

Localization of polymer chains in the system of two penetrable interfaces

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The problem of localization of polymer chains in a system containing two penetrable interfaces within the mean-field approximation is investigated. We study the saturation of the polymer chain in the limiting case of zero bulk concentration. We obtain a non-monotonous behavior of the amount of adsorbed polymers as a function of the distance between the interfaces.

Изучена локализация полимерных цепочек в системе двух прозрачных интерфейсов в рамках приближения среднего поля. Исследовано состояние насыщения полимерной цепочки в предельном случае нулевой концентрации полимера вдали от интерфейсов. Получена немонотонная зависимость количества адсорбированных мономеров как функция расстояния между интерфейсами.

Polymer chains can be adsorbed at surfaces or at penetrable interfaces. Penetrable interfaces reside in 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]. The understanding of polymers in environments 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 because confinement in the adsorbed state, and the excluded volume repulsion between the monomers [4]. The latter is responsible for the formation of large loops and tails and thus for an extended adsorption layer [5]. 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 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, for example, [4]), thus neglecting fluctuation effects around the most probable polymer state function (ground state dominance) within a given geometry and external potentials. 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 [4, 6]. One of the merits of the mean field model is to provide exact solutions of the corresponding stationary nonlinear Schrödinger equation (SNLSE) for piece-wise constant potentials.

In this work we will demonstrate the formalism for the exact solution of the mean-field polymer adsorption problem for the system of two penetrable potential traps. We investigate the saturation

behavior of polymers in such environments. At first, we introduce the model for the well known case of a single interface, and after we present the exact solution for the case of two penetrable interfaces.

It is well known that polymer chain statistics is dominated by the ground state solution of the Edwards equation (see [7]) given by

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

where $u(x)$ 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, $U_{ext}(x)$ 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 interfaces where the localization takes place in the direction perpendicular to the interfaces only. The ground state dominance argument can be easily seen from the formal solution of the partition function for the chain given by

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

where the index k counts the various solutions of Eq.(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 $U_{ext}(x)$ can be written as

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

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 (1), which formally corresponds to the time-independent Schrödinger equation for the function u , takes the form:

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

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

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

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

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

$$\frac{\partial u}{\partial x}|_{+0} - \frac{\partial u}{\partial x}|_{-0} = -\frac{6}{a^2} \cdot \kappa \cdot u|_0 . \quad (7)$$

The localized (ground) state solution of Eq.(5) satisfying the boundary conditions (6),(7) reads:

$$u(x) = \frac{\sqrt{3\kappa}}{a} \cdot e^{-3\kappa|x|/a^2} , \quad (8)$$

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

$$\lambda_l = -3\kappa^2/(2a^2) . \quad (9)$$

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

If we describe the real chain 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 $c(x)$ [4, 8, 9]: $U_{ev}(x) = k_B T \cdot v \cdot a \cdot c(x)$, where v 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 $c(x) \sim |u(x)|^2$ for ground state dominance (GSD) [4]. Thus, Eq.(1) can be rewritten as follows:

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

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

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

Rescaling the variables according to:

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

where l is the excluded volume length (EV-length) as well as introducing the dimensionless state function according to $u \rightarrow \sqrt{a}u$, we can rewrite the SNLSE (11) in the following standard form:

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

where the sign function $\sigma = \pm 1$ (excluded volume $v > 0$ and $v < 0$, respectively) stands for repulsion and attraction between monomers, respectively. In order to return to the initial parameters of the system the 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 [10]):

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

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

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

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

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

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

where the parameter ξ is equal to

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

The parameter x_0 can only be negative. The solution (17) is completely characterized by the value of the parameter ξ (or λ). The parameter x_0 is expressed in terms of ξ due to the boundary condition (15) which for our solution (17) can be rewritten as

$$2\xi \cdot \coth(\xi x_0) = -\kappa. \quad (19)$$

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

Equation (13) requires the condition of normalization which defines, in fact, 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 considered to belong to a single chain and particular effects of the chain ends are ignored. 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.(4)), in the nonlinear case the normalization leads to the relation between the parameters ξ and N (or λ and N). Substituting our solution (17) into the integral (20) and taking into account the relation (19) between x_0 and ξ , we can finally obtain the dependence $N = N(\xi)$ or, vice versa, $\xi = \xi(N)$ (or $\lambda = \lambda(N)$). For our system ($v > 0; \kappa > 0$) we arrive at the following result:

$$N = \kappa - 2 \cdot \xi. \quad (21)$$

It is shown in Ref.[10] that three different types of nonlinear localized states can exist for Eq.(13) depending on the relations between the parameters v and κ . In the first case ($v < 0; \kappa > 0$) 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 ($v < 0; \kappa < 0$) has the amplitude maxima located symmetrically on both sides of the interface. And the last (third) case ($v > 0; \kappa > 0$) corresponds to our physical situation.

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

$$\lambda_l = -\kappa^2/4. \quad (22)$$

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

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

Substituting in Eq.(23) our solution (17) 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 [10]):

$$E = \lambda_l \cdot N - \frac{N^3}{12} + \frac{\kappa \cdot N^2}{4}. \quad (24)$$

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 (24) with respect to N and using relation (21) for $N(\xi)$, 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.

Let us 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 (12) has the following form (compare with (3)):

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

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

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

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

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 .

Eq.(26) reduces to the corresponding homogeneous equation of the form (16) in the regions outside the interfaces with the following boundary conditions:

$$u|_{\pm d+0} = u|_{\pm d-0}, \quad (27)$$

$$\frac{du}{dx}|_{\pm d+0} - \frac{du}{dx}|_{\pm d-0} = -\kappa \cdot u|_{\pm d}. \quad (28)$$

Again, we consider 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 [11]: in-phase symmetric state (IS), anti-symmetric state (A) and anti-phase asymmetric (inhomogeneous) state (AA). The state with the asymmetric distribution of the density near two interfaces splits off in a bifurcation way from the anti-symmetric solution. However, as the ground state is dominant, we are only interested in the *in-phase symmetric solution* (IS) which in the regions $x < -d$ (1), $x > d$ (2) and $|x| < d$ (3) has the following form:

$$u_{1,2}(x) = \mp \frac{\xi}{\sinh[\xi(x-x_{1,2})]}, \quad u_3(x) = \frac{q'\eta}{\text{cn}(\eta x, q)}, \quad (29)$$

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

$$q' = \sqrt{1-q^2} \quad \text{and} \quad \eta = \xi/\sqrt{2q^2-1}, \quad (30)$$

where ξ is defined in (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 straight forward manner. The solution (29) is one-parameter and is completely characterized by the value of the parameter ξ (or λ). Other two parameters q and x_1 (or x_2) are expressed in terms of ξ from the boundary conditions (27),(28) which for our solution (29) can be rewritten as

$$\frac{\xi}{\sinh[\xi(d-x_2)]} = \frac{q'\eta}{\text{cn}(\eta d, q)}, \quad (31)$$

$$\frac{q'\eta^2 \cdot \text{sn}(\eta d, q) \cdot \text{dn}(\eta d, q)}{\text{cn}^2(\eta d, q)} + \frac{\xi^2 \cdot \cosh[\xi(d-x_2)]}{\sinh^2[\xi(d-x_2)]} = \frac{\kappa \cdot \xi}{\sinh[\xi(d-x_2)]}. \quad (32)$$

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, 11, 12]. Via the symmetry of the localized state, we can denote $A_1 = A_2 \equiv A$. Then the boundary conditions (31),(32) in terms of the amplitude A can be rewritten as follows:

$$A = u(-d) = u(d) = \frac{\xi}{\sinh[\xi(d-x_2)]} = \frac{q'\eta}{\text{cn}(\eta d, q)}, \quad (33)$$

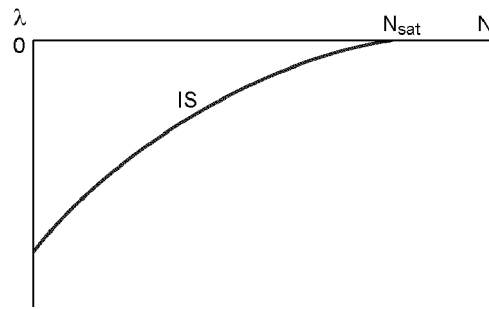


Fig. 1. The dependence $\lambda(N)$ for the in-phase symmetric (IS) state in the system with a positive excluded volume.

$$\sqrt{A^2 - q'^2 \eta^2} \cdot \sqrt{A^2 + q^2 \eta^2} + A \sqrt{A^2 + \xi^2} = \kappa \cdot A. \tag{34}$$

Eq.(34) can be reduced to the form

$$\sqrt{A^4 + A^2 \xi^2 - q^2 q'^2 \eta^4} + A \sqrt{A^2 + \xi^2} = \kappa \cdot A. \tag{35}$$

These three relations (33),(34) (or (33),(35)) determine the parameters A , x_2 and q as functions of the parameters ξ 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 $\xi \rightarrow 0$ (or $\lambda \rightarrow 0$). In the limit $\kappa d \gg 1$ (weak coupling between interfaces) the problem reduces to the study of 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 [11].

After the substitution of our (IS) solution (29) into 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 (IS) state terminates at the edge of the spectrum of linear waves ($\lambda = 0$), and the profile of this spatially localized state near the interfaces have the form of algebraic solitons with power-law asymptotic behavior at large distances [13]. This case corresponds to the situation when 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 $\lambda = 0$, can not be localized in the system.

Taking into account the symmetry of the in-phase symmetric (IS) solution (29) and calculating the total number of monomers, we come to the following exact result:

$$N = \int_{-\infty}^{+\infty} |u|^2 dx = 2\xi [\coth[\xi(d - x_2)] - 1] + 2\eta \cdot \frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} - 2\eta E(\text{am}(\eta d, q), q) + 2q'^2 \eta^2 d, \tag{36}$$

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 the boundary conditions (33),(34) (or (35)).

Using relation (31), we can eliminate parameter x_2 and then rewrite Eq.(36) in the form

$$N = 2 \left[\sqrt{\frac{q'^2 \eta^2}{\text{cn}^2(\eta d, q)} + \xi^2} - \xi \right] + 2\eta \frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} - 2\eta \cdot E(\text{am}(\eta d, q), q) + 2q'^2 \eta^2 d. \tag{37}$$

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

$$\lambda \rightarrow 0 \quad \text{and} \quad \xi \rightarrow 0. \tag{38}$$

In this case we can rewrite the solution (29) for $u_{1,2}(x)$ in the form

$$u_{1,2}(x) = \mp \frac{\xi}{\sinh[\xi(x - x_{1,2})]} \approx \mp \frac{1}{x - x_{1,2}}, \quad (39)$$

and, as it follows from (33), the amplitude at the interface is equal to

$$A \approx \frac{1}{d - x_2}. \quad (40)$$

If we suppose that $\eta d \ll 1$, then from (33) we have $A \approx q'\eta \ll 1$. Substituting this expression into the boundary condition (34) (or (35)), we come to the following result for the parameter q :

$$q^2 \approx \frac{1}{2} \cdot \left(1 + \frac{\xi^2}{2\kappa^2}\right). \quad (41)$$

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

$$\eta = \frac{\xi}{\sqrt{2q^2 - 1}} \approx \sqrt{2} \cdot \kappa, \quad (42)$$

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 $\xi \ll 1$ 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 not small too, and the boundary condition (33) can be rewritten as

$$A \approx \frac{1}{d - x_2} \approx \frac{1}{\sqrt{2}} \cdot \frac{\eta}{\text{cn}(\eta d, 1/\sqrt{2})}. \quad (43)$$

The dependence of the parameter $q = q(\xi, d)$ (or, equivalently, $\eta = \eta(\xi, d)$), which is necessary in order to obtain N in (37), in this case should be found after the substitution A from (43) into the boundary condition (35). In this general case, as a result of this substitution, we come to the following equation for the variable η :

$$\eta^2 \text{cn}^3(\eta d, 1/\sqrt{2}) + 2\kappa^2 \cdot \text{cn}(\eta d, 1/\sqrt{2}) - 2\sqrt{2} \cdot \kappa \cdot \eta = 0. \quad (44)$$

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

$$g_\eta = \eta/\kappa \quad \text{and} \quad y = \kappa d. \quad (45)$$

We note the y gives the *overlap* of the interfaces 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.(45), we obtain

$$g_\eta^2 \cdot \text{cn}^3(g_\eta \cdot y, 1/\sqrt{2}) + 2 \cdot \text{cn}(g_\eta \cdot y, 1/\sqrt{2}) - 2\sqrt{2} \cdot g_\eta = 0 \quad (46)$$

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/surfaces, energy of the system, and the force acting between two penetrable traps.

Now let us introduce the reduced monomers number $n_{sat} = N_{sat}/\kappa$. Then in the saturation limit $\xi \rightarrow 0$ ($N(\xi, d) \rightarrow N_{sat}(d)$) we have $q \rightarrow 1/\sqrt{2}$, and the expression (37) transforms into

$$\begin{aligned} n_{sat} \approx & \frac{\sqrt{2} g_\eta}{\text{cn}(g_\eta y, 1/\sqrt{2})} + 2g_\eta \frac{\text{sn}(g_\eta y, \frac{1}{\sqrt{2}}) \text{dn}(g_\eta y, \frac{1}{\sqrt{2}})}{\text{cn}(g_\eta y, \frac{1}{\sqrt{2}})} - \\ & - 2g_\eta \cdot \text{E}(\text{am}(g_\eta y, 1/\sqrt{2}), 1/\sqrt{2}) + g_\eta^2 y. \end{aligned} \quad (47)$$

Here the function $g_\eta(y)$ is the solution of Eq.(46). Thus, the solution of Eq.(47) has the universal (scaling) form: $n_{sat} = n_{sat}(y)$ for different values of the parameters κ and d . The numerical solution for $n_{sat}(y)$

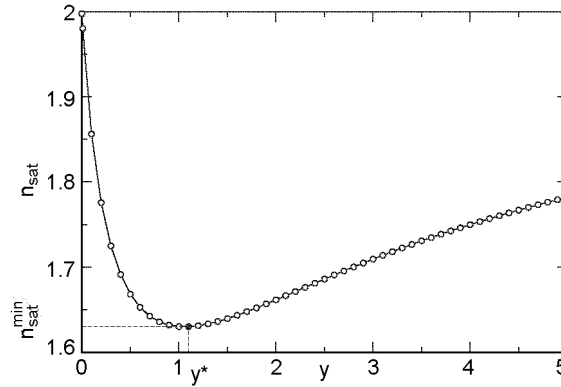


Fig. 2. The dependence $n_{sat}(y)$ at the saturation threshold.

is presented in Fig.2. 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 for $d \rightarrow 0$ when monomers start to escape outside the region confined by two penetrable interfaces into the tails on the both sides of the interfaces, and reaches its maximum value $n_{sat}^{max} = 2$ for $d = 0$ (strong overlap, $y \ll 1$).

In the limiting case $y \ll 1$ (strong overlap) we have $g_\eta \approx \sqrt{2} - 2\sqrt{2} \cdot y$ and from Eq.(47) we obtain the following result for the function n_{sat} :

$$n_{sat} \approx 2 - 2y, \tag{48}$$

where we took into account the correction to the expression (41) for the parameter q , $q^2 \approx \frac{1}{2} \cdot (1 + \frac{\xi^2}{2\kappa^2}) + 2 \cdot y$.

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 [11]. 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 can not be of an arbitrary length. It is limited by the maximum length of a chain, viz., by the total number of monomers multiplied by the statistical segment length of the chain, $d_{max} = (N - 1)a$. The minimal distance d_{min} is defined by the parameter a .

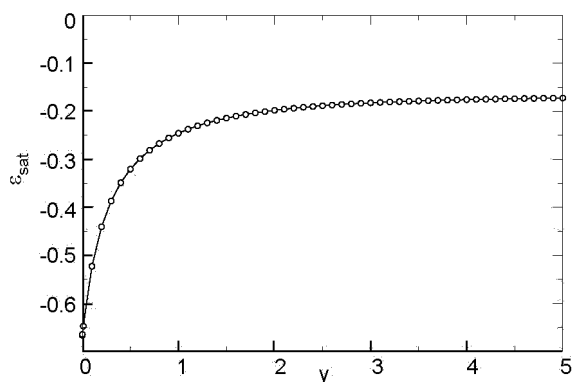
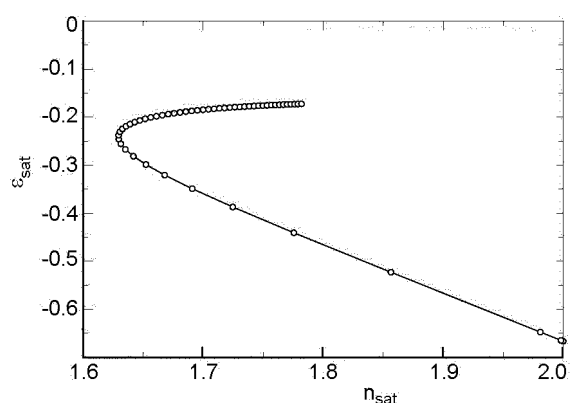
The total energy (per unit area) of the system E is defined by the integral

$$E = \int_{-\infty}^{+\infty} \{ |\frac{\partial u}{\partial x}|^2 + \sigma |u|^4 - \kappa [\delta(x + d) + \delta(x - d)] \cdot |u|^2 \} dx. \tag{49}$$

Substituting the ground state solution (29) into Eq.(49) and taking into account the boundary condition (33), we find the 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 $\varepsilon_{sat} = E_{sat}/\kappa^3$. Then, we obtain in the limit case $\xi \rightarrow 0$:

$$\begin{aligned} \varepsilon_{sat} \approx & \frac{\sqrt{2} g_\eta^3}{3 \operatorname{cn}^3(g_\eta y, 1/\sqrt{2})} \cdot [1 + \sqrt{2} \cdot \operatorname{sn}(g_\eta y, 1/\sqrt{2}) \cdot \\ & \cdot \operatorname{dn}(g_\eta y, 1/\sqrt{2})] - \frac{g_\eta^2}{\operatorname{cn}^2(g_\eta y, 1/\sqrt{2})} - \frac{g_\eta^4 y}{6}. \end{aligned} \tag{50}$$

Using the solution of $g_\eta(y)$ given by Eq.(46) we obtain a single variate function $\varepsilon_{sat}(y)$. The minimum value of ε_{sat} , as it follows from (50), is equal to $\varepsilon_{sat}^{min} = -2/3$. The universal dependence $\varepsilon_{sat} = \varepsilon_{sat}(y)$ is presented in Fig.3. The energy of the saturated system is thus a monotonously increasing function of the distance between the traps. Note that the condition of saturation, however, implies an exchange of

Fig. 3. The dependence $\varepsilon_{sat}(y)$ at the saturation threshold.Fig. 4. The dependence $\varepsilon_{sat}(n_{sat})$ at the saturation limit.

chains by changing the distance according to the result given in Fig.2. Thus, the system is considered in equilibrium with free chains in 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 [14]. 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.4 we display the dependence of 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 between interfaces d_1 and d_2 that can be easily seen from the dependence for the total number of monomers presented in Fig.2. Thus, there exist a high energy phase (large separation) and a low energy phase (close interfaces).

So far, we described localized states with zero concentration at infinity ($u(x) \rightarrow 0$ 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.

We have obtained exact solutions for the problem of adsorption of real polymer chains in systems containing two adsorbing interfaces within the mean-field approximation. Using the exact solution for the SNLSE on intervals of constant potentials opens the possibility to treat various localization problems for polymer chains using the appropriate boundary conditions.

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 [4]. 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. We have found that the saturation density of monomers behaves non-monotone 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. The changing of the distance between the interfaces changes the number of chains adsorbed.

Furthermore, we found the exact expression for the energy of the system which turned out to be strictly negative. The non-monotonous behavior of the saturation density of polymers as a function of the distance between the interfaces results in “two-phase” behavior of the free energy as a function of the amount of adsorbed polymers (see Fig.4). A low-energy phase corresponds to small distances between the interfaces, and a high-energy phase corresponds to large distances between them.

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Локалізація полімерних ланцюжків в системі з двома прозорими інтерфейсами

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Вивчено локалізацію полімерних ланцюжків у системі з двома прозорими інтерфейсами у рамках наближення середнього поля. Досліджено стан насичення полімерного ланцюжка у граничному випадку нульової концентрації полімеру далеко від інтерфейсів. Одержано немонотонну залежність кількості адсорбованих мономерів як функцію відстані між інтерфейсами.