## Derivation of the bending stiffness from REBO potential

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This document is to show that the dihedral term in the  $2^{nd}$  generation Brenner bond order potential (REBO) has a significant contribution to the bending stiffness calculation.

Based on the Eq. (20) in Ref. [1], the bending modulus is calculated as the second derivative with respect to curvature.

$$C_b = \frac{\partial \hat{W}}{\partial \kappa^2}$$

where  $\hat{W}$  is the effective strain energy density after interlattice relaxation  $\eta$ , and is defined by Eq. (9) in Ref. [1].

 $\hat{W}(\mathbf{F}, \mathbf{K}) = W(\mathbf{F}, \mathbf{K}, \eta(\mathbf{F}, \mathbf{K}))$ 

In the Appendix B of Ref. [1], it was shown that the derivative of W with respect to  $\eta$  vanishes, thus

$$C_b = \frac{\partial W}{\partial \kappa^2}$$

In Ref. [1] Eq. (21), the bending modulus is calculated through bond lengths and bond angles. And Ref. [1] very clearly stated that this expansion is for a potential depends only on bond lengths and angles (and not on dihedral angles)

The approach taken in Eq. (21) is correct when applied to the  $1^{st}$  generation Brenner potential [2]. However, the  $2^{nd}$  generation of Brenner bond order potential (REBO) [3] does come with a dihedral term  $b^{DH}$ . Therefore, the contribution from the dihedral term has to be considered additionally.

For the 2<sup>nd</sup> generation potential, the bond order term is

$$\overline{b}_{ij} = \frac{1}{2} [b_{ij}^{\sigma - \pi} + b_{ji}^{\sigma - \pi}] + b_{ij}^{\pi}$$
  
where  $b_{ij}^{\pi} = \prod_{ij}^{RC} + b_{ij}^{DH}$ 

Following Eq. (7) in Ref. [1],

$$W(\mathbf{F}, \mathbf{K}, \eta) = \frac{1}{S_0} \sum_{i=1}^3 [V_R - \overline{b}_{ij} V_A] = \frac{1}{S_0} \sum_{i=1}^3 [V_R - \overline{b}_{ij}^0 V_A - b_{ij}^{DH} V_A]$$
$$C_b = \frac{\partial W}{\partial \kappa^2} = \frac{1}{S_0} \frac{\partial^2}{\partial \kappa^2} \left( \sum_{i=1}^3 [V_R - \overline{b}_{ij}^0 V_A] \right) - \frac{1}{S_0} \sum_{i=1}^3 \frac{\partial^2 (b_{ij}^{DH} V_A)}{\partial \kappa^2}$$
where  $\overline{b}_{ij}^0 = \frac{1}{2} [b_{ij}^{\sigma - \pi} + b_{ji}^{\sigma - \pi}] + \Pi_{ij}^{RC}$ . The radical term  $\Pi_{ij}^{RC}$  vanishes for solid state structures.

Due to the way Eq. (21) was taken, only the contribution from  $\overline{b}_{ij}^{0}$  was calculated. The contribution from  $b_{ij}^{DH}$  was ignored.

Here I show how the dihedral term  $b_{ij}^{DH}$  makes a contribution to the bending modulus calculation.

According to the REBO paper [3],

$$b_{ij}^{DH} = T_{ij}(N_i^t, N_j^t, N_{ij}^{conj}) \left[ \sum_{k \neq i, j} \sum_{l \neq i, j} (1 - \cos^2(\Theta_{ijkl}) f_{ik}^c(r_{ik}) f_{jl}^c(r_{jl})) \right]$$

where  $T_{ij}$  is a constant for solid state structures,  $\Theta_{ijkl}$  is the space angle between the bond ik and bond jl, and for moderate deformation, the cutoff functions can be considered as constant 1.

Following the same approach taken in the Appendix B of Ref. [1], at ground state,

$$\frac{\partial^{2}(b_{ij}^{DH}V_{A})}{\partial\kappa^{2}} = V_{A} \frac{\partial^{2}b_{ij}^{DH}}{\partial\kappa^{2}} = T_{ij}V_{A} \sum_{k \neq i, j} \sum_{l \neq i, j} \frac{\partial^{2}}{\partial\kappa^{2}} [\sin^{2}(\Theta_{ijkl})]$$
$$\frac{\partial^{2}}{\partial\kappa^{2}} [\sin^{2}(\Theta_{ijkl})] = \frac{\partial}{\partial\kappa} [2\sin\Theta_{ijkl}\cos\Theta_{ijkl}\cos\Theta_{ijkl}} \frac{\partial\Theta_{ijkl}}{\partial\kappa}] = \frac{\partial}{\partial\kappa} [\sin2\Theta_{ijkl}} \frac{\partial\Theta_{ijkl}}{\partial\kappa}]$$
$$= 2\cos2\Theta_{ijkl} \left(\frac{\partial\Theta_{ijkl}}{\partial\kappa}\right)^{2} + \sin2\Theta_{ijkl}} \frac{\partial^{2}\Theta_{ijkl}}{\partial\kappa^{2}}$$

At ground state,  $\Theta_{ijkl}$  goes to zero. Thus,

$$\frac{\partial^2}{\partial \kappa^2} [\sin^2(\Theta_{ijkl})] = 2 \left(\frac{\partial \Theta_{ijkl}}{\partial \kappa}\right)^2$$
$$\frac{\partial^2 (b_{ij}^{DH} V_A)}{\partial \kappa^2} = 2T_{ij} V_A \sum_k \sum_l \left(\frac{\partial \Theta_{ijkl}}{\partial \kappa}\right)^2$$

The dihedral angles depend on the curvature and the bond directions. Take zigzag nanotube for example, bond ij can be either perpendicular, or  $\pi/6$  to the circumferential direction.



The dihedral angle can be calculated as a function of curvature from three dimensional geometry. For the bond perpendicular to the circumferential direction, among the four dihedral angles,  $\Theta$ ijk111 =  $\Theta$ ijk212 = 0,  $\Theta$ ijk112 =  $\Theta$ ijk211.

For the bond  $\pi/6$  to the circumferential direction,  $\Theta_{ijk}212 = 0$ ,  $\Theta_{ijk}112 = \Theta_{ijk}211$ .

Similar observation is taken for armchair nanotube. For the bond parallel to the circumferential direction, among the four dihedral angles,  $\Theta$ ijk111 =  $\Theta$ ijk212 = 0,  $\Theta$ ijk112 =  $\Theta$ ijk211.

For the bond  $\pi/3$  to the circumferential direction,  $\Theta ij1k2l2 = 0$ ,  $\Theta ij1k1l2 = \Theta ij1k2l1$ .



The analytical results of the dihedral angles are obtained, but too long to show here. Plots of the dihedral angles and their derivatives are shown in following figures

For armchair nanotubes



The derivatives of the dihedral angles with respect to curvature



For zigzag nanotubes



Derivative of dihedral angles with respect to the curvature



Bond direction	dΘij1k111/dK	dΘij1k112/dK	dΘij1k2l1/dK	dΘij1k2l2/dK
Perpendicular	0	$\frac{\sqrt{3}}{2}r_0$	$\frac{\sqrt{3}}{2}r_0$	0
π/6	$\sqrt{3}r_0$	$\frac{\sqrt{3}}{2}r_0$	$\frac{\sqrt{3}}{2}r_0$	0
Parallel	0	$\frac{\sqrt{3}}{2}r_0$	$\frac{\sqrt{3}}{2}r_0$	0
π/3	$\sqrt{3}r_0$	$\frac{\sqrt{3}}{2}r_0$	$\frac{\sqrt{3}}{2}r_0$	0

The final results of  $\frac{\partial \Theta_{ijkl}}{\partial \kappa}$  at ground state are shown in the table

For atom i on an armchair nanotube, among the 3 bonds surrounding it, one is parallel to the circumferential direction, the other two bond are  $\pi/3$  to it.

$$\sum_{i=1}^{3} \frac{\partial^{2} (b_{ij}^{DH} V_{A})}{\partial \kappa^{2}} = \frac{\partial^{2} (b_{ij}^{DH} V_{A})}{\partial \kappa^{2}} |_{0} + 2 \frac{\partial^{2} (b_{ij}^{DH} V_{A})}{\partial \kappa^{2}} |_{\pi/3}$$
$$= 2T_{ij} V_{A} \left( \sum_{k} \sum_{l} \left( \frac{\partial \Theta_{ijkl}}{\partial \kappa} \right)^{2} |_{0} + 2 \sum_{k} \sum_{l} \left( \frac{\partial \Theta_{ijkl}}{\partial \kappa} \right)^{2} |_{\pi/3} \right) = 21T_{ij} V_{A} r_{0}^{2}$$

Exactly same result is obtained for zigzag.

Therefore, the bending stiffness including the contribution of the dihedral term is

$$C_{b} = \frac{\partial W}{\partial \kappa^{2}} = \frac{1}{S_{0}} \frac{\partial^{2}}{\partial \kappa^{2}} \left( \sum_{i=1}^{3} [V_{R} - \overline{b}_{ij}^{0} V_{A}] \right) - \frac{1}{S_{0}} \sum_{i=1}^{3} \frac{\partial^{2} (b_{ij}^{DH} V_{A})}{\partial \kappa^{2}}$$
$$= -\frac{\sqrt{3}V_{A}}{4} \frac{\frac{1}{2} d(b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi})}{d\cos\theta} - \frac{14\sqrt{3}T_{ij}V_{A}}{3}$$

Here S<sub>0</sub> is the area of a hexagon.  $S_0 = \frac{3\sqrt{3}}{2}r_0^2$ 

The first part is directly taken from Ref [1], and the second part is the contribution of the dihedral term.

On Brenner's REBO paper [3], Tij = -0.00809675. In our atomistic simulation, for some reason, Tij is taken as half of this number. In this case,

$$C_{\rm b} = 2.246 \times 10^{-19} \,\rm Nm$$

Following is a comparison between our atomistic simulation and the above theoretical analysis. They match exactly.



This is about twice of what Ref [1] gives  $(1.1 \times 10^{-19} \text{ Nm})$ . Ref. [4] took a different approach, but ignored the contribution of the dihedral term for the 2<sup>nd</sup> generation Brenner potential too. Their result is identical to Ref. [1].

## Reference

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