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Polymer desorption under pulling: A dichotomic phase transition

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The structural properties and phase behavior of a self-avoiding polymer chain on an adhesive substrate, subject to pulling at the chain end, are described by means of a grand canonical ensemble approach. We derive analytical expressions for the probability distributions of the basic structural units of an adsorbed polymer, such as loops, trains, and tails, in terms of the adhesive potential ϵ and applied pulling force f. In contrast to conventional, $f=0$, polymer adsorption, the chain detachment transition under pulling turns out to be of first (rather than second) order, albeit it is *dichotomic*, i.e., no coexistence of different phase states exists. Also, the hitherto controversial value of the critical adsorption exponent ϕ is found to depend essentially on the degree of interaction between different loops so that $0.34 \leq \phi \leq 0.59$. The theoretical predictions are verified by means of extensive Monte Carlo simulations.

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The manipulation of single polymer chains has turned recently into an important method for understanding their mechanical properties and characterization of the intermolecular interactions [1,2], triggered essentially by the progress in atomic force microscopy (AFM) [3] and by the development of optical and magnetic tweezer techniques [4]. This rapid development has been followed by theoretical considerations, based on the mean-field approximation [5], which provide important insight into the mechanism of polymer detachment from adhesive surfaces under an external pulling force. A comprehensive study by Skvortsov *et al.* [6] examines the case of a Gaussian polymer chain. We also note here the close analogy between the forced detachment of an adsorbed chain and the unzipping of a double-stranded DNA molecule. Recently, DNA denaturation and unzipping have been treated by Kafri *et al.* [7] using the grand canonical ensemble (GCE) approach [8,9] as well as Duplantier's analysis of polymer networks of arbitrary topology [10]. An important result concerning the properties of adsorbed macromolecules under pulling turns out to be the observation [7] that the universal exponents (which govern polymer statistics) undergo renormalization due to excluded volume effects, leading thus to a change of the order of the DNA melting transition from second to first order. In this work we use similar methods to describe the structure and detachment of a single chain from a sticky substrate when the chain end is pulled by an external force.

Starting with conventional (i.e., force-free) adsorption, we recall that an adsorbed chain is build up from loops, trains, and a free tail. One can treat these basic structural units statistically by means of the GCE approach [8,9] where the lengths of the buildings blocks are not fixed but may rather fluctuate. The GCE partition function is then given by

$$\Xi(z) = \sum_{N=0}^{\infty} \Xi_N z^N = \frac{V_0(z)Q(z)}{1 - V(z)U(z)}, \tag{1}$$

where z is the fugacity and $U(z)$, $V(z)$, and $Q(z)$ denote the GCE partition functions of loops, trains, and tails, respectively. The building block adjacent to the tethered chain end is allowed for by $V_0(z)=1+V(z)$. The partition function of the loops is defined as $U(z)=\Sigma_{n=1}^{\infty}(\mu_3 z)^n/n^{\alpha}$, where μ_3 is the three-dimensional connective constant and α is the exponent that governs surface loop statistics. It is well known that for an *isolated* loop $\alpha=1-\gamma_{11}\approx 1.39$ [11]. We will argue below that α changes value due to the excluded volume interaction between a loop and the rest of the chain. The train GCE partition function reads $V(z)=\Sigma_{n=1}^{\infty}(\mu_3 wz)^n/n^{1-\gamma_{d=2}}$, whereby one assumes that each adsorbed segment gains an additional statistical weight $w=\exp(\epsilon)$ with the dimensionless adsorption energy $\epsilon=\varepsilon/k_BT$. Finally, the GCE partition function for the chain tail is defined by $Q(z)=1+\Sigma_{n=1}^{\infty}(\mu_3 z)^n/n^{\beta}$. For an isolated tail $\beta=1-\gamma_1\approx 0.32$ [11], but again the excluded volume interactions of a tail with the rest of the chain increase the value of β. Using the *generating function* method [12], Ξ_N is obtained as $\Xi_N=(z^*)^{-N}$ where the pole z^* is given by the condition $V(z^*)U(z^*)=1$ so that the free energy is $F=k_BTN\ln z^*$ and the fraction of adsorbed monomers $n=-\partial \ln z^*/\partial \ln w$. In terms of the so called *polylog function*, which is defined as $\Phi(\alpha,z)=\Sigma_{n=1}^{\infty}z^n/n^{\alpha}$ [13], the equation for z^* reads ($\gamma_{d=2}=1.343$ [11])

$$\Phi(\alpha,\mu_3 z^*)\Phi(1-\gamma_{d=2},\mu_2 w z^*) = 1. \tag{2}$$

A nontrivial solution for z^* in terms of w (or the adsorption energy ϵ) appears at the *critical adsorption point* (CAP) $w=w_c$ where w_c is determined from $\zeta(\alpha)\Phi(1-\gamma_{d=2}, \mu_2 w_c/\mu_3)=1$ and $\zeta(\alpha)$ is the Riemann function. In the vicinity of the CAP the solution attains the form

$$z^*(w) \approx [1 - A(w-w_c)^{1/(\alpha-1)}]\mu_3^{-1}, \tag{3}$$

where A is a constant. Then the average fraction of adsorbed monomers is $n \propto (\epsilon-\epsilon_c)^{1/(\alpha-1)-1}$. A comparison with the well-known scaling relationship $n \propto (\epsilon-\epsilon_c)^{1/\phi-1}$ where ϕ is the so-called *adsorption* (or *crossover*) *exponent* [11] suggests that

$$\phi = \alpha - 1. \tag{4}$$

This result, derived first by Birshtein [9], is of principal importance. It shows that the exponent ϕ, which describes polymer adsorption at criticality, is determined by α, which governs the polymer loop statistics. If loops are treated as isolated objects, then $\alpha=1-\gamma_{11}\approx 1.39$ so that $\phi=0.39$. In contrast, excluded volume interactions between a loop and the rest of the chain lead to an increase of α and ϕ, as shown below.

From the expression for $U(z)$, given above, and Eq. (3), we have $P_{\text{loop}}\approx(\mu_3 z^*)^l/l^{1+\phi}\approx\exp[-c_1(\epsilon-\epsilon_c)^{1/\phi}]/l^{1+\phi}$. This is valid only for $\epsilon>\epsilon_c$ since a solution for Eq. (2) for subcritical values of the adhesive potential ϵ does not exist. Nontheless, even in the subcritical region, $\epsilon<\epsilon_c$, there are still monomers that occasionally touch the substrate, creating thus single loops at the expense of the tail length. The partition function of such a loop-tail configuration is $Z_{l-t}=(\mu_3^l/l^{1+\phi})\mu_3^{N-l}/(N-l)^\beta$. On the other hand, the partition function of a tail conformation with no loops whatsoever (i.e., of a nonadsorbed tethered chain) is $Z_t=\mu_3^N N^{\gamma_1-1}$. Thus the probability $P^<_{\text{loop}}(l)$ to find a loop of length l next to a tail of length $N-l$ can be estimated as $P^<_{\text{loop}}(l)=Z_{l-t}/Z_t \propto N^{1-\gamma_1}/l^{1+\phi}(N-l)^\beta$ at $\epsilon<\epsilon_c$. In the vicinity of the CAP, $\epsilon\approx\epsilon_c$, the distribution will be given by an interpolation between the expressions above. Hence, the overall loop distribution becomes

$$P_{\text{loop}}(l)=\begin{cases}\dfrac{1}{l^{1+\phi}}\exp[-c_1(\epsilon-\epsilon_c)^{1/\phi}l], & \epsilon>\epsilon_c,\\[2mm] \dfrac{A_1}{l^{1+\phi}}+\dfrac{A_2N^{1-\gamma_1}}{l^{1+\phi}(N-l)^\beta}, & \epsilon=\epsilon_c,\\[2mm] \dfrac{N^{1-\gamma_1}}{l^{1+\phi}(N-l)^\beta}, & \epsilon<\epsilon_c.\end{cases}\tag{5}$$

The same reasoning for a tail leads to the distribution

$$P_{\text{tail}}(l)=\begin{cases}\dfrac{1}{l^{\beta}}\exp[-c_1(\epsilon-\epsilon_c)^{1/\phi}l], & \epsilon>\epsilon_c,\\[2mm] \dfrac{B_1}{l^{\beta}}+\dfrac{B_2N^{1-\gamma_1}}{l^{\beta}(N-l)^{1+\phi}}, & \epsilon=\epsilon_c,\\[2mm] \dfrac{N^{1-\gamma_1}}{l^{\beta}(N-l)^{1+\phi}}, & \epsilon<\epsilon_c.\end{cases}\tag{6}$$

In Eqs. (5) and (6), A_1, A_2, B_1, and B_2 are constants. Close to the CAP, these distributions are expected to attain a U-shaped form (with two maxima at $l=1$ and $l\approx N$), as predicted for a Gaussian chain by Gorbunov *et al.* [14]. For the average loop length L the GCE partition function for loops yields $L=z\partial U(z)/\partial z|_{z=z^*}=\Phi(\alpha-1,\mu_3 z^*)/\Phi(\alpha,\mu_3 z^*)$. At the CAP, L diverges as $L\propto 1/(\epsilon-\epsilon_c)^{1/\phi-1}$. The average tail length S is obtained as $S=z\partial Q(z)/\partial z|_{z=z^*}=\Phi(\beta-1,\mu_3 z^*)/[1+\Phi(\beta,\mu_3 z^*)]$. Again, using the polylog function, one can show that at ϵ_c the average tail length diverges as $S\propto 1/(\epsilon-\epsilon_c)^{1/\phi}$.

Consider the number of configurations of a tethered chain in the vicinity of the CAP as an array of loops which end up with a tail. Using the approach of Kafri *et al.* [7] along with Duplantier's [10] graph theory of polymer networks, one may write the partition function Z for a chain with $\mathcal{N}$ building blocks: $\mathcal{N}-1$ loops and a tail. Consider a loop of length M while the length of the rest of the chain is K, that is, $M+K=N$. In the limit of $M\gg 1$, $K\gg 1$ (but with $M/K\ll 1$), one can show [15] that $Z\sim\mu_3^M M^{\gamma^s_{\mathcal{N}}-\gamma^s_{\mathcal{N}-1}}\mu_3^K K^{\gamma^s_{\mathcal{N}-1}-1}$ where the surface exponent $\gamma^s_{\mathcal{N}}=2-\mathcal{N}(\nu+1)+\sigma_1+\sigma_1^s$ and σ_1 and σ_1^s are critical bulk and surface exponents [10]. The last result indicates that the effective loop exponent α becomes

$$\alpha=\gamma^s_{\mathcal{N}-1}-\gamma^s_{\mathcal{N}}=\nu+1.\tag{7}$$

Thus, $\phi=\alpha-1=\nu=0.588$, in agreement with earlier Monte Carlo findings [16]. One should emphasize, however, that the foregoing derivation is mean-field-like (Z appears as a product of loop and rest-of-the-chain contributions), which overestimates the interactions and increases significantly the value of α, serving as an upper bound. The value of α, therefore, is found to satisfy the inequality $1-\gamma_{11}\leqslant\alpha\leqslant 1+\nu$, i.e., it depends on loop interactions, $0.39\leqslant\phi\leqslant 0.59$.

Using the GCE approach, we treat now the case of self-avoiding polymer chain adsorption in the presence of a pulling force, thus extending the consideration of Gaussian chains by Gorbunov *et al.* [17]. Under a pulling force f, the tail GCE partition function $Q(z)$ in Eq. (1) has to be replaced by $\tilde{Q}(z)=1+\Sigma_{n=1}^{\infty}[(\mu_3 z)^n/n^\beta]\int d^3r\,P_n(\mathbf{r})\exp(fr_\perp/T)$ where $P_n(\mathbf{r})$ is the end-to-end distance distribution function for a self-avoiding chain [18]. After some straightforward calculations, $\tilde{Q}(z)$ can be written as

$$\tilde{Q}(z)=1+a_1\tilde{f}^\theta\Phi(\psi,z\mu_3\exp(a_2\tilde{f}^{1/\nu})).\tag{8}$$

Here the dimensionless force $\tilde{f}=fa/k_BT$, and the exponents $\psi=1-\nu$ and $\theta=(2+t-3\delta/2)/(\delta-1)$ with $t=(\beta-3/2+3\nu)/(1-\nu)$ and $\delta=1/(1-\nu)$. The function $\tilde{Q}(z)$ has a branch point at $z^\#=\mu_3^{-1}\exp(-a_2\tilde{f}^{1/\nu})$, i.e., $\tilde{Q}(z)\sim 1/(z^\#-z)^{1-\psi}$. One may, therefore, conclude that the total GCE partition function $\Xi(z)$ has two singularities on the real axis: the pole z^*, and the branch point $z^\#$. It is known (see, e.g., Sec. 2.4.3. in [12]) that for $N\gg 1$ the main contributions to Ξ_N come from the pole and the branch singular points, i.e.,

$$\Xi_N\sim C_1(z^*)^{-N}+\frac{C_2}{\Gamma(1-\psi)}N^{-\psi}(z^\#)^{-N}.\tag{9}$$

Thus, for large N, only the smallest of these points matters. On the other hand, z^* depends on the dimensionless adsorption energy ϵ only [i.e., on $w=\exp(\epsilon)$] whereas $z^\#$ is controlled by the external force $\tilde{f}$. Therefore, in terms of the two *control parameters* ϵ and $\tilde{f}$, the equation $z^*(\epsilon)=z^\#(\tilde{f})$ defines the critical transition line between the adsorbed phase and the force-induced desorbed phase. In the following this line will be called the *detachment line* (DL). Below it, $f<f_D$, or above it, $f>f_D$, either z^* or $z^\#$, respectively, contributes to Ξ_N. The control parameters ϵ_D and $\tilde{f}_D$ that satisfy this equation denote the detachment energy and detachment force, respectively. On the DL the system undergoes a first-order phase transition. The DL itself terminates for $\tilde{f}_D\to 0$ in the CAP, ϵ_c, where the transition becomes of second order. In the vicinity of the CAP the detachment force $\tilde{f}_D$ vanishes as $\tilde{f}_D\sim(\epsilon-\epsilon_c)^{\nu/\phi}$. This first-order adsorption-desorption phase transition under pulling has a clear dichotomic nature (i.e., it follows an "either-or" scenario): in the thermodynamic limit $N\to\infty$ there is no phase coexistence. The configurations are

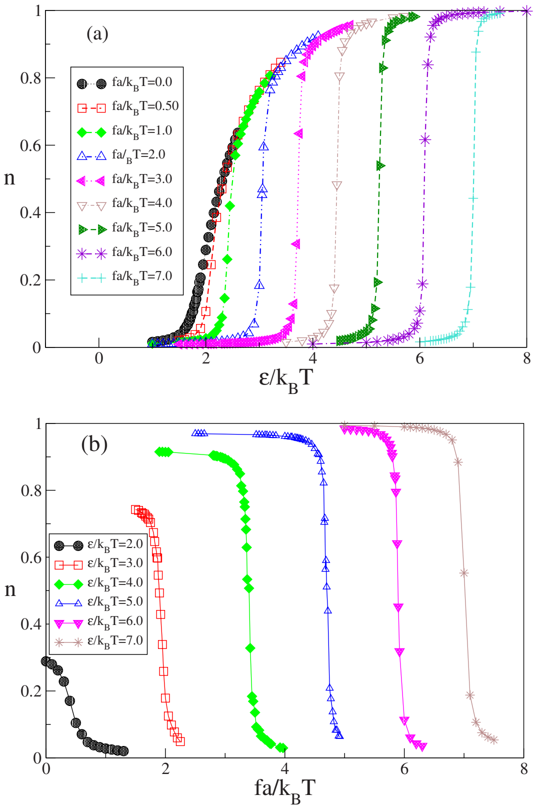

FIG. 1. (Color online) (a) Order parameter n against the surface potential ϵ for various pulling forces. The chain has length $N=128$. (b) n vs f for several surface potentials ϵ.

divided into adsorbed and desorbed dichotomic classes. Metastable states are completely absent. Moreover, the mean loop length L remains finite upon crossing the DL. In contrast, the average tail length S diverges close to the DL. Indeed, at $\tilde{f}<\tilde{f}_D$ the average tail length is given by $S=\tilde{f}^{\theta}\Phi(\psi-1,z^*(w)/z^{\#}(\tilde{f}))/[1+a_1\Phi(\psi,z^*(w)/z^{\#}(\tilde{f}))]$. At the DL, $z^*=z^{\#}$, it diverges as $S\propto\tilde{f}_D/(\tilde{f}_D-\tilde{f})$.

Recently, it has been realized [19] that the DL, when represented in terms of dimensional variables, force f_D versus temperature T, goes (at a relatively low temperature) through a maximum, i.e., the desorption transition shows reentrant behavior. Such behavior was predicted earlier [20–22] in a different context, namely, of DNA unzipping, and also in the coil-hairpin transition [23]. Below we demonstrate that this result follows directly from our theory. Indeed, the solution of Eq. (2) at large values of ϵ (or at low temperature) can be written as $z^*\approx \mathrm{e}^{-\epsilon}/\mu_3$ so that the DL, $z^*=z^{\#}$, in terms of dimensionless parameters is monotonic, $\tilde{f}_D\propto[\epsilon_D-\ln(\mu_3/\mu_2)]^{\nu}$. Note, however, that the same DL, if represented in terms of the dimensional control parameters, force f_D versus temperature T_D (with a fixed dimensional energy ε_0), shows a nonmonotonic behavior $f_D=T_D[\varepsilon_0/T_D-\ln(\mu_3/\mu_2)]^{\nu}/a$, as found earlier for DNA unzipping [20]. This curve has a maximum at a temperature given by $T_D^{\max}=(1-\nu)\varepsilon_0/\ln(\mu_3/\mu_2)$. At very low T, however, the expression for $P_n(\mathbf{r})$ [18] predicts divergent chain deformation [20], i.e., it becomes unphysical. One can readily show that in this case the correct behavior is given by $fa=\varepsilon_0+T\ln(\mu_3/\mu_2)$.

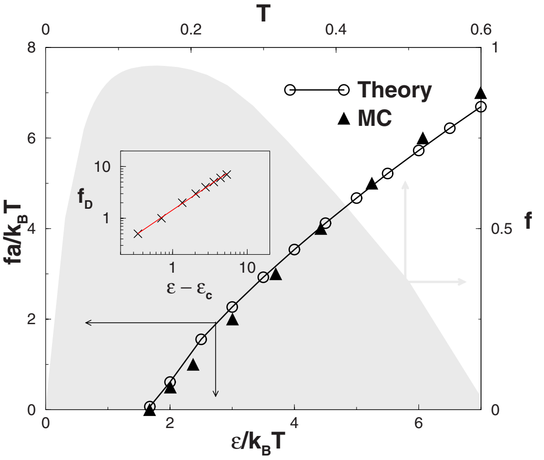

FIG. 2. (Color online) Critical detachment force $f_D=fa/k_BT$ against the surface potential ε/k_BT. Full and empty symbols denote MC and theoretical results. A double logarithmic plot of f_D against $\epsilon-\epsilon_c$ with $\epsilon_c=1.67$ is shown in the inset, yielding a slope of 0.97 ± 0.02, in agreement with the prediction $f_D\propto(\epsilon-\epsilon_c)^{\nu/\phi}$. The shaded area shows the same phase diagram as derived by numeric solution of Eq. (2); in dimensional f (right axis) against T (top axis) units this appears *reentrant*.

We have investigated the force-induced desorption of a polymer by means of extensive Monte Carlo (MC) simulations using a coarse-grained off-lattice bead-spring model [24] of a polymer. Figure 1(a) shows the variation of the order parameter n (average fraction of adsorbed monomers) with changing adhesive potential ϵ at fixed pulling force, whereas Fig. 1(b) depicts n vs force fa/T for various ϵ. The abrupt change of the order parameter is in close agreement with our theoretical prediction. Using the values of f_D and ϵ_D at the DL in the thermodynamic limit $N\rightarrow\infty$, one can construct an adsorption-desorption phase diagram for a polymer chain under pulling, Fig. 2, which is among the central results of this work. The detachment lines obtained from MC data and the numerical representation of $z^*=z^{\#}$ almost coincide, and the slope of f_D vs $(\epsilon-\epsilon_c)$ is close to unity, according to the prediction $f_D\propto(\epsilon-\epsilon_c)^{\nu/\phi}$. Also indicated by the shaded area in Fig. 2 is the reentrant image of the same phase diagram, obtained when the numerical solution of Eq. (2) is plotted in dimensional units of f versus T. In Fig. 3(a) we show the probability distribution function of tail lengths at different strengths of adsorption in the absence of pulling. This confirms the U shape of $P(s)$ predicted by Eq. (6). While for $s\rightarrow1$ the agreement with Eq. (6) is perfect, for $s\rightarrow N$ the long tails are slightly overestimated by Eq. (6). This small discrepancy reflects the dominance of our single loop and tail approximation—multiple loops would effectively reduce the tail size. Figure 3(b) shows the divergency of S close to the critical point ϵ_c. For a chain of finite length N, the tail length divergence at $\epsilon\rightarrow\epsilon_c$ is replaced by a rounding into a plateau since $S\rightarrow N$ but away from ϵ_c the measured slope extrapolates to the theoretical prediction $S\propto1/(\epsilon-\epsilon_c)^{1/\phi}$. In the presence of a pulling force one observes a remarkable feature of the order parameter probability distribution—the absence of two peaks in the vicinity of the critical strength of adsorption, $\epsilon_D\approx6.095\pm0.03$, which still

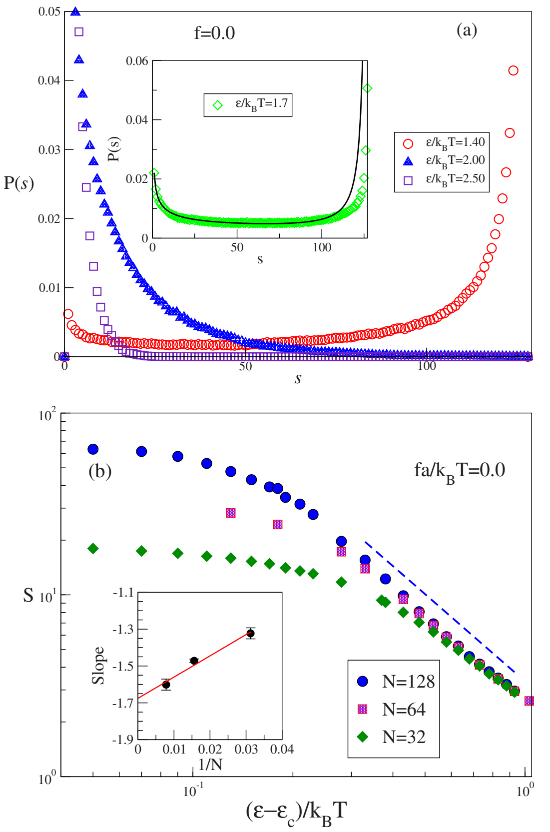

FIG. 3. (Color online) (a) Tail length distribution $P(s)$ for different surface potentials close to ϵ_c in a polymer of length $N=128$ with no pulling force. In the inset $P(s)$ at $\epsilon=\epsilon_c$ (symbols) is compared to the prediction Eq. (6) (full line). (b) Average tail length S against $(\epsilon-\epsilon_c)/k_BT$ plotted for various chain lengths in log-log coordinates. In the inset the slopes of these curves extrapolate for $1/N\to 0$ to $1/\phi$ (thermodynamic limit).

keeps the polymer adsorbed at pulling force $fa/k_BT=6.0$ (Fig. 4). At ϵ_D the distribution $H(n)$ is flat, indicating huge fluctuations so that *any* value of n is equally probable. Close to ϵ_D, one observes a clear maximum in $H(n)$, indicating a desorbed chain with $n\approx 0.01$ for $\epsilon=6.05$, or a completely adsorbed chain with $n\approx 0.99$ for $\epsilon=6.15$. This lack of bimodality in $H(n)$ manifests the dichotomic nature of the desorption transition, which rules out phase coexistence.

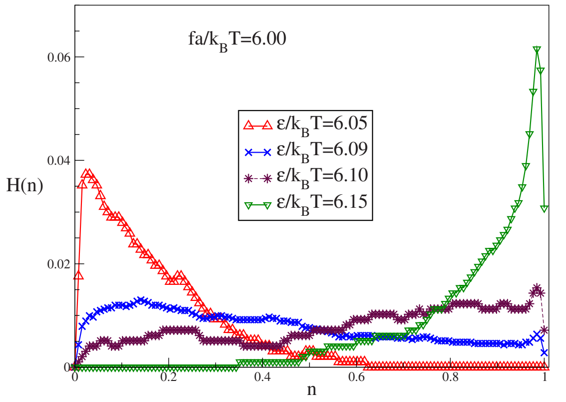

FIG. 4. (Color online) Order parameter distribution for pulling force $fa/k_BT=6.0$ and different adhesion strengths ϵ/k_BT. Here $N=128$ and the threshold value of the surface potential for this force is $\epsilon_D\approx 6.095\pm 0.03$. The values $\epsilon/k_BT=6.09$ and 6.10 are on each side of the DL.

In conclusion, we have shown that the force-induced desorption of a self-avoiding polymer chain can be properly described by means of the GCE approach, yielding the average size and probability distribution functions of all basic structural units as well as their variation with changing force or strength of adhesion. The detachment transition is proved to be of first order, albeit dichotomic in nature, thus ruling out phase coexistence. The critical line of desorption, while monotonic when plotted in dimensionless units of detachment force against surface potential, becomes reentrant in units of force against temperature. In addition, we show that the crossover exponent ϕ governing polymer behavior at criticality depends essentially on interactions between different loops so that $0.39\leqslant\phi\leqslant 0.59$. All these predictions appear in good agreement with our MC simulation results.

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