

Continuum formulation of the Scheutjens-Fleer lattice statistical theory for homopolymer adsorption from solution

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(Received 27 June 2005; accepted 24 August 2005; published online 28 October 2005)

Homopolymer adsorption from a dilute solution on an interacting (attractive) surface under static equilibrium conditions is studied in the framework of a Hamiltonian model. The model makes use of the density of chain ends $n_{1,e}$ and utilizes the concept of the propagator G describing conformational probabilities to locally define the polymer segment density or volume fraction φ ; both $n_{1,e}$ and φ enter into the expression for the system free energy. The propagator G obeys the Edwards diffusion equation for walks in a self-consistent potential field. The equilibrium distribution of chain ends and, consequently, of chain conformational probabilities is found by minimizing the system free energy. This results in a set of model equations that constitute the exact continuum-space analog of the Scheutjens-Fleer (SF) lattice statistical theory for the adsorption of interacting chains. Since for distances too close to the surface the continuum formulation breaks down, the continuum model is here employed to describe the probability of chain configurations only for distances z greater than $2l$, where l denotes the segment length, from the surface; instead, for distances $z \leq 2l$, the SF lattice model is utilized. Through this novel formulation, the lattice solution at $z=2l$ provides the boundary condition for the continuum model. The resulting hybrid (lattice for distances $z \leq 2l$, continuum for distances $z > 2l$) model is solved numerically through an efficient implementation of the pseudospectral collocation method. Representative results obtained with the new model and a direct application of the SF lattice model are extensively compared with each other and, in all cases studied, are found to be practically identical. © 2005 American Institute of Physics. [DOI: 10.1063/1.2075027]

I. INTRODUCTION

A few years ago, a hierarchical (macroscopic and microscopic) methodology was presented for studying surface effects on polymer solutions under both equilibrium (static) and nonequilibrium (flowing) conditions.¹ The approach is based on the judicious choice of a set of primary (independent) field variables defining the state of the system at the macroscopic (continuum) level. Then, a complete set of governing equations is developed through the use of the generalized bracket formalism of nonequilibrium thermodynamics.² The resulting governing equations involve the extended free energy H of the system and are valid both in the bulk and in the interfacial region. In a subsequent publication,³ the methodology was applied to the case of a polymer solution flowing past a noninteracting, planar solid

surface (a hard wall). In that work, the resulting model equations were solved numerically providing a number of interesting results for the effect of the wall on chain conformation, chain segment density, and velocity field in the interfacial region.

Here, the methodology is extended to the case of a polymer solution near an adsorbing surface under static equilibrium conditions, a problem which has received a great deal of attention in the past years.^{4–29} The interest in this problem is driven by the key role that adsorbed polymer layers play in a variety of technological applications, including their use as stabilizers in colloidal systems, lubricants, coating promoters, and many others. The new work offers a quantitative description of the homopolymer adsorption problem in continuum space by establishing also a one-to-one correspondence with the original lattice statistical theory of Scheutjens-Fleer (SF);¹⁸ the latter is generally considered as the most successful theory of polymer adsorption from the solution presented so far. The formalism is general enough

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and can be straightforwardly extended to nonequilibrium (flowing) conditions to investigate shear flow effects on the structure of the adsorbed layer.

The key in the new model is that microscopic and macroscopic field variables are consistently coupled with each other in the context of the Hamiltonian description^{2,30} by using both the number density of chain ends and the number density (or volume fraction) of polymer segments as variables in the analysis; the two densities are connected to each other with an integral equation by invoking the concept of the propagator for the definition of chain conformations. This equation plays the role of an integral constraint for the governing equations of the Hamiltonian model, as derived in the framework of the generalized bracket formalism. In the absence of flow, the governing equations reduce to a minimization problem for the system free energy; this ensures that the chemical potential of all chain conformations is constant everywhere in the adsorbed layer. A closed set of model equations is thus derived which is seen to constitute the exact continuum-space analog of the SF lattice statistical theory. Since for distances too close to the surface, the continuum formulation breaks down, the continuum model is employed to describe the probability of chain configurations only for distances z greater than $2l$, where l denotes the segment length; instead, for distances $z \leq 2l$, the SF lattice model is utilized. This is the second important feature of the present work; the lattice solution at $z=2l$ provides the boundary condition (B.C.) for the continuum model, thus totally avoiding the need for the derivation and/or specification of a continuum B.C. Numerically solving the resulting hybrid (lattice for distances $z \leq 2l$, continuum for distances $z > 2l$) model equations exactly (and not approximately) for any chain length through a novel implementation of the pseudospectral element method is the third unique feature of this work.

The rest of the paper is organized as follows: Section II presents the model equations and establishes the analogy with the SF lattice model.¹⁸ In Sec. III, we present the spectral collocation method used to solve the resulting equations numerically, without invoking an expansion of the partition function to a series of eigenfunctions. In Sec. IV, we present representative numerical results for the segment density profile, free segment probability, and partition function for some representative values of the variables of the problem (chain length N , energy of adsorption χ_s , bulk segment volume fraction ϕ_b , and Flory-chi parameter χ), together with a detailed comparison with the data obtained through a direct application of the SF model. Finally, in Sec. V, we outline our conclusions.

II. MODEL EQUATIONS: ANALOGY WITH THE SCHEUTJENS-FLEER LATTICE MODEL

A. General formalism

Assuming incompressibility (i.e., a constant total mass density ρ_0 for the polymer solution), the following set of primary (independent) field variables is chosen to define the state of the system in the context of the two-fluid Hamiltonian model employed here: The polymer chain number density n_1 , the total momentum density $\mathbf{M}=\rho_0\mathbf{v}$, where \mathbf{v} is

the total velocity field, and an internal structural parameter $\mathbf{C}=\rho_0n_1\mathbf{c}$, where \mathbf{c} is a second-order tensor representing the average conformation of polymer molecules (that is, their conformation in an overall sense). For an isolated Rouse chain, \mathbf{c} can be identified with the second moment tensor of the distribution function for the chain end-to-end vector averaged over all chains.

In the Hamiltonian formalism, the polymer solution is characterized by a free-energy functional H , which is the sum of a kinetic-energy term H_k and an internal free-energy term H_i ,

$$H \equiv H_k + H_i + \int [h_k(z) + h_i(z)]Adz, \quad (1)$$

where h_k is the kinetic energy and h_i the internal free-energy density, A stands for the surface area in the xy plane of the coordinate system, and z denotes the space coordinate perpendicular to the surface. (Note that in Refs. 1 and 3, the coordinate normal to the solid boundary had been denoted by y , and not by z .) The internal free-energy density h_i is considered to be a function of n_1 , \mathbf{C} , and position vector \mathbf{r} .

The set of governing equations is derived by invoking the generalized bracket formalism of nonequilibrium thermodynamics and in general includes the momentum equation, the constitutive equation, and the concentration equation. To close this set of equations one needs further to do the following:

- (i) Account for the connectivity of segments in chains. This is achieved by introducing the concept of the propagator. Under no flow conditions, such a propagator is denoted as $G(z, n; z_0)Adz$ and is proportional to the thermodynamically weighted number fraction of n -segment long subchains that start at z_0 above the surface and end at z within dz .
- (ii) Specify the way of counting chains. Following Ref. 1, this is achieved by introducing as reference points the chain ends. The polymer segment volume fraction ϕ is then related to the density of chain end points $n_{1,e}$ through the propagator G by the following consistency relation:

$$\phi(z) = \sum_{n=0}^{N-1} \int_0^\infty \frac{1}{2} n_{1,e}(z_0) P(z, n; z_0) dz_0. \quad (2)$$

$P(z, n; z_0)$ in Eq. (2) is defined as

$$P(z, n; z_0) \equiv G(z, n; z_0) \frac{\int_0^\infty G(z', N-1-n; z) dz'}{\int_0^\infty G(z', N-1; z_0) dz'} \\ \equiv G(z, n; z_0) \frac{Z(N-1-n, z)}{Z(N-1; z_0)}, \quad (3)$$

where $Z(n, z_0)$ denotes the partition function of an n -segment long subchain starting at distance z_0 above the surface,

$$Z(n, z_0) \equiv \int_0^\infty G(z, n; z_0) dz, \quad (4)$$

and expresses the *joint probability* that a chain with

its origin at z_0 above the surface will reach z (within dz) in n steps and its remaining part will be above the confining boundary.³¹

- (iii) Define the internal part of the free-energy density h_i . If χ_s denotes the adsorption energy parameter (in $k_B T$ units), φ_s the polymer-segment-surface fraction (representing the segment volume fraction at $z=0$), and u_s the adsorption energy of a solvent molecule, then, under equilibrium conditions, h_i is given through (see Ref. 1)

$$\begin{aligned} \frac{h_i}{\rho_0 k_B T} &= u_s - \varphi_s \chi_s \delta(z) \\ &+ \frac{1}{2} n_{1,e}(z) \ln \left[\frac{n_{1,e}(z)}{2} \frac{N}{Z(N-1, z)} \right] \\ &+ (1 - \varphi(z)) \ln(1 - \varphi(z)) + \chi \varphi(z) (1 - \varphi(z)). \end{aligned} \quad (5)$$

B. The polymer segment profile

When no flow is applied on the polymer solution, the governing equations (see Ref. 1) reduce to the following equilibrium condition:

$$\left. \frac{\delta H_i}{\delta n_{1,e}} \right|_z = \left. \frac{\delta H_i}{\delta n_{1,e}} \right|_b, \quad \forall z \geq 0, \quad (6)$$

where the subscript b refers to bulk conditions. Equation (6) ensures that the chemical potential for all chain conformations is constant everywhere ($\forall z \geq 0$) in the interfacial region. By calculating the Volterra derivative $\delta H_i / \delta n_{1,e}$ based on expression (5) for h_i , using $(\partial h_{\text{mix}} / \partial \varphi)(z_0) = -\ln(1 - \varphi(z_0)) - 2\chi\varphi(z_0)$ corresponding to a Flory-Huggins expression for the random mixing term (see Ref. 1), solving for $n_{1,e}$,

$$\begin{aligned} \ln \left[\frac{n_{1,e}(z)}{n_{1,b}} \right] &= \ln Z(N-1, z) + \int_0^\infty [\ln(1 - \varphi(z_0)) + 2\chi\varphi(z_0)] \\ &\times \left[\sum_{n=0}^{N-1} P(z_0, n; z) - \sum_{n=0}^{N-1} P(z_0, n; \infty) \right] dz_0, \end{aligned} \quad (7)$$

and substituting back to (2) leads to the following expression for the segment volume fraction:

$$\begin{aligned} \varphi(z) &= \frac{\varphi_b}{N} \sum_{n=0}^{N-1} Z(N-1-n, z) \\ &\times \int_0^\infty \left[\frac{e^{\int_0^{z_1} [\ln(1-\varphi(z_1)) + 2\chi\varphi(z_1)] \sum_{n=0}^{N-1} P(z_1, n; z_0) dz_1}}{e^{\ln(1-\varphi_b) + 2\chi\varphi_b}} \right] \\ &\times G(z, n; z_0) dz_0, \end{aligned} \quad (8)$$

where φ_b denotes the bulk value.

Equation (8) is an exact expression; however, it appears to involve two sums and two integrals whose calculation restricts its applicability practically to rather short chain length systems. To cope with it, we make the approximation that $P(z_1, n; z_0) \cong \delta(z_1 - z_0) \delta(n)$; simple algebraic manipulations then lead to the following formula for $\varphi(z)$:

$$\begin{aligned} \varphi(z) &= \frac{\varphi_b}{N} \sum_{n=0}^{N-1} Z(N-1-n, z) \\ &\times \int_0^\infty e^{[(\ln(1-\varphi(z_0)))/(1-\varphi_b)] + 2\chi(\varphi(z_0) - \varphi_b)} G(z, n; z_0) dz_0, \end{aligned} \quad (9)$$

which can also be written in a more compact form, if we define the quantity $p(z)$ through

$$p(z) \equiv \exp(-\Delta U(z)), \quad (10)$$

where

$$\Delta U(z) \equiv -\ln \left(\frac{1 - \varphi(z)}{1 - \varphi_b} \right) - 2\chi(\varphi(z) - \varphi_b), \quad (11)$$

(in units of $k_B T$), as

$$\varphi(z) = \frac{\varphi_b}{N} \sum_{n=0}^{N-1} Z(N-1-n, z) \int_0^\infty p(z_0) G(z, n; z_0) dz_0. \quad (12)$$

C. Analogy with the SF lattice theory

The above analysis allows us to make the following analogies with the SF lattice theory:

- (i) The partition function $Z(n, z_0)$ in the continuum theory is identified with the end-segment probability $P(i, s)$, i.e., the probability that the end segment of an s -mer is in layer i , in the SF theory.
- (ii) Equation (7) is identical to the corresponding equilibrium condition of the SF theory [see Eqs. (22) and (23) in Ref. 18] defining the number n_d of polymer molecules in conformation d .
- (iii) The sum $\sum_{n=0}^{N-1} P(z_0, n; z)$ that appears inside the integral on the right-hand side of (7) is the contribution to the segment fraction at plane z_0 of all possible paths through which a chain starting at z can reach z_0 ; it corresponds therefore to the number of segments $r_{i,d}$ that conformation d has at layer i in the SF theory.
- (iv) The quantity $p(z)$ defined by Eq. (10) is identified with the free segment probability p_i in layer i with respect to the bulk solution in the SF theory [see Eqs. (24), (38), and (39) in Ref. 18]. The correction due to the adsorption potential does not appear in Eq. (10), since, in the hybrid model introduced here, the continuum model does not apply for distances $z \leq 2l$.
- (v) The quantity $\Delta U(z)$ defined by Eq. (11) is identified with the *self-consistent field* derived by Helfand and co-workers¹⁴⁻¹⁶ and used throughout the work of Ploehn *et al.*,²¹ Ploehn and Russel,²² and in the SF lattice statistical theory [see Eqs. (24), (38), and (39) in Ref. 18].
- (vi) Equation (8) for the segment profile $\varphi(z)$ is very similar (but not identical) to the corresponding expression reported by SF in their lattice model [Eq. (45) in Ref. 18]. The difference lies in the form of the term involving the free segment probabilities. The analog of the

complicated term $\{e^{\int_0^z [\ln(1-\varphi(z_1))+2\chi\varphi(z_1)] \sum_{n=0}^{N-1} P(z_1,n;z_0) dz_1}\} / [e^{\ln(1-\varphi_b)+2\chi\varphi_b}]$ in the continuum model, which was further approximated by $p(z_0)$ in Eq. (12), is the much simpler term $1/p(z)$ in the lattice model. This small discrepancy between the two descriptions is related to the use of Boltzmann correction factors in the lattice model when converting subchain probabilities $P_{k(t,c)} \times (t=1, \dots, s-1)$ and $P_{k(t,c)} (t=s+1, \dots, r)$ not sharing the intermediate segment s to subchain probabilities $P_{k(t,c)} (t=1, \dots, s)$ and $P_{k(t,c)} (t=s, \dots, r)$ sharing s [see Eq. (27) in Ref. 18]; no such Boltzmann correction factors are introduced in the present continuum theory.

Given the slight discrepancy between continuum and lattice models in the use of Boltzmann correction factors, our continuum theory is formulated here only for distances z greater than two segments long from the surface (i.e., for $z > 2l$) for which one can safely assume that $p(z) \cong 1$; furthermore, the same use of the Boltzmann correction factor in the equation for the polymer segment volume fraction will be made as in the original SF lattice model. In contrast, for distances $z \leq 2l$ the discrete version will be adopted (see Sec. II D below) in which adsorption energy effects on the free segment probability are explicitly accounted for. By expanding $p(z)$ in a Taylor series in terms of the variable $\varphi(z) - \varphi_b$, one can show that the assumption $p(z) \cong 1$ for $z > 2l$ is strictly valid for conditions such that $|\varphi(z) - \varphi_b| \leq 10^{-1} \forall z > 2l$, which, as the SF work demonstrated, is an excellent approximation. Indeed, as can be seen in Table I of the Scheutjens-Fleer's first paper,¹⁸ for all lattice layers except the first two, $p(z)$ deviates only infinitesimally from 1. Consequently,

$$\varphi(z) = \frac{\varphi_b}{N} e^{\Delta U(z)} \sum_{n=0}^{N-1} Z(n,z) Z(N-1-n,z). \quad (13)$$

This is the equation that we will use here to calculate $\varphi(z)$ from the partition function $Z(n,z)$ for all distances $z > 2l$. It is also identical to the expression that Ploehn *et al.*²¹ and Ploehn and Russel²² heuristically introduced in their analytical work to relate $\varphi(z)$ to $Z(n,z)$. According to (13), to calculate the segment volume fraction profile, one needs to determine the partition function $Z(n,z_0)$; this is discussed in Sec. II D.

D. The equation for the self-consistent mean field and the propagator

By analogy with the SF lattice model, the total potential $\Delta U(z)$ is taken to be the sum of (a) the self-consistent field (SCF) U_{SCF} , accounting for segment-segment and segment-solvent interactions, and (b) the surface adsorption potential U_{ads} , accounting for the preferential adsorption of polymer segments over solvent molecules on the surface,

$$\Delta U(z) = U_{\text{SCF}} + U_{\text{ads}}. \quad (14)$$

Since Flory's polymer solution theory³² is employed here, and by accounting for nonlocal effects in the way analyzed by Hong-Noolandi,³³

$$U_{\text{SCF}} = -\ln \frac{(1-\varphi)}{(1-\varphi_b)} - 2\chi(\varphi - \varphi_b) - 2\lambda_1 \chi \frac{d^2 \varphi}{dz^2} \quad (15)$$

(in $k_B T$ units). The constant λ_1 denotes the fraction of nearest neighbors in the adjoining lattice layers and equals $\frac{1}{6}$ in a cubic and $\frac{1}{4}$ in a hexagonal lattice.

As far as the form of the adsorption potential is concerned, for a surface potential with a length scale comparable to the length of the Kuhn segment and an adsorption energy χ_s (in units of $k_B T$) per segment relative to the solvent, U_{ads} is described through the "sticky" condition [see also Eq. (5)]:

$$\frac{U_{\text{ads}}(z)}{k_B T} = \begin{cases} \infty, & z < 0 \\ -\chi_s, & z = 0 \\ 0, & z > 0. \end{cases} \quad (16)$$

The partition function (or integrated propagator) $Z(n,z)$ obeys the Edwards diffusion equation³¹ subject to an appropriate set of initial and boundary conditions as dictated by the physics of the problem. Unfortunately, the corresponding initial-boundary value (ibv) problem suffers from two shortcomings:

- (i) The first is numerical and is associated with the discontinuity of the potential $\Delta U(z)$ at $z=0$.
- (ii) The second is conceptual and is associated with the use of the diffusion equation even down to length scales smaller than one segment length.

To deal with these two shortcomings, a hybrid model is proposed here by treating the SF lattice model as the BC for the continuum Edwards model. According to this model:

- (i) The continuum approach applies only for distances $z > 2l$;
- (ii) for distances $z \leq 2l$, the lattice description is kept; and
- (iii) at $z=2l$, the two descriptions should match each other.

The most important aspects of such a hybrid model are the following:

- (i) It consistently extends the original SF lattice theory to continuum space by avoiding the use of approximate or obscure boundary conditions.
- (ii) All nice features of the SF lattice theory (such as the correct description and consistent implementation in the model of segment-segment, segment-solvent, and segment-surface interactions, the correct treatment of excluded volume effects, the incorporation of end effects, the calculation of tail configurations, etc.) are kept in the model.
- (iii) The continuum equations are derived through the Hamiltonian formalism of continuum mechanics that ensures the internal, thermodynamic consistency of the resulting equilibrium conditions.
- (iv) It does not suffer from limitations related to the size

of chains for which numerical calculations can be carried out. On the contrary, computations with truly long chains (longer than $N=100\,000$) are possible with the new model; these can be used to derive scaling laws describing the spatial dependence of the volume fraction of segments in tails and loops, which are

still lacking. Detailed results from such computations will be presented in a forthcoming paper.³⁴

Mathematically, the new hybrid (lattice for $z \leq 2l$, continuum for $z > 2l$) self-consistent-field model is described by the following set of equations:

$$\left\{ \begin{array}{l} \frac{\partial Z(n,z)}{\partial n} = \frac{l^2}{6} \frac{\partial^2 Z(n,z)}{\partial z^2} - \Delta U(z)Z(n,z), \\ \Delta U(z) = -2\chi(\varphi(z) - \varphi_b) - \ln\left(\frac{1 - \varphi(z)}{1 - \varphi_b}\right) - 2\lambda_1\chi \frac{d^2\varphi}{dz^2}, \\ \varphi(z) = e^{\Delta U(z)} \frac{\varphi_b}{N} \sum_{n=0}^{N-1} Z(n,z)Z(N-1-n,z), \end{array} \right. \quad z > 2l, \quad (17a)$$

$$\left\{ \begin{array}{l} e^{\Delta U_z} Z_{n+1,z} = Z_{n,z} + \lambda_1(Z_{n,z-1} - 2Z_{n,z} + Z_{n,z+1}), \\ \Delta U_z = -(\chi_s + \lambda_1\chi)\delta_{z-1} - 2\chi(\langle\varphi_z\rangle - \varphi_b) - \ln\left(\frac{1 - \varphi_z}{1 - \varphi_b}\right), \\ \varphi_z = e^{\Delta U_z} \frac{\varphi_b}{N} \sum_{n=1}^N Z_{n,z}Z_{N-1-n,z}, \end{array} \right. \quad z \leq 2l, \quad (17b)$$

with initial and boundary conditions specified according to the following rules:

$$\text{at } n=0, \quad Z(n,z) = 1, \quad \forall z \geq 0,$$

$$\text{at } z=0, \quad \left\{ \begin{array}{l} e^{\Delta U_z} Z_{n+1,z} = Z_{n,z} + \lambda_1[0 - 2Z_{n,z} + Z_{n,z+1}], \quad \forall n \geq 1, \\ \Delta U_z = -(\chi_s + \lambda_1\chi) - 2\chi(\varphi_z - \varphi_b) - \ln\left(\frac{1 - \varphi_z}{1 - \varphi_b}\right) - 2\lambda_1\chi(0 - 2\varphi_z + \varphi_{z+1}), \end{array} \right.$$

$$\text{at } z=\infty, \quad Z(n,z) = 1, \quad \forall n \geq 0. \quad (18)$$

Note here that in writing down Eqs. (17b) and (18) referring to the lattice model, the convention has been made²⁶ that z and n should appear as subscripts and not as continuum variables; further, $n=1, \dots, N$.

The full form of the hybrid (lattice-continuum) problem of Eqs. (17) and (18) has never been addressed so far. Simplifications of it, however, arising by assuming an approximation for the B.C. and by expanding the partition function $Z(n,z)$ into a series of eigenfunctions, have been considered in a number of works.²⁴⁻²⁷ It is the purpose of this paper to address and solve the new model exactly without any expansion of $Z(n,z)$ to eigenfunctions.

III. METHOD OF COMPUTATION

To solve the governing equations of the hybrid model, Eqs. (17) and (18), we note that these involve three strongly

coupled subproblems: The inner or lattice problem describing chain configurations at $z=0$, $z=l$, and $z=2l$; the outer or continuum problem describing chain configurations at distances beyond $z=2l$ from the surface; and the matching problem at $z=2l$. The three problems are solved here with the pseudospectral element method^{35,36} in a stagewise fashion as follows (see proposed algorithm below):

- (i) First, an initial guess is made for the propagator $Z_{n,z}$ at the matching layer, $z=2l$, which allows one to solve the outer problem for all distances $z > 2l$ through pseudospectral iterations and a numerical calculation of the respective Jacobian.
- (ii) The solution of the continuum model at all distances $z > 2l$, thus also at $z=3l$, is utilized to solve the lattice model at $z=l$ and $z=2l$.
- (iii) The solution of the inner or lattice problem provides a new guess for the continuum model at $z=2l$ and the pseudospectral iterations continue until convergence.

```

.....
assume  $\varphi(z) \forall z > 0$ 
1  continue
   assume  $Z_{n,z}, n=1, \dots, N$  at  $z=2l$ 
11 continue
   solve the outer problem, Eq. (17a), to obtain  $Z(s, z)$  for  $z > 2l, \forall s=0, \dots, 1$ 
   use  $Z(s, z)$  for  $z=3l$  to solve the inner (lattice) problem, Eq. (17b), to obtain  $Z_{n,z}$  at  $z=2l$ 
       is  $Z_{n,z}$  at  $z=2l$  equal to its previous value for all  $n=1, \dots, N$ ?
           if (not) update guess and go to 11
           if (yes) continue
       end if
   continue
   calculate  $\varphi(z) \forall z > 0$  using Eq. (13)
       is  $\varphi(z)$  equal to its previous value  $\forall z > 0$ ?
           if (not), update  $\varphi(z) \forall z > 0$  and go to 1
           if (yes) finished
       end if

```

Proposed algorithm for the calculation of the new hybrid (lattice-continuum) model, Eqs. (17) and (18).

Lattice and continuum descriptions of the propagator at $z=2l$ differ in nature: in the lattice model, $Z_{n,z}$ at $z=2l$ is known for all values of n from 1 up to chain length N ; in contrast, in the continuum model, $Z(n, z)$ is known only at the N_c collocation points with N_c being typically a small number compared to N (and, usually, independent of N); for example, $N_c=31$ up to 41. $Z_{n,z}$ and $Z(n, z)$ values at $z=2l$ are therefore matched through interpolation (or, equivalently, extrapolation). Also, in the method followed here, the segment volume fractions at the nodal points have been chosen to be the unknown functions; for the matching problem, the unknown functions include the values of the lattice propagator, $Z_{n,z}, n=1, \dots, N$ at $z=2l$.

As far as the numerical method is concerned, we mention that in pseudospectral approximation, a function $f(\xi)$ is represented in one dimension as a truncated series of Chebyshev polynomials,³⁶

$$f(\xi) = \sum_{i=0}^{N_c} a_i T_i(\xi), \quad (19)$$

where $\xi \in [-1, +1]$, $T_i(\xi)$ is the i th-order Chebyshev polynomial, N_c is the upper limit of the truncated series, and a_i is the coefficient of the i th-order term; the latter are determined by the solution of the problem. The Chebyshev polynomials are eigenfunctions of a singular Sturm-Liouville problem and can be expressed, in the interval $\vartheta \in [0, 2\pi]$, as

$$T_i(\cos \vartheta) = \cos(i\vartheta). \quad (20)$$

The grid points are defined as the extrema of the highest-order Chebyshev polynomial,

$$\xi_k = \cos\left(\frac{\pi k}{N_c}\right). \quad (21)$$

From (19), it is apparent that the derivatives of the function f can be expressed analytically by differentiating the right-hand side. In an alternative formulation, the coefficients a_j can be expressed in terms of the values f_j of the function

f at the discrete N_c points. Then the discrete values of the first derivative can also be expressed in terms of f_j 's with a linear operation of the form³⁶

$$\left. \frac{df}{d\xi} \right|_j = \sum_{k=0}^{N_c} D_{jk} f_k, \quad (22)$$

where D_{jk} is the jk th component of the derivative matrix \mathbf{D} defined as

$$D_{jk} = \frac{C_j (-1)^{k+1}}{C_k \xi_j - \xi_k} \quad (j \neq k), \quad D_{jj} = -\frac{\xi_j}{2(1 - \xi_j^2)}, \quad (23)$$

$$D_{00} = -\frac{2N_c^2 + 1}{6} = -D_{N_c N_c},$$

with the coefficients C_j given by

$$C_0 = C_{N_c} = 2, \quad C_j = 1 \quad (1 \leq j \leq N_c - 1). \quad (24)$$

Higher-order derivatives are defined in exactly the same way. Alternatively, the derivatives can be calculated by utilizing a fast Fourier transform (FFT), since a different way of defining the Chebyshev interpolation is through a Fourier one in a suitably mapped circular domain.³⁵

In the pseudospectral approximation, the expressions for the derivatives are substituted in the original system of equations, which thus involves only the discrete values f_j . Mesh refinement is achieved by increasing the order of the truncated series in Eq. (19). Since the governing equations are solved in the transformed domain, the derivatives of the transformation need also to be defined. For computational convenience, one can approximate the coordinates of the original domain (e.g., z) by an analytic function of the coordinate (e.g., ξ) in the transformed domain through a similar spectral expansion. For example, $z \in [l, \infty)$ can be mapped onto $\xi \in [-1, +1]$ by using

$$z = l - L \ln\left(\frac{1 - \xi}{2}\right), \quad (25)$$

where L is a constant setting the length scale of the mapping. In addition, to avoid the appearance of negative values for

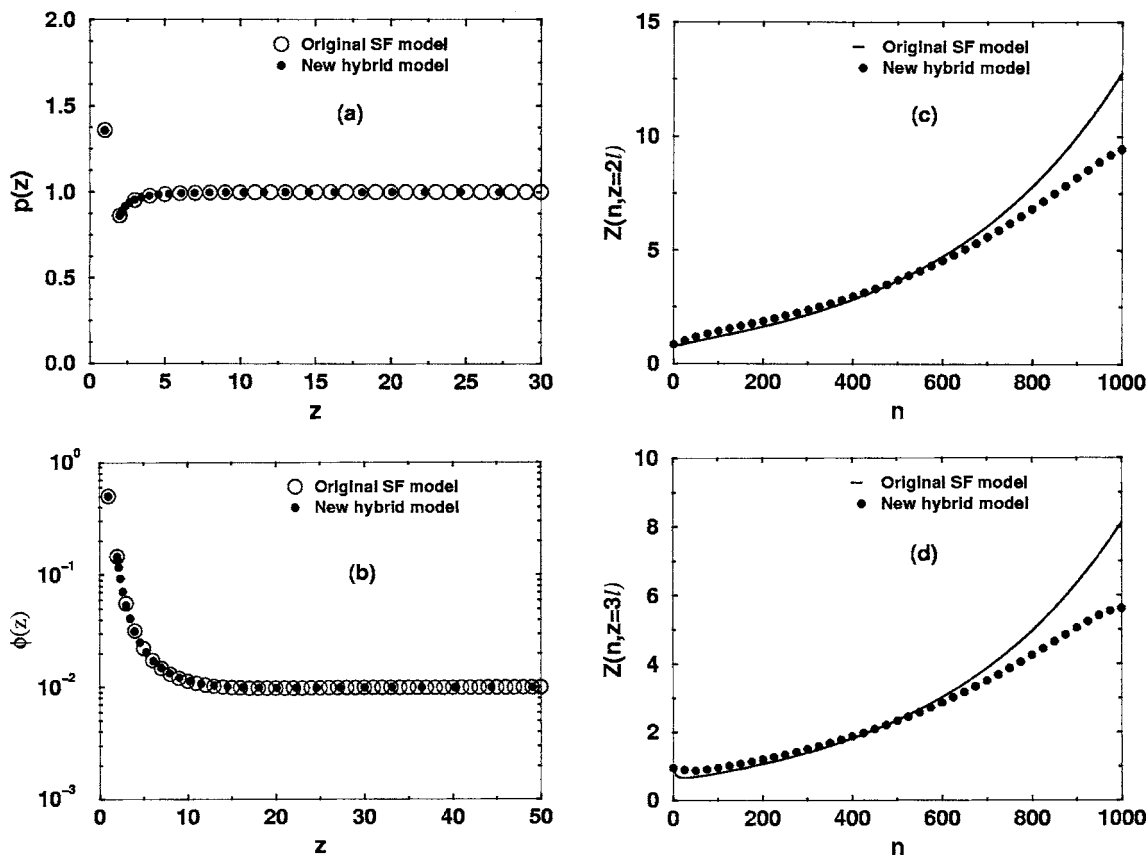


FIG. 1. (a) The z profile of the free segment probability $p(z)$. (b) The z profile of the segment density $\phi(z)$. (c) Equilibrium values of the propagator $Z(n, z)$ in the hybrid model as a function of n , at $z=2l$ (i.e., at the matching layer). (d) Equilibrium values of the propagator $Z(n, z)$ in the hybrid model as a function of n at $z=3l$ (i.e., at the layer that follows the one where continuum and lattice descriptions are matched). Also shown for comparison are the results obtained with the original SF model for the same set of input data: $N=1000$, $\phi_b=10^{-2}$, $\chi_s=1$, and $\chi=0$ (corresponding to an athermal solvent).

$Z(n, z)$ in the course of the spectral iterations that could destroy the convergence of the numerical algorithm, it is best if one works with the auxiliary function $F(n, z)$ defined through $Z(n, z) \equiv \exp(F(n, z))$; $F(n, z)$ is then the unknown function actually employed in the numerical calculations.

For chain lengths N longer than about 100, the calculation of the volume fraction $\phi(z)$ through the sum of Eq. (26) becomes the most CPU time-consuming step and practically prevents studying systems of length N higher than 1000. To speed up computations, the sum can be approximated by its equivalent (continuum) integral form through

$$\phi(z) = e^{\Delta U(z)} \phi_b \int_0^1 Z(s, z) Z(1-s, z) ds, \quad (26)$$

where $s \equiv n/N$; the resulting integral can then be calculated pseudospectrally by transforming it to the scalar product of two vectors (see Appendix).

With an appropriate initial guess, the proposed numerical scheme solves each of the three subproblems within three to four iterations with a relative error of less than 10^{-8} . This has allowed us to calculate systems of practically any chain length within modest CPU time and little memory requirements. Representative results from these calculations for a value of chain length $N=1000$ are reported and discussed in Sec. IV of this paper. Computations with significantly longer chains (up to $N=100\,000$) will be presented in a forthcoming publication.³⁴

IV. RESULTS: DETAILED COMPARISON WITH THE SF LATTICE MODEL

In this section, we present a selection of numerical results for the dependence of the polymer volume fraction $\phi(z)$ on parameters related to the polymer-solvent-surface system. The data are presented for $N=1000$, $\chi_s=1$, and two different values of ϕ_b (equal to 10^{-6} and 10^{-2}) and χ (equal to 0.0 and 0.5). All results have been obtained by approximating the unknown functions $Z(n, z)$ or $F(n, z)$ in the pseudospectral method with a series of Chebyshev polynomials of degree up to the order $N_c=41$ along both n and z , see Eq. (19); of course, in all cases studied, the data were thoroughly checked for convergence with mesh refinement. The comparison with the SF model was always made for the case of a simple cubic lattice ($\lambda_1 = \frac{1}{6}$).

Parts (a) and (b) of Figs. 1–4 present examples from the numerical calculations of the new work with the hybrid (lattice-continuum) model for the variation of the free segment probability $p(z)$ and segment volume fraction $\phi(z)$ profiles with distance z from the surface and their dependence on solvent quality and bulk polymer volume fraction. Also shown in the figures are the results of the numerical calculations with the original SF lattice model. The agreement between the two sets of data is striking; in all cases studied, the obtained $\phi(z)$ and $p(z)$ profiles practically coincide. The excellent agreement between the classical SF lattice and the new hybrid models is further demonstrated in parts (c) and

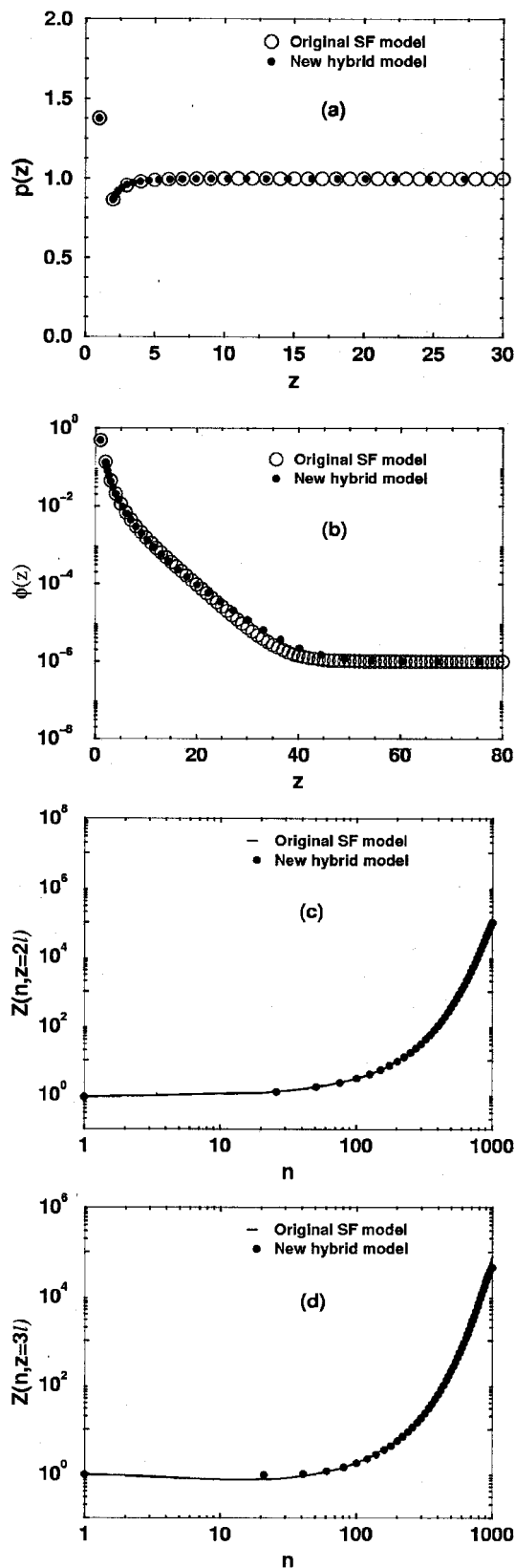


FIG. 2. Same as with Fig. 1 but for the following set of input data: $N = 1000$, $\phi_b = 10^{-6}$, $\chi_s = 1$, and $\chi = 0$ (corresponding to an athermal solvent).

(d) of Figs. 1–4 where the comparison is extended to the level of the propagator $Z(n, z)$ at $z = 2l$ (the matching layer) and at $z = 3l$ (the layer right next to the matching one). Two sets of data are shown in these figures: the first set (full lines)

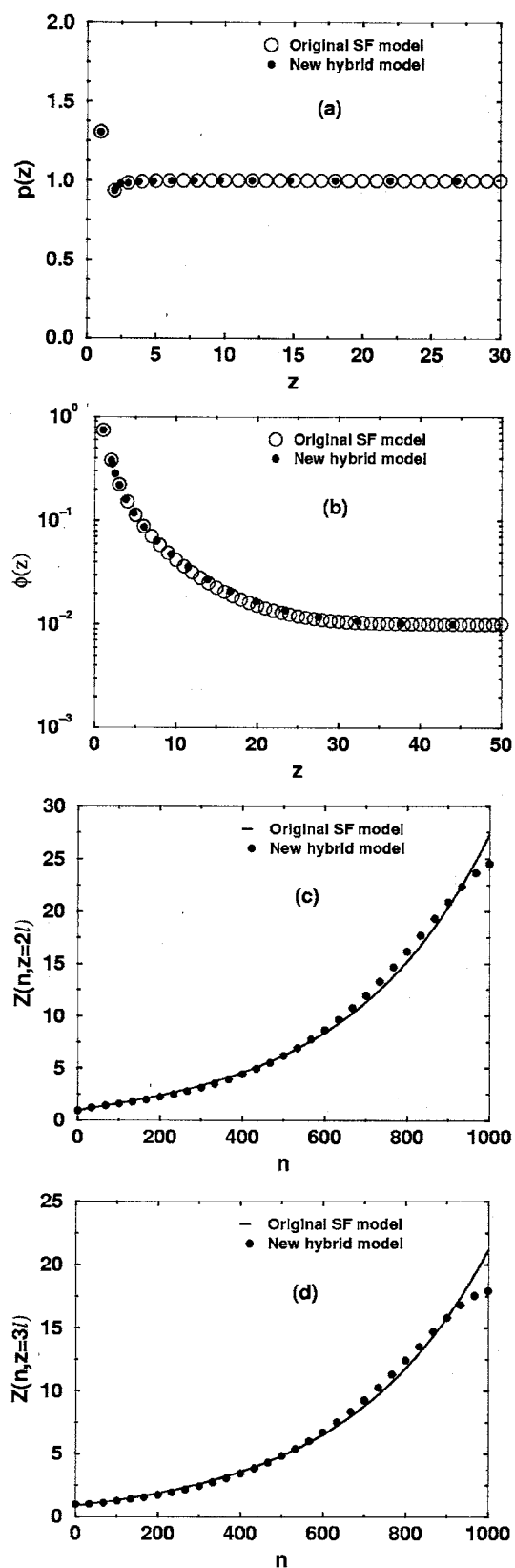


FIG. 3. Same as with Fig. 1 but for the following set of input data: $N = 1000$, $\phi_b = 10^{-2}$, $\chi_s = 1$, and $\chi = 0.50$ (corresponding to a theta solvent).

corresponds to the results obtained through a direct application of the classical SF lattice model while the second (filled circles) to the results obtained with the new model; when $z = 2l$, these data refer to the lattice part of the hybrid model at

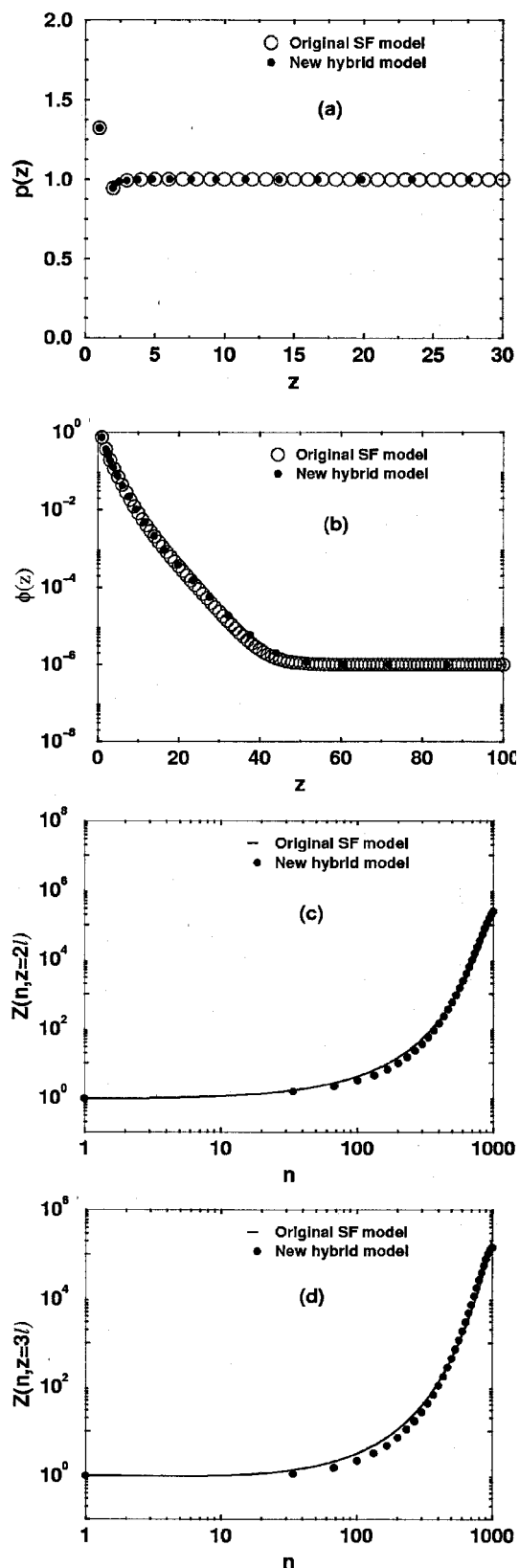


FIG. 4. Same as with Fig. 1 but for the following set of input data: $N=1000$, $\phi_b=10^{-6}$, $\chi_s=1$, and $\chi=0.50$ (corresponding to a theta solvent).

the matching layer, while when $z=3l$, the data refer to its continuum part at the layer right next to the matching layer. For both layers, the agreement with the SF lattice model is remarkable, except for the largest n values where some con-

sistent deviations are observed between lattice and continuum models. The origin of these deviations is believed to be connected with the loss of accuracy when the lattice recurrence relation is transformed into the Edwards diffusion equation through the use of a Taylor expansion in both n and z . An effort to get a diffusion equation which will be truly second-order accurate in z and first-order accurate in n by systematically and consistently keeping higher-order terms in the relevant Taylor expansions is currently in progress.³⁷

An interesting point to make in the data presented in Figs. 1(b)–4(b) is the following: although in most cases the segment density $\phi(z)$ decreases continuously with increasing distance z from the surface, there are instances (e.g., when $\chi=0.0$) where far away from the surface (e.g., for $18l \leq z \leq 44l$) $\phi(z)$ becomes slightly lower than ϕ_b . This has also been observed by SF and causes $\phi(z)$ at long distances from the surface to approach ϕ_b from below. It has been attributed to the effects related to the buildup of the adsorbed layers in terms of loops and tails, and will be discussed more extensively in the next paper, when the power laws obeyed by the tail and loop profiles in the limit of infinitely long chains will be analyzed.

Further, it should be mentioned that lattice and continuum models can be matched not only at the second layer but also at any other layer beyond that. For example, parts (a)–(d) of Fig. 5 compare the data obtained for the free segment probability $p(z)$, the concentration profile $\phi(z)$, and the propagator $Z(n, z)$ with the new hybrid and the original SF lattice models when lattice and continuum descriptions in the former are matched at the third layer (i.e., at $z=3l$). The results have been obtained for $N=1000$, $\phi_b=10^{-2}$, $\chi_s=1$, and $\chi=0.0$. The agreement of the two sets of results is again remarkable.

V. CONCLUDING REMARKS

We have presented a continuum, mean-field formulation of the lattice-based SF statistical theory for the adsorption of interacting chain molecules. The case of a dilute polymer solution subject to a short-range adsorbing boundary condition over a planar solid surface coinciding with the $z=0$ plane of a Cartesian coordinate system has been treated. The new theory employs a hybrid description of the problem; at distances z from the surface greater than $2l$, the description is in continuum space formulated on the Edwards diffusion equation; instead, at distances $z \leq 2l$, the description is discrete following the original SF lattice model. The resulting hybrid model is solved numerically in a three-step approach through an efficient implementation of the pseudospectral collocation method. In addition to formulating the complete set of model equations, a robust computational methodology has been presented for the numerical solution of the resulting hybrid-model equations, valid for any chain length and solvent quality system.

Detailed results presented for the dependence of the polymer segment concentration $\phi(z)$ on distance z from the surface have been shown to agree remarkably well with the SF lattice model for the case of a simple cubic lattice. The comparison with the SF lattice model has also been made at

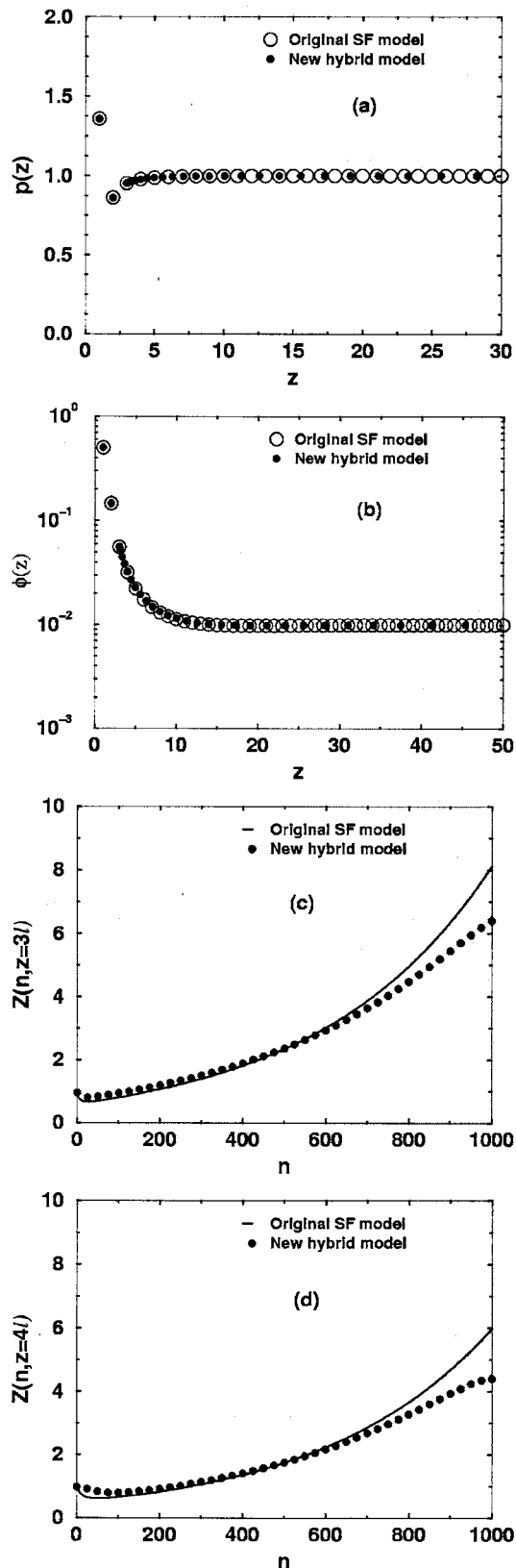


FIG. 5. Same as with Fig. 1 but with lattice and continuum descriptions in the new hybrid model matched at the third layer (i.e., at $z=3l$).

the level of the propagator at the matching layer as well as at the layer right next to that. Except for the highest ranking n values for which some systematic deviations have been recorded between lattice and continuum descriptions, the agreement between the two models is again striking.

Additional results concerning the adsorbed amount Γ , the surface coverage θ , the bound fraction p , the excess amount Γ_{exc} , the root-mean-square thickness t_{rms} , and the statistics of trains, loops, and tails and their scaling laws in the limit of infinitely long chains will be presented in the next paper.³⁴

ACKNOWLEDGMENT

Financial support through a NATO Collaborating Research Grant between Delaware (USA) and Patras (Greece), No. CRG 973023, is greatly appreciated.

APPENDIX: CALCULATION OF THE SEGMENT VOLUME FRACTION

To cast the calculation of the segment volume fraction into the dot product of two vectors, we notice that in the Chebyshev approximation,

$$\begin{aligned} \varphi(z) &= e^{\Delta U(z)} \varphi_b \int_0^1 Z(s, z) Z(1-s, z) ds \\ &= e^{\Delta U(z)} \varphi_b \sum_{j=0}^{N_c} \sum_{k=0}^{N_c} a_j(z) a_k(z) g_{jk}, \end{aligned} \quad (\text{A1})$$

where

$$\begin{aligned} g_{jk} &= \int_0^1 T_j(s) T_k(1-s) ds \\ &= \int_0^\pi \cos(j\vartheta) \cos(k(\pi-\vartheta)) \frac{\sin \vartheta}{2} d\vartheta. \end{aligned} \quad (\text{A2})$$

The matrix \mathbf{g} , which can be calculated once and then tabulated, is symmetric; therefore it can be diagonalized. Thus,

$$\mathbf{g} = \mathbf{Q} \cdot \mathbf{D} \cdot \mathbf{Q}^T, \quad (\text{A3})$$

where \mathbf{D} is the diagonal matrix formed by the eigenvalues of \mathbf{g} ,

$$\mathbf{D} = \text{diag}(d_1, d_2, \dots, d_{N_c}). \quad (\text{A4})$$

On the other hand, the matrix $\mathbf{a}(z)$ of the unknown Chebyshev coefficients at position z above the surface can be calculated by considering the Chebyshev approximation of the partition function $Z(n, z)$ or, equivalently, of $Z(s, z)$ where $s \equiv n/N$ at the nodal points,

$$Z(s, z) = Z(i, z) = \sum_{j=0}^{N_c} a_j(z) T_j(i), \quad i = 0, 2, \dots, N_c, \quad (\text{A5})$$

which is of the form

$$\mathbf{Z} = \mathbf{T} \cdot \mathbf{a}, \quad (\text{A6})$$

with

$$T_i(j) = \cos\left(\frac{(i-1)(j-1)}{(N_c-1)}\pi\right). \quad (\text{A7})$$

The matrix \mathbf{T} and its inverse \mathbf{T}^{-1} can also be calculated once and then tabulated. By inverting Eq. (A6), we get

$$\mathbf{a} = \mathbf{T}^{-1} \cdot \mathbf{Z}. \quad (\text{A8})$$

By combining Eqs. (A8) and (A1), the expression for the segment volume fraction $\varphi(z)$ at position z above the surface becomes

$$\begin{aligned} \varphi &= e^{\Delta U(z)} \varphi_b(\mathbf{a}^T \cdot \mathbf{g} \cdot \mathbf{a}) \\ &= e^{\Delta U(z)} \varphi_b(\mathbf{a}^T \cdot \mathbf{Q} \cdot \mathbf{D} \cdot \mathbf{Q}^T \cdot \mathbf{a}) \\ &= e^{\Delta U(z)} \varphi_b(\mathbf{V}^T \cdot \mathbf{D} \cdot \mathbf{V}) \\ &= e^{\Delta U(z)} \varphi_b \sum_{j=1}^{N_c} d_j V_j^2, \end{aligned} \quad (\text{A9})$$

where

$$\mathbf{V} = \mathbf{Q}^T \cdot \mathbf{C}. \quad (\text{A10})$$

According to Eqs. (A9) and (A10), $\varphi(z)$ at every position z above the surface can be easily calculated spectrally through the dot product of the vectors $\mathbf{d}=(d_1, d_2, \dots, d_{N_c})$ and \mathbf{V}^2 .

¹V. G. Mavrantzas and A. N. Beris, J. Chem. Phys. **110**, 616 (1999).

²A. N. Beris and B. J. Edwards, *Thermodynamics of Flowing Systems* (Oxford University Press, New York, 1994).

³V. G. Mavrantzas and A. N. Beris, J. Chem. Phys. **110**, 628 (1999).

⁴R. Rubin, J. Chem. Phys. **43**, 2392 (1965); J. Res. Natl. Bur. Stand., Sect. B **69B**, 301 (1965); **70B**, 237 (1966).

⁵C. A. J. Hoeve, E. A. DiMarzio, and P. Peysner, J. Chem. Phys. **42**, 2558 (1965); C. A. J. Hoeve, *ibid.* **43**, 3007 (1965); **44**, 1505 (1966).

⁶A. Silberberg, J. Chem. Phys. **46**, 1105 (1967); **48**, 2835 (1968).

⁷K. Motomura and R. Matuura, J. Chem. Phys. **50**, 1281 (1969).

⁸R. J. Rubin, J. Chem. Phys. **51**, 4681 (1969).

⁹P.-G. de Gennes, Rep. Prog. Phys. **32**, 187 (1969).

¹⁰F. Th. Hesselink, J. Phys. Chem. **73**, 3488 (1969); **75**, 65 (1971).

¹¹F. Th. Hesselink, J. Colloid Interface Sci. **50**, 606 (1975).

¹²R.-J. Roe, J. Chem. Phys. **60**, 4192 (1974); **62**, 490 (1975).

¹³A. K. Dolan and S. F. Edwards, Proc. R. Soc. London, Ser. A **343**, 427 (1975).

¹⁴E. Helfand, J. Chem. Phys. **62**, 999 (1975); E. Helfand and A. M. Sapse, *ibid.* **62**, 1327 (1975).

¹⁵E. Helfand, *Macromolecules* **9**, 307 (1976); T. A. Weber and E. Helfand, *ibid.* **9**, 311 (1976).

¹⁶E. Helfand and A. M. Sapse, J. Polym. Sci., Polym. Symp. **54**, 289 (1976).

¹⁷Y. Lepine and A. Caille, Can. J. Phys. **36**, 403 (1978).

¹⁸J. M. H. M. Scheutjens and G. J. Fleer, J. Phys. Chem. **83**, 1619 (1979); **84**, 178 (1980).

¹⁹P.-G. de Gennes, *Macromolecules* **13**, 1069 (1980); **14**, 1637 (1981); **15**, 492 (1982).

²⁰E. Eisenriegler, K. Kremer, and K. Binder, J. Chem. Phys. **77**, 6296 (1982).

²¹H. J. Ploehn, W. B. Russel, and C. M. Hall, *Macromolecules* **21**, 1075 (1988).

²²H. J. Ploehn and W. B. Russel, *Macromolecules* **22**, 276 (1989).

²³H. J. Ploehn, Ph.D. thesis, Princeton University, 1988.

²⁴A. N. Semenov and J.-F. Joanny, Europhys. Lett. **29**, 279 (1995).

²⁵A. N. Semenov, J. Bonet-Avalos, A. Johner, and J. F. Joanny, *Macromolecules* **29**, 2179 (1996); A. Johner, J. Bonet-Avalos, C. C. van der Linden, A. N. Semenov, and J. F. Joanny, *ibid.* **29**, 3629 (1996).

²⁶G. J. Fleer, J. van Male, and A. Johner, *Macromolecules* **32**, 825 (1999); **32**, 845 (1999).

²⁷A. A. Gorbunov, A. M. Skvortsov, J. van Male, and G. J. Fleer, J. Chem. Phys. **114**, 5366 (2001).

²⁸J. de Joannis, C.-W. Park, J. Thomatos, and I. A. Bitsanis, *Langmuir* **17**, 69 (2001).

²⁹J. de Joannis, R. K. Ballamudi, C.-W. Park, J. Thomatos, and I. A. Bitsanis, Europhys. Lett. **56**, 200 (2001).

³⁰V. G. Mavrantzas and A. N. Beris, Phys. Rev. Lett. **69**, 273 (1992); **70**, 02659 (1993).

³¹S. F. Edwards, Proc. Phys. Soc. London **85**, 613 (1965).

³²P. J. Flory, J. Chem. Phys. **10**, 51 (1942).

³³K. M. Hong and J. Noolandi, *Macromolecules* **14**, 727 (1981).

³⁴V. G. Mavrantzas, A. N. Beris, F. Leemakers, and G. J. Fleer (unpublished).

³⁵C. Canuto, M. Y. Hussaini, A. Quarteroni, and T. A. Zang, *Spectral Methods in Fluid Mechanics* (Springer, New York, 1987).

³⁶B. Fornberg, *A Practical Guide to Pseudo-spectral Methods* (Cambridge University Press, Cambridge, 1996).

³⁷V. G. Mavrantzas and A. N. Beris (unpublished).