

Title: Enhanced flow of water through nanotubes

Date: Mar 04, 2015 02:00 PM

URL: <http://pirsa.org/15030109>

Abstract: <p>We investigate through non-equilibrium molecular dynamic simulations the flow of anomalous
 fluids inside rigid nanotubes. Our results reveal an anomalous increase of the overall mass flux
 for nanotubes with sufficiently smaller radii. This is explained in terms of a transition from a
 single-file type of flow to the movement of an ordered-like fluid as the nanotube radius increases.
 The occurrence of a global minimum in the mass flux at this transition reflects the competition
 between the two characteristic length scales of the core-softened potential. Moreover, by increasing
 further the radius, another substantial change in the flow behavior, which becomes more evident at
 low temperatures, leads to a local minimum in the overall mass flux. Microscopically, this second
 transition is originated by the formation of a double-layer of flowing particles in the confined
 nanotube space. These nano-fluidic features give insights about the behavior of confined isotropic
 anomalous fluids.</p>

What is the mystery?

Why should we care?

What are the clues?

What is our hypothesis?

What are our results?

How can we use these anomalies?

Conclusions

Our Group



What is the mistery?

M. Chaplin, <http://www1.lsbu.ac.uk/water/>

Such a simple liquid

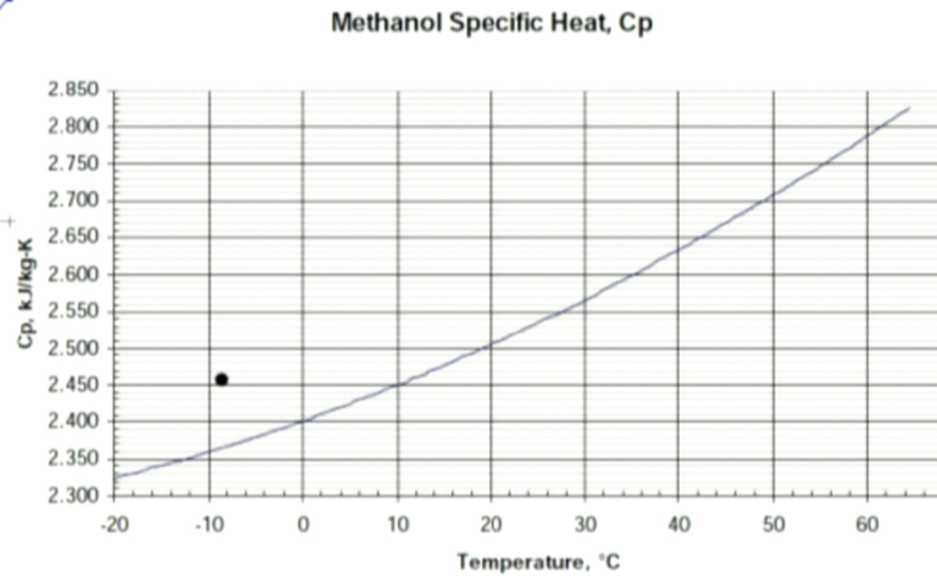
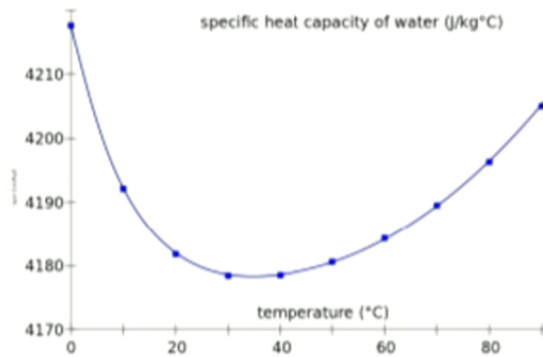
72 anomalies



Specific Heat

methanol: Lombari, Ferrari, Salvetti, CPL 300 (99)

$$\blacktriangleright C_P = \left\{ \frac{\partial Q}{\partial T} \right\}_P$$

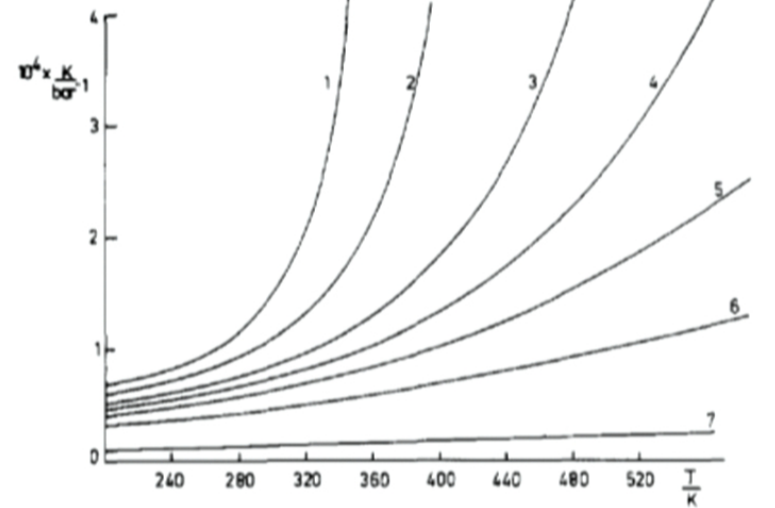
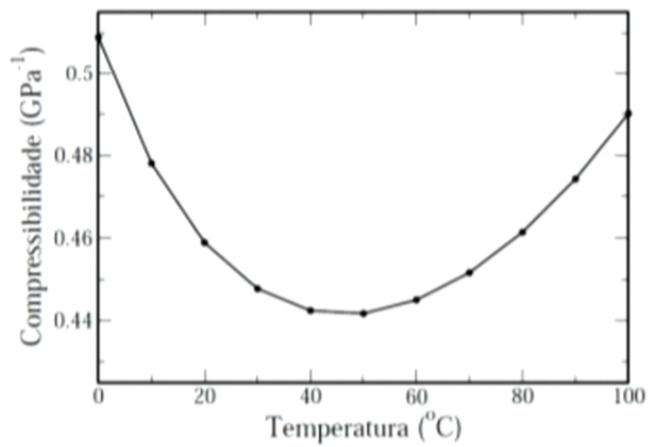


Compressibility

water: Speedy, Angell, JCP 65, 351 (76)

toluene: Minassian, Bouzar, Alba, JPC 92, 487 (88)

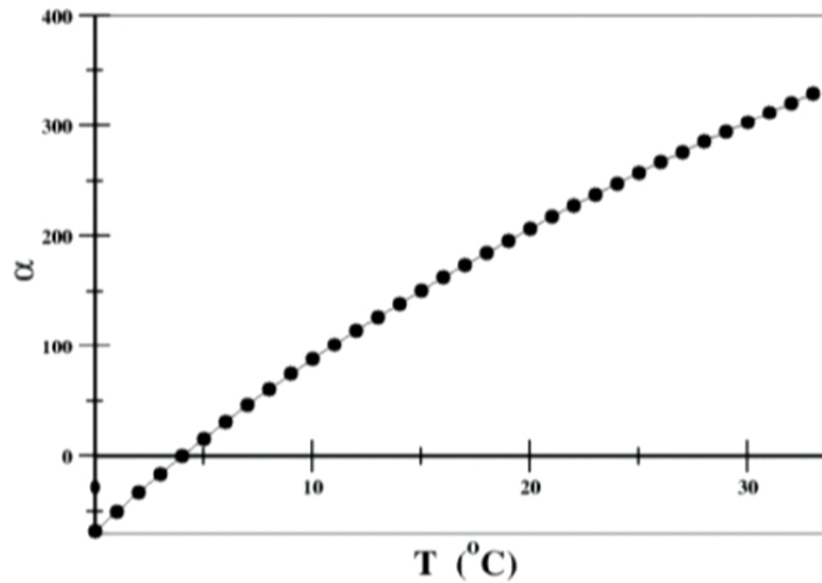
$$\triangleright K_T = -\frac{1}{V} \left\{ \frac{\partial V}{\partial P} \right\}_T$$



Thermal Expansion

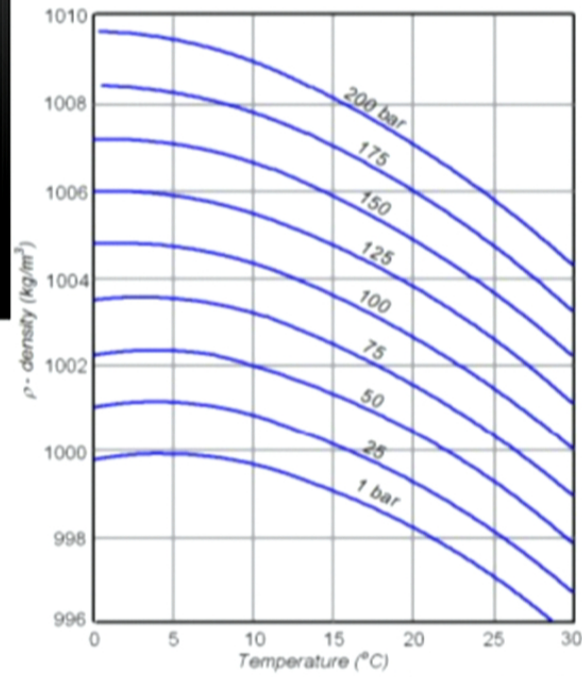
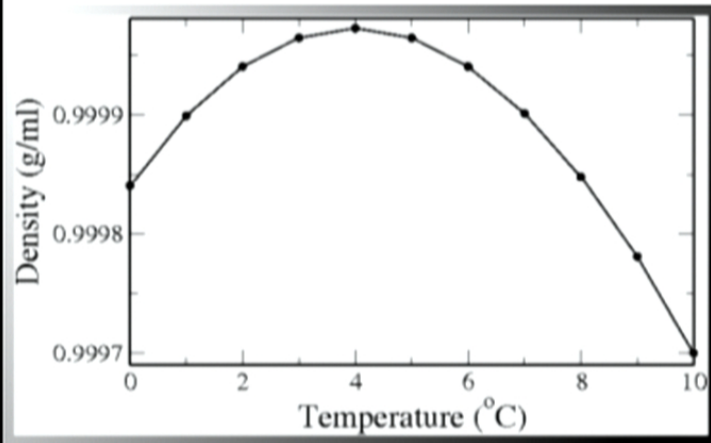
Kell, J. Chem. Eng. Data 20, 97 (75)

$$\alpha_P = \frac{1}{V} \left\{ \frac{\partial V}{\partial T} \right\}_P$$



Density

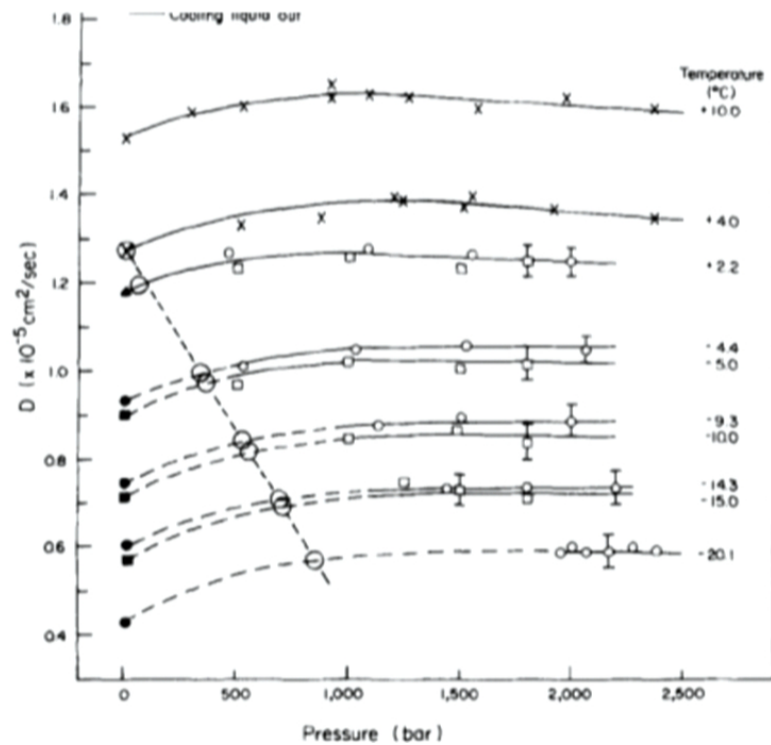
Kell, J. Chem. Eng. Data 12, 66 (67)



Diffusion

Angell, Finch, Bach 65, 3063 (76)

► $\langle r(t)r(0) \rangle = 6Dt$



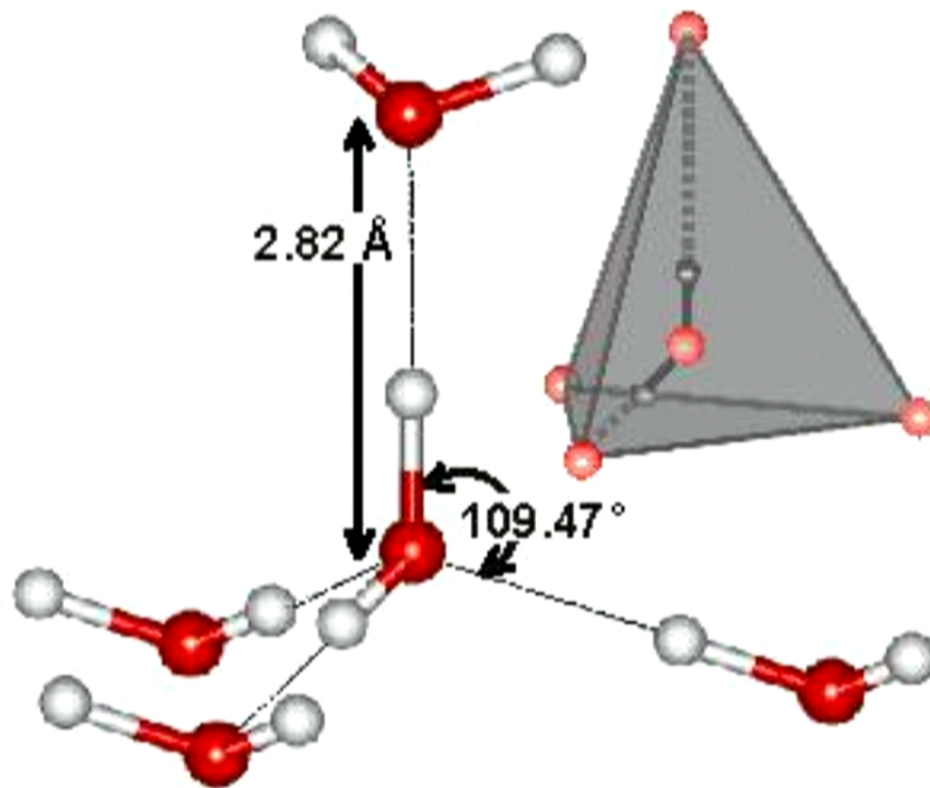
Why should we care?

- ▶ Specific Heat, Thermal Conductivity, High Vaporization Heat – Life
- ▶ Low Compressibility – More land
- ▶ Density – Rivers freeze on top
- ▶ Diffusion anomaly – Transport of nutrients

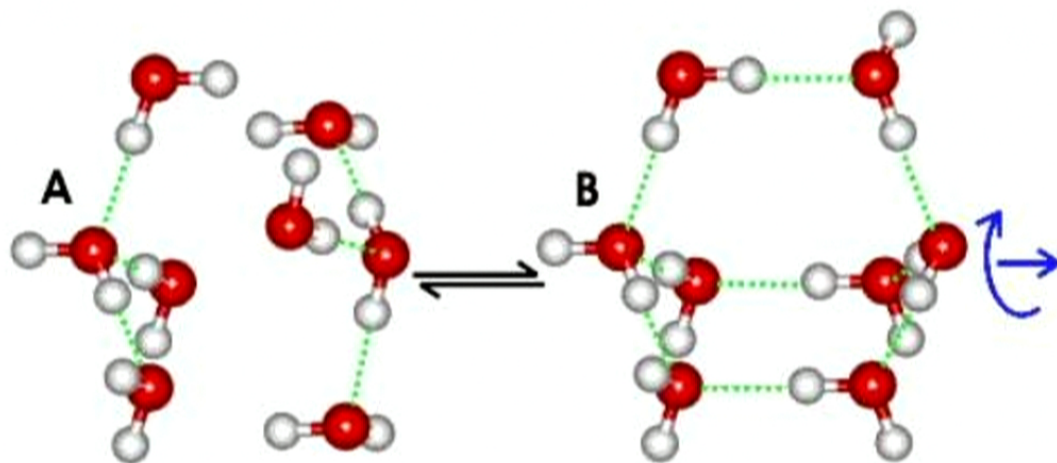
What are the clues?

- ▶ Bonds
- ▶ Polarizability
- ▶ Agreggates

Water Molecule



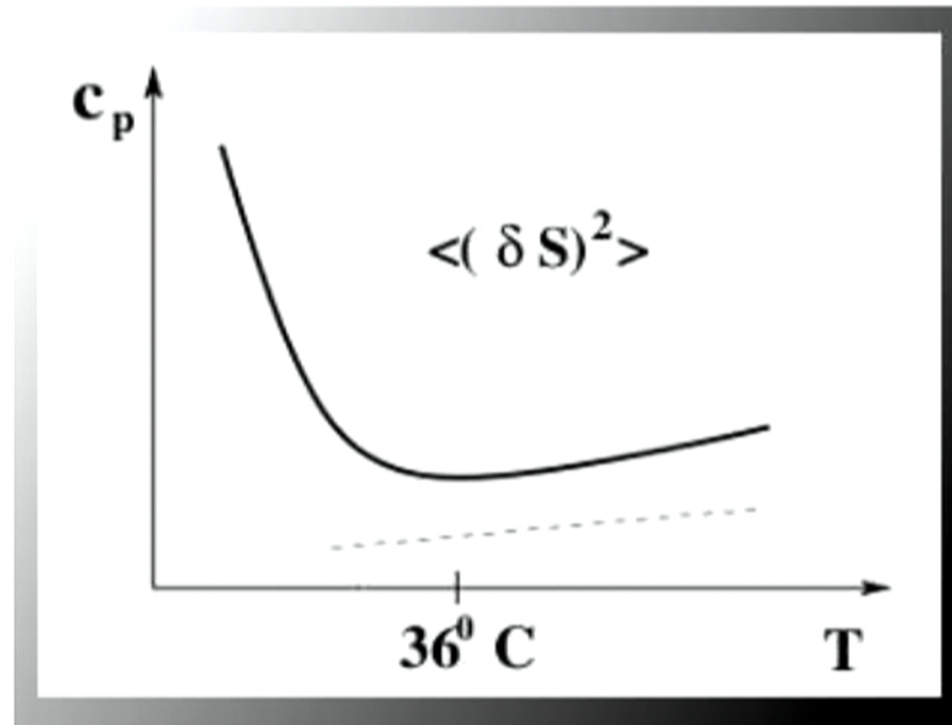
Two Scales



Specific Heat = Fluctuation in the Entropy

Stanley, Pramana 53, 53 (99)

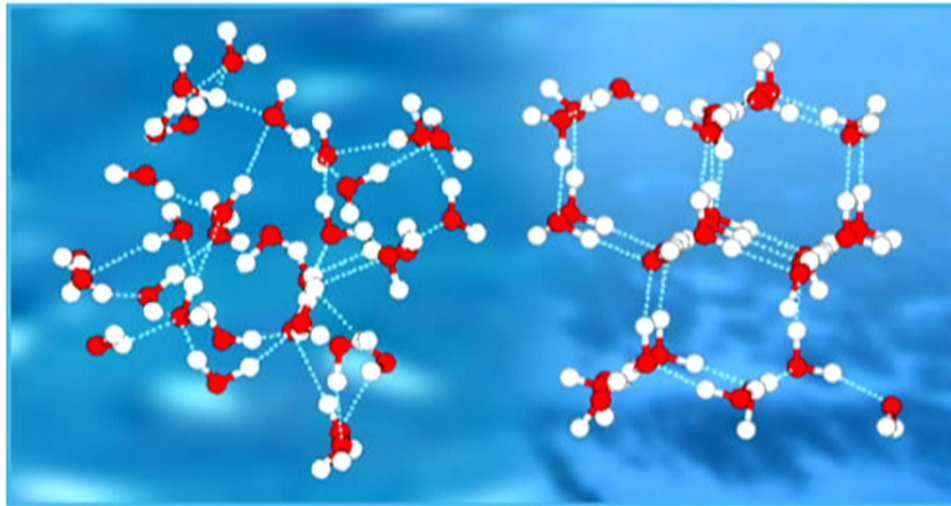
▶ $C_p \propto \langle (S - \langle S \rangle)^2 \rangle$



Specific Heat = Fluctuation in the Entropy

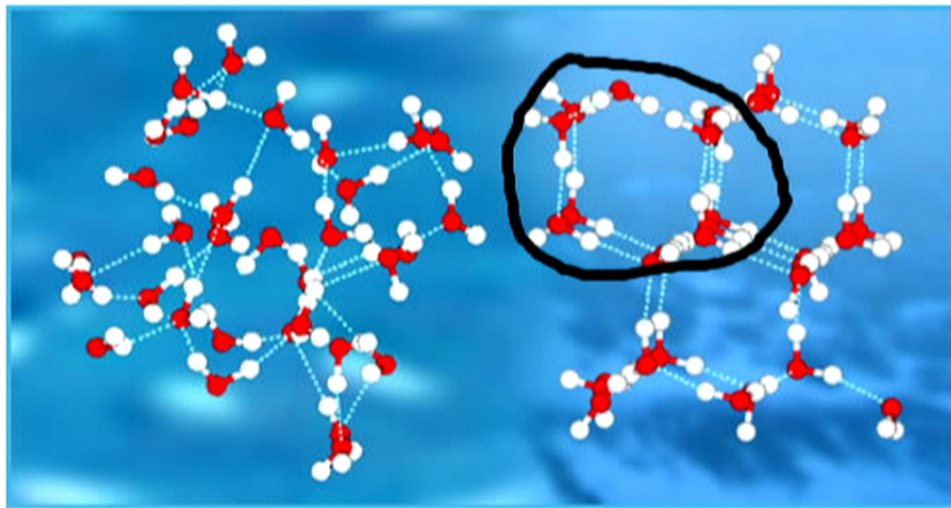
Stanley, Pramana 53, 53 (99)

▶ $C_p \propto \langle (S - \langle S \rangle)^2 \rangle$



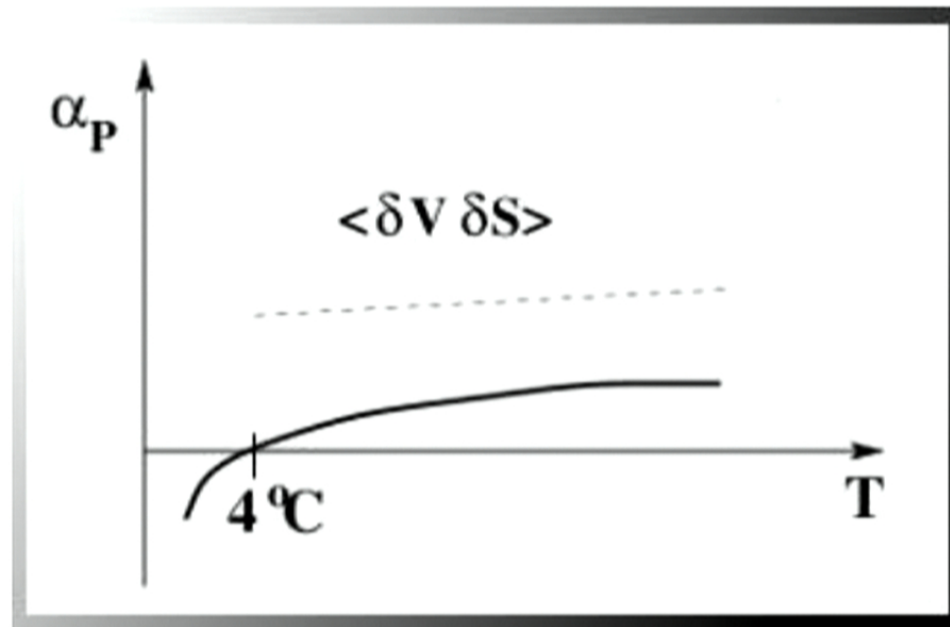
Specific Heat = Fluctuation in the Entropy

▶ $C_p \propto \langle (S - \langle S \rangle)^2 \rangle$



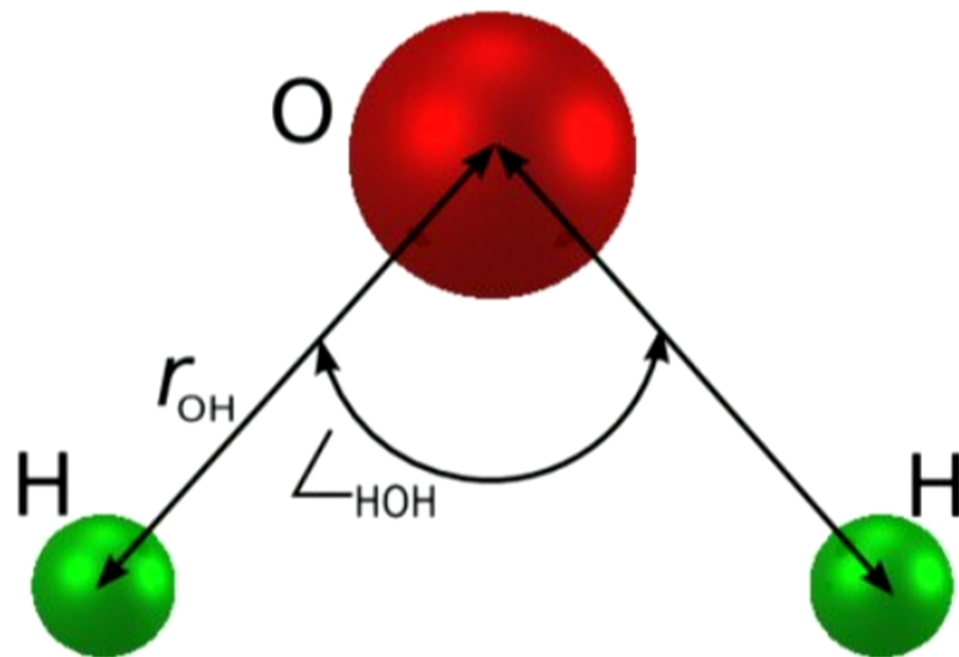
Thermal Expansion = Fluctuation in the Volume and Entropy

▶ $\alpha \propto \langle (S - \langle S \rangle)(V - \langle V \rangle) \rangle$



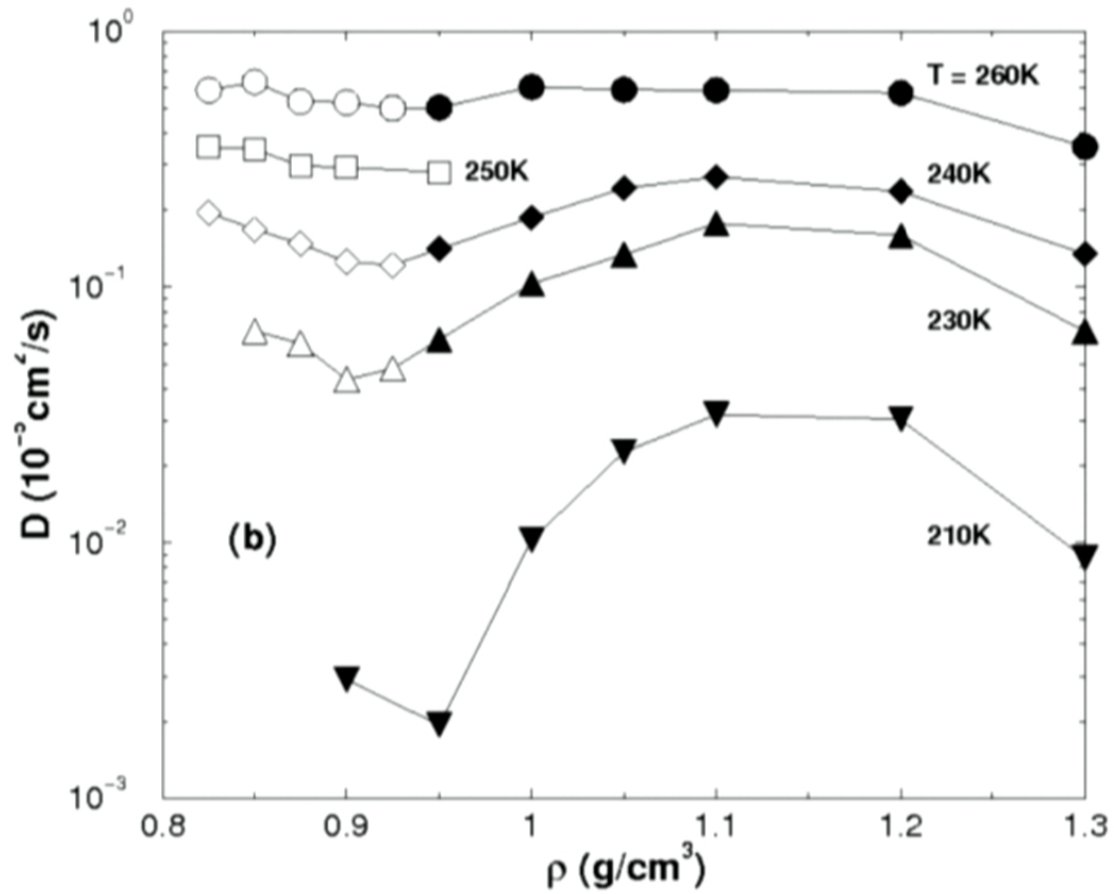
Diffusion - SPC/E

Berendsen, Grigera, Straatsma, JCP 91, 6269 (87)



Diffusion - SPC/E

Netz, Starr, Stanley, Barbosa JCP 115, 344 (01)

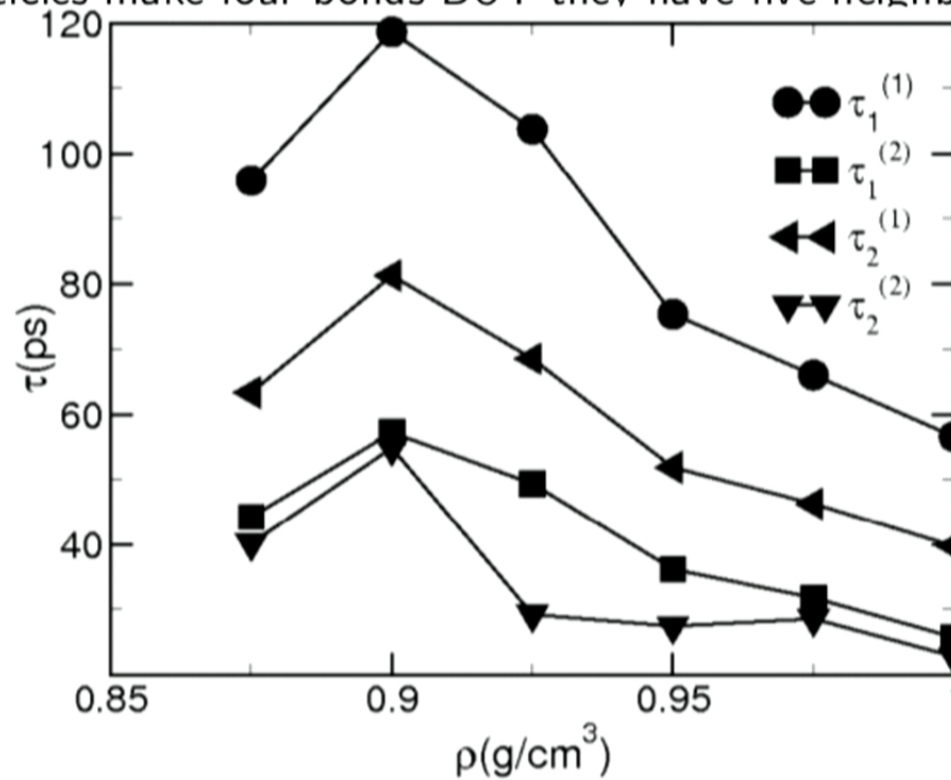


Rotation Diffusion - SPC/E

Netz, Starr, Barbosa, Stanley, JML 101, 159-168 (02)

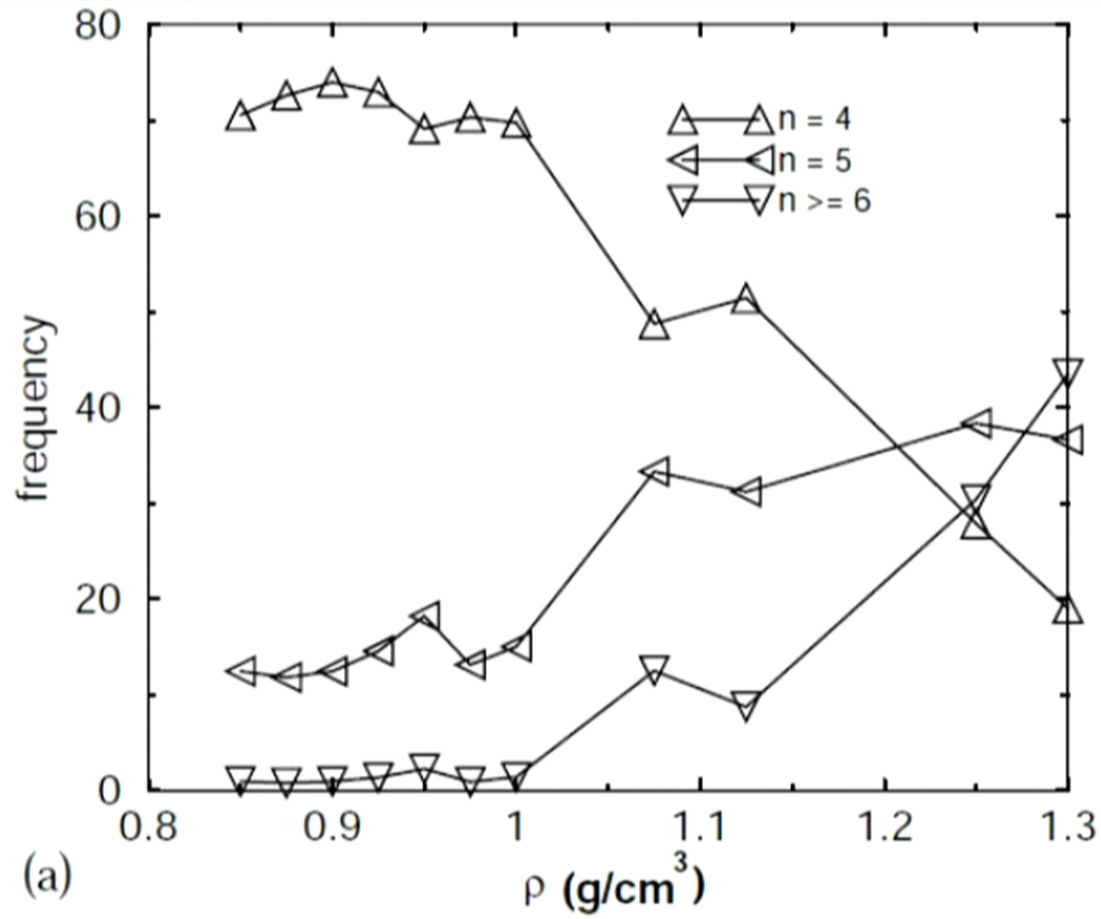
Mazza, Giovanbaptista, Stanley, Starr, PRE 76, 31203 (07)

- ▶ Particles make four bonds BUT they have five neighbors!!!



Frequency - SPC/E

Netz, Starr, MCB and Stanley, Physica A 314, 470 (2002)

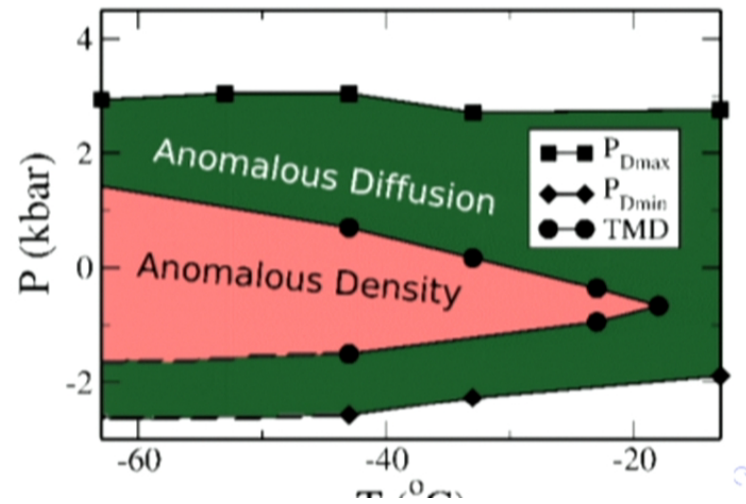
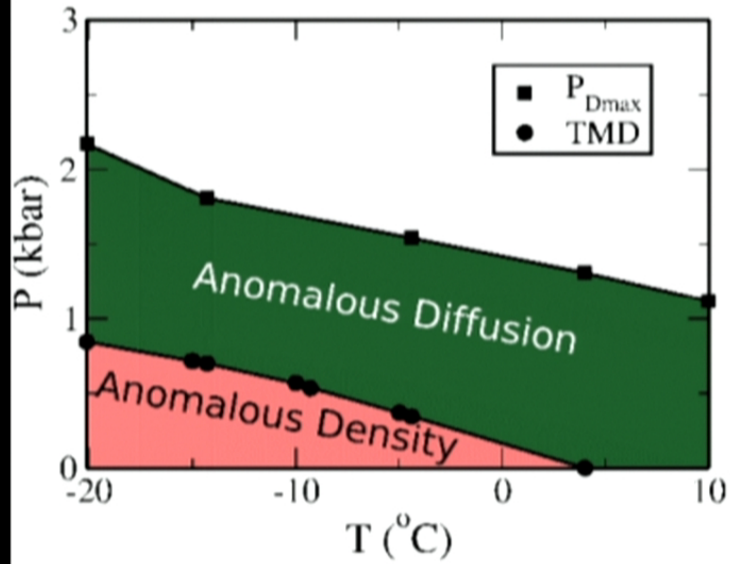


(a)

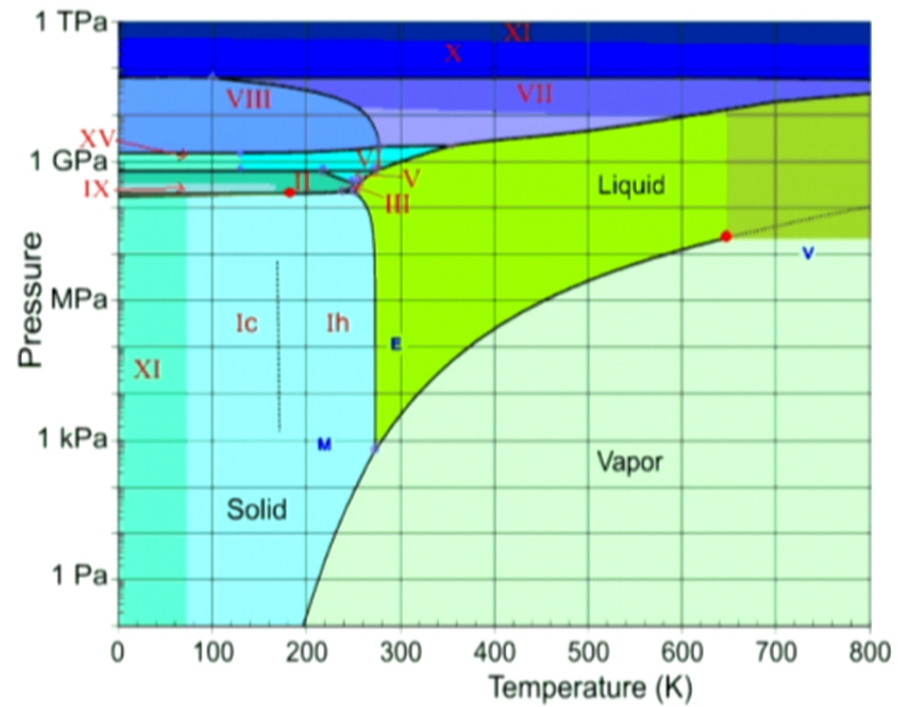
Water SPC/E

Angell, Finch, Bach 65, 3063 (76)

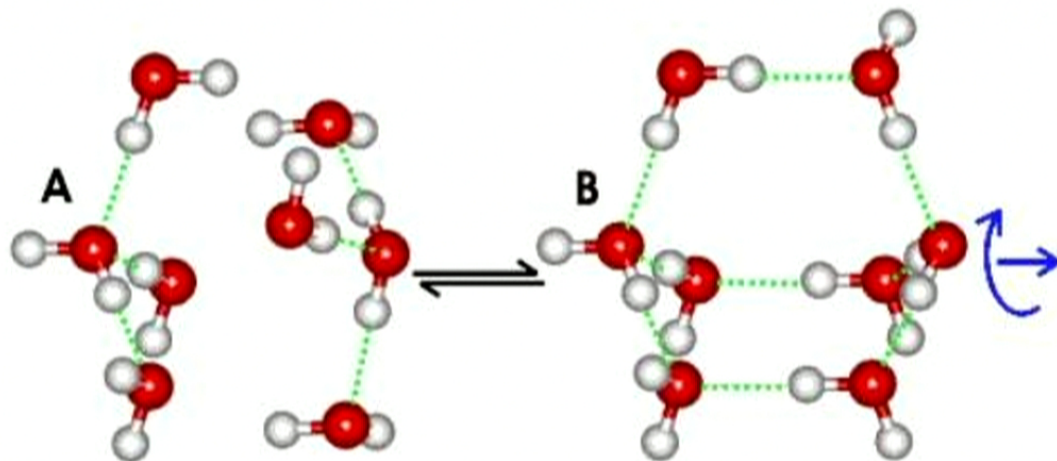
Netz, Starr, Stanley, Barbosa JCP 115, 344 (01)



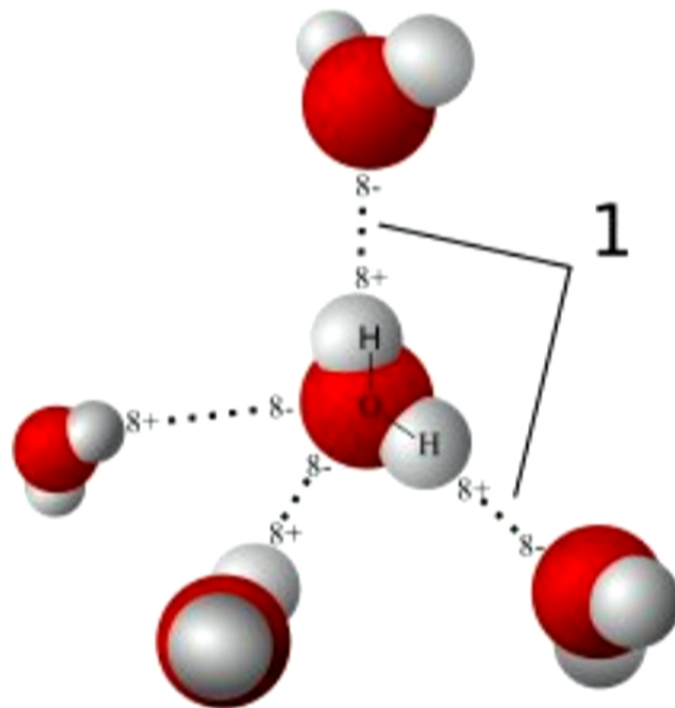
Water Phase Diagram



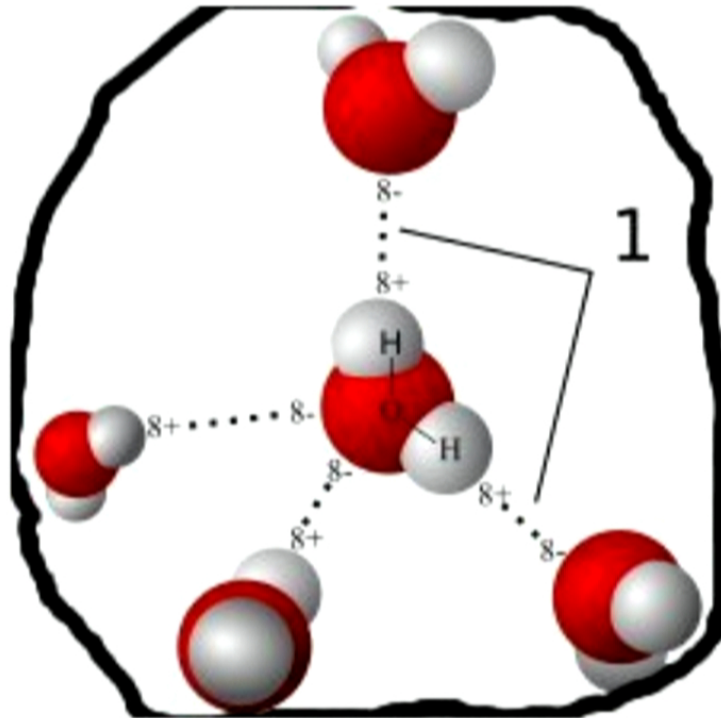
Two Length Scales Potential



Structure

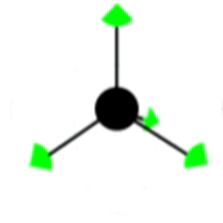
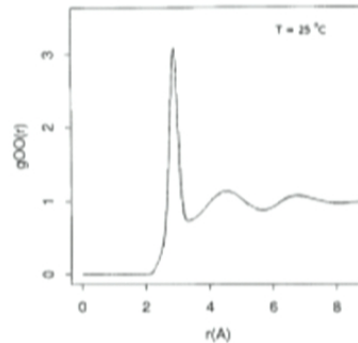


Structure



Effective Potential

- ▶ Radial Distribution Function of WATER:



$$\sigma_o = 2,86 \times 10^{-10} m$$
$$\epsilon = 0,006 \frac{kcal}{mol}$$

- ▶ Ornstein-Zernike Equation:

$$h(r) = g(r) - 1 = c(r) + \rho \int c(r - r') h(r') dr'$$

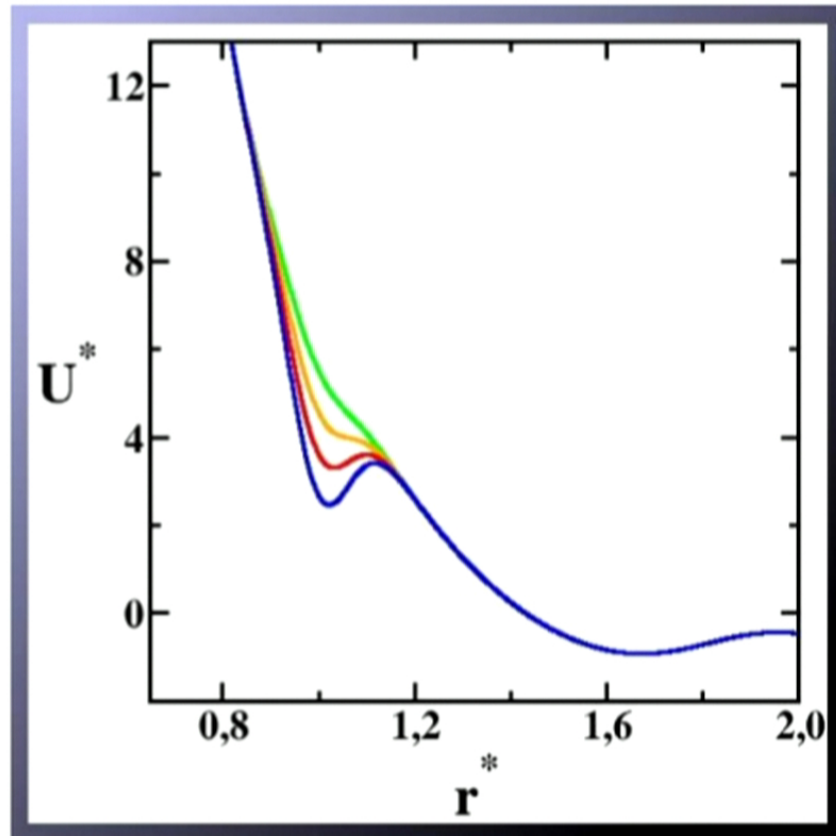
- ▶ Hypernetted Chain Approximation (HNC):

$$U(r) = k_B T \{g(r) - 1 - \ln[g(r)] - c(r)\}$$

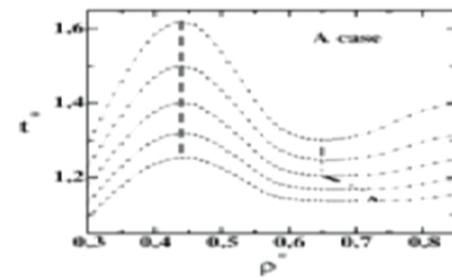
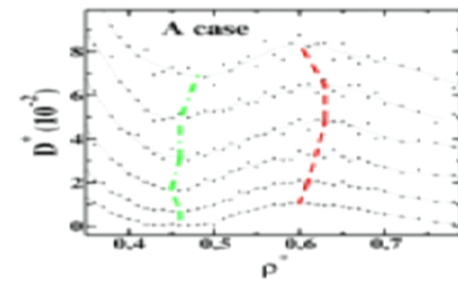
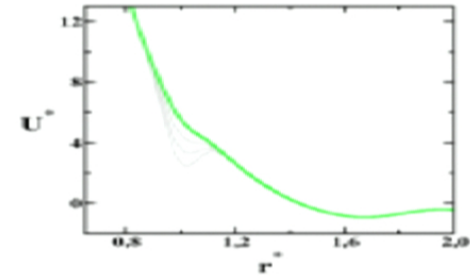
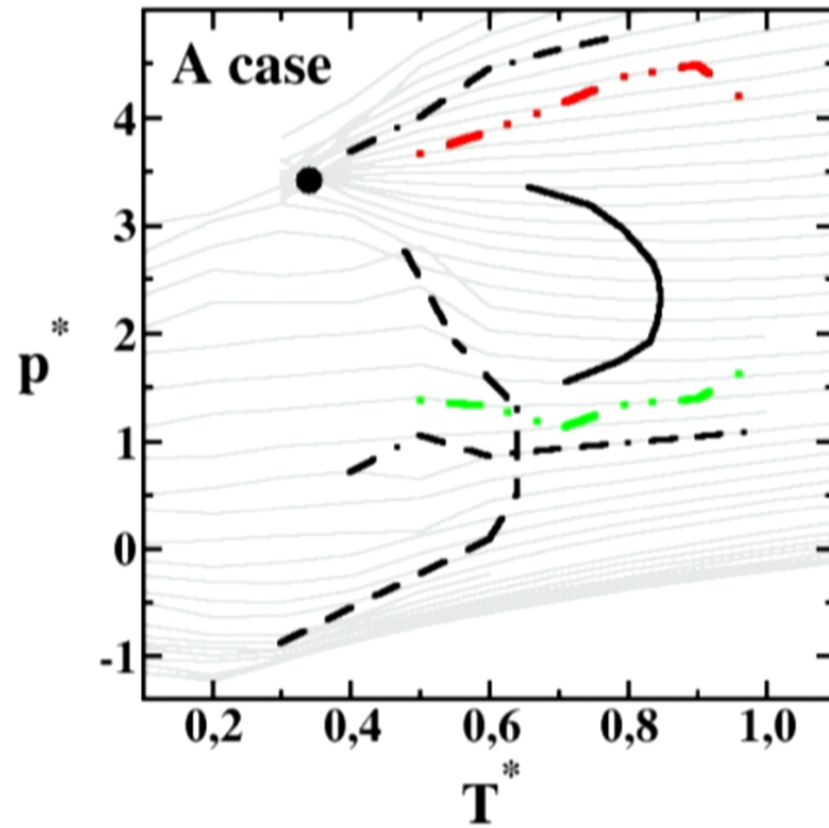


Effective Potential

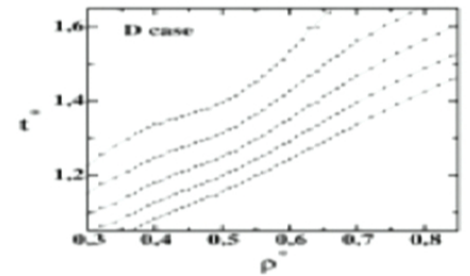
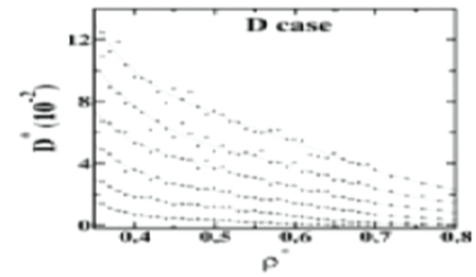
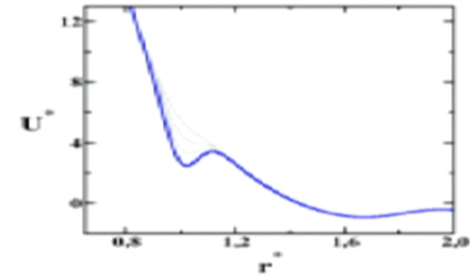
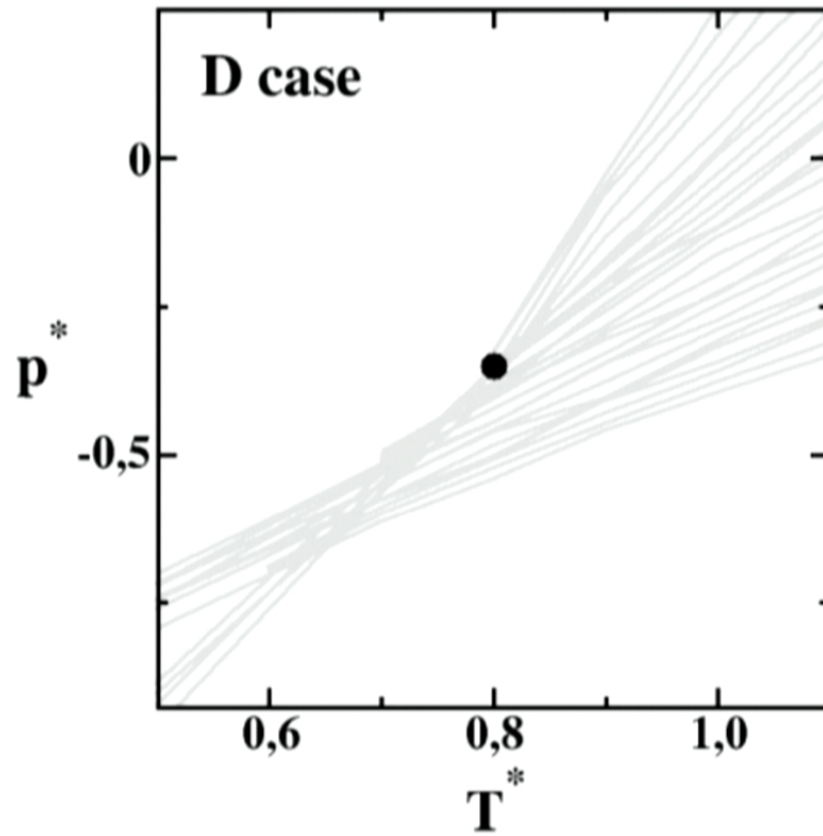
Barraz, Salcedo, Barbosa, JCP 131, 094504 (09)



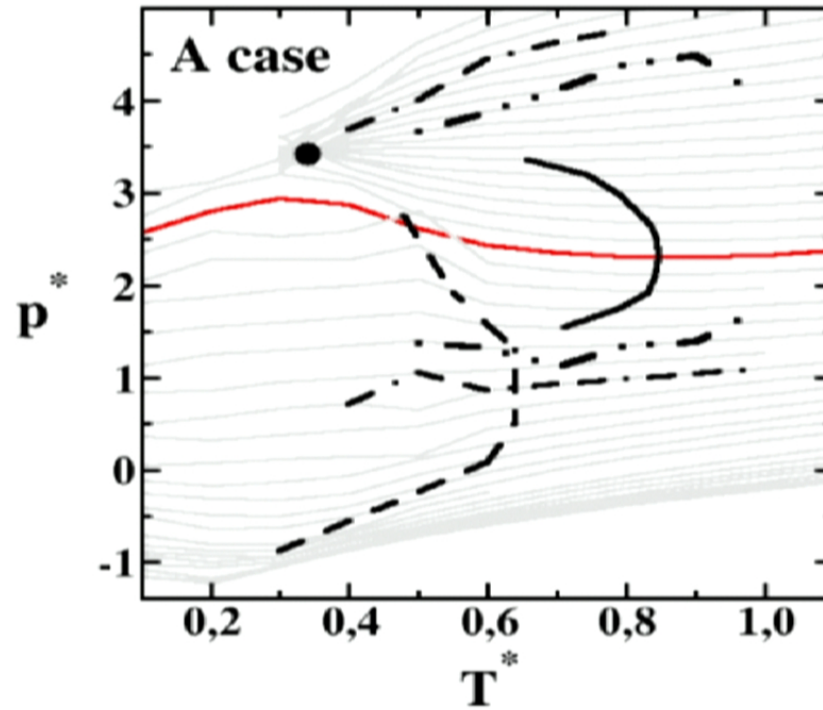
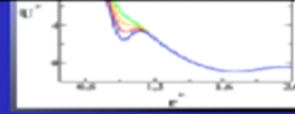
Phase Diagram



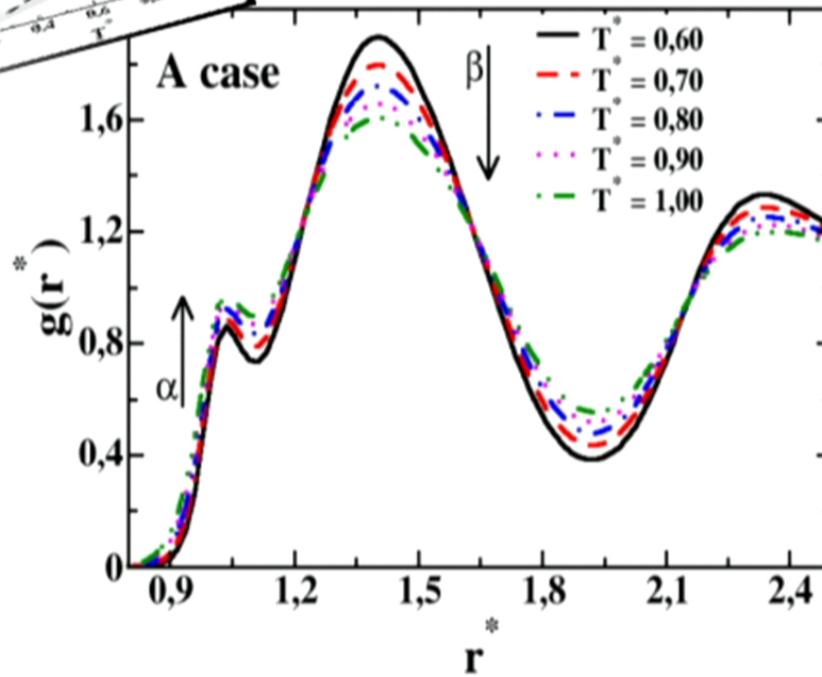
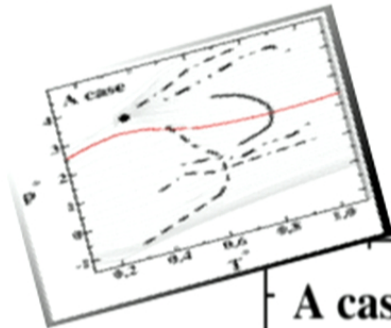
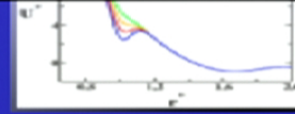
Phase Diagram



Radial Distribution Function

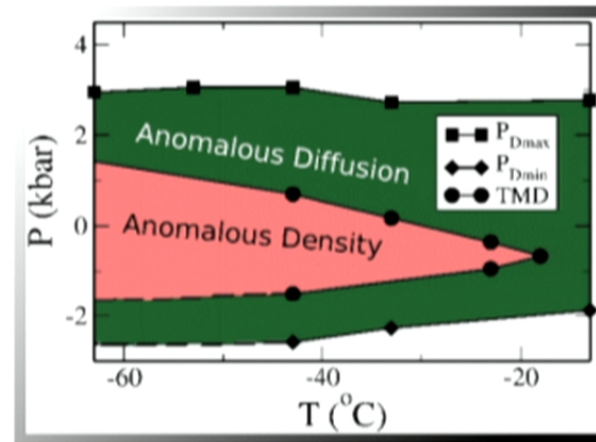
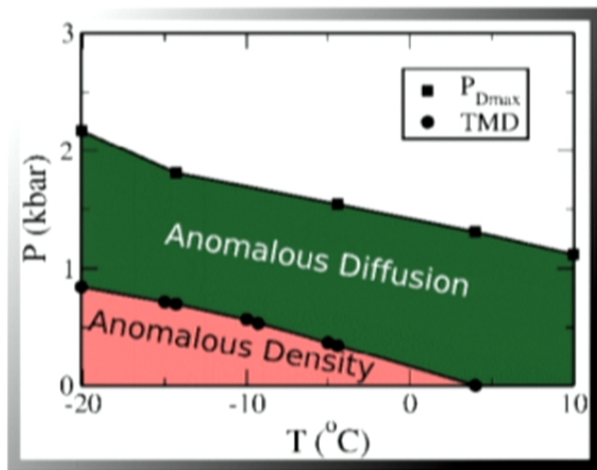
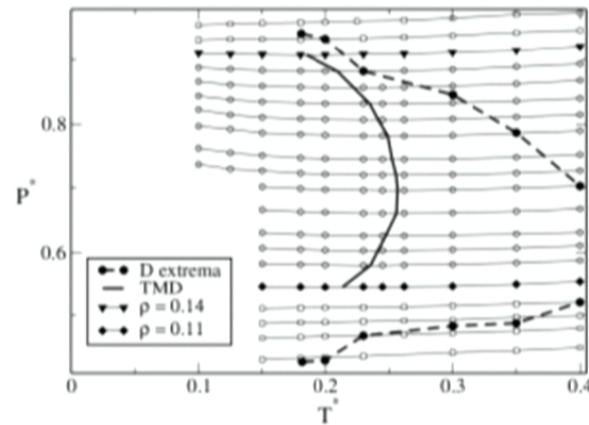


Radial Distribution Function



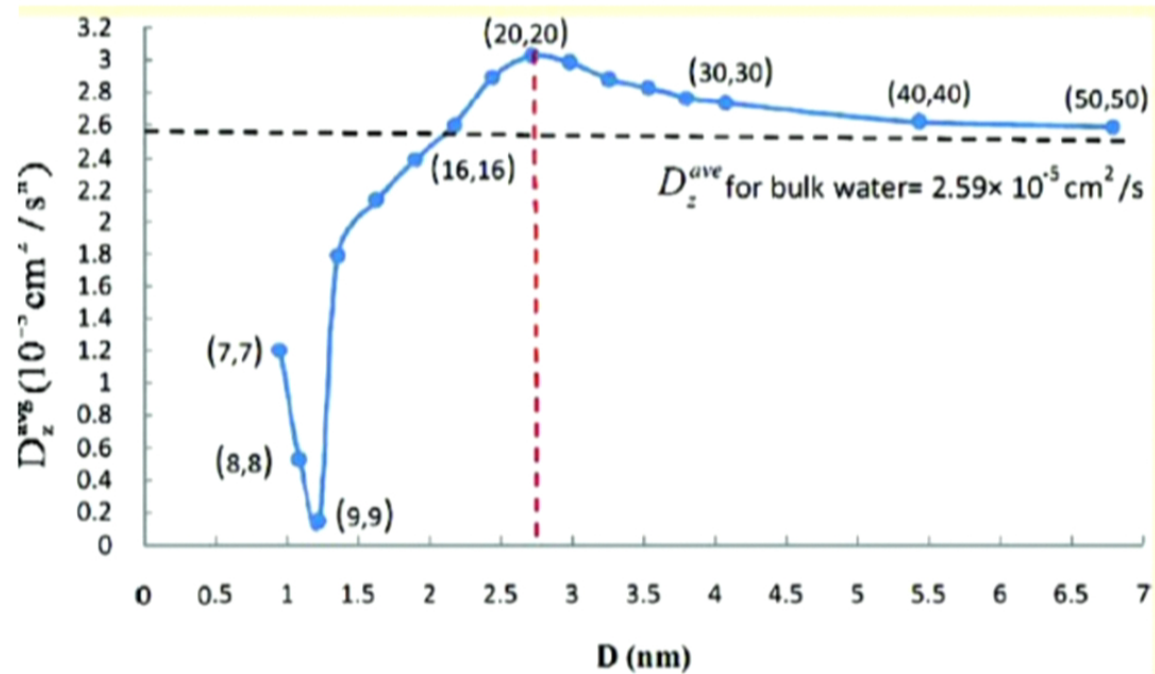
Bulk Phase Diagram Effective Potential

A. B. de Oliveira, P. Netz and MCB JCP124, 84505 (2006)



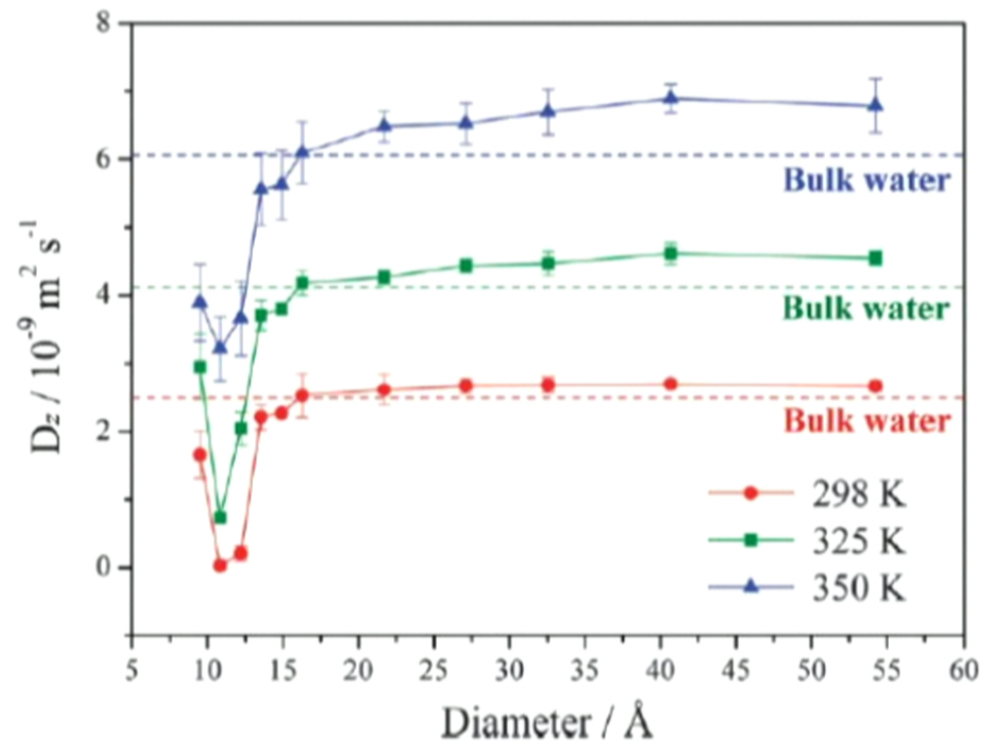
Mystery 1- Diffusion in Nanotubes

A.B. Farinami, JPCB 115, 12145 (2012)-SPC/E



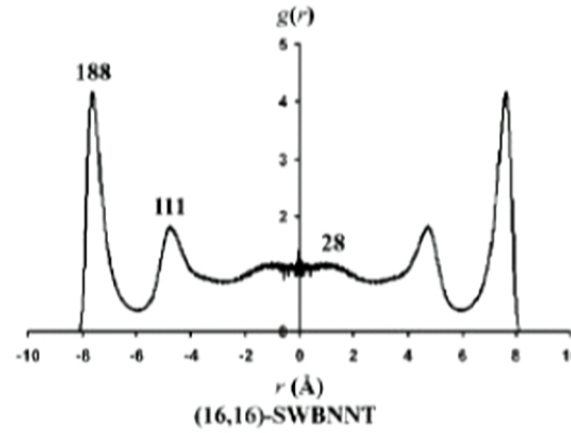
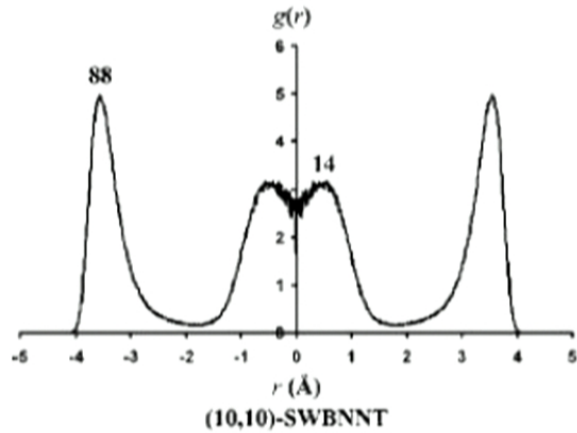
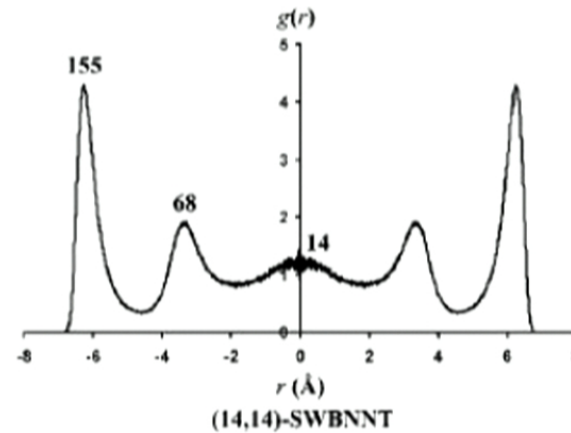
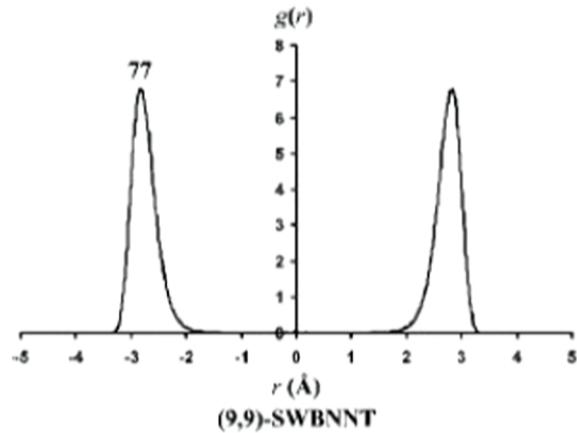
Diffusion in Nanotubes - Temperatures

Y. Zheng, PCCP 14, 964 (2012) - TIP4P-EW



Distribution in Nanotubes - Simulations

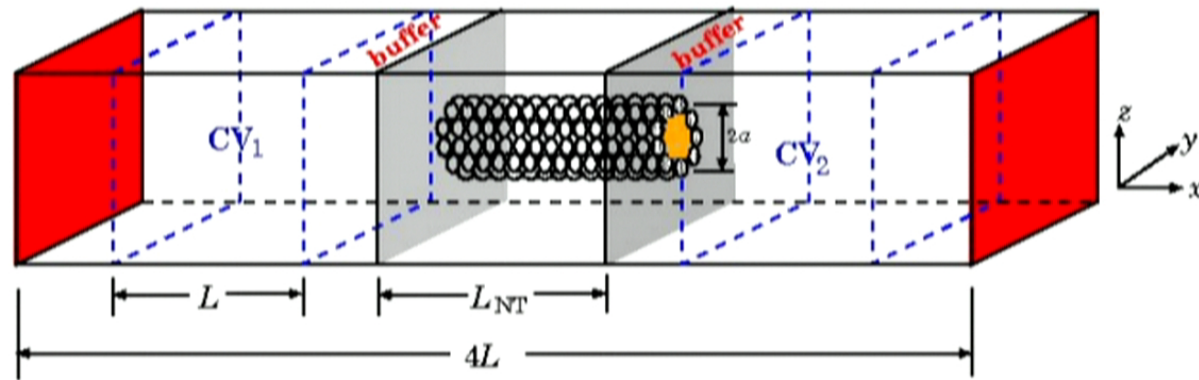
T. Nanok, JCPA 113, 2103 (2009) - SPC/E



Navigation icons: back, forward, search, etc.

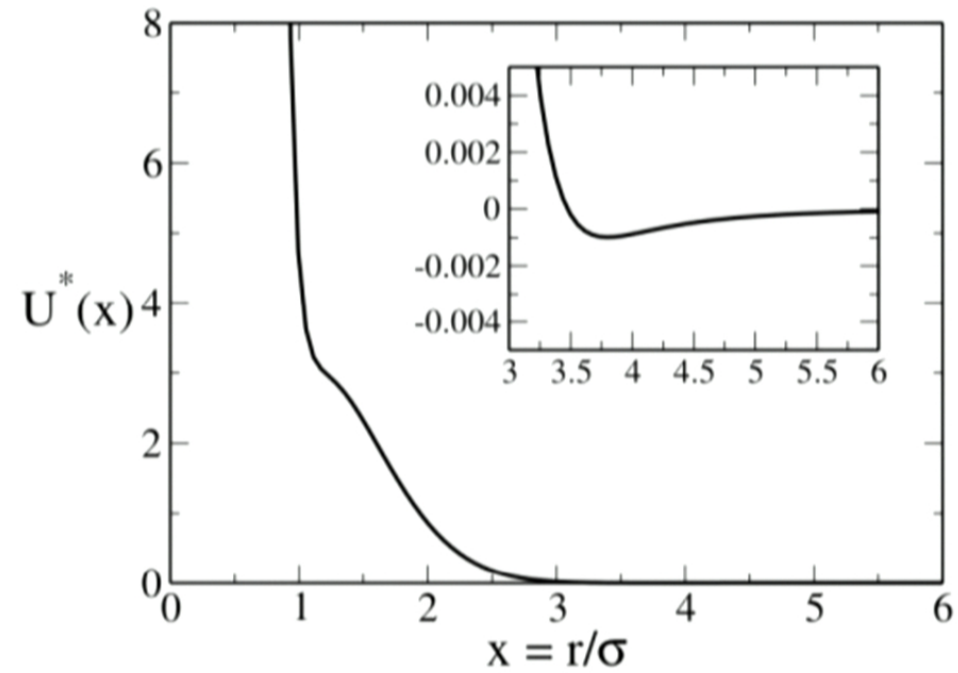
Model for Confining

J. R. Bordin, A. Diehl and MCB, JCP 137, 084504 (2012)

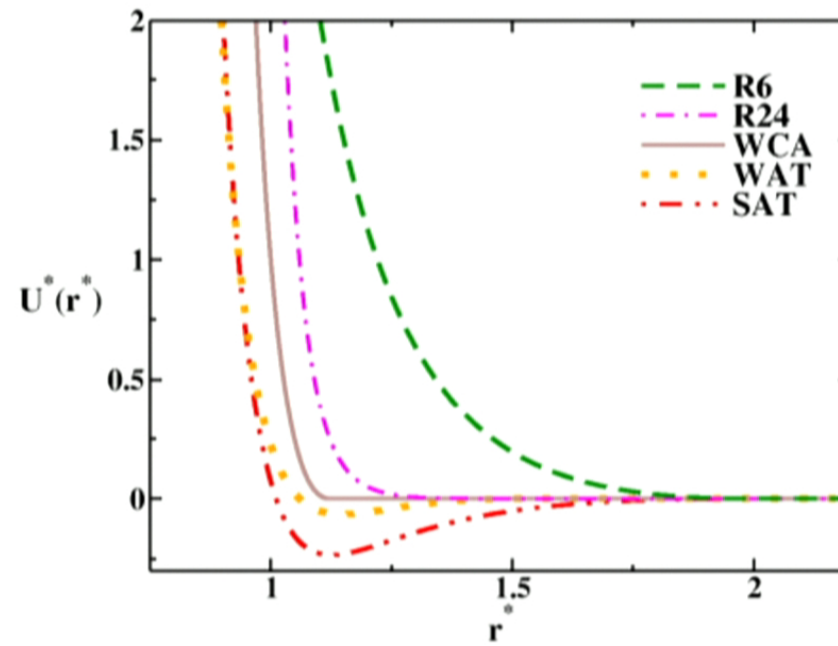


Fluid-Fluid Effective Potential

A. B. de Oliveira, P. Netz and MCB JCP124, 84505 (2006)

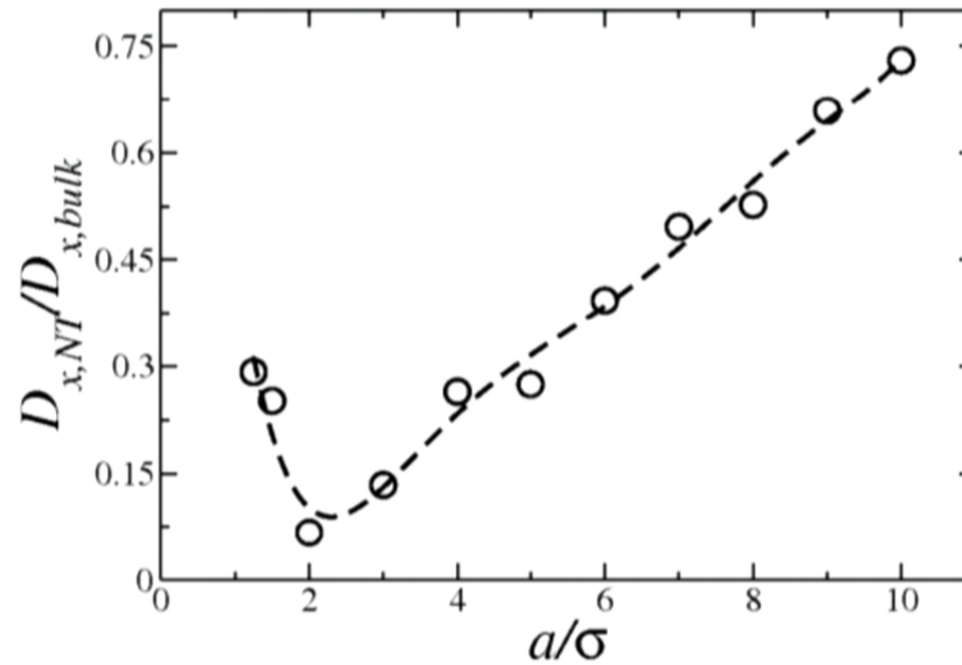


Fluid-Wall Effective Potential



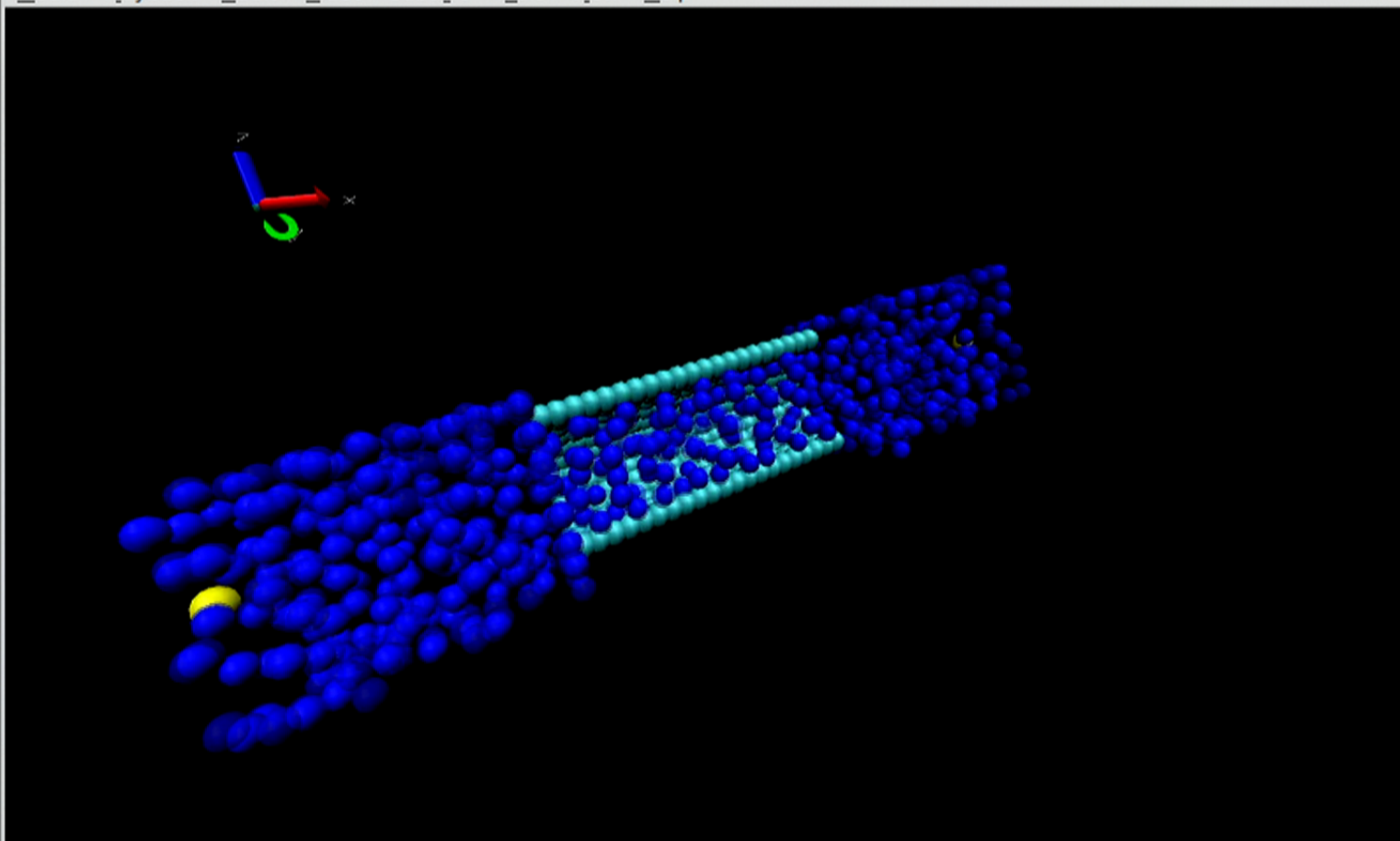
Diffusion

J. R. Bordin, A. B. de Oliveira, A. Diehl and MCB, JCP 137, 084504 (2012)



NPTa4.mpg - VLC media player

Media Playback Audio Video Subtitle Tools View Help



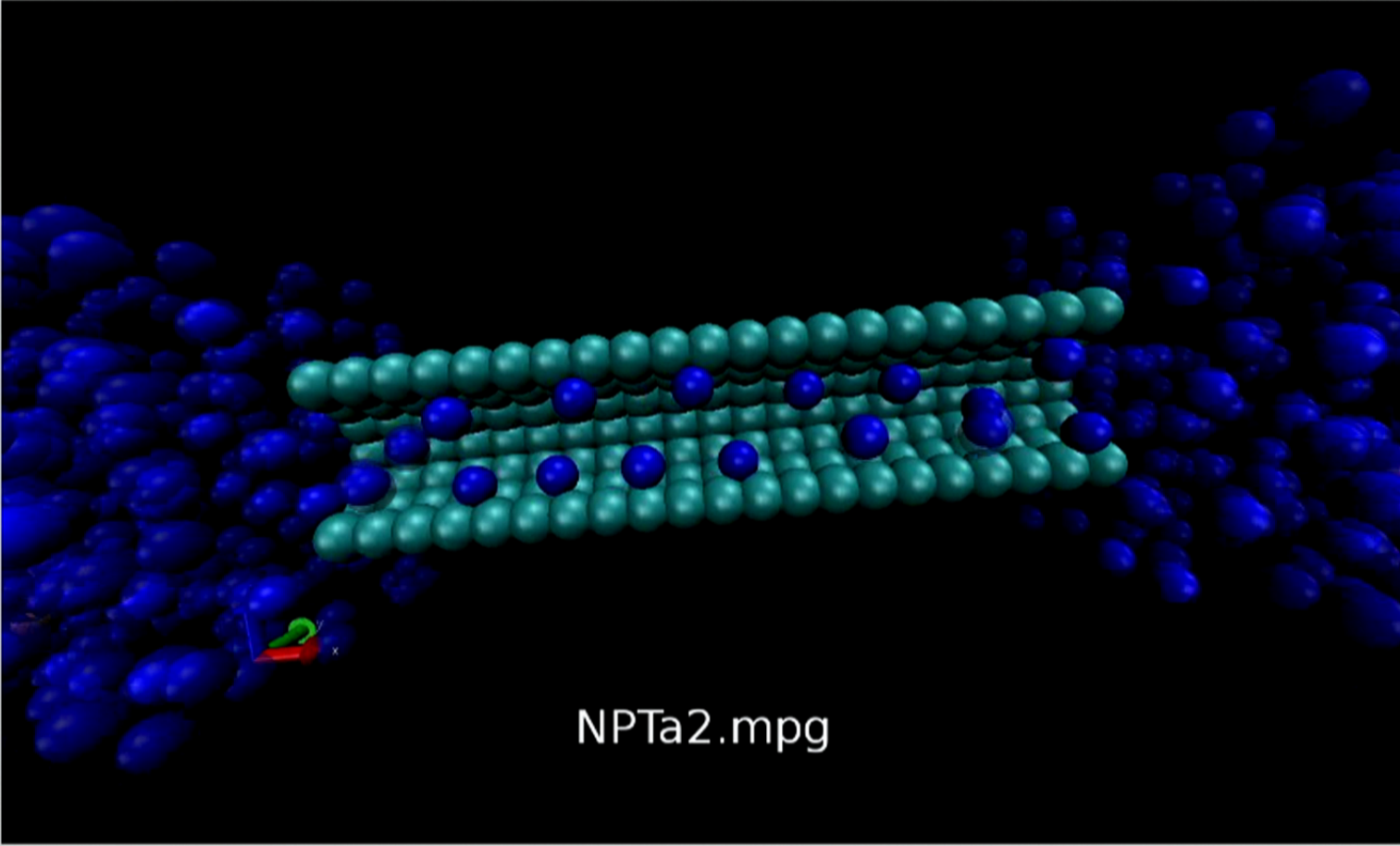
00:00 00:00

Applications Places System Ter... wat... NPT... -1 °C Wed Mar 4, 14:52 en

The image shows a 3D molecular simulation of a lipid bilayer. The lipid molecules are represented by blue spheres (hydrophilic heads) and yellow spheres (hydrophobic tails). A single yellow sphere is highlighted in the foreground. The simulation is displayed in a 3D perspective view with a coordinate system (x, y, z) in the upper left corner. The VLC media player interface is visible at the top and bottom, showing the file name 'NPTa4.mpg' and the system tray with the date and time 'Wed Mar 4, 14:52'.

NPTa2.mpg - VLC media player

Media Playback Audio Video Subtitle Tools View Help



NPTa2.mpg

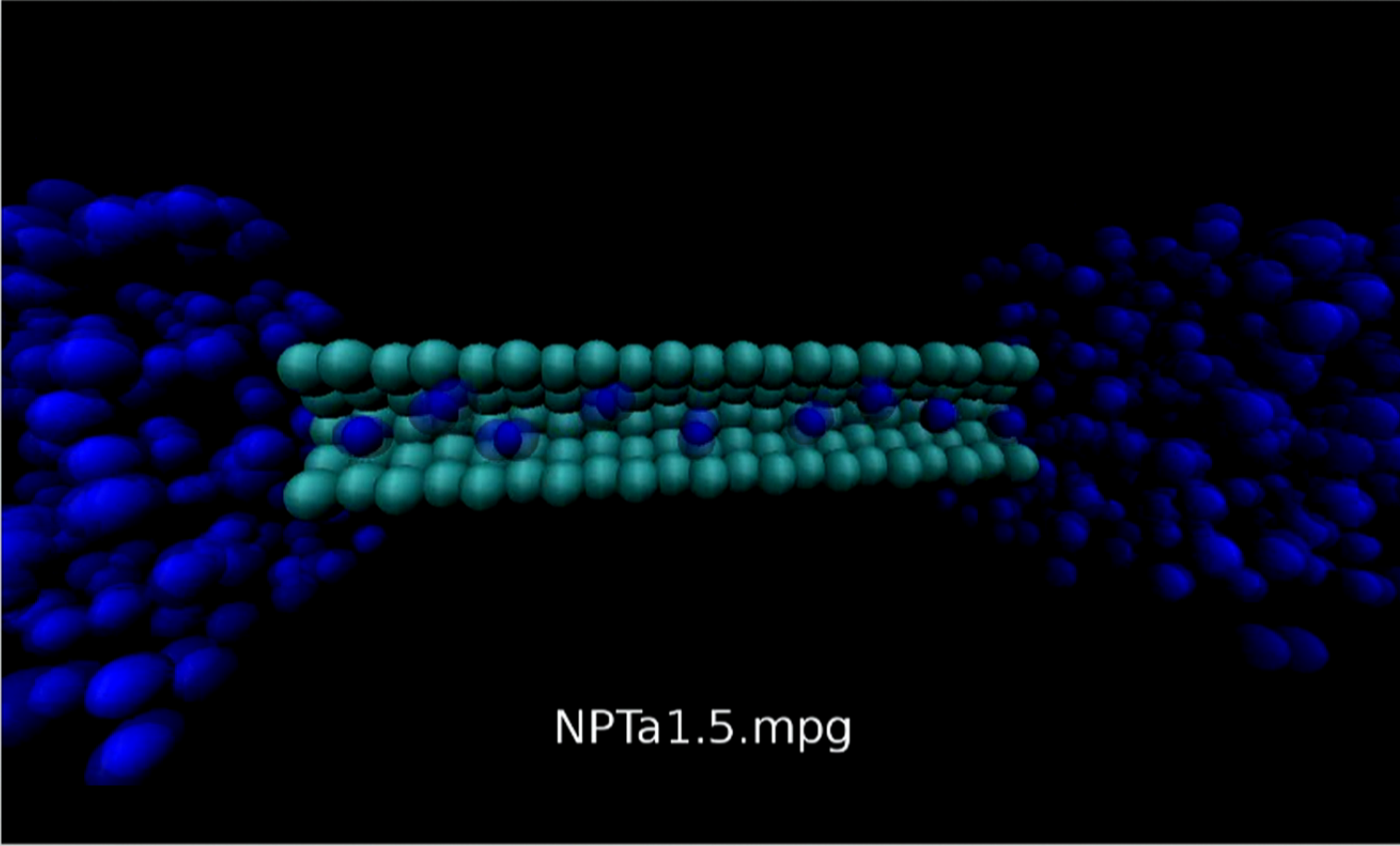
00:00 00:00

Applications Places System Ter... wat... NPT... -1 °C Wed Mar 4, 14:52 en

The image shows a screenshot of a VLC media player window displaying a molecular simulation. The simulation depicts a lipid bilayer, with a protein embedded in the center. The lipid tails are represented by light blue spheres, and the head groups are represented by darker blue spheres. The protein is shown as a complex structure of red, green, and blue spheres. The VLC interface includes a menu bar, a playback progress bar, and a system tray at the bottom.

NPTa1.5.mpg - VLC media player

Media Playback Audio Video Subtitle Tools View Help



NPTa1.5.mpg

00:00 00:00

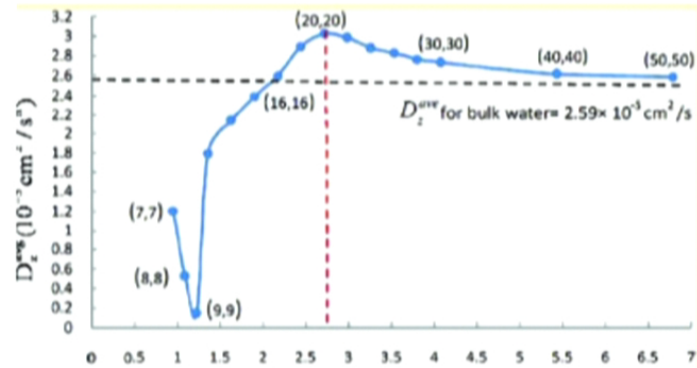
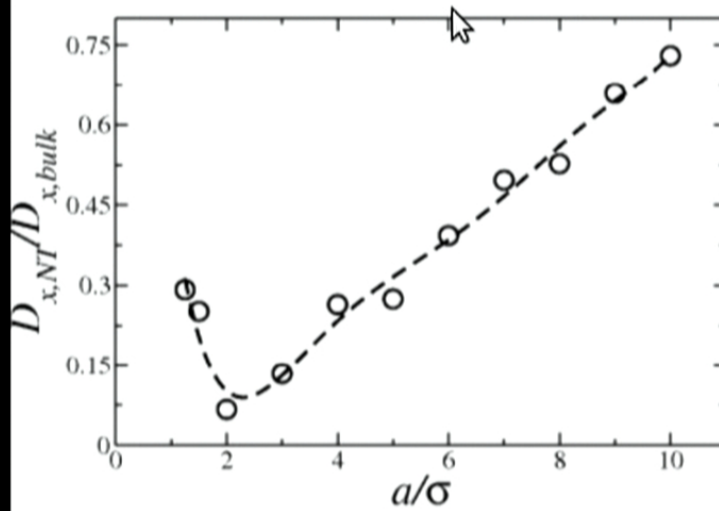
Applications Places System Ter... wat... NPT... -1 °C Wed Mar 4, 14:52 en

The image shows a screenshot of a VLC media player window. The title bar reads "NPTa1.5.mpg - VLC media player". The menu bar includes "Media", "Playback", "Audio", "Video", "Subtitle", "Tools", "View", and "Help". The main video area displays a 3D molecular simulation of a lipid bilayer with a protein channel. The lipids are represented by blue and cyan spheres, and the protein is shown as a central structure. The text "NPTa1.5.mpg" is overlaid at the bottom of the video area. The playback controls at the bottom show a progress bar from 00:00 to 00:00, and various control icons. The system tray at the very bottom shows the application dock with "Applications", "Places", and "System", along with open windows for "Ter...", "wat...", and "NPT...", and system status including "-1 °C", "Wed Mar 4, 14:52", and "en".

Diffusion

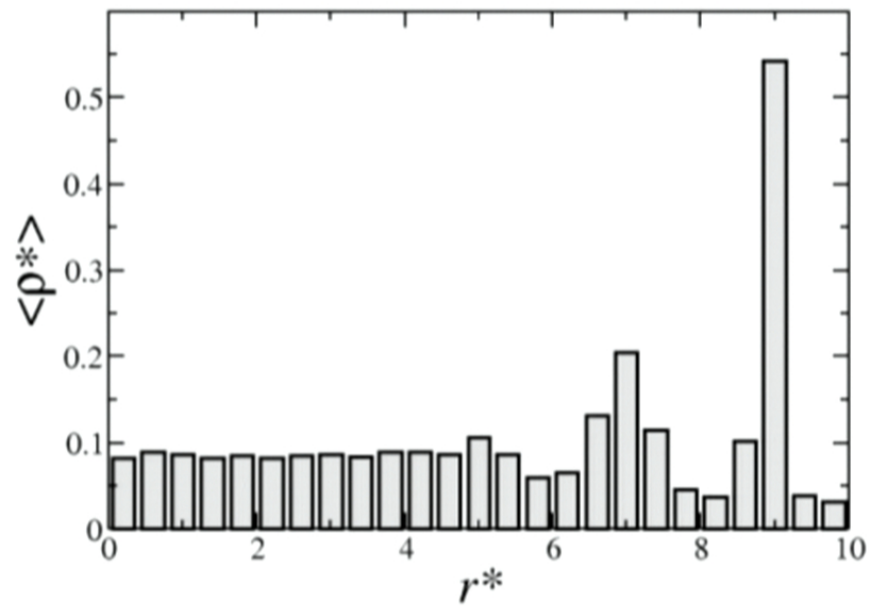
A.B. Farinami, JPCB 115, 12145 (2012)

J. R. Bordin, A. B. de Oliveira, A. Diehl and MCB, JCP 137, 084504 (2012)



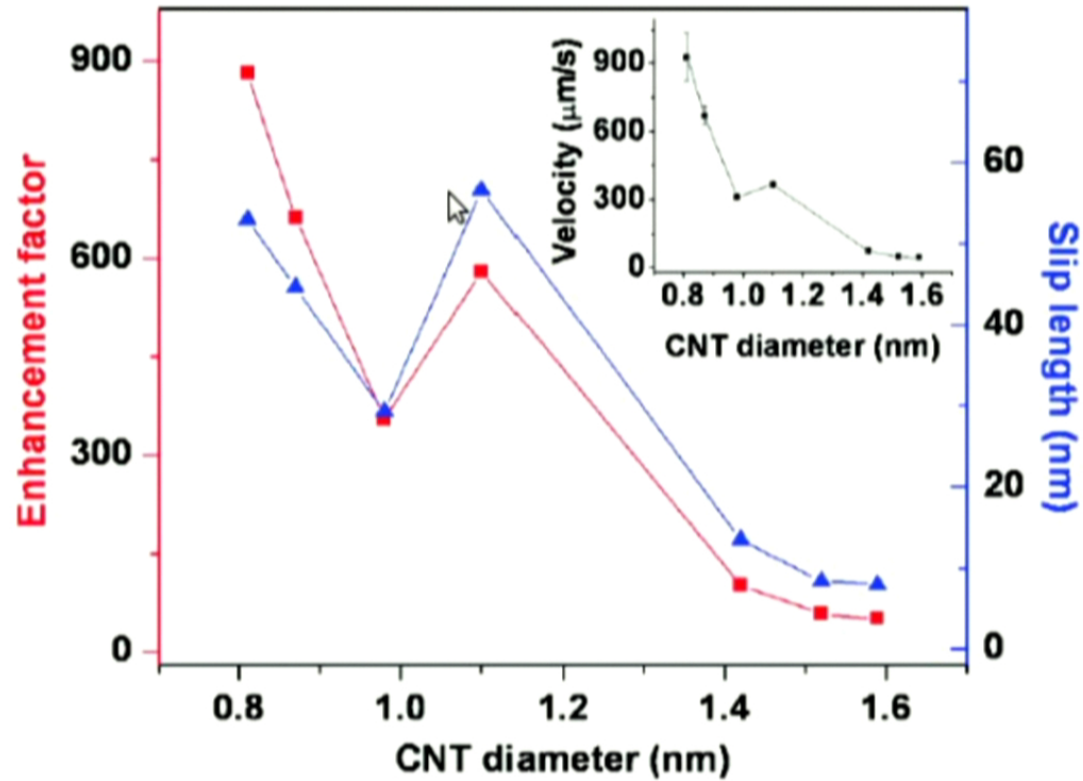
Density vs. $r - a=10$

J. R. Bordin, A. B. de Oliveira, A. Diehl and MCB, JCP 137, 084504 (2012)



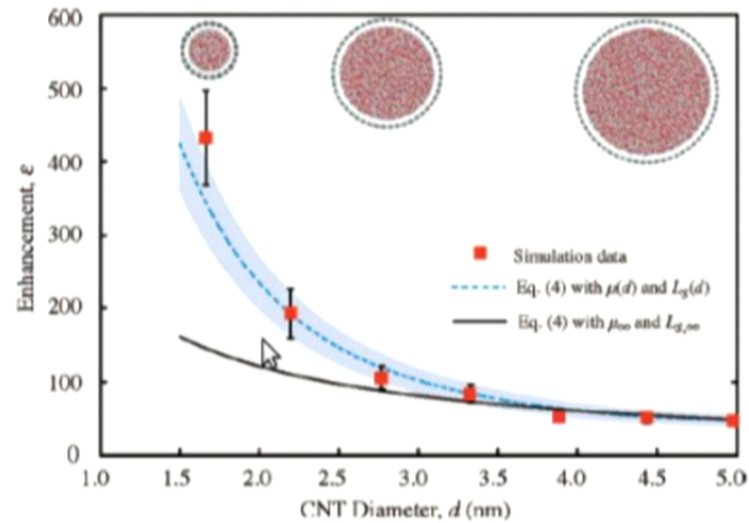
Mystery 2- Flux in Nanotubes

X. Qin et al, Nanoletters 11, 2173 (2011) - experimental - SPC/E



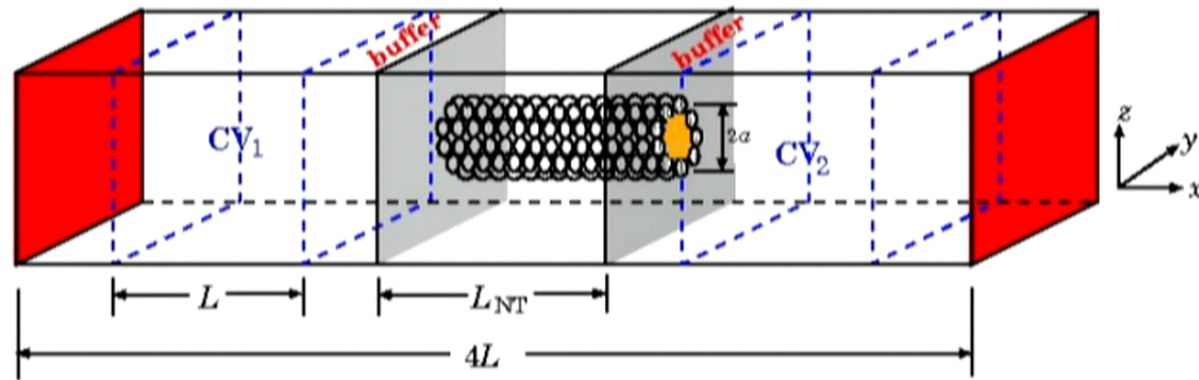
Water Channel - Enhancement Flow

J. A. Thomas and A. J. H. McGaughey, Nanoletters 8, 2788 (2008)



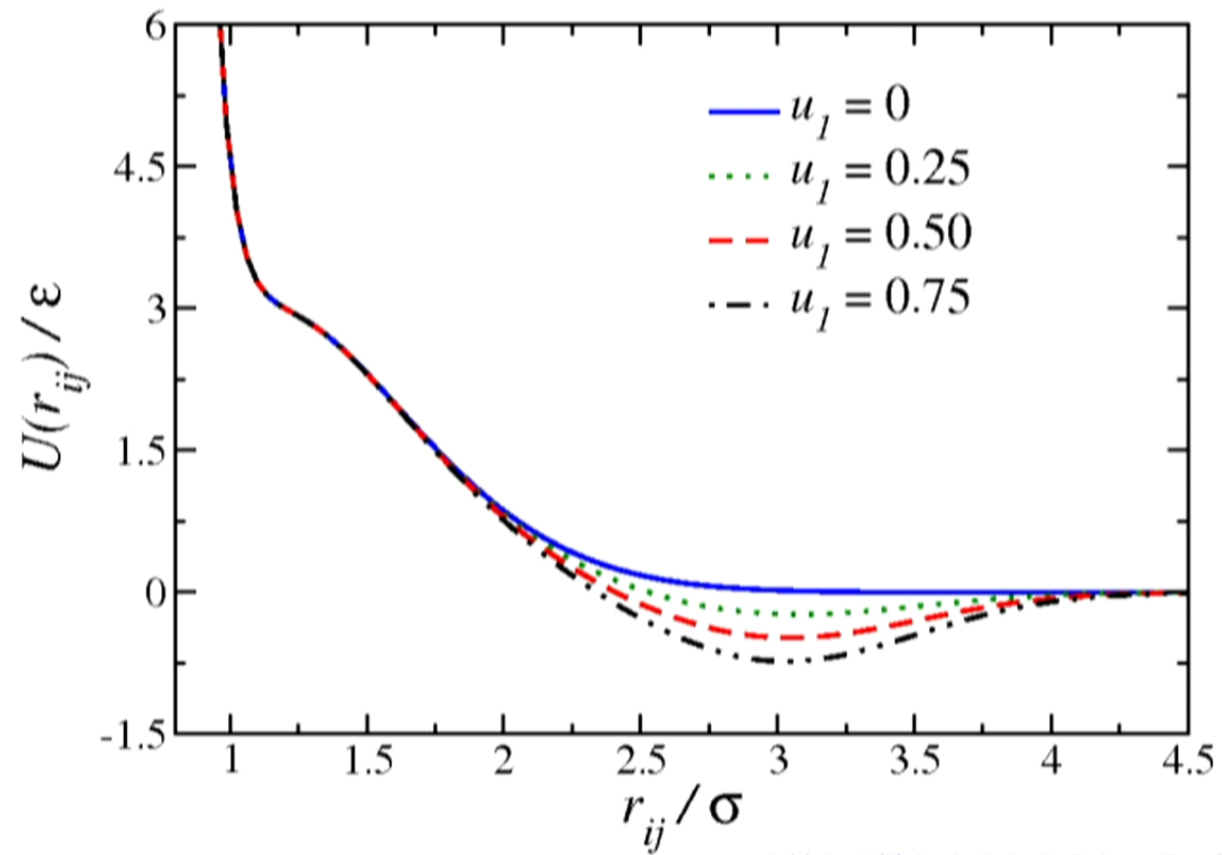
Model for Nanotubes

J. R. Bordin, A. Diehl and MCB, JPCB 117, 7047(2013)



Fluid-Fluid Effective Potential

J. da Silva and MCB, JCP 133, 244506 (2010)



Enhancement Flow

J. R. Bordin, A. Diehl and MCB, JPCB 117, 7047 (2013)

$$\langle v_x \rangle = \gamma_{HP} \frac{\Delta p}{L_{NT}}$$

$$\gamma_{HP} = \frac{a^2}{8\eta}$$

$$\eta = \frac{k_B T}{3\pi\sigma D_x}$$

$$\langle v_x \rangle = \gamma_{MD} \frac{\Delta p}{L_{NT}}$$

$$\epsilon = \frac{\gamma_{MD}}{\gamma_{HP}} \quad (1)$$



Enhancement Flow

J. R. Bordin, A. Diehl and MCB, JPCB 117, 7047 (2013)

$$\langle v_x \rangle = \gamma_{HP} \frac{\Delta p}{L_{NT}}$$

$$\gamma_{HP} = \frac{a^2}{8\eta}$$

$$\eta = \frac{k_B T}{3\pi\sigma D_x}$$

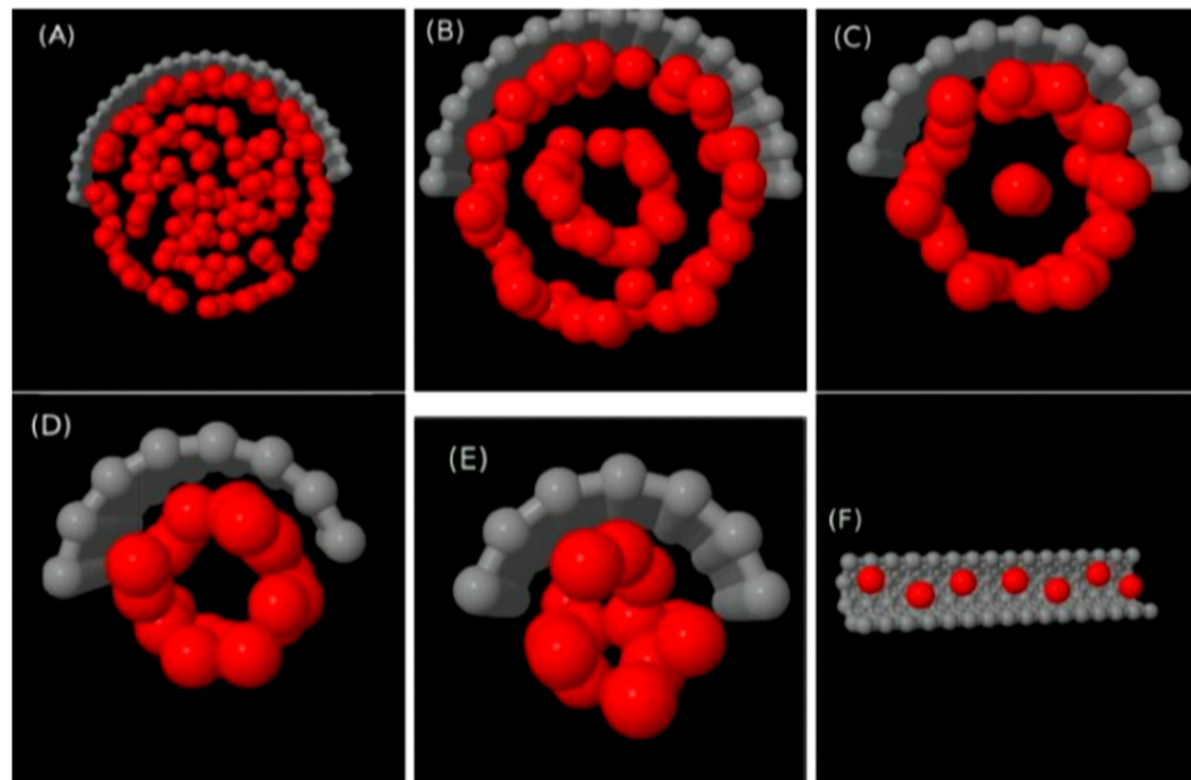
$$\langle v_x \rangle = \gamma_{MD} \frac{\Delta p}{L_{NT}}$$

$$\epsilon = \frac{\gamma_{MD}}{\gamma_{HP}} \quad (1)$$



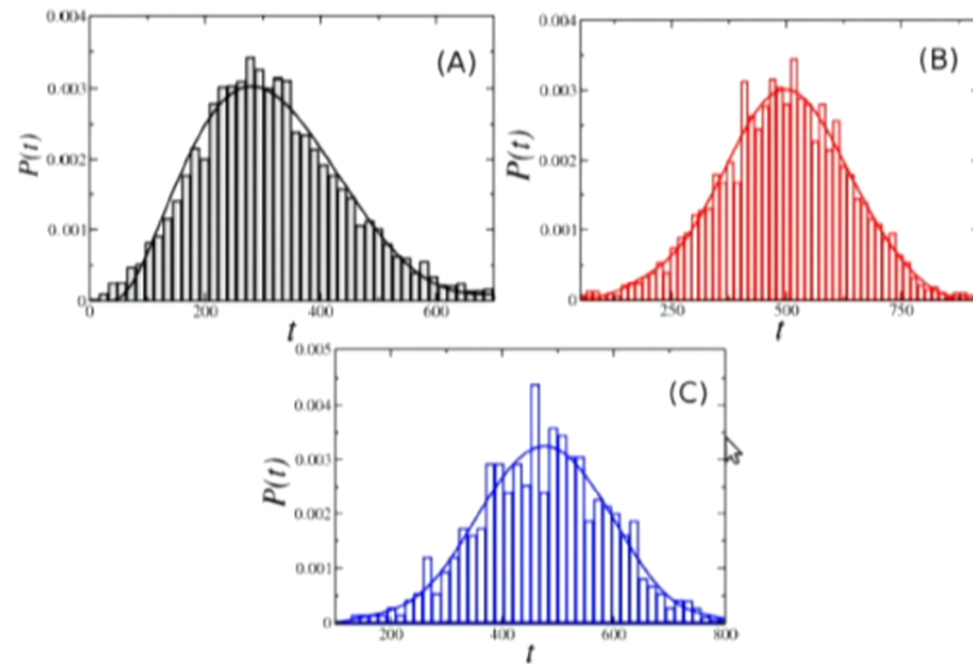
Layers - Attractive

J. R. Bordin, A. Diehl and MCB, JPCB 117, 7047(2013)



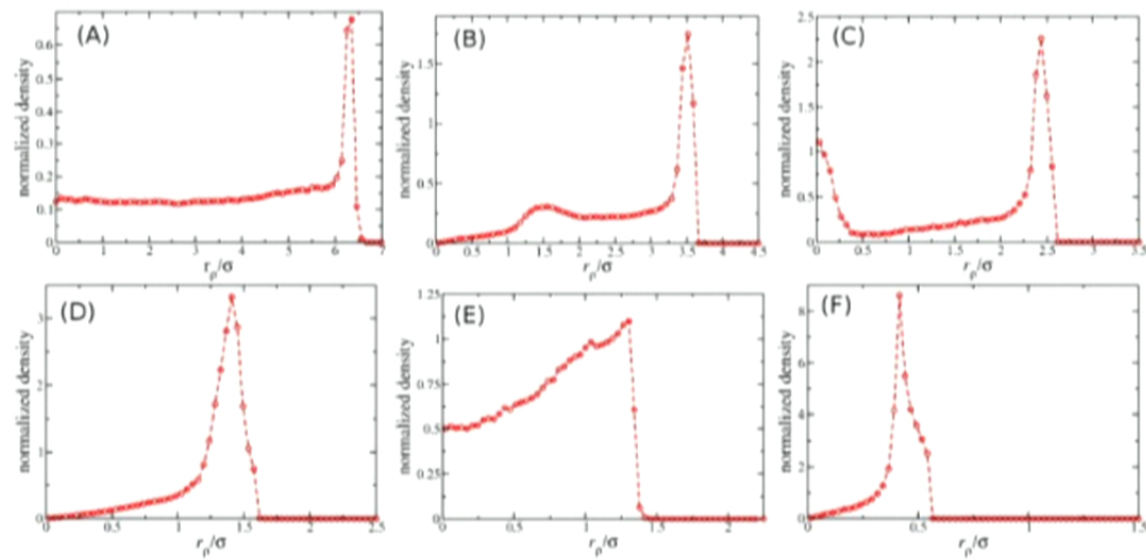
Distribution - Attractive

J. R. Bordin, A. Diehl and MCB, JPCB (2013)



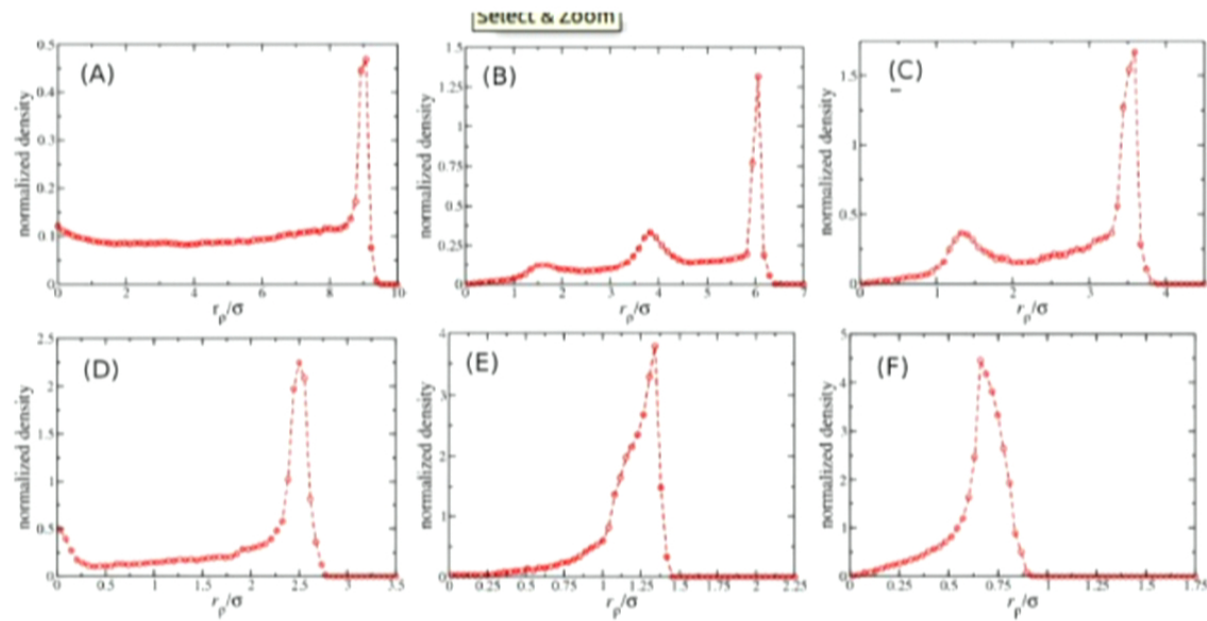
Density - Attractive

J. R. Bordin, A. Diehl and MCB, JPCB (2013)



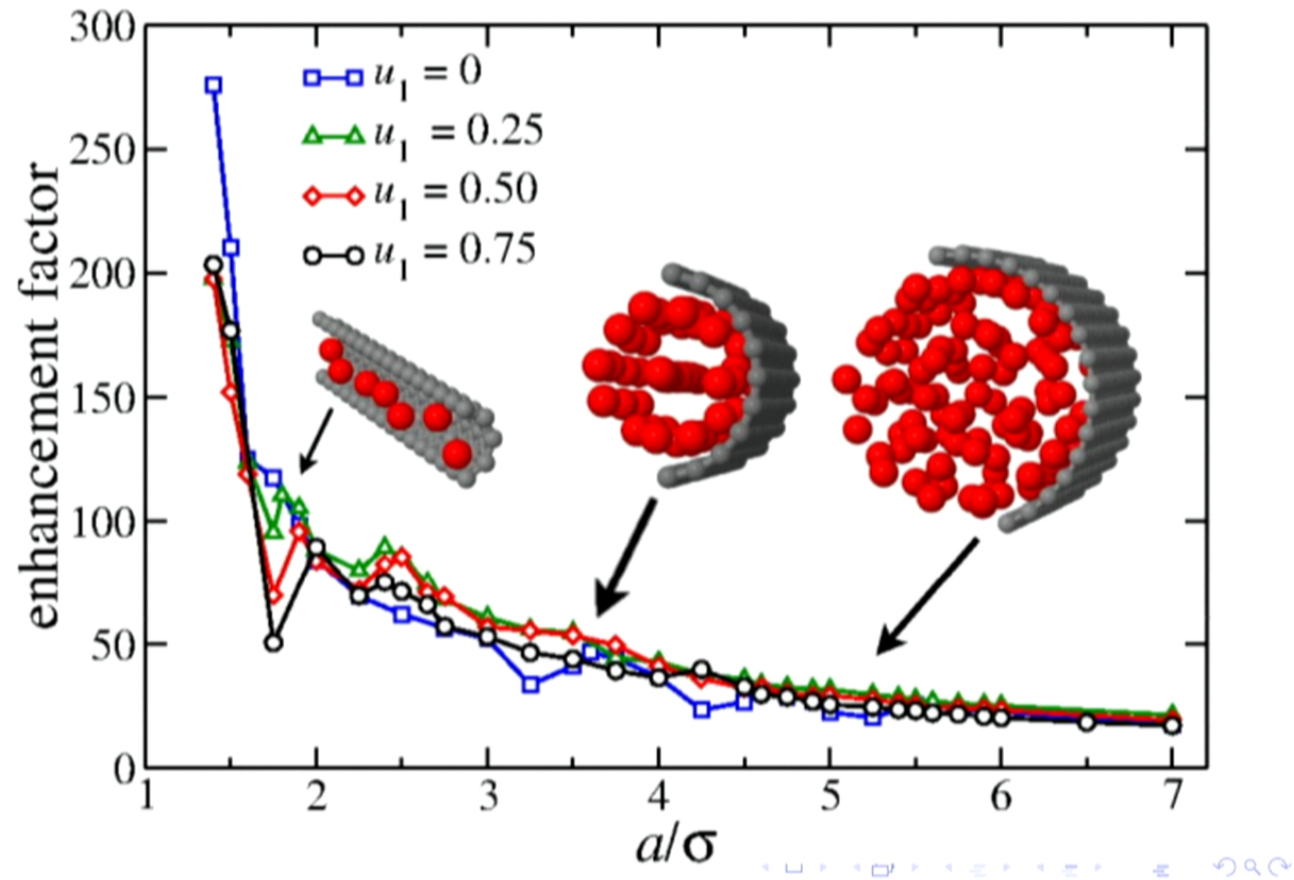
Density - Repulsive

J. R. Bordin, A. Diehl and MCB, JPCB (2013)



Enhancement Flow

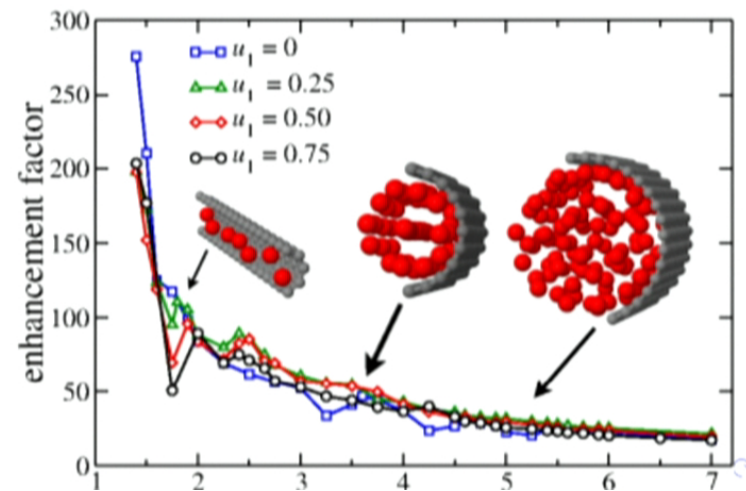
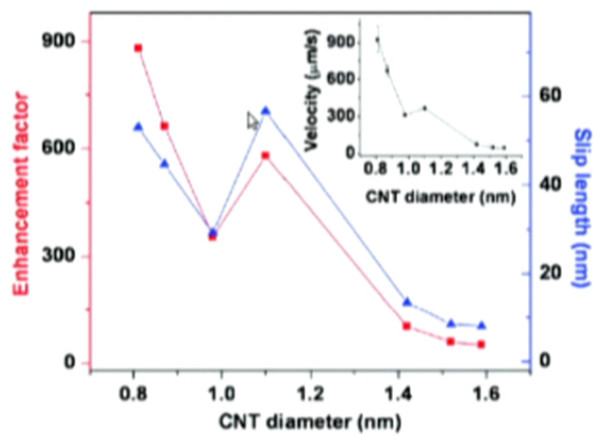
J. R. Bordin, A. Diehl and MCB, JPCB 117, 7047(2013)



Enhancement Flow

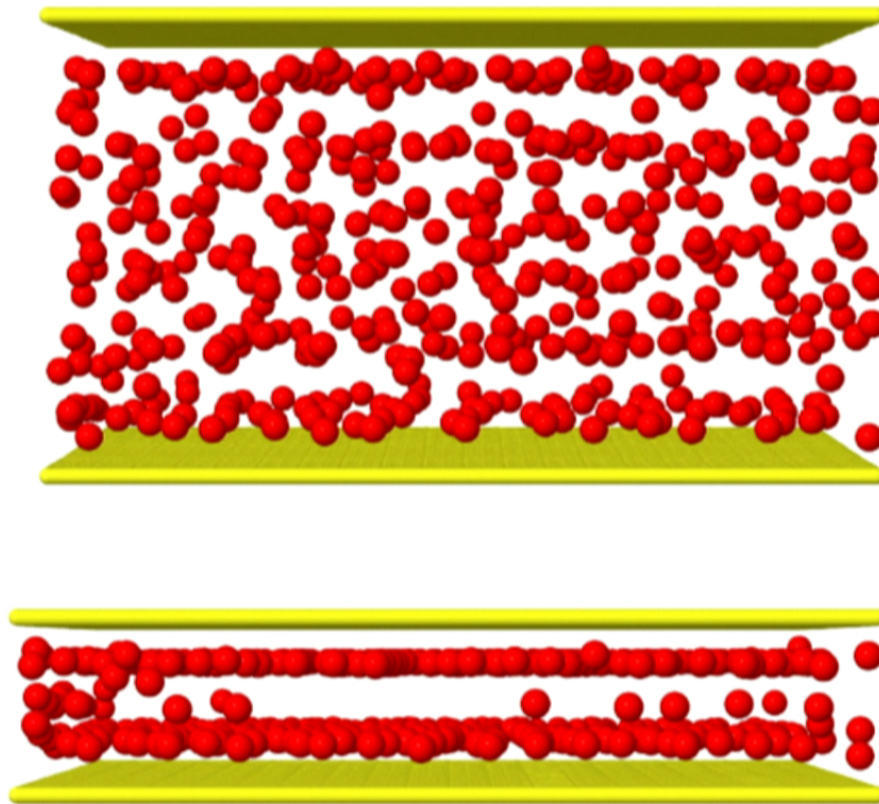
X. Qin et al, Nanoletters 11, 2173 (2011)

J. R. Bordin, A. Diehl and MCB, JPCB 117, 7047(2013)

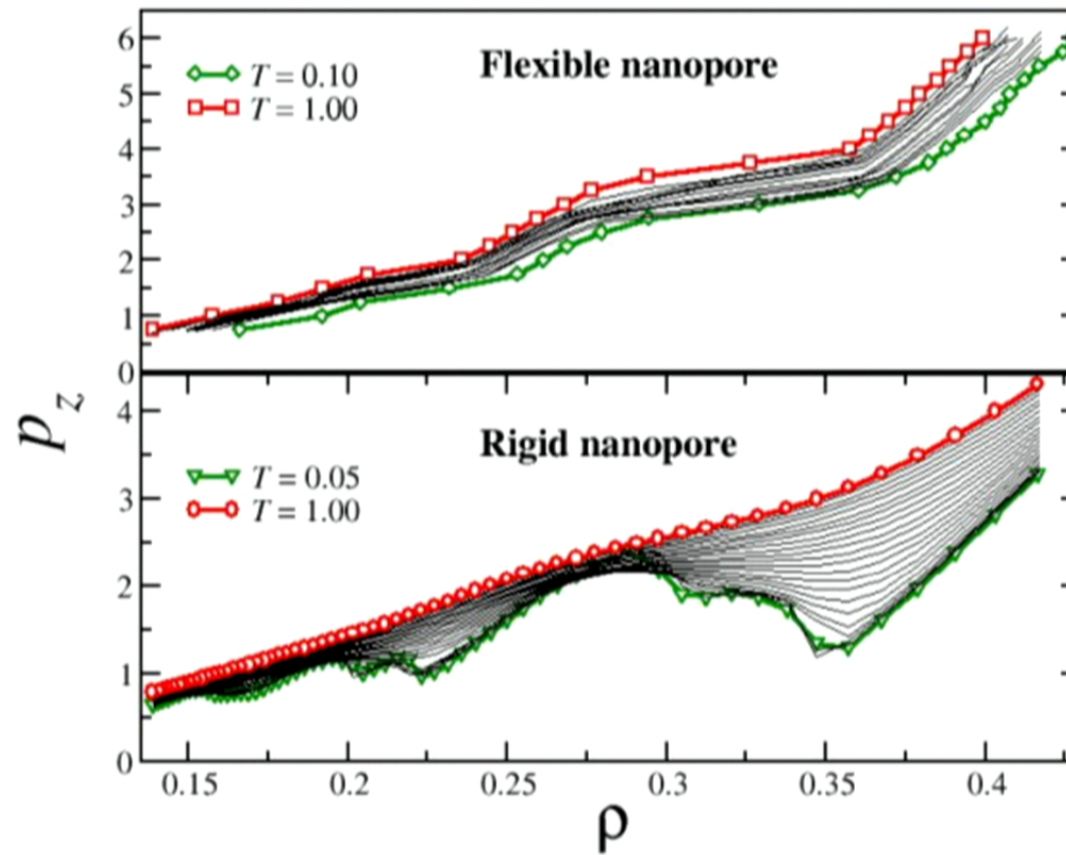


Mystery 3 - What happens if the tubes are flexible?

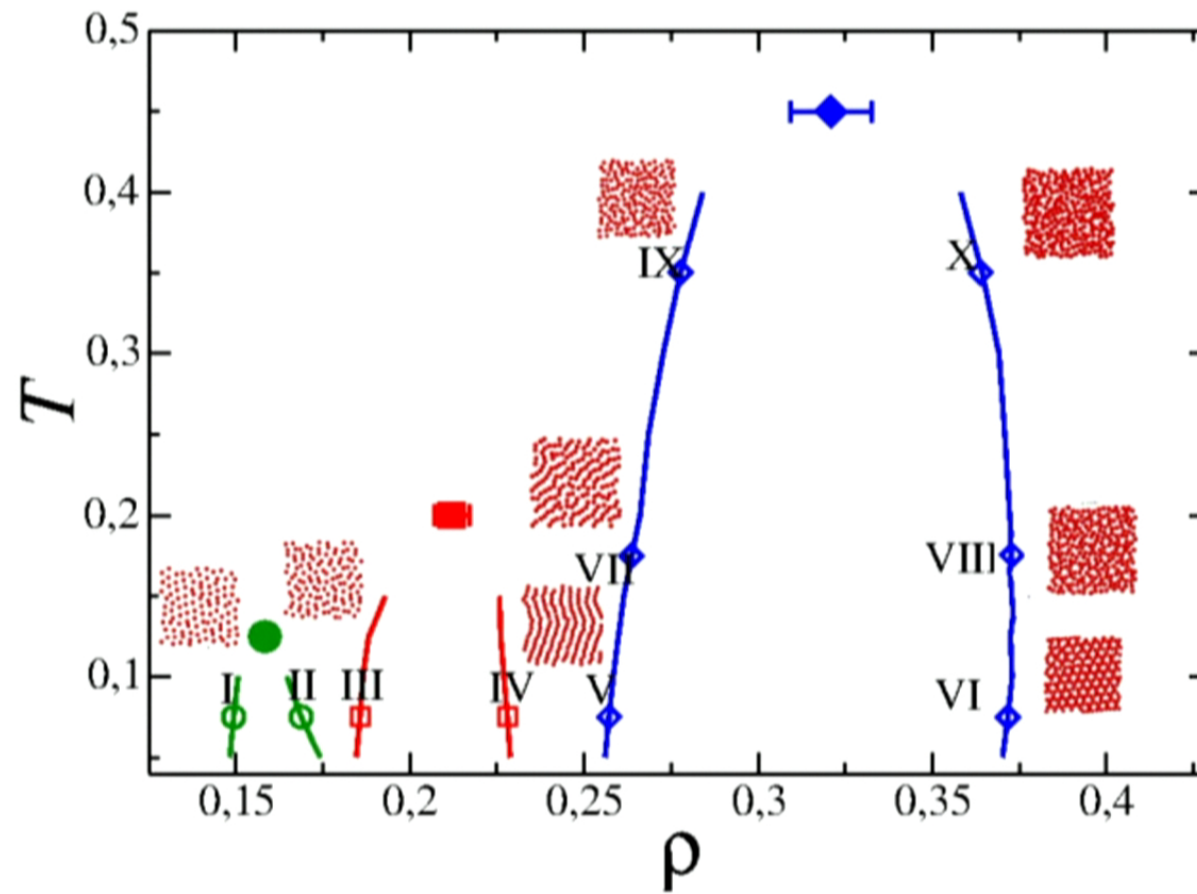
L.B. Krott and MCB PRE 89 012110 (2014)



Pressure vs. Density



T vs. Density

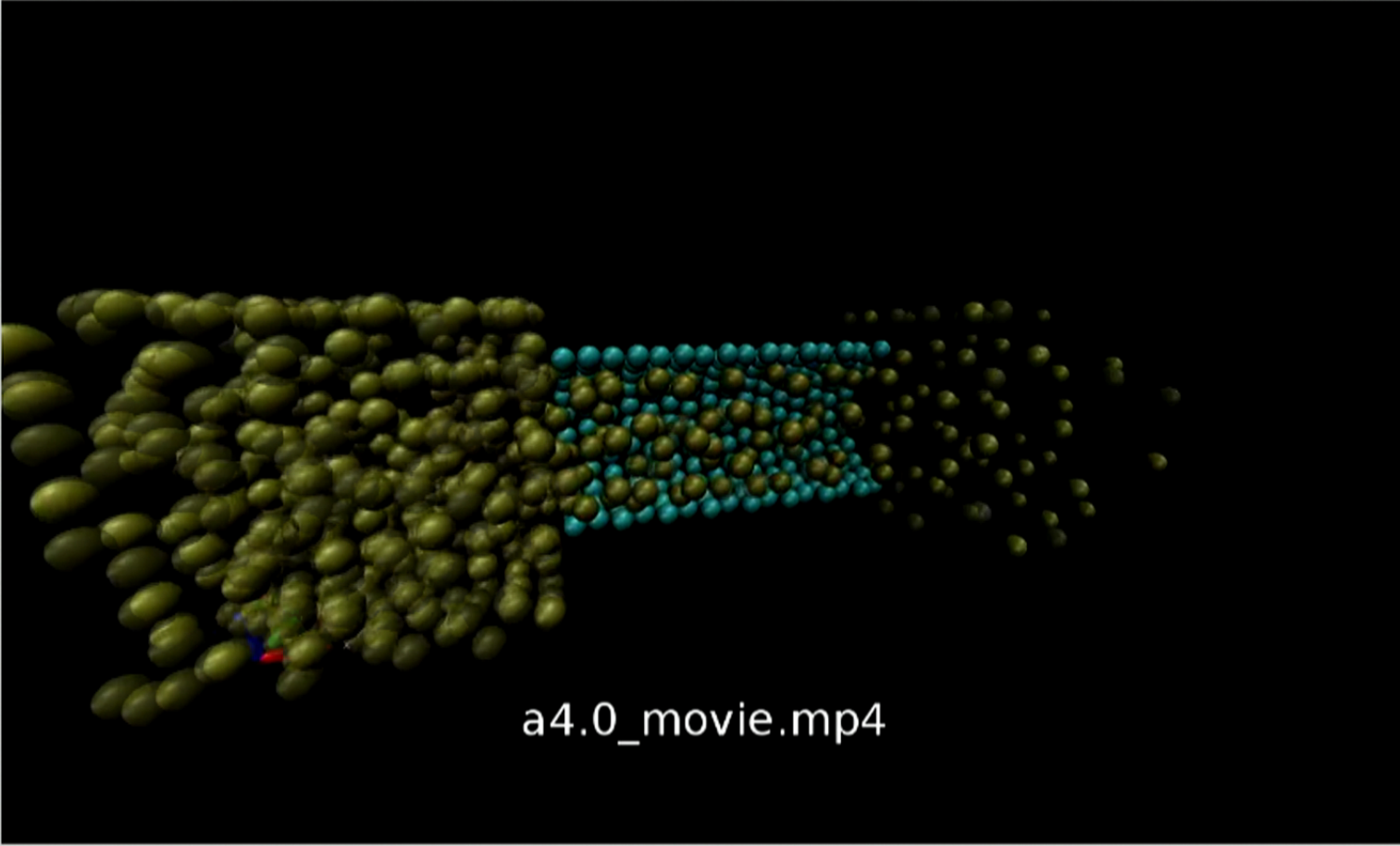


Conclusions

- ▶ Diffusion increases
- ▶ Enhancement Flow
- ▶ Anomalies if rigid walls

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