

COMMUNICATION

A Post-Processing Program for ReaxFF Simulation of Chemical Structural Model of Coal

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Abstract: A post-processing program for ReaxFF simulation of chemical structural model of coal is designed by C++ codes. The results of tests for the program show good agreements with known coal chemistry. The distributions of particular molecules, hydrogen bonds, π - π stacking interactions and cleavage/cross-linking reactions can be summarized by this program. These informations are hard to directly obtained from the ReaxFF results for such a complex system as coal. Furthermore, this program could find out the specific sites of a noncolvant interactions and cleavage/cross-linking reactions, and refine the corresponding molecular geometries. This is helpful to understand the thermal reaction mechanisms of coal.

AMS subject classifications: 68U05, 68U07

Key words: Chemical Structural Model, Coal, ReaxFF, Intermolecular Interaction

Coal is the primary energy resource in China. It takes nearly 70% of our total energy consumption [1]. In order to make full use of coal, coal reactions are widely performed, such as coal pyrolysis [2], liquefaction [3], gasification [4], etc. These reactions are closely related to structures of coal samples. From the beginning of the 21st century, more and more researchers have begun to study chemical structural models of coal [5], which could represent the statistical structures of corresponding coal samples. So far, more than 130 kinds of chemical structures have been proposed. Based on these models, the thermal reactions and properties of coal can be simulated by molecular dynamics simulation or quantum chemical calculations [6].

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Reactive Force Field (ReaxFF) molecular dynamics simulation is a method developed by van Duin [7]. With this method, van Duin examined the structural transformations and chemical processes associated with the coal char at very high temperatures (3000~4000 K) [8]. Since then, the ReaxFF has been used to study coal reactions. E. Salmon used the ReaxFF method to reproduce the thermal decomposition of the Morwell brown coal [9]. X. X. Li and L. Guo have performed coal pyrolysis at 1000~2000 K by ReaxFF simulation [10]. They obtained the sequence of gas generation and product profiles. So, the ReaxFF simulation has been successfully used to explain thermal reactions of coal.

However, our previous work has identified that thermal reactions system of coal in ReaxFF simulation is much too complex at high temperatures. In this system, there are many non-covalent interactions between molecular fragments, such as hydrogen bond and π - π stacking interaction. Hundreds of molecules could react with each other and produce new molecules at every time step. Furthermore, it also includes thousands of coupled reaction pathways, involving cleavage reaction and cross-linking reaction. All of the above simulation results are necessary for the study of the thermal reactions of coal. But they are hardly counted by manual work. In this communication, we describe a new designed post-processing program for ReaxFF simulation of chemical structural model of coal by C++ codes. In this program, we can easily count the number of molecules and intra-/inter-molecular interactions at every time point in the ReaxFF simulation. The geometries of reactants and products in the cleavage or cross-linking reactions could also be obtained by this program, which is difficult to be directly observed in so many atoms.

In order to study the geometrical changes of atoms and molecules in the program, an appropriate data structure is needed to represent each atom and molecule, and then the chemical reaction process. Our study on the chemical reactions of coal is focused on the ReaxFF simulation system containing C, H and O elements.

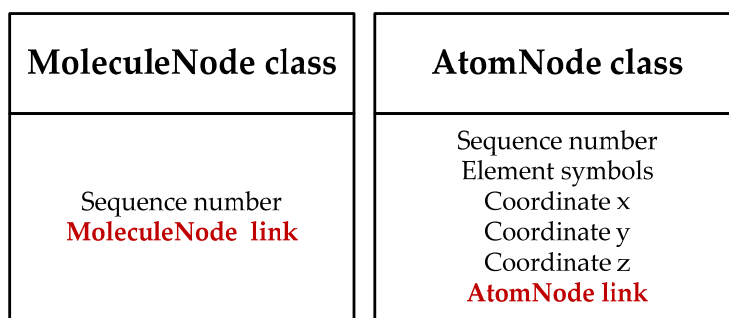


Figure 1: The molecular and atomic link node class structure.

From the raw data, each atom's location in each time point has been given. Therefore, linklist is used to mark each atom and its location is apposite. Then all atoms in one molecule can be linked together to represent the molecule's inclusion [11]. The molecular and atomic link node class is shown in **Figure 1**.

In the molecular node class, it only has one information—the molecule sequence number (abbreviation as **MSN**). At the start time point, each molecule will be given an MSN which starts from 1, until all the molecules are labeled. In the start time point, all the MSNs are continuous. As the simulation proceeds, a molecule may crack, and a new molecule may form (its atom may come from another molecule). An old MSN may disappear, and a new MSN is given to mark the new molecule. In the atom node class, it contains not only the atom sequence number (abbreviation as **ASN**), but also element symbols (C, H and O) and spatial coordinates (x, y, z), which are given in raw data. Each ASN is given to mark one atom and it will not change in the entire reaction process. That means that the ASN identifies each atom uniquely. The coordinates are gotten from raw data, which will update at each time point and fill in the atom node class. After building this data structure, every atom could be linked to a molecule. It is easy to move the atom from one molecule to another. Also, it is easy to find out the number and types of these atoms.

At the zero time point, the main tasks are reading the raw data and turning it into a linklist. First, all the atoms and their locations in raw data of zero time point are read into a float array (Array[i]), which is used to save the atom coordinates (Array[i].x, Array[i].y and Array[i].z). Then this array is traversed and each Array[i] is turned into an atom node. The flow chart of the turning work is shown in **Figure 2**. Because coordinates of each atom have been saved into the array, it is easy to calculate the distance of two atoms A and B (l_{AB}) using the following formula:

$$l_{AB} = \sqrt{(x_A - x_B)^2 + (y_A - y_B)^2 + (z_A - z_B)^2}$$

If l_{AB} is longer than the sum of their van der Waals radius (short for N), it can be considered that there is no bond between the two atoms A and B. If not, they must be connected with a bond and in the same molecule. Then the two nodes should be connected together. If the two atoms belong to different molecules, we can move all the atoms in the larger MSN molecule to the smaller one.

In order to decrease the amount of calculation, the one-dimensional distance of coordinates (x, y or z) between two atoms should be calculated first, which are defined as x_A-x_B , y_A-y_B and z_A-z_B . If the distance of one-dimensional coordinate is longer than the sum of van der Waals radius, the atoms cannot be connected by a bond. There is no need to do extra work [12]. After calculating all the atoms, it should form a linklist as shown **Figure 3**. Every atom is linked to one molecule.

As the ReaxFF simulation proceeds, some atoms may dissociate from one molecule and form a new molecule or connect with another molecule [13]. No matter what reaction it is, the results can be calculated from the coordinates of all the other atoms near this atom (shown in **Figure 4**).

Then, the distance between each atom and all the other atoms nearby ($|x_A - x_B| < N$, $|y_A - y_B| < N$ and $|z_A - z_B| < N$) should be calculated. If the atom is not in the same molecule at the last time point, it means that this atom has dissociated from the original molecule. The link node

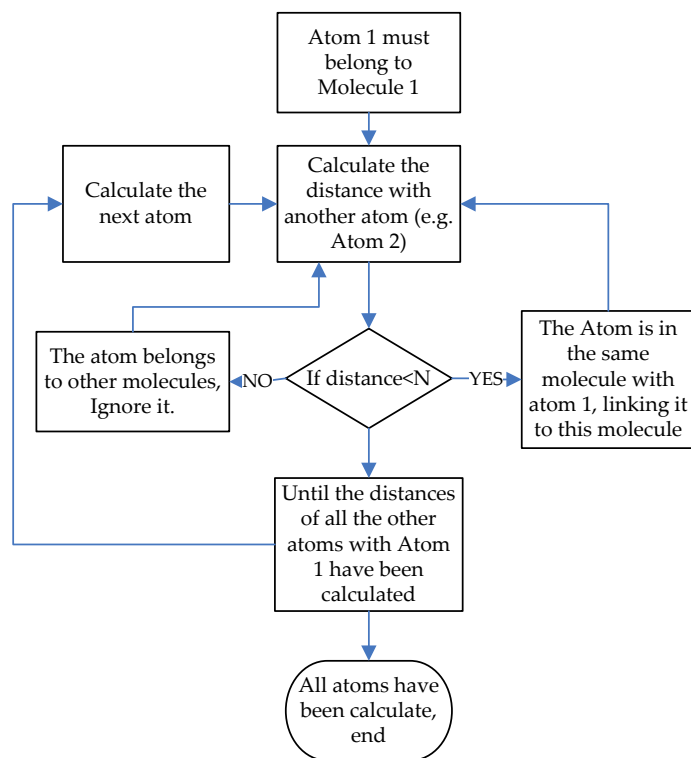


Figure 2: The flow chart of created linklist.

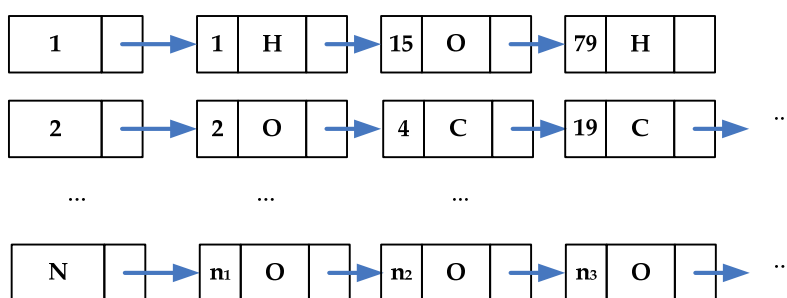


Figure 3: One example of created linklist.

of this atom should be moved from the original molecular linklist and linked to a new molecule. However, atoms near the calculated atom may belong to two or more molecules. It is needed to find out whose MSN should be given to a new molecule. First, all the connected atoms are traversed to find out the smallest MSN, which is given to the new molecule. If the new molecule is formed by several dissociated fragments, its MSN must duplicate another molecule. After the above calculations, it is also necessary to traverse all the molecules to find out whether there are duplicate sequence numbers. If there is a duplicate sequence number, a new MSN should be given to one of them [14].

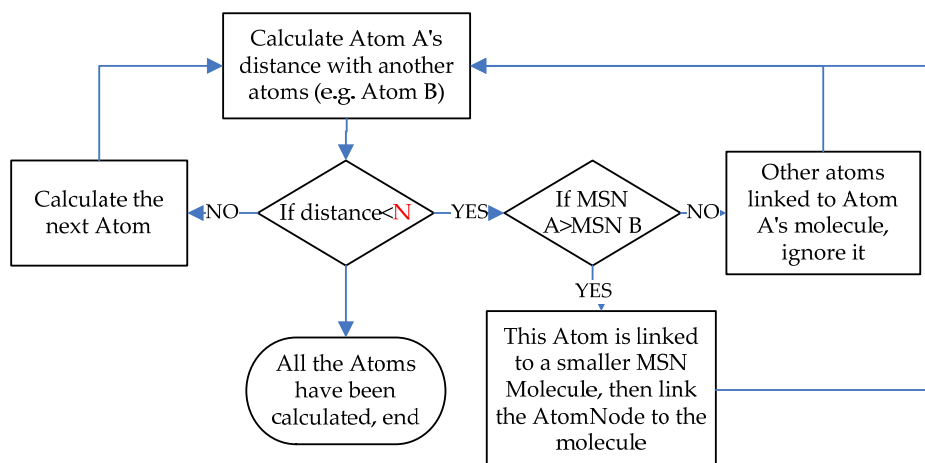


Figure 4: The flow chart of other time point calculation.

The number of molecules can be got by counting all the molecular nodes. By traversing each molecular linklist, the number of C, H and O atoms of each molecule can be counted and the molecular formula is obtained. Then, the molecules at each time point can be classified by the specified rules.

To get the number of hydrogen bonds, it is needed to traverse the linklists of all the molecules to find out all the H atoms connected with two or more O atoms (O··H··O). A hydrogen bond can be conformed if all the following requirements are satisfied: 1) the O··H··O angle is 150-180° [15,16]; 2) one O··H distance is typically ~1.10 Å and the other O··H distance is less than 2.00 Å [17]. The calculation of angle uses the following formula:

$$\cos(\vec{\alpha}, \vec{\beta}) = \frac{x_1 y_1 + x_2 y_2 + x_3 y_3}{\sqrt{x_1^2 + y_1^2 + z_1^2} + \sqrt{x_2^2 + y_2^2 + z_2^2}}$$

By traversing all the linklists, we can also obtain the aromatic structural units in the ReaxFF simulation system. The π - π stacking interaction could then be determined. The most favorable configurations of π - π stacking interaction are sandwich, perpendicular T-shaped

and parallel-displaced geometries [18]. If two structural units satisfied the above geometries and the distance between them is less than particular values (sandwich: 3.50 Å, perpendicular T-shaped: 4.80 Å, parallel-displaced: 1.50 Å), it can be considered that there is a π - π stacking interaction between the structural units.

The cleavage and cross-linking reactions, which are common in the thermal reactions of coal, could be conformed by comparing the atom status of the two neighboring time points. If one atom is no longer bonded to the calculated atom, it can be considered that there is a cleavage reaction. If a new atom appears to connect with the calculated atom, it can be considered that there is a cross-linking reaction. Then sums of all the atoms' cleavage and cross-linking reactions can be counted up. Half of the sums are the number of cleavage and cross-linking reactions.

Tests are performed to verify rationality of this program. In the ReaxFF simulation, 100 Wender model [19] molecules (a chemical structural model for lignite) are added to a periodic cell. We have annealed the periodic cell to lower temperature to get stable conformations. ReaxFF simulations are then performed at 1000 K and 100 MPa. The results of geometry at each time point are shown as follows (unit: Å):

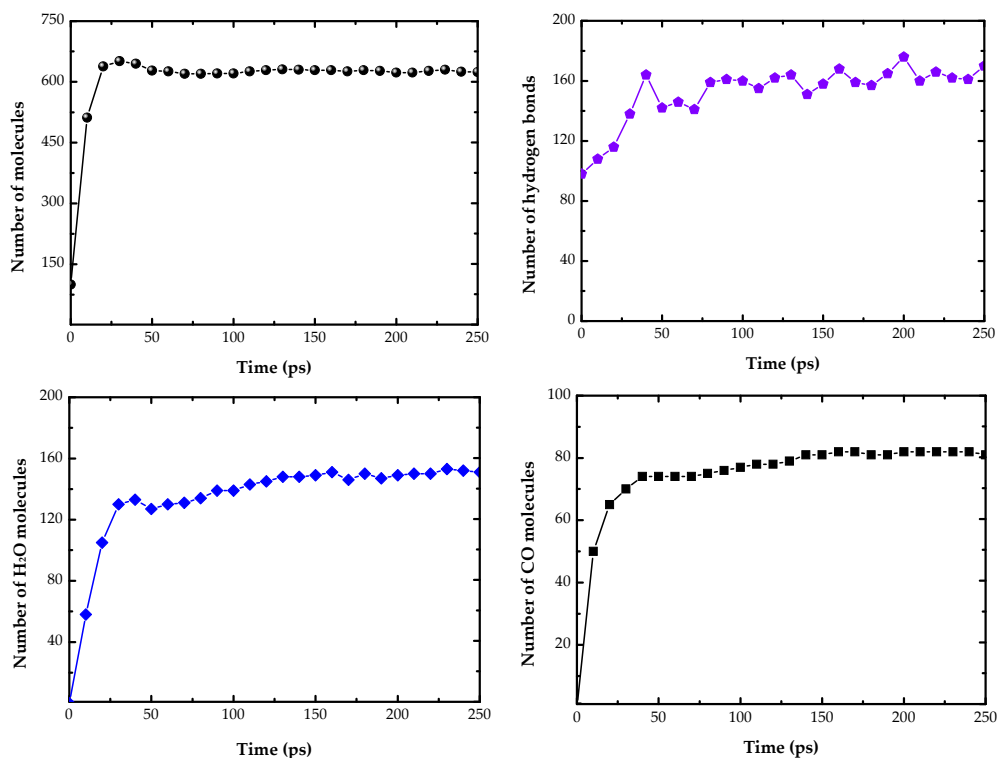


Figure 5: Distributions of total molecules, hydrogen bonds, H₂O and CO obtained by the designed program.

C	47.24113	2.88138	12.13957
C	47.45226	4.32766	11.71154
C	46.35471	5.14203	11.33834
.....			

This data could be further processed by the designed program. All the results show good agreements with known coal chemistry. Part of results are depicted in **Figure 5**, including distributions of total molecules, hydrogen bonds, H₂O and CO. The geometry of a sandwich -type π - π stacking interaction at 15.50 ps in the ReaxFF simulation could be refined from the entire atom coordinates of the system (see **Figure 6**). The distance between two structural units is 3.30 Å. We can also obtain a concrete reaction as well as the geometries of its reactants and products. As shown in **Figure 7**, a cleavage reaction of C-O bond is found out by the designed program, which is hard to be observed by eyes in a system with so many atoms.

In summary, we have presented a post-processing program for ReaxFF simulation of chemical structural model of coal. By processing the the ReaxFF results, the distributions of particular molecules, hydrogen bonds, π - π stacking interactions, cleavage reactions and cross-linking reactions could easily be obtained. Furthermore, this program could find out

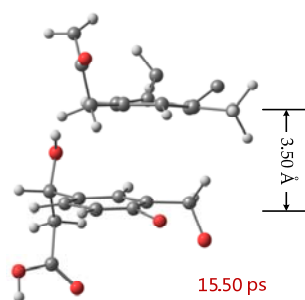


Figure 6: π - π stack interaction between units refined by the designed program (some atoms in the background are omitted).

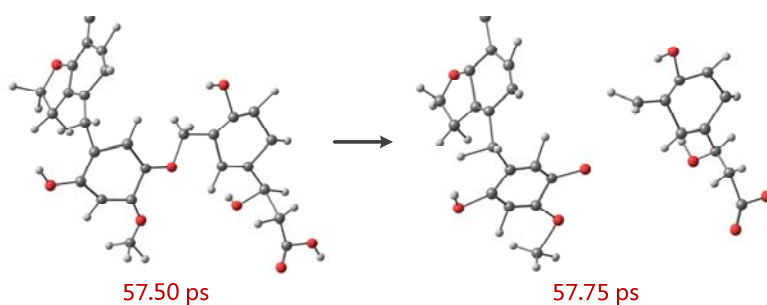


Figure 7: A cleavage reaction in ReaxFF simulation obtained by the designed program.

the specific site of a non-covalent interaction or a reaction in ReaxFF simulation, and refine the coordinates of corresponding reactions. So, this program is helpful to understand the structure and the thermal reactions of coal.

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