Interpenetrations in polymer brushes

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In this Note, we consider a system of two polymer brushes[1] grafted on rigid flat surfaces separated a distance d apart. At plate separations d less than the sum of the individual equilibrium brush heights h^*, the polymer chains grafted on opposing surfaces interfere with each other causing the brushes to either penetrate each other or to compress with no interpenetration, or some combination of the two. The self-consistent-field (SCF) formalism of Milner, Witten, and Cates (MWC)[2] predicts that no interpenetration occurs for brushes in the "classical" limit of large chain length N. Hence, only compression of the brushes can occur. Since the SCF calculations neglect effects which could be important for experimentally relevant chain lengths, it is important to simulate realistic model systems to study the validity and the applicability of the theoretical calculations.

We report results from Monte Carlo simulations in a lattice model[3] of two polymer coated square plates separated a distance d apart. We choose the parameters of our calculations (chain length, grafting density, etc.) in the lattice model closely following a previous numerical-SCF calculation by Shim and Cates,[4] so that it is possible to make a *direct comparison* of our results to those obtained from numerical SCF calculations. We also carry out off-lattice simulations, and, after suitable rescaling of the parameters, we have checked that the results obtained in the lattice simulations are not influenced by the underlying lattice structure.

The lattice model consists of a simple cubic lattice of dimensions $L_x \times L_y \times (d+1)$ with $L_x = L_y = 40$, and d varying from 7 to 15. Periodic boundary conditions in the x and y directions are employed. The polymer chains consist of N_i monomers each, and σ_i is the surface coverage at plate i, where $i = 1,2$ refers to plate 1 and plate 2, respectively. Figure 1 shows the Monte Carlo results for the monomer density profiles for $d = 7$, along with the corresponding density profiles obtained by Shim and Cates in their numerical SCF work. The density profiles for only the left plate are superimposed in Fig. 2 for various plate separations. It is evident from Figs. 1 and 2 that both compression and interpenetration effects are present in this system.

Comparing the results to the numerical-SCF calculations of Shim and Cates[3] we find that their SCF method appears to work reasonably well to produce the general functional form for the density profiles even for these very short chain lengths. There are, however, systematic differences from the Monte Carlo results. For example, the SCF results tend to underestimate the monomer density at the grafting surfaces. To quantify the interpenetration between opposing brushes, Shim, and Cates have defined an interpenetration parameter

$$\beta(d) = \frac{d}{\theta_1 \theta_2} \sum_{z=0}^{d} \phi_1(z)\phi_2(z),$$

where $\phi_1(z)$ and $\phi_2(z)$ are the density profiles for the two

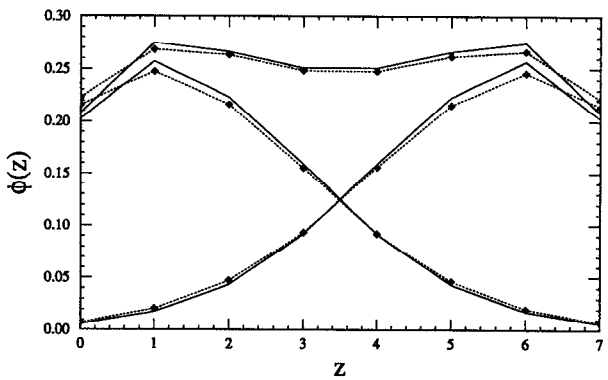

FIG. 1. Density profile $\phi(z)$ as a function of distance z from one of the grafting plates in the symmetric case of coverages $\sigma_1 = \sigma_2 = 0.05$, chain lengths $N_1 = N_2 = 20$ and distance between plates $d = 7$. This plot shows the total density and the contribution coming from each of the two brushes separately. The symbols and the dotted lines are the results of the lattice simulation whereas the continuum line is the result of the SCF calculation of Ref. 4.

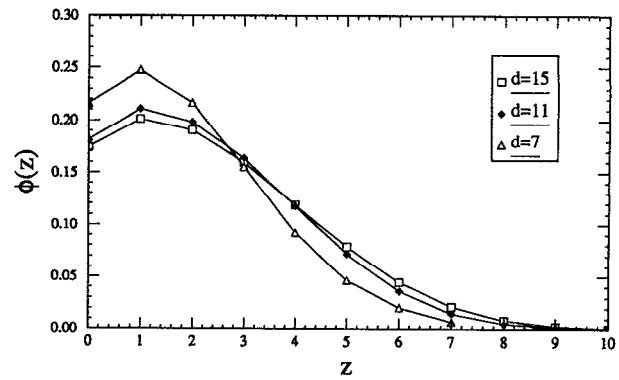

FIG. 2. Density profiles for one of the brushes corresponding to the $d = 15$, 11, and 7 to show the effect of compression on the density profile.

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TABLE I. Comparison of the interpenetration parameter β (see text) obtained in lattice Monte Carlo simulations and numerical SCF calculations.

N_1	σ_1	N_2	σ_2	d	β_{SCF}	β_{MC}
20	20	0.05	0.05	15	0.021	0.012
20	20	0.05	0.05	11	0.148	0.131
20	20	0.05	0.05	7	0.478	0.497
40	40	0.025	0.025	11		0.534
40	40	0.025	0.025	7	0.777	0.838
20	40	0.05	0.025	7	0.595	0.656

plates, and θ_1 and θ_2 are given by $\theta_1=\Sigma_{z=0}^{d}\phi_1(z)$; $\theta_2=\Sigma_{z=0}^{d}\phi_2(z)$. Table I compares the interpenetration values calculated from the Monte Carlo results to the SCF calculations of Shim and Cates.

For chains end-grafted at opposing surfaces, the Monte Carlo results, thus show that both compression and interpenetration effects are present as the plate separation is decreased, instead of the "classical limit" picture[2] which predicts an absence of interpenetration of the brushes in such situations. This discrepancy may be attributable to the fact that the simulations correspond to the "nonclassical" regime of short chains.

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