

ELASTIC BEHAVIOR OF COMB-LIKE POLYMER CHAINS*

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Abstract Three-dimensional Monte Carlo simulations of comb-like polymer chains with various backbone lengths N_b , arm lengths N_a and arm densities m are carried out to study the elastic behavior of comb-like polymer chains. The radius of gyration, the shape factors and bond length in different cases during elastic process are calculated, and it is found that the comb-like polymer molecules with longer backbone or shorter arm are more close to linear chains. But the arm density m affects the chain conformation non-monotonously. Some thermodynamic properties are also studied. Average Helmholtz free energy and elastic force f all increase with elongation ratio λ for all chains.

Keywords: Comb-like polymer; Monte Carlo simulations; Bond fluctuation model.

INTRODUCTION

The molecular architecture of polymer networks strongly influences their mechanical and chemical behavior, and the chain conformation and chain dynamics are long-standing problems of polymer science. Comb polymers are one of the significant molecular frameworks because such polymer can be cross-linked to form networks (gels and rubbers), or many properties of comb polymers can be modified by introducing branches in the field of nematic order^[1], polymer mix^[2, 3], dope, film^[4–6], polymer liquid crystal^[7–10], medicament system *etc.* Especially, the geometric and topologic conformations of comb polymers as well as thermodynamic properties are quite different from those of a general linear chain due to steric repulsion. At the same time, it is a burgeoning field that many scientists bring forward varied fresh theories and make experiments to account for the problems in practical applications, someone even has rarely consistent results, for example, the rubber elasticity. In the 1930's, this important phenomenon was first studied^[11] by using a Gaussian chain model. Later, many scientists put forward theories to non-Gaussian chain models^[12, 13]. These years, computer simulation has become a powerful tool to study network physical properties because it can be used to characterize the network on a microscopic level. Calculations of elastomeric properties of polymer networks have conventionally used theories and models based on the behavior of a collection of average chains, with all chains responding identically to external forces. To explain practical elasticity behavior comb polymers were performed using Monte Carlo simulations here.

In this paper, we studied the formation of comb polymer networks with a range of precursor polymer chain lengths and cross-link concentrations using Monte Carlo simulations. Our purpose here is to explore the elastic characters and thermodynamic properties of comb polymer chains by statistical thermodynamic method. In this model, we can clearly discuss the elasticity in terms of the chemical structure.

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MODEL AND METHOD

Models

The polymer network was studied using the bond fluctuation model (BFM) in three-dimensions on a simple cubic lattice^[14–16], which has been widely used in recent years to investigate the structure and dynamics of a great variety of polymer systems^[15, 17–19].

The polymer chain is modeled as a self-avoiding walk on a lattice. Each monomer in the model occupies a $2 \times 2 \times 2$ cube of sites on a cubic lattice^[20] and is connected to another monomer by a predetermined set of bond vectors. Next neighbors along the chain must be within a certain bond distance, so that the chain cannot cross itself. The bond vectors are built through all possible permutations and sign inversions of the following vector families:

$$\mathbf{B} = P(2, 0, 0) \cup P(2, 1, 0) \cup P(2, 1, 1) \cup P(3, 0, 0) \cup P(3, 1, 0) \cup P(2, 2, 1) \quad (1)$$

here $P(a, b, c)$ represents the set of all permutations and sign combinations of $\pm a, \pm b, \pm c$. The total number of possible configurations per bond is 108, as opposed to six for the simple cubic lattice, two consecutive bonds in the BFM can take 87 different bond angles^[15] as opposed to two ($0^\circ, 90^\circ$) for the simple cubic lattice. Even though the BFM is a lattice-based model, it does not suffer from the very discrete nature of the simple self-avoiding walk on a cubic lattice, whilst retaining the cheap overlap test characteristics of a lattice model. Note that the bond length between two consecutive beads can take five different values: 2, $\sqrt{5}$, $\sqrt{6}$, 3, and $\sqrt{10}$. This is justified by considering that different local conformations produce segments of the backbone of differing length. To simulate such a model, only one type of move needs to be considered, namely the random jump of one bead in a randomly chosen lattice direction by single lattice spacing. The trial is accepted only if both the excluded volume and bond length constraints remain unviolated. This model clearly lends itself to the Monte Carlo simulation technique rather than molecular dynamics. The set $\mathbf{B}$ (Eq. (1)) is chosen to satisfy the constraints of both excluded volume between monomers and topological entanglement between chains. No more than one monomer is permitted to occupy the same site and the entanglement constraint denies two chains to pass through each other for the excluded volume constraint. If the movement breaks the excluded volume constraint, or the new bond vectors between the moved monomer and its neighbors are out of the set $\mathbf{B}$, it will be rejected.

Energy

To generate the chains, it is integrant to calculate the interaction energy along the BFM model. In this paper, we have to consider the (Metropolis)^[15, 20–22] transition probability Ω :

$$\Omega = \min[1, \exp(-\Delta E/k_B T)] \quad (2)$$

for accepting or rejecting a move, which is allowed according to the excluded volume and bond vector restrictions, but involves an energy change ΔE :

$$\Delta E = E_{\text{new}} - E_{\text{old}} \quad (3)$$

where E_{old} and E_{new} represent the energy before and after a move respectively. When the bond length between two consecutive beads is equals to 2, $\sqrt{5}$ or $\sqrt{6}$, the interaction energy minus 1 (in unit of $k_B T$) because shorter distance means more compact structure. If $\Delta E < 0$, then this move is reasonable and can be accepted; on the contrary, if $\Delta E \geq 0$, we could use Eq. (2) to estimate whether this site should move unceasingly or not. After a great deal of steps, we can get the low energy chains.

Comb-like Polymer Chains

To distinguish from real comb polymers, a comb-like polymer model (seen in Fig. 1) was considered in our paper with N_b backbone beads and f arms, each comprising N_a beads, randomly distributed along the backbone. It is useful to define the branching density $m = fN_b$, so the total number of beads is:

$$N = N_b + f \cdot N_a = N_b(1 + m \cdot N_a) \quad (4)$$

Here, we adopt the different values of N_a , N_b , m and f to study their effect on the comb-like polymer chains. At the same time, for the case of $m = 0$ and $N_a = 0$, we can get linear chains with the same length to compare the characteristics with the comb-like polymer backbone chains.

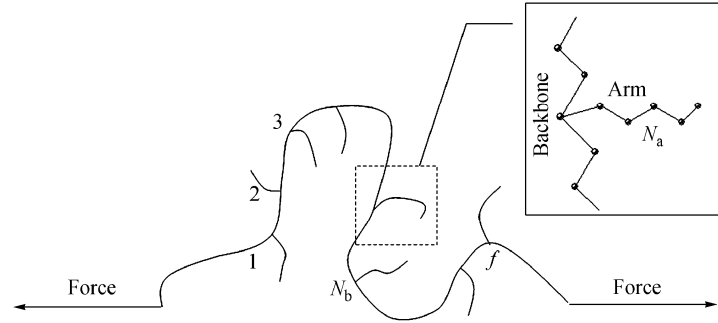


Fig. 1 Sketch map of a comb-like polymer chain under elongation
The force acts along the backbone direction, N_a -arm length, N_b -backbone length, f -arm number, m -arm density.

In our past papers^[23–26], when a force F acts on a polymer chain, the beads in the chains elongate the distance r along the force direction, while compress and draw back r' in the direction vertical to the force direction, and a lot of conformations would vanish. If the force $F = 0$, this is the isolated chain, and the minimum of the end-to-end distance is $r_{\min}$. If $F \neq 0$, the minimum of the end-to-end distance becomes $r_{\min} + r'$. We can get the change of conformations by this method, seen in Fig. 1. Assuming the force acts on the chain in the direction of r -axis, the partition function of the system is

$$Z(r) = \sum_i \exp(-E_i / k_B T) \quad (5)$$

where $\sum_i$ is the sum of the conformations whose r -axis component of end-to-end distance is greater than $r_{\min} + r$. This parameter is useful to study the thermodynamic behavior.

Deformation along one of the axes independently decreases the number of chain conformation. The elongation ratio λ can be obtained from the root-mean-square of end-to-end distance with deformation:

$$\lambda = \frac{\sqrt{\langle R^2 \rangle_r}}{\sqrt{\langle R^2 \rangle_0}} \quad (6)$$

where $\langle R^2 \rangle_r$ is the mean-square end-to-end distance of polymer chains with moving r along the direction of force and $\langle R^2 \rangle_0$ is the mean-square end-to-end distance of comb-like polymer chains without elongation.

The mean-square of end-to-end distance $\langle R^2 \rangle$ is a concise measure of configuration, which is defined as:

$$\langle R^2 \rangle_r = \frac{\sum_i R_i^2 e^{-E_i / kT}}{\sum_i e^{-E_i / kT}} \quad (7)$$

The mean-square of radius of gyration $\langle S^2 \rangle$ is another measure of configuration, which is a measure of the size of the spatial domain pervaded by the configuration. $\langle S^2 \rangle$ is defined as

$$\langle S^2 \rangle_r = \frac{\sum_i S_i^2 e^{-E_i / kT}}{\sum_i e^{-E_i / kT}} \quad (8)$$

where $\sum_i$ is the sum of the conformations whose r -axis component of end-to-end distance is greater than $r_{\min} + r$.

From the partition function, we can derive the average free energies of comb-like polymer chains under various elongation ratios λ :

$$\langle A \rangle = -RT \ln Z(r) \quad (9)$$

For the number of the conformation is so large that the partition function $Z(r)$ is expressed as:

$$Z(r) = Z_0 \frac{M_r}{M} \quad (10)$$

where Z_0 is the partition function of systems without elongation, and it is independent on the elongation ratio λ , and only depends on chain lengths and the type of comb-like polymer chains. M is the total number of samples, and M_r is the number of samples whose x -axis components of diameters are greater than $r_{\min} + r$. Therefore:

$$\langle A \rangle = -k_B T \ln Z_0 - k_B T \ln \frac{M_r}{M} \quad (11)$$

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

$$\langle A' \rangle \equiv \langle A \rangle + k_B T \ln Z_0 = -k_B T \ln \frac{M_r}{M} \quad (12)$$

At the same time, elastic force f can be obtained from the dependence of $\langle A \rangle$ on the elongated distance along the force direction^[23–28]:

$$f = \frac{\partial \langle A \rangle}{\partial r} \quad (13)$$

According to Newton's third law, the force f is the elastic force stored in the polymer chains. The energy contribution to the elastic force f_U is also defined by

$$f_U = \frac{\partial \langle U \rangle}{\partial r} \quad (14)$$

We know $\langle A \rangle = \langle U \rangle - TS$, so we can also calculate the entropy contribution to the elastic force f_s :

$$f_s = \frac{\partial(-TS)}{\partial r} = f - f_U \quad (15)$$

RESULTS AND DISCUSSION

Molecular Size and Shape

As one of basal parameters the radius of gyration $\langle S^2 \rangle$ in different conditions is shown in Fig. 2 as a function of elongation ratio λ . In Fig. 2(a), we calculate the case of $N_a = 5$, $m = 0.5$, and different $N_b = 40, 60$ and 80 . The curves separate regularly from each other with the certain intervals. It can be obtained that the radius of gyration $\langle S^2 \rangle$ increases with the number of back-bone beads clearly. When N_b increases, the total number N of the comb-like polymer chain increases synchronously, the dimensional 'globular' volumes of the chains also extend to increase so that the radius of gyration $\langle S^2 \rangle$ increases certainly. Figure 2(b) is under the conditions of fixed $N_b = 40$ and $m = 0.5$, and different arm lengths $N_a = 3, 5$ and 7 . The results are similar to Fig. 2(a), the curves rise with the arm length of the chain. But at large elongation ratios, some parts of curves superpose together, the reason may be that with elongation ratio increasing the influence of N_a is weakened while the influence of the backbone strengthens for the elongation is along the backbone direction. The curve with pentacles is for linear polymer chains with the same $N_b = 40$. It can be seen that the comb-like polymer chains have larger size than

linear chains at small elongation ratios, but the curve rises abruptly while $\lambda > 1.5$. At the beginning of the elongation, the interactions among the arms force the chains to expand their volume, and this effect becomes stronger for longer arms. With the increase of the elongation ratio, the external force weakens these interior interactions so that the shapes of the linear chains change greatly. To study the effect of the arm density m , we calculate the results with different m values 0.25, 0.5 and 0.75 (Fig. 2c). Large value m means more arms, and the interaction is more complex in affecting the shape of chains. From this figure we can find out that with the small value of the arm density the interior interactions influence the shape greatly, so $\langle S^2 \rangle$ reduces while m increasing. This is in agreement with the previous experiments. But when m is large enough to make chains entangled together, the structures change more tightly. In general, the radius of gyration $\langle S^2 \rangle$ all increases with the elongation ratio, and these figures show the shapes' changes in the process of tensile elongation obviously. Furthermore longer backbone or side-chain leads to larger $\langle S^2 \rangle$ while more arms affect it non-monotonously.

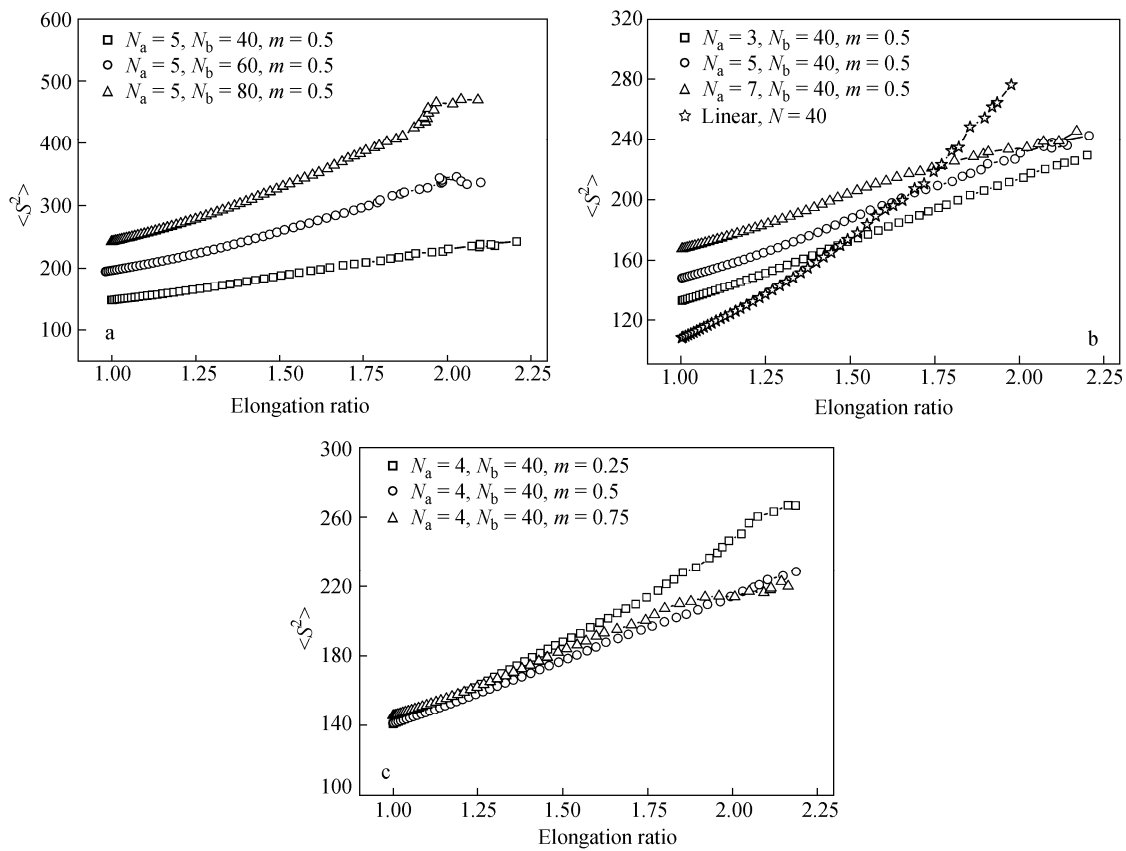


Fig. 2 The radius of gyration $\langle S^2 \rangle$ as a function of elongation ratio λ
a) Different N_b ; b) Different N_a ; c) Different m

In order to investigate the shape of the comb-like polymer chains in the tensile elongation in more detail. Here we consider the radius of gyration tensor S , defined as:

$$S = \frac{1}{n+1} \sum_{i=0}^n S_i S_i^T = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{pmatrix} \quad (16)$$

Here $S_i = \text{col}(x_i, y_i, z_i)$ is the position of atom i in a frame of reference with its origin at the center of mass.

The tensor S can be diagonalized to form a diagonal matrix with three eigenvalues L_1^2 , L_2^2 and L_3^2 ($L_1^2 \leq L_2^2 \leq L_3^2$). Solc and Stockmayer were the first use $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ to measure the shape of flexible polymer chains^[29, 30], and they estimated the ratios to be 1:2.7:11.7 based on a random walk of 100 bonds on a simple cubic lattice using Monte Carlo (MC) technique^[29, 30].

Another parameter^[31–33] characteristic of the shape of molecules may be obtained by combining the reduced components of s^2 to a single quantity that varies between 0 (sphere) and 1 (rod):

$$\langle \delta^* \rangle = 1 - 3 \left\langle \frac{L_1^2 L_2^2 + L_2^2 L_3^2 + L_3^2 L_1^2}{(L_1^2 + L_2^2 + L_3^2)^2} \right\rangle \quad (17)$$

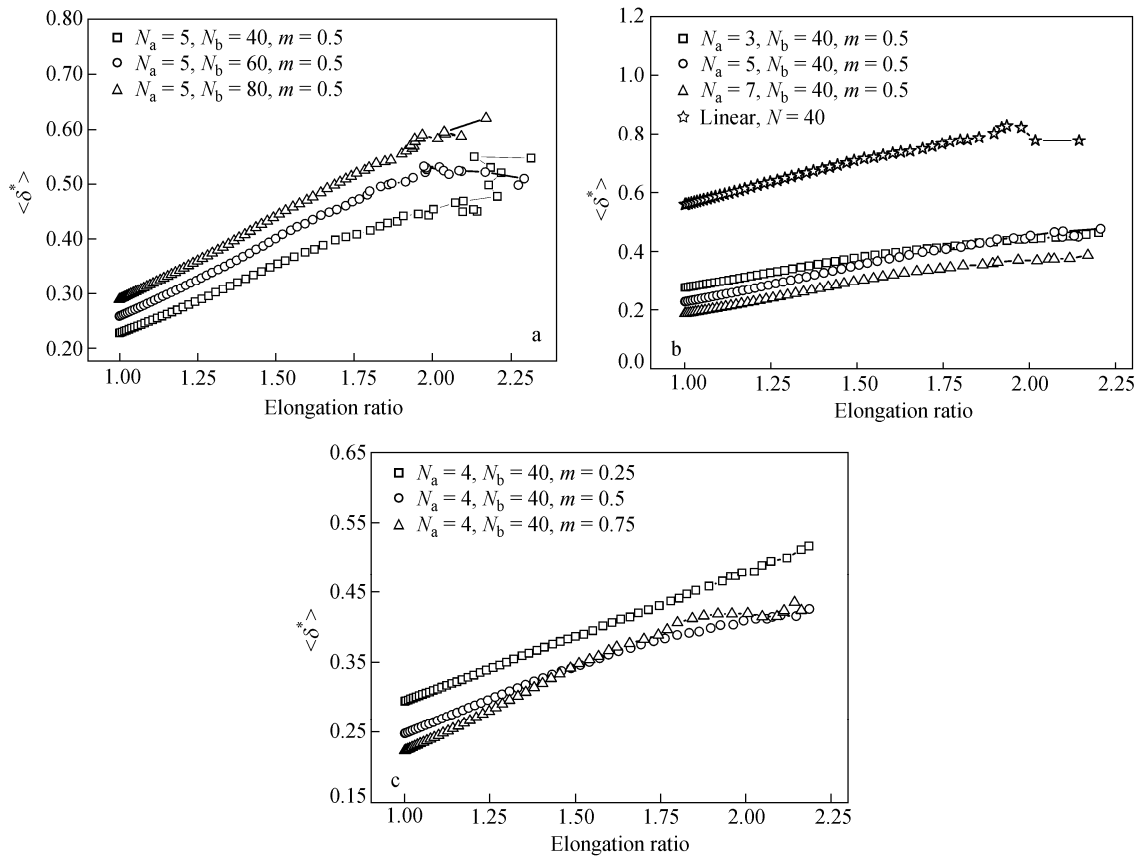


Fig. 3 $\langle \delta^* \rangle$ as a function of elongation ratio λ
a) Different N_b ; b) Different N_a ; c) Different m

The results are shown in Fig. 3 respectively. Evidently the shape factor $\langle \delta^* \rangle$ all increases with the elongation that is hypothetically to say that the chains all extend from sphere to rod along the elongation direction and indicate that during the process of elongation asphericity increases. We can get the conclusion from Fig. 3(a) that the value of $\langle \delta^* \rangle$ ranges from 0.23 to 0.28 without the elongation and increases with the backbone length N_b . Longer backbones can generate more conformations, which make chains more flexible. In Fig. 3(b), we fix N_b and m , and $\langle \delta^* \rangle$ all reduces with arm length so the curve of the linear chains with the same backbone length is on the top of the pictures. The slopes are all smaller than those in Fig. 3(a), which means that the parameter of the arm length is more important than backbone length for the shape of the comb-like polymer chains. Though we exert the force along the backbone direction, the comb-like polymer chains are not easy to be elongated with more side-chains. We can obtain the similar information from Fig. 3(c) for different arm density

m . The values of $\langle \delta^* \rangle$ increase while m reduces at small elongation ratio but there is a turning point for m during the elongation process. The reason may be that the interactions among the arms will be strengthened with the number of side chains increasing, and the chains trend to be rigid because of more difficult internal rotation. At the same time, more side chains will increase the distance between beads and reduce these interactions. Once this exceeds the steric effect, the chain will become flexible again. This conclusion is accordant to the above discussion suitably. In a word, with the increase of the elongation ratio, the shapes of the comb-like polymer chains change from sphere to rod approximatively, but the arms slower these deformations more evidently because their interior interactions change the flexibility of chains.

The bond length of chains certainly will change during the elongation process. We list the mean-square bond length $\langle b^2 \rangle$ as a function of elongation ratio λ in Fig. 4, for different backbone length, arm length and arm density, respectively. With increasing these three parameters the mean square bond length all decreases, that is to say $\langle b^2 \rangle$ is in inverse proportion to the total number N of the chains for more beads can form more compact structure which requires shorter bond length.

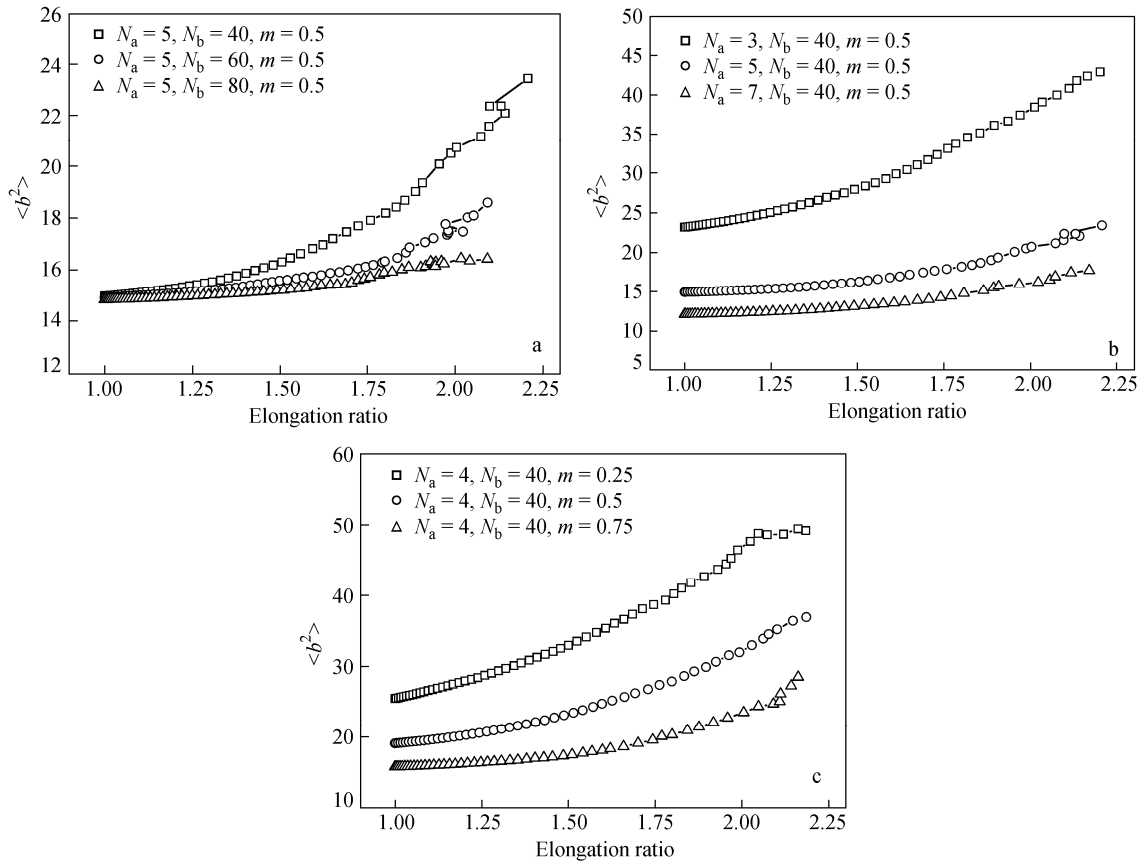


Fig. 4 Mean-square bond length $\langle b^2 \rangle$ as a function of elongation ratio
a) Different N_b ; b) Different N_a ; c) Different m

Then we compare the comb-like polymer chains to the linear chains with the same total number of chains by the factor g :

$$g = \langle S^2 \rangle_{\text{comb}} / \langle S^2 \rangle_{\text{linear}} \quad (18)$$

As already mentioned, $g = 0.5$ for unperturbed chains^[31]. In Fig. 5, we calculate two types of the comb-like chains with the same $N = 160$ to compare with the linear chain. We notice that g is a decreasing function of

elongation ratio λ for all simulated chains. At the same elongation ratio λ , the value of g with longer backbone length is larger than that with more arms that is to say the behavior of the chains with long backbone and less arms is more closed to the linear chains.

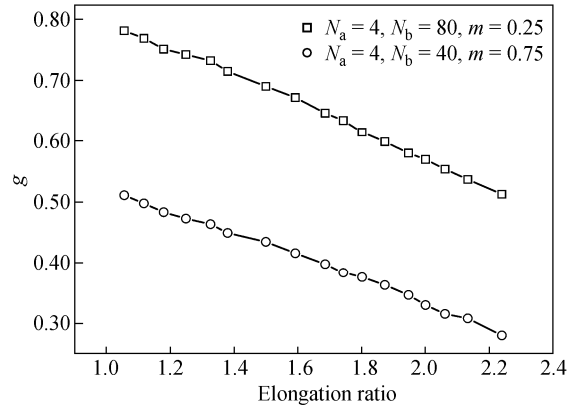
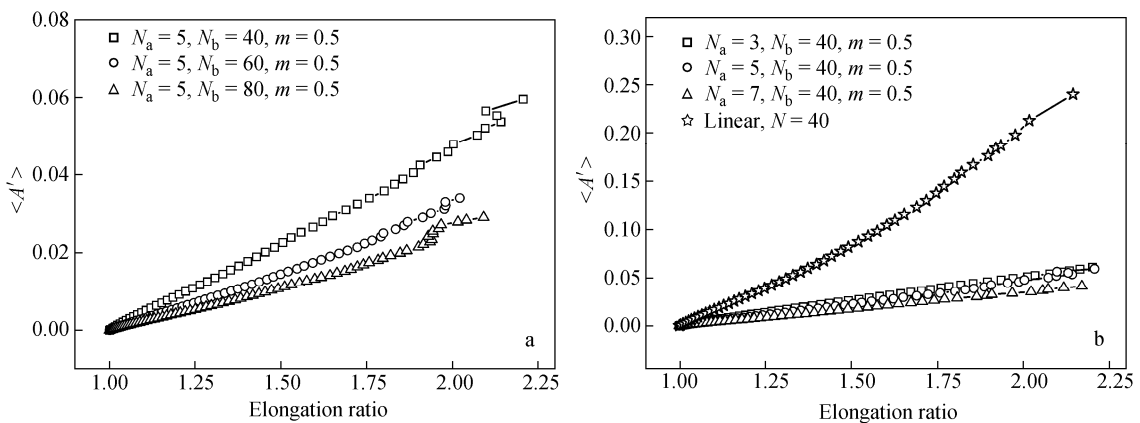


Fig. 5 G-value of $g = \langle S^2 \rangle_{\text{comb}} / \langle S^2 \rangle_{\text{linear}}$ as a function of elongation ratio for comb-like chains with the same chain length $N = 160$

From above discussion we can get some rules that first the arm density affects the comb-like polymer chain structures more effectively than the other parameters. More arm beads need more room to form the stable three-dimension structures. At the same time the increase of backbone length only adds the new segment to the formed chains simply. At last, the correlation of the elongation ratio λ to the chain structure is less important here. At large elongation ratios λ the angles just show a little change because the formed steady structures are not easy to change.

Thermodynamic Properties

In fact, energy changes exist in the process of tensile elongation. The changes of average conformations lead to increases (or decreases) of thermodynamic properties of comb-like polymer chains. Here we first calculate the average free energy and the average energy per bond according to Eq. (12), and the results are shown in Fig. 6 and Fig. 7, respectively.



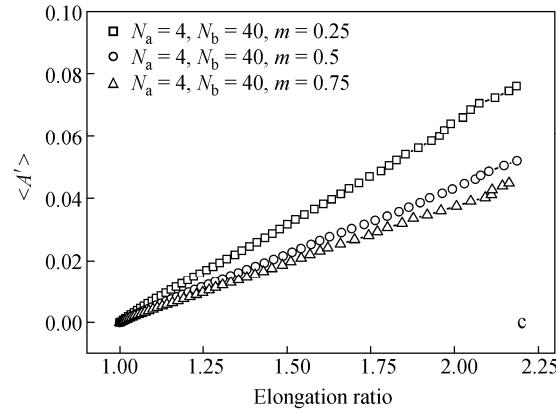


Fig. 6 $\langle A' \rangle$ per bond as a function of elongation ratio for comb-like polymer chains
a) Different N_b ; b) Different N_a including the linear chains; c) Different m

$\langle A' \rangle$ all increases with the elongation ratio λ , and at the same elongation ratio, this parameter decreases with the increase of N_b , N_a or m respectively. In Fig. 6(b), we add the curve with open pentacles for the linear chains to show that the other curves are far below it which explains that the arm affects the average free energy weightily. In Fig. 7, we draw the average energy per bond as a function of elongation ratio. This parameter seems to be independent of the elongation ratio, and the values of average energy almost fix and reduce with the increase of arm length and arm density. That is to say more arm beads can affect availably the comb-like polymer to form the stable structures.

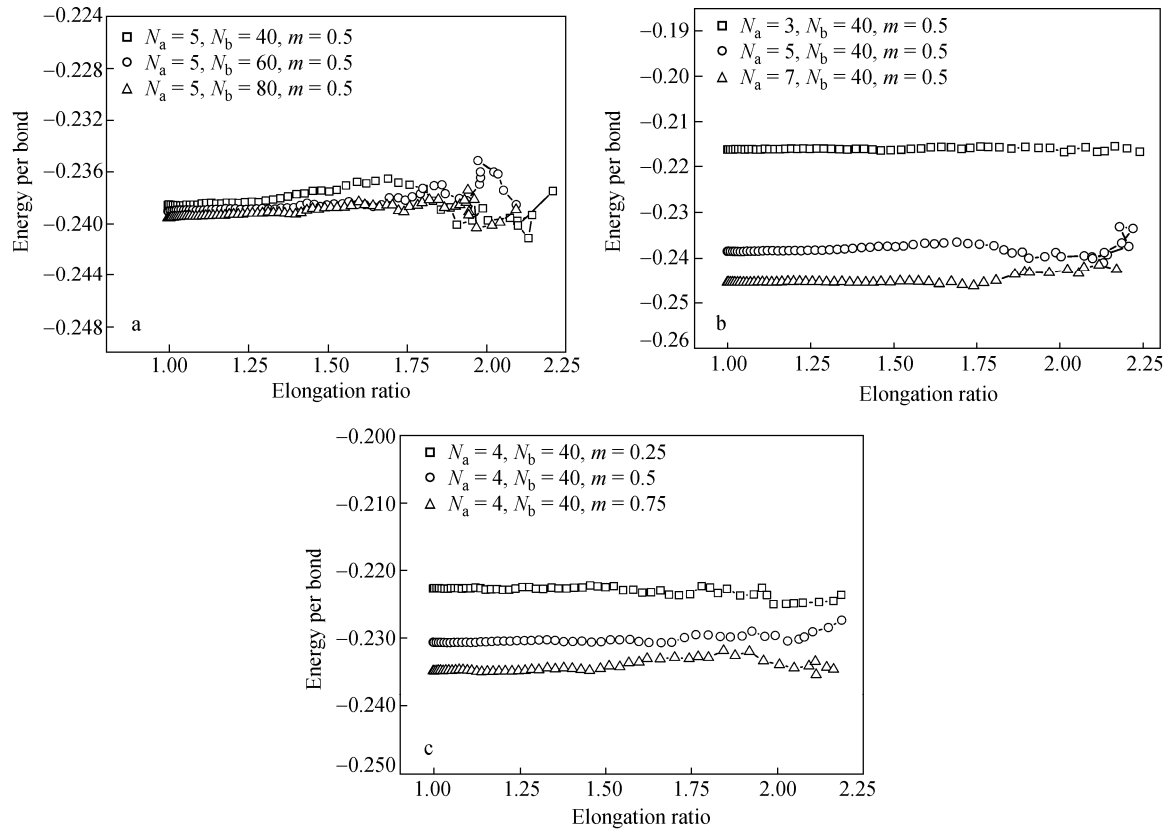


Fig. 7 Average energy per bond as a function of elongation ratio for comb-like chains
a) Different N_b ; b) Different N_a ; c) Different m

The elastic force stored in a chain is calculated according to Eq. (13), and the results are shown in Fig. 8. We can see that elastic force f all increases with elongation ratio λ , only in large elongation ratios there are some waves. According to Eq. (14), we calculate another elastic force f_U , shown in Fig. 9, the values of the elastic force f_U all don't change greatly with the backbone length, arm length or arm density.

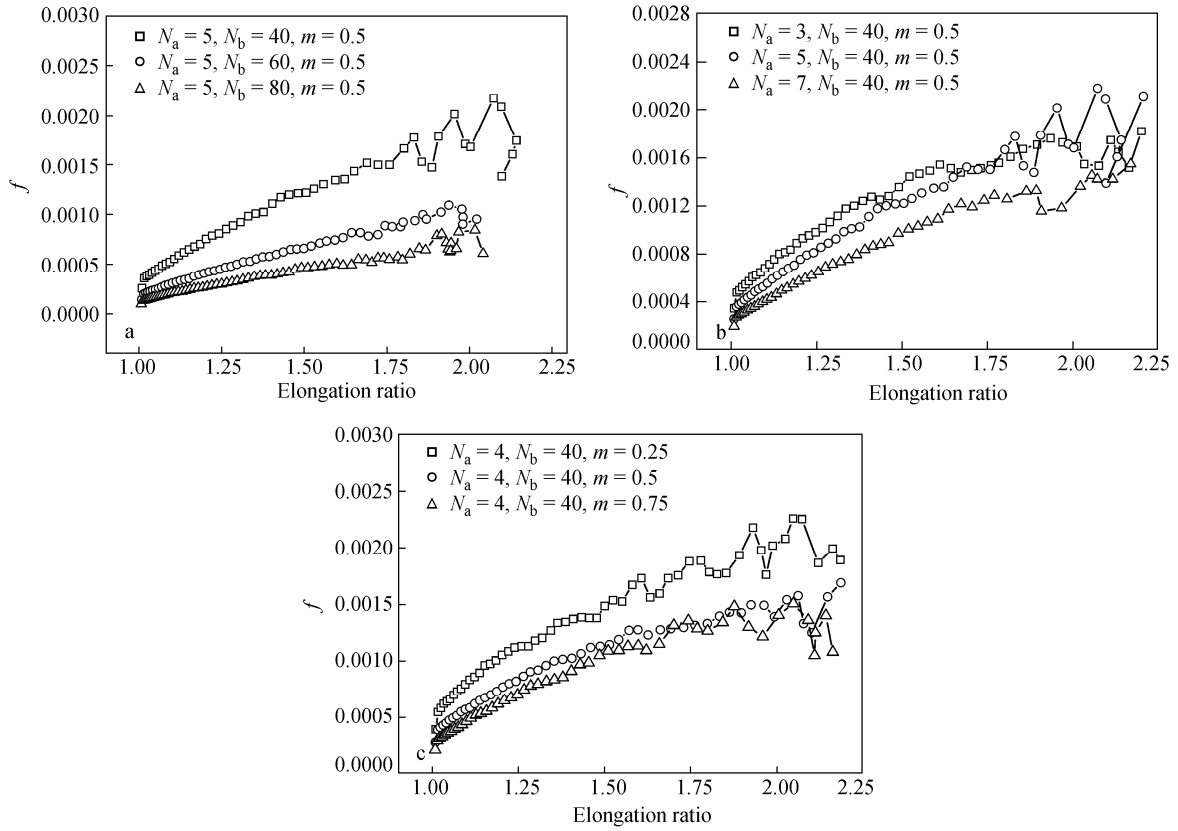
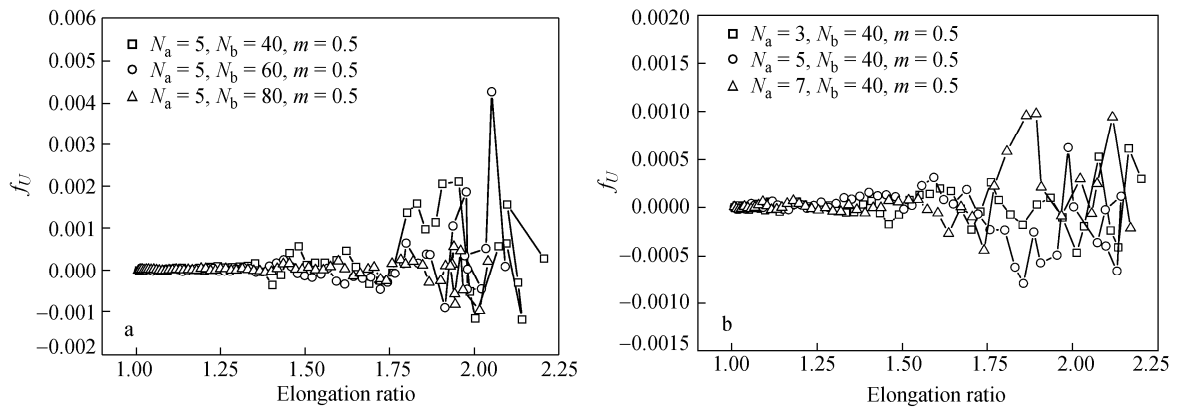


Fig. 8 Force f as a function of elongation ratio for comb-like chains
a) Different N_b ; b) Different N_a ; c) Different m



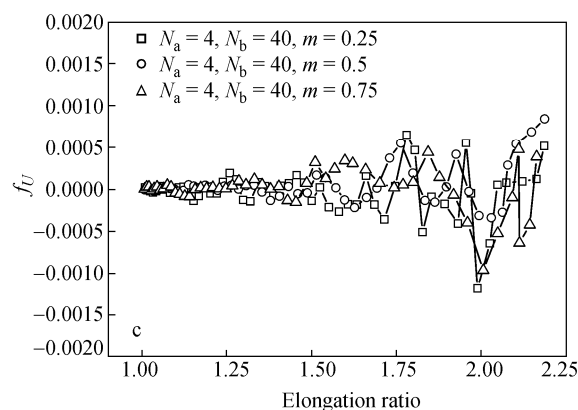


Fig. 9 f_U as a function of elongation ratio for comb-like chains
a) Different N_b ; b) Different N_a ; c) Different m

CONCLUSIONS

In this paper, we calculate the radius of gyration, the shape factors and bond length in different cases during an elongation process and find out that the comb-like polymer chain with longer backbone or shorter arm is more close to linear chain. But arm density m affects the chain conformation non-monotonously. Some thermodynamic properties are also studied here. Although the structure of real comb polymer molecules is complex and it is difficult to understand it clearly, our investigation may provide some insights into the microscopic mechanism of comb polymer molecules. And in some sense, our simulation has revealed some elastic properties of comb polymer chains.

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