# Monte Carlo study of polymer chains end-grafted onto a spherical interface

Raúl Toral
*Instituto de Estudios Avanzados and Departament de Física, Consejo Superior de Investigaciones Científicas and Universitat de les Illes Balears, 07071 Palma de Mallorca, Spain*

Amitabha Chakrabarti
*Department of Physics, Kansas State University, Manhattan, Kansas 66506*
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We report results from a Monte Carlo simulation of many polymer chains end-grafted onto the outer surface of a sphere. We find that for small values of the radius of the grafting sphere, the monomer density profiles are quite different from what is obtained in the case of a flat interface. As the radius of the sphere is increased further, we find that the profiles resemble those obtained in the flat case. However, even for a large value of the radius, the density profiles cannot be described by a parabolic form. We have also studied the scaling behavior of the density profile and find that the scaling hypothesis works reasonably well to describe the height of the polymer brush and the density of monomers at the grafting surface. We also investigated the density profile of the free chain ends for different values of the radius of the spherical interface, different chain lengths, and different surface coverages. Self-consistent-field theory suggests the existence of an exclusion zone near the surface from which the chain ends are expelled. We do not observe a definite exclusion zone for most of the values of chain length, radius, and surface coverage studied here. However, some evidence of an exclusion zone is found in one case with high surface coverage.

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## I. INTRODUCTION

Recently, there has been considerable interest in the study of configurational properties of polymer chains terminally attached or end-grafted to an interface. This study is relevant to many aspects of polymer science and technology [1,2] because the long-range repulsion provided by the polymer brushes modify the interaction between two such grafted surfaces. Earlier studies focused on the case of a planar interface mainly because it is the easiest situation to analyze theoretically. Analytical as well as numerical studies have provided a reasonable understanding of the structure of the brushes formed in the case of a planar interface. Polymers end-grafted onto spherical interfaces, however, are particularly important for stabilization of colloidal suspensions. For example, stabilization can be achieved in a standard latex paint by grafting polymers onto the spherical latex particles. Thus a proper understanding of the conformational properties of polymers grafted onto a spherical interface is extremely important.

For a planar interface, theoretical treatments of the grafted polymer brush have been carried out by using phenomenological scaling arguments [3,4] and self-consistent-field (SCF) method [5–8]. The SCF method is essentially a mean-field approach but it offers a detailed prediction of the brush properties such as the monomer density profile. Usually, this quantity needs to be evaluated numerically [6,9] within the SCF formalism. Recently, however, a simplified SCF method has been developed by Milner, Witten, and Cates (MWC) [8] and by Zhulina and co-workers [10,11]. The MWC theory is based on the assumption of long, strongly stretched chains and weak excluded-volume interactions and is argued to be exact in the long-chain limit. The MWC calculations predict a parabolic form for the density profile, which is well supported by recent Monte Carlo [12,13] and molecular-dynamics [14] simulations. These simulations found general agreement to the parabolic form except for a depletion zone 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, which is in agreement with the results of the SCF model. The quantitative agreement between numerical studies and the SCF theory is also quite good for more complicated situations such as polydisperse chains [12,13,15] grafted on a flat surface and chains grafted on an interacting surface [16–18].

Recently, the SCF method has been extended to the case of chains grafted on a curved surface. For a convex surface and melt condition, Semenov [7] finds that the parabolic form is no longer a self-consistent solution and suggests that the free chain ends should be excluded from a zone near the grafting surface in order to regain self-consistency. Ball, Marko, Milner, and Witten (BMMW) [19] have developed a quantitative theory under melt conditions, where they find the chain configurations and free energy in a closed form for a convex cylindrical surface. They also find the existence of an exclusion zone from which the free chain ends are expelled. Although the good solvent case and the spherical interface case have not been solved in detail, the above authors expect a similar behavior in these situations as well.

Numerical studies have been carried recently to test

 

some of these predictions for convex interfaces. Murat and Grest [20] carried out molecular-dynamics simulations for a cylindrical grafting surface but found no evidence of an exclusion zone except in the extreme situation where the cylinder is replaced by a line. Such exclusion zones have also been observed in another special limiting case of star polymers [21]. It should be noted here that definite exclusion zones have only been observed in the case of an interacting planar grafting surface [18].

In a recent publication, Dan and Tirrell [22] used a numerical SCF method for chains grafted on cylindrical and spherical interfaces. The authors found good agreement with the theoretical predictions of BMMW including some evidence of an exclusion zone. However, we should point out that SCF calculations make a mean-field approximation, i.e., they replace the full statistical-mechanical problem by a single-chain self-consistent problem. Thus the SCF calculations neglect effects of correlations between chains, which might be important in many real experimental situations.

In this paper, we carry out a detailed Monte Carlo study of polymer chains grafted onto a sphere. The advantage of a Monte Carlo study is that these calculations do not make any mean-field approximations, although it is difficult to investigate large-chain-length, high-surface-coverage systems, due to the massive amount of computer time required in such a study. The chain lengths and surface coverages accessed in this study, however, compare well to those used in the numerical self-consistent-field calculations of Dan and Tirrell and are relevant in many experimental situations. We calculate the monomer density profile and the density of the free chain ends for various surface converges as well as different chain lengths. In Sec. II we describe the numerical model and the methods of calculations. In Sec. III we present the results and in Sec. IV we conclude with a brief summary and discussion of the results.

## II. MODEL AND NUMERICAL PROCEDURE

We consider polymer chains grafted onto the outer surface of a sphere of radius $R$. The polymer chains are modeled by the so-called pearl-necklace model [23]. In this model one considers the polymer chains to be made out of $N$ monomers connected by rigid rods. Each monomer is modeled as a hard sphere of diameter unity. The distance between successive monomer centers along a chain is set to be $l=1.1$ times the diameter. The first ("head") monomer of each chain is permanently anchored onto the sphere and consecutive monomers are added by executing a self-avoiding random walk starting from the first monomer. The only interactions considered are the self- and mutually avoiding ones: the monomer spheres cannot penetrate each other or the grafting sphere. In order to be able to achieve all the possible configurations of the system, a Monte Carlo dynamics is introduced. In such dynamics, the monomer movements are simulated by "kink jumps" appropriate for this off-lattice model [23].

We have considered two different values for the radius $R$ of the grafting sphere, two different values for the chain length $N$, and three different values for $N_p$, the number of grafted chains. The total number of monomers in the system is given by $N_t=N_p\times N$. The surface coverage $\sigma$ is defined as

$$\sigma=\frac{N_p}{4\pi R^2} . \tag{1}$$

To put the chains onto the sphere we use a modified version of the existing method of growing and equilibrating chains simultaneously [24]. One by one, the chains are grafted at random locations on the sphere in the following way: first, one tries to place the head monomer at some location on the surface of the grafting sphere such that it does not overlap with any other existing monomers. The center of the head sphere is at a distance of $R+\frac{1}{2}$ from the center of the grafting sphere. If it has not been possible to put the head in $N_1=1000$ trials, the whole existing system is equilibrated $N_e=2$ units of time. We define our unit of time as $N_p\times N$ kink-jump movements (where, in this case, $N_p$ is the number of chains present in the system at that time). Once the head is in location, we put on the remaining $N-1$ monomers one by one. Every monomer is placed randomly with its center at a distance $l$ from the center of the previous monomer. If the monomer overlaps with either the sphere or any of the existing monomers, it is removed and we try to put it on again. If, after $N_2=5$ trials, we fail to put on a monomer, the whole chain is removed and the system is equilibrated $N_e$ units of time and the process starts again.

Once all the chains have been placed the final equilibration starts. In this equilibration process, every monomer is tried to move $N_0$ units of time (i.e., a total of $N_0\times N_t$ trials). We have used for $N_0$ a number much larger than the relaxation time of a single chain. For example, $N_0=10^5$ for run 3 (see Table I). After this initial equilibration, different quantities of interest are recorded every $N_3=10$ steps over a total length of $N_4$ units of time, which depends on the particular run (for example, $N_4=6\times 10^5$ for run 1 and $N_4=6000$ for run 12.

Among other quantities, we have computed the monomer density profile $\phi(r)$, defined as

$$\phi(r)=\frac{(\text{number of monomers with distance to origin between } r-\frac{1}{2} \text{ and } r+\frac{1}{2})}{4\pi r^2} . \tag{2}$$

The definition of $\phi(r)$ is such that the following normalization holds:

$$\int_0^\infty d^3r\,\phi(r)=N_t . \tag{3}$$

The end-chain density $\epsilon(r)$ is defined as

$$\epsilon(r)=\frac{(\text{number of end monomers with distance to origin between } r-\frac{1}{2} \text{ and } r+\frac{1}{2})}{4\pi r^2} \tag{4}$$

which is also normalized such that

$$\int_0^\infty d^3r\,\epsilon(r)=N_p\ . \tag{5}$$

We have also monitored the behavior of the average radius of gyration $\langle R_g \rangle$ and the average end-to-end distance $\langle R_e \rangle$. Special care has been taken that the computed magnitudes correspond to equilibrium configurations by ensuring that the results do not depend on time.

## III. RESULTS

As mentioned earlier, we have considered two different values for the radius of the grafting sphere ($R=5,11.18$), two different values for the chain length ($N=50,100$), and three different values for the number of grafted chains ($N_p=25,50,100$). Thus in all we have studied twelve different cases, as listed in Table I. In this table we show the average radius of gyration $\langle R_g \rangle$ and the average end-to-end distance $\langle R_e \rangle$ of the chains in each case. We find that for both $R=5$ and 11.18, the chains stretch more and more as the surface coverage increases.

In Figs. 1 and 2 the monomer density profile $\phi(r)$ is plotted versus distance $r$, after subtracting the minimum distance to the origin, i.e., $r=r_0-(R+\frac{1}{2})$ where $r_0$ is the distance measured from the center of the grafting sphere. In Fig. 1(a) we show the monomer density profile for chain length $N=50$ for different surface coverages and for the grafting sphere radius $R=5$. We find that the shape of the profile is very different from that obtained for a flat grafting surface [12]. For flat surfaces, the density profile is given by a parabolic form except for distances very near the grafting surface, where a small depletion zone is found. In the present case, we find that the profiles are concave downward and the depletion zone near the grafting surface is less pronounced. It is also clear from this figure that the extent of the depletion zone increases with decreasing $\sigma$. The corresponding density profiles for $N=100$ (and $R=5$) are shown in Fig. 1(b). A similar dependence of the density profile curves on surface coverage is observed in this figure.

TABLE I. Some characteristics of the polymer brush grafted on a spherical interface for various surface coverage ($\sigma$) and chain lengths ($N$). Here $R$ is the radius of the grafting sphere, $N_p$ is the total number of grafted polymer chains, $\langle R_g \rangle$ is the average radius of gyration of the chains, and $\langle R_e \rangle$ is the average end-to-end distance of the chains. Note that runs *a* and *b* corresponding to one *free chain* in solution are also included for comparison. Density profiles for runs 1–12 are analyzed in the text.

| Run | $R$ | $N_p$ | $\sigma$ | $N$ | $\langle R_g \rangle$ | $\langle R_e \rangle$ | $R/\langle R_e \rangle$ |
|---|---|---|---|---|---|---|---|
| *a* | | | | 50 | 5.16 | 12.77 | |
| *b* | | | | 100 | 7.77 | 18.95 | |
| *c* | 5.0 | 1 | | 50 | 5.23 | 13.47 | |
| 1 | 5.0 | 25 | 0.08 | 50 | 5.41 | 14.75 | 0.34 |
| 2 | 5.0 | 50 | 0.16 | 50 | 5.72 | 16.19 | 0.31 |
| 3 | 5.0 | 100 | 0.32 | 50 | 6.14 | 18.09 | 0.28 |
| *d* | 5.0 | 1 | | 100 | 7.90 | 19.96 | |
| 4 | 5.0 | 25 | 0.08 | 100 | 8.56 | 23.95 | 0.21 |
| 5 | 5.0 | 50 | 0.16 | 100 | 9.05 | 25.78 | 0.19 |
| 6 | 5.0 | 100 | 0.32 | 100 | 9.68 | 29.10 | 0.17 |
| *e* | 11.18 | 1 | | 50 | 5.23 | 13.66 | |
| 7 | 11.18 | 25 | 0.016 | 50 | 5.36 | 14.42 | 0.78 |
| 8 | 11.18 | 50 | 0.032 | 50 | 5.44 | 14.81 | 0.75 |
| 9 | 11.18 | 100 | 0.064 | 50 | 5.64 | 15.86 | 0.70 |
| *f* | 11.18 | 1 | | 100 | 7.95 | 20.44 | |
| 10 | 11.18 | 25 | 0.016 | 100 | 8.21 | 22.42 | 0.50 |
| 11 | 11.18 | 50 | 0.032 | 100 | 8.49 | 23.45 | 0.48 |
| 12 | 11.18 | 100 | 0.064 | 100 | 9.19 | 26.52 | 0.42 |

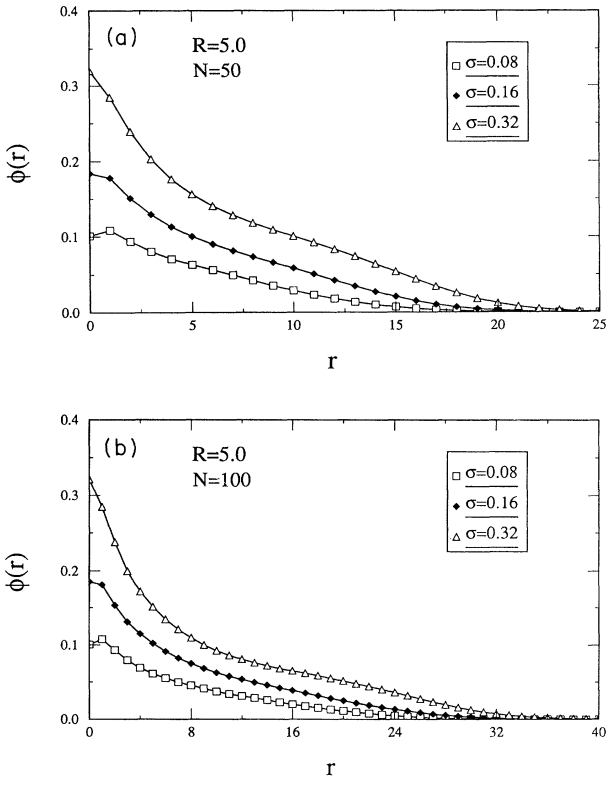


FIG. 1. (a) Density profile from Monte Carlo simulations for polymer chains grafted on a sphere of radius $R=5$ for different coverages and chain length $N=50$. (b) Same as in (a) except $N=100$.

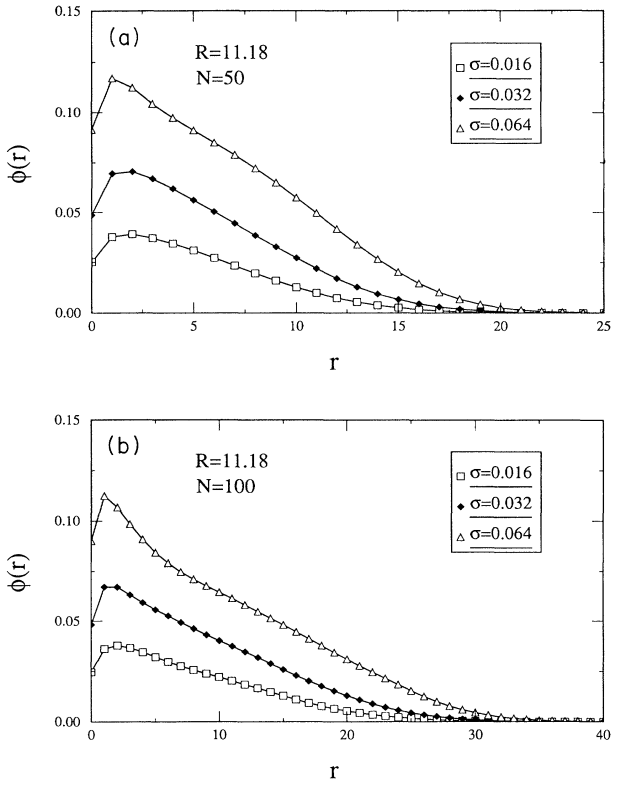


FIG. 2. (a) Same as in Fig. 1(a) except $R=11.18$. (b) Same as in (a) except $N=100$.

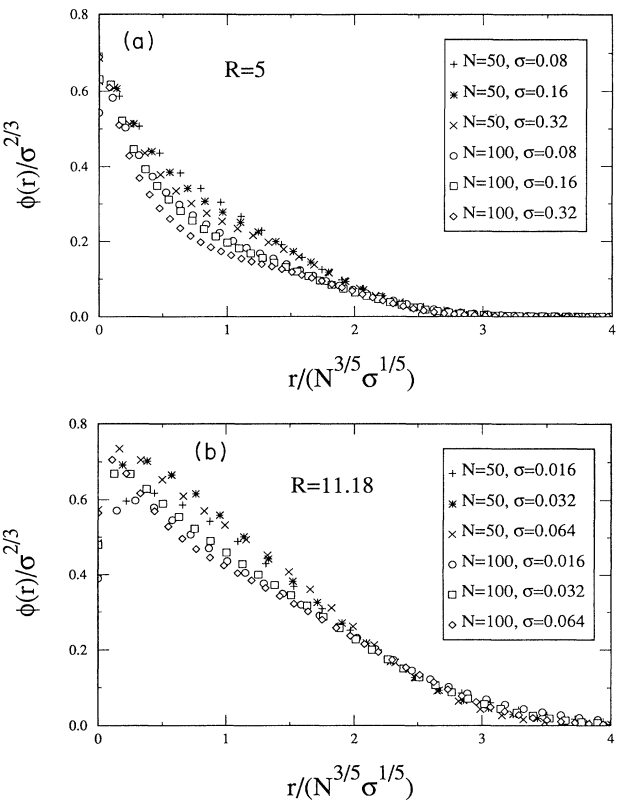


FIG. 3. (a) Test of scaling predictions [Eqs. (6) and (7); see text] for a fixed sphere radius $R=5$, by plotting the rescaled monomer density $\phi(r)/\sigma^{2/3}$ vs the rescaled distance $r/(N^{3/5}\sigma^{1/5})$. (b) Same as in (a) except $R=11.18$.

We now show the monomer density profiles for different surface coverages in the case of a grafting sphere radius $R=11.18$. In Fig. 2(a) we show such profiles for $N=50$ and in Fig. 2(b) we show the corresponding results for $N=100$. In each of these cases we have the same number of polymer chains $N_p$ as in the case of $R=5$, but since the surface area is now five times larger, the surface coverages are smaller in each case by the same factor of 5. In Figs. 2(a) and 2(b) we observe that the profiles are concave upward in contrast to what is found when $R=5$. In this respect the shape of the profile is similar to the one obtained for a flat grafting surface although the profiles in the present case cannot be properly represented by a parabolic form. Thus, even when the radius of the grafting surface is only about ten times larger than the monomer size, the profiles start to resemble those for the flat interface, particularly for the moderate surface coverages considered here. Another interesting observation is that now the depletion zone near the grafting surface is larger than what is seen before for $R=5$ and resembles again those seen for a flat interface.

In Fig. 3 we study the scaling behavior of the density profile for $R=5$ and $N=50$ and 100. Scaling theory suggests that in the limit of star polymers [25] ($R\to 0$) the density profile should scale as

$$\phi(r)\sim\sigma^{2/3}r^{-4/3} . \tag{6}$$

In this same limit the average brush height is expected to scale as

$$h\sim N^{3/5}\sigma^{1/5}R^{2/5} . \tag{7}$$

In order to test these predictions for a fixed value of $R$, we plot $\phi(r)/\sigma^{2/3}$ vs $r/(N^{3/5}\sigma^{1/5})$ in Figs. 3(a) and 3(b) for $R=5$ and 11.18, respectively. We find that the scaling hypothesis works particularly well for the brush height as the scaled density goes to zero at the same point for different chain lengths and surface coverages. Scaling also seems to work around the peak of the profile close to the grafting surface. However, the details of the density profile for intermediate values of $r$ do not seem to scale well. This is probably due to the fact that for the $R$ values considered here, the scaling regime is not properly accessed yet for chain lengths $N=50$ and 100. Also, there seems to be definite differences for the shape of the scaled profiles for $R=5$ and 11.18. This is evident in Fig. 4, where we plot $\phi(r)/\sigma^{2/3}$ vs $r/(N^{3/5}\sigma^{1/5}R^{2/5})$ in order to scale out the $R$ dependence of the brush height. As mentioned earlier, the shape of the profiles are quite different for $R=5$ and 11.18. It seems, then, that the above general scaling description developed for star polymers does not work over the range of values of $R$ and $N$ considered here. In fact, for the star polymer description to be valid, the radius of the grafting sphere must be much smaller than the average brush height. If we consider the average end-to-end distance $\langle R_e\rangle$ to be a measure of the brush height, the above criterion implies that

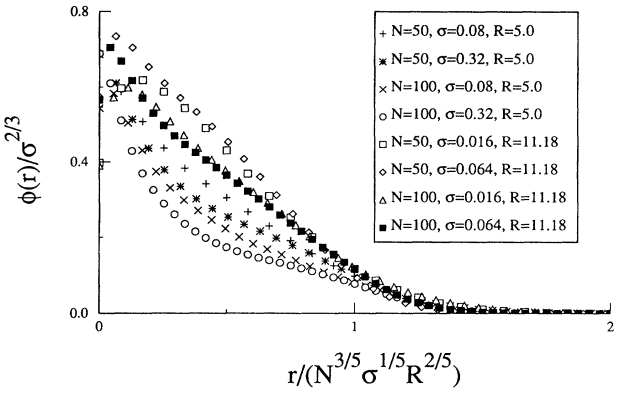


FIG. 4. Test of scaling predictions [Eqs. (6) and (7); see text] by plotting the rescaled monomer density $\phi(r)/\sigma^{2/3}$ vs the rescaled distance $r/(N^{3/5}\sigma^{1/5}r^{2/5})$ for both $R=5$ and 11.18.

the ratio $R/\langle R_e \rangle$ must be much smaller (larger) than unity in the star (flat) limit. This ratio of $R/\langle R_e \rangle$ for different runs is listed in Table I. We point out that our values for this ratio are far from the limiting value for the star polymer and so it is not surprising that the scaling relations do not hold satisfactorily for the simulation results.

In Figs. 5(a) and 5(b) we show log-log plots of the scaling data from Figs. 3(a) and 3(b), respectively. If we fit the data with a straight line for small values of the scaling variable $r/(N^{3/5}\sigma^{1/5})$, we find corresponding power-law exponents in the density profile in the range $(-0.6,-0.5)$ for $R=5$ and $(-0.4,-0.3)$ for $R=11.18$. These values of the exponents are much smaller than the expected value of $-\frac{4}{3}$ obtained from scaling arguments in star polymers. Again, we point out that the scaling regime for which Eqs. (6) and (7) are valid has not been accessed for the chain lengths and surface coverage considered here for each value of $R$.

We now analyze the data for the chain-end density $\epsilon(r)$. In Figs. 6(a) and 6(b) we plot $\epsilon(r)$ vs $r$ for $R=5$ and for different surface coverages. The chain lengths considered in these figures are $N=50$ and 100, respectively. The corresponding figures for $R=11.18$ are shown in Figs. 7(a) and 7(b) for $N=50$ and 100, respectively. For a convex interface, the self-consistent-field theory of BMMW generally suggests the existence of an exclusion zone near the surface from which the chain ends are expelled. For $R=11.18$ we do not find any evidence of an exclusion zone near the grafting surface either for $N=50$

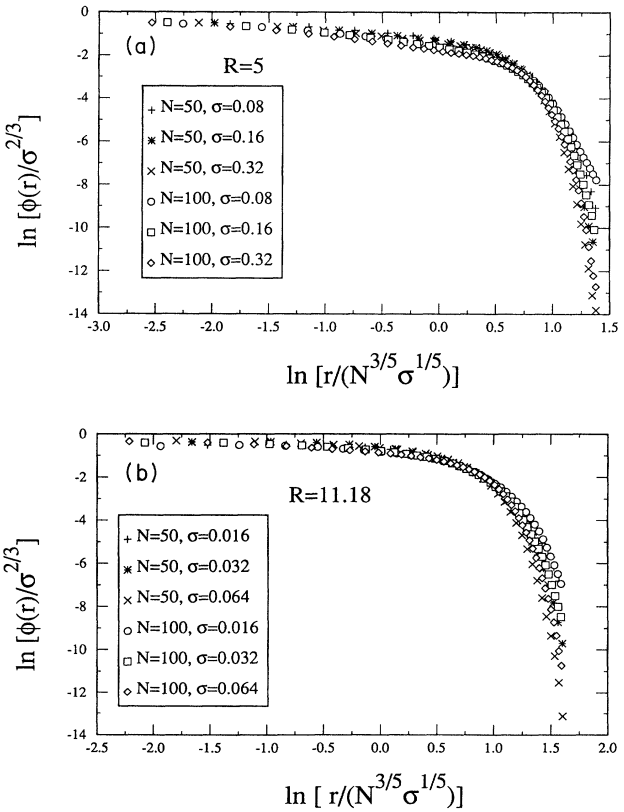


FIG. 5. Log-log plot of the density profile in Fig. 3(a) ($R=5$). The slope of the lines for small values of the scaling variables $r/(N^{3/5}\sigma^{1/5})$ yields an exponent in the range $(-0.6,-0.5)$. (b) Log-log plot of the density profile in Fig. 3(b) ($R=11.18$). The slope of the lines for small values of the scaling variables $r/(N^{3/5}\sigma^{1/5})$ yields an exponent in the range $(-0.4,-0.3)$.

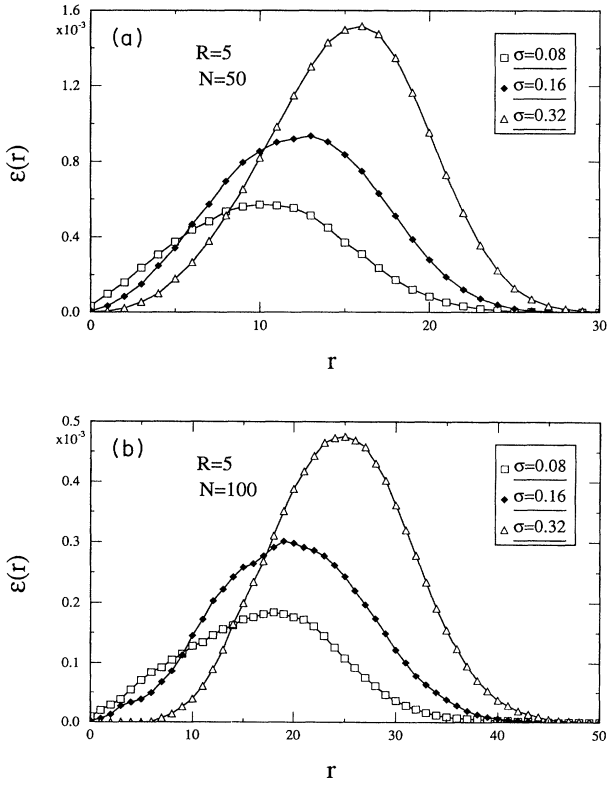


FIG. 6. (a) Density of free chain ends from Monte Carlo simulations for polymer chains grafted on a sphere of radius $R=5$ for different surface coverages and chain length $N=50$. There is no strong evidence of an exclusion zone here. (b) Same as in (a) except $N=100$. Note the existence of an exclusion zone for the largest surface coverage ($\sigma=0.32$).

or for $N=100$. For $R=5$, there is no strong signature of an exclusion zone for $N=50$ either, for any of the three different surface coverages considered here. However, in Fig. 6(b) one finds some evidence of an exclusion zone for $N=100$ and $\sigma=0.32$. This exclusion zone is reasonably large and extends to about 7–8 times the size of a monomer. We point out that the monomer density near the grafting surface is only about 0.3 in this case and thus the exclusion of end monomers does not seem to be due to the crowding of many monomers near the grafting surface [20]. It is also interesting to note that the exclusion zone is only prominent for the most "starlike" of all the runs in which the ratio $R/\langle R_e \rangle$ takes the smallest value (0.17), as shown in Table I.

We note that the SCF predictions of the presence of an exclusion zone might not be applicable for a typical Monte Carlo simulation with chain lengths of $N=50$ or 100 due to finite-chain-length effects on the chain-end density profile. The theoretical values of the width of the exclusion zone for such ratios of brush height to sphere radius $h/R$ is expected to be only a small fraction of the brush height, i.e., a few monomer sizes. On the other hand, finite-chain-length effects (not considered in analytical SCF theories) may modify the chain-end density profile near the surface over a distance of the same order of magnitude [26]. Thus, unless one can consider much larger chain lengths and higher values of surface coverage, a definite confirmation of the exclusion zone will not be possible. An estimate [26] of the fraction of the brush height over which one expects chains to fluctuate away from the SCF distributions is given by $f=(R_f/h)^{4/3}$ where $R_f$ is the "free chain radius" in solution conditions similar to that in the brush. If we consider $R_f \approx N^{1/2}$ and $h \approx R_e$ then $f$ varies in the range 0.2–0.3 for the different cases considered here. For the case of $N=100$ and $\sigma=0.32$ $f=0.24$, $\langle R_e \rangle=29.1$ and the distance over which finite-chain-length effects are important is about $0.24\times 29.1=7$ monomer sizes. Since the dead zone observed in Fig. 6(b) is of the same order of magnitude, we believe that we are just approaching the regime where BMMW theory is applicable. Thus simulations with much larger chain lengths are necessary to resolve this important issue definitely. Such a simulation seems to be beyond reach at this point due to computer time limitations.

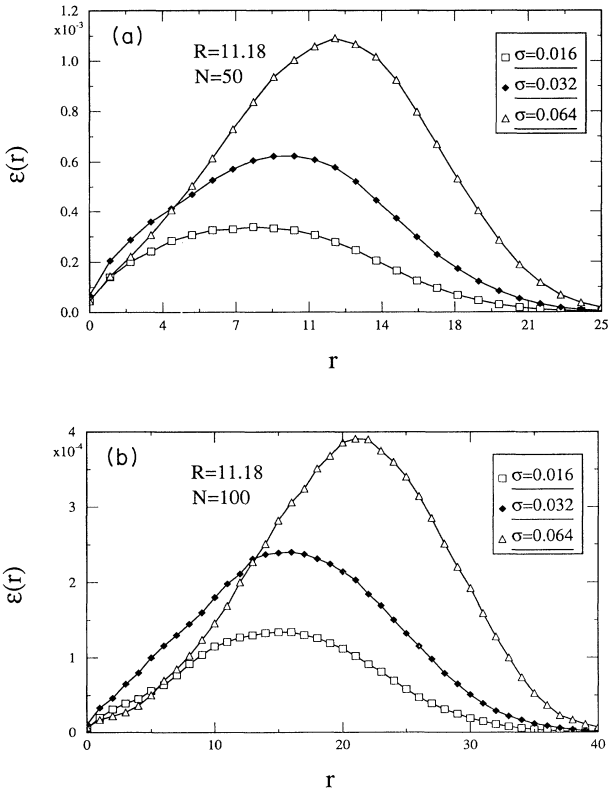


FIG. 7. (a) Density of free chain ends from Monte Carlo simulations for polymer chains grafted on a sphere of radius $R=11.18$ for different coverages and chain length $N=50$. We do not see any strong evidence of an exclusion zone here. (b) Same as in (a) except $N=100$. We do not see any strong evidence of an exclusion zone here.

## IV. CONCLUSIONS

We have carried out a Monte Carlo simulation of many polymer chains grafted onto a spherical interface. We have studied the monomer density profile and the density of the free chain ends for various values of surface coverages, chain length, and radius of the grafting sphere. For small values of the radius of the grafting sphere, we find that the density profiles are quite different from those obtained in the case of a flat interface. As the radius of the sphere is increased further, we find that the profiles resemble those obtained in the flat case, although the former cannot be described by a parabolic form.

We have also studied the scaling behavior of the density profile. The star scaling description discussed here is appropriate only in the limit of $R/h \to 0$. We find that the scaling hypothesis works reasonably well to describe the height of the polymer brush and the density of monomers near the grafting surface. However, we find systematic deviations from scaling for intermediate values of the rescaled distance, indicating that the details of the scaled density profile still depend on parameters such as the radius of the spherical interface for the values of chain lengths and surface coverages considered in this simulation.

Finally, we have investigated the density of the free chain ends for different values of the radius of the spherical interface, chain lengths, and surface coverage. Self-consistent-field theory suggests the existence of an exclusion zone near the surface from which the chain ends are expelled. We do not observe a definite exclusion zone for most of the values of chain length, radius and surface coverage studied here. However, some evidence of an exclusion zone is found in one case, namely, for $R=5$, $N=100$, and $\sigma=0.32$. We note that exclusion zones are difficult to detect in a Monte Carlo simulation since the width of the exclusion zone is comparable to the length scale over which finite-chain-length effects in density are important.

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