

## Localization in a simple multichain catalytic absorption model

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys. A: Math. Gen. 31 1965

(<http://iopscience.iop.org/0305-4470/31/8/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.104

The article was downloaded on 02/06/2010 at 07:23

Please note that [terms and conditions apply](#).

## Localization in a simple multichain catalytic absorption model

Sergei Nechaev†

Institut de Physique Nucléaire, Division de Physique Théorique‡, 91406 Orsay Cedex, France

Received 4 August 1997, in final form 28 November 1997

**Abstract.** We consider the phase transition in the ensemble of  $n$  polymer chains developing on the halfline  $x \geq 1$ . All chains are independent of each other in all points except the origin  $x = 1$ , where the point well is located. The well depth depends on the number of beads of different chains simultaneously staying at the point  $x = 1$ . We show that if the well depth grows faster than  $\frac{3}{2}n \ln n$  with  $n$ , then all chains become localized simultaneously at the origin in the limit  $n \gg 1$ . In the conclusion we discuss the connection of the above defined problem with the phase transition in the copolymer chain with a quenched random sequence of monomers using the replica approach.

### 0. Introduction

Problems dealing with the localization of polymer chains in potentials of various geometries compel much attention of both chemists and physicists. For the first group these problems are naturally connected with creating new materials possessing specific technological properties (for instance, catalysts [1] or ion-containing and surface-active substances [2]). Meanwhile, for physicists the consideration of path localization has remained since the 1970s as the testing ground for developing the new methods to investigate polymer absorption in different geometries, wetting phenomena and kinetics of chemical reactions.

The phenomenon of polymer chain absorption (without self-interactions) is rather well understood at present both for homo- [3–7, 15] and heteropolymer [8–14] cases. The simple diffusion approach [6, 7, 15] provides complete understanding of the absorption of homopolymer chains as well as of block copolymers in complicated geometries. These results can also be explained beautifully by scaling estimates [16]. More advanced renormalization group methods [8] and power-series analysis [10] applied to random chains with a disordered sequence of links are also widely used and give exhaustive information about the thermodynamic properties of ideal polymers near the phase transition point from the delocalized (Gaussian) to the localized (absorbed) regimes. A similar mathematical formalism has been applied to a phase transition in solid-on-solid (SOS) models with quenched impurities [17]. Many conclusions obtained by renormalization group (RG) analysis in [8] correlate with the results in [17].

Problems dealing with 2D wetting in a periodic potential are related to this theme as well. In [18], using a generalized transfer matrix method, we were able to find the exact solution for the critical depinning phase transition for an ideal (nonself-avoiding) chain.

† Also at: LD Landau Institute for Theoretical Physics, 117940 Moscow, Russia. E-mail address: nechaev@landau.ac.ru

‡ Unité de Recherche des Universités Paris XI et Paris VI associée au CNRS.

Finally, it is worthwhile to mention that the model considered below has some features of the so-called ‘zero’s range-exclusion process’ [19, 20] arising in connection with traffic models. Also, similar problems appeared in the course of investigation of the ‘autolocalization’ phenomena [21] and in the theory of multicomponent chemical reactions on traps immersed in an immobile ‘matrix’ [22, 23].

This paper is organized as follows. In section 1 we formulate the simple model of ‘catalytic absorption’ and put forward the question of our main interest; section 2 is devoted to the solution of one- and two-chain problems; the phase transition in the  $n$ -chain model for  $n > 2$  is treated in section 3; while in section 4 we present conjectures about the connection of the multiparticle catalytic absorption with the random copolymer absorption at the point well.

### 1. Multichain model of catalytic absorption at the point well

Consider the one-dimensional lattice  $\mathbb{Z}^+$ , i.e. the set of integer points on the halfline  $x \geq 1$ ,  $\{x\} = \{1, 2, 3, \dots\}$ . Take  $n$  independent  $N$ -step chains on  $\mathbb{Z}^+$ , simultaneously starting at the point  $x = 1$ . All these paths are free, i.e. they do not interact either with any external potential, or with each other at any point except the point  $x = 1$ . At  $x = 1$  the interaction of a given chain with the well is described by the potential  $U(x_1, x_2, \dots, x_n)$  (the index  $i \in [1, n]$  labels the different chains):

$$U(x_1, x_2, \dots, x_n) = \begin{cases} 0 & \text{if } x_i \neq 1 \text{ for all } i \in [1, n] \\ w(1) & \text{if } x_i = 1; x_j \neq 1 \text{ for all } \{j \neq i; j \in [1, n]\} \\ w(2) & \text{if } x_i = 1, x_j = 1; x_k \neq 0 \\ & \text{for all } \{k \neq j \neq i; k \in [1, n]\} \\ \dots & \\ w(n) & \text{if } x_1 = 1, x_2 = 1, \dots, x_n = 1 \end{cases} \quad (1.1)$$

where

$$0 \leq w(1) \leq w(2) \leq \dots \leq w(n). \quad (1.2)$$

The equation (1.1) reflects the fact that the depth of the potential well depends on the number of different chains’ beads *simultaneously* located at the point  $x = 1$ . Let us stress that  $w(i)$  is the ‘individual’ potential, i.e. the potential per one bead in a cluster of  $i$  particles simultaneously located at the point  $x = 1$ . The ‘integral’ well depth for the cluster of  $i$  particles we denote as

$$\mathcal{U}(i) = iw(i).$$

To avoid possible confusions let us emphasize that we consider only the *statistical* problem dealing with enumeration of different trajectories on the lattice  $\mathbb{Z}^+$  with appropriate Boltzmann weights at the boundary. Our problem should not be mixed with the *probabilistic* problem concerning the derivation of the invariant measure for the random walks developed on the lattice  $\mathbb{Z}^+$  with appropriate local transition probabilities (see for example [24]). This probabilistic approach does not deal with the polymer chain statistics and is not regarded in our paper. The difference between the ‘polymer’ and the ‘random walk’ problems is clearly shown in [25].

It is very straightforward to derive the recursion relations describing the process under investigation. Consider the partition function (the number of trajectories),  $Z_N(x_i)$ , of some

arbitrary  $N$ -step path on the halfline  $x_i \in [1, \infty)$  starting at the point  $x = 1$  and ending at the point  $x_i$  ( $x_i \in \mathbb{Z}^+$ ). The function  $Z_N(x_i)$  satisfies the equations,

$$\begin{cases} Z_{N+1}(x_i) = Z_N(x_i + 1) + Z_N(x_i - 1) & (x_i \geq 2) \\ Z_{N+1}(x_i) = e^{U(x_1, \dots, x_i, \dots, x_n)} Z_N(x_i + 1) & (x_i = 1) \\ Z_N(x_i) = 0 & (x_i \leq 0) \\ Z_{N=0}(x_i) = \delta_{x_i, 1}. \end{cases} \quad (1.3)$$

The same recursion relations as equation (1.3) should be written for all functions  $Z_N(x_i)$  where  $i \in [1, n]$  and the potential  $U(x_1, \dots, x_i, \dots, x_n)$  is defined in equation (1.1).

We are interested in the situation when different chains on  $\mathbb{Z}^+$  are very large ( $n \gg 1$ ) and the number of steps of each chain tends to infinity ( $N \rightarrow \infty$ ).

We expect that in the thermodynamic limit  $N \rightarrow \infty$  and for  $n \gg 1$  the absorption transition into a localized state at the point  $x = 1$  is sensitive to the shape of the function  $w(n)$ . Namely, if  $w(n)$  grows rather slow with  $n$  (for the precise criteria of the growth see section 3) we could expect that the phase transitions occur in each individual chain independently; while if  $w(n)$  is rather a sharp function of  $n$ , various types of *collective* localizations are expected. The interplay between the entropy loss and the energy gain in the localized states makes the phase behaviour of the system under consideration extremely rich.

The most attention in our work is paid to determination of the critical shape of the function  $w(n)$  at which the localization transition occurs simultaneously in all  $n$  ( $n \rightarrow \infty$ ) random walks.

It could be useful to define precisely what we mean under the ‘localization’ of the polymer chain. Let  $F(N) = \ln Z(N)$  be the free energy of the  $N$ -step path on the halfline  $\mathbb{Z}^+$  with the point well of depth  $\mathcal{U}$  at the point  $x = 1$ . This model can be described via the recursion relation with specific boundary conditions (cf equation (1.3)). It is known that there exists some critical value  $\mathcal{U} = \mathcal{U}_{\text{cr}} > 0$  which separates two different behaviours of the free energy:

$$\lim_{N \rightarrow \infty} \frac{1}{N} [F(N) - F_0(N)] = \begin{cases} 0 & \text{for } \mathcal{U} < \mathcal{U}_{\text{cr}} \\ \Lambda > 0 & \text{for } \mathcal{U} > \mathcal{U}_{\text{cr}} \end{cases} \quad (1.4)$$

where  $F_0(N) = N \ln 2$  is the trivial part associated with the total number of trajectories on  $\mathbb{Z}^+$ .

The value  $\mathcal{U}_{\text{cr}}$  we call the ‘localization transition point’. It signals the separation of the highest eigenvalue  $\Lambda$  from the continuous spectrum of our recursion relation for given boundary conditions (see appendix A for some details).

## 2. Exact solutions of the catalytic absorption model for $n = \{1, 2\}$

### 2.1. Solution for $n = 1$

Let us start with the simplest situation when  $n = 1$ , i.e. we have a single chain on  $\mathbb{Z}^+$  interacting with the potential well at the origin, i.e. the problem of a ‘polymer absorption’.

In this case equations (1.1)–(1.3) degenerate to the following:

$$U(x) = \begin{cases} 0 & \text{if } x \neq 1 \\ w(1) & \text{if } x = 1 \end{cases} \quad (2.1)$$

and

$$\begin{cases} Z_{N+1}(x) = Z_N(x+1) + Z_N(x-1) & (x \geq 2) \\ Z_{N+1}(x) = e^{U(x)} Z_N(x+1) & (x = 1) \\ Z_N(x) = 0 & (x \leq 0) \\ Z_{N=0}(x) = \delta_{x,1}. \end{cases} \quad (2.2)$$

The solution of the one-particle problem is very straightforward. The equations (2.2) can be rewritten as follows:

$$Z_{N+1}(x) = Z_N(x-1) + Z_N(x+1) + \delta_{x,1}(e^{w(1)} - 1)Z_N(x+1) \quad (x \geq 1) \quad (2.3)$$

completed by the boundary  $Z_N(x=0) = 0$  and initial  $Z_{N=0}(x) = \delta_{x,1}$  conditions.

Perform the substitution

$$Z_N(x) = 2^N \mathcal{Z}_N(x). \quad (2.4)$$

Comparing (2.4) with (1.4) we see that  $F(N) - F_0(N) = \ln \mathcal{Z}_N$ . Let us use now the Fourier–Laplace transform

$$\tilde{\mathcal{Z}}(q, s) = \sum_{N=0}^{\infty} s^N \sum_{x=0}^{\infty} \sin \frac{\pi x q}{l} \mathcal{Z}_N(x)$$

and introduce the new variable  $k = \frac{\pi q}{l}$ . After simple algebra we arrive at the following integral equation for the function  $\tilde{\mathcal{Z}}_N(k, s)$ :

$$\frac{1}{s} \tilde{\mathcal{Z}}(k, s) - \frac{1}{s} \sin k = \cos k \tilde{\mathcal{Z}}(k, s) + \sin k (e^{w(1)} - 1) \frac{1}{\pi} \int_0^{\pi} dk \sin 2k \tilde{\mathcal{Z}}(k, s) \quad (2.5)$$

which leads to the following expression:

$$\mathcal{Z}(x=2, s) \equiv \frac{1}{\pi} \int_0^{\pi} dk \sin 2k \tilde{\mathcal{Z}}(k, s) = \frac{\frac{1}{\pi} \int_0^{\pi} dk \frac{\sin k \sin 2k}{1-s \cos k}}{1 - s(e^{w(1)} - 1) \frac{1}{\pi} \int_0^{\pi} dk \frac{\sin k \sin 2k}{1-s \cos k}}. \quad (2.6)$$

The divergence of the function  $\frac{1}{\pi} \int_0^{\pi} dk \sin 2k \tilde{\mathcal{Z}}(k, s)$  occurs when the denominator in equation (2.6) is set to zero:

$$e^{w_{\text{cr}}^{(1)}} - 1 = \frac{1}{s \frac{1}{\pi} \int_0^{\pi} dk \frac{\sin k \sin 2k}{1-s \cos k}} \Big|_{s \rightarrow 1} \rightarrow 1. \quad (2.7)$$

This equation determines the critical value  $w(1) \equiv w_{\text{cr}}^{(1)}$  which corresponds to the localization transition point. Thus, in the thermodynamic limit  $N \rightarrow \infty$  (i.e. when  $s \rightarrow 1$ ) we have  $w_{\text{cr}}^{(1)} = \ln 2$ . In appendix A we recall briefly some relevant information concerning the origin of second-order phase transitions.

## 2.2. Solution for $n = 2$

**2.2.1. General ansatz.** Consider now two different paths on the halfline, simultaneously developing in ‘time’  $t$  ( $1 \leq t \leq N$ ). These chains are independent of each other at all points  $x = \{2, 3, \dots\}$  except the point  $x = 1$ . Let us call the current coordinates of the first and the second paths  $x_1(t)$  and  $x_2(t)$  correspondingly. The potential (equation (1.1)) now reads

$$U(x_1, x_2) = \begin{cases} 0 & \text{if } x_1 \neq 1 \text{ and } x_2 \neq 1 \\ w(1) & \text{if } \{x_1 = 1 \text{ and } x_2 \neq 1\} \text{ or } \{x_1 \neq 1 \text{ and } x_2 = 1\} \\ w(2) & \text{if } x_1 = 1 \text{ and } x_2 = 1. \end{cases} \quad (2.8)$$

Thus, effectively we have the *single* trajectory in two dimensions developing in the first quarter of the  $(x_1, x_2)$ -plane with specific boundary conditions. In order to simplify the corresponding equations, it is very convenient to choose the embedding lattice as shown in figure 1. The equations for the joint partition function,  $Z_N(x_1, x_2)$ , in the two-dimensional (2D) case (for  $n = 2$ ) become slightly more tricky than in the one-dimensional (1D) case (for  $n = 1$ ).

We can derive the recursion relation for the partition function  $Z_N(x_1, x_2)$  which is the 2D extension of equation (2.3):

$$\begin{aligned} Z_{N+1}(x_1, x_2) = & \Delta_{x_1, x_2} Z_N(x_1, x_2) + \delta_{x_1, 1}(e^{w(1)} - 1)\Delta_{x_2} Z_N(x_1 + 1, x_2) \\ & + \delta_{x_2, 1}(e^{w(1)} - 1)\Delta_{x_1} Z_N(x_1, x_2 + 1) \\ & + \delta_{x_1, 1}\delta_{x_2, 1}(e^{2w(2)} - 2e^{w(1)} + 1)Z_N(x_1 + 1, x_2 + 1) \end{aligned} \quad (2.9)$$

where

$$\Delta_{x_i} \Psi(x_i) \equiv \Psi(x_i - 1) + \Psi(x_i + 1) \quad (i = \{1, 2\}) \quad (2.10)$$

and

$$\begin{aligned} \Delta_{x_1, x_2} \Psi(x_1, x_2) \equiv & \Psi(x_1 - 1, x_2 - 1) + \Psi(x_1 - 1, x_2 + 1) \\ & + \Psi(x_1 + 1, x_2 - 1) + \Psi(x_1 + 1, x_2 + 1). \end{aligned} \quad (2.11)$$

The equation (2.9) is valid for  $x_1 \geq 1, x_2 \geq 1$  and should be completed by the boundary and initial conditions,

$$\begin{cases} Z_N(x_1 = 0, x_2 \geq 1) = Z_N(x_1 \geq 1, x_2 = 0) = Z_N(x_1 = 0, x_2 = 0) = 0 \\ Z_{N=0}(x_1, x_2) = \delta_{x_1, 1}\delta_{x_2, 1}. \end{cases} \quad (2.12)$$

We search the solution of equations (2.9)–(2.12) in the form of the following ansatz:

$$Z(x_1, x_2) = \bar{Z}_N(x_1, x_2) + W_N(x_1, x_2). \quad (2.13)$$

The function  $\bar{Z}_N(x_1, x_2) = Z_N(x_1) Z_N(x_2)$  is the product of two independent 1D functions, each of them satisfying equation (2.3). Thus, for  $\bar{Z}_N(x_1, x_2)$  we have the recursion relation,

$$\begin{aligned} \bar{Z}_{N+1}(x_1, x_2) = & \Delta_{x_1, x_2} \bar{Z}_N(x_1, x_2) + \delta_{x_1, 1}(e^{w(1)} - 1)\Delta_{x_2} \bar{Z}_N(x_1 + 1, x_2) \\ & + \delta_{x_2, 1}(e^{w(1)} - 1)\Delta_{x_1} \bar{Z}_N(x_1, x_2 + 1) \\ & + \delta_{x_1, 1}\delta_{x_2, 1}(e^{w(1)} - 1)^2 \bar{Z}_N(x_1 + 1, x_2 + 1) \end{aligned} \quad (2.14)$$

which is analogous to (2.9) but has an improper Boltzmann weight at the ‘main corner’ point  $(x_1 = 1, x_2 = 1)$ .

In order to compensate the difference in the Boltzmann weight at the point  $(x_1 = 1, x_2 = 1)$  we add to the function  $\bar{Z}_N(x_1, x_2)$  the nonmultiplicative part  $W_N(x_1, x_2)$  describing the ‘absorption at the *main corner*’. This function is defined by the recursion relations,

$$\begin{cases} W_{N+1}(x_1, x_2) = \Delta_{x_1, x_2} W_N(x_1, x_2) + \delta_{x_1, 1}\delta_{x_2, 1}\gamma_2 W_N(x_1 + 1, x_2 + 1) \\ W_N(x_1 = 1, x_2 \geq 2) = W_N(x_1 \geq 2, x_2 = 1) = W_N(x_1 \leq 0, x_2 \leq 0) = 0 \\ W_{N=0}(x_1, x_2) = \delta_{x_1, 1}\delta_{x_2, 1} \end{cases} \quad (2.15)$$

where the extra ‘main corner’ Boltzmann weight  $\gamma_2$  is chosen to reproduce the right Boltzmann weight  $\beta^{(2)}$  at the point  $(x_1 = 1, x_2 = 1)$  (see equations (2.8) and figure 3)

$$\gamma_2 = e^{2w(2)} - e^{2w(1)} - 2. \quad (2.16)$$

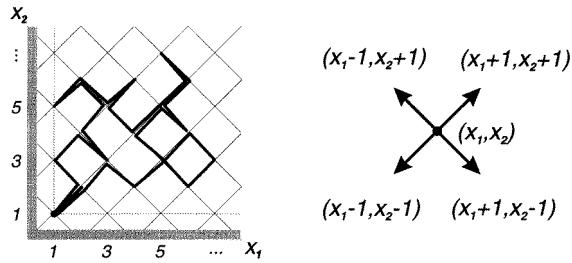


Figure 1. The lattice ( $x_1 > 1, x_2 > 1$ ) with (a) zero's boundary conditions; (b) allowed moves.

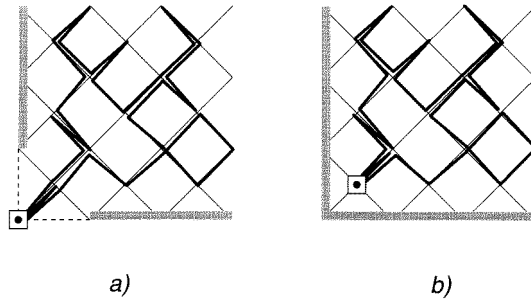


Figure 2. (a) The auxiliary 2D lattice used in the computation of the nonmultiplicative contribution  $W_N(x_1, x_2)$ —see equation (2.15); (b) the same lattice as in (a) but with another boundary condition at the 'main corner'.

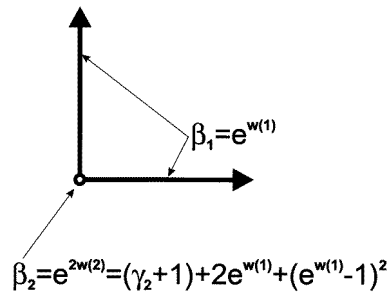


Figure 3. Computation of the 2D extra Boltzmann weight at the 'main corner'.

It is easy to check the validity of our choice of  $\gamma_2$ ,

$$\underbrace{(\gamma_2 + 1)}_{W_N(x_1, x_2)} + \underbrace{(e^{w(1)} - 1)^2 + 2e^{w(1)}}_{Z_N(x_1)Z_N(x_2)} = e^{2w(2)} \equiv \beta^{(2)}. \quad (2.17)$$

The equations (2.15) correspond to the situation shown in figure 2(a), where we marked the point at which the Boltzmann weight  $\gamma_2$  is located by the symbol  $\blacksquare$ .

As stated in section 1 we are interested in the determination of the phase transition point of the function  $Z_N(x_1, x_2)$  (for  $n = 2$  and  $N \gg 1$ ). Generalizing the arguments of section 2.1 it is easy to verify that the transition to the localized state occurs at the divergence point of the function  $Z(x_1 = 2, x_2 = 2, s)$  (as in equation (2.6)):

$$\mathcal{Z}_{N \rightarrow \infty}(x_1 = 2, x_2 = 2) = \frac{1}{\pi^2} \int_0^\pi \int_0^\pi dk_1 dk_2 \sin 2k_1 \sin 2k_2 \tilde{\mathcal{Z}}(k_1, k_2, s \rightarrow 1) \quad (2.18)$$

where

$$Z_N(x_1, x_2) = 4^N \mathcal{Z}_N(x_1, x_2) \quad W_N(x_1, x_2) = 4^N \mathcal{W}_N(x_1, x_2) \quad (2.19)$$

and

$$\tilde{\mathcal{Z}}(k_1, k_2, s) = \sum_{N=0}^{\infty} s^N \sum_{x_1=0}^{\infty} \sum_{x_2=0}^{\infty} \sin x_1 k_1 \sin x_2 k_2 \mathcal{Z}_N(x_1, x_2)$$

(cf equation (2.4)).

Substituting the ansatz (2.13) into (2.18) we see that the divergence of the function  $Z_{N \rightarrow \infty}(x_1 = 2, x_2 = 2)$  is determined:

- either by the divergence of the ‘one-particle’ function  $Z_{N \rightarrow \infty}(x_i = 2)$  ( $i = \{1, 2\}$ )
- or by the divergence of the ‘main corner’ part  $W_{N \rightarrow \infty}(x_1 = 2, x_2 = 2)$

and everything depends on which of these two functions diverges first in the phase space of parameters  $\{w(1), w(2)\}$  (recall that according to equation (1.2) we have a restriction  $0 \leq w(1) \leq w(2)$ ).

The behaviour of the function  $Z_N(x_i)$  ( $i = \{1, 2\}$ ) has been well studied in section 2.1; so, let us concentrate our efforts on the solution of equations (2.15).

2.2.2. *Phase transition point of the ‘main corner’ part  $W_N(x_1, x_2)$ .* The partition function  $W(N) \equiv W_N(x_1 = 1, x_2 = 1)$  where  $N$  is even can be written in the following form. Let us introduce the auxiliary functions:

(1)  $\Omega(N) \equiv \Omega_N(x_1 = 1, x_2 = 1)$ —the number of closed paths, starting at the point  $(x_1 = 1, x_2 = 1)$ , finishing at the same point after  $N$  steps for the first time and satisfying the boundary conditions in figure 2(a);

(2)  $V(N) \equiv V_N(x_1 = 2, x_2 = 2)$ —the number of  $N$ -step closed paths, starting and finishing at the point  $(x_1 = 2, x_2 = 2)$  and satisfying the boundary conditions in figure 2(b).

The following identity can be derived immediately:

$$\Omega(N + 2) = V(N) \equiv 4^N \mathcal{V}(N). \quad (2.20)$$

The function  $W(N)$  admits the representation

$$W(N) = \sum_{k=1}^{N/2} (\beta^{(2)})^k \sum_{\{N_1 + \dots + N_k = N\}} \prod_{i=1}^k \Omega(N_i) \quad (2.21)$$

where the upper limit in the first sum can be set to infinity because the condition  $N_1 + \dots + N_k = N$  ensures the right cut of the sum;  $\beta^{(2)} = \gamma_2 + 1$  is the Boltzmann weight of the potential well at the origin.

Using the Kronecker  $\delta$ -function:

$$\delta(x) = \frac{1}{2\pi i} \oint \frac{dz}{z^{1+x}} = \begin{cases} 0 & x \neq 0 \\ 1 & x = 0 \end{cases}$$

where  $x = N - N_1 - \dots - N_k$ , we may rewrite equation (2.21) as follows:

$$\begin{aligned} W(N) &= \sum_{k=0}^{\infty} (\beta^{(2)})^k \frac{1}{2\pi i} \oint dz z^{-N-1} \sum_{N_1=2}^{\infty} \dots \sum_{N_k=2}^{\infty} z^{N_1 + \dots + N_k} \prod_{i=1}^k \Omega(N_i) \\ &= \frac{1}{2\pi i} \oint dz z^{-N-1} \frac{1}{1 - \beta^{(2)} \sum_{N=2}^{\infty} z^N \Omega(N)}. \end{aligned} \quad (2.22)$$

The appearance of the pole in the last expression signals the separation of the localized mode from the continuous part of the spectrum corresponding to the function  $W(N)$  (cf



(2.3) and equations in appendix A). Using the identity (2.20) we obtain the equation on the transition point (for  $N \rightarrow \infty$ ):

$$\beta_{\text{cr}}^{(2)} = \lim_{z \rightarrow 4} \frac{1}{\sum_{N=0}^{\infty} \left(\frac{z}{4}\right)^N \mathcal{V}(N)} \equiv \lim_{s \rightarrow 1} \frac{1}{\sum_{N=0}^{\infty} s^N \mathcal{V}(N)} \quad (2.23)$$

where  $s = \frac{z}{4}$ .

The function  $V_N(x_1, x_2)$  satisfies the recursion relation in the absence of any potentials,

$$V_{N+1}(x_1, x_2) = \Delta_{x_1, x_2} V_N(x_1, x_2) \quad (2.24)$$

with the boundary and initial conditions shown in figure 2(b):

$$\begin{cases} V_N(x_1 = 1, x_2 \geq 2) = V_N(x_1 \geq 2, x_2 = 1) = V_N(x_1 = 1, x_2 = 1) = 0 \\ V_{N=0}(x_1, x_2) = \delta_{x_1, 2} \delta_{x_2, 2}. \end{cases} \quad (2.25)$$

Using the Laplace and the 2D sin-Fourier transforms and performing the shift in equation (2.24)  $\{x_1 \rightarrow x_1 - 1, x_2 \rightarrow x_2 - 1\}$  we arrive at the standard equation for the function  $\mathcal{V}_N(k_1, k_2, s)$ ,

$$\mathcal{V}_N(k_1, k_2, s) = \frac{\sin k_1 \sin k_2}{1 - s \cos k_1 \cos k_2}. \quad (2.26)$$

Thus, we obtain the final expression,

$$\sum_{N=0}^{\infty} s^N \mathcal{V}(N) = \frac{1}{\pi^2} \int_0^{\pi} \int_0^{\pi} dk_1 dk_2 \frac{\sin^2 k_1 \sin^2 k_2}{1 - s \cos k_1 \cos k_2}. \quad (2.27)$$

Evaluating the last integral at the point  $s = 1$  we obtain the following numerical value for the ‘2D main corner’ transition point,

$$\beta_{\text{cr}}^{(2)} \equiv \gamma_2 + 1 = \frac{\pi}{4 - \pi} \approx 3.660. \quad (2.28)$$

**2.2.3. Phase diagram for two-particle system.** Collecting the results of the sections 2.2.1 and 2.2.2 we conclude that the transition from the delocalized to the absorbed state is determined:

- either by the equation  $\beta_{\text{cr}}^{(1)} \equiv e^{w_{\text{cr}}(1)} = 2$  (the ‘single-chain’ contribution);
- or by the equation  $\beta_{\text{cr}}^{(2)} = \gamma_2 + 1$ , i.e.  $e^{2w(2)} - e^{2w(1)} - 1 = \frac{\pi}{4 - \pi}$  (the two-particle ‘main corner’ contribution).

The complete phase diagram is drawn in figure 4. For  $w(1) > \ln 2$  the influence of the potential  $w(2)$  disappears, while for  $0 < w(1) < \ln 2 \approx 0.693$  the ‘induced’ localization can occur for

$$w(2) > \frac{1}{2} \ln \left( e^{2w(1)} + \frac{4}{4 - \pi} \right)$$

just due to the simultaneous interactions between two random walks at the origin.

It is worthwhile to mention that the ‘collective’ localization can appear even for  $w(1) < 0$ . Suppose, for example, we have the situation:

$$w(1) = -\infty \quad w(2) > 0$$

i.e. each particular chain cannot visit the origin, but there is an energy gain for two chains to be trapped at the origin simultaneously. In this case for

$$w(2) > w_{\text{cr}}(2) = \frac{1}{2} \ln \frac{4}{4 - \pi} \approx 0.769$$

the chains become localized.

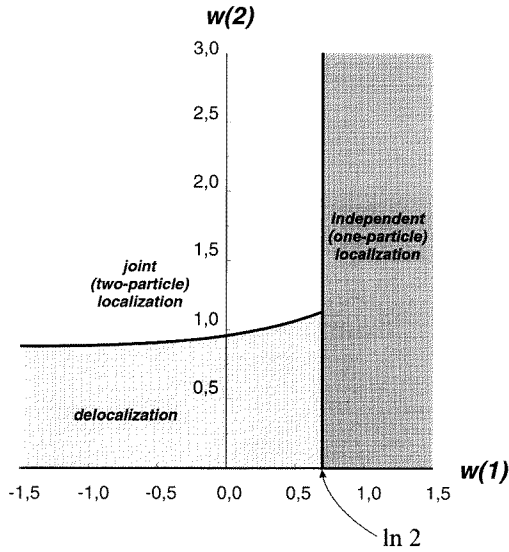


Figure 4. The phase diagram for the two-particle catalytic absorption model.

### 3. Phase transitions in catalytic absorption model for $n > 2$

#### 3.1. Solution for $n = 3$

The equation for the three-particle partition function  $Z_N(x_1, x_2, x_3)$  reads

$$\begin{aligned}
 Z_N(x_1, x_2, x_3) = & \Delta_{x_1, x_2, x_3} Z_N(x_1, x_2, x_3) + \delta_{x_1, 1} (e^{w(1)} - 1) \Delta_{x_2, x_3} Z_N(x_1 + 1, x_2, x_3) \\
 & + \delta_{x_2, 1} (e^{w(1)} - 1) \Delta_{x_1, x_3} Z_N(x_1, x_2 + 1, x_3) \\
 & + \delta_{x_3, 1} (e^{w(1)} - 1) \Delta_{x_1, x_2} Z_N(x_1, x_2, x_3 + 1) \\
 & + \delta_{x_1, 1} \delta_{x_2, 1} (e^{2w(2)} - 2e^{w(1)} + 1) \Delta_{x_3} Z_N(x_1 + 1, x_2 + 1, x_3) \\
 & + \delta_{x_1, 1} \delta_{x_3, 1} (e^{2w(2)} - 2e^{w(1)} + 1) \Delta_{x_2} Z_N(x_1 + 1, x_2, x_3 + 1) \\
 & + \delta_{x_2, 1} \delta_{x_3, 1} (e^{2w(2)} - 2e^{w(1)} + 1) \Delta_{x_1} Z_N(x_1, x_2 + 1, x_3 + 1) \\
 & + \delta_{x_1, 1} \delta_{x_2, 1} \delta_{x_3, 1} (e^{3w(3)} - 3e^{2w(2)} + 3e^{w(1)} - 1) Z_N(x_1 + 1, x_2 + 1, x_3 + 1).
 \end{aligned}
 \tag{3.1}$$

Generalizing the ansatz (2.13) to the three-dimensional (3D) case we search the solution of equation (3.1) in the form

$$\begin{aligned}
 Z_N(x_1, x_2, x_3) = & \overline{W}_N(x_1, x_2) Z_N(x_3) + \overline{W}_N(x_1, x_3) Z_N(x_2) \\
 & + \overline{W}_N(x_2, x_3) Z_N(x_1) + W_N(x_1, x_2, x_3)
 \end{aligned}
 \tag{3.2}$$

where:

- (a) the functions  $Z_N(x_i)$  for  $i \in [1, 3]$  are defined by equation (2.3);
- (b) the functions  $\overline{W}_N(x_i, x_j)$  ( $i \neq j$ ;  $\{i, j\} \in [1, 3]$ ) are defined by the recursion relations (2.15) with the replacement

$$\gamma_2 \rightarrow \overline{\gamma}_2 = e^{2w(2)} - 2e^{w(1)} - 1
 \tag{3.3}$$

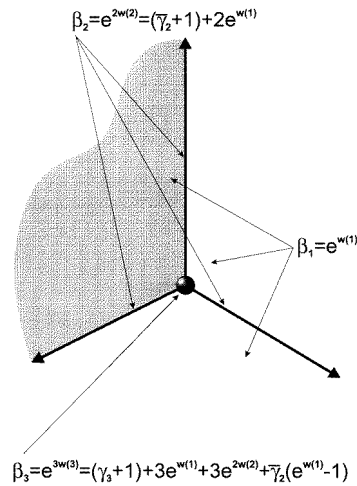


Figure 5. Computation of the Boltzmann weights  $\bar{\gamma}_2$  and  $\gamma_3$ .

(c) the function  $W_N(x_1, x_2, x_3)$  is determined as follows:

$$\left\{ \begin{array}{l} W_{N+1}(x_1, x_2, x_3) = \Delta_{x_1, x_2, x_3} W_N(x_1, x_2, x_3) + \delta_{x_1, 1} \delta_{x_2, 1} \delta_{x_3, 1} \gamma_3 \\ \quad \times W_N(x_1 + 1, x_2 + 1, x_3 + 1) \\ W_N(x_1 = 1, x_2 \geq 2, x_3 \geq 2) = W_N(x_1 \geq 2, x_2 = 1, x_3 \geq 2) \\ \quad = W_N(x_1 \geq 2, x_2 \geq 2, x_3 = 1) = 0 \\ W_N(x_1 = 1, x_2 = 1, x_3 \geq 2) = W_N(x_1 = 1, x_2 \geq 2, x_3 = 1) \\ \quad = W_N(x_1 \geq 2, x_2 = 1, x_3 = 1) = 0 \\ W_{N=0}(x_1, x_2) = \delta_{x_1, 1} \delta_{x_2, 1} \end{array} \right. \quad (3.4)$$

where

$$\gamma_3 = e^{3w(3)} - 3e^{2w(2)}e^{w(1)} + 6e^{2w(2)} - 6e^{w(1)} - 4. \quad (3.5)$$

Let us check the consistency of equations (3.3)–(3.5) (see figure 5):

$$\left\{ \begin{array}{l} (\bar{\gamma}_2 + 1) + 2e^{w(1)} = e^{2w(2)} \\ (\gamma_3 + 1) + 3e^{w(1)} + 3e^{2w(2)} + (\bar{\gamma}_2 + 1)(e^{w(1)} - 1) = e^{3w(3)}. \end{array} \right. \quad (3.6)$$

The arguments of the section 2.2.2 can be easily extended to the 3D case. Skipping the intermediate computations we present the final result for the value of the Boltzmann weight at the ‘3D main corner’ transition point,

$$\beta_{cr}^{(3)} = \left( \frac{1}{\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi dk_1 dk_2 dk_3 \frac{\sin^2 k_1 \sin^2 k_2 \sin^2 k_3}{1 - \cos k_1 \cos k_2 \cos k_3} \right)^{-1} \approx 7.856. \quad (3.7)$$

The localization phase transition is now determined:

- either by the equation  $\beta_{cr}^{(1)} = 2$ , i.e.

$$w_{cr}^{(1)} = \ln 2 \quad (3.8)$$

(the one-particle contribution);

- or by the equation  $\beta_{cr}^{(2)} = \bar{\gamma}_2 + 1 = \frac{\pi}{4 - \pi}$ , i.e.

$$w_{cr}^{(2)} = \frac{1}{2} \ln \left( 2e^{w(1)} + \frac{\pi}{4 - \pi} \right) \quad (3.9)$$

(the two-particle contribution);

- or by the equation  $\beta_{\text{cr}}^{(3)} = \gamma_3 + 1 = 7.856$ , i.e.

$$w_{\text{cr}}(3) = \frac{1}{3} \ln(3e^{2w(2)}e^{w(1)} - 6e^{2w(1)} + 6e^{w(1)} + 10.856) \tag{3.10}$$

(the three-particle ‘main corner’ contribution).

### 3.2. Solution for arbitrary $n$

The general ansatz for arbitrary values of  $n$  reads†

$$\begin{aligned} Z_N(x_1, x_2, \dots, x_n) = & \overline{W}_N(x_1, \dots, x_{n-1})Z_N(x_n) + \text{all permutations} \\ & + \overline{W}_N(x_1, \dots, x_{n-2})\overline{W}_N(x_{n-1}, x_n) + \text{all permutations} \\ & + \overline{W}_N(x_1, \dots, x_{n-3})\overline{W}_N(x_{n-2}, x_{n-1}, x_n) + \text{all permutations} \\ & + \dots + \overline{W}_N(x_1, \dots, x_{\frac{n}{2}})\overline{W}_N(x_{\frac{n}{2}+1}, \dots, x_n) + \text{all permutations} \\ & + W_N(x_1, \dots, x_n) \end{aligned} \tag{3.11}$$

where

$$\begin{cases} \overline{W}_{N+1}(x_1, \dots, x_j) = \Delta_{x_1, \dots, x_j} \overline{W}_N(x_1, \dots, x_j) \\ \quad + \delta_{x_1, 1} \dots \delta_{x_j, 1} \overline{\gamma}_j \overline{W}_N(x_1 + 1, \dots, x_j + 1) & (2 \leq j \leq n - 1) \\ W_N = 0 & \text{in all subsections containing the point } (x_1 = 1, \dots, x_j = 1) \\ \overline{W}_{N=0}(x_1, \dots, x_j) = \delta_{x_1, 1} \dots \delta_{x_j, 1} \end{cases} \tag{3.12}$$

and

$$(\overline{\gamma}_j + 1) + C_j^1 e^{(j-1)w(j-1)} + C_j^2 e^{(j-2)w(j-2)} + \dots = e^{jw(j)}. \tag{3.13}$$

Equations (3.11)–(3.13) produce the following relation for the Boltzmann weight at the ‘ $n$ -dimensional main corner’,  $\gamma_n$ :

$$\begin{aligned} (\gamma_n + 1) + C_{n-1}^1 (\overline{\gamma}_1 + \overline{\gamma}_{n-1}) + C_{n-1}^2 (\overline{\gamma}_2 + \overline{\gamma}_{n-2}) \\ + \dots + (e^{w(1)} - 1) \overline{\gamma}_{n-1} + \overline{\gamma}_2 \overline{\gamma}_{n-2} + \dots + \overline{\gamma}_{\frac{n}{2}} \overline{\gamma}_{\frac{n}{2}+1} = e^{nw(n)} \end{aligned} \tag{3.14}$$

cf (3.6).

The singular points of the functions  $Z_N(x_i)$ ,  $\overline{W}_N(x_i, x_j), \dots$ , in the  $n$ -particle model are located at

$$\beta_{\text{cr}}^{(j)} = \begin{cases} \overline{\gamma}_j + 1 & \text{for } 1 \leq j \leq \frac{n}{2} \\ \gamma_n & \text{for } j = n - 1 \end{cases} \tag{3.15}$$

where each value of  $\beta_{\text{cr}}^{(j)}$  is defined by the equation

$$\beta_{\text{cr}}^{(j)} = \left( \frac{1}{\pi^j} \int_0^\pi \dots \int_0^\pi dk_1 \dots dk_j \frac{\sin^2 k_1 \dots \sin^2 k_j}{1 - \cos k_1 \dots \cos k_j} \right)^{-1} \tag{3.16}$$

and  $\gamma_j$  are the recursive solutions of equation (3.14).

† This equation is written for even values of  $n$ , the generalization to the odd values of  $n$  is very straightforward.

### 3.3. Phase transition in the $n$ -particle system for $n \gg 1$

Now we are in a position to give the answer to the question raised in section 1: ‘what should be the critical shape of the function  $w(n)$  (for  $n \gg 1$ ) to have the simultaneous collective  $n$ -particle localization in the system?’ For simplicity later on we suppose  $n$  to be even. The answer is very straightforward.

The condition on the critical shape  $w_{\text{cr}}(n)$  providing the joint  $n$ -particle localization is defined by setting  $w(n) \equiv w_{\text{cr}}(n)$  in the equations (3.15)–(3.16).

The approximate evaluation of the integral (3.16) for  $n \gg 1$  gives us (with the exponential accuracy—see appendix B for details)

$$\beta_{\text{cr}}^{(n)} = \exp\left(\frac{3}{2}n \ln n - \frac{1}{2}n \ln \frac{\pi e^3}{54} + O(\ln n)\right). \quad (3.17)$$

We drop in equation (3.16) all terms growing with  $n \rightarrow \infty$  slower than  $\exp(\text{constant } n)$ .

Substituting (3.13) into (3.16) and taking into account that all Boltzmann weights are positive, it is easy to conclude that for  $n \gg 1$

$$e^{nw_{\text{cr}}(n)} = e^{\frac{3}{2}n \ln n} \quad (3.18)$$

where we kept the leading asymptotics (for  $n \rightarrow \infty$ ) only. Thus, we arrive at the following final conclusion.

- If the function  $w(n)$  grows faster than  $w_{\text{cr}}(n) = \frac{3}{2} \ln n$  then all  $n \gg 1$  chains are localized simultaneously in the point well located at the origin  $x = 1$  of the halfline  $\mathbb{Z}^+$ .

Recall that  $w(n)$  is the depth of the potential well for each chain bead localized at the origin. Thus the ‘integral’ critical depth,  $\mathcal{U}_{\text{cr}}(n) = nw_{\text{cr}}(n)$  per cluster of  $n$  particles has the following asymptotic behaviour,  $\mathcal{U}_{\text{cr}}(n) = \frac{3}{2}n \ln n$ .

## 4. Discussion: Connection with the random heteropolymer absorption problem

The above mentioned problem has a direct application to the old problem of random copolymer absorption at the point well. Namely, consider a polymer chain on  $\mathbb{Z}^+$  with a point well located at the origin and suppose that the well depth depends on the current ‘time’ (i.e. on the chain bead’s number) located at the point  $x = 0$ . The partition function  $\Theta_N$  of such a system can be written as a sum over all available paths,

$$\Theta_N(x_N) = \mathcal{N} \sum_{\{x_1, \dots, x_{N-1}\}} \prod_{j=1}^N \{g(|x_j - x_{j-1}|) e^{U_j(x_j)}\} \quad (4.1)$$

where  $\mathcal{N}$  is the normalization constant,  $g(|x_j - x_{j-1}|)$  is the local transition matrix and the potential  $U_j(x_j)$  is a random variable of  $j$ . Write  $U_j(x_j)$  as follows:

$$U_j(x_j) = \begin{cases} \frac{1 + \sigma_j}{2} \varepsilon_1 + \frac{1 - \sigma_j}{2} \varepsilon_2 & \text{for } x_j = 0 \\ 0 & \text{for } x_j > 0 \end{cases} \quad (4.2)$$

where  $\varepsilon_{1,2}$  are some positive constants and  $\sigma_j$  is the random variable defined as follows:

$$\sigma_j = \begin{cases} +1 & \text{with the probability } p \\ -1 & \text{with the probability } 1 - p. \end{cases}$$

Write (4.1) in the form of recursion relations:

$$\begin{cases} \Theta_{N+1}(x) = \Theta_N(x+1) + \Theta_N(x-1) & (x \geq 1) \\ \Theta_{N+1}(x) = e^{U_N} \Theta_N(x+1) & (x = 0) \\ \Theta_N(x) = 0 & (x < 0) \\ \Theta_{N=0}(x) = \delta_{x,0}. \end{cases} \quad (4.3)$$

Performing the shift  $x \rightarrow x + 1$  (cf (2.3)) rewrite (4.3) as follows:

$$\begin{cases} \Theta_{N+1}(x) = \Delta_x \Theta_N(x) + (e^{U_N} - 1) \delta_{x,1} \Theta_N(x+1) & (x \geq 1) \\ \Theta_N(x) = 0 & (x = 0) \\ \Theta_{N=0}(x) = \delta_{x,1} \end{cases} \quad (4.4)$$

where  $\Delta_x$  is defined in (2.10).

The partition function  $\Theta_N(x)$  is a random variable which depends on the quenched random pattern of realizations of the potential  $U_j$  ( $j \in [1, N]$ ). To find the reliable thermodynamic quantity in quenched ensembles we have to average the free energy  $\ln \Theta_N$  over the distribution of all random sequences  $\{\sigma_1, \sigma_2, \dots, \sigma_N\}$ . We realize the corresponding computations in the framework of the replica approach.

Averaging the  $n$ s power of the partition function  $\langle \Theta_N^n(x) \rangle = \Phi_N(x_1, \dots, x_n)$ , we obtain:

$$\begin{aligned} \Phi_{N+1}(x_1, \dots, x_n) &= \Delta_{x_1, \dots, x_n} \Phi_N(x_1, \dots, x_n) \\ &+ \langle e^{U_N} - 1 \rangle \sum_{i=1}^n \delta_{x_i, 1} \Delta_{x_1, \dots, \cancel{x_i}, \dots, x_n} \Phi_N(x_1, \dots, x_{i-1}, x_i + 1, x_{i+1}, \dots, x_n) \\ &+ \langle (e^{U_N} - 1)^2 \rangle \sum_{i > j}^n \delta_{x_i, 1} \delta_{x_j, 1} \Delta_{x_1, \dots, \cancel{x_i}, \dots, \cancel{x_j}, \dots, x_n} \\ &\times \Phi_N(x_1, \dots, x_{i-1}, x_i + 1, x_{i+1}, \dots, x_{j-1}, x_j + 1, x_{j+1}, \dots, x_n) \\ &+ \dots + \langle (e^{U_N} - 1)^n \rangle \delta_{x_1, 1} \dots \delta_{x_n, 1} \Phi_N(x_1 + 1, \dots, x_n + 1) \end{aligned} \quad (4.5)$$

where the operator  $\Delta_{x_1, \dots, x_j}$  is the  $j$ -dimensional discrete Laplacian—cf (2.9)–(2.11) and

$$\langle (e^{U_N} - 1)^j \rangle = p(e^{\epsilon_1} - 1)^j + (1 - p)(e^{\epsilon_2} - 1)^j = \langle \gamma_j \rangle. \quad (4.6)$$

The solution of equation (4.5) reads (cf (3.11)):

$$\begin{aligned} \Phi_N(x_1, \dots, x_n) &= \overline{\Phi}_N(x_1, \dots, x_{n-1}) Z_N(x_n) + \text{all permutations} \\ &+ \overline{\Phi}_N(x_1, \dots, x_{n-2}) \overline{\Phi}_N(x_{n-1}, x_n) + \text{all permutations} \\ &+ \dots + \overline{\Phi}_N(x_1, \dots, x_{\frac{n}{2}}) \overline{\Phi}_N(x_{\frac{n}{2}+1}, \dots, x_n) + \text{all permutations} \\ &+ W_N(x_1, \dots, x_n) \end{aligned} \quad (4.7)$$

where the functions  $\overline{\Phi}_N(x_1, \dots, x_k)$  satisfy the master equations ( $k \in [1, n]$ )

$$\begin{cases} \overline{\Phi}_N(x_1, \dots, x_j) = \Delta_{x_1, \dots, x_j} \overline{\Phi}_N(x_1, \dots, x_j) \\ \quad + \delta_{x_1, 1} \dots \delta_{x_j, 1} \overline{\gamma}_j \overline{\Phi}_N(x_1 + 1, \dots, x_j + 1) \quad \{x_1, \dots, x_j\} \geq 1 \\ \overline{\Phi}_N = 0 \quad \text{in all subspaces containing the point } (x_1 = 1, \dots, x_k = 1) \\ \overline{\Phi}_{N=0}(x_1, \dots, x_n) = \delta_{x_1, 1} \dots \delta_{x_n, 1}. \end{cases} \quad (4.8)$$

Using the results of the previous sections one can conclude that the averaged moments of the quenched heteropolymer partition function,  $\langle \Theta_N \rangle, \langle \Theta_N^2 \rangle, \dots, \langle \Theta_N^n \rangle$  exhibit singular behaviour at the set of points being the solutions of equation (3.15) where  $\beta_{cr}^{(1)} = 2$  (see

equation (2.7)) and  $\beta_{\text{cr}}^{(j)}$  for  $j \in [2, n]$  is given by equation (3.16). Recall that we restrict ourselves to the case:  $\varepsilon_1 > 0$  and  $\varepsilon_2 > 0$ .

The ‘true critical point’ of the localization transition in all averaged moments of the partition function  $\Theta_N$  (in the thermodynamic limit  $N \rightarrow \infty$ ) can be obtained using the following simple procedure. We fix some arbitrary value  $\varepsilon_2$  and find the *minimal* value  $\varepsilon_1^{\text{cr}}(\varepsilon_2, j)$  among all solutions of equation (3.15) for  $j \in [1, n]$ .

It is easy to check that for all  $1 \leq j \leq n$  and any arbitrary choice of  $\varepsilon_2$ , the minimal value  $\varepsilon_1^{\text{cr}}$  corresponds just to  $j = 1$ . It means that *all moments of the random copolymer partition function,  $\Theta_N^j$ , averaged over the quenched disorder in monomer types diverge at the same point as the ‘one-particle’ part (i.e. the ‘annealed’ copolymer partition function),  $\langle \Theta_N \rangle$ .*

Of course, our consideration has an obvious crucial shortcoming connected with the fact that the replica approach presented above does not allow us to properly take the limit  $n \rightarrow 0$ . Thus, the computations performed in section 4 cannot be regarded as a proof of the conjecture that the phase transition points of copolymers with quenched and annealed chemical sequences coincide. However, the consistency of our investigation with other speculations on that subject [8, 17] at least gives hope that our conclusion is correct.

### Acknowledgments

I am very grateful to G Uimin, S Korshunov and A Grosberg for useful suggestions concerning the model itself and for critical comments regarding its possible application to the heteropolymer problem. Also I would like to thank H Spohn for his conjectures and for drawing my attention to [19, 20]. I highly appreciate valuable discussions of the problem with G Oshanin, A Comtet, S A Gredeskul and V Tchijov.

### Appendix A

The partition function  $\mathcal{Z}_N(x = 2)$  (see equation (2.5)) can be restored by means of the Mellin transform

$$\mathcal{Z}_N(x = 2) = \frac{1}{2\pi i} \oint ds \mathcal{Z}(s, x = 2) s^{-N-1}. \quad (\text{A.1})$$

On the complex plane the function  $\mathcal{Z}(s)$  has a square-root branching point at  $s = 1$  and a cut along  $]1, +\infty[$ . The function  $\mathcal{Z}(s)$  has a simple pole at the point  $s = s_0$  provided the equation (2.7) holds,

$$1 - s(e^w - 1) \frac{1}{\pi} \int_0^\pi dk \frac{\sin k \sin 2k}{1 - s \cos k} = 0. \quad (\text{A.2})$$

If there exists a pole at  $s_0$ , it gives the main contribution to the integral (A.1) and we have

$$\mathcal{Z}_N(x = 2) = s_0^N \text{Res } \mathcal{Z}(s, x = 2)|_{s=s_0 < 1}.$$

This situation is called the ground-state dominance. The chain is in the localized state and the free energy of the chain is given by  $F(N) - F_0(N) = N \ln(s_0)$ .

From (A.2) we can conclude that the localization transition appears just at  $w = w_{\text{cr}}$ , where

$$e^{w_{\text{cr}}} = 1 + \frac{\pi}{s_0 \int_0^\pi dk \frac{\sin k \sin 2k}{1 - s_0 \cos k}} = \frac{1}{s_0} \left( 1 - \sqrt{1 - s_0^2} \right)^2 \Big|_{s_0 \rightarrow 1} = 2. \quad (\text{A.3})$$

Equation (A.3) gives the asymptotic solution of equation (A.2). Expanding equation (A.2) in power series of  $\delta = \sqrt{1-s}$  near the branching point  $s_0 = 1$  up to the first leading term, we obtain

$$e^w \approx e^{w_{cr}} - 2\sqrt{2}\sqrt{1-s_0}. \tag{A.4}$$

Hence,

$$s_0 \approx 1 - \frac{1}{8}(e^{w_{cr}} - e^w)^2. \tag{A.5}$$

Thus, the phase transition is of second order because

$$\lim_{N \rightarrow \infty} \frac{1}{N} [F(w - w_{cr}|N) - F_0(N)] \sim \ln(s_0) \sim (w - w_{cr})^2. \tag{A.6}$$

When  $w \leq w_{cr}$  we have

$$\lim_{N \rightarrow \infty} \frac{1}{N} [F(w|N) - F_0(N)] = 0.$$

Then the spectrum of equation (2.3) is continuous and the chain is delocalized.

### Appendix B

Let us estimate the value of the integral  $I_n = (\beta^{(n)})^{-1}$  (see equation (3.7)) for  $n \gg 1$

$$I_n = \frac{1}{\pi^n} \int_0^\pi \dots \int_0^\pi dk_1 \dots dk_n \frac{\sin^2 k_1 \dots \sin^2 k_n}{1 - \cos k_1 \dots \cos k_n}. \tag{B.1}$$

Changing the variables  $k_i = q\pi$  and expanding the nominator and denominator of the fraction in (B.1) up to the first nonvanishing term, we obtain

$$I_n \approx \frac{1}{2^{n-1}} \int_{-1}^1 \dots \int_{-1}^1 dk_1 \dots dk_n \frac{k_1^2 \dots k_n^2}{k_1^2 + \dots + k_n^2}. \tag{B.2}$$

Passing to the  $n$ -dimensional spherical coordinate system we arrive, after simple algebra, at the following expression:

$$I_n = \frac{(\sqrt{\pi})^{n-1}}{3n-2} \prod_{l=1}^{n-1} \left\{ \frac{1}{9l^2-1} \frac{\Gamma(\frac{3l}{2})}{\Gamma(\frac{3l-1}{2})} \right\}. \tag{B.3}$$

In the limit  $n \gg 1$  we find the asymptotic expression of the function  $I_n$  with the exponential accuracy,

$$I_n = \exp \left( -\frac{3}{2}n \ln n + \frac{1}{2}n \ln \frac{\pi e^3}{54} + O(\ln n) \right). \tag{B.4}$$

This asymptotic expression has been used in the derivation of equation (3.18).

### References

- [1] Katz O, Avnir D and Ottolenghi M 1995 *J. Phys. Chem.* **99** 14 893
- Blum J, Rosenfeld A and Avnir D 1996 *J. Mol. Catal. A: Chemical* **107** 217
- [2] Khokhlov A R and Dormidontova E E 1997 *Sov. Phys.-Usp.* **40** 109
- [3] Binder K 1983 *Phase Transitions and Critical Phenomena* vol 10, ed C Domb and J Lebowitz (New York: Academic)
- [4] Grosberg A Yu and Shakhnovich E I 1986 *Sov. Phys.-JETP* **64** 493
- [5] Zhulina E B, Skvortsov A M and Birshtein T M 1981 *Vysokomolec. Soedin. A (USSR)* **23** 304
- [6] Birshtein T M 1982 *Vysokomol. Soedin. A (USSR)* **24** 1828
- [7] Birshtein T M and Borisov O V 1991 *Polymer* **32** 916



- [8] Grosberg A Yu and Shakhnovich E I 1986 *Sov. Phys.-JETP* **64** 1284
- [9] Grosberg A Yu and Shakhnovich E I 1986 *Biophys. (USSR)* **31** 1139
- [10] Obukhov S P 1987 *Sov. Phys.-JETP* **66** 1125
- [11] Shakhnovich E I and Gutin A M 1989 *Europhys. Lett.* **8** 327  
Shakhnovich E I and Gutin A M 1989 *J. Phys. A: Math. Gen.* **22** 1647
- [12] Shakhnovich E I and Gutin A M 1989 *J. Physique* **50** 1843
- [13] Frederickson G H and Milner S T 1991 *Phys. Rev. Lett.* **67** 835
- [14] Garel T and Orland H 1988 *Europhys. Lett.* **6** 307
- [15] Grosberg A Yu, Izrailev S F and Nechaev S K 1994 *Phys. Rev. E* **50** 1912
- [16] de Gennes P G 1975 *J. Physique* **37** 1445
- [17] Forgas G *et al* 1991 *Phase Transitions and Critical Phenomena* vol 14, ed C Domb and J Lebowitz (New York: Academic)
- [18] Nechaev S K and Zhang Y C 1995 *Phys. Rev. Lett.* **74** 1815
- [19] Krug J and Ferrari P A 1996 *J. Phys. A: Math. Gen.* **29** L465
- [20] Evans M R 1997 *Preprint* cond-mat/9705006
- [21] Lifschitz I M and Gredeskul S A 1970 *Sov. Phys.-JETP* **30** 1197
- [22] Oshanin G S and Blumen A 1998 *J. Chem. Phys.* **108** 1140
- [23] Cardy J 1996 *J. Phys. A: Math. Gen.* **29** 1897
- [24] Feller W 1966 *An Introduction to Probability Theory and its Applications* vol 1 (London: Wiley)
- [25] Ternovsky F F, Nyrkova I A and Khokhlov A R 1992 *Physica* **184A** 342