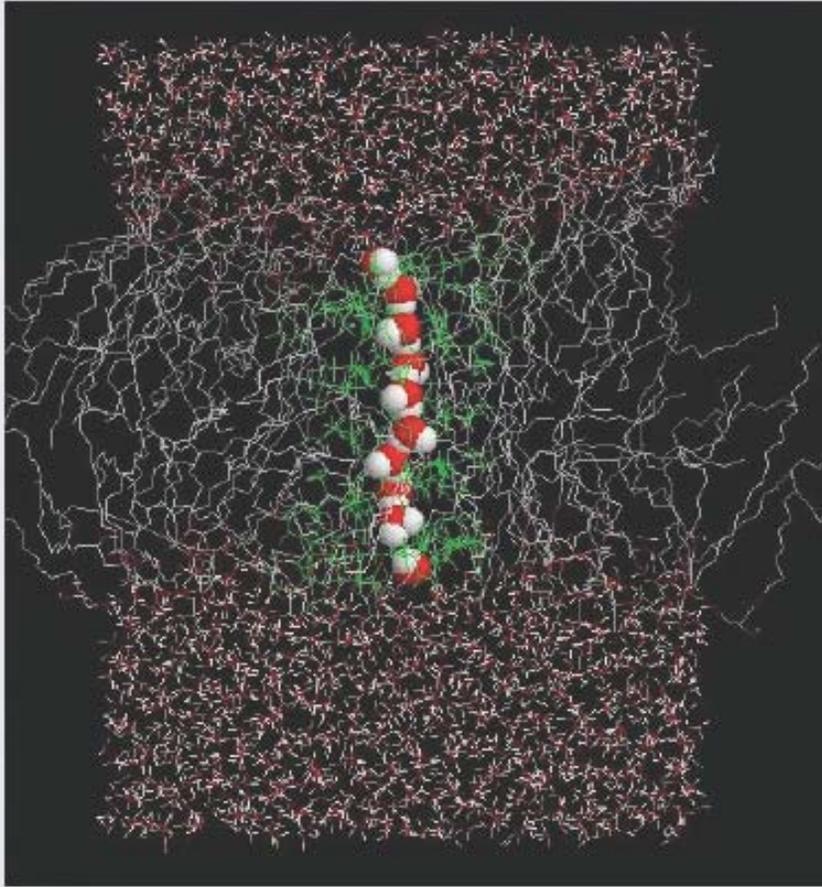


The resultant ‘glassy’ structures were relatively disordered, but it was possible to discern that most of the molecules preferred to freeze along the interior of the nanotube wall in a ‘square-ice’ pattern. This is similar to the proposed structure of Koga *et al.* [Nature 412 (2001) 802] where nanotube-ice forms as a square-ice sheet that is wrapped into a cylinder inside the SWNT. Using this structure as our starting point, we then investigated whether it might be energetically favorable to add additional water molecules inside of the square-ice tube. We found that adding up to 14 additional water molecules per 40 Å of the nanotube in the form of a connected ‘water chain’ results in about the same energy per water-molecule.

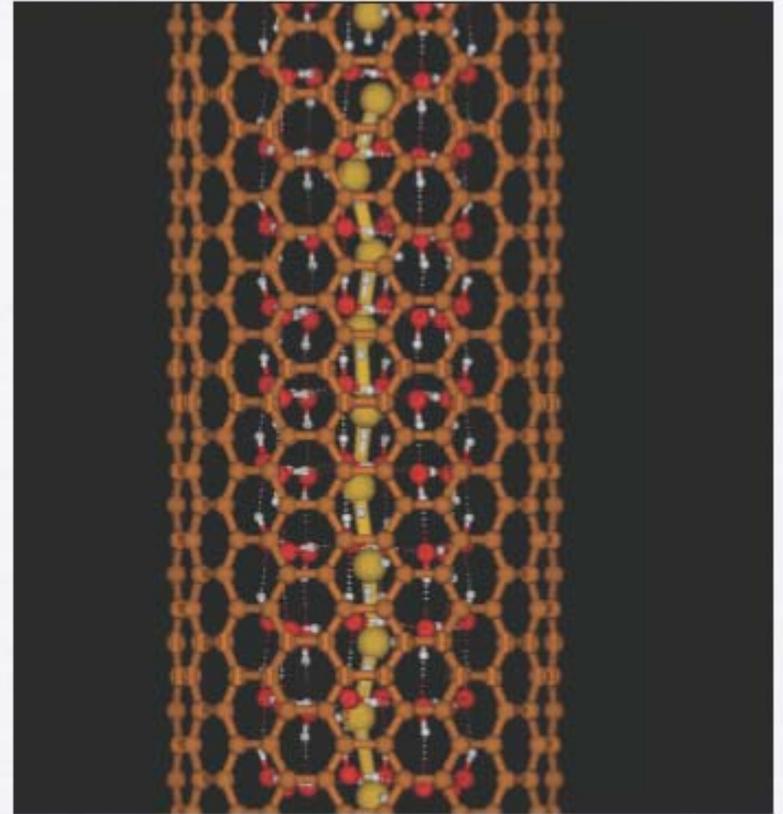


**Proposed structure of nanotube-water. The interior “chain” water molecules have been colored yellow to distinguish them from the exterior “wall” water molecules (colored red).**

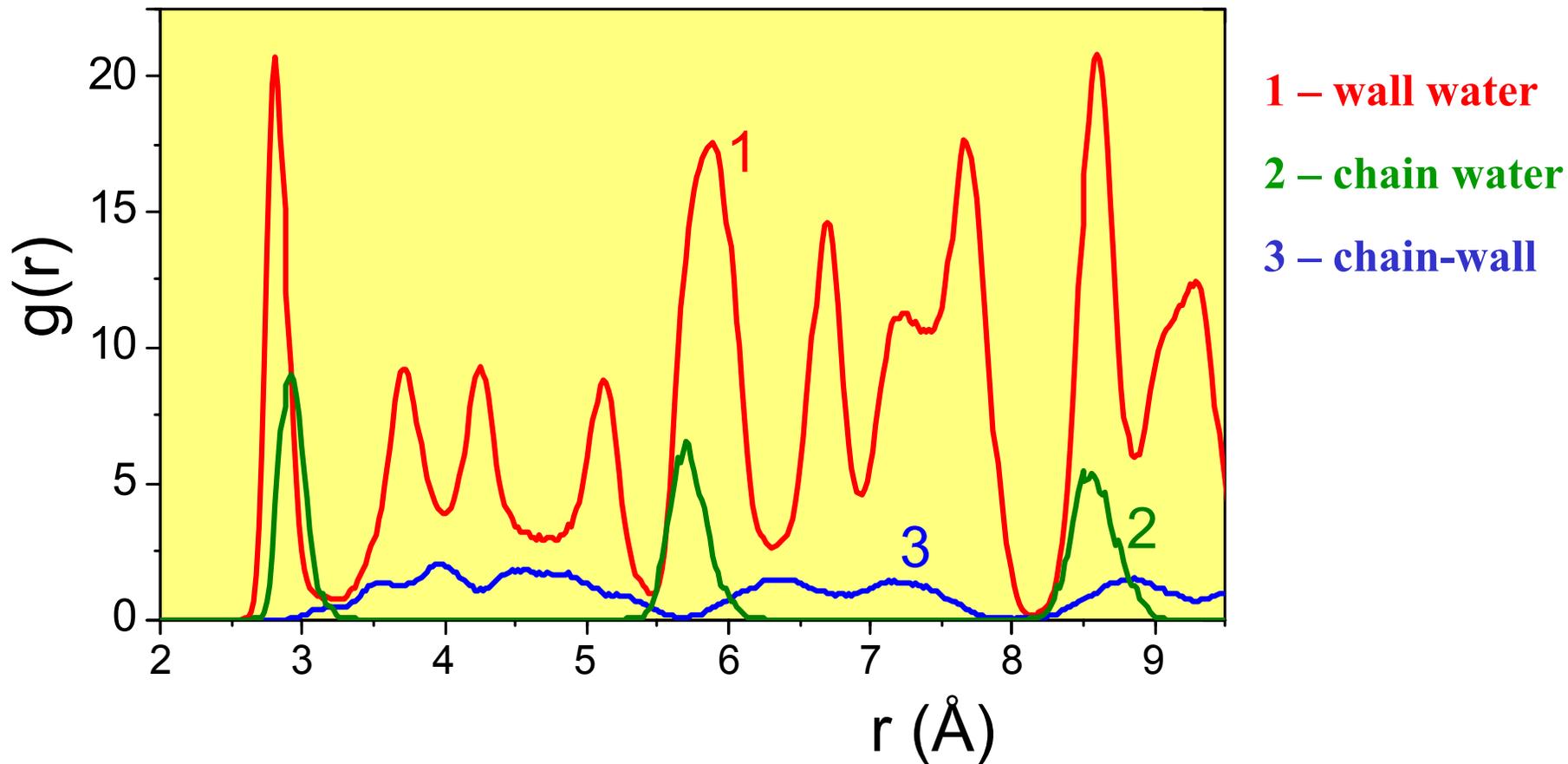
Succinyl linked gramicidin A channel in GMO bilayer (From simulation by Zhen Qin)



Proposed Nano-ice structure



Reminiscent of biological water channels.



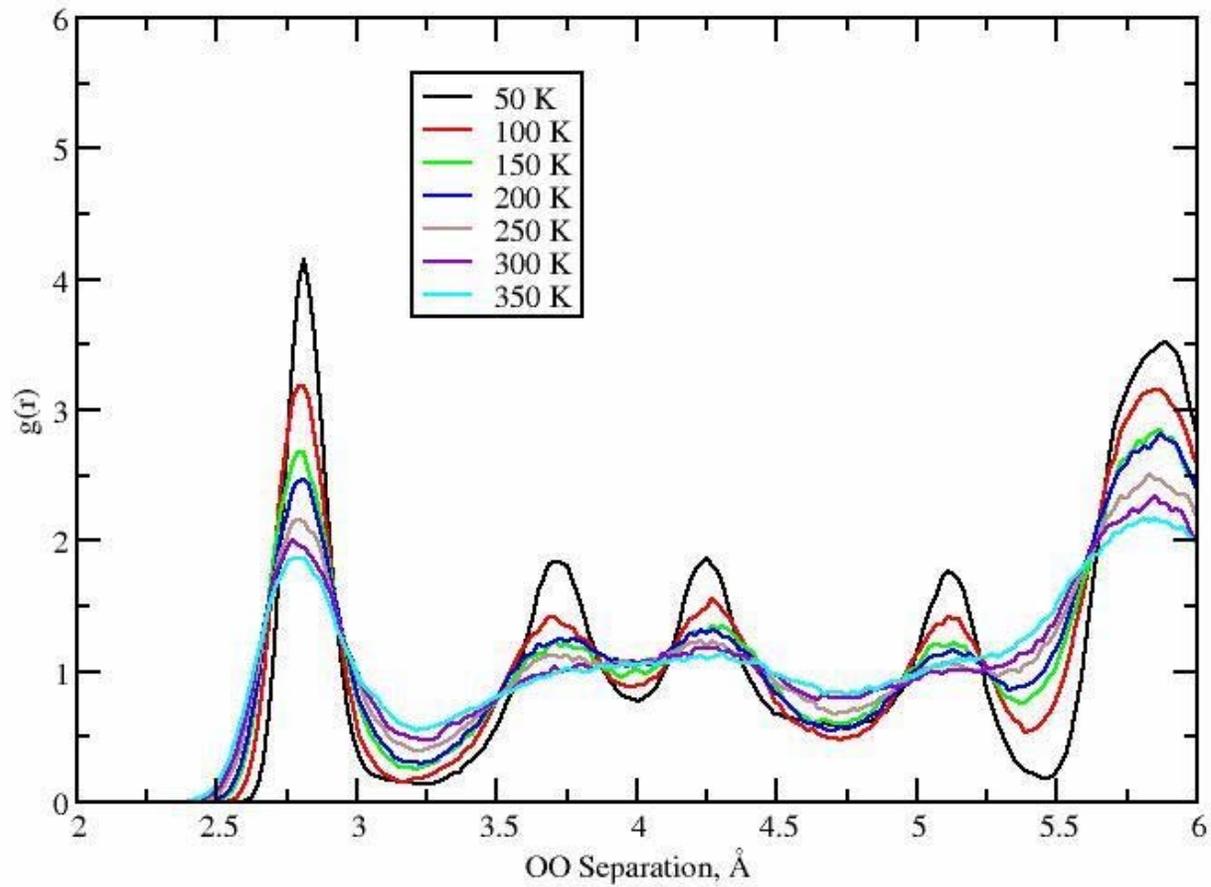
Calculated O-O RDF functions for nanotube-water.

**Chain** and **wall** waters are very structured.

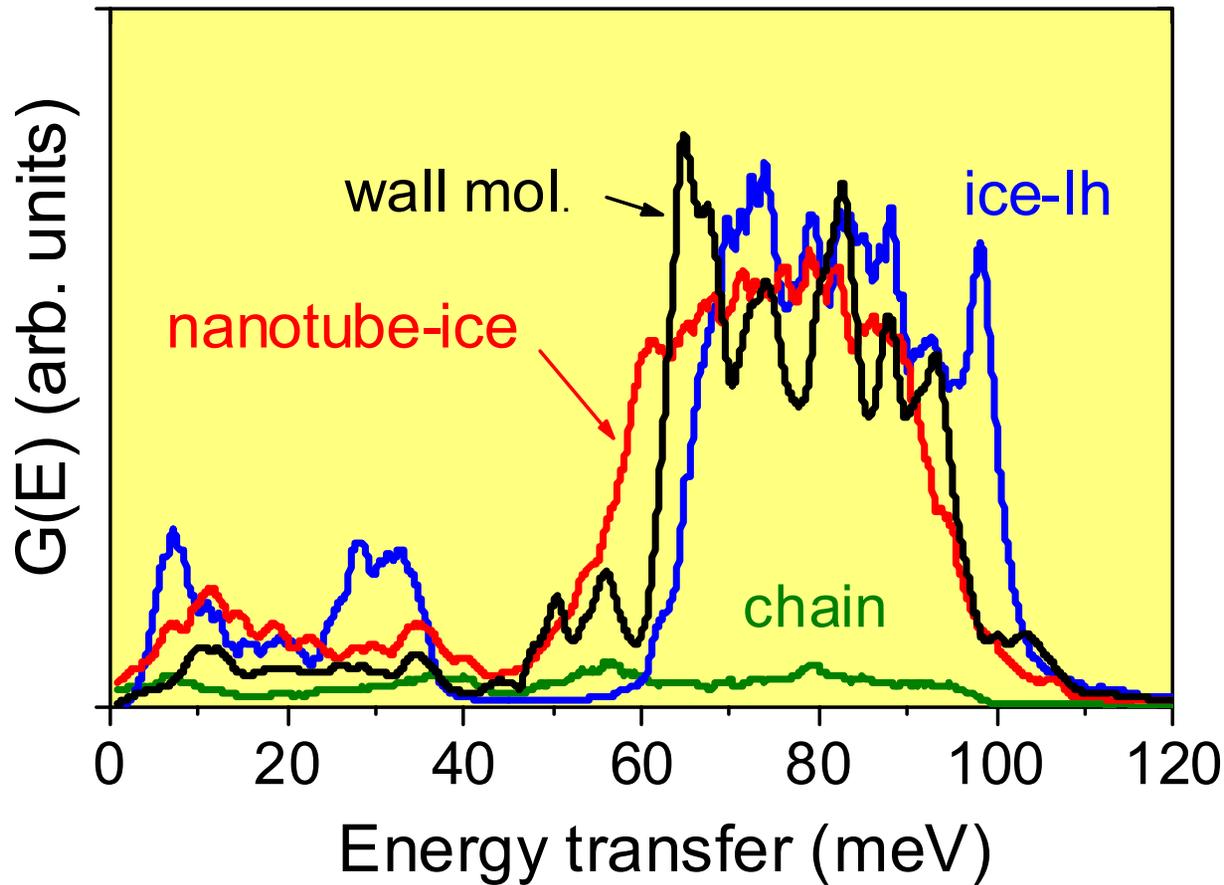
Very little structure between **chain and wall** water molecules.

Chain molecules have less than 2-fold coordination – much less than in the bulk liquid.

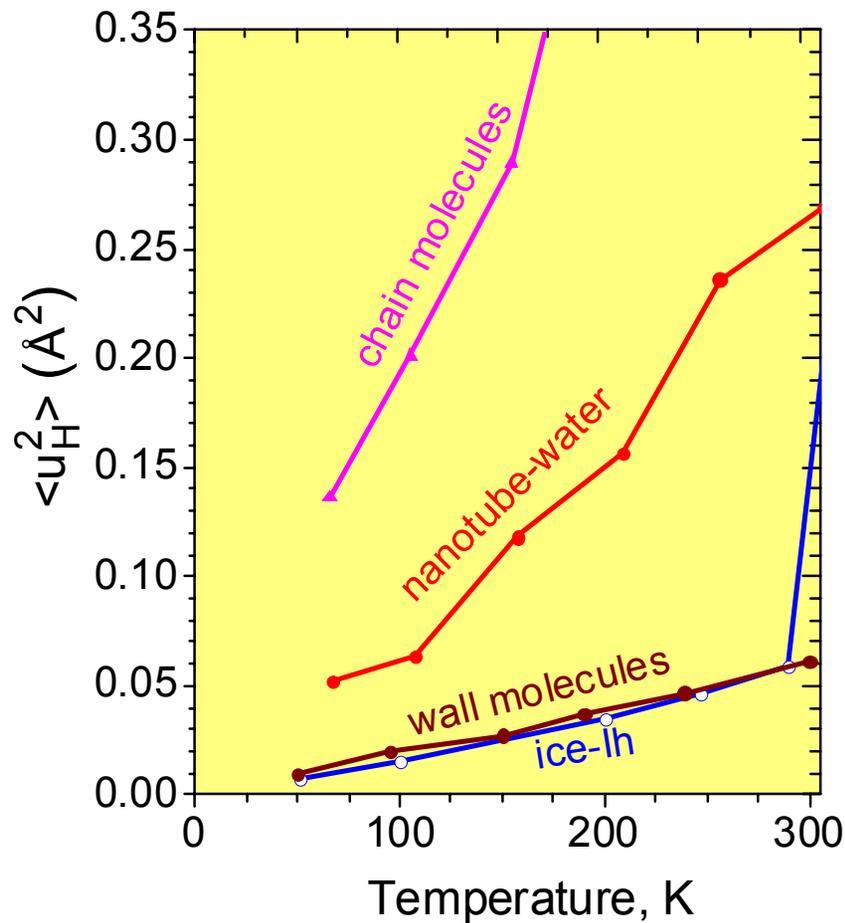
## Nano-Ice RDF's



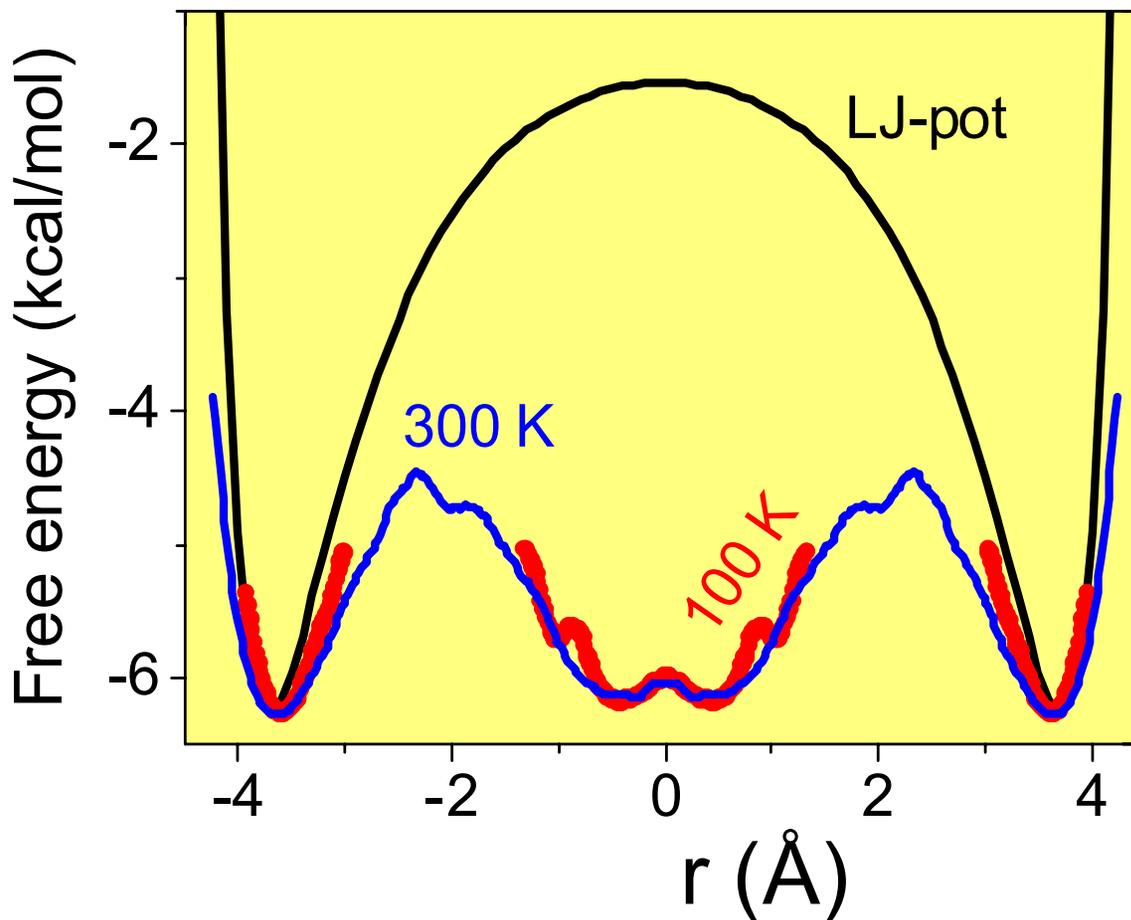
Temperature behavior of calculated RDF function for nanotube-water



Calculated vibrational spectra for **nanotube-ice**, wall molecules alone and **chain water** in nanotube-ice, compared with **ice-Ih**.



Calculated  $\langle u_H^2 \rangle$  for **nanotube-ice**, **wall molecules alone** and **chain water** in nanotube-ice, compared with **ice-Ih**.



**Free energies across the nanotube walls for water molecules in nanotube-water/ice at 100 K (red) and 300 K (blue). The L-J potential (black) provides the minima for location of individual water molecules initially entering the SWNT.**

# Summary

ND and INS measurements in parallel with MD simulations clearly showed the entry of **water into open-ended SWNT** and identified an **ice-wall plus water-chain structure**. The **soft dynamics** of nanotube-water/ice arises mainly from the **drastic change in hydrogen-bond connectivity of the central water-chain**. An average coordination number of 1.86 was found due to continually breaking/forming of the hydrogen bonds between a water molecule with its two nearest neighbors even at ~50 K. **Anomalously enhanced thermal motions in the water-chain**, interpreted by a low-barrier, flattened, highly anharmonic potential well, explains the large mean-square displacement of hydrogen and fluid-like behavior of nanotube-water at temperatures far below the nominal freezing point. This behavior agrees qualitatively with the expected water and proton transport via the nominally hydrophobic inner region of transmembrane proteins such as aquaporin, gramicidin, and bacteriorhodopsin [Y. Kong and J. Ma, Proc. Natl. Acad. Sci. USA **98**, 14345 (2001); R. Pomes and B. Roux, Biophys. J. **82**, 2304 (2002); J.K. Lanyi, J. Phys. Chem. B **104**, 11441 (2000)].

## *Further Studies*

- **Water confined in nanotubes appears to be in an intermediate state having both solid- and fluid-like properties. Its nature has to be further clarified.**
- **\*A stretched (negative-pressure), low-density state of water in nature?**
- **\*The existence of a new critical point (continuous solid-liquid transition)?**

\* Poole *et al.* (1992), Stanley *et al.* (2002), Harrington *et al.* (1997), Dciotino *et al.* (1997), Netz *et al.* (2001)