# Theory of photoluminescence decay and electric-field-dependent energy relaxation in disordered materials at low temperature

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**Abstract.** We present a systematic and exact evaluation of diffusivity, energy, photo-luminescence (PL) decay and photoconduction for systems with energetic and positional disorder in the low-temperature limit. Whereas most quantities can be calculated analytically in the long-time limit (slowing down of relaxation), the PL requires explicit calculation of the total transition probability $G_{ij}(t)$. The problem can be solved by a step-by-step approximation for a simplified PL model, emphasising the diffusional aspect. Finite electric fields lead to drastic modifications of relaxation laws at low temperature. We derive a formalism which can be applied with great generality in particular to amorphous semiconductors, quantum-well superlattices and disordered organic materials.

## 1. Introduction

The relaxation of energy and diffusion of excitations in structures characterised by a density of localised states is a problem of great current interest in amorphous semi-conductors, quantum wells and superlattices [1–4]. Exact analytic methods and Monte Carlo simulations have been used to study this problem [5–8]. Effective-medium tech-niques, which are usually very accurate at high temperatures, turn out to be quite misleading at low $T$. Exciton relaxation and photoconductivity data taken on amorphous silicon and benzophenone glass at very low $T$ do indeed confirm the slow relaxation rates (freezing-in) predicted by theory [9–12]. Recent Monte Carlo simulations by Ries and Bässler suggest that the excitons freeze-in even when the Coulomb forces are taken into account [13, 14]. In this paper we examine the effect of electric fields on energy relaxation and photoluminescence (PL) in amorphous semiconductors and superlattice structures. The electric field produces qualitative changes in the time dependence and suggests novel resonance-type phenomena.

Basically the problem consists of studying the following phenomenon: imagine a density of states $\rho(\varepsilon)$ characterised by a mobility edge $\varepsilon_c$ or mobility edges (for particles and holes). An 'electron' is excited above $\varepsilon_c$ from which point onwards it will relax more slowly having to hop from site to site in a random system of localised states. Since this process takes place usually at a band edge, the density of states $\rho(\varepsilon)$ is a rapidly decreasing function of energy (exponential or Gaussian). This in turn implies that the number of

available relaxation sites is rapidly depleted with each jump at very low temperatures. The consequent phenomenon of 'freezing-in' of excitations has been demonstrated in various glassy and amorphous substances [9–11].

This paper is concerned with the effect of an electric field on this relaxation process at low temperatures. From the above discussion, the reader can immediately infer the importance that an applied field will have for the long-time low-temperature relaxation: in the presence of a field, the number of relaxation sites is greatly enhanced in the field direction. Indeed the particle can now, even at $T = 0$, drift in the field direction and always find a site of lower energy to relax into. Though linear response theory obviously breaks down, mean-field theories become acceptable again in the presence of electric fields because the excitation eventually reaches a 'steady state' for which the concept of an effective medium is again meaningful. This is, of course, not so for zero field and zero temperature where there is no 'steady state'. The generality of the above phenomena should now be evident and its wide range of applicability in most areas of solid-state physics has also been demonstrated.

At zero temperature and in the absence of an electric field, the transport problem can be solved exactly for certain classes of disorder (random distribution of sites and energies); see [12].

The $T = 0$ theory can be extended to finite, but low, $T$ by approximate consideration of the number of additional sites available at finite temperatures. The principal features will be outlined, with emphasis on the change of relaxation laws.

The paper is organised as follows. After this introduction we will give a brief description of the *theory* and principal methods of the formalism, relying heavily on former papers and results [14]. Section 5 summarises the principal *analytical* (asymptotic) results for the different situations of interest. In § 6 we will present some typical *numerical* results showing the transition between the various regimes and give some important results and predictions regarding typical experimental situations. Finally we consider the very important problem of photoconductivity (carrier drift) at low temperatures and finite electric fields. Recombination and generation are not treated in this paper. We show that linear response theory cannot be applied to this situation. A new formalism is therefore required and this is discussed with emphasis on amorphous semiconductors. Some of the most interesting applications of our formalism will be to the field of superlattices and quantum-well (QW) physics, in particular superlattice photodetection [15, 16]. We shall discuss this topic in detail in a future paper.

The last section of this paper is a summary of the material covered and a presentation of the main conclusions and future perspectives with suggestion for new experiments.

## 2. Theory of transport and relaxation at low temperatures

In a series of papers [17], we have developed the theory of current and energy decay in disordered systems. Starting with the master equation for incoherent motion (for simplicity without loss terms) we recall that the carrier density $n_i(t)$ at site $i$ obeys

$$\mathrm{d}n_i/\mathrm{d}t = - \sum_j W_{ij} n_i(t) + \sum_j W_{ji} n_j(t). \tag{1}$$

The experimental quantities of interest can be calculated from the Green function $G_{ij}(t)$, which is the formal solution (1). In Laplace space the solution can be written

$$G_{ij}(p) = G_{ii}^0 \left( \delta_{ij} + \sum_l W_{il} G_{lj} \right) \tag{2}$$

with the local Green function $G_{ii}^0$ in Laplace space $p$ given by

$$G_{ii}^0 = \frac{1}{p + \Sigma_l W_{il}}. \tag{3}$$

'Barred' quantities are understood as configurationally averaged, keeping the initial and final sites $i, j$ fixed, i.e. $\bar{G}_{ij} = \langle G_{ij} \rangle_{ij}$, etc.; the transfer rates are denoted by $W_{ij}$. The diffusivity $D_i(t)$ and energy relaxation function $E_i(t)$ are given explicitly by

$$D_i(t) = \partial \left( \sum_j R_{ij}^2 \bar{G}_{ij}(t) \right) \Big/ \partial t \tag{4}$$

$$E_i(t) = \sum_j \varepsilon_j \bar{G}_{ij}(t). \tag{5}$$

Averaging has to be done using the density-of-states (DOS) function $\rho(\varepsilon_j)$. Typical shapes are exponential for DOS tails in amorphous semiconductors and Gaussian in disordered organic material. The other 'input parameters' of the theory are the transition probabilities $W_{ij}$, depending on the interaction under consideration. Two typical situations arise:

(i) exciton singlet transfer

$$W_{ij} = \nu_0 (R_0/R_{ij})^6 f(\Delta \varepsilon_{ij}/kT) \tag{6}$$

(ii) electronic carrier transport or triplet excitonic transition

$$W_{ij} = \nu_0 f(\Delta \varepsilon_{ij}/kT) \exp(-2\alpha R_{ij}). \tag{7}$$

The energy- and temperature-dependent part has been summarised in $f(x)$, which is typically of exponential form

$$f(x) = \exp[-\tfrac{1}{2}(x + |x|)] \qquad x = (\varepsilon_j - \varepsilon_i)/kT. \tag{8}$$

The broad distribution of transition probabilities due to the exponential dependence on energy and space is the characteristic *label* of this kind of disorder. At finite (high) temperatures we have successfully applied the effective-medium approximation (EMA) for solving the transport problem in good agreement with Monte Carlo (MC) simulations and experiment [5].

At low (zero) temperature, the relaxation process is always directed downwards in energy and therefore the energy equation (5) simplifies to (in Laplace space)

$$E_i = \varepsilon_i \langle G_{ii}^0 \rangle_i + \sum_l \langle G_{ii}^0 W_{il} \rangle_{il} E_l \tag{9}$$

which allows an explicit solution [12]

$$E(\varepsilon, p) = \varepsilon G(\varepsilon) + g_1(\varepsilon) \int^\varepsilon d\varepsilon' \, \rho(\varepsilon') \varepsilon' G(\varepsilon') \exp \left( \int_{\varepsilon'}^\varepsilon d\varepsilon'' \, \rho(\varepsilon'') g_1(\varepsilon'') \right) \tag{10}$$

with $\bar{G}(\varepsilon, p) = G(\varepsilon)$ or $G(\varepsilon, p)$ and

$$g_1(\varepsilon) = [1 - pG(\varepsilon)]/n(\varepsilon) \tag{11}$$

where $n(\varepsilon)$ is the ratio of sites with energies lower than $\varepsilon$. Similar equations can be

derived for the diffusivity and number of new sites visited. The main point is that the only quantity that requires explicit calculation is the *local* Green function. Therefore the problem has considerably simplified.

## 3. The luminescence decay

Regarding the *luminescence* decay, things are not as easy. The general formalism has been developed in [18] and therefore only a brief summary up to that point will be given here.

Starting with the general expression for the luminescence decay of light with energy $\varepsilon$ emitted from $\rho(\varepsilon_i)\Delta\varepsilon_i$ excitons starting at energy $\varepsilon_i$ at $t = 0$ and diffusing to energies $(\varepsilon_j, \varepsilon_j + \Delta\varepsilon_j)$ at time $t$,

$$\Delta L(\varepsilon_i, \varepsilon_j, \varepsilon, t) = \int \Delta\varepsilon_j\Delta\varepsilon_j\rho(\varepsilon_i)\rho(\varepsilon_i)G_{ij}(t)|M(\varepsilon_i, \varepsilon_j)|^2 \, \mathrm{d}R_i \, \mathrm{d}R_j \tag{12}$$

the key quantity is the *non-local* propagator $\bar{G}_{ij}(t)$. The other important parameter is the matrix element $M(\varepsilon_i\,\varepsilon_j)$, mainly reflecting the specific model and/or experimental situation regarding recombination under consideration. As we want to look at the general *diffusional* aspect of the luminescence decay, we neglect the energy dependence of matrix elements $M$ and recombination (loss) rates $\lambda$ (by simply putting them constant), so that

$$L_{ij} = \frac{\Delta L \, \mathrm{e}^{\bar{\lambda}t}}{\Delta\varepsilon_i\Delta\varepsilon_j|M|^2} = \int \mathrm{d}R_i \, \mathrm{d}R_j \, \bar{G}_{ij}(t)\rho(\varepsilon_i)\rho(\varepsilon_j) \tag{13}$$

is therefore the quantity of interest.

The exact multi-step expansion reads (in Laplace space)

$$G_{ij}(p) = G_{ij}^0\delta_{ij} + \Delta G_{ij}^{(1)} + \Delta G_{ij}^{(2)} + \dots \tag{14}$$

with

$$\Delta G_{ij}^{(1)} = W_{ij}\frac{1}{p + \Sigma_i}\frac{1}{p + \Sigma_j} \tag{15}$$

$$\Delta G_{ij}^{(2)} = \sum_l W_{il}W_{lj}\frac{1}{p + \Sigma_i}\frac{1}{p + \Sigma_l}\frac{1}{p + \Sigma_j} \tag{16}$$

$$\varepsilon_i = \sum_l W_{il} + \lambda_i \tag{17}$$

still including the loss term $\lambda_i$.

Transforming the products (in Laplace space) into convolution integrals (in time space), we arrive at

$$\Delta G_{ij}^{(2)}(t) = \frac{\Sigma_l \, W_{il}W_{lj}}{\Sigma_i - \Sigma_j}\left(\frac{\exp(-\Sigma_l t) - \exp(-\Sigma_j t)}{\Sigma_j - \Sigma_l} - \frac{\exp(-\Sigma_l t) - \exp(-\Sigma_i t)}{\Sigma_i - \Sigma_l}\right). \tag{18}$$

The configurational average results in

$$\langle\Sigma_i\rangle = \langle\Sigma_l \, W_{il}\rangle \rightarrow n \int \mathrm{d}r \, \mathrm{d}\varepsilon \, \rho(\varepsilon)W(r, \varepsilon) = n(\varepsilon_i)\bar{W} \tag{19}$$

(at $T = 0$, $\bar{W} = (\pi/6)n\alpha^{-3}$). Therefore

$$\langle\Delta G_{ij}^{(1)}(t)\rangle = \frac{\rho(\varepsilon_i)\rho(\varepsilon_j)}{n(\varepsilon_i) - n(\varepsilon_j)}[G(\varepsilon_j, t) - G(\varepsilon_i, t)] \tag{20}$$

$$\langle\Delta G_{ij}^{(2)}(t)\rangle = \frac{\rho(\varepsilon_i)\rho(\varepsilon_j)}{n(\varepsilon_i) - n(\varepsilon_j)}[G(\varepsilon_j, t)E(\beta(n_i - n_j)) + G(\varepsilon_i, t)E(\beta(n_j - n_i))] \tag{21}$$

$$E(x) = \int_0^x \mathrm{d}x'(1 - \mathrm{e}^{-x'})/x' \tag{22}$$

whereas for $T = 0$

$$G(\varepsilon, t) = \mathrm{e}^{-n(\varepsilon)\beta(t)} \tag{23}$$

$$\beta(t) = n \int \mathrm{d}\mathbf{r} \, (1 - \mathrm{e}^{-tW(r)}) \tag{24}$$

with $W(r)$ representing the position-dependent factor of the transition rates. Again, the PL has been expressed in a systematic way by the *local* Green function although the solution is not accurate enough at long times due to the multi-step expansion.

## 4. The influence of an electric field

Extension to *finite* (low) *temperatures* and *electric field F* is now simple and possible by proper calculation of $\bar{G}_{ij}(t, F)$.

### 4.1. Finite external electric field F

In general the influence of electric fields in hopping conduction is complicated by effects such as the variation of wavefunctions [17], percolation effects [19] and new mobility laws [20]. Again, we want to confine ourselves to the pure diffusional aspect at very low $T$ $(T \to 0\ \mathrm{K})$. Here the main effect is on energy, manifesting itself by enhancement of the number of accessible sites *in* the field direction. Introducing the electrochemical energy $E_i = \varepsilon_i - eFx_i$, the energy condition (at $T = 0$) reads (see figure 1)

$$E_j = \varepsilon_j - eFx_j < \varepsilon_i - eFx_i = E_i. \tag{25}$$

Therefore sites with single site energies $\varepsilon_j > \varepsilon_i$ at $F = 0$ become accessible *in* the field direction, resulting in improved (accelerated) relaxation.

The calculation can be started from the general expression

$$G_{ii}(t) = \exp\left(-n \int \mathrm{d}\mathbf{r} \, \mathrm{d}\varepsilon \, \rho(\varepsilon)[1 - \exp(-W_{ij}t)]\right). \tag{26}$$

Carrying out the (anisotropic) integration in $(\varepsilon, r)$ space, following (25), we arrive at $(T = 0)$

$$\ln G_{ii} = -n2\pi \int_0^\infty \mathrm{d}r \, r(1 - \mathrm{e}^{-tW(r)}) \int_{-r}^r \mathrm{d}x \, n(\varepsilon_i + eFx). \tag{27}$$

Further evaluation and asymptotic regimes will be considered in the next sections, where we also consider the photoconductivity.

The field dependence of the PL decay can now be calculated from the solution of (27) within the multiple-step expansion to the desired accuracy by applying (20) or (21).

### 4.2. Finite (low) temperature T

As mentioned already above, the finite-temperature situation is complicated in general, requiring different methods for low (zero) temperature (exact solution, see above)

**Table 1**

|  | Gaussian | Exponential |
|---|---|---|
| Density of states, $\rho(\varepsilon)$ | $(1/x^{1/2}\sigma)\,\exp[-(\varepsilon/\sigma)^2]$ | $\exp(\varepsilon/\varepsilon_0)$ |
| Energy relaxation (asymptotic), $E(\varepsilon, t)$ | $-\sigma[3\ln(\ln\,\nu_0 t)]^{1/2}$ | $-\varepsilon_0\ln(\ln\,\nu_0 t)$ |

and high $T$ (EMA). Guided by the comparison of exact $T = 0$ theory and MC simulation at low $T$, we see that the main effect of temperature is an enhancement of the transition possibilities due to states lying higher in energy. This can be incorporated into the theory by calculating the finite-temperature Green function $G_i(\varepsilon, T) \equiv G(\varepsilon_i, t, T)$:

$$\ln G(\varepsilon_i, t, T) = -n \int_{-\infty}^{\varepsilon_i} \mathrm{d}\varepsilon_j\, \rho(\varepsilon_j) \int_0^\infty \mathrm{d}r\{1 - \exp[-tW(r_i\varepsilon_{ij})]\}$$

$$= \ln G(\varepsilon, t, T = 0) - n \int_{\varepsilon_i}^\infty \mathrm{d}\varepsilon_j\, \rho(\varepsilon_j)$$

$$\times \int_0^\infty \mathrm{d}r[1 - \exp(-t\,\mathrm{e}^{-2\alpha r_\mathrm{e}}\,\mathrm{e}^{-\beta(\varepsilon_j - \varepsilon_i)})] \tag{28}$$

with exponential dependence of the transition rates in space and energy, to be explicit.

Evaluation, of course, is now more involved, but armed with the solution of (28), calculation of PL and other quantities is straightforward using the formalism presented above.

## 5. Analytical and asymptotic solution

Although the theory presented above requires explicit and numerical evaluation for a full solution, some interesting features can already be extracted by analytical methods.

First, we look at the *energy decay* at $T = 0$ K and $F = 0$ V cm$^{-1}$. This case can be calculated from the general solution (equations (10) and (11)) by expansion in the long-$t$, small-$p$ limit [21]. This procedure can also be applied to the diffusivity and number of new sites visited:

$$E(\varepsilon, t \to \infty) = n^{-1}\left(\frac{n(\varepsilon)}{-\ln G(\varepsilon, t)}\right) \tag{29}$$

with $n^{-1}$ the inverse of $n(\varepsilon)$, the occupation number function.

Of special importance are the Gaussian and exponential DOS models (see table 1). These have to be compared with the simple logarithmic $kT\ln\nu_0 t$ behaviour at high temperatures (exponential DOS model). This slowing down of relaxation is a direct consequence of the change in time dependence of $\bar{G}_{ij}(t)$ at $T = 0$ K.

*Asymptotic* behaviour ($t \to \infty$) evaluation of (23) results in

$$G(\varepsilon, t) = \exp[-(\ln \nu_0 t)^3 nn(\varepsilon)(\pi/6)\alpha^{-3}]. \tag{30}$$

Assuming $\ln G^{-1} = 1$ for the cut-off energy $E$ between mobilised and immobilised states, one finds

$$E(t) = n^{-1} \left( \frac{6\alpha^3}{\pi n (\ln \nu_0 t)^3} \right) \tag{31}$$

which is virtually equation (29)!

We can therefore conclude that the asymptotic energy decay can be calculated from the Green function directly. This is of valuable help for the more complex situations, involving temperature or field.

At *short times*, the EMA is completely sufficient both at low and high temperatures

$$G_{ii}(t \to 0) = 1 - (\Sigma_i)t = \exp[-\langle \Sigma_i \rangle t] \tag{32}$$

e.g. simple exponential decay in contrast to the approximate power-law decay at $T = 0\,\mathrm{K}$, $t \to \infty$ (equation (30)).

The multi-step expansion essentially is an expansion in time and transition steps. This can be seen by expanding the exponentials in (19) and (21) (and using (24)):

$$\langle \Delta G_{ij}^{(1)}(t \to 0) \rangle \sim \rho(\varepsilon_i)\rho(\varepsilon_j)\beta(t). \tag{33}$$

$\beta(t) = \bar{W}t$ at short times, in agreement with the general expression (24). Thus

$$\langle \Delta G_{ij}^{(2)}(t \to 0) \rangle \simeq \frac{\rho_i \rho_j}{n_i - n_j} \{(1 - \beta n_j)[\beta(n_i - n_j) - \tfrac{1}{4}\beta^2(n_i - n_j)^2]$$
$$+ (1 - \beta n_i)[\beta(n_j - n_i) - \tfrac{1}{4}\beta^2(n_j - n_i)^2]\} \tag{34a}$$

$$\langle \Delta G_{ij}^{(2)}(t \to 0) \rangle = \rho_i \rho_j \tfrac{1}{2}\beta^2(n_i - n_j) \tag{34b}$$

which is quadratic in $t$ at short times and proportional to the number of sites *between* initial and final states. One can also see that the two-step contribution dominates when $\beta(t)(n_i - n_j) \gg 1$, i.e. at long times and large occupation-number difference. On the other hand, as $G(\varepsilon, t)$ already exhibits the correct long-time asymptotic power-law decay, qualitatively correct results can already be obtained by considering $\langle \Delta G_{ij}^{(n)} \rangle$ alone. At the end of the next section, we will explore the behaviour quantitatively by numerical calculation.

The *field* dependence, e.g. (27), can be approximated in the two limiting cases $F \to 0$ and $F \to \infty$.

(i) $F \to 0$:

$$\ln G_{ii} \simeq \ln[G_{ii}(F = 0)] - O(F^2) \tag{35}$$

i.e. square dependence of field.

(ii) $F \to \infty$:

$$\int_{-r}^{r} \mathrm{d}x\, n(\varepsilon + eFx) \to r$$

therefore

$$\ln[G_{ii}(F \to \infty)] = -n4\pi \int_0^\infty \mathrm{d}r\, r^2 (1 - \mathrm{e}^{-tW(r)})/2 \tag{36}$$

i.e. 'simulating' a constant DOS of $\tfrac{1}{2}$!

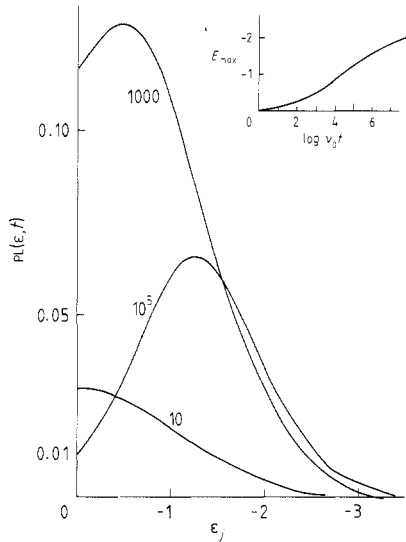**Figure 1.** Spectrum ($\varepsilon_j$) of transient photo-luminescence for three (dimensionless) different times ($\nu_0 t = 10, 1000, 10^5$) and Gaussian density of states (width $\sigma = 1$). Start energy $\varepsilon_i = 0$, $n\alpha^{-3} = 0.01$. Inset shows time-dependent shift of the peak energy $E_{max}$ (in units of $\sigma$).

Physically, *half* of the whole sites of the system (in forward field direction) are accessible, independent of the DOS shape. The situation therefore is very similar to the well known temperature dependence of hopping at the Fermi level, again exhibiting the close relation between temperature and field, but with constraints in geometry (half-space).

Similar to equation (31) the *energy* decay can be calculated approximately for the exponential DOS model

$$E(t, F) = E_0 - (eF/2\alpha) \ln \nu_0 t - 3\varepsilon_0 \ln(\ln \nu_0 t) \tag{37}$$

again confirming the enhancement of the relaxation by the field in a similar way to temperature (compare second and third terms!). Equation (37) should be compared to the mean-field result quoted in [12]. Effective-medium theories are again reasonable even at $T = 0$ for sufficiently large $F$.

## 6. Numerical results

The *PL decay* (without field and/or temperature) within the one-step approximation has already been published in [18]. We therefore present here only the *corrected* spectrum for the *Gaussian* DOS model (figure 1) at three different time steps. The initial energy $\varepsilon_i$ lies at the centre of the distribution. At short times ($\nu_0 t = 10$) PL is low and monotonically decreasing. The onset of diffusion is reflected in the enhancement of PL at $\nu_0 t = 1000$. At longer times PL is decreasing again due to the recombination. The shift in energy of the PL maxima is plotted explicitly in the inset showing the slow energy decay in the Gaussian DOS at $T = 0$ K. Further results for this DOS model will be given elsewhere. Instead, in the following, we will concentrate on the *exponential* DOS model ($\varepsilon_0 = 1$ energy unit, $\varepsilon_i = 0$ and $n\alpha^{-3} = 0.01$ in the following). Figure 2 shows the quenching of the PL with external electrical field for two different times ($\nu_0 t = 10^4$ and $10^5$) and final energies ($\varepsilon_j = -1, -2$). There is a non-trivial crossover
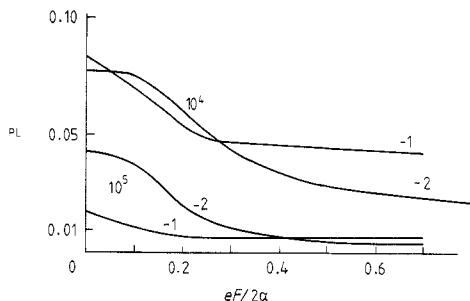
**Figure 2.** The field dependence of PL for two different times ($\nu_0 t = 10^4$, $10^5$) and final energies ($-1$, $-2$), as indicated by the values on the curves. Exponential DOS ($\varepsilon_0 = 1$), $n\alpha^{-3} = 0.01$. Start energy $\varepsilon_i = 0$. Figure shows quenching of PL with field. (Energy in units of $\varepsilon_0$.)
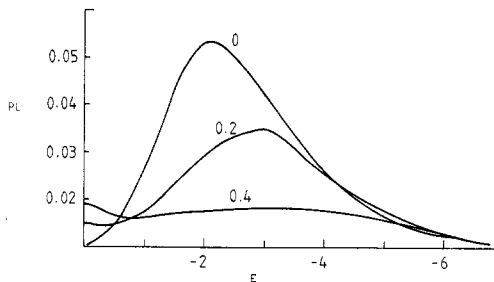
**Figure 3.** Spectrum of PL at fixed time ($\nu_0 t = 10^5$) and various electric fields ($eF/2\alpha = 0$, $0.2$, $0.4$). Other parameters as in figure 2. Plot shows broadening of spectrum with field. (Energy in units of $\varepsilon_0$.)
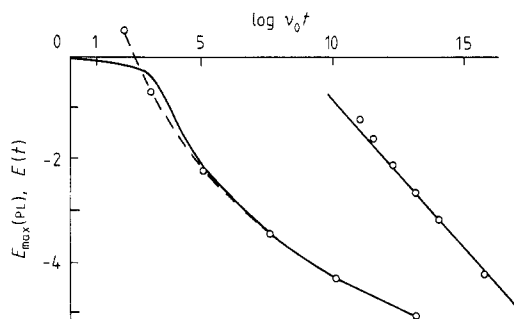


**Figure 4.** A plot of peak energy of PL spectrum (left, full curve) versus time compared to asymptotic decay law from equation (31) (exponential DOS model), $\varepsilon_0 = 1$. The broken curve represents the curve $E(t) = 5 - 3\varepsilon_0 \ln(\ln \nu_0 t)$ where $\varepsilon_0 = 1$. The curve $-\ln(\ln \nu_0 t)$ is also shown (right, full curve). (Energies are in units of $\varepsilon_0$.)

between the two different energies at a given time. Owing to the chosen (long) time, the PL is lower at $10^5$ for all fields and both energies.

Figure 3 exhibits the change of the transient PL spectrum (at a given time $\nu_0 t = 10^5$) with field. Mainly two features are important:

(i) The shift of the PL peak to lower energies with increasing magnitude of the field. This reflects the enhancement of 'diffusion' with electric field.

(ii) The broadening of the spectrum with field, mainly indicating the increase of transition probabilities at higher fields. Additionally the spectrum is broad sloped at high fields and short times.

In this case the maximum is not well defined with some spurious behaviour at small energies.

Next we will consider some typical behaviour of the *energy* decay. As already stated in the preceding sections, the time decay of the PL maximum can be approximated well by the cut-off energy of the local Green function $G(\varepsilon, t)$. To this aim we compare the expression, given by (31), with peak energy $E_{\max}(\text{PL})$, estimated from the full spectrum at different times (not shown here). Figure 4 shows that for times larger than $10^4$ the coincidence is nearly complete. Therefore in the following the energy decay will always be calculated from the cut-off energy of $G(\varepsilon, t)$.

The main result of the present paper is the change in time dependence of the energy decay with field, for $T = 0$, which is plotted in figure 5.
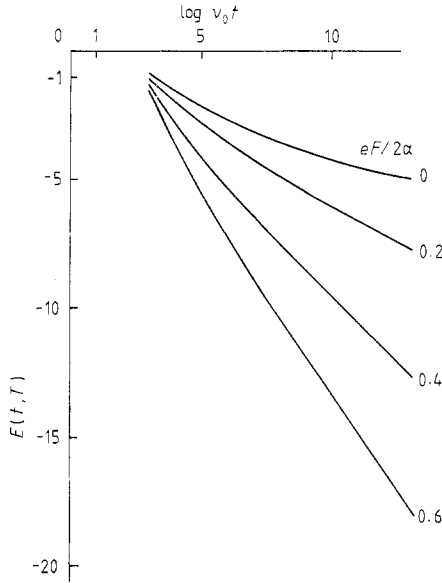
**Figure 5.** The field dependence of energy decay at $T = 0$ K. The figure shows the transition from slow $\ln(\ln \nu_0 t)$ decay at $F = 0$ to $\ln \nu_0 t$ law at higher fields (exponential DOS model), $n\alpha^{-3} = 0.01$, exponential $\rho(\varepsilon)$ with $\varepsilon_0 = 1$. (Energies are in units of $\varepsilon_0$.)
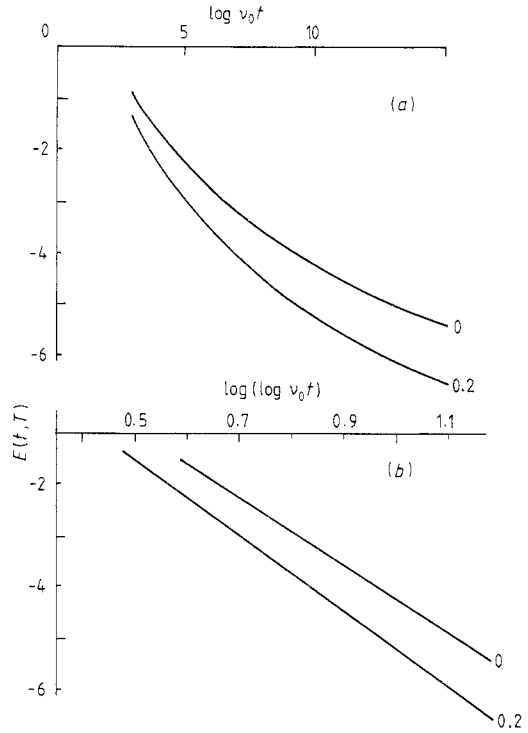
**Figure 6.** Energy decay for $T = 0$ and $T = 0.2$ (exponential DOS model, slope $\varepsilon_0 = 1$): (a) $E(t, T)$ versus log $\nu_0 t$; (b) $E(t, T)$ versus log(log $\nu_0 t$). This figure shows scaling of energy at low $T$ ($\varepsilon_0 \rightarrow \varepsilon_0 + 0.5T$ approximately), $n\alpha^{-3} = 0.01$. (Energies are in units of $\varepsilon_0$.)

One observes the transition from the very slow double-logarithmic relaxation without the field, characteristic of *non*-activated hopping-*down* motion, to the 'activated', simple logarithmic behaviour. The last law is also typical for high-temperature hopping relaxation [21] or multiple trapping [1].

Note that the field is playing the *role of temperature* at $T = 0$ K!

The enhancement of relaxation at low, but finite, temperature can be calculated approximately from the finite-temperature Green function (equation (28)). In figure 6(a) $E(t, T)$ is plotted against log $\nu_0 t$, comparing the $T = 0$ and $T = 0.2$ relaxation energy (which is $\varepsilon$, the slope of the exponential DOS tail). To show the decrease of slope more quantitatively, the same curves are plotted in figure 6(b) versus log(log $\nu_0 t$). As argued from general reasons already in the preceding sections, the decay law at finite $T$ is still double-logarithmic, but with increased slope ($\varepsilon_0 + 0.5\,T$) (this follows approximately from the figure). Therefore, *energy scaling is sufficient to describe low-T relaxation*! Of course, owing to the limited Ansatz, the precise transition to the high-$T$ situation cannot be given within the present approach. But this was not the goal and scope of the present investigation.

The last figure in this paper shows the extension of the formalism due to equation (21) by including the two-step contributions into the calculation. Figure 7 has to be compared with figure 4 from [22]. The plot covers a very large range in time, obviously
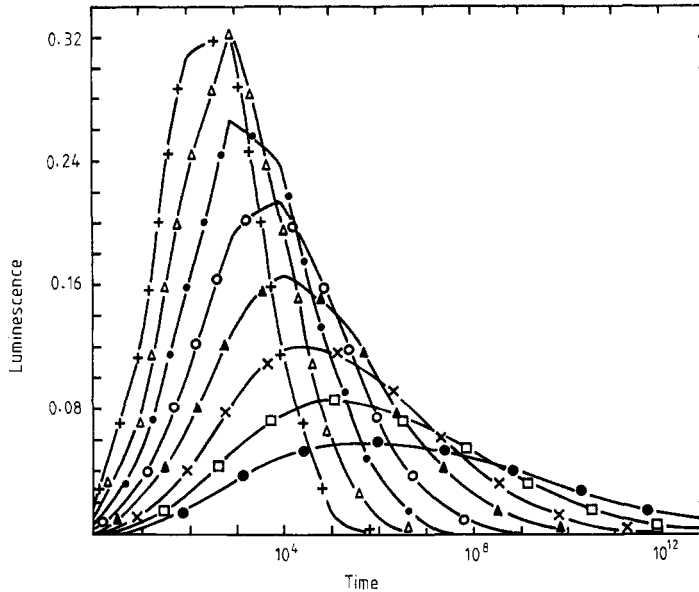
**Figure 7.** PL decay for various final energies ($\varepsilon_j = -1$, $-2$, $-3$) within the two-step approximation (exponential DOS model, $\varepsilon_i = 0$, $\varepsilon_0 = 1$). This figure shows the importance of higher-order terms at long times. The different symbols correspond to: $\varepsilon_j = -0.5$ (+), $-1$ ($\triangle$), $-1.5$ ($\bullet$), $-2$ ($\bigcirc$), $-2.5$ ($\blacktriangle$), $-3$ ($\times$), $-3.5$ ($\square$) and $-4.0$ ($\bullet$).

larger than the validity of the theory. The main effect of the two-step terms is the enhancement and shift of the PL maxima.

The effect is quantitatively substantial, indicating the need for an extension of the theory. Nonetheless the qualitative behaviour is still correct within the low-step expansions.

## 7. The field dependence of the 'photocurrent'

One of the most important quantities in the theory of relaxation in semiconductors, whether bulk, amorphous, thin films or superlattices [3, 18], is the behaviour of the photocarrier drift $I_p$ as a function of time, initial energy and elastic field. In the regime where linear responsive theory is valid ($eFR/kT_e \ll 1$) and where $T_e$ can be an effective hot electron temperature, there is a simple relation between $I_p(\varepsilon, t)$ and $D(\varepsilon, t)$ as given by (4).

Knowledge of the latter is therefore sufficient. At low temperatures and in band tails we are however easily in the regime $eF\bar{R} \geqslant kT_e$ because the density of states can be very small ($\bar{R}$ is large). Here one can no longer use linear response ideas and it is crucial to compute $I_p$ from first principles. We write therefore in Laplace space $p$

$$I_p(\varepsilon_i; p) = p \sum_j R_{ij} G_{ij}(p) \tag{38}$$

and using (2) we have

$$I_i(\varepsilon_i, p) = \sum_l R_{il} W_{il} G_{il}^0(p) + \sum_l G_{il}^0(p) W_{il} I_l(p) \tag{39}$$

where $I_l(p) = I_l(\varepsilon_l, p)$. At low temperatures, back jumps or loop processes to the same

site are very improbable (zero for $T = 0$) and it is therefore justified to decouple the configurational averages so that

$$I(\varepsilon_i, p) = I_0(\varepsilon_i, p) + \int\int d\varepsilon_l \, \rho(\varepsilon_l) \, dR_l \, G(\varepsilon_i, p)W(\varepsilon_i; \varepsilon_l, R_{il})I(\varepsilon_l; p) \tag{40}$$

where

$$I_0(\varepsilon_i; p) = \left( \int d\varepsilon_l \, \rho(\varepsilon_l) \int dR_l \, R_{il}W_{il} \right) G(\varepsilon_i, p). \tag{41}$$

We can conventionally rewrite this in time space as

$$I_0(\varepsilon_i, t) = V(\varepsilon_i, F)G(\varepsilon_i, t; F) \tag{42}$$

where $G(\varepsilon, t; F)$ is given by (27) and $V$ is a drift velocity, which is straightforward to evaluate for any model of $W_{ij}$.

Equation (39) is an integral equation exactly soluble at $T = 0$ when $F = 0$. For finite $F$ the energies $\varepsilon_\mu$ are given by $(\varepsilon_\mu^0 - eF \cdot R_\mu)$ so that there is a correlation between position and energy.

Let us consider (42) in two limits: (i) short time $t\Sigma_j \ll 1$, i.e. the particle has time to make a single jump to '$j$'; and (ii) $t\Sigma \gg 1$, i.e. the time is long enough so that memory of the initial energy is lost and $I(\varepsilon, t) \sim I(t)$. From the work in [15, 16] we know that the energy-dependent diffusivity curves eventually *merge into a single universal time decay curve*.

For case (i) we consider the first-order term $\Delta G_{ij}^{(1)}(t)$ contributing to $I_p$ for $t\Sigma_j \ll 1$; $I_p(\varepsilon, t)$ is given by (42).

Equation (42) is valid as long as the photocurrent is larger than the effective current of the effective new 'energy level' reached after the first (relaxation) jump, etc. Thus if $\varepsilon_1$ is the effective energy after the first jump, we have ($\varepsilon_1 < \varepsilon$)

$$I_p(\varepsilon, t) \sim V(\varepsilon, F)G(\varepsilon, F; t) \tag{43a}$$

$$I_p(\varepsilon, t) \sim V(\varepsilon_1, F)G(\varepsilon_1, F; t) \tag{43b}$$

etc., with $(43a) \leqslant (43b)$. In this 'iterative' way of looking at the short-time photoresponse, the mean energy relaxation rate as a function of time or number of steps is obviously a highly relevant quantity. Substituting the energy relaxation function $E(\varepsilon, t)$ (figures 5 and 6) instead of $\varepsilon$ in $(43a)$ should give us an excellent representation of the short-time photocurrent. When the rates $W_{ij}$ represent non-linear tunnelling rates as shown for example in [23], for superlattice and quantum-well systems, the combination $(43a)$ with $E(\varepsilon, F; t)$ and $V(E(\varepsilon, t); F)$ is the appropriate short-time photocurrent relaxation. In such cases we have negative differential resistance (NDR) effects and the possibility of space-charge oscillations with effective time-dependent internal electric fields. This time dependence will therefore modulate $V(\varepsilon, F) \rightarrow V(\varepsilon, F(t))$ and consequently lead to oscillations in the photocurrent decay (see [24]).

In the long-time limit (40) can be solved immediately to give

$$I(p)_{p \to 0} \sim \frac{\int I_0(\varepsilon'; p)f_e(\varepsilon') \, d\varepsilon'}{p \int G(\varepsilon', p)f_e(\varepsilon') \, d\varepsilon'} \tag{44}$$

or in time space ($T \to 0$)

$$I(t)_{t \to \infty} \sim \left\langle \frac{\Sigma_{j,i} f_{i,e} R_{ij} W_{ij}}{\Sigma_{i,j} f_{i,e} W_{ij}} \right\rangle \sum_i \left\langle \frac{1}{\Sigma_j f_{i,e} W_{ij}} \right\rangle^{-1} \tag{45}$$

where $f_{i,e}$ is an effective electronic distribution function established in the quasi-steady

state with an electric field present. Basically we can assume that $f_{i,e}$ is the same as the Fermi function with an effective electric-field-dependent temperature $T_e(F)$. Equation (45) is also a good approximation at low $T$; at higher $T$ when $eFR/kT_e < 1$, it is better to use the generalised transport theory developed in [25].

The effective field-dependent distribution function can be evaluated rigorously using the analogous energy, field and time-dependent relaxation equation (equation (39) for energy relaxation). We can then define $f_{i,e}$ using

$$E(\varepsilon, t)_{t \to \infty} = \frac{\sum_i f_{i,e} \varepsilon_i}{\sum_i f_{i,e}}. \tag{46}$$

Knowing the LHS we can determine $T_e$ for a given $\rho(\varepsilon)$. For most situations $E(\varepsilon, t)_{t \to \infty} \propto kT_e$.

Equation (46) together with an analogous relation for $E(\varepsilon, t)$ using (45) allows a determination of $kT_e$.

Yet another, and for the present purpose more convenient, way to characterise the steady state is to introduce the concept of a demarcation energy $\bar{E}$ such that the transfer rate above $\bar{E}$ is roughly the same as the net transfer rate to states below $\bar{E}$, i.e.

$$\sum_{\substack{\varepsilon_j < \bar{E} \\ R_j}} W(\bar{\varepsilon}; \varepsilon_j; R_{ij}) = \sum_{\substack{\varepsilon_j > \bar{E} \\ R_j}} W(\bar{\varepsilon}; \varepsilon_j; R_{ij}) \tag{47}$$

where $\varepsilon_j$ is the field free energy.

The evaluation of these relations naturally now depends on the actual system considered, superlattice, bulk semiconductor, etc. As a simple application, consider a semiconductor with a constant $\rho(\varepsilon)$. Using the theory developed in [5], we have a very elegant way of calculating the conductivity at long time.

This method, described in detail in [17], is not entirely equivalent to the $T = 0$ formula as given by (45) (for the latter we can use (26) and integrate over all times). In many respects, however, the following formula is more accurate because it is not restricted to $T = 0$ and allows back jump processes within the effective-medium description. Strictly speaking we are not at $T = 0$ but always at some $T_e > T$ when $F$ is finite.

From [5], defining $\sigma$ to be the effective jump rate from a site ($\varepsilon_i = 0$, $R_i = 0$) we have

$$1 = n \int d\mathbf{R} \int d\varepsilon_j \, \rho(\varepsilon_j) \frac{W(\mathbf{R}_j, \varepsilon_j)}{W(\mathbf{R}_j, \varepsilon_j) + \sigma} \tag{48}$$

where

$$W(\mathbf{R}; \varepsilon_j) = \begin{cases} \nu_0 \exp(-2\alpha|\mathbf{R}| - |\varepsilon_j - e\mathbf{F} \cdot \mathbf{R}|/kT) & \varepsilon_j - e\mathbf{F} \cdot \mathbf{R} > 0 \\ \nu_0 \exp(-2\alpha|\mathbf{R}|) & \varepsilon_j - e\mathbf{F} \cdot \mathbf{R} \leq 0 \end{cases} \tag{49}$$

where $W(\mathbf{R}; \varepsilon)$ is the energy- and distance-dependent jump rate, and $n$ is the density of sites. The prefactor $\nu_0$ can itself be a function of field and temperature but we shall treat it as a constant for simplicity.

At $T = 0$ only down jumps are allowed, so that if $\bar{\varepsilon}$ is an effective hot electron demarcation energy in the steady state, we have

$$\rho(\varepsilon) = 1/\omega \qquad \varepsilon \text{ in } [0, \bar{\varepsilon} + eFR \cos \theta] \tag{50}$$

for a jump to a site $R_j$.

Substituting in (46) we obtain

$$1 = 2\pi n \int \mathrm{d} R \int_{[\bar{\varepsilon} + eFR \cos \theta] > 0} [\bar{\varepsilon} + eFR \cos \theta] R^2 \sin \theta \, \mathrm{d}\theta \, \frac{1}{\nu_0^{-1} \sigma \, \mathrm{e}^{+2\alpha R} + 1}. \tag{51}$$

Writing $\sigma = \nu_0 \, \mathrm{e}^{-2\alpha \bar{R}}$, we can use (51) to obtain an effective jump distance $\bar{R}$. In order to obtain $\bar{\varepsilon}$ we need to know the average energy relaxed in a jump. This is obtained by noting that the particle can hop anywhere into the band from $[0, \bar{\varepsilon} + eF \cdot R]$ so that the average energy lost by the particle is

$$\varepsilon_R \sim \int_0^{\bar{\varepsilon} + eF\bar{R}/2} \varepsilon' \rho(\varepsilon') \, \mathrm{d}\varepsilon' \Big/ \int^{\bar{\varepsilon} + \rho F\bar{R}/2} \rho \, \mathrm{d}\varepsilon' = \frac{\bar{\varepsilon} + eF\bar{R}/2}{2}. \tag{52}$$

For steady state we have that

$$\varepsilon_R = eF\bar{R}/2 \tag{53}$$

so that the average energy lost just corresponds to the average energy gained by the field and $\bar{\varepsilon} \sim eF\bar{R}/4$.

Equation (51) can now be solved easily to give

$$\mathrm{e}^{-2\alpha\bar{R}} = \exp[-(64\alpha^4 W/2\pi n eF)^{1/4}]. \tag{54}$$

Note that for $kT > eF\bar{R}$ we would obtain the usual '$T^{1/4}$ law' for hopping conduction.

Note also that the long-time limit of the 'carrier drift velocity' can be evaluated using (51) and thus we have

$$I(p \to 0) = \left(\frac{4W}{2\pi n eF}\right)^{1/4} \nu_0 \exp\left[-2\alpha \left(\frac{4W}{2\pi n eF}\right)^{1/4}\right]. \tag{55}$$

## 8. Conclusion, outlook and extension

The multi-step expansion has been shown to be a fruitful tool to calculate various quantities of interest in non-equilibrium relaxation via localised states. Interestingly enough the limitations due to low number of relaxation steps, normally included into the calculation, can be overcome by an explicit solution $\bar{G}_{ij}(t)$! The method is similar to the one used for energy relaxation (equation (10)), resulting in a closed expression for the non-local Green function at $T = 0$ K.

Details of the derivation and further (numerical) calculations will be given in a future paper.

Results have been presented primarily for the photoluminescence and energy decay functions and their field and (low-) temperature dependence. Some of the most interesting and widely studied systems are quantum wells and in particular exciton relaxation in QW structures [25].

Common observations are:

(i) quenching of PL with external field,

(ii) broadening of the spectrum,

(iii) shift of peak energy.

In order to treat the field-dependent photoluminescence and photocurrent relaxation in QW and superlattices, the present theory would need to be extended to allow for excitonic processes. This includes mainly the effect of the Coulomb force on the electron–hole drift and diffusion in the system. One of the most interesting aspects of such a system is caused by the non-linear electric-field-dependent hopping probabilities [23]. These effects could easily be included in the present definition of the jump rate $W(\varepsilon_i, \varepsilon_j, R)$, and have been discussed in detail in [23]. The present formalism is easily adapted to superlattices and QW whenever the 'carriers', or luminescing pairs have a negligible Coulomb coupling.

Systematic experimental investigations of the field-dependent time decay of luminescence and photocurrents are surprisingly lacking in both amorphous and crystalline systems. We therefore hope that the present theoretical study and its precise predictions will encourage definite experimental work in this direction.

The change of energy decay with field from $\ln(\ln \nu_0 t)$ at $T = 0$ K to $\ln \nu_0 t$ explores once again quantitatively the intimate relation between electric field and temperature ($\ln \nu_0 t$ is the typical high-$T$ relaxation law).

We have also developed a theory of photoconductivity which can be applied to the high-field domain and can be used for practically all situations of interest including superlattices, ordered and disordered systems. We have evaluated the short-time and long-time carrier drifts for a simple model system. Application of the formalism to more complex situations is straightforward.

# References

[1] Tiedje A and Rose A 1981 *Solid State Commun.* **37** 49
  Hvam J M and Brodsky M H 1981 *J. Physique Coll.* **42** C4 551
[2] Kirby P B, Paul W, Ray S and Tauch J 1982 *Solid State Commun.* **42** 533
[3] Esaki L 1984 *Proc. 17th Int. Conf. Physics of Semiconductors (San Francisco) 1984* (New York: Springer)
[4] Hegarty J, Goldner L and Sturge M D 1984 *Phys. Rev.* B **70** 7345
  Ryan J F 1985 *Physica* B/C **134** 403
[5] Movaghar B, Grünewald M, Ries B, Bässler H and Würtz D 1986 *Phys. Rev.* B **33** 5545
[6] Huber D L 1983 *J. Chem. Phys.* **78** 2530
[7] Tamor M A 1987 *Phys. Rev.* B **35** 15729
[8] Blumen A, Klafter J, White B S and Zumofen G 1984 *Phys. Rev. Lett.* **53** 1301
[9] Wilson B A, Kerwin T and Harbinson J 1985 *Phys. Rev.* B **31** 7953
[10] Richert R and Bässler H 1986 *J. Chem. Phys.* **84** 3567
[11] Monroe D 1985 *Phys. Rev. Lett.* **54** 146
[12] Movaghar B, Ries B and Grünewald M 1986 *Phys. Rev.* B **34** 5574
[13] Ries B and Bässler H 1987 *J. Mol. Electron.* **3** 15
[14] Ries B, Bässler H, Grünewald M and Movaghar B 1988 *Phys. Rev.* B **37** 5508
[15] Capasso F, Mohammed K and Cho A Y 1986 *Appl. Phys. Lett.* **48** 478
[16] Movaghar B 1988 *Semicond. Sci. Technol.* submitted
[17] Movaghar B, Grünewald M, Pohlmann B, Schirmacher W and Würtz D 1983 *J. Stat. Phys.* **30** 315
[18] Movaghar B, Grünewald M and Ries B 1987 *Disordered Semiconductors* ed. M Kastner, G A Thomas and S R Ovshinsky (New York: Plenum) p 723
[19] Böttger H and Bryksin V V 1980 *Phil. Mag.* B **42** 297
[20] Böttger H and Bryksin V V 1985 *Hopping Conduction in Solids* (Berlin: Akademie) p 244

[21] Grünewald M and Movaghar B 1987 *J. Non-Cryst. Solids* **98** 113
[22] Kask J A, Mendez E E and Morkoc H 1985 *Appl. Phys. Lett.* **46** 173
[23] Movaghar B, Leo J and Mackinnon A 1988 *Semicond. Sci. Technol.* **3** 397
[24] Tarucha S, Ploog K and von Klitzing K 1987 *Phys. Rev.* B **36** 4558
[25] Miller D A B, Chemla D S, Danen T C, Gossard A C, Wiegmann W, Wood T H and Burras C A
        1985 *Phys. Rev.* B **32** 1043