# Time-Dependent Development of the Coulomb Gap

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(Received 14 December 1998)

We show that the time development of the Coulomb gap in a Coulomb glass can involve very long relaxation times due to electron rearrangement and hopping. We find that an applied magnetic field reduces the rate of electron hopping and, hence, Coulomb gap formation. These results are consistent with recent conductance experiments on thin semiconducting and metallic films. [S0031-9007(99)09201-7]

PACS numbers: 73.50.–h, 71.23.An, 71.23.Cq, 72.20.My

The competition between interactions and disorder results in glassy dynamics that are often associated with very long relaxation times extending over many decades. One might not expect the same to be true in an electronic system since electrons typically respond very quickly. However, in this paper we show that in the presence of strong disorder, electrons can indeed have very long relaxation times. This occurs in a Coulomb glass which is an insulator with randomly placed electrons that have Coulomb interactions. Heavily doped semiconductors and disordered metals are examples of such systems. Coulomb interactions between localized electrons result in a so-called Coulomb gap in the single particle density of states that is centered at the Fermi energy [1–3]. We have done a calculation in which we follow the time development of the Coulomb gap. In order to produce this gap, electron rearrangement must occur and the associated hopping can involve very long time scales.

These long relaxation times are consistent with recent experiments on thin semiconducting [4,5] and metallic [6] films which have shown that in the presence of strong disorder, electronic systems can relax very slowly. These films were grown on insulating substrates which separated them from a gate electrode that regulated the electron density, and hence the chemical potential, of the film. The conductance $G$ was measured as a function of the gate voltage $V_G$. If $V_G$ sat at a particular value, $V_0$, for a long time and then was varied over a range of voltages, there was a dip in the conductance centered at $V_0$ [7]. We identify this dip with the Coulomb gap in the density of states because the value of the conductance depends on the density of states at the Fermi energy [5,8]. In Mott's picture of variable range hopping, the hopping conductivity increases when the density of states at the Fermi energy increases, since there are then more states to which an electron at the Fermi energy can hop [3]. We identify sweeping $V_G$ by varying the chemical potential without allowing time for equilibration. In effect the sweeps scan the density of states. Thus we expect the conductance to increase with the density of states and hence as the gate voltage $V_G$ moves away from $V_0$.

In the experiments, if the gate voltage was changed suddenly from, say, $V_0$ to $V_1$, the conductance had a very fast initial rise, followed by a period of rapid relaxation, which in turn was followed by a long period of very slow relaxation. In some cases the relaxation was logarithmic in time. Our interpretation of this is that when the gate voltage is changed, the Fermi energy changes, and time-dependent relaxations arise because the system must dig a new hole in the density of states at the new Fermi energy and remove the old hole at the old Fermi energy. Indeed, Vaknin, Ovadyahu, and Pollak [5] found that subsequent sweeps of the gate voltage revealed that the old dip in the conductance at $V_0$ fades with time while a new dip centered at $V_1$ increased with time. The dip in the conductance and the long time relaxation were present only at very low temperatures, not at higher temperatures ($T \gtrsim 20$ K).

Ovadyahu and Pollak [4] also found that in a magnetic field ($H = 9$ T) the long time relaxation rate associated with a change in the gate voltage was even slower. In addition to the spin mechanism that they propose [4], this result is consistent with the fact that the magnetic field reduces the spatial extent of the electron wave functions in the directions transverse to the field. This reduces the wave function overlap of neighboring electrons, resulting in a decrease of the electron hopping rate and hence a decrease in the rate at which a Coulomb gap forms. This is confirmed by our calculations.

Our model of the Coulomb glass follows that of Baranovskiĭ, Shklovskiĭ, and Éfros (BSE) [9]. In this model, the electrons occupy the sites of a periodic lattice, and the number of electrons is half the number of sites. Each site has a random on site energy $\phi_i$ chosen from a uniform distribution extending from $-A$ to $A$. Thus, $g_0$, the density of states without interactions, is flat. A site can contain zero or one electron. In order to follow the time development of the Coulomb gap, we assume that the Coulomb interactions are turned on at time $t = 0$. The Hamiltonian can be written as

$$H = \sum_i \phi_i n_i + \sum_{i>j} \frac{e^2}{\kappa r_{ij}} n_i n_j \theta(t), \qquad (1)$$

where the occupation number $n_i$ equals $\frac{1}{2}$ if site $i$ is

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occupied and $-\frac{1}{2}$ if site $i$ is unoccupied, $e$ is the electron charge, $\kappa$ is the dielectric constant, and the step function $\theta(t)$ is 0 for $t < 0$ and 1 for $t \geq 0$.

The Coulomb gap arises because the stability of the ground state with respect to single electron hopping from an occupied site $i$ to an unoccupied site $j$ requires [3]

$$\Delta_i^j = \varepsilon_j - \varepsilon_i - \frac{e^2}{\kappa r_{ij}} > 0\,, \tag{2}$$

where the single-site energy $\varepsilon_i = \phi_i + \sum_j \frac{e^2}{\kappa r_{ij}} n_j$. So we need to subtract from the density of states those states which violate this stability condition. This leads to [9,10]

$$g(\varepsilon,t) = g_0 \prod_{j>i} \left[ 1 - a_0^3 \int_{-A}^{A} d\varepsilon'\, g(\varepsilon',t)\theta\left(\frac{e^2}{\kappa r_{ij}} + \varepsilon - \varepsilon'\right) F(n_i' = 1, n_j' = 0)\theta\big(t - \tau_{ij}(\varepsilon',\varepsilon,r_{ij})\big) \right], \tag{3}$$

where the single-site energy $\varepsilon_i = \varepsilon$, $\varepsilon_j = \varepsilon'$, and $a_0$ is the lattice constant. $n_i' = n_i + 1/2$; so $n_i' = 1$ if site $i$ is occupied and 0 if site $i$ is unoccupied. $F(n_i', n_j')$ is the probability that donors $i$ and $j$ have occupation numbers $n_i'$ and $n_j'$, respectively, while all other sites have their ground state occupation numbers $\tilde{n}_k'$. $\tau_{ij}^{-1}$ is the number of electrons which jump from site $i$ to site $j$ per unit time. $\theta(t - \tau_{ij})$ represents the fact that at time $t$, the primary contributions to the change in the density of states will be from those hops for which $\tau_{ij} < t$ [11]. In writing Eq. (3), we assume that these hops together with phonons have equilibrated the system as much as is possible at time $t$. The hopping rate $\tau_{ij}^{-1}$ is given by [3]

$$\tau_{ij}^{-1} = \gamma_{ij}^{o} \exp\left(-\frac{2r_{ij}}{a}\right)[1 + N(\Delta_i^j)]F(n_i' = 1, n_j' = 0)\,, \tag{4}$$

where $a = \kappa a_B$ is the effective Bohr radius of a donor, and $a_B$ is the usual Bohr radius ($a_B = \hbar^2/me^2$). We will set the mass $m$ equal to the electron mass so that $a_B = 0.529$ Å. $N(\Delta_i^j)$ is the phonon occupation factor and reflects the contribution of phonon assisted hopping. We are also allowing for spontaneous emission of phonons since we are considering a nonequilibrium situation in which electrons hop in order to lower their energy. The coefficient $\gamma_{ij}^{o}$ is given by [3]

$$\gamma_{ij}^{o} = \frac{E_1^2 |\Delta_i^j|}{\pi d s^5 \hbar^4} \left[\frac{2e^2}{3\kappa a}\right]^2 \frac{r_{ij}^2}{a^2} \left[1 + \left(\frac{\Delta_i^j a}{2\hbar s}\right)^2\right]^{-4}\,, \tag{5}$$

where $E_1$ is the deformation potential, $s$ is the speed of sound, and $d$ is the mass density. Following BSE, we can derive a self-consistent equation for the density of states $g(\varepsilon,t)$,

$$g(\varepsilon,t) = g_0 \exp\left[ -\frac{1}{2} \int_{-A}^{A} d\varepsilon'\, g(\varepsilon',t) \int_{a_0}^{\infty} dr\, 4\pi r^2 F\big(n(\varepsilon) = 1, n(\varepsilon') = 0\big)\theta\left(\frac{e^2}{\kappa r} + \varepsilon - \varepsilon'\right)\theta\big(t - \tau(\varepsilon',\varepsilon,r)\big) \right]. \tag{6}$$

At low energies large distances play an important role and so we have replaced the sum by an integral over $r$ in the exponent. The origin is at site $i$. $n(\varepsilon)$ is the occupation probability of a site with energy $\varepsilon$. $\tau(\varepsilon',\varepsilon,r)$ is given by (4) with $r_{ij}$ replaced by $r$, $\varepsilon_i$ replaced by $\varepsilon$, and $\varepsilon_j$ replaced by $\varepsilon'$.

Since it is not clear how the stability condition of Eq. (2) can be applied to finite temperatures, we will confine our calculations to the case of $T = 0$. In this case the phonon occupation factor $N(\Delta_i^j) = 0$ and the electron occupation factor $F(n_i = 1, n_j = 0) = 1$, if $\varepsilon_i < 0$ and $\varepsilon_j > 0$. Otherwise $F(n_i = 1, n_j = 0) = 0$. We set the Fermi energy $\mu = 0$. We can solve Eq. (6) iteratively on the computer. For the first iteration we start with $g(\varepsilon',t) = g_0$ and calculate $g(\varepsilon,t)$. This is then used as the input for $g(\varepsilon',t)$ in the next iteration. Because successive iterations converge by alternating above and below the correct answer with decreasing amplitude, after the first two iterations we use the average of the input and output of a given iteration as the input for the next iteration. After 11 iterations the typical difference between successive iterations is typically less than 1 part in $10^5$. Because there is particle-hole symmetry, we only need to calculate $g(\varepsilon,t)$ for $\varepsilon < 0$. Figure 1a shows the density of states $g(\varepsilon,t)$ as a function of energy at different times, while Fig. 1b shows $g(\varepsilon,t)$ as a function of time at different energies. Notice the development of the Coulomb gap occurs over many decades in time. The functional form of the time dependence of $g(\varepsilon,t)$ varies with the energy $\varepsilon$ and with $g_0$. For example, at the Fermi energy $g(\mu,t) \sim \ln t$ for $g_0 = 2 \times 10^5$ states/K Å$^3$ and $g(\mu,t) \sim t^{-0.05}$ for $g_0 = 6.25 \times 10^5$ states/K Å$^3$. After an infinite amount of time, the density of states at the Fermi energy $\mu$ goes to zero and $g(\varepsilon) \sim \varepsilon^2$. For finite times, $g(\varepsilon) \sim |\varepsilon|$ in the vicinity of the Fermi energy, though there will be thermal smearing at finite temperatures. For different values of the initial density of states $g_0$, we find the same qualitative behavior as a function of time with the depth of the dip $g_0 - g(\mu,t)$ increasing as $g_0$ increases. Figure 2 shows that the width $W$ of the dip increases with $g_0$. Experimentally the width $W$ increases with the carrier concentration $n$ [5]. This is consistent with our results since the noninteracting density of states $g_0$ increases with $n$, though other parameters such as $\kappa$ may also depend on $n$. The range of widths in Fig. 2 is comparable to that deduced from experiment [5].

The temporal development of the Coulomb gap is qualitatively consistent with the experimental observation of the long time relaxation of the conductance after the

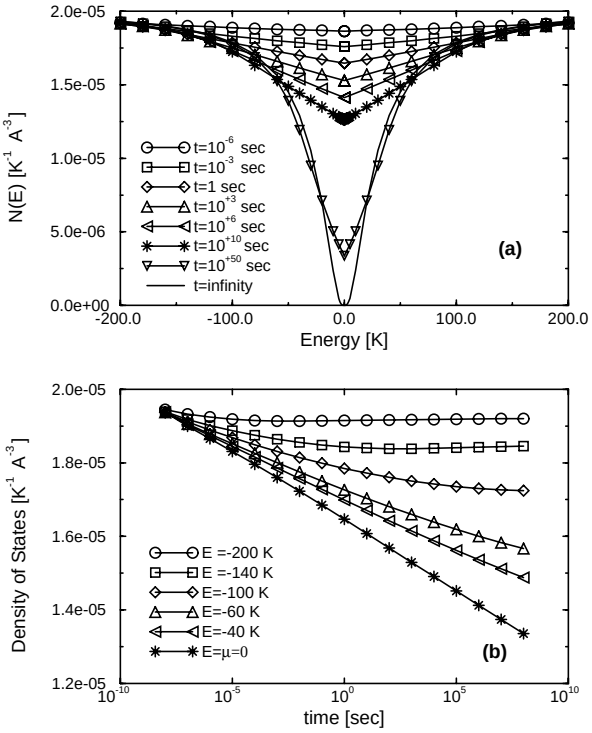


FIG. 1. (a) Density of states $g(\varepsilon)$ as a function of energy for different times. (b) Density of states as a function of time for various energies. Parameters used are $g_0 = 2 \times 10^5$ states/K Å$^3$, $T = 0$, $A = 10^4$ K, $\kappa = 10$, $d = 7.18$ g/cm$^3$, $s = 5.0 \times 10^5$ cm/sec, $E_1 = 5 \times 10^3$ K, and $a_0 = 4$ Å. The density $d$ is chosen to be that of $In_2O_3$. The energy is measured from the Fermi energy $\mu = 0$.

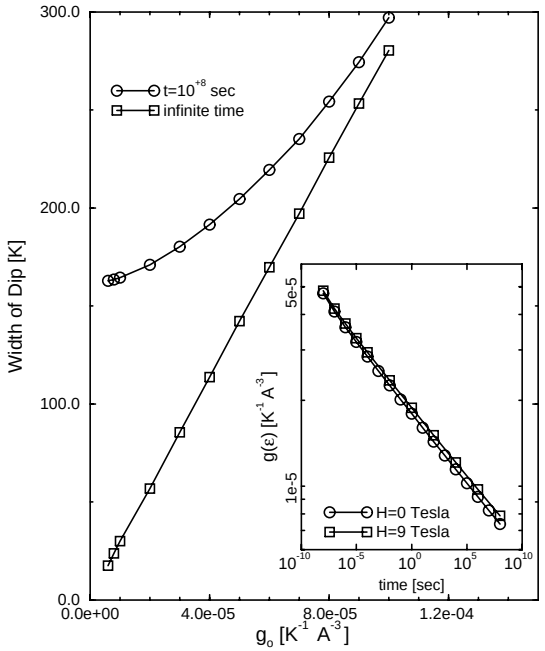


FIG. 2. Width of the Coulomb gap as a function of $g_0$ at $t = 10^{+8}$ sec and at infinite time. The width is measured at halfway between the minimum $g(\mu)$ and the maximum $g_0$ in the density of states. Inset: Density of states $g(\varepsilon)$ as a function of time for different values of the magnetic field $H$. For both curves the energy $\varepsilon = \mu$ and $g_0 = 6.25 \times 10^{-5}$ states/K Å$^3$. The rest of the parameters are the same as in Fig. 1 for both the inset and the main figure.

gate voltage $V_G$ has been changed. The exact relation between the conductance and the density of states is difficult to ascertain in this case because the system is not in equilibrium. However, it is reasonable to assume that the conductance reflects the density of states at the Fermi energy. A well-known example is Mott's formula for conductivity $\sigma$ due to variable range hopping [3].

$$\sigma = \sigma_o \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right], \tag{7}$$

where $T_0 = \alpha/[k_B g(\mu) a^3]$, $\alpha$ is a numerical constant, and $g(\mu)$ is the density of states at the Fermi energy. While strictly speaking this equilibrium formula does not apply to our nonequilibrium situation, we see qualitatively that an increase (decrease) in $g(\mu)$ leads to an increase (decrease) in the conductivity. In the experiments, rapidly sweeping the gate voltage $V_G$ varies the chemical potential without allowing time for equilibration. Relating the conductance to the density of states means that the sweeps over $V_G$ scan the density of states. To get a qualitative feel for this connection, we will use Eq. (7). We identify $g(\mu)$ with $g(\varepsilon)$ and use $T_0 = \alpha/[k_B g(\varepsilon) a^3]$. For most of the scan the density of states has the linear form $g(\varepsilon) = g(\varepsilon_0) + \alpha(\varepsilon - \varepsilon_0)$ where $\varepsilon_0$ and the slope $\alpha$ are constants. The exponent of $1/4$ is appropriate for this case. The experiments on indium oxide [4] were done at 4.11 K, so we set $T = 4$ K and use the $g(\varepsilon)$ shown in Fig. 1. The result is shown in Fig. 3.

Ovadyahu and Pollak noticed that when a magnetic field is applied to their indium oxide films, the relaxation rate decreases and the magnetoresistance is positive [4]. They attributed this to a reduced hopping rate resulting from the fact that a polarized spin cannot hop onto a site that is already occupied. Our scenario suggests an additional mechanism since the magnetic field reduces the wave function overlap in the direction transverse to the field. The reduced overlap means a lower hopping rate and a longer relaxation time. Shklovskiĭ and Éfros [12–14] studied the effect of a magnetic field on variable range hopping. Since the average hopping distance far exceeds the mean distance $R$ between impurities, the hopping electron scatters from many other donor sites. As a result, when the magnetic field is transverse to the direction of tunneling, the wave function decays as $\exp(-\rho/b)$. Here we have adopted cylindrical coordinates with the magnetic field along the $z$ axis and $\rho$ is the radial coordinate transverse to the $z$ axis. The parameter $b = \lambda/|\ln A|$ where the magnetic length $\lambda = \sqrt{c\hbar/eH}$, and $A$ describes the scattering and depends on the magnetic field $H$. For all values of $H$, Shklovskiĭ [14] has shown that $b$, and hence the wave function overlap, decreases as the magnetic field increases. The functional form of $A$ depends on the strength of the field. In the indium oxide experiments [4] $H = 9$ T. Since this is in a weak field regime

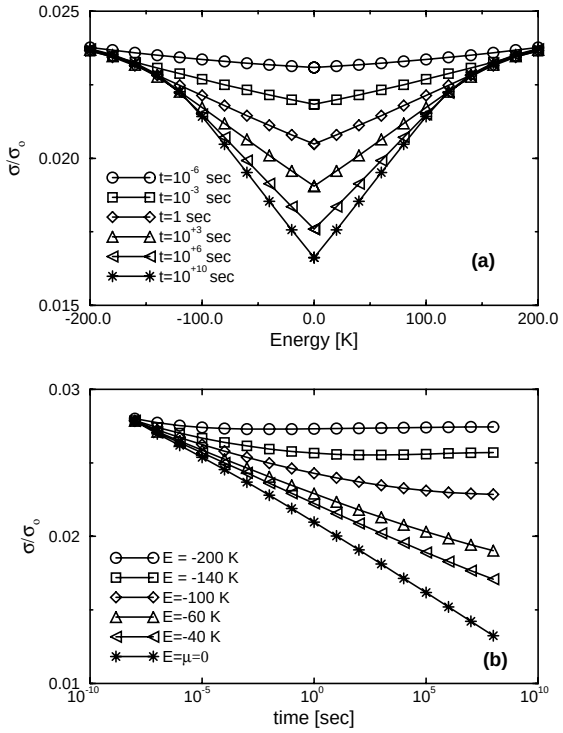


FIG. 3. (a) Dimensionless conductivity $\sigma/\sigma_0$ as a function of energy for different times. (b) Dimensionless conductivity $\sigma/\sigma_0$ as a function of time for various energies. The conductivity of both (a) and (b) are calculated using Mott's formula (7) with $T = 4$ K, $a = 5.29177$ Å, and $\alpha = 2.23$. The rest of the parameters are the same as in Fig. 1.

where $\lambda \gg a$ and $R \ll \lambda^2/a$, we can make the approximation $b \approx a[1 - (a/\lambda)^{4/3}]$ where $a$ is the effective Bohr radius. For a weak field we expect the hopping rate to go as $\tau_{ij}^{-1} \sim \gamma_{ij}^{o} \exp[-2r_{ij}/f(z/\rho_{ij})]$ where the function $f(0) \equiv b$ and $f(\infty) \equiv a$. It is difficult to make a quantitative comparison to the density of states at $H = 0$ since we do not know the prefactor $\gamma_{ij}^{o}$. To get a qualitative feel for the effect of the magnetic field, we can use the $H = 0$ form of $\gamma_{ij}^{o}$ found in Eq. (5), and in Eq. (4) for $\tau_{ij}^{-1}$, we replace $\exp(-2r_{ij}/a)$ with $\exp(-2r_{ij}/b)$. This is a reasonably good approximation since for a field of 9 T and a dielectric constant of 10, $a = 5.29$ and $b = 5.162$ Å. The $T = 0$ result for the density of states at $H = 0$ and $H = 9$ T is shown in the inset of Fig. 2. Both curves start at the same value of $g(\varepsilon = \mu) = g_0$ at time $t = 0$. Notice that the curve at 9 T is slightly above the zero field curve indicating that the relaxation is slower in a magnetic field. This is qualitatively consistent with experiment [4]. To differentiate between our mechanism and spin effects, note that our mechanism predicts that the magnetoresistance is greater when the field is perpendicular to the current than when it is parallel, whereas the magnetoresistance should be isotropic in the field if spin effects dominate.

The experiments found that the dip in the conductance as a function of gate voltage $V_G$ and the long relaxation times of the conductance following a change in $V_G$ were present only at low temperature. These features were not observed at $T \gtrsim 20$ K. From Eqs. (3) and (4), we see that an increase in temperature will affect $g(\varepsilon, t)$ in two ways. First, the thermal smearing of the occupation factor $F(n_i', n_j')$ will fill in the Coulomb gap to some extent. Second, as the number of phonons increases with temperature, there is an increase in the phonon assisted hopping of electrons. We expect that this leads to a rapid rearrangement of electrons on time scales that are too short to observe experimentally. As a result, no dips in the conductance and no long time relaxation were seen experimentally at higher temperatures. It is difficult to calculate these effects because it is not clear how to generalize the stability condition (2) to finite temperatures. In addition the system is not in equilibrium and hence temperature is not well defined for the electrons. However the absence of the conductance dips at higher temperatures is consistent with our scenario.

To summarize, we have shown that the time development of the Coulomb gap in a Coulomb glass can involve very long time scales due to electron hopping and rearrangement. These results are consistent with conductance experiments on disordered semiconducting and metallic films. Although we have only considered single electron hops, these hops are dependent upon previous hops of other electrons through their cumulative effect on the single particle density of states. We expect multielectron processes to also contribute to the conductance, particularly at long time scales.

I would like to thank Hervé Carruzzo for helpful discussions. This work was supported in part by ONR Grant No. N00014-96-1-0905 and by funds provided by the University of California for the conduct of discretionary research by Los Alamos National Laboratory.

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