Molecularly Linked Gold Nanoparticle Films As a Platform for Studying the Influence of Strong Coulomb Interactions on Charge Transport through a Metal-Insulator Transition

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Chemistry
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Abstract

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Low temperature charge transport properties of butanedithiol-linked gold nanoparticles films are investigated and the importance of strong Coulomb effects through percolation metal-insulator transition is studied. Butanedithiol-linked gold nanoparticle films are tuned through the metal-insulator transition through film thickness and signatures of strong Coulomb effects are observed throughout the transition. In particular, 1) films in the thin limit are observed to be insulators (conductance, \( g \), goes to zero as temperature, \( T \), goes to zero), and conductance follows \( g = A \exp\left(\frac{-T_o}{T}\right)^{1/2} \) at low \( T \), where \( A \) and \( T_o \) are temperature-independent variables. This behaviour is predicted by the Efros-Shklovskii Variable Range Hopping model, and comes from the optimization of electron tunnelling process (favouring short distances) and on-site Coulomb charging barrier of the metal clusters (favouring long distances). Additionally, 2) films in the thick limit behave as metals (\( g \) goes to non-zero as \( T \) goes to zero), and \( g = g_o + \beta T^{1/2} \) at low \( T \), where \( g_o \) is conductance due to inelastic scattering and \( \beta \) is a constant. A \( T^{1/2} \) term is predicted by a correction of the conventional Fermi Liquid Theory by Altshuler and Aronov, in which electron-electron interactions are enhanced by disorder. And finally, 3) films at intermediate thickness, near the metal-insulator transition and just barely beyond the metallic regime, exhibit a zero-bias conductance peak. This phase is reminiscent of an exotic metallic phase seen in transition metal compounds near the metal-insulator transition, and is predicted by the Hubbard model near the metal-insulator transition in which Coulomb charging and charge delocalization effects are important, resulting in strong electron correlations. In this regime in which electron correlations are strong, transition metal compounds are known to exhibit many exotic behaviours (such as high \( T_c \) superconductivity in cuprates, and colossal magnetoresistance in manganites); molecularly linked nanoparticle films provide a new platform to understand such important strong electron correlation phenomena.
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Chapter 1

Introduction

The effects of strong coulomb interactions between charge carriers as they delocalize can lead to exotic phases of matter. [1–4] For example, in transition metal oxides (such as cuprates), spatially confined \( d \) or \( f \) orbitals result in strong electron-electron repulsion and an associated energy cost for having multiple electrons occupying the same orbital. These materials also afford means for tuning the degree to which electron delocalize e.g. via doping or high pressure. When electron-electron interaction dominates, the materials are observed to be insulators and when delocalization (i.e. kinetic energy) dominates, the materials are observed to be metals. Remarkably, in the regime where both interactions and delocalization effects are significant, the materials exhibit correlated motion and exotic phenomena such as well studied high Tc superconductivity. [5] Despite being well studied, the exact underlying mechanism behind this phenomenon is not well understood; however, it is widely believed that strong, Coulomb-driven electron-electron interactions combined with electron delocalization play critical roles.

Strong Coulomb effects are known to be important in nanostructured materials, and have lead to interesting optoelectronic and electronic behaviours. [6–8] Such effects are discussed at length later in the thesis, but for the moment, to clarify briefly why this is the case, the energy required to charge a metal nanosphere with a quantum of charge, \( e \) can be calculated. For a metal sphere of capacitance \( C \), and since \( V_C \equiv Q/C \), where \( V_C \) is the voltage required to charge a capacitor with charge \( Q \), this energy is given by

\[
E_C = \int V_C dQ = \frac{e^2}{2C}.
\]

(1.1)

In the case of a sphere, then
\[ C = 4\pi \varepsilon_0 \varepsilon_r R_{NP}, \] (1.2)

\( R_{NP} \) is the radius of the nanoparticle, \( \varepsilon_0 \) is the permittivity of vacuum, and \( \varepsilon_r \) is the dielectric constant of the surrounding material. Note that for \( R_{NP} \sim 1 \) nm, \( E_C \sim 700 \) meV. This is much larger than room temperature fluctuations of \( k_B T \sim 25 \) meV, where \( k_B \) is the Boltzmann constant and \( T \) is temperature. The energy required to charge the nanosphere with two electrons is similarly large also. Therefore, attaching the sphere to a voltage source and increasing the electric potential of an initially neutral metal nanoparticle will result in no electrons hopping on until a critical potential is reached, at which point a single electron will hop on. The suppression of charge transfer onto or off the sphere below this threshold is called Coulomb Blockade. Increasing the potential further will result in a similar threshold below which no additional electrons hop on, until another critical potential is reached, at which point two electrons will occupy the metal sphere. This staircase like charging leads to Coulomb staircase in charge transport through a nanoparticle. [7, 9, 10] Both Coulomb blockade and staircase phenomena are important in understanding electronic properties of nanostructured materials and will be discussed further in the next chapter.

Charges can be made to flow through nanostructures in a variety of ways. One approach that is central to this thesis is that pre-fabricated nanostructures (such as metal nanoparticles) can be “self-assembled” to form macroscopic assemblies. Self-assembly is a simple approach for fashioning materials that exploits various interactions (i.e. van der Waals forces, electrostatic interactions, hydrogen bonding, etc) between nanostructures to form larger structures. [6, 8, 11] For example, saturated carbon chains with -SH end group, called alkanethiols (one -SH end group) can self assemble onto gold surface and will form densely packed ordered monolayers due to the van der Waals interaction between the carbon chain, and the thiol-gold covalent bonding. [12] In the case of bi-functional alkanes, one thiol end group will form a bond with the gold substrate, while the other functional group can remain free to bond to other nanostructures to form hierarchical nanostructures. [6, 8] This is a so-called “bottom-up” approach for making materials using pre-fabricated nanostructures. This approach has advantages over traditional top-down approach, which consists of having a bulk material be etched away to produce a desired nanoscale pattern (e.g. e-beam lithography [13]), in that properties of the assemblies are tunable through choice of nanostructure building blocks and assembly architecture. In addition, self-assembly allows for independent control over size, shape, and chemical composition of individual building blocks. In particular, assemblies consisting of metal nanoparticles separated by a molecular spacer have been shown to exhibit behavior that ranges from insulating to metallic [6, 14–19], depending on choice of molecules and thickness of the assemblies.
Pre-fabricated nanoparticles are commonly synthesized in liquid phase and capped with a molecular capping agent to prevent aggregation. For the simple case of metal nanoparticles suspended in an organic solvent and capped with an organic ligand, self-assembled films can be formed onto macroscopic substrates using a method as simple as drop casting: a droplet of nanoparticle solution can be cast onto a liquid or solid surface, the organic solvent evaporates and the nanoparticle film self-assembles on the surface with the capping ligands serving as interparticle molecular spacers. Collier et al. [20] used this approach with silver nanoparticles to form 2-dimensional monolayers on a water surface. They further controlled interparticle distance through compression. They found that at a critical interparticle distance (< 5 angstroms), the films underwent a transition from an insulator to metal and exhibited metallic-like optical behaviour. They used a Mott-Hubbard model to describe the metal-insulator transition. [21] This model, first proposed by Mott [22], is discussed later in Chapter 4 of the thesis. In short, the model considers a lattice of atoms with electrons on each lattice site such that the electrons can interact with each other via on-site repulsion (which raises potential energy) and electrons can delocalize via inter-site coupling (which contributes to kinetic energy). Here, silver nanoparticles act as sort of ‘artificial atoms’ occupying the lattice sites. As inter-site coupling increases (i.e. interparticle spacing decreases), initially localized electrons can become itinerant, resulting in a metal-insulator transition.

Capping ligands can also be replaced with bi-functional molecules, enabling cross-linking of neighbouring nanoparticles and the formation of connected networks. One such method to achieve cross-linked
nanoparticles is called ‘layer-by-layer self assembly’. In this method, a functionalized solid substrate is alternately immersed in (1) a solution of nanoparticles which bind to the surface and (2) a solution of excess bi-functional molecules which replace the capping ligand of the gold nanoparticle, leaving one functional end group free. Repeat exposure to solutions of gold nanoparticles and molecular linkers leads to formation of a film containing clusters of molecularly-linked gold nanoparticles. Film thickness can be controlled through the number of immersion cycles. Previous low temperature charge transport studies have shown that these nanoparticle films can be metallic (that is, conductance tends to a non-zero finite value at zero temperature) when sufficiently short or conjugated linkers are used (such as butanediithiol [23], 3-mercaptopropionic acid [24] and 1,4-phenylene bis(dithiocarbamate) [14]. Films are insulators (conductance tends to zero as temperature goes to zero) when longer or less conjugated linkers are used (such as dodecanediithiol [16]). Focusing on n-alkanediithiols \( (C_nS_2H_{2n+2}) \) of various lengths as cross-linkers and using gold nanoparticles \( (d = 15 \text{ nm}) \), Zabet-Khousosi et al. showed that, in the limit of thick films, films were insulating for \( n > 5 \), and metals for \( n < 5 \) (see Figure 1.1). Strictly speaking, films made by this process of alternately immersing a substrate in solutions of nanoparticles and molecular cross-linkers are not a realization of the Mott-Hubbard model as described above. Differences include that fact that for sufficiently thin films, percolation effects play important roles. Also, such films are not ordered, while the Mott-Hubbard model assumes an ordered lattice. Nevertheless, a number of studies have reported exponential dependence of resistance on n-alkane chain lengths [14–16,19] and one would expect that varying chain length should change interparticle coupling in the same spirit as the Mott-Hubbard picture. Furthermore, applying the criterion for critical interparticle spacing for the Mott-Hubbard metal-insulating transition, Zabet-Khousosi found that the calculated value was consistent with the observed critical length of \( n \sim 5 \) for n-alkanediithiol. To illustrate this, consider the simplest picture of an ordered lattice filled with hydrogen atoms at zero \( T \) with variable lattice spacing \( s_H \). In the limit \( s_H \) goes to infinity, the overlap between the hydrogen electronic wave function is negligible, and electrons are localized on individual atoms. For conduction to occur, electrons have to transfer between neutral atoms, creating positive and negative charged ions. This transfer requires an energy \( U \), arising from the difference between ionization energy (IE) and electron affinity (EA) of hydrogen atoms. \( U \), known as Hubbard energy, is energy cost to transfer electron from one atom to another and forming an electron-hole pair. [22]

\[
U = \int \int \frac{e^2}{4\pi \epsilon r_{12}} |\Psi(r_1)|^2 |\Psi(r_2)|^2 d^3r_1 d^3r_2 \quad (1.3)
\]

where \( \Psi(r) \) is the wave function of the hydrogen atom and \( \epsilon = \epsilon_o \epsilon_r \). For 1s,
\[ \Psi(r) \propto e^{-\frac{r}{a_0}}, \]  

(1.4)

where \( a_0 \) is the Bohr radius: \( a_0 = \frac{4\pi \epsilon_0 \hbar^2}{m_e e^2} \), where \( \hbar \) is Planck’s constant, \( m_e \) is the mass of an electron and \( e \) is the electron charge. For hydrogen atom, it was found that \( U = 0.625 \frac{e^2}{4\pi\epsilon a_0} \). Due to this energy cost, conductance at 0 K is suppressed and electrons are localized on lattice sites. For finite \( s_H \), the overlap between wave function is nonzero, give rise to energy bands. Then the energy gap for conduction becomes \( E_g = U - \frac{\Delta_1 \Delta_2}{2} \) (see Figure 1.2). The width of energy bands \( \Delta \), depend on the magnitude of overlap integrals, \( \gamma \), between atomic wave function: \( \Delta_1 \approx \Delta_2 \approx 2z_c \gamma \) where \( z_c \) is the coordination number of atoms in the lattice. \( \gamma \) is given by

\[ \gamma = \int \Psi_i \star (r) H \Psi_j (r) d^3r, \]  

(1.5)

where \( H \) is the Hamiltonian of lattice, and \( i \) and \( j \) represent nearest neighbour sites distance \( s_H \) apart. For a hydrogen atom,

\[ \gamma \approx \frac{e^2}{4\pi\epsilon a_0} \left( 1 + \frac{a}{a_0} \right) e^{s_H/a_0}. \]  

(1.6)

Note the pre-exponent factor term with \( s_H \) is negligible relative to exponent term. Thus \( \gamma \) exponentially increases with decreasing \( s_H \). Additionally, \( \Delta \) also increases as \( s_H \) decreases, and at \( U = \frac{\Delta_1 + \Delta_2}{2}, E_g = 0 \), that is the energy gap disappears and lattice becomes metallic. Taking \( \Delta_1 = \Delta_2 \) and \( z_c = 6 \), then \( U \approx 12\gamma \). Using equation 1.6 and the value of \( U \) given for a hydrogen atom, then \( s_H \approx 4.5a_0 \). This is the criterion for the onset of metallic behavior. An analog of the Mott-Hubbard metal-insulator transition can be realized using molecularly linked metal nanoparticles where nanoparticles serve as artificial atoms. Here, the energy gap arises from nanoparticle charging energy. The energy bands come from an overlap between nanoparticle wave functions

\[ \Psi_{NP}(r) \propto e^{-\alpha r}, \]  

(1.7)

where \( \alpha \) is the decay constant of the wave function outside of the nanoparticle. According to the step-potential model,

\[ \alpha \approx \sqrt{2m^* \phi \hbar}, \]  

(1.8)

where \( m^* \) is effective mass of electrons, \( \phi \) is barrier height. Here, using the analogy to hydrogen atom,
As mentioned, short n-alkanedithiol linkers \((n \leq 4)\) are observed to allow electrons to delocalize through connected nanoparticle pathways in thick films. As a result, in addition to using n-alkanedithiol chain length and thereby interparticle spacing to tune thick films through the metal-insulator transition, one can also use butanedithiol as the cross-linker for gold nanoparticles and use film thickness to tune through a percolation metal-insulator transition. [23] In the thin film limit, nanoparticles form small isolated networks on a substrate, and films exhibit thermally activated transport due to Coulomb charging energy barriers associated with charging the clusters with quantized charge carriers during charge transport. As films grow thicker, nanoparticle networks grow and coalesce until at least one sample spanning pathway forms at a so-called “percolation threshold”. At this point, electrons remain itinerant even at low temperatures, and the film is just barely metallic. The film still contains many isolated networks which continue to present Coulomb charging barriers and which contribute to the conductance via thermally assisted processes. As the film becomes thicker still, more isolated networks coalesce to form sample spanning pathways, and the film becomes increasingly conducting.
Goal of Thesis  In view of the ability of molecularly-linked metal nanoparticle films to undergo a percolation-driven insulator-to-metal transition from an insulating phase in which Coulomb barriers inhibit charge transport to a metallic phase in which charges delocalize, the region near the transition is expected to exhibit a phase in which both Coulomb charging and charge delocalization are important, i.e. a phase associated with strongly correlated electron phenomena. As mentioned previously, it is in such phases that transition metal compounds exhibit exotic behaviours, suggesting that this transition regime in molecularly-link nanoparticles may be a target of opportunity for observing and better understanding such phenomena. In this thesis, I measure and analyse charge transport properties of butanedithiol linked gold nanoparticle films through a percolation-driven metal-insulator transition, and in particular, focus on the properties near the transition in both the insulating and metallic phases. I observe behaviours that are indicative of strong electron correlations. In addition, near the metal-insulator transition, I observe an emergence of a phase with a zero-bias conductance peak, which is reminiscent of a so-called “exotic metallic” behaviour seen in transition metal compounds, such as vanadium oxide and nickel sulfide doped with selenium, near their insulator-to-metal transition. The Hubbard model has been used to explain the physics underlying these transition metal compounds, including the emergence of this exotic phase. I propose that qualitatively similar phenomena occur in the nanostructured system studied here.

Outline of Thesis  In Chapter 2, I will discuss how strong Coulomb effects arise in various nanostructured systems, including Coulomb Blockade and Coulomb staircase phenomena in a nanoparticle embedded in a tunnel junction and charging barrier for a nanoparticle embedded in a metal film. In Chapter 3, I will discuss prior experimental work on the role of Coulomb effects on transport through molecularly-linked gold nanoparticle films through the percolation Metal-Insulator Transition, and discuss various hopping transport models in insulating films. In Chapter 4, I discuss the concepts on the role of Coulomb interactions on charge delocalization, including correction to conductivity of disordered metals due to electron-electron interactions and the effects of strong electron correlations in the Hubbard Model. In Chapter 5, I will discuss experimental methods such as nanoparticle synthesis and self-assembly. Chapters 6 to 9 are based on publications on which I was co-author (Chapter 6) [26] or primary author (Chapters 7-9) [23, 27, 28]. Chapter 6 discusses an experiment highlighting the importance of eliminating contact resistance in order to probe film transport properties. It also discusses a 4-probe transport measurement technique for doing this and its application to thin films. Chapter 7 discusses an experiment reporting observation of a zero-bias conductance peak near the metal-insulator transition. Chapter 8 discusses transport measurements on both insulator and metal phases near the
metal-insulator transition and highlights signatures of Coulomb effects that persist throughout on both sides of the transition. Chapter 9 discusses a study in which the metal-insulating was driven using a combination of percolation and ionic liquid gating approaches, confirming previous observations obtained using percolation alone.
Chapter 2

Importance of Coulomb Effects in Nanostructured Systems

2.1 Single Nanoparticle Embedded in a Tunnel Junction

The ability to manipulate devices on the single electron level has been of great interest [7] and has led to the development of single electron transistors and other single electron devices. [29,30]

The simplest case to consider is a very small capacitance tunnel junction between two electrodes. The small capacitance of the junction leads to electrons requiring to overcome a charging barrier. At low $T$, when electrons have insufficient thermal energy to overcome the charging barrier, this barrier may result in blocking current flow through the junction until a critical potential bias is reached. This blockage regime, called Coulomb Blockade, has been observed in simple small-area tunnel junctions between nanoelectrodes. [31]

To illustrate the effect, consider that the voltage $V_C$ required to charge the junction with a single electron is given by

$$V_C = \frac{e}{C},$$

where $C$ is the capacitance of the junction. For a parallel plate junction, $C = A_C \epsilon_\circ \epsilon_r / s_C$, where $A_C$ is the area of each plate, $\epsilon_\circ$ is the permittivity of vacuum, $\epsilon_r$ is the dielectric constant of the material between the plate, and $s_C$ is the distance between plates. Then,
Chapter 2. Importance of Coulomb Effects in Nanostructured Systems

\[ V_C = \frac{\epsilon_s C}{A_C \epsilon_0 \epsilon_r} \]  

(2.2)

And the charging energy becomes

\[ E_C = \int V_C dQ = \frac{e^2}{2C}. \]  

(2.3)

In this entirely classical model, if \( A_C \sim 1 \text{ nm}^2 \), then \( E_C \sim 1 \text{ eV} \). For \( k_B T > E_C \), thermal fluctuation can overcome the charging energy. At room temperature, \( k_B T \sim 25 \text{ meV} \). Here, the emergence of single electron charging effects are seen: at \( T = 0 \text{ K} \), when voltage \( V \) is below \( V_C \), there is no charge transfer (i.e. no current). As \( T \) increases, \( V \) needed to charge the junction decreases as some energy comes from thermal fluctuation.

Single electron charging effects have also been observed using conducting nanoparticles situated between nanospaced electrodes. Here, Coulomb blockade effects have been observed since electrons must overcome an energy barrier in order to charge (or discharge) the conducting nanoparticle, leading to a current suppression in the current-voltage characteristics under a threshold voltage. In addition to this current suppression, as the voltage is increased, another threshold voltage will result in two electrons favorably occupying the nanoparticle, leading to a current ‘step’ in the current-voltage characteristics. This effect, known as Coulomb staircase, has been observed using scanning tunneling microscopy (STM) [9, 32]. In one such early experiment, Hanna et al. measured a granular gold surface in which the two-junction system was created by the grain between the tip of the STM and the bulk of the sample. Later, this effect was seen in charge transport in which individual conducting nanoparticles were fabricated between nanospaced electrodes through electron-beam lithography and reactive-ion etching of an insulating substrate before thin-film evaporation of aluminum. [10] This resulted in an aluminum nanoparticle with an aluminum oxide tunnel barrier sandwiched between two electrodes, in which current vs. bias voltage could be studied.

This behaviour can be described using a semiclassical model. The semiclassical orthodox model, the tunnel junction between electrode-nanoparticle surface is approximated as a parallel capacitor, \( C_j \), and resistor, \( R_j \) and the system is approximated as two junctions in series (see Figure 2.2). Then, the voltage dropped across each junction is

\[ V_j = \frac{C_1 C_2}{C_j C_\Sigma} V, \]  

(2.4)

where \( C_\Sigma = C_1 + C_2 \).
The electron tunneling rate ($\Gamma$) where $\pm$ denotes electron tunneling in/out of junction $j$ is given by

$$\Gamma_j^\pm = \frac{1}{e^2 R_j} \int_0^\infty f(E)[1 - f(E - \Delta E_j^\pm)]dE \quad (2.5)$$

where $f(E)$ is the Fermi function:

$$f(E) = \frac{1}{1 + \exp[(E - E_F)/k_BT]} \quad (2.6)$$

and $\Delta E_j^\pm$ is the change in energy in the system as the electron tunnels through the junction: $\Delta E_1^\pm = \Delta U_C^\pm \pm eV_1$ and $\Delta E_2^\pm = \Delta U_C^\pm \pm eV_2$, where $\Delta U_C$ is the energy change when the charge on the nanoparticle is changed by $\pm e$,

$$\Delta U_C^\pm = \frac{(Q \pm e)^2}{2C_\Sigma} - \frac{Q^2}{2C_\Sigma} = \left(\pm \frac{2Q}{e}\right)E_C. \quad (2.7)$$

Solving the integral for the transmission rate,

$$\Gamma_j^\pm = \left(\frac{1}{e^2 R_j}\right)\left(\frac{-\Delta E_j^\pm}{1 - \exp(\Delta E_j^\pm/k_BT)}\right) \quad (2.8)$$

At $T = 0$ K, then

$$\Gamma_j^\pm(T = 0K) = \begin{cases} \frac{-\Delta E_j^\pm}{e^2 R_j} & \text{for } \Delta E_j^\pm < 0 \\ 0 & \text{for } \Delta E_j^\pm \geq 0 \end{cases} \quad (2.9)$$

Assuming $R_1 = R_2$, $C_1 = C_2$, and $Q = 0$ (i.e. initially charge neutral), then the threshold voltage is $|V_C| = \frac{2E_C}{e}$.

And the current is

$$I = e(\Gamma_1^+ - \Gamma_1^-) = e(\Gamma_2^+ - \Gamma_2^-) = \begin{cases} \frac{V - |V_C|}{2R_j} & \text{for } V > |V_C|, \\ 0 & \text{for } |V_C| < V < |V_C|, \\ \frac{V + |V_C|}{2R_j} & \text{for } V < -|V_C| \end{cases} \quad (2.10)$$

Therefore there is a 'switch' voltage that can turn on the current at $V_C$ and below this voltage no current flow (Coulomb Blockade). The differential conductance ($g \equiv \frac{dI}{dV}$) at zero $T$ is simply

$$g(T = 0) = \frac{dI}{dV}(T = 0) \approx \begin{cases} \frac{1}{2R_j} & \text{for } |V| > |V_C|, \\ 0 & \text{for } |V| < |V_C|. \end{cases} \quad (2.11)$$
Figure 2.1: Coulomb staircase current-voltage curve for a gold nanoparticle single electron transistor along with orthodox model fit (offset for clarity). Reprinted with permission from reference [33]. Copyright 2004 American Institute of Physics (doi: 10.1063/1.1695203).

Note that multielectron charging has not been considered. As mentioned previously, increasing the voltage further will lead to a current step at a critical potential, or a Coulomb staircase effect, in the current-voltage characteristic, as seen in Fig. 2.1.

For non-zero $T$, and $V = 0$, and the regime where $k_B T \ll E_C$,

$$\Gamma_j^{\pm}(T, 0V) = \frac{E_C}{e^2 R_j} \exp \left(\frac{-E_C}{k_B T}\right) \tag{2.12}$$

Conductance inside the Coulomb blockade regime (i.e. about zero bias voltage) comes from electrons with energies greater than $E_C + E_F$. The number of these electrons can be calculated by integrating the Fermi-Dirac distribution.

$$\int_{E_C+E_F}^{\infty} f(E)dE \approx \int_{E_C+E_F}^{\infty} \frac{dE}{1 + \exp\left[(E - E_F)/k_B T\right]} \tag{2.13}$$

$$\propto \int_{E_C+E_F}^{\infty} \exp[-(E - E_F)/k_B T]dE \tag{2.14}$$

$$= (k_B T)\exp\left(\frac{-E_C}{k_B T}\right) \approx \exp\left(\frac{-E_C}{k_B T}\right) \tag{2.15}$$

Note that the Fermi-Dirac distribution was approximated by the Boltzmann distribution and the temperature dependence of the pre-exponential factor $k_B T$ is negligible compared to that of the exponential term.

To get the differential conductance at zero-bias voltage, consider

$$g(V = 0) = \frac{\partial I}{\partial V}(0V) = e \left(\frac{\partial \Gamma_1^+}{\partial V}(0V) - \frac{\partial \Gamma_1^-}{\partial V}(0V)\right) \tag{2.16}$$
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The tunneling rate in equation 2.8 can be written as

$$
\Gamma_1^\pm \approx \frac{\Delta E_1^\pm}{e^2 R_1} \exp \left( \frac{-\Delta E_1^\pm}{k_B T} \right) = -\frac{k_B T (u \pm v)}{e^2 R_1} e^{-u \pm v}, \quad (2.17)
$$

where $u = E_C/k_B T$ and $v = eV/2k_BT$. Then

$$
\frac{\partial \Gamma_1^\pm}{\partial V} = \frac{\partial \Gamma_1^\pm}{\partial v} \approx -\frac{1}{2eR_1} \left[ \pm e^{-u \pm v} \pm (-u \pm v)e^{-u \pm v} \right] \quad (2.18)
$$

For at zero-bias,

$$
g(V = 0) \approx -\frac{1}{2R_1} [(e^{-u} - ue^{-u}) - (-e^{-u} + ue^{-u})] \quad (2.19)
$$

$$
= -\frac{1}{R_1} (1 - u)e^{-u} = -\frac{1}{R_1} \left( 1 - \frac{E_C}{k_B T} \right) \exp \left( -\frac{E_C}{k_B T} \right) \approx \frac{1}{R_1} \frac{E_C}{k_B T} \exp \left( -\frac{E_C}{k_B T} \right) \quad (2.20)
$$

Once again, the conductance can be approximated to be

$$
g(T, V = 0) \approx \exp \left( -\frac{E_C}{k_B T} \right) \quad (2.22)
$$

For a metal sphere, $C = 4\pi\varepsilon_0 \varepsilon_r R_{NP}$, where $R_{NP}$ is the radius of the NP. As such, the conductance varies as $\sim e^{-E_C/T}$, which is reminiscent of a simple activated, or Arrhenius, process, in which the activation energy is inversely proportional to nanoparticle size. This behaviour was confirmed by Zabet-Khosousi et al. In their study [34], they trapped single gold nanoparticles of various sizes ($d = 2.5; 5.0,$ and $10$ nm) in a break-junction through electrostatic trapping, and measured current vs. voltage (see Figure 2.3).

### 2.2 Coulomb Charging Barrier for a Nanoparticle Embedded in a Metal Film

In addition to being observed in individual nanoparticles, single electron charging effects have also been observed in nanoparticle assemblies. [6, 8] For example, various groups [16, 24, 35–38] have found that molecularly linked gold nanoparticle films, cross linked with alkanedithiol of various linker lengths and nanoparticle sizes, exhibit Arrhenius behaviour at $T$ down to $\sim 100$ K, and some have observed current
Figure 2.2: A metal sphere connected to two metal electrodes through tunnel junctions (top) and a representative schematic in which the double tunnel junctions are modelled as two parallel capacitor and resistor in series (bottom).

Figure 2.3: Current-voltage curve for gold nanoparticle of various sizes between break-junction with molecular spacers (data) and data generated from a modified orthodox model (lines). Reprinted with permission from reference [34]. Copyright 2005 American Physical Society (doi: 10.1103/PhysRevLett.94.096801).
suppression in the current-voltage characteristic reminiscent of Coulomb blockade. Activation energies extracted from IV curves and conductance vs. temperature plots have shown to be 10 to 50 meV. Additionally, activation energies varied with both nanoparticle size [39] and linker length [16, 37]. The results were found to be in good agreement with a model taking nanoparticles in an ensemble into account, with some exceptions as will be discussed further.

To get an idea how activation energy may vary with nanoparticle size or linker length in an assembly, consider a system of metal spheres is surrounded by other metal spheres. This picture can be simplified, as per Figure 2.4, to a metal sphere of radius $R_{NP}$ embedded in a conducting matrix with some insulating shell of thickness $s_M$. Then the capacitance is

$$C = 4\pi\varepsilon_0\varepsilon_r \left( \frac{1}{R_{NP}} - \frac{1}{R_{NP} + s_M} \right)^{-1} = 4\pi\varepsilon_0\varepsilon_r \frac{R_{NP}(R_{NP} + s_M)}{s_M}$$

(2.23)

and so the charging energy becomes

$$E_C = \frac{e^2}{8\pi\varepsilon_0\varepsilon_r R_{NP}(R_{NP} + s_M)}$$

(2.24)

This equation predicts how charging energy varies with the size of the nanoparticle, as well as the insulating spacer length and dielectric constant. As nanoparticle size increases, $E_C$ decreases, as observed by many groups including Brust [35] and Leibowitz et al. [40]. Additionally, as molecule spacing $s_M$ decreases, so does $E_C$, as observed by various groups [34, 37] measuring gold nanoparticle films cross-linked with alkanedithiols of various alkane-chain lengths. Wang et al. [15] varied both gold nanoparticle sizes ($d = 2$ to 4 nm) and alkanedithiol linker length ($s_M = 0.8$ to 2 nm) and found excellent agreement with equation 2.24.

Wessels et al. [14] studied gold nanoparticles ($d = 4$ nm) cross-linked with organic linkers composed of different cores (benzene or cyclohexane) and different metal-binding functional groups (thiol or dithiocarbamate). Nanoparticle films cross-linked with molecules with a conjugated core (benzene) were observed to have conductivity one order of magnitude higher than films cross-linked with molecules with a non-conjugated core (cyclohexane). Interestingly, when using 1,4-phenylene-bis(dithiocarbamate) (PBDT), films exhibited metallic-like behaviour (conductivity decreases with increasing temperature). PBDT is 1.1 nm and is highly conjugated. Metallic behaviour in nanoparticle films have also been seen when using alkanedithiol linkers $n \leq 4$ (i.e., $\leq 0.7$ nm). This will be explored further in the next chapter.
Figure 2.4: A metal sphere surrounded by metal spheres in a dielectric medium of dielectric constant $\epsilon_r$ (left) can be approximated as a metal nanoparticle of radius $R_{NP}$ in conducting matrix with an insulating separator of distance $s_M$ (right).
Chapter 3

Prior Experimental Work on the Role of Coulomb Effects on Transport through Molecularly-Linked Gold Nanoparticle Films

3.1 Percolation Metal-Insulator Transition in Nanoparticle Films

As discussed in Chapter 2, nanostructure assemblies composed of metal nanoparticles with molecular spacers can exhibit Arrhenius behaviour, in which the activation energy for electron transport is governed by the charging energy of individual nanoparticles, $E_a = E_C = \frac{e^2}{2C}$. When the tunnel junction barrier between nanoparticles is sufficiently small (that is, molecules are sufficiently short or conjugated), electron wavefunction at a nanoparticle increasingly overlaps with that of neighbouring nanoparticles, and eventually electrons delocalize. The orthodox model derived in Chapter 2 breaks down.

This can be illustrated by looking at the uncertainty principle: $\Delta E \Delta t \geq \hbar/2$. Taking $\Delta E$ to be the charging energy, and $\Delta t$ as the charging time for tunnelling, $\Delta t = RC$, where $R$ and $C$ are the representative resistance and capacitance of the tunnel junction, respectively, as approximated by the
orthodox model (see Figure 2.2). Then $\frac{e^2}{2C} (RC) \geq \frac{1}{2}$, thus $R \geq \frac{1}{h}e^2$.

So for $g \equiv \frac{1}{R} > \frac{2e^2}{h} \sim (13 \text{ k} \Omega)^{-1}$ (called, the quantum of conductance, where the factor of 2 comes from considering spin degeneracy), $\Delta t$ is very short such that $\Delta E$ becomes sufficiently large to overcome $E_c$ even at $T = 0$. Single electron charging effects are then suppressed as quantum coupling becomes strong, charges become delocalized, and film exhibits metallic behaviour. This is consistent with reports of metallic behaviour discussed in section 2.2 in which metallic behaviour was observed using short (butanedithiol [16,23]) or conjugated (1,4-phenylene-bis(dithiocarbamate) [14] linkers.

In butanedithiol-linked gold nanoparticle films, for example, electrons are observed to delocalize between connected nanoparticles. As a result, in addition to driving an insulator-metal transition by changing choice of molecule, an insulator-metal transition can be driven by varying film thickness and percolation. Metal-insulator transition can be tuned, then, through film thickness. This can be easily controllable through layer-by-layer self assembly, as mentioned in Chapter 1.

### 3.2 Hopping Transport in Insulating Films

In band theory, a finite gap exists between valence band and conduction band for insulators. The gap, called the band gap, defines the energy needed for electrons to absorb in order to participate in the conduction band (i.e., participate in conductance) which, for non-zero $T$, can be overcome through thermal energy. Thus, it is expected that conductance increases with $T$ (e.g., Arrhenius). Metals, on the other hand, have no band gap, and instead, conductance is limited by scattering. Thus conductance tends to decrease with $T$, since lowering $T$ lessens phonon scattering effects.

As discussed in Chapter 2, Coulomb charging effects can lead to Arrhenius behaviour (see also equation 2.22), which has been observed by many groups studying both the optical [14,40] and electronic [14–16] properties of molecularly linked gold nanoparticle films. Some groups have found, however, at lower $T$, conductance deviates from Arrhenius behaviour. [16–18] This has also been seen in thin granular metals [41–44], doped semiconductors [45] and quantum dot assemblies [46,47]. They found that

$$g \sim \exp\left[\left(-\frac{T_c}{T}\right)^{\nu_H}\right],$$

where $0 < \nu_H \leq 1$. A model was proposed by Mott [22] to explain this behaviour in doped semiconductors. While Arrhenius transport assumes nearest neighbour hopping, Mott’s Variable Range Hopping (VRH) model allows electrons to optimize tunneling nearby vs. hopping further to find a site of accessibly low energy $E_a$. Mott derived $\nu_H = 1/4$ for 3D systems, and $\nu_H = 1/3$ for 2D systems. [22]
For many systems, however, including granular metals [41–44] and molecularly linked gold nanoparticle films [17–19], particularly near an insulator-metal transition where charges are tending to delocalize more, $\nu_H = 1/2$. As described further below, Efros and Shklovskii (ES) attributed this behaviour to strong coulomb effects [48], although alternate theories also exist [17,49,50]. One challenge to ES model comes from extracted hopping distance values from fitted data; in granular metals and in molecularly linked gold nanoparticle films, hopping distances ranges from tens to thousands of nanometers - surprisingly long distances for tunneling processes. Furthermore, Dunford et al. [19] found that hopping distances tended to increase closer to the insulator-metal transition. They proposed an alternate theory called Quasilocalized Hopping, which will be discussed in the following section.

Nanoparticle assemblies can also exhibit metallic behaviour [14, 16, 19, 23, 24, 38, 51, 52] but transport properties of the metallic behaviour has not been as well explored, particularly close to the metal-insulator transition. Several groups have found that nanoparticle films that were cross-linked with sufficiently short linkers and were of sufficient thickness exhibited metallic behaviour [14, 16, 51, 52] at room temperature and conductance decreased with increasing temperature; however, resistivity of these films were usually many orders larger than the bulk metallic counterpart. For example, Wessels et al. [14] found that the resistivity of films consisting of 6 layers of 1,4-phenylene-bis(dithiocarbamate)-linked 4 nm Au nanoparticles was 8x10^{-4} \Omega m at 295 K. Musick et al. [52] reported resistivities of 5x10^{-6} \Omega m for 12 layers of 2-mercaptoethanol linked 11 nm gold nanoparticles, which is about 200 times higher than bulk gold (2.4x10^{-8} \Omega m). This indicated that electron scattering was enhanced in these films compared to bulk gold. Zabet-Koushosi et al. [16] also found that conductance decreased much more rapidly with temperature for metallic molecularly linked gold nanoparticle films relative to bulk gold, providing more evidence of enhanced electron scattering.

The most well studied nanoparticle assembly system, studied by the Dhirani group, is butanedithiol-linked gold nanoparticle films. These films undergo a percolation insulator-metal transition with increasing film thickness. Well beyond the transition on the metallic side, conductance decreases with increasing $T$. [23, 27] Near the transition on the metallic side, conductance may increase with $T$ at higher $T$, yet remain finite as $T \to 0$. When nanoparticle films just become metallic, a single sample spanning pathway of connecting nanoparticles exist to provide finite conductance at $T = 0$, however several thermally activated pathways still exist. As $T \to 0$, those pathways shutdown, and conductance behaves as equation 3.1. Deeper into the metallic regime, it is expected that

$$g = g_0 + \beta T^q,$$  \hspace{1cm} (3.2)
where \( g_0 \) is the conductivity due to inelastic scattering, and \( q \) depends on dominant scattering process (i.e. phonon-electron scattering, or electron-electron scattering). According to conventional Fermi Liquid theory, electron-electron scattering leads to \( q = 2 \). When considering disorder, however, Coulomb interactions are enhanced (due to electron’s tendency to diffuse), and Altshuler and Aronov calculated \( q = 1/2 \) using perturbation theory. As will be further discussed in Chapter 8, this description agrees remarkably well for butanedithiol linked gold nanoparticle films in the metallic regime, and at low \( T \) when higher term scattering processes (i.e. phonons) shut down. In summary, molecularly-linked nanoparticle films exhibit strong Coulomb phenomena in charge transport, including ES VRH in the insulating regime and Altshuler-Aronov disorder-mediated electron-electron interactions just beyond the insulator-metal transition on the metallic side. In the following section, the derivation of various transport models previously mentioned are discussed.

### 3.2.1 Mott’s Variable Range Hopping

In an insulator, localized electrons acquire thermal energy \( k_B T \) in order to overcome an activation energy barrier \( E_a \) and to conduct. The probability, \( p \), that the electron will absorb \( E_a \) thermally is given by the Boltzmann distribution as \( p \sim \exp(-\frac{E_a}{k_B T}) \). If \( E_a \) is fixed, then transport is simple activated, or Arrhenius, given by

\[
g = A_A \exp \left( -\frac{E_a}{k_B T} \right),
\]

where \( A_A \) is the pre-exponential factor. Consider now that the activation energy \( E_a \) at a site is not fix and can vary site-to-site, electrons may not simply want to ‘hop’ to it’s nearest neighbour, but may hop further in order to find a site with a lower activation energy \( E_a \), as illustrated in Figure 3.1. However, the mechanism in which localized electrons hop (tunneling) favours shorter distances.

We assume that the density of states (number of localized states per unit energy per unit volume) near the Fermi level is constant, that is \( \rho(E) = \rho_0 \), where \( \rho_0 \) is the density of states at the Fermi level. So for electrons to go from site \( i \) to site \( j \), \( E_j - E_i \leq \Delta W_E \), where \( \Delta W_E \) is some energy band. So the number of available states within \( \Delta W_E \) per unit area is given by \( \Delta N_s = \rho_0 \Delta W_E \). Thus the average energy interval (that is, \( \Delta N_s = 1 \)) will be

\[
\Delta W_E = \begin{cases} 
\frac{1}{\rho_0 \pi r_h^2}, & \text{dim = 2} \\
\frac{3}{4\rho_0 \pi r_h}, & \text{dim = 3}
\end{cases}
\]

(3.4)
The probability of electrons tunneling some distance \( r_h \) is \( e^{-2\alpha r_h} \). Additionally, the probability of acquiring energy \( \Delta W_E \) thermally is given by Boltzmann distribution \( e^{-\Delta W_E / k_B T} \). So the hopping probability is the product of both probabilities given by:

\[
P \sim \exp \left( -2\alpha r_h - \frac{\Delta W_E}{k_B T} \right), \tag{3.5}
\]

where \( \alpha^{-1} \) is the attenuation length of electron wave function, and \( \Delta W_E \) is the activation energy required to overcome for electrons to hop onto that site.

Optimizing for \( r_h \) such that \( \frac{dP}{dr_h} = 0 \) gives rise to \( r_{opt} \), that is optimized hopping distance. This gives rise to the following results.. for dim = 2,

\[
\frac{dP}{dr_h} = \left( -2\alpha + \frac{2}{\rho_\circ \pi k_B T r_{opt}^3} \right) \exp \left( -2\alpha r_{opt} - \frac{1}{k_B T r_{opt}^3} \right) = 0
\]

\[
r_{opt} = \left( \frac{1}{\alpha \rho_\circ \pi k_B T} \right)^{1/3} \tag{3.6}
\]

Put that back into the probability,

\[
P \sim \exp \left[ -2\alpha \left( \frac{1}{\alpha \rho_\circ \pi k_B T} \right)^{1/3} - \alpha^{2/3} \left( \frac{1}{\rho_\circ \pi k_B T} \right)^{1/3} \right] \sim \exp \left[ -\frac{3\alpha^{2/3}}{\rho_\circ \pi k_B T} \right] \tag{3.8}
\]

Then,

\[
g = A_M \exp \left[ - \left( \frac{T_{c,M}}{T} \right)^{1/3} \right], \tag{3.9}
\]

where \( T_{c,M} = \frac{3^3 \alpha^2}{\pi k_B \rho_\circ T} \).

For the 3-dimensional case, similarly,
\[
\frac{dP}{dr_h} = \left(-2\alpha + \frac{9}{4\rho_o \pi k_B T r_{\text{opt}}^4}\right) \exp\left(-2\alpha r_{\text{opt}} - \frac{3}{4\rho_o \pi k_B T r_{\text{opt}}^3}\right) = 0 \quad (3.10)
\]

\[
r_{\text{opt}} = \left(\frac{9}{8\alpha \rho_o \pi k_B T}\right)^{1/4} \quad (3.11)
\]

So put that back into \( P \).

\[
P \sim \exp\left[-2\alpha \left(\frac{3}{4\rho_o \pi k_B T}\right)^{1/4} - \frac{3\alpha^{3/4}}{(\rho_o^{1/3} \pi k_B T)^{1/4}}\right] \sim \exp\left[-\frac{5\alpha^{3/4}}{(\rho_o^{1/3} \pi k_B T)^{1/4}}\right] \quad (3.12)
\]

Then,

\[
g = A_M \exp\left[-\left(\frac{T_{o,M}}{T}\right)^{1/4}\right], \quad (3.13)
\]

where \( T_{o,M} = \frac{512\alpha^3}{\pi k_B \rho_o} \).

### 3.2.2 Efros-Shklovskii Varible Range Hopping

Efros and Shklovskii looked at systems in which Coulomb interactions are strong. In these systems, they argued that for an electron hopping from a filled site \( i \) \((E_i < E_F)\) to empty site \( j \) \((E_j > E_F)\), the energy change is given by

\[
\Delta E_{ij} = E_j - E_i - \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r r_{ij}} > 0. \quad (3.14)
\]

The last term comes from the Coulomb attraction between the electron-hole pair at sites \( j \) and \( i \). If \( \Delta E_{ij} < 0 \), the hopping would occur spontaneously and \( E_j \) would not be above the Fermi level.

\[
r_{ij} > \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r \Delta E_{ij}}. \quad (3.15)
\]

For small \( \Delta E_{ij} \), that is electrons to find empty sites close to the Fermi level, \( r_{ij} \) is large, that is electrons must hop long distances. This means that the number of sites near \( E_F \) must be very low, and vanish at \( E_F \).

The concentration of sites within energy bandwidth \( \Delta W_E \) must not exceed \( \Delta N_s \approx r_{ij}^{-3} = \frac{(4\pi \varepsilon_0 \varepsilon_r \Delta W_E)^3}{e^6} \), and since \( \rho(\Delta W_E) = \Delta N_s/\Delta W_E \),

\[
\rho(\Delta W_E) \approx \frac{(4\pi \varepsilon_0 \varepsilon_r)^3 \Delta W_E^2}{e^6} \quad (3.16)
\]
Therefore, density of states vanishes $\sim \Delta W_E^2$ as $\Delta W_E \to 0$. This is in direct contradiction to Mott’s assumption that the density of states near $E_F$ is constant.

This result is observed as a ‘soft’ Coulomb gap, since DOS vanishes only at $E_F$ (see Figure 3.2).

$\Delta N_s$ can be calculated using

$$\Delta N_s = \int_0^{\Delta W_E} \rho(E) dE = \frac{(4\pi\epsilon_0\epsilon_r)^3 \Delta W_E^3}{3e^6}$$  \hspace{1cm} (3.17)

Much like for the derivation of Mott’s VRH, the average energy interval is calculated by setting

1 = $\Delta N_s$ x Volume;

$$\Delta W_E = \left(\frac{9}{4\pi}\right)^{1/3} \left(\frac{e^2}{4\pi\epsilon_0\epsilon_r r_{ij}}\right)$$  \hspace{1cm} (3.18)

The probability of hopping is given by

$$P \sim \exp\left(-2\alpha r_h \left(\frac{9}{4\pi}\right)^{1/3} \frac{e^2}{4\pi\epsilon_0\epsilon_r r_h k_B T}\right),$$  \hspace{1cm} (3.19)

Therefore,

$$\frac{dP}{dr_h} = \left(-2\alpha + \left(\frac{9}{4\pi}\right)^{1/3} \frac{e^2}{4\pi\epsilon_0\epsilon_r r_{opt} h^2 k_B T}\right) \exp\left(-2\alpha r_{opt} - \left(\frac{9}{4\pi}\right)^{1/3} \frac{e^2}{4\pi\epsilon_0\epsilon_r r_{opt} k_B T}\right) = 0$$ \hspace{1cm} (3.20)

$$r_{opt} = \sqrt{\left(\frac{9}{4\pi}\right)^{1/3} \frac{e^2}{8\pi\epsilon_0\epsilon_r \alpha k_B T}}$$  \hspace{1cm} (3.21)

Re-include it into $P$,

$$g = A_E \exp\left[-\left(\frac{T_0}{T}\right)^{1/2}\right]$$  \hspace{1cm} (3.22)

Where $T_0 \approx \frac{e^2 \alpha}{4\pi\epsilon_0\epsilon_r k_B}$.

From this, a few useful equations can be extracted to compare with experimental results:

$$r_{opt} = \frac{1}{4\alpha} \left(\frac{T_0}{T}\right)^{1/2}$$  \hspace{1cm} (3.23)

$$\Delta W_{E, opt} = \frac{k_B}{2} (T_0 T)^{1/2}$$  \hspace{1cm} (3.24)
Figure 3.2: Density of states near Fermi energy vanishes to zero resulting in a ‘soft’ Coulomb gap.

3.2.3 Quasilocalized Hopping in Nanoparticle Films

Even though variable range hopping (VRH) models were derived for doped semiconducting system, previous studies [19] have shown that it describes charge transport behaviour in insulating molecularly linked nanoparticle films. That is, when filling fraction (nanoparticle coverage on the substrate) is low, or when $T$ is high, nearest neighbour hopping occurs, and Arrhenius behaviour is observed. [34] When filling fraction increases, but $\Delta E_{ij}$ dominates, Mott-VRH is observed. [22] When filling fraction increases further, as more and more nanoparticles are added, near the metal-insulator transition, Coulomb interactions increase, that is $\Delta E_{ij} \ll \frac{e^2}{4\pi\varepsilon_r \varepsilon_0 h}$, Efros Shklovskii (ES)-VRH behaviour is observed. [6,45] However, extracted physical parameters showed that results in molecularly-linked nanoparticle films were counter-intuitive to what was expected from the model: tunneling distances, $\alpha$, was found to be too large (on the order of $\mu m$ for samples near metal-insulator transition). Additionally, as filling fraction increases, $r_{opt}$ increases; whereas, in the VRH model, as site density increases, $r_{opt}$ should decrease. In the example given above, $\phi \sim 1 \text{ eV}$ (the estimated value for the linker used in this study, butanedithiol). Then tunneling distance estimation is $\sqrt{\frac{\hbar^2}{2m_e \phi}} \sim 0.2 \text{ nm}$.

The authors proposed an alternative model, given the results, called Quasilocalized hopping. [19] In nanoparticle films, much like granular metallic films, nanoparticles attached via short molecular linkers can facilitate delocalization between metallic nanoparticles, providing a sort of ‘quasilocalization’ of the electron. As films grows, nanoparticle cluster size increases. Now electrons are quasilocalized on these isolated metallic networks, and can hop from cluster to cluster. The cluster size increases until sample spanning pathway emerges and the film becomes metallic. But before that, when still insulating, electrons wanting to hop onto another cluster must overcome a single electron charging energy of the
metallic cluster. So $E_C = \frac{e^2}{2C}$, where $C$ is the capacitance of the cluster size. Assuming the capacitance scales with cluster size, that is $C \sim 2\pi\varepsilon_\epsilon\epsilon_rL_Q$, where $L_Q$ is the length of the cluster. So

$$E_C = \frac{e^2}{4\pi\varepsilon_\epsilon\epsilon_rL_Q}.$$  \hspace{1cm} (3.25)

We also assume within the metallic clusters, electrons scatter at defects (as per metals). Assuming that the transmission probability per defect is $\Gamma_Q$ ($\Gamma_Q < 1$), so puddles with $n_Q$ scattering sites per unit length (see Figure 3.3), then the transmission rate is given by

$$\Gamma_Q^{n_QL_Q} = \exp(-n_QL_Q\log(\Gamma^{-1})).$$  \hspace{1cm} (3.26)

Then there is a similar competition giving rise to

$$P \sim \exp(-n_QL_Q - \frac{e^2}{\varepsilon_\epsilon\epsilon_rL_Qk_BT}),$$  \hspace{1cm} (3.27)

leading to similar $T$-dependence as ES-VRH.
Chapter 4

Concepts on the Role of Coulomb Interactions on Charge Delocalization

4.1 Altshuler-Aronov correction to Conductivity of Disordered Metals due to Electron-Electron Interactions

In metals, conductance goes to a finite value as $T \rightarrow 0$ K and is limited by electron scattering processes. According to Drude theory of metals, conductivity of a metal is given by

$$\sigma = \eta e^2 \tau / m_e,$$

(4.1)

where $\eta$ is the charge density, $m_e$ is the mass of electron, and $\tau$ is the mean free time, and is determined by electron scattering processes. According to Matthiessen’s rule,

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{elastic}}} + \frac{1}{\tau_{\text{inelastic}}},$$

(4.2)

where $\tau_{\text{elastic}}$ is the mean free time for elastic scattering processes (i.e. impurity or defect scattering) and $\tau_{\text{inelastic}}$ is the mean free time for inelastic scattering processes (i.e. electron-electron or electron-phonon scattering). Conductivity thus can be written as
\[
\sigma(T)^{-1} = \sigma_o^{-1} + \sigma_1(T)^{-1}
\]  
(4.3)

where \(\sigma_o\) is the conductivity due to elastic scattering which is a \(T\) independent process. The behavior of \(\sigma\) with \(T\) depends on the dominant scattering process, which may in itself also depend on \(T\):

\[
\sigma(T) = \sigma_o + B_M T^q
\]  
(4.4)

where \(q\) depends on dominant scattering process (i.e. phonon-electron scattering, or electron-electron scattering). At high \(T\), electron-phonon scattering dominates and \(\sigma\) decreases linearly with \(\frac{1}{k_B T}\). At lower \(T\), electron-phonon scattering diminishes, and, in metals in which electron-electron interactions are sufficiently strong, electron-electron scattering may dominate, leading to \(q = 2\). However, with a sufficiently disordered system, electrons can diffuse. Using perturbation theory, Altshuler and Aronov \([55, 56]\) showed this leads to enhanced electron-electron interactions and in this limit, \(q = 1/2\). At low \(T\), then

\[
\sigma(T) = \sigma_o + B_A T^{1/2}
\]  
(4.5)

where \(B_A\) is some coefficient. This behaviour has been seen in systems of doped semiconductors on the metallic side \([56–58]\) and has been applied to butanedithiol-linked gold nanoparticle films in a study described in Chapter 8.

### 4.2 Hubbard Model and Strong Electron Correlations

Earlier, three regimes of interest in molecularly linked gold nanoparticle films through the metal-insulator transition were identified, and potential Coulomb effects in two limits were discussed: the insulating regime and the metallic regime. In the transition regime, the film is composed of a mixture of metallic pathways and isolated clusters. The film is metallic in the sense that conductance is finite at \(T = 0\) K; at finite \(T\), thermal energy may aid in conductance by activating electron hopping onto the isolated clusters. Thus \(g\) increases with increasing \(T\).

In this regime, however, electron interactions are expected to still be important. Note that while band theory had been able to adequately predict behaviour of conventional metals and insulators, it does not adequately capture the physics in materials in which electron interactions are significant. A Hubbard model, however, does take it into account and can act as a sort of guide. \([2]\) The Hubbard
Hamiltonian $H$ is given by

$$ H = \sum_{<i,j>,\sigma_s} t_{ij} C^\dagger_{i,\sigma_s} C_{j,\sigma_s} + U \sum_i n^\dagger_{i,\uparrow} n_{i,\downarrow} \quad (4.6) $$

where $C^\dagger_{i,\sigma_s}$ ($C_{j,\sigma_s}$) are creation (annihilation) operators for electrons at site $i$ ($j$) and spin $\sigma_s$ ($\uparrow$ or $\downarrow$), $t_{ij}$ is the transfer energy, $U$ is the on-site Coulomb repulsion energy, $n_{i,\sigma} = C^\dagger_{i,\sigma} C_{i,\sigma}$ is the number operator, and the first sum is over nearest neighbors and spins.

The Hubbard model describes a simple picture of a lattice in which electrons can hop from site to site, and interact. [2, 59–62] While the model is of an ordered lattice, and molecularly linked gold nanoparticle films are strongly disordered (as discussed in earlier sections), this model can, nevertheless, provide some insights into the interplay between potential energy (arising from Coulomb repulsion) favouring localization (second term dominates) and kinetic energy favouring delocalization (first term dominates). When potential energy $U$ dominates, the model predicts a Mott Insulator with upper and lower bands (called Hubbard bands) located $\pm U/2$ from the Fermi energy; when kinetic energy dominates, the model predicts a broad band at the Fermi energy with bandwidth $W$, as described by band theory for a metal. When both potential and kinetic energies are comparable, interestingly, the model predicts a quasiparticle peak (or Abrikosov-Suhl resonance) appearing as a third narrow band between the upper and lower Hubbard bands. This quasiparticle peak has been observed in strongly correlated materials. [63–69]

Using butanedithiol linked gold nanoparticle films, our studies have shown for the first time a zero-bias conductance peak, reminiscent of the Abrikosov-Suhl predicted by the Hubbard model near the metal-insulator transition. [23, 27] Given that I observe signatures of strong correlations (quasiparticle peak) predicted by the Hubbard Model, despite nanoparticle films being strongly disordered, I propose a Percolative Hubbard Model in its place, as I discuss further in Chapter 7.
Chapter 5

Experimental Methods

5.1 Gold Nanoparticle Synthesis and Characterization

Gold nanoparticles were synthesized using a modified version of Brust et al. [35] First, a 25 mL aqueous solution of 40 mM HAuCl₄ (hydrogen tetrachloroaurate) was prepared and added to a 50 mL solution of 50 mM of tetraoctylammonium bromide (TOAB) in toluene. TOAB acts as a phase transfer agent, transferring Au³⁺ from the aqueous phase to the organic phase, and forming small clusters of Au³⁺ in the organic phase, resulting in a nanoparticle (NP). This mixture was stirred for 20 minutes and the aqueous colourless layer was discarded. Next, a 25 mL aqueous solution of ~10 mM sodium borohydride was added and the solution was mixed for ~ 18 hours. The aqueous layer was removed again, and the dark ruby organic phase was washed three times with 50 mL of 0.1 M sulfuric acid, 1.0 M potassium carbonate, and deionized water, respectively. The organic phase was then dried by vacuum filtration through magnesium sulphate. The final Au NP solution was stored in the refrigerator. The NP size distribution is determined by optimization of free energy (minimizing surface energy by forming bigger clusters vs. maximizing entropy by having many smaller clusters) and thus depends on conditions during synthesis. A TEM sample was taken (see Figure 5.1 for characterization), and the average NP size was found to be \( d = 5.3 \text{ nm} \pm 1.1 \text{ nm} \).

5.2 Self Assembly of Nanoparticle Films

Nanoparticle films (NPF) were prepared through a layer-by-layer self assembly process. NPF devices are assembled on a functionalized glass substrate with pre-deposited gold electrodes. Details are as follows.
Figure 5.1: a) UV-Vis absorbance of Au NP in toluene, b) TEM of Au NP with a scale bar of 20 nm, and c) histogram of Au NP showing average d = 5.3 nm ± 1.1 nm.

**Substrate Preparation** Substrates for transport measurements are prepared in the following order: Glass slides of desired size (usually ~10 mm x ~10 mm) are cut with a carbide tip scribe from a microscope slide (1 mm thick), cleaned by sonication in methanol and acetone for 10 minutes each, and then immersing the slides in hot piranha (3:1 H₂SO₄/H₂O₂) for 30 minutes. The clean slides were then functionalized by immersion into a boiling 40 mM toluene solution of 3-aminopropyldiethoxymethylsilane for 20 minutes. Gold electrodes of desired pattern were then thermally deposited onto the glass slides with a shadow mask. Indium solder was used to attach magnet wires onto the electrodes before NPF assembly.

**Self Assembly of Nanoparticle Films** NPF are self-assembled by alternating immersion of the slides in Au NP solution for 1-4 hours, and linker solution (usually 1,4-butanedithiol) for 10-20 minutes (see Figure 5.2). Figure 5.3 shows characterization of Au NPFs including UV-Vis, showing that approximately the same amount of material is being added each immersion cycle.
Figure 5.2: Schematic representation of layer-by-layer self assembly of nanoparticle films.
Figure 5.3: a) UV-Vis absorbance of Au NPF with immersion cycle, b) Absorbance at 800 nm of Au NPF at immersion cycle 1-8, showing approximately linear growth, c) SEM of LBL through immersion cycles.
Chapter 6

Influence of Low Energy Barrier Contact Resistance in Charge Transport Measurements of Gold Nanoparticle+Dithiol-based Self-Assembled Films


Author Contributions P. Joanis prepared samples and performed measurements resulting in data found in Figure 6.2, 6.4, 6.5, 6.6, 6.7. M. Tie prepared samples and performed measurements resulting in data found in Figure 6.3. P. Joanis prepared Figure 6.2. A.-A. Dhirani prepared Figure 6.1a and 6.1c. M. Tie prepared all other figures (Figure 6.1b, 6.1d, 6.1c, and 6.3 to 6.7), did all data analysis and provided feedback to the manuscript. A.-A. Dhirani provided guidance in experimental and theoretical direction and wrote the manuscript.
6.1 Abstract

Gold-thiol self-assembly is a widely employed strategy for engineering electronic devices using molecules and other nanostructures as building blocks. However, device behavior is expected to be governed by both building block architecture and contact effects. In order to elucidate the role of the latter in such devices, we have studied conductance of n-butanedithiol-linked Au nanoparticle (NP) films using different types of electrode configurations, namely, four-probe vs. two-probe and break junctions before vs. after dielectric break down of contact resistance. We find that contact resistance is governed by transport across a small barrier which can dominate device behavior when temperatures and resistances of the self-assembled devices are low. Accounting for such contact resistance reveals a more precise picture of device behavior in these regimes, including in the present system film properties near the onset of the percolation insulator-to-metal transition and beyond.

6.2 Introduction

Since electronic properties of matter at nanometer length scales are both remarkable and controllable via synthesis, there is vigorous ongoing effort to use nanostructures as building blocks to engineer and study interesting and potentially useful electronic devices. [70] There are, however, a number of challenges that arise in this effort. One is that such nanostructures must inevitably be “wired” to each other or to external electrodes. Given the small length scales involved, self-assembly - that is, exploiting a natural tendency for functional groups to interact with each other or with surfaces - is a commonly used strategy to overcome this challenge, thiol-gold being the most widely studied interaction. Another key challenge is that the electronic properties of self-assembled, nanostructured devices are influenced not just by the nanostructures themselves but by the contacts as well; indeed, in some instances, contact resistance dominates overall device behavior. Conductance can vary depending on molecule binding site and orientation [71] as well as electrode geometry. [72] Aromatic molecules can exhibit a transition from tunnelling to field emission that depends on the molecular terminal functional group (thiol vs. isocyanide) as well as the type of metal contact. [73] Molecules can also exhibit different resistance depending on molecular terminal group – electrode contact [74, 75] and cis-trans conformations. [75] The terminal functional group and the type of metal may influence the nature of a surface dipole, the alignment of the molecular energy levels relative to Fermi level of the metal, and thereby even the dominant charge carrier (electron vs. hole) flowing through the molecule. Aromatic molecules with dicarbamate terminal functional groups self-assembled on a gold surface exhibit 80 times higher
currents than those with thiol terminal function groups. \[76\] Contacts can have important implications for commercial devices. Comparing indium tin oxide, gold and surface oxidized gold contacts for organic light emitting diodes, surface oxidized gold contacts yield the best performance due in part to the low sheet resistance of the underlying gold and improved injection barrier provided by the surface oxide. \[77\] Studies of nanostructured electronic devices thus far have focused on fundamentally two-probe geometries, in which a bias voltage (\(V\)) is applied across a device containing nanostructure(s), and the devices responses (current, \(I\), and its derivatives with voltage, \(\frac{dI}{dV}\), \(\frac{d^2I}{dV^2}\), etc.) include contributions from contact resistances. In some cases, a three-terminal or transistor-type geometry has been employed. \[70\] These are fundamentally two-probe devices as well, in which a third “gate” electrode can subject nanostructures being interrogated to an electric field. In the present study, we employ a so-called four-probe method to interrogate electrical properties of a self-assembled nanostructured system, probing both the nanostructured system+contact resistance as well as just the nanostructured system itself and thereby revealing the role of the contact resistance. Fig. 6.1a is a diagram of our four probe set up, and Fig. 6.1b is a simplified resistor network equivalent. \(R_{F12}\), \(R_{F23}\), and \(R_{F34}\) are the film resistances between probes 1 and 2, 2 and 3, and 3 and 4, respectively. \(R_{C1}\), \(R_{C2}\), \(R_{C3}\) and \(R_{C4}\) are the contact resistances between film and probes 1, 2, 3 and 4, respectively. We can use Fig. 6.1b as an example to illustrate the four probe method. A known current, \(I\), flows from probe 1 to 4, through the outer contacts and the film. The total voltage, \(V_{14}\), required to drive this current depends on both the outer contact resistances and the film resistance. By Ohms law, \(V_{14} = IR_t\), where \(R_t\) is the total resistance of the film plus two contact barriers, \(R_t = R_{C1} + R_{F12} + R_{F23} + R_{F34} + R_{C4}\). This would be a standard two probe measurement which includes contact contributions. Note that a large ratio of contact resistance to total resistance leads to a large ratio of voltage drop across the contacts to the total voltage applied (“voltage divider” effect). In the four-probe method, the voltage difference between probes 2 and 3, \(V_{23}\), is measured using high impedance buffers, which do not allow current to flow across \(R_{C2}\) nor \(R_{C3}\) but rather force all of the current through the film. As a result, 1) by Ohms law, the voltage drops across these contact resistances is zero, and \(V_{23}\) is also the voltage drop across \(R_{F23}\); and 2) the current flowing through \(R_{F23}\) is \(I\). Notwithstanding the presence of contact resistances, we obtain the film resistance in terms of measured quantities: \(R_{F23} = \frac{I}{V_{23}}\). This illustration assumed Ohms law, i.e. that \(I\) varies linearly with \(V\) and \(\frac{dI}{dV}\) is a constant. In general, \(\frac{dI}{dV}\) tends to vary with \(V\). Determining \(\frac{dI}{dV}\) in this common situation using the four probe method is discussed in the supplementary information section.

Self assembled nanoparticle systems can exhibit a variety of remarkable electronic [6] and optical properties [78] and are currently of great interest. [79–81] Using a ‘bottom up’ approach, self assembly affords control over nanoparticle size, linker length, and assembly architecture. This tunability enables
a potential for complex architectures and behaviours, making such systems a favourable proving ground for a variety of applications ranging from single-electron devices to biosensing technologies. [80] For the nanostructured system in the present study, we use self-assembled films containing gold nanoparticles (NP) + n-butanedithiol linker molecules, and use thermally deposited gold films as contacts. Since this system is based on thiol-gold self-assembly, it serves as a test-bed that is of interest. Also, this system can exhibit a wide range of behaviours, from non-metallic behaviour with high film resistance to metallic behavior with low film resistance. [6, 14, 35–37, 52] As film thickness increases, the sizes of “clusters” of metallic, linked nanoparticles grow, until at a percolation transition there are sample spanning metallic clusters. Concurrently, film resistance drops and contact resistance becomes more significant. Previous studies of charge transport in these systems have interrogated film properties using the two-probe method. As films become thicker and film resistance goes down (i.e. near metal-insulator transition and in the metallic regime), contact resistances become more significant and in the metal regime in fact can dominate. In this work, we study film properties as a function of temperature using the four probe method, enabling measurements of both film + contact resistance as well as just film resistance itself. We also use the two-probe method to study break junctions with nanoparticle films bridging the junctions. Both electrode configurations were used to study films with increasing thickness across the metal-insulator transition. Our four-probe data shows the existence of a contact resistance with a small energy barrier, exhibiting tunnelling behavior at low temperatures and voltages and thermally assisted transport at higher temperature. Our break junction samples in the thick film regime initially exhibited the presence of the barrier, but application of a large voltage caused a sudden, irreversible drop in resistance and resulted in clear metallic behaviour. We speculate that this might be due to the breakdown of the contact barrier. This work shows that the two-probe method can exhibit voltage and temperature dependence due to a small barrier tunnelling which has a potential to obscure film properties and that, in order to study film properties more accurately, especially in metallic regime and near metal-insulator transition, it is important to account for this contact barrier using the four-probe method.

6.3 Experimental Section

Butanedithiol used to link Au NPs was purchased from Sigma-Aldrich and used as received. Au NPs were synthesized as described in Section 5.1. Transmission electron microscopy yielded an average NP diameter of 5.0±0.8 nm. NP films on the glass slides with pre-deposited Au electrodes were self-assembled as described in Section 5.2. The amount of NP deposited per immersion cycle depended on NP solution
Figure 6.1: (a) Four-probe electrode configuration with gold electrodes and a self assembled butanedithiol-linked gold nanoparticle film. (b) A typical four configuration represented by a simplified resistor network. (c) Four-probe configuration enabling a control measurement with aluminum electrodes, aluminum oxide contact barrier, outer gold electrodes, and a thermally deposited thin gold film. Two separate measurements are possible: a two probe measurements between outer gold electrodes (minimal contact resistance) and a four probe measurements using two inner aluminum electrodes and outer gold and aluminum electrodes. (d) Photos of (i) our sample and (ii) our control sample represented in (a) and (c), respectively. Any two inner aluminum electrodes can be used for the four-probe method; extra electrodes were deposited to increase sample yield.
concentration and immersion time. As a result, room temperature film resistance was monitored after each NP/dithiol immersion cycle, and self-assembly was continued until a desired resistance was reached.

Four ~ 6 mm long, ~ 200 nm thick Au electrodes separated by 2 mm were thermally deposited on to the glass slides using shadow masks. Copper magnet wires were attached to the Au electrodes using indium solder before NP film self-assembly. Fig. 6.1d (i) shows our sample after NP film self-assembly. Control samples shown in Fig. 6.1d (ii), were made similarly. Glass substrates, 20 mm x 10 mm x 1 mm in size, were cleaned and functionalized as above. Then five 8 mm long, 250 µm wide and 150 nm thick aluminum electrodes were thermally deposited 3 mm apart on the glass slides using shadow masks and left in air to grow a surface oxide layer. A thin gold film, 200 µm wide and 21 nm thick was then deposited across the aluminum electrodes, and subsequently, two gold pads 150 nm thick were deposited on the outer edges of the gold film. Copper magnet wires were attached using indium.

To interrogate NP film properties over smaller length scales, we also studied films employing a 2-probe, break junction electrode configuration. To fashion these devices, glass substrates, 4 mm x 8 mm x 1 mm in size, were cut from microscope slides, cleaned and functionalized as per Section 5.1. The substrates were next placed in a vacuum chamber where a 100 µm wide and 8 mm long Au wire was deposited by metal evaporation using a shadow mask. A 100 µm stretch in the middle of the wire was 16 nm thick, and the rest of the wire was 150 nm thick. Electrodes were connected to the electronics using copper magnet wires and indium solder before NP self-assembly. The sample was immersed in liquid nitrogen and a gradually increasing voltage was applied until the wire broke due to electromigration.

Figs. 6.2a and 6.2b, respectively, show scanning electron microscope images of break junctions before and after self-assembly of a NP film. Break junctions exhibited gaps with widths that ranged from a few
microns to a few nanometers (the latter is estimated from measurements of tunnel currents). A thick NP film is clearly visible in Fig. 6.2b. It obscures the break junction gap, and its edges can be seen as excess material to the sides of the electrodes has been wiped away.

Two- and four-probe methods were used to measure film+contact and film properties, respectively. To improve signal-to-noise, (differential) conductance \( g = \frac{dI}{dV} \) was measured directly by using lockin techniques, rather than by measuring \( I \) vs. \( V \) across the film and numerically differentiating (see Appendix). A sinusoidal voltage modulation \( \tilde{V} \), 10 mV, 10 Hz to 200 Hz depending on sample resistance) from a lockin was summed with a DC bias, \( \bar{V} \), using a summing amplifier. The sum was applied to the first electrode of the sample. The resulting current was converted to a voltage using another amplifier. This voltage was input to a data acquisition card (DAC, National Instruments PCIMIO 16X) to measure its DC component and to the lockin to measure its sinusoidal component. The lockins output was recorded using a second channel of the DAC. In the four-probe method, the DC voltage drop across middle electrodes 2 and 3 was measured using a third channel of the DAC via an operational amplifier to ensure no current was drawn. The sinusoidal component of the voltage drop across the middle electrodes was measured using a second lockin, whose output was measured using a fourth channel of the DAC. Low pass filters were sometimes used to reduce noise. In the four-probe method, these various inputs were used to determine the conductance of the film as a function of voltage drop across the film (not the total voltage drop) as described in the Appendix. Conductances vs. voltage for our samples were measured at different temperatures \( T \) down to \( \sim 2 \) K using a physical property measurement system (PPMS). Measurements for control samples were performed down to \( \sim 77 \) K by slowly lowering/raising the samples in a L-N\(_2\) dewar. Two four-probe and five two-probe samples were studied in detail up to \( \sim 30 \) and \( \sim 60 \) dithiol/NP exposures, respectively. No hysteresis was observed when voltage sweeps were repeated.

To further test the electronics and software, an additional control measurement was performed using commercial resistors arranged as per Fig. 6.1b. To simulate metallic samples with high contact barrier, ‘contact resistances’ (RCs) of 10 k\( \Omega \pm 10\% \) and ‘film resistance’ (RF) of 1 k\( \Omega \pm 10\% \) were used. These values were confirmed using a multimeter. Using the four-probe method, \( R_{F23} \) was found to be 0.98 k\( \Omega \).

### 6.4 Results and Discussion

Fig. 6.3 shows \( g \) vs. \( T \) and \( g \) vs. \( V \) data for our control sample. Control measurements to determine the thermally deposited Au films properties were performed using a two-probe configuration using outer gold electrodes which have minimal contact resistance (see Fig. 6.3a and b). Two-probe measurements
including film and tunnel oxide contact effects were performed using the outer electrodes (i.e. gold and aluminum outer electrode, see Fig. 6.3c and 6.3d). Four-probe measurements to determine films resistance despite contact resistances were performed using an outer gold electrode to drive current, an outer aluminum electrode with an oxide barrier to measure current, and two central aluminum electrodes with oxide barriers to measure voltage drop across the film (see illustration in Fig. 6.1c and data in Fig. 6.3e-f). Fig. 6.3a and 6.3b, obtained with minimal contact resistance, show that the gold film exhibits typical metallic behavior. Namely, conductance decreases as temperature increases, and conductance is independent of bias. Fig. 6.3c and 6.3d, obtained with an aluminum oxide tunnel junction in series with the gold film, indicate the presence of an energy barrier since conductance increases with temperature and with bias. Fig. 6.3c inset shows an Arrhenius plot that yields an activation temperature of 1.64 K. Fig. 6.3e and 6.3f show that $g$ vs. $T$ and $g$ vs. $V$ data of the film itself obtained via the four-probe method behave similarly as data in Fig. 6.3a and 6.3b obtained with minimal contact resistance. Film resistance at 290 K was found to be $\sim 81$ Ω between the gold pads with minimal contact resistance using the two-probe configuration and $\sim 66$ Ω between aluminum electrodes with aluminum oxide tunnel junction contact resistance using the four-probe configuration. Since the length of the film between aluminum electrodes is about 0.8 that between the gold pads, the film resistance between the aluminum is expected to be $\sim 81$ Ω x 0.8 or $\sim 65$ Ω, in reasonable agreement with the value determined using the four-probe method. Using the four-probe method, we are able to obtain film behaviour even with a large ($\sim 30$ kΩ) contact resistance in series. Note that the resistivity of gold is $2.214\times10^{-8}$ Ωm at 293 K [82]. Taking our film dimensions as $\sim 16$ mm long, $\sim 0.2$ mm wide and $\sim 21$ nm thick, the expected resistance measured in the two-probe configuration is expected to be $\sim 84$ Ω, in reasonable agreement with our results.

Fig. 6.4a and 6.4b show conductance vs. temperature data obtained for a 12-NP/dithiol exposure cycle film without and with contact resistance, respectively, using the same four-probe device. That is, data in Fig. 6.4a show 4-probe data using the outer and inner pairs of electrodes of a four-probe device; data in Fig. 6.4b show two-probe data obtained using just the outer pair electrodes. Film conductance (Fig. 6.4a) tends to zero as temperature drops implying that the film is insulating: the density of states vanishes at the Fermi level and electrons have to overcome an energy barrier in order to conduct. The presence of the energy barrier in the film is further evidenced by conductance increasing as temperature increases. The figure inset shows an energy barrier of 24 K. The ln $g$ vs. $\frac{1}{T}$ plots level off at low temperatures due to the conductance being approximately zero. A number of studies have found that NP films can exhibit energy barriers arising from single electron charging of isolated NPs or clusters of linked NPs (“Coulomb blockade”). [36] The data in Fig. 6.4b, which includes contact effects, is similar to
Figure 6.3: Normalized conductance ($g$) vs. temperature ($T$) at zero bias from 77 K to 300 K and normalized conductance vs. voltage ($V$) at 77 K for a thermally deposited gold film obtained using various electronic configurations. a) and b) Two-probe measurements with minimal contact resistance exhibiting film properties. c) and d) Two-probe measurements with aluminum oxide tunnel junction in series exhibiting combined film and contact resistance properties. e) and f) Four-probe measurements with aluminum oxide tunnel junction in series exhibiting film properties. Normalization factors are in (a) $1.2 \times 10^{-2}$ S at 290 K, (b) $1.9 \times 10^{-2}$ S at 2 V, (c) $3.8 \times 10^{-5}$ S at 290 K, (d) $3.7 \times 10^{-5}$ S at 3 V, (e) $1.5 \times 10^{-2}$ S at 290 K, and (f) $1.7 \times 10^{-2}$ S at 0 V.
Figure 6.4: Normalized conductance $g$ vs. temperature $T$ data obtained using a non-metallic, 12 exposure cycle Au NP/butanedithiol film. (a) Four-probe data showing film conductance (main panel) and $\ln g$ vs. $\frac{1}{T}$ with a linear fit (inset). The conductance at 250 K is $1 \times 10^{-5}$ S, and the slope of the inset fit is 24.0 K. (b) Two-probe data showing conductance of the film and contacts combined in series (main panel), and $\ln g$ vs $\frac{1}{T}$ with a linear fit (inset). The conductance at 250 K is $3 \times 10^{-6}$ S, and the slope of the inset fit is 39.5 K. Temperature values: 2 K to 10 K in 1 K steps, 10 K to 30 K in 2 K steps 30 K to 50 K in 5 K steps, 50 K to 100 K in 10 K steps, 100 K to 200 K in 20 K steps, 200 K to 250 K in 5 K steps.

that in Fig. 6.4a. The Arrhenius plot shown in the inset yields a slope of 40 K for film + contact. Since film and contact resistances add in series, when film resistance is high, film resistance can dominate over contact resistance. As a result, conductances of the film with and without contacts behave similarly.

Fig. 6.5a shows film conductance vs. temperature for the same sample after 18 NP/dithiol exposures. This data was obtained using the four-probe electrode configuration to remove contact effects. Note that this time, film conductance tends to a finite, non-zero value at low temperatures, implying that the film satisfies the definition of a metal: the density of states at the Fermi level does not vanish and the electrons are not required to overcome an energy barrier in order to conduct. Nevertheless, as temperature increases, conductance still increases. The figure inset shows an energy barrier corresponding to 11 K. Typically for metals conductance decreases with increasing temperature due to increasing phonon density and increasing electron-phonon scattering. Here, the film has just crossed the percolation threshold (there is at least one sample spanning metallic pathway for current to flow), and the film is only “just” metallic. [36] That is, the film is a mixture of mostly non-metallic pathways and some metallic pathways. At higher temperatures, conductance is dominated by the larger number of non-metallic pathways. As temperature drops, these pathways shut down rapidly, and conductance drops. At the lowest temperatures, just the metallic pathways conduct, conductance tends to a non-zero value,
Figure 6.5: Normalized conductance $g$ vs. temperature data $T$ obtained using a metallic, 18 exposure cycle Au NP/butanedithiol film and a four-probe electrode configuration. (a) Four-probe data showing metallic film conductance (main panel) and $\ln g$ vs. $\frac{1}{T}$ with a linear fit (inset). The conductance at 250 K is $2 \times 10^{-4}$ S, and the slope of the inset fit is 11.4 K. (b) Two-probe data showing conductance of the metallic film and contacts combined in series (main panel) and $\ln g$ vs. $\frac{1}{T}$ with a linear fit (inset). The conductance at 250 K is $4 \times 10^{-5}$ S, and the slope of the linear fit is 14.8 K. Temperatures values are the same as in Fig. 6.4.

and the film satisfies the definition of a metal.

Fig. 6.5b shows 2-probe conductance vs. temperature data of the same film measured using just the outer two electrodes of the four-probe device. In contrast with the four-probe data shown in Fig. 6.5a that exclude contact effects and reveal metallic film behaviour, the data in Fig. 6.5b contain both film and contact effects in series, and the conductance exhibits non-metallic behaviour: it tends to zero as temperature drops. This indicates that the contact resistance comprises an energy barrier, and Fig. 6.5b inset yields an energy barrier corresponding to 15 K. It should be noted that it is difficult to extract a reliable value for the energy barrier of the contact from this data since film and contact conductances are combined in series and both include significant thermally assisted components. However as film become more metallic and contact barrier effects become more prominent, we can use the results from film + contact to get a clearer picture of contact behaviour, as discussed further below.

Fig. 6.6 shows conductance vs. temperature obtained using the same sample with 25 dithiol-Au NP exposure cycles. Figs. 6.6a and 6.6b, respectively, show data from four-probe and outer two-probe measurements. In both cases, conductance tends to a finite, non-zero value as temperature decreases. In the case of the four-probe measurement (Fig. 6.6a), as temperature decreases, film conductance increases for most of the temperature range by only $\sim 2\%$. This behavior can be attributed to temperature dependent electron - phonon scattering as seen in typical metals. Others [83] have also attributed this
change to a combination of tunnelling and an increasing tunnelling distance with increasing temperature due to thermal expansion. For a portion of the temperature range at the lower end, conductance drops by 4% as temperature drops, as this film likely still contains some non-metallic pathways that contribute to the conductance and that shut down at lower temperatures. In the case of the two-probe measurements (Fig. 6.6b), as temperature decreases, film+contact conductance increases slightly for a portion of the temperature range and then drops over a majority of the range by ~30%. The significantly larger drop in the two-probe conductance data compared to the four-probe data evidently reflects the influence of the thermally assisted contact barrier. We note that the two- and four-probe conductance data are not completely Arrhenius anywhere. Estimates for high and low temperature barriers are: 0.35 K (film) and 2.6 K (film and contact) above 10 K; 0.032 K (film) and 0.35 K (film and contact) from 2 K to 5 K. This result is consistent with studies by others [76] which found, using two-probe measurements, that ethanedithiol-linked gold nanoparticle film can exhibit metallic behaviour and barriers of ~2 K above 80 K.

The above data obtained using macroscopic electrodes comparing two- and four-probe measurements show that two-probe measurements can be strongly influenced by barrier effects at lower film resistances. We show a similar conclusion can be reached using break junctions and just two-probe measurements.
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(Figs. 6.7a-c). In these samples, electrodes are closely spaced and thus contact resistance is emphasized, especially for very thick films for which film resistances are relatively low and a significant fraction of the total applied voltage is dropped across the contact resistances. Fig. 6.7a was obtained using a film prepared using 10 dithiol/Au NP immersion cycles. The right inset shows that at temperatures drops, conductance tends to zero rapidly, and this film is therefore likely non-metallic. An Arrhenius plot (left inset) yields an energy barrier corresponding to 98 K at high temperatures. Conductance vs. voltage data in the main panel show that conductance increases with increasing voltage, consistent with the presence of energy barrier(s) to current flow. Fig. 6.7b and 6.7c shows film behaviour of the same sample after 50 dithiol/Au NP immersion cycles. Conductance vs. temperature tends to a finite, non-zero value as temperature drops, implying that the film has become metallic, but conductance decreases with decreasing temperature, implying the presence of an energy barrier. Although current may flow via thermally assisted pathways in the film, it is likely that a small barrier across which tunnelling can occur at low temperatures and voltages is present because as temperature drops, conductance plateaus at the lowest temperatures and becomes approximately constant - a hallmark of tunnelling. Also, conductance vs. voltage exhibits supra-linear behaviour at low temperatures (Fig. 6.7b, right inset). However, as temperature increases, eventually by 160 K, the barrier is overcome thermally, and conductance transitions to metallic film behaviour: conductance vs. voltage becomes approximately ohmic up to ~ 1 V (Fig. 6.7b, left inset). An Arrhenius plot yields barriers corresponding to 12 K above a temperature of 20 K and 0.03 K below a temperature of 10 K.

For samples with sufficiently thick films, as voltage is increased, we eventually observe that the conductances of break junction devices can suddenly and irreversibly increase 10-100 fold. We attribute this to dielectric break down of the contact that is induced in such samples since thick films possess relatively low film resistance and most of the voltage is then dropped across the contacts. Break down is much more common in narrow break junction rather than macroscopic devices due to the higher current densities that arise. Metallic film behaviour is easily identified after this breakdown (see Fig. 6.7d). As temperature drops, conductance increases over most of the temperature range, plateaus and then tends to a finite non-zero value at low temperature (Fig. 6.7d, inset). Also, conductance vs. voltage is ohmic for low voltages (Fig. 6.7d, main panel). This behavior was observed with all five break junction samples studied.

The above-discussed four-probe measurements show that a contact resistance arises at the interface between the NP film and the butanethiol-functionalized gold electrodes. Four-probe conductance of the 25 NP/dithiol exposure metallic film, as shown in Fig. 6.6a, exhibits small barriers in the film itself that correspond to temperatures ranging from 0.3 K to 0.03 K. Given that the film contains particles
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Figure 6.7: Conductance behaviour of a NP/butandithiol film obtained using two-probe break junction electrodes. (a) Conductance behaviour for a non-metallic 10 dithiol/Au NP cycle film before break down of contact resistance. Conductance vs. voltage at various temperatures (main panel), conductance vs. temperature at zero bias (right inset) and Arrhenius plot (left inset). The conductance at 300 K is $1 \times 10^{-5}$ S. Temperature values: 1 K steps from 2 K to 10 K, 2 K steps from 10 K to 20 K, 16 steps spaced linearly in $1/T$ from 20K to 300K. A linear fit to the Arrhenius plot above 10 K has a slope of 98 K. Below 10 K, the conductance is almost zero, and a linear fit yields a flat line. (b) Conductance behaviour for a metallic 50 dithiol/Au NP film before break down of contact resistance. Conductance vs. voltage at various temperatures (main panel), at 2 K (right inset) and from 80 K to 180 K (left inset). The conductance at 300 K is $7 \times 10^{-4}$ S. Temperature values: 1 K steps from 2K to 10 K, 2 K steps from 10 K to 20 K, 14 steps spaced linearly in $1/T$ from 20 K to 110 K, 10 K steps from 110 K to 300K. (c) Conductance vs. temperature (inset) and Arrhenius plot of conductance at zero bias (main panel) for the same sample as (b). A linear fit to the Arrhenius plot above 20 K has a slope of 12 K and from 2 K to 10 K a slope of 0.03 K. (d) Conductance behaviour for the same metallic 50 dithiol/Au NP film as in (b) and (c) after break down of contact resistance. Conductance vs. voltage at various temperatures (main panel) and vs. temperature at zero bias (inset). The conductance at 300 K is $10^{-2}$ S. Temperature values: 1 K steps from 2 K to 10 K, 2 K steps from 10 K to 30 K, 5 K steps from 30 K to 50 K, 10 K steps from 50 K to 100 K, 20 K steps from 100 K to 300 K.
with different sizes and likely different background charges, the existence of a range of energies and
the above-mention values point to single electron charging barriers (Coulomb blockade) in the film. The
 corresponding two probe measurements, which include both film and contact effects, exhibit significantly
 larger barriers that correspond to temperatures ranging from \(\sim 3\) K to 0.3 K. Again the existence of a
 range of barriers, the gradual change of activation energies from high temperature to low temperature
 (see Arrhenius plot in Fig. 6.6b) and their values again suggest Coulomb blockade effects. Such barriers
can arise from linked nanoparticle clusters near the electrode interface that have poor ohmic contact
with nanoparticle film.

It is also possible that contact barriers can arise due to molecular contacts. A number of experimental
and theoretical studies of alkanedithiols ranging from butanedithiol to decanedithiol have shown that
self assembled monolayers, formed from either vapour and liquid phases, can exist in mixed lying-
down and standing-up phases on thermally deposited, poly-crystalline Au (111) surfaces and on single
crystals. \[84–86\] These studies have also shown that as alkane chain length decreases, the lying-down
phase becomes more favoured, and for butanedithiol, only the lying-down phase is formed. As NP self-
assemble on a butaneditiol-functionalized Au electrode surface, at least one of the thiols has to weaken
its interaction with the surface and interact with the NP. In principle a weak interaction with the NP,
caused by strong butanedithiol-surface interaction or steric hindrance due to other molecules, could lead
to non-ohmic contact with the gold NP film and result in a small contact resistance. A small barrier
can arise from a surface dipole and contact potential generated at the contact with the Au NP film. \[84\]
Due to the large curvature of the NPs arising from their small radius, the standing-up phase should be
more favoured by butanedithiols on NPs. This is consistent with the observation that conductance vs.
temperature behaviour of thick NP films is metallic, rather than through- or over-barrier that would be
expected if inter-NP contacts were poor. This is also consistent with facile dielectric breakdown occurring
in the break junction samples. Had there been inter-NP barriers throughout the film, voltage drops would
occur throughout the film as well, while if the barriers were located primarily at the interface between the
NP film and deposited Au electrodes (as the combined two- and four-probe data indicate), voltage drops
would be much more concentrated at these regions and, therefore, much more effective in generating
breakdown. These results suggest that, in order to reduce such contact resistance, short molecules that
favour a standing-up phase are preferable when self-assembling architectures on electrodes. At the same
time, they also demonstrate that four-probe methods are effective in overcoming such contact resistances
and thereby enabling studies of the electronic properties of such architectures themselves.
6.5 Conclusion

In summary, we have found that if two-probe conductance vs. temperature measurements of a material 1) contain contributions from a small contact barrier as well as metallic and non-metallic components of the material; and 2) conductance tends to a finite, non-zero value as temperature drops (satisfying the definition of a metal), then one can safely conclude that the material is a metal. If, however, conductance tends to zero, the role of contact resistance must be carefully analyzed to determine the nature of the material. Using a two-probe break junction with sufficiently thick butanedithiol-linked Au NP films, we showed that we could observe a breakdown of contact resistance and thereby study conductance of metallic films themselves down to low temperatures where barrier effects would have otherwise dominated. Also, by using a four-probe electrode geometry, we could distinguish film vs. film+contact behaviour, enabling identification of metallic films closer to the insulator-to-metal transition. This study shows that being able to study conductance of nanoengineered materials unobscured by contact effects is desirable as it can better reveal behaviours exhibited by nanoengineered materials themselves.

6.6 Appendix

6.6.1 Two-probe and Four-probe measurements

Two-probe measurement For low current (< 5 mA) two probe measurements, a small modulation voltage, \( \tilde{V} \), was combined with a DC bias voltage, \( V \), using a homemade summing amplifier. The summed voltage was then applied to the sample. The resulting current, \( I(\tilde{V} + V) \), was amplified using a current-to-voltage convertor (gain resistor \( R_g \) and output voltage \( R_g I(\tilde{V} + V) \)) and then input to a lockin amplifier. Since

\[
R_g I(\tilde{V} + V) = R_g I(\tilde{V}) + R_g \tilde{V} \frac{\partial I(\tilde{V})}{\partial \tilde{V}} + ...\number{6.1}
\]

and the lockin monitors the sinusoidal component of its input, its output, \( R_g \tilde{V} \frac{\partial I(\tilde{V})}{\partial \tilde{V}} \), is proportional to conductance (see Fig. 6.8). The conductance was recorded as a function of DC bias voltage using a data acquisition card. \( \tilde{V} \) is dropped across both the film and the contacts, and \( \frac{\partial I(\tilde{V})}{\partial \tilde{V}} \) vs. \( \tilde{V} \) includes contributions from both.

For high current (> 5 mA) two probe measurements, the summed voltage was applied to the sample and a known test resistor, \( R_{test} \), in series. The voltage drop across the test resistor was input to an op-amp buffer and its averaged, time-independent component, \( \tilde{V}_m \), was recorded. The sinusoidal component of the voltage drop, \( \tilde{V}_m \), was also monitored using a lockin. This information was used to determine the
Figure 6.8: A schematic of an arbitrary current vs. voltage curve showing the effect of a small voltage modulation.

The current, $I$, across the sample and the test resistor are equal:

$$I(\bar{V} + \tilde{V}) \approx I(\bar{V}) + \bar{V} \frac{\partial I(\bar{V})}{\partial \bar{V}} \approx \bar{V}_m + \tilde{V}_m$$  \hspace{1cm} (6.2)

Comparing sinusoidal components gives

$$\frac{\partial I(\bar{V})}{\partial \bar{V}} \approx \frac{\tilde{V}_m}{\bar{V}_m R_{test}}$$  \hspace{1cm} (6.3)

This result can be used to determine conductance of the sample as a function of voltage applied across the sample since the voltage drop across the sample is determined by subtracting the total voltage applied and the measured voltage drop across the test resistor.

Four-probe measurement  Fig 6.9 shows a schematic of the four-probe electrode configuration. DC and AC voltages ($\bar{V}$ and $\tilde{V}$ respectively) are summed and applied to probe 1; current, $I(\bar{V} + \tilde{V})$, flows in/out of probe 4. A voltage drop is measured across probe 2 and probe 3 using high input impedance operational amplifiers ensuring that essentially no current flows in/out of these probes. Therefore, the current flowing through the sample between probes 2 and 3 is also $I(\bar{V} + \tilde{V})$. This current induces a voltage drop across the film itself between probes 2 and 3 that has both DC and AC components. Since no current flows through probes 2 and 3, by Ohms law, the voltage drop measured across probes 2 and 3 is also the voltage drop across the film itself between these probes, notwithstanding the presence of
contact resistances.

The conductance of the film itself, excluding contact effects, as a function of the voltage dropped across the film ($V_{23}$, which is also the DC component of the voltage drop measured across probes 2 and 3, as mentioned) is

$$\frac{dI}{dV_{23}} = \frac{dI}{dV} \frac{dV}{dV_{23}} = \frac{df}{dV}$$

(6.4)

$\frac{df}{dV}$ can be measured as described above. $V_{23}$ varies with $\tilde{V}$ as shown schematically in Fig. 6.10. When $\tilde{V}$ is modulated by $\tilde{V}$, the response $\tilde{V}_{23}$ changes by $\tilde{V}$, which can be measured across probes 2 and 3 using a second lockin:

$$V_{23} = V_{23}(\tilde{V} + \tilde{V}) = V_{23}(\tilde{V}) + \tilde{V} \frac{\partial V_{23}(\tilde{V})}{\partial \tilde{V}}$$

(6.5)

Thus,

$$\tilde{V}_{23} = \tilde{V} \frac{\partial V_{23}(\tilde{V})}{\partial \tilde{V}}$$

(6.6)

and the conductance of the film as a function of $\tilde{V}_{23}$ is given in terms of measurable quantities:

$$\frac{dI}{dV_{23}} = \frac{dI}{d\tilde{V}} \frac{\tilde{V}}{\tilde{V}_{23}}$$

(6.7)
Figure 6.10: A schematic graph showing an arbitrary response of the voltage drop across probes 2 and 3 as a function of the total applied drive voltage. The graph also shows the effects of an arbitrary modulation drive on the response voltage.
Chapter 7

Conductance peaks and Exotic Metallic Behavior in a Nanoengineered Material: signatures of correlated quasiparticles


Author Contributions  M. Tie prepared samples and performed measurements resulting in data found in Figure 7.2, 7.4, 7.5, 7.6 and 7.7. P. Joanis prepared samples and performed measurements resulting in data found in Figure 7.3. M. Tie prepared all figures, data analysis, and contributed to writing the manuscript. Y. Suganuma provided STM image for Figure 7.1b and provided manuscript feedback. A.-A. Dhirani provided guidance in experimental and theoretical direction and contributed to writing the manuscript.
7.1 Abstract

We have studied conductance ($g$) of 1,4-butanedithiol-linked Au nanoparticle films (NPFs) through a percolation Mott-Hubbard insulator-to-metal transition (MH-MIT) from a Mott insulating phase with significant nanostructure-induced Coulomb charging barriers to a metallic phase. Near the transition, the NPFs traverse an exotic metallic phase exhibiting a pseudogap-like behavior and a zero-bias conductance peak. The peak decays rapidly with increasing temperature, yielding power law fits with an average exponent of $3.8 \pm 2.9$ and surviving in some samples up to remarkably high temperatures of $\sim 20$ K. We propose that the peak is an Abrikosov-Suhl resonance previously observed in non-nanoengineered, correlated materials near MH-MITs. Since nanostructures can be controllably synthesized over a wide range of parameters, the study highlights an opportunity to use "nanoengineered correlated materials" as a powerful new platform to study this exotic metallic phase and electron correlations.

7.2 Introduction

In the present study, we explore the potential of nanostructures to serve as building blocks for "nanoengineered correlated materials" with a similar competition, particularly near a Mott-Hubbard insulator-to-metal transition (MH-MIT). The competition is achieved using 1) Au nanoparticles (NPs) which results in strong Coulomb interactions, 2) short 1,4-butanedithiol (HS(CH$_2$)$_4$SH) linkers between NPs which facilitate delocalization, and 3) a percolation-driven transition to tune the materials between a Mott insulating phase dominated by Coulomb charging barriers [7,29] and a metallic phase [14,16,37,38]. Using a two-probe configuration, in previous studies we found that these systems can exhibit strong Coulomb interactions and a MH-MIT [16,36]. Here, we study such films across the transition using a four-probe configuration to eliminate electrode contact resistance in order to better reveal film properties, especially near the MH-MIT and on the metallic side when film resistances can be low and contact resistance can be significant [26]. We also use a tunnel junction, two-probe configuration to interrogate density of states of the films. Near the transition, four-probe and tunneling conductance ($g$) measurements reveal a peak which we attribute to an Abrikosov-Suhl (AS) resonance that has been previously observed in non-nanoengineered, strongly correlated systems near MH-MITs [63–69]. We propose that a percolation Hubbard model, as a refinement of the usual Hubbard model, can capture the percolative nature of the MH-MIT in the present system.
7.3 Experimental Method

Both four-probe and tunnel junction samples were fabricated on glass substrates cut from microscope slides. The substrates were prepared as per Section 5.2. For four-probe samples, \( \sim 6 \) mm long, 200 nm thick, 0.2 mm wide gold (Au) electrodes separated by 2 mm were thermally deposited on to the mercaptosilane functionalized glass slides using shadow masks. For tunnel junction samples, \( \sim 3 \) mm long, 3 mm wide, 175 nm thick aluminum electrodes separated by \( \sim 0.25 \) mm were used. The aluminum electrodes were exposed to air to grow an oxide layer that served as the tunnel barrier. For both types of samples, copper magnet wires were soldered to the electrodes using indium before film self-assembly. Butanedithiol used to link Au NPs was purchased from Sigma Aldrich and used as received. Au NPs in toluene were synthesized using the method described in Section 5.1. NPFs were self-assembled on the mercaptosilane functionalized glass slides with pre-deposited electrodes by the method described in Section 5.2. With increasing NP/dithiol immersion cycles, “clusters” of molecularly-linked NPs grow and become sample spanning at a percolation threshold. Further immersion cycles cause clusters to grow still larger. Fig. 7.1b shows a scanning tunneling microscope image of an NP film (NPF) self-assembled on a silicon/silicon oxide surface after 4 immersion cycles. Although the particles are linked.
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with dithiol molecules, individual NPs in the film are clearly resolved. Methods for NPF self assembly and characterization of NPFs are shown in Section 5.2. Figure 5.1b shows a transmission electron microscope image of individual gold NPs used to fashion the NPFs. The NPs have an average diameter of $\sim 5$ nm. Ultraviolet-visible (UV-vis) absorption spectroscopy of isolated NPs in solution (Fig. 5.1a) exhibits a plasmon peak at $\sim 540$ nm. Figure 5.3a shows UV-vis absorption spectra of dithiol-linked NPFs on amiosilanized glass sildes with one (bottom curve) to eight (top curve) immersion cycles. The plasmon peak shifts to longer wavelengths with increasing number of immersion cycles due to NP coupling in the NPFs. The absorption grows approximately linearly with number of immersion cycles, indicating that a constant amount of material is added to the NPFs per cycle (see Fig. 5.3b). Atomic force microscopy measurements done on three samples showed an average of 3.5 nm per immersion cycle (see Figure 7.2 for an example of an AFM image for 31 immersion cycles sample.) The amount of NP deposited per immersion depended on NP solution concentration and immersion time. As a result, room temperature film resistance was monitored after each NP/dithiol immersion cycle and self-assembly was continued until a desired resistance was reached. Circuitry and analysis used for four-probe measurements are described in detail in Section 6.3. Conductance was determined at various temperatures down to 2 K using a Quantum Design PPMS. To confirm reproducibility, the evolution of eight tunnel junction and ten four-probe samples were studied in detail, each at several NPF thicknesses.

7.4 Results and Discussion

Figure 7.3a shows the evolution of $g$ vs. temperature ($T$) for samples S12, S18 and S25 with 12, 18 and 25 immersion cycles, respectively. Since S12’s zero-bias $g$ vanishes at low $T$, it has an energy gap at the Fermi energy and is an insulator. The gap is also evidenced by zero-bias $g$ suppression at low $T$ (Fig. 7.3b), which can be attributed to charging barriers [36] and electron-electron interactions [58]. Previous studies have shown that NPFs with small numbers of immersion cycles can exhibit significant Coulomb barriers and that charges flow between clusters via a combination of tunneling and thermally and/or voltage assisted processes [14, 17, 36, 37, 87, 88].

Figure 7.3a shows that S25 is a metal: $g$ remains nonzero at low $T$s, implying the existence of current pathways that have no energy gap at the Fermi level. As an insulating NPF such as S12 is subjected to more immersion cycles, clusters generally grow and charging barriers decrease. Eventually, clusters span the sample, and the film becomes metallic. Some vestiges of thermally assisted $g$ are observed at lower $T$s. At higher $T$s from $\sim$50 K to 300 K, $g$ drops due to increasing electron-phonon scattering. Fig. 7.3c reinforces this picture: $g$ vs. voltage ($V$) is nearly Ohmic, with $<1\%$ zero-bias suppression at low $T$s.
Figure 7.2: Atomic force microscopy data of a 4-probe sample with 31 immersion cycles, intentionally scratched to allow thickness measurements. (a) Deflection image and (b) trace of the cross section. Thickness is approximately 90 nm.
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Figure 7.3: Four-probe conductance ($g$) data for an NPF at 12, 18 and 25 immersion cycles (S12, S18 and S25, respectively). (a) Zero-bias $g$ vs. $T$. The data at each immersion cycle are normalized to their respective values at 300 K, $1.1\times10^{-5}$, $1.9\times10^{-4}$ and $3.5\times10^{-3}$ $\Omega^{-1}$ in order of increasing immersion cycles. Corresponding $g$ vs. voltage ($V$) sweeps at various $T$s for (b) S12, (c) S25 and (d) S18. The $g$ vs. $V$ sweeps at each $T$ are normalized to their respective values at (b) -90 mV and (d) -2 mV.
Figure 7.3a shows that S18 exhibits intermediate behavior. Non-zero $g$ at the lowest T's implies that the sample is a metal by definition; however, unlike typical metals, $g$ increases significantly with increasing T's. This T dependence is “pseudogap-like” in the sense that it can be generated by a density of states that is gapless at and increases away from the Fermi level. Quite remarkably, this intermediate sample also exhibits a zero-bias conductance peak that grows rapidly with decreasing T below 4 K (Fig. 7.3d). We observed such a peak in five out of ten four-probe samples studied and explored a number of potential explanations for its origin. Magnetic impurities are known to generate zero-bias conductance peaks via the Kondo effect; however, magnetic field induced Zeeman splitting of the peak, expected in the magnetic Kondo effect, was not observed (see Fig. 7.4). For a Kondo peak that vanishes by $T_K \sim 4$ K, using $k_B T_K = g_e \mu_B B$ where $k_B$ is Boltzman’s constant, $\mu_B$ is the Bohr magneton, and $g_e \sim 0.4$ (a thiol bound to gold has a charge transfer of $\sim 0.4e$ per molecule [89]), we expect to observe the zero-bias peak in $g$ vs. $V$ to split by $B \sim 15$ T and, therefore, zero-bias $g$ to drop with increasing magnetic field. For such a sample, we varied magnetic field upto 10 T. We observed a drop in the zero-bias magnetoconductance by 4 T, but peaks in $g$ vs. $V$ at both 0 T and 4 T appeared unchanged. Beyond 4 T, zero-bias magnetoconductance did not exhibit any further systematic drop. In addition, a Kondo peak is expected to exhibit a log T dependence; however, we found that our data is better fit with a power law of T rather than log T or Arrhenius behavior (see Fig. 7.5d and Fig. 7.6). In principle, Joule heating can also generate a zero-bias $g$ peak in typical metals: as bias magnitude increases, more current flows, T increases due to Joule heating, and increased electron-phonon scattering decreases $g$. Data for another NPF obtained at 6, 9, 13 immersion cycles, all of which are metallic (Fig. 7.5a),
Figure 7.5: Four-probe control measurements exploring potential explanations for the zero-bias conductance peak observed in Figure 7.3 (d). (a) $g$ vs. $V$ sweeps normalized at $-45$ mV and obtained at $2$ K using a film at 6, 9 and 13 immersion cycles (S6, S9 and S13, respectively; sweeps offset for clarity). (a, inset) A magnified version of a $g$ vs. $V$ sweep for S13. (b) Zero-bias $g$ vs. $T$ data for S6, S9 and S13, normalized to their values at 300 K, $5 \times 10^{-4}$, $2 \times 10^{-3}$ and $8 \times 10^{-3} \Omega^{-1}$, respectively. (c) $g$ vs. $V$ sweeps at various $T$s for a different film with 11 immersions. (d) The zero-bias $g$ vs. $T$ behavior corresponding to (c) with an inset of log–log plot of zero-bias conductance peak ($g_p$) vs. $T$. The slope yields a power law, $g_p \propto T^{-\nu}$, with exponent $\nu = 3.43$. 
provide evidence excluding a Joule heating model. A Joule heating model predicts that current and heating increase monotonically with bias voltage magnitude, while $g$ vs. $V$ data in Fig. 7.5a are non-monotonic. $g$ vs. $V$ plots all exhibit zero-bias conductance peaks; but eventually at larger bias voltage magnitudes, $g$ increases, as observed using insulating samples (Fig. 7.3, S12) and attributed to charging barriers/electron-electron interactions. With increasing immersion cycles ($S6 \rightarrow S9 \rightarrow S13$ in Fig. 7.5a), the zero bias peaks and $g$ increases at larger bias voltage magnitudes both become less pronounced, and $g$ tends to become Ohmic. Although we use In to solder magnet wire to electrodes and In superconducts below 3.4 K, we can rule out Andreev reflections at NPF-In contacts as the cause of the peak since we use a four-probe method. This explanation is excluded also by data in Fig. 7.5c for another sample that exhibited a zero-bias peak that persisted up to remarkably high $T_s$ - almost 20 K, well above the superconducting transition temperature of In. This zero-bias peak is readily observed also in the zero-bias $g$ vs. $T$ data (Fig. 7.5d) and fits a $T^{-\nu}$ power law reasonably well with $\nu = 3.43$. Values of $\nu$ varied from sample-to-sample, ranging from 1.3 to 8.5 with an average value of 3.8 ± 2.9. This rapid drop of zero-bias $g$ with increasing $T$ exhibited by the metallic phase near the MIT contrasts with the slow drop exhibited by metals due to electron-phonon scattering well beyond ($S25$ in Fig. 7.3a and S13 in Fig. 7.3).
7.5b), providing strong indication that the two phases are qualitatively different.

Since \( g \) for a tunnel junction is proportional to density of states of materials it contacts, we also measured NPF \( g \) using an aluminum oxide (\( \text{Al}_x\text{O}_y \)) tunnel junction (\( \text{Al}/\text{Al}_x\text{O}_y/\text{NPF}/\text{Al}_x\text{O}_y/\text{Al} \)) to explore whether the zero-bias peak is associated with increased NPF density of states at the Fermi energy (Fig. 7.7). Having an \( \text{Al}_x\text{O}_y \) tunnel junction in series with the NPF has an added benefit of reducing current and Joule heating effects. Metal samples exhibited thermally assisted \( g \) which plateaued to a non-zero value at low \( T \)s. The plateau is a hallmark of electron tunneling which becomes \( T \) independent when thermal fluctuations are much smaller than tunneling barrier heights. At higher \( T \)s when the tunnel barriers are thermally overcome, \( g \) vs. \( V \) data for a majority of samples exhibited zero bias suppression which can be attributed to charging barriers/electron-electron interactions as for insulating four-probe samples (Fig. 7.3b). One of the eight samples exhibited a clear zero-bias peak that became more pronounced at lower \( T \)s. Since \( g \) for the tunnel junction geometry is proportional to the product of the density of states of aluminum and the NPF, we attribute the zero-bias peak to the density of states of the NPF. We speculate that the peak is observed with a lower sample yield using \( \text{Al}_x\text{O}_y/\text{NPF} \) two-probe geometry compared with \( \text{Au/NPF} \) four-probe geometry due to a combination of factors. Near contacts, NPFs comprise a mixture of metallic and insulating current pathways, and tunnel current exponentially favors barriers that are lowest/thinnest. Consequently, current can likely find the metallic pathways more easily when flowing through barrierless contacts rather than tunnel barriers. This picture is consistent with a previous magnetoconductance study of metallic NPFs using tunnel junction contacts [90].

To interpret the remarkable metallic behavior exhibited by NPFs near the MIT, we use the one-band Hubbard Hamiltonian \((H)\) as a guide:

\[
H = \sum_{<i,j>,\sigma_s} t_{ij} C_{i,\sigma_s}^\dagger C_{j,\sigma_s} + U \sum_i n_{i,\uparrow} n_{i,\downarrow} \tag{7.1}
\]

where \( C_{i,\sigma_s}^\dagger \) (\( C_{j,\sigma_s} \)) are creation (annihilation) operators for electrons at site \( i \) (\( j \)) and spin \( \sigma_s \) (\( \uparrow \) or \( \downarrow \)), \( t_{ij} \) is the transfer energy, \( U \) is the on-site Coulomb repulsion energy, \( n_{i,\sigma_s} = C_{i,\sigma_s}^\dagger C_{i,\sigma_s} \) is the number operator, and the first sum is over nearest neighbors and spins. The first sum is the total kinetic energy, and the second is the total potential energy. The Hubbard model is the simplest picture of a lattice with electrons that can transfer from site-to-site and interact [2, 59–62]. Key parameters describing its solution are \( U \) and bandwidth \((W)\) determined by the total kinetic energy. In the half-filled Hubbard model, a tendency for on-site repulsion \( U \) to yield an insulator competes with a tendency for site-to-site transfer to yield a broad band metal. The model predicts that in the limit that \( U/W \) is small, electrons
are delocalized, yield a metal, and are described by band theory with a band at the Fermi energy with bandwidth $W$. In the opposite limit that $U/W$ is large, electrons are localized, yield Mott insulators, and are described by localized states which yield upper/lower Hubbard bands with bandwidths $\sim W$ located $\pm U/2$ from the Fermi energy. Remarkably, when $U \sim W$, in addition to the upper/ lower Hubbard bands, the model predicts the density of states has a third quasiparticle (QP) peak or AS resonance. The QP peak is located between the upper/ lower Hubbard bands at the Fermi energy and appears at $T_s$ below $T^*$, which characterizes the QP peak width. The QP peak describes coherent electrons at $T_s$ below $T^*$. Above $T^*$, this coherent phase is thermally destroyed and the peak disappears, leaving behind incoherent transitions from the lower to the upper Hubbard bands. The QP peak appears at a critical value of $U/W$, and increases in strength with decreasing $U/W$. As $U/W$ decreases further, eventually the gap between the upper/ lower Hubbard band closes. This QP peak has been observed in a number of strongly correlated systems ranging from quasi-two dimensional organic molecular crystals [68] to transition metal oxides [63,64,66,67,69] and calcogenides [65]. The kinetic and potential energy terms of the microscopic Hubbard model thus, respectively, capture the macroscopic behavior exhibited by NPFs in the limit that the number of immersion cycles is large ($U \ll W \rightarrow$ Ohmic, metallic behavior) and small ($U \gg W \rightarrow$ zero bias $g$ suppression and insulating behavior due to charging barriers). In between ($U \sim W$), the model predicts a QP peak, as observed, and exotic Fermi liquid metal with strongly interacting, correlated electrons. The Hubbard model can be mapped onto the Anderson impurity (AI) model in the limit of infinite dimensions, and yields the QP peak in analogy to the Kondo resonance.

Figure 7.7: Control measurements exploring potential explanations for the zero-bias conductance peak observed in Fig. 7.3 (d). The conductance vs. voltage sweeps were obtained at various temperatures using aluminum/aluminum oxide tunnel junction contacts and two different films, each with 12 immersion cycles. The conductance vs. voltage sweeps at each temperature in (a) are normalized to their respective values at -1.5 V. The insets show the corresponding conductance vs. temperature behavior.
In view of the NPF architecture, the AI model itself provides a microscopic perspective of the present system in terms of clusters interacting with a NPF environment. Such a description has been used to estimate activation energies exhibited by insulating NPFs [14,36,37,87].

A refinement of Hubbard lattice model can serve to accommodate the percolative manner in which NPFs grow (Fig. 7.8). In a percolative Hubbard lattice model, a lattice site becomes occupied by an NP with some probability, and a group of adjacent occupied sites constitutes a cluster of linked NPs. The potential energy varies from site-to-site ($U_i$). $U_i$ to place a second electron at occupied sites depends on the size and environment of the cluster within which the site is located since smaller, more isolated clusters have smaller capacitances and are more difficult to charge. Due to the exponentially decaying tunneling wavefunction of NPs beyond their surfaces, wavefunction overlap and, therefore, $t_{ij}$ decrease from nearest-neighbour to next-nearest-neighbor transfer, etc. Depending on local filling, $U_i$ and $t_{ij}$ have a distribution of values. As the lattice fills and clusters grow, $U_i$ tend to smaller values and $t_{ij}$ tend to larger values until at a threshold, before a lattice spanning cluster forms (the classical percolation MIT), a quantum percolation MH-MIT is expected. An AS resonance would still be expected as electrons delocalize and acquire large effective masses due to correlations. There are still some noteworthy differences between the present system and such a percolation Hubbard lattice model, the most obvious being that the present system is spatially disordered. Also, in practice there can be a distribution of background charges that can affect $U_i$. However, these various sources of disorder evidently are not sufficient to prevent NPFs from becoming metals, and percolation lattice models have been useful in modeling MITs in various disordered materials, including granular [91] and strongly correlated systems [92–94]. Interestingly, a number of studies have shown that nano-scale structures are common in correlated systems [4]. As transitions proceed, competing phases nucleate and grow in a percolative manner, much like the percolation-driven transition exhibited by the nanoengineered class of materials discussed here.
Figure 7.8: Schematic showing a percolation Hubbard lattice model for the nanoparticle film. A 1-dimensional row array is used for illustration. As the number of immersion cycles increases, lattice sites are filled with nanoparticles, and linked nanoparticles form metallic clusters that grow. $U_i$ and $t_{ij}$ vary from site-to-site depending on local filling. Because of interactions between nanoparticles, $U_i$ tends to decrease and bandwidth tends to increase with increasing filling fraction. The evolution of density of states (DOS) of array with increasing filling fraction is shown on the left.
Chapter 8

Conductance of Molecularly-Linked Gold Nanoparticle Films Across an Insulator-to-Metal Transition: from hopping to strong Coulomb electron-electron interactions and correlations


Author Contributions  M. Tie prepared samples, performed measurements, analysed data, and contributed to writing the manuscript. A.-A. Dhirani provided guidance in experimental and theoretical direction and contributed to writing the manuscript.
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8.1 Abstract

We study the influence of Coulomb effects on conductance ($g$) of 1,4-butanedithiol-linked gold nanoparticle (NP) films near a percolation insulator-to-metal transition. On the insulating side, $g \sim \exp[-(T_o/T)^{-1/2}]$ where $T$ is absolute temperature, a behavior predicted by Efros-Shklovskii’s theory for charges optimizing pathways that accommodate Coulomb charging barriers. On the metallic side below $\sim 20K$, $g$ varies linearly with $T^{1/2}$. Such a correction to $g(T = 0)$ is predicted by Altshuler-Aronov’s theory for Fermi liquid metals when disorder mediates electron-electron ($e-e$) Coulomb interactions. Remarkably, in the present system, the $T^{1/2}$ component of $g$ is significant compared to $g(T = 0)$, and fitting to Altshuler-Aronov’s theory yield elastic scattering lengths that are anomalously small - much smaller than the distance between atoms (Ioffe-Regel limit required for metals). Previous studies of materials such as fullerites, layered organic salts and transition metal compounds have also reported such anomalously small scattering lengths and large $T^{1/2}$ components and attributed them to strong Coulomb mediated $e-e$ correlations, which we believe is likely the case in the present system as well. This study highlights a potential opportunity to use molecularly-linked nanoparticle films as a new platform to study strongly correlated electrons in a controlled fashion.

8.2 Introduction

Coulomb effects can be significant in both insulators and metals. In a variety of insulating materials such as films of deposited materials [44,95,96] and chemically synthesized nanoparticles (NPs), [14,17–19,37,46,47,50,97] Coulomb charging energies give rise to large energy barriers that electrons have to overcome in order to conduct. As a result, conductance ($g$) vanishes exponentially as $T \to 0K$: 

$$g \sim \exp[-(T_o/T)^{\nu_H}],$$

where $T_o$ is a constant and $T$ is absolute temperature. In such materials when charges are well localized, that is far from any insulator-to-metal transition, Coulomb effects dominate, and these materials exhibit simple activated behavior with $\nu_H = 1$. $T_o$ is then related to the Coulomb charging energy by $k_B T_o = e^2/2C_S$ where $C_S$ is the total capacitance of the grain/dot to be charged, $k_B$ is Boltzmann’s constant and $e$ is electron charge. In semiconductors with sufficient doping, Efros and Shklovskii showed that Coulomb effects can be manifest through variable range hopping (VRH). [48] In this process, electrons may hop from site-to-site by thermally overcoming charging barriers and tunneling. The hopping probability
depends on the distance, \( z \), between dopant sites as

\[
P \sim \exp(-2z/\xi - \Delta E/k_B T),
\]

(8.2)

where \( \xi \) is the localization length and \( \Delta E \sim e^2/z \) is the Coulomb interaction energy. The first term in equation (2) arises from tunneling and the second from thermally assisted transport. Optimizing the probability by solving \( dP/dz = 0 \) results in \( \nu_H = \frac{1}{2} \).

For metals, conductance is no longer limited by energy barriers; instead, electrons remain delocalized even as \( T \to 0 \) K. Transport is limited by scattering, and at low \( T \), conductivity takes the form

\[
\sigma(T) = \sigma_0 + AT^q,
\]

(8.3)

where the temperature independent term arises from elastic impurity scattering and additional \( T \)-dependent terms arise from phonon scattering or \( e-e \) collisions. [53] In the clean limit, \( e-e \) collisions according to conventional fermi liquid theory yield \( q = 2 \). In the presence of disorder, electrons have a tendency to diffuse. Altshuler and Aronov showed that this provides electrons with more opportunity to interact and leads to enhanced \( e-e \) interactions. In this limit, \( q = \frac{1}{2} \). [55,98] At low \( T \), the \( T^{1/2} \) term dominates other \( T \)-dependent terms, and conductivity is given by [54,99,100]

\[
\sigma(T) = \sigma_0 + AT^{1/2},
\]

(8.4)

where the coefficient \( A \) in equation (4) is given by Altshuler and Aronov [55,56] as

\[
A = \lambda \left( \frac{k_B \tau}{\hbar} \right)^{1/2} \left( \frac{E_F \tau}{\hbar} \right)^{-2} \sigma_0,
\]

(8.5)

\( \sigma_0 \) is given by Boltzmann transport,

\[
\sigma_0 = \eta e^2 \tau / m^*.
\]

(8.6)

\( \lambda \approx 1, \eta \) is the electron density, \( \tau \) is the scattering time, and \( m^* \) is the effective mass. This behavior has been reported on the metallic side of insulator-to-metal transitions in disordered materials such as doped semiconductors [57,58,101] and transition metal oxides. [92,102,103] A theoretical study showed that equation (4) was also applicable to granular metals with strong intergranular coupling in the limit of low temperatures. [104]

Recently, there has been increasing interest in molecule-linked nanoparticle films (MNPFs) as they
can exhibit a wide range of behaviors from an insulating state, with Coulomb barriers being important, to a metallic state. An attractive feature of MNPFs is that their behavior can be easily tuned through choice of NP (e.g. size, shape and chemical composition), molecular linker (e.g. chemical moieties that perform the linking, degree of conjugation, length, other functionalities that can be incorporated, etc), and film architecture (e.g. degree of order, film thickness). [6, 8] The insulating state occurs in the limit that NPs are weakly coupled, and Coulomb charging energies present large barriers to conduction. MNPFs exhibit energy barriers that correlate well with the single electron charging energy for a NP surrounded by a shell (the shell representing the surrounding film); that is, \( E_c = \frac{e^2}{8\pi\epsilon_\sigma\epsilon_r} \left( \frac{1}{\zeta^2} - \frac{1}{s^2} \right) \) where \( \epsilon_r \) is the dielectric constant, \( \zeta \) is the radius of the NP and \( s \) is the inter-NP separation. [6, 14, 18, 36]. Examples of linkers that yield insulating MNPF using gold NPs include alkanedithiols containing more than five carbons, [16, 37] dithiolated terthiophene, [18] 1,4-bis(mercaptoethyl) benzene/cyclohexane and 1,4-bis(mercaptoacetamido) benzene/cyclohexane. [14] Sufficiently thick MNPFs fashioned using alkanedithiols with four or fewer carbons, [16,37] and 1,4-phenylene -bis(dithiocarbamate) [14] exhibit metallic behavior. MNPF behavior can also be controlled via film thickness. As films are self-assembled by immersing a functionalized substrate alternately in gold NP and linker solutions, more material is deposited, clusters of linked NPs grow and cluster charging energies decrease. Eventually, MNPFs cross a percolation threshold and transition from an insulating to a metallic state. [16, 36, 105] Interestingly, near the transition, both Coulomb interaction and electron delocalization are expected to be important, and we have shown that in this regime, butanedithiol-linked gold NP films exhibit a conductance peak at zero bias, which we attribute to an Abrikosov-Suhl resonance. [2,23,59]

To our knowledge, studies of Coulomb effects in MNPFs have focused primarily on the insulating state and barriers generated by charging effects. However, if Coulomb effects are significant in the insulating state near the insulator-to-metal transition, they are expected to persist on the metallic side, and be especially important near the transition. Also, disorder that is inherent in self-assembled MNPFs is expected to enhance \( e - e \) effects in the metallic state.

Here we study \( g vs T \) of MNPFs through the insulator-to-metal transition, and find that, near the transition at low temperatures, \( g vs T \) exhibits exponential behavior (equation (1) with \( \nu_H = \frac{1}{2} \)) on the insulating side and \( T^{1/2} \) behavior on the metallic side. By fitting these behaviors to theory, we extract hopping distances and \( e - e \) scattering lengths, respectively. The latter are found to be anomalously short near the transition, which we attribute to strong \( e - e \) interactions that can generate strong \( e - e \) correlations in MNPFs.
8.3 Experimental Method

MNPFs were fabricated by first preparing the glass substrates as per Section 5.2. Four 8 mm long and 150 nm thick gold electrodes separated by $\sim 2$ mm were thermally deposited onto the glass slides. Indium solder was used to attach magnet wires before MNPF assembly. Gold NPs ($d \sim 5$ nm) were synthesized as per Section 5.1. Butanedithiol, which was used to link gold NPs, was purchased from Sigma-Aldrich and used as received. MNPFs were self-assembled on the glass substrates with predeposited gold electrodes as per Section 5.2. A total of 10 samples were made. For each of the samples, $g$ of the MNPFs was measured as a function of $T$ for various numbers of immersion cycles through the insulator-to-metal transition. A total of 31 $g$ vs $T$ measurements were conducted using the 10 samples.

The measurements were conducted using a physical property measurement system (PPMS) from room temperature down to 2 K. A 10 mV ac voltage supplied by a Stanford Research Systems lockin (model SR830DSP) was applied across the outer electrodes and the resulting current was amplified using a homemade current-to-voltage amplifier. The output of the amplifier was fed back into the lockin, and the output of the lockin, which is proportional to the total differential conductance ($G$) and includes contributions from contact resistances, was recorded by a National Instruments PCIMIO 16X data acquisition card. The associated ac voltage drop across the inner two electrodes ($V_{inner}$) was measured using high impedance voltage followers and a second lockin amplifier. Film conductance ($g$) was found as described in Section 6.3.

8.4 Results and Discussion

Figure 8.1 shows all 31 $g$ vs $T$ data sets, each normalized to its respective $g$ at 300 K. Of the 31 data sets, 30 go down to 2 K and one to 15 K, as the conductance of the latter became too small to measure at lower temperatures. MNPF conductance at 2 K for the 30 data sets measurements range from $0.0164$ (top) to $4.85 \times 10^{-8}$ Ω$^{-1}$ (bottom). Figure 8.1 (inset) shows $g$ vs $T$ at low temperatures from 2 to 20 K. As $T \rightarrow 0$, conductance clearly vanishes for the bottom four data sets (insulating behavior, blue symbols) and goes to a finite number for the top ten (metallic behavior, red symbols). For the more conducting, metallic MNPFs, conductance decreases with increasing temperature at high $T$, a signature of electron-phonon scattering effects also seen in bulk metals. One data set exhibits an obvious peak below 3 K, which we attribute to an Abrikosov-Suhl resonance based on previous work, and which remarkably is visible in these data sets at this scale. [23] The remaining 17 data sets tend to near $g = 0$ at $T = 0$ K, and the associated MNPFs are near and straddle the insulator-to-metal transition (black symbols). Table 8.1
Figure 8.1: Conductance ($g$) vs Temperature ($T$) for various butanedithiol-linked gold nanoparticle films with various numbers of dithiol/nanoparticle immersion cycles. Conductance is normalized to $g(300 \text{ K})$. Values of $g(300 \text{ K})$ range from $0.0155$ to $7.63 \times 10^{-6} \Omega^{-1}$. (Inset) Magnification of the data shown in the main panel at low temperatures. The data have been normalized to $g(20 \text{ K})$. Values of $g(20 \text{ K})$ range from $0.0164$ to $1.35 \times 10^{-6} \Omega^{-1}$. 
lists log of the resistances at 2 K \([\log(r_{2K})]\) for these MNPFs. Since we are primarily interested in the regime around the transition, we focus on these 17 data sets for further analysis.

We explore various \(T\) dependencies for the conductance behavior through the insulator-to-metal transition. We confine our analysis to \(T < 20\) K to reduce contributions from higher temperature scattering processes. Figure 8.2 shows an Arrhenius plot, \(\ln[g/g(20\text{ K})]\) vs \(T^{-1}\), for the 17 data sets. None of the data sets exhibits linear, Arrhenius behavior. Figure 8.3a shows \(\ln[g/g(20\text{ K})]\) vs \(T^{-1/2}\) and figure 8.3b \(g/g(20\text{ K})\) vs \(T^{1/2}\) for the same data sets over the same temperature range. For clarity and to avoid overlapping curves, data sets are divided into two groups based on \(\log(r_{2K})\) ranges (namely, i) 3.79 to 4.21 and ii) 4.37 to 6.10), and the two groups are offset in both figures 8.3a and 8.3b. In the \(\ln[g/g(20\text{ K})]\) vs \(T^{-1/2}\) plot, the data sets corresponding to the less conducting films exhibit linear behavior as evidenced by their \(R^2\) values (see Table 8.1 and Fig. 8.4). This indicates that \(\nu_H = \frac{1}{2}\) behavior dominates on the more insulating side of this range. Note that although \(\nu_H = \frac{1}{2}\) is expected in an ES VRH picture of charges hopping between localized sites at various locations, for example between dopant sites in a semiconductor, a microscopic basis for the \(\nu_H = \frac{1}{2}\) behavior for films with metallic
Figure 8.3: a) $\ln[g/g(20 \text{ K})]$ vs $T^{-1/2}$ and b) $g/g(20 \text{ K})$ vs $T^{1/2}$ for various molecularly-linked gold nanoparticle films. $\log(r_{2K})$ values of the films range from 3.79 to 4.21 (group i) and 4.37 to 6.10 (group ii). Plots for the two groups of data sets are offset for clarity.
grains, particularly near an insulator-to-metal transition, needs to be clarified. In ES VRH, \( T_0 \) is given by
\[
T_0 = \frac{2e^2}{\pi\epsilon_r k_BT}\xi
\]
and the optimal hopping length \( z_{\text{opt}} \) is given by
\[
z_{\text{opt}} = \frac{\xi}{4}\left(\frac{T}{T_0}\right)^{1/2}.
\]
\( T_0 \) extracted from fits to data in figure 8.3a can be used to determine \( \xi \) and \( z_{\text{opt}} \), using \( \epsilon_r = 2.34 \) for alkanes [6]. The results are shown in Table 8.2. Both \( \xi \) and \( z_{\text{opt}} \) are on the order of \( \mu\text{m} \) and tend to increase with increasing conductance. In the present system, if charges hop between localized sites (for example on a NP), one would expect that more sites should be available as filling fraction increases, and the hopping distances should decrease closer to the insulator-to-metal transition, contrary to observation. A potential solution is to reinterpret the length \( z \) in equation (2) as the size of clusters \( L \) so that
\[
P \sim \exp\left(-\frac{2L}{\xi} - \frac{\Delta E}{k_BT}\right).
\]
In this case, the Coulomb energy barrier becomes associated with the single electron charging energy for a cluster \( \Delta E = E_c = e^2/2C_\Sigma \) where \( C_\Sigma \sim L \) and \( \Delta E \sim e^2/L \) in analogy with ES VRH. The Arrhenius term in equation (2) favors larger clusters that are easier to charge, while the decaying exponential term favors smaller clusters. This picture implies that charges traverse paths with optimal cluster sizes that can be quite large and grow as the granular film approaches the insulator-to-metal transition. Scaling arguments would then suggest that the clusters are actually insulating; [53] however, we find empirically that localization length scales are also very large and increase as the insulator-to-metal transition is approached. A proposed co-tunneling mechanism by which electrons can tunnel through an array of grains may account for this long range, exponentially dependent transport. [106]

Table 8.1: Conductance \((g)\) at 300 K, 20 K and 2 K for 17 data sets shown in figure 8.3. \( R^2 \) values are given for linear fits to data using \( g \) vs \( T^{1/2} \) and \( \ln g \) vs \( T^{-1/2} \). \( \Delta R^2 \) is given by \( R^2 \) of \( g \) vs \( T^{1/2} \) fit plot minus \( R^2 \) of \( \ln g \) vs \( T^{-1/2} \) fit.

<table>
<thead>
<tr>
<th>Label</th>
<th>( \log_{(10^2)} )</th>
<th>( g_{300K} )</th>
<th>( g_{20K} )</th>
<th>( g_{2K} )</th>
<th>( R^2 )</th>
<th>( R^2 )</th>
<th>( \Delta R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.79</td>
<td>3.44</td>
<td>1.63</td>
<td>0.99781</td>
<td>0.96559</td>
<td>0.03222</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.97</td>
<td>4.51</td>
<td>2.30</td>
<td>1.06</td>
<td>0.94636</td>
<td>0.04494</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.08</td>
<td>6.18</td>
<td>2.66</td>
<td>0.820</td>
<td>0.99785</td>
<td>0.03053</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.09</td>
<td>9.47</td>
<td>5.44</td>
<td>0.871</td>
<td>0.97359</td>
<td>0.01911</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.13</td>
<td>4.63</td>
<td>2.14</td>
<td>0.747</td>
<td>0.99660</td>
<td>0.01012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.17</td>
<td>5.90</td>
<td>2.50</td>
<td>0.671</td>
<td>0.99766</td>
<td>0.00641</td>
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<td></td>
</tr>
<tr>
<td>4.21</td>
<td>3.15</td>
<td>1.64</td>
<td>0.619</td>
<td>0.98768</td>
<td>0.00577</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.37</td>
<td>5.05</td>
<td>2.56</td>
<td>0.425</td>
<td>0.99148</td>
<td>0.00829</td>
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<td></td>
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<tr>
<td>5.06</td>
<td>1.97</td>
<td>0.658</td>
<td>0.0861</td>
<td>0.99926</td>
<td>0.00580</td>
<td></td>
<td></td>
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<tr>
<td>5.27</td>
<td>1.74</td>
<td>0.561</td>
<td>0.0542</td>
<td>0.99951</td>
<td>0.00051</td>
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</tr>
<tr>
<td>5.40</td>
<td>2.35</td>
<td>0.586</td>
<td>0.0401</td>
<td>0.99405</td>
<td>0.00276</td>
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<tr>
<td>5.63</td>
<td>1.98</td>
<td>0.487</td>
<td>0.0232</td>
<td>0.99177</td>
<td>0.00637</td>
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<tr>
<td>5.73</td>
<td>1.58</td>
<td>0.411</td>
<td>0.0184</td>
<td>0.99161</td>
<td>0.00776</td>
<td></td>
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</tr>
<tr>
<td>5.80</td>
<td>1.80</td>
<td>0.450</td>
<td>0.0159</td>
<td>0.99236</td>
<td>0.00757</td>
<td></td>
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</tr>
<tr>
<td>5.89</td>
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<td>0.320</td>
<td>0.0130</td>
<td>0.98725</td>
<td>0.01172</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.93</td>
<td>1.56</td>
<td>0.387</td>
<td>0.0117</td>
<td>0.98989</td>
<td>0.00852</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.10</td>
<td>0.916</td>
<td>0.229</td>
<td>0.00801</td>
<td>0.99333</td>
<td>0.00647</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8.3a shows that as conductance increases, the data sets appear less linear, as expected: as
Table 8.2: Localization length, $\xi$, and optimal hopping distances, $z_{opt}$, for eight insulating films determined using the ES-VRH model.

<table>
<thead>
<tr>
<th>$\log(r_{2K})$</th>
<th>$\xi$ ($\mu$m)</th>
<th>$z_{opt}$, 2 K ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.27</td>
<td>2.42</td>
<td>2.07</td>
</tr>
<tr>
<td>5.40</td>
<td>1.84</td>
<td>1.81</td>
</tr>
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<td>5.63</td>
<td>1.42</td>
<td>1.59</td>
</tr>
<tr>
<td>5.73</td>
<td>1.39</td>
<td>1.57</td>
</tr>
<tr>
<td>5.80</td>
<td>1.18</td>
<td>1.45</td>
</tr>
<tr>
<td>5.89</td>
<td>1.30</td>
<td>1.52</td>
</tr>
<tr>
<td>5.93</td>
<td>1.16</td>
<td>1.44</td>
</tr>
<tr>
<td>6.10</td>
<td>1.20</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Films become metallic ($g(T = 0) \neq 0$), MNPFs can no longer obey $\nu_H = 1/2$ behavior, which yields $g \to 0$ as $T \to 0$. To explore an alternate description for metallic films, Figure 8.3b plots $g$ vs $T^{1/2}$ for the same data sets. In this plot, the data for the more insulating samples that obey $\nu_H = 1/2$ behavior appear less linear than in figure 8.3a as expected. However, as the films become more conducting, $g$ vs $T^{1/2}$ plots appear more linear (see Fig. 8.4). To confirm these trends, we fit straight lines to the 17 data sets on both $\log g$ vs $T^{-1/2}$ and $g$ vs $T^{1/2}$ plots, and subtracted the respective $R^2$ values for each type of fit. The results are plotted in Fig. 8.5 as a function of $\log(r_{2K})$. The more conducting sample yield larger $R^2$ values using $g$ vs $T^{1/2}$ fits and the less conducting using $\log g$ vs $T^{-1/2}$. This linear $g$ vs $T^{1/2}$ behavior [eq. (4)] can be understood in terms of the disordered nature of the films. Films with a sufficient number of immersion cycles cross a percolation threshold and become metallic with finite $g(T = 0 \text{ K})$. As $T \sim 0 \text{ K}$, the temperature independent term in equation (4) is likely limited by electron scattering from strong disorder in the films as charges inevitable encounter NP surfaces as they flow. Disorder in the metallic state would also likely mediate temperature-dependent, $e-e$ interactions which leads to the $T^{1/2}$ term in equation (4). The data in Fig. 8.3b imply that $e-e$ Coulomb interactions are in fact remarkably important in these systems at low temperatures near the insulator-to-metal transition. The contribution of the $T^{1/2}$ term is comparable to that of the temperature independent term and is observed to quite high temperatures on the order of $\sim 20 \text{ K}$.

The importance of $e-e$ Coulomb interactions can also be gauged by calculating scattering lengths, $l$. Since $\tau = \frac{l}{\nu_F} = \frac{\imath m}{\hbar k_F}$ and $\eta = \frac{k_F^2}{3\pi^2}$, where $\nu_F$ and $k_F$ are the Fermi velocity and wavevector, respectively, $\sigma_0$ in equation (4) is determined by $l$ assuming $k_F$ is known:

$$\sigma_0 = \frac{e^2 k_F^2 l}{3\pi^2 \hbar}.$$  \hspace{1cm} (8.7)

We used these results and data for our four most conducting samples of the 17 data sets shown in Fig. 8.3b (which provided the best agreement to equation (4)) to calculate $l$ near the transition. We use
conductance, \( g_0 \), determined from fit intercepts, to determine \( \sigma_0 \) using 
\[
g_0 = \frac{\sigma_0 w}{t}
\]
where \( t, w, \) and \( \ell \) are film thickness, width and length respectively. \( w \) and \( \ell \) are known from the sample geometry film thickness \( t \) is estimated using 3.5 nm per immersion cycle (determined by atomic force microscopy). Using \( k_F \) for bulk gold as an approximation, namely 
\[
k_F = 1.21 \times 10^{10} \text{ m}^{-1}
\]
calculated values for \( l \) are 0.01, 0.007, 0.002, and 0.0004 Å (see Table 8.3). Note that \( k_F l \ll 1 \) for these metallic samples near the insulator-to-metal transition. We also analyzed conductance for 2 films that were in the highly metallic limit where conductance varies linearly with immersion cycles. These highly metallic films yield scattering lengths of 1.1 and 1.2 Å and \( k_F l \sim 1 \). Since \( k_F l \ll 1 \) near the insulator-to-metal transition and \( k_F l \sim 1 \) in the deeply metallic regime, correlations are much stronger near the transition.

Table 8.3: Calculated scattering length, \( l \), conductance, \( g_0 \), thickness \( t \), width \( w \) and length \( \ell \) and conductivity \( \sigma_0 \) for eight films.

<table>
<thead>
<tr>
<th>log((T_{2K}))</th>
<th>( g_0 ) (S)</th>
<th>( t ) (nm)</th>
<th>( \ell ) (mm)</th>
<th>( w ) (mm)</th>
<th>( \sigma_0 ) (S/m)</th>
<th>( l ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.78</td>
<td>0.0165</td>
<td>70</td>
<td>2.0</td>
<td>3.5</td>
<td>1.3x10^5</td>
<td>1.2</td>
</tr>
<tr>
<td>1.86</td>
<td>0.0138</td>
<td>67</td>
<td>2.0</td>
<td>3.1</td>
<td>1.4x10^5</td>
<td>1.1</td>
</tr>
<tr>
<td>3.79</td>
<td>9.08x10^-3</td>
<td>98</td>
<td>2.5</td>
<td>2.0</td>
<td>1160</td>
<td>0.01</td>
</tr>
<tr>
<td>3.97</td>
<td>5.55x10^-5</td>
<td>81</td>
<td>2.5</td>
<td>2.0</td>
<td>840</td>
<td>0.007</td>
</tr>
<tr>
<td>4.13</td>
<td>1.82x10^-5</td>
<td>67</td>
<td>2.0</td>
<td>2.4</td>
<td>228</td>
<td>0.002</td>
</tr>
<tr>
<td>4.08</td>
<td>3.3x10^-6</td>
<td>56</td>
<td>2.0</td>
<td>2.4</td>
<td>60</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

Remarkably, scattering lengths near the insulator-to-metal transition seem to be smaller than smallest gold-gold atom spacing of 2.8 Å, and MNPFs in this regime seem to violate the Ioffe-Regel limit for metals, namely that \( k_F l \geq 1 \). In our system, electron scattering from nanoparticle surfaces is expected to be strong within clusters, and given that NP diameters are \(~ 5 \text{ nm}\), the Boltzmann model predicts that scattering lengths are expected to be of this order at low temperatures. The Altshuler-Aronov model extends the Boltzmann model in the limit that \( k_F l \gg 1 \) to include enhanced \( e-e \) interactions mediated by defects, and correctly predicts a \( T^{1/2} \) correction term to the Boltzmann \( \sigma_0 \) conductance at low temperatures, even though \( k_F l \ll 1 \) near the insulator-to-metal transition in the present system.

Taking that the Altshuler-Aronov model correctly associates the \( T^{1/2} \) behavior with \( e-e \) Coulomb interactions, the anomalously small scattering lengths suggest that \( e-e \) interactions are very strong in these systems near the insulator-to-metal transition and lead to a break down of the Boltzmann model and the Ioffe-Regel limit which assume that electrons can be effectively treated as independent. This picture is further reinforced by the relative size of the contribution of the \( T^{1/2} \) term in equation (4).

Rewriting equation (4) as

\[
\sigma(T) = \sigma_0 (1 + a T^{1/2}),
\]

we find \( a = 0.67, 0.83, 4.4, 19 \) for four data sets from Fig. 8.3b with the largest conductance, that is
the $T^{1/2}$ correction is significant compared to the temperature independent Boltzmann component. For comparison, a previous study of SrTi$_{1-x}$Ru$_x$O$_3$, which is known to be a disordered strongly correlated system, reported $T^{1/2}$ behavior near an insulator-to-metal transition ($x \sim 0.7$) and $a = 0.40 \sim 0.47$. A number of previous studies of strongly correlated systems such as fullerites, layered organic salts and transition metals have reported that the Boltzmann model yields anomalously small scattering lengths that violate the Ioffe-Regel limit and have attributed them to strong $e-e$ correlations and breakdown of the independent electron picture [107–109]. The results in the present study suggest that MNPFs form another class of materials with strongly correlated electrons - one with a potential to serve as a promising new test bed to study such exotic phenomena in view of the control afforded by these nanostructured materials.

8.5 Conclusion

We have found that Coulomb effects play an important role in the conductance of MNPFs on both the insulating and metallic sides near a percolation insulator-to-metal transition. On the insulating side, Coulomb charging barriers lead to thermally assisted charge transport. On the metallic side, disorder leads to significant Coulomb $e-e$ interactions and anomalously small scattering lengths indicating that electrons in MNPFs are strongly correlated. These results are significant in that they highlight an opportunity to use MNPFs as a new platform to control and study strong $e-e$ interactions given the tunability inherent in MNPFs.
Figure 8.4: a) \( \ln [g/g(20 \text{ K})] \) vs \( T^{-1/2} \) and b) \( g/g(20 \text{ K}) \) vs \( T^{1/2} \) with linear fits for various molecularly-linked gold nanoparticle films. \( \log(r_{2K}) \) value of each film is indicated on the right side of the graph, ranging from 3.79 (top line, first graph) to 6.10 (bottom line, last graph). Plots are offset for clarity.
Figure 8.5: A comparison of the goodness of fits using $g/g(20 \text{ K})$ vs $T^{1/2}$ and $\ln[g/g(20 \text{ K})]$ vs $T^{-1/2}$ models for various films near the insulator-to-metal transition.
Chapter 9

Electrolyte-Gated Charge Transport in Molecularly-Linked Gold Nanoparticle Films: the transition from a Mott insulator to an exotic metal with strong electron-electron interactions


Author Contributions M. Tie prepared samples, performed measurements, analysed data, and contributed to writing the manuscript. A.-A. Dhirani provided guidance in experimental and theoretical direction and contributed to writing the manuscript.
9.1 Abstract

Strong electron-electron interactions experienced by electrons as they delocalize are widely believed to play a key role in a range of remarkable phenomena such as high Tc superconductivity, colossal magnetoresistance, and others. Strongly correlated electrons are often described by the Hubbard model, which is the simplest description of a correlated system and captures important gross features of phase diagrams of strongly correlated materials. However, open challenges in this field include experimentally mapping correlated electron phenomena beyond those captured by the Hubbard model, and extending the model accordingly. Here we use electrolyte gating to study a metal-insulator transition (MIT) in a new class of strongly correlated material, namely nanostructured materials, using 1,4-butanedithiol-linked Au nanoparticle films (NPFs) as an example. Electrolyte gating provides a means for tuning the chemical potential of the materials over a wide range, without significantly modifying film morphology. On the insulating side of the transition, we observe Efros-Shklovskii variable range hopping and a soft Coulomb gap, evidencing the importance of Coulomb barriers. On the metallic side of the transition, we observe signatures of strong disorder mediated electron-electron correlations. Gating films near MIT also reveals a zero-bias conductance peak, which we attribute to a resonance at the Fermi level predicted by the Hubbard and Anderson impurity models when electrons delocalize and experience strong Coulomb electron-electron interactions. This study shows that by enabling large changes in carrier density, electrolyte gating of Au NPFs is a powerful means for tuning through the Hubbard MIT in NPFs. By revealing the range of behaviours that strongly correlated electrons can exhibit, this platform can guide the development of an improved understanding of correlated materials.

9.2 Introduction

Nanostructured materials offer a new platform to study strongly correlated materials. For example, gold nanoparticle films (NPFs) can exhibit well known strong Coulomb charging effects, in which the nanostructured nature of films and the resulting small capacitances lead to Coulomb energy barriers associated with placing one or more electrons onto nanoparticles. [6,7,36] This leads to thermally assisted conductance, including Arrhenius charge transport or variable range hopping (VRH), i.e. insulating behavior. [44,47,97] In addition, some studies have shown that cross linking the nanoparticles in NPFs using short or conjugated molecular linkers, such as butanediithiol [23], 3-mercaptopyropionic acid [24], and 1,4-phenylene bis(dithiocarbamate) [14], can lead to electron delocalization between NPs and metallic film behavior. As a function of some tuning parameter, namely filling fraction, films can be tuned
through a percolation insulator-metal transition (MIT). Near the transition, both Coulomb charging and delocalization effects become significant, and NPFs exhibit strong electron correlations. [23,27]

Electrostatic gating using a silicon/silicon oxide back gate provides another means to tune the electronic properties of nanostructured materials. For example, the number of charge carriers in single electron transistors can be tuned to reveal signatures of Coulomb blockade and Coulomb oscillation. [10,110] Silicon back gate devices have also been used to alter the conductance of Au NPFs by shifting the Coulomb blockade gap and to store analogue information by modifying trapped charge distributions. [111] The capacity to change charge carrier density using electrostatic gating increases linearly with the dielectric constant of the gate insulator and varies inversely with insulator thickness. The ability to change carrier density in silicon back gate devices is limited by several factors, including the minimum oxide thickness required to prevent shorting through defects and dielectric breakdown voltage of the oxide.

Recently, electrolyte gating has emerged as a powerful tool for tuning the chemical potential of a variety of compounds. [112–119] Ionic liquids (IL) have been particularly useful due to their high breakdown voltages (4 - 6 V) and electrochemical stability. When a voltage is applied between a gate electrode and the material, an electrical double layer (EDL) on the nanometer scale is induced between the IL and the material. An advantage shared by this and the Si-gate approaches is that the gate voltage can be varied continuously while keeping the film morphology the same. An additional advantage of electrolyte gating approach is that the double layer’s size being nanometer in scale results in a large capacitance and large induced surface charge densities, causing the chemical potential of the film to shift significantly. [112, 113, 115, 120–124]. In this paper, we use IL gating to tune butanedithiol-linked Au NPFs through an MIT and to reveal signatures of strong electron correlations in this system.

9.3 Experimental Method

Figs. 9.1a and b show a schematic diagram of the Au NPF device. Au NPs (5.3 nm ± 1.1 nm) are synthesized using a modified Brust method [37, 87] as described in Section 5.1. Fig. 5.1a and Fig. 5.1b show a UV-vis absorption spectrum and a TEM image of the synthesized Au NPs, respectively. The Au NP linker, 1,4-buthanedithiol, is purchased from Sigma Aldrich and is used as received. DEME-TFSI (Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide) is used as the IL in the present study. No attempt has been made to optimize our choice of IL, however this IL has been well studied for electrolyte gating [125] and has been extensively used for a wide range of materials. [115, 117–121] DEME-TFSI is purchased from Sigma Aldrich and handled under argon gas in order to minimize exposure to oxygen. To fabricate devices, 10 mm x 12 mm x 1 mm glass slides were
Figure 9.1: a) Schematic of a device with a four terminal + gate electrode configuration and an IL droplet. b) Side view schematic of device showing the EDL upon application of a negative gate voltage.

Functionalized as detailed in Section 5.2. 150 nm thick gold electrodes are thermally deposited onto the functionalized slides in a four-probe + gate electrode configuration as represented in Fig. 9.1a. Electrodes have the following dimensions: source-drain electrodes are 2.5 mm x 1.5 mm, a coplanar gate electrode is 2 mm x 8 mm, and voltage sensing electrodes are 0.2 mm x 2 mm with 1 mm spacing between them. Although a 4-probe electrode configuration is shown schematically in Fig. 9.1a, some slides are prepared with as many as 7 electrodes. In all cases, the two outer electrodes are used as source-drain electrodes, and the inner electrodes are used pairwise to measure voltage drops across the NPF, yielding as many as 4 sample measurements per device.

Au NPFs are self assembled on the glass slides with pre-deposited gold electrodes by alternately immersing the slides in Au NP and 1,4-butanedithiol solutions. Film characterization can be found in Section 5.2. Fig. 5.3b and Fig. 5.3c, respectively, show absorbance at 800 nm and SEM images of NPF at multiple immersion cycles. The linear increase in absorbance with number of immersion cycles indicates approximately a constant amount of gold is added per immersion cycle. Since there is variability from sample to sample due to factors such as variations in nanoparticle solution concentration and substrate functionalization, samples are prepared near MIT using room temperature conductance, rather than number of immersion cycles, as a guide. In total, 11 devices are studied in detail, with room temperature resistances ranging from \( \sim 5 \, \text{k\Omega} \) to \( \sim 50 \, \text{k\Omega} \). Room temperature conductivity, \( \sigma \), is calculated using \( g = \sigma \frac{wd}{l} \), where \( g, w, d \), and \( l \) are the sample conductance, width, thickness, and length, respectively. We confirm that films are approximately uniformly conducting at room temperature by reducing film width by wiping away a portion of the NPF and observing that the conductance decreases correspondingly. After a NPF is deposited on a slide, the sides and back of the slide are wiped using a methanol dampened kimwipe to remove excess material, and indium solder is used to attach magnet wires to the gold pads. 5 \( \mu \text{L} \) of IL is deposited onto the device using a micropipette such that the IL covers both the NPF and gate electrode (see Fig. 9.1a,b). The device is then immediately transferred
into a Physical Property Measurement System (PPMS) and cooled to 240 K.

Film conductance is measured using a 4-probe lockin technique in which a low frequency (<100 Hz) 10 mV ac voltage plus a variable dc source-drain voltage ($V_{SD}$) is applied across the source-drain electrodes. The total conductance, including film plus contact contributions, is measured across the outer electrodes using the lockin. The ac voltage across a pair of inner electrodes is measured using buffers to ensure no current is drawn, and, therefore the voltage drop measured equals that across the film, despite any contact resistance. Film conductance is then calculated at different dc bias voltages using a voltage divider approach (see Section 6.3 for more detail). Any gate voltages are applied and varied at 240 K, rather than at room temperature, to suppress electrochemical reactions. The sample is kept at 240 K, and a constant gate voltage is applied for at least 30 minutes to allow $g$ to equilibrate due to the large charging time constant. The sample is then cooled at a rate of 2 K/min down to 2 K. DEME-TFSI freezes to a glassy state at 180 K so bias voltages are applied only below 180 K. Leakage current between gate and drain electrodes is monitored throughout the experiment. At 240 K, leakage current remains below 100 nA, but rapidly drops below 1 nA as temperature is lowered.

### 9.4 Results and Discussion

Fig. 9.4 shows the influence of gate voltage ($V_G$) on a film that has a room temperature conductivity of $26 \, \Omega^{-1} \text{cm}^{-1}$. The film is near the metal-insulator transition on the insulating side (see Fig. 9.3 for $g$ vs. temperature, $T$, plots for this sample). The data shown are representative of the range of behaviors exhibited by all of our samples. In Fig. 9.4a shows one type of behavior observed. As $V_G$ is swept from $0 \, \text{V} \rightarrow 2 \, \text{V} \rightarrow -2 \, \text{V} \rightarrow 0 \, \text{V}$, $g$ changes hysteretically and reversibly, exhibiting only a small offset at the
Figure 9.3: $g$ vs. gate voltage between a) $\pm 1.25$ V (first sweep), b) $\pm 2$ V (second sweep), c) $\pm 1$ V (third sweep) and d) $g$ vs. temperature data obtained using an Au NPF with room temperature conductivity of $26 \, \Omega^{-1} \, \text{cm}^{-1}$. Colour symbols in a) to c) correspond to points at which $g$ vs. temperature data shown in d) were obtained.
end of the cycle when $V_G$ returns to zero. The change in $g$ between $\pm 2$ V normalized to the average value is approximately 22%. For comparison, we measured the change in conductance of a thermally deposited 16 nm thick metallic gold film between gate voltages of $\pm 2$ V, and observed a 3 % change (see Fig. 9.2). Others have reported changes in thermally deposited metallic gold films up to 10 % at low temperatures between gate voltages $\pm 4$ V. [120]

To quantify the effect of gate voltage on our devices, we calculate induced charge carrier density and correlate with respect to changes in $g$. As previously reported [120,125], electrochemical effects can be significant in gated IL systems. The charge induced by the EDL itself, $Q_C$, can be extracted from leakage current flowing through the gate ($I_G$) and total charge $Q_T = \int I_G dt$, where $t$ is time, using a chronocoulometry method as follows. [126] Fig. 9.4c (inset) shows $I_G$ vs. time as $V_G$ changes from 0.5 V to 1 V. After the change, $I_G$ exhibits a spike due EDL charging at short times and a nonzero persistent current at longer times. The latter is due to a net diffusive current flow that maintains the gradient across the EDL and diffusion of species participating in electrochemical reactions. This persistent $I_G$ results in a $Q_T \sim t^{0.5}$ behavior at large $t$. $Q_C$ due to EDL charging is then determined by the intercept of a linear fit to the $Q_T$ vs. $t^{0.5}$ plot (Fig. 9.4c). We find $Q_C$ varies approximately linearly with $V_G$ (see Fig. 9.4d inset), and the slope yields a capacitance of 9.08 $\mu$F/cm$^2$ for the EDL, which is close to a previously reported value of 6 - 8 $\mu$F/cm$^2$. [127] Near MIT, the NPF film has a mixture of metallic and insulating pathways. However at 240 K, the film is rather conducting, and we can approximate the film as being uniform. We can calculate the 2D average induced charge carrier density using $n_{2D} = Q_C/eS$, where $S$ is the surface area of the film. The 3D induced carrier density is given by $n_{3D} = n_{2D}/\xi$, where $\xi$ is the average screening length in the NPF. Fig. 9.4d shows $\Delta g = \frac{g(V_G=0 V) - g(V_G)}{g(V_G=0 V)}$ vs. $n_{2D}$. The data exhibit an approximately linear relationship. Our data indicate that $n_{2D}$ at 2 V is $\sim 2 \times 10^{14}$ cm$^{-2}$, which is comparable to a value of $9 \times 10^{13}$ cm$^{-2}$ reported by Petach et. al. for EDL charging of thermally deposited thin gold films at room temperature [127]. Assuming $n_{2D}$ is induced approximately uniformly throughout the film thickness, we find that the intrinsic charge carrier density of our film to be $n \sim 5 \times 10^{20}$ cm$^{-3}$, much smaller than the value for bulk gold, $5.90 \times 10^{22}$ cm$^{-3}$, since the NPFs are close to the MIT. Other mechanisms that have been proposed by previous studies may also contribute to $\Delta g$, such as a reversible oxidation of gold [127] or electrochemical doping via hydrogen from water impurities [128]. In addition, shallow energy wells can trap charges, which can contribute to gating and the hysteresis observed.

Fig. 9.4b shows another behavior that is commonly observed. Here using the same sample, $V_G$ is cycled once again (continuing from the end of the sweep shown in Fig. 9.4a) from $0$ V $\rightarrow$ $1$ V $\rightarrow$ $-1$ V $\rightarrow$ $0$ V. At 1 V, there is a sudden, large and irreversible change in $g$. This change occurs after multiple cycles
Figure 9.4: Conductance vs. gate voltage ($V_G$) cycle of a nanoparticle film at 240 K between a) 2 V and -2 V and subsequently b) 1 V and -1 V. c) Leakage current at the gate electrode vs. time as $V_G$ steps from 0.5 V to 1 V (inset) and the resulting total charge $v$. time$^{0.5}$ (main panel). The solid line is a linear fit whose intercept is used to calculate EDL charge. d) Electric double layer charge vs. gate voltage (inset), and normalized change in conductance vs. 2D charge density induced by the double layer (main panel).
varying gate voltage using this sample. We suspect that after multiple sweeps, eventually dielectric breakdown occurs, leading to shorts in the film and an increase in conductance. To reduce the influence of this effect, we studied many samples, each at a particular number of immersion cycles, rather than one or a few samples at multiple immersion cycles.

In view of the significant hysteresis exhibited by $g$ vs $V_G$, the gate voltage is used to adjust the value of $g$ at 240 K, and then $g$ vs $T$ and $g$ vs source-drain voltage ($V_{SD}$) are measured at lower temperatures for various films near MIT. Fig. 9.7a - c show data for three different films at different stages near the metal-insulator transition with room temperature conductivities of 25 $\Omega^{-1}$ cm$^{-1}$, 33 $\Omega^{-1}$ cm$^{-1}$ and 91 $\Omega^{-1}$ cm$^{-1}$ corresponding to a film very near MIT, a film near MIT but clearly on the metallic side, and a film deeper into the metallic regime, respectively. We do not believe Joule heating has any significant effects, as we outline in the Appendix section below. Data for additional samples exhibit similar behaviors and are shown in Fig. 9.5 and Fig. 9.6.

Fig. 9.7a shows results using a film very close to the MIT. The curves from top to bottom correspond to decreasing $V_G$, from 0 V to -3 V. The top inset shows that film conductance at $V_{SD} = 0$ V approaches zero as $V_G$ decreases, and at $V_G = -3$ V, film conductance remains close to zero even as $V_{SD}$ varies over $\pm 0.5$ V. Given the distinction between an insulator vs. metal, i.e. that $g$ tends to zero (insulator) or not (metal) as $T$ and $V_{SD}$ tend to zero, the sample at $V_G = -3$ V seems to be close to the boundary. At higher gate voltages, $g$ continues to exhibit strong suppression at $V_{SD} = 0$ V, which is overcome at higher source-drain voltages consistent with a presence of Coulomb barriers. Such barriers can also be overcome by increasing $T$, and indeed in all cases, as $T$ increases, $g$ at $V_{SD} = 0$ V increases rapidly. That is, in addition to any potential metallic pathways that conduct at the lowest temperatures, all films contain a significant number of thermally assisted (insulating) pathways.

Fig. 9.7b shows results obtained using a different film that is more on the metallic side of the MIT. In this case as gate voltage varies, $g$ at 2 K and $V_{SD} = 0$ V does not drop to zero as in Fig. 9.7a implying that the sample in Fig. 9.7b is deeper into the metallic phase. Remarkably the bottom curve in fact reveals a zero bias conductance peak. A magnified view of the zero-bias region is shown in the bottom right inset for clarity. Such peaks have been observed previously in NPFs tuned through MIT using film thickness and percolation rather than gate voltage as tuning parameters [23] and are discussed further below.

Fig. 9.7c shows results obtained using a film that is further still into the metallic regime. In the inset, the bottom curve ($V_G = 0$ V) is closer to the MIT while the top curve ($V_G = 2$ V) is further into the metallic state since $g$ at $V_{SD} = 0$ V is higher. In both cases, $g$ vs. $V_{SD}$ is suppressed at 0 V, with the more conducting film exhibiting suppression that is more readily overcome with increasing $V_{SD}$ implying
Figure 9.5: a) $g$ vs. temperature ($T$), b) $g$ vs. voltage, c) $\ln[g/g(20\text{ K})]$ vs. $T^{-1/2}$ and d) $g/g(20\text{ K})$ vs. $T^{1/2}$ at different gate voltages ($V_{\text{GATE}}$) for an Au NPF with room temperature conductivity of 21 $\Omega^{-1}\text{cm}^{-1}$.
Figure 9.6: a) $g$ vs. temperature ($T$), b) $g$ vs. voltage, c) $\ln[g/g(20 K)]$ vs. $T^{-1/2}$ and d) $g/g(20 K)$ vs. $T^{1/2}$ at different gate voltages ($V_{GATE}$) for an Au NPF with room temperature conductivity of 23 $\Omega^{-1}$cm$^{-1}$. 
smaller Coulomb barriers. Also, although at both gate voltages, $g$ increases with $T$, the temperature data exhibit a cross-over: compared with the film at $V_G = 0$ V, the film at $V_G = 2$ V is more conducting at 2 K, and its conductance increases more slowly with $T$, i.e. it is deeper into the metallic phase and has insulating pathways with smaller barriers (see also $T$ analysis discussed below).

Given the nanostructured nature of the films and the likely importance of Coulomb barriers generated by potentially small capacitances in the films (i.e. Coulomb blockade and e-e interactions) and/or disordered mediated, strong e-e scattering, we test for two $g$ vs $T$ dependencies:

$$g = g_0 \exp[-(T_0/T)^{1/2}], \quad (9.1)$$

where $g_0$ and $T_0$ are constants - the Efros-Shklovskii variable range hopping (ES VRH) model for insulators (Fig. 9.8a-c); and

$$g = A + BT^{1/2}, \quad (9.2)$$

where $A$ and $B$ are constants - the $T^{1/2}$ model for metals, as predicted by Altshuler and Aronov (Fig. 9.8d-f). The ES-VRH functional form can be derived by optimizing exponential decay ($\exp[-2\zeta/\ell]$), where $\zeta$ is the hopping distance and $\ell$ is the localization length, which favours small $\zeta$, and Arrhenius behavior ($\exp[-E/k_BT]$), where $E \sim 1/\zeta$ due to Coulomb interactions, which favours large $\zeta$. The Coulomb barrier leads to suppression of density of states near the Fermi energy $D \sim (E - E_F)^2$ (soft Coulomb gap). Optimizing $\zeta$ leads to the ES-VRH form in equation (1) and an optimal distance $\zeta_{\text{opt}} = (\ell/4)(T_0/T)^{1/2}$, where $T_0 = 2e^2/(\pi e^2 k_B \ell)$. Although originally developed for doped semiconductors [48] where $\zeta$ is the hopping distance between randomly spaced dopants, ES-VRH behavior has also been observed in a number of insulating materials, including nanostructured materials [6, 19, 46, 129] and thermally deposited films with metallic grains [130]. Altshuler and Aronov [54] derived the $T^{1/2}$ model for electrons in disordered metallic systems in which the disorder leads to enhanced electron-electron correlations. Their calculation in a limit of long distances between disorder sites relative to the Fermi wavelength predicts equation (2) and $D \sim (E - E_F)^{1/2}$ near the Fermi energy. [98,130] We have shown previously that NPFs near a percolation driven MIT on the metallic side exhibit a strong $T^{1/2}$ contribution, presumably due to such disorder enhanced e-e correlation behavior. [27]

We confine our analysis of $g$ vs $T$ data shown in Fig. 9.7a-c to below 20 K (see Fig. 9.8) to focus on effects that dominate at low $T$. Fig. 9.8 shows that as the various films transition from being more insulating to metallic (Fig. 9.7a $\rightarrow$ 9.7c), overall the data transition from exhibiting ES-VRH (Fig. 9.8a) to $T^{1/2}$ (Fig. 9.8f) behavior, confirming the importance of Coulomb effects on both sides of the
Figure 9.7: $g$ vs. $V_{SD}$ at 2 K or 20 K (insets) and $g$ vs. $T$ (main panel) for various Au NPFs and gate voltages. The samples have room temperature conductivities of a) $25 \Omega^{-1}\text{cm}^{-1}$, b) $33 \Omega^{-1}\text{cm}^{-1}$ and c) $91 \Omega^{-1}\text{cm}^{-1}$.
MIT. Also, for a given device, as $V_G$ varies and low $T$ zero bias $g$ increases, i.e. films go deeper into the metallic state, Fig. 9.8 shows that the magnitudes of the slopes in the ES-VRH plots, $T_o$, decrease, i.e. effective barrier heights decrease. Consistent with this trend, as metallicity increases, slopes of $g$ vs $V_{SD}$ increase as well, which suggest that Coulomb barriers are becoming more easily overcome at lower $V_{SD}$ and conduction becomes more facile. As films go deeper into the metallic state, films still have many insulating pathways and effective fits using ES-VRH continue to yield $T_o$ that decreases and $\zeta_{opt}$ that increases, i.e. charges become more delocalized. Best fit values of localization length $\ell$ and optimal hopping length $\zeta_{opt}$ at 2 K are given in Table 9.1. Typically $\zeta_{opt}$ is order $\sim 1 \mu$m. Additional evidence for both ES VRH and $T^{1/2}$ effects are seen in $g$ vs $V_{SD}$ data. On the metallic side of MIT, the film that exhibits $T^{1/2}$ behavior also exhibits $g \sim V_{SD}^{1/2}$ (see Fig. 9.8f, main panel and inset at $V_G = 2$ V). Towards the insulating side, films exhibit $g \sim V_{SD}^2$, consistent with ES VRH and a soft Coulomb gap (note the shapes of the $g$ vs. voltage minima near MIT in Figs. 9.7a and b insets, as well as a more detailed analysis shown in Fig. 9.9 to Fig. 9.11). We noted earlier that the film discussed in Fig. 9.7a appeared to be close to the MIT at $V_G = -3$ V. Fig. 9.7a bottom inset shows a magnified view of $g$ vs. $V_{SD}$ data at $V_G = -3$ V for both 2 K and 20 K. The film appears to be just barely metallic, with weak electron-electron correlation effects giving rise to a small cusp-like shape (sub-linear $V_{SD}$ behaviour) near zero $V_{SD}$. At higher temperatures, when the low T effects of electron-electron correlations wash away, a clear quadratic behaviour dominates (top curve, 20 K and Fig. 9.9). Remarkably, Fig. 9.8 indicates that the $T^{1/2}$ correction to the $T = 0$ K value of conductance is significant, suggesting that although the derivation of the $T^{1/2}$ correction is performed in a perturbative limit, it appears to work well even in the strongly interacting regime. The coefficient $B$ in equation (2) is given as

$$\begin{align*}
B = \lambda \left( \frac{k_B \tau}{\hbar} \right)^{1/2} \left( \frac{E_F \tau}{\hbar} \right)^{-2} \sigma_o,
\end{align*}$$

(9.3)

where $\sigma_o = ne^2\tau/m = A$, $\tau$ is the scattering time, $k_B$ is the Boltzmann constant, $m$ is the effective mass, $\hbar$ is Planck’s constant, and $\lambda \sim 1$. Using this equation and $B/A$ from Fig. 9.8f ($V_G = 2$ V curve), we obtain a scattering length of 0.09 Å. This is much smaller than the inter-atomic distance for Au, indicating very strong electron-electron interactions and a breakdown of the assumptions of the model. Nevertheless, the prediction of a square root behavior apparently is still successful.

Given the results from Fig. 9.7 and 9.8 - namely that NPFs undergo an insulator-to-metal transition across which electrons experience strong Coulomb interactions (ES-VRH to $T^{1/2}$ behavior), and $g$ exhibits a zero-bias peak near MIT (Fig. 9.7b inset) - we propose that the density of states (DOS) evolves across the transition as shown in Fig. 9.12a. Fig. 9.12b shows a qualitative physical picture of
Figure 9.8: a) - c) $\ln(g/g(20\text{ K}))$ vs. $T^{-1/2}$ and d) - f) $g/g(20\text{ K})$ vs. $T^{1/2}$ plots of the $g$ vs $T$ data shown in Fig. 9.7 a) - c), respectively. f) also shows $g$ vs. $V^{1/2}$ of the data shown in Fig. 9.7 c) at $V_G = 2\text{V}$.
Figure 9.9: a) $g$ vs. voltage ($V$) and b) $g$ vs. $V^2$ for an Au NPF with room temperature conductivity of 25 $\Omega^{-1}$cm$^{-1}$ at gate $= -3$ V and $T = 20$ K.

Figure 9.10: a) $g$ vs. voltage ($V$) and b) $g$ vs. $V^2$ at gate $= 0$ V and $T = 5$ K for Au NPF with room temperature conductivity of 91 $\Omega^{-1}$cm$^{-1}$.
Figure 9.11: a) $g$ vs voltage ($V$) with a $V^2$ fit to the background data excluding the zero bias peak at gate = -3 V, $T = 2$ K for an Au NPF with room temperature conductivity of $33 \, \Omega^{-1}\text{cm}^{-1}$. b) $g$ vs. voltage and c) $g$ vs $V^2$ at gate = -3 V for the same sample as in a) at $T = 60$ K by when the peak in a) has disappeared.
Table 9.1: Localization length ($\ell$) and optimal hopping length ($\zeta_{opt}$) at 2 K extracted from slopes of $\ln[g/g(20 K)]$ vs. $T^{-1/2}$ plots in Fig. 9.8.

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Figure 9.12: a) A schematic of the DOS of a Au NPF and b) an illustration depicting electron hopping (curved arrows) and metallic transport (straight arrows) through a NPF as NP filling fraction increases and the NPF traverses an insulator-to-metal transition. Due to the disordered nature of NPF, actual DOS may be a mixture of the three scenarios in a).

transport processes than can occur. At low filling fraction, the film is insulating: the low energy occupied states are separated from the higher energy unoccupied states by a Coulomb gap. As NPF filling fraction increases, clusters of linked NPs grow, and eventually, at a (classical) percolation threshold, the film possesses sample spanning clusters. At the onset of the metallic phase, the gap between lower and upper bands must close. However, the film still possesses a large number of insulating pathways that comprise “impurity” clusters of linked nanoparticles that can also contribute to conduction. Deep into the metallic regime, metallic pathways dominate, and only a small background of isolated impurity clusters and thermally assisted pathways contribute to $g$.

Remarkably, near the MIT, conductance exhibits a zero-source-drain voltage peak, and this is reflected in Fig. 9.12b. middle panel by a proposed peak in the DOS at the Fermi energy when the
film is near MIT. Peaks near the Fermi energy have been previously reported in photoemission studies of strongly correlated transition metal compounds near MIT. [65–67] Theoretically, the simplest model that can account for strong electron-electron correlations and the peak is the lattice Hubbard model:

$$H = \sum_{<i,j>,\sigma} t_{ij} C_{i,\sigma}^\dagger C_{j,\sigma} + U \sum_i n_{i,\uparrow} n_{i,\downarrow},$$

(9.4)

where the first term is the kinetic energy due to hopping between nearest neighbor sites, and the second term is the electron-electron interaction energy. $C_{i,\sigma}^\dagger$ ($C_{j,\sigma}$) are creation (annihilation) operators for electrons at site $i$ ($j$) and spin $\sigma$ ($\uparrow$ or $\downarrow$), $t_{ij}$ is the transfer energy, $U$ is the on-site Coulomb repulsion energy, $n_{i,\sigma} = C_{i,\sigma}^\dagger C_{i,\sigma}$ is the number operator, and the first sum is over nearest neighbors and spins. This model has been used to describe MIT in transition metal compounds [63], where the confined nature of open $d$ and $f$ orbitals leads to strong Coulomb repulsion $U$ when an orbital is occupied by multiple electrons, and electron delocalization can be driven by some tuning parameter. The Hubbard model can be approximately mapped onto the Anderson impurity model, and dynamic mean field theory predicts a peak in DOS at the Fermi level near a Hubbard MIT. The peak is associated with a strongly correlated exotic metallic state in which Coulomb electron-electron repulsion and delocalization are both significant. [62,68] In this regime, electrons acquire large effective masses and experience strong scattering. In NPFs, the competition between Coulomb effects (generated by disorder and charging energies of nanoparticle clusters) and electron delocalization apparently result in similarly strong correlations near MIT. Using the lattice Hubbard model as a guide, we propose a percolation Hubbard picture of NPFs; as lattice sites are filled, eventually adjacent sites become occupied and form a metal cluster of linked nanoparticles in which electrons are delocalized, posses higher kinetic as well as experience lower $U$. At low filling fraction, Coulomb barriers of small, isolated nanoparticle clusters dominate, and conductance is dominated by thermally activated processes. Near MIT on the insulating side, electrons exhibit ES-VRH as they optimize their choice of pathways: smaller clusters are easier to traverse than larger clusters but are more difficult to charge. As filling fraction increases, the clusters grow and electrons become more delocalized, as reflected by an increasing $\zeta_{opt}$ (see Table 9.1). Eventually, the films become metallic, and exhibit strong $T^{1/2}$ scattering term likely due to the large number of NP interfaces. The energy of the film transitions from being dominated by charging energy to kinetic energy. In between, both effects compete, and a resonance at the Fermi level appears. In view of the mixed insulator/metal composition of the film, an Anderson impurity model, which predicts a resonance at the Fermi level, may also be viewed as a reasonable picture of this system.

The present study shows that NPFs can be tuned through the Hubbard MIT by gating, which
modulates carrier density and in turn the Fermi energy. This approach for tuning the NPF near MIT also reveals several key features of the Hubbard MIT, including strong Coulomb interactions, changes in \(g\) at zero source-drain voltage and low temperature, and signatures of strong electron-electron interactions, including \(T^{1/2}\) behavior and a zero-bias peak - a key signature of strong correlations near a Hubbard MIT. Furthermore, changing gate voltage reveals a correlation between increasing \(g\) at 2 K and decreasing Coulomb barriers. By enabling changes in charge carrier density and kinetic energy, gating provides a means for altering the balance between Coulomb repulsion and kinetic energy and thereby provides a powerful means for tuning through the Hubbard MIT in Au NPFs.

9.5 Appendix - Joule Heating

To determine whether Joule heating may be an issue when applying large source-drain voltage (\(V_{SD}\)), we consider our most conducting sample (for which such heating would be strongest), namely the film discussed in Fig. 9.7c inset (top curve, \(V_G = 2\) V and \(T = 2\) K).

The power is \(P = V^2/R = gV^2\), where \(V\) is voltage, \(R\) is resistance and \(g\) is conductance. Assuming that heating is driven by some fraction, \(f\), of the power, then \(\Delta E = fP = C\Delta T\), where \(f \leq 1\), \(C\) is the heat capacity and \(\Delta T\) is the change in temperature. So \(\Delta T = \frac{fV^2}{C}\).

From \(\Delta T \sim V^2\), we expect that as \(V_{SD}\) increases, the \(g\) increases at least quadratically with \(V\) as follows:

From \(g\) vs. \(T\) data (Fig. 9.7a main), without Joule heating driven by \(V\), \(g \sim T^{1/2}\) (see Fig. 9.8f). From Altshuler and Aronov theory for disorder enhanced electron-electron correlations, we expect \(g \sim V^{1/2}\).

Then neglecting Joule heating due to \(V\), \(g_0 = a + bT^{1/2} + c(T)V^{1/2}\). Conductance with Joule heating becomes \(g = a + b(T+\Delta T)^{1/2} + c(T+\Delta T)V^{1/2}\). For small \(\Delta T\), \(g \sim a + bT^{1/2} + 0.5T^{-1/2}\Delta T + c(T)V^{1/2} + c'(T)V^{1/2}\Delta T\).

Since \(\Delta T \sim V^2\), \(g \sim V^{5/2}\). However, qualitatively, Fig. 9.7c insets show that \(g\) increases sublinearly with \(V\); indeed, Fig. 9.8f inset shows that \(g \sim V^{1/2}\). As such, we do not believe Joule heating contributes significantly to our \(g\) vs. \(V_{SD}\) results.
Chapter 10

Conclusion

In this thesis, the influence of strong Coulomb interactions on charge transport through the metal-insulator transition is studied in molecularly-linked gold nanoparticle films, and the emergence of exotic phenomena is observed. In Chapter 6, I show that contact effects can play a significant role in transport properties of thin films, and a four-probe transport measurement technique that eliminates contact resistance is discussed. This technique is used in subsequent chapters. In Chapter 7, film conductance of 1,4-butanedithiol linked gold nanoparticle films (NPF) is studied through a percolation metal-insulator transition, and near the transition, the NPF traverses an exotic metallic phase exhibiting a pseudogap-like behavior and zero-bias conductance peak. This peak is reminiscent of an Abrikosov-Suhl resonance seen in non-nanoengineered, correlated materials near Mott-Hubbard metal-insulator transition, and is predicted by the Hubbard and Anderson Impurity model when electrons delocalize and experience strong Coulomb electron-electron (e-e) interactions. In Chapter 8, I show that Coulomb effects play an important role in the conductance of the NPFs on both the insulating and metallic sides near the percolation metal-insulator transition. In particular, on the insulating side, Coulomb charging barriers lead to thermally assisted charge transport, and on metallic side, disorder leads to significant Coulomb e - e interactions and anomalously small scattering lengths, indicating that electrons in the NPFs are strongly correlated. In Chapter 9, I use electrolyte gating as an alternate means to tune the chemical potential of the NPFs without significant modification to film morphology. Tuning through the metal-insulator transition using electrolyte gating reveals behaviors in the NPFs similar to what has been observed in percolation driven metal-insulator transition: a soft Coulomb gap (showing the importance of Coulomb barriers) on the insulating side, an Abrikosov-Suhl-like resonance in conductance very near the transition, and signatures of strong disordered mediated e - e correlations on the metallic side.
Strong electron correlation is known to be key behind exotic effects seen in transition metal compounds such as high $T_C$ superconductivity in cuprates and colossal magnetoresistance seen in manganites. Due to the immense potential for applications of these materials and due to the fact that they are scientifically interesting, strong correlated materials have received much attention. Despite this, the underlying mechanism behind strong correlation is poorly understood. Previously, strong correlations have been observed in only a few classes of materials, most notably transition metal compounds. By providing evidence of strong correlations in molecularly linked nanoparticle films, the present work shows nanoengineered materials can serve as a new platform to study these exotic effects. There are several advantages to using nanoengineered materials over transition metal compounds, including tunable properties through choice of nanostructure building blocks and assembly process, as well as ease of fabrication and general robustness of the produced materials. The role of disorder should be noted, however, as the many sources for disorder in molecularly linked nanoparticle films, and in nanoengineered materials more generally, present a theoretical challenge. Some sources of disorder, such as NP size dispersion and non-lattice assembly arrangement, may be reduced through further size-selective processing or changing assembly methods. Some sources of disorder, such as nanoparticle interface effects and disorder of molecule assembly on nanoparticle surfaces, are inherent to nanostructured materials and may not be fully eliminated.

A natural next step in this work would be to take advantage of the tunability of nanoengineered materials in order to affect the observed exotic behaviors. For example, in the case of the NPFs near the metal-insulator transition, the interaction between delocalized electrons and Coulomb charging barriers (via isolated clusters) gives rise to a zero-bias resonance peak at the Fermi level, as predicted by the Hubbard and Anderson impurity models. The metal-insulator transition, however, occurs in a narrow range of film thickness in which sample spanning metallic pathways exist alongside sufficiently numerous and accessible isolated clusters. As a future project, fabricating films doped with ‘spacer’ layers (that is, replacing some gold nanoparticles with more atom-like building blocks - building blocks in which electrons are more strongly localized) can aide in slowing down the percolation driven metal-insulator transition by allowing clusters to remain more isolated, strengthening the interactions between delocalized electrons and isolated clusters, and thus produce a more robust (i.e. higher temperature) zero-bias conductance peak. In addition to this, NPFs can be varied in other ways: varying linker molecules and architecture may change film properties as well. For example, linker molecules with a non-zero net charge may affect local charge carrier density of the films by trapping charges. Additionally, film architecture can be varied through use of alternate assembly methods: e.g. through use of a Langmuir trough, nanoparticles can form a close packed lattice structure, increasing nanoparticle density and reducing
disorder in nanoparticle arrangement. Other ways to reduce disorder include reducing nanoparticle size
distribution through alternative synthesis methods or post-processing methods such as size selective
precipitation.

While the above mentioned examples are only a few ways in which NPFs can be varied, nanoengineered materials provides endless possibilities for research into the rich and complex area of strongly
correlated materials.
Bibliography


