

Diffusion and relaxation of energy in disordered systems: Departure from mean-field theories

B. Movaghar

Long Range Research Laboratory, GEC Research Limited, East Lane, Wembley, Middlesex HA9 7PP England, United Kingdom

B. Ries

Fachbereich Physikalische Chemie, Philipps-Universität Marburg, D-3550 Marburg, Federal Republic of Germany

M. Grünewald

Dornier Medizintechnik G.m.b.H. Abteilung HT13, Industriestrasse 15, D-8034 Germering, Federal Republic of Germany

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We present exact analytical and Monte Carlo results for zero-temperature diffusion and energy relaxation of excitations describable by Master-equation dynamics. We demonstrate the freezing-in of relaxation at very low temperatures caused by "isolated" sites and clusters and observed experimentally in glassy benzophenone. Similar effects observed in semiconductor quantum-well structures and probably related to exciton trapping in disordered states caused by well-width fluctuations can be explained along the same lines. Asymptotic laws are derived and compared to Monte Carlo results. We also demonstrate that the departure from mean-field theories, serious for energy relaxation, is not so important for the diffusivity of excitations.

INTRODUCTION

In a previous series of papers which we shall hereafter refer to as I, II and III and given, respectively, by Refs. 1, 2 and 3, we considered the problem of nonequilibrium diffusion and energy relaxation of excitations in disordered systems using direct Monte Carlo simulations and analytic approximations which we have called the "effective-medium approximation" (EMA). There is a wide range of problems for which the knowledge of the time and energy-dependent diffusivity $D(\epsilon, t)$ is essential,^{4,5} these include charge and exciton transport, luminescence and photoconductivity,⁶⁻⁸ and experimental observations of energy relaxation in organic and inorganic semiconductors.⁹⁻¹¹ To this we can now also add the interesting phenomena of energy transport and time-resolved luminescence in semiconductor quantum-well structures (QW) and superlattices.¹²⁻¹⁴ In I we compared Monte Carlo simulations to analytic theory for time dependence and dependence on the initial energy of the excitation. This provides a rather rigorous test for the approximation techniques employed. We found excellent agreement for all quantities of physical interest [energy relaxation function $E(\epsilon, t)$ and diffusivity $D(\epsilon, t)$] down to temperatures of the order of 50 K. Below 50 K, discrepancies begin to appear between exact simulations and EMA techniques. We have discussed the source of these discrepancies in I and have demonstrated the inadequacy of the EMA at low temperatures and in the long-time limit. The effective-medium approach always tends to overestimate the number of relaxation paths in the long-time limit and this leads to a considerably more rapid decay of energy for long times since it does not allow for "dead ends" (isolated sites and clusters) in the network of the random walk. Such dead ends, i.e., sites from which it is difficult to escape at low temperature can lead to very slow energy re-

laxation in the long-time regime as $T \rightarrow 0$. In order to account for the "freezing-in" of excitations at very low temperatures in disordered systems, it is essential to take proper account of the site correlations involved in the sequential jump process.

In the present paper we develop a theory of relaxation and diffusion in disordered systems which is exact at $T=0$ and will provide a good approximation at low temperatures. In this way we are now in a position to tackle the problem from the other extremity. Our results will demonstrate the drastic change that occurs in the relaxation of energy in the long-time limit. Though energy relaxation and diffusivity are simply related to each other, the change in the long-time limit introduced by the freezing-in of excitations at low temperature is much more evident in $E(\epsilon, t)$. Only energy relaxation experiments will in practice be able to distinguish between exact and mean-field predictions in the present problem. The recent measurements of energy relaxation in benzophenone glasses¹¹ at low temperatures agree with the Monte Carlo calculations and indeed exhibit serious discrepancies with the EMA predictions. We shall now remedy this discrepancy between analytic approach and experiment (real and Monte Carlo) taking of course Monte Carlo as the true guide of accuracy.

BASIC FORMALISM

Recall from paper I or from Refs. 1, 2, or 3 the master equation for the dynamics of incoherent excitation transport

$$\frac{dn_i}{dt} = - \sum_j W_{ij} n_i(t) + \sum_j W_{ji} n_j(t), \quad (1)$$

where $n_i(t)$ is the occupational density of site i characterized by position \mathbf{R}_i , energy ϵ_i at time t . The transfer rates W_{ij} , can for our purposes, be abbreviated as

$$W_{ij} = \begin{cases} v_0 F(|\mathbf{R}_{ij}|) \exp[-(\epsilon_j - \epsilon_i)/k_B T], & \epsilon_j > \epsilon_i \\ v_0 F(|\mathbf{R}_{ij}|), & \epsilon_j < \epsilon_i \end{cases} \quad (2)$$

with

$$F(|\mathbf{R}_{ij}|) = \exp(-2\alpha |\mathbf{R}_{ij}|) \quad (3)$$

for charge transport and triplet (exchange) exciton transport or

$$F(|\mathbf{R}_{ij}|) = \left| \frac{R_0}{|\mathbf{R}_{ij}|} \right|^S, \quad \frac{R_0}{|\mathbf{R}_{ij}|} < 1 \quad (4)$$

applicable to multipolar exciton transfer, $S=6$ corresponds to the Förster dipole-dipole transfer rates, v_0 is a prefactor measured in s^{-1} , α^{-1} and R_0 are localization lengths and can, in principle, be energy dependent.

The probability $G_{ij}(t)$ of finding the excitation at site j at time t given that it started at time $t=0$ at site i is the formal solution of the master equation which in the space of the Laplace variable p can be written in the form

$$G_{ij}(p) = \int_0^\infty G_{ij}(t) e^{-pt} dt, \quad (5)$$

$$G_{ij}(p) = \frac{\delta_{ij}}{p + \sum_\mu W_{i\mu}} + \frac{1}{p + \sum_\mu W_{i\mu}} \sum_l W_{il} G_{lj}(p). \quad (6)$$

The quantity of interest, however, is the restricted configurationally averaged quantity $\bar{G}_{ij}(p)$ defined by

$$\bar{G}_{ij}(p) = \int \prod_{\mu (\neq i, j)} d\mathbf{R}_\mu d\epsilon_\mu \frac{\rho(\epsilon_\mu)}{(\Omega)^{N-2}} G_{ij}(p), \quad (7)$$

where Ω is the volume and $\rho(\epsilon)$ is the normalized distribution function of site energies assumed to be independent from each other.

In the general case (finite T), (6) can only be solved using approximation techniques. Once $\bar{G}_{ij}(p)$ is known we have all the information needed to calculate the quantities of physical interest

$$E(\epsilon_i, t) = \sum_j \bar{G}_{ij}(t) \epsilon_j, \quad (8)$$

$$L(\epsilon_i, \epsilon_j, t) = \frac{N^2}{\Omega} \int d\mathbf{R}_{ij} \int_{\epsilon_i - \delta_i}^{\epsilon_i + \delta_i} d\epsilon'_i \rho(\epsilon'_i) \int_{\epsilon_j - \delta_j}^{\epsilon_j + \delta_j} d\epsilon'_j \rho(\epsilon'_j) \bar{G}(\epsilon'_i, \epsilon'_j, \mathbf{R}_{ij}, t) l(\epsilon'_j). \quad (13)$$

By invoking the real-space Fourier transform $\bar{G}(\epsilon_i, \epsilon_j; t, \mathbf{k})$ we can replace this expression by

$$L(\epsilon_i, \epsilon_j, t) = \frac{N^2}{\Omega} \int_{\epsilon_i - \delta_i}^{\epsilon_i + \delta_i} d\epsilon'_i \rho(\epsilon'_i) \int_{\epsilon_j - \delta_j}^{\epsilon_j + \delta_j} d\epsilon'_j \rho(\epsilon'_j) \bar{G}(\epsilon'_i, \epsilon'_j; t, \mathbf{k}=\mathbf{0}) l(\epsilon'_j). \quad (14)$$

THE $T=0$ LIMIT

The $T=0$ limit gives us a unique opportunity to present what is essentially an "exact" solution to the probability function and desired quantities on a disordered network. At $T=0$ there are no back jumps and no loop processes in the random walk of excitations, thus each jump rate be-

$$D(\epsilon_i, t) = \frac{\partial}{\partial t} \left[\frac{1}{6} \sum_j \bar{G}_{ij}(t) R_{ij}^2 \right], \quad (9)$$

which refer to time and initial energy-dependent energy relaxation and diffusivity of a particle following a pulse at time $t=0$, respectively.

In the field of energy relaxation in semiconductors and quantum wells, one often works with the concept of effective temperature $T_e(\epsilon, t)$, which, naturally, also depends on the initial energy of the excited particle and time t ; the effective temperature can be defined by the relation

$$E(\epsilon, t) = \frac{\int_0^\infty e^{-\epsilon'/k_B T_e} \rho(\epsilon') \epsilon' d\epsilon'}{\int_0^\infty \rho(\epsilon') e^{-\epsilon'/k_B T_e} d\epsilon'}. \quad (10)$$

For a free particle type density of states $\rho(\epsilon) \sim \epsilon^{1/2}$ we have

$$E(\epsilon, t) = C k T_e(\epsilon, t), \quad (11)$$

where C is a proportionality constant.

In the limit $t \rightarrow \infty$, $E(\epsilon, t)$ and, thus, $T_e(\epsilon, t)$ become independent of ϵ and finally

$$T_e(\epsilon, t) |_{t=\infty} \equiv T. \quad (12)$$

However, this is only for $T > 0$ and strictly at $t = \infty$ because of freezing-in effects which can prevent particles from reaching true thermodynamic equilibrium in the long-time limit. Thus at $T=0$ the excitation can be blocked forever in a local minimum if the transfer rates have finite range. On the other hand, for infinite range hopping it is always permissible to relax and equilibrium will eventually be reached. It is the functional form of this approach to equilibrium which is the subject matter of this paper.

Finally, let us consider another quantity of interest which is the luminescence intensity $L_{ij}(t)$ obtained at time t and in the energy interval $(\epsilon_j, \epsilon_j \pm \delta_j)$ from excitations excited in the region $(\epsilon_i, \epsilon_i \pm \delta_i)$. This quantity can be written in terms of the probability function $G_{ij}(t)$ and luminescence probability l_j as

tween a pair of sites W_{lk} can be considered an independent variable which is distributed according to a probability function $Q(W_{lk})$. The excitation moves effectively on a Cayley tree with diminishing coordination number. The Cayley tree itself has been discussed in detail in Ref. 15, where it has been shown how the configurational averages can be carried out exactly. At $T=0$ the absence of back

jumps makes the problem rather easy; furthermore, the distinction between bond averaging and site averaging is of no consequence.

Returning to Eq. (6) we can now take the configurational average on both sides keeping (i, j) fixed and write in the space of the Fourier variable \mathbf{k}

$$\begin{aligned} \rho(\varepsilon_j) \bar{G}(\varepsilon_i, \varepsilon_j; \mathbf{k}, p) \\ = \bar{G}_{ii} \delta(\varepsilon_i - \varepsilon_j) + \int d\varepsilon_l S(\mathbf{k}, \varepsilon_l) \Theta(\varepsilon_i - \varepsilon_l) \\ \times \rho(\varepsilon_l) \rho(\varepsilon_j) \bar{G}(\varepsilon_l, \varepsilon_j; \mathbf{k}, p), \end{aligned} \quad (15)$$

where

$$\begin{aligned} nS(\mathbf{k}, \varepsilon_i) = \frac{1}{n(\varepsilon_i)} \int \left\langle \frac{W_{ij}}{p + W_{ij} + \sum_{l \neq j} W_{il}} \right\rangle_{ij} \\ \times e^{i\mathbf{k} \cdot \mathbf{R}_{ij}} d\mathbf{R}_{ij} \end{aligned} \quad (16)$$

and

$$\bar{G}_{ii}(p) = \left\langle \frac{1}{p + \sum_l W_{il}} \right\rangle_i, \quad (17)$$

with

$$n(\varepsilon) = \int_{-\infty}^{\varepsilon} \rho(\varepsilon') d\varepsilon'. \quad (18)$$

The angular brackets denote configurational average and index i outside denotes that the corresponding site is to be kept fixed.

The averages (7) can be evaluated exactly by going over to time space

$$\bar{G}_{ii}(t) = \left\langle \exp \left[- \sum_l W_{il}(t) \right] \right\rangle_i; \quad (19)$$

for the models (2) we can rewrite this as^{16,17}

$$\bar{G}_{ii}(t) = \exp \left[n \int d\varepsilon_k \int d\mathbf{R}_k \rho(\varepsilon_k) (e^{-tW_{ik}} - 1) \right], \quad (20)$$

where $n = N/\Omega$ is the site density. At $T=0$ we can replace this with

$$\bar{G}_{ii}(t) = \exp \left[nn(\varepsilon) \int d\mathbf{R}_k (e^{-v_0 F |\mathbf{R}_{ik}| t} - 1) \right] \quad (21)$$

and the spatial integral can be carried out analytically for Förster-like rates [Eq. (4)]. For exponential rates [Eq. (3)] we can split (20) roughly into two region (1) $\bar{v}t < 1$ and (2) $\bar{v}t > 1$ with

$$\bar{G}_{ii}(t) \sim \begin{cases} \exp[-n(\varepsilon)\bar{v}t], & \bar{v}t < 1 \\ \frac{1}{t_1^{\rho(\varepsilon_i)\alpha_d(t)}}, & \bar{v}t > 1 \end{cases} \quad (22a)$$

$$\quad (22b)$$

where

$$\bar{v} = v_0 n \int F |\mathbf{R}_{ij}| d\mathbf{R}_{ij}, \quad (23)$$

$$\rho(\varepsilon_i) = \frac{1}{\bar{v}} n(\varepsilon_i) \bar{v} / v_0, \quad (24)$$

$$\alpha_d(t) = [\ln(v_0 t)]^{d-1}, \quad (25)$$

and $t_1 = v_0 t$, where d is the dimensionality of the lattice and can be extended to fractal values.¹⁸ Since $\alpha_d(t)$ is a weak function of t we can in some applications replace it with a constant evaluated at $t = \tau$ which is some critical hop time.

Note also that

$$nS(\mathbf{k}, \varepsilon_i) |_{\mathbf{k}=0} = \frac{1}{n(\varepsilon_i)} [1 - p \bar{G}_{ii}(p)]. \quad (26)$$

Transforming (15) into a differential equation allows an explicit solution for $\bar{G}(\varepsilon_i, \varepsilon_j; \mathbf{k}, p)$. However, we shall not derive this here but concentrate on the quantities $E(\varepsilon, t)$ and $D(\varepsilon, t)$.

Using (15) we can write the energy relaxation function $E(\varepsilon, p)$ in Laplace space as

$$E(\varepsilon_i, p) = \varepsilon_i \bar{G}_{ii}(p) + \int_{-\infty}^{\varepsilon_i} \frac{g(\varepsilon_i, p)}{n(\varepsilon_i)} \rho(\varepsilon_l) E(\varepsilon_l, p) d\varepsilon_l, \quad (27)$$

where

$$g(\varepsilon_i, p) = \left\langle \frac{\sum_{\mu} W_{i\mu}}{p + \sum_{\mu} W_{i\mu}} \right\rangle. \quad (28)$$

Converting (27) into a differential equation and solving, we find

$$\begin{aligned} E(\varepsilon, p) = \varepsilon G(\varepsilon, p) + \int_{-\infty}^{\varepsilon} \varepsilon' G(\varepsilon', p) \rho(\varepsilon') g_1(\varepsilon') \\ \times e^{[L(\varepsilon') - L(\varepsilon)]} d\varepsilon', \end{aligned} \quad (29)$$

where

$$g_1(\varepsilon') = \frac{g(\varepsilon', p)}{n(\varepsilon)} \quad (30)$$

and

$$G(\varepsilon, p) = \bar{G}_{ii}(p) |_{\varepsilon_i = \varepsilon}, \quad (31)$$

$$\begin{aligned} [L(\varepsilon') - L(\varepsilon)] = \int_{\varepsilon}^{\varepsilon'} d\varepsilon'' \left[\rho(\varepsilon'') g_1(\varepsilon'') \right. \\ \left. + \frac{d}{d\varepsilon''} \ln[g_1(\varepsilon'')] \right]. \end{aligned} \quad (32)$$

The exact $E(\varepsilon, t)$ for a given $\rho(\varepsilon)$ can now be evaluated using a numerical Laplace inversion routine for all times and energies. In this paper we shall discuss the analytical structure of the result as much as possible and in particular the long-time behavior.

Using the definition of $g_1(\varepsilon)$ we can convert (32) into the form

$$\begin{aligned} [L(\varepsilon') - L(\varepsilon)] = \int_{\varepsilon}^{\varepsilon'} d\varepsilon'' \left[\frac{d}{d\varepsilon''} \ln[1 - pG(\varepsilon'', p)] \right. \\ \left. - pG(\rho, \varepsilon'') \frac{d}{d\varepsilon''} \ln[n(\varepsilon'')] \right], \end{aligned} \quad (33)$$

from which we obtain the extremely useful simplification which states that as $p \rightarrow 0$ ($t \rightarrow \infty$) the right-hand side (rhs) vanishes. Alternatively, we can expand

$$\exp[L(\epsilon') - L(\epsilon)] \sim 1 + \frac{[L(\epsilon) - L(\epsilon')]}{1!} + \dots \quad (34)$$

as $t \rightarrow \infty$ only the first term remains in (34), thus we can achieve a systematic expansion (in the long-time limit) of $E(\epsilon, t)$ by using (34).

Keeping only the first term in (34), we now find

$$E(\epsilon, t) \sim (-) \int_{-\infty}^{\infty} \int_0^t d\epsilon' \frac{\epsilon' \rho(\epsilon')}{n(\epsilon')} \bar{G}(t - \tau, \epsilon') \times \frac{\partial \bar{G}(\tau; \epsilon')}{\partial \tau} d\tau \quad \text{as } t \rightarrow \infty, \quad (35)$$

where $G(t, \epsilon)$ is given by (21). To proceed to the next step and keep the result as general as possible we first note that

$$G(\epsilon, t) = [S(t)]^{-n(\epsilon)}. \quad (36)$$

This follows directly from (21) and is valid for any model of the type (2) with infinite-range hopping.

The relation (36) now allows us to convert the time integral

$$F(t, \epsilon') = (-) \int_0^t G(t - \tau, \epsilon') \frac{\partial G(\tau, \epsilon')}{\partial \tau} d\tau \quad (37)$$

into the form

$$F(t, \epsilon') = -n(\epsilon') \frac{\partial G[n(\epsilon'), t]}{\partial n(\epsilon')} + [n(\epsilon')]^2 \int_0^t d\tau G(\tau) G(t - \tau) \times \frac{S'(t - \tau)}{S(t - \tau)} \ln \left[\frac{S(\tau)}{S(t - \tau)} \right]. \quad (38)$$

To first order in $n(\epsilon')$ we keep only the first term in (38) and substitution into (35) then yields

$$E(\epsilon, t) \sim \int_{-\infty}^{\epsilon} d\epsilon' \rho(\epsilon') \epsilon' G(\epsilon', t) \ln[S(t)] + O(n^2) \quad \text{as } t \rightarrow \infty. \quad (39)$$

To a good approximation this integral can be written as

$$E(\epsilon, t) \sim \hat{n}^{-1}(\{\ln[S(t)]\}^{-1}) + c' \quad \text{as } t \rightarrow \infty, \quad (40)$$

where the function $\hat{n}^{-1}(x)$ is the inverse function to the integrated density of states, i.e.,

$$n(y) = x \implies y = \hat{n}^{-1}(x) \quad (41)$$

and c' a constant which is $\equiv 0$ when $n(\epsilon = -\infty) = 0$.

Note that in the long-time limit there is no longer any dependence on the initial energy of the excitation. Note also that when $S(t)$ is an exponential in time $S(t) \sim e^t$ then (39) is exact because the second term vanishes identically. In fact in this case we can present an explicit solution to $E(\epsilon, t)$ valid for all energies and all times. This is the subject of the following section.

THE EFFECTIVE-MEDIUM APPROXIMATION

Before looking at the exact results, it is instructive to rederive the EMA results of I using the present approach in the limit $T=0$. In the framework of the EMA we approximate the configurational average over the probability

function by an average over the "self-energy," thus the particle does not jump into the true medium but only into the averaged medium; in other words

$$\bar{G}_{ii}(p) \simeq \frac{1}{p + \left\langle \sum_{\mu} W_{i\mu} \right\rangle} = \frac{1}{p + p(\epsilon_i) \nu_0}, \quad (42)$$

where $p(\epsilon_i)$ is given by (24). The Laplace inverse of $\bar{G}(\epsilon, p)$ is now a simple exponential, furthermore the second term on the rhs of Eq. (38) vanishes identically for all p . Thus we now have ($t_1 = \nu_0 t$)

$$E(\epsilon, t) = \epsilon e^{-p(\epsilon)t_1} + \bar{\nu} \int_{-\infty}^{\epsilon} \epsilon' \rho(\epsilon') e^{-p(\epsilon')t_1} d\epsilon'. \quad (43)$$

Consider the following two examples.

Firstly, the exponential tail

$$\rho(\epsilon) = e^{-|\epsilon|/\epsilon_0} \epsilon_0^{-1}. \quad (44)$$

Here

$$E(\epsilon, t) = -\epsilon_0 [\ln(\bar{\nu}t) + \gamma] - \epsilon_0 \int_{\bar{\nu}t/k(\epsilon)}^{\infty} s^{-1} e^{-s} ds \quad (45)$$

with $k(\epsilon) = e^{-|\epsilon|/\epsilon_0}$ and $\gamma = 0.57721\dots$ is Euler's constant.

It follows easily that

$$E(\epsilon, t) \sim -\epsilon_0 \ln(\bar{\nu}t) \quad \text{as } t \rightarrow \infty. \quad (46)$$

This result is in complete agreement with the self-consistent numerical evaluation of $E(\epsilon, t)$ at low T for an exponential tail given in Refs. 2 and 3. The $\ln t$ dependence is clearly visible in Fig. 4 of Ref. 2.

Secondly,

$$\rho(\epsilon) = \frac{1}{W}, \quad [-W, 0] \quad (47)$$

$$E(\epsilon, t) = -W \left[1 - \frac{|\epsilon|}{W} e^{-\bar{\nu}t(1 - |\epsilon|/W)} \right] + \frac{W}{\bar{\nu}t} (1 - e^{-\bar{\nu}t(1 - |\epsilon|/W)}) - |\epsilon| e^{-(1 - |\epsilon|/W)\bar{\nu}t}, \quad (48)$$

and therefore

$$E(\epsilon, t) \sim -W + \frac{W}{\bar{\nu}t} \quad \text{as } t \rightarrow \infty. \quad (49)$$

Note that (46) and (49) are in complete agreement with the general relation (40) since $S(t) = \exp(\bar{\nu}t)$ and thus $\hat{n}^{-1}(\{\ln S(t)\}^{-1})$ behaves as $-\epsilon_0 \ln(\bar{\nu}t)$ and $1/\bar{\nu}t$, respectively. Indeed from the preceding section it follows that the basic quantity is $G(\epsilon, t)$, given this function in whatever form approximate or exact then determines the corresponding long-time behavior of $E(\epsilon, t)$.

THE EXACT BEHAVIOR OF $E(\epsilon, t)$

We have seen from (39) how $G(\epsilon, t)$ determines the behavior of $E(\epsilon, t)$ in the long-time domain. For the model given by (22b) and using (34) we can Laplace invert (29) exactly to obtain $(\alpha_d \bar{\nu} / \nu_0 = \alpha_0)$

$$E(\varepsilon, t) \sim \frac{\varepsilon}{(t_1)^{\alpha(\varepsilon)}} + \int_{-\infty}^{\varepsilon} d\varepsilon' \left[\varepsilon' \frac{\rho(\varepsilon')}{n(\varepsilon')} \frac{1}{\Gamma(1-\alpha(\varepsilon'))} \left(1 - \frac{\Gamma(1-\alpha(\varepsilon'))}{\Gamma(1-2\alpha(\varepsilon'))} \exp[-\alpha(\varepsilon') \ln t_1] \right) \right] + O \left[\frac{1}{t_1} \right]^{2\alpha(\varepsilon)} \quad \text{as } t \rightarrow \infty, \quad (50)$$

where $\Gamma(x)$ is the Γ function and

$$\alpha(\varepsilon) = \alpha_d n(\varepsilon). \quad (51)$$

This result is valid as long as (22b) is true for any $\rho(\varepsilon)$. When $\alpha(\varepsilon) \ll 1$, we can expand the Γ function and thus to first order in $\alpha(\varepsilon)$ all Γ 's can be replaced by 1 in Eq. (50). If $\rho(\varepsilon)$ is exponential it follows then from (50) that

$$E(\varepsilon, t) \sim -\varepsilon_0 \ln(\ln t_1^{\alpha_0}) \quad \text{as } t \rightarrow \infty \quad (52a)$$

a considerable slowing down of relaxation in comparison to be effective medium result (45). Again this result is in complete agreement with (40) since using (36), $S(t) = t^{\alpha_0}$ and $n^{-1}(x) = \varepsilon_0 \ln x$. The more general derivation (39) suggests further that it is permissible to replace α_0 with the fully time-dependent form $[\alpha_d(t) \bar{v}/v_0]$ as given by (22b) but interesting enough this form does not change the functional dependence on t_1 since $\alpha_d \sim (\ln t_1)^{d-1}$, but the prefactor ε_0 is rescaled so that

$$E(\varepsilon, t) \sim -\varepsilon_0 \tilde{d} [\ln(\ln t_1)] \quad \text{as } t \rightarrow \infty. \quad (52b)$$

The exponential tail model is appropriate for amorphous semiconductors and probably also for the description of the localized interface state in two-dimensional quantum-well structures (see Ref. 13). For disordered organic systems, however, we know that $\rho(\varepsilon)$ is well described by a Gaussian of the form

$$\rho(\varepsilon) = \frac{1}{(\sigma^2 \pi)^{1/2}} e^{-(\varepsilon/\sigma)^2}. \quad (53)$$

Unfortunately $n(\varepsilon)$ is now the complementary error function and $n^{-1}(x)$ is not easily obtained. However, we can approximate $n(\varepsilon)$ with

$$n(\varepsilon) = \frac{\sigma}{|\varepsilon| \sqrt{\pi}} \rho(\varepsilon), \quad (54)$$

which is exact as $\varepsilon \rightarrow -\infty$ and a reasonable approximation when ε is in the tail of the Gaussian. Using (40) and incorporating the weak prefactor to $\rho(\varepsilon)$ in (54) into an effective α_0 we have

$$E(\varepsilon, t) \sim -\sigma [\ln(\ln t_1^{\alpha_0(t)})]^{1/2} \quad \text{as } t \rightarrow \infty, \quad (55)$$

where $\alpha_0(t)$ can again be time dependent and obtainable from (22b). When the prefactor to (54) is set $\simeq 1$, $\alpha_0(t) = [\bar{v}/6v_0] \alpha_d(t)$ in (55).

When α_0 is taken to be t independent we can always obtain a more accurate estimate of $E(\varepsilon, t)$ in the intermediate time domain by using (50) instead of (40). The effect of using the fully time dependent form for $\alpha_0(t)$ is to replace $\sigma \rightarrow \sqrt{\tilde{d}} \sigma$ in the asymptotic form (55).

THE SHORT-TIME DOMAIN

In the short-time domain ($\bar{v}t < 1$) we can always use the EMA, this also directly follows from (22a) which tells us that $G(\varepsilon, t)$ is exponential in time. For a given model $\rho(\varepsilon)$ we can then use (43) which is rather easy to analyze.

THE FÖRSTER-TYPE TRANSFER RATES

For singlet excitons one often has transfer rates of the type (4) the corresponding $G(\varepsilon, t)$ is given in Ref. 19 and can be written as

$$G(\varepsilon, t) = \exp \left[-\frac{\pi^{d/2}}{\Gamma(1+d/2)} \Gamma(1-d/S) \times R_0^d n(\varepsilon) (t v_0)^{d/S} \right]. \quad (56)$$

From (40) we find (d is the dimensionality and can be fractal)

$$E(\varepsilon, t) \sim -\varepsilon_0 \ln(\gamma_d t_1^{d/S}) \quad \text{as } t \rightarrow \infty \quad (57)$$

when $\rho(\varepsilon)$ is exponential. Note that this gives the same functional form as a single exponential except for the renormalization of $\varepsilon_0 \rightarrow \varepsilon_0(d/S)$ in the $t \rightarrow \infty$ limit.

THE DIFFUSIVITY IN THE LIMIT $T=0$

Let us now consider the diffusion of excitation in the limit that $T=0$.²⁰ First recall the definition of $D(\varepsilon, t)$ in Laplace space

$$D(\varepsilon_i, p) = \frac{1}{6} p^2 \left\langle \sum_j R_{ij}^2 G_{ij}(p) \right\rangle_i. \quad (58)$$

Substituting (15) into (58) and using the sum rule we have

$$\sum_j \bar{G}_{ij}(p) = \frac{1}{p}, \quad (59)$$

$$\frac{D(\varepsilon_i, p)}{p} = \frac{D_0(\varepsilon_i, p)}{p} + \int_{-\infty}^{\varepsilon_i} \frac{g(\varepsilon_i, p)}{n(\varepsilon_i)} p(\varepsilon_1) \frac{D(\varepsilon_1, p)}{p} d\varepsilon_1, \quad (60)$$

where

$$D_0(\varepsilon_i, p) = \frac{1}{6} p \left\langle \frac{\sum_l R_{il}^2 W_{il}}{p + \sum_l W_{il}} \right\rangle_i. \quad (61)$$

Thus (60) differs from (6) only by the replacement D_0 for $[\varepsilon G(\varepsilon, p)]$. We can therefore solve the problem using the same technique with the appropriate replacement.

The quantity $D_0(\varepsilon, p)$ can be evaluated in time space in the same way this

$$\hat{L}^{-1} \left[\frac{D_0(\varepsilon, p)}{p} \right] = \left\langle \left[\sum_l \frac{R_{il}^2}{6} W_{il} e^{-W_{il}t} \prod_{k(\neq l)} e^{-W_{ik}t} \right] \right\rangle_i. \quad (62)$$

To a good approximation we can replace the rhs with

$$D_0(\varepsilon, t) \sim \frac{\bar{r}^2}{6}(\varepsilon, t) \frac{d}{dt} [G(\varepsilon, t)], \quad (63)$$

where $\bar{r}^2(\varepsilon, t)$ is a weak function of t which we shall replace with the constant

$$\bar{r}^2 = \frac{\int F(|\mathbf{R}|) R^2 d\mathbf{R}}{\int F(|\mathbf{R}|) d\mathbf{R}}. \quad (64)$$

Note that (63) with (64) is exact in the EMA. Using (63) we now find

$$\frac{D_0(\varepsilon, p)}{p} = \frac{\bar{r}^2}{6} [1 - pG(\varepsilon, p)]. \quad (65)$$

Substituting into (61) then yields, in the long-time limit,

$$D(\varepsilon, p) = D_0(p, \varepsilon) + \int_{-\infty}^{\varepsilon} d\varepsilon' \frac{\bar{r}^2}{6} \frac{\rho(\varepsilon')}{n(\varepsilon')} p [1 - pG(\varepsilon', p)]^2 \times \left[1 + \frac{L(\varepsilon) - L(\varepsilon')}{1!} + \dots \right]. \quad (66)$$

Using (63) we can now rewrite the result in real time as

$$[D(\varepsilon, t)]_{\text{long times}} = \frac{\bar{r}^2}{6} \frac{S'(t)}{S(t)} \frac{1}{\ln[S(t)]} \times (1 - e^{-[\ln S(t)]n(\varepsilon)}) \quad (67)$$

plus lower-order terms.

We can exactly rewrite this as

$$D(\varepsilon, t) \sim \frac{r^2}{6} \left[\frac{\delta}{\delta t} \ln \left[\frac{\ln G^{-1}(\varepsilon, t)}{n(\varepsilon)} \right] \right] \text{ as } t \rightarrow \infty, \quad (68)$$

a rather useful result which allows us to determine $D(\varepsilon, t)$ given $G(\varepsilon, t)$ directly, in the long-time limit.

In the framework of the EMA, $D(\varepsilon, t)$ can be written as

$$D(\varepsilon, t) = \frac{1}{6} \bar{r}^2 v_0 p(\varepsilon) e^{-p(\varepsilon)t_1} + \frac{1}{6} \bar{r}^2 v_0^2 \int_{-\infty}^{\varepsilon} p^2(\varepsilon') t e^{-p(\varepsilon')t_1} d\varepsilon' \quad (69)$$

and for an exponential $p(\varepsilon)$

$$D(\varepsilon, t) = \frac{1}{6} \bar{r}^2 \frac{1}{t} (1 - e^{-p(\varepsilon)t_1}). \quad (70)$$

Note that (70) is in complete agreement with (45) with $G(\varepsilon, t)$ given by the EMA. For $\rho(\varepsilon)$ exponential and $G(\varepsilon, t)$ given by (42) we now find (α_0 is a constant)

$$D(\varepsilon, t) \sim \frac{\bar{r}^2}{6} \left[\frac{1}{\ln t_1^{\alpha_0}} \right] \frac{\alpha_0}{t}, \quad (71)$$

which is a slightly stronger decay than in EMA. The interesting feature here is the considerably weaker influence

of the “freezing-in” on $D(\varepsilon, t)$ than on $E(\varepsilon, t)$. The $\ln t_1$ term in the denominator would, in practice, be almost impossible to detect by direct measurement, whereas this is not the case for $E(\varepsilon, t)$: the distinction between $\ln t_1$ and $\ln(\ln t_1)$ is considerable. Nevertheless (71) does give the interesting result that the exact long-time decay of $D(\varepsilon, t)$ can be stronger than $1/t$ as shown above for an exponential density of states. Given $G(\varepsilon, t)$ for a model $\rho(\varepsilon)$ we can immediately deduce the corresponding $D(\varepsilon, t)$ for long times. Equation (67) should as a matter of fact represent a reasonable approximation also for intermediate times.

SUMMARY FOR AN EXPONENTIAL $\rho(\varepsilon)$

Consider $\rho(\varepsilon) = \varepsilon_0^{-1} e^{-|\varepsilon|/\varepsilon_0}$ and $t \rightarrow \infty$:

$G(\varepsilon, t)$	$E(\varepsilon, t)$	$D(\varepsilon, t)$
$\exp[-p(\varepsilon)t_1]$	$-\varepsilon_0 \ln t_1$	$\frac{1}{6} \bar{r}^2 \frac{1}{t}$
$\frac{1}{t_1^{\alpha_0 n(\varepsilon)}}$	$-\varepsilon_0 \ln(\ln t_1^{\alpha_0})$	$\frac{1}{6} \bar{r}^2 \frac{1}{t} \frac{1}{(\ln t_1^{\alpha_0})}$
$\exp[-n(\varepsilon)\gamma_d t_1^{d/S}]$	$-\varepsilon_0 \ln(\gamma_d t_1^{d/S})$	$\frac{1}{6} \bar{r}^2 \frac{1}{t} \frac{d}{S\gamma_d}$

(72)

DISCUSSION AND THE EFFECT OF FINITE T

Figure 1 illustrates the “freezing-in” of energy relaxation for a Gaussian $\rho(\varepsilon)$ at low T as calculated by the Monte Carlo technique (for a description of the Monte Carlo technique used see Ref. 20). The analytical asymptotic law (55) is plotted for comparison. The trend is remarkably well reproduced by (55); Fig. 2 is again a comparison of Monte Carlo with asymptotic form (55) when

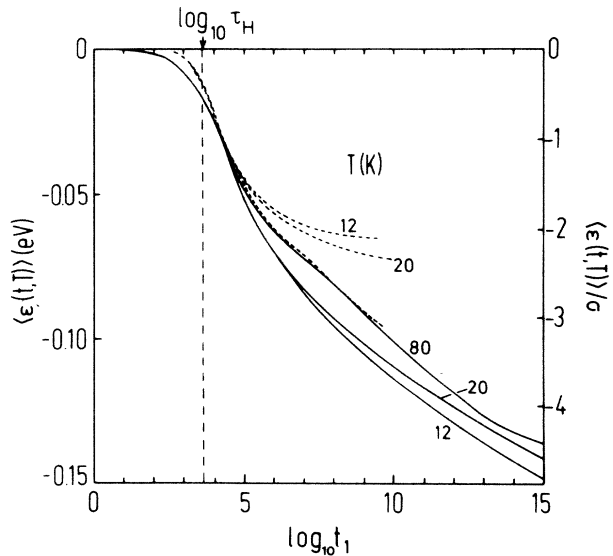


FIG. 1. A comparison of Monte Carlo simulations (dashed line) ($\sigma = 31$ meV; $2an^{-1/3} = 10$; $t_1 = v_0 t$) with effective-medium theory (solid line) $\tau_H = (\bar{v})^{-1}$ as given by (23).

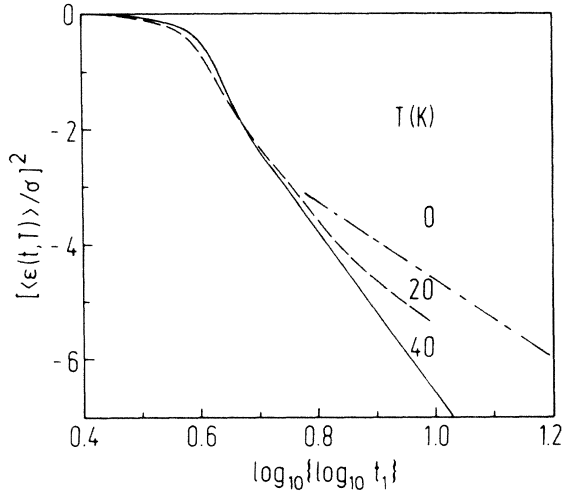


FIG. 2. The Monte Carlo evaluation of squared of the energy function (8) plotted against $\log_{10}\log_{10}t_1$ for two different temperatures $T=20$ K (dashed line) and $T=40$ K (solid line) ($\sigma=31$ meV; $2\alpha n^{-1/3}=10$; $\varepsilon=0$). The $T=0$ curve represents the asymptotic law (55) for the Gaussian model, with α_0 from (22b), $t_1 = \nu_0 t$ and energy in units of σ . The absolute position of the theory curve is arbitrary.

$\rho(\varepsilon)$ is a Gaussian at different temperatures. Again the agreement is very satisfactory. We should remember that the theory curve (dashed dotted) is evaluated for $T=0$ and therefore slower in decay than the Monte Carlo values. It is also very interesting to observe that the finite- T decays are well represented by the $T=0$ asymptotic law provided the *effective slope is made T dependent* see Figs. 1 and 2. Thus we conclude that at low T we can use the asymptotic forms and to first approximation renormalize the slopes, i.e., $\varepsilon_0 \rightarrow \varepsilon_0(T)$ (exponential) and $\sigma \rightarrow \sigma(T)$ Gaussian. For Förster rates this immediately follows from Eq. (B4) of Ref. 19, where $G(\varepsilon, t)$ is evaluated at finite T . Thus we can conclude that the asymptotic forms are reasonable representations also for intermediate times and low T . Figure 3 illustrates the difference between the power law decay of $G(\varepsilon, t)$ and the exponential decay on $E(\varepsilon, t)$ for $\alpha=0.1$ and for the exponential band tail model (44) in the intermediate time domain. Though for the present value of the parameters the curves are not yet truly in the asymptotic domain, we see that the influence of the power law on the slowing down of $E(\varepsilon, t)$ is considerable. Figure 4 corresponds to the same situation except that we have now considered the long-time region and have compared with the asymptotic law (52). Compare with the measurements of energy relaxation on GaAs-Al_xGaAs_{1-x} multiple quantum well by Matsumoto *et al.* (Ref. 13) and, in particular, with the data of Ryan *et al.* [Ref. 14(b), Figs. 1 and 4].

The experimental curve in Ref. 13 exhibits an almost perfect linear time dependence over the region $t > 100$ ps. The theoretical single pulse curve shown in Figs. 3 and 4 do exhibit what could be interpreted as an almost linear regime in the relevant time domain. However we must remember that the measured values refer to an average

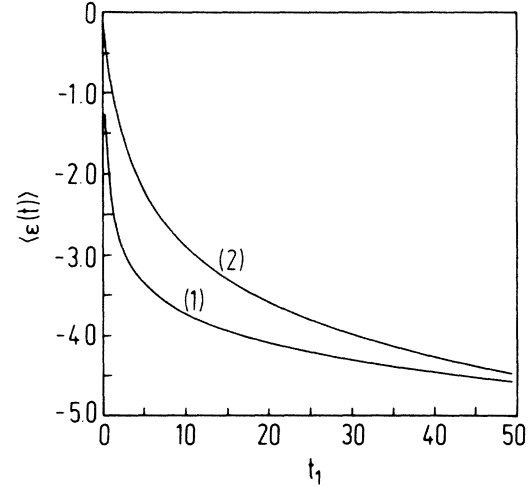


FIG. 3. A comparison of effective medium [curve (2)] from (45) in the text and "exact" energy relaxation as calculated by Eq. (50) curve (1) in the intermediate time domain for an exponential density of states (44). Note the difference in the energy lost per unit time ($\alpha_0=0.1$). (Time is $t_1 = \nu_0 t$; $\varepsilon_0=1$; $\varepsilon=0$.)

and not to a single δ pulse. The experimental curve is related to $E(\varepsilon, t)$ by the equation

$$[\bar{E}(t)]_{\text{expt}} = \frac{\int_{-\infty}^{\infty} \rho(\varepsilon') E(\varepsilon', t) f(\varepsilon') d\varepsilon'}{\int_{-\infty}^{\infty} \rho(\varepsilon') f(\varepsilon') d\varepsilon'} \quad (73)$$

where $f(\varepsilon')$ is the probability function for the exciton distribution after having thermalized into the localized states caused by the interface disorder (well-width fluctuations).

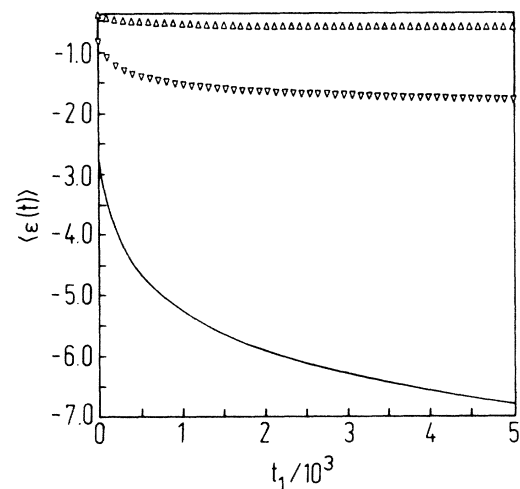


FIG. 4. Same as in Fig. 3 except for the longer-time scale. The asymptotic $-\varepsilon_0 \ln\{\ln t_1\}$ law is plotted for comparison. Solid line: EMA Eq. (45); upper triangular "exact" as defined by Eq. (50); lower triangles represent $-\varepsilon_0 \ln(\ln t_1)$, which is the asymptotic law (52) up to a constant energy shift. Note that the "linearity" of the decay with time in the two upper curves is somewhat misleading and has to do with the energy scale, i.e., if plotted on the same scale as the experimental diagram in Ref. 13 it would look more like Fig. 3. Compare $d \langle \varepsilon(t) \rangle / dt$ in the lower and upper curves.

The initial distribution can be found experimentally as shown in Ref. 13. Direct comparison of $E(\epsilon, t)$ with experiment can be expected in the long-time domain since $E(\epsilon, t)$ becomes independent of start energy at long times and therefore can be taken outside the integral in (73). This is then consistent with the linear domains exhibited by Figs. 3 and 4 in the “long-time” regions. Note, however, that EMA has the same feature and that the true distinction between “exact” and “EMA” are in the energy relaxed/per unit time which are considerably different in the two cases as shown by Figs. 3 and 4 [see also, Fig. 4, Ref. 14(b)].

We shall not pursue this analysis further in this paper but only note that (1) the exact structure of the system which lead to isolated sites and clusters does indeed considerably slow down the relaxation rate in the relevant time domain as observed experimentally and (2) the improved theory does indeed appear to exhibit an almost linear region even for a sharp initial pulse. We should remember also that a rigorous calculation would have to use the power $G(\epsilon, t)$ given by (21). This function starts off as being exponential when $\bar{\nu}t < 1$ [effective-medium region curve (2) of Fig. 3] and then gradually becomes a power law [curve (1) of Fig. 3] $\bar{\nu}t \gg 1$.

Let us now consider the interesting work due to Kastner,²¹ Monroe,²² and more recently due to Wilson *et al.*²³ Kastner derived Eq. (52b) with $\epsilon_0 \rightarrow \epsilon_0 \bar{d} = 3\epsilon_0$ for an exponential tail using a hop optimization technique. It is interesting to observe that the optimization method corresponds here to be strictly asymptotic domain of our solution. One can presumably apply the optimization method for other forms of $\rho(\epsilon)$ as well. Kastner’s result has recently been used by Wilson and co-workers to explain the photoluminescence shift as a function of time and temperature in *a*-Si:H.

One must remember that all the above considerations apply in a real experiment only to the time domain *prior to the onset of recombination*. The recombination rates λ_i can themselves be random variables as discussed in Ref. 1. The approximation of replacing the $\{\lambda_i\}$ with $\langle \lambda_i \rangle = \bar{\lambda}$ then implies that all the above results for $E(\epsilon, t)$ and $D(\epsilon, t)$ must be multiplied by a factor $\exp[-\bar{\lambda}t]$.

Let us now consider the effect of finite temperatures. The influence of temperature works in two different directions. On the one hand, temperature will increase the number of possible jump sites allowing now both upward and downward jumps in energy. In Eq. (27) the integral over energy will now run over all energies with the rules given by (2). The second modification is that (a) backward jumps are now allowed and (b) walks over closed loops are now also permitted. The latter immediately implies that the averaging procedure of treating each bond effectively as an independent variable is no longer exact. Point (a) means that the self-energy entering the denominator of the probability functions is now finite as dis-

cussed in detail in I, II, and III. Point (b) formally represents a formidable problem. In reality, however, we can take care of loop correlations by an effective renormalization of site densities as shown in detail in Ref. 15. Essentially what one does is to replace the true correlations by effective pair correlations only with a renormalized density (or mean-site separation), this then takes care of percolation effects. The procedure is only allowed in infinite range hopping problems where there is no true percolation threshold. The influence of correlations here is only to renormalize the density of the effective network. At very low temperatures we therefore suggest that the neglect of backward jumps, i.e., the retainment of W_{ij} of (20) represents a reasonable approximation. Thus the local correlation function $G(\epsilon, t)$ must now be evaluated at finite T using (20). The function $G(\epsilon, t)$ as given by (20) at finite T has been evaluated (in several references particular.^{16,19}) The asymptotic laws derived here retain their validity at low T provided the “slopes” are allowed to vary with T . For the more general solution we note that the integral equation (6) is now unfortunately not simply soluble, low- T expansions are possible but will not be discussed in the present paper. Approximations should be checked using Monte Carlo techniques. Finally let us recall that in the short-time regime we can always use the EMA but the extension to finite T is not much more straightforward since the integral equation in energy remains.

We have presented an exact zero-temperature relaxation and diffusion theory for excitations whose dynamics obey a master equation and where the bonds W of the network are independently distributed according to a distribution $Q(W)$. We have presented exact asymptotic decay laws for $E(\epsilon, t)$ and $D(\epsilon, t)$. We have also demonstrated the effect of the “freezing-in” of excitations on “isolated” clusters and have compared our results with the Monte Carlo simulations. Experimentally, the effect has been observed in the energy relaxation of Benzophenone glasses and in semiconductor QW structures.

In this paper we have focused our attention on a comparison theory versus “exact” Monte Carlo simulation, and a qualitative analysis of experiments on QW structures in the long-time regime. A quantitative comparison with the QW data requires, in addition to the above theory, knowledge of the distribution function $f(\epsilon)$ for the thermalized excitations in Eq. (73). This will be considered in a future paper.

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¹B. Movaghar, M. Grünewald, B. Ries, and H. Bässler, Phys. Rev. B 33, 5545 (1986).

²M. Grünewald, B. Movaghar, B. Pohlmann, and D. Würtz, Phys. Rev. B 15, 8191 (1985); Proceedings of the International

Conference on Amorphous and Liquid Semiconductors, Rome, 1985 [J. Non-Cryst. Solids 77/78, 163 (1985)].

³M. Grünewald, B. Pohlmann, B. Movaghar, and D. Würtz, Philos. Mag. B 49, 341 (1984).

- ⁴H. Bässler, *Phys. Status Solidi B* **107**, 9 (1981).
- ⁵D. L. Huber, in *Laser Spectroscopy of Ions, Molecules, and Solids*, edited by W. M. Yen and P. M. Selzer (Springer-Verlag, Berlin, 1981); *J. Chem. Phys.* **78**, 2530 (1983); W. Schirmacher, *Solid State Commun.* **39**, 893 (1981).
- ⁶G. Pfister and H. Scher, *Acta Phys. Pol.* **27**, 747 (1978).
- ⁷H. Scher and E. W. Montroll, *Phys. Rev. B* **12**, 2455 (1975).
- ⁸T. Tiedje and A. Rose, *Solid State Commun.* **37**, 49 (1981); J. M. Hvam and M. H. Brodsky, *J. Phys. (Paris) Colloq.* **42**, C4-551 (1981).
- ⁹D. Monroe, J. Orenstein, and M. Kastner, *J. Phys. (Paris) Colloq.* **42**, C4-561 (1981).
- ¹⁰K. D. Rockwitz and H. Bässler, *Chem. Phys.* **70**, 307 (1982).
- ¹¹R. Richert and H. Bässler, *Chem. Phys. Lett.* **118**, 235 (1985).
- ¹²E. Göbel, H. Jung, Z. Kuhl, and K. Ploog, *Phys. Rev. Lett.* **51**, 1588 (1983).
- ¹³T. Takagahara, *Phys. Rev. B* **31**, 6552 (1985); Y. Masumoto, S. Shionoya, and H. Kawaguchi, *ibid.* **29**, 3324 (1984); J. Hegarty, L. Goldner, and M. D. Sturge, *ibid.* **30**, 7346 (1984).
- ¹⁴(a) S. F. Ryan, R. A. Taylor, A. J. Tarberfield, and J. M. Worlock, in *Abstracts of the Yamada Conference on Two Dimensional Systems EP2Ds VI Kyoto, 1985* (unpublished), p. 712; (b) *4th International Conference on Hot Electrons in Semiconductors, Innsbruck, Austria, 1985* (North-Holland, Amsterdam, 1985), p. 404.
- ¹⁵B. Movaghar and W. Schirmacher, *J. Phys. C* **14**, 589 (1981).
- ¹⁶T. E. Orlowski and H. Scher, *Phys. Rev. Lett.* **54**, 220 (1985).
- ¹⁷M. Inokuti and F. Hirayama, *J. Chem. Phys.* **43**, 1973 (1965).
- ¹⁸M. Klafter, A. Blumen, and G. Zumofen, *J. Phys. (Paris)* **45**, L49 (1984).
- ¹⁹R. Parson and R. Kopelman, *J. Chem. Phys.* **82**, 3692 (1985), and references therein.
- ²⁰G. Schönherr, H. Bässler, and M. Silver, *Philos. Mag. B* **44**, 47 (1981); **44**, 369 (1981).
- ²¹M. Kastner, *J. Non-Cryst. Solids* **35/36**, 807 (1980).
- ²²D. Monroe, *Phys. Rev. Lett.* **54**, 146 (1985).
- ²³B. A. Wilson, T. P. Kerwin, and J. Harbison, *Phys. Rev. B* **31**, 7953 (1985).