The effect of filling on the low-temperature energy diffusion in disordered hopping systems

1996 J. Phys.: Condens. Matter 8 L637

(http://iopscience.iop.org/0953-8984/8/43/002)

J. Phys.: Condens. Matter **8** (1996) L637–L642. Printed in the UK

LETTER TO THE EDITOR

The effect of filling on the low-temperature energy diffusion in disordered hopping systems

V I Arkhipov† and G J Adriaenssens

Laboratorium voor Halfgeleiderfysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Heverlee-Leuven, Belgium

Received 5 August 1996

Abstract. The low-temperature energy relaxation of charge carriers in a disordered hopping system is considered, taking into account the filling of hopping sites by localized carriers. A non-linear equation for the occupation probability is derived and solved under the condition of a constant total density of excited carriers. A characteristic time for the appearance of a quasi-Fermi level is estimated.

The energy relaxation of charge carriers and optical excitations in disordered hopping systems that are characterized by a broad energy distribution of hopping sites is a problem of current interest in the study of both organic and inorganic disordered materials [1–5]. This process is shown to be responsible for such phenomena as the time-dependent red-shift in photoluminescence spectra in amorphous semiconductors [1] and conjugated polymers [3, 6, 7], low-temperature carrier recombination and photoconductivity [2, 5], high-field carrier transport at low temperatures [8] etc. A very important characteristic feature of low-temperature relaxations is that only jumps to deeper energies are allowed and that, consequently, the energy distribution of localized carriers always remains in non-equilibrium. As long as the total density of hopping sites is finite, localized states belonging to the deep tail of the distribution will be sooner or later filled by carriers. At longer times this filling will strongly affect the relaxation kinetics. Thus, independently of the level of initial excitation, the filling effect should be taken into account when the low-temperature kinetics of carriers in a hopping system is considered. As far as we know, no attempt at examining this problem has appeared in print. In the present letter we make such an attempt under the assumption that the total carrier density is not changed during the energy relaxation.

We start from the standard initial condition where at $t = 0$ free carriers have been generated and become trapped with uniform probability in a distribution of localized states. Since at low temperatures, only downward carrier jumps are possible, most of the carriers generated at $t = 0$ will occupy 'metastable' hopping sites from which jumps to an empty deeper energy site at some later time t remain possible. At the initial time, $t = 0$, all sites are, obviously, metastable and the density of metastable states (DMS), $g_d(E, t)$, is simply equal to the total density of states (DOS), $g(E)$. In a spatially completely disordered system, distances to deeper hopping sites, accessible for the next jump, are characterized by a broad distribution such that some of the states are still metastable at any time. The probability $w(r, t)$ for a carrier to stay until the time t in a state separated from the nearest accessible

† Permanent address: Moscow Engineering Physics Institute, Kashirskoye Shosse 31, Moscow 115409, Russia.

0953-8984/96/430637+06$19.50

neighbour by the distance r can be obtained directly from the standard Poisson distribution. Indeed, given a jump probability per unit time of $\lambda = \nu_0 \exp(-2\gamma r)$, where ν_0 is the attempt-to-jump frequency and γ is the inverse localization radius, the Poisson distribution

$$P_n(t) = \frac{(\lambda t)^n}{n!} \exp(-\lambda t)$$

describes the distribution of the number of jumps, n, in a time interval t. We are interested in $w(r, t)$, the no-jump term where $n = 0$, of that distribution:

$$w(r, t) = \exp[-\nu_0 t \exp(-2\gamma r)]. \tag{1}$$

At the time t satisfying equation (1), the probability density, W, of finding the nearest deeper hopping neighbour for a state with the energy E at the distance r is also given by the Poisson formula as

$$W(E, r, t) = \exp[-n(E, r, t)] \frac{\partial n(E, r, t)}{\partial r} \tag{2}$$

where $n(E, r, t)$ is the density of localized states with energies exceeding E within the sphere of radius r vacant at the time t. (The energy scale is chosen so that deeper states have higher energies.) In a completely disordered system the function $n(E, r, t)$ takes the form

$$n(E, r, t) = \frac{4\pi r^3}{3} \int_E^\infty \mathrm{d}E' \left[g(E') - \rho(E', t) \right]. \tag{3}$$

where $\rho(E, t)$ is the energy distribution of localized carriers at the time t. Combining equations (1) and (2) and integrating over the coordinate yields the probability $\varphi(E, t)$ for a hopping site with the energy E to be a metastable state at the time t:

$$\varphi(E, t) = \int_0^\infty \mathrm{d}r \ \frac{\partial n(E, r, t)}{\partial r} \ \exp[-n(E, r, t)] \exp[-\nu_0 t \exp(-2\gamma r)]. \tag{4}$$

The energy-independent exponential term in the integrand of equation (4) represents a very steep function of the variable r around $r = r_j = (1/2\gamma)\ln(\nu_0 t)$ such that the following approximation becomes possible:

$$\begin{cases} \exp[-\nu_0 t \exp(-2\gamma r)] \approx 0 & r < r_j(t) \\ & r_j(t) = (1/2\gamma) \ln(\nu_0 t) \\ \exp[-\nu_0 t \exp(-2\gamma r)] \approx 1 & r > r_j(t). \end{cases} \tag{5}$$

This approximation allows an evaluation of the integral in equation (4) as

$$\varphi(E, t) = \exp\left\{ -n\left[E, \frac{1}{2\gamma} \ln(\nu_0 t), t \right] \right\} \tag{6}$$

or equivalently, with the use of equation (3):

$$\varphi(E, t) = \exp\left[-\frac{\pi}{6\gamma^3} [\ln(\nu_0 t)]^3 \int_E^\infty \mathrm{d}E' \left[g(E') - \rho(E', t) \right] \right]. \tag{7}$$

With the above probability, the DMS can be written as

$$g_d(E, t) = \varphi(E, t) g(E). \tag{8}$$

Invoking once more the initial assumption of energy-independent capture constants, the distribution of localized carriers, $\rho(E, t)$, may be calculated as a product of the DMS and a function of time $\chi(t)$:

$$\rho(E, t) = \chi(t) g_d(E, t). \tag{9}$$

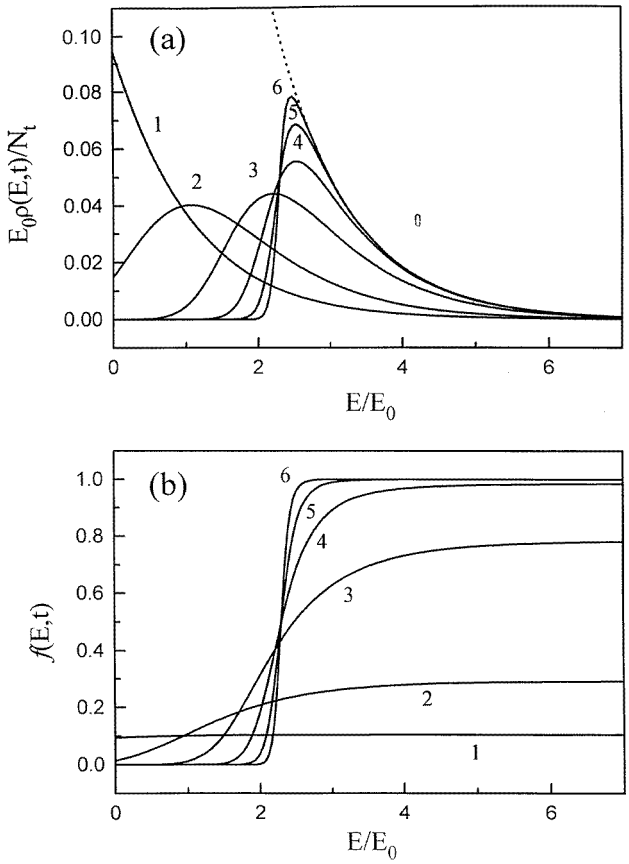

Figure 1. Temporal evolution of the energy distributions of (a) the localized carrier density, $\rho(E,t)$, and of (b) the occupation probability, $f(E,t)$, for an exponential DOS function (dotted line): $g(E) = (N_t/E_0)\exp(-E/E_0)$. The ratios $\pi N_t/6\gamma^3 = 0.01$ and $p_0/N_t = 0.1$ were chosen. Curves 1 to 6 correspond to $\nu_0 t$-values of 10, 10^3, 10^5, 10^7, 10^9, and 10^{11} respectively.

An energy- and time-dependent occupation probability $f(E,t)$, defined through

$$f(E,t) = \frac{\rho(E,t)}{g(E)} = \frac{\chi(t)g_d(E,t)}{g(E)} = \chi(t)\,\varphi(E,t) \tag{10}$$

then reads

$$f(E,t) = \chi(t)\exp\left[-\frac{\pi}{6\gamma^3}\left[\ln(\nu_0 t)\right]^3 \int_E^\infty \mathrm{d}E'\; g(E')\left[1 - f(E',t)\right]\right] \tag{11}$$

where the definition (10) was used to replace the $\rho(E',t)$ of equation (7) with $g(E')f(E',t)$. Equation (11) represents an integral equation for the occupation probability. To solve this equation one should convert it into a partial differential equation. Differentiating equation (11) with respect to energy yields

$$\frac{\partial f(E,t)}{\partial E} - \frac{\pi}{6\gamma^3}\left[\ln(\nu_0 t)\right]^3 g(E) f(E,t)\left[1 - f(E,t)\right] = 0. \tag{12}$$

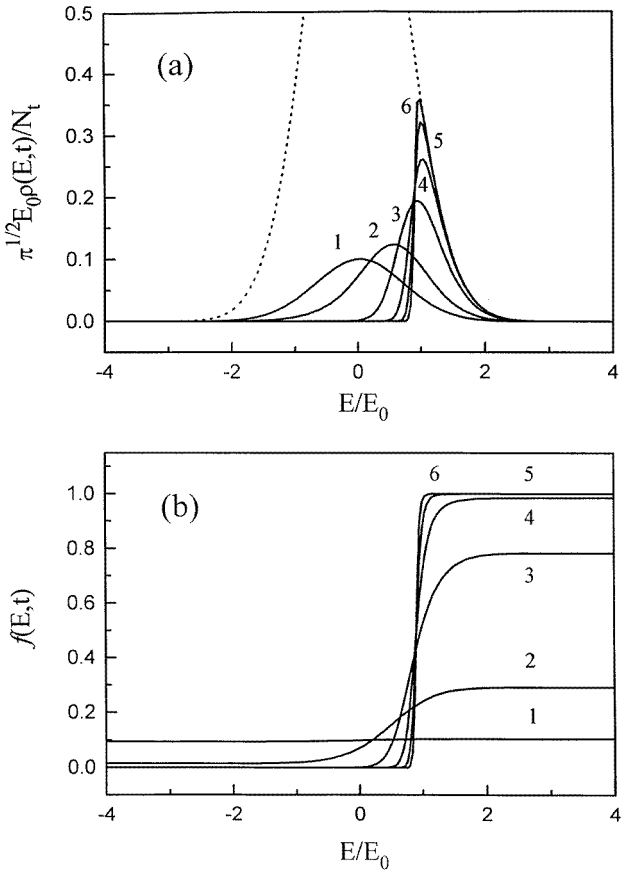

Figure 2. Temporal evolution of the energy distributions of (a) the localized carrier density, $\rho(E,t)$, and of (b) the occupation probability, $f(E,t)$, for a Gaussian DOS function (dotted line). The parameter values are identical to the ones for figure 1.

Equation (12) can be easily solved. The solution reads

$$f(E,t) = \left\{1 + \left[\frac{1}{f(\infty,t)} - 1\right] \exp\left[\frac{\pi}{6\gamma^3}\,[\ln(\nu_0 t)]^3\, N(E)\right]\right\}^{-1} \tag{13}$$

where $N(E)$ is the density of localized states whose energies, E', exceed E:

$$N(E) = \int_E^\infty \mathrm{d}E'\; g(E') \tag{14}$$

and the function $f(\infty,t)$ is calculated below by making use of the normalization condition. In the absence of recombination the total number of generated carriers, p_0, remains the same in the course of energy relaxation, and the function $f(E,t)$ must meet the following condition:

$$\int_{-\infty}^\infty \mathrm{d}E'\; g(E') f(E',t) = p_0. \tag{15}$$

Substituting equations (13) and (14) into equation (15) and integrating over energy yields

the following expression for the function $f(\infty, t)$:

$$f(\infty, t) = \frac{1 - \exp[-(\pi p_0/6\gamma^3)\,[\ln(\nu_0 t)]^3]}{1 - \exp[-(\pi N_t/6\gamma^3)\,[\ln(\nu_0 t)]^3]} \tag{16}$$

where N_t is the total density of localized states. Substituting equation (16) into equation (13) then finally leads to an expression for the occupation probability for the hopping sites as a function of the primary system parameters:

$$f(E,t) = \left\{1 + \frac{\exp[-(\pi p_0/6\gamma^3)\,[\ln(\nu_0 t)]^3] - \exp\left[-(\pi N_t/6\gamma^3)\,[\ln(\nu_0 t)]^3\right]}{1 - \exp[-(\pi p_0/6\gamma^3)\,[\ln(\nu_0 t)]^3]} \times \exp\left[\frac{\pi}{6\gamma^3}\,[\ln(\nu_0 t)]^3\, N(E)\right]\right\}^{-1}. \tag{17}$$

When the filling effect is important the energy distribution of localized carriers is often described in terms of a time-dependent quasi-Fermi level. Equation (17) allows us to estimate the applicability of this approach to the problem of hopping carrier relaxation. Using the traditional definition of the quasi-Fermi level, E_{QF}, as $f(E_{QF}, t) = 1/2$ one gets,

$$N(E_{QF}) = \frac{6\gamma^3}{\pi}\,[\ln(\nu_0 t)]^{-3} \times \ln\left\{\frac{1 - \exp[-(\pi p_0/6\gamma^3)\,[\ln(\nu_0 t)]^3]}{\exp[-(\pi p_0/6\gamma^3)[\ln(\nu_0 t)]^3] - \exp\left[-(\pi N_t/6\gamma^3)[\ln(\nu_0 t)]^3\right]}\right\}. \tag{18}$$

Equation (18) predicts that the stationary position of the quasi-Fermi level characterized by the condition

$$N(E_{QF}^{st}) = p_0 \tag{19}$$

will be established for times longer than t_{QF},

$$t_{QF} = \frac{1}{\nu_0} \exp\left[\left(\frac{6\gamma^3}{\pi p_0}\right)^{1/3}\right] \tag{20}$$

provided that p_0 remains small with respect to N_t. Time-dependent energy distributions of localized carriers and of the occupation probability are shown on figures 1 and 2 for an exponential and a Gaussian distribution of hopping sites. The ratio of the total density of generated carriers, p_0, to the total density of localized states, N_t, was put at 0.1.

In conclusion, the discussion of energy diffusion and relaxation in a disordered hopping system is extended to the consideration of the effect of hopping site filling. This phenomenon must be taken into account every time a many-particle problem, such as those of carrier recombination, photoconductivity, photoluminescence, etc, is analysed under low-temperature conditions. As one can see from figures 1 and 2 the energy distribution of carriers at shorter times mimics the normal 'small-signal' energy relaxation—see e.g. [1, 3]. At longer times the filling effect becomes dominant and an immobile demarcation energy level is established for times exceeding t_{QF}. The characteristic time t_{QF} exponentially increases with decreasing concentration of excess carriers—see equation (20). The principle result of the present letter is the occupation probability function given by equation (17). This function will have to be applied in the future to consideration of low-temperature carrier recombination in disordered hopping systems and similar problems.

VIA acknowledges a fellowship from the KU Leuven. This work was supported by the Belgian Nationaal Fonds voor Wetenschappelijk Onderzoek.

References

[1] Grünewald M and Movaghar B 1989 *J. Phys.: Condens. Matter* **1** 2521
[2] Shklovskii B I, Fritzsche H and Baranovskii S D 1989 *Phys. Rev. Lett.* **62** 2989
[3] Arkhipov V I, Bässler H and Rudenko A I 1992 *Phil. Mag.* B **65** 615
[4] Baranovskii S D, Faber T, Hensel F, Thomas P and Adriaenssens G J 1996 *J. Non–Cryst. Solids* **198–200** 214
[5] Arkhipov V I and Adriaenssens G J 1996 *J. Phys.: Condens. Matter* **8** 7909
[6] Kersting R, Lemmer U, Deussen M, Bakker H J, Mahrt R F, Kurz H, Arkhipov V I, Bässler H and Göbel E O 1994 *Phys. Rev. Lett.* **73** 1440
[7] Arkhipov V I, Bässler H, Deussen M, Göbel E O, Kersting R, Kurz H, Lemmer U and Mahrt R F 1995 *Phys. Rev.* B **52** 4932
[8] Marianer S and Shklovskii B I 1992 *Phys. Rev.* B **46** 13 100