Origin of Stretched Exponential Relaxation for Hopping-Transport Models

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We propose a novel geometric approach to the description of the relaxation phenomena in complex condensed-matter systems. It is shown within a fairly general random site hopping model that the stretched exponential decay law, $\exp[-(t/\tau)^{\beta}]$, originates from the simple and general geometric features of a random distribution of transport and trapping sites in the 3D space. The value of the variable stretching index β is determined by the localization radius of hopping electrons. The possibilities for generalization of the obtained results and interpretation of the relevant experimental data are discussed.

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It is now widely accepted that the stretched exponential function, known since the middle of the 19th century as the Kohlrausch law [1],

$$n(t) = n(0)\exp[-(t/\tau)^{\beta}], \tag{1}$$

with the stretching index β ranging from 0 to 1, fits surprisingly well a great variety of relaxation phenomena in complex condensed-matter systems; see [2–5] and references therein. Often, the Kohlrausch law is associated with the structural relaxation in glasses and polymers [2,4]. However, it is known also for spin and magnetic glasses [6,7], amorphous silicon [8], and other systems. Recently, stretched exponential relaxation distinguished by a variable value of β and a fairly long range of the relaxation time t was found in $LiNbO_3$:Fe crystals [9]. This system, in contrast to glasses and polymers, is expected to obey the established basic concepts of the solid state theory.

The ubiquitous character of the stretched exponential relaxation has encouraged theorists to search for microscopic models compatible with Eq. (1). And such models, which are far from trivial, were found. One of the most known findings of this kind is the model of hierarchically constrained dynamics which implies triggering of slower relaxation processes after completion of faster ones [10]. A number of microscopic lattice models are based on special assumptions about fractal structure of the medium [11]. An overview of the models based on the idea of scale-invariant distribution of relaxation times can be found in [5].

Unfortunately, most of the models of the stretched relaxation have no clear physical basis. Partially, it is caused by the absence of a satisfactory theory of the glassy state. The known models give no clear answer to the simple and fundamental questions: What and why make the stretched relaxation so general? What is the underlying property of the medium responsible for the stretched behavior? The current estimates of the status of the Kohlrausch law range from "It is largely a convenient phenomenological tool without fundamental significance" [12] to "It is one of Nature's best-kept secrets" [4].

The main purpose of this Letter is to link the origin of the stretched exponential behavior with simple and general geometrical properties inherent in hopping relaxation systems. These properties are the subject of stochastic geometry [13]; they are the quintessence of randomness, which is widely recognized as the common feature of all complex condensed-matter systems. Our results do not pretend to cover the whole spectrum of random systems. They show, however, a new way of how to treat the stretched exponential relaxation.

The basic model to be studied is not much different from that considered by many authors. Transport and trapping sites are distributed randomly in the 3D space with the concentrations N_0 and N_T, respectively. Initially, electrons occupy the transport sites with the same probability $p_0 \ll 1$. Further, they walk by hops from site to site and recombine with the traps. The rate of an elementary transition process W is expected to be a sharply decreasing function of the hopping distance R. Note that the randomness naturally appears in the above "continuous" model in contrast to the "lattice" random models; see, e.g., [11]. A number of statistical properties of randomly placed dots (of Poisson ensembles) are known within the probability theory [14]; some special geometric aspects have been analyzed within the percolation theory [15,16].

Now we formulate the geometrical problem in question. Consider an arbitrary initial transport site and an arbitrary trap. An electron can move from this site to the trap in many different ways. Each particular way (let us label it i) can be characterized by the maximum hopping distance $R_i^{\max}$; see also Fig. 1. By varying i one can minimize $R_i^{\max}$ over the ways leading to the chosen trap. Lastly, by minimizing this value over all traps (the nearest trap is not necessarily the optimum one), we obtain a

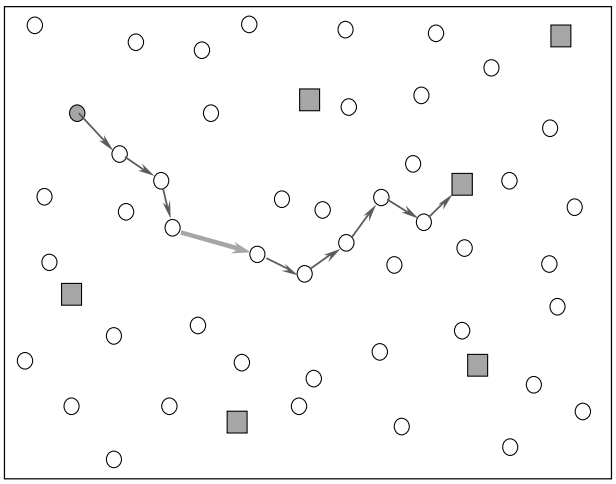

FIG. 1. Schematic representation of randomly placed sites. The solid circle shows an initial electron position, the open circles and solid squares mark the empty transport sites and the traps, respectively. The arrows show one of the ways leading to recombination and including the critical hop; this transition is indicated by the thick arrow.

certain value of R, which is the absolute minimum among the maximum hopping distances for the chosen initial transport site. For an ensemble of the initial transport sites we have therefore a unique distribution function $F(R)$, which is the probability for the mini-max hopping distance to be equal to R. This function is a quantitative geometric characteristic of the random distribution of the transport and trapping sites. It can be introduced for the space of any dimension. According to the definition, $\int_0^\infty F(R)dR = 1$. To the best of our knowledge, the formulated geometrical problem was never considered in the literature.

It seems difficult to find the "geometric" function $F(R)$ in analytical form. But some of its features are clear. Consider the most important case $N_0 \gg N_T$, when the trapping events occur, in average, after many hops over the transport sites. It is evident that $F(R)$ peaks at $R \sim \bar{R}$, where $\bar{R} = (3/4\pi N_0)^{1/3}$ is the characteristic distance between the transport sites. The asymptotic behavior for $R \gg \bar{R}$ is determined by those isolated sites that have no nearest neighbors at the distance smaller than $\approx \bar{R}$. In other words, the function $F(R)$ tends here to the probability of having a nearest neighbor at distance R, $F_p \equiv 4\pi R^2 N_0 \exp(-4\pi N_0 R^3/3)$. The peak of $F(R)$ is expected to be sharper than that of $F_p(R)$ and occur at $R > \bar{R}$.

Why is the introduced geometric function $F(R)$ expected to be of great importance for the description of the decay law? We argue that the mini-max distance R characterizes the bottleneck for the elementary hopping processes leading to relaxation if the rate W is a sharply decreasing function of the hopping distance R. This assertion is in line with the experience accumulated during the studies (analytical, numerical, and experimental) of transport phenomena in random infinite media on the basis of the percolation theory [15,16]. The point is that there is a great number of ways (for a chosen initial site) leading to recombination and including a single section with the critical mini-max distance R; see Fig. 1. The rate $W(R)$ is minimum (among the elementary rates) for all these ways. Multiplicity of the ways enhances strongly the inflow of electrons to and the outflow from the bottleneck. The number of alternative ways depends essentially on the space dimension; in the 3D case the bottleneck is more pronounced than that in the 2D case.

With the concept of the bottleneck accepted, we have for the decay function $f(t)$,

$$f = \int_0^\infty F(R) \exp[-W(R)t]dR. \tag{2}$$

This can be regarded as a kind of the parallel channel model [5] with the relaxation rate spread determined by the distribution $F(R)$. According to Eq. (2), $f(0) = 1$, $f(\infty) = 0$. The decay law depends indeed on the function $W(R)$. For electron hopping processes it can conventionally be chosen as

$$W = \nu \exp(-2R/a), \tag{3}$$

where ν is an R-independent factor and a is the localization radius of the electron wave function ($N_0 a^3 \ll 1$). An exponential decrease of the hopping rate $W(R)$ is sufficient for employment of the bottleneck concept [16]; the smaller a, the better for our theory.

The asymptotic behavior of $f(t)$ for large t is determined by the shape of $F(R)$ in the limit of large R; it has been specified above. Accordingly, we have for $t \to \infty$, $f \to \exp[-(\pi/6)N_0 a^3 \ln^3(\nu t)]$, which differs from the Kohlrausch law. Thus our hope is that $f(t)$ is fitted by Eq. (1) within a long time interval $0 < t \lesssim t_0$.

Our further studies are based on numerical simulations. First, using the Monte Carlo method, we have solved the geometrical part of the problem. Typically, we chose random coordinates of 1000 transport sites within a 3D volume. The number of traps (their coordinates were chosen similarly) varied from 25 to 100, i.e., the ratio N_0/N_T ranged from 40 to 10. For a chosen transport site we calculated the mini-max distance R using the periodic boundary conditions. By choosing different initial sites and different realizations of the site coordinates, we accumulated progressively statistics of the mini-max distance. It was also made sure that increasing N_0 from 1000 to 3000 (with the same ratio N_0/N_T) does not affect the shape of $F(R)$. This means that the trapping sites located very far from the nearest ones are negligible. Increasing ratio N_0/N_T severely complicated the simulation procedure.

Figure 2 shows our numerical results. The difference between $F(R)$ and $F_p(R)$ is evident. The larger N_0/N_T, the sharper the peak of $F(R)$ and the stronger its shift to the

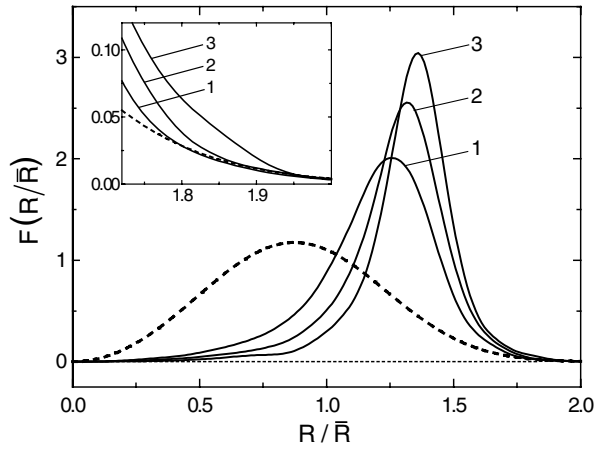

FIG. 2. The function $F(R)$ for three values of N_0/N_T; the solid lines 1, 2, 3 are plotted for $N_0/\mathrm{N}_T = 10, 20, 40$ and the dotted line is the nearest-neighbor distribution $F_p(R)$. The inset shows in detail $F(R)$ for large values of $R/\bar{R}$.

right. For $R > 1.8\bar{R}$ the function $F(R)$ is already very close to $F_p(R)$; the value of $F(R)$ is very small in this region. The data of Fig. 2 fit well the percolation theory [15]. As follows from this theory, the value of R_m corresponding to the maximum of $F(R)$ tends to the critical radius $R_c \simeq 1.4\bar{R}$ in the limit $N_0/N_T \to \infty$. The value of $R_m/\bar{R}$ for curves 1, 2, and 3 is $\simeq 1.25$, 1.32, and 1.36, respectively; it approaches $R_c/\bar{R}$ from below.

Next, using the data on $F(R)$ and Eqs. (2) and (3), we have calculated the decay function $f(t)$. The solid lines 1–9 in Fig. 3 show numerical results obtained for different combinations of N_0/N_T and $\bar{R}/a$. The dotted lines show the best fit by the stretched exponential function. This fit is surprisingly good within the whole range of N_0/N_T and during at least 3–5 decades of the relaxation time; the larger $\bar{R}/a$, the longer the fitting range. The far tail of the relaxation function does not obey the Kohlrausch law in accordance with the asymptotic behavior of $F(R)$. The crossover to the nonstretched relaxation occurs at very small values of $f(t)$.

The value of the index β depends on N_0/N_T and $\bar{R}/a$. The main tendencies of this dependence are clear from Fig. 4. One sees that the stretching index grows smoothly with increasing N_0/N_T and decreases with increasing ratio $\bar{R}/a$. The range of variation of β is rather big, from 0.9 to 0.2. The characteristic time τ is proportional to ν^{-1} and grows exponentially with increasing $\bar{R}/a$.

Lastly, we have performed direct 3D Monte Carlo simulations. We followed an electron located initially at an arbitrary transport site up to its trapping event and accumulated statistics of the survival time. To accelerate the calculations, we restricted ourselves to the hops to several neighboring sites, located not further than $2\bar{R}$ from the current electron position. Nevertheless, the direct simulations were highly time consuming; they could not be performed in a volume sufficient for a full-scale comparison with the data of the previous calculations. The main purpose of these simulations was an examination of the validity of our geometrical approach.

Figure 5 shows the results obtained for three values of N_0/N_T and their fit by the stretched exponential function. This fit is rather good. Furthermore, the values of the stretching index β are also in a good agreement with those obtained earlier; see Fig. 4.

We have shown, therefore, that our geometrical approach grasps the essence of the relaxation problem and leads (within the model considered) to the decay function that is very close to the stretched exponent within several decades of the relaxation time and a wide range of variable parameters. Being apparently simple, the model used allows for anomalous diffusion [17] and includes critical phenomena and multifractal structures [15]. It certainly

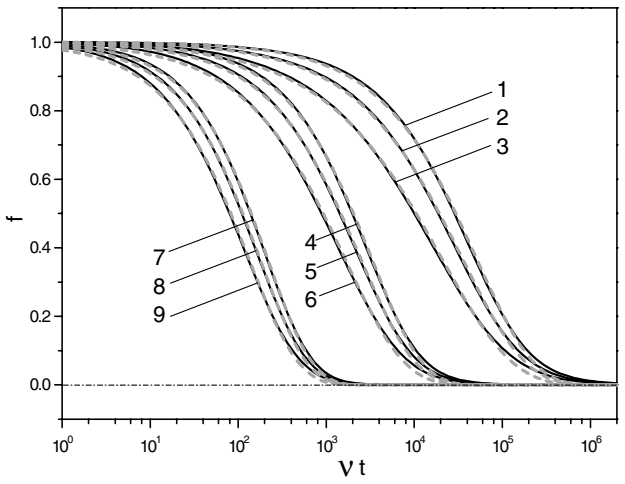

FIG. 3. The relaxation function $f(t)$ for several values of the ratios N_0/N_T and $\bar{R}/a$. The chosen parameters are as follows. 1: $(N_0/\mathrm{N}_T = 40, \bar{R}/a = 4)$; 2: (20, 4); 3: (10, 4); 4: (40, 3); 5: (20, 3); 6: (10, 3); 7: (40, 2); 8: (20, 2); 9: (10, 2).

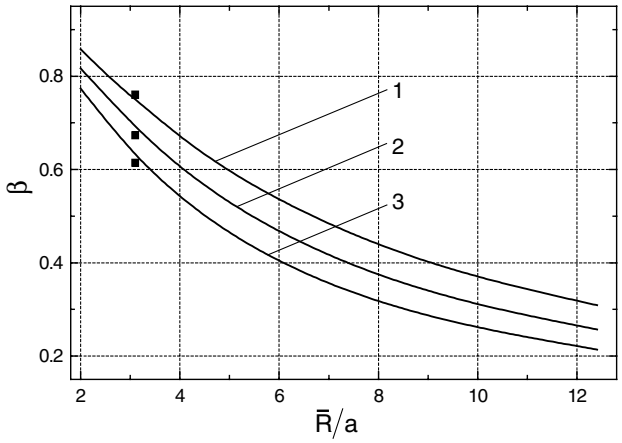

FIG. 4. Dependence of the stretching index β on $\bar{R}/a$; the curves 1, 2, and 3 are plotted for $N_0/N_T = 40$, 20, and 10. The solid squares correspond to the direct simulations.

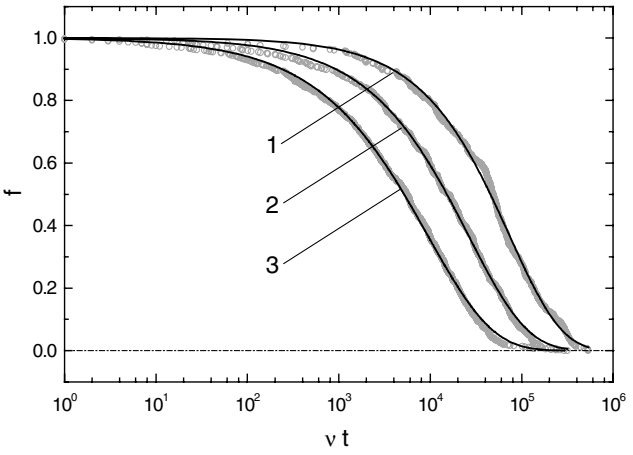

FIG. 5. The decay law (squares) obtained by the direct simulations for $aN_0^{1/3} = 1/5$. The cases 1, 2, and 3 correspond to $N_0/N_T = 40$, 20, and 10. The solid lines are the fit.

possesses many features generic for relaxation phenomena in complex condensed-matter systems.

Generally, the preexponential factor ν in Eq. (3) depends on the temperature T. Quite often, e.g., for the polaron hopping models [18], $\nu \propto \exp(-\epsilon_a/k_BT)$, where $\epsilon_a \approx 10^{-1}$ eV is an activation energy. This representation leads indeed to an activation dependence of the characteristic time τ entering the Kohlrausch law. Such a dependence is detected for electron relaxation in $LiNbO_3$ crystals [9].

Explanation of the temperature dependence of the index β (its temperature growth is mentioned in [8,9]) requires a generalization of our model. The most challenging possibility is, probably, taking into account the influence of the energy difference between the centers on the jump rate W. The effect of the energy disorder cannot often be neglected and leads to nontrivial temperature dependences [16,18]. Within the percolation theory, this effect can, for certain cases, be treated by a transition from the 3D to the 4D space; see Chap. 9 of [16]. Possibly, this idea is applicable to our geometric approach.

It is worth mentioning that our theory explains well the stretched behavior within a wide interval of the relaxation time covering almost the whole range of the relaxing quantity, $f_0 \lesssim f(t) \leq 1$ with $f_0 \ll 1$, which is of prime importance for experiment. This is a big advantage over the classic results [19] showing, under certain assumptions, that the far tail of the decay function follows the Kohlrausch law with the stretching index $\beta = 3/5$; see also [4,11].

Strictly speaking, our model is adequate for electronic disordered systems. It can hardly be trivially readdressed to structural and spin glasses. However, it would not be practical to expect a universal solution to the whole problem of stretched relaxation. We believe that our geometric approach carries some generic features of relaxation phenomena in complex condensed-matter systems. It can be useful, in particular, for structural glasses where heuristic configuration-space models are used to compensate the absence of basic theory.

In conclusion, we have proposed and justified a novel geometric approach to the description of relaxation phenomena in disordered condensed-matter systems. Within a rather general continuous random walk model, this approach has allowed us to establish a close relation between the geometric properties of randomly distributed centers and the stretched exponential decay function and has thus given a new insight into the origin and status of the Kohlrausch law. Within our model, this law has to be considered as a highly useful approximation covering the main body of relaxation times and input parameters.

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