Localization in Simple Multiparticle Catalystic Absorption Model

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Abstract

We consider the phase transition in the system of \( n \) simultaneously developing random walks on the halfline \( x \geq 0 \). All walks are independent on each others in all points except the origin \( x = 0 \), where the point well is located. The well depth depends on the number of particles (i.e. steps of different random walks) simultaneously staying at the point \( x = 0 \). We consider the limit \( n \gg 1 \) and show that if the well depth grows faster than \( \frac{3}{2}n \ln n \) with \( n \), then all random walks become localized simultaneously at the origin. In the conclusion we discuss the connection of the above defined problem with the phase transition in the copolymer chain with quenched random sequence of monomers considered in the frameworks of replica approach.

Key words: random walk, phase transition, localization, polymer and random copolymer absorption, replica method

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Introduction

Problems dealing with the localization of random walks in potentials of various geometries compel much attention of different groups of scientists: both chemists and physicists. For the first group these problems are naturally connected with creating a new materials possessing specific technological properties (for instance, catalysts [1] or ion containing and surface active substances [2]). Meanwhile, for physicists the consideration of random walks localization remains since 70’s the firing ground for elaborating the new methods of the investigation of a polymer absorption in different geometries, wetting phenomena and kinetics of chemical reactions.

The phenomenon of polymer chain absorption is rather well understood at present both for homo–[3]–[7], [15] and heteropolymer [8]–[14] cases. The simple diffusive approach [6, 7, 15] provides complete understanding of an absorption of homopolymer chains as well as of block–copolymers in complicated geometries. These results can be beautifully explained also 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 an exhaustive information about the thermodynamic properties of ideal polymers near the point of phase transition from the delocalized (Gaussian) to the localized (absorbed) fluctuation regimes. The similar mathematical formalism has been applied to a description of a phase transition in solid–on–solid (SOS) models with quenched impurities [17]. Many conclusions obtained by RG analysis in [8] correlate with the results in [17].

Problems dealing with 2D wetting subject to a layer of periodic potential could be attributed 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.
Finally, it is worthwhile to mention that the model considered below has some features of so-called "zero’s range process" [14, 21] emerged in connection with traffic models. Also, similar set of problems appeared in course of investigation of the "autolocalization" phenomena [21] and in the theory of multicomponent chemical reactions on traps immersed in an immovable "matrix" [22, 23].

The present paper is organised 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–particle problems; the consideration of the phase transition in the n–particle model for $n > 2$ is given 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 Multiparticle 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 $x \geq 0$, $\{x\} = \{0, 1, 2, 3, \ldots \}$. Take $n$ independent $N$–step simplest random walks on $\mathbb{Z}^+$, simultaneously starting at the point $x = 0$. All these walks are free, i.e. they do not interact neither with any external potential, nor with each others in all points except the point $x = 0$. At the point $x = 0$ the interaction of a given random walk with the well is described by the potential $U(x_1, x_2, \ldots, x_n)$ (the index $i \in [1, n]$ lables the different random walks):

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

(1.1)

where

$$0 \leq U^{(1)} \leq U^{(2)} \leq \cdots \leq U^{(n)}$$

(1.2)

and

$$U^{(i)} \equiv f(i); \quad i \in [1, n]$$

(1.3)

The equations (1.1)–(1.3) reflect the fact that the depth of the potential well depends on the number of particles (i.e. steps of different random walks) simultaneously located at the point $x = 0$—see Fig.1. Let us stress that $U^{(i)}$ is the "individual" potential, i.e. the potential per one particle in a cluster of $i$ particles simultaneously located at the point $x = 0$. The "integral" well depth for the cluster of $i$ particles we denote as $U(i) = i U^{(i)} = i f(i)$.

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 random walk on the halfline $x_i \in [0, \infty)$ 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:

$$\begin{cases} Z_{N+1}(x_i) = Z_N(x_i + 1) + Z_N(x_i - 1) & (x_i \geq 1) \\ Z_{N+1}(x_1) = e^{U(x_1, \ldots, x_1, \ldots, x_n)} Z_N(x_i + 1) & (x_i = 0) \\ Z_{N=0}(x_i) = \delta_{x_i, 0} \end{cases}$$

(1.4)
The same "equations of motion" (as Eq.(1.4)) should be written for all functions $Z_N(x_i)$ where $i \in [1,n]$ and the potential $U(x_1, \ldots, x_i, \ldots, x_n)$ is defined in Eq.(1.1).

We are interested in the situation when the number of particles jumping on $\mathbb{Z}^+$ (i.e. the number of different random walks) is very large ($n \gg 1$) and the number of steps of each random walk tends to infinity ($N \to \infty$).

We expect that in the thermodynamic limit $N \to \infty$ and for $n \gg 1$ the absorption transition into localized state at the point $x = 0$ is sensitive to the shape of the function $f(n)$. Namely, if $f(n)$ grows rather slowly with $n$ (for the precise criteria of the growth see the Section 3) we could expect that the phase transitions occur in each individual random walk independently; while if $f(n)$ is rather sharp function of $n$, various types of collective localization are expected. The interplay between the entropy loss and the energy gain in the localized states makes the phase behavior of the system under consideration extremely rich.

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

To avoid further misunderstandings let us define precisely what we mean under the "localization" of the random walk. Let $F(N)$ be the free energy of the $N$–step random walk on the halfline $\mathbb{Z}^+$ with the point well of depth $U$ at the origin $x = 0$. This model can be described via the diffusion–type equation with specific boundary conditions (compare to Eq.(1.4)) and there exists some critical value $U = U_{cr} > 0$ which separates two different behaviors of the free energy:

$$
\lim_{N \to \infty} \frac{1}{N} F(N) = \begin{cases} 0 & \text{for } U < U_{cr} \\ \Lambda > 0 & \text{for } U > U_{cr} \end{cases}
$$

The value $U_{cr}$ we call the "localization transition point". It signals the separation of the highest eigenvalue $\Lambda$ from the continuous spectrum of the diffusion–type equation.

## 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 simplest random walk on $\mathbb{Z}^+$ interacting with the potential well at the origin.

In this case Eqs.(1.1)–(1.4) degenerate to the following ones:

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

and

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

Thus, for $n = 1$ we have only one particle jumping on the halfline and the problem is nothing else as a simple absorption at the "point well" located at the origin $x = 0$. 

3
The solution of the one–particle problem is very straightforward. Let us make the shift \( x \rightarrow x + 1 \).

Now the equations (2.3) can be rewritten as:

\[
Z_{N+1}(x) = Z_N(x - 1) + Z_N(x + 1) + \delta_{x,1} \left(e^{U(1)} - 1\right) Z_N(x + 1) \quad (x \geq 1)
\]

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

Perform the substitution

\[
Z_N(x) = 2^N Z_N(x)
\]

and use the Fourier–Laplace transform

\[
\tilde{Z}(q, s) = \sum_{N=0}^{\infty} s^N \sum_{x=0}^{\infty} \sin \frac{\pi x q}{l} Z_N(x)
\]

Introducing the new variable \( k = \frac{\pi q}{l} \), we arrive at the following integral equation for the function \( \tilde{Z}_N(k, s) \):

\[
\frac{1}{s} \tilde{Z}(k, s) - \frac{1}{s} \sin k = \cos k \tilde{Z}(k, s) + \sin k \left(e^{U(1)} - 1\right) \frac{1}{\pi} \int_0^\pi dk \sin 2k \tilde{Z}(k, s)
\]

After simple algebra we get

\[
Z(x = 2, s) \equiv \frac{1}{\pi} \int_0^\pi dk \sin 2k \tilde{Z}(k, s) = \frac{1}{\pi} \int_0^\pi dk \frac{\sin k \sin 2k}{1 - s \cos k} \frac{1}{\pi} \int_0^\pi dk \frac{\sin k \sin 2k}{1 - s \cos k}
\]

The divergence of the function \( \frac{1}{\pi} \int_0^\pi dk \sin 2k \tilde{Z}(k, s) \) occurs at the critical value \( U(1) = U_{cr}^{(1)} \) (corresponding to the localization transition point) when the denominator in Eq.(2.6) is set to zero:

\[
e^{U_{cr}^{(1)}} - 1 = \left. \frac{1}{s} \frac{1}{\pi} \int_0^\pi dk \frac{\sin k \sin 2k}{1 - s \cos k} \right|_{s \to 1} \to 1
\]

Thus, in the thermodynamic limit \( N \to \infty \) (i.e. when \( s \to 1 \)) we have \( U_{cr}^{(1)} = \ln 2 \).

2.2 Solution for \( n = 2 \)

2.2.1 General ansatz

Consider now two particles jumping on the halfline, i.e. two trajectories of random walks simultaneously developing in "time" \( t \) \( (0 \leq t \leq N) \). These trajectories are independent on each others in all points \( x = \{1, 2, \ldots\} \) except the point \( x = 0 \). Let us call the current coordinates of 1st and 2nd random walks \( x_1(t) \) and \( x_2(t) \) correspondingly. The potential (Eq.(1.1)) reads now:

\[
U(x_1, x_2) = \begin{cases} 
0 & \text{if } x_1 \neq 0 \text{ and } x_2 \neq 0 \\
U(1) & \text{if } \{x_1 = 0 \text{ and } x_2 \neq 0\} \text{ or } \{x_1 \neq 0 \text{ and } x_2 = 0\} \\
U(2) & \text{if } x_1 = 0 \text{ and } x_2 = 0
\end{cases}
\]
Thus we have the 2D random walk 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 it is shown in Fig.3. The equations for the joint partition function, \(Z_N(x_1, x_2)\), in 2D–case (for \(n = 2\)) become more tricky than in 1D–case (for \(n = 1\)).

Performing the shift \(x_1 \to x_1 + 1\) and \(x_2 \to x_2 + 1\) (see Fig.3), we can derive the recursion relation for the partition function \(Z_N(x_1, x_2)\) which is the two–dimensional extension of Eq.(2.3):

\[
Z_{N+1}(x_1, x_2) = \Delta_{x_1, x_2} Z_N(x_1, x_2) + \delta_{x_1, 1} \left( e^{U(1)} - 1 \right) \Delta_{x_2} Z_N(x_1 + 1, x_2) + \delta_{x_2, 1} \left( e^{U(1)} - 1 \right) \Delta_{x_1} Z_N(x_1, x_2 + 1) + \delta_{x_1, 1} \delta_{x_2, 1} \left( e^{2U(2)} - 2e^{U(1)} + 1 \right) Z_N(x_1 + 1, x_2 + 1)
\]

(2.9)

where

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

(2.10)

and

\[
\Delta_{x_1, x_2} \Psi(x_1, x_2) \equiv \Psi(x_1 - 1, x_2 - 1) + \Psi(x_1 - 1, x_2 + 1) + \Psi(x_1 + 1, x_2 - 1) + \Psi(x_1 + 1, x_2 + 1)
\]

(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:

\[
\left\{
\begin{array}{l}
Z_N(x_1 = 0, x_2 \geq 0) = Z_N(x_1 \geq 0, x_2 = 0) = Z_N(x_1 = 0, x_2 = 0) = 0 \\
Z_{N=0}(x_1, x_2) = \delta_{x_1, 1} \delta_{x_2, 1}
\end{array}
\right.
\]

(2.12)

It is easy to check that Eqs.(2.9)–(2.12) describe properly our model (taking into account the shift \(x_{1,2} \to x_{1,2} + 1\)):

(i) For \(x_1 \geq 2\) and \(x_2 \geq 2\) we have a simple diffusion without any interactions;

(ii) For \(x_1 = 1\) and \(x_2 \geq 2\) (or for \(x_1 \geq 2\) and \(x_2 = 1\)) the Boltzmann weight \(\beta^{(1)}\) of the random walk steps located at the point \(x_1 = 1\) (or \(x_2 = 1\)) reads

\[
\beta^{(1)} = \left( e^{U(1)} - 1 \right) + 1 = e^{U(1)}
\]

(2.13)

(iii) For \(x_1 = 1\) and \(x_2 = 1\) the Boltzmann weight \(\beta^{(2)}\) of the steps of two different random walk simultaneously located at the point \(x_1 = 1, x_2 = 1\) reads

\[
\beta^{(2)} = \left( e^{2U(2)} - 2e^{U(1)} + 1 \right) + 2 \left( e^{U(1)} - 1 \right) + 1 = \left( e^{U(2)} \right)^2.
\]

(2.14)

Let us search the solution of Eqs.(2.9)–(2.12) using the following ansatz

\[
Z_N(x_1, x_2) = Z_N(x_1) Z_N^{\text{free}}(x_2) + Z_N(x_2) Z_N^{\text{free}}(x_1) + W_N(x_1, x_2)
\]

(2.15)

where:

a) The "one–particle" partition function \(Z_N(x_i) (i = \{1, 2\})\) is the same as in Eq.(2.3);
b) The term $Z_N^{\text{free}}(x)$ is defined as follows

$$
\begin{align*}
Z_N^{\text{free}}(x) &= \Delta x Z_N^{\text{free}}(x) \quad (x \geq 1) \\
Z_N^{\text{free}}(x) &= 0 \quad (x = 0) \\
Z_N^{\text{free}}(x=0) &= \delta_{x,1}
\end{align*}
$$

(2.16)

and has the sense of “free” partition function without any potential on the halfline $x > 0$;

c) The last term $W_N(x_1, x_2)$ describes the “absorption at the main corner” and has the ”nonmultiplicative nature” being determined by the recursion relations:

$$
W_{N+1}(x_1, x_2) = \Delta x_{1,2} W_N(x_1, x_2) + \delta_{x_1,1} \delta_{x_2,1} \gamma_2 W_N(x_1 + 1, x_2 + 1)
$$

(2.17)

where

$$
\begin{align*}
W_N(x_1 = 1, x_2 \geq 2) &= W_N(x_1 \geq 2, x_2 = 1) = W_N(x_1 \leq 0, x_2 \leq 0) = 0 \\
W_{N=0}(x_1, x_2) &= \delta_{x_1,1} \delta_{x_2,1}
\end{align*}
$$

(2.18)

and the ”main corner” Boltzmann weight

$$
\gamma_2 = e^{2U^{(2)}} - 2e^{U^{(1)}} + 1
$$

(2.19)

is chosen such that Eq.(2.15) reproduces the right weight $\beta^{(2)}$ at the point $(x_1 = 0, x_2 = 0)$ (see Eqs.(2,3) and (2,14)).

The equations (2.17)–(2.18) correspond to the situation shown in Fig.4a, where we marked the point at which the Boltzmann weight $\gamma_2$ is located by the sign $\Box$.

As it has been 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 $\tilde{N} \gg 1$. Generalising 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 Eq.(2.16)):

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

(2.20)

where

$$
Z_N(x_1, x_2) = 4^N Z_N(x_1, x_2); \quad W_N(x_1, x_2) = 4^N W_N(x_1, x_2)
$$

(2.21)

and

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

(compare to Eq.(2.4)).

Substituting the ansatz (2.15) into (2.20) we see that the divergence of the function $Z_{\rightarrow \infty}(x_1 = 2, x_2 = 2)$ is determined:

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

and everything depends on the fact which of these two functions diverges first (i.e. for smaller values of $\{U^{(1)}, U^{(2)}\}$) in the phase space of parameters $\{U^{(1)}, U^{(2)}\}$ (recall that according to Eq.(1.2) we have a restriction $0 \leq U^{(1)} \leq U^{(2)}$).

The behavior of the function $Z_N(x_i)$ for $i = \{1, 2\}$ has been well studied in Section 2.1, so, let us concentrate the efforts on the solution of Eqs.(2.17)–(2.18).
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, it is possible to represent 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 the Fig.4a;

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 the Fig.4b;

The following identity can be derived immediately:

$\Omega(N + 2) = V(N) \equiv 4^N V(N)$ (2.22)

The function $W(N)$ admits the representation

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

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

Introducing 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 $x = N - N_1 - \ldots - N_k$, we may rewrite Eq.(2.23) as follows:

$$W(N) = \sum_{k=0}^{\infty} (\beta^{(2)})^k \frac{1}{2\pi i} \oint \frac{dz}{z^{-N-1}} \sum_{N_1=2}^{\infty} \ldots \sum_{N_k=2}^{\infty} z^{N_1 + \ldots + N_k} \prod_{i=1}^{k} \Omega(N_i)$$

$$= \frac{1}{2\pi i} \oint dz z^{-N-1} \frac{1}{1 - \beta^{(2)}} \sum_{N=2}^{\infty} z^N \Omega(N)$$

(2.24)

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 $W(N)$. Using the identity (2.22) we get the equation on the transition point (for $N \to \infty$):

$$\beta^{(2)}_{cr} = \lim_{z \to 4} \frac{1}{\sum_{N=0}^{\infty} \left(\frac{z}{4}\right)^N V(N)} \equiv \lim_{s \to 1} \frac{1}{\sum_{N=0}^{\infty} s^N V(N)}$$

(2.25)

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

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

$$V_{N+1}(x_1, x_2) = \Delta_{x_1, x_2} V_N(x_1, x_2)$$  \hfill (2.26)

with the boundary conditions shown in Fig.4b:

$$
\begin{align*}
V_N(x_1 = 1, x_2 \geq 2) &= V_N(x_1 \geq 2, x_2 = 1) = V_N(x_1 = 1, x_2 = 1) = 0 \\
V_N=0(x_1, x_2) &= \delta_{x_1,2} \delta_{x_2,2}
\end{align*}
$$  \hfill (2.27)

Using the 2D–Fourier and Laplace transforms and performing the back shift in Eq.(2.26) \{x_1 \to x_1 - 1, \ x_2 \to x_2 - 1\} we arrive at the standard equation for the function $V_N(k_1, k_2, s)$:

$$V_N(k_1, k_2, s) = \sin k_1 \sin k_2$$  \hfill (2.28)

Thus, we get the final expression:

$$\sum_{N=0}^{\infty} s^N V(N) = \frac{1}{\pi^2} \int_0^\pi \int_0^\pi dk_1 dk_2 \frac{\sin^2 k_1 \sin^2 k_2}{1 - s \cos k_1 \cos k_2}$$  \hfill (2.29)

Evaluating the last integral at the point $s = 1$ we obtain the following numerical value for the "main corner" transition point:

$$\beta^{(2)}_{cr} = \beta_2 + 1 = \frac{\pi}{4 - \pi} \approx 3.65979$$  \hfill (2.30)

### 2.2.3 Phase diagram for 2–particle system

Collecting the results of the Sections 2.2.1 and 2.2.2 we conclude that the localization transition from the delocalized to the absorbed state is determined:

- either by the equation $\beta^{(1)}_{cr} = e^{U^{(1)}_{cr}} = 2$ (the "one–particle" part);
- or by the equation $\beta^{(2)}_{cr} = \gamma_2 + 1$, i.e. $e^{2U^{(2)}_{cr}} - 2e^{U^{(1)}_{cr}} + 2 = \frac{\pi}{4 - \pi}$ (the two–particle "main corner" part).

The complete phase diagram is drawn in Fig.5. For $U^{(1)} > \ln 2$ the influence of the potential $U^{(2)}$ disappears, while for $0 < U^{(1)} < \ln 2 \approx 0.693$ the "induced" localization can occur for

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

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 $U^{(1)} < 0$. Suppose, for example, such situation:

$$U^{(1)} = -\infty; \quad U^{(2)} > 0$$

i.e. each particular random walk cannot visit the origin, but there is an energy gain for two random walks to stay at the origin simultaneously. In this case for

$$U^{(2)} > U^{(2)}_{cr} = \frac{1}{2} \ln \left(\frac{\pi}{4 - \pi} - 2\right) \approx 0.253$$

the trajectories become localized.
3 Phase transitions in catalytic absorption model for \( n > 2 \)

3.1 Solution for \( n = 3 \)

The equation for the 3–particle partition function \( Z_N(x_1, x_2, x_3) \) reads:

\[
Z_N(x_1, x_2, x_3) = \Delta_{x_1,x_2,x_3} Z_N(x_1, x_2, x_3) + \\
\delta_{x_1,1} \left( e^{U(1)} - 1 \right) \Delta_{x_2,x_3} Z_N(x_1 + 1, x_2, x_3) + \\
\delta_{x_2,1} \left( e^{U(1)} - 1 \right) \Delta_{x_1,x_3} Z_N(x_1, x_2 + 1, x_3) + \\
\delta_{x_3,1} \left( e^{U(1)} - 1 \right) \Delta_{x_1,x_2} Z_N(x_1, x_2, x_3 + 1) + \\
\delta_{x_1,1} \delta_{x_2,1} \left( e^{2U(2)} - 2 e^{U(1)} + 1 \right) \Delta_{x_3} Z_N(x_1 + 1, x_2 + 1, x_3) + \\
\delta_{x_1,1} \delta_{x_3,1} \left( e^{2U(2)} - 2 e^{U(1)} + 1 \right) \Delta_{x_2} Z_N(x_1 + 1, x_2, x_3 + 1) + \\
\delta_{x_2,1} \delta_{x_3,1} \left( e^{2U(2)} - 2 e^{U(1)} + 1 \right) \Delta_{x_1} Z_N(x_1, x_2 + 1, x_3 + 1) + \\
\delta_{x_1,1} \delta_{x_2,1} \delta_{x_3,1} \left( e^{3U(3)} - 3 e^{2U(2)} + 3 e^{U(1)} - 1 \right) Z_N(x_1 + 1, x_2 + 1, x_3 + 1)
\]

(3.1)

Generalising the ansatz (2.15) to the 3D–case we may search the solution of Eq.(3.1) in the form:

\[
Z_N(x_1, x_2, x_3) = Z_N(x_1) Z_N^{\text{free}}(x_2, x_3) + Z_N(x_2) Z_N^{\text{free}}(x_1, x_3) + Z_N(x_3) Z_N^{\text{free}}(x_1, x_2) + W_N(x_1, x_2) Z_N^{\text{free}}(x_3) + W_N(x_1, x_3) Z_N^{\text{free}}(x_2) + W_N(x_2, x_3) Z_N^{\text{free}}(x_1) +
\]

(3.2)

\[
W_N(x_1, x_2, x_3)
\]

where:

a) The partition function \( W_N(x_i, x_j) \) \((i \neq j; \{i,j\} \in [1,3])\) is the same as in Eq.(2.17);

b) The functions \( Z_N^{\text{free}}(x_i) \) and \( Z_N^{\text{free}}(x_i, x_j) \) \((i \neq j; \{i,j\} \in [1,3])\) describe the contributions of one–

and two–dimensional free random walks with zero’s boundary conditions (compare to Eq.(2.15));

c) The function \( W_N(x_1, x_2, x_3) \) is determined as follows:

\[
\begin{cases}
W_{N+1}(x_1, x_2, x_3) = \Delta_{x_1,x_2,x_3} W_N(x_1, x_2, x_3) + \delta_{x_1,1} \delta_{x_2,1} \delta_{x_3,1} \gamma_3 W_N(x_1 + 1, x_2 + 1, x_3 + 1) \\
W_N(x_1 = 1, x_2 \geq 2, x_3 \geq 2) = W_N(x_1 \geq 2, x_2 = 1, x_3 \geq 2) = W_N(x_1 \geq 2, x_2 \geq 2, x_3 = 1) = 0 \\
W_N(x_1 = 1, x_2 = 1, x_3 \geq 2) = W_N(x_1 = 1, x_2 \geq 2, x_3 = 1) = W_N(x_1 \geq 2, x_2 = 1, x_3 = 1) = 0 \\
W_{N=0}(x_1, x_2) = \delta_{x_1,1} \delta_{x_2,1} \\
\end{cases}
\]

with \( \gamma_3 = e^{3U(3)} - 3 e^{2U(2)} + 3 e^{U(1)} - 1 \).

In order to check the validity of ansatz (3.2) let us compute the values of the Boltzmann weights at the boundaries:

1. \textit{At the planes:}

\[
\begin{align*}
x_1 &= 0 \quad (x_2 > 0, x_3 > 0) \\
x_2 &= 0 \quad (x_1 > 0, x_3 > 0) \\
x_3 &= 0 \quad (x_1 > 0, x_2 > 0) \\
\end{align*}
\]

\[
\beta^{(1)} = \left( e^{U(1)} - 1 \right) + 1 = e^{U(2)}
\]

(3.4)
2. At the lines:

\[
\begin{align*}
(x_1 = 0, x_2 = 0) & \quad x_3 > 0 \\
(x_1 = 0, x_3 = 0) & \quad x_2 > 0 \\
(x_2 = 0, x_3 = 0) & \quad x_1 > 0
\end{align*}
\]

\[
\beta^{(2)} = e^{2U^{(2)}} - 2e^{U^{(1)}} + 1 + 2(e^{U^{(1)}} - 1) + 1 = e^{2U^{(2)}}
\]

(3.5)

3. At the ”main corner” point:

\[
(x_1 = 0, x_2 = 0, x_3 = 0) : \quad \beta^{(3)} = e^{3U^{(3)}} - 3e^{2U^{(2)}} + 3e^{U^{(1)}} - 1 - 3(e^{U^{(1)}} - 1) - 3(e^{2U^{(2)}} - 2e^{U^{(1)}} + 1) + 1 = e^{3U^{(3)}}
\]

(3.6)

The arguments of the Section 2.2.2 can be easily extended to the 3D–case. Skipping the intermediate computations we bring the final result for the value of the Boltzmann weight at the ”main corner” transition point:

\[
\beta^{(3)}_{cr} = \left(\frac{1}{\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi dk_1 dk_2 dk_3 \frac{\sin^2 k_1 \sin^2 k_2 \sin^2 k_3}{1 - \cos k_1 \cos k_2 \cos k_3}\right)^{-1} \approx 7.856
\]

(3.7)

The localization phase transition is now determined:

- either by the equation \( \beta^{(1)}_{cr} = 2 \), i.e.
  \[ U^{(1)}_{cr} = \ln 2 \]  
  (the one–particle part);

- or by the equation \( \beta^{(2)}_{cr} = \gamma_2 + 1 = \frac{\pi}{4 - \pi} \), i.e.
  \[ U^{(2)}_{cr} = \frac{1}{2} \ln \left(2e^{U^{(1)}} + \frac{\pi}{4 - \pi} - 2\right) \]  
  (the two–particle ”main corner” part);

- or by the equation \( \beta^{(3)}_{cr} = \gamma_3 + 1 = 7.856 \), i.e.
  \[ U^{(3)}_{cr} = \frac{1}{3} \ln \left(7.856 + 3e^{2U^{(2)}} - 3e^{U^{(1)}}\right) \]  
  (the three–particle ”main corner” part).

3.2 Solution for arbitrary \( n \)

The general ansatz for arbitrary values of \( n \) reads

\[
Z_N(x_1, x_2, \ldots, x_n) = Z_N(x_1)Z_N^{\text{free}}(x_2, \ldots, x_n) + \text{all permutations} + \right.
\]

\[
W_N(x_1, x_2)Z_N^{\text{free}}(x_3, \ldots, x_n) + \text{all permutations} + \\
W_N(x_1, x_2, x_3)Z_N^{\text{free}}(x_4, \ldots, x_n) + \text{all permutations} +
\]

\[
\ldots + \\
W_N(x_1, \ldots, x_{n-1})Z_N^{\text{free}}(x_n) + \text{all permutations} + \right.
\]

\[
W_N(x_1, \ldots, x_n)
\]

(3.11)
Eq.(3.11) produces the following recursive relation for the value \( \gamma_n \):

\[
\gamma_n = e^{nU(n)} - C_n^1 \gamma_{n-1} - C_n^2 \gamma_{n-2} - C_n^3 \gamma_{n-3} - \ldots
\]  

(3.12)

completed by the initial condition \( \gamma_0 = 1 \).

The localization transition in the \( n \)-particles model occurs at the values \( \beta_{ct}^{(j)} \) \( (j = 2, 3, 4, \ldots, n) \) defined by the equation

\[
\beta_{ct}^{(j)} = \gamma_j + 1 = \left( \frac{1}{\pi^j} \int_0^\pi \cdots \int_0^\pi dk_1 \cdots dk_j \frac{\sin^2 k_1 \cdots \sin^2 k_j}{1 - \cos k_1 \cdots \cos k_j} \right)^{-1}
\]  

(3.13)

where \( \gamma_j \) are the recursive solutions of Eq.(3.12).

### 3.3 Phase transition in the \( n \)-particle system for \( n \gg 1 \)

Now we are in position to give the answer to the question raised in Section 1: “What should be the critical shape of the function \( f(n) \) (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 \( f_{ct}(n) \) providing the joint \( n \)-particle localization is defined by setting \( U_{ct}^{(n)} \equiv f_{ct}(n) \) in the equation (3.12) with \( \gamma_j \) extracted from (3.13).

The approximate evaluation of the integral (3.13) for \( n \gg 1 \) gives us (with the exponential accuracy—see Appendix for details):

\[
\gamma_n = \exp \left( \frac{3}{2} n \ln n - \frac{1}{2} n \frac{\pi e^3}{54} + O(\ln n) \right)
\]  

(3.14)

We drop in Eq.(3.13) all terms growing with \( n \to \infty \) slower than \( \exp(\text{const} n) \).

Substituting (3.13) into (3.11) it is easy to conclude that for \( n \gg 1 \) the term \( \gamma_n \) has the maximal value in the sum (3.11):

\[
\gamma_n = e^{\frac{3}{2} n \ln n}
\]  

(3.15)

where we kept the leading asymptotics (for \( n \to \infty \)) only.

Estimating the sum (3.11) with the same accuracy, we arrive at the following final conclusion:

- If the function \( f(n) \) grows faster than \( f_{ct}(n) = \frac{3}{2} \ln n \) then all \( n \gg 1 \) particles are localized simultaneously in the point well located at the origin \( x = 0 \) of the halfline \( \mathbb{Z}^+ \).

Recall that \( U^{(n)} \) is the depth of just the \( n \)-particle well. Thus the ”integral” critical depth, \( U_{ct}(n) = n U_{ct}^{(n)} \) per the cluster of \( n \) particles (i.e. steps of different random walks at the point \( x = 0 \)) has the following asymptotic behavior

\[
U_{ct}(n) = \frac{3}{2} n \ln n
\]
4 Instead of discussion: Connection with random heteropolymer absorption problem

The above mentioned problem has a direct application to the old problem of the random copolymer absorption at the point well. Namely consider the random walk on \( \mathbb{Z}^+ \) with the point well located at the origin and suppose that the well depth depends on the current "time" (i.e. the number of the random walk step) at the point \( x = 0 \). The partition function \( \Theta_N \) of such process one can write as a sum over all random walk paths

\[
\Theta_N(x_N) = \mathcal{N} \sum_{\{x_1, \ldots, x_{N-1}\}} \prod_{j=1}^{N} \left\{ g(|x_j - x_{j-1}|) e^{U_j(x_j)} \right\}
\]  

(4.1)

where \( \mathcal{N} \) is the normalization constant, \( g(|x_j - x_{j-1}|) \) is the local transition probability and the potential \( U_j(x_j) \) is the random variable of \( j \). Suppose that \( U_j(x_j) \) allows the following representation:

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

(4.2)

where \( \varepsilon_1, \varepsilon_2 \) 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 form of recursion relations:

\[
\begin{cases} 
\Theta_{N+1}(x) = \Theta_N(x+1) + \Theta_N(x-1) & (x \geq 1) \\
\Theta_N(x) = e^{U_N(x)} \Theta_N(x+1) & (x = 1) \\
\Theta_N(x) = 0 & (x < 0)
\end{cases}
\]  

(4.3)

Performing the shift \( x \to x + 1 \) rewrite (4.3) as follows

\[
\begin{cases} 
\Theta_{N+1}(x) = \Delta_x \Theta_N(x) + \left(e^{U_N} - 1\right) \delta_{x,1} \Theta_N(x+1) & (x \geq 1) \\
\Theta_N(x) = 0 & (x = 0)
\end{cases}
\]  

(4.4)

The partition function \( \Theta_N(x) \) is the random variable which depends on the quenched random pattern of realisations of the potential \( U_j \) \( (j \in [1, N]) \) at the origin. To find the reliable thermodynamic quantity we have to average the free energy \( \ln \Theta_N \) over the distribution of all random sequences \( \{\sigma_1, \sigma_2, \ldots, \sigma_N\} \). The corresponding computations we realise in the frameworks of the replica approach.
Averaging the $n$th power of the partition function $\langle \Theta_N^n(x) \rangle = \Phi_N(x_1, \ldots, x_n)$, we get:

$$
\Phi_N+1(x_1, \ldots, x_n) = \Delta_{x_1,\ldots,x_n} \Phi_N(x_1, \ldots, x_n) + 
\left\langle e^{U_N} - 1 \right\rangle \sum_{i=1}^{n} \delta_{x_i,1} \Delta_{x_1,\ldots,x_n} \Phi_N(x_1, \ldots, x_i - 1, x_i + 1, x_i + 1, \ldots, x_n) + 
$$

$$
\left\langle e^{U_N} - 1 \right\rangle^2 \sum_{i>j}^{n} \delta_{x_i,1} \delta_{x_j,1} \Delta_{x_1,\ldots,x_n} \Phi_N(x_1, \ldots, x_i - 1, x_i + 1, x_i + 1, \ldots, x_{j-1}, x_j + 1, x_j + 1, \ldots, x_n) + 
$$

$$
\left\langle e^{U_N} - 1 \right\rangle^n \delta_{x_1,1} \ldots \delta_{x_n,1} \Phi_N(x_1 + 1, \ldots, x_n + 1)
$$

(4.5)

The solution of Eq. (4.5) reads (compare to (3.11)):

$$
\Phi_N(x_1, x_2, \ldots, x_n) = \bar{\Phi}_N(x_1) Z_N^{\text{free}}(x_2, \ldots, x_n) + \text{all permutations} + \bar{\Phi}_N(x_1, x_2) Z_N^{\text{free}}(x_3, \ldots, x_n) + \text{all permutations} + \bar{\Phi}_N(x_1, x_2, x_3) Z_N^{\text{free}}(x_4, \ldots, x_n) + \text{all permutations} + \cdots + \bar{\Phi}_N(x_1, \ldots, x_{n-1}) Z_N^{\text{free}}(x_n) + \text{all permutations} + \bar{\Phi}_N(x_1, \ldots, x_n)
$$

(4.6)

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

$$
\begin{align*}
\bar{\Phi}_N(x_1, \ldots, x_j) &= \Delta_{x_1,\ldots,x_j} \bar{\Phi}_N(x_1, \ldots, x_j) + \delta_{x_1,1} \ldots \delta_{x_j,1} \bar{\Phi}_N(x_1 + 1, \ldots, x_j + 1) \quad \{x_1, \ldots x_j \} \geq 1 \\
\bar{\Phi}_N(\text{at least one } x_i \geq 2 \text{ and all others } x_j = 1) &= 0 \quad \{i \neq j \} \in [1, j] \\
\bar{\Phi}_N=0(x_1, \ldots, x_n) &= \delta_{x_1,1} \ldots \delta_{x_n,1}
\end{align*}
$$

(4.7)

and by $\bar{\tau}_j$ we denote the averaged values of the Boltzmann weights:

$$
\bar{\tau}_j = \left\langle \left( e^{U_N} - 1 \right)^j \right\rangle = p (e^{\varepsilon_1 - 1})^j + (1-p) (e^{\varepsilon_2 - 1})^j
$$

(4.8)

Using the results of the previous Sections one can conclude that the averaged moments of the quenched heteropolymer partition function, $\langle \Theta_N \rangle, \langle \Theta_N^2 \rangle, \ldots, \langle \Theta_N^n \rangle$ exhibit the singular behavior at the set of points being the solutions of following equations:

$$
\beta^{(j)}_{\varepsilon_1} = \bar{\tau}_j + 1 = p (e^{\varepsilon_1 - 1})^j + (1-p) (e^{\varepsilon_2 - 1})^j + 1
$$

(4.9)

where $\beta^{(2)}_{\varepsilon_1} = 2$ (see Eq. (2.7)) and $\beta^{(j)}_{\varepsilon_1}$ for $j \in [2, n]$ is given by Eq. (3.13). Recall that we restrict ourselves with 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 $N \to \infty$) can be obtained using the following simple procedure. We fix some arbitrary value $\varepsilon_2$ and find the minimal value $\varepsilon^{\text{cr}}_1(\varepsilon_2, j)$ among all solutions of Eq. (4.9) 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 $\varepsilon^{\text{cr}}_1$ corresponds just to $j = 1$. It means that all moments of the random copolymer partition function, $\Theta^j_N$,
averaged over the quenched disorder in monomer types diverge at the same point as the "one–particle" part (i.e. "annealed" copolymer partition function), ⟨ΘN⟩.

Of course, our consideration has an obvious crucial shortcoming connected with the fact that the replica approach presented above does not allow us to take properly the limit n → 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.

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A Appendix

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

$$I_n = \frac{1}{\pi^n} \int_0^\pi \cdots \int_0^\pi dk_1 \cdots dk_n \frac{\sin^2 k_1 \cdots \sin^2 k_n}{1 - \cos k_1 \cdots \cos k_n} \quad (A.1)$$

Changing the variables $k_i = q\pi$ and expanding the nominator and denominator of the fraction of (A.1) up to the first non vanishing term, we get:

$$I_n \approx \frac{1}{2^{n-1}} \int_{-1}^1 \cdots \int_{-1}^1 dk_1 \cdots dk_n \frac{k_1^2 \cdots k_n^2}{k_1^2 + \cdots + k_n^2} \quad (A.2)$$

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

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

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

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

This asymptotic expression has been used in the derivation of the equation (3.15).
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Figure Captions

Fig.1. The schematic representation of the multiparticle absorption model.

Fig.2. The choice of the lattice for the 2D–random walk in the first quarter \((x_1 > 0, x_2 > 0)\) and the possible local moves of the walker.

Fig.3. The lattice \((x_1 > 1, x_2 > 1)\) with zero’s boundary conditions obtained from the lattice shown in Fig.2 by the shift \(x_{1,2} \to x_{1,2} + 1\).

Fig.4. (a) The auxiliary 2D–lattice used in the computation of the nonmultiplicative contribution \(W_N(x_1, x_2)\)—see Eq.(2.17); (b) The same lattice as in (a) but with another boundary condition at the "main corner".

Fig.5. The phase diagram for the two–particle catalytic absorption model.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5

The diagram illustrates the transition between various states of localization and delocalization as a function of two parameters $U^{(1)}$ and $U^{(2)}$. The regions are labeled as follows:

- **Joint (two-particle) localization**
- **Independent (one-particle) localization**
- **Delocalization**

The curve delimiting these regions is marked by $\ln 2$. The x-axis represents $U^{(1)}$ and the y-axis represents $U^{(2)}$.