Abstract

Charge Transport in Self-Assembled Nanoparticle–Molecule Systems

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Doctor of Philosophy

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University of Toronto

2009

Charge transport in self-assembled gold nanoparticle (NP)–alkanedithiol (HS(CH₂)nSH) systems are investigated using break-junctions. A remarkably simple and reproducible method to fabricate break-junctions using electromigration is described. Using the break-junctions, self-assembled NP systems are studied in two limits: (1) at the single-NP and (2) at the NP-array limits.

Single-NP devices exhibit Coulomb-blockade (CB) conductance suppressions at low temperatures. Contrary to predictions of an “Orthodox” theory, temperature-dependence of conductance inside CB exhibits multiple activation energies ($E_a$): A small $E_a$ at low temperatures, and a larger $E_a$ at high temperatures. The small $E_a$ is independent of NP size and is attributed to an energy state at the metal–molecule contact, whereas the larger $E_a$ scales with NP size and is attributed to NPs’ charging energy. Importantly, a significant (∼5–100fold) discrepancy is observed between values of charging energies obtained from $E_a$ and CB thresholds. To account for the discrepancy, a new model is proposed in which electrons can temporarily be localized at the energy states at the contacts and lose energy. The model is supported by ultraviolet photoelectron spectroscopy which shows energy states close to Fermi level likely arising from gold–thiolate bonds. A suitably modified Orthodox theory can successfully explain the experimental observations. These results underscore the critical role of metal–molecule contacts in influencing energy-profiles of molecular junctions.
Resistance–temperature dependencies of alkanedithiol-linked NP films show evidence of a metal–insulator transition (MIT) as $n$ is varied. The MIT occurs at $n = 5$ and is explained in the context of a Mott-Hubbard model. Furthermore, all metallic films exhibit temperature coefficients of resistance that are smaller than that of bulk gold, and all insulating films exhibit a universal behavior, $R \propto \exp\left[(T_0/T)^\nu\right]$, with $\nu = 0.65$. These observations are discussed in terms of temperature-independent elastic scattering and competitive thermally activated processes, respectively.

The ability to tune properties of NP films thru an MIT implies that materials near the transition may be viewed as semiconductors. To explore this analogy, application of these materials in fabricating field-effect transistors is briefly described. These results highlight the utility of NP films as a platform for studying charge transport.
Acknowledgements

I would like to express my deepest gratitude, special thanks and sincere appreciations to all those who helped, supported and encouraged me throughout my graduate study:

First to my thesis advisor, Prof. Al-Amin Dhirani, for support, guidance and insightful comments;

To my advisory committee members, Prof. John Polanyi, Prof. Dwayne Miller, and Prof. Gilbert Walker, for their advice and generous support;

To my colleagues in the Dhirani group, Yoshi, Jordan, Paul, Jeff, Brian, Ken, and Jimmy, for company and assistance;

To the Goh and Scholes groups at the Chemistry Department and the Birgeneau and Wei groups at the Physics Department for access to laboratory equipment;

To my undergraduate advisor, Prof. Davar Boghaei, for his continuous support;

To supporting organizations, University of Toronto, Ontario’s Ministry of Research and Innovation, Ontario’s Ministry of Training, and Natural Science and Engineering Research Council for Canada, for financial assistance;

To all dear Torontonian friends and families for companionship;

Finally, to my beloved family in Iran for support, patience, and encouragement, and to my love, Lili.
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Part I

Introduction
Self-Assembled Nanoparticle–Molecule Systems

1.1 Electronic Properties of Nanostructured Materials

Nanoscale materials often exhibit electronic properties that are much different from the properties of their corresponding bulk material. A fundamental quantity that describes electrical properties of a material is conductance, $g$, that is defined as the ratio between current, $I$, and an applied bias voltage, $V_b$:

$$g = \frac{I}{V_b}. \quad (1.1)$$

$g$ for a macroscopic conductor obeys Ohm’s law,

$$g = \sigma \frac{A}{L}, \quad (1.2)$$

where $A$, $L$, and $\sigma$ are the cross sectional area, length, and electrical conductivity of the conductor, respectively. Electron transport at the macroscopic scale is a diffusive process, and conductance of the conductor is limited because of charge scattering. A classical theory of conduction in conductors is the Drude model in which scattering is
characterized by a mean free path, $\ell$. $\ell$ is an average distance that charge can travel before it is scattered. Conductivity depends on $\ell$ and the density of charge carriers, $\eta$:\(^1\)

$$\sigma = \frac{\eta e^2 \ell}{mv}. \quad (1.3)$$

Here $e$, $m$ and $v$ represent charge, mass and velocity of conducting electrons, respectively.

Conductance of a nanoconductor usually does not obey Ohm’s law. As the size of a conductor decreases, several effects that are negligible at the macroscopic scale become increasingly important. Some of these effects are as follows.

1. Sizes of nanoconductors are usually smaller than the bulk mean free path of electrons (at least in one dimension). For instance, $\ell$ for bulk Au at room temperature is $\sim 41$ nm. Therefore, electron transport in nanoconductors is no longer a diffusive process as described by Ohm’s law. For normal conductors, as $L$ becomes small, $g$ can exhibit values quantized in units of $g_Q$,\(^2\)

$$g_Q = \frac{2e^2}{h}, \quad (1.4)$$

where $h$ is Planck’s constant. In this limit, electron transport is ballistic; i.e., there is no scattering along the conduction pathway [1].

2. When the size of a conductor becomes comparable with the de Broglie wavelength of electrons, electrons can exhibit discrete energy levels due to quantum confinement, similar to the situation in a particle-in-a-box model. Quantum confinement can exist in one, two, or three dimensions, such as in graphene, nanowires, and nanoparticles, respectively. For example, energy level spacing, $\delta$, in a metallic nanoparticle (NP) is given by

$$\delta \approx \frac{4E_F}{3N}, \quad (1.5)$$

---

\(^1\)In this dissertation, it is assumed that electrons are the main charge carriers

\(^2\) $g_Q$ is a limiting value of conductance for the case of a ballistic conductor with only one transport channel. If $M$ channels are present, the limiting value of conductance become $Mg_Q$. 
where $E_F$ is the Fermi energy of the bulk material (assumed to be the same for the NP) and $N$ is the number of atoms in the NP. Therefore, $\delta$ depends on the NP volume and increases as the NP radius, $r$, is reduced: $\delta \propto r^{-3}$. For a gold NP with $r = 1$ nm and $E_F = 5.5$ eV, $\delta \sim 10$ meV.

3. Addition of extra charges on nanostructures can occur in a discrete manner, because of their small capacitances. Consider an isolated conducting particle with a capacitance $C$. The energy required to add a charge $Q$ to the particle is

$$E_c = \int_0^Q Vdq = \int_0^Q \frac{q}{C}dq = \frac{Q^2}{2C},$$

(1.6)

where $V$ is the electrostatic potential. For a spherical particle with radius $r$ and charge $Q$,

$$V = \frac{Q}{4\pi \varepsilon_r \varepsilon_0 r},$$

(1.7)

and

$$C = 4\pi \varepsilon_r \varepsilon_0 r,$$

(1.8)

where $\varepsilon_0$ is the permittivity of vacuum, and $\varepsilon_r$ is the dielectric constant of the surroundings. As $r$ decreases, $C$ decreases and $E_c$ grows. For very small particles, $E_c$ can be so large that charging of the particle becomes quantized. For example, for a nanoparticle with $r = 5$ nm, the single-electron charging energy is $e^2/2C \sim 140$ meV, much larger than the energy provided by thermal fluctuations at room temperature ($k_B T \approx 25$ meV, where $k_B$ is Boltzmann’s constant and $T$ is temperature).

4. The contact between electrodes and nanostructures can strongly influence the overall conductance of electrode–nanostructure–electrode junctions. The continuum density of states in the electrodes can significantly affect the discrete electronic levels in the nanostructure through shifting or broadening of the electronic levels. In addition, formation of chemical bonds at electrode–nanostructure interfaces
can influence energy level alignments and modify potential energy profiles in the junctions.

Arrays of nanostructures can also exhibit interesting properties. Properties of nanostructure arrays are determined by the properties of the individual nanostructures as well as their interactions and arrangements in the arrays. For example, charges on one nanostructure can polarize neighboring nanostructures and can affect single-electron charging energies of the nanostructures in the arrays. In addition to such classical coupling effects, quantum coupling can also play an important role. Quantum coupling can impact the rate of charge transfer between nanostructures and, in the limit of strong coupling, can result in electron delocalization between nanostructures. The arrangement of nanostructures in the arrays can also give rise to important effects such as percolation and disorder-driven electron localization.

Nanostructured materials, therefore, exhibit a rich range of electronic behavior and have been the subject of extensive study. Researchers from a variety of disciplines, ranging from chemistry and physics to materials and electrical engineering, are attempting to develop new experimental tools and theoretical frameworks to understand electronic behaviors of these materials. Such an understanding not only is essential to realization of miniaturized electronic devices, but can also provide valuable insights into many chemical and biological processes that involve charge transfer at the nanoscale. These include electrochemistry, spectroscopy, chemical and biological sensing, and energy conversion.

1.2 Self-Assembly

In order to study electronic properties of nanostructured materials, they should be fabricated on support structures and should ultimately be attached to macroscopic electrodes. Nanoscale fabrication techniques can be classified into two broad categories: “top-down” or “bottom-up” approaches. The top-down approach involves down-scaling patterning
of materials to the nanometer scale. In a top-down approach such as lithography, one starts with bulk material and etches away unwanted material to create patterned nanostructures. In contrast, the bottom-up approach involves formation of materials starting with components that are atomic and/or molecular in size. Bottom-up assembly may involve arrangement of one or many different types of components, producing structures that exhibit properties that represent a combination of component properties.

Self-assembly is a bottom-up method that involves spontaneous and directional assembly of nanostructures into complex architectures via specific interactions such as van der Waals, electrostatic, or hydrogen bonding \[2\]. Self-assembly can result in robust structures that are formed by either thermodynamically or kinetically favored pathways. This method is commonly used in nature for the creation of complex biological structures such as cells.

Self-assembly offers several advantages over top-down approaches and is the method used in this thesis. Top-down approaches based on optical lithography, though facile and inexpensive, are limited to fabrication of structures with minimum size features of \(\sim 100\) nm. Electron-beam lithography is capable of producing features of the order of \(\sim 5\) nm. However, unlike optical lithography which is a parallel process (many features can be patterned at once), e-beam lithography is a serial process (patterns are made one at a time) and is slow and expensive and requires specialized equipment. Self-assembly, in contrast, is fast and cost-effective and can produce features well below the limits of lithography. It also permits access to a wide range of material components. For example, pre-fabricated NPs and molecules with a variety of electronic structures and chemical functionalities can be assembled to form composite structures with a wide range of electro-chemical properties. Self-assembly also provides a powerful approach for fabrication of integrated nanoscale devices using wet chemical methods. For example, chemically synthesized NPs can be attached to macroscopic support structures using organic linker molecules. It should be noted that self-assembly has a number of limitations.
1. **Self-Assembled Nanoparticle–Molecule Systems**

![Figure 1.1: Schematic of an ideal SAM of hexanedithiol on gold. Sulfur, carbon, and hydrogen atoms are shown in red, black, and white, respectively.](image)

For example, self-assembled monolayers and related structures may have defects which may affect electronic characteristics. Also, the self-assembly process requires relatively weak, thermally labile surface bonds. Nevertheless, self-assembly provides a route to bridge the nano and macroscopic scales.

In this thesis, Au NPs and $\alpha,\omega$-alkanedithiol, $\text{HS(CH}_2\text{)}_n\text{SH}$, molecules are used as prototype self-assembly components, since their properties are well-known and they can be obtained easily. Au NPs with controlled sizes can be synthesized in aqueous or organic solvents using established procedures and are stable for long periods of time (up to several months). Au NPs themselves are of interest for a variety of reasons. They exhibit remarkable electronic behaviors (such as single-electron charging as mentioned above), optical behaviors (such as surface-plasmon resonance), enhanced surface reactivity, and improved catalytic activity [3, 4]. The latter is due to large surface-to-volume ratios of NPs [3, 4]. In addition, biocompatibility of Au NPs has enabled fabrication of NP–biomolecule hybrid assemblies in which biomolecules retain their bioactivities [5]. Au NPs are being extensively investigated for applications in many biological and medical areas such as in biosensing [5], drug delivery [6], and cancer therapy [7].

Alkanedithiols with various chain lengths are commercially available. They bind strongly to gold and those with sufficiently long alkane chains, i.e. $n \geq 6$, can form ordered and packed self-assembled monolayers (SAMs) on gold substrates (see figure 1.1) [8]. The formation of SAMs is driven by van der Waals interactions between alkane
chains [8]. In the SAMs of alkanedithiols, one end of the molecules is attached to the substrate, forming gold-thiolate bonds. The other thiol end is free, providing a “sticky” surface for attachment of Au NPs. Repeated self-assembly of alkanedithiols and Au NPs on a substrate can result in multilayered structures in which the NPs are cross-linked by the molecules [9]. Alkanedithiols, therefore, can act as spacers and can control NP–substrate or NP–NP separation distances [9]. Linker molecules themselves may possess non-trivial charge transport properties [10]. For example, films comprising molecules such as conjugated hydrocarbons exhibit higher conductivities than those comprising saturated hydrocarbons of similar length [11]. Hence, the molecules can influence electronic properties of electrode–molecule–NP or NP–molecule–NP junctions.

1.3 Overview of the Thesis

The objective of this thesis is to explore charge transport in nanostructured systems that are prepared by self-assembly of gold NPs and alkanedithiol molecules. Systems in two particularly interesting limits are studied: (1) single NPs and (2) NP arrays. Studies of both systems yield valuable insight into phenomena involved in charge transport at the nanoscale. These phenomena include tunneling, single-electron charging, energy loss at metal–molecule contacts, coupling, percolation, metal–insulator transition, variable-range hopping, and scattering. This thesis describes insights gained by systematically varying structures of the NP–molecule systems as described below.

1.3.1 Charge Transport in Self-Assembled Single-Nanoparticle Devices

Single-NP devices can be prepared by forming SAMs of alkanedithiol on gold electrodes, and then bridging the gap between the SAMs with a gold NP. Given the size of NPs and the length of alkanedithiols, device preparation requires fashioning of electrodes with
nanometer separations. This is a central challenge in nanostructured electronics. Issues related to electrodes such as size and separation, contact resistance, energy loss, stability, ease and cost of fabrication are all important considerations. To address these issues, several approaches have been commonly employed [12, 13, 14, 15, 16]. These involve vertical electrode geometries such as sandwich junctions and scanning probe microscopy, or horizontal geometries such as break junctions (BJs) created by mechanical breaking or electromigration. The latter are straightforward to prepare and mass-produce, and can be extended to accommodate a third (gate) electrode.

In this thesis, BJ electrodes are used. The BJs are prepared using a non-lithographic approach, based on electromigration, that the author and co-workers have recently developed and published [17]. The method involves the following steps: First, 100-µm-wide, 8-nm-thick gold wires are deposited onto glass substrates through shadow masks, and next, nanometer-sized gaps in the wires are created by passing large currents through the wires at 77 K. The method provides a remarkably simple and reproducible approach for fabricating robust BJs. An important benefit of the method is that it is relatively fast, straightforward, and inexpensive, and since it does not require lithography, it can be performed using commonly available equipment. Also, given that the BJs are supported on solid substrates, they are mechanically stable. This property makes them suitable for studying charge transport as a function of temperature, magnetic field, etc. [18, 19, 20].

After electrode fabrication, SAMs are formed on the BJs by immersing substrates into ethanol solutions of alkanedithiols for ~1 h. Then, chemically synthesized Au NPs are incorporated in the gap between electrodes using two methods: (1) self-assembly of Au NPs from solution onto electrodes and (2) electrostatic trapping. Three different sizes of Au NPs are used: 2.5, 5, and 10 nm. The NPs are capped with alkanethiols, \( \text{CH}_3(\text{CH}_2)_{n-1}\text{SH} \), to prevent NP aggregation both in solution and on electrode surfaces. Different lengths of linkers and capping ligands, i.e. \( n = 4 \) and \( 6 \), are used. Single-NP devices are characterized by scanning electron microscopy (SEM) and room-temperature...
conductance measurements. Current–voltage characteristics of the devices are measured as a function of temperature down to liquid helium temperatures. Results are then analyzed in context of a semiclassical “Orthodox” theory of metal–insulator–nanoisland–insulator–metal (MINIM) systems [21, 22].

In MINIM systems, single-electron charging of the central islands strongly affects electron flow through the systems. These systems are, therefore, known as “single-electron devices” (SEDs). When a bias voltage is applied to an SED, the central island must first charge up to a certain threshold voltage before even a single electron can flow through the system. At low temperatures, electron transfer at voltages below the threshold is suppressed and current is zero. This phenomenon is known as “Coulomb Blockade” (CB). Above the threshold, electrons can charge the island and current starts to flow. At even higher voltages, where it is energetically favorable to charge the island with multiple electrons, incremental steps in current can be observed. These steps are known as “Coulomb staircases” (see Figure 1.2, curve a).

Traditionally, SEDs have been prepared using top-down approaches, such as electron-beam lithography and multiple-angle deposition–oxidation–deposition processes [25, 26, 23, 24, 27]. The SEDs have been extensively studied because of their potential applications in spectroscopy, information storage, thermometry, etc. [28]. Electron transport in these non-self-assembled SEDs has been successfully described by the Orthodox theory. Figure 1.2 shows a fit to experimental data obtained using the orthodox theory (curve b). The fit is in excellent agreement with the data.

In contrast, SEDs that are prepared by molecular self-assembly have been reported to exhibit behaviors that deviate from predictions of the Orthodox theory [29, 30]. An important source of the deviation may be that the Orthodox theory treats the molecular SAMs as simple insulating barriers. Molecules, however, can exhibit more complex behaviors [10], ranging from nonuniform voltage drops [31] as a result of multi-barrier potentials [32] to electron–molecular orbital interactions, which in turn can give rise to
Figure 1.2: (a) Experimental current–voltage characteristics of a non-self-assembled SED showing a central Coulomb blockade gap and three Coulomb staircases. Data are obtained by probing a small indium droplet using a scanning tunneling microscope at 4 K. Indium droplets were prepared by evaporation on an Al/Al₂O₃ substrate. Inset shows schematic of the experiment. (b) Numerical fit to the experimental data obtained using the Orthodox theory. The fit curve is shifted by 0.2 nA for clarity. Reprinted with permission from References [23, 24]. Copyright 1989 and 1991 American Physical Society.
1. SELF-ASSEMBLED NANOPARTICLE–MOLECULE SYSTEMS

processes such as resonant tunneling and oxidation-reduction [33]. In addition, metal–molecules contacts can strongly affect properties of self-assembled SEDs (see below). These effects, which are absent in traditionally prepared SEDs, are not considered by the Orthodox theory.

Phrased another way, studies of self-assembled SEDs not only can provide important information about single-electron charging of the NPs, but they can also provide new valuable insight into charge transport through the molecules. In fact, self-assembled single-NP devices enable a novel route to study conductance of molecular junctions. Demonstrating the utility of this approach to study charge transport in molecular junctions is one of the important results presented in this thesis. This approach offers two key features: (1) it does not require fabrication of electrodes with gap sizes equal to or less than the sizes of molecules (typically 1–2 nm), and (2) the NPs (or generally, nanostructures) provide a practical means to analyze the energy of charges that traverse the junction. The latter is possible because of the single-electron charging of NPs and is implemented via “thermo-voltammetric” spectroscopy in which energy scales of the junctions are probed by independently varying bias voltage ($V_b$) and temperature ($T$).

Variable-$V_b$ and variable-$T$ measurements provide two independent means for determining energy scales, here NP charging energies ($E_c$), as follows. At low $T$, SEDs exhibit current and conductance suppressions below the CB bias thresholds ($\Delta V_{CB}$). $E_c$ thus can be obtained from $\Delta V_{CB}$ at low $T$. As $T$ increases, electrons are able to overcome $E_c$ thermally, and as one may expect, conductance follows an Arrhenius behavior. According to the Orthodox theory, the Arrhenius activation energy ($E_a$) is equal to $E_c$. Therefore, $E_c$ can be obtained from $E_a$, too. Results show that values of $E_c$ obtained in both ways scale with NP size, confirming that they are in fact due to single-electron charging effects. However, a significant discrepancy is observed between values of $E_c$ determined from $\Delta V_{CB}$ and $E_a$, the former being larger by a factor of $\sim 5–100$.

To account for the discrepancy, a number of published extensions to the Orthodox
theory are considered. These include cotunneling, voltage-induced barrier suppression, and self-heating. Given that none of the aforementioned extensions are able to justify the discrepancy, a new model is proposed. The proposed model considers a multi-barrier potential profile for the molecular junction which in turn gives rise to a voltage divider effect. The model contends that metal–molecule contacts introduce small barriers in the conduction pathway of electrons and introduce energy states close to the Fermi level of the metal. The barrier and the energy states likely arise from interfacial dipoles and gold–thiolate bonds, respectively. Electrons can be temporarily localized at the energy states and lose energy. As a result, only a fraction of $V_b$ is applied to the NP and, hence, a larger $\Delta V_{CB}$ is needed to overcome the NP charging energy. The author and co-workers have described these results and the model in References [17, 34].

Further experimental evidence supporting the proposed model is provided by detailed study of $V_b$-dependencies of $E_a$ and by ultraviolet photoelectron spectroscopy (UPS). Detailed Arrhenius analyses reveal that there are in fact multiple activation energies associated with the self-assembled single-NP devices. There is a larger $E_a$ which is attributed to the NP charging since it scales with NP size. There is also a smaller $E_a$ which varies less significantly with NP size and is assigned to the small barrier at the metal–molecule interface. Accordingly, a number of modifications to the Orthodox model are proposed. These modifications are able to explain successfully the experimental findings. UPS provides a means to directly probe electronic structures of SAMs on substrates. UPS spectra of alkanedithiol SAMs on gold exhibit two features that further support the proposed model: (1) the spectra exhibit an energy state close to the Fermi level of gold due to the formation of a gold–thiolate bond, and (2) the spectra exhibit a reduction in gold’s work function due to the interfacial dipole. The author and co-workers have described these results in Reference [35].

This study demonstrates the critical role of metal–molecule contacts in influencing energetics of molecular electronic devices. In particular, it shows that energy loss at
metal–molecule contacts is an important issue and should be considered in electronic studies and applications of molecular junctions. It also highlights the value of thermovoltammetric spectroscopy as a tool for studying charge transport in nanostructures.

1.3.2 Charge Transport in Self-Assembled Nanoparticle Films

NP films represent a novel class of granular materials. Granular materials consist of grains embedded in insulating matrices and exhibit properties that depend on architecture and composition of the materials [36]. Conventional granular films, that is, those that are usually prepared by deposition methods such as thermal evaporation, sputtering, chemical vapor deposition, electroless deposition, etc., have been extensively studied [36]. They are typically disordered and usually exhibit three distinct electronic regimes:

1. An insulating regime, where the volume fraction of grains is small and the grains form isolated islands.

2. A bulk regime, where the concentration of grains is large enough that the isolated islands merge and form continuous pathways through the film.

3. A transition regime, where a transition from insulating to bulk regimes occurs at a critical concentration of grains (percolation threshold). Above the threshold at least one sample spanning pathway is established throughout the film.

In conventional granular films, film thickness influences both grain size and inter-grain spacing, both of which strongly impact film properties. For example, varying spacing between metallic grains can induce a metal–insulator transition. Varying grain size in the insulating regime influences single-electron charging energies and in the bulk regime influences length scale of elastic scattering at grain surfaces. Independent control of grain size and spacing in conventional granular materials can be achieved to a degree by co-deposition of insulating and non-insulating material, but control over uniformity of grain size and spacing at the sub-nanometer scale is not generally possible.
1. **Self-Assembled Nanoparticle–Molecule Systems**

Self-assembled molecularly linked NP (ML-NP) films, on the other hand, represent a new, exquisitely controlled platform for systematically exploring structure–property relationships in granular films. In this approach, the increased control is possible since NPs and molecules with desired properties can be separately synthesized by wet chemical methods and subsequently organized into assemblies. Properties of individual NPs depend on their size, shape, and composition and, therefore, are tunable using recent advances in synthetic methods. Coupling between NPs can be controlled, for example, by varying their separations through use of molecular linkers. Thickness of films can be controlled by alternately self-assembling NPs and linker molecules on a surface. Arrangement of NPs is controllable through to a degree the assembly process. Also, spatial disorder can be controllably introduced in otherwise ordered systems by varying NP size distribution.

The flexibility to independently control grain size, grain spacing, and film thickness combined with a broad range of choices for the NPs and molecules and the manner in which they can be arranged into materials has provided new opportunities in materials science. It has also enabled applications ranging from conductance switching (transistors) \([37]\) and information-storage \([38]\) to proof-of-principle demonstration of chemical/biological sensing \([39, 40, 41, 42, 43, 44, 45, 46]\), surface-enhanced Raman scattering \([47]\), conductive coatings \([48]\), and catalysis \([49]\).

In this thesis, ML-NP films are prepared by a stepwise self-assembly (SSA) method \([50, 51]\). The method involves alternate immersions of a substrate into solutions of NPs and linker molecules with intervening rinse steps. ML-NP films prepared by the SSA method possess a number of noteworthy features \([52, 53]\):

1. Given that in these films strong (covalent) bonds are used to attach NPs to each other and to the substrate, the films are mechanically stable. As a result, the films can be immersed in solutions without significant re-dispersion.

2. Properties of the films can be controlled via the choice of linker molecules. Studies
of Au NP films comprising short alkanedithiols (such as 1,4-butanedithiol) have reported metallic-like charge transport [54], while studies of films comprising long alkanedithiols (such as 1,8-octanediethiol) have reported thermally activated transport [9]. Also, studies of NP films comprising conjugated hydrocarbons have reported higher film conductivity than that of NP films comprising saturated hydrocarbons of similar length [11]. The molecules can have various chemical structure (such as saturated or conjugated) and functionality (such as redox-activity, catalytic-activity, or bio-activity). Our group, for example, has prepared multilayer films of Au NPs cross-linked with ferrocene derivatives, in which the ferrocene moieties retain their redox-active properties [55]. This feature together with the good stability of the films, highlight a possibility of modifying electrochemical properties of electrode surfaces using the self-assembled ML-NP films.

3. The overall thickness of the films can be controlled by varying the number and duration of immersion cycles. Experiments have shown that alternate immersions in 0.5 mM \( \alpha, \omega \)-alkanediethiol/toluene solution (10 min) and Au NP/toluene solution (\( \sim 1 \text{--} 2 \) h) result in an approximately linear increase in film absorption determined through UV/vis spectroscopy [54]. This indicates that an approximately constant amount of Au NPs are added with each immersion cycle.

Au NPs and \( \alpha, \omega \)-alkanediethiol molecules, HS(CH\(_2\))\(_n\)SH, are used to construct ML-NP films. It will be shown that by systematically varying lengths of molecules from \( \sim 0.5 \) nm \( (n = 2) \) to \( \sim 1.6 \) nm \( (n = 10) \) in increments of \( \sim 0.1 \) nm (one CH\(_2\) unit), bulk film properties can be tuned from metallic to insulating: NP films comprising short linkers \( (n \leq 5) \) exhibit metallic behavior, i.e. their conductances remain finite as \( T \rightarrow 0 \); whereas, NP films comprising long linkers \( (n \geq 5) \) exhibit thermally activated conductances and are insulators. Films of alkanedithiol-linked Au NPs, therefore, provide a controlled testbed for studying metal–insulator transition (MIT) in granular materials. This feature of the ML-NP films is also demonstrated in this dissertation. Results are explained in the con-
text of a Mott-Hubbard model for MITs. The model is based on a lattice of atoms with electrons that interact via on-site repulsion and intersite coupling. As intersite coupling increases, initially localized electrons can become itinerant, resulting in an MIT.

Results also show that all metallic films \( n \leq 5 \) exhibit temperature coefficients of resistance \( R \) that are smaller than that of bulk gold. This observation suggests that \( T \)-independent elastic scattering dominates \( R \) of the metallic films. Furthermore, all insulating films \( n \geq 5 \) exhibit a universal scaling behavior,

\[
R \propto \exp \left[ \left( \frac{T_0}{T} \right)^{\nu} \right],
\]

where \( T_0 \) is a constant with temperature units, and \( \nu = 0.65 \). This behavior can be explained in terms of competitive thermally activated processes. The author and co-workers have presented these results in a number of publications [56, 57, 58].

The ability to tune electronic properties of ML-NP films through MITs enables intriguing new electronic applications. For example, ML-NP films with properties intermediate those of metals and insulators can be thought of as semiconductors. Just like semiconductors, conductance of these films can be controlled by applying an electric field using a gate electrode in a field-effect transistor (FET) configuration. Our lab has demonstrated two examples of FET-type applications of ML-NP films. These applications include conductance switching [37] and multi-valued data storage [38], and are briefly described in this dissertation.

The remaining parts of the thesis are organized as follows. Part II describes general experimental techniques that are common to studies of both single NPs and ML-NP films. In Parts III and IV, charge transport phenomena in single-NP devices and ML-NP films are discussed, respectively. Each part starts with theoretical descriptions of the transport phenomena, followed by experimental results and discussions. Part V provides appendices including theoretical derivations of tunneling current formulae, a model for simulating tunneling current in presence of a small barrier, computer simulation codes, and a list of abbreviations.
Bibliography


[58] ———, “Metal-insulator transition in molecularly linked nanoparticle films,” 2008, Handbook of Nanophysics, in preparation. 1.3.2
Part II

General Experimental Techniques
Gold Nanoparticles

Three different sizes of Au NPs were used: 2.5, 5, and 10 nm. Depending on the NP size and the NP capping group, different synthetic methods were employed. NPs were characterized by UV/vis spectroscopy, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Details are as follows.

2.1 Nanoparticle Synthesis

The key to successful synthesis of NPs is to prevent contamination of foreign particles which can serve as premature nucleation centers for NP growth. To minimize inorganic contaminations, all glassware was cleaned with hot, freshly prepared, aqua regia (3:1 HCl/HNO₃) for \(\sim 30\) min and flushed with distilled, deionized water (DDW). To remove organic contaminants, the glassware was then cleaned with hot, freshly prepared, piranha (3:1 H₂SO₄/H₂O₂) and rinsed with DDW. The glassware was used immediately after drying in an oven at \(\sim 110^\circ\)C. All chemical reagents were purchased and used as received.

5 and 10 nm Nanoparticles in Water

Au NPs in water were synthesized using a citrate reduction method developed by Slot and Geuze [1]. To make 100 mL of the NP solution, two solutions were prepared: (1) a
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gold solution, containing 1 mL of 1% (wt.) hydrogen tetrachloroaurate (H\textsubscript{Au}Cl\textsubscript{4}) diluted with DDW to 80 mL, and (2) a reducing solution, containing 4 mL of 1% sodium citrate, 0 to 5 mL of 1% tannic acid, and 25 mM potassium carbonate (the same volume as tannic acid), diluted with DDW to 20 mL. The volume of tannic acid was selected based on the NP size desired. For 5 and 10 nm NPs, 0.5 and 0.05 mL were used, respectively. The two solutions were heated on a hotplate to 60 °C, monitored by a thermometer. Then, the reducing solution was quickly added to the gold solution under continued heating and vigorous stirring. After stirring for ~10 min or when the reaction was complete (indicated by color change from orange to dark, ruby red), the solution was brought to boil, then removed from the hotplate and left to cool down under ambient conditions. The NP solutions were stored at room temperature.

5 nm Nanoparticles in Toluene

Thiol-free ~ 5 nm Au NPs in toluene were synthesized using a method developed by Brust et al. [2]. 0.394 g (1.00 mmol) of hydrogen tetrachloroaurate trihydrate was dissolved in 25 mL of DDW in an erlenmeyer flask, producing an orange solution. 1.47 g (2.50 mmol) of tetraoctylammonium bromide was dissolved in 50 mL of spectroscopy-grade toluene and added to the flask. The mixture was vigorously stirred for ~10 min until the aqueous phase (bottom layer) became clear. The mixture was then transferred to a separatory funnel and the aqueous layer was removed. The organic layer was collected in an erlenmeyer flask, and 0.400 g (10.6 mmol) of sodium borohydride dissolved in 25 mL of DDW was added. This solution was stirred for ~18 hours, and the aqueous phase was removed again. The ruby red organic phase was washed three times with 50 mL each of 0.1 M sulfuric acid, 1.0 M potassium carbonate, and DDW, respectively. After each washing step, the aqueous layer was removed. The organic phase was then dried by vacuum filtration through magnesium sulphate. The NP solution was diluted to ~200 mL with additional spectro-grade toluene and refrigerated.
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2.5 nm Nanoparticles in Toluene

Hexanethiol-capped ~ 2.5 nm Au NPs were synthesized in toluene following Brust’s procedure [3]. 30 mL of a 30 mM aqueous solution of hydrogen tetrachloroaurate was mixed with 80 mL of a 50 mM solution of tetraoctylammonium bromide in toluene. The two-phase mixture was vigorously stirred until the aqueous phase became clear. The aqueous phase was removed and 170 mg hexanethiol was added to the organic phase. 25 mL of a 0.4 mM freshly prepared aqueous solution of sodium borohydride was slowly added with vigorous stirring. The solution was stirred for ~ 3 h, and the organic phase was isolated. The NP solution had a dark brown color and was stored in a fridge.¹

2.2 Nanoparticle Capping

The citrate stabilized 5 and 10 nm NPs were capped with alkanethiols as follows. In a 20 mL scintillation vial, 5 mL of the aqueous NP solution was mixed with 5 mL chloroform, and 5 μL alkanethiol was added to the organic (bottom) layer. The mixture was stirred vigorously under argon for ~ 12 h, after which the aqueous layer was discarded and the organic layer was transferred into a plastic tube. To ensure that most NPs were transferred, additional 1–2 mL portions of chloroform were added to the vial. The solution was sonicated for ~ 1 min and then added to the content of the tube. To extract NPs, a solution of 1:1 ethanol/methanol (the same volume as the NP solution) was mixed with the NP solution, and the volume of the mixture was reduced to a few mL under a flow of air. The mixture was then centrifuged, and a resulting precipitate was collected. The precipitate was washed with ethanol and methanol, dried with nitrogen, and finally dissolved in chloroform. Using this method, solutions of hexanethiol- and butanethiol-capped 5 and 10 nm Au NPs were prepared. The NP solutions, except butanethiol-capped 10 nm NPs, were stable at room temperature for at least several weeks.

¹These NPs were prepared and characterized by P.-E. Trudeau.
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Figure 2.1: Typical UV/vis spectra of (a) thiol-free 5 nm NPs in toluene, (b) citrate-stabilized 10 nm NPs in water, and (c) hexanethiol-capped 10 nm NPs in chloroform.

2.3 Nanoparticle Characterization

Solutions of 5–25 nm Au NPs exhibit a maximum absorbance in UV/vis spectra in the range of ∼ 515–530 nm. Figure 2.1 shows a peak at 527 nm for 5 nm Au NPs in toluene. This maximum absorbance is due to a surface plasmon resonance (SPR). SPR arises from a coherent oscillation of free electrons in the conduction band of metal NPs induced by the electromagnetic field of an incoming light wave [4, 5]. When the frequency of the field becomes resonant with the coherent electron oscillation, a strong absorption in the spectrum is observed. The frequency and width of the SPR peak depend on the size and shape of the metal NP as well as on the dielectric constant of the NP surroundings. For example, 10 nm Au NPs in water exhibit a peak at 517 nm, while hexanethiol-capped
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10 nm NPs in chloroform exhibit a peak at 538 nm. A change in inter-NP spacing can also influence the SPR peak. A decrease in the inter-NP spacing usually shifts the peak to higher wavelengths [6]. NP aggregates exhibit peaks around ~ 600 nm.

The sizes of NPs were determined using TEM. Figures 2.2 and 2.3 show typical TEM images of two types of Au NPs, 5 nm NPs in toluene and 10 nm NPs in water, respectively. TEM samples were prepared by drop-casting NP solutions on carbon-coated copper grids. A histogram of NP diameters for a typical batch of 5 nm NPs in toluene is shown in Figure 2.4.

Alkanethiol-capped NPs were also characterized by SEM. Figure 2.5 shows a typical SEM image of hexanethiol-capped 10 nm NPs self-assembled on a hexanethiol-functionalized gold wire. The gold wire, 55 nm thick, was prepared by thermal deposition on a glass slide (see Section 3.1) and was functionalized by immersion into a 0.5 mM ethanol solution of hexanethiol for 1 h. The slide was then rinsed with ethanol, dried with nitrogen, and immersed in a NP solution for 20 min. After rinsing with chloroform and drying with nitrogen, the slide was mounted on an SEM sample holder using a double-sided carbon tape. The gold wire was electrically connected to the sample holder using a conductive carbon tape. SEM images showed no significant NP aggregation or size change upon capping. Figure 2.5 shows that most (~ 95%) of the NPs are isolated and only small fractions of them form dimers (~ 4.8%) or trimers (~ 0.2%).
Figure 2.2: TEM images of 5 nm Au NPs prepared in toluene and drop-cast on a carbon-coated copper grid. Images were taken using an FEI Tecnai 20 microscope at the Advanced Bioimaging Centre in Mount Sinai Hospital.
Figure 2.3: TEM images of 10 nm Au NPs prepared in water and drop-cast on a carbon-coated copper grid. Images were taken using a Hitachi S-5200 microscope at the Centre for Nanostructure Imaging in the Department of Chemistry.
Figure 2.4: Histogram of NP diameters for a toluene solution of thiol-free 5 nm Au NPs. The histogram is obtained using TEM images as in Figure 2.2.
Figure 2.5: SEM image of hexanethiol-capped 10 nm NPs self-assembled on a hexanedithiol-functionalized gold wire. The image was taken using a Hitachi S-5200 SEM at the Centre for Nanostructure Imaging in the Department of Chemistry.
Chapter 3

Nanometer-Spaced Electrodes

Samples for electronic studies were prepared on BJs formed by electromigration. Our lab has developed a fast, straightforward, and reproducible method for fabricating BJs using 100 µm wide gold wires. Details are provided in this chapter.

3.1 Electrode Deposition

Gold wires were deposited on glass substrates by metal evaporation in a vacuum chamber (see Figure 3.1). Glass substrates, 5 mm × 8 mm × 1 mm, were cut from glass microscope slides (Corning) using a diamond glass cutter (Wale Apparatus Co.). This particular size of the substrate was chosen because of the size limitations of the SEM sample holder. The glass substrates, along with all glassware, were cleaned by immersion in a hot piranha solution (3:1 H₂SO₄/H₂O₂) for no less than 30 min. Then, they were rinsed thoroughly with copious amounts of DDW and dried with nitrogen gas.

To improve adhesion of gold to glass, two types of adhesion layers were used: a thin layer of chromium and a self-assembled monolayer of mercaptosilane. In absence of an adhesion layer, gold wires may easily peel off and this restricts chemical treatments of the wires. First, the deposition method involving chromium is described.
3. Nanometer-Spaced Electrodes

Figure 3.1: Photographs of the (a) exterior and (b) interior of a vacuum chamber used for depositing metal electrodes. (c) Diagram illustrating metal-vapor deposition. A metal source is evaporated via resistive heating in a vacuum chamber; atoms move ballistically and condense on a substrate while film thickness is monitored. Reprinted with permission from Reference [7]. Copyright 2008 J. L. Dunford.
3. Nanometer-Spaced Electrodes

Figure 3.2: (a) Schematic of a gold wire deposited on a glass substrate using a chromium adhesion layer. The electromigration circuit is also shown. (b) Schematic of the deposition setup.

After cleaning the glass substrates, they were immediately transferred to a vacuum chamber, and wires were deposited by evaporating metals through a shadow mask. The structure of a wire is illustrated in Figure 3.2(a). The wire consists of two thick parts (~100 µm wide, 4 mm long, and 63 nm thick) and one thin middle part (~100 µm wide, 100 µm long, and 8 nm thick). The thick parts were created first by depositing 1.5 nm Cr (chromium-plated tungsten rods; Kurt J. Lesker) followed by 55 nm Au (99:999% pellets; Kurt J. Lesker) through the shadow mask while a magnet wire (Belden 8085) was tightly attached to the mask. The shadow mask consisted of 100 µm wide slits machined in a 150 µm thick metal shim. The magnet wire was oriented perpendicular to the slits and was held in place using screws (see Figure 3.2(b)). Metals were deposited at an initial pressure of ~1 µT and a rate of ~0.1 Å/s for Cr and ~2 Å/s for Au. Thickness was monitored in situ using a quartz thickness monitor (Leyfold Inficon XTM/2). After each metal deposition step, the chamber was backfilled with nitrogen to ambient pressure. The magnet wire was then cut and the thin part of the wire was created by depositing an additional 8 nm of Au at a rate of ~0.1 Å/s. Note that in this method there is no adhesion layer underneath the thin part of the wire.
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Figure 3.3: Current–voltage (blue ■) and conductance–voltage (red ●) characteristics of a gold wire during electromigration.

To functionalize glass substrates with mercaptosilane, clean substrates were placed in a vial containing 10 mL toluene. The vial was then sealed with a rubber stopper, and a needle was injected into the stopper to allow release of pressure. The vial was heated on a hotplate until toluene started to boil. Then, 0.1 mL of 3-mercaptopropyltrimethoxysilane, HS(CH₂)₃Si(OCH₂CH₃)₃, was quickly injected. After the solution boiled for 20 min, the glass slides were removed, rinsed with toluene and DDW, and dried after each rinsing step. The substrates were then annealed in an oven at ∼ 110 °C for 10 min, rinsed with DDW and dried, and quickly transferred to the vacuum deposition chamber. Gold wires were deposited on the silanized substrates following the procedure described above, except that the Cr deposition step was skipped. Note that in this method adhesion layers are present underneath both thick and thin parts of the wires.

3.2 Electromigration

Nanometer gaps in the thin parts of the wires were created by electromigration at 77 K [8]. Figure 3.2(a) shows an electromigration circuit. A voltage ramp was applied across the wire and a 2.3 Ω resistor in series. An analog power supply (Hewlett Packard E3620A) was
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Figure 3.4: Current–voltage characteristics of representative break junctions.

used to ramp voltage ($V$) at a rate of 60 mV/s and measure current ($I$). Figure 3.3 shows typical current–voltage ($I - V$) and conductance–voltage ($I/V - V$) characteristics of a wire during electromigration at 77 K. The wire was deposited using a Cr adhesion layer. Wires deposited on silanized slides showed similar behaviors as well. As voltage increased, conductance gradually decreased, until at a break point ($V_b$), the conductance suddenly dropped by more than 8 orders of magnitude. Resulting BJs exhibited resistances ($R$) ranging from $10^8$ to $10^{13}$ Ω. Figure 3.4 shows $I - V$ characteristics of three representative BJs with resistances of $3.3 \times 10^9$, $2.0 \times 10^{10}$ and $> 10^{12}$ Ω. More than 80% of the BJs exhibited $R \gtrsim 10^9$ Ω and these were used for sample preparation.

Figure 3.5 shows break-point parameters for several BJs. Generally, higher currents ($I_b$) are required to break wires with lower resistances ($R_b = V_b/I_b$). This suggests that a critical current density ($J$) is required to break the junctions; for lower $R_b$ junctions, cross-sectional areas are larger, and therefore, higher $I_b$'s are required. Gradual decreasing of this area prior to the final break can also account for the steadily decreasing $I/V$ prior
to the break as seen in Figure 3.3. Typical break-point values of current density ($J_b \sim 100 \text{ mA/(100 } \mu\text{m} \times 15 \text{ nm)} \approx 10^{11} \text{ A/m}^2$) and voltage ($V_b \sim 2.5–5 \text{ V}$) are comparable with those reported for similar BJs [9, 10].

Figures 3.6 show optical microscopy photographs of a gold wire deposited using a Cr adhesion layer (a) before, (b)–(e) during, and (f) after electromigration at room temperature. Photographs (b)–(e) were taken after increasing the voltage to $\sim 2$, 3, 4, and 5 V, respectively. The photographs show that voids are gradually formed in the wire. The voids develop in a slit-like manner resulting in a gap along the width of the wire [11]. The gradual growth of voids is consistent with the gradual decrease of conductance during electromigration.

### 3.3 Break Junction Characterization

BJs were characterized using SEM. Samples were mounted on SEM sample holders using double-sided carbon tapes. Both electrodes were electrically connected to the sample holders using conductive carbon tapes. To reduce charging of glass substrates and the risk of electrostatic discharge, images were obtained at relatively low voltages of 1.0–2.0 kV. Figures 3.7(a)–(d) show SEM images of a typical gold wire after electromigration.
Figure 3.6: Optical microscopy photographs of a gold wire deposited using a Cr adhesion layer (a) before, (b)–(e) during, and (f) after electromigration at room temperature. The photographs were obtained using an Olympus BH-2 optical microscope with 1000× magnification and a Nikon Coolpix 8400 digital camera.
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Figure 3.7: (a)–(d) SEM images of a typical gold wire deposited using a Cr adhesion layer after electromigration. Images (b), (c) and (d) are magnifications of highlighted regions in (a), (b) and (c), respectively. A red line in (d) shows a possible location of a nanometer gap in the break junction. (e) SEM image of the wire before electromigration. The images were obtained using a Hitachi S-5200 SEM.
The wire was deposited using a Cr adhesion layer. Figure 3.7(a) shows a gap between Au electrodes. The width of the gap ranges from nanometers to microns. In the micron-range gap regions, many Au islands, a few 100 nm in diameter, are observed (Figure 3.7(b)). Such islands are known to generate Coulomb blockade effects in some BJs [12]. However, contributions of these islands to the conductance of the NP samples are negligible in our experiments, since the resistance of BJs are more than 2–3 orders of magnitude larger than the resistance of the samples with self-assembled NPs as will be discussed in Chapter 7. Figures 3.7(c,d) show magnified images of a nanometer-range gap region. The Au electrodes exhibit a gyroid-like structure which may obscure the identification of the gap. The gyroid-like structure is likely formed due to heating of the thin part of the gold wire during electromigration. In Figure 3.7(d), a possible location of a nanometer gap is highlighted. The size of the gap, estimated from SEM images, is < 10 nm. By comparing the resistance of the BJs with published results for mechanically controlled BJs with variable gap size [13], the width of the gap is estimated to be ≲ 5 nm at the narrowest region. An SEM image of the thin gold wire before electromigration is also shown in Figure 3.7(e). Note that since there is no adhesion layer underneath the thin part, gold forms a nonuniform film in this region.

BJs prepared on silanized substrates also exhibit nanometer gaps. Such BJs typically exhibit 1–3 regions with electrode separations in the nanometer range. Figure 3.8 shows representative SEM images of a BJ with a gap that is approximately 1–2 nm wide in the narrowest region (for additional SEM images, see attachment 1). These BJs generally exhibit fewer islands in the gap and more continuous film structure as compared to those created without an adhesion layer. Studies of gold films evaporated on mercaptosilane-functionalized glass substrates have shown that gold can form atomically flat films on these substrates because of the strong Au–S interactions [14]. The BJs on silanized substrates also often exhibit voids that are sharply truncated. The sharp edges can be

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1The attachment is available in the pdf version of the thesis.
Figure 3.8: SEM images of a typical BJ created on a mercaptosilane-functionalized glass substrate. Image (b) is a magnification of a highlighted region in (a), displaying a gap with an approximately 1–2 nm width. The images were obtained using a Hitachi S-5200 SEM.
attributed to gold crystal facets that are formed upon heating/cooling of the junctions during/after electromigration.

3.4 Break Junction Failure

BJs are highly susceptible to damage by electrostatic discharge once they are attached to wires. Figure 3.9 shows SEM images of a junction before and after being damaged. Electrostatic discharge mainly damages regions where electrode separations are smallest. To avoid such damage, samples must be meticulously kept grounded as much as possible. The body, tweezers, the soldering iron, sample mounts and measurement instruments must be also grounded when handling samples. A recommended procedure for measuring $I - V$ characteristics of a BJ using a Keithley 428 current amplifier is as follows. First ground both electrodes of the BJs. To do this, first ground wires and then attach them to the electrodes. Then, turn on a “Zero Check” button on the front panel of the Keithley current amplifier. Next, connect different parts of the measurement circuit using BNC cables (see Figure 3.10). Finally, turn off zero check and unground the sample. To remove the sample from the circuit, ground the sample first and then turn on zero check.
Figure 3.9: SEM images of a junction (a) before and (b) after being damaged by electrostatic discharge. Red circles highlight damaged regions.
Figure 3.10: Schematic of a circuit used for measuring current–voltage characteristics of a break-junction sample.
4.1 Electrical Leads and Contacts

Copper magnet wires (Belden 8085) were used as electrical leads. A few millimeters of insulation on each end of wires was stripped with a razor blade. The copper wires were attached to sample electrodes using indium (99.999%; ESPI). The indium was soldered to gold electrodes using a Weller EC1002 soldering iron at a temperature range of \( \sim 200 - 260 \, ^\circ\text{C} \). Indium has a low melting point (approximately 170 \(^\circ\text{C}\)) and exhibits good wettability to clean gold and glass surfaces. However, wettability of indium was poor on molecularly functionalized gold or glass. This poor wettability was noticeable often when attempting to solder copper wires to samples. Even when soldering was successful, indium contacts would occasionally become disconnected when immersing samples in various solutions or during variable-temperature measurements. To ensure mechanically strong connections, indium was always initially spread on glass and then was drawn over gold electrodes.

Indium can become a superconductor at temperatures below \( \sim 6 \, \text{K} \) and this may affect electronic properties of samples. For example, some metallic NP films exhibit a drop in resistance when cooled below 6 K (see Section 12.4, Figure 12.8). The resistance drop is \( \sim 0.3 \, \Omega \) and is attributed to indium-sample contact resistances. This value is
negligible compared to the resistances of the samples studied in this thesis: single-NP devices, insulating NP films, and metallic NP films exhibit resistances in the ranges of $\sim 10^6-10^8 \ \Omega$, $\sim 10^4-10^6 \ \Omega$, and $\sim 10-10^2 \ \Omega$, respectively.

To connect samples to measurement instruments, coaxial BNC cables were used. The copper magnet wires were attached to inner pins of the BNC cables using solder tail connectors. Bodies of the BNC cables were grounded. All connections were shielded to remove electrical noise using boxes wrapped with aluminum foil.

4.2 Electronic Equipment

Several simple home-made devices using operational amplifiers, including summing amplifiers, $I-V$ converters, and voltage followers, were built for electronic measurements. Circuit diagrams of these devices are shown in Figure 4.1. In all devices, LF411CN operational amplifiers were used. Supply voltages of the operational amplifiers were provided using 15 V dc power supplies built in our lab. The $I-V$ converter had interchangeable resistors, $R_{gain}$, with values ranging from $10^3-10^9 \ \Omega$ in logarithmic increments.

Depending on the magnitude of current involved in the measurements, two types of dc sources and meters were used. For experiments involving low currents ($< 1 \ mA$), bias was applied using a digital data acquisition card (National Instruments PCIMIO 16X), current was converted to voltage using a current amplifier (either home-made or commercial Keithley 428), and voltage was measured using the data acquisition card. Voltage outputs/inputs of the data acquisition card were controlled/measured using a computer program (LabView 6i). For high-current experiments, such as electromigration, an analog power supply (Hewlett Packard E3620A) was used to apply voltage and measure current. Current and voltage were then recorded by measuring voltages across a known resistor in series with the sample using home-made voltage followers and the data acquisition card.
4. Electrical Measurements

Figure 4.1: Circuit diagrams of (a) a summing amplifier, (b) an $I - V$ converter, and (c) a voltage follower used for electronic measurements.
For experiments involving ac signals, a digital function generator (Stanford Research Systems DS345) and a lock-in amplifier (Stanford Research Systems SR310) were also used. The function generator created an ac voltage output $V_{ac}$,

$$V_{ac} = V_0 \cos 2\pi ft,$$

where $V_0$ is the maximum voltage amplitude, $f$ is frequency, and $t$ is time. $V_{ac}$ was added to the dc output of the data acquisition card, $V_{dc}$, using a home-made summing amplifier. The total voltage, $V_{dc} + V_{ac}$, was applied to the sample and current was then converted to voltage using a current amplifier. The resulting voltage was simultaneously measured using the data acquisition card and the lock-in amplifier. The lock-in amplifier measures the ac component of the voltage at the frequency $f$ (or some multiple of $f$ if desired) and provides a dc output voltage proportional to $dI/dV(V_{dc})$ as follows. The current is a function of the total voltage applied to the sample, i.e., $I = I(V_{dc} + V_{ac})$. Expanding about $V_{dc}$ yields the following:

$$I(V_{dc} + V_{ac}) = I(V_{dc}) + \frac{dI}{dV}(V_{dc}) \cdot V_{ac} + \cdots$$

$$= I(V_{dc}) + \frac{dI}{dV}(V_{dc}) \cdot V_0 \cos 2\pi ft + \cdots \quad (4.2)$$

The lock-in’s output, measured at frequency $f$, is proportional to the coefficient of $\cos 2\pi ft$; therefore, apart from known amplification factors, the lock-in’s output is given by $dI/dV(V_{dc}) \cdot V_0$. The exact output of the lock-in at the frequency $f$ is given by

$$V_{\text{lock-in}} = \frac{(dI/dV) \cdot V_0 \cdot R_{\text{gain}} \cdot N_{\text{expand}} \cdot (10 \ V)}{V_{\text{sens}}}, \quad (4.3)$$

where $N_{\text{expand}}$ is a dimensionless amplification factor and $V_{\text{sens}}$ is the lock-in’s sensitivity. $N_{\text{expand}}$ and $V_{\text{sens}}$ are parts of the lock-in settings. Harmonic frequencies of $2f$, $3f$, $\ldots$ yield the second, third, $\ldots$ derivatives of $I$ versus $V$, respectively.
4.3 Cryostats

To control temperature in the range of 77 to 300 K, a home-made liquid nitrogen cryostat were used. The cryostat consisted of a liquid nitrogen dewar and a home-made long stick. The stick was used to adjust the position of samples in the dewar and consisted of four parts (see Figure 4.2): a 10 cm long aluminum cap, a 10 cm long copper rod, a 1.5 m long aluminum tube, and an electric box. Samples were mounted on the copper rod. A teflon ribbon was used to wrap the samples and hold them in place, and also isolate them from the aluminum cap. The cap was attached to the copper rod using a screw. Samples were connected to the electric box using magnet wires that were passed through the aluminum tube. Temperature was measured using a thermocouple positioned near the sample. Temperature was controlled by (1) adjusting the height of the sample above the liquid nitrogen surface inside the dewar and (2) using a resistive heater. The power of the heater was adjusted by a temperature controller (Scientific Instruments 9700) through an active feedback.

To control temperature down to liquid helium temperatures, a physical property measurement system (PPMS; Quantum Design) was used. The PPMS was capable of controlling temperature from 1.800 to 350.00 K with 1 mK resolution below 10.00 K and a maximum heating rate of 10 K/min. Samples were mounted on a “resistivity puck” (Quantum Design) using high-vacuum silicon grease (Dow Corning) and were soldered to electrical pads of the puck using indium and magnet wires (Figure 4.3(a)). To avoid electrostatic discharge, all electrical pads were grounded before mounting samples. The puck was then inserted into the PPMS at ambient temperature and pressure. A “heat capacity” cable (Quantum Design) was used to make electrical contact feed-throughs to pins inside the PPMS sample chamber. These pins were also grounded before sample insertion. Prior to cooling, the sample chamber was purged with He vapor, sealed, and vented at room temperature at least three times. If the PPMS chamber and particularly its impedance valve are not sufficiently purged, water vapor can condense, restricting
4. Electrical Measurements

valve operation, and reducing temperature stability below 10 K. The helium dewar was typically refilled every 2 to 3 days, and an outer liquid nitrogen jacket was refilled on a daily basis. When the PPMS was not in use, its temperature controller was shut down to minimize the rate of helium consumption.
Figure 4.2: (a) Schematic of the home-made liquid nitrogen cryostat. (b) Schematic of the stick used for inserting samples in the liquid nitrogen dewar.
4. Electrical Measurements

Figure 4.3: (a) Photograph of a Quantum Design resistivity puck. (b) Cutaway view of a Quantum Design PPMS.
Bibliography


Part III

Charge Transport in Self-Assembled Single-Nanoparticle Devices
Chapter 5

Theory of Single Tunnel Junctions

Single-NP devices are comprised of two junctions in series. Transport through each junction can be described by electron tunneling. Before discussing charge transport in double-junction systems, it is insightful to start with a single tunnel junction where two macroscopic metal electrodes are separated by vacuum (Section 5.1). Then, a molecular junction is considered where a molecule forms the insulator between the electrodes (Section 5.2).

5.1 Metal-Insulator-Metal Junctions

When two electrodes are brought sufficiently close to each other, electrons can tunnel between the electrodes. A treatment of tunneling through a potential barrier starting from Schrodinger’s equation is provided in Appendix A. This section describes an extension of that treatment, namely tunneling between two one-dimensional metal electrodes subjected to a potential energy difference $V_b$ (Figure 5.1) [1, 2, 3].

Tunneling is an elastic process; that is, the electron’s initial and final energies are equal. Also, electrons must leave from a filled state of one electrode and enter an empty state of the other electrode to satisfy Pauli’s exclusion principle. The probability of
Figure 5.1: Energy diagrams for a single tunnel junction at (a) $V_b = 0$ and (b) $V_b > 0$. Gray areas show the Fermi-Dirac distributions in electrodes. Red lines represent energy states available for electron tunneling from electrode 1 to 2. Dotted lines show effects of image forces on the potential barriers.
finding a filled energy state in a metal electrode is given by the Fermi–Dirac distribution,

\[ f(E) = \frac{1}{1 + e^{(E-\mu)/k_B T}}, \]  

(5.1)

where \( \mu \) is the chemical potential. At absolute zero, the Fermi–Dirac distribution becomes a step function and represents the highest occupied energy (or the Fermi energy, \( E_F \)) of the electrode. The combined probability of finding a filled state in one electrode and an empty state in the other electrode, both with energy \( E \), is then \( f(E) \times [1 - f(E)] \), assuming that the electrodes are identical.

When a positive bias voltage \( (V_b > 0) \) is applied to an electrode, its chemical potential is shifted to \( \mu - eV_b \). The Fermi–Dirac distribution for the electrode is then expressed by

\[
\frac{1}{1 + e^{\left(E - (\mu - eV_b)\right)/k_B T}} = \frac{1}{1 + e^{\left(E + eV_b - \mu\right)/k_B T}} = f(E + eV_b).
\]  

(5.2)

The probability of finding filled and empty states in the electrodes thus changes to \( f(E) \times [1 - f(E + eV_b)] \).

Electrons tunneling between the electrodes encounter a potential energy barrier whose height, when \( V_b = 0 \), is given by

\[ U = \phi + E_F - E, \]  

(5.3)

where work function, \( \phi \), is defined as the difference between the Fermi and vacuum energy levels (see Figure 5.1a). Work functions for clean metals in vacuum are typically in the order of a few eV. For \( V_b > 0 \) (Figure 5.1b), the barrier height at a distance \( x \) within the barrier varies linearly with \( x \):

\[ U(x) = \phi + E_F - E - \frac{eV_b x}{L}. \]  

(5.4)

Note that \( U \) adopts appropriate values at \( x = 0 \) and \( L \).

In a proximity of a metal electrode, an electron polarizes the electrode’s surface and creates an image with an opposite charge that in turn exerts an attractive force on the electron. In a tunnel-junction geometry, image charges themselves generate image charges...
in the other electrode, and an electron is affected by all of the resulting forces. Simmons [4] has discussed in detail the influence of image forces on the shape of a potential barrier between planar electrodes. He showed that the image force reduces the height and the width of the barrier, and the image potential can be approximated by

\[ U_{\text{image}} = -1.15 \frac{e^2 \ln 2}{16\pi\varepsilon_0} \frac{L}{x(L-x)}. \] (5.5)

The modified barrier height is then expressed as

\[ U(x) = \phi + E_F - E - \frac{eV_b x}{L} - 1.15 \frac{e^2 \ln 2}{16\pi\varepsilon_0} \frac{L}{x(L-x)}. \] (5.6)

As a first approximation, one can replace the barrier height by an average value given by [1]

\[ \overline{U} = \frac{1}{L} \int_0^L U(x) dx. \] (5.7)

At room temperature, thermal fluctuations in electron energy are on the order of \( k_B T \approx 25 \) meV, much smaller than typical barrier heights. Therefore, except at high temperatures or voltages, charge transport between electrodes is forbidden classically. Electrons can, however, tunnel through the potential barrier (see Appendix A). The tunneling transmission probability, \(|T|^2\), in the limit of a thick barrier, decays exponentially with the barrier width \((L)\),

\[ |T|^2 \sim e^{-2\kappa L}, \] (5.8)

where \( \kappa \) is the decay constant. \( \kappa \) depends on the barrier height,

\[ \kappa = \sqrt{\frac{2mU}{\hbar}}, \] (5.9)

where \( m \) is the mass of electron and \( \hbar \) is Planck’s constant. Assuming that the electrodes are clean and made of gold and approximating the barrier height with the work function \((\phi \approx 5.1 \text{ eV})\), one finds \( \kappa \approx 1.1 \text{ Å}^{-1} \) and

\[ |T|^2 \sim e^{-2.2L/\text{Å}} \approx 10^{-L/\text{Å}}. \] (5.10)
Therefore, the tunneling transmission probability drops by $\sim 1$ order for every 1 Å increase in the barrier width.

The rate of electron tunneling from electrode 1 to 2 at energy $E$, $\Gamma_{1\rightarrow 2}(E)$, can be obtained using Fermi’s golden rule,

$$\Gamma_{1\rightarrow 2}(E) = 2\frac{2\pi}{\hbar} \rho(E) \rho(E + eV_b)|T(E)|^2 f(E)[1 - f(E + eV_b)],$$  \hspace{1cm} (5.11)

where $\rho$ represents the density of states of the electrodes and the factor of 2 arises from the spin degeneracy of electrons. Integrating the contributions from all energies, one obtains an expression for the total tunneling rate from electrode 1 to 2:

$$\Gamma_{1\rightarrow 2} = 2\frac{2\pi}{\hbar} \int_{0}^{+\infty} \rho(E) \rho(E + eV_b)|T(E)|^2 f(E)[1 - f(E + eV_b)]dE.$$  \hspace{1cm} (5.12)

Similarly, the rate of electron tunneling from electrode 2 to 1 is given by

$$\Gamma_{2\rightarrow 1} = 2\frac{2\pi}{\hbar} \int_{0}^{+\infty} \rho(E) \rho(E + eV_b)|T(E)|^2 [1 - f(E)]f(E + eV_b)dE.$$  \hspace{1cm} (5.13)

The net rate of electron tunneling between the two electrodes, $\Gamma$, can be obtained by subtracting equations 5.12 and 5.13:

$$\Gamma = \Gamma_{1\rightarrow 2} - \Gamma_{1\rightarrow 1}.$$  \hspace{1cm} (5.14)

The tunneling current (i.e. the rate of charge flow) between the electrodes is then given by:

$$I = e\Gamma = \frac{4\pi e}{\hbar} \int_{0}^{+\infty} \rho(E) \rho(E + eV_b)|T(E)|^2[f(E) - f(E + eV_b)]dE.$$  \hspace{1cm} (5.15)

At low bias voltages ($eV_b \ll E_F$) and at room temperature, energy levels close to the Fermi level dominate in tunneling. Therefore, one can simplify the expression for current (equation 5.15) by approximating the density of states and the tunneling transmission with their respective values at $E_F$:

$$I = \frac{g_0}{e} \int_{0}^{+\infty} [f(E) - f(E + eV_b)]dE,$$  \hspace{1cm} (5.16)
5. Theory of Single Tunnel Junctions

where

\[ g_0 = \frac{4\pi e}{\hbar} \rho(E_F)^2 |T(E_F)|^2. \]  \hspace{1cm} (5.17)

Note that \( g_0 \) defined here is different from the quantum of conductance, \( g_Q \). The integral in equation 5.16 can be solved analytically (see Appendix D) and is equal to \( eV_b \). The tunneling current at low bias then becomes

\[ I = g_0 V_b. \] \hspace{1cm} (5.18)

Equation 5.18 indicates that \( g_0 \) is the tunneling conductance at low bias:

\[ \frac{dI}{dV_b} = g_0. \] \hspace{1cm} (5.19)

Since \( g_0 \) depends on \( |T(E_F)|^2 \sim \exp(2\kappa L) \), the tunneling conductance drops exponentially with electrode separation,

\[ g_0 \sim e^{-\beta L}, \] \hspace{1cm} (5.20)

where \( \beta = 2\kappa \approx 2.2 \, \text{Å}^{-1} \) for clean Au electrodes. Note that \( g_0 \) does not exhibit explicit temperature dependence, and therefore, tunneling conduction is often characterized by its temperature independence.

At large biases, higher order voltage terms in the tunneling current expression become significant. For example, bias reduces the barrier height according to equation 5.4 and modifies \( |T(E_F)|^2 \). By taking this into account, one obtains an exponential dependence of tunneling current on bias (see Appendix B for derivation),

\[ I(V_b) \propto e^{-2\kappa_0 L} \sinh \left( \frac{eV_b\kappa_0 L}{2\Phi} \right), \] \hspace{1cm} (5.21)

where \( \kappa_0 \equiv \sqrt{(2m\Phi)/\hbar} \) is the decay constant at zero bias.

5.2 Metal-Molecule-Metal Junctions

The discussion in section 5.1 can also be applied to a junction in which a molecule is placed between the electrodes. In this case, the effective barrier height for tunneling
depends on the alignment of the Fermi level of the electrodes with respect to the highest occupied and lowest unoccupied orbitals of the molecule (HOMO and LUMO). If conduction is dominated by electron (or hole) transport, then the effective height, $\phi_{\text{eff}}$, can be approximated by $E_{\text{LUMO}} - E_F$ (or $E_F - E_{\text{HOMO}}$) [5]. Barrier heights for metals with molecules are usually smaller than those for clean metal electrodes, and this leads to smaller values of $\beta$. For example, Frisbie and co-workers [6, 7, 8] have studied $I - V$ characteristics of self-assembled monolayers of alkanethiols with various chain lengths on Au substrates using CP-AFM and observed $\beta \approx 0.9 \, \text{Å}^{-1}$. They have also found that monolayers of oligophenylene-thiols exhibit higher conductances with a smaller value of $\beta \approx 0.4 \, \text{Å}^{-1}$, likely due to smaller HOMO–LUMO energy gaps and closer positioning of the Fermi level to frontier orbitals in conjugated oligophenylene-thiols than in saturated alkanethiols [9].

Treatments of charge transport through molecular junctions taking into account molecular orbitals have been reviewed in a number of articles [9, 10, 11, 12, 13, 14]. One treatment that has been extensively studied is based on a traditional molecular model of charge transfer in donor–bridge–acceptor (D–B–A) systems [15]. This “superexchange” model was originally proposed by McConnell [16] to describe the rate of charge-transfer reactions in solution. In the superexchange model, charge transfer is mediated by virtual states, namely, $D^+ – B^– – A$ or $D – B^+ – A^–$ for electrons or holes, respectively. The rate of charge transfer, $k_{\text{CT}}$, is given by

$$k_{\text{CT}} \sim e^{-\beta' r_{\text{DA}}}, \quad (5.22)$$

where $r_{\text{DA}}$ is the distance between the donor and the acceptor,

$$\beta' = \frac{2}{a} \ln \left( \frac{\Delta E_B}{V_B} \right), \quad (5.23)$$

$a$ is the length of the bridge unit, $\Delta E_B$ is the energy of the mediating states ($D^+ – B^– – A$ or $D – B^+ – A^–$) relative to the ground state ($D – B – A$), and $V_B$ is the coupling energy between
two adjacent units. Using typical values of $\Delta E_B/V_B = 10$ and $a = 5$ Å, equation 5.23 gives $\beta' = 0.92$ Å$^{-1}$ [10].

Nitzan [17] has derived an approximate relationship between $k_{CT}$ and molecular conductance under a number of assumptions (e.g., that the electronic structure of the molecule does not considerably change upon attaching to the electrodes):

$$g \approx \frac{8e^2}{\pi^2\Gamma_D\Gamma_A} \left( \frac{k_{CT}}{\text{DOS}} \right),$$

(5.24)

where DOS represents a Franck–Condon weighted density of vibronic states and $\Gamma_D$ and $\Gamma_A$ are, respectively, widths of the donor and the acceptor levels due to their couplings to the electrodes. The latter depend on the finite lifetime of an electron on the molecule adsorbed on the metal surface. Using typical values of $\Gamma_D = \Gamma_A \approx 0.5$ eV, equation 5.24 yields

$$g \sim 5 \times 10^{-19} \frac{k_{CT}}{\text{DOS}}.$$ 

(5.25)

The agreement between equation 5.25 and experimental values is quite remarkable [11]. For example, Smalley et al. [18] have measured the rate of charge transfer through self-assembled monolayers of ferrocene-terminated alkanethiolates on gold electrodes using an electrochemical approach. For molecules with 9-carbon alkane chains, they measured $k_{CT} \approx 10^4$ s$^{-1}$. Using DOS $\approx 7 \times 10^{-6}$ (eV)$^{-1}$ [11] one obtains $g \approx 7 \times 10^{-10}$Ω$^{-1} = (1.4 \text{ G} \Omega)^{-1}$, which is consistent with the value reported by Frisbie and co-workers for self-assembled monolayers of nonanethiolates on gold [6].
Orthodox Theory of Double Tunnel Junctions

A NP incorporated between two electrodes (see Figure 6.1) can exhibit distinct single-electron charging effects. In order for current to flow between electrodes via the NP, an electron has to occupy the NP, a process that requires overcoming NP’s charging energy, $E_c$. In this Chapter, an Orthodox theory for such a device is reviewed. An experimentally accessible consequence of the theory is that $E_c$ influences both $T$- and $V_b$-dependent behavior of the device. This important result is derived.

Figure 6.1 shows an equivalent circuit for a double tunnel junction with a nanoparticle

![Figure 6.1: Schematic and equivalent circuit of a double tunnel junction with a nanoparticle island.](image)
island, as is described by the Orthodox theory \[19, 20, 21, 3\]. Each junction \(j\) \((j = 1, 2)\) is modeled as a parallel combination of a capacitance, \(C_j\), and a resistance, \(R_j\). The junction capacitances determine the voltage dropped across each junction \((V_j)\),

\[
V_j = \frac{C_1C_2}{C_\Sigma} V_b \tag{6.1}
\]

where \(C_\Sigma = C_1 + C_2\). The junction resistances control the electron tunneling rates through each junction \((\Gamma_j^\pm\), where \(+/-\) refers to electrons tunneling on/off the NP):

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

\[
= \frac{1}{e^2R_j} \Delta E_j^\pm \frac{-\Delta E_j^\pm}{1 - \exp(\Delta E_j^\pm/k_BT)} \tag{6.2}
\]

For the solution of the integral in equation 6.2, see Appendix D. \(\Delta E_j^\pm\) is the change in the energy of the system as a single electron tunnels through junction \(j\) and charges the NP. From electrostatic energy considerations, \(\Delta E_j^\pm\) is determined by the voltage across the junction \((V_j)\) and the energy required to change the charge of the NP by \(\pm 1e\) \((\Delta U^\pm)\) (see Figure 6.2):

\[
\Delta E_1^\pm = \Delta U^\pm \mp eV_1, \tag{6.3}
\]
6. Orthodox Theory of Double Tunnel Junctions

\[ \Delta E_2^\pm = \Delta U^\pm \pm eV_2, \]  
\[ \Delta U^\pm = \frac{(Q \pm e)^2}{2C_\Sigma} - \frac{Q^2}{2C_\Sigma}. \]

\( Q \) is the NP charge and can be written in the form of

\[ Q = Ne + Q_0, \]  
where \( N \) is an integer and \( Q_0 \) is a fractional charge.

Current can be calculated by averaging the difference of tunneling rates in the forward and reverse directions over an ensemble of \( N \):

\[ I = -e \sum_{N=-\infty}^{+\infty} \rho(N) \left( \Gamma_1^+(N) - \Gamma_1^-(N) \right) \]
\[ = -e \sum_{N=-\infty}^{+\infty} \rho(N) \left( \Gamma_2^-(N) - \Gamma_2^+(N) \right), \]  
where \( \rho(N) \) is the ensemble distribution of \( N \). \( \rho(N) \) can be obtained from a steady state consideration [20]:

\[ \rho(N) \left( \Gamma_1^+(N) + \Gamma_2^+(N) \right) = \rho(N+1) \left( \Gamma_1^-(N+1) + \Gamma_2^-(N+1) \right). \]  
Given the following normalization condition for \( \rho(N) \),

\[ \sum_{N=-\infty}^{\infty} \rho(N) = 1, \]  
one obtains

\[ \rho(N) = \frac{\prod_{i=-\infty}^{N-1} x(i) \prod_{i=N+1}^{+\infty} y(i)}{\sum_{j=-\infty}^{+\infty} \left( \prod_{i=-\infty}^{j-1} x(i) \prod_{i=j+1}^{+\infty} y(i) \right)}, \]  
where

\[ x = \Gamma_1^+ + \Gamma_2^+, \]  
\[ y = \Gamma_1^- + \Gamma_2^-. \]  
Thus, one can numerically solve equation 6.7 to obtain \( I(V_b) \).
6. Orthodox Theory of Double Tunnel Junctions

It is possible, however, to obtain a simple expression for \( I(V_b) \) for a symmetric system where \( R_1 = R_2 \), \( C_1 = C_2 \), and \( Q_0 = 0 \). Under these assumptions, one obtains

\[
V_j = \frac{V_b}{2},
\]

(6.13)

\[
\Delta U^\pm = \frac{e^2(1 \pm 2N)}{2C_\Sigma} = E_c(1 \pm 2N).
\]

(6.14)

At absolute zero, the equation for tunneling rates (equation 6.2) reduces to

\[
\Gamma_j^\pm(T = 0) = \begin{cases} 
-\frac{\Delta E_j^\pm}{2eR} \Delta E_j^\pm < 0, \\
0 \quad \Delta E_j^\pm \geq 0.
\end{cases}
\]

(6.15)

Therefore, as \( T \to 0 \), the tunneling rates vanish if

\[
\Delta E_j^\pm \geq 0.
\]

(6.16)

The inequality 6.16 yields voltage thresholds of Coulomb blockade (\( V_{CB} \)). Inside the Coulomb blockade region, there is no excess charge on the NP and \( N = 0 \). Thus, from equations 6.3, 6.4, 6.13, 6.14, and 6.16 one obtains:

\[
|V_{CB}| = \frac{2E_c}{e}.
\]

(6.17)

Current at absolute zero is then given by

\[
I(T = 0) \approx e \left( \Gamma_1^+ - \Gamma_1^- \right) \approx \begin{cases} 
\frac{V_b - |V_{CB}|}{2R} \quad V_b > |V_{CB}|, \\
0 \quad -|V_{CB}| < V_b < |V_{CB}|, \\
\frac{V_b + |V_{CB}|}{2R} \quad V_b < -|V_{CB}|.
\end{cases}
\]

(6.18)

Differential conductance \( (dI/dV_b) \) at absolute zero is

\[
\frac{dI}{dV_b}(T = 0) \approx \begin{cases} 
\frac{1}{2R} \quad |V_b| > |V_{CB}|, \\
0 \quad |V_b| < |V_{CB}|.
\end{cases}
\]

(6.19)
As the temperature rises, conductance inside the CB region increases as well. Inside the CB region and at a temperature range of $0 < k_B T \ll E_c$, the tunneling rate (equation 6.2) becomes

$$
\Gamma_1^\pm \approx \frac{\Delta E_1^\pm}{e^2 R} e^{-\Delta E_1^\pm/k_B T} \\
= \frac{1}{e^2 R} \left( E_c + \frac{eV_b}{2} \right) \exp \left( \frac{-E_c \pm eV_b/2}{k_B T} \right) \\
= \frac{k_B T}{e^2 R} (\epsilon \mp v) e^{-\epsilon \mp v}, \tag{6.20}
$$

where $\epsilon \equiv E_c/k_B T$ and $v \equiv eV_b/2k_B T$. Differential conductance inside the CB region is then given by

$$
\frac{dI}{dV_b} \approx e \left( \frac{d\Gamma_1^+}{dV_b} - \frac{d\Gamma_1^-}{dV_b} \right) \\
= e \left( \frac{dv}{dV_b} \right) \left( \frac{d\Gamma_1^+}{dv} - \frac{d\Gamma_1^-}{dv} \right) \\
= e \left( \frac{e}{2k_B T} \right) \left( k_B T \right) \left[ e^{-\epsilon + v}(\epsilon - v - 1) - e^{-\epsilon - v}(-\epsilon - v + 1) \right] \\
= \left( \frac{e^{-\epsilon}}{2R} \right) \left[ (\epsilon - 1) (e^v + e^{-v}) - v (e^v - e^{-v}) \right] \\
= \left( \frac{e^{-\epsilon}}{R} \right) \left[ (\epsilon - 1) \cosh v - v \sinh v \right]. \tag{6.21}
$$

Thus, conductance at zero bias is

$$
\frac{dI}{dV_b}(V_b = 0) \approx \frac{\epsilon - 1}{R} e^{-\epsilon} \\
\approx \frac{E_c}{Rk_B T} e^{-E_c/k_B T}. \tag{6.22}
$$

Equation 6.22 shows that zero-bias conductance approximately follows an Arrhenius behavior with an activation energy equal to $E_c$. Zero-bias conductance essentially arises from electrons that have energies higher than $E_c + E_F$. The number of these electrons can be calculated using the Fermi–Dirac distribution:

$$
\int_{E_c + E_F}^{\infty} f(E) dE = \int_{E_c + E_F}^{\infty} \frac{dE}{1 + \exp[(E - E_F)/k_B T]} \\
\approx \int_{E_c + E_F}^{\infty} e^{-(E-E_F)/k_B T} dE \\
= k_B T e^{-E_c/k_B T} \propto e^{-E_c/k_B T}. \tag{6.23}
$$
In the above equations, the Fermi–Dirac distribution is approximated by the Boltzmann distribution. Also, the temperature dependence of the pre-exponential term, $k_B T$, is neglected compared with that of the exponential, $\exp(-E_c/k_B T)$.

Equations 6.17 and 6.22 provide two independent ways of obtaining $E_c$: (1) from the CB voltage thresholds at low temperatures, and (2) from Arrhenius activation energies at zero bias. This key result will be revisited in Section 8.3.
Device Preparation

Self-assembled single-NP devices were prepared using BJs. First, monolayers of alkanedithiols were self-assembled on the BJs. This was done by immersing slides in 0.5 mM ethanol solutions of α,ω-alkanedithiols for ∼1–2 h. The slides were then rinsed thoroughly with ethanol, dried with nitrogen gas, and then dipped in very dilute freshly prepared solutions of alkanethiol-capped Au NPs. The NPs were capped to avoid particle aggregation, and dilute NP solutions were used to reduce the probability of capturing multiple NPs in the gap between electrodes.

To monitor capture of NPs two approaches were employed: (1) self-assembly of NPs from solution onto electrodes, and (2) electrostatic trapping [22, 23, 24, 25]. Devices prepared using both approaches exhibited similar behaviors.

7.1 Self-Assembly

In this approach, BJs were immersed in NP solutions for periods of ∼5 min. Junction resistances were measured at room temperature using a digital multimeter after removing samples from NP solutions, rinsing with solvent, and drying with nitrogen. Samples that showed significant drops in resistance, ∼2–3 orders of magnitude or more, were used for device characterizations and electrical measurements. If no significant resistance
change was observed, samples were immersed again in the NP solutions for additional 5 min periods. This procedure was repeated until junction resistances dropped or total immersion time exceeded ∼ 20–30 min. The success rate of this method was about 25%.

Devices were characterized using SEM. SEM images were taken after measuring electrical properties of the devices. The devices were mounted on SEM sample holders using double-sided carbon tapes. Both device electrodes were attached to the sample holders using conductive carbon tapes. To reduce charging of glass substrates and the risk of electrostatic discharge, images were obtained at relatively low voltages of 1.0–2.0 kV. Note that exposing the devices to high-energy focused electron beams can cause irreversible changes in the structure and electronic properties of the devices possibly due to the coalescing of NPs. Figure 7.1 shows SEM images of a representative 10 nm NP device. Note that NPs are mostly isolated and only small fractions of them form dimers (7%) or trimers (0.6%). It is highly likely that single NPs (rather than chains of multiple NPs) bridge the gap, although the possibility of having single NPs in parallel cannot be excluded, given the large width of the BJs.

7.2 Electrostatic Trapping

In this method, an ac voltage was applied to the BJs while they were immersed in NP solutions. The ac voltage generates a spatially varying electric field concentrated in the gap between electrodes. NPs can be polarized by the electric field and experience an attractive force toward the region of the highest field intensity (Figure 7.2(a)). To facilitate capturing of a single NP, a resistor in series with the BJ was used as discussed below. After the electrostatic trapping process, samples were rinsed with chloroform and left to dry.
Figure 7.1: SEM image of a section of a BJ. Solid white lines show the location of the gap between electrodes, and boxed regions highlight regions with nanometer-sized gaps. (b),(c) Magnified images of boxed regions in (a) after depositing 10 nm NPs.
7. Device Preparation

Figure 7.2: (a) Schematic showing the principle of electrostatic trapping. (b) Schematic of the setup for electrostatic trapping ($V_{\text{peak-peak}} = 7$ V at 1 kHz and $R_s = 12$ MΩ).

The setup for electrostatic trapping is illustrated in Figure 7.2(b). A function generator (Stanford Research systems DS345) was used to apply $V_{\text{peak-peak}}$ up to 10 V at 1 kHz across the BJ while it was immersed in a NP solution. A 12 MΩ resistor was connected in series ($R_s$). Conductance was measured using a current amplifier (Keithley 428) with a 100-µs low-pass filter and a lock-in amplifier (Stanford Research Systems SR310). To monitor capture of NPs, conductance was measured as a function of time. Data obtained during electrostatic trapping using three BJs and different NP solutions are presented in Figure 7.3. Conductance of the BJs in NP solutions for $V_{\text{peak-peak}}$ 7 V were stable to $< 0.1 \%$ for long periods of time exceeding 30 min. When $V_{\text{peak-peak}}$ was increased to 7 V (or some times higher), within a minute, conductance exhibited sudden discrete jumps, often fluctuated, and eventually stabilized. In some cases, the fluctua-
Figure 7.3: Conductance of three different BJs as a function of time as (a) hexanethiol-capped 5 nm NPs, (b) butanethiol-capped 5 nm NPs, and (c) hexanethiol-capped 10 nm NPs were electrostatically trapped. BJs were coated with self-assembled monolayers of hexanethiol.

tions ranged between the original and stabilized values as shown in Figure 7.3(b) and (c). These step-like jumps along with initial fluctuations suggest single NP binding, with an initial period of “electronic annealing” of the NP-electrode interaction. This behavior was highly reproducible: ~85% of the samples showed steps in conductance and ~50% showed fluctuations.

Consistent observation of NP binding only after $V$ is increased sufficiently indicates that there is a threshold voltage required to bind NPs strongly to the BJs. A possible origin of this threshold is a need for the alkanedithiol linker molecules to penetrate through the NPs’ ligand shell in order to strongly bind the NPs. An associated barrier must be overcome by the force NPs experience during electrostatic trapping. The force (also known as the dielectrophoresis force) depends on the volume and the dielectric constant of NPs, as well as the amplitude of the electric field [26].

The existence of a binding threshold voltage was exploited to limit the number of captured NPs to only one through use of a series resistor ($R_s = 12 \text{ M}\Omega$). Initially, the
resistance of the BJ (> 1 GΩ) is much higher than $R_s$. Therefore, voltage is mainly dropped across the BJ. When voltage crosses the threshold, the first NP is trapped, and the junction resistance drops to values comparable to $R_s$. Hence, due to a voltage-divider effect, the voltage across the BJ drops significantly below the threshold inhibiting binding of additional NPs. The existence of a threshold implies that the binding process is self-limiting and again points to trapping of a single NP.

### 7.3 Electrical measurements

Current–voltage characteristics of the single-NP devices were measured as a function of temperature from ~ 3 to 300 K using the PPMS. Voltage was applied using the data acquisition card at a rate of 1 mV/50 ms. Current was measured using an $I - V$ converter with a built-in low-pass filter. Differential conductances of the devices were then obtained by numerically differentiating current–voltage data using a Savitzky–Golay method with 2nd degree polynomial smoothing over 40 data points (80 mV). Of 40 devices studied, 14 failed during variable-temperature measurements, and the rest exhibited stable characteristics below ~ 150–200 K. Above this temperature range, some devices exhibited sudden fluctuations in current–voltage characteristics (not shown).

---

1Conductances of the BJs measured during electrostatic trapping using ac voltages (~ 40 nΩ$^{-1}$) are higher than those obtained from differentiating $I - V$ data (< 1 nΩ$^{-1}$). This is probably due to capacitive characteristics of the BJs and/or the measurement circuit.
Chapter 8

Discrepancy between Charging Energies obtained from Voltage Thresholds and Activation Energies

8.1 Coulomb Blockade Voltage Thresholds

Figure 8.1 illustrates typical $I - V_b$ curves of devices made with three different NP sizes near liquid helium temperatures (2.2–4.2 K). Clear current suppressions are observed. The width of suppressions increases with decreasing NP size as also shown in Figure 8.2. This correlation suggests that the suppressions are due to single-electron charging of NPs, that is, Coulomb Blockade (CB). At low $|V_b|$, the energy provided by $e|V_b|$ is insufficient to charge the NP by single electrons; therefore, the electron flow is suppressed. At sufficiently high $|V_b|$, i.e. outside of CB, electrons can charge the NPs and current starts to flow.

Out of the 26 devices which tolerated low temperature excursions, three exhibited $I - V_b$ curves with prominent Coulomb staircases. $I - V_b$ and $dI/dV - V_b$ curves of a device exhibiting Coulomb staircases are shown in Figure 8.3. Generally, the $I - V_b$ curves
8. Discrepancy between Charging Energies obtained from Voltage Thresholds and Activation Energies

**Figure 8.1:** Typical $I - V_b$ curves of single-NP devices with 2.5, 5, and 10 nm NPs near liquid helium temperatures (2.0–4.2 K). Inset: Schematic of the single-NP device.

**Figure 8.2:** Correlation between the CB voltage ranges and the reciprocal of nanoparticle's diameter.
8. Discrepancy between Charging Energies obtained from Voltage Thresholds and Activation Energies

Figure 8.3: (a) $I - V_b$ and (b) $dI/dV - V_b$ curves of a single-nanoparticle device exhibiting Coulomb staircases. The device is comprised of hexanedithiol linkers and hexanethiol-capped 10 nm NPs. The Coulomb staircases are observed at voltage intervals of $\sim 180$ mV.

appear symmetric with respect to voltage, consistent with a symmetric double junction geometry and the physical construction of the devices. The Orthodox theory predicts that Coulomb staircase are only observed when double junctions have significantly different resistances and capacitances.

In a symmetric double junction, the voltage range of Coulomb blockade ($\Delta V_{CB}$) is given by the following relationship (see equation 6.17),

$$\Delta V_{CB} = \frac{4E_c}{e},$$  \hspace{1cm} (8.1)

where $E_c = e^2/C_\Sigma$, and $C_\Sigma$ is the total capacitance of the double junction. $C_\Sigma$ can be estimated from self-capacitances of isolated spherical NPs (equation 1.8). Using a value of 2.6 for dielectric constant of alkanedithiols [27], one obtains $C_\Sigma \approx 0.72, 1.4, \text{ and } 2.9 \ \text{aF}$, and $E_c \approx 110, 55, \text{ and } 28 \ \text{meV}$, for 2.5, 5, and 10 nm NPs, respectively. Note that these values of $E_c$ are in fact overestimates, since the presence of electrodes and perhaps surrounding NPs should raise the capacitance of the junction beyond that of an isolated sphere. Nevertheless, $E_c$ grows as the NP size decreases, as observed.

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8. Discrepancy between Charging Energies obtained from Voltage Thresholds and Activation Energies

Figure 8.4: $dI/dV$ vs $V_b$ for a typical 10 nm NP device at various temperatures (5 K and 10–150 K in increments of 10 K). (Inset) $I$ vs $V_b$ of the sample at the same temperature range.

8.2 Activation Energies

Figure 8.4 shows differential conductance ($dI/dV$) of a typical 10 nm NP sample from 4.2 to 150 K. As the temperature increases, $dI/dV$ inside the CB region improves as electrons are better able to overcome the NP charging energy thermally. Orthodox theory predicts that $dI/dV$ at zero bias follows an Arrhenius behavior, with an activation energy arising from NP charging (equation 6.22). Arrhenius plots of $dI/dV$ at $V_b = 0$ for three NP sizes are shown in Figure 8.5 confirming Arrhenius behavior.\(^1\) Observed activation energies are $\sim 9.2 \pm 2.2$ meV for 10 nm NPs (average over 14 samples), 21 ± 6 meV for 5 nm NPs (average over 9 samples), and 88 ± 20 meV for 2.5 nm NPs (average over 3 samples).

\(^1\)Note that the Arrhenius plots in Figure 8.5 are shown in high temperature ranges ($T \gtrsim 30$ K). For full-temperature range Arrhenius plots see Section 9.1.
8. Discrepancy between Charging Energies obtained from Voltage Thresholds and Activation Energies

Figure 8.5: Arrhenius plots of $dI/dV$ for typical devices with three nanoparticle sizes

Figure 8.6 shows that the activation energies vary inversely with $d$, confirming that the activation energies arise from single-electron charging of NPs.

8.3 The Discrepancy

Fundamentally, one might expect that an electron should be able to gain energy to overcome the charging energy from the electrical potential or from thermal fluctuations on equal footing. Comparison of $E_c$ obtained from the two independent variable-$V_b$ and variable-$T$ measurements represents an important consistency check and can provide new insight. Table 8.1 shows estimated and experimental values of $E_c$ obtained from the two measurements. Data indicate that there is a significant discrepancy between charging energies determined via the two approaches, the former yielding larger values. More than 75% of the samples exhibited discrepancies in the range of $\sim 5$–28. Others exhibited even larger ($\sim 78$–100 fold) discrepancies. It is noteworthy that data did not exhibit a systematic relationship between the length of linker or capping molecules and
8. DISCREPANCY BETWEEN CHARGING ENERGIES OBTAINED FROM VOLTAGE THRESHOLDS AND ACTIVATION ENERGIES

**Figure 8.6:** Correlation between the activation energies and the reciprocal of nanoparticle’s diameter.

**Table 8.1:** Estimated and experimental values of charging energies.

<table>
<thead>
<tr>
<th>NP diameter</th>
<th>Isolated-sphere model</th>
<th>$e\Delta V_{CB}/4$</th>
<th>$E_a$</th>
<th>$e\Delta V_{CB}/4E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 nm</td>
<td>110 meV</td>
<td>516 $\pm$ 238 meV</td>
<td>88 $\pm$ 20 meV</td>
<td>5.7 $\pm$ 0.7</td>
</tr>
<tr>
<td>5.0 nm</td>
<td>55 meV</td>
<td>101 $\pm$ 21 meV</td>
<td>21 $\pm$ 6 meV</td>
<td>4.8 $\pm$ 0.4</td>
</tr>
<tr>
<td>10 nm</td>
<td>28 meV</td>
<td>52 $\pm$ 33 meV</td>
<td>9.2 $\pm$ 2.2 meV</td>
<td>5.9 $\pm$ 0.5</td>
</tr>
</tbody>
</table>

To account for these observations, a number of published extensions to the Orthodox theory are considered. These include cotunneling [28, 29], voltage-induced barrier suppression [30], and self-heating [31, 32].

### 8.3.1 Cotunneling

Cotunneling involves a concerted transport of two electrons through different junctions. Inside the CB region, while sequential transfer of single electron across the double junctions is prohibited, cotunneling of the two electrons through different junctions can cause a finite current [28, 29]:

$$I(V_b) = \frac{h}{24\pi^2e^2R_1R_2} \left( \frac{1}{\Delta E_1} + \frac{1}{\Delta E_2} \right)^2 ((eV_b)^2 + (2\pi k_B T)^2) V_b.$$  \hspace{1cm} (8.2)
However, cotunneling current is negligible when the resistances of junctions are much larger than the quantum of resistance, $R_Q = 1/g_Q = 1.3 \times 10^4 \, \Omega$ (see equation 1.4). In the samples studied, junction resistances are $10^8 \, \Omega$ or larger, corresponding to cotunneling currents less than $10^4$ times smaller than the tunneling current. In addition, cotunneling would give rise to smaller CB voltage thresholds since it allows current to flow inside the CB region. Therefore, cotunneling cannot account for the observed discrepancy.

### 8.3.2 Voltage-induced Barrier Suppression

The Orthodox theory based on equation 6.2 assumes that $I - V_b$ characteristics of tunnel junctions are linear. This is a valid first order approximation when the voltage drop across the junction is small compared to the tunneling potential barrier. An applied bias voltage is expected to suppress the average barrier height (see equation 5.4) and generate a non-linear $I - V_b$ curve at sufficiently high $V_b$ (for example, see equation 5.21). As will be discussed in Section 9.2, $I - V_b$ data outside the CB regions do exhibit curvature and imply a presence of small barriers. Although modifications of the Orthodox theory to include voltage-induced barrier suppression can account for such non-linearities, they do not affect CB thresholds and cannot explain the discrepancy.

### 8.3.3 Self-Heating

Energy dissipation in the central island and/or electrodes due to electron-electron and electron-phonon interactions may lead to self-heating and unequal temperatures for electron distributions in the bath, electrodes and the island. Studies of self-heating in single-electron devices [31, 32] have shown that electron temperature in the electrodes remains close to that of the bath ($T_b$), while the electron temperature of the island ($T_e$) is determined by the rate of heat generated via tunneling electrons and the rate of heat transfer
8. Discrepancy between Charging Energies obtained from Voltage Thresholds and Activation Energies

to the lattice via electron–phonon interactions:

\[ P = \Sigma \Omega (T_e^5 - T_{ph}^5), \]  

\[ (8.3) \]

where \( P \) is the electrical power, \( \Sigma \) is the electron–phonon coupling parameter characteristic of the island material, \( \Omega \) is the volume of the island, and \( T_{ph} \) is the temperature of phonons in the lattice assumed to be the same as \( T_e \). A typical value of \( \Sigma \Omega \) was reported to be \( \sim 20 \text{ pW/K}^5 \) \[31\].

In order to force the \( I - V_b \) data to fit the Orthodox theory, \( T_e \) should exceed \( T_{ph} \) by \( \gtrsim 5 \) times (the minimum value of the discrepancy):

\[ P = \Sigma \Omega T_{ph}^5 \left[ \left( \frac{T_e}{T_{ph}} \right)^5 - 1 \right] = 3 \times 10^3 \Sigma \Omega T_{ph}^5. \]  

\[ (8.4) \]

\( P \) can be estimated from typical values of \( I \) and \( V_b \):

\[ P_{\text{avg}} = I \cdot V_b \approx (1 \text{ nA})(1 \text{ V}) = 1 \text{ nW}. \]  

\[ (8.5) \]

Hence, at \( T_{ph} = 4 \text{ K} \), one gets \( \Sigma \Omega = 0.3 \text{ fW/K}^5 \), which is 60 000 times smaller than its reported typical value and implies a physically unreasonable small coupling parameter.

The situation becomes worse at higher \( T_{ph} \). At room temperature, the desired \( T_e \) should exceed the melting point of gold (1340 K). Therefore, the self-heating model cannot account for the difference in the two energy scales.

8.3.4 Voltage-Divider Effect

The fact that the ratio of the charging energies determined through variable-\( V_b \) and variable-\( T \) measurements are not correlated with the NP size suggests that the discrepancy is not related to single-electron charging of the NPs. Also, estimates of \( E_c \) are in better agreement with values determined from activation energies than voltage thresholds. Both of these observations can be reconciled by assuming that electrons do not simply tunnel elastically through the molecules between the electrodes and the NP, but
rather may lose some energy enroute. One scenario is that electrons may be temporarily localized at a potential well within the junction and lose energy at that site. This scenario results in incoherent electron tunneling and generates a voltage-divider effect as follows. For a single barrier such as that in Figure 8.7(a), current flows by elastic tunneling and loses the applied potential energy \((eV_j)\) entirely in the NP. However, considering a multi-barrier junction potential (Figure 8.7(b)), fractions of electron energy would drop across each barrier. Eventually, only a fraction of the bias voltage \((\xi V_j\), where \(\xi\) is a voltage-division factor\) is applied to the NP, and correspondingly larger voltage thresholds would be required to charge the NP than otherwise would be needed. It is noteworthy that this scenario is similar to a case where multiple NPs in series bridge the gap between electrodes. However, based on SEM images (see Figure 7.1), this possibility can be ruled out.

Detailed analysis of device behaviors, discussed below, suggests that the localization sites are flanked by small and large barriers. Given that the devices are composed of gold–alkanedithiol–gold NP junctions and that long alkane chains of alkanedithiols present large tunneling barriers (see Section 5.2), localization sites are most likely at or near gold–thiolate interfaces \([33]\). Since the probability of electron energy loss via coupling to phonons in the molecule (inelastic tunneling) is small \([34]\), we propose that the energy loss occurs in the electrode via image charges \([35]\). The multi-barrier potential profile shown in Figure 8.7(b), in addition to the voltage-divider effect, can give rise to complex \(T\)-dependent transport mechanisms. Such mechanism are discussed in the next section, providing further support for the proposed model.
Figure 8.7: Schematic diagrams of potential energy for (a) a single-barrier tunnel junction, and (b) a multi-barrier junction. Single-headed arrows represent electron pathways across the barriers.
Thermo-Voltammetry: Voltage Dependence of Arrhenius Analysis of Conductance

Further insight into energy barriers present in self-assembled single-NP devices can be obtained from detailed examinations of device Arrhenius behaviors, especially as a function of bias voltage. This approach, which we call “thermo-voltammetric” spectroscopy, is explored in this chapter.

9.1 Activation Energy vs Voltage

9.1.1 Zero–Bias Peaks in Activation Energies

Figure 9.1 shows $dI/dV$ of the same device as in Figure 8.4 displayed as Arrhenius plots ($\ln(dI/dV)$ vs $1/T$) at various voltages. Note that the Arrhenius plots deviate from straight lines. Given that slopes of Arrhenius plots represent activation energies, we define the differential activation energy ($E_a$) as being proportional to the derivative of the Arrhenius plots:

$$E_a \equiv -k_B \frac{\partial \ln(dI/dV)}{\partial(1/T)}.$$

(9.1)

Figure 9.1 indicates qualitatively that $E_a$ varies with both $V_b$ and $T$. 
Figure 9.1: Arrhenius plots of $dI/dV$ for the 10 nm NP device shown in Figure 8.4 at various bias voltages.
9. Thermo-Voltammetry: Voltage Dependence of Arrhenius Analysis of Conductance

Figure 9.2: $E_a$ vs $V_b$ at various temperatures for (a) the 10 nm NP device shown in Figure 8.4 and (b) a 5 nm NP device. Insets: $E_a$ vs $T$ at zero bias.

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9. **Thermo-Voltammetry: Voltage Dependence of Arrhenius Analysis of Conductance**

To aid interpretation of these results, Figure 9.2a plots $E_a$ vs $V_b$ at various temperatures for the same device. Figure 9.2a is obtained by numerically differentiating the data in Figure 9.1. For a given temperature, $E_a$ vs $V_b$ exhibits a peak at zero bias. Figure 9.2a shows two remarkable features of the heights and the widths of the zero-bias peaks:

1. At zero bias, when charges can only overcome energy barriers thermally, the size of the energy barrier increases with temperature. Inset shows $E_a$ at zero bias as a function of temperature. Two plateaus are observed: as $T \to 10$ K, $E_a \to 2.5$ meV, and as $T \to 100$ K, $E_a \to 8.3$ meV. This implies presence of multiple energy barriers in the system. For $T > 120$ K, $E_a$ gradually decreases with increasing temperature due to Fermi–Dirac distribution (see below).

2. Widths and heights of the zero-bias peaks represent independent measurements of the energy barrier through $V_b$ and $T$, respectively. However, values of the energy barrier obtained by varying $V_b$ are significantly larger than those obtained by varying $T$ by a factor of $\sim 27$ in the sample shown.\(^1\)

To demonstrate the effect of NP size, Figure 9.2b shows $E_a$ vs $V_b$ for a 5 nm NP device at various temperatures. The behavior is qualitatively similar to that of the 10 nm NP device. Zero-bias peak height vs temperature again show two plateaus. Values of the energy barrier obtained from peak widths are also significantly larger ($\sim$ tenfold in the sample shown) than those obtained from peak heights. These observations are highly reproducible. Of 23 samples studied, all samples exhibit discrepancies between values of the energy barrier obtained from varying $V_b$ and $T$. Also, all exhibit multiple $E_a$ as a function of $T$. The high-$T$ $E_a$'s vary significantly with NP size. Average values are $9.2 \pm 2.2$ meV for 10 nm NPs, and $20.5 \pm 6.1$ meV for 5 nm NPs, approximately doubling as the NP size is halved. Therefore, the high-$T$ $E_a$ is attributed to single-electron charging of NPs, as was discussed in Chapter 8. The low-$T$ $E_a$'s vary less significantly with NP

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\(^1\)Peak widths are obtained from $x$-intercepts of linear fits to data near 0 V.
size and from sample to sample for a fixed NP size. Their values are $3.5 \pm 1.2$ meV for 10 nm NPs and $4.6 \pm 2.6$ meV for 5 nm NPs. We propose that the low-$T$ $E_a$'s are attributed to a molecular state within the junction and will be discussed further below.

### 9.1.2 Predictions of the Orthodox Theory

To model and better understand the dependence of $E_a$ on $V_b$ and $T$, let us revisit the predictions of the Orthodox theory. Equation 6.21 indicates that inside the CB region, i.e. for $0 < eV_b < 2E_c$, $dI/dV$ is given by the following relationship:

\[
\frac{dI}{dV} \approx \left(\frac{e^{-\epsilon}}{2R}\right) [(\epsilon - 1)e^v - ve^v]
\]

\[
= \left(\frac{e^{-\epsilon+v}}{2R}\right) (\epsilon - 1 - v)
\]

\[
\approx \left(\frac{E_c - eV_b/2}{2Rk_B T}\right) e^{-(E_c-eV_b/2)/k_B T}.
\]  

Therefore, the activation energy decreases linearly with $V_b$:

\[
E_a = E_c - \frac{e|V_b|}{2}. 
\]  

Outside the CB region,

\[
\frac{dI}{dV} \approx \frac{1}{2R}. 
\]

Hence, the activation energy vanishes. Figure 9.3 shows $E_a$ vs $V_b$ at various temperatures calculated using the Orthodox theory. Consistent with the above equations, $E_a - V_b$ curves exhibit peaks at zero bias. According to the Orthodox theory, the height and the width of the peak represent $E_c$ and $e\Delta V_{CB}$, respectively, and the width-to-height ratio of the peaks should be equal to 4. For the calculation shown, $E_c = 15.3$ meV and $\Delta V_{CB} = 61.2$ mV. Inset shows the variation of peak height with temperature. As temperature rises, $E_a$ gradually decreases, since approximating the Fermi-Dirac distribution with the Boltzmann distribution (see equation 6.23) becomes less accurate at high temperatures.

The existence of zero–bias peaks is correctly predicted by the Orthodox theory; however, magnitudes of the experimentally observed peaks relative to their widths and their
Figure 9.3: $E_a$ vs $V_b$ at various temperatures according to the Orthodox theory. Parameters: $C_1 = C_2 = 2.6$ aF, $R_1 = R_2 = 100$ MΩ, $Q_0 = 0$. Left inset: an equivalent circuit for a double junction system. Right inset: $E_a$ vs $T$ at zero bias.
temperature dependence exhibit large discrepancies when compared with the theoretical predictions. Experimentally observed width-to-height ratios are much larger than the predicted values. Also, observed peak heights increase with temperature to a maximum and then decrease, while the Orthodox theory predicts that they should steadily decrease with temperature.

The discrepancy between charging energies obtained from voltage thresholds and activation energies was discussed in Section 8.3. There, we proposed a mechanism that could lead to a voltage-divider effect in order to account for the discrepancy. As further support for the proposed model, here we discuss extensions of the Orthodox theory and compare results with the above-described experimental observations. Two extensions which yield progressively improved agreement with the observations are discussed.

### 9.1.3 Extension to the Orthodox theory: Series-State Model

To accommodate the proposed voltage-divider effect, an energy state \( E_s \) in series with the NP is considered. Note that in principle more than one state may be present in the junctions. For instance, multiple series states may exist at the interfaces between the two electrodes and the molecules and/or the NP and the molecules. In this case, the applied voltage would be divided among all the states. However, to simplify calculations, a single series-state is considered.

Figure 9.4 illustrates a proposed potential energy diagram for an electrode–molecular-state–NP–electrode system. The system is considered to consist of two sections in series: a molecular junction and a single-NP double junction. \( I - V \) characteristics of the two sections were calculated separately using equation 6.2 for tunneling rates with some modifications that will be discussed below.

Tunneling rates \( \Gamma_s^\pm \) to (+) or from (-) the molecular state are taken to be given by:

\[
\Gamma_s^\pm = \frac{1}{e^2 R_s} \frac{-\Delta E_s^\pm}{1 - \exp(\Delta E_s^\pm / k_B T)},
\]

(9.5)
9. Thermo-Voltammetry: Voltage Dependence of Arrhenius Analysis of Conductance

Figure 9.4: Schematic diagram of potential energy for an electrode–molecular-state–nanoparticle–electrode system. A vertical dashed line divides the system in two sections in series: a molecular junction and a single-NP double junction.
9. Thermo-Voltammetry: Voltage Dependence of Arrhenius Analysis of Conductance

where $\Delta E_s^\pm = E_s \mp eV_s$, $V_s$ is the voltage drop between the state and the electrode, and $R_s$ is a tunneling resistance. Note that equation 9.5 represents a simplified treatment of tunneling to the molecular state. Factors such as broadening of the energy state are neglected. Also, in the derivation of equation 9.5, it is assumed that junctions have linear $I - V_b$ characteristics. Because of the presence of a small tunneling barrier between the electrode and the state, the tunneling current in the molecular junction can become a nonlinear function of voltage. Equation 5.21 indicates that $I - V$ of a junction with a small tunneling barrier can be described by a sinh function. In a series expansion of tunneling current vs voltage, the first nonlinear term is, therefore, proportional to $V^3$.

To incorporate this nonlinearity in the model, $R_s$ is considered to be voltage dependent as follows:

$$R_s = \frac{R_{s,0}}{1 + \alpha V_s^2}, \quad (9.6)$$

where $R_{s,0}$ is the tunneling resistance at zero bias, and $\alpha$ is a coefficient that depends on barrier height and temperature. As is shown in Appendix C, at sufficiently high temperatures, $\alpha$ decreases with increasing temperature. This variation arises since as temperature increases, electrons can with increasing probability thermally overcome small tunneling barriers, and the transport mechanism transitions from through-barrier transport (tunneling or field emission) to over-barrier emission which has a weaker voltage dependence.

$I - V$ characteristics of the molecular junction can be calculated from the following equation:

$$I_s = e(\Gamma_s^+ - \Gamma_s^-). \quad (9.7)$$

$I - V$ characteristics of the single-NP double junction were calculated using the standard Orthodox theory. Since the molecular junction and the single-NP double junction are in series, currents passing through the two junctions are the same, and voltages across each junction are added. To obtain $I - V$ of the overall system, the following procedure was used. For a given value of $I$, the corresponding voltage across the molecular state ($V_s$) was determined using the $I - V$ curve of the molecular junction by interpolation.
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Figure 9.5: $E_a$ vs $V_b$ at various temperatures according to the series-state extension to the Orthodox theory. Parameters: $C_1 = C_2 = 2.6$ aF, $R_1 = R_2 = 100$ MΩ, $Q_0 = 0$, $E_a = 5.3$ meV, $R_s = 10$ MΩ, $\alpha = 125$ V$^{-2} \times (1 - T/100$ K), $\xi = 0.05$. Lower inset: the equivalent circuit used in the model. Upper inset: $E_a$ vs $T$ at zero bias.

A similar procedure was used to obtain voltage across the NP ($V_{NP}$). Bias voltage ($V_b$) was then calculated using the following equation,

$$V_b = V_s + \frac{V_{NP}}{\xi}, \quad (9.8)$$

where $\xi$ was input to the model. Conductance was then obtained by numerically differentiating $I - V_b$ data.

Figure 9.5 shows $E_a$ vs $V_b$ at various temperatures calculated using the series-state model. The data were obtained assuming that the voltage drop across the molecular state was 20 times larger than that across the NP (i.e., $\xi = 0.05$). A comparison between data
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Figure 9.6: Schematic of a single-NP device showing two possible current pathways. The electrodes and the NP are covered with self-assembled monolayers of alkanedithiol and alkanethiol, respectively. The NP is bound to one electrode and may or may not be bound to the other electrode. Blue arrows show two possible current pathways between the electrodes.

in Figure 9.3 and Figure 9.5 reveals that the series-state model captures observations of zero–bias peaks with widths that are \( \sim 20 \) times larger than peak heights as a result of the voltage division. However, the series-state model fails to explain the increase of \( E_a \) with \( T \).

9.1.4 Extension to the Orthodox theory: Series-Parallel Model

The observation of multiple \( E_a \) as a function of temperature can be rationalized assuming multiple current pathways in parallel: one in which a small \( E_a \) is dominant and is overcome at low temperatures, and another in which a large \( E_a \) is dominant and is overcome only at higher temperatures. As discussed earlier in Section 9.1.1, the larger \( E_a \) is attributed to the NP charging and the smaller one to the molecular state. Figure 9.6 depicts a possible scenario that can generate this transport mechanism. In this scenario, current can flow between the electrodes either (1) directly or (2) through the NP. The NP pathway has a large \( E_a \) but a small resistance, whereas the direct pathway
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Figure 9.7: $E_a$ vs $V_b$ at various temperatures according to the series-parallel extension to the Orthodox theory. Parameters: $C_1 = C_2 = 2.6$ aF, $R_1 = R_2 = 100$ MΩ, $Q_0 = 0$, $E_s = 5.3$ meV, $R_{s,0} = 10$ MΩ, $\alpha = 125$ V$^{-2} \times (1 - T/100$ K), $\zeta = 0.05$, $R_{p,0} = 10$ GΩ. Left inset: the equivalent circuit used in the model. Right inset: $E_a$ vs $T$ at zero bias.

includes a smaller $E_a$ and a larger resistance (note that resistances of the BJ$s$ prior to NP self-assembly were $\sim$ 2–3 orders of magnitude larger than those of the NP devices). At low temperatures, current through the NP pathway is suppressed because of the large charging energy of the NP, thus current flows mainly via the direct pathway. As temperature increases, the NP pathway gradually opens and, because of to its smaller resistance, eventually is favored.

In the series-parallel model, $I - V_b$ characteristics of the device were obtained by adding currents passing through the direct pathway and the NP pathway at a given bias voltage. $I - V_b$ data of the NP pathway were calculated as described in the previous section. $I - V_b$
data for the direct pathway were calculated using equation 9.5 for tunneling rates. \( E_s \), \( V_s \) and \( \alpha \) were taken to be the same as above, but the junction resistance at zero bias (\( R_{p,0} \)) was taken to be 100 times larger than the resistance of the NP pathway. Figure 9.7 shows \( E_a \) vs \( V_b \) curves at various temperatures calculated for the series-parallel model. The shapes of the curves and their temperature dependence are in agreement with the experimental observations, providing strong support for the proposed model. At low temperatures, the zero–bias peak width and peak height are small because of the small \( E_a \) of the direct pathway. As temperature increases, \( E_a \) approaches the charging energy of the NP. As a result, the zero–bias peak width and height grow with temperature as observed experimentally.

9.2 Arrhenius Pre-factor vs Voltage

9.2.1 Zero–Bias Peaks in Arrhenius Pre-factors

Further support for the proposed model can be obtained by inspecting pre-exponential factors of conductance. Following the Arrhenius analysis, \( dI/dV \) is factorized as:

\[
\frac{dI}{dV} = g_{\text{preexp}} e^{-E_a/k_B T}.
\] (9.9)

\( g_{\text{preexp}} \) can be obtained from data by multiplying \( dI/dV \) (from Figure 8.4) by \( \exp(E_a/k_B T) \) (from Figure 9.2a). Figure 9.8 shows \( g_{\text{preexp}} \) vs \( V_b \) at various temperatures for the 10 nm (a) and the 5 nm (b) NP devices. Again, data exhibit zero–bias peaks whose heights and widths vary with temperature. Insets show peak heights as a function of temperature at zero bias. As temperature increases from 10 K, peak heights increase from values close to zero up to a maximum, and then start to decrease as temperature increases further. Furthermore, \( g_{\text{preexp}} \) beyond the zero–bias peaks shows a strong dependence on both voltage and temperature. At low temperatures, \( g_{\text{preexp}} \) in the high-voltage range improves with voltage. As temperature increases, the voltage-dependence of \( g_{\text{preexp}} \) weakens, and at \( T \)
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∼ 100 K, $g_{\text{preexp}}$ becomes almost independent of voltage.

9.2.2 Predictions of the Orthodox Theory

The various versions of the Orthodox theory described above also predict the existence of zero–bias peaks in $g_{\text{preexp}} - V_b$ plots. Figure 9.9 shows $g_{\text{preexp}}$ vs $V_b$ at various temperatures obtained from the standard Orthodox theory. Three features are noteworthy:

1. Plots exhibit peaks around zero bias;

2. Peak heights decrease with temperature; and

3. Outside of the peaks, $g_{\text{preexp}}$ is almost constant.

To understand these features, let us revisit the Orthodox theory. From equation 9.2, $g_{\text{preexp}}$ inside the CB region is given by

$$g_{\text{preexp}} \approx \frac{E_c - e|V_b|/2}{2RkT}.$$  \hspace{1cm} (9.10)

g_{\text{preexp}}$ has a maximum at zero bias and decreases with increasing $|V_b|$. This zero–bias peak again represents CB, and the peak width corresponds to $\Delta V_{\text{CB}}$. In addition, $g_{\text{preexp}}$ at zero bias is inversely proportional to temperature. Therefore, the peak height decreases with increasing temperature (see Figure 9.9(inset)). Outside the CB, $g_{\text{preexp}}$ is given by

$$g_{\text{preexp}} \approx \frac{1}{2R}.$$  \hspace{1cm} (9.11)

Therefore, it is a constant determined by the resistances of the tunnel junctions. The resistance limits the rate of current flow, and is assumed to be independent of voltage and temperature in the standard Orthodox theory. Once again, these theoretical predictions are inconsistent with experimental observations.
Figure 9.8: Pre-exponential factor of conductance ($g_{\text{preexp}}$) vs voltage at various temperatures for the (a) 10 nm and (b) 5 nm NP devices. Insets: $g_{\text{preexp}}$ vs $T$ at zero bias.
Figure 9.9: \( g_{\text{preexp}} \) vs \( V_b \) at various temperatures calculated using the standard Orthodox theory. Inset: \( g_{\text{preexp}} \) vs \( T \) at zero bias.
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Figure 9.10: \( g_{\text{preexp}} \) vs \( V_b \) at various temperatures calculated using (a) the series-state and (b) the series-parallel extension to the Orthodox theory. Insets: \( g_{\text{preexp}} \) vs \( T \) at zero bias.

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9.2.3 The Series-State and Series-Parallel Extensions to the Orthodox theory

Figure 9.10 illustrates predictions of the series-state and the series-parallel extensions to the Orthodox theory. Figure 9.10a shows results of including only the voltage-divider effect. Zero–bias peak widths are $\sim 20$ times larger than those in Figure 9.9 as experimentally observed. However, the temperature-dependence of both the peak height and the voltage-dependence of $g_{\text{preexp}}$ outside the zero–bias peak are not consistent with the observations. Figure 9.10b shows results of including the parallel pathways. The results are qualitatively in excellent agreement with the experimental data. The model captures the observed broad peak widths relative to the peak heights (the discrepancy). Also, zero–bias peak widths, peak heights, and $g_{\text{preexp}}$ outside the CB, all follow the observed trends with respect to both $V_b$ and $T$. The peak width represents the CB voltage range in the NP pathway and increases as the NP pathway becomes dominant at higher temperatures. The peak height is proportional to $E_a/Rk_BT$. As temperature increases and current via the NP pathway increases, $E_a$ grows and $R$ drops, resulting in an overall growth of the peak height with temperature up to certain temperatures. Outside the CB, $g_{\text{preexp}}$ now depends on both voltage and temperature. At low temperatures, electrons have to tunnel through small barriers. Therefore, $I - V_b$ is nonlinear and conductance improves with voltage (see Appendix C). At high temperatures, electrons are able to overcome the small barriers thermally, but still have to tunnel through large barriers (presented by alkane chains). Therefore, the voltage-dependence of conductance decreases as temperature increases.

9.3 Ultraviolet Photoelectron Spectroscopy

To test the assumption of the proposed model, namely the presence of a molecular energy state close to the Fermi level, we performed ultraviolet photoelectron spectroscopy (UPS)
of hexanedithiol SAMs on gold. UPS allows us to directly probe the electronic structure of the metal–molecule interface.

The principle of UPS is as follows. In UPS, a beam of monochromatic photons with energy $h\nu$ ejects electrons from the valence/conduction band region of a material. There are two groups of photo-emitted electrons [36]:

1. Primary electrons that are emitted from atomic layers near the material surface without experiencing inelastic collisions. The kinetic energy ($E_k$) of this group of electrons can be related to their binding energy ($E_b$) within the material, where the binding energy is defined as the difference between the Fermi energy ($E_F$) and the electron energy ($E$) in the material:

$$E_b = E_F - E.$$  (9.12)

Electrons with maximum kinetic energies originate from the Fermi level; that is, when $E_b = 0$,

$$E_k = h\nu - \phi,$$  (9.13)

where $\phi$ is the material’s work function. More generally, $E_k$ is given by

$$E_k = h\nu - E_b - \phi.$$  (9.14)

2. Secondary electrons that undergo inelastic collisions, likely with other bound valence-band electrons. This group of electrons generates a featureless peak in the low-$E_k$ (or high-$E_b$) region of the spectrum. In typical UPS spectra, the secondary electrons generate features characterized by sharp cutoff edges that correspond to electrons with vanishing kinetic energies. When $E_k = 0$, $E_b = E_{cutoff}$. The cutoff energy ($E_{cutoff}$), therefore, can be used to determine $\phi$ from UPS spectra according to the following relationship:

$$\phi = h\nu - E_{cutoff}.$$  (9.15)
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UPS was performed using a modified PHI 5500 system with a hemispherical electron energy analyzer. UPS spectra were obtained using a 21.2 eV He I source, a pass energy of 5.85 eV, and a takeoff angle of 75°. Binding energies were referenced with respect to the Fermi level. For some UPS measurements, a -25 V bias was applied to samples to improve the determination of cutoff energies. Samples consisted of 55 nm thick Au films deposited on clean glass slides in a separate vacuum chamber. Samples were then immediately immersed into a 0.5 mM solution of hexanedithiol in ethanol for 1.5 h, rinsed thoroughly with ethanol, and dried with nitrogen. Prior to the measurements, all samples were stored under argon in darkness to avoid contamination and oxidation. UPS spectra were obtained without further sample cleaning.

Figure 9.11 shows UPS spectra of a deposited gold film and a gold film coated with a hexanedithiol SAM. The photoelectron spectrum of Au exhibits features at 2–10 eV arising from the ionization of valence band orbitals near the Au surface. Upon the self-assembly of hexanedithiol, the intensities and locations of these features are significantly modified, indicating chemical bonding between the Au substrate and the molecules. The cutoff edge of the UPS spectra are also modified by the molecular SAM. It is known that alkanethiols lower the work function of gold by ~1.0 eV [37] due to the presence of interfacial dipoles [37, 38, 39, 40].

Another feature of the UPS spectra is a peak at ~1.4 eV that is present in the Au+dithiol spectrum but is absent in the Au spectrum (see inset). This peak is attributed to an energy level localized at the gold–thiolate interface. Similar observations have been reported by others [37, 41, 42, 43, 44, 45]. For example, Alloway et al. [37] have observed peaks at ~1.4 eV in UPS spectra of alkanethiols SAMs on Au. Peak intensities decrease with increasing length of the alkane chain (from 3 to 18 carbon atoms), suggesting that the peaks arise from an electronic state localized near the metal–molecule contact since the drop in intensity can be attributed to electron attenuation in the SAMs with increasing alkane chain length. Zangmeister et al. [43] have observed a similar peak in the UPS
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**Figure 9.11:** UPS spectra of a deposited gold film and a gold film coated with a self-assembled monolayer of hexanedithiol (Au+dithiol). A dotted line shows the energy of the photon (21.2 eV). The difference between the photon energy and the cutoff energy of the spectrum represents the work function of the substrate. Inset: UPS spectra taken near the Fermi level. * indicates a peak at 1.4 eV in the spectrum of Au+dithiol.
Figure 9.12: Schematic of the proposed multi-barrier potential profile for Au-alkanethiol.

spectrum of SAMs of benzenethiol on Au. The observation of similar energy levels in the spectra of saturated and conjugated molecules indicates that the organic structure of the molecules has no significant effect on this energy level. Given that such a peak has been only observed in the spectra of chemisorbed SAMs and is absent in the spectra of physisorbed molecules [35, 41, 46], the energy level can be ascribed to the Au–S interaction.

9.4 Conclusion

Self-assembled single-NP devices provide a powerful means to study charge transport through molecular junctions enabling measurements in which voltage and temperature are independently varied. Results reveal multiple activation energies associated with the junctions. The larger energy is attributed to the NP charging and scales with the NP size. The smaller energy is attributed to a barrier at the metal–molecule contact. Results also show a discrepancy between charging energies obtained from CB voltage thresholds and activation energies. The discrepancy is explained by proposing a voltage-divider effect which arises from electrons’ energy loss at the metal–molecule contact. Accordingly, we
propose a new multi-barrier energy profile for the molecular junction (Figure 9.12) that is consistent with all the observations. We propose that there is a small barrier at the metal–molecule contact, which likely arises from interfacial dipoles. There is a larger tunneling barrier which is presented by the alkane chain and its height is determined by the relative alignment of molecular orbitals and the Fermi level. We also propose that there is an energy state at the Au–S interface where electrons can be localized and lose energy. Based on the proposed multi-barrier potential profile, a number of modifications to the Orthodox theory are considered. The modified model is able to successfully explain experimental findings. These results highlight the critical role of metal–molecule contacts in influencing energetics of molecular electronic devices.
Bibliography


Part IV

Charge Transport in Self-Assembled Nanoparticle Films
Chapter 10

Some Factors Influencing Electronic Properties of Nanoparticle Films

The BJs discussed in Part III can also be used to study electronic properties of NP arrays. Three dimensional arrays of ML-NPs can be prepared by alternately immersing BJs in solutions of alkanedithiols and NPs for sufficiently long immersion times. This approach offers an advantage for studying bulk film properties since it facilitates overcoming percolation thresholds as fewer immersion cycles are needed to bridge the closely spaced electrodes with a ML-NP film. Studies of bulk ML-NP films have generally reported two limiting behaviors:

1. An insulating limit where NPs are electronically isolated and electrons are strongly localized on the NPs. This is the case for very large insulating linker molecules, e.g. long alkanedithiols, and is referred to as the “weak coupling limit”.

2. A metallic limit where electrons are delocalized between NPs. This is the case for sufficiently small (yet nonzero) inter-NP separation and is allowed through electronic wave function overlap between NPs, similar to atomic wave function overlap in molecules. This situation is referred to as the “strong coupling limit”.

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Observation of these two limits, combined with a possibility of varying average inter-NP separation one C-C bond at a time, raises an intriguing prospect of exploring MITs in these ML-NP films. This prospect represents the main focus of this Part of the thesis.

In the weak coupling regime, conductance through a NP–molecule film is governed by tunneling through molecules and single-electron charging of the NPs. The NPs, thus, can be considered as being connected by local conductances, \( g \),

\[
g \propto e^{-\beta s} e^{-E_c/k_BT}, \tag{10.1}
\]

where \( \beta \) is the tunneling decay constant, \( s \) is the inter-NP surface-to-surface separation, \( E_c \) is the single-electron charging energy, \( E_c = e^2/2C \), and \( C \) is capacitance. Obtaining an exact expression for \( C \) is a nontrivial problem and requires taking into account cross-capacitances since charges on one NP can polarize neighboring NPs. A simple approach is to approximate the neighboring NPs as a conducting continuum separated from the central NP by an insulating shell \([1]\), as shown in Figure 10.1. In this approximation, the capacitance of the NP is

\[
C = 4\pi \epsilon_0 \epsilon_r \left( \frac{1}{r} - \frac{1}{r+s} \right)^{-1} = 4\pi \epsilon_0 \epsilon_r \frac{r(r+s)}{s}, \tag{10.2}
\]

and the charging energy can be expressed as

\[
E_c = \frac{e^2}{8\pi \epsilon_0 \epsilon_r} \left( \frac{1}{r} - \frac{1}{r+s} \right) = \frac{e^2}{8\pi \epsilon_0 \epsilon_r} \frac{s}{r(r+s)}. \tag{10.3}
\]

Equation 10.3 predicts that \( E_c \) increases as \( r \) decreases or \( s \) increases:

\[
\frac{\Delta E_c}{E_c} = -\Delta r \left( \frac{1}{r} + \frac{1}{r+s} \right) \approx -2 \Delta r \frac{r}{r} \quad (r \gg s), \tag{10.4}
\]

\[
\frac{\Delta E'_c}{E_c} = \Delta s \left( \frac{1}{s} - \frac{1}{r+s} \right) = \Delta s \left( \frac{1}{s(r+s)} \right) \approx \frac{\Delta s}{s} \quad (r \gg s). \tag{10.5}
\]

A number of studies have confirmed the importance of tunneling \([2, 3, 4, 5]\) and single-electron charging \([6, 7, 8, 9, 10, 11]\) in weakly coupled NP films. Studies of films of \( \text{CH}_3(\text{CH}_2)_{n-1}\text{S}\)-capped Au NPs \([2, 3]\) and HS(\(\text{CH}_2\))_nSH-linked Au NPs \([6, 7, 11]\) have reported that film conductivities exhibit an exponential dependence on \( n \). This observation
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Figure 10.1: (a) Conducting NP of radius $r$ separated from neighboring NPs by an average distance $s$. The NPs are embedded in an insulating medium with dielectric constant $\epsilon_r$. (b) NP in (a) is modeled as a sphere separated from a conducting surrounding by an insulating shell with thickness $s$ and dielectric constant $\epsilon_r$.

suggests that the length of the molecules controls the inter-NP surface-to-surface separation, $s$. The typical observed value of $\beta$ is $\sim 1.0 \text{ Å}^{-1}$, consistent with values reported by studies of metal–molecule–metal tunnel junctions (see Section 5.2). These studies have also reported that the NP films exhibit Arrhenius $T$-dependence with activation energies that generally increase with decreasing $r$ and increasing $n$, according to the trends predicted by equations 10.4 and 10.5, respectively.

Equation 10.1 for conductance predicts that as $T \to 0$, $g$ vanishes. Therefore, films of weakly coupled NPs are electronically insulating. Note that equation 10.1 is only applicable when $g$ is smaller than the quantum of conductance, $g_Q$ (equation 1.4). This requirement ensures that charges can flow by tunneling and yet are sufficiently localized so that charge states of the NPs are well-defined. This can be understood in terms of the energy–time uncertainty principle:

$$\Delta E \Delta t \geq \frac{h}{2}. \quad (10.6)$$

Taking $\Delta E$ as the energy change due to (dis)charging, $\Delta E \approx E_c$, and $\Delta t$ as the (dis)charging time due to tunneling, $\Delta t \approx RC$, one gets

$$\frac{e^2}{2C} (RC) \geq \frac{h}{2} \Rightarrow g = \frac{1}{R} \leq \frac{e^2}{h}. \quad (10.7)$$
Figure 10.2: Effect of inter-NP separation (as determined by the length of alkyl chains in the NP ligand shell) on the density of states of CH$_3$(CH$_2$)$_{n-1}$S-capped 1.7 nm Au NPs. The spectrum of a pure gold foil is shown for comparison. Reprinted with permission from Reference [16]. Copyright 2005 American Physical Society.

The factor of 2 in equation 1.4 arises from electron’s spin degeneracy. For $g > g_Q$, $\Delta t$ is very short such that $\Delta E$ becomes sufficiently large to overcome $E_c$. Single-electron charging effects are then suppressed as quantum couplings become strong and charges become delocalized [12, 13, 14, 15].

Such quantum coupling transitions are expected for NP films when wave function overlap between NPs becomes sufficiently strong. Valence-band photoemission spectroscopy of CH$_3$(CH$_2$)$_{n-1}$S-capped Au NPs [16] has shown that for $n \geq 9$ the density of states at the NP Fermi level vanishes due to the charging energy of the NPs. For $n = 6$, the density of states at the Fermi level increases (Figure 10.2). This can be attributed to electron delocalization for sufficiently small inter-NP separation. Optical spectroscopy of NP films have also shown evidence of quantum coupling. Heath and co-workers [17, 18, 19, 20] studied linear and nonlinear optical response of CH$_3$(CH$_2$)$_{n-1}$S-capped Ag NP monolayers as a function of inter-NP separation. They utilized a Langmuir trough to compress NP
monolayers from $\delta/2r \approx 1.7$ to 1.1, where $r$ is the NP radius and $\delta$ is the center-to-center NP separation ($\delta = 2r + s$). They found that, for $\delta/2r > 1.3$, linear optical responses (e.g., reflectance) could be well-described by a classical coupling model involving changes in polarizability [19] or dielectric constant [20]. For smaller values of $\delta/2r$, predictions of the classical model diverged strongly from experimental observations. Nonlinear response (e.g., second-order susceptibility) exhibited an exponential dependence on $\delta/2r$, implying strong quantum coupling between NPs. For $\delta/2r < 1.2$, optical properties of the monolayer resembled those of a thin metallic Ag film. The transition to delocalized behavior was reversible upon increasing the inter-NP separation.

In the strong coupling regime, electron delocalization can overcome the single-electron charging energy, and as a result, bulk NP films can exhibit metallic behavior, i.e. their conductance remains finite as $T \to 0$. In order for a film of strongly coupled NPs to exhibit global metallicity, the film must cross a percolation threshold. At the threshold, strongly coupled NPs that form metallic “superclusters” combine to form at least one continuous, sample-spanning metallic pathway. Although at or just above the transition, the sample may be dominated by nonmetallic conduction, as $T \to 0$, nonmetallic pathways shut down, and at absolute zero, conductance remains nonzero. Below the threshold, however, metallic superclusters are electronically isolated, and overall, the film is nonmetallic. Our group [21, 22, 23] has studied percolation effects in strongly coupled NP films by varying film thickness. NP films were prepared by stepwise self-assembly using sufficiently short cross-linker molecules (i.e. 1,4-butanedithiol) to ensure strong inter-NP coupling. Films exhibited conductivities that depended strongly on the number of NP/linker exposure cycles. Figure 10.3 shows normalized conductivity as a function of temperature for butanediol-linked Au NP films prepared with 3–9 immersion cycles. Films prepared with $\leq 5$ immersion cycles exhibit thermally activated conductivities, i.e. $d\sigma/dT > 0$; whereas films prepared with $\geq 6$ cycles exhibit metallic-like behavior, i.e. $d\sigma/dT < 0$.
Figure 10.3: Normalized conductivity vs temperature for 1,4-butanedithiol-linked Au NP multilayer films with 3–9 layers. Dashed lines are fits obtained using an effective-medium approximation model. Reprinted with permission from Reference [21]. Copyright 2002 American Institute of Physic.
This Part describes results of studying electronic properties of HS(CH$_2$)$_n$SH-linked Au NPs in the bulk regime, i.e. above the percolation threshold. In these films, inter-NP coupling is controlled by systematically varying the length of linker molecules from $\sim 0.5$ nm ($n = 2$) to $\sim 1.6$ nm ($n = 10$), in increments of $\sim 0.1$ nm (one CH$_2$ unit). Measurements of resistances ($R$) at both 2 K and 200 K, variation of $R$ with $T$ at intermediate temperatures, as well as changes in $R$ after annealing, all point to an MIT occurring at $n = 5$. The transition is explained in the context of a Mott-Hubbard model for MITs. Electronic properties of the NP films below and above the MIT are studied. Applications of NP films near the MIT are also briefly described.
Chapter 11

Film Preparation and Characterization

ML-NP films were prepared via stepwise self-assembly on BJs. NPs 5.0 ± 0.8 nm in diameter and stabilized by tetraoctylammonium-bromide ligands in toluene were used. Since the ligands are weakly attached to the Au NPs, they can be readily exchanged by alkanedithiols, enabling attachment of Au NPs to thiol-terminated surfaces. BJs were fabricated using gold wires deposited on glass slides with Cr adhesion layers as described in Section 3.1. Electrodes were functionalized by immersion in 0.5 mM ethanol solutions of alkanedithiols for 1 h, rinsing with ethanol, and drying with nitrogen. Multilayer NP films were then prepared by alternately immersing samples in toluene solutions of Au NPs for ~ 30–60 min and 0.5 mM alkanedithiols for ~ 10 min with intervening toluene rinse steps.

Films were also prepared on transparent glass substrates and conducting silicon substrates for optical spectroscopy and SEM characterization, respectively. To self-assemble NPs on these substrates, the substrates were functionalized with a monolayer of 3-aminopropylmethyldiethoxysilane, \( \text{NH}_2(\text{CH}_2)_3\text{Si(CH}_3)(\text{OCH}_2\text{CH}_3)_2 \), following a procedure described in Section 3.1, except that aminosilane was used instead of mercaptosilane. Subsequent layers of NPs and alkanedithiols were self-assembled as described above.
Figure 11.1 shows representative UV/vis spectra of films of Au NPs linked with butanedithiol. Films made with other alkanedithiols exhibited similar spectra. The UV/vis spectra exhibit peak red shifts compared to the surface-plasmon resonance peak of NPs in toluene (see Section 2.3). An inset in Figure 11.1 shows a linear increase in maximum absorbance vs the number of cycles indicating that each immersion adds approximately the same amount of NPs. Ellipsometry measurements [8] have shown an approximately linear increase of average film thickness with the number of cycles.

Figure 11.2 shows SEM images of films of Au NPs linked with butanedithiol after 1, 2, and 3 immersion cycles. The images are consistent with the above observations:
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Figure 11.2: SEM images of a butanedithiol-linked Au NP film. Films were prepared on a silicon substrate after 1, 2, and 3 immersion cycles. Reprinted with permission from Reference [21]. Copyright 2002 American Institute of Physics.

Figure 11.3: STM image of a butanedithiol-linked Au NP film. The film was prepared on a doped-silicon/silicon-oxide substrate with four immersion cycles. Tip bias and current set point were -1.2 V and 0.1 nA, respectively. Reprinted with permission from Reference [24]. Copyright 2005 American Chemical Society.
With increasing number of immersion cycles, more NPs are added resulting in a decrease of average inter-NP separation and an increase of average film thickness. The images show that after the first immersion cycle, NPs are mostly isolated and dispersed over the substrate. As the number of cycles increases, newly deposited NPs are attached either to previously deposited NPs, forming “superclusters” of ML-NPs, or to uncovered regions of the substrate, seeding new superclusters. Figure 11.3 shows a scanning tunneling microscope (STM) image of a film of Au NPs linked with butanedithiol, prepared with four immersion cycles on silicon substrate. The STM image, consistent with the SEM images in Figure 11.2, illustrates that the NP film is highly disordered.

Figure 11.4 shows changes in the conductance of NP films vs the number immersion cycles. The conductances generally increase after each cycle because of the increase of film thickness as discussed above. For \( n = 2 \) and 3, as the number of cycles increases, conductances change initially very slowly, then rapidly and finally at a constant rate. These observations suggest that a percolation transition occurs, and eventually in the bulk limit, the number of current pathways increases in proportion to the average thickness of the film. As \( n \) increases, the region of rapid change seems to occur at lower number of cycles, until for \( n \geq 5 \) this region is no longer observed. For large \( n \), conductance varies nonuniformly with the number of cycles. These nonuniform variations may be due to changes in orientation and conformation of alkanedithiols on NPs’ surfaces [25].
**Figure 11.4:** Normalized conductance of typical films of Au NPs linked with alkanedithiols with various chain lengths as a function of number of immersion cycles. Conductances are normalized with respect to their maximum values. Offsets are added for clarity. Inset: Film resistance after the 10th cycle as a function of the number of methylene groups in the linkers.
Metal–Insulator Transition

12.1 Experimental Results

Figure 12.1 shows resistances ($R$) of multilayer films of 5 nm Au NPs cross-linked with alkanedithiols, HS(CH$_2$)$_n$SH with various $n$, as a function of temperature. At low temperatures, two distinct types of behaviors are observed: films with $n \leq 4$ exhibit finite resistances and are metallic; films with $n \geq 6$ exhibit rapidly increasing resistances and are insulating. Both types of behaviors are observed among films with $n = 5$. At intermediate temperatures, temperature coefficient of resistance (TCR) provides another means to compare behavior of samples:

$$\text{TCR} \equiv \frac{1}{R} \left(\frac{dR}{dT}\right).$$

(12.1)

Metals and insulators are known generally to exhibit positive and negative TCR, respectively. This trend is followed by films with $n \leq 4$ and $n \geq 6$, respectively. For $n = 5$, samples with finite resistances at low temperatures exhibit positive TCR, except one which is indicated by an arrow, and samples with rapidly increasing resistances at low temperatures exhibit negative TCR.
Figure 12.1: Normalized resistances of multilayer films of HS(CH$_2$)$_n$SH-linked Au NPs vs temperature. Inset: Resistance of the films at 200 K as a function of $n$. 
Figure 12.1(inset) shows resistances of the films at 200 K as a function of \( n \). As \( n \) increases from 2 to 5, resistance changes by less than an order of magnitude for metallic samples. Going from metallic to insulating samples with \( n = 5 \), resistance jumps by 2 orders. Thereafter, resistance changes by another \( \sim 2 \) orders for insulating samples \( (n \geq 5) \). This change can be attributed to the exponential growth of tunneling resistances with distance,

\[
R \propto \exp(\beta n),
\]

where \( \beta \) is a constant. The observed \( \beta \) is \( \sim 0.9 \), in agreement with reported values for alkanedithiols in single-molecule junctions (see Section 5.2). The observed trends were highly reproducible: All 12 samples with \( n \leq 4 \) and 22 samples with \( n \geq 6 \) showed metallic and insulating behavior, respectively. Of 12 samples with \( n = 5 \), 7 showed metallic and 5 showed insulating behaviors.

### 12.2 Mott-Hubbard Metal–Insulator Transition

The above results can be understood in the context of the Mott-Hubbard model for MITs, proposed originally for a lattice of hydrogen atoms [26, 27]. Consider such a lattice at absolute zero and with variable lattice spacing, \( s \). In the limit \( s \to \infty \), overlap between atomic wave functions is negligible, and electrons are localized on individual atoms. For conduction to occur, electrons have to transfer between neutral atoms, creating positively and negatively charged ions. This transfer requires an energy, \( U \), arising from the difference between the ionization energy (IE) and the electron affinity (EA) of hydrogen atoms. \( U \) is known as the Hubbard energy and is the energy cost of transferring an electron from one atom to another and forming an electron-hole pair [27]:

\[
U = \int \int |\psi(r_1)|^2 \frac{e^2}{4\pi\epsilon r_{12}} |\psi(r_2)|^2 d^3r_1d^3r_2.
\]

\( \psi(r) \) is the wave function of the hydrogen atom. For a 1-s state,

\[
\psi(r) \propto e^{-r/\alpha_0},
\]

\( \alpha_0 \) is the Bohr radius.
where $a_0$ is the Bohr radius:

$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}. \quad (12.5)$$

$U$ has been evaluated and is given by $[27]$

$$U = \frac{5}{8} \frac{e^2}{4\pi\varepsilon a_0}. \quad (12.6)$$

Because of this energy cost, conduction at zero bias is suppressed, and the lattice is insulating.

For finite $s$, the overlap between atomic wave functions is nonzero and gives rise to energy bands as per the band theory of solids. The energy gap for conduction, $E_g$, then reduces to (see Figure 12.2)

$$E_g = U - \frac{\Delta_1 + \Delta_2}{2}. \quad (12.7)$$
The widths, $\Delta_i$, of energy bands, $i$, depend on the magnitude of overlap integrals, $\gamma$, between atomic wave functions,

$$\Delta_1 \approx \Delta_2 \approx 2z\gamma,$$

(12.8)

where $z$ is the coordination number of atoms in the lattice. $\gamma$ is given by

$$\gamma = \int \psi_i^*(r)H\psi_j(r)d^3r,$$

(12.9)

where $H$ is the Hamiltonian of the lattice, and $i$ and $j$ represent nearest-neighbor sites at a distance $s$ apart. For hydrogen atoms, the overlap energy integral is given by

$$\gamma \approx \frac{e^2}{4\pi\epsilon a_0} \left(1 + \frac{s}{a_0}\right) e^{-s/a_0}.$$  

(12.10)

Note that the dependence of the pre-exponential term on $s$ is negligible, compared with that of the exponential term. $\gamma$, therefore, increases exponentially with decreasing $s$.

The bandwidths $\Delta_1$ and $\Delta_2$ also increase as $s$ decreases, and at

$$U = \frac{\Delta_1 + \Delta_2}{2},$$

(12.11)

the energy gap for conduction disappears, and the lattice becomes metallic. Taking $\Delta_1 = \Delta_2$ and $z = 6$, the condition given by equation 12.11 can be written as

$$U \approx 12\gamma.$$  

(12.12)

Using equations 12.6 and 12.10 for $U$ and $\gamma$, one obtains

$$s \sim 4.5a_0,$$

(12.13)

which is the Mott-Hubbard criterion for the onset of metallic behavior [28].

An analogous Mott-Hubbard MIT can be realized in NP films where NPs serve as artificial atoms. In NP films, the energy gap arises from the NP charging energy (i.e. Coulomb gap). The energy bands arise from the overlap between NP wave functions:

$$\psi(r) \propto e^{-kr},$$

(12.14)
where $\kappa$ is the decay constant of wave function outside of the NP. According to a step-potential model (see Appendix A), $\kappa$ is given by

$$\kappa = \frac{\sqrt{2m^*\phi}}{\hbar},$$  \hspace{1cm} (12.15)

where $m^*$ is an effective mass of electron, $\phi$ is the barrier height (i.e. the energy difference between NP’s Fermi level and vacuum), and $\hbar$ is the reduced Planck’s constant. $\kappa$ provides a useful length scale in the Mott-Hubbard criterion for the MIT (see equations 12.4 and 12.14):

$$a_0 \sim \frac{1}{\kappa}.$$  \hspace{1cm} (12.16)

Taking $\phi \approx 1.4$ eV and $m^* \approx 0.4 \times$ mass of electron reported for gold–alkanedithiolate–gold tunnel junctions [29], one obtains

$$\kappa \approx 4 \text{ nm}^{-1}.$$  \hspace{1cm} (12.17)

Applying the Mott-Hubbard criterion (equation 12.13), one finds a critical NP separation for MIT to be

$$s \sim \frac{4.5}{4 \text{ nm}^{-1}} = 1.1 \text{ nm}.$$  \hspace{1cm} (12.18)

This estimated value is consistent with the length of 1,5-pentanediol linkers and the observation of the MIT at $n = 5$.

To test whether observed metallic behavior is a result of Mott-Hubbard MIT rather than of direct metal–metal contacts between NPs, the NP films were annealed under a nitrogen atmosphere. The NP films were mounted on an aluminum platform and heated on a hotplate inside a glove bag. The glove bag was purged with nitrogen to prevent oxidation. Temperature was monitored using a thermocouple attached to the aluminum platform close to the NP film. Film resistance was measured using a digital multimeter. The annealed samples initially followed trends in resistance shown in Figure 12.1. Eventually, samples with $n \leq 5$ showed sudden drops of 30–50% in resistance at $100 \pm 20$ °C. Figure 12.3 shows typical resistance vs temperature data obtained during
annealing of a metallic pentanedithiol-linked NP film. The results are in agreement with a study showing that, using mass spectroscopy and electron microscopy, annealing releases dithiols, which in turn induces metal–metal contacts between NPs and drops in resistance \[10\]. This suggests that before annealing alkanedithiols indeed protect Au NPs from aggregation and point to a Mott-Hubbard mechanism of metallic behavior observed.

The observation of both metallic and insulating behaviors among \(n = 5\) samples suggests that other parameters besides \(n\) can influence the MIT. They include distributions in NP sizes and inter-NP separations for a given \(n\) (likely due to presence of solvent or tetraoctylammonium-bromide ligands, or orientation of linkers), and fluctuations in electrostatic potentials due to trapped charges.
12.3 Examples of Metal–Insulator Transition in Other NP–Molecule Systems

MITs as a function of inter-NP separation have also been reported in a number of other studies involving NP–molecule systems. Redmond and co-workers [30, 31] studied an MIT in CoPt$_3$ NP films by tuning inter-NP separation via thermal annealing. They prepared multilayer films of 3.8 nm CoPt$_3$ NPs on interdigitated arrays of electrodes by drop-casting. The NPs were stabilized with 1-adamantanecarboxylic acid and hexadecylamine ligands. As-prepared films exhibited high resistances exceeding 1 TΩ at room temperature. After annealing under reducing conditions (5% H$_2$, 95% N$_2$ for 1 h), films generally exhibited decreased inter-NP separation and film resistances (Figure 12.4). Films annealed at 80°C exhibited room-temperature resistances on the order of $\sim$ 100 MΩ, thermally activated behavior between 3–300 K, and rapidly climbing $R$ as $T$ decreased near 3 K. At $T = 3$ K, these films also displayed Coulomb blockade in $I–V$ characteristics. Films annealed at 100°C exhibited room-temperature resistances of $\sim$ 190 kΩ and exhibited linear $I–V$ characteristics at all measured temperatures. $R$ vs
12. Metal–Insulator Transition

$T$ data of these films displayed two regions: a region of positive TCR for $80 < T < 300$ K, and another of negative TCR for $4 < T < 80$ K. As temperature approached 3 K, resistances tended to finite values, implying that these films were metallic by definition. Increasing the annealing temperature to 150°C produced films with room-temperature resistances of $\sim 1$ kΩ. These films exhibited linear $I – V$ curves, positive TCR for $4 < T < 300$ K, and resistances that tended to finite values at 4 K, consistent with metallic behavior.

Heath and co-workers have studied electronic properties of Ag NP monolayers using impedance spectroscopy [32] and STM [33, 34]. They utilized a Langmuir trough to prepare NP monolayers with $\delta/2r$ ranging from $\sim 1.7$ to 1.1, where $r$ is the NP radius and $\delta$ is the center-to-center NP separation: $\delta = 2r + s$. Figure 12.5 shows impedance spectra of propanethiolate-capped 3.5 nm Ag NPs and shows three distinct behaviors at various NP separations. For $\delta/2r > 1.3$, spectra could be modeled using an equivalent RC circuit. For $1.2 < \delta/2r < 1.3$, characteristic RC time constants decreased rapidly with decreasing inter-NP separation. Such behavior is consistent with an increasing tunneling rate between NPs. Below $\delta/2r = 1.2$, the film exhibited a transition from an RC- to an inductive-type of behavior, suggesting a transition to metallic conductance. Figure 12.6 shows results of STM studies using monolayers of decanethiolate and hexanethiolate-capped 2.6 nm Ag NPs. Inter-NP separations in these monolayers were $\sim 1.1$ and 0.6 nm, respectively. Normalized conductances of the NP monolayers also strongly depended on $\delta/2r$. At $\delta/2r \approx 1.4$, normalized conductance at zero bias vanished at low temperatures. At $\delta/2r \approx 1.2$, its value at zero bias was equal to 1 and was temperature independent from 300 to 20 K. Since tunneling conductance in STM at low bias is proportional to $\rho_{\text{tip}}(E_F)\rho_{\text{sample}}(E_F)$, normalized conductance, defined as $(dI/dV)(V/I)$, provides a good approximation to the local density of states. At zero bias, insulators exhibit a vanishing density of states. Metals exhibit a finite density of states and a normalized conductance equal to 1.
Figure 12.5: Plot of the frequency-dependent dielectric modulus, $M$, in the complex plane, for a Langmuir monolayer of propanethiolate-capped 3.5 nm Ag NPs at various surface pressures. Insets show equivalent circuits of the monolayer in metallic and nonmetallic limits, respectively. Reprinted with permission from Reference [32]. Copyright 1998 American Physical Society.
Figure 12.6: Normalized density of states (DOS) vs voltage for films of (a) decanethiolate-capped and (b) hexanethiolate-capped 2.6 nm Ag NPs at different temperatures. Data obtained using scanning tunneling microscopy. Reprinted with permission from Reference [33]. Copyright 1999 American Physical Society.

Scanning electrochemical microscopy (SECM) has also ben employed to study MITs in Langmuir monolayers of alkanethiolate-capped Ag and Au nanoparticles [35, 36]. SECM permits surface characterization of a substrate immersed in a solution of redox-active electrolyte [37]. In SECM, an ultramicroelectrode typically serves as the tip, and its position with respect to a substrate can be varied. Voltage is applied between the tip and a reference electrode, and current is measured between the tip and a counter electrode. In contrast with STM current, SECM current arises from redox of species at the ultramicroelectrode tip. When the tip is far from the substrate, the current is driven by the diffusion of redox species between the solution and the tip. When the tip is brought
Figure 12.7: SECM approach curves obtained using a hexanethiolate-capped 4 nm Ag NP monolayer at various Langmuir trough pressures: (1) 0 mN m$^{-1}$ (open barrier position); (2) 11 mN m$^{-1}$; (3) 22 mN m$^{-1}$; (4) 42 mN m$^{-1}$; and (5) 56 mN m$^{-1}$ (closed barrier position). $i$ and $i_L$ are the tip current at a given tip-substrate distance ($d$) and in the bulk, respectively. Dotted lines represent theoretical fits assuming substrates are insulating (lower) or conducting (upper). Reprinted with permission from Reference [35]. Copyright 2001 American Chemical Society.
close to the substrate, the vicinity and the nature of the substrate perturbs the current. An insulating substrate can hinder diffusion of redox species toward the tip and thereby reduce the current; that is, the closer the tip is to the substrate, the smaller is the current. In contrast, a conducting substrate can increase the current by regenerating a portion of the reacted species at its surface. The regenerated species can react again at the tip and increase the tip current. Therefore, SECM offers a means of distinguishing between insulating and conducting substrates and can be used to probe lateral conductivity of the substrates. Figure 12.7, reported by Quinn et al. [35], shows SECM approach curves using hexanethiolate-capped 4 nm Ag NP monolayers obtained at various Langmuir trough surface pressures. At surface pressures below and above 42 mN m\(^{-1}\), respectively, the monolayers exhibited a decrease and increase in SECM current as the SECM tip approached the monolayers. Such a transition was reversible upon changing the surface pressure.

### 12.4 Metallic Behavior

Although bulk ML-NP films with sufficiently short linker molecules behave as metals, they still exhibit electrical behavior that reflects the presence of their nanoscale components. Figure 12.8 shows normalized resistance of metallic ML-NP films \((n \leq 5)\) and thermally deposited 15 nm thick gold wires vs temperature. Above 100 K, resistance varies linearly with temperature. TCR values, obtained by fitting straight lines to the data above 100 K, are shown in a lower inset. For comparison a value of bulk Au is also shown. TCR of the NP films are in the range of \(~0.001–0.002\ \text{K}^{-1}\) and do not exhibit a systematic trend with \(n\). However, they are lower than the TCR of bulk Au \((\sim 0.0055\ \text{K}^{-1})\) by more than a factor of 2. Lack of a systematic trend in TCR vs \(n\) likely arises due to film disorder. Below 10 K, film resistances vary slowly (less than 1\%) and tend to finite values as temperature decreases (upper inset). The tendency of resistance toward a
**Figure 12.8:** Resistance of metallic films of alkanedithiol-linked Au NPs ($n \leq 5$) and thin gold wires normalized to their values at 200 K vs temperature. Upper Inset: Residual resistance of metallic samples extrapolated as $T \to 0$ vs type of samples. Lower Inset: TCR of the metallic samples at 200 K vs type of samples. The same symbols are used to represent sample types in both insets (see abscissa) and main panel.
finite value at very low temperature indicates that these films are fundamentally metallic.

Conductivities of Au NP films are generally lower than that of bulk Au ($\sigma_{Au} = 4.5 \times 10^5 \, \Omega^{-1} \text{cm}^{-1}$) [38]. The highest value reported for Au NP films is $\sigma = 2 \times 10^5 \, \Omega^{-1} \text{cm}^{-1} \approx 0.5\sigma_{Au}$, as reported by Liu et al. [39] for films consisted of 15 layers of 4.8 nm Au NPs prepared using an ionic stepwise self-assembly method. They used Au NPs encapsulated with cationic polymer molecules, poly(diallyldimethylammonium chloride). The NPs were attached to anionic polymer molecules, poly S-119, via electrostatic attractions. Other studies have reported conductivities in the range of $\sim 10^1$–$10^3 \, \Omega^{-1} \text{cm}^{-1}$ [5, 40].

According to the Drude theory of metals, the conductivity of a metal is given by

$$\sigma = \frac{\eta e^2 \tau}{m},$$  \hspace{1cm} (12.19)

where $\eta$ is the density of conducting electrons and $\tau$ is mean free time. $\tau$ is determined by electron scattering, which can be categorized as elastic (e.g., impurity or defect scattering) and inelastic (e.g., electron-electron or electron-phonon scattering). The mean free time associated with these processes can be written as (Matthiessen’s rule)

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{elastic}}} + \frac{1}{\tau_{\text{inelastic}}},$$ \hspace{1cm} (12.20)

and the conductivity of metals can be written as

$$\sigma^{-1} = \sigma_0^{-1} + \sigma(T)^{-1}.$$ \hspace{1cm} (12.21)

At very low temperatures, $\tau_{\text{elastic}}$ dominates since it is independent of temperature. At higher temperatures, $\tau_{\text{inelastic}}$ becomes significant and gives rise to a temperature-dependent conductivity. Assuming that the rate of inelastic scattering due to electron–phonon interactions increases as $\sim k_B T$, metallic conductivity decreases as $\sim 1/k_B T$ and resistivity increases linearly with temperature.

The observation of lower $\sigma$ and TCR in Au NP films compared with bulk gold suggests that electron-scattering processes are strongly enhanced in NP films. Elastic electron-scattering decreases zero-temperature conductivity ($\sigma_0$ in equation 12.21), which in turn
gives rise to smaller values of TCR. Temperature-independent elastic scattering dominates the conductivity of metallic NP films since sizes of NPs are typically much smaller than the mean free path, \(\ell\), of electrons in the bulk material. For example, in a film of 5 nm Au NPs, the time scale for elastic scattering can be estimated as

\[
\tau_{\text{elastic}} \approx \frac{\ell}{v_F} \approx \frac{5 \times 10^{-9}}{1.4 \times 10^6} \text{ m/s} = 3.6 \text{ fs},
\]

where \(v_F\) is the Fermi velocity of electrons in gold. For bulk gold, \(\ell = 41\) nm and \(\tau_{\text{elastic}} \approx 29\) fs at 300 K [41]. At 300 K, the time scale for inelastic scattering due to phonons is

\[
\tau_{\text{inelastic}} \approx \frac{\hbar}{k_B T} \approx 25 \text{ fs}.
\]

Our lab has shown the importance of elastic scattering in ML-NP films near MITs by studying magnetoresistance of the films using superconducting electrodes. [42, 43, 44, 45, 46].

### 12.5 Insulating behavior

Detailed examinations of \(R - T\) data show that all insulating ML-NP films exhibit a universal behavior (Figure 12.9)

\[
R = R_0 \exp \left[ \left( \frac{T_0}{T} \right)^\nu \right],
\]

where \(R_0\), \(T_0\) and \(\nu\) are fitting parameters. An upper inset in Figure 12.9 shows that \(T_0\) increases with \(n\) implying an increase in activation energy with increasing inter-NP separation. A lower inset indicates that \(\nu = 0.65\).

Previous studies of transport mechanisms through insulating ML-NP films have often found two types of \(T\)-dependencies: \(\nu = 1\) and \(\nu = 1/2\). The fact that the observed power lies between these two values suggests that a combination of both mechanisms is operating. To examine this in more detail, \(\ln(R)\) is analyzed vs \(T^{-1}\) and \(T^{-1/2}\) for all insulating films; Figure 12.10 shows behavior of a typical film with \(n = 5\). Below \(\sim 100\)
Figure 12.9: $\ln(R/R_0)$ vs $\ln(T/T_0)$ for all insulating samples ($n \geq 5$). $R_0$ and $T_0$ are fitting parameters. 678 points are overlaid. Upper Inset: Variation of $T_0$ with $n$. Lower Inset: $\ln(\ln(R/R_0))$ vs $\ln(T/T_0)$ showing a linear relationship. The best fit slope is 0.65.
K, \( \ln(R) \) tends to \( T^{-1/2} \) and at higher temperatures to \( T^{-1} \) (Arrhenius) behavior. Insets show slopes of best fit lines to \( T^{-1} \) and \( T^{-1/2} \) behavior for various \( n \). \( T_0 \) (Figure 12.9 inset) and best fit slopes (Figure 12.10 insets) exhibit similar trends.

**Figure 12.10:** Resistance of a typical insulating sample with \( n = 5 \) plotted vs (a) \( T^{-1} \) and (b) \( T^{-1/2} \). Solid lines represent best linear fits for respective data. Insets: Slopes of the linear fits vs \( n \).
12. Metal–Insulator Transition

Table 12.1: Fit parameters for insulating alkanedithiol-linked nanoparticle films obtained from $T^{-1}$ and $T^{-1/2}$ fits.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$E_a$ [meV]</th>
<th>$T_{0}^{ES}$ [K]</th>
<th>$r_{hop}(2$ K) [nm]</th>
<th>$r_{hop}(100$ K) [nm]</th>
<th>$\Delta W_{hop}(100$ K) [meV]</th>
</tr>
</thead>
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<td>5</td>
<td>9.2</td>
<td>780</td>
<td>41</td>
<td>5.7</td>
<td>12</td>
</tr>
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<td>6</td>
<td>13.6</td>
<td>1534</td>
<td>29</td>
<td>4.1</td>
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<td>23</td>
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<tr>
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<tr>
<td>10</td>
<td>18.8</td>
<td>2564</td>
<td>22</td>
<td>3.2</td>
<td>22</td>
</tr>
</tbody>
</table>

Arrhenius behavior can arise from single-electron charging of NPs as discussed in Chapter 10:

$$R \propto e^{E_a/k_B T} \approx e^{E_c/k_B T},$$

(12.25)

where $E_c$ is the charging energy, $E_c = e^2/2C$, and $C$ is the capacitance of NPs. Table I lists activation energies ($E_a$) extracted from the slopes of $T^{-1}$ fits. $E_a$ increases with $n$, implying that $C$ decreases correspondingly. As the inter-NP separation increases, the contribution of neighboring NPs to $C$ decreases. The observed trend is in qualitative agreement with equation 10.3. Taking $\epsilon_r = 2.6$ and $s = 1.6$ nm for decanedithiol, equation 10.3 gives $E_c \approx 44$ meV which is of the same order as the values observed.

A $T^{-1/2}$ behavior is predicted by a variable-range hopping (VRH) model. VRH, introduced by Mott [47] and extended by Efros and Shklovskii [48, 49] to accommodate strong Coulomb interactions, is based on an interplay between tunneling and activated processes. In the VRH model, charge carriers are considered to be localized on sites, $i$, with energies $E_i$. Carriers can generate current by acquiring energy thermally and hopping to another site with energy gap $\Delta E_{ij}$ (Figure 12.11)

$$\Delta E_{ij} = E_j - E_i.$$  

(12.26)

Hopping to the nearest-neighbor site is not always the most favorable process, since there
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**Figure 12.11:** Schematic energy diagram of energy states according to the variable-range hopping model. Short horizontal lines show localized states. Red arrows represent electrons. Black arrows show electron hopping from an occupied site to an empty site. Dashed lines represent an energy band of width $\Delta W$ around the Fermi level.

is a larger probability of finding sites at larger distances, $r_{ij}$, that present lower $\Delta E_{ij}$. A countervailing consideration is that it is more difficult to tunnel to sites at larger $r_{ij}$. Optimization of these two processes leads to a fractional $\nu$ as follows.

Consider a system with a constant density of localized states ($\rho$, number of localized states per unit energy per unit volume) near the Fermi level:

$$\rho(E) = \rho(E_F). \quad (12.27)$$

Note that “volume” in general may vary with dimension: in 1D, it is a length; in 2D, in it an area; etc. Suppose a charge hops from an occupied state $i$ ($E_i < E_F$) to an empty state $j$ ($E_j > E_F$) within a small band $\Delta W$:

$$E_j - E_i \leq \Delta W. \quad (12.28)$$
The concentration of states ($\Delta N$, number of states per unit volume) in the bandwidth $\Delta W$ is given by

$$\Delta N = \rho(E_F)\Delta W.$$  \hfill (12.29)

Therefore, the average separation between sites $i$ and $j$ is

$$r_{ij} \approx \Delta N^{-1/D} = [\rho(E_F)\Delta W]^{-1/D},$$  \hfill (12.30)

where $D$ is the dimensionality of the system. The probability of tunneling from site $i$ to $j$ is

$$P_{\text{tunnel}} \propto e^{-2\kappa r_{ij}}.$$  \hfill (12.31)

The probability of acquiring an energy $\Delta W$ thermally is given by the Boltzmann distribution,

$$P_{\Delta W} \propto e^{-\Delta W/k_B T}.$$  \hfill (12.32)

The probability of hopping is then given by the product of these two probabilities, since an electron at site $i$ needs to absorb energy $\Delta W$ and tunnel elastically to site $j$:

$$P_{\text{hop}} = P_{\text{tunnel}}P_{\Delta W} \propto e^{-2\kappa r_{ij}}e^{-\Delta W/k_B T} = \exp \left[ -2\kappa r_{ij} - \frac{1}{k_B T \rho(E_F) r_{ij}^D} \right].$$  \hfill (12.33)

$P_{\text{tunnel}}$ decreases exponentially with $r_{ij}$, and $P_{\Delta W}$ increases with $r_{ij}$. Maximizing $P_{\text{hop}}(r_{ij})$ gives rise to an optimum hopping distance, $r_{\text{hop}}$,

$$\frac{dP_{\text{hop}}(r_{ij})}{dr_{ij}} = 0 \Rightarrow r_{\text{hop}} = \left( \frac{D}{2\kappa \rho k_B T} \right)^\nu,$$  \hfill (12.34)

where

$$\nu = \frac{1}{D + 1}.$$  \hfill (12.35)

The conductivity given by the optimized hopping probability then has a temperature dependence of the form given by

$$g \propto \exp \left[ - \left( \frac{T_0}{T} \right)\nu \right],$$  \hfill (12.36)
where
\[ T_0 = \frac{k_D}{k_B \rho(E_F)}. \] (12.37)

Equation 12.34 shows that \( r_{\text{hop}} \) varies with temperature and decreases as \( T^{-\nu} \). In nearest-neighbor hopping, the hopping length, given by the distance between nearest neighbors, does not vary with temperature, and conductivity exhibits Arrhenius behavior.

In a system where Coulomb interactions are important, Efros and Shklovskii (ES) [48, 49] showed that a \( \nu = 1/2 \) behavior arises. They argued that, in the presence of Coulomb interactions, \( \Delta W \) has the following relationship with \( r_{ij} \):
\[ \Delta W \propto \frac{e^2}{4\pi\epsilon r_{ij}}. \] (12.38)

By substituting equation 12.38 in the expression for \( P_{\text{hop}} \) (equation 12.33) and following the derivation for Mott-VRH, one obtains
\[ g \propto \exp \left[ - \left( \frac{T_{0}^{E^S}}{T} \right)^{\frac{1}{2}} \right], \] (12.39)
where
\[ T_{0}^{E^S} = \beta \frac{e^2 \kappa}{4\pi \epsilon k_B}, \] (12.40)
and \( \beta \) is a numerical coefficient in the order of 1 [49]. The optimum hopping distance, \( r_{\text{hop}} \), and hopping energy gap, \( \Delta W_{\text{hop}} \), in the ES-VRH model are given by
\[ r_{\text{hop}} = \frac{1}{4\kappa} \left( \frac{T_{0}^{E^S}}{T} \right)^{\frac{1}{2}}, \] (12.41)
\[ \Delta W_{\text{hop}} = \frac{k_B}{2} \left( \frac{T_{0}^{E^S}}{T} \right)^{\frac{1}{2}}. \] (12.42)

\( T_{0}^{E^S} \) can be obtained from fitting the ES-VRH model to experimental data. Other parameters such as \( \kappa, r_{\text{hop}}, \) and \( \Delta W_{\text{hop}} \) can then be calculated from \( T_{0}^{E^S} \).

Table 12.1 lists \( r_{\text{hop}} \) at 2 and 100 K obtained from fitting the ES-VRH model to the data. \( r_{\text{hop}} \) is calculated using equations 12.40 and 12.41,
\[ r_{\text{hop}} = \frac{\beta e^2}{16\pi \epsilon \epsilon_0 k_B \sqrt{T_{0}^{E^S} T}}, \] (12.43)
and taking $\beta = 1$ and $\epsilon_r = 2.6$. As temperature increases, $r_{\text{hop}}$ decreases and at $\sim 100$ K, $r_{\text{hop}}$ becomes comparable to the size of the NPs. Therefore, around $\sim 100$ K, a cross-over from variable-range hopping to nearest-neighbor hopping occurs and films start to exhibit Arrhenius behavior as observed. Calculated values of $\Delta W_{\text{hop}}$ at 100 K are also in good agreement with the activation energies obtained from the Arrhenius fits to the data at high temperatures.

Although the ES-VRH model predicts the observed trend in temperature dependence of conductance, it often yields parameters that are physically unreasonable. Several experimental studies on NP films have reported hopping distances and localization lengths ($\xi \equiv 1/\kappa$) that are as large as hundreds of nanometers, too large to be consistent with tunneling required by hopping [23, 50, 51, 52, 53, 54]. Table 12.1 also shows that $r_{\text{hop}}$ at 2 K are much larger than typical tunneling distances which are expected to be in the order of 1 nm. Note that $r_{\text{hop}}$ is even larger at lower temperatures. Therefore, modifications to the existing model are necessary. Our group has developed a “quasi-localized hopping” model to describe the $T^{-1/2}$ behavior in butanedithiol-linked Au NP films near the MIT [23]. A number of studies have also considered a cotunneling process (see Section 8.3.1) to account for long-range hopping through multiple NPs [52, 55, 56, 57]. These mechanisms have yet to be explored experimentally.

### 12.6 Applications of Nanoparticle Films near Metal–Insulator Transition

Observation of MIT in ML-NP films as a function of linker length or film thickness suggests a remarkable possibility of preparing materials with properties interpolating between metals and insulators. Metals exhibit no energy gap ($E_g$) between valence and conduction bands, while insulators exhibit $E_g$ that are very large compared to $k_B T$. Conventionally, materials with intermediate values of $E_g$ (i.e. $E_g \sim k_B T$) are viewed as
semiconductors and have found important electronic applications, notably in field-effect transistors (FETs). For semiconductors, charge carriers can be generated by thermal excitation across the energy gap; however, the density of charge carriers is usually not so high as to cause complete screening of electric field inside the material. This property enables control over the flow of charge carriers via application of an electric (gate) field in an FET configuration. Conductance can be switched between a maximum (“ON”) and a minimum (“OFF”) value as the electric field is varied.

From this perspective, ML-NP films with $E_g \sim k_B T$, too, can be viewed as semiconductors and can be exploited as functional elements of FETs. $E_g$ for ML-NP films can be controlled through Mott-Hubbard MIT in bulk films or through percolation-driven MIT in strongly coupled NP films. In the former, $E_g$ depends on inter-NP coupling according to equation 12.7, and in the latter, $E_g$ depends on the size of superclusters of strongly coupled NPs. In this section, two applications of “semiconducting” ML-NP films, namely conductance switching and information storage, are briefly described.

Figure 12.12 shows conductance vs bias ($V_b$) and gate ($V_g$) voltages for a butanedithiol-linked 5 nm Au NP film prepared with four deposition cycles. Note that the NP films comprising butanedithiol exhibit an MIT as a function of number of deposition cycles (see Figure 10.3). Here, the number of deposition cycles is chosen such that films are below the percolation threshold and are nonmetallic. The films are prepared on Si/SiO$_2$ substrates. Two electrodes, source and drain, are attached to the films using indium soldering, and the silicon substrate is used as a gate electrode. The drain electrode is electrically grounded, and voltages are applied to the source and gate electrodes.

At $V_g = 0$, clear conductance suppression is observed with a dip at zero bias (Figure 12.12b). This is due to single-electron charging of an array of superclusters of ML-NPs in the film. A gate effect results in an approximately linear shift of the conductance dip away from zero bias. For example, at $V_g = +1$ and -1 V, the conductance dip shifts to $V_b = +1$ and -1 V, respectively (Figure 12.12c,d). The variation of the conductance dip with
Figure 12.12: (a) Differential conductance map as a function of bias and gate voltages at 77 K. The map is obtained using a four-layer films of butanedithiol-linked Au NPs. (b-d) Differential conductance vs bias voltage at various gate voltages: (b) $V_g = 0$ V, (c) $V_g = +1$ V, and (d) $V_g = -1$ V. Reprinted with permission from Reference [58]. Copyright 2005 Institute of Physics.
12. Metal–Insulator Transition

Figure 12.13: Conductance maps of a four-layer film of butanedithiol-linked Au NPs as a function of $V_b$ and $V_g$. The maps are obtained at 77 K after applying various $V_g$ to the film during cooling: (a) $V_g = -5$ V, (b) $V_g = 0$, and (c) $V_g = +5$ V. Reprinted with permission from Reference [58]. Copyright 2005 Institute of Physics.

$V_g$ suggests that the gate voltage shifts the charging energy of the superclusters, in turn shifting CB threshold voltages [24]. At $V_b = 0$, conductance increases with increasing $|V_g|$. This effect forms the principle of conductance switching in FETs.

Another important application of semiconductors and FETs is information storage. The ML-NP films can also be used for this purpose. Information can be “recorded” by applying $V_g$ while the film is slowly cooled. Below a threshold temperature ($\sim 175$ K), the CB gap remains shifted even after $V_g$ is turned off. That is, the value of $V_g$ is effectively recorded. The recorded value of $V_g$ can be “read” through the shift in CB gap. Figure 12.13 shows maps of differential conductance vs $V_b$ and $V_g$ obtained at 77 K, demonstrating stored $V_g$ of -5, 0, or +5 V applied during cooling. Upon warming the film, the CB gap becomes weaker and eventually at $\sim 175$ K vanishes. Therefore, the stored information can be “erased”. Since $V_g$ can be varied continuously, the NP films
can be used as analog memory storage devices.

The ability to store values of $V_g$ in the conductance maps can be attributed to redistribution of background charges in the ML-NP film. Above the threshold temperature, mobile background charges can redistribute in order to cancel gate-induced electric fields. As the temperature is lowered, eventually these charges can become trapped or “frozen”, creating a charge glass that generates gating fields even after $V_g$ is removed. There are several possible places where charges may be trapped, including on NPs, linker molecules, SiO$_2$ substrate and/or interfaces [58]. The electric field induced by trapped charges then can be measured at 77 K via CB charge sensing inherent in the ML-NP film.

### 12.7 Conclusion

The self-assembled ML-NP films exhibit bulk properties that are controllable from the bottom up. Au NPs represent the conductive component of the assemblies, and their size-tuneable properties can be controlled by chemical synthetic methods. Molecules can control inter-NP separations and influence the rate of charge transfer between NPs. Furthermore, molecules can confer functionalities (such as electro-chemical or biorecognition) in the assemblies. Properties of the films can be further controlled via assembly procedure. Film thickness and film order/disorder are controllable.

The controlled functionality afforded by self-assembled NP–molecule systems has enabled a host of new opportunities, both fundamental and applied. These systems have enabled systematic studies of electronic phenomena ranging from single-electron charging to MITs. In terms of applications, there has been particular interest in exploiting functionality of the NP–molecule systems for electronic, chemical, and biological sensing. Given this functionality and in view of the desirable features of electronics (such as low cost, scalability, integrability, etc.), this area will likely continue to represent a significant target of opportunity for future studies.
Bibliography


energies and percolation effects in molecularly linked nanoparticle films,” J. Chem.

in molecularly linked Au nanoparticle arrays near the metal–insulator transition,”

11.3, 12.6

“Self-assembly of gold nanoclusters on micro- and nanoelectronic substrates,” J.

p. 1, 1982. 12.2


[29] W. Wang, T. Lee, and M. A. Reed, “Elastic and inelastic electron tunneling in

H. Weller, and G. Redmond, “Manipulating the charging energy of nanocrystal

[31] A. J. Quinn and G. Redmond, “Artificial atom solids based on metal nanocrystals:
12.4, 12.3


Part V

Appendices
Tunneling through a 1D Potential Barrier

According to quantum mechanics, an electron can tunnel through a potential energy barrier whose height, $V_0$, is greater than the electron’s energy, $E$. Consider, for example, the energy diagram for a 1D potential barrier shown in Figure A.1, where the potential energy is equal to $V_0$ between $x = 0$ and $x = L$ and zero everywhere else. Schrodinger’s equation for such a system is

$$
\begin{align*}
-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V_0\psi(x) &= E\psi(x) & 0 \leq x \leq L, \\
-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} &= E\psi(x) & \text{otherwise.}
\end{align*}
$$

Here $m$ is the mass of electron and $\hbar$ is the reduced Planck’s constant. By solving equation A.1, one finds electronic wave functions, $\psi$, in regions I, II, and III:

$$
\begin{align*}
\psi_I(x) &= Ae^{i\alpha x} + Be^{-i\alpha x}, \\
\psi_{II}(x) &= Ce^{\kappa x} + De^{-\kappa x}, \\
\psi_{III}(x) &= Fe^{i\alpha x},
\end{align*}
$$

where

$$
\begin{align*}
\alpha &= \frac{\sqrt{2mE}}{\hbar}, \\
\kappa &= \frac{\sqrt{2m(V_0 - E)}}{\hbar},
\end{align*}
$$

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A. Tunneling through a 1D Potential Barrier

Figure A.1: Energy diagram of a 1D square potential barrier.

and $A$, $B$, $C$, $D$, and $F$ are constants. In the above equations, the terms $Ae^{i\alpha x}$, $Be^{-i\alpha x}$, and $Fe^{i\alpha x}$ represent incident, reflected, and transmitted parts of the wave function, and note that $Ce^{\kappa x}$ and $De^{-\kappa x}$ correspond to growing and decaying exponential components of the wave function inside the barrier, respectively.

To find the constants $B$, $C$, and $D$ relative to $A$, one can apply the following boundary conditions:

\[
\psi_1(0) = \psi_{II}(0), \quad (A.7)
\]
\[
\psi_{II}(L) = \psi_{III}(L), \quad (A.8)
\]
\[
\left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_{II}}{dx}\right|_{x=0}, \quad (A.9)
\]
\[
\left.\frac{d\psi_{II}}{dx}\right|_{x=L} = \left.\frac{d\psi_{III}}{dx}\right|_{x=L}. \quad (A.10)
\]

Resulting equations are as follows:

\[
A + B = C + D, \quad (A.11)
\]
\[
i\alpha A - i\alpha B = \kappa C - \kappa D, \quad (A.12)
\]
\[
Ce^{\kappa L} + De^{-\kappa L} = Fe^{i\alpha L}, \quad (A.13)
\]
\[
\kappa Ce^{\kappa L} - \kappa De^{-\kappa L} = i\alpha Fe^{i\alpha L}. \quad (A.14)
\]
The transmission probability through the barrier, $|T|^2$, is then calculated by

$$
|T|^2 = \left| \frac{F}{A} \right|^2 = \left| \frac{4i\alpha\kappa e^{-i\alpha L}}{(i\alpha + \kappa)^2 e^{-\kappa L} - (i\alpha - \kappa)^2 e^{\kappa L}} \right|^2. \quad (A.15)
$$

The expression for $|T|^2$ can be simplified using a thick-barrier approximation, in which

$$
\kappa L \gg 1. \quad (A.16)
$$

The result is

$$
|T|^2 = \left| \frac{4i\alpha\kappa e^{-i\alpha L}}{(i\alpha - \kappa)^2 e^{\kappa L}} \right|^2 = \frac{16\alpha^2\kappa^2}{(\alpha^2 + \kappa^2)^2} e^{-2\kappa L}
\quad (A.17)
$$

The pre-exponential factor is typically in the order of $\sim 1$, and therefore, the exponential factor is the most significant:

$$
|T|^2 \approx e^{-2\kappa L}. \quad (A.18)
$$

The transmission probability decays exponentially with the barrier width, and the decay constant, $\kappa$, depends on the barrier height as described by equation A.6.

In the thick-barrier approximation, the growing exponential term in the expression of $\psi_\Pi$ (equation A.3) can be neglected since, from the boundary conditions (equations A.9 and A.10), one can obtain

$$
\left| \frac{C}{D} \right|^2 = e^{-4\kappa L}. \quad (A.19)
$$

In the limit of $\kappa L \gg 1$, the probability of the growing exponential term, $|C|^2$, becomes much smaller than that of the decaying exponential term, $|D|^2$. Therefore, the wave function in the barrier region decays exponentially with distance:

$$
\psi_\Pi(x) \approx e^{-\kappa x}. \quad (A.20)
$$

with a decay constant equal to $\kappa$.

The above equations can be extended to describe a barrier potential with a slowly varying arbitrary shape using the WKB approximation. For a barrier with the potential
A. Tunneling through a 1D Potential Barrier

**Figure A.2:** Arbitrary potential barrier approximated by a series of square barriers with widths of $\Delta x$.

profile of $V(x)$, the tunneling transmission can be approximated by

\[ |T|^2 \approx \exp \left( -\frac{2}{\hbar} \int_0^L \sqrt{2m(V(x) - E)} \, dx \right). \tag{A.21} \]

Equation A.21 can be rationalized as follows. The potential barrier can be considered as a series of square barriers with widths of $\Delta x$ where the $i$th square barrier has a height of $V_i$ (Figure A.2). The probability of transmission through the barrier $V(x)$ then can be written as a product of the probabilities of tunneling through the square barriers:

\[ |T|^2 \approx \prod_i \exp \left( -\frac{2}{\hbar} \sqrt{2m(V_i - E)} \Delta x \right) = \exp \left( -\sum_i \frac{2}{\hbar} \sqrt{2m(V_i - E)} \Delta x \right). \tag{A.22} \]

Substituting the sum in the above equation by an integral in the limit of $\Delta x \to 0$, one gets the WKB approximation. In the average barrier height approximation, equation A.21 is simplified by replacing the potential barrier $V(x)$ with a constant average potential $\overline{V}$:

\[ |T|^2 \approx \exp \left( -\frac{2}{\hbar} \sqrt{2m(\overline{V} - E)} L \right) = e^{-2\kappa L}, \tag{A.23} \]

where

\[ \kappa = \frac{\sqrt{2m(\overline{V} - E)}}{\hbar}. \tag{A.24} \]
Tunneling Current at Intermediate Bias

Here, an expression for tunneling current is derived by taking into account the voltage dependence of the barrier height. It is assumed that $eV_b \ll \phi$, so that electron transport is dominated by tunneling. The tunneling transmission according to the WKB approximation (equation A.21) is then given by

$$\ln |T|^2 \approx -\frac{2}{\hbar} \int_0^L \sqrt{2m \left( \phi + E_F - E - \frac{eV_b x}{L} \right)} \, dx$$

$$= -\frac{2\sqrt{2m\phi}}{\hbar} \int_0^L \left( 1 + \frac{E_F - E}{\phi} - \frac{eV_b x}{\phi L} \right)^{1/2} \, dx$$

$$\approx -\frac{2\sqrt{2m\phi}}{\hbar} \int_0^L \left( 1 + \frac{E_F - E}{2\phi} - \frac{eV_b x}{2\phi L} \right) \, dx$$

$$= -\frac{2\sqrt{2m\phi}}{\hbar} \left( 1 + \frac{E_F - E}{2\phi} - \frac{eV_b}{4\phi} \right) L$$

$$= -2\kappa_0 L + \frac{E_F - E}{\xi} + \frac{eV_b}{2\xi}, \quad (B.1)$$

where

$$\kappa_0 = \frac{\sqrt{2m\phi}}{\hbar}, \quad (B.2)$$

$$\xi = \frac{\phi}{\kappa_0 L}. \quad (B.3)$$

Substituting equation B.1 into the expression for tunneling current (equation 5.15),
B. Tunneling Current at Intermediate Bias

one finds

\[ I \approx \frac{4\pi e}{h} \rho(E_F)^2 e^{-2\kappa_0 L} e^{eV_b/2k} \int_0^{+\infty} e^{(E-E_F)/\xi} \left[ \frac{1}{1 + e^{(E-E_F)/k_B T}} - \frac{1}{1 + e^{(E-E_F+eV_b)/k_B T}} \right] dE. \]  

(B.4)

By introducing an integration variable \( y \),

\[ y \equiv e^{(E-E_F)/k_B T}, \]  

(B.5)

and taking \( \exp(-E_F/k_B T) \approx 0 \) in the lower limit of the integral after exchanging variables, one gets

\[ I \approx \frac{4\pi e}{h} \rho(E_F)^2 e^{-2\kappa_0 L} e^{eV_b/2k} \int_0^{+\infty} y^{k_B T/\xi} \left[ \frac{1}{1 + y} - \frac{1}{1 + y e^{eV_b/k_B T}} \right] \frac{k_B T}{y} dy. \]  

(B.6)

The above integral can be solved analytically using the following relationship:

\[ \int_0^{+\infty} \frac{y^{a-1}}{1 + by} dy = \frac{\pi b^{-a}}{\sin(\pi a)}. \]  

(B.7)

Thus,

\[ I \approx \frac{4\pi e}{h} \rho(E_F)^2 e^{-2\kappa_0 L} e^{eV_b/2k} \frac{\pi k_B T}{\sin(\pi k_B T/\xi)} \left[ 1 - e^{-eV_b/\xi} \right] \]  

\[ = \frac{8\pi e \xi}{h} \rho(E_F)^2 e^{-2\kappa_0 L} \frac{\pi k_B T}{\sin(\pi k_B T/\xi)} \sinh \left( \frac{eV_b}{2\xi} \right). \]  

(B.8)

\( \pi k_B T/\xi \) is typically a small quantity. Its value for Au (\( \phi \approx 5.1 \text{ eV} \)) at room temperature is \( \sim 0.18 \). Therefore,

\[ \frac{\pi k_B T/\xi}{\sin(\pi k_B T/\xi)} \approx 1. \]  

(B.9)

The tunneling current then can be written as

\[ I \approx \frac{8\pi e \xi}{h} \rho(E_F)^2 e^{-2\kappa_0 L} \sinh \left( \frac{eV_b}{2\xi} \right). \]  

(B.10)
Appendix C

Tunneling in Presence of a Small Barrier

Equation 5.21 for tunneling current is derived assuming that the barrier height is much larger than the applied electrical potential, $eV_b$, and thermal fluctuations, $k_B T$. In the large-barrier limit, tunneling current and conductance weakly depend on temperature. For small barriers, however, other mechanisms such as field emission and thermionic emission can become important. As a result, current and conductance may vary significantly with voltage and temperature. This appendix presents results of $I - V_b$ and $dI/dV - V_b$ simulations for a junction with a small barrier at a temperature range of 10–150 K.

Let's start with a general expression for the tunneling current as is given by equation 5.15:

$$I \propto \int_{0}^{+\infty} |T(E)|^2 [f(E) - f(E + eV_b)] dE.$$  \hspace{1cm} (C.1)

The expression for transmission, $|T(E)|^2$, depends on the transport mechanism. Figure C.1 shows three possible mechanisms. For $E < E_F + \phi - eV_b$, electrons have to tunnel through a trapezoidal barrier with a barrier height given by

$$U(x) = \phi + E_F - E - \frac{eV_b x}{L}.$$  \hspace{1cm} (C.2)
C. Tunneling in Presence of a Small Barrier

Figure C.1: Schematic energy diagram for a tunnel junction with a small barrier.
C. Tunneling in Presence of a Small Barrier

Tunneling transmission, $|T(E)|_{\text{tun}}^2$, is then expressed by

$$|T(E)|_{\text{tun}}^2 \approx \exp \left[ -\frac{2}{\hbar} \int_0^L \sqrt{2mU(x)} dx \right]$$

$$= \exp \left[ -\frac{2}{\hbar} \int_0^L \sqrt{2m \left( \phi + E_F - E - \frac{eV_b x}{L} \right)} dx \right]$$

$$= \exp \left[ -\frac{4L\sqrt{2m} (\phi + E_F - E)^{3/2}}{3\hbar} \right]$$

Note that both barrier width and barrier height decrease linearly as $E$ increases, and at $E = E_F + \phi$, the barrier vanishes. In this energy range, electrons tunnel only through a portion of the distance between electrodes and travel through the rest classically. This process is known as “field emission” and occurs when $eV_b$ becomes comparable to $\phi$.

Field-emission transmission, $|T(E)|_{\text{FE}}^2$ is given by

$$|T(E)|_{\text{FE}}^2 \approx \exp \left[ -\frac{4L\sqrt{2m} (\phi + E_F - E)^{3/2}}{3\hbar} \right]$$

For $E > E_F + \phi$, energies of electrons are higher than the potential energy of the barrier, hence, electrons can travel classically between the electrodes. This situation only occurs when electrons gain sufficient thermal energy to be able to overcome the barrier.

This process is, therefore, known as “thermionic emission”. For thermionic emission,

$$|T(E)|_{\text{TE}}^2 \approx 1.$$
C. Tunneling in Presence of a Small Barrier

Figure C.2: \(dI/dV\) vs \(V_b\) at various temperatures calculated for a tunnel junction with a barrier height, \(\phi\), of 20 meV. Data are normalized to the minimum value of \(dI/dV\). \(T = 10\)–\(150\) K in increments of 10 K. Red solid lines are quadratic fits to the data. Blue solid lines represent \(dI/dV\) vs \(V_b\) for a junction with \(\phi = 1\) eV at the same temperature range as above.

The final expression for current then can be written as

\[
I \propto \int_{0}^{E_F+\phi-eV_b} |T(E)|_{\text{tun}}^2 \left[ f(E) - f(E + eV_b) \right] dE \\
+ \int_{E_F+\phi-eV_b}^{E_F+\phi} |T(E)|_{\text{FE}}^2 \left[ f(E) - f(E + eV_b) \right] dE \\
+ \int_{E_F+\phi}^{+\infty} \left[ f(E) - f(E + eV_b) \right] dE. \tag{C.7}
\]

Using equations C.3, C.5, and C.7, one can numerically obtain \(I - V_b\) data for a junction with a small barrier. \(dI/dV\) can then be obtained by numerically differentiating the \(I - V_b\) data. The source code used for simulating data is presented in Appendix E.1.

Figure C.2 shows \(dI/dV\) vs \(V_b\) calculated for a tunnel junction with \(\phi = 20\) meV. For comparison, data for a junction with \(\phi = 1\) eV are also shown. For the small-barrier junction, \(dI/dV\) varies strongly with both voltage and temperature. At low temperatures,
C. Tunneling in Presence of a Small Barrier

\[ \frac{dI}{dV} \approx g_0(1 + \alpha V_b^2), \]  
(C.8)

where \( g_0 \) is the zero-bias conductance and \( \alpha \) is a coefficient. Red solid lines in Figure C.2 represent quadratic fits to the data. Variations of \( g_0 \) and \( \alpha \) with temperature and barrier height are shown in Figure C.3.

Figure C.3a shows that \( g_0 \) for the small-barrier junction increases as temperature increases, whereas \( g_0 \) for the large-barrier junction remains constant. For the small-
C. Tunneling in Presence of a Small Barrier

Barrier junction, \( g_0 \) can be thought of as the sum of two components: a temperature-independent tunneling component, \( g_{\text{tun}} \), and a thermally activated component, \( g_{\text{th}}(T) \):

\[
 g_0 = g_{\text{tun}} + g_{\text{th}}(T) = g_{\text{tun}} \left( 1 + Ae^{-B/T} \right). \tag{C.9}
\]

Figure C.3b shows that \( g_{\text{th}} \) follows an Arrhenius trend with an activation energy of 10 meV. Figure C.3c shows that \( \ln(g_{\text{tun}}) \) is a linear function of \( \sqrt{\varphi} \). This dependence is consistent with the tunneling mechanism of conduction (see Section 5.1 and equation 5.20):

\[
 g_{\text{tun}} \propto e^{-2\kappa L} = \exp \left( -2\sqrt{2m\varphi L} \right). \tag{C.10}
\]

The observed temperature dependence of \( g_0 \), therefore, can be explained as follows. At low temperatures, electrons can only tunnel through the barrier and conductance depends weakly on temperature. As temperature increases, electrons can thermally overcome the small barrier, and conductance increases due to the over-barrier thermionic emission.

Figure C.3d shows that \( \alpha \) for the small-barrier junction initially increases with temperature to a maximum value, \( \alpha_{\text{max}} \), and then drops as temperature increases further. For the large-barrier junction, however, \( \alpha \) is close to zero and is independent of temperature. Figure C.3e shows that \( \alpha_{\text{max}} \) depends on barrier height and decreases as barrier height increases, as expected. Note that the voltage dependence of conductance arises from barrier height suppression induced by the applied bias voltage. This effect becomes more pronounced as the barrier becomes smaller.

The initial growth of \( \alpha \) with temperature can be understood given that as temperature increases the contribution of field emission to conduction increases as well. In the field emission region, bias reduces both the height and the width of the barrier giving rise to a stronger dependence of conductance on voltage. However, at sufficiently high temperatures, thermionic emission dominates and \( \alpha \) starts to decrease. Figure C.3f shows that
C. Tunneling in Presence of a Small Barrier

\( T_{\text{max}} \), i.e. the temperature at which \( \alpha \) is maximum, is linearly proportional to the barrier height. This supports the idea that the drop in \( \alpha \) arises from over-barrier thermionic emission.
Some Useful Integrations

The integral in equation 5.16 can be solved analytically. By introducing an integration variable $y \equiv \exp[(E - E_F)/k_B T]$, taking $\exp(-E_F/k_B T) \approx 0$ in the lower limit of the integral after exchanging variables, and defining $a \equiv \exp(eV_b/k_B T)$ for simplification, one gets

$$\int_0^{+\infty} [f(E) - f(E + eV_b)]dE$$

\[= \int_0^{+\infty} \left[ \frac{1}{1 + e^{(E-E_F)/k_B T}} - \frac{1}{1 + e^{(E+eV_b-E_F)/k_B T}} \right] dE \]

\[= k_B T \int_0^{+\infty} \left[ \frac{1}{y(1 + y)} - \frac{1}{y(1 + ay)} \right] dy \]

\[= k_B T \left[ \ln \frac{1 + ay}{1 + y} \right]_0^{+\infty} \]

\[= k_B T [\ln(a) - 0] \]

\[= eV_b. \quad (D.1)\]
The integral in equation 6.2 can be solved similarly. In the following equations, variable $b$ is introduced for simplification: $b \equiv \exp(-\Delta E_j^\pm / k_B T)$.

$$\int_0^{+\infty} f(E) [1 - f(E - \Delta E_j^\pm)] dE$$

$$= \int_0^{+\infty} \frac{1}{1 + e^{(E-E_F)/k_B T}} \left[ 1 - \frac{1}{1 + \exp[(E - \Delta E_j^\pm - E_F)/k_B T]} \right] dE$$

$$= k_B T \int_0^{+\infty} \frac{1}{1 + y} \left[ 1 - \frac{1}{1 + by} \right] \frac{dy}{y}$$

$$= k_B T b \int_0^{+\infty} \frac{dy}{(1 + y)(1 + by)}$$

$$= k_B T b \left[ \frac{b}{b - 1} \int_0^{+\infty} \left[ \frac{b}{1 + by} - \frac{1}{1 + y} \right] dy \right]$$

$$= \frac{k_B T}{1 - 1/b} \left[ \ln(1 + by) - \ln(1 + y) \right]_0^{+\infty}$$

$$= \frac{k_B T}{1 - 1/b} [\ln(b) - 0]$$

$$= \frac{-\Delta E_j^\pm}{1 - \exp(\Delta E_j^\pm / k_B T)}. \quad \text{(D.2)}$$
IDL Codes

The following codes are written in Research Systems, Inc. (RSI) Interactive Data Language (IDL) version 6.2 programming environment.

E.1 Tunneling in Presence of a Small Barrier

The following program calculates $I - V$ and $dI/dV - V$ data for a tunnel junction at various temperatures. Input variables are barrier height, $\phi$, barrier width, $L$, Fermi energy, $E_F$, voltage array, $V_{1D}$, and temperature array, $T_{1D}$.

```
FUNCTION FD, eps ;The Fermi-Dirac distribution function
    COMMON constants, e, k, hbar, m
    COMMON variables, phi, L, T, V, EF
    result = DOUBLE(1/(1+EXP(eps*e/k/T)))
    RETURN, result
END

FUNCTION T_tun, eps ;Transmission function for tunneling
    COMMON constants, e, k, hbar, m
    COMMON variables, phi, L, T, V
```
A = DOUBLE(4.*L*SQRT(2.*m*e)/3./hbar)
B = DOUBLE((phi-eps)^1.5/V)
C = DOUBLE((phi-eps-V)^1.5/V)
result = DOUBLE(EXP(-A * (B - C)))
RETURN, result

FUNCTION T_FE, eps ;Transmission function for field emission
    COMMON constants, e, k, hbar, m
    COMMON variables, phi, L, T, V
    A = DOUBLE(4.*L*SQRT(2.*m*e)/3./hbar)
    B = DOUBLE((phi-eps)^1.5/V)
    result = DOUBLE(EXP(-A * B))
    RETURN, result
END

FUNCTION T_TE, eps ;Transmission function for thermionic emission.
    result = MAKE_ARRAY(N_ELEMENTS(eps), VALUE=1.0, /DOUBLE)
    RETURN, result
END

;---------------------------Main Program---------------------------

PRO tunneling

;Constants
COMMON constants, e, k, hbar, m
E. IDL Codes

\[ e = \text{DOUBLE}(1.6\times10^{-19}) \text{ \; \text{Electron charge \quad [C]} \]
\[ k = \text{DOUBLE}(1.38\times10^{-23}) \text{ \; \text{Boltzmann's constant \quad [J/K]} \]
\[ \hbar = \text{DOUBLE}(1.05\times10^{-34}) \text{ \; \text{Planck's constant \quad [Js]} \]
\[ m = \text{DOUBLE}(9.11\times10^{-31}) \text{ \; \text{Electron mass \quad [kg]} \]

; Variables

\text{COMMON variables, \text{phi}, \text{L}, \text{T}, \text{V}}
\[
    \phi = \text{DOUBLE}(0.020) \text{ \; \text{Barrier height \quad [eV]} \]
\[
    L = \text{DOUBLE}(0.1\times10^{-9}) \text{ \; \text{Barrier width \quad [m]} \]
\[
    E_F = \text{DOUBLE}(4.5) \text{ \; \text{Fermi energy \quad [eV]} \]

; Generate arrays for voltage, temperature, current, and conductance.

\[
    V_{\text{max}} = \text{DOUBLE}(0.05) \text{ \; \text{Maximum voltage \quad [V]} \]
\[
    V_{\text{min}} = -V_{\text{max}} \text{ \; \text{Minimum voltage \quad [V]} \]
\[
    V_{\text{step}} = \text{DOUBLE}(0.001) \text{ \; \text{Voltage step \quad [V]} \]
\[
    V_{\text{num}} = \text{ROUND}((V_{\text{max}}-V_{\text{min}})/V_{\text{step}}+1) \text{ \; \text{Number of elements in the voltage array}} \]
\[
    V_{1\text{D}} = \text{FINDGEN}(V_{\text{num}})/(V_{\text{num}}-1)*(V_{\text{max}}-V_{\text{min}})+V_{\text{min}} \text{ \; \text{Voltage array}} \]
\[
    \text{zero} = V_{\text{num}}/2 \text{ \; \text{Index of the zero voltage element}} \]
\[
    T_{\text{max}} = 200.0 \text{ \; \text{Maximum temperature \quad [K]} \]
\[
    T_{\text{min}} = 10.0 \text{ \; \text{Minimum temperature \quad [K]} \]
\[
    T_{\text{num}} = 20 \text{ \; \text{Number of elements in the temperature array}} \]
\[
    T_{1\text{D}} = \text{FINDGEN}(T_{\text{num}})/(T_{\text{num}}-1)*(T_{\text{max}}-T_{\text{min}})+T_{\text{min}} \text{ \; \text{Temperature array}} \]
\[
    I = \text{MAKE_ARRAY}(V_{\text{num}},T_{\text{num}}) \text{ \; \text{Current array}} \]
\[
    dI_dV = \text{MAKE_ARRAY}(V_{\text{num}},T_{\text{num}}) \text{ \; \text{Conductance array}} \]

\text{FOR \text{jj} = 0, T_{\text{num}}-1 \text{ \ DO BEGIN} \text{ \ \ ;Temperature loop} \]
E. IDL Codes

\[
T = T1D[jj] \\
I[zero, jj] = 0.0 \\
\]

\[
\text{FOR } j = \text{zero+1, Vnum-1 DO BEGIN} \quad ; \text{Positive voltage loop} \\
V = \text{DOUBLE}(V1D[j]) \\
\]

; Find the lower and upper limits of the integral for current
; by finding the energy range in which \( \text{FD(eps)} - \text{FD(eps+V)} \geq 1e-6 \).
\[
\text{eps} = \text{DOUBLE(FINDGEN(4001)/4000.0*2.0*EF - EF}) \quad ; \text{Energy array} \\
f = \text{DOUBLE(\text{FD(eps)} - \text{FD(eps+V)})} \\
\text{Erange} = \text{eps}[\text{WHERE(ABS(f) GE 1e-6)}] \\
\text{Emin} = \text{MIN(Erange)} \quad ; \text{Lower limit of integral} \\
\text{Emax} = \text{MAX(Erange)} \quad ; \text{Upper limit of integral} \\
\]

; Generate an energy array for tunneling.
\[
\text{E1} = \text{Emin} \\
\text{E2} = \phi - V \\
\text{Enum} = \text{MAX}([400, (\text{E2-E1})/0.0001]) \\
\text{eps_tun} = \text{FINDGEN(Enum)}/(\text{Enum}-1)*(\text{E2-E1})+\text{E1} \\
\]

; Generate an energy array for field emission.
\[
\text{E1} = \phi - V \\
\text{E2} = \phi \\
\text{Enum} = \text{MAX}([400, (\text{E2-E1})/0.0001]) \\
\text{eps_FE} = \text{FINDGEN(Enum)}/(\text{Enum}-1)*(\text{E2-E1})+\text{E1} \\
\]

; Check if the upper limit of integral is greater than the
E. IDL Codes

;barrier height. If so, generate an energy array for thermionic emission, otherwise set the energy equal to the barrier height.

IF Emax GT phi THEN BEGIN
   E1 = phi
   E2 = Emax
   Enum = MAX([400,(E2-E1)/0.0001])
   eps_TE = FINDGEN(Enum)/(Enum-1)*(E2-E1)+E1
ENDIF ELSE eps_TE = phi

;Combine energy arrays and transmission arrays.
eps = [eps_tun, eps_FE, eps_TE]
Tr = [T_tun(eps_tun), T_FE(eps_FE), T_TE(eps_TE)]

;Ensure that the energy array has no repeated values.
range = UNIQ(eps)
eps = eps[range]
Tr = Tr[range]

;Ensure that the elements of the transmission array have finite values.
range = WHERE(FINITE(Tr))
eps = eps[range]
Tr = Tr[range]

;Again, find the energy range in which FD(eps)-FD(eps+V) >= 1e-6.
   f = DOUBLE(FD(eps)-FD(eps+V))
   range = WHERE(ABS(f) GE 1e-6)
;Calculate current in the positive voltage range
;using the numerical integration method INT_TABULATED.
I[j,jj] = INT_TABULATED(eps[range], Tr[range] * $ (FD(eps[range])-FD(eps[range]+V)))

ENDFOR ;Positive voltage loop

;Set current in the negative voltage range to the inverse of current
;in the positive voltage range.
I[0:zero-1,jj] = REVERSE(-I[zero+1:Vnum-1,jj])

;Calculate conductance.
dIdV[*,jj] = DERIV(V1D,I[*,jj])

ENDFOR ;Temperature loop

END
E.2 Orthodox Model

The following function calculates $I - V$ data for a double tunnel junction according to the Orthodox model. Arguments are junction resistances, $R_1$ and $R_2$, junction capacitances, $C_1$ and $C_2$, residual charge, $Q_0$, temperature, $T$, infinity, $\text{Inf}$, voltage array, $\text{voltage}$, voltage-dependence coefficient, $\text{alfa}$, distribution function for the number of excess charges, $\text{rho}$, and a boolean parameter, $\text{check\_inf}$, for verifying if $\text{Inf}$ is sufficient for the given voltage array. The function returns the calculated current array, $\text{current}$.

FUNCTION orthodox, R1=R1, R2=R2, C1=C1, C2=C2, Q0=Q0, T=T, $\text{Inf}=\text{Inf}$, Voltage=Voltage, alfa=alfa, rho=rho, $\text{check\_inf}=\text{check\_inf}$

;Constants

$e =$ DOUBLE(1.6e-19) ;Electron charge [C]
$h =$ DOUBLE(6.626e-34) ;Planck’s constant [Js]
$k =$ DOUBLE(1.38e-23) ;Boltzmann constant [J/K]
$m =$ DOUBLE(9.11e-31) ;Electron mass [kg]

;Parameters

IF N_ELEMENTS(R1) EQ 0 THEN $
R1 = 1.0e8 ;Resistance of junction 1 [ohm]

IF N_ELEMENTS(R2) EQ 0 THEN $
R2 = 1.0e9 ;Resistance of junction 2 [ohm]

IF N_ELEMENTS(C1) EQ 0 THEN $
C1 = 10.0 ;Capacitance of junction 1 [F/e]

IF N_ELEMENTS(C2) EQ 0 THEN $
C2 = 10.0 ;Capacitance of junction 1 [F/e]
E. IDL Codes

```idl
IF N_ELEMENTS(Q0) EQ 0 THEN $
Q0 = 0.0 ;Residual charge [e]

IF N_ELEMENTS(T) EQ 0 THEN $
T = 4.0 ;Temperature [K]

IF N_ELEMENTS(Inf) EQ 0 THEN $
Inf = 10 ;Infinity

IF N_ELEMENTS(voltage) EQ 0 THEN $
voltage = FINDGEN(1001)*0.001-0.5 ;Voltage array

IF N_ELEMENTS(alfa) EQ 0 THEN $
alfa = 0.0 ;Voltage-dependence coefficient [1/V^2]

IF N_ELEMENTS(check_inf) EQ 0 THEN $
check_inf=0 ;If check_inf = 1 then the program verifies
;if Inf is sufficient.

;Create an array for number of excess electrons from -Inf to Inf.
sizeN = 2*Inf + 1
N1D = FINDGEN(sizeN) - Inf

;Create sizeN by sizeV matrices. Rows represent number of excess
;electrons and columns represent voltage.
sizeV = N_ELEMENTS(voltage)
genN = REPLICATE(1, sizeV)
genV = REPLICATE(1, sizeN)
N = genN##N1D
V = voltage##genV

;Calculate energy change of the system.
```
E. IDL Codes

\[ Ct = C1 + C2 \quad ; \text{Total capacitance} \]

\[ V1 = \frac{C2 \times V}{Ct} \quad ; \text{Voltage across junction 1} \]

\[ V2 = \frac{C1 \times V}{Ct} \quad ; \text{Voltage across junction 2} \]

\[ E1p = \text{DOUBLE} \left( \frac{1.0}{Ct} \left( 0.5 + (N + Q0) \right) - V1 \right) \quad ; \text{charging via junction 1} \]

\[ E1m = \text{DOUBLE} \left( \frac{1.0}{Ct} \left( 0.5 - (N + Q0) \right) + V1 \right) \quad ; \text{discharging via junction 1} \]

\[ E2p = \text{DOUBLE} \left( \frac{1.0}{Ct} \left( 0.5 + (N + Q0) \right) + V2 \right) \quad ; \text{charging via junction 2} \]

\[ E2m = \text{DOUBLE} \left( \frac{1.0}{Ct} \left( 0.5 - (N + Q0) \right) - V2 \right) \quad ; \text{discharging via junction 2} \]

;Calculate electron tunneling rates.

\[ \text{newR1} = \frac{R1}{1 + \alpha1 \times (V1^2)} \]

\[ \text{newR2} = \frac{R2}{1 + \alpha2 \times (V2^2)} \]

\[ R1p = -\text{DOUBLE} \left( \frac{E1p}{\text{newR1}} \left( 1 - \exp \left( \frac{E1p \times e}{k \times T} \right) \right) \right) \quad ; \text{charging via junc.1} \]

\[ R1m = -\text{DOUBLE} \left( \frac{E1m}{\text{newR1}} \left( 1 - \exp \left( \frac{E1m \times e}{k \times T} \right) \right) \right) \quad ; \text{discharging via junc.1} \]

\[ R2p = -\text{DOUBLE} \left( \frac{E2p}{\text{newR2}} \left( 1 - \exp \left( \frac{E2p \times e}{k \times T} \right) \right) \right) \quad ; \text{charging via junc.2} \]

\[ R2m = -\text{DOUBLE} \left( \frac{E2m}{\text{newR2}} \left( 1 - \exp \left( \frac{E2m \times e}{k \times T} \right) \right) \right) \quad ; \text{discharging via junc.2} \]

;Calculate the distribution function.

\[ x = R1p + R2p \quad ; \text{total rate of charging} \]

\[ y = R1m + R2m \quad ; \text{total rate of discharging} \]

\[ t1 = \text{DOUBLE} \left( \text{PRODUCT} (x, 1, /\text{CUMULATIVE}) \right) \]

\[ t2 = \text{SHIFT} (t1, [1, 0]) \quad ; \text{the product of } x \text{ from } -\text{Inf} \text{ to } N-1 \]

\[ t2[0, \ast] = 0.0 \]

\[ t3 = \text{DOUBLE} \left( \text{REVERSE} \left( \text{PRODUCT} \left( \text{REVERSE} (y), 1, /\text{CUMULATIVE} \right) \right) \right) \]

\[ t4 = \text{SHIFT} (t3, [-1, 0]) \quad ; \text{the product of } y \text{ from } N+1 \text{ to } \text{Inf} \]

\[ t4[\text{sizeN-1}, \ast] = 0.0 \]

\[ t5 = \text{TOTAL} (t2 \times t4, 1) \]

\[ t6 = t5 \# \# \text{genV} \]
E.3 Series-Parallel Extension to the Orthodox Model

The following program calculates $I-V$ data according to the series-parallel extension to the Orthodox model. Input parameters are charging energy of the single-electron device, $E_{SED}$, resistance of the single-electron device, $R_{SED}$, activation energy of the molecular junction, $Es$, resistances of the series and parallel junctions, $Rs$ and $Rp$, voltage-dependence coefficient, $alfa_0$, and its temperature dependence $alfa_T$, and voltage division factor, $xi$. To obtain $I-V$ of series junctions, first $I-V$ data for each junction are calculated. Next, for given values of current, corresponding voltages for each junction are interpolated and then added together. To obtain $I-V$ of parallel junctions, $I-V$
of the junctions are first calculated and then, for given values of voltages, currents are added.

**PRO model**

;Constants

\[ k = \text{DOUBLE}(1.38e-23) \; \text{Boltzmann constant [J/K]} \]
\[ e = \text{DOUBLE}(1.60e-19) \; \text{Electron charge [C]} \]
\[ \hbar = \text{DOUBLE}(1.05e-34) \; \text{Planck’s constant [Js]} \]
\[ m = \text{DOUBLE}(9.11e-31) \; \text{Electron mass [kg]} \]

;Parameters

\[ E_{\text{SED}} = 0.0153 \; \text{Charging energy of the device [eV]} \]
\[ R_{\text{SED}} = 1.0 \; \text{Resistance of the device} \]
\[ E_s = 0.0053 \; \text{Activation energy of the molecular junc. [eV]} \]
\[ R_s = 0.1 \times R_{\text{SED}} \; \text{Resistance of the series junction} \]
\[ R_p = 100 \times R_{\text{SED}} \; \text{Resistance of the parallel junction} \]
\[ \alpha_0 = 50000.0 \; \text{Voltage dependence of resistance [1/V^2]} \]
\[ \alpha_T = 0.010 \; \text{Temperature dependence of alfa [1/V^2/K]} \]
\[ \xi = 20.0 \; \text{Voltage division factor for the series junc.} \]
\[ \xi_p = 10.0 \; \text{Voltage division factor for the parallel junc.} \]

;Create voltage and temperature arrays.

\[ V_{\text{step}} = 0.001 \]
\[ V_{\text{max}} = 0.1 \]
\[ V_{\text{min}} = -V_{\text{max}} \]
\[ V_{\text{num}} = \text{ROUND}((V_{\text{max}}-V_{\text{min}})/V_{\text{step}})+1 \]
\[ V1\text{D} = \text{Findgen}(V_{\text{num}}) \times V_{\text{step}} + V_{\text{min}} \; \text{zero} = V_{\text{num}}/2 \; \text{Voltage array} \]
T = [7.0,8,9,10,11,12,14,16,18,20,25,30,35,40,45,50,55,60,65,70,75,$
80,85,90,95,100] ; Temperature array
Tnum = N_ELEMENTS(T)
Vsys = MAKE_ARRAY(2*Vnum,Tnum, VALUE=!VALUES.F_NAN)
Isys = MAKE_ARRAY(2*Vnum,Tnum, VALUE=!VALUES.F_NAN)

FOR j = 0, Tnum-1 DO BEGIN ; Temperature loop
  alfa = alfa_0*(1-alfa_T*(T[j]-MIN(T)))
  IF alfa LT 0.0 THEN alfa = 0.0

  ; Calculate current for the single-electron device.
  I1 = DOUBLE(orthodox(C1=0.025/E_SED, C2=0.025/E_SED, R1=R_SED,$
                      R2=R_SED, T=T[j], Voltage=V1D, Inf=1))

  ; Calculate current for the series molecular junction.
  I2 = DOUBLE(orthodox(C1=0.025/Es, C2=0.025/Es, R1=Rs, R2=Rs,$
                      T=T[j], alfa=alfa, Voltage=V1D, Inf=1))

  ; I1 and I2 may have different ranges. Find the smaller range and
  ; recalculate I1 or I2 within this range.
  IF I1[0] GT I2[0] THEN BEGIN ; I1 has the smaller current range.
    temp = MIN(ABS(I2-I1[0]),Vi)
    temp = MIN(ABS(I2-I1[Vnum-1]),Vf)
    IF Vi EQ zero THEN Vi = zero-1
    newV1 = V1D
    newI1 = I1
    ; Recalculate I2.
E. IDL Codes

IF Vf EQ zero THEN Vf = zero+1
newV2 = DOUBLE((Findgen(Vnum)/(Vnum-1))*(V1D[Vf]-V1D[Vi])+V1D[Vi])
newI2 = DOUBLE(orthodox(C1=0.025/Es, C2=0.025/Es, R1=Rs, R2=Rs, $ T=T[j], alfa=alfa, Voltage=newV2, Inf=1))
ENDIF ELSE BEGIN ;I2 has the smaller current range.
    ;Recalculate I1.
newV2 = V1D
newI2 = I2
temp = MIN(ABS(I1-I2[0]),Vi)
temp = MIN(ABS(I1-I2[Vnum-1]),Vf)
IF Vi EQ zero THEN Vi = zero+1
IF Vf EQ zero THEN Vf = zero+1
newV1 = DOUBLE((Findgen(Vnum)/(Vnum-1))*(V1D[Vf]-V1D[Vi])+V1D[Vi])
newI1 = DOUBLE(orthodox(C1=0.025/E_SED, C2=0.025/E_SED, R1=R_SED, $ R2=R_SED, T=T[j], Voltage=newV1, Inf=1))
ENDELSE

;Combine the two current arrays.
Imax = MIN([MAX(newI1),MAX(newI2)])
Imin = MAX([MIN(newI1),MIN(newI2)])
Iseries = [newI1[WHERE((newI1 LE Imax) AND (newI1 GE Imin))], $ newI2[WHERE((newI2 LE Imax) AND (newI2 GE Imin))]]
Iseries = Iseries[SORT(Iseries)]
Iseries = Iseries[UNIQ(Iseries)]

;Given the IV curves, interpolate voltages for each junction that
;correspond to Iseries.
E. IDL Codes

V1 = DOUBLE(INTERPOL(newV1,newI1,Iseries))
V2 = DOUBLE(INTERPOL(newV2,newI2,Iseries))

;Ensure that V1 and V2 arrays have no repeated values.
range = UNIQ(V1)
Iseries = Iseries[range]
V1 = V1[range]
V2 = V2[range]
range = UNIQ(V2)
Iseries = Iseries[range]
V1 = V1[range]
V2 = V2[range]
Inum = N_ELEMENTS(Iseries)

;Calculate the overall voltage.
Vseries = V2+V1*xi

;Calculate I-V for the parallel junction.
Iparallel = orthodox(C1=0.025/E_s, C2=0.025/Es, R1=Rp, R2=Rp, T=T[j], alfa=alfa, Voltage=Vseries/xi_p, Inf=1)

;The overall voltage and current arrays.
Vsys[0:Inum-1,j] = Vseries
Isys[0:Inum-1,j] = Iseries+Iparallel

ENDFOR ;Temperature loop
E. IDL Codes

END
Abbreviations

BJ Break junction
CB Coulomb blockade
CP-AFM conductive-probe atomic force microscope
D–B–A donor-bridge-acceptor
DDW distilled deionized water
DOS density of states
EA electron affinity
ES Efros and Shklovskii
FET field-effect transistor
HOMO highest occupied molecular orbital
IE ionization energy
LUMO lowest unoccupied molecular orbital
MINIM metal-insulator-nanoisland-insulator-metal
MIT metal–insulator transition
ML-NP molecularly linked nanoparticle
NP nanoparticle
PPMS physical property measurement system
SAM self-assembled monolayer
F. Abbreviations

SECM  scanning electrochemical microscope/microscopy
SED  single-electron device
SEM  scanning electron microscope/microscopy
SPR  surface plasmon resonance
SSA  stepwise self-assembly
STM  scanning tunneling microscope/microscopy
TCR  temperature coefficient of resistance
TEM  transmission electron microscope/microscopy
UPS  ultraviolet photoelectron spectroscopy
UV/vis  ultraviolet/visible
VRH  variable-range hopping
WKB  Wentzel-Kramers-Brillouin

\( a_0 \)  Bohr radius of hydrogen atom
\( \alpha \)  numerical coefficient
\( ac \)  alternating current
\( A \)  cross-sectional area
\( \beta \)  decay constant
\( C \)  capacitance
\( C_\Sigma \)  total capacitance
\( \delta \)  energy level spacing,
  nanoparticle center-to-center core separation
\( D \)  dimensionality
\( \Delta \)  widths of energy bands
\( \Delta E \)  change in energy
\( \Delta N \)  number of states per unit volume
\( \Delta t \)  change in time
F. ABBREVIATIONS

$\Delta U$ charging energy

$\Delta V_{CB}$ Coulomb blockade voltage range

$\Delta W$ energy bandwidth

$e$ electron charge

$\epsilon$ permittivity

$\epsilon_0$ permittivity of vacuum

$\epsilon_r$ dielectric constant

$\eta$ charge carrier density

$E$ energy

$E_a$ Arrhenius activation energy,
    differential activation energy

$E_b$ binding charging

$E_c$ charging energy

$E_{\text{cutoff}}$ cutoff energy

$E_F$ Fermi energy

$E_g$ energy gap

$E_k$ kinetic energy

dc direct current

$f$ Fermi-Dirac distribution,
    frequency

$\phi$ barrier height,
    work function

$g$ conductance

$g_0$ tunneling conductance at zero bias

$g_{\text{preexp}}$ pre-exponential factor of conductance

$g_Q$ quantum of conductance

$\gamma$ overlap integral
**F. Abbreviations**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>electron tunneling rate, energy level broadening</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>reduced Planck’s constant</td>
</tr>
<tr>
<td>$I$</td>
<td>current</td>
</tr>
<tr>
<td>$I_b$</td>
<td>break-point current</td>
</tr>
<tr>
<td>$J$</td>
<td>current density</td>
</tr>
<tr>
<td>$J_b$</td>
<td>break-point current density</td>
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<td>$k_B$</td>
<td>Boltzmann’s constant</td>
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<tr>
<td>$k_{CT}$</td>
<td>charge transfer rate</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>decay constant</td>
</tr>
<tr>
<td>$\ell$</td>
<td>mean free path</td>
</tr>
<tr>
<td>$L$</td>
<td>distance between electrodes</td>
</tr>
<tr>
<td>$m$</td>
<td>mass of electron</td>
</tr>
<tr>
<td>$m^*$</td>
<td>effective mass of electron</td>
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<td>chemical potential</td>
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</tr>
<tr>
<td>$n$</td>
<td>number of methylene groups</td>
</tr>
<tr>
<td>$\nu$</td>
<td>temperature exponent</td>
</tr>
<tr>
<td>$N$</td>
<td>number of atoms, number of electrons</td>
</tr>
<tr>
<td>$P$</td>
<td>power, probability</td>
</tr>
<tr>
<td>$Q$</td>
<td>nanoparticle charge</td>
</tr>
<tr>
<td>$Q_0$</td>
<td>residual charge</td>
</tr>
<tr>
<td>$r$</td>
<td>distance, nanoparticle radius</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$r_{DA}$</td>
<td>donor-acceptor distance</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density of states, ensemble distribution</td>
</tr>
<tr>
<td>$R$</td>
<td>resistance</td>
</tr>
<tr>
<td>$R_b$</td>
<td>break-point resistance</td>
</tr>
<tr>
<td>$R_{gain}$</td>
<td>gain resistance</td>
</tr>
<tr>
<td>$R_Q$</td>
<td>quantum of resistance</td>
</tr>
<tr>
<td>$R_s$</td>
<td>series resistance</td>
</tr>
<tr>
<td>$s$</td>
<td>inter-nanoparticle surface-to-surface separation</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>conductivity</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>electron-phonon coupling parameter</td>
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<tr>
<td>$t$</td>
<td>time</td>
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<tr>
<td>$\tau$</td>
<td>mean free time</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$T_0$</td>
<td>bath temperature</td>
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<tr>
<td>$T_e$</td>
<td>electron temperature</td>
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<tr>
<td>$T_{ph}$</td>
<td>phonon temperature</td>
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<tr>
<td>$</td>
<td>T</td>
</tr>
<tr>
<td>$U$</td>
<td>barrier height, Hubbard energy</td>
</tr>
<tr>
<td>$U_{image}$</td>
<td>image potential</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity</td>
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<tr>
<td>$v_F$</td>
<td>Fermi velocity</td>
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<tr>
<td>$V$</td>
<td>voltage</td>
</tr>
<tr>
<td>$V_b$</td>
<td>bias voltage, break-point voltage</td>
</tr>
<tr>
<td>$V_g$</td>
<td>gate voltage</td>
</tr>
</tbody>
</table>
F. Abbreviations

$V_{\text{CB}}$  Coulomb blockade voltage threshold

$\xi$  voltage-division factor

$\psi$  wave function

$x$  distance

$z$  coordination number