

Adsorption of polymer chains at two impenetrable interfaces

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We study the problem of adsorption of polymer chains in a system containing two impenetrable attracting interfaces within the mean-field approximation. We find the exact solution of this mean-field polymer adsorption problem that is controlled by a single scaling variable describing the coupling between the impenetrable interfaces due to the polymer chains. At the saturation point we obtain the total number of adsorbed monomers, the total energy of the system and the force acting between impenetrable interfaces that is turned to be strictly attractive and monotonously decaying towards zero for increasing distance between the interfaces.

The problems of adsorption of polymer chains at interfaces and surfaces have always been a focus of attention of theoretical and applied polymer physics. The understanding of physics of real polymers at surfaces/interfaces can lead to novel applications [1–3]. From a practical point of view, adsorption phenomena in polymeric solutions are very important for such processes as lubrication, adhesion and surface protection, as well as interaction between interfaces and polymers. The excluded volume effects lead to saturation effects at surfaces or interfaces.

The effects of excluded volume interactions can be understood using mean-field concepts [4]. This approach has been applied already to the formation of adsorption layers onto solid surfaces, see [4], and to the interaction between two solid surfaces propagated by adsorbed polymer layers [5, 6]. 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 [7]. Using a renormalized free-energy functional, de Gennes has also extended the mean-field approach to incorporate correlation effects in good solvent conditions. 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, 8].

In our previous work [9] we studied the problem of adsorption of polymer chains in the system of two penetrable interfaces within the mean-field approximation.

The saturation state of the polymer system in the limiting case of zero bulk concentration was investigated. We obtained a non-monotonous behavior of the amount of adsorbed polymers as a function of the distance between the interfaces for such a system. At the saturation point, we found also the total energy of the system and the force acting between the interfaces.

In the present Letter we study the other case, viz., the adsorption of a polymer chain confined by two impenetrable attracting interfaces (hard walls) and compare the results with those obtained in [9] for the system of two penetrable interfaces. Such a problem has been investigated before (see [7, 10]). We find the exact solution for this mean-field polymer adsorption problem within the ground-state dominance approximation (GSDA) and investigate the saturation behavior of a polymer chain in such environments.

The nonlinear equation describing such a system is the corresponding Edwards equation [11] (the statistics of a polymer chain is dominated by the ground state solution of this equation):

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

where $u(x)$ is the part of the state function of the polymer chain corresponding to the eigenvalue λ , a is the length of a statistical Kuhn segment, $U_{ext}(x)$ is the potential energy of a segment at the position x , and $k_B T$ denotes the usual product of Boltzmann's constant and absolute temperature. For simplicity, we use only one coordinate because of the symmetry of the potential. We will study parallel plane interfaces where the localization takes place in the direction perpendicular to them.

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

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

where the index k counts the various solutions of Eq. (1). 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 two impenetrable interfaces (traps) and in the absence of excluded volume effects the external potential $U_{ext}(x)$ can be written as

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

where the interfaces are characterized by the value of the parameter κ ; $2d$ is the distance between interfaces. Note, that the parameter κ has the dimension of a length scale.

Then, Eq. (1) can be rewritten in the following form:

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

The x axis is directed perpendicular to the interfaces.

The solution of Eq. (4) reduces to the solution of the corresponding homogeneous equation

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

in the region between the interfaces with the following boundary conditions at $x = \pm d$:

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

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

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, 12, 13]:

$$U_{ev}(x) = k_B T \cdot v \cdot a \cdot c(x), \quad (8)$$

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 [4]. Thus, Eq. (1) can be rewritten as follows:

$$\lambda u = -\frac{a^2}{6} \frac{d^2 u}{dx^2} + va|u|^2 u + \frac{U_{ext}(x)}{k_B T} u. \quad (9)$$

In the presence of two impenetrable interfaces the external potential $U_{ext}(x)$ takes the form (3) and the nonlinear equation for a real polymer chain takes the following final form:

$$\lambda u = -\frac{a^2}{6} \frac{d^2 u}{dx^2} + va|u|^2 u - \kappa [\delta(x+d) + \delta(x-d)] u. \quad (10)$$

Rescaling the variables according to:

$$\frac{2}{|v|} \lambda \rightarrow \lambda, \quad \frac{2\sqrt{3}}{a\sqrt{|v|}} \kappa \rightarrow \kappa, \quad \frac{x}{l} \rightarrow x, \quad (11)$$

where $l = a/\sqrt{3|v|}$ is the excluded volume length (EV-length), as well as introducing the dimensionless state function according to $\sqrt{a}u \rightarrow u$, we can rewrite the stationary nonlinear Schrödinger equation (10) in the following rescaled form:

$$\lambda u = -\frac{d^2 u}{dx^2} + 2\sigma|u|^2 u - \kappa [\delta(x+d) + \delta(x-d)] u, \quad (12)$$

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 (11) have to be applied once.

The Lagrangian density corresponding to Eq. (12) has the following form:

$$L = -\left|\frac{du}{dx}\right|^2 - \sigma|u|^4 + \kappa [\delta(x+d) + \delta(x-d)] |u|^2 + \lambda |u|^2. \quad (13)$$

The solution of Eq. (12) reduces to the solution of the corresponding homogeneous equation

$$\frac{d^2 u}{dx^2} + \lambda u - 2\sigma|u|^2 u = 0 \quad (14)$$

in the region between the interfaces with the following boundary conditions (compare with (6),(7)):

$$u|_{\pm d+0} = u|_{\pm d-0}, \quad (15)$$

$$\frac{du}{dx}|_{\pm d+0} - \frac{du}{dx}|_{\pm d-0} = -\kappa u|_{\pm d}. \quad (16)$$

As the ground state is dominant, we can omit the modulus and rewrite Eq. (14) in the form

$$\frac{d^2 u}{dx^2} + \lambda u - 2\sigma u^3 = 0. \quad (17)$$

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 interfaces ($\kappa > 0$). The monomers are confined between impenetrable interfaces and cannot penetrate through them. Consequently, the density in the region outside the slit between interfaces is equal to zero. Because the ground state is dominant, we are only interested in the symmetric solution which in the region between the interfaces ($|x| < d$) has the following form (compare with the solution in [9]):

$$u(x) = \frac{q'\eta}{\text{cn}(\eta x, q)}. \quad (18)$$

Here the parameters η is equal to

$$\eta = \xi / \sqrt{2q^2 - 1}, \quad (19)$$

where

$$\xi = \sqrt{-\lambda}. \quad (20)$$

The function $\text{cn}(\eta x, q)$ is the Jacobi elliptic function with modulus q ; $q' = \sqrt{1 - q^2}$; 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 potentials in a straight forward manner. The solution (18) is a one-parameter and is completely characterized by the value of the parameter ξ (or λ).

Equation (12) requires the condition of normalization that defines, in fact, the total number of monomers in the system per (dimensionless) unit area:

$$N = \int_{-\infty}^{+\infty} u^2(x) dx = \int_{-d}^{+d} u^2(x) dx. \quad (21)$$

Indeed, 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.

Note that in the nonlinear case the normalization leads to the relation between the parameters ξ and N (or λ and N). Substituting our solution (18) into the integral (21) we can finally obtain the dependence $N = N(\xi)$ and the inverse dependence $\xi = \xi(N)$ (or $\lambda = \lambda(N)$). For our system ($v > 0; \kappa > 0$) we arrive at the following exact result:

$$N = 2\eta \left[\frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} - \text{E}(\text{am}(\eta d, q), q) + q'^2 \eta d \right], \quad (22)$$

where $\text{E}(\varphi, q)$ is the elliptic integral of the second type and $\text{am}(\phi, q) = \arcsin[\text{sn}(\phi, q)]$ is the elliptic amplitude.

Let us study the behavior of our system at the *saturation limit*:

$$\lambda \rightarrow 0 \quad (\text{or } \xi \rightarrow 0). \quad (23)$$

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.

It was shown in Ref. [9] that in this limit case we come the following expression for the parameter q : $q \approx 1/\sqrt{2}$. Again, we have the same equation for the variable η , as for the system in [9]:

$$\eta^2 \text{cn}^3(\eta d, 1/\sqrt{2}) + 2\kappa^2 \text{cn}(\eta d, 1/\sqrt{2}) - 2\sqrt{2}\kappa\eta = 0. \quad (24)$$

Introducing new scaling variables according to

$$g_\eta = \eta/\kappa \quad \text{and} \quad y = \kappa d, \quad (25)$$

it is possible to reduce the parameter κ in the equation (24). After the substitution of the variables (25) in the Eq. (24) we obtain the following equation with the formal solution $g_\eta(y)$:

$$g_\eta^2 \text{cn}^3(g_\eta y, 1/\sqrt{2}) + 2\text{cn}(g_\eta y, 1/\sqrt{2}) - 2\sqrt{2}g_\eta = 0. \quad (26)$$

Further we shall use the function $g_\eta(y)$ for the calculation of the physical characteristics of the system, such as the number of monomers trapped between attracting interfaces, the total energy of the system, and the force acting between two impenetrable interfaces.

Now let us introduce the reduced monomers number $n_{\text{sat}} = N_{\text{sat}}/\kappa$. At the saturation limit (23) we have $N(\xi, d) \rightarrow N_{\text{sat}}(d)$ and $q \rightarrow 1/\sqrt{2}$, and the expression (22) transforms into

$$n_{\text{sat}} \approx 2g_\eta \frac{\text{sn}(g_\eta y, 1/\sqrt{2}) \text{dn}(g_\eta y, 1/\sqrt{2})}{\text{cn}(g_\eta y, 1/\sqrt{2})} - 2g_\eta \text{E}(\text{am}(g_\eta y, 1/\sqrt{2}), 1/\sqrt{2}) + g_\eta^2 y, \quad (27)$$

where $g_\eta(y)$ is the numerical solution of the transcendental Eq.(26). The dependence (27) $n_{\text{sat}} = n_{\text{sat}}(y)$ has the universal scaling form for different values of the parameters κ and d . The numerical solution for $n_{\text{sat}}(y)$ is presented in Fig. 1.

For penetrable interfaces in [9], $n_{\text{sat}}(y)$ decreases with the scaling variable y tending to its minimum value

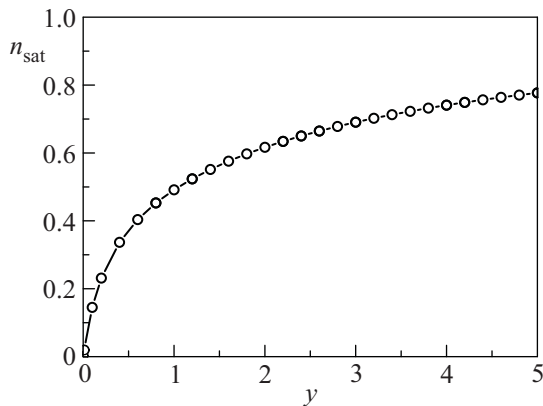


Fig. 1. The dependence $n_{\text{sat}}(y)$ at the saturation threshold

for some value y^* and increases again for $y \rightarrow 0$. In contrast to this case, for impenetrable interfaces the dependence $n_{\text{sat}}(y)$ monotonically decreases and vanishes for $y \rightarrow 0$, because in this case (under consideration) monomers cannot penetrate to the tails outside the space confined by the interfaces.

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, $d_{\text{max}} = (N - 1)a$. The minimal distance d_{min} is defined by the parameter a .

Eq. (12) can be alternatively derived from a variational principle using the energy functional $E[u]$ (per unit area) (see Ref. [4])

$$E = \int_{-\infty}^{+\infty} \left\{ \left| \frac{\partial u}{\partial x} \right|^2 + \sigma |u|^4 - \kappa [\delta(x+d) + \delta(x-d)] |u|^2 \right\} dx. \quad (28)$$

Note that, like in [9], the eigenvalue λ plays the role of the chemical potential for monomers bound in the adsorbed state.

Substituting the solution (18) into the integral (28), we find the exact expression for the total energy of the system:

$$E = \frac{4q^2 \eta^3}{3} \frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}^3(\eta d, q)} + \frac{2(1-2q^2)\eta^3}{3} \times \left\{ \frac{\text{sn}(\eta d, q) \text{dn}(\eta d, q)}{\text{cn}(\eta d, q)} - E[\text{am}(\eta d, q)] \right\} - \frac{2\kappa q^2 \eta^2}{\text{cn}^2(\eta d, q)} + 2q^2 \left(\frac{1}{3} - q^2 \right) \eta^4 d. \quad (29)$$

Again, we can introduce the scaling variables g_η and y (25) and define the appropriately reduced energy of the system $\varepsilon_{\text{sat}} = E_{\text{sat}}/\kappa^3$. Then, we obtain in the saturation limit ($\xi \rightarrow 0$):

$$\varepsilon_{\text{sat}} \approx \frac{2g_\eta^3}{3} \frac{\text{sn}(g_\eta y, 1/\sqrt{2}) \text{dn}(g_\eta y, 1/\sqrt{2})}{\text{cn}^3(g_\eta y, 1/\sqrt{2})} - \frac{g_\eta^2}{\text{cn}^2(g_\eta y, 1/\sqrt{2})} - \frac{g_\eta^4 y}{6}. \quad (30)$$

Using the solution $g_\eta(y)$ given by Eq.(26), we obtain a single variate function $\varepsilon_{\text{sat}}(y)$. The minimum value of ε_{sat} , as it follows from (30), is equal to $\varepsilon_{\text{sat}}^{\text{min}} = -2$. The universal dependence $\varepsilon_{\text{sat}} = \varepsilon_{\text{sat}}(y)$ is presented in Fig. 2. Thus, the energy of the saturated system is

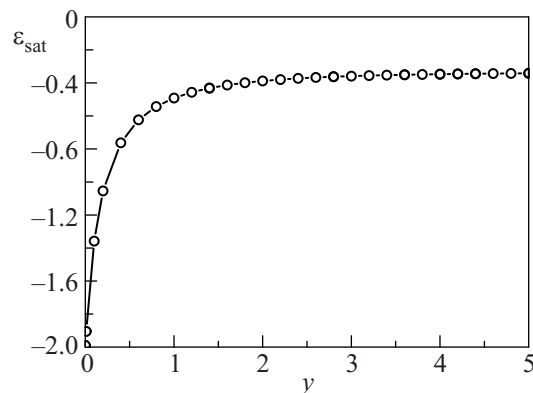


Fig. 2. The dependence $\varepsilon_{\text{sat}}(y)$ at the saturation threshold

a monotonously increasing function of the distance between the interfaces.

If we compare the dependencies $\varepsilon_{\text{sat}}(y)$ for the system of two solid walls and for the system of two penetrable interfaces, we can conclude that over all the range of the scaling variable y we have $\varepsilon_{\text{sat}}^{\text{hard walls}}(y) < \varepsilon_{\text{sat}}^{\text{penetr interf}}(y)$. The number of monomers localized between the hard walls at the saturation limit is much smaller as compared to the case of two penetrable interfaces.

Also, we can calculate an important characteristics of the system for practical measurements, viz., the force per unit area acting between the interfaces. In the general case $F = -dE(d, \lambda)/dd$, and at the saturation limit we have

$$F_{\text{sat}} = -\frac{dE_{\text{sat}}(d)}{dd} = \frac{2\eta^3(\eta'd + \eta)}{3\text{cn}^4(\eta d, \frac{1}{\sqrt{2}})} + 2\eta^2 [\eta' - \kappa(\eta'd + \eta)] \cdot \frac{\text{sn}(\eta d, \frac{1}{\sqrt{2}}) \text{dn}(\eta d, \frac{1}{\sqrt{2}})}{\text{cn}^3(\eta d, \frac{1}{\sqrt{2}})} + \frac{\eta [\eta^2(\eta'd + \eta) - 18\kappa\eta']}{9\text{cn}^2(\eta d, \frac{1}{\sqrt{2}})} - \frac{\eta^3(14\eta'd + 5\eta)}{18}. \quad (31)$$

The parameter $\eta' \equiv d\eta/dd$ is found by differentiation of Eq. (24).

If we introduce the reduced force $f_{\text{sat}} = F_{\text{sat}}/\kappa^4$ and the new function $g_{\eta'}(y) = \eta'/\kappa^2$, then we can rewrite Eq.(31) in the following form:

$$f_{\text{sat}} = \frac{2g_{\eta'}^3(g_{\eta'}y + g_{\eta'})}{3\text{cn}^4(g_{\eta'}y, \frac{1}{\sqrt{2}})} + 2g_{\eta'}^2[g_{\eta'}(1-y) - g_{\eta'}] \times \\ \times \frac{\text{sn}(g_{\eta'}y, \frac{1}{\sqrt{2}}) \text{dn}(g_{\eta'}y, \frac{1}{\sqrt{2}})}{\text{cn}^3(g_{\eta'}y, \frac{1}{\sqrt{2}})} + \\ + \frac{g_{\eta'}[g_{\eta'}^2(g_{\eta'}y + g_{\eta'}) - 18g_{\eta'}]}{9\text{cn}^2(g_{\eta'}y, \frac{1}{\sqrt{2}})} - \frac{g_{\eta'}^3(14g_{\eta'}y + 5g_{\eta'})}{18}, \quad (32)$$

where

$$g_{\eta'}(y) = \frac{g_{\eta'}\mu(y)}{2g_{\eta'}\text{cn}^3(g_{\eta'}y, \frac{1}{\sqrt{2}}) - y\mu(y) - 2\sqrt{2}}, \quad (33)$$

$$\mu(y) = \left[3g_{\eta'}^2\text{cn}^2(g_{\eta'}y, \frac{1}{\sqrt{2}}) + 2 \right] \text{sn}(g_{\eta'}y, \frac{1}{\sqrt{2}}) \text{dn}(g_{\eta'}y, \frac{1}{\sqrt{2}}), \quad (34)$$

and $g_{\eta'}(y)$ is the solution of Eq.(26).

For different values of the parameter κ we obtain the universal dependence $f_{\text{sat}} = f_{\text{sat}}(y)$ presented in Fig. 3. In the limit $y \rightarrow 0$ we have $g_{\eta'} \approx \sqrt{2}$, $g_{\eta'} \approx -2\sqrt{2}$

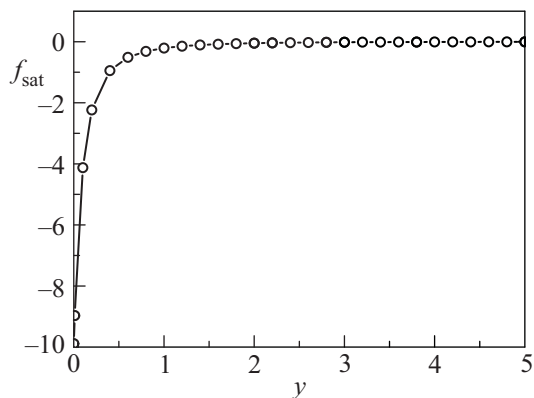


Fig. 3. The dependence $f_{\text{sat}}(y)$ at the saturation threshold

and the minimum value of f_{sat} from Eq.(32) is equal to $f_{\text{sat}}^{\text{min}} = -10$.

If we compare the forces acting between two hard walls and between two penetrable interfaces, we can see that both dependences tend to zero for large values of y and $|f_{\text{sat}}^{\text{hard walls}}(y)| > |f_{\text{sat}}^{\text{penetr interf}}(y)|$ over all the range of the variable y .

To summarize, we obtained the exact solution for the problem of adsorption of a real polymer chain between two impenetrable attracting interfaces within the mean-field approximation. We described adsorbed states at the saturation limit. This can be realized for the adsorption from highly diluted polymer solutions and strongly attracting interfaces as discussed above.

For the saturation limit, we 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 (the coupling parameter of the interface-polymer system). We found the total number of monomers adsorbed at the interfaces (hard walls), the total energy of the system, which turned out to be strictly negative, and the forces acting between both interfaces due to the interface-polymer coupling. The forces turned out to be attractive and monotonously approaching zero with increasing the distance between the interfaces. Also, we performed the comparison of our results with those obtained in [9] for the array of two penetrable interfaces.

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