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Hot Electron Dynamics and Impurity Scattering on Gold Nanoshell Surfaces

by

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A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree

Doctor of Philosophy

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Abstract

Hot Electron Dynamics and Impurity Scattering on Gold Nanoshell Surfaces

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Recent ultrafast pump-probe experiments studying the relaxation rate of an optically excited hot electron distribution on Au/Au$_2$S gold nanoshells indicate that this relaxation rate can be modified by the chemical environment surrounding the shell. This work will begin a theoretical investigation of the effect of chemical adsorbates – solvents and impurities – upon nanoshell hot electron dynamics. The effects of water, polyvinyl alcohol (PVA), sulfur, p-aminobenzoic acid, p-mercaptobenzoic acid and propylamine adsorbates are examined for their electronic interaction with a noble metal surface. p-Aminobenzoic acid is found to have a very large dipole moment when adsorbed to the metal surface, in contrast to p-mercaptobenzoic acid, propylamine and water. This correlates well to the experimentally observed results where nanoshells dispersed in an aqueous solution with p-aminobenzoic acid display a faster relaxation rate compared to nanoshells dispersed in a pure water, aqueous propylamine or aqueous p-mercaptobenzoic acid environments.

This thesis will also introduce a non-equilibrium Green’s function approach, based on the formalism developed by Baym and Kadanoff, to model the dynamics of a hot electron distribution. The model will be discussed in terms of a simple potential scattering mechanism, which may in later work be expanded to include more complex electron-electron and electron-phonon interactions.

Lastly acoustic oscillation modes are calculated for solid gold spheres and gold-silicon nanoshells. These modes describe an effect of electron-phonon coupling between the hot electron distribution and the nanoshell lattice, whereby the electronic energy is converted into mechanical energy.
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I wish to thank my parents, Matha I. Wolfgang and Lozure G. Wolfgang, for their support and understanding during my time in school. It has been a long and difficult effort, an effort that never would have been possible without their love and support.

Lastly, I would like to thank Bobbie Ross. I have been drawing selfishly on her strength to complete my work here at Rice, and now that I am done, I plan to spend the rest of my life paying her back. I will love every minute of it.
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Dedication

In memory of my father:

Lozure Gene Wolfgang

8/31/25 - 9/1/93
Chapter 1

Introduction

Over the last ten years the interest in science at the nanoscale level has grown at a remarkable rate. Involving systems as small as 100 atoms, the physical description of nanoscale devices eludes a purely classical approach, being small enough to exhibit behavior of a discrete set of interacting states, while being too large to approach with any modern quantum mechanical technique. Existing in this physical middle ground, nanoscale device physics allows for the study of condensed matter physics in the region between the well defined bulk (systems involving approximately $10^{23}$ atoms) and atomic physics (systems involving < 10 atoms). However, the recent interest in nanoscale physics does not stem from purely academic roots, but rather from the promise of novel new devices that take advantage of the physical phenomena characteristic for systems of this size.

Nanoshells, roughly spherical nanoparticles on the order of 100 nm in diameter, are examples of such nanoscale devices. The nanoshell, consisting of a dielectric core surrounded by a thin layer of gold ($\sim$ 5-20 nm thick), has garnered a great deal of interest due to its remarkable optical properties. Nanoshells exhibit electromagnetic absorption in the range of 500-3000 nm, where the peak value for absorption is determined by the ratio of the shell thickness to total shell radius. Control of the nanoshell
growth process allows for the construction of nanoscale devices capable of absorbing light at specific wavelengths, tailor made to need.

Though the optical absorbance of gold nanoshells can be determined using extensions of the classical electromagnetic approach developed by Mie, a full understanding of the charge dynamics of the metal nanoshell, strongly perturbed into a highly excited state by the absorbance of this radiation, can only be understood through modern quantum mechanical considerations. Although many-body calculations have been performed to describe the independent electron dynamics of nanoparticles [1], these calculations ignore the effects of the nanoshell environment. Recent experiments by R. D. Averitt and S. Westcott [2, 3, 4] at Rice University indicate that the influence of the environment upon the ultrafast electron dynamics of optically excited nanoshells is anything but straightforward, and certainly not negligible.

The experiments by Averitt and Westcott indicate that the dynamics of the hot electronic distribution created by optical excitation can be influenced by changes in the nanoshell's local solvent/embedding medium environment. Even more remarkable, these experiments indicate that the means of environmental influence are not due to electron-phonon coupling between the surrounding media and the shell, but rather the result of a purely electronic perturbation of the nanoshell's electronic structure. Such electronic interactions between the nanoshell and the local environment may be the result of a chemical interaction between the shells and the solvent or impurities
in the solvent. These molecules may be able to adsorb on the metal shell surface and locally perturb the electric potential of the metal surface. Such perturbations might then allow for efficient scattering of the shell’s optically generated hot electron distribution, thereby influencing the dynamic electronic properties of the shell – such as the lifetime of this hot electron excitation. Although such plasmon scattering has been shown for the case of a continuous surface [5, 6, 7, 8, 9, 10], no evidence, until now, has suggested an electronic mechanism for scattering of the hot-electron distribution on nanoparticles.

This thesis will investigate the role of the chemical environment of the nanoshell upon the dynamics of the optically generated hot electron distribution. This investigation will be done in the context of the experiments performed by Averitt and Westcott, examining the the specific chemical environments used in their ultrafast pump-probe spectroscopy measurements of nanoshell electron dynamics. In Chapter 1, a brief introduction to the optical properties will be made, along with a description of the experiments of Averitt and Westcott that motivated this work. Chapter 2 will address the role of impurities on the nanoshell surface, and how they might alter the hot electron dynamics. In Chapter 3 a rigorous method for studying the hot electron dynamics will be introduced, with some preliminary results based on a very simple scattering mechanism. Lastly, Chapter 4 will discuss how electron-phonon coupling of the hot electron distribution to the nanoshell lattice can produce radial mechanical
oscillations of the nanoshell. Though not discussed in the context of the chemical surface impurity potential scattering described above, it may be an important factor in observing coupling of the hot electron distribution to the nanoshell lattice. Most importantly it illustrates how the optically induced electronic excitation can be converted into mechanical energy. The general formalism to calculate these oscillations will be discussed and some results will be given.
Chapter 2

Experimental Motivation

Recent ultrafast optical studies on nanoshells by S. Westcott and R. Averitt indicate that the change in observed relaxation time of a gold nanoshell’s hot electron distribution created by the laser pump pulse is 1) an environmental effect of the shells surrounding medium and 2) that the influence of the surrounding medium is primarily an electronic, not phonon, based scattering mechanism. Such results contradict currently accepted theory for hot electron relaxation of gold nanoparticles, which claims that electron-phonon coupling between the hot electron distribution and the gold lattice is the dominant channel for electronic relaxation of this excited state. While certainly electron-phonon coupling to the gold lattice describes the long time scale (\(\sim\)ps) relaxation channel of the excited electron distribution, this new experimental evidence suggests that electronic mechanisms, such as a surface impurity potential suggested in this work, play a strong role in modifying the hot electron relaxation rates.

In this section a brief overview of the optical properties of nanoshells will be provided. The ultrafast pump-probe spectroscopy measurements by S. Westcott will then be introduced, describing how the hot electron dynamics are modified by their surrounding medium, and are electronic in nature.
2.1 Optical Properties of Gold Nanoshells

Figure 2.1 depicts the structure of a gold nanoshell. A nanoshell, with diameter on the order of \( \sim 50-120 \) nm, consists of a dielectric core of radius \( r_1 \) with dielectric function \( \epsilon_1 \) surrounded by a thin layer of gold of thickness \( r_2 - r_1 \), with dielectric function \( \epsilon_2 \), embedded in a medium described by the dielectric function \( \epsilon_3 \). Electromagnetic absorbance spectral measurements indicate that these gold nanoshells absorb radiation in the 500-3000 nm wavelength range, and that the absorbance is dependent on the structure of the gold shell. The optical properties of gold particles have long been studied, and have found a reasonably good explanation using the classical electrodynamic approach of Mie [11], successfully describing the 520 nm absorbance of gold colloid. The modern extension of Mie theory to gold nanoshells provides a solution to its absorbance spectra, where the absorbance peak value is found to depend upon the ratio of the shell thickness \( (r_2 - r_1) \) to the total shell radius \( r_2 \) [12, 13].

Though able to predict the absorbance spectra of the gold nanoparticles, classical Mie theory provides no insight as to the absorption mechanism. Optical measurements on the absorption of light by gold particles and films indicate that this absorbance arises due to a collective excitation of the conduction electrons, a plasmon, excited by the incident radiation. The position of this plasmon resonance is then determined by the geometry of the shell.
The modeling of the decay of this excited state, the primary focus of this work, is not a simple problem. Initial excitation of the shell is believed to create a highly non-equilibrium electronic distribution that equilibrates to a smeared hot Fermi distribution of electrons within the first picosecond. This hot electron distribution is then scattered by a variety of mechanisms, including, but, as this thesis hopes to suggest, not limited to, coupling to the gold lattice. Relaxation of the gold nanoshell occurs very rapidly, in the order of ~ 10 picoseconds. To measure such fast electronic equilibration, techniques such as ultrafast optical pump-probe spectroscopy (of particular interest here) are used. Very briefly, this technique utilizes two incident beams (of the same or different frequencies) to monitor the electron relaxation dynamics. The first pulse, a high intensity beam, creates the excited electronic state in the gold nanoparticle. The second beam, much weaker and tuned to the energy of the excited electron distribution of the nanoparticle, probes the hot electron distribution by measuring the change in transmission of this beam as a function of time. After the initial electronic excitation of the shell by the pump beam, a positive change in probe beam transmission is observed – an effect referred to as photo-bleaching – resulting from the vacancy created in the equilibrium conduction electron distribution. Simply stated, since there are now fewer electrons available to absorb the incident radiation, as most have already been promoted to the highly excited electronic state, less of the incident
probe beam energy is absorbed. As the hot electron distribution equilibrates, the change in probe beam transmission returns to its pre-excitation state [14, 15].

A simple phenomenological model by Anisimov [16, 17] has been used to describe the relaxation of hot electron distributions. Known as the two-temperature model (TTM), this approach connects the changes in electronic and lattice temperature through thermal diffusion and an empirically derived electron-phonon term (Eqs. 2.1)

\[
C_e(T_e) \frac{\delta T_e}{\delta t} = \nabla \cdot (\kappa \nabla T_e) - G(T_e - T_l) + H(\vec{r}, t)
\]

\[
C_l(T_l) \frac{\delta T_l}{\delta t} = G(T_e - T_l)
\]

(2.1)

where \(C_e\) and \(C_l\) are the electron and lattice specific heat, \(T_e\) and \(T_l\) are the electron and lattice temperatures, \(H(\vec{r}, t)\) is the laser energy density, \(\kappa\) the thermal conductivity of gold, and \(G\) the empirical electron-phonon coupling constant. This equation has been used to successfully model the hot electron decay for gold nanoshells and provides a model for the time response of the normalized change in transmission, \(\Delta T/T\), measured in pump-probe spectroscopy measurements (Eq. 2.2).

\[
\frac{\Delta T}{T} = \left[1 - e^{\frac{-t}{\tau_r}}\right]e^{\frac{-t}{\tau_d}} + \Upsilon_{off}.
\]

(2.2)

In Eq. 2.2, \(\tau_r\) is the time for the equilibration of the hot, non-equilibrium electronic distribution (created initially by the incident pump beam) to relax into a hot Fermi distribution \((\tau_r \ll 1\ \text{ps})\). \(\tau_d\) is the relaxation time of the hot Fermi distribution and
\( \tau_{off} \) is an offset compensating for the increased lattice temperature resulting from the long-time scale electron-phonon coupling. Using the above model (Eq. 2.2), the relaxation times of the hot electron distribution, \( \tau_d \), will be discussed in light of new experimental data.

### 2.2 Measurements of Hot Electron Relaxation Rates

A series of experiments performed by R. Averitt and S. Westcott [4] regarding the relaxation rates of Au/Au$_2$S nanoshells [18, 2], indicates that contrary to popular belief, electronic scattering mechanisms may indeed play a strong role in the relaxation of the hot Fermi electron distribution when considering the nanoshell environment. Three specific experiments can be cited to support this claim.

The first experiment investigates the effect of the embedding medium upon the nanoshell relaxation rate. Relaxation rates for shells dispersed in water and polyvinyl alcohol (PVA) were examined. The experimentally measured relaxation lifetimes were 5.0 ps for shells dispersed in water and 1.37 ps for shells dispersed in PVA. Clearly, some environmental effect introduced by PVA must be contributing to the more efficient relaxation of the hot electrons.

The second and third experiments addressed the question of relaxation mechanism. The second experiment compared the relaxation rates of nanoshells dispersed in water and D$_2$O. Since the phonon spectrum of D$_2$O is different from that of water, any
effects relating to electron-phonon coupling between the nanoshell and its environment should be observed. Measured relaxation rates for nanoshells dispersed in D$_2$O were 4.7 ps, in perfect agreement with the results for water. This result indicates that no environmental electron-phonon coupling was responsible for the observed relaxation rate in water.

To check if this effect was unique to the water/D$_2$O system, the third experiment investigated the role of temperature dependence upon nanoshells dispersed in PVA. By changing the temperature of the sample the number of available phonon modes is changed. Such a change should be evident in the measured relaxation rates of nanoshells at different temperatures. Measurements of nanoshells dispersed in PVA were made at room temperature and 40 K. The relaxation rate measured for the room temperature system was 1.32 ps and the rate for the 40 K system was 1.34 ps. Again, no notable difference was found for the relaxation rate when the phonon density of the system was changed. This result indicates that the primary interaction between the embedding medium and the nanoshell is mostly electronic.

Further experiments by S. Westcott were performed in order to examine the role of adsorbed impurities on the nanoshell surface with respect to hot electron relaxation. An experiment involving increasing concentrations of p-aminobenzoic acid in an aqueous nanoshell system indicated that the nanoshell relaxation times decreased with increasing concentration, stabilizing at a relaxation time of 1.7 ps. A simi-
lar experiment involving increasing the concentration of p-mercaptobenzoic acid in an aqueous nanoshell environment had no effect on the nanoshell relaxation rate. Lastly, propylamine—possessing the same head group as p-aminobenzoic acid, but without the benzene ring or polar carboxylic acid tail—introduced into an aqueous nanoshell system in increasing concentrations, also had no effect on the hot electron relaxation rates.

These experiments strongly suggest that nanoshell hot electron relaxation times depend upon the environmental conditions surrounding the shell. Further, the experiments indicate that the relationship between the nanoshell and its embedding medium is mostly electronic. It remains to be determined how the local environment interacts electronically with the nanoshell to influence hot electron relaxation. This thesis will investigate this relationship on the premise that chemical adsorption of solvent or impurity molecules on the nanoshell surface can perturb the electronic potential at the shell surface. These defects of the electronic potential can then contribute to hot electron relaxation. The strength of these defects will be dependent upon the way in which the solvent or impurity molecules adsorb on the nanoshell surface. Precedent for the modification of hot electron relaxation rates exists for metal surfaces where the presence of defects in the form of adsorbates or structural defects can create a perturbation of the metal electronic potential [5, 19, 10, 20].
In Chapter 2, a theoretical, quantum chemical investigation will be performed, addressing the chemical relationship between the nanoshell electron dynamics and the shell’s local environment. Specifically, the interaction between water, PVA, sulfur (reflective of possible surface impurities acquired during sample preparation), p-aminobenzoic acid, p-mercaptobenzoic acid, propylamine, and the nanoshell surface will be investigated. These systems will be examined for perturbations of the nanoshell electronic surface structure. Such perturbations can create defect potentials that can lead to electron scattering and be responsible for the observed changes in the measured hot electron relaxation rates.
Figure 2.1  Schematic drawing of nanoshell structure. $r_1$ is the radius of the dielectric core, $r_2 - r_1$ is the thickness of the metal shell, $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$ are the dielectric functions for the dielectric core, metal shell and embedding environment, respectively.
Chapter 3

Impurity Models

3.1 Introduction

Hot electron relaxation for Au/Au$_2$S nanoshells has been shown, in some cases, to be affected by the local environment. In this chapter, this environmental effect will be examined using quantum chemical techniques. \textit{Ab Initio} computational methods will be used to develop models of the interaction of the gold nanoshell surface and the surrounding medium, and used to qualitatively discuss the experimental results of Chapter 1. Specifically, this chapter will address the interaction of water, polyvinyl alcohol (PVA), p-aminobenzoic acid, p-mercaptobenzoic acid, propylamine, and the role of atomic impurities such as sulfur upon the electron dynamics of Au/Au$_2$S nanoshells.

3.2 \textit{Ab Initio} Cluster Models

The investigation of the interaction between the nanoshell surface and solvent media will be accomplished through the use of computational empirical and \textit{ab initio} quantum chemistry methods. Empirical methods will be used to obtain initial conformational information, such as impurity position and orientation above the nanoshell
surface. These methods utilize a method known as molecular mechanics, where the forces between the atoms in a molecule/cluster are solved using a Newtonian approach. Force equations are solved classically using empirical interaction parameters that have been validated experimentally. Geometry optimization is accomplished by minimizing the forces acting on the system within a given set of constraints (empirical data on bond lengths and angles). Due to the simplicity of this approach, it is easily extended to large systems and has been found to be very useful for studying the effects of solvent environments upon physical systems where it is necessary to describe each solvent molecule explicitly. However, this modeling approach is very inexact, as it approaches the solution from a phenomenological technique. Hence, it is only used in situations where it may provide an initial geometry guess to be used later, in more exact quantum mechanical calculations, or where due to the limitations of computational expense, no other model will suffice [21].

*Ab initio* methods involve the solution of Schrödinger's equation to obtain eigenstates and eigenenergies of the molecular system. Due to the complex nature of the full solution to a direct approach of Schrödinger's equation, the solution is approximated using a mathematically equivalent approach. In this work, all *Ab initio* simulations will utilize the Density Functional formalism originally proposed by Kohn and Sham [22, 23]. Here the Schroedinger equation is rewritten in terms of the electron density and solutions are achieved iteratively using a self consistent approach. The
benefit of a Density Functional approach is the inclusion of exchange and correlation effects as a function of electron density. terms unknown to simpler methods such as Hartree-Fock. The computational algorithm used for this work was developed using the local spin density approximation developed by von Barth and Hedin [24], where the exchange-correlation energy is approximated by the exchange-correlation energy for a free electron gas. Our scalable, parallel algorithm utilizes a numerical atomic basis set to form the molecular orbital solutions – a linear combination of these basis orbitals – and obtain the electronic structure and minimum energy conformation of small atomic systems [25].

A complete numerical model of a nanoshell in a solvent environment, in excess of $10^7$ atoms, is far beyond the means of modern computational resources. In order to study these solvent/shell systems, the shell will be approximated by a metal surface and only a few (or in some cases only one) solvent/impurity molecules will be studied. In addition to the difficulties involved with the size of the system to be studied, another difficulty arises as to atom type. Gold, atomic number 79, is so large that the core electrons are relativistic [26, 27, 28, 29, 30, 31, 32]. The chemistry of relativistic atoms is a topic beyond the scope of this study, and is, in fact, an entire area of research unto itself. However, for the case of gold nanoshells, the hot electron excitation involves only the valence electron distribution. For this study, gold will be replaced with copper atoms. Though chemically more reactive, it presents a similar
valence shell and does not suffer from the relativistic problems associated with the heavier elements, such as gold.

In the following sections the interaction between solvent/impurity and the nanoshell surface will be examined by studying the dipole moment and effective potential (Coulomb + exchange/correlation) created by the solvent/impurity + metal surface model. Relative binding strength, dipole moment, and atomic charge will be used to make an argument correlating the induced impurity potential to hot electron relaxation times.

3.3 PVA and Water

The initial investigation revealing the strong environmental dependence of hot electron relaxation dynamics of gold nanoshells by R. Averitt and S. Westcott (Chapter 1) compared the relaxation of Au/Au₂S nanoshells in a water environment to similar shells dispersed in a polyvinyl alcohol medium. These studies, as mentioned previously, illustrate via a temperature and isotope study, that the relaxation must involve an electron-electron scattering mechanism. A defect potential created by the interaction between the solvent environment and the nanoshell free metal surface might serve to perturb this hot electron distribution created in pump-probe measurements, scattering the highly excited electron distribution and decreasing the relaxation time. Such effects, as mentioned earlier, have been observed on metal surfaces
[6, 20, 8, 33, 7], and might be extended to the hot relaxation of metal nanoshells. As discussed in Chapter 1, nanoshells dispersed in PVA have a much higher hot electron decay rate than do similar shells dispersed in water. Clearly, in order to understand this solvation effect, the interaction between PVA, water and the metal shell must be examined.

The first attempt to model the solvent/shell interaction for PVA and water examined a single solvent molecule adsorbed on a metal (copper) surface. PVA, a long hydrocarbon polymer, $-[CH_2CHOH]_n-$, was approximated, initially, by a single, appropriately terminated polymer unit (monomer). An ab initio geometry optimization was performed on the solvent molecules, independent of the metal surface, to determine the minimum energy conformation of the molecules. This minimum energy conformation was then used as an initial guess for solvent orientation above the metal surface. The optimized solvent molecules were set at fixed distances above the metal surface, from 0.5 - 10.0 atomic units (au), and single point energy calculations were performed. This energy calculation determined, roughly, the minimum energy point above the metal surface – the position of the adsorbed solvent molecule. This procedure was performed for different lateral positions above the metal surface, searching for the minimum energy position along the metal surface. Lastly, a geometry optimization was performed on the adsorbate molecules above the metal surface
to calculate their minimum energy state and obtain the electronic structure for the solvent/metal adsorbate system.

Though modeling a single solvent molecule adsorbed on the metal surface allows for a basic understanding of the interaction, it does not provide a realistic model for solvation of the nanosphere itself. Global coordination effects, especially in the case of the polymer environment, PVA, are not represented in the simple single adsorbate model. In an attempt to address this issue, though, as mentioned earlier, beyond our current computational ability, multiple solvent molecules (longer polymer chains) were modeled on a larger metal surface lattice. Trimer PVA strands on a metal lattice were modeled in a similar method to the single molecule adsorbate method described above. In the case of the PVA trimer, investigations of all orientations above the metal lattice is computationally impractical since the conformation space to be investigated is immense and replete with local minimization points, obfuscating the actual minimum energy position. To make this study tractable, a molecular mechanics calculation was performed, suggesting local minima to use as starting points for ab initio calculations.

Lastly, multiple polymer strands above a large metal surface, reflective of the PVA density surrounding the nanoshell, was compared to a model of the nanoshell surface with the appropriate density of water surrounding the shell. The geometry for these models was obtained solely by molecular mechanical means. The final electronic
structure was calculated using a semi-empirical Hartree-Fock approach utilizing a ZINDO (Zerner Intermediate Neglect of Differential Overlap) Hamiltonian. Although the eigenstates and subsequent electronic structure would not be comparable to the previous \textit{ab initio} calculations, such a calculation might further aid in describing any global effect due to the solvation of the nanosphere.

### 3.4 PVA and Water: Results

The optimized positions of water and the PVA monomer above a copper (111) surface are shown in Figures 3.1 and 3.2. In both cases, the oxygen atom of each solvent molecule adsorbs closely to the metal surface. Measuring the distance between this oxygen and the metal surface along a vector normal to the copper surface, the adsorbate-oxygen distance is found to be 4.45 au for PVA and 3.9 au for water. Using a Mulliken population analysis, where the molecular orbitals (eigenstate solutions, being linear combination of the atomic orbital basis) are projected onto the atomic basis, the electronic occupation (charge) of each atom in the molecule can be determined. In both cases, a negative charge, \(-0.315 \, e_o\) for PVA and \(-0.310 \, e_o\) for water, is found on the adsorbed molecule. This charge state indicates that although the oxygen-surface distance may be different for the two solvent molecules, the electronic character of the metal/solvent interaction is quite similar.
The dipole moment of the solvent/metal complexes can be calculated and used as a rough measurement of the impurity defect created on the metal surface as a result of the adsorbed solvent molecule. Figures 3.3 and 3.4 show the calculated dipole moment and total self-consistent energy as a function of distance for the solvent/metal complexes for water and PVA, respectively. The figures show the energy and dipole of un-optimized structures as a function of distance, with the final optimized value highlighted. The dipole moments for the optimized solvent/metal structures are 1.44 and 1.49 Debyes for the water and PVA (EtOH) adsorbates, respectively. Again, no noticeable difference is observed for the electronic behavior of the two adsorbates on the copper surface.

As a further measure of the impurity defect induced by the solvent adsorbate molecule, the effective potential induced by the defect was plotted against the solvent/metal surface. Determination of the defect-induced impurity potential was accomplished by taking the difference between the effective potential (Coulomb + exchange/correlation) for the solvent/metal complex and the bare metal cluster. The resultant defect-induced potential indicates the extent of the adsorbate perturbation into the copper model surface. The results of this calculation appear in Figs. 3.5 and 3.6. Though difficult to quantify, these images seem fairly similar on examination of their influence at the metal interface. Similar screening effects due to the free electron surface localize the perturbation at the first atomic layer.
Figure 3.7 shows the results of single point energy calculations for a PVA trimer (three repeat units) at different distances above the metal surface. As expected, the dipole moment increases with increasing polymer length for the solvent/metal complex. To quantitatively address the effect of polymer length and dipole moment for a comparison to water, a measure of dipole moment/area was taken. Using a molecular mechanics approach, multiple PVA trimers were allowed to relax on a model gold surface to determine the solvent coverage density. A similar solvation model involving multiple water molecules and the same gold surface was used to determine the water coverage. Using this information, the dipole moment/au² could be approximated. The calculation gave values of 0.0666 Debye/au² for the PVA/metal surface and 0.0428 Debye/au² for the water/metal surface. Although the PVA does indicate a larger dipole moment per area value, it is well within the margin of error for a molecular mechanics calculation.

Comparison of the above data for PVA and water – including atomic charge state, dipole moment and effective potential – yield no definitive answer to explain the observed experimental difference in relaxation between nanoshells dispersed in water and PVA. However, this calculation fails to address the issues surrounding immersion of nanoparticles in a polymer matrix. It can not account for phenomena associated with long chain polymers adsorbing to the shells. The polymer density surrounding the shell, the short range mechanical forces that orient the shell/polymer
complex can not be studied here. However, reasonable attempts have been made that indicate that even with maximal coverage, the differences between water and PVA environments can not adequately explain the dramatic experimental variation in electronic relaxation times between the solvents.

3.5 Atomic Impurities

Experimental evidence indicates that the observed difference in hot electron relaxation must be an electronic effect. However, the above discussion of the electronic influence of the embedding media, water or PVA, upon the metal shell surface, indicates that the differences in these solvents are not significant enough to explain the observed change in relaxation rate. To explain the strong variation of nanoshell relaxation rate in different media, another scattering mechanism must be found.

A possible solution to this problem may concern the growth process of the Au/Au$_2$S nanoshell. Grown in aqueous solution, the shells exist with a number of chemical intermediates including sulfur and sodium. These compounds, in aqueous solution, may not strongly adsorb to the nanoshell surface, but rather weakly interact with the metal surface, coordinating around the nanoshell [34]. The process of removing the shells from solution and embedding them in the PVA matrix might induce adsorption of these chemical intermediates upon the metal shell surface. Such adsorbed impurities, found on the nanoshell in the PVA environment, might induce
a perturbation in the surface electronic potential and help to more effectively scatter the hot electron distribution.

One such possible impurity adsorbing to the nanoshell surface might be atomic sulfur. Of all elements, sulfur is well known to be one of the most reactive with gold. The change in effective potential near adsorbed sulfur atoms could very well create the impurity potential necessary to affect electronic relaxation.

To model a sulfur impurity on a gold surface, a model similar to the water/copper complex described above is created. For the model discussed here, the interaction between atomic sulfur and a 31 atom Cu(111) lattice will be studied. *Ab initio* calculations were performed for sulfur atom positions translated laterally and perpendicularly across the surface of the Cu lattice in order to determine the minimum energy position – the most probable location for sulfur adsorption. From the equilibrium electronic structure of the sulfur/copper complex the charge state, dipole moment and effective potential could be determined. Similar calculations were done for water adsorbed on the same 31 atom Cu(111) lattice. The sulfur/metal complex could then be compared to the water/metal complex so that any differences that might influence hot electron scattering of the gold nanoshells can be observed.
3.6 Atomic Impurities: Results

Figure 3.9 shows the equilibrium position of sulfur above the copper cluster. This equilibrium position yields a charge state of \(-0.282\ e_o\) for the sulfur adsorbate and a dipole moment of \(1.54\) for the sulfur/copper impurity. These factors of themselves yield little indication of a strong interaction with the gold surface relative to water where the charge state for the adsorbed oxygen is \(-0.310\ e_o\) and the dipole for the water/copper complex is \(1.44\) Debye. However, analysis of the effective potential for the sulfur/copper and water/copper systems shows a major difference. Figure 3.10 shows the effective potential for sulfur adsorbed on a copper lattice. Compared to the effective potential of water adsorbed on the copper cluster (Fig. 3.5), the difference is clear. Sulfur creates a perturbation in the metal surface potential that is orders of magnitude greater in extent than the perturbation created by water. Such an impurity on a nanoshell would introduce a strong variation in the local electronic structure near the adsorption site inducing a defect potential that could influence the surface scattering of the hot electron distribution, allowing for faster relaxation rates.

Unfortunately, due to the uncontrolled way in which such impurities adsorb to the nanoshell surface, it is difficult to determine experimentally if indeed this is the source of the observed relaxation times. A sulfur impurity proves to be a greater challenge, as observation of sulfur impurities on a gold surface becomes confused with sulfur present in the Au/Au$_2$S nanoshell and aqueous environment. However, this model
does provide proof that strong perturbation of the nanoshell free electron surface by environmental factors (here, surface adsorbates) is possible.

3.7 Molecular Adsorbates

Since confirmation of the presence of impurities adsorbed during the Au/Au$_2$S nanoshell manufacturing process proves difficult, experiments involving the controlled exposure of impurity molecules to an aqueous suspension of nanoshells was performed. These experiments, as mentioned earlier, involved the introduction of p-aminobenzoic acid (p-ABA), p-mercaptobenzoic acid (p-MBA) and propylamine to the nanoshell solution. Experimental pump-probe measurements of nanoshell relaxation rates indicated that the p-MBA had only a small effect (increasing the concentration caused eventual stabilization of the relaxation time at the relaxation time of water), while increasing concentrations of p-ABA induced a clear relaxation rate increase. Introduction of propylamine (a molecule with the same binding group as p-ABA where a short chain alkane group is substituted for the benzioc acid group of p-ABA) in increasing concentration also resulted in no observed change of the hot electron relaxation rate. In this section, the three impurity molecules, p-ABA, p-MBA, and propylamine will be modeled with a metal (copper) surface to address the adsorbate/metal interaction.
The modeling of the p-ABA, p-MBA and propyamine interaction with a nanoshell surface was accomplished using methods similar to those already discussed for the PVA/copper, water/copper and S/copper adsorbate/metal systems. The adsorbate molecules were modeled independently of the metal surface to find their minimum energy configuration in the gas phase. These minimum energy configurations were introduced to the 31 atom Cu(111) surface model and translated laterally and along the surface normal to locate the minimum energy adsorbate positions. Lastly, geometry optimization was done to fine tune the adsorbate conformation on the Cu surface. Initial studies of the minimum energy conformations for both p-ABA and p-MBA above a metal surface using a molecular mechanics approach indicated that both impurities had minima when the plane of the benzene ring was parallel to the metal surface plane for calculations done in vacuum (without the solvent, water). Inclusion of the solvent using an explicit water solvation scheme in a periodic box stabilized the carboxylic acid functional group, changing the minimum energy state of the impurity molecules to an orientation where the benzene ring is perpendicular to the metal surface (Fig. 3.11). Since an explicit water solvation scheme is not possible in an \textit{ab initio} approach – the number of atoms required being well beyond computational limits – the impurity molecules' electronic structure was calculated in vacuum. To prevent the unphysical relaxation of the impurity molecules to the parallel benzene state, the \textit{ab initio} geometry optimization calculations constrained
the molecules so that the benzene ring remained perpendicular to the metal surface plane.

Once the minimum energy conformation was determined, the atomic charge states, dipole moment and effective potential could then be calculated.

### 3.8 Molecular Adsorbates: Results

The nitrogen/copper surface plane distance for p-ABA measured along the surface normal was found to be 5.94 au, and the sulfur/copper surface plane distance for p-MBA was 5.96 au. Figure 3.12 indicates dipole strength as a function of distance for both p-ABA and p-MBA. Dipole measurements at the adsorbate minimum energy position gave a value of 2.27 au for the p-ABA/copper complex and 0.93 au for the p-MBA/copper complex. Figure 3.13 and 3.14 show the effective potential for the p-ABA/copper and p-MBA/copper models. Though p-mercaptobenzoic acid has a strong potential above the Cu surface (≈5 au) this perturbation is relatively well screened out at the first atomic layer (≈5 au). This is not the case for p-aminobenzoic acid, where the effective potential penetrates the first atomic layer. This perturbation of the electric potential at the surface of the nanoshell could influence the hot electron decay.

From the above data, a clear correlation can be drawn between dipole strength, effective potential and hot electron relaxation rates. The p-ABA, with larger dipole
moment, perturbs the free electron surface of the nanoshell significantly when compared to p-MBA and water. The interaction between p-MBA and the copper surface is very similar to the interaction between water and the same copper surface model (see above), indicating that like PVA, it does not significantly alter the shell free electron surface to create a new channel for hot electron relaxation.

Calculation of propylamine adsorbed to a copper surface shows that, adsorbed at its equilibrium position (4.96 au above the Cu plane), propylamine yields a dipole moment of 1.54 au (Fig. 3.15), a value close to that of water (1.44 au). This indicates that the strong polarizability of p-ABA, due to the carboxylic acid group, allows for a greater perturbation of the nanoshell electronic potential at the surface adsorption site. Since p-MBA and propylamine both present dipole moments less than or equal to that of water, no change is observed for the hot electron relaxation rate in those systems.
Figure 3.1 Minimum energy conformation for water adsorbed on 31 atom Cu(111) cluster model.
Figure 3.2  Local minimum energy position for single PVA monomer (ethanol) adsorbed on 31 atom Cu(111) cluster model.
Figure 3.3  Dipole Moment and Total SCF (Self-Consistent Field) Energy as a function of distance for water adsorbed on a 31 atom Cu(111) surface model. Values for minimum energy configuration are indicated by the open circles.
Figure 3.4  Dipole Moment and Total SCF Energy as a function of distance for PVA monomer (ethanol) adsorbed on a 31 atom Cu(111) surface model. Values for minimum energy configuration are indicated by the open circles.
Figure 3.5  Effective potential plot for H$_2$O adsorbed on a 31 atom Cu(111) surface. Figure is a cross section of the water/copper complex, the plane of the diagram normal to the surface plane. The dashed line represents the surface of the copper lattice. The inset picture indicates the adsorbate location relative to the figure. Above the dashed line is the adsorbate molecule, below is the copper bulk.
Figure 3.6 Effective potential plot for PVA monomer (ethanol) adsorbed on a 31 atom Cu(111) surface. Figure is a cross section of the water/copper complex, the plane of the diagram normal to the surface plane. The dashed line represents the surface of the copper lattice. The inset picture indicates the adsorbate location relative to the figure. Above the dashed line is the adsorbate molecule, below is the copper bulk.
Figure 3.7  PVA trimer dipole moment and total SCF energy as a function of distance (average) between the PVA oxygen and the Cu Surface.
Figure 3.8 Effective potential plot for PVA trimer $HO - [CH_2CHOH]_3 - H$, adsorbed on a 31 atom Cu(111) surface. Figure is a cross section of the water/copper complex, the plane of the diagram normal to the surface plane. The dashed line represents the surface of the copper lattice. The inset picture indicates the adsorbate location relative to the figure. Above the dashed line is the adsorbate molecule, below is the copper bulk.
Figure 3.9  Minimum energy conformation of sulfur atom adsorbed on a 31 atom Cu(111) Surface.
Figure 3.10 Effective potential plot for sulfur adsorbed on a 31 atom Cu(111) surface. Figure is a cross section of the water/copper complex, the plane of the diagram normal to the surface plane. The dashed line represents the surface of the copper lattice. The inset picture indicates the adsorbate location relative to the figure. Above the dashed line is the adsorbate atom, below is the copper bulk.
Figure 3.11  Minimum energy conformations for p-ABA. Top: Benzene plane is perpendicular to metal surface plane, the stable state in a water solvation model. Bottom: Benzene plane is parallel to metal surface plane, the stable state for a model calculation in vacuum.
Figure 3.12  Dipole Moment as a function of distance for p-ABA and p-MBA adsorbed on a 31 atom Cu(111) surface model.
Figure 3.13  Effective potential plot for p-aminobenzoic acid adsorbed on a 31 atom Cu(111) surface. Figure is a cross section of the water/copper complex, the plane of the diagram normal to the surface plane. The dashed line represents the surface of the copper lattice. The inset picture indicates the adsorbate location relative to the figure. Above the dashed line is the adsorbate molecule, below is the copper bulk.
Figure 3.14  Effective potential plot for p-mercaptobenzoic acid adsorbed on a 31 atom Cu(111) surface. Figure is a cross section of the water/copper complex, the plane of the diagram normal to the surface plane. The dashed line represents the surface of the copper lattice. The inset picture indicates the adsorbate location relative to the figure. Above the dashed line is the adsorbate molecule, below is the copper bulk.
Figure 3.15 Propylamine dipole moment and total SCF energy as a function of distance (average) between the propylamine nitrogen and the Cu Surface.
Chapter 4

Modeling Non-Equilibrium Dynamics

4.1 Introduction

The electronic environment of a gold nanoshell after excitation by a laser pump pulse is a strongly interacting, non-equilibrium system. Phenomenological approaches have been developed to explain the relaxation of the hot electron system, using a solution to the Boltzmann transport equation [35], by treating the hot electron gas using Fermi liquid theory [36, 37, 38, 39], and by implementation of the two-temperature model (TTM). The two temperature model (Eqs. 2.1) couples the change in electronic temperature and lattice temperature via an electron-phonon coupling mechanism. Though thermal conductivity is taken into account, the TTM remains too simple to explain variations in relaxation rate due to essentially non-linear quantum mechanical mechanisms such as impurity scattering. Recent one-electron quantum kinetic approaches [40], though appropriate for metal films, may not apply directly to nanoshells because of their limited size and discrete phonon spectrum.

Solutions of non-equilibrium systems using the formalism of Kadanoff and Baym [41, 42], should be able to account for impurity scattering mechanisms as well as electron-phonon coupling. The approach involves the solution to a non-linear set of
Green's functions describing electron occupation as a function of time. By introducing impurity and electron-phonon scattering mechanisms and varying their strengths, the dynamics of a hot-electron distribution such as one created on gold nanoshells can be studied.

This chapter will first discuss the basic non-equilibrium formalism developed by Kadanoff and Baym. Next a simple preliminary implementation of this formalism will be discussed and the role of impurity dynamics in this model will be qualitatively examined.

4.2 Non-equilibrium Green's Function Formalism

The non-equilibrium Green's function method developed by Kadanoff and Baym describes the dynamics of complex interacting systems, such as that found during hot electron relaxation in gold nanoshells. For purposes of this discussion, a simple Hamiltonian describing a interacting system will be used

\[ H = \sum_{k,\sigma} \epsilon_{k,\sigma} n_{k,\sigma} + \sum_{k,k',\sigma} V_{k,k'} c_{k',\sigma}^\dagger c_{k,\sigma} \]  

(4.1)

where \( \epsilon \) and \( n \) represent the energy and occupation of the electronic state \( k \), \( c_k \) and \( c_{k',\sigma}^\dagger \) are the annihilation and creation operators for states \( k \) and \( k' \) and \( V_{k,k'} \) is the interaction potential coupling states \( k \) and \( k' \). To investigate the dynamics of this interacting system, namely the occupation of electronic states over time, a two time
Green's function approach is implemented where

\[ G^<(t, t') = \langle c^\dagger(t')c(t) \rangle \]
\[ G^>(t, t') = \langle c(t)c^\dagger(t') \rangle \] (4.2)

defined in the Heisenberg representation, measure correlation in the many body system. Of particular interest is \( G^< \). When \( t = t' \) for the creation and destruction of particles of the same energy, \( k = k' \), \( G^< \) measures the occupation of the state \( k \). To describe the dynamics of a correlated, non-equilibrium system, a solution must be found for the time dependence of \( G^< \).

Baym and Kadanoff introduced a time dependent Dyson equation approach to this problem. Before discussing this approach, it is necessary to define the following generic retarded and advanced Green's functions

\[ iG^R(t, t') = [G^>(t, t') \mp G^<(t, t')]\theta(t - t') \]
\[ -iG^A(t, t') = [G^>(t, t') \mp G^<(t, t')]\theta(t' - t) \] (4.3)

where the upper/lower signs are for bosons/Fermions and \( \theta \) is the Heavyside function.

Using an implementation of the Kadanoff and Baym approach successfully used to model the low temperature dynamics of electron transport in quantum dots as well as charge transfer between atoms and surfaces [43, 44, 45, 46], \( G^< \) is found to satisfy the following set of coupled equations

\[
\left[ i \frac{\partial}{\partial t} - \varepsilon_{k\sigma}(t) \right] G^<_{k'k\sigma}(t, t') = \sum_{k''} \int_{-\infty}^{\infty} d\tilde{t} \Sigma^R_{kk''\sigma}(t, \tilde{t}) G^<_{k''k'\sigma}(\tilde{t}, t')
\]
\[
+ \sum_{k''} \int_{-\infty}^{\infty} d\bar{t} \, \Sigma_{kk''}^{<}(t, \bar{t}) G_{k''\sigma}(\bar{t}, t'),
\]

\[
\left[ i \frac{\partial}{\partial t'} - \varepsilon_{k\sigma}(t') \right] G_{kk'\sigma}^{<}(t, t') = \sum_{k''} \int_{-\infty}^{\infty} d\bar{t} \, G_{kk''\sigma}(t, \bar{t}) \Sigma_{k''k'\sigma}^{<}(\bar{t}, t') + \sum_{k''} \int_{-\infty}^{\infty} d\bar{t} \, G_{kk''\sigma}(t, \bar{t}) \Sigma_{k''k'\sigma}^{A}(\bar{t}, t'),
\]

where \( \varepsilon \) is the energy of level \( k \), and \( \Sigma^{>,<,R,A} \) are the “less than”, “greater than”, retarded and advanced self energies, respectively. In the many body formalism, the self energy describes the interactions of the system and is a term that can be chosen to include impurity scattering and electron-phonon coupling. The \( \Sigma^{R,A} \) can be obtained by using the relation for \( G^{A,R} \) (Eq. 4.3) where \( \Sigma \) is substituted for \( G \).

The retarded and advanced Green’s functions satisfy the following Dyson equations

\[
\left[ i \frac{\partial}{\partial t} - \varepsilon_{k\sigma}(t) \right] G_{kk'\sigma}^{A,R}(t, t') = \delta_{k,k'} \delta(t - t') + \sum_{k''} \int_{-\infty}^{\infty} d\bar{t} \, \Sigma_{kk''\sigma}^{A,R}(t, \bar{t}) G_{k''k'\sigma}^{A,R}(\bar{t}, t'),
\]

\[
\left[ -i \frac{\partial}{\partial t'} - \varepsilon_{k\sigma}(t') \right] G_{kk'\sigma}^{A,R}(t, t') = \delta_{k,k'} \delta(t - t') + \sum_{k''} \int_{-\infty}^{\infty} d\bar{t} \, G_{kk''\sigma}^{A,R}(t, \bar{t}) \Sigma_{k''k'\sigma}^{A,R}(\bar{t}, t'),
\]

These four equations and initial boundary conditions form a closed set, from which solutions for \( G^{<} \) can be obtained.
4.3 Numerical Implementation

The solution for $G_{k,k'}(t, t')$ is formidable. It requires the solution of a four dimensional matrix that scales as $k^2 \times m^2$ for $k$ interacting levels and $m$ time steps. Therefore, the computational demands can become quite expensive.

To assist in the numerical solution of the above Dyson equations, a few substitutions will be introduced to simplify equations 4.4-4.7. First a phase will be introduced

$$G_{kk'}(t, t') \equiv \tilde{G}_{kk'}(t, t') \exp \left[ -i \int_{t_0}^{t} d\tau \epsilon_{k\sigma}(\tau) + i \int_{t_0}^{t'} d\tau \epsilon_{k'\sigma}(\tau) \right], \quad (4.8)$$

it is also helpful to define

$$\tilde{G}_{kk'}^{R}(t, t') \equiv -i\theta(t - t') g_{kk'}(t, t'),$$
$$\tilde{G}_{kk'}^{A}(t, t') \equiv i\theta(t' - t) g_{kk'}(t, t'),$$

these definitions allow the “less than” Green’s function to be rewritten as

$$\frac{\delta}{\delta t} \tilde{G}_{kk'}(t, t') = \sum_{k''} \int_{-\infty}^{t'} dt \tilde{\Sigma}_{kk''\sigma}(t, \bar{t}) g_{k'k''\sigma}^{*}(t', \bar{t})$$
$$- \sum_{k''} \int_{-\infty}^{t} dt \tilde{\sigma}_{kk''\sigma} \tilde{G}_{k'k''\sigma}^{*}(\bar{t}, t'),$$

where $g_{k'k''\sigma}^{*}(t', \bar{t})$ is the complex conjugate of $g_{k'k''\sigma}(t', \bar{t})$ and $\sigma_{kk'}$ is found by replacing $\tilde{G}$ with $\tilde{\Sigma}$ and replacing $g$ with $\sigma$ in Eqs. 4.9. The retarded Green’s function becomes

$$\frac{\delta}{\delta t} g_{kk'}(t, t') = -\sum_{k''} \int_{t'}^{t} dt \tilde{\sigma}(t, \bar{t}) g_{k'k''\sigma}(\bar{t}, t'),$$

To solve this system numerically, a Crank-Nicholson implicit scheme will be used.

This approach to the solution of an integro-differential equation is of order $\Delta t^2$ in
accuracy and has been shown to be a stable method for describing similar systems, such as heat diffusion. Numerical integration of these coupled equations will occur on a two dimensional time grid (in \( t \) and \( t' \)). If the grid spacing is \( \delta \) then a function of \( t \) and \( t' \), such as \( g_{kk'} \), can be expressed as \( F(t, t') = F(i\delta, j\delta) \), where \( i \) and \( j \) are integers. Setting \( m = t \) and \( n = t' \), Eqs. 4.10 and 4.11 can be written as

\[
\tilde{G}_{kk', \sigma}(m, n) = \tilde{G}_{kk', \sigma}(m - 1, n) + \sum_{k''} \frac{1}{2} \delta^2 \sum_{i=m-1}^{m} \left[ \sum_{j=0}^{n} c_j \tilde{\Sigma}_{kk'' \sigma}(i, j) g_{k'' k'}(n, j) - \sum_{j=0}^{i} c_j \sigma_{kk'' \sigma}(i, j) \tilde{G}_{k'' k \sigma}(i, n) \right] \quad (4.12)
\]

\[
g_{kk', \sigma}(m, n) = g_{kk', \sigma}(m - 1, n) - \sum_{k''} \frac{1}{2} \delta^2 \sum_{i=m-1}^{m} \sum_{j=n}^{n} c_j \sigma_{kk'' \sigma}(i, j) g_{k'' k' \sigma}(j, n) \quad (4.13)
\]

where \( c_j = 1/2 \) for \( j = 0, n, i \) and 1 for all other values of \( j \).

Moving all terms of time \((m,n)\) to the right-hand side of Eq. 4.13 and applying the conditions \( g_{kk'}(t, t) = \delta_{k, k'} \) arising from equal-time commutation relations, the final form of the retarded Green’s function can be written as

\[
g_{kk', \sigma}(m, n) + \frac{1}{4} \delta^2 \left[ \sigma_{kk', \sigma}(m, n) + \sum_{k''} \sigma_{kk'' \sigma} g_{k'' k' \sigma}(m, n) \right] = g_{kk', \sigma}(m - 1, n) - \frac{1}{2} \delta^2 \left[ \frac{1}{2} \sigma_{kk', \sigma}(m - 1, n) \right.

+ \sum_{k''} \left. \frac{1}{2} \sigma_{kk'' \sigma}(m - 1, m - 1) g_{k'' k' \sigma}(m - 1, n) + \sum_{i=m-1}^{m} \sum_{j=n+1}^{i-1} \sigma_{kk'' \sigma}(i, j) g_{k'' k' \sigma}(j, n) \right] \quad (4.14)
\]

The final form of the discrete “less than” Green’s function is more complex, the boundary conditions being different for \( t \neq t' \) and \( t = t' \) cases. For the \( t \neq t' \) case,
the final form for the "less than" Green's function can be written as

\[
\tilde{G}_{kk'}(m, n) = \frac{1}{4} \delta^2 \left[ \tilde{\Sigma}_{ kk'}(m, n) + \sum_{k''} \sigma_{kk''}(m, m) \tilde{G}_{kk''}(m, n) \right] \\
= \tilde{G}_{kk'}(m - 1, n) + \frac{1}{4} \delta^2 \tilde{\Sigma}_{ kk'}(m - 1, n) \\
+ \frac{1}{2} \delta^2 \sum_{k''} \left\{ \sum_{i=m-1}^m \left[ \sum_{j=0}^{n-1} \tilde{\Sigma}_{ kk''}(i, j) g_{kk''}(n, j) \right] - \sum_{j=0}^{n-1} \sigma_{kk''}(i, j) \tilde{G}_{kk''}(j, n) \right\} \\
- \frac{1}{2} \sigma_{kk''}(m - 1, m - 1) \tilde{G}_{kk''}(m - 1, n) \right\}
\]  
(4.15)

For equal times, \( t = t' \), the solutions to Eq. 4.4 and its conjugate Eq. 4.5 must agree. More rigorously, at \( t = t' \), the condition \( \frac{d}{dt} \equiv \frac{d}{dt} \left|_{t=t'} \right. \) must hold. Application of this condition to discretized forms of Eqs. 4.4 and 4.5 yields the final form of the "less than" Green's functions for \( t = t' \)

\[
\tilde{G}_{kk'}(m, m) - \frac{1}{2} \delta^2 \tilde{\Sigma}_{ kk'}(m, m) + \frac{1}{4} \delta^2 \sum_{k''} \left[ \sigma_{kk''}(m, m) \tilde{G}_{kk''}(m, m) \right] \\
+ \sum_{k''} \left[ \sigma_{kk''}(m, m) \tilde{G}_{kk''}(m - 1, m - 1) \right] = \tilde{G}_{kk'}(m - 1, m - 1) \\
+ \frac{1}{2} \delta^2 \tilde{\Sigma}_{ kk'}(m - 1, m - 1) - \frac{1}{4} \delta^2 \sum_{k''} \left[ \sigma_{kk''}(m - 1, m - 1) \tilde{G}_{kk''}(m - 1, m - 1) \right] \\
+ \tilde{G}_{kk''}(m - 1, m - 1) \tilde{G}_{kk''}(m - 1, m - 1) + \frac{1}{2} \delta^2 \sum_{i=m-1}^m \sum_{j=0}^{n-1} \left[ \tilde{\Sigma}_{ kk''}(i, j) g_{kk''}(i, j) \right] \\
- \sigma_{kk''}(i, j) \tilde{G}_{kk''}(j, i) + g_{kk''}(i, j) \tilde{\Sigma}_{ kk''}(j, i) - \tilde{G}_{kk''}(i, j) \sigma_{kk''}(i, j) \right) 
\]  
(4.16)

The retarded Green's function matrix is solved using the equal time commutation condition, setting the diagonal elements of \( g_{kk'} = \delta_{kk'} \). Matrix elements in \((t, t')\) are solved outward from the diagonal towards the upper right and lower left corners. The
solution of $\tilde{G}^<$ requires the solution of $g$ and the initial $t = 0$ occupation of all states $k$. The “less than” Green’s function matrix is solved down the diagonal, from top left corner to the bottom right. From this, the occupation of the $k$ electronic states as a function of time can be examined since at equal times, $\tilde{G}^<_{kk}(t, t) = G^<_k(t, t) = n_k(t)$. For both the “less than” and retarded Green’s functions, each step in $(t, t')$ requires the solution of $k^2$ simultaneous equations, and is accomplished through the use of fast linear algebra routines found in the Engineering and Scientific Software Library (ESSL) produced by IBM for RS6000 and SP2 Unix workstations.

4.4 Preliminary Calculations

In this thesis, Numerical implementation of the non-equilibrium Green’s function approach discussed above has only been attempted for degenerate states of the simple Hamiltonian of Eq. 4.1. This model, though unphysical, does help to illustrate the importance of impurity adsorbates for hot electron relaxation. The impurity scattering term of Eq. 4.1, $V_{k,k'} c_{k',\sigma}^\dagger c_{k,\sigma}$, models, phenomenologically, how an impurity potential, $V$, may couple electronic states, scattering (unoccupying) a state $k$ into (occupying) a state $k'$. The two-level problem was examined to check the integrity of the model. For two degenerate states, one occupied, the other unoccupied at $t = 0$, an oscillatory behavior is observed in the occupation number of each state. This result is in agreement with the analytical solution to this model (Fig. 4.1). Increasing the
coupling strength, $V$, increases the frequency of this oscillation, again as predicted by the analytical solution (Fig. 4.2). Though not a remarkable result in itself, it does indicate that impurities, by increasing the coupling constant, induce a new channel for hot electron relaxation. The stronger this impurity potential, the more effective the scattering.

Future implementations of this approach should include non-degenerate electronic states, electron-phonon coupling, and more realistic, energy conserving impurity scattering terms. This model will allow such interactions to be studied in depth, so that a deeper understanding of electronic relaxation mechanisms, especially with respect to nanoshells, may be gained.
Figure 4.1  Test of Non-Equilibrium Greens Function Implementation. Calculation performed for degenerate states, one occupied \((n=1)\) the other unoccupied at \(t=0\). Top: Analytic solution for two-level problem with scattering potential, \(V = 0.007\). Bottom: Result of calculation using Green's function approach for \(V = 0.007\).
Figure 4.2  Effect of $V$ on Occupation Number. Results of Green's function calculation where the dashed line represents a calculation with $V = 0.05$ and the solid line reflects an identical calculation with $V = 0.01$. 
Chapter 5

Acoustic Mode Oscillations of Gold Nanoshells

5.1 Introduction

Recent ultrafast pump-probe spectroscopy experiments involving metal nanoparticles indicate that rapid heating of the metal nanoparticle can result in the excitation of acoustic radial oscillations (breathing modes) [47, 48, 49, 50]. It is believed that the oscillations occur as a result of fast electron-phonon coupling between the hot electron distribution created by the femtosecond pulse and the gold lattice. A hot electron distribution is created in the nanoparticle by means of a femtosecond laser pulse. This energy is transferred to the nanoparticle lattice, inducing an initial expansion of the particle. Since such heating of the gold lattice is isotropic, only radial oscillations are involved. Radial expansion of the nanoparticle changes the electron density of the particle, in turn changing the particle’s plasmon resonance energy. The probe signal, due to the change in the plasmon resonance, experiences a shift in absorption. Since this shift directly corresponds to the acoustic oscillation of the nanoparticle, the frequency of the oscillation is the measured oscillation frequency of the absorption.

It is reasonable to suggest that pump-probe spectroscopy of Au/Au₂S and Au/Si nanoshells might excite the acoustic modes of this more complex structure. In this
chapter a theoretical description of acoustic radial oscillations will be presented, based on a continuum elastic model. This model will be applied to the case of gold nanoshells and the results will be discussed.

5.2 Theory

Following the formalism presented by Lamb [51] and Love [52], the equation of motion of a three dimensional elastic body is given by [53]

\[
\rho \delta^2 \mathbf{D}/\delta t^2 = (\lambda + 2\mu) \nabla (\nabla \cdot \mathbf{D}) + \mu \nabla \times \nabla \times \mathbf{D}
\]  
(5.1)

where \( \mathbf{D} \) is the displacement, \( \lambda \) and \( \mu \) are Lamé's constants and \( \rho \) is the density. For the simple case of a uniform, homogeneous sphere, a stress free boundary condition is applied at the sphere surface, \( r = a \).

\[
\sigma_{rr}|_{r=a} = \left[ \left( \lambda + 2\mu \right) \frac{\delta}{\delta r} + \frac{2\lambda}{r} \right] D_r + \frac{\lambda}{r} \left( \frac{\delta}{\delta \theta} + \cot \theta \right) D_\theta + \frac{\lambda}{r \sin \theta} D_r = 0
\]  
(5.2)

\[
\sigma_{r\theta}|_{r=a} = \mu \left[ \left( \frac{\delta}{\delta r} \right) D_\theta + \frac{1}{r} \frac{\delta D_r}{\delta \theta} \right]_{r=a} = 0
\]  
(5.3)

\[
\sigma_{r\psi}|_{r=a} = \mu \left[ \left( \frac{\delta}{\delta r} - \frac{1}{r} \right) D_\psi + \frac{1}{r \sin \theta} \frac{\delta D_r}{\delta \psi} \right]_{r=a} = 0
\]  
(5.4)

where \( \sigma_{xx} \) are the radial components of the stress tensor in spherical polar coordinates.

To obtain a solution for Eq. 5.1, the displacement, \( \mathbf{D} \), is expressed as a combination of scalar, \( \phi_0 \), and vector potentials, \( \Phi_1, \Phi_2 \) (\( \Phi_i = (r \phi_i, 0,0) \))

\[
\mathbf{D} = \nabla \phi_0 + \nabla \times \Phi_1 + \nabla \times \nabla \times \Phi_2
\]  
(5.5)
Using the above expression for \( \mathbf{D} \), the general solution for Eq. 5.1 is found, where

\[
\phi_i(r, t) = \sum_{l,m} A_{l,m}^i j_l \left( \frac{\omega_{l,m} r}{v_i} \right) Y_l^m(\theta, \psi) e^{-i\omega_{l,m}t} \tag{5.6}
\]

where \( j_l \) are spherical Bessel functions, \( Y_l^m \) are spherical harmonics, \( \omega \) is the angular frequency, \( v_0 \) is the longitudinal sound velocity \( (v_0 = \sqrt{(\lambda + 2\mu)/\rho}) \) and \( v_1 \) and \( v_2 \) are the transverse sound velocities \( (v_1 = v_2 = \sqrt{\mu/\rho}) \). Applying the stress tensor boundary conditions from Eqs. 5.2-5.4, two eigenvalue equations can be derived. The first solution, Eq. 5.7, defines toroidal oscillations - oscillations that do not change the volume of the sphere (Fig. 5.1). The second eigenvalue equation, Eq. 5.8, defines oscillations that include volume oscillations of the sphere (Fig. 5.1).

\[
\dot{j}_{l+1}(\eta) - \frac{l-1}{\eta} j_l(\eta) = 0 \tag{5.7}
\]

\[
2\dot{j}_{l+1}(\xi) \frac{\xi}{\eta^2} \left[ 1 + \frac{(l-1)(l+2)}{\eta} \left\{ \frac{j_{l+1}(\eta)}{j_l(\eta)} - \frac{l+1}{\eta} \right\} \right] + j_l(\xi) \left[ -\frac{1}{2} + \frac{(l-1)(2l+1)}{\eta^2} \left\{ 1 - \frac{2l(l-1)(2l+1)}{\eta^2} \frac{j_{l+1}(\eta)}{j_l(\eta)} \right\} \right] = 0 \tag{5.8}
\]

Here, \( \eta = \omega a/v_0 \) and \( \xi = \omega a/v_1 \). For the case of nanoparticles excited during pump-probe experiments, the exchange of energy from the hot electron distribution to the lattice is assumed to be radially isotropic. Isotropic heating allows only for the radial \( (l=0) \) modes to be excited, modes described by Eq. 5.8. The roots of Eq. 5.8 then yield the normal modes of oscillation for simple, homogeneous nanospheres and can serve as the first approximation to the normal modes of nanoshells.
For the case of a nanoshell, a solid core with a layer of a second material, Equation 5.1 results in an eigenvalue equation whose roots yield the normal radial modes of the shell. Solutions for the radial modes come from solving a series of coupled equations for describing oscillation of the shell material and the core material. Boundary conditions are similar to those of the solid sphere, where elements of the stress tensor were set to zero at the sphere radius. In addition, the elements of the stress tensor at the interface are matched, so that the net change is zero. The coupled equations can be solved as a 6x6 determinant set to zero, the l=0 roots yielding the normal radial modes of vibration.

5.3 Normal Mode Calculations

Solutions of the vibrations of a solid sphere with radius, R = 46.5 nm, are found in Table 5.3 for timescales appropriate for observation under ultrafast pump-probe spectroscopy measurements(11-2 ps).

The numerical solutions for the nanoshell model are shown in Table 5.1. Solutions to the 6x6 determinant discussed above were obtained by a search algorithm, stepping through values of mode frequencies and looking for a zero value. As indicated by Table 5.2, the normal mode spectrum for the nanoshell is much more complex than that of a simple sphere. It should be noted that this calculation for the modes of a shell is dependent upon the zero cutoff used to determine an actual zero solution of the
6x6 determinant. This arbitrary zero designation, the difference between a numerical zero and an actual zero, will cause the number of normal modes to increase as the numerical value of zero used to determine a solution increases. However, it is clear that regardless of the numerical error, the solution to the spherical shell is much more complex. For this work, numerical zero was calculated as any solution to the determinant less than $10^{-20}$.

Assuming the use of a continuum model is valid to model nanoshells with very thin gold layers, the solutions of the shell calculation indicate a large number of modes available for excitation. Because of this, it is unlikely that such modes will be observable during ultrafast pump-probe measurements. A finite dispersion of nanoshell geometries, coupled with the number of available oscillatory modes to excite, should cause any shift in the plasmon resonance measured by the probe beam to be “washed-out”.

However, it is unclear if the continuum model for the gold nanoshell system does, in fact, apply. With a thin gold layer, on the order of only a few nanometers thick, the oscillatory modes should depend upon the number of atomic layers present. This discreteness may violate the continuum model for thin layers and require other approaches such as an empirical molecular mechanics method for a reliable solution.
**Table 5.1** Periods of Normal Modes (l=0) for Gold Nanosphere (R=46.5 nm)

<table>
<thead>
<tr>
<th>Period (×10⁻¹² s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.4</td>
</tr>
<tr>
<td>4.8</td>
</tr>
<tr>
<td>3.2</td>
</tr>
<tr>
<td>2.4</td>
</tr>
</tbody>
</table>

**Table 5.2** Periods of Normal Modes (l=0) for Gold-Silicon nanoshell (Rᵢ = 43 nm, Rₒ = 46.5 nm)

<table>
<thead>
<tr>
<th>Period (×10⁻¹² s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.8</td>
</tr>
<tr>
<td>5.7</td>
</tr>
<tr>
<td>5.2</td>
</tr>
<tr>
<td>4.8</td>
</tr>
<tr>
<td>4.5</td>
</tr>
<tr>
<td>4.3</td>
</tr>
<tr>
<td>3.9</td>
</tr>
<tr>
<td>3.6</td>
</tr>
<tr>
<td>3.3</td>
</tr>
<tr>
<td>3.0</td>
</tr>
<tr>
<td>2.8</td>
</tr>
<tr>
<td>2.6</td>
</tr>
<tr>
<td>2.5</td>
</tr>
<tr>
<td>2.3</td>
</tr>
<tr>
<td>2.2</td>
</tr>
<tr>
<td>2.1</td>
</tr>
</tbody>
</table>
Figure 5.1 Schematic view of vibrational modes of a solid sphere. Top: Toroidal solutions (Eq. 5.7). Solutions involve oscillation of the shell in directions tangent to the shell surface. Bottom: Spheroidal solutions (Eq. 5.8). Solutions include oscillations that have components normal to the sphere. $l=0$ isotropic modes are depicted above.
Chapter 6

Conclusion

This thesis has examined how environmental factors, such as the solvent and impurities found within the solvent, can influence hot electron relaxation times for gold nanoshells. Working from experimental data collected by R. Averitt and S. Westcott, the interaction between the local nanoshell environment and the shell’s free electron surface has been found to be mostly the result of electronic scattering mechanisms. In order to gain an understanding of how the solvent and solvent impurities can influence the surface electronic structure of the gold nanoshell, thereby modifying the hot electron relaxation, the specific solvents and impurities were modeled using empirical and \textit{ab initio} quantum chemical approaches.

Experimental data indicated that nanoshells dispersed in polyvinyl alcohol experienced a faster relaxation time than shells dispersed in water. However, attempts made to model PVA and water environments on a noble metal surface seem to indicate that, as far as the metal electronic structure is concerned, very little difference exists in the way these two solvents interact with the metal surface. Although these chemical models are by no means exact, they suggest that there may be some other mechanism, possibly a solvent impurity such as sulfur, present during nanoshell syn-
thesis that might perturb the nanoshell surface potential strongly enough to influence hot electron relaxation.

Sulfur adsorbates were then modeled on the nanoshell surface. A strong interaction between sulfur and the noble metal substrate model, evident in plots of the sulfur/noble metal effective potential, indicates that perturbation of the nanoshell surface potential is possible as a result of surface adsorbates. However, in the case of sulfur, this type of adsorbate is difficult to experimentally detect, as the sulfur of the Au$_2$S core is indistinguishable from sulfur adsorbed on the shell surface.

Further pump-probe measurements by S. Westcott involved experiments designed to allow control of the adsorption of impurities on the nanoshell surface. Hot electron relaxation times could be continuously modified (reduced) by increasing the concentration of p-aminobenzoic acid in an aqueous suspension of gold nanoshells, until reaching a saturation point. Similar experiments where the impurity molecule, p-mercaptobenzoic acid, was added in increasing concentrations had no effect. These two molecules were modeled using empirical and \textit{ab initio} means to determine their effects on the metal surface potential. Striking differences were observed between these two molecules and their interactions with the noble metal surface. p-Aminobenzoic acid strongly perturbed the electronic potential of the noble metal, while p-mercaptobenzoic acid’s effect was no more significant than the calculations performed for water. This calculation presents strong indications that the interaction
between metal surface and environment is electronic in nature and that the strength of this interaction is due to the chemical nature of the relationship between the impurity and noble metal surface.

In the third section of this thesis, the formalism and implementation of a non-equilibrium Green's function method for describing nanoshell dynamics was introduced. The use of such an approach allows for a detailed understanding of the dynamics of hot electron distributions. Being a quantum mechanical analogue of the Boltzmann transport equations, the role of electron-impurity, electron-phonon and electron-electron interactions in hot electron relaxation can be studied in detail. This method, currently implemented only for degenerate electronic states under a simple impurity scattering model, suggests that electronic factors can have a strong influence on hot electron relaxation.

Lastly, calculations for acoustic oscillations of gold nanoshells have been presented. Although not directly related to the principle topic of this thesis, impurity scattering, it does concern the role of electron-phonon coupling between the hot electron distribution and the nanoshell lattice. The formalism of Lamb, and later by Nishiguchi, is presented in the case of oscillations of a solid sphere. Next the formalism of Tamura, et.al. is introduced, providing the solution of acoustical oscillations of spherical layered structures, such as nanoshells. These modes, though not experimentally de-
tected, may illustrate a means by which the optical excitation of nanostructures can be converted into mechanical energy.

The study of hot electron relaxation for gold nanoshells indicates that this system can be strongly influenced by environmental factors. By taking advantage of this strong coupling to the environment, the lifetimes of the excited electronic distribution can be controlled and adapted to suit a specific need. Applications where a rapid recovery time of the optical absorption, such as optical filters or detectors, can be realized by modifying the embedding medium of the nanoshells. The possible acoustic modes of gold nanoshells suggest conversion of optical to mechanical energy. This mechanical energy might be harnessed to create future optically driven nano-devices such as optically driven mechanical pumps or motors. Certainly more work into the nature of the electronic properties of gold nanoshells is warranted so that the novel properties of these nanoparticles may be utilized.
Bibliography


