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Simulation of the Critical Adsorption of Semi-Flexible Polymers *

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The critical adsorption of semi-flexible polymer chains on attractive surfaces is studied using Monte Carlo simulations. The results reveal that the critical adsorption point of a free polymer chain is the same as that of an end-grafted one. For the end-grafted polymer, we find that the finite-size scaling relation and the maximum fluctuation of adsorbed monomers are equivalent in estimating the critical adsorption point. The effect of chain stiffness on the critical adsorption is also investigated. The surface attraction strength for the critical adsorption of semi-flexible polymer chain decreases exponentially with an increase in the chain stiffness; In other words, lower adsorption energy is needed to adsorb a stiffer polymer chain. The result is explained from the viewpoint of the free energy profile for the adsorption.

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The adsorption of polymer chains onto attractive surfaces is a focused area in polymer science, as well as in biological systems. The adsorbed polymer can modify the property of surface and it plays important roles in many technological and biological applications.[1−4] The surface has a significant impact on the property of adsorbed polymers. For instance, the statistical size and diffusive behavior of adsorbed polymers are significantly changed.[5−9] Hence, the adsorption of polymers has received extensive study from experiments, theory and simulations.[4−14]

A single polymer chain near an attractive surface can exhibit a phase transition from a desorbed state to an adsorbed state when the attraction strength of the surface is beyond the critical adsorption point (CAP).[10] Many methods have been developed to estimate the CAP; for instance, the finite-size scaling approach, the behavior of mean square radius near the CAP, the heat capacity, and the maximum fluctuation of the surface contact number M.[6,7,10,11,15] A mathematical model widely used for studying polymer adsorption is the self-avoiding walk (SAW) chain interacting with an attracting surface. Every walk contacting with the surface is denoted as a surface contact with an interaction energy $-\varepsilon_{\rm PS}$. The surface contact number M serves as an order parameter. Near the CAP, the dependence of M on the polymer chain length N and surface attraction $\varepsilon_{\rm PS}$ were expressed using a finite-size scaling relation and the CAP was estimated.[15] Moreover, it was found that the fluctuation of M or the heat capacity reaches a maximum at CAP.[6,11]

In most of the previous studies, a flexible SAW polymer chain was usually adopted to study the adsorption of polymers.[11,14,15] However, in real biosystem, most polymers, such as double-strand DNA and proteins, are semi-flexible.[16] Because stiff polymers are ubiquitous and crucial, it is meaningful to consider the influence of the stiffness on the adsorption.[17−19] Molecular dynamics (MD) simulations on adsorption of a single end-grafted polymer chain found that stiffer chains can be adsorbed more easily; i.e., more monomers are adsorbed on surface at the same surface attraction strength.[20] Dynamic Monte Carlo (MC) simulation and pruned-enriched Rosenbluth method found that the critical adsorption transition temperature of end-grafted polymers increases with the chain stiffness.[18,21]

In this Letter, we study adsorption of semi-flexible polymer chains on attractive, flat surfaces using dynamic MC simulation. We compare the adsorption of a free polymer chain with that of an end-grafted one. The free polymer chain can diffuse randomly above the surface or adsorbed on the surface, whereas for the case of the end-grafted polymer chain, one end of the chain is grafted and unmovable on the surface. The flat surface is placed at $z = 0$. The simulation system is a cubic with size $L_{\rm s}$ in all the x, y and z directions. Periodic boundary conditions (PBC) are adopted in the x and y directions, while in the z direction we place a repulsive surface to prevent the polymer chain from leaving the system. To eliminate the size effect of the finite simulation size, $L_{\rm s}$ is set to be larger than the contour length of the polymer chain.

A coarse-grained bead-spring model is adopted to model the polymer chain. The polymer chain of length N is composed of N sequentially linked monomers. The monomers are modeled as spherical beads of diameter σ. The bond potential for bonds, pairwise repulsive potential between non-bonded monomers, and

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bending potential for adjacent bonds are taken into account.[22]

The bond potential is expressed by the finitely extensible nonlinear elastic (FENE) potential for two bonded monomers,

$$U_{\rm FENE}=\begin{cases} -\frac{k_{\rm F}}{2}(r_{\rm max}-r_{\rm eq})^2\ln\left[1-\left(\frac{r-r_{\rm eq}}{r_{\rm max}-r_{\rm eq}}\right)^2\right], \\ \qquad \text{for } 2r_{\rm eq}-r_{\rm max}<r<r_{\rm max}, \\ \infty, \ \text{otherwise}, \end{cases} \tag{1}$$

where $r_{\rm eq}$ is the equilibrium bond length, $r_{\rm max}$ is the maximum bond length, and $k_{\rm F}$ is the elastic coefficient. The pairwise repulsive potential between non-bonded monomers adopts the Weeks–Chandler–Andersen (WCA) model,

$$U_{\rm WCA}(r)=\begin{cases} \varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-2\left(\frac{\sigma}{r}\right)^{6}+1\right], & \text{for } r<\sigma, \\ 0, & \text{for } r\geqslant\sigma, \end{cases} \tag{2}$$

where ε is the WCA interaction strength. The bending potential used between adjacent bonds is

$$U_{\rm bend}=\frac{1}{2}k_\theta(\theta-\theta_0)^2, \tag{3}$$

where θ is the bond angle between two neighboring bonds, and k_θ is the bending rigidity. The energy minimum is set at $\theta_0=\pi$. The stiffness of the polymer chain is dependent on k_θ. The polymer is completely flexible at $k_\theta=0$, semi-flexible at finite k_θ, and rod-like at infinitely large k_θ.

The attractive surface at $z=0$ is assumed to be a thick surface. The polymer-surface interaction is described by the following integrated Lennard–Jones (LJ) potential[22]

$$U_{\rm LJ}(z)=\begin{cases} 2\pi\rho_{\rm s}\sigma^3\varepsilon_{\rm PS}\left[\frac{1}{90}\left(\frac{\sigma}{z}\right)^9-\frac{1}{6}\left(\frac{\sigma}{z}\right)^3\right]+{\rm U}_0, \\ \qquad \text{for } z<z_{\rm c}, \\ 0, \quad \text{for } z\geqslant z_{\rm c}, \end{cases} \tag{4}$$

where z is the distance between monomer and surface, and U_0 is used to shift the value of LJ potential to 0 at $z=z_{\rm c}$. In the simulation, the surface density $\rho_{\rm s}=1$ and the cut-off distance $z_{\rm c}=2.5\sigma$ are used. Here $\varepsilon_{\rm PS}$ is denoted as the polymer-surface interaction strength.

The dynamics of polymer chains can be achieved through small random move of monomers. We choose a monomer randomly and move it by a very small step in the x, y and z directions. All the small steps are random values within $(-0.15\sigma,\ 0.15\sigma)$. The acceptance of move is judged by the Metropolis algorithm; i.e., this trial move will be accepted with a probability $p=\min[1,\exp(-\Delta E/k_{\rm B}T)]$, where ΔE is the energy shift due to the trial move.

In the present work, $k_{\rm B}T=1$ and $\sigma=1$ are set as the units of energy and length, respectively, where $k_{\rm B}$ is the Boltzmann constant, and T is the temperature. Other parameters used in the work are the equilibrium bond length $r_{\rm eq}=0.8$, the maximum bond length $r_{\rm max}=1.3$, the elastic coefficient $k_{\rm F}=200$, and the WCA interaction strength $\varepsilon=1$. The variable parameters are the bending rigidity k_θ and the polymer-surface interaction strength $\varepsilon_{\rm PS}$. Our simulation results are averaged over 1000 independent samples and the statistical errors are small.

The state of a polymer chain is dependent on $\varepsilon_{\rm PS}$. The order parameter for the adsorption transition is the number of surface contacts M, which is defined as the number of monomers adsorbed on the surface. In our simulation, a monomer will be defined as an adsorbed monomer if the distance between the monomer and the surface is less than 1. Many previous studies have shown that the dependence of M on $\varepsilon_{\rm PS}$ and N can be expressed by a finite-size scaling relation[15]

$$\begin{aligned} M=N^{\varphi}[a_0+a_1(\varepsilon_{\rm PS}-\varepsilon^*_{\rm PS})N^{1/\delta} \\ +O((\varepsilon_{\rm PS}-\varepsilon^*_{\rm PS})^2N^{2/\delta})] \end{aligned} \tag{5}$$

when $\varepsilon_{\rm PS}$ is close to CAP $\varepsilon^*_{\rm PS}$ of an infinitely long chain. At $\varepsilon^*_{\rm PS}$ we have a power law relation[10]

$$M=a_0N^{\varphi}. \tag{6}$$

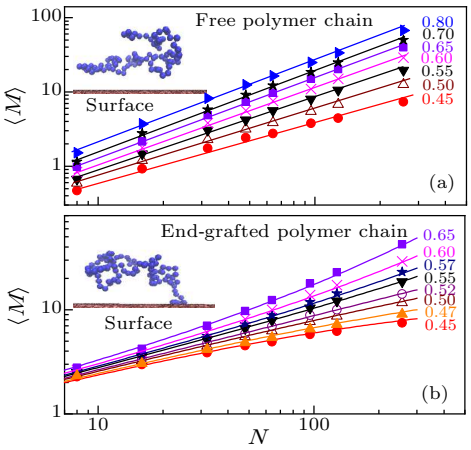

Fig. 1. The log-log plot of the number of surface contacts M versus chain length N at different polymer-surface attraction strengths $\varepsilon_{\rm PS}$ for flexible ($k_\theta=0$) free (a) and end-grafted (b) polymer chains. The straight lines in plot (a) are guides for the eyes. The curves in plot (b) are the fit of Eq. (5) with CAP $\varepsilon^*_{\rm PS}=0.52$, exponents $\varphi=0.52$ and $\delta=1.9$. The insets show the sketches of the free polymer chain and the end-grafted one in (a) and (b), respectively.

The dependence of M on N is plotted in Fig. 1 for the flexible ($k_\theta=0$) free and end-grafted polymer chains. It is interesting to see that all the curves are linear on the log-log plot for the free polymer chain (Fig. 1(a)). In other words, we are unable to estimate $\varepsilon^*_{\rm PS}$ from the finite-size scaling relation. For the free polymer chain, we find the power law relation $M\sim N^{\varphi}$ for all $\varepsilon_{\rm PS}$, while the exponent φ increases

with $\varepsilon_{\rm PS}$. For the end-grafted polymer, the dependence of M on N can be described by Eq. (5) as shown in Fig. 1(b). The CAP of the end-grafted flexible polymer chain is estimated as $\varepsilon^*_{\rm PS} = 0.52$. The exponents $\varphi = 0.52$ and $\delta = 1.9$ for the end-grafted flexible polymer chain are close to $\varphi = 0.54$ and $\delta = 1.78$ estimated for an end-grafted SAW lattice polymer chain.[15]

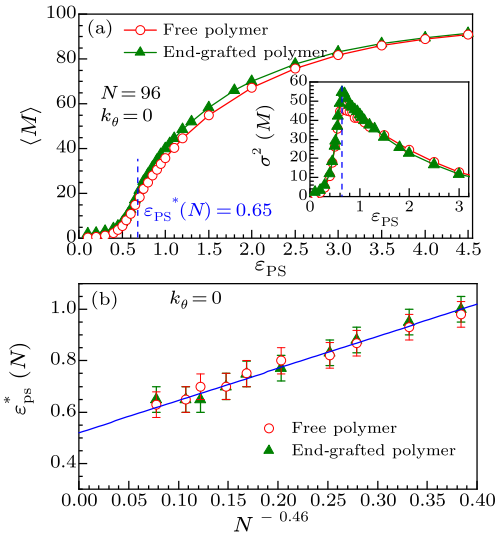

Fig. 2. (a) Plot of the mean surface contact number $\langle M \rangle$ as a function of $\varepsilon_{\rm PS}$ for free and end-grafted polymer models with bending rigidity $k_\theta = 0$. The inset shows its fluctuation as a function of $\varepsilon_{\rm PS}$. Here, polymer length is $N = 96$. (b) Plot of the critical adsorption point $\varepsilon^*_{\rm PS}(N)$ against $N^{-0.46}$ for the free and end-grafted polymer chains with bending rigidity $k_\theta = 0$.

The results of Fig. 1(a) show that it is unable to estimate CAP of the free polymer chain by the finite-size scaling law. We therefore use the maximum fluctuation of the order parameter to determine the CAP.[6,11] The fluctuation of the number M of surface contacts is calculated by

$$\sigma^2(M) = \langle M^2 \rangle - \langle M \rangle^2. \tag{7}$$

Figure 2(a) presents the dependence of M on the polymer-surface attraction strength, $\varepsilon_{\rm PS}$, for the free and end-grafted polymer chains with polymer length $N = 96$. The behavior of M is similar for both the polymer chains. Here $\langle M \rangle$ is roughly 0 at small $\varepsilon_{\rm PS}$. It increases steeply with $\varepsilon_{\rm PS}$ in the mediate $\varepsilon_{\rm PS}$ region, and at last it approaches the value of the polymer length N at large $\varepsilon_{\rm PS}$. The change of $\langle M \rangle$ from 0 to a large value indicates that the polymer chain exhibits a phase transition from a desorbed state to an adsorbed state. At the phase transition point the fluctuation is largest because of continuous adsorption and desorption.[23] The inset of Fig. 2(a) presents the fluctuation of M; i.e., $\sigma^2(M)$, for both the polymer chains. We find the behavior of $\sigma^2(M)$ is roughly the same for both the polymer chains. It is interesting to find that the positions of the peak of $\sigma^2(M)$ are also roughly the same for both the free and end-grafted polymer chains. The value of CAP, $\varepsilon^*_{\rm PS}(N)$, is estimated to be 0.65 ± 0.05 for both the polymer chains of $N = 96$. Here the error bar 0.05 is the minimum interaction step used in the simulation.

Using the maximum fluctuation method, $\varepsilon^*_{\rm PS}(N)$ is estimated for different polymer lengths N. We find that $\varepsilon^*_{\rm PS}(N)$ is roughly the same for both the free and end-grafted polymers. As shown in Fig. 2(b), $\varepsilon^*_{\rm PS}(N)$ decreases with increasing N and the dependence of $\varepsilon^*_{\rm PS}(N)$ on N can be roughly expressed as $\varepsilon^*_{\rm PS}(N) = 0.52 + 1.25N^{-0.46}$ for the flexible polymer at $k_\theta = 0$. We obtain $\varepsilon^*_{\rm PS} = 0.52$ for the infinitely long polymer $N \to \infty$, in agreement with that estimated for the end-grafted polymer chain using the finite scaling relation, as presented in Fig. 1(b).

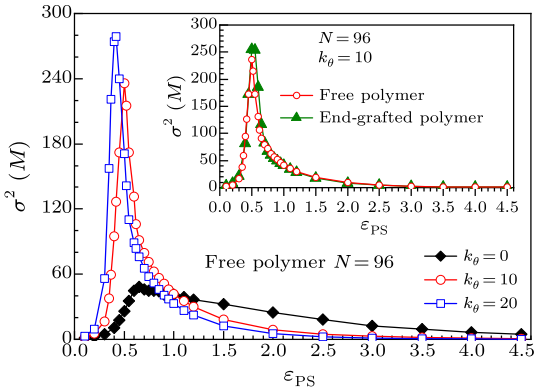

Fig. 3. The dependence of the fluctuation of the contact number, $\sigma^2(M)$, on the polymer-surface attraction $\varepsilon_{\rm PS}$ for the free polymer of length $N = 96$ with different bending rigidities $k_\theta = 0$, 10 and 20. The inset presents $\sigma^2(M)$ of free polymer and end-grafted polymer at $k_\theta = 10$.

The influence of bending rigidity on the CAP is further studied. Figure 3 presents the dependence of $\sigma^2(M)$ on $\varepsilon_{\rm PS}$ for the free polymer of different bending rigidities. We find the peak shifts to small $\varepsilon_{\rm PS}$ with increasing k_θ, representing that the CAP becomes smaller with increasing k_θ, meaning that it is easy to adsorb a stiff polymer.[18,21] The inset of Fig. 3 compares the peak position of the free polymer with that of the end-grafted polymer at $k_\theta = 10$. This shows that both the polymer chains have roughly the same $\varepsilon^*_{\rm PS}$. Thus we can conclude that, for the same rigidity ($k_\theta = 0$ or > 0), both the free and end-grafted polymers have the same CAP.

Using the maximum fluctuation of M, the values of $\varepsilon^*_{\rm PS}(N)$ are estimated for both the free and end-grafted polymers with different k_θ. The phase diagram of desorbed/adsorbed polymer against $\varepsilon_{\rm PS}$ and k_θ is presented in Fig. 4 for the polymer of length $N = 96$. We find that the phase boundary is roughly the same for both the polymer chains. It is also shown that the value of $\varepsilon^*_{\rm PS}(N)$ is reduced as k_θ increases. This is consistent with the conclusion obtained for the adsorption

of end-grafted polymers using the MD simulation and the pruned-enriched Rosenbluth method.[18,21] Therefore, we can conclude that the stiffer the polymer chain is, the smaller the $\varepsilon^*_{\rm PS}$ will be. In other words, for the same adsorbing surface, the adsorption of a stiff polymer chain takes place at higher temperature than a flexible one.

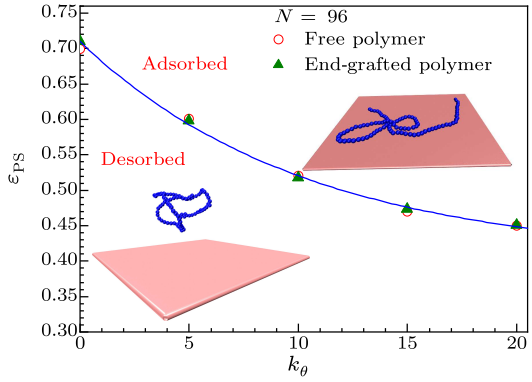

Fig. 4. Phase diagram of desorbed/adsorbed polymer against the polymer-surface attraction $\varepsilon_{\rm PS}$ and the bending rigidity k_θ for the polymer of length $N = 96$. The phase boundary can be expressed approximately as $\varepsilon^*_{\rm PS} = \varepsilon^*_{PS,\infty} + \Delta\varepsilon \exp(-k_\theta/k^*_\theta)$. The insets show the snapshots of desorbed and adsorbed free polymer chain.

The dependence of $\varepsilon^*_{\rm PS}$ on k_θ for both the free and end-grafted polymers can be expressed approximately as

$$\varepsilon^*_{\rm PS} = \varepsilon^*_{\rm PS,\infty} + \Delta\varepsilon \exp(-k_\theta/k^*_\theta). \tag{8}$$

We find $\varepsilon^*_{\rm PS,\infty} = 0.405$, which refers to the critical adsorption point of a rod-like polymer ($k_\theta \to \infty$) for $N = 96$. Here $\Delta\varepsilon$ is the critical adsorption strength difference between the flexible polymer and the rod-like polymer, and k^*_θ may be the separation point that separates a flexible polymer at small k_θ from a stiff one at large k_θ. The physical meaning of k^*_θ deserves further study. For the polymer of length $N = 96$, $k^*_\theta = 10.3$ is estimated.

This dependence of $\varepsilon^*_{\rm PS}$ on k_θ can be understood through the free energy of the system. The free energy can be expressed as $F = U - TS$ with U being the energy and S the entropy. As the intra-polymer interaction is repulsive, U is mainly referred to the polymer-surface attraction energy. Compared to that of desorbed polymer, both U and S are decreased when the polymer is contacted with the surface. The gain of adsorption energy ΔU and the loss of conformational entropy ΔS are dependent on $\varepsilon_{\rm PS}$; i.e., $\Delta F = \Delta U - T\Delta S$ is dependent on $\varepsilon_{\rm PS}$.

The adsorption energy difference ΔU can be calculated in the simulation. The dependence of ΔU on $\varepsilon_{\rm PS}$ is sketched in Fig. 5 for both the completely flexible polymer chain ($k_\theta = 0$) and the semi-flexible polymer chain ($k_\theta > 0$). Our simulation shows that the surface attraction energy for the semi-flexible polymer chain is larger than that of the completely flexible polymer chain; i.e., ΔU of the semi-flexible polymer chain lies lower. Because the conformational number or conformational entropy of the completely flexible polymer chain is larger than that of the semi-flexible one, the entropic term $T\Delta S$ of the completely flexible polymer chain is then also larger; i.e., $T\Delta S$ of the completely flexible polymer chain lies lower. The loss of conformational entropy, $T\Delta S$, is also presented in Fig. 5 for both the chains.

It is well known that, at CAP, the free energy F of the adsorbed polymer is equal to that of the desorbed polymer; i.e., the loss of conformational entropy $T\Delta S$ due to the adsorption is compensated for by the gain of adsorption energy ΔU.[24,25] Then it is obvious to see that $\varepsilon^*_{\rm PS}$ decreases with increasing k_θ. This is consistent with our simulation results. In other words, the stiff polymer needs less adsorption energy to compensate for the loss of conformational entropy as the entropy of the stiff polymer chain is lower.

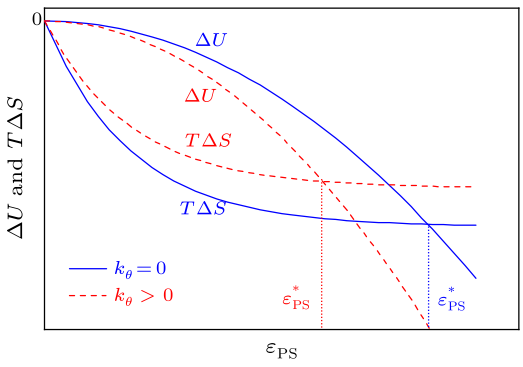

Fig. 5. Sketch of dependence of the adsorption energy difference ΔU and the loss of entropy $T\Delta S$ on the polymer-surface attraction $\varepsilon_{\rm PS}$.

The stiffness of a semi-flexible polymer chain is usually described by the persistence length $L_{\rm p}$. We have checked the relationship between $L_{\rm p}$ and k_θ for the present polymer model. Here $L_{\rm p}$ is calculated based on the following equation[26]

$$\boldsymbol{R} \cdot \boldsymbol{b}_1/b_1 = L_{\rm p}[1 - \exp(-L/L_{\rm p})], \tag{9}$$

with $\boldsymbol{R} \cdot \boldsymbol{b}_1/b_1$ the projection of the end-to-end vector $\boldsymbol{R}$ on the first bond vector $\boldsymbol{b}_1$, and $L = (N-1)b$ the contour length. The mean bond length $b \approx 0.826\sigma$ is close to $r_{\rm eq}$ in Eq. (1). The value of b is roughly independent of k_θ, indicating that it is mainly controlled by the FENE potential. We find that $L_{\rm p}$ is roughly the same as that calculated from the tangent-tangent correlation function $\langle \boldsymbol{b}_i \cdot \boldsymbol{b}_{i+s} \rangle = b^2 \exp(-sb/L_{\rm p})$. The dependence of $L_{\rm p}$ on k_θ is plotted in Fig. 6, where $L_{\rm p}$ increases linearly with k_θ for the present polymer chain model, and the dependence of $L_{\rm p}$ on k_θ can be expressed approximately as

$$L_{\rm p} = b \cdot k_\theta/k_{\rm B}T. \tag{10}$$

Such a linear relation between $L_{\rm p}$ and k_θ is consistent with the prediction for DNA chains.[27]

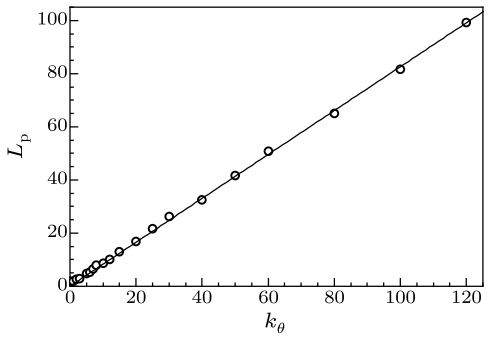

Fig. 6. Plot of the persistence length $L_{\rm p}$ versus the bending rigidity k_θ. The straight line is Eq. (10) with $k_{\rm B}T = 1$.

In summary, the critical adsorption of a semi-flexible polymer on attractive homogeneous surface has been studied by the MC method. The critical adsorption point $\varepsilon^*_{\rm PS}$ is determined from the maximum fluctuation of adsorbed monomers for both the free and the end-grafted polymer chains. The results reveal that $\varepsilon^*_{\rm PS}$ is the same for both the systems. We find that $\varepsilon^*_{\rm PS}$ decreases with the increasing bending rigidity k_θ. In other words, less attractive energy is needed to adsorb a stiffer polymer. This result is explained from the free energy profile of different k_θ. The main reason is that a stiffer polymer chain has less conformational entropy.

References

[1] Milner S T 1991 *Science* **251** 905
[2] Besteman K, Lee J O, Wiertz F G M, Heering H A and Dekker C 2003 *Nano Lett.* **3** 727
[3] Zhou Z and Hartmann M 2013 *Chem. Soc. Rev.* **42** 3894
[4] Duan X, Zhang R, Ding M, Huang Q, Xu W S, Shi T and An L 2017 *Polymer* **122** 125
[5] Chang C M, Lau Y G, Tsai J C and Juan W T 2012 *Europhys. Lett.* **99** 48008
[6] Li Y W, Wüst T and Landau D P 2013 *Phys. Rev. E* **87** 012706
[7] Descas R, Sommer J and Blumen A 2004 *J. Chem. Phys.* **120** 8831
[8] Yang Q H, Wu F, Wang Q and Luo M B 2016 *J. Polym. Sci. Part. B: Polym. Phys.* **54** 2359
[9] Zhou J, Zhang Z, Lan Y, Zhao Y, Lei F, Li H, Li P, Xu H and Huang Q 2017 *Polymer* **132** 235
[10] Eisenriegler E, Kremer K and Binder K 1982 *J. Chem. Phys.* **77** 6296
[11] Sumithra K, Brandau M and Straube E 2009 *J. Chem. Phys.* **130** 234901
[12] Tian W D and Ma Y Q 2013 *Chem. Soc. Rev.* **42** 705
[13] Polotsky A A, Leermakers F A M and Birshtein T M 2015 *Macromolecules* **48** 2263
[14] Ziebarth J D, Gardiner A A, Wang Y M, Jeong Y, Ahn J, Jin Y and Chang T 2016 *Macromolecules* **49** 8780
[15] Luo M B 2008 *J. Chem. Phys.* **128** 044912
[16] Kowalczyk S W, Hall A R and Dekker C 2010 *Nano Lett.* **10** 324
[17] Stepanow S 2001 *J. Chem. Phys.* **115** 1565
[18] Hsu H P and Binder K 2013 *Macromolecules* **46** 2496
[19] He L, Dong Z and Zhang L 2016 *J. Polym. Sci. Part. B: Polym. Phys.* **54** 1829
[20] Kramarenko E Y, Winkler R G, Khalatur P G, Khokhlov A R and Reineker P 1996 *J. Chem. Phys.* **104** 4806
[21] Sintes T, Sumithra K and Straube E 2001 *Macromolecules* **34** 1352
[22] Yang X, Yang Q H, Fu Y, Wu F, Huang J H and Luo M B 2019 *Polymer* **172** 83
[23] Li H, Gong B, Qian C J and Luo M B 2015 *Soft Matter* **11** 3222
[24] Guttman C M, Di Marzio E A and Douglas J F 1996 *Macromolecules* **29** 5723
[25] Gong Y and Wang Y M 2002 *Macromolecules* **35** 7492
[26] Wu F, Fu Y, Yang X, Sun L Z and Luo M B 2019 *J. Polym. Sci. Part B: Polym. Phys.* **57** 912
[27] Geggier S and Vologodskii A 2010 *Proc. Natl. Acad. Sci. USA* **107** 15421