

## Phase transition in a heteropolymer chain at a selective interface

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We consider the localization transition of a heteropolymer chain without volume interactions consisting of two types of links — “hydrophobic” ( $A$ ) and “hydrophilic” ( $B$ ) at a selective oil-water interface: the  $A$  links are repelled from the water into the oil whereas  $B$  links prefer to be located in the water. We study the behavior of the free energy near the point of transition from a delocalized (Gaussian) to a localized (adsorbed) regime for two basic models: chains with periodic ( $A$ - $B$ - $A$ - $B$ - $\dots$ ) and “annealed random” sequences of links. We show that the transition is sensitive to the type of direct repulsive interaction of the links with the interface, and can be of “fourth” order in particular cases.

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### I. INTRODUCTION

Heteropolymers are one of the most important subjects in the physics of disordered systems mainly due to obvious biological applications. In the present paper we consider a very simple schematic model that exhibits the phenomenon of a heterogeneity-induced coil-to-globule transition. Our model is a two-letter  $A$ - $B$  heteropolymer embedded in such a surrounding that say,  $A$ , particles prefer to stay in the left half-space while  $B$  particles prefer the right half-space. Obviously there is a sort of frustration in this system, because the complete separation of  $A$  particles to the left and  $B$  particles to the right is forbidden by the polymer bonds which, therefore, play the role of the disorder. Being adsorbed at the surface between left and right half spaces, polymer chain tends to be localized in the following sense. The excursions of the chain are determined by the competition between the energy gain of dissolution of monomers in the preferable half space and the entropy loss due to the localization of the chain at the interface. Such a confined state is, therefore, the typical globular phase of a polymer chain and the transition from the delocalized state to the localized one is the typical coil-to-globule phase transition [1]. To our knowledge such a model was proposed first by Garel *et al.* in Ref. [2].

There was remarkable progress in the field of het-

eropolymer theory in the last few years [3–10]. In particular, it is connected with the successful theoretical investigation of the phenomenon of spin-glass-like phase transitions for heteropolymer globules, solutions, and melts [7–9]. Our model is, however, the opposite limiting case to that considered in these works. To explain this point, let us stress that in the approach of the investigations cited above the basic assumption is that the formation of a dense structure of the chain is caused by “homopolymer” effects, for example by averaged poor-solvent effects, while the “heteropolymer” effects are responsible for important features of the chain behavior just in the globular phase.

Our goal here is completely different, namely we investigate in detail the coil-to-globule transition induced by the presence of a heterogeneous sequence of links. This is why we restrict ourselves to the following simplifications:

(i) The polymer chain is ideal (i.e., without any volume interactions or excluded volume effects);

(ii) The sequence of links is (a) periodic or (b) “annealed” rather than the more difficult case of quenched randomness [2].

It turns out that even with these simplifications there are some delicate and unexpected effects, including:

(1) The system is very sensitive to the potential acting at the interface;

(2) There is a special point in the phase space of external parameters at which the phase transition belongs to another universality class than the usual phase transitions for adsorbing polymers.

The model considered here is closely related to the widely investigated phenomenon of polymer chain adsorption [3–6,11–14]. It is well understood at present both for homopolymer [3,12–14] and heteropolymer cases

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[4–6]. The simple diffusive approach [13] provides a complete understanding of an adsorption of the homopolymer chains as well as of a block copolymers in different complicated geometries. These results can be beautifully explained also by scaling estimates [15]. More advanced renormalization group methods [4] and power series analysis [6] applied to random chains with a disordered sequence of links are also widely used and give an exhaustive information on the thermodynamic properties of ideal polymer chains near the point of phase transition from delocalized (Gaussian) to localized (adsorbed) regimes. Recently, we noticed that the same mathematical formalism has been applied to a description of the phase transition in restricted solid-on-solid models with quenched impurities [16]. Many conclusions obtained by renormalization group (RG) analysis in Ref. [4] correlate with the results in Ref. [16].

In our model we investigate the localization transition by the transfer matrix methods. To have explicit results, it turns out to be convenient to “lift” the transfer matrix defined on a one-dimensional (1D) space to a three-dimensional space. This will be explained in Sec. III, where also the dependence on the potential at the interface has been studied. In Sec. IV we consider a polymer with annealed disorder in the links sequence. An alternative approach would be to use first returns of the polymer to the interface as in the necklace model [17]. Along this route the existence of a localized phase for quenched disorder has been proved [18,19].

## II. DESCRIPTION OF THE MODEL

Let us consider 3D “beads-on-the-string” model of polymer chain without volume interactions consisting of two types of beads (chain links), namely “hydrophobic” (A) and “hydrophilic” (B). The polymer chain is immersed in a solvent that consists of water and oil separated by the planar interface. Thus the potentials for the two types of chain links are (Fig. 1)

$$\begin{aligned}\varphi(A, \mathbf{r}) &= \begin{cases} u & \text{if } x > 0 \\ -u & \text{if } x < 0, \end{cases} \\ \varphi(B, \mathbf{r}) &= \begin{cases} -u & \text{if } x > 0 \\ u & \text{if } x < 0, \end{cases} \end{aligned} \quad (2.1)$$

where  $x$  denotes the coordinate orthogonal to the planar interface. In addition there is a potential at the interface that is crucial for the structure of the phase diagram and which we will retain below. Still we suppose  $\varphi(A, \mathbf{r}) = \varphi(B, \mathbf{r}) = 0$  if  $x = 0$ .

Let us characterize the sequence of links by  $\alpha_j \in \{A, B\}$  with  $j$  labeling the links along the chain. Then the potential per a whole chain,  $\Phi(\{\alpha_j\}, \mathbf{r})/T$ , is given by

$$\frac{1}{T} \Phi(\{\alpha_j\}, \mathbf{r}) = \frac{1}{T} \sum_{j=1}^N \varphi(\alpha_j, x_j) \quad (2.2)$$

with

$$\varphi(\alpha_j, x_j) = u \sigma_j \theta(x_j). \quad (2.3)$$

Here  $\sigma_j$  is an indicator of the link type

$$\sigma_j = \begin{cases} +1 & \text{if the } j\text{th link is “A”} \\ -1 & \text{if the } j\text{th link is “B”}, \end{cases} \quad (2.3a)$$

and  $\theta(x_j)$  is the symmetric Heaviside function

$$\theta(x_j) = \text{sgn}(x_j) = \begin{cases} +1 & \text{if } x_j > 0 \\ -1 & \text{if } x_j < 0. \end{cases} \quad (2.3b)$$

Let us choose for the single segment distribution the Gaussian function

$$g(\mathbf{r}_j - \mathbf{r}_{j-1}) = \left( \frac{3}{2\pi a^2} \right)^{3/2} \exp \left\{ -\frac{3(\mathbf{r}_j - \mathbf{r}_{j-1})^2}{2a^2} \right\}. \quad (2.4)$$

In all further calculations we absorb the temperature in the potential by setting  $T = 1$  and normalize distances such that for the average segment length we have  $a = 1$ . Since the potential depends only on the  $x_j$ , we can integrate over the coordinates parallel to the interface. Then in (2.4)  $g(\mathbf{r}_j - \mathbf{r}_{j-1})$  is replaced by the one-dimensional Gaussian kernel, still denoted by  $g(x - x')$  and the Green function satisfies the recursion relation

$$G_{N+1}(x) = e^{-\varphi(\alpha_{N+1}, x)} \int_{-\infty}^{\infty} dx' g(x - x') G_N(x'). \quad (2.5)$$

The potential takes different constant values on each half line, which makes it difficult to work directly with

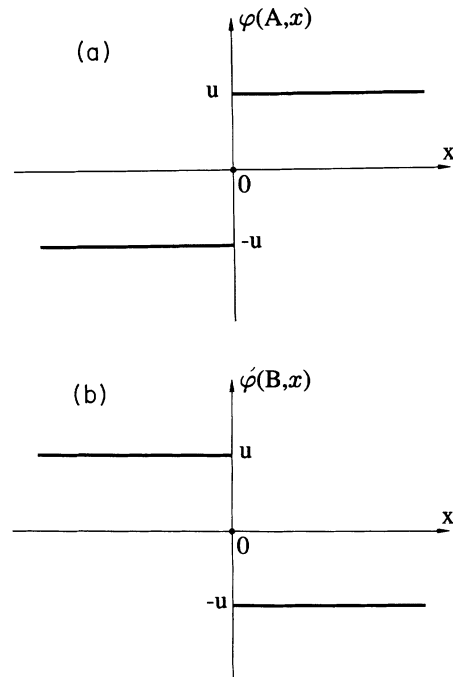


FIG. 1. The potential  $\varphi(\alpha, x)$  acting on: (a) “hydrophobic” (A) links; (b) “hydrophilic” (B) links.

(2.5). Our main idea is to regard the random walk on the 1D half line (or, the 1D "first return" problem) as the radial part of the random walk in a free 3D space [20,21]. There are then two 3D spaces, one for the right and one for the left half lines. Once the walk arrives at the origin, it can pass to the other 3D space. We have to add a repulsive  $\delta$ -function potential at the origin in order to compensate the entropy advantage: just at this point the chain can stay in the same 3D space or transfer to another one. The strength of the  $\delta$ -function potential has to be adjusted such that the right behavior of the 1D random walk is reproduced.

We index the 3D spaces by  $\{+, -\}$  and denote the corresponding Green functions by  $\Gamma_N^+$ ,  $\Gamma_N^-$ . They satisfy the recursion relations

$$\begin{aligned} \Gamma_{N+1}^+(\mathbf{x}) &= e^{-u\sigma_{N+1}} \int d^3x' g(\mathbf{x} - \mathbf{x}') \Gamma_N^+(\mathbf{x}') \\ &\quad + \gamma \delta(\mathbf{x}) \int d^3x' g(\mathbf{x} - \mathbf{x}') \\ &\quad \times [\Gamma_N^+(\mathbf{x}') + \Gamma_N^-(\mathbf{x}')], \end{aligned} \quad (2.6a)$$

$$\begin{aligned} \Gamma_{N+1}^-(\mathbf{x}) &= e^{u\sigma_{N+1}} \int d^3x' g(\mathbf{x} - \mathbf{x}') \Gamma_N^-(\mathbf{x}') \\ &\quad + \gamma \delta(\mathbf{x}) \int d^3x' g(\mathbf{x} - \mathbf{x}') \\ &\quad \times [\Gamma_N^-(\mathbf{x}') + \Gamma_N^+(\mathbf{x}')], \end{aligned} \quad (2.6b)$$

which in matrix form are rewritten as

$$\Gamma_{N+1}(\mathbf{x}) = \hat{\mathbf{M}}_{N+1} \hat{\mathbf{g}} \Gamma_N(\mathbf{x}'), \quad (2.7)$$

where

$$\Gamma_N(\mathbf{x}) = \begin{pmatrix} \Gamma_N^+(\mathbf{x}) \\ \Gamma_N^-(\mathbf{x}) \end{pmatrix},$$

$$\hat{\mathbf{M}}_N = \begin{pmatrix} e^{-u\sigma_N} + \gamma\delta(x) & \gamma\delta(x) \\ \gamma\delta(x) & e^{u\sigma_N} + \gamma\delta(x) \end{pmatrix}. \quad (2.7')$$

Here  $\hat{\mathbf{g}}$  is the integral operator with the Gaussian kernel  $g(x - x')$ . We used the fact that the potential is constant on each half line. As shown in the Appendix [Eqs. (A.8) and (A.12)] the strength of the  $\delta$  function has to be fixed at

$$\gamma = \gamma_{\text{cr}} = \frac{1}{2} \left( \frac{3}{2\pi} \right)^{-3/2} \zeta^{-1}(3/2), \quad (2.8)$$

where  $\zeta$  is Riemann  $\zeta$  function. With this adjustment

$$G_N(\pm|x|) \simeq \Gamma_N^\pm(\mathbf{x}), \quad |x| = |\mathbf{x}|. \quad (2.9)$$

### III. ADSORPTION OF A PERIODIC CHAIN

We consider a polymer chain with a periodic sequence of links,

$$\{\sigma^{(N)}\} = \{-1, +1, -1, +1, \dots\}. \quad (3.1)$$

As mentioned already the adsorption depends sensitively on the direct interaction of the chain links with the interface. We study the following two situations:

(a) The direct interaction of the chain with the interface does not depend on the link type. In this case the statistical weight of a link at the interface takes the value

$$\lambda_j = e^{-u_0} \quad \text{for all } \sigma_j. \quad (3.2)$$

This definition generalizes Eq. (2.5) where  $u_0 = 0$  was assumed.

(b) The direct interaction of links with the interface depends on the link type. This means that the interface can be regarded as a semipenetrable membrane with some kind of selective interaction with chain links. In this case the Boltzmann weight of a link at the interface reads

$$\lambda_j = e^{-\frac{u_0}{2}(1-\sigma_j)} = \begin{cases} e^{-u_0} & \text{if } \sigma_j = 1 \\ 1 & \text{if } \sigma_j = -1. \end{cases} \quad (3.3)$$

We will show that (a) and (b) lead to rather different phase diagrams for the polymer chain.

Performing the Fourier transform in (2.7) (compare with the Appendix) and taking into account that the statistical weight of the  $N$ th link at the interface is  $\lambda_N$ , we obtain a matrix equation valid for an arbitrary sequence of links,

$$\begin{aligned} \Gamma_{N+1}(\mathbf{k}) &= \hat{\mathbf{A}}_{N+1} g(\mathbf{k}) \Gamma_N(\mathbf{k}) + \frac{\gamma_{\text{cr}}}{(2\pi)^3} \lambda_{N+1} \hat{\mathbf{B}} \\ &\quad \times \int d^3k' g(\mathbf{k}') \Gamma_N(\mathbf{k}'), \end{aligned} \quad (3.4)$$

where  $g(\mathbf{k}) = \exp(-\mathbf{k}^2/6)$  and the matrices  $\hat{\mathbf{A}}_N$ ,  $\hat{\mathbf{B}}$  are defined by

$$\hat{\mathbf{A}}_N = \begin{pmatrix} e^{-u\sigma_N} & 0 \\ 0 & e^{u\sigma_N} \end{pmatrix}, \quad \hat{\mathbf{B}} = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}. \quad (3.5)$$

For the periodic sequence (3.1) of links the matrix  $\hat{\mathbf{A}}_N$  takes only two different expressions depending on whether the loop between the neighboring passages of the interface consists of even or odd number of links, namely

$$\hat{\mathbf{A}}_{2N+1} = \begin{pmatrix} e^u & 0 \\ 0 & e^{-u} \end{pmatrix}, \quad \hat{\mathbf{A}}_{2N} = \begin{pmatrix} e^{-u} & 0 \\ 0 & e^u \end{pmatrix}. \quad (3.6)$$

In the components  $\Gamma_N^\pm$  of the spinor  $\Gamma_N$  the recursion relations written only at even link numbers read

$$\begin{aligned}
\Gamma_{2N+2}^+(\mathbf{k}) &= g^2(\mathbf{k})\Gamma_{2N}^+ + g(\mathbf{k})\frac{\gamma_{\text{cr}}}{(2\pi)^3}e^{-u}\lambda^{(\text{od})}\int d^3k'g(\mathbf{k}')[\Gamma_{2N}^+(\mathbf{k}') + \Gamma_{2N}^-(\mathbf{k}')] \\
&+ \frac{\gamma_{\text{cr}}}{(2\pi)^3}\lambda^{(\text{ev})}\int d^3k'g^2(\mathbf{k}')[e^u\Gamma_{2N}^+(\mathbf{k}') + e^{-u}\Gamma_{2N}^-(\mathbf{k}')] \\
&+ A\frac{2\gamma_{\text{cr}}^2}{(2\pi)^3}\lambda^{(\text{ev})}\lambda^{(\text{od})}\int d^3k'g(\mathbf{k}')[\Gamma_{2N}^+(\mathbf{k}') + \Gamma_{2N}^-(\mathbf{k}')], \quad (3.7a)
\end{aligned}$$

$$\begin{aligned}
\Gamma_{2N+2}^-(\mathbf{k}) &= g^2(\mathbf{k})\Gamma_{2N}^- + g(\mathbf{k})\frac{\gamma_{\text{cr}}}{(2\pi)^3}e^u\lambda^{(\text{od})}\int d^3k'g(\mathbf{k}')[(\Gamma_{2N}^+(\mathbf{k}') + \Gamma_{2N}^-(\mathbf{k}')] \\
&+ \frac{\gamma_{\text{cr}}}{(2\pi)^3}\lambda^{(\text{ev})}\int d^3k'g^2(\mathbf{k}')[e^u\Gamma_{2N}^+(\mathbf{k}') + e^{-u}\Gamma_{2N}^-(\mathbf{k}')] \\
&+ A\frac{2\gamma_{\text{cr}}^2}{(2\pi)^3}\lambda^{(\text{ev})}\lambda^{(\text{od})}\int d^3k'g(\mathbf{k}')[\Gamma_{2N}^+(\mathbf{k}') + \Gamma_{2N}^-(\mathbf{k}')]. \quad (3.7b)
\end{aligned}$$

Here  $\lambda^{(\text{ev})}$  and  $\lambda^{(\text{od})}$  denote the statistical weights at the interface of even and odd links correspondingly and  $A$  is the constant

$$A = \frac{1}{(2\pi)^3}\int d^3k g(\mathbf{k}) = \left(\frac{3}{2\pi}\right)^{3/2}.$$

Equations (3.7a) and (3.7b) can be solved by the Laplace transform. Let us introduce the generating functions

$$Z^\pm(s, \mathbf{k}) = \sum_{N=0}^{\infty} s^{2(N+1)}\Gamma_{2N}^\pm(\mathbf{k}), \quad (3.8a)$$

$$Z_1^\pm(s) = \sum_{N=0}^{\infty} s^{2(N+1)}\frac{1}{(2\pi)^3}\int d^3k g(\mathbf{k})\Gamma_{2N}^\pm(\mathbf{k}), \quad (3.8b)$$

$$Z_2^\pm(s) = \sum_{N=0}^{\infty} s^{2(N+1)}\frac{1}{(2\pi)^3}\int d^3k g^2(\mathbf{k})\Gamma_{2N}^\pm(\mathbf{k}). \quad (3.8c)$$

The functions  $Z_1^\pm(s)$  and  $Z_2^\pm(s)$  satisfy a system of linear algebraic equations with corresponding determinant  $\det(s)$ . The coefficients in this system depend on functions

$$L_1(s) = \frac{1}{(2\pi)^3}\int d^3k \frac{sg(\mathbf{k})}{1 - sg^2(\mathbf{k})}, \quad (3.9a)$$

$$L_2(s) = \frac{1}{(2\pi)^3}\int d^3k \frac{sg^2(\mathbf{k})}{1 - sg^2(\mathbf{k})}, \quad (3.9b)$$

$$L_3(s) = \frac{1}{(2\pi)^3}\int d^3k \frac{sg^3(\mathbf{k})}{1 - sg^2(\mathbf{k})}. \quad (3.9c)$$

They are well defined on the interval  $[0,1]$  and may be extended analytically on the whole complex plane except the cut  $]1, \infty[$ . The solution for  $Z_1^\pm(s)$ ,  $Z_2^\pm(s)$  can be found in the standard way

$$Z_1(s) \equiv Z_1^+(s) + Z_1^-(s) = \frac{D_1(s)}{\det(s)},$$

where  $D_1$  is some analytic function depending on  $\{L_{1,2,3}(s), u, \lambda^{(\text{ev})}, \lambda^{(\text{od})}\}$ . The function  $G_{2N}(x=0)$  may be extracted from the integral

$$G_{2N}(x=0) = \frac{1}{2\pi i}\oint ds Z_1(s)s^{-2N-2} \quad (3.10)$$

by integrating along a contour that encircles the origin  $s=0$  and does not surround any singularity of the function  $Z_1(s)$  (cf. Appendix and Fig. 5 for further details).

It is well known [1,3] that the existence of a separated pole of the function  $Z_1(s)$  corresponds to a localized state of the chain. Thus we should analyze equation  $\det(s) = 0$ . The relation between the values  $u$ ,  $\lambda^{(\text{ev})}$ , and  $\lambda^{(\text{od})}$  corresponding to the localization transition point can be extracted from the condition  $\det(s) = 0$  at the point  $s=1$ ,

$$\det(s)|_{s=1} \equiv \det[L_1(s), L_2(s), L_3(s)]|_{s=1} = 0. \quad (3.11)$$

The behavior of the free energy per monomer near the transition point in the localized phase up to constants is given by

$$\begin{aligned}
f(u, \lambda^{(\text{ev})}, \lambda^{(\text{od})}) &\equiv \lim_{N \rightarrow \infty} \frac{1}{N} F(u, \lambda^{(\text{ev})}, \lambda^{(\text{od})}) \\
&= \text{const} \times \ln(s_0), \quad (3.12)
\end{aligned}$$

where  $s_0$  is the pole closest to the origin which is determined by

$$\det(s_0) = \det[L_1(s), L_2(s), L_3(s)]|_{s=s_0} = 0. \quad (3.13)$$

When calculating the corresponding determinant, we get the following expression

$$\begin{aligned}
\det(s) &= \left(1 - 2L_2(s)\gamma_{\text{cr}}\lambda^{(\text{od})}\cosh(u)\right) \\
&\times \left(1 - 2L_2(s)\gamma_{\text{cr}}\lambda^{(\text{ev})}\cosh(u)\right) \\
&- 4L_1(s)\gamma_{\text{cr}}^2\lambda^{(\text{ev})}\lambda^{(\text{od})}[L_3(s) + A]. \quad (3.14)
\end{aligned}$$

The functions  $L_1(s)$ ,  $L_2(s)$ , and  $L_3(s)$  have simple asymptotics near the point  $s = 1$  (with an accuracy up to the leading terms of order  $\sqrt{1-s}$ )

$$L_1(s) \simeq (1 - 2^{-3/2})\Gamma^0(1) - \frac{3^{3/2}}{4\pi}\sqrt{1-s}, \quad (3.15a)$$

$$L_2(s) \simeq 2^{-3/2}\Gamma^0(1) - \frac{3^{3/2}}{4\pi}\sqrt{1-s}, \quad (3.15b)$$

$$L_3(s) \simeq (1 - 2^{-3/2})\Gamma^0(1) - \left(\frac{3}{2\pi}\right)^{3/2} - \frac{3^{3/2}}{4\pi}\sqrt{1-s}, \quad (3.15c)$$

with

$$\Gamma^0(1) = \frac{1}{2\gamma_{cr}} = \left(\frac{3}{2\pi}\right)^{3/2} \zeta(3/2)$$

[cf. Eq. (A.5)]. Collecting Eqs. (3.13)–(3.15) and substituting them into (3.12) we get the expression for the free energy near the transition point

$$f(u, \lambda^{(ev)}, \lambda^{(od)}) = \text{const} \times \left( \frac{\det(s)}{\frac{d}{ds} \det(s)} \Big|_{s=1} \right)^2. \quad (3.16)$$

One can check that the denominator is finite near the point  $s = 1$  for all values of  $u, \lambda^{(ev)}, \lambda^{(od)}$ .

### A. Link-type independent interaction with the interface

Equation (3.11) at the transition point for  $\lambda^{(ev)} = \lambda^{(od)} = e^{u_0}$  [cf. (3.2)] takes the form

$$e^{u_0} = 2^{-3/2} \cosh(u) + (1 - 2^{-3/2}). \quad (3.17)$$

We do not have to consider the second pole of  $Z_1(s)$ , since its contribution to the integral (3.10) may be neglected when  $N$  is large.

The phase diagram in the coordinates  $(u, u_0)$  is presented in Fig. 2. As can be seen from (3.17), for  $u_0 = 0$  the adsorption point is at  $u \equiv u_{tr} = 0$ . The order of the phase transition is obtained using Eq. (3.16) which near the critical point yields the following asymptotics

$$f(u - u_{tr}) = \text{const} \times u^4 \quad (3.18)$$

— a very unconventional dependence for ordinary second-order adsorption transitions in polymer chains. The direct physical arguments for this behavior will be given in the Conclusion.

For all other values  $u_0 = \text{const} > 0$  the free energy scales like in an ordinary second-order phase transition,

$$f(u - u_{cr}) = \text{const} \times (u - u_{cr})^2, \quad (3.19)$$

where  $u_{cr}$  is the solution of (3.17) for fixed value of  $u_0$ .

We also would like to draw the attention to the follow-

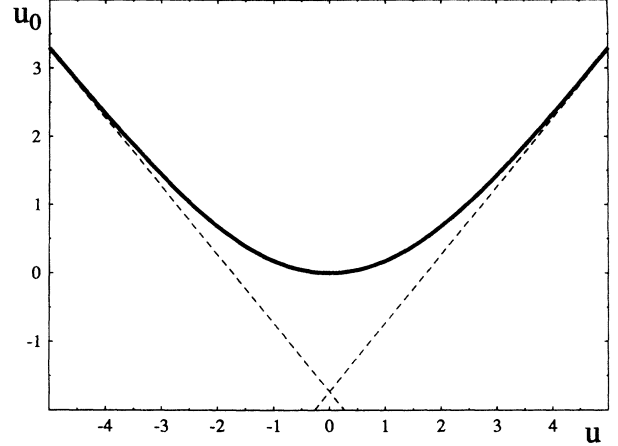


FIG. 2. The phase diagram for the link-type independent interaction of the periodic chain with the interface.

ing fact. We expand (3.17) for large values of  $u_0$  and  $u$ . When  $u_0 \rightarrow \infty$  and  $u \rightarrow \infty$  we get

$$u_0 = u - \frac{5}{2} \ln(2). \quad (3.20)$$

This means that for each value of  $u$  we can find a compensating value of  $u_0$  such that the chain is critical.

### B. Link-type dependent interaction with the interface

For  $\lambda_j$  obeying Eq. (3.3) we have  $\lambda^{(od)} = 1$ ,  $\lambda^{(ev)} = e^{-u_0}$ . In this case the equation for the transition point reads

$$e^{u_0} = \frac{(1 - 2^{-3/2})^2 + 2^{-3/2} \cosh(u) [1 - 2^{-3/2} \cosh(u)]}{1 - 2^{-3/2} \cosh(u)} \quad (3.21)$$

(we consider only one solution as explained before). In contrast to Eq. (3.20) for  $u_0 \rightarrow \infty$  Eq. (3.21) has the limiting point,  $u_{lim}$ , which is determined by the relation

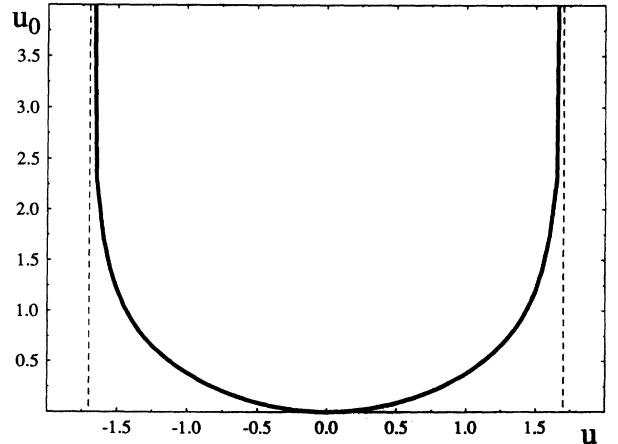


FIG. 3. The phase diagram for the link-type dependent interaction of the periodic chain with the interface.

$$\cosh(u_{\text{lim}}) = 2^{3/2}. \quad (3.22)$$

This means that there exist such values of  $u > u_{\text{lim}}$  corresponding to the localized phase of polymer chain which cannot be forced into the delocalized phase by increasing  $u_0$ . The phase diagram in coordinates  $(u, u_0)$  for this case is presented in Fig. 3. Other aspects of the transition resembles the one considered in the preceding section. In particular, it is of "fourth order" for  $u_0 = 0$  and of second order for all other values  $u_0 = \text{const} > 0$  and  $0 < u < u_{\text{lim}}$ .

#### IV. LOCALIZATION TRANSITION IN HETEROPOLYMER WITH ANNEALED DISORDER IN LINKS TYPES

We now turn to the possible case of a localization transition in a heteropolymer chain where the function of links types  $\alpha(j)$  is a random function of the segment number  $j$ .

There exist two principal different models of a random heteropolymer.

(i) A heteropolymer with "quenched" disorder in link types along the chain. In this model it is supposed that the sequence of link types in a given polymer chain cannot be changed through thermal fluctuations, but can be different only for different chains. The main difficulty in the investigation of the thermodynamic behavior of this system is connected with the problem which is well known in spin glasses – one should average the free energy over possible realizations of sequences  $\alpha(j)$  rather than the partition function. Some aspects of this problem in the context of our model were considered in Refs. [2,18]. In the present paper we do not tackle this set of problems.

(ii) A heteropolymer with "annealed" disorder in link types along the chain. In this model it is allowed for the link types to change the places in a given polymer, which means that the polymer chain is considered in complete equilibrium state and one should average the partition function over possible realizations of the sequences  $\alpha(j)$ . Despite the fact that this type of model is much easier to handle as compared to the case of polymers with quenched disorder, it is also of great interest. As an illustration of such systems we mention the homopolymer chain in the region of coil-to-helix transition [22]. Another even more interesting example of the system with annealed disorder in the sequence of links is given in Ref. [23]. In this work the aqueous solution of polyethylene oxide is considered. Each monomer is supposed to have two possible states, one with and the other without hydrogen bond to the water molecule. The sequence of states along the chain is, of course, not frozen, but allowed to change (see also Ref. [24]).

We turn to the problem of adsorption of an annealed heteropolymer at a selective interface.

We assume that there is a correlation between the nearest-neighbor link types. This means that we replace the potential per monomer,  $\varphi(\alpha_j, x_j)$ , [cf. (2.3)] by  $\psi(\alpha_j, \alpha_{j+1}, x_j)$  of the form

$$\begin{aligned} \psi(\alpha_j, \alpha_{j+1}, x_j) &= \varphi(\alpha_j, x_j) - \frac{1}{2}\mu(\sigma_{j+1} + \sigma_j)^2 \\ &= \varphi(\alpha_j, x_j) - \mu\sigma_j\sigma_{j+1} + \text{const}. \end{aligned} \quad (4.1)$$

The parameter  $\mu$  can be considered as the chemical potential of the  $(A-B)$  contacts on the chain ( $-\infty < \mu < \infty$ ). Note that in the limit  $\mu \rightarrow -\infty$  only the periodic link type sequence  $\{-, +, -, +, \dots\}$  survives and we are back to the case studied in Sec. III.

The corresponding expression for the Green function  $Z_N(x_N, \sigma_N)$  has the form

$$\begin{aligned} Z_N(x_N, \sigma_N) &= \sum_{\sigma_1=\pm 1} \dots \sum_{\sigma_{N-1}=\pm 1} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \prod_{j=0}^{N-1} dx_j \\ &\times \prod_{j=1}^N g(x_j - x_{j-1}) \\ &\times \exp \left\{ - \sum_{j=1}^N \psi(\alpha_j, \alpha_{j+1}, x_j) \right\} \end{aligned} \quad (4.2)$$

with the statistical weight  $\lambda$  of the link at the interface defined as in (3.2). We deduce the recursion relation for the Green function in the usual way,

$$\begin{aligned} Z_{N+1}(x, \sigma) &= e^{-u\sigma\theta(x)} \sum_{\sigma'=\pm 1} e^{\mu(\sigma\sigma'+1)} \\ &\times \int_{-\infty}^{\infty} dx' g(x - x') Z_N(x', \sigma'). \end{aligned} \quad (4.3)$$

The solution of Eq. (4.3) is obtained by generalizing the approach described in Secs. II and III. First we introduce the Green functions on the half lines  $x > 0$  and  $x < 0$  and the Green functions in corresponding 3D spaces

$$\begin{aligned} Z_N(x > 0, \sigma = +1) &\rightarrow P_N^+(\mathbf{x}), \\ Z_N(x > 0, \sigma = -1) &\rightarrow M_N^+(\mathbf{x}), \\ Z_N(x < 0, \sigma = +1) &\rightarrow P_N^-(\mathbf{x}), \\ Z_N(x < 0, \sigma = -1) &\rightarrow M_N^-(\mathbf{x}). \end{aligned}$$

The functions  $P_N^\pm(\mathbf{x})$  and  $M_N^\pm(\mathbf{x})$  satisfy the recursion generalizing Eqs. (2.6). It is more convenient to present the corresponding equation in the matrix form. Let us define the four-component spinor

$$\mathbf{V}_N(\mathbf{x}) = \begin{pmatrix} P_N^+(\mathbf{x}) \\ M_N^+(\mathbf{x}) \\ M_N^-(\mathbf{x}) \\ P_N^-(\mathbf{x}) \end{pmatrix}.$$

After Fourier transform this spinor satisfies the following equation [compare to (3.4)]

$$\begin{aligned} \mathbf{V}_{N+1}(\mathbf{k}) &= \hat{\mathbf{A}}g(\mathbf{k})\mathbf{V}_N(\mathbf{k}) \\ &+ \frac{\gamma_{\text{cr}}}{(2\pi)^3} \lambda \hat{\mathbf{C}} \int d^3k' g(\mathbf{k}') \mathbf{V}_N(\mathbf{k}'), \end{aligned} \quad (4.4)$$

where  $\lambda = e^{-u_0}$  and the matrices  $\hat{\mathbf{A}}$  and  $\hat{\mathbf{C}}$  are as follows:

$$\hat{\mathbf{A}} = \begin{pmatrix} e^{-u+2\mu} & e^{-u} & 0 & 0 \\ e^u & e^{u+2\mu} & 0 & 0 \\ 0 & 0 & e^{-u+2\mu} & e^{-u} \\ 0 & 0 & e^u & e^{u+2\mu} \end{pmatrix},$$

$$\hat{\mathbf{C}} = \begin{pmatrix} e^{2\mu} & 1 & 1 & e^{2\mu} \\ 1 & e^{2\mu} & e^{2\mu} & 1 \\ 1 & e^{2\mu} & e^{2\mu} & 1 \\ e^{2\mu} & 1 & 1 & e^{2\mu} \end{pmatrix}. \quad (4.5)$$

Upon introducing

$$\mathbf{Q}_N(\mathbf{k}) = \begin{pmatrix} Q_N^{(1)}(\mathbf{k}) \\ Q_N^{(2)}(\mathbf{k}) \end{pmatrix} = \begin{pmatrix} P_N^+(\mathbf{k}) + M_N^-(\mathbf{k}) \\ P_N^-(\mathbf{k}) + M_N^+(\mathbf{k}) \end{pmatrix}, \quad (4.6)$$

equation (4.4) takes the form

$$\mathbf{Q}_{N+1}(\mathbf{k}) = \hat{\mathbf{D}}g(\mathbf{k})\mathbf{Q}_N(\mathbf{k}) + \frac{\gamma_{\text{cr}}}{(2\pi)^3}(1 + e^{2\mu})\lambda\hat{\mathbf{T}} \times \int d^3k' g(\mathbf{k}')\mathbf{Q}_N(\mathbf{k}'), \quad (4.7)$$

where

$$\hat{\mathbf{D}} = \begin{pmatrix} e^{-u+2\mu} & e^{-u} \\ e^u & e^{u+2\mu} \end{pmatrix}, \quad \hat{\mathbf{T}} = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}. \quad (4.8)$$

The generating function

$$\Theta(\mathbf{k}, s) = \sum_{N=0}^{\infty} s^{N+1} \mathbf{Q}_N(\mathbf{k}) \quad (4.9)$$

transforms the functional Eq. (4.7) to the algebraic one which allows us to obtain the condition on the relation between  $\{u, u_0, \mu, s = s_0\}$  at which there appears a gap in the transfer matrix spectrum. As it was mentioned above, this corresponds to the localization transition in the system. The location of the highest eigenvalue is determined by the equation

$$\det(s) = \det \left| \hat{\mathbf{E}} - \frac{\gamma_{\text{cr}}}{(2\pi)^3}(1 + e^{2\mu})\lambda \int d^3k sg(\mathbf{k}) \times \left( \hat{\mathbf{E}} - \hat{\mathbf{D}}sg(\mathbf{k}) \right)^{-1} \hat{\mathbf{T}} \right| = 0, \quad (4.10)$$

where  $\hat{\mathbf{E}}$  is the identity matrix.

Equation (4.10) for  $\hat{\mathbf{D}}$  and  $\hat{\mathbf{T}}$  given by (4.8) reads

$$\det(s) = 1 - (1 + e^{2\mu})\lambda \frac{2\gamma_{\text{cr}}}{(2\pi)^3} \int d^3k \frac{sg(\mathbf{k})}{\Delta(s, \mathbf{k})} - (1 - e^{4\mu}) \cosh(u)\lambda \frac{2\gamma_{\text{cr}}}{(2\pi)^3} \int d^3k \frac{s^2 g^2(\mathbf{k})}{\Delta(s, \mathbf{k})} = 0, \quad (4.11)$$

where

$$\Delta(s, \mathbf{k}) = -(1 - e^{4\mu})s^2 g^2(\mathbf{k}) - 2 \cosh(u)e^{2\mu}sg(\mathbf{k}) + 1 \equiv -(1 - e^{4\mu})[g^{(1)} - sg(\mathbf{k})][g^{(2)} - sg(\mathbf{k})]. \quad (4.12)$$

Integration gives us the following equation:

$$\det(s) = 1 - (1 + e^{2\mu})\lambda \frac{\gamma_{\text{cr}}}{b(u, \mu)} \times \left[ \Gamma^0\left(\frac{s}{g^{(1)}}\right) - \Gamma^0\left(\frac{s}{g^{(2)}}\right) \right] - (1 - e^{4\mu}) \cosh(u)\lambda \frac{\gamma_{\text{cr}}}{b(u, \mu)} \times \left[ g^{(1)}\Gamma^0\left(\frac{s}{g^{(1)}}\right) - g^{(2)}\Gamma^0\left(\frac{s}{g^{(2)}}\right) \right] = 0, \quad (4.13)$$

where

$$b(u, \mu) = \sqrt{1 + e^{4\mu} \sinh^2(u)},$$

$$g^{(1)} = \frac{b(u, \mu) - e^{2\mu} \cosh(u)}{1 - e^{4\mu}}, \quad (4.14)$$

$$g^{(2)} = -\frac{b(u, \mu) + e^{2\mu} \cosh(u)}{1 - e^{4\mu}}.$$

The function  $\Gamma^0(s)$  is defined in the Appendix [Eqs. (A.5)].

The point  $s = g^{(1)}$  is the closest to the origin branching point of the function  $\det(s)$  so it determines the critical point  $(u, u_0, \mu)$  (compare to  $s = 1$  for periodic chain).

The phase diagrams calculated from (4.13) are presented in Fig. 4. As before, the chain is localized in the region under the curve and delocalized in the region above the curve.

Let us consider the limit  $\mu \ll -1$ . Expanding (4.13) and (4.14) up to the first leading terms of order  $\exp(2\mu)$  we obtain the following algebraic equation on the transition point:

$$e^{u_0} = 1 + (\cosh u - 1) \left\{ 2^{-3/2} + e^{2\mu} \left[ (1 - 2^{-3/2}) \cosh u + C \right] \right\}, \quad (4.15)$$

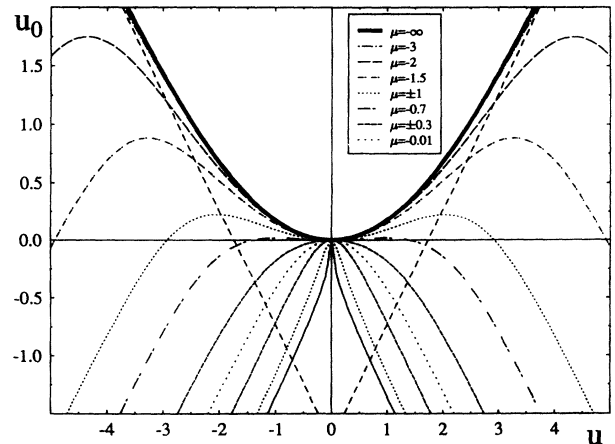


FIG. 4. Phase diagrams for the chain with annealed disorder in link sequence.

where  $C$  is the numerical constant

$$C = 2^{-3/2} + \frac{2}{\sqrt{\pi}\zeta(3/2)} \int_0^\infty dy \frac{y^{1/2} e^{-2y}}{(1 + e^{-y})^2} \approx 0.414895.$$

The region of applicability of Eq. (4.15) is restricted by the inequality

$$e^{2\mu} \cosh(u) \ll 1. \quad (4.16)$$

Equation (4.15) turns to (3.17) in the limit  $\mu \rightarrow -\infty$ , when the annealed sequence is the most likely in ideal periodic (antiferromagnetic) order.

In the opposite limit  $|\mu| \ll 1$  we get from (4.13) and (4.14)

$$e^{u_0} = \frac{1}{\cosh(u)} \{1 + \mu [2 - 1/\zeta(3/2)] \tanh^2(u)\}. \quad (4.17)$$

It can be seen from Eqs. (4.13) and (4.17) and Fig. 4 that the phase transition in the annealed heteropolymer with the nearest-neighbor correlations has some interesting features:

(a) For  $u_0 \geq 0$  the localization occurs only when  $\mu$  is less than some limiting value  $\mu_{\text{lim}} < 0$ .

(b) When  $u_0 < 0$  there is always a region where the chain is localized ( $u < u_{\text{cr}}$ ) and a region ( $u > u_{\text{cr}}$ ) where it is not localized.

(c) When  $u_0 = 0$  or when  $u_0$  has the maximum value for the localization transition to appear,  $\mu < \mu_{\text{lim}}$  being fixed, the transition is of the “fourth” order. In all other cases when a transition exists it is of the second order.

## V. CONCLUSION

Let us first discuss some qualitative mean-field type considerations for the localization transition in the periodic heteropolymer. We can write the free energy  $F$  of the chain as a sum of two parts:  $F_{\text{el}}$  and  $F_{\text{int}}$ , where  $F_{\text{el}}$  is the “elastic” (or, entropic) contribution to the free energy and  $F_{\text{int}}$  is the potential energy of the chain links. Let us assume that the chain is localized near the interface over some length  $l$  (we will minimize afterwards the free energy with respect to  $l$ ). We estimate  $F_{\text{el}}$  and  $F_{\text{int}}$  using the de Gennes’ arguments for adsorption [25] as follows:

$$F_{\text{el}} \sim -\frac{N}{l^2}, \quad F_{\text{int}} \sim \frac{N}{l} \langle u \rangle$$

where  $\langle u \rangle$  is the mean value of the energy of links near the interface averaged over translations of the chain over one period and  $\langle u \rangle$  is determined only by small scale fluctuations and can be estimated as

$$\langle u \rangle = ue^u - ue^{-u} |_{u \rightarrow 0} \simeq 2u^2.$$

Minimizing the free energy  $F(l) = F_{\text{el}} + F_{\text{int}}$  with respect to  $l$  we get

$$l_{\text{eq}} \sim \frac{1}{u^2}.$$

Thus the free energy of the chain near the transition point equals

$$F \sim Nu^4,$$

which is consistent with our exact result of Sec. III.

We briefly summarize our main findings.

The problem of heteropolymer chain statistics at a selective interface can be “lifted” to a problem of a random walk in two communicating 3D spaces. This approach enables us to solve exactly the problem of localization of a periodic heteropolymer chain at the interface and to show that this phase transition has the following unexpected features:

(a) For the pure step potential defined by Eq. (2.1) the phase transition is of “fourth” order.

(b) The transition is very sensitive to the direct repulsive-type interaction of the links with the interface, which is reflected in the phase diagrams shown in Figs. 2 and 3. We believe that this fact could play an important role in chemistry as a possible method to change the interface tension between two liquids by means of adsorbing polymers of different chemical structures at that interface.

This approach also enables us to consider the problem of phase transition in an annealed heteropolymer at the interface and to show that the absence or the presence of the localization point depends strongly on the value of the interaction constant of the nearest-neighbor correlations in the link sequence.

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## APPENDIX

The function  $\Gamma_N(\mathbf{x}, \gamma)$  satisfies the following recursion relation in 3D space:

$$\Gamma_{N+1}(\mathbf{x}, \gamma) = [1 + 2\gamma\delta(\mathbf{x})] \int d^3x' g(\mathbf{x} - \mathbf{x}') \Gamma_N(\mathbf{x}', \gamma), \quad (A1)$$

or, in terms of transfer operator

$$\Gamma_{N+1}(\mathbf{x}, \gamma) = \hat{\mathbf{q}} \Gamma_N(\mathbf{x}, \gamma),$$

[compare to (2.7)], where  $\hat{\mathbf{q}}$  is an integral operator defined as

$$\hat{\mathbf{q}}\psi(\mathbf{x}) = [1 + 2\gamma\delta(\mathbf{x})] \int d^3x' g(\mathbf{x} - \mathbf{x}') \psi(\mathbf{x}'). \quad (A2)$$

The point  $\gamma = \gamma_{\text{cr}}$  corresponds to the point of phase transition from a delocalized (for  $\gamma < \gamma_{\text{cr}}$ ) to a localized



(for  $\gamma > \gamma_{cr}$ ) regimes. In addition the asymptotics of 3D Green function  $\Gamma_N(\mathbf{x} = 0)$  just at the critical point  $\gamma_{cr}$  coincides with the asymptotics of Gaussian random walk on a line. Let us give now a brief derivation of the asymptotic behavior of the Green function  $\Gamma_N(\mathbf{x})$  at the transition point  $\gamma_{cr}$ . Taking Fourier and Laplace transforms we obtain

$$\Gamma_N(\mathbf{k}) = \int d^3x \Gamma_N(\mathbf{x}) \exp(i\mathbf{k} \cdot \mathbf{x}),$$

$$\Gamma(s, \mathbf{k}) = \sum_{N=1}^{\infty} s^N \Gamma_N(\mathbf{k}), \quad s \leq 1.$$

Now by (A1) the function  $\Gamma(s, \mathbf{k})$  satisfies the following equation:

$$\begin{aligned} \frac{1}{s}[\Gamma(s, \mathbf{k}) - s] &= g(\mathbf{k})\Gamma(s, \mathbf{k}) \\ &+ \frac{2\gamma}{(2\pi)^3} \int d^3k' g(\mathbf{k}')\Gamma(s, \mathbf{k}'), \end{aligned} \quad (\text{A3})$$

where  $g(\mathbf{k}) = \exp(-\mathbf{k}^2/6)$ . We assume the initial conditions to be  $\Gamma_0(\mathbf{k}) = 1$ . Equation (A3) has the solution at  $\mathbf{x} = 0$

$$\Gamma(s, \mathbf{x} = 0) \equiv \frac{1}{(2\pi)^3} \int d^3k g(\mathbf{k})\Gamma(s, \mathbf{k}) = \frac{\Gamma^0(s)}{1 - 2\gamma\Gamma^0(s)} \quad (\text{A4})$$

where  $\Gamma^0(s)$  is defined as

$$\Gamma^0(s) = \frac{1}{(2\pi)^3} \int d^3k \frac{sg(\mathbf{k})}{1 - sg(\mathbf{k})} = \left(\frac{3}{2\pi}\right)^{3/2} \sum_{t=1}^{\infty} \frac{s^t}{t^{3/2}}. \quad (\text{A5})$$

One can easily obtain an expression for negative argument of  $\Gamma^0(s)$

$$\Gamma^0(-s) = 2^{-1/2}\Gamma^0(s^2) - \Gamma^0(s). \quad (\text{A5}')$$

The Green function  $\Gamma_N(\mathbf{x} = 0)$  can be restored by means of the Mellin transform

$$\Gamma_N(\mathbf{x} = 0) = \frac{1}{2\pi i} \oint ds \Gamma(s, \mathbf{x} = 0) s^{-N-1}. \quad (\text{A6})$$

On the complex plane the function  $\Gamma(s)$  has a square root branching point at  $s = 1$  and a cut along  $]1, +\infty[$ .  $\Gamma(s)$  has a simple pole at the point  $s = s_0$  provided the following equation holds [3]:

$$1 - 2\gamma\Gamma^0(s_0) = 0 \quad (\text{A7})$$

(cf. Fig. 5). If there exists a pole at  $s_0$ , it gives the main contribution to the integral (A6) and we have

$$\Gamma_N(\mathbf{x} = 0) = s_0^N \text{Res}\Gamma(s, \mathbf{x} = 0)|_{s=s_0 < 1}.$$

This situation is called the ground state dominance [1]. The largest eigenvalue of transfer operator  $\hat{\mathbf{q}}$  equals  $1/s_0$ . The chain is in the localized state and the free energy of the chain is given by  $F = N \ln(s_0)$ .

From (A7) we can conclude that the localization tran-

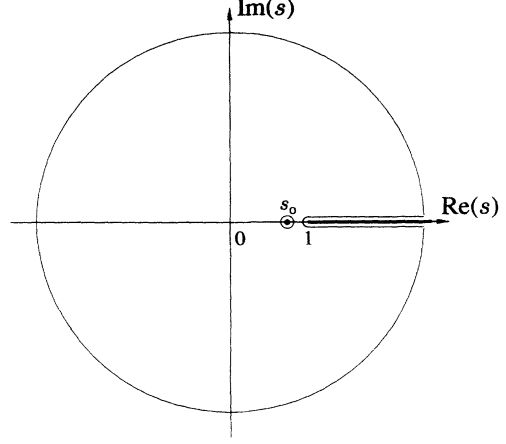


FIG. 5. The integration contour for the function  $\Gamma(s)$  [Eq. (A10)] on the complex plane  $\{\text{Im}(s), \text{Re}(s)\}$ .

sition appears at  $\gamma = \gamma_{cr}$ , where

$$\gamma_{cr} \equiv \frac{1}{2\Gamma^0(s_0 = 1)} = \frac{1}{2} \left(\frac{3}{2\pi}\right)^{-3/2} \zeta^{-1}(3/2). \quad (\text{A8})$$

We obtain the solution of Eq. (A7) up to the first leading term expanding the function  $\Gamma^0(s)$  in a power series of  $\sqrt{1-s}$  near the branching point  $s = 1$  (cf. Fig. 5). This yields

$$\Gamma^0(s) = \Gamma^0(1) - \frac{3^{3/2}}{\pi\sqrt{2}}\sqrt{1-s}, \quad (\text{A9})$$

and

$$s_0 = 1 - \frac{2\pi^2}{27} \left(\frac{\gamma - \gamma_{cr}}{2\gamma\gamma_{cr}}\right)^2. \quad (\text{A10})$$

Thus the transition is of the second order because

$$\lim_{N \rightarrow \infty} \frac{1}{N} F(\gamma - \gamma_{cr}) \sim \ln(s_0) \sim (\gamma - \gamma_{cr})^2. \quad (\text{A11})$$

To calculate the asymptotics of  $\Gamma_N(\mathbf{x} = 0)$  at the transition point we substitute (A9) into (A6) and integrate along the cut edges. Then

$$\Gamma_N(\mathbf{x} = 0, \gamma_{cr})|_{N \rightarrow \infty} = \frac{\sqrt{2\pi}}{3^{3/2}} \frac{1}{(2\gamma_{cr})^2} \frac{1}{N^{1/2}}. \quad (\text{A12})$$

When  $\gamma \leq \gamma_{cr}$  we have

$$\lim_{N \rightarrow \infty} \frac{1}{N} F(\gamma) = 0.$$

Then the spectrum of the transfer operator  $\hat{\mathbf{q}}$  is continuous and the chain is delocalized.

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