Development of an Importance Sampling Single Chain Mean Field Theory for Polymer Adsorption onto a Flat Wall

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ABSTRACT: In this work we have introduced an importance sampling methodology in the framework of the single chain mean field theory (SCMF), to describe the adsorption of moderately long polymers onto solid surfaces. Since the method is based on the generation of self-avoiding chain conformations, excluded volume correlations along the chain backbone are maintained, leading to the proper scaling behavior in the properties depending on one-chain statistics, unlike the self-consistent field theories based on ideal (Markovian) chains. The formulation presented is general and is expected to be very useful for future applications. Because of its mean field nature, the methodology does not require large computer capabilities. As an application of the methodology given here, we present novel results on the profiles of the end-monomer distributions for two chain lengths and different bulk concentrations.

1. Introduction

Polymer adsorption has been extensively studied in recent years, from both experimental and theoretical points of view,[1] due to the great number of applications of polymers near interfaces. Polymer adsorption also has a fundamental interest since it represents a case of a confined polymeric system, together with polymers in pores, grafted layers, microstructures in polymer blends, and copolymer solutions, among many others. In forthcoming papers, we will address the behavior of relatively short polymers (on the order of 10^2 Kuhn segments) adsorbed onto flat[2] and curved interfaces.[3] Our work embraces (i) the development of a suitable non-Markovian self-consistent field theory, (ii) a comparison of the results for flat interfaces with Monte Carlo data from independent authors, and (iii) an analysis of the behavior of polymers adsorbed onto curved interfaces. This article is concerned only with the first point and its overall goal is to demonstrate the utility of this kind of non-Markovian mean field theory and give novel results in polymer adsorption.

Polymer adsorption has attracted a lot of attention for a long time.[4−7] In the past decade, a new insight was found in the analysis of the internal structure of the adsorbed layer[1,9,10] from mean field models based on Edwards' equation. However, despite the qualitative interest, these mean field treatments did not properly reproduce neither the scaling laws[8] nor the experimental data.[11] The theoretical treatment that we will discuss in this paper is based on the *single chain mean field* theory (SCMF), introduced by Ben-Shaul, Szleifer, and co-workers.[14,15] This theory was originally developed to study the structure of micellar aggregates in the absence of solvent molecules and later was generalized to longer chains in the presence of solvent.[16,17] The application of the theory to grafted polymers as well as its use in the treatment to micellar aggregates is given elsewhere.[18,19]

The SCMF theory may be placed between full-scale computer simulations (Monte Carlo and molecular dynamics) and simple analytical approaches based on order-parameter theories of the Cahn−Hilliard−de Gennes type.[7] Computer simulations provide a numerical solution of the model system, although the detailed description of all the molecular interactions dramatically reduces the size of the systems to be simulated. In addition, the existence of topological barriers between conformations requires long simulations to obtain an adequate sampling of the conformational space. Because of these intrinsic difficulties, MC studies on polymer adsorption are rather scarce in the literature. The Cahn−Hilliard−de Gennes approach, despite being limited to very long polymers, is illustrative. Effectively, this approach can correctly reproduce the scaling exponents in these properties based on the one-chain behavior, if the excluded volume correlations are properly taken into account by a local swelling of the chain.[10] One has to keep in mind, however, that its validity is limited to the $N \to \infty$ scaling limit and that it is mean field in essence.

The SCMF approach is also a mean field theory constructed from the free energy of a self-avoiding chain in a self-consistent field. Thus, intrachain interactions are exactly described while interactions with other molecules (other polymers and solvent) are calculated in a self-consistent mean field approximation. Such a procedure differs from the self-consistent field approaches based on Edwards' equation (referred to as SCF, from now on) in that it recognizes a non-Markovian nature of the conformational probability distribution of the chain. In the SCMF approach, distant segments along the chain backbone can be correlated due to their direct excluded volume interactions if they are close in space. In other words, if one constructs the SCMF propagator in the same spirit as in Edwards' theory,[12,13] then

$$G_{\mathrm{SCMF}}(\boldsymbol{r},\boldsymbol{r}';N) \neq \int \mathrm{d}\boldsymbol{r}'' \, G_{\mathrm{SCMF}}(\boldsymbol{r},\boldsymbol{r}'';n)G_{\mathrm{SCMF}}(\boldsymbol{r}'',\boldsymbol{r}';N-n) \quad (1.1)$$

indicates that the propagator is thus *non-Markovian*. The chain propagator has been defined as the statistical

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weight of a self-avoiding chain in the mean field, as given from the expression

$$G_{\mathrm{SCMF}}(\mathbf{r},\mathbf{r}';N) = \int_{\mathrm{r}_0=\mathbf{r}}^{\mathrm{r}_N=\mathbf{r}'} \mathcal{D}\,\gamma \mathrm{e}^{-H_{\mathrm{mf}}[\gamma]/kT} \qquad (1.2)$$

where γ denotes an arbitrary *self-avoiding* conformation of the chain, $\mathcal{D}\gamma$ is an integration only over these self-avoiding conformations of the chain, and $H_{\mathrm{mf}}[\gamma]$ is the mean field energy (to be given later on). Therefore, the calculation of any average property of the system requires the knowledge of all (or a representative sample) of the possible single-chain configurations of the chain model, and not only of the statistically independent partial propagators $G(\mathbf{r},\mathbf{r}'';n)$, with $n < N$, as is the case in the Markovian self-consistent field (SCF) theories. Therefore, in view of this fact, we will explicitly make the distinction between Markovian SCF theories and the non-Markovian SCMF.

The application of the SCMF theory to polymer adsorption has some of the difficulties encountered in MC simulations as, for instance, the treatment of narrow and deep adsorbing wells. In this paper, we will review the mathematical framework of the SCMF theory and further develop an optimal sampling strategy of the polymer configurational space for the sampling to be statistically significant for the properties that we want to describe. Previous versions of the SCMF theory use a homogeneous sampling of the one-chain conformational space, a strategy that gives good results in situations such as micellar aggregates of short molecules,[19] as well as in tethered polymeric layers.[18] However, in polymer adsorption problems, where bulk as well as interfacial properties have to be properly described, a homogeneous sampling for chains of about 100 monomers already requires an overwhelmingly large number of conformations to be significant.

The rest of the paper is organized as follows. In section 2, we introduce the theoretical details of the SCMF theory, in a point to point formulation, together with the importance sampling method used for the evaluation of the configurational space integrals. Section 3 is devoted to a qualitative analysis of polymer adsorption onto a flat solid surface, as predicted by our method, and a brief discussion of the novel results obtained for the end-monomer distribution. Finally, section 4 is reserved for a discussion of the topics that have arisen in this work as well as to the conclusions that can be drawn.

2. The Single Chain Mean Field Theory

The starting point of the theory is to consider that all polymer molecules are statistically independent so that the state of the system is completely characterized by the knowledge of the one-chain configurational probability distribution, $P[\gamma]$, together with the solvent molecule number density field $c_{\mathrm{s}}(\mathbf{r})$. One can obtain the polymer density profile and all other average conformational and thermodynamic properties from the knowledge of these two magnitudes. A given configuration of the polymer is denoted by γ, standing for the set of vectors, $\{\mathbf{r}_i[\gamma]\}$, indicating the position of the centers of the $i = 1 \dots N$ monomers of the chain, N being the polymerization index.

The Helmholtz free energy functional of the system is then written in terms of the probability distribution function of one single chain and the density profiles of polymers and solvent molecules. The minimization of the free energy provides the functional form of the latter quantities in terms of the parameters describing the system. Thus, the free energy is constructed by considering a term corresponding to the internal energy, $U[\gamma, c_{\mathrm{s}}(\mathbf{r}), c(\mathbf{r})]$, which takes into account the inter- and intramolecular interactions, including the interactions of the polymer segments with the adsorbing surface. The entropic contribution to the free energy contains the conformational entropy of the chains as well as the entropy of mixing of the polymer and solvent molecules. Hence, the mean field free energy functional of the polymer−solvent system in a given volume of space is given by the expression[17,23]

$$F[P[\gamma], c_{\mathrm{s}}(\mathbf{r})] = kT\mathcal{N}_{\mathrm{p}}\int \mathcal{D}\gamma(P[\gamma]\ln P[\gamma]) + kT\int_V \mathrm{d}\mathbf{r}\, c_{\mathrm{s}}(\mathbf{r}) \ln\phi_{\mathrm{s}}(\mathbf{r}) + \int \mathcal{D}\gamma P[\gamma] U[\gamma, c_{\mathrm{s}}(\mathbf{r}), c(\mathbf{r})] \qquad (2.1)$$

In this equation, k is Boltzmann's constant, and $\mathcal{N}_{\mathrm{p}}$ is the number of polymers in the volume. The local volume fraction of solvent molecules is given by $\phi_{\mathrm{s}}(\mathbf{r}) = v_{\mathrm{s}}c_{\mathrm{s}}(\mathbf{r})$, where $c_{\mathrm{s}}(\mathbf{r})$ is the local solvent number density, and v_{s} is the volume occupied by one solvent molecule. Moreover, the symbol $\mathcal{D}\gamma$ denotes here an integration with respect to *all the allowed configurations* of the chain, which may be both ideal or self-avoiding configurations, depending on the model used. The independent macroscopic variables in the free energy functional eq 2.1 are T, $\mathcal{N}_{\mathrm{p}}$, and V, since the system is considered to be incompressible. Hence, the accessible volume is filled either by solvent molecules or by polymer segments. If N_{s} denotes the total number of solvent molecules in the volume, the incompressibility assumption implies that

$$V = v_{\mathrm{p}}N\mathcal{N}_{\mathrm{p}} + v_{\mathrm{s}}N_{\mathrm{s}} \qquad (2.2)$$

where v_{p} and v_{s} are the volumes of a polymeric and solvent molecule, respectively.

In eq 2.1, $U[\gamma, c_{\mathrm{s}}(\mathbf{r}), c(\mathbf{r})]$ is the energy of a given configuration γ in a solvent density field $c_{\mathrm{s}}(\mathbf{r})$ and local monomer density $c(\mathbf{r})$. Thus, here we assume that the interaction energy can explicitly depend not only on the configuration but also on the local monomer number density,

$$c(\mathbf{r}) \equiv \int \mathcal{D}\gamma P[\gamma] \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i[\gamma]) \qquad (2.3)$$

as well as on the solvent density $c_{\mathrm{s}}(\mathbf{r})$. This interaction energy can include both intrachain and interchain interactions, as well as interactions with external fields (as for example, adsorbing surfaces). Hence, the energy term can be further decomposed into three contributions, according to

$$U[\gamma, c_{\mathrm{s}}(\mathbf{r}), c(\mathbf{r})] = U_{\mathrm{intra}}[\gamma] + U_{\mathrm{inter}}[\gamma, c_{\mathrm{s}}(\mathbf{r}), c(\mathbf{r})] + U_{\mathrm{ext}}[\gamma] \qquad (2.4)$$

The first term on the right-hand side of this equation corresponds to the intrachain monomer−monomer interactions, which is a function only of every configuration. The second term stands for the interactions of the chain with the solvent as well as with monomers of other chains. The third term in eq 2.4 corresponds to the interaction with external fields (for example, interaction with adsorbing surfaces).

The short-range hard-core repulsions are taken into account by means of both the generation of self-avoiding configurations of the chains, as well as through the *volume filling* constraint, describing the repulsive interaction with the molecules of the environment. This condition has to be satisfied at every point in the volume (volume filling constraint) and is stated as

$$\phi(\mathbf{r}) + \phi_s(\mathbf{r}) = 1 \tag{2.5}$$

satisfied in a mean field way. The average monomer volume fraction is given by

$$\phi(\mathbf{r}) \equiv \int \mathcal{D}\gamma P[\gamma] \sum_{i=1}^{N} v_p \delta(\mathbf{r} - \mathbf{r}_i[\gamma]) = v_p c(\mathbf{r}) \tag{2.6}$$

Hence, the mean field interaction is nonhomogeneous and varies depending on the distribution of the monomers of polymer and solvent as a function of the distance from the surface. In this work, we have assumed that the excluded volume per monomer is constant and independent of the chain conformation. The importance of such an approximation will be discussed later on.

Thus, introducing the constraint as a Lagrange multiplier field $\pi(\boldsymbol{r})$, one can finally write

$$F[P[\gamma], c_s(\boldsymbol{r})] = kT\mathcal{N}_p \int \mathcal{D}\gamma (P[\gamma] \ln P[\gamma]) + kT\int_V \mathrm{d}\boldsymbol{r}\, c_s(\boldsymbol{r}) \ln\phi_s(\boldsymbol{r}) + \int \mathcal{D}\gamma P[\gamma] U[\gamma, c_s(\boldsymbol{r}), c(\boldsymbol{r})] + \int_V \mathrm{d}\boldsymbol{r}\, \pi(\boldsymbol{r})\{\phi(\boldsymbol{r}) + \phi_s(\boldsymbol{r}) - 1\} \tag{2.7}$$

The free-energy functional given by eq 2.7 deserves some comments. In the first place, our description involves some degree of coarse-graining. Effectively, eq 2.5 is meaningful only in a coarse-grained sense since it cannot be strictly satisfied at a length scale smaller than the size of the monomers or solvent molecules. Notice that the constraint eq 2.5 introduces into the free energy functional eq 2.7 the effect of the hard core repulsive forces between particles, which are not included in U. In density functional theories of inhomogeneous fluids (DFT), the repulsive forces are accounted for by the inclusion of the appropriate excess contributions to the free energy functionals.[20−22] These excess contributions may depend on the density at a given field point (local DFT) or on a weighted average of the density in a given environment of the field point (nonlocal DFT).[24,25] Regarding eq 2.5, our SCMF formulation is therefore *local*, in the DFT terminology, due to the fact that monomers as well as solvent molecules are considered as point particles. However, eq 2.7 also depends on the self-avoiding conformations of one chain. Hence eq 2.7 is in this respect nonlocal, since the finite size of the monomers is fully accounted for in the chain conformations. This character is of great importance in the description of the effects of the excluded volume correlations along the chain. For consistency, however, we will consider our formalism as *local*, and phenomena such as the oscillatory density profile near an attractive hard wall, with a wavelength on the order of the monomer (solvent) size, lie beyond the scope of this work.[20] In the second place, since interchain interactions are considered only through the local average monomer density, both in the expression of $U_{\mathrm{inter}}[\gamma, c_s(\boldsymbol{r}), c(\boldsymbol{r})]$ as well as in the volume-filling constraint eq 2.5, the interchain correlations are ignored in the SCMF theory. It is thus expected that our formalism reproduces mean field results in properties such as the dependence of the critical density with the temperature in polymer phase separation. Nevertheless, our theory is suitable for the description of properties related to the long length scale features of the polymers, in the spirit of the usual mesoscopic descriptions of polymers in solution. It is also important to realize that, due to the fact that our formulation keeps the self-avoidance of the chain into account, it is expected that the description of properties related to one-chain features will yield the appropriate exponents, unlike mean field theories based on Markovian statistics (SCF).

In this work, we concentrate on the description of the structure of polymer adsorption onto a planar surface, when the polymers are flexible and moderately long. To simplify the forthcoming analysis, it is convenient to introduce here the specific model that we will use in this paper. We will consider here polymers composed of N monomers described as a sequence of spherical particles of diameter l freely joined with each other by rigid connectors at a fixed distance l between their centers, and exerting hard-core repulsions between themselves and with the solvent molecules. Thus, the intrachain contribution to the energy U is zero. As far as attractive intermolecular interactions are concerned, we make no distinction between the solvent molecules and polymer segments (they are energetically identical); thus, the solvent−solvent and solvent-segment interactions can be ignored by properly defining the origin of the energies. Therefore, on the right-hand side of eq 2.4, only the contribution due to the interaction of the monomers with external fields will be nonzero. In particular, we will consider an attractive square well potential of an energy depth ϵ and a width d, on the order of magnitude of the monomer size, located at the surface of the adsorbing wall, to model the adsorption of monomers at its surface. Therefore, the energetic contribution is simply given by the expression

$$U[\gamma, c_s(\boldsymbol{r}), c(\boldsymbol{r})] = U_{\mathrm{ext}}[\gamma] = \epsilon\int \mathrm{d}\boldsymbol{r}\, \theta(d - |z - z_0|) \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i[\gamma]) \tag{2.8}$$

where z_0 is the position of the solid repulsive surface and θ is the Heavyside function, $\theta(x)$, which is 0 when the argument x is negative and 1 elsewhere. The effect of the infinitely repulsive wall is implicitly taken into consideration by discarding any polymer conformation such that the center of at least one monomer i is $|z_i| < |z_0|$ in the sums over the conformational space of the chain. With this restriction, no contribution of the hard wall should appear in eq 2.8.

From eq 2.1, by evaluating

$$\frac{\delta F}{\delta P[\gamma]} = 0 \tag{2.9}$$

$$\frac{\delta F}{\delta c_s(\boldsymbol{r})} = 0 \tag{2.10}$$

one obtains the equations satisfied by the fields that minimize the free energy eq 2.1 subject to the constraint given in eq 2.5. The solution of eq 2.9 yields the probability distribution of a given conformation γ

$$P[\gamma] = A\mathrm{e}^{-H_{\mathrm{mf}}[\gamma]/kT} \tag{2.11}$$

The second equation, eq 2.10, gives the solvent density profile

$$c_{\mathrm{s}}(\boldsymbol{r}) = B\mathrm{e}^{-v_{\mathrm{s}}\pi(\mathbf{r})/kT} \tag{2.12}$$

In eq 2.11, A is a normalization constant arising from the condition

$$\int \mathcal{D}\gamma P[\gamma] = 1 \tag{2.13}$$

and $H_{\mathrm{mf}}[\gamma]$ is the mean field Hamiltonian for a given conformation γ

$$H_{\mathrm{mf}}[\gamma] \equiv \int \mathrm{d}\boldsymbol{r}\, [v_{\mathrm{p}}\pi(\boldsymbol{r}) + \epsilon\theta(d - |z - z_0|)]\sum_{i=1}^{N}\delta(\boldsymbol{r} - \boldsymbol{r}_i[\gamma]) \tag{2.14}$$

In eq 2.12, the constant B is given by the condition

$$N_{\mathrm{s}} = \int \mathrm{d}\boldsymbol{r}\; c_{\mathrm{s}}(\boldsymbol{r}) \tag{2.15}$$

where N_{s} is the total number of solvent molecules in the volume.

Equations 2.11 and 2.12 explicitly depend on the yet unknown Lagrange multiplier field $\pi(\boldsymbol{r})$. This field can be determined by substituting the expressions for the probability distribution as well as the solvent concentration into the constraint eq 2.5. We then obtain

$$v_{\mathrm{s}}N_{\mathrm{s}}\frac{\mathrm{e}^{-v_{\mathrm{s}}\pi(\mathbf{r})/kT}}{\int \mathrm{d}\boldsymbol{r}\; \mathrm{e}^{-v_{\mathrm{s}}\pi(\mathbf{r})/kT}} + v_{\mathrm{p}}\mathcal{N}_{\mathrm{p}}\frac{\int \mathcal{D}\gamma \mathrm{e}^{-H_{\mathrm{mf}}[\gamma]/kT}\sum_{i=1}^{N}\delta(\boldsymbol{r} - \boldsymbol{r}_i[\gamma])}{\int \mathcal{D}\gamma \mathrm{e}^{-H_{\mathrm{mf}}[\gamma]/kT}} = 1 \tag{2.16}$$

The solution of the previous equation permits the calculation of the Lagrange multiplier field $\pi(\boldsymbol{r})$, which completely determines the mean field probability distributions and, from the latter, all relevant properties of the system.

2.1. Calculation at a Fixed Chemical Potential. As previously mentioned, the choice of the total number of chains in the system $\mathcal{N}_{\mathrm{p}}$ and the volume V is required to obtain the solution of the mean field $\pi(\boldsymbol{r})$ from eq 2.16. However, since we want to describe inhomogeneous systems, fixing the total number of chains in the volume does not give us a priori the knowledge of the bulk polymer density. Thus, it is convenient to eliminate $\mathcal{N}_{\mathrm{p}}$ in eq 2.16 in favor of the bulk polymer density, through the chemical potential μ.

With this purpose in mind, let us consider the partition function of one chain in the mean field, as given by the configurational integral

$$\mathcal{Z}_{\mathrm{p}} \equiv \frac{1}{l_{\mathrm{p}}^{D}}\int \mathcal{D}\gamma \mathrm{e}^{-H_{\mathrm{mf}}[\gamma]/kT} \tag{2.17}$$

where l_{p} stands for the de Broglie wavelength[26] of one monomer and D is the dimensionality of the chain configurational space. From the mean field point of view, we can relate the statistical weight of one chain with the chemical potential from the relation

$$\mathcal{Z}_{\mathrm{p}} = \mathcal{N}_{\mathrm{p}}\mathrm{e}^{-\mu_{\mathrm{p}}/kT} \tag{2.18}$$

where μ_{p} is the polymer chemical potential. For the solvent field, one has

$$\mathcal{Z}_{\mathrm{s}} \equiv \frac{1}{l_{\mathrm{s}}^{3}}\int_V \mathrm{d}\boldsymbol{r}\; \mathrm{e}^{-\pi(\mathbf{r})v_{\mathrm{s}}/kT} = N_{\mathrm{s}}\mathrm{e}^{-\mu_{\mathrm{s}}/kT} \tag{2.19}$$

where here l_{s} corresponds to the de Broglie length for the solvent molecules and μ_{s} is the solvent chemical potential. In an incompressible system, however, the only independent chemical potential is the so-called *exchange chemical potential* μ due to the fact that the addition of one chain to the system has to be compensated with the removal of the equivalent volume of solvent molecules. Thus, in our context μ is given by

$$\mu = \mu_{\mathrm{p}} - N\frac{v_{\mathrm{p}}}{v_{\mathrm{s}}}\mu_{\mathrm{s}} \tag{2.20}$$

Therefore, without loss of generality, we can choose $\mu_{\mathrm{s}} = 0$ in eq 2.19, which fixes the scale of the chemical potential of the polymer, and can identify μ_{p} with the exchange chemical potential μ in eq 2.18. In addition, it follows that

$$\frac{1}{l_{\mathrm{s}}^{3}}\int_V \mathrm{d}\boldsymbol{r}\; \mathrm{e}^{-\pi(\mathbf{r})v_{\mathrm{s}}/kT} = N_{\mathrm{s}} \tag{2.21}$$

We will further consider that our system is in thermodynamic equilibrium with a homogeneous system of the same volume. Hence, both systems share the same chemical potential. For such a homogeneous system, the one-chain partition function Z_{p}^{0} can also be evaluated from eq 2.17, with the corresponding mean field Hamiltonian given by

$$H_{\mathrm{mf}}^{0}[\gamma] \equiv \int \mathrm{d}\boldsymbol{r}\; v_{\mathrm{p}}\pi^{0}(\boldsymbol{r})\sum_{i=1}^{N}\delta(\boldsymbol{r} - \boldsymbol{r}_i[\gamma]) = v_{\mathrm{p}}\pi^{0}N \tag{2.22}$$

where no interface potential has been introduced. The second equality follows from the fact that π^0 is a constant if the system is macroscopically homogeneous. Thus, the equilibrium condition between the inhomogeneous and the homogeneous systems allows us to write

$$\mathrm{e}^{-\mu/kT} = \frac{Z_{\mathrm{p}}}{\mathcal{N}_{\mathrm{p}}} = \frac{Z_{\mathrm{p}}^{0}}{\mathcal{N}_{\mathrm{p}}^{0}} \tag{2.23}$$

with

$$\frac{Z_{\mathrm{p}}^{0}}{\mathcal{N}_{\mathrm{p}}^{0}} = \frac{Nv_{\mathrm{p}}}{l_{\mathrm{p}}^{D}\phi^{0}V}\,\mathrm{e}^{-v_{\mathrm{p}}\pi^{0}N/kT}\int \mathcal{D}\gamma = \frac{Nv_{\mathrm{p}}}{l_{\mathrm{p}}^{D}\phi^{0}V}\left[\frac{l_{\mathrm{s}}^{3}}{v_{\mathrm{s}}}(1 - \phi^{0})\right]^{Nv_{\mathrm{p}}/v_{\mathrm{s}}}\int \mathcal{D}\gamma \tag{2.24}$$

where we have defined the bulk monomer volume fraction, from the properties of the homogeneous system as being $\phi^0 \equiv v_p N \mathcal{N}_p^0/V$. The second equality follows after eliminating $e^{-\pi^0}$ using eq 2.21, together with the incompressibility condition eq 2.5. Hence, the constraint equation to be solved after the introduction of the bulk monomer density as an independent parameter is

$$\frac{v_s}{l_s{}^3} e^{-v_s\pi(\mathbf{r})/kT} + \frac{V\phi^0}{N}\left[\frac{v_s/l_s{}^3}{1-\phi^0}\right]^{v_p N/v_s} \frac{\int \mathcal{D}\gamma e^{-H_{mf}[\gamma]/kT} \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i[\gamma])}{\int \mathcal{D}\gamma} = 1 \quad (2.25)$$

Notice the conformational space volume included in the denominator of the second term on the left-hand side of this last expression. This volume has also to be sampled by means of Monte Carlo techniques, as we will see in the next subsection. In addition, the value of v_s/l_s in eq 2.25 is immaterial for our purposes since it can be absorbed into π, which is the quantity to be determined. Of course, the numerical values of both l_p and l_s will affect the total free energy of the system, but this will not be reflected in the profiles that we calculate since they are carried out at a fixed temperature.

2.2. Importance Sampling of the Phase Space of One Single Self-Avoiding Chain. The solution of the constraint equation, eq 2.25, involves integrations over the one-chain configurational space. These integrations can, in principle, be carried out analytically for ideal chains, where monomers can overlap. However, in the case of self-avoiding chains, such an analytic evaluation is virtually impossible for chains with more than a few monomers. One way to overcome this difficulty is to evaluate the configurational integrals by means of the Monte Carlo method. It is crucial to realize at this point that the exact description of the self-avoiding chain conformations maintains the excluded volume correlations along the chain despite the fact that the interchain interactions and the effect of the solvent is taken at the mean field level. The use of ideal-chain conformations in the evaluation of the configurational space integrals transfers all the intrachain excluded volume repulsions to the mean field $\pi(\boldsymbol{r})$, smoothing out these intrachain correlations. Thus, properties depending on one-chain statistics will be sensitive to the method of evaluation of the configurational space integrals, something that will be seen in the values of the exponents in the power-law behavior of the different properties that we will discuss later on. On the other hand, the numerical nature of the generation of self-avoiding chain conformations limits the length of the chains that can effectively be treated in the framework of SCMF by several orders smaller than with calculations based on Markovian statistics.[1]

In our case, the presence of an adsorbing potential of strength on the order of kT and of a narrow width on the order of the monomer size, makes the uniform sampling of the one-chain configurational space inefficient, since most of the configurations generated in this way have an irrelevant statistical weight. Therefore, here we develop the theory for a general biased sampling and discuss the *optimal sampling* for a given situation of interest.

To evaluate the integral of a given function $f[\gamma]$ over the configurational space of a chain by means of the Monte Carlo method, we use the formula[27]

$$\int \mathcal{D}\gamma f[\gamma] \simeq \frac{1}{\Lambda}\sum_{\alpha=1}^{\Lambda} \frac{f[\gamma_\alpha]}{\mathcal{P}_B[\gamma_\alpha]} \quad (2.26)$$

where Λ is the total number of sampling points in the configurational space and $\mathcal{P}_B[\gamma]$ is the probability distribution of the biased sampling. It is convenient for our purposes to relate $\mathcal{P}_B[\gamma]$ with a statistical weight $w[\gamma]$, which we refer to later on

$$\mathcal{P}_B[\gamma] = \frac{w[\gamma]}{\int \mathcal{D}\gamma w[\gamma]} \quad (2.27)$$

Therefore, aiming at a numerical evaluation of the constraint equation, the conformational space integrations in the second term on the right-hand side of eq 2.25 can be rewritten in terms of a sum over the Monte Carlo samples, giving

$$\frac{\int \mathcal{D}\gamma e^{-H_{mf}[\gamma]/kT} \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i[\gamma])}{\int \mathcal{D}\gamma} \simeq \frac{\sum_{\alpha=1}^{\Lambda} e^{-H_{mf}[\gamma\alpha]/kT} \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i[\gamma_\alpha])/w[\gamma_\alpha]}{\sum_{\alpha=1}^{\Lambda} 1/w[\gamma_\alpha]} \quad (2.28)$$

Notice that the phase space volume in the denominator has also been calculated by means of the same biased Monte Carlo sampling, so that the normalizing factors $\int \mathcal{D}\gamma w[\gamma]$ cancel out.

The averages of a given variable $A(\boldsymbol{r},\boldsymbol{r}_i[\gamma])$ can then be performed in a similar way

$$\langle A(\boldsymbol{r})\rangle = \frac{\int \mathcal{D}\gamma e^{-H_{mf}[\gamma]/kT} A(\boldsymbol{r},\boldsymbol{r}_i[\gamma])}{\int \mathcal{D}\gamma e^{-H_{mf}[\gamma]/kT}} \, e \, \frac{\sum_{\alpha=1}^{\Lambda} e^{-H_{mf}[\gamma\alpha]/kT} A(\boldsymbol{r},\boldsymbol{r}_i[\gamma_\alpha])/w[\gamma_\alpha]}{\sum_{\alpha=1}^{\Lambda} e^{-H_{mf}[\gamma\alpha]/kT}/w[\gamma_\alpha]} \quad (2.29)$$

Furthermore, considering eq 2.28, the constraint eq 2.25 is rewritten as

$$e^{-v_s\pi(\mathbf{r})/kT} + \frac{V\phi^0}{N}\left[\frac{1}{1-\phi^0}\right]^{v_p N/v_s} \times \frac{\sum_{\alpha=1}^{\Lambda} e^{-H_{mf}[\gamma\alpha]/kT} \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i[\gamma_\alpha])/w[\gamma_\alpha]}{\sum_{\alpha=1}^{\Lambda} 1/w[\gamma_\alpha]} = 1 \quad (2.30)$$

where the factor $v_s/l_s{}^3$ has been absorbed into $\pi(\boldsymbol{r})$.

Finally, to end this section, it is important to also realize that the most efficient sampling of the conformational space is that done with a distribution given by the absolute value of the integrand itself, i.e., using[27]

$$w[\gamma] = |f[\gamma]| \tag{2.31}$$

in integrals of the form of eq 2.26. Hence, the choice $w[\gamma] = e^{-H_{mf}[\gamma]/kT}$ will be a convenient choice to make the samples relevant for the problems at hand.

3. Results

In this section we will describe the procedures employed to numerically implement the importance sampling SCMF previously given, which will be applied to the case of adsorption of polymers onto a plane wall. In particular, results for loop monomer as well as tail monomer volume fraction profiles are obtained. Furthermore, end-monomer distributions are obtained for the first time, to the best of our knowledge.

3.1. Numerical Calculation Details. The solution of the SCMF problem has been done from a sampling of the configurational space of *off-lattice* polymers of 100 and 200 monomers, in cubic boxes of size $L = 115.32l$ and $L = 226.92l$, respectively, l being the monomer length. The adsorbing wall has a thickness of $2.72l$ and its mid plane is located at $z = 0$, occupying the center of the simulation box. Hence, the repulsive hard surfaces are at the planes $z = \pm 1.36l$ (which corresponds to $|z_0| = 1.86l$ with respect to the position of the centers of the monomers). The wall is rigid and cannot be penetrated by the chain beads. The wall has a certain thickness, larger than the size of a monomer, to prevent that chains could be divided by the wall in the process of numerically generating and modifying the conformations. Adsorption takes place because we have introduced a square well potential at the surface of the plane, according to eq 2.8, whose width available to monomers is $d = 1.86l$ and different values of ϵ on the order of kT have been used. Since periodic boundary conditions in the three directions of space are considered, the size of the box has been chosen such that the chains never reach the two adsorbing surfaces at one time, even when fully extended.

The chains are modeled as pearl necklaces of nonoverlapping beads of diameter l, whose centers are separated a fixed distance equal to the bead diameter, and where the chain is fully flexible. As mentioned, the excluded volume per monomer has been taken as being independent of the conformation of the chain, and is estimated to be $v_p = 1.86l^3$, assumed as constant in this work. This value corresponds to an estimate of the net excluded volume per monomer in a chain (approximately one-half of the volume excluded by an isolated monomer). In this work, we have chosen that the excluded volume of the whole chain be independent of the conformation γ and equal to v_pN, for simplicity requirements, and instead focus our attention on the importance sampling methodology. This assumption is taken to simplify the problem as much as possible, although it is rather crude. We will see in ref 2, however, that this approximation is enough to properly describe the monomer volume fraction profiles of adsorbed chains due to the fact that the loops and tails, formed upon polymer adsorption, only marginally overlap.[6] Due to this effect, the excluded volume correlations are not screened by the local density. The scaling results obtained for polymer adsorption are usually constructed upon this fact.

Because of the macroscopic translational symmetry of the system in the directions parallel to the wall, the mean field Lagrange multiplyer $\pi(\mathbf{r})$ is considered to be a function of the z coordinate only. Hence, the box has been divided into layers of thickness $\delta = 1.86\ l$, parallel to the plane, inside of which π is taken as constant. This choice permits us to have a reasonable precision on the spatial variation of π and, at the same time, the volume of the layer is large enough for eq 2.5 to make sense.

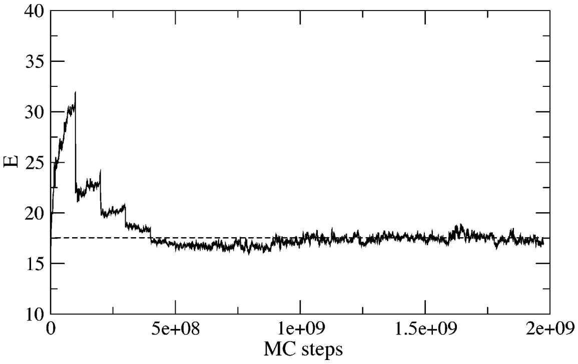

Figure 1. Variation of the energy of the configurational file, $E = -\sum_\gamma H_{mf}(\gamma)$, with Monte Carlo (MC) steps for a system with $N = 100$, $f^0 = 0.058$, and $\epsilon = -0.35kT$.

To evaluate the configurational space integrals in eqs 2.28 and 2.29 by means of a Monte Carlo procedure, a *configurational file* is created. In this file, the coordinates of all the monomers of the polymer, corresponding to a large number of different configurations (usually 2×10^4), are stored together with the numerical value of its bias weight $w[\gamma]$. The sums over all the configurations in the averages (eq 2.30) will simply be replaced by sums over the sample of configurations stored in the configurational file. At the beginning of the simulation, this configurational file is filled by a uniform distribution, $w[\gamma] = 1$, of conformations. It contains a collection of statistically independent self-avoiding chains whose first monomer is randomly located inside the simulation box. It is clear that the direct use of this initial sample in eqs 2.28 and 2.29 will be rather inefficient. Effectively, due to the narrow and deep adsorbing well, only a few of these configurations will be statistically relevant for the adsorption problem (in particular those that have monomers inside the adsorbing well). To overcome this difficulty, a bias field is introduced aiming at gathering together a large number of configurations around the most relevant part of the chain configurational space. Once the bias field has been chosen, the configurational file is transformed so that the chains are distributed according to the selected bias $w[\gamma]$. To obtain this new *equilibrated* configurational file, a chain is randomly selected and its configuration modified by an elementary movement picked at random (crankshaft, reptation or simple overall translation of the chain). The statistical weight of the new configuration with respect to the bias field is then compared with the old one, and accepted or rejected according to the Metropolis rule.[28] The procedure is repeated a large number of times, until indicators such as the sum of the energy with respect to the bias field of the conformations in the configurational file (Figure 1) or that of the conformations in contact with the adsorbing well are stationary in a statistical sense (see Figure 2). Once this point is reached, the stored configurations are distributed according to the prescribed statistical weight $w[\gamma]$. With respect to multichain Monte Carlo simulations, the acceptance rate is much larger since the topology of the

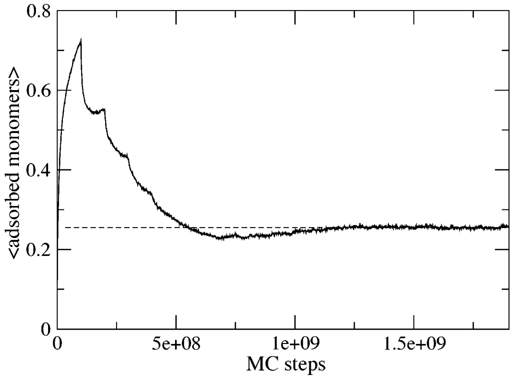

Figure 2. Variation of the average number of adsorbed monomers of the configurational file with respect to Monte Carlo (MC) steps for a system with $N = 100$, $f^0 = 0.058$ and $\epsilon = -0.35kT$.

energy space is smoother for a chain in a mean field than in a multichain system.

In our calculations, with the purpose of obtaining a statistically significant configurational file, we have chosen the Boltzmann weight of the chains in the mean field

$$w[\gamma] \propto \mathrm{e}^{-H_{\mathrm{mf}}[\gamma]/kT} \tag{3.1}$$

where $H_{\mathrm{mf}}[\gamma]$ is given in eq 2.14, as the bias. Of course, since $\pi(r)$ is not known a priori, an iterative procedure has to be used to recalculate the field while relaxing the conformations of the configurational file, until a stationary value is obtained. In fact, we initially choose $\pi^{(0)}(\mathbf{r}) = 0$ in eq 2.14 and define $w^{(0)}[\gamma]$ from eq 3.1. After about 10^8 Metropolis steps, eq 2.30 is used to recalculate $\pi^{(1)}(\mathbf{r})$ and, hence, $w^{(1)}[\gamma]$ from the actual sample in the configurational file. The Metropolis process is initiated again for other 10^8 steps. The whole process is repeated until a stationary value of π is obtained. The dynamic process of relaxation of the configurational file toward the optimal sample is analogous to a diffusion process in a nonlinear potential field. The detailed balance property of the transition probabilities satisfied by the Metropolis rule ensures that the proper thermodynamic equilibrium distribution will be reached after a large enough number of steps are taken.[28,29] In Figures 1 and 2 are shown, respectively, the evolution of two indicators (energy and adsorbed monomers) of the relaxation of the configurational file, as functions of the MC steps. Notice the sharp jumps due to the recalculation in the iterative procedure of the mean field Hamiltonian used as a bias field.

It is crucial to realize that performing averages by means of sums over the configurations in the configurational file has some advantages with respect to the usual procedure used in Monte Carlo simulations, since the configurations are recorded and the probability distribution of each one is known. Effectively, once the samples are correctly distributed in the configurational file, eq 2.30 can be solved for different values of the parameters that define the physical problem, i.e., the adsorption energy ϵ and the bulk density f^0. This produces a new Lagrange multiplier field $\pi(\mathbf{r})$ from which the mean field Hamiltonian $H_{\mathrm{mf}}[\gamma]$ as well as the physical probability distribution $P[\gamma]$ are determined for the new conditions. Hence, the range of applicability of a given sampling is only limited by its statistical relevance for the physical conditions that one wants to analyze. Effectively, a sampling suitable for a dilute bulk solution may not be statistically relevant when concentrated solutions are used, although it could still be relevant at intermediate concentrations. In practice, only two sets of samples with different biases have been used to cover the range of concentrations from dilute to close to melt conditions.

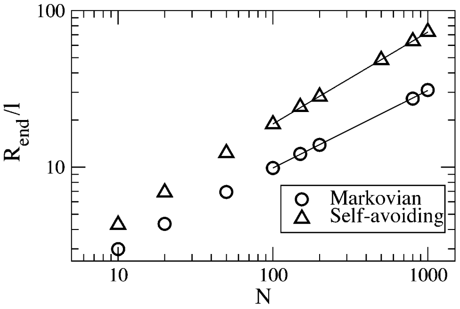

Figure 3. End-to-end distance corresponding to self-avoiding and Markovian chains, obtained from SCMF method, as a function of chain length. Solid lines show the fitted power law, $N \geq 100$; $R_{\mathrm{end}}/l = 1.27N^{0.587}$, for the case of self-avoiding walk chains (triangles), and $R_{\mathrm{end}}/l = 1.02N^{0.495}$ for Markovian chains (circles).

Table 1. Values of Radius of Gyration and End-to-End Distances Corresponding to Self-Avoiding Walk (SAW) as Well as Markovian Chains, Obtained from the Single Chain Mean Field Method, for Different Chain Lengths[a]

	N					
	32	100	200	1000	A	ν
$R_{\mathrm{g}}^{\mathrm{SAW}}/l$	3.69	7.45	11.29	29.34	0.49	0.593
$R_{\mathrm{end}}^{\mathrm{SAW}}/l$	9.33	18.79	28.22	73.28	1.27	0.587
$R_{\mathrm{g}}^{\mathrm{Markov}}/l$	2.32	4.06	5.70	12.92	0.41	0.499
$R_{\mathrm{end}}^{\mathrm{Markov}}/l$	5.52	9.85	13.88	31.07	1.02	0.495

[a] The coefficient A and the exponent ν are the results of a fit of the data plotted in Figure 4, for $N \geq 100$, of the form $R_{\mathrm{g,end}}/l = AN^{\nu}$

In the case that ideal overlapping instead of self-avoiding chains are generated in the sampling, the procedure followed is the same except for the fact that there is no energy penalty if monomers overlap. Notice that the generation of ideal chains in the sampling effectively eliminates the excluded volume correlations along the chains, due to the fact that the intrachain excluded volume repulsions are incorporated into the mean field $\pi(\mathbf{r})$. This fact leads to a sampling with more compact conformations that will produce a different qualitative behavior. In this case, the results issued from SCMF theory should quantitatively agree with SCF calculations.

3.2. Structure of the Adsorbed Layer As Predicted by SCMF. Let us first consider the predictions of the one-chain properties for a homogeneous system. In Figure 3, we show the functional dependence of the end-to-end distance of the chains with respect to the number of segments N, in a system with a homogeneous polymer density, as obtained from our SCMF methodology. We compare the SCMF results obtained from the generation of self-avoiding (or non-Markovian) chains with those of overlapping (Markovian) chains. The numerical results of the end-to-end distance as well as the radius of gyration for both kinds of chains are listed in Table 1.

Notice that the physical problem posed in both cases is exactly the same, but the methodology differs in the allowed conformations of the chains in the mean field, that is, in the choice of the reference state on which the

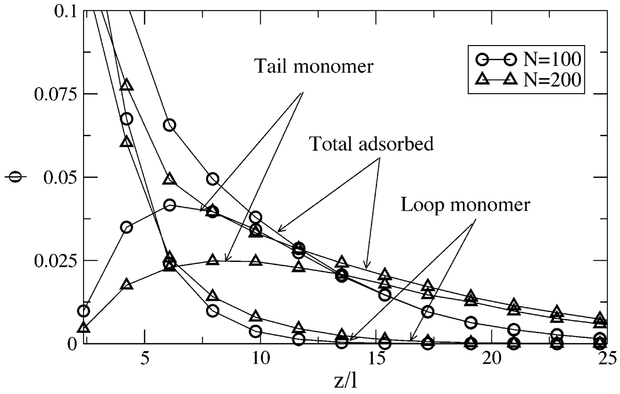

Figure 4. Representation of loop, tail and adsorbed monomer volume fraction profiles, obtained from the single chain mean field method (SCMF), corresponding to chains of $N = 100$ (circles) and $N = 200$ (triangles) at bulk monomer volume fractions $\phi^0 \simeq 0.058$ and $\phi^0 \simeq 0.033$, respectively. In both cases, $\epsilon = -0.35kT$.

mean field is built. The power law behavior found for the radius of gyration with self-avoiding chains in the sampling is very close to that observed in excluded volume statistics, $R_g \sim lN^\nu$, with $\nu \simeq {}^3/_5$.[30,31] On the other hand, the results for ideal chains are compatible with Gaussian (ideal chain) statistics, yielding an exponent $\nu \simeq {}^1/_2$.

It is important to mention that the results found for R_g as well as for R_{end}, by means of the SCMF calculations for both, self-avoiding and ideal chains, are independent of the bulk monomer concentration c^0 used in the calculations. Therefore, the SCMF formulation used in this work cannot properly describe the crossover between excluded volume statistics in dilute solution and ideal chain statistics in a melt, as given by the scaling expression

$$R_g \sim l(l^3c^0)^{-1/8}N^{1/2} \tag{3.2}$$

Thus, the theory cannot properly predict the screening of the excluded volume correlations along the chain backbone by the local monomer concentration[6] in the bulk. Thus, the chains are excessively swollen even at large bulk concentrations.[18] This effect is especially noticeable when long chains in semidilute solutions are considered. However, it is irrelevant for short chains where the SCMF method has mainly been applied[19] since the overlap concentration is then much higher. It is also irrelevant for the structure of the adsorbed layer due to the marginal overlap of loops and tails in the inhomogeneous region; i.e., no screening of the excluded volume correlations occur in the region of the inhomogeneity. SCF calculations, in turn, predict ideal chain statistics at all concentrations.

Let us consider adsorption on a plane wall using only self-avoiding chains from now on. Figure 4 shows typical results of the internal structure of the layer obtained by means of SCMF. In this case, we present results for loop, tail and adsorbed monomer volume fractions for two different chain lengths, $N = 100$ and $N = 200$, at bulk monomer fractions $\phi^0(N = 100) \simeq 0.058$ and $\phi^0(N = 200) \simeq 0.033$, corresponding roughly to half of the overlap concentration $\phi^* \equiv 3v_pN/4\pi R_g{}^3$ in each case. The adsorption energy is $\epsilon = -0.35kT$, above the threshold of adsorption, the latter estimated to be around $\epsilon = -0.28kT$ from our calculations (a similar value is obtained in MC simulations reported in ref 33). Below this energy value, monomer depletion in the first layer near the wall is observed. In Figure 5, we have represented the adsorbed monomer volume fraction profile of the previous systems using a logarithmic scale. The figure shows that there is a regime near the wall that can be considered as following a power-law decay. The exponent obtained from the fit is -1.26 for $N = 100$ and -1.23 for $N = 200$, both very close to the scaling exponent $-4/3 \simeq -1.33$, obtained in the limit $N \to \infty$.[7]

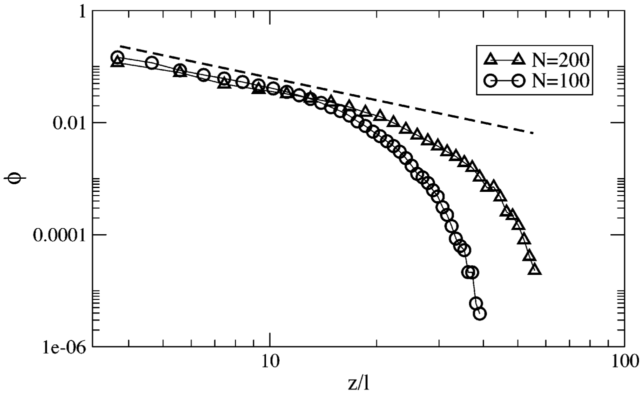

Figure 5. Representation of the adsorbed monomer volume fraction profiles corresponding to chains of $N = 100$ (circles) and $N = 200$ (triangles), obtained from single chain mean field approach (SCMF), at bulk monomer volume fractions $\phi^0 \simeq 0.058$ and $\phi^0 \simeq 0.033$, respectively. In both cases, $\epsilon = -0.35kT$. The dashed line corresponds to a power law of -1.33.

Although there is a reasonable agreement between our numerical exponent and the scaling results (valid in the $N \to \infty$ limit), we have found that indeed the initial apparent power-law decay depends in fact on the bulk concentration in this regime of chain lengths[2]. This fact indicates that we are not in the asymptotic long chain $N \to \infty$ scaling regime. In our case and for the studied chain lengths the $-{}^4/_3$ exponent is only found if the concentration is near the crossover. This fact has already been pointed out in refs 34 and 35, with which our results quantitatively agree. A detailed discussion of the structure of the adsorbed layer predicted by this methodology in comparison with Markovian SCF as well as Monte Carlo simulations will be given in ref 2. In this latter reference, the concentration dependence of the exponents in the decay of the monomer density is discussed.

Together with the monomer volume fraction profiles, we have also obtained the end-monomer distribution profile, which is shown in Figure 6 using a logarithmic scale. The end-monomer distribution is a difficult quantity to obtain from simulations, since the relevant property scales as the number of chains in the system, instead of as the number of monomers. This number is usually too small to obtain good statistical sampling for an acceptable computer time. The reasonable quality of our data indicates the adequacy of the importance sampling method introduced in this work in the solution of the SCMF problem. The end-monomer distribution is of special theoretical interest since its decay near the adsorbing wall involves the so-called *magnetic susceptibility* exponent $\gamma \simeq 1.162$ in $d = 3$ (or $\gamma = 1$ in $d = 4$, which is also the value corresponding to the Markovian mean field), which is independent of the Flory exponent ν.[6] Scaling arguments for $N \to \infty$ predict a decay of the form

$$c_{end}(z) \sim z^{-\beta/\nu} \tag{3.3}$$

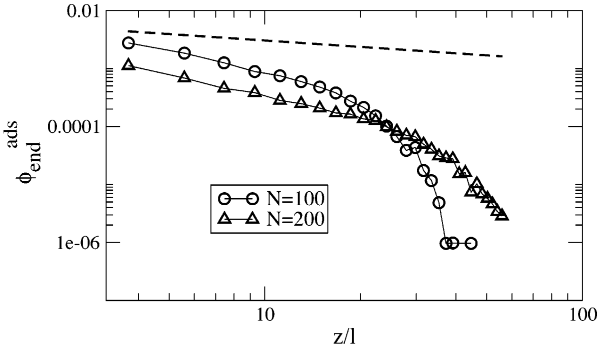

Figure 6. End-monomer distribution profiles, corresponding to the adsorbed chains obtained from single chain mean field method (SCMF), for $N = 100$ (circles) and $N = 200$ (triangles) at bulk monomer volume fractions $\phi^0 \simeq 0.058$ and $\phi^0 \simeq 0.033$, respectively. The dashed line corresponds to a power law of -0.532. In both cases $\epsilon = -0.35kT$.

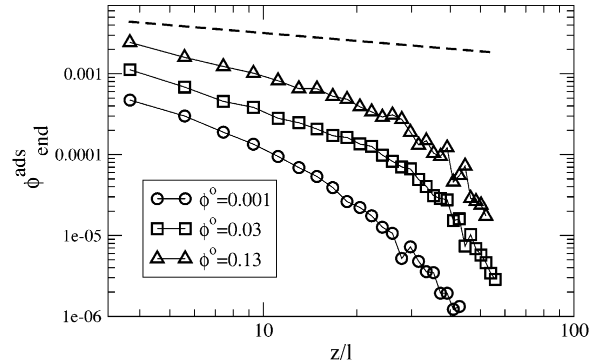

Figure 7. End-monomer distribution profiles, corresponding to the adsorbed chains obtained from single chain mean field method (SCMF), for different bulk monomer volume fractions ($f^0 = 0.001, 0.03, 0.13$). $N = 200$ and $\epsilon = -0.35kT$. The dashed line corresponds to a power law of -0.532.

where $\beta = (d\nu - \gamma)/2$, d being the dimension of space. The numerical value obtained here is $\beta/\nu \simeq 1.4$ and $\beta/\nu \simeq 1.18$ for $N = 100$ and $N = 200$, respectively, while the scaling predictions are $\beta/\nu \simeq 0.532$. For this particular property, the asymptotic predictions and the numerical SCMF results in the initial decay rate are more disparate than in the case of the total monomer density. Again, this apparent power-law behavior is a function of the concentration, giving a flatter profile as concentration increases. This fact indicates that our results cannot be directly compared with scaling predictions because the latter are only valid in the asymptotic limit $N \to \infty$, and the finite size effects seem to be very important for the polymer lengths considered here. Scaling predictions for Gaussian chains ($d = 4$, $\nu = {}^1/_2$ and $\gamma = 1$) give an exponent $\beta/\nu = 1$, valid only in the limit $N \to \infty$, which seems to be closer to our results. However, SCF calculations with Gaussian chains for a chain length $N = 200$ give an exponent $\beta/\nu \simeq 1.6$[36] higher than our SCMF results with self-avoiding conformations.

To end this section, the end-monomer distribution for different bulk concentrations is represented in Figure 7, in which $N = 200$ and $\epsilon = -0.35kT$. As already observed in the case of the monomer profiles, the initial power-law decay depends on the concentration and, therefore, we can again conclude that such short chains do not display the asymptotic regime expressed by the scaling exponents.

4. Discussion and Concluding Remarks

In this paper we have reviewed the single chain mean field methodology and introduced an importance sampling strategy that has allowed us to find new results for the case of polymer adsorption onto a flat interface. In ref 2, a detailed comparison with Monte Carlo data as well as self-consistent field calculations will be done, in support of the validity of our mean field methodology as far as quantitative results are concerned.

In comparison with previous applications of the SCMF methodology, the importance sampling introduced here has allowed us to find results for difficult quantities such as the end distribution of the adsorbed chains, even with the use of a limited number of conformations in the sampling. In our calculations, different bias fields have been tested, all aimed at gathering a large number of polymers in the vicinity of the adsorbing wall. However, the most efficient sampling, has been a bias field that coincides with the mean field energy of chain, $H_{mf}[\gamma]$, according to eq 2.14. When the configurational file has been relaxed to the Boltzmann weight, in view of eq 3.1, we can consider that all the samples are equally relevant for the averages.

A point that is in need of further improvement in our methodology is that we have chosen a dynamical procedure to relax the chains in the configurational file to the desired distribution based on the Metropolis rule. Because of the nature of the topological barriers appearing in polymer adsorption this procedure is computationally expensive, although more efficient than in equivalent Monte Carlo calculations, due to the smooth variation of the mean field.

One of the major advantages of the procedure discussed in this work comes from the fact that the physical problem and the sampling of the phase space are independent events. In this way, similar in spirit to histogram reweighting techniques in Monte Carlo simulations,[37] the same sampling in the configurational file can be used for different physical conditions. The problem reduces to computing the Lagrange multiplier field π for the actual conditions but from a sampling obtained under different conditions. In fact, the ability of this procedure is limited by the relevance of the sampling for a given physical problem. In the range of bulk concentrations that we have currently analyzed, ranging from very dilute to semidilute, two sample sets have been used. One set is obtained under dilute bulk conditions and the other set at conditions near the crossover concentration. In the same way, the adsorption energy used in the generation of the sampling has in general been set to be smaller than kT to increase the probability of desorption and permit a faster relaxation of the structure of the layer as well as to have a reasonably populated bulk. However, the sample obtained in this way can be used to describe reversible but strong adsorption situations with ϵ up to $1kT$.

As far as the results are concerned, we have obtained a qualitative description of the adsorbed layer that is in agreement with the actual picture, based on the SCF calculations of Scheutjens and Fleer[1] as well as with the theoretical work of the two order parameter theory and scaling.[8,9] Furthermore, original results on the polymer end distributions are presented. The quality of our results are indicators of the adequacy of the importance sampling method that we have developed in this work. The results, however, do not agree with the predicted scaling behavior and show a dependence on the bulk concentration, as has also been reported for other properties of polymers of similar length.[35] The agreement of the results of our methodology with Monte Carlo simulations for these properties will be discussed in ref 2. Thus, it seems that finite size effects are very important in the properties of adsorbed layers of moderately long polymeric chains. Finally, the lack of screening of the excluded volume correlations in the SCMF theory employed in this work is due to the fact that the overall excluded volume of a given conformation has been considered to be independent of the conformation itself. Here we have focused our attention on the development of an importance sampling treatment that has allowed us to obtain clear results for adsorption problems. In forthcoming works, we will explicitly take such an effect into consideration in the theory.

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