

Mean-field treatment of polymer chains trapped between surfaces and penetrable interfaces

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We study the exact solutions for the problem of adsorption of polymers in a system containing two interfaces within the mean-field ground-state dominance approximation both for penetrable and nonpenetrable interfaces. We discuss the case of saturation of the polymer double layer for the limiting case of zero bulk concentration. Here, the exact solution is controlled by a single scaling variable which describes the coupling between the interfaces due to the polymer chains. For the case of penetrable interfaces we obtain a nonmonotonous behavior of the amount of adsorbed polymers as a function of the distance between the interfaces. This leads to a high- and a low-energy phase for the double layer with respect to the amount of polymers localized. At the saturation point, the force acting between the interfaces is strictly attractive and monotonously decaying toward zero for increasing interface distance for both types of interfaces. The exact solution for the chemical equilibrium state of the polymer double layer with a semidilute bulk state is governed by two scaling variables and explicit concentration dependence can be removed. The scaling variables describe the ratio between the interface distance and the bulk correlation length and the ratio between the localization length of the interfaces and the bulk correlation length, respectively. Using the exact solution on intervals of constant potentials opens the possibility to treat various localization problems for polymer chains using the appropriate boundary conditions.

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I. INTRODUCTION

Polymer chains can be adsorbed at surfaces or at penetrable interfaces. Penetrable interfaces emerge on structured surfaces or in layered environments. The latter can be formed in microphase separated block copolymers, liquid crystalline or lipid systems. Here, interfaces between two media can act as attractive and penetrable interfaces for both alternating and random copolymers as has been shown previously [1]. Structured surfaces carrying a striped pattern of alternating polymer affinity represent an interface system in two dimensions [2]. The understanding of polymers in environments of multiple interfaces can lead to applications for selection and recognition of polymer properties [3,4]. An exact solution for ideal chains in a layered structure has been recently presented by Chervanyov and Heinrich [5]. The adsorption of ideal chains on a periodically patterned surface has been studied by Stepanow and Fedorenko [6].

In the adsorbed state, conformations of localized chains are the result of the interplay between adsorption energy, entropy reduction because of confinement in the adsorbed state, and the excluded volume repulsion between the monomers [7]. The latter is responsible for the formation of large loops and tails and thus for an extended adsorption layer [8]. Only excluded volume of monomers leads to saturation effects at surfaces or interfaces. Thus, taking into account excluded volume effects is most important to understand the physics of real polymers close to surfaces or interfaces.

Unfortunately, it is virtually impossible to solve the many chain problem for a polymer adsorption including all effects

of conformation statistics and excluded volume. On the other hand, the effects of excluded volume interactions can be understood using mean-field concepts, see [7], thus neglecting fluctuation effects around the most probable polymer state function (ground-state dominance) within a given geometry and external potentials. This approach has been applied already to the formation of adsorption layers onto solid surfaces, see [7], and the interaction between two solid surfaces propagated by adsorbed polymer layers [9,10]. Using mean-field arguments it has been shown by de Gennes that forces between impenetrable interfaces mediated by adsorbing polymers in thermal equilibrium are always attractive [11]. Using a renormalized free-energy functional, de Gennes has also extended the mean-field approach to incorporate correlation effects in good solvent conditions. Moreover, as has been shown by Semenov *et al.*, the ground-state dominance approach of the mean-field model can be improved, for instance, by explicitly including the effect of chain ends [12]. Generally, the mean-field model can be considered as a versatile tool to understand the essential effects of excluded volume interactions in many chain systems under geometric constraints, boundary conditions, and external potentials [7,13]. One of the merits of the mean-field model in the ground-state dominance approach is to provide exact solutions of the corresponding stationary nonlinear Schrödinger equation (SNLSE) for piecewise constant potentials, so that even complex potential environments can be treated analytically using the appropriate boundary conditions. Moreover, solutions of the SNLSE are important in many directions of modern nonlinear physics such as, for example, nonlinear periodic structures in optics [14] or Bose-Einstein condensation [15].

In this work we will demonstrate the formalism for the exact solution of the mean-field polymer adsorption problem for an array of two potential traps within the ground-state dominance approximation (GSDA). We will consider the

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case of penetrable as well as impenetrable traps. In particular we investigate the saturation behavior of polymers in such environments and we show that there exists a general and exact scaling at the saturation point. Furthermore, we investigate the problem of finite bulk density for both penetrable and solid interfaces.

The rest of the work is organized as follows: In Sec. II we introduce the model for the well-known case of a single interface. In Sec. III we present the exact solution for the case of two penetrable interfaces and we discuss the scaling at the saturation point. The case of two hard walls is solved in Sec. IV. We consider the case of finite bulk concentration in Sec. V.

II. LOCALIZATION OF POLYMER CHAINS AT AN ADSORBING INTERFACE

It is well known that polymer chain statistics is dominated by the ground-state solution of the Edwards equation [16] given by

$$\lambda\psi(x) = -\frac{a^2}{6}\frac{d^2\psi(x)}{dx^2} + \frac{1}{k_B T}U_{\text{ext}}(x)\psi(x). \quad (2.1)$$

Here, $\psi(x)$ is the part of the state function of the polymer chain associated with the eigenvalue λ , a is the length of a statistical (Kuhn) segment, $U_{\text{ext}}(x)$ denotes the potential energy of a segment at the position x , and $k_B T$ denotes the usual product of Boltzmann's constant and absolute temperature. For simplicity, we have used only one spatial coordinate related with the symmetry of the potential. We will study plane surfaces and interfaces where the localization takes place in the direction perpendicular to the surface and/or interface only. The ground-state dominance argument can be easily seen from the formal solution of the partition function (under the constraints of fixed end points) for the chain given by

$$Z(x, x') = \sum_k \exp(-N\lambda_k)\psi_k(x)\psi_k(x'), \quad (2.2)$$

where the index k counts the various solutions of Eq. (2.1). Now, for large values of N the lowest value for λ , the ground-state solution, dominates the partition function. In the following we will only consider the ground-state solution, so we drop the index k for simplicity.

In the presence of an interface (trap) and in the absence of excluded volume effects, the external potential $U_{\text{ext}}(x)$ can be written as

$$U_{\text{ext}}(x) = -k_B T \kappa \delta(x), \quad (2.3)$$

where the interface is characterized by the positive value of the parameter $\kappa > 0$ in the case of attraction of monomers by the interface and by the negative value of $\kappa < 0$ in the opposite case, the repulsion of monomers from the interface. Note that κ has the dimension of a length scale which might be considered as the (microscopic) extension of the trap.

Then, the Edwards equation (2.1), which formally corresponds to the time-independent Schrödinger equation for the function ψ , takes the form

$$\lambda\psi(x) = -\frac{a^2}{6}\frac{d^2\psi(x)}{dx^2} - \kappa\delta(x)\psi(x), \quad (2.4)$$

where the x axis is directed perpendicular to the interface. In such a linear system a localized polymer state can exist only in the case of an attractive interface ($\kappa > 0$).

The solution of Eq. (2.4) reduces to the solution of the homogeneous equation

$$\frac{a^2}{6}\frac{d^2\psi(x)}{dx^2} + \lambda\psi(x) = 0 \quad (2.5)$$

in the regions $x > 0$ and $x < 0$ with the following boundary conditions at $x=0$:

$$\psi|_{+0} = \psi|_{-0}, \quad (2.6)$$

$$\left.\frac{\partial\psi}{\partial x}\right|_{+0} - \left.\frac{\partial\psi}{\partial x}\right|_{-0} = -\frac{6}{a^2}\kappa\psi|_0. \quad (2.7)$$

Generally, there are two scenarios which can be considered. First, there exists solutions of Eq. (2.5) with zero density $|\psi(x)|^2$ at infinity. They correspond to truly localized state functions. We note already at this point that this type of solution also describes nonequilibrium (under-saturated) surface states in the case of excluded volume interaction. The second type of solution is obtained for finite density for $x \rightarrow \infty$ of the form $|\psi(x \rightarrow \infty)|^2 = c$. The latter solution does not exist for the linear problem (without excluded volume), as a ground-state solution, as can be directly seen from Eq. (2.5).

The localized (ground-) state solution of Eq. (2.5) satisfying the boundary conditions (2.6) and (2.7) reads

$$\psi(x) = \frac{\sqrt{3\kappa}}{a} e^{-3\kappa|x|/a^2}, \quad (2.8)$$

and the eigenvalue λ corresponding to this localized state is equal to

$$\lambda_l = -3\kappa^2/(2a^2). \quad (2.9)$$

The region of the localization of solution is characterized by the localization length $L \sim a^2/(3\kappa)$.

If we describe the chain with excluded volume interactions in a self-consistent field, we suppose the interactions between monomers are repulsive and local. The presence of other segments provides repulsive potential proportional to the density $c(x)$ [7,17,18]: $U_{ev}(x) = k_B T \nu ac(x)$, where ν is the (dimensionless) excluded volume parameter. Consequently, one can describe each chain as an ideal chain subjected to an external potential $U_{ev}(x)$. The density $c(x)$ is proportional to $c(x) \sim |\psi(x)|^2$ for ground-state dominance (GSD) [7]. In this approximation the solvent should be considered as marginal [19]. It serves as the simplest approximation which reflects the interplay between excluded volume effects and conformational entropy as pointed out in the Introduction. Using these arguments, Eq. (2.1) can be rewritten as follows:

$$\lambda \psi = -\frac{a^2}{6} \frac{d^2 \psi}{dx^2} + \nu a |\psi|^2 \psi + \frac{1}{k_B T} U_{\text{ext}}(x) \psi. \quad (2.10)$$

In the presence of an interface, the external potential $U_{\text{ext}}(x)$ takes the form (2.3) and the nonlinear equation for a polymer chain takes the following final form:

$$\lambda \psi = -\frac{a^2}{6} \frac{d^2 \psi}{dx^2} + \nu a |\psi|^2 \psi - \kappa \delta(x) \psi. \quad (2.11)$$

Rescaling the variables according to

$$\lambda \rightarrow \frac{2}{|v|} \lambda, \quad \kappa \rightarrow \frac{2\sqrt{3}}{a\sqrt{|v|}} \kappa, \quad x \rightarrow \frac{x}{l}, \quad l = \frac{a}{\sqrt{3|v|}}, \quad (2.12)$$

where l is the excluded volume (EV) length as well as introducing the dimensionless state function according to $\psi \rightarrow \sqrt{|v|} \psi$, we can rewrite the SNLSE (2.11) in the following standard form:

$$\lambda \psi = -\frac{d^2 \psi}{dx^2} + 2\sigma |\psi|^2 \psi - \kappa \delta(x) \psi, \quad (2.13)$$

where the sign function $\sigma = \pm 1$ (excluded volume $\nu > 0$ and $\nu < 0$, respectively) stands for repulsion and attraction between monomers, respectively. In order to return to the initial parameters of the system the transformations (2.12) must be applied once.

The solution of Eq. (2.13) reduces to the solution of the corresponding homogeneous equation in the regions $x > 0$ and $x < 0$ supplemented with the following boundary conditions at $x = 0$ (see Ref. [20]):

$$\psi|_{+0} = \psi|_{-0}, \quad (2.14)$$

$$\left. \frac{\partial \psi}{\partial x} \right|_{+0} - \left. \frac{\partial \psi}{\partial x} \right|_{-0} = -\kappa \psi|_0. \quad (2.15)$$

These boundary conditions are obtained by integration of the eigenvalue equation around the δ singularities. However, we note that this type of boundary conditions has been introduced by de Gennes, see Ref. [7], using the argument that the adsorptive region of the potential is much smaller as compared to the relevant length scales of the adsorption profile. Following de Gennes' approach our results are applicable to any class of short-ranged potentials (taking into account that then the boundary conditions replace a more complicated exact solution). Using this argument, the formal singularities imposed by the δ functions can be avoided.

As the ground state is dominant, we can omit the modulus and rewrite Eq. (2.13) in the regions outside the interface in the form

$$\frac{d^2 \psi}{dx^2} + \lambda \psi - 2\sigma \psi^3 = 0. \quad (2.16)$$

Our physical system corresponds to the case of the repulsion between monomers $\sigma = +1$ (excluded volume $\nu > 0$) and the attraction of monomers by the interface ($\kappa > 0$). In this case we have the following expression for the solution satisfying

the boundary conditions and having zero density at infinity [$\psi(x) \rightarrow 0$ for $|x| \rightarrow \infty$]:

$$\psi(x) = \frac{\epsilon}{\sinh[\epsilon(|x| - x_0)]}, \quad (2.17)$$

where the parameter ϵ is equal to

$$\epsilon = \sqrt{-\lambda}. \quad (2.18)$$

The parameter x_0 can only be negative. The solution (2.17) is completely characterized by the value of the parameter ϵ (or λ). The parameter x_0 is expressed in terms of ϵ due to the boundary condition (2.15) which for our solution (2.17) can be rewritten as

$$2\epsilon \coth(\epsilon x_0) = -\kappa. \quad (2.19)$$

It can be seen from this relation, that, as a consequence of $x_0 < 0$, κ can only be positive in the case of $\nu > 0$, i.e., the localized state exists only in the case of attracting interface.

Equation (2.13) requires the condition of normalization which defines, in fact, the total number of monomers per (dimensionless) unit area,

$$N = \int_{-\infty}^{+\infty} |\psi(x)|^2 dx. \quad (2.20)$$

We note that in the standard framework of the GDSA all monomers in the system are considered to belong to a single chain and particular effects of the chain ends are ignored. A generalization of the mean-field equations beyond the ground-state dominance has been developed by Semenov and co-workers, see Ref. [12]. For simplicity, we denote N as the total number of monomers in the system. Note that in contrast to the case of a linear system [see Eq. (2.4)], in the nonlinear case the normalization leads to the relation between the parameters ϵ and N (or λ and N). Substituting our solution (2.17) into the integral (2.20) and taking into account the relation (2.19) between x_0 and ϵ , we can finally obtain the dependence $N = N(\epsilon)$ or, vice versa, $\epsilon = \epsilon(N)$ [or $\lambda = \lambda(N)$]. For our system ($\nu > 0; \kappa > 0$) we arrive at the following result:

$$N = \kappa - 2 \cdot \epsilon. \quad (2.21)$$

It is shown in Ref. [20] that three different types of nonlinear localized states can exist for Eq. (2.13) depending on the relations between the parameters ν and κ . In the first case ($\nu < 0; \kappa > 0$) (1) the interface is attractive, and the maximum of the amplitude of the localized state is at the point of the interface (trap). The localized state in the case ($\nu < 0; \kappa < 0$) (2) has the amplitude maxima located symmetrically on both sides of the interface. The last (third) case ($\nu > 0; \kappa > 0$) (3) coincides with the case under consideration. The dependence $\lambda = \lambda(N)$ for all possible nonlinear localized states are shown in Fig. 1.

The maximum value of parameter N in our case (curve 3) is equal to $N_{\text{sat}} = \kappa$. This point corresponds to the limit case of $\lambda \rightarrow 0$ (or $\epsilon \rightarrow 0$). No more monomers can be added to the interface in this case. Thus, this point corresponds to the saturated state of the interface. We note that an eigenvalue of

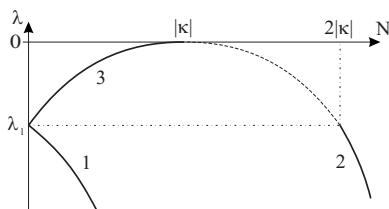


FIG. 1. Dependence $\lambda = \lambda(N)$ for three possible types of localized states: ($\nu < 0; \kappa > 0$) (curve 1), ($\nu < 0; \kappa < 0$) (curve 2), and ($\nu > 0; \kappa > 0$) (curve 3). Dependence 3 corresponds to our physical situation.

the linear system λ_l is given in rescaled units by

$$\lambda_l = -\kappa^2/4. \quad (2.22)$$

Equation (2.13) can be alternatively derived from a variational principle using the energy functional $E[\psi]$ (see Ref. [7]),

$$E = \int_{-\infty}^{+\infty} \left(\left| \frac{\partial \psi}{\partial x} \right|^2 + \sigma |\psi|^4 - \kappa \delta(x) |\psi|^2 \right) dx. \quad (2.23)$$

Substituting in Eq. (2.23) our solution (2.17) and using expression (2.21), we find the following relation between the total energy E and the total number of monomers in the chain N (see [20]):

$$E = \lambda_l N - \frac{N^3}{12} + \frac{\kappa N^2}{4}. \quad (2.24)$$

The first term in this relation describes the energy of N non-interacting monomers in the chain and corresponds to the description of the system in the linear approximation; the second term describes the energy of interaction of monomers in a pure soliton (as if the interface were absent); and the third term describes the interaction of bound monomers through an interface. Note that the sign of the trap (sign of κ) determines only the last term, for $\kappa > 0$ the presence of attractive interface *increases* the energy of the localized state (the interface attracts the monomers which repel each other).

Differentiating expression (2.24) with respect to N and using relation (2.21) for $N(\epsilon)$, we can easily verify the validity of the relation $\partial E / \partial N = \lambda$. So the eigenvalue λ plays the role of *chemical potential* for monomers bound in the localized state.

III. LOCALIZATION OF POLYMER CHAINS AT TWO INTERFACES

Let us describe a polymer chain in the system of two penetrable interfaces. In the presence of two interfaces, the external potential $U_{\text{ext}}(x)$ in the initial variables (2.12) has the following form [compare with (2.3)]:

$$U_{\text{ext}}(x) = -k_B T \kappa [\delta(x+d) + \delta(x-d)], \quad (3.1)$$

where the interfaces are characterized by the value of the parameter κ . As before, in the case of attraction of monomers by interfaces the parameter κ is positive, $\kappa > 0$, the x axis is

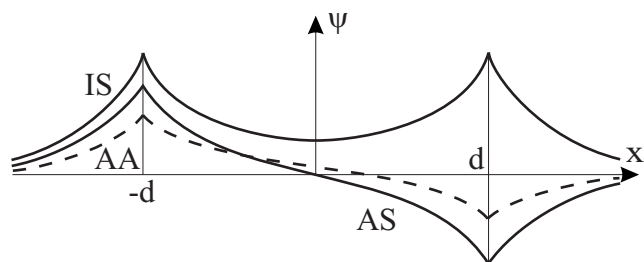


FIG. 2. Profile of all possible solutions localized near two attractive interfaces in the case of a positive excluded volume. Profile (IS) represents the in-phase symmetric state, (AS) is the antisymmetric state, and (AA) is the antiphase asymmetric state.

directed perpendicular to the interfaces, and $2d$ is the distance between interfaces.

Using the transformations (2.12) by means of which Eq. (2.13) had been obtained, we obtain the rescaled SNLSE as follows:

$$\lambda \psi = -\frac{d^2 \psi}{dx^2} + 2\sigma |\psi|^2 \psi - \kappa [\delta(x+d) + \delta(x-d)] \psi, \quad (3.2)$$

where the sign function $\sigma = \pm 1$ for repulsion and attraction between monomers, respectively, and, as before, we use the initial symbols of variables λ , x , d , and κ .

Equation (3.2) reduces to the corresponding homogeneous equation of the form (2.16) in the regions outside the interfaces with the following boundary conditions:

$$\psi|_{\pm d+0} = \psi|_{\pm d-0}, \quad (3.3)$$

$$\frac{d\psi}{dx} \Big|_{\pm d+0} - \frac{d\psi}{dx} \Big|_{\pm d-0} = -\kappa \psi|_{\pm d}. \quad (3.4)$$

Again, we consider positive excluded volume ($\sigma = +1$) and the attraction of monomers by interfaces ($\kappa > 0$).

We shall discuss in this section the spatially localized states having zero density far from the interfaces [$\psi(x) \rightarrow 0$ for $|x| \rightarrow \infty$]. The “bulk” states with nonzero density at infinity shall be considered in Sec. V.

Let us study the states of the first kind (“localized” states). For a positive excluded volume, three different types of stationary localized states can exist [21]: in-phase symmetric state (IS), antisymmetric state (AS), and antiphase asymmetric and/or inhomogeneous state (AA). All these dependencies are shown in Fig. 2. The state with the asymmetric distribution of the density near two interfaces splits off in a bifurcation way from the antisymmetric solution (as against the system with a negative excluded volume). AS and AA states must be excluded from our consideration because for the ground state $\psi < 0$ is not possible.

As the ground state is dominant, we are only interested in the in-phase symmetric solution which in the regions $x < -d(1)$, $x > d(2)$, and $|x| < d(3)$ has the following form:

$$\psi_{1,2}(x) = \mp \frac{\epsilon}{\sinh[\epsilon(x-x_{1,2})]}, \quad \psi_3(x) = \frac{q' \eta}{\text{cn}(\eta x, q)}, \quad (3.5)$$

with $x_2 < d$ and $x_1 = -x_2$. Here $\text{cn}(\eta x, q)$ is the Jacobi elliptic function with modulus q . Also, we introduce

$$q' = \sqrt{1-q^2} \quad \text{and} \quad \eta = \epsilon/\sqrt{2q^2-1}, \quad (3.6)$$

where ϵ is defined in (2.18). The elliptic modulus q varies in the range from $1/\sqrt{2}$ to 1.

The advantage of our method to compare with other approaches is that we deal with the exact solution. This makes it possible to consider all piecewise constant potential forms in a straightforward manner. The solution (3.5) is one parameter and is completely characterized by the value of the parameter ϵ (or λ). The other two parameters q and x_1 (or x_2) are expressed in terms of ϵ from the boundary conditions (3.3) and (3.4).

Because two interfaces attract the monomers, a convenient characteristic of a localized state is represented by the amplitudes $A_1 = \psi(x=-d)$ and $A_2 = \psi(x=d)$ at these interfaces [2,4,21]. Using the symmetry of the localized state, we can denote $A_1 = A_2 \equiv A$. Then, the boundary conditions (A1) and (A2) in terms of the amplitude A can be rewritten as follows:

$$A = \psi(-d) = \psi(d) = \frac{\epsilon}{\sinh[\epsilon(d-x_2)]} = \frac{q' \eta}{\text{cn}(\eta d, q)} \quad (3.7)$$

and

$$\sqrt{A^4 + A^2 \epsilon^2 - q^2 q'^2 \eta^4} + A \sqrt{A^2 + \epsilon^2} = \kappa A. \quad (3.8)$$

For details, see the Appendix.

The relations (3.7) and (3.8) determine the parameters A , x_2 , and q as functions of the parameters ϵ and d . In the general case it can be exactly resolved numerically.

However, a solution can be obtained analytically for the limiting cases $\kappa d \gg 1$ and $\epsilon \rightarrow 0$ (or $\lambda \rightarrow 0$). In the limit $\kappa d \gg 1$ (weak coupling between interfaces) the problem reduces to the study of an effective system of two coupled anharmonic oscillators with a ‘‘hard’’ nonlinearity when the eigenvalue λ increases with the amplitude of the solution. This problem is described analytically in more detail in Ref. [21].

After the substitution of three different types of solutions for the in-phase symmetric state (IS), antisymmetric state (AS), and antiphase asymmetric state (AA) into the integral (2.20) defining the total number of monomers in the chain, we can finally obtain the dependencies $N=N(\epsilon)$ and the inverse dependencies $\epsilon=\epsilon(N)$ [or $\lambda=\lambda(N)$] which are presented in Fig. 3.

Far from the bifurcation point ($\lambda \rightarrow 0$) the analysis within the simplified model of two coupled anharmonic oscillators does not hold, but it can be shown that the dependencies for IS, AS, and AA states terminate at the edge of the spectrum of linear waves ($\lambda=0$), and the profiles of these spatially localized states near the interfaces have the form of algebraic solitons with power-law asymptotic behavior at large distances [22]. This case corresponds to the situation when the total number of monomers tends to its maximum value. A

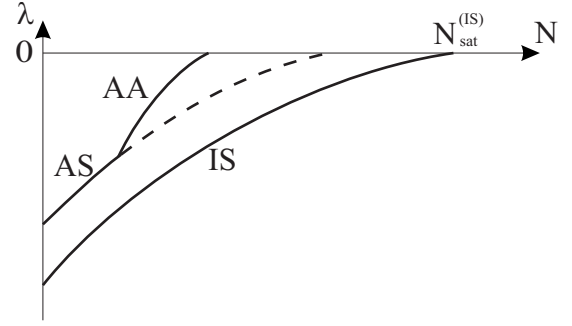


FIG. 3. The dependencies $\lambda(N)$ for the in-phase symmetric (IS) state, antisymmetric (AS) state, and antiphase asymmetric (AA) state in the system with a positive excluded volume.

total number of monomers greater than the maximum values $N_{\text{sat}}^{(\text{IS})}$, $N_{\text{sat}}^{(\text{AS})}$, and $N_{\text{sat}}^{(\text{AA})}$, corresponding to the boundary of the band of linear bulk waves $\lambda=0$, cannot be localized in the system.

In the following, we focus on the IS state which is realized for the polymer profile. Taking into account the symmetry of the (IS) solution (3.5) and calculating the total number of monomers, we come to the following exact result:

$$\begin{aligned} N &= \int_{-\infty}^{+\infty} |\psi|^2 dx = 2 \int_d^{+\infty} |\psi_2|^2 dx + 2x \int_0^d |\psi_3|^2 dx \\ &= 2\epsilon \{ \coth[\epsilon(d-x_2)] - 1 \} + 2\eta \frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} \\ &\quad - 2\eta E[\text{am}(\eta d, q), q] + 2q'^2 \eta^2 d, \end{aligned} \quad (3.9)$$

where $E(\varphi, q)$ is the elliptic integral of the second type and $\text{am}(\varphi, q) = \arcsin[\text{sn}(\varphi, q)]$ is the elliptic amplitude. Two parameters $x_2 = x_2(\epsilon, d)$ and $q = q(\epsilon, d)$ are determined from the boundary conditions (3.7)(A3) [or (3.8)].

Using relation (A1), we can eliminate parameter x_2 and then rewrite Eq. (3.9) in the form

$$\begin{aligned} N &= 2 \left(\sqrt{\frac{q'^2 \eta^2}{\text{cn}^2(\eta d, q)} + \epsilon^2 - \epsilon} \right) + 2\eta \frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} \\ &\quad - 2\eta E[\text{am}(\eta d, q), q] + 2q'^2 \eta^2 d. \end{aligned} \quad (3.10)$$

This is still the exact result.

Let us study the behavior of the system at the saturation point defined by

$$\lambda \rightarrow 0 \quad \text{and} \quad \epsilon \rightarrow 0. \quad (3.11)$$

As shown in the Appendix, in this case the amplitude can be written as

$$A \approx \frac{1}{d-x_2} \approx \frac{1}{\sqrt{2} \text{cn}(\eta d, 1/\sqrt{2})}. \quad (3.12)$$

The dependence of the parameter $q = q(\epsilon, d)$ [or, equivalently, $\eta = \eta(\epsilon, d)$], which is necessary in order to obtain N in (3.10), in this case should be found after the substitution A from (3.12) into the boundary condition (3.8). In this general case, as a result of this substitution, we come to the following transcendental equation for the variable η :

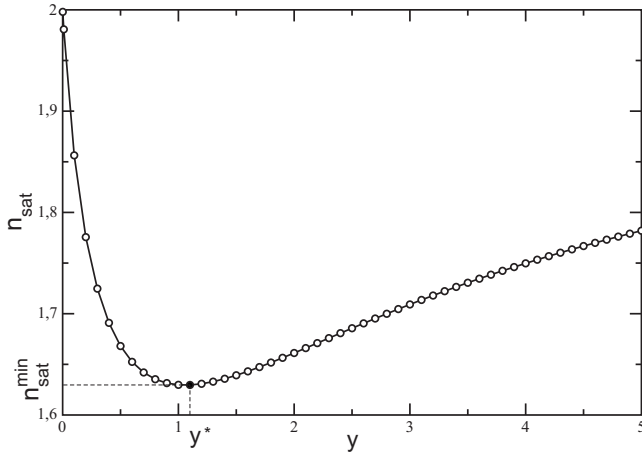


FIG. 4. The dependence $n_{\text{sat}}(y)$ at the saturation threshold. The plot is obtained by numerically solving Eqs. (3.15) and (3.16).

$$\eta^2 \text{cn}^3(\eta d, 1/\sqrt{2}) + 2\kappa^2 \text{cn}(\eta d, 1/\sqrt{2}) - 2\sqrt{2}\kappa\eta = 0. \quad (3.13)$$

It is now possible to reduce one variable by introducing the scaling variables

$$g_\eta = \eta/\kappa \text{ and } y = \kappa d. \quad (3.14)$$

We note that y gives the overlap of the interface profiles in terms of the linear solution. Here, $y \ll 1$ corresponds to strongly overlapping interfaces, and $y \gg 1$ corresponds to a weak overlap. Using Eq. (3.14), we obtain

$$g_\eta^2 \text{cn}^3(g_\eta y, 1/\sqrt{2}) + 2 \text{cn}(g_\eta y, 1/\sqrt{2}) - 2\sqrt{2}g_\eta = 0 \quad (3.15)$$

with the formal solution $g_\eta(y)$. Further we shall use this function for the calculation of the physical characteristics of the system, such as the number of monomers trapped between interfaces and/or surfaces, energy of the system, and the force acting between two penetrable traps and two solid walls.

Now let us introduce the reduced monomers number $n_{\text{sat}} = N_{\text{sat}}/\kappa$. Then in the saturation limit $\epsilon \rightarrow 0$ [$N(\epsilon, d) \rightarrow N_{\text{sat}}(d)$] we have $q \rightarrow 1/\sqrt{2}$, and expression (3.10) transforms into

$$n_{\text{sat}} = \frac{N_{\text{sat}}}{\kappa} \approx \frac{\sqrt{2}g_\eta}{\text{cn}(g_\eta y, 1/\sqrt{2})} + 2g_\eta \frac{\text{sn}(g_\eta y, 1/\sqrt{2})\text{dn}(g_\eta y, 1/\sqrt{2})}{\text{cn}(g_\eta y, 1/\sqrt{2})} - 2g_\eta E[\text{am}(g_\eta y, 1/\sqrt{2}), 1/\sqrt{2}] + g_\eta^2 y. \quad (3.16)$$

Here the function $g_\eta(y)$ is the solution of Eq. (3.15). Thus, the solution of Eq. (3.16) has the universal (scaling) form $n_{\text{sat}} = n_{\text{sat}}(y)$ for different values of the parameters κ and d . The numerical solution for $n_{\text{sat}}(y)$ is presented in Fig. 4. Starting from a large distance, d , between interfaces (weak overlap, $y \gg 1$), the saturation parameter n_{sat} decreases with d as the “bridge” (formed by the overlapping tails of the profile) between interfaces becomes more powerful, and tends to its minimum value $n_{\text{sat}}^{\text{min}} \approx 1.63$ at a characteristic

distance given by the unique value $y^* \approx 1.11$. It increases again for $d \rightarrow 0$ when monomers start to escape outside the region confined by two penetrable interfaces into the tails on both sides of the interfaces, and reaches its maximum value $n_{\text{sat}}^{\text{max}} = 2$ for $d=0$ (strong overlap, $y \ll 1$).

In the limiting case $y \ll 1$ (strong overlap), we have $g_\eta \approx \sqrt{2} - 2\sqrt{2}y$ and from Eq. (3.16), we obtain the following result for the function n_{sat} :

$$n_{\text{sat}} \approx 2 - 2y, \quad (3.17)$$

where we take into account the correction to the expression (A6) for the parameter q ,

$$q^2 \approx \frac{1}{2} \left(1 + \frac{\epsilon^2}{2\kappa^2} \right) + 2y. \quad (3.18)$$

In the opposite limiting case $y \gg 1$ the interaction (overlapping) between two traps is small only in the small-amplitude limit when the description of the system can be reduced to a model of coupled “hard” anharmonic oscillators [21]. Such a description is valid only in the region $1 - \lambda/\lambda_l \ll |\lambda_l|$, where the eigenvalue $\lambda_l = -\kappa^2/4$ ($\epsilon = \kappa/2$).

A few words are necessary about the range of validity of the obtained solution. Physically, the distance d between two interfaces cannot be arbitrarily large. In previous work about ideal chains in an array of traps [2] we have shown that for large distances between the interfaces the GSDA fails and a combination of ground states and excited states dominates the statistics, see also [5]. In this case the chain is localized around one trap only. This can be interpreted as a crossover from “bridging” to “nonbridging.” In accordance with this intuitive result the obtained ground-state solution should not be valid for very large distances. An obvious limitation would be given by a distance larger than the stretching length of a chain, viz., by the total number of monomers multiplied by the statistical segment length of the chain, $d_{\text{max}} = (N-1)a$. On the other hand, a minimal distance d_{min} for the interpretation of our results is defined by the parameter a .

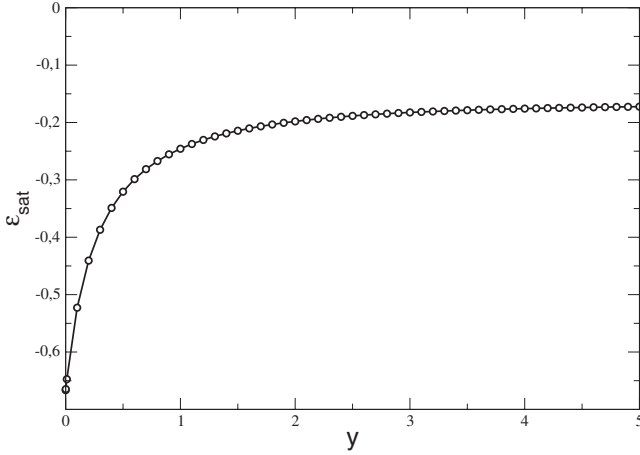
The total energy (per unit area) of the system E is defined by the integral

$$E = \int_{-\infty}^{+\infty} \left(\left| \frac{\partial \psi}{\partial x} \right|^2 + \sigma |\psi|^4 - \kappa [\delta(x+d) + \delta(x-d)] |\psi|^2 \right) dx. \quad (3.19)$$

Substituting the ground-state solution (3.5) into Eq. (3.19) and taking into account the boundary condition (3.7), we can find the following exact expression for the total energy of the system. Again, we can introduce the scaling variables y and g_η and define the appropriately reduced energy of the system $\epsilon_{\text{sat}} = E_{\text{sat}}/\kappa^3$. Then, we obtain in the limit case $\epsilon \rightarrow 0$,

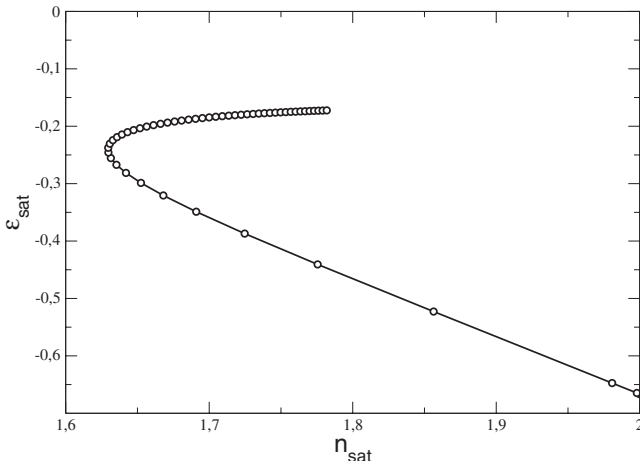
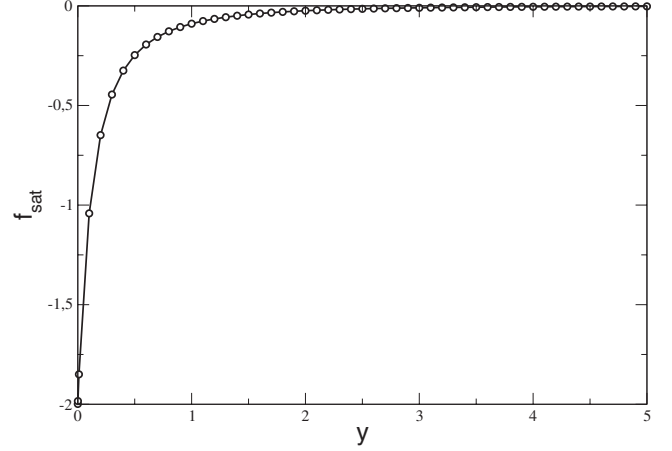
$$\epsilon_{\text{sat}} \approx \frac{\sqrt{2}g_\eta^3}{3 \text{cn}^3(g_\eta y, 1/\sqrt{2})} [1 + \sqrt{2} \text{sn}(g_\eta y, 1/\sqrt{2})\text{dn}(g_\eta y, 1/\sqrt{2})] - \frac{g_\eta^2}{\text{cn}^2(g_\eta y, 1/\sqrt{2})} - \frac{g_\eta^4 y}{6}. \quad (3.20)$$

Using the solution of $g_\eta(y)$ given by Eq. (3.15) we obtain a


 FIG. 5. The dependence $\varepsilon_{\text{sat}}(y)$ at the saturation threshold.

single variate function $\varepsilon_{\text{sat}}(y)$. The minimum value of ε_{sat} , as it follows from (3.20), is equal to $\varepsilon_{\text{sat}}^{\text{min}} = -2/3$. The universal dependence $\varepsilon_{\text{sat}} = \varepsilon_{\text{sat}}(y)$ is presented in Fig. 5. The energy of the saturated two-trap system is thus a monotonously increasing function of the distance between the traps. Note that the condition of saturation, however, implies an exchange of chains by changing the distance according to the result given in Fig. 4. Thus, the system is considered in equilibrium with free chains in a highly dilute solution ($c \rightarrow 0$), which are populating the interfaces until saturation is reached. Note that there is no contradiction between the requirement of saturation and a highly diluted bulk solution for an adsorption strength per monomer (related by κ) of the order of a few kT [23]. In particular, for changes of the distance between the interfaces, where the saturation value n_{sat} is decreased, chains must be released because of over-saturation (positive free energy excess).

In Fig. 6 we display the dependence of the function ε_{sat} from n_{sat} . This clearly indicates two different values (branches) of the total excess energy of the two-interface system for the same value of the total number of monomers N localized at the interfaces. These branches corresponding to the same value of the parameter N are related to two different distances between interfaces d_1 and d_2 that can be


 FIG. 6. The dependence $\varepsilon_{\text{sat}}(n_{\text{sat}})$ at the saturation limit.

 FIG. 7. The dependence $f_{\text{sat}}(y)$ at the saturation threshold.

easily seen from the dependence for the total number of monomers depicted in Fig. 4. Thus, there exist a high-energy phase (large separation) and a low-energy phase (close interfaces).

From the total excess energy we can also calculate the force (per unit area) acting between the interfaces which is an important characteristic for practical measurements. In the general case $F = -dE(d, \lambda)/dd$. If we introduce the new function $g_{\eta'}(y) = \eta'/\kappa^2$ and the reduced force $f_{\text{sat}} = F_{\text{sat}}/\kappa^4$, then we obtain in the saturation limit

$$\begin{aligned}
 f_{\text{sat}} = & -\frac{\sqrt{2}g_{\eta'}^2g_{\eta'}}{\text{cn}^3(g_{\eta'}y, 1/\sqrt{2})} \\
 & \times [1 + \sqrt{2} \text{sn}(g_{\eta'}y, 1/\sqrt{2})\text{dn}(g_{\eta'}y, 1/\sqrt{2})] \\
 & - \frac{\sqrt{2}g_{\eta'}^3(g_{\eta'}y + g_{\eta'})\text{sn}(g_{\eta'}y, 1/\sqrt{2})\text{dn}(g_{\eta'}y, 1/\sqrt{2})}{\text{cn}^4(g_{\eta'}y, 1/\sqrt{2})} \\
 & \times [1 + \sqrt{2} \text{sn}(g_{\eta'}y, 1/\sqrt{2})\text{dn}(g_{\eta'}y, 1/\sqrt{2})] \\
 & + \frac{2g_{\eta'}^2(g_{\eta'}y + g_{\eta'})\text{sn}(g_{\eta'}y, 1/\sqrt{2})\text{dn}(g_{\eta'}y, 1/\sqrt{2})}{\text{cn}^3(g_{\eta'}y, 1/\sqrt{2})} \\
 & + \frac{2g_{\eta'}g_{\eta'}}{\text{cn}^2(g_{\eta'}y, 1/\sqrt{2})} - \frac{g_{\eta'}^4}{2}. \tag{3.21}
 \end{aligned}$$

For different values of the parameter κ we have the universal dependence $f_{\text{sat}} = f_{\text{sat}}(y)$ which is presented in Fig. 7. In the limit $y \rightarrow 0$ we have $g_{\eta'} \approx -2\sqrt{2}$, and the minimum value of f_{sat} from Eq. (3.21) is equal to $f_{\text{sat}}^{\text{min}} = -2$. This behavior is in agreement with that predicted by de Gennes in Ref. [9].

IV. ADSORPTION OF POLYMER CHAINS BETWEEN TWO HARD WALLS

In this section we describe the adsorption of a polymer chain confined by two hard but attractive walls and compare the results with those obtained in the preceding section for the system of two penetrable interfaces. This situation has been extensively studied before, see Refs. [11,12]. Our first aim is to provide the exact solution of the mean-field equa-

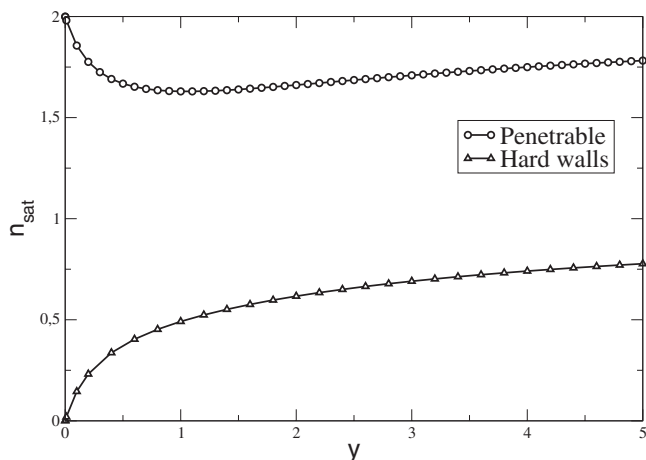


FIG. 8. The dependencies $n_{\text{sat}}(y)$ for two penetrable interfaces and $n_{\text{sat}}^c(y)$ for the confined system of two hard walls.

tion in the GSDA and to discuss it at the saturation point. Second, we compare the solution with that of the geometrically unconstrained system. In fact, the problem of hard walls can be considered as part of the solution for the system of penetrable interfaces.

The nonlinear equation (SNLSE) describing such a system has the form of the eigenvalue equation (2.16) with the boundary conditions (3.3) and (3.4). Now, monomers confined between the surfaces cannot penetrate through them. Consequently, the density in the region outside the slit between the surfaces is equal to zero. The solution between the interfaces ψ_3 has the form presented in (3.5).

The total number of monomers (reduced value n_{sat}^c) confined in the system in the saturation limit is represented by the following expression [compare with (3.16)]:

$$n_{\text{sat}}^c \approx 2g_\eta \frac{\text{sn}(g_\eta y, 1/\sqrt{2}) \text{dn}(g_\eta y, 1/\sqrt{2})}{\text{cn}(g_\eta y, 1/\sqrt{2})} - 2g_\eta E[\text{am}(g_\eta y, 1/\sqrt{2}), 1/\sqrt{2}] + g_\eta^2 y. \quad (4.1)$$

The function $g_\eta(y)$ is the solution of Eq. (3.15).

In Fig. 8 we compare the solutions $n_{\text{sat}}^c = N_{\text{sat}}^c / \kappa$ for the confined system and $n_{\text{sat}} = N_{\text{sat}} / \kappa$ for the system of two penetrable interfaces as functions of the scaling variable y . For penetrable traps, $n_{\text{sat}}(y)$ decreases with the distance d between interfaces tending to its minimum value for some distance and increases again for $d \rightarrow 0$. In contrast to the previous case, for solid walls the dependence $n_{\text{sat}}^c = n_{\text{sat}}^c(y)$ monotonically decreases and vanishes for $d \rightarrow 0$, because in this case, monomers cannot penetrate to the tails outside the space confined by the interfaces.

At the saturation limit ($\varepsilon \rightarrow 0$) the total energy of the confined system has the following form [compare with (3.20)]:

$$\varepsilon_{\text{sat}}^c \approx \frac{2g_\eta^3 \text{sn}(g_\eta y, 1/\sqrt{2}) \text{dn}(g_\eta y, 1/\sqrt{2})}{3 \text{cn}^3(g_\eta y, 1/\sqrt{2})} - \frac{g_\eta^2}{\text{cn}^2(g_\eta y, 1/\sqrt{2})} - \frac{g_\eta^4 y}{6}. \quad (4.2)$$

We can compare the dependencies $\varepsilon_{\text{sat}}^c = E_{\text{sat}}^c / \kappa^3$ for the sys-

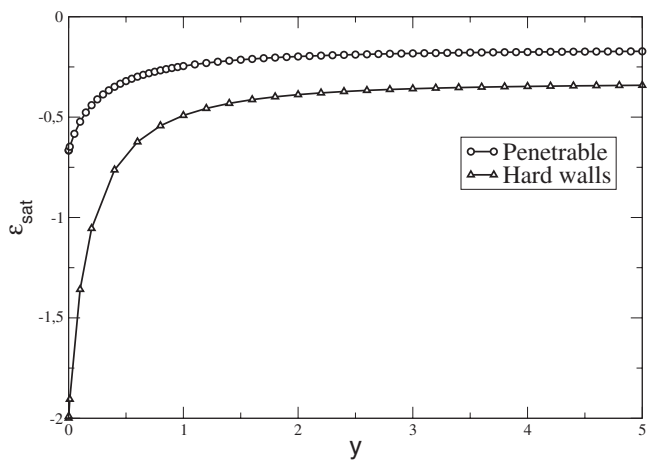


FIG. 9. The dependencies $\varepsilon_{\text{sat}}(y)$ for two penetrable interfaces and $\varepsilon_{\text{sat}}^c(y)$ for the confined system of two solid walls.

tem of solid walls and $\varepsilon_{\text{sat}} = E_{\text{sat}} / \kappa^3$ for the system of two penetrable interfaces in Fig. 9. It can be seen from the figure that over all of the ranges of the allowed distances d we have $\varepsilon_{\text{sat}}^c < \varepsilon_{\text{sat}}$. However, it should be also noted that the number of monomers (chains) localized in the slit between the hard walls at the saturation threshold is much smaller as compared to the case of two penetrable interfaces, see Fig. 8.

In Fig. 10 we compare the forces $f_{\text{sat}} = F_{\text{sat}} / \kappa^4$ and $f_{\text{sat}}^c = F_{\text{sat}}^c / \kappa^4$ acting between two penetrable interfaces and between two hard walls, respectively. We can see from the figure that both functions tend to zero for large distances d (see Ref. [9]) and $|f_{\text{sat}}^c| > |f_{\text{sat}}|$ over all the ranges of distances d .

V. FINITE BULK CONCENTRATION

So far, we have described localized states with zero concentration at infinity [$\psi(x) \rightarrow 0$ for $|x| \rightarrow \infty$] having “dynamical” equilibrium at the saturation limit (N_{sat}). This can be approximately realized for highly diluted bulk solutions and strongly attracting interfaces as discussed above. Another

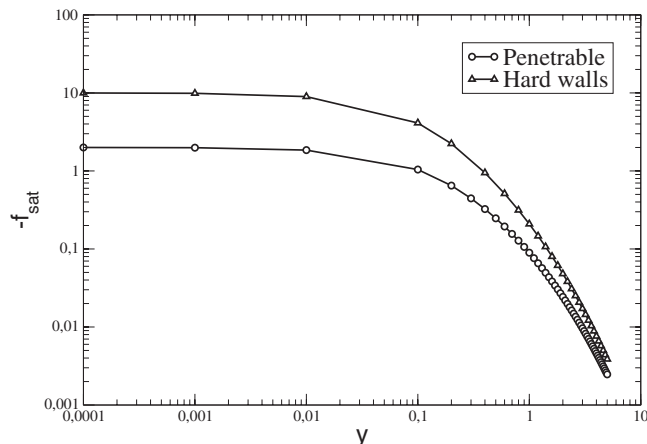


FIG. 10. Comparison of $f_{\text{sat}}(y)$ between two penetrable interfaces and $f_{\text{sat}}^c(y)$ between two hard walls.

sort of equilibrium takes place in the system with nonzero density far from the interface [7,17]. In this case our system is in chemical equilibrium with the bulk, different from that given by the solution (2.17) at the saturation point.

Let us start again by reconsidering the case of a single trap. Finite concentration in the bulk is defined by

$$|\psi(x)|^2 \rightarrow c \quad \text{for } |x| \rightarrow \infty. \quad (5.1)$$

The eigenvalue equation has the form of Eq. (2.16) [or (2.13)]. The solution in this case has the following form [7]:

$$\psi(x) = \frac{1}{\xi} \coth\left(\frac{|x-x_0|}{\xi}\right), \quad (5.2)$$

where the parameter $\xi = \sqrt{2/\lambda}$. The parameter x_0 can only be negative and it is expressed in terms of ξ due to the boundary condition at $x=0$ as follows:

$$\sinh\left(\frac{2x_0}{\xi}\right) = -\frac{4}{\kappa\xi}. \quad (5.3)$$

It can be easily seen from this relation, that, because $x_0 < 0$, parameter κ is positive. With the fixed concentration in the bulk [$|\psi(x \rightarrow \infty)| \rightarrow \sqrt{c}$], we have the following relation for the solution (5.2):

$$\lambda = 2c, \quad (5.4)$$

and the (mean-field) correlation length takes the form

$$\xi = \sqrt{\frac{2}{\lambda}} = \frac{1}{\sqrt{c}}. \quad (5.5)$$

Let us now return to the system of two attractive interfaces. We also note the existence of the ‘‘bulk’’ states with the finite concentration at infinity according to Eq. (5.1). As before (see Sec. III) there is a repulsion between monomers, and the eigenvalue equation has the form of Eq. (3.2). The solution in this case in the regions $x < -d(1)$, $x > d(2)$, and $|x| < d(3)$ has the following form:

$$\psi_{1,2}(x) = \mp \frac{1}{\xi} \coth\left(\frac{x-x_{1,2}}{\xi}\right), \quad (5.6)$$

$$\psi_3(x) = \frac{q'\chi}{\text{cn}(\chi x, q)}, \quad (5.7)$$

where $x_2 < d$ and $x_1 = -x_2$. Also, we have introduced the parameter

$$\chi = \frac{1}{\xi\sqrt{1/2 - q^2}}. \quad (5.8)$$

The elliptic modulus q varies in the range from 0 to $1/\sqrt{2}$. Using Eq. (5.1) we again obtain the relations (5.4) and (5.5).

As before, we introduce the amplitudes at the interfaces $A_1 = A_2 \equiv A$ and rewrite the boundary conditions (3.3) and (3.4) for the solutions (5.6) and (5.7) as follows:

$$\begin{aligned} A &= \sqrt{c} \coth[\sqrt{c}(d-x_2)] \\ &= \sqrt{2c} \sqrt{\frac{1-q^2}{1-2q^2}} \text{cn}^{-1}\left(\sqrt{\frac{2c}{1-2q^2}} d, q\right), \end{aligned} \quad (5.9)$$

$$A^2 - c + \sqrt{A^4 - 2cA^2 - 4c^2 \frac{q^2 q'^2}{(1-2q^2)^2}} = \kappa A. \quad (5.10)$$

Relations (5.9) and (5.10) determine the parameters A , x_2 , and q as functions of the characteristics c and d .

At this point we can again eliminate one of the three parameters c , d , and κ by introducing the scaling variables as follows:

$$s = A\xi, \quad k = \kappa\xi, \quad \delta = d/\xi, \quad (5.11)$$

thus eliminating the explicit concentration dependency from the solution. Using (5.11) we can rewrite Eqs. (5.9) and (5.10) as

$$s = \coth(\delta - \tilde{x}_2) = \sqrt{2} \sqrt{\frac{1-q^2}{1-2q^2}} \text{cn}^{-1}\left(\sqrt{\frac{2}{1-2q^2}} \delta, q\right), \quad (5.12)$$

with $\tilde{x}_2 = x_2/\xi$ and

$$s^2 - 1 + \sqrt{s^4 - 2s^2 - 4 \frac{q^2 q'^2}{(1-2q^2)^2}} = ks. \quad (5.13)$$

If we use Eq. (5.13) to obtain $q(s, k)$, the amplitude can be formally obtained from Eq. (5.12) as

$$s = f_s(k, \delta). \quad (5.14)$$

Then, we obtain from the first equation (5.12) the formal solution for the constants $\tilde{x}_{1,2} = \tilde{x}_{1,2}(k, \delta)$. Thus, the exact solution for the amplitudes as well as for the profile can be expressed as a function of the scaled distance between the interfaces, δ , and the scaled interface attraction, k .

For large values of $\delta = d/\xi$, i.e., when the distance between the interfaces is much bigger than the correlation length, the coupling effects between the interfaces should become irrelevant (screened by the semidilute solution between the interfaces). Then, the individual interfaces are in equilibrium with the solution and Eq. (5.2) holds for each interface with a respective shift of the x axes. On the other hand, if the distance between the interfaces is much smaller than the correlation length and amplitude is much higher than \sqrt{c} ($s \gg 1$) the inner solution should be only weakly perturbed by the finite concentration and the results of the preceding section hold approximately.

As an example we compare the dependencies for the scaled amplitude $s = s(k)$ for the fixed values of the parameter δ in Fig. 11. Thus, if the interface distance is smaller than the bulk correlation length the amplitude grows approximately linear with increasing interface attraction.

Other combinations of the three relevant length scales can be used to express the role of the interface overlap or the role of the concentration based on the exact relations given by Eqs. (5.6)–(5.10).

VI. CONCLUSIONS

We have obtained exact solutions for the problem of adsorption of polymer chains with excluded volume interactions in systems containing two adsorbing interfaces using

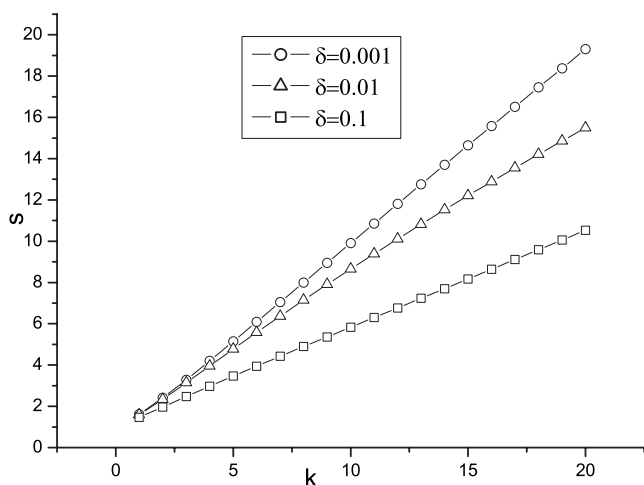


FIG. 11. The dependencies for the scaled amplitude $s=s(k)$ for the various values of the parameter $\delta=0.001, 0.01, 0.1$.

the ground-state approximation. An example for such a scenario could be interfaces onto nanostructured surfaces. Using the exact solution for the SNLSE on intervals of constant potentials opens the possibility to treat various problems of localization for polymer chains using the appropriate boundary conditions. The analysis of the special functions relevant for the actual problem is worked out very well and both analytical and numerical solutions can be obtained.

For the case of zero bulk concentration we have considered the polymer layer at the saturation limit. This scenario is realized if adsorption takes place from a highly diluted polymer solution. Because of the huge gain of free energy per chain in polymer adsorption, highly diluted polymer solutions lead to saturated surface states, see [7]. For the saturation limit we have derived an exact scaling solution, where the only relevant control parameter is the measure of the overlap between the interfaces given by the scaling variable $y=\kappa d$ which can be considered as the coupling parameter of the interface-polymer system.

In a marked difference to a polymer localized between two hard walls, for the case of penetrable interfaces, the saturation density of monomers behaves *nonmonotone* as a function of the distance between the interfaces. When the distance becomes small, the polymer double layer can relax excluded volume constraints by forming larger loops and tails in the outside region of the interfaces. Thus, the capacity of the double interface to localized polymers displays a minimum value $n_{\text{sat}}^{\text{min}} \approx 1.63$ at a characteristic value of the coupling parameter $y^* \approx 1.11$, see Fig. 4. Furthermore, we found the exact expressions for the energy of the double layer and for the force which is acting between both interfaces due to the polymer-interface coupling. Both the penetrable and nonpenetrable interfaces of the energy are strictly negative and the corresponding forces are attractive and monotonously approaching zero with increasing the distance between the interfaces. We note that the system is taken at the dynamical equilibrium of the saturation point; changing the distance between the interfaces also changes the number of chains adsorbed.

The nonmonotonous behavior of the saturation density of polymers as a function of the distance between two pen-

etrable interfaces yields to a “two-phase” behavior of the free energy as a function of the amount of adsorbed polymers, see Fig. 6. A low-energy phase corresponds to small distances between the interfaces, and a high-energy phase corresponds to large distances between the interfaces.

We have also solved the case of finite bulk concentration where the polymer double layer is in chemical equilibrium with the surrounding solution. Here, we have shown that two scaling variables (corresponding to three relevant length scales) control the exact solution and the explicit concentration dependence can be removed. One variable can be chosen as the ratio between the interface distance and the (mean-field) correlation length of the solution and the second variable gives the ratio of the interface length (inverse value of κ) and the correlation length of the solution.

In this work we have used a δ potential approximation for the traps which can be considered of the (standard) limiting case of a steplike potential where the high-affinity part is much more narrow compared to the low affinity part, thus simplifying the structure of the interfaces. In forthcoming works our method will be applied to real interface, where the attraction depends on the concentration inside the interface (surface), a problem noted already by de Gennes, as well as to the adsorption of a polymer chain in a periodic array of interfaces [2,4,24].

The authors are grateful to Professor A. S. Kovalev for useful discussions.

APPENDIX: BOUNDARY CONDITIONS AND SOLUTIONS FOR THE TWO PENETRABLE INTERFACES

As noted in Sec. III the solution (3.5) is one parameter and is completely characterized by the value of the parameter ϵ (or λ). Here, we derive the equation to fix the other two parameters, q and x_1 (or x_2) are expressed in terms of ϵ , using the boundary conditions (3.3) and (3.4). For our solution (3.5) the boundary conditions can be rewritten as

$$\frac{\epsilon}{\sinh[\epsilon(d-x_2)]} = \frac{q'\eta}{\text{cn}(\eta d, q)}, \quad (\text{A1})$$

$$\begin{aligned} & \frac{q'\eta^2 \text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}^2(\eta d, q)} + \frac{\epsilon^2 \cosh[\epsilon(d-x_2)]}{\sinh^2[\epsilon(d-x_2)]} \\ & = \frac{\kappa\epsilon}{\sinh[\epsilon(d-x_2)]}. \end{aligned} \quad (\text{A2})$$

Using the amplitudes at the interfaces (see Sec. III), we obtain Eq. (3.7). For the second boundary condition, we obtain

$$\sqrt{A^2 - q'^2 \eta^2} \sqrt{A^2 + q^2 \eta^2} + A \sqrt{A^2 + \epsilon^2} = \kappa A. \quad (\text{A3})$$

Equation (A3) can be reduced to the form given by Eq. (3.8).

At the saturation point defined by Eq. (3.11), we can rewrite the solution (3.5) for $\psi_{1,2}(x)$ in the form

$$\psi_{1,2}(x) = \mp \frac{\epsilon}{\sinh[\epsilon(x - x_{1,2})]} \approx \mp \frac{1}{x - x_{1,2}}, \quad (\text{A4})$$

and, as it follows from (3.7), the amplitude at the interface is equal to

$$A \approx \frac{1}{d - x_2}. \quad (\text{A5})$$

If we suppose that $\eta d \ll 1$, then from (3.7) we have $A \approx q' \eta \ll 1$. Substituting this expression into the boundary condition (A3) [or (3.8)], we come to the following result for the parameter q :

$$q^2 \approx \frac{1}{2} \left(1 + \frac{\epsilon^2}{2\kappa^2} \right). \quad (\text{A6})$$

However, this means that the parameter η , which is equal to

$$\eta = \frac{\epsilon}{\sqrt{2q^2 - 1}} \approx \sqrt{2}\kappa, \quad (\text{A7})$$

is not small in the limiting case $\eta d \ll 1$ because the parameter κ has an arbitrary value. This means that the parameter q is close to $1/\sqrt{2}$. Thus, the inequality $\epsilon \ll 1$ leads to the limit case for the parameter q , viz., $q \rightarrow 1/\sqrt{2}$.

Now, we suppose that distance, d , is not small. The amplitude A is also not small, and the boundary condition (3.7) can be rewritten as given by Eq. (3.12).

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