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Interpenetration of two polymer chain globules

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Abstract

Molecular dynamics was performed in a model system of two chain globules so that a process of the two globules merging was just simulated. It was found that this merging process was recognized as two stages, the wetting stage and the interpenetration stage. The interpenetration does not occur to partially encountered segments of the two globules, even though the chain segments are in the molten state. In the first stage, the touched two globules change their shapes rapidly from a sphere to a half-ball respectively. This obviously shows that the change in shape is mastered by the surface tension. In the second stage, the interpenetration happens to the two-chain sphere with an initial structure of each chain in a half-ball shape. A different molecular mechanism of chain diffusion has been found for this system. It is the chain loop crawling among the globule surface. Characterization of the interpenetration process was carried out by several means of analyzing the trajectory files. It was found that in the interpenetration stage there is a fast evolution and a lentitude period. The interpenetration is a conformational entropy driving process, and takes a half time for the lentitude period, which regards just 15% of total free energy difference.

Keywords: Interpenetration; Globule; Molecular dynamics

1. Introduction

One of the longstanding subjects in polymer physics is the interpenetration process of polymer chains. This process is the very step for polymer chain condensation from the dilute solution to the aggregation state. Such condensed multiple chain system possesses a structure that polymer chains form entanglement network, which thus establishes the mechanical property of polymers.

Without chain interpenetration a single chain has different properties from that of normal bulk polymer. Bu and Xue et al. found that the single chain samples have higher crystallinity [1] and very rapid crystallization rate [2–4] compared with the usual crystallization process in isotactic polystyrene and polycarbonate. The glass transition temperature of atactic polystyrene [5] and polycarbonate [6] was also found lower than that of the normal bulk.

When heating up single chain particles or pauci chain particles in forming a film [7], merging occurs to the neighboring particles. This merging accompanied the interpenetration of polymer chains, even though monitoring this process was very difficult in the last stage. Using small angle neutron scattering to observe the melting of a few deuterated polyethylene chains within normal polyethylene bulk [8], the crystal mat with the deuterated chains undergoes a conformational explosion from a regular super-folded sheet structure into a random coil configuration in just a few seconds. This result thus dispels a usual doubt that the migration of chain segments in the bulk is very slow. When precipitating from a dilute solution in the pool solvent, polystyrene chains become tiny globules, which are merging together at room temperature. This merging process was found very slow [9].

In most cases, to minutely determine the degree of interpenetration is difficult. But using the non-radiative energy transfer between fluorescent labels, Morawetz [10] characterized the degree of interpenetration in solutions. He found the emission spectrum exhibited a marked dependence on the concentration of the solution that the samples were derived, even though this method cannot be applied to bulk system and solid particle merging process.

By means of experiments, we know many things about the interpenetration. However, detailed information about chain motions in the penetration process is much difficult to

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be observed. Molecular dynamics (MD) provides a useful implement to understand molecules motion between chains at atomestic level. Many works have reported on the interpenetration behavior of polymer interface [11–14]. Additionally, the globules merging process is a different source to explore interpenetration of polymer chains. Recently Chuang et al. [15] used a two globules model to investigate this kind of aggregation process in solution. In their simulation, two globules could not interpenetrate each other unless external force applied. Obviously, MD on aggregation of two-chain coils in vacuum is a good simulation on the phenomenon that two globules merging in the pool solvent.

In the present study, we used two chains to simulate the globules merging process by means of MD, and to study the interpenetration behavior between chains. In the simulation, two stages were distinguished for this merging process. One is the wetting stage and the other is the interpenetration stage. Differently from Chuang's work that mainly emphasizes on the first stage, we focused on the second stage. Several means were used to characterize the second stage, such as the distance between two globule centers, the overlapped atomic density area of both chains, and the first neighbor peak of inter-chain radial distribution function. The free energy of the process is also calculated from the mean force between chains in a time-zone average. Some details about this process were discussed as well.

2. Methodology

Polyethylene (PE) chains were used in the present simulation. Each of the chains consists of 300 CH_2, which are the united atoms. This approximation was used in many papers to study collapse [16], crystallization [17,18], and glass temperature transition [19,20] of the PE. In this model, no charge is added. The simulation circumstance here is in vacuum, which has the distinct advantages of supplying a poor solvent. The simulation was performed using Cerius2™. The force field parameters come from Dreiding II [21]. The time evolution was used of the canonical (constant T) Nose–Hoover method. The integration step was 2 fs for all simulations and the cut-off distance for the Lennard–Jones potential was 9 Å. The temperature was set at 600 K. The initial coil structure was obtained from MD run of a PE chain in all trans conformation at 600 K. At such high temperature, the chain had a great deal of mobility and collapsed into a contact globule. During the process, van der Waals attractive interaction between segments plays an important role as studied at 300 K [17]. In first 50 ps the total energy and radius of gyration turned to constant values till 300 ps. The last structure was used as the initial coil structure in the present study.

This globule obtained from MD has remarkably different size with coils in bulk and solute. The lack of interaction between the chain and other chains or solvent molecules in simulation causes the chain segments compact together. The radius of gyration R_g of the globule is about 9.8 Å. For the chain in unperturbed state with the same number of bonds, the $\langle R_g^2 \rangle$ is proportional to $\langle r^2 \rangle/6$ ($\langle r^2 \rangle$ is the mean-square end-to-end distance). From the characterization ratio C_∞, the $\langle R_g \rangle$ in bulk was estimated about 28.4 Å, which is more than three times in size than that of simulated globule.

In the present study, a model adopted is a two-coil system. The two globules were apart from each other with a distance of 20.5 Å. The edge distance of the two coils was about 6–7 Å. This is structure at 0 ps in the simulation. No external force was applied. MD was running in vacuum at 600 K. The use of such high temperature is for avoiding crystallization of the polyethylene chains, and also to speed up the process so that we can monitor it within a reasonable duration.

3. Results and discussion

3.1. Two stages of two globules merging

After analyzing trajectory files of the process, we found that this globule merging process can be divided into two stages, the wetting stage and the interpenetration stage. In the first stage, the two globules are coming close to each other and touching each other. However, when part chains of the globules met together, the interpenetration did not happen to these encountered segments, even the chains were in the molten state. The two partially touched globules change their shapes rapidly from a sphere to a half-ball, as the potential energy sharply drops down for the two. In the first stage, surface tension obviously plays an important role to drive the two balls to touch each other and change their shapes for reducing the surface area in forming a new ball with a double volume.

The two globules entering the first stage takes a while, it likes those mentioned by Chuang et al. [15] that the globules collide many hundreds of times before merging and before aggregation starts. In the present study, we did not pay attention on the efficiency of the globules collision, but the second stage.

3.2. The second stage: interpenetration

The present study indicates that interpenetration starts in the second stage. Structure evolution of the two coils is shown in Fig. 1. The two coils from the snapshot at 50 ps are intermingling through the snapshot at 100, 1000, 6000, and 9000 ps. When we measure the distance between two coil centers, Fig. 2 shows the value versus time, the distance describes the coil centers in the second stage are coming close up. Obvious descent appears before ~6 ns. However, potential energy of the system appears randomly. When we measure the radius of gyration for each coil, the two curves show their difference through the second stage, see Fig. 3.

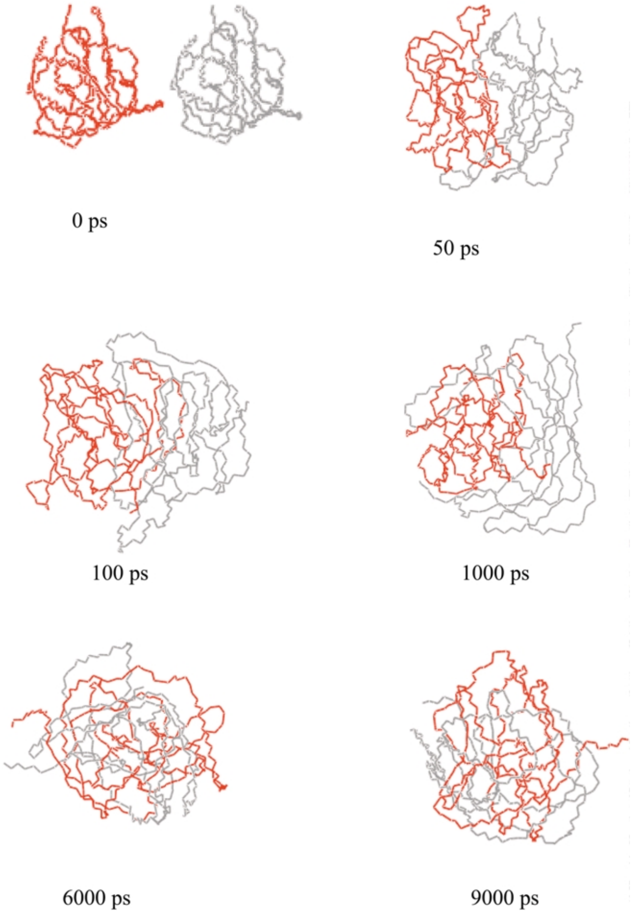

Fig. 1. The snapshot of the coils at 0, 50, 100, 1000, 6000, 9000 ps.

At the beginning of the stage, one of the radii of gyration is much larger than that of the other. This indicating that at this moment one coil just envelops the other. Later, one can find some inverted situations that the one being encircled now counterattacks. Near 12 ns, the two coils gain almost the same size of the radius of gyration. Fig. 3 records a struggling history of the two coils for occupying the bigger room, which possesses double volume than before.

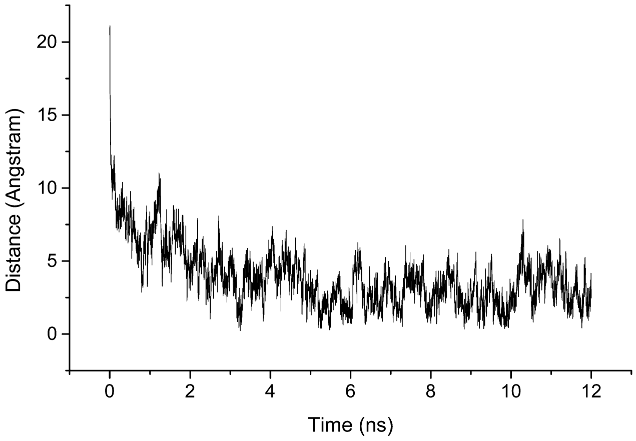

Fig. 2. The distance between the centers of two coils versus time.

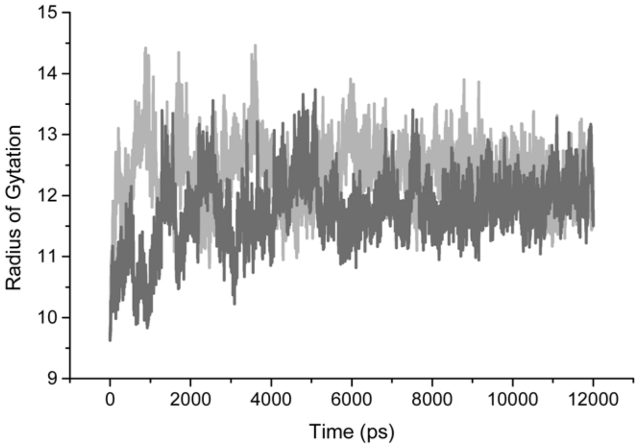

Fig. 3. The radius of gyration of two coils as a function of time.

3.3. Different molecular mechanism of chain diffusion

The chains themselves are complicated objects that strongly interact with many neighbors by being tangled up with them. The process of interpenetration is very much complicated than the simple Brownian motion. In the bulk circumstance, because of the constraining effect of the surrounding chains, the chain has to wriggle along the tube, which is de Gennes' reptation model. In our system, monitoring the snapshots of the coil structures from the trajectory files, we found that since the coil system has considerable surface area, chain penetration has chance to undergo a different way from the reptation.

Fig. 4 shows the other way of the interpenetration, which was found in the present study. That is, the chain segment loop bestrows the globule surface. A labeled segment of a loop is at the top of the globule in Fig. 4A. Along with the evolution of the system, Fig. 4B–D show the labeled segment gradually being covered and migrated inside the globule. The case of the segment loop encircling each other among the surface does frequently appear in the simulation as shown in Fig. 3. In addition, chain ends were also found to keep floating on the surface. The activation energy of chain migration is of course lower for the chain on the surface than that for the chain inside the globule. This is a possible reason for the chain diffusion having different mechanism.

3.4. Characterization with atomic density

In order to characterize the degree of interpenetration, we used a method of projection of all atoms into the axis of coil centers. The axis was divided into 0.5 Å intervals. The atoms in each chain were projected into different interval according the space position of atoms. The density of atom projection was calculated using the atom number in every interval of axis divided by the total atom number of each chain. The profiles of atomic density along the axis for the initial structure and at various moments are shown in Fig. 5.

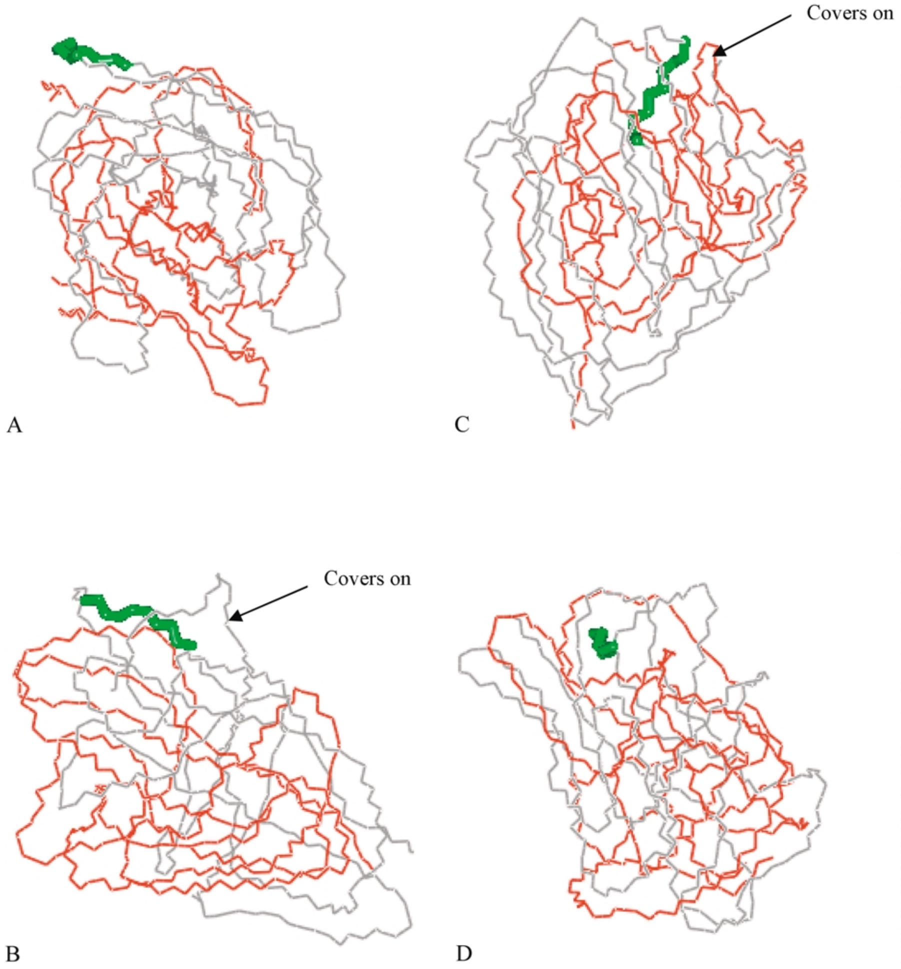

Fig. 4. The chain loop diffusion among the coil surface. A: a segment in a loop covers other chains, B: this segment is covered by another loop, C: the segment is being covered by another dark loop, D: the segment is under the loops.

One can find that overlapped area of the two peaks is getting larger. Use of the overlapped area versus the time in making a plot, Fig. 6 shows the points increasing before 6 ns, and a plateau appears after. This kinetic feature is that we obtained by using the method of the atomic density projection. A fast evolution takes place before 6 ns and is followed by a lentitude period.

3.5. Characterization with RDF

Second way to characterize the degree of interpenetration is use of the inter-chain radial distribution function (RDF). This method follows a procedure, in which one needs to sit on everywhere of one chain to count each neighbor chain within certain distance, if the neighbor chain is the other chain. For a system consisted of chain-A and chain-B, total number of inter-chain atom pairs is $N_{\mathrm{A,B}}$ with a volume of V. For a specific distance of i, the number of inter-chain atom pairs is $N^{i}_{\mathrm{A,B}}$, the normalized population is

$$g'_{\mathrm{A,B}} = \frac{V}{v(r_i) - V(r_i - 1)} \frac{N'_{\mathrm{A,B}}}{N_{\mathrm{A,B}}} \quad (1)$$

Fig. 7 shows the population of the inter-chain interaction pairs within 40 Å. The lowest curve is for the population of the initial structure of the two coils. The curve above it is for an average of the structures collected at 1–50 ps. The next upper curve is for an average of 50–100 ps. In turn, the curves are for the average of 100–200 ps, 200–300 ps, and 300–400 ps. First peak in the figure is located at ~5 Å, which is just the position for the first neighbor chain. This peak is growing up during the process. When making a plot of intensity of the first neighbor peak versus the time, the points in Fig. 8 increase until reaching 6 ns. The plateau is met again. The characterizations by above methods indicate that no feature or difference is in the plateau area. However, in the view of radius of gyration of each chain as shown in Fig. 3 one can find that even in the plateau area difference between the two radii of gyrations does exist. This means that something still changes inside and we need more efficient characterization.

3.6. Mean force

We then turn to mean force of the coils since it relates to

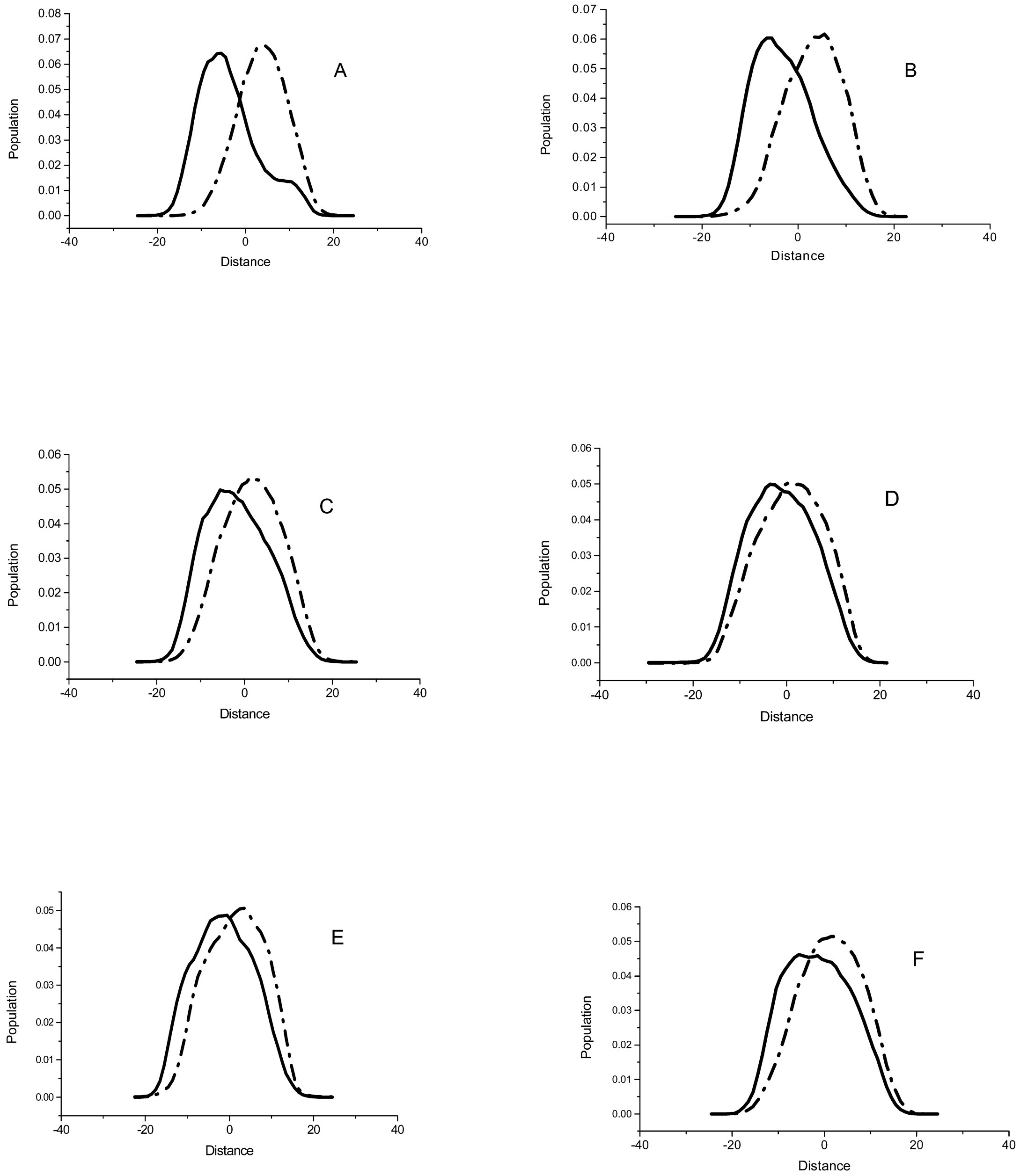

Fig. 5. The projection of all atoms on the axis along the coil centers for each coil. A: all snapshots from 1 to 1000 ps; B: all snapshots from 1000 to 2000 ps; C: all snapshots from 3000 to 4000 ps; D: all snapshots from 5000 to 6000 ps; E: all snapshots from 7000 to 8000 ps; F: all snapshots from 8000 to 9000 ps.

free energy of the process. The mean force is such measured that when the two coils apart from each other with a distance of r, one chain will be applied a force from the other chain. This force is a sum of forces of every pair atoms between the two coils. Since with certain distance one chain has thousands of conformations, each conformation would be applied a different force from one another. Therefore, for a distance of r, all of the conformations within the globule have an averaged force, which is the mean force, $\langle f(r) \rangle$. We have to obtain the mean force as a function of r. However, during the merging simulation, we cannot fix the r between coils to receive many conformations from dynamics. But we can use the time zone average to collect many conformations and make mean values. In the time zone average, the distance becomes an averaged value. The mean forces obtained in such a way are plotted in Fig. 9. The mean force increases with a descent of distance between the coil centers.

3.7. The degree of interpenetration

To know the degree of interpenetration is obviously important goal in the present study. Since we obtained the mean force for each averaged state where the two coils interpenetrate to certain extent during the process, the work made by the environment can be correlated to the driving

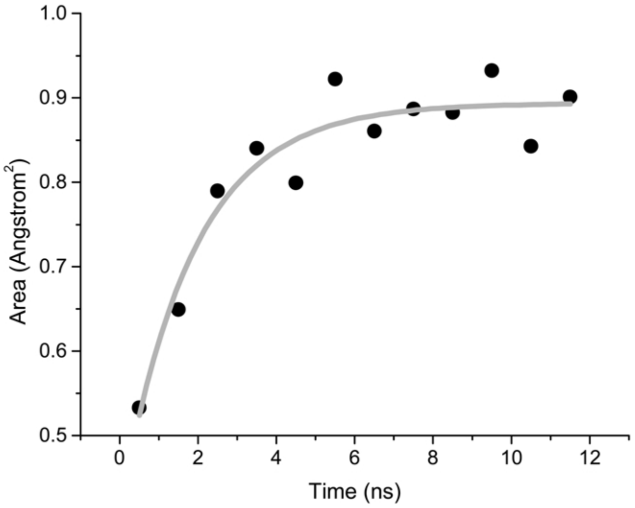

Fig. 6. The overlapped area calculated from the atom number distribution in Fig. 5 versus time.

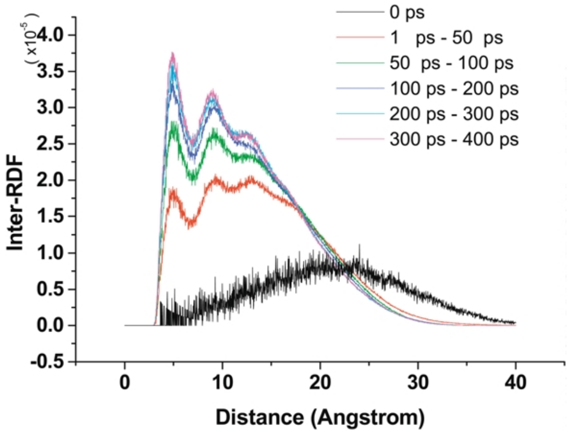

Fig. 7. The inter-molecular radius distribution function from 1 to 400 ps. See text.

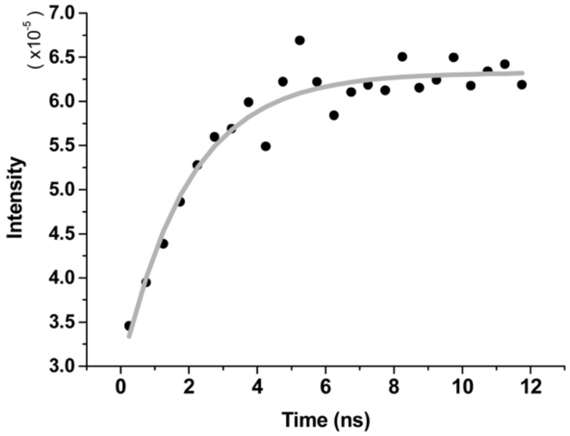

Fig. 8. The intensity of the first neighbor peak of inter-RDF as a function of simulation time. The line is fit the data using exponential function.

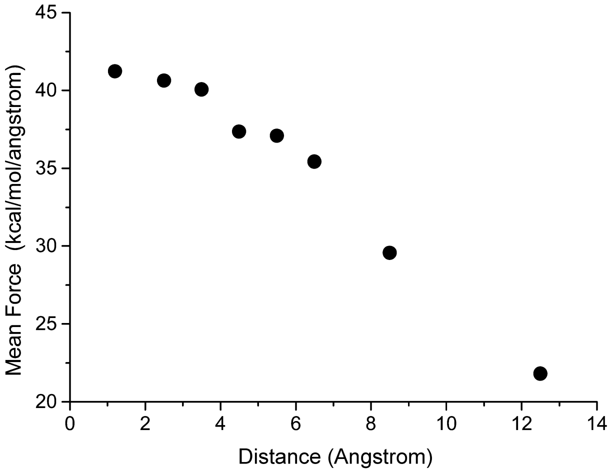

Fig. 9. The calculated mean force as a function of the distance of two coil-centers when the coils move to each other.

force, or the free energy. This can be calculated by an

$$A(r) = \int_0^r \langle f(\bar{r}) \rangle \mathrm{d}r \tag{2}$$

integration of the mean force, as shown in Fig. 10a.

This free energy describes fully interpenetrated two coils in a separation process. According to the thermodynamics,

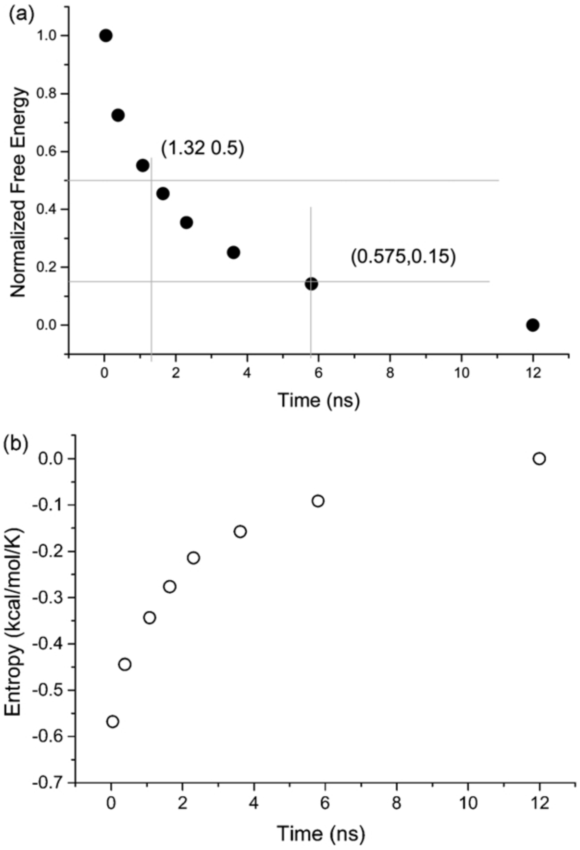

Fig. 10. a: The free energy as a function of simulation time. b: The entropy change as a function of simulation time

the entropy can then be obtained

$$S(r) = \frac{U(r) - A(r)}{T} \tag{3}$$

Where T donates the temperature at 600 K, $U(r)$ is the internal energy in the system. Because this simulation is based on the NVT canonical ensemble and the kinetic energy is keep constant, the difference of internal energy is substituted by the difference of the potential energy. At every r state, the entropy is obtained when setting $A(0) = 0$. Using the relation between the distance and simulation time, this entropy change is expressed as a function of simulation time, as shown in Fig. 10b. The entropy almost gets to a balance at about 6 ns. A little change with the entropy exists beyond 6 ns, showing the last period of the process. Therefore, the entropy plays an important role in the last period of the interpenetration process.

Obviously, the free energy is the best measure for the degree of the interpenetration process. According to normalized free energy, in the second stage, the interpenetration takes a half of the duration for ~85% of the course, and a half time for the rest ~15%. The rate of the simulated process is about 0.08 nm/ns, which is much faster than the rate of the crystalline mat explosion [9]. This is because that the molecular weight of our model is such smaller and the running temperature so higher. It is the very temperature of 600 K to have the interpenetration process observed. Otherwise, to make the interpenetration happening at lower temperature, we need also the external force to overcome the “entanglement force”, as was experienced before [15].

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