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

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Abstract. We consider the adsorption of a random heteropolymer onto an interface within the model of Garel *et al.* [1] by taking into account random self-interactions and ternary repulsive 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 2nd Legendre transform. Our study reveals a complex behaviour of the localization of the heteropolymer. In particular, we predict a reentrant localization transition for moderate values of the asymmetry of the distribution function of the monomer sequences along the heteropolymer.

PACS. 05.70.Np Interface and surface thermodynamics – 61.41.+e Polymers, elastomers, and plastics – 64.70.-p Specific phase transitions

1 Introduction

The behaviour of heteropolymers at interfaces 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 biosensors, pattern recognition applications, glues, paints etc. [18]. Experiments [19,20] and numerical simulations [21,22] have shown that a random heteropolymer may localize, reinforcing the interface between two incompatible solvents and reduces 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. In the case of 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 the B-half-plane. Obviously there is a sort of frustration in such system because the complete separation of A monomers into one-half plane 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 causes random self-interactions between the monomers, may have a considerable impact on their bulk thermodynamic behavior [23], which consists in a segregation into A-rich and B-rich domains. In the case of a single heteropolymer in a solvent the random self-interactions favor the collapse of the heteropolymer [24,25]. The self-interactions between monomers may play an important role for adsorption as it was noticed in [4–26]. However, the influence of random 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 [27]. In the present paper we will consider the influence of the binary random monomer-monomer interactions and ternary repulsive interactions on the localization behavior of a random heteropolymer onto an interface.

The article is organized as follows. Section 2 introduces the model and the formalism. In Section 3 we present our results. Section 4 contains the conclusions.

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2 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 of the monomer 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 [28] over the trajectories $\mathbf{r}(s)$ $(0 \leq s \leq N)$ of the polymer chain

$$\begin{aligned} Z\{\zeta(s)\} = \int D\mathbf{r}(s) \exp\Bigg\{ &-\frac{d}{2a^2}\int_0^N \mathrm{d}s \left(\frac{\partial \mathbf{r}}{\partial s}\right)^2 \\ &+w\int_0^N \mathrm{d}s\ \zeta(s)\mathrm{sgn}[z(s)] + \chi_0 \int_0^N \mathrm{d}s \\ &\times \int_0^N \mathrm{d}s'\ \zeta(s)\zeta(s')\delta\left(\mathbf{r}(s)-\mathbf{r}(s')\right) \\ &-\lambda \int_0^N \mathrm{d}s \int_0^N \mathrm{d}s' \int_0^N \mathrm{d}s'' \delta\big(\mathbf{r}(s) \\ &-\mathbf{r}(s')\big)\delta\left(\mathbf{r}(s')-\mathbf{r}(s'')\right)\Bigg\}, \end{aligned} \qquad (1)$$

where a is the Kuhnian segment length, $z(s)$ is the Cartesian component of $\mathbf{r}(s)$ in d-dimensions transversal to the interface, w, χ_0, and λ are measured in units of k_BT. 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

$$P(\{\zeta(s)\}) \propto \exp\left[-\frac{1}{2\varDelta_0}\int_0^N (\zeta(s)-\zeta_0)^2\,\mathrm{d}s\right]. \qquad (2)$$

The distribution function (2) of the random "charges" $\zeta(s)$ is completely characterized by its two moments, $\langle\zeta(s)\rangle = \zeta_0$ with ζ_0 being related to the asymmetry in the composition of the copolymer, and $\langle\zeta(s)\zeta(s')\rangle = \zeta_0^2 + \varDelta_0\delta(s-s')$, where $\varDelta_0$ being the variance of the distribution. The choice of the interaction potential as a step function is legitimate, if the interface width is much smaller than the size of an average excursion loop. For positive w the monomers with $\zeta(s) > 0$ favor the right half-plane. The third term in the exponential of equation (1) describes the short-range random interactions between monomers, where χ_0 is the effective interaction potential (the second virial coefficient). The sign of this term in (1) is chosen such that for $\chi_0 > 0$ the like monomers attract each other while the unlike monomers repel each other. The last term in equation (1) corresponds to ternary repulsive interactions, which prevents the heteropolymer from the collapse due to attractive binary self-interactions. The model described by equation (1) admits that the random 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, but is not so simple.

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 $\langle ...\rangle$ means average with the distribution function (2). The partition function Z^n can be written as

$$Z^n = \int \prod_{\alpha=1}^{n} D\mathbf{r}_\alpha(s)\exp\left\{-H_0 - H_{int}\right\}, \qquad (3)$$

where

$$H_0 = \frac{d}{2a^2}\int_0^N \mathrm{d}s \sum_{\alpha=1}^{n}\left(\frac{\partial \mathbf{r}_\alpha}{\partial s}\right)^2, \qquad (4)$$

$$\begin{aligned} H_{int} = &-w\int_0^N \mathrm{d}s\ \zeta(s)\sum_{\alpha=1}^{n}\mathrm{sgn}[z_\alpha(s)] \\ &-\chi_0\int_0^N \mathrm{d}s\int_0^N \mathrm{d}s'\ \zeta(s)\zeta(s')\sum_{\alpha=1}^{n}\delta\left(\mathbf{r}_\alpha(s)-\mathbf{r}_\alpha(s')\right) \\ &+\lambda\int_0^N \mathrm{d}s\int_0^N \mathrm{d}s'\int_0^N \mathrm{d}s''\sum_{\alpha=1}^{n}\delta\left(\mathbf{r}_\alpha(s)-\mathbf{r}_\alpha(s')\right) \\ &\times\delta\left(\mathbf{r}_\alpha(s')-\mathbf{r}_\alpha(s'')\right). \end{aligned} \qquad (5)$$

To average over $\zeta(s)$ in (3) we expand (3) in Taylor series in powers of H_{int}, carry out the average, and re-exponentiate the obtained expression. This allows us to write the result of the average in the exponential as

$$\begin{aligned} \ln\left(\langle\exp\{-H_{int}\}\rangle\right) = &-\langle H_{int}\rangle \\ &+\frac{1}{2}\left(\langle H_{int}^2\rangle - \langle H_{int}\rangle^2 + ...\right). \end{aligned} \qquad (6)$$

Restricting the expansion in (6) to quadratic terms in H_{int} we obtain

$$\langle Z^n\rangle = \int\prod_{\alpha=1}^{n} D\mathbf{r}_\alpha(s)\exp\left\{-\int_0^N \mathcal{L}_n\ \mathrm{d}s\right\}, \qquad (7)$$

with

$$\begin{aligned}\mathcal{L}_n = {} & \frac{d}{2a^2}\sum_{\alpha=1}^{n}\left(\frac{\partial \mathbf{r}_\alpha(s)}{\partial s}\right)^2 - w\zeta_0\sum_{\alpha=1}^{n}\mathrm{sgn}(z_\alpha(s)) \\ & - \frac{1}{2}w^2\Delta_0\sum_{\alpha,\beta=1}^{n}\mathrm{sgn}(z_\alpha(s))\mathrm{sgn}(z_\beta(s)) - 2w\chi_0\zeta_0\Delta_0 \\ & \times \sum_{\alpha,\beta=1}^{n}\mathrm{sgn}(z_\alpha(s))\int_0^N \delta\left(\mathbf{r}_\beta(s)-\mathbf{r}_\beta(s')\right)\,\mathrm{d}s' \\ & - \chi_0\zeta_0^2\sum_{\alpha=1}^{n}\int_0^N \delta\left(\mathbf{r}_\alpha(s)-\mathbf{r}_\alpha(s')\right)\,\mathrm{d}s' - 2\chi_0^2\zeta_0^2\Delta_0 \\ & \times \sum_{\alpha,\beta=1}^{n}\int_0^N \mathrm{d}s'\int_0^N \mathrm{d}s''\delta\left(\mathbf{r}_\alpha(s)-\mathbf{r}_\alpha(s')\right) \\ & \times \delta\left(\mathbf{r}_\beta(s)-\mathbf{r}_\beta(s'')\right) - \chi_0^2\Delta_0^2\sum_{\alpha\neq\beta}^{n}\int_0^N \delta\left(\mathbf{r}_\alpha(s)-\mathbf{r}_\alpha(s')\right) \\ & \times \delta\left(\mathbf{r}_\beta(s)-\mathbf{r}_\beta(s')\right)\,\mathrm{d}s' - \frac{\chi_0^2\Delta_0^2}{a^d}\sum_{\alpha=1}^{n}\int_0^N \delta\left(\mathbf{r}_\alpha(s)\right. \\ & \left. -\mathbf{r}_\alpha(s')\right)\,\mathrm{d}s' + \lambda\sum_{\alpha=1}^{n}\int_0^N \mathrm{d}s'\int_0^N \mathrm{d}s''\delta\left(\mathbf{r}_\alpha(s)\right. \\ & \left. -\mathbf{r}_\alpha(s')\right)\delta\left(\mathbf{r}_\alpha(s')-\mathbf{r}_\alpha(s'')\right). \qquad (8)\end{aligned}$$

Notice that we have considered the term proportional to $\chi_0^2\Delta_0^2$ for $\alpha \neq \beta$ and $\alpha = \beta$ separately. For $\alpha = \beta$ there appears the term $\delta(0)$, which becomes finite, $\delta(0) \simeq a^{-d}$, by using the Kuhnian length a as a microscopic cutoff.

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 [5]).

In the following we will preaverage $\mathcal{L}_n$ over the transversal and longitudinal coordinates $z_\alpha(s)$ and $\mathbf{r}^{\shortparallel}_\alpha(s)$ appearing in (8) under the integrals over the contour length. This will reduce (8) to a quantum mechanical Hamiltonian. The idea is as following. First we will separate the delta functions in equation (8) in in-plane and in transversal components: $\delta(\mathbf{r}) = \delta(\mathbf{r}^{\shortparallel})\delta(z)$. The preaveraging over the transversal coordinates will be performed by using the transversal Green's function $G(z,N;z',0)$, which we represent as series over the eigenfunctions $\psi_k(z)$ as

$$G(z,z';N) = \sum_k \mathrm{e}^{-N\varepsilon_k}\psi_k(z)\psi_k^*(z'). \qquad (9)$$

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

$$-\frac{\partial G}{\partial N} = -\frac{a^2}{2d}\partial_z^2 G + \frac{U(z)}{T}G, \qquad (10)$$

which is remarkably similar to the Schrödinger equation for a quantum particle in an external potential [28]

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

The mapping of the latter onto equation (10) occurs by using the following replacements: $t \to \mathrm{i}N$, $\hbar \to T$, $a^2/T \to d/m$. In the case of a discrete spectrum with the energy of the ground state being negative, the main contribution in the series (9) for large N originates from the ground state (ground state dominance) [32]. In the approximation of the ground state dominance we take into account only one term ($k = k_0$) in (9). Due to the use of GSD the average over $z_\alpha(s)$ does not affect the integration over s, so that the preaveraging of the terms in equation (8) containing only one delta-function gives

$$\langle\rho(\mathbf{r}_\alpha)\rangle = \left|\psi_{k_0}(z_\alpha)\right|^2\langle\rho(\mathbf{r}^{\shortparallel}_\alpha)\rangle, \qquad (11)$$

where $\rho(\mathbf{r}^{\shortparallel}_\alpha) = \int_0^N \delta(\mathbf{r}^{\shortparallel}_\alpha - \mathbf{r}^{\shortparallel}_\alpha(s))\mathrm{d}s$. Preaveraging in a similar way the terms which are bilinear in delta-functions gives

$$\langle\rho(\mathbf{r}_\alpha)\rho(\mathbf{r}_\beta)\rangle = \left|\psi_{k_0}(z_\alpha)\right|^2\left|\psi_{k_0}(z_\beta)\right|^2\left\langle\rho(\mathbf{r}^{\shortparallel}_\alpha(s))\rho(\mathbf{r}^{\shortparallel}_\beta(s''))\right\rangle. \qquad (12)$$

The seventh term in equation (8) can be written in form of equation (12), but due to the missing of one integration over the contour length it contains the factor $1/N$, so that it can be neglected for large N. We now will consider the preaveraging over the longitudinal coordinates $\mathbf{r}^{\shortparallel}_\alpha(s)$. The fifth and the last but one term, and the last term in equation (8) are the second and the third virial coefficients, respectively. The balance between them prevents the polymer from complete collapse. We will treat the averages $\langle\rho(\mathbf{r}^{\shortparallel}_\alpha)\rangle$, $\langle\rho(\mathbf{r}^{\shortparallel}_\alpha(s))\rho(\mathbf{r}^{\shortparallel}_\beta(s''))\rangle$ on the level of the Flory theory [34]. As it is well-known the free energy associated with the 2nd and the 3rd virial coefficients can be written as

$$F = -(\chi_0^2\Delta_0^2/a^d + \chi_0\zeta_0^2)\frac{N^2}{R^{d_{\shortparallel}}} + \lambda\frac{N^3}{R^{2d_{\shortparallel}}}, \qquad (13)$$

where $d_{\shortparallel} = d - 1$. The extremum of F with respect to R gives $R^{-d_{\shortparallel}} = (\chi_0^2\Delta_0^2/a^d + \chi_0\zeta_0^2)/(2\lambda N)$. This value of R permits to estimate the average density in equation (11) as $\langle\rho(\mathbf{r}^{\shortparallel}_\alpha)\rangle = (\chi_0^2\Delta_0^2/a^d + \chi_0\zeta_0^2)/(2\lambda)$, and similarly $\langle\rho(\mathbf{r}^{\shortparallel}_\alpha(s))\rho(\mathbf{r}^{\shortparallel}_\alpha(s''))\rangle = ((\chi_0^2\Delta_0^2/a^d + \chi_0\zeta_0^2)/(2\lambda))^2$. In doing so we omit the influence of the interface on the balance between the 2nd and 3rd virial coefficient. This is legitimate to the lowest order we are considering in the present work.

Carrying out the preaveraging in (8) by using equations (11, 12) gives the effective replica Hamiltonian as

$$\begin{aligned}H_n = &-D\sum_{\alpha=1}^{n}\nabla_z^2 - w\zeta_0\sum_{\alpha=1}^{n}\mathrm{sgn}(z_\alpha)\\ &-\frac{1}{2}w^2\Delta_0\sum_{\alpha,\beta=1}^{n}\mathrm{sgn}(z_\alpha)\mathrm{sgn}(z_\beta) - 2w\chi_0\zeta_0\Delta_0\sigma\\ &\times\sum_{\alpha,\beta=1}^{n}\mathrm{sgn}(z_\alpha)\,|\psi(z_\beta)|^2 - 2\chi_0^2\zeta_0^2\Delta_0\sigma^2\\ &\times\sum_{\alpha,\beta=1}^{n}|\psi(z_\alpha)|^2\,|\psi(z_\beta)|^2 - (\chi_0\Delta_0^2+\zeta_0^2)\chi_0\sigma\\ &\times\sum_{\alpha=1}^{n}|\psi(z_\alpha)|^2 + \lambda\sigma^2\sum_{\alpha=1}^{n}|\psi(z_\alpha)|^4, \qquad (14)\end{aligned}$$

where we have introduced the notation $D = a^2/2d$, and $\sigma = (\chi_0^2\Delta_0^2/a^d + \chi_0\zeta_0^2)/(2\lambda)$. Due to the preaveraging the problem becomes effectively one dimensional.

The investigation of the adsorption of a random heteropolymer chain is now equivalent to the study of the ground state of the Hamiltonian H_n given by equation (14). In treating the case without the self-interactions (the case which is obtained from equation (14) by putting $\chi_0 = 0$ and $\lambda = 0$) Stepanow *et al.* [5] applied a novel variational principle for the 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

$$0 = -G^{-1} + G_0^{-1} + H_n^{int}, \qquad (15)$$

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

$$F(G) = -\mathrm{tr}\,\ln(G) + \mathrm{tr}\,G_0^{-1}G + \mathrm{tr}\,H_n^{int}G, \qquad (16)$$

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^{int} is the interaction part of the Hamiltonian, and ω is Laplace conjugate to the chain's length N. The functional $F(G)$ given by equation (16) is the particular case of the generating functional of the 2nd Legendre transform in Quantum Field Theory and Statistical Physics [35–37]. Notice that without preaveraging of $\rho(\mathbf{r}_\alpha)$ according to equations (11, 12) the problem under consideration does not reduce to a quantum mechanical problem and instead of (16) we have to use the extremum principle associated with the second Legendre transform [36,37]. Assuming the ground state dominance we choose the n-replica trial Green's function as

$$G(k_1,k_2;z,z';t) = \prod_{\alpha=1}^{n}\exp(-\varepsilon_k t)\psi(k_1,k_2;z_\alpha)\psi(k_1,k_2;z'_\alpha), \qquad (17)$$

where the trial wave function is used as

$$\psi(k_1,k_2;z_\alpha) = \sqrt{\frac{2k_1k_2}{k_1+k_2}}\left(\mathrm{e}^{-k_1z_\alpha}\vartheta(z_\alpha) + \mathrm{e}^{k_2z_\alpha}\vartheta(-z_\alpha)\right). \qquad (18)$$

Notice that the energy $\varepsilon_k = -Dk_2^2$ is negative, and is a function of k_2. Computing the terms in (16) by using (17) and (18) gives the extremum functional as

$$\begin{aligned}F(k_1,k_2) = &\ln(\omega+n\varepsilon_k) + \frac{n(Dk_1k_2-\varepsilon_k)}{\omega+n\varepsilon_k}\\ &-\frac{nw\zeta_0}{\omega+n\varepsilon_k}\left(\frac{k_2-k_1}{k_1+k_2}\right)\\ &-\frac{n}{2}\frac{\Delta_0w^2}{\omega+n\varepsilon_k} - \frac{n(n-1)}{2}\frac{\Delta_0w^2}{\omega+n\varepsilon_k}\left(\frac{k_2-k_1}{k_1+k_2}\right)^2\\ &-\frac{n\chi_0\sigma(\chi_0\Delta_0^2+\zeta_0^2)}{\omega+n\varepsilon_k}\frac{k_1k_2}{k_1+k_2}\\ &-\frac{n^2w\chi_0\zeta_0\Delta_0\sigma}{\omega+n\varepsilon_k}\frac{2k_1k_2}{k_1+k_2}\left(\frac{k_2-k_1}{k_1+k_2}\right)\\ &-\frac{(n+3n^2)}{12}\frac{2\zeta_0^2\chi_0^2\Delta_0\sigma^2}{\omega+n\varepsilon_k}\left(\frac{2k_1k_2}{k_1+k_2}\right)^2\\ &+\frac{1}{3}\frac{n\lambda\sigma^2}{\omega+n\varepsilon_k}\left(\frac{2k_1k_2}{k_1+k_2}\right)^2. \qquad (19)\end{aligned}$$

The stationarity conditions

$$\partial F/\partial k_1 = \partial F/\partial k_2 = 0, \qquad (20)$$

give in the limit $n = 0$ the following equations

$$\begin{aligned}&3k_1^3 + 9k_1^2k_2 + 9k_1k_2^2 + 3k_2^3 + 6\zeta(k_1+k_2) + 6\Delta(k_1-k_2)\\ &-3\chi^2\Delta^2\sigma k_2(k_1+k_2) - 3\chi\zeta^2\sigma k_2(k_1+k_2) - 4\zeta^2\chi^2\Delta\sigma^2k_1k_2^2\\ &+8\lambda\sigma^2k_1k_2^2 = 0, \qquad (21)\end{aligned}$$

$$\begin{aligned}&3k_1^3k_2 + 9k_1^2k_2^2 + 9k_1k_2^3 + 3k_2^4 + 3\zeta(k_1^2-k_2^2) - 6\Delta k_1k_2\\ &-3\chi^2\Delta^2\sigma k_1k_2(k_1+k_2) - 3\chi\zeta^2\sigma k_1k_2(k_1+k_2)\\ &-(2\zeta^2\sigma+\Delta)\chi^2\Delta\sigma k_1^2k_2^2 + 4\lambda\sigma^2k_1^2k_2^2 = 0, \qquad (22)\end{aligned}$$

where we have introduced new quantities $\Delta = \Delta_0w^2$, $\zeta = \zeta_0w$, $\chi = \chi_0/w^2$ and have put $D = 1$. The 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.

3 Results

The localization of a random heteropolymer was studied in [5] (see also [6–15]) without taking into account the self-interactions between the monomers. It was found in [5] that the localization-delocalization transition occurs at the temperature $T_c = \frac{2\Delta_0}{3\zeta_0}$, where the parameter k_1 becomes zero and thence the localization length $\xi_1 = 1/k_1$

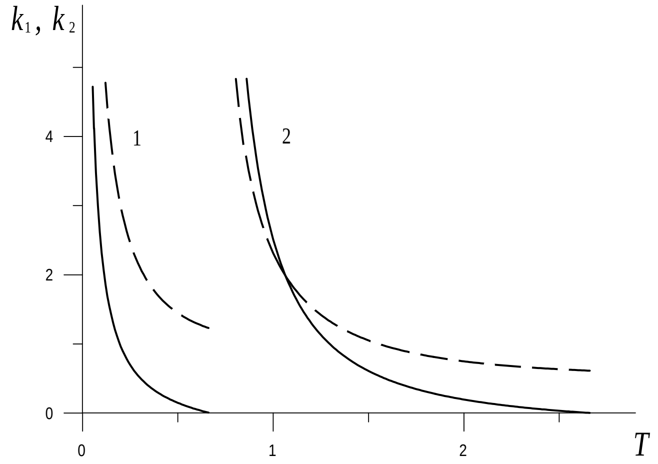

Fig. 1. Dependence of k_1 (solid line) and k_2 (dashed line) as functions of the temperature at $\zeta_0 = 1$, $\Delta_0 = 1$, $w_1 = 1$, $\lambda_1 = 1$. Curves 1, 2 correspond to $\chi_1 = 0.1$; 2, respectively.

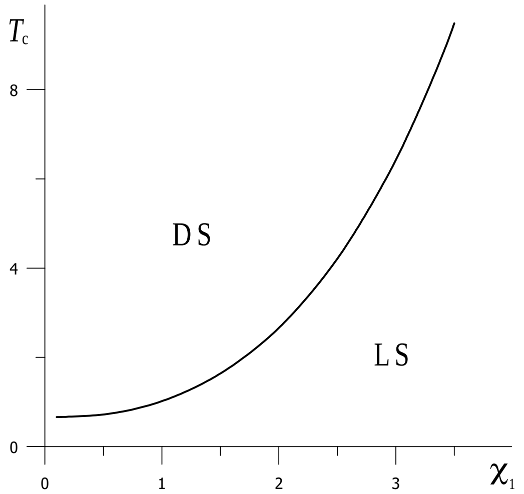

Fig. 2. The critical temperature T_c *vs.* χ_1 (values of all parameters are the same as in Fig. 1). LS and DS is the abbreviation for localized and delocalized state.

becomes infinite. The value of T_c coincides exactly with that found in [9] by using a different method. The condition $k_1 = 0$ means that the heteropolymer delocalizes in the right half-plane ($z > 0$). This is in agreement with equation (1) according to which for $\chi > 0$ the charges with $\zeta(s) > 0$ prefer to be in the right half-plane. For the ideal heteropolymer ($\chi_0 = 0$, $\lambda = 0$) we have recovered the results of [5] with values $k_1^0 = \sqrt{6\Delta}/9$ and $k_2^0 = 2k_1^0$ for statistically symmetric heteropolymer, $\zeta_0 = 0$. The asymmetry of the ground state for $\zeta_0 = 0$ is the consequence of the breaking of the symmetry of the distribution function of the monomer sequences $P(\{\zeta(s)\})$ due to the interface [5]. Besides the conformations with average charge being zero, there are also conformations containing a charge excess. It is clear that among the charge sequences $\zeta(s)$ which are favorable for localization (negative charge excess $-\delta\zeta$), there are also charge sequences (positive charge excess $\delta\zeta$) disfavoring the localization. According to the Gaussian distribution of charge sequences the charge excess for a piece of the polymer containing N monomers is of order $\sqrt{N}$. In studying the localization of the heteropolymer with $\zeta_0 > 0$ the copies of the heteropolymer with excess of charge sequences, which is favorable for adsorption, are present in the solution with higher amount than the copies with the opposite charge excess.

Unfortunately, the equations (21, 22) cannot be analyzed analytically, so that we solve them numerically. First we have examined the influence of the random monomer-monomer interaction on the localization lengths. In Figure 1 we show the dependence of k_1 and k_2 as a functions of the temperature at fixed λ_1 ($\lambda = \lambda_1/T$), w_1 ($w = w_1/T$), and for two different values of the strength of random self-interactions χ_1 ($\chi_0 = \chi_1/T$). Together with Figure 2 it shows that the random self-interactions shift the critical temperature to higher values *i.e.* they favor the localization.

Notice that at the transition point ($k_1 = 0$, the delocalization occurs in the right-half plane) the penetration length of the polymer in the left half-plane $1/k_2$ is not zero. According to the ansatz $\varepsilon_k = -Dk_2^2$ the binding energy at the transition differs from zero too. This occurs already in the case $\lambda = 0$ and χ_0 considered in [5] and can be explained as follows. In the case of adsorption onto an asymmetric interface, where the adsorption is due to the contact interaction with the interface, the adsorption energy as well as the penetration length of the polymer into the repulsive half-plane are zero at the transition [29]. This is the generic case for localization of quantum particles in potential wells [30]. However, in the present problem there is no direct interaction with the interface. The adsorption is the consequence of a collective organization of the heteropolymer on both sides of the interface [1], so that the heteropolymer penetrates the both parts of the interface and due to this the nonzero value of k_2 at the transition is expected. The penetration of the heteropolymer into the left half-plane $z < 0$ will be accompanied by the energy win, so that also the adsorption energy is expected not to be zero at the transition. The free energy in this approximation is simply the one-replica binding energy. Thus, in agreement with [5] the adsorption of the heteropolymer onto an interface is the first-order transition. Figure 3 shows the dependence of k_1 and k_2 on the temperature at fixed χ_1 for two different values of the strength of the ternary interactions λ_1. Figure 4 gives the critical temperature as a function of λ_1. Figures 3, 4 show that as expected the repulsive ternary interactions disfavor the localization of the heteropolymer.

Figure 5 shows the dependence of k_1 and k_2 as a function of the asymmetry parameter ζ_0 for two different values of χ_1. For larger value of χ_1 the heteropolymer is always localized. At small ζ_0 the inverse localization length k_1 first decreases in agreement with the expectation that the increase of the asymmetry parameter drives

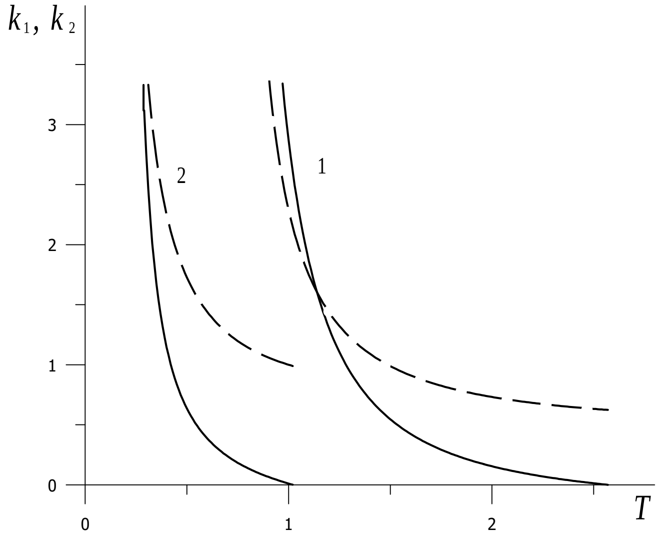

Fig. 3. Dependence of k_1 (solid line) and k_2 (dashed line) as functions of the temperature at $\zeta_0 = 1$, $\Delta_0 = 1$, $w_1 = 1$, $\chi_1 = 1$. Curves 1, 2 correspond to $\lambda_1 = 0.2$;1, respectively.

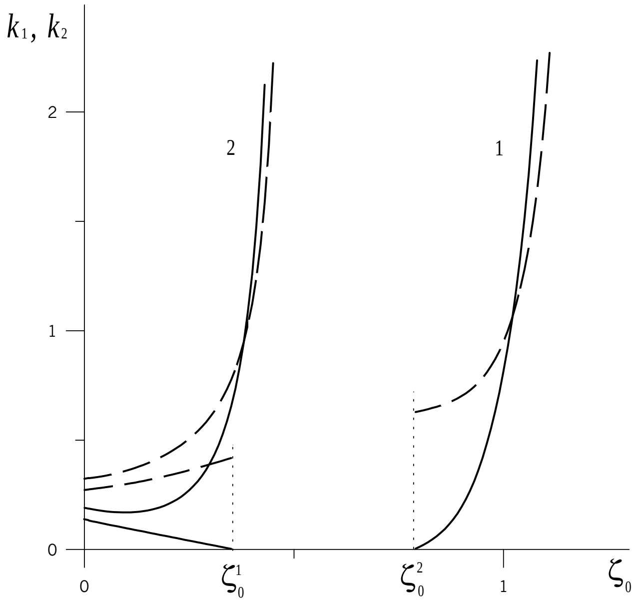

Fig. 5. Dependence of k_1 (solid line) and k_2 (dashed line) as functions of the asymmetry parameter ζ_0 at $\Delta_0 = 1$, $\lambda_1 = 0.01$, $T = 2$ for two values of χ_1 (curves 1, 2 correspond to $\chi_1 = 0.3$ and 1, respectively).

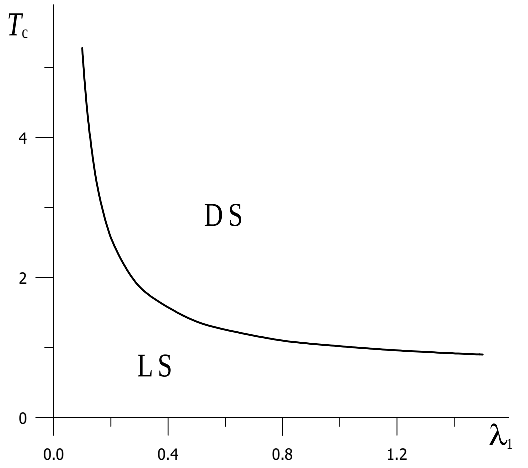

Fig. 4. The critical temperature T_c *vs.* λ_1 (values of all parameters are the same as in Fig. 3). LS and DS is the abbreviation for localized and delocalized state.

the heteropolymer to the delocalization transition. However, at higher values of the asymmetry k_1 and k_2 begin to increase, so that the heteropolymer will be more and more squeezed at the interface. This unusual behaviour can be explained due to the interplay between the random self-interactions and the selectivity of the solvents on both sides of the interface. The random self-interactions being attractive for the monomers of the same kind results in a decrease of the size of the blobs on both sides of the interface. This tendency to collapse, which is due to the attractive interactions between the monomers of the same kind, is accompanied by the tendency to a microphase separation [31] between the monomers of different kind. The repulsive interaction between the monomers of different kind will reinforce the microphase separation. The decrease of the size of the blobs, and the reorganization of the monomers within the blobs has the consequence that the blobs will win energy if the A-rich part of the blob will be in A'-solvent and its B-rich part will be in the B'-solvent, with the obvious consequence that the contacts of the blobs with the interface will be reinforced, which will favor the localization of the heteropolymer. The random self-interactions influence to great extent the larger blobs, *i.e.* the blobs which are on the right side of the interface, while similar to the case of the excluded volume interactions the effect of the interaction is proportional to $\chi\sqrt{N}$ with N being the number of monomers in the blob. The number of monomers in the blobs on the right side of the interface is expected to increase with the asymmetry parameter ζ_0. Due to this the tendency to collapse (which is expected to be prevented by ternary interactions) and the reorganization of the monomers in blobs (micro-phase separation) is more pronounced for blobs in the right half-plane. Thus, the interplay of the random monomer-monomer interactions and the selectivity of the solvent favors the localization of the heteropolymer. According to the expectation that this reorganization will be more pronounced for the blobs on the right side of the interface will explain that for even larger values of ζ_0 the inverse lengths k_1 and k_2 change the places: k_1 becomes larger than k_2. This marks the strong localization of the heteropolymer, which is due to the random self-interactions. The effect of the asymmetry on the binary random interactions can be seen in the effective replica Hamiltonian (14), where ζ_0 appears in combination of the strength of the binary random interactions χ_0, *i.e.* it enforces the effect of random self-interactions. Notice that within the present method we cannot study directly the reorganization of the

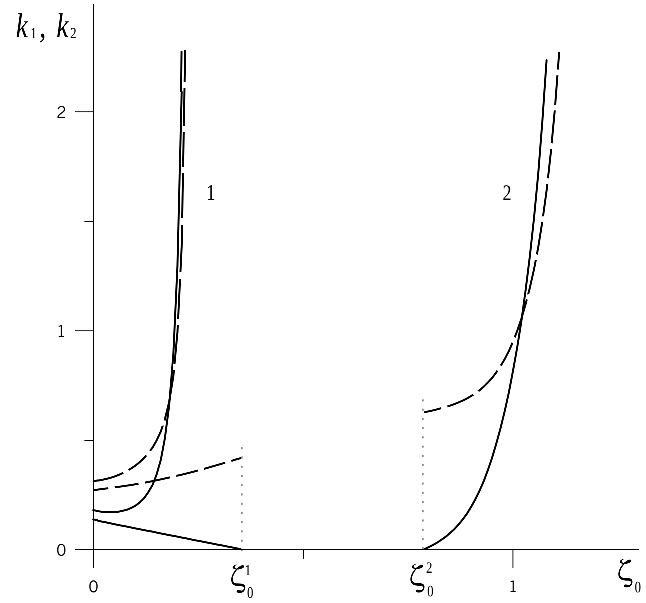

Fig. 6. Dependence of k_1 (solid line) and k_2 (dashed line) as functions of the asymmetry parameter ζ_0 at $\varDelta_0 = 1$, $\chi_1 = 0.3$, $T = 2$ for two values of λ_1 (curves 1, 2 correspond to $\lambda_1 = 0.0001$ and 0.01, respectively).

heteropolymer at the interface, but see its consequences for adsorption. The strong increase of k_1 and k_2 means that the heteropolymer practically lies on the interface. The increase of the localization energy, which is proportional to k_2^2, gives an additional support of this picture. It is intuitively clear that the repulsive ternary interactions cannot prevent this regime of the strong localization of the heteropolymer.

For smaller $\chi_1 > 0$ or high T (see Fig. 5, curve 1), the increase of k_1 and k_2 for large enough ζ_0 shown in curve 2 of Figure 5 results in a rather more striking behaviour. In the range $\zeta_0 \leq \zeta_0^1$ the increase of the asymmetry drives the heteropolymer towards delocalization transition, which occurs at ζ_0^1. We expect that in this regime the self-organization of the heteropolymer is not advanced, since the effect of the random interactions is weak. For intermediate values of the asymmetry parameter, $\zeta_0^1 < \zeta_0 < \zeta_0^2$, with ζ_0^1 and ζ_0^2 depending on χ, there is the window where the polymer is delocalized. For $\zeta_0 > \zeta_0^2$ the polymer localizes again, *i.e.* there is a reentrant localization transition of the heteropolymer, the behaviour, which is expected to have the same reason as the behaviour of the curve 2 of Figure 5 for large asymmetry parameter ζ_0, and is expected to be due to the nontrivial self-organization of the heteropolymer at the interface.

Figure 6 shows the dependence of k_1 and k_2 on the asymmetry parameter ζ_0 for fixed χ_1 and for two different values of λ_1. The behaviour is qualitatively the same as in Figure 5. The increase of λ_1 drives the heteropolymer towards delocalization, and favors the reentrant transition.

The analysis of equations (21–22) at ζ_0^1, ζ_0^2, and at $k_1 = 0$, where (21–22) considerably simplify, yields that for small χ and $\varDelta$, and large λ the asymmetry parameter ζ_0^2 increases, when χ and $\varDelta$ decreases, and increases with increase of λ. This in agreement with the above consideration. Thus, as expected the decrease of $\varDelta$ drives ζ_0^2 to infinity.

Notice that the behaviour shown in Figure 5 is limited to the model of Gaussian distributed charge sequences we are considering here. The mapping of this model to the model with bimodal distributed charge sequences, which is more preferable from the experimental point of view, demands to restrict the asymmetry parameter by a maximal value $\zeta_0^{\max}$ being of order of magnitude comparable with the width $\sqrt{\varDelta_0}$ of the distribution function of charge sequences [26]. Thus, the experimentally relevant range of the asymmetry parameter is restricted to $\zeta_0 < \zeta_0^{\max}$, so that the reentrant transition we have predicted is expected to be of experimental interest for $\zeta_0^2 < \zeta_0^{\max}$. Although at $\zeta_0 = \zeta_0^{\max}$ the heteropolymer is on average homopolymer, due to the difference of the variance $\varDelta_0$ from zero the typical polymer is still heterogeneous. Notice that both the reentrant transition and the strong increase of k_1 and k_2 occur at relatively small ζ_0.

Although the above results are derived by using approximations, primarily the preaveraging procedure, which is the key point permitting us to reduce the localization with random-self interactions to a quantum mechanical problem, we expect that because these predictions are supported by qualitative arguments, the complex behaviour of the random heteropolymer at the interface revealed in the present work is not the artifact of approximations.

4 Conclusion

We have considered the adsorption of a random heteropolymer onto an interface within the model by Garel *et al.* [1] by taking into account the random binary self-interactions and ternary repulsive 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 2nd Legendre transform. We have found that random self-interactions favor the localization of the random heteropolymer driving the delocalization transition to larger values of asymmetry, while on the contrary the ternary repulsive interactions disfavor the localization. The localization of the heteropolymer with random self-interactions shows a complex behaviour consisting in a reentrant localization transition at moderate values of the asymmetry parameter ζ_0 in the appropriate range of values of parameters of the model.

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