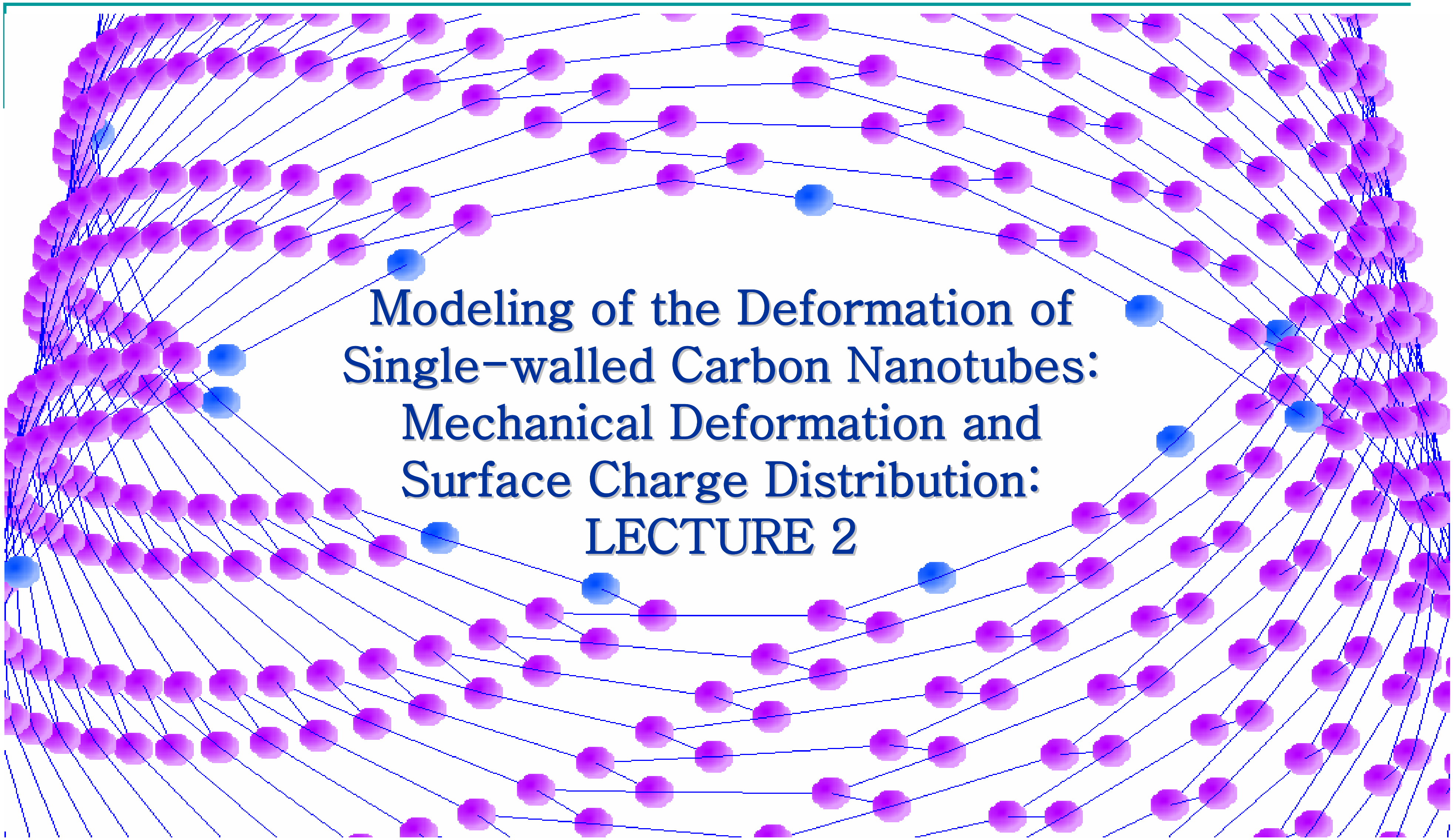

Modeling of the Deformation of Single-walled Carbon Nanotubes: Mechanical Deformation and Surface Charge Distribution: LECTURE 2

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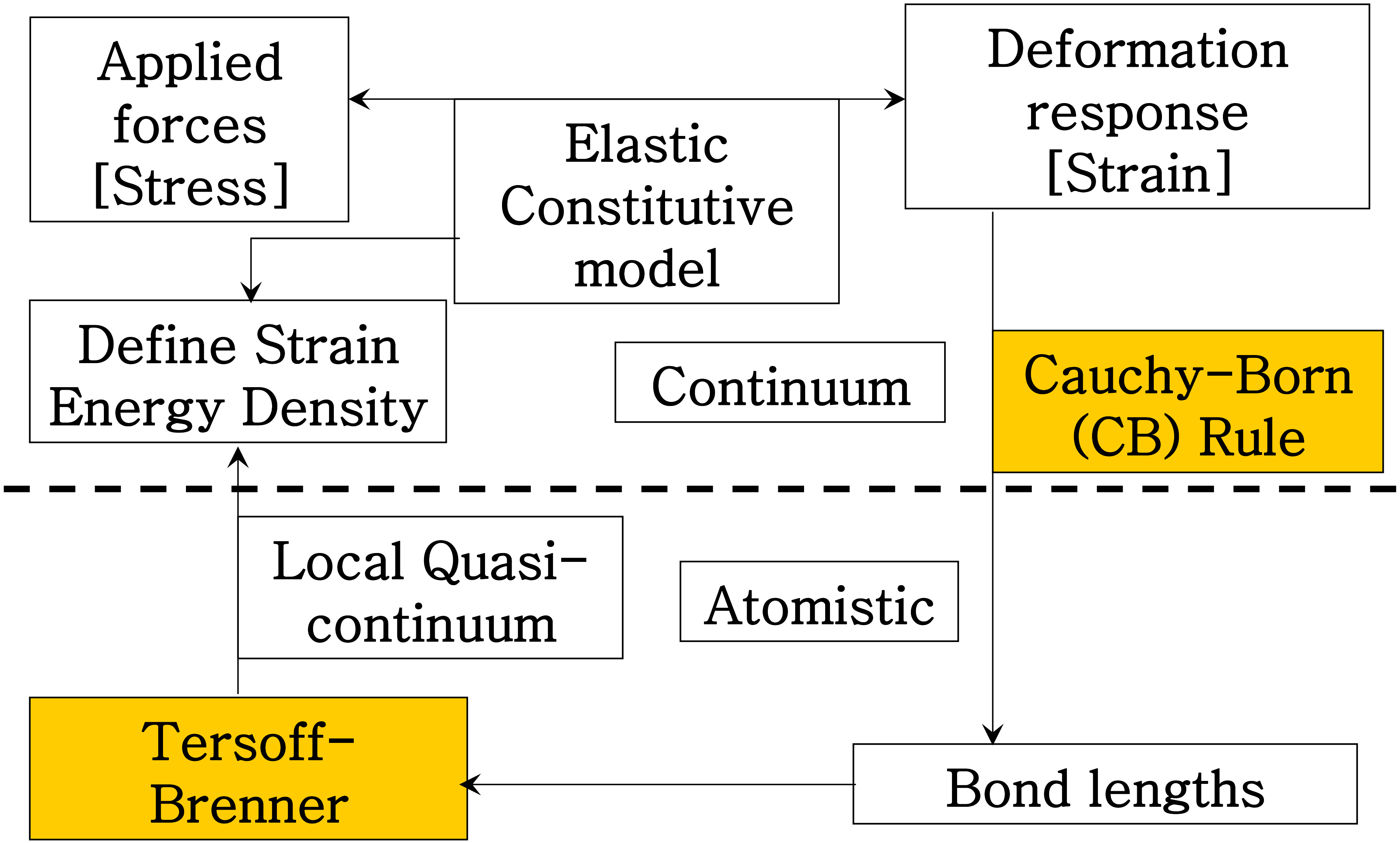
Lecture-1 Summary

- Carbon nanotube (CNT) nomenclature:
  - Chirality – chiral, armchair and zig-zag CNTs
  - Single-walled nanotubes (SWNTs), nanotube bundles, multi-walled nanotubes (MWNTs)
- Experiments on CNT electromechanical oscillators
- Mechanical modeling approaches for CNTs:
  - Multi-scale paradigms
  - Overview of present work on SWNTs
- Course outline

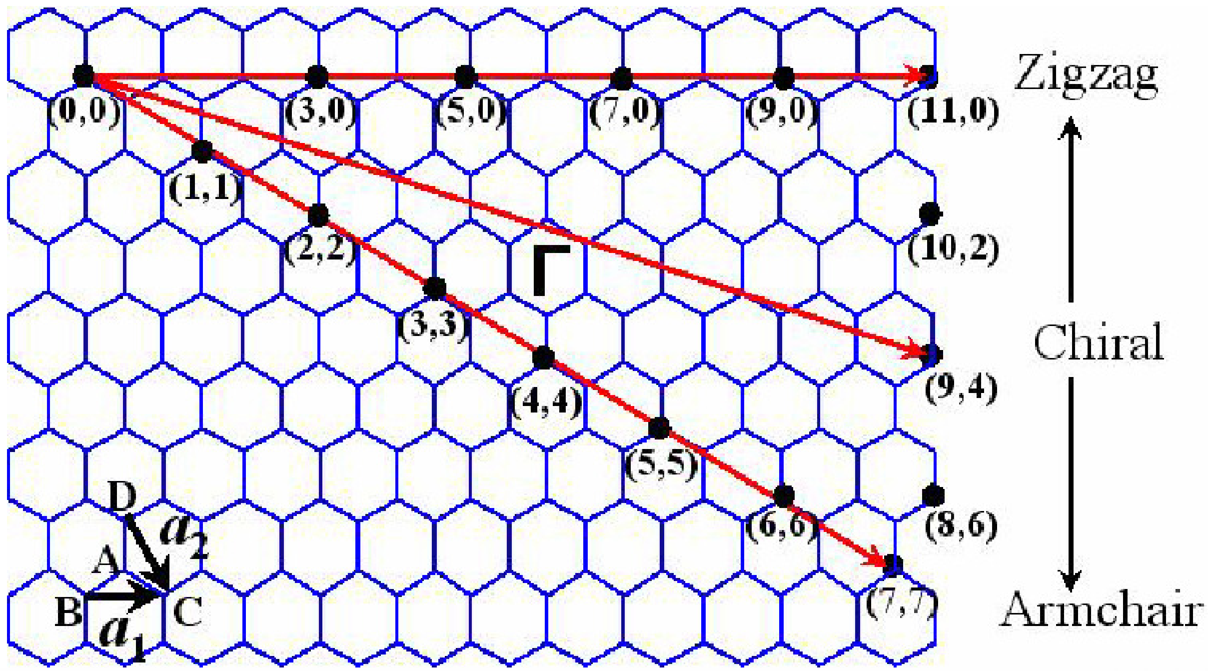
Local QC Approach: Overview

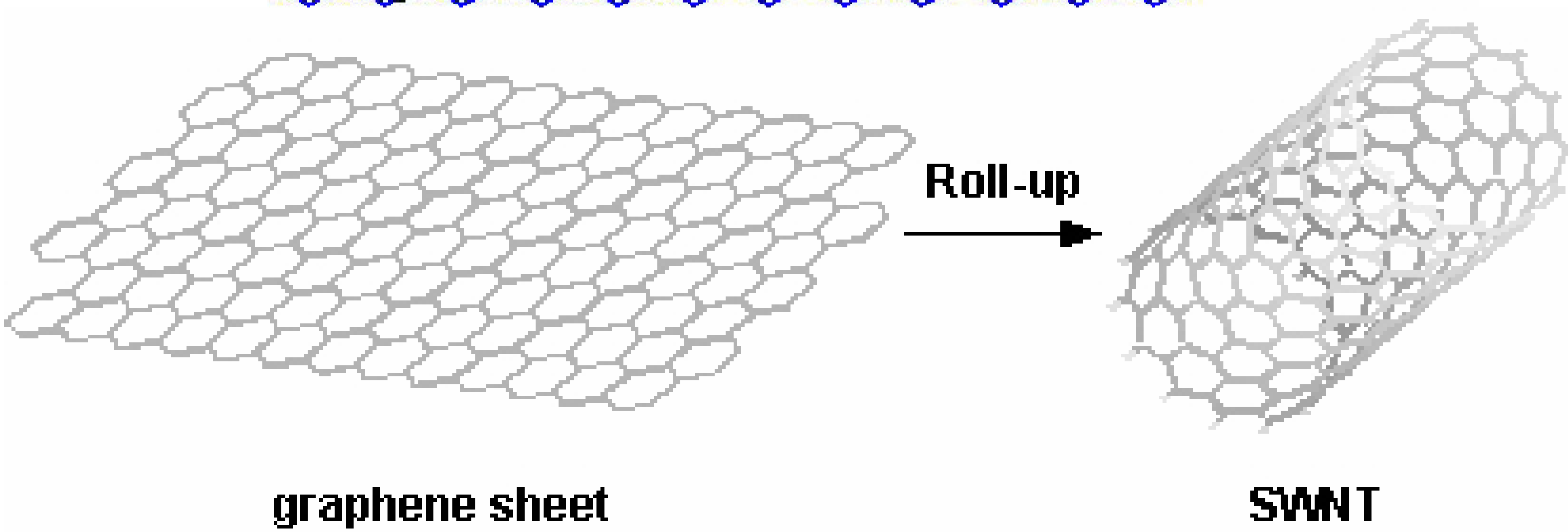


Lecture-2 Overview

- 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

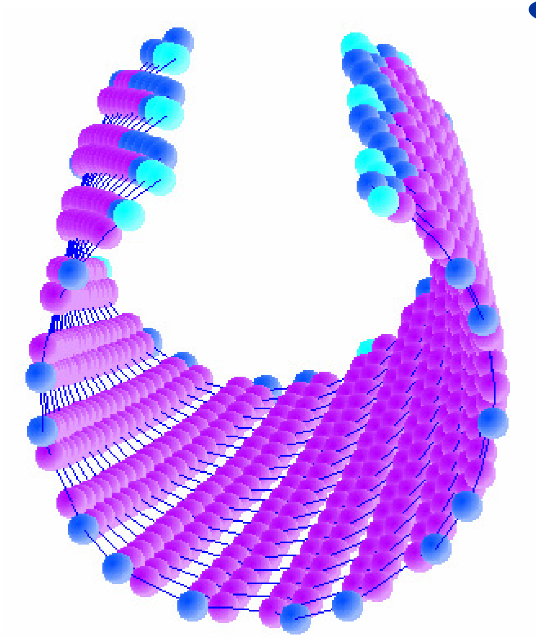
Hexagonal Graphene Lattice (n,m)→ SWNT

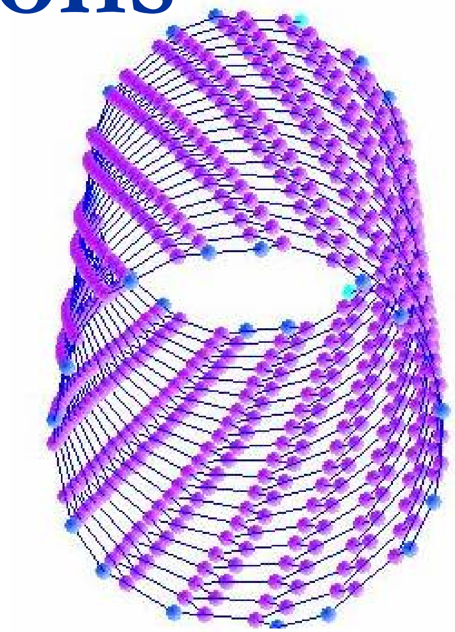




Structural Configurations

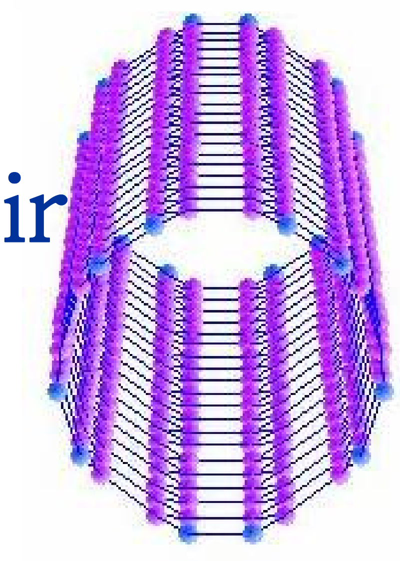
Roll-up

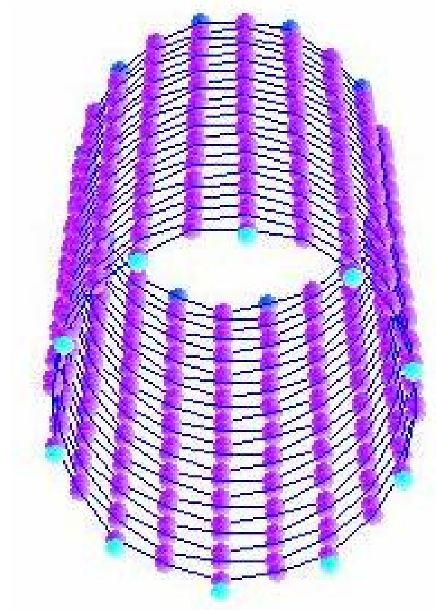




Chiral (9,6)

Armchair (5,5)





Zig-zag (10,0)

Tersoff-Brenner Interatomic Potential

$$V\left(a(i,j)\right)=V_R\left(a(i,j)\right)-\overline{B}(i,j)V_A\left(a(i,j)\right)$$

V_R → Repulsive term

$\overline{B}$ → Multi-body coupling term

V_A → Attractive term

a(i,j): Bond length between atoms 'i' and 'j'

$$V_R(a)=\frac{D^{(e)}}{S-1}\exp\left[-\sqrt{2S}\beta\left(a-R^{(e)}\right)\right]f_c(a)$$

$$V_A(a)=\frac{D^{(e)}S}{S-1}\exp\left[-\sqrt{2/S}\beta\left(a-R^{(e)}\right)\right]f_c(a)$$

$$f_c(a)=\begin{cases}1 & a<R^{(1)}\\ \frac{1}{2}\left\{1+\cos\left[\frac{\pi\left(a-R^{(1)}\right)}{R^{(2)}-R^{(1)}}\right]\right\} & R^{(1)}\le a\le R^{(2)}\\ 0 & a>R^{(2)}\end{cases}$$

Tersoff-Brenner (TB) Interatomic Potential

Multi−body coupling term $\overline{B}(i,j)=\frac{1}{2}\left[B(i,j)+B(j,i)\right]$

Where: $B(i,j)=\left[1+\sum_{k\neq i,j}G(\theta(i,j,k))\,f_c(a(i,k))\right]^{-\delta}$

With: $G(\theta)=a_0\left[1+\frac{{c_0}^2}{{d_0}^2}-\frac{{c_0}^2}{{d_0}^2+(1+\cos\theta)^2}\right]$

10 parameters with 2 sets of values:

Parameter	Value (set 1)	Value (set 2)
$D^{(e)}$	6.325 eV	6.00 eV
S	1.29	1.22
β	15 nm^{-1}	21 nm^{-1}
$R^{(e)}$	0.1315 nm	0.1390 nm
$R^{(1)}$	0.17 nm	0.17 nm
$R^{(2)}$	0.20 nm	0.20 nm
δ	0.80469	0.5
a_0	0.011304	0.00020813
${c_0}^2$	19^2	330^2
${d_0}^2$	2.5^2	3.5^2

Mapping Planar Graphene to SWNT

Chiral (circumferential) vector: $\mathbf{\Gamma} = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$

Circumference: $\Gamma = \sqrt{\mathbf{\Gamma}.\mathbf{\Gamma}}$

$$= \sqrt{n^2 a_1^{\ 2} + m^2 a_2^{\ 2} + nm\left(a_1^{\ 2} + a_2^{\ 2} - a_3^{\ 2}\right)}$$

Chiral angle: $\phi = \cos^{-1}\left(\dfrac{\mathbf{\Gamma}.\boldsymbol{a}_1}{\Gamma a_1}\right)$

Cylindrical atomic coordinates on the SWNT:

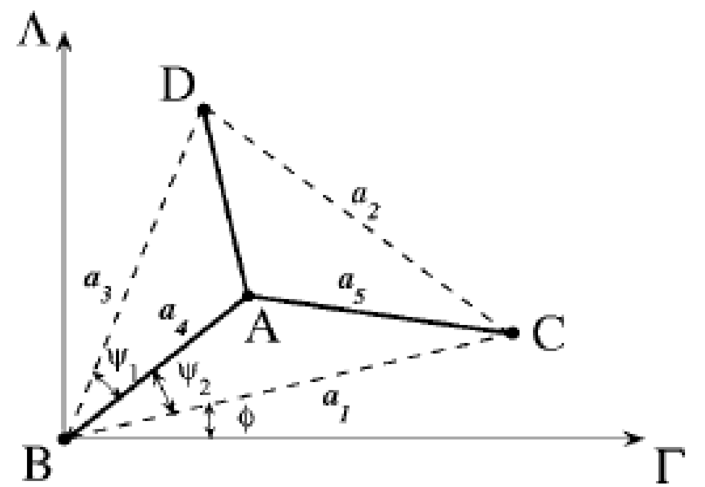
$$R(A) = R(B) = R(C) = R(D) = d/2 = \Gamma/2\pi$$

$$\Theta(A) = \frac{2a_4\cos\left(\psi_2 + \phi\right)}{d} \qquad Z(A) = a_4 \sin\left(\psi_2 + \phi\right)$$

$$\Theta(B) = 0 \qquad Z(B) = 0$$

$$\Theta(C) = \frac{2a_1\cos\left(\phi\right)}{d} \qquad Z(C) = a_1 \sin\left(\phi\right)$$

$$\Theta(D) = \frac{2a_3\cos\left(\psi_1 + \psi_2 + \phi\right)}{d} \qquad Z(D) = a_3 \sin\left(\psi_1 + \psi_2 + \phi\right)$$



Rep atom ‘A’ with nearest neighbors ‘B’, ‘C’ and ‘D’

Mapping Planar Graphene to SWNT

Bond length: $a^{(0)}(X,Y)=\sqrt{\frac{d^2}{2}\left[1-\cos\left(\Theta(Y)-\Theta(X)\right)\right]+\left(Z(Y)-Z(X)\right)^2}$

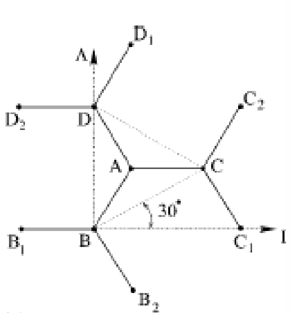
$$\text{where } X,Y \in \{A,B,C,D\}$$

Energy of rep atom ‘A’: $V=\frac{1}{2}\left[V\left(a(A,B)\right)+V\left(a(A,C)\right)+V\left(a(A,D)\right)\right]$

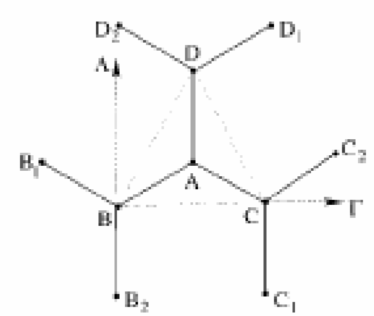
This is completely expressed in terms of parameters $\boldsymbol{a}_k$, k=1,2,3,4,5

These parameters can be obtained using: $\frac{\partial V}{\partial a_k}=0,\ k=1,2,3,4,5$

Additional lengths required by the TB interatomic potential:



Armchair

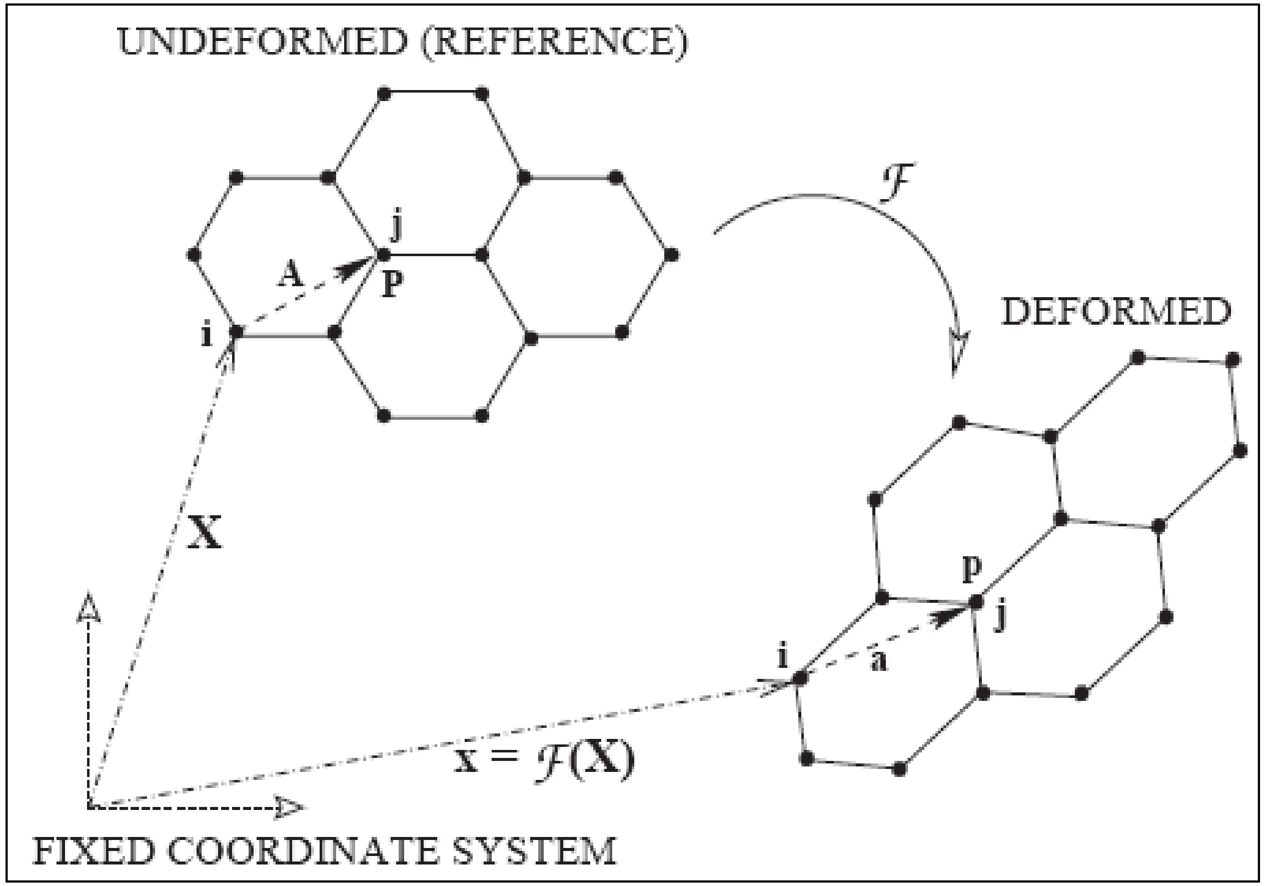


Zigzag

$$a(B,B_1)=a(C,A) \qquad a(D,D_2)=a(C,A)$$
$$a(B,B_2)=a(D,A) \qquad a(C,C_1)=a(D,A)$$
$$a(C,C_2)=a(B,A) \qquad a(D,D_1)=a(B,A)$$
$$a(A,B_1)=a(C,B) \qquad a(A,B_2)=a(D,B)$$
$$a(A,C_1)=a(D,C) \qquad a(A,C_2)=a(B,C)$$
$$a(A,D_1)=a(B,D) \qquad a(A,D_2)=a(C,D)$$

Cauchy-Born (CB) Deformation Rule

- i, j : carbon atoms
- $\mathcal{F}$: Deformation map
- **A** : Undef bond vector
- **a** : Deformed bond vector
- $\mathbf{a} = \mathcal{F}(\mathbf{X} + \mathbf{A}) - \mathcal{F}(\mathbf{X})$



- Expand RHS → Taylor series about **X,** with $\mathbf{F} = \nabla\mathcal{F}$,

$$\mathbf{a} = \mathbf{F}(\mathbf{X}) \cdot \mathbf{A} + \frac{1}{2!}\nabla\mathbf{F}(\mathbf{X}):(\mathbf{A} \otimes \mathbf{A}) + \frac{1}{3!}\nabla\nabla\mathbf{F}(\mathbf{X})\lozenge(\mathbf{A} \otimes \mathbf{A} \otimes \mathbf{A}) + \text{h.o.t}$$

Cauchy-Born (CB) Deformation Rule

- Deformed C–C bond vector: a, Undeformed bond vector: A, Continuum deformation gradient: F(X)

$$a = F(X).A$$

- CB Hypothesis: F(X) derived from continuum deformation – assumed to be uniform at the atomic scale
- Present work → Investigate applicability of the CB rule for *inhomogeneous* deformations.

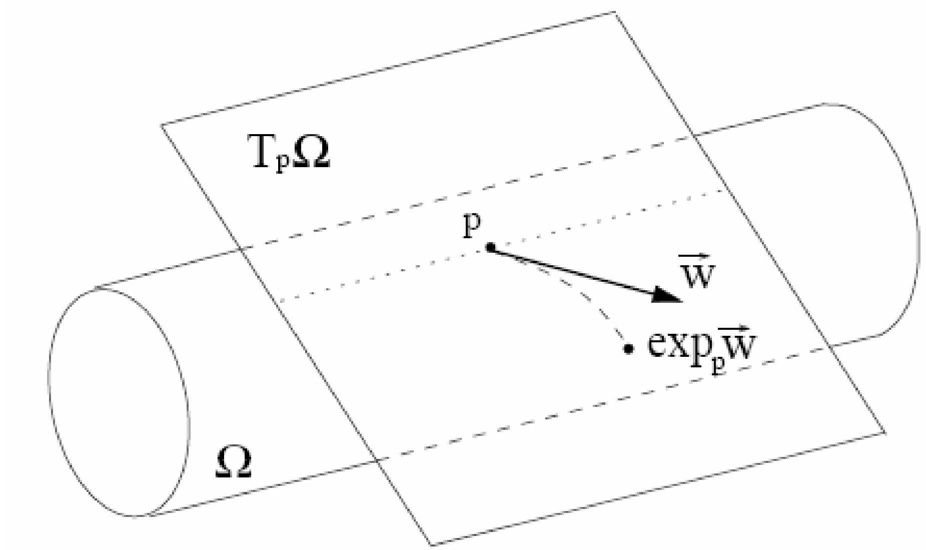
Key idea: Use Mean value theorem to obtain a location at which to evaluate F to get the infinite Taylor series

$$\boldsymbol{a} = \mathfrak{F}(\mathbf{X}+\mathbf{A}) - \mathfrak{F}(\mathbf{X})$$

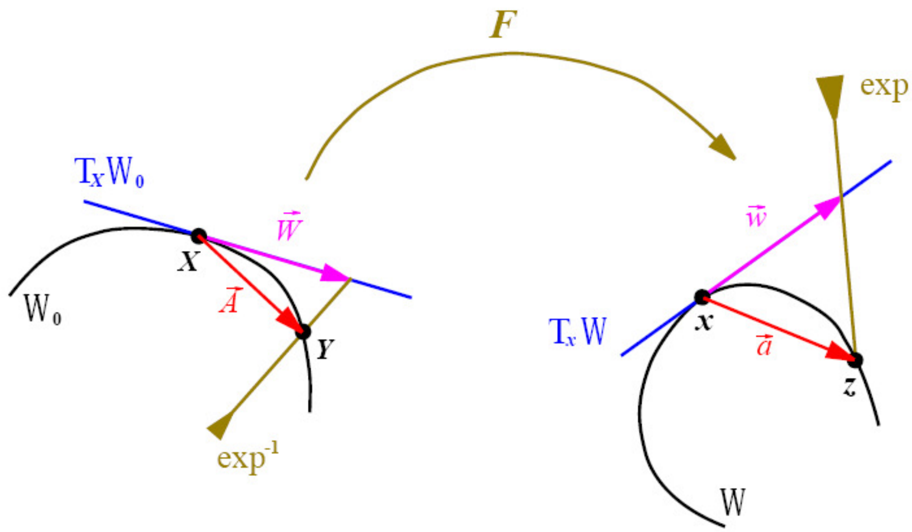
$$= \nabla\mathfrak{F}(\mathbf{X}_{\alpha}) \bullet \mathbf{A} = \mathbf{F}(\mathbf{X}_{\alpha}) \bullet \mathbf{A}$$

Curved Membrane Modification of CB

- Curved membranes: Continuum F(X) maps tangent space at X on manifold
- Exp Map modification (Geodesics) [Arroyo et al., 2002]
- Standard CB rule replaced by a composition of 3 operations:
  - ‘unwrap’ undeformed geodesic
  - apply CB rule
  - ‘wrap’ deformed geodesic



[Arroyo et al., 2002]

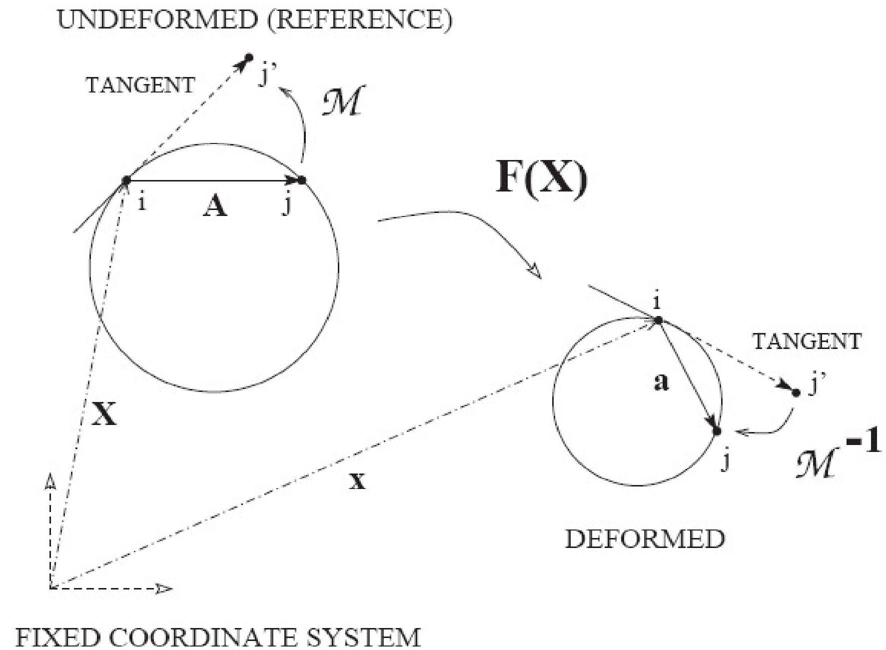


Born Rule: $\vec{a} = \mathbf{F}\,\vec{A}$

Proposed Rule: $\vec{a} = \exp_{\mathbf{x}} \circ \mathbf{F} \circ \exp_{\mathbf{X}}^{-1} \vec{A}$ $\qquad \vec{a} = \mathcal{F}_{\Phi} \vec{A}$

[Arroyo et al., 2002]

Bond Lengths



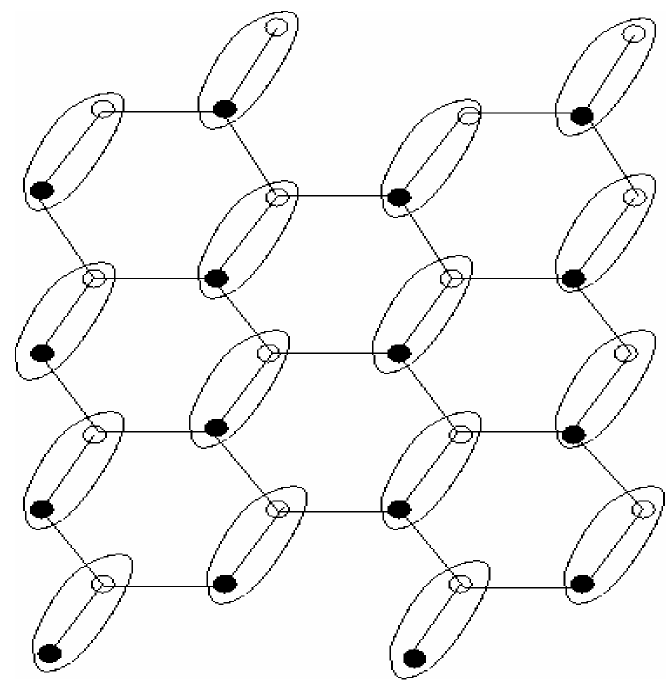
Using Exp Cauchy–Born rule:

$$\mathbf{a} = M^{-1}\mathbf{F}(\mathbf{X})M\mathbf{A}$$

Graphene:

Bravais multi-lattice [2 Sub-lattices]

Hexagonal Lattice + 2 basis atoms



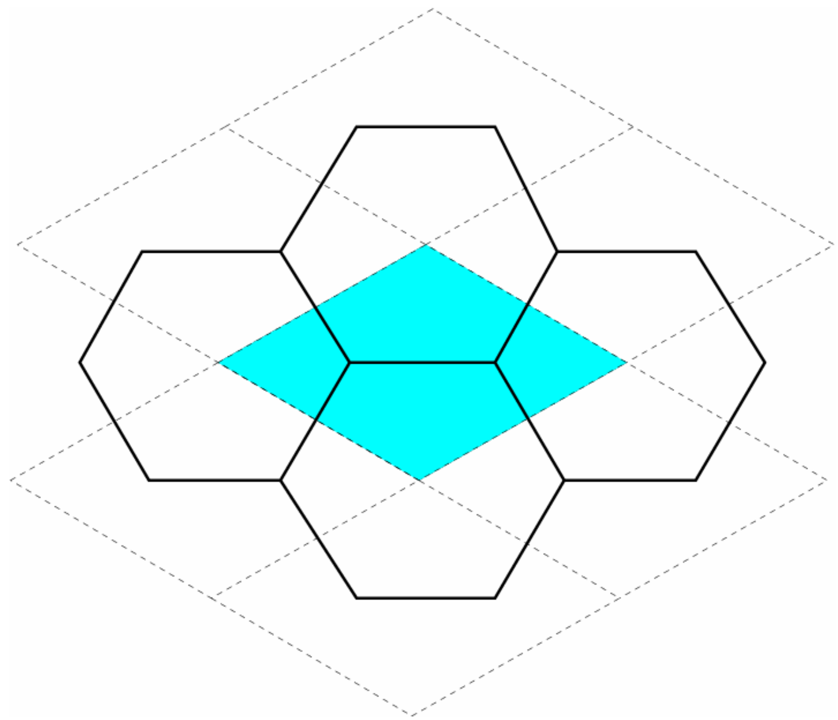
$$\mathbf{a}(i, j) = M^{-1}\mathbf{F}(\mathbf{X})M[\mathbf{A}(i, j) + \boldsymbol{\eta}]$$

when ‘i’ ,‘j’ lie on different sub-lattices,

and η = 0 otherwise

Local QC: Define Strain Energy Density

Shaded area → Rep unit cell of area $\boldsymbol{\Omega}_{\text{cell}}$ on a planar graphene sheet



$$W(\mathbf{E}, \boldsymbol{\eta}(\mathbf{E})) \equiv \hat{W}(\mathbf{E}) = \frac{\sum_{cell} V[a(i,j)\{\mathbf{E}\}]}{\boldsymbol{\Omega}_{cell}}$$

η chosen such that $\left.\dfrac{\partial W}{\partial \boldsymbol{\eta}}\right|_{\mathbf{E}} = \mathbf{0}$

η: Internal variable obtained numerically by energy minimization for each imposed deformation

Stress-Strain Relationship

Stress: Requires a wall thickness for definition – 3.35 Å (from literature) used in both QC and DFT

$$\mathbf{T} = \frac{d\hat{W}}{d\mathbf{E}} = \left.\frac{\partial W}{\partial \mathbf{E}}\right|_{\boldsymbol{\eta}} + \left.\frac{\partial W}{\partial \boldsymbol{\eta}}\right|_{\mathbf{E}} \cdot \frac{d\boldsymbol{\eta}}{d\mathbf{E}}$$

$$= \left.\frac{\partial W}{\partial \mathbf{E}}\right|_{\boldsymbol{\eta}}$$

Second Piola–Kirchhoff Stress Tensor

$$\left[\text{since, } \left.\frac{\partial W}{\partial \boldsymbol{\eta}}\right|_{\mathbf{E}} = \mathbf{0} \right]$$

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