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Pressure induced structural transformation in nano-particles and carbon nano-tubes

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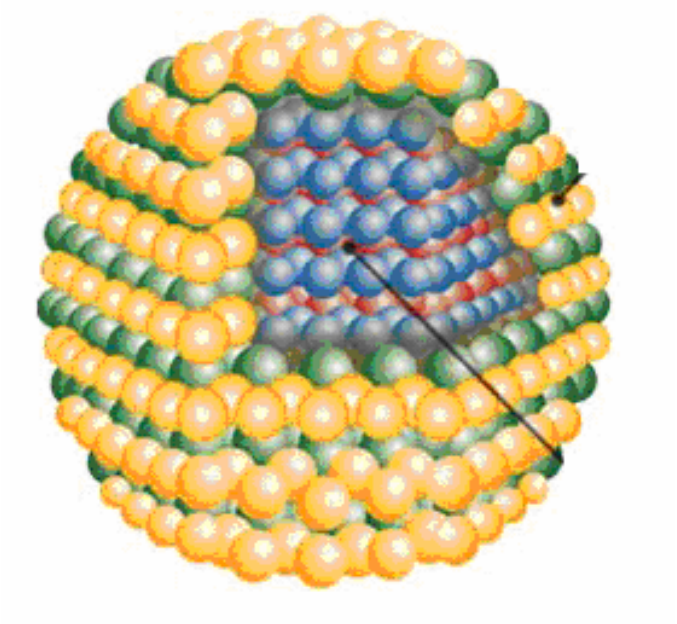
Outline:

- **Introduction**
- **Constant-pressure MD method for finite system**
- **Some applications:**
  - ***(1) Melting of nano-particles***
  - ***(2) Solid-solid transition in nano-particles***
  - ***(3) Pressure-induced hard-soft transition of CNTs***
- **Summary**

Why finite systems under pressure?



- Nanocrystal has much larger surface to volume ratio, influence elastic and thermodynamic properties

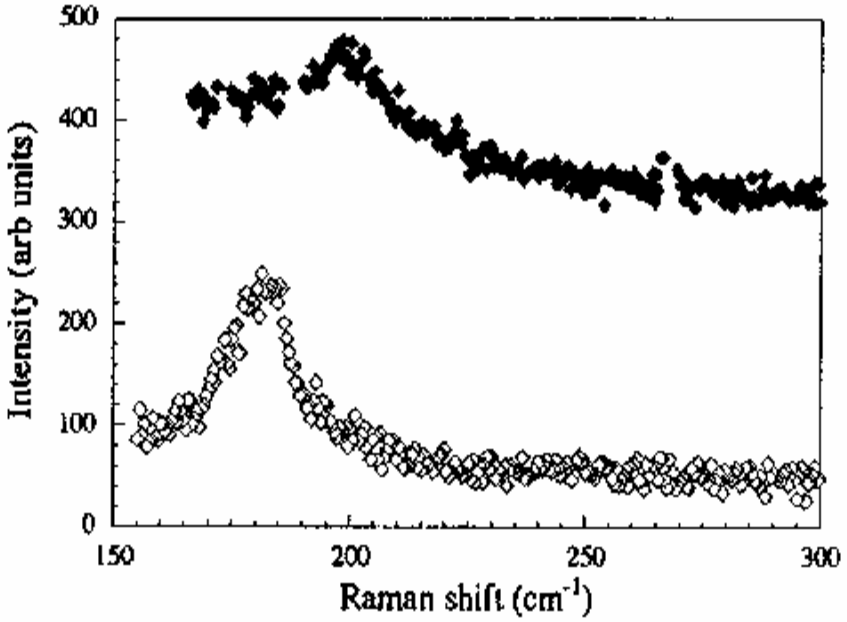
  How different the small is?

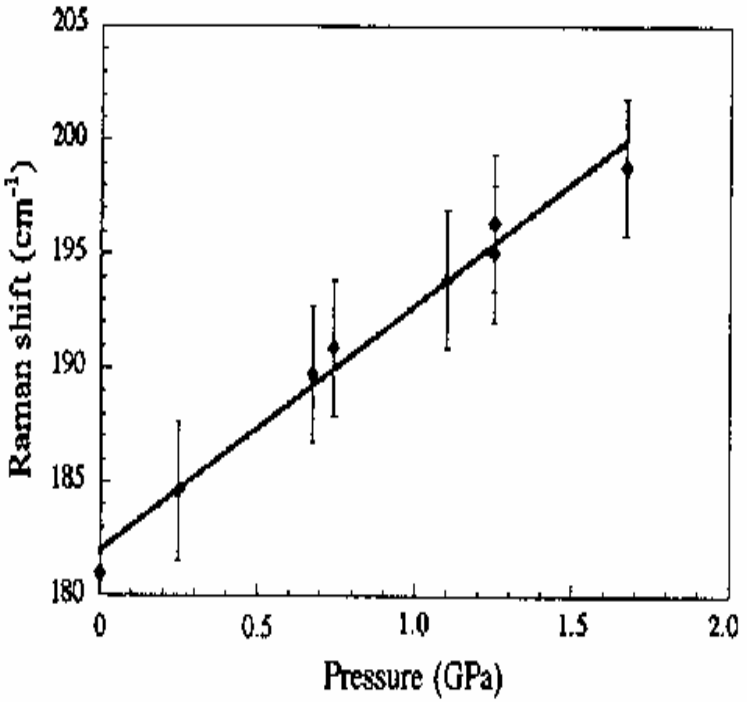
- Helping to understand the micro-mechanism of bulk material

Carbon Nano-tube under the pressure:

Exp. Observation

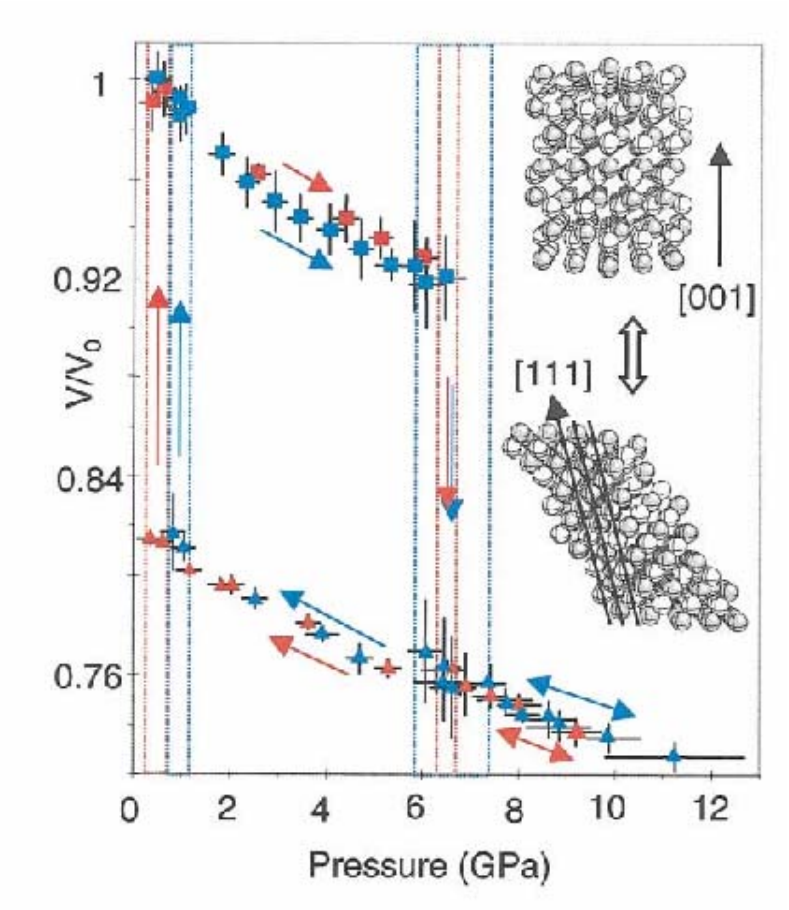
Breathing mode disappeared at P=1.7 GPa

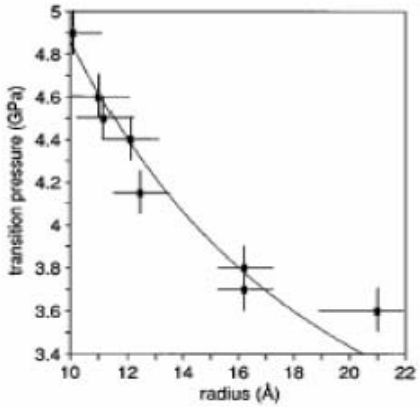




Peters et al. PRB, 61(5939)

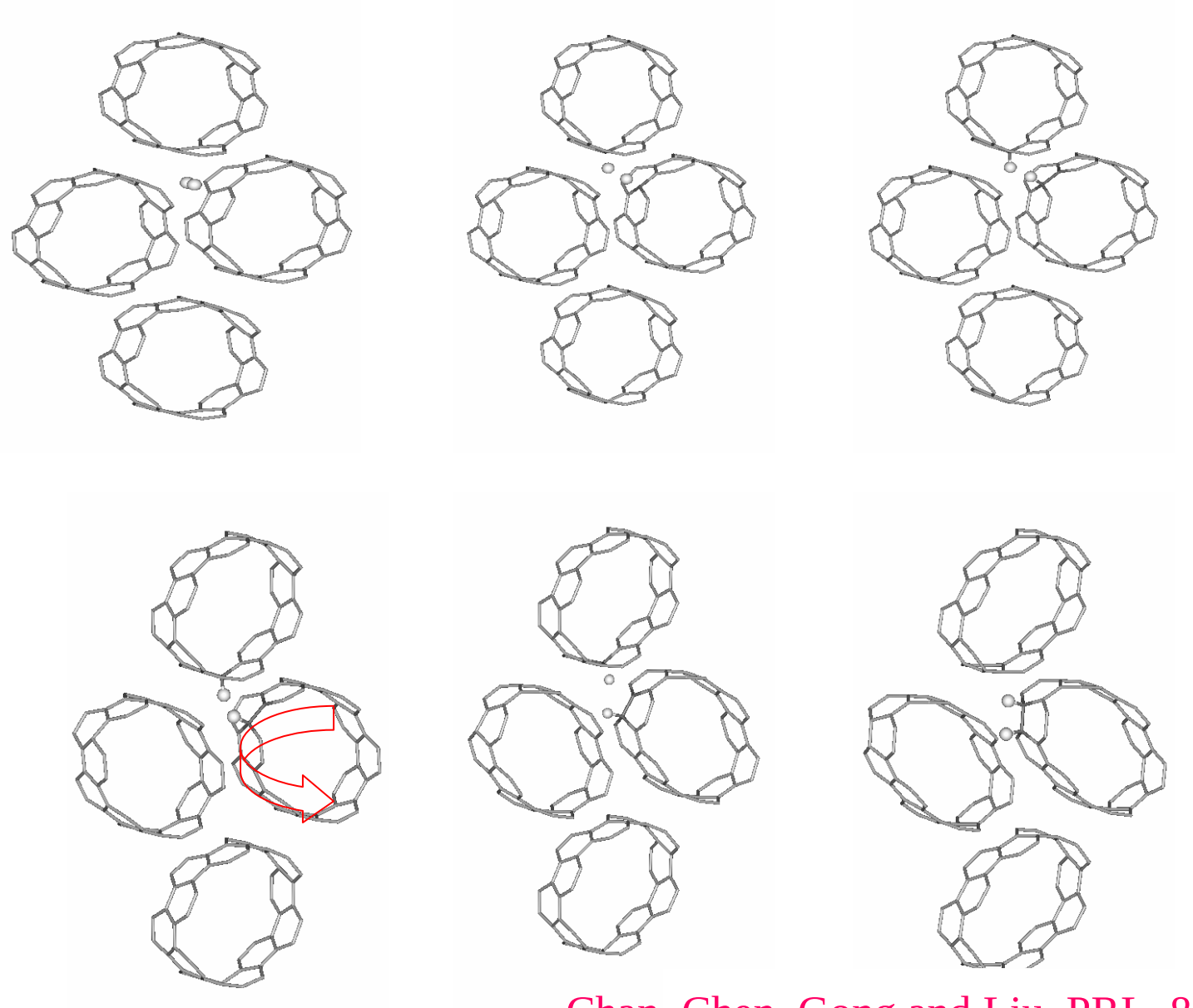
Structural transformation of CdSe





Wurtzite to rock salt transformation pressure vs. size of CdSe nanocrystals (Alivisatos group).

Pressure induced H_2 dissociation in tube bundles:



Chan, Chen, Gong and Liu, PRL, 8720(2001)

- **Conventional constant-pressure MD:**

Parrinello-Rahman

$$H = \sum_{i}^{N} \frac{1}{2} m_i \dot{\vec{R}}_i^2 + \Phi(\{\vec{R}_i\}) + \frac{1}{2}\mu\dot{\Omega}^2 + P\Omega$$

Where volume: $\Omega = \vec{a} \times \vec{b} \cdot \vec{c}$

Finite system without any periodicity:???

We propose:

JPCM 14, L487(2002)

$$L = \sum_{i}^{N} \frac{1}{2} m_i \dot{\vec{R}}_i^2 - \Phi(\{\vec{R}_i\}) - P_{ext}\Omega(\{\vec{R}_i\})$$

Where volume is the whole volume of the finite system.

If we write the volume of the system into in following form

$$\Omega = \Omega(R_{ij}^3)$$

One can easily prove that:

$$P_{ext} = P_{\text{int}} = \frac{1}{3\Omega}\left(\sum_{i}^{N} m_i \dot{\vec{R}}_i^2 - \sum_{i}^{N} \vec{R}_i \cdot \nabla\Phi\right)$$

Motion of Equations:

$$\frac{d^2 R_i}{dt^2} = -\nabla_i \Phi - P_{ext} \nabla_i \Omega$$

Main Features:

Computation overhead is small!
Parameter free!
Easy to code, either in DFT based code or MD!

How to calculate volume of a finite system:

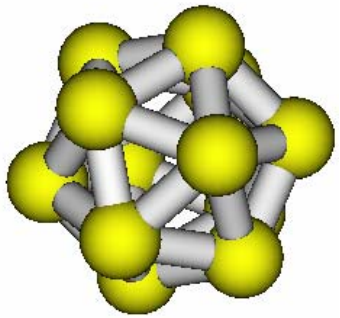
$$\sum_{i}^{N} \vec{R}_i \cdot \nabla \Omega = 3\Omega \qquad \Omega = \Omega(R_{ij}^3)$$

A simplest scheme: atomic sphere to approximate WS cell (not too bad for the metal system)

$$\Omega = \sum_i \gamma_i \frac{4\pi}{3} \sum_{j \neq i} \left(\frac{r_{ij}}{2}\right)^3$$

γ_i constant,
r_{ij} interatomic distance

A good approximation: the volume of the polyhedron



Recent Progress by M. Cococcioni et al. : PRL(2005)

The volume is defined from the charge density:

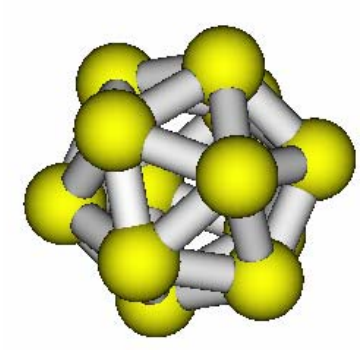
$$V_q = \int d\mathbf{r}\,\vartheta(\rho(\mathbf{r}) - \alpha),$$

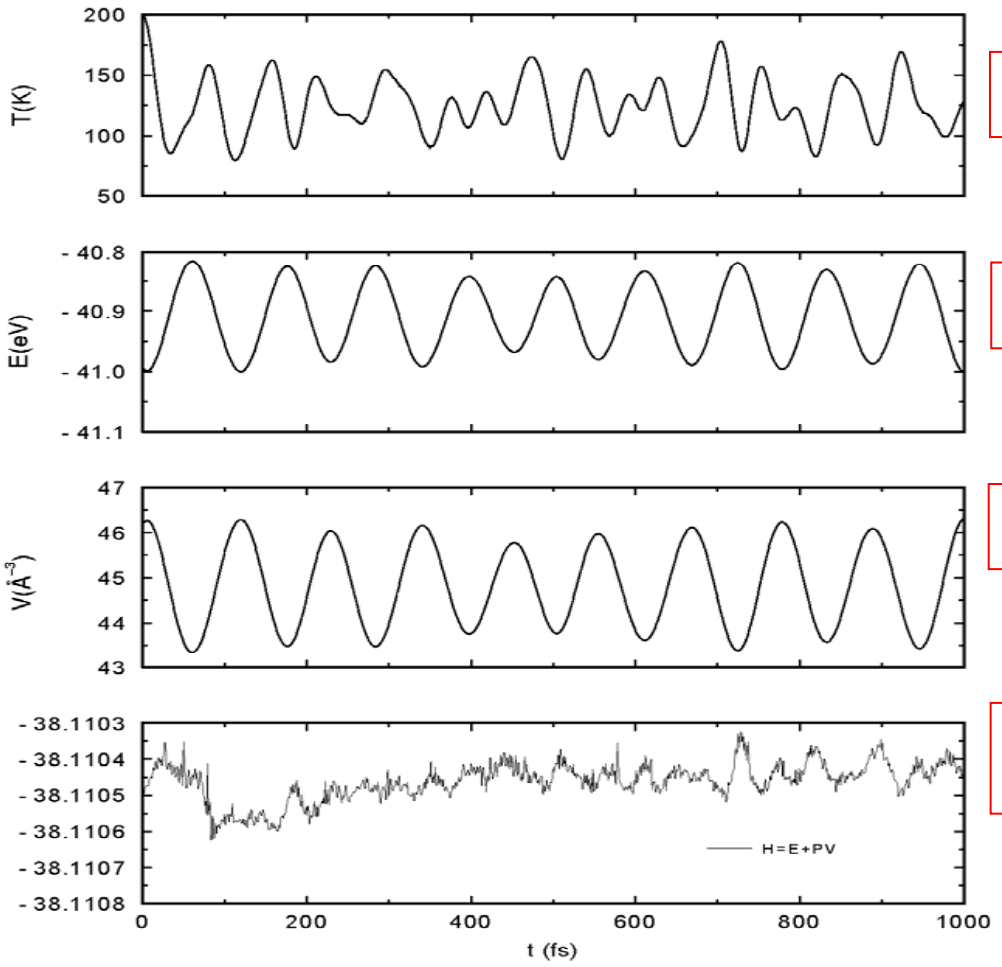
If the step function is approximated by a gaussian:

$$\Phi_V(\mathbf{r}) = P\frac{\delta V_q}{\delta\rho}\Big|_{\rho=\rho(\mathbf{r})} = \frac{P}{\sigma\sqrt{2\pi}}e^{-(\rho(\mathbf{r})-\alpha)/2\sigma^2}.$$

Constant Pressure in Ab-initio MD

Al_{13} cluster at 10 GPa





Constant Temperature

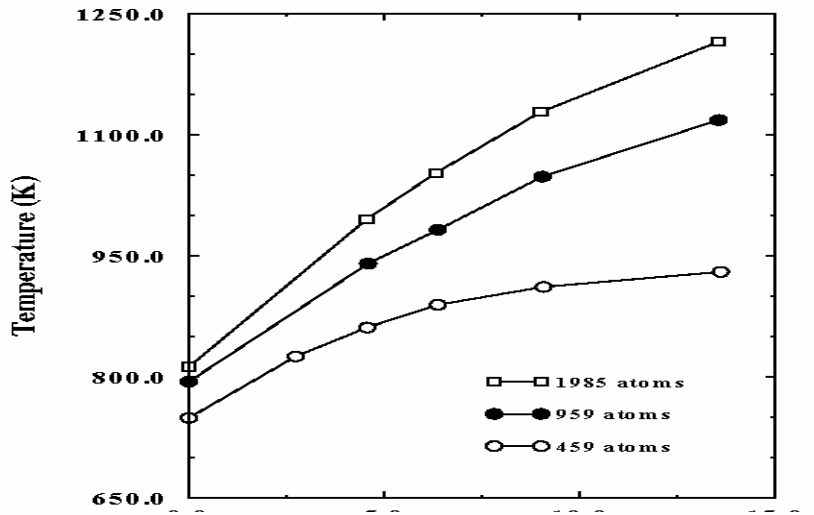
Total energy fluctuation

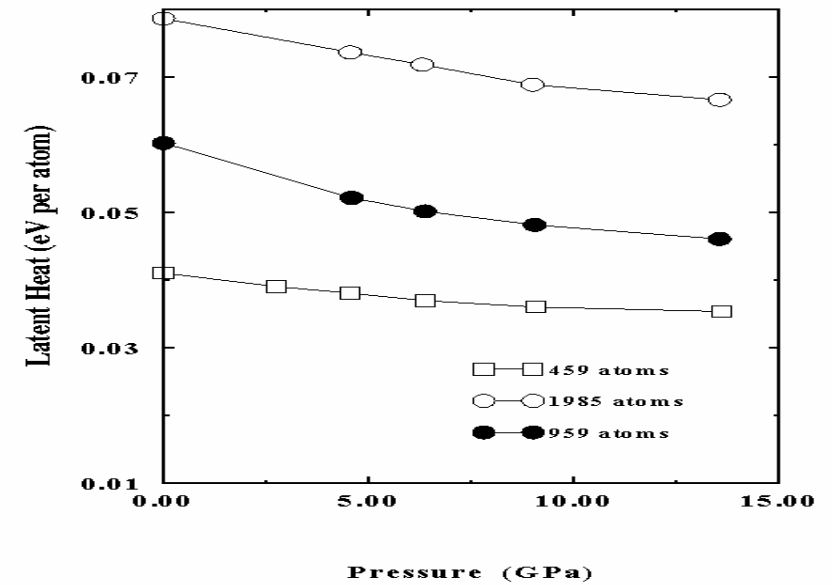
Volume fluctuation

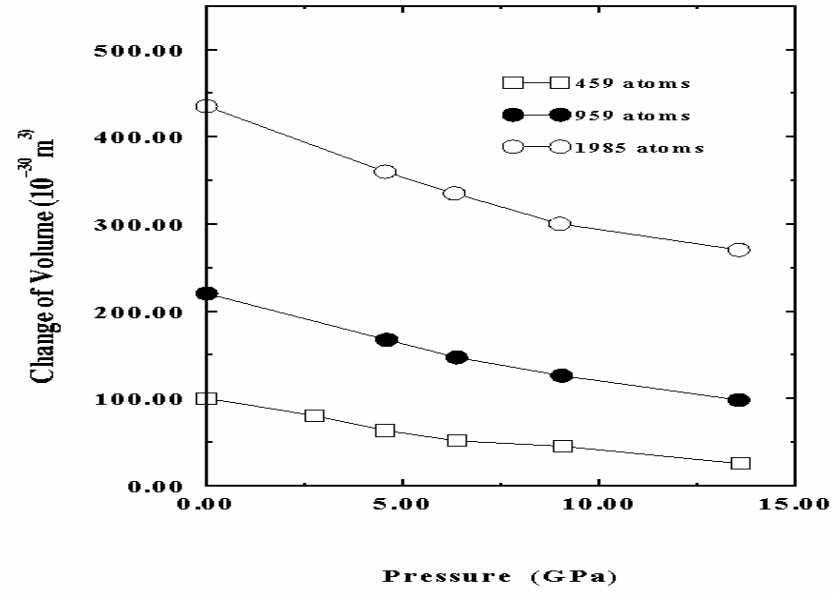
Constant Enthalpy

Melting of small Ni particles under pressure:

(classical MD with Sutten-Chen potentials)





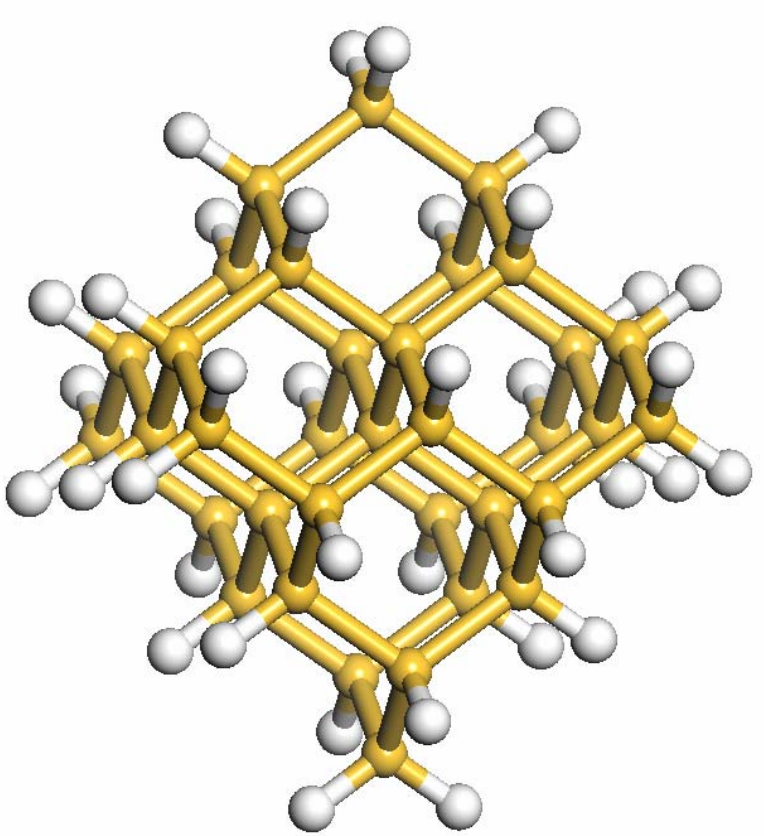


$$\frac{dp}{dT} = \frac{l}{T(V_2 - V_1)}$$

Ni particles: Small is the same!

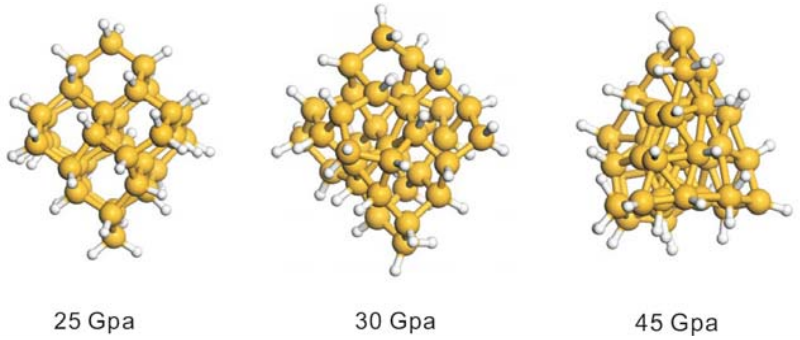
Si cluster under pressure

- Si_{35} saturated with 36 hydrogen atoms
  - Si_{35} structure is cut from bulk silicon.
  - Constant pressure is exposed on Si atoms.



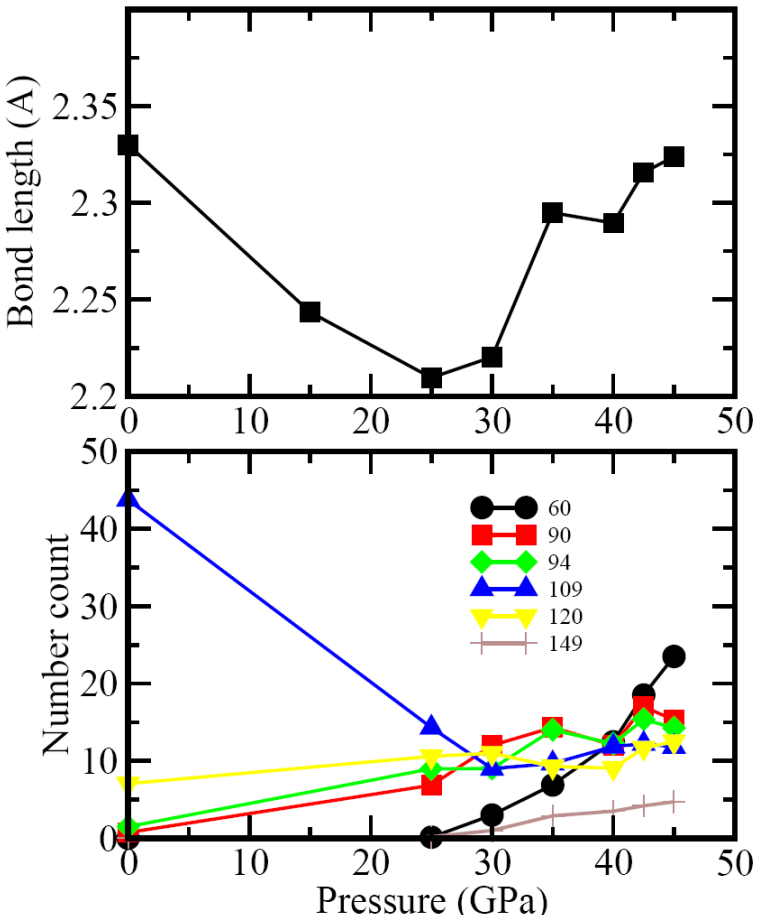
Si_{35} cluster under pressure

Structure changes at 30 GPa



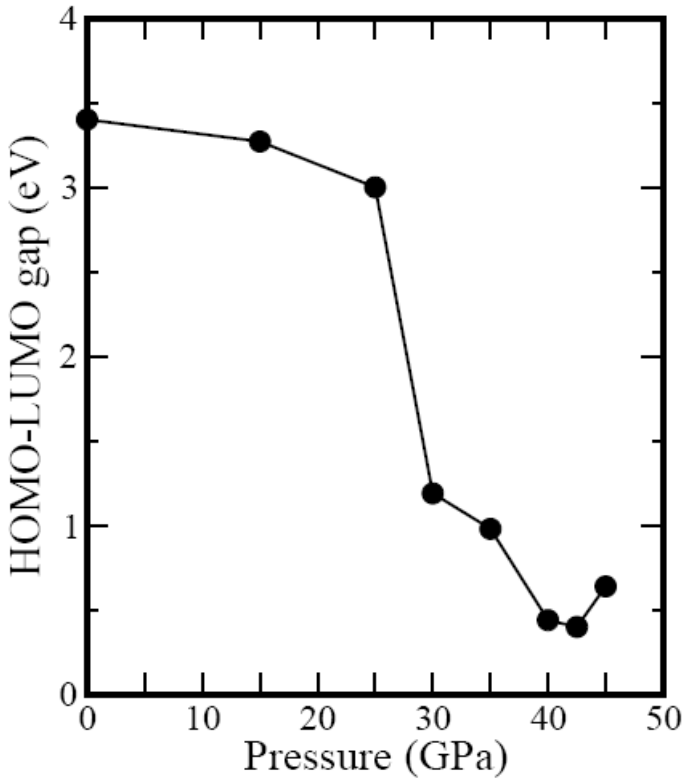
Bond length and angle

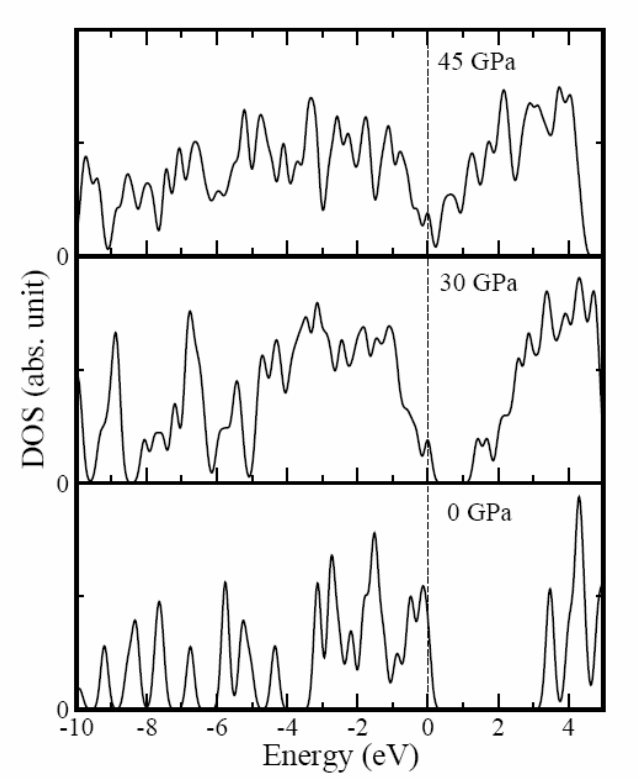
- Bond length increase beyond P_c
- 60 degree angle which refers to hexagonal structure appears.



Si_{35} cluster under pressure

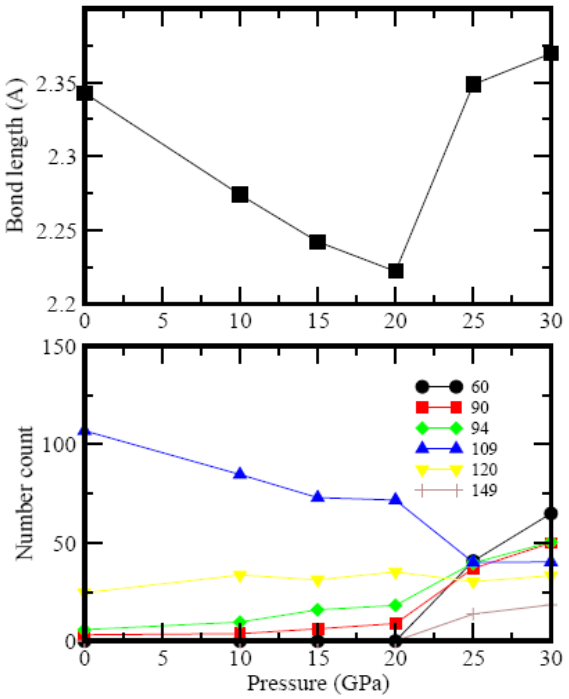
- Metallization driven by pressure
  —HOMO-LUMO gap decreases

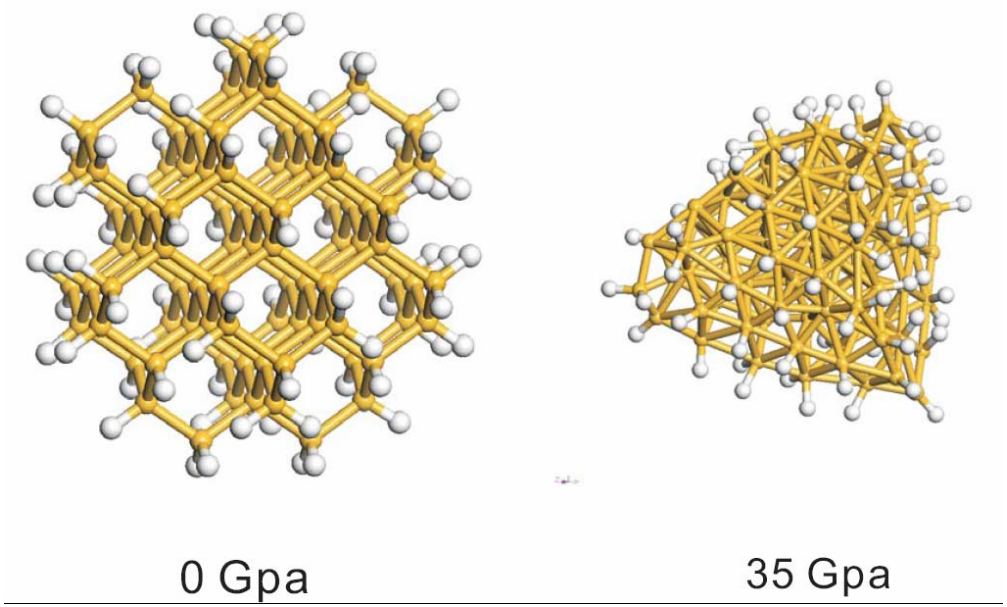




Si_{87} cluster under pressure

Si_{87} has a lower P_c



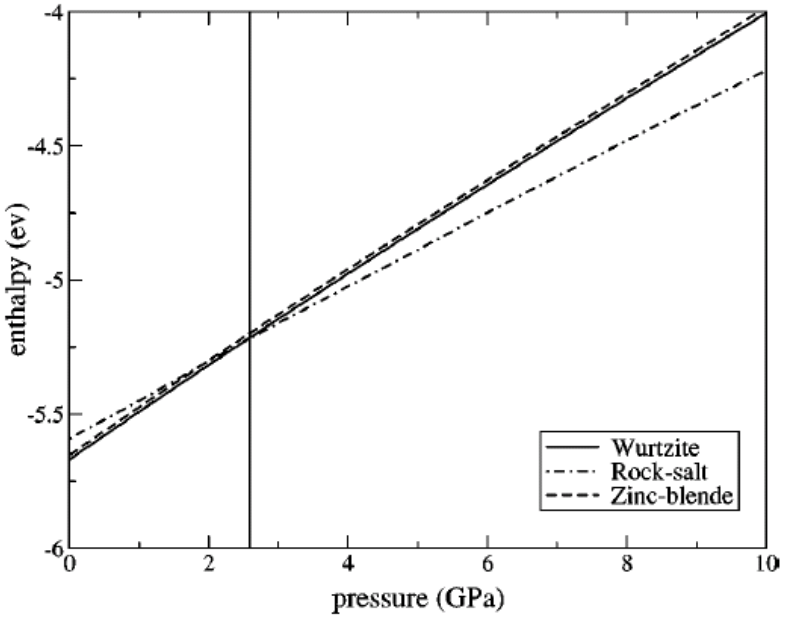


Pressure Induced Structure transformation of large CdSe particles

Classical Potential:

$$V_{ij} = \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij}\left\{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right\}$$

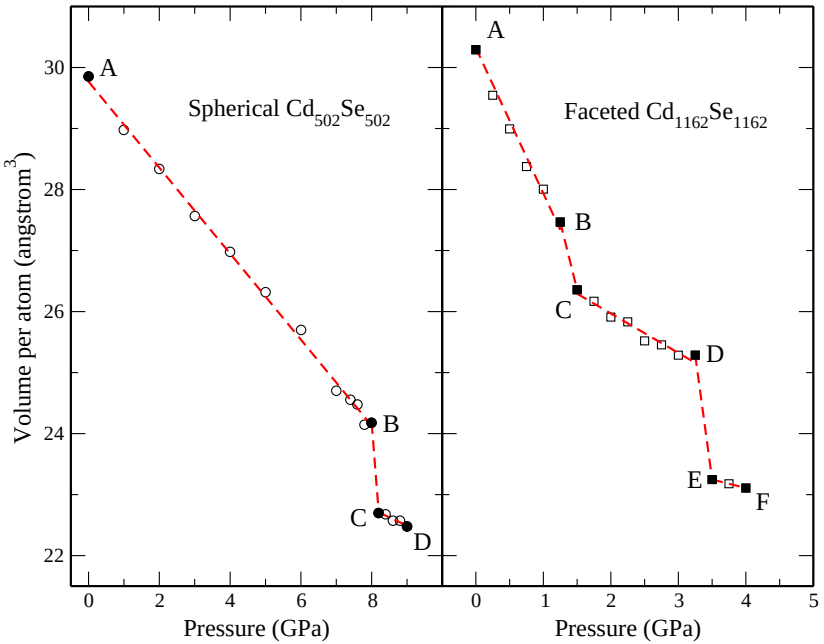
	q	σ (Å)	ϵ (K)
Cd	1.18	1.98	16.8
Se	−1.18	5.24	14.9

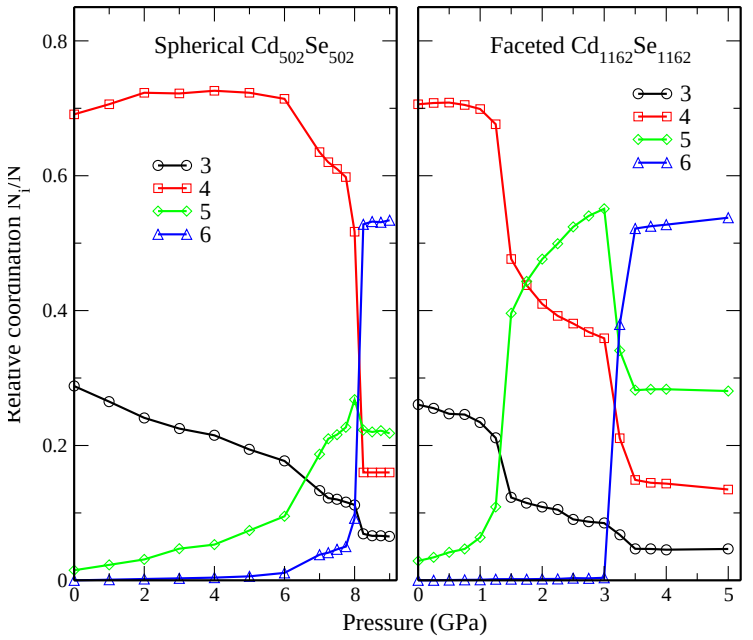


The two-body potential consists of long-range Coulomb part and a short-range part. The phase transformation of bulk CdSe from wurtzite structure to rocksalt structure occurs at about **2.5** GPa, in agreement with experimental measurements.

E. Rabani, J. Chem. Phys. **116**, 258 (2002)

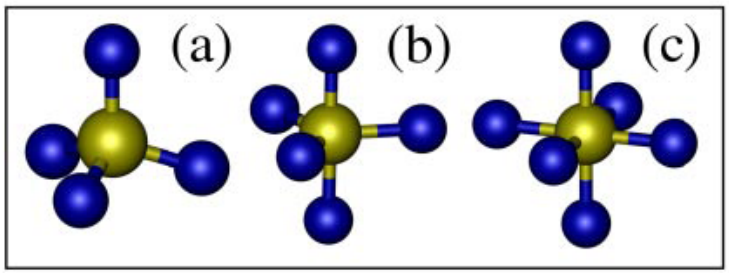
Transformation path



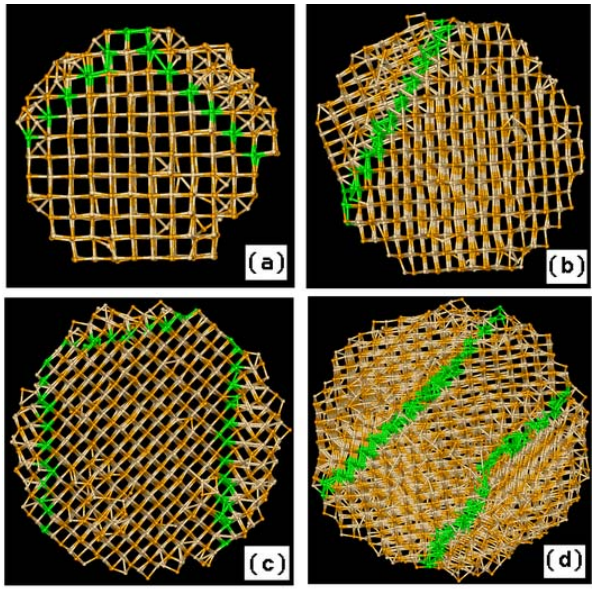


Spherical: Wurtzite → Rocksalt

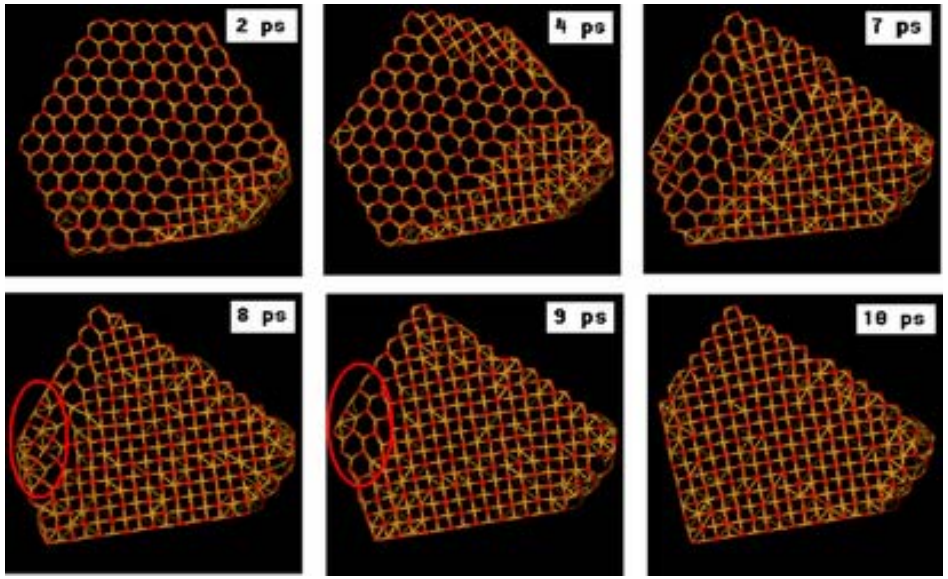
Faceted: Wurtzite → h-MgO(five coordinated) → Rocksalt



Domains after transformation

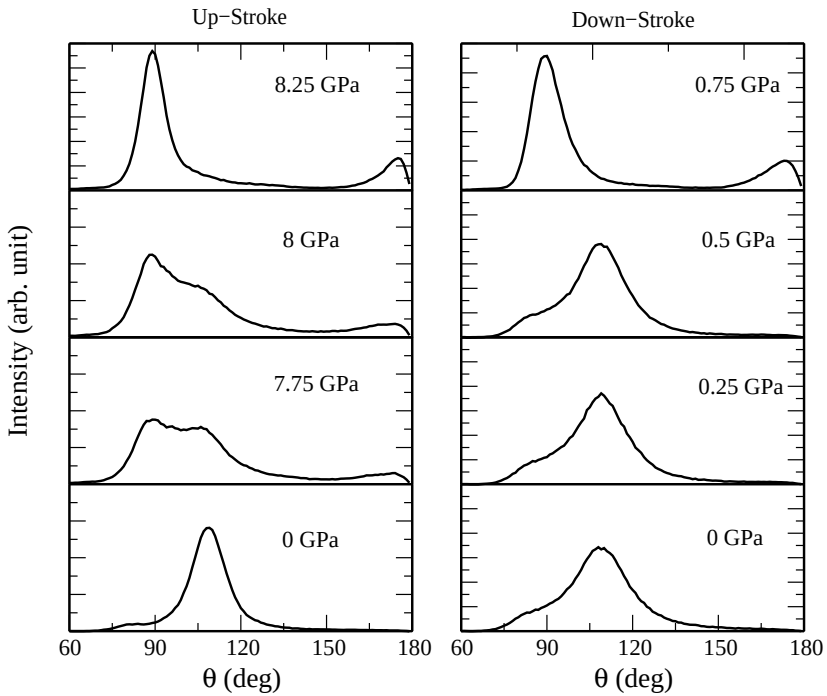


Strain domains after the structural transformation in spherical nanocrystals. The grain boundary is show as green atoms



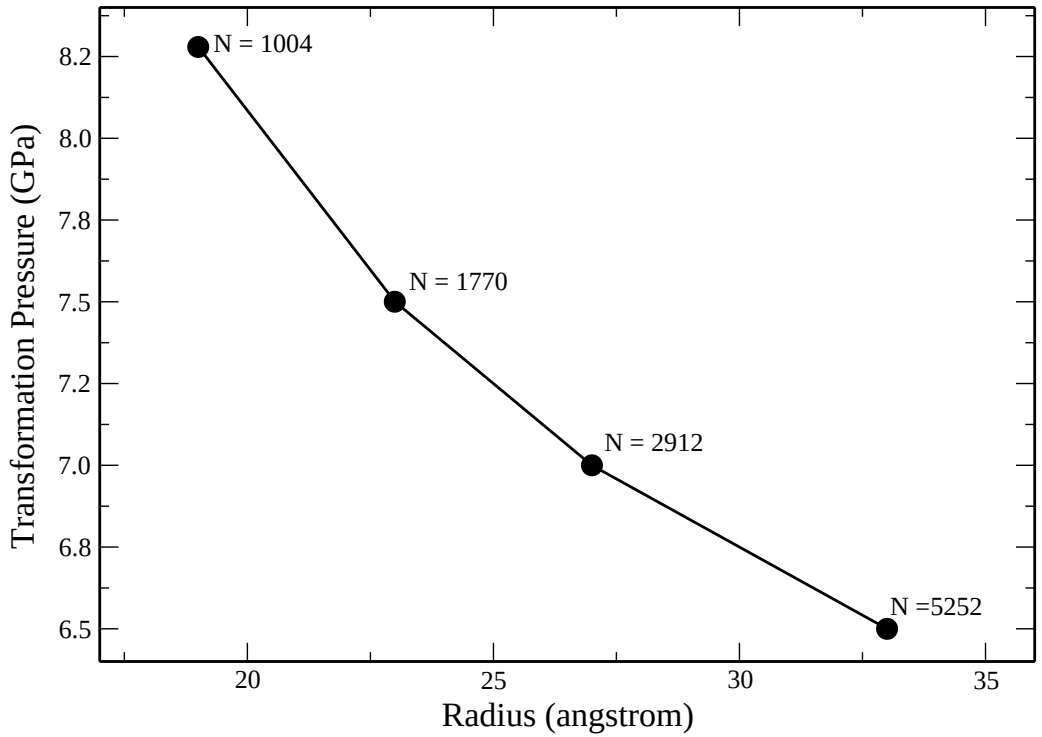
The snapshots of the MD simulation for the faceted $Cd_{1162}Se_{1162}$ nanocrystal transforming from five-fold coordination structure to rocksalt structure.

The hysteresis behavior

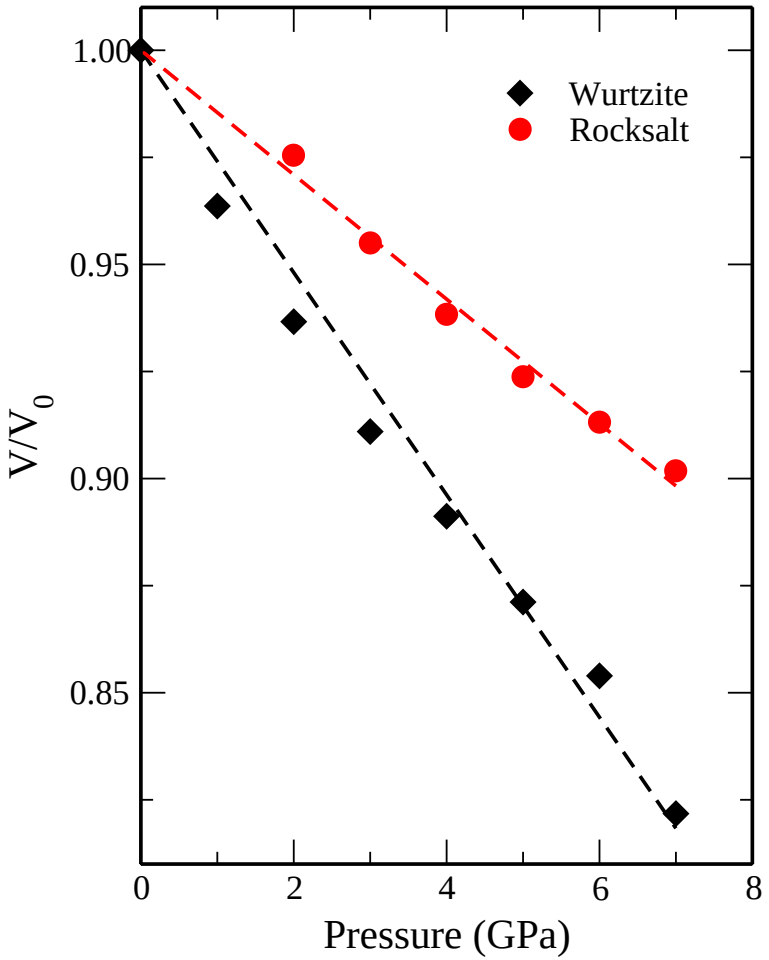


Averaged bond angle distribution of spherical $Cd_{502}Se_{502}$ nanocrystals.

Size effect on the transformation pressure



Variation of the transformation pressure with radius for nanocrystals at 300 K. With increasing nanocrystal size, the transformation pressure approaches the bulk value from above.



Volume as a functions of external pressure for spherical $Cd_{502}Se_{502}$ nanocrystal. The data can be fit with a linear volume compressibility of B_0 = **38.5** GPa for wurtzite and B_0 = **68.8** GPa for rocksalt

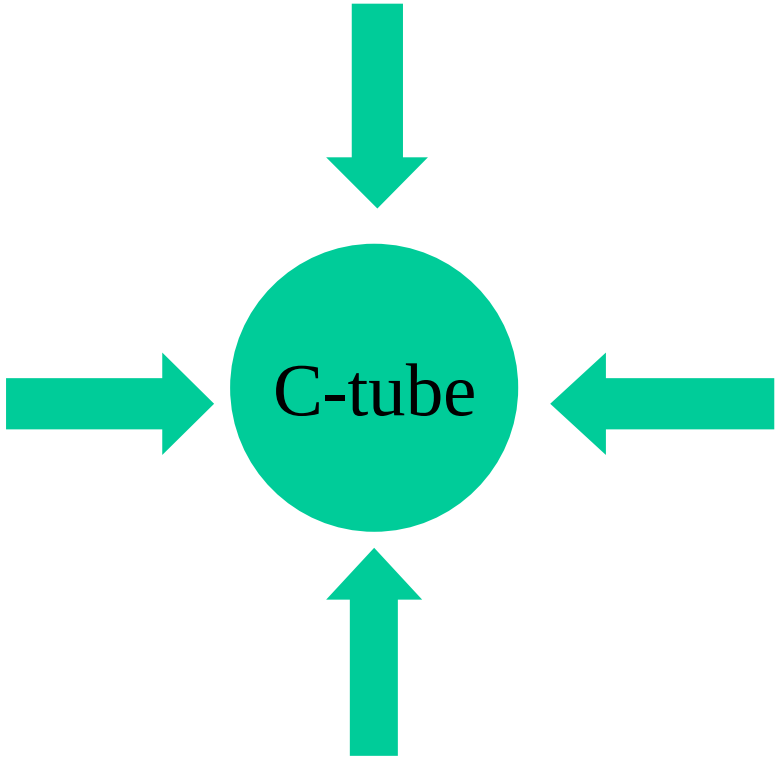
Bulk modulus

Physical constants	Wurtzite	Rock salt
B_0 (GPa)	37±5	74±2
B_0'	11±3	
V_0 (m^3)	5.62×10^{-29}	4.36×10^{-29}
c_1 (N/m)	0.34	0.63
c_2 (N/m) (Å^2)	84	83

Radius 21 angstrom

S. H. Tolbert and A. P. Alivisatos,
J. Chem. Phys. **102**, 4642 (1995).

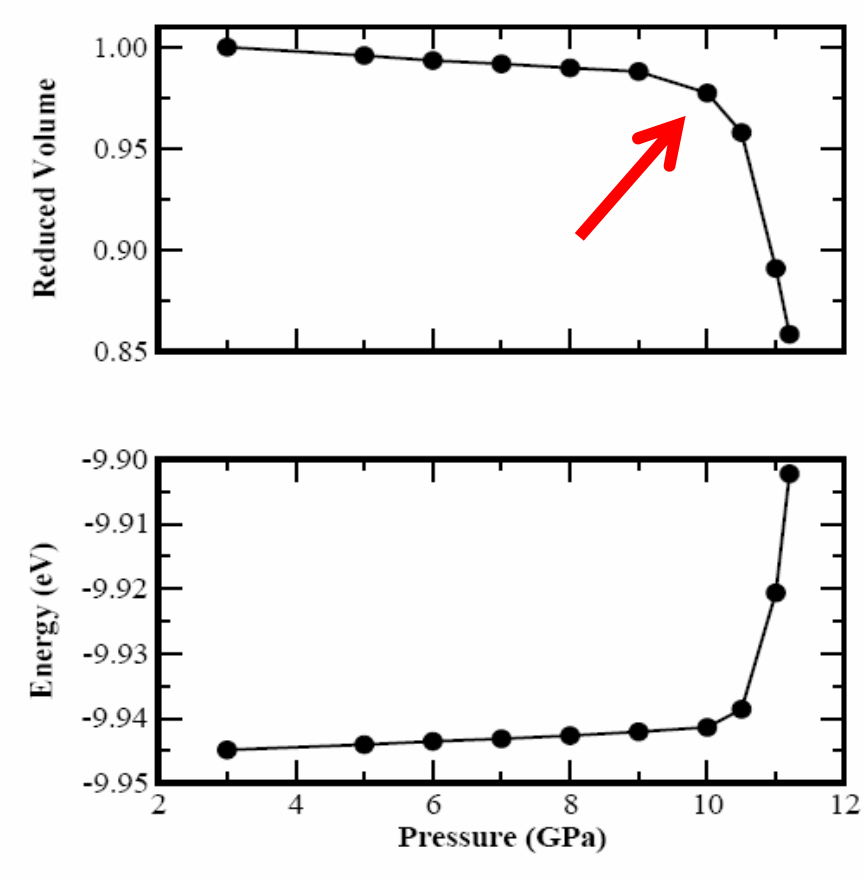
Schematic show of carbon tube under hydrostatic pressure

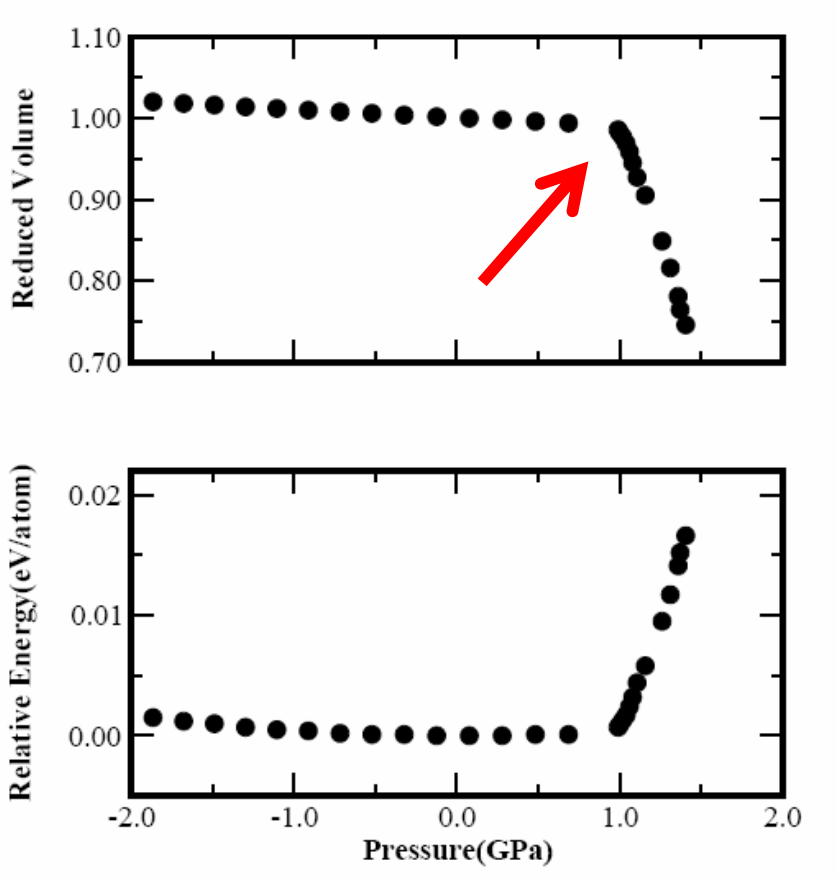


Periodic boundary condition in axial direction

PRB70, 165417(2004)

Pressure Induced hard-soft transition in CNTBs

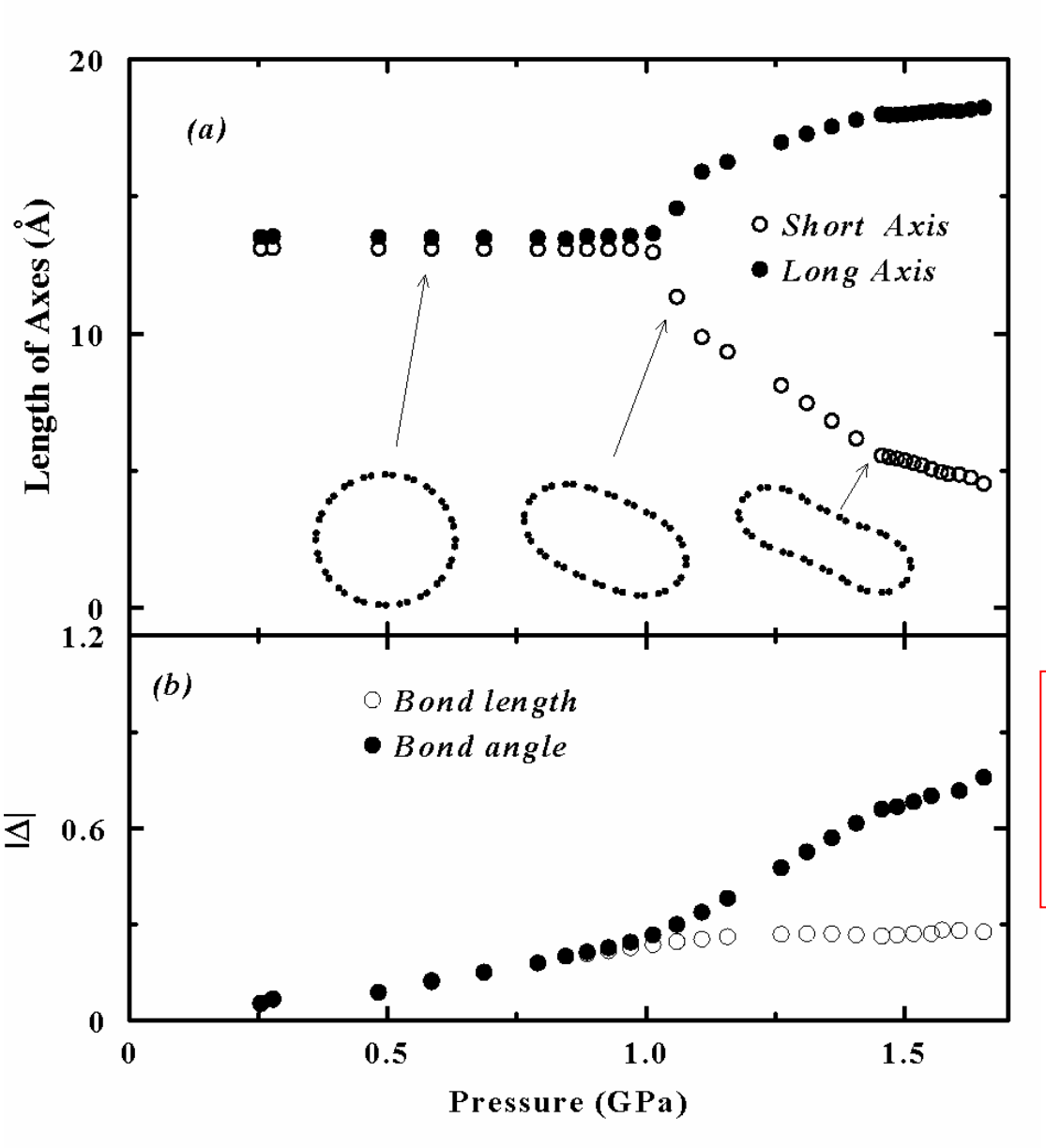




Ab-initio MD, (6, 6)

MD, (10,10)

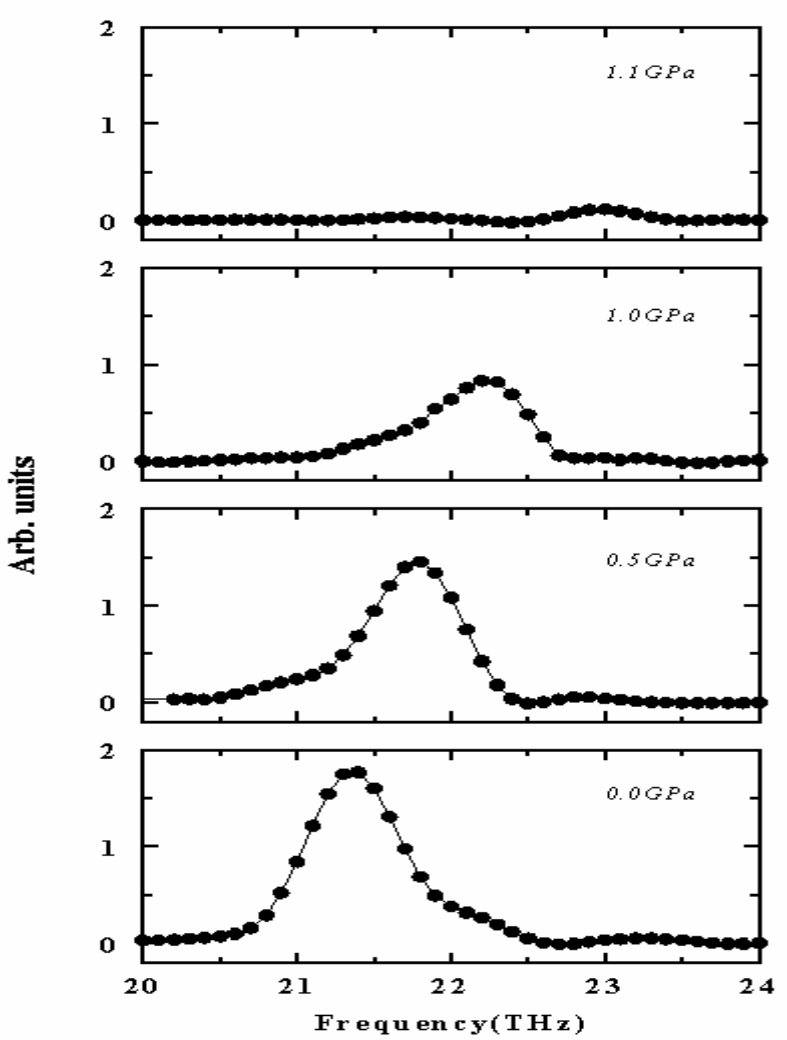
Shape Changes under pressure

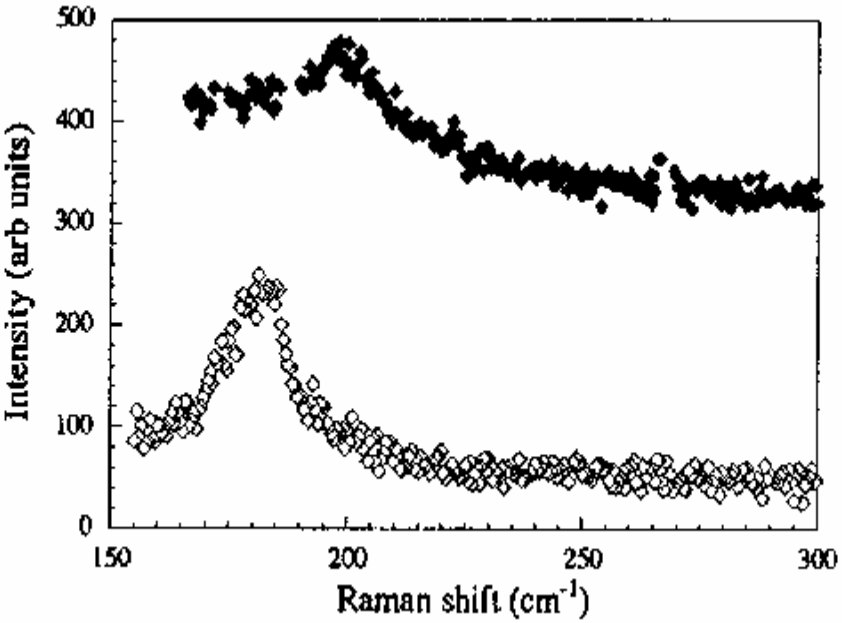


Shape change with hard-soft transition

Bond angle responsible to the pressure after the change

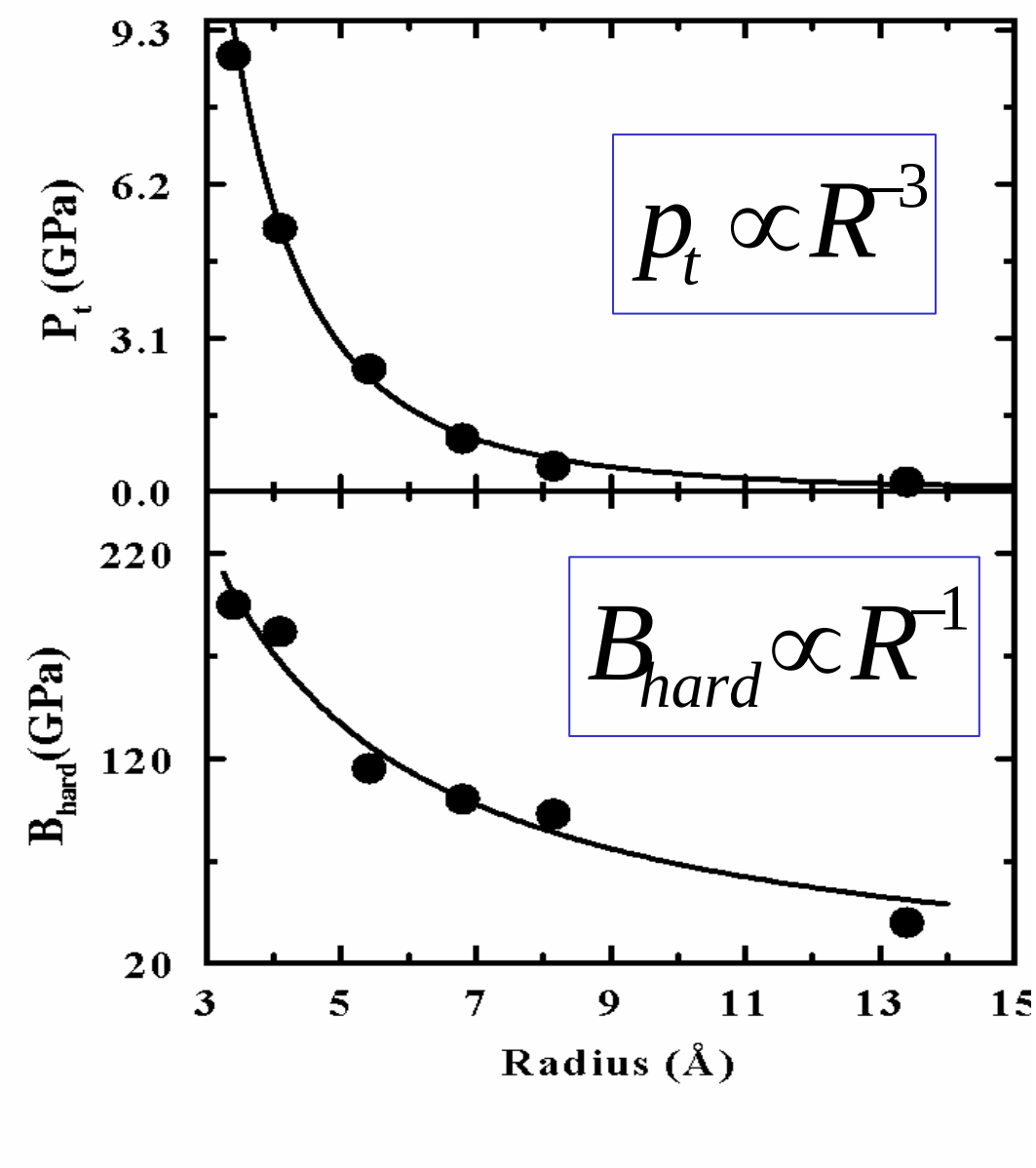
Softening the breath mode of the Carbon tube:





Peters et al. PRB, 61(5939)

Size dependence of transition pressure



Elastic model for tube under pressure:

- Elastic energy of the tube per unit length:

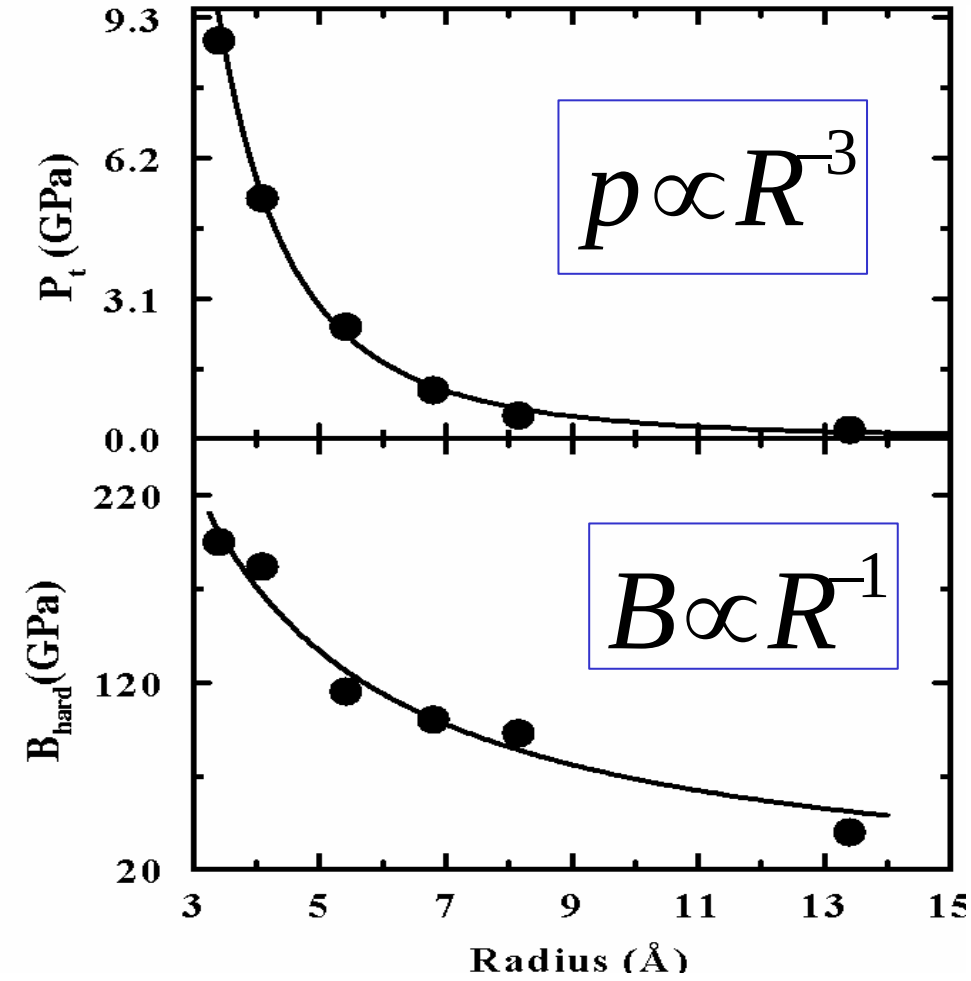
$$E = \frac{D}{2}\oint \frac{1}{\rho^2} dl + \frac{C}{2}\oint \left(\frac{\oint dl - L_0}{L_0}\right)^2 dl + PA,$$

where $D = Yh^3/12(1-\nu^2)$ and $C = Yh/(1-\nu^2)$

Y: Youngs modulus
ν: Poisson ratio
h: thickness of tube
A: area of tube cross section
L_0: perimeter of thue cross section

Size dependence of transition pressure and bulk modulus: Simulation and modeling

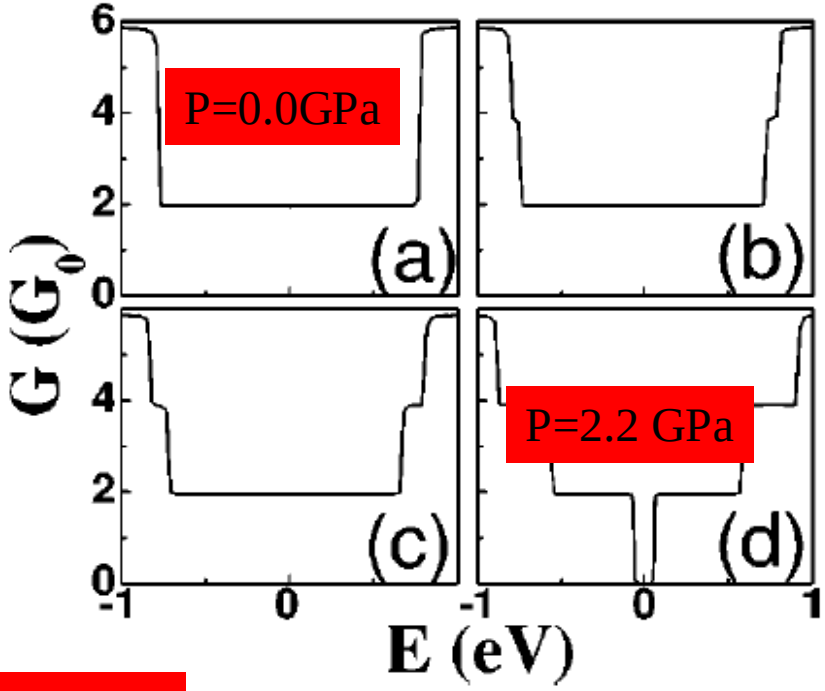
$$P_t = \frac{3D}{R_0^3(1+\epsilon_c)^3} \approx \frac{3D}{R_0^3}, \qquad B_h = \frac{C}{2R_0}.$$



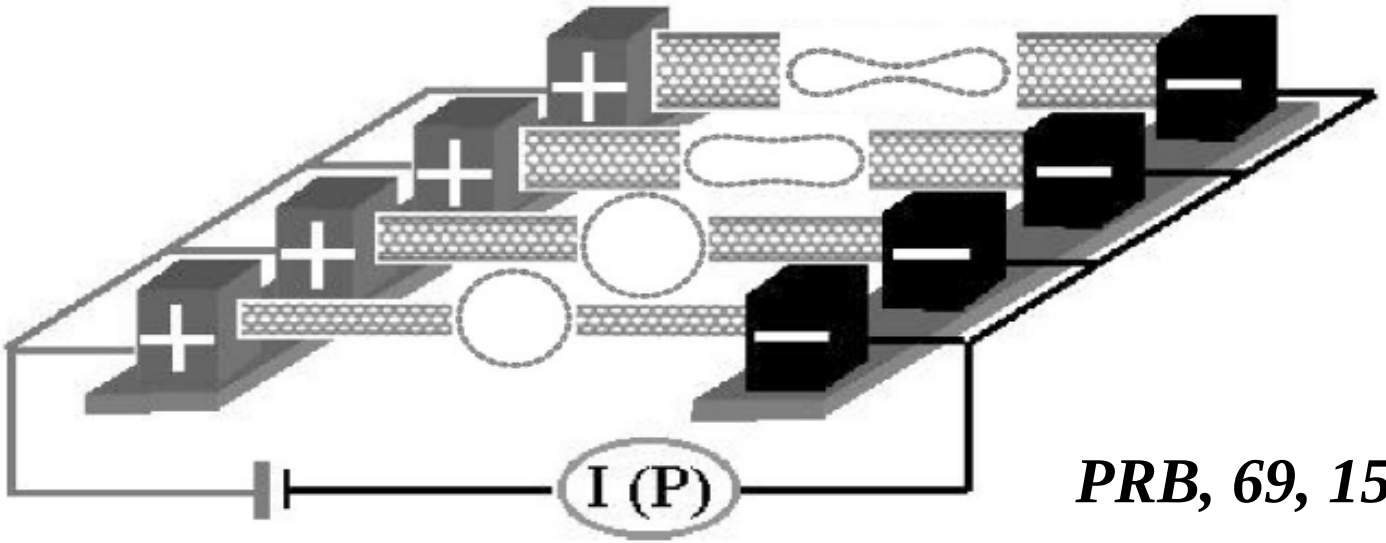
$D = 0.76eV$

In agreement with available data

Conductivity of CNT Under Pressure:

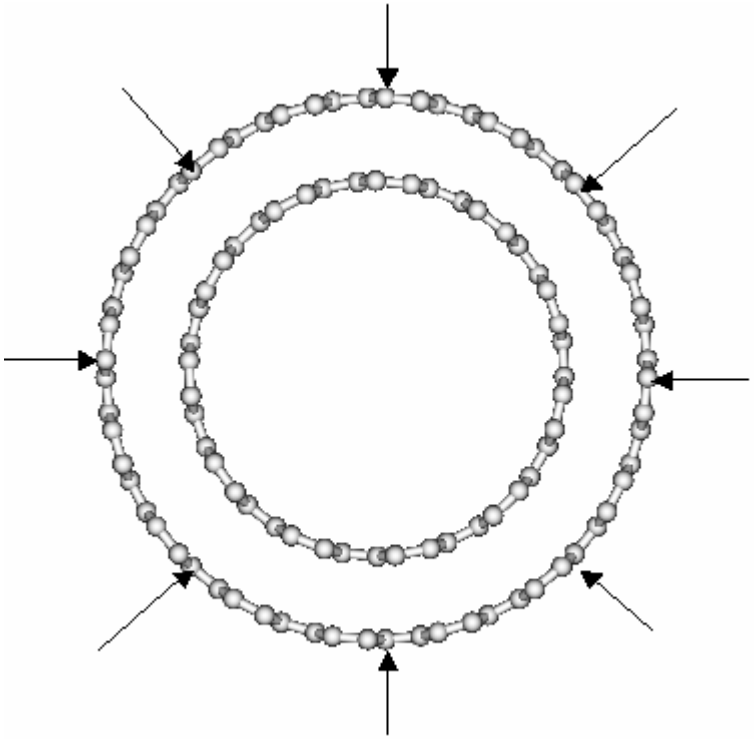


Conceptional Pressure Sensor:



PRB, 69, 153406

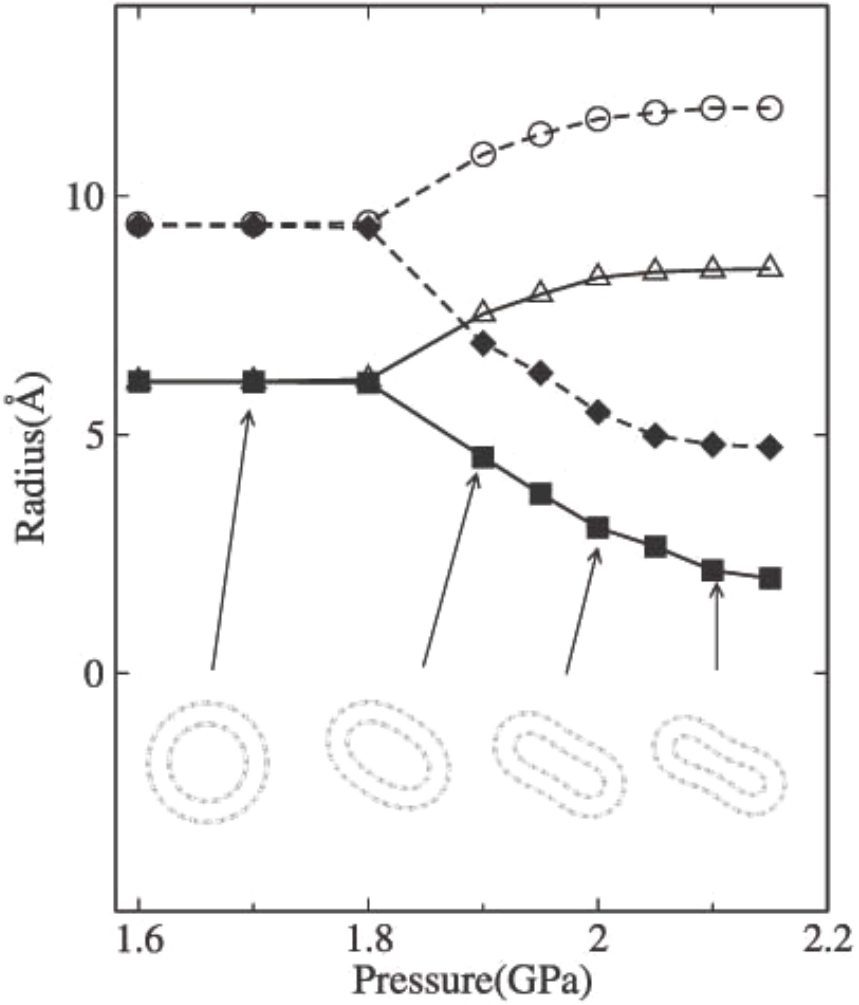
Double Wall Carbon nano-tube Under Pressure:



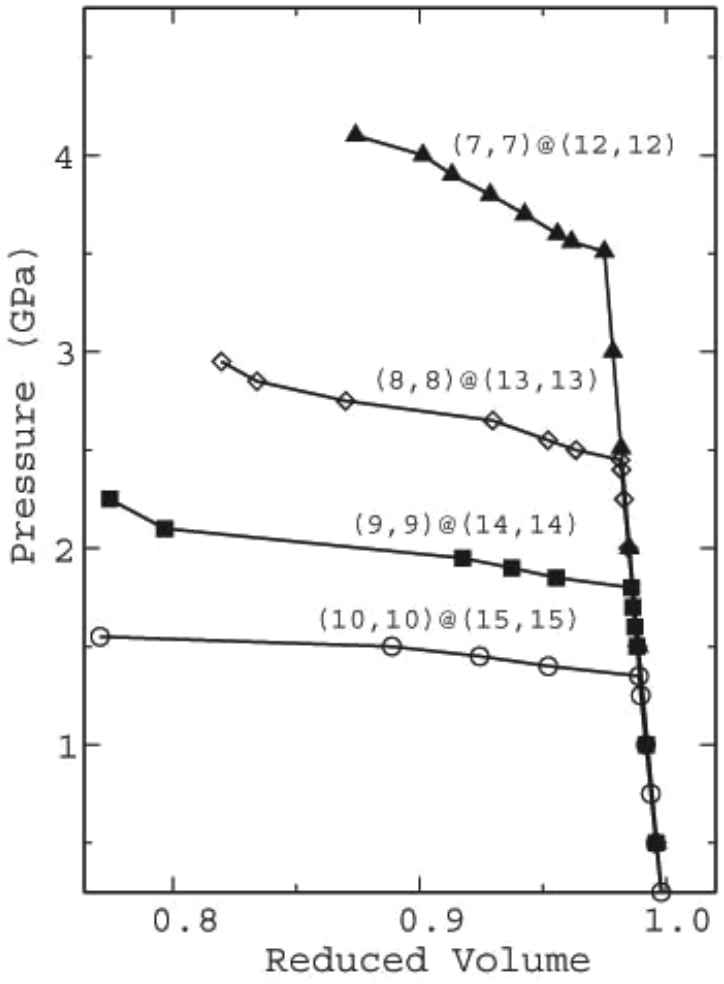
outer tube: uniform pressure

inner tube: response to the VdW potential

YE et al. PRB72, 035454(2005)

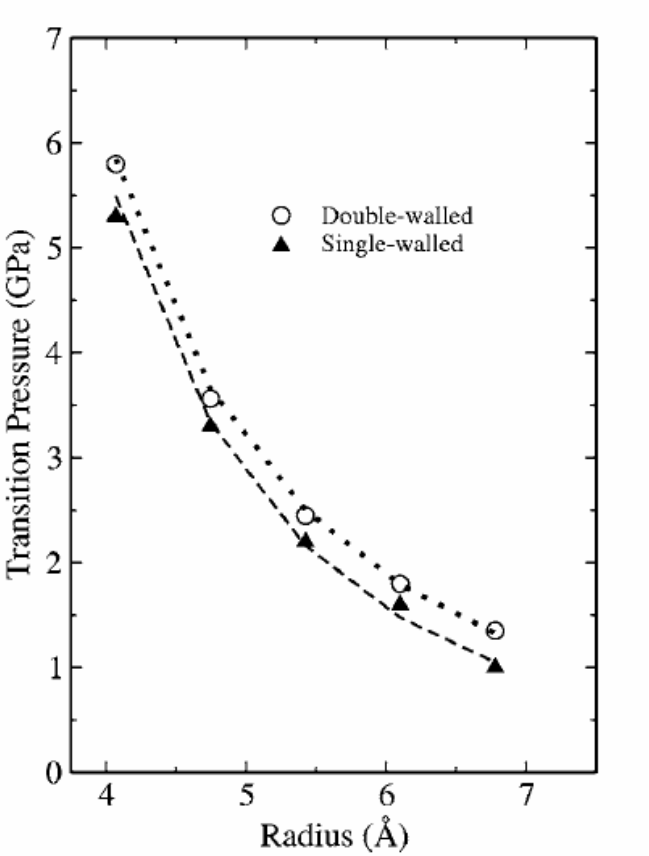


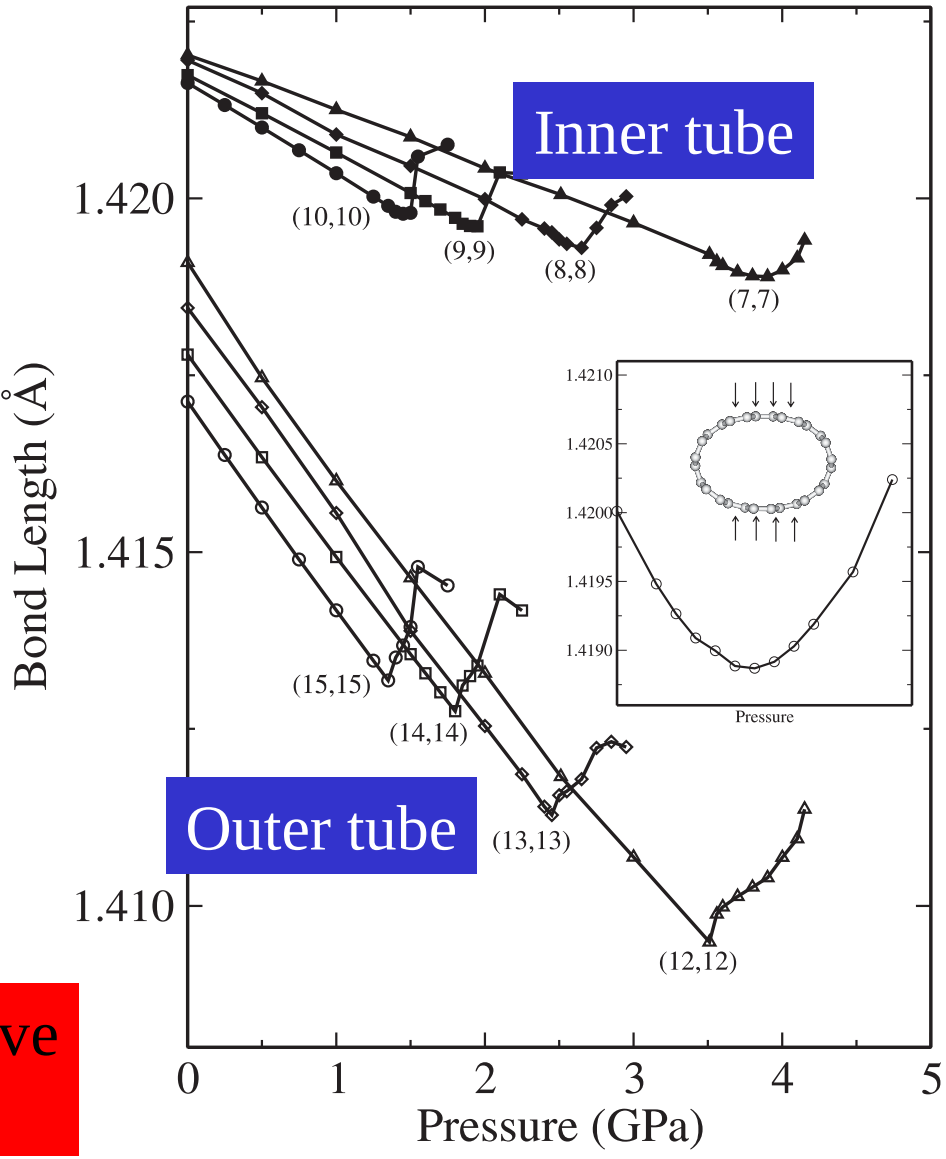
The long radius, short radius of tube as a function of pressure for (9,9)@(14,14) nanotube. At the same pressure, outertube and innertube collapse from circle to oval



Pressure as a function of the reduced volume for DWCNTs at 300 K. The discontinuity of the slopes indicates hard-soft transition under hydrostatic pressure

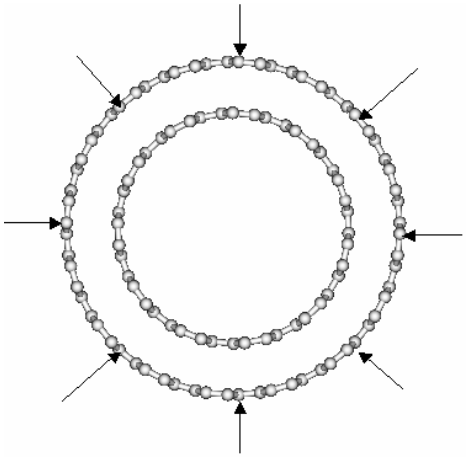
Transition pressure for Double-walled tubes

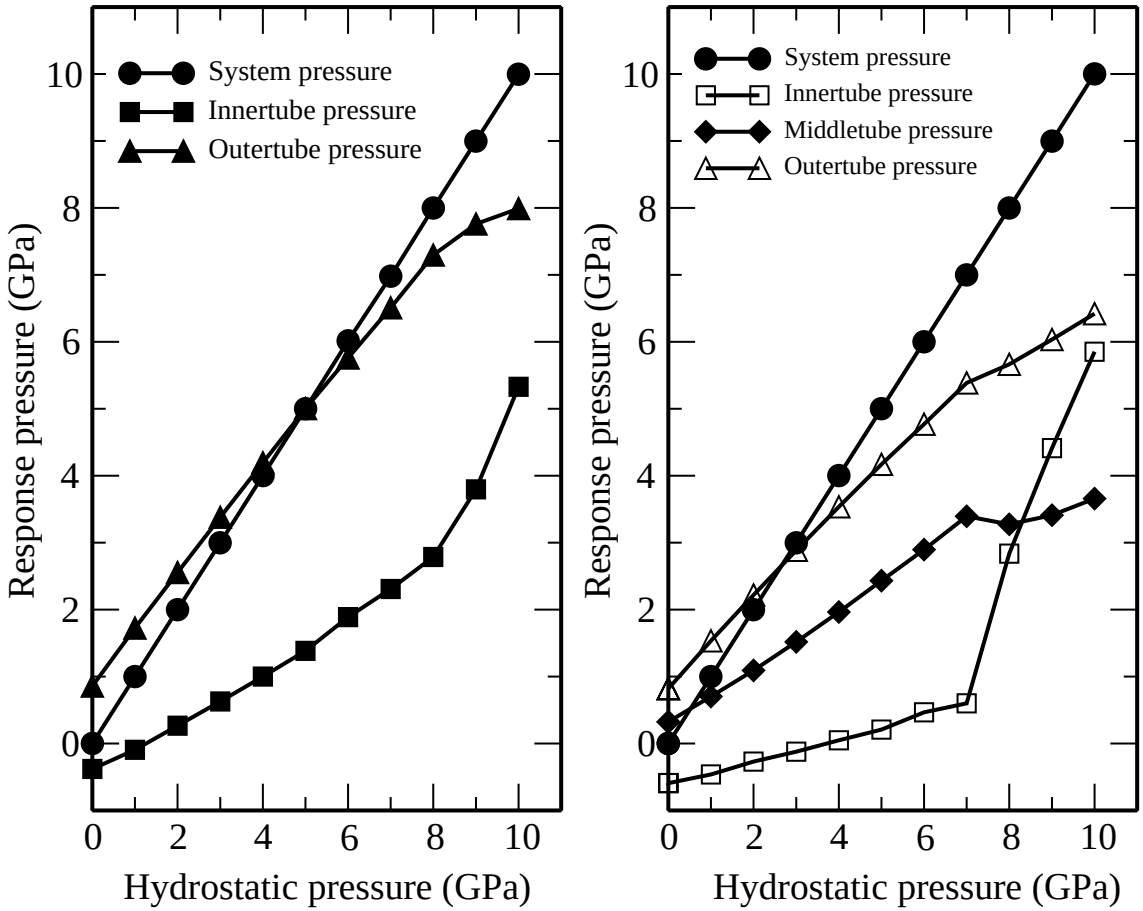




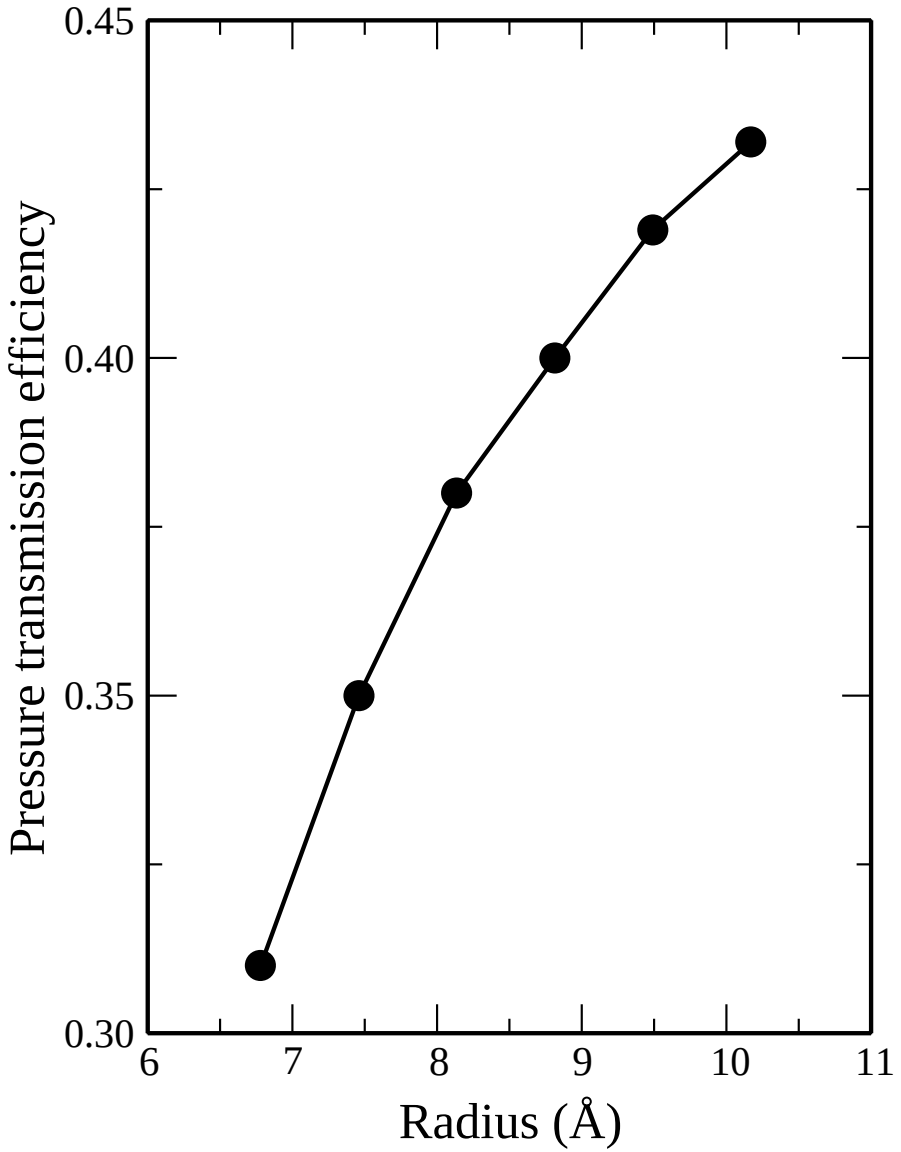
Inner and outer tuber have different behavior

Pressure transfer Efficiency from outer Inner tuber





Response pressure as a function of the external hydrostatic pressure for (5,5)@(10,10) DWCNT(left) and (5,5)@(10,10)@(15,15) TWCNT(right). The fitted relation of leftpanel relation is y=0.31x-0.36, we define x as the pressure transmission efficiency

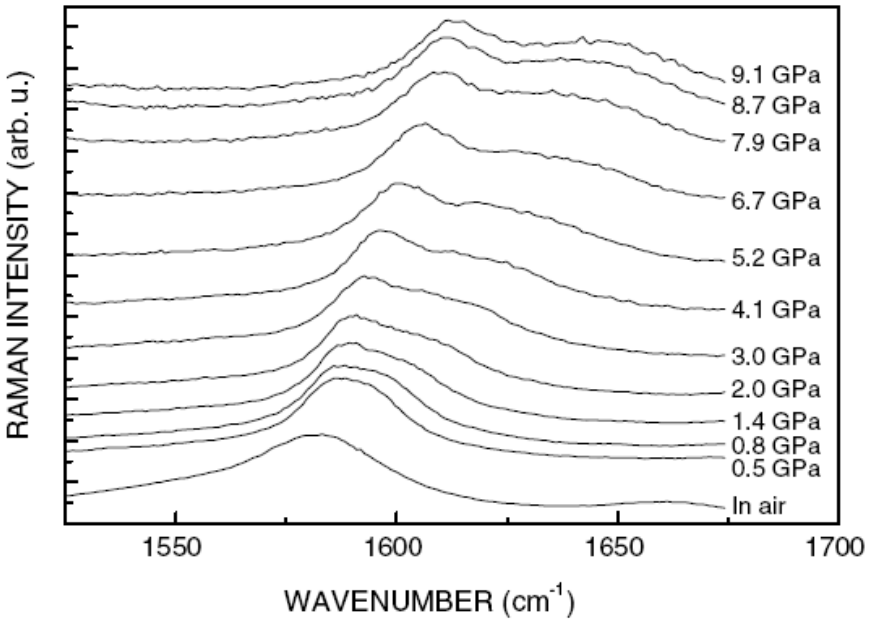


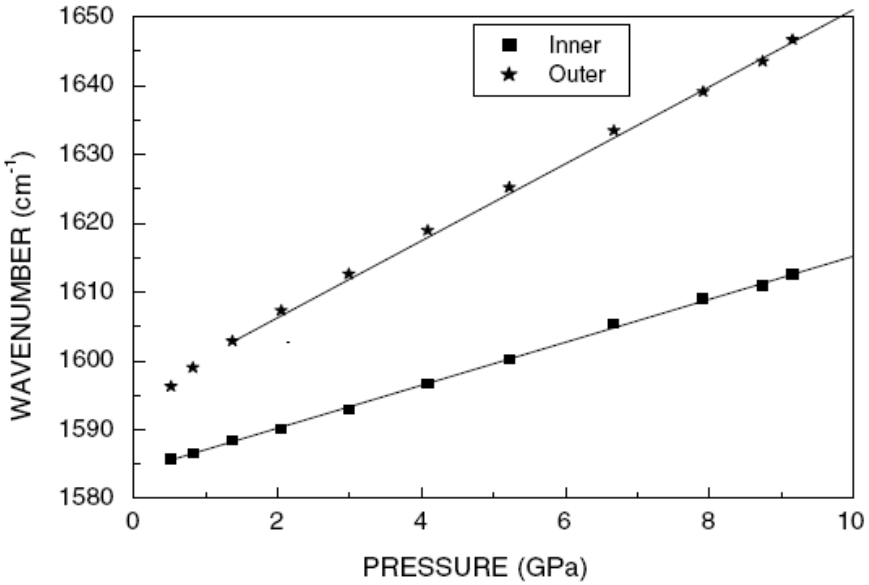
The transmission efficiency increases as tube radius increases

The pressure transmission efficiency of DWCNT as a function of the outertube radius.

Ye et al. PRB (2007)

Raman spectra of double-walled carbon nanotube in the region of optical mode at different hydrostatic pressure.

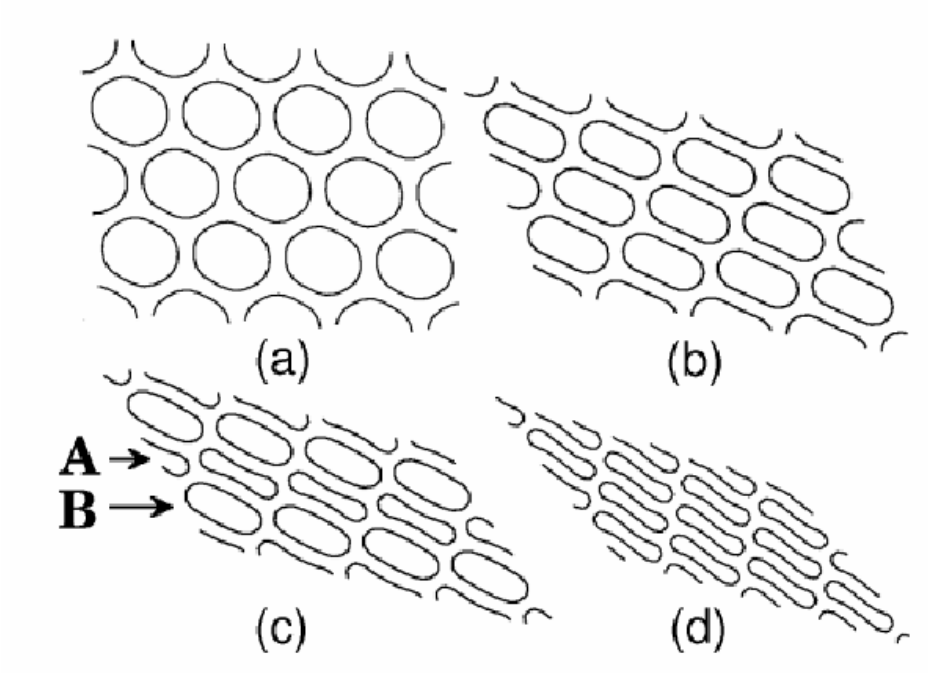




*The radius of the inner tube is **5** angstrom, the pressure coefficient of the inner tube is 3.11 cm-1/GPa, the outer tube is 5.59 cm-1/GPa. The pressure coefficient of the inner tube is 45% samller than the outer tube's*

P. Puech, H. Hubel, D. J. Dunstan, R. R. Bacsa, C. Laurent, and W. S. Bacsa, Phys. Rev. Lett. **93**, 095506 (2004).

Tube lattice Under pressure:

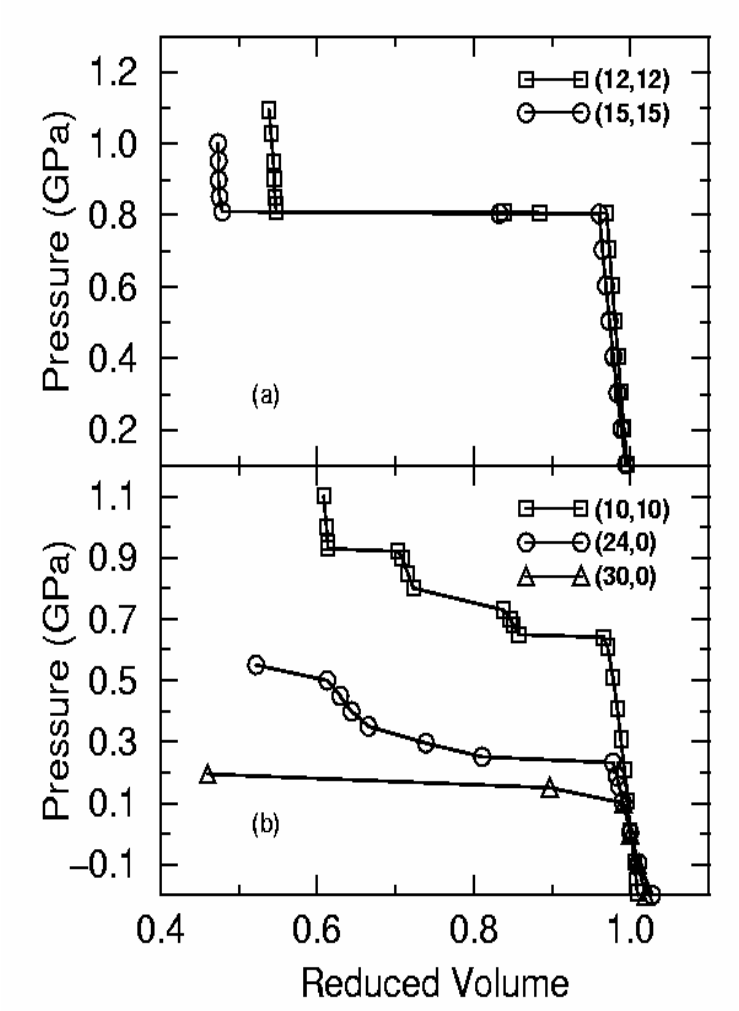


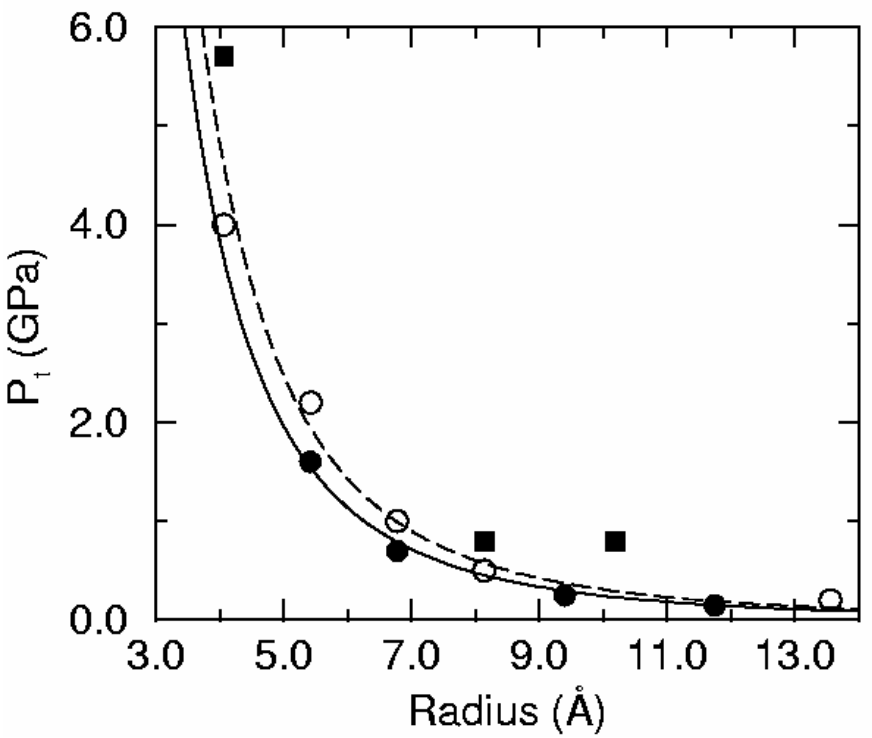
-

	Enery/atom (eV)			PV/atom	enthalpy/atom
	E	E_1	E_2	(eV)	(eV)
A	-7.366	-7.330	-7.318	0.012	-7.354
B	-7.378	-7.342	-7.341	0.021	-7.357
Δ	0.012	0.012	0.023	0.009	0.003

Zhang, Liu and Gong, PRB70, 035422(2004), PRL93, 149601(2004)

Transition pressure: isolated tube and lattice





Symmetry and Radius Dependent

Summary:

- A new algorithm for constant pressure MD for finite system, which provides a window to study the properties of finite-system.

- Applications:

  Si cluster has a higher transition pressure than bulk. Larger clusters, lower P_c. Pressure driven Si cluster to simple hexagonal-like structure, not β -tin!

A hard-soft transition of carbon notube is identified.

……..

Thank You!

Martonark, Molteni and Parrinello Proposed(PRl, 2001):

$$L = \frac{1}{2}\sum_i \mu \int d\mathbf{r}\,|\dot{\psi}_i(\mathbf{r})|^2 + \frac{1}{2}\sum_I M_I \dot{\mathbf{R}}_I^2 - E[\{\psi_i\},\{\mathbf{R}_I\}] + \sum_{i,j}\Lambda_{ij}(\langle\psi_i|\psi_j\rangle - \delta_{ij})$$
$$+ \frac{1}{2}\sum_I m\dot{\mathbf{X}}_I^2 - \sum_{I,J} V_{C\text{-}L}(|\mathbf{R}_I - \mathbf{X}_J|) - \sum_{I<J} V_{L\text{-}L}(|\mathbf{X}_I - \mathbf{X}_J|).$$

N_L: No. of atom for pressure transfer medium.

Large enough!

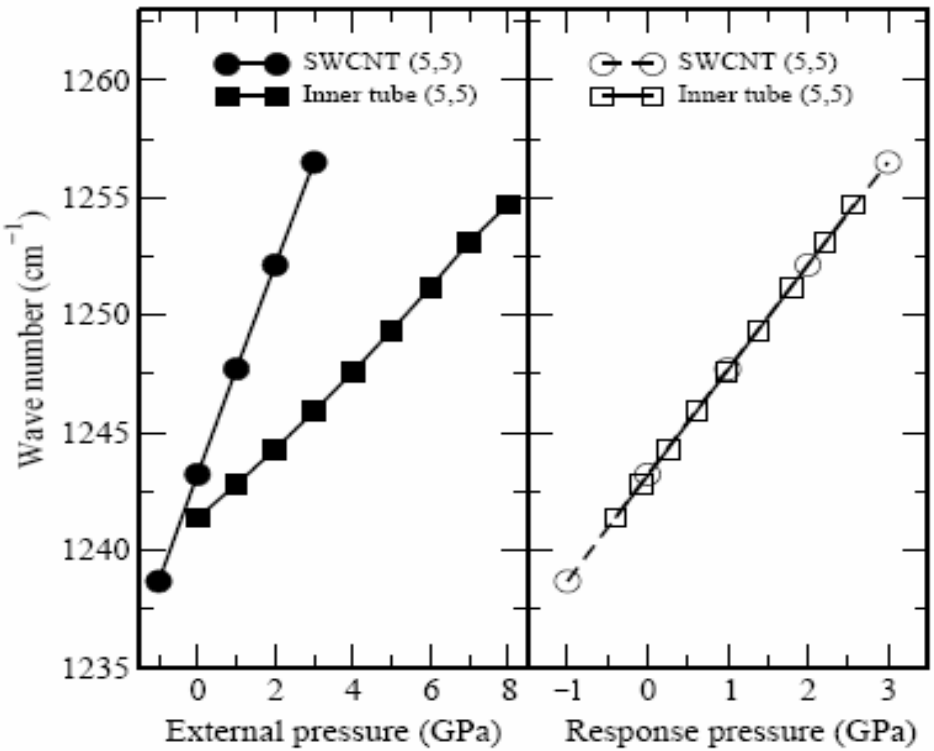
$V_{C\text{-}L}$: Interaction between cluster and medium.

Accurate!

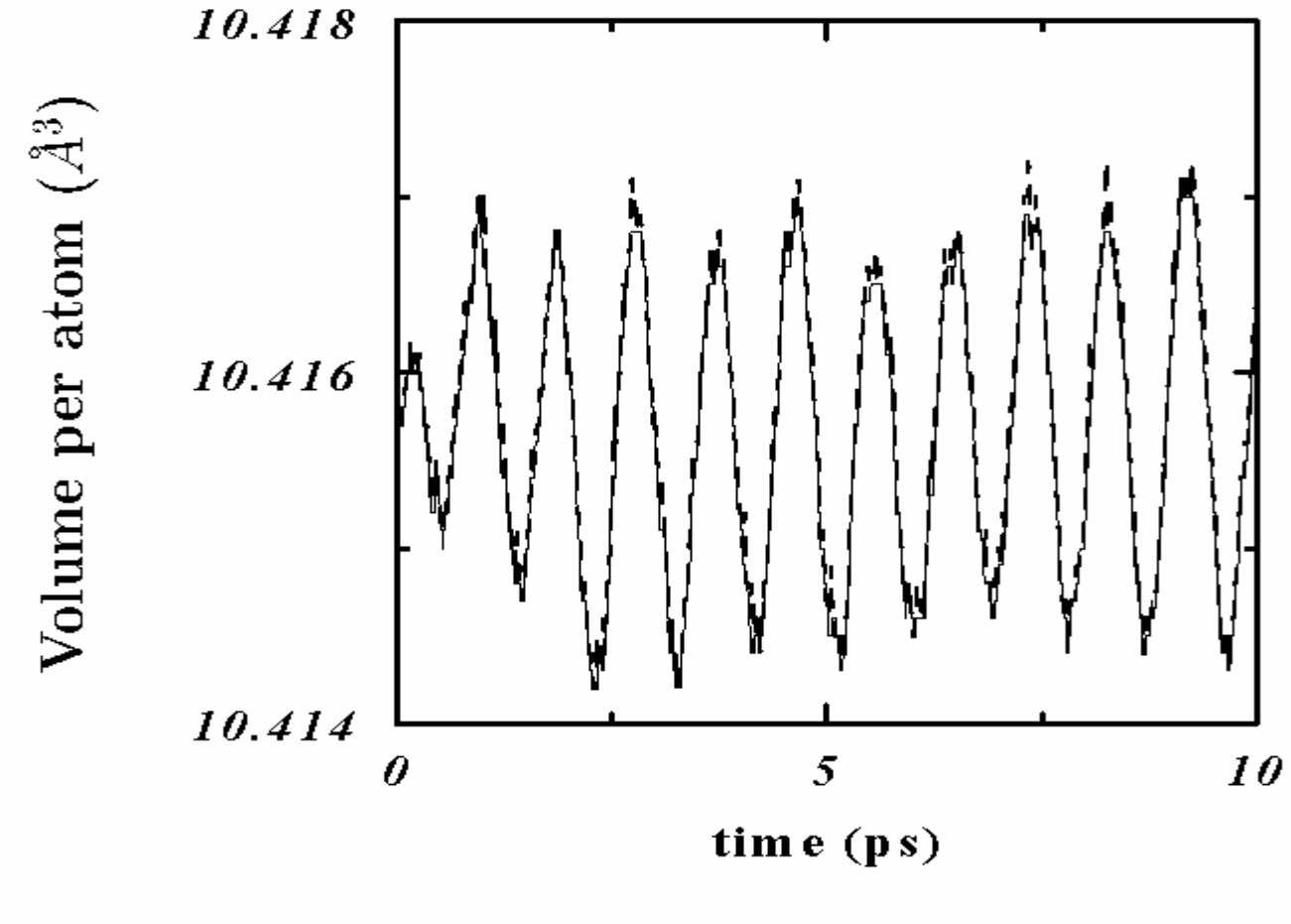
$V_{L\text{-}L}$: Interaction for the atoms in the medium.

Good!

simple，but large computational overhead!

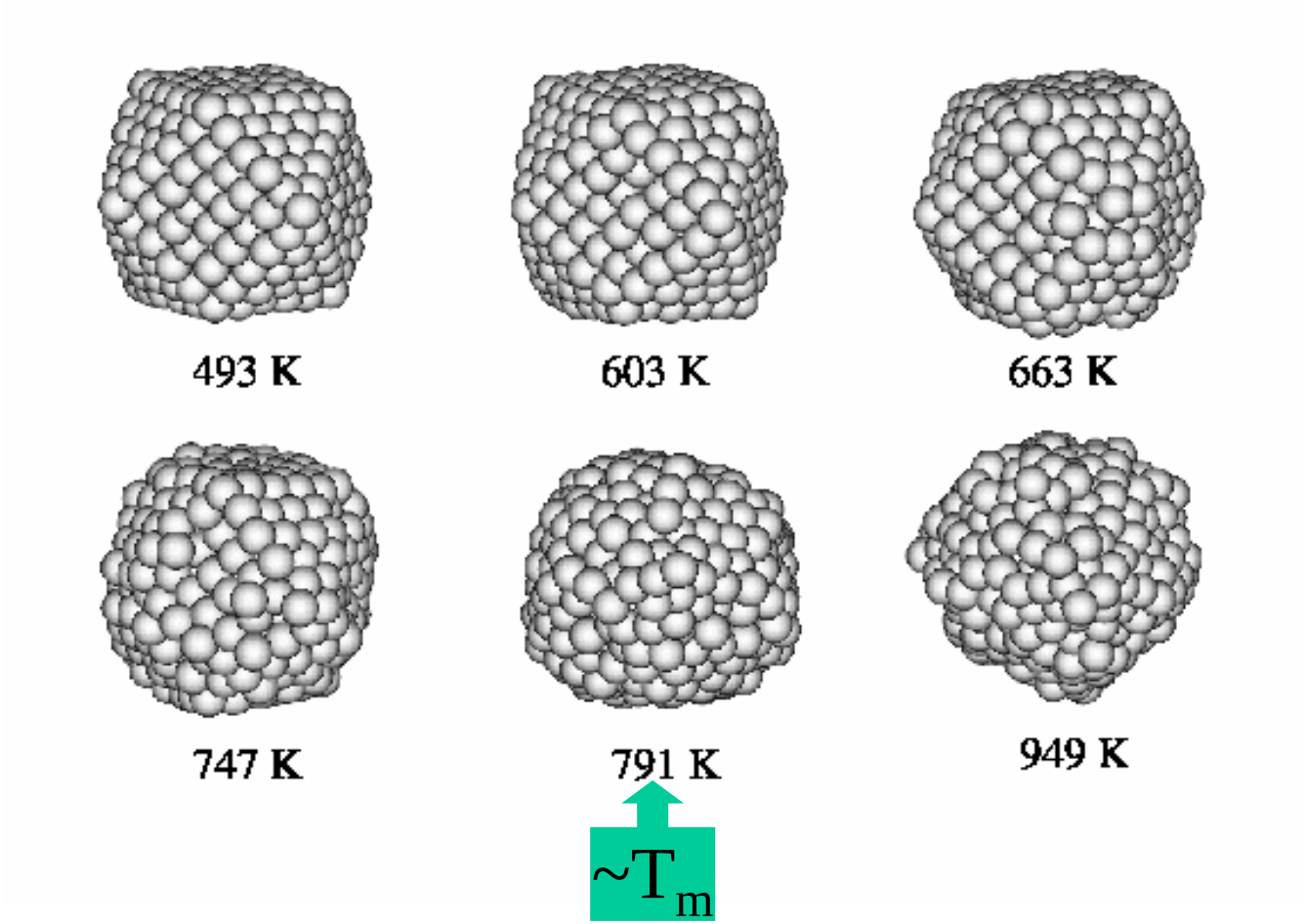

SWCNT (5,5)
Inner tube (5,5)
SWCNT (5,5)
Inner tube (5,5)
Wave number (cm^{-1})
1260
1255
1250
1245
1240
1235
0
2
4
6
8
−1
0
1
2
3
External pressure (GPa)
Response pressure (GPa)

Validity of the volume decomposition:



Comparison between the “exact” and atomic volume:
The agreement is good!

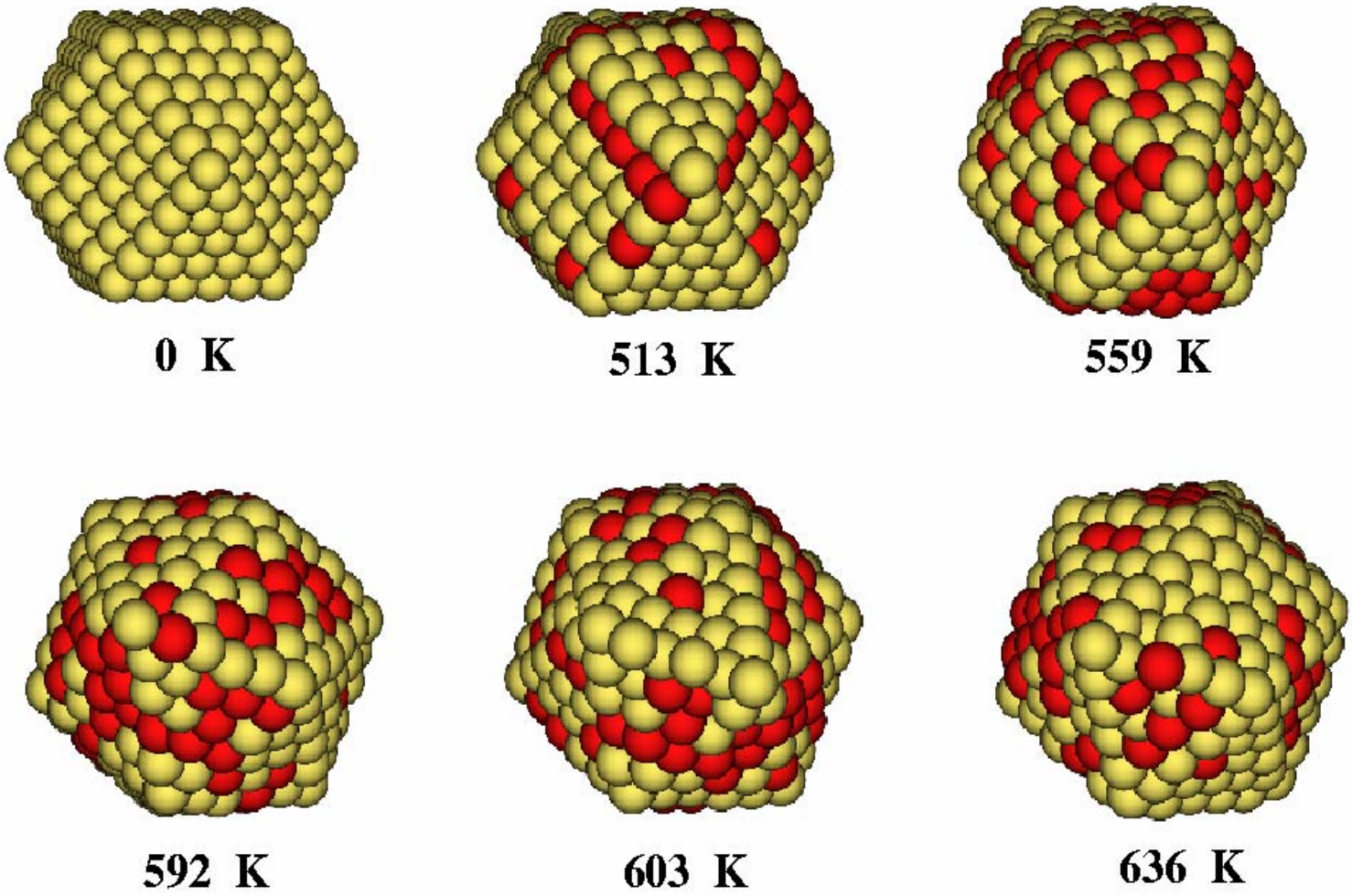
Temperature Dependence: Structure of Ni_{561} without Pressure



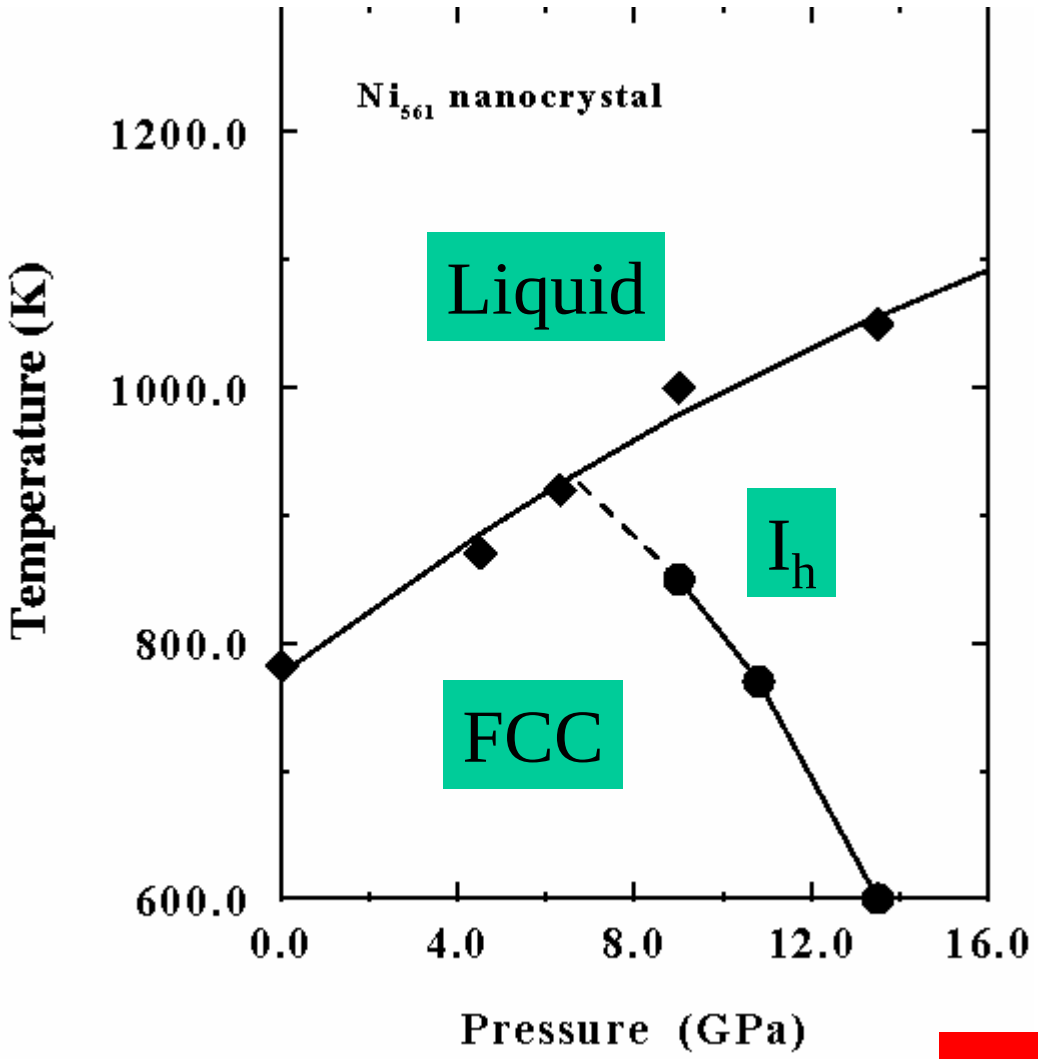
No structure transition before melting!

Temperature dependence: structure Ni_{561} under pressure 10GPa

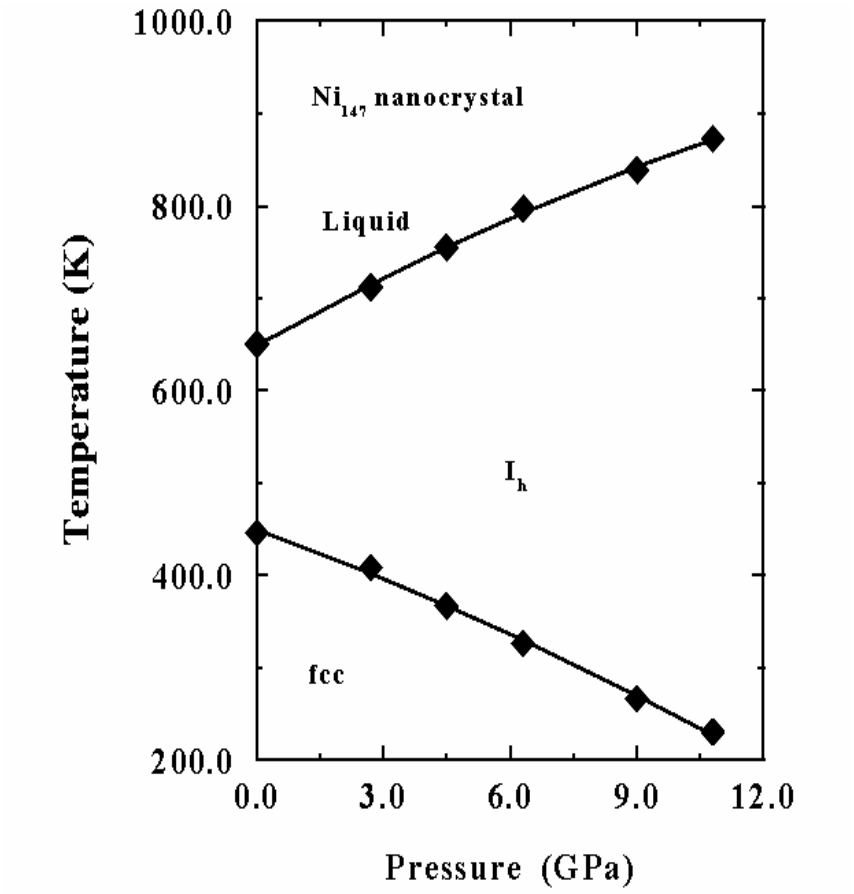
FCC-like structure to Icosahedral structure transition

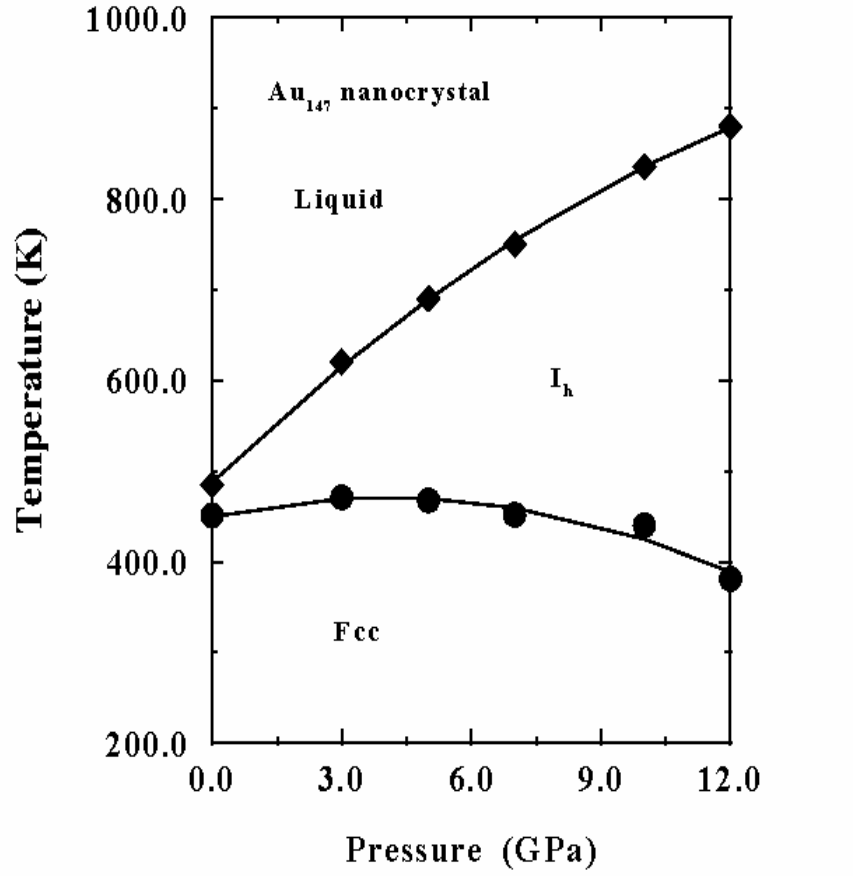


“Phase Diagram of nano-particle Ni”

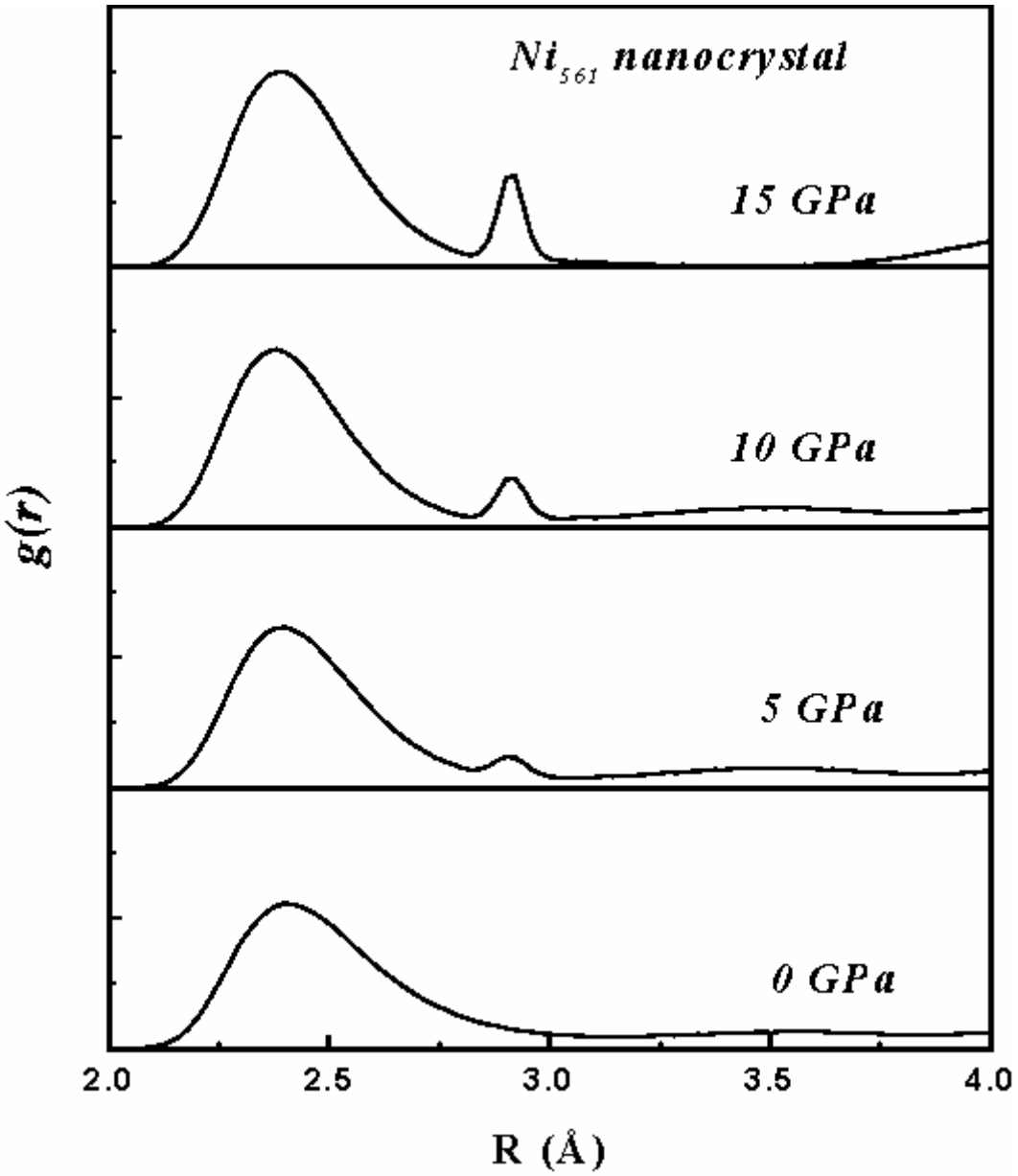


Small is different!


1000.0
800.0
600.0
400.0
200.0
Temperature (K)
Ni147 nanocrystal
Liquid
Ih
fcc
0.0
3.0
6.0
9.0
12.0
Pressure (GPa)


1000.0
800.0
600.0
400.0
200.0
Temperature (K)
Au147 nanocrystal
Liquid
Ih
Fcc
0.0
3.0
6.0
9.0
12.0
Pressure (GPa)

Under pressure: bcc-Ni locally appeared.



The critical transition pressure is defined by the conditions $\frac{d^2E}{d\omega^2}|_{\omega=1}=0$ and $\frac{dE}{d\epsilon}|_{\omega=1}=0$, which give rise to

$$P_t = \frac{3D}{R_0^3(1+\epsilon_c)^3} \approx \frac{3D}{R_0^3},$$

$$\epsilon_c = -\frac{5D}{2CR_0^2}.$$

The ratio of bulk modulus in hard and soft phase:

$$\frac{B_s}{B_h} = \frac{19}{12}(\frac{h}{R_0})^2.$$

$$\frac{B_s}{B_h} \propto (\frac{h}{R_0})^2 \approx 0.01$$

- Pressure:

  powerful tool to explore the meta-stability,
  phase transitions of solids,
  new structures, new physics, new properties…

- size effect, surface effect:

  more rich physics in meta-stability!