Thermodynamics of Confined Nano-Phases; The Role of Molecular Simulation

Keith E. Gubbins
North Carolina State University

Where is Raleigh?

Where is Raleigh?

OUTLINE

1. Review of atomistic simulation methods:

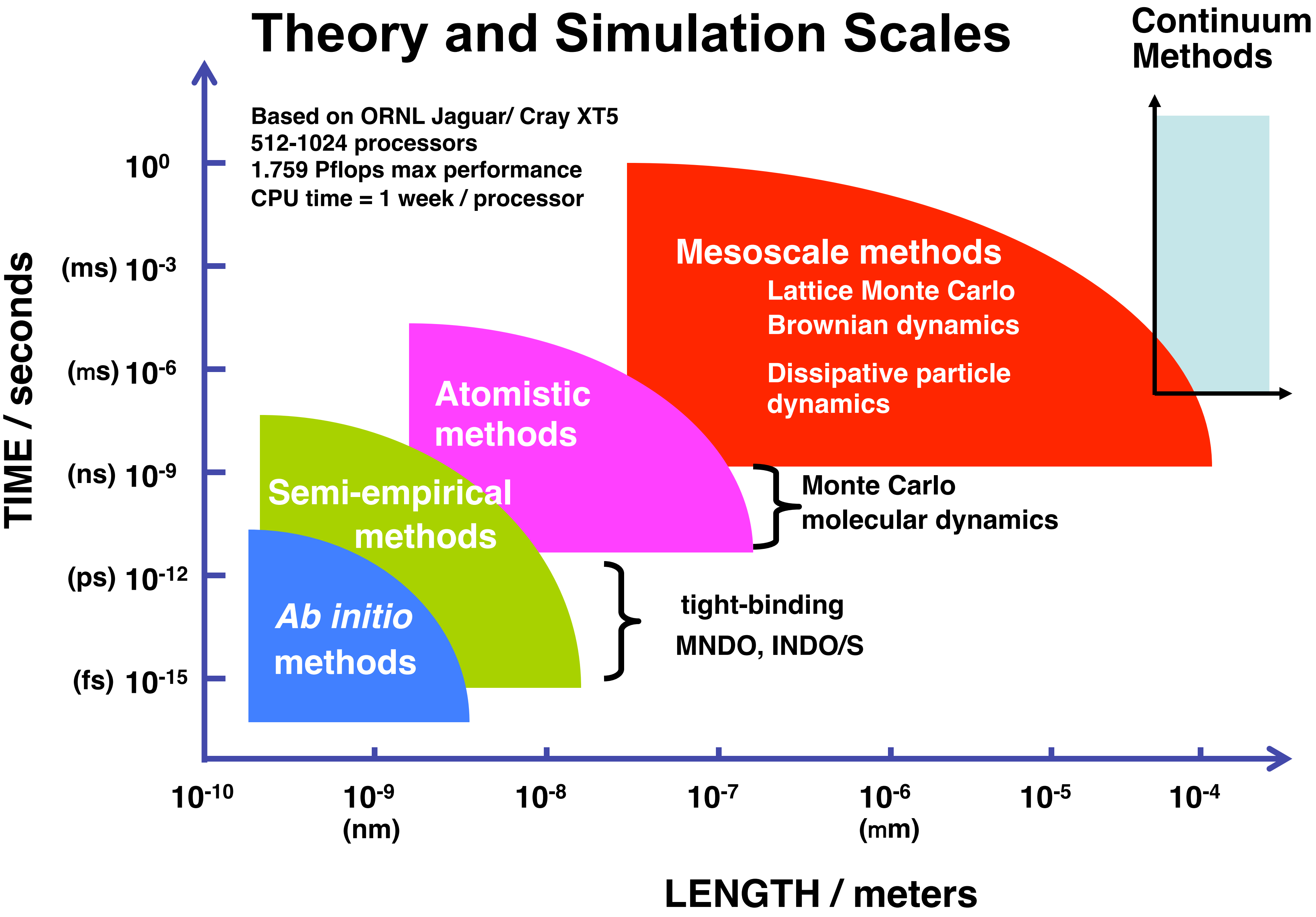
    Classical statistical mechanics
    Molecular Dynamics method
    Monte Carlo method

2. Some applications to confined nano-phases:

    Introduction to nanoporous materials and adsorption
    Phase changes
    Pressure effects in nanopores
    Diffusion in nanopores

3. Conclusion

Theory and Simulation Scales



Based on ORNL Jaguar/ Cray XT5
512-1024 processors
1.759 Pflops max performance
CPU time = 1 week / processor

TOP 500 SUPERCOMPUTERS*

Name, Site	Cores	PetaFlops
1. Titan, Oak Ridge Nat Lab	560,640	17.6
2. Sequoia, Lawrence Liverm.	1,572,864	16.3
3. K Computer, Riken, Japan	705,024	10.5
4. Mira, Argonne NL	786,432	8.2
5. JuQueen, Julich, Germany	393,216	4.1

* www.top500.org, November 2012

Common Assumptions

- Can treat kinetic energy of molecular motion and potential energy due to intermolecular interactions classically
- We often treat small molecules as rigid, and neglect any effects of the electronic or vibrational state of the molecules on their intermolecular force field. $P_i = P_i^{class} P_i^{quant}$. For large molecules (proteins, polymers, etc.) flexibility is included using classical force fields.
- We shall often assume that the N-body intermolecular potential energy can be written as a sum of isolated two-body (pair) interactions (neglect 3-body and higher n-body interactions)

Time vs. Ensemble Averages: the Ergodic Hypothesis

- Experimental observations are time averages over system behavior as it fluctuates between many quantum states *(i)*, e.g. for the energy *U*

$$U = \lim_{\tau\to\infty} \frac{1}{\tau} \sum_i E_i \Delta t_i$$

- Alternatively, imagine a very large number, *M*, of replicas of the system, all at the same *N*, *V* and *T*, then at some instant average over all of them to get the average energy

$$U = \lim_{M\to\infty} \sum_i E_i \rho_i$$

The *ergodic hypothesis* states that these two kinds of average give the same result for *U.*

Classical Distribution Laws

- Canonical Ensemble System at fixed N,V,T can exist in many possible configurational states with different energies E. Probability of observing system in a particular state n is given by the *Boltzmann distribution law*,

$$\rho = \frac{e^{-\beta E}}{Q} \qquad (1) \qquad \beta = 1/kT$$

- Grand Canonical Ensemble System is at fixed temperature, volume and chemical potential, *μ*

$$\rho_{\mu VT}(\mathbf{r}^N) = \frac{1}{\Xi}\sum_N \frac{z^N}{\Lambda^{3N} N!}\exp\left[-\beta\mathcal{U}\left(\mathbf{r}^N\right)\right] \qquad z = \exp(\mu / kT)$$

Atomistic Simulation Methods

- References:
  - A. R. Leach, *Molecular Modelling*, 2nd ed., Ch. 6, 8, Prentice Hall (2001)
  - D. Frenkel and B. Smit, *Understanding Molecular Simulation*, 2nd ed., Academic Press (2002)
  - M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford (1987)

Atomistic Simulation Methods - General Features

- In these methods the equations of statistical mechanics are solved numerically. The two principal methods are Monte Carlo (MC) and Molecular Dynamics (MD)

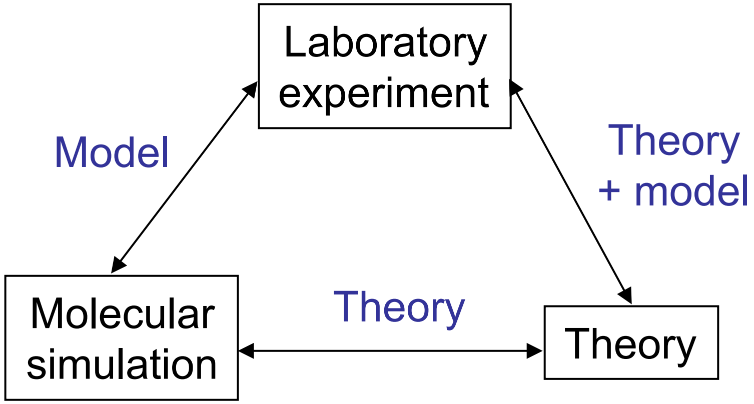
- In atomistic (molecular) simulation we must first specify the molecular model:
  - <u>For fluids</u> this consists of specifying equations for the intermolecular and intramolecular forces (the 'force field'), molecular mass
  - <u>For some heterogeneous systems, e.g. colloids, composites, fluid-solid systems,</u> we often need to specify, in addition, the space coordinates of solid atoms, and this becomes part of the model

- The equations of statistical mechanics are then solved 'exactly', without further approximation

Atomistic Simulation Methods - General Features

- Uses:

1. Test model by comparing simulated and experimental properties. Then use model in further simulations to carry out "experiments" not possible in the laboratory, e.g. critical points for molecules that decompose below T_c, properties of molten salts, long-chain hydrocarbon properties at very high pressures, properties of confined nano-phases, etc.
2. Fundamental studies, e.g. to determine the range of validity of Kelvin's equation, Fick's law of diffusion, Newton's law of viscosity, etc.
3. Industrial applications include design of new products (drugs, polymers, catalysts, solvents, crystal growth inhibitors, etc.) and data prediction for process simulators.
4. Test theories by comparing theory and simulation



Features Common to MC and MD

- We will get accurate results for our model system, provided:
  - *N* is large enough
  - run is long enough
  - we avoid metastability trapping
  - unwanted boundary effects are minimized

- Runs typically involve *N* up to 100,000 and real times up to 10-100 ns. However, with current machines it is possible to study *N* up to several billions, and times up to 1 μs.

Differences Between MC and MD

- MD gives information about dynamical behavior, as well as equilibrium, thermodynamic properties. Thus, transport properties can be calculated. MC can only give static, equilibrium properties

- MC can be more easily adapted to other ensembles:
  - μ, V, T (grand canonical)
  - N, V, T (canonical)
  - N, P, T (isobaric-isothermic)

- In MC motions are artificial - in MD they are natural

- In MC we can use special techniques to achieve equilibrium quickly. For example, can 'observe' formation of micelles, slow phase transitions. In MD we cannot 'speedup' equilibration.

Brief Account of MD

Molecular Dynamics (MD)

- Molecules move naturally under their own intermolecular forces.
- Positions and velocities of each molecule are followed in time by solving Newton's (and Euler's, for non-spherical molecules) equations of motion.
- Then

$$A_{average} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A\left[\underline{p}^N(t), \underline{r}^N(t) \right] dt$$

- According to the ergodic hypothesis, the time average and ensemble averages are equal, so

$$A_{average} = \langle A \rangle$$

- First MD in 1957 for hard spheres: B. J. Alder and T.E. Wainwright, *J. Chem. Phys.* **27**, 1208 (1957)

Berni J. Alder (1925-)

Standing: Berni Alder
Sitting: Mary Ann Mansigh
Tom Wainwright
(ca.1962)

Credit: http://photos.aip.org/history/Thumbnails/ald賀

´_berni_c1.jpg

ca. 2008

Credit: http://news.engineering.ucdavis.edu/das
/index.html?param=7a4517ac456c72b8558a673435c20a62

- First MD in 1957 (Lawrence Berkeley NL): B. J. Alder and T.E. Wainwright, *J. Chem. Phys.* **27**, 1208 (1957)
- Born in Germany as a Swiss citizen
- Came to United States in 1941 prior to US's entrance into WWII
- PhD from Caltech working with John Kirkwood (although not thesis advisor)
- After PhD went to Livermore National Lab and worked with Edward Teller
  - Worked on developing equations of state for weapons development
  - Taught in the Chemistry Department at Berkeley
- Developed the Molecular Dynamics method with Tom Wainwright (1955 – 1956).
- Teller predicted MD would not be competitive with Monte Carlo as it was more complicated

MD: Newton’s equations

- How does it work?
  - Newton’s equations of motion for the *N*-particle system:

$$\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i \qquad (1) \qquad\qquad i = 1,2,3,\ldots.N$$

where:

$$\mathbf{F}_i = -\frac{\partial \mathrm{U}}{\partial \mathbf{r}_i} = \text{Force acting on particle } i$$

$$\ddot{\mathbf{r}}_i = \frac{d^2\mathbf{r}_i}{dt^2} = \text{Acceleration of particle } i$$

$$m_i = \text{Mass of particle } i$$

  - In MD these equations are solved numerically to obtain the time evolution of the system under the given potential.

MD: Newton's equations

- How does it work?
  - Newton's equations of motion for the *N*-particle system:

$$\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i \qquad (1)$$

  - In order to solve this set of 3*N* second-order differential equations, we need 6*N* initial conditions:
    - Initial positions are chosen to avoid having large forces at the beginning of the simulation. For small molecules (e.g. Ar, H_2O) this can be done by placing atoms on a lattice (e.g. fcc). For complex systems (e.g. a protein), need to first use a minimization ('Molecular Mechanics') algorithm.
    - Initial velocities are sampled from a Maxwell-Boltzmann distribution.

MD: Verlet’s Method

- Loup Verlet [*Phys. Rev.* 159, 98 (1967)] was one of the first to carry out MD for a realistic continuous intermolecular potential (Lennard-Jones) and his algorithm is still widely used. The position of molecule *i* at time *t*+d*t* is related to the position at time *t* by a Taylor series:

$$\mathbf{r}_i(t+\delta t)=\mathbf{r}_i(t)+\delta t\,\dot{\mathbf{r}}(t)+\frac{1}{2!}(\delta t)^2\,\ddot{\mathbf{r}}_i(t)+\frac{1}{3!}(\delta t)^3\,\dddot{\mathbf{r}}_i(t)+\mathrm{O}\left(\delta t^4\right) \qquad (2)$$

- Similarly, for time *t*-d*t* we have:

$$\mathbf{r}_i(t-\delta t)=\mathbf{r}_i(t)-\delta t\,\dot{\mathbf{r}}_i(t)+\frac{1}{2!}(\delta t)^2\,\ddot{\mathbf{r}}_i(t)-\frac{1}{3!}(\delta t)^3\,\dddot{\mathbf{r}}_i(t)+\mathrm{O}\left(\delta t^4\right) \qquad (3)$$

where $\dot{\mathbf{r}}_i = d\mathbf{r}_i / dt = \mathbf{v}_i =$ velocity of molecule i, and

$\ddot{\mathbf{r}}_i = d^2\mathbf{r}_i / dt^2 = \mathbf{a}_i = \mathbf{F}_i/\mathrm{m}_i =$ acceleration of molecule i.

MD: Verlet’ s Method

- If we add equations (2) and (3), we get:

$$\mathbf{r}_i(t+\delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i\left(t-\delta t\right) + \frac{\left(\delta t\right)^2}{m_i}\mathbf{F}_i\left(t\right) + \mathrm{O}\left(\delta t^4\right) \tag{4}$$

- If we subtract (3) from (2), we find:

$$\mathbf{v}_i(t) = \dot{\mathbf{r}}_i(t) = \frac{1}{2\delta t}\left[\mathbf{r}_i\left(t+\delta t\right) - \mathbf{r}_i\left(t-\delta t\right)\right] + \mathrm{O}\left(\delta t^3\right) \tag{5}$$

- Equation (4) is used to obtain the positions at time *t*+d*t*,
- Equation (5) is used to calculate the velocities at time *t*.

MD: The time step

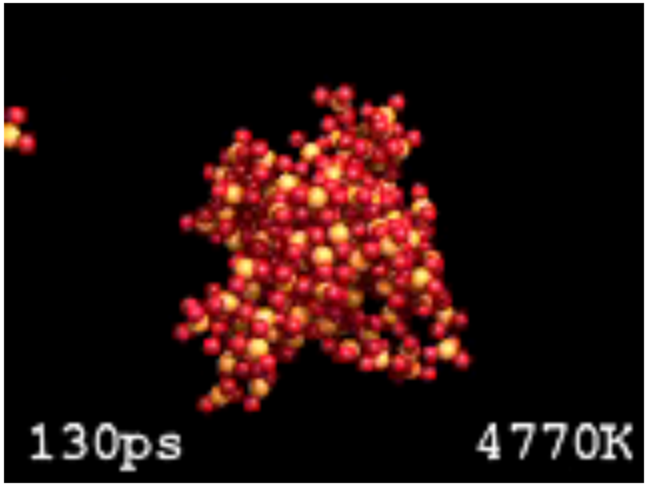
- The time step d*t* should be:
  - Small enough so that truncation errors from the numerical method are negligible. This is usually tested by monitoring the total energy of the system as a function of time. If energy is not conserved, it means that d*t* is too big.
  - Big enough so that the desired real time is covered with a minimum number of time steps.
- A rule of thumb is that the energy of the system should be constant to within 0.01% over the run. Typically, this requires us to pick d*t* ~ one tenth of the characteristic time of the fastest vibration in the system. For atoms or rigid molecules this is usually of the order of 10 fs = 10^{-14} s. Thus, for a typical system it takes ~ 100000 time steps to model 1 ns of real time. For flexible molecules we may need a time step of about 1 fs=10^{-15}s.

MD: The time step

- It is possible to look at longer time scales by removing the fastest degrees of freedom from the system. Some ways to do this are:
  - Treat the parts of the system involved in the fast mode (e.g. C-H vibrations) as a single particle, *i.e.* coarse grain out the fast degrees of freedom. This is done, for example, in the “united atoms” force fields.
  - Constrain the fast modes.
- The contribution of the fast modes to the system’s properties, if needed, must be added later. This assumes that the dynamics of the faster modes are uncoupled from the rest of the system.

Molecular Dynamics of a Nanoparticle

- Unlike MC, the motion of the particles in a MD simulation is realistic.



An evaporating LaF_3 cluster
from an MD simulation.
(From V. Bulatov's web site)

The Monte Carlo Method

- Suppose we want to calculate $\langle A \rangle$, the ensemble average of $A(x_1, x_2, \ldots, x_i, \ldots x_N) = A(x^N)$, where $x_i = \underline{r}_i$ for spherical and $x_i = \underline{r}_i, w_i$ for nonspherical molecules.

- Examples of A are U (internal energy), P (pressure), pair correlation function $g(x_1, x_2)$, etc. For the canonical ensemble

$$\langle A \rangle = \frac{\int dx^N A\left(x^N\right) \exp\left(-\mathrm{U}/kT\right)}{\int dx^N \exp\left(-\mathrm{U}/kT\right)} = \int dx^N A\left(x^N\right) \rho\left(x^N\right)$$

where

$$\rho\left(x^N\right) = \frac{\exp\left[-\mathrm{U}\left(x^N\right)/kT\right]}{\int dx^N \exp\left[-\mathrm{U}\left(x^N\right)/kT\right]} =$$

probability density
for state x^N

The Monte Carlo Method

- In MC simulations the average is approximated by generating a large number of trial configurations x^N using a random number generator, and replacing the integrals by sums over a finite number of configurations. Simple numerical integration methods (Simpson’s rule, quadrature, random sampling) do not work – too many variables, too many overlaps.

- Importance sampling: If configurations can be sampled with probability $\rho(x^N)$, i.e. proportional to $\exp[-\mathcal{U}(x^N)/kT]$, we expect these configurations will be the ones contributing most to the average in. Then

$$\langle A \rangle = \frac{1}{n_c} \sum_{j=1}^{n_c} A(j)$$

where n_c = total number of configurations. Metropolis *et al*. showed how to implement importance sampling (N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953))

The Monte Carlo Method

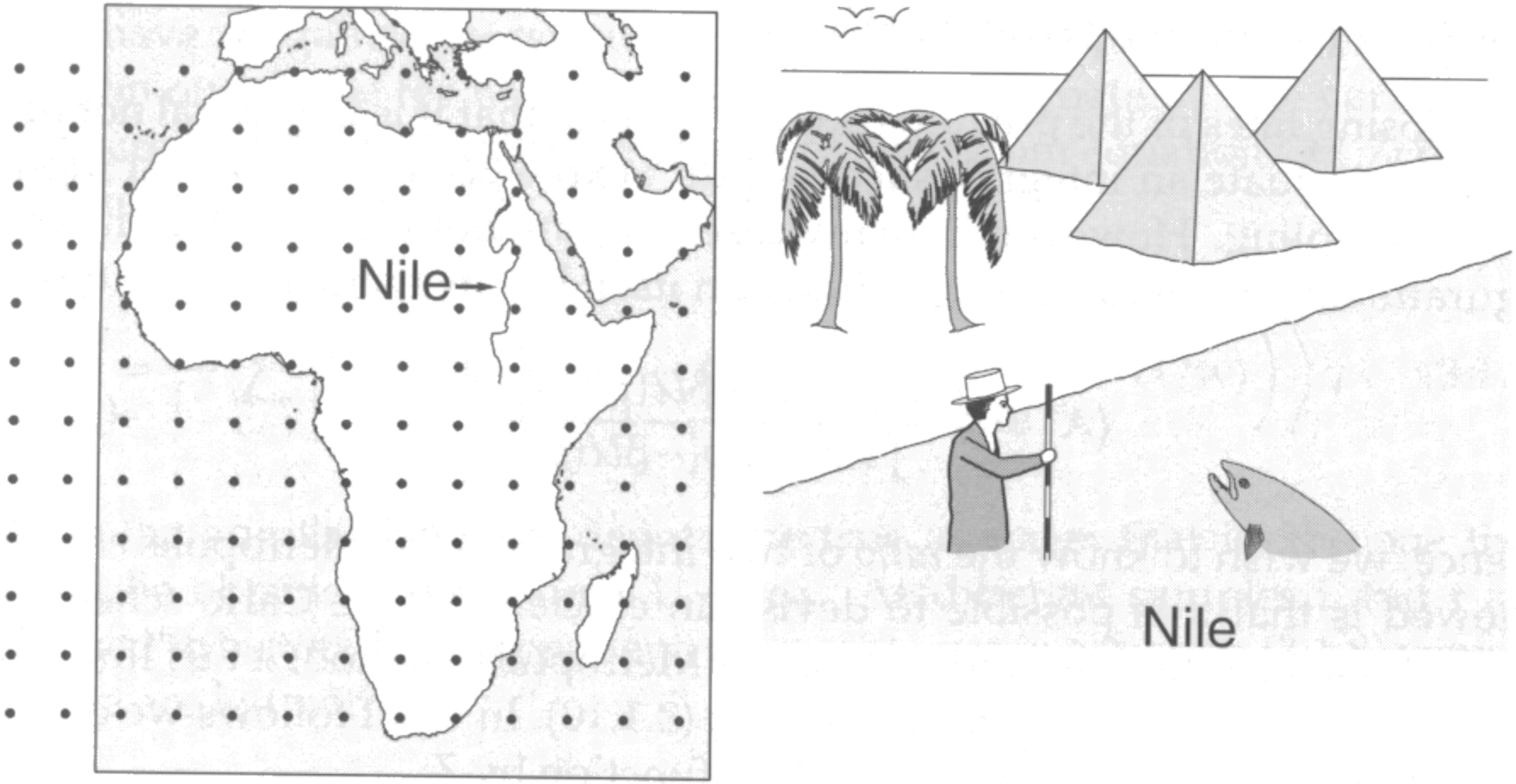


Figure 3.1: Measuring the depth of the Nile: a comparison of conventional quadrature (left), with the Metropolis scheme (right).

taken from D. Frenkel and B. Smit, *Understanding Molecular Simulation*, 2nd ed. (2002)

Microscopic Reversibility

When the MC run reaches thermodynamic equilibrium the rate of change from configuration *m* to *n* must equal the rate of the reverse change from *n* to *m*, otherwise the system would not remain at equilibrium. This leads (see Allen & Tildesley) to the condition of *microscopic reversibility* (also called the condition of *detailed balance*):

$$\frac{P_{m\to n}}{P_{n\to m}} = \frac{\rho_n}{\rho_m}$$

This is the *central equation in MC*

The Metropolis MC Method

- The usual scheme for putting Metropolis into practice is

1) A randomly chosen molecule i is made to undergo a random displacement $\Delta \underline{r}$ from its initial position to a new position within a cube of length l, centered on the original position of i. Usually l is chosen so that ~50% of trial moves are accepted. If l is too small we get a higher acceptance rate, but this may not sample all configurations efficiently. If l is too large most trials are rejected
2) Calculate $\mathcal{U}(x^N)_n$ and $\Delta\mathcal{U} = \mathcal{U}(x^N)_n - \mathcal{U}(x^N)_m$
3) If $\Delta\mathcal{U}$ is negative, i.e. $\rho_n/\rho_m > 1$, the move is accepted
4) If $\Delta\mathcal{U}$ is positive, i.e. $\rho_n/\rho_m < 1$, the move is accepted with probability $\rho_n/\rho_m = \exp[-\Delta\mathcal{U}/kT]$. The decision to accept or reject the move is made by generating a random number *z* with a value between 0 and 1. If $z \leq \exp[-\Delta\mathcal{U}/kT]$ the move is accepted, otherwise it is rejected. If it is rejected the old state m is again counted as the new configuration in the chain.

Applications of Atomistic Simulation to Confined Nano-Phases

Nanoporous materials and adsorption
Phase changes
Pressure effects in nanopores
Diffusion in nanopores

Research Group

Keith Gubbins

Malgorzata Sliwinska-Bartkowiak

Cody Addington

Katherine Phillips

Ying-Chun (Lucy) Liu

Teresa Bandosz

Joshua Moore

Jeremy Palmer

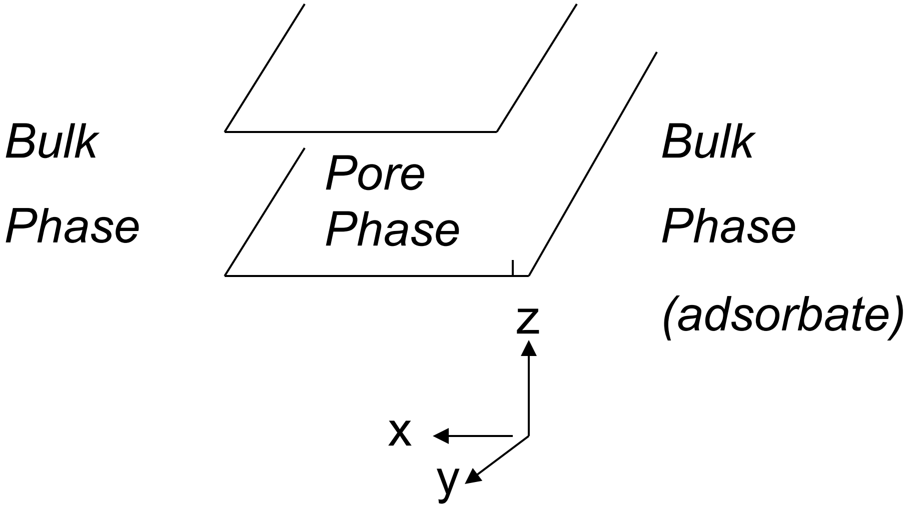
Liangliang (Paul) Huang

Yun Long

Andrew Santos

EQUILIBRIUM CONDITIONS FOR THE CONFINED NANOPHASE

Thermodynamic & Mechanical Equilibrium



Bulk

Phase

Pore

Phase

Bulk

Phase

(adsorbate)

$$T_{bulk} = T_{pore}$$ (thermal)

$$\mu_{bulk} = \mu_{pore}$$ (chemical)

$$\nabla \bullet \mathbf{P} = 0$$ (mechanical)

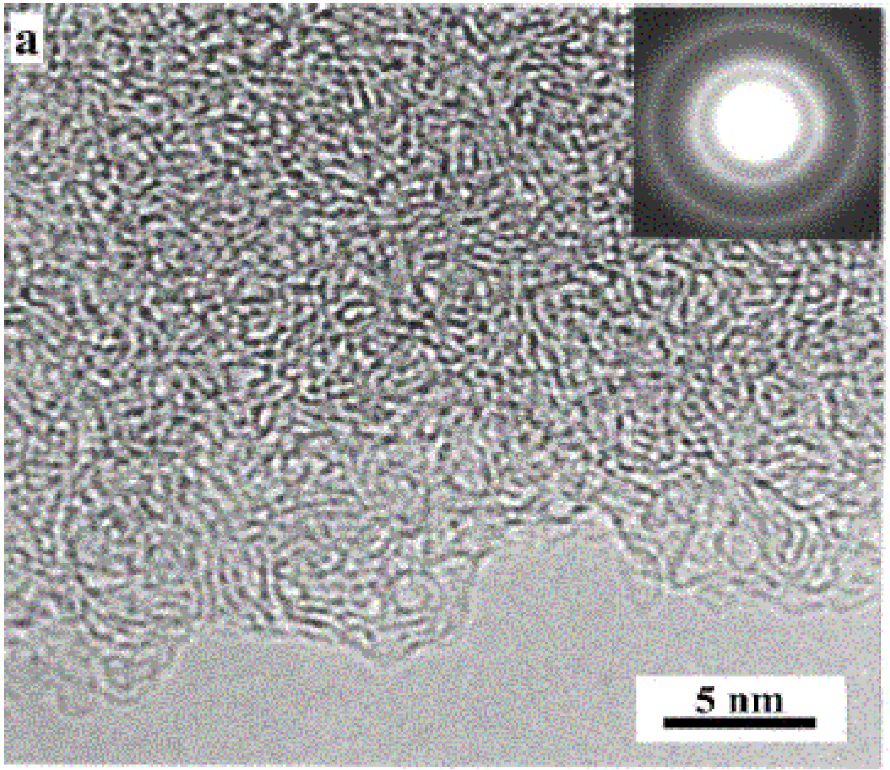
We usually use semi-grand ensemble Monte Carlo simulation to bring the pore phase to equilibrium with the bulk phase. The pore is in direct contact with an infinite reservoir of molecules. .

SOME NANOPOROUS MATERIALS

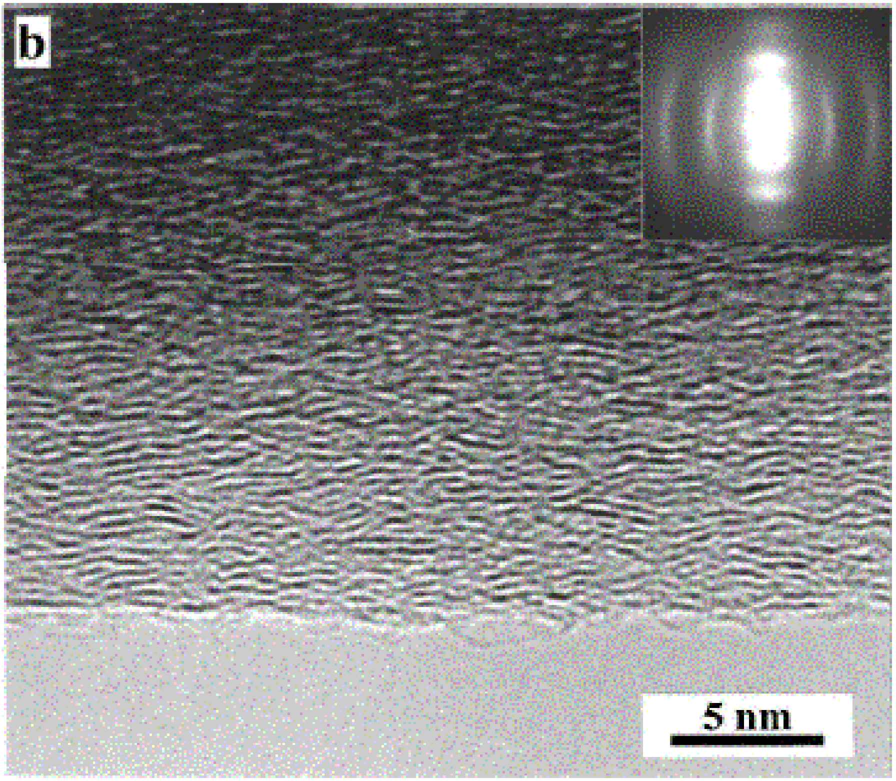
Material	Surface	Pore Shape	Pore Width, nm
A. Crystalline			
Aluminosilicate	O, Al, Si	Cylinder, cage	0.3-1.0
*Mica (SFA)	O, K^+	Slit	
Gallophosphates	O, P	Cylinder	<1.0
*Metal Organic Framework	O, M	Cage	1 up
*Carbon nanotube	C	Cylinder	2-10
B. Regular			
*CMK Mesoporous C	C	Cylinder	2-10
*Templated matls (e.g. SBA)	O, Al, Si	Cylinder	2-15
*KIT silica	O	Cylinder	10 up
*PMO	O	Cylinder	2-8
C. Disordered			
Porous glasses	O, Si	Cylinder	$5\text{-}10^4$
Pillared clays	O, Si, Al	Slit+pillars	>0.5
*Activated carbon fiber	C	Slit	0.6-1.5
*Carbide-derived carbon	C	Slit	0.3-2.0
*Hierarchical carbons	C	Sphere, cylinder	5, 100
*Carbon aerogels	C	Sphere	30

Porous Carbon Materials

Example of graphitisable and non-graphitisable carbons



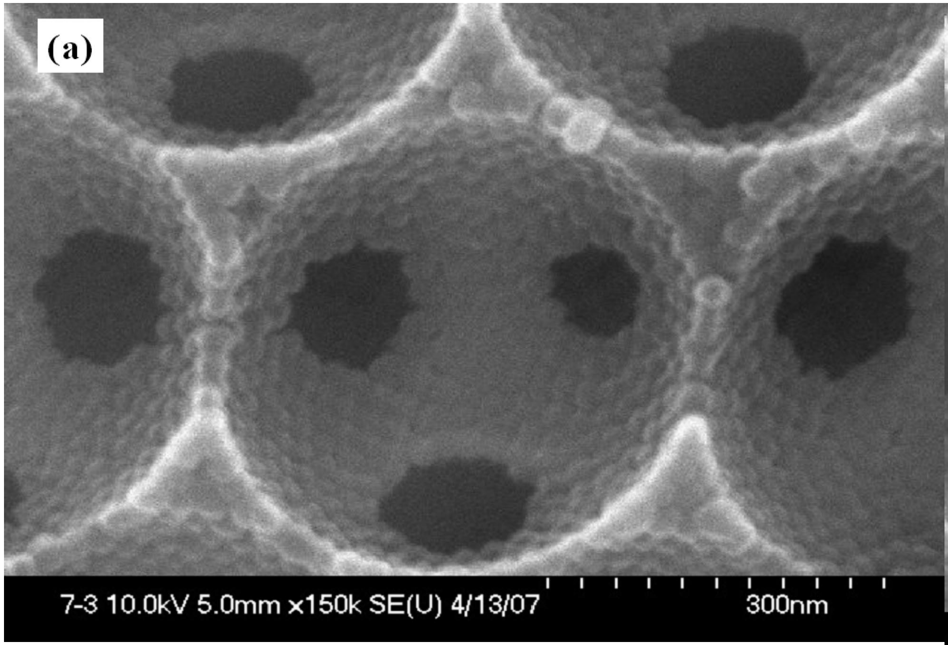
Carbon prepared by pyrolisis of sucrose in argon at 1000º C (non-graphitisable)



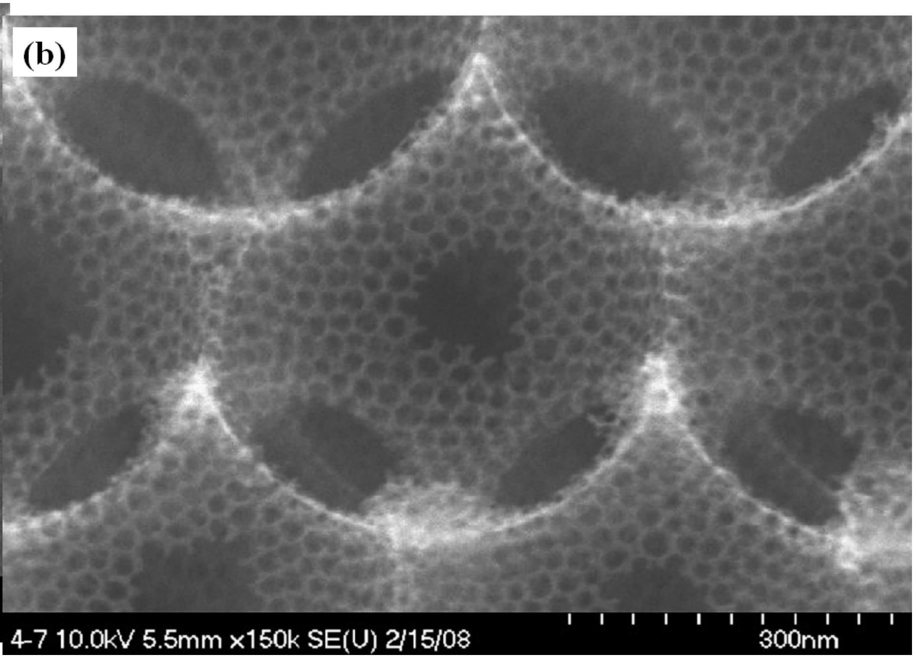
Carbon prepared by pyrolisis of anthracene in argon at 1000º C (graphitisable)

Harris et al. (Philosophical Magazine Letters, 2000)

Hierarchical Porous Materials



Ordered hierarchical nanostructured silica



Ordered hierarchical nanostructured carbon

B.Z. Fang, J.H. Kim, M. Kim and J.S. Yu, Chem. Mater., **21**, 789 (2009).

Some Effects of Confinement

- Shifts in bulk phase transitions & new phases

  L.D. Gelb, K.E. Gubbins, R. Radhakrishnan and M. Sliwinska-Bartkowiak, "Phase Separation in Confined Systems", *Reports on Progress in Physics*, **62**, 1573-1659 (1999).
  C. Alba-Simionesco et al., "Effects of Confinement on Freezing and Melting", *Journal of Physics: Condensed Matter*, **18**, R15-R68 (2006)

- Selective adsorption of certain components

$$S_{12} = \frac{(x_1 / x_2)_{pore}}{(x_1 / x_2)_{bulk}} = selectivity\ \ for\, 1$$

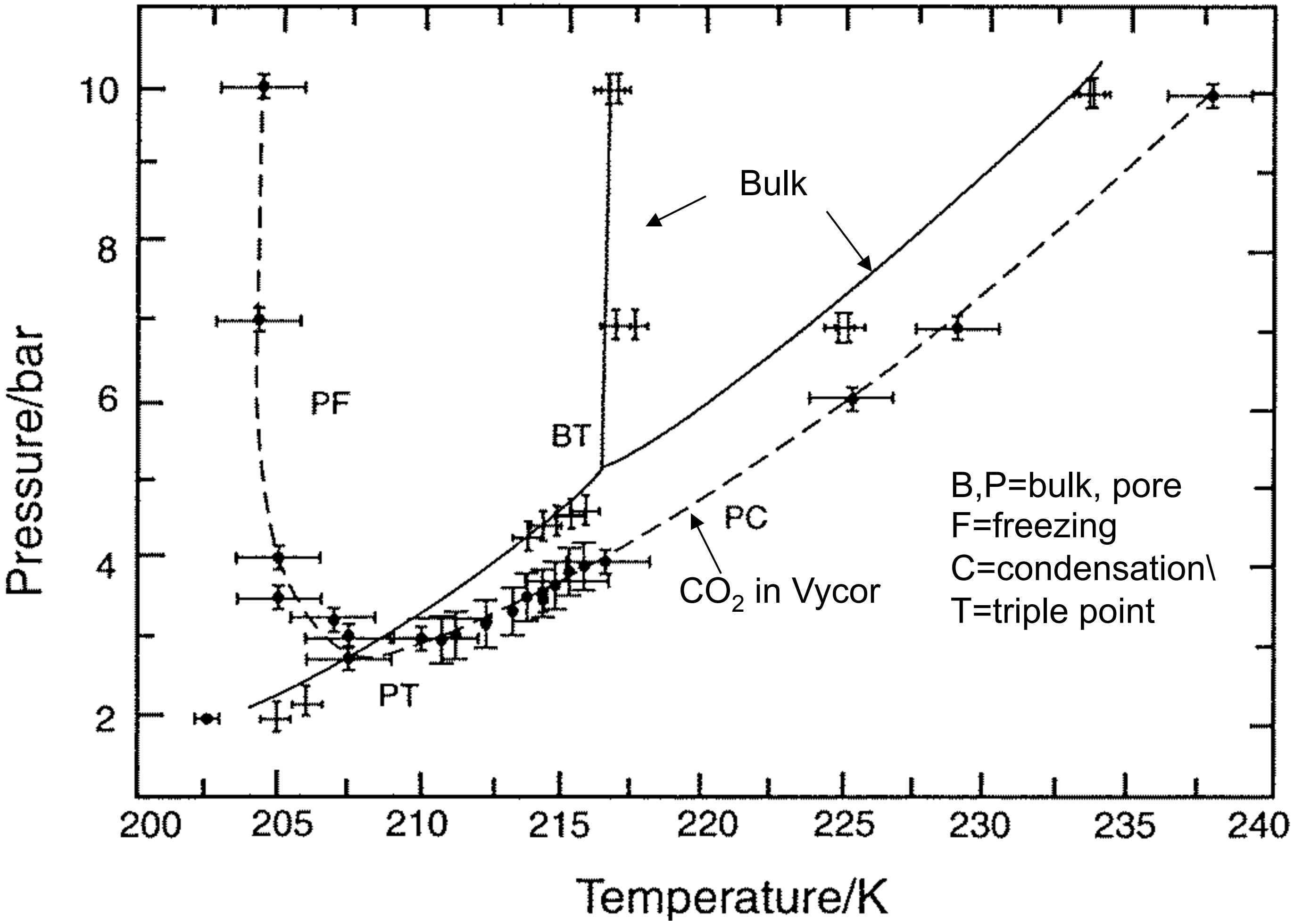
- Compression of adsorbed surface layers – high pressure effects
- Novel diffusion mechanisms – e.g. single file
- Large effects on chemical reactions - yield, rate, mechanism

PHASE CHANGES IN NANOPORES

- **The Variables**
  - Temperature (bulk phase)
  - Pressure (bulk phase)
  - Composition (bulk phase)
  - Pore shape (slit, cylinder, sphere, etc.)
  - Pore width (H or D)
  - Properties of the adsorbent material (chem. composition, wall roughness, connectivity, etc.)
  - Properties of the adsorbate (confined phase)

The influence of the adsorbent and adsorbate can, to a large extent, be summarized by the wettability – the degree to which the adsorbate phase wets the walls of the solid adsorbent

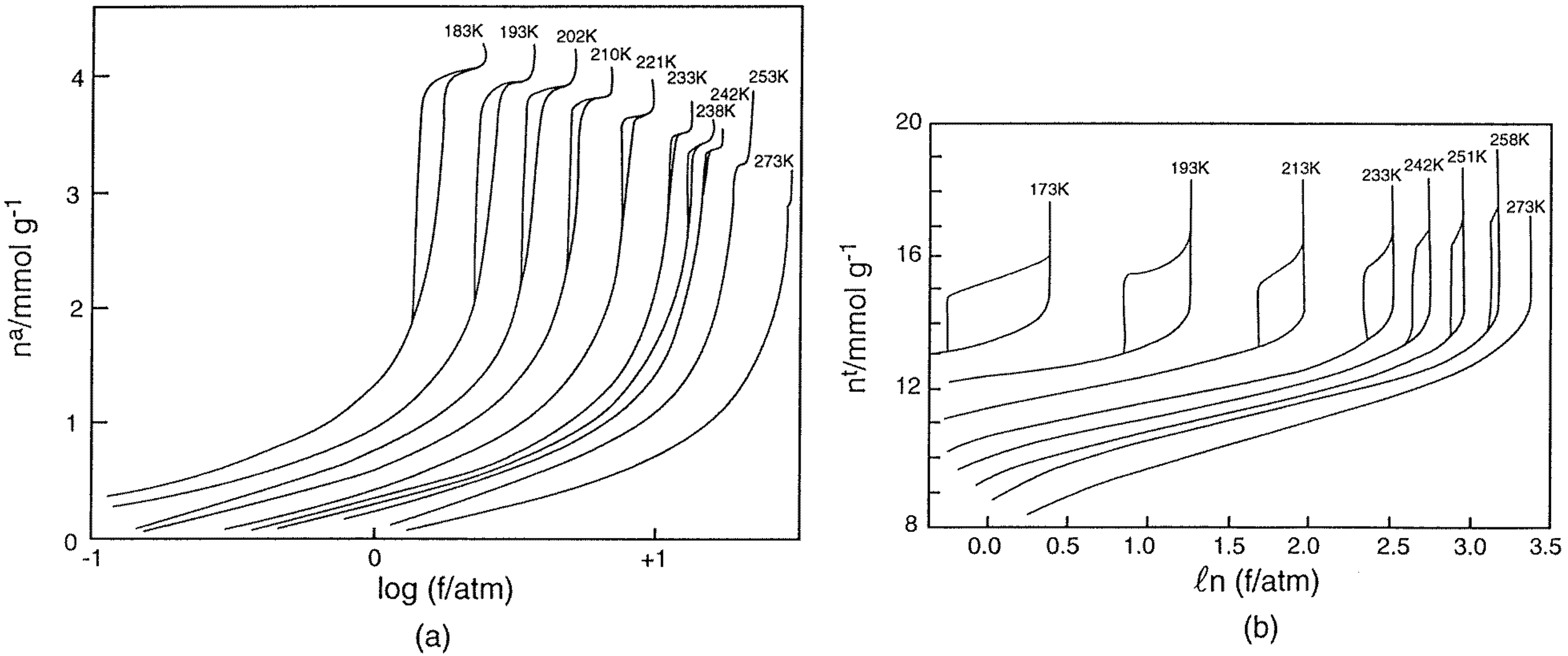
Pressure-Temperature Phase Diagram from Positron Annihilation: CO_2 in Vycor (α~1)



B,P=bulk, pore
F=freezing
C=condensation\
T=triple point

A. Alam and coworkers. See L. D. Gelb *et al*., “Phase separation in confined systems”, Rep. Prog. Phys., 62, 1573 (1999).

Adsorption Isotherms and Capillary Condensation for Xenon in (a) Vycor Glass, (b) Active Carbon

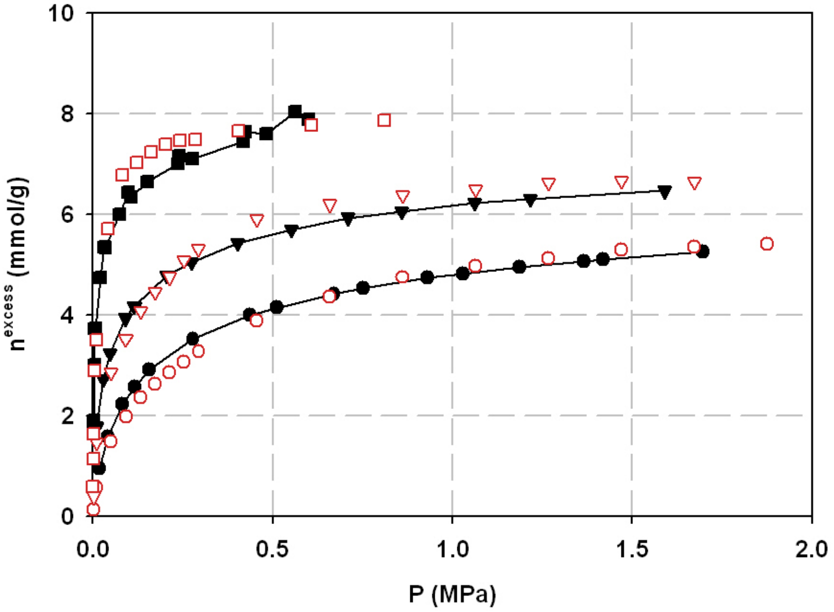


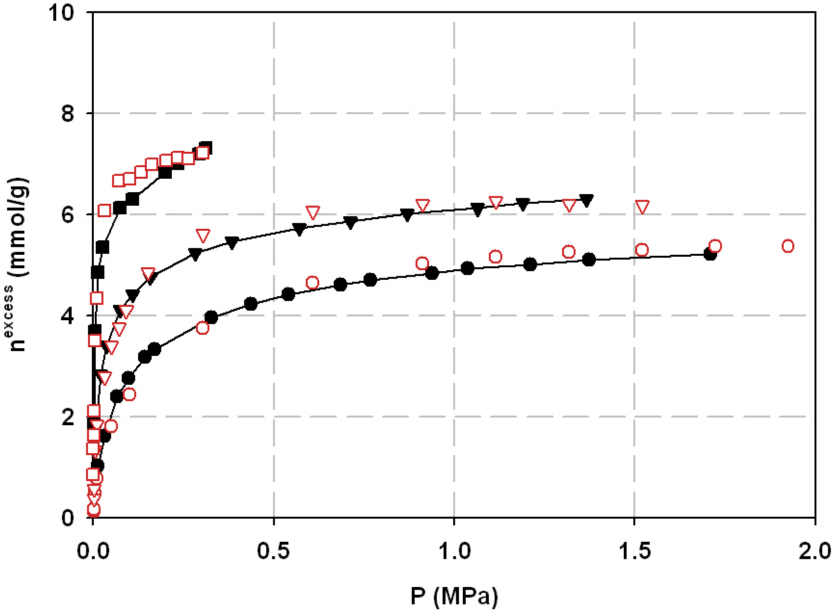
Vycor Glass

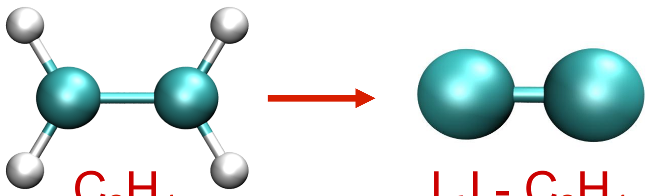
Active Carbon

From D.H. Everett et al. L. D. Gelb *et al.*, “Phase separation in confined systems”, Rep. Prog. Phys., 62, 1573 (1999).

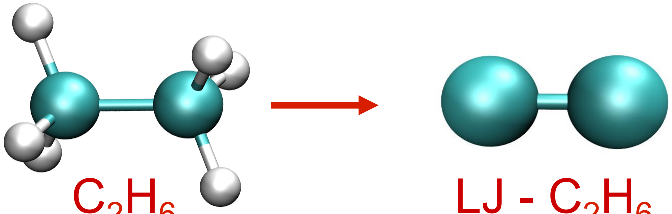
BPL (HRMC): Hydrocarbon Adsorption







C_2H_4 LJ - C_2H_4



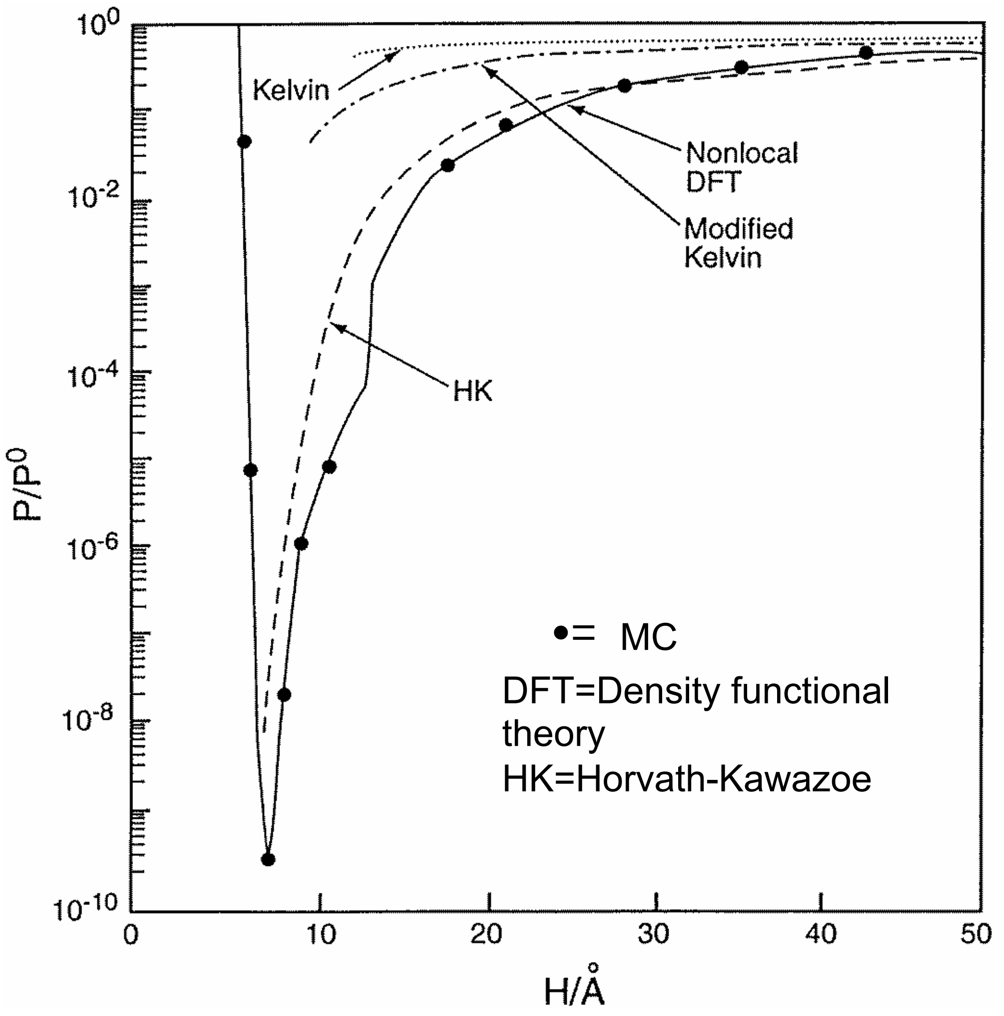
C_2H_6 LJ - C_2H_6

Experimental Data: Reich et al. ,
Ind. Eng. Chem. Process Des. Dev. ,3, 1980

□ ○ △ Simulation
■ ● ▲ Experiment

PORE FILLING PRESSURE vs. PORE WIDTH NITROGEN, 77 K: BREAKDOWN OF KELVIN EQUATION

N_2 in slit-shaped carbon pores



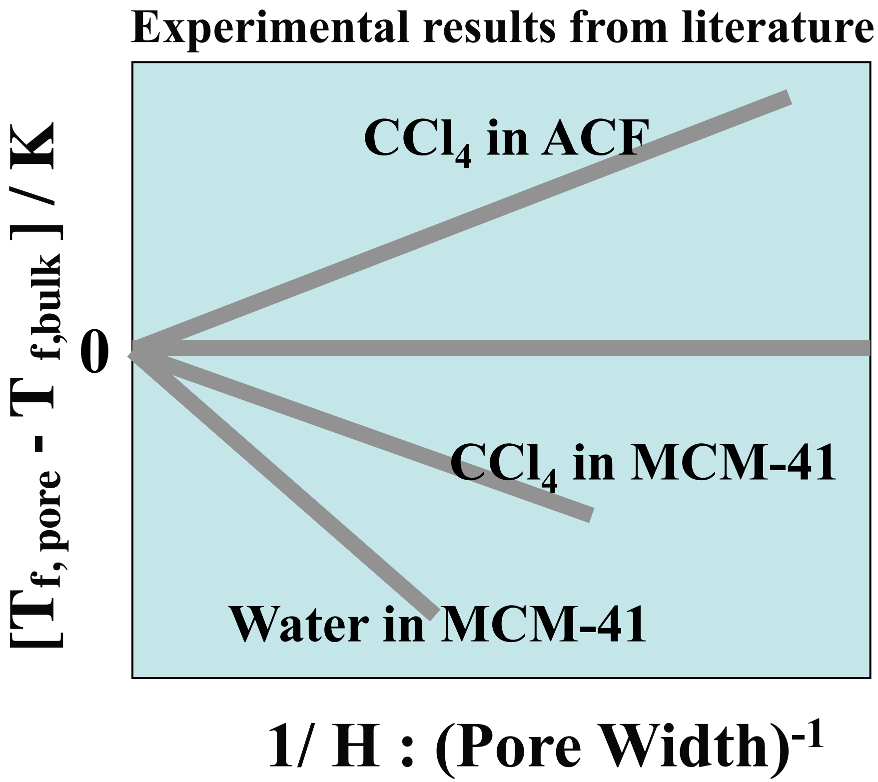
● = MC

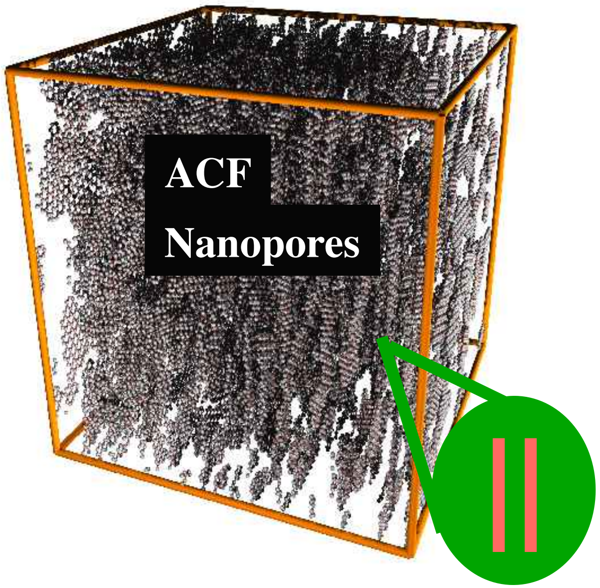
DFT=Density functional theory

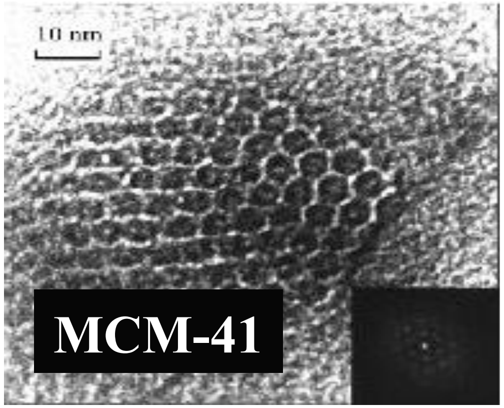
HK=Horvath-Kawazoe

L. D. Gelb *et al*., “Phase separation in confined systems”, Rep. Prog. Phys., 62, 1573 (1999).

Freezing in Porous Media







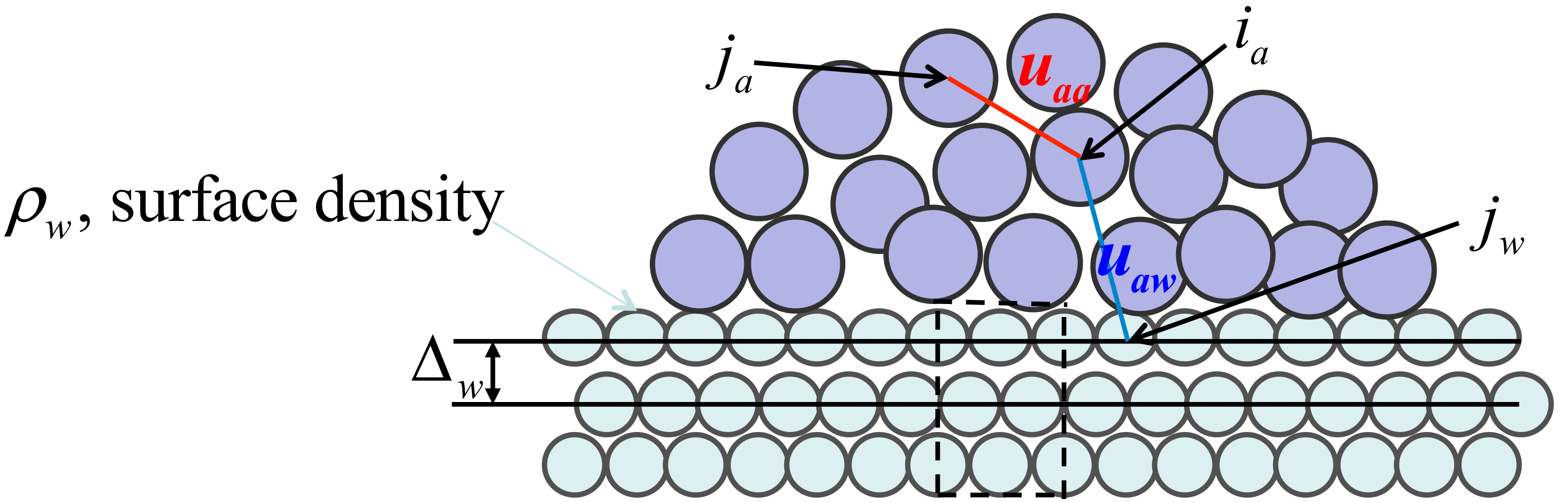
Theory of Corresponding States:

$$T^*_{f,pore} = f\left(H^*, \alpha, \sigma_{fw}/\sigma_{ff}\right)$$

$$T^*_{f,pore} = k\frac{T_{f,pore}}{T_{ff}}; H^* = \frac{H}{H_{ff}} \qquad \alpha = \frac{U_{fw}}{U_{ff}} = \frac{\rho_w \varepsilon_{fw} \sigma^2_{fw} \Delta}{\varepsilon_{ff}}$$

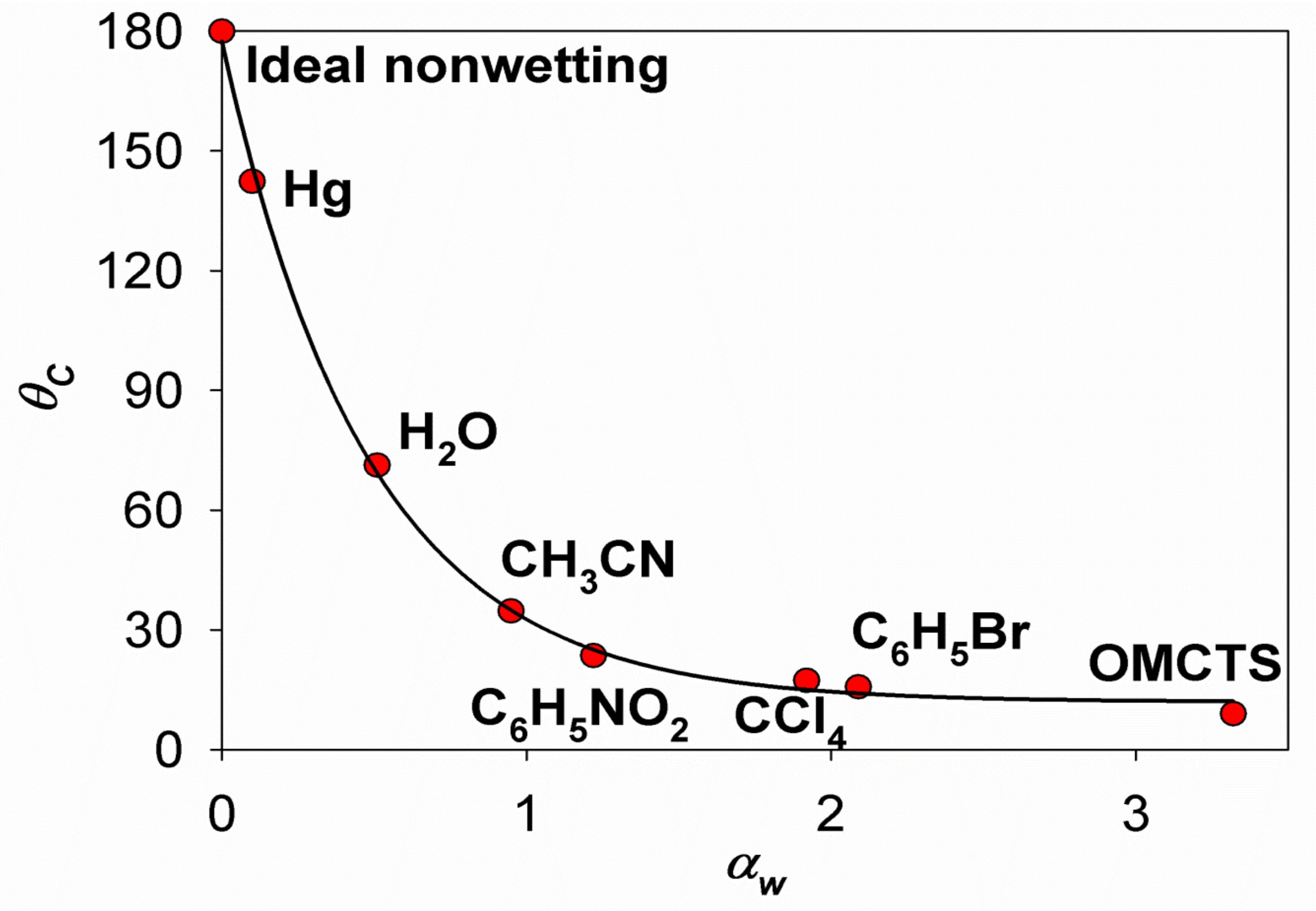
L.D. Gelb, K.E. Gubbins, R. Radhakrishnan and M. Sliwinska-Bartkowiak, “Phase Separation in Confined Systems”, *Reports on Progress in Physics*, **62**, 1573-1659 (1999).

Wetting at the Nanoscale

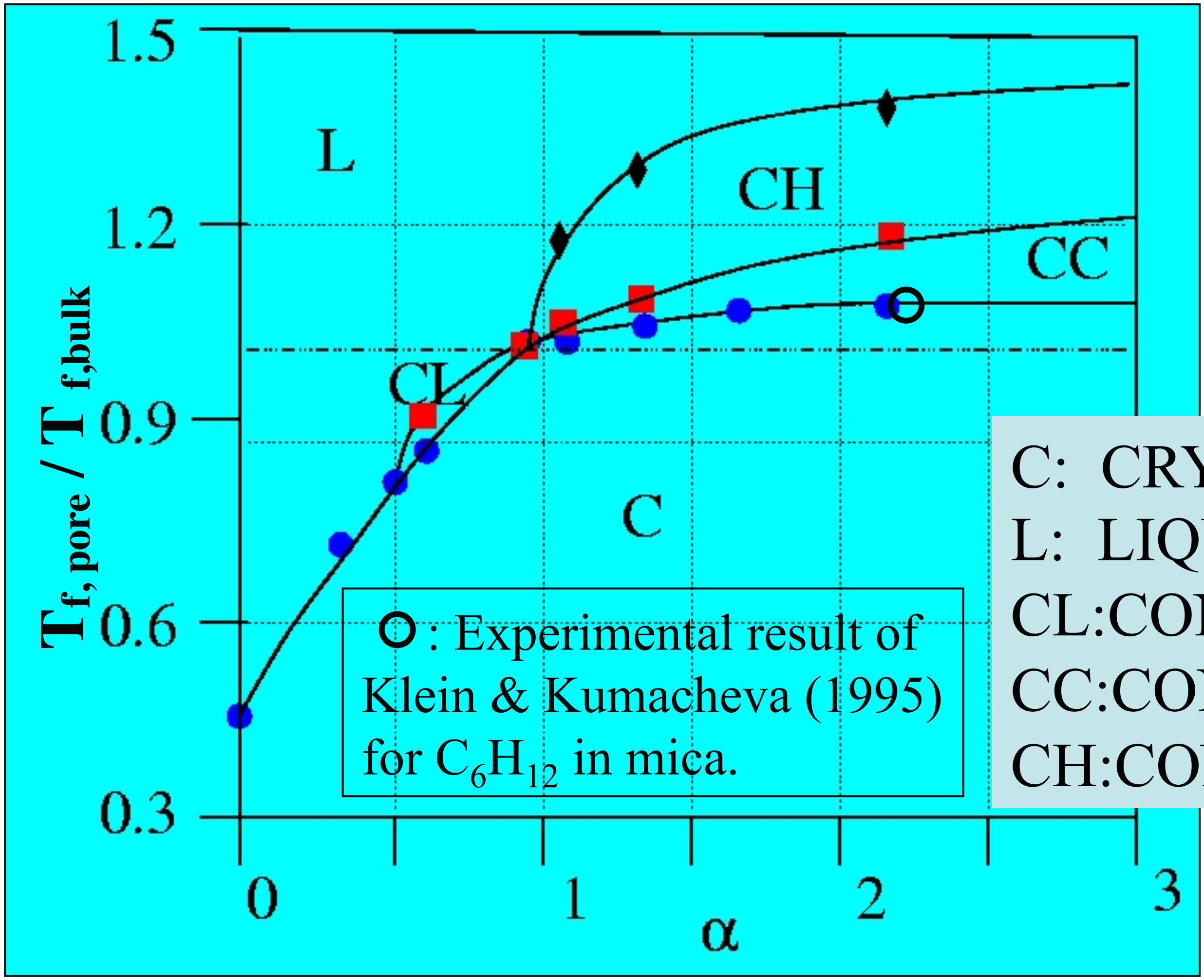


$$\begin{aligned}\alpha_w &= \frac{\text{adsorbate−wall (aw) interaction}}{\text{adsorbate−adsorbate (aa) interaction}}\\ &= C\sigma_{aw}^2\rho_w\Delta(\varepsilon_{aw}/\varepsilon_{aa})\\ &= microscopic\ wetting\ parameter\end{aligned}$$

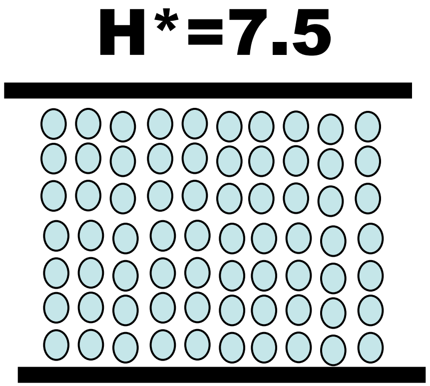
Contact angle on graphite vs. wetting parameter
Courtesy M. Śliwinska-Bartkowiak



Global Freezing Diagram for Carbon Slit Pore, H*=7.5 from GCMC simulation

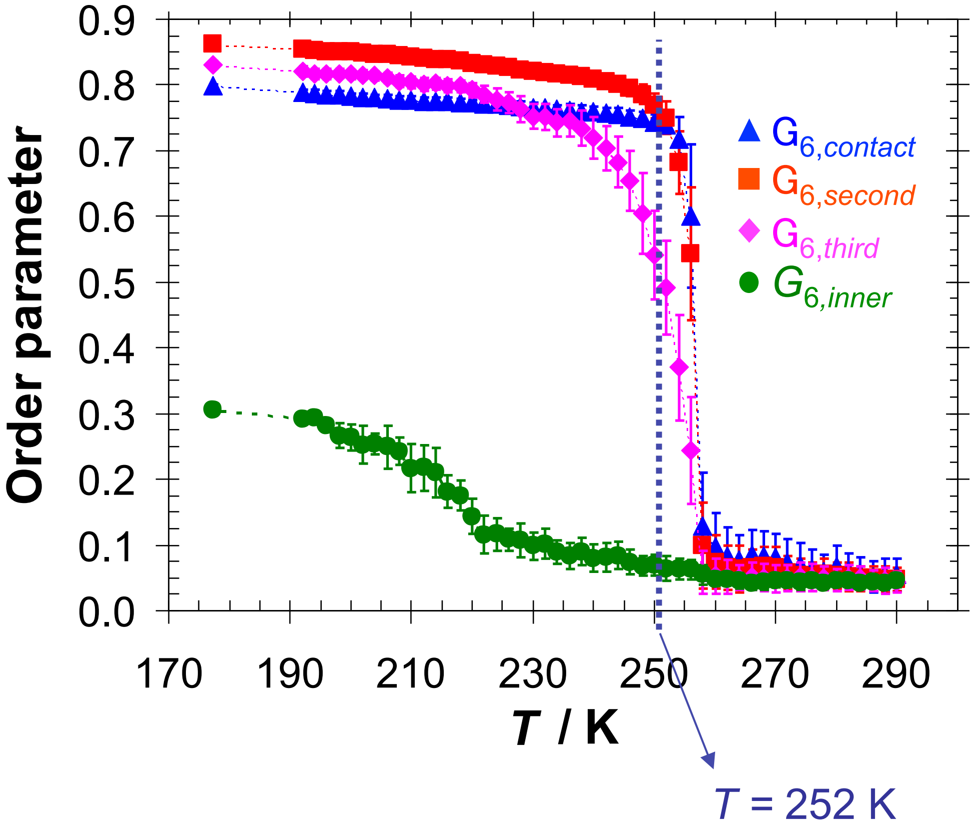


○ : Experimental result of Klein & Kumacheva (1995) for C_6H_{12} in mica.



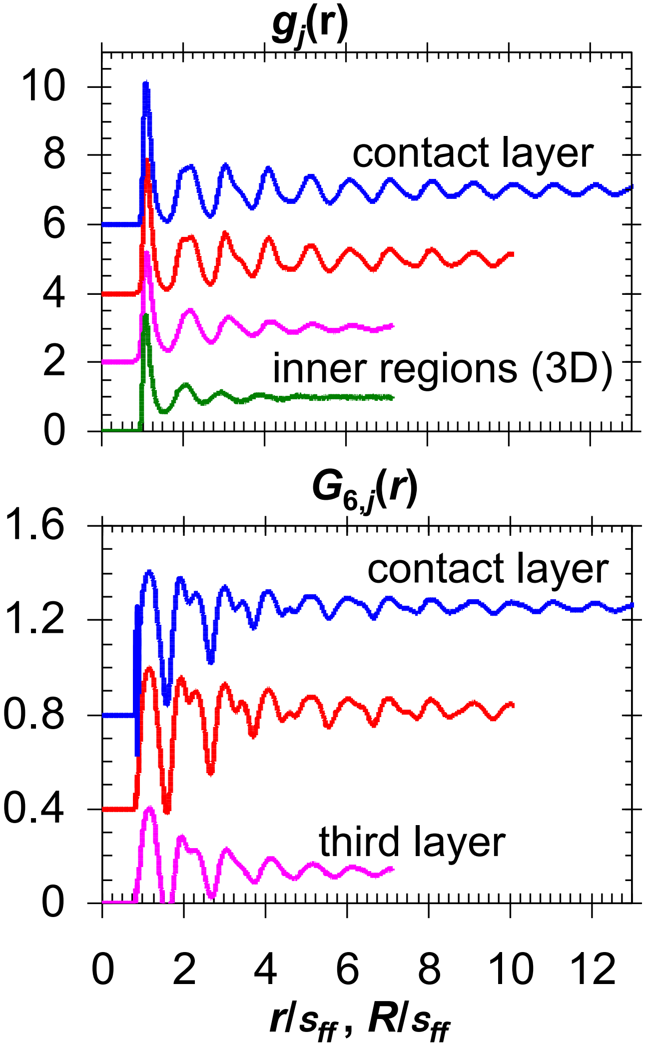
C: CRYSTALLINE
L: LIQUID
CL:CONTACT-LIQUID
CC:CONTACT-CRYSTAL
CH:CONTACT-HEXATIC

Freezing of Argon in Multi-Walled Carbon Nanotubes, *D* = 5.0 nm, GCMC



T = 252 K

T = 252 K **(phase C)**



F. R. Hung *et al.*, *J. Chem. Phys.* **122**, 144706 (2005)

Pressure Enhancement due to Confinement

High pressure phenomena observed in bulk phases often occur for nanophases confined in nanoporous materials, even though the bulk gas pressure is low, ~1bar or less.

High pressures in pores are of interest because:

1. They directly reflect the intermolecular forces.
2. Understanding these effects would open the way to design of nano-reactors, new materials.
3. They lead to structural deformation that in turn affects adsorption & other material properties.
4. They may provide a connection with bulk properties

High Pressure Effect: Experimental Studies of Dimerization of NO: $2NO=(NO)_2$

$$x_{(NO)_2} / x_{NO}^2 = (K / K_\phi)P \sim P$$

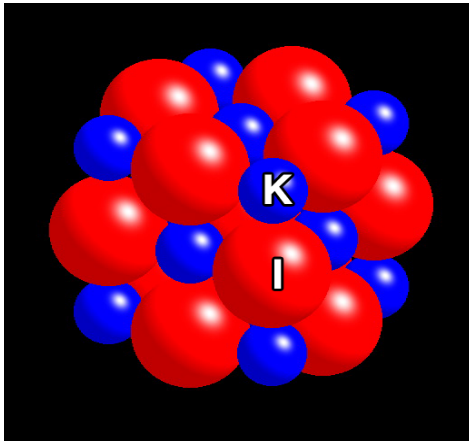
Porous Material	Method	T/K	Mole % $(NO)_2$ Bulk	Mole % $(NO)_2$ Confined	Ref.
Activated Carbon Fibers, H=0.8 nm	Magnetic Susceptibility	298-423	<<1	98-100	1
(10,10) SWCNT H=1.35 nm	FTIR	103-136	≤1	100	2

1. K. Kaneko et al., Langmuir, **5**, 960 (1989)
2. O. Byl, P. Kendratyuk and J.T. Yates, *J. Phya. Chem. B*, **107**, 4277 (2005)

High Pressure Effect: Phase Transition in KI

Induction of High Pressure Solid Phase Transition

Bulk Phase Potassium Iodide (K. Asaumi et al., *PRB* (1983))



NaCl type fcc

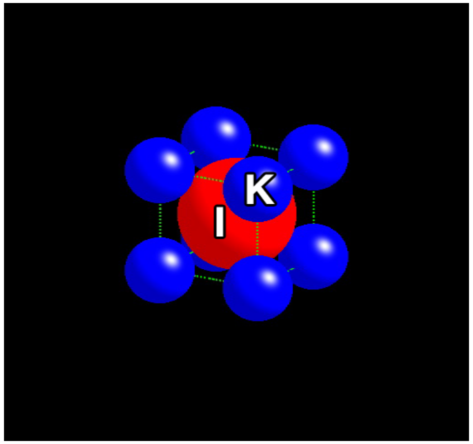
a = 0.706 nm

Phase transition

1.9 GPa

(1900 MPa)

(19,000 bar)



CsCl type cubic

a = 0.413 nm

Confined KI

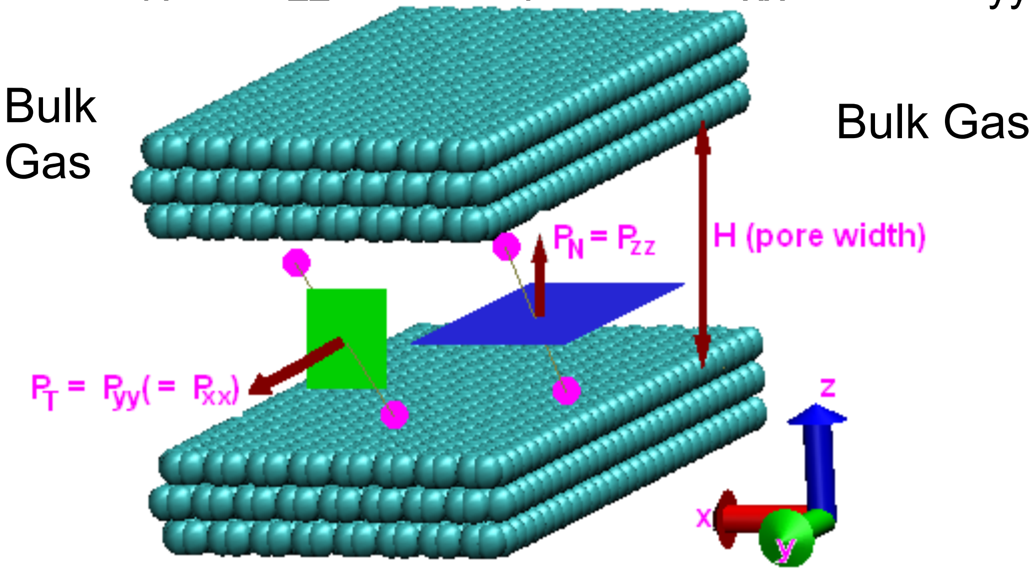
Phase transition from fcc (NaCl type) to modified cubic (CsCl type) below 1 bar in porous carbons is observed by: K. Urita et al., J.A.C.S., 133, 10344 (2011)

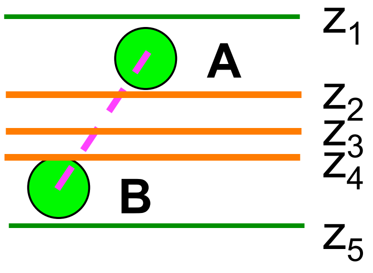
Pressure in Inhomogeneous Phases

- Pressure in inhomogeneous phases is a 2nd-order tensor:

$$\mathbf{P}(\mathbf{r}) = \begin{bmatrix} P_{xx} & 0 & 0 \\ 0 & P_{yy} & 0 \\ 0 & 0 & P_{zz} \end{bmatrix} = \mathbf{P}_{kinetic} + \mathbf{P}_{configurational}$$

- In slit pore, pressure has only two independent components and depends only on *z* (the direction normal to the wall): $P_N = P_{zz}$ and $P_T(z) = P_{xx}(z) = P_{yy}(z)$





Irving-Kirkwood definition of configurational contribution

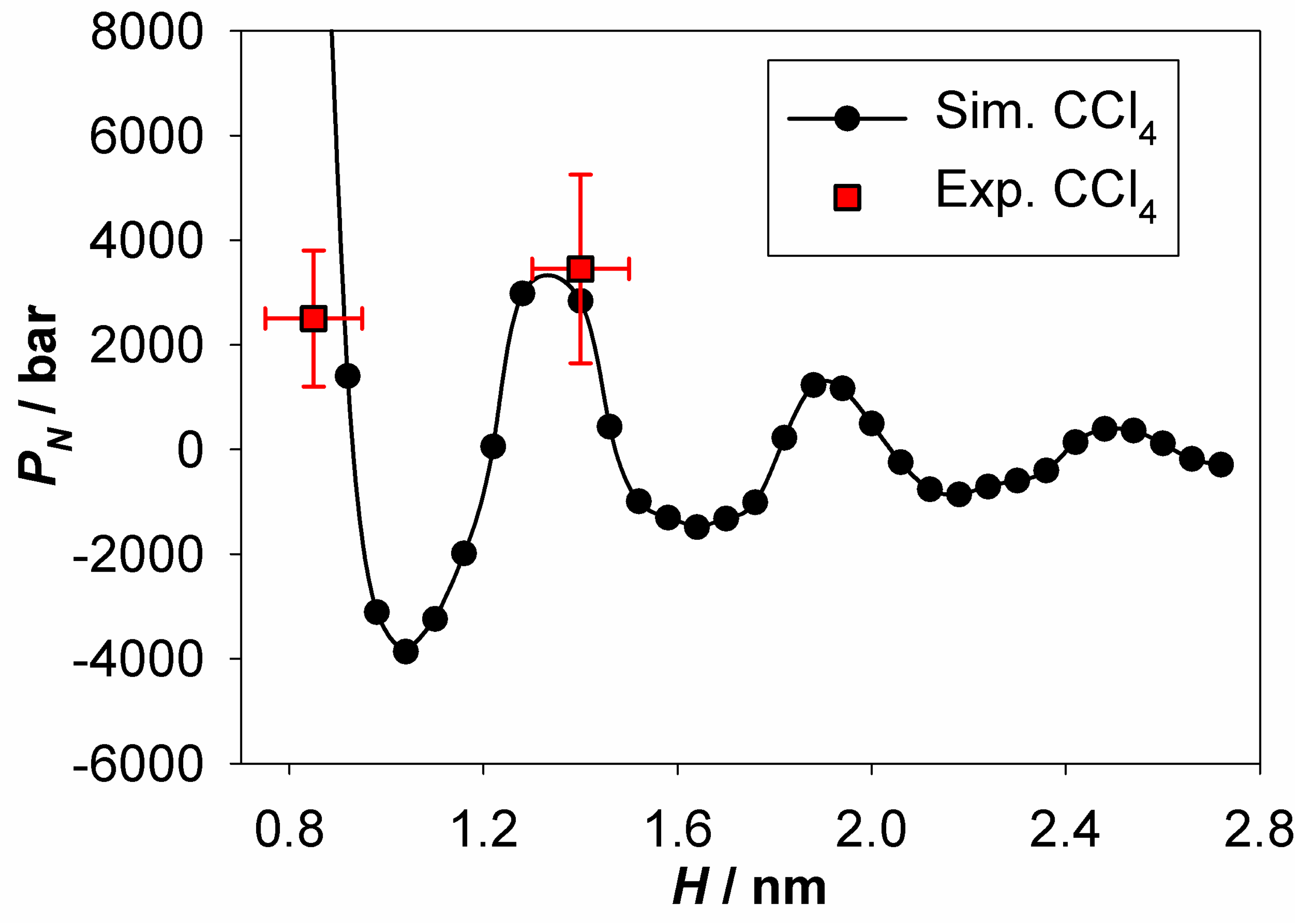
Pressure Tensor: Thermo Route

For a system of volume *V* with *N* molecules at temperature *T*, if we make small volume changes Δ*V* by extending or contracting the system in the *α* direction (*α* = *x*,*y* or *z*), then

$$P_{\alpha\alpha} = Lim_{\Delta V \to 0} - \left(\frac{\partial A}{\partial V_0} \right)_{N,T} = \rho(\mathbf{r})kT + Lim_{\Delta V \to 0} kT \ln < e^{-\Delta U_{\alpha\alpha}/kT} >_0$$

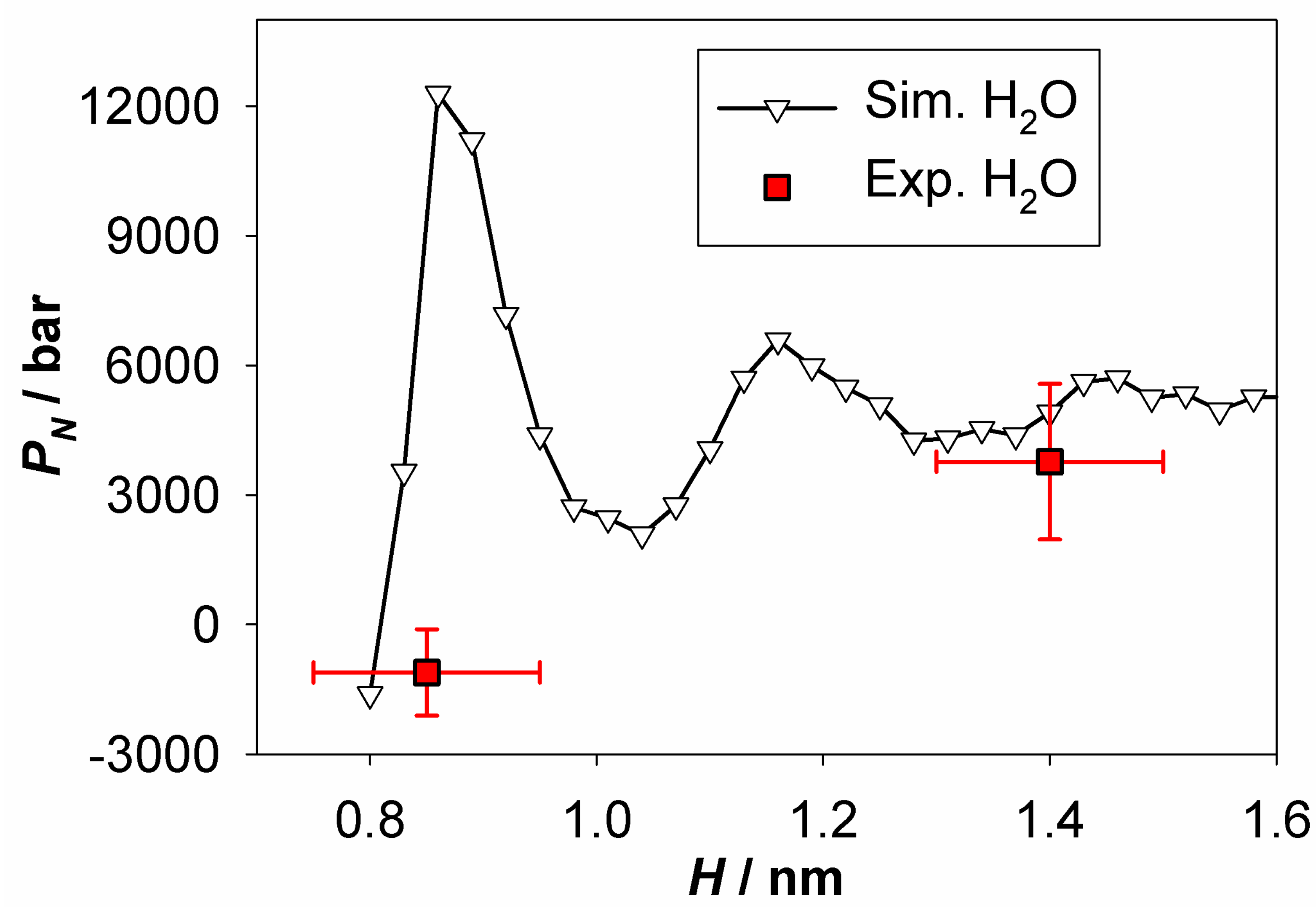
where the ensemble average is over the unpertubed (volume *V*) system. For slit pores the two routes to the pressure tensor give the same results (within statistical errors). This volume pertubation route has the merit that it includes any effects of surface fluctuations (capillary waves).

Normal pressure of CCl_4 in ACF
T = 300 K, P_{bulk} = 1.0 bar



H. Drozdowski et al, *PCCP*, **14**, 7145 (2012)

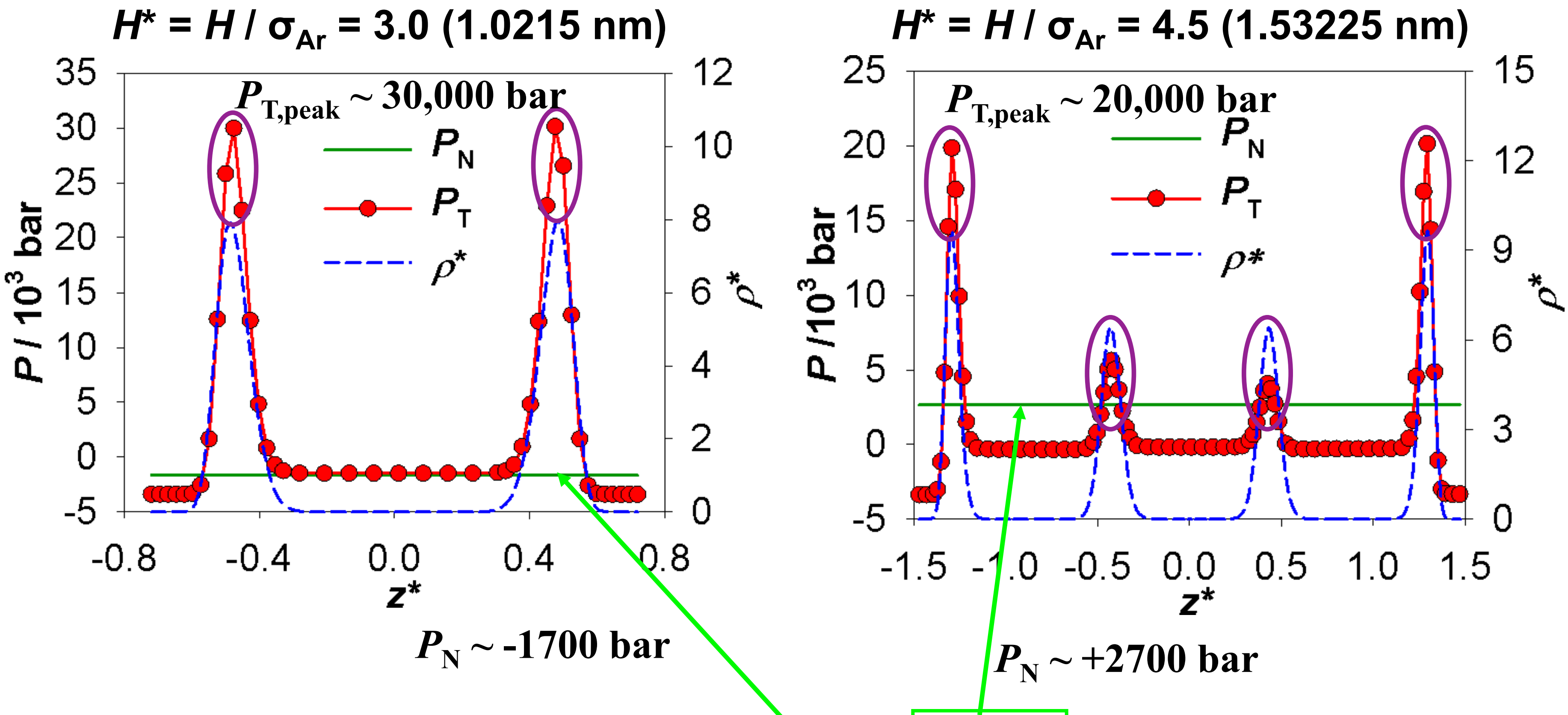
Normal pressure of water in ACF
T = 300 K, P_{bulk} = 1.0 bar



H. Drozdowski et al, *PCCP*, **14**, 7145 (2012)

Ar in Slit Carbon Pores: Pressure Profiles

P_{bulk} = 1.0 bar, T = 87.3 K (b.p.)



$H^* = H / \sigma_{Ar}$ = 3.0 (1.0215 nm)

$P_{T,peak}$ ~ 30,000 bar

P_N ~ -1700 bar

$H^* = H / \sigma_{Ar}$ = 4.5 (1.53225 nm)

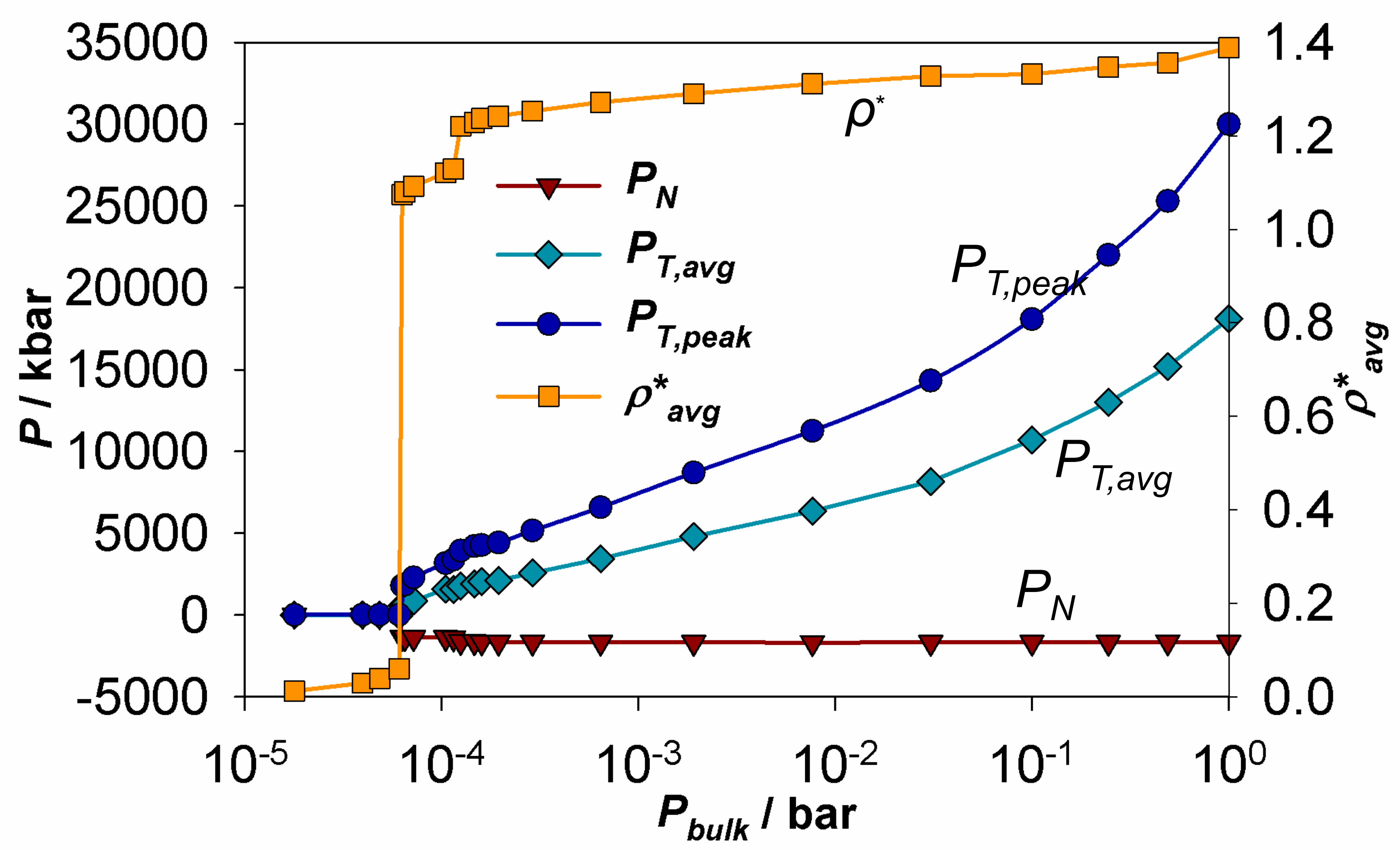
$P_{T,peak}$ ~ 20,000 bar

P_N ~ +2700 bar

- P_N is constant, can be negative or positive, enhanced by ~ 1,000x.
- P_T is very large locally, enhanced ~ 10,000x, follows the density profile.
- In silica pores, the enhancement factor is one order smaller in magnitude.

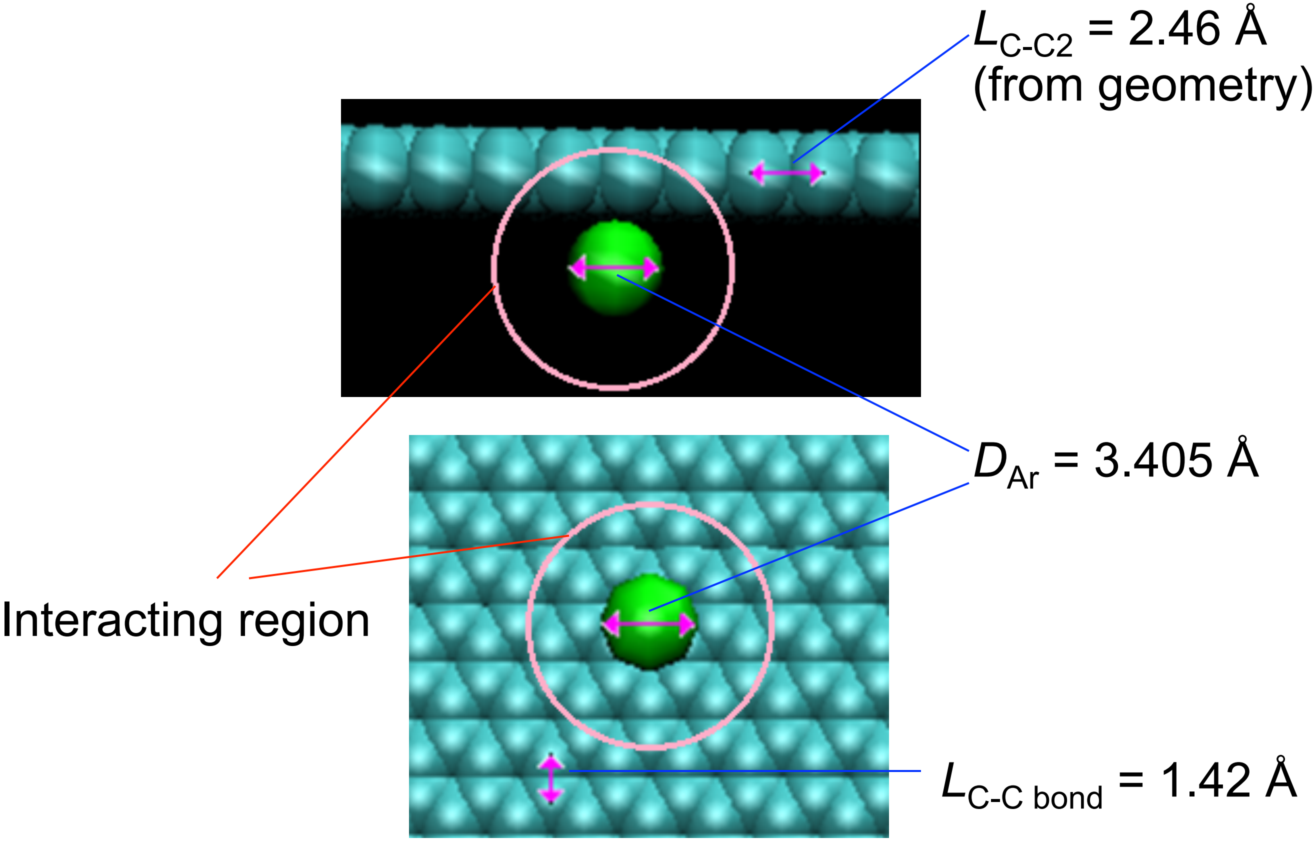
Yun Long, Jeremy C. Palmer, Benoit Coasne, Małgorzata Śliwinska-Bartkowiak and Keith E. Gubbins, "Pressure enhancement in carbon nanopores: A major confinement effect", *Physical Chemistry Chemical Physics*, **13**, 17163-17170 (2011)

Effect of Bulk Pressure
T = 87.3 K, *H** = 3.0 (1.0215 nm)



$P_T \alpha \exp(P_{bullk})$. This (approx) exponential dependence was predicted from a simple model for solid-liquid coexistence in pores by Miyahara et al, JCP, 2000

Argon Interacting with a Graphene Surface

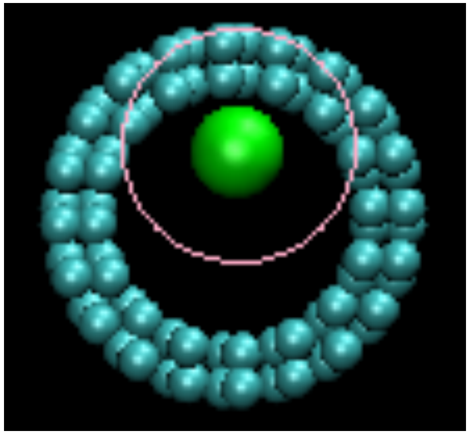


$L_{\text{C-C2}} = 2.46$ Å
(from geometry)

$D_{\text{Ar}} = 3.405$ Å

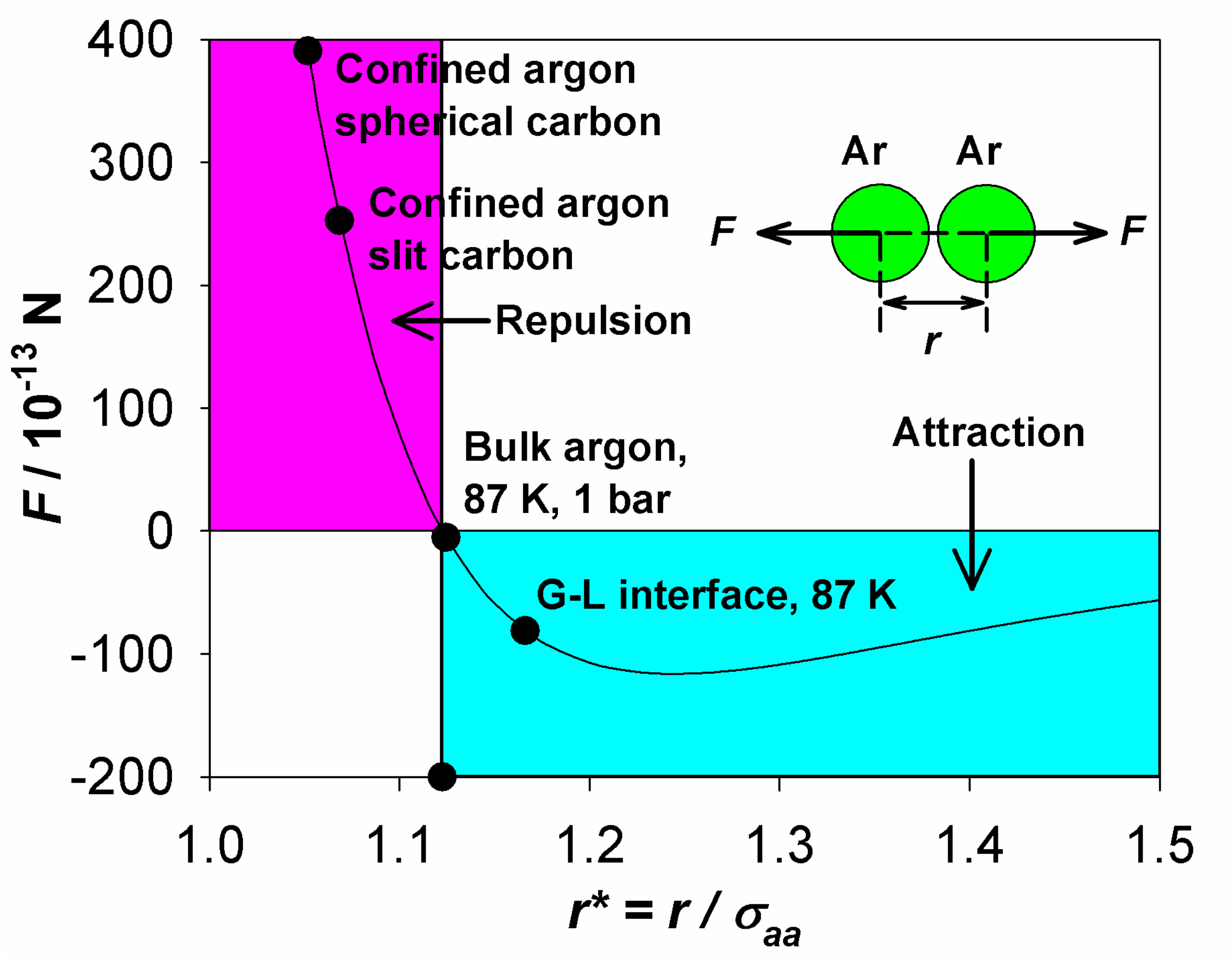
Interacting region

$L_{\text{C-C bond}} = 1.42$ Å

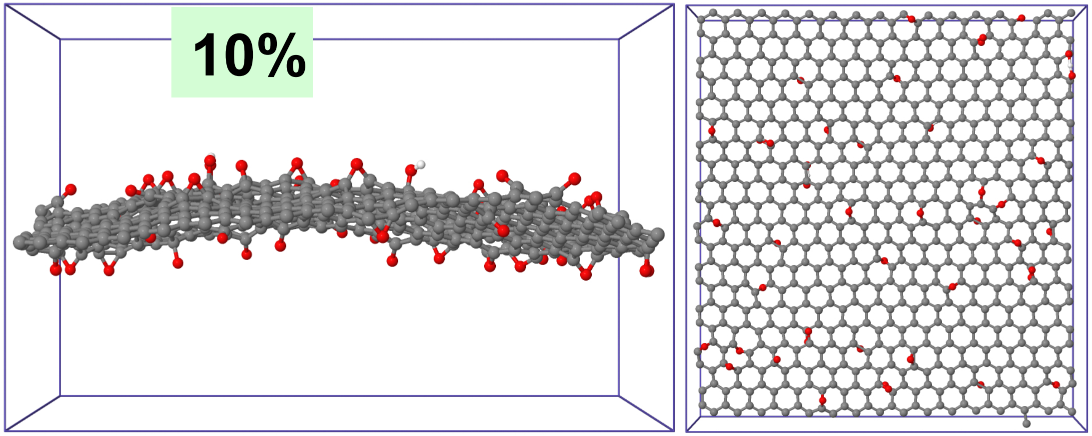


The C atoms are close-packed in graphene layer, so the overall C-Ar interaction is very strong. This leads to compression of the argon molecules in the plane parallel to the walls. The Ar molecules experience repulsive forces, leading to large positive tangential pressures

Intermolecular Pair Force and Most Probable Separation Distances

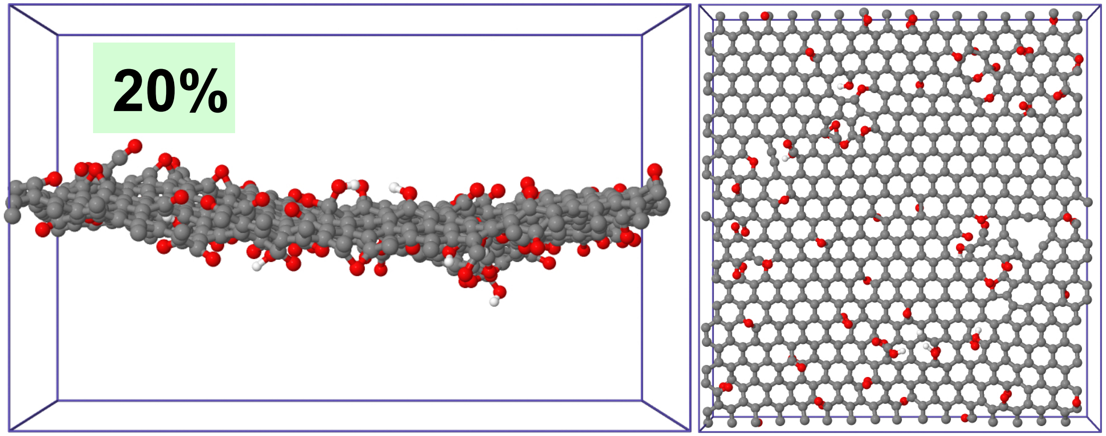


Effect of Surface Roughness. Functionalized Graphene Surface (Paul Huang)



Hydroxyl & epoxy groups on surface cause curvature

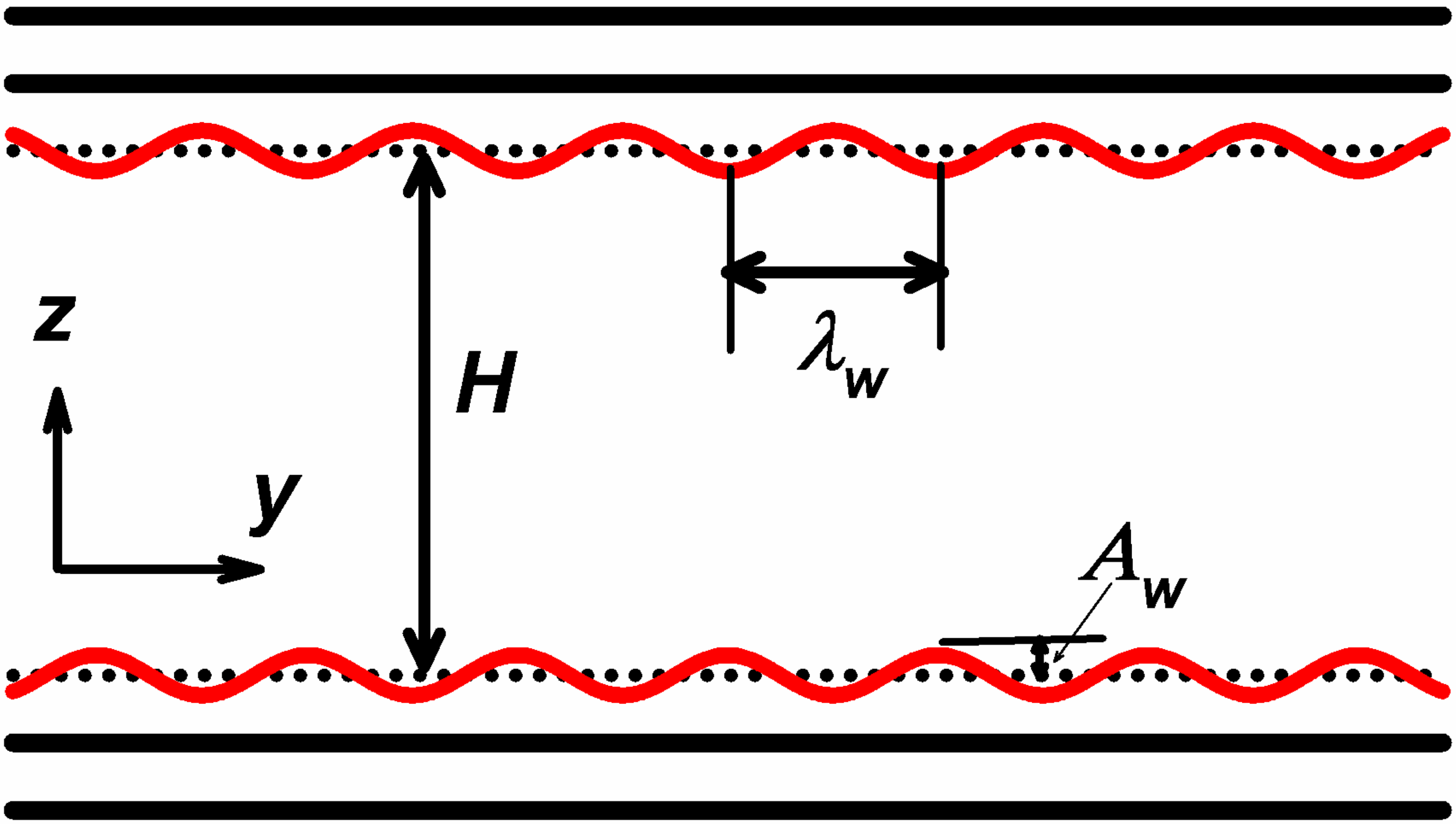
Hydroxyl, epoxy, vacancy



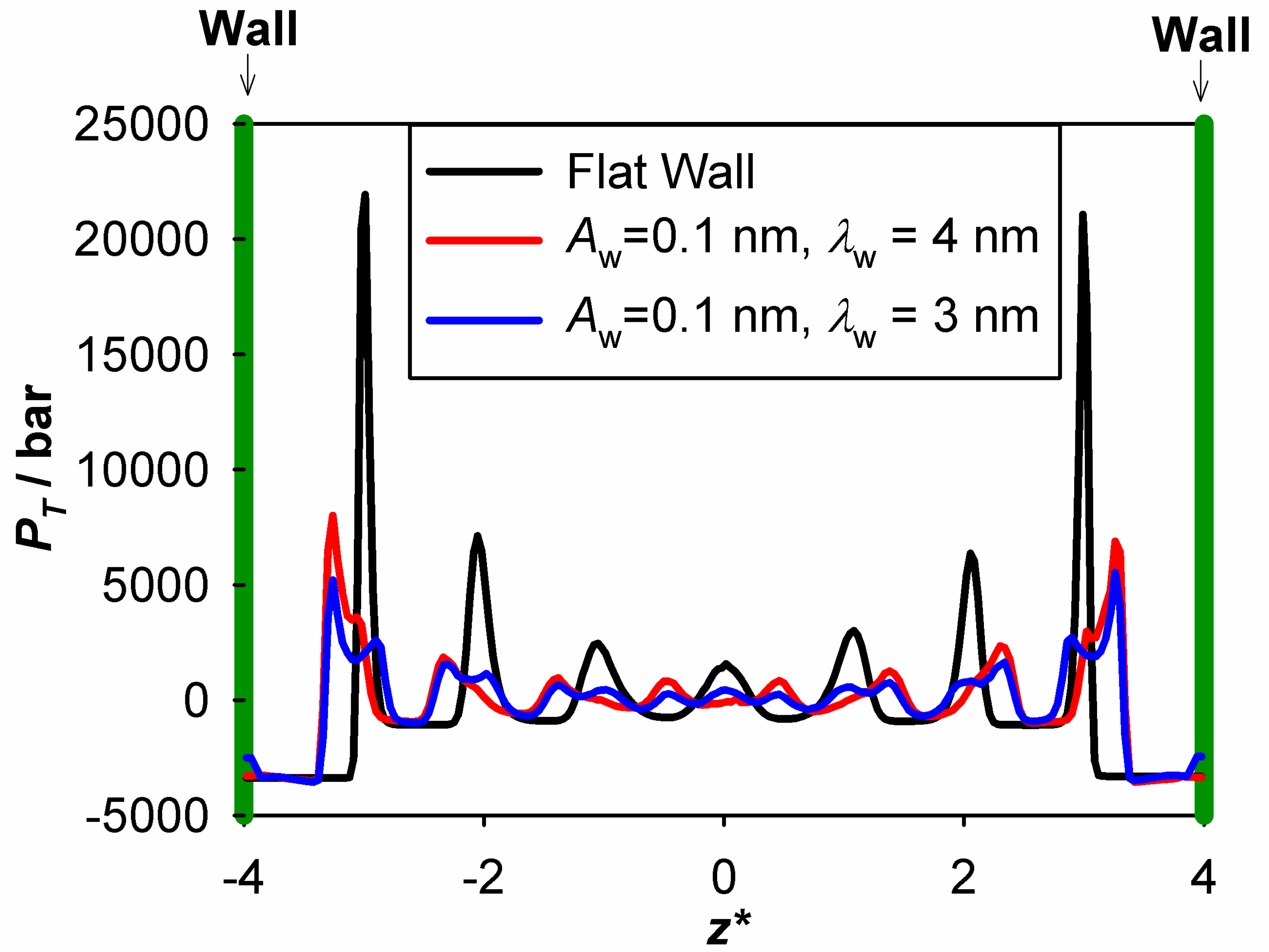
Box size: 4.3 x 4.0 x 2.5 nm

from ReaxFF reactive molecular dynamics

Model for Rough-Wall Slit Pore



Tangential Pressure Profile of Ar in Slit Pores with Surface Roughness, 87.3 K, 1 bar Bulk Pressure

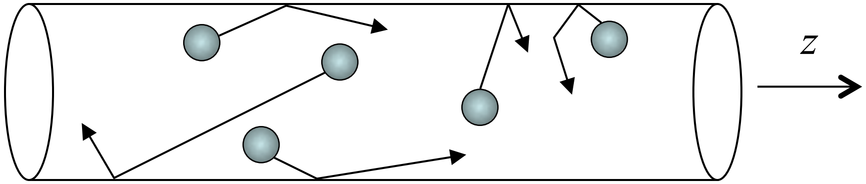


DIFFUSION MECHANISMS IN NANO-PORES

Ballistic (free flight: short times)

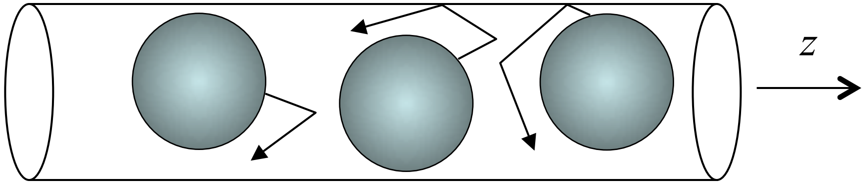
$$\lim_{t\to 0}\left\langle\left[z(t)-z(0)\right]^2\right\rangle = 2Et^2$$

Fickian Diffusion: longer times



$$\lim_{t\to \infty}\left\langle\left[z(t)-z(0)\right]^2\right\rangle = 2Dt$$

Single-file Diffusion: longer times

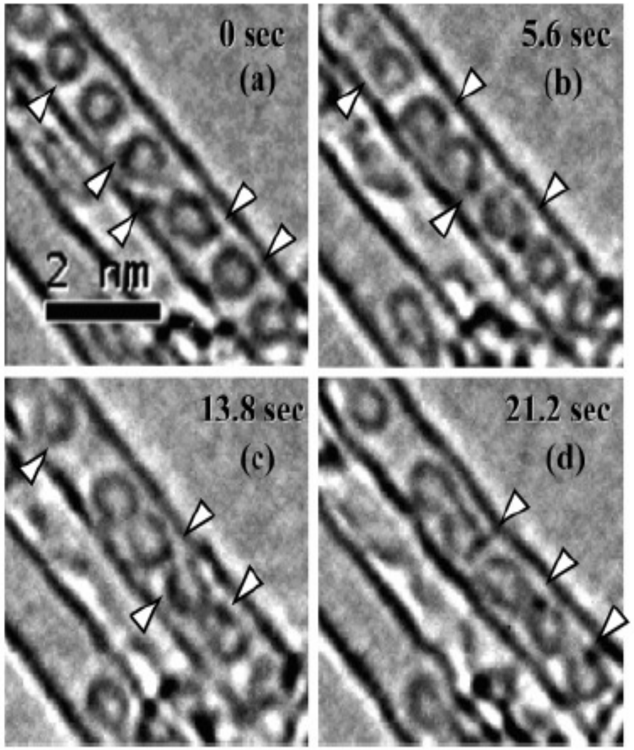


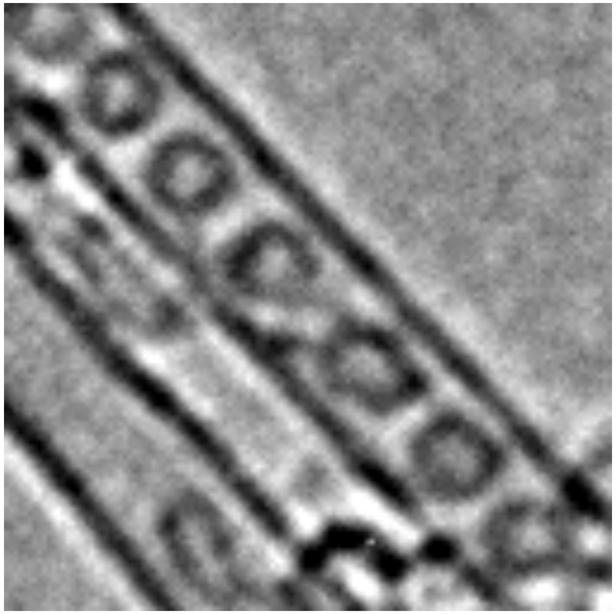
$$\lim_{t\to \infty}\left\langle\left[z(t)-z(0)\right]^2\right\rangle = 2F\sqrt{t}$$

D is the self-diffusivity; F is the single file mobility

High Resolution TEM of C_{60} peapods in Single-Walled Carbon Nanotubes (SWNT)

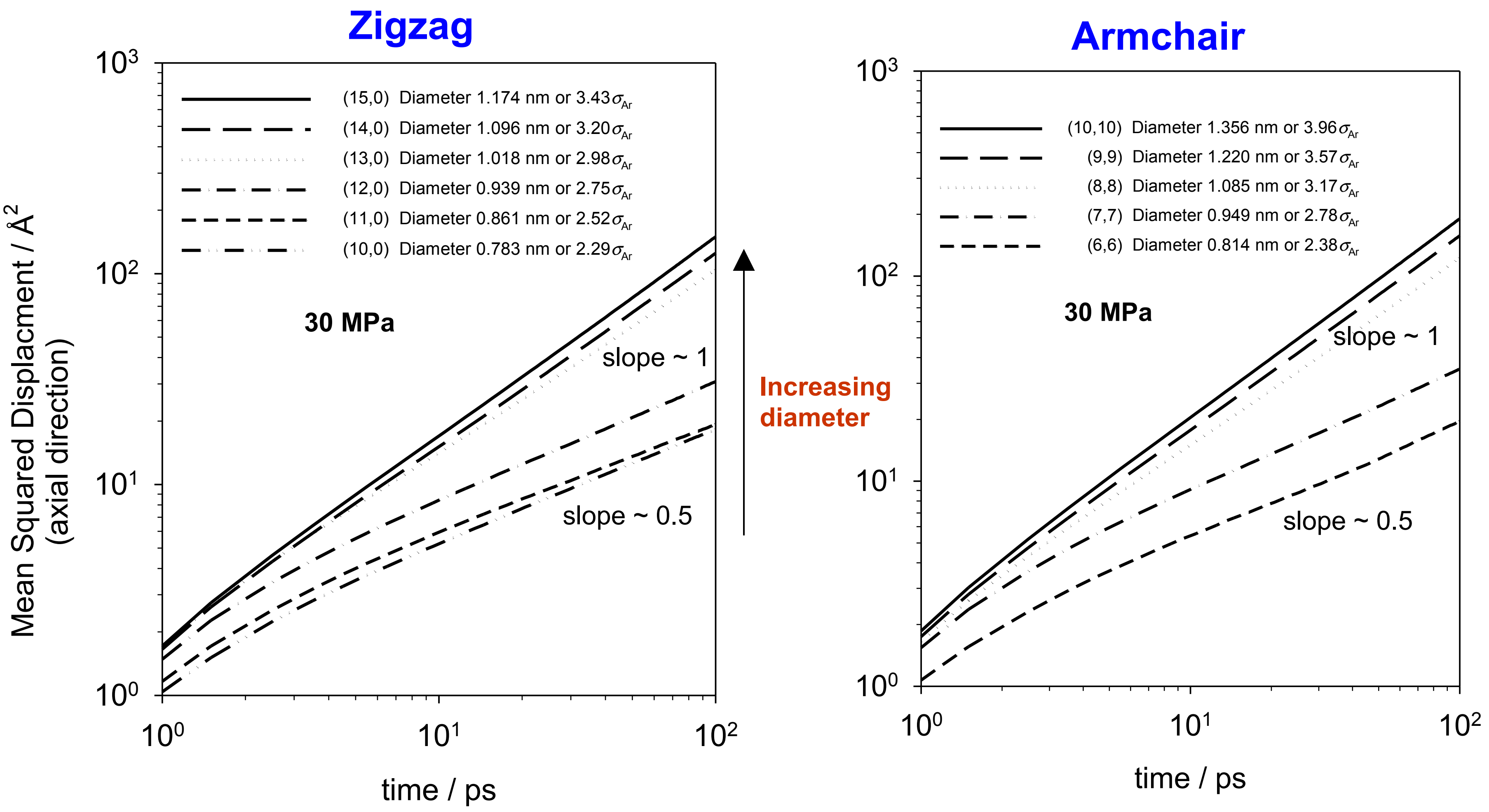
Figure 3 from B.Y. Sun, et. Al, *JACS*, **127**, 17972-17973 (2005).





Time-dependent HRTEM images of $(CsC_{60})_n$ in SWNT taken at 0, 5.6, 13.8, and 21.2 s (arrows point to Cs. The movie speed is ca. 5 times faster than the real time).

Mean Squared Displacement of Argon in Armchair and Zigzag SWNTs at 298 K (T*=2.40)

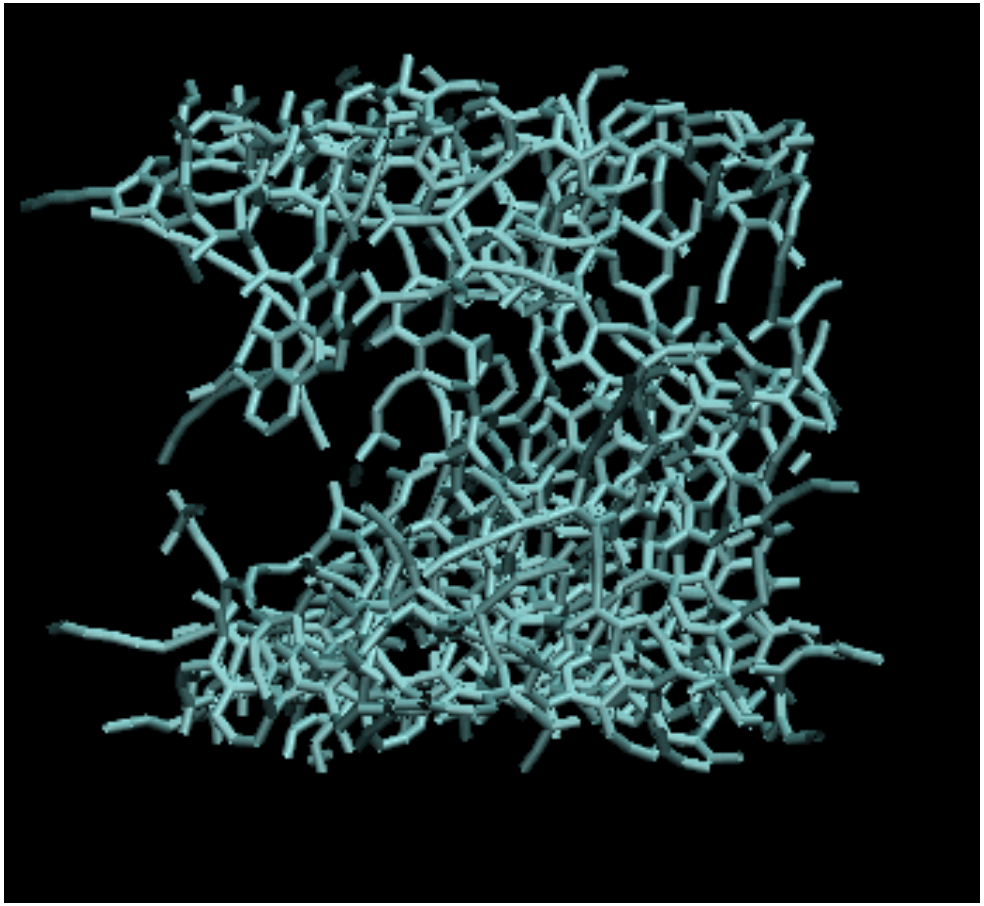


Transition from single file to Fickian occurs at a pore diameter of about 2.80σ_{Ar}

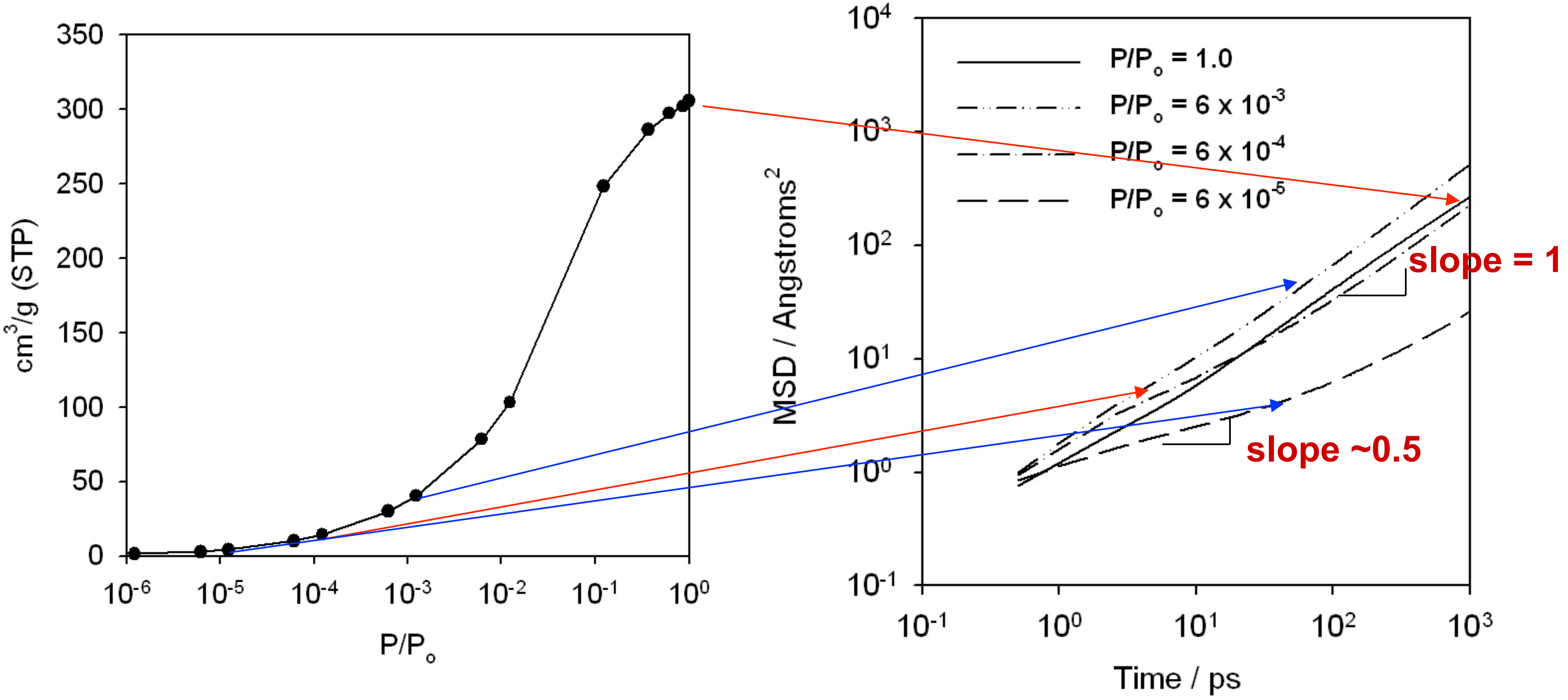
BPL Activated Carbon

Disordered Microporous Carbon: Modeled by Hybrid Reverse Monte Carlo

J.C. Palmer et al., *Carbon*, **47**, 2904 (2009).

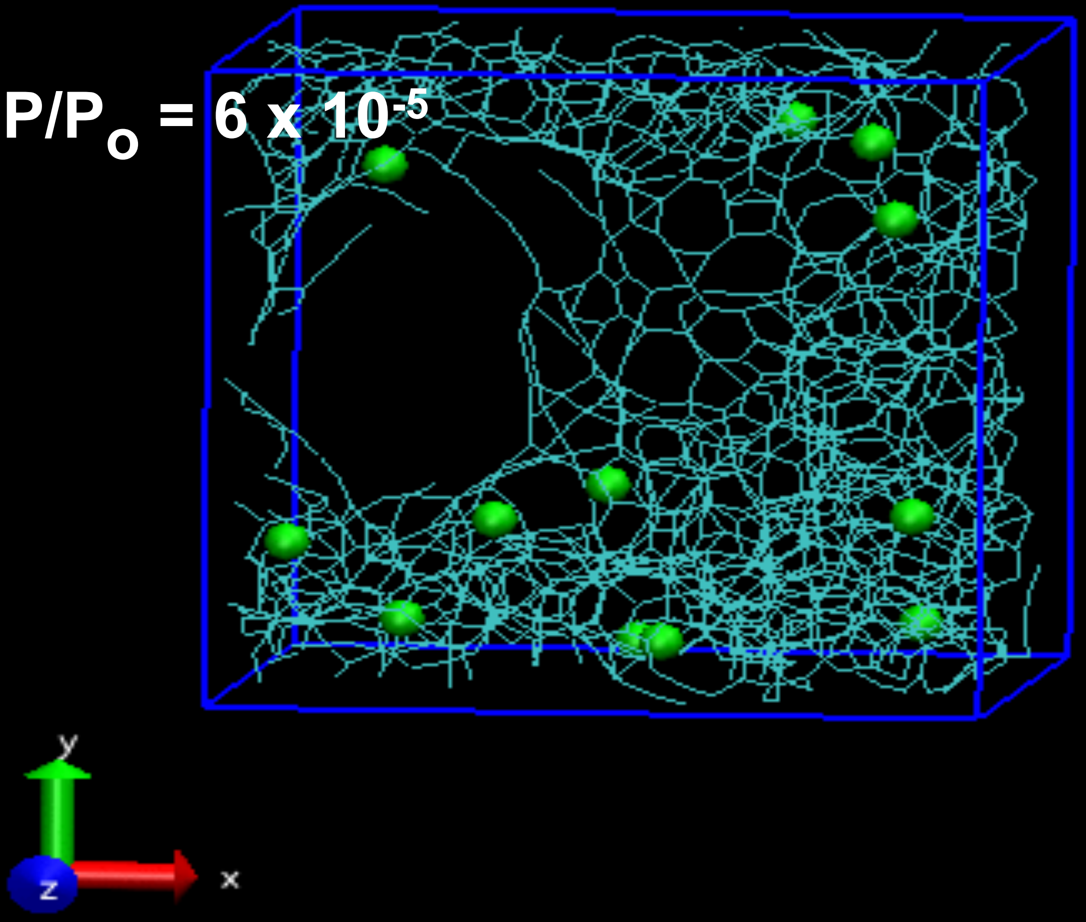


BPL Activated Carbon
Ar Adsorption and Diffusion at 120 K



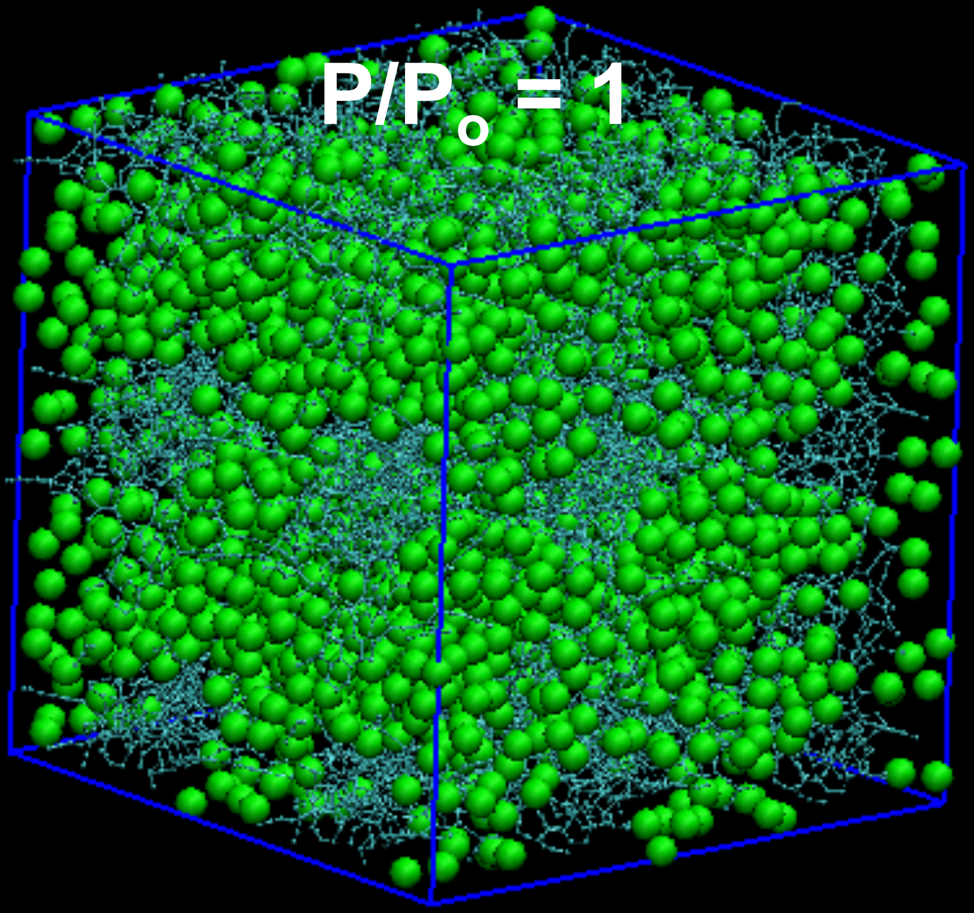
As you increase pressure, we might expect that the diffusion rate (MSD) will decrease as the packing of more particles slows the total movement. However, below ~$P/P_o = 6 \times 10^{-3}$ the MSD actually increases with increasing pressure, because at low P molecules are trapped in small pores, but increasingly occupy larger pores as P increases.

$P/P_o = 6 \times 10^{-5}$



Note: This is a movie of a very small system so that it is easy to see movement of the particles at low pressure. Our actual simulations involve at least 2,000 fluid atoms for all pressures in NVE MD

BPL Activated Carbon
Ar Diffusion at 120 K



Conclusions and Future Needs

- MC and MD play an important role in understanding confinement effects, and can provide results for properties that cannot yet be measured in the lab (e.g. pressures, structures).
- Phase transition shifts in nanopores depend strongly on wetting characteristics of the solid.
- Pressure in confined nanophases can be greatly enhanced at liquid temperatures – by several orders of magnitude for P_N and by up to 8 orders for P_T. In-pore pressures are sensitive to bulk pressure, wetting, wall roughness.
- Need to develop methods for quantitative or semi-quantitative description of multi-modal diffusion in materials with a range of pore sizes.

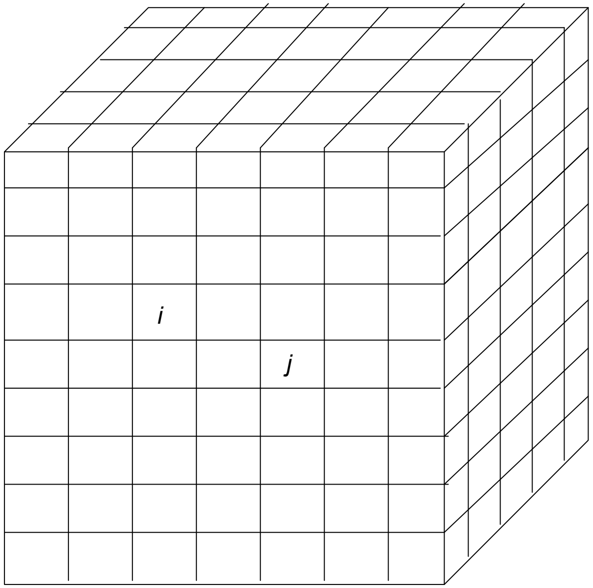
Thank you for your attention!

Questions?
Suggestions?
Complaints?

THEORY & MODELING AT DIFFERENT SCALES

- At present theory/modeling is done at 4 different scales:
- The electronic scale. Matter is made up of electrons, protons, etc. and obeys quantum mechanics. The most rigorous approach. Also the most costly.
- The atomistic scale. Matter is made up of atoms, & obeys statistical mechanics. We don't explicitly account for the electrons, protons, etc., and so we lose the electronic detail.
- The meso scale. Matter is made up of small chunks of matter, each containing a number of atoms. No rigorous basis for meso-scale methods. We now lose both the electronic and atomic detail.
- The continuum scale, treat matter as a continuum. Bulk matter obeys well known macroscopic laws of conservation, and constitutive equations (Fick's Law, Fourier's Law, Newton's Law, etc.)

The Microcanonical Ensemble and Ensemble Averaging



A microcanonical ensemble is a collection of replicas of the system of interest, with all replicas having the same number of molecules, *N*, energy *E*, and volume *V*. Although each replica is in the same thermodynamic state as the system of interest, at any instant in time the various members of the ensemble will occupy many different quantum states (e.g. states *i* and *j* for two of the ensemble members shown).

Features Common to MC and MD

- Equilibration

  This simulation period can be monitored in several ways:

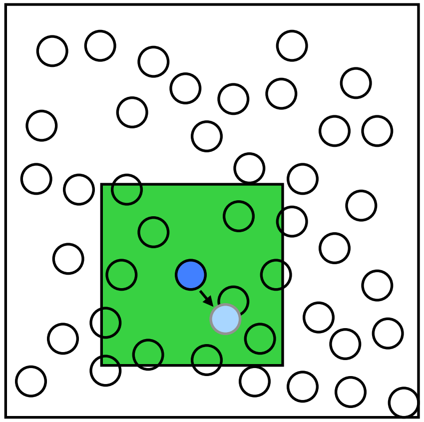
  - Check instantaneous values of properties: potential energy, pressure, etc.
  - If initial configuration was a lattice, track the “melting” of the lattice by monitoring order parameters measuring translational order (e.g., Verlet) and/or rotational order (e.g. Viellard-Baron). For definitions, see Leach, pp. 321-323; Allen & Tildesley, pp. 171-172.
  - Monitor mean squared displacements of molecules
  - Check radial distribution

The Ergodic Hypothesis

First Postulate.

The observed time average ($\tau \rightarrow \infty$) of a property of the system is equal to the ensemble average of the property, in the limit $M \rightarrow \infty$.

Displacement Trial Moves

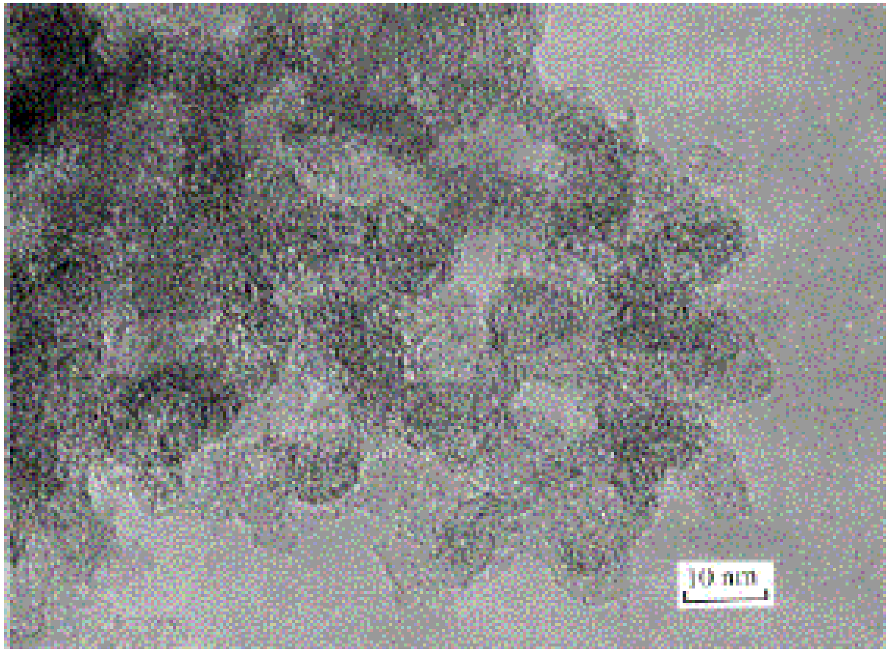


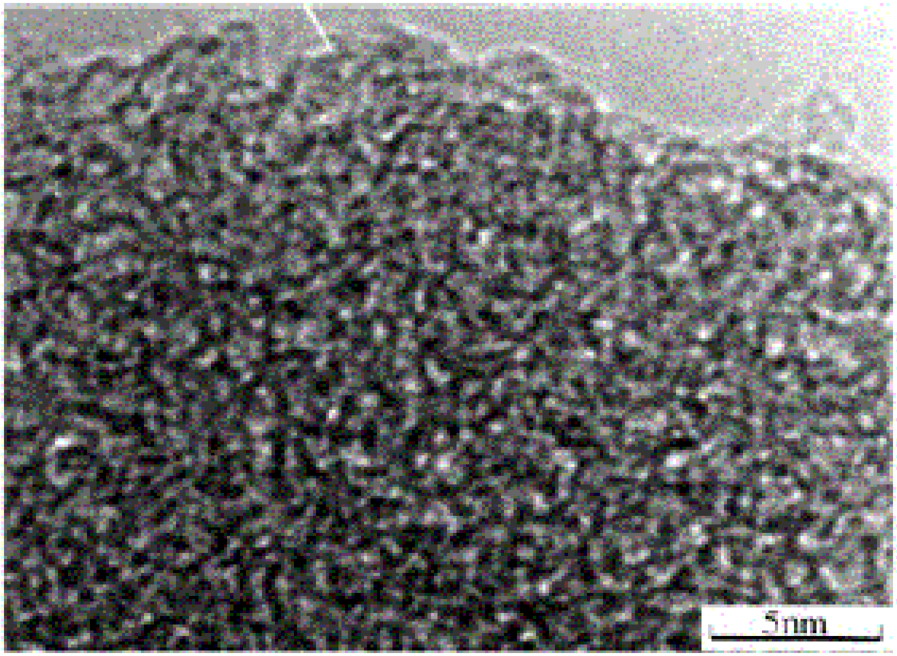
- New configuration has same volume and number of molecules
- Basic trial
  - displace a randomly selected atom to a point chosen with uniform probability inside a cubic volume of edge l centered on the current position of the atom
- The probability, $P_{m\rightarrow n}$, of acceptance of a move from a configuration *m* with coordinates $(x_1, x_2, \ldots, x_i, \ldots x_N)_m$ to a new configuration *n* with coordinates $(x_1, x_2, \ldots, x_i, \ldots x_N)_n$, is proportional to the probability density of the final state, *n*,

$$P_{m\rightarrow n} \,\alpha\, \rho_n$$

- For this trial move, probability ratios derived for the canonical (NVT) ensemble are the same in other common ensembles $(NPT,\ mVT,$ etc.), so the algorithm described here pertains to them as well.
- Speedup algorithm by the introduction of clever trial moves
  - reptation, crankshaft moves for polymers
  - multi-molecule movements of associating molecules
  - many more

Porous Carbon Materials

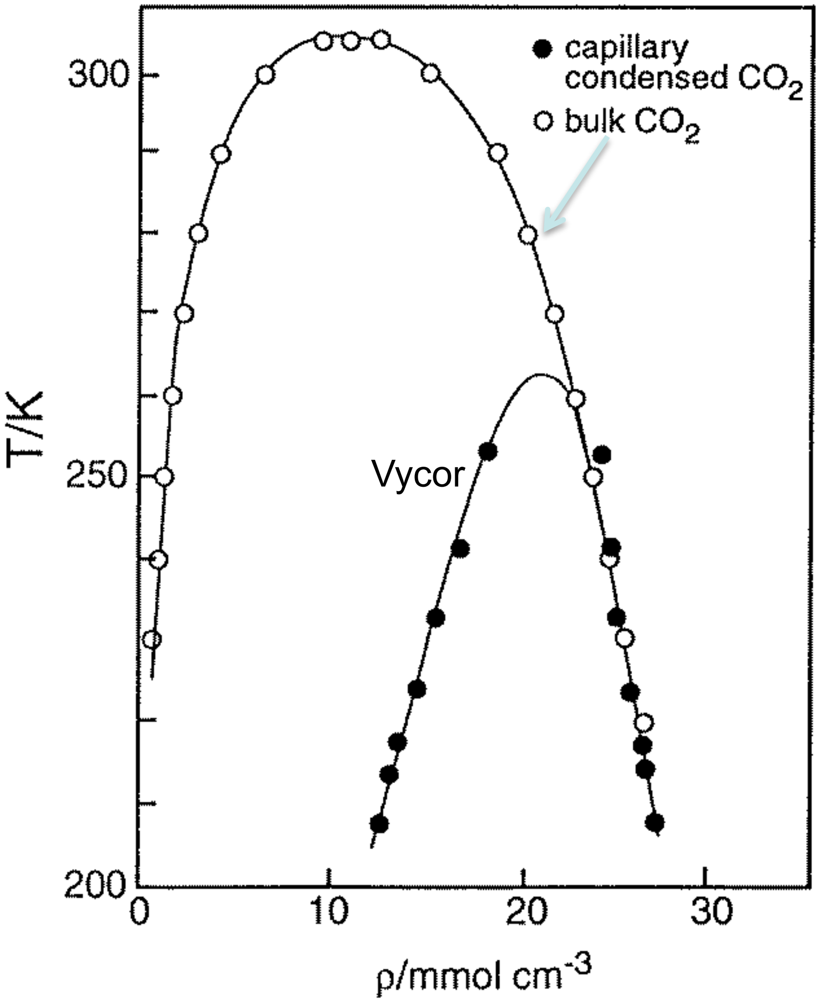




TEM image of a carbon aerogel
Hanzawa et al. (Adsorption, 1998)
Aerogels are mesoporous materials that contain some micropores

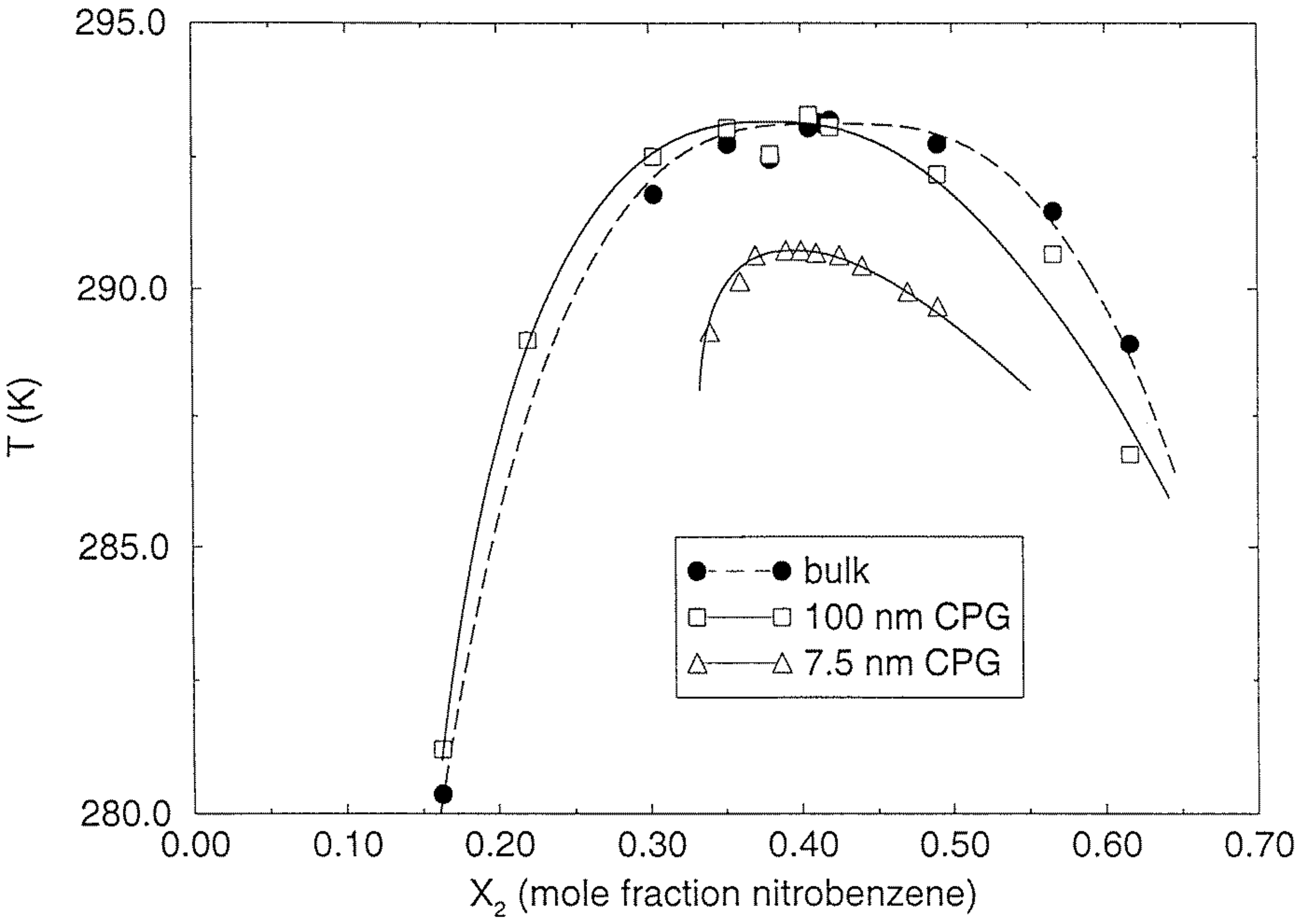
TEM of a pitch based activated carbon fibre. Light areas are pores, grey areas are pore walls. The pores are modeled as slit shaped.
Gelb et al. (Rep. Prog. Phys, 1999)

‘Hysteresis Phase Diagram” for CO2/Vycor



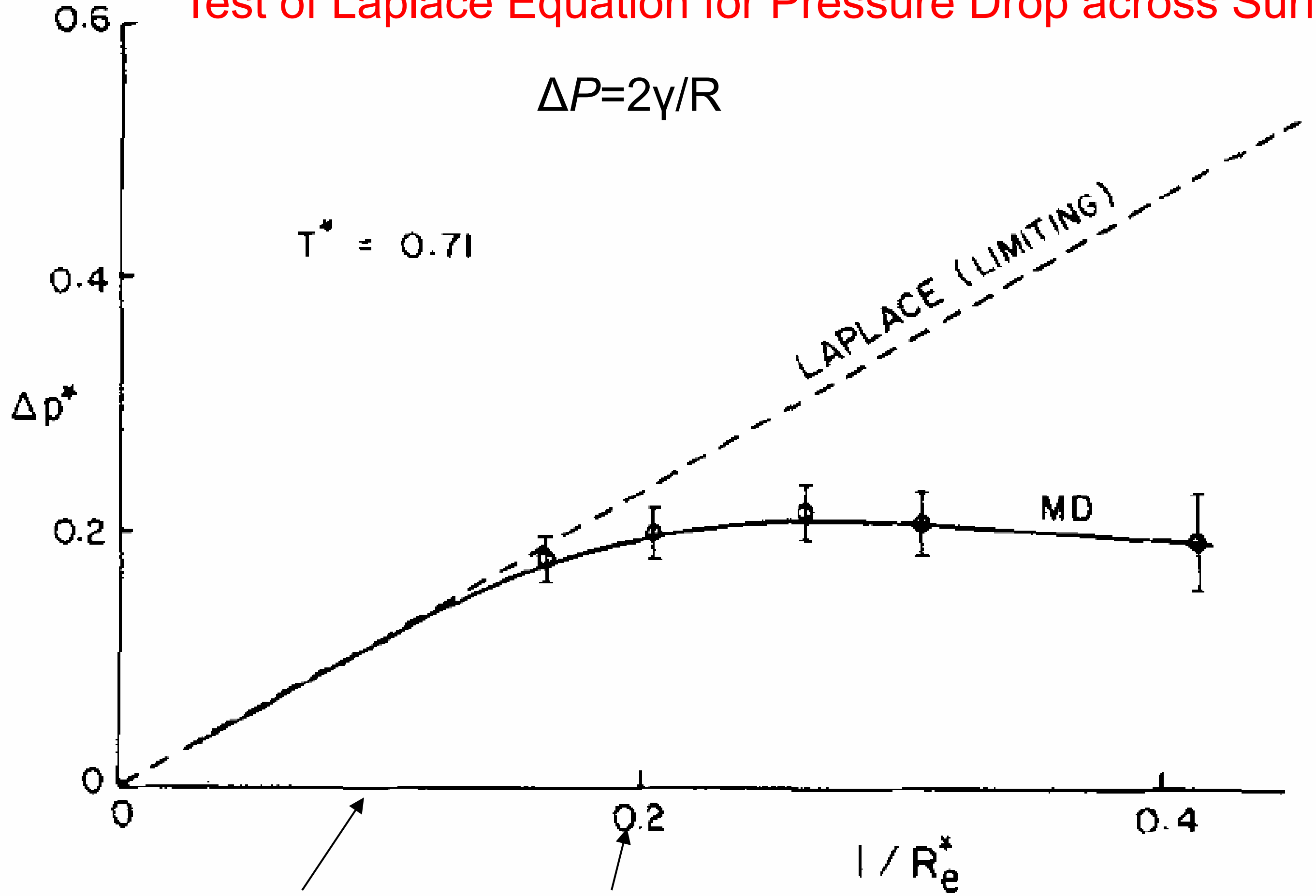
D.H. Everett et al. See also L. D. Gelb *et al.*, “Phase separation in confined systems”, Rep. Prog. Phys., 62, 1573 (1999).

Liquid-Liquid Equilibria: Nitrobenzene/n-Hexane in Controlled Pore Glass



M. Sliwinska-Bartkowiak et al. See also L. D. Gelb *et al.*, "Phase separation in confined systems", Rep. Prog. Phys., 62, 1573 (1999).

Test of Laplace Equation for Pressure Drop across Surface of a Drop



$\Delta P = 2\gamma/R$

R=10σ

R=5σ

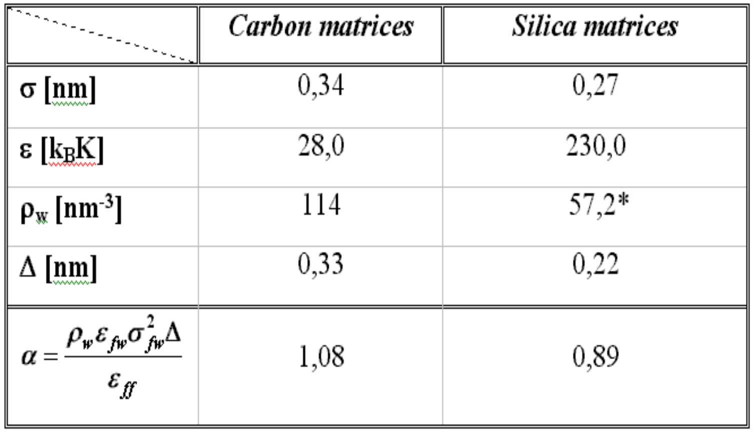
Test of the Laplace equation for the difference in pressure across the surface of a Lennard-Jones liquid drop of equimolar radius R_e. The Laplace equation is $\Delta p = 2\gamma_s/R_s$. Similar breakdown occurs for the Kelvin, Gibbs-Thomson, Young's, …equations.

S.M. Thompson *et al.*, "A molecular dynamics study of liquid droplets", JCP, 81, 530 (1984).

MELTING OF LIQUIDS IN CYLINDRICAL PORES

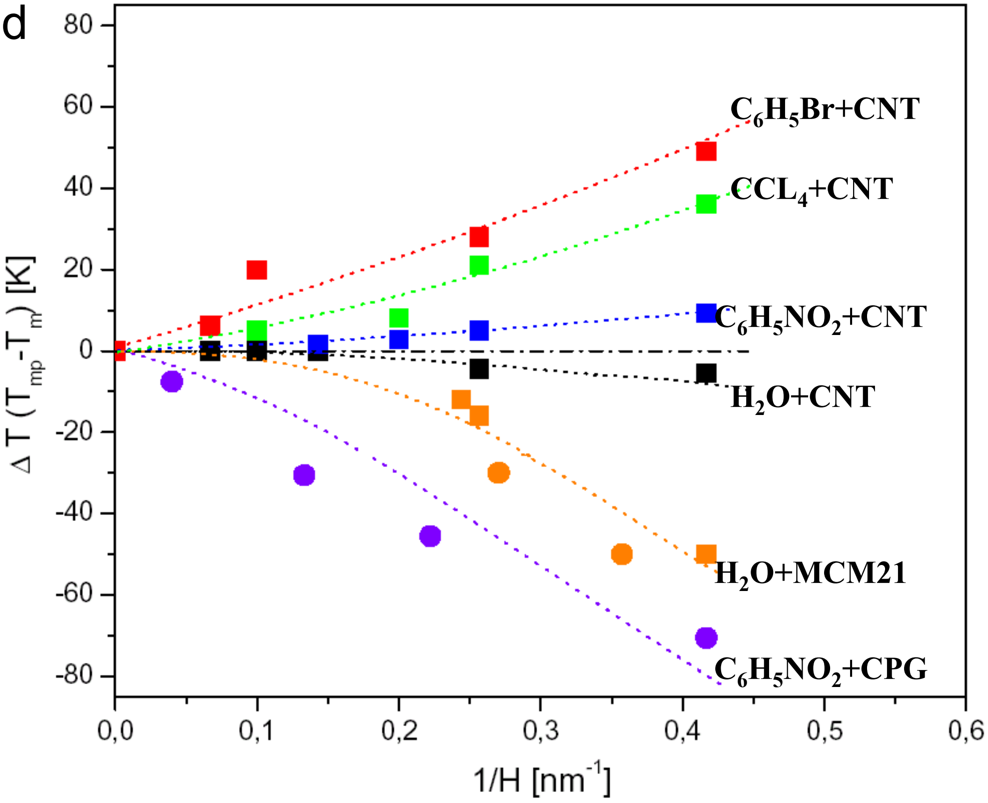
Results obtained by dielectric method

α for water



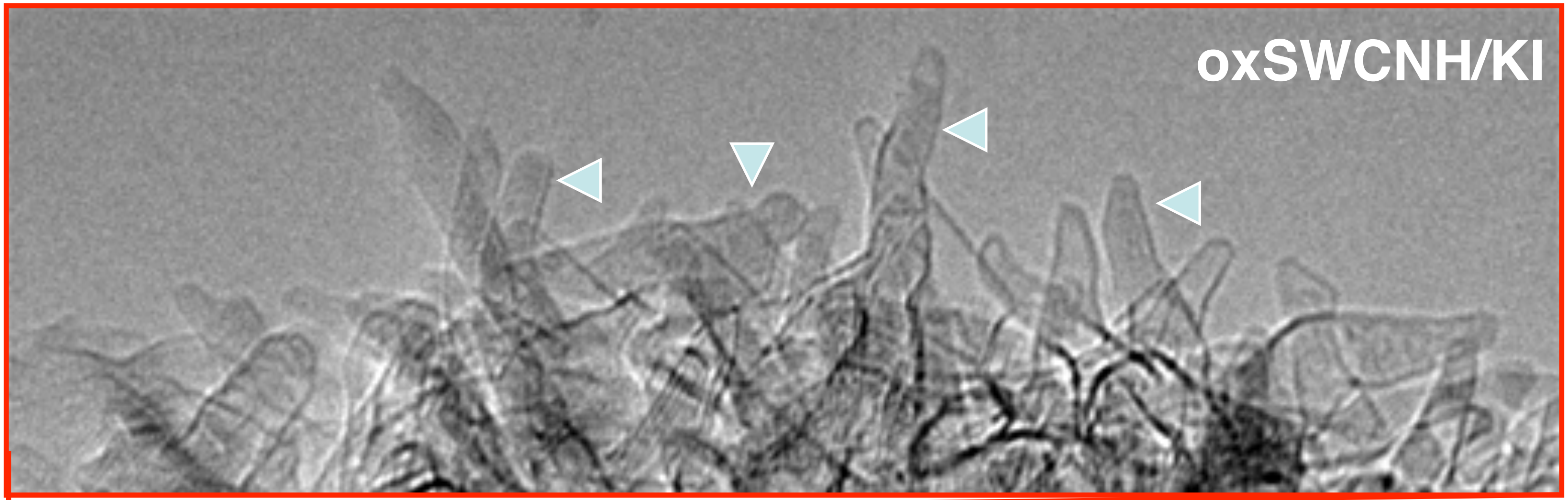
	Carbon matrices	*Silica matrices*
σ [nm]	0,34	0,27
ε [$k_B K$]	28,0	230,0
ρ_w [nm^{-3}]	114	57,2*
Δ [nm]	0,33	0,22
$\alpha = \frac{\rho_w \varepsilon_{fw} \sigma_{fw}^2 \Delta}{\varepsilon_{ff}}$	1,08	0,89

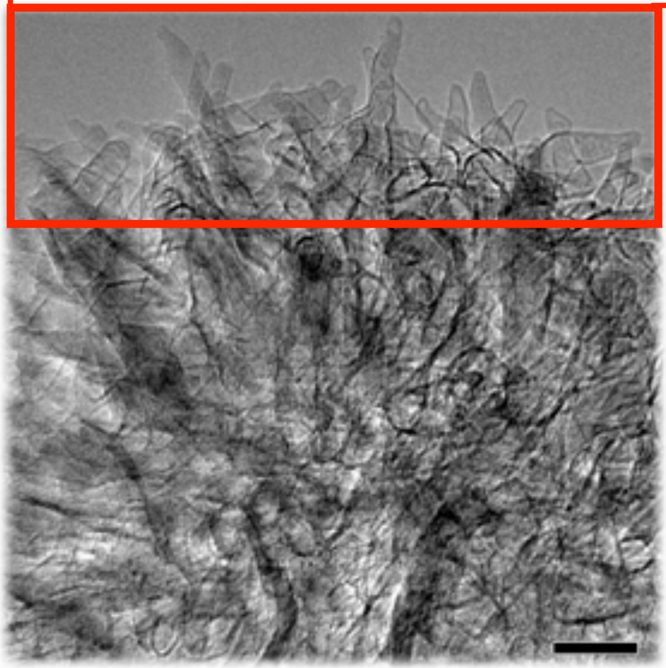
$$\alpha_{carbon} > \alpha_{silica}$$



Increase of melting temperature of liquids confined in carbon nanopores relatively to the silica nanopores

TEM images (from K. Kaneko)

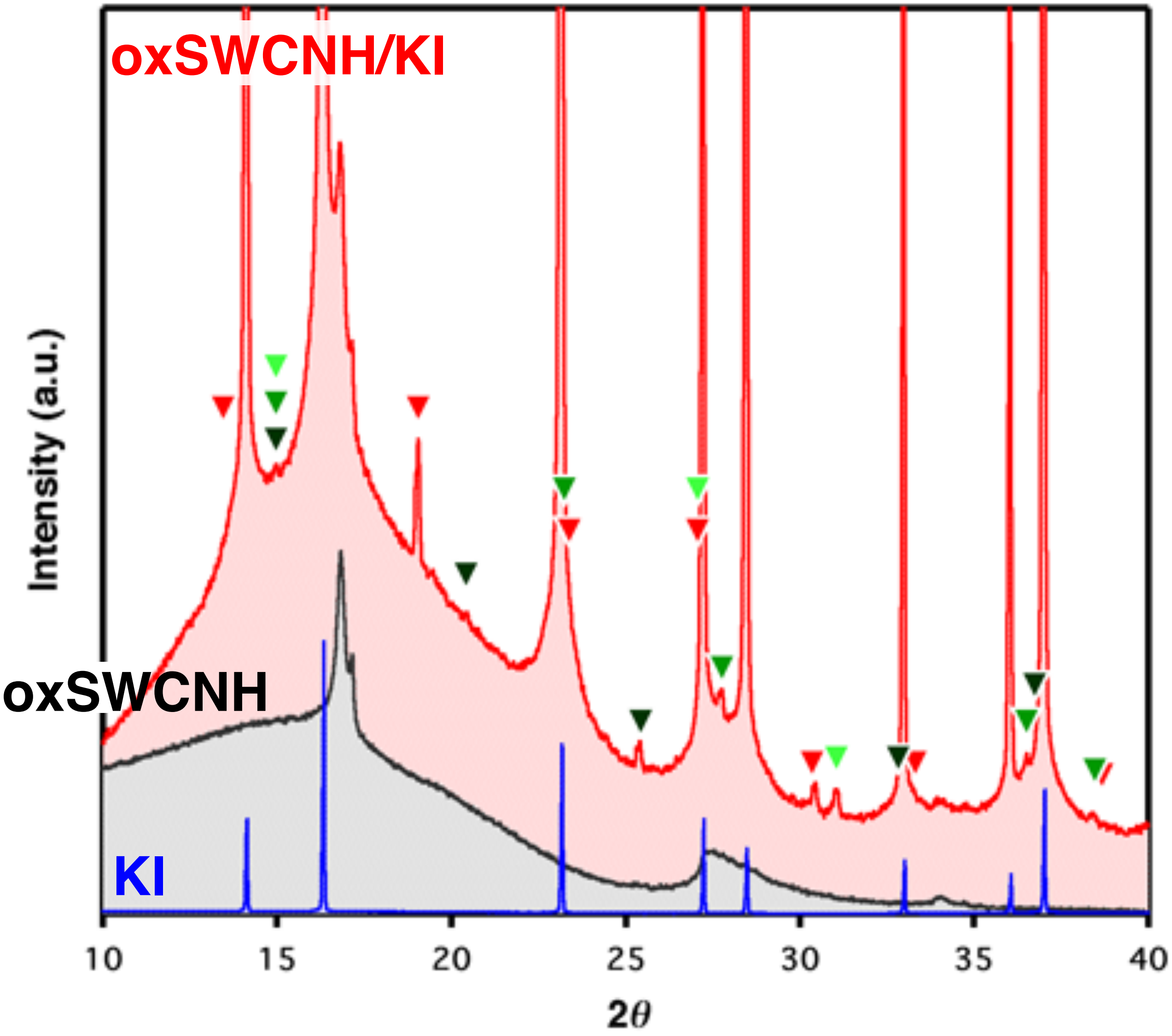




KI crystal in nanohorn

XRD for KI/SWCNH (from K. Kaneko)

λ = 1.003 Å (SPring-8)



Ambient pressure

f.c.c. [Fm$\bar{3}$m]

a = b = c

0.706 nm

***High-pressure phase* (1.9 GPa)**

cubic [Im$\bar{3}$m]

▼ **a = b = c**

0.429 nm

tetragonal

[I4/mmm]

a = 0.385 nm

▼ **b = c**

0.214 nm

▼ **b = c**

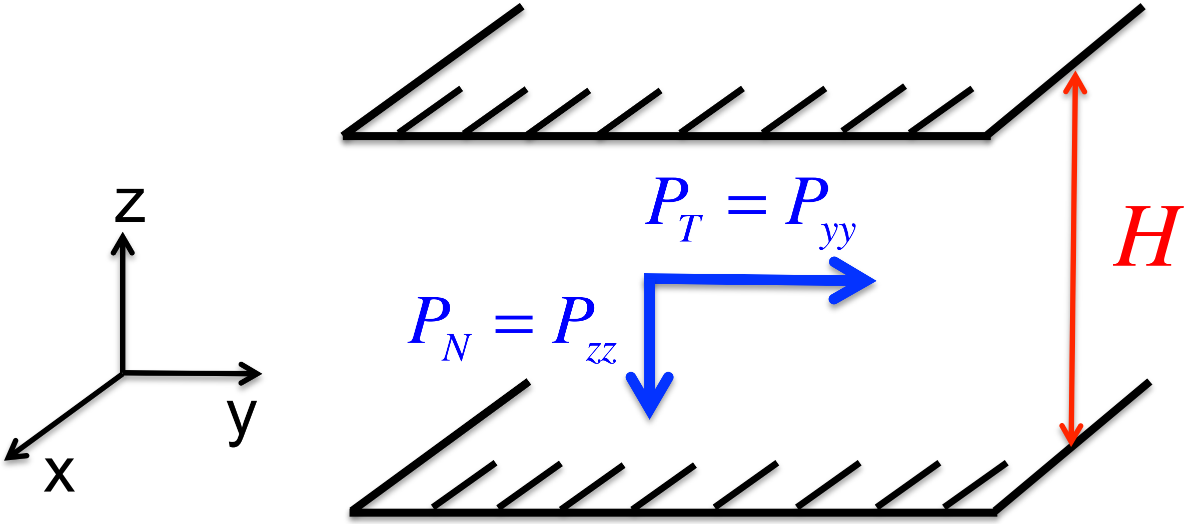
0.249 nm

▼ **b = c**

0.283 nm

Pores of Simple Geometry: Mechanical Equilibrium

Slit Pore

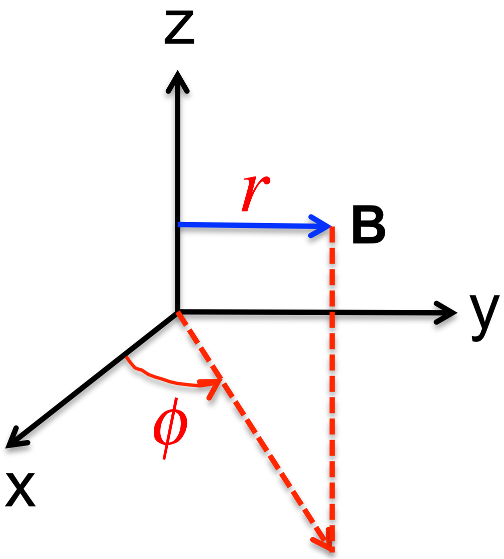


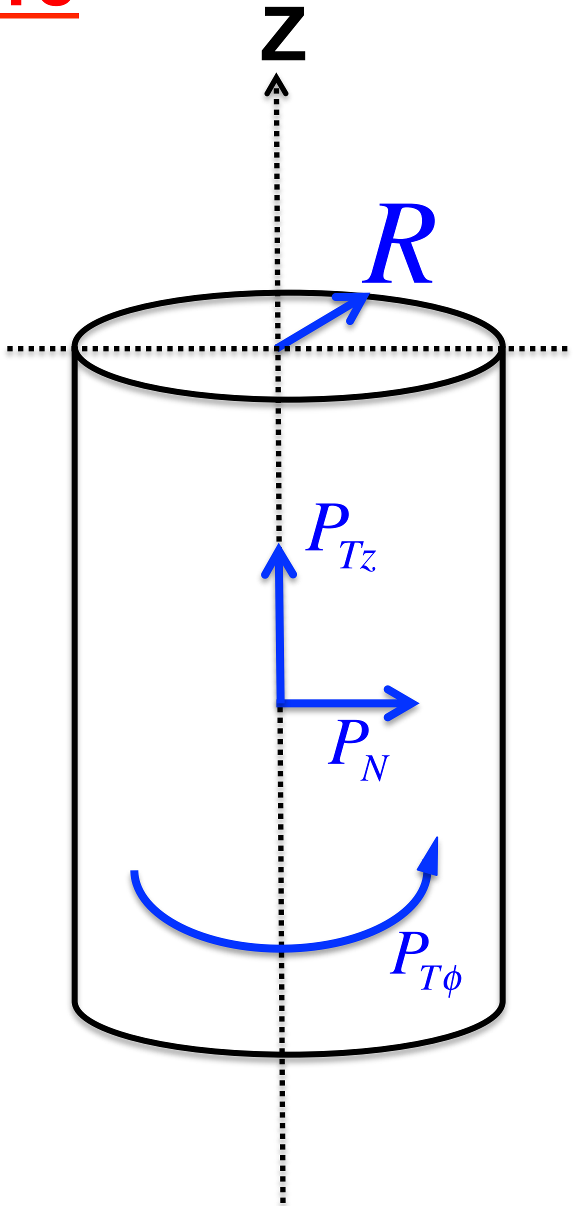
$$\nabla \bullet P = 0$$

$$\frac{\partial P_T(z)}{\partial x} = \frac{\partial P_T(z)}{\partial y} = 0$$

$$\frac{\partial P_N}{\partial z} = 0 \qquad (P_N = const.)$$

Cylindrical Pore





$$\nabla \bullet P = 0$$

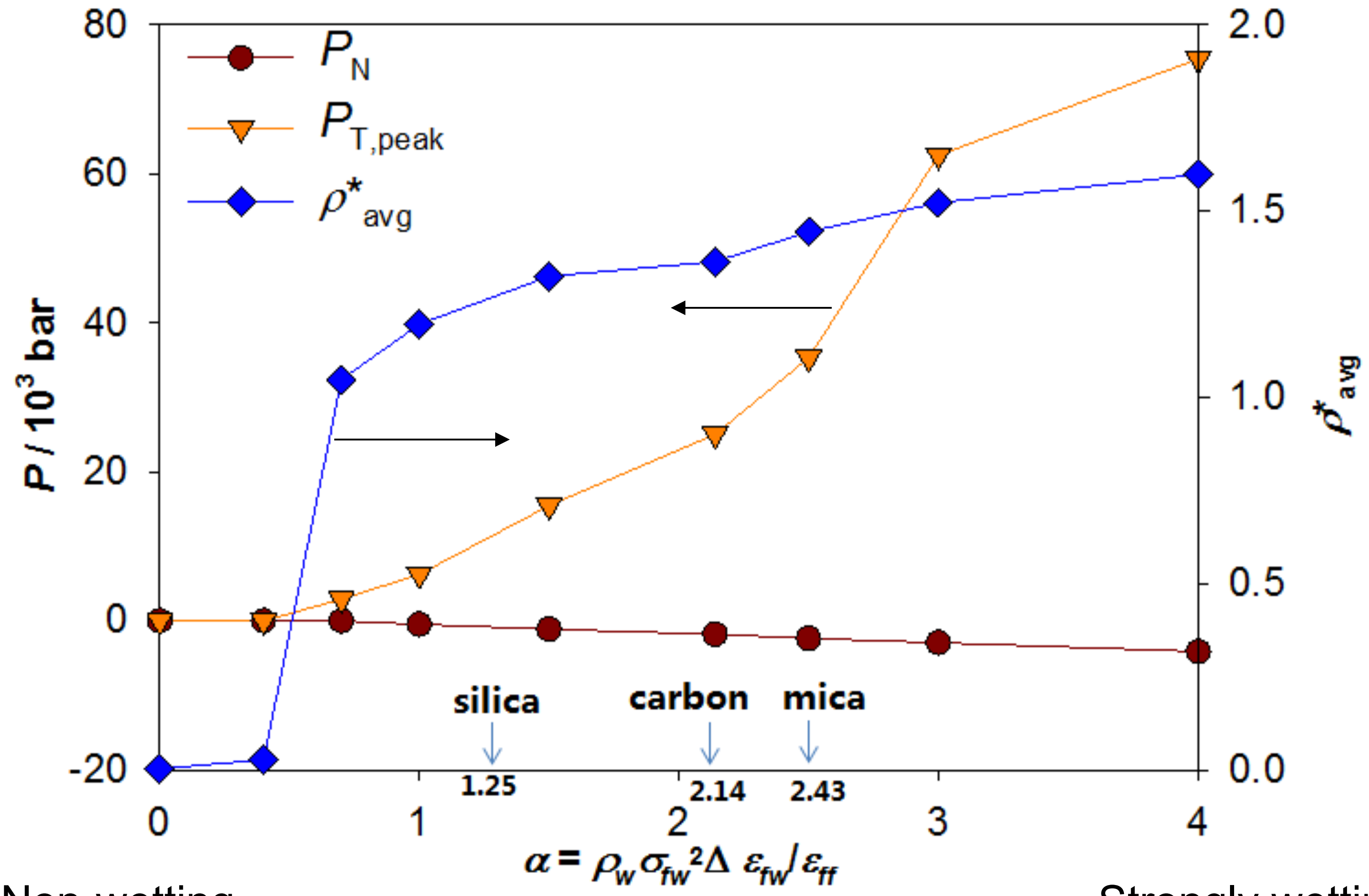
$$\frac{\partial}{\partial r}\left(rP_N(r)\right) = P_{T\phi}(r)$$

$$\frac{\partial P_{T\phi}(r)}{\partial \phi} = 0$$

$$\frac{\partial P_{Tz}(r)}{\partial z} = 0$$

Effects of material & adsorbate

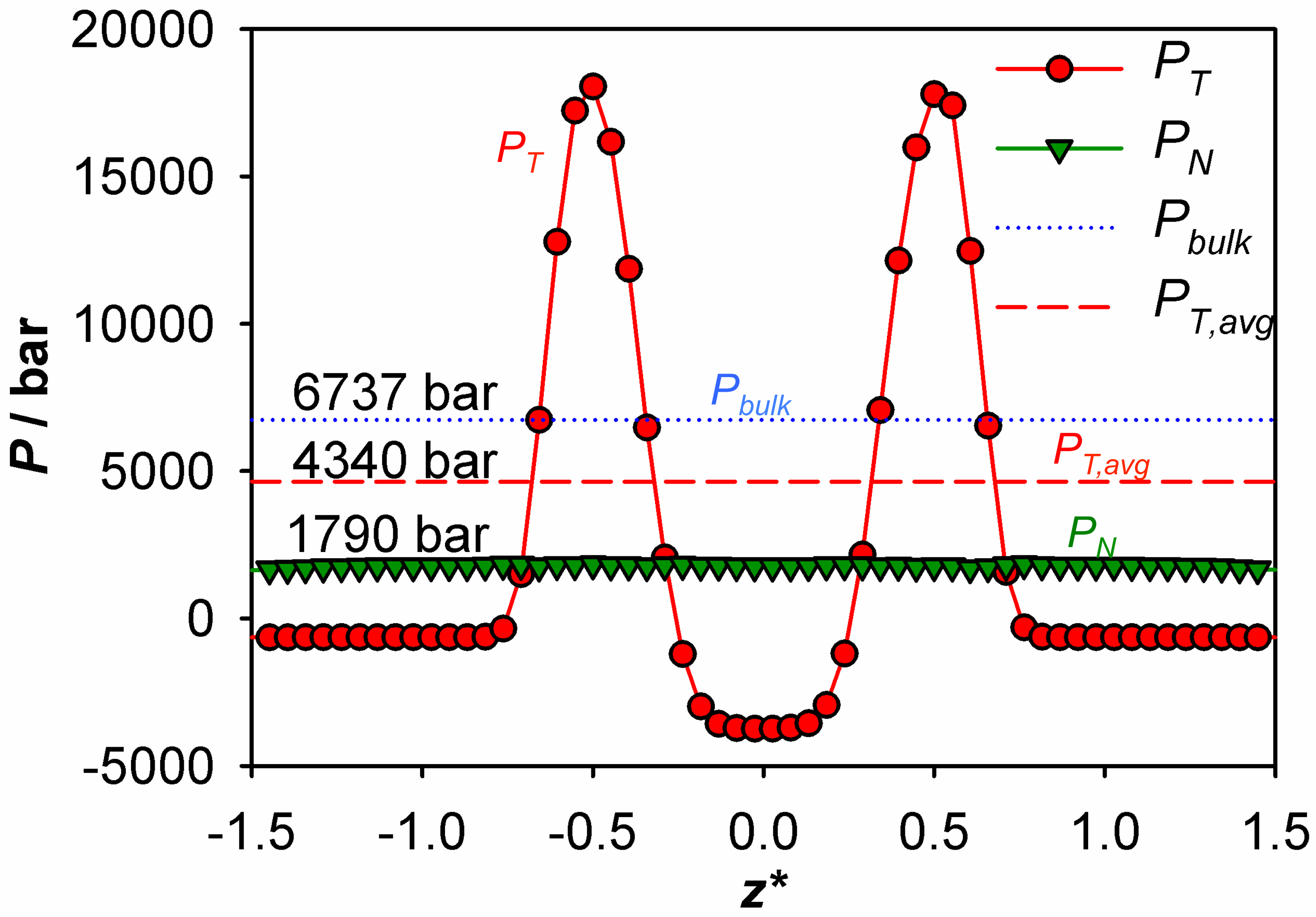
$H^* = 3.0$, $T = 87.3$ K, $P_{bulk} = 1.0$ bar



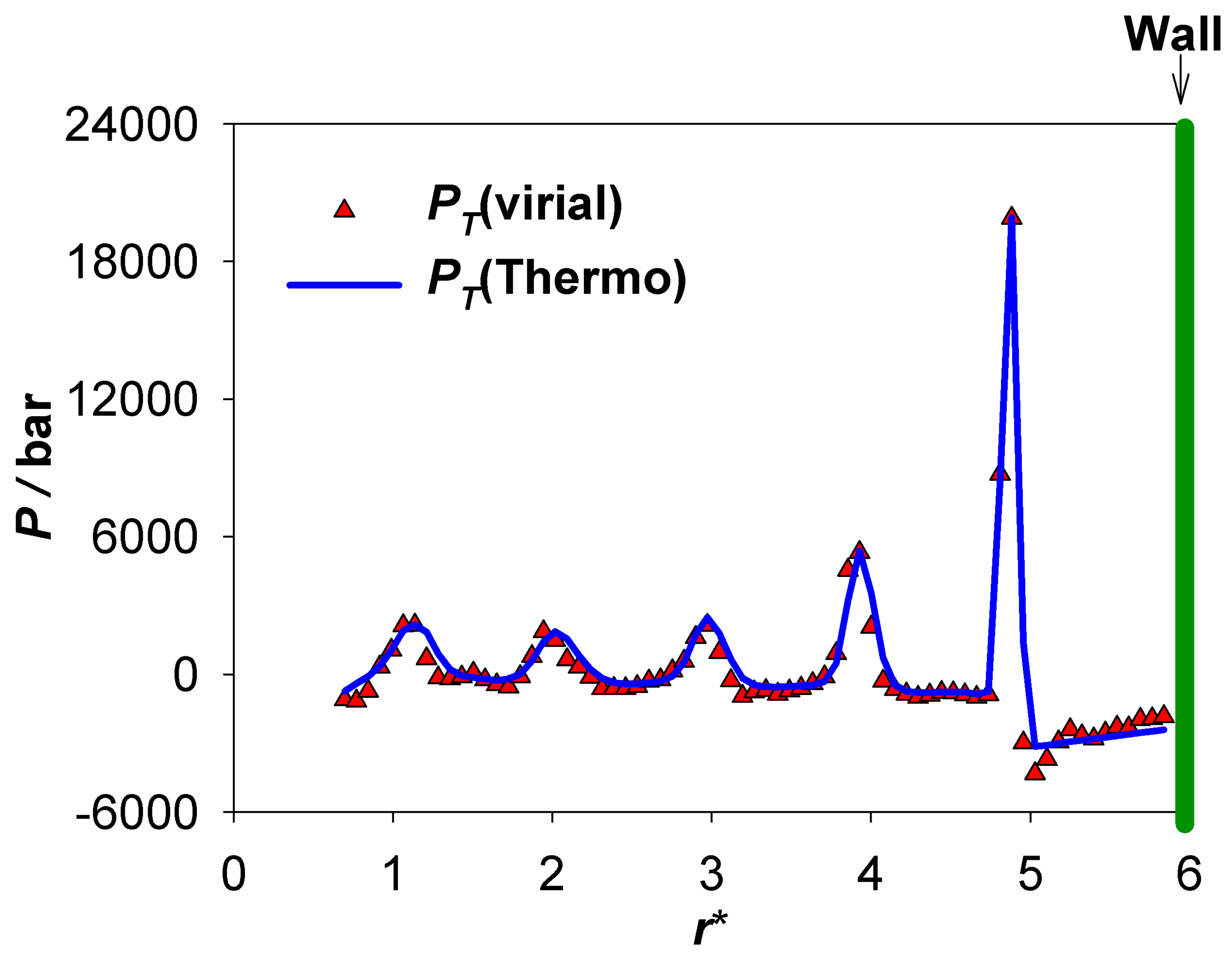
Non-wetting

Strongly wetting

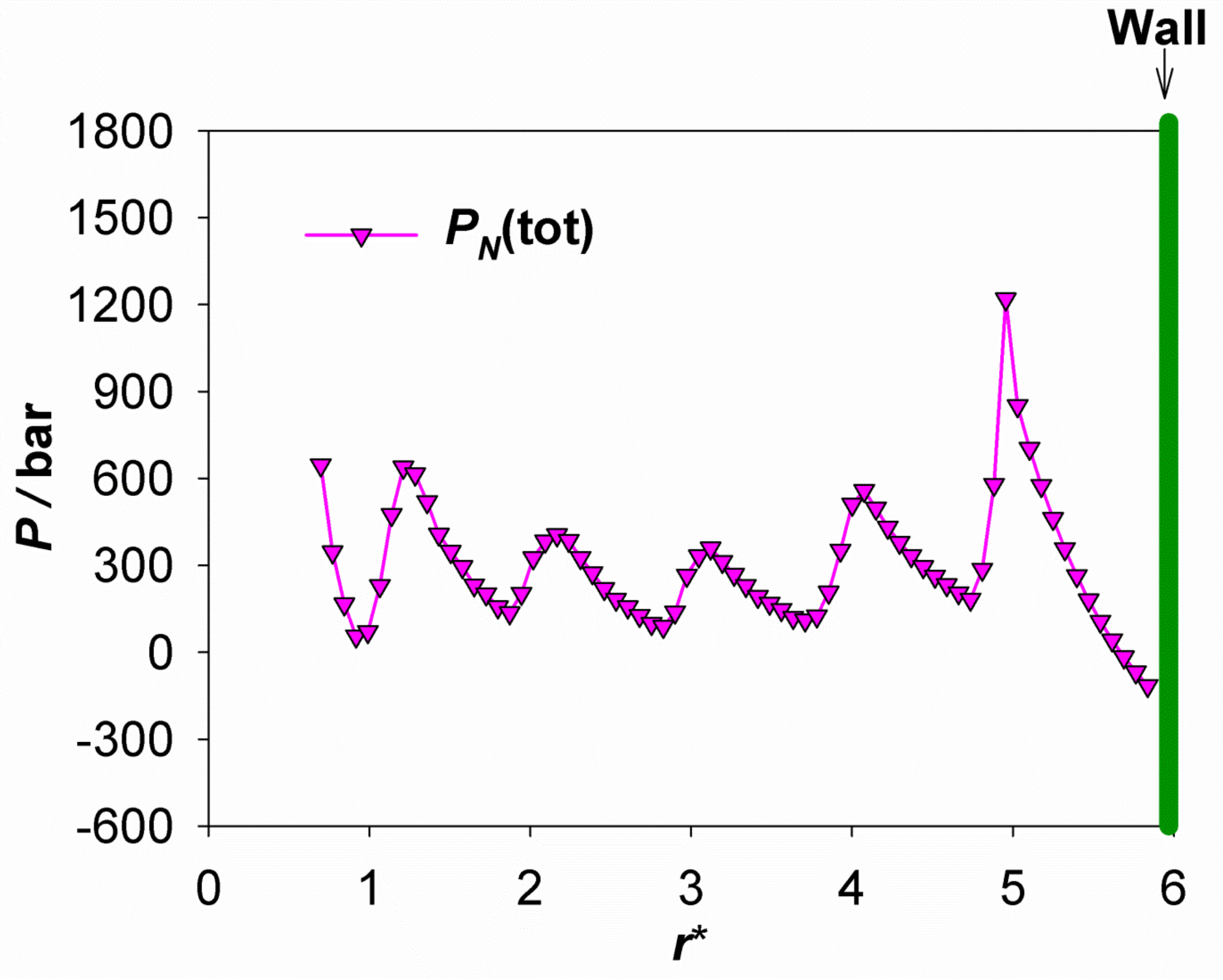
Hg intrusion and pressure *reduction* in carbon slit pore (H* = 3.0) at 300 K: *α*=0.1



Tangential Pressure Profile of Ar in a Spherical Pore (D = 4 nm), at 87.3 K, 1 bar Bulk Pressure

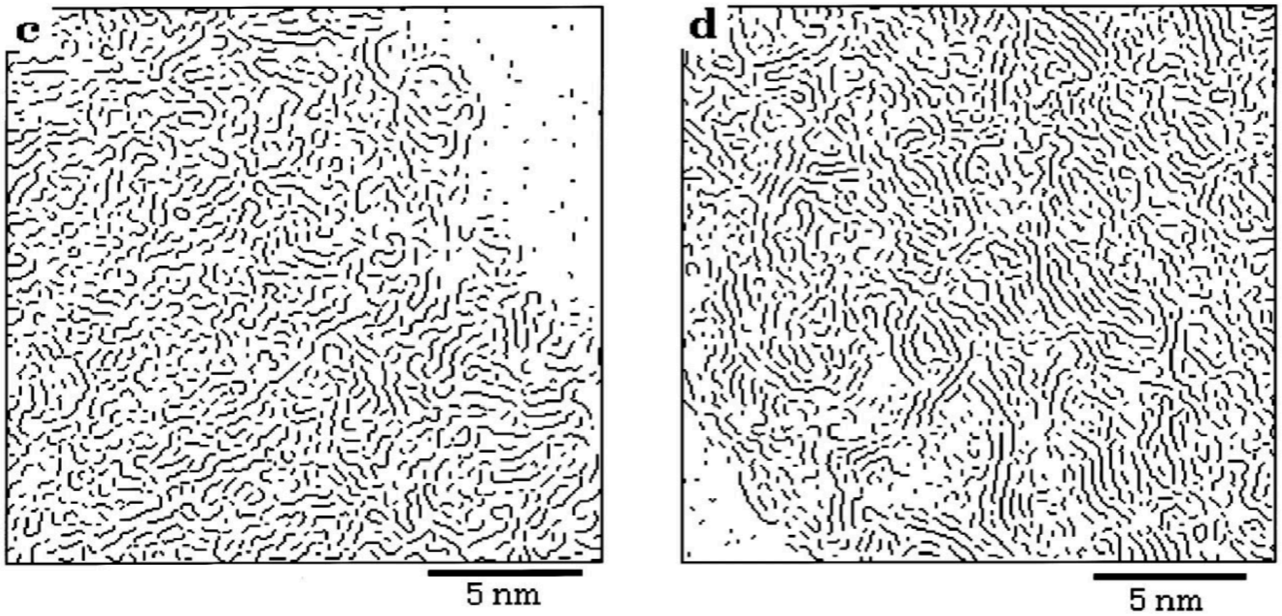


Normal Pressure Profile of Ar in a Spherical Pore (*D* = 4 nm), at 87.3 K, 1 bar Bulk Pressure



J. Jagiello Model of Surface Roughness

phenol formaldehyde resin char (PFC), Carbon, 38, 1977 (2000)



Layer distance
~ 0.38 nm

Layer diameter:
3.4 nm ~ 3.9 nm

$$z = \frac{1}{2} H + A_W \cos\left(\frac{2\pi}{\lambda_W} y\right)$$