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Transport Theory for Extended and Localised States

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TRANSPORT THEORY FOR EXTENDED AND LOCALISED STATES

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1. Introduction

The study of electron transport in severely disordered systems is only just beginning. A general understanding of the behaviour of simple liquid metals may be obtained from Boltzmann transport theory which we review in Section 2. This is a good place to start because, apart from having application to liquid metals we may also put the results in a form having wider validity than their derivation might suggest. In particular we find that the static conductivity and thermopower may be expressed as Kubo-Greenwood formulae[1]. These formulae have been used a great deal to analyse transport data for amorphous semiconductors as we discuss in Section 3.

It is characteristic of disordered systems that some of the electron states are localised. Transport through these states takes place through a hopping mechanism which has received much attention in recent years. We review the general formalism in Section 4 and make simple applications to ac conductivity and dc conductivity in Sections 5 and 6. Finally in Section 7 we outline a unified theory of both ac and dc hopping conductivity which has been developed in the last two years.

Hopping transport is one characteristic feature of amorphous semiconductors. Another is anomalous carrier pulse propagation. In crystalline semiconductors, subjected to a steady electric field, injected carrier pulses are usually found to be drifted Gaussians. In amorphous semiconductors such simple behaviour is seldom observed. We discuss the marked anomalies which arise and the reasons for them in Section 8. At one time a hopping theory was used to discuss the origin of the anomalies[2]. More recent treatments point to trapping as the most likely mechanism[3-7].

Boltzmann transport theory is treated in most books on crystalline solid state physics. The author has given a review in a previous Spring College[8] and applications to liquid metals have recently been reviewed by March[9]. The book by Mott and Davis[1] is outstanding in its treatment of many topics in non-crystalline materials. Hopping conductivity has been reviewed by several authors[10-16] and anomalous carrier pulse propagation is discussed at length by Pfister and Scher[2] on the basis of a hopping model.

2. Boltzmann Transport Theory

2.1. Introduction

Let us suppose that the electron states may be labelled by a wave vector $\underline{k}$ and that scattering from $\underline{k}$ to $\underline{k}'$ is weak. Then we may describe the electron system by a semi-classical electron distribution function $f(\underline{k}, \underline{r}, t)$, which

depends on position $\underline{r}$ and time t as well as $\underline{k}$, and satisfies the Boltzmann equation

$$\frac{\partial f}{\partial t} + \underline{v}.\underline{\nabla} f + \frac{1}{\hbar}\underline{F}.\underline{\nabla}_k f = \left(\frac{\partial f}{\partial t}\right)_c \qquad (2.1)$$

Here: $f = f(\underline{k}, \underline{r}, t)$, $\underline{v}$ is the velocity of an electron in state $\underline{k}$ and $\underline{F}$ is the classical force. The right hand side of (2.1) describes the effect of collisions and has the form

$$\left(\frac{\partial f}{\partial t}\right)_c = \int \{f'[1 - f]\, P(\underline{k}', \underline{k}) - f[1 - f']\, P(\underline{k}, \underline{k}')\} d\underline{k} \qquad (2.2)$$

where $f' = f(\underline{k}', \underline{r}, t)$ and $P(\underline{k}', \underline{k})$ describes the scattering rate from $\underline{k}'$ to $\underline{k}$. We suppose that f is normalised so as to be equal to the probability that state $\underline{k}$ (with spin up) is occupied and that spin flips are forbidden. Then $P(\underline{k}', \underline{k}) = (\Omega/8\pi^3)$ times the transition rate from $\underline{k}'$ to $\underline{k}$ in a volume Ω and is independent of Ω. The physical interpretation of the solution of equation (2.1) is provided by the following expressions for the electron density n, the electric current density $\underline{J}$ and the heat flux vector $\underline{Q}$:

$$n = \frac{1}{4\pi^3} \int f\, d\underline{k} \quad , \qquad (2.3)$$

$$\underline{J} = -\frac{e}{4\pi^3} \int f\, \underline{v}\, d\underline{k} \quad , \qquad (2.4)$$

$$\underline{Q} = \frac{1}{4\pi^3} \int f[\varepsilon - \varepsilon_F]\, \underline{v}\, d\underline{k} \quad . \qquad (2.5)$$

In these equations we ignore spin splitting and give equal weights to the contributions from both spin orientations; ε is the energy of state $\underline{k}$ and ε_F is the chemical potential.

2.2. Solution of Boltzmann's Equation

The formalism comprised in equations (2.1) to (2.5) is often applied to crystalline metals and semiconductors and details are given in most textbooks on solid state physics. A review has been given by the author in a previous Spring College[8]. To determine the transport properties of the electrons in a particular energy band we use the functional dependence of ε upon $\underline{k}$ for that band and interpret $\underline{v}$ as the corresponding group velocity $\hbar^{-1}\underline{\nabla}_k\varepsilon$. The formalism becomes particularly simple for an isotropic system in which details of the band structure are averaged out so that ε depends only on $k = |\underline{k}|$. We confine our attention to this case. Our results are then particularly appropriate to liquid metals which are the subject of Professor Beck's lectures[17]. They also provide a useful, but idealised, description of crystalline metals and semiconductors. In the interest of simplicity we consider only static situations, so that $\partial f/\partial t = 0$. We also suppose that a weak, uniform electric field $\underline{E}$ is applied and that the magnetic field vanishes. Finally, we allow weak gradients of ε_F and temperature. Then we may solve (2.1) by expanding in powers of the small quantities $\underline{E}$, $\underline{\nabla}\varepsilon_F$ and $\underline{\nabla}T$.

In zero the order we write $f = f_0$ and determine f_0 from

$$\left(\frac{\partial f_0}{\partial t}\right)_c = 0 \tag{2.6}$$

Now, $P(\underline{k}', \underline{k})$ satisfies the detailed balance condition

$$\frac{P(\underline{k}', \underline{k})}{P(\underline{k}, \underline{k}')} = \exp[\beta(\varepsilon' - \varepsilon)] \tag{2.7}$$

where $\beta = (k_BT)^{-1}$ with k_B denoting Boltzmann's constant and T denoting the temperature at the point $\underline{r}$; $\varepsilon = \varepsilon(\underline{k})$ and $\varepsilon' = \varepsilon(\underline{k}')$. It follows immediately that (2.6) may be satisfied by making the integrand in (2.2) vanish. Thus we find that f_0 is just the Fermi-Dirac function of the energy:

$$f_0(\varepsilon) = [\exp\{\beta(\varepsilon - \varepsilon_F)\} + 1]^{-1} \tag{2.8}$$

where β and ε_F are arbitrary functions of $\underline{r}$.

In first order we write

$$f = f_0 + f_1 \tag{2.9}$$

and find from (2.1) that f_1 is determined by the linearised Boltzmann equation

$$\underline{v}.\underline{\nabla}f_0 - \frac{e\underline{E}}{\hbar}.\underline{\nabla}_k f_0 = \left(\frac{\partial f_1}{\partial t}\right)_c \tag{2.10}$$

In this equation $(\partial f_1/\partial t)_c$ denotes the linearised collision term:

$$\left(\frac{\partial f_1}{\partial t}\right)_c = \int \Gamma(\underline{k}', \underline{k}) \left(\frac{f_1'}{f_0'(1 - f_0')} - \frac{f_1}{f_0(1 - f_0)}\right) d\underline{k}' \tag{2.11}$$

where $f_1 = f_1(\underline{k}, \underline{r}, t)$, $f_1' = f_1(\underline{k}', r, t)$, $f_0 = f_0(\varepsilon)$, $f_0' = f_0(\varepsilon')$ and the function $\Gamma(\underline{k}', \underline{k})$ is the thermal equilibrium electron flux from $\underline{k}'$ to $\underline{k}$ per unit volume of $\underline{k}$ space:

$$\Gamma(\underline{k}', \underline{k}) = f_0'(1 - f_0)\, P(\underline{k}', \underline{k}) \tag{2.12}$$

We see immediately from (2.7) and (2.8) that $\Gamma(\underline{k}', \underline{k})$ is symmetrical, i.e.: $\Gamma(\underline{k}', \underline{k}) = \Gamma(\underline{k}, \underline{k}')$.

In solving (2.10) it is convenient to use the relations

$$\underline{\nabla}f_0 = -\frac{df_0}{d\varepsilon}[\underline{\nabla}\varepsilon_F + T^{-1}\nabla T(\varepsilon - \varepsilon_F)] \tag{2.13a}$$

$$\frac{1}{\hbar}\underline{\nabla}_k f_0 = \frac{df_0}{d\varepsilon}\underline{v} \tag{2.13b}$$

on the left-hand side. To simplify the subsequent analysis we introduce on the right-hand side, the relaxation time $\tau = \tau(\varepsilon)$ by writing

$$\left(\frac{\partial f_1}{\partial t}\right)_c = -\frac{f_1}{\tau} \tag{2.13c}$$

Then we have

$$f_1 = \tau\frac{df_0}{d\varepsilon}\underline{v}.[e\underline{E}' + T^{-1}\underline{\nabla}T(\varepsilon - \varepsilon_F)] \tag{2.14}$$

where $\underline{E}' \equiv \underline{E} + e^{-1}\underline{\nabla}\varepsilon_F$ is the electromotive force.

2.3. Formulae for the transport coefficients

We obtain formulae for the transport coefficients by substituting (2.9) into (2.4) and (2.5). Thus we find with the aid of (2.14) that

$$\begin{aligned} \underline{J} &= \sigma.\underline{E}' + L.\underline{\nabla}T \\ \underline{Q} &= M.\underline{E}' + N.\underline{\nabla}T \end{aligned} \tag{2.15a}$$

where

$$\sigma = -\frac{e^2}{4\pi^3}\int \underline{v}\,\underline{v}\;\tau\frac{df_0}{d\varepsilon}\,d\underline{k}$$

$$L = -\frac{e}{4\pi^3 T}\int \underline{v}\,\underline{v}\;\tau\frac{df_0}{d\varepsilon}\,(\varepsilon - \varepsilon_F)\,d\underline{k} \qquad (2.16)$$

$$M = \frac{e}{L\pi^3}\int \underline{v}\,\underline{v}\;\tau\frac{df_0}{d\varepsilon}\,(\varepsilon - \varepsilon_F)\,d\underline{k}$$

$$N = \frac{1}{4\pi^3 T}\int \underline{v}\,\underline{v}\;\tau\frac{df_0}{d\varepsilon}\,(\varepsilon - \varepsilon_F)^2\,d\underline{k}$$

In crystals σ, L, M and N are tensors For liquid metals they reduce to scalars which are obtained from (2.16) by replacing the dyadic $\underline{v}\,\underline{v}$ by the scalar $v^2/3$. Equations (2.15a) are the "theorists form" of the transport equations in which $\underline{E}'$ and $\underline{\nabla T}$ are taken as the independent variables. In the "experimentalists form" $\underline{J}$ and $\underline{\nabla T}$ are the independent variables. Thus we have

$$\begin{aligned} \underline{E}' &= \rho\,\underline{J} + S\underline{\nabla T} \\ \underline{Q} &= \Pi\,\underline{J} - \kappa\underline{\nabla T} \end{aligned} \qquad (2.15b)$$

where the (scalar) resistivity ρ, thermopower S, Peltier coefficient Π and thermal conductivity κ are given by

$$\begin{aligned} \rho &= \sigma^{-1} \\ S &= -\sigma^{-1}L \\ \Pi &= \sigma^{-1}M \\ \kappa &= \sigma^{-1}ML - N \end{aligned} \qquad (2.17)$$

The Onsager relations

$$M = -TL \qquad (2.18a)$$

i.e.

$$\Pi = TS \qquad (2.18b)$$

are trivially obvious from equations (2.16) and (2.17).

2.4. Conductivity and thermopower

We are primarily concerned with the most commonly measured transport coefficients σ and S. By writing $d\underline{k} = 4\pi k^2\,(dk/d\varepsilon)d\varepsilon$ and $v = \hbar^{-1}\,d\varepsilon/dk$ in the scalar form of the above equations we readily find that

$$\sigma = -\int \frac{df_0}{d\varepsilon}\,\sigma(\varepsilon)d\varepsilon \qquad (2.19)$$

$$S = \frac{k_B}{e}\int \frac{df_0}{d\varepsilon}\,\frac{\sigma(\varepsilon)}{\sigma}\,\frac{(\varepsilon - \varepsilon_F)}{k_B T}\,d\varepsilon \qquad (2.20$$

where

$$\sigma(\varepsilon) = \frac{e^2}{12\pi^3\hbar}\,4\pi k^2\,v\,\tau \qquad (2.21)$$

is the "conductivity at energy ε". For liquid metals the electron statistics are degenerate and we find from (2.8) that $df_0/d\varepsilon \simeq -\,\delta(\varepsilon - \varepsilon_F)$. Hence, we easily obtain the familiar results

$$\sigma \simeq \sigma(\varepsilon_F) \qquad (2.22)$$

$$S \simeq -\frac{\pi^2}{3e}\,k_B^2\,T\,\frac{d\sigma(\varepsilon_F)/d\varepsilon}{\sigma(\varepsilon_F)} \qquad (2.23)$$

For n-type semiconductors with a conduction band edge at ε_c which is several $k_B T$ away from ε_F the electron statistics are non-degenerate. Hence equation (2.8) reduces to $f_0 \simeq \exp[\beta(\varepsilon_F - \varepsilon)]$ and we have

$$\sigma = \beta\int \exp[\beta(\varepsilon_F - \varepsilon)]\sigma(\varepsilon)\,d\varepsilon$$

$$S = -\frac{k_B}{e}\left(\frac{\varepsilon_c - \varepsilon_F}{k_B T}\right) + A \qquad (2.24)$$

where

$$A = -\int \frac{df_0}{d\varepsilon}\,\frac{\sigma(\varepsilon)}{\sigma}\,\frac{\varepsilon - \varepsilon_c}{k_B T}\,d\varepsilon \qquad (2.25)$$

is the "heat of transport" in units of k_BT.

We see that (2.20) specifies S as k_B/e times the average carrier energy measured relative to ε_F calculated with the weighting factor $-df_0/d\varepsilon\ \sigma(\varepsilon)$. This result is thought to have validity outside the domain of Boltzmann transport theory in which we have derived it[1].

2.5. The Einstein relation

In equations (2.15) $\underline{E}'$ denotes the emf $\underline{E} + e^{-1}\nabla\varepsilon_F$. Hence, under isothermal conditions the current density takes the form

$$\underline{J} = \sigma\underline{E} + e^{-1}\sigma\nabla\varepsilon_F \tag{2.26}$$

where ε_F is determined from the equation for the electron density

$$n = \frac{1}{4\pi^3}\int f_0\ d\underline{k} \tag{2.27}$$

to which f_1 makes no contribution. The first term in equation (2.26) is the current density due to the electric field. We identify the second term as the current density $eD\nabla n$ due to diffusion and, by writing $\underline{\nabla}n = \underline{\nabla}\varepsilon_F(dn/d\varepsilon_F)$, we obtain the Einstein relation:

$$\sigma = e^2D(dn/d\varepsilon_F) \tag{2.28}$$

Equation (2.28) is the most general form of the Einstein relation and it is valid for both degenerate and non-degenerate statistics. For non-degenerate statistics, however, the relation is usually expressed in an alternative form by noting that $f \simeq \exp[\beta(\varepsilon_F - \varepsilon)]$. Hence n is proportional to $\exp(\beta\ \varepsilon_F)$ and $dn/d\varepsilon_F = \beta n$. Thus we have

$$\mu = eD/k_BT \tag{2.29}$$

where $\mu = \sigma/en$ is the electron drift mobility. It should be emphasised, as a preamble to the next sub-section, that equation (2.29) is valid only for non-degenerate statistics.

2.6. Energy dependent diffusivity and mobility[92]

We may rewrite equation (2.27) for n in the form

$$n = \int f_0\ N(\varepsilon)\ d\varepsilon \tag{2.30a}$$

where

$$N(\varepsilon) = \frac{4\pi k^2}{4\pi^3\ d\varepsilon/dk} \tag{2.30b}$$

is the density of states. When equation (2.30a) is differentiated with respect to ε_F we see from (2.8) that

$$\frac{dn}{d\varepsilon_F} = -\int \frac{df_0}{d\varepsilon}\ N(\varepsilon)\ d\varepsilon \tag{2.31}$$

By substituting this result into equation (2.28) and using equation (2.19) we find that the diffusion coefficient D may be expressed in the form

$$D = \langle\ D(\varepsilon)\ \rangle \tag{2.32}$$

where

$$D(\varepsilon) = \frac{\sigma(\varepsilon)}{e^2N(\varepsilon)} \tag{2.33}$$

in the "energy-dependent diffusivity" and the angular brackets signify an average taken with the weighting factor $-N(\varepsilon)\ df_0/d\varepsilon$. We see immediately from equations (2.21) and (2.30b) and (2.33) that

$$\begin{aligned} D(\varepsilon) &= \tfrac{1}{3}\ v^2\tau \\ &= \tfrac{1}{3}\ \lambda^2\tau^{-1} \end{aligned} \tag{2.34}$$

where v, τ and the mean free path $\lambda = v\tau$ are all evaluated at energy ε.

We may rewrite (2.33) in a form which is often used in discussions of amorphous semiconductors:

$$\sigma(\varepsilon) = e\ N(\varepsilon)k_BT\ \mu(\varepsilon) \tag{2.35}$$

where

$$\mu(\varepsilon) = \frac{eD(\varepsilon)}{k_BT} \tag{2.36}$$

is usually referred to as the "mobility at energy ε". This terminology is a little unfortunate but has now become firmly established. The factors k_BT actually cancel out of equations (2.35) and (2.36) to yield the simpler equation

$$\sigma(\varepsilon) = e^2N(\varepsilon)\ D(\varepsilon) \tag{2.37}$$

which has the same physical content. Thus $\mu(\varepsilon)$ as given by (2.36) is simply $D(\varepsilon)$ scaled by a factor e/k_BT to give it the <u>dimensions</u> of mobility. The scaling factor does not change the physical interpretation of $D(\varepsilon)$ which is that of a diffusion constant. Indeed, we may readily verify from equations (2.22), (2.28), (2.31) and (2.37) that, for degenerate statistics, the macroscopic diffusion constant is just $D(\varepsilon_F)$ whereas $\mu(\varepsilon_F)$ as given by equation (2.36) has no simple macroscopic interpretation. By way of illustration we consider electrons with a constant effective mass m^*. Then

$$\mu(\varepsilon_F) = \frac{e\tau(\varepsilon_F)}{m^*}\ \frac{2\varepsilon_F}{3k_BT} \tag{2.37}$$

in which we recognise the first factor as the drift mobility.

For non-degenerate statistics $\mu(\varepsilon)$ has a more reasonable interpretation. We readily verify that the macroscopic mobility in this case is $\sigma/en = < \mu(\varepsilon) >$ where the angular brackets have the same significance as in equation (2.32). Unfortunately, this simple result becomes invalid as soon as the statistics become degenerate to any degree.

2.7. <u>Hall mobility and ac conductivity</u>

To determine the low-field Hall mobility $\mu_H = \sigma_{xy}/B\sigma_{xx}$ we must include a Lorentz force term $-e\underline{v} \times \underline{B}$ in the classical force $\underline{F}$ entering into Boltzmann's equation (2.1). The calculation of μ_H is elementary but tedious for isotropic systems[8]. We find that $\mu_H = \mu$ for degenerate statistics and

$$\mu_H = \mu << \tau^2 >>/<< \tau >>^2 \tag{2.38}$$

for general statistics and a constant effective mass. In equation (2.38) the double angular brackets indicate an average calculated with a weighting factor $-df_0/d\varepsilon$ times the <u>integrated</u> density of states.

The current density response to an ac electric field $\mathrm{Re}[\underline{E}\exp(-i\omega t)]$ may be calculated by keeping the time derivative in Boltzmann's equation (2.1). For degenerate statistics the result is $\mathrm{Re}[\sigma(\omega)\ \underline{E}\ \exp(-i\omega t)]$ where $\sigma(\omega)$ is given by the Drude formula:

$$\sigma(\omega) = \sigma[1 - i\omega\tau(\varepsilon_F)]^{-1} \tag{2.39}$$

For general statistics the general behaviour is the same as that predicted by the Drude formula but $\tau(\varepsilon_F)$ is replaced by an appropriate, frequency-dependent, average of $\tau(\varepsilon)$.

2.8. <u>Conclusion</u>

To evaluate the formulae for the transport coefficients we require τ. For elastic scattering between plane wave states $\underline{k}$ and $\underline{k}'$ the behaviour of each individual scatterer is usually described by the differential scattering cross-section $\sigma(\theta)$ where θ is the angle between $\underline{k}$ and $\underline{k}'$. The correlations in the positions of an assembly of scatterers with density n_s may be allowed for by multiplying $\sigma(\theta)$ by the static structure factor $a(K)$ where $K = 2k\sin\theta/2$ is the magnitude of the scattering wave vector $\underline{k}' - \underline{k}$. With this notation, τ^{-1} is given by the well known formula:

$$\frac{1}{\tau} = n_s v\ 2\pi \int \sigma(\theta)(1 - \cos\theta)\ a(K)\ \sin\theta\ d\theta \tag{2.40}$$

In semiconductors we usually assume completely random scatterers, so that $a(K) = 1$, and calculate $\sigma(\theta)$ in the Born approximation. In liquid metals $a(K)$ is usually taken from X-ray or neutron scattering data and $\sigma(\theta)$ is calculated from the ion-core phase shifts. This topic will be persued by Professor Beck[17].

When we turn to inelastic scattering, we find that τ is not very well-defined[8]. Nevertheless, very often an approximate relaxation time may be introduced which provides good physical insight. When this is not possible it becomes necessary to solve the linearised Boltzmann equation by numerical or variational methods. Some examples are given in reference 8.

3. Applications of Kubo-Greenwood Formulae

3.1. Introduction

Equations (2.19) and (2.20) are usually known as Kubo-Greenwood formulae[1]. In the one-electron approximation they have validity outside the domain of Boltzmann transport theory. When the transport mechanism is different from that assumed in Section 2, what changes is $\sigma(\varepsilon)$, equations (2.19) and (2.20) remain intact. We quote them again here for convenience:

$$\sigma = -\int \frac{df_0}{d\varepsilon}\,\sigma(\varepsilon)\,d\varepsilon \qquad (3.1)$$

$$S = \frac{k_B}{e}\int \frac{df_0}{d\varepsilon}\,\frac{\sigma(\varepsilon)}{\sigma}\,\frac{(\varepsilon - \varepsilon_F)}{k_BT}\,d\varepsilon \qquad (3.2)$$

The first relation is easily justified for electrons moving in a disordered static potential. We give a derivation in Section 3.2. Accepting (3.1) for the moment we may immediately give a heuristic derivation of (3.2). Equation (2.18), expressing Onsager symmetry, and (2.15), expressing the linear transport relations have general validity. Hence $S = \Pi/T$ where the Peltier coefficient is the ratio of $\underline{Q}$ to $\underline{J}$ when $\underline{\nabla}T = 0$. For the electric field $\underline{E} = (E_x, 0, 0)$, $\underline{J} = (\sigma E_x, 0, 0)$ and we see from (3.1) that the contribution to σE_x from energies between ε and $\varepsilon + d\varepsilon$ is $-E_x(df_0/d\varepsilon)\,\sigma(\varepsilon)\,d\varepsilon$. The corresponding contribution to Q_x in the heat flux vector $\underline{Q} = (Q_x, 0, 0)$ is obtained by dividing by $-e$ and multiplying by $\varepsilon - \varepsilon_F$. Thus we obtain (3.2). The argument used here is obviously not rigorous. Nevertheless equation (3.2) is usually assumed to be generally valid[1].

3.2. Derivation of the conductivity formula[1,8]

As the nomenclature implies, equation (3.1) may be derived from the Kubo formula[18] for the conductivity $\sigma(\omega)$ at frequency ω. A very simple approach is possible when we recognise that the real part $\sigma_1(\omega)$ of $\sigma(\omega)$ is equal to $2/|E|^2$ times the time-averaged power absorption density P in an electric field $(E_x, 0, 0)$ with $E_x = \mathrm{Re}[E\exp(-i\omega t)]$. The perturbation of the Hamiltonian produced by E_x for one electron is $eE_x x$ and this produces a transition rate W_{mn} between any pair of one-electron states m and n which we may calculate using Fermi's Golden Rule:

$$W_{mn} = \frac{2\pi e^2}{\hbar}\,\frac{|E|^2}{4}\,|\langle n|x|m\rangle|^2\,[\delta(\varepsilon_n - \varepsilon_m - \hbar\omega) + \delta(\varepsilon_n - \varepsilon_m + \hbar\omega)] \qquad (3.3)$$

The corresponding power dissipation if m is known to be occupied and n is known to be empty is $W_{mn}(\varepsilon_n - \varepsilon_m)$. In thermal equilibrium the probability of the initial condition necessary for the absorption to take place is $f_m^0(1 - f_n^0)$ where $f_m^0 = f_0(\varepsilon_m)$ is the Fermi-Dirac function (2.8). Hence we have, considering a volume Ω,

$$\sigma_1(\omega) = \frac{\pi e^2}{2\hbar\Omega}\sum_{mn} (\langle n|x|m\rangle)^2\,(\varepsilon_n - \varepsilon_m)\,f_m^0(1 - f_n^0)$$

$$\times\,[\delta(\varepsilon_n - \varepsilon_m - \hbar\omega) + \delta(\varepsilon_n - \varepsilon_m + \hbar\omega)]$$

$$= \frac{\pi e^2\omega}{2\Omega}\sum_{mn} |\langle n|x|m\rangle|^2\,\delta(\varepsilon_n - \varepsilon_m - \hbar\omega)$$

$$\times\,[f_m^0(1 - f_n^0) - f_n^0(1 - f_m^0)]$$

$$= \frac{\pi e^2\omega}{2\Omega}\sum_{mn} |\langle n|x|m\rangle|^2\,\delta(\varepsilon_n - \varepsilon_m - \hbar\omega)\,(f_m^0 - f_n^0) \qquad (3.4)$$

In the second line we have interchanged the dummy variables m and n and have used the properties of the δ-function and the hermiticity of $\langle m|x|n\rangle$.

In the one-electron approximation

$$[x, H] = \frac{1}{2m_e}[x, p_x^2] = \frac{i\hbar}{m_e}\,p_x \qquad (3.5)$$

where H is the one-electron Hamiltonian and m_e is the free electron mass. It follows that

$$\langle n|x|m\rangle\,(\varepsilon_n - \varepsilon_m) = \frac{i\hbar}{m_e}\langle n|p_x|m\rangle \qquad (3.6)$$

and (3.4) may be written in the equivalent form:

$$\sigma_1(\omega) = \frac{\pi e^2 \hbar}{2\Omega m_e^2} \sum_{mn} |\langle n|p_x|m\rangle|^2 \, \delta(\varepsilon_n - \varepsilon_m - \hbar\omega) \times \frac{[f_0(\varepsilon_m) - f_0(\varepsilon_m + \hbar\omega)]}{\hbar\omega}$$

In the limit ω → 0 we therefore have

$$\sigma = \sigma_1(0) = -\frac{\pi\hbar}{2\Omega m_e^2} \sum_{mn} |\langle n|p_x|m\rangle|^2 \, \delta(\varepsilon_n - \varepsilon_m) \frac{df_0(\varepsilon_m)}{d\varepsilon_m} = -\int \frac{df_0}{d\varepsilon} \sigma(\varepsilon) \, d\varepsilon \tag{3.7}$$

with

$$\begin{aligned} \sigma(\varepsilon) &= \frac{\pi e^2 \hbar}{2\Omega m_e^2} \sum_{mn} |\langle n|p_x|m\rangle|^2 \, \delta(\varepsilon - \varepsilon_n) \, \delta(\varepsilon - \varepsilon_m) \\ &= \frac{\pi e^2 \hbar\Omega}{2m_e^2} N^2(\varepsilon) \, p_x^2(\varepsilon)_{av} \end{aligned} \tag{3.8}$$

where

$$N(\varepsilon) = \frac{1}{\Omega} \sum_n \delta(\varepsilon - \varepsilon_n) \tag{3.9}$$

is the density of states (counting both spin orientations) and $p_x^2(\varepsilon)_{av}$ is the average of $|\langle n|p_x|m\rangle|^2$ calculated with the weighting factor $\delta(\varepsilon - \varepsilon_m)\,\delta(\varepsilon - \varepsilon_n)$.

3.3. Localised and extended states

We see from the above discussion that σ(ε) is determined by the matrix elements of p_x between states with energy ε. For this reason the distinction between extended and localised states is of great importance in the theory of electron transport in disordered systems. As the name implies: extended states, like Bloch functions, run right over the macroscopic volume Ω of the system while localised states, like impurity wave functions, are confined to a microscopic volume. The two types of state cannot co-exist at the same energy because any coupling of a localised state to an extended one will lead to delocalisation[1].

Let us consider a single energy band for which N(ε) has the form shown in Fig. 1. For weak disorder most of the states are extended. Localised states arise only in the tails of N(ε), as indicated by the cross-hatching, and are due to extreme fluctuations of the potential. The localised states are separated from

the extended states by "mobility edges" ε_c and ε_c'. The reason for this nomenclature is made clear below. As the disorder increases ε_c and ε_c' move towards the centre of the band and coalesce at a critical value of the disorder. Thereafter all the states in the band are localised. This is called an Anderson transition[1].

3.4. Behaviour of σ(ε)

When T → 0 the conductivity σ in equation (3.1) approaches $\sigma(\varepsilon_F)$. Now, we see from the discussion of Section 3.2 that $\sigma(\varepsilon_F)$ is determined by the matrix elements of p_x between states having the energy ε_F. Moreover, it follows from (3.6) that all these matrix elements vanish if $\langle n|x|m\rangle$ is well defined - which it is for localised states. Consequently $\sigma(\varepsilon_F) = 0$ when ε_F lies in the region of localised states. This argument breaks down when ε_F lies in the region of extended states because $\langle n|x|m\rangle$ diverges. Thus $\sigma(\varepsilon_F) \neq 0$ in this case.

We are therefore led to picture σ(ε) as vanishing when ε lies outside the region between ε_c and ε_c' and the reason for calling these energies "mobility edges" is apparent. In the extended state region σ(ε) > 0. The behaviour of σ(ε) as ε approaches a mobility edge remains controversial. Mott supposes that it attains a minimum value

$$\sigma_{min} = 0.026 \, e^2/\hbar a = 610/a \ \Omega^{-1} \ cm^{-1} \tag{3.9}$$

where a is a typical interatomic dimension measured in Angstroms. We may derive this result very easily from (2.21), by arguing that the minimum value of the mean freepath $v\tau \sim a$ and $k \sim 1/a$ which gives $\sigma_{min} = e^2/3\pi^2 ha$. There is considerable experimental evidence to support this contention[1]. Nevertheless, it may be that σ(ε) reaches a value in the order of σ_{min} near the mobility edge and then drops rapidly to zero. It would not be easy to tell the difference from experimental data.

Since (3.8) must agree with (2.21) for weakly scattered free electrons with $N(\varepsilon) = 4\pi k^2/4\pi^3\hbar v$, $v = \hbar k/m_e$ and $\lambda = v\tau$ we have

$$p_x^2(\varepsilon)_{av} = \frac{2\pi\hbar^2}{3} \frac{\lambda}{\Omega} \tag{3.10}$$

Mott supposes that a result of this form has general validity for extended states with λ being the phase coherence length of the wavefunction[1]. If this is the case, and if λ reaches a minimum value of a, $p_x^2(\varepsilon)_{av}$ is fixed and we see from (3.8) that σ(ε) becomes proportional to the square of the density of states.

For temperatures above absolute zero the coupling of electrons to the phonons gives $\sigma(\varepsilon)$ a small but non-vanishing value in the localised state regions. Transport through these states proceeds by a hopping mechanism as we discuss in detail later on. For the moment we concentrate on general applications of the Kubo-Greenwood formulae without detailed discussion of the transport mechanism.

3.5. N-type semiconductor transport

In amorphous semiconductors the transport properties are determined by carriers in states near the "pseudo-gap" in the density of states shown schematically in Fig. 2. At room temperature the transport properties are usually thought to be dominated by either holes in extended states in the valence band or electrons in extended states in the conduction band. In either case the statistics are non-degenerate because ε_F is located near the middle of the gap[1]. To be definite we consider n-type material. Then we may write $f_0(\varepsilon) \simeq \exp[\beta(\varepsilon_F - \varepsilon)]$ in the conduction band and ignore the valence band states altogether. The Kubo-Greenwood formulae (3.1) and (3.2) therefore become

$$\sigma = \int \sigma_D(\varepsilon)\ \exp[\beta(\varepsilon_F - \varepsilon)]d\varepsilon \tag{3.11}$$

$$S = -\frac{k_B}{e}\int \frac{\sigma_D(\varepsilon)}{\sigma k_B T}\exp[\beta(\varepsilon_F - \varepsilon)]\ (\varepsilon - \varepsilon_F)d\varepsilon \tag{3.12}$$

where, by expressing $\sigma(\varepsilon)$ in the form (2.35), we have introduced a "differential conductivity":

$$\sigma_D(\varepsilon) = \sigma(\varepsilon)/k_BT = e\ N(\varepsilon)\ \mu(\varepsilon) \tag{3.13}$$

There have been a number of different treatments of these equations and we mention some of them briefly here.

In the most elementary treatment we set $\sigma(\varepsilon) = \sigma(\varepsilon_c)$ for $\varepsilon > \varepsilon_c$ and $\sigma(\varepsilon) = 0$ for $\varepsilon < \varepsilon_c$. Then we have immediately

$$\sigma = \sigma(\varepsilon_c)\exp[-\ \beta(\varepsilon_\sigma - \varepsilon_F)] \tag{3.14}$$

$$S = -\frac{k_B}{e}\left[\frac{\varepsilon_S - \varepsilon_F}{k_BT} + A\right] \tag{3.15}$$

with $\varepsilon_\sigma = \varepsilon_S = \varepsilon_c$ and $A = 1$. If $\varepsilon_c - \varepsilon_F = W - \gamma T$, where W and γ are constants we see that a plot of log σ against β has an activation energy (slope) W and $\beta = 0$ intercept $\sigma(\varepsilon_c)\ \exp(\gamma/k_B)$ while a plot of Se/k_B against β has an activation energy W and $\beta = 0$ intercept $1 - \gamma/k_B$. A great deal of experimental data for many amorphous semiconductors exhibits this sort of general behaviour but the slopes and intercepts are very sensitive to the method of preparation[1].

A material which has been studied very extensively in recent years is a - Si prepared by the glow discharge decomposition of silane and the experimental data on σ and S have been investigated by several authors for both doped and undoped samples. Le Comber and Spear made the first detailed investigations of this material at Dundee and the work of the Dundee group will be reviewed by Professor Spear[19]. They have often analysed their data on the assumption that there are three transport channels: extended states, tail states and donor states[20]. Friedman[21] has made a careful analysis of Dundee data on the basis of equations (3.11) to (3.13) using the values of $N(\varepsilon)$ determined by Le Comber and Spear[20] and making reasonable assumptions about the variation of $\mu(\varepsilon)$ across the mobility edge. Spear and co-workers have also emphasised the importance of the temperature dependence of both ε_F and possibly ε_c in determining the behaviour of σ and S and the variation of this behaviour from sample to sample[22, 23].

The transport problem which has received most attention in recent years is the observation that while (3.14) and (3.15) are valid for a - Si, ε_σ is frequently greater than ε_S and the difference $\varepsilon_\sigma - \varepsilon_S$ varies from one sample to another. The simplest explanation is that the mobility involved in $\sigma(\varepsilon_c) = e\ N(\varepsilon_c)\ \mu(\varepsilon_c)\ k_BT$ is activated with an activation energy $\varepsilon_\mu - \varepsilon_\sigma - \varepsilon_S$ but then the dependence on preparation method is hard to understand. Döhler[24] has emphasised that one may actually determine the differential conductivity (3.13) from experimental data on S and σ provided it is supposed that $\sigma_D(\varepsilon)$ is independent of β. To do this we write equations (3.11) and (3.12) in the form

$$\sigma(\beta)e^{-\beta\varepsilon_F} = \int_{-\infty}^{\infty} \sigma_D(\varepsilon)e^{-\beta\varepsilon}\ d\varepsilon \tag{3.16}$$

$$\frac{eS}{k_B} = -\frac{e^{\beta\varepsilon_F}}{k_BT}\int_{-\infty}^{\infty} \sigma_D(\varepsilon)e^{-\beta\varepsilon}(\varepsilon - \varepsilon_F)d\varepsilon \tag{3.17}$$

We see from (3.16) that $\sigma(\beta)\exp(-\beta\varepsilon_F)$ is the Laplace transform of $\sigma_D(\varepsilon)$. Hence we may determine $\sigma_D(\varepsilon)$ by inverting the transform once ε_F is known as a function of β. To determine that we differentiate equation (3.16) with respect to β and use (3.17) to show that

$$\frac{d\varepsilon_F}{d\beta} = -\frac{1}{\beta}\left[\frac{eS}{K_B} - \frac{d\log\sigma(\beta)}{d\beta}\right] \tag{3.18}$$

The right-hand side of this equation is known from experiment. Hence ε_F may be determined to within an additive constant which depends on the origin of energy. Consequently $\sigma_D(\varepsilon)$ may be determined apart from an arbitrary shift on the energy scale. Döhler finds that $\sigma(\varepsilon)$ increases rapidly by several orders of magnitudes over a few tenths of an electron volt and depends on doping. This is consistent with the sort of behaviour to be expected near a mobility edge but the details are hard to understand because no transport model is assumed.

Grunwald and Thomas[25] have shown that it is also possible to explain some of the data using a variable-range hopping model but to do so requires what are probably unrealistic assumptions about the distribution of tail states and its doping dependence..

The most recent and most promising treatment of the problem is due to Overhof and Beyer[26] who suggest that ε_μ is due to long range fluctuations of ε_c caused by charged defects in the material. The value of ε_σ is determined by extreme fluctuations while ε_S involves an average and is consequently less. These authors emphasise the importance of the quantity

$$\begin{aligned} Q &= \log\sigma + eS/k_B \\ &= \log\sigma(\varepsilon_c) - \varepsilon_\mu\beta \end{aligned} \tag{3.19}$$

where we have used equations (3.14) and (3.15). We see that Q does not involve ε_F explicitly and is much more indicative of the transport mechanism (as opposed to the electron distribution) than either σ or S individually which do involve ε_F. A plot of Q against β is usually a straight line over a much wider temperature range than is the case for either log σ or S. Moreover the slope ε_μ depends on preparation which one would expect if it is determined by fluctuations of ε_c.

3.6. Conductivity near the mobility edge

Götze and co-workers have developed an unusual and interesting approach to the problem of conductivity in random systems[27 - 30]. The theory provides formulae for both ac and dc conductivity. We outline the dc calculation here. Free electrons with an effective mass m* are considered and it is supposed that they are scattered by a random potential. A relaxation time τ depending on frequency and the location of the Fermi level is introduced and this determines the conductivity when T = 0. In the Boltzmann transport regime τ^{-1} is given by (2.40) with $\varepsilon = \varepsilon_F = \hbar^2 k_F^2/2m^*$ and it is supposed, for simplicity that there is a cut-off in the Fourier transform of the scattering potential such that $a(K)\,\sigma(\theta)$ is constant for $K < K_0$ and zero for $K > K_0$. Then

$$\begin{aligned} \tau &\propto \varepsilon_F^{-\frac{1}{2}}\ , \quad 2k_F < K_0, \\ &\propto \varepsilon_F^{3/2}\ , \quad 2k_F > K_0. \end{aligned} \tag{3.20}$$

Götze goes beyond the Boltzmann transport regime by relating the frequency dependent τ to the density fluctuations in the system, as perturbed by the scattering, which also involve τ in the simplest approximation. Thus a self-consistency condition arises which can be solved numerically. For weak coupling the solution falls slightly below the Boltzmann result (3.20) at high energies but, and this is the important point, τ drops to zero at a mobility edge ε_c, varying as $(\varepsilon - \varepsilon_c)^{\frac{1}{2}}$ as indicated in Fig. 3. For $\varepsilon < \varepsilon_c$ τ becomes imaginary and the dc conductivity vanishes.

A mobility edge is thus predicted by the theory but $\sigma(\varepsilon)$ falls continuously to zero as ε approaches ε_c from above and a minimum metallic conductivity does not appear in the formalism. Belitz and Götze have therefore looked again at experimental data on the dc conductivity of Sb doped Ge, $La_{1-x}\,Sr_x\,VO_3$ and $Gd_{1-x}\,Sr_x\,VO_3$ in which variation of ε_F shows up a transition from semiconducting (activated) to metallic (temperature-independent) behaviour. This has been interpreted as an Anderson transition in the sense that ε_F moves through the mobility edge ε_c. There seems little doubt that this is the case[1]. However, the data does not seem to provide good evidence for a minimum metallic conductivity (as has sometimes been suggested[1]) because Belitz and Götze can fit it with reasonable parameter values by using the $\sigma(\varepsilon)$ derived from their model in the Kubo-Greenwood formula (3.1).

4. Hopping Transport Theory: General Formalism

4.1. Introduction

The states in the tails of the conduction band and valence band of an amorphous semiconductor are localised. Electrons move amongst these states by "hopping" from full states to empty states. The treatment of electron transport involving this mechanism is usually described by a rate equation which is the analogue of Boltzmann's equation for localised states. We use this approach here. As in all transport problems the same results may be obtained by considering the expectation values of appropriate correlation functions in thermal equilibrium. For hopping conductivity the appropriate equilibrium variable is the mean square distance moved by a hopping electron in time t. Thus: we may calculate the diffusivity from a study of a random walk problem and then use the Einstein relation to obtain the conductivity. This approach has attracted the interest of several authors[12, 31 - 38]. We do not use it here because for degenerate statistics the random walk is necessarily an artificial one since, in the real system, the electrons get in each others way. Instead we proceed as in Section 2 to introduce a weak field into the rate equation and calculate the perturbations of the occupation probabilities of the localised states which it produces. We shall see how the random walk formalism arises in this context. However, for calculating transport coefficients the Boltzmann equation approach is more direct and is easier to use because, for weak fields, it reduces to Kirchhoff's equations for an equivalent RC network[39].

4.2. Miller-Abrahams equivalent circuit

We follow previous treatments given by the author and regard the localised states as defining sites which may be occupied by one, and only one, electron. Let f_m and R_{mn} be respectively the occupation probability of site m and the transition rate from m to n. Then the f_m's are determined by the rate equations

$$\frac{df_m}{dt} = \sum_n [f_n(1 - f_m)R_{nm} - f_m(1 - f_n)R_{mn}] \tag{4.1}$$

Let us write ε_m for the unperturbed energy of site m and U_m for the perturbation of ε_m produced by the applied field. We suppose that R_{mn} satisfies the detailed balance relation

$$\begin{aligned}\frac{R_{mn}}{R_{nm}} &= \exp[\beta(\varepsilon_m + U_m - \varepsilon_n - U_n)] \\ &\simeq \exp[\beta(\varepsilon_m - \varepsilon_n)]\,[1 + \beta\,(U_m - U_n)]\end{aligned} \tag{4.2}$$

for small applied fields. When $U_m = 0$ for all m, f_m reduces to the thermal equilibrium form

$$f_m^0 = [\tfrac{1}{2}\exp\{\beta(\varepsilon_m - \varepsilon_F)\} + 1]^{-1} \tag{4.3}$$

This is just the Fermi function (2.8) modified by a factor of 0.5 in front of the exponential to take account of the fact that only one electron, but with either spin orientation, may occupy site m. When $U_m \neq 0$ it is convenient to write

$$f_m = f_m^0 - \frac{df_m^0}{d\varepsilon_m}\phi_m \tag{4.4}$$

where ϕ_m remains to be determined. When equations (4.2) and (4.4) are substituted into equation (4.1) we find that to first order in ϕ_m and U_m, the linearised rate equations are

$$C_m \frac{d}{dt}(V_m + Ex_m) = \sum_n g_{mn}(V_n - V_m) \tag{4.5}$$

where

$$C_m = - e^2\, df_m^0/d\varepsilon_m \tag{4.6a}$$

$$g_{mn} = e^2\, \beta f_m^0(1 - f_n^0)\, R_{mn}^0 \tag{4.6b}$$

$$V_m = - [Ex_m + e^{-1}\,\phi_m] \tag{4.6c}$$

In equations (4.5) and (4.6) we have written

$$U_m = eEx_m \tag{4.7}$$

to specialise to the case when a uniform electric field E is applied in the positive x direction. In equation (4.6b) R_{mn}^0 is the equilibrium value of R_{mn}.

Equations (4), (5) and (6) have a simple interpretation. We see from (4.3) and (4.4) that ϕ_m may be regarded as the local change of chemical potential at site m. Hence V_m in equation (4.6c) is the local change of the electrochemical potential $\phi_m + eEx_m$ multiplied by $-e^{-1}$ for convenience of notation. We refer to V_m simply as the "voltage" at site m. The particle current which flows from n to m is proportional to the electrochemical difference between the two sites. In equation (4.5) we have introduced a factor -e so that the <u>electric</u> current from n to m appears as $g_{mn}(V_n - V_m)$. The quantity g_{mn} is given by equation (4.6b). It follows from the detailed balance relation (4.2) in zero field that $g_{mn} = g_{nm}$. Thus g_{mn} is a positive, symmetrical conductance. Finally, we note that the left-hand side of equation (4.5) is the time-rate of change of the electric charge on site m and that c_m in (4.6a) is positive and may be interpreted as a capacitance. Hence, equations (4.5) are Kirchhoff's equations for the RC network shown in Fig. 4 where the ground potential is zero and the voltage generators sustain the applied potential at each site. This point of view was originally introduced by Miller and Abrahams[39] and it has proven to be very fruitful.

4.3. <u>Conductivity formulae</u>

There are several alternative ways to write a general formula for the conductivity $\sigma(\omega)$ at frequency ω. Let us suppose that E has a time factor $\exp(-i\omega t)$. Consider a large cube of side L inside an infinite specimen. The current density across the coordinate plane at x is

$$J(x) = L^{-2} \sum_{mn} g_{mn}(V_m - V_n)\ \theta(x - x_m)\ \theta(x_n - x) \qquad (4.8)$$

where the unit step functions exclude contributions from pairs of sites for which the inequalities $x_m < x < x_n$ are not satisfied. The current density is independent of x when $L \to \infty$. We may therefore average over x from 0 to L and divide by E to obtain the conductivity formula

$$\sigma(\omega) = \frac{1}{\Omega E} \sum_{mn} (x_n - x_m)\ \theta(x_n - x_m)\ g_{mn}(V_m - V_n)$$

$$= \frac{1}{2\Omega E} \sum_{mn} g_{mn}\, V_{mn}\, x_{nm} \qquad (4.9)$$

where $\Omega = L^3$, $V_{mn} = V_m - V_n$ and $x_{nm} = x_n - x_m$. In the first line of (4.9) terms with $x_n < x_m$ are excluded. In the second line we have used the symmetry of g_{mn} to include them.

We may also obtain a simple formula for the real part $\sigma_1(\omega)$ of $\sigma(\omega)$ by noting that the Joule heat generated in Ω is the sum of the Joule heats developed in the individual conductances. Thus we find that

$$\sigma_1(\omega) = \frac{1}{2\Omega|E|^2} \sum_{mn} g_{mn} |V_{mn}|^2 \qquad (4.10)$$

when $\omega \to 0$, E and V_{mn} are real and the modulus signs may be removed from (4.10). It will be noticed that there is no difficulty in taking the limit $\omega \to 0$ in either (4.9) or (4.10). However, to use either formula we must first obtain an approximation to V_{mn}. We discuss ways of doing this in Sections 5, 6 and 7.

Our final task in this sub-section is to obtain an explicit formula for $\sigma(\omega)$ by introducing a Green's matrix to solve equations (4.5). Let us write

$$q_m = C_m(V_m + Ex_m) \qquad (4.11)$$

for the charge on site m. We consider a finite system and introduce row matrices $\underline{q}$ and $\underline{x}$ whose nth columns are q_n and x_n respectively and the square matrices W and C whose (mn)th elements are respectively:

$$W_{mn} = -\, g_{mn}/C_m + \delta_{mn} \sum_n g_{mn}/C_m \qquad (4.12a)$$

$$C_{mn} = C_m\, \delta_{mn} \qquad (4.12b)$$

Then, assuming a time factor $\exp(-i\omega t)$, the linearised rate equations (4.5) take the matrix form

$$-i\omega\underline{q} = -\,\underline{q}W - E\underline{x}\,CW\ . \qquad (4.13)$$

Writing

$$G = (W - i\omega)^{-1} \qquad (4.14)$$

for the Green's matrix we have

$$\underline{q} = E\underline{x}\,C\,WG \qquad (4.16)$$

The conductivity is equal to $-i\omega/E$ times the x-component of the dipole moment density. Hence

$$\sigma(\omega) = -\frac{i\omega}{\Omega}\, \underline{x}\, CWG\, \underline{\tilde{x}} \tag{4.17}$$

where $\underline{\tilde{x}}$ is the transpose of $\underline{x}$. It only remains to write this formal result in a more recognisable form.

4.4. The Einstein Relation

To rewrite equation (4.17) in the form of an Einstein relation we require to notice some elementary properties of G. We see from (4.14) that W commutes with G and

$$1 + i\omega\, G = WG = GW \tag{4.18}$$

Taking the mnth matrix element of this equation and summing over n we obtain

$$1 + i\omega \sum_n G_{mn} = 0 \tag{4.19}$$

since, from (14.12a),

$$\sum_n W_{mn} = 0 \tag{4.20}$$

Finally, we notice that the detailed balance relation $g_{mn} = g_{nm}$ means that the conductance matrix $g = CW$ is symmetrical. It follows that $S = C^{-\frac{1}{2}} g C^{-\frac{1}{2}} = C^{\frac{1}{2}}\, WC^{-\frac{1}{2}}$ is symmetrical. Hence

$$\begin{aligned} CG &= -\frac{C}{i\omega}\left[1 + \frac{W}{i\omega} - \frac{W^2}{\omega^2} + \ldots.\right] \\ &= -\frac{C^{\frac{1}{2}}}{i\omega}\left[1 + \frac{S}{i\omega} - \frac{S^2}{\omega^2} + \ldots.\right]C^{\frac{1}{2}} \end{aligned} \tag{4.21}$$

is also symmetrical, i.e.

$$C_m\, G_{mn} = C_n\, G_{nm} \tag{4.22}$$

To carry out the algebra we substitute for WG in (4.17) from (4.18) and eliminate the diagonal elements of G with the aid of (4.19). Thus we have

$$\begin{aligned} \sigma(\omega) &= -\frac{i\omega}{\Omega}\left[\sum_m x_m\, C_m \sum_{n\neq m} (1 + i\omega G)_{mn}\, x_n - \sum_m x_m\, C_m \sum_{n\neq m} (1 + i\omega G)_{mn}\, x_m\right] \\ &= \frac{\omega^2}{\Omega} \sum_{mn} x_m\, C_m\, G_{mn}\, (x_n - x_m) \qquad (4.23) \\ &= -\frac{\omega^2}{2\Omega} \sum_{mn} C_m\, G_{mn}\, (x_m - x_n)^2 \end{aligned}$$

In the last line of (4.23) we have symmetrised the summand and have made use of (4.22).

Equation (4.23) provides a formal expression for $\sigma(\omega)$. To put it in its most easily interpretable form we note that the electron density is

$$n = \Omega^{-1} \sum_m f_m^0 \tag{4.24}$$

where f_m^0 is given by equation (4.3). Hence

$$\frac{dn}{d\varepsilon_F} = -\,\Omega^{-1} \sum_m \frac{df_m^0}{d\varepsilon_m} \tag{4.25}$$

which, with (4.6a), allows us to write (4.23) in the form of an Einstein relation:

$$\sigma(\omega) = e^2 \frac{dn}{d\varepsilon_F}\, D(\omega) \tag{4.26}$$

with

$$D(\omega) = -\tfrac{1}{2}\omega^2 \frac{\sum_m \left|\frac{df_m^0}{d\varepsilon_m}\right| \sum_n G_{mn}\, (x_m - x_n)^2}{\sum_m \left|\frac{df_m^0}{d\varepsilon_m}\right|} \tag{4.27}$$

being a frequency dependent diffusivity.

4.5. The associated random walk

It follows from equation (4.14) that G_{mn} is the causal Fourier transform of $P_{mn}(t)$ where

$$\frac{d}{dt} P_{mn} = -\sum_\ell \left[W_{en}\, P_{m\ell} - W_{n\ell}\, P_{mn}\right],\ t > 0,\ P_{mn} = \delta_{mn}\ ,\ t = 0. \quad (4.28$$

We see that the diagonal elements of W are not involved in this equation. Moreover $-W_{\ell n} = g_{\ell n}/C_\ell$ is positive and may be regarded as a hop rate.

Hence $P_{mn}(t)$ may be interpreted as the probability that a single particle will be found on n at time t, given that it was on m at time 0 and that it hops between sites with the rate $-W_{\ell n}$. Consequently, the sum over n in equation (4.27) is the Fourier transform of the mean square distance moved by the particle in time t. The sum over m averages this quantity over sites with a weighting factor $df^0_m/d\varepsilon_m$.

The connection of the hopping conductivity problem with random walks is contained in equations (4.26) and (4.27). For non-degenerate statistics $df^0_m/d\varepsilon_m = -\beta f^0_m$ and we readily find that $-W_{\ell n} = R^0_{\ell n}$. Hence the particle is hopping with the thermal equilibrium hop rate and the site averaging in (4.27) is done with a Boltzmann weighting factor. In that case the relevant random walk problem is the actual random walk of any one electron in the hopping system because non-degenerate statistics imply that the electron density is so low that the electrons never get in each others way. For degenerate statistics $df^0_m/d\varepsilon_m \neq -\beta f^0_m$ and $W_{mn} \neq R^0_{mn}$. The relevant random walk is therefore an artificial one and the site averaging is also done in an artificial way which takes proper account of the degenerate statistics. A random walk picture, all be it an artificial one, makes an appearance even in this case because of the particular structure of the linearised rate equations[12].

5. Hopping Conductivity: ac conductivity

5.1. The pair approximation

Assuming a time factor $\exp(-i\omega t)$, we see from equation (4.5) that $V_m \to Ex_m$ when $\omega \to \infty$ so that both equations (4.9) and (4.10) yield the same asymptotic limit

$$\sigma(\infty) = \frac{1}{2\Omega}\sum_{mn} g_{mn}\, x_{mn}^{\;2} \qquad (5.1)$$

The existence of a non-zero high frequency limit to $\sigma(\omega)$ is due to our tacit assumption that the hops take place instantaneously which introduces δ-functions into the current response. It is easy to expand $\sigma(\omega)$ in powers of ω^{-1} but the convergence is too slow for the series to be of any value. A much more successful expansion when $\omega \neq 0$ is in powers of the site density n_s. Since double sums are involved in the general formulae for $\sigma(\omega)$ the leading term in the expansion is proportional to n_s^2 and it is obtained by summing the contributions from all pairs of sites calculated by treating each pair as being isolated from all other sites. This is the "pair approximation" originally introduced by Pollak and Geballe[40].

Let us consider an arbitrary pair of sites m and n. Then Kirchhoff's equations (4.5) reduce to

$$-i\omega\, C_m(V_m + Ex_m) = g_{mn}\, V_{nm} \qquad (5.2a)$$

$$-i\omega\, C_n(V_n + Ex_n) = -\, g_{mn}\, V_{nm} \qquad (5.2b)$$

so that

$$V_{mn} = -\frac{Ex_{mn}}{g_{mn}\, Z^p_{mn}} \qquad (5.3)$$

where

$$Z^p_{mn} = \frac{1}{g_{mn}} - \frac{1}{i\omega C_m} - \frac{1}{i\omega C_n} \qquad (5.4)$$

when this result is substituted into (4.9) we obtain the pair approximation to $\sigma(\omega)$:

$$\sigma(\omega) = \frac{1}{2\Omega}\sum_{mn} x^2_{mn}/Z^p_{mn} \qquad (5.5)$$

which remains to be system averaged. Before doing that we notice that (5.5) yields the exact result (5.1) when $\omega \to \infty$ and that it gives $\sigma(0) = 0$ because $Z^p_{mn} \to \infty$ when $\omega \to 0$. Thus, the pair approximation becomes progressively worse as ω is reduced. Nevertheless, it is frequently used to analyse data for audio and video frequencies provided that $\sigma_1(\omega) \gg \sigma(0)$.

5.2. The r-hopping model

A special case which is often considered is what we shall call the r-hopping model. It is defined by

$$g_{mn} = g_a \exp(-2\alpha r_{mn}) \qquad C_m = C \qquad (5.6)$$

where α, g_a and C are constants. To arrive at a model of this type we consider non-degenerate electrons in a band of states whose width is small compared to

k_BT. Then $f_m^0 \to f$, a constant much less than one so that $C = e^2\beta f$. Moreover, if we suppose that the hop rate between two sites a distance r_{mn} apart is $R_0 \exp(-2\alpha r_{mn})$ then $g_a = R_0 C$, i.e. $R_0 = g_a C^{-1}$ is the natural unit of frequency in the problem. For sites randomly distributed with a density n_s the system average of equation (5.5) yields:

$$\sigma(\omega) = \frac{2\pi}{3} n_s^2 g_a(-i\omega\tau_0) \int_0^\infty \frac{r^4\,dr}{1 - i\omega\tau} \tag{5.7}$$

where

$$\tau = \tau_0 e^{2\alpha r} \tag{5.8a}$$

with

$$\tau_0 = (2R_0)^{-1} \tag{5.8b}$$

When $\omega \to \infty$ we obtain

$$\sigma(\infty) = (g_a\alpha)\frac{\pi}{2}(n_s\alpha^{-3})^2 \tag{5.9}$$

At lower frequencies we use this result to normalise $\sigma(\omega)$ so that

$$\frac{\sigma(\omega)}{\sigma(\infty)} = \frac{4}{3}\alpha^5(-i\omega\,\tau_0)\int_0^\infty r^4\,dr\left[\frac{1}{1+\omega^2\tau^2} + \frac{i\omega\tau}{1+\omega^2\tau^2}\right] \tag{5.10}$$

The real and imaginary parts of the integral in (5.10) are easily approximated at low frequencies[40 - 42]. When $\alpha n_s^{-1/3} \gg 1$ and $\omega\,\tau_0 \ll 1$ we find that $\omega\,\tau/[1 + \omega^2\,\tau^2]$ has a sharp peak at

$$r_\omega = \frac{1}{2\alpha}\log(\omega\tau_0)^{-1} \tag{5.11}$$

which is the value of r at which $\omega\tau = 1$. We may readily integrate $\omega\tau/[1 + \omega^2\,\tau^2]$ over all r to obtain the value $\pi/4\alpha$. Thus $\omega\tau/[1 + \omega^2\,\tau^2]$ may be approximated by

$\pi/4\alpha\;\delta(r - r_\omega)$. Similarly $[1 + \omega^2\,\tau^2]^{-1} \simeq \theta(r_\omega - r)$. When these results are substituted into (5.10) we obtain immediately

$$\frac{\sigma_1(\omega)}{\sigma(\infty)} = \frac{\pi}{3}(\omega\tau_0)\;(\alpha r_\omega)^4 \tag{5.12a}$$

$$\frac{\sigma_2(\omega)}{\sigma(\infty)} = -\frac{4}{15}(\omega\tau_0)\;(\alpha r_\omega)^5 \tag{5.12b}$$

$$\frac{\sigma_2(\omega)}{\sigma_1(\omega)} = -\frac{2}{5\pi}\log(\omega\tau_0) = -\,0.293\,\log_{10}(\omega\tau_0) \tag{5.12c}$$

It is usually supposed that $\tau_0 \sim 10^{-13}\ s^{1}$. Then r_ω decreases slowly with increasing ω for frequencies in the typical experimental range of 1 kHz to 1 MHz. Consequently both $\sigma_1(\omega)$ and $\sigma_2(\omega)$ show a slightly sub-linear frequency dependence which is often approximated by a ω^s with

$$s = \frac{d\log\sigma_1(\omega)}{d\log\omega} = 1 - \frac{4}{\log\omega\tau_0} \tag{5.13}$$

being the slope of the real part of $\sigma_1(\omega)$ on a log-log plot. The frequency dependence of s and the ratio $\sigma_2(\omega)/\sigma_1(\omega)$ is very weak and is usually not discernable in experimental data.

5.3. The AHL model

In the r-hopping model we consider a very narrow band. It is of interest to go to the opposite extreme of a very wide band. The simplest model for this case is one introduced several years ago by Ambegaokar Halperin and Langer[43] to describe dc conductivity. It is defined by

$$g_{mn} = g_a\,\exp(-s_{mn}) \tag{5.14}$$

where the conductivity exponent s_{mn} is given by

$$s_{mn} = 2\alpha r_{mn} + \frac{1}{2}\beta[|\varepsilon_m| + |\varepsilon_n| + |\varepsilon_m - \varepsilon_n|] \tag{5.15}$$

where the site energies are measured from the Fermi level plus $k_BT\log 2$. The energy-dependent exponential factor in (5.14) arises from asymptotic approximations to Fermi and Bose factors in equation (4.6b) for g_{mn}. To carry out the configuration average we suppose that the sites are uniformly distributed in space with a density n_s and uniformly distributed in energy over a wide band width W with a density of states $\rho_F = n_s/W$. Then the system average of (5.5) becomes:

$$\sigma(\omega) = \frac{2\pi}{3} \rho_F^2 g_a \int d\varepsilon_1 \int d\varepsilon_2 \int_0^\infty r^4 \frac{(-i\omega\tau)Qe^{-2\alpha r}}{1 - i\omega\tau} dr \tag{5.16}$$

where

$$Q = \exp[-\tfrac{1}{2}\beta\{|\varepsilon_1| + |\varepsilon_2| + |\varepsilon_1 - \varepsilon_2|\}] \tag{5.17}$$

and

$$\tau^{-1} = \left(\frac{1}{C_1} + \frac{1}{C_2}\right) g_a Qe^{-2\alpha r} \tag{5.18}$$

We suppose that $W >> k_BT$. Then the major contribution to the energy integrals in (5.16) comes from the neighbourhood of $\varepsilon_1 = \varepsilon_2 = 0$ and the limits of integration may be extended to infinity.

When $\omega \to \infty$ we have

$$\sigma(\infty) = (g_a\alpha) \frac{\pi}{2} (n_s\alpha^{-3})^2 \bar{Q} \tag{5.19}$$

where

$$\bar{Q} = W^{-2} \int_{-\infty}^{\infty} d\varepsilon_1 \int_{-\infty}^{\infty} d\varepsilon_2 \, Q = 6(k_BT/W)^2 \tag{5.20}$$

Equation (5.19) differs from our result (5.9) for r-hopping only by the factor $\bar{Q}$. Moreover, the frequency dependence of $\sigma(\omega)$ obviously still has the same general character as before and we may roughly evaluate (5.14) by giving τ its value when $\varepsilon_1 = \varepsilon_2 = 0$. Thus we write τ as in equation (5.8) with R_0 equal to the transition rate in thermal equilibrium for $r = 0$ and $\varepsilon_1 = \varepsilon_2 = 0$. Then our previous evaluation of $\sigma(\omega)/\sigma(\infty)$ goes through unaltered except for the reinterpretation of $\sigma(\infty)$ and τ_0. At low frequencies the final result is

$$\sigma_1(\omega) = (g_a\alpha)\, \pi^2(\rho_F k_B T\alpha^{-3})^2\, \omega\tau_0(\alpha r_\omega)^4 \tag{5.21}$$

with r_ω given by (5.11) and $\sigma_2(\omega)/\sigma_1(\omega)$ given by (5.12c). This result differs from (5.12a) only in that n_s^2 is replaced by $6(\rho_F k_BT)$. It was originally derived by Austin and Mott with a slightly different numerical factor[44]. The simple approximation used to evaluate the integral in (5.16) has been criticised recently by Pramanik and Islam[45]. The integral has therefore been evaluated numerically. The approximate results quoted here are found to be substantially correct[46].

5.4. General Debye Models

The basic structure of the pair approximation is of the Debye type[47]:

$$\sigma(\omega) = -\, i\omega\left\langle\frac{\chi_0}{1 - i\omega\tau}\right\rangle \tag{5.22}$$

where the angular brackets signify an average and the choice of χ_0, τ and the average define the model. In the energy-dependent case we took $\tau = \tau_0 \exp(2\alpha r)$, $\chi_0 \sim r^2$ and the probability distribution in r was proportional to $4\pi r^2$. In the AHL model we again, in the end, put $\tau = \tau_0 \exp(2\alpha r)$ but took $\chi_0 \sim Qr^2$ and the probability distribution of r, ε_1 and ε_2 was proportional to $4\pi r^2 W^{-2}$. Another variant which has attracted considerable interest in recent years is the "classical barrier hopping model" originally introduced by Pike[48] but discussed extensively by Elliott[47, 49, 50] for chalcogenide glasses. In these materials the absence of spin resonance signals suggests that one is concerned with the hopping of <u>pairs</u> of electrons between D^+ and D^- centres. (An account of the defect centres found in amorphous semiconductors is given in this Spring College by Professor Davis[91] and in the book by Mott and Davis[1].) Elliott supposes that the hops are thermally activated over a Coulomb barrier of the form

$$W = W_m - 2e^2/\varepsilon\pi r \tag{5.23}$$

where ε is the electrical permitivity of the material and r is the spatial separation of the two sites. Then we have

$$\tau = \tau_1 \exp(-\beta/r) \tag{5.24}$$

where $\tau_1 = \tau_0 \exp(W_m/k_BT)$ and $\beta = 2e^2/\varepsilon\pi k_BT$. The real part of the conductivity has the form $\omega(r_\omega)^6$ in this case, the additional two powers of r_ω arising in the evaluation of the Debye integral because the exponent in τ involves r^{-1}.

The optimum distance for ac absorption r_ω is determined as before by the equation $\omega\tau = 1$, which gives for Elliott's model,

$$r = \frac{\beta}{\log(\omega\tau_1)} = \frac{\beta}{W_m/k_BT + \log\omega\tau_0} \tag{5.25}$$

Consequently $\sigma_1(\omega) \sim \omega^s$ with

$$s = 1 - \frac{6}{W_m/k_BT + \log\omega\tau_0} \tag{5.26}$$

where, for most chalcogenides, below about 200 K the frequency-dependent term may be neglected in comparison to W_m/k_BT. Consequently: $s = 1 - 6k_BT/W_m$ which increases with decreasing T as is often observed[47, 49, 50]. Recent Shimakawa[52] has pointed out that at high temperatures it is possible to identify additional components in the ac conductivity which he associates with single electron hops between D^0 and D^+ or D^- centres. The D^0 centres are thermally activated from D^+ and D^- centres as the temperature rises[1, 92].

5.5. Conclusion

The strong frequency dependence associated with ac hopping conductivity is due to the highly disordered state of the materials under consideration. For a random walk on a regular Bravais lattice the mean square distance moved in time t is easily seen to be strictly proportional to t for all t. The Fourier transform of this ramp function is proportional to ω^{-2} and consequently, from equation (4.27) we see that $D(\omega)$ is independent of ω. The fact that $\sigma_1(\omega)$ increases with ω is also indicative of hopping in a disordered system. This behaviour is to be contrasted with the decrease of $\sigma_1(\omega)$ with increasing ω which we see from (4.39) is characteristic of Boltzmann transport involving extended states.

6. Hopping Transport: dc conductivity and thermopower

6.1. Introduction: the r-hopping model.

In the early 1970's several groups realised that the calculation of dc hopping conductivity involves ideas taken from percolation theory[43, 53, 54]. To illustrate the sort of considerations involved we discuss first of all the r-hopping model for which the ac conductivity has already been calculated in Section 5.2. by using the pair approximation. We have to go outside this approximation to calculate the dc limit. Taking finite clusters containing two or more sites can never yield a non-zero value of $\sigma(0)$ because the mean

squared distance moved by a particle hopping in such a cluster must remain finite for large times. To calculate $\sigma(0)$ it is therefore necessary to consider an infinite system.

We easily obtain a formal expression for $\sigma(0)$ by taking the dc limit of equation (4.10):

$$\sigma(0) = \frac{1}{2\Omega E^2}\sum_{mn} g_{mn} V_{mn}{}^2 \tag{6.1}$$

This equation has been used to evaluate $\sigma(0)$ for large systems modelled on a computer[14]. To proceed with an analytical derivation of $\sigma(0)$ we take the system average of (6.1) to obtain

$$\sigma(0) = \frac{2\pi}{E^2} n_s^2 \int_0^\infty r^2\, g(r)\, \Delta V^2(r)\, dr \tag{6.2}$$

where $g(r) = g_a \exp(-2\alpha r)$ and $\Delta V^2(r)$ is the mean square voltage drop between two sites separated by a distance r. The quantity $P(r) = g(r)\,\Delta V^2(r)$ is the mean power dissipated in the conductance $g(r)$ joining the sites. When r is large $\Delta V^2(r) = E^2r^2/3$ because there is an electric field of magnitude E oriented in the x direction. Hence $P(r)$ grows exponentially as r decreases. Eventually, however, an optimum separation r_p for power absorption will be reached and $P(r)$ falls off again when r is reduced still further. This is because $g(r)$ behaves essentially like a short circuit when $r \to 0$. Thus $\Delta V^2(r) \to 0$ but a non-zero current flows through $g(r)$ which is determined by the currents in the neighbouring conductances. For $r < r_p$ it is therefore convenient to rewrite $P(r)$ in the form $I^2(r)/g(r)$ where $I^2(r)$ is the mean square current through $g(r)$. To make $P(r)$ continuous at r_p we must have $I^2(r_p) = g^2(r_p)\,E^2r_p{}^2/3$. For simplicity we neglect the variation of $I^2(r)$ when $r < r_p$. Thus, finally we arrive at the ansatz:

$$\begin{aligned} g(r)\,\Delta V^2(r) &= g(r)\,E^2r^2/3, \quad r > r_p, \\ &= \frac{g^2(r_p)}{g(r)}\,E^2r_p{}^2/3, \quad r < r_p. \end{aligned} \tag{6.3}$$

When this is substituted into (6.2) the integral may be evaluated immediately. When αr_p is large we obtain the simple result:

$$\sigma(0) = \frac{2\pi}{3} n_s^{\,2} r_p^{\,4} (g_a/\alpha) e^{-2\alpha r_p} \tag{6.4}$$

The behaviour of $\sigma(0)$ is dominated by the final exponential factor in (6.4). For dimensional reasons r_p is proportional to $n_s^{-1/3}$. Percolation theory comes in to determine the constant of proportionality. The argument is an asymptotic one concerning the behaviour of the system as $\alpha \to \infty$ with n_s fixed. There is then an enormous spread in conductance values. As α increases, all the conductances with r greater than a chosen value, r_0 say, can be omitted from the network without affecting $\sigma(0)$ because they become exponentially small compared with those which are retained. This argument is valid provided that removing all the conductances with $r > r_0$ does not cause the infinite network to break into isolated islands so that dc conductivity becomes impossible. The critical value of r_0 for which the network just falls apart is called the critical percolation radius. It is identical to the value of r for which P(r) has its maximum value when αr_p is large.

Henceforth we interpret r_p as the critical percolation radius. Its value may be determined on a computer by shrinking identical spheres centred on random sites until no continuous paths of overlapping spheres remain[54, 55]. Thus we find that the percolation criterion which determines r_p takes the form: the mean number of neighbours with $r < r_p$ is equal to N_p where $N_p = 2.7$ in 3D, 4.5 in 2D and 2.1 in 4D (which we shall need later in energy-dependent problems). Our current problem is three dimensional and we therefore have

$$\frac{4\pi}{3} r_p^3 n_s = N_p = 2.7 \tag{6.5}$$

which determines r_p completely. In Fig. 5 the full curve was calculated from (6.2) by using the ansatz (6.3) with r_p given by (6.5); the points were obtained by solving Kirchhoff's equations for a system containing 2500 sites and substituting the voltage drops calculated in this way into the sum (6.1)[56]. The agreement between the analytical and computed results is extremely good and should serve to remove any lingering doubts about the validity of the above argument. The lower dashed curve in Figure 5 is the low density approximation (6.4); the upper dashed is obtained by setting $r_p = 0$ in (6.3).

6.2. The AHL model

We may extend the discussion in Section 6.1 to the case when the conductance between two sites involves the site energies as well as the intersite distance. To be definite we consider the AHL model discussed in Section 5.3. Then the conductance exponent s_{mn} given in (5.15) replaces $2\alpha r$ and the configuration average of (6.1) reduces to

$$\sigma(C) = \frac{2\pi\rho_F^2}{E^2} \int d\varepsilon_1 \int d\varepsilon_2 \int r_{12}^2\, g_{12}\, \Delta V_{12}^2\, dr_{12} \tag{6.6}$$

where ΔV_{12}^2 is the mean square voltage drop across the conductance g_{12}. To evaluate (6.6) we generalise the ansatz (6.3):

$$\begin{aligned} g_{12}\, \Delta V_{12}^2 &= g_a \exp(-s_{12})\, E^2 r^2/3, \quad s_{12} > s_p, \\ &\doteq g_a \exp(s - 2s_p)\, E^2 r_p^2/3, \quad s_{12} < s_p, \end{aligned} \tag{6.7}$$

where the critical percolation exponent s_p is determined by the criterion that the mean number of conductances emanating from site 1 with $s_{12} < s_p$ is $N_p = 4.5$ (the value for 4D hyperspheres). Once s_p is fixed, r_p is determined as a function of ε_1 and ε_2 by setting $s_{12} = s_p$ in equation (5.15).

A problem arises in identifying the mean number of neighbours emanating from site 1 with $s_{12} < s_p$ because, as we see from (5.15), there can be no neighbours at all which satisfy the percolation criterion when $\varepsilon_1 > k_B T\, s_p$. These sites must therefore play a negligible role in the dc conductivity and we solve the problem by excluding them altogether in calculating s_p. Then the mean number of sites with $\varepsilon_1 < s_p k_B T$ per unit volume is $2\,\rho_F\, s_p\, k_B T$ while the mean number of conductances per unit volume with $s_{12} < s_p$ is

$$B = \frac{1}{2}\rho_F^2 \int d\varepsilon_1 \int d\varepsilon_2 \int 4\pi^2\, dr \tag{6.8}$$

where the factor of 1/2 prevents double counting. Since each conductance is connected to two sites, the percolation criterion is

$$\frac{2B}{2\rho_F\, s_p\, k_B T} = N_p = 4.5 \tag{6.9}$$

Thus we find that [8]

$$s_p = \left(\frac{4\ 0\ N_p\ \alpha^3 \beta}{\pi \rho_F} \right)^{1/4} \tag{6.10}$$

which leads the Mott's famous $T^{1/4}$ law for hopping conductivity by degenerate electrons[1]. It is usual to speak of "variable range" hopping in this case because of the interplay of distance and energy variations which determines the critical percolation exponent s_p. When the ansatz (6.7) is used to evaluate $\sigma(0)$ in (6.6) the final result is[8]

$$\sigma(0) = 2\alpha\ g_a \frac{4\pi}{3} (\rho_F\ k_B T)^2 \frac{1}{s} \left(\frac{s_p}{2\alpha} \right)^6 e^{-s_p} \tag{6.11}$$

when s_p is large. In Figure 6 the dashed curve is a plot of $\sigma(0)$ calculated from (6.11). The dots are calculated by solving Kirchhoff's equations for 2197 sites [57]. They are believed to be overestimates because only twelve neighbours to each site were taken into account in the calculations[56, 57]. The significance of the full and dash-dot curves is explained in Section 7.

6.3. More general models

The general idea behind the application of percolation theory to the calculation of $\sigma(0)$ is easily extended to more general cases. We may vary the density of states so as to deal with tail states and two-dimensional impurity bands may be handled as well[12, 14]. The idea that percolation theory determines the exponent in $\sigma(0)$ is now over a decade old. The notion that the simple ansatz that we have used for the mean square voltage drop between two sites could also be successful in predicting the prefactor is taking longer to gain acceptance. Suffice it to say that it has worked well in every case for which numerical results are available.

6.4. Thermopower

An entirely satisfactory theory has yet to be developed because of the intimate involvement of the phonons in the hopping process which should be taken into account[59]. There has therefore been some controversy in the literature[60, 61]. However, it is usually assumed that the mean energy $\frac{1}{2}(\varepsilon_m + \varepsilon_n)$ is transported when an electron hops from m to n[62, 63]. Then, on the basis of the argument given in Section 3.1. we find that the thermopower for a hopping system is given by

$$S = -\frac{1}{eT} \frac{\sum\limits_{mn} g_{mn}\ V_{mn}\ x_{nm}\ [\frac{1}{2}(\varepsilon_m + \varepsilon_n) - \varepsilon_F]}{\sum\limits_{mn} g_{mn}\ V_{mn}\ x_{nm}} \tag{6.12}$$

where V_{mn} is the voltage drop between sites m and n produced by an applied electric field. For non-degenerate statistics a result of the standard type (2.24) is obtained. At low temperatures the statistics become degenerate. For extended state conduction in metals the result is that S is proportional to T as in equation (2.23) because the mean energy transported relative to the Fermi level is proportional to $(k_B T)^2$. In the hopping case the significant range is $s_p\ k_B T$ leading to a $T^{\frac{1}{2}}$ dependence of S[62, 63] because s_p is proportional to $T^{-1/4}$. Moreover, we see from (4.3) that the peak of $-df_m^0/d\varepsilon_m$ occurs at $\varepsilon_F + k_B T \log 2$ when the hopping sites can only be singly occupied. This leads to an additional constant term $- k_B \log 2/e$ when $T \to 0$[1, 64]. When the Hubbard U is finite (rather than infinite as we have assumed),, S again tends to a constant value when $T \to 0$ but the value of the constant depends on the details of the model[59, 64].

7. Hopping Conductivity: Unified Theory

In Sections 6 and 7 we have approached the calculation of ac and dc hopping conductivity along entirely different routes. There is a clear need for a unified treatment. This problem has been approached recently by Movaghar and co-workers[35 - 37] through the random walk formalism and by Butcher and Summerfield[65, 58] via the Miller and Abrahams equivalent circuit. We outline the latter approach because it is very simple. The pair model equations (5.2) are modified by the addition of extra terms $-Y(\varepsilon_m)(V_m + Ex_m)$ and $-Y(\varepsilon_n)(V_n + Ex_n)$ on the right-hand sides of (5.2a) and (5.2b) respectively. $Y(\varepsilon_m)$ and $Y(\varepsilon_n)$ are average admittances which take account of the effect of the rest of the network on the pair (m,n). They are determined from a modified mean field equation:

$$Y(\varepsilon_m) = B^{-1} \int d\varepsilon_n\ \rho(\varepsilon_n) \int 4\pi r_{mn}{}^2 \left(\frac{1}{g_{mn}} + \frac{1}{Y(\varepsilon_n) - i\omega C_n} \right)^{-1} dr_{mn} \tag{7.1}$$

Once this equation is solved, the pair equations (5.2), modified as indicated above, may be solved immediately to yield V_{mn} for insertion into (4.9) prior to system averaging. The correction factor B is chosen so that the theory yields the correct percolation threshold in percolation problems involving cut-offs in the conductances. We find that $B = N_p$ or two and three dimensional R-hopping, while $B = 4.4$ for the AHL model[58].

Details of the calculations are in the course of publication[58]. By way of illustration we show in Figures 7 and 8 the real and imaginary parts of $\sigma(\omega)$ for a 3D R-hopping model. The model is studied numerically in reference 66. It should be noted that it differs from the R-hopping model defined by equation (5.6) by the multiplication of g_{mn} by an additional factor $(\alpha r_{mn})^{3/2}$. The full curves in Figures 6 and 7 are derived as indicated here. The points are obtained by solving Kirchhoff's equations for 1600 sites[66] and the dashed curve is taken from the unified random walk theory[37]. In Figure 6 we make a corresponding comparison for the dc conductivity calculated for the AHL model. The full curve is the unified equivalent circuit theory result[58], the dots are computer points[57], the dashed curve is obtained using percolation theory[8] and the dot-dash curve is obtained from the barrier hopping hopping model of Movaghar et al[37].

The availability of a unified theory is very useful for the interpretation of experimental data. It is all too easy to fit either ac data or dc data but not both. A preliminary study[67] indicates that the data of Pollak and Geballe[40] for impurity bands in c - Si is in fair agreement with the theory. The data of Kahlert[68] for impurity bands in c - GaAs is in excellent agreement with the theory as far as dc conductivity is concerned but the theory fails completely to account for the rapid rise of ac conductivity which is observed. In these cases the only unknown is the density of states curve. Excellent experimental data is also available[69, 70] for a - Ge which exhibits $T^{1/4}$ behaviour when $\omega = 0$. Very few of the relevant parameters are known in this case. The dc behaviour is easily fitted using the AHL model but the characteristic hopping frequency has an unacceptably high value in the order of 10^{21} Hz [67]. Again the rapid rise of the ac conductivity which is observed is not predicted by the theory. In this connection it should be noted that the excellent agreement between theory and experiment for a - Ge shown in Figure 8 of reference 37 is incorrect; the frequency axis has been scaled inappropriately to achieve it.

8. Anomalous Carrier Pulse Propagation and Trap-controlled Transport

8.1. Introduction

Let us consider a plate-like specimen with the spatial coordinate x measured across the plate as shown in Figure 9. Suppose that a pulse of electrons with number density $n(x, t)$ is created at one end by uniform illumination over the cross-section of the plate. This may be achieved

by shining light through a transparent electrode (see Figure 9). In this Section we address the question of how the carrier pulse will move and distort when an electric field $E(x, t)$ is applied in the negative x direction.

To study carrier pulse propagation experimentally it is usual to monitor the total current density in the positive x direction:

$$I(t) = J(x, t) - \varepsilon\frac{\partial E(x, t)}{\partial t} \qquad (8.1)$$

where $J(x, t)$ is the electric current density due to the electrons and ε is the electrical permitivity. The minus sign appears in front of the displacement current because $E(x, t)$ has been taken in the negative x direction to make the electron pulse move in the positive x direction. Maxwell's equations show that the total current density is equal to the curl of the magnetic field and is therefore non-divergent. For the one-dimensional situation under discussion here this means that $I(t)$ is independent of x (as our notation implies) and may be monitored outside the specimen. The behaviour of $I(t)$ depends on the boundary conditions produced by the circuit external to the specimen. We suppose, for simplicity, that the potential difference between the ends of the specimen is held constant. Then we may average (8.1) over the specimen length L to express $I(t)$ as the spatial average of $J(x, t)$:

$$I(t) = \frac{1}{L}\int_0^L J(x, t)\,dx \qquad (8.2)$$

$I(t)$ is the quantity that we wish to calculate. To do so we use the charge conservation equation

$$\frac{\partial J(x, t)}{\partial x} - e\frac{\partial n(x, t)}{\partial t} = 0 \qquad (8.3)$$

where $n(x, t)$ is the total electron density. We stress the word total here because we will subsequently be concerned with situations in which some electrons cease to contribute to $J(x, t)$ because they drop into traps. Nevertheless, the trapped electrons continue to contribute to $n(x, t)$. Theories of carrier pulse propagation differ from one another in the relation which is supposed to exist between $J(x, t)$ and $n(x, t)$ in equation (8.3). We review the conventional theory in the next sub-Section. The pulse is a drifted Gaussian; $I(t)$ is constant while the pulse remains in the specimen and falls away after a transit time proportional to L/E at which the pulse passes out of the far end. This sort of behaviour is observed in most crystalline semiconductors. It is the basis of the method for measuring carrier drift mobility originally pioneered by Shockley and Haynes[71] for crystalline semiconductors and developed by Spear and co-workers for amorphous semiconductors[1].

In amorphous semiconductors $I(t)$ often behaves completely differently. Indeed on a linear-linear plot it frequently droops to zero in an apparently featureless way. Replotting on log-log paper reveals small-time behaviour proportional to $t^{-1+\alpha}$, and large-time behaviour proportional to $t^{-1-\alpha}$ where α is a constant between 0 and 1. One may identify a "transit time" t, by interpolating between these two regimes and it is found that $t_T \sim (L/T)^{1/\alpha}$. Finally, $\log I(t)$ against $\log t$ plots for different values of t_T (i.e. for different values of E or L) can be superimposed by scaling.

What we have described above may be called archetypal anomalous carrier pulse propagation. We show a good example in Figure 10. More complicated data can arise and there may be a switch to conventional carrier pulse propagation as the temperature varies[1, 2]. Nevertheless, archetypal behaviour is observed often enough for us to seek a general explanation of it in the properties of amorphous semiconductors. A possible explanation was advanced by Scher and Montroll[32]. They suggested that the anomalies were to be expected if one was concerned with hopping carriers. We review the theory in Section 8.3. Qualitative, it makes the right predictions but quantitatively it seems unlikely to be correct. More recently it has been emphasised by several authors[3 - 7] that trapping is a more likely explanation. It is a remarkable fact that the central equation in the theory is formally the same in both cases which makes the two possibilities hard to distinguish on a qualitative basis. Nevertheless, the bulk of the quantitative evidence would appear to favour trapping effects as being dominant. We review the trap-controlled case in Section 8.4. and the theory of archetypal anomalous carrier pulse propagation in Section 8.5.

8.2. Conventional carrier pulse propagation

It is supposed in the conventional theory of carrier pulse propagation that

$$J(x, t) = - en(x, t)\,\mu E + eD\,\frac{\partial n(x, t)}{\partial x} \tag{8.4}$$

where μ and D are respectively the electron mobility and diffusivity. These quantities are taken to be constant and are related by the Einstein relation (assuming non-degenerate statistics)

$$\mu = \frac{eD}{k_B T} \tag{8.5}$$

We also neglect the effect of carrier space charge on E which is identified with the constant applied potential difference divided by L.

When (8.4) is substituted into (8.3) we therefore obtain the familiar equation

$$\frac{\partial n}{\partial t} + v_D\,\frac{\partial n}{\partial x} = D\,\frac{\partial^2 n}{\partial x^2} \tag{8.6}$$

where $v_D = \mu E$ is the electron drift velocity. We impose the boundary condition

$$n(x, 0) = n_0\,\delta(x),\ t = 0. \tag{8.7}$$

Then the appropriate solution of (816) may be obtained by elementary methods:

$$n(x, t) = \frac{n_0}{(4\pi Dt)^{1/2}}\exp\left[-\frac{(x - v_D t)^2}{4Dt}\right] \tag{8.8}$$

To determine $I(t)$ we substitute this result into (8.4) and then use (8.2). If the peak of the pulse is well away from the ends of the specimen the diffusion term in (8.4) integrates to zero while the conduction current term yields $-en_0 v_D$. The pulse approaches the far end of the specimen at a transit time $t_T = L/v_D = L/\mu E$. The spatial width of the pulse is then proportional to $t_T^{1/2}$ and this will be reflected in a trailing edge on $I(t)$ with time-width proportional to $(L/E)^{\frac{1}{2}}$.

8.3. Carrier pulse propagation involving hopping

Let us suppose that the electrons in the pulse reach a local equilibrium at temperature T and move by hopping. We have seen in Section 4 that the that the diffusivity $D(\omega)$ becomes strongly frequency dependent in this case. Moreover, assuming non-degenerate statistics, the Einstein relation is preserved at frequency ω so that the frequency dependent mobility $\mu(\omega)$ is given by (see Section 4.4.):

$$\mu(\omega) = e\, D(\omega)/k_B T \tag{8.9}$$

These observations suggest that we modify (8.4) by taking its Fourier transform and replacing the constants μ and D by the frequency dependent quantities $\mu(\omega)$ and $D(\omega)$. Thus we have:

$$J(\omega) = -\, eE\mu(\omega)\ n(\omega) + e\, D(\omega) \frac{\partial}{\partial x} n(\omega) \tag{8.10}$$

where $J(\omega)$ and $n(\omega)$ are the Fourier transforms of $J(x, t)$ and $n(x, t)$ respectively. Equation (8.4) is regained by neglecting the frequency dependence of $\mu(\omega)$ and $D(\omega)$. Inverting the transform we have

$$J(x, t) = -\frac{e^2 E}{k_B T} \int_{-\infty}^{t} d(t - \tau)\ n(x, \tau)\ d\tau + e \frac{\partial}{\partial x} \int_{-\infty}^{t} d(t - \tau)\ n(x, \tau)\ d\tau \tag{8.11}$$

where

$$d(t - \tau) = \frac{1}{2\pi} \int D(\omega)\ e^{-i\omega(t - \tau)}\ d\omega. \tag{8.12}$$

Thus we must make equation (8.4) non-local in time because of the strong frequency dependence of $D(\omega)$. It is not difficult to verify the validity of (8.11) by studying in detail the behaviour of the hopping Green's function in the long wavelength limit[72 - 78].

8.4. Carrier pulse propagation involving trapping

We suppose that the current density $J(x, t)$ is carried by electrons in a conduction band according to the equation

$$J(x, t) = -en_c(x, t)\ \mu_c E + eD_c \frac{\partial n_c(x, t)}{\partial x} \tag{8.13}$$

Where $n_c(x, t)$ is the carrier density in the conduction band, μ_c is their mobility and D_c is their diffusivity which we take to be constants related through the Einstein relation. Without traps equation (8.13) reduces to the conventional relation (8.4). The traps make themselves felt because $n_c(x, t)$ is different

from the total electron density $n(x, t)$ which appears in the particle conservation equation (8.3). We are here discussing trap-controlled band conduction for simplicity. The argument may be generalised to deal with trap-controlled hopping[2, 6].

To describe the traps we use the linear rate equations[4, 6]:

$$\frac{\partial p_j}{\partial t} = n_c\, C_j - p_j\, R_j \tag{8.14}$$

where C_j is the capture rate and R_j is the release rate of the jth type of trap. To solve these equations we suppose that the carrier pulse is injected into the conduction band at $x = 0$ when $t = 0$ and that at that time all the traps are empty. Then the Fourier transform of (8.14) yields

$$-i\omega\, p_j\ (\omega) = n_c(\omega)\ C_j - p_j(\omega) R_j \tag{8.15}$$

in an obvious notation. Hence

$$p_j\ (\omega) = \frac{n_c(\omega)\ C_j}{R_j - i\omega} \tag{8.16}$$

The total electron density is

$$n(x, t) = n_c(x, t) + \sum_j p_j \tag{8.17}$$

By taking the Fourier transform of (8.17) and using (8.16) we obtain immediately

$$n_c(\omega) = n(\omega) \left\{1 + \sum_j \frac{C_j}{R_j - i\omega}\right\}^{-1} \tag{8.18}$$

When this result is inserted into the Fourier transform of (8.13) we see that we obtain an equation of identical structure to (8.10) but where now

$$\mu(\omega) = \mu_c \left\{1 + \sum_j \frac{C_j}{R_j - i}\right\}^{-1} \tag{8.19}$$

and $D(\omega)$ is determined by the Einstein relation (8.9).

We see that there is a formal identity between the equation which determines the carrier pulse shape for hopping and trap-controlled carriers.

8.5. Archetypal anomalous carrier pulse propropation

For very long times the carrier pulse propagation is controlled by the dc value $\mu(0)$ of $\mu(\omega)$. Thus the pulse eventual converts to the drifted Gaussian predicted by the conventional transport equations. Anomalous carrier pulse propagation arises at times prior to that for which the approximation $\mu(\omega) \approx \mu(0)$ is valid. The nature of the propagation is then determined by the frequency dependence of $\mu(\omega)$. In the hopping case we have seen in Section 4 that there is large frequency range in which the ac conductivity has a power-law dependence on ω. The ac mobility therefore exhibits similar behaviour. The work of Noolandi[4] may be interpreted as showing that quite simple trap distributions can lead to power-law behaviour for the effective mobility defined in (8.19). We show below that such a power-law dependence of $\mu(\omega)$ on ω leads immediately to the archetypical anomalous carrier pulse propagation described in Section 6.1.

Let us suppose, then, that

$$\mu(\omega) = \mu_i(-i\omega\tau_0)^{1-\alpha} \tag{8.20}$$

where μ_i, τ_0 and α are constants with $0 < \alpha < 1$. We shall see below that the frequency dependence of the mobility will, of itself, cause an injected carrier pulse to spread out. The diffusion term in equation (8.10) is not necessary for this purpose and may be neglected at sufficiently long times. This situation is in complete contrast to the conventional one when the diffusion term can never be neglected. We note that our neglect of any dc contribution to conventional carrier pulse propagation which we discussed above will never take place for the model under discussion. When diffusion is neglected the Fourier transform of equation (8.3) yields

$$\frac{d}{dx}[\mu(\omega)\, n(\omega)E] - i\omega\, n(\omega) = n_0\, \delta(x) \tag{8.21}$$

where we have imposed the boundary condition (8.7). Equation (8.21) may be integrated immediately to give

$$n(\omega) = \frac{n_0}{\mu(\omega)E} \exp[i\omega x/E\mu(\omega)]\, \theta(x) \tag{8.22}$$

The unit step function $\theta(x)$ appears in $n(\omega)$ because, with the field pointing in the negative x direction (as we suppose), the electrons must move in the positive x direction.

When the Laplace transform (8.22) is inverted we have the pulse shape formula:

$$n(x,\ t) = \theta(x)\, \frac{n_0}{2\pi} \int_{-\infty}^{\infty} \frac{\exp[-i\omega(t - x/E\mu(\omega))]}{E\mu(\omega)}\, d\omega \tag{8.23}$$

For arbitrary $\mu(\omega)$ this integral must be evaluated numerically. However, there are two especially simple cases. Firstly, when $\alpha \rightarrow 1$ so that (8.20) gives $\mu(\omega) = \mu_1$ a constant. Then we immediately obtain the expected result:

$$n(x,\ t) = n_0\, \delta(x - \mu_1 Et) \tag{8.24}$$

Secondly, when $\alpha = \frac{1}{2}$ then we may write (8.18) in the form

$$n(\omega) = -\, 2\, \frac{n_0}{2ikD_e} \exp[ikx]\, \theta(x) \tag{8.25a}$$

where

$$D_e = (\mu_1 E)^2\, \tau_0 \tag{8.25b}$$

is an effective diffusion constant and

$$k = (i\omega/D_e)^{\frac{1}{2}} \tag{8.25c}$$

We may immediately verify from equation (8.8), with $v_D = 0$ (or from the conventional diffusion equation, which is rather easier) that

$$n(x,\ t) = \frac{2\, n_0}{(4\pi D_e t)^{\frac{1}{2}}} \exp(-x^2/4D_e t)\, \theta(x) \tag{8.26}$$

We begin to see the seeds of archetyped anomalous carrier pulse propagation in the simple result (8.26). It will be recalled that we have neglected diffusion altogether. Nevertheless the pulse diffuses rather than drifts into the region $x > 0$ with an effective diffusion constant D_e determined by the electric field. The peak of the pulse remains at $x = 0$ for all t. The factor of 2 in equation (8.26) keeps $n(x,\ t)$ normalised to n_0 for all t since none of the electrons move into the region $x < 0$. It is easy to verify that $n(x,\ t)$ is proportional to $t^{-\alpha}$ times a function of x and t in the combination x/t^{α}. In Figure 11[79] we show pulse shapes calculated for various values of α as functions of $(x/t^{\alpha})/E\mu_1\tau_0^{\,1-\alpha}$.

To study the behaviour of I(t), which is what is measured experimentally, we substitute (8.22) into the first term of (8.10) and invert the transform to obtain the conduction current density

$$J(x,\ t) = -\frac{n_0 e}{2\pi}\int_{-\infty}^{\infty} d\omega e^{-i\omega t}\ \theta(x)\ \exp[i\omega x/E\mu(\omega)] \qquad (2.27)$$

Then I(t) follows from equation (8.2) when we invert the order of integration. Thus we find that

$$I(t) = -\frac{n_0 e}{2\pi}\int_{-\infty}^{\infty} d\omega e^{-i\omega t}\ \frac{e^{iqL} - 1}{iqL} \qquad (8.28)$$

where $q = i\omega/E\mu(\omega)$ which is proportional to ω^{α} when $\mu(\omega)$ has the power law form (8.20). We consider times which are long enough for diffusion to be neglected but still short enough to ensure that no significant part of the carrier pulse has reached the far end of the specimen. Then we may let $L \to \infty$ in (8.27) which removes the exponential term. Making the change of variable $u = \omega t$ we find that

$$I(t) \sim \frac{E}{L}\, t^{\alpha-1},\ t \to 0. \qquad (8.29)$$

On the other hand, when $t \to \infty$ we are concerned with small ω, i.e. with small q. The leading terms in the factor of the integrand in (8.28) involving q are

$$\frac{e^{iqL} - 1}{iqL} \sim 1 + \tfrac{1}{2}\, iqL \qquad (8.30)$$

The first term yields a δ-function which may be ignored. The second term gives

$$I(t) \sim \frac{L}{E}\, t^{-1-\alpha} \qquad (8.31)$$

Finally, we may define a transit time t_T by equating (8.29) and (8.30). We see that

$$t_T \sim \left(\frac{L}{E}\right)^{\frac{1}{\alpha}} \qquad (8.32)$$

Equations (8.29), (8.31) and (8.32) are the salient qualitative features observed in archetypal anomalous carrier pulse propagation. The ability to superpose curves of I(t) for different transit times follows immediately from the power-law behaviour which is exhibited in these equations and stems from the power-law behaviour assumed for $\mu(\omega)$.

8.6. Comparison with experiment

The addition of dc term to the mobility function modifies the behaviour found above[77, 78, 80]. As an example we show in Figure 11 n(x, t) calculated as a function of $x/\mu_0 E\tau_0$ for various values of $T = t/\tau_0$ when

$$\mu(\omega) = \mu_0 + \mu_1\ (-i\omega\tau_0)^{1-\alpha} \qquad (8.33)$$

with $\alpha = 0.5$ and $\mu_1/\mu_0 = 100$ [80]. We note in particular that the peak of the pulse drifts away from the origin in contrast to the behaviour found when in sub-Section 8.5. when $\alpha = 0.5$ and $\mu_0 = 0$. This is always the case when $\mu_0 \neq 0$ [80]. Consequently, the total current settles down to a constant value after a time t_2 determined by the relative strengths of the ac and dc contributions to $\mu(\omega)$. For anomalous carrier pulse propagation to occur we must have $t_T \ll t_2$. For a hopping mechanism it is possible to estimate the ac and dc contributions to $\mu(\omega)$ from ac and dc conductivity data. The values of t_2 calculated on this bases for a - Se are always very large compared to estimates of t_T and yet this material shows a transition from conventional to anomalous carrier pulse propagation at 143 K [79]. Moreover, the values of α should correlate with the powers of ω arises in ac conductivity. The degree of correlation is very poor[79] and we conclude that trapping is more likely to be the mechanism involved in most cases in which anomalous carrier pulse propagation has been observed.

9. Conclusion

In this brief review of the theory of electron transport in disordered solids we have given most weight to the hopping mechanism because the theory of that is now well developed within the framework of the rate equation formalism. The rate equations themselves have been taken as intuitive. They may of course be derived from first principles[16] or from a master equation[81].

In recent years there has been a great deal of work on calculations of the Hall effect for hopping electrons[82 - 88]. The Hall mobility is small but not zero. However, the calculations remain of academic interest because the Hall effect has so far defeated all attempts to measure it in a hopping system.

Our discussion of transport by electrons in extended states has necessarily been more tenuous because the simple picture afforded by a rate equation is not generally valid. We have concentrated on concepts which are commonly used in the analysis of experimental data. The treatment of conductivity for electrons near a mobility edge which has been developed recently by Götze and co-workers[27 - 30] has not yet been used very much. Nevertheless, it would appear to be the most promising new approach to a more general theory. None of the properties of amorphous materials are understood very well from a quantitative point of view. There are always a great many unknown parameters in any transport theory which can be adjusted so as to give apparent agreement between the theory and experiment. The most obvious case in which this obstacle to progress can be easily overcome is impurity bands in crystalline semiconductors. Further experimental work on these systems would be extremely valuable. This is particularly so at the present time because a theoretical understanding of the effect of Coulomb interaction on their transport properties is beginning to emerge[1, 15, 16, 89, 90].

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Figure Captions

Fig. 1. Density of states for a single band showing localised state regions (cross-hatched) bounded by mobility edges at ε_c and ε_c'.

Fig. 2. Density of states near the pseudogap in an amorphous semiconductor showing the localised state region (cross-hatched) extending from a mobility edge ε_v in the valence band to a mobility edge ε_c in the conduction band. The Fermi level ε_F is near the middle of the pseudo gap.

Fig. 3. Schematic plot of the relaxation time at zero frequency calculated by Belitz and Götze[30]. Dashed line: Boltzmann transport regime. Full line: solution of the self-consistent equation.

Fig. 4. The Miller-Abrahams equivalent circuit.

Fig. 5. Dc conductivity as a function of density for the r hopping model. Full curve: full analytical formula (6.2), (6.3) and (6.5). Upper dashed curve: calculated from (6.2) with $r_p = 0$. Lower dashed curve: calculated from (6.4) and (6.5). Points: computed directly for a system of 2500 sites[56].

Fig. 6. Dc conductivity as a function of $T^{-0.25}$ for an AHL model with $\alpha n_s^{-1/3} = 3.4$ and $W = 10$ meV. Dashed curve: calculated from (6.11). Dots: computed using a full numerical solution of Kirchhoffs equations for 2199 sites[57]. Full curve: calculated from the extended pair approximation equations[58]. Dash-dot curve: calculated from the barrier hopping model[37].

Fig. 7. Real part $\sigma_1(\omega)$ of the ac conductivity for a three dimensional R-hopping system as a function of $\omega_1 = \omega/R_0$. The full curve is calculated using the extended pair approximation[58, 65]. The dashed curve is obtained from the unified random walk theory[37]. The points are obtained by using a full numerical solution of Kirchhoff's equations for 1600 sites[66].

Fig. 8. Imaginary part $\sigma_2(\omega)$ of the ac conductivity for a three dimensional R-hopping system as a function of $\omega_1 = \omega/R_0$. The full curve is calculated using the extended pair approximation[58, 65]. The dashed curve is obtained from the unified random walk theory[37]. The points are obtained by using a full numerical solution of Kirchhoff's equations for 1600 sites[66].

Fig. 9. Schematic diagram of the experimental arrangement for observing carrier pulse propagation. The potential difference V across the specimen (cross-hatched) is held constant and the total current I(t) is monitored.

Fig. 10. Superposed log I - log t plots for 1:1 TNF:PVK with the applied voltages indicated[32].

Fig. 11. The function $f_\alpha(s) = n(x, t)/(n_0 E\mu_1 t^\alpha \tau_0^{1-\alpha})$ plotted against $s = (x/t^\alpha)/E\mu_1 \tau_0^{1-\alpha}$ for the values of α shown[79].

Fig. 12. Carrier density as a function of $x/\mu_0 E \tau_0$ for various values of $T = t/\tau_0$ when $\mu(\omega) = \mu_0[1 + 100 (-i\omega\tau_0)^{\frac{1}{2}}]$[80].

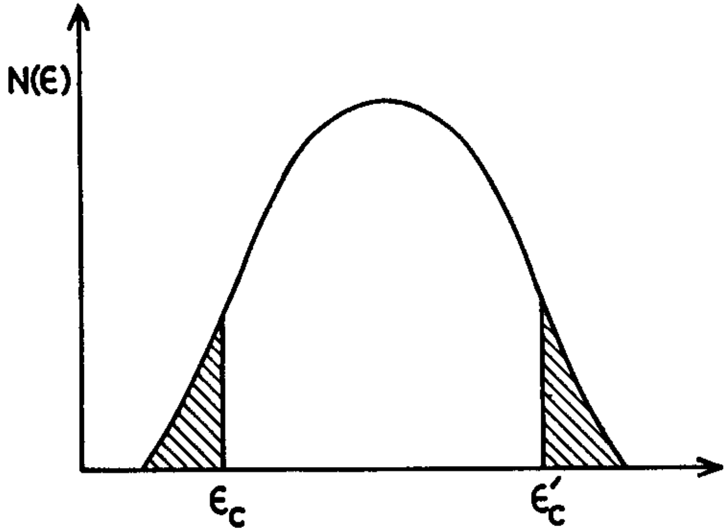

Fig.1

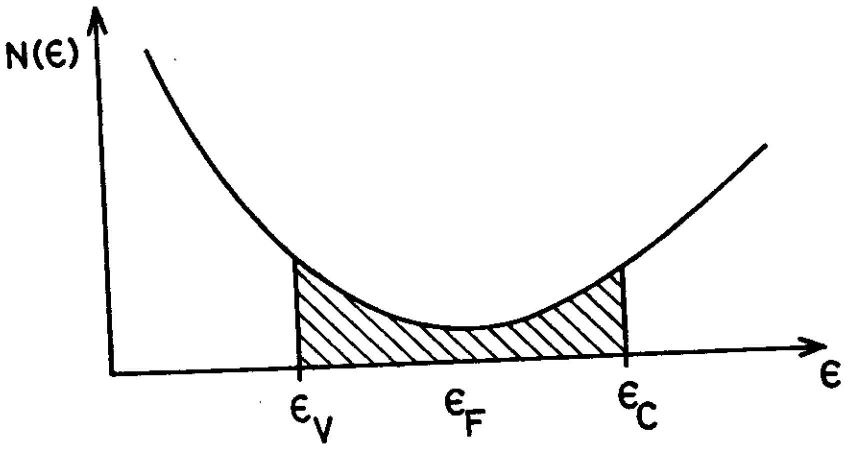

Fig. 2

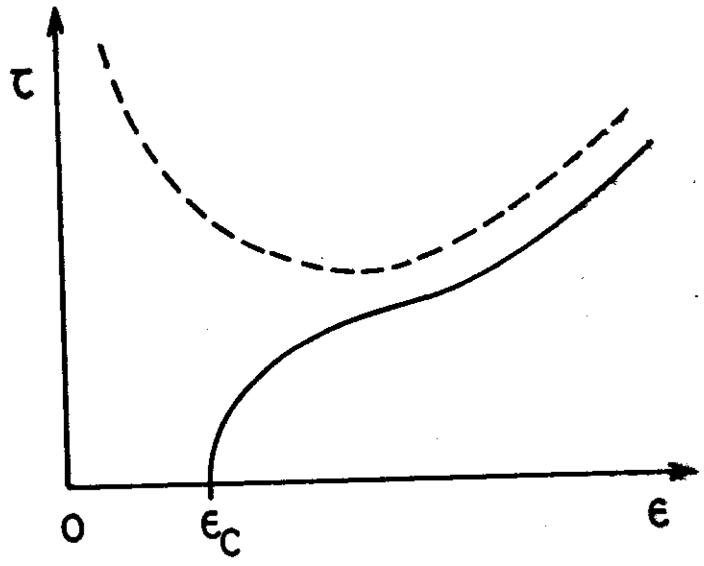

Fig. 3

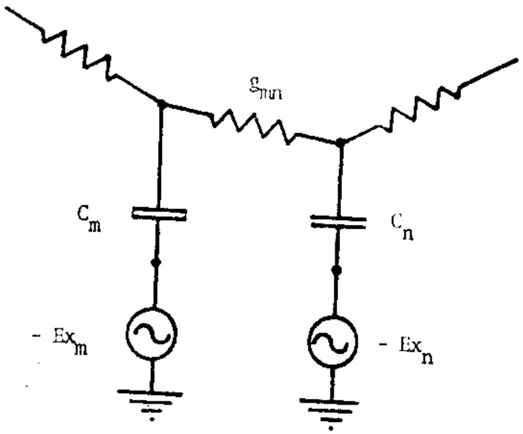
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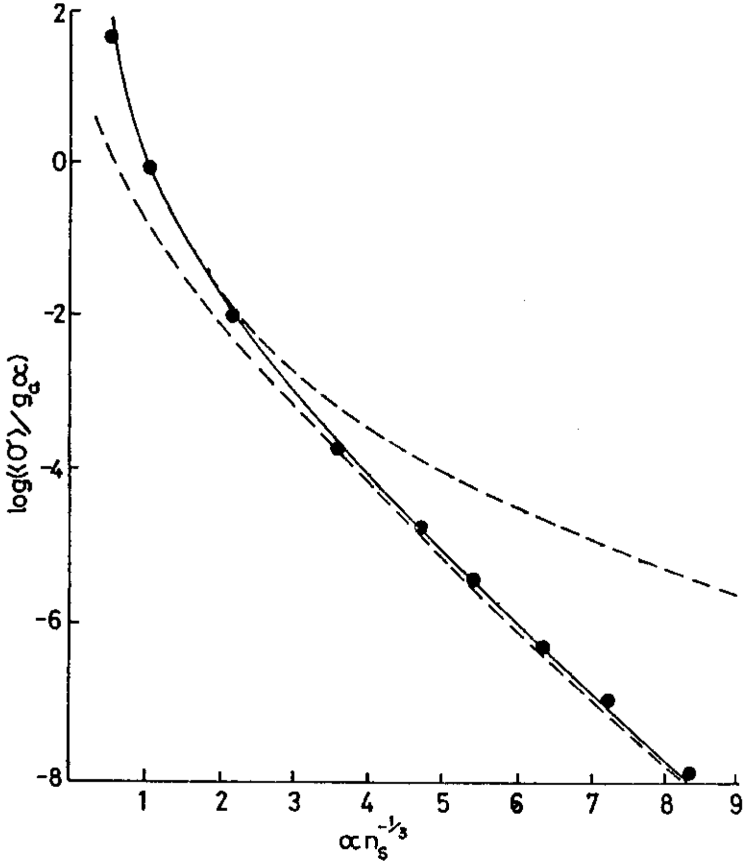
Fig. 4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$\alpha n_s^{-1/3}$

FIG. 5

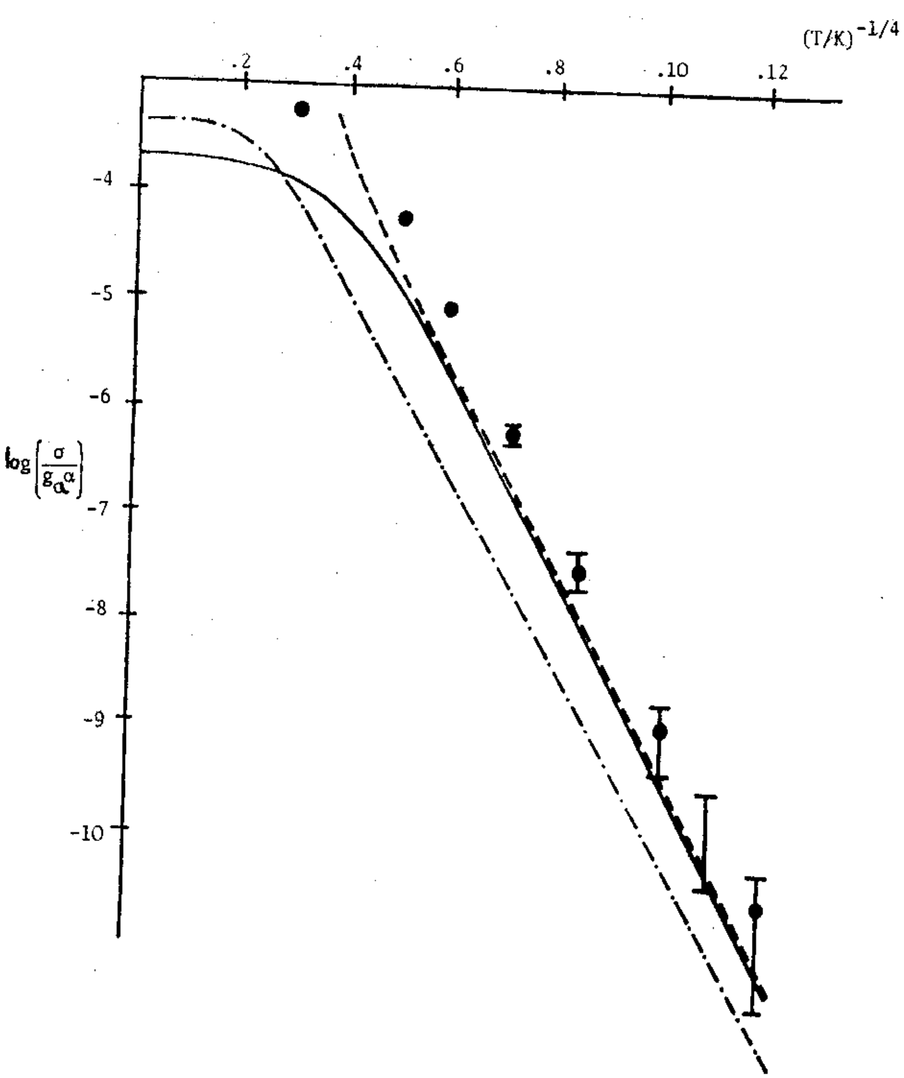
(T/K)$^{-1/4}$
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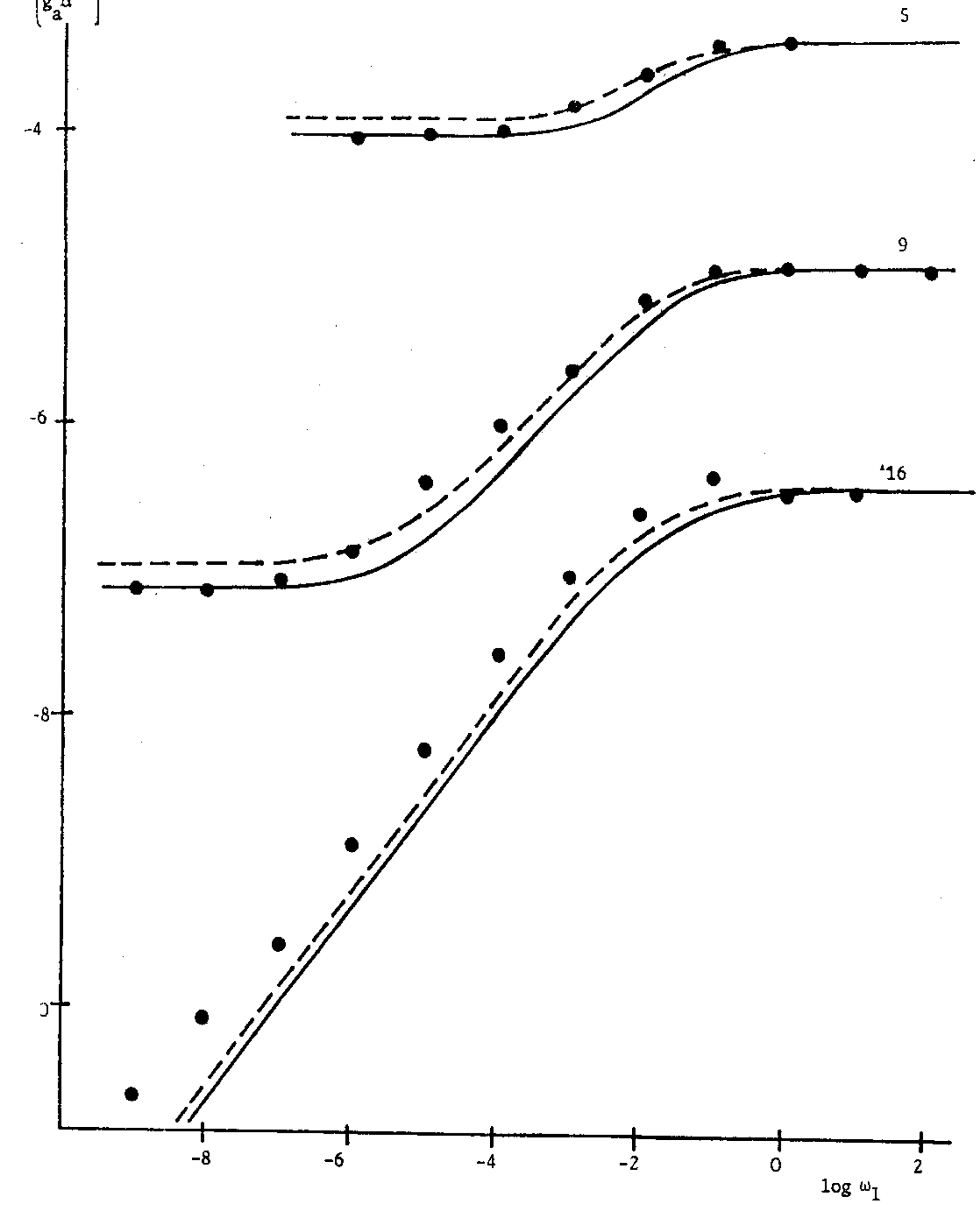
Fig. 6.


log$\left(\frac{\sigma_1(\omega)}{g_a^{\alpha}}\right)$
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0
-8
-6
-4
-2
0
2
log ω_I

Fig. 7.

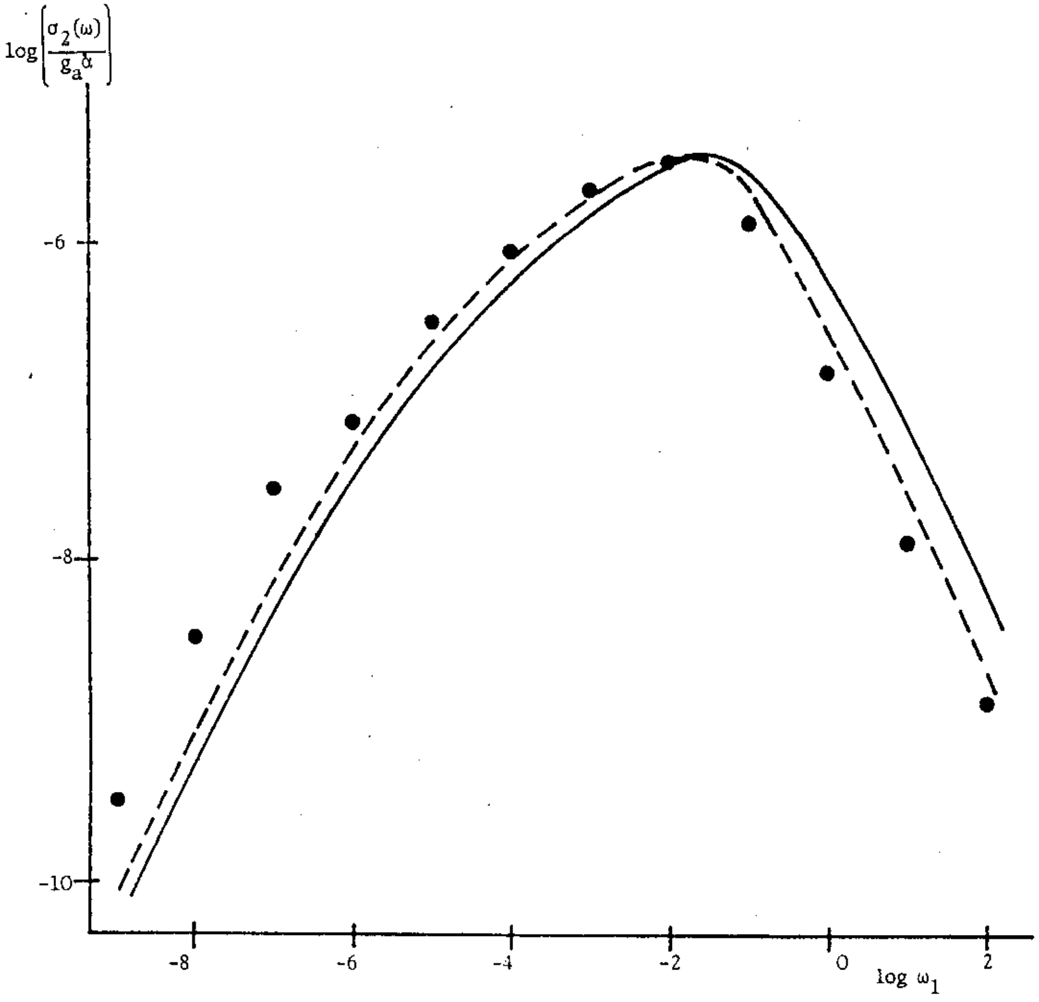
$\log\left(\frac{\sigma_2(\omega)}{g_a\alpha}\right)$
-6
-8
-10
-8
-6
-4
-2
0
2
$\log \omega_1$

Fig. 8.

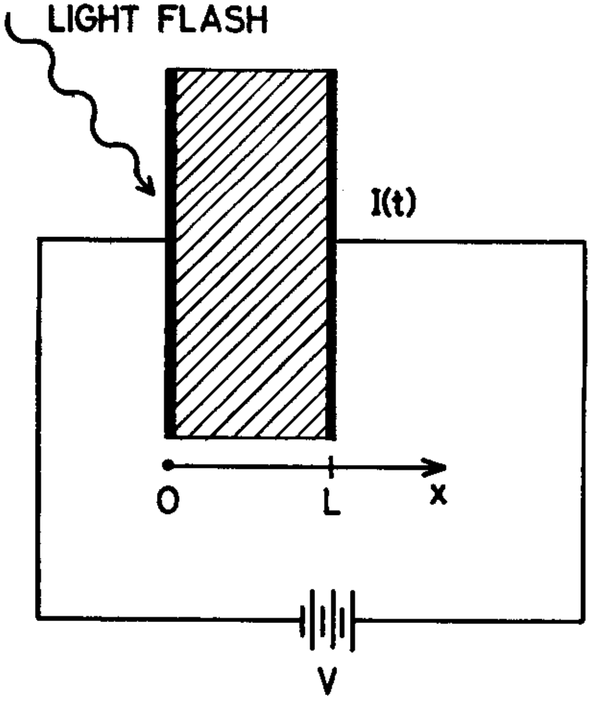
LIGHT FLASH
I(t)
O
L
x
V

Fig.9

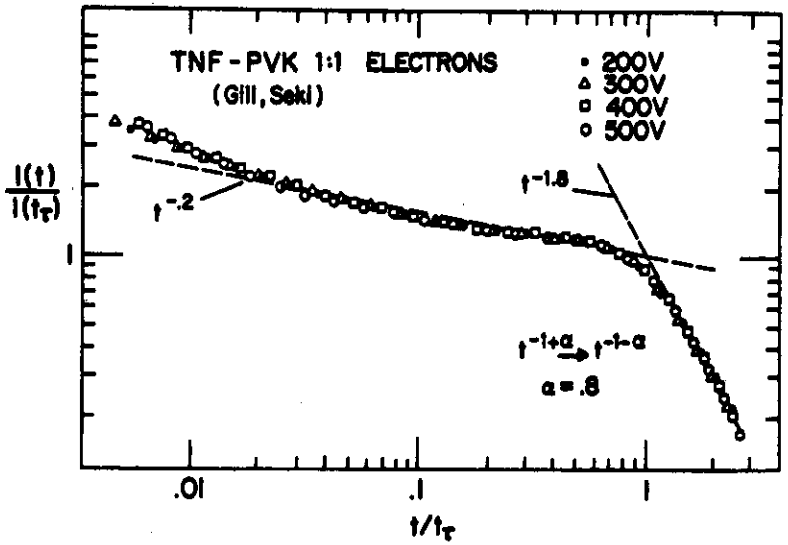
TNF - PVK 1:1 ELECTRONS
(Gill, Seki)
• 200V
△ 300V
□ 400V
○ 500V
I(t)/I(t_τ)
1
t^-.2
t^-1.8
t^-1+α → t^-1-α
α = .8
.01
.1
1
t/t_τ

Fig. 10

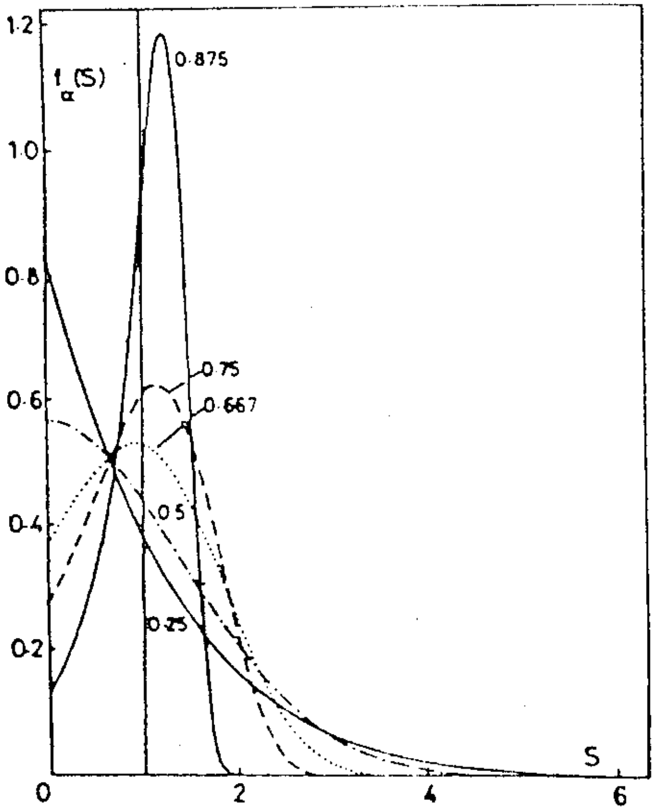
f_α(S)
1.2
1.0
0.8
0.6
0.4
0.2
0
2
4
6
S
0.875
0.75
0.667
0.5
0.25

Fig. 11.

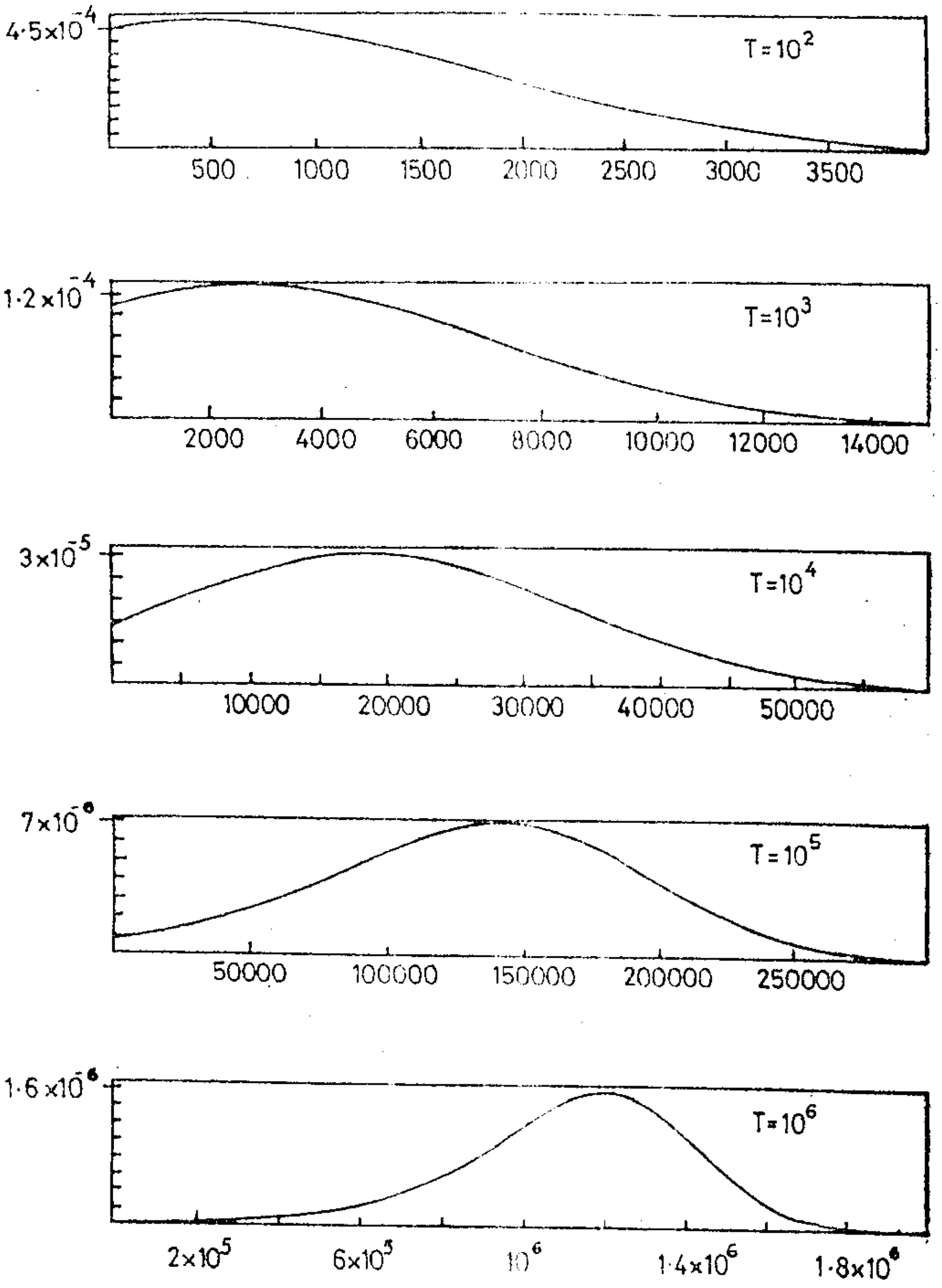
4·5×10^-4
T=10^2
500
1000
1500
2000
2500
3000
3500
1·2×10^-4
T=10^3
2000
4000
6000
8000
10000
12000
14000
3×10^-5
T=10^4
10000
20000
30000
40000
50000
7×10^-6
T=10^5
50000
100000
150000
200000
250000
1·6×10^-6
T=10^6
2×10^5
6×10^5
10^6
1·4×10^6
1·8×10^6

Fig. 12.