POLARIZATION AND SELF-ASSEMBLY AT METAL-ORGANIC INTERFACES:
MODELS AND MOLECULAR-LEVEL PROCESSES

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POLARIZATION AND SELF-ASSEMBLY AT METAL-ORGANIC INTERFACES:
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Dissertation

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ABSTRACT

This dissertation contributes to the understanding of driving forces of self-assembly processes leading to the growth and self assembly of metal nanostructures for nanoelectronic, sensor, and drug delivery applications. It remains difficult to image and characterize molecular-level processes by measurement alone so that we have employed molecular simulation to gain more insight into two aspects: (1) the contribution of induced charges in metal nanostructures to the interaction with biomolecules and ionic liquids, (2) and the mechanism of gold nanorod growth. Polarization at \{111\} and \{100\} surfaces of gold in contact with water and peptides of different charge state contributes to the binding strength and plays a role in the assembly of metal nanostructures. We computed the attractive energy using the concept of image charges and molecular dynamics simulation in all-atomic resolution. Attractive interactions amount to between $-50$ and $-70$ mJ/m$^2$, corresponding to $-0.6$ kcal/mol per water molecule and variable amounts per amino acid in peptides depending on the charge state (0 to $-10$ kcal/mol). The main contribution to adsorption on \{111\} surfaces stems from soft epitaxial interactions and the net contribution of polarization to adsorption is smaller. On surfaces with poor epitaxial fit of the solute molecules such as \{100\} surfaces, the main contribution to adsorption can be made by polarization, particularly for charged peptides and ionic liquids. Therefore, the magnitude of interfacial polarization can modulate the binding strength of biomolecules or surfactants versus solvent to metal surfaces.
The mechanism of shape regulation in the growth of gold nanorods in ionic liquids (ILs) such as 1-Ethyl-3-methylimidazolium ethyl sulfate is initiated by silver underdeposition and modulated by induced surface charge which decreases in the order {110}, {100}, and {111} for gold surfaces. Attractive effect of induced charges is quantified based on our previous work on polarization at metal-biomolecular interfaces in solution. Higher surface corrugation increases the induced charge so that the side surfaces of gold nanorods synthesized in imidazolium based ionic liquids are formed by {110} and {100} faces, in which a higher contribution of induced charges by -2.3 kcal/mol-molecule compared to {111} surfaces accounts for the thermodynamic stability observed in TEM. In a nonionic solvent like water, surface energies of all three faces {110}, {100}, and {111} are about the same and lead to different surface bounds of gold nanorods in combination with capping agents. The adsorption energy of IL molecules on the gold surfaces changes as a function of the number of molecules per unit area depending on packing constraints and network strength between cations and anions. The adsorption energy per molecule saturates once flat-on molecular multilayers are formed. We suggest that the balance between induced charges, soft epitaxy, and silver underdeposition contributes to the anisotropic growth of gold nanorods in a given solvent.
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\]

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CHAPTER I

INTRODUCTION

Synthesis of metal nanostructures, especially nanoparticles and nanorods with dimensions on the order of 1 nm to 1 μm has become a focus of materials science due to the versatile applications that occur as a consequence of anisotropy in such structures.\(^1\) Anisotropic nanostructures have high surface to volume ratio leading to large fraction of atoms on the surface,\(^2\) which gives them new and novel properties that are shape and size dependent. The dependence of optical properties on shape and size as well as the confinement of electrons at the nano level in these structures results in applications as optoelectronic devices.\(^3,4\)

Template controlled synthesis of nanostructures has gained specific importance in recent years because of the high degree of tunability possible through the process. This tunability is a result of the polar head group that self assembles and packs itself in a manner that serves as a template for the nanostructure. There is an epitaxial relationship between the final nanostructure and the self assembled amphiphilic molecules that form nano-reactors.\(^5\) By tuning the self assembly through choice of organic template, the aspect ratio and morphology of the resulting nanostructure can be controlled. Role of the polar head group is not fully understood, although it is hypothesized that the metal precursor atoms are attracted to it. These molecular organic templates are especially important because of the ease of their removal and the ability to functionalize the

1
resulting nanostructure for specific applications in catalysis and as sensors.\textsuperscript{6,7} Some templates that are commonly used are surfactants (e.g. hexadecyl-trimethyl-ammonium bromide, (CTAB)), polymers (e.g. Polyvinylpyrrolidone (PVP)), ionic liquids (e.g. 1-ethyl-3-methylimidazolium ethylsulfate (EMIMES)), and biomacromolecules (e.g. peptides and modified DNA/RNA). The focus of the present study relates to the forces at play in the adsorption/desorption of CTAB, EMIMES, and gold-binding peptides and the templating mechanism of these molecules on metal surfaces. Specifically the polarization energy resulting from the contact of gold with gold-binding peptides in solution and ionic liquids is analyzed. A hypothesis for anisotropic growth of nanorods primarily through differential in polarization energies at different surfaces of gold (\{111\}, \{100\}, and \{110\}) is put forth.

Molecular simulation is particularly feasible for template directed syntheses as the dimensions of the interface at which nucleation and growth occur as well as the dimensions of the macro-molecule are relatively small.\textsuperscript{8} Forces of non-covalent nature can be easily computed through discrete analyses of electrostatic forces and total energies. The decoupling of the forces at play is desired for understanding the mechanism of templating. Geometrical and stereo chemical matching play pivotal roles\textsuperscript{9-12} and can be visualized and compared by analyzing trajectories of macromolecules in solution on metal surfaces. Adsorption energies as well as binding sites have experimental validations with the aid of Surface Enhanced Raman Spectroscopy (SERS),\textsuperscript{13,14} electrochemical data,\textsuperscript{15} Fourier Transform Infrared (FTIR) spectroscopy and Thermo Gravimetric Analysis (TGA),\textsuperscript{2} and databases of interfacial free energies and adsorption of macromolecules on specific substrates.\textsuperscript{8,16}
The electrical double layer that forms on metals in contact with solutions has been the subject of interest of chemists for well over a century. Orientation of organics on the metal layer in solution with water has been calculated through free energy arguments, and been posited as playing a crucial role in their adsorption.\textsuperscript{15} Competition of aliphatics with water has been considered in detail in electrochemical calculations dating back to forty years. The relative free energies can vary by 2.5 kcal/mol at zero potential of the electrode surface depending on whether the hydrocarbon end or the polar group end is in contact with the surface. Hydrocarbon in contact with surface gives lower energies. However, this calculation does not take into account geometrical and stereo chemical matching that occurs in templated assembly. Hence, dynamics of the simulation are important so as to analyze competing thermodynamic and kinetic behaviors. This has also been seen with the occurrence of the gold \{110\} facet in templated growth of nanorods, although the \{110\} surface is not thermodynamically favored (discussed in brief in 1.1). Image energies, which are the interaction energies of the polar solvent and solute with surface induced charge of the metals, (visualized as images of the solvent and solute in the metal), have been analyzed in simplified electrochemical calculations and considered as significant in surfactant and aliphatic based solutions.\textsuperscript{15,17}

These image energies and orientational effects have not been correctly included in the analyses of adsorption of surfactants and other macro-molecules in recent calculations using molecular dynamics or ab-initio forms. It has been acknowledged that electrostatic forces, as also the solvent, play a major role in the formation of nanostructure morphology.\textsuperscript{17} Hence, it is logical that image energies would play a role too. There is a
need, therefore, to quantify image energies for solutions of peptides, surfactants, and ionic liquids on metals.

The summation of these image energies are most accurately done through a cell-based cutoff which takes into account the exact form of both lateral and vertical interactions of original with image atoms in a given number of layers of cells. These values indicate a competition mechanism for the organic with water, and also highlight the importance of the location of images on the metal surface. The analysis has been extended to complement the understanding of binding mechanisms of ionic liquids and surfactants in addition to free energy and adsorption arguments. In the case of ionic liquids, differential in polarization energies is the driving factor towards differential adsorption of the molecules on gold surfaces (\{111\}, \{110\}, \{100\}) and outranks soft-epitaxy as the driving force because of absence of polar water molecules which screen induced charges for peptides and surfactants in solution.

Additionally, anisotropy is kinetically driven and has a number of contributing factors.\textsuperscript{18,19} Concentration of reactant, pH, and the morphology of the initial seed all play a role. Surfactant can play the roles of stabilizer, dispersant, or a size-directing agent.\textsuperscript{19} Ionic liquids play the role of stabilizers and growth-directing agents through an electrosteric mechanism (Chapter 5).

1.1. Statement of the Problem

The mechanisms in the binding of surfactants to metals are not fully understood. There is experimental data to corroborate a bilayer templated assembly of nanorods through a reverse micelle formation of the surfactant that acts as a “soft template”.\textsuperscript{20-22}
However, the specific binding of the surfactant to different facets and the formation of \(\{110\}\) surfaces in gold need theoretical investigation, as the \(\{110\}\) surfaces are the least stable,\(^{23}\) undergo reconstruction,\(^{24}\) and in addition do not occur in the thermodynamically directed synthesis of single-crystalline seeds.\(^{25}\) Similarly, adsorption of peptides on gold involves a variety of forces that include stereo chemical and geometrical matching.\(^{25}\) Including the image energies (hereby referred to as the polarization energies because the energies are a result of the polarization of the charge distribution on the metal surface because of the highly polar water solvent plus the zwitterionic peptide) can point to better accuracy in the values of adsorption energies already calculated.\(^{27}\) The adsorption energies need to be augmented with the orientation as well as the polarization energies of the ionic liquids and surfactants to form an accurate, quantified view of the mechanism of organic templating in the formation of nanostructures.

1.2. Importance of the Study

If the mechanisms of nanostructure formation through organic molecular templating are understood in an accurate, quantitative manner, then anisotropy can be guided through a controlled assembly using factors and permutations suggested by models. There is a stated need to control the anisotropy so as to control the functionality of the target device that is to be fabricated from the nanostructure.

These models can then, also, be used to study the metal-organic interface in a DSSC: Dye-Sensitized Solar Cell (more specifically the adsorption of the dye on the TiO\(_2\) anatase in the presence of an electrolyte). The orientation of the dye is understood to play a crucial role in the adsorption mechanisms, and the need to study the dynamics of
the anchoring of dyes on the titania anatase is recognized. However, previous models both for dyes and surfactants on metals, fail to include polarization of the dye/surfactant in the electrolyte/medium and/or fail to capture the dynamics, as most of them employ first principles or plane wave implementation of density functional theory. Accurate values for adsorption can be calculated in an approach similar to that of the adsorption of surfactants/ionic liquids/peptides and dynamic trajectories that show the stereo chemistry can be obtained using the appropriate validated parameters for metals and oxides.

More broadly, the specific interaction of biomacromolecules with nanoparticles has been the topic of significant interest because of their varied applications in transcription, inhibition, gene expression, sensors, diagnostics, light harvesting, labeling, and actuation. The analytical tools developed from the calculation of polarization energies and templating mechanisms can also be used to get an insight into the quantitative aspects of biomacromolecule-nanoparticle interaction for various geometries of the nanoparticle, specifically the role of polarization energies in guiding adsorption of organics on shaped surfaces in addition to arguments of epitaxial and geometrical fit.
2.1. Introduction

Anisotropy in nanoparticles is the functional basis for a wide variety of applications in modern materials science. Directional properties in metal nanostructures afford tuning of electrical, magnetic, optical, structural, and adsorptive properties. These can be used for fabrication of composites, storage media, films, sensors, optical switches, molecular gates and catalysts.\textsuperscript{1,33-35} The applications of size and shape controlled metal nanostructures have raced ahead of the ability to synthesize them in narrow, controlled distributions and morphologies.\textsuperscript{8} There is a need for understanding of the forces at play during the formation of these nanostructures. A quantitative outlook of interfacial forces involved and the degree to which they influence adsorption and desorption of molecules on these inorganic surfaces would explicitly answer some of the questions related to the experimental observations of anisotropic growth and specific binding.\textsuperscript{8,35,36}

Understanding these interactions at the organic-inorganic interfaces is especially important for structures of face-centered cubic (fcc) metals, such as Ag, Au, and Pd, in the absence of a crystallographic driving force that would lead to anisotropy.\textsuperscript{1} Thermodynamics should favor the formation of faceted spheres. The components that would drive anisotropy in this case would be the interactions between metal precursors,
reducing agents, solvent, and a surfactant/polymer/ionic/biomacromolecular species that would stabilize and/or template the formation of the anisotropic metal nanostructure.

2.2. Modulating Morphology and Specific Interaction

Morphological control of particles can be achieved through either i) growth-based or ii) template-based synthesis approach. Growth-based approach refers to precipitation mechanisms, while template-based approach refers to nucleation and growth mechanisms on templates, involving size-directing agent(s) acting as stabilizers or templates or both. The pre-existing structure of the template causes epitaxial growth that commonly involves geometrical and stereochemical matching.8

Growth directed syntheses have focused on a range of inorganic compounds including biomineral precipitation, with a focus on CaCO3,37-39 and precipitation of metals,40 metal oxides, and semi conducting compounds.41-59 Growth-directing agents guide the assembly of these compounds and there is specific interest in understanding the mechanisms of phase stability, plane orientation, and other physiological factors involved in growth-based syntheses.

Solution-based precipitation can either occur through a direct precipitation of the metal from the solution with the use of suitable reducing agents, or preparation of a fine dispersion of metal compounds followed by reduction of the compounds in gas or liquid phase.19 Pressure and temperature are kinetic variables that can control growth, especially in the second mechanism.

Solvent plays a major role in the synthesis of nanoparticles through these solution-based routes. With increasing polarity of solvent, dissolution of metal salts
increases, leading to a number of syntheses of metal nanoparticles in alcohol based media.\textsuperscript{60-64} Surfactants act as dispersants in this case, and aggregation occurs due to electrostatic interactions resulting from the polarity of the solvent. Alcohols serve as solvents and reducing agents, and would need a dispersant like a surfactant, in addition, as described above. Polyols (e.g. glycerol) serve the triple function of solvents, reducing agents, and dispersants. Cu and Ni nanoparticles have been prepared using polyols.\textsuperscript{65}

For a hematite system it has been shown that the shape regulation is dependent on adsorption of the organic molecule.\textsuperscript{44} Specific adsorption of sulfate ions is observed for planes of hematite, and this controls the morphology of the resulting nanostructure. Shear rate can also be used to guide morphology in titanate compounds in addition to the concentration of precursor/complexing agent.\textsuperscript{53,54}

Template-directed syntheses commonly involve microemulsions and micelles, creating pockets of growth, with the confinement of the reacting species to produce a resulting nanostructure that bears resemblance to the initial structure on which growth occurs. These systems can be seen as nano-reactors where the transport and diffusion of species become a controlling factor in the overall synthesis. The “aggregation-template” mechanism of growth of CdS rods is illustrated in Figure 2.1.
Simple thermodynamic arguments cannot explain the formation of structures having non-equilibrium shapes, e.g. \{110\} surfaces of Au have the highest energy and gold nanorods containing \{110\} surfaces can be obtained via CTAB bilayer mechanism. In this case, packing of the polar head group is a main parameter that guides the geometrical matching of the template and resulting nanostructure. The charge of the polar head group can also be used to advantage, and when complemented with the
use of ultraviolet radiation, it is seen that only the polar groups that are positively charged reduce gold. Molecular dynamics calculations in conjunction with experimental tools of small-angle neutron scattering, and surface force microscopy have been used to analyze the formation of rigid, rod-like polystyrene particles from a dendrimer template.

Combination of self-assembly with templated synthesis results in complex nanostructures. This is because of the interlocking of reverse micelles and microemulsions with specific faces of the nanoparticle crystal. Pressure and temperature can be used as kinetic controls in synthesis of CdSe rods, used in photovoltaics. Mesoporous silica can change from particles to rods by using cationic surfactants.

2.2.1. Organic Templates as Size-Directing Agents

Organic compounds are used in a wide variety of roles, such as templates, stabilizers, and modifiers. Easy removal of organics has resulted in their popularity in the synthetic applications mentioned above. Organics have been variously used as templates for size and shape control.

Monolayers of surfactants have been commonly seen to template the nucleation and growth of metal nanoparticles, resulting in geometrical and stereochemical matching of the monolayer with the nanocrystal lattices via a mechanism of epitaxial growth. Lattice matching occurs in the growth of Barium Fluoride. X-ray diffraction was used to observe this matching phenomenon. CTAB has a unique propensity to produce rods of varying anisotropy. The synthesis scheme is illustrated in Figure 2.2.
Figure 2.2. Gold nanorod synthesis through seed-mediated approach using CTAB as surfactant. TEM of nanorods (avg. length 500 nm) on bottom right (ref. 86).

With spherical seeds starting from 3.5-4 nm, nanorods of 20-30 nm width, and 600 nm lengths can be produced. Aspect ratios, defined as length to width ratio, in the range of 2 to 25 can be obtained. Smaller seeds are seen to produce higher aspect ratio of nanorods.\textsuperscript{87} The presence of Ag\textsuperscript{+} increases the yield significantly to ~100% from 20-40%, but decreases the aspect ratio to a maximum of 6 with Ag\textsuperscript{+} ions present.\textsuperscript{88} Also, a number of shapes such as blocks, cubes, and tetrapods can be formed by using the above method.\textsuperscript{89} Hence, this may be a synthetic route to produce shape-controlled silver nanoparticles.
The positively charged quaternary ammonium headgroup shows preferential binding to the \{100\} and \{110\} faces of Au, since the \{111\} faces are densely packed. It is hypothesized, that side faces are stabilized by the headgroup binding and this results in growth along the [110] axis. Sides are not well defined and may be either \{100\} or \{110\} or both (Figure 2.3).

Figure 2.3. Schematic of the gold nanorod. The pentagonal end faces are all \{111\}. Growth direction is along [110]. Sides are either \{111\} or \{110\} (ref. 86).

Figure 2.4. Zipping mechanism in the formation of Au-nanorod through CTAB mediated synthesis (ref. 86).
The effect of the headgroup is not fully understood. Hence, the need for modeling to understand the adsorption and templating mechanism. Tail length also affects the anisotropy. CTAB forms a bilayer that is experimentally observed through FTIR and thermogravimetric measurements. Tails of CTAB interlock to form a bilayer, with one layer of cationic headgroups facing the metal and the other facing the aqueous solvent (Figure 2.4). The aspect ratio of Au-nanorod depends on the tail length of CTAB.\textsuperscript{86} Longer the chain length, better is the stabilization of nanorod in the zipped bilayer intermediate shown above.\textsuperscript{86}

CTAB is one of the most commonly used organic molecules for making anisotropic nanostructures of metals.\textsuperscript{22,90} It templates the growth of nanoparticles to nanorods. In some mechanisms that have been put forward, CTAB is seen to serve as soft-template.\textsuperscript{20-22,90,91} Tunability exists in the aspect ratio of gold nanorods through CTAB serving as a structure-directing template.\textsuperscript{92} Ionic Liquids (ILs) act as solvent and capping agents.\textsuperscript{36} They present an alternative route to nanorod synthesis that is eco-friendly. Reaction mechanism is kinetic based. [EMIM][ES] attachment has been hypothesized as being similar to that of CTAB. We analyze the difference in the two mechanism of synthesis from ionic liquids and surfactants in Chapter 5. Transport and thermodynamic driving forces also play a key role. ILs attach to the low density facet of gold, if a weak reducing agent is used.

Morphologies of gold nanorods can be varied through the introduction of different inorganic ions that control the seed formation, thereby controlling the resulting nanostructure that is templated on the seeds.\textsuperscript{26,93} Morphology can also be tuned with
change in the concentration of silver-ion resulting in variations in yield and aspect ratio in gold nanorods through CTAB mediated synthesis.

2.2.2 Peptides and Bio-Molecules as Organic Templates

Biomacromolecules acting as templates have found applications in bio-detection and imaging,\textsuperscript{94} achieved through optical tuning of as synthesized nanoparticles. Organic ligands\textsuperscript{32} have been engineered to impart nanoparticles with catalytic, transportation, and sensing properties.\textsuperscript{95,96} Other uses include therapeutic devices, implants and interfacial bio-compatibility.\textsuperscript{97} Some of the applications are summarized in Figure 2.5.

Bio-molecules such as peptides, DNA, enzymes, and antibodies can functionalize nanoparticles to have recognition patterns, also called motifs, on the surface that would serve as detectors and as connectors in hybrid assemblies. Nanoparticles can also serve as a scaffold for attaching to ligand with a range of resulting functionalities, as shown in Table 2.1.
Peptides have been used to synthesize gold nanoparticles, by reduction of the H\(\text{AuCl}_4\) precursor, with great control on size distribution as also formation of self assembling arrays of nanoparticles. Two peptides used for this purpose are A3 and Flg.
The peptides A3 and Flg are used in our study of polarization at the metal-biomolecular interface. A3 contains the tyrosine residue which has been hypothesized as reducing the HAuCl₄ precursor.³⁵

Figure 2.6. TEM micrographs of gold nanoparticles by reduction of HAuCl₄ in the presence of the peptides A) A3-Flg and B) Flg-A3. Scale bar is 50 nm (ref. 35).

Narrower distribution of nanoparticles is obtained through reduction with A3-Flg or Flg-A3 peptide sequences than with either A3 or Flg peptide alone. The peptide sequences not only reduce the gold salt precursor but also coat the surface of the nanoparticles, lending both stability and selective functionality through surface activation. As can be discerned from the figure above, hexagonal patterns are formed. This ability to
self assemble 2D arrays can have useful electronic and optical properties.\textsuperscript{98} The ability to self-associate into 2-D patterns also gives the possibility of tuning these assemblies according to interparticle spacing or particle size.

By simulating and understanding interactions, the inorganic binding of peptides can be lent robustness. Literature exists on mechanisms of interaction of peptides with metals, although a quantified outlook is missing.\textsuperscript{99,100}

DNA is comparable in size to nanocrystals and forms standard secondary and tertiary structures, making it ideal for template based syntheses of nanocrystals. It has suitable mechanical\textsuperscript{101-105} and molecular-recognition properties.\textsuperscript{106} On the other hand it has poor electrical conductivity. Modification of ssDNA is possible at specific sites so as to covalently bind to nanocrystals, forming a number of patterns (Figure 2.7). Resulting conjugates hybridize to form complementary ssDNA.\textsuperscript{107}
Figure 2.7. Patterns formed by DNA-based assembly of nanocrystals. These patterns vary from collinear to triangular. Optical properties of nanocrystals depend on spacings and hence can be tuned. DNA creates nonperiodic, and specific structures that are not available through other organic templates (ref. 107).

The formation of silver ion-DNA complex is based on ion-exchange and selective localization of the silver ion along the DNA backbone. Reduction of silver ion on the skeleton leads to formation of silver aggregates in the form of nanowires (Figure 2.8).
Figure 2.8. DNA–assisted silver wire formation. Electrode patterns with dimensions can be seen in the top left corner. The 100x100µm boxes are bonding pads. a, Two different sequences of oligonucleotides are attached to the electrodes. b, Connection of electrodes by 1-DNA bridge connecting the two electrodes. c, Bridge formation with concentration of silver-ion. d, DNA skeleton has metallic silver aggregates bound to it. e, Silver wire formation, fully developed (ref. 108).

The approach of using DNA as a polyanion structured template can also be extended to polymers like PPV. DNA based nanoparticle complexes have a number of
applications and can be synthesized using a range of materials. DNA, being anionic, is extremely receptive to cationic nanoparticles. Interaction is through electrostatic attraction. Monolayer protected nanoparticles serve as scaffolds for nucleic acids. These nanoparticles can have their monolayer tuned for stability, which has applications in drug release. Charge-mediated endocytosis gives adsorption of DNA-nanoparticle, which has an overall positive complex, on the cell membrane. These complexes are eventually absorbed onto the cells. There is cooperative binding of DNA with EtBr, through an interplay of electrostatic and intercalation mechanisms that can be exploited for interactions with monolayer protected nanoparticles.

Antiangiogenic properties of Au-nanoparticles have led to their use in cancer treatment. Nanoparticle-protein complexation results in lessened denaturation of proteins at the air-water interface. Binding is also guided by the hydrophobic/hydrophilic nature of constituent amino acids. Length of linkers, with amino acids serving as linkers for peptides, can tune nonspecific interactions. Amino acid interaction with materials underlines the basis of the peptide interactions which can be used to template the formation of a variety of nanostructures and devices. Protein 3rGBP inhibits the growth of Au{111} crystal face in solution. It is important to understand which parts of the structure cause templating, and self-assembly and how. Peptide nanodomains can be formed on metal by tuning specific interactions, with insight gained from atomistic simulation, that occur during self-assembly. Molecular dynamics can aid NMR data set to see specific binding sites and the conformation of the bound protein.

The majority of 3rGBP is available for interaction with the nanoparticle surface, since the intramolecular forces are weak. Particular surfaces, e.g. {111}, can serve as
nanoscale building block, if nanotemplates of peptide can be formed on them. Geometrical and symmetry matching exist in such nanodomains. The lack of internal stability in the peptide, 3rGBP\textsubscript{1} being a self-associating peptide, leads to intermolecular forces. Some amino acids of 3rGBP\textsubscript{1} have been recognized as disorder promoting. Nonbonding interactions and intrinsic disorder contribute to the 3-D structure of the nanoparticle-protein complex. Number of contacts of the peptide with gold guides the diffusion processes, promoting long-range order. Surface recognition leads to use as template, and tuning of linkage to metals and other materials. Heterostructures can be formed through such linkage tuning.

In summary, we have seen that bio-functionalization\textsuperscript{33} of nanoparticles opens up a number of avenues in the applications of nanoparticles. These are summarized in Figure 2.9. The binding of these peptides and other biomacromolecules to nanoparticles is not fully understood. Specific peptide sequences that bind to nanoparticles are generated experimentally through a phage display technique illustrated in Figure 2.10. The dependence of binding on the sequence of peptides can be discerned through quantification of the binding phenomena and adsorption/desorption mechanisms. Peptides can control both the assembly and disassembly of complexes, which gives reversible control on processes.\textsuperscript{33} Au nanoparticles can thus be used as probes for gene-expression by modification through oligonucleotides.\textsuperscript{125}
Figure 2.9. Various applications of biofunctionalized nanoparticles (BFNs) (ref. 32).
2.2.3. Specific Adsorption of Organic Molecules on Inorganic Surfaces

Binding of surfactants to different surfaces to give faceted growth or cause reconstruction of a high-energy metal surface is well documented.\textsuperscript{25,126} The lack of a commonly accepted experimental or theoretical approach towards quantifying the adhesion energy of organic surfactant on a given surface of the nanocrystal results in no generic method for the choice of surfactant. Hence, modeling can lead to understanding
of the forces at play which would help in a better choice of template and/or surfactant that can be used in the syntheses of nanoparticles.\textsuperscript{127}

CTAB is expected to bind stronger to \{110\} facet than to \{111\} or \{100\} as seen through TGA.\textsuperscript{25} It is also seen than in formation of a nanostructure of octahedral geometry, the net growth rate on \{100\} exceeds the one on \{111\}, but it is not known which plays bigger role: i) strong surfactant binding or ii) size-dependent surface energies. In PVP-mediated synthesis of metal nanoparticles, growth is in direction opposite to where PVP would adsorb.\textsuperscript{24,128} In presence of Gold Binding Proteins (GBPs) Au forms hexagonal crystals. Gold Binding Proteins show preferential binding to Au \{111\}, but it is not understood why.

In electrochemistry, specific adsorption depends on the hydration number of the ion/molecule.\textsuperscript{15} Hydration number is the experimental variable that is measurable. Primary hydration lessens specific adsorption when compared to ions that are not hydrated. Image energy has been reported as contributing towards specific binding as would be discussed in the next section. Specific adsorption is independent of charge on metal, the effect being known as super-equivalency in adsorption. Super-equivalency would mean that even on a neutral metal surface in contact with polar solvents/surfactants specific adsorption would be observed if energy can be gained by the ion/molecule from adhesion to the metal.

2.2.4. Experimental Observations of Physical Adsorption in Surface Enhanced Raman Spectroscopy (SERS) and Electrochemistry and the Effect of Molecular Orientation
Raman scattering is enhanced by the adsorption of molecules on the surface and termed Surface Enhanced Raman Spectroscopy (SERS). The two possible mechanisms of enhancement are electromagnetic and chemical.\textsuperscript{13} In the case of physical adsorption it is mostly an electromagnetic mechanism, and can be understood by the classic electrostatic example of a polarizable metal sphere placed in an external electric field. Induced field on the surface may be due to induced charges produced as a result of a polar molecule on the metal surface. This causes changes in resonance condition of the surface plasmons, which varies with orientation and separation of adsorbate from the surface of the metal.\textsuperscript{14}

The study of adsorption of neutral molecules on electrochemical interfaces has been extensively done.\textsuperscript{129-131} Pyridine at the mercury electrode has been the subject of Raman studies.\textsuperscript{132-135} Plots of free energy versus coverage show abrupt changes. These changes are hypothesized as resulting from the perpendicular orientation of the pyridine molecule on the electrode. Pyridine is physisorbed on Hg, as well as Ag\textsuperscript{14} and, at higher surface coverage or small fields, it orients itself perpendicular to the metal surface. It is suggested that for negatively charged surfaces the N lone pair would point away from the surface.

Solvent orientation at metal surfaces (Figure 2.11) has been considered important towards understanding the adsorption of molecules on the electrochemical interface.\textsuperscript{14,15} Expressions have been derived for ratios of number density of molecules with dipoles pointing up to those with dipoles pointing down in terms of the electric field, interaction energy of the dipoles, and the co-ordination number of surrounding dipoles.

Image energy created due to adsorption of pyridine on silver, creates a dipole of which only the perpendicular component of polarizability is considered as contributing to
the Raman spectra. The other components are ignored as a non-linear approximation (they involve higher terms of the induced electric field and the polarizability of the adsorbate). This means that orientation of the pyridine on the silver electrode is important in determining the Raman spectra (Figures 2.12, 2.13).

Figure 2.11. Schematic model of the adsorption of the pyridine molecule on the Ag electrode with no counter ions present. Different orientations of Pyridine and water are shown (ref. 14).
Figure 2.12. Schematic showing the separation of the center of the pyridine molecule from the image plane (distance R). On the right is the plot of the logarithm of Raman intensity enhancement as a function of R. As can be seen from the graph, enhancement of several orders of magnitude can result from the surface-image dipole mechanism (ref. 14).
Fig. 2.13. Image dipole orientation on (a) positively charged surface, (b) negatively charged surface, and (c) local polarization induced due to adsorption of pyridine with counter ions (ref. 14).

Orientation of aliphatic molecules in solution on the electrochemical surface has been studied in detail.\textsuperscript{15,136} From free energy calculations it is concluded that the hydrocarbon group points towards the metal while the polar group points towards water. This is the thermodynamically favored argument. In nanorod formation, we see the opposite of the thermodynamic argument for zipped mechanism involving CTAB mediated synthesis of gold nanorods. It leads us to conclude that some kinetic factors, templated growth, or chelation mechanisms wherein the counter ions are epitaxially bound to the gaps in metal surface, are at play.
The fact that the orientation of molecules makes a difference in image energy is illustrated below (Figure 2.14) by showing the interactions resulting from two different orientations of water molecule with its induced dipole. The difference in energies for the two orientations is calculated to be about 0.9 kcal/mol.\textsuperscript{15}

![Image interactions for two opposing orientations of water molecules on the surface. The difference in energies is calculated to be around 0.9 kcal/mol (ref. 15).](image)

2.3. Kinetic Shape and Size Control in Nanocrystal Formation

The inorganic core of nanocrystals requires stabilization. Organic surfactants play a major role in the stabilization and hence the final shape and size of the nanostructure. If the selective adhesion to the inorganic surfaces is used in conjunction with control of kinetic parameters (Figures 2.15, and 2.16), then a variety of shapes and sizes can be formed.\textsuperscript{128}
Figure 2.15 shows shape control through kinetics. In a) we see a high growth regime where the high energy facets grow quicker compared to the lower-energy facets. In b) we see shape control through adhesion. If the organic moiety binds selectively to a facet, then the growth of that facet can be slower compared to other facets which results in rod/disk like shapes. In c) complex shapes are formed by the sequential elimination of a high-energy facet by the persistent growth of a low energy facet. In d) dendritic branching occurs because of the existence of more than one crystal structure in the same domain.
Figure 2.16. Anisotropic growth of nanoparticles. (a) CdSe nanorod (scale bar 50 nm) and (b) Co nanodisks (scale bar 100 nm) by kinetic shape control and selective adhesion. The introduction of an organic that selectively binds to a facet effectively lowers the energy of that facet (ref. 127).
Focusing of growth can be obtained by controlling the monomer concentration. At high monomer concentration, the critical size is small, resulting in growth of all particles (Figure 2.17). Smaller particles grow at larger rates than bigger particles, resulting in size focusing. However, if the monomer concentration goes below a threshold, the smaller nanocrystals are depleted as the larger ones grow, resulting in broadening of the size distribution. Hence, a control of monomer concentration gives a control on the size distribution.
CHAPTER III
CONCEPTS OF MOLECULAR SIMULATION

3.1. Introduction

A simulation involves assumption and/or formulation of a model, application of the model under a given set of pre-determined conditions, analysis of the results, and finally interpretation of the results as per the final goals of the simulation (e.g. comparison with experiment or understanding of a set of interactions). Applications of materials simulations span a wide range of fields as diversified as polymers, electronics, photonics, structural materials, fuels, (commodity, specialty, and agricultural) chemicals, and pharmaceuticals.

Simulation methods can be classified into four broad fields according to the size of the system and the properties under investigation.

a) Quantum-mechanical methods: These study the electronic structure, conductivity, chemical reactivity of molecules up to a maximum of 1000 permissible atoms.

b) Classical methods: These study systems in full atomistic detail, without the explicit consideration of the electronic structure. Behavior of organics in solution or interface can be studied using classical models. A maximum of 100,000 atoms can be considered under these schemes.
c) Mesoscale methods: These are suitable for studying systems at the µm scale, where no atomistic detail is considered and atoms or groups of atoms can be represented by one bead or unit. Morphologies and entanglement networks of polymers can be studied through these models.

d) Finite element methods: These solve sets of Partial Differential Equations (PDEs) to look at mechanical properties of the system under study. These models are used to look at anything from structural analysis to crystallization patterns.

Molecular Dynamics (MD) and Monte Carlo (MC) fall into category b. The focus of this work is investigation of interactions through force-field based MD calculations, followed by analyses. Force-field is a set of parameters (like bond length, angles, vibrational constants, connectivities between molecules, well depths, etc.) that are used to calculate interactions according to potentials described in the system. From the potential, forces can be calculated, which would further give velocities and co-ordinates according to Newton’s laws.

Figure 3.1. Schematic showing the relationship between theory, experiment, and simulation (ref. 137).
Figure 3.1 shows the relationship between simulation, theory, and experiment. There are models in which sufficient theoretical insight is available, but experimental investigation is difficult (e.g. growth dynamics of a nanostructure, or intermediates in catalysis, or charge transfer on the TiO$_2$ anatase in a solar cell). For these cases, modeling would provide data that can at later stage be validated through experiment. Alternatively, models can be validated with experimental values through some physical parameter (semi-empirical validation), and then simulations carried out to analyze other parameters of interest. Similarly, there are systems where complexity is high, and the Hamiltonian for the energy can be obtained. However, simulation can switch on and switch off a number of interactions to better analyze the forces at play and their comparative roles in the dynamics of the system (e.g. templated growth of a nanostructure).

There are also situations where numerical experiments are the best bet because carrying out experiment is not desirable or feasible (e.g. reactor meltdown, buried interface between nanoparticle and biomolecule). In all of these cases, the role of simulation is not to fit experimental curves, but to augment theory and experiment in better understanding the dynamics and processes of the system at hand.\textsuperscript{137}

3.2. Molecular Dynamics: Methods

Molecular dynamics uses the Newton’s equations of motion to equilibrate a chosen/given model system of $N$ particles until the properties do not change with time. After equilibration the values of the system that are needed (temperature, pressure, energies, co-ordinates, etc.) are sampled by averaging. Many times, these averages are
only taken after equilibration has been reached, or the fluctuation in block averages is within a certain error. The fluctuation in block averages is commonly seen by plotting energies vs. time and looking at averages over blocks of time that are representative fractions of the total.

The time step is defined as the smallest period over which the integration of the forces occur, according to the Newton’s laws of motion. A commonly used time-step is femto second ($10^{-15}$ seconds) for molecular dynamics (MD) simulations. In many ways MD can be seen as a numerical experiment, analogous to physical experiments.\textsuperscript{138} An MD scheme is illustrated below (Figure 3.2).
Initialize; choose N atoms that represent the model system. e.g. construct a periodic box with metal surface and organic in solution.

Calculate forces by differentiating the total potential (two-body, three-body, four-body, many-body; as applicable).

Calculate co-ordinates by choosing an integrator to integrate equations of motion (commonly used integrator is Verlet integrator).

Sample the system to get averages.

Repeat MD loop till equilibration. Check for block averages to see fluctuations.

Figure 3.2. Flowchart for a typical molecular dynamics simulation used to study the systems at hand.

In MD simulations of metal-organic interface, periodic boundary conditions (PBC) are used. PBC means the model system interacts with the images around it, and the forces are calculated till a mentioned cut-off. This scheme can mimic bulk behavior but with considerably less computing effort.

Verlet integrator integrates equations of motion according to the following scheme:-

\[
\ddot{r}(t + \Delta t) = 2\ddot{r}(t) - \ddot{r}(t - \Delta t) + \frac{\dot{F}(t)}{m} \Delta t^2
\]
\[ + O(\Delta t^4). \quad (3.1) \]

The advantage of the algorithm is that it does not require velocity calculation to get the new co-ordinates. By using cut-offs for the forces (typical forces that require cut-offs are van-der Waals, and Coulomb) and PBC considerable computing cost is saved. Summation of electrostatic forces in a system with PBC is done in the fastest possible manner by Ewald summation which sums the interactions in Fourier space. However, Ewald summation assumes a charge neutral system with no net dipole.\textsuperscript{139} The zero net dipole assumption is unjustified and hence cell-based summation is sometimes used to accurately carry out the electrostatic interactions in solutions with highly polar solvents or large dipoles (zwitterionic structures). In cell-based summation, all atoms are translated into the periodic box without breaking any bonds and the interaction of the original box is considered with a layer of cells surrounding it.

3.3. Monte Carlo: Methods

Monte Carlo (MC) simulation assumes a stochastic mechanism to look at time-dependence of models for which evolution is not defined according to a set of equations (e.g. MD uses Newton’s equations). The evolution of the system involves a number of iterations from random formations. If these iterations from dissimilar albeit random formulations of the system agree within the error bounds permissible then the system evolution can be studied and sampled through MC simulation. Examples include diffusion limited aggregation, where the particle moves in a random fashion, until it encounters a seed and then sticks to it. Nucleation and growth can be studied through MC,
and growth-mediated syntheses would make good systems for MC investigation (while template-mediated syntheses would make good systems for MD investigation).

MC operates through a probabilistic mechanism wherein a move is accepted or rejected with a probability that depends on the energy of the new system after the move. A move can be anything from the rotation about a bond, translation of particle, reptation of polymer chain, or shrinking of the box by a small volume. One of the popular algorithms employs the Metropolis Scheme:

Take the energy difference: \( \Delta E = E_{n+1} - E_n \) \hspace{1cm} (3.2)

Accept the new move with the probability: \( p_{acc,MC} = \min[1, e^{-\Delta E/k_BT}] \) \hspace{1cm} (3.3)

If the move is accepted, the old structure is set as the new structure, otherwise the old structure remains. MC methods can also be classified as on-lattice and off-lattice. In on-lattice MC the particles/beads sit on lattice sites whereas in off-lattice MC, the coordinates are freely chosen.

3.4. Parameters for Models under Study

The energy of the system is calculated from a specified set of interactions. Potentials in the model can be two-body (bonds, van-der-Waals, Coulomb interactions), three-body (angles, bond-angle cross terms), four-body (torsions, out-of-plane terms), many-body potentials (used in embedded atom models, and bond order models). Many-body potentials are not under study in the systems and models in the course of this work.

The potential energy of the system can then be broken down as:

\[
E_{pot}(r_1, r_2, \ldots, r_N) = E_{Bond} + E_{Angle} + E_{Torsion} + E_{Out-of-plane} + E_{Coulomb} + E_{vdW}
\] \hspace{1cm} (3.4)
First four terms represent bonded interactions while the last two represent non-bond interactions.

\[
E_{\text{Bond}} = \sum_{ij} k_i (r - r_0)^2
\]

\[
E_{\text{Angle}} = \sum_{ijk} k_{ij} (\phi - \phi_0)^2
\]

\[
E_{\text{Torsion}} = \sum_{ijkl} f(k_{ijl}, \theta, \theta_0)
\]

Figure 3.3. Schematic showing the bonded interactions in a molecule.

\(r_0\) and \(\theta_0\) are obtained from known trends or X-Ray crystal structures. \(k_i\) and \(k_0\) can be obtained from either simple classical estimates or quantum chemical calculations. Alternatively, the Raman spectra of the molecule can be simulated using an assumed value of the vibrational constants and the result compared with experiment. This can be done in a loop till there is agreement between the two spectra (simulated and experimental).

3.5. Ensembles in MC and MD Simulations

A collection of systems (particles, molecules, polymers) in different energy states is known as an ensemble.

NVT ensemble: Number of particles (N), volume (V), and temperature (T) are fixed. This is also known as canonical ensemble. Diffusivity, thermal conductivity, and viscosity can be calculated in MD with this ensemble. Pressure (P), and internal energy
(U) and the structure (for comparison with X-ray, neutron-scattering experiments) can be calculated using MC/MD methods.

NPT ensemble: Number of particles (N), pressure (P), and temperature (T) are fixed. This is also known as isothermal-isobaric ensemble. The ensemble gives dimensional flexibility in contrast to NVT. Used mainly in MD systems, to calculate response to shear, strain, density variation, and also to study morphologies of non-equilibrated systems, allowing them greater degrees of freedom to revert to favorable energy conformations.

µVT ensemble: Chemical potential (µ), volume (V), and temperature (T) are fixed. This is also known as grand canonical ensemble. Used in MC simulation of equilibrated systems in contact with bulk fluids. Equilibration is achieved through addition and deletion of particles. A number of simulations are required to get the properties of the system at various points. This is used to study colloidal systems, fluid, and multicomponent mixtures. The ensemble fails for dense systems.

Gibbs ensemble: This ensemble is used to study phase equilibria for fluid phases. Two boxes are brought in contact and a thermodynamic equilibrium is established through displacement, and volume, and molecular exchange between the boxes. The number of particles (N), volume (V), and temperature average (T) is constant for both boxes taken together. This method can be used to validate force-fields as well as analyze critical points in phase diagrams.
Two additional ensembles less commonly used are NVE (fixed number of particles (N), volume (V), and energy (E)), also known as microcanonical ensemble and NPH (fixed number of particles (N), pressure (P), and enthalpy (H)), also known as isobaric-isenthalpic ensemble.
CHAPTER IV

POLARIZATION AT METAL-BIOMOLECULAR INTERFACES IN SOLUTION

4.1. Introduction

The interaction of proteins, peptides, and surfactants with metal surfaces is of great promise for the assembly of metal nanostructures with potential applications in nanoelectronics, sensors, medical technology, and bioinspired materials.\textsuperscript{35,86,99,100,140-147} Peptides with high affinity to Au and Pd surfaces have been identified by phage display techniques \textsuperscript{33,35,99,100,141,142,144} and specific non-covalent binding has been explained by complementarity of the molecular structure of the peptide to epitaxial fcc lattice sites on the metal surface.\textsuperscript{147} Accordingly, the binding strength of the peptide correlates with the surface energy of the metal and with competitive epitaxial binding preferences of sp\textsuperscript{2} and sp\textsuperscript{3} hybridized groups in comparison to solvent molecules on a given metal surface.\textsuperscript{59,147-149} Differential peptide adsorption as a function of curvature and roughness of metal nanoparticles can also be explained using the concept of molecular epitaxy.\textsuperscript{150} Alternatively, covalently assisted binding is possible through R–S–Au\textsubscript{n} bonds of Cys-containing peptides and thiols to gold surfaces.

A yet much less considered contribution to the binding strength is polarization of the metal surface through the typically polar and often ionic environment created by solvents, surfactants, peptides, or DNA. It has long been known that electrons and other
point charges experience an attractive image potential near metal surfaces and numerous reports explain the effect of point charges and single molecules on metal surfaces in vacuum and in the gas phase. Yet few studies deal with polarization in solution or in the solid state, and approximations such as hard sphere electrolytes as well as the focus on interfacial capacity have not provided quantitative thermodynamic insight related to the competitive adsorption of organic and biological matter onto metal nanostructures in aqueous solution. The lack of quantitative knowledge of attraction mediated by induced charges is also related to the difficulty to measure such effects as separate contributions to adsorption experimentally and, thus, shortage of experimental data. At the same time, the impact of polarization on the self-assembly of surfactants and biomolecules on metal surfaces is undeniable, especially on metal surfaces of irregular geometry. The aim of our contribution is a first quantitative evaluation of the effects of induced charges on metal surfaces using a physically justified computational approach for systems up to millions of atoms on nanosecond time scales. We will discuss the impact of the image potential as an additional contribution to epitaxial and covalent binding on even metal surfaces with water, peptides of different charge state, and amino acids.

Attractive polarization occurs in response to exterior charges in the vicinity of a grounded metal surface. Electrons enter or exit through the ground, or free valence electrons redistribute at the metal surface without grounding, to maintain the interior of the metal free of electric fields (figure 4.1). The induced, complementary electric field can be thought of as mediated by image charges. According to a classical continuum model for distances $z - z_{sf} > 2.5$ Å from the top atomic layer of the metal surface, the
attractive image potential $E_{im}$ felt by a charged species $q$ is proportional to $-\frac{q^2}{4(z - z_{im})}$.

The image plane $z_{im}$ is located close to the jellium edge $z_{im} = z_{S/S} + \frac{d}{2} + \delta$ with a small system-dependent offset $\delta$ (figure 4.1A). At distances $z - z_{S/S} < 2.5$ Å, the classical continuum model overestimates the attraction and alternative models such as discrete classical models perform better.  

Figure 4.1. Concept of induced charge and image potential on a gold $\{111\}$ surface as example (A) in vacuum and (B) in contact with a peptide solution. (A) In vacuum, a point charge $+q$ causes opposite charges to enter through the ground and locate at the surface of the metal (pink negative charges) to generate an electrical field opposite to that created by $+q$. The image potential can be calculated assuming a classical image charge $-q$ (Bardeen 1940 (ref. 151); Lang & Kohn 1973 (ref. 153) ). Positions of the jellium edge (broken line) and of the image plane (solid line) are shown. (B) In contact with a peptide solution, we find a dense collection of multipoles which is overall charge-neutral but typically of nonzero dipole moment on time average. The electrons in the metal rearrange similarly at the surface to counterbalance the local electric field at the solution interface.
(grounding is not required). The image potential can be computed on the assumption of a mirror image of the collection of all atomic charges (shaded in pink). $\delta_v$ and $\delta$, represent system-dependent small offsets between the image plane and the jellium edge in vacuum and in the condensed phase. $z_{s0}$ and $z_{sf}$ represent the average position of the first atomic layer of the solution and of the metal at the interface. The arithmetic mean ("interface edge") characterizes the position of the image plane which maps the first atomic layer of the solution onto the first atomic layer of the metal.

To analyze the contribution of induced charges to adsorption of water and peptides on metal surfaces, we use example systems which have been characterized in experiment $^{35, 99, 144}$ and by molecular dynamics (MD) simulation under neglect of polarization$^{147, 168}$. Using these previously reported equilibrium MD conformations over a period of several nanoseconds, we determined polarization energies a-posteriori for a range of positions of the image plane. This decoupling of MD and image potential is only a first approximation as induced charges and the associated image potential remain difficult to integrate into the MD algorithm (see section 4.2). Nevertheless, we discuss likely changes in molecular conformation and interface structure due to the added image potential and show that the a-posteriori calculation yields polarization energies of quantitative to semi-quantitative value.

To our knowledge, the contribution of image charges to adsorption in such all-atomic models has not been computed before and we begin with a derivation of the governing equations (section 4.2). Then we employ the previously described model systems (section 4.3) of approximately $3 \times 3 \times 5$ nm$^3$ dimension that consist of even Au
metal interfaces with pure water, a solution of a non-charged, and a solution of a charged biomolecule in solution were analyzed by example of the charge-neutral dodecapeptide A3 and the threefold negatively charged octapeptide Flg-Na₃. The MD simulation relies on the biomolecular force field CVFF extended for fcc metals and provides access to length scales of multiple nanometers, time scales of multiple nanoseconds, and realistic peptide concentrations in chemical detail. Strong epitaxial adsorption and a high degree of direct surface contact was reported for both peptides on Au \{111\} surfaces and weak epitaxial adsorption and a low degree of direct surface contact on Au \{100\} surfaces. The analysis of the image potential on the basis of MD simulation promises physically justified results as biomolecular force fields include atomic charges in very good agreement with experimentally determined dipole moments.

Potential alternative methods to determine the influence of induced charges include hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) and full electronic structure calculations such as density functional theory (DFT). However, QM/MM methods could introduce a significant dependence of atomic charges on basis sets or pseudopotentials, substantial disagreement with experimental dipole moments, and uncertainty in the image potential. Electronic structure (DFT) calculations would be computationally a million times more expensive and limit the system size to peptide fragments, few water molecules, and equilibration times to picoseconds to probe the image potential. Therefore, these methods were not further pursued here. Previous DFT calculations on subsystems, nevertheless, were detrimental to verify the absence
of significant covalent bonding between peptides (excluding Cys) and metal surfaces in aqueous solution. The force field models employed here neglect residual amounts of charge transfer and covalent bonding across the metal-biological interface and remain a good approximation due to the gain in length and time scales. A limitation of all methods is also the difficulty to define an exact position of the image plane (see section 4.2.1.). A typical uncertainty of ±0.1 Å introduces more uncertainty in the image potential than many other details. Yet the classical continuum method \(^{160,161}\) is a simple and good approximation to estimate polarization on metal interfaces as the distance between the top atomic layer of the metal surface and the first layer of atoms in solution is on the order of 2.5 Å, including some shorter individual distances down to 2.0 Å of less significant statistical weight (table 4.1).

The outline of the paper is as follows. In Section 4.2, we discuss the location of the image plane and introduce novel computational algorithms to compute the image potential of metal-biomolecular interfaces in solution. In Section 4.3, we explain details of the models, computation, and analysis. Section 4.4 is dedicated to the results and discussion, including the total polarization energy per surface area of the metal, the contribution to the polarization energy by water, peptides, amino acids, and the net contribution of polarization to peptide adsorption on the metal surface. The paper concludes with a summary in Section 4.5.
Figure 4.2. Models of the peptides in the simulation. (A) Peptide A3 was identified from a phage display library and is charge-neutral. (B) Peptide Flg-Na₃ is a common binding motif to Au \{111\} and Pd \{111\} surfaces and contains 3 Na⁺ ions to compensate three negative charges on the Asp side chains. Peptide models were employed in zwitterionic form and the charge state of the side chains corresponds to pH = 7.
Table 4.1. Properties of Au {111} and {100} surfaces in contact with water and peptide solutions, including the average position of the jellium edge $z_{Jel}$ and of the first layer of solution atoms $z_{Sol}$ relative to the first layer of metal atoms $z_{Sf}$, the polarization energy $E_{pol}$ per surface area, per water molecule and per amino acid of the peptides in contact with the metal surface assuming an image plane located at the jellium edge.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$z_{Jel} - z_{Sf}$ ($\text{Å}$)</th>
<th>$z_{Sol} - z_{Sf}$ ($\text{Å}$)</th>
<th>$E_{pol}$ per surface area ($\text{mJ/m}^2$)</th>
<th>$E_{pol}$ per H$_2$O ($\text{kJ/mol}$)</th>
<th>$E_{pol}$ per amino acid ($\text{kJ/mol}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au {111}</td>
<td>1.1773</td>
<td>2.535 ±0.005</td>
<td>$-55 \pm 5$</td>
<td>$-2.38$ (1st layer)</td>
<td>$-40$ to ±0 (avg. −8.4)</td>
</tr>
<tr>
<td>Au {100}</td>
<td>1.0196</td>
<td>2.299 ±0.005</td>
<td>$-60 \pm 10$</td>
<td>$-2.18$ (1st layer)</td>
<td>$-29$ to ±0 (avg. N. A.)</td>
</tr>
</tbody>
</table>

*Average over all systems (water, A3, Flg-Na$_3$).*
4.2. Computation of the Image Potential


The computation of the image potential, which we call equally polarization energy here, depends on the position of the image plane. In vacuum, the image plane \( z_{im} = z_{sj} + \frac{d}{2} + \delta_v \) is typically located near or slightly above the jellium edge (figure 4.1A) which corresponds to a plane located half a lattice spacing \( d/2 \) above the top atomic layer of a given metal surface.\(^\text{152, 161, 160-162}\) Surface state energies from photoemission and inverse photoemission measurement indicate metal-dependent locations of the image plane relative to the jellium edge \( \delta_v \) between \(-0.13 \text{ Å} \) (inwards) and \(+0.26 \text{ Å} \) (outwards).\(^\text{160}\) Low values of \( \delta_v \) are associated with higher total electron density of the metal, proportional to higher atomic number, for example \( \delta_v \) (Au) < \( \delta_v \) (Ag) < \( \delta_v \) (Cu).\(^\text{154, 161}\) The image plane can additionally shifted inwards (1) due to movement of charges, forcing a response of the electron gas and partial loss of the image potential and (2) through the approach of charged entities closer than 2.5 Å to the surface atomic plane of the metal which causes image saturation and non-linearity and would otherwise result in overestimates of the image potential.\(^\text{160,161}\) On the contrary, the application of external electric fields and charge transfer at electrode surfaces can shift the image plane outwards up to \( \delta_v = +0.8 \text{ Å} \).\(^\text{153,162}\)

In contrast to vacuum, the presence of a condensed phase brings charged species very close to the surface (figure 4.1B) so that the electron density of the metal is pushed inwards and non-linear effects are more important. An inward shift of the mirror plane
\( \delta_i - \delta_v \) up to \(-0.5 \, \text{Å}\) was reported for mercury-water interfaces in theoretical models.\(^{162}\), \(^{163}\) In consideration of experimental data,\(^{160}\) a zero shift or a small negative shift \( \delta_i = 0 \) \(\pm 0.2 \, \text{Å}\) of the image plane relative to the jellium edge on Au and Pd surfaces appears best justified.\(^{160}\) The mirror image of the first atomic layer of water molecules and organic solutes is then anticipated on or slightly below the surface atomic plane of the metal similar as shown in figure 4.3B, with some tendency toward figure 4.3C. For a chosen metal interface, the position of the image plane remains fixed at this position in the absence of applied electric fields and nanoscopic flow.

4.2.2. Image Potential in Solution.

To our knowledge, numerical expressions for the image potential in all-atomic models containing solute molecules, explicit solvent, and ions have not been developed and are introduced in this section. We begin with a brief summary of the image potential of single point charges in vacuum, and then derive the image potential for a collection of charged molecules such as water, peptides, and ions in contact with metal surfaces.

Let us consider first a single point charge (figure 4.1A). For simplicity, we assume the vertical distance of the original charge \( q \) from the image plane \( z - z_{im} \) (figure 4.1A) to be \( z/2 \), leading to a distance \( z \) between the original charge and the image charge along the \( z \) axis. According to Coulomb’s law, the attractive force on the original charge \( q \) due to the pertinent image charge \( -q \) equals \( F_{im} = -\frac{1}{4\pi\varepsilon_0} \frac{q^2}{z^2} \). The image potential corresponds to the energy gain of moving the original charge \( q \) from \( \infty \) on the \( z \) axis to a final position \( z/2 \). The integration variable is \( d(z'/2) \) due to the symmetry
constraint of the image: when the original charge moves downward by \(-d(z'/2)\), the image moves upwards by \(d(z'/2)\) so that their distance decreases by \(-dz'\). Therefore, the image potential for a single ion at a large distance \(z/2\) from the image plane on the metal surface is:\textsuperscript{151, 153, 160, 161}

\[
E_{im} = -\int_{\infty}^{\infty} \hat{E}_{im} d\left(\frac{z'}{2}\right) = -\int_{\infty}^{\infty} -\frac{1}{4\pi\varepsilon_0} \frac{q^2}{z'^2} \left(\frac{z'}{2}\right) = \left[ -\frac{1}{4\pi\varepsilon_0} \frac{q^2}{2z'} \right]_{\infty}^{z} = -\frac{1}{4\pi\varepsilon_0} \frac{q^2}{2z}. \tag{4.1}
\]

Hereby, the denominator \(2z\) equals twice the vertical distance \(z\) between original charge and image charge.

The situation is similar for multipolar, overall neutral molecules such as water \(\text{H}(+0.41\text{e})-\text{O}(-0.82\text{e})-\text{H}(+0.41\text{e})\), peptides, and condensed aqueous interfaces (figure 4.1B).\textsuperscript{163} Then, the “imprint” of the opposite charge distribution of the dense liquid phase across the image plane creates the image potential. The evaluation of this potential includes all pairwise interactions between original charges and image charges, under additional consideration of periodic images of image charges. Original charges \(q_i\) and image charges \(q_j\) can then differ in absolute value, in \(x\) and \(y\) coordinate, and deviate from the \(\pm z/2\) symmetry along the \(z\) axis. Therefore, the expression for the image potential between a pair of a charged atom \(i\) and another image charge \(j\) changes to:

\[
E_{im}^{ij} = -\frac{1}{4\pi\varepsilon_0} \int_{\infty}^{z} \frac{q_i q_j}{(z'+\Delta z_{ij})^2 + (x_i - x_j)^2 + (y_i - y_j)^2} d\left(\frac{z'}{2}\right). \tag{4.2}
\]

Equation (4.2) allows different charges, a possible horizontal offset \(d_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2}\), and a nonzero asymmetry in \(z\) direction \(\Delta z_{ij} = -z_i - z_j\) as part of the vertical distance \(z_{ij} = z_i - z_j = 2z_i - z_i - z_j = z' + \Delta z_{ij}\). The positive
coordinate \( z_i \) and the negative coordinate \( z_j \) can be freely chosen and still conform with the previous definition of the \( z \) coordinate \( z = z / 2 \) and with the integration variable \( d(z'/2) \). Evaluation of the integral in equation (4.2) yields the image potential:

\[
E_{im}^{ij} = -\frac{q_i q_j}{4\pi\varepsilon_0} \left[ \frac{1}{2d_{ij}} \tan^{-1}\frac{z_{ij}}{d_{ij}} \right] = \frac{q_i q_j}{4\pi\varepsilon_0} \left[ \frac{\pi}{2} - \tan^{-1}\frac{z_{ij}}{d_{ij}} \right]. \tag{4.3}
\]

Equation (4.3) is the exact expression for the image potential between one pair of a charged atom \( i \) and an image charge \( j \). The image potential depends on the vertical distance \( z_{ij} \), regardless of whether it is symmetrically or asymmetrically intersected by the image plane. For the overall charge neutral system, however, every asymmetric pair \( z_i/z_j \) is accompanied by another asymmetric pair of opposite orientation. The position of the image plane is solely dictated by the positions of the image charges. For \( d_{ij} \to 0 \), it can be shown that equation (4.3) converges into equation (4.1).

The image potential for the full system is given by a summation over all pairwise Coulomb interactions across the image plane as shown in equation (4.3), including the interactions between \( N \) original charges \( i \) and corresponding \( N \) image charges \( j \) as well as the interactions between original charges and periodic images of image charges in the \( xy \) plane under the condition of overall charge neutrality \( \sum_{i=1}^{N} q_i = 0 \):

\[
E_{im} = \sum_{i=1}^{N_{\text{original}}} \sum_{j=1}^{N_{\text{image}}} \frac{q_i q_j}{4\pi\varepsilon_0} \left[ \frac{\pi}{2} - \tan^{-1}\frac{z_{ij}}{d_{ij}} \right]. \tag{4.4}
\]
Equation (4.4) is the exact expression for the full image potential with respect to an image plane determined by the coordinates of the given image charges \( j \), located at half the separation \( z_{ij} \) between original charges and their corresponding image charges \((i = j)\).

For a simplified algorithmic implementation using common Ewald and Particle-Particle-Particle Mesh (PPPM) methods instead of the less convenient \( \tan^{-1} \) function in equation (4.4), it is instructive to compare the integrands of the exact formula

\[
\frac{1}{z_{ij}^2 + d^2} d\left(\frac{z_{ij}'}{2}\right)
\]

for the image potential to a hypothetical, extended version of the image potential of single ions

\[
\frac{1}{z_{ij}^2 + d^2} d\left(\sqrt{z_{ij}^2 + d^2}\right)
\]

including a horizontal offset \( d \neq 0 \) in the integration variable. The latter expression yields a larger absolute value of the integral due to the augmented integration variable and corresponds to half the summation of Coulomb interactions as in equation (4.1). We thus obtain an upper bound of the absolute value of the (negative) polarization energy as:

\[
|E_{im}| < \left| \sum_{i=1}^{N_{\text{original}}} \sum_{j=1}^{N_{\text{image}}} \frac{q_i q_j}{4 \pi \varepsilon_0} \frac{1}{2 |\vec{r}_i - \vec{r}_j|} \right|.
\]  

(4.5)

This formula can be extended into a Coulomb summation over all interactions in the total pool of \((2N)\) original charges and image charges for the location of the image plane (IP) (i) at the desired distance \( z_{im} \) and (ii) at a distance \(-\infty\) far below for which \( E_{im} \) (equation (4)) equals zero. The benefit is the applicability of common Ewald and Particle-Particle-Particle Mesh (PPPM) schemes and division by two.
The first term in equation (4.6) includes original-original, original-image, and image-image interactions and the second term subtracts original-original and image-image interactions, leading to the desired estimate of the polarization energy. We note that $E_{im}$ is negative so that equation (4.6) yields a lower value than the exact formula equation (4.4). A position of the image plane at $z_{im} - 300 \text{ Å}$ in the second term can be regarded sufficient to reduce the image potential to zero. Typical dipole lengths of $\sim 2 \text{ Å}$ (in the presence of counter ions $>10 \text{ Å}$) are then much smaller than the minimum distance of the mirror image of 600 Å.

In this section, we have derived two methods to compute the image potential at metal-aqueous interfaces in atomistic detail (equations (4.4) and (4.6)). Consideration of positions of the image plane slightly away from the jellium edge (figure 4.3 A-C) helps understand the nature of the image potential and the sensitivity of computed results with regard to the exact position of the image plane. A reference position far below the metal surface (figure 4.3D) is required when using Ewald and PPPM procedures (equation (4.6)).
Figure 4.3. Illustration of different positions of the image plane $z_{im}$ on the Au {111} surface in contact with peptide A3 and water. Corresponding mirror images are shaded in pink. The image plane is shown (A) above the interface edge, (B) at the interface edge (~0.1 Å above the jellium edge), (C) near the first layer of metal atoms, and (D) far below the interface edge, equal to zero image potential as employed in equation (4.6).

4.3. Computational Details

4.3.1. Molecular Models and Force Field.

Molecular models and the force field have been previously described. We employed six model systems composed of {111} and {100} surfaces of gold in contact with water and aqueous solutions of peptides Flg-Na$_3$ and A3 in all atomic resolution.
Vertical metal slabs of at least 1.2 nm thickness with a surface area of \(28.84 \times 29.97 \text{ Å}^2\) for Au \{111\} surfaces and \(28.5474 \times 28.5474 \text{ Å}^2\) for Au \{100\} surfaces were built using multiples of the metal unit cell according to X-Ray data\(^{165}\). Models of the peptides were prepared according to the sequence of amino acids (figure 4.2) in different configurations (extended, helical, random coil) and extensively equilibrated by molecular dynamics simulation on the Au \{111\} and \{100\} surfaces in the presence of 1000 explicit water molecules at a density of the liquid phase of 1000 kg/m\(^3\). The corresponding peptide concentration was 56 mM, and the effective concentration was lower due to isolation of one peptide molecule per simulation box and limited peptide-peptide interactions through periodic boundary conditions. We employed the graphical interfaces of Materials Studio\(^{166}\) and Hyperchem\(^{167}\) to prepare initial model configurations.

For molecular dynamics simulations, the CVFF\(^{169}\)–METAL\(^{165}\) force field (no cross no morse version) was employed which includes accurate Lennard-Jones parameters for fcc metals. The potential energy consists of the sum of the bond, angle, torsion, out of plane, Coulomb and van-der-Waals energies. Computed metal-water interface tensions\(^{165}\) and the strength of metal-peptide interactions in aqueous solution were found to be in very good agreement with experimental data and ab-initio studies\(^{147}\).

The possibility of quantitative thermodynamic consistency between biomolecular force fields and validated extensions for inorganic components using standard combination rules has also been previously demonstrated\(^{147}\). Nevertheless, further validation of the accuracy and limitations of Lennard-Jones interactions between the metal and other molecules will be very helpful.
4.3.2. Molecular Dynamics Simulation.

Equilibrium configurations of the Au-water and Au-water-peptide systems were initially obtained by energy minimization (1000 steps) and subsequent molecular dynamics simulation in the NVT ensemble using various peptide start conformations on the surface. A spherical cutoff at 1.2 nm was employed for van-der-Waals interactions and Ewald summation for Coulomb interactions using high accuracy of $10^{-6}$ kcal/mol. The total simulation time exceeded 5 ns for the metal-peptide-water systems (1 ns sufficient for metal-water interfaces) with a time step of 1 fs and temperature control by the Andersen thermostat at 298.15 K. 500 snapshots from the equilibrium trajectory were chosen for each system to analyze polarization energies. For visualizations of representative structures and further details, see Heinz et al. 2009 (ref. 147).

4.3.3. Analysis.

The first step in the analysis involved the definition of the image plane. The average $z$ coordinate of the superficial layer of gold atoms $z_{sf}$ was obtained as an average over all gold atoms in the first atomic layer over 500 snapshots with negligible uncertainty ($\pm 0.002$ Å). Nevertheless, individual atoms differed in $z$ coordinate nearly up to 1 Å in the course of molecular dynamics of the fcc surface. The average $z$ coordinate of the first atomic layer of the liquid surface $z_{sol}$ was determined as an average over the 150 nearest atoms above the \{111\} Au surface and over the 141 nearest atoms above the \{100\} Au surface in each snapshot as an average over 500 snapshots, corresponding to the same number of atoms per surface area. Using the values of $z_{sol}$ and $z_{sf}$ (table 4.1),
we defined a default position of the image plane \( z_{im} = 0 \) Å at the interface edge 

\( \left( z_{Sol} + z_{Sy} \right) / 2 \) (figure 4.3). The statistical uncertainty of ±0.005 Å was negligible although the perceived uncertainty on the basis of visual inspection was ±0.1 Å. The position of the image plane was then varied in 17 steps from \( z_{im} = +0.3 \) Å to \( z_{im} = -300 \) Å to evaluate the image potential for each position.

The second step in the analysis involved the generation of image charges and the computation of the total polarization energy per surface area (figure 4.4). For each snapshot of each system, a copy of all atoms in the solution phase, including peptide, counter ions, and water, was reflected on the image plane as shown in figure 4.3 with opposite atomic charges. Periodicity in the \( z \) direction was eliminated and the polarization energy was computed using equation (4.4) as an average over all 500 snapshots, using the coordinates and point charges of the original atoms and of the image atoms. For this purpose, original atoms were translated into the box without dissecting charge-neutral molecules. We employed a cell-based cutoff for Coulomb interactions between original charges \( i \) and image charges \( j \), including 5 layers of cells in the \( x \) and in the \( y \) direction for the image charges \( j \) to take into account sufficient periodic replicas (a total of \( 11^2 = 121 \) cells in the \( xy \) plane for the image charges). Approximate results using the Ewald method according to equation (4.6) were also obtained.

The third step in the analysis involved the breakdown of polarization energies per water molecule in the first and second molecular layers on the gold \{111\} and \{100\} surfaces in contact with water (figure 4.5). The density profile of water oxygen atoms was recorded as an average over all 500 snapshots of the gold-water interfaces and
partitioned into first, second, and residual water layers on the basis of visual inspection (figure 4.5). The partition is apparent from significant changes in the O density along the z coordinate. Given the dimensions of the simulation box, the first molecular layer of water on the {111} surface contained on average 99 water molecules (8.7 Å² per molecule) and the second layer 75 water molecules. The first molecular layer of water on the {100} surface contained on average 98 water molecules (8.3 Å² per molecule) and the second layer 71 water molecules. The polarization energy per water molecule was then computed by running the summation in equation (4) selectively for the original atoms i of the water molecules in the respective molecular layer and over the images j of all original atoms and their periodic replicas in 5 layers of cells as an average over 500 snapshots, similar as described for the entire system.

The fourth step in the analysis involved the breakdown of polarization energies per peptide molecule and per each constituting amino acid (figure 4.6). For this purpose, the summation in equation (4.4) was carried out selectively for the original atoms i of a given amino acid residue including counter ions and over the images j of all original atoms and their periodic replicas in 5 layers of cells as an average over 500 snapshots, similar as described for the entire system. The polarization energy per peptide corresponds to the sum of the polarization energy of all constituting amino acid residues including counter ions.

As a last step, the net contribution of polarization to peptide adsorption was determined as the difference between the polarization energy of the adsorbed peptides on the metal surface in solution compared to that of pure water adsorbed on the metal surface, using the difference in total polarization energy per surface area. The net
contribution of polarization to peptide adsorption was also independently estimated from the balance of the polarization energy of the peptide and loss of polarization energy of the corresponding amount of replaced surface-bound water. The latter approximation neglects reorientation of water molecules in contact with the peptide compared to their orientation in the absence of peptide.

4.4. Results and Discussion

On the basis of the molecular dynamics model, we attempt a first quantitative evaluation of the contribution of induced charges to the adsorption of water and biomolecules in solution on metal surfaces. Such polarization remains difficult to quantify in experiment and no laboratory data have been available. We analyze total polarization energies per surface area for water and peptide solutions on gold \{111\} and \{100\} surfaces, average contributions by water molecules, peptides, constituting amino acids, as well as the net contribution of polarization to peptide adsorption on the metal surfaces. We find that the net contribution of polarization to adsorption is an order of magnitude smaller than epitaxial contributions on \{111\} surfaces or covalent bonds. In contrast, polarization can be the major contribution to adsorption of highly charged peptides on epitaxially unattractive \{100\} metal surfaces (table 4.2).

Visualizations of the metal-peptide-water systems in atomic detail as seen in molecular dynamics simulation can be found in Heinz et al. 2009 (ref. 147). Peptides A3 and Flg-Na₃ are in direct contact and strongly bound to \{111\} surfaces in aqueous
solution, and weakly bound to \{100\} surfaces with less direct contact and at least a partial water interlayer between the metal surface and the peptide.

4.4.1. Total Polarization Energy per Surface Area.

A first impression of the magnitude of charge-induced polarization can be formed on the basis of the polarization energy per surface area (figure 4.4). The image plane is positioned stationary near the jellium edge between the first layer of metal atoms $z_{sf}$ and the first layer of solution atoms $z_{sol}$ (table 4.1), although some ambiguity about the exact position of the image plane causes uncertainty in image potential (section 4.2.1). It is thus instructive to follow the magnitude of the image potential across the range of possible positions of the image plane, which also reveals further insight into the nature of charge-induced polarization and can play a role in the calculation of the image potential (equation (4.6)). The polarization energy on Au \{111\} and on Au \{100\} surfaces is significant near the jellium edge and increases to zero when the image plane would shift towards the metal (figure 4.4).

On the Au \{111\} surface, the polarization energy per surface area with reference to the jellium edge amounts to between $-50$ mJ/m$^2$ and $-55$ mJ/m$^2$ for water, a solution of the charged peptide Flg-Na$_3$, and a solution of the neutral peptide A3 (figure 4.4a). When the position of the image plane is hypothetically varied, similar polarization energies are observed for all three systems across the range of positions, related to comparable polarity of the peptides in comparison to water. Differences in polarization energy for the metal-peptide solution interfaces in comparison to pure metal-water interfaces indicate the net contribution of polarization to peptide adsorption (table 4.2,
A hypothetical outward shift of the image plane toward the first layer of solution atoms would decrease the polarization energy by multiples, and a hypothetical shift toward the first atomic layer of Au (at $z_{im} = -1.27 \, \text{Å}$) would increase the polarization energy to $-15 \, \text{mJ/m}^2$.

On the Au $\{100\}$ surface, the polarization energy per surface area with reference to the jellium edge is between $-50 \, \text{mJ/m}^2$ and $-70 \, \text{mJ/m}^2$ for water, a solution of peptide A3, and a solution of peptide Flg-Na$_3$ (figure 4.4b). The polarization energy is then mainly determined by water molecules in direct contact with the surface and enhanced by the polarity of ionic groups in the peptides. Significant polarization is particularly seen for Flg-Na$_3$, consistent with a significant net contribution of polarization to adsorption on the Au $\{100\}$ surface (table 4.2, section 4.4.4).

At hypothetical inward positions of the image plane $z_{im}$ between $-5$ and $-10 \, \text{Å}$, the polarization energy per surface area exhibits tail contributions different from zero (figure 4.4). These nonzero contributions result from net dipole moments in the simulation box in spite of overall charge neutrality. The smallest tail contribution for water ($-5 \, \text{mJ/m}^2$) on the Au $\{111\}$ and Au $\{100\}$ surfaces is associated with molecular orientation of water molecules through hydrogen bonds and a short dipole length. The intermediate tail contribution for peptide Flg-Na$_3$ ($-7 \, \text{mJ/m}^2$) on the Au $\{111\}$ surface (figure 4a) arises from a larger dipole length between carboxylate anions and individual Na$^+$ cations.$^{147}$ A high tail contribution for peptide A3 ($-10 \, \text{mJ/m}^2$) on the Au $\{111\}$ surface (figure 4a) is associated with the large distance of $\sim 30 \, \text{Å}$ between the positively charged N terminal and the negatively charged C-terminal end. On the Au $\{100\}$ surface, a smaller tail contribution for peptide A3 ($-6 \, \text{mJ/m}^2$) is found related to surface
detachment of the peptide. A high tail contribution for peptide Flg-Na$_3$ (−14 mJ/m$^2$) is caused by several large distances >10 Å between anionic groups and Na$^+$ cations related to separation of the peptide from the surface by a water interlayer. The difference in tail contributions for a given system relative to pure water also indicates net contributions of polarization to peptide adsorption.

The polarization energy per surface area of −50 mJ/m$^2$ is significant on an absolute scale, however, it amounts only to 3% of the surface tension $\gamma_{SV} = 1540$ mJ/m$^2$ of the gold {111} surface on a relative scale. The attractive nature of the image potential tends to lower the metal-aqueous interface tension $\gamma_{SL}$. The interface tension suggested by the Young equation $\gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \theta$, in which contact angles of polar and nonpolar liquids on clean noble metal surfaces are $\theta = 0^\circ$, may thus be further reduced by 50 mJ/m$^2$. A trend in this direction was indicated by simulation.

Polarization energies per surface area were also computed using the approximate method equation (4.6) using Ewald techniques. Results are similar for the image plane positioned near the jellium edge, lower for an outward (solution) shift of the image plane due to the modification of the integrand, and higher for an inward (surface) shift of the image plane. A loss of tail contributions occurs due to an arbitrary assumption of zero dipole moment on the system in the Ewald summation scheme.
Figure 4.4. Polarization energy per surface area as a function of the position of the image plane (A) on the Au \{111\} surface and (B) on the Au \{100\} surface in contact with water.
and peptide solutions. The position of the image plane is near the jellium edge and other positions serve to illustrate the nature of charge-induced polarization. Differences in polarization energy between a peptide solution and pure water indicate the net contribution of induced charges to adsorption.

4.4.2. Contribution by Water.

The density profile of water molecules above the Au \{111\} and \{100\} surfaces, represented by the water oxygen atoms, indicates the formation of two distinct molecular layers and a rather continuous distribution of water molecules further away from the surface (figure 4.5). The polarization energy per surface area of $-50 \text{ mJ/m}^2$ with respect to the jellium edge (figure 4.4) translates into an attraction of $-2.4 \text{ kJ/mol}$ surface-bound water molecule on the Au \{111\} surface and of $-2.2 \text{ kJ/mol}$ surface-bound water on the Au \{100\} surface. A water molecule in the second molecular layer is attracted only by $-0.13 \text{ kJ/mol}$ on the Au \{111\} surface and by $-0.14 \text{ kJ/mol}$ on the Au \{100\} surface. Water molecules further away from the metal surface make negligible contributions (figure 4.5 and table 4.1). The associated increase in molecular mobility with increasing distance from the surface, driven both by loss in molecular epitaxy and in polarization, is consistent with an increase in dielectric constant from 6 to 32 to 78.5 in the first water layer, the second water layer, and bulk water on a metal surface reported by measurements and calculations.\textsuperscript{15}

The averaged total attraction per water molecule in the first molecular layer on the Au surface ranges between $-8$ and $-12 \text{ kJ/mol}$ in classical MD simulation.\textsuperscript{165} Experimental results or data from other computational methods on the adsorption of bulk
water on Au surfaces were not available, however, a similar attraction of $-10$ kJ/mol of single water molecules to Au $\{111\}$ surfaces in vacuum was reported by DFT calculations.\textsuperscript{172} The contribution of polarization of $-2.3$ kJ/mol to total water adsorption of $\sim-10$ kJ/mol is therefore on the order of 20%. A test using an additional surface attraction of 20\% in molecular dynamics models under neglect of polarization slightly shortens the distance of water molecules from the surface and increases the maximum-to-minimum ratio in the density profile. However, considerable differences in molecular orientation (layering) at the metal-water interface were only observed when the surface attraction of the metal was increased in excess of 100\%.\textsuperscript{165}
Figure 4.5. Density profile of water in contact with the metal surfaces, showing the distribution of water oxygen atoms along the z axis. (A) On the Au \{111\} surface and (B) on the Au \{100\} surface. The average polarization energy per mol water molecules in the
first two molecular layers is indicated, assuming that the image plane is located at the jellium edge.

4.4.3. Contribution by Peptides and Amino Acids.

The polarization energy per peptide molecule $E_{\text{pol}}^P$ varies as a function of chemistry of the peptide and type of metal surface between $-20$ and $-80$ kJ/mol peptide (table 4.2), as shown in more detail by contributions of individual amino acids as an average over 500 snapshots (figure 4.6).

On the Au $\{111\}$ surface in aqueous solution, peptides A3 and Flg-Na3 experience strong non-covalent epitaxial interactions and are $\sim$80% in direct contact during molecular dynamics. Polarization energies of $-80$ and $-82$ kJ/mol peptide, respectively, are associated with a loss of polarization energy of $\sim$30 replaced surface-bound water molecules and considerably smaller than epitaxial binding energies exceeding $-200$ kJ/mol (table 4.2). The composition of the polarization energy by individual amino acids varies in a wide range. In the peptide A3 on the $\{111\}$ surface, the positively charged N-terminal $^1$Ala residue exhibits the highest contribution to polarization of $-40$ kJ/mol, followed by the negatively charged C-terminal $^{12}$Phe (figure 4.6a). All other polar residues such as Tyr and Ser contribute less than $-10$ kJ/mol to polarization and contributions below $-5$ kJ/mol are made by lowly polar Gly, Ala, Met, and Pro residues. Therefore, the total attraction by induced charges of peptide A3 is primarily caused by the long distance between the charged N- and C-terminal ends and the resulting large dipole moment. In the peptide Flg-Na3 on the Au $\{111\}$ surface, the
polarization energy is primarily mediated by residues with a net charge, too (figure 4.6b). A large contribution of −30 kJ/mol is seen for Lys in combination with neighboring Asp residues which exhibit positive contributions. The observation of positive contributions to polarization underlines that contributions from groups with a net charge must be considered jointly with corresponding groups of opposite charge in an overall charge neutral system. Less than −10 kJ/mol are contributed by the bipolar Lys residue and by sodium counter ions in combination with neighboring Asp residues. The neutral N-terminus and Tyr made only minor contributions.

On the Au {100} surface in aqueous solution, peptides A3 and Flg-Na3 are not attracted by epitaxy and at least a partial water interlayer is found between the metal surface and the peptides. The polarization energy of −23 and −77 kJ/mol peptide, respectively, is then significant in relation to the small total attraction (table 4.2). In the peptide A3 on the Au {100} surface, the comparatively small polarization energy of −23 kJ/mol arises predominantly from the dipole between the positively charged N-terminal Ala and the negatively charged C-terminal Phe. Other residues make virtually no contribution (figure 4.6a). The loss of surface contact compared to the Au {111} surface and the absence of electrically charged amino acids other than N-terminal and C-terminal ends leads to loss of polarization. In the peptide Flg-Na3 on the Au {100} surface, the total polarization energy of −77 kJ/mol includes large contributions of −20 kJ/mol by negatively charged Asp residues in combination with sodium counter ions (figure 4.6b). Charged groups in the peptide and counter ions are spatially further separated (>10 Å) in comparison to the average peptide structure on the Au {111} surface, leading to a similarly high polarization energy and significant tail contributions at image plane.
positions < 5 Å (figure 4.4b). Minor contributions to polarization are made by the electrically neutral residues 1Asp, 2Tyr, and 8Lys.

As polarization energies were excluded in the iterative MD simulation (section 4.3), the additional attraction by polarization modifies reported peptide conformations on the metal surface:^{147} amino acid residues of lowest polarization energy are likely found closer to the metal surface than under neglect of polarization. On the {111} surface with peptides strongly bound by molecular epitaxy and in direct surface contact, some additional polarization does not appreciably affect the structure of the interface. Equally, peptide detachment from the surface is unfavorable as it would result in loss of epitaxial binding strength and in polarization energy. On the {100} surface with peptides weakly bound to the surface and water molecules located between the surface and the peptide, polarization likely alters the reported interface structure. Attractive polarization brings highly polar amino acid residues closer to the surface and decreases the number of water molecules in the interlayer between the peptide and the surface. In the peptide A3 on the {100} surface, tighter surface contact of the polar end groups may occur and decrease the polarization energy, while additionally released surface-bound water molecules partially offset this gain in polarization energy (table 4.2). In the peptide Flg-Na3 on the Au {100} surface, tighter surface contact of several charged residues is also likely. However, closer surface contact does not enhance epitaxial binding and up to +60 kJ/mol in polarization energy must be afforded to release 26 surface-bound water molecules. Therefore, the charged peptide Flg-Na3 may prefer adsorption states between direct contact with the metal surface of low net attraction and with a distance of about one water interlayer between the surface and the peptide of maximum attraction. Further detachment from the
{100} surface is unfavorable for both A3 and Flg-Na3 peptides due to increasing ultimate loss of polarization energy.

In conclusion, we find that amino acids of low polarity contribute less than $-5$ kJ/mol to the polarization energy of peptides even when in direct epitaxially driven contact with the surface. Amino acids with net charges and counter ions, including N terminal and C terminal groups, contribute up to $-40$ kJ/mol to the polarization energy. Contributions by polarization are superseded in the presence of covalent and significant epitaxial attraction such as on the Au {111} surface but can otherwise control adsorption such as on the Au {100} surface.
Figure 4.6. Contributions of constituting amino acids to the polarization energy of (A) peptide A3 and (B) peptide Flg-Na₃ including three sodium ions in aqueous solution on Au {111} and {100} surfaces. The image plane was located at the jellium edge.
Table 4.2. Net contribution of polarization to peptide adsorption on even Au surfaces

$E_{Pol}^N$ in comparison to the net contribution of epitaxial interaction $E_{E}^N$. The main contributions are the polarization energy per peptide $E_{Pol}^P$ and the approximate loss in polarization energy by replaced surface-bound water $E_{Pol}^W$.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Peptide</th>
<th>Net attraction by polarization$^a$</th>
<th>Net attraction by epitaxy$^b$</th>
<th>Contributions to net attraction by polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_{Pol}^N$ (kJ/mol)</td>
<td>$E_{E}^N$ (kJ/mol)</td>
<td>Peptide $E_{Pol}^P$</td>
</tr>
<tr>
<td>Au {111}</td>
<td>A3</td>
<td>−28 ±4 [−6 ±16]</td>
<td>−260 ±20</td>
<td>−80</td>
</tr>
<tr>
<td></td>
<td>Flg-Na₃</td>
<td>−12 ±4 [−10 ±16]</td>
<td>−260 ±20</td>
<td>−82</td>
</tr>
<tr>
<td>Au {100}</td>
<td>A3</td>
<td>−16 ±12 [+10 ±16]</td>
<td>−38 ±20</td>
<td>−23</td>
</tr>
<tr>
<td></td>
<td>Flg-Na₃</td>
<td>−80 ±20 [−69 ±8]</td>
<td>0 ±20</td>
<td>−77</td>
</tr>
</tbody>
</table>

$^a$ Exact values from the difference in polarization energy of the peptide solution relative to a pure aqueous interface for an image plane located at the jellium edge (figure 4). The values in square brackets are simplified additive estimates $E_{Pol}^P + E_{Pol}^W$.

$^b$ From Heinz et al. 2009.(ref.147) Using the more accurate CHARMM-METAL force field, lower epitaxial adsorption energies of $−160$ kJ/mol (A3) and $−80$ kJ/mol (Flg-Na₃) on {111} surfaces were reported.$^{27}$

$^c$ Estimates from an average number count of replaced surface-bound water molecules.
4.4.4. Net Contribution to Peptide Adsorption.

The net contribution of induced charges to peptide adsorption \( E_{\text{pol}}^N \) equals the difference between the polarization energy at the metal-peptide-water interface and at the neat metal-water interface (figure 4.4). It is thus smaller than the polarization energy by the peptide alone and compared to the net contribution of non-covalent epitaxial interaction to peptide adsorption \( E_{\text{EE}}^N \) (table 4.2) as previously reported.\(^{147}\)

On the Au \{111\} surface, the net contribution of induced charges to peptide adsorption is about an order of magnitude less than the contribution of molecular epitaxy, and thus negligible in first approximation (table 4.2). The net contribution of polarization to peptide adsorption is only between \(-10\) and \(-30\) kJ/mol peptide compared to the total peptide adsorption energy on the order of \(-200\) kJ/mol, owed to the high degree of surface contact and epitaxial fit of the peptides A3 and Flg-Na\(_3\). The absolute contribution of polarization by the peptides of \(-80\) kJ/mol peptide is reduced by the similar polarity of \(~30\) displaced water molecules to between \(-10\) and \(-30\) kJ/mol. The similar polarity of peptide and solvent thus largely eliminates a competitive advantage in polarization of one component over the other, as evidenced by similar polarization energies per surface area and similar tail contributions (figure 4.4a). On this surface, strong molecular epitaxy thus creates a high energy barrier for surface detachment of peptides regardless of induced charges.

On the Au \{100\} surface, the net contribution of induced charges to peptide adsorption plays a major role (table 4.2). The charge-neutral peptide A3 shows a net attraction of \(-16\) kJ/mol due to polarization and of \(-38\) kJ/mol due to weak epitaxial interaction. The significant relative contribution of polarization likely decreases the
distance of the charged terminal groups (Figure 4.6a) to the metal surface compared to MD simulation under neglect of polarization. More direct contact of other peptide residues with the metal surface, however, is unlikely due to their small contribution to polarization and unfavorable replacement of more surface-bound water molecules (Figure 4.6a). The highly charged, surface-detached peptide Flg-\(\text{Na}_3\) exhibits a net attraction due to induced charges to the \{100\} surface of \(-80\) kJ/mol which dominates over zero epitaxial attraction (table 4.2). This attraction draws the peptide closer to the metal surface than observed in MD simulation, although an increased degree of direct contact with the metal surface causes a penalty up to \(+60\) kJ/mol by release of surface-bound water molecules and enforces unfavorable epitaxial contact. Therefore, the peptide Flg-\(\text{Na}_3\) can be partially in direct contact with the metal surface yet the energetically favored position is at a distance of a water layer away from the surface.

Therefore, the net contribution of polarization to peptide adsorption is minor on metal surfaces with strong epitaxial attraction and significant, or dominant for highly charged peptides, on metal surfaces with weak epitaxial attraction.

4.5. Conclusion

The interaction of metal surfaces with biomolecules and water encompasses interfacial polarization due to induced charges in addition to non-covalent epitaxial and covalent bonding interactions. Polarization by induced charges remains difficult to measure so that a computational approach was developed and applied as a first step to evaluate the nature and magnitude of charge-induced polarization. Using all-atomic models in classical molecular dynamics simulation and the concept of image charges in a
a-posteriori computation of the image potential, we determined the influence of induced charges on even Au surfaces on the interfacial structure and adsorption of water, peptides, and corresponding single amino acids. The polarization energy per surface area amounts to between $-50$ and $-70$ mJ/m$^2$ for aqueous and biomolecular interfaces. Molecular contributions by surface-bound water molecules ($-2.3$ kJ/mol) and peptide residues (0 to $-40$ kJ/mol per amino acid) are comparable on average due to similar polarity. Charged amino acids with a large time-averaged distance between cationic and anionic groups are most strongly attracted to the metal surface due to polarization. On metal surfaces with favorable epitaxial interactions and direct surface contact of peptides such as Au $\{111\}$, the net contribution of polarization to peptide adsorption is small. On metal surfaces with weak epitaxial attraction and a remaining water interlayer between the surface and the peptide such as Au $\{100\}$, the net contribution of induced charges to peptide adsorption is significant or even dominant. For the highly charged octapeptide Flg-Na$_3$ on an Au $\{100\}$ surface, for example, adsorption is entirely driven by polarization up to $-80$ kJ/mol peptide. Contributions of polarization to biomolecular adsorption decrease with increasing distance of the peptide from the surface and can range several nanometers for charged peptides compared to only about one nanometer for non-covalent epitaxial interactions.

This investigation is a first step toward quantitative understanding of polarization on metal nanostructures. When the polarity of biomolecules and solvent would differ more substantially from the solvent such as in ethers or hydrocarbons as opposed to water, adsorption onto metal surfaces would be more strongly influenced by induced charges. In addition to even metal surfaces investigated here, the geometry of edges and curved
surfaces of nanorods and nanoparticles likely affects the adsorption of organic surfactants and peptides by different strength of induced electric fields which can be investigated using the proposed model. The integration of polarization forces into molecular dynamics and QM/MM algorithms would also be desirable.
CHAPTER V
FACET RECOGNITION OF GOLD NANORODS BY IONIC LIQUIDS

5.1. Introduction

Anisotropic nanostructures have found applications ranging from sensing and imaging to opto-electronic devices.\textsuperscript{145,174-181} The low cytotoxicity of gold, and the tunable NIR absorbance of gold nanostructures make it especially attractive for bio-imaging. Hence, the control of shape and size of gold nanorods is an interesting material science problem. Considerable effort has been expended towards synthesis of gold nanorods from surfactants such as Cetyl trimethyl ammonium bromide (CTAB).\textsuperscript{181,182} Ionic Liquids (ILs) present a green alternative to cytotoxic surfactants like CTAB, leading to increased interest in IL based synthesis of nanostructures.\textsuperscript{183-188}

In addition to green chemistry, ILs offer other advantages over surfactants in synthesis. They stabilize nanoparticle formation because of their high ionic charge, polarity and the ability to form networks through weak H-bonding.\textsuperscript{189} These “supra-molecular” networks give directionality to the self-assembling metal. The low interfacial energies of ILs mean that they are excellent dissolving agents. ILs also have low melting points (as low as -96°C)\textsuperscript{190} and are liquid over a wide temperature range up to 400°C.\textsuperscript{191}

Growth mechanisms of nanostructures in surfactants likely involve capping of the higher energy faces with surfactants\textsuperscript{192-194} yet there is no universal theory that explains anisotropic evolution of nanostructures.\textsuperscript{192} Studies on nanoparticle formation in ILs\textsuperscript{189,195}
have not been extended to nanorods and do not provide an explanation of growth mechanisms of nanorods in ILs.

The present study analyzes interactions contributing to anisotropic nanorod formation in ILs. Molecular dynamics and DFT calculations were performed to obtain adsorption energies, contour charge densities, polarization energies, and visualize the molecular arrangement of 1-Ethyl-3-methylimidazolium ethyl sulfate ([EMIM][ES]) on gold surfaces to analyze network formation. We observed the formation of networks of 1 nanometer range among the IL molecules.

It has been reported that a monolayer of silver preferentially deposits on the higher energy (Au{110}, Au{100}) surfaces. We hypothesize that underdeposition is followed by attachment of surfactant or capping agent through attractive polarization and soft epitaxy. Specifically, in the case of [EMIM][ES], molecules attach themselves to the high energy surfaces by attraction through differential in attractive forces from induced surface charge (or polarization). The order of these two processes becomes clear with experimental evidence of no silver nanorods being formed without Ag present. Ag helps in breaking the initial symmetry. These two processes of silver underdeposition, and adsorption of IL molecule through attractive polarization combined limit the growth of high energy surfaces of {110}, and {100}, and support the growth on the side twinned {111} end surfaces as seen by TEM of the grown nanorods. Figure 1 shows the hypothesis that charts the mechanisms for growth of nanorods in IL and contrasts it with growth of nanorods in surfactants. We also found that both nanorod and nanoparticle formation is highly specific to the choice of IL, since the IL-Au interaction depends
strongly on both the anion and cation. The anion effect on nanoparticle synthesis has been analyzed experimentally\textsuperscript{195} and fits our observations.

Figure 5.1. Contrast between growth of gold seed crystals mediated (A, B) by the ionic liquid [EMIM][ES] and (C) by a surfactant (CTAB). A Ag\textsuperscript{+} helps create \{110\} and \{100\} surfaces by underdeposition (ref. 196) and increases attraction of EMIMES to these surfaces leading to their stabilization. Adsorption energies (including epitaxial and induced charge contributions) also support the preferential adsorption of EMIMES to \{110\} and \{100\} surfaces. B When there are no Ag\textsuperscript{+} ions, there is no driving force to form higher energetic \{110\} and \{100\} surfaces. Spherical nanoparticles are formed and
EMIMES also stabilizes the bounding \{111\} facets. Nanorod growth in the presence of CTAB in water, which leads to formation and stabilization of \{110\} and \{100\} surfaces even without Ag\(^+\) ions. In the case of CTAB better packing of the surfactant is observed on the \{110\} surface. CTAB does not need Ag\(^+\) ions for anisotropic nanorod formation. Br\(^-\) ions placing themselves in lattice spaces and preferential epitaxy of the alkyl chains through geometrical matching to grooves on the \{110\} surface are the dominant mechanisms of adsorption.

5.2. Methods

5.2.1. Models

All models for the gold-ionic liquid systems were constructed using the graphical interface of Materials Studio 4.0. The force field used has been validated for metal-aqueous and metal-biological interfaces.\(^{165}\) Metal surfaces were built using multiples of unit cell from X-ray data for \{100\} unit cell. The \{111\} and \{110\} unit cells were extracted from the \{100\} unit cell. A minimum of 1.2 nm thickness (z-direction) and 2x2 nm\(^2\) surface areas were constructed. For adsorption energy computations, the z-direction was extended to 50 nm total (Figure 5.2).

\([\text{EMIM}]\text{[ES]}\) in liquid was maintained at 1.2391 gm/cm\(^3\) for computation of average energy per molecule, density, and vaporization energies. Physical properties of \([\text{EMIM}]\text{[ES]}\) and Imidazole were computed and compared to experimental values for validation of the force field. Vaporization energies at 298.15 K obtained for \([\text{EMIM}]\text{[ES]}\) and Imidazole were within 1.5\% of reported values.\(^{197,198}\) NPT simulations to obtain densities of Imidazole and \([\text{EMIM}]\text{[ES]}\), gave values within 2\% for Imidazole and 8\% for
[EMIM][ES]. Dipole moment obtained for Imidazole gives deviation of 1.5% from reported value.\textsuperscript{198}

For classical MD simulations the PCFF-Metal force field was used (no cross terms no morse potential) with accurate LJ potential for FCC metal.\textsuperscript{165} DFT computations were carried out using the PAW potential which have greater accuracy than the ultra soft potentials.\textsuperscript{199} VASP was used for all DFT computations and LEV00 and TETR tools used for visualization.\textsuperscript{200} Although the increased size of the basis set increases the computation time, the accuracy gains are significant.
Figure 5.2. Schematic illustration for the calculation of adsorption energy for per EMIMES molecule on gold surface for a monolayer. The \{110\} surface is shown in the
figure. Five different conformations of [EMIM][ES] were used for statistics. 

\[ E_{\text{adsorption per molecule for first monolayer}} = \frac{(E_A - (E_{(Bavg)x6}) - E_C)}{6}. \]

5.2.2. Computational Details

A minimum of five conformations were taken for adsorption energy computations, with a dynamics of 400 ps for single computation, and an average of 2 ns total simulation time over multiple computations for the same system. The final trajectories were extracted for analysis every time a new computation for the same system was repeated, preceded by equilibration of 100 ps. The conformation of IL molecules on the gold surfaces was minimized by annealing at 800 K for 400 ps. A spherical cutoff of 1.2 nm was employed for van der Waals interactions. Ewald accuracy for Coulomb interactions was kept at $10^{-6}$, but relaxed to 1 for annealing since we were interested in the conformations and not the energy of the system.

For DFT calculations, used to map the contour charge densities of single [EMIM][ES] on Au \{111\} surface, we employed the LDA approximation, PAW pseudopotentials, an energy cutoff at 400 eV, and plane waves (4 x 2 x 1 k points for Au unit cell having 54 atoms). The final equilibrated structure was used for calculation of contour charge densities.

5.2.3. Analysis

First step in the analysis is to obtain contour charge densities. The final equilibrated trajectory of the DFT computation was used to extract the charge densities. The charge densities were extracted in x and y directions, at a number of different
positions crossing the vertical plane (z direction) between the molecule and the gold surface. These charge densities in e/Å$^3$ were then plotted using Origin.

Second step in the analysis is to obtain adsorption energies of the IL molecules on different gold surfaces. The IL molecule is annealed on the gold surface at 800K with a dynamics of 400ps, and then the final trajectory is used for dynamics at 298.15K for 400 ps, preceded by a minimization of 100ps. A minimum of five conformations are taken, and the total time for each simulation exceeds 2ns since multiple computations were carried out for the same system. Adsorption energies are computed as per the schematic in Figure 5.2. The difference in energies between the molecules on surface subtracted from i) the average energies of IL molecules in liquid multiplied by the number of molecules and ii) the energy of gold, gives the adsorption energy of IL on gold surface (Figure 5.2). EMIM][ES] was approximated as having an area of 70 Å$^2$ which gives coverage of ≈17 % per molecule on all three surfaces. This is consistent with the visualization of six molecules on the first layer of all three surfaces in snapshots from trajectories of bulk IL on gold surfaces. The coverage is increased up to 200% (bilayer), followed by computations for 300% and 400%.

Third step in the analysis is computation of polarization energies for gold-ionic liquid systems which were carried out by placing the image plane at the interface edge using trajectories for 400 ps obtained by placing the bulk IL (30 molecules) on all three gold surfaces. The exact formulation for image energies is detailed in our previous work.$^{201}$ Placing the image atoms at the interfacial edge maps the first atomic layer of the solution to the first atomic layer of the metal atoms, and is justified for all three surfaces of {100}, {110}, and {111} according to surface state energy calculations.$^{160}$ from
photoemission and inverse photoemission measurements in addition to self-consistent calculations that show weak dependence of the image plane with change in crystallographic face of the metal. Using the methodology described in our previous work, the first layer of gold atoms was obtained with negligible error for all three surfaces. A similar approach is employed to obtain the solution edge for IL molecules. The average of the metal surface edge and solution edge gives the interfacial edge and the image atoms are reflected on this followed by a translation downwards to obtain values for different placement of image planes. The image energies were obtained per molecule for a bilayer by computing the contribution of each layer wherein the energies are summed over only the first and second layers and all image atoms. Finally, the polarization energies are added to the adsorption energies obtained in step two to get the total adsorption energies from epitaxial and attractive polarization.

Fourth step in the analysis involves approximating the network strength of the IL on the three gold surfaces. Two approaches are taken to quantify networks. First, the average length of the 3x3 network over 20 snapshots is extracted for all three systems of gold {111}, {110}, and {100} -IL. Second, the number of [EMIM]⁺ cations with parallel orientation to the gold surface is extracted over the same 20 snapshots.

5.3. Results and Discussion

5.3.1. Adsorption Mechanism

The contour charge densities (Figure 5.3) show favorable orientation of the imidazolium ring in the [EMIM]⁺ parallel to gold surface {111} using DFT computation. We also see the contour charge densities on the planes to be opposite to the charge distribution in the molecule and equal in relative magnitude. Specifically, for the
alkyl side chain and the imidazolium nitrogens, there is maximum distortion. This favors the hypothesis that attractive polarization plays a major role in the adsorption of IL on gold surfaces.

Figure 5.3. Charge density contour plot for [EMIM][ES] on Au{111} surface for two planes: Plane 2: in the ring plane, and Plane 1 midway between the ring plane and the top surface atomic layer. Also shown is the top view of cross-section across the [EMIM][ES] molecule. All charge densities are in e/Å$^3$.

Ionic Liquids, with high distribution of charges on individual atoms, experience attractive forces by polarization as visualized above in Figure 5.3, due to induced charges on the metal (gold) surface. A model for anionic adsorption on gold in colloidal systems has been previously proposed, though not quantified.$^{202,203}$ Quantification of image energies for two gold-binding peptides in solution, and with water over gold have
recently been reported.\textsuperscript{201} With no water present to screen polarization as in the case of peptides in solution, the effect of attractive polarization by individual molecules is magnified in the case of ILs close to the gold surface due to the high charges on individual atoms. The differential in polarization energies between the Au\{111\} and the Au\{110\}, and Au\{100\} surface is a maximum of 2.3 kcal/mol-molecule versus 1.2 kcal/mol-molecule for epitaxial attraction (Figure 5.4A). This is a significant differential in adsorption energies from attractive polarization, and can be said to result in preferential attachment of [EMIM][ES] to the open surfaces of \{110\} and \{100\}.

Figure 5.4B further shows the variation in adsorption energies with development of layers through increased surface coverage of IL on the \{110\} surface. We observe that the favorable conformations of the IL are lost when the first monolayer is formed. This can be seen in a peak (loss of adsorption energy) in Figure 5.4B for the first monolayer (6 molecules), and also for 12 molecules (bilayer). The values reach saturation as the number of molecules is increased. This is because the IL molecules reach bulk behavior after the first bilayer. The layering leading to a bilayer can be seen in Figure 5.5, 5.6, and 5.7.

Figure 5.8 shows the orientation of the networks on gold surfaces for \{111\}, \{100\} and \{110\} surfaces. The average networks are stronger and larger on \{110\} surfaces compared to the \{111\} surfaces whereas the number of favorable orientations is higher on \{111\} surfaces than the \{110\} surface. The average network distance is lower by 0.1 Å on the \{100\}, and by 0.04 Å on the \{111\} surfaces compared to the \{110\} surface, while the favorable conformations per 6 molecules in a bilayer is 4 for \{111\}, and 1 for \{110\}. These point to slight epitaxial favor for the \{111\} and \{100\} surfaces
by the IL which is much less when compared to the attractive polarization energy that favors the more openly packed \{110\} surface. Also, it shows that the network distances can be manipulated to vary the attraction of IL molecule on the nanostructures by either choosing different geometries of the IL or a highly faceted nanostructure.

Figure 5.4. A. Epitaxial and Polarization Energies per molecule of \([\text{EMIM}]\)[\text{ES}] on the three gold surfaces, \{111\}, \{110\}, and \{100\}. The epitaxial energies are for a bilayer of \([\text{EMIM}]\)[\text{ES}] on the gold surface. B. Variation of adsorption energy, including the polarization energy per molecule with surface coverage of \([\text{EMIM}]\)[\text{ES}] on gold surface. 1 \([\text{EMIM}]\)[\text{ES}] molecule occupies 17 % of the surface area. Surface area of model
surfaces was 4 nm$^2$.

Figure 5.5. Network formation of ionic liquid ([EMIM][ES]) on the Au {110} surface. Each anion has three cations as its nearest neighbors and vice versa. The number of ionic liquid molecules in the first layer and the second layer is six molecules, for all three surfaces. We can observe the loss in favorable conformations when the first monolayer is formed. A shows 50% coverage, B shows 100% coverage, C shows 150% coverage, D shows 200% coverage.
Figure 5.6. Network formation of ionic liquid ([EMIM][ES]) on the Au \{111\} surface. A shows 50\% coverage, B shows 100\% coverage, C shows 150\% coverage, D shows 200\% coverage.

Figure 5.7. Network formation of ionic liquid ([EMIM][ES]) on the Au \{100\} surface. A shows 50\% coverage, B shows 100\% coverage, C shows 150\% coverage, D shows 200\% coverage.
Figure 5.8. Network formation of IL on {100}, {111} and {110} surfaces. There is a greater percentage of flat on [EMIM]$^+$ cations parallel to the surface on {111} and {100} as compared to {110}.

5.3.2. Shape Control

The governing factor in the shape control of gold nanorods synthesized from imidazolium based ILs is silver underdeposition. Deposition of submonolayers of Ag (0) on gold surfaces can occur at potentials less than that required for bulk deposition of Ag on Au. This phenomenon, known as underdeposition or “underpotential deposition” (UPD), is significant for acidic conditions where the reduction potentials needed are higher than for basic pH. For example, potential needed for deposition at pH=3 is about 0.3 V higher than that at pH= 8. UPD is possible if the work function of the adsorbate is lower than that of the substrate. Greater the difference in work function, the more the chances of underpotential deposition. For Ag-Au pair, work-function differences between {100}, {110}, and {111} surfaces are 0.83 , 0.85, and 0.57 eV respectively. Clearly underdeposition would be favored on the higher energy surfaces of {110} and {100}. The differential has been explained as occurring through
stabilization of the ion core of Ag on Au by greater co-ordination on the more openly packed Au{110} and Au{100} surfaces (Figure 5.9). XPS measurements in CTAC-mediated synthesis of nanorods further validate the preferential UPD on the more openly packed surfaces, and the agreement between theoretical and experimental coverage increases with the [Ag]/[Au] and the increasing anisotropy of the resultant nanostructures.

Figure 5.9. Ag (0) deposited on Au{110}, {100}, and {111} surfaces. Number of nearest neighbors for the {110} surface is 5 (including one in the second layer), {100} surface is 4, and the {111} surface is 3. Stabilization of the Ag (0) ion cores by higher number of neighboring atoms facilitates preferential underdeposition on the higher energy surfaces of Au {110} and to a lesser extent, Au {100}.

The underpotential deposition shifts, which is a measure of how much the potential for submonolayer deposition has been reduced compared to bulk deposition, have been calculated as 0.12 V for Au {111}/Ag$^+$, 0.17 V for Au {100}/Ag$^+$, and 0.28 V for Au {110}/Ag$^+$ systems.$^{196}$ We propose that most of the Au{110} surface is covered by an adlayer of Ag and lesser deposition occurs on the Au{100} surface. This is followed by favorable attachment of [EMIM][ES] to the Au {110} and Au{100} surfaces.
through attraction by induced surface charge. Slow growth on the high energy surfaces, \{110\} and \{100\}, results in the side faces of the nanorod being abundant in them, even though they are thermodynamically unfavorable. End faces of Au\{111\} grow the fastest, with no adlayer and no [EMIM][ES] attached to them. The growth direction is along Au[100] as for the two side surfaces, the Au\{100\} surface is less impeded than the Au\{110\} surface.

Experimentally, it has been observed that in the absence of Ag\(^{+}\), there is no nanorod formation for IL mediated synthesis,\(^{36}\) whereas for CTAB mediated synthesis nanorods are formed, with different geometries depending on ratio of Au\(^{+}\) to Ag\(^{+}\) present (ratio of Au\{100\} to Au\{110\} surfaces on the synthesized nanorod changes with [Ag\(^{+}\)]).\(^{196,205}\) This underlines the critical role of silver underdeposition in anisotropic evolution of gold nanorods synthesized with ILs. It has also been hypothesized that the growth of Au nanoparticles in [EMIM][ES] in the absence of Ag\(^{+}\) happens through Ostwald Ripening.\(^{195}\) Ostwald Ripening is the process by which smaller crystals agglomerate or coalesce into larger shapes to minimize surface energy. In the absence of shape regulation through the deposition of Ag (0) to higher energy facets, the nanoparticles thermodynamically grow into larger diameters with facets of \{111\} dominating the XRD peaks.\(^{195}\)

The role of the anion has been examined in detail for IL mediated Au nanoparticle formation.\(^{189,195}\) Anions have a strong influence on nanoparticle formation acting as nucleating agents and/or as stabilizers. The size of the nanoparticle formed depends on the stabilization provided by the anion. Methanesulfonate (MS) anions are more stabilizing than ethyl sulfate (ES) anions for the same imidazolium cation (EMIM).
MS mediated synthesis gives a uniform range of nanoparticles at lower temperatures that are smaller in size when compared to the ES mediated synthesis. Stabilization of Au nanocluster increases with softness of the ligand/anion. Hence H$_2$O has the least stabilization, whereas Cl$^-$ hinders nanoparticle growth because it is very stabilizing. This stabilization based on hardness/softness of the ligand is due to binding occurring as a result of HOMO of the ligand having enough energy to overlap with the LUMO of the metal.

While a bilayer stabilization similar to surfactants has been hypothesized in the formation of gold nanoparticles from ILs that have anions with long chains (lauryl sulfate), the role of IL anion in nanorod formation, or selective stabilization of surfaces has not been explored. We hypothesize that anisotropy would increase with greater stabilization of the more openly packed surfaces of Au $\{110\}$ and Au $\{100\}$) with anion. Contour charge densities stress the importance of sulfate anion (Figure 5.3C). Electro-Steric stabilization resulting from the networks formed by the IL on the Au surface is the most reasonable explanation in the light of the 3x3 network formation and the increased role of attractive polarization in differential adsorption. The various mechanisms, outlined above, have been summarized as our hypothesis in Figure 5.1.

To further explore the role of networks, the C-H--O bond distance for the first layer of [EMIM][ES] on the different Au surfaces is measured as an indirect indicator of the network strength. The networks are more compact for $\{110\}$ surfaces when compared to $\{100\}$ and $\{111\}$ surfaces. Every cation is bound to three anions and vice versa. The nature of these H-bonds has been studied for amino acid residues and such network formation has also been reported in ILs. The C$^\alpha$ for the amino acid residues is similar
to the methyl, or ethyl carbons in the imidazole cation. This specific co-ordination for [EMIM][ES] (3 anions to each cation, and vice versa) would change for ILs with different cations and the network formation would be a function of the geometry of the molecule. The structure of imidazolium salts in solid has been reported\textsuperscript{210} to be a 3x3 network and the existence of such a network in the solution state, esp. close to the gold surface indicates the presence of weak intramolecular bonds and immobilization akin to a frozen layer close to the gold surface.

A flat-on bilayer observed in our DFT computation and IL layering on \{111\} surface is consistent with studies of methylimidazole at Cu electrode surfaces. The local area of gold near the positively charged imidazolium cation was reported as negative due to induced fields to counter the positive dipole, and a flat on configuration was seen using SERS analysis for methylimidazole on Copper surface.\textsuperscript{211}

5.4. Conclusion

A growth mechanism for gold nanorods in [EMIM][ES] has been proposed. Epitaxial fit influences nanorod formation to a lesser extent in Ionic Liquids than it does in surfactants. Attractive polarization energies on the more openly packed surfaces of Au\{110\} are higher by -2.3 kcal/mol-molecule when compared to the Au\{111\} surface. Preferential deposition of Ag(0) adlayer on the Au\{110\} surface is favored due to differential in the work function of Au-Ag pair for \{110\} plane exceeding that of the \{100\} and \{111\} planes. It is proposed that, in the absence of an epitaxial driving force, silver underdeposition breaks the symmetry (perfect symmetry of nanostructure being a spherical nanoparticle) in synthesis of nanorods from [EMIM][ES], and it is
complimented by attraction through induced charges due to the highly ionic [EMIM][ES] on the gold surface. Induced charges favor attachment of [EMIM][ES] molecules to the already restricted surfaces of Au{110} and Au{100}.

There is no data for Au nanorod formation using [EMIM][MS] or [EMIM][TfO]. Change in anisotropy from change in anions for the IL, keeping the (imidazolium) cation constant, would give us more insight into the specific Au-IL interaction and a broader picture of IL-mediated Au-nanorod synthesis.

These arguments do not take into account surface reconstruction, which is seen in IL-mediated nanorod formation. However, Herringbone reconstruction is minor for Au{111} surfaces at the scale of 1 nm, and has been neglected in the present study.
CHAPTER VI
CONCLUSION

The molecular level mechanisms involved in the self assembly of organics (biomolecules, surfactants, and ionic liquids) at metal surfaces have been the subject of experimental and theoretical investigation. The quest is to tailor molecules with specific binding properties and patterns on nanoparticles and metal surfaces with applications in electronic devices, drug delivery, and catalysis as well as control the anisotropy of nanostructure formation so as to tune functionality for applications in plasmon resonance, opto-electronics, and bio-imaging. Molecular level processes involved at the metal-organic interface can be broken down into i) non-covalent soft-epitaxial interactions through geometrical fit by co-ordination of polarizable atoms in favorable configurations, or adaptation through conformational flexibility of long chains to epitaxial grooves on the first, second, and third layers of even metal surfaces, ii) covalent bonding interactions like Au-thiol linkages and iii) attraction of organics through induced charges by interfacial polarization. A comparison of the “relative magnitudes” of i) and iii) for metal-bimolecular (peptides), and metal-ionic liquid (1-ethyl-3-methylimidazolium ethyl sulfate: [EMIM][ES]) interfaces has been done. Classical molecular dynamics simulations with all-atomic models have been used in conjunction with a-posteriori computation of polarization energies to determine contributions of the stated mechanisms (i) and iii) to interfacial structure and selective adsorption at different Au surfaces.
A hypothesis for anisotropic formation of gold nanorods, synthesized from imidazolium based Ionic Liquids (IL) solvents, driven primarily by attraction through induced charges has been proposed.

Adsorption of organics at metal surfaces depends on nature of the solute (organic), the solvent (water/hydrocarbon/epoxy), and the geometry as well as the packing of the surface (metal, e.g. gold). For the biomolecule-metal interface in solution, adsorption at the closely packed Au \{111\} surface is dictated by soft-epitaxial interactions between the peptide (both charged and neutral) and the even metal surface. Contribution of interfacial polarization is found to be small, if not negligible. However, for the more openly packed Au \{100\} surface, which has a water interlayer between the metal and peptide, interfacial polarization dominates the adsorption mechanism for the charged peptide. This demonstrates that for molecules with weak epitaxial fit, and high distribution of charges on individual atoms, attraction through induced polarization is the governing mechanism for adsorption. A breakdown of polarization energy contribution by individual amino acids also indicates an increase in attraction with increase in distance (averaged over the trajectory) between the cationic and anionic groups for charged residues.

Ionic Liquid (IL) molecules have high distribution of charges on individual atoms. There are no water molecules to compete for adsorption at the metal-organic interface for IL-metal systems. A possible mechanism of IL adsorption could be through geometrical fit of highly polar atoms (S, N, O) to epitaxial grooves of the even metal surface, similar to peptide adsorption on gold. However, with increasing coverage of the IL ([EMIM][ES]) on gold, the differential in adsorption energy per molecule is negligible and within the standard deviation for the different surfaces (Au \{111\}, Au \{110\}, and

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Au \{100\} ). This points to a mechanism other than soft-epitaxy, that directs selective adsorption of the IL leading to observed anisotropy in gold nanorods synthesized from imidazolium based salts. The side faces of the nanorods are the thermodynamically less favored Au \{110\} and Au \{100\} surfaces which have a computed differential of \( \approx 11 \) mJ/m\(^2\) in added attractive polarization energies of [EMIM][ES] in comparison to the more closely packed Au \{111\} surface. Combined with a favorable tendency of monolayer deposition of Ag(0) on the Au \{110\} and Au \{100\} surfaces, interfacial polarization dictates anisotropic formation of gold nanorods synthesized from imidazolium based salts.

ILs also form networks through intra and inter weak hydrogen bonding. These networks depend on the geometry of the cation and anion and could serve as a template for shapes other than rods (stars, dendrites, etc.) if combined with control of attractive induced charges through change of side groups on the anion (increasing length of side chain would lead to increasing charge on the negative O in the anion and increased stabilization through induced charge but also decreased stabilization due to steric disruption of the micelle). These mechanisms can be summed up as “electro-steric” in nature.

Mechanisms involved in nanorod synthesis from ILs (no solvent) differs from those synthesized in surfactants (e.g. CTAB) in solution, in that the surfactant molecules form bilayers by co-ordination through conformational flexibility of the large aliphatic groups to epitaxial grooves on gold. Soft-epitaxy plays the major role in surfactant mediated synthesis and surfactants act as hard capping agents, whereas interfacial polarization drives IL-mediated synthesis of gold nanorods and ILs act as soft capping
agents which can tune surface geometry of resultant nanostructure by changing the anion (which changes both the IL network and magnitude of attraction through induced charges) while also having the added advantage of being eco-friendly.

Estimation of contributions through polarization has been the subject of electrochemical calculations, and was considered as a significant energy that could influence selective adsorption.\textsuperscript{15,17} However, it has been seen as marginal by some authors, or not considered at all in dynamics simulations.

Polarization energy contributions have been quantified in the present study and their role highlighted in the interaction of even metal interfaces with biomolecules and ionic liquids. With change in geometry, visualization of surface potential provides a tool for determining favorable epitaxial binding sites.\textsuperscript{51} A feasible extension of the present model would be to include attractive polarization energy contributions to adsorption at shaped metal surface geometries through changes in induced potential tracked as a function of changes in induced electric field. These induced electric potential maps could be combined with surface potential maps to give an integral view of adsorption so as to include the contribution of both long range forces, van der Waals and Coulomb, at edges and curves of metal nanostructures.
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