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Free-energy profiles and scaling in polymer brushes

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Monte Carlo simulations have been performed for an unattached polymer in a grafted polymer layer (a polymer brush). The simulations employ a non-Boltzmann sampling method to calculate the free energy of the unattached chain as a function of its vertical position in the brush, $W(z)$, and the free energy per chain in the grafted layer, f. Contrary to other recent reports, we find grafting conditions where the variation of f is consistent with scaling and analytical self-consistent field (SCF) theories. The free-energy profile, $W(z)$, also follows a form predicted from SCF theory.

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When polymers are attached by one end to a surface, they often become crowded, stretch away from the surface, and form a "brush" [1,2]. Due to their unique architecture, brushes have fascinating physical properties which can be exploited in several ways. Brushes have found extensive use, for example, in stabilizing colloidal dispersions [3], they can be used to control the transport of macromolecules through narrow pores [4], and they can serve as synthetic analogues to naturally occurring biological membranes [5]. The steric stabilization provided by grafted polymers has even been used to design drugs to fight a strain of the influenza virus [6].

Two opposing driving forces govern the properties of grafted polymer layers in good solvents. Scaling analyses [7] and self-consistent field (SCF) theories [8,9] quantify the balance between the free-energy cost of chain stretching and the free-energy gain of solvation. When these two free-energy components are described by the theory of semidilute solutions [10], both scaling and SCF theories predict the following asymptotic scaling of the free energy per chain in the grafted layer, f:

$$f \sim N\sigma^{5/6}, \tag{1}$$

where N is the chain length and σ is the surface grafting density. In contrast, a mean-field (MF) treatment of stretching and solvation predicts a different scaling law: $f_{\mathrm{MF}} \sim N\sigma^{2/3}$. Nevertheless, both free-energy expressions lead to the same scaling law for the brush height, $h \sim N\sigma^{1/3}$, which has been confirmed through computer simulations [11–13] and experiments [14]. These measurements cannot directly test the free energy scaling, however, and in principle, other free-energy expressions may give rise to the same scaling law for h. A few recent studies have examined the free-energy variation through computer simulation [15] and mean-field theory [16], but their results were not consistent with either scaling law for f given above. The discrepancy raises questions about the conditions, if any, where the asymptotic free-energy scaling laws are valid. This issue must be resolved because the conformational free energy plays a central role in determining important properties of polymer brushes, including their ability to resist deformation and provide steric stabilization.

The free energies of chain stretching and solvation have additional consequences for kinetic processes in grafted layers. During the fabrication of a brush, for example, end-adsorbing chains that arrive near the grafting surface encounter a large free-energy barrier to adsorption, because they must stretch beyond their equilibrium dimensions and sacrifice contact with the solvent in order to enter the grafted layer [17,18]. The resistance to adsorption can be quantified by the free-energy profile $W(z)$, defined as the free-energy change that accompanies the translation of the adsorbing end of the free chain from far outside the brush to a position z within the brush. Ligoure and Leibler [17] and Milner [18] have analyzed the form of $W(z)$ in studies of adsorption kinetics, while Halperin and Alexander [19] have considered $W(z)$ in the context of expulsion from grafted layers. Each treatment has predicted a different functional form for $W(z)$, however, and no computational studies have yet been reported to evaluate these theoretical predictions.

Here, we report the first direct numerical calculation of the free-energy profile, $W(z)$, for a free chain within a grafted polymer layer. We conduct Monte Carlo (MC) simulations of unattached polymer chains within monodisperse brushes on flat surfaces; the simulations employ a non-Boltzmann sampling method to obtain $W(z)$ accurately even in regions of very high free energy. Since the free chain is structurally identical to the grafted chains, the free-energy profile evaluated at the grafting surface, $W(0)$, yields the free energy per chain in the brush, f. We can therefore test the scaling law in Eq. (1) in a model system with an exact numerical solution of its statistical mechanics. Although recent studies [15,16] have not found support for the scaling laws given above, our results do agree with Eq. (1) and, along with measurements of forces between grafted layers [20], give support to the earlier theoretical treatments [7,8].

In principle, the free-energy profile can be obtained from MC simulations of a free chain and a grafted layer by accumulating $P(z)$, the probability of finding the first segment of the free chain at a distance z from the grafting surface, and using the relationship $W(z) \propto -k_BT \ln P(z)$. This approach fails, however, for brushes of moderate or high grafting density. In these cases, the probability of finding the free chain within the brush is very small, and the statistical uncertainty in $P(z)$ is overwhelming. To alleviate this problem, we use a simple form of non-Boltzmann sampling [21] to calculate

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$W(z)$. We assume that the first segment of the free chain, and *only* this segment, contains a fictitious "charge" that couples to an external field such that the total free energy of the free chain becomes $W(z)+Fz$. Since the external field affects only the first segment of the free chain, the field does not perturb the global structure of the free or grafted chains [22]. In the presence of the external field, the free-energy profile is given by

$$W(z)=F(z_0-z)-k_BT\ \ln\frac{P(z)}{P(z_0)}\,, \qquad (2)$$

where z_0 is chosen outside the brush so that $W(z_0)=0$. The simulation box is finite in the z direction, so $P(z_0)$ remains nonzero. Furthermore, the free chain is not allowed to adsorb irreversibly when it comes into contact with the surface, so it continues to sample the region within the brush. The resulting free energy contains contributions from chain stretching and solvation, but it does not contain the binding energy of the adsorbing group [7].

For computational simplicity, the simulations are performed with a lattice model similar to the bond fluctuation model of Carmesin and Kremer [23]. Each polymer segment occupies one site on a "primary" cubic lattice with a lattice constant $a_P=1$, and the bond lengths are allowed to fluctuate among the values 1, $2^{1/2}$, and $3^{1/2}$. Excluded volume interactions are enforced for the segments on the primary lattice. By virtue of the lattice geometry, the midpoints of all bonds must lie on a "secondary" lattice with a lattice constant $a_S=a_P/2$, and the crossing of polymer chains can be rigorously forbidden by tracking the locations of the midpoints on the secondary lattice and enforcing a separate "excluded volume" condition for the bond midpoints on the secondary lattice. In this way, the proper chain topology is strictly preserved [24]. The initial configurations of the grafted chains are generated following Lai and Binder [13], and the free chain is initially grown as a random coil outside the brush. The anchoring segments of the grafted chains are allowed to move in the plane of the grafting surface, so these degrees of freedom are annealed. Periodic boundary conditions are applied in the x and y directions, while impenetrable walls are present in the z direction; the lattice dimensions are chosen so that periodic images do not interact. Approximately 10^6 MC steps were used for equilibration; on the order of 10^7 steps were used to accumulate statistics for $P(z)$. We report energy in units of k_BT, length in units of a_P. Since the excluded volume interactions in the lattice model are athermal, the grafted chains are in effect immersed in a good solvent.

The first simulation results concern the scaling of the free energy per chain in the brush, shown in Fig. 1 as f/N versus σ in logarithmic coordinates. The solid line passing through most of the simulation data corresponds to $f/N\sim\sigma^{5/6}$, indicating that Eq. (1) describes the scaling behavior of the chain free energy very well, even for chains as short as $N=10$. In contrast, the mean-field free-energy expression ($f_{\mathrm{MF}}\sim N\sigma^{2/3}$) is not appropriate for the good (athermal) solvent conditions studied here. Although Eq. (1) is valid at moderate grafting densities, deviations from the scaling law become evident below an N-dependent "overlap density." The lower limit of the scaling regime is delineated by the dimensionless quantity d/R_g, where d is the average distance between grafting points. Taking $d\approx\sigma^{-1/2}$, the free energy departs from Eq. (1) when d/R_g is below a constant of order unity. The scaling relationship in Eq. (1) should also fail at high grafting densities when the free-energy expressions used for chain stretching and solvation become invalid. Deviations from the scaling law are not pronounced, however, as long as $h/R_g<5$ [25].

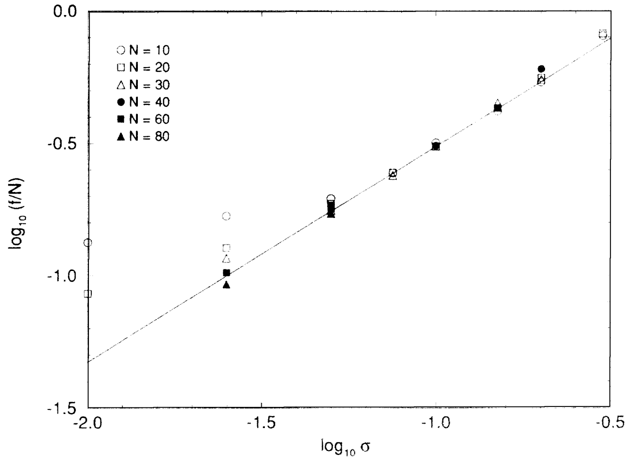

FIG. 1. Free energy per chain normalized by chain length, f/N, versus grafting density, σ, in log-log format for chain lengths ranging from $N=10$ to 80. The solid line indicates the variation predicted by Eq. (1).

In recent MD simulations of brushes at constant surface pressure [15], Grest examined the scaling of the free energy per chain through the variation of the surface osmotic pressure per unit area, Π_a, and the relationship $\Pi_a=\sigma^2(\partial f/\partial\sigma)$. The scaling law in Eq. (1) predicts $\Pi_a\sim N\sigma^{11/6}$, but the MD simulations measured $\Pi_a\sim\sigma^x$, with $x=2.5\pm0.2$ for brushes in good solvents. Furthermore, a recent mean-field theory of Carignano and Szleifer [16] has suggested that, for finite chain lengths, Π_a is best expressed in a virial expansion in the density profile and there may be no region of scaling behavior for the conformational free energy, f. (Any scaling exponents for f would be only apparent exponents for a narrow region of σ.) Nevertheless, the data in Fig. 1 show no systematic deviation from Eq. (1) for values of σ where the grafted chains are moderately stretched. There is no clear source for the discrepancy between the MD simulations, the recent mean-field theory, the current MC simulations, and the earlier analytical theories; the disagreement may simply arise because the onset of scaling behavior is sensitive to the details of the molecular model.

Our final result concerns the free-energy profile, $W(z)$, which has been calculated from Eq. (2) for several different grafting conditions. The universal character of the free-energy profile can be illustrated by presenting scaled coordinates in which $W(z)$ can be reduced to a master curve for a wide range of N and σ. The scaling law in Eq. (1) suggests that $W(z)$ should be normalized by $N\sigma^{5/6}$ in constructing the universal curve for the free-energy profile. Furthermore, the

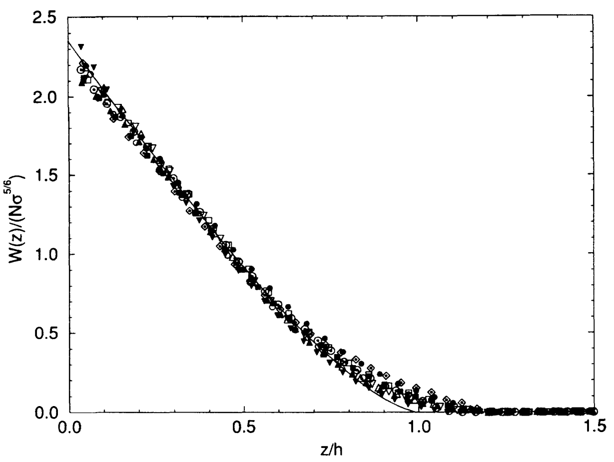

FIG. 2. Normalized free-energy profile, $W(z)/(N\sigma^{5/6})$, versus dimensionless distance z/h. Empty symbols are data for chains of length $N=30$, filled symbols are for $N=40$, and symbols with dots are for $N=60$. Diamonds, circles, squares, upright triangles, and upside-down triangles correspond to values of $\sigma=0.025$, 0.05, 0.10, 0.15, and 0.20, respectively. The solid line corresponds to Eq. (3).

natural choice for the dimensionless measure of distance is z/h, where h is the brush height. In Fig. 2, we present the free energy profile in these scaled coordinates for several values of N and σ [25]. The data do indeed collapse to a single curve, which has several notable features.

The free-energy profile is nearly linear for $(z/h)<0.50$. Near the grafting surface, an incoming free chain therefore faces a nearly constant resistance during its approach to the surface. Halperin and Alexander [19] have predicted a linear free-energy profile based on a simple picture of the grafted layer and the adsorption process. They assume that the density profile of grafted segments is uniform [7] and that the portion of the free chain within the brush is stretched uniformly while the portion of the free chain outside the brush is unperturbed. Although these assumptions are not satisfied in general, they become better approximations as the free chain approaches the surface; the form of $W(z)$ then becomes very close to the predicted linear profile. Milner presented a more detailed analysis based on an analytical SCF theory and derived the following form for the free-energy profile [18]:

$$W(z)=\frac{2f}{\pi}\{\cos^{-1}(z/h)-(z/h)[1-(z/h)^2]^{1/2}\}, \quad (3)$$

where f is again the free energy per grafted chain. Referring to Fig. 2, the normalized simulation data are consistent with this expression throughout most of the brush. Since Eq. (3) was derived from a mean-field expression for the chain stretching and solvation energies, it is not expected to be exact for athermal solvents. The quantitative corrections for good solvent conditions should be small, however, as they are for the density profile in the analytical SCF treatment [26]. Deviations from the SCF result may also be expected due to the depletion of segment density near the hard wall [27]. The quantitative effects of the depletion layer are masked by the statistical uncertainty in the calculated free energies.

To summarize, we have used Monte Carlo simulations with a non-Boltzmann sampling method to investigate the free energy of polymer chains in brushes. The free energy per grafted chain, f, agrees well with the predictions of scaling and SCF theories for moderate grafting density in good solvents [7,8]. This result should add to the ongoing discussion of free energy scaling in grafted polymer layers [15,16]. The free energy profile for a free chain entering a brush, $W(z)$, can be expressed universally by using the scaled coordinates $W(z)/(N\sigma^{5/6})$ versus z/h; the normalized profile agrees well with the form obtained by Milner from an analytical SCF theory [18]. The form of $W(z)$ can be incorporated in models used to design and optimize the processes that are used to fabricate polymer brushes on both laboratory and industrial scales.

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[22] To test this statement, we have performed a few very long "brute force" simulations with $F=0$; they yield results that are identical to much shorter simulations performed with finite values of F. For the highest grafting densities, $Fb/k_BT \approx 1/2$, where b is the Kuhn segment length of the free chain in solution.

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[25] We define the brush height as $h=(8/3)\langle z\rangle$, where $\langle z\rangle$ is the first moment of the segment density profile, $\varphi(z)$, since $\varphi(z)$ is approximately parabolic and $\langle z\rangle=(3/8)h$ is an exact result for parabolic profiles.

[26] For good solvents, the analytic SCF theory predicts very small corrections to the mean-field parabolic density profile. See Ref. [8].

[27] Although we have not shown the segment density profile, $\varphi(z)$, it does indicate a slight depletion of tethered chain segments in the first few lattice layers. Similar density profiles have been observed in the previous simulation studies cited in the text.