11-14-2017

Diffusion on Silver Nanorod Surfaces: Mechanisms of Fast Diffusion at Low Temperature

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Ag nanorods may serve as sensors in the detection of trace amounts of chemical agents, even single molecules, through surface enhanced Raman spectroscopy (SERS). However, thermal coarsening of Ag nanorods near room temperature limits their applications. In this work, we examine this thermal instability through molecular dynamics simulations and molecular statics calculations in order to elucidate the process. From these computational methods, it is realized that the thermal instability of Ag nanorods is the result of rapid surface diffusion, and we hypothesize that the thermal stability can be enhanced by the addition of a thin dielectric cap. This hypothesis is then tested through the use physical vapor deposition, electron microscopy characterization, and SERS tests. It is shown that the proposed method is effective in stabilizing both morphology and sensitivity of Ag nanorods, confirming the findings of the computational study and the prediction based on those findings. The results of this work extend the applicability of Ag nanorods as chemical sensors to higher temperatures.
Diffusion on Silver Nanorod Surfaces: Mechanisms of Fast Diffusion at Low Temperature

Lou Michael Bachenheimer

B.S., University of Connecticut, 2010

A Dissertation
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
at the
University of Connecticut
2017
APPROVAL PAGE

Doctor of Philosophy Dissertation

Diffusion on Silver Nanorod Surfaces:
Mechanisms of Fast Diffusion at Low Temperature

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AKNOWLEDGEMENTS

I would like to start by thanking my amazing wife Kelley, whose patience, support, and understanding were instrumental to me completing this dissertation. Just like in so many other cases, I couldn’t have done it without you. Similarly, I have to thank my family. I’m truly blessed to have such a massive support network.

Next, I would like to thank my major advisor Dr. Hanchen Huang and co-advisor Dr. Stephen Stagon for their invaluable guidance and mentoring over the past six years. The combination of critical analysis and optimistic support yielded a fantastic environment for learning.

I would also like to thank my collaborators Dr. Paul Elliott and again Dr. Stephen Stagon for their aid in running experimental studies.

Finally, I would like to thank my associate advisors Dr. Eric Jordan and Dr. Michael Pettes for their aid in completing my doctoral studies and continuing support.
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<tr>
<td>Å</td>
<td>Angstroms</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>Δt</td>
<td>Change in time / Timestep</td>
</tr>
<tr>
<td>∇</td>
<td>Del operator</td>
</tr>
<tr>
<td>ε</td>
<td>Lennard-Jones depth</td>
</tr>
<tr>
<td>σ</td>
<td>Lennard-Jones intercept</td>
</tr>
<tr>
<td>μ</td>
<td>Chemical potential</td>
</tr>
<tr>
<td>μVT</td>
<td>Grand canonical ensemble</td>
</tr>
<tr>
<td>ρ</td>
<td>Change in electron charge density</td>
</tr>
<tr>
<td>φ</td>
<td>EAM pairwise potential term</td>
</tr>
<tr>
<td>Γ</td>
<td>Jump frequency</td>
</tr>
<tr>
<td>a</td>
<td>Acceleration</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volts</td>
</tr>
<tr>
<td>E</td>
<td>Energy</td>
</tr>
<tr>
<td>E\textsubscript{a}</td>
<td>Activation energy</td>
</tr>
<tr>
<td>E\textsubscript{k}</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>E\textsubscript{T}</td>
<td>Thermal energy</td>
</tr>
<tr>
<td>EAM</td>
<td>Embedded Atom Model</td>
</tr>
<tr>
<td>EBPVD</td>
<td>Electron Beam Physical Vapor Deposition</td>
</tr>
<tr>
<td>F</td>
<td>Force</td>
</tr>
<tr>
<td>FCC</td>
<td>Face center cubic</td>
</tr>
<tr>
<td>FEA</td>
<td>Finite Element Analysis</td>
</tr>
<tr>
<td>GLAD</td>
<td>Glancing Angle Deposition</td>
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<tr>
<td>k\textsubscript{B}</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>k\textsubscript{e}</td>
<td>Coulomb’s constant</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>L</td>
<td>Lagrangian</td>
</tr>
<tr>
<td>LAMMPS</td>
<td>Large-scale Atomic/Molecular Massively Parallel Simulator</td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>MEP</td>
<td>Minimum Energy Path</td>
</tr>
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<td>MS</td>
<td>Molecular Statics</td>
</tr>
<tr>
<td>n</td>
<td>Number of system degrees of freedom</td>
</tr>
<tr>
<td>ns</td>
<td>Nanoseconds</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometers</td>
</tr>
<tr>
<td>N</td>
<td>Number of atoms</td>
</tr>
<tr>
<td>NEB</td>
<td>Nudged Elastic Band</td>
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<td>NPT</td>
<td>Canonical ensembles</td>
</tr>
<tr>
<td>NVE</td>
<td>Micro canonical ensemble</td>
</tr>
<tr>
<td>NVT</td>
<td>Canonical ensembles</td>
</tr>
<tr>
<td>OAD</td>
<td>Oblique Angle Deposition</td>
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<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
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<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>q</td>
<td>Electric charge</td>
</tr>
<tr>
<td>Q</td>
<td>Electric charge</td>
</tr>
<tr>
<td>r</td>
<td>Distance between two particles</td>
</tr>
<tr>
<td>s</td>
<td>Seconds</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>SERS</td>
<td>Surface Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>T_0</td>
<td>Desired temperature</td>
</tr>
<tr>
<td>Tm</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-High Vacuum</td>
</tr>
<tr>
<td>v</td>
<td>Atomic vibrational frequency</td>
</tr>
<tr>
<td>v</td>
<td>Velocity</td>
</tr>
<tr>
<td>v'</td>
<td>Initial velocity</td>
</tr>
<tr>
<td>V</td>
<td>Potential energy / Volume</td>
</tr>
<tr>
<td>x</td>
<td>Position</td>
</tr>
<tr>
<td>x'</td>
<td>Initial position</td>
</tr>
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</table>
Chapter 1: Introduction

1.1: Introduction

This section presents our motivation for studying materials and nanotechnology. Before we get into the specifics problem addressed in this dissertation, we must first understand the basis for studying materials and nanotechnology.

Material science has been a major focus of engineering since ancient times, consisting of creating or combining materials in order to elicit desired properties. A classic and simple example is the bimetallic strip used in thermostats. By understanding the properties of each metal, the thermostat engineer knows that one metal will have a greater expansion than the other when exposed to heat. Attaching the two metal strips together to create a bimetallic strip will result in a material that will bend as temperature increases. While this example is a simple one, it touches on all three major factor of material science: process, structure, and properties. The process is how each material is made. In this example, the process would be how each metal was forged from the corresponding ores and then how the metals were combined to form the bimetallic strip. The structure of a material is the atomic structure,
which describes how the individual atoms form the materials crystal structure. The structure of a material is important in order to understand where, atomically, the material properties come from. Finally, the material properties are the descriptors of how the material reacts in different situations, such as stress, strain, or expansion due to heat as used in our bimetallic strip example.

1.1.1: Experimentation vs Modeling

Historically, material properties were studied and measured empirically through macro-scale experimentation. In order to measure thermal expansion, for example, samples would be heated to different temperatures and the expansion would be recorded. While this method of material property study is certainly effective, it does have several restrictions. First and foremost among these restriction is the fact that experimental procedures do not explain why the properties are what they are, and as such can not be used to predict properties for new materials. This severely limits the ability to design new materials to have specifically desired properties.
Modern technology partially alleviates this restriction with discoveries such as the scanning tunneling microscope by IBM in 1981.\(^1\) The ability to experimentally view nanostructure, commonly considered to be structure with at least one dimension less than 100 nanometers (nm), allows experimental scientists to at least partially view the crystallographic explanations of material properties. However, there is still a limit on just how small something can be while still being experimentally observable,\(^2\) as there is also a limit on how small of a timespan can be experimentally observed.

The second and third restrictions on experimental studies into material science are the cost of the physical materials to be tested and the potential risk of testing under dangerous conditions. For example, if one wished to experimentally discover the melting point of a diamond, he or she would have to purchase not only the diamond, but also the equipment to heat the sample to over 4500 K\(^3\) as well as temperature shielding to maintain safety. Furthermore, the scientists experiment would likely fail at first due to the fact that diamond will sublimate rather than melt if not kept under extreme pressure.

As an alternative to experimental studies, one can instead utilize modeling. Modeling resolves many of the primary issues resulting from empirical experimentation, but has its own limitations. Modeling easily deals with the cost and danger issues that experimental
studies struggle with, since when doing modeling all one needs is a computer. There is also no direct limitation on size, as different models can be applied for scales. For example, macro scale materials can be studied by utilizing finite element analysis (FEA), which subdivides the larger object into smaller elements. Since these elements are significantly small and share boundaries, they can then be solved by a series of boundary value differential equations. On the smallest level, density functional theory (DFT) can be used to model individual electrons, capturing the quantum mechanical effects in a material. Molecular Dynamics (MD) has a slightly larger scale than DFT and treats entire atoms as individual particles that can then be treated classically. The scale of a model has its own inherent limitations. Smaller scale modeling - such as DFT - can be more accurate as they make less assumptions. However since each electron must be modeled, far more computing power is necessary to run a computational simulation. MD, by comparison, makes the assumption that each atom can be treated as a single particle, and can therefore model a larger object over a longer timescale than DFT while using the same amount of computing power. While the advent of super computing has drastically increased the ability to model smaller scales, computing power is still fundamentally limited, and as such proper modeling requires a
multiscale approach, where the proper modeling technique is used for the proper size and time scale. Figure 1 below shows an example of how multiscale modeling is used.

Figure 1: Multiscale modeling utilizes the proper modeling technique for the timescale and size scale.  

While modeling has distinct advantages over empirical experimentation, such as being able to model smaller scales with less cost and less risk, experimental methods have advantages as well. Since modeling relies on assumptions and a direct input of physics, be it quantum mechanics for DFT, interatomic physics for MD, or continuum mechanics for FEA,
the accuracy of the model is dependent on the accuracy of the inputs. For example, using an inaccurate formula to describe the potential energy between two atoms in MD would result in inaccurate simulation results. Even if all the data and physics is highly accurate, it is possible for the modeler to miss a relevant parameter, resulting in simulation artifacts. Experimental studies are based on physical observation, and as such they are often more accurate.

In order to conduct a proper investigation, one should use both experimental and modeling methods. Experimental methods are used to generate the constants and physics entered into the model. A model can then be used to investigate scales too small for experimentation in order to better understand to root atomic cause of material properties. Finally, these simulation results can be used to make predictions that can then be tested experimentally.

1.1.2: Nanotechnology

As stated earlier, material science is the study of the process, structure, and properties of a material. Just like a material science engineer can use his or her knowledge
of material properties to design a material with specifically desired properties, such as the bimetallic strip mentioned earlier, nanotechnology is also about designing materials to have specific properties. In nanotechnology, however, the nanomaterial can be engineered at the nanoscale to produce properties otherwise unobtainable. For example, capacitance is a function of surface area. By coating the surfaces with nanoparticles, the effective surface area and thus capacitance can be increased. Nanomaterials often possess material properties unique to their size scale. Surface effects, for example, have a much larger influence on the nanoscale, where a larger percentage of the structure’s atoms form said surface. Nanoscience, the pure research of nanostructures, has enormous scientific importance as it helps scientists understand the root crystallographic causes of properties observed in the bulk material. Similarly, nanoscience is also crucial to explain observed macro-scale phenomena.

1.2: Problem Statement

While Ag nanorods have technological importance in many fields, sensing, sealing and electronics are amongst the leaders. Ag nanoparticles can be used in surface-enhanced
Raman scattering (SERS) in order to potentially enhance them by a factor of $10^{11}$, meaning individual molecules can be detected. However, this phenomenon is highly dependent on substrate surface morphology. Ag nanorods can also be used to achieve low temperature metallic sealing. This is due to the fact that even at low temperature Ag nanorods will quickly merge into a film, as shown in figure 2.

Figure 2: SEM of Ag nanorods (a) immediately following fabrication and (b) after 10 s of annealing in air at 475 K (less than 0.4 Tm)

Several reports in the past using other materials such as Cu or Au have suggested that the surface beings to pre-melt, which leads to morphological change. This is not well-understood as the bulk melting temperature of Ag is 965°C and while melting point depression due to nanoscale effects in smaller nanoparticles has been shown, the size of
these structures is well over that of nanoscale size effects. While the diffusion has been widely reported, there is little understanding of the mechanisms allowing fast diffusion at such low temperature. Further, there is little knowledge on the mechanism by which Ag nanorods can merge into a film at low temperature. Understanding what occurs at the atomic level during this process will lead to an ability to potentially inhibit diffusion for use in SERS or enhance it for use in low temperature metallic sealing.

1.3: Proposed Solution

In order to address this issue, a Ag nanorod must first be modeled. Once this is complete, molecular dynamics simulations will be used to model the behavior of atoms on the surface of the Ag nanorod. Looking at the results of the MD simulation, atoms that move on the surface will be identified and the different mechanisms they use to jump from one location to another will be observed. Next, molecular statics (MS) simulations will be used to examine each observed jump mechanism. The nudged elastic band (NEB) method will be used to determine the energy barrier that must be overcome for each jump mechanism. By examining the energy barriers for each of the jump mechanisms used for surface diffusion,
a better understanding of the surface diffusion enforced thermal instability will be achieved, and predictions on how to prevent it will be made. Finally, in order to test the veracity of the simulations, the predictions will be experimentally tested. The nanostructures will be grown using physical vapor deposition (PVD) and the samples will be tested using figure microscopy.

1.4: Background

Before presenting any specifics on the methods or results used, we will first go over the necessary background information needed in order to understand MD, MS, PVD, and SERS.

1.4.1: Molecular Dynamics

Molecular dynamics (MD) is a method for modeling atomic structures in which an entire atom is treated as a single particle. This is done by making use of the Born-Oppenheimer approximation and results in a simulation process much less computationally expensive than standard quantum mechanical models. This allows for models consisting of
$10^9$ atoms and for simulations up to nanoseconds in length. In quantum mechanics, particles are described via wave functions and the interactions between particles are described by an energy potential. By treating the entire atom as a point mass, the system can be treated using only classical mechanics, provided there is an accurate function for calculating interatomic potential energy.

In order to understand MD, one must first understand the classical mechanics used to formulate it. Newton’s second law states that sum of the forces acting on an object is equal to mass times acceleration:

$$\Sigma F = m \cdot a$$  \hspace{1cm} (1)

Assuming a constant instantaneous acceleration and integrating with respect to time yields the following:

$$v = v^i + a \cdot \Delta t$$  \hspace{1cm} (2)

In equation (2) above, $\Delta t$ is the change in time, $v$ is velocity, $v^i$ is initial velocity, and $a$ is acceleration. Integrating again with respect to time yields the following:

$$x = x^i + v^i \cdot \Delta t + \frac{a}{2} \cdot \Delta t^2$$  \hspace{1cm} (3)

In equation (3) above, $x$ is position and $x^i$ is initial position. Keep in mind that in the equations above, $F$, $a$, $v$, and $x$ are each vectors, and as such contain $x$, $y$, and $z$ components. When setting up the initial model, each atom is assigned an initial position $x^i$ and an initial velocity
If we assume acceleration to be known (calculating acceleration will be explained shortly) and we then assign a timestep, \( \Delta t \), for use in the model, the simulation can begin. For each atom, start by calculating the acceleration vector affecting it. Then use equation (2) and equation (3) to calculate the new position and velocity vectors respectively. Once this has been done for every atom in the model, the simulation will have been advanced by a timestep of \( \Delta t \). At this point, one uses the new positions to calculate the new acceleration effecting each atom and simply repeats to process above, using the recently calculated positions and velocities to calculate the next set of positions and velocities.

While the process described above seems simple at first, there are several major factors still to consider. First, how is the acceleration acting on each atom calculated? Second, how are boundary conditions, temperature, and pressure controlled? And finally, how do you determine what the timestep value must be?

**1.4.1.1: Interatomic Potentials**

The backbone of a MD simulation is the interatomic potential. This is the model that describes how atoms interact with one another and allows one to calculate the acceleration
acting on each atom. If one rearranges equation (1) we see that acceleration can be defined as the sum of the forces divided by mass.

\[ a = \frac{\Sigma F}{m} \]  \hspace{1cm} (4)

Thus, in order to calculate the acceleration of an atom, one must first calculate each force acting on it. This is where the interatomic potential comes into play. The interatomic potential describes the potential energy on one atom based on the distance from one or more other atoms. Since force is related to potential energy as shown below in equation (5), if one can calculate the potential energies then one can calculate the forces.

\[ F = -\nabla V(x) \]  \hspace{1cm} (5)

In equation (5) above, \( \nabla \) is a three-dimensional derivative and \( V(x) \) is potential energy as a function of position.

The simplest form of potential is called a pairwise potential. In a pairwise potential, only two atoms are considered: The atom in question and one other atom acting on it. A classic example of a pair potential is electrostatic potential, derived from Coulomb’s Law:

\[ V(r) = k_e \cdot q \cdot \frac{Q}{r} \]  \hspace{1cm} (6)

In equation (6) above, \( k_e \) is Coulomb’s Constant, \( q \) is the charge of the atom in question, \( Q \) is the charge of the atom acting on the atom in question, and \( r \) is the distance between the
two atoms. If there were many atoms acting on the atom in question, as is most likely the case, equation (6) could be used for each one, yielding the force each atom exerts on the atom in question.

While the coulombic potential is simple and easy, it only models a repulsive force. In actuality, atoms will experience both an attractive and a repulsive force. The classical example of this in a pairwise potential is the Lennard-Jones potential, as shown in figure 3 below:

![Lennard-Jones potential](image)

Figure 3: Lennard-Jones potential shown in red. Repulsive and attractive components shown in blue. \(^16\)

\[
V_{LJ}(r) = 4 \cdot \varepsilon \cdot \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]
\]  \(\text{(7)}\)
In the Lennard-Jones potential, equation (7) above, \( \varepsilon \) is the depth of the potential well and \( \sigma \) is the finite distance at which the potential energy equals zero. The first term of the equation, the \( r^{12} \) term, represents the repulsive portion of the potential. This term describes Pauli repulsion, which is the repulsive force that is caused when two atoms get close enough for electron orbitals to overlap. The second term of equation (7), the \( r^6 \) term, represents the attractive portion of the potential. This term describes van der Waals forces, which attract atoms together at longer distances. When these attractive and repulsive terms are combined to form the Lennard-Jones potential, a potential energy well is formed, as seen in figure 3 above. This potential well represents the minimum potential energy position, and as such the ideal distance between the two atoms. If the atoms move closer together, Pauli repulsion will push them apart. If the atoms move farther apart, van der Waals forces will pull them together. The exact energy minimum at the bottom of the potential well represents the equilibrium separation distance.

While the potential itself is certainly important for describing the energetic minimum, there is another crucial value when setting up a MD simulation. As the distance between the two atoms increases, the potential energy decreases as the graph in figure 3 approaches zero. With only two atoms being considered, this does not seem to be much of an issue.
However, with thousands of atoms, each being effected by each other atom, the number of calculationsskyrockets. In order to mitigate this, interatomic potentials are made to have a distinct “cutoff distance” after which the interaction is assumed to be zero. Since the potential energy approaches zero as distance increases anyway, this assumption can be made without any significant effect. In the Lennard-Jones potential, this cutoff distance is usually set to $2.5 * \sigma$. With a proper cutoff distance in place, each atom is only effected by a small set of atoms near it, and thus the number of calculations decreases drastically. This also allows for the computational process to be split among computer processors.

With the cutoff distance in place, one hits the issue of having to calculate the distance between each and every atom in order to determine which are within the cutoff. In an effort to make this process more computationally efficient, a “neighbor list” is created for each atom, consisting of all the neighboring atoms within the cutoff distance. Since atoms move, a “skin” is added around the cutoff distance to include atoms that could potentially move within range, and these atoms in the skin are also included in the neighbor list. Both the cutoff distance and this skin can be seen depicted below in figure 4. There are two main factors here that need to be considered: First, how thick does the skin need to be, and second, how often does the neighbor list need to be updated? Both of these factors depend
on how much atomic motion and vibration is expected. A thicker skin and more frequent neighbor list refreshes will make it less likely an atom will be missed, but will also slow down the simulation.

Another method used here, in concert with neighbor lists, are domain lists. Domain lists are formed by first taking the entire simulation cell, or model, and dividing it up into smaller sections, often rectangular prisms or cubes. Each edge of the rectangular prism must
be greater than the cutoff distance in order to ensure that any atom in the domain can only have neighbors in its own domain or an adjacent domain. This means that when refreshing neighbor lists, only atoms in adjacent domains need be considered, speeding up computation. Figure 5 below depicts how domains can be set up in a two-dimensional example.

Figure 5: Domain setup for a two-dimensional example. An atom in the center domain (blue) can only have neighbors from the surrounding domains (green).
While neighbor lists require a distance calculation, domain lists only require dividing up the simulation cell and can be updated much more quickly. In addition, each domain can then be set up in separate processors running in parallel in order to speed up the simulation further.

As stated earlier, the Lennard-Jones potential is a pairwise potential, meaning it models the interaction between two distinct atoms. While this type of approach is sufficient for inert atoms, more complicated atomic structures pose a significant problem for a pairwise potential. In these situations, a multi-body potential is needed. In a multi-body potential, multiple atoms are considered at once, allowing for more accurate atomic interactions.

While there are many distinct multi-body potentials, the one used in this dissertation is called the embedded atom model (EAM). The EAM, seen below in equation (8), combines a pairwise potential with a multi-body effect in order to produce accurate results.\textsuperscript{18,19}

$$V_{EAM} = \sum_i V_i = \sum_i F(\bar{\rho}_i) + \frac{1}{2} \sum_{i \neq j} \varphi(r_{ij})$$

$$\bar{\rho}_i = \sum_{j \neq i} \rho(r_{ij})$$

Equation (8) gives the potential energy acting on atom “i” by all atoms “j”.

\textsuperscript{18,19}
The first term in the EAM potential, the $\rho$ term, is the multi-body effect. Specifically, $\rho$ is the change of the electron charge density from atom “j” at the location of the atom in question, atom “i”. The variable $r_{ij}$ is the distance between atom “i” and atom “j”, and since $\rho$ depends on the location of atom “i”, $\rho$ must therefore be a function of $r_{ij}$. $\bar{\rho}_i$ is then the total electron charge density at the location on atom “i” and is the sum of the contributions of all atoms “j”. Just like in other potentials, the EAM potential has a cutoff distance, so only nearby atoms “j” need be considered, speeding up computation. $F(\bar{\rho}_i)$ is then the total energy required to embed the atom in question (atom “i”) into the existing system (all atoms “j”), as shown in figure 6 below, and is referred to as the total embedding energy.

Figure 6: The total embedding energy is the energy required to embed atom “i” into the system of atoms “j”.
While the first term in the EAM potential takes multiple atoms into account, the second term in the EAM potential shown in equation (8), the $\varphi$ term, represents the pairwise component. Just like in the Lennard-Jones potential or the Coulomb potential, this term only considers two atoms at a time and is a function of the distance between those two atoms. In order to find the total energy acting on a given atom, atom “$i$”, one must sum each of the individual interactions with each other atom “$j$” within the cutoff distance. This term describes the core repulsive forces that result when atoms get too close to each other.

When the multi-body and pairwise terms are combined to form the full EAM potential, there is a significant improvement in accuracy over the Lennard-Jones potential. The dependence on local electron energy density yields a significant improvement when modeling metals specifically. Since the simulations reported in this dissertation use Ag atoms, an EAM potential is used. When using a EAM potential, a file containing the relevant tabulated data is uploaded. The first line of the EAM file will contain information relevant to the specific atom type. This includes the atomic number, atomic mass, lattice constant, and crystal structure type. The second line contains information about the rest of the file. This includes the number of tabulated values for each variable, the spacing used for those arrays, and the cutoff distance. Finally, the file includes tabulated data values for each of
the three functions. These include the embedding energy $F(\bar{\rho}_i)$, the effective charge function, and the density function $\rho(r_{ij})$. The values included in these tables are derived from both experimental methods and quantum mechanical calculations. The values are tested extensively, but it is still a best practice to test the complete potential before use. This can be done by using the potential to calculate known properties such as elastic constants and surface energy.

1.4.1.2: Boundary conditions, temperature, and pressure

As stated earlier, in addition to the interatomic potential needed in order to calculate the acceleration experienced by an atom, boundary conditions, temperature, and pressure must be considered. The boundaries in a simulation can be physical, such as a surface, or unphysical, such as the end of the simulation cell. Temperature control can also be problematic due to the innate nature of temperature for the size scale. On the atomic level, temperature is simply the velocities of the atomic vibrations. This means that temperature can be controlled directly by artificially scaling atomic velocity, but this will also directly affect
the simulation. Atomic level pressure must be measured in terms of atomic stress, or virial stress.

As stated earlier, a boundary can be either physical or unphysical. For the physical boundaries, the interatomic potential should handle them appropriately. When it comes to unphysical boundaries however, the boundary conditions must be set up when first initializing the simulation cell. The simulation cell is the complete set of atoms to be included in the simulation as well as the physical shape that will contain them. The entire simulation must occur in the simulation cell, so its boundaries represent the limits of where any atom can move to.

Before discussing the types of boundaries for a simulation cell, one must first discuss the size limitations for the simulation cell constrained by said boundaries. The first size limitation is perfectly recognizable: the simulation cell cannot be too large. In general, the larger a simulation cell ones uses, the more atoms will be required to fill said simulation cell. As mentioned earlier, there is a limit to computational power available due to the limitations of modern computer technology. If the size of the model grows significantly large, a different modeling scale must be used. The current limit for simulations is an order of magnitude of $10^9$ atoms. There are other boundary options that can be utilized to simulate larger systems
using MD, and these will be discussed in detail later. While less intuitive, there is also a limitation on how small a simulation cell can be. When first modeling a simulation cell, one must take care that the cell has enough room for atoms to experience the necessary interactions with neighboring atoms. This concept will become much more important as we discuss the different specific boundary types.

There are two primary types of boundary condition that can be set for a standard simulation cell: fixed boundaries and free boundaries. In macroscale continuum mechanics, visualizing these two boundary types is fairly straightforward. A fixed boundary cannot move or rotate and a free boundary can. On the atomic scale, a free boundary will consist of a free surface of atoms. These atoms will be able to move without any external stresses or restrictions, and the surface will evolve naturally.

In order to accomplish a fixed boundary on a molecular level, one can instead represent a fixed boundary by “freezing” a group of atoms along said boundary. In order to freeze atoms, there are two options. The first method of freezing is to simply exclude the atoms from the timestep integration. When taking this approach, one must make sure to still include their interaction with the neighboring atoms that are not frozen. Another approach to freezing a group of atoms is simply keep their positions constant. Regardless of
which method is chosen, there are several considerations that must be kept in mind. First, one must remember that temperature on the atomic scale is defined by the velocities of the atoms. A group of atoms that remain perfectly stationary are effectively an area at absolute zero! For this reason, care must be taken when managing temperature, which will be discussed later. A second consideration is the cutoff distance, and this will lead us into a third type of boundary condition, the infinite boundary.

Often times when conducting a MD simulation, one will wish to model a boundary that continues infinitely. This could be the case if one is modeling the surface of a macro scale material. Remember, on the atomic scale most macro scale objects are effectively infinitely large. An atom 1 cm from a surface is effectively infinitely away from an atom on that surface, and thousands of times farther away than the cutoff distance. In order to model an infinite boundary, an area of atoms at least one full cutoff distance deep must be added to that boundary and then frozen. This will ensure that any atom in the original simulation cell can have full interactions with the frozen boundary atoms. There should also be a full cutoff distance between the surface being studied and the frozen atoms, as seen in Figure 7 below. This will mitigate effect caused by the unphysical frozen atoms by making sure none
of the original atoms have to interact with the frozen atoms, but instead interact with atoms in the buffer zone.

![Diagram](image)

**Figure 7:** By adding one cutoff distance of buffer atoms and one cutoff distance on frozen atoms, an infinite boundary can be simulated.

As stated earlier, often times the simulation cell will not be able to contain nearly enough atoms. The number of atoms in a macro scale object is on the order of $10^{23}$, which is fourteen orders of magnitude larger than the maximum number of atoms that can be
contained in the largest MD simulation cell. In order to mitigate this problem, there is a fourth boundary type that can be employed: periodic boundaries. When a periodic boundary is used, the simulation cell is effectively copied and placed on the other side of the simulation cell. If, for example, the simulation cell was a cube with a periodic boundary orthogonal to the x-axis, then the simulation would effectively be an infinite repetition of the simulation cell along the x-axis. So if, as shown in figure 8 below, an atom were to move out of the right side of the simulation cell, it would then enter the left side of the simulation cell. Similarly, an atom near the right edge would be effected by atoms near the left edge. A cube with periodic boundaries in all three directions would effectively be an infinite bulk, with the simulation completely surrounding itself with duplicates. One must note that if periodic boundary conditions are being used, the minimum size of the simulation cell in that direction must be the cutoff distance. If a complete cutoff distance is not used in a direction with periodic boundaries, an atom would be able to interact with its own replica, which means it would interact with itself, resulting in unphysical artifacts.
In most cases, a combination of boundary types will be used. For example, if one wished to simulate an infinite surface, he or she would use periodic boundaries on the x and y directions, an infinite boundary in the negative z direction, and a free boundary in the positive z direction. If, as done later in this dissertation, one wished to model an infinitely long cylinder, one would model a cylinder of atoms at least one cutoff distance tall with cylinder’s axis along the z direction. The x and y directions would be left with free boundaries and the z direction would have periodic boundaries applied.
In order to control the temperature, the velocities of the atoms must be controlled. This can be done in several different ways, either directly or indirectly. The simplest method is to directly scale the velocities of each atom in the simulation. To start, equation (9) below shows the definition of kinetic energy:

\[ E_k = \frac{1}{2} m v^2 \]  

In the equation above, \( m \) represents mass and \( v \) represents velocity. Thermal energy can be expressed using equation (10).

\[ E_T = \frac{n}{2} k_B T \]  

In the equation above, \( n \) represents the system’s degrees of freedom, \( k_B \) is the Boltzmann constant, and \( T \) represents temperature. Setting equation (9) equal to equation (10) provides a method of relating velocity to temperature.

\[ \frac{1}{2} m v^2 = \frac{n}{2} k_B T \]  

In equation (11) above, \( m \) is the mass of the particle and \( v \) is the root mean square speed of the system. Simplifying yields the following expression for temperature as a function of root mean square speed:

\[ T(v) = \frac{n k_B}{m v^2} \]
When direct velocity scaling is implemented, the magnitude of each atom’s velocity vector is scaled periodically in order to maintain the desired system temperature. Since the velocity of every atom in the system is scaled, their relative velocities remain constant. While this method will indeed control the temperature, directly interfering with particle velocities is inherently unphysical and will enforce and unrealistic distribution of atomic velocities. In an actual system, the speed of each atom will be distributed according to a Boltzmann distribution, where an atom’s individual velocity related to its local surroundings. This means that the speeds will be proportional to $e^{-E/k_BT}$.  

A similar method that can be used to control the temperature of the system is the Berendsen thermostat, seen below in equation (12), which uses a differential equation to maintain temperature. Unfortunately, the Berendsen thermostat suffers from the same distribution issue as velocity scaling.

$$\frac{dT}{dt} = \frac{T_0-T}{w}$$

A better method of controlling the system temperature, and the method used in the simulation in this dissertation, is the Nosé-Hoover thermostat. In the Nosé-Hoover thermostat, the system is coupled to a single imaginary, or “virtual”, particle that functions as a heat bath for the entire system. By allowing every atom the ability to interact and
exchange energy with this virtual particle, constant temperature can be maintained. In order to do this, an additional degree of freedom is added to the system. The virtual particle is introduced to the system by adding the following Lagrangian:

\[ L_{\text{virtual}} = g \cdot k_B \cdot T_0 \cdot \ln(s) \]  

(13)

This will then modify the equations of motion by adding a “friction” coefficient \( Q \) to the acceleration equation, where \( Q \) is the coefficient for velocity.

\[ \dot{Q} = \frac{1}{M} \cdot (m \cdot v^2 - k_B \cdot T_0) \]  

(13)

In equation (13) above, \( M \) is the mass of the virtual particle. By comparing equation (13) to equation (11) one notices that when the average kinetic energy of the system equals the desired average kinetic energy, which means the temperature is equal to the desired temperature, then \( Q \) will equal zero and will not have any effect. Since it is proportional to velocity, the larger the difference between the actual temperature and the desired temperature becomes, the more of an impact the Nosé-Hoover thermostat will have. This helps to make it an excellent method of maintaining a temperature equilibrium.

Regardless of which method is used to control temperature, it is important not to include any “frozen” atoms in the process. Since these frozen atoms will all have velocities
of zero, they are all effectively at 0K, or absolute zero, and will drastically lower the average temperature of the system if included.

Finally, the pressure of the system must sometimes be controlled as well. On the atomic scale pressure, and thus stress, is measured as virial stress. The virial stress tensor can be defined as follows:

$$\tau_{ij} = \frac{1}{V} \sum_k \left( -m^k \cdot (v^k_i - \bar{v}_i) \cdot (v^k_j - \bar{v}_j) + \frac{1}{2} \sum l f^{kl} \cdot (x^l_i - x^k_i) \right)$$  \hspace{1cm} (14)

In equation (14) above, V represents the volume of the system, k and l are atoms in the domain, \( m^k \) is the mass of atom “k”, \( v^k_i \) is the \( i^{th} \) component of the velocity of atom “k”, \( \bar{v}_i \) is the \( i^{th} \) component of the average velocity of all atoms in the volume, \( v^k_j \) is the \( j^{th} \) component of the velocity of atom “k”, \( \bar{v}_j \) is the \( j^{th} \) component of the average velocity of all atoms in the volume, \( f^{kl} \) is the \( j^{th} \) component of the force applied on atom “k” by atom “l”, \( x^l_i \) is the \( i^{th} \) component of the position of atom “l” and \( x^k_i \) is the \( i^{th} \) component of the position of atom “k”. The first term represents the kinetic energy of the atoms that are colliding with the interface while the second term is equivalent to the engineering definition of pressure.

With the concept of atomic level pressure established, it is possible to control is using similar methods to those used to control temperature. Direct scaling can be applied to the simulation cell dimensions, thus adding or removing stress. The Berendsen method can again
be used to monitor via a differential equation, or a Nosé-Hoover barostat can be applied that
again makes use of a virtual particle. As with thermostats, this the simulations in this
dissertation will use the Nosé-Hoover barostat.

Now that boundary conditions, temperature control, and pressure control have all
been examined, it is important to look at the different types of thermodynamic ensembles
that can be used. There are three types of thermodynamic ensembles: micro canonical,
canonical, and grand canonical. The ensembles determine which thermodynamic values will
be kept constant in order to run the simulation.

In a micro canonical ensemble, or NVE ensemble, the values held constant are the
number of atoms (N), the volume of the system (V), and the total energy of the system (E).
Since no thermostat is included, this ensemble is best used in isolated or periodic systems
with no heat being transferred.

There are two types of canonical ensembles, NVT and NPT. In each of the two, the
number of atoms (N) and the temperature (T) are held constant. In NVT, the volume is also
held constant. In NPT, the pressure is also held constant. In either example, energy is no
longer constrained to be constant. Canonical ensembles are useful when a thermostat or
barostat is needed.
Finally, in a grand canonical ensemble, or $\mu VT$ ensemble, the values held constant are the chemical potential ($\mu$), the volume of the system (V), and the temperature (T). While not used often in MD simulations due to the limitations of MD, grand canonical ensembles are used for modeling phase changes such as thermal evaporation.

1.4.1.3: Timesteps

The final portion of setting up an MD simulation is to choose an appropriate timestep, $\Delta t$. The timestep is the amount of simulated time that passes with each iteration of the model. Just like when thinking of the framerate in a video, when a larger timestep is used detail can be missed. In addition, larger timesteps can miss crucial atomic motion, and any error will be propagated as the simulation continues. On the reverse side, while smaller timesteps can be more accurate, they will also result in more iterations being needed in order to simulate the same amount of time. This will result in an increase of required computing power. The goal is thus to set the timestep just small enough so that it will capture all relevant atomic motion. This means that typical timesteps range from between five to ten percent of the atomic vibrational period. In metals, this equates to a timestep of
one femtosecond. In metals, heat is transferred by the motion of electrons, but in ceramics heat is transferred by phonons. Phonons are waves of atomic vibration, and as such simulations of ceramics will require a timestep roughly ten times smaller than that used when simulating metals. The accuracy of the simulation is still never perfect, as the timestep is never zero. As such, errors will always propagate as a simulation runs. This is another reason why a multiscale modeling approach is often required, as MD simulations have an inherent limit to length.

At this point, the entire MD process can be modeled. As shown in figure 9 on the next page, the first step is to assign initial values to position, velocity, and time and choose an appropriate timestep. Next, acceleration is calculated and equations of motion are used to predict the next values of position and velocity. Boundary conditions, temperature, and pressure are then controlled as needed and the calculated new positions and velocities are corrected. At this point, any physical properties of interest are calculated and recorded. Finally, the time is advanced by one timestep and the process is repeated.
Figure 9: Simplified model of MD simulation.

1.4.2: Molecular Statics

While MD simulations are used for observing the motion of atoms, molecular static (MS) calculations are used when time does not need to advance. In MS, atoms are not moved to simulate motion. Instead, atoms are moved in order to minimize the total
potential energy of the system. The end result is every atom being moved to the local minimum energy position, or equilibrium location. While MS has issues modeling structures with thermal fluctuation, it remains an excellent tool for calculating local energies and this is how MS was used in this dissertation.

Minimization methods work by calculating potential energy from the interatomic potential and the atom positions, then moving atoms slightly and calculating the total potential energy again to see if it decreased, and repeating. A commonly used method is the conjugate gradient method. This method assumes that the best method of minimization is to move atoms in the direction of steepest decent. The gradient of the energy is used to determine this direction. Once the direction is determined, the system can be reduced to a single degree of freedom and can be minimized to find the optimal position. The process is then repeated until a local minimum for the total energy is reached.

The minimization method used here in the MS calculations is called the quick-min method. This method was developed by Sheppard in 2008 and uses damped dynamics to move atoms to their minimum energy positions.

The specific reason MS was used in this dissertation was to utilize the nudged elastic band (NEB) method. The NEB method is used to calculate the minimum energy path
(MEP) an atom can take in order to move from one location to another. When a NEB calculation is set up, the atom in question is given an initial and final position. Two replicas of the simulation cell are then made. In replica 1, the moving atom is placed in its starting position. In replica 2, the moving atom is placed in its final position. The two replicas are then minimized, as discussed earlier, in order to make sure that the initial and final positions of the atom in question are indeed local energy minima. Next, a user-provided number of replicas are created. In each replica, the atom in question is placed evenly along a straight path between the initial and final positions. For example, if five replicas were made, replica 1 would be the system with the moving atom in the minimized initial position. Replica 5 would be the system with the moving atom in the minimized final position. Replicas 2, 3, and 4 would respectively have the moving atom ¼, ½, and ¾ of the way between the minimized initial and minimized final positions. Figure 10 below shows an example with all twenty-four replicas superimposed together. In the figure, the grey atoms represent a FCC 111 surface and the orange atoms form an A-type step on said surface. Here the atom to be moved is shown in yellow. All 24 replicas are superimposed in the figure, and one can see that the moving atom is distributed evenly along a line connecting the initial and final positions. Each replica is exactly the same, with the exception of the moving atom’s location.
Figure 10: 24 NEB replicas superimposed, before any minimization. The moving atom is shown in yellow.

Once the different replicas are set up, artificial inter-replica spring forces are imposed in order to yield a smooth path. This means that the yellow atom in replica 3 will have two additional forces acting on it, as if a spring connected it to itself in replica 2 and another spring connected it to itself in replica 4. With these inter replica spring forces in place, the moving atom in each replica form a chain, each one connected to the next by an invisible spring. The overall effect is similar to an elastic band. These inter-replica forces are needed to keep the atom’s location in each replica close to its location in neighboring replicas and
thus model the path the atom will take while it moves. If the inter-replica forces were not included, the atom might appear to “teleport” between replicas!

With the inter-replica spring forces added, the next step is to run an energy minimization for each replica. Typically, each replica is minimized separately on its own processor in order to be computationally efficient. Once each replica has been minimized, saddle points are found to insure that the replicas will accurately show the full MEP. At this point, viewing all of the replicas superimposed over each other will show the MEP the atom can take as it moves from start to finish, as shown in figure 11 below:

![NEB replicas superimposed](image)

Figure 11: 24 NEB replicas superimposed, after minimization. The moving atom, shown in yellow, follows the minimum energy path as shown.
Figure 12: Simplified model of the NEB method.

By plotting the atom’s location with respect to replica number, one can see the physical path the atom will most likely take as it travels from start to finish. Similarly, by plotting the atom’s energy with respect to replica number, one can see the MEP. The energy plot for the motion shown in figure 11 can be seen in figure 13 on the next page.
Figure 13: Energy curve for MEP shown in figure 11. Change in energy is plotted with respect to replica number.

The more neighbors the atom has, the lower its energy. Another way to think of this is that the more neighbors the atom has, the harder it is to move as more atoms are holding it in place. The motion, or diffusion, of an atom on a surface, or “adatom”, is governed by the following Arrhenius equation:\(^{31}\)

\[
\Gamma = \nu \cdot e^{-\frac{E_a}{k_B T}}
\]

In equation (13) above, \(\Gamma\) represents the frequency of diffusion jumps, \(\nu\) represents the vibrational frequency of the adatom, \(E_a\) is the activation energy, \(k_B\) is the Boltzmann constant,
and T is the temperature. The higher the activation energy, the less often an adatom is to make a jump and diffuse. For this reason, the activation energy is also referred to as the diffusion energy or diffusion barrier.

Looking again at figure 13, one can calculate the diffusion barrier for a given jump by subtracting the initial energy from the maximum energy. For example, if one wished to calculate the diffusion barrier for an adatom to break away from the kink site onto an A-type 111 step, as shown in figure 11 moving from the left to the right, one could follow the same motion on figure 13. Starting from the left, the initial change in energy is 0.00 eV. As the adatom moves to the right, it must go through a maximum energy of 0.47 eV. This means that the process has a diffusion barrier of 0.47 eV.

Now, what if one were to look at the same process in reverse? When moving from the right to the left, an atom would start with a local energy of 0.22 eV. As it moves along the MEP energy curve in figure 13, it reaches a maximum energy of 0.47 again. Subtracting these, one sees that the diffusion barrier is only 0.25 eV.

The same process has a different diffusion barrier depending on direction. Since the diffusion barrier is 0.47 eV when going from left to right but only 0.25 eV when going from right to left, one can conclude that it is less likely for an adatom to break away from a kink
site than it is for adatom to join a kink site. Looking again at the image shown in figure 11, this makes sense; an adatom moving from left to right has to break more bonds, and as such it is more difficult to do.

Understanding the diffusion barriers for the different jump mechanism on the surface of a material can yield to a much better understanding of how atoms will tend to move on said surface, and thus how the surface will grow or decay.

1.4.3: Physical Vapor Deposition

Physical vapor deposition (PVD) is a process used to fabricate nanomaterials. In PVD, a source material and a substrate are placed at opposite ends of a vacuum chamber. Once the vacuum is established, the source material is vaporized and the vapor phase atoms move through the chamber until forming a thin film on the substrate. Many different methods are available for vaporizing the source target, and each has its own benefits and weaknesses, but the PVD process as a whole is both simple and versatile.

In order to create nanostructures, the substrate is often set at a high angle. This is known as glancing angle deposition (GLAD) or oblique angle deposition (OAD). 32,33 This
method is successful due to a shadowing effect on the substrate. While these first nanostructure were initially found in 1959, the technology has matured rapidly since. 34,35 These include numerous pure metallic nanostructures, including simple structures such as thin films, but also complex structures such as helixes or zig-zags.

In GLAD, the substrate can be moved or rotated, resulting in the ability to create different structures. By maintaining a constant flux angle ($\alpha$) during GLAD PVD, cylinders of atoms can be grown. These cylinders will all grow at an incline, with the angle between the cylinders’ axis and the substrate being constant. Cylinders of atoms on the nanoscale, that is with diameters less than 100 nm, are referred to as “nanorods”.

In the early 2000s, a research team at RPI managed to grow Cu nanorods and tested the limits on nanorod size. They found that if the deposition rate was increased, the diameter of the nanorods would decrease. 36-39 Eventually, a critical diameter of 30 nm was found. If the deposition rate was increased any more, the nanorods would grow too close together and merge, losing their unique properties. By 2013, however, a team of researchers from the University of Connecticut were able to use noble-metals, or metals resistant to corrosion, to grow the smallest ever nanorods. These were only 10 nm in diameter, 40 and opened up many new application possibilities.
There are several different methods of PVD, including magnetron sputtering, ion bombardment, pulsed laser deposition (PLD), thermal evaporation, and electron beam PVD. In each of these methods, the base mechanics of PVD remain the same, as shown in figure 14 below. The difference is how the vaporized source atoms enter the chamber.

Figure 14: In a basic PVD chamber, the source material is vaporized and travels through a vacuum to the substrate.

Often, as seen in figure 14, a thin quartz crystal is placed in the chamber orthogonal to the source. As atoms are deposited on the crystal, mass is added. This will result in a
slight change in vibrational frequency, which can then be used to calculate how much mass is being added. This technique, called a quartz crystal microbalance, allows one to see the deposition rate during fabrication.

The first method of adding the vaporized source atoms mentioned is magnetron sputtering. In magnetron sputtering, a very strong magnetic field and a very strong electric field are generated underneath the source material. A noble gas, often Argon (Ar), is then passed through the chamber directly above the source material. As the gas moves through the magnetic field, atoms become ionized as electrons are stripped away. Now electrically charged, the Ar ions are quickly accelerated towards the source material. The combination of the low ambient pressure and the energetic impact of the Ar ions with the source material surface result in atoms from the source material being blasted off. These source atoms then form the vapor that passes through the chamber to the substrate. An advantage of using magnetron sputtering is that it does not require as high of a vacuum as other methods. It also requires less cooling as the process takes place at a lower temperature. Unfortunately, due to the fact that the magnets have fixed locations beneath the source material, grooves will be etched into the source, resulting in non-uniform source utilization. In addition, the rate at which atoms are knocked off the source, and thus the deposition rate, are dependent
on the strength of the magnetic and electric fields. This results in less manual deposition rate control when compared to other PVD methods. Furthermore, the addition of gas to the PVD chamber will lower decrease the vacuum, which can result in impurities in the nanostructures. At higher deposition rates, more gas will enter the chamber, and thus increase the risk of impurities further.

Another method of activating the source material for PVD mentioned earlier is ion bombardment. Ion bombardment, also referred to as ion beam sputtering, is quite similar to magnetron sputtering. Whereas magnetron sputtering used magnetic fields to create ions, ion beam sputtering uses an external ion source. By firing an external ion beam at the source material, atoms will again be knocked off and into the vacuum chamber. This allows greater control, as both the ion beam energy and flux can be adjusted separately. This allows much greater control over the deposition rate. However, just like with magnetron sputtering, impurities can result from the addition of particles to the PVD vacuum chamber.

A similar method to ion beam deposition is pulsed laser deposition (PLD). In PLD, a high-energy laser is shot at the source target. This is similar to the ion bombardment, but no particles enter the vacuum – with the exception of photons. By pulsing the laser at regular intervals, a “plume” of vaporized atoms forms from the source material. This plume
contains not only individual atoms, but also electrons and small clusters of atoms. While the
impurity issue from magnetron sputtering is resolved, the inconsistency of the plume results
in its own complications. The high energy of the laser also leads to a high deposition rate,
which makes this method more suited for growing epitaxial films than nanostructures.

In order to have better control over the deposition rate, a fourth – and much simpler
- PVD method can be used. Thermal evaporation PVD leverages an electric resistance heater
placed directly beneath the source material. By establishing ultra-high vacuum (UHV)
conditions in the PVD chamber, the evaporation (or even sublimation) temperature of the
source material can be depressed to a point that can be reached by the conductive heating.
While this method is certainly simple, the UHV restriction means oxides cannot be deposited.
Furthermore, the maximum temperature of the heating element will impose a direct limit on
what source materials can be used. Also, there will inevitably be a delay between adjusting
the heater and the desired adjustment to deposition rate while the source either heats up
or cools down. Finally, the newly vaporized atoms will have a lower energy than those
formed with the previously mentioned methods. This results in mostly “line of sight”
deposition between the source material and the substrate. This can result in greater surface
roughness.
The final PVD method mentioned earlier in electron beam PVD, or EBPVD. As this is the method utilized later in this dissertation, more detail on its procedure will be provided. EBPVD is similar to thermal evaporation PVD, but instead of heating the entire source material, a thin electron beam is used to vaporize a small local area. As can be seen in figure 15 on the next page, an electron beam can be guided to hit different area on the source material. Where the electron beam hits, the area is locally super-heated and vaporized. Since the vaporization is local and the electron beam can be moved, the deposition rate delay seen in thermal evaporation PVD is eliminated. This, combined with the ability to control the electron beam’s power, results in excellent control over deposition rate. Since particles are not being added to the vacuum, the impurity issue from magnetron sputtering is eliminated. This results in the ability to grow extremely pure thin films and nanostructures. While PLD created a plume of atoms, ions, and electrons, EBPVD can achieve much better control. With direct control over both the pressure of the PVD chamber and the power of the electron beam, proper vaporization can be achieved for many source materials. Furthermore, the electron beam has the ability to produce very high energy densities. This results in a wide variety of materials that can be used as a source and thus deposited. One
downside to EBPVD is the cooling requirement, but this can be resolved by integrating a
water cooling system.

Figure 15: Schematic of electron beam PVD. The high-energy electron beam is guided to
strike the source material, locally superheating and vaporizing it.
1.5: Dissertation objectives:

There are three primary objectives of this dissertation. First and foremost is to gain a better understanding of the root cause of Ag nanorod instability. The second objective is to use this better understanding to predict a method of preventing or mitigating this instability. Finally, the third primary objective is to test this method of stabilization.

In order to gain a better understanding of the root cause of Ag nanorod instability, MD simulations were used to simulate Ag nanorods. By investigating these simulation results, the dominant surface diffusion mechanisms were identified. MS NEB calculations were then used to better understand the diffusion barrier for these dominant mechanisms. With these modeled, the cause of the instability was understood to be rapid surface diffusion.

With this knowledge, it could be seen that kink sites on the nanorod surface are integral to the surface diffusion that resulted in the Ag nanorod instability. This allowed the prediction that capping the nanorods with a thin layer of dielectric material would slow the surface diffusion, and thereby increase the thermal stability of the Ag nanorods.
Finally, EBPVD was used to fabricate Ag nanorods. Both electron microscopy and Raman spectroscopy were used to test the nanorods thermal stability with and without a thin capping layer of TiO$_2$. This would test the prediction made based on the understanding gained from the MD simulations of surface diffusion. The electron microscopy would show both thermal stability and reveal the nanorods’ core-shell morphologies. The use of surface enhanced Raman spectroscopy would further demonstrate the thermal stability of capped Ag nanorods as sensors.

Control over the coarsening of Ag nanorods may have widespread affects in technology, such as sensing or low temperature metallic sealing.
Chapter 2: Simulation and Modeling

2.1: Validating the model

Before describing the modeling methods used, one must first establish that the model is an accurate description of the physical world. In order to accomplish this, each of the necessary assumptions made when setting up the model must be examined thoroughly. The simulations presented here will be done using Ag nanorods, so the assumptions must be viable for modeling Ag at that scale.

We also note that all simulations are run using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). LAMMPS is a set of open source molecular modeling software available at http://lammps.sandia.gov. 46

The first set of necessary assumptions are those implicit to the MD method itself. The largest of these is the use of the Born-Oppenheimer approximation 14 which allows one to treat an entire atom, electrons included, as a single point mass. This assumption is a fundamental requirement of MD, and has been repeatedly shown to be accurate when simulating metals such as Ag. 18,19,47
Another assumption implicit to the MD method is that the limited timescale that can be possibly simulated will be able to provide results that translate to usable understanding. The longest simulations set up will only run for 200 ns. While this is on the upper limit of what could be simulated due to the number of atoms and the available computational power, it is still drastically less than any macro-scale timeframe. However, these simulations will not be looking for full degradation of the nanorod, but rather the mechanism that results in said degradation. If the effect is indeed the result of rapid surface diffusion, a simulation lasting 200 ns should be more than enough to see any relevant diffusion jump mechanisms. This can be shown quantitatively through the Arrhenius diffusion equation, equation (13), which is repeated below for convenience.

\[ \Gamma = v \cdot e^{-\frac{E_a}{k_B T}} \]  

(13)

Many more assumptions are specific to the simulation(s) they are being used for, and will as such be investigated later when those specific methods are discussed. There are, however, two major overlaying assumptions that must first be addressed: The first is that the specific EAM potential being used accurately models the system. As previously stated, the interatomic potential is the backbone of MD, and must be accurate in order to obtain any usable results. The second is that the findings are indeed the result of surface diffusion, and
not simply an artifact caused by Rayleigh instability. These two potentially major concerns will be addressed now.

2.1.1: Interatomic potential

The specific interatomic potential used in these simulations and calculations is the Ag EAM potential developed by Williams et al. because it has been successfully used to replicate the crystal structure, lattice constant, elastic constants, and surface formation energies of FCC Ag. Before using the potential however, these parameters were rechecked for accuracy. By comparing simple calculation results to accepted values, the interatomic potential can be validated.

The first parameter checked was the lattice constant. In order to test this, a simulation cell was set up to model bulk Ag. The cell was a cube with all periodic boundaries. Ag has a lattice constant of 4.09 angstroms (Å) and as such the simulation cell dimensions must be exact multiples of this in order to use periodic boundaries. The simulation cell must match up perfectly edge to edge so it can be repeated through the periodic boundaries. For this simulation cell, the sides were assigned lengths of 12.27 Å, slightly above two cutoff distances.
The simulation cell was evenly filled with FCC Ag atoms such that the periodic boundaries would simulate bulk FCC Ag. The energy was then minimized, calculated, and recorded. The simulation cell was then expanded and contracted, effectively increasing and decreasing the lattice constant, and for each value the energy was minimized, calculated, and recorded. It was then confirmed that a lattice constant of 4.09 Å indeed yielded the lowest total energy. Therefore, it was confirmed that the interatomic potential accurately replicates the lattice constant.

Next, a similar process was used to confirm that the interatomic potential accurately replicates the elastic constants. The same simulation cell used to confirm the lattice constant was again used here. The simulation cell was then deformed both positively and negatively in each direction, applying strain. It was also subjected to shear strain by deforming one side of the simulation cell while holding the other stationary. By calculating the stresses resultant from each of these strains, the elastic constant could then be computed and confirmed to match the accepted value.

Finally, the surface energy must be replicated accurately. Since many of the calculations will involve surface energy, it is extremely crucial that the interatomic potential be able to model this accurately. In order to test the interatomic potential’s calculated surface
energy, a simulation cell was set up as follows: The x and y directions, corresponding to the [\bar{1}11] and [1\bar{1}1] crystallographic directions, were again set up with periodic boundaries and side lengths of 12.27 Å, slightly above two cutoff distances. The z direction, however, was set up differently. The simulation cell was 45 Å tall, with atoms occupying the center 36.81 Å portion, or about six cutoff distances. The boundaries were free boundaries. This would simulate an infinite plane with a thickness of six cutoff distances. Each face of the plane would then be an infinite \{111\} surface. By calculating the energy of this system and comparing it the bulk energy and then dividing by two since there are two surface, the top and the bottom, the surface energy was calculated. Again, this was shown to be in good agreement with the accepted value, proving that the chosen EAM interatomic potential would be suitable for the surface energy calculations planned.

2.1.2: Rayleigh Instability

Rayleigh instability is the phenomenon of a stream of fluid breaking into droplets.\(^{48}\)

Rayleigh instability is named for Lord Rayleigh, who in the late nineteenth century showed theoretically that a vertically falling liquid with a circular cross-section would sometimes break
apart into a stream of droplets. Specifically, it would break apart if the liquid’s wavelength was larger than its circumference. This phenomenon is the result of surface tension effects, as the liquid breaks into droplets in order to conserve energy.

On the nanoscale, this effect is paralleled in nanorods. Just like streams of liquid breaking into a stream of droplets in order to minimize surface tension, thin nanorods can break into an array of nanospheres in order to minimize surface energy. Since this dissertation is examining the degradation of nanorods, it must be shown that the degradation being observed in the simulations is in fact the result of rapid surface diffusion, and not simply Rayleigh instability.

In order to examine whether Raleigh instability is a factor for Ag nanorods of these sizes, a simulation cell was set up to include an entire nanorod, with each end free. The simulation was run using an NVE ensemble with time steps of 0.001 ps and temperature controlled via a Nose-Hoover thermostat. 20,22

This diffusion was investigated by simulating 5 nm diameter nanorods with each end terminated in a conical tip similar to those observed in experiments. 48 An axial length of 20 nm was used as it was long enough such that tip effects at each nanorod end would be distinct. An axial direction of [111] was chosen as it corresponded to nanorods growing at a roughly
17.5° from the (111) substrate, as seen in SEM images. A schematic of a 5 nm diameter <111> oriented Ag nanorod is shown below in figure 16.

![Schematic of Ag nanorod](image)

Figure 16: Schematic of <111> oriented Ag nanorod with a diameter of 5 nm. A-type and B-type (111) steps are shown in blue and red respectively.

Variation of the axial direction results in a nanorod with the same morphological features as the [111] orientation shown in Fig 16, with the only difference being the spacing between surface steps, as shown in figure 17 below. Our proposed method, however, is
diffusion based and solely the result of the morphology. The simulations were run at various
temperatures for 200 ns. In order to avoid any artifacts due to the initial tip configuration,
the first 20 ns were used to reach steady state conditions, after which the jump rate remained
relatively constant.

Figure 17: Ag nanorod grown on (111) surface at 20°.

The results are shown in figure 18 on the next page. Figure 18(d) shows the effective
radius as a function of axial position. The blue, green, and red lines correspond to 20 ns, 110
ns, and 200 ns respectively. It is clear from this figure that as time progresses, the nanorods
widen near the ends while the length decreases. While the nanorods in these simulations are
only 5 nm in diameter, it is clear that the widening is the result of diffusion and not Rayleigh
instability due to the fact that the nanorod widens at all axial positions. Since Rayleigh instability is a related to diameter, if it is not present in 5 nm diameter Ag nanorods it cannot be present in the larger nanorods simulated in this dissertation.

Figure 18: Simulation cell at (a) 20 ns (b) 110 ns and (c) 200 ns, and (d) effective radius as a function of axial position showing a decrease in length corresponding with an increase in width. The blue, green, and red lines correspond to 20 ns, 110 ns, and 200 ns respectively.

2.2: Surface Dynamics
With the simulation method validated, we must now explain the various computational methods used for the simulations and calculations in this dissertation. The computational methods can be divided up into two approaches: MD and MS.

2.2.1: MD Methods

A set of MD simulations was used to investigate diffusion on the sides of the Ag nanorod that represent the majority of the surface area. As previously stated, in order for our proposed mechanism of diffusion enforced thermal instability to occur there must be rapid diffusion on the nanorod sides, as well as diffusion up and down the nanorod sides. This diffusion was investigated by simulating an infinite Ag nanorod at several constant temperatures. In addition to investigating the diffusion on the nanorod sides, the constant surface area of this second set of MD simulations allows for the creation of a diffusion plot, which can then be used to show a correlation to temperature. The simulation cells contain either 20 nm or 30 nm diameter nanowires of FCC silver, oriented with their axis along the [111] direction, as shown in figure 19 below.
Figure 19: Molecular dynamics simulation set-up with (a) a schematic of the structure of the nanorod, (b) a segment of the nanorod with (111) A-type steps in red and (111) B-type steps in blue, and (c) a representative simulation cell colored according to potential energy, with red and blue representing highest and lowest potential energy respectively.

The axial orientation was again set to [111] direction. Different diameter nanorods were simulated to ensure that the results are independent of simulation cell size. The cells had an axial length of 4.25 nm (scaled according to temperature) and were periodic in the axial direction in order to simulate an infinitely long nanowire.

The MD simulations were run using a timestep of 0.001 ps with temperature controlled through a Nose-Hoover thermostat. An NVT ensemble was used to bring the simulation
to temperature, after which an NVE ensemble was enforced. The individual atomic energies and numbers of first and second nearest neighbors were recorded for each atom to be used when identifying diffusion jumps.

2.2.2: MS Methods

A set of MS calculation was set up to examine the MEP and determine the associated diffusion barrier for each dominant surface diffusion jump mechanism observed in the MD simulation results. The diffusion barriers for atomic motion around the nanorod must be small enough to allow for rapid diffusion. In addition, there must be a low diffusion barrier mechanism for atoms to move up and down the nanorod side in order for the nanorod to degrade by shrinking and widening until it merges with its neighbors. Therefore, the diffusion energy barrier for each relevant jump type must be known. The relevant jump types were first identified by analyzing the diffusion jumps observed in the results of the second set of MD simulations. For every jump, the number of nearest neighbors of the jumping atom was counted before and after each jump. Jumps could be identified by the distance an atom travels, the change in atomic coordination, and by examining the atom’s energy curve for local energy minimums. Combining these with the morphology shown in figure 19 allows for the
identification of the jump type. The various jump types are shown and explained in detail in the Results and Discussion section of this dissertation. The energy barriers for each jump type observed in the second set of MD simulations were then determined via MS simulations, specifically by using the nudged elastic band (NEB) algorithm 6,7 to find the minimum energy path (MEP). The minimization was done using the quick-min minimizer 28 as described earlier in the introduction. The static simulation cell was 31.813x30.055x63.757 Å or about 5x5x10 cutoff distances. The vertical axis was again the [111] direction, with periodic boundary conditions in the [-11-1] and [11-1] directions.
Chapter 3: Simulation results

3.1: MD results

The MD results identified several commonly occurring jump mechanisms. First, atoms move along the A and B type steps that make up much of the nanorod surface morphology. These jump mechanisms can be seen below in figures 20-23.

Figure 20: Observed jump mechanism along A-type [111] step.
Figure 21: Observed jump mechanism along B-type [111] step.

Figure 22: Observed mechanism for breaking away from a kink site along A-type [111] step.
Figure 23: Observed mechanism for breaking away from a kink site along B-type [111] step.

While the above figures show the mechanisms for atoms to move around the nanorod, adatoms must also diffuse up and down the nanorod sides, axially, in order for the rapid diffusion to result in the experimentally observed thermal instability. The nanorod surface morphology is primarily composed of six (110) sides and six (112) sides, alternating around the nanorod to form a dodecagon. The sides made up primarily of B-type steps are the (110) sides and the sides made up primarily of A-type steps are the (112) sides. Figure 24 below shows a close up view of the different side morphologies.
Figure 24: Morphologies of (110) and (111) sides.

As one approaches the intersection between a (110) side and a (112) side, the length of the steps decreases. As such, the kink sites density increases. As we saw earlier, the diffusion process begins when atoms break away from these kink sites. Atoms also make use of kink sites to move axially along the nanorod. The mechanism for this axial motion is shown in figure 25 on the next page. 92.1% of axial motion was found to use this mechanism.
Figure 25: An atom breaks away from a kink site (a) and then moves along the step edge (b).

Upon reaching the end of the step (c) it can drop down into another kink site (d).
In addition, this set of MD simulations was used to determine the most active diffusion events on an infinite Ag nanorod surface at varied temperatures, as well as to investigate the correlation to temperature. For each constant temperature simulation, the jump rate was determined by taking the slope of a plot of total jumps with respect to time, normalized by the number of jumping atoms. By plotting these jump rates with respect to inverse temperature on a semi-log plot, as shown in figure 26 below, the dominant diffusion energy barriers can be calculated from the slopes. A clear transition in diffusion mechanism was seen in nanorods around 0.4 Tm, as shown by the slope change in figure 26. This transition resulted from a change in the dominant diffusion energy barrier from 0.23 eV to 0.55 eV. Furthermore, there was less than a 5% difference in the barriers calculated from the 20 nm and 30 nm diameter simulations, showing that the results are independent of simulation cell size. These barriers corresponded to different diffusion mechanisms dominating the diffusion on the nanorod sides.
Figure 26: Diffusion plot showing a clear change in the dominant diffusion type. The slopes above and below 0.4 Tm correspond to diffusion energy barriers of 0.55 eV and 0.23 eV respectively.

3.2: MS Results

The MS simulations were used to determine the diffusion barriers and determine the dominating mechanism for the above and below the critical temperature of 0.4 Tm. NEB calculations were done for each diffusion mechanism observed in the MD simulations. In the dynamic simulations, a clear transition in diffusion mechanism was seen in both the 20 nm
and 30 nm nanowires at around 475 K. This transition resulted from a change in the dominant diffusion energy barrier from about 0.25 eV to 0.55 eV. These barriers corresponded to two different diffusion processes: the lower being the energy required to move along a step and the higher being the energy required to break away from a kink site. Thus, at about 475 K atoms begin to break away from kink sites and diffuse along the nanowire surface steps. To further elucidate this process, NEB simulations were run for A type and B type steps on the (111) surface. The energy barriers for moving along an A type and B type step were found to be 0.25 eV and 0.31 eV respectively, and the energy barriers for breaking away from a kink site along an A type and B type step were found to be 0.47 eV and 0.51 eV respectively, as shown in Table 1 below. Comparing these values to the dominant energy barriers calculated from the dynamics simulations, which were 0.23 and 0.55 eV respectively, one can see that the shift in dominant diffusion mechanisms observed in the dynamics results in fact represents more atoms breaking away from kink sites and onto steps, with good agreement. The diffusion barrier for axial movement was found to be 0.34 eV.
Table 1: Summary of Diffusion Barriers

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Mechanism</th>
<th>Energy Barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-type step</td>
<td>Along Step</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Break away</td>
<td>0.47</td>
</tr>
<tr>
<td>B-type step</td>
<td>Along Step</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>Break away</td>
<td>0.51</td>
</tr>
<tr>
<td>Compare to MD</td>
<td>Along Step</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>Break away</td>
<td>0.55</td>
</tr>
<tr>
<td>Kink site</td>
<td>Move axially</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Figures 27-30 show the MEP energy curves for these diffusion mechanisms. The change in energy is plotted with respect to diffusion coordinate, which here is the NEB replica number.

Figure 27: MEP energy curve for an atom moving along an A-type step. Change in energy is plotted with respect to diffusion coordinate.
Figure 28: MEP energy curve for an atom moving along a B-type step. Change in energy is plotted with respect to diffusion coordinate.

Figure 29: MEP energy curve for an atom breaking away from a kink site and onto an A-type step. Change in energy is plotted with respect to diffusion coordinate.
Figure 30: MEP energy curve for an atom breaking away from a kink site and onto a B-type step. Change in energy is plotted with respect to diffusion coordinate.

With this understanding, we understand that the rapid surface diffusion depends heavily on kink sites. With free motion up or down the nanorod sides, the nanorod will logically grow shorter and wider in order to reach a state of decreased surface energy. This was indeed observed in the MD results when ruling out Rayleigh instability, and figure 18 indeed shows the nanorod decreasing in length while increasing in width. Eventually, this will result in the nanorods growing wide enough to merge, as depicted in figure 31 below.
Figure 31: Comic representation of Ag nanorods shortening and growing wider, eventually merging and becoming a film.

With the importance of kink sites to this process, especially those near the nanorod tip, better understood, we predict that blocking these kink sites with a cap of a thin dialectic layer will prevent the thermal instability of Ag nanorods.
Chapter 4: Experimental confirmation

Ag and other noble metal nanorods have applications as sensors for the detection of trace amounts of chemical agents through surface enhanced Raman scattering (SERS). Such nanorods lead to an enhancement of as much as $10^8$ to the intrinsically weak Raman signal. Additionally, the large surface-to-volume ratio of the metallic nanorods is optimized when they are well separated and small, as this group realized recently. The optimal surface-to-volume ratio decreases if the nanorods start to coarsen, and geometric “hot spots”, which enhance the Raman signal, are lost. Over time, even at or near room temperature in ambient, Ag nanorods coarsen. Indeed, SERS experiments indicate that the enhancement factor may degrade by up to 80% after 30 days of ambient storage.

With this in mind, as well as our understanding from the simulation results, we propose that capping the nanorods with a dielectric layer will prevent this thermal instability. To demonstrate the feasibility of this conceptual proposal, we use PVD to grow Ag nanorods with a titanium dioxide (TiO$_2$) capping layer; and we use scanning electron microscopy (SEM), transmission electron microscopy (TEM), and SERS to characterize the thermal stability and Raman enhancement of Ag nanorods under various annealing temperatures.
4.1: Empirical Methods

Before presenting the results, we briefly describe the methods of sample preparation and characterization. Capped Ag nanorods are grown using electron beam PVD with an oblique or glancing flux incidence angle of 86°.\textsuperscript{59,60} The nanorods are grown on ultrasonically cleaned Si \{001\} wafers with native oxide. The source materials are 99.99\% Ag pellets (Kurt J Lesker Co.) and 99.99\% TiO\textsubscript{2} pieces (Kurt J Lesker Co.) and are deposited from a Fabmate \textsuperscript{TM} liner (Kurt J Lesker Co.). The vacuum chamber is a stainless steel tank approximately 45 cm tall and 25 cm diameter. The source to substrate distance is approximately 35 cm. The substrates are placed onto a precision machined mount at the top of the chamber and the source material is placed into the electron beam hearth at the base. The chamber is then evacuated to a base pressure of 1x10\textsuperscript{-4} Pa for at least six hours. The working pressure is 1x10\textsuperscript{-3} Pa for Ag and 1x10\textsuperscript{-2} Pa for TiO\textsubscript{2}. Ag nanorods are grown to a height of 500 nm at a deposition rate of 10 nm/s, measured by quartz crystal microbalance, and are then removed from the vacuum chamber. The substrates with the nanorods that serve as the control are separated and placed under vacuum storage while the substrates with the nanorods that are
to be capped with TiO$_2$ are returned to the chamber at the same orientation. TiO$_2$ is then deposited at a rate of 0.1 nm/s to a total thickness of 5 nm.

The nanorod samples are then removed from their respective vacuum chambers and are immediately characterized using SEM, TEM, and Raman microscopy. The scanning electron microscope is an FEI Quanta 250, with a field emission source, the transmission electron microscope is a FEI Technai 12, and the Raman system is a Renishaw Raman 2,000. Thermal annealing is performed in air on a laboratory hot plate, which is controlled and monitored via K-type thermocouple. Annealing temperature of the plate surface is first stabilized, then the nanorod samples are added, and timing begins. When the annealing time completes, the samples are immediately removed from the hot surface and allowed to cool in air before SEM imaging. Raman spectroscopy is performed using a 514.5 nm wavelength laser operating at a power of 0.5 mW, a magnification of 50 times, and a sampling time of 60 seconds. Samples are sensitized in a solution of 5 mM Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)ruthenium(II) dye (N719) (Sigma Aldrich) in 99.9 % ethanol (Sigma Aldrich) for 12 hours. After sensitization, samples are immediately removed and rinsed with ethanol five times before performing Raman spectroscopy.
4.2: Experimental Results

As a reference point, Figure 32 shows the annealing behavior of uncapped Ag nanorods. The as-grown uncapped Ag nanorods are well separated; Figure 32(a). After annealing at 50°C for 10 minutes, the uncapped Ag nanorods substantially merge with one another; Figure 32(b). This morphological change of Ag nanorods at 50°C indicates that, to facilitate SERS sensing at temperature even slightly above room temperature, special processing is necessary to enhance their thermal stability. It is also interesting to note that annealing at 100°C for 10 minutes leads to complete collapse of the uncapped Ag nanorods; inset of Figure 32(b).
Figure 32: SEM images of Ag nanorods (a) as fabricated and (b) after annealing at 50°C for 10 minutes, with the inset showing collapsed Ag nanorods after annealing at 100°C for 10 minutes.

As shown in Figure 33(a), the morphology of Ag nanorods capped with TiO₂ resembles that of the uncapped ones in Figure 32(a). However, the TEM image reveals that the capped Ag nanorod carries a coating layer on the top; Figure 33(b). The electron diffraction pattern of multiple nanorods indicates that the cap has both amorphous and crystalline regions; the bottom of Figure 33(b).
Figure 33: (a) SEM image of capped Ag nanorods as grown, (b) TEM image of a single Ag nanorod with TiO$_2$ capping primarily at the nanorod tip (top), and electron diffraction pattern of multiple Ag nanorods (bottom).

Next, we put the thermal stability of these capped Ag nanorods to the test under various annealing temperatures. Figure 34 below shows the morphology of capped Ag nanorods that are annealed under various temperatures for 10 minutes. Annealing at 100°C for 10 minutes leads to little visible change to the morphology of the capped Ag nanorods; Figure 34(a). In contrast, for the uncapped Ag nanorods, annealing at 100°C for 10 minutes leads to complete collapse; and even annealing at 50°C for 10 minutes leads to substantial coarsening, as shown in Figure 32. That is, the capping, as we propose, is effective in stabilizing the morphology of Ag nanorods; we will come back to the SERS sensitivity of the capped Ag nanorods later. Pushing the stability further, we have characterized the morphology of the capped Ag nanorods at higher temperatures – 200°C, 300°C, and 400°C –
as shown in Figures 34(b)-34(d). Morphological changes at 200°C are easily visible, although the capped Ag nanorods remain separated. The total collapse of the capped Ag nanorods occurs at 400°C; in contrast, the uncapped Ag nanorods collapse at 100°C.

Figure 34: SEM images of Ag nanorods with TiO$_2$ capping after annealing for 10 minutes at (a) 100°C, (b) 200°C, (c) 300°C, and (d) 400°C.
Having established the effectiveness of TiO$_2$ capping in stabilizing the morphology of Ag nanorods, we next characterize the effectiveness in maintaining the SERS sensitivity. Figure 35(a) shows the SERS spectra of as grown Ag nanorods, with and without TiO$_2$ capping. The capping does not substantially perturb the spectrum, before annealing for 10 minutes. The peak at 1540.18 1/cm is of particular relevance in sensing, because it is the most dominating N719 peak, and the dominance of this peak is consistent for all substrates and annealing levels tested here, and in the works of Qui et al. and Lee et al. For annealed nanorods, we measure the intensity at this dominating Raman shift location, 1540.18 1/cm, and divide it by the intensity of uncapped Ag nanorods as fabricated at the same shift location. This normalized SERS intensity of the annealed Ag nanorods changes as a function of annealing temperature; Figure 35(b). Without capping, the normalized SERS intensity precipitously decreases to 0.04 after annealing at 100°C, from 1.00 at room temperature; corresponding to the morphological change in Figure 32. With TiO$_2$ capping, the normalized SERS intensity decreases to 0.93 at 100°C from 0.97 at room temperature; corresponding to the enhanced morphological stability shown in Figure 34.
Figure 35: (a) Raman spectra of N719 dye on Ag nanorod arrays as fabricated, and (b) Normalized SERS intensity as a function of annealing temperature of the Ag nanorod arrays.
Chapter 5: Summary and conclusions

5.1: Summary

By combining multiscale modeling with experimental methods, a solution to thermal instability in Ag nanorods was found. As discussed previously, Ag nanorods have many uses in diverse technologies, including sensing, sealing, and electronics. However, Ag nanorods are thermally unstable, and will quickly degrade into a film, even at low temperature. By modeling Ag nanorods using MD simulations, the dominant surface diffusion mechanisms were observed. By testing these mechanisms via NEB calculations, the associated diffusion barriers were calculated. This understanding of the atomic mechanism for rapid surface diffusion enforced thermal instability allowed for the prediction of a fabrication method that would enhance thermal stability. Specifically, this was capping Ag nanorods with a thin dielectric layer. This method was then tested experimentally. EBPVD was used to fabricate Ag nanorods with and without a thin TiO$_2$ cap. These nanorods were annealed and tested with SEM imaging and TEM imaging to show the enhanced thermal resistance. They were then tested with Raman microscopy to ensure that SERS sensitivity was maintained.
5.2: Conclusions and Key Findings

The thermal instability in Ag nanorods was shown to be the result of rapid surface diffusion. Furthermore, it was shown that this diffusion enforced thermal instability could be mitigated by applying a thin dielectric cap of TiO$_2$. Computer simulations of Ag nanorods showed that kink sites on the surface play a significant role in the rapid surface diffusion that results in thermal instability. Furthermore, the instability depends on atoms diffusing off the nanorod tip to diffuse down the sides, allowing the nanorods to shorten and fatten until merging with their neighbors. With this insight, we were able to predict that if the surface diffusion was prevented through the means of a thin dielectric capping layer, the thermal stability would be enhanced. This was indeed the case. The morphology of capped Ag nanorods is stable up to at least 100°C; in contrast, the morphology of uncapped Ag nanorods becomes unstable even slightly above room temperature. The capped Ag nanorods remain separate at 300°C; in contrast, the uncapped Ag nanorods completely collapse at 100°C. As SERS sensors, TiO$_2$ capped Ag nanorods are nearly as sensitive as the uncapped ones at room temperature, but Raman microscopy showed that capped Ag nanorods were over 23 times
more sensitive than uncapped Ag nanorods after annealing at only 100°C for 10 minutes. This discovery opens the door for Ag nanorod use in technology where rapid degradation previously limited their usage.
Bibliography:


31. Diffusion equation reference


40. S. P. Stagon and H. C. Huang, Nanotechnology Reviews 2.3 (2013).


