Water: A Complex Liquid

Marcia C. Barbosa

What is the mistery?

Why should we care?

What are the clues?

What is our hypothesis?

What are our results?

What do we predict?

Conclusions

Our Group

What is the mistery?

M. Chaplin, Water structure and science (2010).

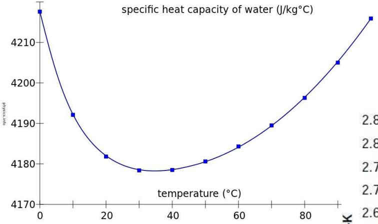
Such a simple liquid

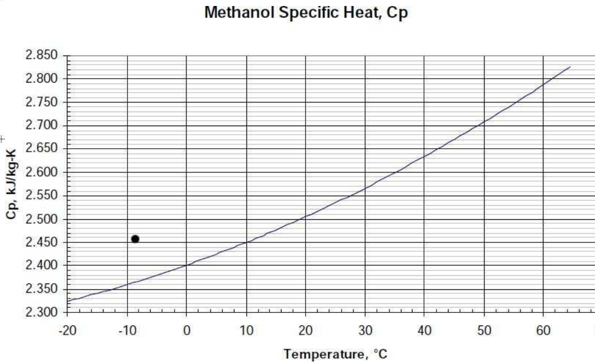
69 anomalies

Specific Heat

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

- $C_P = \left\{\frac{dQ}{dT}\right\}_P$



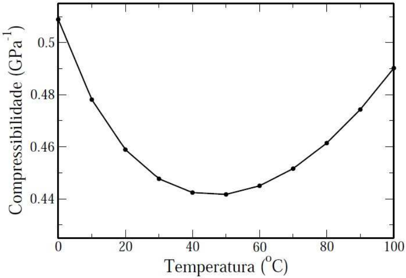


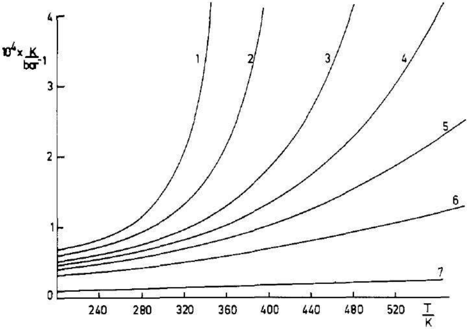
Compressibility

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

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

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

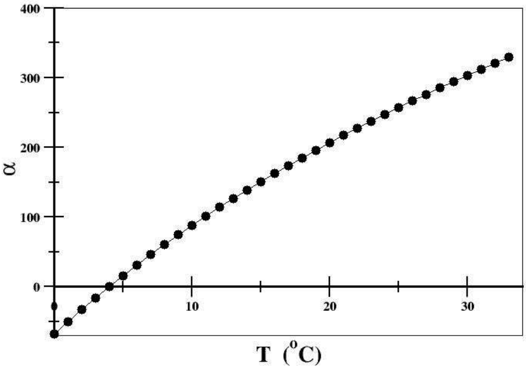




Thermal Expansion

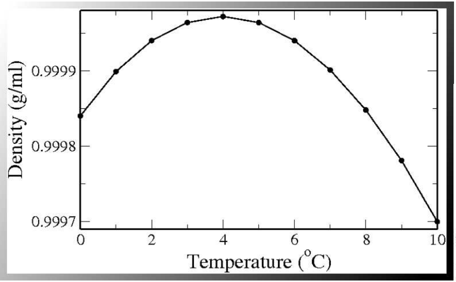
Kell, J. Chem. Eng. Data 20, 97 (75)

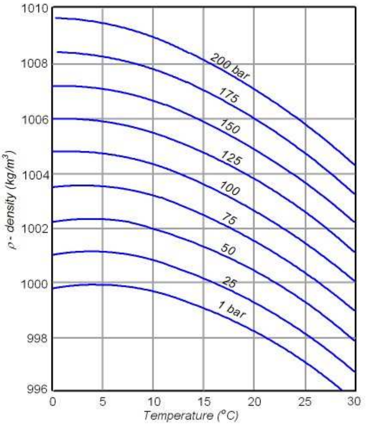
- $\alpha_P = \frac{1}{V}\left\{\frac{\partial V}{\partial T}\right\}_P$



Density

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

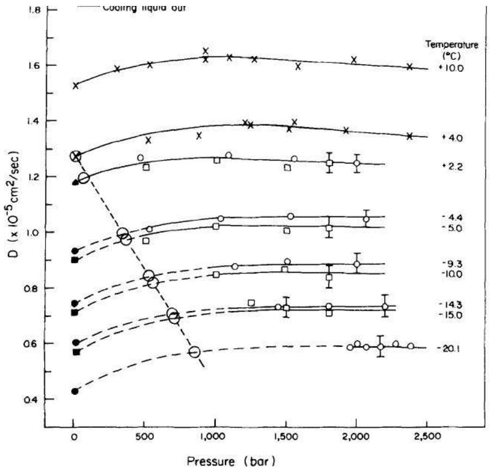




Diffusion

Angell, Finch, Bach 65, 3063 (76)

- $\langle r(t) r(0) \rangle = 6Dt$



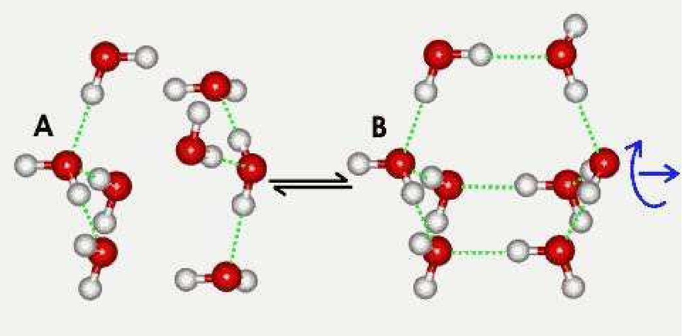
Why should we care?

- Specific Heat, Thermal Coductivity, 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

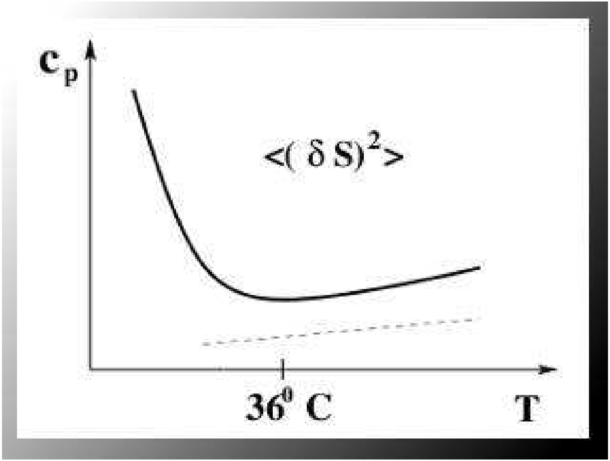
Two Scales



Specific Heat = Fluctuation in the Entropy

Stanley, Pramana 53, 53 (99)

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



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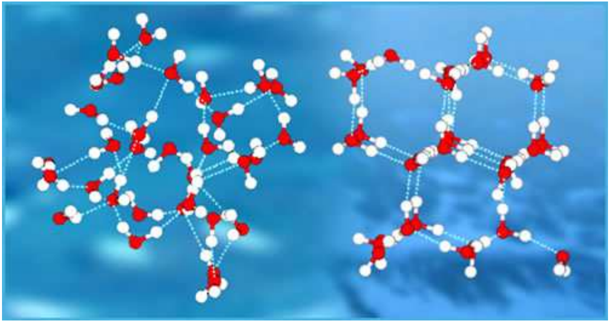

Specific Heat = Fluctuation in the Entropy

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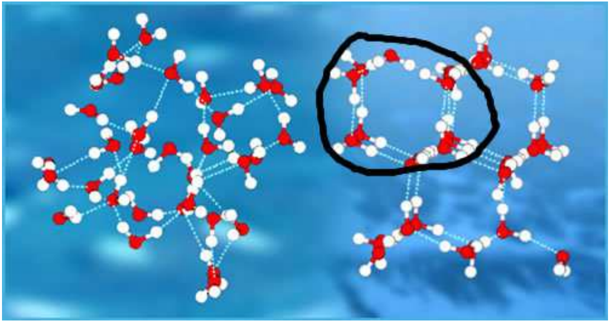
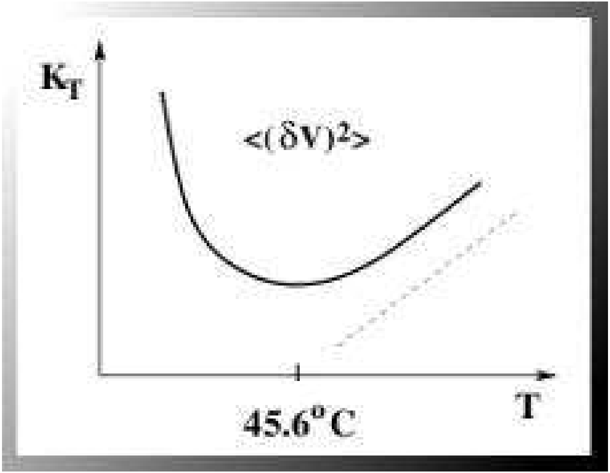


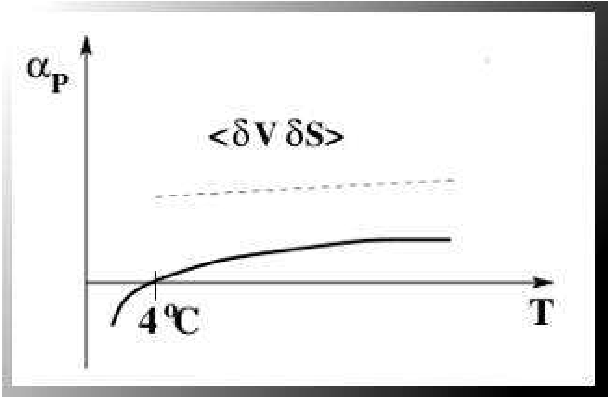
Compressibility = Fluctuation in the Volume

- $K_T \propto \langle (V - \langle V \rangle)^2 \rangle$



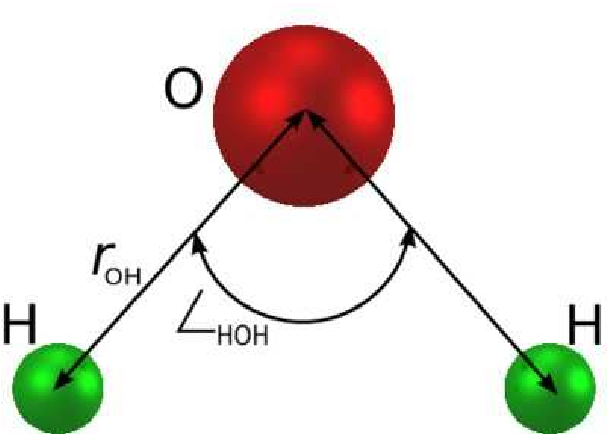
Thermal Expansion = Fluctuation in the Volume and Entropy

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



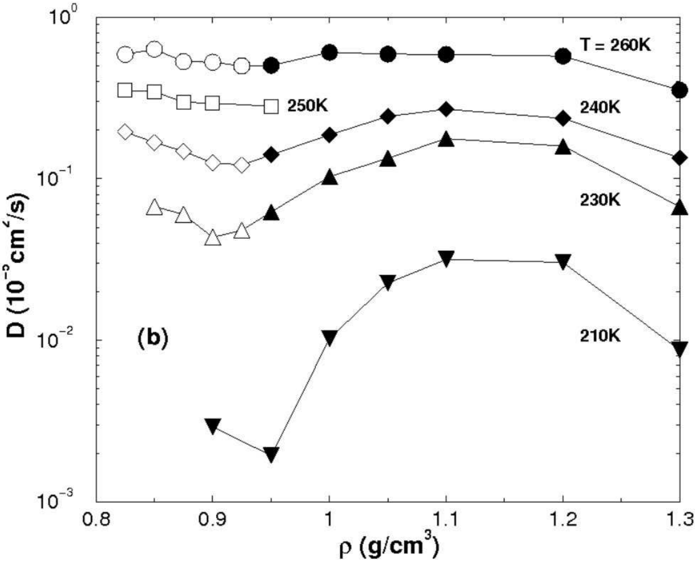
Diffusion - SPC/E

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



Diffusion - SPC/E

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

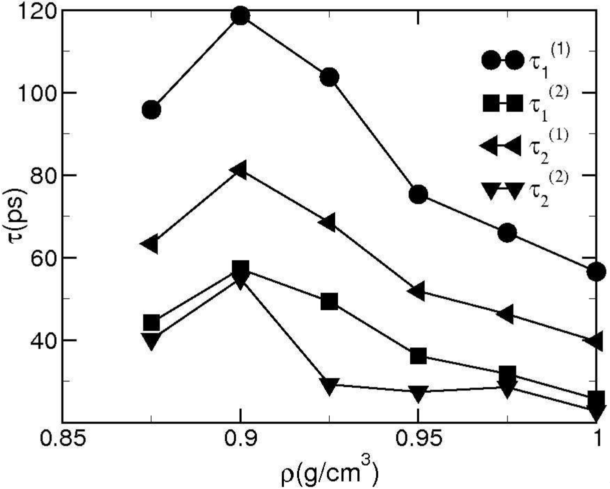


Rotation Diffusion - SPC/E

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

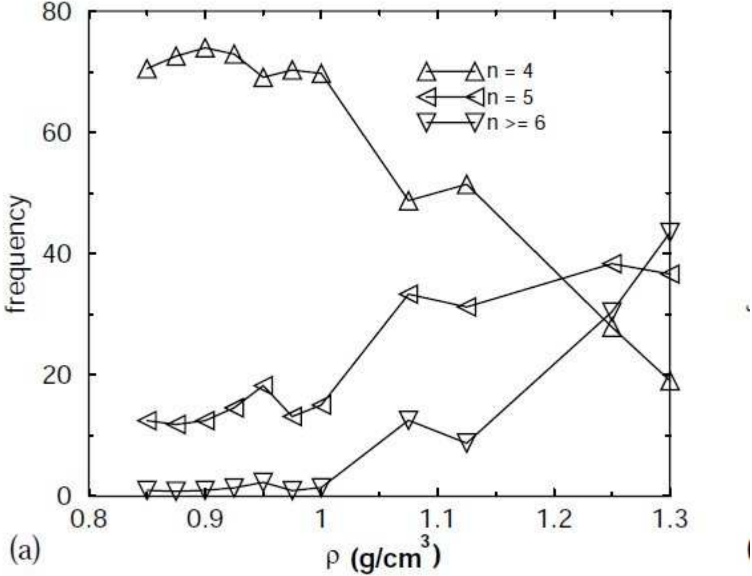
Mazza, Giovanbaptista, Stanley, Starr, PRE 76, 31203 (07)

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



Frequency - SPC/E

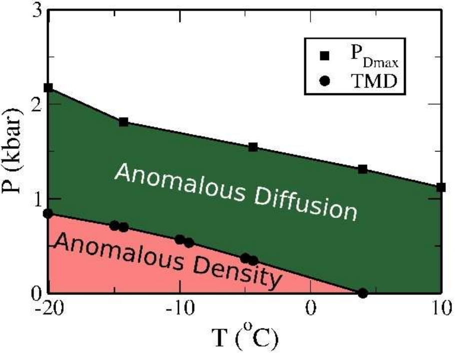
Netz, Starr, MCB and Stanley, Physica A 314, 470 (2002)

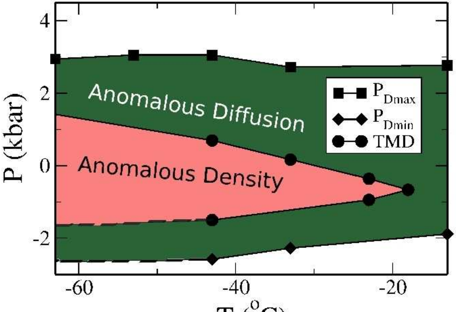


Water SPC/E

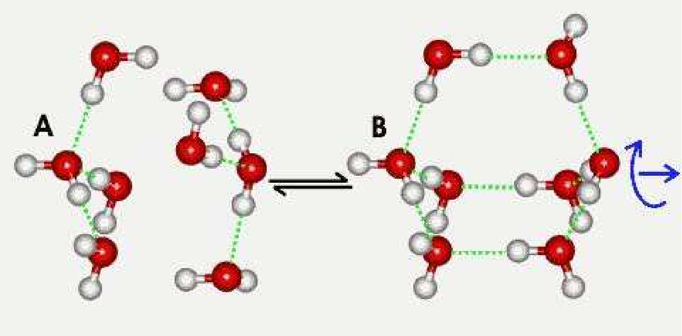
Angell, Finch, Bach 65, 3063 (76)

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

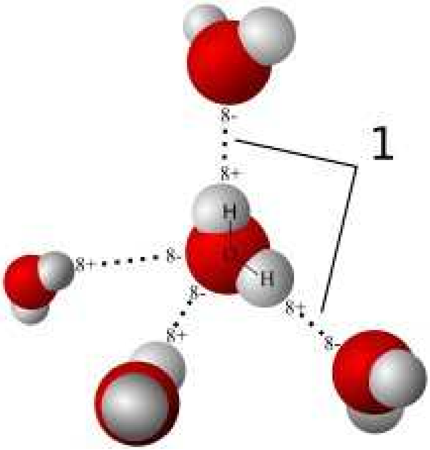




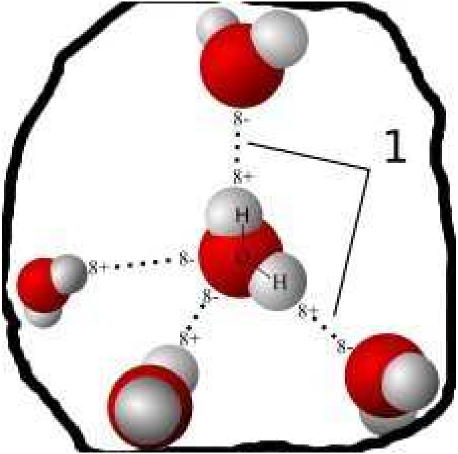
Two Length Scales Potential



Structure

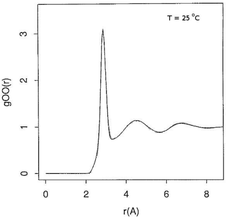


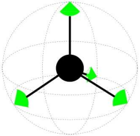
Structure



Effective Potential

- Radial Distribution Function of WATER:





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

- Ornstein-Zernike Equation:

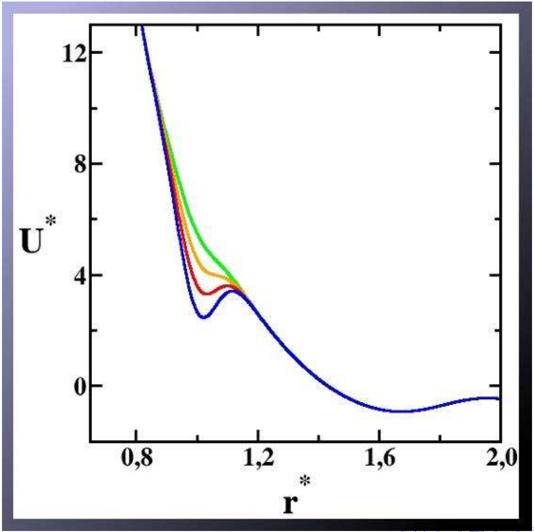
$$h(r) = g(r) - 1 = c(r) + \rho \int c(r - r')h(r')dr'$$

- *Hypernetted Chain Approximation* (HNC):

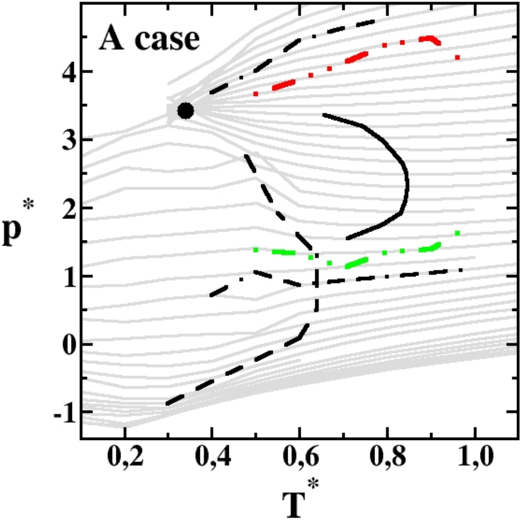
$$U(r) = k_B T\{g(r) - 1 - \ln[g(r)] - c(r)\}$$

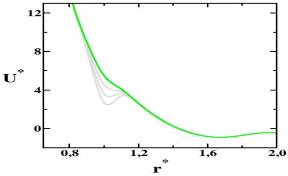
Effective Potential

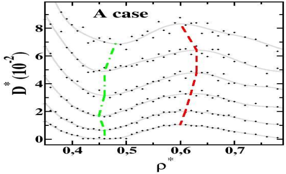
Barraz, Salcedo, Barbosa, JCP 131, 094504 (09)

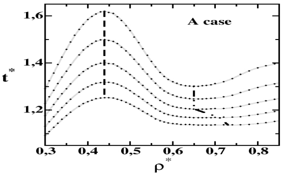


Phase Diagram









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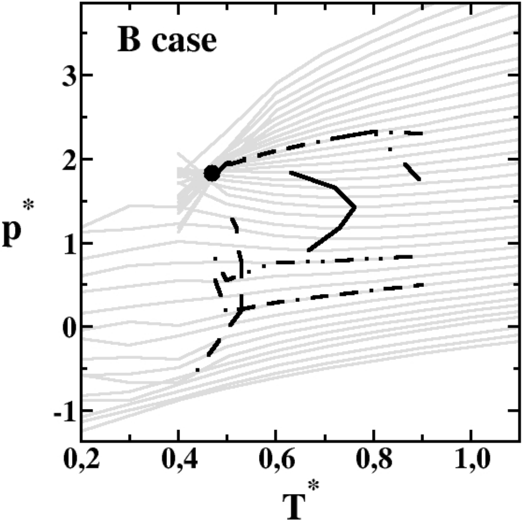

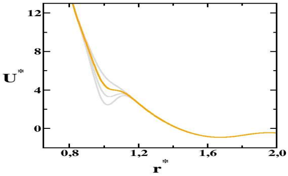

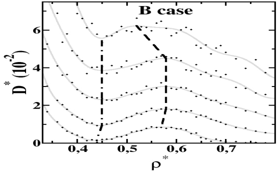

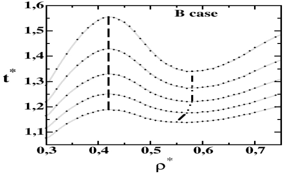

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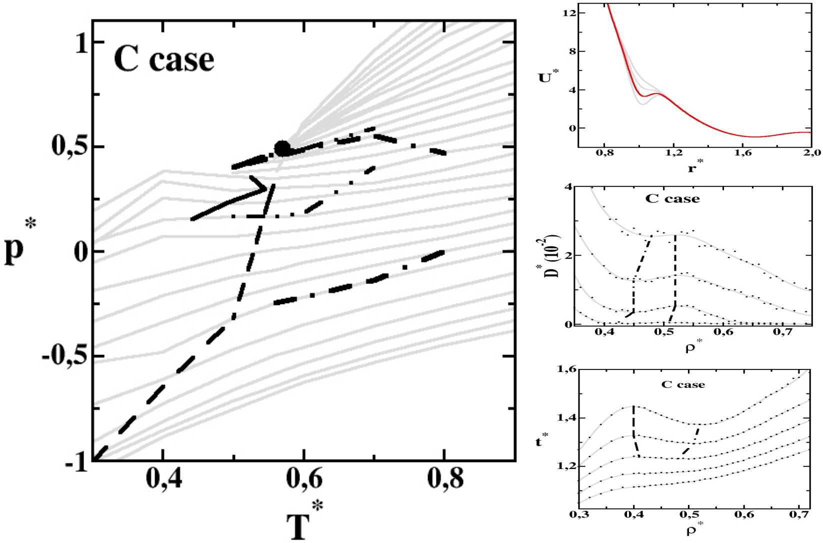

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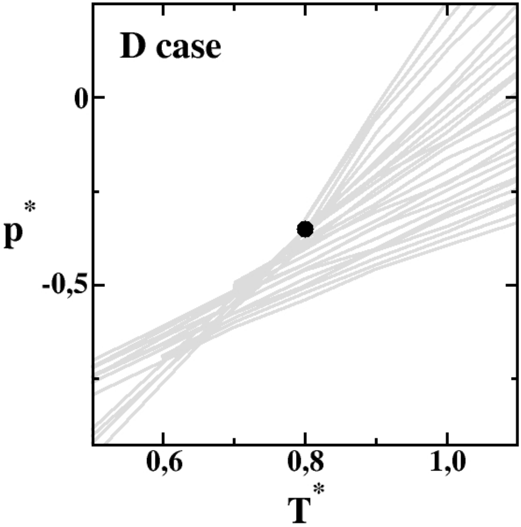
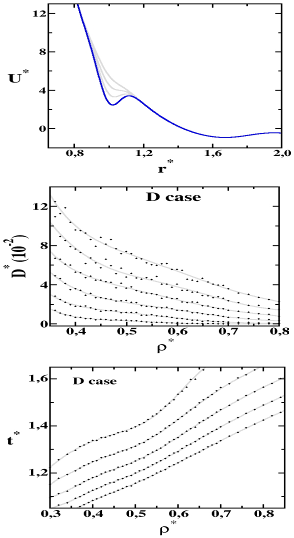
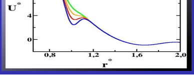
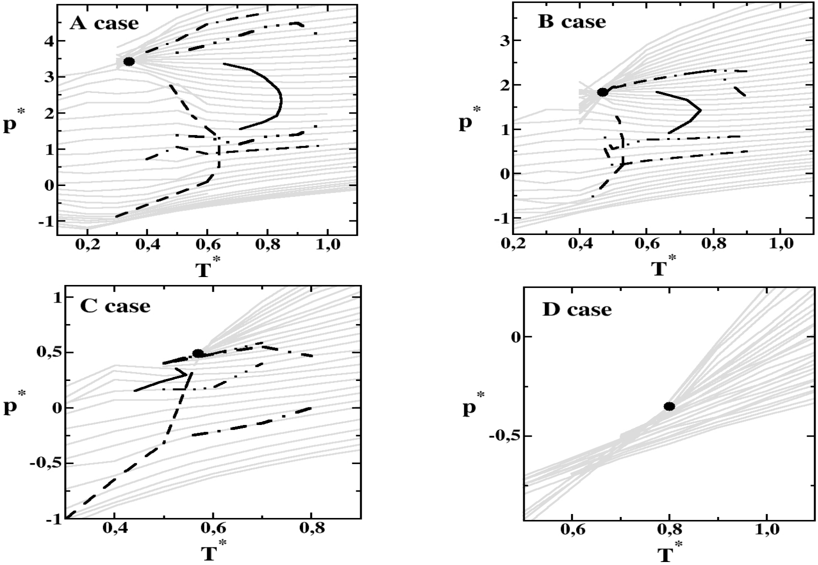




Critical Points





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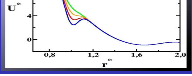
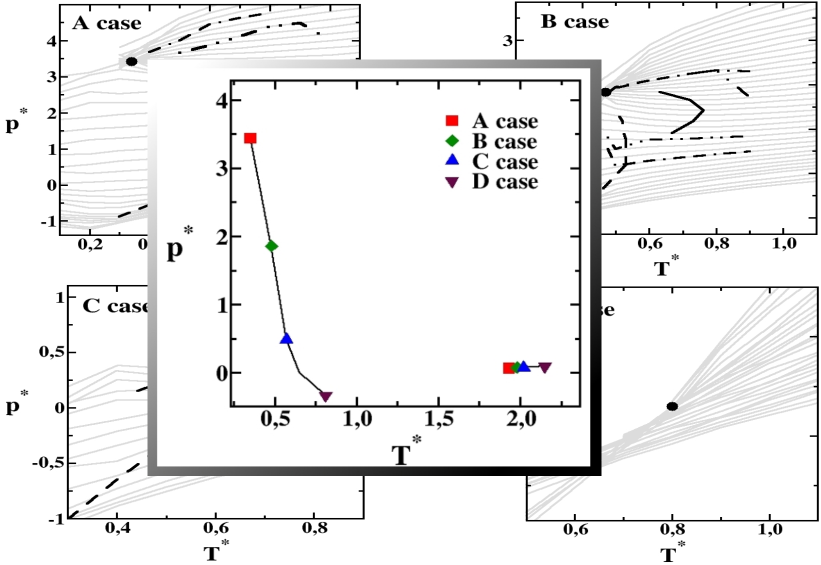
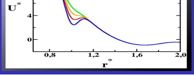
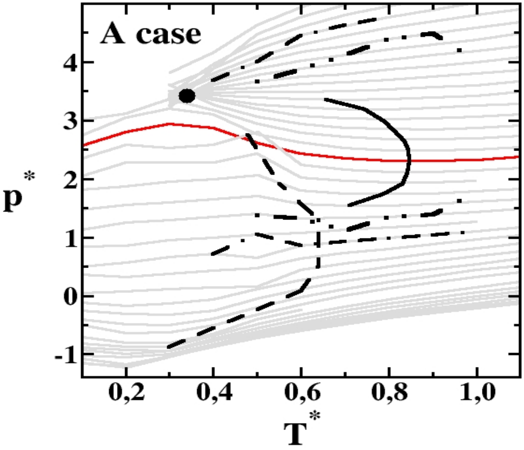




Radial Distribution Function





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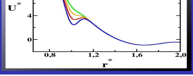
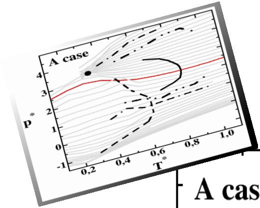
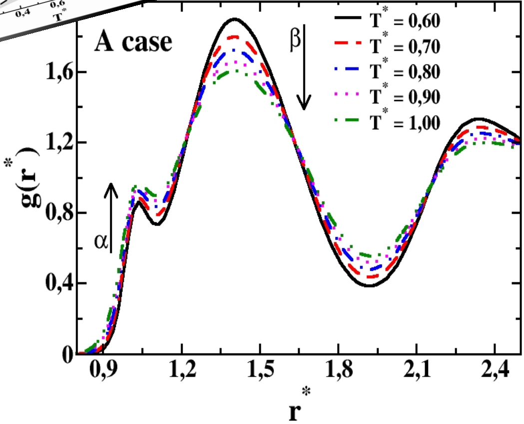
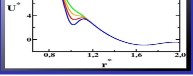
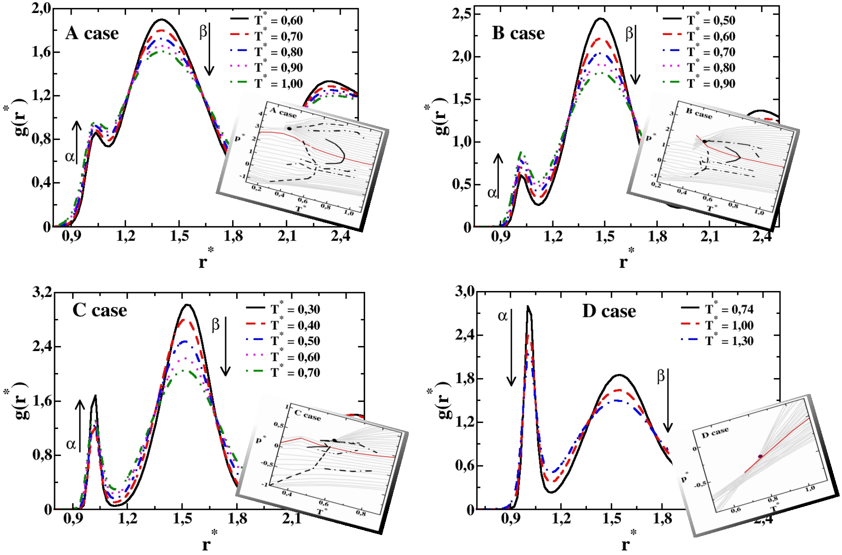






Radial Distribution Function





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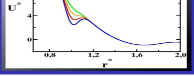
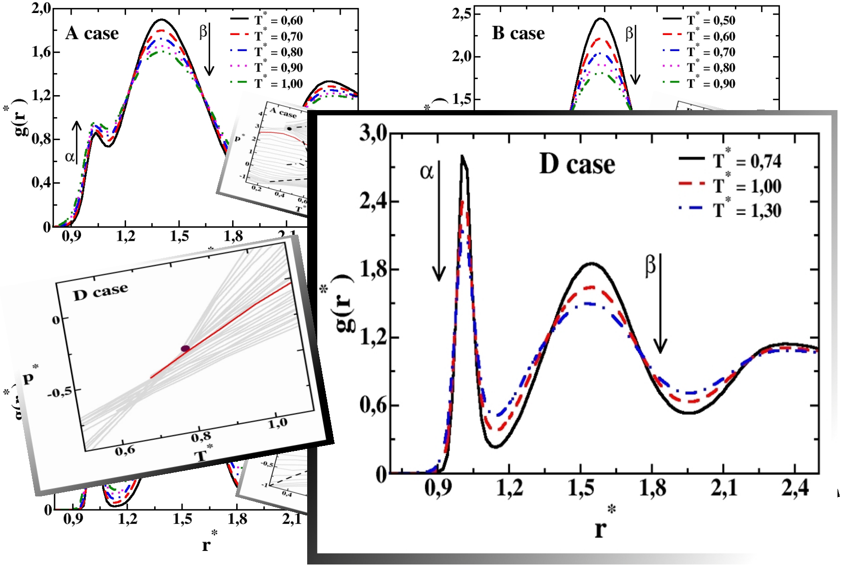
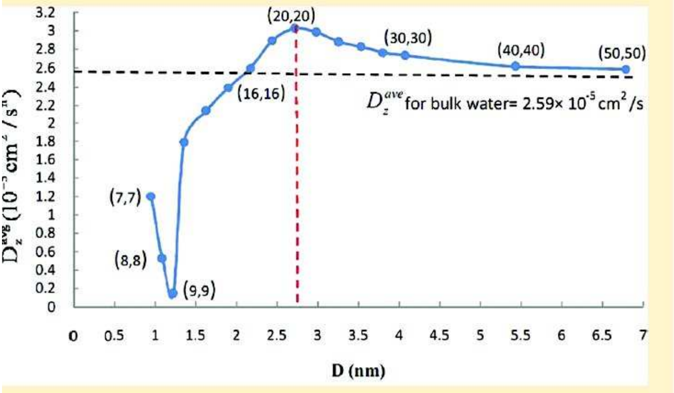


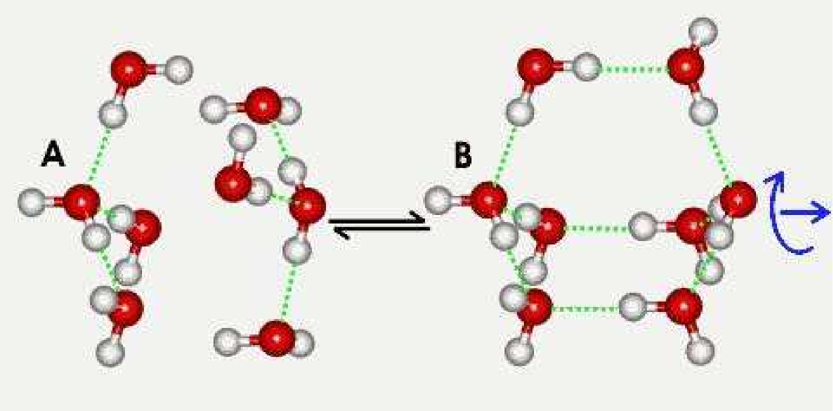


Rapid Flow in Nanotubes - Simulations

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

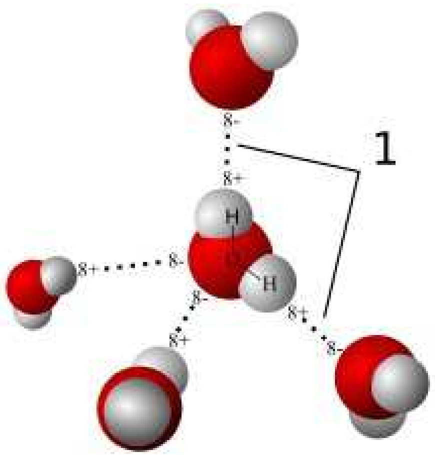


Water Channels- What is our Model?



Structure

N. M. Barraz, E. Salcedo and MCB, JCP 135 104507 (2011)



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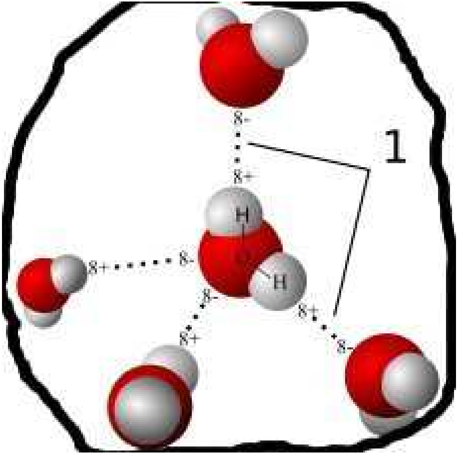
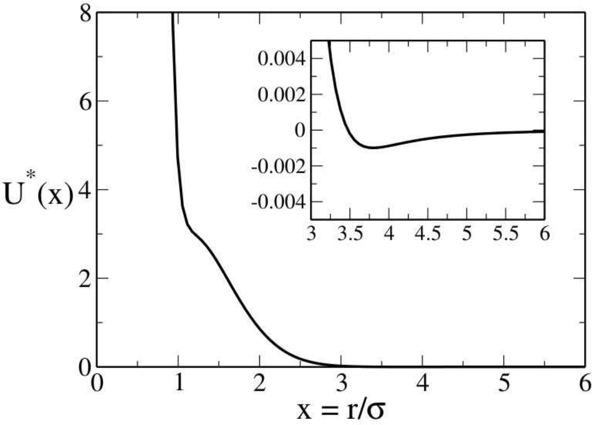
N. M. Barraz, E. Salcedo and MCB, JCP 135 104507 (2011)



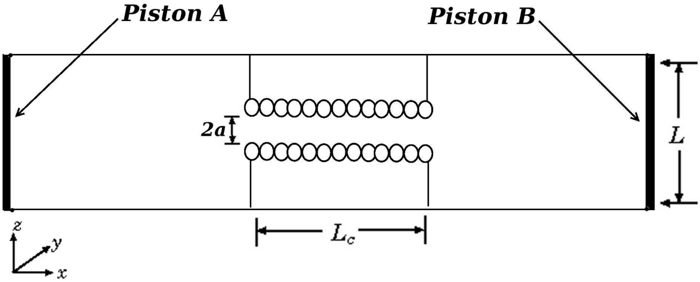
Effective Potential

A. B. de Oliveira, P. E. Netz, T. Colla and MCB, JCP 124 84505 (2006)



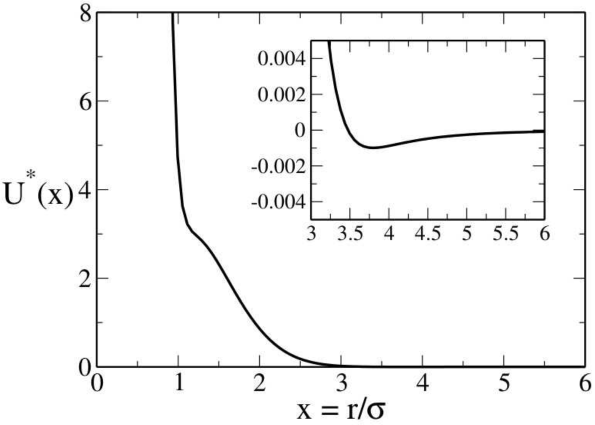
Model for Confining

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



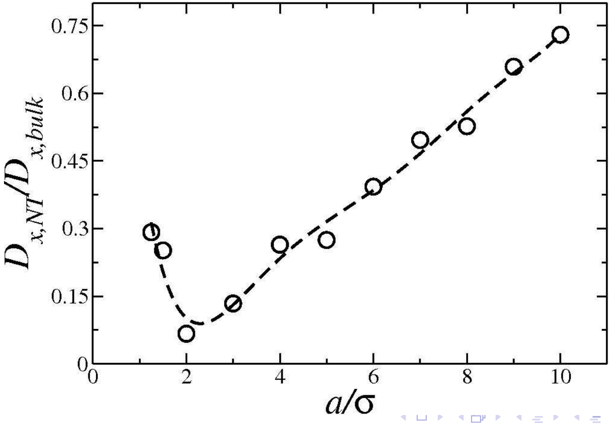
Effective Potential

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



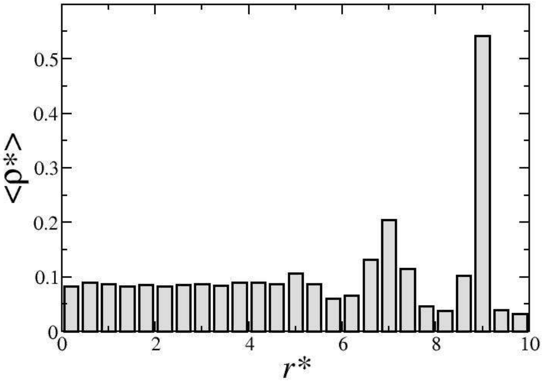
Diffusion

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



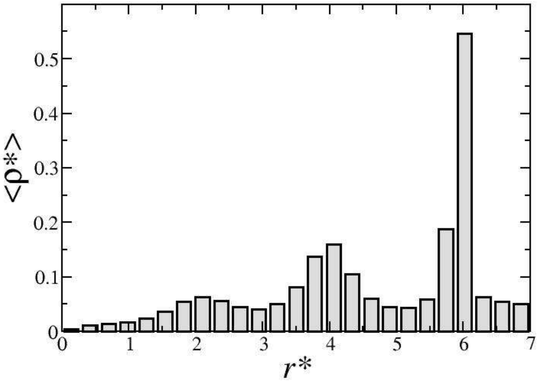
Density vs. r - a=10

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



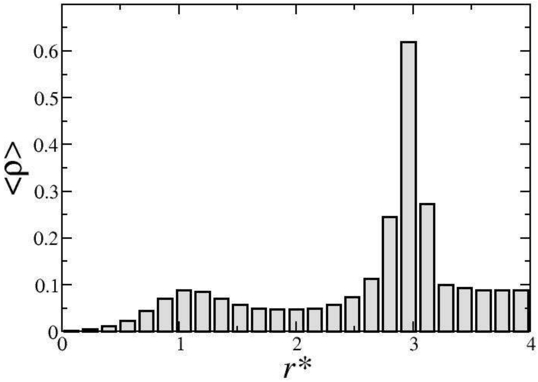
Density vs. r - a=7

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



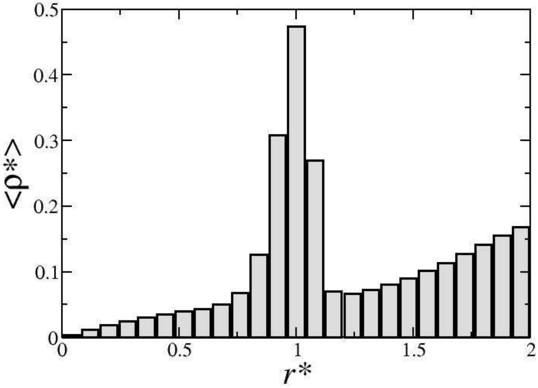
Density vs. r - a=4

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



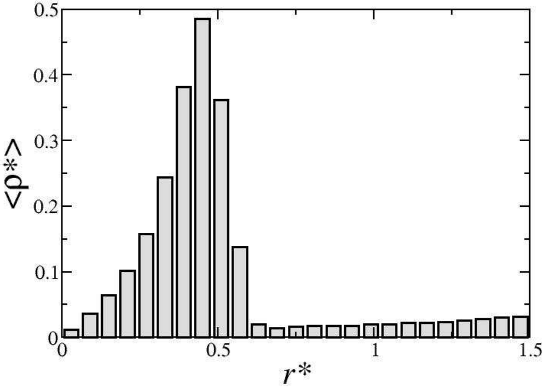
Density vs. r - a=2

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



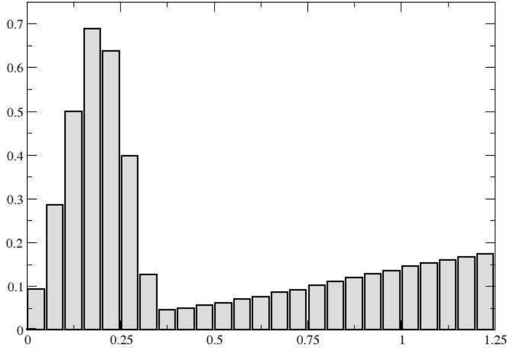
Density vs. r - a=1.5

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



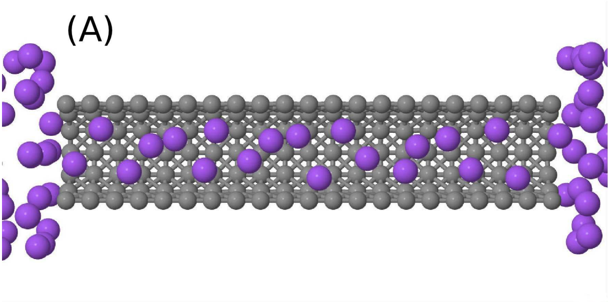
Density vs. r - a=1.25

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



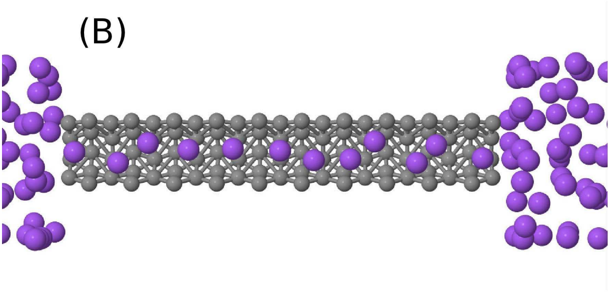
Density vs. r - a=1.25

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



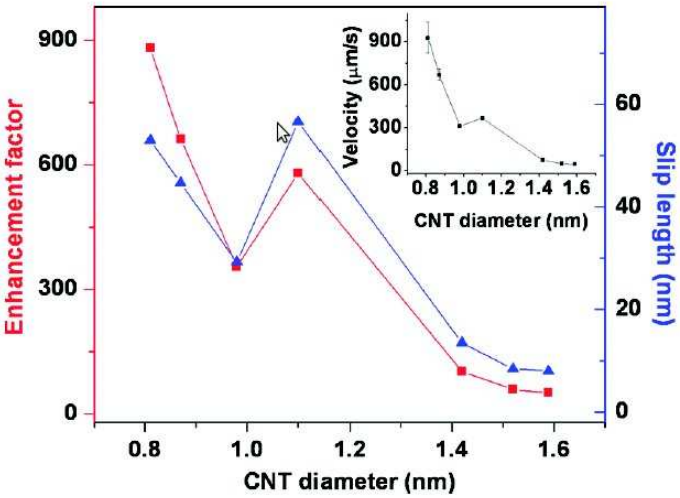
Density vs. r - a=1.25

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



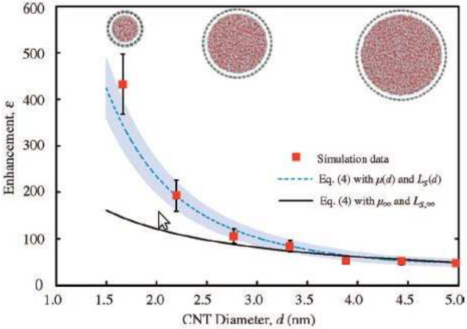
Flux in Nanotubes

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



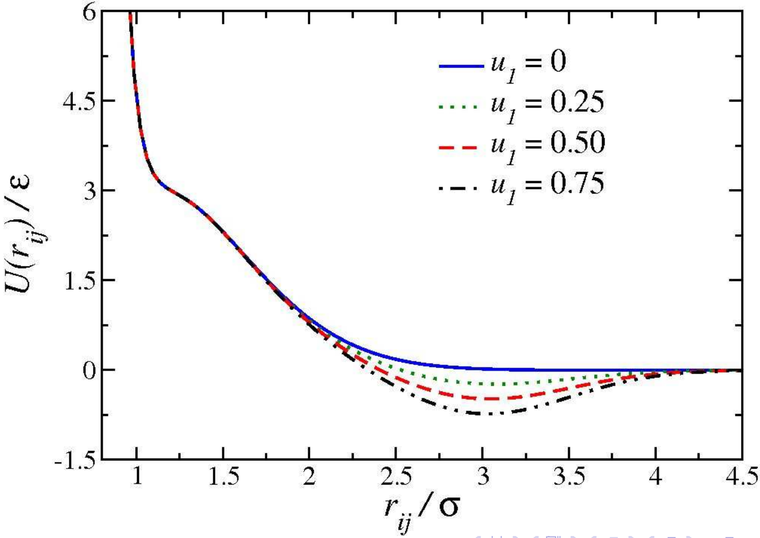
Water Channel - Enhancement Flow

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



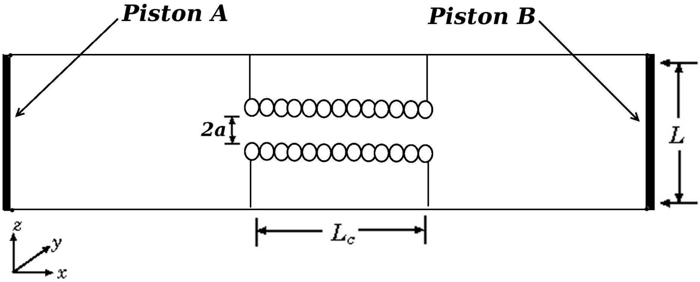
Effective Potential

J. da Silva and MCB, JCP (2010)



Model for Nanotubes

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



Enhancement Flow

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

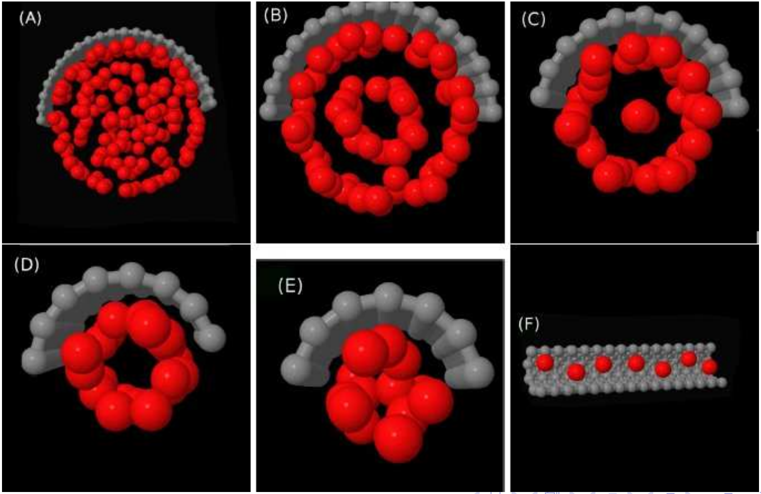
$$\begin{aligned}\langle v_x \rangle &= \gamma_{HP} \frac{\Delta p}{L_{NT}} \\ \gamma_{HP} &= \frac{a^2}{8\eta} \\ \eta &= \frac{k_B T}{3\pi\sigma D_x}\end{aligned}$$

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

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

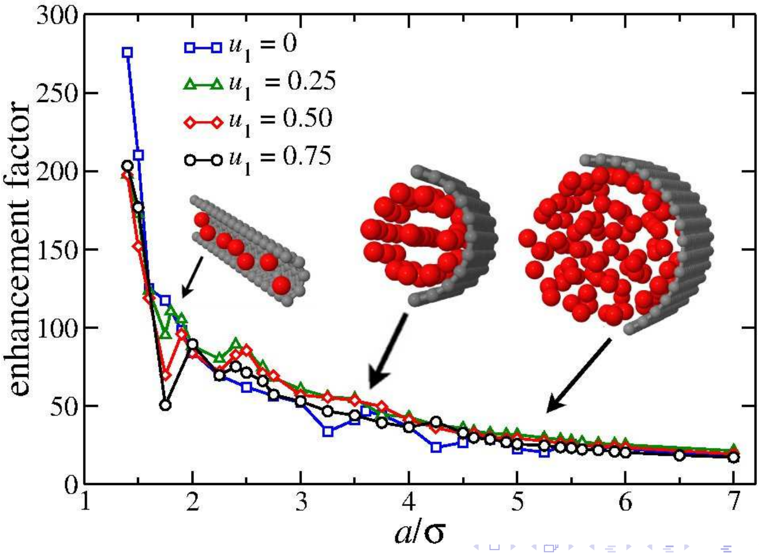
Layers

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



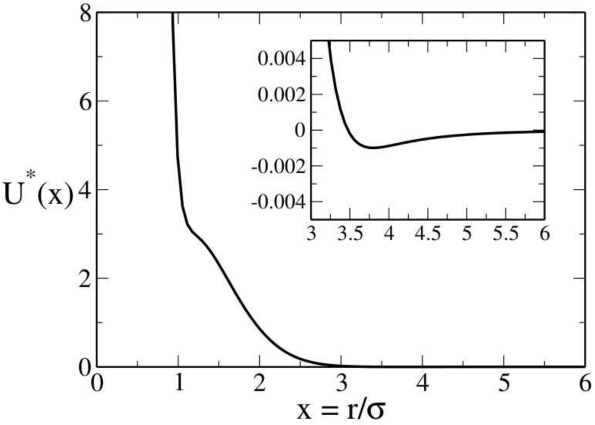
Enhancement Flow

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



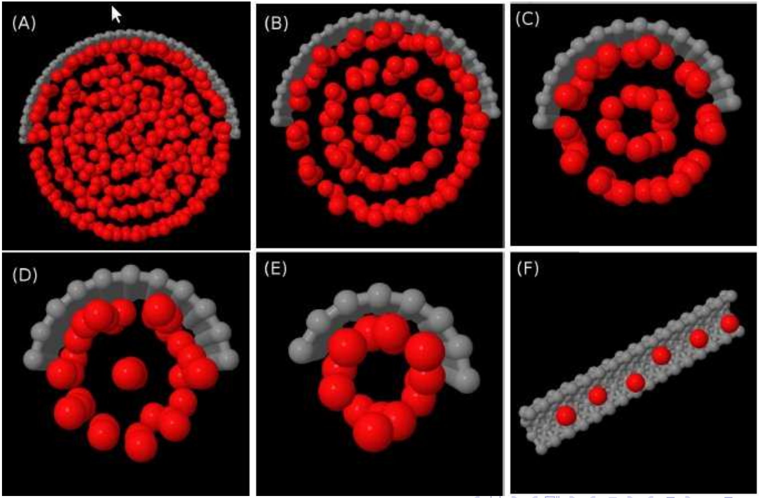
Potential

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



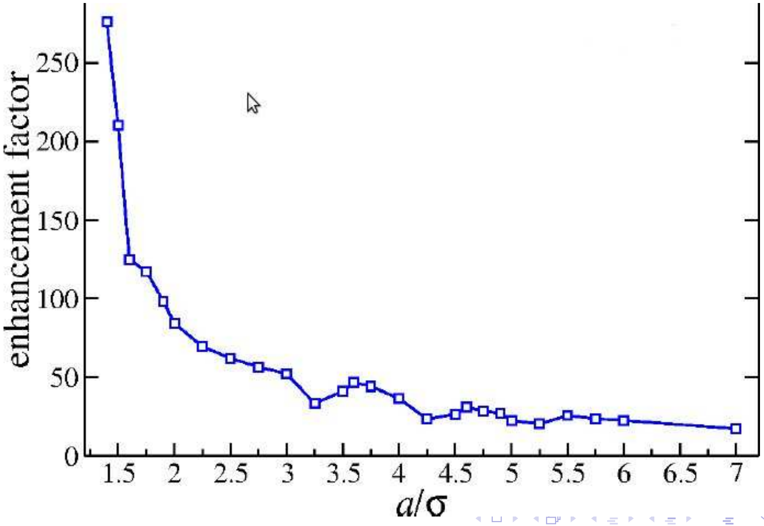
Layers

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



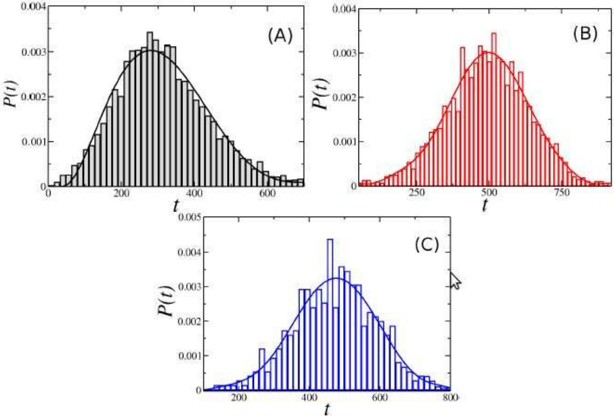
Enhancement Flow

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



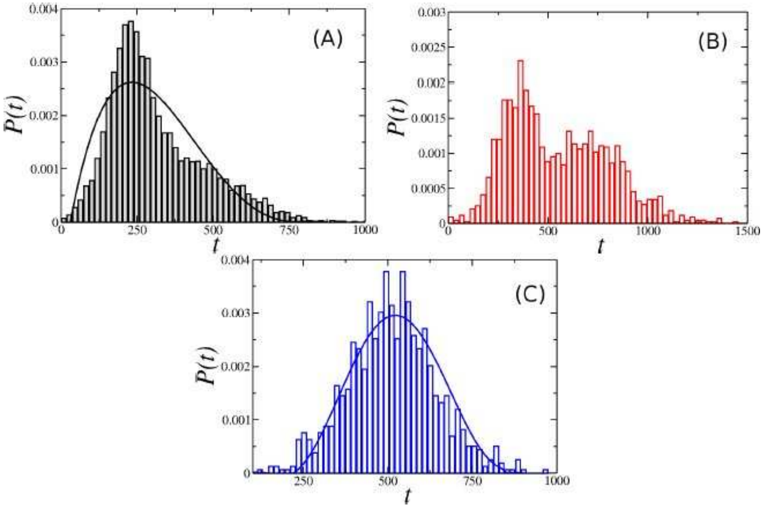
Distribution - Attractive

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



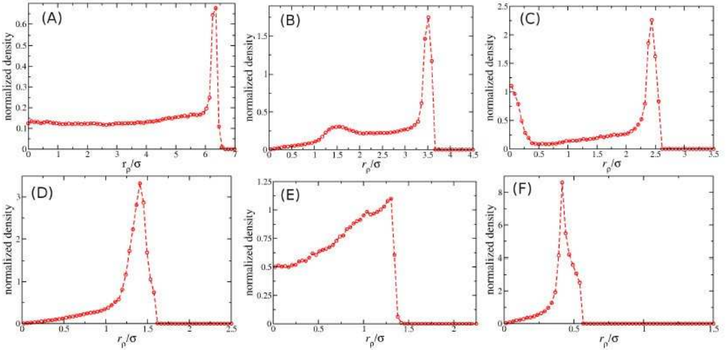
Distribution - Repulsive

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



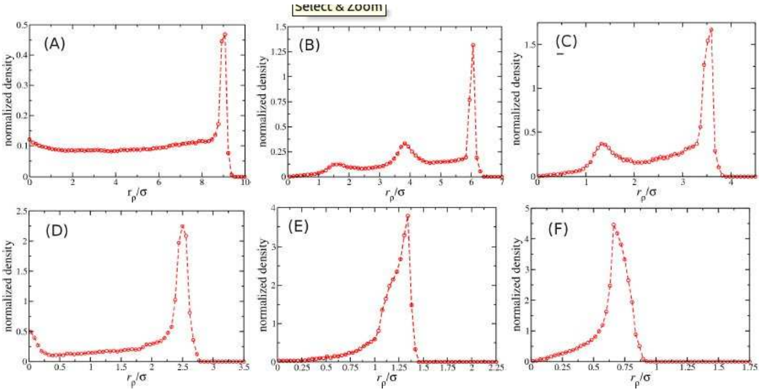
Density - Attractive

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



Density - Repulsive

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



Conclusions

- Effective Model Reproduces the Thermodynamic Anomalies of Water

- Effective Model Reproduces the Dynamic Anomalies of Water