

# ADSORPTION OF POLYMER CHAINS AT PENETRABLE INTERFACES

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We investigate the problem of adsorption (localization) of polymer chains in the system of two penetrable interfaces within the mean-field approximation. The saturation of the polymer system in the limit case of zero bulk concentration is studied. We find the exact solution of this mean-field polymer adsorption problem that opens the possibility to treat various localization problems for polymer chains in such environments using the appropriate boundary conditions. The exact solution is controlled by a single scaling variable that describes the coupling between the interfaces due to the polymer chains. We obtain a nonmonotonic behavior of the amount of adsorbed polymers as a function of the distance between the interfaces. This leads to a high-energy and a low-energy phase for the double layer with respect to the amount of polymers localized. At the saturation point, we find the total energy of the system and determine the force acting between the interfaces to be strictly attractive and to monotonically decay to zero for interface distance increases.

## 1. INTRODUCTION

The localization of polymer chains at surfaces or at penetrable interfaces is of great interest from both theoretical and technological standpoints because of its various applications. From a practical point of view, adsorption phenomena in polymeric solutions are important in processes such as lubrication, adhesion, and surface protection, as well as in biological processes of interaction between membranes and polymers.

Penetrable interfaces reside in structured surfaces or in layered environments that can be formed in microphase separated block copolymers, liquid crystalline or lipid systems. Here, it has been shown [1] that interfaces between two media can act as attractive and penetrable interfaces for both alternating and random copolymers. The understanding of polymers in envi-

ronments of multiple interfaces can lead to novel applications for selection and recognition of polymer properties [2, 3].

In the adsorbed state, conformations of localized chains are the result of the interplay between adsorption energy, entropy reduction due to confinement in the adsorbed state, and the excluded volume repulsion between the monomers [4]. The last effect is responsible for the formation of large loops and tails and hence for an extended adsorption layer [5]. Only the excluded volume of monomers leads to saturation effects at surfaces or interfaces. Therefore, taking excluded volume effects into account is most important for understanding the physics of real polymers close to surfaces or interfaces.

Unfortunately, it is virtually impossible to solve the many chain problem for polymer adsorption including all effects of conformation statistics and excluded volume. On the other hand, the effects of excluded vo-

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lume interactions can be understood using mean-field concepts (see, e. g., [4]), thus neglecting fluctuation effects around the most probable polymer state function (ground state dominance) in a given geometry and external potentials. Generally, the mean-field model can be regarded as a versatile tool for understanding the essential effects of excluded volume interactions in many chain systems under geometric constraints, boundary conditions, and external potentials [4, 6]. One of the merits of the mean-field model is that it provides exact solutions of the corresponding stationary nonlinear Schrödinger equation (NLSE) for piecewise constant potentials. We note that the solutions of the NLSE are also very important in many directions of modern nonlinear physics such as nonlinear periodic structures in optics [7], Bose–Einstein condensations in optical lattices [8], and many others.

In this work, we propose a formalism for exactly solving the mean-field polymer adsorption problem for the system of two penetrable interfaces. We investigate the saturation behavior of polymers in such environments. In subsection 2.1, we introduce the model for a single penetrable interface, and in subsection 2.2, we present the exact solution in the case of two penetrable interfaces.

## 2. LOCALIZATION OF POLYMER CHAINS AT ADSORBING PENETRABLE INTERFACES

It is well known that polymer chain statistics is dominated by the ground state solution of the Edwards equation (see [9]) given by

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

where  $u(x)$  is the part of the state function of the polymer chain associated with the eigenvalue  $\lambda$ ,  $a$  is the length of a statistical (Kuhn) segment,  $U_{ext}(x)$  is the potential energy of a segment at the position  $x$ , and  $k_B T$  is the usual product of Boltzmann's constant and absolute temperature. For simplicity, we use only one spatial coordinate related to the symmetry of the potential. We study plane interfaces where the localization occurs in the direction perpendicular to the interfaces only.

The ground state dominance argument can be easily seen from the formal solution for the partition function of the chain given by

$$Z(x, x') = \sum_k \exp\{-N\lambda_k\} u_k(x) u_k(x'), \quad (2)$$

where the index  $k$  counts the various solutions of Eq. (1). For large values of  $N$ , the lowest value of  $\lambda$  (the ground state solution) dominates the partition function. In what follows, we only consider the ground state solution, and drop the index  $k$  for simplicity.

### 2.1. Polymer chain localization at an adsorbing interface

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

$$U_{ext}(x) = -k_B T \kappa \delta(x). \quad (3)$$

Here, the interface is characterized by a positive value of the parameter  $\kappa$  in the case of attraction of monomers by the interface and by a negative value of  $\kappa$  in the opposite case, the repulsion of monomers from the interface. We note that the parameter  $\kappa$  has the dimension of length. Then Edwards equation (1), which formally corresponds to the time-independent Schrödinger equation for the function  $u$ , takes the form

$$\lambda u(x) = -\frac{a^2}{6} \frac{d^2 u(x)}{dx^2} - \kappa \delta(x) u(x), \quad (4)$$

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. (4) reduces to the solution of the homogeneous equation

$$\frac{a^2}{6} \frac{d^2 u(x)}{dx^2} + \lambda u(x) = 0 \quad (5)$$

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

$$u|_{+0} = u|_{-0}, \quad (6)$$

$$\left. \frac{du}{dx} \right|_{+0} - \left. \frac{du}{dx} \right|_{-0} = -\frac{6}{a^2} \kappa u|_0. \quad (7)$$

The localized ground state solution of Eq. (5) satisfying boundary conditions (6) and (7) is given by

$$u(x) = \frac{\sqrt{3\kappa}}{a} \exp\left(-\frac{3\kappa|x|}{a^2}\right), \quad (8)$$

and the eigenvalue  $\lambda$  corresponding to this localized state is

$$\lambda_l = -\frac{3\kappa^2}{2a^2}. \quad (9)$$

The region of localization of the solution is characterized by the localization length

$$L \sim \frac{a^2}{3\kappa}.$$

If we describe the real chain in a self-consistent field, we suppose that the interactions between monomers are repulsive and local. The presence of other segments provides a repulsive potential proportional to the density  $c(x)$  [4, 10, 11]:

$$U_{ev}(x) = k_B T v a c(x),$$

where  $v$  is the (dimensionless) excluded volume parameter. Consequently, we can describe each chain as an ideal chain subjected to the external potential  $U_{ev}(x)$ . The density  $c(x)$  is proportional to  $|u(x)|^2$  for ground state dominance [4]. Thus, Eq. (1) can be rewritten as

$$\lambda u = -\frac{a^2}{6} \frac{d^2 u}{dx^2} + v a |u|^2 u + \frac{1}{k_B T} U_{ext}(x) u. \quad (10)$$

In the presence of an interface, the external potential  $U_{ext}(x)$  takes the form (3) and the nonlinear equation for a real polymer chain finally becomes

$$\lambda u = -\frac{a^2}{6} \frac{d^2 u}{dx^2} + v a |u|^2 u - \kappa \delta(x) u. \quad (11)$$

Rescaling the variables as

$$\frac{2}{|v|} \lambda \rightarrow \lambda, \quad \frac{2\sqrt{3}}{a\sqrt{|v|}} \kappa \rightarrow \kappa, \quad \frac{x}{l} \rightarrow x, \quad (12)$$

where

$$l = \frac{a}{\sqrt{3|v|}}$$

is the excluded volume length, and introducing the dimensionless state function according to  $\sqrt{a}u \rightarrow u$ , we can rewrite SNLSE (11) in the standard form

$$\lambda u = -\frac{d^2 u}{dx^2} + 2\sigma |u|^2 u - \kappa \delta(x) u, \quad (13)$$

where the sign function  $\sigma = \pm 1$  (with the respective excluded volume  $v > 0$  and  $v < 0$ ) stands for repulsion and attraction between monomers.

To return to the initial parameters of the system, transformations (12) have to be applied once.

The solution of Eq. (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. [12]):

$$u|_{+0} = u|_{-0}, \quad (14)$$

$$\left. \frac{du}{dx} \right|_{+0} - \left. \frac{du}{dx} \right|_{-0} = -\kappa u|_0. \quad (15)$$

Because the ground state is dominant, we can omit the modulus and rewrite Eq. (13) in the regions outside the interface as

$$\frac{d^2 u}{dx^2} + \lambda u - 2\sigma u^3 = 0. \quad (16)$$

Our physical system corresponds to the case of repulsion between monomers ( $\sigma = +1$ , excluded volume  $v > 0$ ) and 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 far from the interface ( $u(x) \rightarrow 0$  for  $|x| \rightarrow \infty$ ):

$$u(x) = \frac{\xi}{\text{sh}[\xi(|x| - x_0)]}, \quad (17)$$

where

$$\xi = \sqrt{-\lambda}. \quad (18)$$

The parameter  $x_0$  can only be negative.

The solution in (17) is completely characterized by the value of the parameter  $\xi$  (or  $\lambda$ ). The parameter  $x_0$  is expressed in terms of  $\xi$  due to boundary condition (15), which for our solution (17) can be rewritten as

$$2\xi \text{cth}(\xi x_0) = -\kappa. \quad (19)$$

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

Equation (13) requires the normalization condition, which in fact defines the total number of monomers per (dimensionless) unit area:

$$N = \int_{-\infty}^{\infty} |u(x)|^2 dx. \quad (20)$$

We note that in the standard framework of the mean-field approach, all monomers in the system are assumed to belong to a single chain and particular effects of the chain ends are ignored. For simplicity, we let  $N$  denote the total number of monomers in the system.

We note that in contrast to the case of a linear system (see Eq. (4)), in the nonlinear case the normalization leads to a relation between the parameters  $\xi$  and  $N$  (or  $\lambda$  and  $N$ ). Substituting our solution (17) in (20) and taking the relation (19) between  $x_0$  and  $\xi$  into account, we can finally obtain the dependence  $N = N(\xi)$

or, vice versa,  $\xi = \xi(N)$  (or  $\lambda = \lambda(N)$ ). For our system ( $v > 0$  and  $\kappa > 0$ ), we arrive at the following result:

$$N = \kappa - 2\xi. \tag{21}$$

It is shown in Ref. [12] that three different types of nonlinear localized states can exist for Eq. (13) depending on the relations between the parameters  $v$  and  $\kappa$ . In the first case ( $v < 0$  and  $\kappa > 0$ ), 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 where  $v < 0$  and  $\kappa < 0$  has the amplitude maxima located symmetrically on both sides of the interface. And the last (third) case where  $v > 0$  and  $\kappa > 0$  corresponds to our physical situation.

The maximum value of  $N$  in our case is equal to  $N_{sat} = \kappa$ . This point corresponds to the limit case  $\lambda \rightarrow 0$  (or  $\xi \rightarrow 0$ ). 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 the eigenvalue  $\lambda_l$  of the linear system is given in rescaled units by

$$\lambda_l = -\frac{\kappa^2}{4}. \tag{22}$$

Equation (13) can be alternatively derived from a variational principle using the energy functional  $E[u]$  (see Ref. [4]),

$$E = \int_{-\infty}^{\infty} \left[ \left| \frac{\partial u}{\partial x} \right|^2 + \sigma |u|^4 - \kappa \delta(x) |u|^2 \right] dx. \tag{23}$$

Substituting our solution (17) in Eq. (23) and using expression (21), we find the following relation between the total energy  $E$  and the total number of monomers in the chain  $N$  (see [12]):

$$E = \lambda_l N - \frac{N^3}{12} + \frac{\kappa N^2}{4}. \tag{24}$$

The first term in this relation describes the energy of  $N$  noninteracting 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 the interface. We note that the sign of the trap (the sign of  $\kappa$ ) determines only the last term; for  $\kappa > 0$ , the presence of an attractive interface increases the energy of the localized state (the interface attracts the monomers, which repel each other).

Differentiating expression (24) with respect to  $N$  and using relation (21) for  $N(\xi)$ , we can easily verify the relation

$$\frac{\partial E}{\partial N} = \lambda.$$

Hence, the eigenvalue  $\lambda$  plays the role of chemical potential for monomers bound in a localized state.

### 2.2. Polymer chains localization at two adsorbing interfaces

We describe a polymer chain in the system of two penetrable interfaces. In the presence of two interfaces, the external potential  $U_{ext}(x)$  in the initial variables has the form (compare with (3))

$$U_{ext}(x) = -k_B T \kappa [\delta(x+d) + \delta(x-d)], \tag{25}$$

where the interfaces are characterized by the value of the parameter  $\kappa$ . As before, in the case of attraction of monomers by interfaces the parameter  $\kappa$  is positive, the  $x$  axis is directed perpendicular to the interfaces, and  $2d$  is the distance between the interfaces.

Using transformations (12) by means of which Eq. (13) had been obtained, we obtain the rescaled SNLSE in the form

$$\lambda u = -\frac{d^2 u}{dx^2} + 2\sigma |u|^2 u - \kappa [\delta(x+d) + \delta(x-d)] u, \tag{26}$$

with the sign function  $\sigma = \pm 1$  for the respective cases of repulsion and attraction between monomers, and, as before, we use the initial symbols of variables  $\lambda$ ,  $x$ ,  $d$ , and  $\kappa$ .

The Lagrangian density corresponding to Eq. (26) has the form

$$L = -\left| \frac{du}{dx} \right|^2 - \sigma |u|^4 + \kappa [\delta(x+d) + \delta(x-d)] |u|^2 + \lambda |u|^2. \tag{27}$$

Equation (26) reduces to the corresponding homogeneous equation of form (16) in the regions outside the interfaces with the boundary conditions

$$u|_{\pm d+0} = u|_{\pm d-0}, \tag{28}$$

$$\frac{du}{dx} \Big|_{\pm d+0} - \frac{du}{dx} \Big|_{\pm d-0} = -\kappa u|_{\pm d}. \tag{29}$$

Again, we consider a positive excluded volume ( $\sigma = +1$ ) and the attraction of monomers by interfaces ( $\kappa > 0$ ). For a positive excluded volume, three different types of stationary localized states can exist [13]:

the in-phase symmetric state, the antisymmetric state, and the anti-phase asymmetric (inhomogeneous) state. The state with the asymmetric distribution of the density near two interfaces splits off in a bifurcation manner from the antisymmetric solution. But because 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:

$$\begin{aligned}
 u_{1,2}(x) &= \mp \frac{\xi}{\text{sh}[\xi(x - x_{1,2})]}, \\
 u_3(x) &= \frac{q'\eta}{\text{cn}(\eta x, q)},
 \end{aligned}
 \tag{30}$$

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

$$q' = \sqrt{1 - q^2}, \quad \eta = \frac{\xi}{\sqrt{2q^2 - 1}},
 \tag{31}$$

where  $\xi$  is defined in (18). The elliptic modulus  $q$  varies in the range from  $1/\sqrt{2}$  to 1.

The advantage of our method compared with other approaches is that we deal with the exact solution. This allows considering all piecewise constant potential forms in a straightforward manner. Solution (30) is a one-parameter solution and is completely characterized by the value of the parameter  $\xi$  (or  $\lambda$ ). The other two parameters  $q$  and  $x_1$  (or  $x_2$ ) are expressed in terms of  $\xi$  from boundary conditions (28) and (29), which for our solution (30) can be rewritten as

$$\frac{\xi}{\text{sh}[\xi(d - x_2)]} = \frac{q'\eta}{\text{cn}(\eta d, q)},
 \tag{32}$$

$$\begin{aligned}
 \frac{q'\eta^2 \text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}^2(\eta d, q)} + \frac{\xi^2 \text{ch}[\xi(d - x_2)]}{\text{sh}^2[\xi(d - x_2)]} &= \\
 &= \frac{\kappa \xi}{\text{sh}[\xi(d - x_2)]}.
 \end{aligned}
 \tag{33}$$

Because two interfaces attract the monomers, a convenient characteristics of a localized state is represented by the amplitudes

$$A_1 = u(x = -d)$$

and

$$A_2 = u(x = d)$$

at these interfaces [3, 13, 14]. Due to the symmetry of the localized state, we can set

$$A_1 = A_2 \equiv A.$$

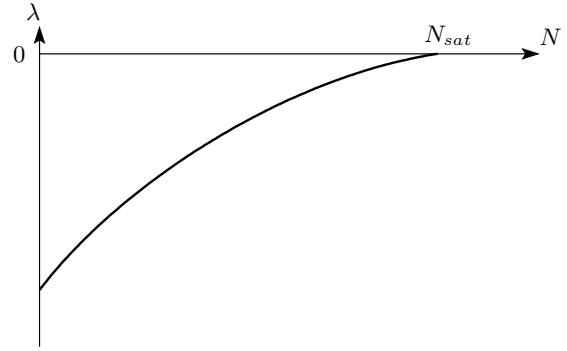


Fig. 1. The dependence  $\lambda(N)$  for the in-phase symmetric state in the system with a positive excluded volume

Then boundary conditions (32) and (33) can be rewritten in terms of the amplitude  $A$  as follows:

$$A = u(-d) = u(d) = \frac{\xi}{\text{sh}[\xi(d - x_2)]} = \frac{q'\eta}{\text{cn}(\eta d, q)},
 \tag{34}$$

$$\sqrt{A^2 - q'^2 \eta^2} \sqrt{A^2 + q^2 \eta^2} + A \sqrt{A^2 + \xi^2} = \kappa A.
 \tag{35}$$

Equation (35) can be reduced to the form

$$\sqrt{A^4 + A^2 \xi^2 - q^2 q'^2 \eta^4} + A \sqrt{A^2 + \xi^2} = \kappa A.
 \tag{36}$$

The three relations in (34) and (35) (or (34) and (36)) determine the parameters  $A$ ,  $x_2$ , and  $q$  as functions of the parameters  $\xi$  and  $d$ . In the general case, it can be exactly solved numerically. However, a solution can be obtained analytically in the limit cases  $\kappa d \gg 1$  and  $\xi \rightarrow 0$  (or  $\lambda \rightarrow 0$ ). In the limit  $\kappa d \gg 1$  (weak coupling between interfaces), the problem reduces to the effective system of two coupled anharmonic oscillators with a “hard” nonlinearity when the eigenvalue  $\lambda$  increases with the amplitude of the solution. This problem is described analytically in more detail in Ref. [13].

After the substitution of our in-phase symmetric solution (30) in the integral (20) defining the total number of monomers in the chain, we can finally obtain the dependence  $N = N(\xi)$  and the inverse dependence  $\xi = \xi(N)$  (or  $\lambda = \lambda(N)$ ), which is presented in Fig. 1. It can be shown that the dependence for the in-phase symmetric state terminates at the edge of the spectrum of linear waves ( $\lambda = 0$ ), and the profile of this spatially localized state near the interfaces has the form of algebraic solitons with a power-law asymptotic behavior at large distances [15]. This case corresponds to the situation where the total number of monomers tends to its maximum value. A total number of monomers

greater than the maximum value  $N_{sat}$ , corresponding to the boundary of the band of linear bulk waves  $\lambda = 0$ , cannot be localized in the system.

Taking the symmetry of the in-phase symmetric solution (30) into account and calculating the total number of monomers, we obtain the exact result

$$N = \int_{-\infty}^{\infty} |u|^2 dx = 2\xi [\text{cth}[\xi(d - x_2)] - 1] + 2\eta \frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} - 2\eta E(\text{am}(\eta d, q), q) + 2q'^2 \eta^2 d, \quad (37)$$

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  $x_2 = x_2(\xi, d)$  and  $q = q(\xi, d)$  are determined from boundary conditions (34) and (35) (or (36)).

Using relation (32), we can eliminate the parameter  $x_2$  and then rewrite Eq. (37) as

$$N = 2 \left[ \sqrt{\frac{q'^2 \eta^2}{\text{cn}^2(\eta d, q)} + \xi^2 - \xi} \right] + 2\eta \frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} - 2\eta E(\text{am}(\eta d, q), q) + 2q'^2 \eta^2 d. \quad (38)$$

We study the peculiarities of our system in the limit case  $\eta d \ll 1$ . (Note that we are not at the saturation limit yet.) It follows from Eq. (34) that  $A \approx q'\eta$ . From boundary condition (36) (or (35)), we then obtain the relation

$$\frac{q\xi}{\sqrt{2q^2 - 1}} = \kappa \quad \text{or} \quad q\eta = \kappa. \quad (39)$$

It follows from (39) that  $\eta = \kappa/q$ , and, taking the inequality  $\eta d \ll 1$  into account, we obtain the following limitation for the distance  $d$ :

$$d \ll q/\kappa \quad \text{or} \quad d \ll 1/\kappa. \quad (40)$$

In this limit case, the total number of monomers (38) can be reduced to the form

$$N \approx 2 \left( 1 - \sqrt{1 - \frac{q'^2}{q^2}} \right) \kappa. \quad (41)$$

We next study the behavior of the system at the saturation point defined by

$$\lambda \rightarrow 0 \quad \text{and} \quad \xi \rightarrow 0. \quad (42)$$

In this case, we can rewrite solution (30) for  $u_{1,2}(x)$  in the form

$$u_{1,2}(x) = \mp \frac{\xi}{\text{sh}[\xi(x - x_{1,2})]} \approx \mp \frac{1}{x - x_{1,2}}, \quad (43)$$

and, as follows from (34), the amplitude at the interface is equal to

$$A \approx \frac{1}{d - x_2}. \quad (44)$$

If we suppose that  $\eta d \ll 1$ , then we have  $A \approx q'\eta$  from (34). Substituting this expression in boundary condition (35) (or (36)), we obtain the following result for the parameter  $q$ :

$$q^2 \approx \frac{1}{2} \left( 1 + \frac{\xi^2}{2\kappa^2} \right). \quad (45)$$

But this means that the parameter  $\eta$ , which is equal to

$$\eta = \frac{\xi}{\sqrt{2q^2 - 1}} \approx \sqrt{2}\kappa, \quad (46)$$

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

We now suppose that the distance  $d$  is not small. The amplitude  $A$  is also not small, and boundary condition (34) can be rewritten as

$$A \approx \frac{1}{d - x_2} \approx \frac{1}{\sqrt{2}} \frac{\eta}{\text{cn}(\eta d, 1/\sqrt{2})}. \quad (47)$$

The dependence of the parameter  $q = q(\xi, d)$  (or, equivalently,  $\eta = \eta(\xi, d)$ ), which is necessary in order to obtain  $N$  in (38), in this case should be found after the substitution of  $A$  from (47) in boundary condition (36). In this general case, as a result of this substitution, we obtain the following equation for the variable  $\eta$ :

$$\eta^2 \text{cn}^3(\eta d, 1/\sqrt{2}) + 2\kappa^2 \text{cn}(\eta d, 1/\sqrt{2}) - 2\sqrt{2}\kappa\eta = 0. \quad (48)$$

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

$$g_\eta = \eta/\kappa \quad \text{and} \quad y = \kappa d. \quad (49)$$

We note  $y$  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. (49), we obtain

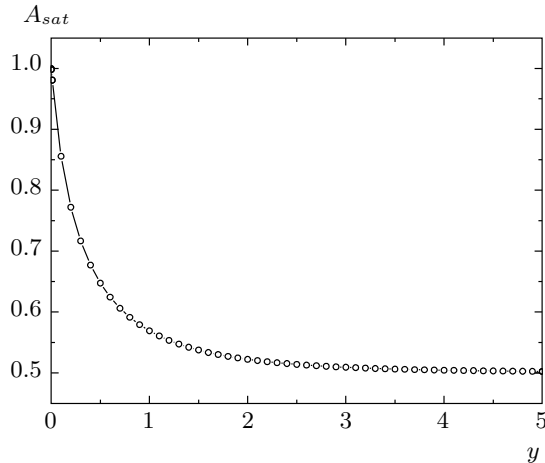


Fig. 2. The dependence  $A_{sat}(y)$  at the saturation threshold

$$g_\eta^2 \text{cn}^3 \left( g_\eta y, 1/\sqrt{2} \right) + 2 \text{cn} \left( g_\eta y, 1/\sqrt{2} \right) - 2\sqrt{2}g_\eta = 0 \quad (50)$$

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

If we introduce the reduced amplitude  $A_{sat} = A/\kappa$  and take definitions (49) into account, then expression (47) can be rewritten as

$$A_{sat} \approx \frac{1}{\sqrt{2}} \frac{g_\eta}{\text{cn}(g_\eta y, 1/\sqrt{2})}. \quad (51)$$

Here, the function  $g_\eta(y)$  is the numerical solution of transcendental equation (50). Hence, dependence (51) has the universal scaling form  $A_{sat} = A_{sat}(y)$  for different values of the parameters  $\kappa$  and  $d$ . The numerical solution for  $A_{sat}(y)$  is presented in Fig. 2.

We now introduce the reduced number of monomers  $n_{sat} = N_{sat}/\kappa$ . Then in the saturation limit  $\xi \rightarrow 0$  ( $N(\xi, d) \rightarrow N_{sat}(d)$ ), we have  $q \rightarrow 1/\sqrt{2}$ , and expression (38) transforms into

$$n_{sat} \approx \frac{\sqrt{2}g_\eta}{\text{cn}(g_\eta y, 1/\sqrt{2})} + 2g_\eta \frac{\text{sn}(g_\eta y, 1/\sqrt{2}) \text{dn}(g_\eta y, 1/\sqrt{2})}{\text{cn}\left(g_\eta y, \frac{1}{\sqrt{2}}\right)} - 2g_\eta \text{E}\left(\text{am}(g_\eta y, 1/\sqrt{2}), 1/\sqrt{2}\right) + g_\eta^2 y, \quad (52)$$

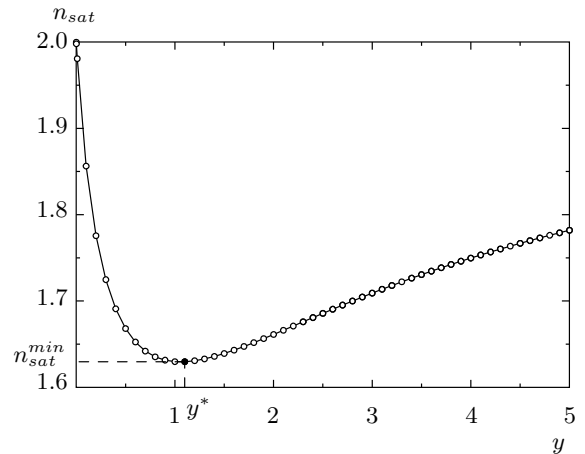


Fig. 3. The dependence  $n_{sat}(y)$  at the saturation threshold

where  $g_\eta(y)$  is the solution of Eq. (50). The dependence  $n_{sat} = n_{sat}(y)$  in (52) also has the universal scaling form for different values of  $\kappa$  and  $d$ . The numerical solution for  $n_{sat}(y)$  is presented in Fig. 3. 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  $n_{sat}^{min} \approx 1.63$  at a characteristic distance given by the value  $y^* \approx 1.11$ . It increases again as  $d \rightarrow 0$  when monomers start to escape from the region confined by two penetrable interfaces into the tails on both sides of the interfaces, and reaches its maximum value  $n_{sat}^{max} = 2$  for  $d = 0$  (strong overlap,  $y \ll 1$ ).

In the limit case  $y \ll 1$  (strong overlap), we have  $g_\eta \approx \sqrt{2} - 2\sqrt{2}y$ ; from Eq. (52), we then obtain the following result for the function  $n_{sat}$ :

$$n_{sat} \approx 2 - 2y, \quad (53)$$

where we included the correction to expression (45) for the parameter  $q$ ,

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

In the opposite limit case  $y \gg 1$ , the interaction (overlap) 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 [13]. Such a description is valid only in the region  $1 - \lambda/\lambda_l \ll |\lambda_l|$ , where the eigenvalue  $\lambda_l = -\kappa^2/4$  ( $\xi = \kappa/2$ ).

The distance  $d$  between two interfaces cannot be arbitrary. It is limited by the maximum length of a chain, i. e., by the total number of monomers times the statistical segment length of the chain,  $d_{max} = (N-1)a$ . The minimal distance  $d_{min}$  is defined by the parameter  $a$ .

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

$$E = \int_{-\infty}^{\infty} \left\{ \left| \frac{\partial u}{\partial x} \right|^2 + \sigma |u|^4 - \kappa [\delta(x+d) + \delta(x-d)] |u|^2 \right\} dx. \quad (54)$$

Substituting ground state solution (30) in Eq. (54) and taking boundary condition (34) into account, we find the exact expression for the total energy of the system:

$$E = \frac{2\xi^3}{3} + \frac{2}{3} \left[ \frac{2q'^2\eta^2}{\text{cn}^2(\eta d, q)} - \xi^2 \right] \sqrt{\frac{q'^2\eta^2}{\text{cn}^2(\eta d, q)} + \xi^2} + \frac{4q'^2\eta^3}{3} \frac{\text{sn}(\eta d, q) \cdot \text{dn}(\eta d, q)}{\text{cn}^3(\eta d, q)} + \frac{2(1-2q^2)\eta^3}{3} \times \left\{ \frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} - E[\text{am}(\eta d, q)] \right\} + 2q'^2 \left( \frac{1}{3} - q^2 \right) \eta^4 d - \frac{2\kappa q'^2 \eta^2}{\text{cn}^2(\eta d, q)}. \quad (55)$$

Again, we can introduce the scaling variables  $y$  and  $g_\eta$  and define the appropriately reduced energy of the system

$$\varepsilon_{sat} = E_{sat} / \kappa^3.$$

In the limit case  $\xi \rightarrow 0$ , we then obtain

$$\varepsilon_{sat} \approx \frac{\sqrt{2}g_\eta^3}{3\text{cn}^3(g_\eta y, 1/\sqrt{2})} \left[ 1 + \sqrt{2} \text{sn}(g_\eta y, 1/\sqrt{2}) \right] \times \left[ \text{dn}(g_\eta y, 1/\sqrt{2}) \right] - \frac{g_\eta^2}{\text{cn}^2(g_\eta y, 1/\sqrt{2})} - \frac{g_\eta^4 y}{6}. \quad (56)$$

Using the solution  $g_\eta(y)$  of Eq. (50), we obtain a single variate function  $\varepsilon_{sat}(y)$ . The minimum value of  $\varepsilon_{sat}$ , as follows from (56), is equal to  $\varepsilon_{sat}^{min} = -2/3$ . The universal dependence  $\varepsilon_{sat} = \varepsilon_{sat}(y)$  is presented in Fig. 4. The energy of the saturated system is thus a monotonically increasing function of the distance between the traps. We note that the condition of saturation implies an exchange of chains by changing the distance according to the result in Fig. 3. Thus, the system is considered in equilibrium with free chains in a highly dilute solution ( $c \rightarrow 0$ ) populating the interfaces until saturation is reached. We note that there is no contradiction between the requirement of saturation and a highly diluted bulk solution for an adsorption

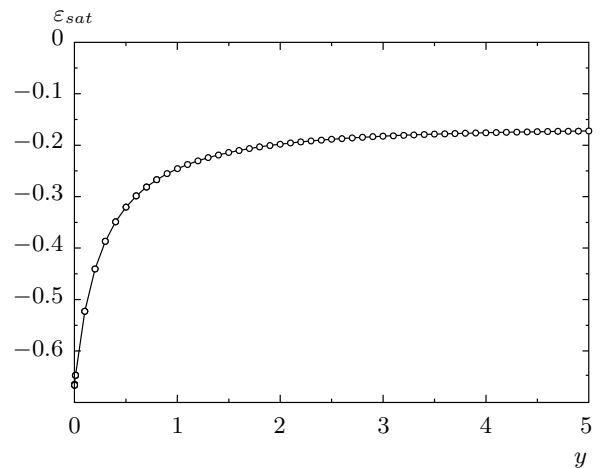


Fig. 4. The dependence  $\varepsilon_{sat}(y)$  at the saturation threshold

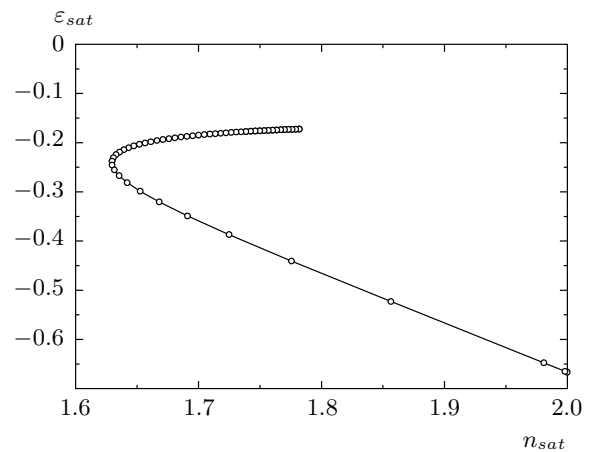


Fig. 5. The dependence  $\varepsilon_{sat}(n_{sat})$  at the saturation limit

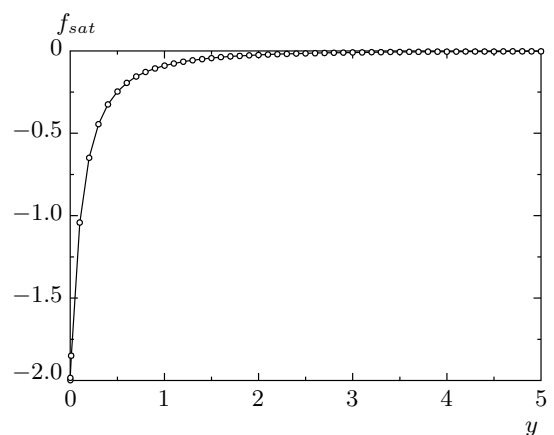


Fig. 6. The dependence  $f_{sat}(y)$  at the saturation threshold



strength per monomer (related by  $\kappa$ ) of the order of a few  $kT$  [16]. In particular, for changes of the distance between the interfaces, where the saturation value  $n_{sat}$  is decreased, chains have to be released because of over-saturation (positive free energy excess).

In Fig. 5, we plot the function  $\varepsilon_{sat}(n_{sat})$ . 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  $d_1$  and  $d_2$  between the interfaces, as

can be easily seen from the dependence for the total number of monomers presented in Fig. 3. Hence, there exist a high-energy phase (large separation) and a low-energy phase (close interfaces).

Also, we can calculate an important characteristic of the system for practical measurements, the force per unit area acting between the interfaces. In the general case,

$$F = -\frac{dE(d, \lambda)}{dd},$$

and at the saturation limit we have

$$F_{sat} = -\frac{dE_{sat}(d)}{dd} = \frac{\sqrt{2} \eta^3 (\eta' d + \eta)}{3} \frac{\sqrt{2} + 3 \operatorname{sn}(\eta d, 1/\sqrt{2}) \operatorname{dn}(\eta d, 1/\sqrt{2})}{\operatorname{cn}^4(\eta d, 1/\sqrt{2})} +$$

$$+ \sqrt{2} \eta^2 \frac{\eta' + \sqrt{2} [\eta' - \kappa (\eta' d + \eta)] \operatorname{sn}(\eta d, 1/\sqrt{2}) \operatorname{dn}(\eta d, 1/\sqrt{2})}{\operatorname{cn}^3(\eta d, 1/\sqrt{2})} +$$

$$+ \frac{\eta [\eta^2 (\eta' d + \eta) - 18\kappa\eta']}{9 \operatorname{cn}^2(\eta d, 1/\sqrt{2})} - \frac{\eta^3 (14\eta' d + 5\eta)}{18}. \quad (57)$$

The parameter  $\eta' \equiv d\eta/dd$  can be easily found by differentiating Eq. (48), which gives

$$\eta' = \frac{\eta [3\eta^2 \operatorname{cn}^2(\eta d, 1/\sqrt{2}) + 2|\kappa|^2] \operatorname{sn}(\eta d, 1/\sqrt{2}) \operatorname{dn}(\eta d, 1/\sqrt{2})}{2\eta \operatorname{cn}^3(\eta d, 1/\sqrt{2}) - d [3\eta^2 \operatorname{cn}^2(\eta d, 1/\sqrt{2}) + 2|\kappa|^2] \operatorname{sn}(\eta d, 1/\sqrt{2}) \operatorname{dn}(\eta d, 1/\sqrt{2}) - 2\sqrt{2} |\kappa|}. \quad (58)$$

If we introduce the reduced force  $f_{sat} = F_{sat}/\kappa^4$  and the new function  $g_{\eta'}(y) = \eta'/\kappa^2$ , then we can rewrite Eq. (57) in the form

$$f_{sat} = -\frac{\sqrt{2} g_{\eta'}^2 g_{\eta'}}{\operatorname{cn}^3(g_{\eta'} y, 1/\sqrt{2})} \left\{ 1 + \sqrt{2} \operatorname{sn}(g_{\eta'} y, 1/\sqrt{2}) \operatorname{dn}(g_{\eta'} y, 1/\sqrt{2}) \right\} -$$

$$- \frac{\sqrt{2} g_{\eta'}^3 (g_{\eta'} y + g_{\eta}) \operatorname{sn}(g_{\eta'} y, 1/\sqrt{2}) \operatorname{dn}(g_{\eta'} y, 1/\sqrt{2})}{\operatorname{cn}^4(g_{\eta'} y, 1/\sqrt{2})} \left\{ 1 + \sqrt{2} \operatorname{sn}(g_{\eta'} y, 1/\sqrt{2}) \operatorname{dn}(g_{\eta'} y, 1/\sqrt{2}) \right\} +$$

$$+ \frac{2g_{\eta'}^2 (g_{\eta'} y + g_{\eta}) \operatorname{sn}(g_{\eta'} y, 1/\sqrt{2}) \operatorname{dn}(g_{\eta'} y, 1/\sqrt{2})}{\operatorname{cn}^3(g_{\eta'} y, 1/\sqrt{2})} + \frac{2g_{\eta'} g_{\eta'}}{\operatorname{cn}^2(g_{\eta'} y, 1/\sqrt{2})} - \frac{g_{\eta'}^4}{2}, \quad (59)$$

where

$$g_{\eta'}(y) = \frac{g_{\eta} [3g_{\eta'}^2 \operatorname{cn}^2(g_{\eta'} y, 1/\sqrt{2}) + 2] \operatorname{sn}(g_{\eta'} y, 1/\sqrt{2}) \operatorname{dn}(g_{\eta'} y, 1/\sqrt{2})}{2g_{\eta} \operatorname{cn}^3(g_{\eta'} y, 1/\sqrt{2}) - y [3g_{\eta'}^2 \operatorname{cn}^2(g_{\eta'} y, 1/\sqrt{2}) + 2] \operatorname{sn}(g_{\eta'} y, 1/\sqrt{2}) \operatorname{dn}(g_{\eta'} y, 1/\sqrt{2}) - 2\sqrt{2}}, \quad (60)$$

and  $g_{\eta}(y)$  is the solution of Eq. (50).

For different values of the parameter  $\kappa$ , we obtain the universal dependence  $f_{sat} = f_{sat}(y)$  presented in Fig. 6. In the limit  $y \rightarrow 0$ , we have  $g_{\eta'} \approx -2\sqrt{2}$ , and the minimum value of  $f_{sat}$  from Eq. (59) is equal to  $f_{sat}^{min} = -2$ . This behavior is in agreement with that predicted by de Gennes in Ref. [4].

### 3. CONCLUSIONS

We have obtained exact solutions for the problem of adsorption of real polymer chains in systems with two adsorbing interfaces within the mean-field approximation. We described localized states with zero bulk con-

centration having “dynamical” equilibrium at the saturation limit. This can be realized for the adsorption from highly diluted polymer solutions and strongly attracting interfaces as discussed above. Because of the huge gain of free energy per chain in polymer adsorption, highly diluted polymer solutions lead to saturated surface states (see [4]). Using the exact solution for the SNLSE on intervals of constant potentials opens the possibility to treat various localization problems for polymer chains in such environments using the appropriate boundary conditions.

For the saturation limit, we derived an exact scaling solution in which the only relevant control parameter is the measure of the overlap between the interfaces given by the scaling variable that can be considered as a coupling parameter of the interface–polymer system. We found that the saturation density of monomers behaves nonmonotonically as a function of the distance between the interfaces, which results in “two-phase” behavior of the free energy as a function of the amount of adsorbed polymers (see Fig. 5). When the distance becomes small, the polymer double layer can relax the excluded volume constraints by forming larger loops and tails in the outer region of the interfaces. Changing the distance between the interfaces changes the number of chains adsorbed. A low-energy phase corresponds to small distances between the interfaces, and a high-energy phase corresponds to large distances between them. We note that the system is taken in the dynamical equilibrium at the saturation point.

We found the energy of the system, which turned out to be strictly negative, and the forces acting between both interfaces due to the polymer–interface coupling. The forces are found to be attractive and to monotonically approach zero with increasing the distance between the interfaces, which is in agreement with the behavior predicted by de Gennes [4].

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