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# Frequency Analysis of Diffusion in 1D Systems with Energy and Spatial Disorder

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**Summary:** We have analyzed the frequency-dependent features of diffusive transport of mobile carriers by hopping in a disordered environment composed of varying energy barriers. We developed a simple approach based on the solution of the master equation for a gradient of concentration (chemical potential) under a sinusoidal perturbation. This method extends the well-known result of the steady state case, $D=\{1/\Gamma\}^{-1}$, to the frequency domain. The results of our calculations are in agreement with the approximate analytical solution of the CTRW formalism. We are able to determine the onset of frequency-dependent diffusivity in terms of probabilities of highest energy barriers.

**Keywords:** ac conductivity; activation energy; diffusion; dispersive transport; hopping

## Introduction

Electronically conducting polymers possess a unique combination of physical and chemical properties making them prospective materials for numerous applications such as in batteries and supercapacitors, sensors and ion release systems. In these applications the organic conductor is embedded in a secondary, ionically conducting phase that shields the electric fields beyond the nanoscopic scale, so that diffusion of electrons becomes the dominant transport mechanism. It is well known that, in the presence of a severe structural disorder, the transport by hopping between localized states introduces dispersion- or frequency-dependent mechanisms. Recently it has been shown that electronically conducting polymers permeated with electrolyte display those effects at moderately high frequencies [1,2]. Therefore, for a realistic description of devices, it is required to extend Fickean diffusion models to account for the dependence of the local diffusivity on factors such as concentration and frequency. Here we describe a first step towards that goal,

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providing a simple method to determine the local diffusivity on a random energy-barrier model system.

## Method

We consider a finite chain of $N$ sites with randomly distributed energy barriers between them. A particle probability current dependent on time flows into site 1 and is extracted at site $N$. The rate equations governing the kinetics of hopping have the form:

$$\frac{\mathrm{d}}{\mathrm{d}t} P_i(t) = \Gamma_{i+1,i} P_{i+1}(t) + \Gamma_{i-1,i} P_{i-1}(t) - \left(\Gamma_{i,i+1} + \Gamma_{i,i-1}\right) P_i(t) \tag{1}$$

where $P_i(t)$ are the site occupation probabilities, and the transition rates are thermally activated with an activation energy related to the height of the barrier to be overcome, $\Gamma = \Gamma_0\, \mathrm{e}^{-\beta E_i}$, where $\beta = 1/k_\mathrm{B}T$. This method deals with noninteracting particles, i.e. neither is Coulomb repulsion taken into account nor is self-exclusion regarded; however, these aspects can be readily incorporated into the formalism.

In order to derive the value of the diffusion coefficient, $D$, we take Fick's first law, $I = -D\nabla n$, where $I$ is the particle current and $n$ the concentration of particles. Then we calculate the diffusion coefficient from the gradient of particle probability at a given current input. We take this gradient from the master equation (1) linearized for a periodic perturbation ($\mathrm{d}/\mathrm{d}t \to \mathrm{i}\omega$, where $\omega$ is the angular frequency). So we get the frequency-dependent diffusion coefficient in one dimension:

$$D(\omega) = \mathrm{Re}\left[\frac{IN}{P_1 - P_N}\right] \tag{2}$$

For low frequencies, this method gives the well-known value $D(\omega = 0) = \left\{1/\Gamma_{i,i+1}\right\}^{-1}$ [3].

## Results

In Fig. 1 the results obtained from numerical calculation of Eq. (2) for a chain of 100 sites are compared with the analytical equation of the continuous time random walk (CTRW) approximation, which takes the form $D(\omega)/D(0) = \left[\mathrm{i}\,\omega/\omega_\mathrm{m}\right]/\log(1+\mathrm{i}\,\omega/\omega_\mathrm{m})$ [4], where $\omega_\mathrm{m} = \sigma(0)p(E_\mathrm{c})/\beta$, $p(E_\mathrm{c})$ being the probability of the highest energy barriers in the distribution. Figure 1 shows that our simple method based on an extension of Fick's law is in agreement with the more sophisticated approaches available in the literature [4,5]. Therefore we obtain the main features of frequency-dependent diffusivity in a random energy barrier system [4], which can be summarized as follows.

The diffusivity becomes independent of the energy barrier probability distribution at low temperatures. The diffusivity becomes frequency-dependent when the frequency is of the order of $\omega_m$ or, in other words, the probability of the highest barrier to be overcome determines the onset of frequency-dependent diffusivity [5]. Then the most important contribution to the dc conductivity is due to the highest barrier, so that a greater part of the barriers become irrelevant to the low-frequency diffusivity. Since the frequency axes in Fig. 1 have not been rescaled in any way, we note that our method describes quite correctly the onset of frequency-dependent diffusivity.

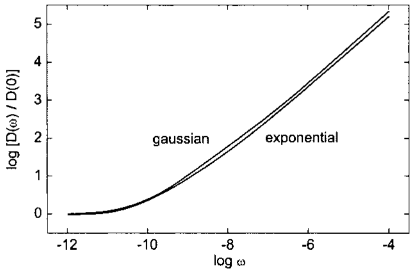

Figure 1. Log-log plot of numerical results of low-temperature normalized diffusivity in 1D system as a function of the frequency for two different energy-barrier distributions. Numerical results based on Eq. (2) (points) are compared with the CTRW approximation (lines).

## Conclusions

We suggested a new and simple procedure to calculate the frequency-dependent diffusion coefficient in one dimension, which enables the application of Fick's law in the analysis of electron transport in organic conductors.

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