SHAPE-SELECTIVE SYNTHESSES
OF GOLD AND COPPER NANOSTRUCTURES:
INSIGHTS FROM DENSITY-FUNCTIONAL THEORY
AND MOLECULAR DYNAMICS

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Abstract

Density-functional theory (DFT) and molecular dynamics (MD) were used to resolve the origins of shape-selective syntheses of \{111\}-faceted Au nanostructures mediated by polyvinylpyrrolidone (PVP) as well as \{100\}-faceted Cu nanostructures mediated by hexadecylamine (HDA) seen in experiment. For the work in PVP on Au surfaces, the hexagonal reconstruction of Au(100) was considered. DFT results indicate that the Au(111) surface covered by the PVP segment, 2-pyrrolidone (2P), has a lower surface energy than the 2P-covered (5 \times 1) Au(100)-hex surface, and that PVP may exhibit a binding affinity for Au(111) comparable to or greater than (5 \times 1) Au(100)-hex. With MD, it is shown that the PVP-covered Au(111) surface has a lower surface energy than the PVP-covered (5 \times 1) Au(100)-hex surface, and that the atactic PVP isosamer chains have a binding affinity for Au(111) comparable to (5 \times 1) Au(100)-hex. Also, the (5 \times 1) Au(100)-hex surface may have a higher flux of Au atoms than the Au(111) surface. Therefore, the Au(111) surface would be thermodynamically and kinetically favored in PVP-mediated syntheses, leading to \{111\}-faceted Au nanostructures. For the work in HDA on Cu surfaces, DFT results show that the HDA-covered Cu(100) surface has a slightly higher surface energy than the HDA-covered Cu(111) surface. However, HDA has a significant binding preference on Cu(100) over Cu(111). Therefore, the Cu(100) surface would be kinetically favored in HDA-mediated syntheses, leading to \{100\}-faceted Cu nanostructures. Further, a metal-organic many-body (MOMB) force field for HDA-Cu interactions was developed based on the DFT work, and the force field was used to resolve the HDA binding patterns on Cu(100) at molecular level. With MD, it is found that decylamine (DA) may be used as an effective capping agent in the synthesis of \{100\}-faceted Cu nanostructures since DA as well as HDA are organized on Cu surfaces and have the same binding preference on Cu(100) over Cu(111). It is also found that the HDA structures on Cu surfaces remain intact in aqueous solution due to hydrophobicity of alkyl tails and long alkyl chains in the HDA molecules, which could prevent Cu oxidation during the synthesis.
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Chapter 1 —
Introduction

In the past two decades, various nanostructures of the late 3d transition metals Cu [2–21] and Ni [22, 23], the late 4d transition metals Ag [20, 24–29], Pd [30], and Ru [31], as well as the late 5d transition metals Au [20, 27, 32–35] and Pt [36–39] have been synthesized in solution phase. In particular, Au nanostructures are of key interest for applications in catalysis [40–43], sensing [44–48], and solar cells [49–51], while Cu nanostructures hold great potential for applications as flexible nanowire electrodes in transparent conducting films [2, 7, 8, 10, 12, 15, 17, 18, 52–55], conductive ink [13], and catalysis [6, 9, 11, 56, 57]. In these applications, the unique and promising properties of these nanocrystals are significantly influenced by their size and shape. Therefore, resolving the detailed mechanism in the synthesis of Au and Cu nanostructures is important to achieve controlled and reproducible products for industrial applications.

In the solution-phase syntheses of Au and Cu nanostructures, polyvinylpyrrolidone (PVP) (cf. Fig. 1.1) [32–35] and hexadecylamine (HDA) (cf. Fig. 1.2) [2, 3, 5–7, 9, 11, 14] respectively serve as capping agents or structure-directing agents (SDA), which bind to and protect surface atoms of the face-centered cubic (fcc) metal seeds during the growth stage of nanocrystals. In experiment, it was observed that \{111\}-faceted Au nanostructures, such as nanotetrahedra and nanoicosahedra, occurred in the PVP-mediated synthesis [32–35], while \{100\}-faceted Cu nanostructures, such as nanowires [2, 14], nanocubes [2, 11], and nanorods [9], occurred in the HDA-mediated synthesis. It is hypothesized that the capping agent binds more strongly to certain crystal facets, which become the most dominant ones in the final shape of nanostructures [58]. Therefore, it is likely that PVP and HDA bind more strongly to Au(111) and Cu(100) respectively to shape \{111\}-faceted Au and \{100\}-faceted Cu nanostructures. In the quest to investigate the formation of these nanostructures, it is
useful to understand how PVP and HDA bind to Au and Cu surfaces, respectively.

**Figure 1.1.** A syndiotactic PVP chain, in which the 2-pyrrolidone rings alternate with respect to the backbone. Oxygen is red, nitrogen is blue, carbon is black, and hydrogen is white.

**Figure 1.2.** An HDA molecule. Nitrogen is blue, carbon is black, and hydrogen is white.

Since it is difficult to directly measure binding energies of the capping agent on different crystal facets with experiments, to probe the origins of facet-selective binding for PVP on Au(111) as well as for HDA on Cu(100), atomistic-scale theoretical methods and molecular-level simulations can provide important insight into the synthesis. For example, recent studies with density-functional theory (DFT) indicate that PVP binds more strongly to Ag(100) than to Ag(111) [59–61], which is likely to facilitate the formation of \{100\}-faceted Ag nanostructures as seen in experiment. Further, the recent study of classical molecular-dynamics (MD) simulations shows how PVP in ethylene glycol solution induces \{100\}-faceted Ag nanocrystals [62] by using the force field describing PVP-Ag interactions [63], which was developed to fit previous DFT results [59]. Using MD, progress can be made in understanding the solution-phase binding of capping agents to nanocrystal surfaces [64–66], solid-liquid interfacial free energies and nanocrystal Wulff shapes [67, 68], as well as kinetic structures and the kinetics of nanocrystal growth [62, 69–72]. In this work, DFT was applied first to investigate the binding-energy differences between crystal facets, and force fields for the binding of capping agents to fcc metal surfaces were developed based on DFT results and
used to perform MD simulations to obtain further information at molecular scale as well as at experimental temperature and timescale.

For studying PVP binding to Au within DFT scale, the repeat unit of PVP was considered according to the recent DFT study which predicts a significant preference for \{100\}-faceted Ag nanostructures in the PVP-mediated synthesis by incorporating the binding-energy difference between Ag(100) and Ag(111) for a PVP repeat unit into a thermodynamic model including PVP chain stiffness [59]. The results from DFT calculations were used to fit an empirical force field for the binding of PVP to Au surfaces [73], and atactic PVP chains at molecular level were described in this work. It is noted that PVP is typically atactic [74,75] (i.e., it has random placement of 2-pyrrolidone rings on both sides of the backbone), although syndiotactic PVP shown in Fig. 1.1 can be synthesized [75].

For modeling PVP binding to Au, it is also important to recognize that the Au(100) surface tends to exhibit hexagonal reconstructions [76–81]. The DFT studies show that in vacuum and in some electrochemical environments, the surface energy of the (5 × 1) hexagonal reconstruction of Au(100) (i.e., (5 × 1) Au(100)-hex) is lower than Au(100) and higher than Au(111) [76–80], and that the tendency for Au(100) to reconstruct can be linked to relativistic electronic effects [79, 80]. Recent experimental work shows that a c(28 × 48) hexagonal reconstruction occurs on Au(100) [81], but such hexagonal reconstruction is beyond the DFT scale. Therefore, (5 × 1) Au(100)-hex was considered along with Au(100) as well as Au(111) surfaces in the PVP/Au systems.

For studying HDA binding to Cu with DFT, it is noted that room-temperature experimental studies with solution nuclear magnetic resonance (NMR) spectroscopy indicate that HDA binds intact to Cu [82] and Ru [31] surfaces via the amine group and that the alkyl chains tilt away from Ru surfaces at high HDA concentrations [31]. A high molar ratio of HDA to Cu, ranging from 3-6, is required to obtain \{100\}-faceted Cu nanostructures [2,3,5–7,9,14]. Therefore, the DFT work focuses on investigating the structures of HDA monolayers on Cu surfaces. Also, solvent can play a role in solution-phase syntheses and water is a typical solvent in HDA-mediated synthesis of Cu nanostructures [2,4,8,9,12,14,17]. In this work,
the solvent and its effects on the Cu surfaces are ignored. It is noted that while Cu is easily oxidized in water, several experimental studies indicate that there is no oxidation of the final Cu nanostructures [2, 4, 8, 14, 17] in aqueous HDA-mediated syntheses, but thin oxide surface layers have also been observed [9, 12]. Thus, water may reach the Cu surfaces to an extent that varies among different synthesis procedures. The work here focuses on the ideal scenario where Cu surfaces are well protected by HDA, but the potential importance of Cu surface oxidation is also acknowledged.

In the DFT work, it is considered that monolayer structures of HDA on Cu may be similar to self-assembled alkanethiol monolayers on Cu surfaces. In recent experimental scanning tunneling microscopy (STM) studies of HDA and dodecylamine on Au(111), de la Llave et al. came to the conclusion that alkylamine monolayers have a similar structure to alkanethiol self-assembled monolayers on Au [83]. Alkanethiols form self-assembled monolayers in which the sulfur atoms bind to the Cu surface and the alkyl tails are oriented away from the surface. Alkanethiols have been reported to form a hexagonal (√3 × √3)R30° overlayer on Cu(111) [84] and Au(111) [85–88], and a hexagonal c(2 × 6) overlayer on Cu(100) was observed using STM [89] and low-energy electron diffraction (LEED) [89,90]. Also relevant are recent results from atomic-force microscopy (AFM) studies of long-chain alkylamines on graphene [91,92]. These studies indicate that long-chain alkylamines form self-assembled monolayers in which the amine group is located close to the graphene surface and the alkyl tails orient normal to the surface plane, in a hexagonal pattern [91,92]. Recent molecular-dynamics simulation studies confirm this structure and show that a long-chain alkylamine monolayer on graphene has a surface coverage of ~0.057 Å⁻² with a hexagonal-like pattern that is incommensurate with the surface [91–93]. Thus, various possible self-assembled monolayer structures of HDA on Cu(100) and Cu(111) are considered.

Further, to resolve the HDA binding patterns on Cu surfaces at molecular level and probe the effect of solvent, water [2, 4, 8, 14, 17], on the dynamics of HDA binding to Cu surfaces with MD simulations, it is required to develop a force field fitting to DFT results in terms of binding energy and optimized geometry for HDA-Cu interactions. Another important
aspect of the force field is the capability to reproduce preferential binding of HDA molecules to the Cu(100) surface consistent with DFT [1] and experimental studies. A similar scenario occurs for PVP, which was found in first-principles DFT calculations to bind more strongly to Ag(100) than to Ag(111) [59, 60]. Since it is difficult to reproduce the \{100\} binding preference with pair potentials [94], a Metal-Organic Many-Body (MOMB) force field [63,70] was previously developed to model this preference for the PVP/Ag system. In the HDA/Cu system, there is charge transfer (in both DFT [1] and experiment [95]) from the amine group of HDA to Cu surface atoms, which plays an important role in dictating \{100\} facet selectivity – a similar scenario occurs for the O atom in the PVP/Ag system [59, 60]. The capability of the MOMB force field to mimic this charge transfer and its ramifications for metal-organic binding conformations is important to its success.

In the study of PVP on Au, the author investigated the origins of the \{111\} facet selectivity for PVP on Au and its relationship to the reconstruction of Au(100) using DFT and MD simulations. The author resolved PVP binding to Au(111), Au(100), and (5 × 1) Au(100)-hex at the segment level using DFT and at the chain level using MD. In the study of HDA on Cu, the author investigated the origins of the \{100\} facet selectivity for HDA on Cu using DFT and MD simulations, and the author resolved the HDA binding patterns on Cu(100) and Cu(111) at the atomistic level using DFT and at the molecular level using MD. With the MOMB force field developed for HDA-Cu interactions in this work, the author also examined the alkylamines with different chain lengths on Cu surfaces as well as the HDA monolayer on Cu surfaces in an aqueous medium using MD simulations.
Chapter 2

Methods

2.1 Density-Functional Theory

2.1.1 Overview

DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP) [96–98], employing projector augmented-wave (PAW) potentials [99] to describe electron-ion core interactions, and the generalized-gradient approximation (GGA) exchange-correlation functional by Perdew, Burke, and Ernzerhof (PBE) [100]. Long-range van der Waals (vdW) interactions were included using the PBE+vdWsurf method [101,102] for polyvinylpyrrolidone (PVP)/Au systems and the DFT-D2 method of Grimme [103] for hexadecylamine (HDA)/Cu systems, where the dispersion coefficient \( C_6 \) and vdW radius \( R_0 \) derived by Ruiz et al. for Cu were used to account for bulk screening effects [102]. Details of the DFT calculations regarding lattice constants and bare surface energies, PVP/Au systems, as well as HDA/Cu systems are included in subsections 2.1.2, 2.1.3, as well as 2.1.4, respectively.

2.1.2 Lattice Constants and Bare Surface Energies

The bulk Au lattice constant \( a_{0,\text{Au}} \) was calculated using an fcc primitive cell built with different lattice parameters ranging between 4.00 and 4.28 Å. A \((12 \times 12 \times 12)\) \( k \)-point grid was used for this primitive cell. The total energy vs. \( a_{0,\text{Au}} \) was plotted and then a third-degree polynomial was fit to the curve. It was found \( a_{0,\text{Au}} = 4.17 \) Å at the location where the derivative of the polynomial was zero. The corresponding bulk Au cohesive energy is \( E_{\text{bulk, Au}} = -3.273 \) eV. These values are in exact agreement with previous PAW-PBE theoretical results [77]. The bulk Cu lattice constant \( a_{0,\text{Cu}} = 3.615 \) Å from experiment [104]. The corresponding bulk Cu cohesive energy is \( E_{\text{bulk, Cu}} = -4.146 \) eV by using an fcc primitive cell.
with a \((12 \times 12 \times 12)\) \(k\)-point grid, and the energy agrees with PAW-PBEsol potential [105].

For calculating the bare surface energies of the three Au surfaces \((\gamma_{\text{Au}})\) and those of the two Cu surfaces \((\gamma_{\text{Cu}})\), a supercell with the smallest repeat unit for each surface in the \(x\)– and \(y\)–directions parallel to the surface was built first. In the \(z\)–direction perpendicular to the surface, there were 23 total layers: 8 vacuum and 15 metal. The 3 surface layers at each of the metal-vacuum interfaces in this periodic cell were relaxed and the 9 central layers were fixed at the bulk termination. \((16 \times 9 \times 1)\), \((16 \times 16 \times 1)\), and \((4 \times 20 \times 1)\) \(k\)-point grids were used for Au(111), Au(100), and \((5 \times 1)\) Au(100)-hex, respectively. \((16 \times 9 \times 1)\) and \((16 \times 16 \times 1)\) \(k\)-point grids were used for Cu(111) and Cu(100), respectively. After geometry optimization, \(\gamma_{\text{metal}}\) was calculated using [106]

\[
\gamma_{\text{metal}} = \frac{E - NE_{\text{bulk}}}{2A_{\text{surf}}},
\]

where \(E\) is the energy of the optimized supercell, \(N\) is the number of metal atoms in the slab, \(E_{\text{bulk}}\) is the energy per metal atom in the bulk crystal, and \(2A_{\text{surf}}\) is the sum of the areas at the top and the bottom of the metal slab. The surface energies of Au(111), Au(100), and \((5 \times 1)\) Au(100)-hex were found to be 0.044, 0.054, and 0.050 eV/Å\(^2\), respectively, in excellent agreement with previous theoretical values [77], although PBE may underestimate surface energies [106]. The surface energies of Cu(111) and Cu(100) were found to be 0.106 and 0.117 eV/Å\(^2\) respectively, in agreement with PAW-PBEsol DFT calculations [105]. The surface energy of Cu(111) is consistent with experiment [107], and the average surface energy of the two Cu surfaces is also consistent with experiment [108].

### 2.1.3 PVP/Au Systems

To model the binding of PVP on Au surfaces within DFT scale, the interaction of 2-pyrrolidone (2P) (cf., Fig. 2.1) with Au surfaces was considered. Experimental studies indicate that PVP binds on Au surfaces via the oxygen in the 2P ring [109,110], which is likely to be the most active group in the repeat unit of the PVP polymer. Three Au surfaces
that could occur during colloidal syntheses were considered: Au(111), Au(100), and (5 × 1) Au(100)-hex (cf., Fig. 2.1). The (5 × 1) Au(100)-hex surface is a model for the (5 × I) (I is an integer) family of quasi-hexagonal reconstructions that have been experimentally observed to occur for Au(100) in vacuum [81,111,112] and electrochemical [113,114] environments.

Figure 2.1. Top-down view of the 2P binding conformations associated with the highest (1) and the lowest (20) binding energies on (5 × 1) Au(100)-hex. Oxygen is red, nitrogen is blue, carbon is black, and hydrogen is white. The red rectangle shows the (5 × 1) unit cell of Au(100)-hex and the numbers within the unit cell indicate relative atom heights (in Å). The light green triangle composed of 2 carbon atoms and 1 oxygen atom indicates the plane of the 2P ring.

The gas-phase 2P molecule was studied using a cubic supercell with side length of 20 Å. The Au surfaces were modeled using 6-layer (4 × 4 × 14) supercells for Au(111) and Au(100) and a (5 × 4 × 14) supercell for (5 × 1) Au(100)-hex. Wave functions were expanded using a kinetic energy cut-off of 400 eV. The Brillouin zone was sampled with a (4 × 4 × 1) Monkhorst-Pack k-point grid and with a Methfessel-Paxton smearing of 0.1 eV. 2P was adsorbed on only one side of the slab. The bottom 3 layers of the Au slabs were fixed at the bulk termination, while all the other atomic coordinates were relaxed using a force-convergence criterion of 0.01 eV/Å (i.e., fmax in LAMMPS). In a previous study [59], it is shown that the computed structure of gas-phase 2P is consistent with experiment [115].
2.1.4 HDA/Cu Systems

Two Cu surfaces that could occur during colloidal syntheses were considered: Cu(111) and Cu(100), and five HDA binding patterns (cf., Table 2.1) were proposed in this work. For \((\sqrt{3} \times \sqrt{3})R30^\circ\)-Cu(111) and p(2 \times 2)-Cu(111), \((\sqrt{3} \times 3 \times 23)\) and \((2 \times 2\sqrt{3} \times 23)\) supercells were used, respectively. For \((5 \times 3)\)-Cu(100), c(2 \times 6)-Cu(100), and p(2 \times 2)-Cu(100), \((5 \times 3 \times 26), (2 \times 6 \times 26),\) and \((2 \times 2 \times 26)\) supercells were used, respectively. For calculating average isolated HDA-Cu binding energy, \((3\sqrt{3} \times 6 \times 23)\) and \((6 \times 4\sqrt{3} \times 23)\) supercells were used for \((\sqrt{3} \times \sqrt{3})R30^\circ\)-Cu(111) and p(2 \times 2)-Cu(111), respectively, and \((5 \times 6 \times 26), (6 \times 6 \times 26),\) and \((6 \times 6 \times 26)\) supercells were used for \((5 \times 3)\)-Cu(100), c(2 \times 6)-Cu(100), and p(2 \times 2)-Cu(100), respectively. The unit to describe supercell geometries in \(x\) and \(y\) axes is nearest neighbor distance, and that in \(z\) axis is the interlayer spacing.

Table 2.1. The proposed HDA binding patterns on Cu(111) and Cu(100) in this work and their corresponding properties defined in section 4.1.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>(\rho_{HDA} (\text{\AA}^{-2}))</th>
<th>(G)</th>
<th>(x) axis</th>
<th>(y) axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\sqrt{3} \times \sqrt{3})R30^\circ)-Cu(111)</td>
<td>0.059</td>
<td>2</td>
<td>(211)</td>
<td>(0\bar{1}1)</td>
</tr>
<tr>
<td>p(2 \times 2)-Cu(111)</td>
<td>0.044</td>
<td>2</td>
<td>(\bar{1}10)</td>
<td>(\bar{1}01)</td>
</tr>
<tr>
<td>(5 \times 3)-Cu(100)</td>
<td>0.061</td>
<td>6</td>
<td>(011)</td>
<td>(0\bar{1}1)</td>
</tr>
<tr>
<td>c(2 \times 6)-Cu(100)</td>
<td>0.051</td>
<td>4</td>
<td>(011)</td>
<td>(0\bar{1}1)</td>
</tr>
<tr>
<td>p(2 \times 2)-Cu(100)</td>
<td>0.038</td>
<td>1</td>
<td>(011)</td>
<td>(0\bar{1}1)</td>
</tr>
</tbody>
</table>

These supercells have six layers of Cu with HDA molecules adsorbing on one side of the slabs, and a vacuum spacing of \(\sim 12\) \(\text{Å}\) between the top of the molecular layer and the top of the supercell was left, as done in recent DFT studies [59, 73]. The cutoff radius for vdW interactions is 40 \(\text{Å}\). The bottom 3 layers were fixed at the bulk termination and all the other atomic coordinates were relaxed using a force-convergence criterion of 0.01 eV/\(\text{Å}\) (i.e., \(f_{\text{max}}\) in LAMMPS). For constructing models for fitting the force field (cf., section 5.1), all the other atomic coordinates were fixed at the DFT-optimized conformation in the directions parallel to the surface plane.

For an HDA molecule in gas phase, a cubic supercell with side length of 25 \(\text{Å}\) was used.
For a hexagonal HDA monolayer in vacuum, an \((J \times \sqrt{3}J \times 40 \, \text{Å})\) supercell was used, where \(J\) varied between 4.0 and 4.4 \(\text{Å}\). Wave functions were expanded using a kinetic energy cut-off of 400 eV, and the Brillouin zone was sampled with a Monkhorst-Pack \(k\)-point grid and with a Methfessel-Paxton smearing of 0.1 eV. For \((\sqrt{3} \times \sqrt{3})R30^\circ\)-Cu(111) and p\((2 \times 2)\)-Cu(111), \((10 \times 6 \times 1)\) and \((8 \times 5 \times 1)\) \(k\)-point grids were used, respectively. For \((5 \times 3)\)-Cu(100), c\((2 \times 6)\)-Cu(100), and p\((2 \times 2)\)-Cu(100), \((4 \times 6 \times 1)\), \((8 \times 3 \times 1)\), and \((8 \times 8 \times 1)\) \(k\)-point grids were used, respectively. For calculating average isolated HDA-Cu binding energy, \((3 \times 3 \times 1)\) and \((3 \times 3 \times 1)\) \(k\)-point grids were used for \((\sqrt{3} \times \sqrt{3})R30^\circ\)-Cu(111) and p\((2 \times 2)\)-Cu(111), respectively, and \((4 \times 3 \times 1)\), \((3 \times 3 \times 1)\), and \((3 \times 3 \times 1)\) \(k\)-point grids were used for \((5 \times 3)\)-Cu(100), c\((2 \times 6)\)-Cu(100), and p\((2 \times 2)\)-Cu(100), respectively. For a hexagonal HDA monolayer in vacuum, a \((10 \times 6 \times 1)\) \(k\)-point grid was used.

2.2 Molecular Dynamics

2.2.1 Overview

The binding of organic molecules on metal surfaces was modeled within the LAMMPS MD simulation code [116,117]. To model interatomic interactions, three different types of potentials were used. An embedded-atom method (EAM) potential was used for Au-Au [118,119] and Cu-Cu [119,120] interactions. To model intra- and intermolecular interactions, a slightly revised CHARMM force field was used for PVP [63,121], and the CHARMM General Force Field (CGenFF) [121,122] implemented in the CGenFF program [123] that performs atom typing and assignment of bond, angle, and dihedral parameters as well as charges by analogy [124, 125] was used for HDA. The CHARMM36 force field files [126] were also used to assign Lennard-Jones parameters to each type of atom in an HDA molecule. It is noted that the CGenFF program [127] and the CHARMM36 general force field [128] have been applied to small organic molecules adsorbed on carbon nanotubes in MD simulations.

The framework of the Metal-Organic Many-Body (MOMB) force field [63,70] was used to model organic-metal interactions. In this potential, atoms \((a)\) in organic molecules interact
with metal surfaces ($S$) mainly via a pair potential ($\phi_{a-S}$) defined as

$$\phi_{a-S}(r_{ij}) = D_{0,a-S} \left[ e^{-2\alpha_{a-S}(r_{ij}-r_{0,a-S})} - 2e^{-\alpha_{a-S}(r_{ij}-r_{0,a-S})} \right] - s_6 f_{\text{damp}}(r_{ij}, R_{0,a}, R_{0,S}) C_{6,a-S} r_{ij}^{-6},$$

(2.2)

where $r_{ij}$ is the distance between atomic species $i$ and $j$. The first term in Eq. (2.2) is a Morse potential with parameters $D_{0,a-S}$, $\alpha_{a-S}$, and $r_{0,a-S}$ to account for the short-range and direct-bonding interactions. The second term in Eq. (2.2) accounts for long-range vdW interactions in the form prescribed by Grimme [103], which has been implemented in the USER-MISC package of LAMMPS [63,70,129]. Here, $s_6$ is a global scaling factor, $f_{\text{damp}}$ is a damping function associated with $r_{ij}$ as well as vdW radii ($R_{0,a}$ and $R_{0,S}$), and $C_{6,a-S}$ is the dispersion coefficient for the $a - S$ interactions. The values of $C_6$ and $R_0$ for atomic species in organic molecules were given by Grimme [103], and those for Cu were given by Ruiz [102] to account for bulk screening effects. A cutoff radius of 5.5 Å and 6.0 Å was used for the Morse potential for PVP-Au and HDA-Cu interactions respectively, and a cutoff radius of 12 Å was used for vdW interactions.

As discussed in Chapter 1, a pair potential does not adequately capture the surface-selective binding observed for the PVP/Au and HDA/Cu systems. It is known from prior studies [63,70] that DFT results can be better matched by including a term in the molecule-surface potential to interface with the EAM potential. This one-way electron density function mimics charge transfer from the organic molecule to the metal surface, consistent with the findings in a recent DFT study of the HDA/Cu system [1]. In the EAM potential for Au, the electron densities supplied one-way from O to Au ($\rho_{O \rightarrow Au}$) were included. In the EAM potential for Cu, the electron densities supplied one-way from N to Cu ($\rho_{N \rightarrow Cu}$) and from amine H to Cu ($\rho_{H \rightarrow Cu}$) were included. These functions are defined as

$$\rho_{O \rightarrow Au}(r_{ij}) = f_O \rho_{Au-Au}(r_{ij})$$

(2.3)

$$\rho_{N \rightarrow Cu}(r_{ij}) = f_N \rho_{Cu-Cu}(r_{ij})$$

(2.4)
\[ \rho_{H\rightarrow Cu}(r_{ij}) = f_H \rho_{Cu-Cu}(r_{ij}) \]  

(2.5)

where the scaling factors \( f_O, f_N, \) and \( f_H \) were used to adjust the amount of electron density supplied from O to Au, from N to Cu, and from amine H to Cu respectively, and \( \rho_{Au-Au} \) as well as \( \rho_{Cu-Cu} \) are the electron density between Au as well as Cu atoms, respectively. Thus, a modified EAM potential for Au (\( \phi_{Au} \)) and for Cu (\( \phi_{Cu} \)) is respectively given as

\[
\phi_{Au} = \sum_{i} F_{Au} \left( \sum_{i \neq j} \rho_{Au-Au}(r_{ij}) + \sum_{i \neq j} \rho_{O\rightarrow Au}(r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{Au-Au}(r_{ij}) ,
\]

(2.6)

\[
\phi_{Cu} = \sum_{i} F_{Cu} \left( \sum_{i \neq j} \rho_{Cu-Cu}(r_{ij}) + \sum_{i \neq j} \rho_{N\rightarrow Cu}(r_{ij}) + \sum_{i \neq j} \rho_{H\rightarrow Cu}(r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{Cu-Cu}(r_{ij}) ,
\]

(2.7)

where \( F_{Au} \) and \( F_{Cu} \) are the Au and Cu embedding energy respectively, which is a function of electron density \( \rho \), and \( \phi_{Au-Au} \) and \( \phi_{Cu-Cu} \) are the pair potential between Au and Cu atoms, respectively. The superscript on the sum indicates the sum runs over the specified species or species pairs. It is noted that \( F_{Au}, \rho_{Au-Au}, \) and \( \phi_{Au-Au} \) were given by the original EAM potential for Au [118, 119], and \( F_{Cu}, \rho_{Cu-Cu}, \) and \( \phi_{Cu-Cu} \) were given by the original EAM potential for Cu [119, 120]. The modified EAM potential was implemented in LAMMPS via the Finnis-Sinclair option [130]. Details of MD simulations regarding lattice constant and bare surface energies of Au, PVP/Au systems, HDA/Cu systems, as well as water/HDA/Cu systems are included in subsections 2.2.2, 2.2.3, 2.2.4, as well as 2.2.5, respectively.

### 2.2.2 Lattice Constant and Bare Surface Energies of Au

The bulk Au lattice constant \( a_{0,Au,MD} = 4.08 \text{ Å} \) from experiment [131]. The corresponding bulk Au cohesive energy is \( E_{bulk,Au,MD} = -3.924 \text{ eV} \) by using a \((15 \times 15 \times 15) \) fcc cell with the EAM potential, and the energy is in exact agreement with previous EAM theoretical results [118].

For calculating the bare surface energies of the two Au surfaces (\( \gamma_{Au,MD} \)), \((18 \times 20 \times 160 \text{ Å})\) and \((20 \times 20 \times 160 \text{ Å})\) supercells were built for Au(111) and \((5 \times 1) \) Au(100)-
hex, respectively. The surface consists of 15 layers, where 3 surface layers at each of the Au-vacuum interfaces were relaxed and 9 central layers were fixed at the bulk termination. After geometry optimization, $\gamma_{\text{Au,MD}}$ was calculated using

$$\gamma_{\text{Au,MD}} = \frac{E_{\text{Au}} - N E_{\text{bulk,Au,MD}}}{2A_{\text{surf}}}$$ \hspace{1cm} (2.8)

where $E_{\text{Au}}$ is the energy of the optimized supercell for the bare Au slabs. The surface energies of Au(111) and (5 × 1) Au(100)-hex were found to be 0.075 and 0.101 eV/Å$^2$, respectively. The value of $\gamma_{\text{Au(111),MD}}$ is consistent with the EAM theoretical value [118] and also close to experiment [108].

### 2.2.3 PVP/Au Systems

The Au surfaces were modeled using rigid (40 × 46 × 60 Å) and (40 × 40 × 60 Å) supercells for Au(111) and (5 × 1) Au(100)-hex, respectively. It is noted that these Au surfaces are flat, with periodic boundary conditions to account for the relatively large nanocrystals grown experimentally [58,132]. The rigid surface consists of 6 layers, where the bottom 3 layers were fixed at the bulk termination, and the top 3 layers were fixed after being optimized using the FIRE algorithm [133] with a force-convergence criterion of 0.01 eV/Å (i.e., $f_{\text{max}}$ in LAMMPS). Two initial orientations of 24 atactic PVP icosamer chains on each Au surface were built: two perpendicular orientations on Au(111) as well as orientations parallel and perpendicular to the (5 × 1) Au(100)-hex unit cell. Initially, the PVP backbones were all in the trans conformation. The MD simulations were conducted in the canonical (NVT) ensemble at 550 K, an experimental temperature [32] for the synthesis of Au nanostructures, with a time step of 1 fs. The Nosé-Hoover thermostat was used to maintain constant temperature, and the instantaneous potential energies and configurations were saved every 0.1 ns.
2.2.4 HDA/Cu Systems

The Cu lattice constant predicted by the EAM potential (3.615 Å [119,120]) agrees well with the experiment [104], as do the cohesive energy, bulk modulus, and shear modulus [120]. For an HDA molecule in the gas phase, a cubic supercell with a side length of 50 Å was used. The two Cu surfaces, Cu(100) and Cu(111), with adsorbed HDA were modeled using supercells with six Cu layers, where the bottom three layers were fixed at the bulk termination and all the other atomic coordinates were relaxed. For the HDA/Cu system in vacuum, a supercell with length of 70 Å in the surface normal was used. Energy minimization was performed using the FIRE algorithm [133] until the maximum force on any Cartesian component of any relaxed atom (i.e., \( f_{\text{max}} \) in LAMMPS) was less than 0.01 eV/Å. The MD simulations were conducted in the canonical (NVT) ensemble at 373 K, an experimental temperature [2, 7, 14] for the HDA-mediated synthesis of Cu nanostructures, with a time step of 1 fs. The Nosé-Hoover thermostat was used to maintain constant temperature, and the instantaneous potential energies and configurations were saved every 0.01 ns and 0.1 ns, respectively. The systems were equilibrated for 5 ns so that final configurations and potential energies were independent of the initial states, and the data within this 5-ns period were extracted for analysis.

2.2.5 Water/HDA/Cu Systems

TIP3P water model [134] implemented in CHARMM36 force field files [126] as well as the CHARMM-Metal force field [94] were used for water intermolecular interactions as well as for water-Cu interactions, respectively. In terms of water-Cu(111) interfacial tension, the error of the CHARMM-Metal force field in conjunction with Simple Point Charge (SPC) water model with respect to experiment is \(~14\%\) [94], and the sensitivity of the CHARMM-Metal force field to SPC and TIP3P water models is \(~2–4\%\) [135]. Thus, quantitatively acceptable description is expected for water-Cu interactions.

First, an fcc (10 \( \times \) 10 \( \times \) 10) cell was built for Cu with a lattice constant of 3.615 Å [119,120], and NPT simulations were performed at 373 K and 1 bar using Nosé-Hoover
barostat to maintain constant pressure. The system was equilibrated for 5 ns, and its corresponding average lattice constant is 3.636 Å, which was employed as Cu lattice constant to construct (5 × 3)-Cu(100) and (√3 × √3)R30°-Cu(111) in aqueous medium. Water molecules were initially placed in simple cubic packing at density ~1 g/cm³ on top of HDA monolayer structures. In the surface normal, ~20 Å were left, where water molecules do not interact with HDA and Cu, to model solvent behavior in the bulk phase. NPT simulations of the water/HDA/Cu systems were performed at 373 K and 1 bar only in the surface normal to equilibrate the size of supercell in z axis for 5 ns. Subsequently, NVT simulations of the water/HDA/Cu systems were performed with the average equilibrated supercell size from NPT simulations. The details of NVT simulations here are the same as those for HDA/Cu systems.
PVP on Au Surfaces with DFT and MD

3.1 2P on Au Surfaces with DFT

3.1.1 2P Binding Sites and Binding Energies

To search for possible binding sites for 2P with DFT, initial binding structures were systematically built, where the oxygen atom was near the high-symmetry sites on each of the Au surfaces. These initial conformations were motivated by experimental spectroscopic studies [109,110], which indicate that PVP binds on Au via the oxygen atom. The total numbers of initial conformations were 12, 7, and 36 for Au(111), Au(100), and (5 × 1) Au(100)-hex, respectively. After geometry optimization, all of the unique binding conformations are shown in Figs. 3.1, 3.2, and 3.3 for Au(111), Au(100), and (5 × 1) Au(100)-hex, respectively. Also, Fig. 2.1 shows the optimized 2P structures with the highest and the lowest binding energies on (5 × 1) Au(100)-hex. In all cases, the oxygen atom of 2P is the closest to the Au surface with a distance of \( d_{O-Au} \) shown in Table 3.1. The plane of the 2P ring indicated in Fig. 2.1 is slightly tilted away from the Au surface plane, forming an angle of \( \theta_{2P-Au} \) reported in Table 3.1. The experimental study with scanning tunneling microscopy (STM) indicates that 2P molecules adsorb intact on Au(111) with their ring planes tilted away from the surface [136].

The binding energies (\( E_{bind,Au} \)) for the 2P conformations on the Au surfaces were calculated using

\[
E_{bind,Au} = E_{2P} + E_{Au} - E_{2P+Au}
\]

(3.1)

where \( E_{2P} \) is the energy of the optimized 2P in the gas phase, \( E_{Au} \) is the energy of the optimized bare Au slabs, and \( E_{2P+Au} \) is the energy of the optimized 2P/Au system. \( E_{bind,Au} \) can be expressed as a sum of two components such that \( E_{bind,Au} = E_{short-range} + E_{vdW} \), where
Figure 3.1. Top-down view of the 5 unique conformations of 2P on Au(111). Oxygen is red, nitrogen is blue, carbon is black, and hydrogen is white.

Figure 3.2. Top-down view of the 4 unique conformations of 2P on Au(100). Oxygen is red, nitrogen is blue, carbon is black, and hydrogen is white.

$E_{\text{short-range}}$ arises from direct chemical bonding and Pauli repulsion at very close separation, and $E_{\text{vdW}}$ is the long-range vdW interactions. Figure 3.4 shows the binding energies for all the optimized 2P conformations and Table 3.1 provides the highest and the lowest binding energies. It can be seen that the binding energies on Au(111) are fairly similar, while the binding energies show a greater variation on Au(100) and (5 × 1) Au(100)-hex.
Figure 3.3. Top-down view of the 20 unique conformations of 2P on (5 × 1) Au(100)-hex. Oxygen is red, nitrogen is blue, carbon is black, and hydrogen is white.

Table 3.1. DFT-calculated quantities described in the text for Au(111), Au(100), and (5 × 1) Au(100)-hex. The values are associated with the strongest (the weakest) 2P binding energies on Au surfaces.

<table>
<thead>
<tr>
<th></th>
<th>Au(111)</th>
<th>Au(100)</th>
<th>(5 × 1) Au(100)-hex</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{O-Au}$ (Å)</td>
<td>2.96(2.58)</td>
<td>2.52(2.95)</td>
<td>2.55(2.73)</td>
</tr>
<tr>
<td>$\theta_{2P-Au}$ (°)</td>
<td>16(17)</td>
<td>20(16)</td>
<td>17(15)</td>
</tr>
<tr>
<td>$E_{bind,Au}$ (eV)</td>
<td>1.05(1.01)</td>
<td>1.12(0.95)</td>
<td>1.13(0.94)</td>
</tr>
<tr>
<td>$\gamma_{2P,Au}$ (eV/Å²)</td>
<td>0.036(0.036)</td>
<td>0.046(0.047)</td>
<td>0.043(0.044)</td>
</tr>
</tbody>
</table>
It can be seen in Fig. 3.4 that vdW interactions are the most dominant contribution to the total binding energies on all three surfaces, which agrees with the previous studies on the binding of 2P on Ag(100) and Ag(111) with DFT [59,60]. As the binding energies of 2P on Au are compared with those on Ag [59,60], it is found that 2P binding energies on Au surfaces are 30–40% stronger than those on Ag surfaces. It is also found that pyridine binding energies on Au surfaces are stronger than those on Ag surfaces using DFT calculations [137]. The stronger binding of 2P on Au surfaces than on Ag surfaces could be attributed to stronger vdW attraction.
3.1.2 Spatially-Resolved Binding Sites for Oxygen Atoms of 2P on Au Surfaces

To gain further insight into how PVP binds on the Au surfaces, the binding locations of the oxygen atoms in the various 2P binding conformations were mapped. These maps are shown for Au(111), Au(100), and (5 × 1) Au(100)-hex in Figs. 3.5, 3.6, and 3.7, respectively. The binding sites reflect the symmetries of the underlying surfaces and it is noted that even very closely spaced binding sites for oxygen atoms can reflect drastically different 2P conformations. A (10 × 10) surface cell in these figures was used because the size approximately corresponds to the Kuhn length of solution-phase PVP, which is ∼9 PVP segments [59]. In this way, a perspective on the length scale involved with PVP binding on these surfaces is provided. For the purpose of discussion, binding energies that fall below 1.0 eV are designated as “low”, those that fall between 1.0–1.06 eV are designated as “medium”, and those higher than 1.06 eV are designated as “high”.

Figure 3.5. The binding sites for oxygen atoms of 2P on Au(111). The binding sites were colored according to their binding energies indicated by the legend.

Figure 3.5 shows that on Au(111) there is a high and uniform density of oxygen binding sites, all with binding energies that fall in the medium range (green) of the energy scale.
Figure 3.6. Similar to Fig. 3.5 except for Au(100).

Figure 3.7. Similar to Fig. 3.5 except for \((5 \times 1)\) Au(100)-hex.
This indicates that there are many possible ways for PVP to contact Au(111), leading to similar macromolecular binding energies. It can be seen in Fig. 3.6 that the distribution of binding-site energies is broader on Au(100) than on Au(111). Figure 3.4 indicates that one of the sites on Au(100) has a higher binding energy than any site on Au(111), but the rest of the binding-site energies on Au(100) are lower than any binding-site energy on Au(111).

Interestingly, the map for (5 × 1) Au(100)-hex in Fig. 3.7 indicates that the oxygen binding sites form stripes of alternating binding energies that follow the repeating pattern: high – low – medium – low – medium – low. There is a unique energy stripe associated with each unique atom in the (5 × 1) unit cell, which suggests a possible correlation between binding energies and local atomic structures of the unit cell. For example, Fig. 2.1 shows the relative heights of surface atoms in the unit cell of the bare (5 × 1) Au(100)-hex surface. While the atom heights are distinct for each different energy stripe, there is no obvious correlation between atom height and binding energy.

On (5 × 1) Au(100)-hex, PVP binding on the high-energy sites is limited with such a heterogeneous distribution of binding-site energies in Fig. 3.7. It can be seen from Fig. 3.4 that there are only three binding-energy sites on (5 × 1) Au(100)-hex that have higher binding energies than the highest on Au(111) and these sites are all located in the high-energy stripe in Fig. 3.7. Thus, if there is sufficient coverage of macromolecular PVP on the (5 × 1) Au(100)-hex surface, the energetic heterogeneity of the segment binding sites may lead to overall PVP binding comparable to or lower than Au(111).

### 3.1.3 2P-Induced Surface Energies of Au

To investigate the surface energies of the Au facets with the optimized 2P binding conformations summarized in Fig. 3.4, the surface energy \( \gamma_{2P,\text{Au}} \) is defined as [138]

\[
\gamma_{2P,\text{Au}} = \frac{(E_{2P+\text{Au}} - NE_{\text{bulk},\text{Au}}) - E_{2P} - (E_{\text{Au,fix}} - NE_{\text{bulk},\text{Au}})/2}{A_{\text{surf}}},
\]  

(3.2)
where $N$ is the number of metal atoms in the slab, $E_{\text{bulk,Au}}$ is the bulk cohesive energy per Au atom, $E_{\text{Au,fix}}$ is the energy of a bare Au slab fixed at the bulk termination, which is the unreconstructed $(1 \times 1)$ surface in all cases, and $A_{\text{surf}}$ is the surface area of the slab at the organic/metal-vacuum interface. The surface energies in Eq. (3.2) reflect the configurations of the supercells, where only one side of the slab was relaxed/reconstructed and adsorbed with 2P. The surface energies for the 2P-covered Au facets ($\gamma_{2P,\text{Au}}$) are shown in Table 3.1 and indicate that 2P-covered Au(111) is the most favored facet thermodynamically. The analysis here shows that the 2P binding energies on Au(100) and $(5 \times 1)$ Au(100)-hex which are stronger than those on Au(111) are not enough to alter the ordering of the surface energies of 2P-covered Au facets from that of bare Au facets, which favors Au(111) (cf., subsection 2.1.2). However, from the DFT calculations alone, it is unclear how segments of a polymer chain would access the various binding sites and how this would affect the overall chain binding energies and the surface energies of PVP-covered Au facets. To resolve these issues, MD simulations of PVP binding on Au surfaces were performed.

### 3.2 PVP on Au Surfaces with MD

#### 3.2.1 PVP Binding Energies on Au Surfaces

MD simulations of an adsorbed atactic PVP oligomer (icosamer) monolayer on Au surfaces in vacuum were performed using the force field (FF) developed in the recent study [73] to probe PVP binding on the Au(111) and the $(5 \times 1)$ Au(100)-hex surfaces. The 2P binding energies with FF agree well with those with DFT, and the FF reveals a repeating striped pattern of oxygen binding sites of 2P on $(5 \times 1)$ Au(100)-hex with high – low – medium – low – medium – low binding energies [73], which is consistent with DFT results in Fig. 3.7. Beginning with two different initial orientations for PVP, the systems were equilibrated for 20 ns for Au(111) and 25 ns for $(5 \times 1)$ Au(100)-hex. These relatively long equilibration times were required so that the final chain configurations and average potential energies were independent of the initial states for these relatively stiff chains with strong surface interactions. Snapshots of
the equilibrated structures of PVP on Au(111) and (5 × 1) Au(100)-hex are shown in Figs. 3.8 and 3.9, respectively. Subsequent to equilibration, the data over 25 ns runs were obtained and analyzed for discussion in this subsection as well as the following two subsections.

**Figure 3.8.** Top-down and side views of the equilibrated configurations of a PVP monolayer on Au(111). The initial orientation of the PVP chains is (a) horizontal, and (b) vertical with respect to the page. Oxygen is red, nitrogen is blue, and carbon is black.

The binding energies of the PVP monolayer on Au(111) and (5 × 1) Au(100)-hex ($E_{\text{bind,Au,MD}}$) were calculated using

$$E_{\text{bind,Au,MD}} = 24\langle E_{\text{PVP}} \rangle + E_{\text{Au,MD}} - \langle E_{\text{PVP+Au}} \rangle,$$  \hfill (3.3)

where $\langle E_{\text{PVP}} \rangle$ is the mean potential energy of one PVP icosamer chain in the gas phase, $E_{\text{Au,MD}}$ is the energy of the optimized bare Au slab using the EAM potential, and $\langle E_{\text{PVP+Au}} \rangle$ is the mean potential energy of the PVP monolayer on the Au surface. In Table 3.2, the binding energy difference between (5 × 1) Au(100)-hex and Au(111) per PVP repeat unit ($\Delta E_{\text{bind,Au,MD}}$ per segment) is shown. This difference is significantly smaller than the large difference obtained in 2P binding energies with DFT (cf., Fig. 3.4), where the largest dif-
Figure 3.9. Top-down and side views of the equilibrated configurations of a PVP monolayer on (5 × 1) Au(100)-hex. The initial orientation of the PVP chains is (a) parallel, and (b) perpendicular to the long axis of the (5 × 1) Au(100)-hex unit cell. Oxygen is red, nitrogen is blue, and carbon is black.

The binding energy difference is 0.08 eV. Also, it can be seen in Table 3.2 that the binding energy difference per unit surface area ($\Delta E_{\text{bind, Au, MD per unit area}}$) is small such that the ordering of the surface energies of the PVP-covered Au facets ($\Delta \gamma_{\text{PVP, Au}}$) does not change from that of the bare Au facets (cf., subsection 2.2.2). This issue is discussed in further detail in the following subsection.

Table 3.2. MD-calculated quantities described in the text with standard errors for difference between (5 × 1) Au(100)-hex and Au(111).

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<tr>
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<th>(5 × 1) Au(100)-hex - Au(111)</th>
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<tr>
<td>$\Delta E_{\text{bind, Au, MD per segment}}$ (eV)</td>
<td>0.013±0.001</td>
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<tr>
<td>$\Delta E_{\text{bind, Au, MD per unit area}}$ (eV/Å$^2$)</td>
<td>0.00039±0.00004</td>
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<tr>
<td>$\Delta \gamma_{\text{PVP, Au}}$ (eV/Å$^2$)</td>
<td>0.026±0.00004</td>
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</table>
3.2.2 PVP-Induced Surface Energies of Au

To probe the surface energies of the Au facets with PVP, the surface energy ($\gamma_{\text{PVP,Au}}$) [138] is defined as

$$\gamma_{\text{PVP,Au}} = \frac{(\langle E_{\text{PVP+Au}} \rangle - N E_{\text{bulk,Au,MD}}) - \langle E_{24\text{PVP}} \rangle - (E_{\text{Au,fix,MD}} - N E_{\text{bulk,Au,MD}})/2}{A_{\text{surf}}},$$

(3.4)

where $E_{\text{bulk,Au,MD}}$ is the bulk cohesive energy per Au atom using the EAM potential, $\langle E_{24\text{PVP}} \rangle$ is the mean potential energy of 24 PVP icosamer chains in a system with the same size as PVP on Au, $E_{\text{Au,fix,MD}}$ is the EAM potential energy of a bare Au slab fixed at the bulk termination, which is the unreconstructed (1 × 1) surface in all cases. The surface energies in Eq. (3.4) reflect the configurations of the supercells, where only one side of the slab was relaxed/reconstructed and adsorbed with PVP.

The difference in surface energy between (5 × 1) Au(100)-hex and Au(111) for PVP-covered Au facets ($\Delta \gamma_{\text{PVP,Au}}$) is shown in Table 3.2, and it indicates that PVP-covered Au(111) facets are thermodynamically favorable. Also, the results suggest that {111} facets would be the most prevalent in the Wulff equilibrium shapes of Au nanostructures because the surface energy of Au(111) interacting with an environment is lower than that of (5 × 1) Au(100)-hex [139].

3.2.3 Oxygen Density Profiles for PVP on Au Surfaces

To further quantify the mechanism by which PVP would induce facet selectivity for Au(111), the oxygen density profiles in the PVP monolayer on Au(111) and (5 × 1) Au(100)-hex were analyzed. Oxygen was chosen because PVP binds on Au surfaces mainly via oxygen according to experiments [109, 110]. Further, since each PVP repeat unit has one oxygen atom, this is also a measure of the PVP segment density. To calculate oxygen density profiles $\rho_O(z)$, the average number of oxygen atoms $\langle N_O \rangle$ was obtained in slices with widths of $h = 0.5$ Å in the z direction perpendicular to the surface plane with the first slice beginning 0.1 Å below the lowest z coordinate of all oxygen atoms. The (5 × 1) Au(100)-hex surface has
a structure where different atoms in the unit cell have different heights (cf., Fig. 2.1), which can affect the density profile. To eliminate this effect, the supercell was also divided into slices along the x direction parallel to the long axis of the \((5 \times 1)\) unit cell, so that each slice covers a row of surface atoms with a constant height. These x slices were then partitioned along the z direction. Thus, the oxygen density is given by

\[
\rho_O(z) = \frac{\langle N_O(z) \rangle}{A_{\text{surf}} h},
\]

where \(h\) is the width of a slice in the z direction. It can be seen in Fig. 3.10 that two oxygen density peaks arise due to the atactic nature of PVP, where 2P rings can be oriented with respect to the backbone in a way that either places oxygen close to the surface or further away from the surface. It is noted that both peaks are higher for Au(111) than they are for \((5 \times 1)\) Au(100)-hex. However, in the inset of Fig. 3.10, there is a higher density on \((5 \times 1)\) Au(100)-hex than on Au(111) for oxygen atoms at \(z\) beyond the two major peaks. The density at these large distances results from loose end segments, which are more prevalent in the “fluffier” PVP monolayer on \((5 \times 1)\) Au(100)-hex than on Au(111) (cf., Figs. 3.8 and 3.9).

The lower density for \((5 \times 1)\) Au(100)-hex near the surface indicates that this surface is not as well protected by PVP as Au(111). This lower density could be a driving force for a higher Au flux to \((5 \times 1)\) Au(100)-hex and more rapid growth of Au(111). The higher density for \((5 \times 1)\) Au(100)-hex at large \(z\) results from loose end segments, and the recent study [62] indicates that the loose end segments can actually aid in attracting Au atoms by pulling them into the PVP monolayer. This type of attraction is more prevalent on \((5 \times 1)\) Au(100)-hex than on Au(111), which is a more compact PVP monolayer. Therefore, Au atoms are more easily incorporated into the PVP monolayer on \((5 \times 1)\) Au(100)-hex than they are on Au(111). Once they enter the PVP monolayer, they diffuse more rapidly through the less dense monolayer near the \((5 \times 1)\) Au(100)-hex surface, leading to a larger arrival rate of Au atoms at this facet and a greater propensity for \{111\}-faceted Au nanostructures.
3.3 Summary

In summary, the origins of facet selectivity for PVP on Au(111) in shape-controlled syntheses of Au nanostructures have been resolved with DFT and MD. With DFT, it is found that the 2P-covered Au(111) surface is thermodynamically favored because it has the lowest surface energy compared with the 2P-covered Au(100) and (5 \times 1) Au(100)-hex surfaces. By probing 2P binding energies and their spatial distribution across the three Au surfaces, it is also found that PVP may exhibit a binding affinity for Au(111) comparable to or greater than (5 \times 1) Au(100)-hex. With MD, it is shown that atactic PVP icosamer chains have a binding affinity for Au(111) comparable to (5 \times 1) Au(100)-hex and that the PVP-covered Au(111) surface has a lower surface energy than the PVP-covered (5 \times 1) Au(100)-hex surface. Further, by examining oxygen density profiles for PVP on the two Au surfaces, it is found that the (5 \times 1) Au(100)-hex surface may have a higher flux of Au atoms than the Au(111) surface.

Figure 3.10. Oxygen density profiles for PVP on Au(111) and (5 \times 1) Au(100)-hex.
thermodynamic and kinetic points of view in this work, \{111\}-faceted Au nanostructures would occur in PVP-mediated syntheses.

Although the generality of the reconstruction on Au(100) for large nanostructures (with dimensions on the order of 100 Å) considered in this work needs to be verified, it is important to point out that this reconstruction has not been considered in relevant studies with semi-empirical potentials [64,140]. It is noted that quasi-hexagonal reconstructions on Au(100) larger than the (5 × 1) superstructure [79,81] may occur during PVP-mediated colloidal growth process. In this case, Au(100)-hex would be more similar to Au(111) and any difference between the two surfaces might be further reduced. Future studies, aimed at characterizing the surface structures of these materials, would be useful in efforts to achieve shape selectivity.
Chapter 4  
HDA on Cu Surfaces with DFT

4.1 Binding Patterns of HDA on Cu

Motivated by experimental studies of alkanethiols on Cu and Au surfaces [84–90], two and three patterns for HDA on Cu(111) and Cu(100) were studied, respectively. These patterns are summarized in Table 2.1, which shows their HDA packing densities ($\rho_{\text{HDA}}$), the number of HDA molecules in the unit cell ($G$), as well as the vectors of the $x$ and $y$ axes in the surface unit cell. $\rho_{\text{HDA}}$ is defined as

$$\rho_{\text{HDA}} = \frac{G}{A_{\text{surf}}},$$

where $A_{\text{surf}}$ is the surface area of the slab.

To probe the geometries and energies of these binding patterns, initial all-trans HDA binding conformations were built for each pattern. Various possible locations of the nitrogen atom with respect to the Cu surface atoms (i.e., atop, bridge, threefold fcc/hcp hollow sites on Cu(111), as well as fourfold hollow sites on Cu(100)) and various orientations of the HDA molecules were considered. As shown in Fig. 4.1, the orientation of a rigid, all-trans HDA molecule with respect to the surface $x − y$ plane can be described in terms of three angles $A$, $B$, and $\Gamma$. $A$ is the tilt angle, which is defined as the angle between the surface normal and the chain axis that connects the nitrogen to the methyl carbon. $B$ is the twist angle, which is the angle between the alkyl chain plane and the tilt plane defined by the surface normal and the chain axis. $\Gamma$ is the orientation angle between the $x − z$ plane and the tilt plane.

Several different measures were used to characterize the binding energetics of the HDA
Figure 4.1. An HDA molecule in Cartesian coordinates with angles $A$, $B$, and $\Gamma$, as defined in the text. The $x-y$ plane is the surface plane, and nitrogen is placed at the origin as the reference point. Nitrogen is blue, carbon is black, and hydrogen is white.

monolayers. The total binding energy per HDA molecule $E_{\text{bind,Cu}}$ is given by

$$E_{\text{bind,Cu}} = \frac{G E_{\text{HDA}} + E_{\text{Cu}} - E_{\text{HDA+Cu}}}{G},$$  \hspace{1cm} (4.2)$$

where $E_{\text{HDA}}$ is the energy of an optimized HDA molecule in the gas phase, $E_{\text{Cu}}$ is the energy of the optimized bare Cu slab, and $E_{\text{HDA+Cu}}$ is the energy of the optimized HDA/Cu system. The total binding energy can be written as a sum of two types of binding energies such that $E_{\text{bind,Cu}} = E_{\text{HDA-HDA}} + E_{\text{HDA-Cu}}$, where $E_{\text{HDA-HDA}}$ and $E_{\text{HDA-Cu}}$ are the intermolecular and molecule-surface binding energies per HDA molecule, respectively. $E_{\text{HDA-HDA}}$ is given by

$$E_{\text{HDA-HDA}} = \frac{G E_{\text{HDA}} - E_{\text{HDA,bind}}}{G},$$ \hspace{1cm} (4.3)$$

where $E_{\text{HDA,bind}}$ is the energy of the HDA molecules (no Cu slab is present) with the same
conformations they have in the optimized HDA/Cu system. $E_{\text{HDA-Cu}}$ is calculated using

$$E_{\text{HDA-Cu}} = \frac{E_{\text{HDA,bind}} + E_{\text{Cu}} - E_{\text{HDA+Cu}}}{G}. \quad (4.4)$$

The molecule-surface binding energy can be written as a sum of two types of binding energies, such that $E_{\text{HDA-Cu}} = \langle E_{\text{HDA-Cu,iso}} \rangle + E_{\text{HDA-HDA,sub}}$. $\langle E_{\text{HDA-Cu,iso}} \rangle$ is average isolated HDA-Cu binding energy, and $E_{\text{HDA-HDA,sub}}$ is substrate-mediated HDA-HDA binding energy since $E_{\text{HDA-HDA}}$ represents the direct interaction that molecules have in the absence of a Cu substrate. $\langle E_{\text{HDA-Cu,iso}} \rangle$ is given by

$$\langle E_{\text{HDA-Cu,iso}} \rangle = \sum_{g=1}^{G} \frac{(E_{\text{HDA,iso,g}} + E_{\text{Cu}} - E_{\text{HDA+Cu,iso,g}})}{G}, \quad (4.5)$$

where $g$ is an index for HDA molecule $g$ in the unit cell, $E_{\text{HDA,iso,g}}$ is the energy of an HDA molecule (no Cu slab is present) in an isolated limit with the same conformation it has in the optimized HDA/Cu layer and $E_{\text{HDA+Cu,iso,g}}$ is the energy of an HDA molecule adsorbed on Cu with the same conformation it has in the optimized HDA/Cu layer in an isolated limit. $\langle E_{\text{HDA-Cu,iso}} \rangle$ measures the average contribution of layer-induced changes in the HDA binding conformation to the interaction of an HDA molecule with the Cu surface. The average distance between HDA nitrogens and Cu surface atoms $\langle d_{\text{N-Cu}} \rangle$ is defined as

$$\langle d_{\text{N-Cu}} \rangle = \langle z_N \rangle - \langle z_{\text{Cu}} \rangle, \quad (4.6)$$

where $\langle z_N \rangle$ and $\langle z_{\text{Cu}} \rangle$ are the average $z$ coordinates of the nitrogen atoms and Cu surface atoms in a unit cell, respectively. The average tilt angle of HDA $\langle A \rangle$ is given by

$$\langle A \rangle = \frac{\sum_{g=1}^{G} A_g}{G}, \quad (4.7)$$

where $A_g$ is the tilt angle for HDA molecule $g$ in the unit cell.

To assess the roles of direct chemical interactions and van der Waals (vdW) interactions
in the binding, Eqs. (4.2)-(4.4) can be written as sums of two components: $E_{\text{short-range}} + E_{\text{vdW}}$, where $E_{\text{short-range}}$ arises from Pauli repulsion and direct chemical bonding at very close separations, and $E_{\text{vdW}}$ is the long-range vdW interaction.

### 4.1.1 Binding Patterns of HDA on Cu(111)

To probe the geometries and energies of the ($\sqrt{3} \times \sqrt{3}$)R30° and the p(2 × 2) overlayers for HDA on Cu(111), initial all-trans HDA binding conformations were built in which the nitrogen atoms were located close to the surface on the atop, bridge, hcp, or fcc high-symmetry sites of Cu(111). For these two patterns, initial HDA conformations with various tilt angles $\Delta$ and uniform $\Gamma$ with the nitrogen atoms located on the atop sites were also considered. The unit cell for the ($\sqrt{3} \times \sqrt{3}$)R30° overlayer contains two HDA molecules and it is also considered that molecules in this pattern could have either uniform or mixed $\Gamma$, where the difference between the two $\Gamma$ is 90°. This is motivated by studies of long-chain alkanethiol monolayers on Au(111), which show the coexistence of uniform and mixed-molecule orientations in a ($\sqrt{3} \times \sqrt{3}$)R30° overlayer using STM [86, 141] and grazing incidence X-ray diffraction (GIXD) [142].

Figure 4.2 shows the HDA structures with the highest $E_{\text{bind,Cu}}$ for the ($\sqrt{3} \times \sqrt{3}$)R30° and the p(2 × 2) patterns. In both these patterns, it is found that after structural optimization, the nitrogen atoms tend to reside on atop sites regardless of their initial binding locations. This is consistent with the DFT study which shows the preferential binding of methylamines on atop sites of Au(111) [143]. The corresponding initial and optimized properties of these patterns are summarized in Table 4.1. Figure 4.3 shows the breakdown of the binding energies in Eqs. (4.2)-(4.4) into short-range and vdW components.

In Table 4.1 and Fig. 4.3, it can be seen that the overall binding energies per HDA molecule for the ($\sqrt{3} \times \sqrt{3}$)R30° and p(2 × 2) patterns are dominated by vdW interactions between HDA molecules (HDA-HDA interactions). Although the HDA-HDA interactions increase with increasing HDA packing density, the HDA-Cu interaction decreases with increasing $\rho_{\text{HDA}}$ such that the binding energy is slightly less at higher coverages. Overall, it
**Figure 4.2.** Top-down and side views of the optimized HDA structure in the unit cell and underlying Cu surface atoms for $((\sqrt{3} \times \sqrt{3})R30^\circ)$-Cu(111) with initial (a) uniform $\Gamma$; (b) mixed $\Gamma$ and for (c) p(2 × 2)-Cu(111). The red rectangle is the unit cell of the pattern. Nitrogen is blue, carbon is black, and hydrogen is white.

**Table 4.1.** The initial (with subscript 0) and optimized properties defined in the text for the two HDA binding patterns on Cu(111). $N_0$ denotes the high-symmetry binding site on which the nitrogen atom was initially placed.

<table>
<thead>
<tr>
<th>$A_0$</th>
<th>$B_0$</th>
<th>$\Gamma_0$</th>
<th>$N_0$</th>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{N-Cu} \rangle$ (Å)</th>
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34
is seen from Fig. 4.3 that HDA-HDA vdW attraction dominates the overall binding energy. The HDA-Cu attraction is relatively weak, in comparison. This is consistent with experimental solution-phase nuclear magnetic resonance (NMR) studies at room temperature [82], which indicate that there is rapid exchange between bound HDA on Cu and free HDA in solution – implying a weak HDA-Cu interaction.

Further considering the HDA-HDA vdW attraction, it is seen in Fig. 4.2 and Table 4.1 that the tilt angle for the p(2 × 2) pattern is much greater than those with the ($\sqrt{3} \times \sqrt{3}$)R30° pattern. This occurs because of the lower HDA packing density for the p(2 × 2) pattern (cf., Table 2.1). A similar phenomenon was observed in experimental studies of long-chain alkanethiol monolayers with IR spectroscopy [87] and near edge X-ray absorption fine structure (NEXAFS) [144,145], where the tilt angle on Cu(111) is ∼12°, which is smaller than that on Au(111) (∼27°) [87].
The difference in tilt angles for alkanethiol monolayers can be attributed to the smaller lattice constant for Cu (3.615 Å) than for Au (4.08 Å) [104]. If HDA binding patterns were the same on both (111) surfaces and the chain axes were normal to the surface plane, the distance between alkyl chains would be shorter on Cu than on Au. Therefore, HDA assumes a greater tilt angle on Au to decrease the distance between the alkyl tails and optimize vDW interactions [142]. Similarly in this study, at lower HDA packing density, the molecules assume a greater tilt angle to optimize their own HDA-HDA interactions. As it can be seen from Table 4.2, for the p(2 × 2) pattern, HDA-HDA interactions increase from 0.90 eV at $\langle \mu \rangle = 1.6^\circ$ to 1.28 eV at $\langle \mu \rangle = 38.8^\circ$. The results here confirm that optimizing HDA-HDA interactions are the main driving force for the greater tilt angle at lower HDA packing density.

Table 4.2. The initial (with subscript 0) and optimized properties defined in the text for p(2 × 2)-Cu(111) with initial different $A$.

<table>
<thead>
<tr>
<th>$A_0$</th>
<th>$B_0$</th>
<th>$\Gamma_0$</th>
<th>$N_0$</th>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{N-Cu} \rangle$ (Å)</th>
<th>$\langle \mu \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.51</td>
<td>0.90</td>
<td>0.61</td>
<td>2.20</td>
<td>1.6°</td>
</tr>
<tr>
<td>10°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.55</td>
<td>0.92</td>
<td>0.63</td>
<td>2.20</td>
<td>11.3°</td>
</tr>
<tr>
<td>20°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.67</td>
<td>1.04</td>
<td>0.63</td>
<td>2.23</td>
<td>25.2°</td>
</tr>
<tr>
<td>30°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.72</td>
<td>1.08</td>
<td>0.64</td>
<td>2.24</td>
<td>30.6°</td>
</tr>
<tr>
<td>40°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.89</td>
<td>1.28</td>
<td>0.62</td>
<td>2.25</td>
<td>38.8°</td>
</tr>
<tr>
<td>50°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.57</td>
<td>0.95</td>
<td>0.62</td>
<td>2.26</td>
<td>32.8°</td>
</tr>
</tbody>
</table>

Similar to the trend seen across surfaces for alkanethiols [87,144,145], it is found that the tilt angles for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern on Cu(111) are relatively small compared to the experimental HDA tilt angle for the $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern on Au(111) ($\sim30^\circ$) in X-ray photoelectron spectroscopy (XPS) [83]. Since the HDA tilt angles on Au(111) are close to those seen experimentally for alkanethiols on Au(111), it is expected that the HDA tilt angle on Cu(111) is also close to that for alkanethiols on Cu(111) ($\sim12^\circ$) [144,145] – although this is not what is found. To establish that the tilt angles found in this work are reasonable, HDA layers with uniform $\Gamma$ and five different initial sets of $A$ and $B$ with the nitrogen atoms initially placed on atop sites were optimized. The initial and optimized properties
are included in Table 4.3. While there is some variation in the optimized tilt angles and binding energies, the largest tilt angle is 9.7°, which is still smaller than that for alkanethiols on Cu(111). It is noted that the experimental uncertainty in the tilt angles for alkanethiols on Cu(111) is high (e.g., 12±10°) [144], so the small tilt angles predicted in this work for HDA on (√3 × √3)R30°-Cu(111) are within acceptable range. However, it is possible that this search has not revealed the most optimal binding configuration and there might be an energetically favored minimum with a larger tilt angle.

Table 4.3. The initial (with subscript 0) and optimized properties defined in the text for (√3 × √3)R30°-Cu(111) with initial different A and B but uniform Γ. The references here (Ref.) have experimental values from which A₀ and B₀ were built.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>A₀</th>
<th>B₀</th>
<th>Γ₀</th>
<th>N₀</th>
<th>E_{bind,Cu} (eV)</th>
<th>E_{HDA-HDA} (eV)</th>
<th>E_{HDA-Cu} (eV)</th>
<th>⟨d_{N-Cu}⟩ (Å)</th>
<th>⟨A⟩</th>
</tr>
</thead>
<tbody>
<tr>
<td>[144,145]</td>
<td>0°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.83</td>
<td>1.39</td>
<td>0.44</td>
<td>2.30</td>
<td>2.6°</td>
</tr>
<tr>
<td>12°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.82</td>
<td>1.36</td>
<td>0.46</td>
<td>2.26</td>
<td>4.6°</td>
<td></td>
</tr>
<tr>
<td>20°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.78</td>
<td>1.32</td>
<td>0.47</td>
<td>2.26</td>
<td>7.1°</td>
<td></td>
</tr>
<tr>
<td>[83]</td>
<td>30°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.79</td>
<td>1.32</td>
<td>0.46</td>
<td>2.26</td>
<td>7.6°</td>
</tr>
<tr>
<td>[87]</td>
<td>12°</td>
<td>45°</td>
<td>60°</td>
<td>atop</td>
<td>1.78</td>
<td>1.33</td>
<td>0.45</td>
<td>2.26</td>
<td>9.7°</td>
</tr>
</tbody>
</table>

It is also interesting to consider the origins of the coverage-dependence of the HDA-Cu interaction, which decreases with increasing coverage. Properties relevant to this interaction are summarized in Table 4.4. Here, it can be seen that ⟨E_{HDA-Cu,iso}⟩ is greater at lower HDA packing density, indicating that the larger tilt angles at low coverage also favor more optimal HDA-Cu bonding. As the coverage increases and the tilt angles decrease, ⟨E_{HDA-Cu,iso}⟩ weakens and there is a net decrease in the HDA-Cu interaction with increasing coverage.

Overall, the HDA binding energy is relatively independent of coverage. Following the model of the Langmuir isotherm [146], this indicates that the HDA surface coverage should be dictated by its concentration in solution. At the relatively high molar ratios of HDA to Cu employed in experimental syntheses of Cu nanostructures (i.e., a molar ratio of HDA to Cu, ranging from 3-6 [2,3,5–7,9,14]), it is expected to observe the high-coverage (√3 × √3)R30° pattern. It is noted that in these dense and self-assembled monolayers, the long and hydrophobic alkyl tails will repel water molecules and prevent Cu oxidation, consistent
Table 4.4. The initial (with subscript 0) and optimized properties defined in the text for the two HDA binding patterns on Cu(111).

<table>
<thead>
<tr>
<th>A_0</th>
<th>B_0</th>
<th>\Gamma_0</th>
<th>E_{HDA-Cu} (eV)</th>
<th>\langle E_{HDA-Cu,iso} \rangle (eV)</th>
<th>E_{HDA-HDA,sub} (eV)</th>
<th>\langle A \rangle</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0°</td>
<td>60°</td>
<td>0.44</td>
<td>0.32</td>
<td>0.12</td>
<td>2.6°</td>
</tr>
<tr>
<td>0°</td>
<td>0°</td>
<td>60°, 150°</td>
<td>0.42</td>
<td>0.26</td>
<td>0.17</td>
<td>0.2°</td>
</tr>
</tbody>
</table>

\[(\sqrt{3} \times \sqrt{3})R30°-Cu(111)\]

p(2 × 2)-Cu(111)

| 40° | 0°  | 60° | 0.62 | 0.44 | 0.18 | 38.8° |

with experimental observations.

As a final note, it is seen that for \[(\sqrt{3} \times \sqrt{3})R30°-Cu(111)\], HDA molecules with mixed \(\Gamma\) have higher total binding energies than those with uniform \(\Gamma\) due to stronger HDA-HDA interactions. This finding is consistent with a previous study of a long-chain alkanethiol monolayer on Au(111) [88]. Using periodic DFT calculations with relatively small unit cells, it is possible that more complex HDA binding patterns could occur with a distribution of orientation angles. Given that the binding energy with mixed \(\Gamma\) is slightly higher than with uniform \(\Gamma\), it seems possible that more complex binding configurations could occur in experiment.

4.1.2 Binding Patterns of HDA on Cu(100)

To probe the geometries and energies of the \((5 \times 3)\), \(c(2 \times 6)\), and \(p(2 \times 2)\) overlayers for HDA on Cu(100), initial all-trans HDA binding conformations in which one nitrogen atom was located close to the surface on the atop, bridge, or four-fold hollow high-symmetry sites of Cu(100) were built. The \((5 \times 3)\) pattern is achieved by translating the \((\sqrt{3} \times \sqrt{3})R30°\) overlayer for HDA on Cu(111) to the Cu(100) surface. A hexagonal-like overlayer on Cu(100) should have an \(n \times 3\) pattern, where \(n\) is an integer if the overlayer is commensurate with the surface. With \(n = 5\), the HDA packing density is closest to that for \((\sqrt{3} \times \sqrt{3})R30°-Cu(111)\), which motivates this study of the \((5 \times 3)\) pattern. For this pattern, one nitrogen atom was initially on a high-symmetry site, while others were evenly spaced hexagonally in
the unit cell. It was considered that the molecules in this pattern could have either uniform or mixed $\Gamma$, where the difference between the two $\Gamma$ is $90^\circ$. This is motivated by the finding for $(\sqrt{3} \times \sqrt{3})R30^\circ$-Cu(111) that HDA molecules with mixed $\Gamma$ have higher binding energies than those with uniform $\Gamma$ (cf., Table 4.1).

For c(2 × 6)-Cu(100), one nitrogen atom was initially on a high-symmetry site, while others were placed hexagonally in the unit cell according to the model proposed by Kondoh et al. [89] for alkanethiols on Cu(100). For the $5 \times 3$ pattern, HDA conformations in which their initial tilt angles were zero were optimized since small tilt angles are found for $(\sqrt{3} \times \sqrt{3})R30^\circ$-Cu(111) (cf., Table 4.1). For the $c(2 \times 6)$ and $p(2 \times 2)$ patterns, initial HDA conformations with various tilt angles, with one nitrogen atom located on the atop site in the unit cell were also considered.

Figure 4.4 shows the HDA structures for the $5 \times 3$, c(2 × 6), and p(2 × 2) patterns with the strongest $E_{\text{bind,Cu}}$ after optimization of each initial configuration. It is found that the nitrogen atoms tend to adsorb close to atop sites, regardless of their initial binding locations, which is the same as for HDA on Cu(111). For the $5 \times 3$ pattern, it is found that while most of the amine groups have a relatively constant height from the surface, typically one or two of the amines reside further from the surface than the rest. For example, going from left to right in Fig. 4.4(a), the $d_{N-Cu}$ are: 2.21, 2.19, 2.18, 2.29, 2.39, and 2.25 Å. Going from left to right in Fig. 4.4(b), the $d_{N-Cu}$ are: 2.19, 2.20, 2.18, 2.23, 2.50, and 2.34 Å.

It is observed that for certain elevated molecules in all the optimized configurations of the $5 \times 3$ pattern, there is no any specific correlation between the amine groups that are elevated and their surface location. This “pop-up” phenomenon can be attributed to the high HDA packing density for this pattern (cf., Table 2.1). When one of the HDA molecules assumes an elevated binding configuration, its HDA-Cu interaction ($E_{\text{HDA-Cu,iso}}$) becomes non-attractive: 0.00 eV and -0.04 eV for the fifth HDA molecule from left in Fig. 4.4(a) and (b), respectively. The “pop-up” molecules are essentially squeezed away from the surface to minimize the total energy.

In Table 4.5 and Fig. 4.5, it is observed that the HDA-Cu interaction increases with
decreasing HDA packing density due to increasing $\langle E_{\text{HDA-Cu,iso}} \rangle$ reported in Table 4.6, and this finding is consistent with the binding of HDA on Cu(111). Although this trend on Cu(100) is offset to a small extent by the increase in $E_{\text{HDA-HDA,sub}}$ with increasing coverage due to attractive, substrate-mediated HDA-HDA interactions, a net decrease in the HDA-Cu interaction with increasing coverage is still observed.

Further, it is observed that the total binding energies per HDA molecule are similar for all the patterns, but the densely packed $(5 \times 3)$ pattern with mixed $\Gamma$ has the highest binding energy. It is noted that only periodic structures with unit cells of limited sizes can be probed using DFT calculations. Given the propensity for mixed $\Gamma$, the lack of exact registry of $n$ atoms with the atop sites, and the “pop-up” tendencies for the $(5 \times 3)$ pattern, it is possible that high-coverage HDA layers have more disordered configurations or that they are even incommensurate with Cu(100).

The structure of an adsorbed layer is dictated by molecule-molecule and molecule-surface
Table 4.5. The initial (with subscript 0) and optimized properties defined in the text for the three HDA binding patterns on Cu(100). $N_0$ denotes the high-symmetry binding site on which the nitrogen atom was initially placed.

<table>
<thead>
<tr>
<th></th>
<th>$A_0$</th>
<th>$B_0$</th>
<th>$\Gamma_0$</th>
<th>$N_0$</th>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{\text{N,Cu}} \rangle$ (Å)</th>
<th>$\langle A \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5 × 3)-Cu(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.93</td>
<td>1.46</td>
<td>0.48</td>
<td>2.25</td>
<td>1.7°</td>
<td></td>
</tr>
<tr>
<td>0°</td>
<td>0°</td>
<td>60°, 150°</td>
<td>atop</td>
<td>2.01</td>
<td>1.52</td>
<td>0.49</td>
<td>2.27</td>
<td>1.8°</td>
<td></td>
</tr>
<tr>
<td>c(2 × 6)-Cu(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40°</td>
<td>0°</td>
<td>60°</td>
<td>atop</td>
<td>1.96</td>
<td>1.41</td>
<td>0.55</td>
<td>2.23</td>
<td>35.9°</td>
<td></td>
</tr>
<tr>
<td>p(2 × 2)-Cu(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td>0°</td>
<td>45°</td>
<td>atop</td>
<td>1.96</td>
<td>1.24</td>
<td>0.72</td>
<td>2.25</td>
<td>50.8°</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.5. The total, HDA-HDA, and HDA-Cu binding energies per HDA molecule, broken down into the short-range and vdW (overall – short-range) components for the three HDA binding patterns on Cu(100) summarized in Table 4.5.
Table 4.6. The initial (with subscript 0) and optimized properties defined in the text for the three HDA binding patterns on Cu(100).

<table>
<thead>
<tr>
<th></th>
<th>( A_0 )</th>
<th>( B_0 )</th>
<th>( \Gamma_0 )</th>
<th>( E_{\text{HDA-Cu}} ) (eV)</th>
<th>( \langle E_{\text{HDA-Cu,iso}} \rangle ) (eV)</th>
<th>( E_{\text{HDA-HDA,sub}} ) (eV)</th>
<th>( \langle A \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((5 \times 3))-Cu(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0°</td>
<td>0°</td>
<td>60°</td>
<td>0.48</td>
<td>0.31</td>
<td>0.17</td>
<td>1.7°</td>
<td></td>
</tr>
<tr>
<td>0°</td>
<td>0°</td>
<td>60°, 150°</td>
<td>0.49</td>
<td>0.33</td>
<td>0.16</td>
<td>1.8°</td>
<td></td>
</tr>
<tr>
<td>c(2 \times 6)-Cu(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40°</td>
<td>0°</td>
<td>60°</td>
<td>0.55</td>
<td>0.42</td>
<td>0.13</td>
<td>35.9°</td>
<td></td>
</tr>
<tr>
<td>p(2 \times 2)-Cu(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td>0°</td>
<td>45°</td>
<td>0.72</td>
<td>0.67</td>
<td>0.05</td>
<td>50.8°</td>
<td></td>
</tr>
</tbody>
</table>

interactions. If the former interactions dominate adsorbate binding, an incommensurate layer is generally expected, while a commensurate layer is expected if molecule-surface interactions dominate. It is noted that for octanethiols on Cu(111) with the \((\sqrt{3} \times \sqrt{3})R30^\circ\) pattern, the binding energy is 3.55 eV using vdW-corrected DFT \([147]\), which is much higher than what is found here. Since the alkyl-tail interactions (per methylene unit) similar for alkanethiols and alkylamines are expected, this implies that alkylamines have significantly weaker interactions with the surface. On the other end of the spectrum, alkylamine layers are incommensurate on graphite \([91–93]\) and it is expected that the alkylamine-surface interaction in this system is dominated by (relatively) weak vdW interactions. Alkylamines on Cu surfaces, in particular the Cu(100) surface, whose symmetry does not match the preferred symmetry for HDA-HDA interactions, fall in between alkanethiol monolayers on metal surfaces and alkylamines on graphite. For these reasons, it is possible that high-coverage HDA overlayers are incommensurate with Cu(100).

In Fig. 4.4 and Table 4.5, it is seen that the tilt angles increase as the HDA packing density decreases (cf., Table 2.1). This is consistent with the finding for HDA on Cu(111) and with the expectations from studies of alkanethiol monolayers \([142]\), as discussed above. It is concluded for HDA on Cu(111) that the higher tilt angle for the pattern at lower HDA packing density optimizes its own HDA-HDA interaction (cf., Table 4.2), and this is the
same for the patterns at lower HDA packing densities on Cu(100) (cf., Tables 4.7 and 4.8 for c(2 × 6) and p(2 × 2), respectively).

**Table 4.7.** The initial (with subscript 0) and optimized properties defined in the text for c(2 × 6)-Cu(100) with initial different A.

<table>
<thead>
<tr>
<th>$A_0$</th>
<th>$B_0$</th>
<th>$\Gamma_0$</th>
<th>$N_0$</th>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{N-Cu} \rangle$ (Å)</th>
<th>$\langle \Lambda \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0°</td>
<td>60° atop</td>
<td>1.71</td>
<td>1.16</td>
<td>0.55</td>
<td>2.16</td>
<td>1.7°</td>
<td></td>
</tr>
<tr>
<td>10°</td>
<td>0°</td>
<td>60° atop</td>
<td>1.74</td>
<td>1.16</td>
<td>0.57</td>
<td>2.17</td>
<td>8.5°</td>
<td></td>
</tr>
<tr>
<td>20°</td>
<td>0°</td>
<td>60° atop</td>
<td>1.84</td>
<td>1.26</td>
<td>0.58</td>
<td>2.18</td>
<td>20.5°</td>
<td></td>
</tr>
<tr>
<td>30°</td>
<td>0°</td>
<td>60° atop</td>
<td>1.97</td>
<td>1.40</td>
<td>0.56</td>
<td>2.21</td>
<td>30.8°</td>
<td></td>
</tr>
<tr>
<td>40°</td>
<td>0°</td>
<td>60° atop</td>
<td>1.96</td>
<td>1.41</td>
<td>0.55</td>
<td>2.23</td>
<td>35.9°</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.8.** The initial (with subscript 0) and optimized properties defined in the text for p(2 × 2)-Cu(100) with initial different A.

<table>
<thead>
<tr>
<th>$A_0$</th>
<th>$B_0$</th>
<th>$\Gamma_0$</th>
<th>$N_0$</th>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{N-Cu} \rangle$ (Å)</th>
<th>$\langle \Lambda \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0°</td>
<td>45° atop</td>
<td>1.33</td>
<td>0.61</td>
<td>0.71</td>
<td>2.14</td>
<td>4.1°</td>
<td></td>
</tr>
<tr>
<td>10°</td>
<td>0°</td>
<td>45° atop</td>
<td>1.36</td>
<td>0.62</td>
<td>0.73</td>
<td>2.15</td>
<td>9.7°</td>
<td></td>
</tr>
<tr>
<td>20°</td>
<td>0°</td>
<td>45° atop</td>
<td>1.44</td>
<td>0.70</td>
<td>0.74</td>
<td>2.21</td>
<td>22.7°</td>
<td></td>
</tr>
<tr>
<td>30°</td>
<td>0°</td>
<td>45° atop</td>
<td>1.72</td>
<td>0.98</td>
<td>0.74</td>
<td>2.20</td>
<td>40.3°</td>
<td></td>
</tr>
<tr>
<td>40°</td>
<td>0°</td>
<td>45° atop</td>
<td>1.89</td>
<td>1.15</td>
<td>0.74</td>
<td>2.23</td>
<td>46.8°</td>
<td></td>
</tr>
<tr>
<td>50°</td>
<td>0°</td>
<td>45° atop</td>
<td>1.94</td>
<td>1.23</td>
<td>0.71</td>
<td>2.26</td>
<td>50.8°</td>
<td></td>
</tr>
<tr>
<td>60°</td>
<td>0°</td>
<td>45° atop</td>
<td>1.96</td>
<td>1.24</td>
<td>0.72</td>
<td>2.25</td>
<td>50.8°</td>
<td></td>
</tr>
</tbody>
</table>

For both Cu(111) and Cu(100), it is noted that patterns with the most favorable HDA-HDA interactions are those with the highest HDA packing density. To test the limit of optimal HDA packing density, a c(2 × 2) overlayer for HDA on Cu(100), with $\rho_{\text{HDA}} = 0.077$ Å$^{-2}$, was also studied. For this pattern, it is found that the overall $E_{\text{bind,Cu}}$, $E_{\text{HDA-HDA}}$, and $E_{\text{HDA-Cu}}$ are 0.21, -0.11, and 0.32 eV, respectively. Thus, the high HDA packing density for this pattern leads to repulsion between HDA molecules, making such a high-density pattern unfavorable.
4.2 Binding-Energy Analysis for a Hexagonal HDA Monolayer in Vacuum

In the studies of HDA patterns on Cu(111) and Cu(100), it is found that HDA-HDA interactions dominate the total binding energies and increase with HDA packing density (cf., Tables 2.1, 4.1, and 4.5). However, there is a limit to this increase for very high packing densities, as it is seen for c(2 × 2)-Cu(100). Thus, there is likely to be an optimal HDA packing density that maximizes the HDA-HDA interaction. To find the optimal HDA packing density, hexagonal HDA monolayers in vacuum were studied, beginning with the HDA structures with uniform Γ in Fig. 4.2(a) and with mixed Γ in Fig. 4.2(b), and the supercell size was varied in the $x$ and $y$ directions to vary the packing density. Figure 4.6 shows the HDA-HDA binding energy for a hexagonal HDA monolayer (ML) in vacuum ($E_{\text{HDA-HDA,ML}}$) as a function of the HDA packing density. It is noted that the optimized hexagonal HDA monolayers have similar structures to those on the Cu surface in terms of $A$, $B$, and $\Gamma$.

$E_{\text{HDA-HDA,ML}}$ is calculated using

$$E_{\text{HDA-HDA,ML}} = \frac{GE_{\text{HDA}} - E_{\text{ML}}}{G},$$  \hspace{1cm} (4.8)

where $E_{\text{ML}}$ is the energy of the optimized HDA ML. Third-degree polynomials (cf., the equations in Fig. 4.6) were fitted to the results, and it is found that for HDA structures with uniform $\Gamma$, the optimal HDA packing density is 0.066 Å$^{-2}$ and the corresponding $E_{\text{HDA-HDA,ML}}$ is 1.57 eV. For HDA structures with mixed $\Gamma$, the optimal HDA packing density is 0.065 Å$^{-2}$, and the corresponding $E_{\text{HDA-HDA,ML}}$ is 1.60 eV. These values are higher than those for (5 × 3)-Cu(100) with uniform and mixed $\Gamma$ (cf., Table 4.5). The finding here indicates that HDA in (5 × 3)-Cu(100) has an overall binding preference over ($\sqrt{3} \times \sqrt{3}$)R30°-Cu(111) due to a closer HDA packing density to the optimal value. On Cu(111), the number of possible HDA binding patterns that are commensurate with the surface is limited by the hexagonal Cu(111) surface geometry. On Cu(100), the square surface geometry allows various hexagonal-like
HDA binding patterns with HDA packing densities closer to the optimal values.

Figure 4.6. The correlation between HDA-HDA binding energy and HDA packing density for a hexagonal HDA monolayer in vacuum.

Although HDA-HDA interactions dominate the total binding energies, HDA-Cu binding energies also play a significant role as discussed above. Taking into account the dependence of \( E_{\text{HDA-Cu}} \) on HDA packing density, it is noted that the values of \( E_{\text{HDA-Cu}} \) for Cu(100) are systematically larger than those for Cu(111). Therefore, the greater binding affinity for HDA on Cu(100) can be attributed not only to higher HDA-HDA interactions but also to higher HDA-Cu interactions.

4.3 Charge-Density Difference Analysis of HDA-Cu Binding

To gain further insight into HDA-Cu binding, the charge-density difference upon binding \( \Delta \rho \) for the high-coverage binding configurations with mixed \( \Gamma \) shown in Figs. 4.2(b) and 4.4(b) was calculated. \( \Delta \rho \) is defined as

\[
\Delta \rho = \rho_{\text{HDA+Cu}} - \rho_{\text{HDA}} - \rho_{\text{Cu}},
\]

(4.9)
where $\rho_{\text{HDA}\text{+Cu}}$ is the charge density of the optimized HDA/Cu system, and $\rho_{\text{HDA}}$ and $\rho_{\text{Cu}}$ are the charge densities of the HDA molecules (in the absence of a Cu slab) and the bare Cu slabs, respectively, with the same geometries as in the optimized HDA/Cu systems.

Figure 4.7 shows charge-density difference plots for the chosen surfaces. These plots were obtained using VESTA [148, 149]. On both surfaces, charge transfer occurs primarily between the amine groups and the Cu surface atoms. Amine groups donate electrons to Cu surface atoms, leading to charge depletion around them and charge accumulation on the Cu surface atoms. This result agrees with a recent solution NMR study [82], which indicates that HDA binds to Cu surfaces via the nitrogen electron doublets in the amine group.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.7}
\caption{Isosurfaces of charge density difference for (a) the structure shown in Fig. 4.2(b) for Cu(111) and (b) the structure shown in Fig. 4.4(b) for Cu(100). An isosurface level of $\pm 0.002 \text{ Bohr}^{-3}$ is used here. The regions of charge accumulation and depletion are yellow and blue, respectively. Nitrogen is blue, carbon is black, and hydrogen is white.}
\end{figure}
4.4 HDA-Induced Surface Energies of Cu

To understand how HDA might alter the relative stabilities of the Cu(100) and Cu(111) surfaces, the surface energies $\gamma_{\text{HDA,Cu}}$ of the high-coverage surfaces shown in Figs. 4.2(b) and 4.4(b) were calculated. $\gamma_{\text{HDA,Cu}}$ is defined as [138]

$$
\gamma_{\text{HDA,Cu}} = \frac{(E_{\text{HDA,Cu}} - NE_{\text{bulk,Cu}}) - E_{\text{HDA,bind}} - (E_{\text{Cu,fix}} - NE_{\text{bulk,Cu}})/2}{A_{\text{surf}}}, \quad (4.10)
$$

where $N$ is the number of metal atoms in the slab, $E_{\text{bulk,Cu}}$ is the energy per Cu atom in the bulk crystal, $E_{\text{Cu,fix}}$ is the energy of a bare Cu slab fixed at the bulk termination, and $A_{\text{surf}}$ is the surface area of the slab at the organic/metal-vacuum interface. Equation (4.10) reflects the configurations of the supercells, in which only one side of the slab was relaxed and adsorbed with HDA. While surface energies calculated in vacuum DFT studies at zero K do not exactly represent the solution-phase environment of experimental syntheses, as discussed above, solvent (water) is unlikely to be present to any significant extent in experimental studies wherein pure Cu nanostructures are synthesized. As discussed above, the near-surface environment in aqueous HDA-mediated Cu nanostructure synthesis is likely similar to the high-density HDA-covered slabs studied here.

Using Eq. (4.10), the surface energies for the HDA-covered Cu(111) and Cu(100) surfaces shown in Figs. 4.2(b) and 4.4(b) are 0.081 and 0.086 eV/Å$^2$, respectively. These values can be compared to those for bare Cu(111) and Cu(100), which is found to be 0.106 and 0.117 eV/Å$^2$, respectively (see subsection 2.1.2). It is apparent that HDA adsorption lowers the surface energies of these facets significantly and that the energy difference between the facets is also reduced by HDA adsorption – to the point that the two surfaces are nearly isoenergetic (within the numerical uncertainty of the calculations). Based on trends observed in calculations of interfacial free energies of Ag(100) and Ag(111) surfaces in solvent [67], it is expected to find a reduction in HDA-Cu interfacial free energies at the temperatures of experimental solution-phase syntheses. Also, considering uncertainties in the optimal HDA structures on Cu surfaces, the exact thermodynamic effect of HDA on Cu nanostructure
shape seems unclear at this point – although HDA adsorption clearly favors \{100\} facets to a greater extent as found for bare Cu in vacuum.

Although the exact thermodynamic effect of HDA on Cu nanocrystal shapes is unclear, there is likely the kinetic effect of HDA adsorption on Cu nanostructures based on analogies to previous theoretical studies of the effect of polyvinylpyrrolidone (PVP) on Ag and Au crystal surfaces [59,60,62,63,70,71,73,150,151]. In these studies, it is found that the strong binding of PVP to Ag(100) compared to Ag(111) leads to better protection of Ag(100) by PVP and a higher Ag flux to Ag(111). Using the framework of the kinetic Wulff construction, this leads to \{100\}-faceted Ag cubes, as is seen experimentally [152]. Since it is also predicted here that HDA binds more strongly to Cu(100) than to Cu(111), a similar scenario may occur in this system and this would be consistent with experimental trends.

4.5 Summary

In summary, dispersion-corrected DFT was used to probe possible structures for adsorbed layers of HDA on Cu(100) and Cu(111). Numerous possible candidate structures at various surface coverages were investigated and detailed information on seven different structures on these surfaces was provided. It is found that HDA binds to these Cu surfaces by donating electrons in the amine groups to the Cu surface atoms, consistent with experiment. It is also found that vdW interactions between the alkyl tails of HDA molecules are stronger than the interaction between the amine group and the Cu surfaces. HDA-tail interactions dominate the overall binding of HDA to Cu for all of the binding configurations investigated here. Strong HDA-tail interactions lead to coverage-dependent tilting of the HDA layers, such that the tilt angle is larger for lower coverages. A similar phenomenon is seen in the binding of alkanethiol molecules to metal surfaces. At full monolayer coverage, the energetically preferred binding configuration for HDA on Cu(100) is a \(5 \times 3\) pattern – although incommensurate structures cannot be ruled out – while the \((\sqrt{3} \times \sqrt{3})R30^\circ\) pattern is preferred on Cu(111). On both these surfaces, higher binding energies were found for configurations with mixed molecular twist angles.
A major motivation for this work is to understand the experimentally observed capability of HDA as a capping agent for producing \{100\}-faceted Cu nanocrystals. Consistent with experiment, it is found that HDA binds more strongly to Cu(100) than to Cu(111). This strong binding stems from the capability of HDA to form more densely packed layers on Cu(100), which leads to stronger HDA alkyl-tail interactions, as well as the stronger binding of the amine group to Cu(100). The surface energies of HDA-covered Cu(100) and Cu(111) surfaces were estimated and it is found that HDA adsorption lowers the surface energies of the bare Cu surfaces. Significantly, HDA adsorption decreases the difference between the bare-surface Cu surface energies to the point at which the HDA-covered surfaces are nearly isoenergetic. It is thus possible that HDA-covered Cu nanocrystals could have different thermodynamic shapes, expressing \{100\} facets to a greater extent, than bare Cu crystals. By drawing analogies to previous theoretical work on understanding the kinetically induced shapes of Ag nanocrystals grown in the presence of PVP, it seems likely that HDA-covered Cu nanocrystals could have kinetic shapes that primarily express \{100\} facets, as is seen experimentally.
Chapter 5

HDA on Cu Surfaces with MD

5.1 Force-Field Fitting

For HDA-Cu interactions described in the pair potential in Eq. (2.2), it is noted that $D_{0,a-S}$, $\alpha_{a-S}$, and $r_{0,a-S}$ are unknown parameters, and $s_6$ may need to be adjusted to better estimate vdW interactions [63, 73]. These parameters were determined for each of four designated atom types ($a$) in an HDA molecule: amine H bonded to N, aliphatic H bonded to C, aliphatic C, and N. Additionally, to mimic the effect of charge transfer from the amine group to the surface, the values of $f_N$ and $f_H$ were determined for the N and the amine H in Eqs. (2.4) and (2.5).

The force-field parameters were determined using the most favored HDA binding patterns on Cu(100) and Cu(111) [cf., Figs. 5.1(a) and 5.2(a), respectively] in the recent DFT study [1]. To carry out the parametrization, these structures were replicated in $(15 \times 12 \times 26)$ and $(7\sqrt{3} \times 12 \times 23)$ supercells for Cu(100) and Cu(111), respectively, where the unit to describe the $x$ and $y$ supercell axes in the surface plane is the nearest-neighbor distance, and that in $z$ direction normal to the surface is the inter-layer spacing. The HDA/Cu system has six Cu layers, where the bottom three layers were fixed at the bulk termination and all the other atomic coordinates were fixed at DFT-optimized configuration. From these configurations, 15 different HDA conformations were generated on each Cu surface by translating the molecules along the $z$ axis normal to the Cu surface. The molecules were translated up to 0.9 Å above and down to 0.5 Å below the original conformation, in 0.1 Å increments, to probe both attractive and repulsive forces exerted by the Cu surface on each atomic species in the molecules. For each fixed HDA conformation, both DFT and force-field calculations were performed to obtain the force and energy profiles for HDA-Cu
interactions. The force profiles were obtained using

\[ F^\text{HDA-Cu}_{mlk} = F^\text{total}_{mlk} - F^\text{HDA}_{mlk}, \]  

(5.1)

where \( F^\text{HDA-Cu}_{mlk} \) is the \( k \) Cartesian component of the force exerted by the Cu surface on atom \( l \) in the HDA conformation \( m \), \( F^\text{total}_{mlk} \) is the total force, and \( F^\text{HDA}_{mlk} \) is the intra- and intermolecular force, which was calculated using the same HDA conformation in a supercell with the same size as for the HDA/Cu system, only without Cu. The energy profiles were obtained using

\[ E^\text{HDA-Cu}_m = E^\text{HDA}_m + E^\text{Cu}_m - E^\text{total}_m, \]  

(5.2)

where \( E^\text{HDA-Cu}_m \) is the interaction energy between the HDA conformation \( m \) and the Cu surface, \( E^\text{HDA}_m \) is the energy of the same HDA conformation in a supercell with the same size without Cu, \( E^\text{Cu}_m \) is the energy of the Cu surface in a supercell with the same size without HDA, and \( E^\text{total}_m \) is the energy of the HDA/Cu system.

The initial values of unknown variables \( (D_{0,a-S}, \alpha_{a-S}, r_{0,a-S}, f_N, f_H, \text{and } s_6) \) were chosen according to the previous study [63], and they were adjusted randomly using a Python-coded algorithm to minimize a cost function. The cost function \( (C) \) indicates the degree of matching between the force field (FF) and DFT and is defined as

\[ C = \sum_{\text{Cu}(100),\text{Cu}(111)} \left( \sum_{m=1}^{M} \sum_{l=1}^{L} \sum_{k=x}^{z} \frac{(F^\text{HDA-Cu,FF}_{mlk} - F^\text{HDA-Cu,DFT}_{mlk})^2}{\sum_{m=1}^{M} \sum_{l=1}^{L} \sum_{k=x}^{z} (F^\text{HDA-Cu,DFT}_{mlk})^2} \right) \]

\[ + w \sum_{\text{Cu}(100),\text{Cu}(111)} \left( \frac{\sum_{m=1}^{M} (E^\text{HDA-Cu,FF}_m - E^\text{HDA-Cu,DFT}_m)^2}{\sum_{m=1}^{M} (E^\text{HDA-Cu,DFT}_m)^2} \right) \]

\[ + w \sum_{m=1}^{M} \frac{(\Delta E^\text{HDA-Cu,FF}_{m,Cu(100)-Cu(111)} - \Delta E^\text{HDA-Cu,DFT}_{m,Cu(100)-Cu(111)})^2}{\sum_{m=1}^{M} (\Delta E^\text{HDA-Cu,DFT}_{m,Cu(100)-Cu(111)})^2}, \]  

(5.3)

Here, the first, second, and third terms correspond to the force, energy, and energy difference
between the two Cu surfaces, respectively. \( m = 1 \) corresponds to the HDA conformation closest to the surface and the conformation furthest from the surface is \( M = 15 \). \( L = 24 \) is the number of atoms per HDA molecule within the vdW cutoff to the surface atoms, and the weighting factor \( w = L^{-1} \) accounts for the fact that the number of energy observations is less than that of forces. In the algorithm, random trial parameter values were generated and only the values that lead to a cost function smaller than the current value are accepted for the next iteration. When the value of the cost function converged to a minimum, \( s_6 = 0.60 \), and the other variables are summarized in Table 5.1.

### Table 5.1

Morse potential parameters \( D_0 \), \( \alpha \), and \( r_0 \) in Eq. (2.2) and the scaling factors for one-way amine H → Cu \( (f_H) \) and N → Cu \( (f_N) \) electron-density functions in Eqs. (2.4) and (2.5).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>( D_0 ) (eV)</th>
<th>( \alpha ) (Å(^{-1}))</th>
<th>( r_0 ) (Å)</th>
<th>( f_H, f_N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>amine H – Cu</td>
<td>0.00176</td>
<td>1.87</td>
<td>2.51</td>
<td>1.29</td>
</tr>
<tr>
<td>aliphatic H – Cu</td>
<td>0.00157</td>
<td>1.64</td>
<td>2.82</td>
<td>–</td>
</tr>
<tr>
<td>C – Cu</td>
<td>0.00103</td>
<td>1.35</td>
<td>4.27</td>
<td>–</td>
</tr>
<tr>
<td>N – Cu</td>
<td>0.00418</td>
<td>4.13</td>
<td>2.31</td>
<td>4.24</td>
</tr>
</tbody>
</table>

#### 5.2 Force-Field Testing

Following parametrization of the force field, its accuracy was tested by performing energy minimization on various DFT-optimized HDA structures on Cu(100) and Cu(111). The details of energy minimization are included in subsection 2.2.4. The HDA binding patterns probed in energy minimization are summarized in Table 5.2, which shows their HDA packing densities \( \rho_{\text{HDA}} \), the number of HDA molecules in the unit cell \( (G) \), as well as the vectors of the \( x \) and \( y \) axes in the surface unit cell. \( \rho_{\text{HDA}} \) is defined as

\[
\rho_{\text{HDA}} = \frac{G}{A_{\text{surf}}},
\]

where \( A_{\text{surf}} \) is the surface area of the slab. Figures 5.1 and 5.2 show representative DFT-optimized HDA structures on Cu(100) and Cu(111), respectively.
Table 5.2. HDA binding patterns on Cu(100) and Cu(111) from DFT [1] and their corresponding properties defined in the text.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>$\rho_{\text{HDA}}$ (Å$^2$)</th>
<th>$G$</th>
<th>$x$ axis</th>
<th>$y$ axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5 × 3)-Cu(100)</td>
<td>0.061</td>
<td>6</td>
<td>(011)</td>
<td>(011)</td>
</tr>
<tr>
<td>c(2 × 6)-Cu(100)</td>
<td>0.051</td>
<td>4</td>
<td>(011)</td>
<td>(011)</td>
</tr>
<tr>
<td>p(2 × 2)-Cu(100)</td>
<td>0.038</td>
<td>1</td>
<td>(011)</td>
<td>(011)</td>
</tr>
<tr>
<td>($\sqrt{3} \times \sqrt{3}$)R30°-Cu(111)</td>
<td>0.059</td>
<td>2</td>
<td>(211)</td>
<td>(011)</td>
</tr>
<tr>
<td>p(2 × 2)-Cu(111)</td>
<td>0.044</td>
<td>2</td>
<td>(T10)</td>
<td>(TT2)</td>
</tr>
</tbody>
</table>

Figure 5.1. Top-down and side views of the DFT-optimized HDA structure in the unit cell and underlying Cu surface atoms for (5 × 3)-Cu(100) with (a) uniform \( \Gamma \) and (b) mixed \( \Gamma \), for (c) c(2 × 6)-Cu(100), as well as for (d) p(2 × 2)-Cu(100) [1]. The red rectangle is the unit cell of the pattern. Nitrogen is blue, carbon is black, and hydrogen is white.

After energy minimization, several different measures [1] were used to characterize the binding energetics and geometries of the HDA structures. The total binding energy per HDA molecule $E_{\text{bind,Cu}}$ is given by

$$E_{\text{bind,Cu}} = \frac{GE_{\text{HDA}} + E_{\text{Cu}} - E_{\text{HDA+Cu}}}{G}, \quad (5.5)$$
Figure 5.2. Top-down and side views of the DFT-optimized HDA structure in the unit cell and underlying Cu surface atoms for \((\sqrt{3} \times \sqrt{3})R30^\circ\text{-Cu}(111)\) with (a) uniform \(\Gamma\) and (b) mixed \(\Gamma\), as well as for (c) \(p(2 \times 2)\text{-Cu}(111)\) [1]. The red rectangle is the unit cell of the pattern. Nitrogen is blue, carbon is black, and hydrogen is white.

where \(E_{\text{HDA}}\) is the energy of an optimized HDA molecule in the gas phase, \(E_{\text{Cu}}\) is the energy of the optimized bare Cu slab, and \(E_{\text{HDA+Cu}}\) is the energy of the optimized HDA/Cu system. The total binding energy can be written as a sum of two types of binding energies such that

\[
E_{\text{bind,Cu}} = E_{\text{HDA-HDA}} + E_{\text{HDA-Cu}},
\]

where \(E_{\text{bind,Cu}}\) is the energy of the HDA/Cu system and \(E_{\text{HDA-HDA}}\) and \(E_{\text{HDA-Cu}}\) are the intermolecular and molecule-surface binding energies per HDA molecule, respectively. \(E_{\text{HDA-HDA}}\) is given by

\[
E_{\text{HDA-HDA}} = \frac{GE_{\text{HDA}} - E_{\text{HDA,bind}}}{G},
\]

where \(E_{\text{HDA,bind}}\) is the energy of the HDA molecules (no Cu slab is present) with the same
conformations they have in the optimized HDA/Cu system. $E_{\text{HDA-Cu}}$ is calculated using

$$E_{\text{HDA-Cu}} = \frac{E_{\text{HDA,bind}} + E_{\text{Cu}} - E_{\text{HDA+Cu}}}{G} .$$

(5.7)

As shown in Fig. 5.3, the geometry of a rigid, all-trans HDA molecule with respect to the surface $x - y$ plane can be described in terms of three angles $A$, $B$, and $\Gamma$. $A$ is the tilt angle, which is defined as the angle between the surface normal and the chain axis that connects the nitrogen to the methyl carbon. $B$ is the twist angle – the angle between the alkyl chain plane and the tilt plane defined by the surface normal and the chain axis. $\Gamma$ is the orientation angle between the $x - z$ plane and the tilt plane. The average distance between HDA nitrogens and Cu surface atoms $\langle d_{\text{N-Cu}} \rangle$ is defined as

$$\langle d_{\text{N-Cu}} \rangle = \langle z_\text{N} \rangle - \langle z_\text{Cu} \rangle ,$$

(5.8)

where $\langle z_\text{N} \rangle$ and $\langle z_\text{Cu} \rangle$ are the average $z$ coordinates of the nitrogen atoms and Cu surface atoms in a unit cell, respectively. The average tilt angle of HDA $\langle A \rangle$ is given by

$$\langle A \rangle = \frac{\sum_{g=1}^{G} A_g}{G} ,$$

(5.9)

where $A_g$ is the tilt angle for HDA molecule $g$ in the unit cell.

The force-field and DFT properties for the three HDA binding patterns on Cu(100) are summarized in Table 5.3, and it can be seen that the FF predicts these properties well for $(5 \times 3)$-Cu(100), c$(2 \times 6)$-Cu(100), and p$(2 \times 2)$-Cu(100). It is noted that the $(5 \times 3)$ pattern with uniform $\Gamma$ shows a larger total binding energy than that with mixed $\Gamma$, which has the opposite trend as is observed in DFT. This can be attributed to the underestimate in $E_{\text{HDA-HDA}}$ for mixed $\Gamma$ by CGenFF, as the fitted force field exhibits good agreement with DFT for the HDA-Cu interaction. HDA structures with different $A$ for c$(2 \times 6)$-Cu(100) and p$(2 \times 2)$-Cu(100) were further tested, and they are shown in Tables 5.4 and 5.5, respectively. In these tables, it can be seen that almost all of the force-field properties match well with
Figure 5.3. An HDA molecule in Cartesian coordinates with angles $A$, $B$, and $Γ$, as defined in the text. The $x − y$ plane is the surface plane, and nitrogen is placed at the origin as the reference point. Nitrogen is blue, carbon is black, and hydrogen is white.

DFT results.

The force-field and DFT properties for the two HDA binding patterns on Cu(111) are summarized in Table 5.6, where it is seen that the force field provides an excellent fit to DFT for $(\sqrt{3} \times \sqrt{3})R30°$-Cu(111) and p(2 × 2)-Cu(111). It is noted that the $(\sqrt{3} \times \sqrt{3})R30°$ pattern with uniform $Γ$ shows a slightly larger total binding energy than that with mixed $Γ$, which is the opposite trend from DFT. As for Cu(100), this can be attributed to the underestimate in $E_{HDA-HDA}$ for mixed $Γ$ by CGenFF. HDA structures with different $A$ for the $(\sqrt{3} \times \sqrt{3})R30°$ and p(2 × 2) patterns were also tested, and they are shown in Tables 5.7 and 5.8, respectively, which show that properties predicted by the force field match well with DFT results.

To summarize the comparison between the force field and DFT, Fig. 5.4 shows the force-field binding energy as a function of the DFT binding energy for the same structure for all the HDA conformations described in the text and some other HDA structures with small
Table 5.3. The force field and DFT [1](in parentheses) properties defined in the text for the three HDA binding patterns on Cu(100). The corresponding DFT-optimized structures are shown in Fig. 5.1.

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>error</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{\text{N-Cu}} \rangle$ (Å)</th>
<th>$\langle \phi \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5 × 3)-Cu(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>uniform</td>
<td>1.96(1.93)</td>
<td>1.44%</td>
<td>1.46(1.46)</td>
<td>0.50(0.48)</td>
<td>2.33(2.25)</td>
<td>0.8°(1.7°)</td>
</tr>
<tr>
<td>mixed</td>
<td>1.87(2.01)</td>
<td>6.60%</td>
<td>1.37(1.52)</td>
<td>0.50(0.49)</td>
<td>2.33(2.27)</td>
<td>0.8°(1.8°)</td>
</tr>
<tr>
<td>c(2 × 6)-Cu(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.94(1.96)</td>
<td>1.38%</td>
<td>1.31(1.41)</td>
<td>0.63(0.55)</td>
<td>2.20(2.23)</td>
<td>31.7°(35.9°)</td>
</tr>
<tr>
<td>p(2 × 2)-Cu(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.93(1.96)</td>
<td>1.47%</td>
<td>1.07(1.24)</td>
<td>0.86(0.72)</td>
<td>2.14(2.25)</td>
<td>50.6°(50.8°)</td>
</tr>
</tbody>
</table>

Table 5.4. The force field and DFT [1](in parentheses) properties defined in the text for c(2 × 6)-Cu(100) with uniform $\Gamma$ and different $\phi$.

<table>
<thead>
<tr>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>error</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{\text{N-Cu}} \rangle$ (Å)</th>
<th>$\langle \phi \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.71(1.71)</td>
<td>0.05%</td>
<td>1.10(1.16)</td>
<td>0.61(0.55)</td>
<td>2.22(2.16)</td>
<td>3.5°(1.7°)</td>
</tr>
<tr>
<td>1.71(1.74)</td>
<td>1.63%</td>
<td>1.09(1.16)</td>
<td>0.62(0.57)</td>
<td>2.19(2.17)</td>
<td>10.1°(8.5°)</td>
</tr>
<tr>
<td>1.84(1.84)</td>
<td>0.15%</td>
<td>1.23(1.26)</td>
<td>0.61(0.58)</td>
<td>2.35(2.18)</td>
<td>23.2°(20.5°)</td>
</tr>
<tr>
<td>1.96(1.97)</td>
<td>0.34%</td>
<td>1.32(1.40)</td>
<td>0.64(0.56)</td>
<td>2.28(2.21)</td>
<td>31.4°(30.8°)</td>
</tr>
<tr>
<td>1.94(1.96)</td>
<td>1.38%</td>
<td>1.31(1.41)</td>
<td>0.63(0.55)</td>
<td>2.20(2.23)</td>
<td>31.7°(35.9°)</td>
</tr>
</tbody>
</table>

Table 5.5. The force field and DFT [1](in parentheses) properties defined in the text for p(2 × 2)-Cu(100) with uniform $\Gamma$ and different $\phi$.

<table>
<thead>
<tr>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>error</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{\text{N-Cu}} \rangle$ (Å)</th>
<th>$\langle \phi \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.36(1.33)</td>
<td>2.71%</td>
<td>0.59(0.61)</td>
<td>0.77(0.71)</td>
<td>2.01(2.14)</td>
<td>4.3°(4.1°)</td>
</tr>
<tr>
<td>1.40(1.36)</td>
<td>3.30%</td>
<td>0.61(0.62)</td>
<td>0.79(0.73)</td>
<td>2.00(2.15)</td>
<td>13.1°(9.7°)</td>
</tr>
<tr>
<td>1.38(1.44)</td>
<td>4.42%</td>
<td>0.59(0.70)</td>
<td>0.79(0.74)</td>
<td>2.06(2.21)</td>
<td>22.4°(22.7°)</td>
</tr>
<tr>
<td>1.94(1.72)</td>
<td>12.31%</td>
<td>1.11(0.98)</td>
<td>0.82(0.74)</td>
<td>2.17(2.20)</td>
<td>46.8°(40.3°)</td>
</tr>
<tr>
<td>1.92(1.89)</td>
<td>1.82%</td>
<td>1.10(1.15)</td>
<td>0.82(0.74)</td>
<td>2.41(2.23)</td>
<td>50.8°(46.8°)</td>
</tr>
<tr>
<td>1.93(1.94)</td>
<td>0.86%</td>
<td>1.10(1.23)</td>
<td>0.82(0.71)</td>
<td>2.36(2.26)</td>
<td>50.7°(50.8°)</td>
</tr>
<tr>
<td>1.93(1.96)</td>
<td>1.47%</td>
<td>1.07(1.24)</td>
<td>0.86(0.72)</td>
<td>2.14(2.25)</td>
<td>50.6°(50.8°)</td>
</tr>
</tbody>
</table>
Table 5.6. The force field and DFT [1](in parentheses) properties defined in the text for the two HDA binding patterns on Cu(111). The corresponding DFT-optimized structures are shown in Fig. 5.2.

<table>
<thead>
<tr>
<th>Γ</th>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>error</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{N-Cu} \rangle$ (Å)</th>
<th>$\langle A \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>uniform</td>
<td>1.86(1.83)</td>
<td>1.45%</td>
<td>1.43(1.39)</td>
<td>0.42(0.44)</td>
<td>2.40(2.30)</td>
<td>2.6°(2.6°)</td>
</tr>
<tr>
<td>mixed</td>
<td>1.84(1.87)</td>
<td>1.68%</td>
<td>1.41(1.45)</td>
<td>0.43(0.42)</td>
<td>2.41(2.28)</td>
<td>0.3°(0.2°)</td>
</tr>
<tr>
<td>p(2 × 2)-Cu(111)</td>
<td>1.82(1.89)</td>
<td>3.86%</td>
<td>1.20(1.28)</td>
<td>0.62(0.62)</td>
<td>2.33(2.25)</td>
<td>38.5°(38.8°)</td>
</tr>
</tbody>
</table>

Table 5.7. The force field and DFT [1](in parentheses) properties defined in the text for $(\sqrt{3} \times \sqrt{3})$R30°-Cu(111) with uniform Γ and different A.

<table>
<thead>
<tr>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>error</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{N-Cu} \rangle$ (Å)</th>
<th>$\langle A \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.86(1.83)</td>
<td>1.45%</td>
<td>1.43(1.39)</td>
<td>0.42(0.44)</td>
<td>2.40(2.30)</td>
<td>2.6°(2.6°)</td>
</tr>
<tr>
<td>1.82(1.82)</td>
<td>0.38%</td>
<td>1.40(1.36)</td>
<td>0.42(0.46)</td>
<td>2.36(2.26)</td>
<td>4.7°(4.6°)</td>
</tr>
<tr>
<td>1.89(1.78)</td>
<td>6.17%</td>
<td>1.45(1.32)</td>
<td>0.44(0.47)</td>
<td>2.43(2.26)</td>
<td>1.8°(7.1°)</td>
</tr>
<tr>
<td>1.90(1.79)</td>
<td>6.28%</td>
<td>1.45(1.32)</td>
<td>0.45(0.46)</td>
<td>2.43(2.26)</td>
<td>1.4°(7.6°)</td>
</tr>
<tr>
<td>1.86(1.78)</td>
<td>4.39%</td>
<td>1.40(1.33)</td>
<td>0.45(0.45)</td>
<td>2.38(2.26)</td>
<td>5.8°(9.7°)</td>
</tr>
</tbody>
</table>

Table 5.8. The force field and DFT [1](in parentheses) properties defined in the text for p(2 × 2)-Cu(111) with uniform Γ and different A.

<table>
<thead>
<tr>
<th>$E_{\text{bind,Cu}}$ (eV)</th>
<th>error</th>
<th>$E_{\text{HDA-HDA}}$ (eV)</th>
<th>$E_{\text{HDA-Cu}}$ (eV)</th>
<th>$\langle d_{N-Cu} \rangle$ (Å)</th>
<th>$\langle A \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.42(1.51)</td>
<td>6.25%</td>
<td>0.89(0.90)</td>
<td>0.53(0.61)</td>
<td>2.25(2.20)</td>
<td>1.6°(1.6°)</td>
</tr>
<tr>
<td>1.46(1.55)</td>
<td>6.33%</td>
<td>0.89(0.92)</td>
<td>0.57(0.63)</td>
<td>2.27(2.20)</td>
<td>14.3°(11.3°)</td>
</tr>
<tr>
<td>1.67(1.67)</td>
<td>0.10%</td>
<td>1.08(1.04)</td>
<td>0.59(0.63)</td>
<td>2.35(2.23)</td>
<td>29.7°(25.2°)</td>
</tr>
<tr>
<td>1.68(1.72)</td>
<td>1.99%</td>
<td>1.06(1.08)</td>
<td>0.62(0.64)</td>
<td>2.24(2.24)</td>
<td>32.4°(30.6°)</td>
</tr>
<tr>
<td>1.82(1.89)</td>
<td>3.86%</td>
<td>1.20(1.28)</td>
<td>0.62(0.62)</td>
<td>2.33(2.25)</td>
<td>38.5°(38.8°)</td>
</tr>
<tr>
<td>1.72(1.57)</td>
<td>9.32%</td>
<td>1.10(0.95)</td>
<td>0.62(0.62)</td>
<td>2.32(2.26)</td>
<td>33.0°(32.8°)</td>
</tr>
</tbody>
</table>
per HDA molecule), which is likely important in reproducing trends in the HDA-mediated syntheses of \{100\}-faceted Cu nanostructures \[2,3,5–7,9,14\].

Figure 5.4. Comparison of total binding energies per HDA molecule predicted by the force field (FF) to those by DFT for the five HDA binding patterns in Table 5.2 [1] and variants of these patterns given in Tables 5.4, 5.5, 5.7, and 5.8. The solid line indicates a prefect fit of the FF to DFT and the dotted lines indicate a 10% error.

5.3 HDA Binding Patterns on Cu(100)

An advantage of having a well-fit force field is that scenarios becoming costly with DFT calculations can be probed. In the recent DFT studies [1], it was unclear whether or not the identified lowest-energy (5 × 3) pattern is indeed the lowest energy or if there is some other
pattern with higher-order periodicity or that is incommensurate with the surface. Thus, various possible overlayer structures for HDA on Cu(100) were probed using classical MD simulations based on the force field.

In the search for possible binding patterns, hexagonal patterns preferred by the HDA molecules that also fit various periodicities of the Cu(100) surface were generated. It became clear that hexagonal patterns can maintain a periodicity of 3 along the [011] direction, then the periodicity along the [011] direction could be adjusted to achieve an (approximate) hexagonal pattern. Table 5.9 lists the various patterns considered in this work, along with their N-atom density $\rho_{\text{HDA}}$, $G$, the vectors of the $x$ and $y$ axes in the surface unit cell, and the binding energy per HDA molecule $E_{\text{bind,Cu,MD}}$ with the standard errors determined in MD simulations.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>$\rho_{\text{HDA}}$ (Å$^{-2}$)</th>
<th>G</th>
<th>$x$ axis</th>
<th>$y$ axis</th>
<th>$E_{\text{bind,Cu,MD}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(13 \times 3)$-Cu(100)</td>
<td>0.063(high)</td>
<td>16</td>
<td>(011)</td>
<td>(0(\bar{1}1))</td>
<td>1.84±0.01</td>
</tr>
<tr>
<td>$(5 \times 3)$-Cu(100)</td>
<td>0.061(high)</td>
<td>6</td>
<td>(011)</td>
<td>(0(\bar{1}1))</td>
<td>1.87±0.01</td>
</tr>
<tr>
<td>$(12 \times 3)$-Cu(100)</td>
<td>0.060(high)</td>
<td>14</td>
<td>(011)</td>
<td>(0(\bar{1}1))</td>
<td>1.88±0.01</td>
</tr>
<tr>
<td>$(19 \times 3)$-Cu(100)</td>
<td>0.059(medium)</td>
<td>22</td>
<td>(011)</td>
<td>(0(\bar{1}1))</td>
<td>1.88±0.01</td>
</tr>
<tr>
<td>$(26 \times 3)$-Cu(100)</td>
<td>0.059(medium)</td>
<td>30</td>
<td>(011)</td>
<td>(0(\bar{1}1))</td>
<td>1.88±0.01</td>
</tr>
<tr>
<td>$(33 \times 3)$-Cu(100)</td>
<td>0.059(medium)</td>
<td>38</td>
<td>(011)</td>
<td>(0(\bar{1}1))</td>
<td>1.88±0.01</td>
</tr>
<tr>
<td>$(7 \times 3)$-Cu(100)</td>
<td>0.058(low)</td>
<td>8</td>
<td>(011)</td>
<td>(0(\bar{1}1))</td>
<td>1.88±0.01</td>
</tr>
<tr>
<td>$(16 \times 3)$-Cu(100)</td>
<td>0.057(low)</td>
<td>18</td>
<td>(011)</td>
<td>(0(\bar{1}1))</td>
<td>1.87±0.01</td>
</tr>
<tr>
<td>$(17 \times 3)$-Cu(100)</td>
<td>0.054(low)</td>
<td>18</td>
<td>(011)</td>
<td>(0(\bar{1}1))</td>
<td>1.75±0.01</td>
</tr>
<tr>
<td>$(\sqrt{3} \times \sqrt{3})R^{30°}$-Cu(111)</td>
<td>0.059(medium)</td>
<td>2</td>
<td>(2(\bar{1}1))</td>
<td>(0(\bar{1}1))</td>
<td>1.81±0.01</td>
</tr>
</tbody>
</table>

For constructing each of the proposed HDA patterns, one nitrogen was initially placed on a high-symmetry site, while others were evenly spaced hexagonally in the supercell. It was considered that the molecules could have uniform $\Gamma$, and their initial tilt angles were zero since small tilt angles were found for $(5 \times 3)$-Cu(100) as well as $(\sqrt{3} \times \sqrt{3})R^{30°}$-Cu(111) in the recent DFT study [1]. The sizes of surface plane for various HDA patterns are shown in Table 5.10, and they are at least twice the unit cell size as well as the vdW cutoff radius.
These ensure that the periodicity of the pattern is not constrained by the supercell size and each of the atoms in the supercell does not interact with its own periodic images in MD simulations. To obtain thermal properties of these patterns, all-atom MD simulations were conducted, and their details are included in subsection 2.2.4.

Table 5.10. The sizes of surface plane for the proposed HDA patterns on Cu(100) and Cu(111) in MD simulations. The unit to describe the x and y supercell axes in the surface plane is the nearest-neighbor distance.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>Surface plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(13 \times 3)$-Cu(100)</td>
<td>$(26 \times 12)$</td>
</tr>
<tr>
<td>$(5 \times 3)$-Cu(100)</td>
<td>$(15 \times 12)$</td>
</tr>
<tr>
<td>$(12 \times 3)$-Cu(100)</td>
<td>$(24 \times 12)$</td>
</tr>
<tr>
<td>$(19 \times 3)$-Cu(100)</td>
<td>$(38 \times 12)$</td>
</tr>
<tr>
<td>$(26 \times 3)$-Cu(100)</td>
<td>$(52 \times 12)$</td>
</tr>
<tr>
<td>$(33 \times 3)$-Cu(100)</td>
<td>$(66 \times 12)$</td>
</tr>
<tr>
<td>$(7 \times 3)$-Cu(100)</td>
<td>$(14 \times 12)$</td>
</tr>
<tr>
<td>$(16 \times 3)$-Cu(100)</td>
<td>$(32 \times 12)$</td>
</tr>
<tr>
<td>$(17 \times 3)$-Cu(100)</td>
<td>$(34 \times 12)$</td>
</tr>
<tr>
<td>$(\sqrt{3} \times \sqrt{3})R30^\circ$-Cu(111)</td>
<td>$(7\sqrt{3} \times 12)$</td>
</tr>
</tbody>
</table>

Two aspects of these binding patterns were characterized. First, the binding energy per HDA molecule $E_{\rm bind,Cu,MD}$ is defined as

$$E_{\rm bind,Cu,MD} = \frac{G\langle E_{\rm HDA} \rangle + \langle E_{\rm Cu} \rangle - \langle E_{\rm HDA+Cu} \rangle}{G},$$

where $\langle E_{\rm HDA} \rangle$ is the average potential energy of an HDA molecule in the gas phase, $\langle E_{\rm Cu} \rangle$ is the average potential energy of the bare Cu slab, and $\langle E_{\rm HDA+Cu} \rangle$ is the average potential energy of the HDA/Cu system.

Second, molecular ordering in these systems was also characterized via the radial distribution functions $g(r)$ for the nitrogen atoms projected onto the $x-y$ plane from equilibrated configurations. $g(r)$ is defined as

$$g(r) = \frac{\langle N_{(r,r+\Delta r)} \rangle}{2\pi r \Delta r \rho_{\text{HDA}}},$$
where \( r \) is the distance between nitrogen atoms projected onto the \( x - y \) plane, \( \langle N_{(r,r+\Delta r)} \rangle \) is the average number of nitrogen-atom pairs with a distance between \( r \) and \( r + \Delta r \). Here, \( \Delta r \) is 0.1 Å at 373 K to decrease the noise while keeping resolution and \( \Delta r \) is 0.001 Å at 0 K for accuracy. For discussion purposes, the \((13 \times 3)\), \((5 \times 3)\), and \((12 \times 3)\) patterns on Cu(100) are designated as high \( \rho_{\text{HDA}} \); the \((19 \times 3)\), \((26 \times 3)\), and \((33 \times 3)\) patterns on Cu(100), and \((\sqrt{3} \times \sqrt{3})R30^\circ\)-Cu(111) as medium \( \rho_{\text{HDA}} \); and the \((7 \times 3)\), \((16 \times 3)\), and \((17 \times 3)\) patterns on Cu(100) as low \( \rho_{\text{HDA}} \).

As it can be seen in Table 5.9, with the exception of the HDA patterns with the highest and lowest density, most HDA patterns on Cu(100) show the same binding potential energy within uncertainty. Moreover, these energetically preferred patterns have a higher binding energy than the \((\sqrt{3} \times \sqrt{3})R30^\circ\) pattern on Cu(111). Since \( E_{\text{bind,MD}} \) on Cu(100) are the same for seven of the patterns, the HDA surface coverage should be dictated by its concentration in solution following the model of the Langmuir isotherm [146].

Figure 5.5 shows \( g(r) \) at 373 K for the patterns in Table 5.9 with a high HDA coverage and a medium-coverage HDA pattern, for comparison. \( g(r) \) for \((5 \times 3)\)-Cu(100) at 0 K is also shown as a series of vertical lines for this perfectly ordered pattern. Here, it is seen that each peak in \( g(r) \) at 373 K is associated with two or three lines at 0 K. This is in contrast to the \((\sqrt{3} \times \sqrt{3})R30^\circ\)-Cu(111) pattern shown in Fig. 5.6, where each peak is associated with one line at 0 K. Two (or three) lines per peak at 373 K can be seen because the \((5 \times 3)\)-Cu(100) pattern is a distorted hexagon, while the \((\sqrt{3} \times \sqrt{3})R30^\circ\)-Cu(111) pattern is a perfect hexagon. It can also be seen that the peaks in \( g(r) \) are mostly centered about the 0 K spectrum—though the \((5 \times 3)\) structure conforms the best to the 0 K spectrum and there is increasing deviation at the other coverages as distance increases. This is an indication that each of the structures is unique.

Figure 5.7 shows \( g(r) \) at 373 K for the patterns in Table 5.9 with a medium HDA coverage. \( g(r) \) for \((5 \times 3)\)-Cu(100) at 0 K is also shown as a series of vertical lines for this perfectly ordered pattern. Here, it can be seen that, unlike the high-coverage patterns, these medium-coverage patterns tend to be shifted toward longer distances compared to the zero-
Figure 5.5. Radial distribution functions \((g(r))\) for nitrogen atoms projected onto the \(x - y\) plane with standard error bars for the three HDA binding patterns on Cu(100) with high HDA packing density and the \((19 \times 3)\)-Cu(100) shown in Table 5.9 at a temperature of 373 K. Vertical lines show \(g(r)\) for \((5 \times 3)\)-Cu(100) at 0 K as a reference.

Figure 5.6. Similar to Fig. 5.5, except for \((\sqrt{3} \times \sqrt{3})R30^\circ\)-Cu(111).
temperature reference for $(5 \times 3)$-Cu(100). Thus, these patterns are unique compared to those at higher coverage. Notable exceptions are the peaks at the third-neighbor distance (3NN) – these peaks are centered on the zero-temperature line and uphold the third-neighbor periodicity in the $[0\overline{1}1]$ direction. Thus, as the coverage changes, structural changes occur along the $[011]$ direction and not along the $[0\overline{1}1]$ direction.

Figure 5.7. Similar to Fig. 5.5, except for the patterns in Table 5.9 with a medium HDA coverage.

Figure 5.8 shows $g(r)$ at 373 K for the patterns in Table 5.9 with a low HDA coverage and the $(33 \times 3)$-Cu(100) pattern for medium HDA coverage. $g(r)$ for $(5 \times 3)$-Cu(100) at 0 K is also shown as a series of vertical lines for this perfectly ordered pattern. Here, there is more variation among curves for the different coverages. Notably, the curve for the lowest-coverage $(17 \times 3)$ pattern is qualitatively different than those for the higher coverages. This curve no longer shows a peak at 3NN since the packing density for this pattern is the lowest such that there is more space for nitrogen atoms to move on the surface (cf., Fig. 5.9 for equilibrated configurations of nitrogen atoms and Cu surface atoms). For discussion purposes, the $(17 \times 3)$ pattern is designated here to indicate the periodicity of optimized nitrogen atoms with respect to the Cu(100) surface at 0 K (cf., Fig. 5.10).
Figure 5.8. Similar to Fig. 5.5, except for the patterns in Table 5.9 with a low HDA coverage and the \((33 \times 3)\)-Cu(100) pattern for medium HDA coverage.

Figure 5.9. Top-down view of the equilibrated nitrogen configurations and underlying Cu surface atoms for \((17 \times 3)\)-Cu(100) at 373 K. Nitrogen is blue.

Figure 5.10. Top-down view of the optimized nitrogen configurations and underlying Cu surface atoms for \((17 \times 3)\)-Cu(100) at 0 K. The red rectangle is the unit cell of the pattern. Nitrogen is blue.
5.4 The Effect of Chain Length on the Assembly of Alkylamines on Cu Surfaces

It is evident that interactions between hydrocarbon tails play a key role in stabilizing the self-assembled monolayer structure of HDA. These tail interactions are expected to weaken as the alkylamine tail shortens, and a set of MD simulations was conducted to investigate this. Pentylamine (PA), decylamine (DA), and HDA initial monolayer structures with a \((5 \times 3)\) pattern on Cu(100) and the \((\sqrt{3} \times \sqrt{3})R30^\circ\) pattern on Cu(111) at 373 K were built to investigate the effect of chain length on the binding of alkylamines to Cu surfaces. The parameters used for the PA/Cu and DA/Cu systems are the same as those for HDA/Cu described previously. After equilibration, Figs. 5.11 and 5.12 show that PA does not form an organized monolayer – some of the PA molecules leave the Cu surfaces. This finding is consistent with a recent MD and atomic-force microscopy (AFM) study [91] that alkylamines with six or fewer carbon atoms do not form a stable self-assembled monolayer on graphene.

It can be seen that DA molecules do form a complete monolayer on Cu surfaces, similar to HDA. The binding energies \(E_{\text{bind},\text{Cu},\text{MD}}\) for DA (i.e., replacing HDA in Eq. (5.10) with DA) on Cu(100) and Cu(111) are \(1.30 \pm 0.01\) and \(1.23 \pm 0.01\) eV respectively.
Figure 5.11. Top-down and side views of the equilibrated (a) PA, (b) DA, and (c) HDA configurations for $(5 \times 3)$-Cu(100) at 373 K. Nitrogen is blue, carbon is black, and hydrogen is white.

Figure 5.12. Top-down and side views of the equilibrated (a) PA, (b) DA, and (c) HDA configurations for $(\sqrt{3} \times \sqrt{3})R30^\circ$-Cu(111) at 373 K. Nitrogen is blue, carbon is black, and hydrogen is white.
5.5 The Effect of Solvent on the Binding of HDA on Cu Surfaces

Systems with aqueous medium/HDA monolayer/Cu surfaces were built for the (5 × 3) pattern on Cu(100) as well as for the (√3 × √3)R30° pattern on Cu(111) to probe the effect of solvent on the binding of HDA on Cu surfaces. MD simulations were performed according to the procedures in the recent study [62], and details of MD simulations are included in subsection 2.2.5. After equilibration, Fig. 5.13 shows that the HDA monolayers in aqueous medium remain intact without significant fluctuation along z axis normal to the Cu surfaces. This is attributed to the long and hydrophobic alkyl tails in the dense self-assembled HDA monolayers that repel water molecules and prevent Cu oxidation, which is consistent with experimental observations [2, 4, 8, 14, 17].

\[\text{Figure 5.13. Side view of the equilibrated HDA configurations for (a)(5 \times 3)-Cu(100) and (b)(\sqrt{3} \times \sqrt{3})R30^\circ-Cu(111) in an aqueous medium at 373 K. Oxygen is red, nitrogen is blue, carbon is black, and hydrogen is white.}\]
5.6 Summary

In summary, force fields for the adsorption of alkylamines on Cu surfaces were successfully parameterized by fitting the force and energy in the force fields to those in the DFT results [1]. The DFT-predicted HDA binding conformations on Cu surfaces were optimized with the force fields, and the force fields in general not only reproduce the DFT results well in terms of binding energy and geometry, but also show the HDA preferential binding for (5 × 3)-Cu(100) over (√3 × √3)R30°-Cu(111) seen in DFT. With MD simulations, the force fields resolved the unique HDA binding patterns on Cu(100) in vacuum. The effect of chain length on the binding of alkylamines on Cu surfaces was examined in vacuum with MD, and it is found that PA cannot form a stable monolayer on Cu surfaces, while DA are organized and have the same binding preference on Cu(100) over Cu(111) as HDA. Finally, the effect of water on the HDA monolayer binding on Cu surfaces was probed with MD, and it is found that the HDA structures on Cu surfaces are intact in an aqueous medium due to the long and hydrophobic alkyl tails in the dense self-assembled HDA monolayers that repel water molecules and prevent Cu oxidation.
Chapter 6  
Conclusions

For shape-selective syntheses of Au nanostructures, the origins of the {111} facet selectivity for PVP on Au and its relationship to the reconstruction of Au(100) have been resolved with DFT and MD. With DFT, it is found that the 2P-covered Au(111) surface has a lower surface energy than the 2P-covered (5 × 1) Au(100)-hex surface, and that PVP may exhibit a binding affinity for Au(111) comparable to or greater than (5 × 1) Au(100)-hex. MD simulations were performed to probe how atactic PVP icosamer chains would affect the overall binding energies and the surface energies of PVP-covered Au facets. With MD, it is shown that the PVP-covered Au(111) surface has a lower surface energy than the PVP-covered (5 × 1) Au(100)-hex surface, and that the PVP chains have a binding affinity for Au(111) comparable to (5 × 1) Au(100)-hex. Also, the (5 × 1) Au(100)-hex surface may have a higher flux of Au atoms than the Au(111) surface by examining oxygen density profiles for PVP on Au surfaces. Therefore, the Au(111) surface would be thermodynamically and kinetically favored in PVP-mediated syntheses, leading to {111}-faceted Au nanostructures as seen in experiment. Future studies, aimed at characterizing the evolution of Au structures in the presence of PVP in solution with MD simulations, would be useful in efforts to achieve shape-controlled syntheses of Au nanostructures.

For shape-selective syntheses of Cu nanostructures, the origins of the {100} facet selectivity for HDA on Cu have been resolved with DFT and MD. With DFT, it is found that the HDA-covered Cu(100) surface has a slightly higher surface energy than the HDA-covered Cu(111) surface. However, HDA with the most favored pattern of (5 × 3) on Cu(100) has a significant binding preference over that of (\(\sqrt{3} \times \sqrt{3}\))R30° on Cu(111) since the HDA packing density on Cu(100) is closer to the optimal one for a hexagonal HDA monolayer in vacuum as well as HDA-Cu interaction on Cu(100) is higher. Therefore, the Cu(100) sur-
face would be kinetically favored in HDA-mediated syntheses, leading to \( \{100\} \)-faceted Cu nanostructures as seen in experiment. Further, a MOMB force field describing HDA-Cu interactions was developed by fitting the force and energy in the force field to those in the DFT work, and the force field was applied in MD simulations to resolve the HDA binding patterns on Cu(100) at molecular level. With MD, it is found that DA may be used as an effective capping agent for synthesizing \( \{100\} \)-faceted Cu nanostructures since DA as well as HDA are organized on Cu surfaces and have the same binding preference on Cu(100) over Cu(111). It is also found that the HDA structures on Cu surfaces remain intact in aqueous solution due to hydrophobicity of alkyl tails and long alkyl chains in the HDA molecules, which could prevent Cu oxidation during the synthesis. Future work, aimed at probing the molecular details of the growth process of Cu nanocrystals mediated by various alkylamines with the MOMB force field in large-scale MD simulations, would be useful to develop strategies for shape-controlled syntheses of Cu nanostructures.
Bibliography


Vita

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Shih-Hsien Liu was born and raised in Taipei, Taiwan. He obtained his B.S.E. and M.S. in Chemical Engineering from National Taiwan University in 2008 and 2010, respectively. After serving in the military at Taiwan Air Force for one year, he started pursuing his Ph.D. in Chemical Engineering at the Pennsylvania State University in 2011, and earned Ph.D. in 2017. His research interests include: 1) developing mathematical models predicting heterogeneous interactions (e.g., metal-organic chemical reactions) for molecular-dynamics (MD) simulations based on first-principles/density-functional theory (DFT) calculations; 2) synthesizing and characterizing inorganic nanomaterials for thin-film solar cell applications. More information about him can be found at the following links:

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