

## **A Brand New Reactive Potential Made Molecular Dynamics on Chemical Reaction Possible**

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**Abstract:**

A new idea is brought in this paper that molecular dynamics with a force field integrated a brand new reactive potential form which considered bond breaking and forming can be used to simulate chemical reaction. As an example, we report here a force field CRACK developed for studying pyrolysis process of n-alkane. CRACK splines together a harmonic well and a shallow Lennard-Jones well: the harmonic well models C-C covalent bond while the Lennard-Jones well models long-range van der Waals forces. These two wells are separated by an energy barrier which controls dissociation and recombination. To validate this new reactive potential form, CRACK has been used to simulate pyrolysis process of n-decane and n-octane by molecular dynamics (MD). The dissociation probabilities as well as product distributions were analyzed and the time history of pyrolysis was illustrated. The research on dissociation probabilities shows that the defined pyrolytic temperature could be altered by changing the displacement constant  $d_e$  which controls the height of dissociation barrier of C-C bond and it was also found that the pyrolytic temperature of n-octane was higher than of n-decane at the same  $d_e$ , which is consistent with the pyrolysis fundamental. The time history of decane pyrolysis revealed an inspirer result that CRACK force field certainly reflected the recombination between free radicals. Another exciting result is that, by analysis of the distribution of pyrolytic products, the main products distribution was observed to transfer from mid-short to mid-long chains and chain distribution tended to shorter or longer with the elevated temperature which is well consistent with the regularity of thermal cracking. We announce that molecular dynamics can be certainly used to simulate the process of chemical reaction as long as reactive potential is proper.

**Keywords:** Reactive potential RPMD, CRACK force field, Pyrolysis, Molecular dynamics

## 2. RPMD and CRACK force field

While developing RPMD, we considered the principle of Transition-State Theory TST as the theoretic basis of RPMD. According to the TST, when two molecules or radicals collide, they can cross the activated complex which corresponds to the saddle point on the potential-energy surface toward the product that can be referred to recombination, vice versa, a hydrocarbon molecule can also dissociate into the smaller molecules by the same way. In brief, we can apply a potential-energy surface called critical dividing surface or reaction path for the bond breaking and forming which has a reactant region and a product region that are separated by a barrier.

Toxvaerd force field is a widely used classical force field. While modifying the force field, each methyl or methylene group of hydrocarbon is treated as the “carbon” particle whose mass is designated as 14 a.m.u for simplifying calculation.

Potential expression in a classically empirical force field includes valence potential terms and non-bonded potential terms. Hereinafter three valence potential terms was changed while considering the bond breaking and free radial recombination:

- 1) Bond-stretching potential  $V_b(r)$  between the two adjacent bonded carbon particles in the same carbon chain;
- 2) Angle-bending potential  $V(\theta)$  among three adjacent bonded carbon particles in the same carbon chain;
- 3) Torsional potential  $V(\phi)$  among four adjacent bonded carbon particles in the same carbon chain.

The function forms of above three potential terms were all modified in RPMD. Among these, the most important modification is developing a bran-new two-body potential term  $V(r)$  by integrating  $V_b(r)$  and van der Waals potential between two special carbon particles.  $V(r)$  is the most important potential term in RPMD.

### 2.1 RPMD potential in CRACK

#### 2.1.1 Two-body potential term $V(r)$ in RPMD

$V(r)$  which contains long-distance van der Waals interaction and bond stretching potential is adapted to express the interaction between two special carbon particles: two adjacent carbon particles in the same chain in the dissociation reactant region or in the recombination product region and two carbon particles which are able to participate in bond breaking or forming in different chains in the dissociation product region or in the recombination reactant region. The potential value is set to zero when two carbon particles are separated infinite far. The expression of  $V(r)$  is:

$$V(r) = V_1(r) + V_0 \quad (1)$$

where  $V_0$  is a constant introduced to ensure that  $V(r)$  trends to zero when two carbon particles are away from infinite distance.

$V_1(r)$ , a subsection function, has different function forms in six different regions:

$$V_1(r) = \begin{cases} \left[ \frac{1}{2} k_s (r - r_0)^2 - de \right] & r \leq r_0 \\ \left[ \frac{1}{2} k_s (r - r_0)^2 - de \right] SW(r, r_0, r_1) & r_0 \leq r \leq r_1 \\ k_a (r - r_1)(\sigma - r) [1 - SW(r, r_1, r_2)] & r_1 \leq r \leq r_2 \\ k_a (r - r_1)(\sigma - r) & r_2 \leq r \leq \sigma \\ 4\epsilon_A \left[ \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right] & \sigma \leq r \leq r_{\min} \\ 4\epsilon \left[ \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right] - (\epsilon_A - \epsilon) & r_{\min} \leq r \leq r_s \end{cases} \quad (2)$$

where  $SW$  is a switch function, by multiplying it any function can be controlled on or off. The expression of  $SW$  is chosen as:

$$SW(r, r_a, r_b) = \begin{cases} 1 & r \leq r_a \\ (r_b - r)^2 (r_b + 2r - 3r_a) / (r_b - r_a)^3 & r_a \leq r \leq r_b \\ 0 & r > r_b \end{cases} \quad (3)$$

In equation (2), the former two parts are bond stretching terms,  $k_s$  is C-C bond force constant,  $r_0$  is 'equilibrium' or referenced bond length,  $r_1$  is the limited bond length beyond which the bond will be considered as near breaking state,  $de$  is an alterable displacement constant which can be used to adjust the depth of potential energy  $V_1(r)$  trap at  $r = r_0$  so can be used to control the dissociation activate energy. The  $r \leq r_1$  region is considered as the bonded region. The third and forth regions are transition region, in which two-body potential transfers from bonded to non-bonded. In this region,  $V_1(r)$  reaches its maximum

when  $r = r_2$ , which corresponds to the energy of activated dissociation or recombination transition state. Where,  $k_a$  is also a parameter used to control the height of energy barrier. The last two parts are  $V_1(r)$  in non-bonded *i.e.* van der Waals interaction region, in which  $V_1(r)$  includes the normal Lennard-Jones potential (LJ 12-6). Here,  $V_0 = \epsilon_A - \epsilon$ ,  $\epsilon_A$  is another adjustable parameter. In CRACK force field, non-bond cutoff is used and worked by multiplying a switch function:

$$V(r) = (V_1(r) + V_0)SW(r, r_s, r_c) \quad r_s \leq r \leq r_c \quad (4)$$

where  $r_s$  and  $r_c$  are respective cut-on and cut-off distance. The values of boundary points in  $V(r)$  are primarily set as follow according to the properties of carbon particles:  $r_0 = 0.4\sigma$ ,  $r_1 = 0.6\sigma$ ,  $r_2 = 0.8\sigma$ ,  $r_{\min} = \sqrt[6]{2}\sigma$ ,  $r_s = 2.3\sigma$ ,  $r_c = 2.5\sigma$ . To ensure the continuity of potential function  $V_1(r)$  at every boundary point, here should be  $k_a = \frac{24\epsilon_A}{\sigma(\sigma - r_1)}$ .

The plot of potential  $V_1(r)$  was shown in Figure 1.

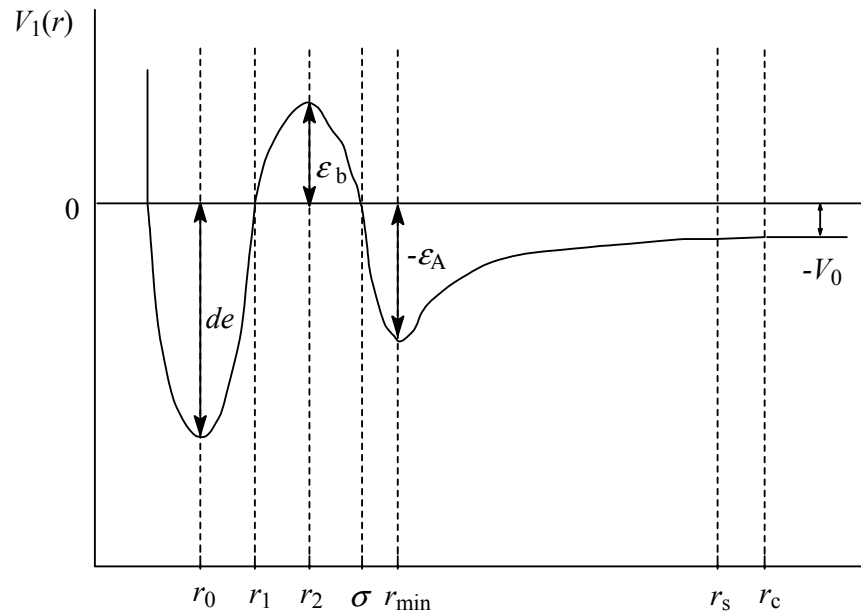


Figure 1. Illustration of  $V_1(r)$  potential curve

### 2.1.2 The other two valence potentials in RPMD

Bond bending potential  $V(\theta)$  among three adjacent carbon particles  $i-j-k$ , which have independent bond lengths and bond angles, is as follow:

$$V(\theta, r_{ij}, r_{jk}) = \frac{1}{2} k_b (\cos \theta - \cos \theta_0)^2 SW(r_{ij}, r_0, r_b) SW(r_{jk}, r_0, r_b) \quad (5)$$

where  $k_b$  and  $\theta_0$  are bond force constant and “equilibrium’ or referenced bond angle (Table 1) respectively. The action of  $SW$  is that the potential would be closed by  $SW$ , viz. equals to zero, once one of the two bond lengths is bigger than  $r_b$ .  $r_b$  is the limited bond length which value is  $r_1$ .

Torsional potential  $V(\phi)$  among four adjacent carbon particles  $i-j-k-l$ , which have independent bond lengths and bond angles in the same carbon chain, is in the form:

$$V(\phi, r_{ij}, r_{jk}, r_{kl}) = V_0(\phi) SW(r_{ij}, r_0, r_b) SW(r_{jk}, r_0, r_b) SW(r_{kl}, r_0, r_b) \quad (6)$$

$$V_0(\phi) = \sum_{i=0}^5 a_i (\cos \phi)^i$$

where,  $a_i$  is force parameter [Toxvaerd 1984],  $\phi$  is corresponding torsion angle.  $SW$  has the similar action as in  $V(\theta)$ .

## 3. MD Simulation

### 3.1 Modelling system

Applying CRACK force field, MD simulation has been performed to explore pyrolysis process of  $n$ -octane and  $n$ -decane systems. One hundred molecules were included in each system, so 800 and 1000 carbon particles were existed in the respective modelling system. The density of modelling boxes was set to  $0.76 \text{ g}\cdot\text{cm}^{-3}$  and  $0.78 \text{ g}\cdot\text{cm}^{-3}$  respectively by controlling the size of modelling boxes. Periodic boundary condition and minimum image convention were applied.

## 4. Results and discussion

### 4.1 Pyrolysis probability and pyrolytic temperature

According to the respective moving trajectory of all carbon particles, the number of pyrolyzed molecular in each system at different simulation time were statistically analyzed by pyrolysis products analysis program. As an example, the number of pyrolyzed molecular in *n*-decane system near the “pyrolytic temperature” at different simulation time was listed in Table 2. Pyrolysis of *n*-decane molecules was found at 710K, and above 715K, the number of pyrolyzed molecular increased notably with time, when CRACK force field was applied. In contrast, pyrolysis was not observed between 500 and 900K when applying Toxvaerd force field.

**Table 2.** The number of pyrolyzed molecules of *n*-decane at different simulation time under varied temperatures ( $de=125\text{kJ/mol}$ )

Force Field	Temperature / K	Time / ps					
		5	10	15	20	25	30
Toxvaerd	500 – 900	0	0	0	0	0	0
CRACK	700	0	0	0	0	0	0
CRACK	710	1	0	1	0	1	1
CRACK	715	3	4	6	5	6	7
CRACK	800	6	8	11	10	12	14

“Pyrolytic temperature”  $T_p$  was defined as the temperature beyond which obvious pyrolysis can be observed (in Table 2 it as 715K, and similar to the others). This can be seen as a concept within microscope reactive kinetics because there is only reactive temperature in petrochemical industry. But here we can discuss the pyrolysis probability and behavior of *n*-alkane through  $T_p$ . Fig. 2 gives the plots of the reciprocal of  $T_p$  vs.  $de$  in the two systems. Both well linear correlations were observed from two plots, which means the relationship between  $de$  and  $T_p$  is similar to that between Arrhenius activate energy and reactive temperature. From fig. 2 we can see that  $T_p$  of *n*-octane and/or *n*-decane system increased with the increase of displacement constants  $de$  which reflected the corresponding increase of dissociation activate energy barrier. This is consistent with TST and RPMD. Another conclusion drawn from Fig. 2 is that pyrolysis happened more easily with the longer chain, which agreed with the fundamental of pyrolysis [Zhang et al 1994].

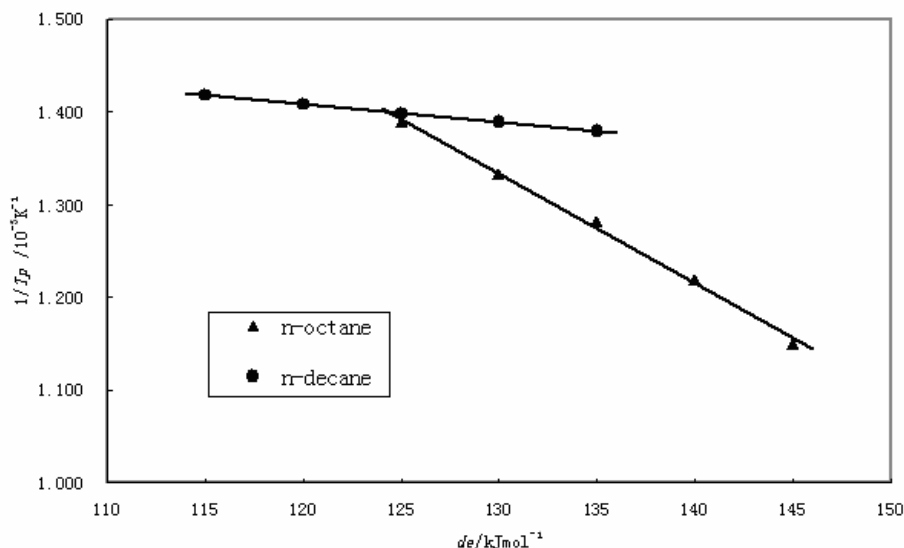


Figure 2. Plot of reciprocal of pyrolytic temperatures  $T_p$  of *n*-octane and *n*-decane systems vs. the displacement constants  $d_e$

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