

# Chapter 4

## Correlated Hopping in Coulomb Glass

### Introduction

In this chapter we shall be concerned with the role of Coulomb interactions on the hopping conduction of localized electrons at low temperatures. In a classic paper, Mott [13] showed that as the temperature is lowered, the conductivity changes from its usual activated form  $\sigma_{dc} \propto \exp(-E_3/k_B T)$  to a form  $\sigma_{dc} \propto \exp[-(T_M/T)^{1/4}]$ . This has been termed 'variable range hopping' (VRH). Following Mott's VRH arguments, there have been numerous efforts to put Mott's work on firmer theoretical foundations. They have been largely based on the rate equation approach of Miller and Abrahams [27]. The linearized rate equation can be solved using standard Green function techniques as applied to disordered systems. Physically, this amounts to calculating the conductivity of a random resistor network which under some conditions also amounts to the calculation of diffusion of a single particle executing a random walk in a disordered medium. The main problem of such approaches lies in incorporating the effects of Coulomb interactions as these are basically single particle approximations of transport. The analysis of Efros and Shklovoski [16, 17] takes into account the Coulomb interactions by incorporating their effect only through the Coulomb gap in the density of states (DOS), which again allows the use of the single particle picture. There have been several efforts [38, 39, 76, 77]

to incorporate the effect of Coulomb interactions on hopping conduction. Building on the work of Dersch et. al [77], Lamba and Kumar [78] have given a detailed many-body treatment to describe the crossover from Mott's to Coulomb gap regime. This crossover has also been well described by some empirical approaches [79, 80].

The purpose of present chapter is to deal with some other aspects of correlated motion of carriers to calculate the dc and ac conductivities in the Coulomb gap regime. In particular, we wish to take into account backward correlations in hopping, which have been observed in numerical simulations of conductivities. In particular, in simulations of Maas *et al* [81], it is seen that when disorder and Coulomb interactions are of comparable strength, the successive carrier hops are strongly correlated. A carrier is likely to jump back to the site from which it came with greater probability than in uncorrelated diffusion. When there is Coulomb gap, this can be physically understood in the following terms. Due to interactions, in the neighborhood of an occupied site, the occupation of other electrons is less than average, i.e there is a 'correlation hole' which in turns reduces the Hartree energy associated with the occupied sites near the Fermi level. Similarly the neighborhoods of unoccupied sites have larger than average occupation of electrons(negative hole), thereby raising their Hartree energy. So when an electron jumps from an occupied site to an unoccupied site, it has to overcome this energy barrier of the order of Coulomb gap. At low temperatures, the relaxation of holes as the carrier jumps is slow, so there should be a tendency to go back to the hole it left behind in the previous jump.

In this chapter, we consider the effect of such correlation by a random walk model and relate the enhanced backward hopping rate to the Coulomb gap by a simple consideration. Correlated random walks [82, 83, 84, 85, 86] are a class of random walks, in which unlike Markovian walks, the memory is not lost after each step. Most of the theoretical work has concentrated on correlated random walks on ordered lattices. Hilfer and Orbach [87] and Hilfer [88] have introduced disorder into this formalism by considering

walks on a bond percolation model. We extend their treatment to a more general class of disordered systems. Our treatment is restricted to memory of one last step only. We use the model to study the behavior of the dc as well as the ac conductivity.

This chapter is organized as follows. In section 1, we give the stochastic interpretation for the diffusion constant. In section 2, we present a brief review of the correlated random walk problem for a pure system with help of an example. In section 3, we set up the correlated random walk formulation for a disordered system. In the section 4, we discuss the model for the backward transition rates. In section 5, the Green function formalism for conductivity is discussed. We will use the effective medium approximation to give an expression for conductivity. Finally the results for the conductivity will be described in section 6.

## 4.1 The Rate Equation

The rate equation approach basically studies the variation in the thermal average of the electron occupation in states localized around particular sites as a linear response to an externally applied electrical field. This charge variation can be related to the conductivity through the continuity equation.

### 4.1.1 The linearized Rate Equation

The development of theory of hopping conduction was started using the one electron semi-classical viewpoint [77]. To determine the dynamics of the system, the classical rate equation is used. The rate equation for thermal average of the occupation number  $f_i(t)$  at site  $i$ , in presence of external fields is,

$$\frac{\partial f_i}{\partial t} = \sum_j [f_j(1 - f_i)W_{ji} - f_i(1 - f_j)W_{ij}] \quad (4.1)$$

where  $W_{ij}$  is the transition rate from an occupied site  $i$  to an empty site  $j$ . The transition rates  $W_{ij} = W_{ij}^0 \exp[\beta(V_{ij} - |V_{ij}|)/2]$  are determined by  $V_{ij} = V_i - V_j$  and equilibrium

transition rate  $W_{ij}^0$ . Here  $V_i$  is the potential at site  $i$  due to an external applied field. In equilibrium, at temperature  $T$ ,  $f_i$  is given by the Fermi-Dirac statics,

$$f_i^0 = [\exp(\beta \{\epsilon_i - \mu\}) + 1]^{-1} \quad (4.2)$$

where  $\beta = 1/k_B T$  and  $\epsilon_i$  is the energy of the site  $i$ .

As mentioned in section 1.5, the rate equation should obey the principle of detailed balance. This comes from the requirement that in equilibrium the total probability of an electron jumping into a state is equal to the probability of an electron jumping out of that state. This condition leads to the following relationship between equilibrium transition probability,

$$\frac{W_{ij}^0}{W_{ji}^0} = \exp[-\beta(\epsilon_j - \epsilon_i)] \quad (4.3)$$

Now linearizing the rate equation and using the equation (4.3), we get the following equation for  $\delta f_i(t) = f_i(t) - f_i^0$ ,

$$\frac{\partial \delta f_i(t)}{\partial t} = - \sum_j C_{ij} F_j^{-1} \delta f_i(t) - \beta \sum_j C_{ij} V_j \quad (4.4)$$

where  $F_j = f_j^0(1 - f_j^0)$  and  $C_{ij}$  is given by,

$$C_{ij} = -\Gamma_{ij} + \delta_{ij} \sum_l \Gamma_{il} \quad (4.5)$$

where  $\Gamma_{ij} = W_{ij}^0 f_i^0(1 - f_j^0)$  are the symmetric equilibrium transition rates. This equation gives a linear relation between the external potential  $V$  and change in occupation numbers at sites. Let the electric field be switched at  $t = 0$ . Using  $\delta f_i(t = 0) = 0$  and Laplace transforming equation (4.4), we get the following equation for  $\delta f(z)$  in matrix notation,

$$\delta f(z) = -i\beta(z + i\underline{C} \underline{F}^{-1})^{-1} \underline{C} \underline{V}(z) \quad (4.6)$$

#### 4.1.2 Generalized Master Equation

In the previous subsection, the role of electron-electron interactions was completely neglected. In presence of interactions Dersch *et al* [77] used Mori-Zwanzig formalism.

[89] to derive the following generalized master equation (GME) for hopping conduction. The method is complicated and only the result will be mentioned.

$$\delta f(z) = -i\beta(z + i\sigma(z)\underline{F}^{-1})^{-1}\sigma(z)\underline{V}(z). \quad (4.7)$$

where  $\sigma(z)$  is a matrix which is defined as,  $\sigma_{ij}(z) = \Gamma_{ij}^1(z) - \delta_{ij} \sum_l \Gamma_{il}^1$ . The  $\Gamma_{ij}^1(z)$  are the generalized transition rates of the system. Their  $z$ -dependence is a consequence of the interactions. If the dynamics of the quantity  $\Gamma_{ij}^1(z)$  is faster than that of the external field then we can make the Markovian approximation and replace  $\Gamma_{ij}^1(z)$  by  $\Gamma_{ij}^1(0)$  and then the equation (4.7) is equivalent to equation (4.6).

It is important to understand that in the Markovian limit, the effect of interactions can still be seen. When an electron jumps from an occupied site to an empty site, then simultaneous relaxation around the sites involved in the jump can lower the energy of the transition. If the relaxation is faster than the characteristic transition times of the system, then the system will obey the Markovian rate equation but with different transitions rates as compared to the non-interacting system. If the system is not able to lose the memory of previous steps, then GME has to be used. This brings us to the correlated random walk interpretation of the GME.

### 4.1.3 Random Walk Interpretation

We consider the situation under a uniform field  $E$  applied in  $x$ -direction. Then  $V_i = -Ex_i$ , where  $x_i$  is the  $x$ -coordinate of site  $i$ . Let us define a matrix  $\underline{S} = \underline{F}^{-1}\underline{C}$  whose matrix elements are given by,  $S_{ij} = S_{ij}^e - \delta_{ij} \sum_l S_{il}^e$ , where  $S_{ij}^e = \Gamma_{ij}/F_i$ . Then equation (4.6) can be reset into the matrix form as,

$$\underline{\delta f} = -\beta e E x^T \underline{F} \underline{S} \underline{G}. \quad (4.8)$$

where the matrix  $\underline{G}$  is defined by the equation,

$$(\underline{S} - i\omega)\underline{G}(\omega) = \underline{I}. \quad (4.9)$$

The matrix  $\underline{G}$  has a simple stochastic interpretation. It is the green function of a single electron performing a Markovian random walk on a lattice with transition rates  $S_{ij}^e$ . Let  $P_{ij}(t)$  be the probability of finding a particle at site  $j$  at time  $t$  when it was at site  $i$  at time  $t = 0$ . The Markovian random walk equation is,

$$\frac{dP_{ij}(t)}{dt} = \sum_k [P_{ik}(t)S_{kj}^e - P_{ij}(t)S_{jk}^e] \quad (4.10)$$

Then Fourier transforming the above equation, one gets,

$$P^F(\omega) = \frac{1}{(\underline{S} - i\omega)} \quad (4.11)$$

where  $P_{ij}^F(\omega)$  is the Fourier transform of  $P_{ij}(t)$ . So we can see that  $P^F(\omega) \equiv \underline{G}(\omega)$  as mentioned.

#### 4.1.4 Conductivity

The whole exercise would be futile unless one is able to write down the formal expression for the conductivity of the system, in terms of the charge fluctuation  $\delta f_i$  calculated above. To do this we define the induced dipole moment density in the  $x$ -direction

$$P_x(t) = -\frac{e}{\Omega} \underline{x}^T \underline{\delta f}(t) \quad (4.12)$$

The  $x$ -component of the current density is then  $J_x(t) = i\omega P_x(t)$  (from the continuity equation). With  $P \propto \sum_i e x_i \delta f_i$  the final expression for the frequency dependent conductivity is,

$$\sigma(\omega) = -\frac{i\omega e^2 \beta}{\Omega} \langle \underline{x}^T \underline{F} \underline{S} \underline{G} \underline{x} \rangle_c \quad (4.13)$$

where the  $\langle \rangle_c$  denote the configuration average. To complete the analogy with random walks the equation (4.13) can be recast into the form,

$$\sigma(\omega) = -\frac{\omega^2 e^2}{2\Omega k_B T} \langle \sum_{ij} X_{ij}^2(\omega) G_{ij}(\omega) F_i \rangle_c \quad (4.14)$$

where  $X_{ij} = x_i - x_j$ . Averaging over all directions the conductivity is,

$$\sigma(\omega) = -\frac{\omega^2 e^2}{6\Omega k_B T} \langle \sum_{ij} R_{ij}^2(\omega) G_{ij}(\omega) F_i \rangle_c \quad (4.15)$$

where  $R_{ij}^2 = (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2$ . If further we assume that all the hopping is taking place in a narrow band around the Fermi level where all the site energies are approximately equal, we can replace  $F_i$  by  $n_C = N_C/N$  i.e., the number of carriers divided by total number of sites. Then the conductivity is related to  $\sum R_{ij}^2 G_{ij}(\omega)$  which is the root-mean square displacement of the random walk. We can then express  $\sigma(\omega)$  as,

$$\sigma(\omega) = \frac{e^2 N_c}{\Omega k_B T} D(\omega) \quad (4.16)$$

which is just Einstein's formula and  $D(\omega)$  the single particle diffusion coefficient,

$$D(\omega) = -\frac{\omega^2}{6} < \frac{1}{N} \sum_{ij} R_{ij}^2 G_{ij}(\omega) >_c \quad (4.17)$$

## 4.2 Review Of The Correlated Random Walks

In a Markovian random walk (MRW) each step is independent of the previous steps. Let us consider a MRW on a translationally invariant lattice. The transitions are limited to nearest neighbors and the transition rate is  $\Gamma$ . The mean square displacement  $< r^2(t) >$  is  $zDt$ , where  $D$  is the diffusion constant and  $z$  is the coordination number. Now for a cubic lattice with spacing  $a$ ,  $D = \Gamma a^2$  and  $z = 2d$ .

Correlated random walks are a class of random walks where the hops are correlated upto a finite number of steps. Correlated walks were first introduced in the discussion of 'persistence of motion' of particles in fluids. After the initial work by Jeans [90] and Smolachowski [91], Fuerth [92] worked out the theory for random walk with persistence in one dimension. He showed that the mean square displacement of a infusoria in a solution shows a definite non-linear time evolution. The correlation or the memory accounts for the fact that the particle have an inertia and thus they persisted to move in the same direction for a time which is not negligible compared to the observation time. The correlated random walks have been used to explain many physical phenomenon.

Two other applications are conformation of polymers [93] and tracer [94] diffusion in

metals. In tracer diffusion when the tracer hops to a vacancy, the vacancy from which it came is certainly behind the tracer particle. So tracer has a larger probability to move back to the vacancy it came from than to another vacancy. Similar phenomenon is observed in polymer chains where certain directions are blocked for each monomer. One can model some of these systems in terms of a correlated random walk which retains the memory of one last step. Let  $d_i$  be the displacement of the  $i^{\text{th}}$  step and let  $R_n - R_0$  be the total displacement in  $n$  steps. Then the square of sum of all displacement is,

$$\langle (R_n - R_0)^2 \rangle = \langle \left( \sum_{i=1}^n d_i \right) \left( \sum_{j=1}^n d_j \right) \rangle \quad (4.18)$$

If the correlation between successive steps is denoted by  $\alpha$ ,  $\alpha = \langle d_i d_{i+1} \rangle$  then it can be shown that  $\langle d_i d_j \rangle$  proportional to  $\alpha^{|i-j|}$ . The general result is that for long times or large number of steps,

$$\frac{\langle (R_n - R_0)^2 \rangle}{\langle (R_n - R_0)^2 \rangle_{un}} \xrightarrow{n \rightarrow \infty} f \quad (4.19)$$

where  $\langle \rangle_{un}$  is denotes the Markovian random walk. So the static diffusion constant is changed by the correlation factor  $f$ . For the two cases mentioned above, the correlation factor is,

$$f = \frac{(1 + \alpha)}{(1 - \alpha)} \quad (4.20)$$

To see this type of correlation let us consider a correlated walk on the linear chain with constant transition rates. The rate for a transition in the same direction as the previous one is denoted by  $\Gamma_f$  and the rate for a transition in the opposite direction is denoted by  $\Gamma_b$ . The conditional probability  $P(n, t)$  of finding the particle at site  $n$  at time  $t$  when it originated at site 0 at  $t = 0$  is split up into two contributions  $P_+(n, t)$  and  $P_-(n, t)$ , where  $+$  and  $-$  indicates that the particle came from site  $n + 1$  or  $n - 1$ , respectively. These quantities obey the following coupled master equations:

$$\frac{d}{dt} P_+(n, t) = \Gamma_f [P_+(n + 1, t) - P_+(n, t)] + \Gamma_b [P_-(n + 1, t) - P_+(n, t)], \quad (4.21)$$

$$\frac{d}{dt} P_-(n, t) = \Gamma_f [P_-(n - 1, t) - P_-(n, t)] + \Gamma_b [P_+(n - 1, t) - P_-(n, t)]. \quad (4.22)$$

This set of master equations is transformed into a set of coupled algebraic equations by Fourier and Laplace transformations,

$$[s + \Gamma_f(1 - e^{ika}) + \Gamma_b]\tilde{P}_+(k, s) - \Gamma_b e^{ika}\tilde{P}_-(k, s) = P_+(k, 0), \quad (4.23)$$

$$-\Gamma_b e^{-ika}\tilde{P}_+(k, s) + [s + \Gamma_f(1 - e^{-ika}) + \Gamma_b]\tilde{P}_-(k, s) = P_-(k, 0). \quad (4.24)$$

where  $\tilde{P}(k, s)$  is the Fourier and the Laplace transform of  $P(r, t)$  in space and time respectively. The initial conditions are  $P_+(k, 0) = P_-(k, 0) = 1/2$ . The conditional probability  $\tilde{P}(k, s)$  is obtained from the solution of equations (4.23) and (4.24) as,

$$\tilde{P}(k, s) = \frac{s + \gamma + (\Gamma_b - \Gamma_f) \cos ka}{s^2 + 2s[\Gamma_b + \Gamma_f(1 - \cos ka)] + 2\Gamma_f\gamma(1 - \cos ka)}, \quad (4.25)$$

where  $\gamma = \Gamma_f + \Gamma_b$  is the total transition rate.

The small- $k$  expansion of  $\tilde{P}(k, s)$  is

$$\tilde{P}(k, s) \rightarrow \frac{1}{s} - \frac{(s + \gamma)\Gamma_f(ka)^2}{s^2(s + 2\Gamma_b)} + \dots \quad (4.26)$$

The asymptotic mean-square displacement is given by the small- $s$  behavior of  $\tilde{P}(k, s)$ ,

$$\langle x^2 \rangle (t) \xrightarrow{t \rightarrow \infty} \frac{\Gamma_f}{\Gamma_b} \gamma a^2 t. \quad (4.27)$$

The resulting static diffusion coefficient is the product of the diffusion coefficient of the uncorrelated random walk,  $\gamma a^2/2$ , times the correlation factor  $f = \Gamma_f/\Gamma_b$ .

### 4.3 Correlated Random Walk in Disordered Systems

Consider the hopping of a single particle in a disordered medium. For a Markovian random walk, we start with writing a master equation for  $P(i, t)$ , which is the conditional probability to find a particle at site  $i$  at time  $t$  if it started from the origin at time  $t=0$ . The effect of correlation is to retain the memory of the last step. So one defines the probability  $P(i, j, t)$  to find a walker at site  $i$  at time  $t$  given that it arrived at  $i$  via a

direct transition from site  $j$ . The probability density  $P(i,t)$  is obtained by summation over all possible histories in  $P(i,j,t)$  as

$$P(i,t) = \sum_j P(i,j,t), \quad (4.28)$$

where sum is over all sites of the system excluding  $i$ . Initial condition that the walker is at the origin ( $o$ ) at time  $t=0$  is  $P(i,0) = \delta_{i,o}$ . A transition rate  $W_{ij}^b$  is assigned to a jump from site  $j$  to site  $i$  if the previous jump was from site  $i$  to site  $j$ . A transition rate  $W_{ij}$  is assigned to a jump from site  $j$  to  $i$  if the particle had jumped to  $j$  from any site except  $i$ . Conditional probability  $P(i,j,t)$  obeys the following master equation [87, 88]

$$\dot{P}(i,j,t) = \sum_{k \neq i} W_{ij} P(j,k,t) + W_{ij}^b P(j,i,t) - \left[ \sum_{k \neq j} W_{ki} + W_{ji}^b \right] P(i,j,t), \quad (4.29)$$

where  $\dot{P}$  implies a time derivative of  $P$ . Defining  $\delta W_{ij} = W_{ij}^b - W_{ij}$ , equation (4.29) can be rewritten as

$$\dot{P}(i,j,t) = W_{ij} P(j,t) + \delta W_{ij} P(j,i,t) - \left[ \sum_k W_{ki} + \delta W_{ji} \right] P(i,j,t). \quad (4.30)$$

Summing over  $j$  in equation (4.30) we get an equation for  $P(i,t)$

$$\dot{P}(i,t) = \sum_j W_{ij} [P(j,t) - P(i,t)] + \sum_j \delta W_{ji} A(j,i,t), \quad (4.31)$$

where we have defined

$$A(i,j,t) = P(j,i,t) - P(i,j,t). \quad (4.32)$$

Using equation (4.30) we can write an equation for  $P(j,i,t)$  and thereby obtain an equation for  $A(i,j,t)$ . One can get a closed set of equations, by replacing  $\sum_k W_{ki}$  by  $W_t$  which is its average over sites,  $W_t = \langle \sum_k W_{ki} \rangle$ . This yields the equation

$$\dot{A}(i,j,t) = W_{ij} [P(i,t) - P(j,t)] - [W_t + 2\delta W_{ij}] A(j,i,t). \quad (4.33)$$

The approximation made here seems physically reasonable for the two-site probabilities.

Using initial conditions  $P(i,0) = \delta_{i,o}$  and  $A(j,i,0) = 0$  and taking Laplace transform of

equations (4.31) and (4.33), we obtain

$$s\bar{P}(i, s) - P(i, 0) = \sum_j [\bar{P}(j, s) - \bar{P}(i, s)] \left[ W_{ij} - \frac{\delta W_{ij} W_{ij}}{s + W_t + 2\delta W_{ij}} \right], \quad (4.34)$$

where  $\bar{P}(i, s)$  denotes the Laplace transform of  $P(i, t)$ . We now make a further assumption by taking  $\delta W_{ij}$  to be site-independent, as we later relate it to the Coulomb gap. Replacing  $\delta W_{ij}$  by its average value  $\delta W_b$ , we get an equation equivalent to the Markovian rate equation, but with a scaled frequency  $\tilde{s} = sf(s)$  where

$$f(s) = \left[ 1 + \frac{\delta W_b}{s + W_t + \delta W_b} \right]. \quad (4.35)$$

equation (4.34) is solved in terms of the Green's function  $G_{ij}(s)$

$$P(i, s) = f(s) \sum_j G_{ij}(\tilde{s}) P(j, 0), \quad (4.36)$$

where in the matrix notation  $\hat{G}$  obeys the equation

$$\hat{G}(\tilde{s} - \hat{W}) = I, \quad (4.37)$$

with

$$\hat{W}_{ij} = W_{ij} - \delta_{ij} \sum_k W_{ki}. \quad (4.38)$$

## 4.4 Model

We consider a system of randomly placed sites with the density  $n$ . Each site has an energy  $\phi_i$ , where  $\phi_i$ 's are randomly drawn from a rectangular distribution taken to be

$$P(\phi) = \frac{1}{2A} \quad |\phi| \leq A, \quad (4.39)$$

$$P(\phi) = 0 \quad |\phi| > A. \quad (4.40)$$

The DOS for this system has the form

$$g(\phi) = g_0 = \frac{n}{2A} \quad |\phi| \leq A. \quad (4.41)$$

In the presence of Coulomb interactions, the single site energies are modified by Hartree terms and take the form

$$\epsilon_i = \phi_i + \sum_j V_{ij} n_j, \quad (4.42)$$

where  $V_{ij} = e^2/\kappa R_{ij}$  denotes the Coulomb interaction between electrons at the sites  $i$  and  $j$ ,  $n_j$  are the site occupation numbers and  $\kappa$  is the dielectric constant of the medium. As shown by Efros and Shklovoski, the stability of the ground state requires that the density of states  $g(\epsilon)$  for the Hartree energies has a gap around the Fermi level  $\epsilon_F$ , and is given by

$$g(\epsilon) = \frac{C (\epsilon - \epsilon_F)^2 \kappa^3}{e^6} \quad |\epsilon - \epsilon_F| \leq \Delta, \quad (4.43)$$

$$g(\epsilon) = g_0 \quad \Delta < |\epsilon - \epsilon_F| < A, \quad (4.44)$$

where  $C$  is a dimensionless constant of order unity and  $\Delta$  is the width of the Coulomb gap, which is obtained by continuity to be

$$\Delta = \frac{e^3 g_0^{1/2}}{\kappa^{3/2}}. \quad (4.45)$$

Next we model  $\delta W_b$ . It is the difference between the probability of jump between sites around the Fermi level, which typically have an energy barrier of  $\Delta$  and the probability of backward hop. At low temperatures  $k_B T \ll \Delta$ , the charge around the hole relaxes at time scales which are much larger than the conduction time scale ( $\sigma_1^{-1}$ ), to be discussed below. So the backward hop is a downward jump in energy  $\Delta$  and we take,

$$\delta W_b = W_t \tanh\left(\frac{\Delta}{k_B T}\right). \quad (4.46)$$

At very low temperatures,  $k_B T \ll \Delta$ ,  $\delta W_b \approx W_t$ , which makes the probability of backward hops quite large. As the temperature increases, this quantity decreases as expected. In this chapter we have focused on the low temperature regime. We further simplify the calculation by working with symmetric transition rates,  $W(R, \epsilon) = \nu_0 \exp\left[-\left(\frac{R}{a} + \frac{\epsilon}{k_B T}\right)\right]$  where  $\nu_0$  is taken to be the phonon Debye frequency. Then for  $k_B T \ll \Delta$  the average

transition rate of the system is

$$W_t = 16\pi (k_B T)^3 a^3 n \kappa^3 / e^6. \quad (4.47)$$

We work in the frequency units of  $\nu_0$ .

## 4.5 Greens Function Formalism for Conductivity

### 4.5.1 Tight Binding Analogy

The calculation of  $G(\omega)$  for our problem requires inversion of a random matrix and such problem arise in a variety of contexts. Propagation of electrons and quantum of vibrational and magnetic excitations in disordered solids involves precisely similar green's functions. It is clear that the Green's function defined in equation (4.9) is similar to the Green's function for the tight binding problem [95, 96, 97, 98]. This analogy has the advantage that we can directly use the methods that have been developed for the tight binding problem.

The first step in building up this analogy is to split the transition probability matrix  $\underline{S}$  into a diagonal and an off-diagonal part and defining the energy and the overlap matrix element of the corresponding tight binding problem as,

$$\epsilon_i = - \sum_k S_{ik}^e \quad (4.48)$$

and

$$t_{ij} = S_{ij}^e \quad (4.49)$$

Then the Green's function for the problem is

$$G_{ij}(\omega) = \langle i | \frac{1}{i\omega - H} | j \rangle \quad (4.50)$$

Where  $H$  is the hamiltonian for the problem which has diagonal elements  $\epsilon_i$  and off-diagonal elements  $t_{ij}$ . We then write down the Dyson Expansion for the Green's function in terms of these elements as,

$$G_{ij}(\omega) = G_{ii}^0 \delta_{ij} + G_{ii}^0 t_{ij} G_{jj}^0 + \sum_k G_{ii}^0 t_{ik} G_{kk}^0 t_{kj} G_{jj}^0 + \dots \quad (4.51)$$

where the unperturbed Green's function  $G_{ii}^0$  is just

$$G_{ii}^0(\omega) = \frac{1}{i\omega - \epsilon_i} \quad (4.52)$$

The series (4.51) is to be summed over all possible paths which start from site  $i$  and end at the site  $j$ . Renormalized Perturbation Expansion technique is a method to handle the problem of path summation [99].

## 4.5.2 Renormalized Perturbation Expansion

We present a brief review of the Renormalized Perturbation Expansion (RPE) for the Green's function. We first discuss the tight-binding system and then extend the considerations to the kind of systems at hand where the onsite energies and hopping amplitudes are related. The details are found in references [1, 95, 96, 97]. The key idea in using the renormalized perturbation expansion, is to take into account the number closed loops in the Dyson expansion [1]. We first define the local self-energy by considering  $G_{ii}(\omega)$ . This involves summation over the set of all paths that start and end at site  $i$ . Clearly this set of paths can be divided into paths that visit site  $i$   $n$  times with  $n = 0, 1, 2, \dots$ . If we denote by  $\Delta_i(\omega)$  the contribution from paths that come back to site  $i$  just once, then the  $G_{ii}(\omega)$  can be written as,

$$G_{ii}(\omega) = \frac{1}{i\omega - \epsilon_i} + \frac{1}{i\omega - \epsilon_i} \Delta_i \frac{1}{i\omega - \epsilon_i} + \dots \quad (4.53)$$

So all the distinct paths are included in the self energy  $\Delta_i$  and the green function  $G_{ii}$  is written as,

$$G_{ii}(\omega) = \frac{1}{i\omega - \epsilon_i - \Delta_i(\omega)} \quad (4.54)$$

An expansion in terms of paths can also be written for  $\Delta_i(\omega)$

$$\Delta_i(\omega) = \sum_{j \neq i} t_{ij} G_{jj}^i(\omega) t_{ji} + \sum_{k \neq i \neq j} t_{ij} G_{jj}^i(\omega) t_{jk} G_{kk}^{i,j}(\omega) t_{ki} + \dots \quad (4.55)$$

where  $G_{jj}^i(\omega)$  is the Green function of the system with site  $i$  removed;  $G_{kk}^{i,j}(\omega)$  is the corresponding Green's function of the system from which site  $i$  and  $j$  are removed.

The higher order terms are built from Green function's in which the previously visited sites have been removed. This procedure is called RPE. We can similarly define the self-energies corresponding to Green function  $G_{kk}^i(\omega)$  etc. as,

$$G_{kk}^i = [i\omega - \epsilon_k - \Delta_k^i]^{-1} \quad (4.56)$$

$$G_{kk}^{i,j} = [i\omega - \epsilon_k - \Delta_k^{i,j}]^{-1} \quad (4.57)$$

The expressions for  $\Delta_k^i$  and  $\Delta_k^{i,j}$  are identical to equation (4.55) with the following restrictions. For example,  $\Delta_k^i$  corresponds to all paths that return to  $k$  once, without visiting the site  $i$ . So we can now write the RPE for  $G_{ij}(\omega)$  as,

$$G_{ij}(\omega) = G_{ii}\delta_{ij} + G_{ii}t_{ij}G_{jj}^i + \sum_k G_{ii}t_{ik}G_{kk}^i t_{kj}G_{jj}^{i,k} + \dots \quad (4.58)$$

In all the above path summations all the repeated indices have been eliminated, so they represent an exact self avoiding expression.

The Tight Binding analogy is however not completely applicable here, as in our problem the energies  $\epsilon_i$  themselves are related to the transfer matrix elements  $t_{ij}$ ,  $\epsilon_i = -\sum_k t_{ik}$ . To bring the RPE closer to our problem [95], it is important to exclude the bond  $(i-j)$  from the green function  $G_{jj}^{(i)}$ . To do this new transfer rates  $g_{ij}$  and green function  $G_{jj}(ij)$  are defined. In  $G_{jj}(ij)$  bond  $(i-j)$  is excluded. The removal of a bond  $(i-j)$  from a site green function  $G_{ii}$  leads to inclusion of all two site loops into the new transfer rates  $g_{ij}$ . The new transfer rate can be written in terms of old rates as,

$$g_{ij} = t_{ij} - t_{ij}G_{jj}^i t_{ji} \quad (4.59)$$

In terms of new site green functions  $g_{ij}$  is,

$$g_{ik} = \frac{t_{ik}/t_{ki}}{1/t_{ki} + G_{kk}(ik)} \quad (4.60)$$

To further write the series, green function like  $G_{jj}(ik, kl, \dots sj)$  have to be defined in which all the bonds previously used by the electron are excluded. The series (4.58) can

be rewritten as,

$$G_{ij}(\omega) = G_{ii}\delta_{ij} + G_{ii}g_{ij}G_{jj}(ij) + \sum_k G_{ii}g_{ik}G_{kk}(ik)g_{kj}^i G_{jj}(ik : kj) + \dots \quad (4.61)$$

where

$$G_{ii} = \left[ i\omega + \sum_k g_{ik} - D_i \right]^{-1} \quad (4.62)$$

where  $D_i$  refers to the summation over all closed loop contributions to the self energy  $\Delta_i$  which include three or more sites. The two site contributions are included in  $\sum_k g_{ik}$  as seen from equation (4.59). Now to first order the green functions at the sites are decoupled from each other. This will allow us to average the series (4.61) term by term.

At this stage the expressions are exact. But an exact solution is possible only for some model systems like the Cayley tree where there are no closed loops. Then the expressions are simplified and it is possible to write down a closed expression for the conductivity. For real systems it is necessary to make approximations. The general idea is to make approximations such that it is possible to recast the expressions for a real system in a form similar to the results for the exactly soluble modes, so that the results of the model system can be carried over to the real systems.

### 4.5.3 Effective Medium Approximation

The basic idea of the effective medium approximation [100] (EMA) is to replace a disordered medium by some effective ordered medium whose parameters are chosen such that they describe the actual medium as closely as possible. Applying the EMA to equation (4.61), by replacing the transfer matrix elements  $g$  by their configuration averages, we can write,

$$\langle G_{ij} \rangle_{ij} = \left( i\omega + \sum_n \langle g_{in} \rangle \right)^{-1} \langle g_{ij} \rangle_{ij} \left( i\omega + \sum_{l \neq i} \langle g_{jl} \rangle \right)^{-1} + \dots \quad (4.63)$$

The configuration average of any quantity  $B$  is defined as,

$$\langle B(R_1, R_2, \dots, R_N : E_1, E_2, \dots, E_N) \rangle = \int BP(R_1, \dots, R_N)g(E_1)\dots g(E_N) \times \prod_{i=1}^N dR_i dE_i \quad (4.64)$$

where  $P(R_1, \dots, R_N)$ , is the  $N$ -site correlation function and the density of states is denoted by  $g(E_i)$ . Usually  $P(R_1, \dots, R_N)$  is approximated by the product of the pair correlation functions, as follows,

$$P(R_1, \dots, R_N) = g_C(R_1 - R_2)g_C(R_2 - R_3)\dots g_C(R_{N-1} - R_N) \quad (4.65)$$

where  $g_C(R_i - R_j)$  denotes the pair correlation function. If the transition rates are symmetric and of the form,

$$W_{ij} = W^1(R_{ij})\nu(|E|/k_B T) \quad (4.66)$$

the Fourier transform of (4.63) can be written as,

$$G_k(\omega) = [i\omega + ng_{k=0}(\omega) - ng_k(\omega)]^{-1} - [i\omega + ng_{k=0}(\omega)]^{-1} \quad (4.67)$$

where

$$G_k(\omega) = n \int e^{-ik \cdot R_{ij}} g_C(R_i - R_j) \langle G_{ij} \rangle_{ij} dR_{ij} \quad (4.68)$$

$$g_k(\omega) = \int e^{-ik \cdot R_{ij}} g_C(R_i - R_j) \langle g_{ij} \rangle_{ij} dR_{ij} \quad (4.69)$$

For symmetric transition rates,  $F_i = F = n_c(1 - n_c)$  where  $n_c$  is the number of particles per site  $n_c = N_c/N$ . Using equations (4.15) and (4.67), the conductivity can be written as

$$\sigma(\omega) = -\frac{e^2}{k_B T} \frac{(i\omega)^2}{6\Omega} F \left. \frac{\partial^2 G_k}{\partial k^2} \right|_{k=0} \quad (4.70)$$

So finally, using equation (4.67) the conductivity can be written as,

$$\sigma(\omega) = \frac{e^2}{k_B T} \frac{N_c(1 - n_c)}{6\Omega} \langle \sum R_{ij}^2 g_{ij}^S \rangle \quad (4.71)$$

where  $S$  denotes symmetric transition rates. Applying the EMA to the expression for  $g_{il}$  in equation (4.60) we can write,

$$\langle g_{ij} \rangle_{ij} = \left( \frac{1}{W_{ij}} + \frac{1}{i\omega + \langle \sum_{l \neq i} g_{jl} \rangle_j} \right)^{-1} \quad (4.72)$$

Substituting (4.72) in (4.71) the conductivity for symmetric hop rates can be written as,

$$\sigma(\omega) = \frac{e^2}{k_B T} \frac{N_c(1-n_c)}{6\Omega} D(\omega) \quad (4.73)$$

where

$$D(\omega) = \left[ \frac{\langle R^2(\omega) \rangle}{6a_p} \right] \sigma_1(\omega) \quad (4.74)$$

and  $\sigma_1(\omega)$  is given as a solution of the following self consistent equation,

$$\sigma_1(\omega) = [\sigma_1(\omega) + i\omega] n a_p \int \int \frac{g(E) g_C(R) W_{ij}}{i\omega + \sigma_1(\omega) + W_{ij}} dR dE \quad (4.75)$$

with  $a_p = 1/e$  and

$$\langle R^2(\omega) \rangle = \left\langle R_{ij}^2 \frac{W_{ij}}{i\omega + \sigma_1(\omega) + W_{ij}} \right\rangle / \left\langle \frac{W_{ij}}{i\omega + \sigma_1(\omega) + W_{ij}} \right\rangle \quad (4.76)$$

## 4.6 Results

Let us now write the expressions for the conductivity for the correlated random walk.

The expression for frequency dependent conductivity can be written as

$$\sigma(\omega) = \frac{(i\omega)^2 e^2 f(\omega)}{6V k_B T} \sum_{ij} \langle F(\epsilon_i) R_{ij}^2 Q_{ij}(\tilde{\omega}) \rangle, \quad (4.77)$$

the transition rates  $g_{ij}$  obey the same self consistent equation but with scaled frequency  $\tilde{\omega}$  replacing  $\omega$ .

$$g_{ij} = \left[ \frac{1}{W_{ij}} + \frac{1}{i\tilde{\omega} + \sum_l g_{jl}} \right]^{-1} \quad (4.78)$$

The self-consistent equation for the average value  $\sigma_1(\omega)$  of  $\sum_j g_{ij}$  can be recast into the form

$$\sigma_1(\tilde{\omega}) = (\sigma_1(\tilde{\omega}) + i\tilde{\omega}) \int \frac{g(\epsilon) W(R, \epsilon) d^3R d\epsilon}{(\sigma_1(\tilde{\omega}) + i\tilde{\omega}) W(R, \epsilon) + 1}, \quad (4.79)$$

and the conductivity is given as

$$\sigma(\omega) = \frac{F e^2}{6V k_B T f(\omega)} \langle R^2(\tilde{\omega}) \rangle \sigma_1(\tilde{\omega}), \quad (4.80)$$

with

$$\langle R^2(\tilde{\omega}) \rangle = \left\langle \frac{R^2 W(R, \epsilon)}{\sigma_1(\tilde{\omega}) + i\tilde{\omega} + W(R, \epsilon)} \right\rangle / \left\langle \frac{W(R, \epsilon)}{\sigma_1(\tilde{\omega}) + i\tilde{\omega} + W(R, \epsilon)} \right\rangle. \quad (4.81)$$

Using transition rates defined in section 4 and the condition  $\Delta \gg k_B T$ , the equation (4.79) can be written in terms of dimensionless variables as

$$\sigma_1(\tilde{\omega}) = (\sigma_1(\tilde{\omega}) + i\tilde{\omega}) p \int \int \frac{\epsilon^2 r^2 dr d\epsilon}{(\sigma_1(\tilde{\omega}) + i\tilde{\omega}) W(r, \epsilon)^{-1} + 1} \quad (4.82)$$

where  $p = 4\pi n a^3 (k_B T)^3 \kappa^3 / e^6 = W_t / 4$ .

We first look at the calculation of conductivity for the uncorrelated system. The previous analysis [96, 97] was done by neglecting the frequency dependence of mean square displacement, which is rather weak. Thus the frequency dependence of conductivity is largely determined by  $\sigma_1(\omega)$ . Analysis of the equation (4.82) shows, that the significant dispersion in  $\sigma_1(\omega)$  sets in only when frequency becomes greater than  $\sigma_1(0)$ . The equation for  $\sigma_1(0)$  is equivalent to the percolation criterion employed by Ambegaokar *et al* [28]. Solving equation (4.82) for  $\omega=0$  one gets

$$\sigma_1(0) = \exp(-u) = \exp \left[ - \left( \frac{180}{p} \right)^{1/6} \right] = \exp \left[ - \left( \frac{T_{es}}{T} \right)^{1/2} \right]. \quad (4.83)$$

In the infinite frequency limit  $\sigma_1(\omega)$  is proportional to the average transition rate of the system  $W_t$ . In the intermediate frequency range the conductivity obeys a power law in frequency,  $\sigma_1(\omega) \propto \omega^s$ . The slope is crudely given by  $s = (u + \ln W_t) / u$ . The slope increases as the temperature  $p$  decreases.

For the correlated walk, the conductivity becomes a function of a scaled frequency  $\tilde{\omega}$  instead of  $\omega$ . The behavior of  $\sigma_1$  as functions of  $\omega$  and  $\tilde{\omega}$  is shown in figs. 4.1 and 4.2 for two different temperatures. The curve for  $\sigma_1(\tilde{\omega})$  shifts to the left with respect to  $\sigma_1(\omega)$  on the frequency scale. The shift depends upon the frequency dependent correlation factor  $f(\omega)$ . As seen from the figs. 4.1 and 4.2, the shift is apparent for frequency range  $\sigma_1(0) < \omega < W_t$ . At high frequencies,  $\omega \gg W_t$ ,  $f(\omega) \approx 1$  so the correlation effects are negligible. Since there is no dispersion in the low frequency range  $\omega < \sigma_1(0)$ , the curves

again coincide. The crossover frequency  $W_t$  is temperature dependent and does not scale with  $\sigma_1(0)$ . Comparison of figs. 4.1 and 4.2 shows that the crossover from correlated to uncorrelated hopping occurs at different frequencies for different temperatures.

The calculation of conductivity with correlated hopping requires computation of the factor  $\langle R^2(\tilde{\omega}) \rangle$ . This leads to the reduction of the conductivity by a factor of  $1/f(\omega)$ . The results for conductivity for two values of  $p$  are shown in figs. 4.3 and 4.4. At temperatures reported here  $f(0)$  is weakly dependent on temperature, so the change in dc conductivity is also weakly dependent on  $p$ , as seen in these figures. At higher frequencies  $\omega > W_t$ ,  $f(\omega) \approx 1$ , so no correlation effects are present and the curves coincide. Enhanced backward correlations increase the slope of conductivity by  $\ln[f(0)]/u$ . This is significant at high temperatures (small  $u$ ). The increase in slope due to backward correlations decreases as temperature decreases ( $u$  increases) as seen in the figures 3 and 4.

We next discuss the scaling of the ac conductivity, which has been seen in numerous studies [101, 102, 103, 104]. The experimental studies show that over a considerable range of temperatures the scaling of the form

$$\sigma(\omega)/\sigma_{dc} = \Psi(\omega/T\sigma_{dc}), \quad (4.84)$$

holds for a wide range of materials, including ionic conductors. In the present calculation we have already seen that the frequency dispersion of conductivity sets in only when  $\omega > \sigma_1(0) \propto T\sigma_{dc}$ . The reason for this is quite apparent in equation (4.79). However the scaling of equation (4.84) requires that  $\sigma(\omega)/\sigma_{dc}$  will not have any temperature dependence apart from that contained in  $\sigma_1(0)$ . This, as in earlier studies [102, 103, 104], is true when the temperatures are low and a Sommerfeld approximation can be made to evaluate the integrals in equations (4.79) and (4.81). Since  $\tilde{\omega} = 0$  for  $\omega = 0$  the equation for  $\sigma_1(0)$  is same for both correlated as well as Markovian hopping. However, for the correlated hopping the difference comes in the evaluation of the dc conductivity in which

there is an additional factor of  $f(0)$ . Thus we can write

$$\sigma(\omega)/\sigma_{dc} = \Psi \left( \frac{\tilde{\omega}}{\sigma_1(0)} \right) = \Psi \left( \frac{\omega f(\sigma_1(0))}{\sigma_{dc} T f(0)} \right). \quad (4.85)$$

This shows that the scaling frequency changes due to correlated diffusion by the factor  $f(\sigma_1(0)/f(0))$ , which has been termed as the Haven ratio [105, 106].

## Concluding Remarks

In this chapter, we have treated the effect of Coulomb interactions on hopping transport through two aspects. These are: (a) depletion of single-particle density of states, which has a dominant effect on the temperature dependence of dc conductivity, (b) the enhanced backward hopping which is a consequence of Coulomb hole (anti hole) around occupied (unoccupied site). The latter aspect has a considerable influence on the ac conductivity in the dispersive regime. We show that the scaling property of conductivity with frequency is still obeyed approximately, but modified by the Haven ratio. This factor had been introduced in the empirical work in an ad hoc manner. Here we have obtained its theoretical value.

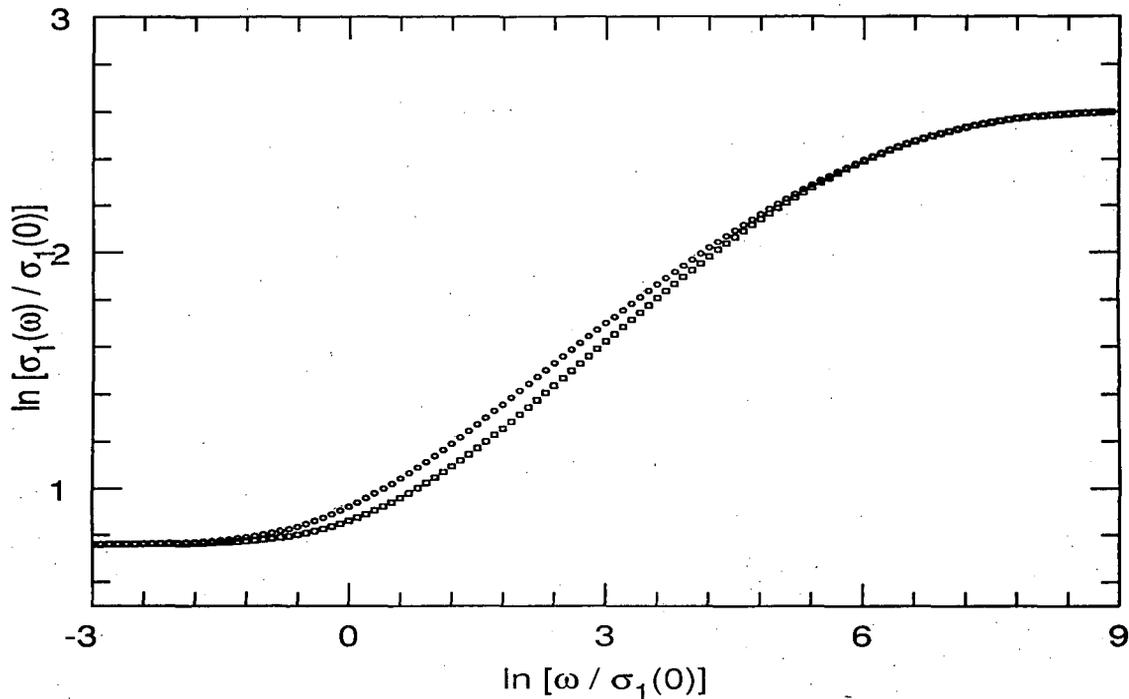


Figure 4.1: Plots of  $\ln[\sigma_1(\omega)/\sigma_1(0)]$  with  $\ln[\omega/\sigma_1(0)]$  for (o) correlated and (□) uncorrelated hopping for  $p=.0002$ .

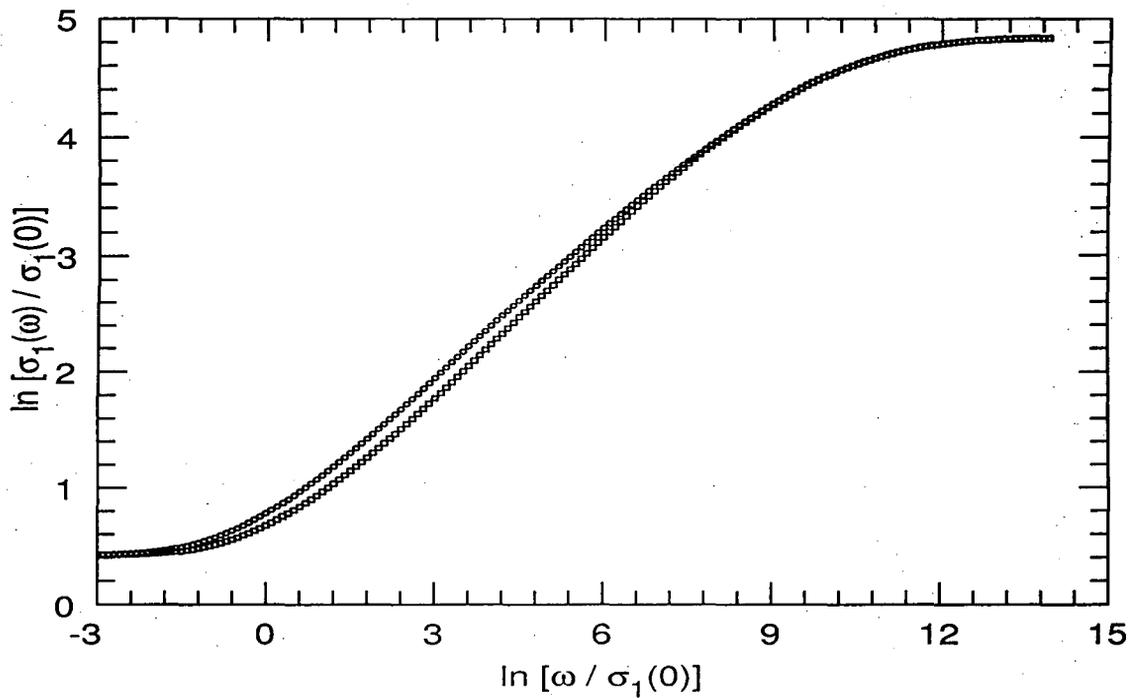


Figure 4.2: Plots of  $\ln[\sigma_1(\omega)/\sigma_1(0)]$  with  $\ln[\omega/\sigma_1(0)]$  for (o) correlated and (□) uncorrelated hopping for  $p=.00002$ .

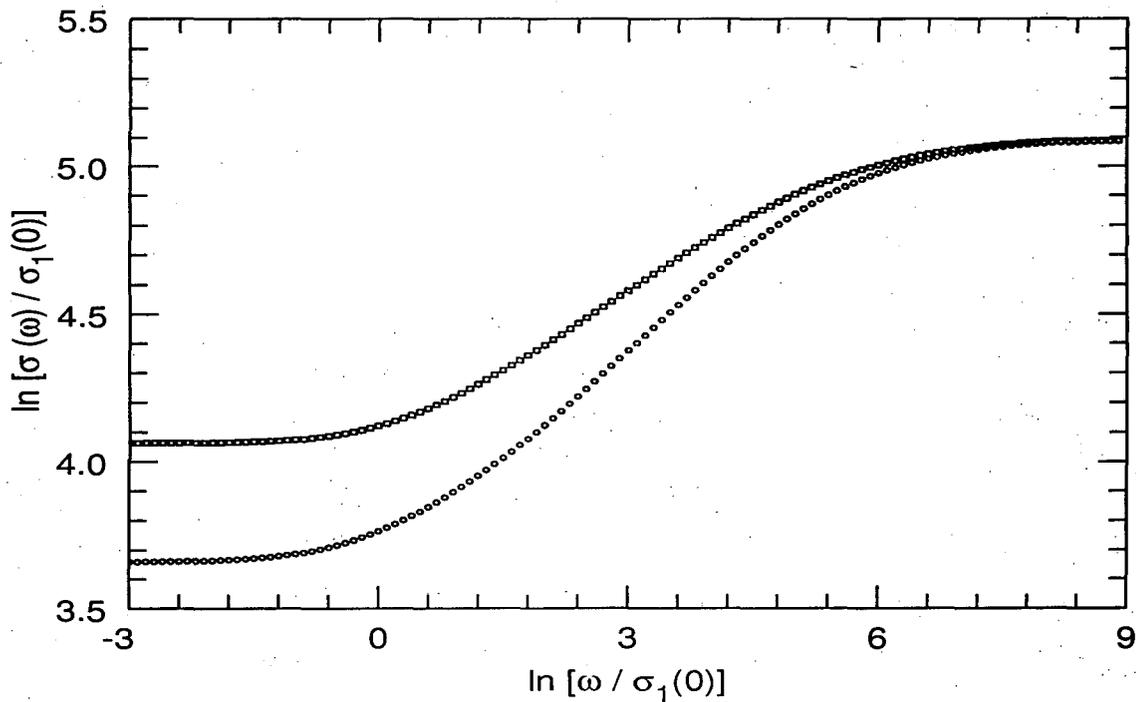


Figure 4.3: Logarithmic plots of scaled conductivity  $\ln[\sigma(\omega)/\sigma_1(0)]$  against scaled frequency  $\ln[\omega/\sigma_1(0)]$  for (○) correlated and (□) uncorrelated hopping for  $p=.0002$ .

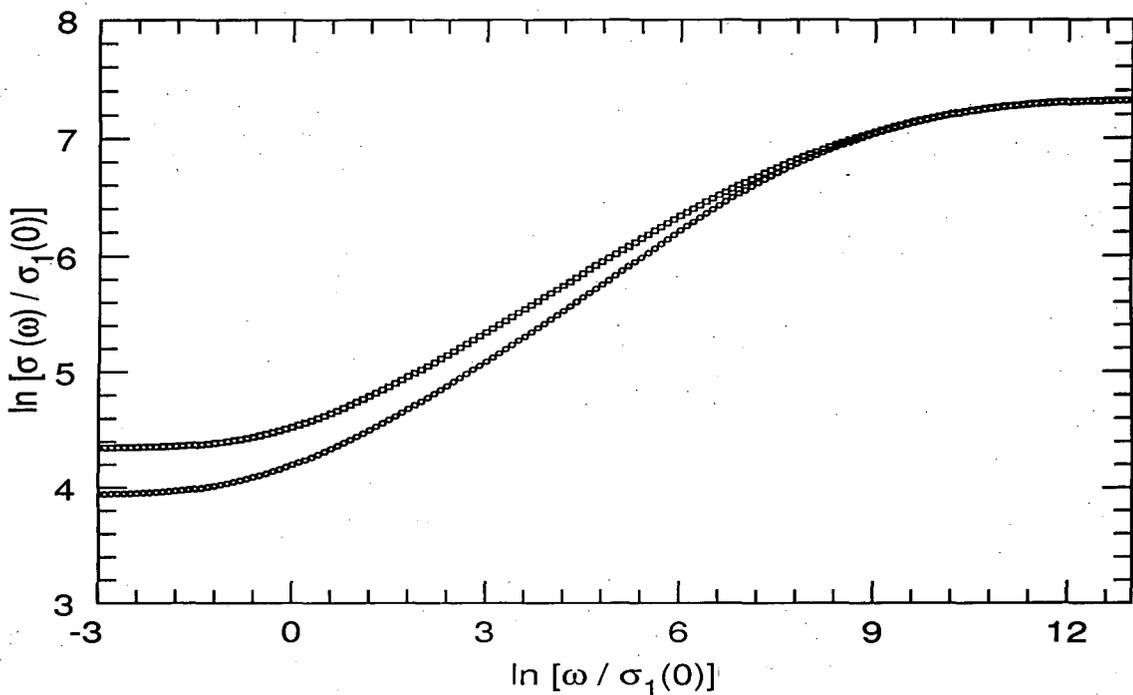


Figure 4.4: Logarithmic plots of scaled conductivity  $\ln[\sigma(\omega)/\sigma_1(0)]$  against scaled frequency  $\ln[\omega/\sigma_1(0)]$  for (○) correlated and (□) uncorrelated hopping for  $p=.00002$ .