Supporting Information for

Development of Reactive Force Field for Fe-C interaction to Visit

Carburization of Iron

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(1) ReaxFF Potential Function

This document contains all the general ReaxFF-potential functions. In the current ReaxFF code all the energy contributions in this document are calculated regardless of system composition. All parameters that do not bear a direct physical meaning are named after the partial energy contribution that they appear in. For example, *pval1* and *pval2* are parameters in the valence angle potential function. Parameters with a more direct physical meaning, like the torsional rotational barriers (*V1, V2, V3*) bear their more recognizable names.

1. Oveall system energy

Equation (1) describes the ReaxFF overall system energy.

$$E_{systerm} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C2} + E_{triple} + E_{tors} + E_{conj} + E_{H-bond} + E_{vdw} + E_{Coulomb}$$
(1)

Below follows a description of the partial energies introduced in eq (1).

2. Bond Order and Bond Energy

A fundamental assumption of ReaxFF is that the bond order *BO'ij* between a pair of atoms can be obtained directly from the interatomic distance *rij* as given in eq (2). In calculating the bond orders, ReaxFF distinguishes between contributions from sigma bonds, pi-bonds and double pi bonds.

$$BO'_{ij} = BO'_{ij}^{\sigma} + BO'_{ij}^{\pi} + BO'_{ij}^{\pi\pi}$$

= exp[$P_{bo1}(\frac{r_{ij}}{r_0^{\sigma}})^{P_{bo2}}$] + exp[$P_{bo3}(\frac{r_{ij}}{r_0^{\pi}})^{P_{bo4}}$] + exp[$P_{bo5}(\frac{r_{ij}}{r_0^{\pi\pi}})^{P_{bo6}}$] (2)

Based on the uncorrected bond orders *BO*', derived from eq (2), an uncorrected overcoordination Δ ' can be defined for the atoms as the difference between the total bond order around the atom and the number of its bonding electrons *Val*.

$$\Delta'_{i} = \sum_{j=1}^{nbond} BO'_{ij} - Val_{i}$$
(3)

ReaxFF then uses these uncorrected overcoordination definitions to correct the bond orders BO'_{ij} using the scheme described in eq (5-11). To soften the correction for atoms bearing lone electron pairs a second overcoordination definition Δ'^{boc} (eq (4)) is used in eqs (10) and (11). This allows atoms like nitrogen and oxygen, which bear lone electron pairs after filling their valence, to break up these electron pairs and involve them in bonding without obtaining a full bond order correction.

$$\Delta_i^{'boc} = \sum_{j=1}^{nbond} BO'_{ij} - Val_i^{boc}$$

$$\tag{4}$$

$$BO_{ij}^{\sigma} = BO_{ij}^{\sigma} * f_{1}(\Delta_{i}^{'}, \Delta_{j}^{'}) * f_{4}(\Delta_{i}^{'}, BO_{ij}^{'}) * f_{5}(\Delta_{j}^{'}, BO_{ij}^{'})$$

$$BO_{ij}^{\pi} = BO_{ij}^{\sigma} * f_{1}(\Delta_{i}^{'}, \Delta_{j}^{'}) * f_{1}(\Delta_{i}^{'}, \Delta_{j}^{'}) * f_{4}(\Delta_{i}^{'}, BO_{ij}^{'}) * f_{5}(\Delta_{j}^{'}, BO_{ij}^{'})$$

$$BO_{ij}^{\pi\pi} = BO_{ij}^{\sigma} * f_{1}(\Delta_{i}^{'}, \Delta_{j}^{'}) * f_{1}(\Delta_{i}^{'}, \Delta_{j}^{'}) * f_{4}(\Delta_{i}^{'}, BO_{ij}^{'}) * f_{5}(\Delta_{j}^{'}, BO_{ij}^{'})$$
(5)

$$BO_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} \tag{6}$$

$$f_{1}(\Delta_{i},\Delta_{j}) = \frac{1}{2} * \left(\frac{Val_{i} + f_{2}(\Delta_{i},\Delta_{j}) + f_{3}(\Delta_{i},\Delta_{j})}{Val_{i} + f_{2}(\Delta_{i},\Delta_{j}) + f_{3}(\Delta_{i},\Delta_{j})} + \frac{Val_{j} + f_{2}(\Delta_{i},\Delta_{j}) + f_{3}(\Delta_{i},\Delta_{j})}{Val_{j} + f_{2}(\Delta_{i},\Delta_{j}) + f_{3}(\Delta_{i},\Delta_{j})} \right)$$
(7)

$$f_{2}(\Delta_{i}',\Delta_{j}') = \exp(-p_{boc1}*\Delta_{i}') + \exp(-p_{boc1}*\Delta_{j}')$$
(8)

$$f_{3}(\Delta_{i}, \Delta_{j}) = -\frac{1}{p_{boc2}} * In\{\frac{1}{2} * [\exp(-p_{boc2} * \Delta_{i}) + \exp(-p_{boc2} * \Delta_{j})]\}$$
(9)

$$f_4(\Delta'_i, BO'_{ij}) = \frac{1}{1 + \exp(-p_{boc3} * (p_{boc4} * BO'_{ij} * BO'_{ij} - \Delta'^{boc}) + p_{boc5})}$$
(10)

$$f_{5}(\vec{\Delta}_{j}, B\vec{O}_{ij}) = \frac{1}{1 + \exp(-p_{boc3} * (p_{boc4} * B\vec{O}_{ij} * B\vec{O}_{ij} - \vec{\Delta}_{j}^{boc}) + p_{boc5})} \quad (11)$$

A corrected overcoordination Δ_i can be derived from the corrected bond orders using eq (12).

$$\Delta_i = -Val_i + \sum_{j=1}^{neighours(i)} BO_{ij}$$
(12)

Equation (13) is used to calculate the bond energies from the corrected bond orders BO_{ij} .

$$E_{bond} = -D_e^{\sigma} * BO_{ij}^{\sigma} * \exp[P_{be1} * (1 - (BO_{ij}^{\sigma})^{P_{be2}})] - D_e^{\pi} * BO_{ij}^{\pi} - D_e^{\pi\pi} * BO_{ij}^{\pi\pi}$$
(13)

3. Lone pair energy

Equation (15) is used to determine the number of lone pairs around an atom. Δ_i^e is determined in eq (7) and describes the difference between the total number of outer shell electrons (6 for oxygen, 4 for silicon, 1 for hydrogen) and the sum of bond orders around an atomic center.

$$\Delta_i^e = -Val_i^e + \sum_{j=1}^{neighours(i)} BO_{ij}$$
(14)

$$n_{lp,i} = \operatorname{int}(\frac{\Delta_i^e}{2}) + \exp\{-p_{lp1} * [2 + \Delta_i^e - 2 * \operatorname{int}(\frac{\Delta_i^e}{2})]^2\}$$
(15)

For oxygen with normal coordination (total bond order=2, $\Delta_{i=4}^{e}$), eq (15) leads to 2 lone pairs. As the total bond order associated with a particular O starts to exceed 2, eq (15) causes a lone pair to gradually break up, causing a deviation Δ_{i}^{lp} , defined in eq (16), from the optimal number of lone pairs $n_{lp,opt}$ (e.g. 2 for oxygen, 0 for silicon and hydrogen).

$$\Delta_i^{lp} = n_{lp,opt} - n_{lp,i} \tag{16}$$

This is accompanied by an energy penalty, as calculated by eq(17).

$$E_{lp} = \frac{p_{lp2} * \Delta_i^{lp}}{1 + \exp(-75 * \Delta_i^{lp})}$$
(17)

4. Overcoordination

For an overcoordinated atom ($\Delta_i > 0$), eqs (18-19) impose an energy penalty on the system. The degree of overcoordination Δ is decreased if the atom contains a broken-up lone electron pair. This is done by calculating a corrected overcoordination (eq (19)), taking the deviation from the optimal number of lone pairs, as calculated in eq (16), into account.

$$E_{over} = \frac{\sum_{j=1}^{nbond} p_{ovun1} * D_e^{\sigma} * BO_{ij}}{\Delta_i^{lpcorr} + Val_i} * \Delta_i^{lpcorr} * \left[\frac{1}{1 + \exp(p_{ovun2} * \Delta_i^{lpcorr})}\right]$$
(18)

$$\Delta_{i}^{lpcorr} = \Delta_{i} - \frac{\Delta_{i}^{lp}}{1 + p_{ovun3} * \exp(p_{ovun4} * \{\sum_{j=1}^{neighbours(i)} (\Delta_{j} - \Delta_{j}^{lp}) * (BO_{ij}^{\pi} + BO_{ij}^{\pi\pi})\})$$
(19)

5. Undercoordination

For an undercoordinated atom ($\Delta_i < 0$), we want to take into account the energy contribution for the resonance of the π -electron between attached under-coordinated atomic centers. This is done by eq (20) where E_{under} is only important if the bonds between under-coordinated atom *i* and its undercoordinated neighbors *j* partly have π -bond character.

$$E_{under} = -P_{under} * \frac{1 - \exp\left(p_{ovun6} * \Delta_{i}^{lpcor}\right)}{1 + \exp\left(-p_{ovun2} * \Delta_{i}^{lpcor}\right)} * f_{6}(BO_{ij,\pi}, \Delta_{j})$$
(20)

$$f_{6}(BO_{ij,\pi}, \Delta_{j}) = \frac{1}{1 + p_{ovun7} * \exp(p_{ovun8} * \{\sum_{j=1}^{neighbours(i)} (\Delta_{j} - \Delta_{j}^{lp}) * (BO_{ij}^{\pi} + BO_{ij}^{\pi\pi})\})}$$
(21)

6. Valence Angle Terms

6.1 Angle energy. Just as for bond terms, it is important that the energy contribution from valence angle terms goes to zero as the bond orders in the valence angle goes to zero. Equations (22-28) are used to calculate the valence angle energy contribution. The equilibrium angle Θ_o for Θ_{ijk} depends on the sum of π -bond orders (SBO) around the central atom *j* as described in eq (25). Thus, the equilibrium angle changes from around 109.47 for sp3 hybridization (π -bond=0) to 120 for sp2 (π bond=1) to 180 for sp (π -bond=2) based on the geometry of the central atom *j* and its neighbors. In addition to including the effects of π -bonds on the central atom *j*, eq (25) also takes into account the effects of over- and under-coordination in central atom *j*, as determined by eq (26), on the equilibrium valency angle, including the influence of a lone electron pair. *Val^{angle}* is the valency of the atom used in the valency and torsion angle evaluation. *Val^{angle}* is the same as *Val^{boc}* used in eq (4) for non-metals. The functional form of eq (27) is designed to avoid singularities when SBO=0 and SBO=2. The angles in eqs (22)-(28) are in radians.

$$E_{val} = f_7 (BO_{ij}) * f_7 (BO_{jk}) * f_8 (\Delta_j) * \{ p_{val1} - p_{val1} * \exp[-p_{val2} * (\Theta_0 - \Theta_{ijk})^2] \}$$
(22)

$$f_7(BO_{ij}) = 1 - \exp(-p_{val3} * BO_{ij}^{p_{val4}})$$
(23)

$$f_{8}(\Delta_{j}) = [p_{val5} - (p_{val5} - 1)*\frac{2 + \exp(p_{val6}*\Delta_{j}^{angle})}{1 + \exp(p_{val6}*\Delta_{j}^{angle}) + \exp(-p_{val7}*\Delta_{j}^{angle})}]$$
(24)

$$SBO = \sum_{n=1}^{neighbours(j)} (BO_{jn}^{\pi} + BO_{jn}^{\pi\pi}) + [1 - \prod_{n=1}^{neighbours(j)} \exp(BO_{jn}^{8})] * (-\Delta_{j}^{angje} - p_{val8} * n_{lp,j})$$
(25)

$$\Delta_{j}^{angje} = -Val_{j}^{angje} + \sum_{n=1}^{neighbours(j)} BO_{jn}$$
(26)

$$SBO2 = 0 \quad if \quad SBO \le 0$$

$$SBO2 = SBO^{p_{val9}} \quad if \quad 0 < SBO < 1$$

$$SBO2 = 2 - (2 - SBO)^{p_{val9}} \quad if \quad 1 < SBO < 2$$

$$SBO2 = 2 \quad if \quad SBO > 2$$

$$(27)$$

$$\Theta_0 = \pi - \Theta_{0,0} * \{ 1 + \exp[-p_{val10} * (2 - SBO2)] \}$$
(28)

6.2 Penalty energy. To reproduce the stability of systems with two double bonds sharing an atom in a valency angle, like allene, an additional energy penalty, as described in eqs (29) and (30), is imposed for such systems. Equation (30) deals with the effects of over/undercoordination in central atom j on the penalty energy.

$$E_{Pen} = p_{pen1} * f_9(\Delta_j) * \exp[-p_{pen2} * (BO_{ij} - 2)^2] * \exp[-p_{pen2} * (BO_{jk} - 2)^2]$$
(29)

$$f_{9}(\Delta_{j}) = \frac{2 + \exp(-p_{pen3} * \Delta_{j})}{1 + \exp(-p_{pen3} * \Delta_{j}) + \exp(p_{pen4} * \Delta_{j})}$$
(30)

6.3 Three-body conjugation term. The hydrocarbon ReaxFF potential contained only a conjugation term, which was sufficient to describe most conjugated hydrocarbon systems. However,

this term failed to describe the stability obtained from conjugation by the $-NO_2$ - group. To describe the stability of such groups a three-body conjugation term is included (eq (31)).

$$E_{coa} = p_{coa1} * \frac{1}{1 + \exp(p_{coa2} * \Delta_{j}^{val})} * \exp[-p_{coa3} * (-BO_{ij} - \sum_{n=1}^{neighbours(i)} BO_{in})^{2}] *$$

$$\exp[-p_{coa3} * (-BO_{jk} + \sum_{n=1}^{neighbours(i)} BO_{kn})^{2}] *$$

$$\exp[-p_{coa4} * (BO_{ij} - 1.5)^{2}] * \exp[-p_{coa4} * (BO_{jk} - 1.5)^{2}]$$
(31)

7. Torsion angle terms

7.1 Torsion rotation barriers. Just as with angle terms we need to ensure that dependence of the energy of torsion angle ω_{ijkl} accounts properly for $BO \rightarrow 0$ and for BO greater than 1. This is done by eqs (32)-(34).

$$E_{tors} = f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) * \sin \Theta_{ijk} * \sin \Theta_{jkl} * \left[\frac{1}{2}V_1 * (1 + \cos \omega_{ijkl}) + \frac{1}{2}V_2 * \exp\{p_{tor1}(BO_{jk}^{\pi} - 1 + f_{11}(\Delta_j, \Delta_k))^2\} * (1 - \cos 2\omega_{ijkl}) + \frac{1}{2}V_3 + (1 + \cos 3\omega_{ijkl})]$$
(32)

$$f_{10}(BO_{ij}, BO_{jk}, BO_{kl}) = [1 - \exp(-p_{tor2} * BO_{ij})] * [1 - \exp(-p_{tor2} * BO_{jk})] * [1 - \exp(-p_{tor2} * BO_{kl})]$$
(33)

$$f_{11}\left(\Delta_{j},\Delta_{k}\right) = \frac{2 + \exp\left[-p_{tor3}^{*}\left(\Delta_{j}^{angle} + \Delta_{k}^{angle}\right)\right]}{1 + \exp\left[-p_{tor3}^{*}\left(\Delta_{j}^{angle} + \Delta_{k}^{angle}\right)\right] + \exp\left[p_{tor4}^{*}\left(\Delta_{j}^{angle} + \Delta_{k}^{angle}\right)\right]}$$
(34)

7.2 Four body conjugation term. Equations (35-36) describe the contribution of conjugation effects to the molecular energy. A maximum contribution of conjugation energy is obtained when successive bonds have bond order values of *1.5* as in benzene and other aromatics.

$$E_{conj} = f_{12} \left(BO_{ij}, BO_{jk}, BO_{kl} \right)^* p_{cot1} * [1 + (\cos^2 \omega_{ijkl} - 1)^* \sin \Theta_{ijk} * \sin \Theta_{jkl}]$$
(35)

$$f_{12} \left(BO_{ij}, BO_{jk}, BO_{kl} \right) = \exp[-p_{\cot 2} * (BO_{ij} - 1\frac{1}{2})^2] * \exp[-p_{\cot 2} * (BO_{jk} - 1\frac{1}{2})^2] * \exp[-p_{\cot 2} * (BO_{kl} - 1\frac{1}{2})^2]$$
(36)

8. Hydrogen bond interactions

Equation (37) described the bond-order dependent hydrogen bond term for a X-H—Z system as incorporated in ReaxFF.

$$E_{H-bon\ d} = p_{hb1} * [1 - \exp(p_{hb2} * BO_{XH})] * \exp[p_{hb3} * (\frac{r_{hb}^0}{r_{HZ}} + \frac{r_{HZ}}{r_{hb}^0} - 2)] * \sin^8(\frac{\Theta_{XHZ}}{2})$$
(37)

9. Correction for C₂

ReaxFF erroneously predicts that two carbons in the C₂-molecule form a very strong (triple) bond, while in fact the triple bond would get de-stabilized by terminal radical electrons, and for that reason the carbon-carbon bond is not any stronger than a double bond. To capture the stability of C₂, the partial energy contribution (${}^{E}C_{2}$) was introduced. Equation (38) shows the potential function used to de-stabilize the C₂ molecule:

$$E_{C_2} = k_{c2} * (BO_{ij} - \Delta_i - 0.04 * \Delta_i^4 - 3)^2 \quad if \quad BO_{ij} - \Delta_i - 0.04 * \Delta_i^4 - 3 > 0$$

$$E_{C_2} = 0 \quad if \quad BO_{ij} - \Delta_i - 0.04 * \Delta_i^4 - 3 \le 0$$
(38)

where Δ_i is the level of under/overcoordination on atom *i* as obtained from subtracting the valency of the atom (4 for carbon) from the sum of the bond orders around that atom and k_{c2} the force field parameter associated with this partial energy contribution.

10. Triple bond energy correction.

To describe the triple bond in carbon monoxide a triple bond stabilization energy is used, making CO both stable and inert. This energy term only affects C-O bonded pairs. Equation (39) shows the energy function used to describe the triple bond stabilization energy.

$$E_{trip} = p_{trip1} * \exp[-p_{trip2} * (BO_{ij} - 2.5)^{2}] \\ * \frac{\exp[-p_{trip4} * (\sum_{k=1}^{neighours(i)} BO_{ik} - BO_{ij})] + \exp[-p_{trip4} * (\sum_{k=1}^{neighours(i)} BO_{jk} - BO_{ij})]}{1 + 25 * \exp[p_{trip3} * (\Delta_{i} + \Delta_{j})]}$$
(39)

11. Nonbonded interactions

In addition to valence interactions which depend on overlap, there are repulsive interactions at short interatomic distances due to Pauli principle orthogonalization and attraction energies at long distances due to dispersion. These interactions, comprised of van der Waals and Coulomb forces, are included for all atom pairs, thus avoiding awkward alterations in the energy description during bond dissociation.

11.1 Taper correction. To avoid energy discontinuities when charged species move in and out of the non-bonded cutoff radius ReaxFF employs a Taper correction, as developed by de Vos Burchart. Each nonbonded energy and derivative is multiplied by a Taper-term, which is taken from a distance-dependent 7th order polynomial (eq (40)).

$$Tap = Tap_{7} * r_{ij}^{7} + Tap_{6} * r_{ij}^{6} + Tap_{5} * r_{ij}^{5} + Tap_{4} * r_{ij}^{4} + Tap_{3} * r_{ij}^{3} + Tap_{2} * r_{ij}^{2} + Tap_{1} * r_{ij} + Tap_{0}$$
(40)

$$Tap_{7} = \frac{20}{R_{cut}^{7}} \qquad Tap_{6} = \frac{-70}{R_{cut}^{6}} \qquad Tap_{5} = \frac{84}{R_{cut}^{5}} \qquad Tap_{4} = \frac{-35}{R_{cut}^{4}}$$
(41)
$$Tap_{3} = 0 \qquad Tap_{2} = 0 \qquad Tap_{1} = 0 \qquad Tap_{0} = 1$$

11.2 van der Waals interactions. To account for the van der Waals interactions we use a distance-corrected Morse-potential (eqs (42-43)). By including a shielded interaction (eq (43)) excessively high repulsions between bonded atoms (1-2 interactions) and atoms sharing a valence angle (1-3 interactions) are avoided.

$$E_{vdw} = Tap * D_{ij} * \{ \exp[\alpha_{ij} * (1 - \frac{f_{13}(r_{ij})}{r_{vdw}})] - 2 * \exp[\frac{1}{2} * \alpha_{ij} * (1 - \frac{f_{13}(r_{ij})}{r_{vdw}})] \}$$
(42)

$$f_{13}(r_{ij}) = \left[r_{ij}^{p_{vdw1}} + \left(\frac{1}{\gamma_w}\right)^{p_{vdw1}}\right]^{\frac{1}{p_{vdw1}}}$$
(43)

11.3 Coulomb Interactions. As with the van der Waals-interactions, Coulomb interactions are taken into account between all atom pairs. To adjust for orbital overlap between atoms at close distances a shielded Coulomb-potential is used (eq (44)).

$$E_{coulomb} = Tap * C * \frac{q_i * q_j}{[r_{ij}^3 + (1 / \gamma_{ij})^3]^{1/3}}$$
(44)

Atomic charges are calculated using the Electron Equilibration Method (EEM)-approach. The EEM charge derivation method is similar to the QEq-scheme; the only differences, apart from parameter definitions, are that EEM does not use an iterative scheme for hydrogen charges (as in QEq) and that QEq uses a more rigorous Slater orbital approach to account for charge overlap.

(2) MEAM Potential Function

1. Total Energy

The total energy E of a system of atoms in the modified embedded-atom method (MEAM) has been shown by the form:

$$E = \sum_{i} \left[F_{i}(\overline{\rho}_{i}) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(R_{ij}) \right]$$
(45)

In this form, the embedding function F_i is the energy to embed an atom of type *i* into the background electron density $\bar{\rho}_i$ at site *i*, ϕ_{ij} is a pair interaction between atoms *i* and *j* whose separation is given by R_{ij} .

2. Pair Interaction

 E_i is the total energy of the direct contribution from the *i*th atom and indirection contribution through its interaction with its neigbors:

$$E_{i} = F_{i}(\frac{\overline{\rho}_{i}}{Z_{i}}) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(R_{ij})$$
(46)

where, Z_i is the number of nearest neighbors of a type-*i* atom of reference structure. The reference structure is always a equilibrium crystal structure of type-*i* atoms.

By limiting the interactions to first neighbors only, a number of important questions about cutoffs or screening was introduced.

$$E_i^u(R) = F_i(\frac{\overline{\rho}_i^0(R)}{Z_i}) + \frac{Z_i}{2}\phi_{ii}(R)$$
(47)

where $\bar{\rho}_i^{0}(R)$ is the background electron density for the reference structure of atom *i* and *R* is the nearestneighbor distance. Here $E_i^u(R)$ is the energy per atom of the reference structure as a function of nearest-neighbor distance. Assuming that $E_i^u(R)$ is known, we derived the pair interaction for type-*i* atoms:

$$\phi_{ii}(R) = \frac{2}{Z_i} \left\{ E_i^u(R) - F_i(\frac{\bar{\rho}_i^0(R)}{Z_i}) \right\}$$
(48)

3. Background Electron Density

The embedded- atom method (EAM) used a linear superposition of spherically averaged atomic electron densities, while in the MEAM, $\bar{\rho}_i$ is augmented by an angularly dependent term. The background electron density at each atomic site *i* is computed considering the directionality of bonding, that is, by combining several partial electron density terms for different angular contributions with weight factors $t^{(h)}$ (h = 1–3). Each partial electron density is a function of atomic configuration and atomic electron density. The atomic electron densities $\rho^{a(h)}$ (h = 0 – 4) are given as:

$$\rho^{a(h)}(R) = \rho_0 \exp\left[-\beta^{(h)}(\frac{R}{r_e} - 1)\right]$$
(49)

where ρ_0 is the atomic electron density scaling factor and $\beta^{(h)}$ decay lengths are adjustable parameters, and r_e is the nearest-neighbor distance in the equilibrium reference structure.

(3) Means Square Displacement

Diffusion coefficient was obtained by calculating the means square displacement (MSD) as follow:

$$MSD = \langle |r(t) - r(0)|^2 \rangle$$
 (50)

$$D = \frac{1}{6} \lim_{\Delta t \to 0} \frac{MSD(t + \Delta t) - MSD(t)}{\Delta t}$$
(51)

where, r represent the position of particle, t is the time and D is the abbreviation of diffusion coefficient.

(4) Arrhenius Equation

The diffusion barrier was fitted by using Arrhenius equation:

$$D(T) = D_0 \exp\left(-\frac{E_a}{\kappa T}\right)$$
(52)

where, E_a is the activation energy, D_0 is the pre-exponential factor and κ is the Boltzmann factor and *T* represents the temperature.

(5) The top view of all structures in Figure 5

(a) The structures with carbon on different sites on Fe(100)



4FS1BS2B-3C 4F4FS1B-c2x2-3C-1

(b): The structures with carbon on different sites on Fe(110)



Sub-4C



(c): The structures with carbon on different sites on Fe(111)

(d): The predicted structures



2dimer5chain-9C

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10chain-10C