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# Application of the Cluster Size Distribution in Binary Randomly Disordered Finite Chains

## Exact Solution of the Random Walk Problem for a Finite Chain with an Arbitrary Concentration of Pure Absorbers

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A closed form is obtained of the length distribution of open and closed clusters in binary randomly disordered finite chains and its first three moments are calculated. It allows to express configurational averages of interest in chains with randomly distributed broken bonds, with randomly distributed infinite masses and related finite disordered systems and to calculate them exactly. A particular case of random walks on a chain with chaotically distributed pure absorbers is considered without any restrictions on the chain length and the number of absorbers. The exact expressions of the averaged survival probability and averaged lifetime of a particle in the chain are obtained and discussed.

Получены аналитические выражения распределений открытых и закрытых кластеров по длинам в ограниченной случайно разупорядоченной бинарной цепочке и вычислены три первых момента указанных распределений. Это позволяет определить конфигурационные средние в цепочке со случайно распределенными разорванными связями, в цепочке со случайно распределенными бесконечными массами и подобных неупорядоченных ограниченных системах в замкнутой, удобнои для точного расчета форме. Полученные результаты использованы для решения задачи случайных блужданий в цепочке с хаотически распределенными абсолютно поглощающими ловушками без каких-либо ограничений на длину цепочки и число ловушек. Найдены точные выражения конфигурационных средних вероятности выживания и времени жизни частицы в цепочке, которые могут быть использованы для описания донорной люминесценции в донор–акцепторных разупорядоченных одномерных системах.

### 1. Introduction

A theory of one-dimensional disordered systems has been elaborated in recent years (cf. [1, 2]). This was stimulated by the extensive experimental work on materials with quasi-one-dimensional properties. From the theoretical point of view these studies are extremely interesting providing a number of exact analytic results that are not available in more complicated cases of two- and three-dimensional disordered systems. Moreover there exist some exactly tractable models with specified kind of disorder, but still very useful for investigations in many aspects. First, they can be relevant to real experimental situations [3]. Second, they give reliable bases for testifying and for comparing approximate approaches to the description of disordered systems [4, 5]. Third, they supply the investigator with a unique opportunity to get an insight into the nature of effects caused by disorder [1 to 7]. In the papers cited the importance to study such models was convincingly demonstrated in the case of infinite systems. Little has been done so far as to finite disordered systems. In particular no attempts were made to consider models discussed in [3, 4, 6, 7] taking into account

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the size effects, though the importance of such considerations is self-evident. The present publication partly fills the gap.

To be more definite a finite chain constituted of two types of structural components distributed at random is in the focus of our discussion. The cluster size distribution and its three first moments are obtained (Section 2) and used (Section 3) in calculations of the exact averaged quantities characterizing random walks on a finite chain with an arbitrary number of pure absorbers regarded as one of the components of a disordered chain. These quantities, the survival probability and lifetime of a particle in a chain with absorbers, proved to be useful for the description of light emission of one-dimensional donor–acceptor disordered systems. We conclude the paper summarizing the main results and putting emphasis on their applications in Section 4.

## 2. Cluster Length Distribution and Its Moments

The observable properties of binary substitutionally disordered systems are tightly linked with the existence of clusters composed, say, of $n$ molecules of type A localized on adjacent sites of a periodical structure. The molecules of a cluster occupy the region with $m$ molecules of type B on its boundary. In an infinite disordered chain the cluster size (length) distribution was used in the exact calculations of some configurational averages [3, 4, 6, 7]. It is also useful for analogous calculations in the case of finite disordered one-dimensional systems, but little additional work should be done to obtain its closed form.

The only two types of clusters consisting of A molecules can exist in a finite chain with full number of sites $N$ on which $N_A$ molecules of the sort A and $N_B$ molecules of the sort B, $N_A + N_B = N$, are randomly distributed: the open ones — with one B molecule on the cluster borders (related to the chain ends) and the closed ones — with two B molecules on the cluster borders (inside the chain). The same can be said about clusters consisting of B molecules. To obtain the cluster length distribution it is necessary to find the full number of open and closed clusters of the length $n$ (correspondingly $p^o(n)$ and $p^c(n)$) in all possible nonequivalent linear configurations of the given number of A and B molecules. Let us get first an expression for $p^c(n)$ of A clusters.

The number of closed clusters of the length $n$ in an arbitrary configuration is equal to

$$\sum_{i=1}^{N_B-1} \delta_{q_i,n}\,, \tag{1}$$

where $q_i$ denotes the length (expressed as the number of sites occupied by A molecules of a cluster) of closed clusters in this configuration, $q_i \in [0, N_A]$, $N_B - 1$ is the limiting number of closed clusters in any configuration. We also introduce the notations $q_0$ and $q_{N_B}$ for the distances between the chain ends and B molecules nearest to them. To find $p^c(n)$ (1) should be summed over all possible configurations which is evidently equivalent to the summation over all values of $q_i$ including $q_0$ and $q_{N_B}$ that satisfy the condition $\sum_{i=0}^{N_B} q_i = N_A$. Thus we have

$$p^c(n) = \sum_{q_0, q_1, \ldots, q_{N_B}=0}^{\infty} \delta_{\sum_{i=0}^{N_B} q_i,\, N_A} \sum_{i=1}^{N_B-1} \delta_{q_i,n}\,. \tag{2}$$

The summation in (2) is easily performed with the help of the Kronecker $\delta$-function integral representation

$$\delta_{n,m} = (2\pi)^{-1} \int_0^{2\pi} \exp\left[i\varphi(n-m)\right] \mathrm{d}\varphi \tag{3}$$

and gives

$$p^{c}(n) = \frac{N_B - 1}{4\pi^2} \int_C dz \int_{C'} dz' \frac{z^{-(N_A+1)}}{(1-z)^{N_B}} \frac{z'^{-(n+1)}}{zz' - 1}, \tag{4}$$

where contours of integrations are unit circles $C$ and $C'$ on the complex plane. Making use of the Cauchy theorem in (4) we get

$$p^{c}(n) = \frac{(N - n - 1)!}{(N_B - 2)!\,(N_A - n)!}. \tag{5}$$

The function $p^{o}(n)$, the full number of open A clusters in all configurations, can be obtained similarly

$$p^{o}(n) = \frac{2(N - n - 1)!}{(N_B - 1)!\,(N_A - n)!}. \tag{6}$$

Note that for the given $N$ $p^{o}(n)$ forms the quadratic matrix $||p^{o}_{N_B,n}||$ with elements defined by the relations

$$\begin{aligned} &p^{o}_{N_B,n} = p^{o}_{N_B,n+1} + p^{o}_{N_B-1,n+1}\,, \\ &p^{o}_{N_B,n} = \begin{cases} 2, & N_B + n = N\,, \\ 0, & N_B + n > N\,, \end{cases} \quad p^{o}_{1,n} = 2\,, \quad n = 1, 2, \ldots, N-1\,. \end{aligned} \tag{7}$$

The matrix corresponding to $p^{c}(n)$ is simply connected with $||p^{o}_{N_B,n}||$ due to the fact that $p^{c}(n) = (N_B - 1)/2\; p^{o}(n)$.

From (5) and (6) one can obtain the cluster length distribution

$$P(n) = \frac{N_B (N_A - 1)!\,(N - n - 1)!}{(N-1)!\,(N_A - n)!} \tag{8}$$

normalized to unity

$$\sum_{n=1}^{N_A} P(n) = 1\,, \tag{9}$$

which defines the probability of existence of an A cluster of the length $n$ in a binary randomly disordered finite chain. The probabilities to find an open and a closed cluster of this length are as follows:

$$P^{o}(n) = \frac{2}{N_B + 1} P(n) \tag{10}$$

and

$$P^{c}(n) = \frac{N_B - 1}{N_B + 1} P(n)\,, \tag{11}$$

respectively.

It can be easily shown that for $N \gg N_B \gg 1$ (8) reduces to the asymptotic form of a distribution of Poisson type,

$$\underset{N \gg N_B \gg 1}{P(n)} \to P_{as}(n) = c_B \exp(-n c_B)\,, \tag{12}$$

where $c_B = N_B/N$.

The moments of the cluster length distribution read as

$$m^{(i)} = \sum_{n=1}^{N_A} n^i P(n)\,. \tag{13}$$

To obtain their explicit dependence on the component concentrations it is convenient to express them in terms of the generating function. Using the obvious relation

$$\frac{(N-n-1)!}{(N_A-n)!}=\frac{\partial^{N_B-1}}{\partial z^{N_B-1}}(1+z)^{N-n-1}\Big|_{z=0}, \tag{14}$$

one can write

$$m^{(i)}=\frac{N_B(N_A-1)!}{(N-1)!}\frac{\partial^{N_B-1}}{\partial z^{N_B-1}}F_i(z)\Big|_{z=0}, \tag{15}$$

where the generating function is

$$F_i(z)=(1+z)^{N-1}\frac{\partial^i}{\partial\alpha^i}\sum_{n=1}^{N_A}\frac{\exp(\alpha n)}{(1+z)^n}\Big|_{\alpha=0}=$$
$$=(1+z)^{N-1}\frac{\partial^i}{\partial\alpha^i}\left\{\frac{(1+z)^{-N_A-1}\exp[(N_A+1)n]-(1+z)^{-1}\exp(\alpha)}{(1+z)^{-1}\exp(\alpha)-1}\right\}\Big|_{\alpha=0}. \tag{16}$$

Advantages of the latter representation of $F_i(z)$ arise from the fact that after differentiating in $\alpha$ the terms containing the multiplier $\exp[(N_A+1)n]$ in (16) include powers of $z$ not higher than $N_B-2$.

In what follows we restrict ourselves to $i=0,1,2,3$. For these values of $i$ we have

$$F_0(z)=z^{-1}[(1+z)^{N-1}-(1+z)^{N_B-1}],$$
$$F_1(z)=z^{-2}\{(1+z)^N-(1+z)^{N_B-1}[(N_A+1)z+1]\},$$
$$F_2(z)=z^{-3}\{(1+z)^N(2+z)-(1+z)^{N_B-1}([(N_A+1)z+1]^2+z+1)\},$$
$$F_3(z)=z^{-4}\{(1+z)^N(6+6z+z^2)-(1+z)^{N_B-1}([(N_A+1)z+1]^3+$$
$$+3(1+z)[(N_A+1)z+1]+(1+z)(2+z))\}. \tag{17}$$

Hence one can see that, after expanding $F_i(z)$ in powers of $z$, just the sum of two polynomials is obtained: the first of power $N-2$ and the second of power $N_B-2$. Introducing for the latter (that makes no contribution to the moments) the notation $-f_i(z)$ we rewrite (17) in a more convenient form,

$$F_0(z)=\sum_{i=1}^{N-1}\frac{(N-1)!\,z^{i-1}}{i!\,(N-1-i)!}-f_0(z), \qquad F_1(z)=\sum_{i=2}^{N}\frac{N!\,z^{i-2}}{i!\,(N-i)!}-f_1(z),$$
$$F_2(z)=\sum_{i=3}^{N}\left(2+\frac{i}{N+1-i}\right)\frac{N!z^{i-3}}{i!\,(N-i)!}+(N+1)z^{N-2}-f_2(z),$$
$$F_3(z)=\sum_{i=4}^{N}\left[6+\frac{6i}{N+1-i}-\frac{i(i-1)}{(N+1-i)(N+2-i)}\right]\frac{N!\,z^{i-4}}{i!\,(N-i)!}+$$
$$+(N+1)(N+6)z^{N-3}+(N+1)(N+2)z^{N-2}-f_3(z). \tag{18}$$

Finally substituting (18) into (15) we get for $i=0$ equation (9) and

$$m^{(1)}=(c_B+N^{-1})^{-1}, \tag{19}$$

$$m^{(2)}=\frac{2-c_B}{(c_B+N^{-1})(c_B+2N^{-1})}, \tag{20}$$

$$m^{(3)}=\frac{6(1-c_B)+c_B(c_B-N^{-1})}{(c_B+N^{-1})(c_B+2N^{-1})(c_B+3N^{-1})}. \tag{21}$$

Relations (5), (6), (8) to (11) and (19) to (21) resulting from them can be applied to calculate the exact configurational average in finie tchains with randomly distrib-

uted infinite masses, randomly distributed broken bonds, etc. As an example the particular case of random walks on finite chains with chaotically distributed traps (absorbers) is considered in the next section.

### 3. Example of an Exactly Solvable Model of a Disordered System. Random Walks on a Finite Chain with Chaotically Distributed Pure Absorbers

The results obtained above can be effectively used in the classical one-dimensional random walk problem. We consider the particular case of randomly distributed pure absorbers which, for infinite chains, was discussed in [7]. The model of "interrupted chain" considered in [3, 4, 6] is very much alike ours.

Random walk motion is equivalently described both by the generating function formalism [8] and the solutions to master equations [1, 7] preferable in employing for our problem.

Let a particle move along a chain jumping from one site of the chain to another with the per second probability $W$. On any site occupied by an absorber a particle is irreversibly removed from the chain with the per second probability $\beta$. The probability $\varrho(r, t)$ to find a particle on the chain site $r$, $r = 1, 2, \ldots, N$, at time $t$, satisfies master equations which read

$$\frac{\partial \varrho(r, t)}{\partial t} = W \sum_{r=1}^{N} [\varrho(r+1, t) + \varrho(r-1, t) - 2\varrho(r, t)] - \beta \sum_{\{k\}} \varrho(k, t) , \tag{22}$$

where $\{k\}$ denotes the summation only over the sites occupied by randomly distributed absorbers. These are associated in the following with B molecules.

We are interested in the probability that at time $t$ the particle still can be found in the chain, the survival probability, averaged over all configurations of the absorber distribution

$$\varrho(t) = \overline{\sum_{r=1}^{N} \varrho(r, t)} , \tag{23}$$

where the bar denotes configurational averaging. If at $t = 0$ the particle was distributed over sites free of absorbers with equal probabilities $N_A^{-1}$, in the case of pure absorbers, $\beta \to \infty$, (23) is reduced to

$$\varrho(t) = \frac{N_A(N_B + 1)}{N} \sum_{n=1}^{N_A} [P^o(n)\, \varrho_n^o(t) + P^c(n)\, \varrho_n^c(t)] , \tag{24}$$

where $\varrho_n^o(t)$, $\varrho_n^c(t)$ are the survival probabilities in open and closed clusters, respectively. The expressions for them follow from the solutions of master equations for $n + 1$ and $n + 2$ site regular chains with one and two pure absorbers on the chain ends. The corresponding expressions are

$$\varrho_n^o(t) = \frac{1}{(2n+1)\, N_A} \sum_{l=1}^{n} \operatorname{tg}^2\left(\pi \frac{n - l + 1}{2n + 1}\right) \exp\left\{-\left[1 - \cos\left(\pi \frac{2l - 1}{2n + 1}\right)\right] 2Wt\right\}, \tag{25}$$

$$\varrho_n^c(t) = \frac{1}{(n+1)\, N_A} \sum_{l=1}^{n} [(-1)^{l+1} + 1] \operatorname{ctg}^2\left[\frac{\pi l}{2(n+1)}\right] \times$$
$$\times \exp\left\{-\left[1 - \cos\left(\frac{\pi l}{n+1}\right)\right] 2\, Wt\right\}. \tag{26}$$

Equations (25), (26) together with (10), (11), and (24) completely define the survival probability of a random walker in a chain of an arbitrary length $N$ with an arbitrary

number $N_B$ of pure absorbers. In particular, (24) implies the effects of fluctuations of the absorber distribution. They are known to be actual in infinite chains [7] leading to the characteristic time dependence of $\varrho(t)$ (see (27)). For the finite chains under consideration a new circumstance comes into play. The survival probability in an open (end) cluster is essentially greater than in a closed one of the same length. This is important and is reflected in the time behaviour of $\varrho(t)$ if $N_B$ is not much greater than unity.

In the limit $N$, $N_B \to \infty$ with $c_B$ remaining finite and $c_B \ll 1$, $2Wt \gg 1$, (24) corresponds to the result of Balagurov and Vax [7]

$$\varrho(t) = \frac{4}{\pi^2}\int_0^\infty x \exp\left(-\frac{c_B^2\pi^2\tilde{t}}{2x^2}\right)\sinh^{-1}(x)\,dx = \begin{cases} 1 - 2\left(\frac{2}{\pi}c_B^2\tilde{t}\right)^{1/2}; & \frac{\pi^2 c_B^2\tilde{t}}{2} \ll 1\,, \\ 8\left(\frac{2c_B^2\tilde{t}}{3\pi}\right)^{1/2}\exp\left[-\frac{3\pi^{2/3}}{2}(c_B^2\tilde{t})^{1/3}\right]; & \frac{\pi^2 c_B^2\tilde{t}}{2} \gg 1\,, \quad \tilde{t} \equiv 2Wt\,, \end{cases} \tag{27}$$

where end effects are ignored. Note that the same characteristic form, $\exp -(\lambda t)^{1/3}$ for long times (but with different $\lambda$), was obtained in [3] for the autocorrelation function (see also [1]) of the randomly interrupted chain. Both these results have the same origin, the complete localization of excitations within clusters, and can be extracted from the behaviour of the density of states near a band edge discussed by Lifshitz [9].

It is interesting to compare (27) with the exact result of (24) to see how end effects manifest themselves. The difference between these two expressions is hard to be seen directly but it is easily exhibited by simple numerical calculations.

We now treat an integral characteristic of the considered process which can be obtained in a closed form and thus, the role of end effects can be simply extracted. The mentioned characteristic is

$$\bar{T} = \int_0^\infty \varrho(t)\,dt = \frac{N_A(N_B+1)}{N}\sum_{n=1}^{N_A}[P^o(n)\,T_n^o + P_n^c(n)\,T_n^c] \tag{28}$$

which has the meaning of the average lifetime of a particle in the chain with pure absorbers. The expressions for lifetime of a particle in open ($T_n^o$) and closed ($T_n^c$) clusters are

$$T_n^o = (6WN_A)^{-1}\,n(n+1)\,(2n+1)\,, \tag{29}$$

$$T_n^c = (12WN_A)^{-1}\,n(n+1)\,(n+2)\,, \tag{30}$$

and coincide with appropriately defined mean first-passage times, the well-known quantities in the random walk theory [8]. Substituting (29), (30) into (28) and using the results obtained above of the moment calculations we get

$$\bar{T} = (12W)^{-1}\,(2 + M + M')\,, \tag{31}$$

where

$$M = 3(c_B + 3N^{-1})\,m^{(2)}\,, \qquad M' = (c_B + 7N^{-1})\,m^{(3)}\,. \tag{32}$$

It can be seen that $\bar{T}$ is practically independent of the chain length when two simple conditions are fulfilled: $N \gg 1$, $c_B \gg 7N^{-1}$. But we would like to stress that end effects are important and manifest themselves in the dependence of $\bar{T}$ on $c_B$ in rather long chains (for example $N \approx 100$) when $c_B$ changes in a wide range ($1 \leqq N_B \leqq$

$\leqq 10$ in our example). This is the direct consequence of two factors: the probability of the existence of a closed cluster is by $(N_B - 1)/2$ (not $N_B$) times greater than that of an open one with the same length; the lifetime of a particle in an open cluster is greater than in a closed one (by four times for sufficiently long clusters).

If the above-mentioned conditions are satisfied the relation between the average lifetime and the absorber concentration is

$$2W\overline{T} = c_B^{-2}. \tag{33}$$

Note that (33) holds even when $c_B$ is close to unity. At the same time one can obtain (33) neglecting end effects and averaging (30) for $n \gg 1$ with the distribution (12), which is a correct procedure only for $c_B \ll 1$.

In the general case (31) and (32) give the exact expression of $\overline{T}$ in a finite chain with an arbitrary number of absorbers, but not larger than $N - 1$ and not smaller than 1 when the result is trivial.

The results obtained in this section are directly applicable to the description of the luminescence decay and the luminescence quantum yield in one-dimensional donor–acceptor systems. For example, let A molecules be donors and their excited state be of the incoherent exciton type characterized by radiative lifetime $\tau$. The excitation amplitude at site $r$ at time $t$ is then exactly $\varrho(r, t) \exp(-t/\tau)$ and consequently, in the case of homogeneous $\delta$-pulse excitation of donors, $\varrho(t) \exp(-t/\tau)$ represents the time dependence of donor molecule luminescence in presence of randomly distributed acceptors (absorbers). It can be also shown that $\eta = \overline{T}\tau^{-1}$ corresponds to the expression of the quantum yield in the case of $\delta$-pulse excitation or quantum yield normalized to unity under stationary and uniform excitation of donors provided that the excitation decay is mainly due to absorption by acceptors. This is the case when $W\tau \gg c_B^{-2}$, i.e. when the incoherent exciton diffusion length is much greater than the mean distance between acceptors.

It should be pointed out that for an infinite donor–acceptor system the above-mentioned results were also discussed in [10], where the expression $\eta = (6W\tau c_B^2)^{-1}$ was obtained. This differs from ours by the factor 1/3. This quantitative discrepancy is due to the fact that the definition of configurational averages used in [10] was not appropriate to the case.

## 4. Conclusions

The length distribution of open and closed clusters in binary randomly disordered finite chains was derived and the first three moments of this distribution were calculated. This allowed us to solve exactly the problem of random walks on a chain with arbitrary number of chaotically distributed pure absorbers. This was done earlier only in the case of infinite chains and small absorber concentrations [7]. The utilization of the presented theory to the description of the donor luminescence quantum yield of one-dimensional donor–acceptor chains was also demonstrated.

Some other fundamental physical quantities of one-dimensional disordered finite systems such as the density of states, the spectral density, the frequency-dependent hopping conductivity, etc. can be found quite similarly. The corresponding calculations are now in progress. These calculations, among other questions of interest, permit to answer the two of primary importance: how long should a disordered chain be to be treated as an infinite one and what kind of deviations from the properties of infinite systems can be expected if end effects come into play. Both these questions are answered here concerning the lifetime of a particle in the presence of pure absorbers ((31) to (33)). As to the time dependence of the survival probability simple

numerical calculations should be done to see the difference between the exact result (24) and (27) which is exact only asymptotically.

The approach used here is restricted to systems with a specified kind of disorder (one of the component relative to the other should be a pure absorber, infinitely large potential, etc.). But still their theoretical studies are very useful providing exact results which serve as basis when treating more realistic cases. Note, in conclusion, that expressions for configurational averages analogous to (24) can be used as a zero approximation in an appropriately defined perturbation, but which is exact in the concentration of perturbed chain sites.

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## References

[1] S. ALEXANDER, J. BERNASCONI, W. R. SCHEIDER, and R. ORBACH, Rev. mod. Phys. **53**, 175 (1981).
[2] I. M. LIFSHITZ, C. A. GREDESKUL, and L. A. PASTUR, Introduction into the Theory of Disordered Systems, Izd. Nauka, Moscow 1982 (in Russian).
[3] S. ALEXANDER, J. BERNASCONI, and R. ORBACH, Phys. Rev. B **17**, 4311 (1978).
[4] T. ODAGAKI and M. LAX, Phys. Rev. Letters **45**, 847 (1980).
[5] T. ODAGAKI and M. LAX, Phys. Rev. B **24**. 5284 (1981).
[6] C. DOMB, A. A. MARADUDIN, E. W. MONTROLL, and G. H. WEISS, Phys. Rev. **115**, 24 (1959).
[7] B. YA. BALAGUROV and V. G. VAX, Zh. eksper. teor. Fiz. **65**, 1939 (1973).
[8] E. W. MONTROLL and G. H. WEISS, J. Math. Phys. (Cambridge) **6**, 167 (1965).
[9] I. M. LIFSHITZ, Adv. Phys. **13**, 483 (1964).
[10] V. M. AGRANOVICH and M. D. GALANIN, Excitation Energy Transfer in Condensed Matters, Izd. Nauka, Moscow 1978 (in Russian).

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