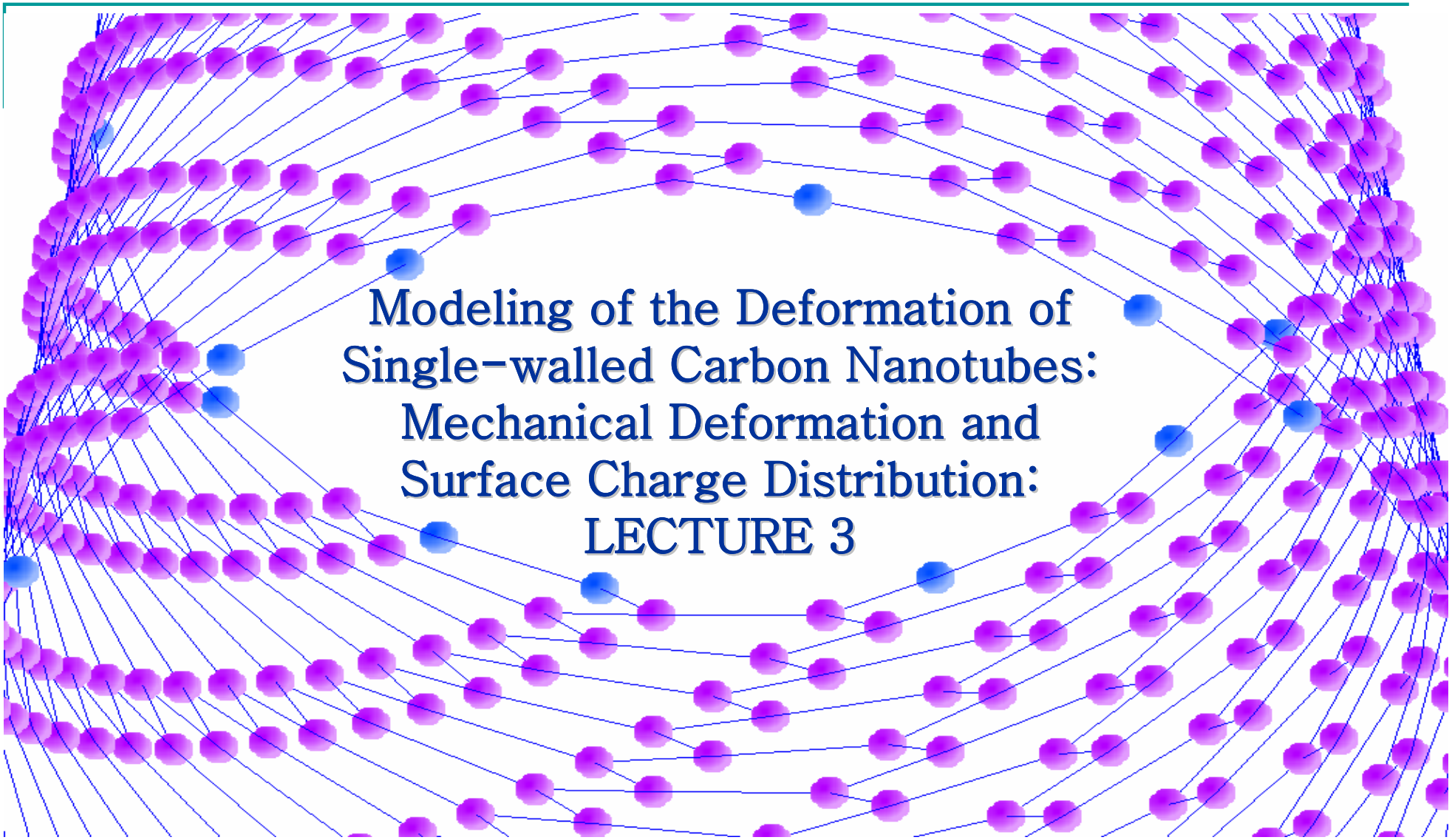

Modeling of the Deformation of Single-walled Carbon Nanotubes: Mechanical Deformation and Surface Charge Distribution: LECTURE 3

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Lecture-2 Summary

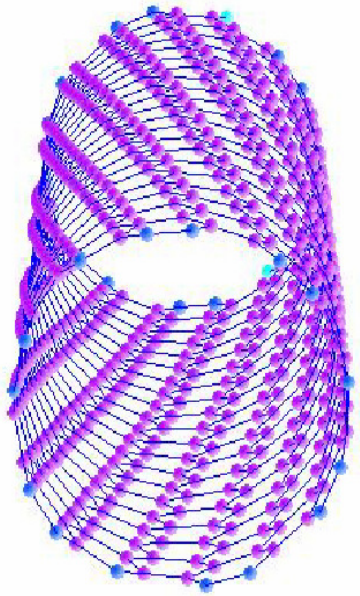
- Tersoff-Brenner multi-body interatomic potential for hydrocarbons
- Mathematically mapping planar and rolled-up graphene sheets: Computing C-C bond lengths
- Cauchy-Born (CB) Rule:
  - Basic hypothesis and deformation rule for bulk solids
  - Modifications for curved membranes (SWNTs)
  - Modifications for complex Bravais lattices (honeycombs)
  - Extension to cases of inhomogeneous deformations
- Zero temperature local QC: Continuum hyperelastic constitutive law using interatomic potentials

Lecture-3 Overview

- Focus on a specific type of deformation: Coupled extension and twist
- Obtain kinematic coupling effects in extension and twist for SWNTs
- Modified CB rule for inhomogeneous deformations
- Stress-strain plots and elastic moduli in extension and twist
- *Ab initio* evaluation of Young's modulus using density functional theory
- Comparison of results from different approaches and concluding remarks

Deformations: Extension and Twist of SWNTs

- Simple class of deformations:
  - Analytic treatment
  - Provides insight into modeling aspects for complex deformations
- Certain SWNTs:
  - Possess twisted atomic structure
  - **Exhibit natural extension-twist coupling**



Deformations: Extension and Twist of SWNTs

Propose a generalized deformation map:

$r = \gamma R$

$\theta = \Theta + f(Z;k)$

$z = (1+\varepsilon) Z$

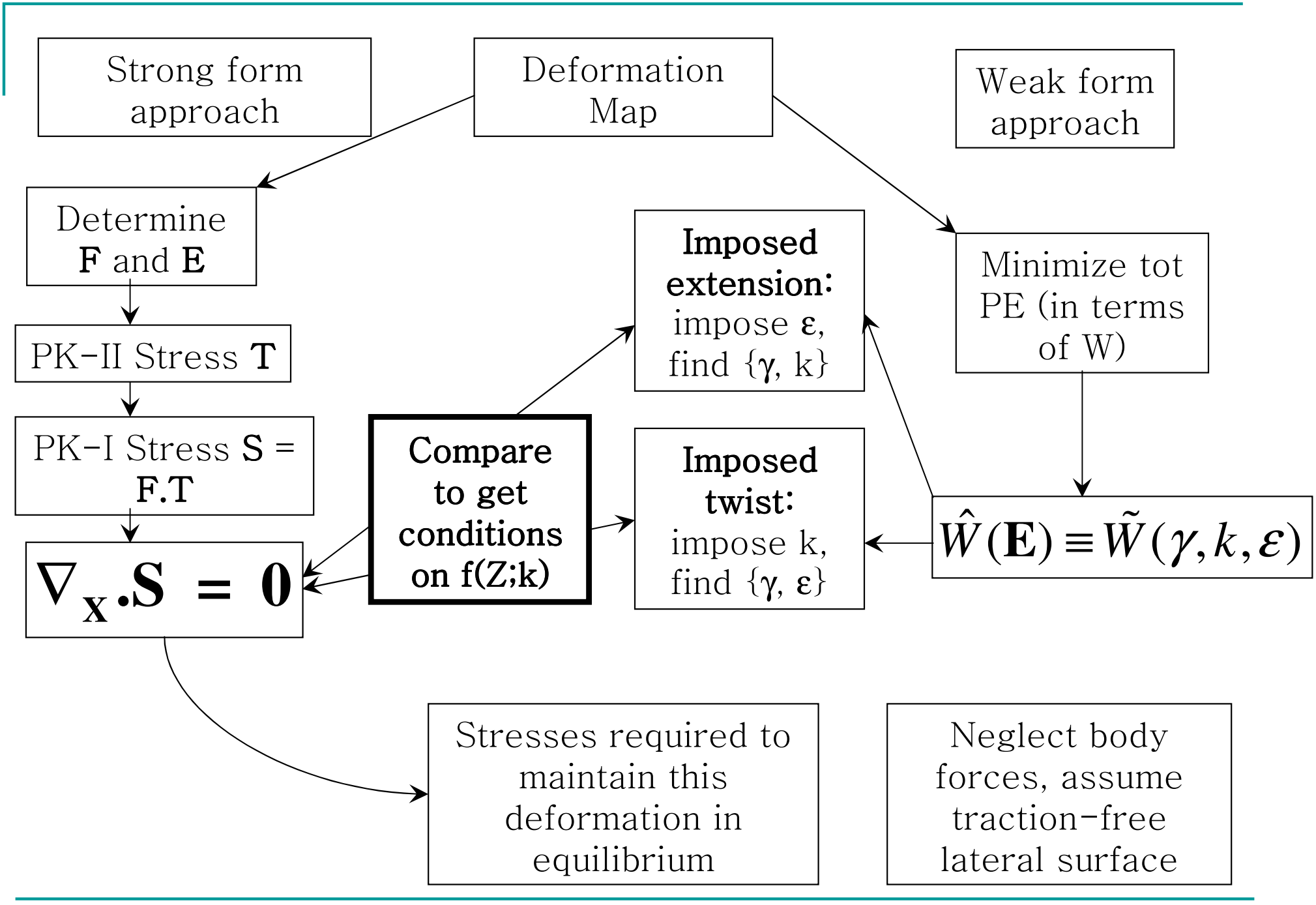
r, R : Def & Undef Radii

θ, Θ : Def & Undef Polar angles

z, Z : Def & Undef Axial coords

- Deformation – inhomogeneous in general → CB rule to be modified!
- Reference cylinder → deformed cylinder.
- f(Z;k) → kZ: Well-known extension-twist deformation, k: Twist per unit undeformed length

f(Z;k): Need to characterize


Strong form approach
Deformation Map
Weak form approach
Determine F and E
PK-II Stress T
PK-I Stress S = F.T
$\nabla_X . S = 0$
Compare to get conditions on f(Z;k)
Imposed extension: impose ε, find {γ, k}
Imposed twist: impose k, find {γ, ε}
Minimize tot PE (in terms of W)
$\hat{W}(\mathbf{E}) \equiv \tilde{W}(\gamma, k, \varepsilon)$
Stresses required to maintain this deformation in equilibrium
Neglect body forces, assume traction-free lateral surface

Equilibrium: Strong Form

- **Axi-symmetric** stress measures (**Θ** independent).

- **Traction-free** BC on the inner and outer **lateral surfaces** of the SWNT

Final set of local equilibrium equations:

$$T_{\Theta\Theta} + 2Rf' T_{\Theta Z} + f'^2 R^2 T_{ZZ} = 0 \ldots (1)$$

$$\frac{\partial}{\partial Z}\left[T_{\Theta Z} + f' RT_{ZZ}\right] = 0 \ldots (2)$$

$$\frac{\partial T_{ZZ}}{\partial Z} = 0 \ldots (3)$$

Equilibrium: Weak Form

Imposed Extension

Satisfies (1) and (2) for **any** f (Z;k) such that:

$$\frac{\partial f'}{\partial k} \neq 0$$

(3) is trivially satisfied.

$$T_{\Theta\Theta} + 2Rf' T_{\Theta Z} + f'^2 R^2 T_{ZZ} = 0 \ldots (1)$$

$$\frac{\partial}{\partial Z}\left[T_{\Theta Z} + f' RT_{ZZ} \right] = 0 \ldots (2)$$

$$\frac{\partial T_{ZZ}}{\partial Z} = 0 \ldots (3)$$

Imposed Twist

Satisfies (1) and (3) for arbitrary 'f'.

Necessary condition to satisfy (2): $f' = \text{constant}$

Bond Length Deformations

- **Undeformed** bond vector between ‘i’ and ‘j’ (**unwrapped geodesic** on the cylinder):

$$\tilde{\mathbf{A}} = R\left(\Theta_j - \Theta_i\right)\mathbf{e}_\Theta + \left(Z_j - Z_i\right)\mathbf{e}_Z$$

r = γ R

θ = Θ + f (Z;k)

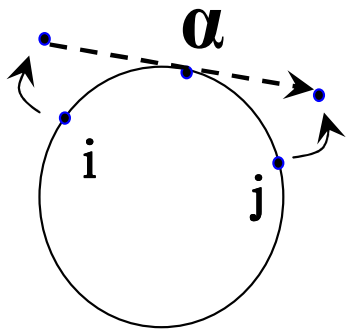
z = (1+ε) Z

- Deformed geodesic vector from **direct map**:

$$\tilde{\mathbf{a}} = \gamma R\left[\left(\Theta_j - \Theta_i\right) + f(Z_j) - f(Z_i)\right]\mathbf{e}_\theta + \left(z_j - z_i\right)\mathbf{e}_z$$

- **CB rule** evaluated at some intermediate point ‘α’:

$$\hat{\mathbf{a}} = \gamma R\left[\left(\Theta_j - \Theta_i\right) + \left(Z_j - Z_i\right) f'(Z_\alpha)\right]\mathbf{e}_\theta + \left(z_j - z_i\right)\mathbf{e}_z$$



Bond Length Deformations (contd…)

- 'Best' **location** to apply the CB rule:

$$f'(Z_\alpha) = \frac{f(Z_j) - f(Z_i)}{Z_j - Z_i}$$

Use Mean-value Theorem in the CB rule!

$$\boldsymbol{a} = \mathcal{F}(\mathbf{X} + \mathbf{A}) - \mathcal{F}(\mathbf{X})$$
$$= \nabla\mathcal{F}(\mathbf{X}_\alpha)\bullet\mathbf{A} = \mathbf{F}(\mathbf{X}_\alpha)\bullet\mathbf{A}$$

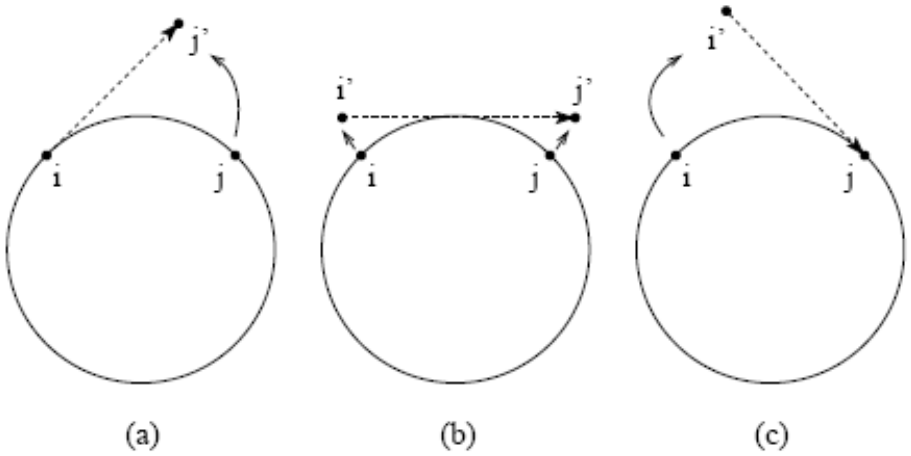
  - Θ_α : Automatically determined – α lies on geodesic

- For $f(Z;k) = k\,Z^2$, $Z_\alpha = (Z_i + Z_j)/2$ --- **Mid-Point**

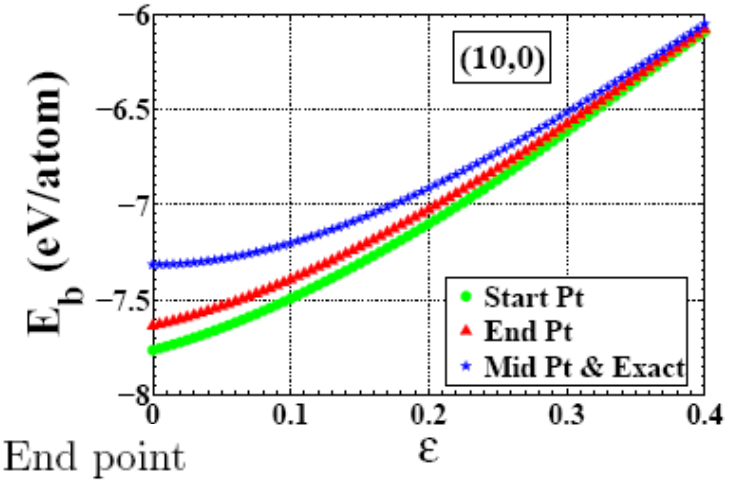
- Note : Bond lengths --- always measured as **Euclidean lengths** between atoms (after wrapping the deformed geodesic back onto the deformed cylinder).

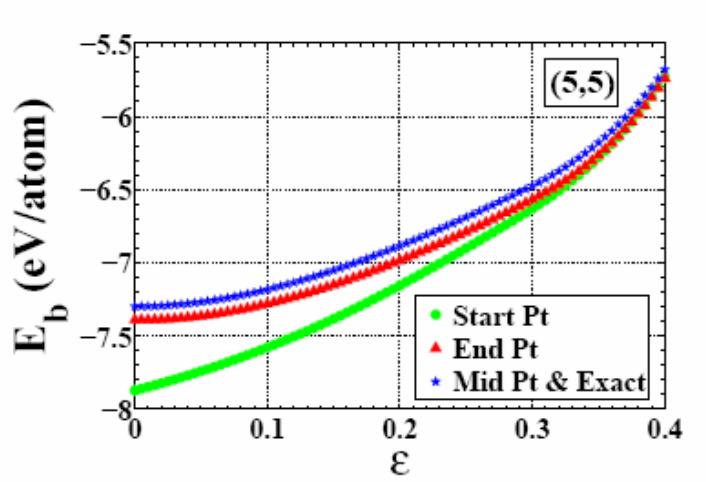
f(Z;k) = k Z^2: Binding energy/atom (E_b) → Comparison of different unwrapping rules

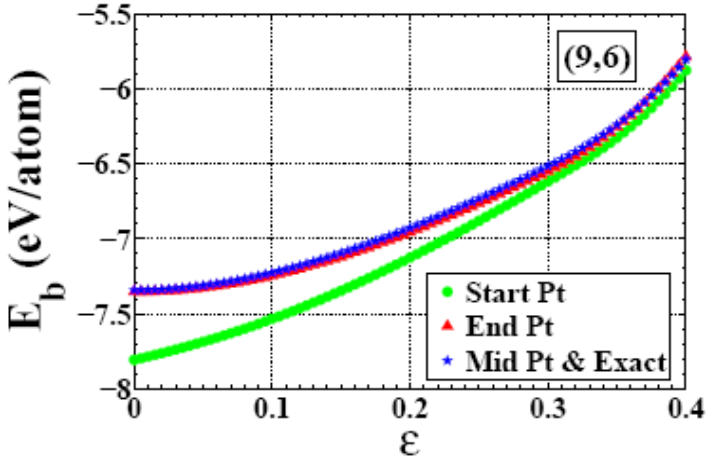
Brenner Parameter Set 1



Various 'unwrapping' rules - (a) Start point, (b) Mid point and (c) End point



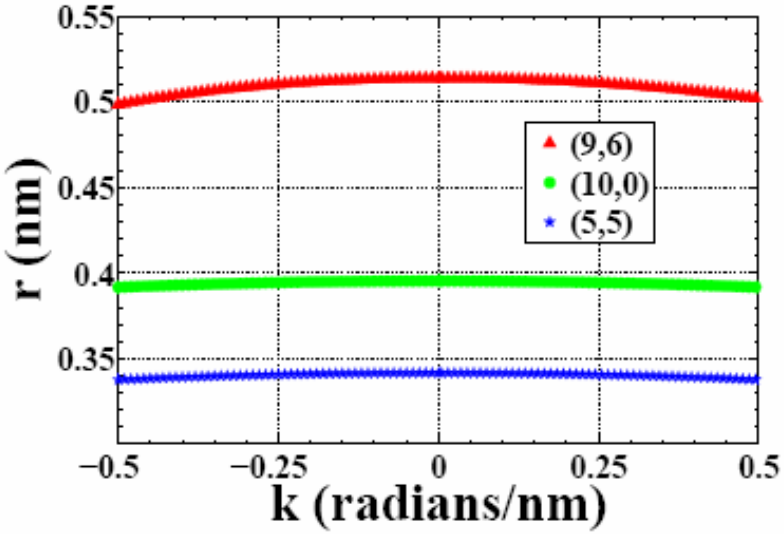


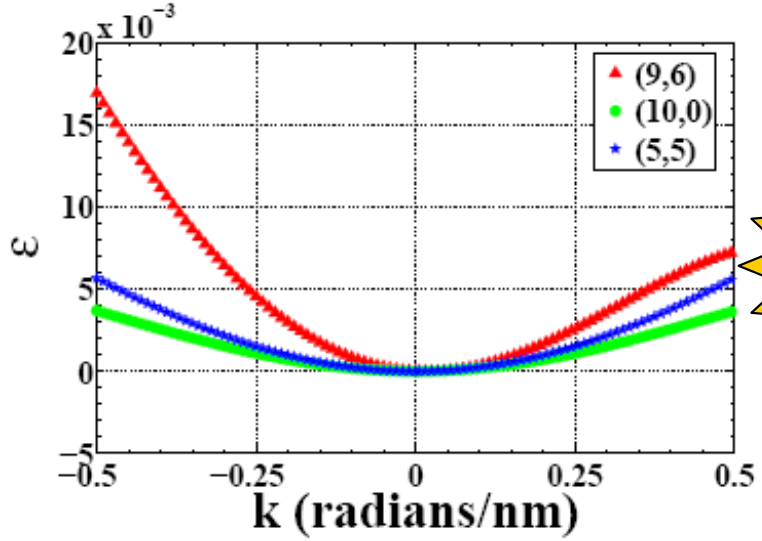


K. Chandraseker, S. Mukherjee, Y. X. Mukherjee, IJSS, to appear, 2006

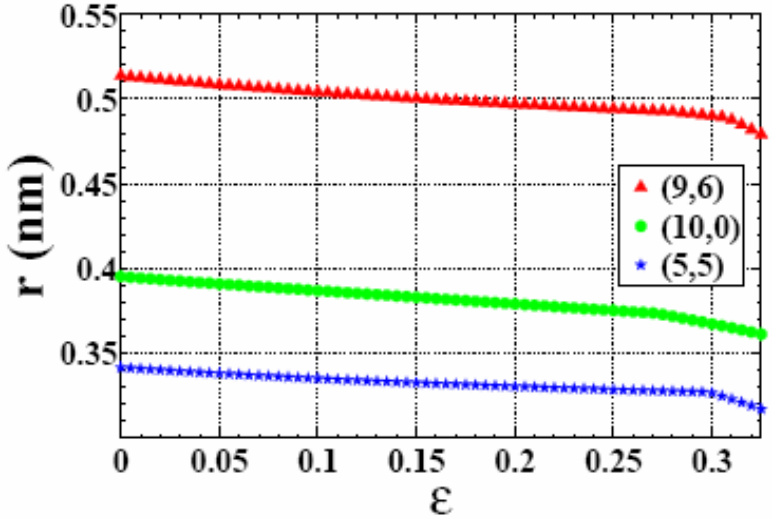
f(Z;k) = k Z: Kinematic Coupling → Indep of 'unwrap' point!

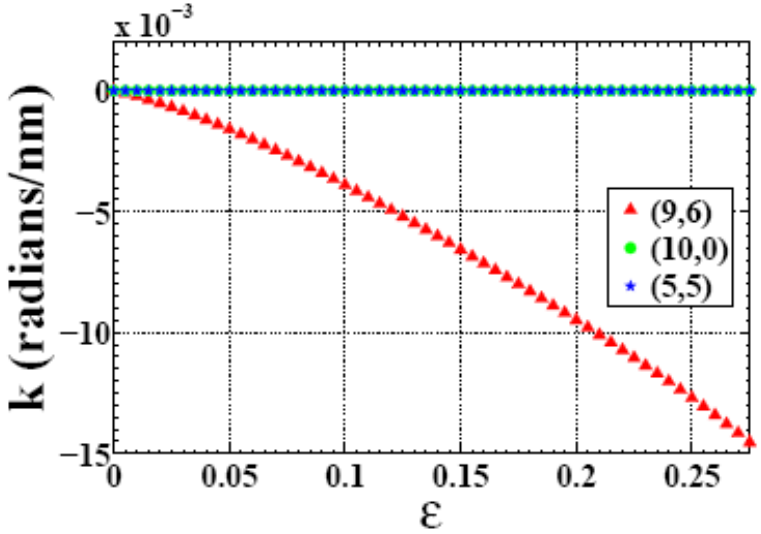
Brenner Parameter Set 1





Chiral asymm!





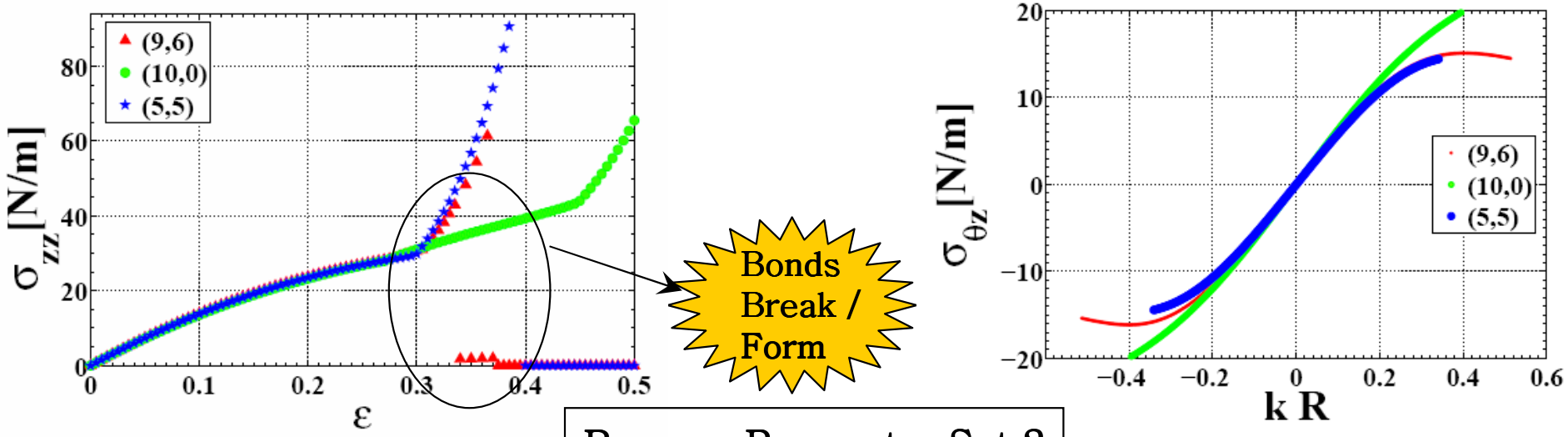
Chiral twists!

Brenner Parameter Set 2: Qualitatively similar results (not shown)

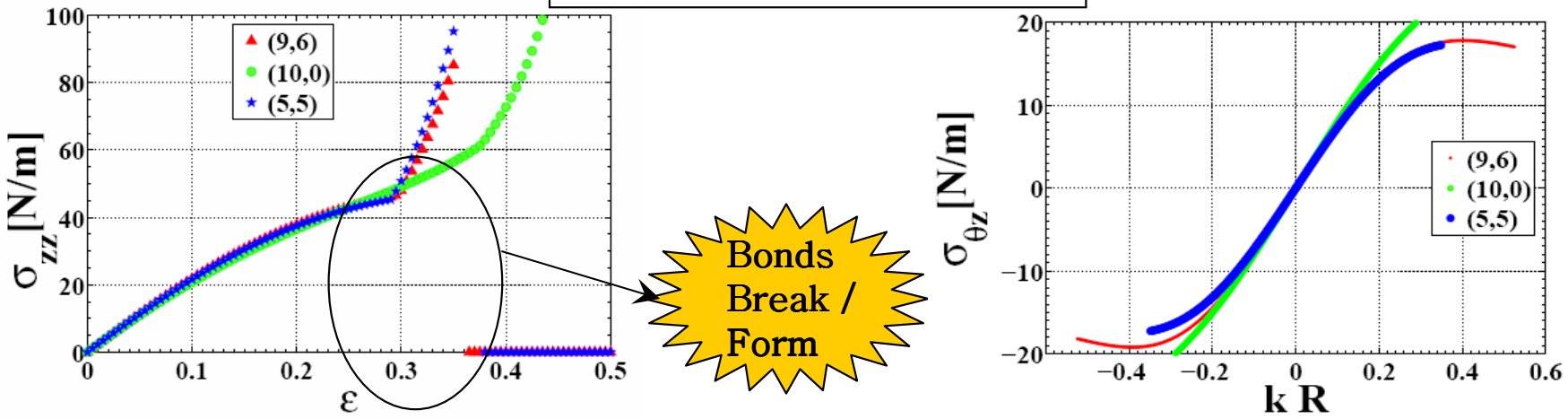
K. Chandraseker, S. Mukherjee, Y. X. Mukherjee, IJSS, to appear, 2006

Stress-Strain Curves in Tension and Torsion: f(Z;k) = k Z

Brenner Parameter Set 1



Brenner Parameter Set 2



Stress–Strain Slopes: (a) Independent of SWNT chirality (b) Parameter set dependent: qualitatively similar, quantitatively different

Coupling Effects on Young's and Shear Moduli

$$\mathbf{C} = \frac{d^2\hat{W}}{d\mathbf{E}d\mathbf{E}} = \frac{\partial^2 W}{\partial \mathbf{E}\partial \mathbf{E}} - \frac{\partial^2 W}{\partial \mathbf{E}\partial \boldsymbol{\eta}} \cdot \left(\frac{\partial^2 W}{\partial \boldsymbol{\eta}\partial \boldsymbol{\eta}}\right)^{-1} \cdot \frac{\partial^2 W}{\partial \boldsymbol{\eta}\partial \mathbf{E}}$$

Young's Modulus (Y)

$$Y = C_{ZZZZ} + \nu^{(e)}_{\Theta\Theta} C_{ZZ\Theta\Theta} + \nu^{(e)}_{\Theta Z} C_{ZZ\Theta Z}$$

Poisson Effect

Induced Twist Effect

$\nu^{(e)}_{\Theta Z}$, $\nu^{(e)}_{\Theta\Theta}$ } Functions of components of $\mathbf{C}$

Shear Modulus (G)

$$G = C_{\Theta Z\Theta Z} + \nu^{(t)}_{\Theta\Theta} C_{\Theta Z\Theta\Theta} + \nu^{(t)}_{ZZ} C_{\Theta ZZZ}$$

Poisson Effect

Induced Extension Effect

$\nu^{(t)}_{ZZ}$, $\nu^{(t)}_{\Theta\Theta}$ } Functions of components of $\mathbf{C}$

Explicit dependence of Y and G on coupling derived

Moduli Values with Wall Thickness of 0.335 nm

Brenner Parameter Set 1

	Y [GPa]
(9,6) Chiral	470
(5,5) Armchair	457
(10,0) Zigzag	464
	G [GPa]
(9,6) Chiral	188
(5,5) Armchair	193
(10,0) Zigzag	177

Zhang et al. (2002): 475 GPa

Brenner Parameter Set 2

	Y [GPa]
(9,6) Chiral	693
(5,5) Armchair	670
(10,0) Zigzag	684
	G [GPa]
(9,6) Chiral	240
(5,5) Armchair	246
(10,0) Zigzag	226

Zhang et al. (2002): 705 GPa

Arroyo & Belytschko (2004): 704 GPa

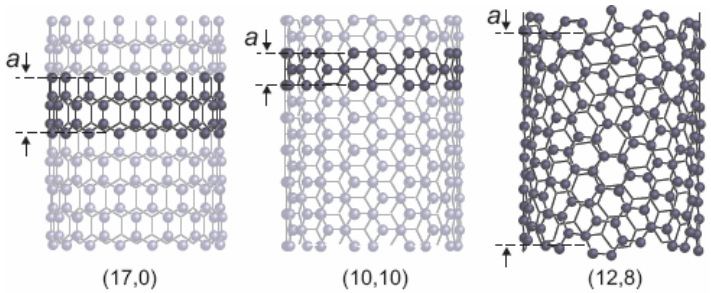
Arroyo & Belytschko (2004): 249 GPa

Most reported experimental / atomistic studies of Y predict ~ 1000 GPa

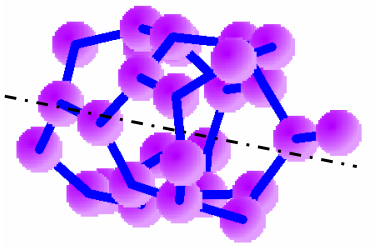
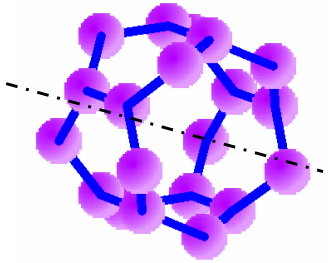
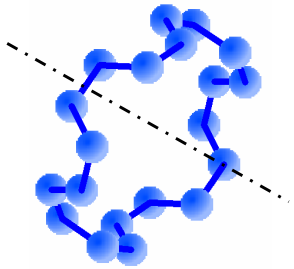
☺ Good agreement (within 3%) between slopes of stress – strain curves and moduli calculation

☹ Moduli are underestimated and parameter set dependent

DFT Unit–cell Relaxations

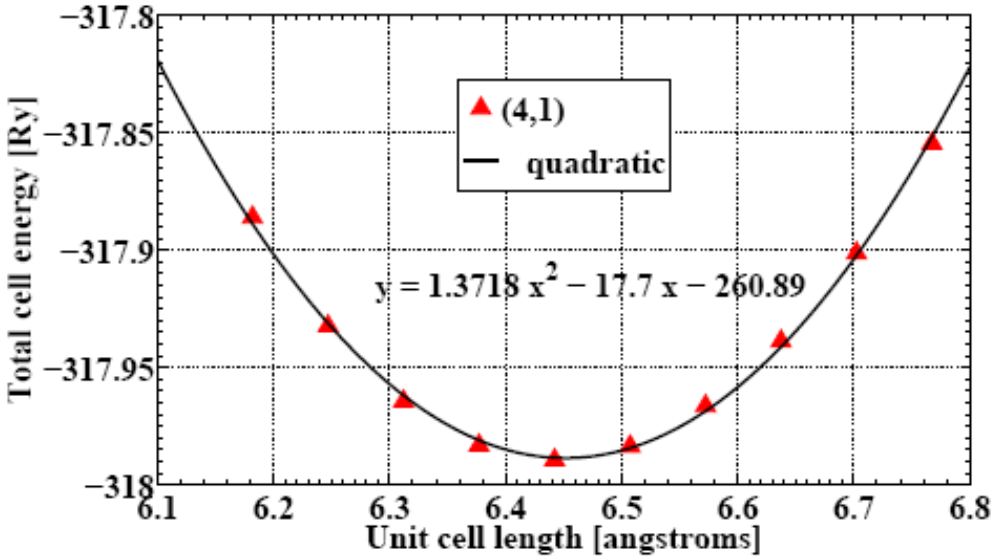


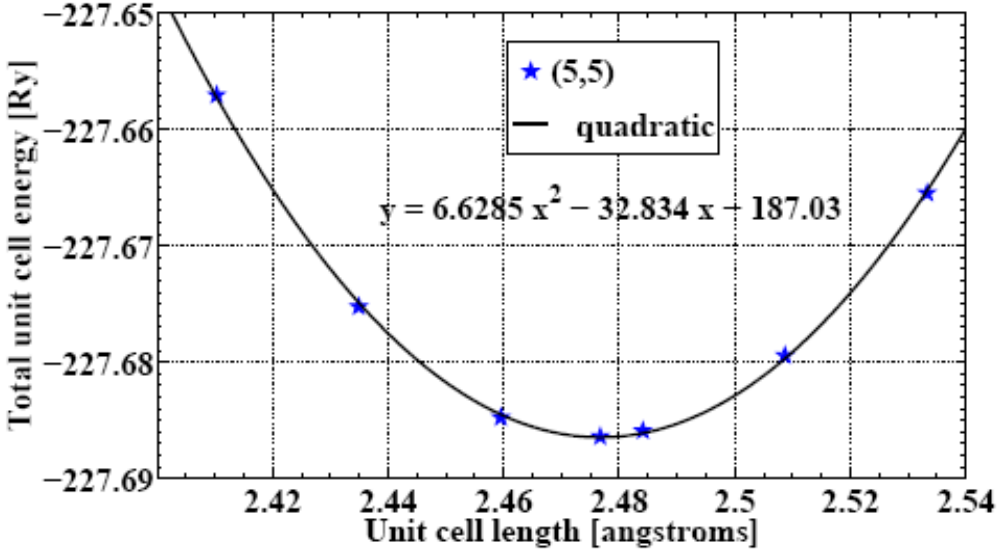
- Construct translational unit cells:

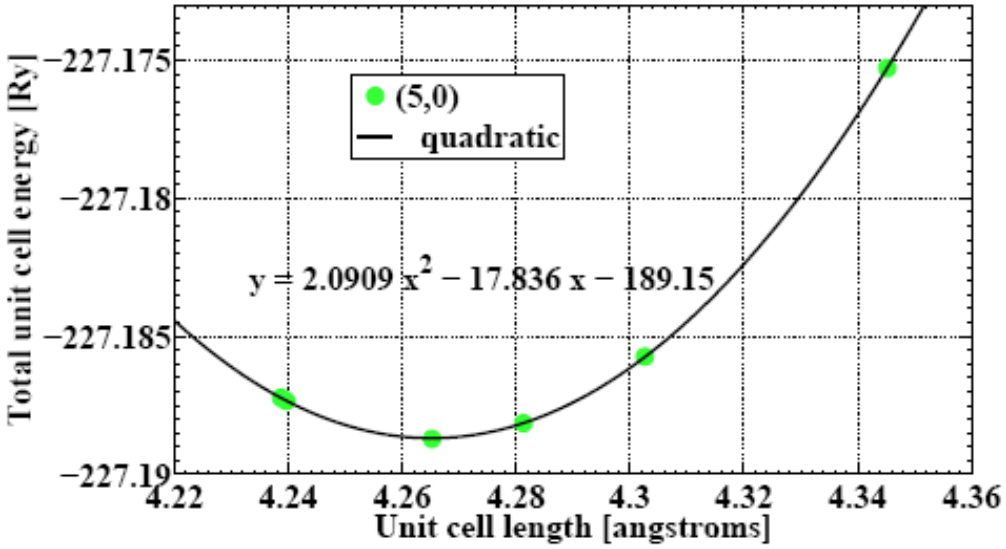
 Chiral (4,1): 28 atoms diameter 3.8 Å, cell length 6.5 Å	 Zigzag (5,0): 20 atoms diameter 4.1 Å, cell length 4.3 Å	 Armchair (5,5): 20 atoms diameter 6.9 Å, cell length 2.5 Å

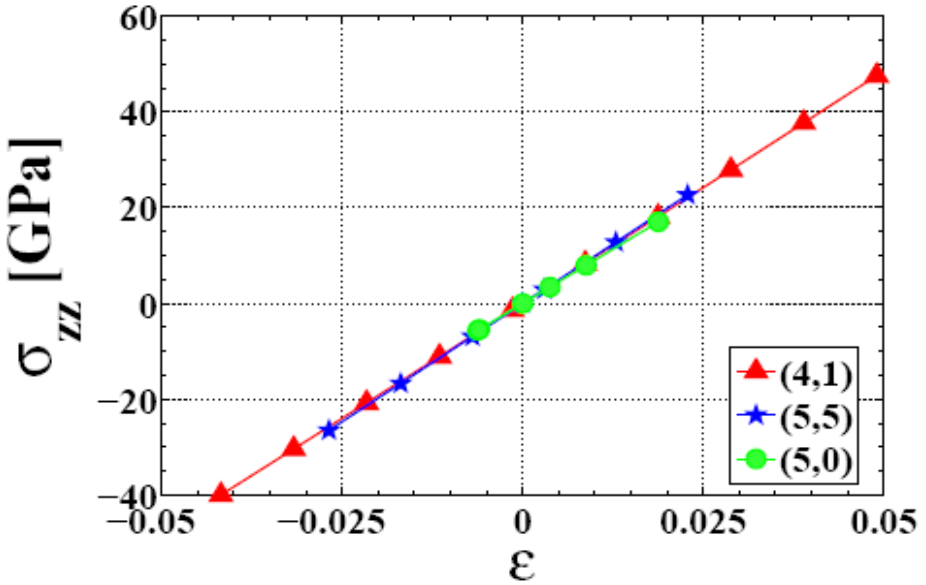
- PWscf Code: PBE–GGA Exchange–Correlation, Ultrasoft Vanderbilt pseudopotentials
- Plane Wave Basis: $E_{cut-off}$ = 50 Ry
- 13.8 Å x 13.8 Å in–plane periodic box dimension [Mielke et al. 2004, Chem. Phys. Lett. 390, pp. 413–420] (create vacuum around SWNT) for tetragonal lattice
- Brillouin zone sampling: 2x2x4 for (5,0), (5,5). Γ–point for (4,1)
- Extension deformations only – no imposed twist

Stress–Strain Curves: Extension









Values of Y: Chiral (4,1) – 965 GPa, Armchair (5,5) – 990 GPa, Zigzag (5,0) – 906 GPa

Concluding Remarks

QC with Empirical Potentials	DFT
☺ Y and G found analytically	☹ Y found numerically
☹ Y and G parameter set dependent	☺ No experimentally fit parameters
☺ Complete stress–strain curves in ~ 1 minute on a desktop PC (2 GHz, 512 MB RAM)	☹ Each data point ~ 10 hours on a desktop PC (2 GHz, 512 MB RAM)
☺ General deformations straightforward in FE framework	☹ Deformations restricted by computational expense and translational periodicity

- QC with empirical potentials: Effect of extension–twist coupling on Y and G explicitly shown with cylindrical reference configuration
- Future directions:
  - DFT–QC bridged approach: computational expense?
  - DFT approach to extract continuum parameter values

Acknowledgements

- Cornell Theory Center: Serial Cluster
- Computing Facility at the Department of Theoretical and Applied Mechanics, Cornell University

References

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- Modifications to the Cauchy-Born Rule: Applications in the deformation of single-walled carbon nanotubes, K. Chandraseker, S. Mukherjee, Y.X. Mukherjee, Int. J. Solids and Structures, to appear, 2006.
- Atomistic-continuum and *ab initio* estimation of the elastic moduli of single-walled carbon nanotubes, K. Chandraseker, S. Mukherjee, submitted, 2006.

Thank you!

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