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Elastic Behavior of Polymer Chains

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The elastic behavior of the polymer chain was investigated in a three-dimensional off-lattice model. We sample more than 10^9 conformations of each kind of polymer chain by using a Monte Carlo algorithm, then analyze them with the non-Gaussian theory of rubberlike elasticity, and end with a statistical study. Through observing the effect of the chain flexibility and the stretching ratio on the mean-square end-to-end distance, the average energy, the average Helmholtz free energy, the elastic force, the contribution of energy to the elastic force, and the entropy contribution to elastic force of the polymer chain, we find that a rigid polymer chain is much easier to stretch than a flexible polymer chain. Also, a rigid polymer chain will become difficult to stretch only at a quite high stretching ratio because of the effect of the entropy contribution. These results of our simulation calculation may explain some of the macroscopic phenomena of polymer and biomacromolecular elasticity.

Key words: Monte Carlo algorithm, Three-dimensional off-lattice model, Elastic behavior, Polymer

I. INTRODUCTION

In recent years, a series of experiments have been performed using the atomic force microscope (AFM) and have provided a wealth of information about the mechanical properties of the single-molecule chains [1-6]. These experiments are clearly related to the details of intermolecular and intramolecular force and the internal structure of the molecule. These investigations reveal the microscopic mechanisms of the deformation process [7-10], such as the folding processes of proteins or DNA. The theoretical studies of the elasticity of the polymer chain began in the 1930s, based on both Gaussian models and non-Gaussian models [11-14]. Considering the effect of various rotational-isomeric states, the effect of the elongation of a polymer chain was discussed by Abe and Flory in 1970 [15]. Then Curro and Mark proposed a non-Gaussian theory of rubberlike elasticity based on rotational-isomeric state and investigated rubberlike elasticity on the basis of distribution functions for end-to-end separation of the chains through Monte Carlo simulations [16,17]. It is well known that the elastic behavior of protein molecules is almost the same as polymer chains, so we may find the general law of the elastic behavior of the biomacromolecule through researching the elastic behavior of the polymer chain. Accordingly, many computational studies of the elastic behavior of both the polymer chain and the biopolymer chain have been undertaken [18-26].

The various biomacromolecular chains have the different chain flexibility because of their distinct chemical structures. For example, most single strand DNA

chains or single strand RNA chains have generally been considered to be flexible chains; but under some conditions, some of the single strand DNA chains or single strand RNA chains may partially fold into double strands on some segments, which then exhibit an obvious rigid behavior, therefore the whole chain appears like a rod-coil chain. Moreover, it is well known that the peptide chains are usually flexible as general polymer chains; but the protein chains are generally considered to be the rigid chains because they currently fold into the stable secondary structure. On the other hand, the different secondary structures also result in the different chain stiffness, for example, the α -helix segment is a rigid segment and a β -sheet segment is a semiflexible segment at the same time. Because of this, we may do a reversed analysis to confirm the spatial structure of the biomacromolecules through detecting their chain flexibility. Therefore, the studies of the elastic behavior of the polymer chain influenced by the chain flexibility should have guiding significance for experiments.

In our simulations, we sampled mass conformations (no less than 10^9) of the polymer chain with various chain flexibilities (flexible, semiflexible, rigid, and rod-coil) through a Monte Carlo algorithm, and then did a statistical analysis based on the non-Gaussian theory of rubberlike elasticity. Thus the change of the mean-square end-to-end distance $\langle R_f^2 \rangle$, the average energy $\langle U \rangle$, the average free energy $\langle A \rangle$, the elastic force F , the contribution of energy to the elastic force F_U , the entropy contribution to elastic force F_S of the polymer chains with the chain flexibility, and the stretching ratio are observed.

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II. SIMULATION METHOD

In the present work, the off-lattice Monte Carlo model developed by Binder and co-workers was used [27], in which each randomly selected bead on the chain was allowed to move around its position. A set of vectors \vec{r}_i , is defined to specify the conformation of the polymer chain in a three-dimensional space, where $i=1,2,\dots,M,\dots,N$, is the rigid segment. The interaction energy E is taken to be:

$$E(\vec{r}_i) = V_{\text{Bond length}} + V_{\text{Bond angle}} + V_{\text{Nonbonded LJ}} \quad (1)$$

The interaction potential between two successive bonded segments is treated as

$$V_{\text{Bond length}} = k \sum_{i=1}^{N-1} (|\vec{r}_{i+1} - \vec{r}_i| - \sigma)^2 \quad (2)$$

where σ is the equilibrium bond length and set as 1.0 and the constant parameter k is assigned 10. The angle potential ($V_{\text{Bond angle}}$) is taken to be

$$V_{\text{Bond angle}} = f \sum_{i=1}^{M-2} (1 + \cos \theta_i)^2 \quad (3)$$

where the bond angle θ_i is formed by three successive beads $i, i+1, i+2$; f is the bending constant: for the flexible, semiflexible, and rigid segment, $f=0.0, 2.0$, and 4.0 , respectively. The nonbonded interaction potential is considered to be between pairs of beads that are separated by at least two bonds, and written as:

$$V_{\text{Nonbonded LJ}} = 2 \sum_{i=1}^{N-2} \sum_{j=i+2}^N \left[\left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^{12} - \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^6 \right] \quad (4)$$

On the basis of the method above, now we will consider the elastic behavior of flexible polymer chain, semiflexible polymer chain, rigid polymer chain, and rod-coil polymer chain when the reduction temperature $T=1.0$. When a force F acts on a polymer chain, the atoms in the chains move a distance r along the force direction (here we suppose that the direction of the force is the z axis), and many of the conformations will vanish. If the force $F=0$, it is an isolated chain, and we assume the minimum of end-to-end distance is r_{min} . If $F \neq 0$, the minimum distance along the force direction becomes $r_{\text{min}}+r$. Assuming the force acts on the chain in the direction of z axis, therefore, the partition function of the system

$$Z = \sum_i \exp -\frac{E_i}{k_B T} \quad (5)$$

where \sum_i is the sum of the conformation whose z -axis component of the end segment is greater than $z_{\text{min}}+z$.

In fact, the partition function is widely used to study the thermodynamic properties, such as the Helmholtz free energy, the average energy, and the elastic force. From the partition function, we can derive the average Helmholtz free energies of polymer chains under various elongation lengths

$$\langle A \rangle = -RT \ln Z(z) \quad (6)$$

The number of conformations is so large for long chains that it is very difficult to count all conformations according to Eq.(5). In this work, the partition function $Z(z)$ can be calculated through

$$Z(z) = Z_0 \times \frac{M_z}{M} \quad (7)$$

where Z_0 is the partition function of system without elongation, M is the total number of samples, and M_z is the number of samples whose z -axis components of the end segments are greater than $z_{\text{min}}+z$. Therefore

$$\langle A \rangle = k_B T \ln Z_0 - k_B T \ln \frac{M_z}{M} \quad (8)$$

For simplicity, we define $\langle A' \rangle$ as

$$\begin{aligned} \langle A' \rangle &\equiv \langle A \rangle + k_B T \ln Z_0 \\ &= -k_B T \ln \frac{M_z}{M} \end{aligned} \quad (9)$$

Because Z_0 is the partition function of polymer chains without elongation, it is independent of elongation lengths, and only depends on chain length and the type of polymer chains. At the same time, elastic force F can be obtained from the dependence of $\langle A \rangle$ on the elongation distance along the force direction:

$$F = \frac{\partial \langle A \rangle}{\partial z} \quad (10)$$

According to Newton's third law, the force F is the elastic force stored in the polymer chains. In the meantime, we can also get average energy $\langle U \rangle$ of polymer chains.

$$\langle U \rangle = \frac{\sum_i E_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \quad (11)$$

The energy contribution to the elastic force F_U is defined by

$$F_U = \frac{\partial \langle U \rangle}{\partial z} \quad (12)$$

As $\langle A \rangle = \langle U \rangle - TS$, we can also calculate entropy contribution to the elastic force F_S :

$$F_S = \frac{\partial (-TS)}{\partial z} \quad (13)$$

In this work, the 31-mers polymer chain is chosen as the object of research. For a rod-coil polymer chain, the length of the rigid segment is assigned 16 mers, so the length of the flexible segment is 15 mers. Therefore, the parameters of this work are: $N=31$, $N_{\text{rod}}=16$, $N_{\text{coil}}=15$, $f_{\text{rod}}=f_{\text{rigid}}=4.0$, $f_{\text{semiflexible}}=2.0$, $f_{\text{flexible}}=f_{\text{coil}}=0.0$.

III. RESULTS AND DISCUSSION

A. Mean-square radius of gyration and mean-square end-to-end distance

In this work the elongation length r is defined as the projection of the end-to-end distance of the polymer chain in the direction of the force (the direction is the z -axis). The mean-square radius of gyration $\langle R_g^2 \rangle$ and the mean-square end-to-end distance $\langle R_f^2 \rangle$ are important in investigating the changes of chain dimensions in the process of tensile elongation which are respectively defined as

$$\langle R_g^2 \rangle_r = \frac{\sum_i R_i^2 e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \quad (14)$$

$$\langle R_f^2 \rangle_r = \frac{\sum_i S_i^2 e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \quad (15)$$

where \sum_i is the sum of conformations whose z -axis component of the end-to-end distance is greater than r , R_i and S_i are the radius of gyration and the end-to-end distance of the i th conformation, respectively. Figure 1 shows the mean-square end-to-end distance $\langle R_f^2 \rangle_r$ as a function of the stretching ratio for homopolymer chains with different stiffness. Here we define L as the ratio of

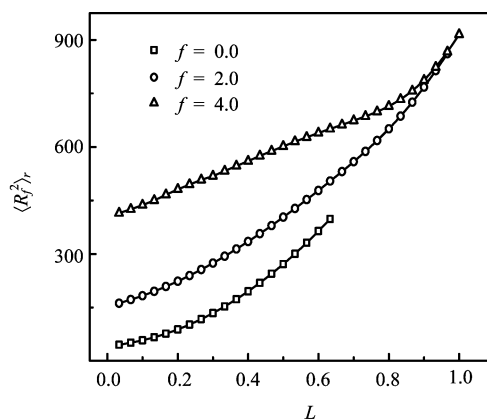


FIG. 1 Mean-square end-to-end distance $\langle R_f^2 \rangle_r$ of the 31-mers polymer chain as a function of L with different chain stiffness.

the end-to-end distance of the whole polymer chain to the chain length of the whole polymer chain. We find that the mean-square end-to-end distance of all kinds of polymer chains increases with L . For the rigid polymer chain, the mean-square end-to-end distance increases linearly with L until L reach 0.8. The gaps of the curves are large at the small-scale deformation. However, with the increasing of the stretching ratio, the gaps of the curves become small, and the mean-square end-to-end distance of the semiflexible polymer chain and the rigid polymer chain are almost coincident at the stretching ratio of 0.97.

We also studied the mean-square end-to-end distance of rod-coil polymer chains as shown in Fig.2. It is obvious that the mean-square end-to-end distance of total polymer chain increases with the stretching ratio, and the mean-square end-to-end distance of the rod segment in the rod-coil polymer chain increases linearly, the same as a rigid polymer chain, but the mean-square end-to-end distance of the coil segment in polymer chain remains stable at first. It looks like the coil segment in polymer chain has not been stretched until the rigid segment in polymer chain has been pulled straight. Is this supposition reasonable?

B. Thermodynamic properties

Energy changes always exist in the process of tensile elongation. The changes of conformations lead to increases (or decreases) of thermodynamics properties for polymer chains. Here we first calculate the average Helmholtz free energy and the average energy according to Eqs.(6)-(12); the results are shown in Fig.3, Fig.4 and Fig.5. Figure 3 presents the average Helmholtz free energy as a function of L for $N=31$ with $f=0.0, 2.0, 4.0$,

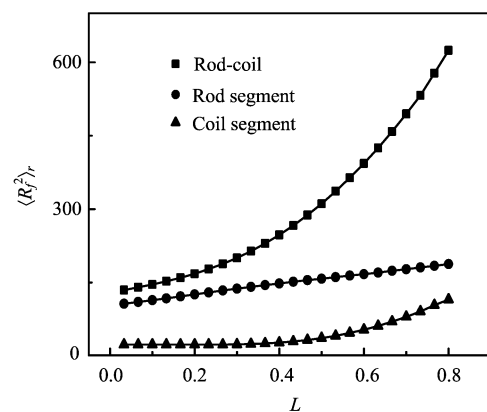


FIG. 2 Mean-square end-to-end distance $\langle R_f^2 \rangle_r$ of total polymer chain, rod segment, and coil segment as a function of the stretching ratio; the length of whole polymer chain is 31 mers, and the length of the rod segment is 16, the length of the coil segment is 15, $f=4.0$ and 0.0 is for the rod segment and the coil segment, respectively.

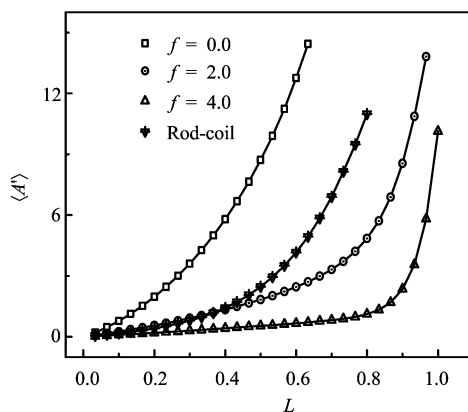


FIG. 3 Average value of $\langle A' \rangle$ as a function of L for polymer chains. The length of the polymer chain is 31-mers, and f means the stiffness of polymer chains to be assigned 0.0, 2.0, and 4.0 for the flexible, semiflexible, and rigid segment, respectively; rod-coil means that the polymer chain is the rod-coil copolymer chain under the conditions $N_{\text{rod}}=16$, $N_{\text{coil}}=15$, $f_{\text{rod}}=4.0$, and $f_{\text{coil}}=0.0$.

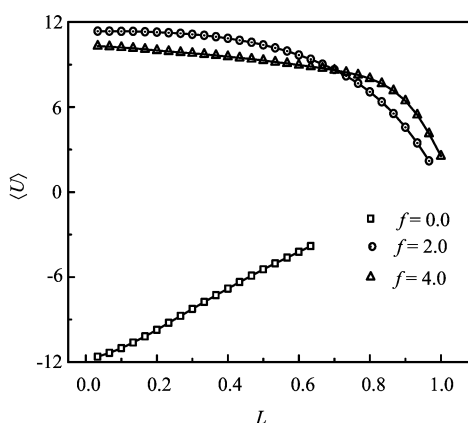


FIG. 4 Average energy as a function of the stretching ratio for the homopolymers with different chain stiffness, $N=31$.

and rod-coil. From Fig.3, we can find that the average Helmholtz free energy increases, with L for the flexible polymer chain and the semiflexible polymer chain, but for the rigid polymer chain the average Helmholtz free energy is almost unchanged before L increases to 0.8. At the same stretching ratio, the values of the average Helmholtz free energy increases while f decreases. It is easily understood that the rigid polymer chains are easily stretched. When a force F acts on the rigid polymer chains, the average Helmholtz free energy has almost no change till a very high stretching ratio. We also find the average Helmholtz free energy of rod-coil polymers, which is between the average Helmholtz free energy of the rigid polymer chain and the average Helmholtz free energy of the flexible polymer chain, increases with L . We can find the average energy of the flexible polymer chains increases linearly with the stretching ratio, but the average energy of the semiflexible polymer chain

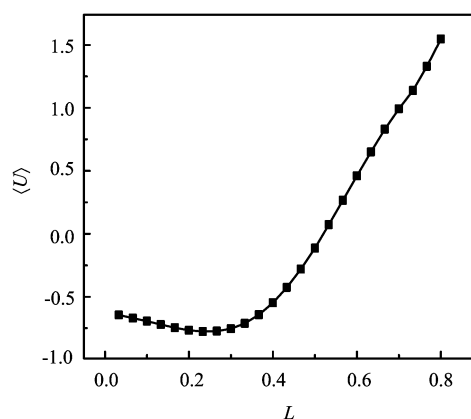


FIG. 5 Average energy as a function of for the rod-coil copolymer chain under the conditions $N_{\text{rod}}=16$, $N_{\text{coil}}=15$, $f_{\text{rod}}=4.0$, and $f_{\text{coil}}=0.0$.

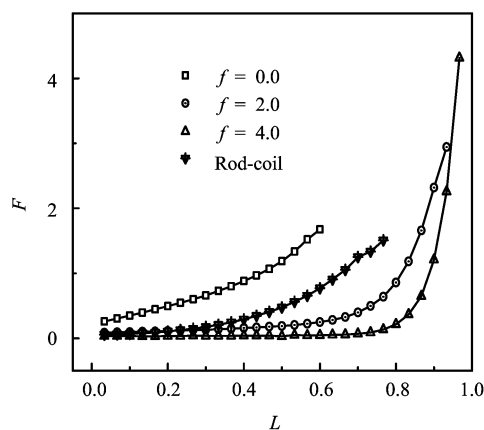


FIG. 6 Elastic force F as a function of L for various polymer chains (flexible, semiflexible, rigid, and rod-coil). The length of the polymer chain is 31-mers, and f means the stiffness of polymer chains to be assigned 0.0, 2.0 and 4.0 for the flexible, semiflexible and rigid segment, respectively; rod-coil means that the polymer chain is the rod-coil copolymer chain under the conditions $N_{\text{rod}}=16$, $N_{\text{coil}}=15$, $f_{\text{rod}}=4.0$, and $f_{\text{coil}}=0.0$.

and the rigid polymer chain decreases sluggishly at first and then decreases sharply. Figure 5 shows that the average energy of rod-coil polymers declines slightly at first, and then rises rapidly.

The elastic force stored in the polymer chains according to Eq.(10), Eq.(12), and Eq.(13) was calculated, and the results are given in Fig.6. The elastic force increases with L for the flexible polymer chain; the elastic force increases slowly for the semiflexible polymer chain when the stretching ratio is less than 0.7 and increases abruptly after L exceeds 0.7. Similar to the semiflexible polymer chain, the elastic force on the rigid polymer chain is nearly unchanged till its abrupt increase at the stretching ratio of 0.8. To obtain the same L , the elastic force of the flexible polymer chain is larger than the elastic force of the rigid polymer chain. Therefore stretching the flexible polymer chain must be much

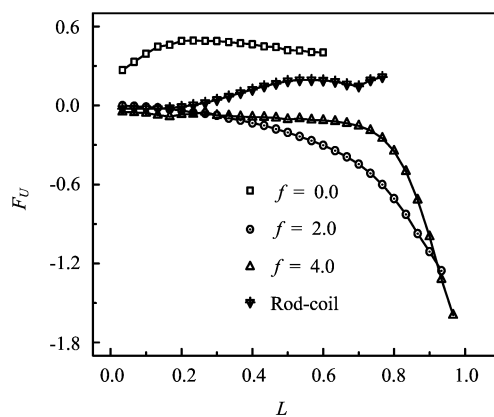


FIG. 7 Energy contribution to elastic force F_U as a function of L for various homopolymers (flexible, semiflexible rigid, and rod-coil). The length of the polymer chain is 31-mers, and f means the stiffness of polymer chains to be assigned 0.0, 2.0 and 4.0 for the flexible, semiflexible, and rigid segment, respectively; rod-coil means that the polymer chain is the rod-coil copolymer chain under the conditions $N_{rod}=16$, $N_{coil}=15$, $f_{rod}=4.0$, and $f_{coil}=0.0$.

more difficult. We also find the value of elastic force of rod-coil polymer increases with the increasing stretching ratio and it is between the value of elastic force of the flexible and rigid polymer chain.

In Fig.7, the change of the energy contribution to the elastic force F_U with the stretching ratio is shown. When the deformation of the polymer chain is not very large, the energy contribution to the elastic force F_U changes little. After the stretching ratio exceeds a certain value the energy contribution to the elastic force decreases quickly. The change of the entropy contribution to the elastic force F_S with the stretching ratio showed an opposite picture (Fig.8): at a small deformation the entropy contribution to the elastic force F_S still seems to be constant; but when the stretching ratio becomes large enough, the entropy contribution to the elastic force F_S begins to increase abruptly.

Now we can answer the question we posed earlier in this work: whether the coil segment in a rod-coil polymer chain will not be stretched until the rigid segment in the same polymer chain has been stretched a certain degree? The average Helmholtz free energy of the flexible polymer chain increases rapidly even when the stretching ratio is very low, but for the rigid polymer chain the change of the average Helmholtz free energy is almost zero at the same stretching ratio. Therefore stretching the flexible polymer chain is much more difficult than stretching the rigid polymer chain. The deformation of the flexible polymer chain may take place only when the increase amplitude of the average Helmholtz free energy of the rigid polymer chain is close to the level of the flexible polymer chain.

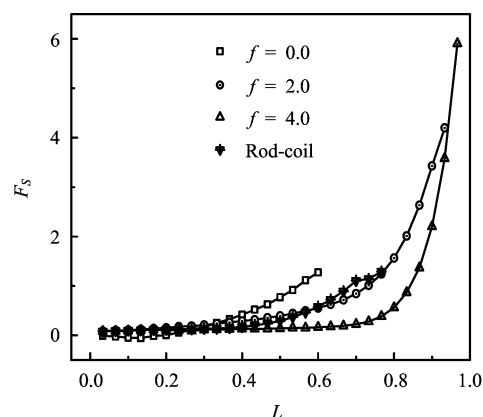


FIG. 8 Entropy contribution to force F_S as a function of L for various homopolymers (flexible, semiflexible rigid, and rod-coil). The length of the polymer chain is 31-mers, and f means the stiffness of polymer chains to be assigned 0.0, 2.0 and 4.0 for the flexible, semiflexible, and rigid segment, respectively; rod-coil means that the polymer chain is the rod-coil copolymer chain under the conditions $N_{rod}=16$, $N_{coil}=15$, $f_{rod}=4.0$, and $f_{coil}=0.0$.

IV. CONCLUSION

In conclusion, we have simulated the stretching process of a simple polymer chain with the Monte Carlo algorithm in a three-dimensional off-lattice model and investigated its elastic behavior. We find that stretching a flexible polymer chain is more difficult than stretching a rigid polymer chain, because the entropy contribution makes the free energy increase rapidly. When a rod-coil polymer chain was stretched the deformation was present in the rod segment first and will not appear in the coil segment until the stretching ratio of the rod segment has become very large. A rigid polymer chain is very easy to stretch (the elastic force F and the free energy $\langle A' \rangle$ is almost zero) when the stretching ratio is low, but when the stretching ratio reaches 0.8, the elastic force F and the free energy $\langle A' \rangle$ begin to increase rapidly. At the same time, average energy $\langle U \rangle$ and the energy contribution to the elastic force F_U decrease, but the entropy contribution to the elastic force F_S increases; therefore, this phenomenon must have been caused by the entropy contribution. For a rod-coil polymer chain, the results of our simulation calculation may explain some of the macroscopic phenomena of polymer and biomacromolecular elasticity.

V. ACKNOWLEDGMENTS

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