Chapter 5

Formation of the Coulomb gap

Introduction

The Coulomb glasses are systems [16, 76] in which electronic states are localized due to disorder and the transport occurs by thermally activated hopping. The familiar examples are impurity bands in doped semiconductors and amorphous semiconductors, in which the Fermi level lies in the region of localized states. The long range Coulomb interactions play a dominant role in the thermodynamic and transport properties of these systems.

In recent years studies of relaxation in Coulomb glasses have revealed some very interesting dynamical features. These studies have been done on disordered semiconducting [107, 108, 109, 110] and metallic films [111, 112] in MOSFET geometry and employ the field effect. By changing the gate voltage in these experiments, one changes the carrier concentration in the film and studies the relaxation of conductivity. The field effect [108] studies reveal that, an abrupt change of gate voltage leads to an increase of conductivity irrespective of whether the electron concentration is increased or decreased by the change. This feature, which seems quite counterintuitive at first sight, is associated with another dynamic aspect. The nonequilibrium conductivity relaxes to its new equilibrium value, which corresponds to equilibrium at the new electron concentration, by a rather slow process characteristic of glassy behavior. This behavior of nonequilibrium conductivity and its relaxation has been a subject of much interest and have been

ascribed to correlations in the Coulomb glass [110, 113, 114].

A key aspect of the correlations in the Coulomb glass is the existence of Coulomb gap [33, 36], which refers to a sharp depletion of the density of states (DOS) for the low energy single-particle excitations. More precisely, in equilibrium the single particle density of states develops a soft gap around the Fermi level. Recently Yu [114] has introduced a physically appealing picture to understand the above-mentioned phenomenon in terms of Coulomb gap. According to her, the main effect of the injection or removal of electrons can be analyzed in terms of an abrupt change in the Fermi level of the system. The main elements of the equilibration process that follows are the formation of Coulomb gap at the new Fermi level and its healing at the old level. Since conductivity is proportional to the density of states of the low energy electron-hole excitations, the first feature of the experiment, namely the rise of conductivity in the nonequilibrium state is nicely understood in this picture. Since in equilibrium the Fermi level is at the bottom of the gap, any change in its position leads to a higher density of states, and hence to the larger conductivity.

The second aspect, concerned with the slow decrease of conductivity, is related to the growth of correlations which lead to the formation of the Coulomb gap at the new Fermi level. The Coulomb gap is basically due to the correlated occupation of sites in equilibrium. Around each occupied (unoccupied) site, there is a depletion (excess) of electrons on the neighboring sites due to Coulomb interactions. As a result, the one-particle Hartree energy is lower for an occupied site than for an unoccupied sites. Thus around the Fermi level for sites with equal site energies, the occupied sites have lower, while the unoccupied sites have higher Hartree energies resulting in a Coulomb gap.

The chapter is organized as follows. In section 1, we present the model for the Coulomb glass. This model is same as that given in sections 1.8.1 and 1.8.2. In section 2, the integral equation for time dependent density of states $g(\epsilon, t)$ is introduced. We then give a model for $g(\epsilon, t)$ based upon the time scaling properties of the integral equation

for $g(\epsilon, t)$. We then solve the integral equation for $g(\epsilon, t)$ and determine the various parameters self-consistently. In section 3, we present the consequences of Coulomb gap formation on conductivity.

5.1 Model

A quantitative way to consider the effect of these correlations on the one-particle excitation density was given by Efros and Shklovskii (ES) [17]. We describe their procedure for a Coulomb glass, formed in the impurity band of a doped and compensated semiconductor. The compensation is such that only half the donor sites are occupied by electrons. For this system the Hamiltonian [16] can be written in terms of site occupation variables n_i in the following way,

$$H = \sum_i \phi_i n_i + \frac{1}{2} \sum_{i \neq j} V_{ij}(n_i - 1/2)(n_j - 1/2), \tag{5.1}$$

here n_i's take value 0 and 1. ϕ_i is the site energy for the localized level around the site R_i, and it is taken to be randomly distributed with a probability distribution which we take to be,

$$\begin{aligned} P(\phi) &= \frac{1}{2A} \quad |\phi| \leq A, \\ P(\phi) &= 0 \quad |\phi| > A. \end{aligned} \tag{5.2}$$

$V_{ij} = e^2/\kappa\,|R_i - R_j|$ is the Coulomb interaction between charges on sites i and j and for convenience the charge on occupied site is taken to be $e/2$ and on unoccupied site to be $-e/2$. The Hartree energy in the ground state, which is the energy needed to add an electron to an empty site i keeping all other charges fixed is given by,

$$\epsilon_i = \phi_i + \sum_j V_{ij} < n_j - 1/2 >, \tag{5.3}$$

where $< n_i >$ denotes the occupation in the ground state configuration. The excitation energy for the process in which an electron from an occupied site i is moved to an

unoccupied site j, keeping all other charges fixed is given by,

$$\Omega_{ji} = \epsilon_j - \epsilon_i - V_{ij} \tag{5.4}$$

Efros and Shklovskii [17] observed that for the ground state the occupation n_i should be such that all possible excitation energies must be positive. The condition on single electron transition requires that the sites with energy difference $\Delta\epsilon$, must be separated in space by a distance greater than $e^2/\kappa\Delta\epsilon$. This translates into a behavior for the density of states $g(\epsilon)$ near the Fermi energy $\mu(\mu = 0$ in the present model) to be [17],

$$g(\epsilon) \propto \epsilon^2 \quad |\epsilon| < \Delta, \tag{5.5}$$

Here Δ is the width of the Coulomb gap given by

$$\Delta^2 = c\frac{\pi}{3} g_o \left(\frac{e^2}{\kappa}\right)^3, \tag{5.6}$$

where $g_o = 1/Ar_{av}^3$ is the density of states for site energies ϕ_i, $r_{av} = n^{-1/3}$ is the average distance between the sites, and c is numerical constant of order one.

5.2 Time Dependent density of States

A more quantitative treatment for the density of states was given by Efros [37] and Baranovskii *et al* [73], who formulated an integral equation for the density of states given by,

$$g(\epsilon) = g_o \exp\left[-\frac{2\pi}{3}\left(\frac{e^2}{\kappa}\right)^3 \int_0^{E_c-|\epsilon|} d\epsilon' \frac{g(\epsilon')}{(|\epsilon| + \epsilon')^3}\right], \tag{5.7}$$

where $E_c = e^2/\kappa r_{av}$. We have written the equation for $\epsilon < 0$. Note that in this model the Coulomb gap is symmetric about the Fermi level. Equation (5.7) arises basically by requiring that $g(\epsilon)$ is reduced from g_o by a factor which is the joint probability of the occurrence of all those transitions that do not obey the stability condition, $\Omega_{ij} > 0$. It is straightforward to see that this equation admits a solution $g(\epsilon) \propto \epsilon^2$ for small ϵ. One can also obtain the constant c of the equation (5.6) to be exp(3).

Now let us return to the consideration of relaxation in Coulomb glass from a nonequilibrium situation, specifically the one which arises by an abrupt change in the density of electrons. As mentioned above, the process of equilibration involves formation of holes (antiholes) around occupied (unoccupied) sites. This is a slow and hierarchical process, as it involves a rather large number of rearrangements at several length scales. As the hop probability decreases exponentially with distance, the relaxation at successively larger length scales require successively larger relaxation times.

Yu [114] has addressed the problem of how the Coulomb gap develops (or heals) in time by generalizing the above integral equation to time dependent situations in the following way. Recall that the rate of the hop between two sites of energies ϵ and ϵ', and separated by a distance r is given by,

$$\tau^{-1}(\epsilon, \epsilon', r) = \nu_0 \exp[-(|\epsilon| + |\epsilon'| + |\epsilon - \epsilon'|)/2kT - 2r/a], \tag{5.8}$$

where a is the localization length of the donor orbitals. Now till a time t, only those transitions occur for which $\tau \leq t$. Incorporating this, leads to the following integral equation for the time-dependent density of states, $g(\epsilon, t)$.

$$g(\epsilon, t) = g_o \exp\left[-\frac{1}{2}\int_{-A}^{A} d\epsilon' g(\epsilon', t) \int_a^{\infty} dr 4\pi r^2 F(n(\epsilon) = 1, n(\epsilon') = 0)\theta(\frac{e^2}{\kappa r} + \epsilon - \epsilon')\theta(t - \tau(\epsilon, \epsilon', r)\right. \tag{5.9}$$

Here $F(n_i, n_j)$ denotes the probability that the donors i and j have occupation numbers n_i and n_j respectively.

The purpose of this chapter is to show that some important features of the solution of equation (5.9) can be obtained analytically. These features have interesting physical implications which should be useful in analyzing the results of the relaxation experiments mentioned above. We consider the situation at zero temperature. With $\epsilon' > 0$, $\epsilon < 0$, $\tau^{-1}(\epsilon, \epsilon', r)$ is given by $\exp(-2r/a)$. Equation (5.9) can be written in terms of the variable $v = e^2/\kappa r$ as,

$$g(\epsilon, t) = g_o \exp\left[-3b \int_0^W d\epsilon' g(\epsilon', t) \int_0^{E_c} \frac{dv}{v^4} \theta(v - |\epsilon| - \epsilon')\theta(t - \tau(v))\right], \tag{5.10}$$

with $\tau(v) = \nu_o^{-1} exp(\frac{2e^2}{a\kappa v})$ and $b = \frac{2\pi}{3}(\frac{e^2}{\kappa})^3$. The presence of theta-function involving time puts a lower limit $E_c(t) = \frac{e^2}{\kappa a \ln(\nu_o t)}$ on the value of v. It is important to distinguish between the two cases: $|\epsilon| > E_c(t)$ and $|\epsilon| < E_c(t)$. On integrating over v, equation (5.10) can be written as,

$$g(\epsilon, t) = g_o \exp\left(-b \int_0^{E_c - |\epsilon|} d\epsilon' g(\epsilon', t) \left[\frac{1}{v_l^3(\epsilon, \epsilon', t)} - \frac{1}{E_c^3}\right]\right), \tag{5.11}$$

where, for $|\epsilon| \leq E_c(t)$,

$$\begin{aligned} v_l(\epsilon, \epsilon', t) &= E_c(t) \quad \epsilon' \leq E_c(t) - |\epsilon| \\ &= |\epsilon| + \epsilon' \quad \epsilon' > E_c(t) - |\epsilon|. \end{aligned} \tag{5.12}$$

On the other hand, for $|\epsilon| > E_c(t)$

$$v_l(\epsilon, \epsilon', t) = |\epsilon| + \epsilon'. \tag{5.13}$$

As t goes to infinity, $E_c(t)$ goes to zero and equation (5.11) reduces to equation (5.7). Further note that the time dependence in the integral equation (5.11) occurs solely through $E_c(t)$.

We solve equation (5.11) under the conditions $A >> E_c >> \Delta >> E_c(t)$ and $a >> r_{av}$. For this purpose, we make the following ansatz for $g(\epsilon, t)$,

$$\begin{aligned} g(\epsilon, t) &= g_\mu(t) + g_1(t)\epsilon + g_2(t)\epsilon^2 \quad 0 < |\epsilon| \leq E_c(t), \\ &= g_3(t)\epsilon^2 \quad E_c(t) \leq |\epsilon| \leq \Delta, \\ &= g_o \quad |\epsilon| > \Delta. \end{aligned} \tag{5.14}$$

Here g_μ, g_1, g_2 and g_3 are to be determined from the integral equation, and their time-dependence occurs through $E_c(t)$. The functional form of the DOS given above is similar to the one given by Yu [114]. Till times, $E_c(t) > \Delta$, the DOS does not change. This can be physically explained by noting that only after jumps exceeding distance $r_\Delta = \frac{e^2}{\kappa\Delta}$ happen, the Coulomb gap is effected. We now substitute the ansatz for $g(\epsilon, t)$ in the

rhs of equation (5.11). We first consider the region $|\epsilon| > E_c(t)$ to determine $g_3(t)$. Neglecting the terms of the order ϵ/E_c and $(\epsilon/\Delta)^2$, one obtains for the equation (5.11),

$$g(\epsilon,t) = g_o \left(\frac{|\epsilon| + E_c(t)}{\Delta}\right)^{bg_3} exp\left[-bG_1(|\epsilon|, E_c(t)) + \frac{3}{2}bg_3 - \frac{g_o}{2\Delta^2}\right], \tag{5.15}$$

where

$$\begin{aligned} G_1 &= \frac{1}{(|\epsilon| + E_c(t))^2}\left[g_\mu \frac{(E_c(t)^2 + 2|\epsilon|E_c(t))}{2\epsilon^2} + \frac{g_1 E_c(t)^2}{2|\epsilon|} - \frac{g_2 E_c(t)(3E_c(t) + 2|\epsilon|)}{2}\right] \\ &+ g_2 \ln\left(\frac{|\epsilon| + E_c(t)}{|\epsilon|}\right). \end{aligned} \tag{5.16}$$

Note that $G_1 \to 0$ as $E_c(t)/|\epsilon| \to 0$, so that at large times the self-consistency requires $bg_3 = 2$, which gives

$$g_3(t) = \frac{cg_o}{\Delta^2}, \tag{5.17}$$

with c=exp(3-1/c), which matches the solution in $t \to \infty$ limit. Next we consider the regime $|\epsilon| < E_c(t)$. Evaluating the integrand in the exponent of equation (5.11) for $|\epsilon|/E_c(t) << 1$, then leads to the self consistent equation,

$$g_\mu + g_1|\epsilon| + g_2|\epsilon|^2 = g_o \left(\frac{|\epsilon| + E_c(t)}{\Delta}\right)^2 exp\left[-b\left(I(0) + \frac{I'(0)|\epsilon|}{E_c(t)} + I''(0)\frac{|\epsilon|^2}{E_c(t)^2}\right)\right], \tag{5.18}$$

where

$$I(0) = \frac{g_\mu}{E_c(t)^2} + \frac{g_1}{2E_c(t)} + \frac{g_2}{3} + \frac{g_o}{2\Delta^2} \quad ; \quad I'(0) = -\frac{3g_o c}{\Delta^2}, \tag{5.19}$$

$$I''(0) = \frac{3g_o c}{2\Delta^2} - \frac{3}{2}\left[\frac{g_\mu}{E_c(t)^2} + \frac{g_1}{E_c(t)} + g_2\right]. \tag{5.20}$$

equation (5.18) is solved by taking,

$$g_\mu = \frac{c_\mu g_o}{\Delta^2} E_c(t)^2 \quad ; \quad g_1 = \frac{c_1 g_o}{\Delta^2} E_c(t) \quad ; \quad g_2 = \frac{c_2 g_o}{\Delta^2}. \tag{5.21}$$

Using the condition $\frac{bcg_o}{\Delta^2} = 2$, we get the following relations between c_μ, c_1, c_2 and c,

$$c_\mu = \exp\left[\frac{-2}{c}\left(c_\mu + \frac{c_\epsilon}{2} + \frac{c_2}{3} + \frac{1}{2}\right)\right], \tag{5.22}$$

$$c_1 = 6c_\mu \quad ; \quad c_2 = \left[12 + \frac{3(c_u + c_1 + c_2)}{c}\right] c_\mu. \tag{5.23}$$

The requirement of the continuity of the density of states at $|\epsilon| = E_c(t)$ yields the relation $c_\mu + c_1 + c_2 = c$. The above equations and the continuity relation yield the following values: $c_\mu = .39$; $c_1 = 2.34$; $c_2 = 5.85$; $c = 8.58$. The value of c is different from one got by solving equation (5.11) for $|\epsilon| >> E_c(t)$. One has to note that our solution is valid in the regions away from $|\epsilon| \cong E_c(t)$ and $|\epsilon| \cong \Delta$. The form of the solution connecting the regimes across $E_c(t)$ and Δ is clearly more complex. The discrepancy in the value of c largely affects the solution in the region $|\epsilon| \approx \Delta$, which our solution does not describe. Though the functional form of the solution is similar to the numerical solution obtained by Yu [114], the time dependence of DOS at Fermi level is given by g_μ which is proportional to $1/[\ln(\nu_o t)]^2$, rather than the power law as obtained by Yu.

5.3 Conductivity

We now present the consequences of the Coulomb gap formation on the relaxation of conductivity in the above nonequilibrium situation. We base our calculation on the work of Movaghar and Schirmacher [95] (4.73, 4.74, 4.75, 4.76). These expressions are based on an effective medium approximation using the renormalized perturbation expansion. The DC conductivity is proportional to σ_1 which obeys the following self consistent equation,

$$1 = \int \frac{g(\epsilon)\, W(R,\epsilon)\, d^3R\, d\epsilon}{\sigma_1 + W(R,\epsilon)} \quad , \tag{5.24}$$

where $W(R,\epsilon) = exp(\frac{R}{a} + \frac{\epsilon}{K_B T})$ are the symmetric transition rates in the units of phonon frequency ν_0. The merit of the approximation is that it incorporates the percolation considerations. The temperature variation of conductivity obeys the Mott's $T^{1/4}$-law [13] if $g(\epsilon)$ is finite and slowly varying at the Fermi level and Efros-Shklovskii's $T^{1/2}$-law [17] if $g(\epsilon) \propto \epsilon^2$.

We now assume that the above formula can also give the conductivity in the non-equilibrium situation. The plausible justification is that the relaxation of the DOS is slower than the time scale over which the steady states of current are achieved. Then one

has a succession of slowly evolving steady states and the time-dependence of conductivity is due to time-dependent DOS, $g(\epsilon, t)$. The equation (5.24) can now be rewritten using the time dependent DOS $g(\epsilon, t)$ as

$$1 = \int \frac{g\,(\epsilon, t)\, W\,(R, \epsilon)\, d^3R\; d\epsilon}{\sigma_1 + W\,(R, \epsilon)} \quad , \tag{5.25}$$

With time $g(\epsilon, t)$ changes from a constant value g_o to one proportional to ϵ^2, so we should see a crossover from Mott's law to ES law in conductivity. We show the solution for σ_1 in fig. 5.1 as function of time. The time axis is taken to be $\Delta/E_c(t)$ which is proportional to $\ln(\nu_o t)$. The main features of this plot can be understood in a simple manner as the solution for equation (5.25) can be phrased in terms of the percolation criterion for hopping conduction due to Ambegaokar et. al. [28]. When $R_c = -ln(\sigma_1/\nu_o)$ is less than $E_c(t)$, it is seen that $R_c \approx \left(\frac{1}{g_\mu r_{av}^3 k_B T}\right)^{1/4}$. Since $g_\mu \propto E_c(t)^2$, $R_c \propto (1/E_c(t))^{1/2}$, the conductivity decreases as time increases. As R_c becomes greater than $E_c(t)$, the conductivity starts to deviate from Mott's law. When $R_c >> E_c(t)$ then $R_c \approx (e^2/\kappa r_{av} k_B T)^{1/2}$ which is a constant and so is the conductivity.

These considerations do not take account of other features of the nonequilibrium conditions prevailing in the experiments. For example, if the addition (depletion) of charge is not homogeneous, there would be an additional diffusive component to the current. Similarly the assumption that the added electrons occupy the lowest available Hartree levels may not be true in the initial stages of the relaxation.

Conclusions

To summarize, we have obtained some significant features of the time devolpment of the Coulomb gap in Coulomb glass, when the system is put into a nonequilibrium state by an abrupt change of the electron density. In particular, we have shown that the density of states at the Fermi level goes to zero accordingly to $1/[ln(\nu_o t)]^2$. The consequences for the relaxation of conductivity are also discussed.

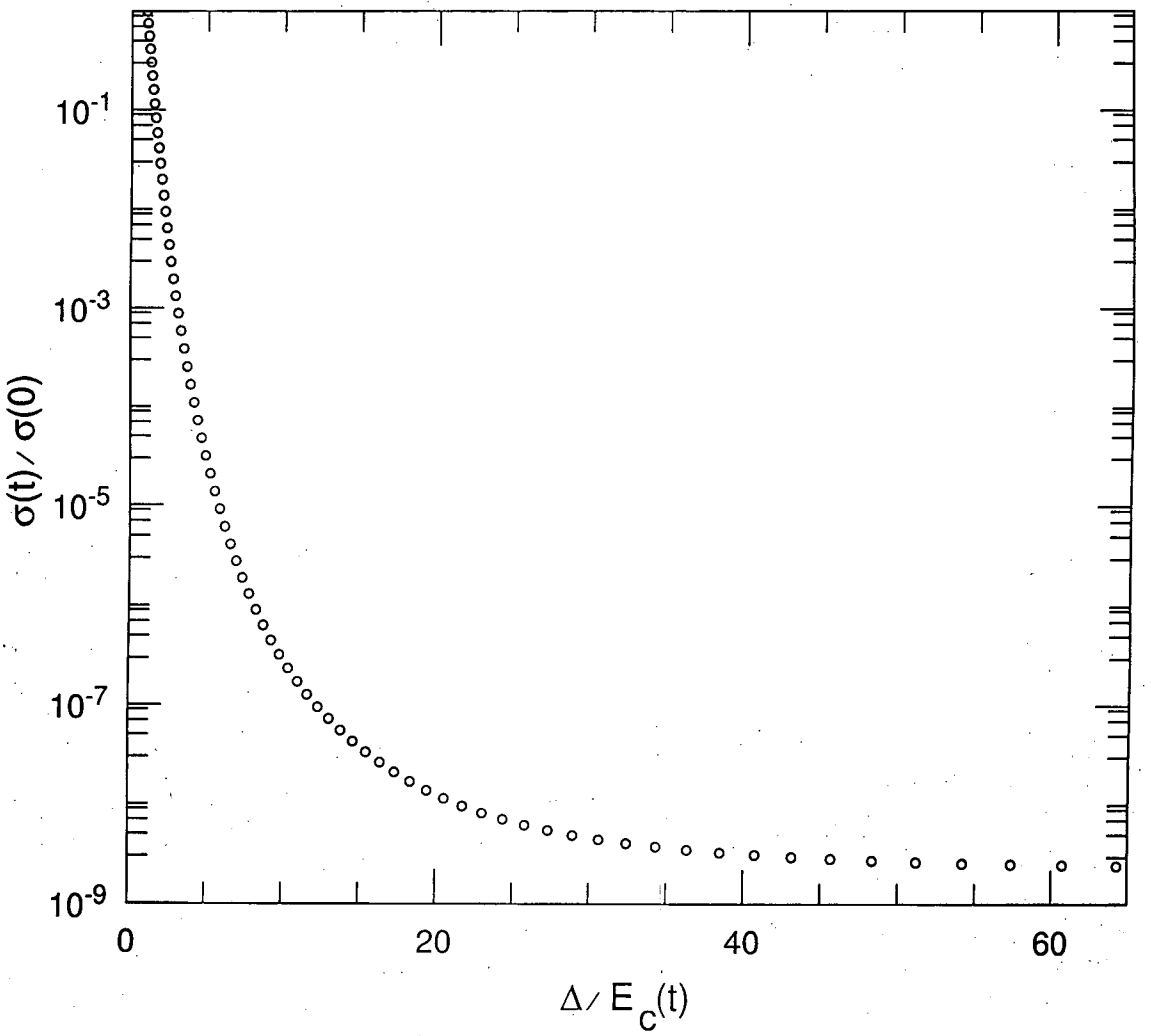

Figure 5.1: Plot of $\sigma_1(t)/\sigma_1(0)$ with $\Delta/E_c(t)$, according to equation (5.25) and the time-dependent density of states given in equation (5.14). $\Delta/E_c(t)$ is proportional to $ln(\nu_o t)$. $\sigma_1(0)$ is calculated with $E_c(0) = \Delta = 300k_BT$, $\sigma_1(0) = 8.11e-5$.