Will Water Flow Through Nanotubes?

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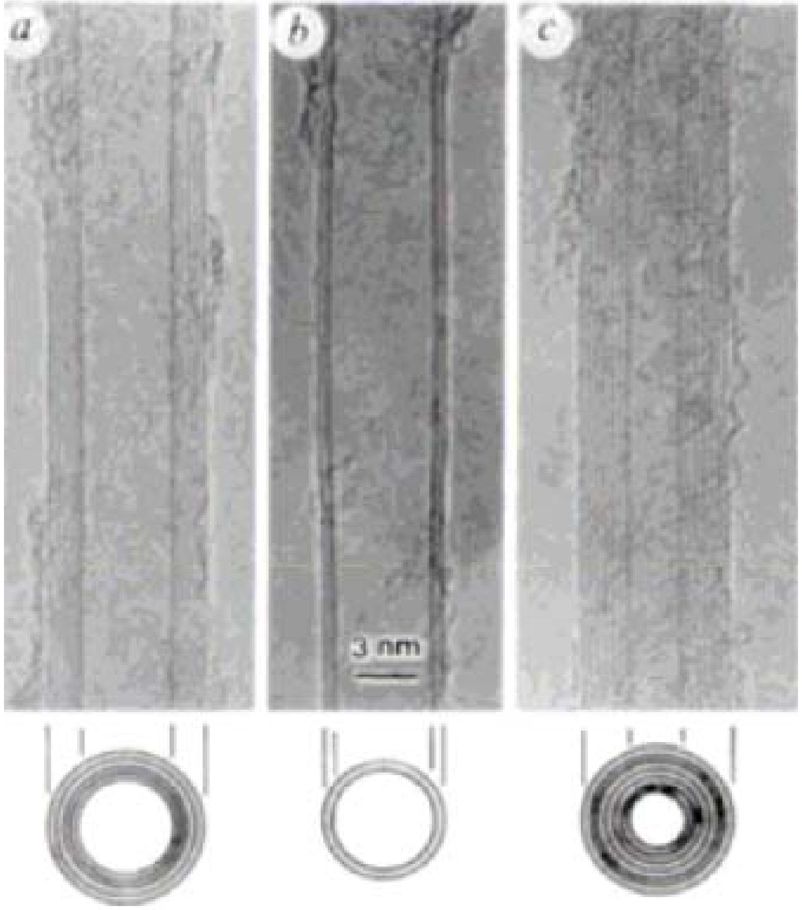
Carbon Nanotubes : A Review

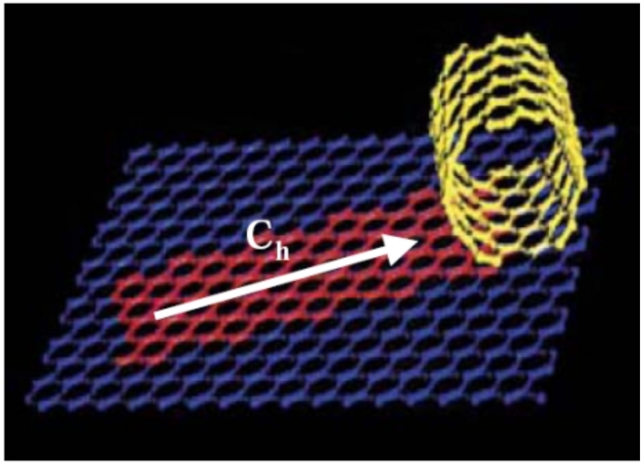
- Allotropes : Diamond, Graphite, Fullerenes and Nanotubes
- 1985 Kroto discovers C_{60} . Axes of Symmetry. 20 hexagons, 12 pentagons
- Molecular scale carbon fibres 1991 – Iijima : Nanotubes
- Novel electrical, mechanical and optical properties.
- Hydrophobicity and Wetting : Idea of Nanofluidic channel
- SWNT’s and MWNT’s
- Arc-Evaporation Method : Bulk quantity of CNT’s

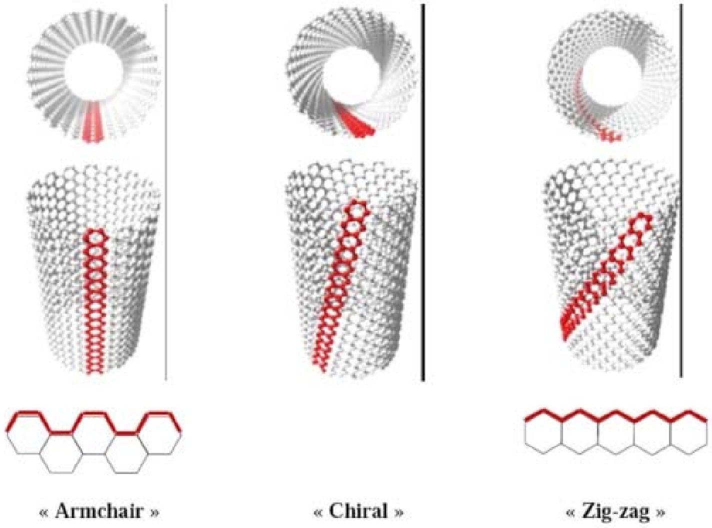


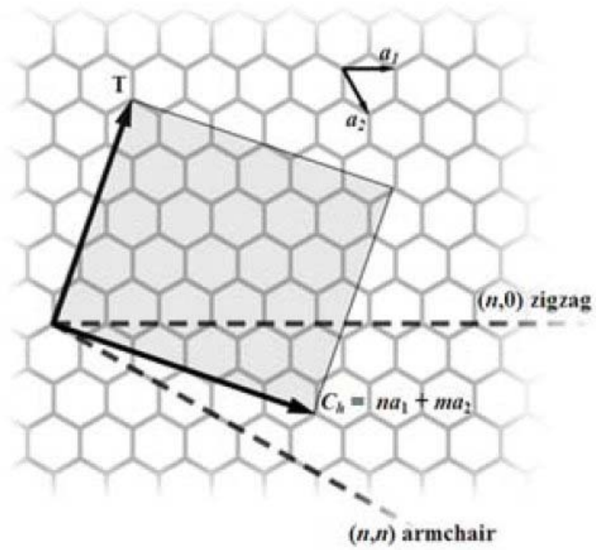
Ref. : Ijima (NEC, Tsukuba, Japan), Helical microtubules of graphitic carbon, Nature, 354, 56 (1991).

Structure and Notation

- Graphene cylinders Hybridization
- $\mathbf{C_h} = n\mathbf{a_1} + m\mathbf{a_2}$
- Zigzag , Armchair, Chiral.
- Unit Cell : T Vector





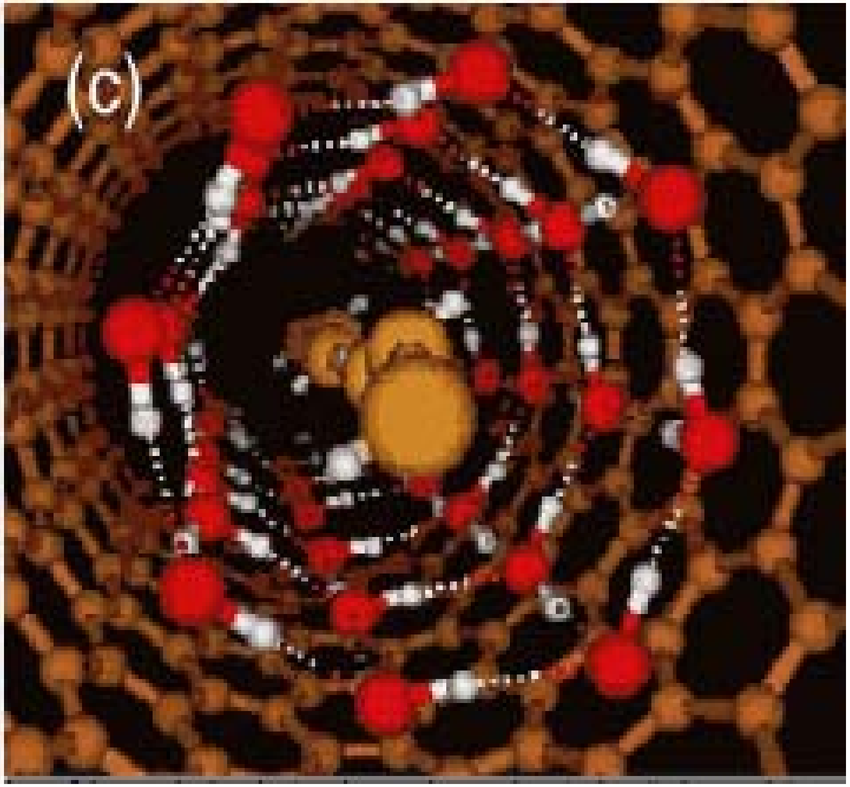


Water at Nanoscale

- Water when confined in nanotubes exhibits 15 polymorphic phases of bulk ice
- Regions in the nanotubes are observed where the liquid-solid interface diminishes.
- Water behaves like a viscous fluid when confined to channels less than two nanometers wide
- Water begins to behave like a solid in the vertical direction, but retains fluidity in the horizontal

Water nano-interactions

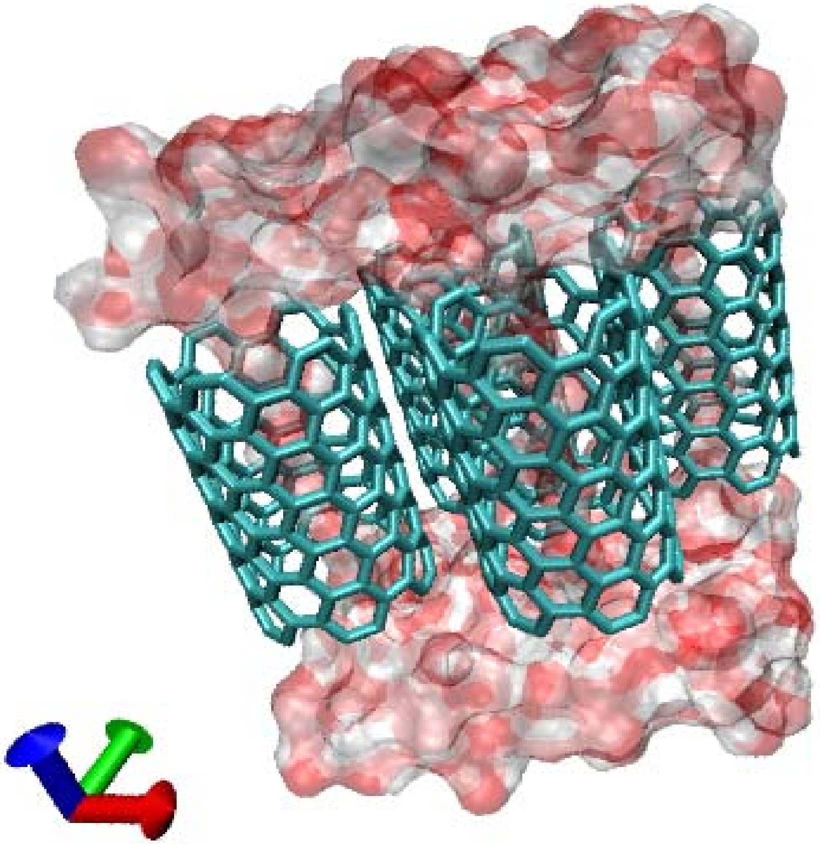
- H-bonding becomes weaker for water close to the nano-tube ends
- Enhanced diffusion noted in Gold nanotubes
- ‘Shell+Chain’ configuration inside carbon nanotubes below 200 K
- High H-bonding fluctuations for this configuration



Water Interactions

- At 210 K the configuration breaks down
- Water entering an 8 Angstrom wide nanotube loses 10kcal/mol on H-bonding
- Gains 4 kcal/mol on van der Waals
- H-bond avg-age –
    - 5.6pS in nanotube
    - 1 pS in bulk
- Better oriented H-bonds inside nanotubes

Computational Chemistry



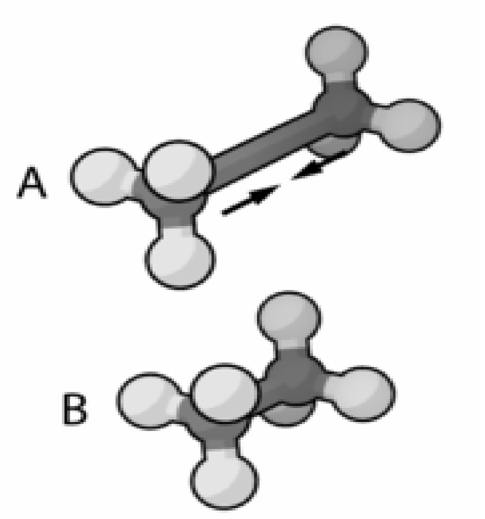
- Setting up virtual experiments
- Explore properties of nanotubes
- Provide a basis for theory development
- Simulation leading to experimental data

Techniques

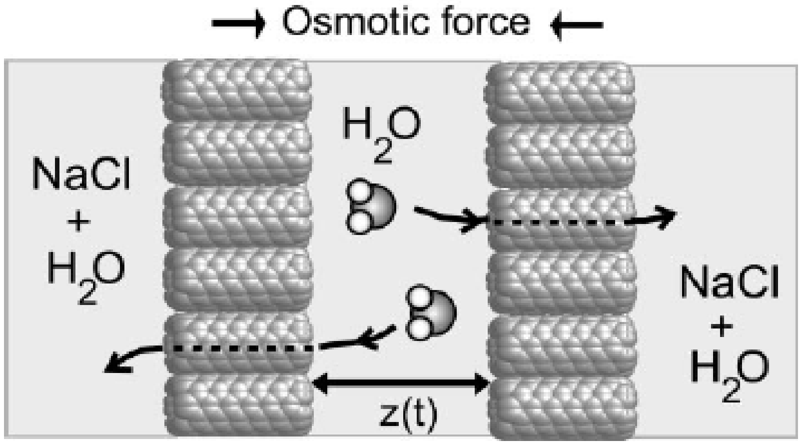
$$V(r^N) = \sum_{bonds} \frac{1}{2}k_b(l - l_0)^2 + \sum_{angles} \frac{1}{2}k_a(\theta - \theta_0)^2$$

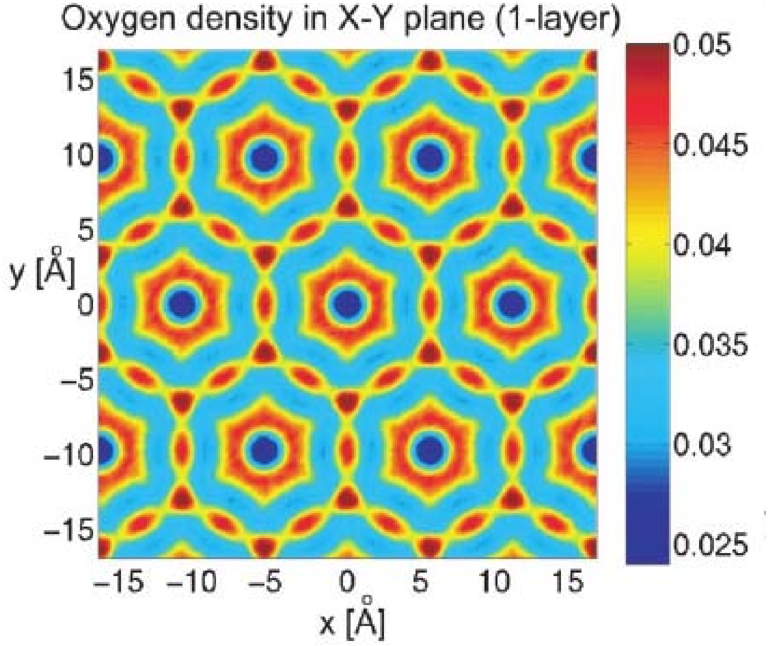
$$+ \sum_{torsions} \frac{1}{2}V_n[1 + \cos(n\omega - \gamma)] + \sum_{j=1}^{N-1} \sum_{i=j+1}^{N} \left\{ 4\epsilon_{i,j} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

- Energy Minimization
- Ab initio methods
- Hartree Fock Methodology and Density Functional Theory
- Classical Molecular Dynamics and force fields



Inferences: Case Study I

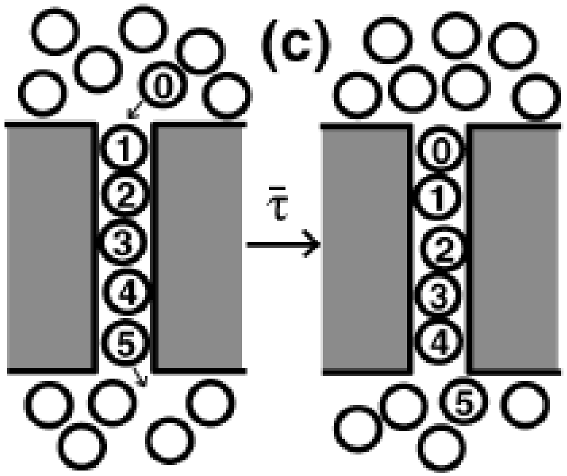


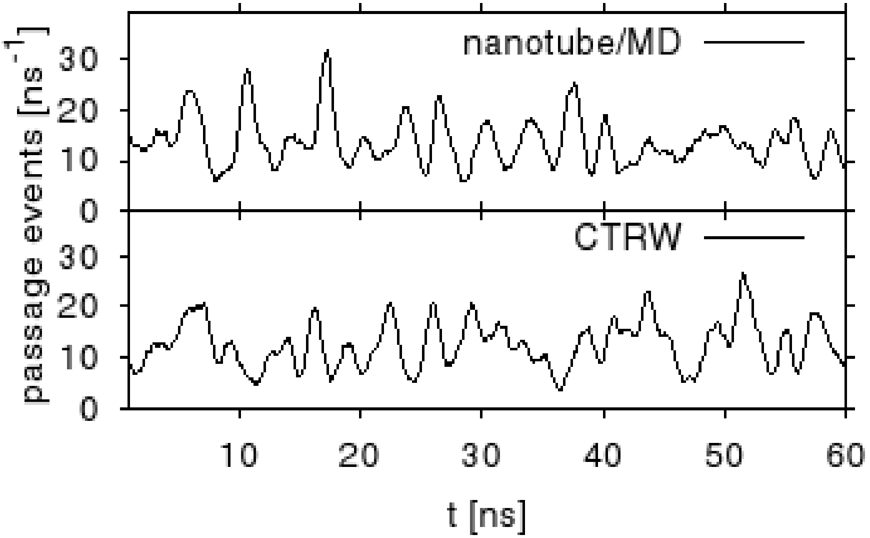

Oxygen density in X-Y plane (1-layer)

- Set up details Hexagonally packed (6,6) nanotubes, van der Waal's forces holding together, amber field, 180ns @ 2fs, Particle Mesh summation
- Results

  Small but frequent back flow against osmotic gradients, narrow channels increase flow rates, nearly frictionless flow, stable 2D pattern of water, well formed H bonding.

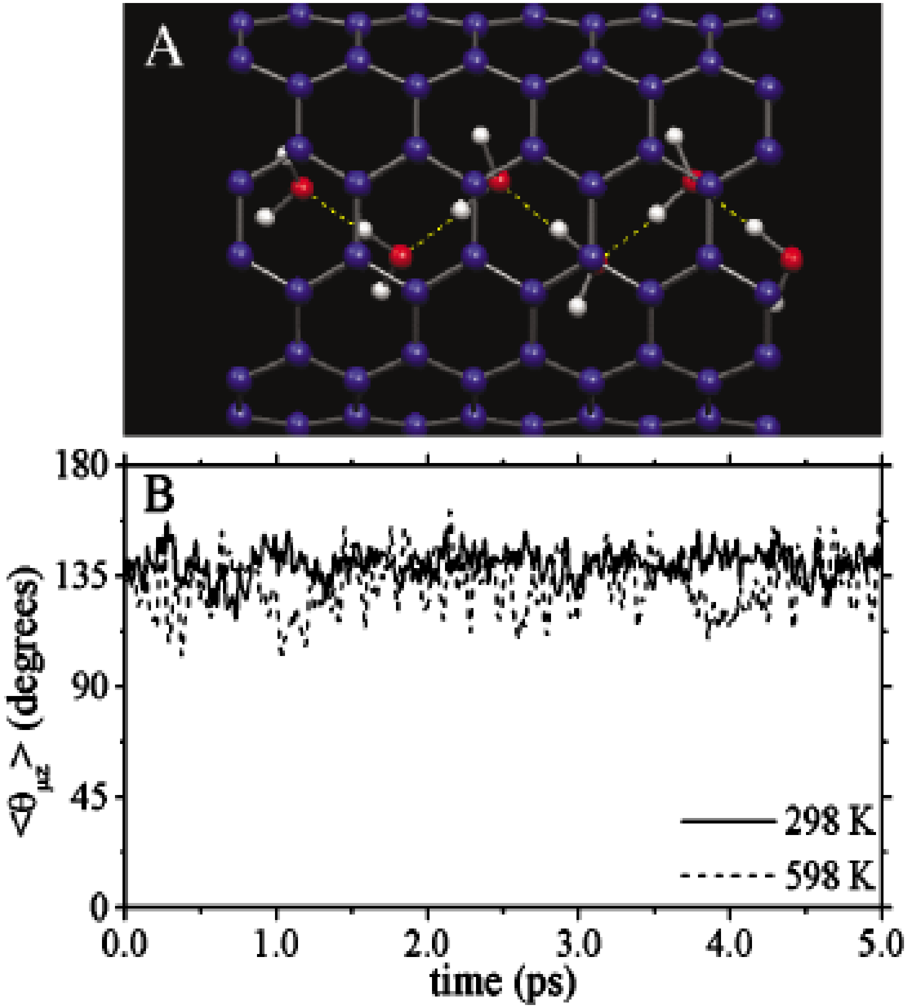
Inferences: Case Study II





- Set up details Water carbon interactions with Lennard- Jones potential, entry and exit events counting.
- Results
  Flow occurs in bursts, collective water motion, can be described as a continuous time random walk model, avg number of translocations tends to a constant while actual follows a random distribution, obtained probabilities of various events.

Inferences: Case Study III



- Set up details

  Use of density functional theory with pseudopotentials for (6.6) CNTs, classical MD for initial data, 2ps @ 1fs steps.

- Results

  Rigidity of water wire, require 598K for water flipping, ordered dipoles at 298K, 2 separate Hydrogens (IR Spectroscopy), calculate dipole moment changes, delocalized proton over water in tube.

Experimental Results

Experiment 1

(Holt *et al)*

- Fabrication of DWNT nanotubes (1-2 nm)
- Developing a nanotube membrane
- Flow rates found to be much greater than predicted by continuum flow model
- Observed flux around 12 molecules per nm^2
- Results match with MD simulations

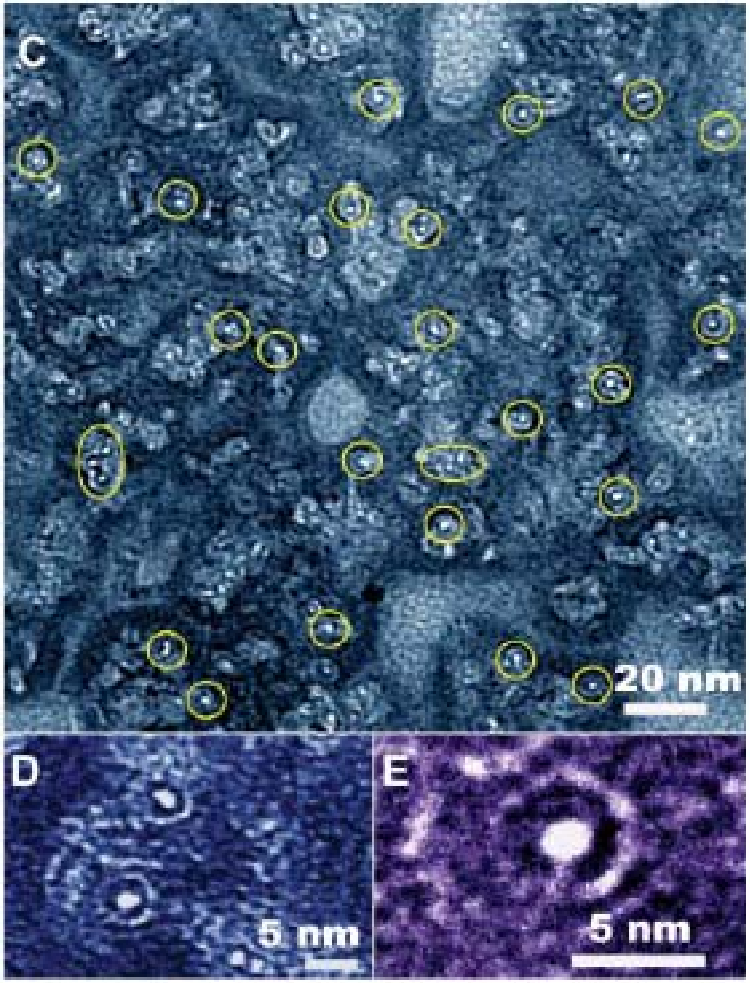
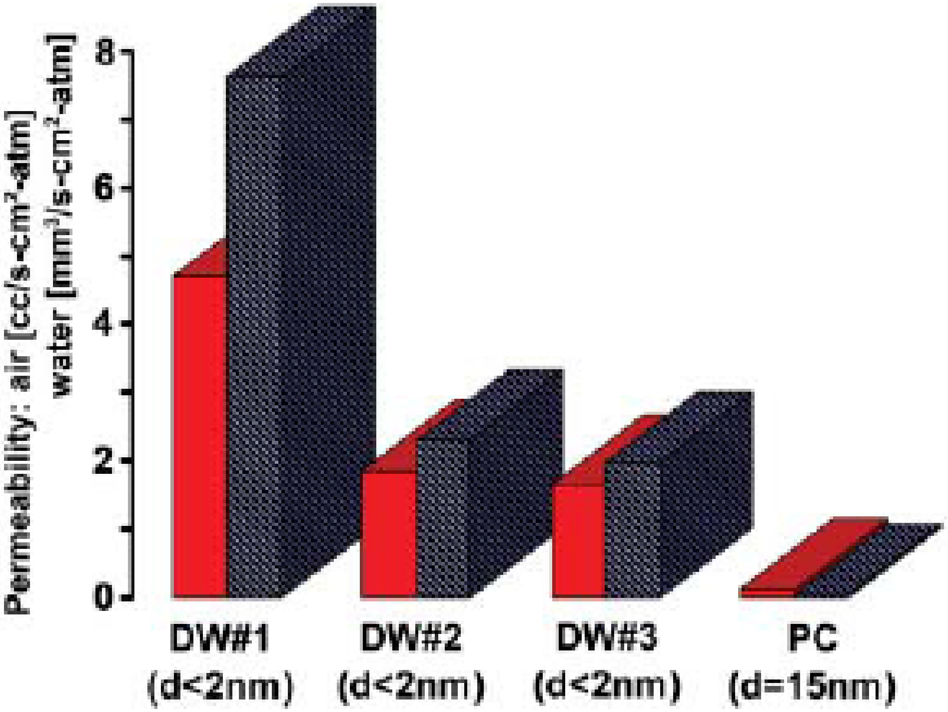


Fig. 4. Air (red) and water (blue) permeability as measured for three DWNT membranes (DW#1, 2, and 3) and a polycarbonate membrane (PC). Despite considerably smaller pore sizes, the permeabilities for all DWNT membranes greatly exceed those of the polycarbonate membrane.

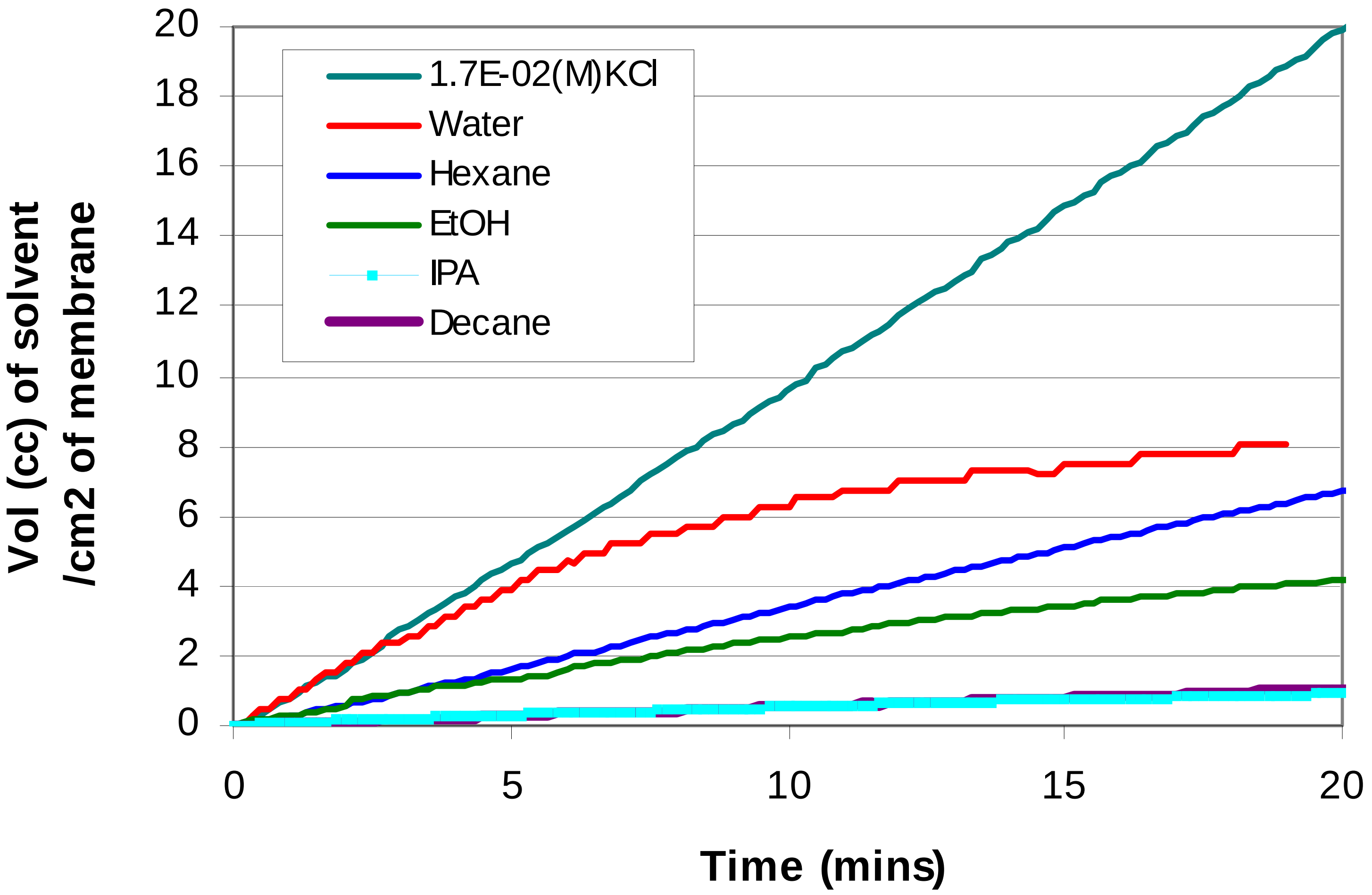


μ

Experiment 2

(M. Majumder, N. Chopra, R. Andrews, B. J. Hinds)

- Membrane of multiwalled carbon nanotubes(7 nm diameter)
- Flow rates found to be four to five orders of magnitude greater than conventional models
- Large slip lengths(3-70 µm)



Flow rates vary with time for hydrogen bonded molecules

Maybe due to flow related ordering or formation of bubbles.

Applications

- Serve as models to study flow through biological channel
  - study energetics of ion translocation through hydrophobic channels
  - study of sensitivity of ion permeabilities with variations in pore width
- Nucleic acid tansport through nanotubes
  - study transport through biological membranes using nanotubes as a model
  - MD simulations show hydrophobic interactions can trap RNA molecules in nanotube pores ---- separation devices ?

Applications

- Water purification
  - nanotube membarnes – high selectivity, high flow rates
  - electochemically control interaction of water with nanotubes
  - still more research required
- Waste water treatment
  - MWNT's -noted for absorption of toxic substances like cadmium, lead, 1,2-dichlorobenzene