Elastic and Piezoelectric Properties of Boron Nitride Nanotube Composites
I: Molecular Dynamics of a Single Wall BNNT

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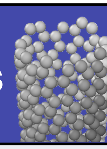
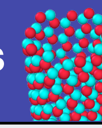
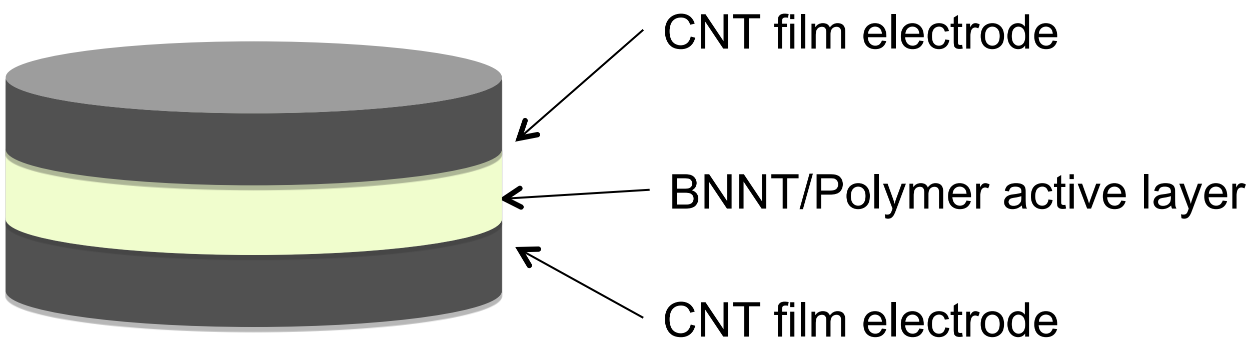
Outline

- Background and motivation
- Piezoelectric molecular dynamics model of boron nitride nanotubes (BNNTs)
- Analytical and simulation results
- Summary

Nanotube Comparison

	Carbon Nanotubes 	Boron Nitride Nanotubes 
Mechanical Properties (Axial Young's Modulus)	1.33 TPa (very stiff)	1.18 TPa (very stiff)
Axial Thermal Conductivity	>3000 W/mK (highly conductive)	~300–3000 W/mK (highly conductive)
Axial Coefficient of Thermal Expansion	~1 x10^{-6} K^{-1} (very low)	~1 x 10^{-6} K^{-1} (very low)
Electric Properties	Metallic or semiconducting	Insulator (6.0 eV band gap, $10^{15\text{-}18}$ ohm-cm) Dielectric strength 2x10^5 V/mm Piezoelectric (0.25-0.4 C/m^2)
Thermal Oxidation Resistance	Stable up to 300-400 °C in air	Stable to over 800 °C in air
Neutron Absorption Cross-Section	C = 0.0035 barn	B = 767 barn (B^{10} ~3800 barn) N = 1.9 barn (Excellent neutron radiation shielding)
Color	Black	White (can be dyed to color)

Langley All-Nanotubes Actuator/Sensor Film



Goal: flexible, mechanically durable, large actuation, high sensitivity

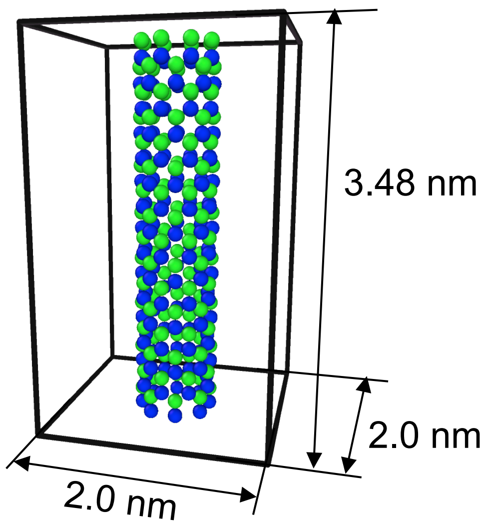
Modeling is essential in achieving these goals

Molecular Dynamics Model of BNNTs

- Define forces between atoms using a given interatomic potential (energy)

$$U_r = \sum_{i,j}\left[V_R(r_{ij}) - B_{ij}V_A(r_{ij})\right]; \quad \vec{F}_i = -\partial U_r/\partial \vec{r}_i$$

- Evolve atoms according to Newton's law: $\vec{a}_i = \vec{F}_i / m_i$



Tersoff – Brenner type of potential:

1. Albe et al., (Rad. Eff. Def. Sol. 141 (1997) 85)
2. Verma – Sekkal: (Nanotechnology 18 (2007) 435711)

Total potential energy:

$$U_r = \frac{1}{2}\sum_{i,j\neq i} V_R(r_{ij}) - B_{ij}V_A(r_{ij}) = \sum_i U_i$$

where:

$$V_R(r_{ij}) = F_c(r_{ij})\frac{D_0}{S-1}\exp\left(-\beta\sqrt{2S}\left(r_{ij}-r_0\right)\right) \quad \text{- repulsive term}$$

$$V_A(r_{ij}) = F_c(r_{ij})\frac{SD_0}{S-1}\exp\left(-\beta\sqrt{2/S}\left(r_{ij}-r_0\right)\right) \quad \text{- attractive term}$$

$$F_c(r_{ij}) = \begin{cases} 1 & r \le R_1 \\ 0.5\left[1+\cos\left(\pi\dfrac{r_{ij}-R_1}{R_2-R_1}\right)\right], & R_1 < r_{ij} \le R_2 \\ 0 & R_2 < r_{ij} \end{cases} \quad \text{- cut-off function}$$

$$B_{ij} = \left(1+\gamma^n P_{ij}^n\right)^{-\frac{1}{2n}}$$

$$P_{ij} = \sum_{k\neq i,j} F_c(r_{ik})G(\theta_{ijk})\exp\left[\lambda^3\left(r_{ij}-r_{ik}\right)^3\right]$$

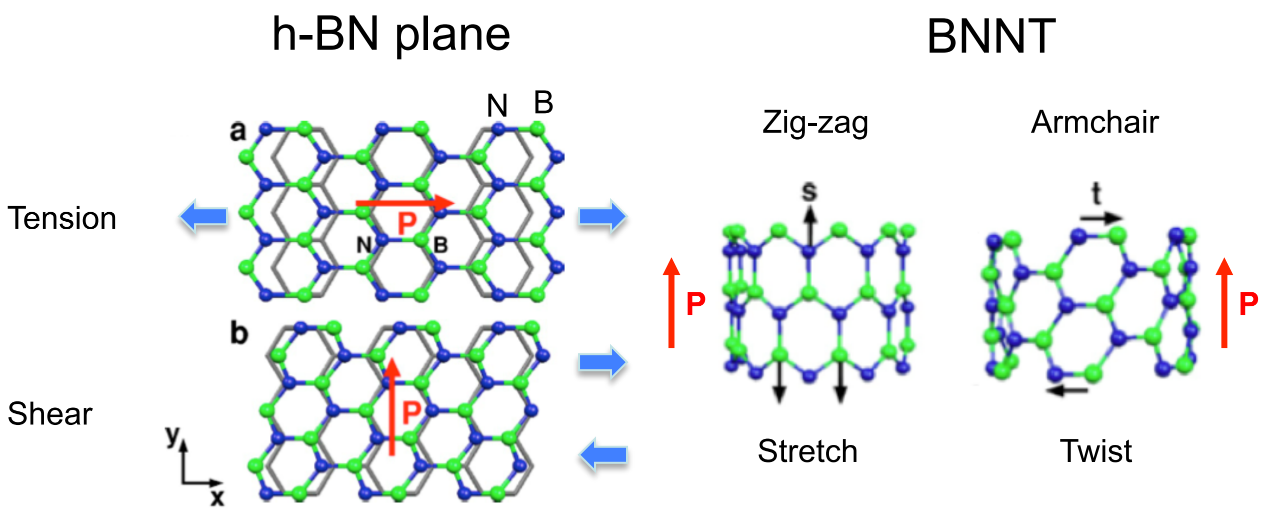
$$G(\theta_{ijk}) = 1+\frac{c_0^2}{d_0^2}-\frac{c_0^2}{d_0^2+\left(h_0-\cos\theta_{ijk}\right)^2} \quad \text{- angular dependent 3-body term}$$

θ_{ijk} is the angle between bonds $i-j$ and $i-k$.

MD models do not currently address the piezoelectric behavior

Piezoelectric Properties of BNNTs

Piezoelectric Effect



(Sai & Mele, PRB 68, (2003) 241405)

Induced polarization, $\vec{p}$, under strain ε_{jk}: $\quad p_i = e_{ijk}\varepsilon_{jk}$

where e_{ijk} - piezoelectric tensor with symmetry:

$$e_{xxx} = -e_{xyy} = -e_{yxy} = -e_{yyx}; \quad e_{xxx} = 0.086 - 0.12\ e / Bohr$$

The MD model has to reproduce the characteristic polarization behavior

MD Model for a Piezoelectric BNNT

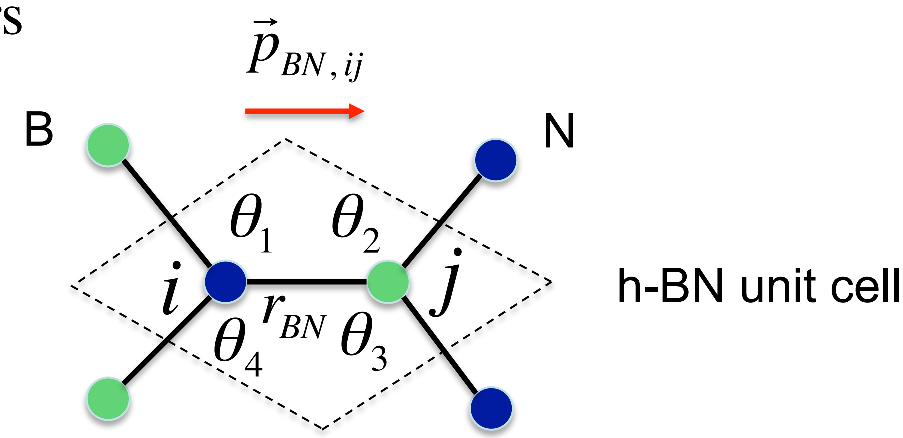
Introduce a dipole term to the interatomic potential

$$U = U_r + U_p; \quad U_p = \sum_{i=\{B\},j=\{N\}} U\left(\vec{p}_{BN,ij}\right)$$

Dipole Parametric Equation:

$$\vec{p}_{BN,ij} = p_0\left[\frac{r_{BN,ij} - r_0}{r_0} + t_\theta \sum_{k=1}^{4}\left(\frac{1}{2} + \cos\theta_k\right)\right]$$

p_0, t_θ - fitting parameters



The dipole term is simple, efficient, and allows for analytic expression of the piezoelectric tensor

Analytical Model for a Piezoelectric BNNT

Shell Theory of the Hexagonal BN Lattice*

During homogeneous deformation the h-BN lattice sustains force equilibrium by shifting the N-sublattice at a shift vector ζ with respect to the B-sublattice.

ζ is determined by the equilibrium condition:

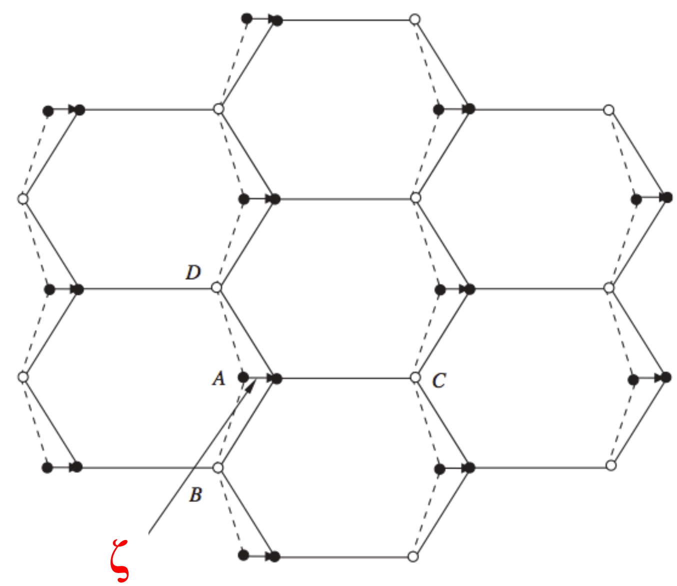
$$\partial\Phi/\partial\zeta_\lambda = 0 \quad \text{with}$$

$$\Phi = \sum_{j=1}^{3} V\left(r_{ij};\cos\theta_{ijk}, k \neq i,j\right) \quad \text{and}$$

$$V\left(r_{ij};\cos\theta_{ijk}\right) = V_R\left(r_{ij}\right) - B_{ij}V_A\left(r_{ij}\right)$$

as a function of the interatomic potential parameters:

Shift between B and N sub-lattices



$$\zeta_\lambda = \frac{2}{3}A\varepsilon_{\alpha\beta}\sum_{j=1}^{3} n_\alpha^j n_\beta^j n_\lambda^j \quad \text{with} \quad A = 1 - \frac{8r_0^2\left(\frac{\partial^2 V}{\partial r_{ij}^2}\right)_0 + 12r_0\left(\frac{\partial^2 V}{\partial r_{ij}\partial\cos\theta_{ijk}}\right)_0}{4r_0^2\left(\frac{\partial^2 V}{\partial r_{ij}^2}\right)_0 + 12r_0\left(\frac{\partial^2 V}{\partial r_{ij}\partial\cos\theta_{ijk}}\right)_0 + 18\left(\frac{\partial^2 V}{\partial\cos\theta_{ijk}\partial\cos\theta_{ijk}}\right)_0 - 9\left(\frac{\partial^2 V}{\partial\cos\theta_{ijk}\partial\cos\theta_{ijl}}\right)_0 + 12\left(\frac{\partial V}{\partial\cos\theta_{ijk}}\right)_0}$$

and for r_{ij} and $\cos\theta_{ijk}$:

$$r_{ij}^2 = r_0^2\left(\delta_{\alpha\beta} + 2\varepsilon_{\alpha\beta}\right)\left(n_\alpha + \zeta_\alpha\right)\left(n_\beta + \zeta_\beta\right) - r_0^4\left[k_{\alpha\beta}\left(n_\alpha + \zeta_\alpha\right)\left(n_\beta + \zeta_\beta\right)\right]^2 / 12$$

$$\cos\theta_{ijk} = \frac{r_0^2}{r_{ij}r_{ik}}\left(n_\alpha^{ij} + \zeta_\alpha\right)\left(n_\lambda^{ik} + \zeta_\lambda\right) \times \left\{\delta_{\alpha\lambda} + 2\varepsilon_{\alpha\lambda} + \frac{r_0^2}{12}k_{\alpha\beta}k_{\gamma\lambda}\left[3\left(n_\beta^{ij} + \zeta_\beta\right)\left(n_\gamma^{ik} + \zeta_\gamma\right) - 2\left(n_\beta^{ij} + \zeta_\beta\right)\left(n_\gamma^{ij} + \zeta_\gamma\right) - 2\left(n_\beta^{ik} + \zeta_\beta\right)\left(n_\gamma^{ik} + \zeta_\gamma\right)\right]\right\}$$

*Song et al., Journal of Nanoscience and Nanotechnology, 8, 3774-3780, 2008.

Expressing Polarization*

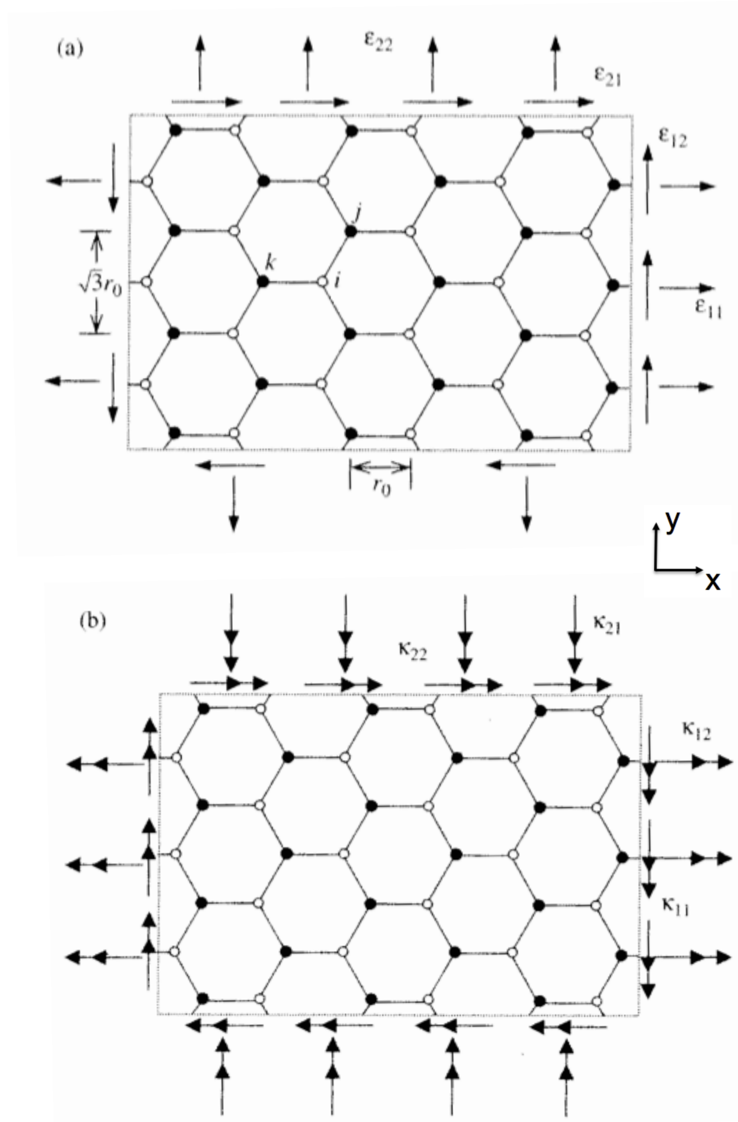
Parametric equation: $\vec{p}_{BN,ij} = p_0 \left[\frac{r_{BN,ij} - r_0}{r_0} + t_\theta \sum_{k=1}^{4} \left(\frac{1}{2} + \cos\theta_k \right) \right]$

Substituting r_{ij}, and $\cos\theta_{ijk}$, and limiting to linear terms of $\varepsilon_{\alpha\beta}$, and $r_0^2\kappa_{\alpha\beta}^2$, excluding rotation, $\varepsilon_{xy} = \varepsilon_{yx}$:

$$\vec{p}_{cell,x} = \frac{p_0}{2\sqrt{3}r_0^2} \left\{ \begin{array}{l} (1+A)(\varepsilon_{xx} - \varepsilon_{yy}) - \frac{r_0^2}{96}(5k_{xx}^2 - 2k_{xx}k_{yy} - 3k_{yy}^2) - \\ -t_\theta \left[3(1-A)(\varepsilon_{xx} - \varepsilon_{yy}) - \frac{r_0^2}{96}(23k_{xx}^2 + 42k_{xx}k_{yy} - 81k_{yy}^2) \right] \end{array} \right\}$$

$$\vec{p}_{cell,y} = -\frac{p_o}{2\sqrt{3}r_0^2} \left[(1+A) - 3t_\theta(1-A) \right] \varepsilon_{xy}$$

General equation expressing polarization of any deformed h-BN layer through the interatomic potential (A and r_0), and two fitting parameters, p_0 and t_θ.



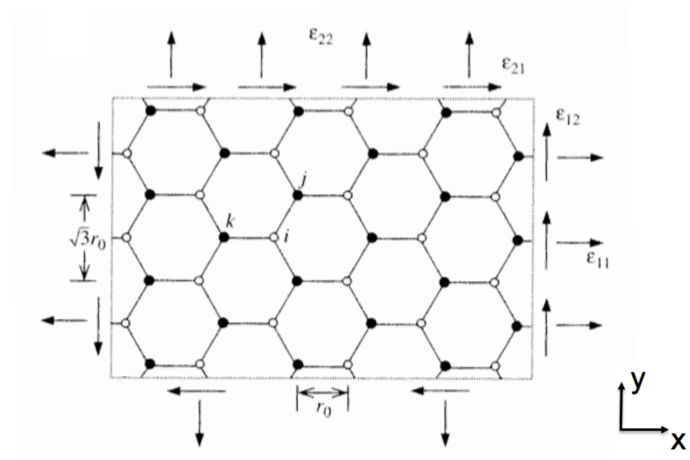
*Yamakov et al., Comp. Mat. Sci., 95, 362-370, 2014.

Polarization of a hexagonal BN Plane

In plane deformation: $\kappa_{\alpha\beta} = 0$

$$p_x = \frac{p_0}{2\sqrt{3}r_0^2}\left[(1+A) - 3t_\theta(1-A)\right]\varepsilon_{xx} - \frac{p_0}{2\sqrt{3}r_0^2}\left[(1+A) - 3t_\theta(1-A)\right]\varepsilon_{yy}$$

$$p_y = -\frac{p_o}{2\sqrt{3}r_0^2}\left[(1+A) - 3t_\theta(1-A)\right]\varepsilon_{xy}$$



Stretched h-BN Plane

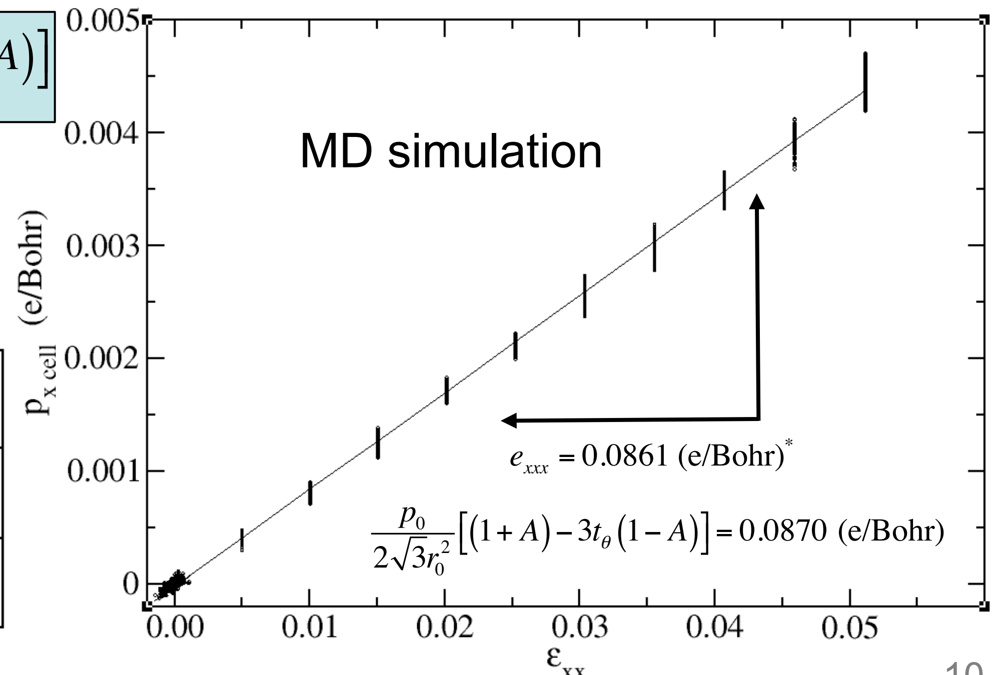
Piezoelectric tensor:

$$p_x = e_{xxx}\varepsilon_{xx} + e_{xyy}\varepsilon_{yy}$$

$$p_y = e_{yxy}\varepsilon_{xy} = e_{yyx}\varepsilon_{yx}$$

$$\boxed{e_{xxx} = -e_{xyy} = -e_{yxy} = -e_{yyx} = \frac{p_0}{2\sqrt{3}r_0^2}\left[(1+A) - 3t_\theta(1-A)\right]}$$

Preserves the hexagonal symmetry



Model Parameters

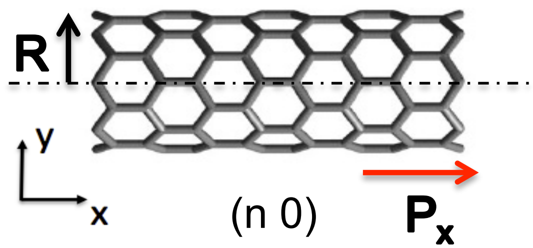
	U_r			p		
	r_0 (nm)	A	E (TPa)	p_0 (e/nm)	t_θ	e_{xxx} (e/Bohr)
Albe et al.	0.1462	0.276	1.11	0.029	-1.4	0.0894
Verma-Sekkal	0.1457	0.241	1.48	0.041	-0.75	0.0870

* N. Sai, EJ. Mele, PRB 68 (2003) 241405

Polarization of a BNNT

Zig-zag (n 0) tube: $\kappa_{xx} = 0; \quad \kappa_{yy} = 1/R; \quad r_0^2 / R^2 << 1$

Folded along x-axis



$$R = n r_0 \sqrt{3}/2\pi$$

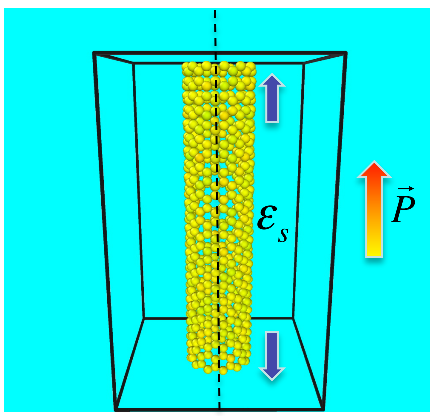
$$p = p_x = \frac{p_o}{2\sqrt{3} r_0^2}\left[(1+A) - 3t_\theta(1-A)\right](1+\nu)\varepsilon_{xx} + \underbrace{\frac{p_0}{64\sqrt{3}R^2}(1-27t_\theta)}$$

Valid in the limit $r_0^2 \kappa_{yy}^2 = r_0^2 / R^2 << 1$

No polarization in twist, ε_{xy}

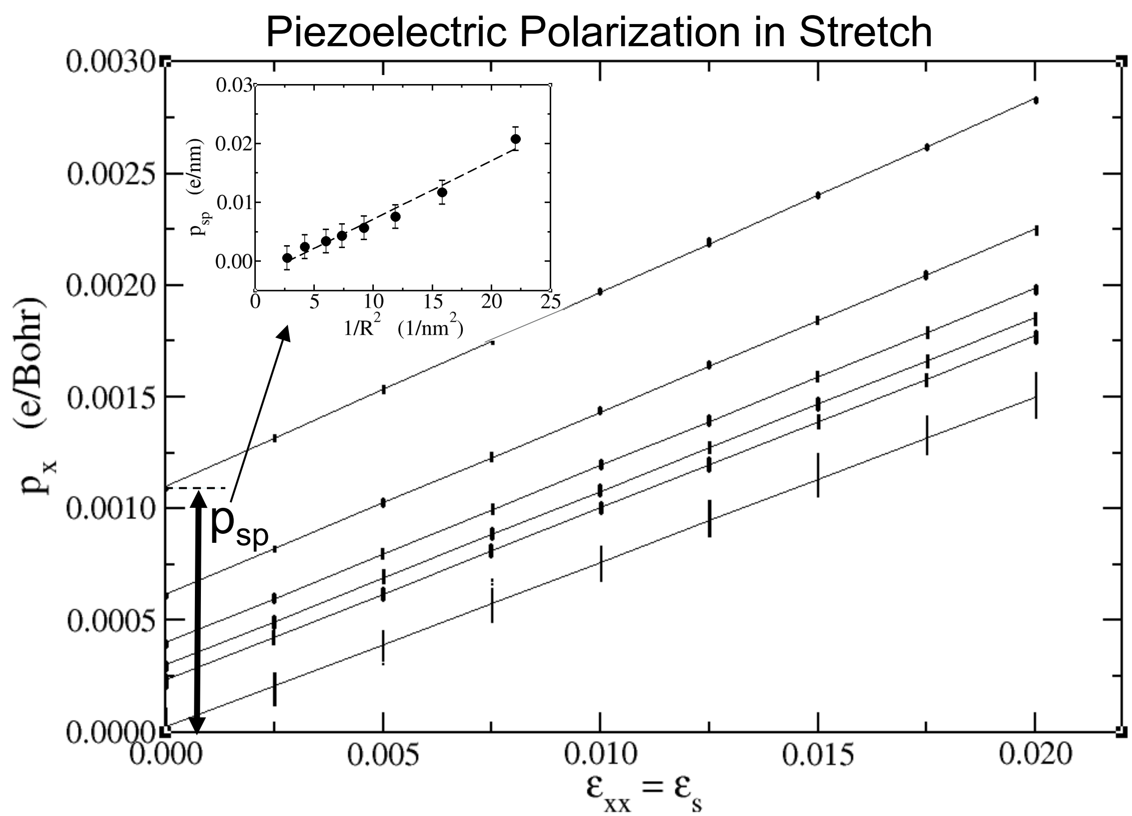
Spontaneous polarization ~ $1/R^2$

$$p_{sp} = const / R^2$$



MD simulation of a BNNT under stretch

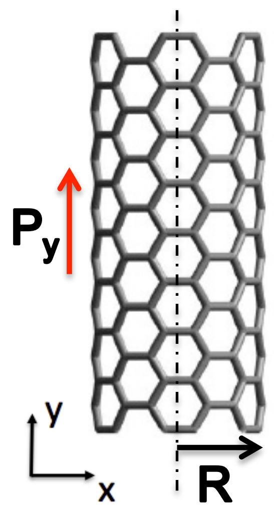
MD Results



Polarization of a BNNT

Armchair tube: (n n) $\kappa_{xx} = 1/R; \quad \kappa_{yy} = 0; \quad r_0^2/R^2 << 1$

Folded along y-axis

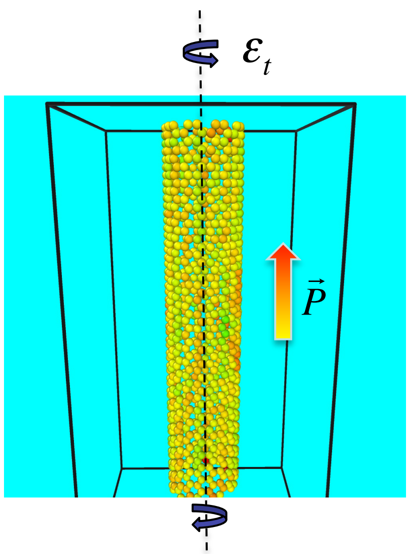


(n n) $R = 3nr_0/2\pi$

$$p = p_y = -\frac{p_o}{2\sqrt{3}r_0^2}\left[\left(1+A\right)-3t_\theta\left(1-A\right)\right]\varepsilon_{xy}$$

No polarization in stretch, ε_{yy}

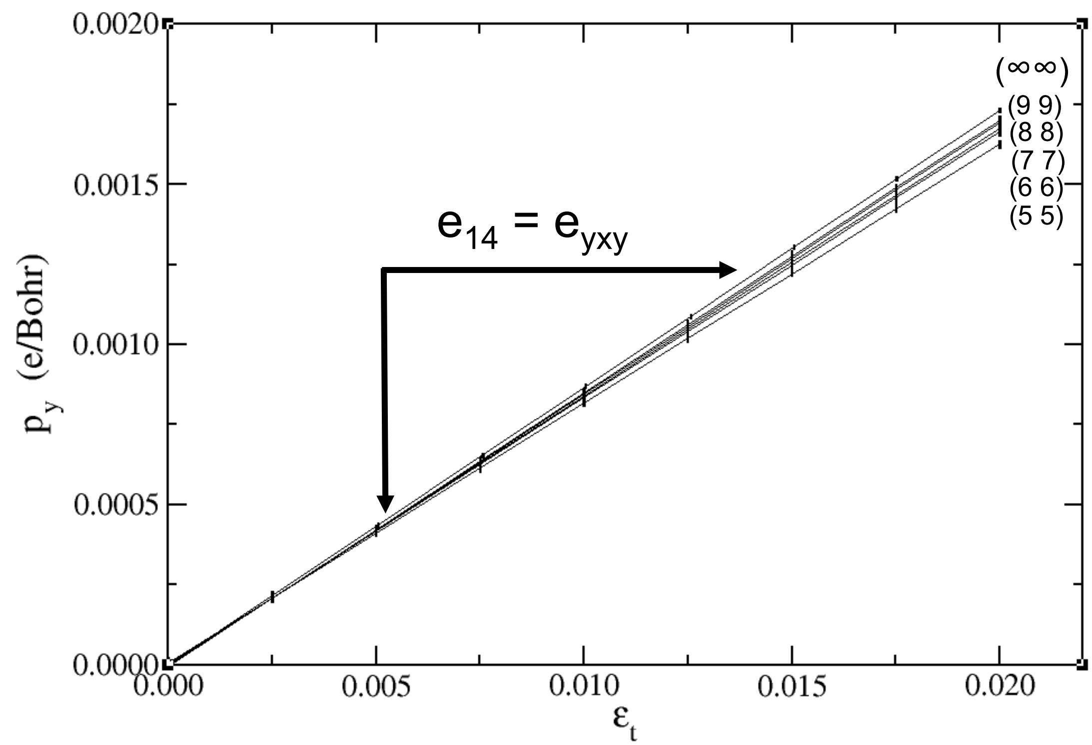
No spontaneous polarization



MD simulation of a BNNT under twist

MD Results

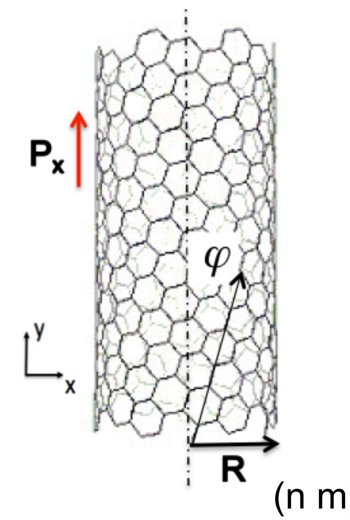
Piezoelectric Polarization in Twist



Polarization of a BN Nanotube

Chiral tube $(n\ m)$ with chiral angle, $\tan\varphi = \dfrac{m\sqrt{3}}{m+2n}$:

Folded at angle φ



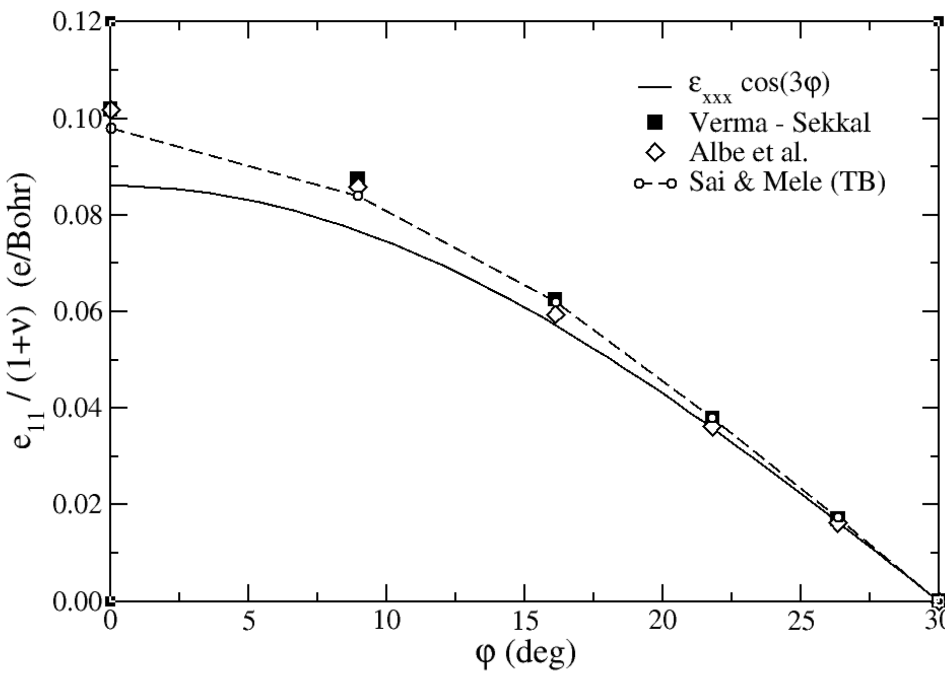
$$p_x = e_{11}\varepsilon_s + e_{14}\varepsilon_t$$

$$e_{11} = \frac{p_o \cos 3\varphi}{2\sqrt{3}r_0^2}\left[(1+A) - 3t_\theta(1-A)\right](1+v)$$

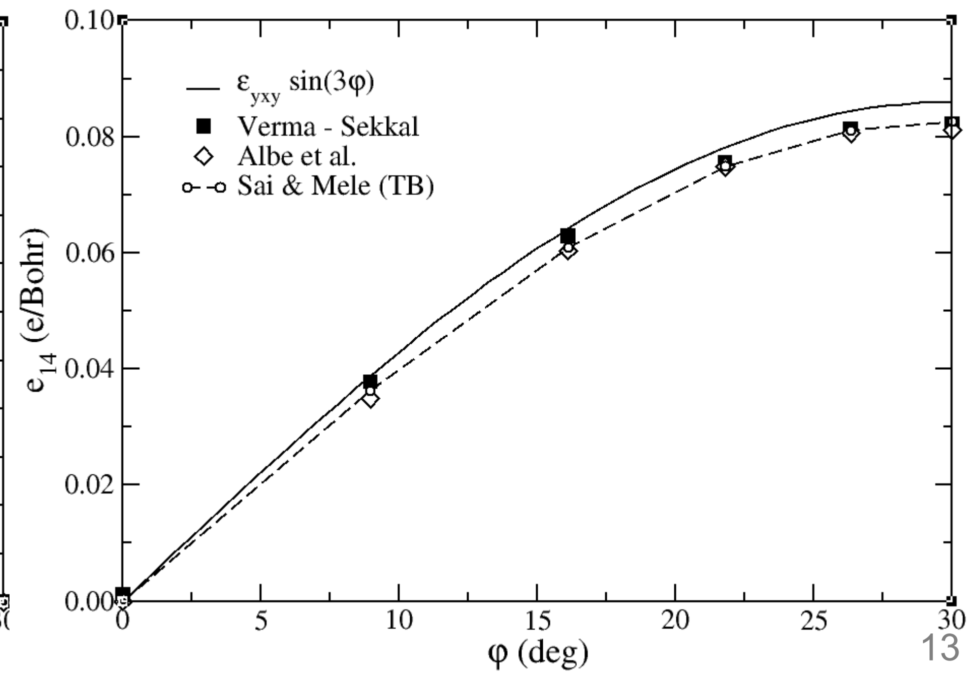
$$e_{14} = -\frac{p_o \sin 3\varphi}{2\sqrt{3}r_0^2}\left[(1+A) - 3t_\theta(1-A)\right]$$

MD Results

Polarization in Stretch



Polarization in Twist



Summary

Parametric equation: $\vec{p}_{BN,ij} = p_0\left[\frac{r_{BN,ij} - r_0}{r_0} + t_\theta \sum_{k=1}^{4}\left(\frac{1}{2} + \cos\theta_k\right)\right]$

- Analytic expression of the piezoelectric coefficients through the interatomic potential

$$e_{xxx} = -e_{xyy} = -e_{yxy} = -e_{yyx} = \frac{p_0}{2\sqrt{3}r_0^2}\left[(1 + A) - 3t_\theta(1 - A)\right]$$

- The model reproduces the piezoelectric properties predicted by first-principle
- The model predicts 1 / R^2 spontaneous polarization of BNNTs

Limitations of the analytical model:

- Valid for small curvature (bending): tubes with $r_0^2/R^2 << 1$, or R > 1 nm (most experimental BNNTs)

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