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Structure of polymer chains end-grafted on an interacting surface

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We use Monte Carlo simulation methods to study the structure of many polymer chains end-grafted on a flat interacting surface. We consider both attractive and repulsive interactions between the grafting surface and the monomers. We also study the effect of short-range and long-range surface interactions. In all cases, the density profiles of the grafted polymer layer obtained from Monte Carlo studies are in good agreement with various recent self-consistent-field calculations. For repulsive potential wells we find the presence of a definite exclusion zone from which the free ends of the chains are repelled. This result is in excellent agreement with the theoretical prediction.

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I. INTRODUCTION

The configurational properties of polymers terminally attached (end-grafted) to an interface are important to many aspects of polymer science and technology [1]. In particular, stabilization of colloidal suspensions can be achieved by end-grafting polymer chains to colloidal particles [2]. These polymer chains provide the long-range repulsion necessary to offset inherent short-range attractive forces (van der Waals attraction) that exist between colloidal particles. In cases where there is high surface coverage (σ) and no surface adsorption, the polymers stretch out normal to the surface forming a polymer "brush." In general, the overall structure of the brushes (e.g., the height and the density profile) depends on the solvent quality, since the equilibrium structure is the result of a free-energy balance between conformational entropy and excluded-volume-interaction energy.

Theoretical treatments of the grafted polymer brush have employed phenomenological scaling arguments [3,4] and self-consistent-field (SCF) methods [5–8]. The scaling arguments of Alexander [3] and de Gennes [4] provide no detailed information of the polymer chain conformations. They do, however, provide scaling relations between the height of the brush, the surface coverage, and the chain length (N). Various studies based on the SCF method have indicated a substantially different monomer density profile from the step-function form assumed by Alexander and de Gennes. Usually, the monomer density profile needs to be evaluated numerically [9–11] in these SCF calculations. Recently, however, a simplified SCF method has been developed by Milner, Witten, and Cates (MWC) [8] based on the assumption of long, strongly stretched chains and weak excluded-volume interactions. Such calculations are argued to be exact in the long-chain limit. MWC found a parabolic form for the density profile. This parabolic density profile is supported by recent Monte Carlo [12,13] and molecular-dynamics [14] simulations for the case of nonadsorbing grafting surfaces. These simulations found general agreement with the parabolic form except for a depletion of monomer concentration very near the grafting surface. It is also found that the free ends of the chains are not excluded from the region near the grafting surface, in agreement with the results of the SCF model. The agreement between numerical studies and the SCF theory is also quite good for more complicated situations such as polydisperse chains [12,15] grafted on a flat surface and chains grafted on a curved surface [16,17].

Recently, the SCF method for chains grafted on a noninteracting flat surface [8] has been generalized by Marques and Johner and by Marko [18] for the case of an interacting grafting surface. These calculations are carried out for both attractive and repulsive interactions between the grafting surface and the polymer chains. For attractive interactions it has been found that the layer thickness depends in a simple way on the total integrated strength of the interaction potential, with no dependence on the particular shape of the potential well. For repulsive interactions, the SCF calculations find exclusion zones (similar to the case of a convex grafting surface [16] with no surface interactions) from which the free chain ends are excluded. None of these predictions has previously been tested in either experiments or in numerical simulations.

In this paper, we carry out a detailed Monte Carlo study of polymer chains grafted on an interacting surface. We calculate the density profile and the density of the free chain ends for various types of surface interactions, both attractive and repulsive. The general agreement between our numerical results and those obtained from SCF calculations is very good. In Sec. II, we describe the numerical model and the methods of calculations. In Sec. III A, we present the results for attractive potentials, both short ranged and long ranged, and compare them with SCF calculations. In Sec. III B, we present the corresponding results for repulsive surface interactions and in Sec. IV, we conclude with a brief summary and discussion of the results.

II. MODEL AND NUMERICAL PROCEDURE

In order to simulate the behavior of many polymer chains terminally anchored to an interacting surface, we have carried out extensive Monte Carlo calculations. We choose a simple cubic lattice with a grafting surface of size $L_x \times L_y$ located at $z=0$. We consider $L_x = L_y = 40$ and use periodic boundary conditions in the x and y directions. Our results are for chains with $N+1$ monomers with $N=49$ and 99. The surface coverage σ is equal to 0.04 in all cases. The number of polymer chains (N_p) present in the system is then given by $N_p = \sigma L_x L_y = 64$. All the monomers in the simulations are subject to excluded-volume interactions, such that a particular lattice site cannot be occupied by more than one chain at a time. We have chosen random initial conditions for the simulation, i.e., for a particular run, one end of each of the N chains is kept fixed at a randomly chosen vacant site on the grafting surface. We define our unit of time, one Monte Carlo step per monomer (MCM), as N_p "N-bead cycles," i.e., N_pN elementary bead-jump attempts. The particulars of an elementary bead-jump attempt depend on the local environment of the randomly chosen monomer and could be one of the following: an end bead jump, a normal internal bead jump or a crankshaft motion. Once all the required chains are grafted, the equilibration process starts. We consider several different interactions between the grafting surface and the monomers in this study. We consider both short-ranged (contact-type) and long-ranged (square-well-type) attractive interactions. For repulsive interactions, we consider only the square-well case. In each of these cases, we use an importance sampling method based on the standard Metropolis algorithm: the new configuration is accepted with probability $\min(1, e^{-\Delta E/k_BT})$, where ΔE is the change in energy produced by the trial update. The starting configurations are equilibrated over 125 000 MCM's, i.e., for about 0.8 billion monomer updates for $N=99$. After the equilibration is done, several different quantities such as the monomer density and the free-chain-end density as a function of distances from the grafting plane are computed over ten sets of trials with 125 000 MCM in each trial. The density profiles for these ten sets are then compared to study if proper equilibration has been reached. For all the cases considered here, we found that the sampling has been carried out in equilibrium situations as evident from the absence of any systematic differences in those ten sets of data. The data were then averaged over these 10 sets to improve the accuracy.

III. RESULTS

A. Attractive surface interactions

We first consider short-range attractive interactions (contact type) between the grafting surface and the monomers. We define χ_s (in units of k_BT) as the difference in the energy of adsorption between a monomer and a solvent molecule. The solvent molecules are considered to be occupying the empty sites of the lattice. The monomers then gain an energy of χ_s only if they lie on the grafting plane located at $z=0$. We consider $N=49$ and 99, $\sigma=0.04$, and $\chi_s=0.5$ in this study. In Fig. 1 we show the density profile for $N=49$ and in Fig. 2 we show the corresponding density profile for $N=99$. In these figures we also show the density profile for the nonadsorbing case [12] for comparison. We compare our numerical results with numerical-SCF calculations based on the work of Hirz [9]. Hirz's calculation is an extension of the Scheutjens-Fleer [6] lattice model for terminally attached chains with attractive surface interactions. In both Figs. 1 and 2 we find that the agreement between Monte Carlo simulations and numerical SCF results are excellent for all values of z, except for $z=0$, where the SCF method seems to underestimate the monomer density.

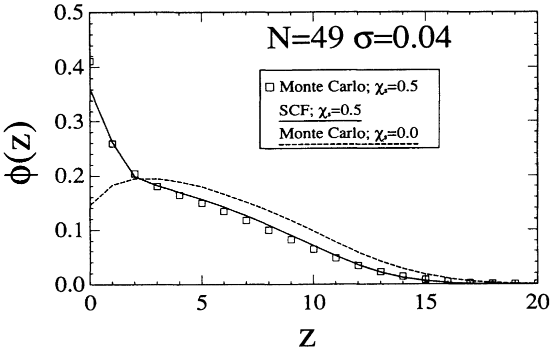

FIG. 1. Density profile from Monte Carlo simulations for contact-type attractive interactions between the grafting plane and the monomers. Here $N=49$ and $\sigma=0.04$. The results from numerical SCF calculations for adsorbing surface (Ref. [9]) and from Monte Carlo calculations for nonadsorbing surface (Ref. [12]) are also included for comparison.

We also compare our results with analytical SCF calculations [18]. In the SCF formulation of MWC [8], the brush height for noninteracting grafting surface is given by

$$h_0 = (12\sigma\omega_0/\pi^2 a)^{1/3} V \ , \tag{1}$$

where ω_0 is the excluded-volume-interaction strength in this model, a is the "packing length," and V is the

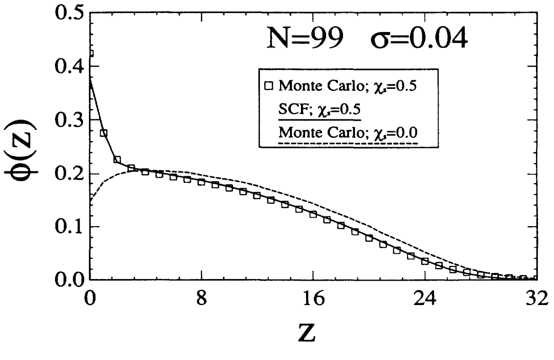

FIG. 2. Same as in Fig. 1 except that $N=99$ here.

volume of each polymer chain. The ideal chain end-to-end distance in this model is given by

$$R_{\mathrm{MWC}}=(3V/a)^{1/2} . \tag{2}$$

For lattice polymers considered in our simulation the end-to-end distance for ideal chains is given by

$$R_{\mathrm{lattice}}=(Nb^2)^{1/2} , \tag{3}$$

where b is the lattice constant. Also, for lattice polymers one should consider $V=Nb^3$, so that the packing length in the MWC model is given by

$$a=3b , \tag{4}$$

in terms of the lattice constant b. From now on, we will set $b=1$ so that all lengths are measured in units of the lattice constant. Then $a=3$ and for lattice polymers the brush height for a noninteracting grafting surface becomes

$$h_0=(12\sigma\omega/\pi^2)^{1/3}N , \tag{5}$$

where $\omega=\omega_0/3$ is the equivalent lattice excluded-volume parameter.

In the SCF theory extended to the case of an interacting grafting surface [18], a relevant parameter is

$$f_s=\frac{\Lambda_s}{\sigma V\omega_0} , \tag{6}$$

where Λ_s is the magnitude of the integral of the surface potential and thus a measure of the total surface interaction. In terms of this parameter f_s the brush height in the presence of surface interactions is given by

$$h=h_0(1-f_s)^{1/3} \tag{7}$$

and it is not expected to depend on the detailed shape of the *attractive* surface potential. For the contact attractive interaction considered in our lattice model, one finds

$$f_s=\frac{\chi_s}{3\sigma N\omega} , \tag{8}$$

with $w\approx0.47$ as computed in Ref. [12] for $N=99$ and $\sigma=0.04$. For $\chi_s=0.5$, $f_s=0.0895$ and thus the predicted value of h is approximately 27 lattice constants from Eq. (7), when we consider $h_0=28$ for this case as found in Ref. [12]. Note that we have computed h_0 in Ref. [12] by fitting the profile to a parabola and computing the distance where this fitted profile vanishes. In the presence of surface interactions we fit the latter part of the profile to a parabola and estimate h to be the height where this fitted function vanishes. The above estimate of h ($h=26.7$) agrees reasonably well with the theoretical prediction ($h=27.0$).

In the SCF theory [18], the monomer distribution is found to be parabolic for distances outside the range of the surface interactions. We find agreement with this prediction for distances larger than several lattice sites from the grafting plane. Actually, for large distances, the density profile for the adsorbing case approaches that for the nonadsorbing case both for $N=49$ and 99 as seen in Figs. 1 and 2. This is expected from the theory since for moderate values of χ_s and large N, h approaches h_0 [Eqs. (7) and (8)]. In experimental situations, then, one expects that for a very short-range attractive surface potential, the density profile will be indistinguishable from the nonadsorbing case for distances away from the grafting surface.

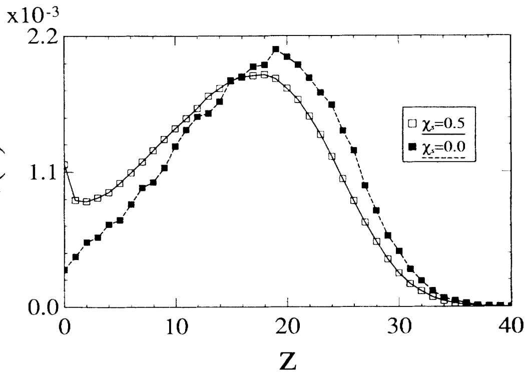

FIG. 3. Chain-end-density profile from Monte Carlo simulations for contact-type attractive interactions between the grafting plane and the monomers. Here $N=99$ and $\sigma=0.04$. The results from Monte Carlo calculations for nonadsorbing surface (Ref. [12]) are also included for comparison.

In Fig. 3 we plot the density of the free chain ends for both the adsorbing case and the nonadsorbing case for $N=99$. The theoretical predictions are that the chain-end density will show a peak at the grafting surface for the adsorbing case, but for large distances away from the grafting surface the chain-end-density profile will be similar to the nonadsorbing case. We find that the density of the free chain ends are larger at the grafting surface for the adsorbing case in agreement with the SCF theory [18]. We also note that the predicted peak at $z=0$ is clearly visible in the simulation. Also, for distances far away from the grafting surface, the chain-end-density profiles for the adsorbing and the nonadsorbing case are qualitatively similar to each other.

Next, we consider the case with longer-range attractive surface interactions. We do not know the existence of any numerical SCF calculations for this case. However, Marques and Johner and Marko [18] have considered this situation in their analytical SCF calculations. In particular, they have considered an attractive square-well potential. In order to compare Monte Carlo results with analytical theory, we have considered an attractive square-well surface potential with depth V_0 (in units of k_BT) and range z_0. We show the density profile for two such situations in Fig. 4 for $N=99$ and $\sigma=0.04$ along with the theoretical profiles calculated by Marko. In each of these cases $z_0=4$ and $V_0=0.1$ and 0.5, respectively. In Fig. 4 the density is rescaled by ϕ_0, the monomer density at $z=0$ for the noninteracting case, and the distance by h_0, the height of the brush in the noninteracting case. The values of ϕ_0 and h_0 are taken from the Monte Carlo simulations of Ref. [12]. As seen in Fig. 4, the general form of the density profiles agree quite well with the theoretical predictions. We should note here that, in this rescaled form, the comparison with theory

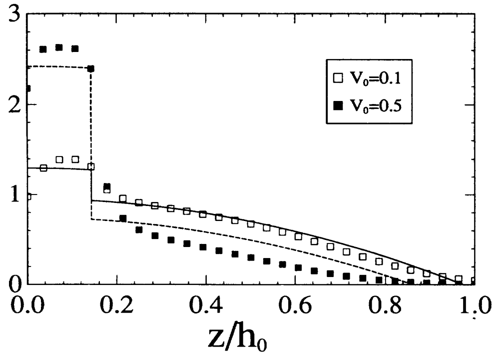

FIG. 4. Density profile for long-range square-well attractive potential for various well depths V_0. Here $N=99$, $\sigma=0.04$, and the range of the potential $z_0=4$ lattice spacings. The lines are predictions of the SCF theory [18].

does not involve any free parameter. We note that the agreement with theory is better for $V_0=0.1$ than for $V_0=0.5$. For the latter case of strong attraction, many monomers fill up the attractive well and the grafted brush ceases to be strongly stretched in the case of the finite chain lengths considered here. This is evident from the relatively small value (approximate 2.3 in this case in contrast to 3.5 for the noninteracting brush) of the ratio of the brush height to the unperturbed chain radius of gyration in this case.

Let us now compare some specific features of the density profile of the grafted layer found in this simulation with the theoretical predictions. The theoretical prediction is that for a grafted layer with a long-range attractive surface interaction, the height of the brush is also given by Eq. (7) independent of the shape of the attractive potential. For the square-well potentials considered here,

$$f_s=\frac{V_0 z_0}{3\sigma N\omega} \tag{9}$$

and as mentioned before we have [12] $h_0=28.0$ for the above values of N and σ. Then, the theoretical value for h [Eq. (7)] is 27.0 and 24.0 for $V_0=0.1$ and 0.5, respectively. This implies that the theoretical density profile should vanish for values of the rescaled height $h/h_0=0.96$ and 0.86, respectively. The theoretical value of h/h_0 agrees well with our numerical estimate for $V_0=0.1$, obtained by fitting the latter part of the profile in Fig. 4 to a parabola. For $V_0=0.5$ the numerical result for h/h_0 is smaller than the predicted value but, as mentioned earlier, in this case the brush is not strongly stretched and a comparison with the SCF theory may not be appropriate.

The profile is expected to show a maximum near z_0 whose strength increases as V_0 increases. The SCF theory [18] predicts that the monomer density at $z=0$ for the attractive case is given by

$$\phi(z=0)\approx\phi_0+\frac{f_s\sigma N}{z_0}\ , \tag{10}$$

where ϕ_0 is the monomer density at $z=0$ for the nonadsorbing case. Note that the SCF theory predicts a parabolic profile for the nonadsorbed case and the simulation results [12] show that there is a small depletion zone near the grafting surface. In order to compare with SCF calculations in the presence of surface interactions, we take the value of ϕ_0 from the parabolic fit to the profile in Ref. [12] rather than its "raw" value at $z=0$. Thus we find $\phi_0\approx0.21$. For $V_0=0.1$ and 0.5 the predicted value of $\phi(z=0)$ are approximately 0.28 and 0.54, respectively and hence $\phi/\phi_0=1.3$ and 2.6 in these cases. Again, these values compare well with the numerical results shown in Fig. 4.

B. Repulsive surface interactions

In this section we consider repulsive interactions between the grafting surface and the monomers. In order to compare with theoretical calculations, we again consider a repulsive square well of height V_0 and range z_0. We consider $z_0=4$ and 9 lattice spacings and $V_0=0.5$ and 1.0 in these studies. In Fig. 5 we plot the density profile for various values of z_0 and V_0 along with theoretical profiles [18]. Again in this rescaled form, the comparison does not involve any free parameters. We find that the density profile shows an abrupt drop near z_0 for all values of V_0 in agreement with the theoretical predictions. We also note that z_0 plays an important role to govern the structure of the brush. For example, for $z_0=4$, the density profile at large distances are very similar both for $V_0=0.5$ and 1.0. On the other hand, the profile extends further out in z for $z_0=9$ and $V_0=1.0$. It seems, then, that the height of the brush is controlled more by the range of the repulsive well than by the strength of it. The value of the density near the grafting surface, however, seems to be controlled by V_0, at least for the relatively strong values of V_0 considered in this study.

In Fig. 6 we plot the chain-end density for the several repulsive well considered above, along with the noninteracting surface case. We find that the overall structure of the chain-end density is governed more by the range of the repulsive well rather than its strength. Moreover, in

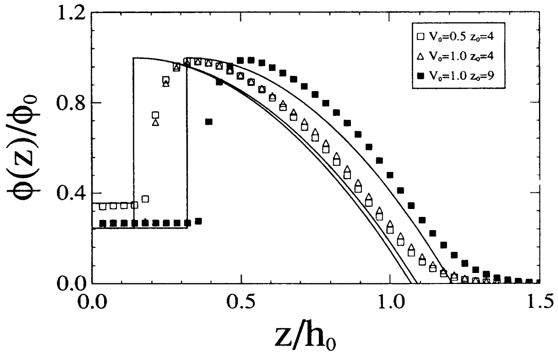

FIG. 5. Density profile for long-range square-well repulsive potential for various well depths V_0 and range z_0. Here $N=99$ and $\sigma=0.04$. The results from Monte Carlo calculations for nonadsorbing surface (Ref. [12]) are also included for comparison. The lines are predictions of the SCF theory [18].

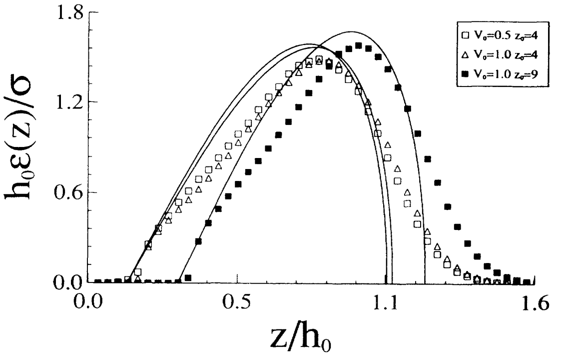

FIG. 6. Chain-end-density profile for long-range square-well repulsive potential for various well depths V_0 and range z_0. Here $N=99$ and $\sigma=0.04$. The results from Monte Carlo calculations for nonadsorbing surface (Ref. [12]) are also included for comparison. The lines are predictions of the SCF theory [18]. Note the existence of an excluded zone for $z \leq z_0$ for the repulsive potentials.

excellent agreement with the SCF theory [18], we find the existence of an excluded zone ranging up to z_0 for all values of V_0 considered here. This simulation definitely observes an exclusion zone in grafted polymer layers. In this case the exclusion zone arises due to the repulsive surface interactions. The prediction of an exclusion zone in the context of a noninteracting convex grafting surface [16] is still unconfirmed in experiment or simulation.

IV. CONCLUSIONS

In this paper we have used Monte Carlo simulation methods to study the structure of many polymer chains grafted on a flat interacting surface. We consider both attractive and repulsive interactions between the grafting surface and the monomers. We compare the results from the Monte Carlo study with recent self-consistent-field calculations. For short-range attractive potentials, numerical SCF calculations has already been carried out. We find excellent agreement between the Monte Carlo results and numerical SCF calculations. We also find that the density profile for this adsorbing case is very similar to that for the nonadsorbing case for distances far away from the grafting surface. This has been predicted in an extension of an analytical calculation based on SCF methods [18].

For longer-range surface interactions we consider square-well type potentials for both attractive and repulsive cases and compare our results with the theoretical predictions. The agreement between the Monte Carlo results and the SCF theory is excellent. For both attractive and repulsive potentials the predicted shape of the profile agrees quantitatively with numerical simulations. For repulsive potential well we also find the presence an excluded zone inside the potential well from which the free ends of the chains are repelled. This is predicted by the SCF theory as well.

We find, then, that for polymer chains grafted on interacting surfaces the SCF theory works quite well. For nonadsorbing cases the theory has already been compared with numerical simulations with excellent agreement. We hope that our simulation would attract more experimental work [19,20] in this direction.

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