Diffusion in a disordered system with a dipole-dipole interaction

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Random walks in a disordered medium with a dipole-dipole transport are studied. It is proved that the long-time asymptotic behavior is of a diffusion character and the diffusion coefficient is determined. The analysis is based on a new, efficient, numerical-modeling method employing direct calculation of the Fourier transform of the propagator and periodic continuation of the system without periodic continuation of the initial condition. © *1995 American Institute of Physics.*

1. Dipole transport in the problem of random walk in disordered media (RWDM) occurs during the migration of localized excitons and spin-polarization transport. The most detailed measurements have been performed for depolarization of fluorescence[1,2] and by the methods of time-varying selective laser spectroscopy,[3,4] stimulated four-wave mixing,[5] and β-NMR (Ref. 6). Different analytical[4,7–13] and numerical[8,14,15] approaches have been used for the theoretical analysis. In particular, in Ref. 11 a general method was developed for calculating the propagator at moderately long times. At present, the most important and complicated question is that of the long-time asymptotic behavior of the process. Although the formulation of the diffusion hypothesis[10,13] is now apparently generally accepted, it has never been proved either theoretically or experimentally. The experimental results of Refs. 4 and 5, where an attempt was made to measure the diffusion coefficient D, differ substantially. The scatter in the values of D, obtained in different theoretical approaches, is even greater (see the discussion in Ref. 13). Here the agreement between the measurements obtained in Ref. 5 and the calculations in Ref. 12 is an exception.

In the present paper we perform a theoretical analysis of the long-time asymptotic behavior for the standard RWDM model with dipole transport. We have formulated a new numerical-modeling method based on the procedure of periodic continuation of the system and we investigated with the aid of this method the Fourier transform $P(\mathbf{k},t)$ of the propagator, which is the observed quantity in experiments on four-wave mixing.[5] As a check, the results were calculated by using two different computer programs and the method was tested on an asymptotically exactly solvable model of dipole transport.[16]

The results obtained yield, in particular, a new value for the diffusion coefficient D. Therefore, the agreement obtained between the values of D in Refs. 5 and 12 is accidental, and the disagreement between this result and our result is apparently due to the fact that in Ref. 5 the very important control measurement of the dependence of the results on the wave vector was not performed (which the authors themselves noted) and the theoretical computational method employed in Ref. 12 has only a heuristic and not a math-

ematical estimate of the rate of convergence and therefore of the accuracy.

The value which we obtained for D falls between the values corresponding to the experiments of Refs. 4 and 5. This shows that new, more accurate measurements must be performed.

2. The migration of localized excitations over a system of randomly distributed (in a regular lattice) impurities is described by the kinetic equation

$$\dot{p}_{ij} = -\sum_m (\nu_{mi} p_{ij} - \nu_{im} p_{mj}), \quad p_{ij}(t=0) = \delta_{ij}, \tag{1}$$

where $p_{ij}(t)$ is the probability of observing an excitation at the time t at the ith impurity site, if it was first observed at the site j. In the standard model of dipole transport $\nu_{ij} = \nu_0 r_0^6 / |\mathbf{r}_i - \mathbf{r}_j|^6$, where ν_0 is the transition rate corresponding to the minimum distance r_0 between the impurities, and $\mathbf{r}_i$ is the radius vector of the ith impurity. The arrangement of the impurities is assumed to be uncorrelated and their concentration is $c \ll 1$. In the limit of low concentrations the characteristic time scale is given by the Förster constant $\beta = (16/9)\pi^3 (r_0^3/\Omega)^2 c^2 \nu_0$, where Ω is the volume of a unit cell. Parametrically, β is identical to the transport rate ν_{ij} over an average distance $\bar{r} = r_0 c^{-1/3}$. In the numerical modeling we considered a simple cubic lattice with a unit cell of size r_0. We singled out in the lattice a cube with an edge $R \gg r_0$, prescribed at the lattice sites a pseudorandom configuration of $N = c(R/r_0)^3$ impurities, and then periodically continued this configuration [but not the initial condition for Eq. (1)] to the entire infinite lattice. A similar method of periodic continuation was employed previously in Ref. 17 for other purposes.

We introduce the quantity

$$\rho_j(\mathbf{k},t) = \sum_m p_{jm}(t) \exp[i\mathbf{k}(\mathbf{r}_m - \mathbf{r}_j)]. \tag{2}$$

The configurational average $\langle \rho_j(\mathbf{k},t) \rangle = P(\mathbf{k},t)$ is the Fourier transform of the propagator and is the directly observed quantity in four-wave mixing experiments. Combining Eqs. (1) and (2), we find that if $\mathbf{r}_i - \mathbf{r}_j = R\mathbf{m}$, where $\mathbf{m} \in Z^3$, then $\rho_i = \rho_j$. Therefore, it is sufficient to solve the finite system of equations

$$\dot{\rho}_i = -(A(\mathbf{k})\rho)_i = -\sum_{j=1}^{N} [W_{ji}(0)\rho_i - W_{ij}(\mathbf{k})\rho_j], \quad \rho_i(\mathbf{k}, t=0) = 1, \tag{3}$$

where i and j now enumerate the sites in the periodicity cube, and

$$W_{ij}(\mathbf{k}) = \sum_{m \in Z^3} \nu_0 r_0^6 |\mathbf{r}_j - \mathbf{r}_i - \mathbf{m}R|^{-6} \exp[i\mathbf{k}(\mathbf{r}_j - \mathbf{r}_i - \mathbf{m}R)]. \tag{4}$$

3. The finite system (3) for small values of $|\mathbf{k}|$ gives the basic information about the asymptotic behavior of the process at long times. We note that by confining attention to small values of $|\mathbf{k}|$ we substantially speed up the calculations, since for $\mathbf{k}=0$ the initial vector (3) is the principal eigenvector of the generator $A(\mathbf{k}=0)$. In the numerical analysis we study the quantity

$$P(\mathbf{k},t|N)=\frac{1}{N}\sum_{i=1}^{N}\rho_i=\langle\bar{0}|\exp[-A(\mathbf{k})t]|\bar{0}\rangle, \tag{5}$$

where $\langle i|\bar{0}\rangle=1/\sqrt{N}$ is the average over all configurations obtained from a given configuration by changing the "central" site. As N increases, $P(\mathbf{k},\ t|N)$ approaches $P(\mathbf{k},t)$. Using the spectral expansion of the Hermitian operator $A(\mathbf{k})$, we find that

$$P(\mathbf{k},t|N)=\sum_{\mu=0}^{N-1}|\langle\mu|\bar{0}\rangle|^2\exp(-a_\mu(\mathbf{k})t);\quad A(\mathbf{k})|\mu\rangle=a_\mu(\mathbf{k})|\mu\rangle. \tag{6}$$

The lowest eigenvalue $a_0(\mathbf{k}\to 0)$ is unique, and $|\langle 0|\bar{0}\rangle|^2=1+O(k^2)$. Introducing the projection operators $\pi=|\bar{0}\rangle\langle\bar{0}|$ and $\bar{\pi}=1-\pi$, we obtain

$$a_0(\mathbf{k})=\langle\bar{0}|A(\mathbf{k})|\bar{0}\rangle+\langle\bar{0}|A(\mathbf{k})\bar{\pi}\,\frac{1}{a_0(\mathbf{k})-\bar{\pi}A(\mathbf{k})\bar{\pi}}\,\bar{\pi}A(\mathbf{k})|\bar{0}\rangle. \tag{7}$$

It thus follows that

$$a_0(\mathbf{k})=D_{\alpha\beta}k_\alpha k_\beta-\sigma k^3+O(k^4)=\bar{a}_0(\mathbf{k})+O(k^4), \tag{8}$$

and the coefficient $\sigma=(\pi^2/12)cr_0^3\nu_0$ is determined completely by the first term in Eq. (7) and can be calculated, for example, by the Poisson–Ewald method.[16] It is convenient to represent the diffusion tensor in the form $D_{\alpha\beta}=(\kappa_{\alpha\beta}/6)\bar{r}^2\beta$. Since the system is isotropic, $D_{\alpha\beta}\to D\,\delta_{\alpha\beta}$ and $\kappa_{\alpha\beta}\to\kappa\delta_{\alpha\beta}$ as $N\to\infty$. To calculate $a_0(\mathbf{k})$ we solved the system of equations (3) numerically, calculated $P(\mathbf{k},\ t|N)$ and approximated it by using the formula

$$P(\mathbf{k},t|N)=\exp(-\bar{a}_0(\mathbf{k})(t+b/\beta))+(\bar{r}k)^2 f\exp(-a_1 t),\quad a_1=(2\pi/R)^2D\kappa_1, \tag{9}$$

and sought values of N and t for which the $\kappa_{\alpha\beta}$, b, f, and κ_1 no longer depended on N, t, $\mathbf{k}$, and c. This procedure is more efficient than direct implementation of Eq. (7).

As a check, the diffusion coefficient was also determined by a different (more rapidly converging) method which follows from the relation

$$\sum_{ij}\rho_i^*A_{ij}(\mathbf{k})\rho_j/\sum_i|\rho_i|^2\to\bar{a}_0(\mathbf{k})\quad\text{as } t\to\infty. \tag{10}$$

4. The proposed method was tested on known, exactly solvable models. In the model of isotropic random walk (MIRW) the propagator is determined by the equation[16]

$$\dot{P}_{xy}=-\sum_z\left[\nu_{zx}\xi_x P_{xy}-\nu_{xz}\xi_z P_{zy}\right],\quad P_{xy}(t=0)=\delta_{xy}, \tag{11}$$

where $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ run through the lattice Z^3, $\nu_{xz}=\nu_{zx}=\upsilon_{z-x,0}$, $\Sigma_x\nu_{x0}x^2<+\infty$, $\{\xi_x\}$ is a set of independent, positive, identically distributed, random quantities with a sufficient number of finite inverse moments.

We now consider a periodic system, leaving the quantities ξ_x independent, when $\mathbf{x}$ runs through the sites of a cube V, centered at zero, with edge R, and setting $\xi_{x+Ry}=\xi_x$ for an arbitrary integer vector $\mathbf{y}$.

By analogy with Eq. (2), we introduce the quantity

$$\rho_x(\mathbf{k},t)=\sum_y P_{xy}(t)\exp[i\mathbf{k}(\mathbf{x}-\mathbf{y})], \tag{12}$$

for which $\rho_{x+Ry}=\rho_x$ and which satisfies the finite system of equations

$$\dot{\rho}_x=-(A(\mathbf{k})\xi\rho)_x=-\sum_{z\in V}[W_{zx}(0)\xi_x\rho_x-W_{xz}(\mathbf{k})\xi_z\rho_z], \quad \rho_x(\mathbf{k},t=0)=1, \tag{13}$$

where $\mathbf{x}$ and $\mathbf{z}$ now lie inside the periodicity cube, and

$$W_{xz}(\mathbf{k})=\sum_{m\in Z^3}\nu_{z,x+mR}\exp[i\mathbf{k}(\mathbf{z}-\mathbf{x}-\mathbf{m}R)]. \tag{14}$$

In the MIRW the quantity $P(\mathbf{k}, t|N)$ [see Eq. (5)] corresponds to

$$\rho_1(\mathbf{k},t)\equiv\langle 0|\exp(-A\xi t)\frac{\kappa_0}{\xi}|0\rangle=\langle 0|\sqrt{\frac{\kappa_0}{\xi}}\exp(-\sqrt{\xi}A\sqrt{\xi}t)\sqrt{\frac{\kappa_0}{\xi}}|0\rangle, \tag{15}$$

$$\langle\mathbf{x}|0\rangle=\frac{1}{\sqrt{N}}; \quad \frac{1}{\kappa_0}=\frac{1}{N}\sum_{x\in V}\frac{1}{\xi_x}; \quad N=R^3.$$

The minimum eigenvalue of the operator $\sqrt{\xi}A\sqrt{\xi}$ is determined by an expression identical to Eq. (7), where $\langle x|\overline{0}\rangle=\sqrt{\kappa_0/(\xi N)}$, with the substitution $A\to\sqrt{\xi}A\sqrt{\xi}$. We note that the second term in Eq. (7) is now a fourth-order term in k which does not contribute to the diffusion coefficient. From the first term we find

$$D=\kappa_0 D_0, \quad D_0=(1/6)\sum_x x^2\nu_{x0}. \tag{16}$$

Here D_0 is a diffusion coefficient on a regular lattice. This answer for large N agrees very well with the expression obtained in Ref. 16 for the diffusion coefficient:

$$D=\kappa D_0; \quad \frac{1}{\kappa}=\left\langle\frac{1}{\xi_0}\right\rangle,$$

where $\langle\ldots\rangle$ is an ensemble average. This means that in the present model the limits $N\to\infty$ and $t\to\infty$ are interchangeable and that the relative accuracy in determining D from Eq. (16) is of the order of $1/\sqrt{N}$. The interchangeability of these limits can also be proved similarly for all models considered in Ref. 18. The numerical algorithm for solving the systems (3) and (13) was checked for MIRW with ξ distributed uniformly on the interval (1, 6), and $\langle 1/\xi\rangle\approx 10/\langle\xi\rangle$. As a result, the value obtained for the diffusion coefficient agreed with Eq. (16) within 10^{-6}.

5. The proposed method models adequately the disordered system (1) as long as the diffusion radius $r_D=\sqrt{6Dt}$ satisfies the condition

$$\varepsilon_D=(2r_D/R)^2=4\kappa\beta t/N^{2/3}<1. \tag{17}$$

In the opposite limit, when $\varepsilon_D > 1$, we obtain the model of transport in a crystal with a complex large unit cell that contains N atoms. For small $c \leqslant 0.1$ and $k \leqslant 0.1 \cdot 2\pi/R$ the value of κ stabilizes within 8% near $\kappa = 0.305$ for all $\beta t \geqslant 10$ and $N \geqslant 150$ and changes monotonically as t and N increase or k and c decrease. For the highest value employed $N \approx 2000$ the criterion (17) holds up to $\beta t_{\max} \approx 130$; for $c = 0.05$ we have the value $\kappa = 0.301(4)$, and $a_1 \approx (2\pi/R)^2 D$. It thus follows that in our main problem (1) and (3), just as in the exactly solvable models,[18] the limits are interchangeable

$$\lim_{t\to\infty}\lim_{N\to\infty} D(t,N) = \lim_{N\to\infty}\lim_{t\to\infty} D(t,N) = D$$

and the long-term asymptotic behavior in the problem under study is diffusion.

For comparison, we point out that in the GAF theory[9] $\kappa_{\mathrm{GAF}} = 0.315$. The phenomenological theory of Refs. 10 and 13 for calculating D employs the Scher–Lax formula[7] and gives $\kappa = \kappa_{\mathrm{SL}} = 0.373$. The modification given in Refs. 12 and 13 of the GAF theory (developed, specifically, for extending the theory to one- and two-dimensional systems) gives $\kappa = \kappa_D = 0.186$, and in Ref. 19 the value $\kappa = \kappa_{\mathrm{GJ}} = 0.49$ was obtained. The experimental data of Ref.4 are consistent with the value $\kappa = \kappa_{\mathrm{SL}}$. The result presented in Ref. 5 corresponds to $\kappa = \kappa_{\mathrm{GKM}} = 0.147(23)$, which gives, when the term σk^3 from Eq. (8) is taken into account correctly, the value $\tilde{\kappa}_{\mathrm{GKM}} = 0.168(26)$ (Ref. 12). Here we ignore the correction for the dipole anisotropy of the transition rates, which amounts to about 10%.[12,13]

We note that the long-term asymptotic behavior for $P(\mathbf{k},t)$ starts for much lower values of βt than for the autocorrelation function $\langle P_{00}(t)\rangle$. This property is realized in all known methods for performing analytical calculations[13,20] and in numerical modeling. This makes it possible to limit the analysis to comparatively small values, $N \approx 500$, to obtain results with adequate accuracy and is one of the most important advantages of our method.

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