CONDUCTIVITY, DRIFT AND DI

JOHN

A thesis submitted

for admission to the

CONDUCTIVITY, DRIFT AND DIFFUSION IN AMORPHOUS SEMICONDUCTORS

BY

JOHN DAVID CLARK

A thesis submitted to the University of Warwick

for admission to the degree of Doctor of Philosophy

August 1980

CONTENTS

List of Illustrations

ACKNOWLEDGEMENTS

I wish to thank Professor P. N. Butcher for his highly competent supervision of this work. Without his abundant patience, ideas, wisdom, encouragement and criticism it could not have been accomplished. I am also grateful to many present and former members of Warwick Physics Department for invaluable discussions, particularly the members of the Theory Group. The interest in this work taken by Dr. G. Rowlands should not go unmentioned.

The Science Research Council made this work possible by providing me with a quota studentship.

I am very grateful to Miss S. Callanan for her very accurate and speedy typing of this thesis.

To Dr. J. M. Marshall of Dundee College of Technology I owe a particular debt. He gave many hours of his time to discussion of this work, sent me some of his computer data and even performed some calculations especially for me. He and Mrs Marshall very kindly gave me hospitality when I visited Dundee.

I am also indebted to the following for helpful discussions, comments and information: Dr. F. W. Schmidlin of Xerox Corporation, A. C. Sharp of Dundee College of Technology and Dr. J. Hirsch of Birkbeck College, London University.

Finally let me thank my parents and family for their support and encouragement; and my former teachers for developing and sustaining my interest in Physics, notably Drs. J. F. Angress and P. G. Williams of Westfield College, London University and Mr. B. Salthouse of Eccles College.

DECLARATION

Except where indicated, the work reported in this thesis is the result of my own independent research. No details of this work have appeared in any thesis or dissertation at this, or any other, institution.

Some parts of the research reported herein have been published in the following:-

1. Conductivities, Drift and Diffusion in Amorphous Semiconductors.
   by P. N. Butcher, J. D. Clark, K. J. Hayden and J. A, McInnes in Proc. 14th Int. Conf. on Amorphous and Liquid Semiconductors, edited by B. L. H. Wilson (Bristol: Institute of Physics) p.973, (1978).
2. Calculations of ac Conductivity and dc Hall Mobility for Hopping Carriers.
   by P. N. Butcher, J. D. Clark, A. A. Kumar and J. A. McInnes, J. Non-Crystalline Solids, 35 and 36, 89 (1980).
3. Numerical Calculations of ac Hopping Conductivity.
   by J. A. McInnes, P. N. Butcher and J. D. Clark.
   Phil. Mag. B. 41, 1 (1980).
4. The Theory of Anomalous Carrier Pulse Propagation (ACPP) in Amorphous Semiconductors.
   by P. N. Butcher and J. D. Clark, Accepted for Phil. Mag. B. (1980).
5. The Theory of ACPP in Amorphous Semiconductors II: Extension to later phases in the life of the pulse.
   by J. D. Clark and P. N. Butcher, Submitted to Phil. Mag. B. (1980).

6. The Theory of ACPP in Amorphous Semiconductors III: Derivation of a Macroscopic Conservation Equation for Carriers Hopping on a Lattice of Sites with Random Positions and Energies.

by P. N. Butcher and J. D. Clark, submitted to Phil. Mag. B. (1980).

John D Clark.

Abstract

Drift mobility experiments in amorphous semiconductors frequently show a particular pattern of non-gaussian, anomalous carrier pulse propagation (ACPP) characterised by a power-law decay of transient current and super-linear dependence on the ratio length/electric field. Such behaviour is predicted whether the transport mechanism be hopping, trap-controlled hopping or trap-controlled band transport.

A new theory of hopping ACPP is developed, based upon regarding the hopping as a random walk on a set of sites with both random positions and random energies. In contradistinction to earlier theories no artificial regular lattice is introduced. This new theory has the advantage of simplicity. A macroscopic equation of motion of the pulses is derived which shows how such ACPP is governed by the ac mobility: its existence may therefore be directly tested by comparison with ac conductivity measurements. Extensive calculations of the pulse-shape are performed. The theory is found to be consistent with computer simulations of hopping pulses. Hopping does not appear to be the dominant ACPP mechanism in chalcogenide glasses. Evidence is emerging that it may be the principal ACPP mechanism in certain doped organic polymers.

A new formulation of trap-controlled hopping is proposed. It is shown that all three proposed mechanisms lead to the same macroscopic pulse propagation equation with an Einstein-like relation and with suitable physical interpretation of involved quantities. This is in contrast to the findings of other authors.

Continuous-time random walk theory of hopping conductivity is reviewed. It is argued that this theory is sound provided it is physically interpreted as a random walk among sites whose random locations are rerandomized immediately after each hop. Reasons for this are discussed.

CHAPTER 1:

Introduction

1a. Aims of Thesis

Conductivity, drift and diffusion of hopping carriers will be considered in terms of random-walk models.

The major part of the thesis is concerned with the development of a theory of the propagation of pulses of hopping charge carriers (electrons or holes) in amorphous semiconductors. It is explained in §1d how such pulses frequently show behaviour which is markedly different from the conventional, gaussian pulses considered in §1c. It is shown in §1b how hopping may be modelled as a random walk among randomly located sites whose energies are randomly distributed. A simple derivation of a macroscopic equation of motion of such pulses is given. This equation shows how the pulses are governed by the ac mobility $\tilde{\mu}(\omega)$ once they have thermalised, and hence by the ac conductivity $\sigma(\omega)$: the two are related via $\sigma(\omega) = ne\tilde{\mu}(\omega)$ where n is the steady-state carrier concentration. This fact allows direct testing of whether steady-state hopping is the mechanism of transport of the pulses since $\sigma(\omega)$ is independently measurable.

The case in which the carriers are out of thermal equilibrium is also briefly considered; criticisms of work on this problem by Schmidlin (1980) are made.

A second, subsidiary theme of this thesis is a review of the random walk theory of hopping conductivity begun by Scher and Lax (1973). It is necessary to simplify the most general model, a random walk on randomly arranged sites to obtain an expression for $\sigma(\omega)$. These authors use a regular simple cubic lattice with the distribution of times a carrier

spends on a given site taken to be the average of such distributions for the random walk on a random lattice. This model gives good values for $\sigma(\omega)$ (McInnes, Butcher, and Clark 1980) yet it has been the subject of controversy (Tunaley 1974, Butcher 1974, Lax and Scher 1977, Kumar and Heinrichs 1980, Schmidlin 1980). The controversy is now in principle settled: the time is therefore ripe for a review that gives a complete, consistent account of this model, taking account of criticisms made of it and including further work using the theory (Butcher 1974, Scher and Montroll 1975, Leal Ferreira 1977, McInnes, Butcher and Clark 1980) and tests of the theory (Scher and Lax 1973, Kahlert 1976).

In the rest of this chapter the problems studied are introduced in more detail. The review of Scher-Lax theory occupies chapter 2; other theories of anomalous carrier pulse propagation are given in chapter 3. In chapters 4-6 the new theory is developed. Chapter 7 is to summarise this work, discuss some points raised by it, suggest future work and conclude the thesis.

1b. Amorphous Semiconductors: Hopping Transport and Random Walks

"Electronic Processes in Non-Crystalline Materials" are the subject of a book by Mott and Davis (1979). Figure 1.1 shows what the density of states near the Fermi level in a three-dimensional amorphous semiconductor might look like. It is an over simplification (Mott and Davis, op.cit. p.211) but shows that, as in crystalline semiconductors, there is a largely full valence band of itinerant electron states and a largely empty conduction band of such states. (Translational symmetry and thus Bloch's theorem (Blatt 1968, p.79)) are of course lost.) The gap between these bands is empty in crystalline semiconductors, but is not so in amorphous ones. There is a reduction in state density and in contradistinction to the band states,

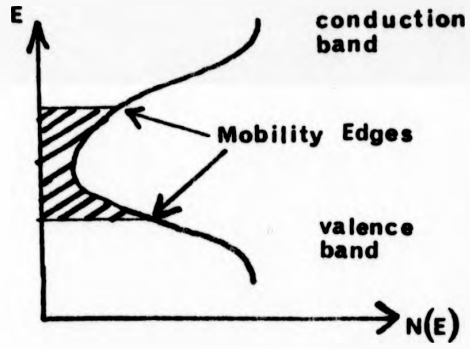


Figure 1.1: Density of States N(E) around the Fermi Level in an amorphous semiconductor. States shown shaded are localised; the other states are itinerant. There is likely in practice to be more structure in N(E) than is shown: the diagram is to illustrate the main point that between valence and conduction bands there exist allowed states, which are localised.

the gap states are localised. In a localised state the expectation value of the electron velocity is zero.

Transport of electrons in the conduction band is possible (Mott and Davis 1979, p. 219). The localised states can also contribute to transport. If some of them are empty, electrons can make transitions (called hops) between them (Figure 1.2). Since the energies of the localised states usually differ the hops must be inelastic. Mott and Davis (1979, p.27) mention photon-activated hopping which gives $\sigma(\omega) \propto \omega^2$; Emin (1976) considers small polaron hopping, found in certain crystals and in vanadate glasses; Butcher and Swierkowski (1980) consider hopping driven by interelectron interactions. But ac conductivity is usually proportional to ω^s, $s < 1$, at low frequencies which seems to preclude the former mechanism. The latter is not thought to have much effect on conductivity (Hearn 1980, private communication). A one-electron picture in which the hops involve emission and absorption of phonons is considered by Miller and Abrahams (1960) who consider hopping among impurity states in compensated crystalline semiconductors, cooled to liquid helium temperatures to suppress band conduction. (It was to explain this conduction that hopping was first proposed by Mott (1956) and Conwell (1956)). Compensation is necessary to cause some impurity sites to become vacant. Such phonon-assisted hopping has achieved some success in describing experimental data in these systems (Butcher, Hayden and McInnes 1977, Butcher and Hayden 1977, Hayden and Butcher 1978, Scher and Lax 1973) though this success is not complete (Kahlert 1976). This is the hopping mechanism envisaged throughout this thesis.

Miller and Abrahams (1960) suppose that the hopping is governed by the rate equations

$$\frac{df_m}{dt} = \sum_n \left[W_{nm} f_n(1-f_m) - W_{mn} f_m(1-f_n) \right] \qquad (1.1)$$

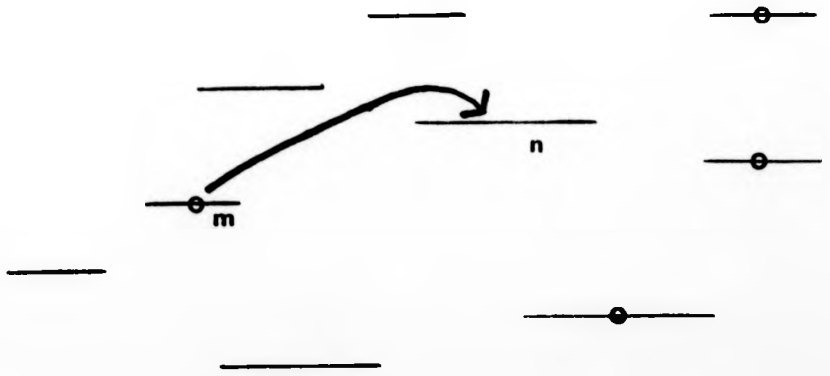


Figure 1.2: A hop from a localised state centred at m to one at centred n involves a transition in r-space.

where f_m is the occupation probability of the m^{th} site and W_{mn} is the transition rate between sites m and n. One imagines a finite number N_s of sites uniformly distributed in volume τ and notes for future reference that the probability of a hop from the m^{th} site known to be occupied at time zero would be $\lambda_m \exp(-\lambda_m t)$ where $\lambda_m = \sum_n W_{mn}$ if all other sites were empty. Barker (1976) derives eqn (1.1) from the Kubo formula (Ziman 1969, p.101). W_{mn} is taken to have the form quoted by Butcher, Hayden and McInnes (1977), viz. eqn (2.24): it is only used explicitly when considering isoenergetic systems. In non-isoenergetic cases, eqn (4.3) is assumed, with W_{mn} depending on distance but not direction of intersite separation.

It is now shown how to use the Miller-Abrahams rate equations (1.1), with a view towards setting up a random-walk picture of hopping. The treatment of Butcher (1976) is followed. In the steady state, the left-hand side of eqn (1.1) vanishes. f_m^o, the steady-state value of f_m is given by

$$f_m^o = \left[1 + \frac{1}{2} \exp\left(\frac{\varepsilon_m - \zeta}{k\Theta}\right)\right]^{-1} \qquad (1.2)$$

where ζ is the electrochemical potential, Θ the absolute temperature, ε_m the energy of the m^{th} site and the factor $\frac{1}{2}$ arises because Coulomb repulsion forbids double occupancy of sites. Detailed balance prevails and it then follows from eqn (1.1) that the steady state transition rates are related by

$$\frac{W_{mn}^o}{W_{nm}^o} = \exp\left|\frac{\varepsilon_m - \varepsilon_n}{k\Theta}\right| \quad . \qquad (1.3)$$

If a weak perturbation (e.g. an electric field) is applied such that to ε_m must be added U_m, it is assumed that

$$\frac{W_{mn}}{W_{nm}} = \frac{W_{mn}^o}{W_{nm}^o}\left|1 + \frac{U_m - U_n}{k\Theta}\right| \qquad (1.4)$$

to first order. If the f_m are perturbed by an amount f_m^1 it is easily shown after some algebra that to first order

$$\frac{df_m^1}{dt} = \sum_n \left[\{ f_n^1 W_{nm}^e - f_m^1 W_{mn}^e \} + \frac{1}{k\Theta} \{ F_n U_n W_{nm}^e - F_m U_m W_{mn}^e \} \right] \tag{1.5}$$

where $W_{mn}^e = f_m^o(1-f_n^o)W_{mn}^o/F_m$ with $F_m = f_m^o(1-f_m^o)$. In the non-degenerate limit $f_m \to f_m^o$.

The formal solution of eqn (1.5) is facilitated by the use of matrix notation. Kets are used to denote column vectors and bras to denote their transposes (but not their hermitian conjugates). The m^{th} element of $|f^1\rangle$ is f_m^1; that of $|U\rangle$ is U_m. Let $\underline{\underline{F}}$ be a diagonal matrix with m^{th} element F_m and let

$$(\underline{\underline{R}})_{mn} \equiv \left[\sum_p W_{mp}^e \right] \delta_{mn} - W_{nm}^e \tag{1.6}$$

where δ_{mn} is Kronecker's symbol. Then eqn (1.5) becomes

$$\frac{d}{dt} |f^1\rangle = - \underline{\underline{R}} \, |f^1\rangle - \frac{1}{k\Theta} \underline{\underline{R}} \, \underline{\underline{F}} \, |U\rangle \, . \tag{1.8}$$

A formal expression for the ac conductivity is now derived. Let an external field $E \exp(-i\omega t)$ be applied in the x-direction such that

$$|U(t)\rangle = eEe^{-i\omega t} \, |x\rangle \, . \tag{1.9}$$

Then

$$|f^1(t)\rangle = e^{-i\omega t} \, |f^1(0)\rangle \, . \tag{1.10}$$

In this thesis the electron charge is denoted "-e" so that $e > 0$. Eqn (1.8) then reduces to

$$(\underline{\underline{R}} - i\omega \underline{\underline{I}}) \, |f^1(0)\rangle = - \frac{eE}{k\Theta} \underline{\underline{R}} \, \underline{\underline{F}} \, |x\rangle \tag{1.11}$$

where $\underline{\underline{I}}$ is the unit matrix. Eqn (1.11) has the formal solution

$$|f^1(0)\rangle = -\frac{eE}{k\Theta}\,\underline{\underline{G}}^T\,\underline{\underline{R}}\,\underline{\underline{F}}\,|x\rangle \qquad (1.12)$$

where $\underline{\underline{G}}$ is the inverse of $(\underline{\underline{R}}^T - i\omega\underline{\underline{I}})$ and the superscript T indicates transposition. Now the dipole moment per unit volume has x-component

$$p_x(t) = -\frac{e}{\tau}\sum_m f_m^1(t)\,x_m$$

$$= -\frac{e}{\tau}\langle x|f^1(t)\rangle \quad . \qquad (1.13)$$

The x-component of current density is $-i\omega p_x(t)$ (Duffin 1973, p.303) so that

$$\sigma(\omega) = \frac{-i\omega p_x(t)}{E\,\exp(-i\omega t)} = \frac{-i\omega e^2}{\tau k\Theta}\langle x|\underline{\underline{F}}\,\underline{\underline{R}}^T\,\underline{\underline{G}}|x\rangle \quad . \qquad (1.14)$$

The disordered systems considered are isotropic so that the choice of x-direction is arbitrary. This equation together with eqn (2.24) is directly solved numerically by: Butcher, Hayden and McInnes (1977), Butcher and McInnes (1978), McInnes and Butcher (1979) and McInnes, Butcher and Clark (1980) for isoenergetic sites with results shown in figures 2.1 and 2.2. McInnes and Butcher (1979) also consider non-isoenergetic dc cases. Analytical evaluation of eqn (1.14) is possible in certain limits: results are listed in Appendix F.

Experimental hopping conductivities often take the form

$$\sigma(\omega) = \sigma_o + \sigma_1\,(-i\omega\tau_o)^{1-\alpha} \qquad (1.15)$$

where $0 < \alpha < 1$, τ_o is a time constant and σ_o and σ_1 are constants (Mott and Davis 1979, p.117; Lakatos and Abkowitz 1971).

The model just described may be interpreted in terms of random walks. In this thesis a random walk in which the walker can only rest at certain

randomly located points in space is called a random walk on a random lattice. A continuous time random walk is in general a random walk with instantaneous hops where the carrier spends a finite, stochastically governed time on each site it visits (though Scher and Lax (1973) use it to mean particularly such a walk on a regular lattice of sites). If each of these times is governed by a probability $\lambda_m \exp(-\lambda_m t)$ with λ_m defined above, the random walk is called markovian: otherwise it is non-markovian.

The matrix $\underline{\underline{G}}$ has a simple interpretation in terms of random walks. Consider now a single electron performing a random walk on the random lattice of sites. Suppose that no other electrons are present, and that the motion of electrons is governed by the set of effective transition rates $\{W^e_{mn}\}$. If this electron is known to be on site m at time zero then the probability $P_{mn}(t)$ that at time t it will be on site n (the mn^{th} element of matrix $\underline{\underline{P}}$) is given by the Kalmogorov equation (Feller 1966)

$$\frac{d}{dt}\left[\underline{\underline{P}}(t)\ \theta(t)\right] = -\ \theta(t)\ \underline{\underline{P}}(t)\ \underline{\underline{R}}^T + \underline{\underline{I}}\delta(t) \qquad (1.16)$$

where $\theta(t)$ is the unit step function and $\delta(t)$ the Dirac delta function. Eqn (1.16) has Fourier transform

$$\hat{\underline{\underline{P}}}(\omega)(\underline{\underline{R}}^T - i\omega\underline{\underline{I}}) = \underline{\underline{I}} \qquad (1.17)$$

where $\hat{\underline{\underline{P}}}(\omega)$ is the causal Fourier transform (see Appendix C) of $\underline{\underline{P}}(t)$. But it was stated above that $\underline{\underline{G}}$ is the inverse of $(\underline{\underline{R}}^T - i\omega\underline{\underline{I}})$: therefore $\underline{\underline{G}} = \hat{\underline{\underline{P}}}(\omega)$ and $\underline{\underline{G}}$ is the causal Fourier transform of $\underline{\underline{P}}(t)$. This random walk interpretation relies upon the fact that the linearisation leading to eqn (1.5) reduces the problem to an effective non-degenerate one. Except in the non-degenerate limit the random walk interpretation is an artificial, albeit very useful, picture.

Scher and Lax (1973) approximate the markovian random walk on a random lattice with a non-markovian random walk on a regular lattice in order to obtain a tractable unified theory of ac and dc conductivity. These authors obtain an expression for the diffusivity

$$\tilde{D}(\omega) \equiv \int_0^\infty e^{i\omega t} \langle V(t)V(0)\rangle dt \qquad (1.18)$$

where the term in angular brackets is the velocity correlation furnction. Lax (1960). This is proportional via. the ac Einstein relation (2.1) to the ac conductivity. These authors take the distribution $\psi(t)$ of times between jumps to be the same for all jumps including the first. Tunaley (1974) points out that this is not so for a non-markovian random walk. Correcting this error removes the ability of $\sigma(\omega)$ to increase with respect to ω as required. This point has been the cause of much controversy. Even now, six years later, Kumar and Heinrichs (1980) and Schmidlin (1980) disagree about whether Tunaley's objection is relevant. Figures 2.1 and 2.2 show that the Scher-Lax conductivity is a good approximation to direct numerical solution of eqn (1.14), suggesting that preoccupation with the fine details of Scher-Lax theory is likely to make one miss the salient question: why does this model give good conductivities? It is this question which sets the tone of chapter 2.

1c. Conventional Carrier Pulse Propagation in Semiconductors

Experiments to measure the drift mobility of charge carriers in crystalline semiconductors were first reported by Haynes and Shockley (1949) and are reviewed in Shockley's (1950) book. It is assumed that the number current density $\underset{\sim}{J}(\underset{\sim}{x},t)$ due to a sheet of carriers, say electrons, of number density $n(\underset{\sim}{x},t)$ is given by

$$\underset{\sim}{J}(\underset{\sim}{x},t) = -\underset{\sim}{E}\mu n(\underset{\sim}{x},t) - D\underset{\sim}{\nabla} n(\underset{\sim}{x},t) \qquad (1.19)$$

where μ is the mobility and D the diffusivity, both assumed constant. In the steady state $\underset{\sim}{J}(\underset{\sim}{r},t)$ vanishes. If the semiconductor is isolated and $\underset{\sim}{E} = -\underset{\sim}{\nabla}V(\underset{\sim}{r})$ then in the steady state the electrons obey Boltzman statistics:

$$n(\underset{\sim}{r},t) \propto \exp\{-eV(\underset{\sim}{r})/k\Theta\} \tag{1.20}$$

It then follows trivially from eqn (1.19) with $\underset{\sim}{J} = 0$ that

$$\mu = \frac{eD}{k\Theta} \tag{1.21}$$

which is the well known dc Einstein relation (Shockely 1950, p.299). This powerful result determines the relative importance of drift and diffusion.

In a drift mobility experiment one imagines a sheet of n_o carriers per unit area, say electrons, injected uniformly onto the yz-plane. The equation of continuity then gives

$$\frac{\partial n(\underset{\sim}{r},t)}{\partial t} = -\underset{\sim}{\nabla}.\underset{\sim}{J} + n_o\delta(x)\delta(t)$$

$$= -E\mu\frac{\partial n(x,t)}{\partial x} + D\frac{\partial^2 n(x,t)}{\partial x^2} + n_o\delta(x)\delta(t)\ , \tag{1.22}$$

from eqn (1.19) and assuming $\underset{\sim}{E} = (-E, 0, 0) =$ constant. The solution of eqn (1.22) is

$$n(x,t) = \frac{n_o}{\sqrt{4\pi Dt}}\ \exp\left[-\frac{(x-\mu Et)^2}{4Dt}\right] \tag{1.23}$$

if the pulse is well away from the ends of the semiconductor. This travelling, broadening gaussian pulse is shown in figure 1.3. The drift velocity μE is uniform. The broadening is caused by the diffusion term and will be referred to as fickian diffusion. In the limit $D \to 0$ eqn (1.23) becomes a uniformly travelling delta function. It will be seen in later sections that in this limit, anomalous pulses are not at all delta-function-like.

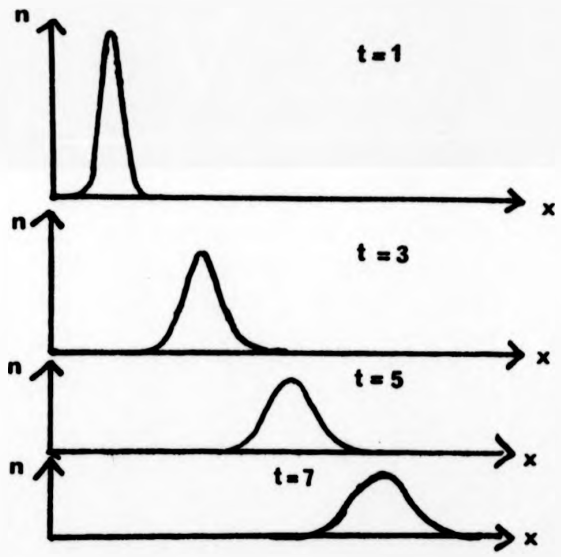


Figure 1.3: Gaussian pulse propagation; plot of n(x,t) vs. x.

Using the methods of Appendix A, one finds that the spatial moments

$$\langle x(t) \rangle = \mu E t \quad ; \tag{1.24}$$

$$\sigma(t) \equiv \sqrt{\langle x^2(t) \rangle - \langle x(t) \rangle^2} = \sqrt{2Dt} \tag{1.25}$$

so that

$$\frac{\langle x(t) \rangle}{\sigma(t)} \propto t^{\frac{1}{2}} \quad . \tag{1.26}$$

The electric current density flowing through the external circuit wired to a semiconductor containing a pulse is shown in Appendix G to be

$$I(t) = - \frac{e}{\ell} \int_0^{\ell} J(x,t) dx \tag{1.27}$$

if the ends of the semiconductor are at $x = 0$ and $x = \ell$ and the voltage drop across the semiconductor is held constant. If the pulse is far from either of these ends, replacing the limits on the integral in eqn (1.27) with $\pm\infty$ will cause very little loss of accuracy. Then from eqns. (1.19) and (1.23) it is easily seen that

$$I(t) = - \frac{e\mu E}{\ell} = \text{constant} \quad . \tag{1.28}$$

As the pulse approaches the extinction electrode, I(t) will rapidly decay to zero, the decay time being essentially proportional to the RMS pulse width $\sigma(t)$. Figure 1.4 shows such transient currents for two different values of E plotted against t/t_1 where the transit time

$$t_1 = \frac{\ell}{\mu E} \quad . \tag{1.29}$$

It is seen that the two curves have different shapes and cannot be exactly superimposed. A similar effect is seen by varying ℓ at constant E. This apparently innocuous property of conventional pulses is not found in the anomalous pulses described in the next section.

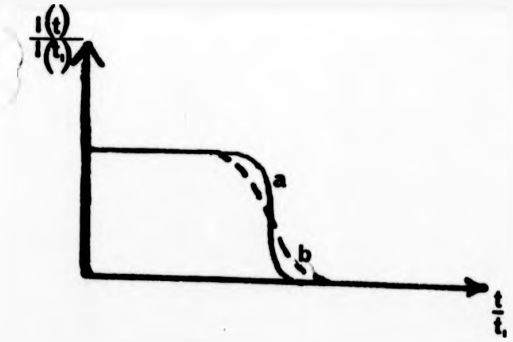


Figure 1.4: Current density I(t) due to a conventional pulse, eqn (1.23): (a) high field; (b) low field. t_1 is the transit time of the pulse.

Drift-mobility experiments of the kind just described provided the first direct evidence of the existence of holes as drifting entities. Furthermore the drift mobilities measured were found to be in good agreement with Hall mobilities (Shockley 1950, p.54 ff). These experiments were thus a valuable confirmation of the theory of transport in crystalline semiconductors.

1d. Anomalous Carrier Pulse Propagation in Semiconductors

It was natural, in view of the above, to perform drift mobility experiments in amorphous semiconductors when studies of these materials began around 1970. Figure 1.5 shows schematically the experimental arrangement.

It quickly became apparent that the pulses are highly non-gaussian in certain materials such as a-As_2Se_3, a-Se (at low temperatures) and in certain molecularly doped organic polymers (see e.g. Pfister and Scher (1978) who review anomalous carrier pulse propagation (hereafter ACPP)). The same salient features, viz.

$$\left.\begin{aligned} I(t) &\propto t^{-(1-\alpha)} \text{ for } t \ll t_1 \ ; \\ I(t) &\propto t^{-(1+\alpha)} \text{ for } t \gg t_1 \ ; \\ t_1 &\propto (\ell/E)^{1/\alpha} \ , \end{aligned}\right\} \qquad (1.30)$$

using the notation of the previous section, are common to many of these experiments. Eqn (1.30), in which $0 < \alpha < 1$, is markedly different to the conventional behaviour of such pulses, eqns (1.28) and (1.29). Figure 1.6 shows current-pulse shapes in a-Se (the prefix means "amorphous"). Figure 1.7 shows those of a-As_2Se_3 and a typical doped polymer.

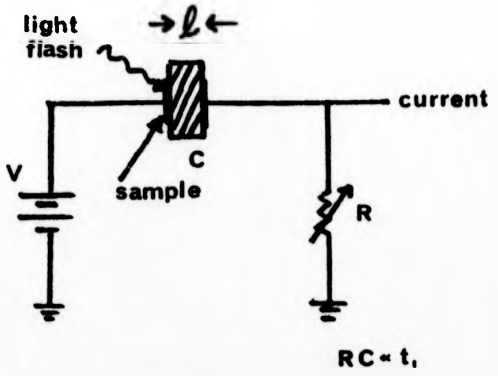


Figure 1.5: Schematic diagram of experimental arrangement. The voltage drop across the semiconductor is held constant. (From Scher and Montroll 1975).

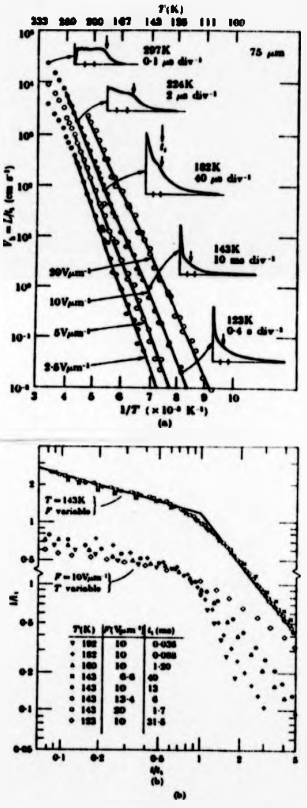
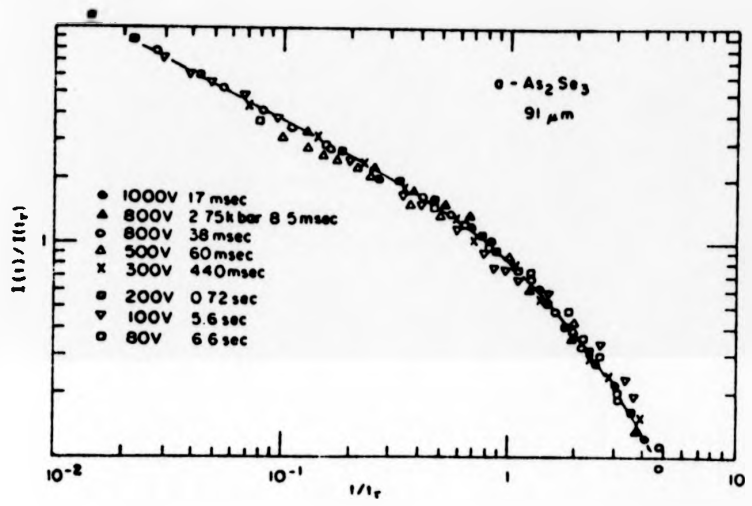


Figure 1.6: Typical anomalous carrier pulse propagation results, for a-Se. F = electric field, t_τ is the transit time called t_1 in this thesis. The insets are current vs. time plots. (From Pfister 1976).



a

FIG. 5. A log*I*-log*t* plot for a-As_2Se_3 for the range of transit time listed in the figure. The measurements by Pfister also include a data set at high pressure (2.75 kbar). The solid line is the theoretical curve.

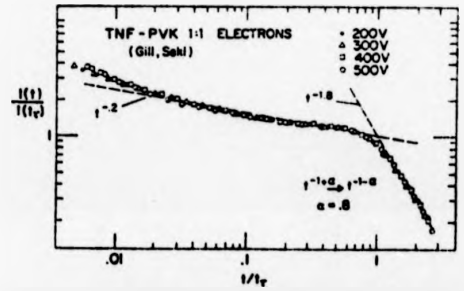


FIG. 6. A log*I*-log*t* plot for 1:1 TNF-PVK measured by Gill and taken from a paper by Seki. The slopes of the dashed lines are −0.2, and −1.8, respectively.

b

Figure 1.7: More anomalous carrier pulse propagation experimental data, showing universality. (a) Measured by Pfister (b) measured by Gill and Seki (From Scher and Montroll 1975).

An intriguing feature of such pulses, shown in figure 1.6 is that at a given temperature, I(t) vs. t/t_1 curves have the same shape and may be superimposed. This feature is known in the pulse-propagation literature as universality (Pfister and Scher 1978). It was seen in the previous section how universality requires the ratio $\langle x(t)\rangle/\sigma(t)$ to be time-independent: eqn (1.26) therefore provides yet more proof that in ACPP the pulses are non-gaussian.

LeComber and Spear (1970) perform drift mobility experiments in a-Si and find evidence, shown in figure 1.8, for the existence of a mobility edge in this material. These authors do not report ACPP. Allan (1978) observes non-gaussian pulses in this material though they do not obey eqn (1.30). It is possible, though by no means certain, that this author sees pulses which are created over a long time period because of contact electrode effects (Abkowitz and Scher 1977).

As Pfister and Scher (1978) point out, any one of three plausible transport mechanisms in amorphous semiconductors can cause ACPP, viz. hopping, trap-controlled band transport and trap-controlled hopping. The last two are reviewed in chapter 3. Scher and Montroll (1975) give a theory of ACPP based on continuous-time random walks on regular lattices; a later simplification of this theory by Leal Ferreira (1977) is given in §2e, where it is shown how this model could be linked to ac conductivity via the artificial quantity $\psi(t)$.

A simpler and more direct theory of hopping ACPP based on random walks on random lattices is devleoped in chapters 4 to 6. It is more general than the Scher-Lax-Montroll model, being able to cope with non-isoenergetic sites. It is based on the ac mobility which is proportional to the directly measurable ac conductivity and is thus physically transparent. This theory is based on the macroscopic pulse propagation equation (MPPE):

$$\frac{\partial n(\underset{\sim}{x},t)}{\partial t} = \left[\frac{e\,\underset{\sim}{E}\cdot\underset{\sim}{\nabla}}{k\Theta} + \nabla^2\right] \int_{-\infty}^{\infty} d\tau\; D(t-\tau)\, n(\underset{\sim}{x},\tau) + n_o \delta(x)\delta(t) \qquad (1.31)$$

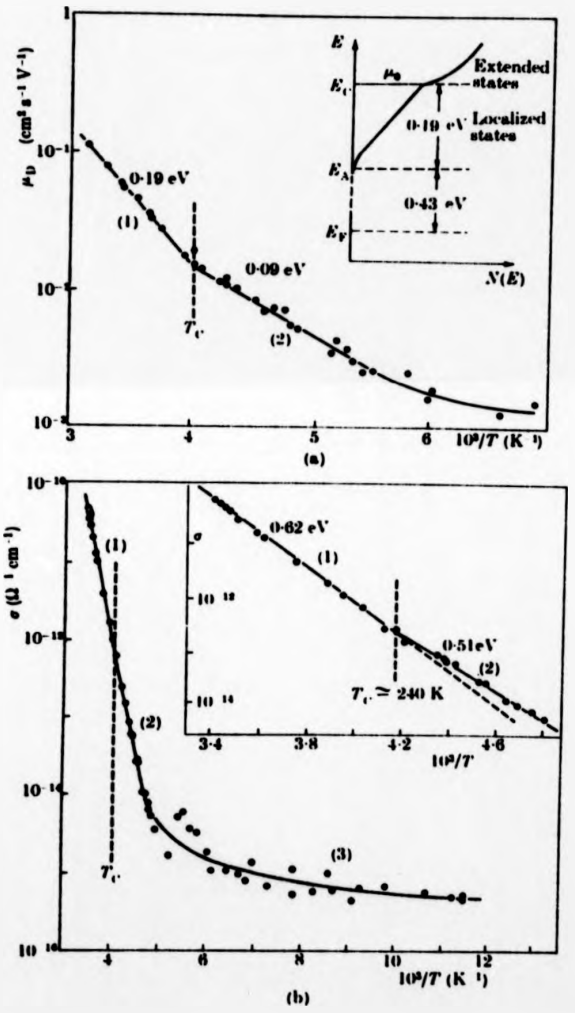


Figure 1.8: Temperature dependence of (a) drift mobility of electrons and (b) conductivity σ in a-Si:H (From LeComber and Spear 1970).

where $n(\underset{\sim}{x},t)$ is the number density of carriers, n_o is the number of carriers per unit area in the pulse and D(t) is the inverse causal Fourier transform of the diffusivity $\tilde{D}(\omega)$ which is related to the ac mobility via the ac Einstein relation

$$\tilde{\mu}(\omega) = \frac{e\tilde{D}(\omega)}{k\Theta} \cdot \tag{1.32}$$

The MPPE is seen to be a generalisation of eqn (1.22); eqn (1.32) is a generalisation of eqn (1.21). A straightforward derivation of eqns (1.31) and (1.32) is given in chapter 4.

The MPPE is shown in chapter 3 to hold for trap-controlled band transport so long as $\tilde{\mu}(\omega)$ and $\tilde{D}(\omega)$ are suitably reinterpreted in terms of the rate of thermalisation with trap (localised) states. Eqn (1.32) is still valid in this case. Controversy exists in the literature (Butcher 1978, Schmidlin 1980) over whether eqns (1.31) and (1.32) can be written down for trap-controlled hopping with yet another physical interpretation of $\tilde{\mu}(\omega)$ and $\tilde{D}(\omega)$. In an attempt to settle this controversy an argument is advanced in chapters 4 and 7 to show how the MPPE and a pseudo-Einstein relation exist for this mechanism, thereby vindicating the conjecture of Butcher (1978) that the MPPE can be written down for any transport mechanism which gives rise to ACPP.

The ACPP theory advanced in this thesis allows much more extensive calculation of pulse shapes n(x,t) than has hitherto been performed (Scher and Montroll 1975, Montroll and Scher 1973, Leal Ferreira 1977). A conductivity of the form of eqn (1.15) is assumed: results are presented in chapters 5 and 6. When the dc term σ_o is set equal to zero the pulse shapes have the elegant form

$$n(x,t) \propto \frac{1}{t^{\alpha}} f_{\alpha}\left(\frac{x}{t^{\alpha}}\right) \tag{1.33}$$

where f_α is a function of α and of x/t^α.

Before this theory is presented, the theory of hopping conductivity due to Scher and Lax will be reviewed. Other ACPP theories are then briefly described.

Chapter 2:

Continuous-Time Random Walk Theory of Hopping Conduction

2a. Introduction

This theory, due to Scher and Lax (1973), models hopping as a non-markovian random walk on a regular lattice of sites. The underlying assumption is that it is not the distance hopped which is important so much as the distribution of times a carrier waits at the various sites it visits, before hopping on to the next sites. This distribution is non-exponential giving rise to a non-markovian random walk. It was seen in the previous chapter that hopping might be more realistically modelled as a markovian random walk among randomly located sites in which the probability of hopping to another site at a given time decays exponentially in time. It will be seen in section 2d that the microscopic details of the hopping process are not well modelled by the theory of Scher and Lax. Nevertheless it will also be seen that this method still yields a conductivity in good agreement with that obtained by direct numerical solution of the rate equations (1.1). Reasons for this are discussed in section 2d following calculation of the conductivity in section 2c. Before that, an account is given of the controversy which developed over whether the Scher and Lax formalism actually gives rise to a frequency-dependent conductivity at all (Tunaley 1974, Lax and Scher 1977, Kumar and Heinrichs 1980). This controversy was settled by Kumar and Heinrichs (op.cit.) who show that the Scher and Lax formalism is equivalent to hopping among randomly located sites whose locations are rerandomised after every hop, as was first demonstrated by Butcher (1974b). Finally in section 2e this theory is used to study ACPP.

The theory calculates the diffusivity $\tilde{D}(\omega)$ which is related to the ac conductivity $\sigma(\omega)$ via the Einstein relation

$$\sigma(\omega) = \frac{ne^2}{k\Theta} \tilde{D}(\omega) \qquad (2.1)$$

where n is the carrier density and Θ the absolute temperature.

Only the limit of non-degenerate carrier statistics is considered. Consideration is also restricted to the case of hopping among isoenergetic sites. There is nothing to stop the theory being extended to consider hopping among sites of widely differing energies though this is not done here.

2b. Formal Expression for the Diffusivity and Discussion of the Controversy Surrounding it.

The diffusivity $\tilde{D}(\omega)$ is defined in equation (1.18). For the present purpose it is to be evaluated for a carrier hopping among sites whose position vector is $\underset{\sim}{\ell}$ and which lie on a simple cubic lattice. Let $\psi(\underset{\sim}{\ell}-\underset{\sim}{\ell}_o, t-t_o)$ be the probability per unit time that a carrier which hopped onto the site at $\underset{\sim}{\ell}_o$ at time t_o will remain there until time $t > t_o$ and then hop directly to the site at $\underset{\sim}{\ell}$. It is important to note that $\psi(\underset{\sim}{\ell}-\underset{\sim}{\ell}_o, t-t_o)$ is defined so that the carrier <u>just arrives</u> at $\underset{\sim}{\ell}_o$ at t_o. It is also helpful, particularly when considering the first hop after starting to observe the system, to define $h(\underset{\sim}{\ell}-\underset{\sim}{\ell}_o, t-t_o)$ as the probability per unit time that a carrier will hop to $\underset{\sim}{\ell}$ at time t given that it <u>is</u> at $\underset{\sim}{\ell}_o$ at time t_o. There is a subtle difference between $\psi(\underset{\sim}{\ell},t)$ and $h(\underset{\sim}{\ell},t)$. The progress of one particular carrier will be followed. The condition that this carrier <u>is</u> at the origin just after t = 0 is expressed as

$$R_o(\underset{\sim}{\ell},t) \equiv \delta_{\underset{\sim}{\ell},o}\, \delta(t-0^+) \qquad (2.2)$$

where $R_o(\underset{\sim}{\ell},t)$ is the probability of finding the carrier to be initially on site $\underset{\sim}{\ell}$ at time t and where the first delta is Kronecker's symbol and the second is a Dirac delta function. $t = 0^+$ is considered to be the time at which observation begins. Now define $R_n(\underset{\sim}{\ell},t)$ as the probability per unit time that this carrier satisfying eqn (2.2) will <u>arrive</u> at $\underset{\sim}{\ell}$ at time t if $n \geq 1$. Then

$$R_1(\underset{\sim}{\ell},t) = h(\underset{\sim}{\ell},t) \ ; \tag{2.3}$$

$$R_n(\underset{\sim}{\ell},t) = \sum_{\underset{\sim}{\ell}'} \int_o^\infty d\tau \ \psi(\underset{\sim}{\ell}-\underset{\sim}{\ell}',t-\tau) \ R_{n-1}(\underset{\sim}{\ell}',\tau), \ n \geq 2 \ . \tag{2.4}$$

In Appendix D the diffusivity of a carrier satisfying eqns (2.2-4) is shown to be

$$\tilde{D}(\omega) = \frac{\tilde{\sigma}^2_{rms}(\omega)}{6} \left\{ \frac{-i\omega\tilde{h}(\omega)}{1-\tilde{\psi}(\omega)} \right\} \tag{2.5}$$

where $\tilde{\psi}(\omega)$ is the causal Fourier transform (see Appendix C) of

$$\psi(t) \equiv \sum_{\underset{\sim}{\ell}} \psi(\underset{\sim}{\ell},t) \ , \tag{2.6}$$

$\tilde{h}(\omega)$ is the causal Fourier transform of

$$h(t) \equiv \sum_{\underset{\sim}{\ell}} h(\underset{\sim}{\ell},t) \tag{2.7}$$

and $\tilde{\sigma}^2_{rms}(\omega)$ is defined by

$$\tilde{\sigma}^2_{rms}(\omega) \equiv \frac{\sum_{\underset{\sim}{\ell}} \underset{\sim}{\ell}\cdot\underset{\sim}{\ell} \ \tilde{\psi}(\underset{\sim}{\ell},\omega)}{\tilde{\psi}(\omega)} \ , \tag{2.8}$$

where $\tilde{\psi}(\underset{\sim}{\ell},\omega)$ is the causal Fourier transform of $\psi(\underset{\sim}{\ell},t)$. It remains to express $\tilde{h}(\omega)$ in terms of $\tilde{\psi}(\omega)$. This is easily done (Feller 1966, Lax and Scher 1977, Kumar and Heinrichs 1980).

Consider a process consisting of two events such that, if the first is known to occur at time zero, the probability per unit time of the occurrence of the second at time t is $\psi_1(t)$. Then the probability per unit time of no second event having yet occurred by time t is

$$\phi_1(t) = \int_t^\infty \psi_1(\tau)d\tau \quad . \tag{2.9}$$

Moreover, the conditional probability per unit time $\psi_1(t|\tau)$ for the second event at time t knowing that exactly a time τ has elapsed since event one, is given by

$$\psi_1(t+\tau) = \psi_1(t|\tau)\ \phi_1(\tau) \quad . \tag{2.10}$$

It follows that $\psi_1(t) = \psi_1(t|0)$. To obtain $h_1(t)$, the distribution of waiting times to the second event if observation started at time zero and the first event occurred at some unknown earlier time, it is necessary to average $\psi_1(t|\tau)$ with respect to $\phi_1(\tau)$ (Lax and Scher 1977):

$$h_1(t) = \frac{\int_o^\infty \psi_1(t|\tau)\ \phi_1(\tau)d\tau}{\int_o^\infty \phi_1(\tau)d\tau} = \frac{1 - \int_o^t \psi_1(\tau)d\tau}{\int_o^\infty t\psi_1(t)dt} \quad . \tag{2.11}$$

The last step in eqn (2.11) is obtained by integrating by parts. The denominator is $\langle t \rangle$, the first moment of t. The causal Fourier transform of eqn (2.11) is

$$\tilde{h}_1(\omega) = \frac{1 - \tilde{\psi}_1(\omega)}{-i\omega\langle t \rangle} \quad . \tag{2.12}$$

Substitution of $\tilde{\psi}$ for $\tilde{\psi}_1$ and $\tilde{h}$ for $\tilde{h}_1$ in eqn (2.12) leads to, in eqn (2.5),

$$\tilde{D}(\omega) = \frac{\tilde{\sigma}^2_{rms}(\omega)}{6\langle t \rangle} \tag{2.13}$$

whose only frequency-dependence is in $\tilde{\sigma}^2_{rms}(\omega)$. It is shown in Appendix H that $\tilde{\sigma}^2_{rms}(\omega)$ decreases as ω increases. This is in qualitative contrast to the observed marked increase in hopping conductivity as ω increases. It will be seen in the next section that Scher and Lax (1973) treat $\tilde{\sigma}^2_{rms}(\omega)$ as a constant and, it would seem, thereby lose their frequency dependence. Yet, as pointed out in the previous chapter, hopping conductivity definitely depends upon frequency. So far this random walk has been treated as a renewal process (Tunaley 1974), i.e. one in which the time between successive events is governed by the same distribution $\psi(t)$.

Fortunately there exists an alternative interpretation of the Scher and Lax formalism which allows this difficulty to be circumvented. Consider the real hopping process, and further consider it modelled as a markovian random walk among randomly located sites in which the probability that a carrier which hopped onto site ℓ at time zero has yet to hop away at time t is

$$Q_\ell(t) = \exp\left[-\sum_{j\neq\ell} W(\underline{r}_j-\underline{r}_\ell)t\right] \tag{2.14}$$

where j labels sites, $W(\underline{r}_j-\underline{r}_\ell)$ is the transition rate from site ℓ to site j and $\underline{r}_j$ is the position of the j^{th} site. The probability per unit time of a hop occurring at time t is

$$\psi^{RM}_\ell(t) = -\frac{dQ_\ell(t)}{dt} = \sum_j W(\underline{r}_j-\underline{r}_\ell)e^{-\sum_j W(\underline{r}_j-\underline{r}_\ell)t} . \tag{2.15}$$

The superscript RM denotes "Random Medium". The probability per unit time of a hop occurring at time t if the carrier was merely observed to be on site ℓ at t=0 is found from eqn (2.11) to be

$$h^{RM}_\ell(t) = \psi^{RM}_\ell(t) \tag{2.16}$$

since $\sum_j W(\underline{r}_j - \underline{r}_\ell)$ is a constant. Exponential waiting-time distributions such as eqn (2.15) are the only ones for which $h_1(t)$ and $\psi_1(t)$ are identical (cf. eqn (2.11)). Since the $\psi_\ell^{RM}(t)$ clearly depend on ℓ (some sites are more strongly coupled to their neighbours than others) this random walk is not a renewal process. The configuration average $\langle Q(t) \rangle$ of eqn (14) over sites ℓ is taken and a waiting-time distribution

$$\psi(t) = - \frac{d\langle Q(t) \rangle}{dt} \tag{2.17}$$

is used in eqn (2.6). This is equivalent to saying: after each hop on the random network of sites, hold the occupied site fixed and rerandomise the positions of all the others. Eqn (2.16) is used to justify also making

$$h(t) = - \frac{d\langle Q(t) \rangle}{dt} \tag{2.18}$$

in eqn (2.7). Eqn (2.11) is thereby over-ridden and in eqn (2.5) $\tilde{h}(\omega)$ and $\tilde{\psi}(\omega)$ are both equal to

$$\tilde{\psi}(\omega) = \tilde{h}(\omega) = 1 + i\omega \langle \tilde{Q}(\omega) \rangle \tag{2.19}$$

where $\langle \tilde{Q}(\omega) \rangle$ is the causal Fourier transform of $\langle Q(t) \rangle$. Thus the process modelled is not quite the renewal process worked out in Appendix D. It is, however, equivalent to such a non-markovian random walk in which the carrier is forced to <u>hop onto</u> the origin at time $t=0^+$, rather than merely be there at that time.

Thus, as pointed out by Kumar and Heinrichs (1980), to whom the above argument is due, the Scher and Lax method of calculating $\tilde{D}(\omega)$ is far from ruined by Tunaley's (1974) argument. Tunaley is quite right in demonstrating that it is insufficient to model the hopping as a renewal process: the adjustment to the random walk just outlined is needed. Physically this

is most easily understood as a markovian random walk on a random lattice whose site positions are rerandomised after every hop (Butcher 1974b).

This section is completed by considering the special case

$$\psi(\underset{\sim}{s},t) = p(\underset{\sim}{s})\ \psi_2(t)$$

$$= p(\underset{\sim}{s})\ \psi(t) \qquad (2.20)$$

if $\sum_{\underset{\sim}{s}} p(\underset{\sim}{s}) = 1$ where $p(s)$ is the probability that the hop will be over a displacement $\underset{\sim}{s}$. Further, let

$$\psi(t) = \lambda e^{-\lambda t} \quad , \qquad (2.21)$$

where λ is constant. Then from eqns (2.5), (2.8) and (2.19),

$$\tilde{D}(\omega) = \frac{1}{6}\lambda \sum_{\underset{\sim}{s}} s^2 p(\underset{\sim}{s}) \qquad (2.22)$$

which is constant. If eqn (2.20) were waived, one would have

$$\tilde{D}(\omega) = \frac{1}{6}\lambda\ \tilde{\sigma}^2_{rms}(\omega) \qquad (2.23)$$

with no more frequency dependence than eqn (2.13). $\psi(t)$ must therefore be non-exponential. In the next section its form is (implicitly) worked out and used to compute conductivity.

2c. Application to Calculation of Conductivity

In Appendix E, equations (2.1), (2.5) and (2.19) are used together with a suitable approximation to $\tilde{\sigma}^2_{rms}(\omega)$ are used to evaluate the conductivity $\sigma(\omega)$ at low and intermediate ω. The mean square displacement per hop is replaced by the mean square nearest-neighbour separation between randomly located sites. The rate of hopping a distance r,

$$W(\underset{\sim}{r}) = R_o(\alpha r)^{\nu}\ e^{-2\alpha r} \qquad (2.24)$$

where ν is a parameter depending on band structure (Miller and Abrahams

1960). It can take values around 1.5-2.0 and two cases are considered in this thesis: $\nu = 3/2$ to allow comparison with numerical calculations by McInnes et.al. (McInnes and Butcher 1979, McInnes, Butcher and Clark 1980) and $\nu = 0$ to examine qualitatively the effect of the most important part of W(r): the exponential. With $\nu = 0$ the dc conductivity is found from eqns (2.1) and (E26) of Appendix E to be

$$\frac{\sigma(0)}{g_a} = 0.062\ B^{-7/4}\ e^{-0.532B^{3/2}} \tag{2.25}$$

where

$$B = \alpha n_s^{-1/3} \tag{2.26}$$

where α comes from eqn (2.24) and n_s is the density of localised electron states, and g_a is defined by

$$g_a = \frac{e^2 R_o}{k\Theta}\frac{n}{n_s}\ , \tag{2.27}$$

n being the carrier density.

The conductivity at non-zero frequencies must be evaluated numerically using the method outlined in Appendix E. Scher and Lax (1973) perform this calculation with $\nu = 0$. The author has performed it with $\nu = 3/2$ (McInnes, Butcher and Clark 1980), with results shown in figures (2.1) and (2.2). These results are compared with those of Butcher, Hayden and McInnes (1977), McInnes and Butcher (1979) (Appendix F, eqn (F1)) and McInnes, Butcher and Clark (1980) (eqn (F5) and Appendix F). It is seen that the dc formulae agree remarkably well for $B \lesssim 9$. By $B = 16$, the Scher and Lax formula, eqn. (2.25) is three-and-a-half orders of magnitude less than eqn (F1) of Butcher et.al. (1977). At intermediate frequencies the two approaches show excellent agreement. Reasons for the failure of the Scher-Lax approach at high frequencies are discussed in appendix E.

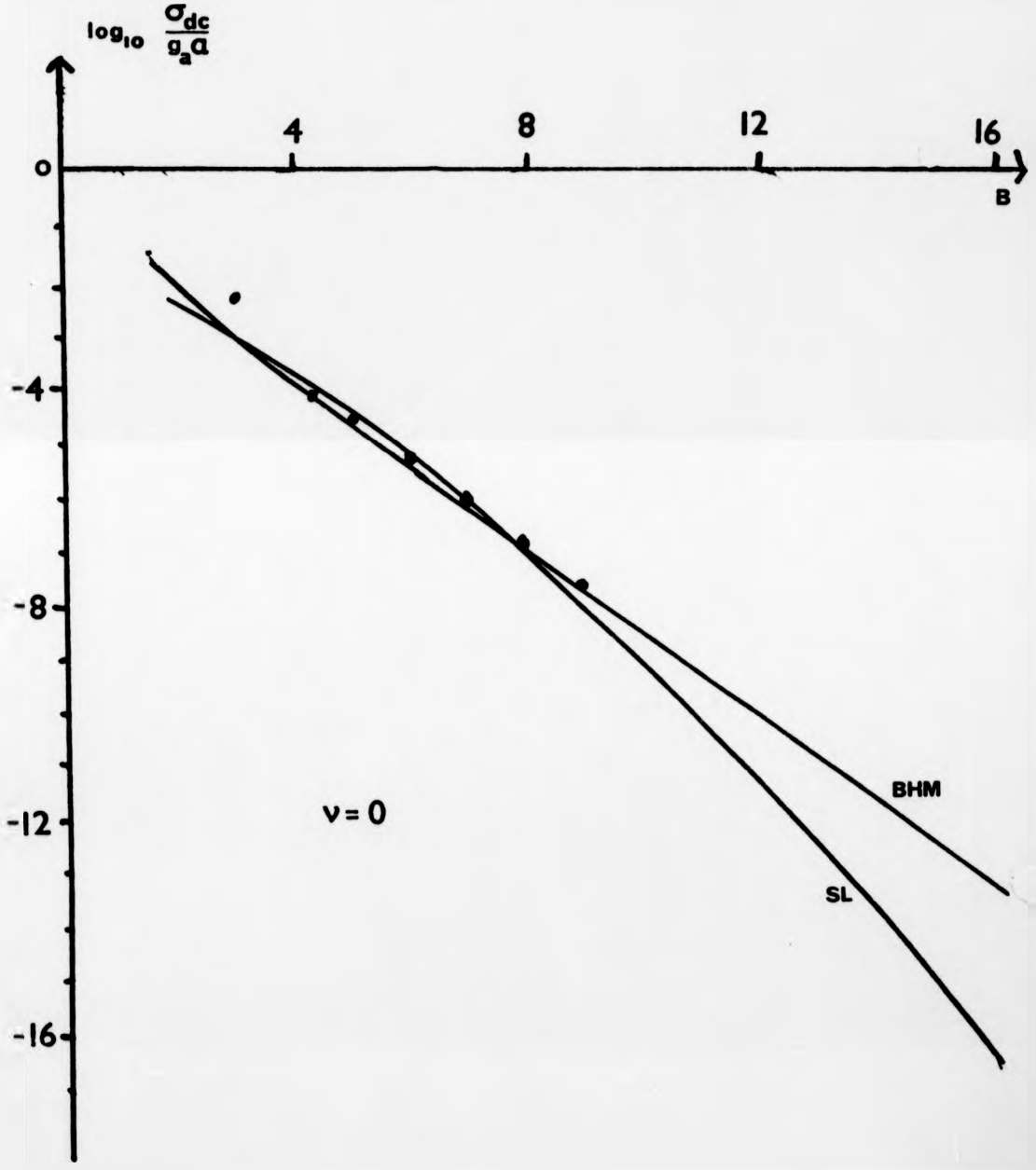


Figure 2.1: Comparison of dc conductivities of Scher and Lax (SL) with Butcher, Hayden and McInnes (1977: BHM = analytic theory, dots = numerical solutions of eqn (1.14)).

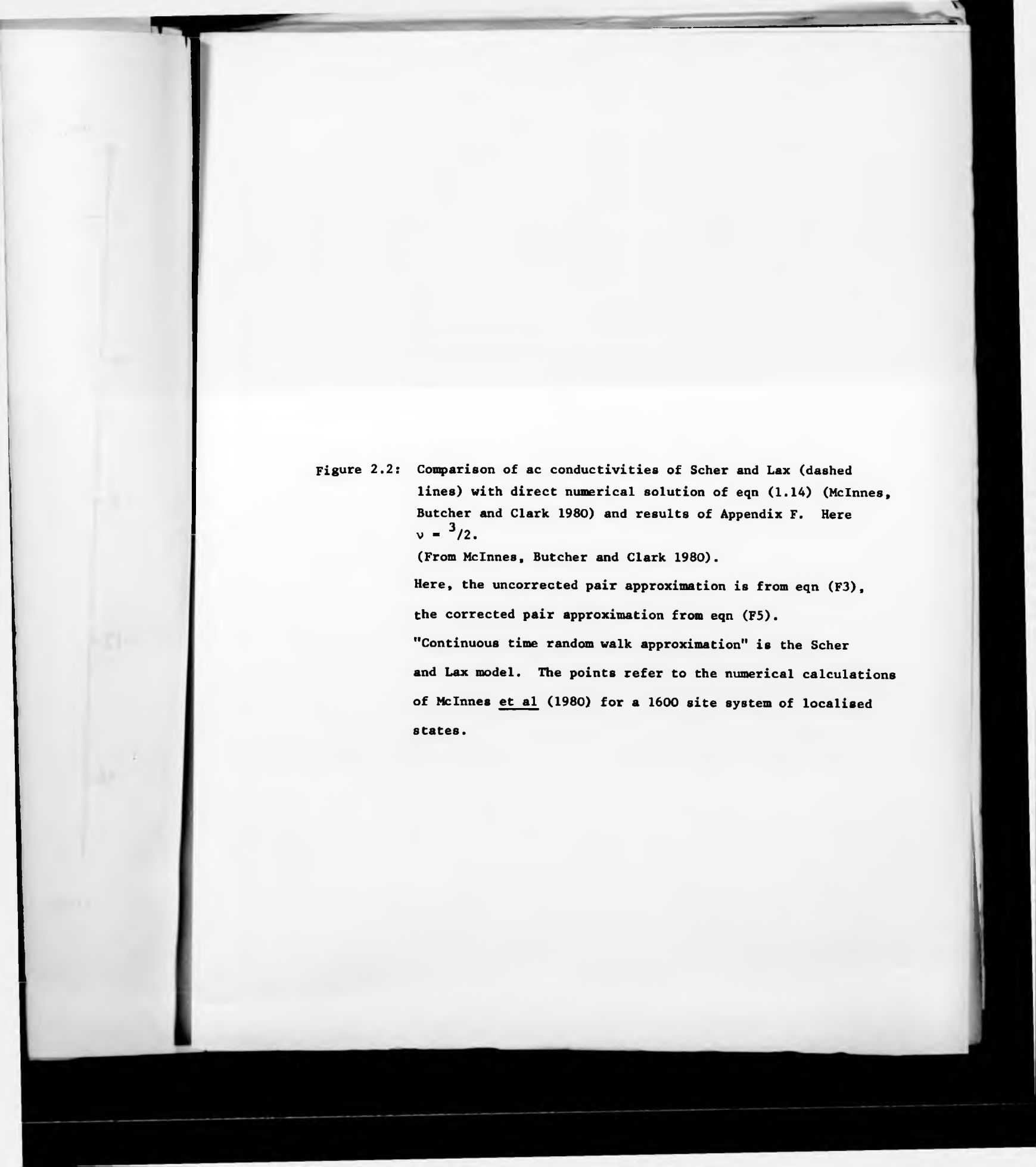
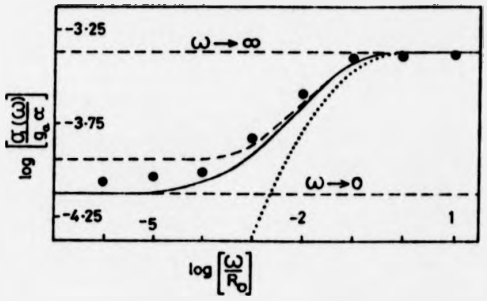
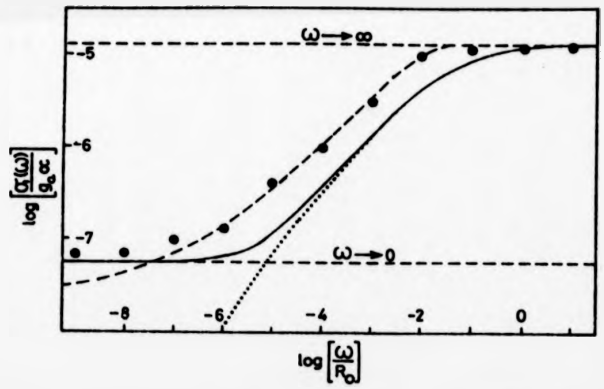


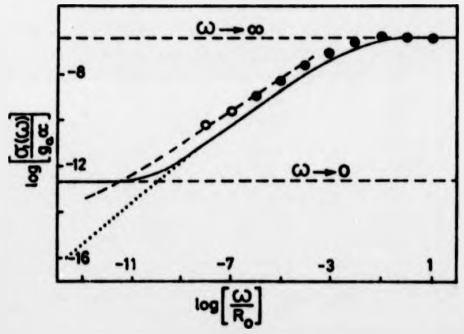
Figure 2.2: Comparison of ac conductivities of Scher and Lax (dashed lines) with direct numerical solution of eqn (1.14) (McInnes, Butcher and Clark 1980) and results of Appendix F. Here $\nu = {}^{3}/_{2}$.
(From McInnes, Butcher and Clark 1980).
Here, the uncorrected pair approximation is from eqn (F3), the corrected pair approximation from eqn (F5). "Continuous time random walk approximation" is the Scher and Lax model. The points refer to the numerical calculations of McInnes et al (1980) for a 1600 site system of localised states.



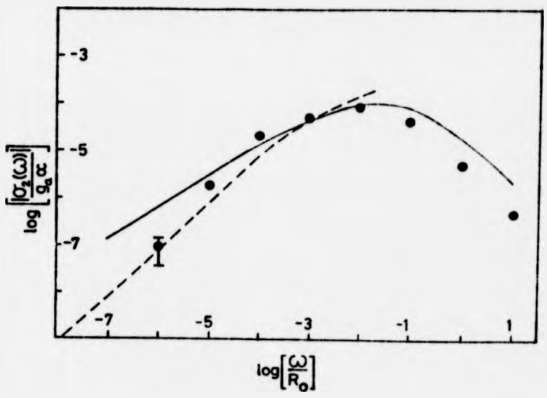
Real component of a.c. conductivity as a function of reduced frequency ω/R_0 for $\alpha n_0^{-1/3} = 5{\cdot}0$. Full curve: corrected pair approximation. Dotted curve: uncorrected pair approximation. Dashed curve: continuous-time, random-walk approximation. Points: computed for 1600-site system.



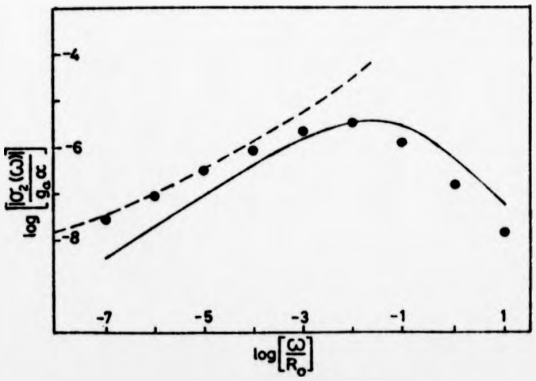
Real component of a.c. conductivity as a function of reduced frequency ω/R_0 for $\alpha n_0^{-1/3} = 9{\cdot}0$. Full curve: corrected pair approximation. Dotted curve: uncorrected pair approximation. Dashed curve: continuous-time, random-walk approximation. Points: computed for 1600-site system.



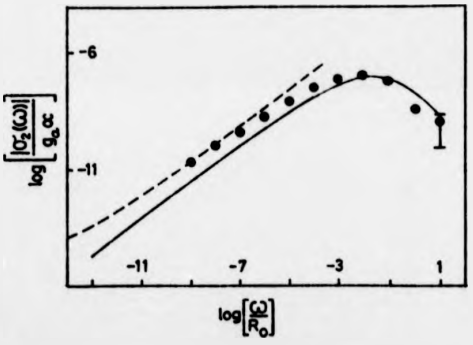
Real component of a.c. conductivity as a function of reduced frequency ω/R_0 for $\alpha n_0^{-1/3} = 16{\cdot}0$. Full curve: corrected pair approximation. Dotted curve: uncorrected pair approximation. Dashed curve: continuous-time, random-walk approximation. Points: computed for 1600-site system. Open points: computed for 1600-site system with a less stringent convergence criterion.



Imaginary component of a.c. conductivity as a function of reduced frequency ω/R_0 for $\alpha n_s^{-1/3}=5{\cdot}0$. Full curve: pair approximation. Dashed curve: continuous-time, random-walk approximation. Points: computed for 1600-site system.



Imaginary component of a.c. conductivity as a function of reduced frequency ω/R_0 for $\alpha n_s^{-1/3}=9{\cdot}0$. Full curve: pair approximation. Dashed curve: continuous-time, random-walk approximation. Points: computed for 1600-site system.



Imaginary component of a.c. conductivity as a function of reduced frequency ω/R_0 for $\alpha n_s^{-1/3}=16{\cdot}0$. Full curve: pair approximation. Dashed curve: continuous-time, random-walk approximation. Points: computed for 1600-site system.

In figures (2.3), (2.4) and (2.5) the conductivity of Scher and Lax is compared with experiment. It is compared by Scher and Lax (1973) themselves with measurements due to Pollak and Geballe (1961) of hopping in narrow impurity bands in n-type compensated silicon and by Kahlert (1976) with his own measurements on n-type compensated gallium arsenide: again hopping in a narrow impurity band is envisaged.

In both comparisons the formula

$$R_o = R_M|\Delta|\ e^{-\Delta/k\Theta} \tag{2.28}$$

is substituted into eqn (2.24), where R_M may be determined absolutely using the theory of Miller and Abrahams (1960) and Δ is an experimentally estimated mean of the energy difference between sites. In figures (2.3) and (2.5)

$$\bar{D}(\Omega) = \frac{\tilde{D}(\omega)}{\frac{1}{6}\tilde{\sigma}^2_{rms}(\omega)e^{\gamma}R_o} \quad . \tag{2.29}$$

$e^{\gamma} = 1.718$ is defined in Appendix E, eqn (E9). Scher and Lax find good agreement with the data of Pollak and Geballe. Kahlert, however, is able to fit either dc or ac conductivity but not both together. Reasons for this discrepancy are not understood. In view of the close agreement with the numerical results of McInnes, Butcher and Clark (1980), one would expect these to fail similarly.

Movaghar, Pohlmann and Sauer (1980) use a Green function method to solve the rate equations and fit the ac conductivity of McInnes et.al (1980) and the measured ac conductivity of amorphous germanium. (Summerfield 1980, to be published) is repeating these calculations without the adjustable parameter used by Movaghar et.al. His preliminary results suggest that this solution of the rate equations also fails to

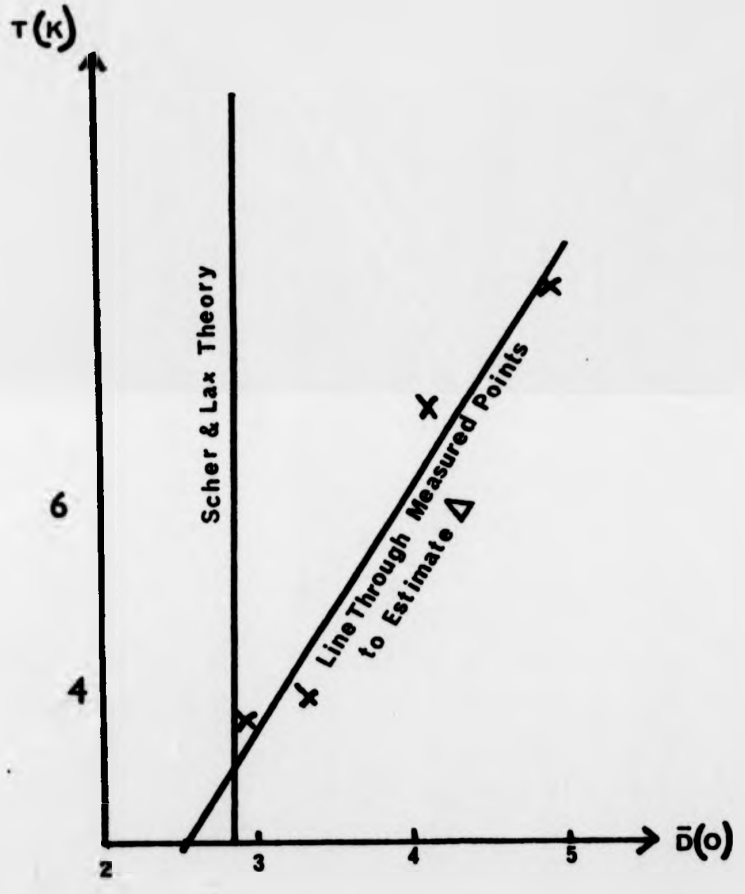


Figure 2.3: Plot of $\overline{D}(O)$ vs temperature used to deduce Δ from eqns (2.28) and (2.29), for compensated Si. Data of Pollak and Geballe (1961) quoted by Scher and Lax (1973).

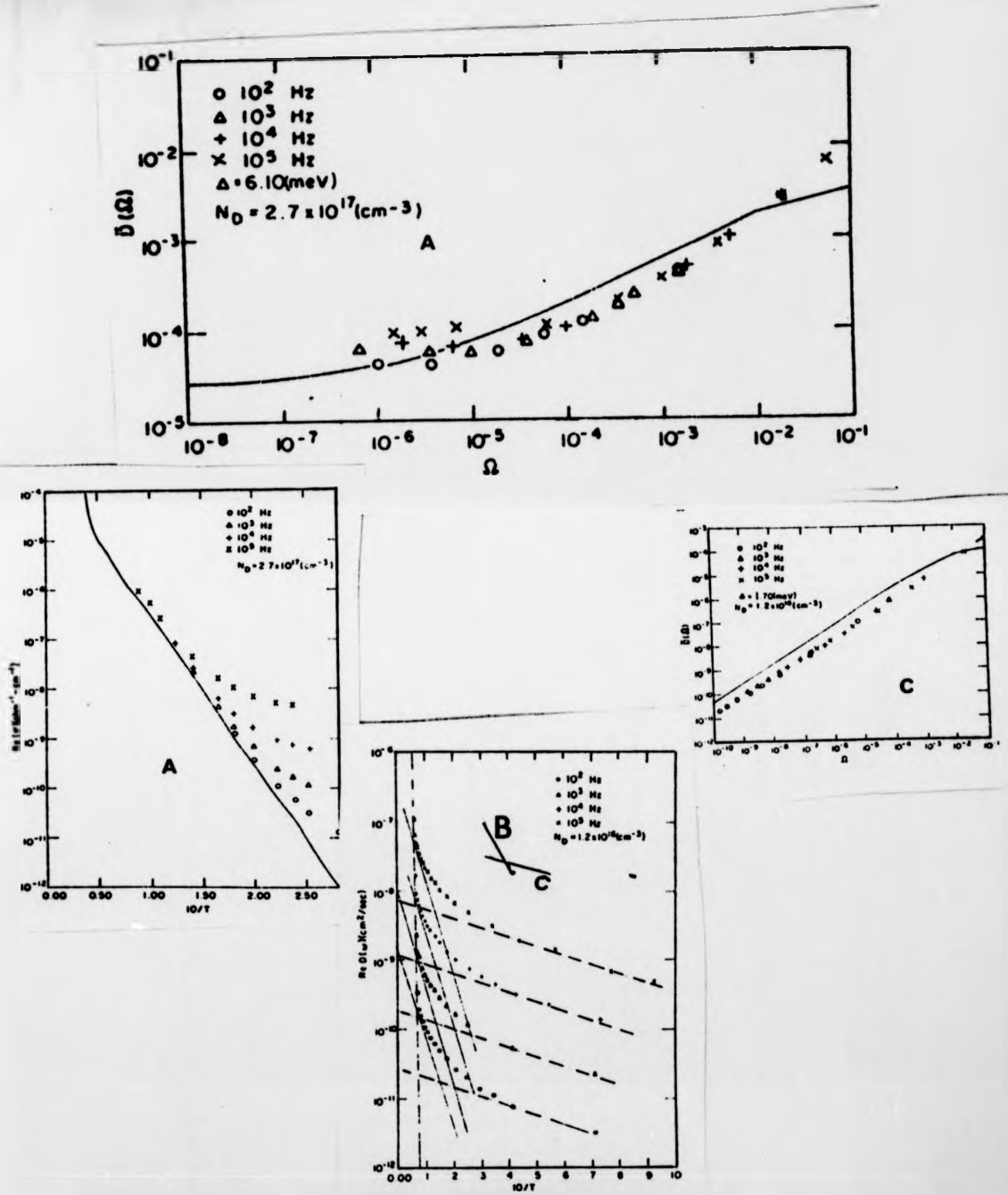


Figure 2.4: Measurements of Pollak and Geballe (1961) of conductivity of compensated silicon. A, B and C refer to different donor concentrations; B and C to different temperature regimes of the same donor concentration. The activation energy of C is fitted. Otherwise there is no fitting. (From Scher and Lax 1973).

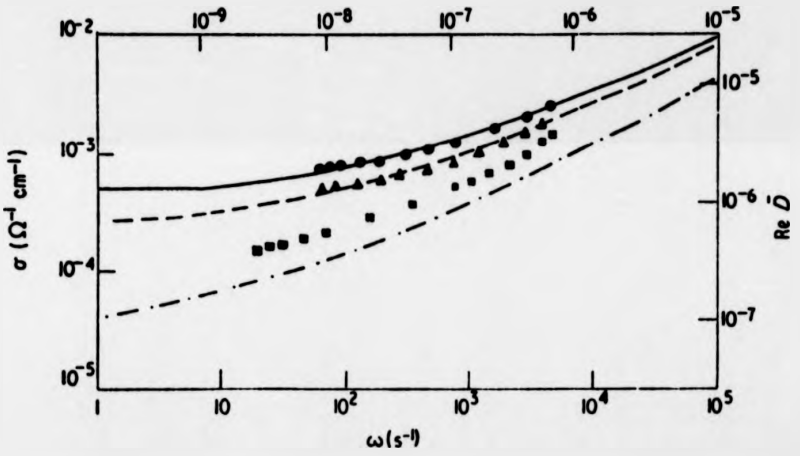


Figure2. Measured conductivity σ versus angular frequency ω (points) and calculated real part of the diffusion constant $\bar{D}$ versus Ω (curves). ■, sample E1415; ▲, sample E1915; ●, sample E2115; chain curve, $\eta = 2{\cdot}12 \times 10^{-3}$; broken curve, $\eta = 2{\cdot}99 \times 10^{-3}$; full curve, $\eta = 3{\cdot}3 \times 10^{-3}$. The lower abscissa scale and left ordinate scale concern the experimental points, the upper abscissa scale and right ordinate scale concern the calculated curves.

Figure 2.5: Data of Kahlert (1976) on compensated GaAs. $\eta = \pi/2B^3$ so that the squares correspond to B = 9.05, triangles to B = 8.07 and circles to B = 7.81. The three curves have been fitted through the points and predict dc conductivities 10^4 times lower than the unfitted theory of Scher and Lax (1973).

describe both dc and ac conductivity together.

2d. Comparison of the Rerandomisation (Scher and Lax) Approach with Hopping on Randomly Located but Fixed Sites.

The rate equation formalism assumes the rate equations (1.1) (Miller and Abrahams 1960). These are then linearised (Butcher 1976). Whether the charge carriers are degenerate or not, the linearised rate equations are equivalent to a random walk on a random lattice of permanently fixed sites (Butcher, op.cit.). Results of calculations of conductivity using this formalism, due to Butcher and co-workers, are given in Appendix F. It was mentioned in §2b that continuous-time random walk theory is equivalent to a random walk among randomly located sites in the special case that the site locations are rerandomised after every hop. This is shown in Appendix H. Such rerandomisation makes an otherwise inextricable diffusivity calculable (Butcher 1974b). In this section simple qualitative arguments are advanced to provide some insight into the consequences of the rerandomisation approximation and thus into the validity of continuous-time random walk theory.

Consider first the limit of very high site densities, $B \to 0$. Then within a favourable hopping distance α^{-1} (cf. eqn (2.24)) there will be very many sites. The probability of hopping to a given site within this range does not depend very greatly on its exact position: the exact site configuration is unimportant. Therefore rerandomising the sites after every hop cannot significantly alter the behaviour of the carriers. The rerandomisation approximation is expected to work well in this regime.

This argument obviously breaks down at the opposite extreme, $B \to \infty$. Naïvely one might expect the rerandomisation approximation to fail in this

case, arguing that carriers really only follow paths along which all the hops are short, but if the sites are rerandomised the carrier keeps getting stuck on sites which after rerandomisation find themselves isolated. However, as figures (2.1) and (2.2) show, the only regime in which this approximation fails is the dc regime for $B \gtrsim 10$. Now Kahlert (1976; see figure 2.5 above) uses, for his measurements, samples with $8 \lesssim B \lesssim 9$; Butcher, Hayden and McInnes (1977) compare their calculations with measurements on compensated (crystalline) germanium with $3 \lesssim B \lesssim 13$. If B is greater than perhaps 3 or 4 the structure of eqn (2.24) is such that hops to the few nearest neighbours will dominate. The regime $B \to 0$ described above is not applicable here: indeed there is an experimentally important intermediate B regime in which the rerandomisation approximation works well.

Consider first the limit of high frequencies. Here the rerandomisation approximation is very good. Eqn (H22), with rerandomisation, gives

$$\tilde{D}^{re}(\infty) = \tilde{D}^{fs}(\infty) \qquad (2.30)$$

where "re" means "rerandomised" and "fs" means "fixed sites": $\tilde{D}^{fs}(\infty)$ is taken from eqn (F7). This result is most easily understood by considering the inverse causal Fourier transform of $\tilde{D}(\omega)$, D(t). The characteristics of D(t) at small t are the inverse causal Fourier transform of the characteristics of $\tilde{D}(\omega)$ at large ω. Imagine two ensembles of systems of hopping sites, all initially identical. In one ensemble the sites rerandomise after every hop; in the other they do not. Now let a carrier be placed at t = 0 on a given initial site in each system of the ensembles. While these carriers are making their first hops, the two ensembles are quite identical. Thereafter they differ. Diffusion in the time regime is shown in Chapter 4 to be governed by the MPPE, eqn (1.31),according

to which at short times only low values of τ come into $D(t-\tau)$. By virtue of the above argument

$$\lim_{t \to 0} D^{fs}(t) = \lim_{t \to 0} D^{re}(t) \qquad (2.31)$$

whence eqn (2.30) immediately follows.

Now consider the dc limit. The diffusivity

$$\tilde{D}(0) = \frac{1}{2} \overset{\sim}{\sigma}^2_{rms}(0)\, \chi(0) \qquad (2.32)$$

where $\overset{\sim}{\sigma}^2_{rms}(0)$ is the mean-square displacement per hop and $\chi(0)$ is the mean hopping frequency. In eqn (2.24) ν is taken to be zero. The following equations are then valid:

$$\sigma^{2\ re}_{rms}(0) = 0.3474\ n_s^{-2/3} \ , \qquad (2.33)$$

$$\sigma^{2\ fs}_{rms}(0) = 2B^2\ e^{-1.72B}\ n_s^{-2/3} \ , \qquad (2.34)$$

$$\chi^{re}(0) = B^{-3/4}\ e^{-0.532\ B^{3/2}}\ R_o \ , \qquad (2.35)$$

$$\chi^{fs}(0) = \pi B^{-3}\ R_o \ , \qquad (2.36)$$

apart from constants of proportionality. The fixed-site results are from Appendix F, eqns (F1) and (F2). The rerandomisation results are from eqns (2.5) and (E26). The rerandomisation completely fails to give good reproductions of eqns (2.34) and (2.36). Yet the resultant diffusivities resemble one another closely for $B \lesssim 10$, as shown in figure (2.1).

The rerandomisation approximation replaces many short hops along favourable paths with much fewer hops over greater distances. Favourable paths cannot exist in this case - since they are destroyed after every hop, the carriers have no chance to follow them. Silver (1977) shows how

the number of hops per unit time can be reduced in this way by several orders of magnitude. He numerically compares a fixed-site random walk with the theory of Scher and Lax (1973).

In the rerandomisation approximation set out in Appendix H hops are essentially to nearest neighbours. Using eqn (E4) and calculating the error as $\left[\langle r_{NN}^2\rangle - \langle r_{NN}\rangle^2\right]^{\frac{1}{2}}$, the nearest-neighbour distance is typically

$$r_{NN} = (0.55 \pm 0.2)\, n_s^{-1/3} \quad . \tag{2.37}$$

The small spread in r_{NN} values is caused by the sharp peak in eqn (E4). Let a further approximation be made: let the distance hopped have a constant value $r_{NN} = 0.55$. Then because of eqn (2.24) the hop rate $\chi^{re}(0)$ would be proportional to $\exp(-\lambda B)$ where λ is a constant. Eqn (2.37) makes this quantity non-exponential. The higher is B the more non-exponential $\chi^{re}(0)$ will be because the variation in hop rate across the range of r_{NN} values will become greater. The sharpness of the peak in eqn (E4) ensures that this effect will not be very great when B is smallish, say 5.0.

In the fixed-site case it is seen from eqn (F1) that if the non-exponential factor in the dc conductivity is neglected as being slowly varying, this conductivity obeys the relation

$$\frac{d\sigma_{BHM}(0)}{dB} = -\sigma_{BHM}(0) \tag{2.38}$$

To understand this equation, Summerfield (1980, private communication) remembers that on a fixed random lattice of sites the carriers will tend to follow likely paths, i.e. paths on which each hop is short compared to $\alpha^{-1} = (B\, n_s^{-1/3})^{-1}$. He then points out that as B increases, likely paths will be destroyed at random because one hop in this path becomes

improbably long. Butcher (1976) derives eqn (2.36) without knowing the conductivity. It then follows from eqn (2.32) that a factor $\exp(-\lambda B)$, λ constant, will appear in eqn (2.34).

At large values of B the rerandomisation conductivity will fall off the faster because in this case the carriers inevitably become trapped for a while every time the rerandomisation leaves the occupied site relatively isolated. The carriers are thus unable to follow likely paths as in the fixed site case. This effect becomes more important as B increases. This effect is responsible for the failure of the rerandomisation approximation in the dc limit when $B \gtrsim 10$. It is thus seen that this approximation works by approximately reversing the roles of $\tilde{\sigma}^2_{rms}(0)$ and $\chi(0)$. It fails to mimic the microscopic behaviour of the carriers but usually yields a good macroscopic description. This state of affairs is crucially dependent on eqn (2.24). If this rate were replaced by a formula such as, say, the Ramp function

$$W(\underset{\sim}{r}) \begin{cases} = R_o\left(1 - \frac{\alpha r}{3}\right), & r < 3\alpha^{-1}, \\ = 0, & r \geq 3\alpha^{-1}, \end{cases} \qquad (2.39)$$

the arguments leading to eqn (2.38) would still hold but those used to justify the roughly-exponential form of eqn (2.35) would fail. (Indeed once a rerandomisation occurs such that no sites fall within a radius $3\alpha^{-1}$ the carrier will become permanently trapped and unable to make further hops. The important point though is that eqn (2.24) must be roughly exponential for eqn (2.35) to work).

2e. Application of Continuous-Time Random Walk Theory to Anomalous Carrier Pulse Propagation

In the preceeding section it was easier to envisage this theory as hopping with site rerandomisation. It will now be more convenient to

switch back to the random-walk-on-regular-lattice picture. Continuous-time random walk theory is applied to ACPP by Montroll and Scher (1973), Shlesinger (1974) and Scher and Montroll (1975). Leal Ferreira (1977) points out that to obtain the salient features of ACPP, eqn (1.30), it is only necessary to consider the continuum limit of the lattice and that diffusion effects are unimportant. This author's calculation is reviewed here since his approximations greatly facilitate the calculation.

The starting point is the Generalised Master Equation (Kenkre, Montroll and Shlesinger 1973):

$$\frac{dP(\underset{\sim}{\ell},t)}{dt} = \int_0^t dt'\phi(t-t') \sum_{\underset{\sim}{\ell}'} [p(\underset{\sim}{\ell}-\underset{\sim}{\ell}')P(\underset{\sim}{\ell}',t')-p(\underset{\sim}{\ell}'-\underset{\sim}{\ell})P(\underset{\sim}{\ell},t')] \ . \qquad (2.40)$$

Here $P(\underset{\sim}{\ell},t)$ is the probability of finding a carrier on the site at $\underset{\sim}{\ell}$ at time t if at t = 0 it was on the site at the origin; $p(\underset{\sim}{\ell})$ is the probability of a hop which displaces the carrier through $\underset{\sim}{\ell}$. As explained in §2b, $\tilde{\psi}(\omega)$ and $\tilde{h}(\omega)$ are equated. Their inverse causal Fourier transforms are therefore equal (i.e. $h(t) = \psi(t)$). $\psi(t)$ is related to the probability $\phi(t)$ of no hop occurring since the last hop at t = 0 via the relation

$$\phi(t) = 1 - \int_0^t \psi(\tau)d\tau \qquad (2.41)$$

(which is called eqn (D16) in appendix D). Eqn (2.40) is derived from first principles by Klafter and Silbey (1980) for the case of a regular lattice with some of its sites occupied by hopping centres. These authors express $\psi(t)$ in terms of the self-energy matrix of the system.

The Laplace transform into u-space of eqn (2.41) is

$$\hat{\phi}(u) = \frac{u\hat{\psi}(u)}{1-\hat{\psi}(u)} \ . \qquad (2.42)$$

The claret (ˆ) symbol is used to denote Laplace transforms. $p(\underset{\sim}{\ell})$ is taken to be non-zero only for

$$\left.\begin{aligned} p(0,\pm1,0) = p(0,0,\pm1) &= \tfrac{1}{6}\ ; \\ p(\pm1,0,0) &= \tfrac{1}{6} \pm bE \end{aligned}\right\} \qquad (2.43)$$

where E is electric field given by $\underset{\sim}{E} = (-E,0,0)$ and b is a constant. Electrons are considered; the calculation for holes has the same form. $P(\underset{\sim}{\ell},t)$ is now taken to be continuous and is Taylor expanded to second order in x. The electrical charge density $\rho(x,t)$ per unit area then obeys the equation

$$\frac{\partial\rho(x,t)}{\partial t} = \int_0^t dt'\phi(t-t')\left[\frac{a_o^2}{6}\frac{\partial^2\rho(x,t')}{\partial x^2} - 2a_o bE\frac{\partial\rho(x,t')}{\partial x}\right] \qquad (2.44)$$

where a_o is the lattice constant. A generation term $q_o\delta(x)\delta(t)$ may be added to the right hand side of eqn (2.44) to represent a constant number n_o electrons per unit area, having total charge q_o, created at $x = 0$ at $t = 0$. The resemblance of eqn (2.44) to the MPPE, eqn (1.31), is obvious. The Laplace transform of eqn (2.44) is*

$$u\hat{\rho}(x,u) = q_o\delta(x) - 2a_o bE\frac{\partial\hat{\rho}(x,u)}{\partial x}\hat{\phi}(u) \qquad (2.45)$$

which is very easily solved to yield

$$\hat{\rho}(x,u) = \frac{\theta(x)\ \exp[-ux/(2a_o bE\hat{\phi}(u))]}{2a_o bE\hat{\phi}(u)} \qquad (2.46)$$

A value of $\psi(t)$ is required which satisfies the normalisation condition $\phi(\infty) = 0$ and gives rise to ACPP-like behaviour. $\theta(x)$ is the unit step function. It is convenient to use

$$\psi(t) = 4W_M\, e^{W_M t}\, i^2\, \mathrm{erfc}\,(W_M t)^{\frac{1}{2}} \qquad (2.47)$$

* The diffusion term is omitted.

where i^2 means "double integral" (Montroll and Scher 1973). Then

$$\lim_{t \to \infty} \psi(t) \propto \frac{1}{t^{1+\frac{1}{2}}} \quad . \tag{2.48}$$

It is shown in Appendix I that the Laplace transform of eqn (2.47) has a very simple form, namely

$$\hat{\psi}(u) = \frac{1}{[1 + (u/W_M)^{\frac{1}{2}}]^2} \tag{2.49}$$

whence

$$\hat{\phi}(u) = \frac{W_M}{1 + 2\ (W_M/u)^{\frac{1}{2}}} \quad . \tag{2.50}$$

This is substituted into eqn (2.46) to yield

$$\hat{\rho}(x,u) = \frac{q_o\ \theta(x)}{2W_M a_o bE} \exp\left\{\frac{-ux[1 + 2(W_M/u)^{\frac{1}{2}}]}{2W_M a_o bE}\right\} \quad . \tag{2.51}$$

The inverse Laplace transform of eqn (2.51) is

$$\rho(x,t) = \frac{q_o}{\pi^{\frac{1}{2}} a_o bE} \exp[-y^2/(W_M t - y)] \left[1 + \frac{y}{2(W_M t - y)}\right] \tag{2.52}$$

(Spiegel 1965, Chapter 2) where $y = x/2a_o bE$. For times $t >> W_M^{-1}$,

$$\rho(x,t) = \frac{\theta(x) q_o \exp[-x^2/(2a_o bEW_M t)]}{\pi^{\frac{1}{2}} a_o bE (W_M t)^{\frac{1}{2}}} \quad . \tag{2.53}$$

This half-gaussian pulse is very far from the conventional diffusionless pulse, eqn (1.23) with lim D → 0.

It is shown in Appendix G that the total current density which would be measured were this semiconductor connected to an ammeter is

$$I(t) = -\frac{d}{dt}\left[\int_0^{\ell}\rho(x,t)dx + \frac{1}{\ell}\frac{d}{dt}\int_0^{\ell}x\rho(x,t)dx\right]$$

$$\propto \frac{1}{(W_M t)^{\frac{1}{2}}}\left\{1 - \exp\left[-\frac{\ell^2}{4(a_o bE)^2 t}\right]\right\} \qquad (2.54)$$

from eqn (2.53), if ℓ is the now length of the semiconductor. Hence if t_1 is the time the pulse takes to cross the semiconductor,

$$I(t) \quad \begin{cases} \propto t^{-\frac{1}{2}} , & t << t_1 ; \\ \propto t^{-3/2} , & t >> t_1 \end{cases} \qquad (2.55)$$

The salient features of ACPP are recovered. Crudely we may take the transit time t_1 to be the time at which the exponent in eqn (2.54) is equal to unity. This gives the remaining salient feature

$$t_1 \propto (\ell/E)^2 . \qquad (2.56)$$

Eqns (2.55) and (2.56) are identical to eqn (1.30) if $\alpha = \frac{1}{2}$.

If one chooses $\psi(t) \sim t^{-(1+\alpha)}$ at large t, then from eqn (2.41), $\phi(t) \sim t^{-\alpha}$. This implies that at low ω, $\hat{\phi}(\omega) \sim (-i\omega)^{-(1-\alpha)}$. Substituting this value into eqns (2.1) and (2.5) yields a diffusivity and thus a conductivity proportional to $(-i\omega)^{1-\alpha}$, like eqn (5.1) (Scher 1976). The above calculation therefore corresponds to having a conductivity proportional to $\omega^{\frac{1}{2}}$.

CHAPTER 3

Review of Other Theories of Anomalous Carrier Pulse Propagation

3a. Introduction

In this section another mechanism commonly proposed for ACPP is reviewed (Marshall and Allan 1978, Noolandi 1977 a,b,c, Schmidlin 1977, 1980, Pfister and Scher 1977). This mechanism is trap-controlled transport. The basis of trap-controlled transport is that carriers in transport states are de-exciting into traps. The concentration of "free" carriers falls causing the transient current density I(t) to fall. It may be trap-controlled band transport (TCBT) in which the carriers are initially excited into extended states in the conduction band, through which they travel but are subject to capture by and release from localised states present in the material. Alternatively it may be trap-controlled hopping (TCH) in which one envisages two types of hopping site: traps in which the carriers spend a long time and transport states with roughly the same energies and a roughly constant mobility which is somewhat higher than that which one would associate with trap states. Both models give rise to the same set of equations though the physical processes involved are of course different. TCBT is discussed by Marshall and Allan (1978), Noolandi (1977 a, b,c) and Schmidlin (1977). TCH is discussed by Pfister and Scher (1978), Noolandi (1977 a, b,c) and Schmidlin (1977, 1980). Both mechanisms can give rise to ACPP. Rudenko and Arkhipov (1979) discuss a variation on TCBT in which the carriers are also allowed to hop between traps: they too find that ACPP is plausible under such circumstances. Indeed they derive a macroscopic equation having the same form as that for TCBT and TCH.

In section 3b, the formal theory of trap-controlled transport is reviewed. In section 3c and in Appendix B it is shown that an arbitrary trap distribution eventually gives rise to gaussian pulses. In section 3d the paper on TCH by Schmidlin (1980) is reviewed.

3b. Formal Theory of Trap-Controlled Transport

This is set up by Schmidlin (1977) and Noolandi (1977a). Both authors use the same method. One imagines free and trapped carriers. In TCBT the "free" carriers are carriers in the conduction band; in TCH they are carriers in states loosely called "transport" states by Schmidlin (op.cit.). In his 1980 paper he suggests that they are states such that their annihilation would hamper the progress of carriers through their neighbourhood in $\underset{\sim}{\chi}$-space whereas traps are states whose annihilation would improve such progress.

To make the theory macroscopic some care must be taken when defining the capture rate $C_j(\underset{\sim}{\chi},t)$ and release rate $\rho_j(\underset{\sim}{\chi},t)$ of carriers from the j^{th} kind of trap at co-ordinates $(\underset{\sim}{\chi},t)$. If the traps are regarded as discrete points these will not be continuous functions. Therefore one "smooths out" the effect of the traps and assumes C_j and ρ_j to be continuous. The additional assumptions that they are independent of position and time are made.

Let $n(\underset{\sim}{\chi},t)$ be the total carrier concentration, $p(\underset{\sim}{\chi},t)$ be the concentration of free carriers and $p_j(\underset{\sim}{\chi},t)$ be the concentration of carriers in the j^{th} kind of trap. These quantities are again "smoothed out". The carriers then obey the conservation equations

$$\frac{\partial n(\underset{\sim}{\chi},t)}{\partial t} = n_o\delta(\underset{\sim}{\chi})\delta(t) - \underset{\sim}{\nabla}\cdot\underset{\sim}{J}_f(\underset{\sim}{\chi},t) \qquad (3.1)$$

$$n(\underset{\sim}{r},t) = p(\underset{\sim}{r},t) + \sum_j p_j(\underset{\sim}{r},t) \tag{3.2}$$

$$\frac{\partial p_j(\underset{\sim}{r},t)}{\partial t} = p(\underset{\sim}{r},t)C_j - p_j(\underset{\sim}{r},t)\rho_j \tag{3.3}$$

where

$$J_f(\underset{\sim}{r},t) = \mu_f \underset{\sim}{E}\, p(\underset{\sim}{r},t) + D_f \underset{\sim}{\nabla} p(\underset{\sim}{r},t) \tag{3.4}$$

is the number current density of free carriers. Eqns (3.1) - (3.4) are Fourier-transformed into $\underset{\sim}{r}\omega$-space. Of the resulting equations the fourth is substituted into the first. The third is used to eliminate the Fourier transform of $p_j(\underset{\sim}{r},t)$ from the second. This is then used to eliminate the Fourier transform of $p(\underset{\sim}{r},t)$ from the first. The resulting equation is inverse Fourier-transformed to give

$$\frac{\partial n(\underset{\sim}{r},t)}{\partial t} = n_o \delta(\underset{\sim}{r},t) + \underset{\sim}{E}.\underset{\sim}{\nabla} \int_{-\infty}^{\infty} \mu(t-\tau)\, n(\underset{\sim}{r},\tau)d\tau$$

$$+ \nabla^2 \int_{-\infty}^{\infty} d\tau\, D(t-\tau)\, n(\underset{\sim}{r},\tau)\ . \tag{3.5}$$

where n_o is the total number of carriers per unit area, and $\mu(t)$ is the inverse Fourier transform of

$$\tilde{\mu}(\omega) \equiv \mu_f \tilde{Q}(\omega) \equiv \mu_f \left[1 - \sum_j \frac{C_j}{\rho_j - i\omega}\right]^{-1} \tag{3.6}$$

and

$$\tilde{D}(\omega) \equiv D_f \tilde{Q}(\omega) \quad . \tag{3.7}$$

Eqn (3.5) has the same mathematical structure as the hopping MPPE, equ (4.33). Use of this fact is made in §5b to show how eqn (3.5) can give rise to ACPP.

This is the source of the central problem of this thesis: both hopping and TCBT can in principle give rise to ACPP making it necessary to look hard for clues as to which mechanism is present in experiments. As Rudenko and Arkhipov (1979) point out it might even be a mixture.

If μ_f and D_f are related by an Einstein relation then a pseudo-ac Einstein relation (Lax 1960, see also next chapter) between $\tilde{\mu}(\omega)$ and $\tilde{D}(\omega)$ will hold. It should perhaps be emphasised that these quantities are not ac mobility and ac diffusivity in the hopping sense (Schmidlin 1979, private communication) so this will not be a genuine Einstein relation. If in the case of TCBT the carrier makes many intraband transitions between each trapping event a dc Einstein relation between μ_f and D_f may be expected since the carriers to all intents and purposes equilibrate within an isolated band. This may be expected to happen in practice. Schmidlin (1977, 1980) claims that in TCH no Einstein relation should hold.

It is pointed out in §5c that the diffusion term in eqn (3.5) is negligible, otherwise the universality feature of ACPP noted in chapter 1 would not be found. However the pulse still disperses. It is convenient (whatever the transport mechanism) to call the contribution of the drift term (involving μ) to $\langle x(t)\rangle$, namely $\langle x(t)\rangle_{dr}$, the shift of the pulse. The contribution $\sigma_{dr}(t)$ of the drift term to the rms spread $\sigma(t)$ defined by eqn (A3) of Appendix A is called the spread of the pulse. The behaviour of these quantities in trap-controlled transport is discussed in the next section.

3c. Behaviour after long times of Trap-Controlled Pulses

Even if diffusion is neglected, such pulses eventually show gaussian broadening whatever the trap distribution. This is essentially because the long-time behaviour of the pulses is dominated by the low-frequency

behaviour of $\tilde{Q}(\omega)$, which may be always expanded in the form

$$\tilde{Q}(\omega) = Q_o + Q_1(-i\omega) + \ldots\ldots \tag{3.8}$$

where Q_o and Q_1 are constants. Consider the spatial moments of such pulses-spatial moments as discussed in Appendix A. Insertion of eqns (3.8) and (3.6) into eqn (A4) yields

$$\langle x(t)\rangle_{dr} = E\mu_f(Q_1 + Q_o t) \ . \tag{3.9}$$

This is the shift of the pulse at large times: the subscript 'dr' indicates that diffusion effects are neglected. The spread of a pulse is defined to be

$$\sigma_{dr}(t) \equiv \sqrt{\langle x^2(t)\rangle_{dr} - \langle x(t)\rangle_{dr}^2} \ . \tag{3.10}$$

In this case it is seen from Appendix A that

$$\sigma_{dr}(t) = E\mu_f\left[2Q_oQ_1t\right]^{\frac{1}{2}} \tag{3.11}$$

as $t \to \infty$. Eqns (3.9) and (3.11) together show that in this limit the effect of the traps is to cause the pulse to shift at constant velocity while spreading like a gaussian pulse. Perhaps it should be emphasised that the cause of this spread is not the same as in a conventional pulse (Fickian diffusion): it is entirely generated by the drift term and is due to the capture and release by traps. There will be a contribution to the spread from the diffusion term. At large times this contribution will be gaussian like (see Appendix A)

3d. Brief review of Trap-Controlled Hopping

The case for invoking trap-controlled hopping may be argued as follows. Pollak (1977) considers hopping among essentially isoenergetic sites (known as r-percolation) and points out that to obtain a nonzero spread it is

necessary for carriers to become delayed by entering isolated sites. But by virtue of this very isolation, the chance of entering such a site is so low that this process is unimportant. In this thesis, this is called the Pollak effect. Pollak therefore writes down the Pauli Master Equation (see Kenkre (1977) for a discussion of master equations) which will only describe conventional pulse propagation. In Chapter 6 this problem is approached from a different point of view and a different conclusion is obtained: Pollak's argument turns out to be over-simple and requires generalising somewhat though a time regime in which the Pollak effect does hold may be found. Be that as it may, his idea is taken up by other authors (Schmidlin 1977, 1980, Pfister and Scher 1977, Noolandi 1977) who propose that to supress the Pollak effect and obtain ACPP, certain sites must exist such that they are easy for carriers to enter but hard to leave. Such sites are called traps and might for example be sites having much lower energies than their neighbours. This mechanism is considered in detail by Schmidlin (1980), who explicitly states that his carriers are out of thermal equilibrium: the transient current I(t) decays largely because the excess number of carriers in highly mobile (transport) states is thermalizing with the traps. That is, this fall in current is caused by more and more carriers becoming trapped. Schmidlin starts his detailed analysis from the same point as that used in this thesis, viz. eqn (4.1). He then splits his hopping states into transport and trapping states. A transport state is defined to be one which, if it were annihilated, would cause the mobility to go down. A trap is defined to be a state whose annihilation would improve the progress of carriers, i.e. increase their mobility. Schmidlin's grounds for doing this are purely intuitive. He then writes down essentially equations (3.1), (3.2) and (3.3), putting his states on a regular lattice although its presence does not affect his results.

On the basis of this approach, Schmidlin concludes that (i) hopping among isoenergetic sites cannot produce the salient features of ACPP, (ii) hopping ACPP and ac conductivity are unrelated, (iii) the claim of Butcher (1978) that all ACPP mechanisms lead to the same macroscopic equation regardless of the microscopic origin and meaning of the quantities is incorrect, (iv) the Einstein relation is invalid for TCH and (v) the theory of Scher and Lax (1973) cannot produce a frequency-dependent conductivity.

Conclusion (v) was discussed and refuted in the previous chapter. Consideration of the first four points will occupy much of the remainder of this thesis. On point (i): a time will be found after which the Pollak effect gives rise to a constant transient current density I(t) but even then the pulse does not behave in a conventional manner. Points (ii) - (iv) are discussed in the next chapter and in Chapter 7. In Chapter 4 it is shown how even if the hopping carriers are out of thermal equilibrium a pseudo-Einstein relation may be constructed.

CHAPTER 4

Derivation of the Macrascopic Pulse Propagation Equation for Hopping Carriers

4a Introduction

Previous authors (Scher and Montroll 1975, Shlesinger 1974, Montroll and Scher 1973, Klafter and Silbey 1980) consider hopping among isoenergetic sites and develop a sophisticated theory of this process as a possible ACPP mechanism. Their method is reviewed in Chapter 2. In Chapter 3 non-isoenergetic hopping as a candidate for an ACPP mechanism is mentioned.

It is my present purpose to show how these two processes can be simply united into one theory according to which the ac mobility of hopping carriers governs the propagation of pulses via this mechanism and an ac Einstein Relation holds. This is done by direct use of a random lattice of sites with both position and energy arbitrarily disordered. In contrast to previous authors' models (Scher and Montroll 1975, Shlesinger 1974, Montroll and Scher 1973, Klafter and Silbey 1980, Bányai and Gartner 1980, Schmidlin 1980) the model used here does not at any stage involve the use of a regular lattice. This problem was first considered by Butcher (1979) who shows that the MPPE is valid for pure diffusion on a lattice of isoenergetic but spatially random sites. A generalisation of this to the case of non-isoenergetic sites and $E \neq 0$ is now presented (Butcher and Clark 1980, to be published).

In contrast to the carriers involved in trap-controlled hopping (Pfister and Scher 1977, Schmidlin 1977, 1980), the carriers are here assumed to be in thermal equilibrium. This is done in the belief that in practice the carriers are likely to thermalise long before reaching the end of the semiconductor.

4b. Basic Assumptions of the Theory

Consider a large, almost infinite, isotropic, homogeneous random lattice of N_s sites with random energies ε_m and positions $\underset{\sim}{r}_m$. A small, constant electric field $\underset{\sim}{E}$ may be applied. The carriers may be electrons or holes. The case of electrons is considered here but the theory for holes is almost identical. The electrons obey Boltzmann statistics and their macroscopic density $n(\underset{\sim}{r},t)$ is assumed to be so slowly varying in $\underset{\sim}{r}$-space that only first and second spatial derivatives of $n(\underset{\sim}{r},t)$ are important. With these assumptions only terms $\sim$ unity, E, k, kE and k^2 are important when calculating the Fourier transform of $\partial n/\partial t$ in $\underset{\sim}{k}\omega$-space. It will turn out that all but the last two of these terms vanish. Space charge is assumed to be negligible.

The following notation is used: column vectors are denoted by kets $|>$ and row vectors by bras $<|$ but in contradistinction to conventional Dirac notation there is no complex conjugation when transposing from bras to kets. Thus $<a|b> = \sum_m a_m b_m$. The Fourier Transform (FT) convention defined in Appendix C is used.

The rate equations of Miller and Abrahams (1960) are assumed to be valid in the Boltzmann limit, i.e.

$$\frac{d}{dt}|f> = -\underset{\approx}{R}|f> + \delta(t)|\delta_s> \tag{4.1}$$

where $|\delta_s>$ has all elements equal to zero except the s^{th} which is equal to unity, f_m is the occupation probability of the m^{th} site and the relaxation matrix $\underset{\approx}{R}$ is defined by

$$\underset{\approx}{R}_{mn} = \left(\sum_p W_{mp}\right)\delta_{mn} - W_{nm} \tag{4.2}$$

where W_{mn} is the transition rate from site m to site n. Note that the W_{nm} on the right hand side of eqn. (4.2) is the nm^{th} not mn^{th} element. It is supposed that Boltzmann statistics apply. Then

$$\exp[-(\epsilon_m + e\underset{\sim}{E}.\underset{\sim}{r}_m)/k\Theta]W_{mn}$$

$$= \exp[-(\epsilon_n + e\underset{\sim}{E}.\underset{\sim}{r}_n)/k\Theta]W_{nm} \quad . \tag{4.3}$$

The $|\delta_s>$ -term corresponds to creation of a carrier on site s at time t = 0. Θ is the absolute temperature. The Fourier Transform of eqn.(4.1) yields

$$-i\omega \; |\tilde{f}> = -\underline{\underline{R}} \; |\tilde{f}> + |\delta_s> \; , \tag{4.4}$$

whence (using $\underline{\underline{I}}$ denote the unit matrix)

$$|\tilde{f}> = \underline{\underline{G}} \; |\delta_s> \equiv (\underline{\underline{R}} - i\omega\underline{\underline{I}})^{-1}|\delta_s> \tag{4.5}$$

where the Green matrix $\underline{\underline{G}}$ obviously satisfies the relations

$$\underline{\underline{I}} + i\omega\underline{\underline{G}} = \underline{\underline{G}}\underline{\underline{R}} = \underline{\underline{R}}\underline{\underline{G}} \quad . \tag{4.6}$$

The Green matrix also has a simple interpretation in terms of a random walk performed by a single particle on an empty lattice (Butcher 1976). Let us define a matrix $\underline{\underline{P}}$ in which the mn^{th} element is the probability that a carrier initially on site m at t = 0 will be on site n at time t. Then $\underline{\underline{P}}$ obeys the Kolmogorov equation (Feller 1966)

$$\frac{d}{dt}[\underline{\underline{P}}(t)\;\theta(t)] = -\theta(t)\;\underline{\underline{P}}(t)\;\underline{\underline{R}}^T + \underline{\underline{I}}\delta(t) \tag{4.7}$$

where $\theta(t)$ is the unit step function. The Fourier transform of eqn. (4.4) may be rearranged to show that

$$\underline{\underline{\tilde{P}}}(\omega) = (\underline{\underline{R}}^T - i\omega\underline{\underline{I}})^{-1} = \underline{\underline{G}}^T \tag{4.7a}$$

where $\underline{\underline{\tilde{P}}}(\omega)$ is the FT of $\underline{\underline{P}}(t)\ \theta(t)$ and the superscript T indicates transposition. Hence using the usual definition of the diffusivity (Lax 1960) one has, assuming isotropy,

$$\tilde{D}(\omega) = \frac{\omega^2}{2}\int_0^\infty e^{-i\omega t} \langle\{x(t) - x(0)\}^2\rangle$$

$$= -\frac{\omega^2}{2}\sum_{ms} G_{ms}\, f_s^o\, (x_m - x_s)^2 \tag{4.8}$$

In this equation the initial sites s have been averaged over with a Boltzmann weighting factor $f_s^o = \xi \exp(-\varepsilon_s/k0)$ with ξ chosen so that $\sum_s f_s^o = 1$.

4c. Derivation of the Macroscopic Continuity Equation

Let us consider a particle created at time zero at site s. The microscopic continuity equation in $k\omega$-space reads

$$-i\omega\,\tilde{N}'(\underset{\sim}{k},\omega) = -i\underset{\sim}{k}\cdot\tilde{\underset{\sim}{J}}(\underset{\sim}{k},\omega) + e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}_s} \tag{4.9}$$

where $\tilde{N}'(\underset{\sim}{k},\omega)$ is the double FT of the microscopic number density $n(\underset{\sim}{r},t)$ and $\tilde{\underset{\sim}{J}}(\underset{\sim}{k},\omega)$ is the double FT of the microscopic number current density. In order to begin the derivation of the corresponding macroscopic equation, rewrite eqn (4.9) in the form

$$-i\omega\tilde{N}(\underset{\sim}{k},\omega) = -i\underset{\sim}{k}\cdot\tilde{\underset{\sim}{v}}(\underset{\sim}{k},\omega)\tilde{N}(\underset{\sim}{k},\omega) + e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}_s} \tag{4.10}$$

where

$$\tilde{\underset{\sim}{v}}(\underset{\sim}{k},\omega) \equiv \tilde{\underset{\sim}{J}}(\underset{\sim}{k},\omega)/\tilde{N}(\underset{\sim}{k},\omega)\ . \tag{4.11}$$

Then seek the Boltzmann configuration average of $-i\underset{\sim}{k}\cdot\underset{\sim}{\tilde{v}}(\underset{\sim}{k},\omega)$ up to terms quadratic in $\underset{\sim}{k}$ and linear in $\underset{\sim}{E}$. One sees from eqn (4.9) that, to this order, one may replace $\tilde{N}(\underset{\sim}{k},\omega)$ by $e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}_s}/(-i\omega)$ in eqn. (4.11). Moreover, to identify $\underset{\sim}{\tilde{J}}(\underset{\sim}{k},\omega)$ recall that $n(\underset{\sim}{r},t)$ is the sum of terms like $f_m\delta(\underset{\sim}{r}-\underset{\sim}{r}_m)$. Hence, using eqn. (4.4), one has

$$-i\omega\tilde{N}(\underset{\sim}{k},\omega) = \langle e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}|-i\omega\tilde{f}\rangle$$

$$= \langle e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}|-\underset{\approx}{R}|\tilde{f}\rangle + \langle e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}|\delta_s\rangle \quad .$$

This equation must be identical to eqn (4.9). Hence

$$-i\underset{\sim}{k}\cdot\underset{\sim}{\tilde{\chi}} = \langle e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}|-\underset{\approx}{R}|\tilde{f}\rangle$$

$$= \langle e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}|-\underset{\approx}{RG}|\delta_s\rangle$$

where we have substituted for $|\tilde{f}\rangle$ from eqn (4.5). When these two results are used in eqn (4.11) one has

$$i\underset{\sim}{k}\cdot\underset{\sim}{\tilde{v}}(\underset{\sim}{k},\omega) = -i\omega\ \langle e^{i\underset{\sim}{k}\cdot(\underset{\sim}{r}_s-\underset{\sim}{r})}|\underset{\approx}{RG}|\delta_s\rangle \qquad (4.12)$$

to second order in $\underset{\sim}{k}$. To keep the theory linear in $\underset{\sim}{E}$ write $\underset{\approx}{R} = \underset{\approx}{R}^o + \underset{\approx}{R}^1$, $\underset{\approx}{G} = \underset{\approx}{G}^o + \underset{\approx}{G}^1$ and $\underset{\sim}{\tilde{\chi}} = \underset{\sim}{\tilde{\chi}}^o + \underset{\sim}{\tilde{\chi}}^1$ where the superscript indicates the power of $\underset{\sim}{E}$ involved and powers higher than the first are ignored. Then eqn (4.9) gives

$$i\underset{\sim}{k}\cdot\underset{\sim}{\tilde{\chi}}^o(\underset{\sim}{k},\omega) = -i\omega\ \langle e^{i\underset{\sim}{k}\cdot(\underset{\sim}{r}_s-\underset{\sim}{r})}|\underset{\approx}{R}^o\underset{\approx}{G}^o|\delta_s\rangle\ ; \qquad (4.13)$$

$$i\underset{\sim}{k}\cdot\underset{\sim}{\chi}^1(\underset{\sim}{k},\omega) = -i\omega\ \langle e^{i\underset{\sim}{k}\cdot(\underset{\sim}{r}_s-\underset{\sim}{r})}|\underset{\approx}{R}^o\underset{\approx}{G}^1 + \underset{\approx}{R}^1\underset{\approx}{G}^o|\delta_s\rangle. \qquad (4.14)$$

It only remains to evaluate the configuration averages of these expressions

accurate to second order in $\underset{\sim}{k}$.

When the exponential in eqn (4.13) is expanded one has

$$i\underset{\sim}{k}\cdot\underset{\sim}{\chi}^{o}(\underset{\sim}{k},\omega) = -i\omega \langle 1|\underline{\underline{R}}^{o}\underline{\underline{G}}^{o}|\delta_s\rangle$$

$$-i\omega i\underset{\sim}{k}\cdot \langle \underset{\sim}{r}_s-\underset{\sim}{r}|\underline{\underline{R}}^{o}\underline{\underline{G}}^{o}|\delta_s\rangle$$

$$-i\omega \langle\{i\underset{\sim}{k}\cdot(\underset{\sim}{r}_s-\underset{\sim}{r})\}^2|\underline{\underline{R}}^{o}\underline{\underline{G}}^{o}|\delta_s\rangle \ . \qquad (4.15)$$

The first term on the right-hand side vanishes because (as is obvious from eqn (4.2)

$$\langle 1|\underline{\underline{R}} = 0 \qquad (4.16)$$

for all $\underset{\sim}{E}$, where $\langle 1|$ has all its elements equal to unity. To find the macroscopic values of the other two terms, weight them with a Boltzmann factor f_s^o. Then, employing eqn (4.6), one obtains from the second term on the right of eqn (4.15):

$$\sum_s f_s^o \langle \underset{\sim}{r}_s-\underset{\sim}{r}|\underline{\underline{I}} + i\omega\underline{\underline{G}}^{o}|\delta_s\rangle = 0 + \sum_{sm} G_{ms}^{o}\, f_s^{o}(\underset{\sim}{r}_s-\underset{\sim}{r}_m) \ , \qquad (4.17)$$

since the contribution from the unit matrix obviously vanishes. To evaluate the remaining term in eqn (4.17), write $\underline{\underline{F}}^{o}$ for a diagonal matrix whose mm^{th} element is f_m^o. Then it follows from eqn (4.3) that $\underline{\underline{R}}^{o}\underline{\underline{F}}^{o}$ and $(\underline{\underline{F}}^{o})^{-1}\underline{\underline{R}}^{o}$ are both symmetric matrices. Moreover from eqn (4.5)

$$\underline{\underline{I}} = \underline{\underline{G}}^{o}\underline{\underline{F}}^{o}\,[(\underline{\underline{F}}^{o})^{-1}\,\underline{\underline{R}}^{o} - i\omega(\underline{\underline{F}}^{o})^{-1}]$$

so that $\underline{\underline{G}}^{o}\underline{\underline{F}}^{o}$, being the inverse of a symmetric matrix, is itself symmetric. The summand in eqn (4.17) is therefore antisymmetric and the sum vanishes.

The Boltzmann average of the final term in eqn (4.15) gives

$$< i\underset{\sim}{k}\cdot\tilde{\underset{\sim}{\chi}}^{o}(\underset{\sim}{k},\omega) > = -i\omega \sum_s f_s^o <(i\underset{\sim}{k}\cdot(\underset{\sim}{r}_s-\underset{\sim}{r}))^2 |\underline{\underline{I}}|\delta_s>$$

$$-i\omega \sum_s f_s^o <(i\underset{\sim}{k}\cdot(\underset{\sim}{r}_s-\underset{\sim}{r}))^2 |i\omega \underline{\underline{G}}^o|\delta_s>$$

$$= -\sum_{\alpha\gamma} k^\alpha k^\gamma \frac{\omega^2}{2} \sum_{ms} (r_s^\alpha - r_m^\alpha)(r_s^\gamma - r_m^\gamma)\, G_{ms}^o f_s^o \qquad (4.18)$$

since the term involving the unit matrix obviously vanishes. In this equation α and γ label cartesian co-ordinate axes. The coefficient of $k^\alpha k^\gamma$ is a second-rank tensor property of the particular configuration of the random system which is being considered. It is supposed that the sum involved is self-averaging and is therefore equal to its configuration average. It is also supposed that the configuration-average yields an isotropic tensor whose identical diagonal elements we denote by $\tilde{D}(\omega)$ (cf eqn (4.8)). Then, omitting the configuration-average to save writing, one has from eqn (4.18)

$$<i\underset{\sim}{k}\cdot\tilde{\underset{\sim}{\chi}}^{o}(\underset{\sim}{k},\omega)> = \sum_{\alpha\gamma} k^\alpha k^\gamma \tilde{D}(\omega)\delta_{\alpha\gamma}$$

$$= -(i\underset{\sim}{k})^2 \tilde{D}(\omega) \qquad (4.19)$$

with $\tilde{D}(\omega)$ given by eqn (4.8). When this approximation to $i\underset{\sim}{k}\cdot\tilde{\underset{\sim}{\chi}}$ is substituted into eqn (4.10) one obtains the double FT of the diffusion term in eqn (1.31).

Let us turn now to the evaluation of $i\underset{\sim}{k}\cdot\tilde{\underset{\sim}{\chi}}^{1}(\underset{\sim}{k},\omega)$ in eqn (4.14). Writing $\underline{\underline{R}} \approx \underline{\underline{R}}^o + \underline{\underline{R}}^1$ in eqn (4.5) and expanding the exponential one obtains the familiar formula of first-order perturbation theory: $\underline{\underline{G}}^1 = -\underline{\underline{G}}^o\underline{\underline{R}}^1\underline{\underline{G}}^o$. When this result is substituted into eqn (4.14) one finds with the aid of eqn (4.6) that $i\underset{\sim}{k}\cdot\tilde{\underset{\sim}{\chi}}^{1}$ may be written in the more convenient form

$$i\underset{\sim}{k}\cdot\underset{\sim}{\chi}^{1}(\underset{\sim}{k},\omega) = \omega^2 \langle e^{i\underset{\sim}{k}\cdot(\underset{\sim}{r}_s-\underset{\sim}{r})}|\underline{\underline{G}}^{o}\underline{\underline{R}}^{1}\underline{\underline{G}}^{o}|\delta_s\rangle$$

$$= \omega^2 \langle 1|\underline{\underline{G}}^{o}\underline{\underline{R}}^{1}\underline{\underline{G}}^{o}|\delta_s\rangle + \omega^2 i\underset{\sim}{k}\cdot\langle \underset{\sim}{r}_s-\underset{\sim}{r}|\underline{\underline{G}}^{o}\underline{\underline{R}}^{1}\underline{\underline{G}}^{o}|\delta_s\rangle \qquad (4.20)$$

where I have ignored terms of negligible order. By setting $\underset{\sim}{k} = 0$ in eqn (4.20) one sees that the 1^{st} term on the right-hand side vanishes. A direct algebraic derivation of this result is easily made. Note first of all that eqn (4.2) implies that $\langle 1|\underline{\underline{R}}^{o} = \langle 1|\underline{\underline{R}}^{1} = 0$. Hence from eqn (4.6), $\langle 1|(\underline{\underline{I}} + i\omega\underline{\underline{G}}^{o}) = 0$ which allows us to replace $\langle 1|\underline{\underline{G}}^{o}$ in eqn (4.20) by $(-i\omega)^{-1}\langle 1|$ and the result follows.

To deal with the second term on the right of eqn (4.20), write

$$\underline{\underline{R}}^{1} = \underline{\underline{R}}^{1+} + \underline{\underline{R}}^{1-} \qquad (4.21)$$

where

$$(\underline{\underline{R}}^{1+})_{mn} = \delta_{mn}\sum_{p} W^{1}_{mp} - \tfrac{1}{2}(W^{1}_{nm} + e^{\beta(\epsilon_n-\epsilon_m)}W^{1}_{mn}) , \qquad (4.22a)$$

$$(\underline{\underline{R}}^{1-})_{mn} = -\tfrac{1}{2}(W^{1}_{nm} - e^{\beta(\epsilon_n-\epsilon_m)}W^{1}_{mn}) . \qquad (4.22b)$$

W^{1}_{mn} is the term in the transition rate W_{mn} which is linear in $\underset{\sim}{E}$ and $\beta = (k\Theta)^{-1}$. Let us first show that the contribution due to $\underline{\underline{R}}^{1+}$ vanishes. It has been noted that the matrices $\underline{\underline{R}}^{o}\underline{\underline{F}}^{o}$ and $\underline{\underline{G}}^{o}\underline{\underline{F}}^{o}$ are symmetric. It follows from eqn (4.22a) that $\underline{\underline{R}}^{1+}\underline{\underline{F}}^{o}$ is also symmetric. The contribution to the system average of $\underline{\underline{R}}^{1+}$ to the term on the right of eqn (4.20) is

$$i\underset{\sim}{k}\cdot\underset{\sim}{\chi}^{1+} = \sum_{ms} \omega^2(\underset{\sim}{r}_m-\underset{\sim}{r}_s)\left[\underline{\underline{G}}^{o}\underline{\underline{R}}^{1+}\underline{\underline{G}}^{o}\underline{\underline{F}}^{o}\right]_{ms} , \qquad (4.23)$$

The transpose of the matrix in square brackets is

$$\left[\underline{\underline{G}}^{o}\underline{\underline{R}}^{1+}\underline{\underline{G}}^{o}\underline{\underline{F}}^{o}\right]^{T} = \underline{\underline{F}}^{oT}\underline{\underline{G}}^{oT}(\underline{\underline{R}}^{1+})^{T}\underline{\underline{G}}^{oT}$$

$$= \underline{\underline{G}}^{o}\underline{\underline{F}}^{o}(\underline{\underline{R}}^{1+})^{T}\underline{\underline{G}}^{oT}$$

$$= \underline{\underline{G}}^{o}\underline{\underline{R}}^{1+}\underline{\underline{F}}^{o}\underline{\underline{G}}^{oT}$$

$$= \underline{\underline{G}}^{o}\underline{\underline{R}}^{1+}\underline{\underline{G}}^{o}\underline{\underline{F}}^{o}$$

since $\underline{\underline{F}}^{o}$ is diagonal. The matrix in square brackets is therefore symmetric so that the sum in eqn (4.23) vanishes. Now, the contribution of $\underline{\underline{R}}^{1-}$ is considered. The decomposition of eqn (4.21) was motivated by the detailed balance relation (4.3) which, when linearised in $\underset{\sim}{E}$, gives the symmetry relations

$$W^{o}_{mn}\, e^{\beta(\varepsilon_m-\varepsilon_n)} = W^{o}_{nm} \quad ,$$

$$e^{-\varepsilon_m}\left[W^{1}_{mn} - e\beta\underset{\sim}{E}\cdot\underset{\sim}{r}_m\, W^{o}_{mn}\right]$$

$$= e^{-\varepsilon_n}\left[W^{1}_{nm} - e\beta\underset{\sim}{E}\cdot\underset{\sim}{r}_n\, W^{o}_{nm}\right]$$

Hence one sees from eqn (4.22b) that

$$R^{1}_{mn} = -\tfrac{1}{2}\, e\beta\, W^{o}_{nm}\, \underset{\sim}{E}\cdot(\underset{\sim}{r}_m-\underset{\sim}{r}_n)$$

$$= -\tfrac{1}{2}\, e\beta\, R^{o}_{mn}\, \underset{\sim}{E}\cdot(\underset{\sim}{r}_m-\underset{\sim}{r}_n) \quad .$$

Therefore

$$(\underline{\underline{G}}^{o}\underline{\underline{R}}^{1-}\underline{\underline{G}}^{o})_{ms} = \tfrac{1}{2}\, e\beta\underset{\sim}{E}\cdot\sum_{pq} G^{o}_{mp}\, R^{o}_{pq}\, (\underset{\sim}{r}_q-\underset{\sim}{r}_p)G^{o}_{qs}$$

$$= \tfrac{1}{2}\, e\beta\underset{\sim}{E}\cdot\{\sum_{q}\underset{\sim}{r}_q\, G^{o}_{qs}\sum_{p} G^{o}_{mp}\, R^{o}_{pq}$$

$$- \sum_{p}\underset{\sim}{r}_p\, G^{o}_{mp}\sum_{q} R^{o}_{pq}\, G^{o}_{qs}\}$$

$$= \tfrac{1}{2}\, e\beta\underset{\sim}{E}\cdot\{\sum_{q}\underset{\sim}{r}_q\, G^{o}_{qs}(\delta_{mq} + i\omega G^{o}_{mq})$$

$$- \sum_{p}\underset{\sim}{r}_p\, G^{o}_{mp}(\delta_{ps} + i\omega G^{o}_{ps})\}$$

where eqn (4.6) in zeroth order has been used. By replacing p with q in the second summation we see that the terms quadratic in $\underline{\underline{G}}^o$ cancel leaving the simple result

$$(\underline{\underline{G}}^o \underline{\underline{R}}^{1-} \underline{\underline{G}}^o)_{ms} = \tfrac{1}{2}\, e\beta\, G^o_{ms}\, \underset{\sim}{E}\cdot(\underset{\sim}{r}_m - \underset{\sim}{r}_s). \tag{4.25}$$

To complete the calculation of $i\underset{\sim}{k}\cdot\tilde{\underset{\sim}{\chi}}^1$ we substitute eqn (4.25) into the second term on the right of eqn (4.20), Boltzmann-average over site s and employ similar arguments as those used to derive eqn (4.19) from eqn (4.18). Thus one finds that

$$i\underset{\sim}{k}\cdot\tilde{\underset{\sim}{\chi}}^1(\underset{\sim}{k},\omega) = i \sum_{\alpha\gamma} k^\alpha E^\gamma \frac{\omega^2}{2} \sum_{ms} (r_m^\alpha - r_s^\alpha)(r_m^\gamma - r_s^\gamma) G^o_{ms}\, f^o_s$$

$$= - i\underset{\sim}{k}\cdot\underset{\sim}{E}\, e\beta\, \tilde{D}(\omega)\ , \tag{4.26}$$

with $\tilde{D}(\omega)$ given by eqn (4.8). Substitution of eqn (4.26) together with eqn (4.19) into eqn (4.10) gives the double FT of the drift term in eqn (1.31). The Einstein relation

$$\tilde{\mu}(\omega) = e\beta\tilde{D}(\omega) \tag{4.27}$$

is thus justified, in contrast to the assertion of Schmidlin (1980) mentioned in section 3d.

4d. The Case of Carriers Not in Thermal Equilibrium

It has hitherto been assumed that the carriers instantaneously thermalise among the available sites. While this is true if the sites are isoenergetic it will not initially be the case in general. It may be that the assumption made in §4a that the carriers thermalise well before reaching the end of the semiconductor is not valid, as suggested by Schmidlin (1980). It is now shown that, be there thermalization or no, an MPPE like eqn (1.31) is still valid and a pseudo-Einstein relation may be constructed. It is seen from equns (4.7a) and (4.8) that

$$\tilde{D}(\omega) = -\frac{\omega^2}{2}\int_0^\infty dt\, e^{i\omega t} \sum_{ms} f_s^o\, P_{sm}(t)(x_m - x_s)^2. \tag{4.28}$$

If the carriers are out of thermal equilibrium a non-equilibrium diffusivity may be defined by

$$\tilde{D}^{NE}(\omega) \equiv -\frac{\omega^2}{2}\int_0^\infty dt\, e^{i\omega t} \sum_{ms} f_s(t)\, P_{sm}(t)(x_m - x_s)^2$$

$$= -\frac{\omega^2}{2}\sum_{ms} \tilde{f}_s(\omega) * G_{ms}(\omega)(x_m - x_s)^2 \tag{4.29}$$

where the symbol * means "convolution", in this case in ω-space, and

$$\lim_{t \to \infty} f_s(t) = f_s^o \tag{4.30}$$

For dilute pulses it is to be expected that the transition rates W_{mn} depend only on the semiconducting medium, not on the charge carriers themselves. Eqns (4.9) to (4.18) inclusive are thus valid except that in the last line of eqn (4.18) $G_{ms}^o(\omega)\, f_s^o$ is replaced by $G_{ms}^o(\omega) * \tilde{f}_s(\omega)$ so that in eqn (4.19) $\tilde{D}(\omega)$ is replaced by $\tilde{D}^{NE}(\omega)$. Furthermore eqns (4.20)

to (4.22b) are unaffected. Eqn (4.23) is no longer vanishing. Instead, let $\underline{\underline{R}}^{+} = \underline{\underline{R}}^{o} + \underline{\underline{R}}^{1+}$ and $\underline{\underline{G}}^{+} = (\underline{\underline{R}}^{+} - i\omega\underline{\underline{I}})^{-1}$. Then eqn (4.20) becomes

$$i\underset{\sim}{k}.\underset{\sim}{\chi}^{1}(\underset{\sim}{k},\omega) = \omega^{2} i\underset{\sim}{k}.\langle \underset{\sim}{r}_{s} - \underset{\sim}{r} | \underline{\underline{G}}^{+}\underline{\underline{R}}^{1-}\underline{\underline{G}}^{+} | \delta_{s} \rangle$$

$$= \omega^{2} i\underset{\sim}{k}.\langle \underset{\sim}{r}_{s} - \underset{\sim}{r} | \underline{\underline{G}}^{o}\underline{\underline{R}}^{1-}\underline{\underline{G}}^{o} | \delta_{s} \rangle + O(kE^{2}) \quad . \tag{4.31}$$

The terms of $O(kE^{2})$ are neglected. Thus only the contribution of $\underline{\underline{R}}^{1-}$ to eqn (4.20) is of appreciable order, and the calculation may be resumed without further worry about $\underline{\underline{R}}^{1+}$. Eqn (4.25) is still valid. In eqn (4.26) $G^{o}_{ms}(\omega)\, f^{o}_{s}$ is replaced by $G^{o}_{ms}(\omega) * \tilde{f}_{s}(\omega)$ so that $\tilde{D}(\omega)$ is replaced by $\tilde{D}^{NE}(\omega)$. Eqn (4.27) therefore generalises to the pseudo-Einstein relation

$$\tilde{\mu}^{NE}(\omega) = e\beta\, \tilde{D}^{NE}(\omega) \quad , \tag{4.32}$$

as mentioned in §3d.

4e. Discussion of the Macroscopic Pulse Propagation Equation

This equation for hopping carriers reads

$$\frac{\partial n(\underset{\sim}{r},t)}{\partial t} = \left[\frac{e\underset{\sim}{E}.\underset{\sim}{\nabla}}{k\Theta} + \nabla^{2}\right]\int_{-\infty}^{\infty} D^{NE}(t-\tau)\, n(\underset{\sim}{r},\tau)\, d\tau$$

$$+ \delta(\underset{\sim}{r}-\underset{\sim}{r}_{s})\delta(t) \quad . \tag{4.33}$$

Eqn (4.33) is of the MPPE form (1.31) as well as the already-mentioned eqn (3.5) of trap-controlled transport. The universality of the MPPE first suggested by Butcher (1978) is thus established in contrast to the claim of Schmidlin (1980) that there is no universal MPPE. Of course, the physical interpretation of D(t) varies from mechanism to mechanism.

Henceforth it is assumed that the hopping carriers are in thermal equilibrium and obey Boltzmann statistics. The superscript "NE" in eqn (4.33) may now be dropped. $\tilde{D}(\omega)$ and $\tilde{\mu}(\omega)$ are genuine ac diffusivity and mobility respectively. Furthermore $\tilde{D}(\omega)$ is related to a directly measurable quantity, the ac conductivity

$$\sigma(\omega) = \frac{ne^2}{k\Theta} \tilde{D}(\omega) \tag{4.34}$$

where n is the equilibrium carrier density. Eqns (4.33) and (4.34) together provide a conceptually simple test of whether steady-state hopping is the ACPP transport mechanism in a given material. In the next two chapters the appropriate theory is developed. The available data on amorphous selenium and amorphous arsenic triselenide do not lend support to such a conclusion, as will be demonstrated. However, new data on a doped organic polymer does suggest hopping ACPP.

Chapter 5:

Pulse Propagation Governed by Power-law Conductivity

5a. Introduction

An ac mobility commonly found in hopping transport (see for example Lakatos and Abkowitz 1971 or Mott and Davis 1979, p.229),

$$\tilde{\mu}(\omega) = \mu_1(-i\omega\tau_o)^{1-\alpha} \tag{5.1}$$

is inserted into the MPPE, eqn (1.31) and the properties of the resulting pulse are investigated. To keep $\mu(t-\tau)$ real (therefore $\tilde{\mu}(\omega) = \tilde{\mu}(-\omega)^*$) and $\tilde{\mu}(\omega)$ single-valued, a branch cut is introduced along the negative imaginary ω-axis. α is assumed to take a value in the open interval (0, 1). Pulse shapes $n(x,t)$ and transient currents flowing through the specimen are calculated for various values of α. Both pure drift and pure diffusion are considered: the question of the relative importance of these two effects in experiments on ACPP is asked - it is concluded that if hopping were the transport mechanism diffusion would be negligible. However once the pulse-shapes for pure drift have been computed, those for pure diffusion may be obtained with very little extra labour. They are therefore included for the sake of generality. It will transpire that in the former case x and t only enter into $n(x,t)$ in the combination x/t^{α} apart from a prefactor $t^{-\alpha}$ to keep $n(x,t)$ normalized and in the latter case x and t will only appear in $n(x,t)$ in the combination $|x|/t^{\frac{1}{2}\alpha}$ apart from a normalizing prefactor $t^{-\frac{1}{2}\alpha}$. Hence in the pure drift case both the mean position of the pulse (the shift) and the rms standard deviation from the mean (the spread)

are proportional to t^{α}. The requirement of Scher and Montroll (1975), known as universality, that these two quantities have a time-independent ratio is therefore automatically satisfied.

The classic salient features of ACPP are reproduced qualitatively. But quantitatively ac conductivity and ACPP measurements in a-As_2Se_3 fail to show the expected agreement leading one to believe that hopping is not the ACPP mechanism in this material.

5b. Calculation of Pulse-Shapes

It is supposed in what follows that $\underset{\sim}{E} = (-E, 0, 0)$ and that a sheet of electrons having uniform density n_o per unit area is injected onto the plane $x = 0$ at time $t = 0$. Then one may replace $\underset{\sim}{r}$ by x, $\underset{\sim}{k}$ by k_x with the x-subscript dropped and $\underset{\sim}{E}$ by -E in the MPPE and its Fourier transforms in $\underset{\sim}{r}\omega$- and $\underset{\sim}{k}\omega$-space. The latter transform becomes

$$-i\omega \tilde{N}(k,\omega) = - \tilde{\mu}(\omega)E\, ik\, \tilde{N}(k,\omega) + n_o \qquad (5.2)$$

in the pure drift case and

$$-i\omega \tilde{N}(k,\omega) = (ik)^2 \tilde{D}(\omega)\, \tilde{N}(k,\omega) + n_o \qquad (5.3)$$

in that of pure diffusion from eqns (4.9) then (4.26) and (4.19) respectively. Rearrangement of eqn (5.2) and transformation into $\underset{\sim}{r}\omega$-space yields

$$\tilde{n}(x,\omega) = \frac{n_o\, 0(x)\, \exp(+i\omega x/\tilde{\mu}(\omega)E)}{\tilde{\mu}(\omega)E} \qquad (5.4)$$

The resulting Fourier integral for n(x,t) may be put into a convenient form by introducing the integration variable $u = - i\omega t$ and the reduced variables: $X = x/L_1$, $T = t/\tau_o$ and $s = X/T^{\alpha}$ where $L_1 = \mu_1 E \tau_o$ is a characteristic length.

Thus one finds that

$$n(x,t) = \frac{n_o\,\theta(X)}{L_1 T^{\alpha}}\, f_{\alpha}(s) \qquad (5.5)$$

where

$$f_{\alpha}(s) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} du\; u^{\alpha-1}\exp(u-su^{\alpha}) \qquad (5.6)$$

with a > 0 so that the integral is along a vertical line in the right-hand u-plane. Since n(x,t) is normalised to n_o, it is immediately seen from eqn (5.5) that $f_{\alpha}(s)$ is normalised to unity.

The pure diffusion case is similarly treated to yield

$$n(x,t) = \frac{n_o}{2L'T^{\frac{1}{2}\alpha}}\; f_{\frac{1}{2}\alpha}\,(|s'|) \qquad (5.7)$$

where $s' = X'/T^{\alpha/2}$ with $X' = x/L'$ where $L' = (D_1\tau_o)^{\frac{1}{2}}$ with $\mu_1 = eD_1/k\Theta$ as the characteristic length for pure diffusion. Thus, the solution of the pure diffusion problem for a particular value of α is simply a symmetrised and scaled version of the pure drift problem with α replaced by $\alpha/2$. Attention is therefore now confined largely to the pure drift problem. It remains to evaluate $f_{\alpha}(s)$. In principle one could re-express eqn (5.6) as an integral with a real integrand along the real axis and evaluate this on the computer, but in practice greater accuracy and reliability are achieved by the following method, applicable when $\alpha = k/m$ where k and m are integers. Then for X > 0 we readily find that

$$\frac{\partial^k n}{\partial T^k} = (-1)^m \frac{\partial^m n}{\partial X^m} \quad . \qquad (5.8)$$

This partial differential equation for n is most easily obtained by manipulating the equation

$$-i\omega\tilde{n}(x,\omega) = -E\tilde{\mu}(\omega)\,\frac{\partial\tilde{n}(x,\omega)}{\partial x} \quad , \tag{5.9}$$

which is eqn (5.2) transformed into $x\omega$-space with the delta function omitted, into a form which may be recognised as the Fourier transform of eqn (5.8). Fortunately, it is easy to solve this partial differential equation: merely substitute for n from eqn (5.5) and an ordinary differential equation for $f_\alpha(s)$ is obtained. Let us consider for example the case $\alpha = \frac{1}{2}$. Then $k = 1$, $m = 2$, eqn (8) reduces to the diffusion equation and the ordinary differential equation for $f_{\frac{1}{2}}(s)$ is

$$f_{\frac{1}{2}}(s) + sf'_{\frac{1}{2}}(s) = -2f''_{\frac{1}{2}}(s) \quad . \tag{5.10}$$

Eqn (5.10) may be solved analytically. The corresponding equation for more general rational values of α must, however, be solved numerically. The method of Merson (1957), a Runge-Kutta method giving an error estimate, is used here to integrate in towards the origin from large values of s. The boundary conditions required to start the integration are obtained from the aysmptotic formula for $f_\alpha(s)$:

$$f_\alpha(s) = \frac{1}{2\pi i}\int_C dz\, \exp(z^{1/\alpha} - sz)$$

$$\sim \frac{(\alpha s)^{\frac{2\alpha-1}{2-2\alpha}}}{\sqrt{2\pi(1-\alpha)}}\, \exp\left[-\left(\frac{1}{\alpha}-1\right)(\alpha s)^{\frac{1}{1-\alpha}}\right] \quad . \tag{5.11}$$

The contour C lies in the right-hand z-plane, passes through the saddle point on the real axis and avoids all the others. The second line of eqn (11) follows when the method of steepest descents (e.g. Matthews and Walker 1965, p. 78) is used to evaluate the integral. It is differentiated as many times as is necessary to obtain sufficient boundary conditions to start the integration at a value of s which is large enough to give 99%

accuracy. The numerical method was easily capable of such accuracy. A test of the accuracy of the solution is provided by checking that $f_\alpha(s)$ is normalised to unity over the range $s > 0$.

In the special case $\alpha = \frac{1}{2}$ eqn (11) is exact and yields

$$n(x,t) = \frac{\theta(X)}{L(\pi T)^{\frac{1}{2}}} \exp\left[-\frac{X^2}{4T}\right] . \qquad (5.12)$$

This "half-gaussian" pulse has a peak which remains at the origin and it expands with an effective diffusion constant L^2/τ_o. This pulse is shown in fig. 5.1. Note the similarity of this pulse to eqn (2.53), calculated by Leal Ferreira (1977) using continuous-time random walk theory. Another simple case is $\alpha = 1/1$ for which one finds the conventional result

$$n(x,t) = \frac{n_o}{LT}\,\delta\left(\frac{X}{T} - 1\right) = n_o\delta(x-\mu_1 Et) . \qquad (5.13)$$

Thus the injected delta-function propagates without spreading, with the carrier drift velocity. The peak of the pulse moves away from the origin and is located at $X = T$, i.e. at $s = 1$.

Other cases were investigated numerically: the results are shown in fig. 5.2. There is a qualitative difference between the results for $\alpha \leq \frac{1}{2}$ and for $\alpha > \frac{1}{2}$. In the former case the peak of the pulse is located at the origin of s and does not move in x-space. But when $\alpha > \frac{1}{2}$ the peak of the pulse is located at a non-zero value of s which implies that the peak propagates in x-space. As $\alpha \to 1$ the peak approaches the point $s = 1$ corresponding to propagation with the carrier drift velocity. But note from fig. 5.2 that the peak moves above $s = 1$ for $\alpha = 3/4$ and 7/8 and approaches $s = 1$ from <u>above</u> as α increases still further. This behaviour is not altogether unexpected. It is easy to show that the mean value of

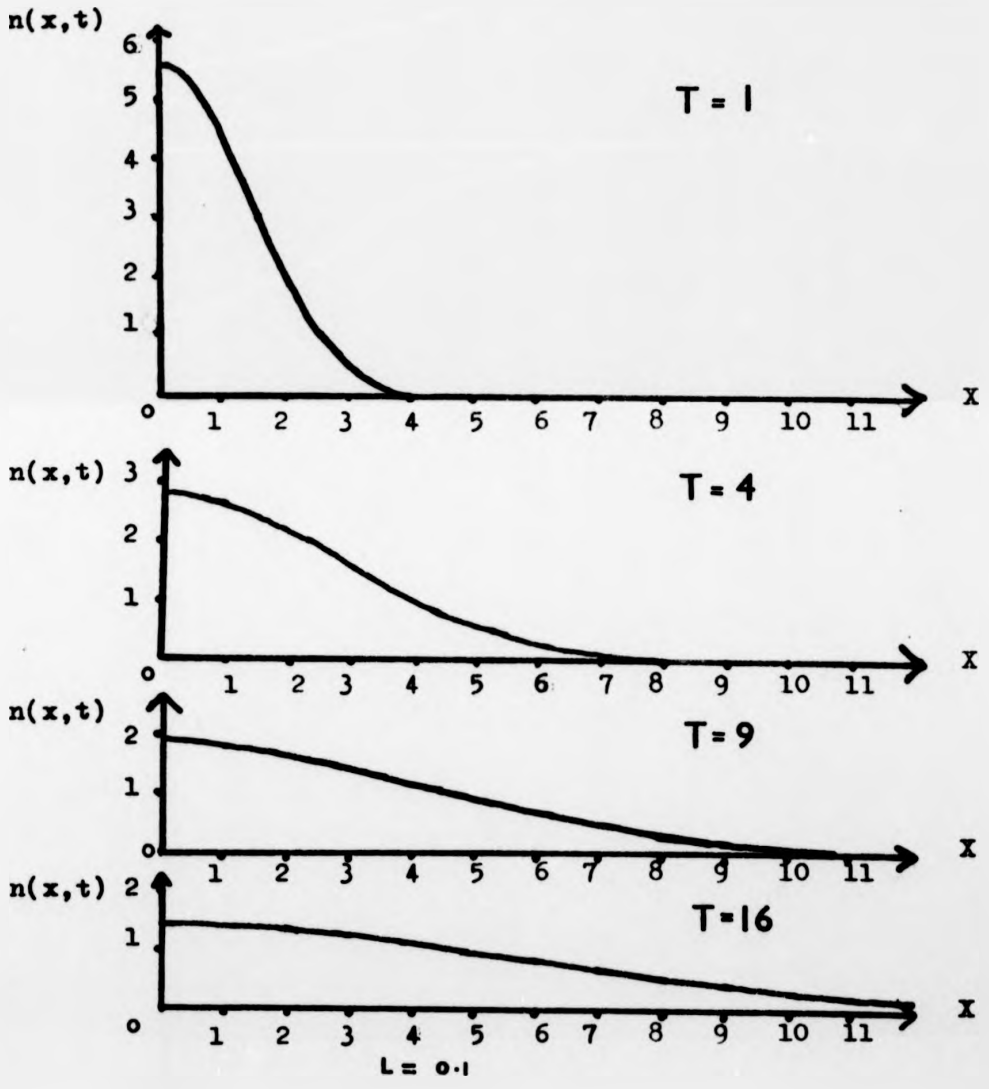


Figure 5.1: Anomalous carrier pulse propagation: The pulse shape when $\alpha = \frac{1}{4}$, eqn (5.12). Pure drift.

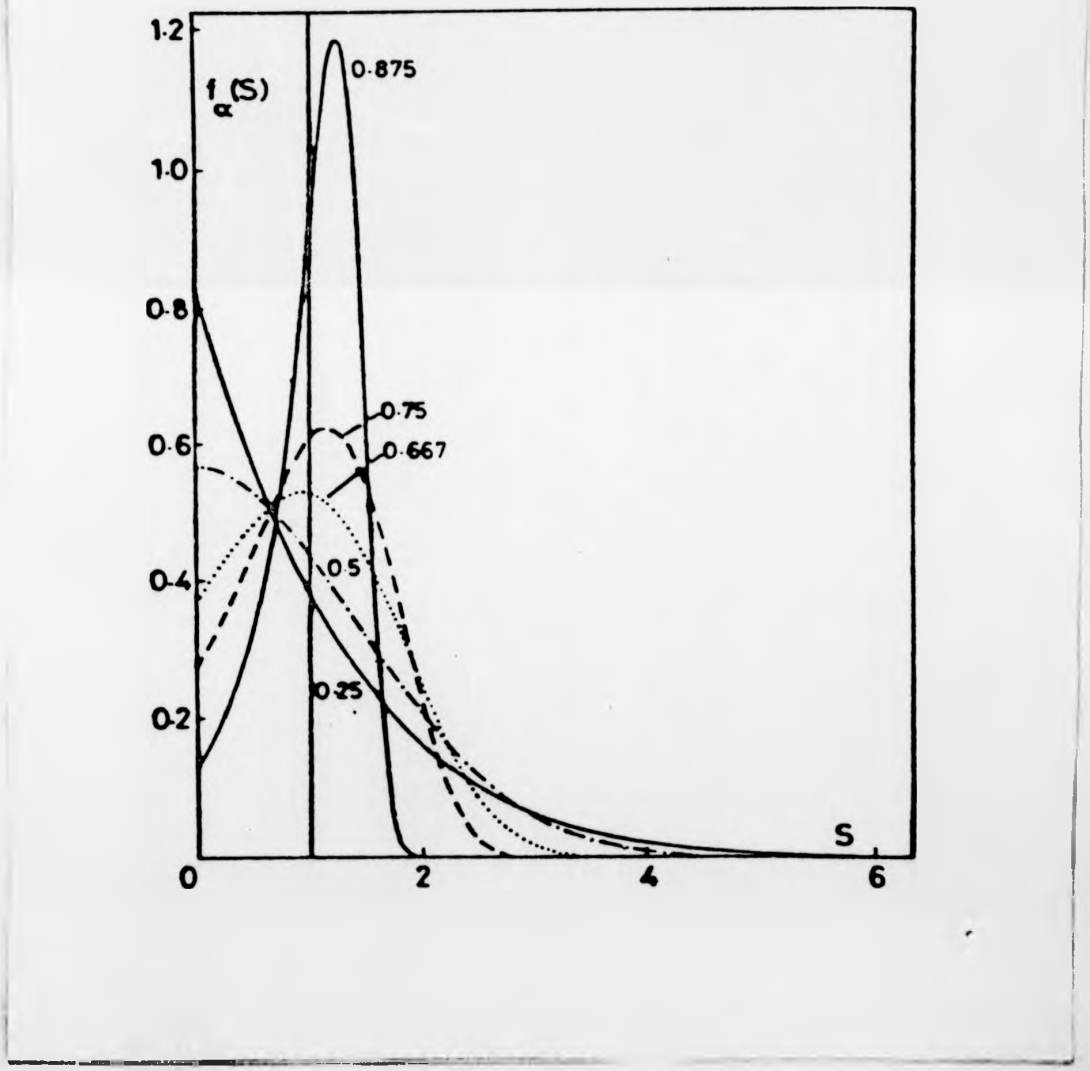


Figure 5.2: Pulse shapes for various (shown) values of α: $f_\alpha(s)$ is plotted against s. The vertical line represents the delta function, eqn (5.13), when $\alpha = 1$. (From Butcher and Clark 1980a).

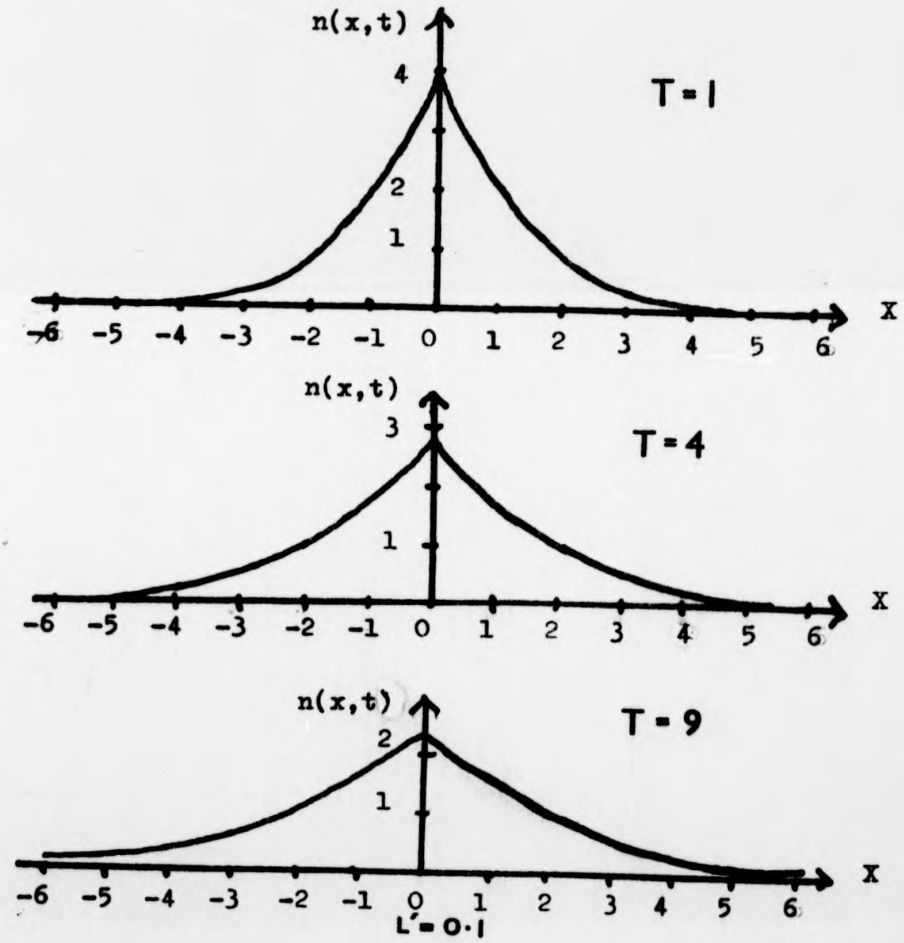


Figure 5.3: Pulse shape for pure diffusion when $\alpha = \frac{1}{4}$.

s behaves in qualitatively the same way. Use of eqns (5.1), (A4) and (A10), Appendix A, yields

$$\langle x(t)\rangle_{dr} = E\mu_1\tau_o \frac{T^\alpha}{\Gamma(1+\alpha)}$$

whence

$$\langle s\rangle_{dr} = \frac{1}{\Gamma(1+\alpha)} \quad . \tag{5.14}$$

It is readily found from a table of gamma functions that $\langle s\rangle_{dr} = 1$ when $\alpha = 0$ and 1. Otherwise $\langle s\rangle_{dr} > 1$, rising to a peak value of 1.13 when $\alpha = 0.46$.

The spread of the pulses is now computed. Use is made of eqns (5.1), (A6), (A4), (A3) and (A10) to give

$$\sigma_{dr}(t) = L_1 T^\alpha \left[\frac{1}{\Gamma(1+2\alpha)} - \frac{1}{\Gamma^2(1+\alpha)}\right]^{\frac{1}{2}} \quad . \tag{5.15}$$

Shlesinger (1977) shows that the quantity in square brackets is always positive. The time-independent ratio of shift (5.14) and spread (5.15), mentioned above, are returned to in the next section after consideration of the pure diffusion process.

This of course occurs when E = 0. The pulse-shape, as mentioned earlier, is obtained by symmetrising and scaling the pure drift result when α is halved. The evolution in time of such a pulse, for $\alpha = \frac{1}{2}$, is shown in figure (5.3). The conventional case arises when $\alpha = 1$. One finds the well-known result

$$n(x,t) = \frac{n_o}{L'(4\pi T)^{\frac{1}{2}}} \exp(-X'^2/4T) \quad . \tag{5.16}$$

The pulse-shape is gaussian and, in particular, is flat at x = 0. When $\alpha < 1$ the pulse has a cusp at the spatial origin (cf figs (5.2) and (5.3)). There is nothing fundamental about this cusp - a more sophisticated model

would not predict it. Use of the ac Einstein relation, eqn (4.27) and eqns (5.1), (A8), (A9) and (A10) yield a variance in s' of

$$\langle s'^2 \rangle_{dif} = \langle x'^2 \rangle_{dif} T^{-\alpha} = \frac{2}{\Gamma(1+\alpha)} \quad . \tag{5.17}$$

The pulse-shapes derived in this section are also valid for trap-controlled band transport if in eqn (3.6) $\tilde{Q}(\omega) = A(-i\omega\tau_o)^{1-\alpha}$ where A is a constant, with a suitable interpretation of τ_o. $n(x,t)$ is the concentration of free carriers plus carriers in traps.

5c. The total current density in the pure drift case

Consider a sample of length ℓ which is driven by a constant-voltage source. Then the total current density is given by the well-known formula (see for example, Scher 1976), derived in Appendix G,

$$I(t) = -\frac{e}{\ell}\int_o^{\ell} J_x(x,t)dx = -\frac{e}{\ell}\frac{d\langle x\rangle}{dt}$$

$$= -\frac{eE}{2\pi\ell}\int_o^{\ell} dx \int_{i\Omega-\infty}^{i\Omega+\infty} d\omega\, \tilde{\mu}_1(\omega)\, \tilde{n}(x,\omega)e^{-i\omega t} \quad . \tag{5.18}$$

The far right-hand side of the first line of eqn (5.18) follows from the equation (1.22) of continuity. The contribution of the diffusion term in the MPPE eqn (1.31) is neglected. In the second line of eqn (5.18), the pure drift contribution to $J_x(x,t)$ has been expressed as a Fourier integral. When $\tilde{n}(x,\omega)$ is calculated from eqn (5.4) and substituted into eqn (5.18) the x-integration may be carried out immediately to yield

$$I(t) = \frac{n_o eL}{2\pi i\tau_o \ell}\int_{a-i\infty}^{a+i\infty} du\, e^{uT}\left\{\exp\left[\frac{-u^{\alpha}\ell}{L_1}\right] - 1\right\} u^{-\alpha}du \quad . \tag{5.19}$$

in which $u = -i\omega\tau_o$.

At short times I(t) may be calculated by letting $\ell \to \infty$ in the integrand of eqn (5.19) because a negligible number of carriers will have reached the end of the specimen. This approach yields

$$I(t) = \frac{-n_o e \ell}{\tau_o \ell \Gamma(\alpha)} \; T^{\alpha-1} \quad . \tag{5.20}$$

A negative sign appears in this equation because we have considered electrons moving in the positive x-direction. For large times one might consider small ℓ in the integrand of eqn (5.19) and expand the exponential. However this leads to a divergent integral: a different approach is needed. Leal Ferreira (1977) provides one. He shows that

$$I(t) = - e \frac{d}{dt} \left[- \int_o^\ell n(x,t)dx + \frac{1}{\ell} \int_o^\ell xn(x,t)dx \right] \quad . \tag{5.21}$$

See Appendix G, eqn (G6). In deriving this equation, note has been taken of the unit step function in eqn (5.5) which implies that no carriers move out of the sample across the boundary located at x = 0. When t is sufficiently large the variation of n(x,t) across the specimen becomes negligible; one may write

$$n(x,t) = n(0,t) = n_o / L_1 \Gamma(1-\alpha) T^\alpha \tag{5.22}$$

using eqn (5.6). Substitution of eqn (5.22) into eqn (5.21) yields

$$I(t) \sim \frac{-n_o e \ell \alpha}{2 L_1 \Gamma(1-\alpha) \tau_o} \; T^{-(1+\alpha)} \tag{5.23}$$

The transit time T_1 in reduced units may be defined by equating the formulae for I(t) given in eqns (5.20) and (5.23). Thus one obtains

$$T_1 = (\ell/E)^{1/\alpha} \left[\alpha \Gamma(\alpha) / 2 (\mu_1 \tau_o)^2 \Gamma(1-\alpha) \right]^{1/2\alpha} \quad . \tag{5.24}$$

Eqns (5.20), (5.23) and (5.24) reproduce the classic salient features, eqn (1.30), of ACPP. However it is shown in §5d that despite this qualitative reproduction of eqn (1.30), there is a serious quantitative discrepancy between the ACPP measurements and ac conductivity measurements in a-As_2Se_3. (The same applies to a-Se but discussion of this is deferred to the next chapter). In analysing the experimental data, diffusion has been neglected. Is this neglect justifiable? To answer this question, comparison is made of eqns (5.15) and (5.17) at experimentally realistic values of the parameters. It is found that

$$\frac{\sigma_{dr}^2}{\sigma_{dif}^2} \sim \frac{L_1^2 T^{2\alpha}}{L^{-2} T^{\alpha}} \sim \frac{eE\, L_1}{k\Theta}\, T^{\alpha} \quad . \tag{5.25}$$

Use may be made of the Einstein relation (4.27) and eqn (5.24) for the reduced transit time T_1 which is substituted into eqn (5.25) to yield

$$\frac{\sigma_{dr}^2}{\sigma_{dif}^2} \sim \frac{eE\ell}{k\Theta} \quad . \tag{5.26}$$

Every quantity in this equation may be measured directly. ℓ, Θ and E are obtained from figs. 2c and 2d of Pfister and Scher (1978): typically $\ell \sim 100\ \mu m$, $E \sim 10\ V\ \mu m^{-1}$ and $\Theta \sim 100$ K in chalcogenide glasses. Then $\sigma_{dr}^2/\sigma_{dif}^2 \sim 10^5$ in experimentally realistic situations: diffusion may indeed be neglected. Furthermore, the time-dependence of eqn (5.25) is such that diffusion becomes steadily less important as the pulse evolves in time.

The identity of current-α and conductivity-α in a hopping system was first noticed by Scher (1976), who finds that (in terms of the SLM* theory) they both arise from a waiting-time distribution $\psi(t) \sim t^{-(1+\alpha)}$. However, Scher does not use this identity to simplify his rather complicated calculations in the manner outlined in this and the previous chapter. But he does point out that despite the intimate theoretical connection

* SLM = Scher-Lax-Montroll, as in Chapter 2.

between ac conductivity and ACPP for hopping systems no correlation has been established experimentally between these two phenomena in the same material. This is consistent with considerations made in §5d and chapter 6 of chalcogenide glasses.

This section is concluded with a final comment on universality. It was mentioned in §1. that in ACPP the current density displays the property

$$\frac{I(t)}{I(t_1)} = g(t/t_1) \tag{5.27}$$

where t_1 is the transit time. g is a function of t/t_1. It may be any well-behaved function of this quantity. The choice of t_1 is actually arbitrary. It follows that

$$\ell nI(t) - \ell nI(t_1) = \ell ng(t/t_1) \equiv h(t/t_1) \tag{5.28}$$

where the definition of $h(t/t_1)$ is obvious by inspection. Hence, taking the time derivative,

$$\frac{I'(t)}{I(t)} = \frac{1}{t_1} h'(t/t_1) = \frac{1}{t} h'(1) \tag{5.29}$$

since the left hand side of eqn (5.29) only depends upon t, allowing one to forget the physical origin of t_1 and set it equal to t. Therefore

$$I(t) = A\, t^{h'(1)} \tag{5.30}$$

where A is an arbitrary constant, $h'(1)$ is obviously a constant. The requirement of universality thus implies a power law form for I(t). This result still holds if $I'(t)$ has a discontinuity at $t = t_1$; $I(t) \propto t^a$ for $t < t_1$ and $I(t) \propto t^b$ for $t > t_1$ where a and b are constants. Because of the form of $f_\alpha(s)$ defined in eqn (5.6), this theory gives a first-principles explanation of universality: if the ratio of shift to spread

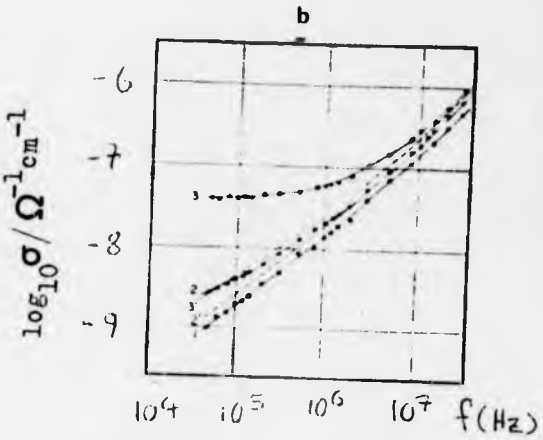
were not constant, it is obvious that universality would not be observed. This is why it is not observed in conventional carrier pulse propagation. If in ACPP account were taken of the diffusion term, the universality would again be lost. This is still true if one were to adapt the calculation to trap-controlled transport using $\hat{Q}(\omega) = A(-i\omega\tau_o)^{1-\alpha}$ in eqn (3.6), where A is a constant.

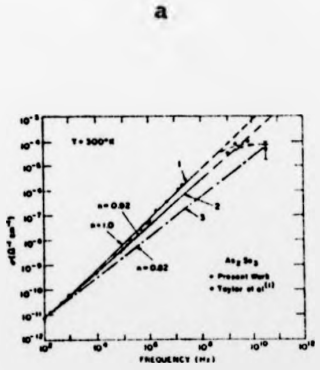
5d. Comparison with Experiments on $a\text{-}As_2Se_3$

Pfister and Scher (1978) give logarithmic plots of t_1 vs. ℓ/E for $a\text{-}As_2Se_3$ which have a slope of -1.85 indicating from eqn (5.24) that $\alpha = 0.55$. On the other hand, Ivkin and Kolomeits (1970) and Lakatos and Abkowitz (1971) measure the ac conductivity of this material. Their results indicate that $\alpha < 0.15$, implying t_1 to be proportional to ℓ/E raised to a power greater than 6.67 which is very different from the observed power of 1.85. These measurements are all shown in fig. 5.4.

This makes it unlikely that if the assumptions of the theory given here are valid, hopping is the ACPP transport mechanism.

In fig. b, the number (1) refers to a temperature of 25°C, (2) to 100°C and (3) to 150°C.





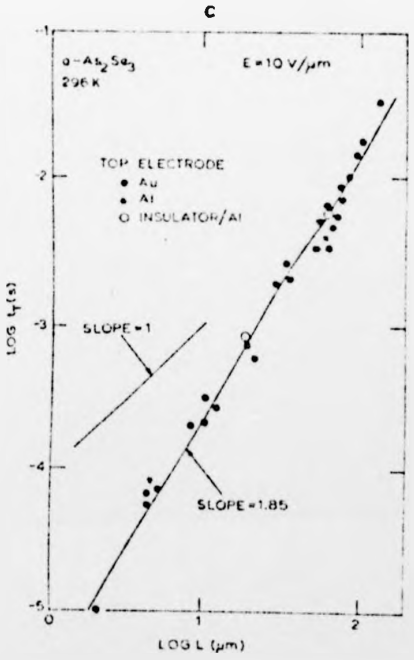


Figure 5.4: Comparison of measurements of ac conductivity and log t_1 vs log(ℓ/E) in ACPP measurements. (From (a) Lakatos and Abkowitz 1971, (b) Ivkin and Kolomeits 1970 and (c) Pfister and Scher 1978). Note how (b) shows that the ac part of the conductivity (dotted lines) is still of power-law form even when it is much smaller than the sum of ac and dc parts (solid line).

CHAPTER 6:

Addition of a dc Term to the Power-Law Mobility:

Behaviour of Hopping Pulses

6a. Introduction

The aim of this chapter is to investigate the effect of a hopping mobility on ACPP when a dc term is added so that eqn (5.1) becomes generalised to

$$\tilde{\mu}(\omega) = \mu_o + \mu_1(-i\omega\tau_o)^{1-\alpha} \qquad (6.1)$$

where μ_o is a constant and the other terms have the same meaning as previously. It will be assumed that the length of the specimen, ℓ, is so great that the pulse never reaches its end at any time considered. This assumption is made to demonstrate how the pulse would evolve in time if it were not absorbed by the extinction electrode. As will be seen, the pulse now eventually ceases to behave like that in fig. 5.1 but instead leaves the creation electrode and starts to travel as a whole with uniform velocity, continuing to spread. Remarkably, this spread is never gaussian, in contrast to the trap-controlled case considered in Chapter 3. It is shown that diffusion is unimportant in real systems. A computer simulation of carriers hopping on a spatially random lattice of isoenergetic sites due to Marshall (1978) is analysed in terms of the theory developed: it is concluded that the theory, together with numerical conductivity calculations of McInnes, Butcher and Clark (1980), describes this simulation well. The chapter is continued with a discussion of work of other authors on the possibility of hopping as an ACPP mechanism. The current density I(t) flowing under these

circumstances is readily found from eqns (5.4), (5.19) and (6.1) to be

$$I(t) = - \frac{eEn_o}{\ell} \left[\mu_o + \frac{\mu_1}{\Gamma(\alpha)} \; T^{\alpha-1} \right] \quad . \tag{6.2}$$

A reduced time

$$T_2 = (\mu_1/\Gamma(\alpha)\mu_o)^{1/1-\alpha} \sim (\mu_1/\mu_o)^{1/1-\alpha} \tag{6.3}$$

may be defined. Much before this time $I(t) \propto T^{\alpha-1}$ as in Chapter 5. Much later I(t) is constant. T_2 is the reduced time at which the change in behaviour of the pulse occurs. Many changes in the behaviour of the pulse will be seen to occur at times $T \sim T_2$: qualitative changes do not occur at times very far from T_2. In §6f agreement is shown between drift mobility and conductivity in a doped polymer.

6b. Behaviour of the Pulse discussed in terms of its Spatial Moments

The case of pure drift is considered first. Eqn (A4) of Appendix A is used, with the value of $\tilde{\mu}(\omega)$ taken from eqn (6.1). The resulting equation is inverse-Fourier-transformed to give the shift

$$\langle x(t) \rangle_{dr} = L_o T + \frac{L_1 T^{\alpha}}{\Gamma(1+\alpha)} \tag{6.4}$$

where L_1 is defined in Chapter 5 and by analogy $L_o = \mu_o E \tau_o$. The second spatial moment is obtained by taking the Fourier transform of eqn (A6) of Appendix A giving

$$\langle x^2(t) \rangle_{dr} = 2 \left[\frac{L_o^2 T^2}{2} + \frac{L_1^2 T^{2\alpha}}{\Gamma(1+2\alpha)} + \frac{2 L_o L_1 T^{1+\alpha}}{\Gamma(2+\alpha)} \right] \quad . \tag{6.6}$$

To obtain eqn (6.6), eqns (6.1) and (6.4) were substituted into eqn (A6) and the inverse Fourier transform was taken. The spread immediately follows from eqns (A3), (6.6) and (6.4):

$$\sigma_{dr} = L_1^{\frac{1}{2}} \left[L_1 T^{2\alpha} \left\{ \frac{2}{\Gamma(1+2\alpha)} - \frac{1}{\Gamma^2(1+\alpha)} \right\} + \frac{2L_o T^{1+\alpha}}{\Gamma(1+\alpha)} \left\{ \frac{1-\alpha}{1+\alpha} \right\} \right]^{\frac{1}{2}} . \qquad (6.7)$$

It was mentioned in section 5b that the first term in braces is always positive. It will be noted that both shift and spread display two distinct regimes of behaviour. The reduced changeover time in each case is of the order of T_2. When $T << T_2$ the ACPP features found in Chapter 5 prevail. When $T >> T_2$, $\langle x \rangle \propto T$ and $\sigma \propto T^{\frac{1}{2}(1+\alpha)}$. Unless $\alpha=0$ this is therefore a regime of constant current density and non-gaussian pulses since σ is not proportional to $T^{\frac{1}{2}}$. That the current density is constant follows from eqn (5.18). The non-gaussian nature of these pulses is in contrast to the trap-controlled case considered in Chapter 3 when gaussian pulses were found to develop after long times. Comparison of eqns (3.8) and (6.1) shows that this is because eqn (6.1) is non-analytic at $\omega=0$ and so cannot be expanded in powers of ω like eqn (3.8).

In the above discussion diffusion was omitted. The case of pure diffusion is now considered, again using the methods of Appendix A. From eqns (A8), (A9) and (A10),

$$\sigma_{dif}^2(t) = 2\left[D_o \tau_o T + \frac{D_1 \tau_o T^{\alpha}}{\Gamma(1+\alpha)} \right] . \qquad (6.8)$$

The Einstein relation (4.34) is invoked giving $D_o = \mu_o k\Theta/e$ and $D_1 = \mu_1 k\Theta/e$. A change in behaviour is again seen at $T \sim T_2$: below T_2 ACPP-like behaviour prevails. Later than T_2, $\sigma_{dif}(t) \propto t^{\frac{1}{2}}$; this is characteristic of conventional diffusion.

In the earlier regime the relative importance of drift and diffusion is considered in section 5b. Diffusion is found to be an unimportant process in experimentally realistic systems. In the regime $T >> T_2$

$$\frac{\sigma^2_{dr}(t)}{\sigma^2_{dif}(t)} \sim \frac{L_o L_1 T^{1+\alpha}}{D_o \tau_o T} \sim \frac{eEL_1 T^{\alpha}}{k\theta} \tag{6.9}$$

using the ac Einstein relation. Remarkably, eqns (6.9) and (5.25) are identical. Since eqn (6.9) applies to a later time regime than eqn (5.25) and $\sigma^2_{dr}/\sigma^2_{dif}$ increases as T increases it follows that if diffusion is irrelevant for $T << T_2$ it is also unimportant for $T >> T_2$. In experimental systems diffusion may be safely neglected. The computer simulation of Marshall (1978) considered later in this chapter is another matter: diffusion plays a noticeable part in the behaviour of Marshall's pulses.

6c. The Pulse-shape n(x,t)

This quantity is calculated using eqns (5.4) and (6.1). The resulting formula

$$\tilde{n}(x,\omega) = \frac{n_o \theta(x) \exp(+i\omega x/\{\mu_o + \mu_1(-i\omega\tau_o)^{1-\alpha}\}E)}{\{\mu_o + \mu_1(-i\omega\tau_o)^{1-\alpha}\}E} \tag{6.10}$$

is inverse Fourier-transformed numerically, giving

$$n(x,t) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} \frac{du\, e^{uT}}{L_o + L_1 u^{1-\alpha}} \exp\left(\frac{-ux}{L_o + L_1 u^{1-\alpha}}\right) \tag{6.11}$$

where $u = -i\omega\tau_o$ and a is a positive constant. To facilitate inversion, eqn (6.11) is mapped onto a real integral along a real contour as follows. As figure (6.1) shows the u-plane has a branch point at the origin and a branch cut along the negative real axis. This corresponds to the cut

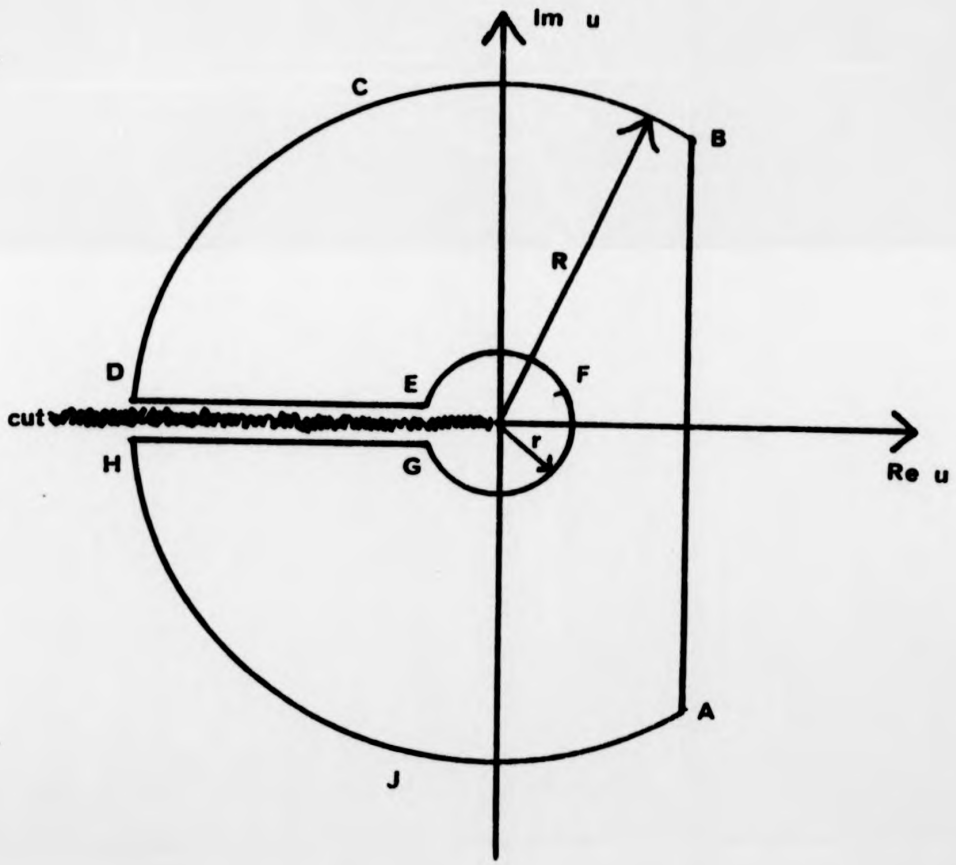


Figure 6.1: The u-plane showing the contour ABCDEFGHJA.

along the negative imaginary ω-axis introduced in §5a. The integral around the contour ABCDEFGHJA vanishes because this contour surrounds no poles. In the limits $R \to \infty$ and $r \to 0$ it is readily seen that

$$\int_A^B f(u)\,du + \int_D^E f(u)\,du + \int_G^H f(u)\,du = 0 \qquad (6.12)$$

where f(u) is the integrand of eqn (6.11). The integral to be performed is thus the sum of integrals from E to D and H to G. When writing these it is convenient to let

$$L(s) = L_o + L_1(se^{i\pi})^{1-\alpha}, \quad k(s) = |L(s)|^2, \quad p(s) = \mathrm{Re}L(s),$$

$$q(s) = \mathrm{Im}\,L(s), \quad h(s) = xsp(s)/k(s) \text{ and}$$

$$g(s) = xsq(s)/k(s). \quad \text{Then}$$

$$n(x,t) = \frac{n_o\theta(x)}{\pi}\int_o^\infty ds\,\frac{e^{h(s)-sT}}{k(s)}\,[p(s)\sin g(s) + q(s)\cos g(s)]\,. \qquad (6.13)$$

Numerical evaluation of this integral is not quite straightforward because the integrand oscillates with a non-uniform period. A routine was developed which integrates eqn (6.13) between successive zeros of sin g(s). Figures 6.2 to 6.5 show the results for cases $L_o = L_1 = 1$, when $\alpha = 0.25$, 0.50 and 0.75 and $L_o = 1$, $L_1 = 100$ for $\alpha = 0.5$. This last case gives qualitatively similar results to the case $\alpha = 0.5$, $L_o = L_1 = 1$. In all these cases the change of shape of the pulse as T goes through T_2 can be clearly seen. In the calculations n_o is always put equal to unity so that there should always be unit area under the pulses. This condition is always satisfied to within better than 2%. In the case $\alpha = \frac{1}{4}$, T = 100 the leading edge of the pulse is omitted because of difficulties encountered with the numerical method.

Figures 6.2 - 6.5: Time evolution of pulses $n(x,t)$ computed from eqn (6.13). Ordinate: $n(x,t)$; Abscissa: x.

Figure 6.2: $\alpha = \frac{1}{2}$, $L_o = L_1 = 1$

Figure 6.3: $\alpha = \frac{1}{2}$, $L_o = 1$, $L_1 = 100$

Figure 6.4: $\alpha = 1$, $L_o = L_1 = 1$

Figure 6.5: $\alpha = 2$, $L_o = L_1 = 1$

From Clark and Butcher (1980).

Fig. 6·2

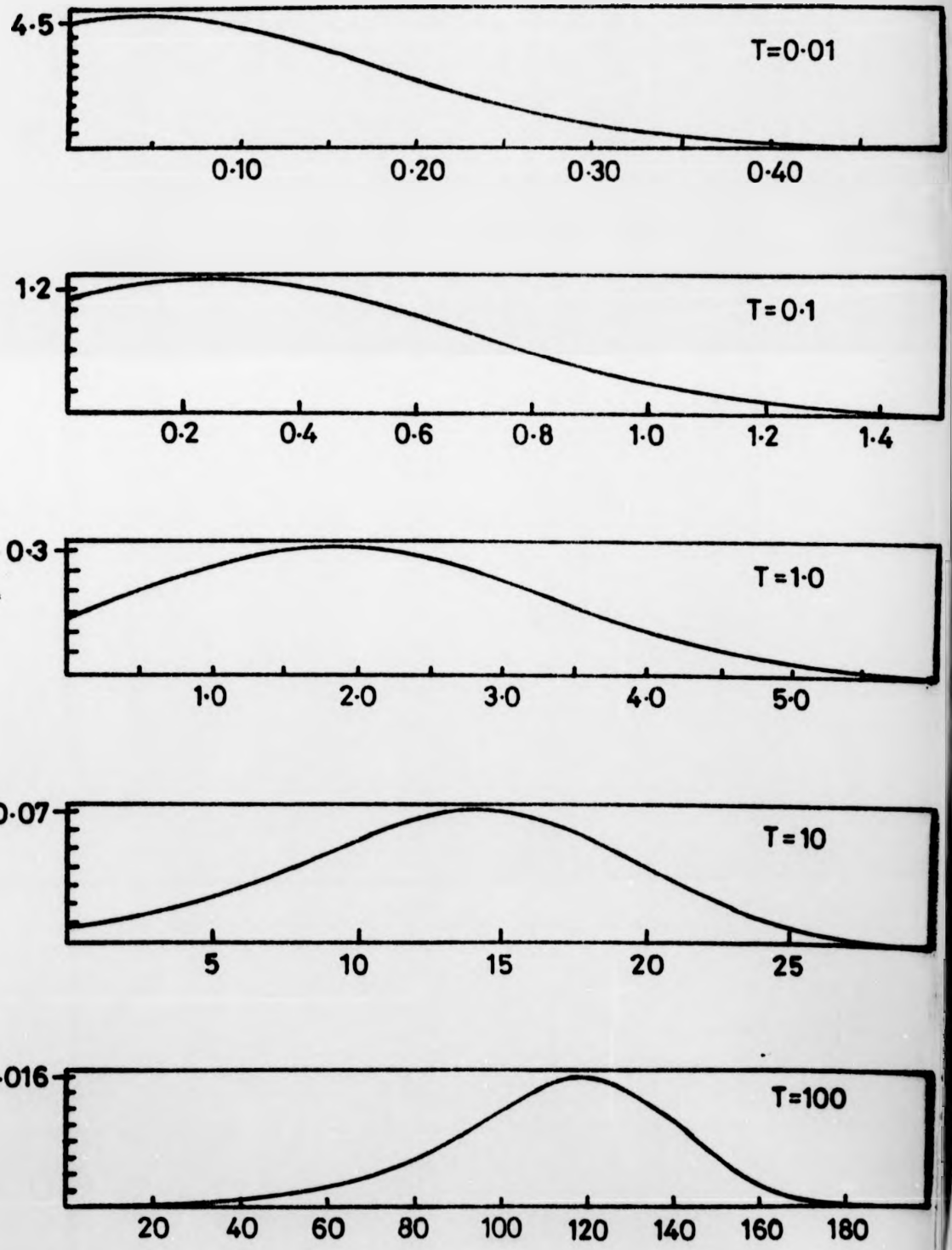

4·5
T=0·01
0·10
0·20
0·30
0·40
1·2
T=0·1
0·2
0·4
0·6
0·8
1·0
1·2
1·4
0·3
T=1·0
1·0
2·0
3·0
4·0
5·0
0·07
T=10
5
10
15
20
25
0·016
T=100
20
40
60
80
100
120
140
160
180

Fig. 6·3

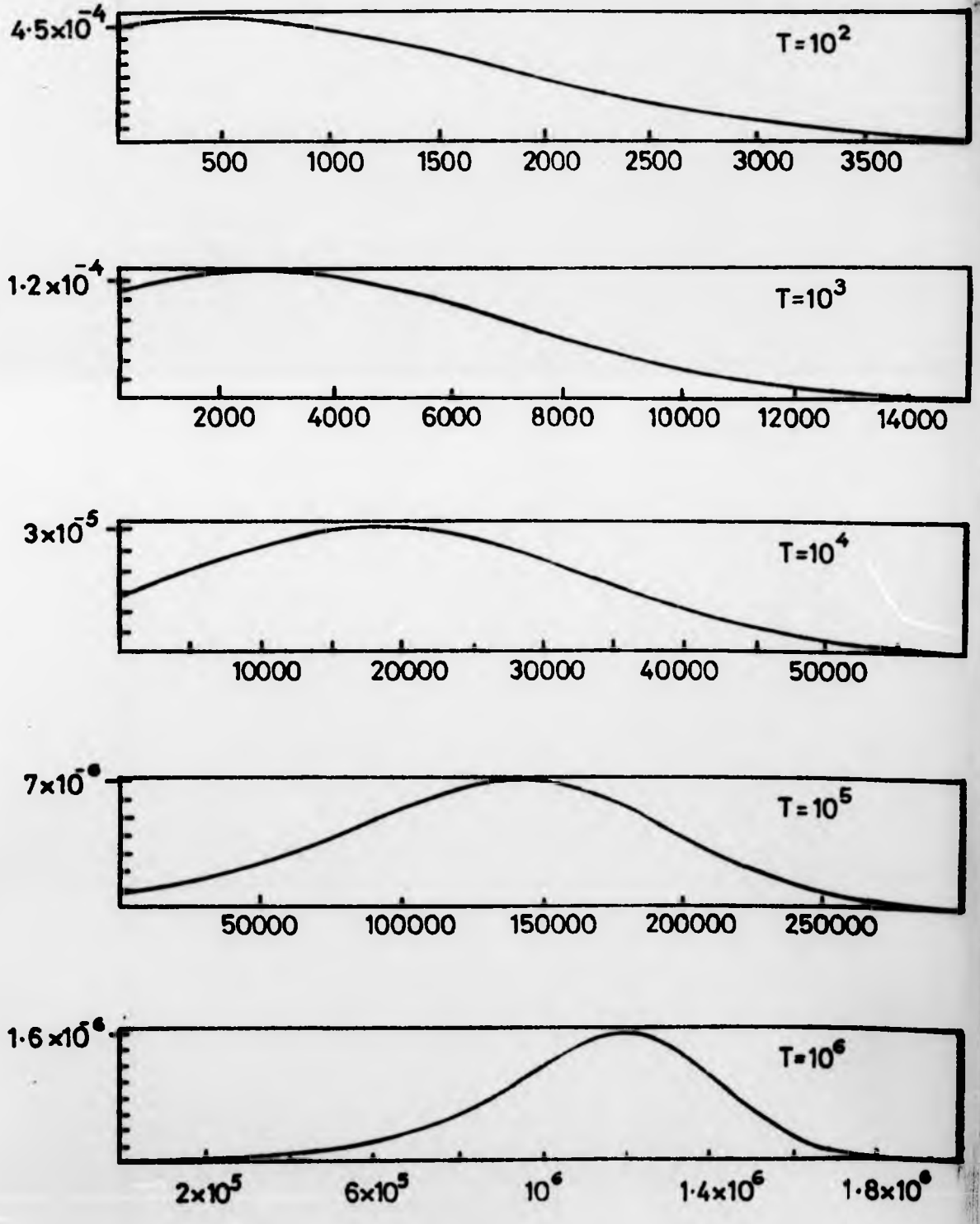

4·5×10⁻⁴
T=10²
500 1000 1500 2000 2500 3000 3500
1·2×10⁻⁴
T=10³
2000 4000 6000 8000 10000 12000 14000
3×10⁻⁵
T=10⁴
10000 20000 30000 40000 50000
7×10⁻⁶
T=10⁵
50000 100000 150000 200000 250000
1·6×10⁻⁶
T=10⁶
2×10⁵ 6×10⁵ 10⁶ 1·4×10⁶ 1·8×10⁶

Fig. 6·4

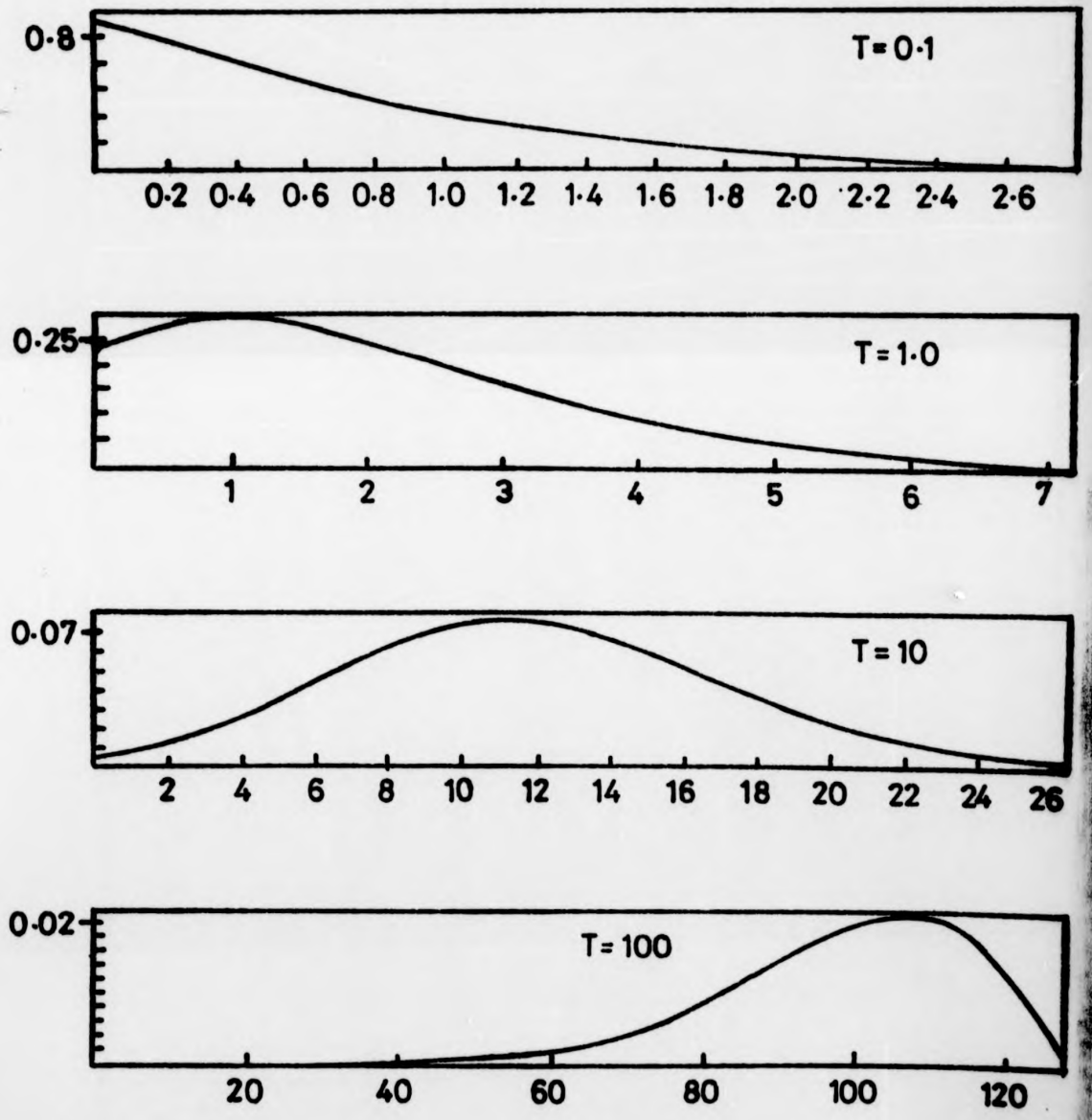
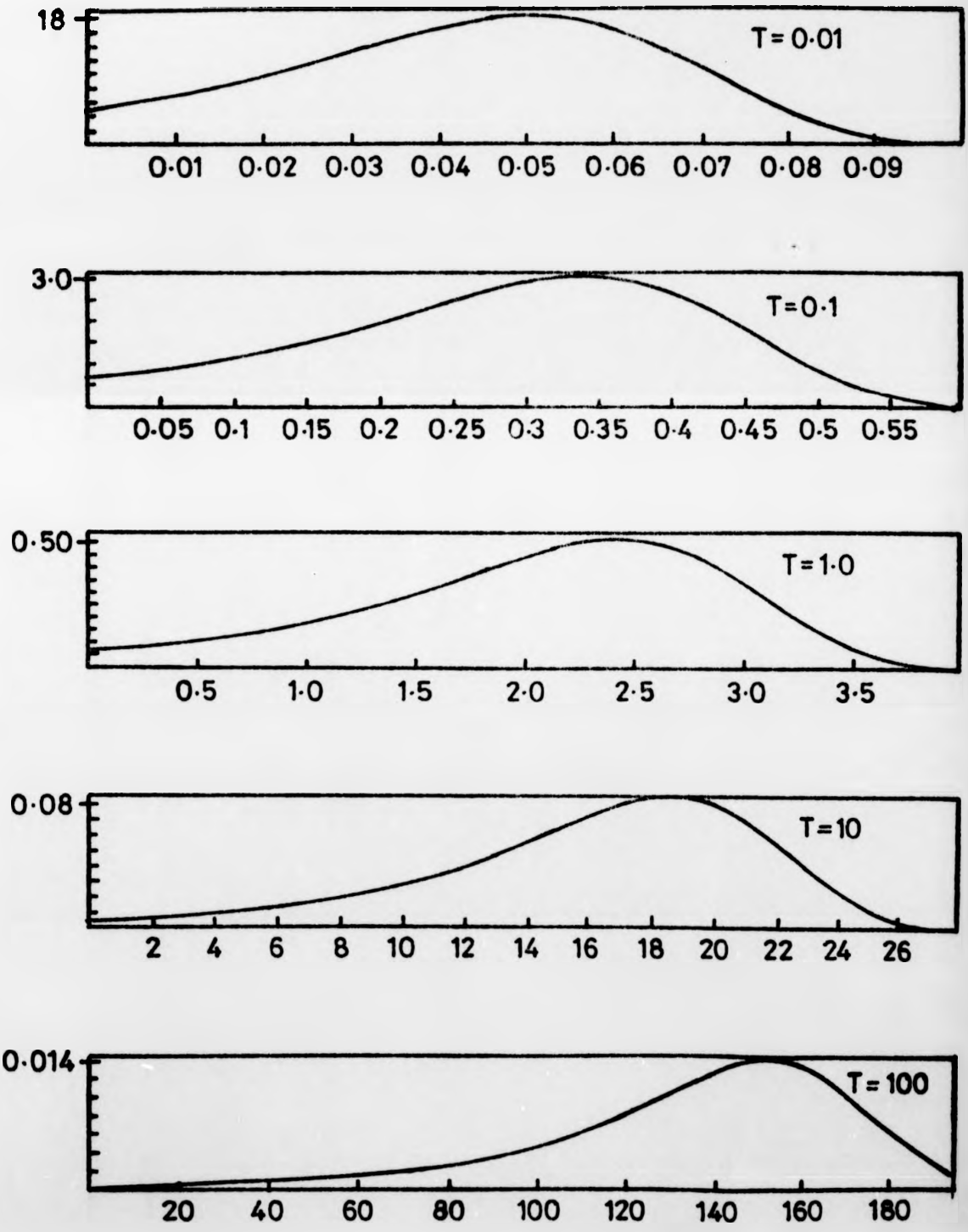

0·8
T= 0·1
0·2 0·4 0·6 0·8 1·0 1·2 1·4 1·6 1·8 2·0 2·2 2·4 2·6
0·25
T= 1·0
1 2 3 4 5 6 7
0·07
T= 10
2 4 6 8 10 12 14 16 18 20 22 24 26
0·02
T= 100
20 40 60 80 100 120

Fig. 6·5

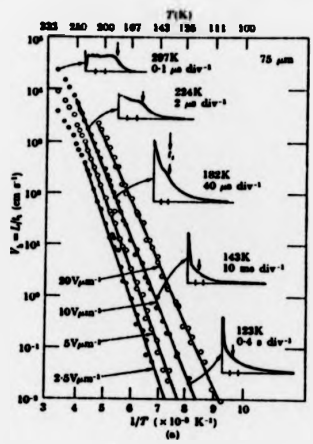

18
T = 0·01
0·01 0·02 0·03 0·04 0·05 0·06 0·07 0·08 0·09
3·0
T = 0·1
0·05 0·1 0·15 0·2 0·25 0·3 0·35 0·4 0·45 0·5 0·55
0·50
T = 1·0
0·5 1·0 1·5 2·0 2·5 3·0 3·5
0·08
T = 10
2 4 6 8 10 12 14 16 18 20 22 24 26
0·014
T = 100
20 40 60 80 100 120 140 160 180

It is perhaps worth emphasising yet again that the pulses in figs. 6.2 - 6.5 arise purely from drift. They contain no diffusion effects. Conventional pulses so treated would be delta-functions. The pulses are therefore anomalous even when $T >> T_2$.

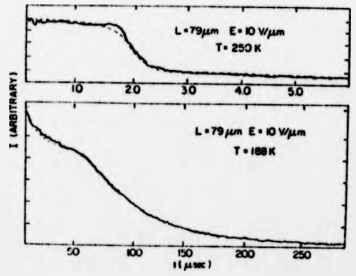
6d. Comparison with Experiments on Amorphous Selenium

Amorphous selenium shows a transition from classic ACPP at 143 K through a transition temperature around 188 K to constant-current carrier pulse propagation at 250 K (Noolandi 1977a, Pfister 1976). This is shown in figure 6.6. If hopping were the transport mechanism this behaviour should be predictable from measurements of ac conductivity at different temperatures. Pfister (op.cit) plots log t_1 vs 1/kΘ and finds a straight line even though the pulses change from $t_1 > t_2$ to $t_1 < t_2$ behaviour. His plot is shown in Fig. 6.6. This strongly suggests that no change of transport mechanism is involved. The transit time varies from milliseconds at 143 K to microseconds at 250 K. If the transport mechanism were hopping then insertion of experimental values of α, τ_o and $\mu_1/\mu_o \equiv \sigma_1/\sigma_o$ (where σ is conductivity) into eqn (6.3) should yield the prediction that $t_2 << t_1$ when $\Theta = 250$ K, $t_2 \sim t_1$ when $\Theta = 188$ K and $t_2 >> t_1$ when $\Theta = 143$ K.

Estimates of τ_o vary from 10^{-11} to 10^{-16}s (Mott and Davis 1979, p226; Butcher and Hayden 1977). Consider $\tau_o \sim 10^{-13}$ s: the large uncertainty will not affect the argument now offered. σ_1/σ_o may be obtained from data extrapolated from Lakatos and Abkowitz (1971) shown in fig. 6.7. It is found that $\sigma_1 \sim 10^{-1}(\Omega\ \text{cm})^{-1}$, roughly independently of temperature. $\sigma_o \sim 10^{-30}$ and 10^{-17} $(\Omega\ \text{cm})^{-1}$ at 143 K and 250 K respectively. By inserting these numbers into eqn (6.3) one learns that $t_2 \sim 10^{16}$ and 10^3 s at 140 and 250 K respectively - that is, 10% of age of the universe and



a



b

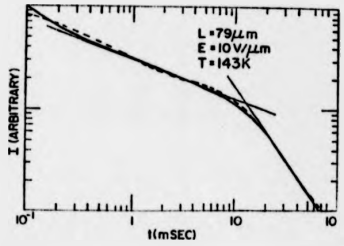


Figure 6.6: Measurements by Pfister (1976) of ACPP in a-Se (a) from Pfister (1976) & (b) from Noolandi 1977a.

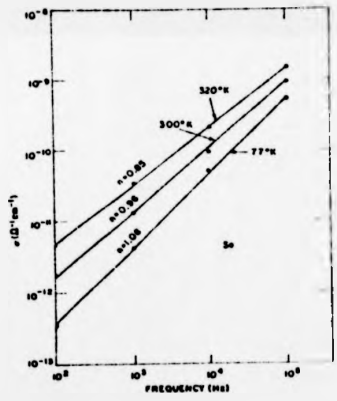


Figure 6.7: Measurements of ac conductivity in a-Se (from Lakatos and Abkowitz 1971).

20 minutes respectively. This is a clear prediction that $t_1 \ll t_2$ in all the data of fig. 6.6.

One may express this discrepancy another way. From the experimental data in figure 6.6 it is clear that $t_1 \gg t_2$ at 250 K. Hence it is true that

$$\mu_o \simeq \frac{\ell}{Et_1} \sim 10^{-2}\ \mathrm{cm}^{-2}(\mathrm{V\ s})^{-1}. \qquad (6.14)$$

Use is now made of the formula $\sigma_o = n_o e \mu_o$ where n_o is the equilibrium carrier concentration, estimated (somewhat uncertainly) to be $\sim 10^{18}\ \mathrm{cm}^{-3}$ (Mott and Davis 1979, p.473). This yields

$$\mu_o \sim 10^{-16}\ \mathrm{cm}^{-2}(\mathrm{V\ s})^{-1}. \qquad (6.15)$$

There is a discrepancy of 14 orders of magnitude between eqns (6.14) and (6.15). Thus even if the estimate of n_o were 10 orders of magnitude out, which is hardly likely, hopping still would not account satisfactorily for the behaviour of pulses in this material.

6e. Analysis of Computer Studies of ACPP

Marshall (1978; 1980a, to be published; 1980b, private communication) performs Monte Carlo simulations of hopping pulses in a box of randomly located isoenergetic sites. He considers the following parameter values: $2 \le B \le 10$ in eqn (2.26); $\nu = 0$ in eqn (2.24) and $eE/k\Theta = 1$ in eqn (4.3). He finds that in all cases $T_2 \ll T_1$. In this section his results are compared via the theory of §§4a-6c with the mobilities of McInnes, Butcher and Clark (1980), cf. figure 2.2 and Appendix F, and Butcher, Hayden and McInnes (1977), eqn (F1) of Appendix F. τ_o is given by eqn (F8).

When B = 5, McInnes et al. find that eqn. (6.1) holds for $\omega\tau_o \lesssim 0.1$ with

$$\frac{D_1}{D_o} = \frac{\mu_1}{\mu_o} = \frac{\sigma_1}{\sigma_o} \simeq 9 \qquad (6.16)$$

where D_1 and σ_1 are diffusivity and condutivity respectively, which are associated via the Einstein relation with μ_1, and D_o and σ_o are similarly defined. These authors also find that in this case, in eqn (6.1)

$$\alpha = 0.78 \pm 0.03 \qquad (6.17)$$

(McInnes 1980, private communication). Then, from eqn (6.3),

$$3.3 \times 10^3 < T_2 < 2.4 \times 10^4 \quad . \qquad (6.18)$$

The small error in eqn (6.17) causes a large error in the inequality (6.18). Marshall (1980b) finds that when B = 5

$$T_2 \simeq 1.9 \times 10^4 \quad ; \qquad (6.19)$$

his data for this value of B are shown in Marshall (1978). This value of T_2 is well within the range of inequality (6.18).

It is now evident that both the simulation of Marshall and the analytic theory developed in this thesis predict that the Pollak effect (§3d) dominates the behaviour of hopping pulses if the sites among which the carriers may hop are isoenergetic. This effect is apparent after the carriers have penetrated a depth of about 5 sites. For a site density $\sim 10^{18}$ cm^{-3} this corresponds to a distance of 500 Å which is much thinner than a typical experimental sample thickness $\sim 10^{6}$Å (Pfister and Scher 1978).

Because of the extreme sensitivity of inequality (6.18) to errors in the value of α , it is perhaps better to take D_1/D_o from eqn (6.16), T_2 from eqn (6.19) and use eqn (6.3) to compute α. Allowing an arbitrary variation of a factor of two either way in eqn (6.16), which sould be ample to allow for the different numbers of interconnected sites in the

two numerical calculations (cf. McInnes and Butcher 1979), and for the fact that McInnes et al. (1980) use $\nu = 3/2$ in eqn (2.24) (which is not expected to affect the argument seriously), one thus finds from figure 6.9 that

$$\alpha = 0.8 \pm 0.06 \tag{6.20}$$

in good agreement with eqn (6.17).

Marshall's "samples" are finite, in spatial extent, in contradistinction to the assumption made at the beginning of this chapter. This author's comparison (1980b) of I(t) computed for B = 7 when the pulse is created (a) at the centre and (b) at the edge (creation electrode) of his "sample" is shown in figure 6.10. It is apparent that the edge has an important but transient effect on the current. It is now argued that this is because the end of the sample acts as a reflecting barrier, away from which carriers diffuse asymmetrically in space. Eqn (5.25) for Marshall's "samples" becomes

$$\frac{\sigma_{dr}^2}{\sigma_{dif}^2} \sim \langle x(t) \rangle_{dr} \tag{6.21}$$

using eqn (6.4) and remembering that a reduced time T_2 has not yet elapsed. For B = 3 Marshall (1978) finds that $\langle x(1000) \rangle \sim 5$ so that drift is barely dominant when t = 1000. From eqns (5.25) and (6.9) diffusion will dominate at much lower times. Chandrasekhar (1943) treats diffusion at a reflecting barrier at x = 0 for a discrete-time random walk on a regular lattice, finding the boundary condition $\partial n_b(x,t)/\partial x = 0$ at the barrier from the fact that

$$n_b(x,t) = n_{nb}(x,t) + n_{nb}(-x,t) \tag{6.22}$$

where n(x,t) is particle density, subscript b means "with barrier" and nb

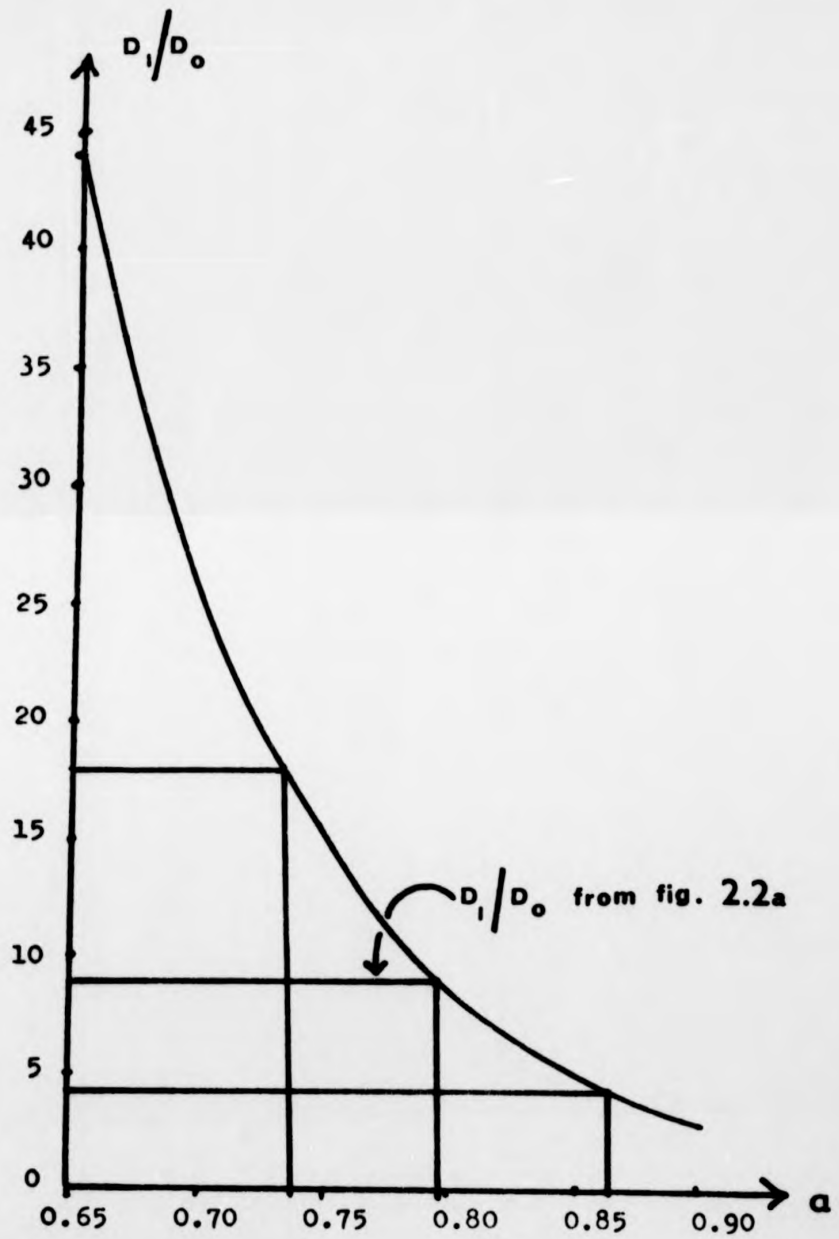


Figure 6.9: Plot of D_1/D_o vs α from eqn (6.3) using T_2 from eqn (6.19).

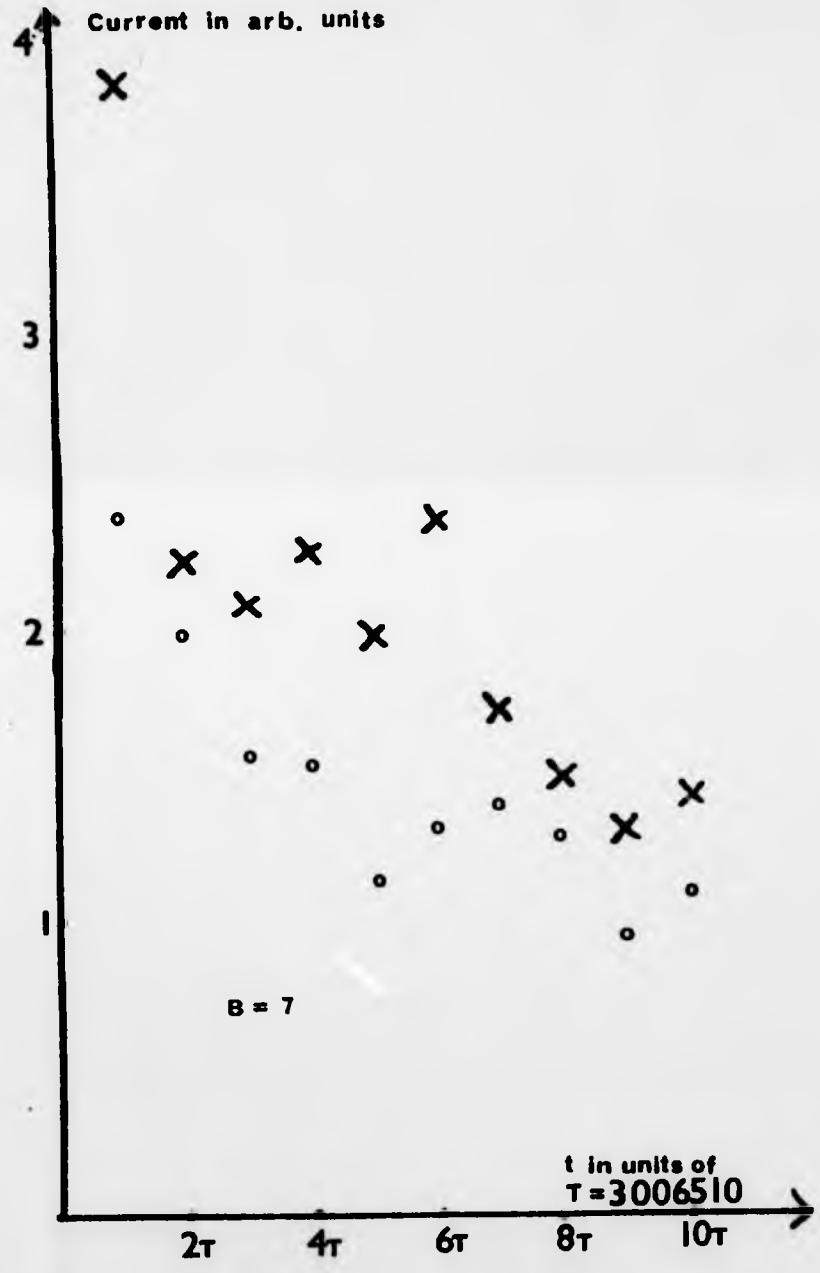


Figure 6.10: Plot of I(t) vs t with B = 7 for pulse created at creation electrode (crosses) and in the centre (circles of the specimen. (From Marshall 1980b).

means no "barrier". If this result is applied to Marshall's simulations via eqns (5.7) and (G5) it follows that

$$I_{dif}(t) \propto T^{-(1-\frac{1}{2}\alpha)} \quad . \tag{6.23}$$

Thus from eqn (6.20) Marshall's initial I(t) is expected to be dominated by a term decaying as $T^{-(0.6 \pm 0.03)}$. In fact analysis of Marshall's work indicates that the decay is nearer $T^{-0.8}$. But the assumption that eqn (6.22) still holds for a continuous-time random walk is crude. In a discrete-time random walk all the carriers are frequent hoppers. In the present case some carriers will be relatively isolated and will hardly ever hop; they will therefore not "feel" the barrier. It is possible that such an effect causes I(t) to decay more rapidly than in eqn (6.23). It is seen from figure 6.11 that Marshall's data for I(t) does not quite fit a simple power-law decay. Surface effects are to be similarly expected at the extinction electrode.

Finally the dc diffusivity D_o for Marshall's system is estimated by making

$$\langle x(t) \rangle = \ell = 50 \quad , \tag{6.24}$$

the "sample" -length (Marshall 1978, 1980a, b) in eqn (6.4). Knowledge of T_2 (Marshall 1980b) gives D_1/D_o from eqn (6.3) for a range of likely values of α, estimated from figure 2.2. The resultant estimate is made using Marshall's (1980b) values of the transit time T_1, and compared in figure 6.12 with D_o found from eqn (F1) and the much cruder estimate of Pollak (1977) quoted by Marshall (1978). The error bars on the simulation data are due to uncertainty in α.

It is concluded from the good agreement in figure 6.12 and the rest

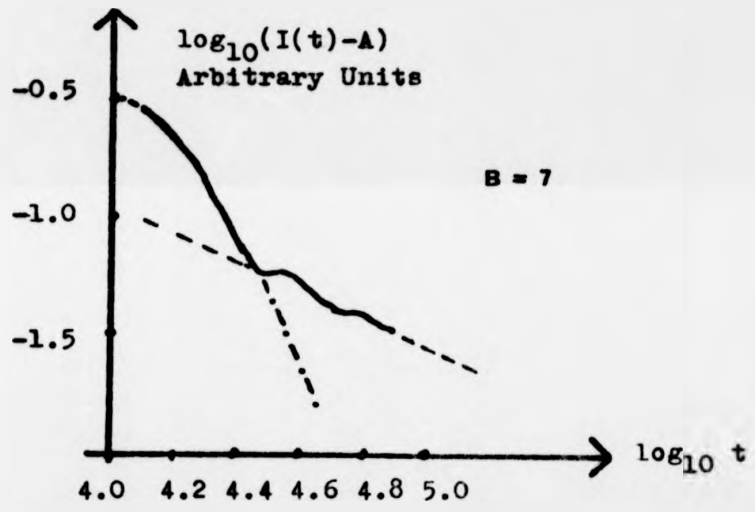


Figure 6.11: Plot of $\log_{10}\{I(t)-A\}$ vs $\log_{10}$ t showing the existence of two time regimes, with change-over time $t = 3 \times 10^4$ in this case (B = 7), cf. transit time $t_1 = 1.1 \times 10^8$. A is an arbitrary constant chosen to emphasise the "kink" in this curve. It is present for all values of B but is more pronounced at high values of B. The dashed and dash-dot lines are extrapolations of the two regimes.

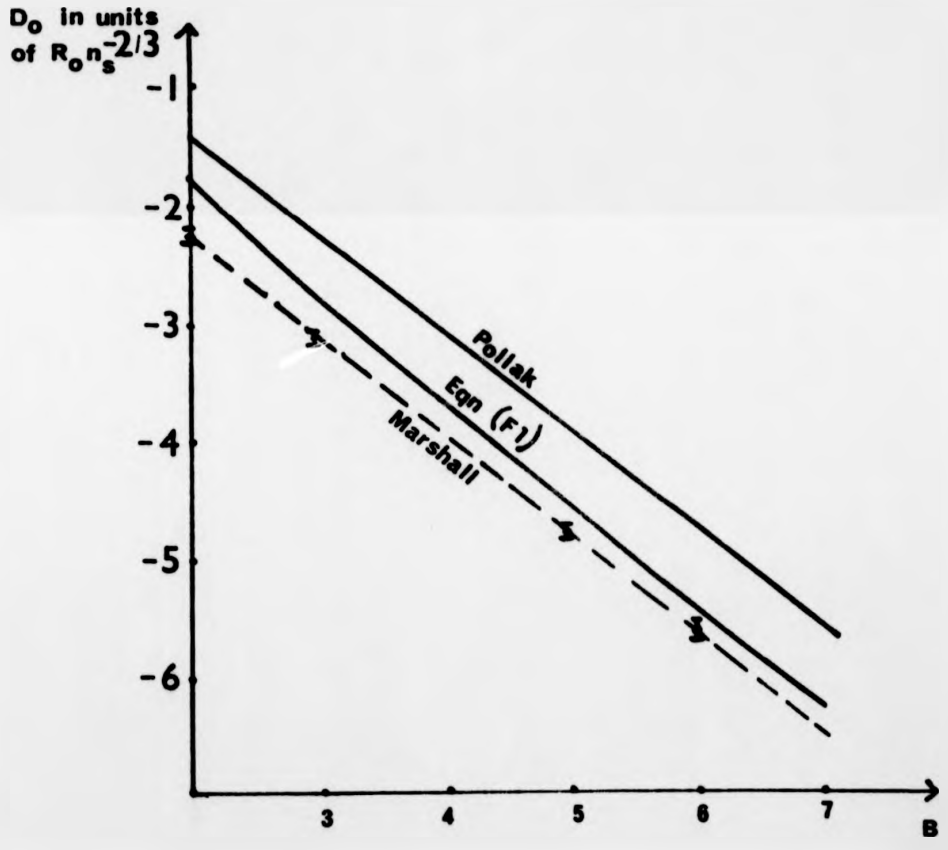


Figure 6.12: Plot of D_o vs B from eqns (6.4), (6.24) and data of Marshall (1980b) (dashed line: error bars due to uncertaintly of α in eqn (6.4)). Eqn (F1) is used to deduce D_o as a function of B. A simpler model (Pollak 1977, quoted by Marshall 1978) is also used to estimate D_o (dotted line).

of §6e that the theory of §§4a-6c provides a good description of ACPP by carriers hopping among bulk isoenergetic sites.

§6f. Comparsion of drift mobility and conductivity in doped Lexan

Lexan is the commercial name of an organic polymer (it is a trademark of the General Electric Co.). It may be doped: conduction then takes place by hopping among the impurities. Troup, Mort, Grammatica and Sandman (1980) dope this material with an organic radical (tri-p-tolylamine) which they describe. Figure 6.13 shows a comparison of the dc conductivity and drift mobility defined by eqn (1.29) as functions of temperature. The similarity of activation energies of these two quantities suggests that the same hopping transport mechanism may be responsible for both. An advantage of such a system is that the nearest neighbour separation is controllable, being computed from the impurity concentration via the method used to derive eqn (E5). Figure 6.14 shows how a drift mobility dependence of the form

$$\mu \propto \langle r^2 \rangle \, e^{-2\alpha r} \tag{6.25}$$

occurs, giving $\alpha^{-1} = 1.1$ Å at $\theta = 295$ K. This form of mobility may be obtained very crudely by saying: the dc Einstein relation (1.21) implies mobility proportional to diffusion which is roughly proportional to mean-square-distance-hopped times mean-hop-rate, whence eqn (6.25).

Thus it seems highly likely that the drift-mobility mechanism in this material is hopping. This is a new result and the theory developed in this thesis offers a method of investigating hopping in this material. The hopping sites probably have similar energies and may therefore be treated as isoenergetic: by virtue of the discussion of the previous section it is to be expected that $t \gg t_2$.

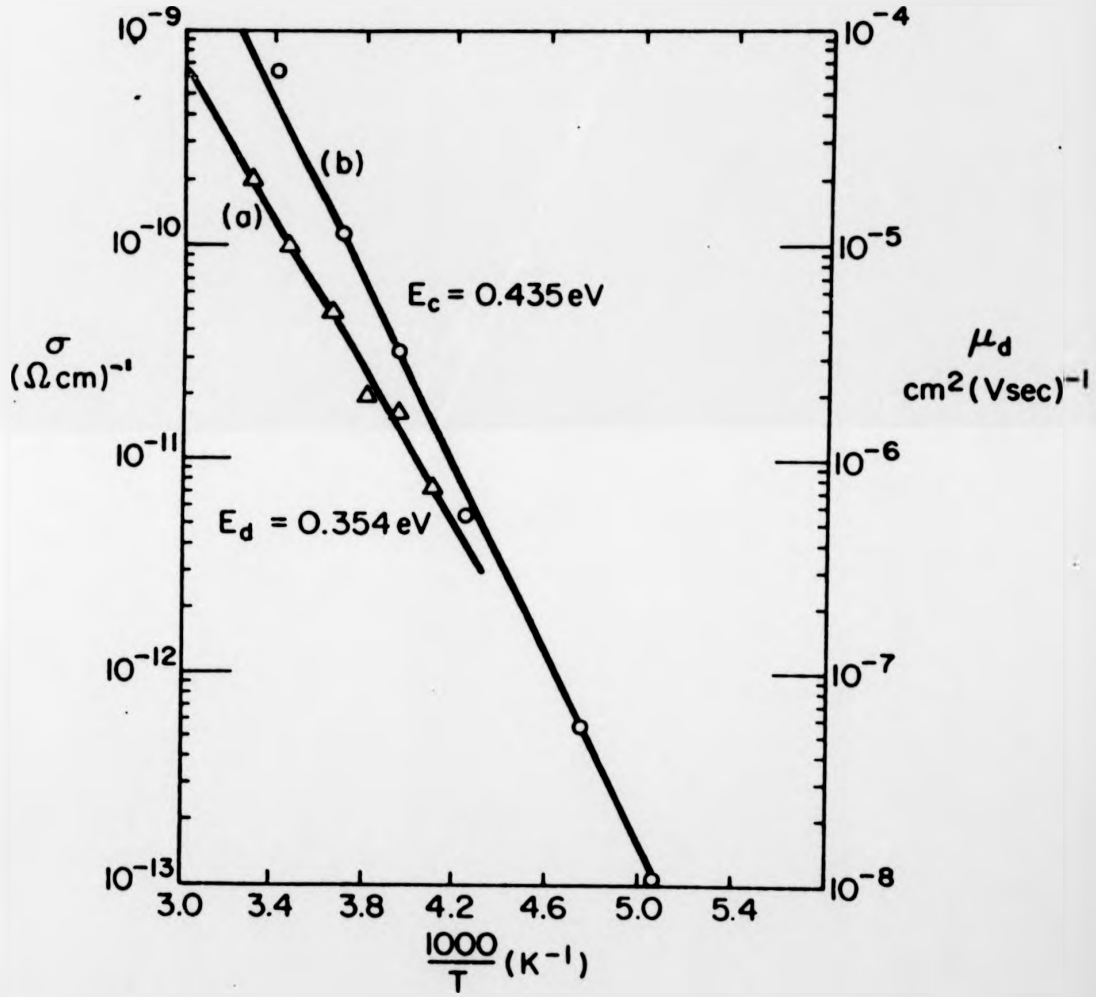


Figure 6.13: Showing activation energies E_D of drift mobility μ_D, and E_c of low-field dc conductivity σ for doped Lexan® (from Troup et al. 1980). T = temperature.

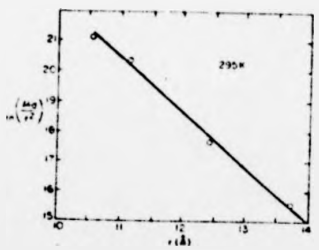


Figure 6.14: Plot of $\ell n(\mu_D/\langle r^2 \rangle)$ vs $\langle r \rangle$, where $\langle\rangle$ indicates mean separation of nearest neighbours, known from the impurity concentration, and μ_D = drift mobility, showing that eqn (6.25) is satisfied for drift mobility in doped Lexan®. (From Troup et al. 1980).

Chapter 7:

Discussion

7a. Introduction

The purpose of this chapter is firstly to summarise the work of this thesis and then to discuss certain points raised by it.

The thesis consists mostly of a theory of ACPP but in chapter 2 a review is also given of the theory of Scher and Lax (1973) and of its subsequent development. The latter is summarised in §7b; the former in §7c. In §§7d to 7f possible weaknesses of the ACPP theory are explored. In §7f the question of thermalisation of the pulse is discussed. A re-definition of trap-controlled hopping is given. In §7g future work and possible future applications of the present ACPP theory are outlined. §7h is the concluding section.

7b. Random Walks and Conductivity I: Rerandomization

It is clear that a one-electron or one-hole theory of hopping conduction may be regarded as a continuous-time random walk on a random lattice of sites. Even if the sites are isoenergetic the diffusivity of a carrier executing such a random walk has not at present been calculated. As a first approximation, Scher and Lax (1973) model such a random walk as a random walk on a regular simple cubic lattice with the effect of the disorder included by making the random walk non-markovian, the distribution $\psi(t)$ of times a carrier spends on a site being taken to be the configuration average of those encountered in a random walk on a random medium. It is $\psi(t)$ rather than distance hopped which is regarded as the important quantity in this process. The lattice

is merely a computational aid and does not correspond to any physical lattice such as the host lattice in a compensated crystalline semiconductor.

Two criticisms of this model are made in the literature. Firstly Tunaley (1974) points out that if the random walk is non-markovian, the distribution h(t) of times from the start of observation to the first jump will differ from $\psi(t)$ in such a way as to make the diffusivity frequency-independent. Yet the experimental diffusivity measured in disordered semiconductors rises steeply with frequency. Butcher (1974) and later Kumar and Heinrichs (1980) circumvent this problem by interpreting the Scher and Lax model as a markovian random walk on a random lattice of sites in which every site except the one currently occupied is rerandomized immediately after every hop. Since this is a markovian random walk its first-jump waiting time distribution is identical to later ones and so the Scher-Lax model may be used in its original form.

The second criticism (Butcher 1974) is that in the dc limit the mean square displacement per hop, $\tilde{\sigma}^2_{rms}(0)$, and the mean hopping frequency $\chi(0)$ are not well modelled as functions of B (eqn (2.26)), the r lattice site density. Yet the facts that the intersite hop rates fall off exponentially with distance hopped and that nearest-neighbour hops dominate mean that the diffusivity, which is proportional to the product $\tilde{\sigma}^2_{rms}(0)\ \chi(0)$, is well produced because the roles of the two quantities are crudely <u>reversed</u> by rerandomization. However for $B \gtrsim 10$ this is no longer so. At densities this low, the fact that sometimes after the sites have been rerandomized the carrier finds itself on an isolated site (which it would be very unlikely to visit were the sites permanently fixed) causes the diffusivity to drop dramatically.

As $\omega \to \infty$ the diffusivity corresponds to $\lim_{\epsilon \to 0} D(\epsilon)$ in the time domain.* At such low times no hops have occurred, therefore nor has any re-randomization, therefore $D(\epsilon)$ must be the same with or without re-randomization. It remains to be understood why the rerandomisation approximation works so well at intermediate frequencies.

Pfister and Scher (1978) use the same continuous-time random walk theory to model both trap-controlled band transport and trap controlled hopping. They show how in each case $\psi(t)$ might be computed. In the former case the lattice parameter is proportional to the applied field E, which suggests that the basic physics of the problem is obscurred by this approach. Schmidlin (1980) points out that the latter case may indeed be so modelled but further suggests that this implies that the Scher-Lax theory of conductivity is invalid. This is in contrast to the findings of the present work which show that within its limitations (viz. rerandomization) the Scher and Lax model works surprisingly well.

7c. Random Walks and Conductivity II: Pulses

In chapters 4-6 a theory is developed which enables one to investigate hopping as a candidate mechanism for ACPP. It is based on a more realistic model of hopping than that just considered, in which the sites are permanently fixed, randomly located and have random energies uncorrelated with their positions. A formal equation of motion of the pulse is derived and it is shown how in thermal equilibrium this equation becomes

$$\frac{\partial n(x,t)}{\partial t} = - E\int_{-\infty}^{\infty} \mu(t-\tau) n(x,\tau) d\tau + n_o \delta(x)\delta(t) \qquad (7.1)$$

where $\mu(t)$ is the inverse causal Fourier transform of the ac mobility

* Epsilon represents a very short time.

$$\tilde{\mu}(\omega) = \frac{\sigma(\omega)}{ne} \qquad (7.2)$$

in which n is the steady state carrier density and $\sigma(\omega)$ is the ac conductivity. Eqns (7.1) and (7.2) allow one to test whether this mechanism of ACPP is actually dominant because $\sigma(\omega)$ may be independently measured, and once this quantity is known it may be substituted into these equations which are then solved to predict the ACPP properties.* In chapters 5 and 6 it was seen how to do this without making use of the unknown quantity n. In the latter case, some knowledge of what constitutes a reasonable value of n is helpful, but as eqns (6.14) and (6.15) show, if the measurements of Lakatos and Abkowitz (1971) are valid, a value of $n \sim 10^{32}$ cm^{-3} would be required for the hopping theory to be valid at 250 K. Since there are only about 10^{23} atoms in a cubic centimetre this is quite ridiculous. In neither a-Se nor a-As_2Se_3 does hopping of electrons or holes as envisaged by, say, Butcher (1976) appear to be the dominant ACPP mechanism.

Pfister and Scher (1977) reach the same conclusion in a-As_2Se_3 on different grounds. They imagine the hopping to be of small polarons and find that the activation energy associated with the drift mobility is too high for such hopping.

The present theory of ACPP rests on the assumptions of §4b, notably (i) that the pulse has thermalised and (ii) that the Miller-Abrahams rate equations (1.1) hold. These assumptions are discussed below.

7d. Possible Failure of the Miller-Abrahams Rate Equations.

In §2c a brief account is given of the evidence which is beginning to emerge that the Rate Equation formalism fails to account for both ac and dc conductivity at one and the same time. (The reported calculations

---

* Extensive solutions of the pulse shapes n(x,t) are given which in the pure power-law case may be adapted to any mechanism.

of Summerfield (1980) and Movaghar, Pohlmann and Sauer (1980) allow site energies to vary).

If this state of affairs is at some future date resolved by a modification of the $|\underset{\sim}{r}|$-dependence of the hop rate W(r), eqn (2.24), the present theory of ACPP will be unharmed. If the E-dependence of the rates turns out not to be given by eqn (4.3) but depends on, say, frequency of applied field, then the theory would require modification.

It may be that eqn (7.1) will be shown to be invalid, but this equation is intuitively appealing:- with what quantity is $\tilde{\mu}(\omega)$ likely to be replaced?

7e. Approximations Inherent in the Pulse Propagation Theory

Schmidlin (1977) discusses space charge, concluding that in principle it will tend to slow down the rate of decay of I(t). Though this author considers trap-controlled transport, his discussion of space-charge is mechanism-independent. He assumes that the space charge is mostly due to an uneven distribution of carriers remaining from pulses previously propagated through the sample. This problem may be controlled by careful choice of electrodes and by using large pulses (Sharfe 1970). There is no detailed quantitative study of this problem known to the author; the *a priori* assumption that space charge is negligible remains to be tested.

The contact electrodes present the experimentalist with a problem (Pfister and Scher 1978). Perfectly ohmic contacts are not easily obtained. Abkowitz and Scher (1977) give a theoretical treatment of this problem, considering effects at the creation electrode. Scher and Montroll (1975) give a crude theoretical treatment of the extinction

electrode, by assuming it to be a perfectly absorbing boundary. Leal Ferreira (1977) is able to treat this electrode by merely truncating his integral over x, eqn (2.54), at this electrode when evaluating I(t), without losing the salient results of Scher and Montroll. This is the justification for using such an approach in this thesis. As pointed out in §6e the theory developed here can only account for behaviour while the pulse is not close to either electrode, especially if the transit time, eqn (6.3), has been exceeded. Before this time the pulses can never, by virtue of their shape, have most of their carriers near the extinction electrode unless α is close to unity in eqn (6.1), which rarely happens (Pfister and Scher 1978). It is in the nature of the integrals in eqns (2.54) and (5.18) that they are over the whole pulse and except when the main bulk of the pulse is near an electrode they should provide good approximations to I(t). This is only a problem when t is very close indeed to zero or if $t >> t_2$ and the pulse is within one or two standard deviations of the extinction electrode. Most of the time the pulse may be regarded as being far from electrodes.

Eqn (6.1) for $\tilde{\mu}(\omega)$ is a crude approximation to the curves shown in figure 2.2. The $\omega \to \infty$ limit is unimportant: here eqn (6.1) is only a poor approximation when $\omega \gtrsim \tau_o^{-1}$. As explained in §6d this corresponds to times $\lesssim 10^{-12}$s which are way below experimentally important times. At the opposite extreme, $\omega \to 0$, eqn (6.1) is non-analytic giving rise to permanently non-gaussian pulses. Intuitively one feels that this is not right, yet measurements of conductivity at conductivities at frequencies much less than t_2^{-1} still support eqn (6.1) (see figures (7.1) and (5.4)). Experiments on ACPP typically take 10-1000 μs, which corresponds to frequencies $\omega \sim 10^3 - 10^5$ Hz implying non-gaussian pulses. It is for this reason that Pollak's (1977) treatment of the constant-current ACPP regime is inadequate: the pulses are still anomalous. As shown in §3c this is not so for trap-controlled band transport.

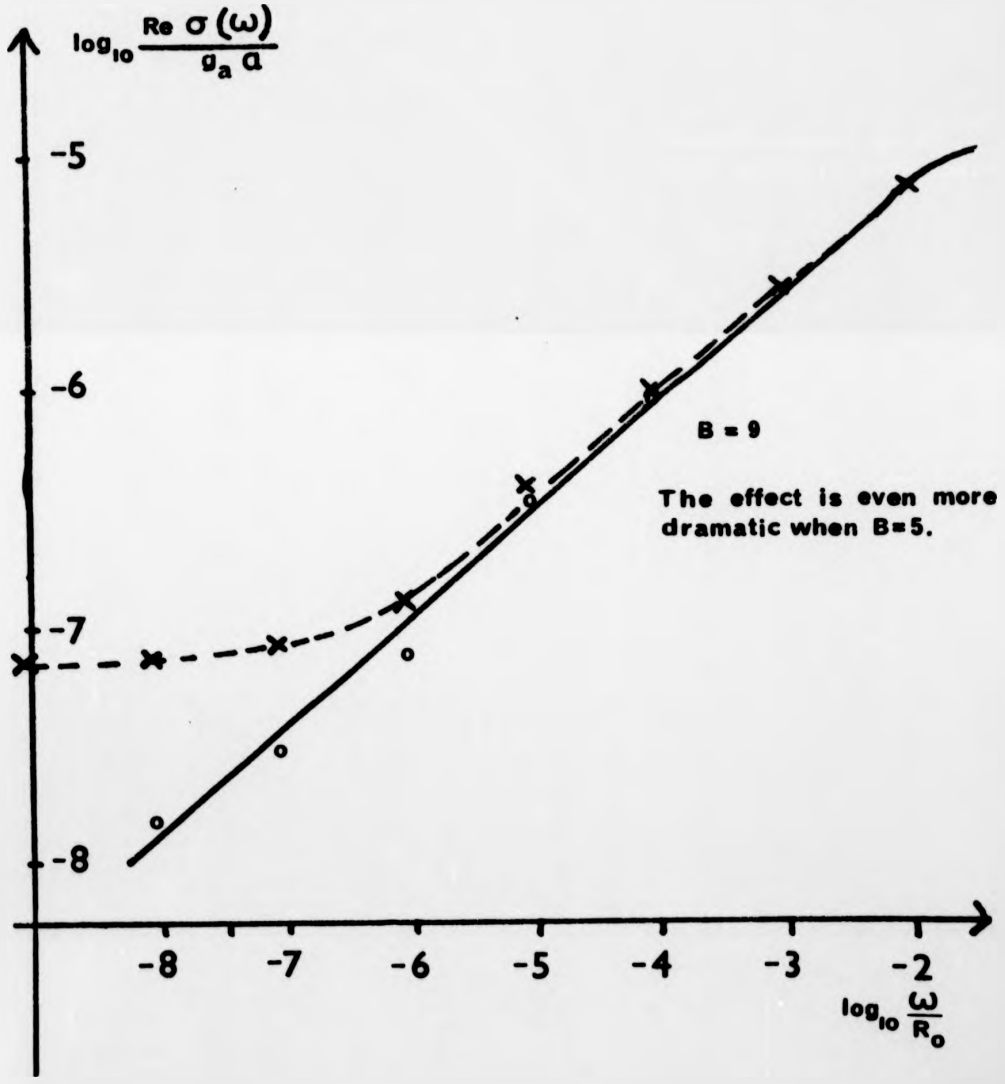


Figure 7.1: Log-log plot of $\sigma(\omega)$ vs ω/R_o (dashed line) and $[\sigma(\omega)-\sigma(0)]$ vs ω/R_o (solid line) deduced from figure 2.2b (data of McInnes, see McInnes, Butcher and Clark 1980). It is seen that Eqn (6.1) represents a reasonable approximation at low frequencies.

Experimental exploitation of this fact as a means of distinguishing mechanisms would be difficult and require prior refinement of the theories to include effects at the extinction electrode, where the pulse-widths manifest themselves.

It has been argued (Schmidlin 1980) that in ACPP one is concerned with hopping over long chains of sites whereas ac mobility is dominated by contributions from small clusters. But in the range of ω-values of interest in ACPP, 10^3 - 10^5 Hz, large clusters of sites still make a large contribution to the ac mobility in this frequency range (McInnes, Butcher and Clark 1980, Butcher and Clark 1980, Lakatos and Abkowtiz 1971, Mott and Davis 1979). It is only at much higher frequencies that the ac mobility is really dominated by contributions from small clusters.

7f. Thermal Equilibrium and Pulse Propagation

The essential difference between the treatments give here and by Schmidlin (1980) of hopping ACPP is that Schmidlin's carriers are out of thermal equlibrium, whereas the present work considers the carriers to have thermalised very soon after their creation. Discussion of this approximation therefore merits a section to itself.

Trap-controlled hopping may be redefined as hopping by carriers out of thermal equlibrium. Such hopping is not governed by the ac mobility, as is pointed out by Schmidlin (1980) but it is governed by the MPPE, with $\tilde{\mu}^{NE}(\omega)$ and $\tilde{D}^{NE}(\omega)$ appearing in it, as in eqn (4.33). This last fact is missed by Schmidlin who also believes that $\tilde{\mu}^{NE}(\omega)$ and $\tilde{D}^{NE}(\omega)$ are not governed by a pseudo-Einstein relation; it is argued in §4d that they are.

This immediately leads one to ask: are the pulses in thermal equilibrium during most of their transit or not? The disagreement between Schmidlin and the present work can only be resolved when the answer to this question is known. (Of course, the pulses are spatially localised and therefore not literally in thermal eqiuilibrium. What is not known is whether or not they are almost in equilibrium). Marshall (1980b) is currently addressing himself to this problem using computer simulations of non-isoenergetic hopping ACPP.

In view of the difficulty in interpreting ACPP experiments which is by now apparent, such computer simulations as those of Marshall (1978, 1980a,b), Marshall and Allan (1979) and Silver (1977) provide a valuable method of examining the behaviour of pulses. (Simulations of hopping conductivity by McInnes et al. (1977, 1978a,b,c, 1979, 1980) are similarly valuable as a means of testing approximations made in analytical theories).

If in a-Se the ACPP mechanism were trap-controlled hopping, a theory of this would have to account for the factor of 10^{14} difference between eqns (6.14) and (6.15). This suggests that it may be more fruitful to try trap-controlled band transport as a mechanism first. It remains to discover the mechanism in a-As_2 Se_3. Those arguments (Schmidlin 1977, Pfister and Scher 1977) which have been advanced to suggest that it is trap-controlled hopping are tentative and their confirmation or otherwise would be made possible by the development of a quantitative theory of trap-controlled hopping.

7g. Future Work

In view of the notorious changes in electrical behaviour from specimen to specimen of apparently the same amorphous material it would help to reinforce the conclusions of §§5d and 6d about ACPP and ac

conductivity measurements if such measurements were carried out on one and the same specimen. Sharp (1979, private communication) has measured ACPP and dc conductivity of a given specimen of a-As_2Se_3; it would be interesting to extend these measurements to include ac conductivity.

Experiments are beginning to reveal agreement between drift mobility and other phenomena. Troup, Mort, Grammatica and Sandman (1980) report agreement between drift mobility and dc conductivity measurements in a doped organic polymer (TTA/Lexan:Lexan is a trademark of General Electric Co.) arranged so that carriers hop between impurities. The present theory offers insight into the behaviour of such simplified systems, which perhaps provide a better "laboratory" for the study of hopping than the more complicated chalcogenide glasses.

In another system, a-Si:H, Noolandi, Hong and Street (1980) report agreement between measured dc drift mobility and that calculated from luminescence data using a model which assumes that the luminescence is due to radiative tunnelling between localised states just below the mobility edge. Refinement of these calculations may provide insight into transport processes in this material.

The question of the extent of thermal equilibrium in hopping pulses is central to the validity of the theory given in this thesis. It is discussed in the previous section. Should the pulses transpire to be well away from thermal equilibrium, a theory of trap-controlled hopping is called for. Production of such a theory could be based on eqn (4.35): Schmidlin (1980) refers to forthcoming work by himself on this difficult subject.

It still remains to discover why ac conductivity theories disagree with experiment.

7h. Conclusions

The Scher-Lax (1973) approximation to the rate equation formalism is soundly based. Reasons why it works so well are becoming clear. The formalism may be extended to describe hopping ACPP. Doubts are beginning to be cast on whether the rate equation formalism is sound.

In addition to hopping, trap-controlled hopping and trap-controlled band transport are commonly proposed ACPP mechanisms. The former is simply hopping by carriers out of thermal equilibrium.

In thermal equilibrium the behaviour of hopping pulses is governed by the ac mobility and hence the ac conductivity. This does not seem to be the case in chalcogenide glasses. Perhaps it would be better to confine ACPP studies to simpler systems until they have been advanced to a degree where they may be applied to chalcogenide glasses.

In any ACPP mechanism, the macroscopic pulse propagation equation of Butcher (1978) is valid, with suitable interpretation of $\tilde{D}(\omega)$ and $\tilde{\mu}(\omega)$, which are proportional via Einstein's relation.

Appendix A:

Methods of Evaluating Spatial Moments of Pulses

The m^{th} spatial moment of a distribution of carriers with number density n(x,t) per unit area is defined to be

$$\langle x^m(t)\rangle \equiv \frac{\int_{-\infty}^{\infty} dx\, x^m\, n(x,t)}{\int_{-\infty}^{\infty} dx\, n(x,t)} \qquad \text{(A1)}$$

for $t > 0$. If the pulse is created at $t = 0$ the moment is undefined for $t < 0$. Any factor $\theta(t)$, where θ is the unit step function, which appears in the value of a spatial moment may therefore be dropped. The denominator of eqn (A1) is then equal to n_o.

The Macroscopic Pulse propagation equation (MPPE) (1.31) for hopping pulses or for trap-controlled pulses is multiplied by x^m and integrated over x to yield

$$\frac{d\langle x^m(t)\rangle}{dt} = \frac{1}{n_o}\int_{-\infty}^{\infty} dx\, x^m \frac{\partial n(x,t)}{\partial t}$$

$$= \frac{1}{n_o}\int_{-\infty}^{\infty} dx\, x^m \int_{-\infty}^{\infty} d\tau \left[D(t-\tau)\frac{\partial^2 n(x,\tau)}{\partial x^2} - E\mu(t-\tau)\frac{\partial n(x,\tau)}{\partial x}\right] . \qquad \text{(A2)}$$

The standard spatial deviation

$$\sigma(t) \equiv \sqrt{\langle x^2(t)\rangle - \langle x(t)\rangle^2} \qquad \text{(A3)}$$

is interesting to calculate; it illustrates succinctly the spatial extent of the pulse.

Eqn (A2) will be used in two limits: pure drift in which the diffusion term is neglected; and pure diffusion when $E = 0$. The subscripts 'dr' and

'dif' are used to indicate the taking of the former and latter limit respectively. The contributions to $\sigma^2(t)$ of drift and diffusion add. When assessing their relative importance it is therefore sufficient to consider them separately. In what follows it will be supposed that as $x \to \pm \infty$, $n(x,t)$ and its spatial derivatives all tend to zero faster than any power of x.

Consider the pure-drift approximation. The first term in the square brackets of eqn (A2) is neglected. The remainder of that equation is integrated by parts over x with m = 1; the resulting equation, when Fourier transformed, yields

$$-i\omega \langle \tilde{x}(\omega) \rangle_{dr} = \frac{E\, \tilde{\mu}(\omega)}{-i\omega} \quad . \tag{A4}$$

The implied algebraic expression for $\langle \tilde{x}(\omega) \rangle$ is then directly inverse Fourier transformed to yield the value of $\langle x(t) \rangle_{dr}$. In order to obtain $\sigma_{dr}(t)$ it is necessary to know $\langle x^2(t) \rangle_{dr}$. This is found by similar means to $\langle x(t) \rangle_{dr}$; in eqn (A2) m is set equal to two. Then

$$\frac{d}{dt} \langle x^2 \rangle = - \frac{E}{n_o} \int_{-\infty}^{\infty} d\tau\ \mu(t-\tau) \int_{-\infty}^{\infty} dx\ x^2\, \frac{\partial n(x,\tau)}{\partial x}$$

$$= \frac{2E}{n_o} \int_{-\infty}^{\infty} d\tau\ \mu(t-\tau) n_o\ \langle x(\tau) \rangle \tag{A5}$$

after integrating by parts once over x. From the Fourier transform of eqn (A5) it follows that

$$\langle \tilde{x}^2(\omega) \rangle_{dr} = \frac{2E\ \tilde{\mu}(\omega) \langle \tilde{x}(\omega) \rangle}{-i\omega} \quad . \tag{A6}$$

This equation is then directly inverse-transformed. The result, together with the square of $\langle x(t) \rangle_{dr}$, is substituted into eqn (A3): this yields $\sigma_{dr}(t)$.

Let us now turn to pure diffusion and set E = 0 in eqn (A2). The first moment is easily seen to vanish as one would expect since the system is now symmetrical in x. From eqn (A2)

$$\frac{d\langle x^2(t)\rangle_{dif}}{dt} = \frac{1}{n_o}\int_{-\infty}^{\infty} d\tau\ D(t-\tau) \int_{-\infty}^{\infty} dx\ x^2\ \frac{\partial^2 n(x,\tau)}{\partial x^2}$$

$$= 2\int_{-\infty}^{\infty} d\tau\ D(t-\tau)\ \theta(t) \qquad \text{(A7)}$$

after integrating by parts over x twice. Eqn (A7) is Fourier transformed to yield

$$-i\omega\ \langle \tilde{x}^2(\omega)\rangle_{dif} = \frac{2\tilde{D}(\omega)}{-i\omega} \quad ; \qquad \text{(A8)}$$

Eqn (A8) is now inverse Fourier transformed to give $\langle x^2(t)\rangle_{dif}$. Clearly

$$\sigma^2_{dif}(t) = \langle x^2(t)\rangle_{dif} \quad . \qquad \text{(A9)}$$

It is interesting to note that $\sigma^2_{dif}(t)$ has the same form as $\langle x(t)\rangle_{dr}$ regardless of model used. This of course is a well known result in the conventional case: it generalises to anomalous carrier pulse propagation.

The conventional drift-diffusion results quoted in chapter 1 may be obtained by setting $\mu(t) = \mu_o\delta(t)$ and $D(t) = D_o\delta(t)$ so that $\tilde{\mu}(\omega) = \mu_o$ and $\tilde{D}(\omega) = D_o$. In the anomalous cases discussed in chapters 3, 5 and 6 use must be made of the Fourier transform of t^{p-1}, $p > 1$. ω is taken to lie in the upper-half plane to ensure convergence. If we restrict ourselves to positive values of t,

$$\int_{-\infty}^{\infty} \theta(t)\ t^{p-1}\ e^{i\omega t}\ dt = \frac{1}{(-i\omega)^p} \int_0^{\infty} dz\ z^{p-1}\ e^{-z}$$

$$= \frac{\Gamma(p)}{(-i\omega)^p} \qquad \text{(A10)}$$

where $z = -i\omega t$ and $\mathrm{Re}\ z > 0$. It follows that the inverse Fourier transform of $(-i\omega)^p$ is $\theta(t)t^{p-1}/\Gamma(p)$.

In the main text $\langle x(t)\rangle_{dr}$ is referred to as the shift of the pulse and $\sigma_{dr}(t)$ as the spread. Neither quantity contains any effect due to diffusion: together they indicate the velocity and spatial extent respectively of the pulse due to the drift term alone.

Appendix B:

Rigorous Treatment of long-time Behaviour of Trap-Controlled Pulses

This problem is treated heuristically in §3c. A less transparent but more rigorous derivation of the same results is now given. Eqn (3.6) for $\tilde{Q}(\omega)$ may be rewritten

$$\tilde{Q}(\omega) = \frac{\prod_{j=1}^{N} (\rho_j - i\omega)}{\prod_{j=1}^{N} (\rho_j - i\omega) + \sum_{j=1}^{N} C_j \left\{ \prod_{m \neq j} (\rho_m - i\omega) \right\}}$$

$$= \frac{P_N^{(1)}(\omega)}{P_N^{(2)}(\omega)} \quad . \tag{B1}$$

$P_M^{(i)}(\omega)$ is shorthand for a polynomial in ω of degree M : i labels particular polynomials. In this case it is obvious by inspection of eqn (B1) which polynomials are meant. Substitution of eqn (B1) via eqn (3.6) into eqn (A4) yields

$$(-i\omega)\langle \tilde{x}(\omega) \rangle_{dr} = \mu_f E \frac{P_N^{(1)}(\omega)}{P_{N+1}^{(3)}(\omega)} \tag{B2}$$

where

$$P_{N+1}^{(3)}(\omega) = (-i\omega)\, P_N^{(2)}(\omega) \quad . \tag{B3}$$

It is convenient to define α_k as minus the k^{th} root of $P_{N+1}^{(3)}(\omega)$ and

$$A_k \equiv P_N^{(1)}(\alpha_k) \left[\frac{d}{d\omega} P_{N+1}^{(3)}(\omega) \right] = \text{constant.} \tag{B4}$$

The first value of α_k, $\alpha_1 = 0$. Spiegel (1965, p.61) shows that the inverse Fourier transform of eqn (B2) is

$$\frac{d\langle x(t)\rangle_{dr}}{dt} = \mu_f E\theta(t)\left[A_1 + \sum_{k=2}^{N} A_k\, e^{-\alpha_k t}\right] \qquad \text{(B5)}$$

where the unit step function $\theta(t)$ may be dropped as explained in Appendix A. Spiegel in fact proves this relation for Laplace transforms but if ω has a small positive-imaginary part the proof he gives is very easily generalised. At very large times eqn (B5) gives

$$\langle x(t)\rangle_{dr} = \mu_f E A_1 t \propto t \quad . \qquad \text{(B6)}$$

The spread of the pulse is evaluated using the technique of Appendix A. Eqn (A6) becomes

$$(-i\omega)\ \langle \tilde{x}^2(\omega)\rangle_{dr} = 2(\mu_f E)^2 \left[\frac{P_N^{(1)}(\omega)}{P_{N+1}^{(3)}(\omega)}\right]^2 \quad . \qquad \text{(B7)}$$

Eqn (B7) is most easily inverse Fourier transformed by direct evaluation of the convolution of the term in square brackets with itself. The effect of the $\theta(t)$ in eqn (B5) is to make the convolution effectively finite. Then

$$\frac{d\langle x^2(t)\rangle_{dr}}{dt} = 2(\mu_f E)^2 \int_0^t d\tau \left[A_1 + \sum_{m=2}^{N+1} A_m e^{-\alpha_m \tau}\right]\left[A_1 + \sum_{k=2}^{N+1} A_k e^{-\alpha_m (t-\tau)}\right]$$

$$= 2(\mu_f E)^2 \int_0^t d\tau \left[A_1^2 + A_1 A_j e^{-\alpha_j \tau} + \ldots + A_1 A_j e^{-\alpha_j (t-\tau)} + \ldots\right.$$

$$+ A_k A_\ell e^{-(\alpha_k - \alpha_\ell)t}\, e^{(\alpha_k - \alpha_\ell)\tau} + \ldots.$$

$$\left. + A_m^2\, e^{-\alpha_m t} + \ldots.\right]$$

$$= 2(\mu_f E)^2\left[A_1^2 t + \ldots + \frac{2A_1A_j}{\alpha_j}(1-e^{-\alpha_j t}) + \ldots.\right.$$

$$\ldots. + \frac{A_kA_\ell}{\alpha_k-\alpha_\ell}(e^{-\alpha_\ell t} - e^{-\alpha_k t}) + \ldots..$$

$$\left. + \frac{A_m^2}{\alpha_m}(1-e^{-\alpha_m t}) + \ldots..\right] \qquad \text{(B8)}$$

where $k \neq \ell$. It immediately follows that

$$\langle x^2(t)\rangle_{dr} = 2(\mu_f E)^2\left[\frac{A_1^2 t^2}{2} + \ldots + \frac{2A_1A_j}{\alpha_j^2}(\alpha_j t + e^{-\alpha_j t} - 1) + \ldots..\right.$$

$$+ \frac{A_kA_\ell}{(\alpha_k-\alpha_\ell)\alpha_k\alpha_\ell}\left[\alpha_k(1-e^{-\alpha_\ell t}) - \alpha_\ell(1-e^{-\alpha_k t})\right]$$

$$\left. + \ldots + \frac{A_m^2}{\alpha_m^2}(\alpha_m t + e^{-\alpha_m t} - 1) + \ldots..\right] \qquad \text{(B9)}$$

Use of eqns (B9), (B6) and (A3) yield a spread

$$\sigma_{dr}(t) = \text{const} \times \mu_f E t^{\frac{1}{2}} \qquad \text{(B10)}$$

as $t \to \infty$. This is precisely what one would expect for gaussian pulses.

Appendix C:

Fourier Transform Conventions Used

A quantity in $\underset{\sim}{x}$t-space might be $f(\underset{\sim}{x},t)$. The following Fourier transforms of $f(\underset{\sim}{x},t)$ are defined.

$$\tilde{f}(\underset{\sim}{x},\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t}\, f(\underset{\sim}{x},t) \quad . \tag{C1}$$

$$F(\underset{\sim}{k},t) = \iiint_{-\infty}^{\infty} d^3\underset{\sim}{x}\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{x}}\, f(\underset{\sim}{x},t) \quad . \tag{C2}$$

$$\tilde{F}(\underset{\sim}{k},\omega) = \iiint_{-\infty}^{\infty} dt\, d^3\underset{\sim}{x}\, e^{-i(\underset{\sim}{k}\cdot\underset{\sim}{x}-\omega t)}\, f(\underset{\sim}{x},t) \quad . \tag{C3}$$

It is seen that a small letter denotes $\underset{\sim}{x}$-space, a capital letter denotes $\underset{\sim}{k}$-space, a tilde ($\sim$) denotes ω-space and its absence denotes t-space. If $f(t)$ were a function of t only and thus $\tilde{f}(\omega)$ a function of ω only it would not matter whether f were a lower case letter or an upper case one.

ω is given a small positive imaginary part to ensure convergence. When such functions as $(-i\omega)^{1-\alpha}$, which would not be analytic unless the ω-plane is cut, occur, the ω-plane is given a branch cut along the negative imaginary axis.

Fourier transforms (C1) where $f(\underset{\sim}{x},t)$ is multiplied by the unit step function $\theta(t)$ are called causal Fourier transforms.

It will sometimes be necessary to take Fourier transforms of qunatities defined on lattices. If the lattice is simple-cubic and has N^3 sites and

periodic boundary conditions, write

$$f(\underset{\sim}{s}) = N^{-3} \sum_{\underset{\sim}{k}} F(\underset{\sim}{k})\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{s}} \quad , \tag{C4}$$

where $f(\underset{\sim}{s})$ is defined on a lattice of sites $\underset{\sim}{s}$ and its Fourier transform $F(\underset{\sim}{k})$ on its reciprocal lattice of sites $\underset{\sim}{k}$, also simple-cubic. Then

$$\begin{aligned} \sum_{\underset{\sim}{s}} f(\underset{\sim}{s})\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{s}} &= N^{-3} \sum_{\underset{\sim}{s},\underset{\sim}{k}'} F(\underset{\sim}{k}')\, e^{i(\underset{\sim}{k}'-\underset{\sim}{k})\cdot\underset{\sim}{s}} \\ &= N^{-3} \sum_{\underset{\sim}{k}'} F(\underset{\sim}{k}')\, N^3 \delta_{\underset{\sim}{k}'\underset{\sim}{k}} \\ &= F(\underset{\sim}{k}) \quad . \end{aligned} \tag{C5}$$

The delta is Kronecker's symbol. Now suppose

$$c(\underset{\sim}{s}) = \sum_{\underset{\sim}{s}'} f(\underset{\sim}{s}-\underset{\sim}{s}')\, g(\underset{\sim}{s}') \quad .$$

Then

$$\begin{aligned} C(\underset{\sim}{k}) &= \sum_{\underset{\sim}{s}} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{s}} \sum_{\underset{\sim}{s}'} e^{i\underset{\sim}{k}\cdot\underset{\sim}{s}'}\, f(\underset{\sim}{s}-\underset{\sim}{s}')\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{s}'}\, g(\underset{\sim}{s}') \\ &= \sum_{\underset{\sim}{s}''} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{x}}\, f(\underset{\sim}{s}'') \sum_{\underset{\sim}{s}'} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{s}'}\, g(\underset{\sim}{s}') \\ &= F(\underset{\sim}{k})G(\underset{\sim}{k}) \quad . \end{aligned} \tag{C6}$$

The convolution theorem for Fourier transforms on lattices is thus established

Appendix D:

Formal Expression for the ac Diffusivity $\tilde{D}(\omega)$ found by Scher and Lax

The starting point is the expression (1.18) for $\tilde{D}(\omega)$, namely

$$\tilde{D}(\omega) = \int_0^\infty dt\ e^{i\omega t} \langle v(t)v(o)\rangle \ . \tag{D1}$$

Define

$$\Delta(t) \equiv \langle\{x(t) - x(o)\}^2\rangle$$

$$= \langle\{\int_0^t v(\tau)d\tau\}^2\rangle \quad . \tag{D2}$$

It is assumed that the carriers exhibit stationary statistics so that the velocity autocorrelation function

$$c(\tau) \equiv \langle v(t+\tau)v(t)\rangle \tag{D3}$$

depends only on τ. It is therefore symmetric in τ. It is clear from eqn (D1) that $\tilde{D}(\omega)$ is the Fourier transform of $\theta(\tau)c(\tau)$ where $\theta(\tau)$ is the unit step function. The Fourier Transform convention of Appendix C is used. Now

$$\Delta(t) = \int_0^t d\tau \int_0^t d\tau'\ c(\tau-\tau')$$

$$= 2\int_0^t d\tau \int_0^\tau d\tau'\ c(\tau-\tau') \tag{D4}$$

therefore

$$\frac{d^2}{dt^2}\Delta(t) = 2c(t) \quad . \tag{D5}$$

It immediately follows that

$$\tilde{D}(\omega) = \frac{1}{2}\int_0^\infty dt\, \frac{d^2}{dt^2}\Delta(t)\, e^{i\omega t}$$

$$= -\frac{\omega^2}{2}\int_0^\infty dt\, e^{i\omega t}\,\Delta(t)$$

$$= -\frac{\omega^2}{6}\int_0^\infty dt\, e^{i\omega t}\,\langle\{\underset{\sim}{r}(t) - \underset{\sim}{r}(o)\}^2\rangle \qquad \text{(D6)}$$

since $\Delta(0)$ and $d\Delta(0)/dt = 0$. Eqn (D6) reduces the problem to one of calculating $\langle\{\underset{\sim}{r}(t)-\underset{\sim}{r}(o)\}^2\rangle$. This is now done for the Scher and Lax (1973) model of a non-markovian random walk on a simple-cubic lattice of sites, with lattice constant a, labelled by position vector $\underset{\sim}{s}$. The relationship of this system to a disordered semiconductor is discussed in Chapter 2, where it is pointed out that in order to obtain a meaningful relationship, the random walk is considered to start with a carrier known to be on site $\underset{\sim}{s}_o$ at time $t = 0^+$. Let $P(\underset{\sim}{s},t|\underset{\sim}{s}_o,0)$ be the probability that such a carrier is on site $\underset{\sim}{s}$ at time t. This has causal Fourier transform $\hat{P}(\underset{\sim}{s},\omega;\underset{\sim}{s}_o)$ (see Appendix C). If $f(\underset{\sim}{s}_o)$ is the probability of $\underset{\sim}{s}_o$ being the initial site eqn (D6) becomes

$$\tilde{D}(\omega) = -\frac{\omega^2}{6}\sum_{\underset{\sim}{s},\underset{\sim}{s}_o} f(\underset{\sim}{s}_o)(\underset{\sim}{s}-\underset{\sim}{s}_o)^2\,\hat{P}(\underset{\sim}{s},\omega;\underset{\sim}{s}_o) \qquad \text{(D7)}$$

Eqn (D7) is a discrete expression for $\tilde{D}(\omega)$. The lattice of sites is taken to have N^3 sites (where N is very large) and periodic boundary conditions. As in section 2, let $R_n(\underset{\sim}{s},t)$ be the probability per unit time that a carrier <u>just arrives</u> at $\underset{\sim}{s}$ during time $t \to t + \Delta t$ in r steps if it was at $\underset{\sim}{s}_o = 0$ at $t = 0^+$. For $n \geq 2$, R_n satisfies eqn (2.4),

namely

$$R_n(\underset{\sim}{\ell},t) = \sum_{\underset{\sim}{\ell}'} \int_0^t d\tau\ \psi(\underset{\sim}{\ell}-\underset{\sim}{\ell}',t-\tau)R_n(\underset{\sim}{\ell}',\tau) \qquad \text{(D8)}$$

where $\psi(\underset{\sim}{\ell}-\underset{\sim}{\ell}',t-\tau)$ is the probability per unit time that a carrier which arrived on the site at $\underset{\sim}{\ell}'$ at time τ jumping to site at $\underset{\sim}{\ell}$ at time t. It is also convenient to define $h(\underset{\sim}{\ell}-\underset{\sim}{\ell}',t-\tau)$, the probability per unit time that a carrier, which was observed to be on the site at $\underset{\sim}{\ell}'$ at time τ, will jump onto the site at $\underset{\sim}{\ell}$ at time t. The boundary condition that the carrier be on site $\underset{\sim}{\ell} = 0$ at $t = 0^+$ is expressed as

$$R_o = \delta_{\underset{\sim}{\ell},o}\ \delta(t-0^+) \qquad \text{(D9)}$$

(though R_o is not a probability of just arriving the symbol R_o is still used). The first delta is the Kronecker symbol, the second a Dirac delta function. The first jumpcannot be treated using eqn (D8) but rather

$$R_1(\underset{\sim}{\ell},t) = \sum_{\underset{\sim}{\ell}'} \int_0^t d\tau\ h(\underset{\sim}{\ell}-\underset{\sim}{\ell}',t-\tau)R_o(\underset{\sim}{\ell}',\tau) = h(s,t) \quad . \qquad \text{(D10)}$$

Eqn (D9) has been used to obtain the last step of eqn (D10). It is convenient to introduce the generating function

$$R(\underset{\sim}{\ell},t,z) \equiv \sum_{n=o}^{\infty} z^n R_n(\underset{\sim}{\ell},t) \quad . \qquad \text{(D11)}$$

$R(\underset{\sim}{\ell},t,1)$ is the probability that a carrier just reaches $\underset{\sim}{\ell}$ at time t. Eqn (D8) is multiplied by z^n and summed over n to yield, with the help of eqns (D9)-(D11),

$$R(\underset{\sim}{\ell},t,z) - z \sum_{\underset{\sim}{\ell}'} \int_0^t d\tau\ \psi(\underset{\sim}{\ell}-\underset{\sim}{\ell}',t-\tau)R(\underset{\sim}{\ell},t,z) = \delta_{\underset{\sim}{\ell},o}\delta(t-0^+) + z[h(\underset{\sim}{\ell},t)-\psi(\underset{\sim}{\ell},t)] \qquad \text{(D12)}$$

The causal Fourier transform of this equation into ω-space is

$$\tilde{R}(\underset{\sim}{s},\omega,z) - z \sum_{\underset{\sim}{s}'} \tilde{\psi}(\underset{\sim}{s}-\underset{\sim}{s}',\omega)\tilde{R}(\underset{\sim}{s},\omega,z) = \delta_{\underset{\sim}{s},o} + z[\tilde{h}(\underset{\sim}{s},\omega)-\tilde{\psi}(\underset{\sim}{s},\omega)] \quad . \tag{D13}$$

A discrete Fourier transformation into $\underset{\sim}{k}$-space, using the convention of Appendix C is made in which $\hat{\tilde{U}}(\underset{\sim}{k},\omega,z)$, $\hat{\tilde{\psi}}(\underset{\sim}{k},\omega)$ and $\hat{\tilde{H}}(\underset{\sim}{k},\omega)$ are the Fourier transforms of $\tilde{R}(\underset{\sim}{s},\omega,z)$, $\tilde{\psi}(\underset{\sim}{s},\omega)$ and $\tilde{h}(\underset{\sim}{s},\omega)$ respectively. Then

$$\hat{\tilde{U}}(\underset{\sim}{k},\omega,z)\left[1 - z\hat{\tilde{\psi}}(\underset{\sim}{k},z)\right] = 1 + \left[\hat{\tilde{H}}(\underset{\sim}{k},\omega) - \hat{\tilde{\psi}}(\underset{\sim}{k},\omega)\right] \quad . \tag{D14}$$

Equation (D14) is very easily solved for $\hat{\tilde{U}}(\underset{\sim}{k},\omega,z)$.

Changing tack somewhat,

$$P(\underset{\sim}{s},t|0,0) = \int_0^t R(\underset{\sim}{s},\tau,1)\phi(t-\tau)d\tau \tag{D15}$$

where

$$\phi(t) = 1 - \int_0^t \psi(t')dt' \tag{D16}$$

where

$$\psi(t) = \sum_{\underset{\sim}{s}} \psi(\underset{\sim}{s},t) \tag{D17}$$

Similarly, let

$$h(t) = \sum_{s} h(s,t) \tag{D18}$$

$\phi(t)$ is the probability that a carrier which hopped onto a given site will remain there until at least time t. The causal Fourier transforms of eqns (D15)-(D18) are taken to yield $\hat{P}(s,\omega;1)$, $\tilde{\phi}(\omega)$, $\tilde{\psi}(\omega)$ and $\tilde{h}(\omega)$ respectively where

$$\tilde{\psi}(\omega) = 1 + i\omega\tilde{\phi}(\omega) \tag{D19}$$

and

$$\tilde{P}(\underset{\sim}{s},\omega;1) = \tilde{R}(\underset{\sim}{s},\omega,1)\left[\frac{1-\tilde{\psi}(\omega)}{-i\omega}\right] \quad . \tag{D20}$$

Eqn (D20) may now be inserted into eqn (D7) to give

$$\tilde{D}(\omega) = -\frac{\omega^2}{6}\left[\frac{1-\tilde{\psi}(\omega)}{-i\omega}\right]\sum_{\underset{\sim}{s}} \underset{\sim}{s}\cdot\underset{\sim}{s}\,\tilde{R}(\underset{\sim}{s},\omega,1) \quad . \tag{D21}$$

It remains to evaluate the sum in eqn (D21). This is most easily done by noting from eqn (C5) that

$$\sum_{\underset{\sim}{s}} s^2\, R(\underset{\sim}{s},\omega,1) = -\nabla_{\underset{\sim}{k}}^2\,\tilde{U}(\underset{\sim}{k},\omega,1)\big|_{\underset{\sim}{k}=0} \tag{D22}$$

where $\tilde{U}(\underset{\sim}{k},\omega,1)$ is taken from eqn (D14). Symmetry causes both $\nabla_{\underset{\sim}{k}}\tilde{\Psi}(\underset{\sim}{k},\omega)\big|_{k=0}$ and $\nabla_{\underset{\sim}{k}}\tilde{H}(\underset{\sim}{k},\omega)\big|_{k=0}$ to vanish but the second derivatives are nonzero at the origin in $\underset{\sim}{k}$-space. The surviving terms in eqn (D22) are therefore

$$-\nabla_{\underset{\sim}{k}}^2\tilde{U}(0,\omega,1) =$$

$$\frac{-\{[1-\tilde{\Psi}(0,\omega)]\,\nabla_{\underset{\sim}{k}}^2\,[\tilde{H}(0,\omega)-\tilde{\Psi}(0,\omega)] + [1+\tilde{H}(0,\omega)-\tilde{\Psi}(0,\omega)]\nabla_{\underset{\sim}{k}}^2\,\tilde{\Psi}(0,\omega)\}}{[1-\tilde{\Psi}(0,\omega)]^2}$$

$$- \text{ vanishing terms.} \tag{D23}$$

Eqn (C5) is again used to show that

$$-\nabla_{\underset{\sim}{k}}^2\,\tilde{\Psi}(0,\omega) = \sum_{\underset{\sim}{s}} s^2\tilde{\psi}(\underset{\sim}{s},\omega) \tag{D24}$$

and

$$-\nabla_{\underset{\sim}{k}}^2\,\tilde{H}(0,\omega) = \sum_{\underset{\sim}{s}} s^2\tilde{h}(\underset{\sim}{s},\omega) \quad . \tag{D25}$$

Using eqns (D17) and (D18) it is seen that $\tilde{H}(0,\omega) = \tilde{h}(\omega)$ and $\tilde{\Psi}(0,\omega) = \tilde{\psi}(\omega)$. A final fact is now all that is needed to simply the formal expression for $\tilde{D}(\omega)$. The mean-square distance $\tilde{\sigma}^2_{rms}(\omega)$ hopped in the first jump cannot differ from that of subsequent jumps, so

$$\tilde{\sigma}^2_{rms}(\omega) = \frac{\sum_{\underline{\ell}} s^2 \tilde{\psi}(\underline{\ell},\omega)}{\tilde{\psi}(\omega)} = \frac{\sum_{\underline{\ell}} s^2 \tilde{h}(\underline{\ell},\omega)}{\tilde{h}(\omega)} \quad . \tag{D26}$$

Substitution of eqns (D26), (D25), (D24), (D23) and (D22) into eqn (D21) yields

$$\tilde{D}(\omega) = \frac{\tilde{\sigma}^2_{rms}(\omega)}{6} \left[\frac{-i\omega\tilde{h}(\omega)}{1-\tilde{\psi}(\omega)}\right] . \tag{D27}$$

This is the expression found by Tunaley (1974). It is not quite the result of Scher and Lax (1973): these authors put $\tilde{h}(\omega)$ equal to $\tilde{\psi}(\omega)$. The justification for doing this is discussed in section 2b.

Appendix E:

Practical Calculation of Conductivity using the Formalism of Scher and Lax

One imagines localised states randomly distributed among the lattice sites. Most sites are unoccupied by such states and may therefore not be visited by the charge carriers. The lattice itself is unphysical and merely a computational aid. The rate of hopping between sites separated by a distance $\underset{\sim}{r}$ is given by eqn (2.24)

i.e.

$$W(\underset{\sim}{r}) = R_o(\alpha r)^{\nu} e^{-2\alpha r} \quad . \tag{E1}$$

The conductivity is calculated using the ac Einstein relation (2.1), with $\tilde{D}(\omega)$ taken from eqn (2.5), i.e. eqn (D27) with $\tilde{h}(\omega) = \tilde{\psi}(\omega)$. In order to use eqn (D27) two contacts are made between this equation and real disordered semiconductors. The first is to make an approximation to $\tilde{\sigma}^2_{rms}(\omega)$; the second is to make an approximation to $\tilde{\psi}(\omega)$. Both will be done in such a manner as to be valid at low frequencies.

$\tilde{\sigma}^2_{rms}(\omega)$ is replaced by a constant, namely $\tilde{\sigma}^2_{NN}$, the mean square distance between nearest neighbours in a spatially random array of N_s localised states enclosed in a volume τ. Now the probability of there being no neighbour to such a state within a radius r is

$$P_A = \left(1 - \frac{4\pi r^3}{3\tau}\frac{N_s}{N_s}\right)^{N_s} \simeq e^{-\frac{4\pi n_s r^3}{3}} \tag{E2}$$

if N_s is very large and $n_s = N_s/\tau$, which is a finite quantity. This relation is easily verified by remembering that the probability of finding a given site within a radius r is $4\pi r^3/3\tau$; the probability of finding it

elsewhere in volume τ is $(1 - 4\pi r^3/3\tau)$. The sites are distributed independently of each other so P_A is found by raising the quantity in brackets to the power N_s - hence eqn (E2). The probability of finding one of N_s sites in a shell of radius $r \to r + dr$ is

$$P_B = 4\pi n_s r^2 dr. \tag{E3}$$

The probability of the nearest neighbour being in this shell is

$$P_{NN}(r)dr = P_A P_B = 4\pi n_s r^2 \, e^{-\frac{4\pi n_s r^3}{3}} \, dr. \tag{E4}$$

The mean square nearest neighbour separation is therefore

$$\sigma_{NN}^2 = 3\beta_1 \int_o^\infty r^4 \, e^{-\beta_1 r^3} \, dr$$

$$= \beta_1^{-2/3} \int_o^\infty X_1^{2/3} \, e^{-X_1} \, dX_1$$

$$= \Gamma(5/3)(3/4\pi n_s)^{2/3} = 0.3474 \, n_s^{-2/3}, \tag{E5}$$

where $\beta_1 = 4\pi n_s/3$ and $X_1 = \beta_1 r^3$. This approximation will clearly fail at densities so high that hops to the nearest localised state are not significantly preferred. It will also fail at very high frequencies when the conductivity comes mostly from a minority of carriers hopping between unusually close states. Its validity at low frequencies and densities is discussed in section 2d.

The second quantity obtained from considering real systems is $\tilde{\psi}(\omega)$. For reasons explained in section 2b, $\tilde{h}(\omega)$ is put equal to $\tilde{\psi}(\omega)$ in eqn (2.5). Actually it is easier to evaluate $\tilde{\phi}(\omega)$, related to $\tilde{\psi}(\omega)$ by eqn (D19), i.e.

$$\tilde{\psi}(\omega) = 1 + i\omega\tilde{\phi}(\omega) = \tilde{h}(\omega) \tag{E6}$$

where the inverse causal Fourier transform of $\tilde{\phi}(\omega)$, $\phi(t)$, is the probability that a carrier which hopped onto some lattice site at t = 0 will not have hopped away at time t. Scher and Lax (1973) evaluate the configuration average of $Q_\ell(t)$, the probability that a carrier which hopped onto site ℓ will remain there for at least time t without hopping away, if ℓ is one of a random network of sites. The causal Fourier transform of this configuration average is then substituted for $\tilde{\phi}(\omega)$. This is equivalent to rerandomising the sites after every hop, a point discussed in Chapter 2, section 2d.

Consider a real localised state ℓ. The probability that a carrier which hopped onto it at time t = 0 will still be there at time t

$$Q_\ell(t) = \exp\left[-\sum_{j\neq\ell} W(\underline{r}_j-\underline{r}_\ell)t\right] \tag{E7}$$

with W given by eqn (E1). This obviously depends on ℓ. An isolated site is more likely to retain carriers than one with many close neighbours. Equations (E7) and (2.14) are identical. The configuration average of $Q_\ell(t)$ is easily found by the method of Thomas, Hopfield and Augustinyak (1965) to be, for very large N_s + finite N_s/τ,

$$\begin{aligned}
\langle Q(t)\rangle &= \tau^{-N_s}\int_\tau\cdots\int_\tau \exp\left[-t\sum_j W(\underline{r}_j)\right] d^3\underline{r}_1\cdots d^3\underline{r}_{N_s} \\
&= \left[\frac{1}{\tau}\int_\tau d^3\underline{r}\left[1+\left\{\exp\left[-tW(\underline{r})\right]-1\right\}\right]\right]^{N_s} \\
&= \left[1+\frac{N_s}{\tau N_s}\int_\tau d^3\underline{r}\,\{e^{-W(\underline{r})t}-1\}\right]^{N_s} \\
&\simeq \exp\left[-\frac{N_s}{\tau}\int_\tau d^3\underline{r}\,\{1-e^{-W(\underline{r})t}\}\right] .
\end{aligned} \tag{E8}$$

The subscript ℓ on $\langle Q_\ell(t)\rangle$ has been dropped to save writing. Since $W(\underline{\chi})$ varies rapidly with $|\underline{\chi}|$, Scher and Lax (1973) take

$$1 - e^{-tW(\underline{\chi})} = \begin{cases} 1 \text{ if } Wt > e^{\gamma} \\ 0 \text{ if } Wt < e^{\gamma} \end{cases} \tag{E9}$$

where $\gamma = 0.5772$ is Euler's constant (Whittaker and Watson 1940). $e^{\gamma} = 1.718$. Eqn (E8) becomes

$$\langle Q(t)\rangle \simeq \exp\left[-4\pi n_s \int_0^{x_2} r^2 dr\right]$$

$$= \exp\left(\frac{-4\pi n_s x_2^3}{3}\right) \tag{E10}$$

where x_2 is the value of $|\underline{\chi}|$ in eqn (E9) at which the left-hand-side changes from 0 to 1. In fact two values of x_2 could satisfy

$$W(x_2)t = e^{\gamma} \tag{E11}$$

when W is taken from eqn (E1): the larger is chosen (see figure E1). For small t, no x_2 will satisfy eqn (E11); eqn (E9) therefore gives a large time approximation to $\langle Q(t)\rangle$. The causal Fourier transform $\langle \hat{Q}(\omega)\rangle$ so generated is thus a low frequency approximation. This $\langle \hat{Q}(\omega)\rangle$ is the desired quantity: it is substituted into eqn (E6) giving

$$\hat{\psi}(\omega) = 1 + i\omega \langle \hat{Q}(\omega)\rangle \quad . \tag{E12}$$

Substitution of eqns (E12) and (E5) into eqn (D27) then yields a diffusivity

$$\hat{D}(\omega) = 0.0579\, n_s^{-2/2} \left[\frac{1}{\langle \hat{Q}(\omega)\rangle} + i\omega\right] \quad . \tag{E13}$$

$\langle \hat{Q}(\omega)\rangle$ remains to be evaluated. This is done from eqn (E10):

$$\langle \hat{Q}(\omega)\rangle = \int_{t_m}^{\infty} dt \, \exp\left[\frac{4\pi n_s x_2^3}{3} + i\omega t\right] \tag{E14}$$

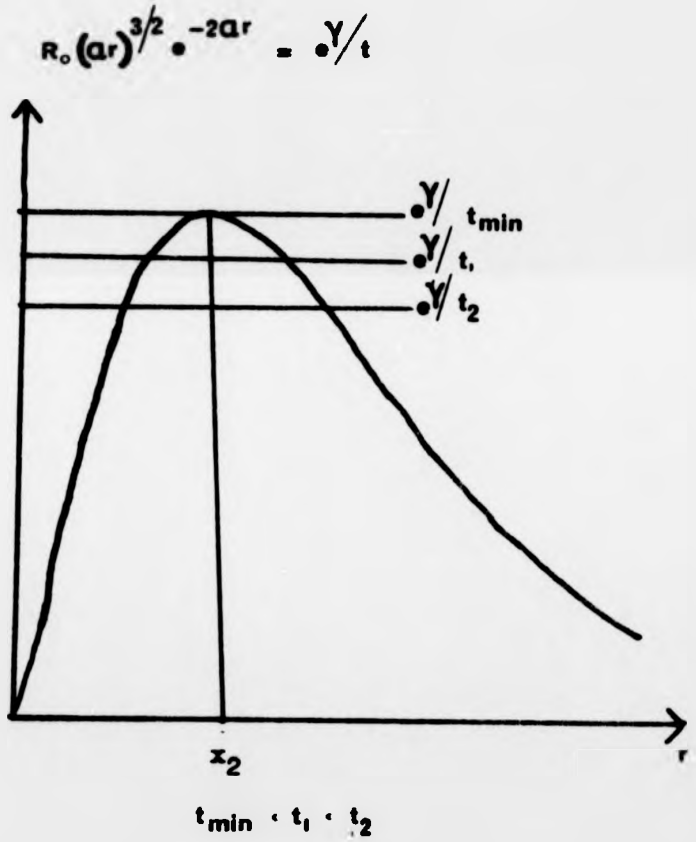


Figure E1: Solutions of eqn (E11), to deduce t_{min}.

where t_m is the lowest t capable of satisfying eqns (E1) and (E11). Let x_m be the corresponding value of x_2 (see figure E1 in which $t_2 > t_1 > t_m$). This occurs when $W(x_2)$ maximises, i.e.

$$W'(x_2) = 0 \quad . \tag{E15}$$

Substitute, from eqn (E11),

$$dt = \frac{-W'(x_2)dx_2}{W^2(x_2)e^{\gamma}} \quad . \tag{E16}$$

Re-express eqn (E1) as

$$W(x_2) = R_o\, e^{-s(x_2)} \tag{E17}$$

where

$$s(x_2) = 2\alpha x_2 - \nu \ell n\, \alpha x_2 \quad . \tag{E18}$$

Then

$$\langle \tilde{Q}(\omega) \rangle = \frac{1}{R_o e^{\gamma}} \int_{\frac{1}{2}\nu}^{\infty} dx_2\; s'(x_2)\; \exp\left[\frac{-4\pi n_s x_2^3}{3} + \frac{i\omega e^{s(x_2)}}{R_o e^{\gamma}} + s(x)\right] \tag{E19}$$

The lower limit, $\frac{1}{2}\nu = x_m$. In order to save writing, let $y = \alpha x_2$ and

$$f(y) = 2y + \frac{i\Omega e^{2y}}{y^{\nu}} - \frac{\mu y^3}{3} \tag{E20}$$

where $\Omega = \omega/R_o e^{\gamma}$ and $\mu = 4\pi/\alpha n_s$. Eqn (E19) becomes

$$\langle \tilde{Q}(\omega) \rangle = \frac{1}{R_o e^{\gamma}} \int_{\frac{1}{2}\nu}^{\infty} \frac{dy}{y^{3/2}} \left(2 - \frac{\nu}{y}\right) e^{f(y)} \tag{E20a}$$

which lends itself readily to estimation by the method of steepest descents (see e.g. Matthews and Walker 1965, p.78). The saddle point used occurs when $e^{f(z)}$ is stationary: this value of z will be called z_o. It satisfies

$$f'(z_o) = 0 = 2 + \frac{i\Omega e^{2z_o}(2-\nu/z_o)}{z_o^{\nu}} - \mu z_o^2 . \qquad \text{(E21)}$$

Furthermore

$$f''(z_o) = |f''(z_o)|e^{i\theta} \text{ (definiton of } \theta)$$

$$= \frac{i\Omega}{z_o^{\nu}} e^{2z_o}\left[\frac{3}{2z_o^2} + (2-\nu/z_o)^2\right] - 2\mu z_o . \qquad \text{(E22)}$$

Near z_o,

$$f(z) \simeq f(z_o) + \frac{f''(z_o)}{2}(z-z_o)^2 . \qquad \text{(E23)}$$

Hence

$$\langle\tilde{Q}(\omega)\rangle \simeq \frac{e^{f(z_o)}(2-\nu/z_o)}{R_o e^{\gamma} z_o^{\nu}} \int_{-\infty}^{\infty} dz\, e^{\frac{1}{2}f''(z_o)(z-z_o)^2}$$

$$\simeq \frac{e^{f(z_o)}(2-\nu/z_o)}{R_o e^{\gamma} z_o^{\nu}} \left[\frac{2\pi}{f''(z_o)}\right]^{\frac{1}{2}} e^{\frac{i}{2}(\pm\pi-\theta)} \qquad \text{(E24)}$$

in accordance with the method of steepest descents. Since from eqn (E14) $\langle\tilde{Q}(0)\rangle$ is real and positive, the positive value of π is chosen.

z_o must be found numerically. Scher and Lax (1973) restrict their attention to the case $\nu = 0$. Their method is generalised to include $\nu \neq 0$ by McInnes, Butcher and Clark (1980). It is not single-valued but the desired value is obvious from consideration of the limit $\omega \to 0$. Sometimes this desired value is obtained by iterating around

$$z_{o(n+1)} = \frac{1}{2}\ln\left[\frac{iz_{o(n)}^{\nu}(2-\nu/z_{o(n)}^2)}{\Omega(2-\nu/z_{o(n)})}\right] \qquad \text{(E25)}$$

which is a rearrangement of eqn (E21). At low frequencies z_o from eqn (E25) tended to converge to the wrong value and had to be found by trial and error. The resulting value is then substituted into eqn (E24) and (E13).

The case $\omega = 0$ may be evaluated analytically, giving

$$\tilde{\sigma}_D(0) = \frac{0.131(0.3989)^{\nu} B^{(6\nu-3)/4} e^{-0.532B^{3/2}}}{(2-2.507\nu B^{-3/2})} R_o n_s^{-2/3} , \qquad \text{(E26)}$$

where B is defined by eqn (2.26).

A problem encountered at high frequencies ($\Omega \gtrsim 3 \times 10^{-2}$) was that the real part of the conductivity began to oscillate. This effect is demonstrated here by the approximate calculation of the case $\nu = 0$, $B = 9$ (eqn (2.26)), $\Omega = 1$. Then in eqn (E20)

$$f(z) = 2z + i\Omega e^{2z} + 0.00575\, z^3$$

$$\simeq 2z + i\Omega e^{2z} . \qquad \text{(E27)}$$

In eqn (E21)

$$f'(z_o) = 2 + 2i\Omega e^{2z_o} = 0 \qquad \text{(E28)}$$

implies that $i/\Omega = e^{2z}$, whence

$$z_o = \frac{1}{2} \ell n \left(\frac{1}{\Omega}\right) + i\pi/4 = i\pi/4 \qquad \text{(E29)}$$

whence

$$e^{f(z_o)} = e^{2z_o + i\Omega e^{2z_o}} = ie^{-1} \qquad \text{(E30)}$$

and $f''(z_o) = 4i\Omega e^{2z_o} = -4$. Substitution of these results into eqns (2.1) (2.27) (E24) and (E13) yields

$$\frac{\sigma(\Omega=1)}{g_a{}^{\alpha}} = -0.967 \times 10^{-3} i \qquad \text{(E31)}$$

whereas more accurate evaluation yields

$$\frac{\sigma(\Omega=1)}{g_a{}^{\alpha}} = 7.04 \times 10^{-6} - 1.001 \times 10^{-3} i \qquad \text{(E32)}$$

which differs from eqn (E31) by about 4%, indicating that the numerical method is reliable. This almost purely imaginary conductivity is not what the physics leads one to expect. Since the numerical method does not fail in this case but gives essentially the same (incorrect) answer as the analytical method, one is led to the conclusion that the low-frequency approximations made have failed when $\Omega = 1$, $B = 9$ and $\nu = 0$ and that similar failure occurs for other values of B and ν at high frequencies.

Appendix F:

Hopping Conductivity Formulae Derived Using the Rate-Equation Formalism

It is beyond the scope of this thesis to give derivations of these formulae. A detailed account of the dc limit is given in the Ph.D. thesis of Hayden (1978); reviews of the work on this topic are given by Butcher (1976, 1979). Whether the carriers be non-degenerate (Boltzmann statistics) or degenerate (Fermi-Dirac statistics), Butcher (1976) shows how the rate equations of Miller and Abrahams (1960), eqn (1.1), may be linearised and reduced to an equivalent non-degenerate markovian random walk on a fixed random lattice. This is compared and contrasted with the theory of Scher and Lax (1973) in section 2d. Only isoenergetic sites are considered here.

The dc conductivity for isoenergetic sites (Butcher, Hayden and McInnes 1977) is, in three dimensions,

$$\frac{\sigma_{BHM}(0)}{g_a{}^{\alpha}} = 0.870\ (0.864B)^{\nu-2}\ e^{-1.728B} \qquad \text{(F1)}$$

where B is defined by eqn (2.26), ν and α by eqn (2.24) and g_a by eqn (2.27). Butcher (1976) shows that for $\nu = 0$, the mean hop rate in the dc limit

$$f^{fs}(0) = \pi R_o B^{-3} \qquad \text{(F2)}$$

where the superscript 'fs' means 'fixed sites' and R_o comes from eqn (2.24).

The high-frequency limit is treated by considering the conductivity due to carriers making reciprocating hops between pairs of sites. The idea is that the conductivity at such frequencies is dominated by such

hops between anomalously close pairs of sites. The result for $\nu = {}^3/2$ is:

$$\langle\sigma^P(\omega)\rangle = \frac{\langle\sigma(\infty)\rangle(-i\omega)\sqrt{2}}{\Gamma({}^{13}/_2)R_o}\int_o^\infty \frac{x^4dx}{1-\sqrt{2}\ i\omega e^x/R_o x^{3/2}} \qquad \text{(F3)}$$

where

$$\langle\sigma(\infty)\rangle = \frac{\pi g_a \Gamma({}^{13}/_2)}{3\sqrt{2}\ (2\alpha)^5} \qquad \text{(F4)}$$

is the infinite-frequency conductivity (McInnes, Butcher and Clark, 1980). The formula (F3) gives rise to zero dc conductivity. A crude approximation to the real conductivity is given by the corrected pair approximation

$$\langle\sigma^C(\omega)\rangle = \sigma_{BHM}(0) + \langle\sigma^P(\omega)\rangle \qquad \text{(F5)}$$

(McInnes, Butcher and Clark 1980, Hayden 1978). Eqn (F5) together with direct numerical solution of the rate equations (1.5) for isoenergetic sites with $\nu = {}^3/2$ (McInnes et al. 1980) is plotted in figure (2.2). When $\nu = 0$,

$$\frac{\langle\sigma^P(\omega)\rangle}{\langle\sigma(\infty)\rangle} = \frac{\langle\hat{D}^P(\omega)\rangle}{\langle\hat{D}(\infty)\rangle} = \frac{(-i\omega\tau_o)}{24}\int_o^\infty \frac{x^4dx}{1-i\omega\tau_o e^x} \qquad \text{(F6)}$$

Butcher (1976), with

$$\langle\hat{D}(\infty)\rangle = \frac{8\pi n_s}{(2\alpha)^5\tau_o} \qquad \text{(F7)}$$

The infinite-frequency equations (F7) and (F4) are exact solutions of the linearised rate equations. In eqns (F6) and (F7)

$$\tau_o \equiv \frac{1}{2R_o} \ . \qquad \text{(F8)}$$

Appendix C:

Total Transient Current Density I(t) Due to a Pulse of Unevenly Distributed Carriers

The method used here is given by Scher (1976) in a review article on ACPP. One imagines the experimental system shown in figure C1 with planar symmetry within the semiconductor and $x_1 - x_2 = \ell$. The current will be measured in the external circuit; the two wires shown form part of a closed circuit. The circuit is arranged so that the applied voltage drop is held constant and ($\underset{\sim}{E} = -E, 0, 0$). The voltage drop between x_2 and x_1 is therefore constant. For definiteness' sake the carriers are taken to be electrons though the final result also holds for holes. Let the semiconductor have dc dielectric constant ϵ. Maxwell's fourth equation for this system is then

$$\underset{\sim}{\nabla} \wedge \underset{\sim}{H} = \underset{\sim}{J} + \epsilon\epsilon_o \frac{\partial \underset{\sim}{E}}{\partial t} = \underset{\sim}{J}_T \qquad \text{(C1)}$$

where $\underset{\sim}{H}$ is magnetic field, $\underset{\sim}{J}$ is current density and $\underset{\sim}{J}_T$ is total current density. This has zero divergence. The divergence theorem (e.g. Morse and Feshback 1953, p.37) then states that

$$\int_\tau \nabla . \underset{\sim}{J}_T \, d\tau = \int_\Sigma \underset{\sim}{J}_T . d\underset{\sim}{\Sigma} = 0 \qquad \text{(C2)}$$

where Σ and τ are defined in figure C1. $\underset{\sim}{J}_T$ vanishes except through the surfaces at x' and x'' within the wire and semiconductor. Thus

$$J_T(x',t)s = J_T(x'',t)S \qquad \text{(C3)}$$

where s and S are defined in figure C1, is the total current density

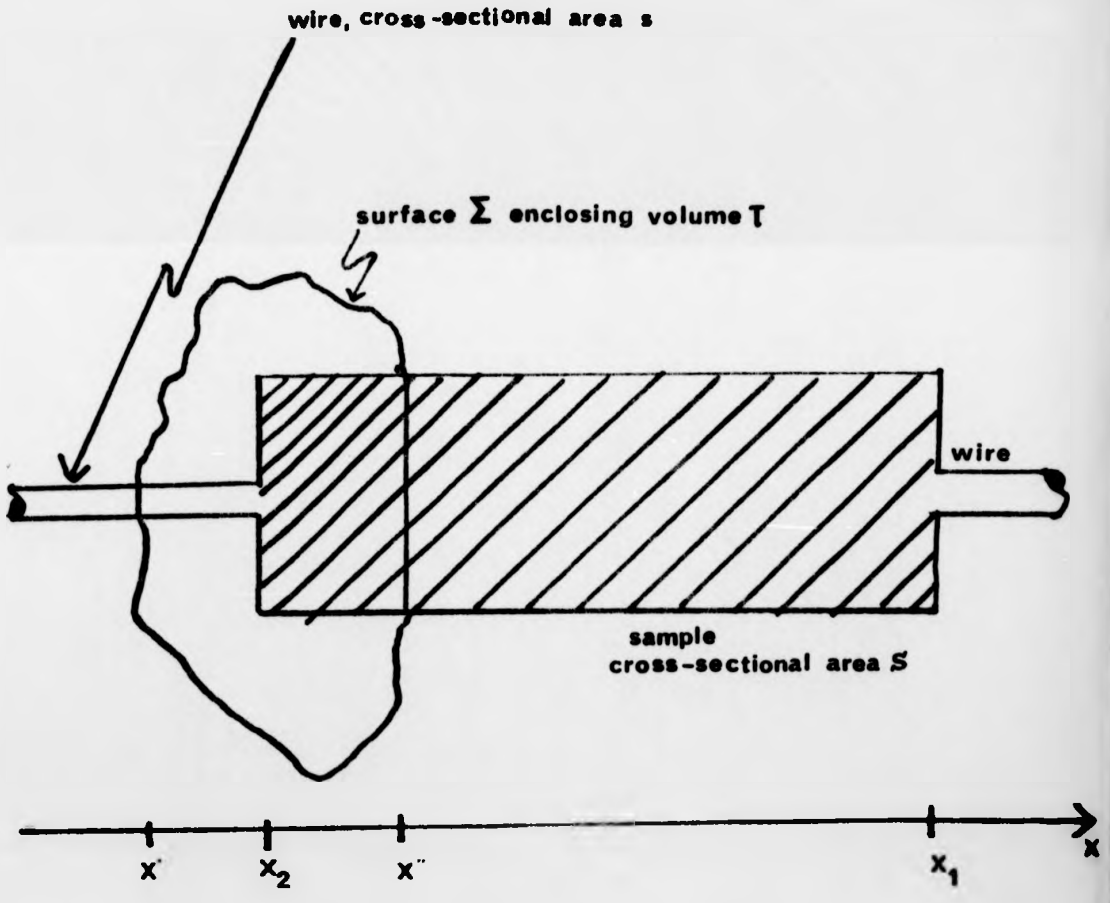


Figure C1: Schematic diagram of experimental system. The voltage drop between x_2 and x_1 is held constant.

flowing through the system. This is true regardless of the values of x' and x": the current flowing in the semiconductor is the same at all x" and therefore equal to its average over x". The current density within the semiconductor

$$I(t) = \frac{1}{\ell}\int_{x_1}^{x_2} J_T(x,t)dx$$

$$= \frac{1}{\ell}\int_{x_1}^{x_2} J(x,t)dx + \frac{\varepsilon\varepsilon_o}{L}\frac{d}{dt}\int_{x_1}^{x_2} E(x,t)dx$$

$$= \frac{1}{\ell}\int_{x_1}^{x_2} J(x,t)dx \quad . \qquad \text{(G4)}$$

The last line of eqn (G4) follows because the second integral of the second line of this equation is the voltage drop across the semiconductor which is held constant; its time derivative thus vanishes. From eqn (1.22), the equation of continuity, it follows that if ℓ is almost infinite,

$$I(t) \approx \frac{1}{\ell}\int_{-\infty}^{\infty} J(x,t)dx$$

$$= -\frac{e}{\ell}\int_{-\infty}^{\infty} x\,\frac{\partial J(x,t)}{\partial x}\,dx$$

$$= -\frac{e}{\ell}\frac{d}{dt}\int_{-\infty}^{\infty} x\,n(x,t)dx$$

$$= -\frac{e}{\ell}\frac{d\langle x\rangle}{dt} \qquad \text{(G5)}$$

from eqn (A1). The equation of continuity also tells us that (Leal Ferreira 1977)

$$I(t) = \frac{1}{\ell}\int_{o}^{\ell} J(x,t)dx$$

$$= \frac{1}{\ell}\left[xJ(x,t)\Big|_0^{\ell} + \int_0^{\ell} x\,\frac{\partial\rho(x,t)}{\partial t}\,dx\right]$$

$$= -\frac{d}{dt}\int_0^{\ell}\rho(x,t)dx + \frac{1}{\ell}\frac{d}{dt}\int_0^{\infty} x\rho(x,t)dx \qquad \text{(G6)}$$

if no current flows in the-x direction at $x = 0^+$.

Appendix H:

Hopping With Site Rerandomization:

The Case of Low Density and High Frequency

It was first realised by Butcher (1974b), to whom the following calculations are due, that the Continuous-Time Random Walk model of Scher and Lax (1973) set out in Chapter 2 is equivalent to hopping on a random lattice of sites with every member of this lattice re-randomized after every hop except the site containing the single carrier being followed. Exponential transition rates, as in eqns (2.14) and (2.15), are assumed. This equivalence is pointed out in Section 2b. The formalism of Chapter 4 is used with suitable modifications. If the sites are isoenergetic eqn (4.8) becomes

$$\tilde{D}(\omega) = -\frac{\omega^2}{2N_s} \sum_{mn} G_{mn}(x_m - x_n)^2 \qquad \text{(H1)}$$

if the system contains N_s sites. It may be seen from eqn (4.5) that if the matrix $\underline{\underline{R}}$ is split into a diagonal part $\underline{\underline{R}}^d$ and an off-diagonal part $-\underline{\underline{R}}^{od}$ then if

$$\underline{\underline{G}}^d \equiv [R^d - i\omega]^{-1} , \qquad \text{(H2)}$$

$$\underline{\underline{G}}^d = \underline{\underline{G}}^d + \underline{\underline{G}}^d \underline{\underline{R}}^{odT} \underline{\underline{G}}^d + \underline{\underline{G}}^d \underline{\underline{R}}^{odT} \underline{\underline{G}}^d \underline{\underline{R}}^{odT} \underline{\underline{G}}^d + \ldots . \qquad \text{(H3)}$$

where the superscript T indicates transposition. That is,

$$G_{mn} = G_{mm}\delta_{mn} + G_{mm}\left[W_{mn} + \sum_p W_{mp} G_{pp} W_{pn} + \ldots\right] G_{nn} . \qquad \text{(H4)}$$

When the sites are isoenergetic and fixed, $f_m = f$ = constant in eqn (4.1). Let $\nu = 0$ in eqn (2.24) to concentrate on the most important part of R_{mn}

viz. $W_{mn} = R_o \exp(-2\alpha|\underset{\sim}{r}_m - \underset{\sim}{r}_n|)$. Eqn (H4) is to be substituted into eqn (H1) with an average over all site locations except m and n. This is done making the simplifying assumption that the sets of site locations available immediately after every hop are statistically independent of one another. Then

$$\tilde{D}^{re}(\omega) = -\frac{\omega^2 n_s}{2} \int d^3\underset{\sim}{r}_n \, \langle G_{mn} \rangle' \, (x_m - x_n)^2 \qquad \text{(H5)}$$

where the superscript "re" means "with rerandomization" and

$$\langle G_{mn} \rangle' = n_s^{-1} \left[\tilde{\psi}^{re}(r_{mn},\omega) + \int d^3\underset{\sim}{r}_p \, \tilde{\psi}^{re}(r_{mp},\omega)\tilde{\psi}(r_{pn},\omega) \right] \tilde{\phi}(\omega) \qquad \text{(H6)}$$

in which

$$\tilde{\psi}^{re}(r_{mn},\omega) = n_s \langle G_{mm} W_{mn} \rangle' , \qquad \text{(H7)}$$

$$\tilde{\phi}^{re}(\omega) = \langle G_{nn} \rangle' \qquad \text{(H8)}$$

and

$$\underset{\sim}{r}_{mn} = \underset{\sim}{r}_m - \underset{\sim}{r}_n , \qquad \text{(H9)}$$

whose x-component is x_{mn}. The n_s in the numerator appears because each term in the double sum (H1) becomes identical after averaging: there are N_s^2 of these. The $1/\tau$ is to normalise the average, where τ = volume and $n_s = N_s/\tau$. When going from eqn (H4) to eqn (H6), it must be remembered that the sites are rerandomized after every hop so that in a term like $G_{mm} \sum_p W_{mp} G_{pp} W_{pn} G_{nn}$ the averaging is performed so that each product in braces when this term is written $\sum_p \{G_{mm} W_{mp}\}\{G_{pp} W_{pn}\}\{G_{nn}\}$ is averaged separately. Primes on angular brackets indicate averaging only over the (N_s-2) sites not involved in the particular hop in question. $\tilde{\phi}^{re}(\omega)$ is the causal Fourier transform of the system average of the probability

that the carrier will remain on a given site without hopping away until at least a time t given that it was on that site at t = 0. Since transition rate densities exponential with respect to time are assumed it does not matter when this carrier entered that site (cf. §2b). It is important to note that this definition is the same as that of $\langle\tilde{Q}(\omega)\rangle$ in eqn (2.19). $\tilde{\psi}^{re}(r_{mn},\omega)$ has a simple stochastic interpretation: it is the causal Fourier transform (see Appendix C) of the probability per unit volume per unit time that at time t the carrier hops to unit volume in the region of $\underset{\sim}{r}_n$ from $\underset{\sim}{r}_m$. Again since exponential transition rates are assumed it does not matter when the carrier entered site m. Let us define

$$\tilde{\psi}^{re}(\omega) \equiv \int d^3\underset{\sim}{r}_n \, \tilde{\psi}^{re}(r_{mn},\omega) \tag{H10}$$

which is the causal Fourier transform of the rate of hopping anywhere at time t; this is the continuum limit of eqn (2.6). Note that it is also the causal Fourier transform of eqn (2.17). Therefore

$$\tilde{\psi}^{re}(\omega) = 1 + i\omega \, \tilde{\phi}^{re}(\omega) \tag{H11}$$

by analogy with eqn (2.19). Substitution of eqn (H10) into eqns (H6) and (H5) shows that the contribution of each term in the series in square brackets in eqn (H6) is $N\tilde{\psi}^{re}(\omega)^{N-1}$ times the contribution of the first term. This is easily seen if, for example, the second term is written

$$\int_{-\infty}^{\infty} d^3\underset{\sim}{r}_n \int d^3\underset{\sim}{r}_p \, (x_m - x_n + x_p - x_p)^2 \, \tilde{\psi}^{re}(r_{mp},\omega) \, \tilde{\psi}^{re}(r_{pn},\omega)$$

since the isotropy of the $\tilde{\psi}$'s ensures that cross-terms like $x_m x_n$ either cancel or vanish. The summation of the series is then trivial. Define

$$\tilde{\sigma}^2_{rms}(\omega) \equiv \frac{3\tilde{\Delta x}^2(\omega)}{\tilde{\psi}^{re}(\omega)} \equiv \frac{3\left|\int d^3\underline{r}_n\, x_{mn}^2\, \tilde{\psi}^{re}(r_{mn},\omega)\right|}{\tilde{\psi}^{re}(\omega)} \quad . \tag{H12}$$

It will be seen that this is the continuum limit of eqn (2.8). With this definition

$$\tilde{D}^{re}(\omega) = -\frac{\omega^2}{2}\left[1 + 2\tilde{\psi}^{re}(\omega) + 3\tilde{\psi}^{re}(\omega)^2 + \ldots.\right]\tilde{\Delta x}^2(\omega)\ \tilde{\phi}^{re}(\omega)$$

$$= -\frac{\omega^2}{2}\ \frac{\tilde{\Delta x}^2(\omega)\tilde{\phi}^{re}(\omega)}{[1-\tilde{\psi}^{re}(\omega)]^2}$$

$$= \frac{\tilde{\sigma}^2_{rms}(\omega)}{6}\left[\frac{-i\omega\tilde{\psi}^{re}(\omega)}{1-\tilde{\psi}^{re}(\omega)}\right] \tag{H13}$$

using eqn (H11). Eqn (H13) is the continuum limit of eqn (2.5) with $\tilde{h}(\omega) = \tilde{\psi}(\omega)$. In view of this and the fact that $\tilde{\psi}^{re}(\omega)$ is the causal Fourier transform of eqn (2.17), the equivalence between the above approach and that of Scher and Lax developed in §§2b and 2c is demonstrated.

In the low density limit hopping to nearest neighbours will dominate. The diagonal element G^d_{mm} becomes

$$G^d_{mm} = \left[\sum_p W_{mp} - i\omega\right]^{-1} = (W_{mn} - i\omega)^{-1} \tag{H14}$$

using eqn (H2). The quantity to be averaged in eqn (H7) is thus approximately $\{W_{mn}/(W_{mn}-i\omega)\}$ if site n is the nearest neighbour to site m. Hence, abbreviating r_{mn} to r,

$$\tilde{\psi}^{re}(r,\omega) \approx \frac{R_o\, e^{-2\alpha r}\, n_s\, e^{-4\pi n_s r^3/3}}{R_o\, e^{-2\alpha r} - i\omega}$$

$$= \frac{n_s\, e^{-4\pi n_s r^3/3}}{1 - 2i\omega\tau_o e^{2\alpha r}} \qquad \text{(H15)}$$

where $2\tau_o = R_o^{-1}$. Figure H1 shows how eqn (H15) may be substituted into eqn (H12). It is seen that $\tilde{\sigma}^2_{rms}(\omega)$ decreases as ω increases. At zero frequency

$$\tilde{\psi}^{re}(\omega) = n_s \exp(-4\pi n_s r^3/3) \qquad \text{(H16)}$$

giving rise to the value of $\tilde{\sigma}^2_{rms}(\omega)$ used by Scher and Lax (1973), eqn (E5),

$$\tilde{\sigma}^2_{rms}(0) = 0.3474\, n_s^{-2/3} \quad . \qquad \text{(H17)}$$

At very high frequencies such that $\omega\tau_o \exp(2\alpha n_s^{-1/3}) \gg 1$, $\tilde{\psi}^{re}(\omega)$ becomes, from eqns (H15) and (2.26),

$$\tilde{\psi}^{re}(\omega) \approx \frac{n_s}{2(-i\omega\tau_o)} \exp\left[-\left\{\frac{4\pi n_s r^3}{3} + 2Bn_s^{1/3} r\right\}\right] \quad . \qquad \text{(H18)}$$

Using the method used to derive eqn (E5) it is easily seen that the mean nearest-neighbour distance is $0.55\, n_s^{-1/3}$ and the mean cubic nearest-neighbour distance is $3/(4\pi n_s)$. For $B \gtrsim 5$ the $2Bn_s^{1/3} r$ term in eqn (H18) is therefore the greater by a factor of 5 at nearest-neighbour distances. When $B = 16$ it is over 17 times greater. Figure H1 shows that now $\sigma^2_{rms}(\infty) \sim \alpha^{-2}$: thus eqn (H18) may be simplified, replacing

$$\exp(-4\pi n_s r^3/3) \text{ by } \exp(-4\pi n_s \alpha^{-3}/3) \approx 1$$

so that

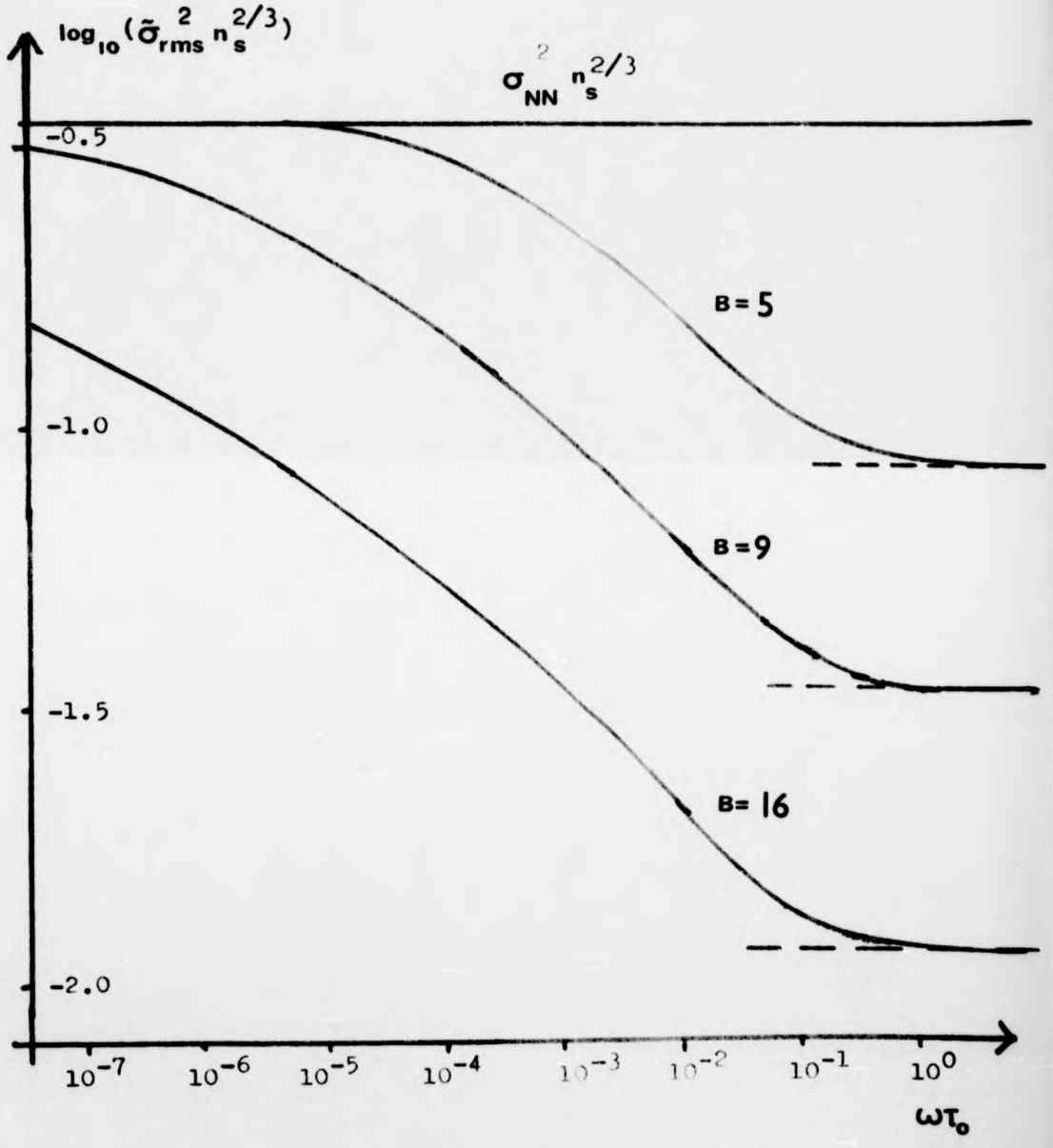


Figure H1: $\tilde{\sigma}^2_{rms}(\omega)$ vs ω from eqns (H12) and (H15) showing how $\tilde{\sigma}^2_{rms}(\omega)$ decreases monotonically with respect to ω and so cannot alone be responsible for ac conductivity. The dashed lines are high-ω limits.

$$\tilde{\psi}^{re}(\omega) = \frac{n_s e^{-2Bn_s^{1/3}r}}{2(-i\omega\tau_o)} \quad . \tag{H19}$$

In eqn (H19), n_s is taken to be very low so that in eqn (H11) $\tilde{\phi}^{re}(\omega) \simeq (-i\omega)^{-1}$. Substitution into eqn (H14) yields

$$\tilde{D}^{re}(\omega) = i\omega n_s \frac{2\pi}{3} \int_o^\infty \frac{r^4 dr}{1-2i\omega\tau_o e^{2\alpha r}} \quad . \tag{H20}$$

Hence

$$\frac{\tilde{D}^{re}(\omega)}{\tilde{D}^{re}(\infty)} = \frac{2(-i\omega\tau_o)}{24} \int_o^\infty \frac{x^4 dx}{1-2i\omega\tau_o e^x} \tag{H21}$$

with

$$\tilde{D}^{re}(\infty) = \frac{8\pi n_s}{(2\alpha)^5 \tau_o} \quad . \tag{H22}$$

Eqn (H15) may also be used to obtain the same dc diffusivity, eqn (E26), as that found by Scher and Lax (1973) (Butcher 1974).

Appendix I:

Laplace Transform of $\psi(t) = 4W_M e^{W_M t}\, i^2\, \mathrm{erfc}\,(W_M t)^{\frac{1}{2}}$

This function and its Lapalce transform (Montroll and Scher 1973; Butcher 1979, private communication) appear in §2e. The operator i^2 is defined by

$$i^2\,\mathrm{erfc}(z) \equiv \int_z^\infty dz' \int_{z''}^\infty dz''\,\mathrm{erfc}(z'') \tag{I1}$$

Lemma 1

$$\begin{aligned} i\,\mathrm{erfc}(z) &= \int_z^\infty 1.\mathrm{erfc}(z')dz' \\ &= -z\,\mathrm{erfc}(z) - \frac{1}{\pi^{\frac{1}{2}}}\int_z^\infty \frac{d}{dy}\left(e^{-y^2}\right) dy \\ &= \frac{e^{-z^2}}{\pi^{\frac{1}{2}}} - z\,\mathrm{erfc}(z) \quad . \end{aligned} \tag{I2}$$

Lemma 2

$$\begin{aligned} i^2\,\mathrm{erfc}(0) &= \pi^{-\frac{1}{2}} \int_0^\infty y^2\, e^{-y^2}\, dy \\ &= \pi^{-\frac{1}{2}} \left[-\tfrac{1}{2}\, y e^{-y^2}\Big|_0^\infty + \tfrac{1}{2}\int_0^\infty e^{-y^2}\, dy \right] \\ &= \tfrac{1}{4} \quad . \end{aligned} \tag{I3}$$

The Laplace transform is now performed. Let $v = u/W_M$.

$$\hat{\psi}(u) = \int_0^\infty e^{-ut}\,\psi(t)\,dt$$

$$= 4\int_0^\infty dt\; e^{-t(v-1)}\; i^2\,\mathrm{erfc}(t^{\frac{1}{2}})$$

$$= 4\left[\frac{e^{-t(v-1)}}{-(v-1)}\quad i^2\,\mathrm{erfc}(t^{\frac{1}{2}})\right]_0^\infty$$

$$-\frac{4}{(v-1)}\int_0^\infty e^{-t(v-1)}\; i\,\mathrm{erfc}(t^{\frac{1}{2}})\,\frac{dt}{2t^{\frac{1}{2}}}$$

$$= \frac{4}{v-1}\,i^2\,\mathrm{erfc}(0) - \frac{4}{v-1}\int_0^\infty e^{-z^2(v-1)}\; i\,\mathrm{erfc}(z)\,dz \qquad \text{(I4)}$$

The second line of eqn (I4) follows from eqn (2.47).

From lemma 1

$$\int_0^\infty e^{-z^2(v-1)}\; i\,\mathrm{erfc}(z)\,dz$$

$$= \int_0^\infty e^{-z^2(v-1)}\left[\frac{e^{-z^2}}{\pi^{\frac{1}{2}}} - z\,\mathrm{erfc}(z)\right]dz$$

$$= \frac{1}{2v^{\frac{1}{2}}} + \frac{1}{2(v-1)}\int_0^\infty dz\left[\frac{d}{dz}\,e^{-z^2(v-1)}\right]\mathrm{erfc}(z)$$

$$= \frac{1}{2v^{\frac{1}{2}}} + \frac{1}{2(v-1)}\left[-1 + \frac{2}{\pi^{\frac{1}{2}}}\,\frac{1}{2}\quad\frac{\pi}{v}\right]$$

$$= \frac{1}{2(1+v^{\frac{1}{2}})} \qquad \text{(I5)}$$

Since erfc(0) = 1. From eqns (I3),(I4) and (I5)

$$\hat{\psi}(u) = \frac{4}{v-1}\left[\frac{1}{4} - \frac{1}{2(1+v^{\frac{1}{2}})}\right]$$

$$= \frac{1}{[1+(u/W_M)^{\frac{1}{2}}]^2} \quad . \tag{I6}$$

It may now be seen how $\psi(t) \sim t^{-3/2}$ as $t \to \infty$. The limit as $t \to \infty$ of $\psi(t)$ is the inverse Laplace transform of

$$\lim_{u \to o} \hat{\psi}(u) \text{ , } \underline{\text{viz.}}$$

$$\lim_{u \to o} \hat{\psi}(u) = 1 - (u/W_M)^{\frac{1}{2}} \tag{I7}$$

whence the required result follows.

REFERENCES

Abkowitz, M. and Scher, H., 1977, Phil. Mag. 35, 1585.

Allan, D., 1978, Phil. Mag. B. 38, 381.

Banyai, L. and Gartner, A., 1980, to appear in Physica A.

Barker, J. R., 1976, J. Phys. C. 9, 4397.

Blatt, F., 1968, Physics of Electronic Conduction in Solids (New York: McGraw-Hill).

Butcher, P. N., 1974, J. Phys. C. 7, 2645.

Butcher, P. N., 1976, in Linear and Nonlinear Electronic Transport in Solids, edited by J. T. Devreese and V. E. van Doren (New York: Plenum Press) pp 341-381.

Butcher, P. N., 1978, Phil. Mag. B, 37, 653.

Butcher, P. N., 1979, (correct year 1980), in Modern Trends in the Theory of Condensed Matter edited by A. Pekalski and J. Przystawa (Berlin: Springer-Verlag).

Butcher, P. N., 1979, private communication. Address: Physics Department, University of Warwick, Coventry, CV4 7AL, U.K.

Butcher, P. N., 1980, Proc. 1979 Conference on Impurity Bands in Solids (Wurzburg, W. Germany. To be published by Taylor and Francis, London).

Butcher, P. N. and Clark, J. D., 1980a, Accepted for Phil. Mag. B.

Butcher, P. N. and Clark, J. D., 1980b, to be published.

Butcher, P. N., Clark, J. D., Hayden, K. J. and McInnes, J. A., 1978, Proc. 14th Int. Conf. on the Physics of Semiconductors, edited by B. L. H. Wilson (Bristol: Institute of Physics) p. 973.

Butcher, P. N., Clark, J. D., Kumar, A. A. and McInnes, J. A., 1980, J. Non-Crystalline Solids, 35 & 36, 89.

Butcher, P. N. and Hayden, K. J., 1977, Proc. 7th Int. Conf. on Amorphous and Liquid Semiconductors, edited by W. E. Spear (Edinburgh: the University) p. 234.

Butcher, P. N., Hayden, K. J. and McInnes, J. A., 1977, Phil. Mag. 36, 19.

Butcher, P. N. and McInnes, J. A., 1978, Phil. Mag. B37, 249.

Butcher, P. N. and Świerkowski, L. 1980, Solid State Commun. 33, 1151.

Chandrasekhar, S., 1943, Rev. Mod. Phys. 15, 1.

Clark, J. D. and Butcher, P. N., 1980, to be published.

Conwell, E. M., 1956, Phys. Rev., 103, 51.

Duffin, W. J., 1973, Electricity and Magnetism, (London: McGraw-Hill).

Emin, D., 1976, in Linear and Nonlinear Electronic Transport in Solids, edited by J. T. Devreese and V. E. van Doren (New York: Plenum Press) pp. 409-434.

Feller, W., 1966, An Introduction to Probability Theory and its Applications, vol. 2, 2nd Edition (New York: John Wiley and Sons).

Hayden, K. J., 1978, Ph.D. Thesis, Warwick University, Coventry, U.K.

Hayden, K. J. and Butcher, P. N., 1978, Phil. Mag. B 38, 603.

Haynes, J. R. and Shockley, W., 1949, Phys. Rev., 75, 691.

Hearn, C. J., 1980, private communication. Address: Physics Department, University of Warwick, Coventry CV4 7AL, U.K.

Ivkin, E. B., and Kolomiets, B. T., 1970, J. Non-Crystalline Solids, 3, 41.

Kahlert, H., 1976, J. Phys. C, 9, 491.

Kenkre, V. M., 1977, in Statistical Mechanics and Statistical Methods in Theory and Practice: A Tribute to Elliot W. Montroll, edited by U. Landman (New York: Plenum Press), p. 491.

Kenkre, V. M., Montroll, E. W. and Shlesinger, M. F., 1973, J. Stat. Phys. 9, 45.

Klafter, J. and Silbey, R., 1980, Phys. Rev. Letts, 44, 55.

Kumar, A. A. and Heinrichs, J., 1980, J. Phys. C., 13, 2131.

Lakatos, A. I. and Abkowitz, M., 1971, Phys. Rev. B., 3, 1791.

Lax, M., 1960, Rev. Mod. Phys. 32, 25.

Lax, M. and Scher, H., 1977, Phys. Rev. Letts., 39, 781.

Leal Ferriera, G. F., 1977, Phys. Rev. B. 16, 4719.

LeComber, P. G. and Spear, W. E., 1970, Phys. Rev. Letts, 25, 509.

Marshall, J. M., 1978, Phil. Mag. B. 38, 335.

Marshall, J. M., 1980a, to appear in Phil. Mag. B.

Marshall, J. M., 1980b, private communications. Address: Physics Department, Dundee College of Technology, Bell St., Dundee DD1 1HG, U.K.

Marshall, J. M. and Allan, D., 1979, Phil. Mag. B. 40, 71.

Marshall, J. M. and Sharp, A. C., J. Non-Crystalline Solids, 35 & 36, 99.

Mathews, J. and Walker, R. L., 1965, Mathematical Methods of Physics (New York: W. A. Benjamin Inc.)

McInnes, J. A., et al. 1977: See Butcher, Hayden and McInnes (1977)
1978a: See Butcher and McInnes (1978)
1978b: See Butcher, Clark, Hayden and McInnes (1978)
1980: See Butcher, Clark, Kumar and McInnes (1980).

McInnes, J. A. and Butcher, P. N., 1979, Phil. Mag. B. 39, 1.

McInnes, J. A., Butcher, P. N. and Clark, J. D., 1980, Phil. Mag. B. 41, 1.

Merson, R. H., 1957, Proc. Symp. Data Processing (Salisbury, S. Australia: Weapons Research Establishment).

Miller, A. and Abrahams, E., 1960, Phys. Rev. 120, 745.

Morse, P. M. and Feshbach, H., 1953, Methods of Theoretical Physics, (New York: McGraw-Hill).

Montroll, E. W. and Scher, H., 1973, J. Stat. Phys, 9, 101.

Mott, N. F., 1956, Can. J. Phys. 34, 1356.

Mott, N. F. and Davis, E. A., 1979, Electronic Processes in non-Crystalline Materials, (Oxford: Clarendon Press).

Movaghar, B., Pohlmann, B. and Sauer, G. W., 1980, Phys. Status Solidi B. 97, 533.

Noolandi, J., 1977a, Phys. Rev. B. 16, 4466.

Noolandi, J., 1977b, Phys. Rev. B. 16, 4474.

Noolandi, J., 1977c, Proc. 7th Int. Conf. on Amorphous and Liquid Semiconductors, edited by W. E. Spear (Edinburgh: The University) pp 224-228.

Noolandi, J., Hong, K. M. and Street, R. A., 1980, Solid State Commun., 34, 45.

Pfister, G., 1976, Phys. Rev. Lett. 36, 271.

Pfister, G. and Scher, H., 1977, Phys. Rev. B. 15, 2062.

Pfister, G. and Scher, H., 1978, Adv. Phys. 27, 747.

Pollak, M., 1977, Phil. Mag. 36, 1157.

Pollak, M. and Geballe, T. H., 1961, Phys. Rev. 122, 1742.

Rudenko, A. I. and Arkhipov, V. I. 1979, Phil. Mag. B. 39, 465.

Scher, H., 1976, in Photoconductivity and Related Phenomena, edited by J. Mort and D. M. Pai (Amsterdam: Elsevier) Ch. 3.

Scher, H. and Lax, M., 1973, Phys. Rev. B. 7, 4491, ibid. 4502.

Scher, H. and Montroll, E. W., 1975, Phys. Rev. B. 12, 2455.

Schmidlin, F. W., 1977, Phys. Rev. B. 16, 2362.

Schmidlin, F. W., 1979, private communication. Adress: Xerox Corporation, Joseph C. Wilson Centre for Technology, Rochester, NY 14644, U.S.A.

Schmidlin, F. W., 1980, Phil. Mag. B. 41, 535.

Scharfe, M. E., 1970, Phys. Rev. B. 2, 5205.

Sharp, A., 1979, private communication. Address: Physics Department, Dundee College of Technology, Bell St., Dundee DD1 1HG, U.K.

Shlesinger, M. F., 1974, J. Stat. Phys. 10, 421.

Shlesinger, M. F., 1977, in Statistical Mechanics and Statistical Methods in Theory and Application: A Tribute to E. W. Montroll, edited by U. Landman (New York: Plenum Press) p. 507.

Shockley, W., 1950, Electrons and Holes in Semiconductors (Princeton: Van Nostrand).

Silver, M., 1977, Proc. 7th Int. Conf. on Amorphous and Liquid Semiconductors, edited by W. E. Spear (Edinburgh: The University) pp. 214-218.

Spiegel, M. R., 1965, Theory and Problems of Laplace Transforms (New York: McGraw-Hill, Schaum Series).

Summerfield, S., 1980, private communication. Address: Physics Department, University of Warwick, Coventry CV4 7AL, U.K.

Thomas, D. G., Hopfield, J. J. and Augustinyak, 1965, Phys. Rev., 140, A202.

Troup, A., Mort, J., Grammatica, S. and Sandman, D. J., 1980, J. Non-Crystalline Solids, 35 & 36, 151.

Tunaley, J. K. E., 1974, Phys. Rev. Letts. 33, 1038.

Whittaker, E. T. and Watson, G. N., 1940, Modern Analysis, 4th Edition (Cambridge: University Press).

Ziman, J. M., 1969, Elements of Advanced Quantum Theory, (Cambridge: University Press).