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Reactive empirical bond-order (REBO) potential

1. A little history of REBO.

The reactive empirical bond-order (REBO) model is a widely-used theory to calculate the potential energy of covalent bonds. In 1988, based on works of Abell [1], Tersoff proposed a many-body energy function [2] parameterized for carbon [3] and multicomponent systems [4]. The expression of the total potential energy of system is a sum of nearest-neighbour pair interactions which depend not only on the coordination of atoms but also on their local atomic environment. A simple parameterized bond order function was used to describe chemical pair bonded interactions. This theory could realistically describe single, double and triple bond energies of carbon structures such as some hydrocarbons and diamond. A significant step was taken by Brenner [5] for conjugated hydrocarbons and carbon system [6] [7] in 1990. He extended Tersoff's potential function by introducing two additional terms into the bond order to describe radical and conjugated bonds.

Because only nearest-neighbour interactions have been considered, the REBO function could be quickly evaluated. This computational efficiency could therefore be well adapted in numeric simulations [8]. In the research works concerning the mechanical properties of CNTs in past 20 years, REBO functions have been used to study the elastic properties [7]-[18] and the structural stabilities (defect, buckling, ultimate strength and bond breaking…) [19]-[25] of CNTs. An acceptable accuracy has been reported in some of these works, by comparing with the experimental, *ab initio* or *tight-binding* results.

Despite numerous successful applications of the first-generation REBO potential functions, they suffer from several drawbacks. First, its form is too restrictive to simultaneously fit equilibrium distances, energies, and force constants for all types of carbon-carbon bonds. Second, the possibility of modelling processes involving energetic atomic collisions is limited because both Morse-type terms go to finite values as the distance between atoms decreases. Third, the absence of dispersion and the non-bonded repulsion term make the potential poorly suited for any system with significant intermolecular interaction. In the simulation of carbon nanotubes under bending strain, the REBO potential has been reported to lead direct inaccuracy at high level of deformation [13]. Finally, it has been reported by Pettifor and co-workers [26] that the neglect of a separate π bond contribution leads to problems with the overbinding of radicals and a poor treatment of conjugacy.
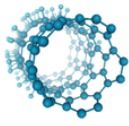
So as to resolve these problems, an adaptive intermolecular reactive bond order (AIREBO) function has been proposed by Stuart and co-workers [27] in 2000. In this theory, the entire system energy was given by the expression

$$E^{\text{total}} = E^{\text{REBO}} + E^{\text{non-bonded}} + E^{\text{single-bond-torsion}}$$

$E^{\text{non-bonded}}$ is the non-bonded interactions term (Lennard-Jones 12-6 potential function), and $E^{\text{single-bond-torsion}}$ represents the torsional interactions about single bonds. Both the repulsive and the attractive pair interaction functions have been modified to simultaneously fit bond properties that could not be fitted by the first-generation Brenner's function. This potential function can be well adapted to reactive systems.

In 2002, Brenner proposed a second-generation reactive empirical bond order function (REBO2) [28]. In which the form of bond energy function were written in similar forms as the Stuart's, but non-bonded interactions and torsional interactions about single bonds were not considered. Recently, in the simulation works using REBO2 [29] [30], a good agreement between numeric and experimental results has been reported.

Considering the study emphasis in this work and the properties (accuracy, computational efficiency and compatibility) of potential function, we employ Brenner's REBO2 potential function in our simulations.

2. REBO2

In this theory, the total chemical binding energy E_b is a collection of that of individual atoms, in which only the nearest-neighbour interactions are considered.

$$E_b = \sum_i \sum_{j(j>i)} \left[V^R(r_{ij}) - b_{ij} V^A(r_{ij}) \right] \tag{1}$$

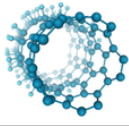where:

V^R is the interatomic repulsion term.

V^A is the interatomic attraction term, which represents bonding from valence electrons. It is assumed to be transferable between different atomic hybridization.

r_{ij} is the distance between atoms i and j.

b_{ij} is the bond order function between atoms i and j that is derived from Huckel electronic structure theory. All many-body effects are included in this function.

2.1. Switching function (cut-off function) $f^c_{ij}(r)$

The switching function restricts the pair interaction to the nearest neighbours:

$$f_{ij}^c(r) = \begin{cases} 1 & r < D_{ij}^{\min} \\ \left[1 + \cos\left(\dfrac{\pi(r - D_{ij}^{\min})}{D_{ij}^{\max} - D_{ij}^{\min}}\right)\right]/2 & D_{ij}^{\min} < r < D_{ij}^{\max} \\ 0 & r > D_{ij}^{\max} \end{cases} \tag{2}$$

where:

$D_{ij}^{\min}$ and $D_{ij}^{\max}$ are the cut-off radius. $[D_{ij}^{\min}, D_{ij}^{\max}]$ defines the interval in which one drives the contribution of interaction smoothly from one to zero. The presence of switching function in the cut-off range must be taken into account in the simulations and the topic is discussed in [31]-[34]. The values employed in this work are $D_{ij}^{\max} = 2\ \overset{\circ}{A}$ and $D_{ij}^{\min} = 1.7\ \overset{\circ}{A}$.

2.2. Interatomic pair term V^R and V^A:

$$V^R(r) = f^c(r)(1 + \frac{Q}{r})A\exp(-\alpha r) \tag{3}$$

$$V^A(r) = f^c(r)\sum_{n=1,3} B_n\exp(-\beta_n r) \tag{4}$$

where:

parameters Q, A, α, B₁, B₂, B₃, β₁, β₂, β₃ are determined by a fitting routine on a given database of molecular properties taken from standard literature references. The resulting values [28] are given in **table 1**.
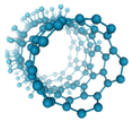
Table 1. Parameters for C-C bond, equations (3) and (4)

	value		value		value
Q (Å)	0.313 460 3	B_1 (eV)	12 388.792	β_1 (Å⁻¹)	4.720 452 3
A (eV)	10 953.544	B_2 (eV)	17.567 406	β_2 (Å⁻¹)	1.433 213 2
α (Å⁻¹)	4.746 539 1	B_3 (eV)	30.714 932	β_3 (Å⁻¹)	1.382 691 3

2.3. the bond order function b_{ij}

$$b_{ij} = \frac{1}{2}\left[b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi} + b_{ij}^{RC} + b_{ij}^{DH}\right] \tag{5}$$

where:

$b_{ij}^{\sigma-\pi}$ depends on the local coordination and bond angles for atoms *i* and *j*, respectively.

b_{ij}^{RC} represent the influence of radical character and π bond conjugations on the bond energy between atoms i and j.

b_{ij}^{DH} depends on the dihedral angle for C-C double bonds.

The value of b_{ij} is larger for stronger bonds.

2.3.1. $b_{ij}^{\sigma-\pi}$

$$b_{ij}^{\sigma-\pi} = \left[1 + \sum_{k(\neq i,j)} f_{ik}^c(r_{ik}) G(\cos(\theta_{ijk})) \exp(\lambda_{ijk}) + P_{ij}(N_i^C, N_i^H)\right]^{-1/2} \tag{6}$$

where:

θ_{ijk} is definited as the angle between vector $\vec{r}_{ij}$ and $\vec{r}_{ik}$.

N_i^C and N_i^H are the numbers of nearest-neighbour carbon and hydrogen atoms, respectively. These are defined by the sums

$$N_i^C = \sum_{k(\neq i,j)}^{\text{carbon atoms}} f_{ik}^c(r_{ik}) \tag{7}$$

and

$$N_i^H = \sum_{l(\neq i,j)}^{\text{hydrogen atoms}} f_{il}^c(r_{il}) \tag{8}$$

P_{ij} represents a bicubic spline.

$G(\cos(\theta_{ijk}))$ represents the contribution that each nearest neighbour makes to the empirical bond order according to the cosine of the angle of the bonds between atoms i and j. A fifth-order polynomial spline is used to approximate $G(\cos(\theta_{ijk}))$.

$$G(\cos(\theta_{ijk})) \approx \sum_{n=0}^{5} a_n (\cos(\theta_{ijk}))^n \tag{9}$$

Note that in the region $0°<\theta<109.47°$, a revised angular function $g_c(\cos(\theta))$ is proposed because the values from $G(\cos(\theta))$ are too large for undercoordinated carbon atoms.

$$g_c(\cos(\theta)) = G_c(\cos(\theta)) + Q(N_i^t)[\gamma_c(\cos(\theta)) - G_c(\cos(\theta))] \tag{10}$$
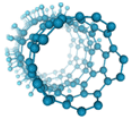
where

$$N_i^t = N_i^C + N_i^H \tag{11}$$

And $Q(N_i^t)$ is defined by

$$Q(N_i^t) = \begin{cases} 1 & N_i^t < 3.2 \\ [1 + \cos(2\pi(N_i^t - 3.2))] / 2 & 3.2 < N_i^t < 3.7 \\ 0 & N_i^t > 3.7 \end{cases} \tag{12}$$

The value of parameters used in this work for $g(\cos(\theta_{ijk})) \approx \sum_{n=0}^{5} a_n (\cos(\theta_{ijk}))^n$ for $N_i^t < 3.2$ is given

in table 2.

Table 2. Parameters for fifth-order polynomial spline approximation, equations (9) and (10)

function	region	a_0	a_1	a_2	a_3	a_4	a_5
g(cos(θ))	*0°<Θ<109.47°*	0.27186	0.48922	-0.43286	-0.56140	1.27111	-0.03793
G(cos(θ))	*109.47°<Θ<120°*	0.69669	5.54440	23.4320	55.9476	69.8760	35.3117
G(cos(θ))	*120°<Θ<180°*	0.28160	1.06200	2.13400	2.53000	1.55200	0.38560

_2.3.2._ b_{ij}^{RC}

$$b_{ij}^{RC} = F_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right) \tag{13}$$

where F is a tricubic spline and N_{ij}^{conj} is a local measure of conjugation in the *i-j* bond.

$$N_{ij}^{conj} = 1 + \left[\sum_{k(\neq i,j)}^{carbon} f_{ik}^c(r_{ik}) H(x_{ik})\right]^2 + \left[\sum_{l(\neq i,j)}^{carbon} f_{jl}^c(r_{jl}) H(x_{jl})\right]^2 \tag{14}$$
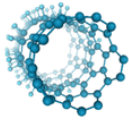
where

$$H(x_{ik}) = \begin{cases} 1 & x_{ik} < 2 \\ [1 + \cos(2\pi(x_{ik} - 2))] / 2 & 2 < x_{ik} < 3 \\ 0 & x_{ik} > 3 \end{cases} \tag{15}$$

and

$$x_{ik} = N_k^t - f_{ik}^c(r_{ik}) \tag{16}$$

The value of N_{ij}^{conj}, which varies from one for nonconjugated bonds to nine for graphite.

2.3.3. b_{ij}^{DH}

$$b_{ij}^{DH} = T_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right)\left[\sum_{k(\neq i,j)}\sum_{l(\neq i,j)}\left(1-\cos^2\left(\Theta_{ijkl}\right)\right)f_{ik}^c\left(r_{ik}\right)f_{jl}^c\left(r_{jl}\right)\right] \tag{17}$$

where

T is a tricubic spline. Its value used in this work is given in table 3.

Θ_{ijkl} is the rotation angle around double bond. It is defined by

$$\Theta_{ijkl} = e_{jik}e_{ijl} \text{ with } e_{jik} = R_{ji} \times R_{ik} \text{ and } e_{ijl} = R_{ij} \times R_{jl}$$

where

e_{jik} and e_{ijl} are the unit vectors in the perpendicular direction to the plans *jik* and *ijl*, respectively.

R is the vector connecting the atoms.

Table 3. Parameters for C-C tricubic spline *T*, equations (17)

N_i^t	N_j^t	N_{ij}^{conj}	$T_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right)$
2	2	9	-0.00809675

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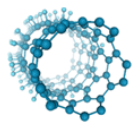
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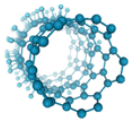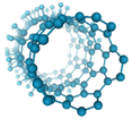
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Appendix A

Interatomic forces calculations by using REBO2 potential energy:

We present an analytical model to calculate the interatomic force by using Brenner's second-generation reactive empirical bond order function (REBO2). The force on an atom **i** is the sum of its all bond interactions. The value of force given by each bond is equal to the negative gradient of the bond potential energy, which has been given in equations (1)-(17).

$$\vec{F}_i = -\vec{\nabla}_i E^{total} \tag{A.1}$$

1. The gradient of interaction pair terms can be expressed as

$$\vec{\nabla} V_{ij}^R = \left(1 + Q/r_{ij}\right)A\exp\left(-\alpha r_{ij}\right)\vec{\nabla} f_{ij}^c - f_{ij}^c\left(\alpha + \alpha Q/r_{ij} + Q/r_{ij}^2\right)A\exp\left(-\alpha r_{ij}\right)\vec{\nabla} r_{ij} \tag{A.2}$$

and

$$\vec{\nabla} V_{ij}^A = \sum_{n=1}^{3} B_n \exp\left(-\beta_n r_{ij}\right)\vec{\nabla} f_{ij}^c - f_{ij}^c\left[\sum_{n=1}^{3}\beta_n B_n \exp\left(-\beta_n r_{ij}\right)\right]\vec{\nabla} r_{ij} \tag{A.3}$$

Where the gradient of switch function f^c is

$$\vec{\nabla} f_{ij}^c(r) = \begin{cases} 0 & r < D_{ij}^{min} \\ -\sin\left(\dfrac{\pi(r_{ij} - D_{ij}^{min})}{D_{ij}^{max} - D_{ij}^{min}}\right)\dfrac{\pi}{2\left(D_{ij}^{max} - D_{ij}^{min}\right)}\vec{\nabla} r_{ij} & D_{ij}^{min} < r_{ij} < D_{ij}^{max} \\ 0 & r > D_{ij}^{max} \end{cases} \tag{A.4}$$

Note that the curve of $\vec{\nabla} f_{ij}^c$ is smoothly continuous in all three intervals.
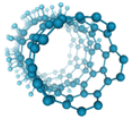
2. The gradient of bond order function b_{ij} can be given by four terms:

$$\vec{\nabla} b_{ij} = \frac{1}{2}\left[\vec{\nabla} b_{ij}^{\sigma-\pi} + \vec{\nabla} b_{ji}^{\sigma-\pi}\vec{\nabla} b_{ij}^{RC} + \vec{\nabla} b_{ij}^{DH}\right] \tag{A.5}$$

2.1 $\vec{\nabla} b_{ij}^{\sigma-\pi}$

It can be obtained as:

$$\vec{\nabla} b_{ij}^{\sigma-\pi} = \frac{-\left(b_{ij}^{\sigma-\pi}\right)^3}{2}\left[\sum_{n=0}^{5} a_n\left(\cos\theta_{pij}\right)^n \exp(\lambda_{pij})\vec{\nabla} f_{ip}^c + \sum_{n=0}^{5} a_n\left(\cos\theta_{qij}\right)^n \exp(\lambda_{qij})\vec{\nabla} f_{iq}^c\right.$$

$$+ \sum_{n=1}^{5} n a_n \left(\cos\theta_{pij}\right)^{n-1} \exp(\lambda_{pij}) f_{ip}^c \vec{\nabla}\cos\theta_{pij} + \sum_{n=1}^{5} n a_n \left(\cos\theta_{qij}\right)^{n-1} \exp(\lambda_{qij}) f_{iq}^c \vec{\nabla}\cos\theta_{qij} + \vec{\nabla}P_{ij} \Bigg] \quad \text{(A.6)}$$

where
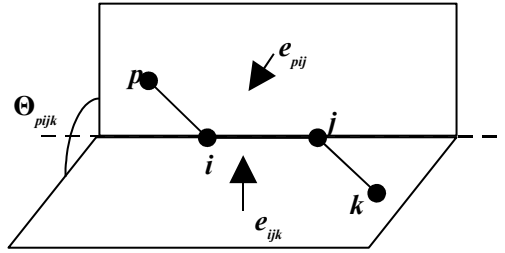
$$\vec{\nabla}\cos\theta_{pij} = \vec{\nabla}\left[\frac{\vec{r}_{ip}\cdot\vec{r}_{ij}}{r_{ip}r_{ij}}\right] = \frac{\vec{\nabla}(\vec{r}_{ip}\cdot\vec{r}_{ij})}{r_{ip}r_{ij}} - \frac{\vec{r}_{ip}\cdot\vec{r}_{ij}}{(r_{ip})^2 r_{ij}}\vec{\nabla}r_{ip} - \frac{\vec{r}_{ip}\cdot\vec{r}_{ij}}{(r_{ij})^2 r_{ip}}\vec{\nabla}r_{ij} \quad \text{(A.7)}$$

2.2 $\vec{\nabla}b_{ij}^{RC}$

$$\vec{\nabla}b_{ij}^{RC} = \vec{\nabla}F_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right) \quad \text{(A.8)}$$

2.3 $\vec{\nabla}b_{ij}^{DH}$

2.3.1 Here we cite an example of calculation of the dihedral angle Θ_{pijk} between two plans defined by 4 atoms *p,i,j,k* in *fig*A1.

*fig*A1: an example of dihedral angle

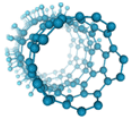$$\cos\Theta_{pijk} = e_{pij}\cdot e_{ijk}$$

Where e_{pij} *and* e_{ijk} are unit vectors in the direction of the cross product. The cosine of dihedral angle can be represented in a form simplified by using double product rules:

$$\cos\Theta_{pijk} = \frac{\vec{r}_{ip}\wedge\vec{r}_{ij}}{r_{ip}r_{ij}\sin\theta_{pij}}\cdot\frac{\vec{r}_{jk}\wedge\vec{r}_{ji}}{r_{jk}r_{ji}\sin\theta_{ijk}} = \left(\frac{\vec{r}_{jk}\cdot\vec{r}_{ip}}{r_{jk}r_{ip}} + \cos\theta_{pij}\cos\theta_{ijk}\right)\frac{-1}{\sin\theta_{pij}\sin\theta_{ijk}} \quad \text{(A.9)}$$

2.3.2 $\vec{\nabla}\cos\Theta_{pijk}$
It can be written as:

$$\vec{\nabla}\cos\Theta_{pijk} = \vec{\nabla}\left[\left(\frac{\vec{r}_{jk}\cdot\vec{r}_{ip}}{r_{jk}r_{ip}} + \cos\theta_{pij}\cos\theta_{ijk}\right)\frac{-1}{\sin\theta_{pij}\sin\theta_{ijk}}\right]$$

$$= \left(\vec{\nabla}\left(\frac{\vec{r}_{jk} \cdot \vec{r}_{ip}}{r_{jk} r_{ip}} \right) + \cos\theta_{ijk} \vec{\nabla}\cos\theta_{pij} + \cos\theta_{pij}\vec{\nabla}\cos\theta_{ijk} \right) \frac{-1}{\sin\theta_{pij}\sin\theta_{ijk}}$$

$$+\cos\Theta_{pijk}\left[\frac{\cos\theta_{ijk}}{\left(\sin\theta_{ijk}\right)^2}\vec{\nabla}\cos\theta_{ijk} + \frac{\cos\theta_{pij}}{\left(\sin\theta_{pij}\right)^2}\vec{\nabla}\cos\theta_{pij} \right] \tag{A.10}$$

Where $\vec{\nabla}\cos\theta$ has been calculated in equation (A.8) and (A.9)

2.3.3 $\vec{\nabla}b_{ij}^{DH}$

So we can easily obtain:

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

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

$$+ T_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right)\left[\sum_{k(\neq i,j)}\sum_{l(\neq i,j)}\left(1-\cos^2\left(\Theta_{ijkl}\right)\right)f_{jl}^c(r_{jl})\vec{\nabla}f_{ik}^c(r_{ik}) \right] \tag{A.12}$$

$$+ T_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right)\left[\sum_{k(\neq i,j)}\sum_{l(\neq i,j)}f_{jl}^c(r_{jl})f_{ik}^c(r_{ik})\left(-2\cos\left(\Theta_{ijkl}\right)\right)\vec{\nabla}\cos\left(\Theta_{ijkl}\right) \right]$$
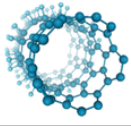
3. Gradient of splines

3.1 $\vec{\nabla}P_{ij}\left(N_i^C, N_i^H\right)$

$$\vec{\nabla}P_{ij}\left(N_i^C, N_i^H\right) = \frac{\partial P_{ij}}{\partial N_i^C}\vec{\nabla}N_i^C + \frac{\partial P_{ij}}{\partial N_i^H}\vec{\nabla}N_i^H$$

where

$$\vec{\nabla}N_i^C = \sum_{k(\neq i,j)}\vec{\nabla}f_{ik}^c(r_{ik}) \quad \text{and} \quad \vec{\nabla}N_i^H = \sum_{k(\neq i,j)}\vec{\nabla}f_{ik}^H(r_{ik})$$

3.2 $\vec{\nabla}F_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right)$

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$$\vec{\nabla} F_{ij}\left(N_i^t, N_j^t, N_{ij}^{conj}\right) = \frac{\partial F_{ij}}{\partial N_i^t}\vec{\nabla} N_i^t + \frac{\partial F_{ij}}{\partial N_j^t}\vec{\nabla} N_j^t + \frac{\partial F_{ij}}{\partial N_{ij}^{conj}}\vec{\nabla} N_{ij}^{conj}$$

Where

$$\vec{\nabla} N_i^t = \vec{\nabla} N_i^C + \vec{\nabla} N_i^H$$

and

$$\vec{\nabla} N_{ij}^{conj} = \vec{\nabla}\left[\sum_{k(\neq i,j)}^{carbon} f_{ik}^c(r_{ik})H(x_{ik})\right]^2 + \vec{\nabla}\left[\sum_{l(\neq i,j)}^{carbon} f_{jl}^c(r_{jl})H(x_{jl})\right]^2$$

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