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Electronic transport in disordered organic and inorganic semiconductors

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Abstract

It is shown that theoretical methods developed for a description of hopping transport in disordered inorganic solids can be also successfully applied to a description of hopping transport in organic disordered materials, such as conjugated polymers, molecularly doped polymers and organic glasses. While the density of localized states (DOS) in inorganic materials is believed to be exponential, a Gaussian DOS has been suggested for organic disordered materials. The most powerful and rigorous theoretical method for the description of variable-range hopping (VRH) in the exponential DOS is based on percolation theory. We show that this percolation approach is also valid for systems with a Gaussian DOS, thus being universal for inorganic and organic disordered materials. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In various disordered inorganic and organic materials, transport of charge carriers at low temperatures is related to incoherent hopping between localized states. Efficient theoretical methods have been developed for inorganic systems. Among the most successful methods, one can note the percolation approach and the approach based on the concept of the transport energy. However, these methods are rarely applied to organic systems. On the contrary, a description of hopping transport in organic materials is often based on the ensemble averaging of hopping rates, which is known to be quite inappropriate for the description of hopping processes. Such a situation is unsatisfactory, since the physics of hopping processes in organic and inorganic solids and the basic models for their description are rather similar [1,2]. In both cases it is assumed that the hopping rate of a charged carrier Γ_{ij} between two localized states *i* and *j* with energies ε_i and ε_j separated by distance r_{ij} is determined by the standard expression [1]

$$\Gamma_{ij} = \Gamma_0 \exp\left\{-\frac{2r_{ij}}{a} - \frac{E_{ij}}{kT}\right\} \equiv \Gamma_0 \exp\{-\xi_{ij}\}, \quad (1)$$

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where Γ_0 is the prefactor, *a* is the localization length, E_{ij} is determined as

$$E_{ij} = \{|\varepsilon_i - \mu| + |\varepsilon_j - \mu| + |\varepsilon_i - \varepsilon_j|\}/2$$
(2)

and μ is the equilibrium Fermi level. It is also usually assumed that the spatial positions of localized states and their energies are at random. The main difference between models for inorganic and organic materials is the choice of the density of localized states (DOS), $g(\varepsilon)$. While for inorganic systems, like amorphous semiconductors, one usually assumes an exponential DOS, for organic materials it is believed that DOS is Gaussian [2]:

$$g(\varepsilon) = \frac{N}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{\varepsilon^2}{2\sigma^2}\right\},\tag{3}$$

where N is the total concentration of localized states.

One of the most fruitful ideas in the field of hopping transport was put forward by Miller and Abrahams [3] who reduced the hopping problem to that of calculating the conductivity of a random network of resistances. According to this approach, the local resistance R_{ij} between sites *i* and *j* corresponds to the inverse hopping rate Γ_{ij} : $R_{ij} = kT/(e^2\Gamma_{ij})$. For one-dimensional systems in which resistances are connected sequentially, the exact result for hopping conductivity can be obtained by averaging the inverse rates or the hopping times [4]. In two- and three-dimensional systems the most advanced method for calculating the hopping conductivity is based on percolation theory [1]. The corresponding approach for the variable-range hopping (VRH) in an exponential DOS was suggested by Grünewald and Thomas [5]. Recently a somewhat modified approach to the same problem was published by Vissenberg and Matters [6]. Being most rigorous, the percolation approach is rather elaborate for calculations and more transparent treatments of the VRH were always searched for. One of the most clear and attractive theoretical approaches to the calculation of temperature-dependent transport coefficients in inorganic disordered solids with an exponential DOS is based on the concept of the transport energy [7–9]. This approach has been extended to systems with a Gaussian DOS [10] and it was recently successfully applied to the calculation of the temperature-dependent carrier drift mobility in organic disordered systems [11]. In [11] we considered non-interacting charge carriers and calculated the temperature dependence of the dc conductivity G(T) in a form

$$G(T) \propto \exp\left\{-C\left(\frac{\sigma}{kT}\right)^2\right\},$$
 (4)

with $C \approx 0.45$, which is very close to the result obtained earlier by computer simulations [12].

Although based on transparent arguments, the method of the transport energy [7–11] is not rigorous. In this report we extend for the first time the consistent percolation approach to organic disordered materials with a rapidly varying Gaussian DOS described by Eq. (3).

2. Percolation theory for hopping in a Gaussian DOS

The standard formulation of the percolation approach is the following. Let us choose some value of the transition rate $\Gamma = \Gamma_0 \exp(-\xi)$ and assume that the bond between two sites i and jexists if $\Gamma_{ii} > \Gamma$ (or equivalently if $\xi_{ii} < \xi$). Then the bond concentration is a function of ξ and it increases with increasing ξ . At some $\xi = \xi_c$ an infinite percolation cluster of interconnected bonds appears, which is responsible for the hopping motion of charged carriers in the dc regime. The critical value ξ_c determines the exponential temperature and concentration dependences of the transport coefficients. According to percolation theory, the infinite cluster appears when the average number of bonds per site $\langle B \rangle$ attains some critical value B_c . Numerical calculations for the percolation threshold in a system of random sites give $B_c \approx 2.7$ [1]. The appropriate bonding criterion for the percolation threshold has the form [13]

$$\langle B(\varepsilon) \rangle = B_{\rm c},$$
 (5)

where we take into account that the number of bonds per site can be energy dependent. Indeed, the number of bonds $B(\varepsilon_i)$ per site with energy ε_i is defined by

$$B(\varepsilon_i) = \int \mathrm{d}\varepsilon_j g(\varepsilon_j) \int \mathrm{d}\mathbf{r_{ij}} \theta \left\{ \xi - \frac{2r_{ij}}{a} - \frac{E_{ij}}{kT} \right\} \tag{6}$$

so that $B(\varepsilon)$ is energy dependent even if the DOS near the Fermi level is constant. The variation of $B(\varepsilon)$ with energy is accounted for by using the averaging procedure [14]

$$\langle B(\varepsilon) \rangle = \frac{\int d\varepsilon g(\varepsilon) B^2(\varepsilon)}{\int d\varepsilon g(\varepsilon) B(\varepsilon)},\tag{7}$$

where it is taken into account that at a given energy ε , the probability for a bond to belong to the infinite cluster is proportional not only to the DOS but also to the number of bonds $B(\varepsilon)$. The bonding criterion determines the percolation threshold $\xi = \xi_c$ and hence the main exponential factor for the conductivity,

$$G = G_0 \exp(-\xi_c). \tag{8}$$

In what follows, we apply the described procedure to calculate the dc conductivity in a Gaussian DOS for three-dimensional systems. After straightforward, though rather elaborate calculations, we obtain from Eqs. (3), ((5)-(7)) the exponent for the conductivity

$$-\xi_{\rm c} = \frac{\mu - \varepsilon_{\rm t}}{kT},\tag{9}$$

where

$$\varepsilon_{\rm t} = -\sqrt{2}\sigma \ln^{1/2} \left\{ \frac{\beta N a^3}{s_{\rm c}^4} \left(\frac{\sigma}{kT}\right)^3 \right\} \tag{10}$$

with $\beta \approx 0.35/(2\sqrt{2B_c}) \approx 0.045$ and the quantity s_c determined by the self-consistent equation

$$s_{\rm c} = -\ln^{1/2} \left\{ \frac{\beta N a^3}{s_{\rm c}^4} \left(\frac{\sigma}{kT} \right)^3 \right\}. \tag{11}$$

The numerator in Eq. (9) is equal to the energy separation between the energy ε_t and the Fermi level. Therefore the energy ε_t can be called the transport energy. It follows from Eqs. (10) and (11) that the parameter s_c and hence the transport energy ε_t only weakly (logarithmically) depend on temperature. On the other hand, the Fermi level μ is generally strongly temperature dependent, being determined by the equation

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}\varepsilon g(\varepsilon)}{1 + \exp((\varepsilon - \mu)/kT)} = n, \tag{12}$$

where *n* is the carrier concentration. At low *n*, one obtains [15]

$$\mu = -\frac{1}{2} \left(\frac{\sigma^2}{kT} \right) - kT \ln\left(\frac{N}{n} \right).$$
(13)

The last term on the right-hand side in Eq. (13) determines a temperature-independent contribution to the conductivity exponent, so that if the temperature variation of the conductivity is described by using a temperature-dependent activation energy, the latter is not the distance between the transport energy and μ but contains only the part that non-linearly varies with temperature. Using Eqs. (8)–(13), one obtains the dependence of the conductivity on the parameters σ/kT and Na^3 . The numerical solution of these equations gives for the temperature dependence of the conductivity Eq. (4) with $C \cong 0.44$ for $Na^3 = 0.001$ and $C \cong 0.38$ for $Na^3 = 0.02$. These values are valid for σ/kT in the interval between 1 and 100. Our previous calculations based on the transport-energy approach [11] give Eq. (4) with $C \cong 0.46$ for $Na^3 = 0.001$ and $C \approx 0.38$ for $Na^3 = 0.02$, in excellent agreement with the percolation approach used in this work.

3. Conclusions

Our results show that the standard percolation approach developed for the description of incoherent hopping transport in inorganic systems can also be successfully applied to the description of hopping transport of charge carriers in organic disordered materials. Calculations within the percolation approach give results in excellent agreement with those obtained by using a more transparent, though less rigorous, approach based on the concept of transport energy [11].

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References

- B.I. Shklovskii, A.L. Efros, Electronic Properties of Doped Semiconductors, Springer, Heidelberg, 1984.
- [2] H. Bässler, Phys. Status Solidi B 175 (1993) 15.
- [3] A. Miller, E. Abrahams, Phys. Rev. 128 (1960) 745.
- [4] K.W. Kehr, T. Wichmann, Mater. Sci. Forum 223&224 (1996) 151.
- [5] M. Grünewald, P. Thomas, Phys. Status Solidi B 94 (1979) 125.
- [6] M.C.J.M. Vissenberg, M. Matters, Phys. Rev. B 57 (1998) 12964.
- [7] D. Monroe, Phys. Rev. Lett. 54 (1985) 146.
- [8] F. Shapiro, D. Adler, J. Non-Cryst. Solids 74 (1985) 189.

- [9] S.D. Baranovskii, P. Thomas, G.J. Adriaenssens, J. Non-Cryst. Solids 190 (1995) 283.
- [10] S.D. Baranovskii, T. Faber, F. Hensel, P. Thomas, J. Phys.: Condens. Matter 9 (1997) 2699.
- [11] S.D. Baranovskii, H. Cordes, F. Hensel, G. Leising, Phys. Rev. B 62 (2000) 13081.
- [12] G. Schönherr, H. Bässler, M. Silver, Philos. Mag. B 44 (1981) 369.
- [13] V.L. Bonch-Bruevich, I.P. Zvyagin, R. Keiper, A.G. Mironov, R. Enderlein, B. Esser, Electronentheorie ungeordneter Halbleiter, Deutscher Verlag der Wissenschaften, Berlin, 1984.
- [14] M. Pollak, J. Non-Cryst. Solids 11 (1972) 1.
- [15] I.P. Zvyagin, A.V. Plyukhin, Moscow Univ. Phys. Bull. 45 (1990) 84.