Stretch transition in a polymer brush

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The behavior of a grafted chain of length K inside an otherwise monodispersed (of length N) polymer brush is investigated. For the case of $K \leq N$, the stretching of the chain increases abruptly as K approaches N, analogous to the coil-stretch transition. By generalizing previous results, we derive the scaling forms for the stretching parameter and its mean square fluctuations. We also extend our investigation to the $K > N$ regime and obtain results for the stretching parameter by scaling calculations. We show that the chain is maximally stretched as $K \to N$ from above. Furthermore, we perform a Monte Carlo simulation using the bond-fluctuation model to study the chain end position and its fluctuations. Our data indicate that both the stretching of the chain and its fluctuation are maximal at $K = N$ and the system exhibits a first-order phase transition. The scaling form for the stretching parameter is verified and the scaling function is obtained.

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I. INTRODUCTION

Polymer chains with one end grafted on a surface have drawn a lot of research interest in recent years (see Refs. [1–3] for a review) because of their numerous application in technologies. Furthermore, such grafted polymer layers are of great theoretical and experimental interests since the stretched configurations of these chains give rise to very unique physical properties. Recently, Klushin and Skvortsov [4] proposed that the grafted polymer layer can be viewed as a critical system in the following sense. Imagine a shorter grafted chain (of length K) inside an otherwise monodispersed polymer brush (of chain length N). The fluctuation of this short chain increases and diverges (proportional to N) as its chain length approaches N from below and the system becomes critical. Such a behavior is reminiscent of some kind of "resonance" effect in which the amplitude of fluctuation grows when the chain is at the "resonant length." Since the theory involved the use of the self-consistent field (SCF) theory, a mean-field approximation, which may not quantitatively describe the system accurately, it is important to have an independent investigation that involves either few or no assumptions. In this situation, computer simulation would be a very desirable method. Furthermore, if the system is truly a critical system, then one expects the system to become critical when the chain length $K \to N$ from *above* also. However, previous studies [4,5] did not include the $K > N$ situation because SCF theory does not give an accurate description for the behavior of a longer chain inside a brush of length $N < K$. Hence it would be desirable to extend the study to the $N < K$ case and obtain results by other means, namely, computer simulations and scaling calculations. Indeed our results indicate that the transition is first order instead of second order, contrary to the results suggested previously in Ref. [4].

In this paper, we investigate a polymer brush with one chain of a different length in a good solvent and characterize its scaling behavior. Previous results by Klushin and Skvortsov [4] for a shorter chain in a brush are generalized to obtain the crossover scaling forms for the finite chain lengths. We also extend the study to the regime for a longer chain in a brush and obtain results for the chain end position using simple scaling calculations. We perform a Monte Carlo simulation, using the bond-fluctuation model, to check upon our proposed scaling forms and the SCF values of the exponents. The simulation study is of interest because conventional analytical SCF methods [6,7] often ignore fluctuation effects which may be qualitatively important in the critical properties. Also these effects can be probed easily in a simulation. This study should provide some fundamental understanding for the fluctuation effects in the grafted polymer layers and also useful information about the dynamical response of the system.

II. TRANSITION BEHAVIOR AND SCALING FORMS

The system we have in mind is a grafted polymer brush composed of monodispersed chains each with N monomers and one end fixed on some impenetrable plane (the x-y plane); the z position of the ith monomer along the chain is labeled by z_i. The grafting density σ is understood to take values that ensure that the system is in the brush regime. It has been shown using the scaling [8] and SCF theory [4,9] and also confirmed by Monte Carlo simulations [8,9] that the chain end fluctuations in a monodispersed grafted polymer layer are anomalously high with $\langle \delta z_N \rangle \sim N$ as compared to the Gaussian-type fluctuations ($\sim N^{1/2}$). By observing the fact that large fluctuations are often associated with a system near second-order phase transitions, Klushin and Skvortsov [4] showed that the chain behavior in a grafted brush corresponds to the vicinity of a coil-stretch transition [10]. We shall briefly go through their arguments here for the sake of completeness. According to SCF

theory [6,7], each monomer is subjected to a parabolic self-consistent potential

$$U(z) = \text{const} - \frac{\pi^2}{8a^2N^2}z^2 \tag{1}$$

for $0 \leq z \leq h$, where h is the brush height and a is the monomer size. This parabolic potential leads to a force in the direction of $+z$, which tends to elongate the chain. Thus the system is in analog with a free-draining chain in an extensional flow [11,12] which is well known to undergo a coil-stretch transition as the flow rate changes. The point is that the critical flow rate for an ideal chain is exactly equal [4] to the factor $\frac{\pi^2}{8a^2N^2}$ in Eq. (1). They also showed that, using SCF theory, a Landau-type free energy for the shorter chain can be written down and at $K = N$, each chain in the brush is exactly at the coil-stretch second-order transition point and thus leads to the strong chain end fluctuations. However, this is in major disagreement with the results of Ref. [11] (using transfer-matrix method), which indicated that the chain under an external parabolic stretching potential undergoes a *first-order* phase transition instead of a second-order transition [4]. One of the purposes of our present work is to attempt to clarify the above discrepancy using Monte Carlo simulations.

A. Short chain behavior in a brush

This transition behavior can better be observed if a single shorter chain of length K is placed inside an otherwise monodispersed brush of length N. The short chain can be considered to be under the action of an external potential given by Eq. (1) and by increasing the length of the shorter chain, the transition can be monitored as $K \to N$. To describe the transition behavior, we follow Ref. [4] and introduce

$$\lambda \equiv 1 - K/N \tag{2}$$

as the tuning parameter for the deviation from the transition point and

$$\eta \equiv \langle z_K \rangle / K \tag{3}$$

for the parameter of chain stretching, which is the order parameter for the phase transition. The mean square deviation of the chain end is denoted by $\langle \delta z_K^2 \rangle$.

Using SCF theory, it was shown that [4] $\langle z_K \rangle$ and $\langle \delta z_K^2 \rangle$ increase dramatically according to the power laws $\langle z_K \rangle \sim \langle \delta z_K^2 \rangle^{1/2} \sim K^{-1/2}\lambda^{-1/2}$ for $1/(N\sigma^{2/3}) \ll \lambda \ll 1$. Corrections to the mean-field behavior may change the values of the exponents and in general one can write down the scaling of the end position of the K chain as

$$\langle z_K \rangle \sim K^{\beta}\lambda^{-\delta} \tag{4}$$

for some exponents β and δ. However, at $\lambda = 0$ ($K = N$ is a true monodispersed brush), $\langle z_K \rangle$ is limited by the brush height and is proportional to K [6–9]. Hence we propose the scaling of η to be of the form

$$\langle \eta \rangle \equiv \frac{\langle z_K \rangle}{K} = f(\lambda^{\frac{\delta}{1-\beta}}K), \tag{5}$$

where $f(x)$ is some scaling function with $f(x) \sim x^{-(1-\beta)}$ for $x \gg 1$.

Similarly, the power law growth of the mean square fluctuation can be written in the form

$$\langle \delta z_K^2 \rangle \sim K^{\alpha}\lambda^{-\gamma} \tag{6}$$

for some exponent α and γ. However, a true divergence of $\langle \delta z_K^2 \rangle$ will not occur since at $\lambda = 0$ ($K = N$) the fluctuation is limited by the brush height. It has been shown both from Monte Carlo simulations [8] and SCF results [9] that $\langle \delta z_K^2 \rangle \propto K^2$ for a monodispersed brush of length K. Thus the fluctuation of the shorter chain can be described in terms of the scaling form

$$\langle \delta\eta^2 \rangle \equiv \frac{\langle \delta z_K^2 \rangle}{K^2} = g(\lambda^{\frac{\gamma}{2-\alpha}}K), \tag{7}$$

where $g(x)$ is some scaling function with $g(x) \sim x^{-(2-\alpha)}$ for $x \gg 1$. Mean-field (SCF) theory predicts the values of these exponents to be [4]

$$\alpha = \gamma = 1, \beta = \delta = \frac{1}{2}. \tag{8}$$

B. The case with $K > N$ ($\lambda < 0$)

In this case, the K chain is longer and one expects that it would assume a "mushroom" configuration [13]. The SCF result will not work in this case since the portion of the K chain above the brush is not stretched. However, one can use a simple scaling calculation to obtain the qualitative behavior of chain stretching as a function of λ as follows. One can picture the mushroomlike K chain consisting of a stretched portion inside the brush and the number of monomers in this portion is very close to N; the rest of the $K - N$ monomers form the head of the mushroom and stay above the brush. Thus the average end position of the K chain can be written as a sum of the heights of these two portions

$$\langle z_K \rangle \simeq a\sigma^{1/3}N + a(K - N)^{\nu}, \tag{9}$$

where a is the monomer size, σ is the surface coverage, and $\nu \simeq 0.59$ is the usual self-avoiding walk exponent. The first term in (9) is the chain length of a monodispersed brush [6–8] and the second term is the dimension of a chain of length $K - N$ in a good solvent. The relative weights of the two terms in (9) may differ by a factor of order unity in reality, but for simplicity they are taken to be the same. In terms of the parameter of chain stretching as defined in (3) and with $\lambda = -|\lambda|$, Eq. (9) can be rewritten as

$$\langle \eta \rangle \simeq \frac{a}{1 + |\lambda|}\left(\sigma^{1/3} + \frac{|\lambda|^{\nu}}{N^{1-\nu}}\right). \tag{10}$$

For $\lambda = 0$ Eq. (10) reduces to the well-known result of a monodispersed brush $\langle \eta \rangle \simeq a\sigma^{1/3}$. It is obvious that $\langle \eta \rangle \to 0$ for $\lambda \to -\infty$ and it is easy to verify that Eq. (10) for $\langle \eta \rangle$ has a single maximum at

$$\lambda_{\max} \simeq -\left(\nu\sigma^{-1/3}\right)^{\frac{1}{1-\nu}}/N \qquad (11)$$

for $N \gg 1$. Thus in the limit of long chain lengths (both K and N are large), $\langle\eta\rangle$ has a peak at $\lambda = 0$ and the chain is stretched maximally at $K = N$. Hence, using simple scaling calculations, we show that the K chain is maximally stretched as $\lambda \to 0-$, which is compatible with the SCF result in the limit $\lambda \to 0+$. Unfortunately, the calculation for $\langle \delta z_K^2 \rangle$ does not follow in a similar way since the fluctuations due to the stretched portion and the rest of the mushroom portion are strongly correlated and cannot be simply added up. These scaling predictions and the values of the exponents from SCF results will be tested in next section by Monte Carlo simulations.

III. SIMULATION DETAILS

The bond-fluctuation model [14] for a macromolecular chain is used in the simulations. Previous simulations using this model [8,13,15,16] have been very successful in exploring the physical behavior of the grafted polymer layers. In the bond-fluctuation model, we consider a box of linear dimensions $L \times L \times M$, where one surface of size $L \times L$ (in the x-y plane) is chosen as a grafting surface and the other $L \times L$ surface at a large distance M apart never restricts the configurations of the grafted chains. We choose the periodic boundary conditions in the x and y directions, while the two other boundaries in the z direction (at $z = 1$ and $z = M$, respectively) are treated as hard impenetrable walls. For the dimensions of the box, we choose $L = 32$ and $M = 3N + 1$. The grafting density is fixed to be 0.093 75, at which the system is well in the brush regime from our previous experience of the system [8]. The anchoring site of the chains in the monodispersed brush are randomly chosen, but strictly self-avoiding grafting at the wall. We simply grow the chains linearly from their anchoring sites in the $+z$ direction as the starting configurations. These linearly stretched chains are then relaxed with the bond-fluctuation algorithm for a long time. Typically, the equilibrium time was chosen many times larger than the characteristic relaxation time of the system of monodisperse grafted polymers [8]. Measurement are then taken for another extended period of Monte Carlo time. Since we are interested in the behavior of a chain of length K in a brush of length N and in general $K \neq N$, the statistics on the K chain is relatively low and extensive Monte Carlo runs are required to accumulate reasonable statistics. We studied brushes with $N = 20$–60 and with a K-chain length up to 120. The cases with $K > N$ are also investigated in addition to the $K < N$ situations. In order to ensure that the results are genuine and not accidental due to statistical fluctuations of the grafting positions, several (typically 5–10) different realizations of grafting sites are simulated and the results are averaged. The end positions of the K chains and their fluctuations are then measured.

IV. SIMULATION RESULTS AND DISCUSSIONS

The simulation results for the parameters of chain stretching as defined in (3) as a function of λ are shown

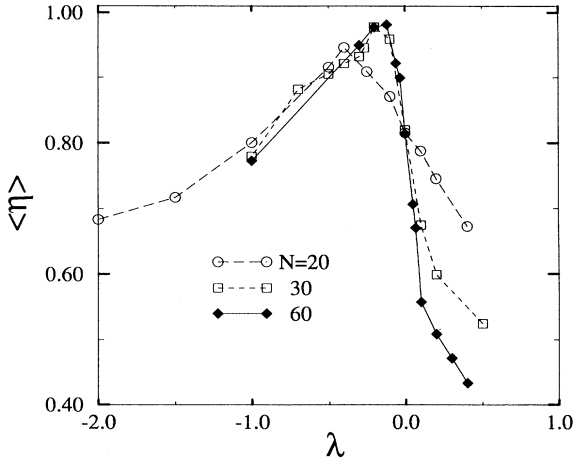

FIG. 1. The parameter of chain stretching $\langle\eta\rangle$ plotted vs λ.

in Fig. 1 in the range of both $K > N$ and $K \leq N$. $\langle\eta\rangle$ shows a peak near $\lambda = 0$, which agrees with the theoretical consideration in Sec. II. Furthermore, the peak occurs at some negative values of $\lambda_{\max}$ for finite N, as predicted in Eq. (11). We also verified that $|\lambda_{\max}|$ decreases as N increases. In Fig. 2 we plot $-\lambda_{\max}$ vs $1/N$; the data fall on a straight line within error bars consistent with the scaling result $\lambda_{\max} \sim 1/N$ in Eq. (11). Also revealed in Fig. 2 is the fact that the transition as $\lambda \to 0+$ gets sharper as the brush length N increases. In the long chain limit ($N \to \infty$), the order parameter $\langle\eta\rangle$ becomes discontinuous, indicating that the phase transition is first order. Furthermore, no hysteresis is observed in our data. The behavior of the order parameter is drawn schematically for $N \to \infty$ in Fig. 3. The $\lambda \leq 0$ behavior in Fig. 3 is easily obtained from Eq. (10), namely, $\langle\eta\rangle \sim 1/(1 + |\lambda|)$. Thus our scaling analysis and Monte Carlo data indicate

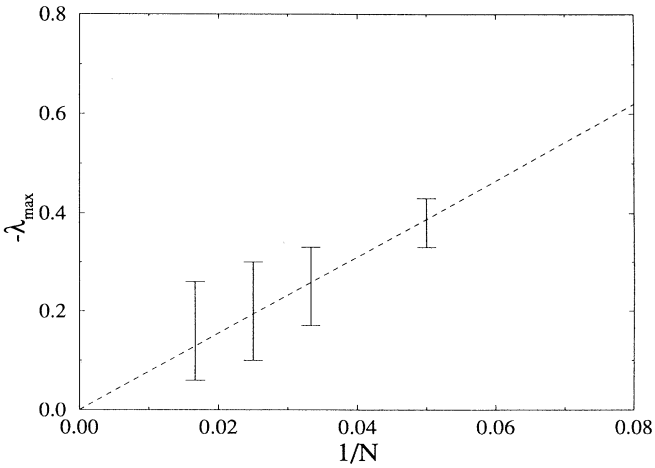

FIG. 2. $-\lambda_{\max}$ versus $1/N$ as suggested in Eq. (11). The straight line is just a guide for the eye.

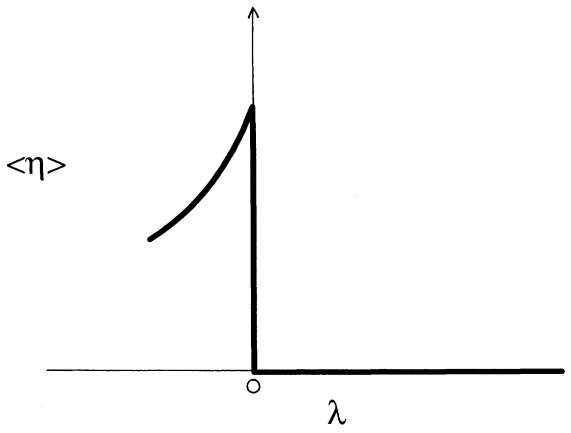

FIG. 3. Qualitative behavior of $\langle\eta\rangle$ as a function of λ in the long chain $N \to \infty$ limit.

that the stretch transition at $\lambda = 0$ is first order, contrary to Ref. [4], which suggested a second-order phase transition. Our result should be compared to the coil-stretch transition of an ideal polymer in an external field in Ref. [11], which also exhibits a first-order transition. A quadratic external potential acting on an end-grafted polymer chain was considered in Ref. [11] and the stretching parameter showed a step function rise to the stretched state as the strength of potential increases. The absence of hysteresis was also found in the transfer-matrix calculations in Ref. [11]. However, there is a slight difference in our case: after the system jumps to the stretched state, the stretching parameter $\langle\eta\rangle$ decreases gradually upon further changing the tuning parameter λ in the $\lambda < 0$ regime. This phenomenon can be easily understood as follows: in the $\lambda < 0$ regime (the K chain is longer), as λ decreases the mushroom portion of the chain increases and hence the whole chain is effectively less stretched. Figure 4 shows the fluctuation $\langle\delta\eta^2\rangle$ versus λ; it peaks around $\lambda = 0$ showing that the fluctuation is maximal at $K = N$, in agreement with the theoretical predictions from the SCF theory. Also shown in the figure is that the peak in $\langle\delta\eta^2\rangle$ becomes sharper as N increases, but the peak value stays constant. This shows that the chain end fluctuation of the K chain is anomalously large at the transition point with $\langle\delta z_K^2\rangle \propto K^2$.

To test for the scaling prediction in Eq. (5), Fig. 5 is a scaling plot with the SCF exponents $\beta = \delta = \frac{1}{2}$ for different values of N. The data fall roughly onto a master curve for $\lambda \geq 0$. However, for $\lambda < 0$, since the SCF theory does not work in this case, we do not expect the data to scale and indeed the data do not collapse in this regime. Unfortunately, the fluctuations $\langle(\delta z_K)^2\rangle$ are very strong near the $\lambda = 0$ transition regime and increase with N; we are unable to obtain results for brushes with $N > 30$ with reasonable uncertainties to draw conclusion about the scaling prediction and the values of the exponents in Eq. (7) at the present stage of computing power. Although we did not verify explicitly the scaling form in Eq. (7), our results do show that a growth in fluctuations at $\lambda = 0$ is approached from above and below.

Using SCF theory, the free energy of the K chain for $\lambda \geq 0$ can be described [4] by a Landau-type free energy (quadratic in η) and thus lead to the suggestion that the associated stretch transition is second order in Ref. [4]. However, it should be noted that this Landau free energy is valid only for $\lambda \geq 0$, and in fact for $\lambda < 0$, the free energy takes a different functional form: the free energy is explicitly nonanalytic at $\lambda = 0$ and actually gives rise to a first-order transition. This stretch transition in a polymer brush has the unique properties that it is first order i.e., the first derivative of the free energy and the order parameter is discontinuous, but at the same time bears many characteristic features that are often seen in second order phase transitions. One such feature is the the absence of hysteresis, which on the contrary was often observed in the first-order coil-stretch transitions of real polymers under elongational flow [17,18]. Another feature is the large fluctuation we

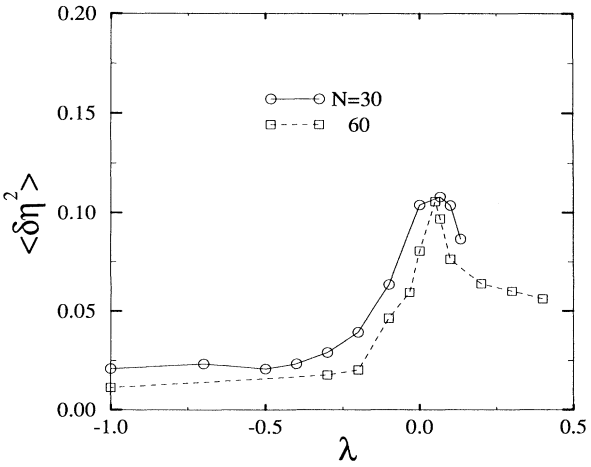

FIG. 4. $\langle\delta\eta^2\rangle$ plotted vs λ for $N = 30$ and 60.

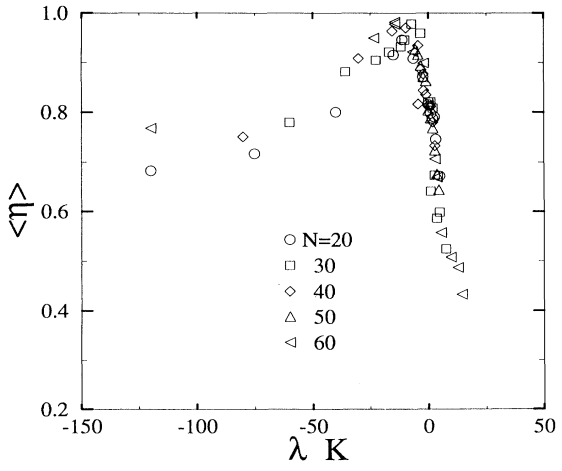

FIG. 5. Scaling plot of $\langle\eta\rangle$ vs λK as suggested in Eq. (5) with $\beta = \delta = 1/2$.

have already seen. Third is the phenomenon of anomalous slowing down, i.e., the relaxation time of the chain is exceptionally large with, $\tau \sim K^3$ (at $\lambda = 0$), which has been shown in Ref. [4] and confirmed by simulations [8]. Very recently, an unusual first-order phase transition that has many features of the second-order transition, including the lack of metastable states and anomalous slowing down, has been shown to exist in the adsorption-stretching transition of an end-grafted Gaussian chain [19,20]. We believe that the stretch transition in the polymer brush can be described by a similar model and some theoretical calculations are in progress. To conclude, our results indicate that the stretched chain configurations in a polymer brush can be understood in terms of a special first-order stretch transition (which is different in nature from the usual coil-stretch transition observed for polymers in elongational flow), thus providing a distinct route to the fundamental understanding of the physical properties of such systems.

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