Adsorption of a random heteropolymer with self-interactions onto an interface

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Abstract

We consider the adsorption of a random heteropolymer onto an interface within the model by Garel et al. \cite{Garel} by taking into account self-interactions between the monomers. Within the replica trick and by using a self-consistent preaveraging procedure we map the adsorption problem onto the problem of binding state of a quantum mechanical Hamiltonian. The analysis of the latter is treated within the variational method based on the 2-nd Legendre transform. We have found that self-interactions favor the localization. The effect is intensified with decrease of the temperature. Within a model without taking into account the repulsive ternary monomer-monomer interactions we predict a reentrant localization transition for large values of the asymmetry of the heteropolymer and at low enough temperatures.

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INTRODUCTION

The behavior of heteropolymers at interface between two immiscible (incompatible) solvents has been intensively studied in recent years [1]-[16] since it has an obvious importance in biological applications (proteins and membranes) [17] and application in different fields of industry such as biosensor, pattern recognition applications, glues, paints etc. [18]. Experiments [19], [20] and numerical simulations [21], [23] have shown that a random heteropolymer may localize, reinforcing the interface between two incompatible solvents and reduce interfacial tension. Recent theoretical efforts have been devoted to understand the fundamental physical mechanism governing the localization of a random copolymer onto an interface [5]-[15].

In the simple model introduced by Garel et al. [1] only the interaction of the monomers with the solvent, but not the self-interactions between the monomers were taken into account. Considering a $A-B$ copolymer at the $A-B$ interface $A$ monomers prefer to be in the $A$-half-plane while $B$ monomers prefer to be in $B$-half-plane. Obviously there is a sort of frustration in such system because the complete separation of $A$ monomers into one-half and $B$ monomers into another half plane is forbidden by polymer bonds. The analysis performed in [1] showed that the localized state of a random heteropolymer chain in the presence of a selective interface can be imagined as consisting of blobs with majority of $A$ monomers and minority of $B$ monomers in the $A$-half-plane and vice versa for the blobs in the $B$-half-plane. It was shown that random copolymer always localizes for statistically symmetric heteropolymer, whereas a delocalization transition was found if the heteropolymer is asymmetric. The heterogeneity in the chemical structure of the polymer, which results in self-interactions between the monomers, may have a considerable impact on their bulk thermodynamic behavior [22], which consists in a segregation into $A$-rich and $B$-rich domains. In the case of a single heteropolymer in solvent the self-interactions favor the collapse of the heteropolymer [24]. The self-interactions between monomers may play an important role for adsorption as it was noticed in [1], [27]. However, the influence of self-interactions on the localization behavior of the random heteropolymer is poorly understood. The effect of the excluded volume in the adsorption of a heteropolymer was recently investigated in [26]. In the present paper we will consider the influence of the direct monomer-monomer interactions on the localization behavior of a random heteropolymer onto an interface.

The article is organized as follows. In Section II we will introduce to the model and the formalism we use. Section III contains our results and Section IV conclusions.

I. MODEL AND FORMALISM

We study the problem of a random heteropolymer by using the model proposed in [1]. Let us consider a long two-letter $A-B$ heteropolymer chain in the presence of the $A'-B'$ interface between two incompatible solvents. Alternation of different type of monomers along the chain is assumed to be random, and each monomer is assumed to interact with an external potential, which takes positive and negative values depending on the position with respect to the interface. The partition function of the polymer in the presence of the interface is given by the following Edwards functional integral [27] over the trajectories $\mathbf{r}(s)$ ($0 \leq s \leq N$) of the polymer chain
\[
Z\{\zeta(s)\} = \int D\mathbf{r}(s) \exp \left\{ -\frac{1}{2a^2} \int_0^N ds \left( \frac{\partial \mathbf{r}}{\partial s} \right)^2 + w \int_0^N ds \, \zeta(s) \text{sgn}[z(s)] + \chi_0 \int_0^N ds \int_0^N ds' \, \zeta(s)\zeta(s') \delta(\mathbf{r}(s) - \mathbf{r}(s')) \right\},
\]

where \(a\) is the Kuhnian segment length, \(z(s)\) is the Cartesian component of \(\mathbf{r}(s)\) transversal to the interface, \(w\) and \(\chi_0\) are measured in units of \(k_B T\). The first term in the exponential of (1) corresponds to the elastic energy of the polymer chain, the second one describes the monomer interaction with the medium, which is governed by the random parameter \(\zeta(s)\), which is assumed to be Gaussian distributed with the distribution function

\[
P\{\zeta(s)\} \propto \exp \left[ -\frac{1}{2\Delta_0} \int_0^N (\zeta(s) - \zeta_0)^2 \, ds \right].
\]

The distribution function (2) of the random “charges” \(\zeta(s)\) is completely characterized by its two moments, \(\langle \zeta(s) \rangle = \zeta_0\) with \(\zeta_0\) related to the asymmetry in the composition of the copolymer, and \(\langle \zeta(s)\zeta(s') \rangle = \zeta_0^2 + \Delta_0 \delta(s - s')\) where \(\Delta_0\) being the variance of the distribution. The interaction potential is chosen as a step function. Such a choice is legitimate, if the interface width is much smaller than the size of an average excursion loop. The last term in Eq.(1) describes the short-rang interaction between monomers, where \(\chi_0\) is the effective interaction potential (the second virial coefficient). The sign of the last term in (1) is chosen so that for \(\chi_0 > 0\) the like monomers attract each other while the unlike monomers repel each other. The model described by Eq.(1) admit that the self-interactions occur independent of whether the monomers are on the left or on the right side of the interface. This may be the case if even the favorable solvent for a given type of monomer is slightly poor. If the favorable solvent is comprised of the same monomers, then the self-interactions between the like monomers in their own medium are expected to be zero. The generalization of the model where the self-interactions are switched off, if they are in their own medium is possible. The effect of ternary interactions, which will prevent the collapse of the blobs of the adsorbed heteropolymer due to attractive self-interactions, will be considered in a separate paper.

The random “charges” \(\zeta(s)\) in (1) are considered as quenched variables, so that in order to obtain the free energy one has to average \(\ln(Z)\) over all possible realizations of monomer sequences. For this purpose we use the replica trick consisting in introduction of \(n\) copies of the system with the same quenched variables \(\zeta(s)\), and using the identity \(\ln(Z) = \lim_{n \to 0} (Z^n - 1)/n\) in averaging over \(\zeta(s)\). Thus, at the intermediate stage we consider the average \(\langle Z^n \rangle\) where \(\langle \ldots \rangle\) means average with the distribution function (2). The partition function \(Z^n\) can be written as

\[
Z^n = \int \prod_{\alpha=1}^n D\mathbf{r}_\alpha(s) \exp \left\{ -H_0 - H_{\text{int}} \right\},
\]

where

\[
H_0 = \frac{1}{2a^2} \int_0^N ds \sum_{\alpha=1}^n \left( \frac{\partial \mathbf{r}_\alpha}{\partial s} \right)^2,
\]

\[
H_{\text{int}} = \int_0^N ds \sum_{\alpha=1}^n \delta(\mathbf{r}(s) - \mathbf{r}(s')) \zeta(s)\zeta(s').
\]
\[ H_{\text{int}} = -w \int_0^N ds \zeta(s) \sum_{\alpha=1}^n \text{sgn}[\mathbf{r}_\alpha(s)] - \chi_0 \int_0^N ds \int_0^N ds' \zeta(s)\zeta(s') \sum_{\alpha=1}^n \delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\alpha(s')). \]

(5)

To average over \( \zeta(s) \) in (5) we expand (5) in Taylor series in powers of \( H_{\text{int}} \), carry out the average, and reexponentiate the obtained expression. This results in writing the result of this reexponentiation as

\[
\ln(\langle \exp \{-H_{\text{int}}\} \rangle) = -\langle H_{\text{int}} \rangle + \frac{1}{2} \langle \langle H_{\text{int}}^2 \rangle \rangle - \langle H_{\text{int}} \rangle^2 + \ldots.
\]

(6)

Restricting the expansion in (6) to quadratic terms in \( L \) we obtain

\[
\langle Z^n \rangle = \int \prod_{\alpha=1}^n D\mathbf{r}_\alpha(s) \exp \left\{ -\int_0^N \mathcal{L}_n \, ds \right\},
\]

(7)

with

\[
\mathcal{L}_n = \frac{1}{2a^2} \sum_{\alpha=1}^n (\frac{\partial \mathbf{r}_\alpha(s)}{\partial s})^2 - w\zeta_0 \sum_{\alpha=1}^n \text{sgn}(\mathbf{r}_\alpha(s)) - \chi_0 \zeta_0^2 \sum_{\alpha=1}^n \int_0^N \delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\alpha(s')) \, ds' - \frac{1}{2} w^2 \Delta_0 \sum_{\alpha,\beta=1}^n \text{sgn}(\mathbf{r}_\alpha(s))\text{sgn}(\mathbf{r}_\beta(s)) - \frac{2}{w} \chi_0 \zeta_0 \Delta_0 \sum_{\alpha,\beta=1}^n \text{sgn}(\mathbf{r}_\alpha(s)) \int_0^N \delta(\mathbf{r}_\beta(s) - \mathbf{r}_\beta(s')) \, ds' - 2\chi_0^2 \zeta_0^2 \Delta_0 \sum_{\alpha,\beta=1}^n \int_0^N ds' \int_0^N ds'' \delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\alpha(s')) \delta(\mathbf{r}_\beta(s) - \mathbf{r}_\beta(s'')) - \chi_0^2 \Delta_0^2 \sum_{\alpha,\beta=1}^n \int_0^N \delta(\mathbf{r}_\alpha(s) - \mathbf{r}_\alpha(s')) \delta(\mathbf{r}_\beta(s) - \mathbf{r}_\beta(s')) \, ds'.
\]

(8)

Notice that \( \mathcal{L}_n \) contains more than one integration over the contour length. Due to this it is not possible to reduce \( \mathcal{L}_n \) to a quantum mechanical Hamiltonian as it is the case, if only a single integration over the contour length appears (see for example [24]). In the following we will preaverage (8) in order to reduce it to a quantum mechanical Hamiltonian. For this purpose let us consider the quantities

\[
\rho(\mathbf{r}_\alpha) = \int_0^N \delta(\mathbf{r}_\alpha - \mathbf{r}_\alpha(s')) \, ds',
\]

(9)

\[
q(\mathbf{r}_\alpha, \mathbf{r}_\beta) = \int_0^N \delta(\mathbf{r}_\alpha - \mathbf{r}_\alpha(s')) \delta(\mathbf{r}_\beta - \mathbf{r}_\beta(s')) \, ds',
\]

(10)

where \( \rho(\mathbf{r}_\alpha) \) is the microscopic density associated with the polymer and \( q(\mathbf{r}_\alpha, \mathbf{r}_\beta) \) is the replica overlap parameter [24]. We will preaverage \( \rho(\mathbf{r}_\alpha) \) and \( q(\mathbf{r}_\alpha, \mathbf{r}_\beta) \) in Eq.(8) over \( \mathbf{r}_\alpha(s') \) and \( \mathbf{r}_\beta(s') \) according to

\[
\langle \rho(\mathbf{r}_\alpha) \rangle = \int_0^N ds \int dZ \int dZ' G(Z, N; z, s)G(z, s; Z', 0) \times \int dR_i \int dR'_i G_0(R_i, N; r_{in}, s)G_0(r_{in}, s; R'_i, 0)
\]

(11)
and similar for \( q(\mathbf{r}_\alpha, \mathbf{r}_\beta) \). \( G_0(R_i; N; r_i, s) \) in (11) is the free Green’s function of the longitudinal degrees of freedom of the polymer. Notice that the average over the longitudinal coordinates of the polymer with the unperturbed Green’s function is an approximation. We use the spectral representation of the transversal Green’s function in Eq.(11) \( G(z, N; z', 0) \) through the eigenfunctions \( \psi_k(z) \)

\[
G(z, z'; N) = \sum_k e^{-N\varepsilon_k} \psi_k(z) \psi_k^*(z').
\]

The Green’s function \( G(z, z'; N) \) satisfies for \( N > 0 \) the differential equation

\[
-\frac{\partial G}{\partial N} = -\frac{a^2}{6} \partial^2_z G + \frac{U(z)}{T} G,
\]

which is remarkably similar to the Schrödinger equation for a quantum particle in an external potential [27]

\[
i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + U(r) \psi.
\]

The mapping of the latter onto Eq.(13) occurs by using the following replacements: \( t \rightarrow iN \), \( \hbar \rightarrow T \), \( a^2/T \rightarrow 3/m \).

In the case of a discrete spectrum with the energy of the ground state being negative, the main contribution in the series (12) for large \( N \) originates from the ground state (ground state dominance) [28]. The preaveraging of \( \rho(\mathbf{r}_\alpha) \) and \( q(\mathbf{r}_\alpha, \mathbf{r}_\beta) \) given by Eqs.(9-10) according to (11) in the approximation of the ground state dominance gives

\[
\langle \rho(\mathbf{r}_\alpha) \rangle \approx \sigma |\psi_{k_0}(z_\alpha)|^2, \\
\langle q(\mathbf{r}_\alpha, \mathbf{r}_\beta) \rangle \approx \sigma |\psi_{k_0}(z_\alpha)|^2 |\psi_{k_0}(z_\beta)|^2,
\]

where \( \sigma = N/S \) is an average monomer density per surface area [29]. We expect that the ratio \( \sigma \) is finite for large \( N \) and \( S \).

The substitution of (14), (15) into the Hamiltonian (8) gives the effective replica Hamiltonian as

\[
H_n = -D \sum_{\alpha=1}^{n} \nabla^2_z - w \zeta_0 \sum_{\alpha=1}^{n} \text{sgn}(z_\alpha) - \chi_0 \zeta_0^2 \sigma \sum_{\alpha=1}^{n} |\psi(z_\alpha)|^2 - \\
\frac{1}{2} w^2 \Delta_0 \sum_{\alpha,\beta=1}^{n} \text{sgn}(z_\alpha) \text{sgn}(z_\beta) - 2w \chi_0 \zeta_0 \Delta_0 \sigma \sum_{\alpha,\beta=1}^{n} \text{sgn}(z_\alpha) |\psi(z_\beta)|^2 - \\
(2\zeta_0^2 \sigma + \Delta_0) \chi_0^2 \Delta_0 \sigma \sum_{\alpha,\beta=1}^{n} |\psi(z_\alpha)|^2 |\psi(z_\beta)|^2,
\]

where we have introduced the notation \( D = a^2/2 \). Due to the average over the longitudinal degrees of freedom of the polymer by using the unperturbed Green’s function, the problem becomes one dimensional.

The investigation of the adsorption of a random heteropolymer chain is equivalent to the study of the ground state of the Hamiltonian \( H_n \) given by Eq.(16). Without taking into
account the self-interactions, the case which is obtained from Eq. (14) by putting \( \chi_0 = 0 \), Stepanow et al. [5] applied a novel variational principle for Green’s function associated with the Hamiltonian \( H_n \). The latter generalizes the well-known Rayleigh-Ritz method in Quantum Mechanics for nonstationary states. The variational principle for the Green’s function can be outlined as follows [5]. The start point is the Dyson equation for the Green’s function \( G \)

\[
0 = -G^{-1} + G_0^{-1} + H_n^{\text{int}},
\]

which is considered as a stationarity condition \( \delta F(G)/\delta G = 0 \) of a functional \( F(G) \), which is found in a straightforward way as

\[
F(G) = -\text{tr} \ln(G) + \text{tr} G_0^{-1} G + \text{tr} H_n^{\text{int}} G,
\]

where the bare Green’s function is defined as \( G_0^{-1} = \omega + H_0 \), with \( H_0 \) being the unperturbed part of the Hamiltonian, \( H_n^{\text{int}} \) is the interaction part of the Hamiltonian, and \( \omega \) is Laplace conjugate to the chain’s length \( N \). The functional \( F(G) \) given by Eq. (18) is the particular case of the generating functional of the 2-nd Legendre transform in Quantum Field Theory and Statistical Physics [30]-[32]. Notice that without preaveraging of \( \rho(\mathbf{r}_a) \) and \( q(\mathbf{r}_a, \mathbf{r}_\beta) \) given by Eqs. (14) the problem under consideration does not reduce to a quantum mechanical problem and instead of (18) we have to use the extremum principle associated with the second Legendre transform [31]-[32]. Assuming the ground state dominance we choose the \( n \)- replica trial Green’s function as

\[
G(k_1, k_2; z, z'; t) = \prod_{\alpha=1}^n \exp(-\varepsilon_k t) \psi(k_1, k_2; z_\alpha) \psi(k_1, k_2; z'_\alpha),
\]

where the trial wave function is chosen as

\[
\psi(k_1, k_2; z_\alpha) = \sqrt{\frac{2k_1k_2}{k_1 + k_2}} \left( e^{-k_1 z_\alpha} \vartheta(z_\alpha) + e^{k_2 z_\alpha} \vartheta(-z_\alpha) \right).
\]

Notice that the energy \( \varepsilon_k = -Dk_2^2 \) is negative, and is a function of \( k_2 \). Computing the terms in (18) by using (19), (20) gives the extremum functional as

\[
F(k_1, k_2) = \ln(\omega + n\varepsilon_k) + \frac{n(Dk_1k_2 - \varepsilon_k)}{\omega + n\varepsilon_k} - \frac{n\omega \zeta_0}{\omega + n\varepsilon_k} \left( \frac{k_2 - k_1}{k_1 + k_2} \right) - \frac{n(\Delta_0 w^2)}{2 \omega + n\varepsilon_k} - \frac{n(n - 1) \Delta_0 w^2}{2 \omega + n\varepsilon_k} \left( \frac{k_2 - k_1}{k_1 + k_2} \right)^2 - \frac{n\chi_0 \zeta_0^2 \sigma}{\omega + n\varepsilon_k} \left( \frac{k_2}{k_1 + k_2} \right) - \frac{n^2 w\chi_0 \zeta_0 \Delta_0 \sigma}{\omega + n\varepsilon_k} \left( \frac{2k_1k_2}{k_1 + k_2} \right) \left( \frac{k_2 - k_1}{k_1 + k_2} \right) - \frac{(n + 3n^2)}{12} \left( \Delta_0^2 \sigma + \Delta_0 \right) \zeta_0^2 \Delta_0 \sigma \left( \frac{2k_1k_2}{k_1 + k_2} \right) \left( \frac{k_2 - k_1}{k_1 + k_2} \right)^2.
\]

The stationarity conditions

\[
\partial F / \partial k_1 = \partial F / \partial k_2 = 0,
\]

(22)
give in the limit \( n = 0 \) the following equations

\[
3k_1^3 + 9k_1^2k_2 + 9k_1k_2^2 + 3k_2^3 + 6\zeta(k_1 + k_2) + 6\Delta(k_1 - k_2) - \\
3\chi^2\sigma k_2(k_1 + k_2) - 2(2\chi^2\sigma + \Delta)\chi^2\Delta\sigma k_1k_2^2 = 0,
\]

(23)

\[
3k_1^3k_2 + 9k_1^2k_2^2 + 9k_1k_2^3 + 3k_2^4 + 3\zeta(k_1^2 - k_2^2) - 6\Delta k_1k_2 - \\
3\chi^2\sigma k_1k_2(k_1 + k_2) - (2\chi^2\sigma + \Delta)\chi^2\Delta\sigma k_1k_2^2 = 0,
\]

(24)

where we have introduced new quantities \( \Delta = \Delta_0w^2, \zeta = \zeta_0w, \chi = \chi_0/w^2 \) and have put \( D = 1 \). Solution of this system of equations gives us the localization lengths \( \xi_1 = 1/k_1 \) and \( \xi_2 = 1/k_2 \), which describe the localization of the random heteropolymer onto the interface.

II. RESULTS

The present problem was studied in [5] (see also [6]–[15]) without taking into account the self-interactions between the monomers. It was found in [3] that the localization-delocalization transition occurs at the temperature \( T_c = \frac{\Delta_0}{\chi_0} \), where the parameter \( k_1 \) becomes zero and localization length \( \xi_1 \) becomes infinite. The value of \( T_c \) coincides exactly with that found in [5] by using a different method. The condition \( k_1 = 0 \) means that the heteropolymer delocalizes in the right hand half plane \( (z > 0) \).

Unfortunately, the equations (23), (24) cannot be solved analytically, so that we analyze them numerically. First we have examined the influence of the monomer-monomer interaction on the localization lengths. In Fig.1,2 we present the dependence of \( k_1 \) and \( k_2 \) as a functions of the asymmetry parameter \( \zeta \) for different values of the parameter \( \chi_0 \). Fig.1 corresponds to \( \chi_0 = 0 \) and recovers the results of [3] with values \( k_1^0 = \sqrt{6\Delta}/9 \) and \( k_2^0 = 2k_1^0 \) for statistically symmetric heteropolymer, \( \zeta_0 = 0 \). At the critical value of the asymmetry \( \zeta_0^c = 2\Delta/3 \), the parameter \( k_1 \) becomes zero, so that the heteropolymer delocalizes in the right hand half-plane. The increase of the parameter \( \chi_0 \) (Fig.2) leads to the increase of the critical value of the asymmetry parameter \( \zeta_0^c \) at which the delocalization transition takes place. This means that the self-interactions favor the localization of the heteropolymer. This can be explained qualitatively as follows. The self-interactions being attractive results in a decrease of the size of the blobs on both sides of the interface, which result in a decrease of their repulsion from the interface. The self-interactions influence to great extent the larger blobs, i.e. the blobs which are on the right hand side of the interface, while as in the case of the excluded volume interactions the effect of interactions is proportional to \( \chi \sqrt{N} \) with \( N \) being the number of monomers in the blob. At given \( \chi_0 > 0 \) and large enough \( \zeta_0 \) and \( T \) (see Fig.2, curve 2) the parameter \( k_1 \) becomes again positive that means that in this range of parameters the polymer is localized. Thus, as a function of the asymmetry parameter \( \zeta_1^0 < \zeta_0 < \zeta_2^0 \) with \( \zeta_1^0 \) and \( \zeta_2^0 \) depending on \( \chi \), there is window where the polymer is delocalized. For \( \zeta_0 < \zeta_1^0 \) the self-interactions favor the localization driving the critical value \( \zeta_0^c \) to larger values. It is surprising that for \( \zeta_0 > \zeta_2^0 \) the polymer localizes again. We interpret this as follows. We expect that in the model under consideration it is reasonable to impose a restriction on the maximal value of the asymmetry parameter \( \zeta_0^{\text{max}} \), which is of order of \( \Delta_0 \) [23], so that \( \zeta_0 < \zeta_0^{\text{max}} \). Although at \( \zeta_0 = \zeta_0^{\text{max}} \) the heteropolymer is on average
homopolymer, due to the difference of the variance $\Delta_0$ from zero the typical polymer is still heterogeneous. The self-interactions between the monomers in Hamiltonian (16), which are attractive between the monomers of the same kind and repulsive between the monomers of different kind, have the tendency to cause a microphase separation between the $A$ and $B$ monomers at large values of asymmetry parameter $\zeta_0$. Then, the polymer can be imagined as consecutive units of microphase separated blobs, each of them prefers to be on the left or on the right with respect to the interface. This is expected to favor the localization of the heteropolymer. We expect that taking into account the incompressibility of the blobs will disfavor the reentrant transition. However, the prediction that the self-organization of the random heteropolymer due to self-interactions will favor the localization will remain valid.

Notice that both $k_1$ and $k_2$ increase with increase of $\zeta_0$ and become equal at some $\zeta_0$ (curve 1 in Fig.2). For larger values of $\zeta_0$ parameter $k_1$ becomes larger than $k_2$. This signals that the blobs on the right hand side of the interface collapses to a size smaller than the blobs on the left hand side, which is reasonable due to the fact that the effect of self-interactions is amplified by the number of monomers in the blob. However, this region is beyond the physical realization of the present model, since we do not take into account the repulsive third virial coefficient, which sets a minimal length for collapsed blobs.

At some value of $\chi$ that corresponds to the temperature at which the microphase separation occurs the parameter $k_1$ is always positive, so that there is no delocalization transition (see curve 2 in Fig.2). Notice that assuming the existence of a maximal value for the asymmetry parameter, $\zeta_0^{\text{max}}$, the reentrant localization transition is limited to $\zeta_0 < \zeta_0^{\text{max}}$, which imposes an inequality on $\chi$ and thus on temperature.

Notice that the parameter $k_1$ becomes infinite at some value of $\chi$. In the symmetric case ($\zeta_0 = 0$) we have found that $k_1$, $k_2$ become infinite at the critical value $\chi_c = 9/(2\Delta)$ (Fig.3). The latter means that the heteropolymer collapses onto the interface. Taking into account the ternary interactions will prevent this.

III. CONCLUSION

We have considered the adsorption of a random heteropolymer onto an interface within the model by Garel et al. by taking into account the self-interactions between the monomers. The use of a preaveraging procedure within the replica method permits to map the present problem to a localization problem associated with a quantum mechanical Hamiltonian. To find the binding state of the latter we use the variational principle based on the 2-nd Legendre transform. We have found that self-interactions favor the localization of the random heteropolymer driving the delocalization transition to larger values of asymmetry. At the appropriate strength of self-interactions we found a reentrant localization transition at sufficiently high values of the asymmetry parameter $\zeta_0$. Although we expect that the part of predictions are physically irrelevant due to not taking into account the repulsive ternary interactions, which will effectuate a minimal collapse length, the qualitative tendencies of self-interactions will remain valid. The method we use can be extended to go beyond the approximations used in the present article. The preaveraging approximation means in fact a restriction of the extremum functional associated with the second Legendre transform to one-loop level, and can be overcomed. It is also possible to include the longitudinal behavior of the heteropolymer into the extremum procedure.
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REFERENCES

[1] T. Garel, A. Huse, S. Leibler, and H. Orland, Europhys. Lett., 8, 9 (1989).
[2] C. Yeung, A. C. Balazs, and D. Jasnow, Macromolecules, 25, 1357 (1992).
[3] A. Grosberg, S. Izrailev, and S. Nechaev, Phys. Rev.E, 50, 3, 1912 (1994).
[4] S. Milner and G. Fredrickson, Macromolecules, 28, 7953 (1995).
[5] S. Stepanow, J.-U. Sommer, and I. Ya. Erukhimovich, Phys. Rev. Lett. 81, 4412 (1998).
[6] V. Ganesan and H. Brenner, Europhys. Lett. 46, 43 (1999).
[7] A. Trovato and A. Maritan, Europhys. Lett. 46, 301 (1999).
[8] A. Maritan, M. P. Riva, and A. Trovato, J. Phys. A 32, L275 (1999).
[9] C. Monthus, Eur. Phys. J. B 13, 111 (2000).
[10] Z. Y. Chen, J. Chem. Phys. 112, 8665 (2000).
[11] X. Châtellier and J.-F. Joanny, Eur. Phys. J. E 1, 9 (2000).
[12] R. Martin, M. S. Causo, and S. G. J. Whittington, Phys. A. 33, 7903 (2000).
[13] C. Monthus, T. Garel, and H. Orland, Eur. Phys. J. B 17, 121 (2000).
[14] N. A. Denesyuk and I.Ya. Erukhimovich, J. Chem. Phys. 113, 3894 (2000).
[15] N. A. Denesyuk, J. Chem. Phys. 114, 4696 (2001).
[16] J-U. Sommer and M. Daoud, Europhys. Lett., 32, 407 (1995).
[17] T. Garel, H. Orland, and E. Pitard, ”Protein folding and heteropolymers”, in ”Spin Glass and Random Fields”, A.P.Young (ed.), Wold Scientific, Singapure (1997) p.387-443.
[18] D. H. Napper, Polymeric Stabilization of Colloidal Suspensions (Cornell University Press, Ithaca, 1979).
[19] C. A. Dai, B. J. Dair, K. H. Dai, C.K. Ober, and E. J. Kramer, Phys.Rev.Lett., 73, 4272 (1994).
[20] H. R. Brown, K. Char, V. R. Deline, P. F. Green, Macromolecules, 26, 4155 (1993); K. Char, H.R. Brown, V. R. Deline, Macromolecules, 26, 4164 (1993).
[21] J-U. Sommer, G. Peng, and A. Blumen, J.Chem. Phys., 105, 8376 (1996).
[22] G. H. Fredrickson and S. T. Milner, Phys. Rev. Lett. 67, 835 (1991).
[23] Z. Y. Chen, J. Chem. Phys., 111, 5603 (1999).
[24] T. Garel, L. Leibler, and H. Orland, J. Phys. II France, 4, 2139 (1994).
[25] L. Gutman and A. K. Chakraborty, J. Chem. Phys., 101, 10074 (1994); ibid 103, 10733 (1995); 104, 7306 (1996); 105, 7842 (1996).
[26] S. Dwyer, M. Trott, and Z. Y. Chen, J. Chem. Phys., 113, 10377 (2000).
[27] S. F. Edwards, Proc. Phys. Soc. London, 85, 613 (1965).
[28] P. G. de Gennes, Scaling Concepts in Polymer Physics (Cornell University Press, Ithaca, NY, 1979).
[29] S. T. Milner and T. A. Witten, Macromolecules, 21, 2610 (1988).
[30] C. de Dominicis and P. C. Martin, J. Math. Phys. 5, 14 (1964); 5, 31 (1964).
[31] A. V. Dobrynin and I. Ya. Erkhimovich, J. Phys. II France, 1, 1387 (1991).
[32] S. Stepanow, A. V. Dobrynin, T. A. Vilgis, and K. Binder, J. Phys. I France, 6, 837 (1996).
Figure captions

Fig.1 Dependence of $k_1$ (solid line) and $k_2$ (dashed line) as a functions of the asymmetry parameter $\zeta_0$ at $\chi_0 = 0$, $\Delta_0 = 1$, $\sigma = 1$, $T = 1$ [5].

Fig.2 Dependence of $k_1$ (solid line) and $k_2$ (dashed line) as a functions of the asymmetry parameter $\zeta_0$ at $\chi_0 = 1$, $\Delta_0 = 1$, $\sigma = 1$ (curves 1, 2 correspond to $T = 0.5; 1$ respectively). Here LS, DS correspond to localized and delocalized states.

Fig.3 Dependence of $k_1$ (solid line) and $k_2$ (dashed line) as a functions of the parameter $\chi$ at $\zeta_0 = 0$, $\Delta_0 = 1$, $\sigma = 1$. $\chi_c$ is equal to $9/(2\Delta)$.
Fig. 1

\[ k_1, k_2 \]

\[ k_1^0 \]

\[ k_2^0 \]

\[ \zeta_0^c \]

\[ \zeta_0 \]
Fig. 2
Fig. 3