ELSEVIER

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 45 (2004) 3547–3554

polymer

www.elsevier.com/locate/polymer

Effects of temperature on elastic behavior of short compact polymers

Linxi Zhang[a,*], Tingting Sun[a,b]

[a]Department of Physics, Wenzhou Normal College, Wenzhou 325027, China
[b]Department of Physics, Zhejiang University, Hangzhou 310027, China

Received 24 January 2004; received in revised form 7 March 2004; accepted 7 March 2004

Abstract

In this paper, we study further to explore the effects of temperature on the elastic behavior of short compact polymers. Average conformations and thermodynamics statistical properties at various temperatures T are calculated here. Different chain lengths N and elongation ratio λ are also considered simultaneously. From the plots of f and f_U vs. elongation ratio at low temperature, we can know that compact polymers are more close to the native states. With temperature decreasing deeply, polymer chains have the tendency to form globular structures. The results are concluded from: the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ increase abruptly with temperature decreasing at low temperature, and both characteristic ratio $\langle R^2\rangle/Nb^2$ and average energy per bond $\langle U\rangle$ decreases abruptly with temperature decreasing at low temperature, here L_1^2, and L_2^2 are the eigenvalues of the radius of gyration tensor S ($L_1^2 \le L_2^2$). We also analyze the relationship between the heat capacity C_V and temperature T for different chain lengths in the process of tensile elongation. The coil-to-globule transition temperature T_c can be estimated from the location of the peak on the heat capacity plot as a function of temperature. The plots of $\langle R^2\rangle$ as a function of chain length N at different temperatures are also shown, and the correlation $\langle R^2\rangle \sim N^\alpha$ is obtained at $T > T_c$ or $T < T_c$, while at $T = T_c$, the plots are irregular, here α depends on temperature and elongation ratio simultaneously. Elastic force (f), energy contribution to elastic force (f_U), and the ratio f_U/f are also discussed at various temperatures. These investigations may provide some insights into elastic behaviors of compact polymers at different temperatures, especially at low temperature.

Keywords: Compact polymer; Elastic behavior; Conformation

1. Introduction

Recently, there are a series of single molecule experiments, in which proteins such as biotin and avidin are stretched by mechanical forces, reveals a lot of information about the mechanical properties of structural proteins and provide detailed insights into intermolecular and intramolecular forces [1–15]. Mechanical experiments of atomic force microscope (AFM) can extract information about free energy landscapes of proteins and study directly the mechanical characteristic of molecular motors and mechanical function in living organisms [3–5,16–19]. These investigations can help us understand the origins of unusual strength exhibited by muscle proteins [16]. Besides the experiments, there also exist the theoretical studies of AFM with some general approaches [20–24]. However, the effects of temperature on the elastic behavior of proteins are always neglected.

Elastic behavior of protein molecule is of great significance in understanding the mechanical characteristic of protein. In fact, the elastic behavior of protein molecule is almost the same as general polymer chain, for example, the changes in Helmholtz free energy are from energy and entropy for both compact polymer (protein) and general polymer. The elasticity is an important phenomenon in polymer physics. Kuhn et al. first studied rubber elasticity using a Gaussian chain model in the 1930s [25,26]. Later on, much effort was put into network theories based on the non-Gaussian models [27,28]. However, in those theories, rubber elasticity is athermal and independent of the chemical structure of polymer chains. Then Abe and Flory discussed the effect of the elongation of a polymer chain on the apportionment of its bonds and bond sequences among various rotational-isomeric states (RIS) [29]. Curro and Mark provided a non-Gaussian theory of rubber-like elasticity based on rotational isomeric state simulations of

---

[*] Corresponding author. Tel.: +86-57187953261; fax: +86-57187951328.

E-mail address: Lxzhang@hzcnc.com (L. Zhang).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.03.025

network chain configurations and investigated rubber-like elasticity on the basis of distribution functions for end-to-end separation r of the chains using the Monte Carlo method [30,31]. However, the thermodynamic properties of rubber-like elasticity have not been investigated in detail. We have discussed the conformational properties, especially the conformational energy, of long polymethylene (PM) chains with respect to rubber elasticity using the RIS model, and the elastic behavior of short PM chains using the enumeration calculation method considering the RIS model and non-local interactions [32–35].

By ‘compact’, we prefer to those conformations of single-chain molecules which are tightly packed, i.e. fully contained within a volume of space (a box) with the minimal (or near minimal) surface/volume ratio [36–38]. Compact polymer is one of the important polymers because proteins are compact polymers [36,37]. Recently Dmitrii and Zhisong investigated the force extension curves of single protein molecules from the probability distribution $P(r)$ [39]. However, the interactions between residues (or atoms) in protein molecules are ignored in their calculations [39]. In fact, the interactions between residues (or atoms) in protein molecules are very important. Perhaps, some special behaviors of elastic forces in protein molecules depend mainly on residue interactions. We have done some work in investigating elastic behaviors of compact polymers. For short compact polymers, we use the enumeration calculation method to study elastic behaviors of compact polymers in the process of tensile elongation [40], and for long protein-like polymers, we use Monte Carlo method to discuss those problems [41]. In these studies, the HP model [36–38, 42–44] is also adopted, and we mainly discussed the change in conformations and thermodynamics properties in the process of tensile elongation. However, the temperature effect has not been considered in those investigations [40, 41]. In this paper, some effects of temperature on the elastic behavior of short compact polymers are discussed by using the enumeration calculation method based on two-dimensional lattice model.

Organization of this paper is as follows: first, we briefly describe the method of calculation. Then we discuss the changes in average conformations at temperature T for different chain lengths in the process of tensile elongation, for example, the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$, and the characteristic ratio of $\langle R^2\rangle/Nb^2$. We also present the scaling relationship between the mean-square end-to-end distance $\langle R^2\rangle$ and chain length N. Some thermodynamics properties are also studied here, such as average energy, Helmholtz free energy and elastic force at different temperatures. At last, heat capacity C_V at temperature T for different chain lengths is also investigated in the process of tensile elongation.

2. Method of calculation

A compact polymer is modeled by a self-avoiding chain of length N on square lattice. The Hamiltonian of the system is

$$H = \sum_{i<j} \varepsilon_{\mu_i\mu_j}\Delta(r_i - r_j) \tag{1}$$

where $\varepsilon_{\mu_i\mu_j}$ is the contact energy between residue types μ_i and μ_j, and $\Delta(r_i - r_j) = 1$ if r_i and r_j are adjoining lattice sites with i and j not adjacent along the chain, and $\Delta(r_i - r_j) = 0$ otherwise. The term in Eq. (1) refers to intramolecular interactions. In the HP model, the hydrophobic energy, or the solvent effects, is a major contributor to the energetics of protein folding. A favorable contact energy, $\varepsilon_{HH} = -1.0$ is assigned to two non-consecutive residues which are one lattice spacing apart, while the other interactions, both ε_{HP} and ε_{PP} are set equal to zero [37,38, 42–44]. In this paper, we only discuss short compact polymer chains with all H sequences. Here, the enumeration calculation method is adopted, and this means that we calculate all the conformations of the chains in the process of tensile elongation.

On the basis of the method above, now we will consider the elastic behavior, especially the conformational energy of short compact polymers. When a force f acts at the ends of a compact polymer chain, the atoms (or residues) in the compact polymer chain move a distance r along the direction of the force. Thus, a lot of conformations vanish, and the number of conformations decreases. In Fig. 1, if the force $f = 0$, this is an isolated chain, and we assume that the minimum of end-to-end distance is $r_{\min}$ (Fig. 1(a)). If the force $f \neq 0$, the minimum of end-to-end distance along the elongated direction becomes $r_{\min} + r$ (Fig. 1(b)). For simplicity, the minimum of end-to-end distance $r_{\min}$ equals to 1 (excluded volume is considered here). If the force acts at the ends of the chain in the direction of x-axis, the partition function of the system is

$$Z(r) = \sum_i \exp(-E_i/k_B T) \tag{2}$$

where $\sum_i$ is the sum of the conformations whose x-axis component of end-to-end distance is greater than r. In fact, our formula is the same as Flory’s expression, i.e. Eq. (7) in Chapter VIII [45] because $\sum_i$ is the sum of all conformations in Flory’s expression, while here $\sum_i$ is the sum of

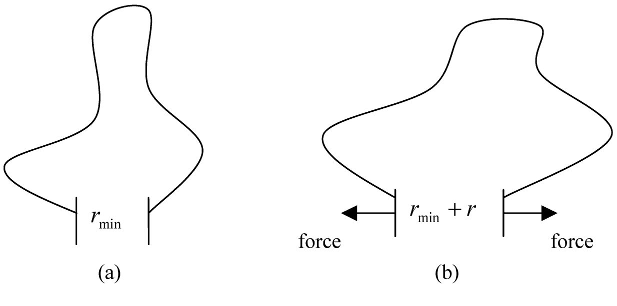


Fig. 1. Conformations of an isolated chain (a) and of a chain with force acting on (b). The minimum of end-to-end distance becomes from r to $r + r_{\min}$ in the process of tensile elongation.

the conformations whose x-axis component of end-to-end distance is greater than r. This leads a difference in the formula between our expression of partition function and Flory's one.

The radius of gyration tensor S is considered here to measure the shape of compact polymer chains, and it is defined as for two-dimensional polymer chain:

$$S = \frac{1}{n+1}\sum_{i=0}^{n} S_i S_i^{\mathrm{T}} = \begin{pmatrix} S_{xx} & S_{xy} \\ S_{xy} & S_{yy} \end{pmatrix} \tag{3}$$

where $S_i = \mathrm{col}(x_i, y_i)$ is the position of bead 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 two eigenvalues L_1^2 and $L_2^2 (L_1^2 \leq L_2^2)$. We will discuss the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ at different temperatures in the process of tensile elongation.

Elongation ratio λ is obtained from the root-mean-square end-to-end distance $\langle R^2\rangle_r^{1/2}$, and we define it as [40]

$$\lambda = \frac{\sqrt{\langle R^2\rangle_r}}{\sqrt{\langle R^2\rangle_0}} \tag{4}$$

where $\langle R^2\rangle_r$ is the mean-square end-to-end distance of compact chains with moving r along the direction of the force and $\langle R^2\rangle_0$ is the mean-square end-to-end distance of compact chains without elongation. In the meantime, the mean-square end-to-end distance $\langle R^2\rangle_r$ is defined as

$$\langle R^2\rangle_r = \frac{\sum_i R_i^2 \, \mathrm{e}^{-E_i/k_\mathrm{B}T}}{\sum_i \mathrm{e}^{-E_i/k_\mathrm{B}T}} \tag{5}$$

where $\sum_i$ is the sum of the conformations whose x-axis component of end-to-end distance is greater than r.

We can also get the average energy $\langle U\rangle$ and Helmholtz free energy $\langle A\rangle$ of the compact chains under various elongation ratio λ, and they are

$$\langle U\rangle = \frac{\sum_i E_i \, \mathrm{e}^{-E_i/k_\mathrm{B}T}}{\sum_i \mathrm{e}^{-E_i/k_\mathrm{B}T}} \tag{6}$$

$$\langle A\rangle = -k_\mathrm{B}T \ln \sum_i \mathrm{e}^{-E_i/k_\mathrm{B}T} \tag{7}$$

In the meantime, the force value f can be obtained from the dependence of free energy $\langle A\rangle$ on the elongated distance along the force direction [32–35,40,41,46]

$$f = \frac{\partial\langle A\rangle}{\partial r} \tag{8}$$

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

$$f_\mathrm{U} = \frac{\partial\langle U\rangle}{\partial r} \tag{9}$$

The heat capacity C_V is defined as [47]

$$C_V = \frac{\langle U^2\rangle - \langle U\rangle^2}{k_\mathrm{B}T^2} \tag{10}$$

3. Results and discussions

3.1. Average conformations

The conformations of proteins are very important because the functions of proteins are determined directly by the structures of proteins. To investigate the changes in the shape of compact polymer in the process of tensile elongation in more detail, we first calculate the radius of gyration tensor S, defined by Eq. (3). The tensor S can be diagonalized to form a diagonal matrix with two eigenvalues L_1^2 and L_2^2 $(L_1^2 \leq L_2^2)$. We plot the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ as a function of temperature T for different chain lengths in the process of tensile elongation, and the results are shown in Fig. 2. Here, $\langle L_2^2\rangle$ is parallel to the direction of elongation and $\langle L_1^2\rangle$ is vertical to the direction of elongation. First, we find that the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ becomes small with elongation ratio increasing for $N = 15$. This means that the polymer chain has been elongated in the direction of force. Here, we pay great attention to the relationship between the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$and temperature T. In this paper, we suppose $k_\mathrm{B} = 1$. In fact, here temperature is in the unit of $|\varepsilon_\mathrm{HH}|/k_\mathrm{B}$. In the region of $T > 3.0$, the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ hardly has any change for certain elongation ratio λ. With temperature T decreases, the value of $\langle L_1^2\rangle/\langle L_2^2\rangle$ increases. At low temperature, the value increases rapidly with decreasing temperature. For $\lambda = 1.0$ and 1.4, the values reach 1.0 at $T = 0.125$. It means that when temperature decreases to one point, compact polymers become globular structure. For $\lambda = 1.8$, compact polymers

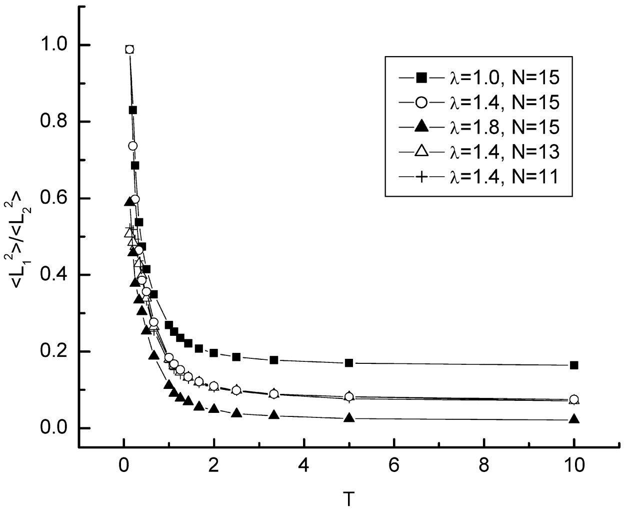


Fig. 2. Ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ vs. T for different chain lengths in the process of tensile elongation. Here, $k_\mathrm{B} = 1$.

approach globular structure at low temperature $T = 0.125$, and the value of $\langle L_1^2\rangle/\langle L_2^2\rangle$ is close to 0.6. We also investigate the relationship between the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ and chain length, and the results are also shown in Fig. 2. In Fig. 2, when $T > 0.4$, the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ is almost the same for different chain lengths, and when $T < 0.4$, the ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ with $N = 15$ is greater than that with $N = 13$ and 11. The ratio of $\langle L_1^2\rangle/\langle L_2^2\rangle$ with $N = 15$ at $T = 0.125$ reaches 1.0, however, the ratio with $N = 13$ and 11 only reach 0.5. It may have some correlations with the largest number of contact of compact polymers. We know the largest number of contact is $t_{\max} = 9$ for $N = 15$, $t_{\max} = 7$ for $N = 13$ and $t_{\max} = 6$ for $N = 11$ [36]. We can conclude at low temperature ($T = 0.125$), the shapes of compact polymers approach globular, especially for long chain without elongation. For example, the number of conformations with the number of contacts $t = 8$ is 2705 for $N = 15$ in our model, and there is almost 40 times large as $t = 9$ (the number of conformations with is 69 for $t = 9$). In fact, we know that for one conformation with $t = 8$ at temperature $T = 0.125$, there is $e^{-E_i(t=8)/k_BT}|_{T=0.125} = e^{8/0.125} = 6.23 \times 10^{27}$; however, for one conformation with $t = 9$ there is $e^{-E_i(t=9)/k_BT}|_{T=0.125} = e^{9/0.125} = 1.86 \times 10^{31} \approx 3000 \times e^{-E_i(t=8)/k_BT}|_{T=0.125}$. So we conclude that at low temperature there exists

$$\langle R^2\rangle_r = \frac{\sum_i R_i^2 e^{-E_i/k_BT}}{\sum_i e^{-E_i/k_BT}} \approx \frac{\sum_{i(t=9)} R_i^2\, e^{-E_i/k_BT}}{\sum_{i(t=9)} e^{-E_i/k_BT}}\Big|_{T=0.125}$$

at $T = 0.125$ for $N = 15$. When elongation ratio increases, the number of conformations of compact polymers decreases and this leads the ratio $\langle L_1^2\rangle/\langle L_2^2\rangle$ to decrease from 1.0 with $\lambda = 1.0$ to 0.6 with $\lambda = 1.8$ at $T = 0.125$. An example is also shown in Fig. 3, and we can know that the shape of 15-bond compact polymer with $t = 9$ approaches globular structure. Here, t is the number of contacts of compact polymer chains.

The mean-square end-to-end distance $\langle R^2\rangle$ is important in investigating the changes in chain dimensions in the process of tensile elongation. Fig. 4(a) shows the plots of the characteristic ratio $\langle R^2\rangle/Nb^2$ ($b = 1$) vs. temperature T for different chain lengths in the process of tensile elongation.

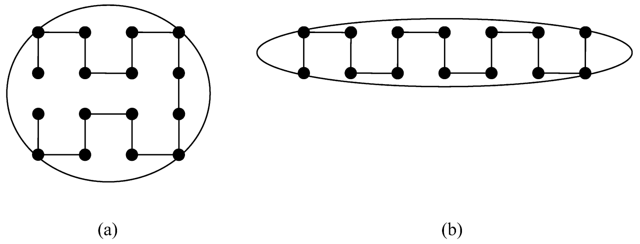
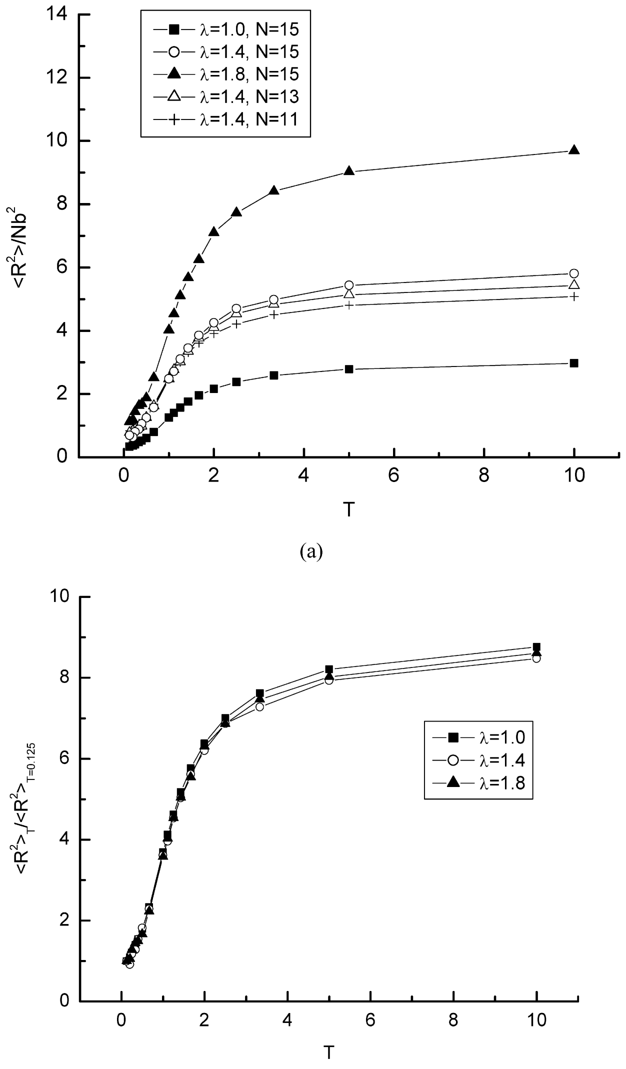

(a) (b)

Fig. 3. Two conformations of 15-bond compact chains with $t = 9$ (a), and $t = 6$ (b), respectively. Here t represents the number of contacts. In (a) ($t = 9$), the shape of compact polymer approaches globular, while in (b) ($t = 6$), the shape is flat.



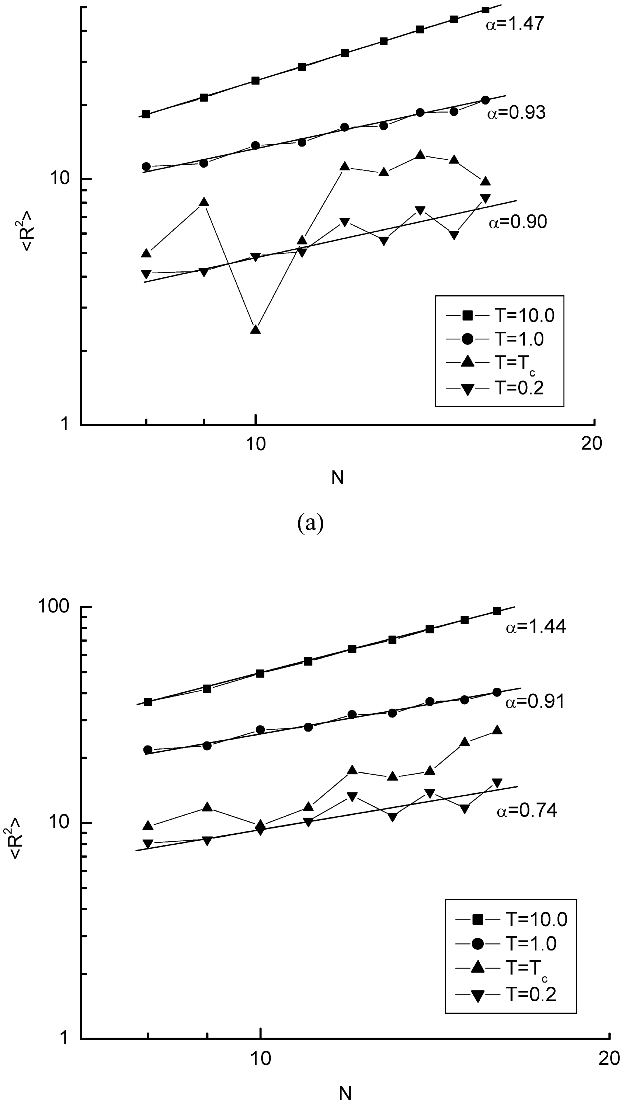
(a)

(b)

Fig. 4. (a) Characteristic ratio $\langle R^2\rangle/Nb^2$ vs. T for different chain lengths in the process of tensile elongation, and (b) ratio of $\langle R^2\rangle_T/\langle R^2\rangle_{T=0.125}$ vs. T for chain length $N = 15$ in the process of tensile elongation. Here, $k_B = 1$.

In the process of tensile elongation, the forces acting on the compact polymer chains do work, therefore the average distances between atoms become large, and $\langle R^2\rangle/Nb^2$ increases with elongation ratio λ. In the meantime, when temperature $T > 3.0$, the characteristic ratio hardly changes with temperature for a certain elongation ratio. When temperature $T < 3.0$, the characteristic ratio decreases rapidly. At low temperature, the characteristic ratio is relatively small, and the chains are more compact. In Fig. 4(a), we also find that the characteristic ratio also increases with chain length increasing when $T > 2.0$, and it is almost independent of chain length when $T < 2.0$ with a given elongation ratio (here $\lambda = 1.4$). In the meantime, we also give the relative ratio of $\langle R^2\rangle_T/\langle R^2\rangle_{T=0.125}$ as a function of temperature T with different elongation ratios for $N = 15$ in the process of tensile elongation in Fig. 4(b). In Fig. 4(b) the ratio of $\langle R^2\rangle_T/\langle R^2\rangle_{T=0.125}$ is almost independent of elongation ratio λ for $N = 15$, and only depends on temperature T.

We also discuss the mean-square end-to-end distance $\langle R^2 \rangle$ as a function of chain length N at different temperatures T. Here, we consider two values of elongation ratio: $\lambda = 1.0$ (without elongation) and $\lambda = 1.4$. First, we introduce a transition temperature T_c, which we will be discussed in more detail later. In Fig. 5(a), there are plots of $\langle R^2 \rangle$ as a function of N at different temperatures without elongation ($\lambda = 1.0$) in double-logarithm scale. At $T = 10.0$, there is a good line, and at $T = 1.0$, it also fits linear although there exists 'parity domino effect' of lattice model. However, at $T = T_c$, there is almost no correlation between $\langle R^2 \rangle$ and N. When $T = 0.2$ ($T < T_c$), it fits also linear too. Here, T_c is a transition temperature. When temperature T is larger than T_c ($T = 1.0$) or smaller than T_c ($T = 0.2$), the plots of $\langle R^2 \rangle$ as a function of N all fit good linear in double-logarithm scale. That means $\langle R^2 \rangle \sim N^{\alpha}$, here $\alpha = 1.47$, 0.93, and 0.90 for $\lambda = 1.0$ at $T = 10.0$, 1.0, and 0.2, respectively. Only at $T = T_c$, the plot has no order. We also find that the scaling exponent of the line increases with temperature T except $T = T_c$. That also means that the value of $\langle R^2 \rangle$ with chain length N changes larger at high temperature. In fact, the theoretical scaling exponent of two-dimensional self-avoiding chain is $\alpha = 1.50$ [48], and our result at $T = 10.0$ ($\alpha = 1.47$) is close to the theoretical one. Double logarithmic plot of $\langle R^2 \rangle$ vs. N at different temperatures with $\lambda = 1.4$ are also shown in Fig. 5(b). The results are similar to Fig. 5(a), therefore, we do not describe in detail here.



(a)

(b)

Fig. 5. Double logarithmic plots of the mean-square end-to-end distance $\langle R^2 \rangle$ vs. chain length N at different temperatures T with (a) $\lambda = 1.0$ and (b) $\lambda = 1.4$. Here, $k_B = 1$.

3.2. Thermodynamics properties

Average energy and average Helmholtz free energy per bond at different temperatures are calculated by Eqs. (6) and (7), and Fig. 6 shows average energy per bond as a function of temperature T for different chain lengths in the process of tensile elongation. We find that average energy per bond for 15-bond compact chain increases with elongation ratio λ, especially at high temperature. The reason may be that the number of contacts for compact polymers becomes smaller in the process of tensile elongation, so average energy per bond increases. However, the difference between different elongation ratios become small at low temperature, especially at $T < 0.30$. In this case, average energy depends mainly on the largest number of contacts, and there almost are the same for the largest number of contacts at $\lambda = 1.0$, 1.4 and 1.8. At temperature $T > 3.0$, all the plots in Fig. 5 are nearly parallel to x-axis. But when temperature drops to $T < 3.0$, average energy per bond also decrease with temperature T. At low temperature, average energy per bond is very low. The reason may be that compact polymers

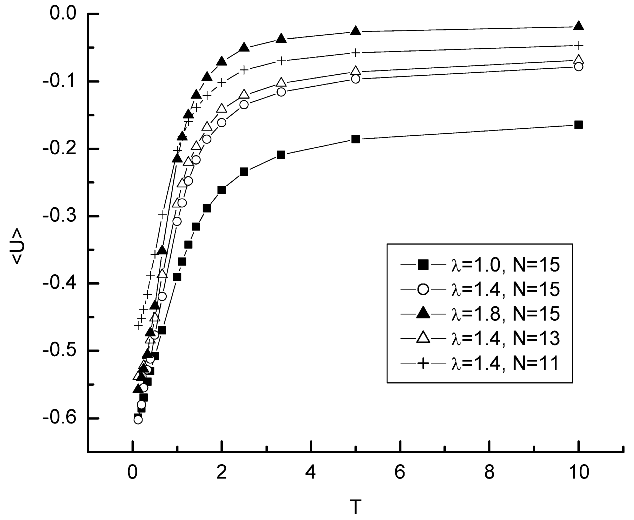


Fig. 6. Average energy per bond $\langle U \rangle$ vs. T for different chain lengths in the process of tensile elongation. Here, $k_B = 1$.

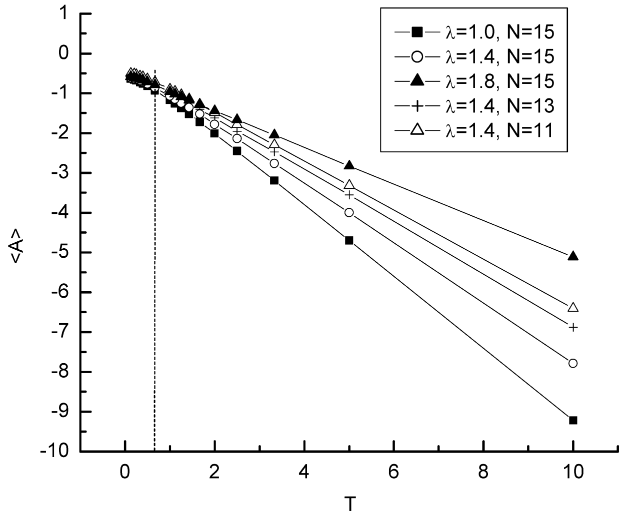


Fig. 7. Average Helmholtz free energy per bond $\langle A\rangle$ vs. T for different chain lengths in the process of tensile elongation. Here $k_B = 1$.

approach globular structure when temperature drops to $T < 0.5$. We also investigate the average energy per bond for different chain lengths with $\lambda = 1.4$. Average energy per bond decreases with increasing chain length. For different chain lengths, compact polymer all approaches globular structure at low temperature.

In Fig. 7, we plot average Helmholtz free energy per bond as a function of temperature T for different chain lengths in the process of tensile elongation. For 15-bond chain, the number of contacts becomes small with elongation ratio increasing, so average Helmholtz free energy per bond increases. Considering the case of $\lambda = 1.4$, average Helmholtz free energy per bond of $N = 13$ is smaller than that of $N = 11$, and larger than that of $N = 15$. The data fall fairly well on a straight line when $T > T_c$ (≈ 0.7) because there is $\langle A\rangle = -k_B T \ln \sum_i e^{-E_i/k_B T}$, so when T is larger, $\sum_i e^{-E_i/k_B T}$ is almost the constant at different temperatures. We can conclude that when $T > T_c$, the plots of average Helmholtz free energy per bond as a function of temperature T fit good linear. When $T < T_c$, there is a different relation between average Helmholtz free energy per bond and temperature.

We calculate the elastic force stored in the short compact polymer chains according to Eqs. (8) and (9). Fig. 8 shows the plots of elastic force per bond as a function of elongation ratio for different chain lengths at different temperatures. We have discussed the case of $T = 1.0$, and concluded that the elastic forces increase slowly with elongation ratio λ for small λ, and increase abruptly for large λ [40]. When temperature drops to $T = 0.4$, the elastic force increases quickly then smoothly. So are 11-bond and 13-bond chains at $T = 0.4$. However, the value of elastic force per bond for 15-bond chain is the largest one and 11-bond is the smallest. This is also in accord with the results in Fig. 7. If temperature drops again to ($T = 0.2$), the trend of the curve for 15-bond chain increases first, then goes smoothly, at last it falls a little. At low temperature, the compact polymer shows its native state evidently. In Fig. 8, we also give the plot of elastic force for 15-bond Gaussian chain. In fact, interactions and self-avoiding are not considered for Gaussian chain. Here, we compare it with 15-bond compact chain at $T = 1.0$. When $\lambda < 2$, the two curves are almost the same. While $\lambda > 2$, elastic force of 15-bond compact chain at $T = 1.0$ is larger than that of 15-bond Gaussian chain. When the chain is most elongated, elastic force becomes smaller with temperature increasing, and the elastic force of Gaussian chain is the smallest one at $T = 1.0$. However, our calculated results have much difference than the experiment results [3,4]. The reason may be that in the AFM experiment one conformation of protein is measured, and after one contact between residues break away, this contact cannot be formed again, while our calculation is the average of many possible conformations. In fact, the AFM experiment results

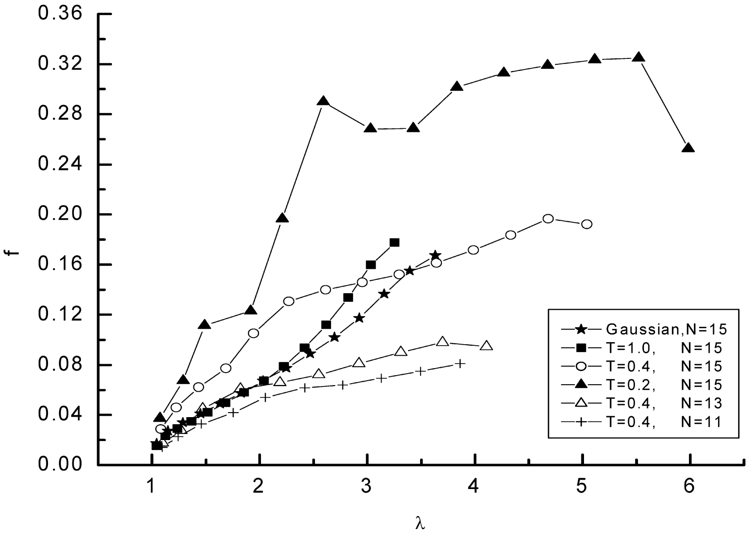


Fig. 8. Elastic force per bond f vs. elongation ratio for different chain lengths at different temperatures. Here, 15-bond Gaussian chain is also considered, and $k_B = 1$.

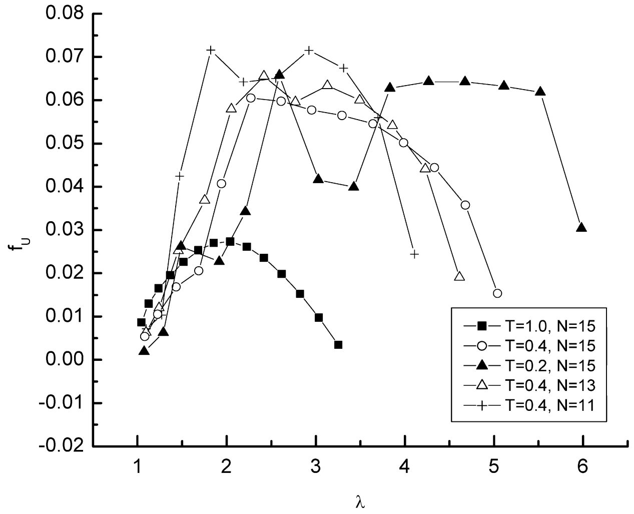


Fig. 9. Energy contribution to elastic force per bond f_U vs. elongation ratio for different chain lengths at different temperatures. Here, $k_B = 1$.

of elastic force of proteins are obtained from non-equilibrium states of proteins; however, our results are from equilibrium states of compact polymers. Because the molecule is stretched by moving the surface, with uniform speed, away from the cantilever, the force is time dependent. This leads there exist some differences between our theoretical results and the experiment ones.

Energy contribution to elastic force f_U is very important to investigate the changes in conformations. Here, we calculate f_U for different chain lengths at different temperatures, and the results are shown in Fig. 9. At $T = 1.0$, the value of f_U increases first, then drops for 15-bond chain [40]. In the region of $\lambda = 1.60-1.80$, there is a maximum one. When temperature decreases ($T = 0.4$), the maximum value of f_U increases. The maximum value of f_U means the number of vanishing conformations is the largest. At $T = 0.4$ for $N = 11$ and 13, there both have two peaks. But for $N = 15$, only one peak is found. In the meantime, at $T = 0.2$, there hardly changes in the region of $\lambda = 3.50-5.50$ for $N = 15$.

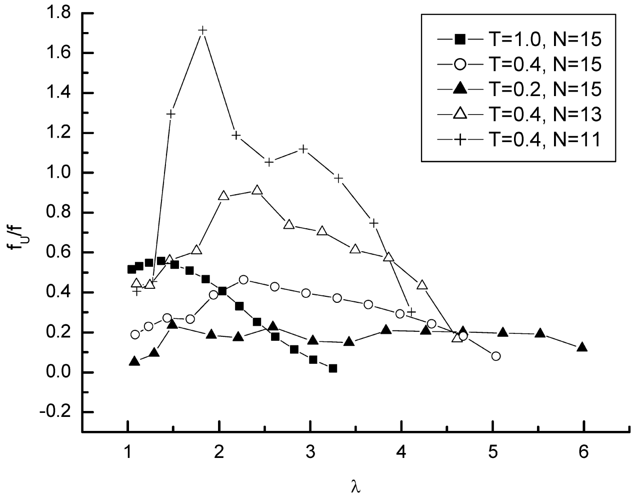
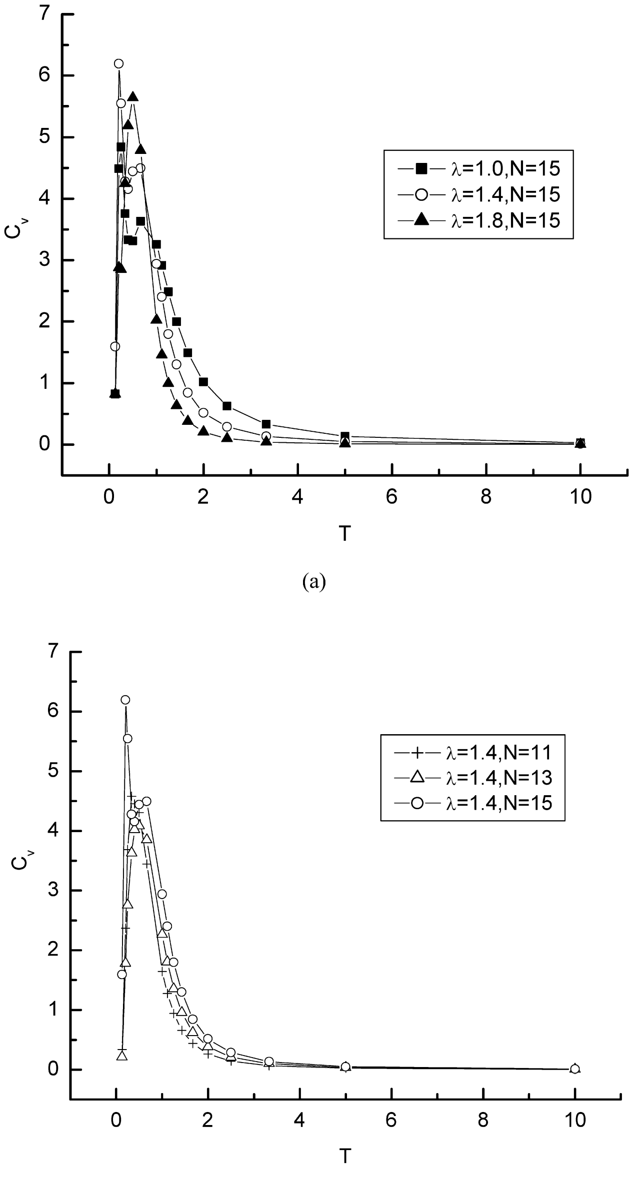


Fig. 10. The ratio f_U/f vs. elongation ratio for different chain lengths at different temperatures. Here, $k_B = 1$.

The ratio f_U/f vs. λ are also considered in Fig. 10. At $T = 0.2$, the value of f_U/f for 15-bond compact chains keep relatively constant in the process of tensile elongation, and the value is about 0.2. As temperature increase to $T = 0.4$, the plot first increases then drops, and it has one peak, and the ratio of f_U/f is greater than that at $T = 0.2$. However, at $T = 1.0$, the value of f_U/f first increases a little then decreases as λ increases. We also consider the ratio of f_U/f at $T = 0.4$ for 11-bond, and 13-bond compact polymers. We find the curves all have one peak, and the maximum value of f_U/f becomes larger with chain length decreasing.

At last, we discuss the heat capacity C_V, and in Fig. 11 it



(a)

(b)

Fig. 11. C_V vs. T for different chain lengths in the process of tensile elongation. Here, $k_B = 1$.

is shown C_V as a function of temperature T for different chain lengths in the process of tensile elongation according to Eq. (10). The coil-to-globule transition temperature T_c can be estimated from the location of the main peak on the heat capacity plot as a function of temperature. Fig. 11(a) shows the plots of C_V as a function of temperature T for 15-bond compact polymer chain with different elongation ratios λ. With $\lambda = 1.0$ and 1.4, we see that besides the subsidiary peak at low temperatures, the specific heat exhibits also a strong, fairly broad peak at a higher temperature which correspond to T_c, and with $\lambda = 1.8$, there is only one peak. We also calculate the heat capacity C_V of compact polymers with $N < 15$. For example, 14-bond compact chain with $\lambda = 1.0$ has also two peaks while others all have only one peak. So, we suppose that if chain length is longer, there may also have two peaks in the plots of C_V as a function of temperature. Besides the main peak corresponding to the collapse transition, there is also a subsidiary peak at a lower temperature. As discussed in Ref. [49], this subsidiary peak presumably describes the roughening transition. Fig. 11(b) shows the plots of C_V as a function of temperature T for 11-bond, 13-bond and 15-bond compact polymer chains with $\lambda = 1.4$. The values of T_c are 0.333, 0.5, and 0.667 for $N = 11$, 13, and 15, respectively. That is said that the value of T_c increases with N at the same elongation ratio. In Fig. 11(a), the values of T_c for 15-bond chain at different elongation ratios are very near, and they are 0.667, 0.667, and 0.5 for $\lambda = 1.0$, 1.4, and 1.8, respectively. The results of these microscopic calculations may explain some macroscopic phenomena of elasticity of compact polymers. The elastic behavior of compact polymers at low temperature can provide some insights into the structure of compact polymers in the native states.

Acknowledgements

This research was financially supported by National Natural Science Foundation of China (Nos. 20174036, 20274040), and Natural Science Foundation of Zhejiang Province (No. 10102). We also thank the referees for their critical reading of the manuscript and their good ideas.

References

[1] Zhuang X, Rief M. Curr Opin Struct Biol 2003;13:88–97.
[2] Zinober RC, Brockwell DJ, Beddard GS, Blake AW, Olmsted PD, Radford SE, Smith DA. Protein Sci 2002;11:2759–65.
[3] Rief M, Gautel M, Oesterhelt F, Fernandez JM, Gaub HE. Science 1997;276:1109–11.
[4] Rief M, Fernandez JM, Gaub HE. Phys Rev Lett 1998;81:4764–7.
[5] Rief M, Pascual J, Saraste M, Gaub HE. J Mol Biol 1999;286:553–61.
[6] Thompson JB, Hansma HG, Hansma PK, Plaxco KW. J Mol Biol 2002;322:645–52.
[7] Pennisi ME. Science 1999;283:168–9.
[8] Oberhauser AF, Hansma PK, Carrion-Vazquez M, Fernandez JM. Proc Natl Acad Sci USA 2001;98:468–72.
[9] Li H, Oberhauser AF, Fowler SB, Clarke J, Fernandez JM. Proc Natl Acad Sci USA 2000;97:6527–31.
[10] Erickson HP. Science 1997;276:1090–2.
[11] Brockwell DJ, Beddard GS, Clarkson J, Zinober RC, Blake A, Trinick J, Olmsted PD, Smith DA, Radford SE. Biophys J 2002;83:458–72.
[12] Best RB, Li B, Steward A, Daggett V, Clarke J. Biophys J 2001;81:2344–56.
[13] Li H, Carrio-Vazquez M, Oberhauser AF, Marsamante PE, Fernandez JM. Nat Struct Biol 2000;7:1117–20.
[14] Oberhauser AF, Badilla-Fernandez C, Carrio Vazquez M, Fernandez JM. J Mol Biol 2002;319:433–47.
[15] Marsalek PE, Lu H, Li H, Carrion-Vazquez M, Oberhauser AF, Schulten K, Fernandez JM. Nature 1999;402:100–3.
[16] Smith BL, Schaffer TE, Viani M, Thompson JB, Frederick NA, Kindt J, Belcher A, Stucky GD, Morse DE, Hansma PK. Nature 1999;399:761–3.
[17] Kellermayer MSZ, Smith SB, Granzier HL, Bustamante C. Science 1997;276:1122–5.
[18] Oberhauser AF, Marszalek PE, Erickson H, Fernandez JM. Nature 1998;393:181–5.
[19] Tskhovrebova L, Trinic JA, Sleep JA, Simmons RM. Nature 1997;387:308–12.
[20] Horie C, Miyazaki H. Phys Rev B 1990;42:11757–61.
[21] Sasaki N, Tsukada M. Phys Rev B 1995;52:8471–82.
[22] Girard C, Bouju X. J Chem Phys 1991;95:2056–64.
[23] Girard C, Bouju X, Martin OJF, Dereux A, Chavy C, Tang H. Joachim Phys Rev B 1993;48:15417–24.
[24] Argento C, French RH. J Appl Phys 1996;80:6081–90.
[25] Kuhn W. Kolloid-Z 1934;68:2–11.
[26] Guth E, Mark H. Lit Chem 1934;65:93–121.
[27] Kuhn W, Guth E. Kolloid-Z 1942;101:248–71.
[28] Treloar LRG. Trans Faraday Soc 1946;42:77–85.
[29] Abe Y, Flory PJ. J Chem Phys 1970;52:2814–20.
[30] Curro JG, Mark JE. J Chem Phys 1984;80:4521–5.
[31] Mark JE. J Phys Chem B 2003;107:903–13.
[32] Linxi Z, Youxing H, Delu Z. Macromol Theory Simul 2001;10:479–84.
[33] Xiaozhen Y, Xianfeng L. Chin J Polym Sci 1998;16:279–82.
[34] Linxi Z, Agen X, Zhouting J, Delu Z. Macromol Theory Simul 2001;10:651–5.
[35] Linxi Z, Zhouting J, Delu Z. J Polym Sci, Polym Phys 2002;40:105–12.
[36] Chan HS, Dill KA. Macromolecules 1989;22:4559–73.
[37] Lau KF, Dill KA. Macromolecules 1989;22:3986–97.
[38] Lau KF, Dill KA. Proc Natl Acad Sci USA 1990;87:638–42.
[39] Dmitrii ME, Zhisong W. J Chem Phys 2002;116:7760–5.
[40] Tingting S, Linxi Z, Jin C, Yu S. J Chem Phys 2004;120:5469–75.
[41] Weiqi Y, Linxi Z. Macromol Theory Simul. Submitted for publication.
[42] Kamtekar S, Schiffer JM, Xiongm H, Babik JM, Hecht MH. Science 1993;262:1680–5.
[43] Dill KA, Bromberg S, Yue K, Fiebig KM, Yee KM, Thomas PD, Chan HS. Protein Sci 1995;4:561–602.
[44] Yue K, Fiebig KM, Thomas PD, Chan HS, Shackhnovich EI, Dill KA. Proc Natl Acad Sci USA 1995;92:325–9.
[45] Flory PJ. Statistical mechanics of chain molecules. New York: Interscience; 1969. p. 308.
[46] Flory PJ. Principles of polymer chemistry. Ithaca, New York: Cornell University Press; 1953.
[47] Lam PM. Phys Rev B 1987;36:6988–92.
[48] de Gennes PG. Scaling concepts in polymer physics. Ithaca: Cornell University Press; 1979.
[49] Dickman R, Schieve WC. J Phys 1984;45:1727–30.