Final Report on DE-FG03-00ER45843: Coulomb Glasses

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Abstract

This is a final report on DE-FG03-00ER45843 entitled “Coulomb Glasses.” The work is continuing under grant DE-FG02-04ER46107 under the DOE Chicago Operations office. During the award period from August 15, 2000 to December 31, 2003, we studied the following:

- 1/f Noise in Coulomb Glasses
- Coulomb glass phase transitions as a function of positional disorder
- A new structural probe of the structural glass transition
- Frequency dependence and equilibration of the specific heat of glass forming liquids
1 Introduction to Electron and Coulomb Glasses

An electron glass is an amorphous insulator with randomly placed electrons. One example of this is a disordered metal. Another example is a doped semiconductor in which the donor and acceptor sites have random positions. In these systems the electrons see a random potential and are localized. We can model this situation with randomly placed sites that have random on-site energies. Electrons sit on some fraction of these sites. If they interact with one another via long range Coulomb interactions, then we have a special case of an electron glass known as a Coulomb glass.

The Coulomb interactions between localized electrons result in a Coulomb gap in the single particle density of states that is centered at the Fermi energy. The Coulomb gap makes the ground state stable with respect to single electron hops [1, 2, 3]. To understand why there is a gap, think of a spin glass analogy [4] where an occupied site corresponds to a site with spin up and an unoccupied site corresponds to a site with spin down. Let \( P(h) \) be the distribution of local fields \( h \). If \( P(h = 0) \neq 0 \), then the spins with \( h = 0 \) can flip easily, which causes other spins to flip and a proliferation of spin flips occurs. So stability of the ground state requires \( P(h = 0) = 0 \). Efros and Shklovskii [2, 3] gave a more formal argument in which they showed that the gap vanishes as \((E - E_F)^2\) in 3 dimensions and as \(|E - E_F|\) in 2 dimensions, where \( E_F \) is the Fermi energy.

Electron and Coulomb glasses are technologically important because they comprise the components of electronic devices in the form of disordered metals, doped semiconductors, and tunnel junctions. We have been studying how slow electron hopping in a Coulomb glass is manifested in low frequency noise and aging [5, 6, 7, 8, 9]. These features can have a deleterious impact on the performance of electronic devices.

2 1/f Noise in Electron and Coulomb Glasses

To an experimenter, noise is a nuisance at best and a serious problem hindering measurements at worst. However noise comes from the fluctuations of microscopic entities and it can act as a probe of what is happening physically at the microscopic scale. Let us set up our notation and define what we mean by noise. Let \( \delta x(t) \) be a fluctuation in some quantity \( x \) at time \( t \). If the processes producing the fluctuations are stationary in time, i.e., translationally invariant in time, then the autocorrelation function of the fluctuations \( \langle \delta x(t_2)\delta x(t_1) \rangle \) will be a function \( \psi(t_2 - t_1) \) of the time difference. In this case the Wiener–Khintchine theorem can be used to relate the noise spectral density \( S_x(\omega) \) to the Fourier transform \( \psi(\omega) \) of the autocorrelation function [10]: \( S_x(\omega) = 2\psi(\omega) \) where \( \omega \) is the angular frequency. 1/f noise, which is ubiquitous and dominates at low frequencies, corresponds to \( S_x(\omega) \sim 1/\omega \).

Low frequency 1/f noise [10, 11, 12] is found in a wide variety of conducting systems such as metals, semiconductors, tunnel junctions [13], and even superconducting SQUIDs [14, 15]. Yet the microscopic mechanisms are still not well understood. In some cases the electrons are in a strongly disordered potential and form an electron glass or a Coulomb
glass. Experimental studies on doped silicon inversion layers have shown that low frequency $1/f$ noise is produced by hopping conduction [16]. Because the systems are glassy, electron hopping can occur on very long time scales which can produce low frequency noise. In the current award period we showed that the resulting noise spectrum goes as $f^{-\alpha}$ where $f$ is frequency and the temperature dependent exponent $\alpha > 1$ [9].

Sliolkovski had suggested that $1/f$ noise is caused by fluctuations in the number of electrons in an infinite percolating cluster [17]. These fluctuations are caused by the slow exchange of electrons between the infinite conducting cluster and small isolated donor clusters. Subsequently Kogan and Shklovskii combined a more rigorous calculation with numerical simulations and found a noise spectrum where $\alpha$ was considerably lower than 1 [18]. Furthermore, below a minimum frequency of order 1–100 Hz, the noise spectral density saturated and became a constant independent of frequency. Their calculations were valid only in the high temperature regime where the impurity band was assumed to be occupied uniformly and long-range Coulomb correlations were essentially neglected. Since then there have been attempts to include the effects of correlations.

In particular, Kozub suggested a model [19] in which electron hops within isolated pairs of impurities produce fluctuations in the potential seen by other hopping electrons that contribute to the current. While leading to $1/f$-type noise within some frequency range, this model also shows low frequency noise saturation due to the exponentially small probability of finding an isolated pair of sites with a long tunneling time. Moreover, the model magnitude is predicted to increase as the temperature $T \to 0$ in contradiction with the recent experimental findings of Massey and Lee [20]. This, in part, led Massey and Lee to the conclusion that the single particle picture is inconsistent with the observed noise behavior. Later work by Shklovskii [21] also found the noise increasing with decreasing temperature in agreement with some experiments [22] but not with the experiments of Massey and Lee [20]. A different approach was proposed by Kogan [23] who considered intervalley transitions as the source of the hopping conduction noise. Unfortunately this approach does not seem to be analytically tractable and is not easily generalizable.

We extended Kogan and Shklovskii's approach [18] by including the energy dependence of the hopping as well as the effects of electron-electron interactions on the single particle density of states $g(e)$. This is essentially a mean field approximation: we assume that charge is carried by electron-like quasiparticles whose interaction with the other charges is taken into account via the single particle density of states. For comparison we also considered the case of noninteracting electrons with a flat density of states.

We showed that $1/f$ noise is produced in a 3D electron glass by charge fluctuations due to electrons hopping between isolated sites and a percolating network at low temperatures. Unlike some of the work mentioned above, our noise spectra did not saturate at low frequencies that are experimentally accessible. The low frequency noise spectrum goes as $\omega^{-\alpha}$ with $\alpha$ slightly larger than 1. With increasing temperature $\alpha$ decreased slightly and then flattened off. The noise amplitude at a fixed frequency is constant at high temperatures but decreases with decreasing temperature. This behavior is due to the presence of activated electron hopping processes which decrease with decreasing temperature. All these results are in good agreement with the recent experiments by Massey and Lee [20]. These results hold true both with a flat, noninteracting density of states and with a density of states that
includes Coulomb interactions. In the latter case, we modeled the density of states with a Coulomb gap that fills in with increasing temperature. For a large Coulomb gap width, this density of states gives a dc conductivity with a hopping exponent \( \delta \approx 0.75 \) which has been observed in recent experiments [24, 25, 26, 27, 28] but never explained [29]. For a small Coulomb gap width, the hopping exponent \( \delta \approx 0.5 \). (The hopping exponent \( \delta \) is defined by \( \sigma(T) = \sigma_0 \exp \left[ -\left( T_0/T \right)^\delta \right] \) where \( \sigma \) is the conductivity, \( T \) is temperature, and \( T_0 \) and \( \sigma_0 \) are constants.)

3 Coulomb Glass Phase Transitions as a Function of Disorder

If you cool a system of interacting electrons hopping between randomly placed sites, it will eventually freeze and become a Coulomb glass. In our first paper on this subject we were able to clearly characterize the nature of the Coulomb glass transition for the first time [30]. It had long been presumed that classically a Coulomb glass undergoes a phase transition analogous to the spin-glass transition [31, 32]. However, the nature of the transition had not been determined, and in fact, there had been no direct demonstration of a finite temperature phase transition.

We did Monte Carlo simulations on three dimensional systems in which half of the sites were occupied by electrons. During each Monte Carlo step, each electron was given the opportunity to hop to a different site with Boltzmann probability. Our results demonstrated, for the first time, that a classical three dimensional Coulomb glass undergoes a finite temperature phase transition in which the positions of the electrons freeze [30]. Using finite size scaling [33], we determined the critical exponents and the transition temperature. We found that the phase transition occurs at a temperature which is an order of magnitude lower than the characteristic interaction energy. We attributed this suppression to the pairing of nearby sites into weakly interacting effective dipoles. In other words, two nearby sites will most likely have one site occupied and the other unoccupied, resulting in an electric dipole. The closer the two sites are, the smaller their dipole moment. These small dipole moments will interact weakly with the rest of the system and will be able to remain active down to temperatures much lower than the bare Coulomb interaction energy.

We also monitored the formation of the Coulomb gap in the single particle density of states as the temperature is lowered. We found that the density of states \( N(\varepsilon) \) at the Fermi energy begins to decrease when the temperature is comparable to the interaction energy. This is an order of magnitude higher than the transition temperature. At temperatures just above \( T_c \), the Coulomb gap is nearly fully formed, and \( N(\varepsilon) \) is more than a factor of 50 smaller than at high temperatures. The temperature dependence of the Coulomb gap agrees qualitatively with capacitance [34] and conductance experiments [35], and should be directly measurable in tunneling experiments.

During the award period we extended this work to study the effect of systematically introducing quenched disorder on a second order crystallization transition. If there is no quenched disorder, a system of electrons with Coulomb interactions in a translationally invariant system will undergo a first order phase transition into a Wigner crystal as the
temperature is lowered [36]. However, if we start with a translationally discrete system, this transition becomes second order. In particular, if we have a cubic lattice of sites with half the sites occupied by electrons, the electrons will undergo a second order crystallization transition in which they are arranged in an face-centered cubic (FCC) configuration as the temperature is lowered. (Sitting on every other site of a cubic lattice results in an FCC configuration.) On the other hand, as we have just discussed, we have shown that when there is off-diagonal quenched disorder, there is a second order phase transition into a Coulomb glass [30].

We have now studied what happens between these two transitions by gradually introducing disorder. We used Monte Carlo simulations to study a half-filled Coulomb system where the disorder comes from the placement of the sites that the electrons can occupy. We chose half-filling in order to take advantage of the particle-hole symmetry which allows us to map the problem onto an Ising spin glass with randomly placed spins that interact with a 1/r potential. An up-spin corresponds to an occupied site, and a down-spin corresponds to an unoccupied site. We used an Ewald sum [37] to determine the long range interaction between sites. First we considered the ordered case where the sites form a cubic lattice. In the ground state the electrons sit on every other site and form a face centered cubic lattice. We confirmed that the ordered case was a second order transition by looking at the staggered magnetization distribution and confirming the absence of phase coexistence at the transition temperature. Then we randomized the placement of the sites by giving a width to the distribution of places where a site can sit in a unit cell. We regulated the amount of disorder by changing the width of the distribution.

For a given amount of disorder, we monitored the second order phase transition as a function of temperature using finite size scaling techniques [33]. This involves calculating the Edwards-Anderson order parameter g which measures to what extent the spins have frozen and have stopped flipping. A good measure of the transition is Binder’s dimensionless parameter \( g = \frac{1}{3}(3 - \langle \sigma^4 \rangle \langle \sigma^2 \rangle^2) \), where \( \langle ... \rangle \) denotes a time (thermal) average. At high temperatures the distribution of \( g \) is Gaussian and \( g \) tends to zero, whereas at low temperatures \( g \) becomes nonzero. At \( T_c \), \( g \) has the same value independent of system size, which means that the curves for \( g \) versus \( T \) for different system sizes cross at \( T_c \). This allowed us to determine \( T_c \).

From scaling the size dependence of these quantities, we deduced the critical exponent \( \nu \). We found that \( \nu \) increased with disorder from \( \nu \approx 0.55 \) in the ordered case to \( \nu \approx 1.3 \) in the fully disordered case. At the same time the transition temperature \( T_c \) decreased by more than a factor of 4 in going from the ordered case to the fully disordered case. We calculated the specific heat and watched how it changed with disorder. In the crystal, the specific heat is a sharp peak while in the strongly disorder Coulomb glass it is a broad bump.

We also monitored how the Coulomb gap changes with disorder. The Coulomb gap corresponds to the local magnetic field distribution in a spin glass. In our previous work [30] we saw that in the strongly disordered case, the dip in the density of states deepens with decreasing temperature and forms the Coulomb gap. In the Wigner crystal, the local field distribution consists of 2 delta functions, one on either side of the Fermi energy. One delta function corresponds to the fact that each occupied site is identical to all the other occupied sites and the other delta function corresponds to the unoccupied sites. So in the crystal, there is a “hard hole” in the sense that there finite energy range centered at the
Fermi energy where the density of states is zero. We monitored how this hole filled in as the delta functions broadened with the gradual introduction of disorder. We also found that the minimum in the density of states increases monotonically with temperature in a way that cannot be described by a simple power law as is sometimes quoted in the literature [38, 39, 40]. A paper describing our results has been accepted for publication in Physical Review B.

4 New Structural Probe of the Glass Transition

The glass transition is still not well understood despite extensive study. Experimentally the glass transition occurs when the relaxation time exceeds the measurement time and particle motion appears to be arrested. There have been two main theoretical approaches to the glass transition: dynamic and thermodynamic. Theories in the first category view the glass transition as a kinetic phenomenon characterized by a growing relaxation time and viscosity [41, 42, 43, 44, 45]. When the relaxation time exceeds the measurement time, particle motion appears to be arrested resulting in the glass transition. One of the most prominent theories espousing this view is the mode coupling theory (MCT) in which ideally the relaxation time diverges at a temperature $T_C$ above the experimental glass transition temperature [43]. The thermodynamic viewpoint attributes the glass transition to an underlying phase transition hidden from direct experimental observation by extremely long relaxation times [41, 42, 46, 47, 48]. In most scenarios there is an underlying second order phase transition associated with a growing correlation length which produces diverging relaxation times as well as diverging static susceptibilities [49, 50, 51, 52, 53, 54]. More recently Mezard and Parisi [48, 55] have argued that the underlying transition is actually a random first order transition signaled by a jump discontinuity in the specific heat.

Experimentally the glass transition is characterized by both kinetic and thermodynamic features. For example in the supercooled liquid kinetic quantities such as the viscosity and relaxation time grow rapidly as the temperature is lowered. When the system falls out of equilibrium below a certain temperature, thermodynamic quantities exhibit features reflecting the glass transition. For example as the system is cooled the specific heat has a step-like form and the dielectric constant exhibits a peak at a frequency dependent temperature.

During the current award period, in an effort to better characterize the glass transition, we introduced a novel probe which we call a generalized compressibility [56, 57]. Unlike the specific heat which monitors energy fluctuations, this linear compressibility is a function of the microscopic structure of the system: it depends solely on the positions of the particles and not on their previous history. Since we do not need to compare the system's state at different times, it is not a dynamic or kinetic quantity. Rather it is a thermodynamic quantity in the sense that it is purely a function of the microstate of the system dictated by its location in phase space. The generalized compressibility is easy to compute numerically, and it is simpler than the dielectric constant which involves both the translation and orientation of electric dipoles. In addition it does not suffer from finite size effects that can often plague measurements of the ordinary compressibility deduced from simulations. The generalized compressibility can be calculated in either the canonical or grand canonical ensembles. In particular it is well defined for a system with fixed volume $V$ and particle number $N$ in
contrast to the ordinary compressibility which is defined for a system that has fluctuations in \( N \) or \( V \). We performed a molecular dynamics simulation on a glass forming liquid consisting of a two component mixture of soft spheres in three dimensions. As the temperature is lowered (or as the density is increased), the generalized compressibility drops sharply at the glass transition, with the drop becoming more and more abrupt as the measurement time increases. At our longest measurement times, the drop occurs approximately at the mode coupling temperature \( T_c \). The drop in the linear generalizer compressibility occurs at the same temperature as the peak in the specific heat which we will discuss in the next section. By examining the inherent structure energy as a function of temperature, we found that our results are consistent with the kinetic view of the glass transition in which the system falls out of equilibrium. (An inherent structure is a particular system configuration whose energy corresponds to the minimum of a basin in the energy landscape.) We found no size dependence and no evidence for a second order phase transition though this does not exclude the possibility of a phase transition below the observed glass transition temperature. We see similar results as the density is increased at fixed temperature. Our results were published in *Physical Review E* [56].

5 Frequency Dependence and Equilibration of the Specific Heat of Glass Forming Liquids

As a glass forming liquid is cooled or compressed, a glass transition occurs when the system falls out of equilibrium, i.e., when the time scale for reaching equilibrium exceeds the observation time [41]. This is often associated with frequency dependent measurements of quantities such as the specific heat [58] and dielectric function [59] where characteristic frequencies systematically decrease with decreasing temperature. We have used molecular dynamics simulations of a three dimensional binary mixture of soft spheres to show that this frequency dependence is associated with long equilibration times.

Like many complex systems, such as proteins and neural networks, the dynamics of the glass transition is strongly influenced by the potential energy landscape [60, 61]. Each point on the energy landscape corresponds to a configuration of the particles in the system and the height at that point is given by the energy of the system. The energy landscape can be used to describe the three ways in which a system can fall out of equilibrium. First a system can become trapped in a metastable minimum where it stays for the duration of the observation time. Second a system can be in an energetically unlikely part of phase space and proceed slowly to a region of the energy landscape where its configurations obey a Boltzmann distribution. As such a nonequilibrium system evolves toward more probable regions of phase space, it exhibits aging which means its properties systematically change with time and do not obey stationarity [62]. The aging time, after which aging stops, is equal to the \( \alpha \) relaxation time which is the characteristic time for the system to forget its initial configuration.

The third way is not widely appreciated and in the current award period we showed that it is an important source of frequency dependence [63]. Namely, even after a glassy system no longer ages and has reached basins with appropriate energies, the system proceeds so slowly
through the energy landscape that it takes a long time to accumulate the large number of statistically independent measurements needed to accurately determine a thermodynamic average. We found from molecular dynamics simulations that a glass forming liquid can undergo a glass transition, as signaled by a peak in the specific heat $C_V$ versus temperature, that is due to insufficient averaging by a system that shows no signs of aging. The distribution of energies that a system samples in a basin of the energy landscape is a subset of the full distribution of energies available to the system. Since this subset has a smaller variance than the full distribution, the resulting specific heat, which is proportional to the variance of the energy, will be smaller when calculated from short time spans than from long time spans. These smaller values account for the values below the peak in $C_V$ on the low temperature side. Going to longer time spans eliminates the peak, though at temperatures below the peak temperature $T_p$, the longer time spans can be orders of magnitude longer than previously recognized equilibration times such as the a relaxation time, the energy correlation time, and the aging time. We found that the increase of the specific heat with time span is mirrored by the increase of the real part of the specific heat with decreasing frequency. We did this by calculating the frequency dependent specific heat from the Fourier sine transform of the energy fluctuation autocorrelation function [64]. We have published our results in Physical Review E [63].

In doing molecular dynamics simulations to calculate the specific heat and the linear generalized compressibility of a glass forming liquid, we used a three dimensional binary mixture of soft spheres with a $1/r^12$ interaction. Our work has made this a very well characterized system and at least one other group is using our results as a benchmark in developing new molecular dynamics techniques [65].

6 Summary

During the award period we studied the following:

- 1/f Noise in Coulomb Glasses
- Coulomb glass phase transitions as a function of positional disorder
- a new structural probe of the structural glass transition
- frequency dependence and equilibration of the specific heat of glass forming liquids
References


