Elastic behavior of adsorbed single compact chains

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Abstract

Elastic behaviors of short single two-dimensional compact chains adsorbed on the attractive surface are investigated in this paper by using the enumeration calculation method. In our model a single compact chain is fixed with one of its end at a position above the impenetrable surface, and then it is pulled away from the attractive surface slowly through elastic force acting. We investigate the chain size and shape of adsorbed compact chains, such as mean-square end-to-end distance per bond $\langle R^2 \rangle/N$ mean-square radii of gyration per bond $\langle S^2 \rangle_x/N$ and $\langle S^2 \rangle_y/N$, shape factors $\langle \delta \rangle$, and fraction of adsorbed monomers f_a in order to illuminate how the size and shape of adsorbed compact chains change during the process of tensile elongation. Especially for strong attraction interaction there are some special behaviors in the chain size and shape during this process. If there exits adsorption interaction, single compact chain is first almost pulled down to the adsorption surface and then moves in the direction of force until to leave the adsorption surface. These changes become more obvious with strong adsorption interaction. Our calculation can show this elastic process of adsorbed compact chains visually and simply. On the other hand, some thermodynamics properties are also studied here. We use average energy per bond, average Helmholtz free energy per bond, elastic force f and energy contribution to elastic force f_u to study the elastic behavior of adsorbed single compact chains in the process of tensile elongation. Elastic force f has a long plateau during the tensile elongation for strong adsorption interaction, which agrees well with experimental and theoretical ones. These investigations can provide some insights into the elastic behaviors of adsorbed protein chains.
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Keywords: Elastic behavior; Adsorbed compact chain; Enumeration calculation method

1. Introduction

In many areas of science including physics, chemistry, biology, material science, and tribology, the adsorption phenomenon is widely used as stabilizers or flocculationg agents for colloidal dispersions [1,2], polymer adhesion [3], biocompatibility [4] and chromatographic separation [5], etc. Furthermore, adsorption of protein molecules on solid interfaces is important in fields like biomedical materials engineering [6], chromatography [7], and nanotechnology [8,9]. The knowledge of adsorption-induced conformational changes of proteins is essential to understand protein adsorption [10,11]. Unfortunately, because of considerable experimental difficulties, detailed information about these conformational changes is sparse [11–16], which hampers the further development of protein adsorption theory.

In the past, scientists were absorbed in studying adsorption of polymer chains in many fields. Various parameters such as the adsorbed amount, surface coverage, layer thickness, average bound fraction of polymer monomers and polymer volume fraction profile normal have been used to describe the conformations of polymer chains adsorbed on a surface [17–26]. Otherwise, the Gaussian model of an adsorbed polymer in an external field has been used to analyze the feature of the phase transitions [27,28]. On the other hand, protein adsorption bears some resemblance to the adsorption of general polymer chains because most of proteins are copolymers and polyelectrolytes. Therefore, the adsorption of proteins is receiving more attentions [29,30]. In fact, protein adsorption plays a key role in a variety of biological processes [6,31,32] and it is of primary importance in many practical applications such as the design of biocompatible materials [33,34], drug carriers [35–37] and biosensors [38,39] among many others. Scientists have known that proteins are large molecules with

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inhomogeneous surfaces that can change their confor-mations driven by the interactions with a surface [40,41].

In recent years, numerous experimental and theoretical studies have been devoted to the adsorption phenomenon onto solid surfaces because of important applications of polymeric materials in industry and daily life. The experiment scientists could measure these parameters more and more exactly while many excellent experimental techniques are developed to study the adsorption phenom-enon. The relative experiment apparatus such as atomic force microscopy (AFM) [42] has been used to study the adsorption phenomenon. Important thing is that single-molecule force spectroscopy (SMFS), based on AFM, has become a versatile platform for studying intermolecular and intramolecular interactions with its extremely high force sensitivity [43]. Recently, Hugel et al. studied the elasticity of single polyvinylamine chains and their desorption from solid surfaces based on SMFS [44]. Cui et al. also measured directly the desorption force of a single polyelectrolyte chain from a substrate [45]. They all observed typical force curves based on SMFS, i.e. force has a long plateau and then drops to zero [44,45]. However, these direct measurements were done on general polymer chains (such as single polyvinylamine chains or single polyelectrolyte chains etc), and interactions between single polymer chains and the substrate are strong. If these interactions between single polymer chains and the substrate are weak, it is difficult to measure elastic force directly based on SMFS. However, simulation investigation can overcome this disadvantage, and can obtain many conformational properties and elastic behavior of adsorbed chains with weak adsorption inter-action. In the meantime, the elasticity of single protein chains has not been investigated by SMFS, and some different elasticity behaviors from general polymer chains may be obtained through simulation investigation, especially for weak adsorption interaction. Proteins are compact polymers [46]. The compact conformations of polymers are important because they are the principal configurations of the native states of globular proteins. 'Compact' refers to those configurations 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, and compact chains can represent protein chains simply [46]. Therefore, in this paper, we use the enumeration calculation method to investigate elastic behavior of single two-dimensional adsorbed compact chains, and it can help us to understand clearly the effect of adsorption interaction on the elastic behavior of single compact chains during this process.

2. Method of calculation

According to the model of a self-avoiding chain of length N on square lattice, the Hamiltonian of the compact chains system with adsorption interaction can be redefined as:

$$E = \sum_{i<j} \varepsilon_{ij}\Delta(r_i - r_j) + V \qquad (1)$$

where ε_{ij} is the contact energy between monomer i and 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, while $\Delta(r_i - r_j) = 0$ otherwise. Here we suppose that $\varepsilon_{ij} = -1$ (in the unit of k_BT) [46]. To simulate the adsorption of chains, it is realized by introduction of attractive contact potential between the attractive surface and chain monomers. The additional item V in Eq. (1) represents the adsorption interaction. In this paper, we only study short two-dimensional compact chains, so the potential applied can be rewritten as:

$$V(y_i) = \begin{cases} 0, & y_i > 0 \\ \varepsilon, & y_i = 0 \end{cases} \qquad (2)$$

where y_i is the distance between i-th monomer in a chain and the adsorption surface, and ε is the value of adsorption interaction energy accordingly ($\varepsilon \leq 0$). In this paper, we only employ the adsorption interaction energy $\varepsilon = 0$, -1, and -3, respectively. As we only discuss short two-dimensional compact chains, so the x-axis certainly means the adsorption surface and the y-axis is vertical to this surface. Because we adopt the enumeration calculation method in this paper, we could count all conformations of short two-dimensional compact chains with different chain length and adsorption energy and study the adsorption phenomena during the process of tensile elongation. In Fig. 1, we draw the sketch map of the absorbed compact chains during this process, and the solid and dashed lines respectively represent two conformations of adsorbed compact chain with one of its end fixed at different positions Y_1 and Y_2. In this model, this is single compact chain actually, and the chain moves slowly along the direction of force, i.e. the value of Y increases slowly. Then we account the total number of conformations with different value Y in terms of the
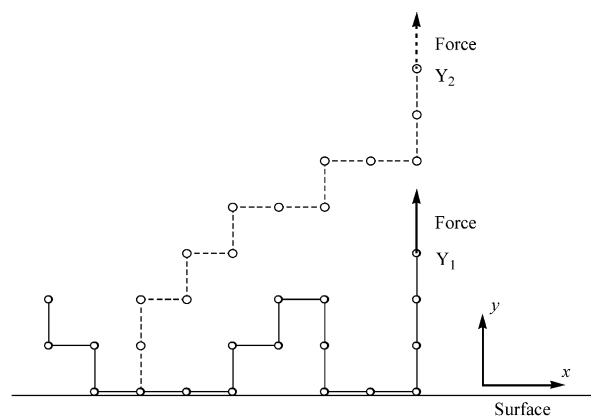

Fig. 1. Sketch map of the absorbed compact chains during the process of tensile elongation. The solid and dashed lines respectively represent two conformations of adsorbed compact chain with the ends at different positions Y_1 and Y_2.

enumeration calculation method. This model is similar to Klushin's model [27,28], and it is easy to compare with the experimental data of SMFS.

At the same time, the partition function of the system is

$$Z(Y) = \sum_i \exp\left(\frac{-E_i}{kT}\right) \tag{3}$$

where $\sum_i$ is the sum of all conformations with one of their ends fixed at position Y. In fact, the partition function is widely used to study the thermodynamic properties of polymer chains. Because the number of conformations for long adsorbed compact chains is very large, we have to use Monte Carlo method to simulate real compact chains, while the enumeration calculation method can only be used to investigate the short compact chain system. Therefore, in this paper we only study short adsorbed compact chains with chain length $N = 13$, 15, and 17, respectively. In fact, the number of conformations for 17-bond adsorbed compact chains at $Y = 17$ is also large (about 6,000,000). In fact, as the tendency of our results for short adsorbed compact chains is the same, therefore, we can predict the results of long adsorbed compact chains from short adsorbed compact chains. We can derive Helmholtz free energy of adsorbed compact chains from the partition function:

$$\langle A(Y)\rangle = -kT \ln Z(Y) \tag{4}$$

This parameter can provide much important thermodynamic information for compact chains [47,48]. 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 [47,49–52]:

$$f = \frac{\partial \langle A \rangle}{\partial Y} \tag{5}$$

According to Newton's third law, the force f is the elastic force stored in the adsorbed compact chains. In the meantime, energy contribution to the elastic force f_u is defined by

$$f_u = \frac{\partial \langle U \rangle}{\partial Y} \tag{6}$$

In fact, elastic behaviors of general polymer chains have been investigated for a long time [53,54]. Of course, elastic behavior of adsorbed compact chains may be different from general polymer chains.

3. Results and discussion

3.1. Chain size and shape

Mean-square end-to-end distance $\langle R^2 \rangle$ is important in investigating the chain size and shape, so we first plot the characteristic ratio $\langle R^2 \rangle/N$ as a function of Y_0 for adsorbed compact chains with different chain length N and different

adsorption energy ε in Fig. 2. Here Y_0 is defined as

$$Y_0 = \frac{Y}{N} \tag{7}$$

here Y is the distance between the last monomer (the point of force acting) and the attractive surface. When Y increases, Y_0 also increases at the same time, and the results could be more similar to each other through adopting the parameter of Y_0 instead of Y. The characteristic ratio of end-to-end distance $\langle R^2 \rangle/N$ (here bond length is unit) decreases slowly for weak attractive interaction, and fast for strong attractive interaction. When $\varepsilon = 0$, the lines with square symbols for 13-, 15-, and 17-bond chains in the bottom of Fig. 2 all gather together, and the change under this condition is not obvious. When $\varepsilon = -1$, i.e. adsorption energy is equal to contact energy, the ratio of $\langle R^2 \rangle/N$ has a little fluctuation. However, when adsorption energy is strengthened to -3, we can observe evidently that $\langle R^2 \rangle/N$ decreases abruptly with Y_0 increasing. For example, for the case of $N = 17$ and $\varepsilon = -3$, the ratio of $\langle R^2 \rangle/N$ decreases from 13.6 to 5.53 in the region of $Y_0 = 0.0$–0.4, then it changes from 5.53 to 5.59 in the region of $Y_0 = 0.40$–0.53, and at last $\langle R^2 \rangle/N$ decreases from 5.59 to 1.17. In Fig. 2, we can also find that compact chains with $\varepsilon = -3$ are all adsorbed on the surface at the beginning of tensile elongation, and this leads to have a large characteristic ratio of $\langle R^2 \rangle/N$. When Y_0 increases, adsorbed compact chains move away from the attractive surface, the shape of adsorbed compact chains changes from a rod (all monomers are adsorbed on the attractive surface) to a sphere slowly and this leads $\langle R^2 \rangle/N$ to decrease. For weak attractive interaction, there are only few monomers of compact chains adsorbed on the attractive surface at the beginning of elongation, this leads to have a small value of $\langle R^2 \rangle/N$, and it decreases slowly during this process. For the case of $\varepsilon = 0$, the chain size of compact chains keeps unchangeable in the process of elongation.

We also measure the parallel and perpendicular mean square radii of gyration of adsorbed compact chains, which
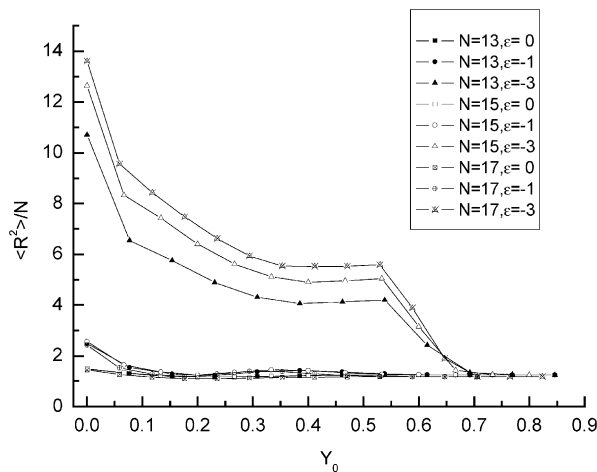

Fig. 2. Characteristic ratio $\langle R^2 \rangle/N$ as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε.

are defined as

$$\langle S^2 \rangle_x = \langle \frac{1}{N+1} \sum_{i=0}^{N} (x_i - x_{c.m.})^2 \rangle = \langle \frac{1}{N+1} \sum_{i=0}^{N} S_{xi}^2 \rangle \qquad (8)$$

$$\langle S^2 \rangle_y = \langle \frac{1}{N+1} \sum_{i=0}^{N} (y_i - y_{c.m.})^2 \rangle = \langle \frac{1}{N+1} \sum_{i=0}^{N} S_{yi}^2 \rangle \qquad (9)$$

here (x_i, y_i) are the coordinate of the i-th monomer in a chain and $(x_{c.m.}, y_{c.m.})$ is the position of the center of a chain. The angular brackets $\langle\rangle$ denote thermodynamic average, and S_{xi} and S_{yi} represent the distance from the i-th monomer to the center position along x- and y-axes, respectively. Fig. 3(a) shows mean-square radius of gyration per bond $\langle S^2 \rangle_x/N$ as a function of Y_0 for adsorbed chains with different chain length and different adsorption energy. When $\varepsilon = 0$ (without adsorption interaction), $\langle S^2 \rangle_x/N$ increases a little during this process. This result is important, and we can get some available information that the adsorbed compact chains without adsorption interaction will extend a little along the
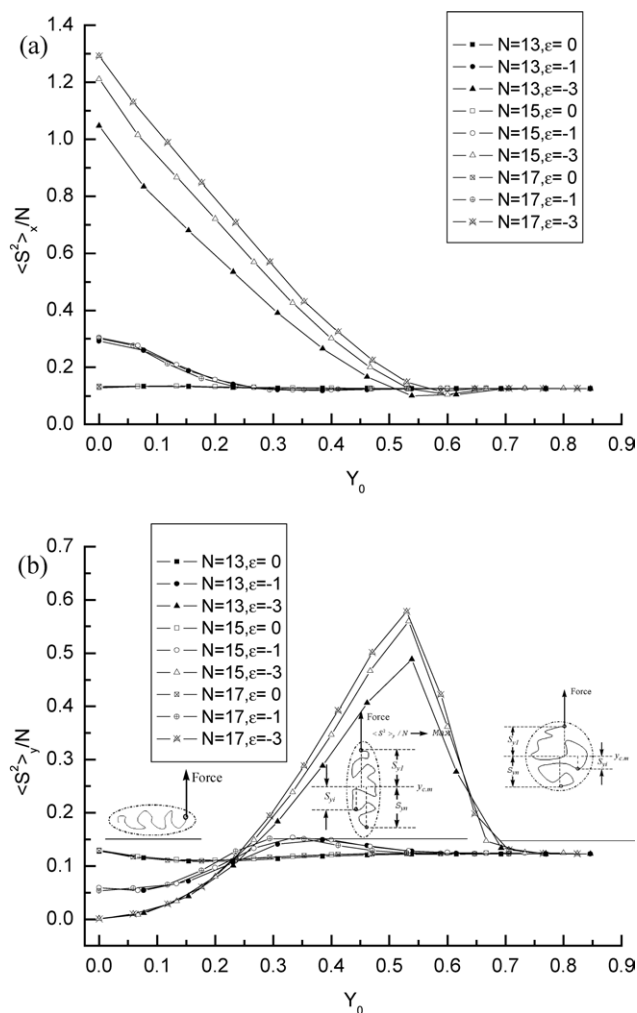

Fig. 3. Mean-square radii of gyration per bond $\langle S^2 \rangle_x/N$ (a) and $\langle S^2 \rangle_y/N$ (b) as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε.

adsorption surface. The data with rings and upper triangles represent the cases of $\varepsilon = -1$ and $\varepsilon = -3$, respectively, and $\langle S^2 \rangle_x/N$ all decreases with Y_0 increasing. This trend is more obvious for strong adsorption interaction. Mean-square radius of gyration $\langle S^2 \rangle_x/N$ as a function of Y_0 is also shown in Fig. 3(b). In Fig. 3(b), we can directly find that when $\varepsilon = 0$, the curves with square symbols decrease a little in the region of small Y_0. When adsorption energy becomes -1, or -3, the curves increase first and then decrease continuously until to the constant value. When $\varepsilon = -1$, the turning point of the curves falls in about $Y_0 = 0.32$, and then this point will move to $Y_0 = 0.53$ for strong adsorption interaction of $\varepsilon = -3$. At the beginning of tensile elongation, $\langle S^2 \rangle_y/N$ decreases with adsorption interaction energy increasing. In the middle of this process, $\langle S^2 \rangle_y/N$ increases with adsorption interaction energy increasing, and when Y_0 is greater than 0.7, $\langle S^2 \rangle_y/N$ are all the same for different adsorption interaction energy. The reason why there exists a maximum value for $\langle S^2 \rangle_y/N$ may be that at this point some monomers are still adsorbed on the attractive surface, and meanwhile other monomers are far away from the attractive surface. In Fig. 3(b), we add three illustrations for adsorbed chains with $\varepsilon = -3$ to express this tensile process. $\langle S^2 \rangle_y/N$ means the average distance of the monomers which leave the center of chains along the direction of y-axis. If this parameter has large value, this means that the monomers are far away from the line of $x = y_{c.m}$, and S_{yi} also have large values accordingly. At the beginning of the tensile elongation, as all the monomers are adsorbed on the attractive surface, the compact chains are horizontal and compressed, and S_{yi} are all close to zero (Fig. 3(b)), this leads to have a small value of $\langle S^2 \rangle_y/N$. In the middle of this process, some monomers are far away from the attractive surface, while the other monomers are still adsorbed on the surface, the compact chains will extend to be the longest one along y-axis and S_{yi} becomes large, therefore, the ratio of $\langle S^2 \rangle_y/N$ reaches to the maximum one (Fig. 3(b)). At the end of this process, as the adsorbed compact chains leave off the attractive surface and become general compact chains, so the value of $\langle S^2 \rangle_y/N$ is far smaller than the maximum one. If the adsorption interaction is weak, it is easy to pull the adsorbed compact chains away from the surface, so this leads the position of the peak to move the left. If there does not exist adsorption interaction, we do not overcome the adsorption interaction, therefore, there does not exist the maximum value for $\langle S^2 \rangle_y/N$.

In order to investigate the change of the shape of adsorbed compact chains in more detail, here we also consider the radius of gyration tensor S, which is defined as:

$$S = \frac{1}{N+1} \sum_{i=0}^{N} S_i S_i^T = \begin{pmatrix} S_{xx} & S_{xy} \\ S_{yx} & S_{yy} \end{pmatrix} \qquad (10)$$

Here $S_i = \text{col}(x_i, y_i)$ is the position of monomer i in a frame of reference with its origin at the center of a chain. The tensor S can be diagonalized to form a diagonal matrix with two eigenvalues L_1^2 and L_2^2 ($L_1^2 \leq L_2^2$). Solc and Stockmayer first

used these parameters in three-dimensional $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ to measure the shape of flexible polymer chains [55,56], and they estimated the ratio to be 1:2.7:11.7 based on a random walk of 100 bonds on a simple cubic lattice using Monte Carlo (MC) method. We also use this parameter to measure the shape and size of chains [47,48]. In Fig. 4, we plot the ratio of $\langle L_1^2 \rangle / \langle L_2^2 \rangle$ as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε. In general, the ratios all decrease with adsorption energy increasing. When $\varepsilon = 0$, the curves with square symbols all increase firstly, and then decrease a little. However, for the cases of $\varepsilon = -1$, and -3, the ratios all increase firstly, then decrease, and at last increase again. Furthermore, comparing with the case of $\varepsilon = 0$, we can find that this change is more evident, and the turning points also can be observed clearly. In Fig. 4, the ratio increases with Y_0 increasing firstly, and then decreases, at last increases again with Y_0 increasing. For $\varepsilon = -1$ it has a maximum value in the range of $Y_0 = 0.17$–0.24, and for $\varepsilon = -3$, it has a maximum one in the range of $Y_0 = 0.34$–0.38. Therefore, we can find that the changes of the shape and size of chains are more complicated during the tensile process, and we will use the following parameter to illuminate the process in detail.

Another parameter [57,58] of the shape of chains can be obtained by combining the reduced components to a single quantity that varies between 0 (sphere) and 1 (rod), and in our two-dimensional compact chain model we redefine the parameter as:

$$\langle \delta \rangle = 1 - 4 \langle \frac{L_1^2 L_2^2}{(L_1^2 + L_2^2)^2} \rangle \qquad (11)$$

$\langle \delta \rangle$ as a function of Y_0 for adsorbed chains with different chain length N and different adsorption energy ε is shown in Fig. 5. There are nine curves that can be divided into three kinds of curves in terms of different adsorption interaction energy. All the curves do not change monotonously. In general, all curves decrease firstly, and then increase, at last
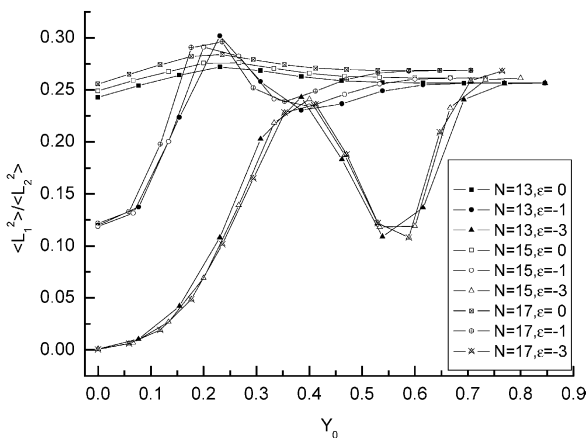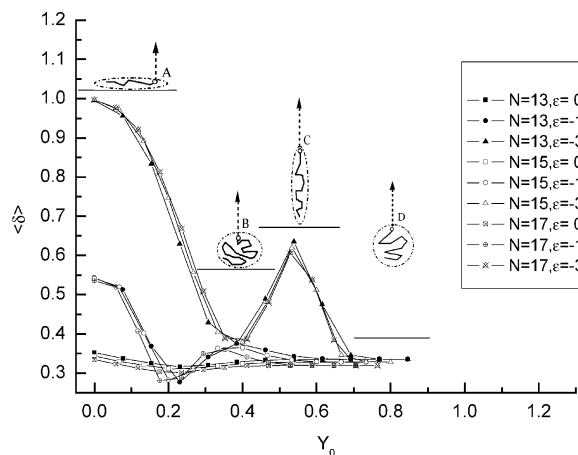

Fig. 5. $\langle \delta \rangle$ as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε.

decrease again. This change is more obvious for strong adsorption interaction. In the case of $\varepsilon = 0$, $\langle \delta \rangle$ is close to 0.34 at $Y_0 = 0.0$. As we all know that under this condition the shape of adsorbed compact chains will trend to be a sphere so that $\langle \delta \rangle$ should be equal to 0.0. However our result is greater than zero. The reason may be that in this paper the chains are restricted in a half of the two-dimensional space ($y \geq 0$) and they are not allowed to pass though the adsorption surface, i.e. x-axis. In the case of $\varepsilon = -1$, $\langle \delta \rangle$ without elongation ($Y_0 = 0$) becomes 0.54, and the reason is that there exists the effect of adsorption interaction, the chains are attracted by the surface, and it affects the shape of the compact chains deeply. However, if adsorption interaction energy becomes -3, we can find $\langle \delta \rangle$ is almost equal to 1 at $Y_0 = 0$. That is to say that the strong adsorption interaction can pull down the compact chains completely and leads the compact chain like a rod. Comparing three adsorption interaction energies in Fig. 5, we can directly get the available information of the shape change after the effect of different adsorption interaction during the process of tensile elongation. To illuminate the shape change visually, we add four sketch maps in Fig. 5 at four turning points of the curves, i.e. positions A, B, C, and D. On the other hand, we select the value of $\langle \delta \rangle$ with the adsorption interaction energy of $\varepsilon = -3$ and chain length $N = 17$ in Fig. 5, and then we discuss this process in detail. At the beginning of elongation (position A), the compact chain is all pulled down to the attractive surface and the shape of chain looks like a rod. Secondly, with Y_0 increasing (position B), the compact chain will extend and the shape trends to be a sphere. Thirdly, if Y_0 increases again (position C) and reaches to the critical point $Y_0 = 0.54$, the chain extend to be a rod shape along the direction of force and a little monomers are adsorbed on the attractive surface yet. Therefore, the value of $\langle \delta \rangle$ is close to 0.65 (Fig. 5). At last, the whole compact chains are all pulled away from the adsorption surface (position D), at this time there is not any effect of the adsorption on compact chains, and therefore the

Fig. 4. Ratio of $\langle L_1^2 \rangle / \langle L_2^2 \rangle$ as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε.

adsorbed compact chains become the general compact chains.

In order to investigate the reason why there exit those properties for adsorbed compact chains during the tensile elongation, we then calculate the fraction of adsorbed monomers f_a, which is defined as:

$$f_a = \frac{N_a}{N+1} \tag{12}$$

here N_a is the number of monomers absorbed on the surface (x-axis), and $N+1$ is the total number of monomers in a chain. In other words, f_a presents the percentage of adsorbed monomers on the horizontal layer of $y=0$, and the results are given in Fig. 6. The curves in Fig. 6 all decrease with Y_0 increasing and f_a increase with adsorption interaction energy increasing at the same value Y_0. For adsorbed compact chains without elongation ($Y_0=0$), f_a is equal to 0.17, 0.44, and 0.92 for $\varepsilon=0$, -1, and -3, respectively. In Fig. 6, we can find that most of compact chain monomers can be attracted by the adsorption surface with strong adsorption interaction, which are in agreement with above discussions.

Here we have used some available parameters to analyze the changes of the chain shape and size using different adsorption interaction during the process of tensile elongation. In general, we can get three conclusions: firstly, the behavior of the adsorbed compact chains without adsorption interaction is far different from the adsorbed compact chain with adsorption interaction during this process. Secondly, the adsorption interaction affects the shape and size deeply, especially for strong interaction. At last, in despite of different chain length and adsorption interaction energy, the chains will all trend to the stable states while the adsorbed compact chain is raised to some height, and the size and shape will also fix in one stable value.
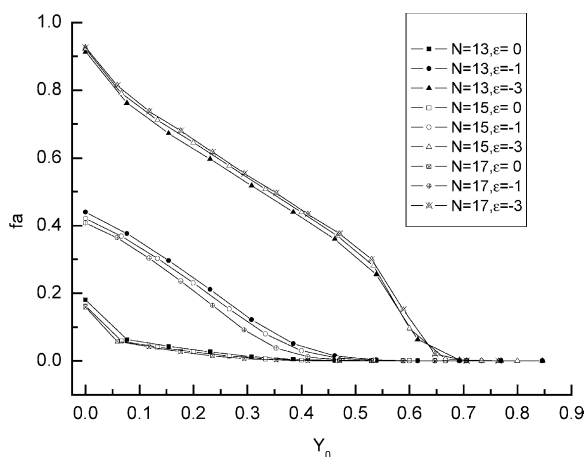
3.2. Thermodynamics properties

Firstly we investigate the average Helmholtz free energy per bond of adsorbed compact chains during the elongation process. The change of conformations leads to the change of thermodynamics properties for adsorbed compact chains in this process. In Fig. 7, we plot average Helmholtz free energy per bond as a function of Y_0 for adsorbed compact chains with different chain length and different adsorption energy. As we use Y_0 instead of Y to get rid of the effect of chain length, the difference between the curves with the same adsorption interaction energy is very small. We first consider the results of adsorbed compact chains without adsorption interaction, and the curves with square symbols in Fig. 7 decreases with Y_0 increasing. Comparing with the cases of $\varepsilon=-1$ and -3, we find that these curves are smooth. The behavior of $\varepsilon=-1$ or -3 is the contrary to $\varepsilon=0$. The average Helmholtz free energy per bond of adsorbed compact chains all increases with Y_0 increasing, especially for strong adsorption interaction. For example, the averages Helmholtz free energy changes from -3.0 to -1.12 for $\varepsilon=-3$, however, the averages Helmholtz free energy only changes from -1.16 to -1.05 for $\varepsilon=0$. This result can also illuminate the importance of adsorption interaction during the elongation process.

Then we plot the average energy per bond as a function of Y_0 for adsorbed compact chain with different chain length N and different adsorption energy ε in Fig. 8. The curves are consistent with the results in Fig. 7. Similarly, the curves for compact chains without adsorption interaction are almost the lines parallel to the x-axis, and there is only a little undulation. Under this condition there is only the contact energy exiting in the adsorbed compact chains, therefore, the average energy per bond changes a little during the elongation process. However, if adsorption interaction exists between the compact chains and the attractive surface, the average energy per bond of adsorbed compact chains will change greatly. At the beginning of the tensile
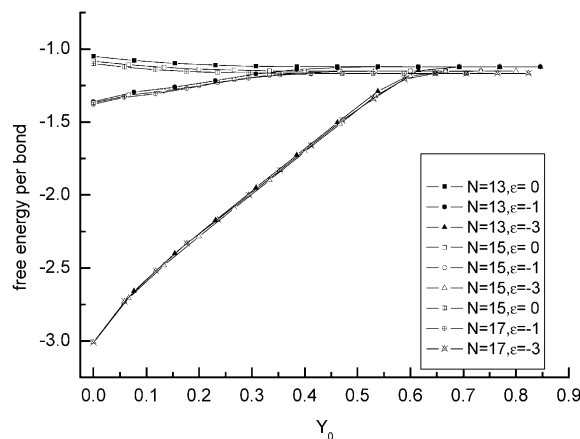

Fig. 6. Fraction of adsorbed segments f_a as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε.

Fig. 7. Helmholtz free energy per bond as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε.
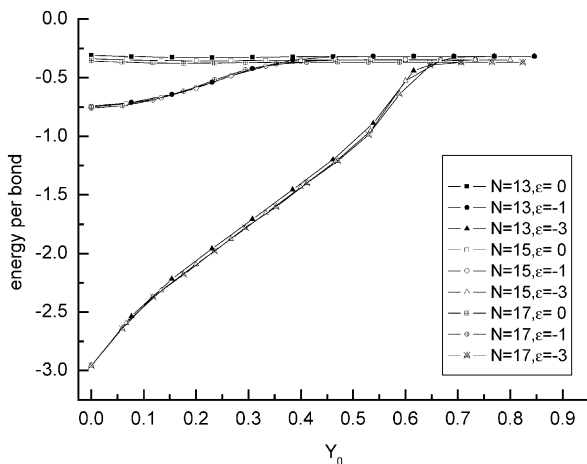
Fig. 8. Average energy per bond as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε.

process, the compact chain ends at low y-layer, therefore, there are more monomers adsorbed by the surface and the total attractive interaction energy will be large. When we raise the adsorbed compact chains again, the number of the adsorbed monomers will decrease, and the total attractive interaction will be weakened certainly. Otherwise, the change is more obvious with adsorption interaction energy increasing.

We also calculate the elastic force f according to Eq. (5), and the results are shown in Fig. 9. In Fig. 9, we can find that the curves of square symbols increase with Y_0 increasing for the case of $\varepsilon = 0$. However, in the cases of $\varepsilon = -1$ and -3, the curves will decrease firstly, then keep constant value, and at last decrease again with Y_0 increasing. This trend is obvious in the case of strong adsorption interaction energy ($\varepsilon = -3$). Those results agree well with those of Klushin [27,28], and experimental results of Hugel and Cui [43–45]. Their results are very similar to our results of $\varepsilon = -3$ in the range of $Y_0 > 0.20$, i.e. the force curve decreases firstly, and has a long plateau and then the force drops to zero [43–45]. The long plateau suggests that the
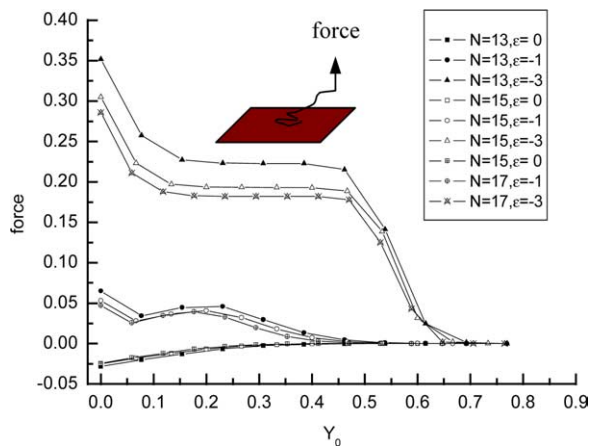
desorption process of polymer chains from the substrate is smooth and that it drops a flat conformation at the interface [44,45]. If the point of force acting is in the interior of adsorbed chain, the force curve may have several long plateaus [44,45]. If the point of force acting is at the end of adsorbed chain, there may exist a long plateau in force curve, see Fig. 9. Of course, if the adsorption interaction is weak, a long plateau in force curve cannot be observed. As we adopt the enumeration calculation, we can also investigate the size and shape in the process of elongation. However, it is very difficult to discuss this question in Klushin's theory. In our previous paper [49], we used another model to study the elastic behaviors of multi-chain systems, and there are adsorbed polymer materials. At the beginning of tensile elongation, there exist many conformations and their last monomers are fixed at positions Y_1, Y_2, …,Y_N, respectively. If a force F acts on this adsorbed polymer material and moves the distance r along the direction of force, the last monomers' positions would accordingly change to Y_1+r, Y_2+r,…, Y_N+r, respectively [49]. However, here we only focus on the elastic behavior of single compact chain and the force only acts on one single chain's end. Therefore, there exist some differences between these two models. In the meantime, another conclusion is that if there does not exist adsorption interaction, there need not any elastic force (i.e. $f < 0$, see the case of $\varepsilon = 0$). At last we calculate energy contribution to elastic force f_u according to the Eq. (6), and f_u as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε is shown in Fig. 10. For the case of $\varepsilon = 0$, f_u increases monotonously a little with Y_0 increasing. However, for the cases of $\varepsilon = -1$, f_u increases firstly and then decreases to the constant value with Y_0 increasing. There appears a peak near $Y_0 = 0.23$, which is consistent with Fig. 4. If the adsorption interaction energy becomes $\varepsilon = -3$, the peak moves right to about $Y_0 = 0.53$. Here we employ the parameter f_a (Fig. 6) with $N = 17$ and $\varepsilon = -3$ as the inset to describe this change. This slope of this curve means the speed of monomers leaving away from
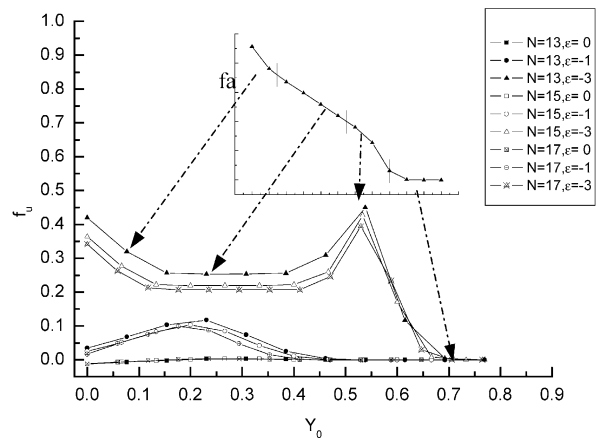

Fig. 9. Elastic force (f) as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε.

Fig. 10. f_u as a function of Y_0 for adsorbed compact chains with different chain length N and different adsorption energy ε.

the surface and there exist four phases according to the slope of this curve. This leads to have different values for f_u during this process. The reason why there exists different behavior of f_u for the cases of $\varepsilon = -1$ and -3 in Fig. 10 may be that there are contact interactions in compact chains, and the adsorption interaction of $\varepsilon = -1$ is equal to the contact interaction, however, the adsorption interaction of $\varepsilon = -3$ is larger than that of the contact interaction.

4. Conclusion

In this paper we perform the enumeration calculation method to study the elastic behavior of short two-dimensional compact chains absorbed on the attractive surface. We first investigate the changes of chain size and shape, such as mean-square end-to-end distance, mean-square radii of gyration, shape factors, and fraction of adsorbed monomers. Our aim is to illuminate how the size and shape of chains changes during the elongation process. Then we also study the thermodynamics properties of adsorbed compact chains. Different elastic behaviors are obtained for adsorbed compact chains. Elastic force decreases abruptly in the small region of elongation, and there exists a long plateau for strong adsorption interaction, which is agreement well with the theoretical and SMFS experiment ones.

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