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The Green's function approach to adsorption of a random heteropolymer onto surfaces

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Received 11 October 2001, in final form 11 February 2002

Published 2 May 2002

Online at stacks.iop.org/JPhysA/35/4229

Abstract

We study the localization of a heteropolymer with Gaussian distributed random sequences onto an homogeneous surface, the problem which is equivalent to the wetting of an interface at a disordered substrate in two dimensions, via replica trick by using the Green's function technique. We present analytical results of the study of one- and two-replica binding states for two particular cases: (i) nearly statistically symmetric copolymer in the vicinity of the threshold of the annealed problem, and (ii) the asymmetric polymer with the interaction part of the annealed Hamiltonian being nearly zero. In both cases, the localization is due to two-replica binding states. In case (i) the two-replica binding state exists both above and below the localization transition of the annealed problem. In case (ii) the energy of the two-replica binding state at the transition is finite. The exact treatment of the one- and two-replica bound states is used to compute the free energy of the random heteropolymer. A schematic phase diagram of the localization–delocalization transition of the random heteropolymer is suggested.

PACS numbers: 61.41.+e, 68.35.Rh, 64.70.-p

1. Introduction

Adsorption of a polymer chain onto a surface is of great practical interest ranging from biological physics to technological applications [1–9] (and references therein). The adsorption of a polymer with heterogeneous sequence structure is relevant in connection with the study of the behaviour of proteins near surfaces. The problem of wetting in two dimensions [10–19] is closely related to the adsorption of a symmetric heterogeneous polymer onto a surface. The polymer adsorption has been studied in connection with the denaturation of double-stranded DNA in solution [17–20] and growth problems [16].

The role of disorder in the adsorption of a random heteropolymer remains a subject of controversy. This question has been addressed recently by several groups [11–19]. The quenched part of disorder is concluded to be irrelevant in [11, 12], while on the contrary, the

work [13] shows that the quenched part of the disorder is marginally relevant, and shifts the transition temperature of the localization. The marginal relevance of the quenched disorder was proved exactly in [14–16].

In this paper, we study the adsorption of a random asymmetric heteropolymer via a replica trick using the Green's function technique. In contrast to the previous studies, the Green's function method allows an exact consideration of one-replica (1r) and two-replica (2r) binding states. Our analysis shows that for a statistically symmetric heteropolymer the 2r binding state exists at the localization transition of the 1r binding state. The exact solution of the two-replica problem at the point where the interaction part of the annealed Hamiltonian is zero, yields that the localization transition is first-order. The one-replica and two-replica localized states are incorporated into a novel and heuristic procedure to compute the quenched free energy.

The paper is organized as follows. Section 2 introduces the model and formalism. Section 3 considers one- and two-replica binding states. Section 4 introduces the computation of the phase diagram. Section 5 contains our conclusions.

2. Model and formalism

The partition function of a polymer containing N segments interacting with the surface is

$$Z = \int Dz(s) \exp \left[-\frac{1}{2l^2} \int_0^N ds \left(\frac{dz(s)}{ds} \right)^2 - \int_0^N ds V_0(z(s)) - \int_0^N ds \zeta(s) V_{\text{int}}(z(s)) \right] \quad (1)$$

where $V_0(z) = (\infty, z \leq 0; 0, z > 0)$ is the repulsive interaction potential with the impenetrable surface, l is the statistical segment length. The heterogeneity of the polymer is described by random Gaussian variables $\zeta(s)$, which are characterized by the moments $\overline{\zeta(s)} = \zeta$, and $\overline{\zeta(s)\zeta(s')} = \zeta^2 + \Delta\delta(s - s')$. If $\zeta = 0$, then the number of monomers which are attracted or repelled from the well is on average the same, so that the heteropolymer is statistically symmetric. In contrast, if $\zeta \neq 0$, there is an excess of monomers, which are repelled from ($\zeta > 0$) or attracted to ($\zeta < 0$) the well. In this case the heteropolymer is asymmetric [2]. The attractive interaction with the surface will be modelled by the potential $V_{\text{int}}(z) = u\delta(z - z^0)$, where z^0 is small but nonzero (see below). This choice of the potential allows the exact treatment of the problem with two replicas, as will be shown below.

Imaging s to be an axis perpendicular to z we interpret equation (1) as a partition function of a directed line interacting with a heterogeneous substrate at $z = 0$, which is the wetting problem. The random variables $\zeta(s)$ are now attributed to the substrate. The wetting interpretation of the polymer problem is a particular case of the relation between the polymer in d dimensions and directed polymer in $d + 1$ dimensions. In the case of wetting, the condition $\zeta \neq 0$ means that on average the interface interacts with the substrate. If $\zeta > 0$, then the interface is repelled from the substrate.

Performing the average over $\zeta(s)$ by using the replica trick we obtain the replica partition function as

$$Z_n = \overline{Z^n} = \int Dz_a(s) \exp \left(-\sum_{a=1}^n \int_0^N ds \left(D \left(\frac{dz_a(s)}{ds} \right)^2 + V_0(z_a(s)) + \zeta V_{\text{int}}(z_a(s)) \right) + \frac{\Delta}{2} \sum_{a,b=1}^n \int_0^N ds V_{\text{int}}(z_a(s)) V_{\text{int}}(z_b(s)) \right) \quad (2)$$

where $D = l^2/2$. The free energy has to be computed as follows:

$$-\beta F = \left. \frac{\partial Z_n}{\partial n} \right|_{n=0}. \quad (3)$$

Due to the fact that (2) contains only the one-fold integral over s , the partition function Z_n can be interpreted as the probability amplitude of a quantum mechanical system of n particles associated with the Hamiltonian

$$H_n = \sum_{a=1}^n (-D\nabla_a^2 + V_0(z_a) - \beta\delta(z_a - z_0)) - \Delta u^2 \sum_{a<b}^n \delta(z_a - z_0) \delta(z_b - z_0) \tag{4}$$

where $\beta = \Delta u^2/2\delta_0 - \bar{\zeta}$ with $\delta_0 = 1/\delta(0)$ being of the order of magnitude equal to the width of the potential well, and $\bar{\zeta} = \zeta u$. The first term in (4) is associated with the annealed average of the free energy. The annealed part of H_n is equivalent to the localization problem of a quantum particle in the vicinity of the wall, and can be solved exactly. The binding problem for (4) with $n = 2$ can also be solved exactly. The replica Hamiltonian (4) was previously discussed in [14, 15] in terms of diagrammatic expansions. The Hamiltonian (4) at given n can be interpreted as a Hamiltonian of n polymers interacting with the surface. The last term in the annealed part of the Hamiltonian describes the attraction of the monomers of each replica to the surface, which is replica independent. The second sum in (4) gives an additional attractive interaction, if the monomers belonging to different polymers (replicas) contact the surface simultaneously. We are not aware if such an interaction can be realized in reality.

Equation (4) at $n = 2$ and for $\beta = 0$ and $V_0(z_a) = 0$ is exactly the Hamiltonian of a quantum particle in a two-dimensional delta potential. As is well known from text books, the binding state in this case exists for infinitesimally weak potential. While $\sum_{a=1}^n V_0(z_a)$ does not possess radial symmetry, the Hamiltonian (4) at $n = 2$ and $V_0(z_a) \neq 0$ does not correspond to a quantum mechanical problem in a radial symmetric two-dimensional potential well with an impenetrable core at the origin.

The Hamiltonian H_n at $n = 2$, $V_0(z_a) = 0$ and $\beta = 0$ is related to the Poland–Sheraga model [20]. The essential difference with the Poland–Sheraga model consists in the fact that all contacts occur at $z = z_0$, i.e. model (4) neglects the wiggling of the zipped polymer pair. It is evident that the last term in (4) favours the localization of replicas.

3. One- and two-replica bound states

To this end, it is convenient to consider the one-replica Green's function, $G(z_1, N; z_1^0) \equiv \langle \delta(z(N) - z_1) \delta(z(0) - z_1^0) \rangle$, associated with the annealed part of Hamiltonian (4). The Laplace transform with respect to N (the variable N plays the role of the imaginary time for the quantum particle) of the perturbation expansion of $G(z_1, N; z_1^0)$ in powers of the attraction strength β is a geometric series, which is summed as

$$G(z_1, p; z_1^0) = G_0(z_1, p; z_1^0) + \beta \frac{G_0(z_1, p; z_0) G_0(z_0, p; z_1^0)}{1 - \beta G_0(z_0, p; z_0)} \tag{5}$$

where $G_0(z_1, p; z_1^0) = (\exp(-|z_1 - z_1^0|\sqrt{p/D}) - \exp(-|z_1 + z_1^0|\sqrt{p/D})) / \sqrt{4Dp}$ is the Laplace transform of Green's function of the diffusion equation in the half space ($z \geq 0$) with the Dirichlet boundary condition at $z = 0$. The equation

$$1 - \beta G_0(z_0, p; z_0) = 1 - \beta(4Dp)^{-1/2}(1 - \exp(-2z_0\sqrt{p/D})) = 0 \tag{6}$$

which is the denominator of the second term in the rhs of equation (5), is the energy eigenvalue condition for 1r (one-replica or one-particle) localized state. Identifying D as $\hbar^2/2m$, equation (6) coincides exactly with the eigenenergy condition for the localization of a quantum particle in an attractive Delta-potential placed at the distance z_0 from the wall. The localized state corresponds to the solution of (6) $p_c > 0$. The energy of the localized state is given by $E_{1,0} = -p_c$. It is easy to see from (6) that the localized state exists for $\beta > \beta_c = D/z_0$.

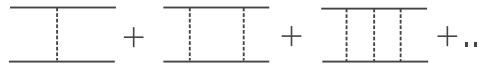


Figure 1. The perturbation expansion of the connected part of the two-replica Green's function. The continuous lines represent the polymers (replicas). The dashed lines are associated with the monomer–monomer interactions.

The inverse Laplace transform of $G(z_0, p; z_0)$ for $N > 0$ in the regime of weak binding ($2z_0\sqrt{p/D} \leq 1$) and $\beta > \beta_c$ is obtained from (5) as

$$G(z_0, N; z_0) \simeq \frac{\sqrt{D}}{\beta z_0} \left(\sqrt{p_c} \exp(Np_c) + \frac{1}{\sqrt{\pi N}} - \frac{p_c z_0}{\sqrt{D}} \exp(Np_c) - \sqrt{\frac{p_c}{\pi D N}} z_0 + \sqrt{p_c} \exp(Np_c) \operatorname{erf}(\sqrt{Np_c}) - \frac{p_c z_0}{\sqrt{D}} \exp(Np_c) \operatorname{erf}(\sqrt{Np_c}) \right) \quad (7)$$

where $p_c = (\beta/\beta_c - 1)^2 D^3 / (\beta^2 z_0^4)$.

To study the effect of the nondiagonal part of H_n in the case $n = 2$ we will consider the connected part of the two-replica Green's function $G_{2,c}(z_1, z_2, N; z_1^0, z_2^0, 0) \equiv \langle \delta(z_1 - z_a(N)) \delta(z_2 - z_b(N)) \delta(z_1^0 - z_a(0)) \delta(z_2^0 - z_b(0)) \rangle_c$, where a and b denote the replica indices ($a \neq b$). The perturbation expansion of Green's function $G_{2,c}(z_1, z_2, N; z_1^0, z_2^0, 0)$ in powers of the interaction (third and fourth terms in (4)) is represented graphically in figure 1. The dotted lines are associated with the two-replica interaction given in equation (4). The ends of the dotted lines are associated with z_0 and the arc length s_i , which are ordered from left to right. An integration over s_i has to be performed. Each part of the continuous line between two consecutive dotted lines is associated with the one-replica Green's function $G(z^0, s_i; z^0, s_{i-1})$. The left (right) external lines are associated with $G(z, N; z^0, s_i)$ ($G(z_0, s_1; z^0, 0)$) (let z be z_1 or z_2 , while z^0 be z_1^0 or z_2^0). The graphical expansion in figure 1, which visualizes the effect of two-replica interaction in H_2 in terms of spacetime ($N = -it$) trajectories, shows that both trajectories contact the surface at the same time. Thus, the return probability to have two consecutive contacts is the square of that for one particle (replica). This suggests that the localization of two particles (replicas) interacting according to (4) is closely related to the localization of one particle in two dimensions. The integral associated with a graph in figure 1 is a folding, so that the Laplace transform with respect to N reduces the perturbation expansion in figure 1 to a geometrical series, which is summed as

$$G_{2,c}(z_1, z_2, p; z_1^0, z_2^0) = \alpha \frac{\tilde{G}_2(z_1, z_2, p; z_0, z_0) \tilde{G}_2(z_0, z_0, p; z_1^0, z_2^0)}{1 - \alpha \tilde{G}_2(z_0, z_0, p; z_0, z_0)} \quad (8)$$

where $\alpha = \Delta u^2$, and $\tilde{G}_2(z_1, z_2, p; z_1^0, z_2^0)$ is the Laplace transform of the product of two one-replica Green's functions $G(z_1, N; z_1^0) G(z_2, N; z_2^0)$. The denominator on the rhs of equation (8) gives the eigenvalue condition for the two-replica bound state. Note that equations (5) and (8) are exact solutions of the integral equations for Green's functions $G(z_1, p; z_1^0)$ and $G_{2,c}(z_1, z_2, p; z_1^0, z_2^0)$ in the delta potentials contained in equation (4). These equations enable one to study 1r and 2r localized states. This is in contrast to the previous studies [11–16] where the delocalized state was studied.

We did not succeed in analysing the eigenvalue condition associated with the denominator of equation (8) analytically in the general case, so now we will consider the following particular cases: (i) approximately statistically symmetric polymer in the vicinity of the localization threshold of the annealed problem, and (ii) the asymmetric polymer under the condition that

the interaction part of the annealed Hamiltonian is approximately zero. The latter case can be realized by tuning the asymmetry parameter ζ . The two-replica partition function for directed polymers with random interactions was previously studied by using the renormalization group method in [14, 15].

3.1. Symmetric polymer

To ensure the existence of the Laplace transform of the one-replica Green's function squared, we introduce a short-time cut-off by replacing $1/N$ by $1/(N + a)$. The cut-off a along the polymer, which in the quantum mechanical context of the problem has the dimensionality of time, can be eliminated in favour of the transversal length a_0 via $a = a_0^2/4D$.¹ The eigenvalue condition for the two-replica localized state, which consists in equality of the denominator of equation (8) to zero, is obtained for small p_c , i.e. in the vicinity of the localization transition of the annealed problem, as

$$0 = 1 - \frac{D\alpha}{\pi z_0^2 \beta^2} \exp(a_0^2 p/4D) \Gamma(0, a_0^2 p/4D) + \frac{p_c^2 D\alpha}{\pi z_0^2 \beta^2} \left(\frac{-2\pi}{\sqrt{p}} + \frac{2z_0}{\sqrt{D}} \exp(a_0^2 p/4D) \Gamma(0, a_0^2 p/4D) \right) \quad (9)$$

where $\Gamma(0, x)$ is the incomplete gamma function. Equation (9) yields for p in the vicinity of the one-replica binding transition, i.e. for small p_c ,

$$p_{2,c} = \frac{4D \exp(-\gamma)}{a_0^2} \exp\left(-\frac{\pi z_0^2 \beta^2}{D\alpha}\right) \quad (10)$$

where γ is the Euler number. The energy $E_{2,c}$ of the two-replica bound state is $-p_{2,c}$. For the symmetric case, $\alpha = 2\beta\delta_0$, $p_{2,c}$ decreases with decreasing δ_0 at fixed $\beta \sim \beta_c$ and z_0 . This ensures the validity of the condition $2z_0\sqrt{p/D} \leq 1$ (weak binding) that we used to derive equation (10). A similar analysis slightly above the annealed threshold also results in equation (10), so that the two-replica bound state exists both below and above the threshold of the one-replica bound state. Result (10) shows that the two-replica bound state already exists at the one-replica localization transition. This finding is in agreement with the result obtained by Nechaev [21] in a related model. This is very reasonable and can be explained qualitatively as follows. The individual interactions with the surface contained in the annealed part of Hamiltonian (4) result in an increase of the probability of finding the monomers of the polymer pair in the vicinity of the surface. This compensates the decrease of the probability, which is due to the wall potential $\sum_{a=1}^n V_0(z_a)$, and thus shifts the threshold to the lower values. Unfortunately, we were not able to study analytically the eigenvalue condition at the localization transition. Such a study will enable the nature of the transition to be clarified. Note that the essential singularity upon α in equation (10) reflects the fact that the 2r interactions are marginally relevant. The latter is in agreement with preceding studies [13–16]. In the quantum mechanical language the 2r interaction in (4) corresponds to one particle in a two-dimensional well, which is marginal as is well known [22]. As a consequence of this, the value $p_{2,c}$ of the 2r bound state is very small at the localization transition of the annealed Hamiltonian, $p_c = 0$. This circumstance makes it difficult to analyse the localization transition numerically.

¹ Note that the case when only the first term in (11) is present corresponds to localization of a QM particle in a shallow two-dimensional potential well. The above procedure gives an exact solution of the problem, if one identifies the length a_0 with the width of the potential well.

3.2. Asymmetric polymer

The asymmetric case (ii), $\beta \rightarrow 0$, where no one-replica localized states exist can be realized by tuning the asymmetry parameter ζ as seen from the definition of β , $\beta = \Delta u^2/2\delta_0 - \bar{\zeta}$. For small β the 1r Green's function may be approximated by its bare value, so that we obtain

$$G^2(z_0, N; z_0) = \frac{1}{4\pi DN} \left(1 - 2 \exp\left(-\frac{z_0^2}{2DN}\right) + \exp\left(-\frac{2z_0^2}{2DN}\right) \right). \quad (11)$$

As above we replace $1/N$ in the first term on the right-hand side of (11) by $1/(N+a)$, where the cut-off a along the polymer can be eliminated in favour of the transversal length a_0 via $a = a_0^2/4D$. The z_0 -dependent terms in (11) are due to the boundary condition at the surface $z = 0$. In the case of adsorption onto an interface only the term $1/(4\pi DN)$ will appear in equation (11), so that in this case the two-replica bound state will exactly coincide with that in a shallow two-dimensional potential well. Using (11) we obtain from (8) the eigenvalue condition for the two-replica bound state as

$$1 + 4\alpha_1 K_0(4\sqrt{\bar{p}/\sigma^2}) - 2\alpha_1 K_0(4\sqrt{2\bar{p}/\sigma^2}) - \alpha_1 \exp(\bar{p})\Gamma(0, \bar{p}) = 0 \quad (12)$$

where $K_0(x)$ is the modified Bessel function of the second kind, $\bar{p} = pa_0^2/D$, $\alpha_1 = \alpha/4\pi D$, $\sigma = a_0/z_0$. Identifying the cut-off a_0 with z_0 gives $\sigma = 1$. It appears that the results are not sensitive to the choice of a_0 . The numerical analysis of equation (12) for different σ ($= 0.8, 1, 1.2$) yields the critical value α_1^c for the localization transition ($= 0.5825, 0.7857, 1.085$). It appears that at the transition $\bar{p}_{2,c}^0$ has a finite value ($= 0.0001, 0.00195, 0.01963$), i.e. the binding transition is a first-order transition. Above the transition, $\alpha_1 > \alpha_1^c$, there are two solutions for $\bar{p}_{2,c}$: $\bar{p}_{2,c} < \bar{p}_{2,c}^0$ and $\bar{p}_{2,c} > \bar{p}_{2,c}^0$. According to the ground state dominance argument, the larger value governs the behaviour of the polymer for large N . The approximate consideration based on the Taylor expansion of the eigenvalue condition (12) for small \bar{p} ,

$$1 - \alpha_1(\gamma + \ln 2 - 2 \ln \sigma) + \alpha_1 \bar{p}(-1 + \gamma + 8 \ln 2/\sigma^2 + \ln \bar{p}) + \dots = 0 \quad (13)$$

is in agreement with the results of numerical consideration of equation (12). The reason for the unusual first-order transition is due to the term $\bar{p} \ln \bar{p}$ in equation (13). The latter is responsible for the lhs of (13) having a minimum at finite \bar{p} , which leads to the first-order transition. The physical reason for the first-order transition is due to the boundary condition at the wall $z = 0$, which results in a reduction in the number of conformations, and drives the transition to be first order.

As we stressed above, the problem associated with the Hamiltonian H_n given by equation (4) for number of replicas $n = 2$ and $\beta = 0$ is closely related to the Poland–Sheraga model [20], which was recently studied in [23–25] by taking into account the excluded-volume interaction between the denatured loops and the rest of the chain. The excluded volume interaction reduces the number of conformations and drives there the transition to the first order. This is similar to the two-replica localized state, where the reduction of the number of conformations is due to the effect of the wall potential $V_0(z)$.

4. The phase diagram

In computing the free energy by using the replica formula (3) and taking into account the one-replica and two-replica binding states, we follow the procedure proposed by one of the authors [26]. In the case only 1r (one-replica) binding state exists, equation (3) gives straightforwardly $-\beta F/N = p_c$. However, the situation is nontrivial when a 2r (two-replica) binding state exists. Taking into account the two-replica states in the two-pair approximation

we obtain the partition function Z_n as

$$Z_n = Z_1^n + \frac{n(n-1)}{2} Z_{2,c} Z_1^{n-2} + \dots = \exp(np_c N) + \frac{n(n-1)}{2} \exp(p_{2,c} N + (n-2)p_c N) + \dots \quad (14)$$

where we have taken into account that Z_1 and $Z_{2,c}$ behave for large N as $\exp(p_c N)$ and $\exp(p_{2,c} N)$, respectively, when both 1r and 2r bound states exist. If no 1r bound state exists, then $Z_1 = 1$. The next terms in (14) contain contributions of ternary and higher pairs. Due to the fact that the replica Hamiltonian (4) does not contain simultaneous ternary interactions, we expect in agreement with [11] that the model we study does not have 3r bound states. Using (3) and (14), the free energy is obtained to be proportional to $\exp((p_{2,c} - 2p_c)N)$, hence the free energy is not an extensive quantity for $p_{2,c} - 2p_c > 0$. This shows that the two-pair approximation (14) is insufficient for computing the free energy. The problem is due to the fact that the exponentially increasing term in (14) that originates from the two-particle bound state does not contain the factor n , as is the case for the 1r bound state. The factor n in the exponential of the latter ensures that it disappears in the limit $n \rightarrow 0$. To overcome the difficulty, we follow [26] and take into account in the expansion of Z_n the term containing the maximal number of unconnected pairs. Then, instead of (14) we obtain

$$Z_{2n} = Z_1^{2n} + \dots + 2^{-n} \frac{\Gamma(2n+1)}{\Gamma(n+1)} Z_{2,c}^{2n/2} \quad (15)$$

where we consider even n . The factor $2^{-n} \Gamma(2n+1)/\Gamma(n+1)$ in equation (15) is the analytical continuation of $(2n-1)!!$ for arbitrary n . The free energy is now obtained from equation (3) as

$$\frac{-\beta F}{N} = p_c + \frac{1}{2} p_{2,c} + \dots \quad (16)$$

The localization length ξ_{loc} can be computed by using $p_{2,c}$ as $\xi_{\text{loc}} \simeq (p_{2,c}/D)^{-1/2}$. The regime (ii) considered above is obtained from (16), if one puts $p_c = 0$. Note the plus sign in front of the 2r energy in (16). The computation of the 2r energy in the two-pair approximation (14) gives in the limit $n \rightarrow 0$ instead of (16) the minus sign in front of the second term. The inconsistency of this result is clearly demonstrated by the nonextensiveness of the free energy computed by using equation (3). The procedure of taking into account the terms with maximal number of pairs can be justified by the following ground state dominance like argument: the term, $\exp(np_{2,c} N)$, dominates over $\exp(p_{2,c} N)$ for large N and $n \geq 1$. The condition $n \geq 1$ is demanded in the procedure of introduction of the replica trick by considering the partition function Z_n with n a positive integer. Thus, in carrying out the limit $N \rightarrow \infty$ one should hold n as a positive integer, and thereafter perform the limit $n \rightarrow 0$. The extensiveness of the free energy in N is *a posteriori* justification of the above procedure. For the peculiarities of the limits $N \rightarrow \infty$ and $n \rightarrow 0$ in the replica treatment of the directed polymer in disordered media see [27].

We will now use the results of the study of 1r and 2r bound states of the replica Hamiltonian (4) to construct the phase diagram of the localization of the heteropolymer in variables $\bar{\zeta}$ and $\alpha_1 = \Delta u^2/4\pi D$, which is shown schematically in figure 2. We know the behaviour at α_1^c and α_1^a from the study of the cases (ii) and (i). The latter corresponds to the localization transition of the annealed Hamiltonian (1r bound state) in the symmetric case ($\bar{\zeta} = 0$). The dotted straight line is the localization line of the annealed Hamiltonian; $\bar{\zeta}_c = -D/z_0$ is the value of the asymmetry parameter in the limit $\alpha_1 \rightarrow 0$. Since the random heteropolymer can arrange at the surface in such a way that pieces of the polymer which are attracted to the surface are in contact with the latter, while the pieces which are repelled are in the loops

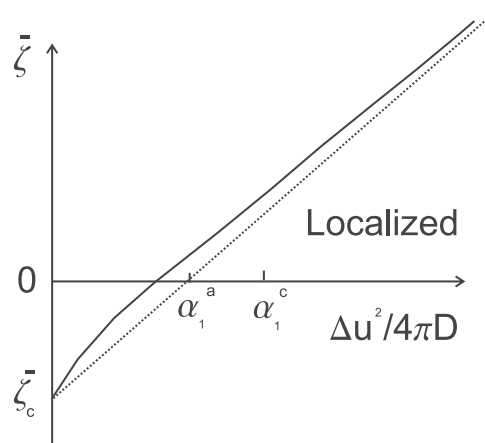


Figure 2. The phase diagram of the localization–delocalization transition. α_1^a marks the localization transition for the annealed symmetric polymer. α_1^c marks the 2r localization transition of the asymmetric heteropolymer, where the interaction part of the annealed Hamiltonian is zero.

and tails (see [4] for a related discussion), the random quenched heteropolymer is expected to localize more easily than the related homopolymer or even more easily than the annealed heteropolymer. The shift of the localization transition to higher temperatures in comparison to that of the annealed heteropolymer can also be understood by using the following simple argument. The realizations of the disorder in the annealed case occur within one copy of the system. The attractive character of the interaction in the annealed case reflects the proper effect of the inhomogeneities of the charge distribution along the heteropolymer. Besides the conformations with average charge being zero, there are also conformations containing charge excess. It is clear that among the charge sequences $\zeta(s)$ which are favourable for localization (negative charge excess $-\delta\zeta$), there are also charge sequences (positive charge excess $\delta\zeta$) disfavouring the localization. According to the Gaussian distribution of charge sequences, the charge excess for the piece of the polymer containing N monomers is of order \sqrt{N} . The configurations with a positive charge excess also contribute to T_c^a . In other words T_c^a is determined by all charge conformations. In the quenched case, the disorder is realized on many (infinite) copies of the system. This makes the situation completely different to the annealed case. In the quenched case, the unfavourable configurations (which correspond to different copies of system) do not contribute to T_c^q , simply because the heteropolymer with such a charge excess does not localize. The consequence of this is that the critical temperature for quenched case T_c^q should be higher than that for the annealed case T_c^a . In other words T_c^q is determined mainly by the part of charge sequences, which favour the localization. This conclusion can be formulated as a statement that the wall breaks the symmetry of the distribution function $P\{\zeta(s)\}$ of charge sequences. This symmetry breaking was applied previously in [28] to understand the asymmetry of the ground state in the case of adsorption of a random heteropolymer onto an interface between two selective solvents.

Note that the downward shift of the critical temperature found in [13] does not contradict our result. Derrida *et al* [13] considered disorder with a bimodal distribution. The latter can be represented in a straightforward way in a form corresponding to dilution. It can be shown by considering the typical length of adsorbed loops that in the case of dilution the critical temperature T_c^{dil} should be lower than the critical temperature of the pure case T_c^{pure} [29].

In the case of the model studied in [1, 18] (the interaction of a random heteropolymer with the three-dimensional point-like potential well) the 2r interactions (4) can be imagined in the quantum mechanical language as the interaction of a quantum particle with a potential well in 2×3 dimensions, which is expected to be irrelevant at the localization transition of the annealed polymer. In the context of the replica approach of the present work this would explain the coincidence of the critical temperature in canonical and microcanonical quenched sequences studied in [18].

The prediction that the quenched part of Hamiltonian (4), which is responsible for 2r bound states, shifts the critical temperature to higher values, has the consequence that the localization line will cut the horizontal axis on the left of the point α_1^q . The continuous line cannot end in the dotted line, while the analysis carried out in (i) in the vicinity of α_1^q applies also along the dotted line, so that the 2r localized state exists there. Thus, the continuous line will be on the left of the dotted line, and it will end in $\bar{\zeta}_c$.

An appealing question which still remains open is the nature of the localization transition along the localization line in figure 2. The present study supports rather the scenario that the localization transition is first order except for the point $\bar{\zeta}_c$, where it is continuous. This is based on our finding that the transition for the asymmetric polymer at α_c , where the interaction part of the annealed Hamiltonian is zero, is a first-order transition. However, more analytic and numeric effort is necessary to resolve this intriguing question.

Note that in the case of adsorption onto an interface the two-replica interactions are marginally relevant, however there is no shift of the critical temperature, because the polymer will be localized for infinitesimal strengths of 1r and 2r interactions.

5. Conclusion

In summary, we have considered adsorption of a random heteropolymer onto a homogeneous surface via a replica trick by using the Green's function technique. We use the exact treatment of one- and two-replica binding states of the replica Hamiltonian to compute the free energy of the random heteropolymer. We have considered analytically two particular cases: (i) an almost statistically symmetric polymer in the vicinity of the threshold of the annealed problem, and (ii) the asymmetric polymer where the interaction part of the annealed Hamiltonian is nearly zero. In the former case, we have obtained that the localization of the polymer is due to the 2r binding state, which exists both above and below the 1r binding state, which corresponds to the localization transition of the annealed problem. We have obtained that in the case (ii) the energy of the 2r binding state at the transition is finite, i.e. the localization is a first-order transition. The one-replica and two-replica localized states are used to compute the quenched free energy, and to construct a schematic phase diagram of the localization–delocalization transition.

Acknowledgments

We acknowledge support from the Deutsche Forschungsgemeinschaft, SFB 418 and grant Ste 981/1-1. SS acknowledges many stimulating discussions with T Garel, H Orland and S Nechaev. We thank R Netz for bringing to our attention the reference [24].

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