Basic 8
Micro-Nano Materials Science and Analysis
-Atomistic simulations in materials science and engineering-

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    [Y. Kinoshita and N. Ohno, *Phys. Rev. B*, 82, 085433 (2010)]

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    [Y. Kinoshita, S. Hase, and N. Ohno, *Phys. Rev. B*, 80, 125114 (2009)]
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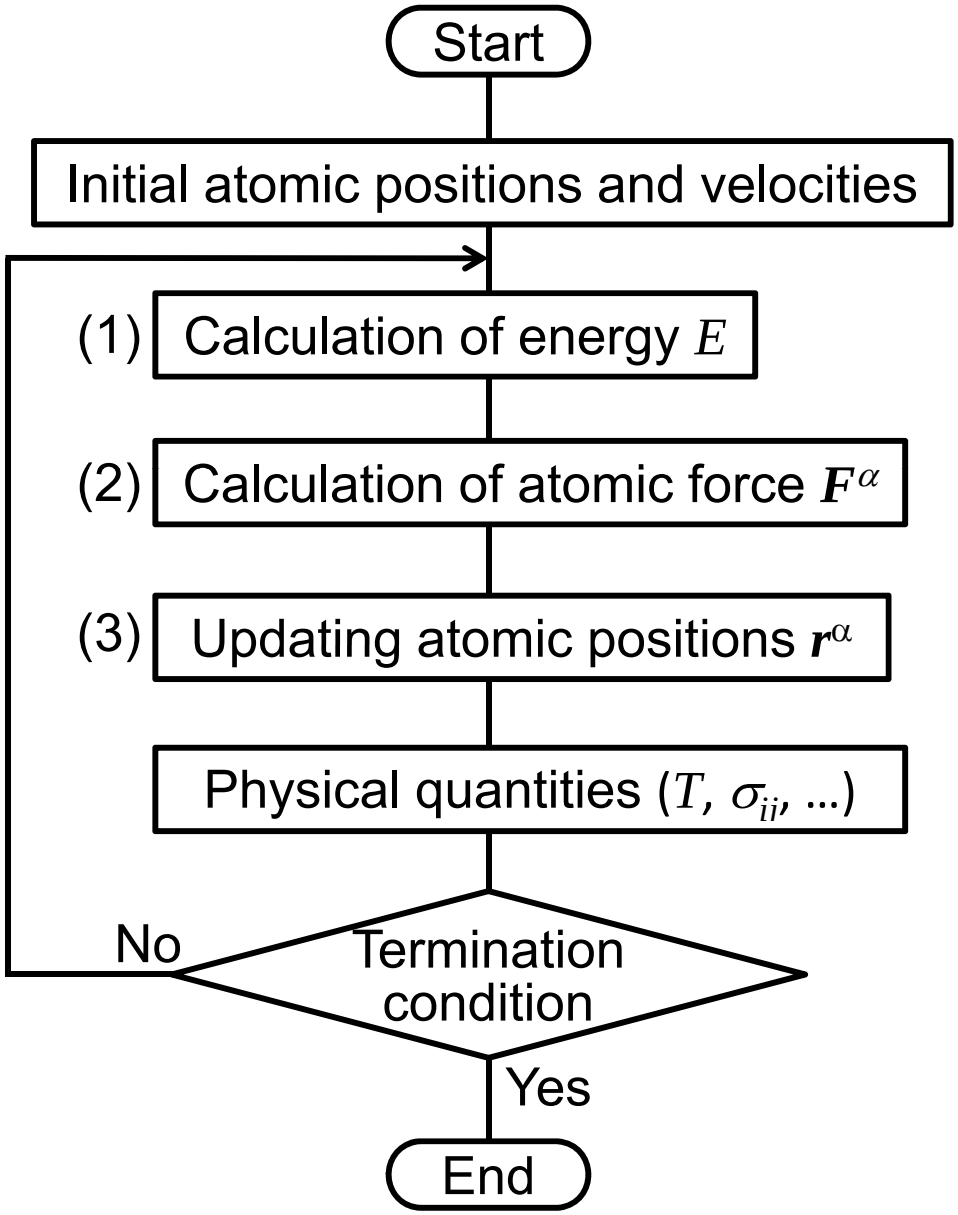
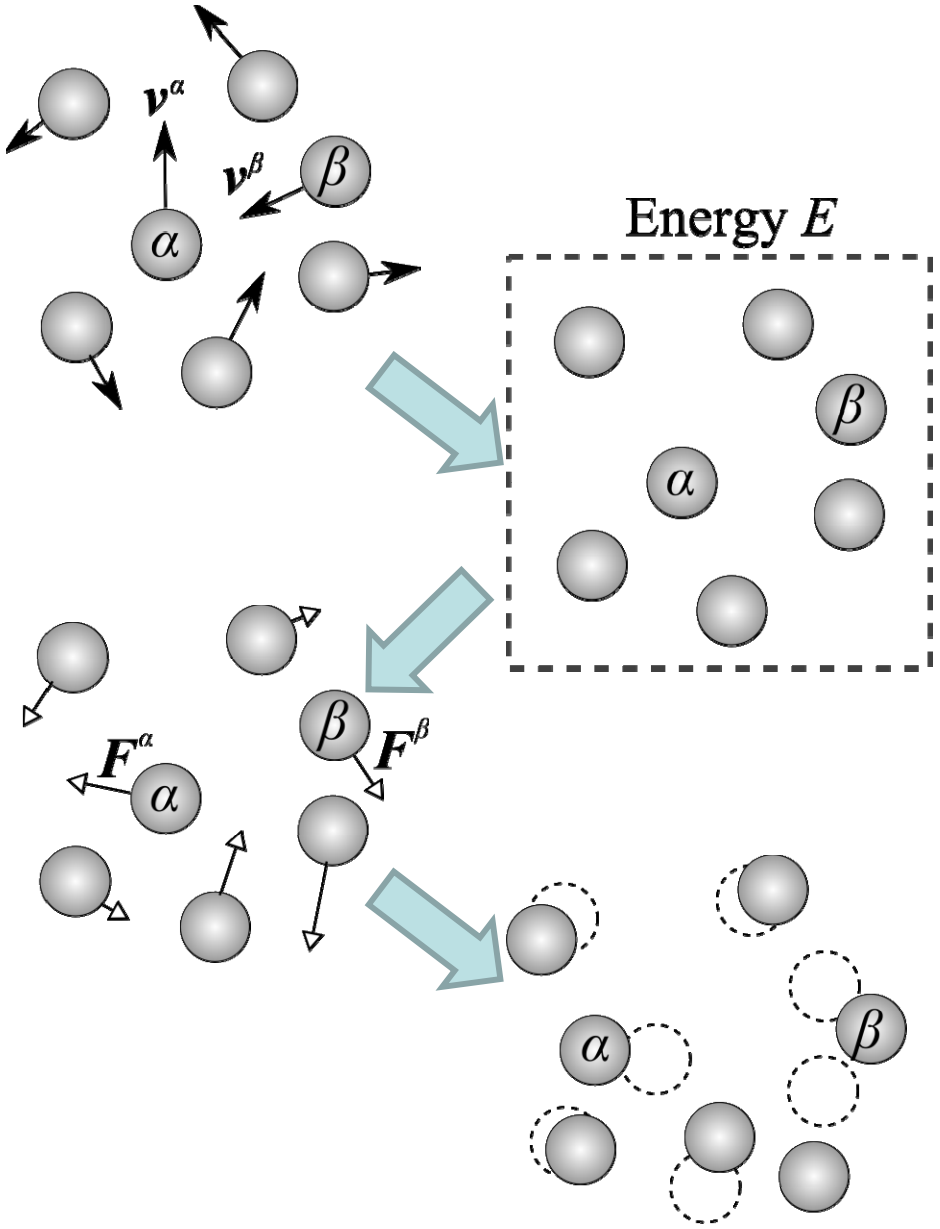
Outline and procedure of atomistic simulations





(1) Calculation of energy E

Non-empirical／First-principles

$$E = \int v_{\mathrm{ext}}(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r} + T[\rho(\boldsymbol{r})] + \frac{1}{2}\int \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}'d\boldsymbol{r} + E_{\mathrm{xc}}[\rho(\boldsymbol{r})]$$

$\rho(\boldsymbol{r})$: Charge density

$v_{\mathrm{ext}}(\boldsymbol{r})$: External field

$T[\rho(\boldsymbol{r})]$: Kinetic energy

$E_{\mathrm{xc}}[\rho(\boldsymbol{r})]$: Exchange-correlation energy

- Based on quantum mechanics
- High accuracy
- High computational cost

Empirical method

$$E = \sum_{\alpha}\sum_{\beta}\phi(r^{\alpha\beta}) \quad \text{(2-body)}$$

$$E = \sum_{\alpha}\sum_{\beta}\sum_{\gamma}\phi(r^{\alpha\beta}, r^{\alpha\gamma}, \theta^{\alpha\beta\gamma}) \quad \text{(3-body)}$$

$r^{\alpha\beta}$: Distance between atom α and β

$\theta^{\alpha\beta\gamma}$: Angle among atom α, β, and γ

- Based on empirical potential
- Low accuracy
- Low computational cost

(2) Calculation of atomic force F^{α}

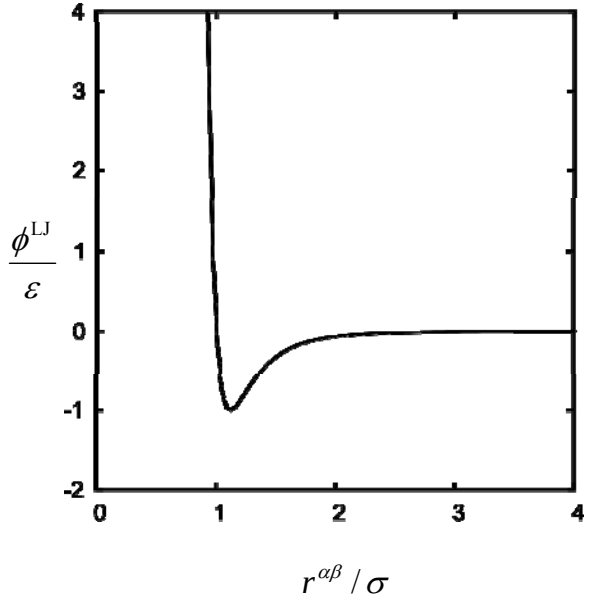
$$\boldsymbol{F}^{\alpha} = -\nabla E, \qquad F_i^{\alpha} = -\frac{\partial E}{\partial r_i^{\alpha}}$$

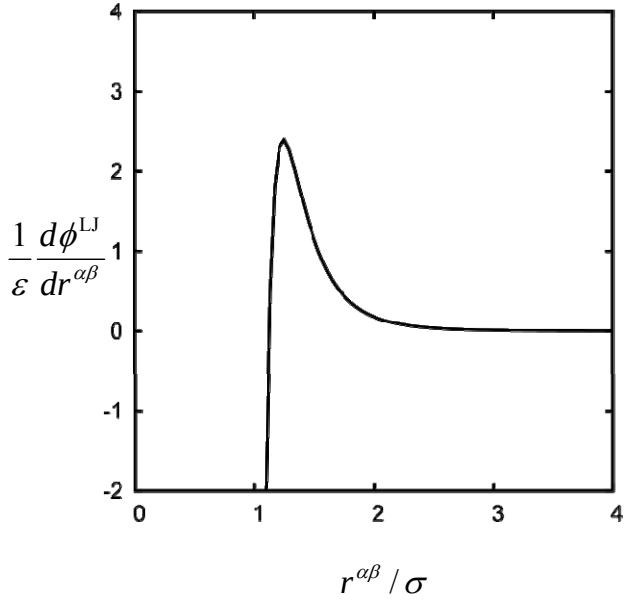
(α : Index of atoms, i : x-, y-, or z-coordinate)

Ex) Lennard-Jones potential (ε, σ : Material constant)

$$\phi^{\mathrm{LJ}}(r^{\alpha\beta}) = 4\varepsilon\left[\left(\frac{\sigma}{r^{\alpha\beta}}\right)^{12} - \left(\frac{\sigma}{r^{\alpha\beta}}\right)^{6}\right], \qquad \frac{d\phi^{\mathrm{LJ}}}{dr^{\alpha\beta}} = -\frac{4\varepsilon}{r^{\alpha\beta}}\left[12\left(\frac{\sigma}{r^{\alpha\beta}}\right)^{12} - 6\left(\frac{\sigma}{r^{\alpha\beta}}\right)^{6}\right]$$

$$E = \frac{1}{2}\sum_{\alpha}\sum_{\beta\neq\alpha}\phi^{\mathrm{LJ}}(r^{\alpha\beta}), \qquad F_i^{\alpha} = -\frac{\partial E}{\partial r_i^{\alpha}} = -\frac{\partial E}{\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial r_i^{\alpha}} = -\sum_{\beta\neq\alpha}\frac{d\phi^{\mathrm{LJ}}}{dr^{\alpha\beta}}\frac{r_i^{\alpha} - r_i^{\beta}}{r^{\alpha\beta}}$$





(3) Updating atomic positions

Molecular Mechanics

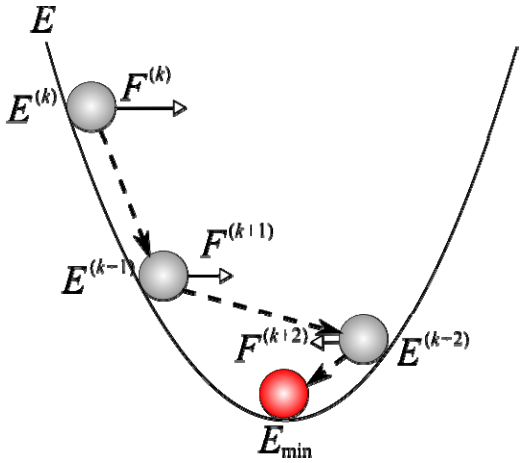
- Energy minimization by an optimization algorithm
- Final (converged) atomic position is important

Ex) Steepest descent method

$$E = E(\boldsymbol{r}), \quad \boldsymbol{r} = [\boldsymbol{r}^{\alpha}, \boldsymbol{r}^{\beta}, \cdots]$$

$$\boldsymbol{r}^{(k+1)} = \boldsymbol{r}^{(k)} - a\nabla E^{(k)}$$

$$= \boldsymbol{r}^{(k)} + a\boldsymbol{F}^{(k)}$$

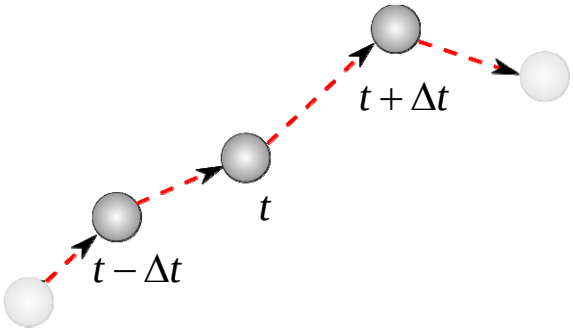


Molecular Dynamics

- Numerical integration of the equation of motion
- Atomic trajectory is important

Ex) Verlet algorithm

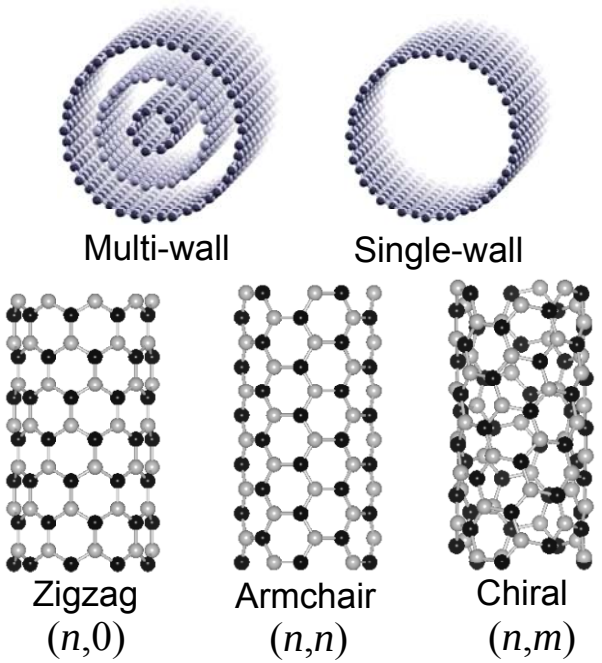
$$\boldsymbol{r}^{\alpha}(t+\Delta t) = 2\boldsymbol{r}^{\alpha}(t) - \boldsymbol{r}^{\alpha}(t-\Delta t) + \frac{\boldsymbol{F}^{\alpha}(t)}{m^{\alpha}}(\Delta t)^2$$



Example of atomistic simulations ~backgrounds~

- Boron nitride nanotube (BNNT)
  - 1994 : Theoretical prediction (A. Rubio et al., *PRB*, *EPL*)
  - 1995 : Experimental synthesis (N. G. Chopra et al., *Science*)

- Structure
  - Multi-wall (MW) > Single-wall (SW)
  - Zigzag > Armchair, Chiral
  - Interwall spacing : 0.33-0.34 nm



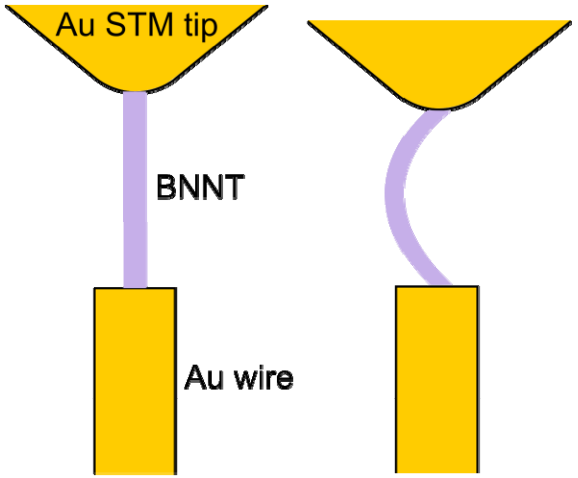
- Properties
  - High mechanical strength
  - High thermochemical stability
  - Electrically insulating, unlike carbon nanotubes

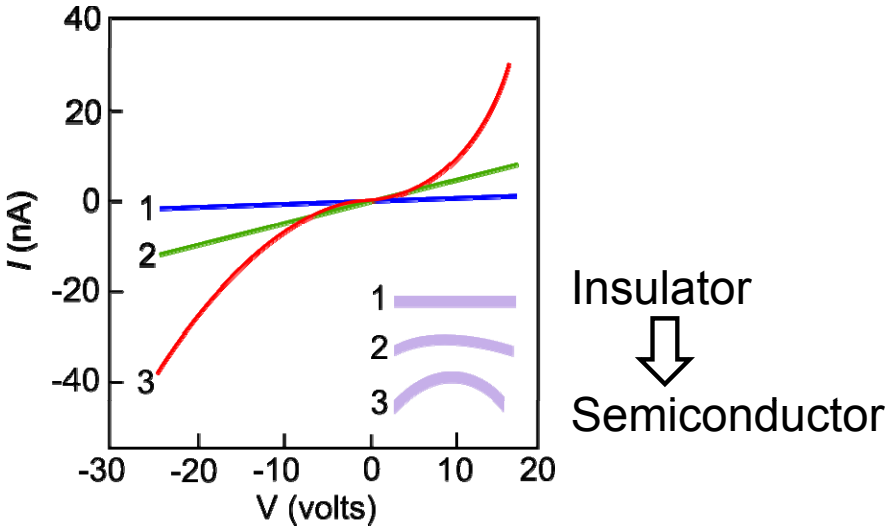
    independent of diameters, chiralities and the number of walls

    ⇨ Nanocoatings for conductive nanowires, nanotubes etc.

Example of atomistic simulations ~backgrounds~

- Bending (experiment) Bai et al., *Nano Lett.*, **7**, 632 (2007)





– Deformation-induced electronic changes:

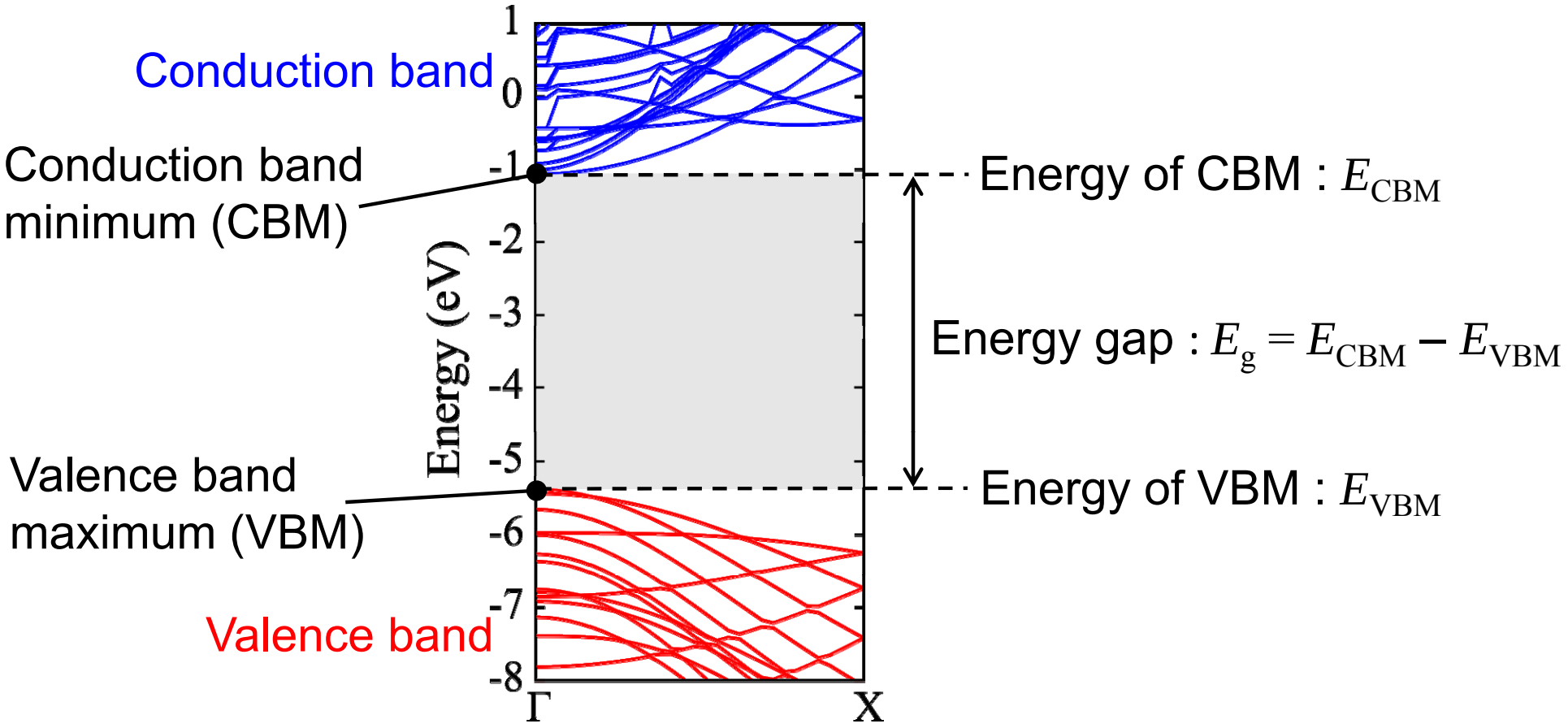
Mechanism? Deformation modes? Feasibility?

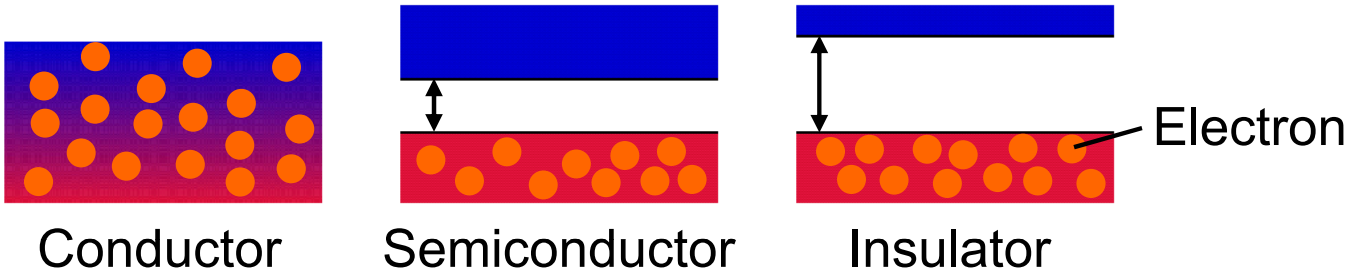
This work:

① Electronic structures of SWBNNTs subjected to tension, torsion, and flattening

② Flattening-induced electronic changes in MWBNNTs

Example of atomistic simulations ~backgrounds~



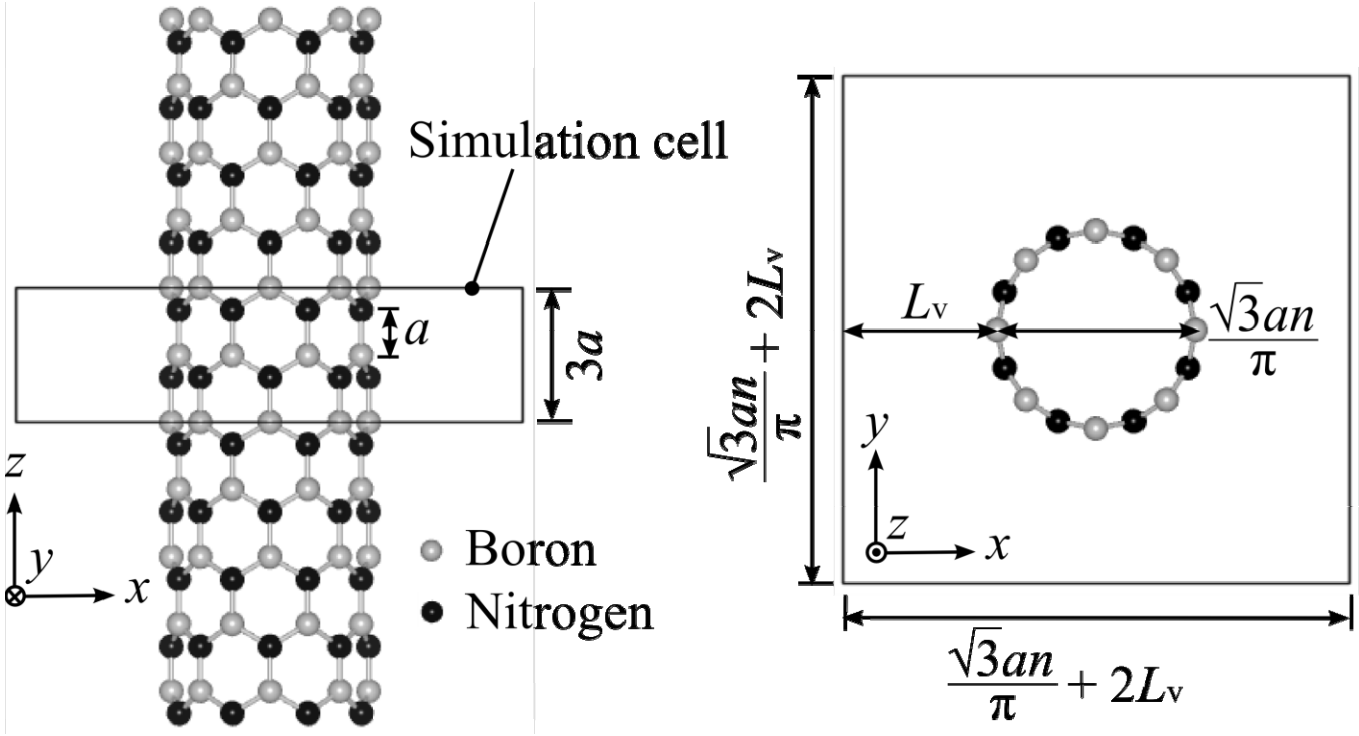


① Electronic structures of SWBNNTs subjected to tension, torsion, and flattening

Y. Kinoshita and N. Ohno, *Phys. Rev. B*, 82, 085433 (2010)

Simulation model

- $(n,0)$ zigzag, $n = 6, 8, 10$



a : Nearest interatomic distance = 0.145 nm

L_v : Length of vacuum region = 0.5 nm

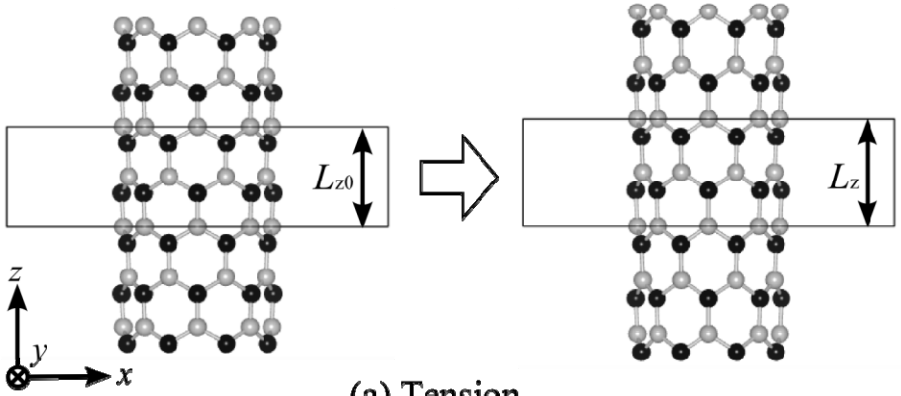
Simulation procedure

- Deformation analyses

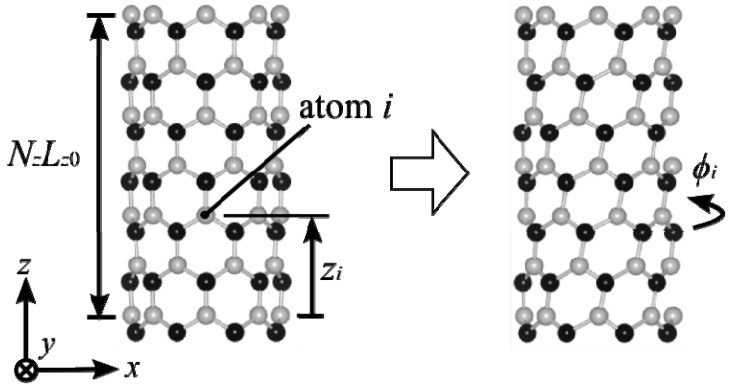
Tensile strain $\varepsilon_{zz} = \dfrac{L_z - L_{z0}}{L_{z0}}$

Specific angle of twist (deg/nm) $\theta = \dfrac{360}{nN_z L_{z0}}$

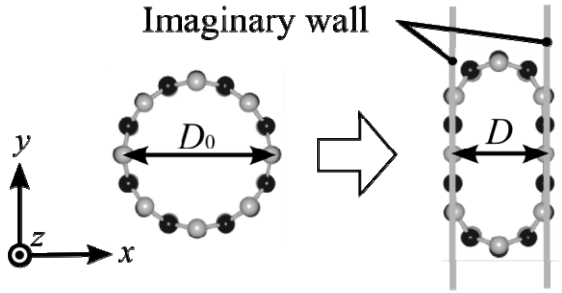
Flattening ratio $\eta = \dfrac{D_0 - D}{D_0}$



(a) Tension



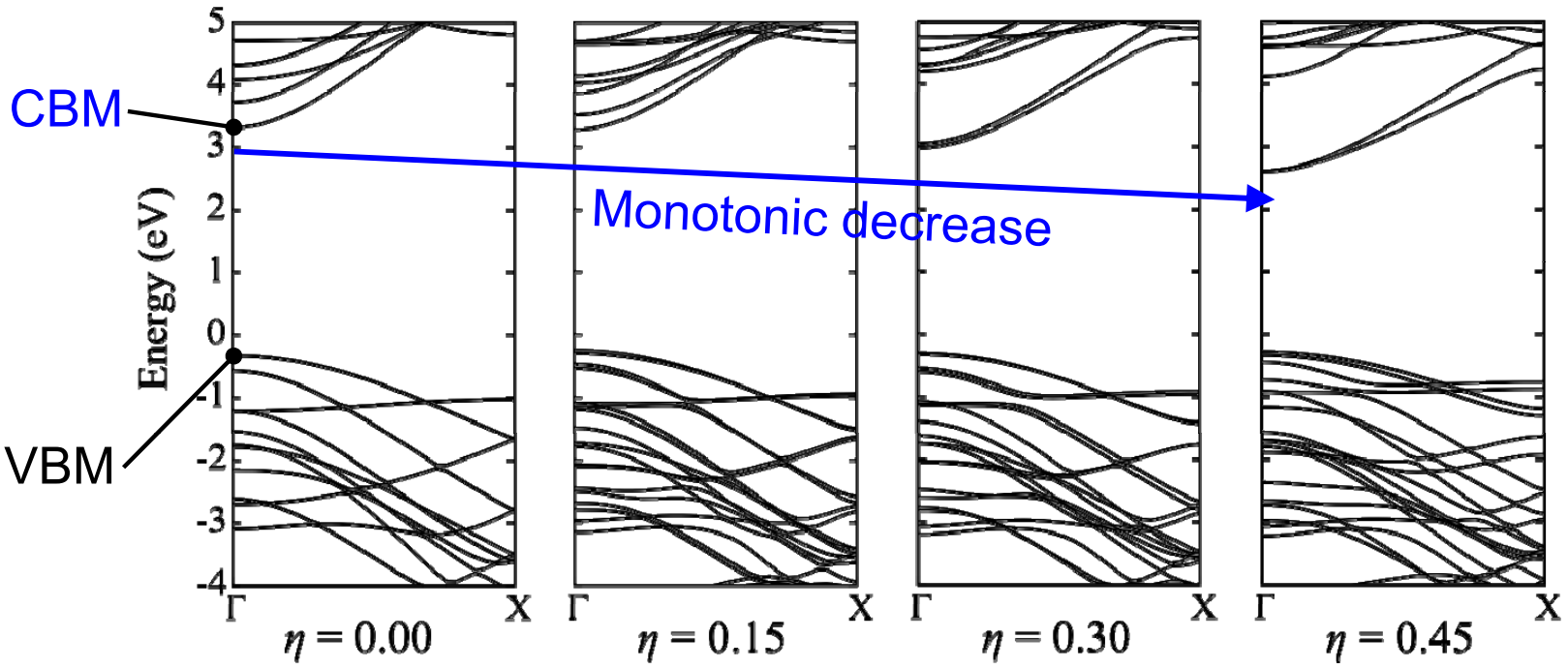
(b) Torsion



(c) Flattening

- Analytical condition
  - First-principles
  - DFT-GGA (PW91)
  - Ultrasoft pseudopotential
  - Cut-off energy : 350 eV
  - k-points: 30 points (Γ-X)

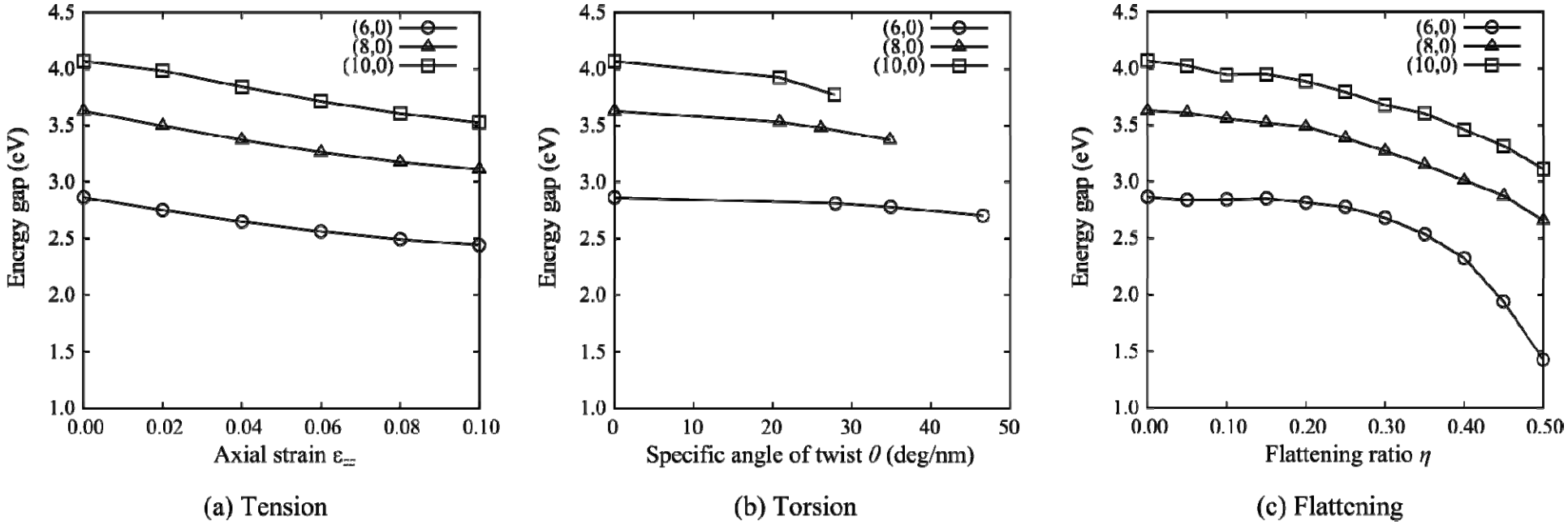
Energy band structure of (8,0) under flattening



- VBM and CBM are located at the Γ point
- Decrease in CBM energy ⇨ Decrease in the energy gap

※ Monotonic decrease in E_{CBM} also under tension & torsion

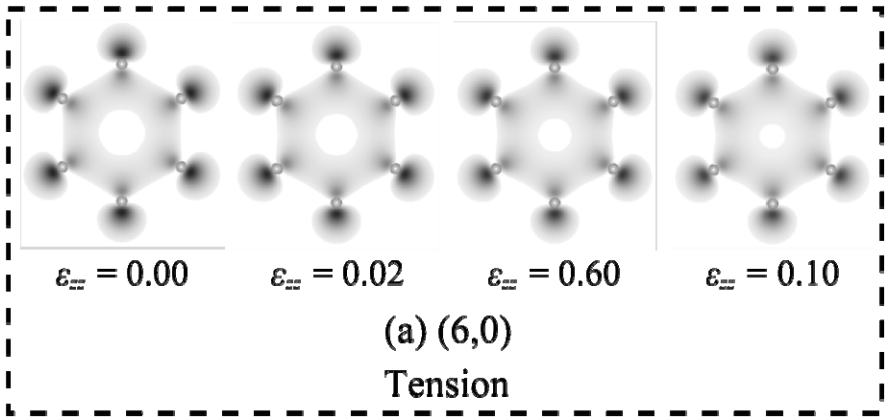
Change in the energy gap

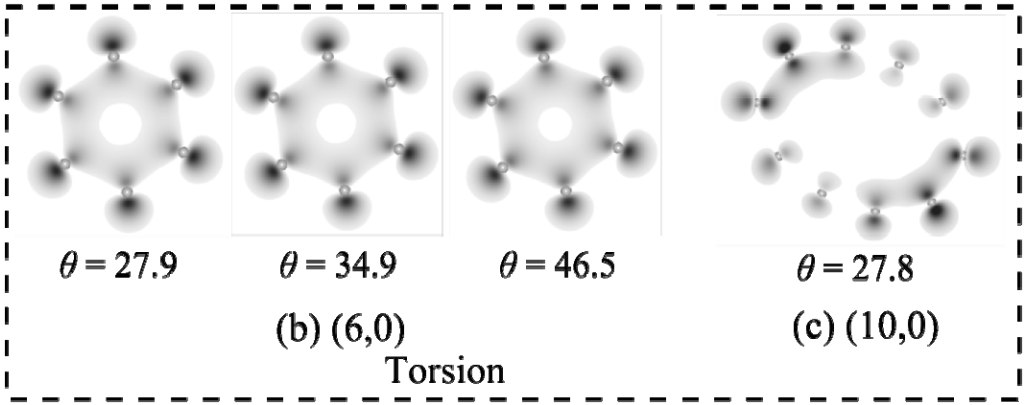


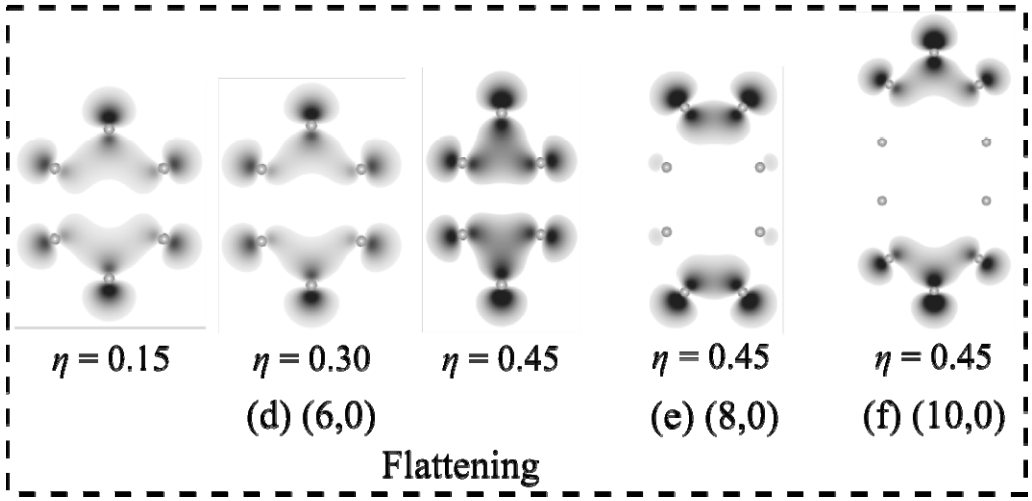
(a) Tension (b) Torsion (c) Flattening

- Tension and torsion
  - The energy gap decreases almost linearly.
  - The rate of decrease hardly depends on the diameter
- Flattening
  - The energy gap decreases quadratically or exponentially
  - The amount of decrease significantly depends on the diameter
  - A few times larger decrease in E_{gap} than tension and torsion

CBM charge density

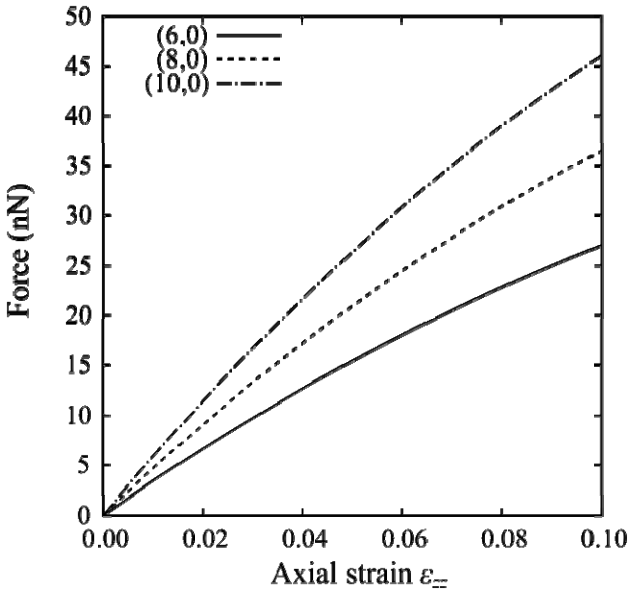




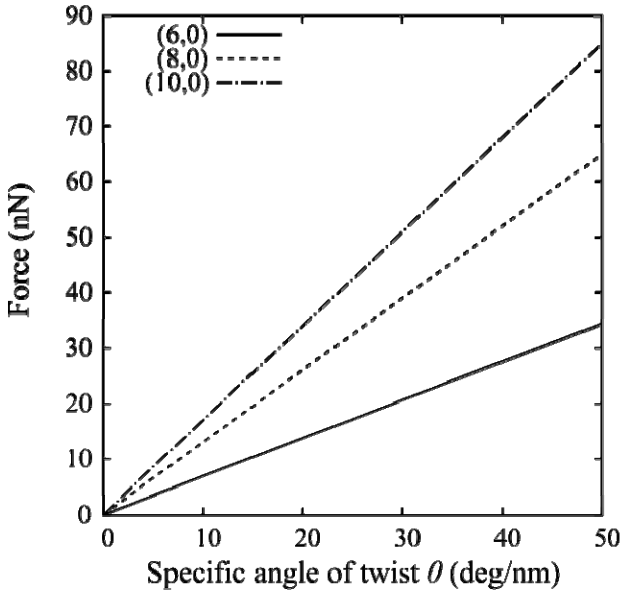


- Bond formation between neighboring boron atoms
  ⇨ Decrease in CBM energy
- Bond strength:
  Flattening > Tension, Torsion

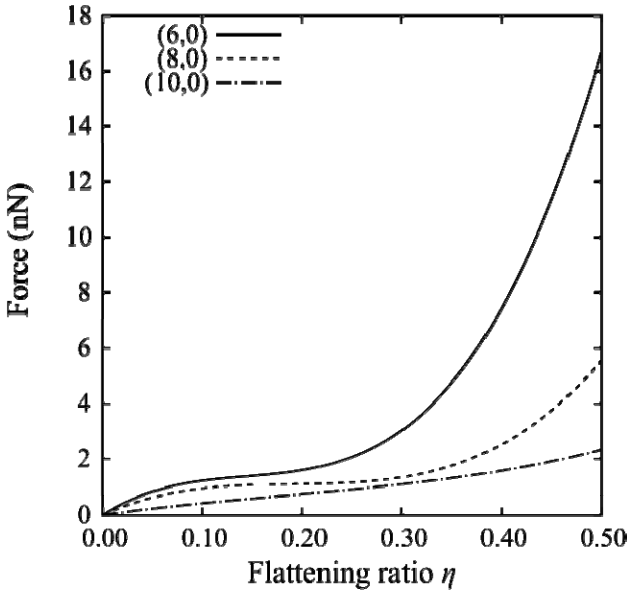
Deformation force



(a) Tension



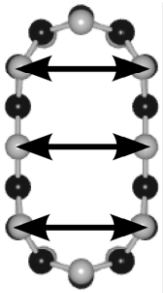
(b) Torsion



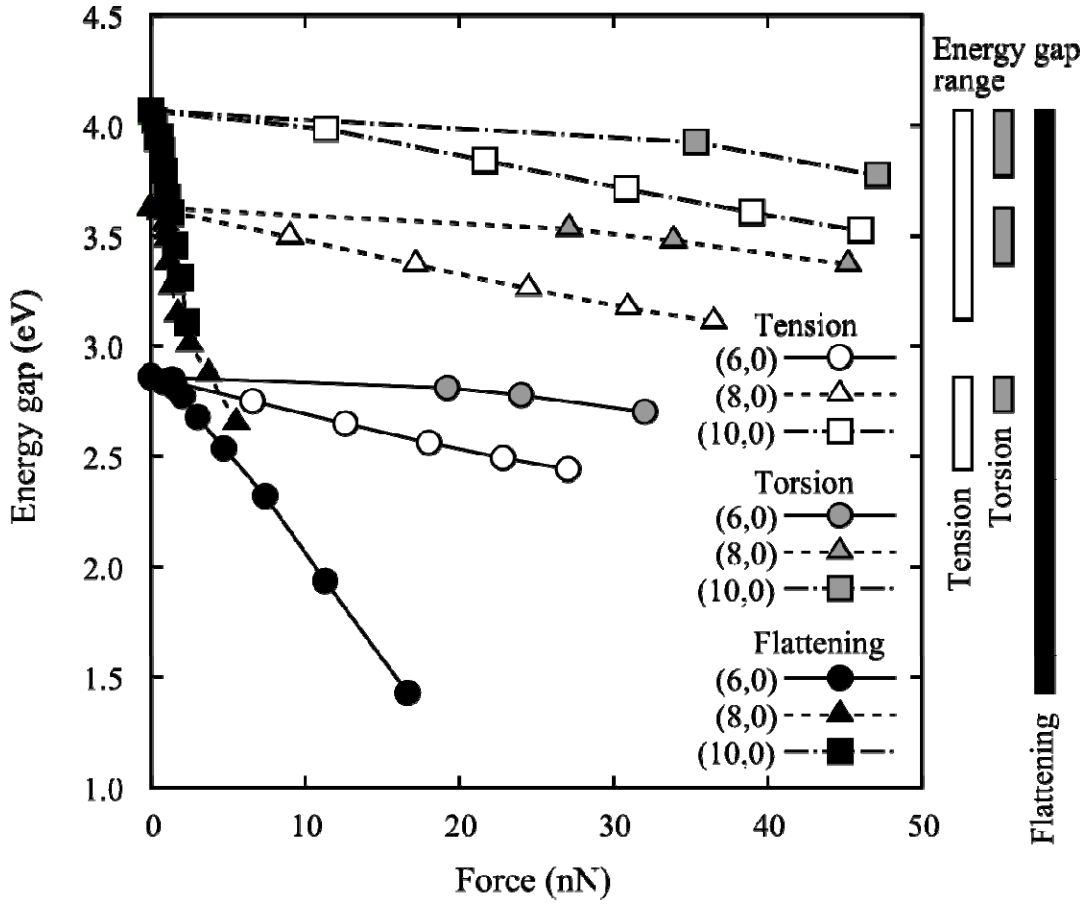
(c) Flattening

- Required force : Flattening << Tension, Torsion
- Forces rapidly increase later under flattening

Repulsive force



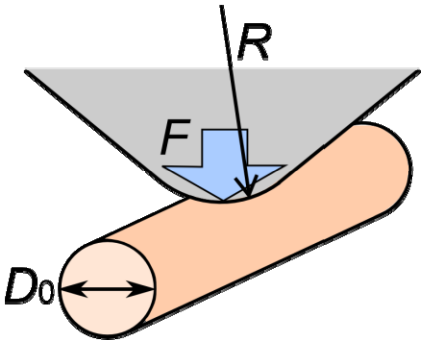
Energy gap vs. Deformation force



- Flattening with a force smaller than that applied for tension or torsion leads to the larger decrease in E_{gap}
- Flattening offers a larger obtainable range of E_{gap} than tension and torsion

Feasibility of flattening BNNTs

- Flattening of CNTs by AFM tip Barboza et al., *PRL*, **102**, 025501 (2009)



$$\frac{FD_0^{3/2}}{(2R)^{1/2}} = \frac{\alpha}{(1-\eta)^{3/2}}\left[\sqrt{2\eta+\eta^2} + \tan^{-1}\left(\sqrt{\frac{\eta}{1-\eta}}\right)\right]$$

F : Force R : AFM tip radius D_0 : Tube diameter

α : const. $= 1.2\times10^{-18}$ [J] η : Flattening ratio

- When $\eta = 0.4,\ R = 30$ nm
  - (6,0) CNT: $F = 15.4$ N/m (Barboza et al.)
  - (6,0) BNNT: $F = 16.8$ N/m (This work)

Flattening BNNTs is technically feasible.

Summary ①

Electronic structures of (n,0) SWBNNTs under tension, torsion, and flattening have been investigated by first-principles.

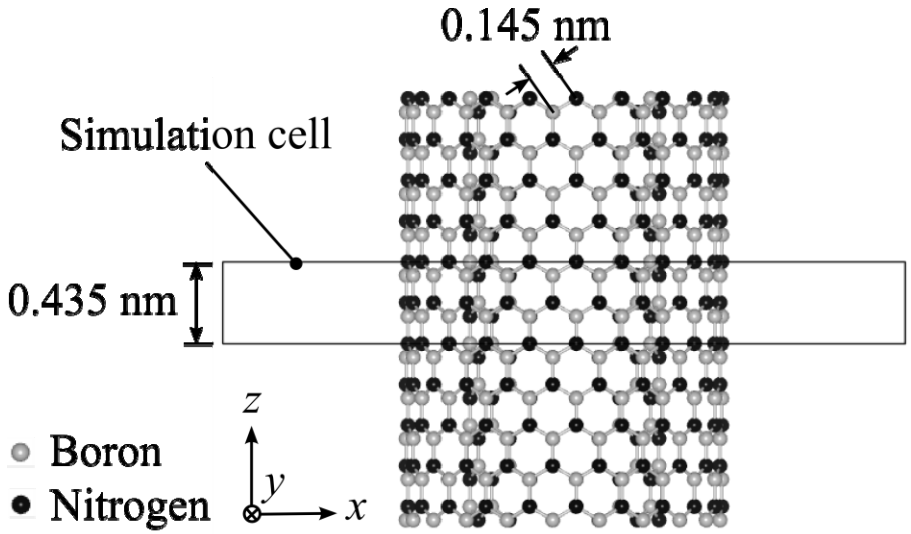
- Tension, torsion, and flattening decrease the energy gaps of SWBNNTs.
- Flattening with a force smaller than that applied for tension or torsion causes a larger decrease in the energy gap.
- The force required for flattening SWBNNTs is not unrealistic.

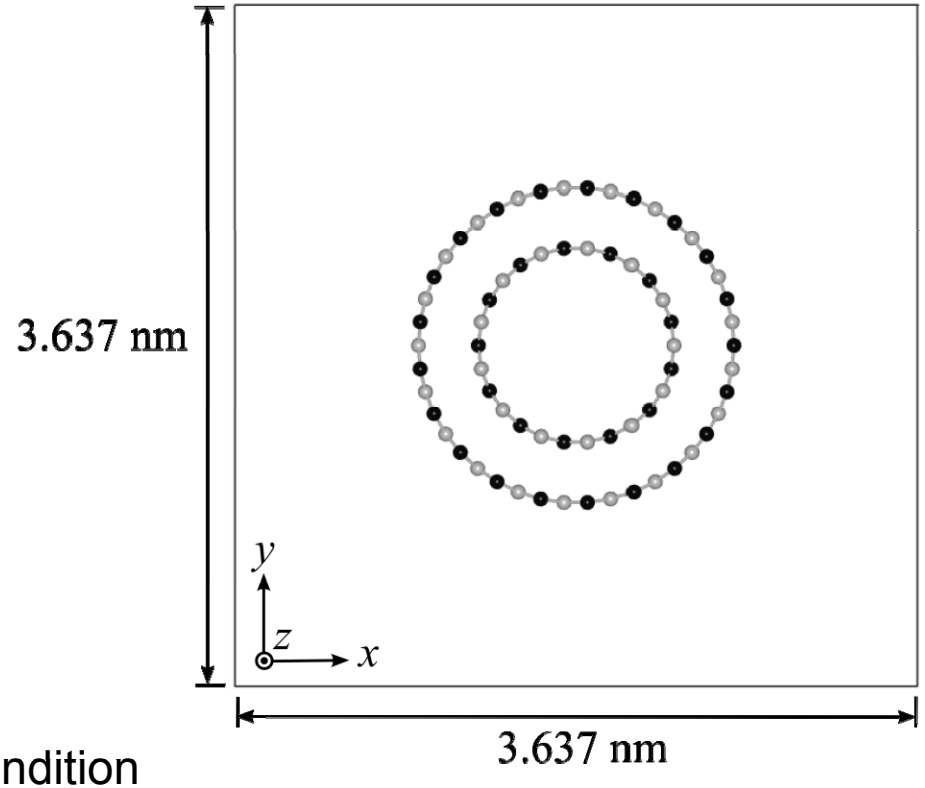
②Flattening-induced electronic changes in MWBNNTs

Y. Kinoshita, S. Hase, and N. Ohno, *Phys. Rev. B*, 80, 125114 (2009)

Simulation model

- $(n,0)$ zigzag, $n^{i+1} - n^{i} = 8$, i : i-th tube from the innermost
  → most stable (S. Okada et al., *PRB*, **65**, 165410 (2002))
  - Single-wall (SW) : (5,0), (13,0), (21,0)
  - Double-wall (DW) : (5,0)@(13,0), (13,0)@(21,0)
  - Triple-wall (TW) : (5,0)@(13,0)@(21,0)

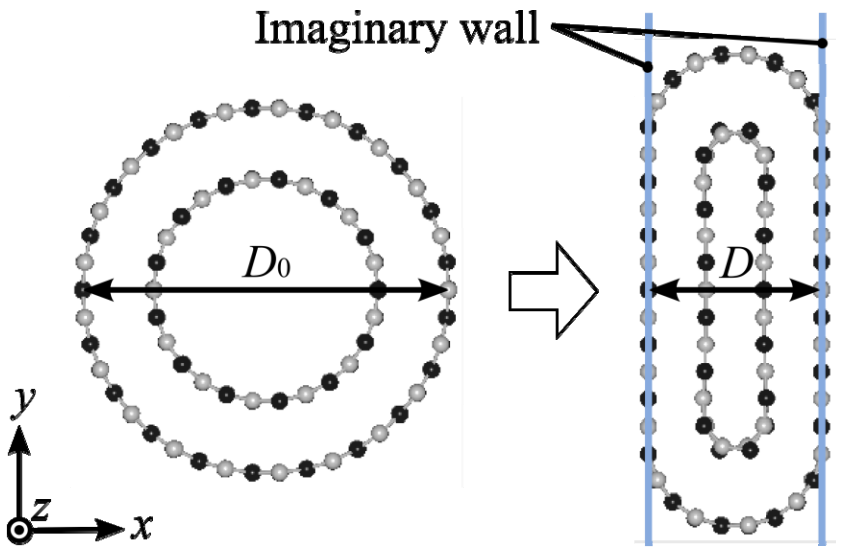




※Three-dimensional periodic boundary condition

Simulation procedure

- Flattening deformation
  - Equilibrium condition
    - Atomic force < 0.01 eV/Å
    - Stress σ_{zz} < 0.01 GPa
  - Under flattening
    - Atomic force < 0.01 eV/Å
    - Strain ε_{zz} = 0



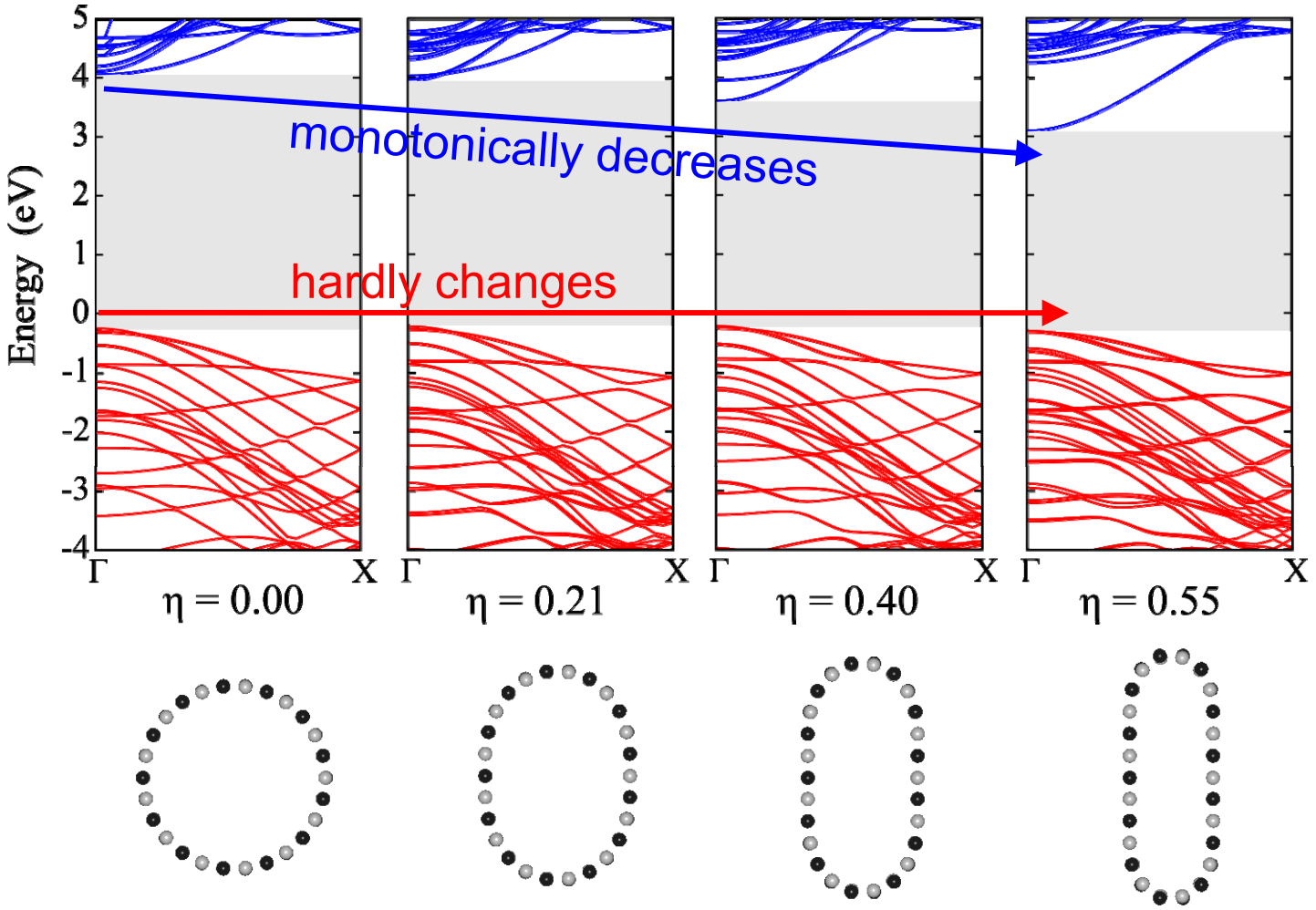
- Analytical condition
  - First-principles
  - DFT-GGA (PW91)
  - Ultrasoft pseudopotential
  - Cut-off energy : 350 eV
  - k-points: 1 x 1 x 4

Flattening ratio : $\eta = \dfrac{D_0 - D}{D_0}$

D_0 : Diameter of the outermost tube at equilibrium

D : Distance between imaginary walls

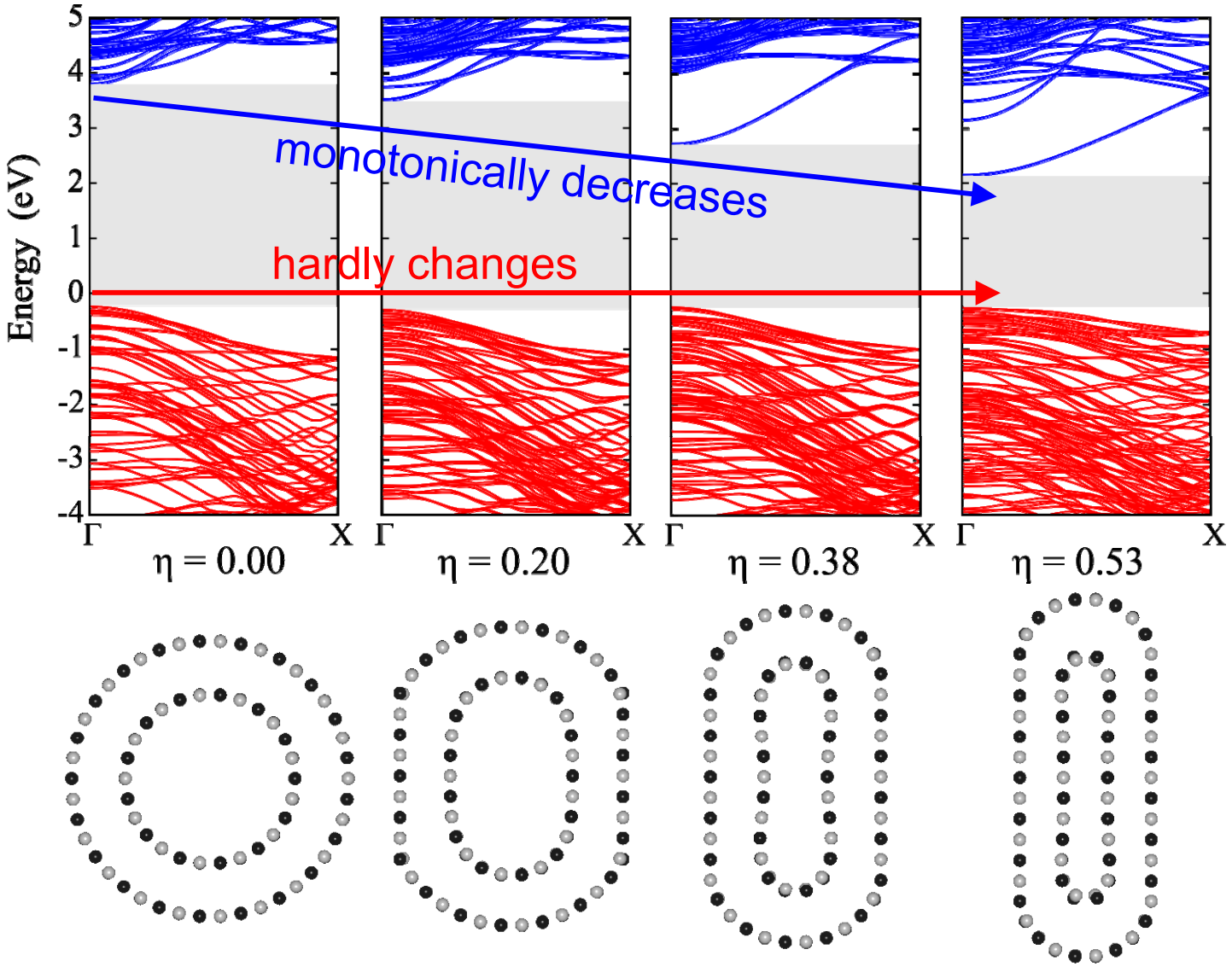
Energy band of (13,0) SW



- E_{CBM} is the main factor in determining E_{g}

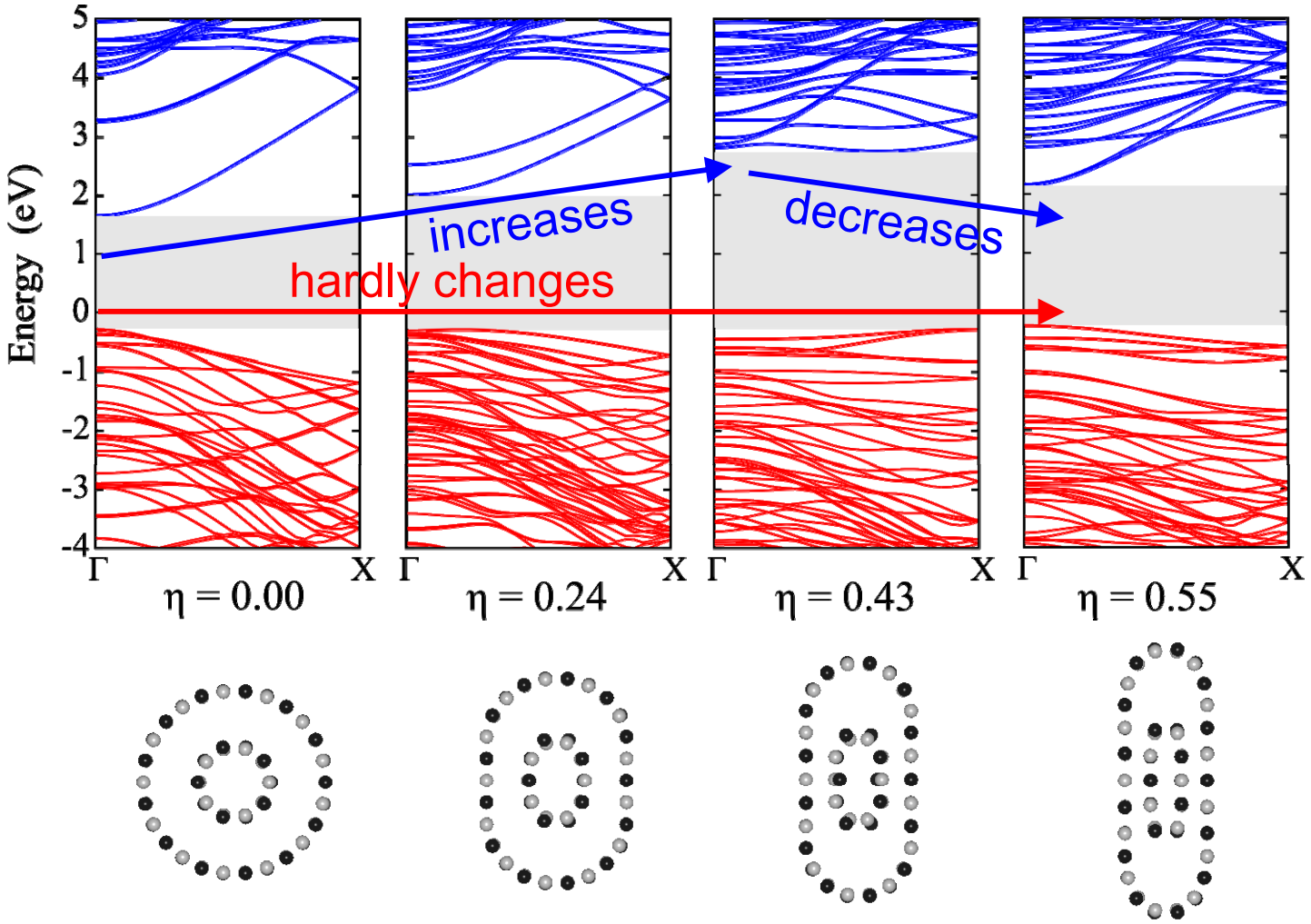
※Tendency of change in band structure :
(5,0) SW, (21,0) SW ≈ (13,0) SW

Energy band of (13,0)@(21,0) DW



- (13,0)@(21,0) DW ≈ SWs

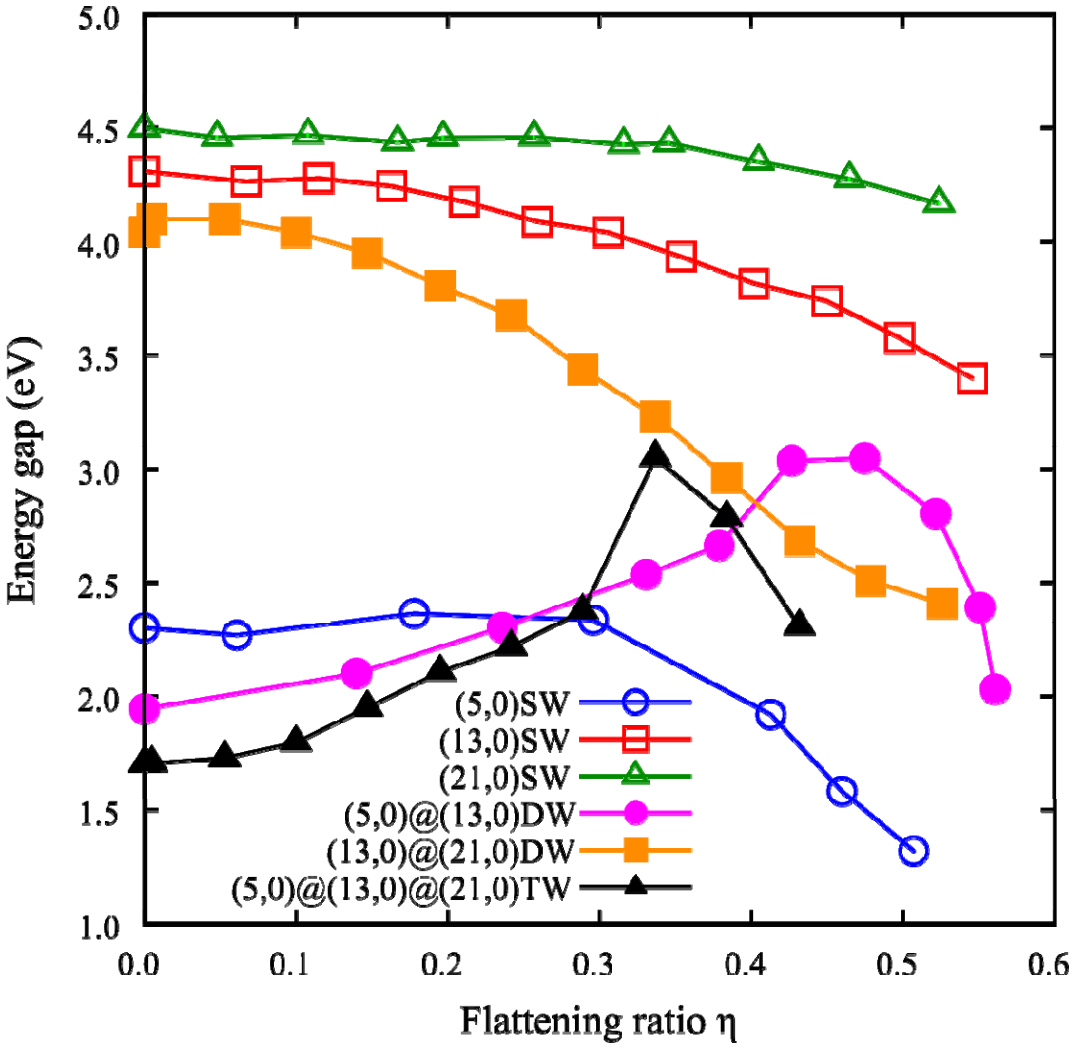
Energy band of (5,0)@(13,0) DW



- E_{CBM} is the main factor in determining E_{g}

※Tendency of change in band structure :
(5,0)@(13,0)@(21,0) TW ≈ (5,0)@(13,0) DW

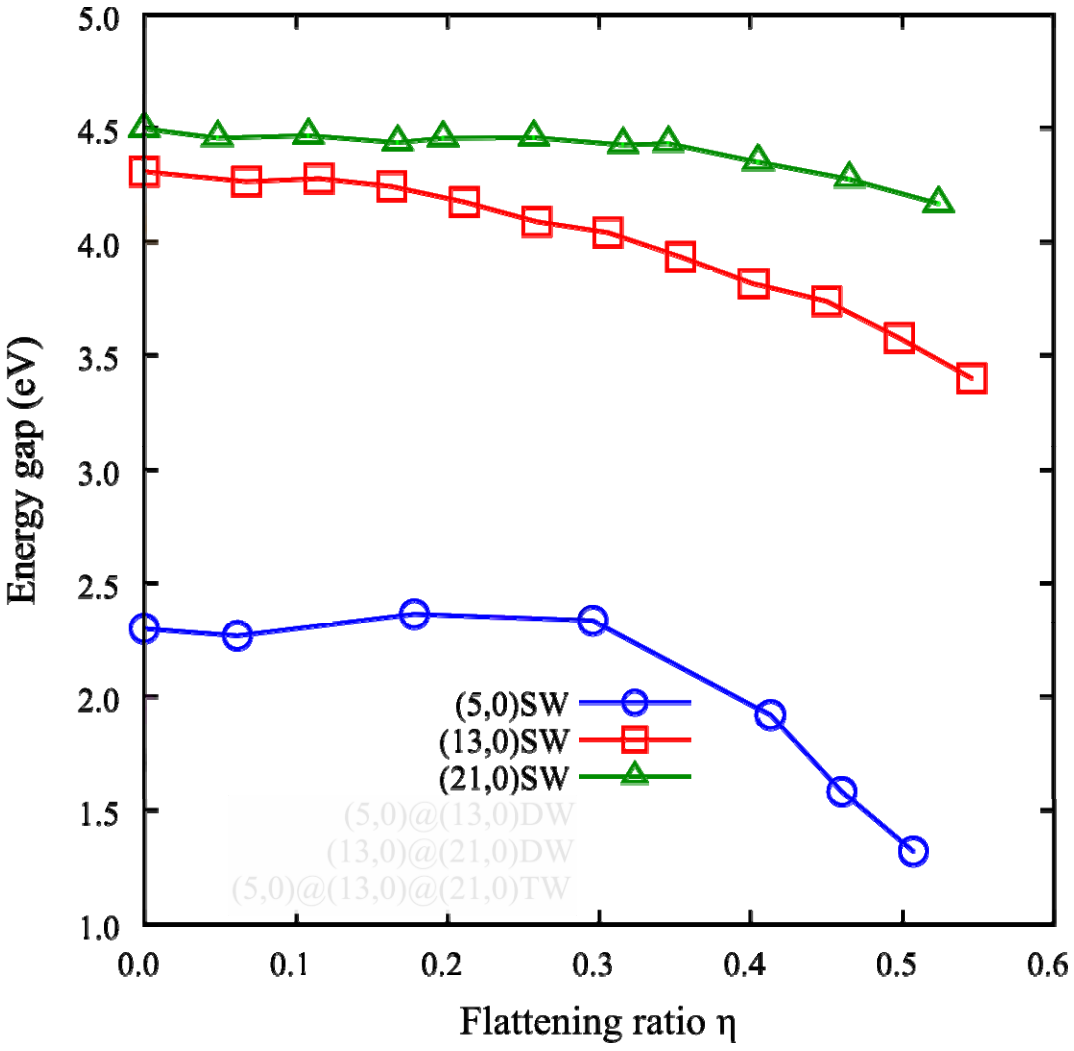
Energy gap vs. Flattening ratio



- ΔE_g in the SWs :
  - * Monotonic decrease
  - * (5,0) > (13,0) > (21,0)
- ΔE_g in (13,0)@(21,0) DW
  - * Monotonic decrease
  - * > (13,0) SW, (21,0) SW
- ΔE_g in (5,0)@(13,0) DW and TW
  - * Increase and then decrease
  - * ↑ to ↓, earlier in TW
- $E_g - \eta$ curves : MWs ≠ SWs

  ⇨ Effects of interwall interaction

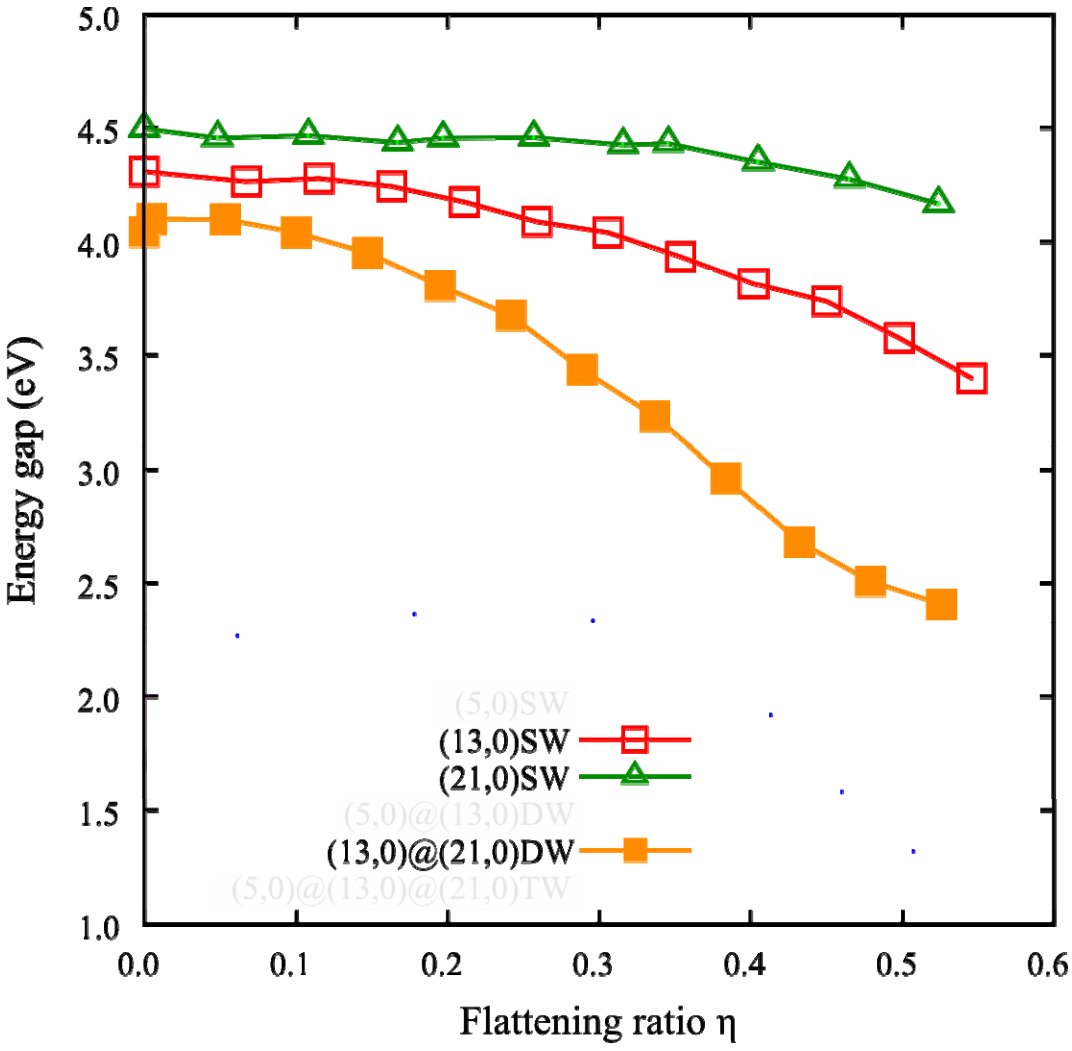
Energy gap vs. Flattening ratio



- ΔE_g in the SWs :
  - * Monotonic decrease
  - * (5,0) > (13,0) > (21,0)
- ΔE_g in (13,0)@(21,0) DW
  - * Monotonic decrease
  - * > (13,0) SW, (21,0) SW
- ΔE_g in (5,0)@(13,0) DW and TW
  - * Increase and then decrease
  - * ↑ to ↓, earlier in TW
- $E_g - \eta$ curves : MWs ≠ SWs

  ➡ Effects of interwall interaction

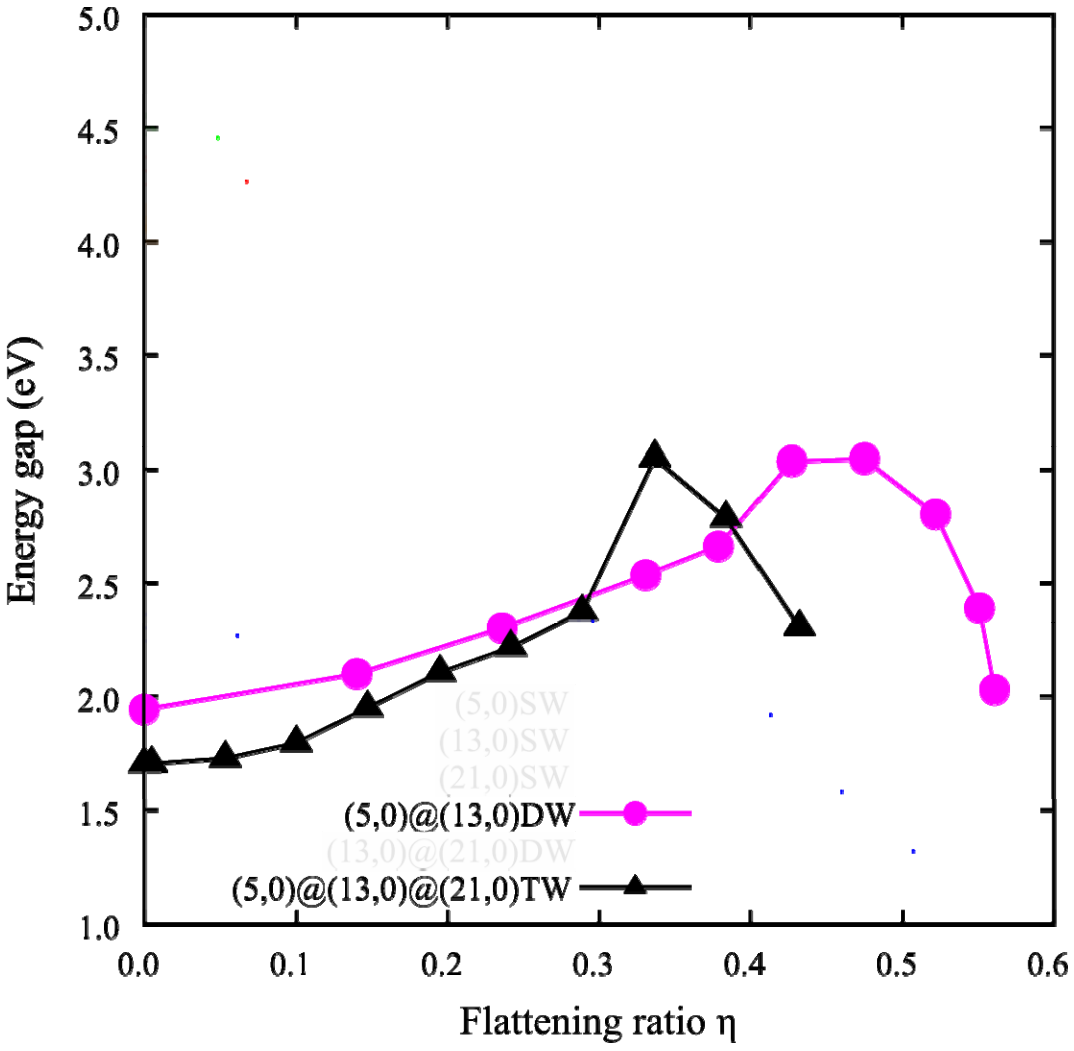
Energy gap vs. Flattening ratio



- ΔE_g in the SWs :
  - * Monotonic decrease
  - * (5,0) > (13,0) > (21,0)
- ΔE_g in (13,0)@(21,0) DW
  - * Monotonic decrease
  - * > (13,0) SW, (21,0) SW
- ΔE_g in (5,0)@(13,0) DW and TW
  - * Increase and then decrease
  - * ↑ to ↓, earlier in TW
- $E_g - \eta$ curves : MWs ≠ SWs

  ⇒ Effects of interwall interaction

Energy gap vs. Flattening ratio



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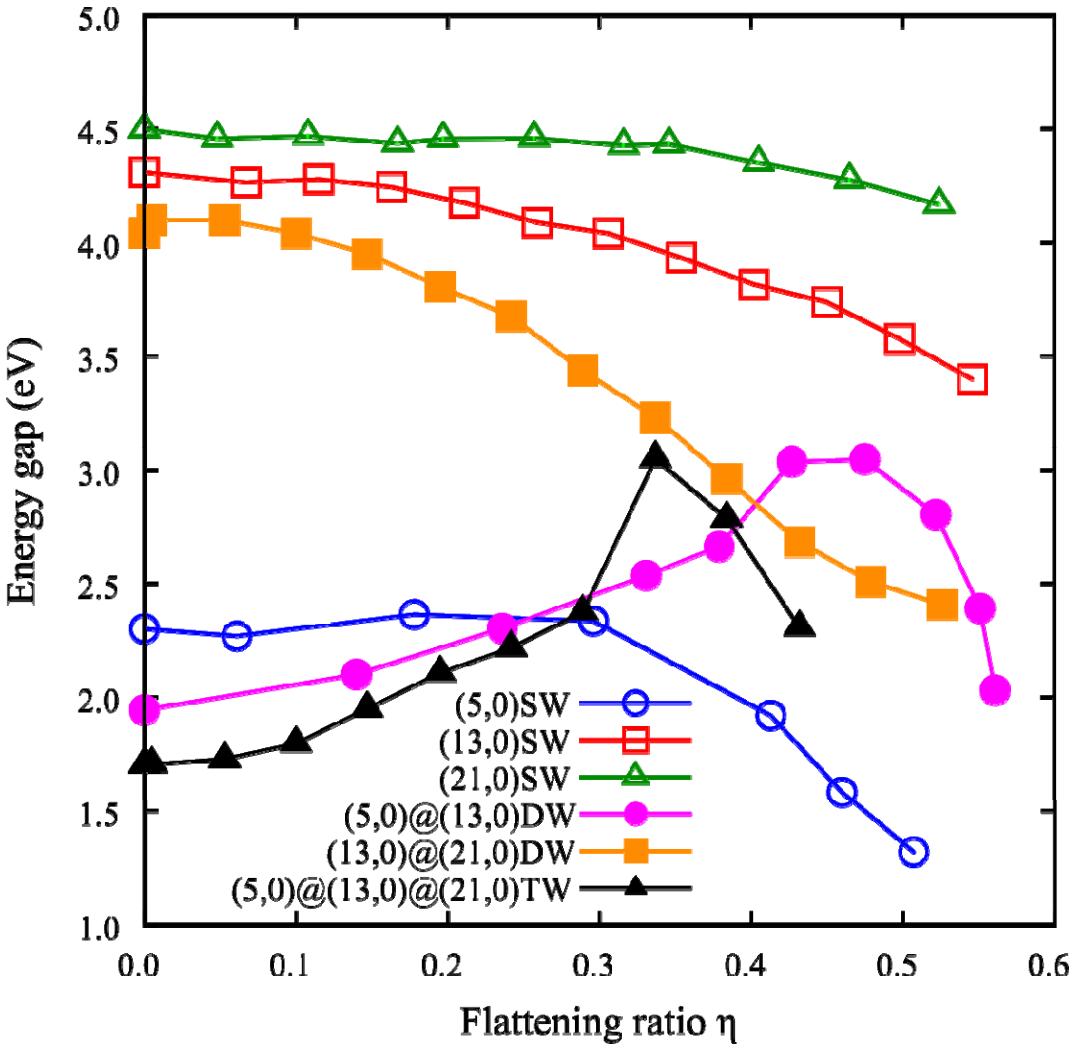
  - ➡ Effects of interwall interaction

Energy gap vs. Flattening ratio



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- ΔE_g in (13,0)@(21,0) DW
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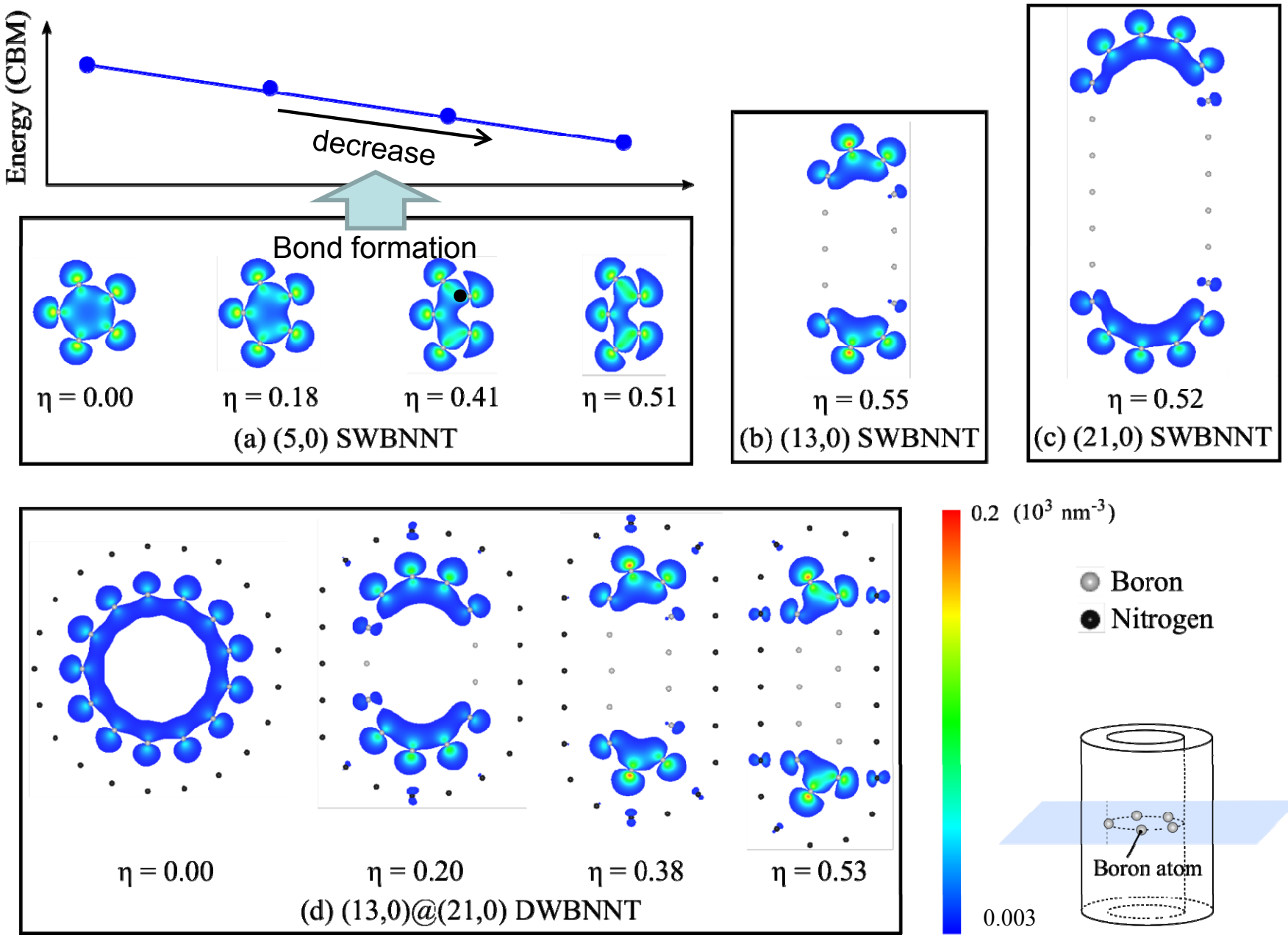
  - * > (13,0) SW, (21,0) SW
- ΔE_g in (5,0)@(13,0) DW and TW
  - * Increase and then decrease
  - * ↑ to ↓, earlier in TW

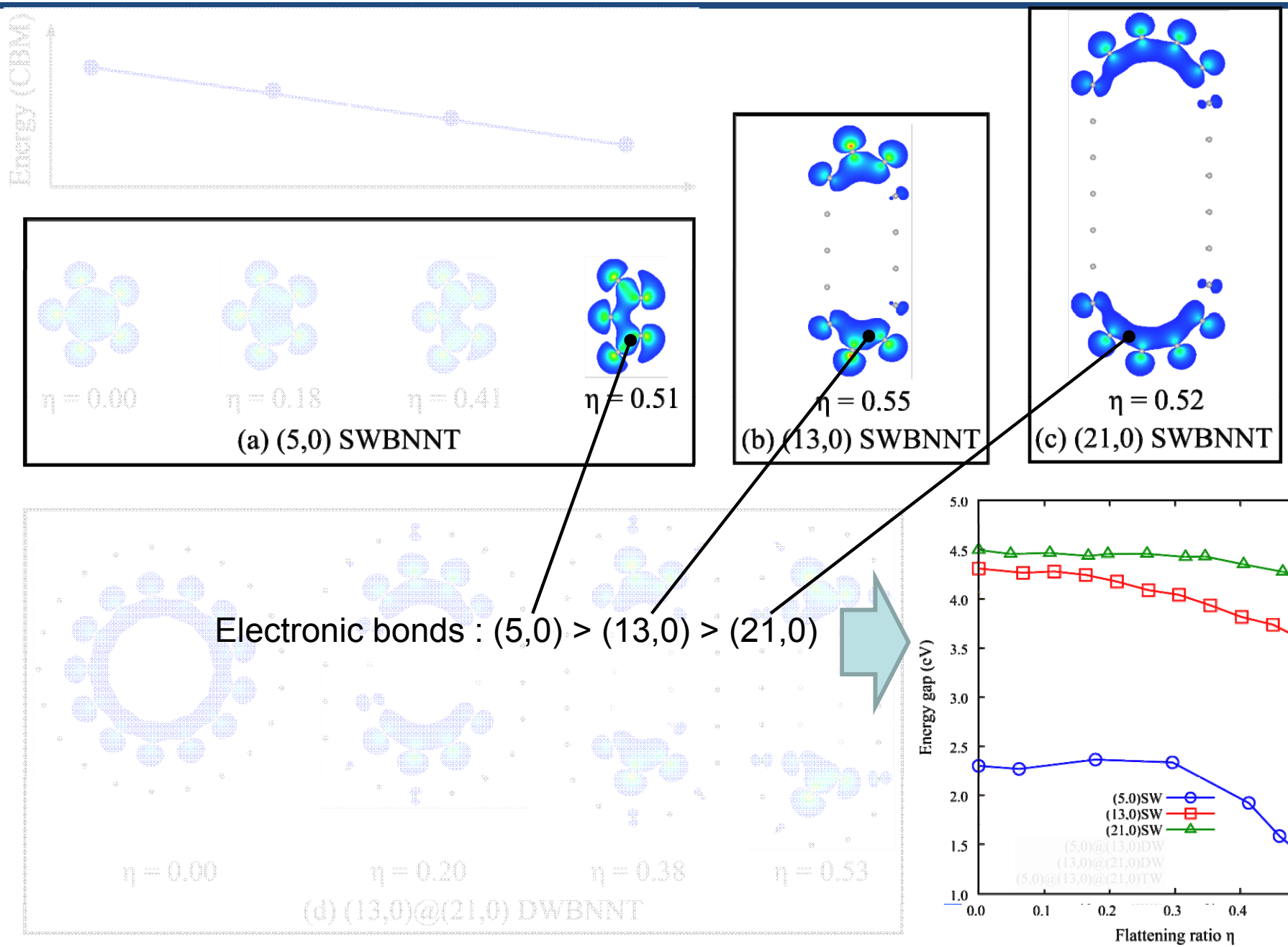
- $E_g - \eta$ curves : MWs ≠ SWs

  ⇨ Effects of interwall interaction

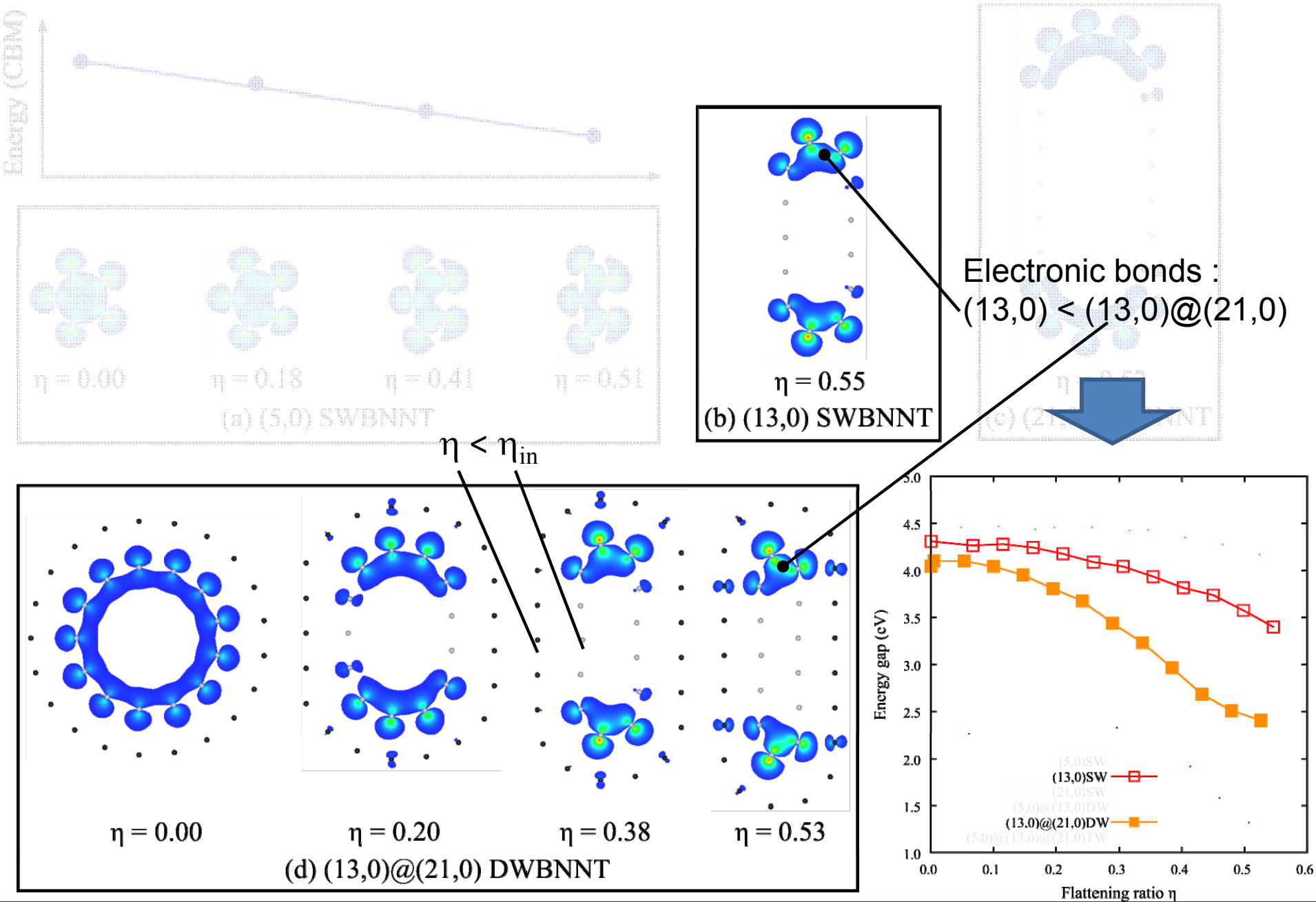
CBM charge density of SWs and (13,0)@(21,0) DW



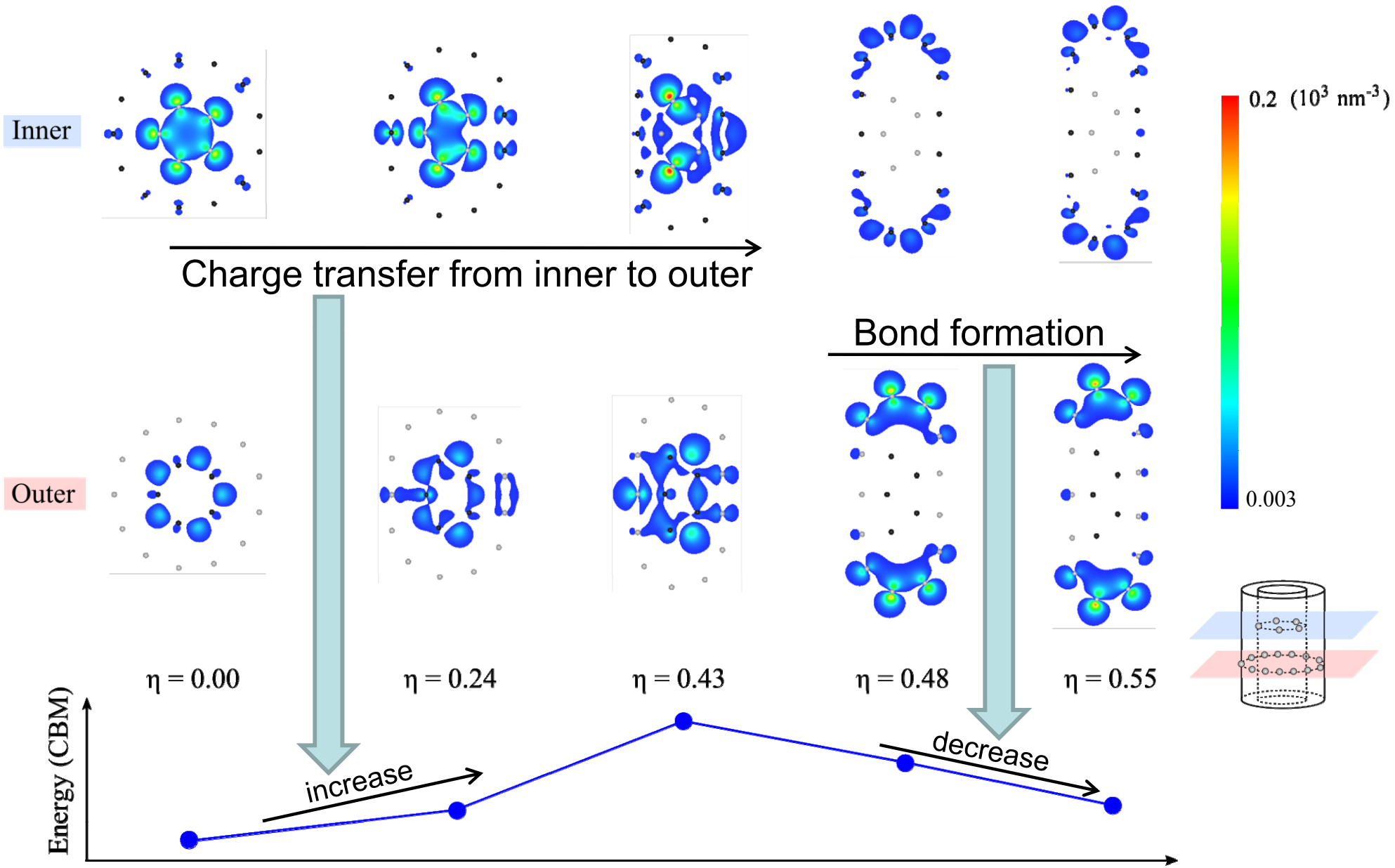
CBM charge density of SWs and (13,0)@(21,0) DW



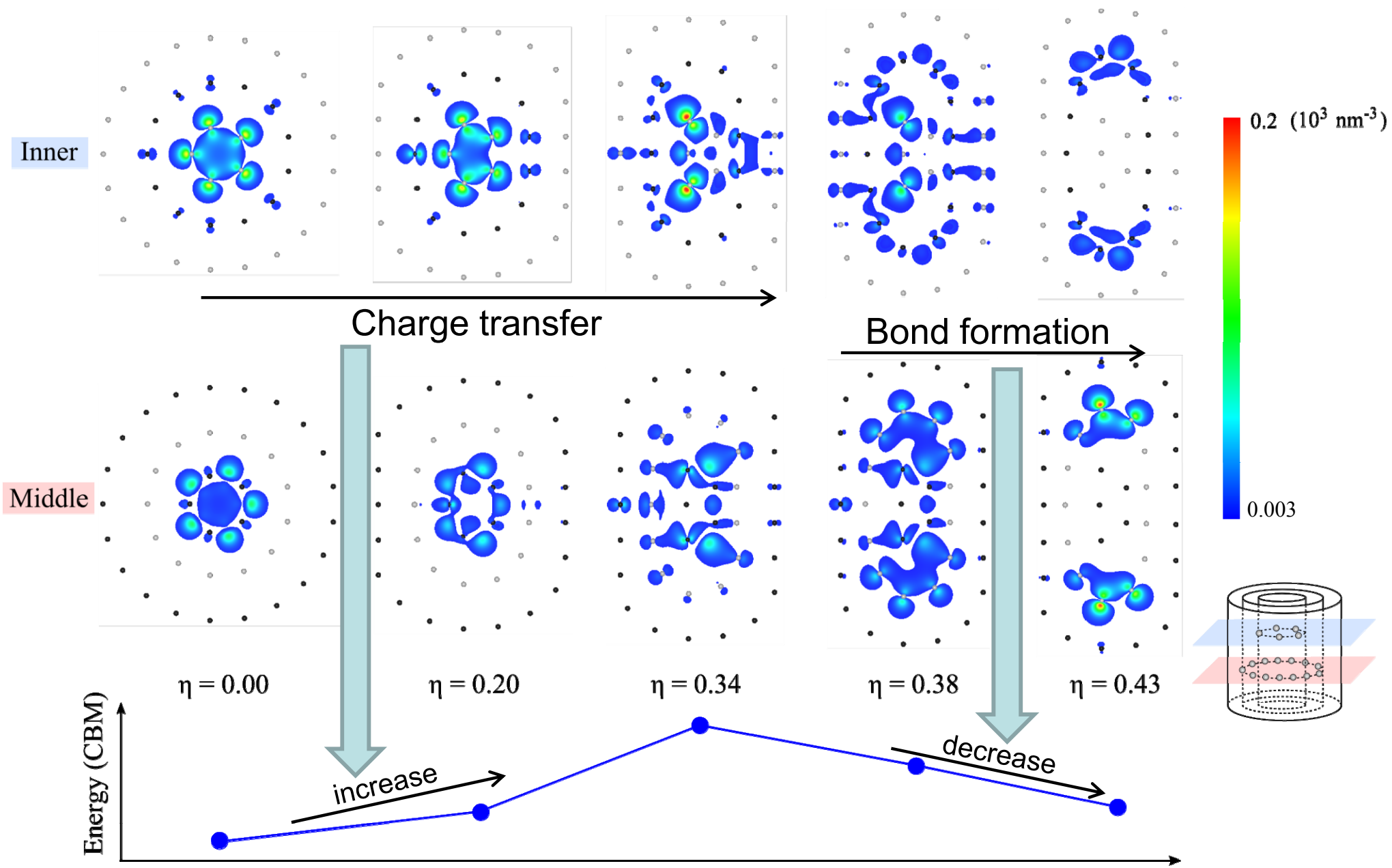
CBM charge density of SWs and (13,0)@(21,0) DW



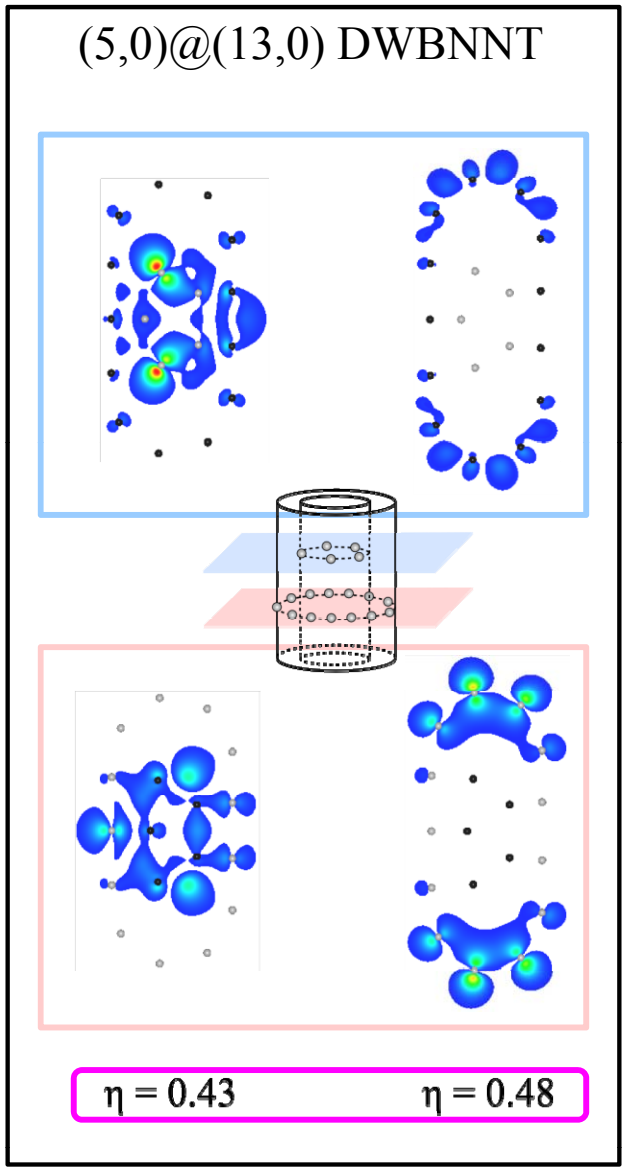
CBM charge density of (5,0)@(13,0) DW

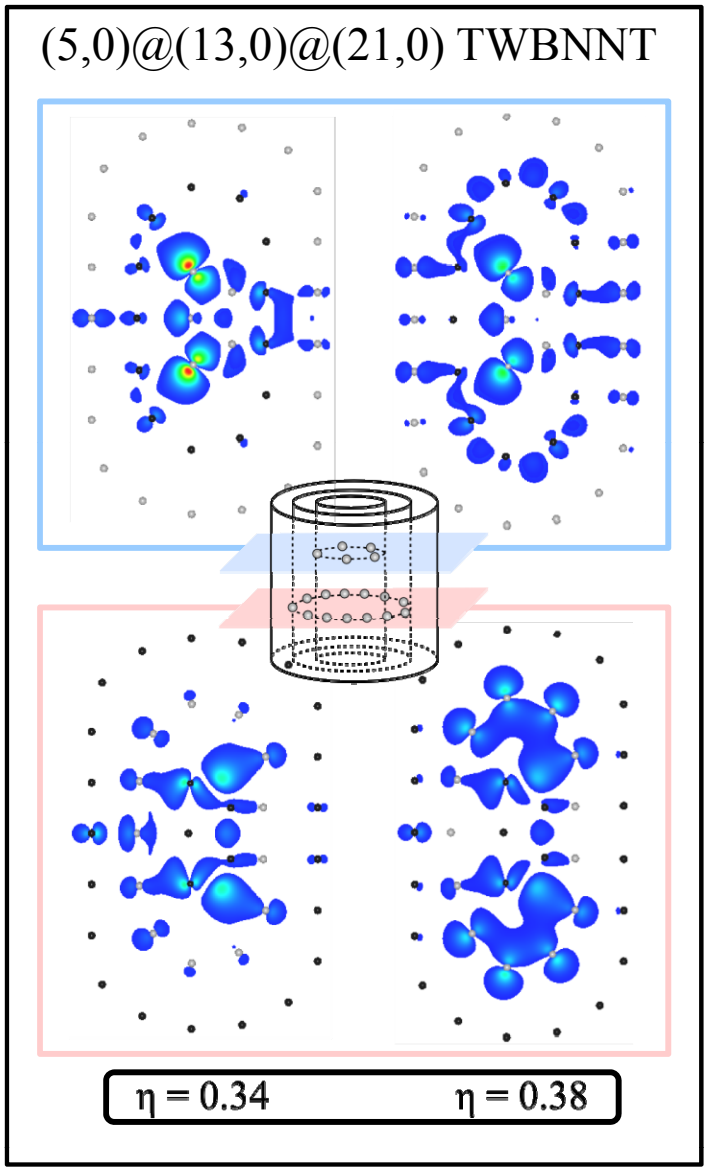


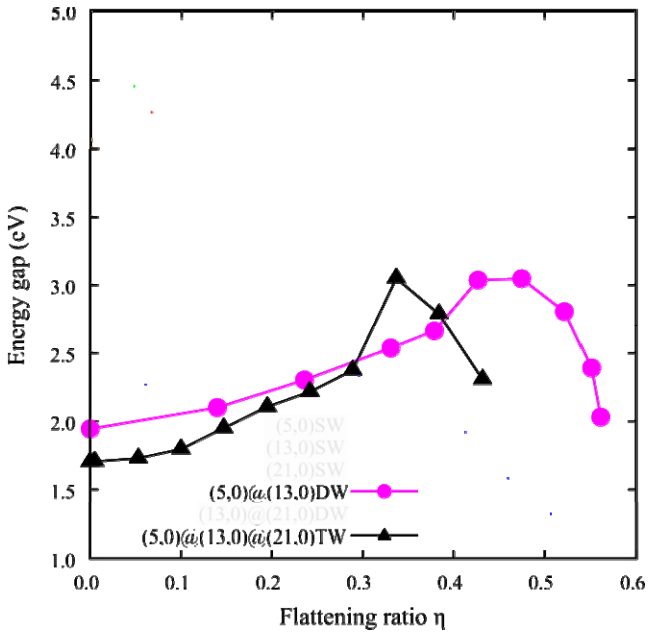
CBM charge density of (5,0)@(13,0)@(21,0) TW



CBM charge density of (5,0)@(13,0) DW and TW







Summary ②

Electronic structures of SW- and MWBNNTs under flattening compression have been investigated using first-principles.

- Single-walled BNNTs (SWBNNTs) :
  - The energy gap monotonically decreases with increasing flattening deformation.
  - The amount of the decrease becomes smaller in proportion to the tube diameter.
- Multi-walled BNNTs (MWBNNTs) :
  - $n_{\mathrm{in}} > n_{\mathrm{c}}$: The energy gap monotonically decreases.
  - $n_{\mathrm{in}} < n_{\mathrm{c}}$: The energy gap first increases and then decreases.

Innermost tube : $(n_{\mathrm{in}}\ ,\ 0)$ zigzag

n_{c} : Critical value, an interger between 5 and 13.

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