

**Geminate pair recombination in molecular systems with correlated disorder**Darius Abramavicius<sup>1</sup> and Leonas Valkunas<sup>1,2</sup><sup>1</sup>*Institute of Physics, A. Gostauto 12, Vilnius 2600, Lithuania*<sup>2</sup>*Department of Theoretical Physics, Faculty of Physics, Vilnius University, Sauletekio Avenue 9, Block 3, 2054 Vilnius, Lithuania*

(Received 29 November 2002; revised manuscript received 1 August 2003; published 23 December 2003)

Influence of the correlation of the disorder on the geminate charge pair recombination is theoretically analyzed. Charge dynamics is considered in one- and three-dimensional systems by means of Monte Carlo simulations. It is demonstrated that the correlation radius of the disorder is the limiting distance factor by discriminating the effect of the disorder in the mobile charge movement. Because of that the concept of the local disorder, which expresses itself in the geminate recombination kinetics, is introduced. The correlation effects express themselves in the intermediate times and are lost in the large-scale movement of the charges. It is demonstrated that the discrepancies between disorder values obtained by the geminate pair recombination kinetics and those from the charge drift studies can be attributed to the correlative effects of the disorder. The radius of the correlation is estimated to reach 17 to 28 lattice constants for the organic semiconductors.

DOI: 10.1103/PhysRevB.68.245203

PACS number(s): 72.20.Ee

**I. INTRODUCTION**

Recent achievement in the development and control of highly sensitive organic materials with well-defined photoconducting properties opened the way of their possible applications in optoelectronics by designing light-emitting diodes,<sup>1,2</sup> transistors,<sup>3,4</sup> photocells,<sup>5</sup> etc. The photorefractive effect, discovered in organic systems<sup>6</sup> and mostly studied in poly(*N*-vinylcarbazole),<sup>7-9</sup> has numerous potentially interesting applications in the real-time holography. The principal properties of molecular systems are very sensitive to the microscopic constraint because of the asymmetry, ordering, and alignment of the molecules in their arrangement. For instance, the conductivity of highly oriented fibrillar polyacetylenes can be comparable to that of copper (up to 10<sup>5</sup> S/cm) and the light emission of such aligned molecular systems is highly polarized.<sup>10</sup>

Dynamics of charge carriers in molecular systems of current technological interests demonstrates complex behavior in various time domains, from femtoseconds to microseconds and even to milliseconds. Charge generation is the very initial event in the sequence of primary processes after the light absorption, taking place in the femtosecond-nanosecond time domain. According to present observations of the charge photogeneration in organic sensitized photoconductors<sup>11,12</sup> or conjugated polymers<sup>13,14</sup> at least two steps are well distinguished. The electron-hole pair of a particular characteristic distance appears on the subpicosecond time scale after absorption of the light quantum,<sup>15</sup> while the subsequent charge separation and/or the geminate recombination of separated charges are much slower, resulting in nanosecond and even longer characteristic times.<sup>16,17</sup> Because of that the very initial stages of the charge separation are related to the unrelaxed charge movement prior to the polaronic state formation<sup>18</sup> while the slower ones are attributed to the polaron type movement—the hopping of the charges.<sup>12</sup>

Various kinds of lattices (for instance, cubic or square) are the basic frameworks used for studies of various aspects of the charge movement in real systems. The energy disorder

plays the major role in determining the dynamics of charges, while the off-diagonal disorder shows only a minor effect on the initial part of recombination dynamics.<sup>19</sup> In addition, from the analysis of the total geminate pair recombination (GPR) kinetics the initial charge separation distance can be deduced.<sup>19</sup> By analyzing the relaxed charge movement on a long time scale, the mobility of charges can be determined. The experimental data of the charge mobility in molecular polymers are in agreement with the model calculations by assuming the characteristic dispersion to be of the order of 0.1 eV in terms of the model, based on the cubic lattice with Gaussian diagonal (energy) disorder.<sup>20</sup> By considering the GPR kinetics within the same model approach, the conclusion of a somewhat smaller amount of the dispersion value of the disorder is obtained.<sup>19,21</sup> This variation of the amount of the disorder depending on the processes under consideration has to be affected by the size of the system, which is involved in the diffusive behavior of the mobile charge. Indeed, the recombination process takes place in the vicinity of the parent chromophore, and the recombination time is comparable to the time required for the charge relaxation in the disordered lattice.

The difference of the disorder value depending on the spatial scale of the processes under consideration can be understood in terms of the correlation size of the disorder, which displays itself in the percolative behavior of the charge dynamics<sup>22,23</sup> or in the kinetic networks for the strong disorder case.<sup>24</sup> The percolation effect in disordered clusters is strongly dependent on the dimensionality of the system.<sup>25</sup> Indeed, the conjugated polymers are often ascribed to one-dimensional systems, while nonconjugated polymers may be treated as systems of higher dimensionality.<sup>26</sup> The correlation effect on the field dependence of the mobility of the charge carrier in molecular-doped polymers (MDP) was demonstrated numerically<sup>27,28</sup> and analytically for a one-dimensional continuum model<sup>29</sup> (see also Ref. 26 for review). Namely, the positive spatial correlation was originated to permanent dipole moments present in the polymeric system,<sup>27,28</sup> while resulting in the Gaussian site energy distribution for the diagonal correlation component.<sup>30</sup> Recently

it was demonstrated that the correlated disorder explains the observed temperature and field dependences of the charge mobility in MDP.<sup>31</sup> The effect of correlations is weaker or even lost on the large scale of movement (larger than typical correlation distances), while it can be appreciable on a small scale of motion. GPR is a typical process caused predominantly by the small scale of the charge movement, especially the initial stage of the recombination kinetics. Therefore, the correlation effect on a short scale of the charge movement with respect to the GPR kinetics will be the main issue under consideration.

## II. MODELING OF CORRELATIONS

Effects of the disorder on the dynamics of the mobile charges can be well demonstrated by Monte Carlo simulations (see, for instance, Refs. 24, 27, 28). The square lattice framework characterized by particular site energies for the mobile particle will be used as the basic structural arrangement to start the simulation procedure. The local inhomogeneity is taken into account as the diagonal disorder (the disorder of the site energies) while the global disorder caused by various tensions in the system results in the correlation effects of the disorder.

### A. One-dimensional lattice model

Let us first consider a one-dimensional lattice composed of  $N$  sites with the site energies  $\varepsilon_x$  specific to any site, where  $x$  enumerates the sites:  $x = 1, 2, \dots, N$ . The uncorrelated disorder can be simply introduced by taking the site energies  $\varepsilon_x$  randomly distributed according to the Gaussian distribution characterized by the mean value, which will be set to 0 for convenience, and by dispersion  $\sigma^2$ . However, to employ correlations, this model fails because this type of description does not contain any information about the correspondence between energies of the different sites. The Fourier analysis is a convenient tool for the correlation effects to be taken into account.

In general, large ( $N \gg 1$ ) systems may be characterized by means of the pair correlation function, which in its turn is defined by the correlation radius, thus giving

$$\langle \varepsilon_x \varepsilon_{x'} \rangle = \sigma^2 \exp\left(-\frac{|x-x'|}{R_c}\right), \quad (1)$$

where  $\langle \dots \rangle$  denotes the statistical average,  $|x-x'|$  is the distance between sites  $x$  and  $x'$ , while  $R_c$  is the correlation radius of the disorder. Here and in the following all distance units are expressed in terms of the lattice constant. The Fourier transformation of the site energies results in mapping of the real space into a corresponding Fourier representation. Thus, the site energies can be related to their inverse transform values:

$$\varepsilon_x = \sigma \sum_{k=-(N-1)}^{N-1} a_k \exp(i\Delta kx), \quad (2)$$

where  $\Delta = 2\pi/N$  and  $k$  determines the numbering of the Fourier component (or a coordinate in the  $k$  space). The ampli-

tude  $a_k$  is a complex number and must obey the relationship  $a_k = a_k^*$  in order for the energy values to be real. Due to the well-known Wiener-Khintchin fundamental theorem,<sup>32</sup> the correlation function is determined as an inverse transformation of a power spectrum of the site energies:

$$\langle \varepsilon_0 \varepsilon_x \rangle = \sigma^2 \sum_k I_k \exp(i\Delta kx), \quad (3)$$

where  $I_k$  is the amplitude of a power spectrum. Since the correlation function is an exponentially decaying function [see Eq. (1)], the power spectrum, which in its turn is the Fourier transform of the correlation function, is determined by the Lorentzian function, giving accordingly

$$I_k = \frac{\Delta}{\pi} \frac{1/R_c}{(\Delta k)^2 + (1/R_c)^2}. \quad (4)$$

In terms of the Fourier coefficients the power spectrum is related to amplitudes  $a_k$  as

$$I_k = |a_k|^2. \quad (5)$$

Thus, by defining the amplitudes of the Fourier series from Eqs. (4) and (5) as

$$|a_k| = \sqrt{I_k}, \quad (6)$$

the correlated site energies can be determined from Eq. (2). In order to get the disordered picture for the energy distribution, the phases of the coefficients  $a_k$  must be random. Thus, assuming

$$a_k = |a_k| \exp(i\varphi_k), \quad (7)$$

where  $\varphi_k$  is a linearly distributed random number drawn from the interval  $[0, 2\pi)$ , the correlated disorder is well defined. It is worthwhile to mention that the relation  $\varphi_k = -\varphi_{-k}$  for the random phase coefficients must be fulfilled.

### B. The correlated energy profile for higher-dimensional lattices

A similar procedure may be applied to the square two-dimensional lattice (and for lattices of higher dimensionality as well) with the correlated disorder. By using the same Fourier transformation procedure as given in Eq. (2), the correlation function for sites  $(x, y)$  and  $(x', y')$  of two-dimensional lattice can be defined as follows:

$$\langle \varepsilon_{x,y} \varepsilon_{x',y'} \rangle = \sigma^2 \exp\left(-\frac{|x-x'|}{R_c}\right) \exp\left(-\frac{|y-y'|}{R_c}\right), \quad (8)$$

with the power spectrum given by

$$I_{k,l} = I_k I_l, \quad (9)$$

where  $I_k$  and  $I_l$  are the power spectra of the one-dimensional behavior along  $x$  and  $y$  axes, as determined in Eq. (4). It is noteworthy that the correlation function for the two-dimensional system can be also defined in a somewhat different way by means of the following definition of the correlation function [compare Eq. (13)]:

$$\langle \varepsilon_{x,y} \varepsilon_{x',y'} \rangle = \sigma^2 \exp\left(-\frac{|r-r'|}{R_c}\right), \quad (10)$$

where  $r = \sqrt{x^2 + y^2}$ . In this case the power spectrum is given by

$$I_{k,l} = \Delta^2 \frac{1}{|k| \pi^2} \frac{1/R_c}{|k|^2 + (1/R_c)^2}, \quad (11)$$

where  $|k| = \Delta \sqrt{k^2 + l^2}$ . The correlated energy profile in this case is the same as for the one-dimensional system. Both definitions provide similar results. Further extension of the presented approach in determining the correlated disorder for higher-dimensional systems is straightforward. Since the  $D$ -dimensional Fourier transformation of the energy spectrum can be determined as follows:

$$\varepsilon_{\mathbf{r}} = \sigma \sum_{k_1, k_2, \dots, k_D = -(N-1)}^{N-1} a_{\mathbf{k}} \exp[i\Delta(\mathbf{k} \cdot \mathbf{r})], \quad (12)$$

where  $\mathbf{r}$  is a  $D$ -dimensional radius vector of the position of a particular lattice node,  $\mathbf{k} = (k_1, k_2, \dots, k_D)$  is the corresponding vector determining the  $D$ -dimensional Fourier transformation, thus, similarly the correlation function is determined as

$$\langle \varepsilon_{\mathbf{r}} \varepsilon_{\mathbf{r}'} \rangle = \sigma^2 \prod_{i=1}^D \exp\left(-\frac{|x_i - x'_i|}{R_c}\right). \quad (13)$$

Therefore, the corresponding power spectrum is given by

$$I_{\mathbf{k}} = \prod_{i=1}^D I_{k_i}, \quad (14)$$

where  $I_{k_i}$  represents the power spectra of the one-dimensional system as defined in Eq. (4). Accordingly, the Fourier coefficients are also related to the one-dimensional coefficients:

$$|a_{\mathbf{k}}| = \prod_{i=1}^D |a_{k_i}|, \quad (15)$$

and, therefore, this procedure may be used for the square lattice of any dimensionality.

### III. GEMINATE PAIR RECOMBINATION

The hopping rate of the mobile charge from  $i$ th molecule to the  $j$ th one in the molecular framework,  $\nu_{ij}$ , is determined by the distance-dependent exponential factor as a result of the overlap of the corresponding electronic wave function and by the energy-dependent factor caused by the electron interaction with the molecular environment (electron solvation) and intermolecular and intramolecular vibrations.<sup>19</sup> Thus,

$$\nu_{ij} = \nu_0 \exp(-2\gamma|\mathbf{r}_i - \mathbf{r}_j|) B_{ij}(\Delta E), \quad (16)$$

where  $\nu_0$  is a frequency prefactor,  $\gamma$  is a wave function overlap factor of particular molecules, and the Boltzmann prefactor is selected to be of the Miller-Abrahams type,<sup>33</sup>

$$B_{ij}(\Delta E) = \begin{cases} \exp[-(\Delta E)/(k_B T)] & \text{if } \Delta E < 0 \\ 1 & \text{if } \Delta E > 0, \end{cases} \quad (17)$$

where  $\Delta E = E_i - E_j \equiv \varepsilon_{x,y} - \varepsilon_{x',y'}$  and  $k_B$  is the Boltzmann constant.

Such a hopping rate is widely used to simulate the diffusion of the mobile charges as well as their mobility in the presence of the external electric field (see Ref. 26 for review). It is worthwhile to mention that the validity of the Miller-Abrahams expression for the hopping rate has been seriously challenged,<sup>34,35</sup> especially for extraction of the parameters from experimental data. However, since this approach is based on the detailed balance, qualitative demonstration of the effect under consideration will be distinguished. By introducing the additional Coulomb field from the parent lattice site, where the countercharge remains set, the process of geminate recombination can be simulated as well. The details of the model simulations have been recently described.<sup>19</sup> To rule out the jump frequency, which determines the time scale of the process under consideration, the dimensionless time will be used, what corresponds to the time unity as

$$[\nu_0 \exp(-2\gamma a)]^{-1}, \quad (18)$$

where  $a$  is the lattice constant. Typically  $2\gamma a$  can be assumed to be of the order of 10.<sup>19</sup> In this case the hopping between the nearest neighbors is predominant (the corresponding mean-jump-time equals 1), while for the diagonal jumps on the square lattice the jump rate is smaller by a factor of 60.

The typical value of the dispersion of the disorder satisfies the following:  $\sigma > k_B T$  even at room temperature.<sup>19-21</sup> Basically the case of  $\sigma/k_B T = 2$  corresponds to the global diagonal disorder of 0.05 eV, while the value  $\sigma/k_B T = 4$  relates to a value of 0.1 eV. The Coulomb energy for the charges between nearest neighbors in the lattice is determined by the lattice constant and by the dielectric constant of the medium typically giving the following value for the ratio:

$$E_C/(k_B T) = \frac{e}{4\pi\epsilon\epsilon_0 a k_B T} = 25-30,$$

see Refs. 19 and 21.

### IV. RESULTS

#### A. Correlated energy landscape of the lattice

Qualitatively, the correlated disorder provides the nonlocal perturbation of the energy landscape of the regular lattice. The corresponding distribution of the energy for the mobile charge obtained by the Fourier-transformation approach described above for the evaluation of the correlated disorder is shown in Fig. 1 for the disordered one-dimensional lattice of 1000 sites with different radii of the correlation. The correlated distribution of the energy landscape depending on the correlation size is evidently distinguished. Statistically, these differences are well determined by the correlation function, which is exponentially dependent on the interpigment distance as shown in Fig. 2. The calculated correlation function

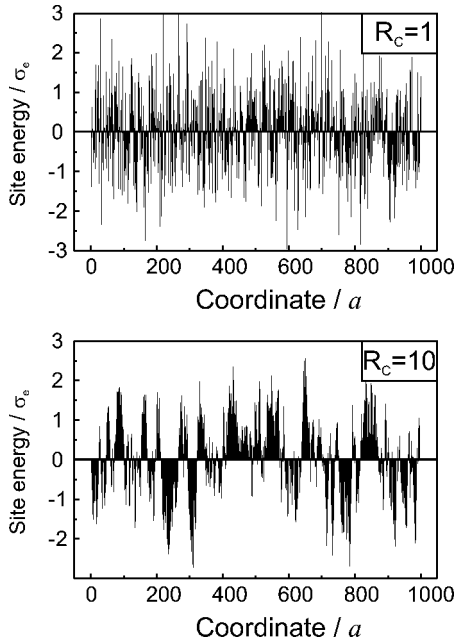


FIG. 1. One-dimensional landscapes of the noncorrelated (a) and correlated (b) disordered lattices.

decays slightly faster than the single-exponential decay function (see the case of  $R_c=1$  in Fig. 2) because of the finite size of the lattice under consideration. Indeed, this deviation disappears for larger lattices containing 10 000 sites (not shown). However, the distribution of the site energies in both cases of the lattices is Gaussian with the dispersion approximately equal to 1.

**B. Diffusion of the mobile charges**

The long-distance movement of the mobile particle under zero external field conditions can be well characterized by the time dependence of the mean value of the square displacement of the particle, i.e., by the  $\langle R^2 \rangle$  dependence on  $t$ , where  $\langle \dots \rangle$  means the statistical averaging.<sup>24</sup> The results of calculations for the one-dimensional lattices of various values of the correlation radii are presented in Fig. 3. It is evident that the regular lattice corresponds to the well-known diffusion-type relationship

$$\langle R^2 \rangle \propto t, \tag{19}$$

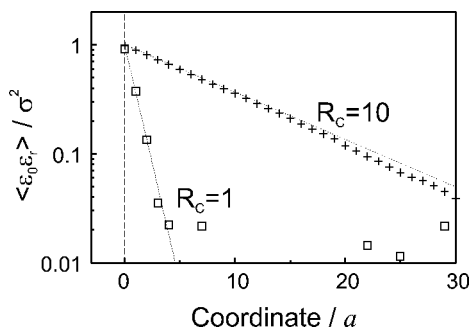


FIG. 2. Correlation functions of the lattices shown in Fig. 1. Dotted lines correspond to the exponential decay.

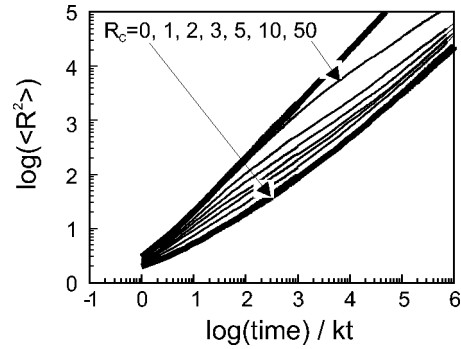


FIG. 3. Time dependence of the calculated mean values of the square displacement for the one-dimensional system with various correlation radii of the disorder. Corresponding values of  $R_c$  are pointed out. Results for the regular lattice and for the lattice of noncorrelated disorder are shown by bold lines. The diagonal disorder value is taken to be  $\sigma=2k_B T$  in calculations.

where the factor of the proportionality is the diffusion coefficient. The process providing this kind of correspondence can be related to the normal diffusion. In the case of the uncorrelated disorder, the long-time behavior of  $\langle R^2 \rangle$  is linearly dependent on time, while the diffusion process is somewhat slower compared to the regular lattice (the corresponding diffusion constant is smaller). This change of the diffusion constant is caused by the different conditions of the movement since in the case of the disordered lattice the mobile particle has to overcome the large potential barriers between the lattice sites. The linear time dependence is reached asymptotically when the particle distribution on the energy scale approaches the thermal equilibrium distribution. Since the mean energy for the particle in the disordered lattice corresponds to the value  $E_{\text{mean}} = \sigma^2/k_B T$ , thus, indeed it takes some time to reach this value for the initially generated particle in the system with the uncorrelated disorder (see Fig. 3).<sup>36</sup> This thermal equilibration time increases with the increase of the disorder, and the intermediate regime of the dispersive hopping becomes more pronounced.<sup>24</sup> The correlation of the disorder expresses itself on the same time scale as the intermediate regime of the dispersive hopping. At shorter times the particle behavior is closer to the case of the regular lattice while for the larger time scale and at larger distances it approaches the case of the diffusion behavior in the lattice with the uncorrelated disorder.

The diffusion in the system of higher dimensions with the correlated disorder is qualitatively similar to that observed in one-dimensional systems (see Fig. 4). At the short times it demonstrates the diffusion type behavior corresponding to the regular lattice, while at longer times it switches into the diffusion of the particle in the lattice with the uncorrelated disorder. Depending on the correlation size, this switching period changes: the larger the radius, the longer the switching period. At short times the particle feels the local disorder, which can be weaker than the global one. Therefore, the diffusion rate of the particle changes in the course of time, being faster at short times and slowing down with time. The characteristic time determining this transition from the short-time to the long-time behavior resembles the correlation ra-

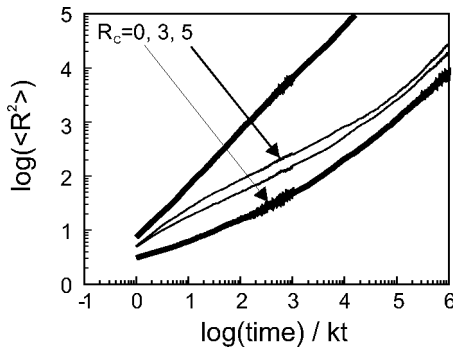


FIG. 4. Time dependence of the calculated mean values of the square displacement for the three-dimensional system with various correlation radii of the disorder. Corresponding values of  $R_c$  are pointed out. Results for the regular lattice and for the lattice of noncorrelated disorder are shown by bold lines. The diagonal disorder value is taken to be  $\sigma = 4k_B T$  in calculations.

dius of the disorder. The case is different in the one-dimensional systems, where the particle faces the sites with increasing disorder values as it moves to the larger distances. Since the particle has no other way to move, the diffusion process turns out to be similar to the diffusion in the system with the uncorrelated disorder. For the higher dimensions the particle has the possibility of avoiding the “high cost” paths and, therefore, the diffusion is slightly faster at the long times in the correlated lattice as compared to the uncorrelated case. This conclusion is validated for the small values of the disorder, which are typical of the disordered polymers as used for calculations. However, in the case of strong disorder the kinetics of the charged particle becomes predominantly one dimensional in the networks of higher dimensions.<sup>24</sup>

### C. Geminate pair recombination

The effect of the correlative disorder on the GPR kinetics is analyzed by assuming that the recombination rate of the charges in the charge transfer state is infinitely fast, i.e., it is assumed that they recombine immediately as soon as the mobile charge reaches its countercharge.

The recombination kinetics as shown in Fig. 5 and Fig. 6 is very sensitive to the changes of the correlation radii. Larger correlations speed up the initial part of the kinetics,

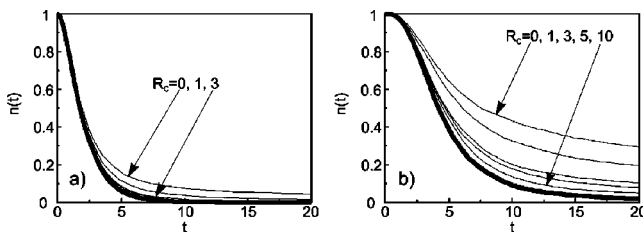


FIG. 5. The GPR kinetics calculated for the one-dimensional lattice with different correlation radii of the disorder (corresponding values are pointed out), while the GPR kinetics for the regular lattice is presented in bold. The initial charge separation radii  $r_0 = 3a$  (a) and  $r_0 = 5a$  (b) are assumed. The diagonal disorder value is taken to be  $\sigma = 2k_B T$  in calculations.

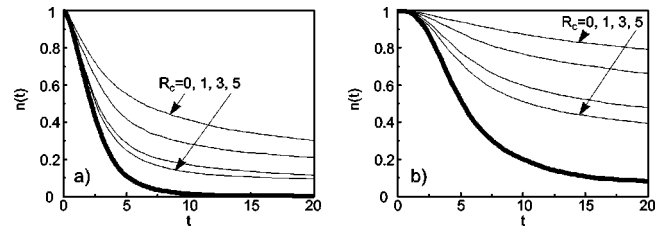


FIG. 6. The GPR kinetics calculated for the three-dimensional lattice with different correlation radii of the disorder (corresponding values are pointed out), the bold curve indicates the GPR kinetics for the regular lattice. The initial charge separation radii  $r_0 = 3a$  (a) and  $r_0 = 5a$  (b) are assumed. The diagonal disorder value is taken to be  $\sigma = 4k_B T$  in calculations.

while the rate at later times of the kinetics approaches the case of the lattice with the uncorrelated disorder. This is in accord with the concept of the local energy disorder described in the Introduction. The initial kinetics originates from the charge pair, which recombines in a few jumps covering the initial charge separation distance. For the correlation radius larger than this initial separation distance, the main part of the GPR kinetics is close to that of the regular lattice. The long-time kinetics being determined by the recombination of the pairs of charges separated at larger distances than the correlation radius resembles the kinetics of the GPR in the lattice with the uncorrelated disorder.

Qualitatively these conclusions are independent of the dimensionality of the system. However, the effect resulting from the interplay between the correlation radius of the disorder and the initial separation distance of the charges is more expressed in three-dimensional systems (Fig. 6) than in the one-dimensional case (Fig. 5).

### V. DISCUSSION

Calculations of time dependence of the mean-squared displacement (see Figs. 3 and 4) qualitatively demonstrate the behavior similar to that obtained in noncorrelated disordered systems.<sup>24</sup> Three regimes corresponding to the regular diffusion at short times, the dispersive hopping regime at intermediate times, and finally the regular diffusion at long times, generally can be distinguished in disordered systems.<sup>37</sup> The correlation of the disorder mainly influences the time scale of the transition between these regimes. The larger the correlation radius, the later transition times are expected, while these times are shorter for larger system dimensions. The effect of the dimension of the system is caused by the difference in the possible diffusion pathways. Indeed, the one-path particle movement in one-dimensional systems and, thus, the absence of other possibilities for the particle to escape from its local position result in larger-cost movements of particles in this case. Therefore, the diffusion characteristic in Fig. 3 has no sharp switching region, and the diffusion manner approaches asymptotically the diffusion in the lattice with the uncorrelated disorder.

Bearing this in mind, the concept of the local disorder dependence of the extension (defined by radius  $R_p$ ) of the region, where the process under consideration takes place,

can be determined by the following equation:

$$\xi(R_p) = \frac{1}{2} \sqrt{\langle [\varepsilon(0) - \varepsilon(R_p)]^2 \rangle} = \sigma \sqrt{1 - \exp(-R_p/R_c)}. \quad (20)$$

Thus, for the distances much shorter than the correlation radius, i.e., for  $R_p \ll R_c$ , the effective width of the energy disorder is  $\xi(r) \ll \sigma$ , while for longer distances, when  $R_p \gg R_c$ , the disorder approaches the bulk value  $\xi(r) \rightarrow \sigma$ .

The GPR process evidently resembles the short-time behavior of the charge movement since it is driven by the Coulomb potential of its counterion. Thus, the GPR kinetics is caused by the competition between the initial charge separation distance and the radius of the correlation. Qualitatively, this competition effect is well distinguished by comparing the kinetics for different correlation radii and with the same radius of the initial charge separation as shown in Fig. 5 and Fig. 6.

The GPR kinetics performed recently claimed the value of the diagonal disorder in the films of poly-*N*-epoxypropylcarbazole to be equal to 0.04 eV.<sup>21</sup> This estimation is lower than 0.1 eV obtained for the similar system from the charge drift studies.<sup>36</sup> This difference can be attributed to the correlation effects of the diagonal disorder described above. Indeed, assuming that the GPR approximately takes place in a region  $R_p = 3$  to 5 of the lattice units, the correlation radius  $R_c$  has to be of the order of 17 to 28 lattice constants according to Eq. (21).

Another parameter determining the GPR kinetics is the initial distance of the charge separation. Evidently the overall GPR kinetics dramatically slows down by increasing the distance of the initial charge separation,  $r_0$ , turning out to be very similar to that for the regular lattice as soon as  $R_c \geq r_0$ , while the change in the correlation radius in the opposite region, when  $R_c < r_0$ , has the largest effect on the kinetics. Comparative studies of the kinetics with the fixed correlation radius and by changing the initial charge separation distance demonstrate the sensitivity of the very initial part of the kinetics. Thus, it becomes evident that both values, the correlation radius and the initial charge separation distance, cannot be determined from fitting the only experimental GPR kinetics, and the analysis of the additional data is needed. It can be obtained, for instance, from estimations of the quantum yield of the total charge separation in the presence of the external electric field. That value is mostly sensitive to  $r_0$ , the parameter of the initial charge separation, while the correlation of the disorder has a minor effect as it follows from the diffusive behavior of the particle. The experimental possibilities of determining the initial charge

separation by means of studies of the transient spectra in the presence of the external electric field were recently demonstrated.<sup>14</sup> This could be another option in determining that value.

The given analysis is qualitative since the time scale used for calculations was renormalized to the charge hopping rate. However, we have to admit that by determining the dimensional scale of time some uncertainties are still remaining since the scaling of the regular lattice is not independent of the time scaling used above. Indeed, by determining the rate of the excitation jump in the regular lattice (the time scaling rate) as

$$k_{\text{reg}} = \nu_0 \exp(-2\gamma a), \quad (21)$$

this value is also related to the dimensional scale of the lattice. Thus, by renormalizing the frequency scale  $\nu_0$ , the same value of the charge jump time can be obtained while rescaling the lattice size. However, the initial charge separation distance and the correlation radius of the disorder are not related to that scaling relationship, therefore, giving an independent effect on the GPR kinetics.

The other type of the electron transfer rate based on the Marcus theory of electron transfer can be used instead of the Miller-Abrahams expression. The concept of reorganization energy reduces the sharp exponential dependence on the electron transfer barrier. However, conclusions obtained in our consideration of the influence of the correlative disorder on the GPR qualitatively will remain.

## VI. CONCLUDING REMARKS

Here we introduce the concept of the local energy disorder, which is usually lower than the energy disorder in the bulk. The geminate pair recombination is predominantly caused by the local energy disorder, therefore, it carries much information about its correlation size. The geminate pair recombination analysis indicates that the disorder values are lower than those obtained from the mobility measurements. This feature of the local disorder is directly related to the correlations of the energy disorder. According to estimations, the correlation effect of the disorder extends over a size comparable to the extension of the motion of the charges in the recombination process in molecular photoconductors covering tens of angstroms.

## ACKNOWLEDGMENT

We are grateful for the support from the Lithuanian State Science and Studies Foundation.

<sup>1</sup>J. Burroughes, D. D. C. Bradley, A. Brown, R. Marks, K. Machay, R. Friend, P. Burns, and A. Holmes, *Nature (London)* **347**, 539 (1990).

<sup>2</sup>D. Brown and A. Heeger, *Appl. Phys. Lett.* **58**, 1982 (1991).

<sup>3</sup>F. Garnier, R. Hailaoui, A. Yassar, and P. Srivastava, *Science* **265**, 1684 (1994).

<sup>4</sup>D. Gundlach, Y. Lin, T. Jackson, and D. Schlom, *Appl. Phys. Lett.* **71**, 3853 (1997).

<sup>5</sup>G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789 (1995).

<sup>6</sup>S. Ducharme, J. C. Scott, R. J. Twieg, and W. E. Moerner, *Phys. Rev. Lett.* **66**, 1846 (1991).

- <sup>7</sup>K. Meerholz, B. L. Volodin, Sandalphon, B. Kippelen, and N. Peyghambarian, *Nature (London)* **371**, 497 (1994).
- <sup>8</sup>W. E. Moerner, S. M. Silence, F. Hache, and G. C. Bjorklund, *J. Opt. Soc. Am. B* **11**, 320 (1994).
- <sup>9</sup>D. Van Steenwinckel, E. Hendrickx, and A. Persoons, *J. Chem. Phys.* **114**, 9557 (2001).
- <sup>10</sup>T. Shimmel, G. Denninger, W. Ries, J. Voit, M. Schwoerer, W. Schoepe, and H. Naarmann, *Synth. Met.* **28**, 1 (1989).
- <sup>11</sup>A. Ruseckas, V. Gulbinas, V. Sundström, A. Undzenas, and L. Valkunas, *J. Phys. Chem. B* **102**, 7365 (1998).
- <sup>12</sup>D. Abramavicius, V. Gulbinas, and L. Valkunas, *Synth. Met.* **109**, 39 (2000).
- <sup>13</sup>L. J. Rothberg, M. Yan, A. W. P. Fung, T. M. Jedju, E. W. Kwock, and M. E. Galvin, *Synth. Met.* **84**, 537 (1997).
- <sup>14</sup>V. Gulbinas, R. Kananavicius, L. Valkunas, and H. Bässler, *Phys. Rev. B* **66**, 233203 (2002).
- <sup>15</sup>L. Valkunas, V. Gulbinas, and S. Jursenas, *J. Lumin.* **121**, 87 (2000).
- <sup>16</sup>K. Watanabe, T. Asaki, and H. Masuhara, *J. Phys. Chem. B* **101**, 5131 (1997).
- <sup>17</sup>D. Abramavicius, V. Gulbinas, A. Ruseckas, A. Undzenas, and L. Valkunas, *J. Chem. Phys.* **111**, 5611 (1999).
- <sup>18</sup>D. Abramavicius, V. Gulbinas, and L. Valkunas, *Chem. Phys. Lett.* **368**, 480 (2003).
- <sup>19</sup>D. Abramavicius, V. Gulbinas, and L. Valkunas, *Mol. Cryst. Liq. Cryst.* **355**, 127 (2001).
- <sup>20</sup>H. Bässler, *Macromol. Chem. Macromol. Symp.* **37**, 1 (1990).
- <sup>21</sup>D. Abramavicius, V. Gulbinas, A. Ruseckas, A. Undzenas, and L. Valkunas, *Mol. Cryst. Liq. Cryst.* **324**, 275 (1998).
- <sup>22</sup>N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1971).
- <sup>23</sup>J. M. Ziman, *Models of Disorder: The Theoretical Physics of Homogeneously Disordered Systems* (Cambridge University Press, Cambridge, 1979).
- <sup>24</sup>R. Brown and B. Esser, *Philos. Mag. B* **72**, 125 (1995).
- <sup>25</sup>D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, revised 2nd ed. (Taylor and Francis, London, 1994).
- <sup>26</sup>M. Pope and C. E. Swenberg, *Electron Processes in Organic Crystals* (Oxford University Press, New York, 1999).
- <sup>27</sup>Y. N. Garstein and E. M. Conwell, *Chem. Phys. Lett.* **245**, 351 (1995).
- <sup>28</sup>Y. N. Garstein and E. M. Conwell, *Phys. Rev. B* **51**, 6947 (1995).
- <sup>29</sup>D. H. Dunlap, P. E. Parris, and V. M. Kenkre, *Phys. Rev. Lett.* **77**, 542 (1996).
- <sup>30</sup>R. H. Young, *Philos. Mag. B* **72**, 435 (1995).
- <sup>31</sup>P. E. Parris, V. M. Kenkre, and D. H. Dunlap, *Phys. Rev. Lett.* **87**, 126601 (2001).
- <sup>32</sup>R. Kubo, M. Toda, N. Hashitsume, *Statistical Physics II: Non-equilibrium Statistical Mechanics* (Springer-Verlag, Berlin, 1985).
- <sup>33</sup>A. Miller and E. Abrahams, *Phys. Rev.* **120**, 745 (1992).
- <sup>34</sup>D. Emin, *Phys. Rev. Lett.* **32**, 303 (1974).
- <sup>35</sup>D. H. Dunlap, *Phys. Rev. B* **52**, 939 (1995).
- <sup>36</sup>H. Bässler, *Phys. Status Solidi B* **175**, 15 (1993).
- <sup>37</sup>I. Rips and J. Jortner, *Chem. Phys.* **128**, 237 (1988).