Packing effects in mixed Lennard-Jones clusters and potential energy functions for alkylthiolates and C60 on the gold (111) surface

Sean Michael Cleary
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Packing effects in mixed Lennard-Jones clusters and potential energy functions for alkylthiolates and C60 on the gold (111) surface

Abstract
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Keywords
Chemistry, Physical

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PACKING EFFECTS IN MIXED LENNARD-JONES CLUSTERS AND
POTENTIAL ENERGY FUNCTIONS FOR ALKYLTHIOLATES AND C_{60}
ON THE GOLD (111) SURFACE

BY
SEAN MICHAEL CLEARY
B.S., UNH, 2002

THESIS

Submitted to the University of New Hampshire
in Partial Fulfilment of
the Requirements for the Degree of

Master of Science
in
Chemistry

December, 2008
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ABSTRACT

PACKING EFFECTS IN MIXED LENNARD-JONES CLUSTERS AND
POTENTIAL ENERGY FUNCTIONS FOR ALKYLTHIOLATES AND
\text{C}_{60} \text{ON THE GOLD (111) SURFACE}

by

Sean M. Cleary

University of New Hampshire, December 2008

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CHAPTER 1

ON THE STABILITY OF HIGH-SYMMETRY MIXED LENNARD-JONES CLUSTERS AS A FUNCTION OF THE MIXED INTERACTION PARAMETERS

Introduction

The study of van der Waals clusters remains an area of active research in both the experimental and the theoretical domains. These nonbonded aggregates of atoms or molecules are a state of matter between free gases and the condensed phases, comprising from two to thousands of individual units. Clusters exhibit vastly different properties from liquids and solids because they have a much larger surface area to volume ratio than do the condensed phases. This gives them a higher proportion of surface-occupying, low-coordinate constituent units and higher surface energy.

Clusters of rare gases are of much theoretical interest in part because they are fairly easily simulated. While, compared to a molecule, a rare gas cluster may have an abundance of local minimal energy structures (LM), their van der Waals “bonds” do not exhibit the angular dependence of conventional chemical bonds. The interactions for spherical atoms can be cheaply but adequately represented by pairwise-additive potentials such as the Lennard-Jones (LJ) 12-6 potential, enabling extensive simulation in a short time.

The global minimum energy structures (GM) for pure clusters (n = 0) of up to 110 LJ atoms have probably been found. Most of these structures are based on
the Mackay icosahedron,\textsuperscript{4} which itself comprises interlinked tetrahedra. This packing scheme will be referred to as PI, for polyicosahedral. However, the most interesting clusters are those that have other types of global minima than icosahedral, such as LJ\textsubscript{38}, whose GM is a truncated octahedron.

Before moving on to contrast different packing structures, it will be worth introducing the concept of magic numbers. At its most basic level, a magic number N is a cluster stoichiometry that is, empirically, significantly more abundant than the neighboring stoichiometries N-1 and N+1. The term itself was borrowed from nuclear physics, where nuclei with magic numbers of protons or neutrons are especially stable. The nuclear magic numbers are 2, 8, 20, 28, 50, and 82 (and 126 for neutrons) and are explained by the shell model of the nucleus;\textsuperscript{5} a magic numbered nucleus a full shell of nucleons. Electrons in atoms have magic numbers as well; 2, 10, 18, 36, 54, and 86 are electronic magic numbers, and correspond to noble gas electron configurations, with a full valence shell.

In clusters, magic numbers may be observed when a ‘packing shell’ is completed. For icosahedral packing, magic numbers occur for cluster stoichiometries that can give icosahedral structures. 13 atoms can give an icosahedral structure, and this structure can be built up by successive addition of adatoms until the next larger complete icosahedron, with 55 atoms, is formed.\textsuperscript{4} Magic numbers may also occur when packing shells are partly filled. This effect is reminiscent of the relatively stable (n-1)d\textsuperscript{5} electron configuration, where the d subshell is half full, which often occur in the transition metals and their ions. Clusters of 19 and 23 atoms may form structures comprising, respectively, two and three interpenetrating icosahedra. 19 and 23 were observed by
mass spectroscopy (MS) to be magic numbers for xenon.\textsuperscript{6}

Whether a number of atoms in a cluster will, experimentally, be observed to be magic is a more complicated issue. For instance, although small clusters of real rare gas atoms pack icosahedrally, the cluster with $N = 13$ has been observed not to be especially abundant for argon, krypton, or xenon, nor $N = 55$ for the former two.\textsuperscript{6} This may, however, be an experimental effect; MS requires ionization, which may lead to fragmentation (more so for the less polarizable and less strongly bound smaller rare gas clusters) and possibly other changes in cluster structure, which is not to mention the effects of the pressure of the gas or other details.

Since all of the work presented in this thesis is theoretical, we will use a purely theoretical definition of magic number: For a given packing style, a number $N$ is magic if $N$ van der Waals bonded particles can pack to form either the packing style’s high-symmetry unit, or structure comprising interpenetrated high-symmetry units. For icosahedral packing, the high-symmetry unit is the icosahedron, so 13, 19, 23, and 55 are all considered magic numbers by this definition. The cubic packing seen in LJ\textsubscript{38} gives complete cuboctahedra at the same $N$ as PI packing gives icosahedra.\textsuperscript{4} A truncated octahedral structure is possible at $N = 38$. The reason LJ\textsubscript{38} has the GM it does is simply that 38 atoms can pack cubically to give high-symmetry structure with a partially filled octahedral shell, whereas they cannot pack icosahedrally to form a high-symmetry polyicosahedral structure. (This ‘principle of maximum symmetry’ is essentially a surface tension effect; it is driven by minimizing the surface area.)

Another useful concept for describing clusters is that of the potential energy surface (PES). In terms of potential energy surfaces (PESs), clusters like LJ\textsubscript{38} exhibit at
least two funnels, areas of configuration space separated by high energy barriers.\textsuperscript{4,7}

Structures in one funnel are more closely related to each other than to structures from the other funnel. Typically, one funnel will be much wider (i.e., contain more LM) than the others, or conversely, one much narrower. Often, as is the case with LJ\textsubscript{38}, the GM will lie in the narrower funnel, which may lead to difficulties in simulations. Successful location of the LJ\textsubscript{38} GM has thus been used as a criterion for judging the quality of global minimization algorithms.\textsuperscript{7-9}

Yet more complicated, and less well-studied, are mixed rare gas clusters. Whereas permuting two atoms (i.e., exchanging their positions) in a pure LJ cluster will not change the structure, exchanging different types of atom in a mixed cluster may lead to a completely different geometry and energy. This leads to more complex PESs. Sabo, Doll, and Freeman\textsuperscript{10} explored the effect, on the energy of the GM, of varying the number \(n\) and interaction parameters of impurity atoms \(Y\), in clusters with formula \(X_{N-n}Y_n\) (\(N = 7, 10, 13\)). (There were always more \(X\) than \(Y\) atoms; thus \(Y\) was the "impurity." ) The GM energy, however, tells little about the GM structure.

More information can be gained from the the ‘core energy,’ the energy of X-X interaction. The geometry of \(X_{N-n}\), here called the inherent structure, defines the core energy. The inherent structure also determines the total cluster geometry. The total packing scheme can be considered a phase, analogously to one particular crystal structure of a solid with polymorphs, and the type of packing scheme is indicated by the core energy. Introducing impurities to a pure cluster can then cause a phase change of sorts, wherein the GM structure changes to one of a different core energy. Hence Sabo, \textit{et al.} plotted core energy as a function of the interaction parameters of pure \(Y\). They showed
systematically that by judicious choice of impurity atom, the inherent structure of $X_{N-n}$ could be controlled.

In dealing with binary LJ clusters, the mixed interaction parameters are usually determined by the Lorentz-Bertholet mixing rules:\(^2\)

$$\sigma_{XY} = (\sigma_{XX} + \sigma_{YY})/2,$$

and

$$\varepsilon_{XY} = (\varepsilon_{XX}\varepsilon_{YY})^{1/2},$$

where $\sigma_{ij}$ is the van der Waals radius of species $i$ and $j$, and $\varepsilon_{ij}$ is their maximum energy of attraction or (potential energy) well depth. Sabo, et al. used this approach and varied the parameters for pure $Y$. However, there is no compelling reason not to fix the parameters for pure $X$-$X$ and $Y$-$Y$ interactions and to vary the mixed ($X$-$Y$) interaction parameters, the equilibrium distance and well depth for interaction for the two types of atom.

White\(^{11}\) found that the GM of $\text{Ar}_3\text{Xe}_8$ using Pullan’s mixed parameters\(^{12}\) was different from the GM using the usual mixing rules. He found a $D_{4d}$ geometry, comprising two argon-capped staggered $\text{Xe}_4$ rings sandwiching the third argon, of higher core energy than the $C_2$ GM found by the Lorentz-Bertholet rules. The fundamental unit of this packing style is, rather than a $\text{Xe}_4$ tetrahedron, a doubly Ar-capped square $\text{Xe}_4$ ring. This is, essentially, a new type of packing, with its own magic stoichiometries, $\text{Ar}_{m+1}\text{Xe}_{4m}$.

At the outset, it was unclear whether the dominant cause of this symmetry change was the Pullan parameters’ larger mixed-interaction energy, or their smaller Ar-Xe equilibrium distance. The former promotes Ar-Xe interaction at the cost of Xe-Xe
bonding, and the latter allows more intercalation of Ar between Xe₄ rings by lowering the
two rings’ separation from (and interaction with) each other.

This D₄d GM is interesting: The series of pure LJₙ has only two known C₄-
containing GMs (n = 6 and 38) for n ≤150, while it contains many C₃- and C₅-containing
GMs (resp., n = 3, 5, 10, 14... and n = 7, 13, 18, 19...).³ The combination of high
symmetry and stacking suggests the possibility of stable structures comprising longer
ordered columns of rings upon rings, with formula Aₙ₊₁(Xeₘ)ₙ, where A is an argon-like
atom and n is the number of Xeₘ rings. We have investigated the possibility as a
function of the mixed interaction parameters, for m = 3, 4, 5 and n = 1, 2, 3, 4.

**Method**

I. Interaction Potential

The Lennard-Jones 12-6 potential² was used, that is

\[
V = \sum_i \sum_{j>i} \varepsilon_{ij} \left( \frac{r_{ij}}{r_{eq}} \right)^{12} - 2 \left( \frac{r_{ij}}{r_{eq}} \right)^6
\]

(3)

where i and j are atomic indices, \( \varepsilon_{ij} \) is the energy well depth, and \( r_{eq} \) is the equilibrium
distance van der Waals bond length. LJ(12-6) is more often used in its \( \sigma_{ij} \) formulation,
where \( \sigma_{ij} \), the collision diameter, is the distance at which i and j are close enough to begin
to be repelled. Their relation ship is \( \sigma_{ij} = 2^{1/6} r_e \); \( V_{ij}(\sigma_{ij}) = 0 \). Since we are investigating
equilibrium geometries, not collisions, \( r_{eq} \) is a more convenient choice of unit. The
values² of \( r_e \) and \( \varepsilon \) for pure interactions are shown in Table 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( r_e ) (Å)</th>
<th>( \varepsilon_{xx}/k_B ) (K)</th>
</tr>
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<tr>
<td>Argon</td>
<td>3.822</td>
<td>119.8</td>
</tr>
<tr>
<td>Xenon</td>
<td>4.602</td>
<td>222.3</td>
</tr>
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</table>
The Lorentz-Bertholet mixing rules work the same way for $r_{mix}^e$ as for $\sigma_{mix}$. However, we hold the Ar and Xe parameters fixed and vary the mixed interaction parameters, referred to simply as $r^e$ and $\varepsilon$, between those for pure Ar and pure Xe. The latter parameter pairs will be designated with subscripts. Lengths and energies are reported, respectively, in reduced units of $r_{XeXe}^e$ and $\varepsilon_{XeXe}$ (≈0.44 kcal mol$^{-1}$).

II. Global Minimum Searches:

Each $A_{n+1}(Xe_m)_n$ structure was initialized with an unoptimized $C_m$ structure such that all neighboring xenon atoms were at $r_{XeXe}^e$ from each other. Each Xe has two neighbors in its own ring and two in any adjacent parallel rings. The structure was then relaxed to its LM, giving the minimum-energy $C_m$ configuration and $V_{Cm}$. This and all other LM in this section were found using the Polak-Ribiere modified conjugate gradient algorithm.$^{14}$

The cluster was reinitialized with the coordinates of LJ$_N$ with the $n + 1$ A atoms occupying random positions in the pure LJ lattice. This pseudo-LJ$_N$ cluster was relaxed to its LM, and this energy taken as a first guess at the low-symmetry$^{14}$ minimum energy, $V_{LS}$. The lowest-energy LS structure was sought by the basin-hopping technique of Wales and Doye,$^7$,$^{15}$ with one modification as noted below. Briefly, a single atom in a cluster of energy $V_{prev}$ was randomly chosen and displaced by a small amount (up to 1 $r_{XeXe}^e$) in a random direction, and then the entire cluster was relaxed to the new LM. This new energy $V_{new}$ was compared to $V_{prev}$ by the Metropolis Monte Carlo acceptance routine:

$$\Delta V = V_{new} - V_{prev},$$

and the move was accepted if $\Delta V \leq 0$, or if
where \( T \) is the temperature (10K for all trials; see below) and \( \xi \) is a random number between zero and one, exclusive. Note that the move was accepted if \( \Delta V = 0 \); that is, \( V_{\text{new}} = V_{\text{prev}} \). If the move failed the acceptance criteria, it was rejected, and the old geometry was retained. Each \( V_{\text{new}} \) found by BH was compared first with \( V_{C_n} \) to ensure their difference, and then with the lowest found \( V_{LS} \). Each \( V_{\text{new}} < V_{LS} \) was saved. In contrast to the original BH routine, every 100th Monte Carlo step was replaced with an A-Xe exchange, followed again by a local minimization and Metropolis acceptance/rejection. The maximum displacement length and temperature were chosen somewhat arbitrarily; these values were able to locate the LJ38 GM and so were used here without further testing.

In all, \( \sim 10^3 N^2 \) steps or permutations were made. The lower of \( V_{C_m} \) and \( V_{LS} \) was taken to be the global minimum energy. Redefining

\[
\Delta V = V_{C_m} - V_{LS}
\]

(6)
gave a convenient measure of the symmetry of the GM; the cluster had a \( C_m \) GM if \( \Delta V < 0 \), and not otherwise.

**Results**

The results are organized according to the columnar structure’s highest symmetry axis \( C_m \), subdivided by the number of rings, \( n \).

1. \( C_3 \): \( A_{n+1}Xe_{3n} \)

\( \Delta V \) for \( n = 1 \) is shown in Figure 1. The x and y axes give respectively \( r^e \) and \( \varepsilon \) in units of the corresponding parameters for Xe-Xe. The core energies (not shown) are all the same as Xe\(_3\) (-3.0). LJ\(_3\) and LJ\(_5\), corresponding to Xe\(_{N-n}\) and Xe\(_N\), are also shown.
here. The analogous pure LJ structures will be useful for comparison in more complex cases. The values of the mixed parameters used by Pullan and given by the Lorentz-Berthollet rules are indicated (respectively) by a square and a circle.

No $C_3$ GMs are observed for $n = 2$, although the core energies and structures are all changed (Figure 2) from octahedral $Xe_6$. These structures are yet less favorable in structures containing three or more rings (not shown). This will be further discussed below.

Figure 1. $\Delta V$ as a function of $r^*$ and $\varepsilon$ for $A_2Xe_5$. Both parameters range from the values for argon up to those of xenon. All GMs but the lower right corner are $C_3$. The structures to the right are pure LJ$_3$ and LJ$_5$. 
II. C₄: Aₙ₋₁Xe₄ₙ

Three families of GMs are observed in the n = 1 case. With high ε and low rₑ, D₄h structures dominate; at larger rₑ and lower ε, the GMs are Cᵥ. Such a division is shown in Figure 3, but the core energies of the GMs reveal more (Figure 4). Structurally, the D₄h structures consist of a Xe₄ square capped above and below the plane, and the Cᵥ comprise tetrahedral Xe₄ with two faces capped by A. There is a GM of a third core energy at large rₑ and intermediate ε belonging to a partly bent-open distorted tetrahedron with an A-A distance of rₑ Ar-Ar. Here we see a change in GM core energy from that of Xe₄. In all cases, the GM is either a variation on Xe₆, or has an Xe₄-like core.
Figure 3: ΔV for A₂Xe₄. The C₄ geometries are GMs in the upper left half of the parameter space. Representative structures are shown in Fig. 4.

Figure 4. Core energies for A₂Xe₄. The dark blue region has a C₄ GM; the lighter two are C₂v. The GM's core structure in the region with V(Xe) = -6 is a tetrahedron; the one -5.25 is a bent rhombus.

With n = 2, Figure 5 shows a broad range of parameter space with C₄ minima. Figure 6 shows that the core energy has also been greatly perturbed (V(Xe₈) ~ -19.82) everywhere but at the largest r² and smallest ε. The same obtains for n = 3 (Figs. 7, 8)
and, to a lesser extent, \( n = 4 \) (not shown), where \( C_4 \) GMs are no longer found in the parameter space surveyed. In these two higher-\( n \) cases, we again see variations on \( \text{Xe}_N \) and \( \text{Xe}_{N,n} \)-like cores, but the \( C_4 \)-containing GMs are completely unlike those of pure Xe.

Figure 5. \( \Delta V \) of \( \text{A}_x\text{Xe}_y \). The large blue region at small \( r^* \) has \( C_4 \) GMs.

Figure 6. Core energy and sample GM structures of \( \text{A}_x\text{Xe}_y \). Several isomers are present. Only the blue region in the lower right has not had its core energy changed \((V(\text{Xe}_y) = -19.8)\).
III. $C_5$: $A_{12+1}Xe_{5n}$

Since a $C_5$ axis is common in pure LJ GMs, this would be the least surprising symmetry axis to find in mixed structures. However, no $C_5$ GMs were observed when $n$
1. The inherent structures found in this parameter space (Figure 9) differ qualitatively from those of Sabo et al., due to our different choice of parameters varied. (They found $C_5$ GMs when $\varepsilon_{YY} > \varepsilon_{XX}$ and $r^e_{YY} \sim r^e_{XX}$.

Figure 9. $\Delta V$ for $A_2Xe_3$. There are no $C_3$ GMs in the phase space surveyed.

Figure 10. Core energies and geometries of $A_2Xe_3$. The energy of L$J_3$ is $\sim 9.1$. 
By contrast, $n = 2$ and 3 show some high-symmetry GMs (Figures 10-14). Remarkably, some of the low-$r^6$ GMs contain the $C_4$ structures observed above for the same $n$. 

![Diagram](image1)

**Fig. 11** $\Delta V$ for $A_3Xe_{18}$. The blue region has $C_2$ GMs.

![Diagram](image2)

**Figure 12.** Core energies and sample geometries for $A_3Xe_{18}$. $V(LJ) = -28.4$. Note the underlying 4-ring motif in three leftmost structures.
Discussion

All of the observed changes in inherent core structure result from changing intracluster forces with the mixed parameters. It was mentioned that $A_2Xe_3$ shows no change in core energy from pure $Xe_3$. The change in GM structure is at first confusing: The $C_3$-containing GM has 6 mixed equilibrium-length bonds and the $C_s$ structure only 5
equilibrium mixed bonds and one A-A bond. The preference for an A-A bond in the second GM can be understood as a function of \( r^e \). When \( r^e \) is large, the two A atoms will be too far apart in the C\(_3\) structure to interact very much, since \( r^e_{AA} \) is fixed. However, the C\(_5\) structure gives a full A-A interaction and still allows the equatorial A to interact somewhat with the xenon across the ring, again because \( r^e \) is large.

The \( \text{A}_2\text{Xe}_4 \) is more interesting because a change in core energy occurs. The phase change between tetrahedron-like and square planar Xe\(_4\) is due to the interplay between nearly balanced forces striving to maximize either Xe-Xe or A-Xe interactions. If we move "up" in \( \varepsilon \) (Fig. 4), the GMs show progressively less Xe-Xe energy and more A-Xe energy, as indicated by the two core energies different from that of pure Xe\(_4\). While two isomers were observed for \( \text{A}_2\text{Xe}_3 \) (Figure 1), they both had the same core Xe-Xe energy as pure Xe\(_3\) (= -3). Here, we see the pure Xe\(_4\) core energy in the C\(_{2v}\) structures, but that of the D\(_{4h}\) isomers is completely distinct. In fact, square planar Xe\(_4\) is not even a minimum for the pure cluster; it is a second-order saddle.

It is at first surprising that, for \( n = 1 \), there are high symmetry GMs for \( m = 3 \) and 4, but not 5. Like the square in the C\(_4\) case, the pentagon is a saddlepoint. The core energy is very high, so the mixed interaction energy would need to be very large to compensate. The GMs in the observed parameter space fall into two categories, both variations on a doubly capped pentagon of 3 Xe and 2 A. At low \( \varepsilon \), the two A atoms are nearest neighbors in the GM; at higher \( \varepsilon \), they are farther apart. In the former case, Xe-Xe energy is maximized, and in the latter, weak A-A interactions are reduced in favor of stronger A-Xe interactions. No matter how much \( \varepsilon \) is increased, \( \varepsilon_{AA} \) remains small.
We have found that C\textsubscript{4} and C\textsubscript{5} columns can be the global minimum energy structures of mixed Lennard-Jones clusters of xenon and an argon-like impurity. Why C\textsubscript{3} columns do not form (in the examined parameter space) may not be immediately obvious. Consider the interaction between two three-membered rings of xenon. If they are allowed to approach each other in an antiparallel configuration, they will approach their minimum-energy separation, where each Xe on each ring is 1.0 reduced length from two members of the other ring. The equilibrium distance between the two rings is \(\sqrt{2}\approx 0.817\). By trigonometry, we can calculate that an atom centered between the two rings in their equilibrium positions (with respect to each other, not the central atom) will be \(\sqrt{2}\) from each atom in the two rings. This distance also applies to larger columns, which are only successions of antiparallel rings. Thus, to maximize A-Xe interactions and maintain optimal ring-ring interactions, a C\textsubscript{3} columnar heteroatom must not have \(r^e\) larger than 0.7071..., which is smaller than \(r^e_{Ar-Ar}\), the smallest \(r^e\) tested. In fact, this optimal \(r^e\) is smaller than the collision diameter \(\sigma_{ArAr}\approx 0.73\). An A atom of the dimensions we examined would “feel” nothing but repulsion between two three-membered rings.

By the same method as used above, it can be shown that the ideal \(r^e\) for C\textsubscript{4} and C\textsubscript{5} structures are 0.823 and 0.951, respectively. The best \(r^e\) for the C\textsubscript{5} axis is very close to 1-hence its frequency in pure LJ clusters and its occurrence at fairly large \(r^e\) here. The optimum \(r^e\) for C\textsubscript{4}, on the other hand, is very close to \(r^e_{Ar-Ar}\). To extend this analysis, a C\textsubscript{6} columnar GM would ideally have \(r^e\approx 1.316\). How large \(\varepsilon\) would need to be to make the C\textsubscript{6} structure the GM is unknown, but such structures may be possible.
Conclusions

We have shown that mixed clusters may have highly symmetric columnar global minimum energy structures. The question arises, however, of the possibility of other, non-columnar high-symmetry GM geometries for mixed LJ clusters, and this question is explored in the following chapter.

The GM structure of a cluster is by definition the most stable structure at zero temperature. At temperatures greater than 0 K, however, one must consider the entire free energies of the clusters, not only their potential energies. The most thermodynamically stable cluster geometry will change with temperature due to different geometries' differing entropies. Study of the most stable geometry for a given cluster requires some type of thermodynamic integration, or integration of the configuration integral. For multi-basin systems, this is reliably performed by parallel tempering.\textsuperscript{16} Parallel tempering is, unfortunately, highly computationally intensive, and its application to mixed LJ clusters was not investigated in this thesis.

A parallel-tempered study of Ar\textsubscript{2}Xe\textsubscript{4} was, however, carried out by White et al.\textsuperscript{17} It was shown that a solid-solid phase transition occurs between the D\textsubscript{4h} GM structure and the second and third lowest-energy structures, which have C\textsubscript{2v} symmetry and a tetrahedral inherent structure. This raises the intriguing possibility of solid-solid phase transitions in other mixed clusters, such as Ar\textsubscript{3}Xe\textsubscript{4}, with its very low-lying\textsuperscript{11} D\textsubscript{4d} GM and the next-lowest energy, low symmetry PI-packed structures. This would be a very interesting system for future work.
CHAPTER 2

NON-COLUMNAR HIGH-SYMMETRY MIXED LJ CLUSTERS

Introduction

Encouraged by our results for columnar GM structures, we systematically sought the GM geometries for all clusters with the general formula Ar$_n$Xe$_m$ for $n + m \leq 19$, $n < m$, in search of other high-symmetry or non-tetrahedral packing-based minimum-energy structures. Portions of these results have been published previously.\(^{18}\)

Method

The same interaction potential was used for the general mixed clusters, except that the GM was initially sought using only the Pullan mixed interaction parameters for Ar-Xe. For a few select interesting stoichiometries, full searches of the parameter space were made as for the columnar clusters.

The GM structures of the general clusters were found by a slightly different method than the columnar clusters. Basin hopping was used as before, but the conjugate gradient minimizer was replaced with Nocedal's implementation of the limited-memory Broyden-Fletcher-Goldfarb-Shanno algorithm (L-BFGS).\(^{19}\) In trial runs, L-BFGS was found to perform consistently faster than the CG minimizer.

The configuration space was also searched differently for these clusters. Since we had no a priori knowledge of potentially interesting structures, only random search methods were used. The clusters were randomly initialized, their energies locally
minimized, and then, rather than moving one particle in a random direction and then minimizing the energy, as above, extensive use of permutation was made. Single-particle displacement moves were made only when the same LM was found five times in a row. The clusters were also periodically reinitialized in a random configuration. In all, a total of \( n^*m^*(m+n)^3 \) moves were made for each cluster. This quantity was chosen arbitrarily to be larger for more-mixed stoichiometries, which have more permutational isomers. This formula for the number of moves was tested on \( \text{Ar}_3\text{Xe}_8 \). It located the (presumably difficult-to-find) GM several times, and was thus deemed suitable for finding high-symmetry minima.

**Results**

In this section, a new notation will be adopted. A given cluster stoichiometry \( \text{Ar}_m\text{Xe}_n \) will be denoted simply by \((m,n)\).

We have classified the interesting GM obtained by the type of packing shown by the xenon core structure. Five distinct classes were observed. Minima based on an (poly)icosahedral xenon core were predominant, as expected, and are not discussed further here. At the opposite extreme lie structures based on a square pyramidal structure comprising a \( \text{Xe}_4 \) ring capped by an argon atom. Previously discussed examples of these GM are the \( D_4 \) structures of \( \text{Ar}_2\text{Xe}_4 \) and \( \text{Ar}_3\text{Xe}_8 \), which in the new notation become \((2,4)\) and \((3,8)\). We shall call this class square-based minima. There was also a number of GM structures found that were closely related to different square-based structures, with lower symmetry. This group of GM will be called the square-derived class.

Some GM showed a combination of square-based and icosahedral packing. Two distinct classes of such hybrid packing schemes were observed. The first involves a
square \( \text{Xe}_4 \) ring stacked on a pentagonal bipyramid, and will be called simply the hybrid class. Finally, the decahedral class shows either decahedral or broken decahedral symmetry. These classes will be discussed individually.

I. Square-Based GM

The four square-based GM all have \( \text{D}_4 \) or higher symmetry. They have stoichiometries (2,4), (3,8), (4,12), and (7,8), and are shown in Figure 1. The only new square-based structure is the fourth, octahedral cluster (7,8). It can be envisaged as formed by the ‘capping’ of four faces of the (3,8) GM with an argon atom, and letting the two \( \text{Xe}_4 \) rings rotate to become parallel. This rotation allows each new capping argon to interact strongly with one additional xenon atom, and creates the observed octahedral symmetry.

II. Square-Derived GM

Four GM were found to be variations on the theme of a square-based GM: (2,8), (2,9), (1,10), and (6,12) (Figure 2). The symmetry of the first three is \( \text{C}_{4v} \), and the fourth is \( \text{C}_{2v} \). (2,8) is (3,8) minus one of its capping Ar, and (2,9) and (1,10) have one and two of the capping Ar replaced by Xe. It should be reiterated that the (1,10) GM has lower symmetry than that of (3,8). Examination of the figure shows that the bottom capping Xe is farther from the central Ar than is the top Xe, because of strain produced by a capping Xe pushing away the Xe in the square ring as it approaches the core Ar.

(6,12) is simply (4,12) with two Ar added. Each new Ar is coordinated to two central-ring Xe and to one Xe on the upper and one on the lower ring.
Figure 1. Side- and high symmetry axial views of the square-based GM. Stoichiometries and symmetries are: (2,4) $D_{4h}$, (3,8) $D_{4d}$, (4,12) $D_{4h}$, and (7,8) $O_h$. Of particular interest is the last, new, structure, which is derived by adding an Ar to four faces of Ar$_3$Xe$_8$. 
Figure 2. The four square-derived GM

Figure 3: Hybrid GM with $m+n=12$: (1,11), (2,10), (3,9), & (4,8)
III. Hybrid GM

For \( m+n=12 \), four stoichiometries had hybrid GM (Figure 3): (1,11), (2,10), (3,9), and (4,8). In each of these structures, a capped \( \text{Xe}_4 \) ring sits on the Ar cap of a pentagonal bipyramid. The second Ar replaces the Xe capping the 4-ring in (1,11), and subsequent argon atoms replace successive 5-ring xenon atoms.

IV. Decahedral GM

The GM for (5,13) and (7,11) show a completely different type of hybrid packing (Figure 4). The inherent structure for both of them is that of a truncated decahedron, with \( D_{5h} \) symmetry. (5,13) has the corners of the decahedral core filled out with argon adatoms. Its relationship to the structure for the pure Lennard-Jones 13-mer\(^3\) is exactly analogous to (7,8)'s relationship to (3,8). Adding Ar atoms to alternate coannular faces causes the initially staggered rings to rotate into a perpendicular position.

In (7,11), the top and bottom Xe atoms of (5,13) are replaced by Ar atoms. The GM structure has \( C_{2v} \) symmetry; it is as if, in the decahedral structure, two adjacent capping Ar pried the two Xe between them apart. The \( D_{5h} \) structure (also shown in Fig. 4) is a local minimum about 0.25 \( \varepsilon_{\text{XeXe}} \) (0.4% of the total binding energy) higher in energy than the GM.
Figure 4. Decahedral and related structures: a. GM of (5,13); b. GM of (7,11); c. Decahedral LM of (7,11)
Discussion

It will be useful to interpret these results in terms of the magic numbers for different packing styles. It will be recalled that most Lennard-Jones clusters, both pure and mixed, show polyicosahedral (PI) packing. This packing scheme has magic numbers that give an icosahedral GM (N = 13, 55, 147...)\(^7\) Other PI magic numbers occur for incomplete icosahedra where one or more new capped pentagons has been added to an existing icosahedral-based structure (N = 19, 23, 26...).\(^3\) Figure 5 shows the GM for Lennard-Jones clusters of 13, 19, 23, and 26, where the lighter-colored atoms in each structure are those added onto the previous magic cluster’s structure.

The previous chapter’s work can be interpreted in terms of magic numbers. That is, we examined the mixed-interaction parameter space for cluster stoichiometries that could be magic for non-icosahedral packing schemes, namely, \(A_{m+1}(Xe_n)_m\). Those stoichiometries are, at least potentially, magic for columnar packing of n-membered Xe rings.

Some of the most interesting new mixed cluster GM found during the present work occur for stoichiometries not magic to either PI or square-based columnar packing schemes. These clusters have no particular preference for one packing structure or another. This is most noticeable when the stoichiometry is nearly magic. The low-symmetry family of hybrid GM falls exactly in such a “no-man’s land.” Their stoichiometries are such that \(N = m + n\) is just under 13, an icosahedral magic number. The geometry of pure LJ\(_{12}\) is just that of LJ\(_{13}\) minus a capping atom, but when the cluster is mixed, the energetics favor a square-on-pentagon structure (at least with the Pullan
mixed interaction parameters). The GM of mixed clusters with $N = 13$ (not shown) are all icosahedrally based.

Figure 5. First four magic numbered pure Lennard-Jones clusters with $N = 13, 19, 23,$ and $26$, with ‘new’ adatoms in grey.
N = 11, a magic number for square-based packing, shows a similar effect. The clusters (2,9) and (1,10) are similar to (3,8) (Fig 2. c and b; Fig. 1 b). It is interesting that (2,8), a nearly-magic stoichiometry, has a GM like (3,8) with one capping Ar removed. Evidently, this C₄ structure is more stable than the icosahedral-based structure for a ten-particle cluster at this stoichiometry. In fact, the (3,8) GM structure is particularly robust, as we shall see.

The most surprising GM located were those of (7,8) and (5,13) (Figs. 1, 4c). Neither of these has a magic stoichiometry for columnar or polyicosahedral structures, but they both contain potentially magic substructures for different packing schemes, respectively the square-based (3,8) and icosahedral (0,13). It was thus surprising when their GM were found to be octahedral and decahedral, respectively. In each case, the Ar adatoms to the magic cluster cause the two Xe rings to rotate torsionally from a staggered configuration into an eclipsed conformer, containing square Xe rings. This eclipsed conformation is, for both the (3,8) and (0,13) clusters, a saddlepoint. The presence of Ar adatoms, though, stabilizes the square-ring-containing configurations. This is, in fact, the same effect as observed in the D₄ᵥ GM of (2,4) compared with (0,4): an otherwise unstable square Xe core structure is stabilized by Ar-capping.

In the case of (5,13), an additional benefit is effected by the rings’ rotation. It was mentioned earlier that the ideal rₑ for an atom in the center of two 5-member rings is 0.951, which comes from the geometry of a regular icosahedron. This means that icosahedral LJ-13, although a magic number, feels strain because its central atom is too large to fit perfectly into the space available. (In the LJ-13 GM, the total energy is minimized when all of the surface atoms have moved slightly farther from the center, and
from each other, until the ‘tension’ of their mutual bonds being stretched cancels the
‘compression’ of the central atom; the equilibrium distances are 0.964 from center-to-
surface and 1.013 between neighboring surface atoms.\textsuperscript{3} Twisting an icosahedron to a
truncated decahedron reduces the structure’s symmetry. The surface atoms are no longer
all equivalent but have been divided into subsets of two axial atoms and ten equatorial
atoms (Figure 6). The central atom lies, respectively, 1.001 and 0.987 from these two
sets of surface atoms. The compression strain on the central atom is thus greatly relieved,
albeit at the cost of interaction between the two rotated rings. This lost ring-ring
interaction energy is more than recovered, in (5,13), by mixed interactions between
capping Ar atoms and the square rings. Part of the reason a decahedral (6,12) GM was
not observed (where Ar replaces the central Xe of (5,13)) is that the decahedral structure
is better suited to a larger than a smaller central atom.

![Icosahedron and truncated decahedron](image)

\textbf{Figure 6.} Icosahedron and truncated decahedron (to scale). In the former,
neighboring surface sites are 1.0 units from each other and 0.951 from the
center; in the latter, nearest-neighbor surface sites are also 1.0 from each
other while the center is 1.00 from the axial sites and 0.99 from equatorial
sites.
A related, but opposed, effect is seen in the \( \text{C}_{2v} \) GM for (7,11) (Fig. 4b). Here, the decahedral symmetry is broken by two capping Ar coming together and splitting a square face of the decahedral core structure. The reason they can do this is that the two pentagonal rings, in this structure, are capped by small Ar atoms, and can deform more easily than Xe-capped 5-rings. As mentioned above, the \( \text{D}_{5h} \) structure for this cluster is a LM, but deformation to the lower-symmetry structure is energetically favored.

The occurrence of icosahedral, decahedral, and close-packed (e.g., octahedral) GM structures for mixed Lennard-Jones cluster is interesting because they represent all of the major packing styles for homogeneously interacting clusters. Both pure Lennard-Jones and real metal atom clusters are believed to pass through size regions where different packing schemes are more stable. This is due to the competition between the tendencies to maximize nearest-neighbor contacts while minimizing strain. At small cluster sizes, icosahedral packing offers the most highly coordinated internal and external atoms, but regular tetrahedra cannot pack to fill all space. This introduces strain, as described above for LJ-13. For some size regimes, decahedral structures are less-strained, and at the bulk scale, strain-free close-packing structures are the most favored. For pure Lennard-Jones clusters, the transition from predominantly icosahedral to decahedral occurs around 1600 atoms, and that from decahedral to close-packing is estimated to occur around \( 10^5 \).21

The cluster-size at which these phase transitions occur is dependent on the particular system. What we have essentially done in the previous chapter is to manipulate the details of the system so as to change the preferred packing structure for a given stoichiometry. We now return to this technique of exploring the parameter space,
and repeat the methodology of the previous chapter on (7,8) to examine the durability of the octahedral/close packed structure with respect to the mixed interaction parameters. The results of this search are shown in Figure 7, over a backdrop qualitatively indicating the core energy of each GM. As in the previous chapter, the mixed Lorentz-Berthollet and Pullan parameters are indicated by a circle and a square, respectively.

The octahedral structure is the GM at low \( r^e \) and fairly large \( e \), as one would expect. The cubic core structure allows a larger \( r^e \) for the central atom than does that of (3,8) (optimal \( r^e = 0.823 \)), but still has a fairly low optimal mixed \( r^e = (\sqrt{3})/2 \approx 0.866 \). As \( r^e \) crosses 0.9 (only 0.01 larger than the Pullan value initially used), the GM changes to a PI structure. The PI GM structures vary with \( e \): larger \( e \) gives more highly mixed, lower core-energy clusters. What is more interesting from the standpoint of non-PI packing schemes is what happens when \( r^e \) is kept small but \( e \) is lowered. When the mixed interaction distance and energy for this cluster stoichiometry are both low, the GM is a multiply face-capped derivative of the (3,8) GM. This \( D_{4h} \) structure thus appears to be a genuine magic number cluster and, in the right region of the mixed interaction parameter space, to be built upon like any other magic numbered scaffold.

The (7,8) cluster was not very close to any magic number stoichiometries for PI packing. But for the (5,13) cluster, the stoichiometry is just short of the nineteen required for a polyicosahedron, yet our mixed interaction parameters gave a different packing style in the GM. So we also carried out an \((r^e, e)\) exploration on this cluster’s GM (Figure 8). Large \( r^e \) leads to PI GM, with the degree of exclusion of Ar atoms decreasing with \( e \), and the decahedral structure is the GM in only a narrow region of the parameter space. At low \( r^e \) and fairly large \( e \), the GM looks like the GM of (6,12) with Pullan’s
parameters, only with one of the Ar adatoms replaced by Xe. This was the only structure
found with a $D_4$ core structure with a Xe adatom.

Figure 7. GM of (7,8) as a function of mixed $r^e$ and $\varepsilon$. 
This work up to now explored stoichiometries only up to $m+n = 19$, but we also investigated the 20-atom $(8,12)$ cluster. This stoichiometry can form a $D_{4h}$ structure like that of $(6,12)$'s GM but with capping $Ar$ added to the other two sides of the column. Preliminary calculations quickly showed that the $D_{4h}$ structure is not the GM when using the Pullan parameters, so the parameter space was not explored more fully. Finding where in the parameters space the possible $D_{4h}$ structure is the GM may be a possible future extension of this work.
Conclusions

We have found that mixed Lennard-Jones clusters may have non-icosahedral GM at stoichiometries that are not magic for icosahedral packing. We found both Ar-capped square-based and hybrid square/icosahedral packing schemes, and showed that magic-number stoichiometries for square-based GM, \((m+1,4m)\), may act as seeds or scaffolds for further cluster growth, as do magic-numbered polyicosahedral GM in pure LJ clusters. Further, for an n-fold symmetric magic number GM, we have shown that adding n additional small adatoms may ‘untwist’ the GM to produce capped square faces. Consistently with our own and others’ earlier work,\(^{10,22}\) we found that the mixed intereaction distance parameter \(r^e\) is more important than the mixed interaction energy in determining the preferred packing scheme.
CHAPTER 3

CONSTRUCTION OF A POTENTIAL ENERGY FUNCTION FOR THE
THIOLATE SULFUR ATOM-Au (111) SURFACE INTERACTION

Introduction

We now move away from rare gas clusters and begin to consider a completely
different system: That of thiolated fullerenes on a gold (111) surface. We would like to
be able to model the dynamics of self-assembly of these functionalized fullerenes. This
process will depend critically upon the interaction of thiolate sulfur atoms and C\textsubscript{60} with
the gold surface. Simulation of self-assembly will require many potential evaluations, so
we would like a potential form for those interactions that is as simple and quick to
evaluate as possible. In this chapter, we parametrize a simple potential energy function
for the thiolate sulfur-Au (111) interaction, and in the next, we do so for C\textsubscript{60}'s interaction
with the same surface.

Background

The crystal structure of bulk gold is face-centered cubic (fcc), with a lattice
constant $a$ of 2.881 Å (Figure 1). The (111) plane cuts through the unit cell such that the
faces in the xy, yz, and xz planes are all split into isosceles triangles. The surface thus
generated (Figure 2) has threefold symmetry. The unit cell of the surface is the rhombus
with two sides given by the displacement vectors from one gold atom to two of its nearest
neighbors.

Alkanethiolates are known to form self-assembled monolayers (SAMs) on this
While the bare Au (111) surface undergoes a 22 x \( \sqrt{3} \) reconstruction, chemisorbed alkane thiolates undo this reconstruction and restore the threefold symmetry, at least at large surface coverages. At these large coverages, the individual alkanethiolates are anchored very nearly five Å from each other, exactly \( \sqrt{3} \) times the Au-Au separation. This distance is the length of the unit cell’s long diagonal (Figure 2), from one site to a nearby site of the same type. Thus, the thiolate sulfur atoms are all bound to the surface at equivalent sites. Exactly which site they are bound to, though, has been controversial.

Figure 1. The unit cell of bulk gold, with shading for depth. The nearest-neighbor distance is 2.881Å. The (111) plane is the plane that contains atoms A, B, and C.
The Au(111) surface has four distinct binding sites: atop sites, where the adatom sits directly above a gold atom in the top layer; bridge sites, where the adatom is above and midway between two neighboring gold atoms; and two 'threelfold' sites, fcc and hcp, where the adatom is centered between three surface gold atoms. The threelfold sites differ by the presence or absence of an Au atom in the second-highest layer of the solid; the hcp site is directly above a second-layer atom and the fcc site is above a third-layer atom but a second-layer vacancy.

Most theoretical work on the thiolate S–Au (111) interaction has used methylthiolate as representative of alkylthiolates generally. Based on density functional theory (DFT) calculations on this system, different researchers have predicted different binding sites and geometries. The plurality of these studies predict a threelfold binding
site for the sulfur atom, but others predicted a bridge binding site or a site between a bridge and fcc site. These studies all agreed, however, that the binding energy is roughly 40 kcal mol\(^{-1}\). Some experimental work strongly indicated an atop binding site, in contrast to the DFT studies. This contradiction was resolved after the present work was completed: the thiolate sulfur atom actually bonds to an adatom of gold which then sits over a threefold site on the (unreconstructed) (111) surface.

Assuming a threefold binding site, Mahaffy, Bhatia, and Garrison found Morse potential parameters for the thiolate S-Au interaction by fitting to earlier theoretical data. The total potential energy for one thiolate sulfur atom is obtained by summing its interaction energies with many surface atoms. They used their Morse potential to determine the diffusion coefficient for thiolates on Au (111) by molecular dynamics.

Self assembly of thiolated fullerenes on a surface involves the diffusion of thiolate sulfur atoms, so we are interested in their potential energy function. The problem with a Morse potential between an adsorbate and a surface is that it is pairwise-additive: the interactions of the adatom with many surface atoms must be calculated. This becomes very time-consuming for large systems. We would like to replace the Morse form of the potential with a non-pairwise additive functional form to reduce computational time. The typical way of representing an atom’s interaction with a surface is by a Lennard-Jones-and-Devonshire potential,

\[
V(x, y, z) = V_0(z) + V_c(x, y, z),
\]

where \(V_0(z)\) is an \((x, y)\)-averaged potential energy between the atom and the surface, and \(V_c(x, y, z)\) is a corrugation potential, representing the effects of the actual surface’s

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periodic variation. $V_0(z)$ is taken to be the larger part of the energy, with $V_c(x,y,z)$ comparatively small. Also, $V_c(x,y,z)$ should decay more rapidly with $z$, so that at large distances, the potential energy does not depend on $x$ or $y$.

We will fit a function of this general form to the values of Mahaffy and coworkers' Morse potential at specific $(x,y,z)$ points over the Au (111) lattice. The functional forms of both $V_0(z)$ and $V_c(x,y,z)$ will contain adjustable parameters, and by 'fitting' the potential function, we mean adjusting the parameters to reproduce the properties of the function fitted to—i.e., the Morse potential—at a few select points. The quality of the fit potential is judged by how well it reproduces the original potential at other points than the ones where it was fit.

**Method and Results**

The thiolate-gold Morse potential, which we will call simply $v_M$, is

$$v_M(r) = D_e \left( \exp(-2\alpha \Delta r) - 2 \exp(-\alpha \Delta r) \right),$$

with

$$\Delta r = r - r_e,$$

where $D_e$, $\alpha$, and $r_e$ are the potential parameters in Table 1, and $r$ is the distance between the thiolate sulfur atom and a given gold surface atom:

$$r = \sqrt{(x_S - x_{Au})^2 + (y_S - y_{Au})^2 + (z_S - z_{Au})^2}.$$ 

| Table 1: Parameters for the Morse Thiolate-Au Potential $v_M$ |
|----------------------|----------------------|
| $D_e$                | 8.763 kcal mol$^{-1}$|
| $\alpha$            | 1.47 Å$^{-1}$        |
| $r_e$               | 2.65 Å              |
The total potential energy for one thiolate sulfur atom over the surface is the sum of its Morse interactions with all of the gold atoms within a certain range, \( r_{\text{cutoff}} \). The total \( V_M(x,y,z) \) due to the interaction with the surface is then

\[
V_M(x,y,z) = \sum_{i, r_i \leq r_{\text{cutoff}}} V_M(r_i).
\]

(5)

In their work, Mahaffy et al. used a cutoff distance for \( v_M \) of 2.5\( r_e \). The cutoff distance is \( \sim 2.3 \) times the gold-gold separation in the Au lattice, so in all of this work, we used a lattice 7 x 7 atoms wide, and three deep. It should be noted that \( v_M \) at the cutoff distance is about 0.05 kcal mol\(^{-1}\), so this value limits the precision of the total \( V_M \).

Table 2: Stationary Points on the Au (111) Surface for \( V_M \)

<table>
<thead>
<tr>
<th>Site</th>
<th>Height (( \text{Å} ))</th>
<th>Energy (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atop</td>
<td>2.36</td>
<td>-30.39</td>
</tr>
<tr>
<td>Bridge</td>
<td>1.99</td>
<td>-40.53</td>
</tr>
<tr>
<td>hcp</td>
<td>1.90</td>
<td>-43.18</td>
</tr>
<tr>
<td>fcc</td>
<td>1.90</td>
<td>-43.18</td>
</tr>
</tbody>
</table>

Table 2 gives the energy-minimizing heights, \( z_{\text{SM}} \), over each of the main sites on the Au (111) lattice, along with each site's minimal energy, \( V_{\text{SM}} \). These quantities are respectively the heights above each site that give the lowest energy, and that energy itself, and the subscripts indicate site-minimized. We will fit our new functional forms at the \((x,y,z)\) coordinates and \( V_{\text{SM}} \) of the atop, bridge, and hcp sites. Since \( V_{\text{SM}} \) for the fcc site is practically degenerate with the hcp site, we will consider the sites identical, and refer to them collectively as the threefold sites. This approximation will give the potential energy function even parity.

Potential energy curves for a thiolate sulfur atom over the threefold, bridge, and
atop sites are shown in Figure 3, Fig. 4 gives the potential energy at a range of \( z \) across the long diagonal of the unit cell, and Fig. 5 shows \( V_{SM} \) everywhere over the lattice.

The potential energy of an atom interacting with a surface varies periodically with the surface's corrugation. We assume that the corrugation can be adequately described by the first order term in the Fourier expansion of the surface (see Appendix), which is given by

\[
Q(x, y) = \cos s_1(x, y) + \cos s_2(x, y) + \cos(s_1(x, y) + s_2(x, y)),
\]

and for the Au (111) surface,

\[
s_1 = \frac{2\pi}{a} \frac{2y}{\sqrt{3}}, \tag{8}
\]

and

\[
s_2 = \frac{2\pi}{a} (x - \frac{y}{\sqrt{3}}), \tag{9}
\]

where \( a \) is the lattice constant (2.881 Å). (We first tried fitting a potential form using the exact Fourier expansion, but this proved problematic, and is not discussed here.)
Figure 3. Mahaffy’s Morse potential energies over the atop, bridge and threefold sites over a range of \( z \).
Figure 4. $V_M$ of thiolate sulfur above the long diagonal of an Au(111) unit cell. The contours run from $V_{\text{3fold}}$ (-43.18 kcal mol$^{-1}$) up to zero. The solid contours represent 20 kcal mol$^{-1}$ and the dashed ones are 2 kcal mol$^{-1}$.
Figure 5. z-minimized potential energy surface of $V_M$ over the Au(111) unit cell. Distances are in Å. The lattice vectors are shown, pointing from one atop site to another.
The assumption that the first-order corrugation is sufficient is very common in the literature,\textsuperscript{32,33} indeed, higher order terms in the Fourier expansion seem only to have been used when the expansion coefficients can be obtained in analytical form. This is possible when the potential to be fitted has the form of a finite polynomial (such as the Lennard-Jones potential), but not for a Morse potential.\textsuperscript{33}

We thus chose a general functional form for the fit potential

\[ V_{\text{fit}}(x, y, z) = V_0(z) + V_1(z)Q(x, y). \]  \hspace{1cm} (10)

The (dimensionless) values of \( Q \) for the threefold, bridge, and atop sites are -1.5, -1, and 3. The effect of the corrugation, then, is always attractive at the former two sites, and always repulsive at the atop site.

We chose conventional functional forms for \( V_0 \) and \( V_1 \) of, respectively, a Morse potential and an exponential decay,

\[ V_1(z) = A \exp(-bz). \]  \hspace{1cm} (11)

\( V_{\text{fit}} \) then has five adjustable parameters: \( D_e, \alpha, \) and \( z_e \) for the Morse potential, and \( A \) and \( b \) for the corrugation potential. These five parameters require five data to be fit exactly. We chose, however, to fit six data points, to try to ensure a broader range of applicability. The data chosen were the \( z_{\text{SM}} \) and \( V_{\text{SM}} \) of the three major sites on the lattice. Recalling that the motivation for this work was to be able to simulate self-assembly of alkylthiolates on Au (111), the most important points to reproduce were the site-minimized energies and heights over the threefold and bridge sites. This is because the energy barrier to diffusion across the surface, of critical importance to self-assembly, is the energy difference between these two sites' minimal energies (2.65 kcal mol\(^{-1}\)).

The potential parameters were fit to the data by optimizing them to minimize the
weighted squared error,

$$\text{err} = \sum_i W_i \left( \frac{X_i - x_i}{X_i} \right)^2,$$

(12)

where the $W_i$ are the weights assigned to each datum, the $X_i$ are the values of $z_{SM}$ and $V_{SM}$ given by $V_M$ (i.e., the data to be fit to), and the $x_i$ are the values predicted by the fit function's parameters. The data for the bridge and threefold sites were given heavier weighting than the atop site. The relative weights ranged from 5:1 to 100:1, but the exact weights used did not matter much. The data for the two lower-energy sites were consistently more easily fit than those for the atop site.

This fit was performed by a grid-based search in the parameter space, where each parameter was varied stepwise over an interval, followed by a Monte Carlo search where the parameters were randomly varied by ± 1%, and only downhill steps (i.e., those that reduced the square error) were accepted. The optimized parameters so obtained are given in Table 3, and the $V_{fit}$'s predicted $z_{SM}$ and $V_{SM}$ at the threefold, bridge, and atop sites, along with the inner turningpoints over the bridge and threefold sites, are compared with the true values for $V_M$ in Table 4. The fit is perfect at the two lower-energy sites, but $V_{fit}$ underestimates the corrugation slightly, so the atop site is 0.11 kcal mol$^{-1}$ too stable, and lies 0.04 Å too low.

Table 3: Parameters for the Fit Potential

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e$ (kcal mol$^{-1}$)</td>
<td>36.8</td>
</tr>
<tr>
<td>$\alpha$ (Å$^{-1}$)</td>
<td>1.178</td>
</tr>
<tr>
<td>$z_e$ (Å)</td>
<td>2.110</td>
</tr>
<tr>
<td>$A$ (kcal mol$^{-1}$)</td>
<td>3630.</td>
</tr>
<tr>
<td>$b$ (Å$^{-1}$)</td>
<td>3.355</td>
</tr>
</tbody>
</table>

The effect of the reduced corrugation shows in Figure 6, where $V_{fit}$ and $V_M$ are
plotted over the same three sites. At small $z$, the fit potential gives slightly lower energies over the atop site and slightly higher energies over the bridge and threefold sites than $V_M$. The fit also gives lower energies at large $z$ than $V_M$. Figure 7 shows $V_{fit}$ and $V_M$, at a range of $z$ over the long diagonal of the unit cell, and Figure 8 zooms in on Fig. 7’s low-energy region with $V$ between $V_{threefold}$ and 25 kcal mol$^{-1}$. At this scale, the discontinuities in $V_M$, as gold atoms pass in and out of the cutoff range for the potential, become visible. Slight asymmetries due to the small difference between the hcp and fcc sites are also apparent.

| Table 4: Stationary and Inner Turning Points (t.p.) of $V_{fit}$ and $V_M$ |
|---------------------------------|-----------------|-----------------|-----------------|
| Site               | $z_{SM}$ (Å), Fit; $V_M$ | $V_{SM}$ (kcal mol$^{-1}$), Fit; $V_M$ |
| Atop               | 2.324; 2.368 | -30.50; -30.39 |
| Bridge             | 1.988; 1.988 | -40.53; -40.53 |
| Threefold          | 1.900; 1.900 | -43.18; -43.18 |
| Bridge t.p.        | 1.360; 1.333 | 0; 0           |
| Threefold t.p.     | 1.204; 1.173 | 0; 0           |

**Discussion**

Our motivation in fitting this potential was to develop a computationally cheap way of simulating the diffusion of thiolated fullerenes across the Au (111) surface, to the end of modeling their self-assembly into ordered patterns. We are mainly interested in situations of fairly low temperature, where the thermal energy is small (the average thermal energy, $RT$, per degree of freedom at 300 K is $\sim 0.6$ kcal mol$^{-1}$). Figure 6 shows clearly that our fit potential represents $V_M$ within this energy range at the bottom of the threefold site’s potential well. It is only around $V = 39$ kcal mol$^{-1}$ that any disagreement appears between $V_{fit}$ and $V_M$ above the threefold or bridge sites.

But of course, $V_{fit}$ was fit above the threefold and bridge sites, so it would be
expected to reproduce $V_M$ over those points rather well. Diffusion depends also on the path between the threefold and bridge sites, so Figures 9 and 10 we compare the minimized energies $V_{SM}$ and $z_{SM}$ for $V_M$ and $V_{fit}$ all along the long diagonal of the unit cell. Between the threefold minima, very small errors are introduced in $V_{SM}$ along the diffusion path due to the small differences between the fcc and hcp sites, differences that our fit ignores. These errors are on the order of 0.05 kcal mol$^{-1}$ the limit of $V_M$'s accuracy (0.05 kcal mol$^{-1}$), so they are acceptable. The energy-minimizing heights $z_{SM}$ along the threefold-to-threefold diffusion path appear indistinguishable for the two potentials. At most, the $z_{SM}$ for $V_{fit}$ deviates from that for $V_M$ by $10^{-3}$ Å in the low energy region.

The fit is not so tight along the path from a threefold site toward an atop site. Because $V_{fit}$ underestimates the surface corrugation, the fit's $V_{SM}$ and $z_{SM}$ become too small. However, the site-minimal energies and heights for $V_M$ are reproduced well everywhere at energies less than the diffusion barrier, which is most important. While diffusion depends exponentially on the energy barrier, it is effected to a lesser but significant degree by the curvature of the potential energy surface, and this fit potential reproduces the curvature of $V_M$ at low energies. We thus have reason to believe that this potential fit has achieved its purpose: to be able to model the low-temperature diffusion of alkylthiolates on the Au (111) surface, based on a prior thiolate sulfur-gold Morse potential for that system.
Figure 6. Fit (symbols) and true potential energies over the three surface sites.
Figure 7. $V_M$ (left) and $V_{fit}$ above the long diagonal of the unit cell. The contours are spaced as in Fig. 4.
Figure 8. $V_M$ (left) and $V_{fit}$ (right) above the long diagonal of the unit cell in the low-energy region. Dashed lines represent 0.5 kcal mol$^{-1}$. Distance along unit cell ($\AA$) vs. Distance ($\AA$):
Figure 9. The minimum energy path, $V_{SM}$, along the long diagonal of the unit cell computed by $V_M$ (line) and $V_{fit}$ (squares).
Figure 10. The energy minimizing heights, $z_{SM}$ along the long diagonal of the unit cell computed by $V_M$ (line) and $V_{fit}$ (squares).
As mentioned, Yu et al.\textsuperscript{29} found the true binding site of alkylthiolates to be atop a gold adatom that sits above a threefold site. So while Mahaffy and coworkers' and our potentials successfully model energies and (x,y) positions on the surface, they predict the wrong heights $z$ of the sulfur atom above the surface. Further research directions may include fitting a Morse potential between thiolate sulfur and one gold atom to reproduce the same data as used by Mahaffy, Bhatia, and Garrison,\textsuperscript{24} and finding a simple form (like Eq. 1 or 10) for the potential energy of the gold adatom on the surface. The gold adatom's interaction with the surface could be modelled by a multi-body potential function like the Sutton-Chen\textsuperscript{34} or Gupta\textsuperscript{35} potentials. How the presence of an attached thiolate sulfur atom would perturb the gold adatom's interactions with the surface would be a much more involved problem.

\textbf{Conclusions}

We successfully found a computationally cheap but accurate potential energy function to model the thiolate sulfur-Au (111) surface interaction. This will enable more extensive simulations in less time than would be possible using the previously available Morse potential form for this interaction.
CHAPTER 4

CONSTRUCTION OF A POTENTIAL ENERGY FUNCTION FOR THE C_{60}-Au (111) INTERACTION

Introduction

We now turn our attention to the interaction of unfunctionalized C_{60} fullerene with the Au (111) surface. The interaction energy between these two species is comparable with that of the gold surface with a thiolate sulfur atom, and thus of interest as the fullerene component of thiolated fullerenes may compete with the thiolate moieties for surface binding sites. The C_{60}-surface interaction must, therefore, be well-accounted for in computational studies of the self-assembly of functionalized fullerenes on the Au (111) surface. When this work was done, no empirical potential function was available for the C_{60}-surface system, unlike the thiolate-surface system in the previous chapter. We therefore set about to develop a functional form for the C_{60}-Au (111) potential and parametrize it to fit the available experimental and computational data.

Background

C_{60} forms monolayers on the Au (111) surface, and like those of thiolates, this process lifts the 22 x 3 reconstruction. In the first study of these monolayers, it was found by scanning tunnelling microscopy (STM) that at 298K, two competing domains form: a $2\sqrt{3} \times 2\sqrt{3}$ R30° lattice, and a 38 x 38 commensurate lattice (Figure 1). The former has a unit cell of fullerenes separated by $2\sqrt{3}$ times the gold lattice constant, very nearly the C_{60}-C_{60} separation in solid fullerene (~10.0 Å), rotated 30° with respect to the underlying Au (111) lattice. It was found by low energy electron diffraction that on
annealing at 625 K, the $2\sqrt{3} \times 2\sqrt{3}$ R30° lattice predominated.\textsuperscript{37} A later scanning
tunnelling spectroscopy study\textsuperscript{38} showed that the metastable commensurate phase was
actually a $7 \times 7$ lattice with respect to the surface, or $2 \times 2$ with respect to C\textsubscript{60} (also shown
in Fig. 1). The fullerene-fullerene distance in this arrangement is 10.1 Å, slightly larger
than the C\textsubscript{60}-C\textsubscript{60} equilibrium separation, and it was determined that in the unit cell, one
fullerene occupies an atop or threefold site and the other three are at bridge sites.

![Figure 1](image)

Figure 1. a. Unit cell of the $2\sqrt{3} \times 2\sqrt{3}$ R30° C\textsubscript{60} lattice on Au(111),
with lattice vectors rotated 30° from the Au(111) lattice vectors. Black
dots represent C\textsubscript{60}s at threefold sites. b. Unit cell of the $7 \times 7$ C\textsubscript{60}
lattice, where gray circles are atop sites and open dots are bridge sites.

What sites C\textsubscript{60} occupies in the stable $2\sqrt{3} \times 2\sqrt{3}$ R30° phase is less certain. An
early STM study indicated\textsuperscript{39} the fullerenes all occupy atop sites with a pentagonal face
toward the surface, but different density functional theory (DFT) calculations have
predicted preferred bridge\textsuperscript{40} and hcp\textsuperscript{41} binding sites, with a hexagonal face down. It was
found by STM that at room temperature, the adsorbed fullerenes can rotate freely about
the axis normal to the gold surface.\textsuperscript{39}
In addition to rotation, diffusion of C$_{60}$ on the Au (111) surface is also known to occur freely at 300K. Isolated fullerenes diffuse too fast at room temperature to be resolved at the STM time scale,$^{36}$ but a later study observed ‘islands’ of two to eight fullerenes diffusing together.$^{42}$

The adsorption enthalpy of a C$_{60}$ monolayer on Au (111) has been experimentally found to lie between 40 and 60 kcal mol$^{-1}$.$^{36,37}$ This includes the energy of C$_{60}$-C$_{60}$ interaction; each fullerene has six nearest neighbors, half as many as each fullerene in solid C$_{60}$. If the C$_{60}$-C$_{60}$ interaction is not changed by interaction with the gold surface, then subtracting half of the enthalpy of sublimation of pure C$_{60}$, with $\Delta H_{\text{sub}} \sim 40$ kcal mol$^{-1}$,$^{43}$ from these gives an adsorption enthalpy between C$_{60}$ and the surface between 20 and 40 kcal mol$^{-1}$. This is of the order of a weak covalent bond. Theoretical studies have predicted that the surface transfers from 0.2 to 0.8 electrons to the fullerene,$^{37,40,41}$ indicating chemisorption.

Additionally, a differential conductance study has been performed$^{44}$ on C$_{60}$ sitting at the junction of two gold plates. The obtained peaks in the conductance with voltage were taken to be resonances with the C$_{60}$-Au vibrational levels. These results were used to calculate a vibrational force constant of 70 N/m = 100 kcal mol$^{-1}$ Å$^{-1}$ for the fullerene-surface ‘bond.’

All of the experimental data are compatible with the results of the DFT study of Wang and Cheng,$^{41}$ whose calculations predicted rotational and diffusional energy barriers of about 2.3 and 3.2 kcal mol$^{-1}$. Because this study fits the experimental data, we parametrized our potential to fit its predictions. For each site, the minimized energies $V_{SM}$ and energy-minimizing heights $z_{SM}$,$^{45}$ above the surface are given in Table 1. (The
distances are from the plane of the surface to the center of mass of the fullerene, and the
subscript is for site-minimal.) As with the Morse potential for thiolate on Au (111) used
in the previous chapter, the two threefold sites were observed to be nearly degenerate.

**Method and Results**

We begin by making the assumption that C\textsubscript{60} can be modeled as a united
‘pseudoatom.’ Girifalco was able to replicate properties of bulk C\textsubscript{60} using this approach
of treating the molecule as a spherical pseudoatom,\textsuperscript{46} so we have reason to expect this
approximation is reasonable. We will then assume the same general Lennard-Jones-and-
Devonshire potential form as we did for the thiolate S-Au (111) interaction,

\[
V(x, y, z) = V_0(z) + V_c(x, y, z). \tag{1}
\]

**Fit Potential Form 1**

We first approximated the C\textsubscript{60}-Au (111) interaction as being due only to
dispersion. While the interaction is very likely at least weakly covalent, there is simply
not enough experimental or computational data available for a more refined treatment.
Additionally, because C\textsubscript{60} is so polarizable (88.9 Å\textsuperscript{3}),\textsuperscript{47} its adsorption energies tend to be
close to the order of weak covalent bonds. For instance, the adsorption energy of a single
molecule of C\textsubscript{60} onto the (111) surface of C\textsubscript{60} is 19.2 kcal mol\textsuperscript{-1} (using Girifalco’s
potential),\textsuperscript{46} two thirds of its likely interaction energy with Au (111). The error due to
neglecting the C\textsubscript{60}-surface bond’s covalency is likely to be small.

At large distances, the dispersive attraction between a polarizable atom and a flat
metal surface is given by\textsuperscript{48}

\[
V_0 = -\frac{C}{(z - z_m)^3}, \tag{2}
\]
where $C$ is derived from the polarizability of the atom and of the surface and $z_m$ is a parameter to account for the "leakage" of electrons out of the metal's bulk and into the space over the surface. $z_m$ serves to convert the actual height, $z$, to the "effective" height. For metals, $z_m$ is usually around half of the interlayer separation, although it has been found to increase with adatom size.

In the present case, we treat $z_m$ as an adjustable parameter to allow the attractive potential to account for $C_{60}$'s polarizable electrons' confinement to the (nearly) spherical shell of carbon atoms around the fullerene center of mass. Instead of devising a separate short-range bonding potential, we assumed that the attractive part of the potential has only this form.

At small separation, the repulsive potential becomes important. For monatomic gases over a surface, it has the form:

$$V_R(x,y,z) = A_R \exp(-a(z-z_e) + D(x,y)),$$

(3)

where $A_R$, $a$, and $z_e$ are parameters, and $D(x,y)$ contains the surface corrugation. We first combine $A_R$ and $\exp(az_e)$ to define

$$A' = A_R \exp(az_e)$$

(4)

and then again assume that the corrugation depends only on the first order terms in the Fourier expansion of the surface. We give $D(x,y)$ the form,

$$D(x,y) = bQ(x,y),$$

(5)

where $Q(x,y)$ has the same meaning as in Chapter 3, and where $b$ is an adjustable parameter, expected to be small. Treating $C$ as a fifth adjustable parameter, we obtain the potential form...
\[ V(x, y, z) = \frac{-C}{(z - z_m)^3} + A'\exp(-az + bQ(x, y)). \] (6)

The unitless values of \( Q(x, y) \) for the threefold, bridge, and atop sites are, as in Chapter 3, respectively -1.5, -1, and 3. Since we will be fitting all of our potential energy functional forms at these sites, which have only one \( Q(x, y) \) value each but an infinite number of \((x, y)\) coordinates, we will henceforth denote the potential simply as \( V(Q, z) \), with the \( x \)- and \( y \)-dependence implicit in \( Q \). As with the thiolate-Au (111) potential, the corrugation will always be repulsive over the atop site and attractive over the bridge and threefold sites (or rather, the corrugation will reduce repulsion over these sites). We again assume degenerate threefold (fcc and hcp) binding sites.

We call this first fitted potential Fit 1. When the \( x \) and \( y \) dependence is replaced simply with \( Q \), Fit 1 has the functional form

\[ V(Q, z) = \frac{-C}{(z - z_m)^3} + A'\exp(-az + bQ). \] (7)

We first set out to fit the parameters to Wang and Cheng’s \( V_{SM} \) and \( z_{SM} \) for \( C_{60} \) over the threefold, bridge, and atop sites of the Au (111) surface (Table 1).

<table>
<thead>
<tr>
<th>Site</th>
<th>( V_{SM} ) (kcal mol(^{-1}))</th>
<th>( z_{SM} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Threefold</td>
<td>-29.2</td>
<td>5.7</td>
</tr>
<tr>
<td>Bridge</td>
<td>-26.0</td>
<td>5.8</td>
</tr>
<tr>
<td>Atop</td>
<td>-19.8</td>
<td>6.1</td>
</tr>
</tbody>
</table>

This functional form proved difficult to fit using the squared-error minimization technique, used in the previous chapter, of searching over a hypergrid in the parameter space and then refining the best-fitting parameters by downhill-only Monte Carlo steps. This is possibly due to the extreme sensitivity of the inverse-cube and the two
exponential parameters; it was difficult to find a suitable range of maximum and minimum parameter values over which to perform a grid search. We then tried fitting it using the *Find* function in Mathcad 2000.\(^51\) This function minimizes the squared error given by Eq. (3.10) using a conjugate gradient local minimization scheme. It is therefore less sensitive to the initial choice of parameters than the grid-based search, and will converge to the nearest squared-error locally-minimizing parameter set.

It may be mentioned that the data fit, in this case, were the \(V(Q, z_{SM}) = V_{SM}\) and \(\nabla_z V(Q, z_{SM}) = 0\) for each site; the *Find* function uses only function and derivative values to find optimized parameters for a fitting function, so a squared error-minimizing parameter set could conceivably give a local potential *maximum* at a site’s \(z_{SM}\) (although this did not occur). In the code we wrote for least squares error minimization, we could minimize the fit potential and find \(z_{SM}\) for each candidate parameter set, and thus directly use the three \(z_{SM}\) as data to be fit.

The *Find* function, too, was unable to find potential parameters that reproduced all three sites’ site-minimized energies and distances. So we then focused on the lower-energy threefold and bridge sites and tried fitting to the values of \(V(Q, z_{SM})\) and \(\nabla_z V(Q, z_{SM})\) for these sites, along with the value of the force constant, \(\nabla_z^2 V(Q, z_{SM})\), at the threefold site. We were able to fit parameters for Fit 1 that reproduced these five data.

The parameters thus obtained are given in Table 2, and the potential energy over each site is shown in Figure 2. The \(C_3\) term for \(C_{60}\)-Au (111) has been estimated\(^52\) to be 245 kcal mol\(^{-1}\) \(\AA^3\), while the fit value is about 40% larger. The \(z_m\) value of 3.9178 Å is very much larger than half the interlayer separation (1.176 Å), but \(C_{60}\) is very much
larger than a rare gas atom. This first potential functional form for the potential, and every form tried subsequently, easily reproduced the force constant at the equilibrium height over the threefold site.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>kcal mol(^{-1}) Å(^3)</td>
<td>342.821</td>
</tr>
<tr>
<td>(z_m)</td>
<td>Å</td>
<td>3.9178</td>
</tr>
<tr>
<td>(A')</td>
<td>kcal mol(^{-1}) Å(^{-1})</td>
<td>4.1727x10(^9)</td>
</tr>
<tr>
<td>a</td>
<td>Å(^{-1})</td>
<td>3.2257</td>
</tr>
<tr>
<td>b</td>
<td>--</td>
<td>0.20839</td>
</tr>
</tbody>
</table>

Table 2: Potential Parameters for Fit 1

Figure 2. Potential energies given by Fit 1. Solid dots are the data fit to.

This first fit fails badly over the atop site. The reason for this is twofold:

Obviously, the potential was not fit to the atop site, but more seriously, \(S\) for the atop site is +3, where it is only -1 and -1.5 at the bridge and threefold sites. This atop site feels an increased repulsion disproportionate to the decreased repulsion over the other two sites.
We next tried other forms for the repulsive potential, but before moving on, we shall point out that the inner turning point over the threefold site is $z \approx 5.2 \text{ Å}$. This gives an surface-C$_{60}$ distance (assuming the C$_{60}$ is oriented with a hexagonal face down) of only 1.95 Å, much smaller than carbon’s Lennard-Jones $\sigma$ value ($\sim 3.5$ Å), but this would be consistent with covalent character to the fullerene-surface interaction.

**Fit Potential Form 2**

Given the problems found with the theoretically justified (assuming C$_{60}$ is well-modeled by a pseudoatom) Fit 1, we then tried a wholly empirical form for the potential, which we will call Fit 2. Since the form of a Morse potential plus an exponential corrugation term worked so well for the thiolate-Au (111) interaction, we chose the same form here:

$$V(z) = V_{\text{Morse}} + A \exp(-bz)'S,$$

(8)

with five adjustable parameters. We performed a grid-based search in the five parameters and improved them by Monte Carlo methods, as above. The resulting parameters are given in Table 3, and the fit’s $V_{\text{SM}}$ and $z_{\text{SM}}$ are given in Table 4 for comparison with Table 1. Fit 2 reproduced the energies and distances (within the error of Wang and Cheng’s data) for the threefold and bridge sites, and was in better agreement for the atop site than Fit 1. However, Fit 2 still could not reproduce the atop site’s minimal energy or height.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_e$</td>
<td>kcal mol$^{-1}$</td>
<td>22.537</td>
</tr>
<tr>
<td>$z_e$</td>
<td>Å</td>
<td>5.9624</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Å$^{-1}$</td>
<td>1.4051</td>
</tr>
<tr>
<td>$A$</td>
<td>kcal mol$^{-1}$</td>
<td>1.9505x10$^{10}$</td>
</tr>
<tr>
<td>$b$</td>
<td>Å$^{-1}$</td>
<td>3.8064</td>
</tr>
</tbody>
</table>

**Table 3: Potential Parameters for Fit 2**
Table 4: Optimized Energies and Heights for Fit 2

<table>
<thead>
<tr>
<th>Site</th>
<th>$V_{SM}$ (kcal mol$^{-1}$)</th>
<th>$z_{SM}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Threefold</td>
<td>-29.12</td>
<td>5.69</td>
</tr>
<tr>
<td>Bridge</td>
<td>-26.10</td>
<td>5.81</td>
</tr>
<tr>
<td>Atop</td>
<td>-17.43</td>
<td>6.20</td>
</tr>
</tbody>
</table>

These difficulties are again due to the sign of $Q$ being negative over the threefold and bridge sites, and positive and larger over the atop site. The corrugation serves to decrease the energies of the former two, and increase that of the latter. Since the atop site has a significantly larger value of $Q$ than the other sites, the corrugation consistently over-increases its energy. We finally decided to try making the corrugation always repulsive.

Fit Potential Form 3

Fit 3 had the form

$$V(Q, z) = V_{Morse} + A \exp(-bz)(Q + 1.5).$$

Adding 1.5 to $Q$ makes the corrugation zero for the threefold site and positive for the other two. Table 5 gives the parameters for this potential, as optimized by the grid/MC search method. With this form, all energies and distances are within the original data’s uncertainties. The energies over each site and the $z$-minimized $V$ along the long diagonal of the Au (111) unit cell are shown in Figures 4 and 5, and $V(z)$ along the same path is shown in Figure 6. Interestingly, the inner turningpoint over the threefold site is again around 5.2 Å.
Table 5: Potential Parameters for Fit 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>De</td>
<td>kcal mol$^{-1}$</td>
<td>29.29</td>
</tr>
<tr>
<td>$z_c$</td>
<td>Å</td>
<td>5.67</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Å$^{-1}$</td>
<td>1.31</td>
</tr>
<tr>
<td>A</td>
<td>kcal mol$^{-1}$</td>
<td>$1.45 \times 10^{15}$</td>
</tr>
<tr>
<td>b</td>
<td>Å$^{-1}$</td>
<td>5.74</td>
</tr>
</tbody>
</table>

Figure 3. The potential energy over the three surface sites given by Fit 3.
Figure 4. Minimum energy path for Fit 3 along the long diagonal of the unit cell. Wang and Cheng's DFT data are solid dots.
Figure 5. Potential energy surface for z and y, the distance along the long diagonal of the unit cell using Fit 3.

Discussion

At first glance, it is not clear why Fit 2 should perform so poorly for the atop site, when a potential of the same form worked so well for the thiolate-surface interaction. We would argue that this is due to the unusually large equilibrium separation between the fullerene and the surface. The $V_{SM}$ and $z_{SM}$ of the threefold, bridge, and atop sites relative to $V_{SM}$ and $z_{SM}$ of the threefold site for the two systems are listed in Table 7. The relative $V_{SM}$ at the three sites are comparable for both systems. But because the
equilibrium distance of the threefold site is so large for C₆₀, the differences in relative
distances are comparatively small.

<table>
<thead>
<tr>
<th>Site</th>
<th>VM/V₃fold</th>
<th>zₛM/zₛM₃fold</th>
<th>VM/V₃fold</th>
<th>zₛM/zₛM₃fold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Threefold</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Bridge</td>
<td>0.94</td>
<td>1.05</td>
<td>0.90</td>
<td>1.02</td>
</tr>
<tr>
<td>Atop</td>
<td>0.70</td>
<td>1.24</td>
<td>0.68</td>
<td>1.07</td>
</tr>
</tbody>
</table>

The thiolate sulfur-Au (111) potential has a large relative distance between the
threefold and atop sites’ energy-minimizing heights, and the effect of the surface’s
corrugation diminishes correspondingly. The C₆₀-Au (111) potential, on the other hand,
has only a small relative distance between the two sites’ energy-minimizing heights. The
exponentially decaying corrugation potential in Fit 2 simply cannot decrease rapidly
enough to reproduce the atop sites’ energetics, because it is constrained by the more
important energetics at the threefold and bridge sites. If the corrugation is always
repulsive, the situation changes. In this case, the threefold site’s energetics are described
entirely by the Morse potential. The corrugation potential then becomes a correction
term for only the atop and the bridge sites, which the two-parameter exponential decay
form used is able to accommodate.

There are two ways the corrugation potential could be modified which might
allow a more conventional form. One is to expand the pre-exponential factor A to

\[ A = A' \exp(bz_1), \] (10)

where A’ and z₁ are new parameters. This would revise the corrugation potential’s
functional form to
\[ V_1(z) = A' \exp(-b(z - z_1)). \]  

This would greatly reduce the size of the pre-exponential factor and make it easier to search the parameter space thoroughly, at the cost of introducing another parameter whose space would also need to be searched.

The \( z_1 \) parameter described above may be related to the definition of \( z \). In this chapter, \( z \) has been the distance from the surface plane to the center-of-mass of the fullerene. A better metric, however, might be the distance from the surface plane to the lowest face of the \( C_{60} \). With this definition of \( z \), the \( z_{sm} \) for the threefold, bridge, and atop sites are respectively 2.4, 2.5, and 2.8 Å. The relative \( z_{sm} \) are then 1.0, 1.05, and 1.17, comparable with the relative \( z_{sm} \) for thiolute sulfur at the three sites. It is possible, then, that a corrugation potential form like that of the thiolute sulfur/Au (111) interaction could work if this definition of \( z \) was used.

Regardless, the form of Fit 3 is adequate to our purposes; it reproduces the sparse known and predicted data on the \( C_{60} \)-Au (111) interaction. This system is not yet well characterized experimentally, but as new information comes to light, the potential can be reparametrized by the same method of grid-based search followed by downhill-only Monte Carlo steps, to accommodate the new facts of the matter. It may be necessary to change the corrugation potential's form or the definition of \( z \) to accommodate new information, but the form we have now is sufficient to model what is now known about the \( C_{60} \)-Au (111) interaction.
APPENDIX

FOURIER EXPANSIONS IN ONE AND TWO DIMENSIONS

Fourier expansion is the expression of a function in terms of trigonometric basis functions with different frequencies. This expansion is most useful for periodic functions. For a function with period L, the basis functions will have angular spatial frequencies or wavevectors

\[ k_n = \frac{2\pi n}{L}, \]  

where \( n \) is an integer from 0 to infinity. The Fourier expansion of this function is

\[ f(x) = \frac{c_0}{2} + \sum_{n=1}^{\infty} c_n \cos(k_n x) + d_n \sin(k_n x), \]  

where the coefficients of the even and odd basis functions are respectively

\[ c_n = \frac{2}{L} \int_0^L f(x) \cos(k_n x) dx, \]  

and

\[ d_n = \frac{2}{L} \int_0^L f(x) \sin(k_n x) dx, \]  

where the factor of \( 2/L \) is to normalize the basis functions, i.e., for \( n > 0 \),

\[ \int_0^L \cos^2(k_n x) dx = \frac{L}{2}, \]  

and the integral of the squared sine function has the same value. For \( n = 0 \), the
integral for the cosine squared is $L$, so $c_0$ as defined by Eq. (3a) must be halved. $c_0$ is just the average value of the function across $L$, and the higher order coefficients give the function's *corrugation*, its deviation from the average as a function of position. For smooth functions, Fourier series converge at small $n$; the coefficients $c_n$ become smaller and smaller with increasing $n$.

If the function is even with respect to reflection across the origin, then only the $c_n$ will be nonzero. This is true for Fourier expansions of higher-dimensional functions, as well. In the body of this thesis, we make the approximation that the potential energy (at a given $z$) is even with respect to reflection across the $xz$ and $yz$ planes, so we will restrict the discussion that follows to even functions, for simplicity.

For a function periodic in two dimensions, the situation is more complicated. In what follows, vectors in the will be written in bold print in the text, and indicated with an arrow or tilde in equations. Let us first consider a periodic function of $\mathbf{r} = x\mathbf{i} + y\mathbf{j}$. The function's values over the entire surface will resemble a repeating two dimensional lattice. If the unit cell of the lattice is a trapezoid described by the lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, then its Fourier expansion is

$$f(\vec{r}) = \frac{c_{00}}{2} + \sum_m \sum_n c_{mn} \cos(\vec{k}_{mn} \cdot \vec{r}),$$

(5)

with $m$ and $n$ being integers not both equal to zero, and the wavevectors are

$$\vec{k}_{mn} = 2\pi m\vec{a}_1 + 2\pi n\vec{a}_2.$$  

(6)

$\vec{a}_1$ and $\vec{a}_2$ are reciprocal vectors defined by their relationship with the surface lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$:

$$\vec{a}_i \cdot \vec{a}_j = \delta_{ij},$$  

(7)
where $\delta_{ij}$ is the Kronecker delta. The coefficients $c_{mn}$ are

$$c_{mn} = \frac{2}{|\mathbf{a}_1||\mathbf{a}_2|} \int_A f(\mathbf{r}) \cos(\mathbf{k}_{mn} \cdot \mathbf{r}) d\mathbf{r},$$

(8)

with the integration carried out over the unit cell, the trapezoid bound by $\mathbf{a}_1$ and $\mathbf{a}_2$. For a function with a rectangular unit cell (Figure 1a) with the lattice vectors

$$\mathbf{a}_1 = L_x \hat{i} \quad & \quad \mathbf{a}_2 = L_y \hat{j},$$

(9)

the reciprocal lattice vectors are simply (Figure 1b)

$$\mathbf{\tilde{a}}_1 = \frac{\hat{i}}{L_x} \quad & \quad \mathbf{\tilde{a}}_2 = \frac{\hat{j}}{L_y},$$

(10)

because the spatial lattice vectors are already orthogonal. In practice, not all of the coefficients $c_{mn}$ need to be considered because of the symmetries of the spatial and reciprocal lattices. Figure 1b shows the reciprocal lattice for a rectangular spatial lattice for $m + n \leq 2$. The Fourier expansion coefficient for a point $(m,n)$ in the reciprocal lattice is equal to that for any other point at the same distance from the origin. That distance from the origin is equal to the spatial frequency in the direction $m\mathbf{\tilde{a}}_1 + n\mathbf{\tilde{a}}_2$, so this is to say that the expansion coefficients for all $(m,n)$ with the same frequency will be equal.

Generally, the spatial frequency of a point in the reciprocal lattice will be

$$\nu_{mn} = \sqrt{(m\mathbf{\tilde{a}}_1 + n\mathbf{\tilde{a}}_2) \cdot (m\mathbf{\tilde{a}}_1 + n\mathbf{\tilde{a}}_2)},$$

(11)

If the reciprocal vectors are orthogonal, as in a rectangular lattice, $\nu$ will reduce to $(m^2/L_x^2 + n^2/L_y^2)^{1/2}$. Finally, each unique $(m,n)$ wavevector in the reciprocal space is only counted once in the summation of Eq. (3). This means that only one of each pair of antiparallel vectors $(m,n)$ and $(-m,-n)$ is included in the sum. The actual coefficients
needed, of a function with the symmetry of this lattice, will be those for (0,0), (1,0), (0,1),
(1,1), (1,-1), (2,0), and so on. From Figure 1b, it can be seen that all of these lie in one
half of the reciprocal lattice.

If the function being expanded has a third dimension, z, in which the function is
not periodic, then the coefficients so obtained will themselves be functions of z. This is
the case, for instance, for an atom’s interaction with a surface. At constant z, the
potential energy will be described completely by one set of expansion coefficients V_{mn},
but if z changes, then the coefficients will also change, so they are better written as
V_{mn}(z).

Let us now return to the Au(111) surface, with its threefold symmetry. This case
is more complicated than a rectangular lattice because its lattice vectors are not
orthogonal. These lattice vectors can be written as

\[ \vec{a}_1 = a\left(\frac{i}{2} + \frac{\sqrt{3}j}{2}\right) \]  \hspace{1cm} (12a)

and

\[ \vec{a}_2 = a\hat{i}, \] \hspace{1cm} (12b)

where a is the lattice constant for gold, 2.881 Å. The potential energy surface for
thiolate sulfur or C_{60} over Au (111) will have the same symmetry and lattice vectors as
the surface. To perform a Fourier expansion of a function of this surface, we require the
surface’s reciprocal lattice vectors. By applying Eq. (7) to Eqs. (12), we obtain

\[ \vec{a}_1 = \frac{2j}{\sqrt{3}a} \] \hspace{1cm} (13a)
and
\[
\tilde{a}_2 = \frac{1}{a} (\hat{i} - \frac{\hat{j}}{\sqrt{3}}). \tag{13b}
\]

The reciprocal vectors are shown in Fig. 2a, and the reciprocal lattice points corresponding to the four lowest spatial frequencies and their distinct directions are shown Fig. 2b. The first nonzero frequency includes the inverse directions \(\tilde{a}_1, \tilde{a}_2,\) and \(\tilde{a}_1 + \tilde{a}_2,\) or \((m \, n) = (1 \, 0), (0 \, 1), (1, 1).\) The second frequency has \((m \, n) = (1 \, -1), (2 \, 1),\) and \((1 \, 2),\) and the third, \((2 \, 0), (0 \, 2),\) and \((2 \, 2).\) We define
\[
s_1 = \vec{k}_{10} \bullet \vec{r} = 2\pi \tilde{a}_1 \bullet \vec{r} = \frac{4\pi y}{\sqrt{3}a} \tag{14a}
\]
and
\[
s_2 = \vec{k}_{01} \bullet \vec{r} = 2\pi \tilde{a}_2 \bullet \vec{r} = \frac{2\pi}{a} \left(x - \frac{y}{\sqrt{3}}\right), \tag{14b}
\]
so the argument of the cosine function for Fourier expansion coefficient \(c_{mn}\)
becomes
\[
\vec{k}_{mn} \bullet \vec{r} = (m\tilde{a}_1 + n\tilde{a}_2) \bullet \vec{r} = ms_1 + ns_2. \tag{15}
\]
Finally, then, the Fourier expansion of the potential energy \(V(x,y,z)\) for a particle anywhere over the Au (111) surface will be
\[
V(x, y, z) = \frac{V_{00}(z)}{2} + V_1(z) (\cos s_1 + \cos s_2 + \cos (s_1 + s_2))
+ V_2(z) (\cos (s_1 - s_2) + \cos (2s_1 + s_2) + \cos (s_1 + 2s_2))
+ V_3(z) (\cos 2s_1 + \cos 2s_2 + \cos (2s_1 + 2s_2)) + ...
\tag{16}
\]
where the $V_i$ are the expansion coefficients for the $i$th spatial frequencies of the reciprocal lattice; e.g. $V_1 = V_{10} = V_{01} = V_{11}$. In the specific case of thiolate sulfur over Au (111), these four terms were the only sizable ones in the expansion at physically relevant $z$. And in all cases, $V_1 > V_2 > V_3$, so the approximation, used in Chapters 3 and 4, that the potential’s corrugation was dependent only upon the first order cosine terms $(\cos(s_1), \cos(s_2), \text{and } \cos(s_1+s_2))$ was good.

![Image](image_url)

**Figure 1.** a) A rectangular lattice, its lattice vectors (solid), and its reciprocal vectors (dashed; not to scale). b) The first few reciprocal vectors of the reciprocal lattice, $m\vec{a}_1+n\vec{a}_2$, for $m + n \leq 2$ (omitting $-2\vec{a}_1$). The vectors can be replaced by $(m,n)$ points sitting where the vectors’ tips are in this representation, omitting all $(-m,-n)$ points. The origin of the lattice is the zeroth-frequency term.
Figure 2. a) The Au(111) surface and its surface lattice vectors \(\mathbf{a}_1\) and \(\mathbf{a}_2\) (solid), and the directions of the reciprocal lattice vectors \(\mathbf{a}^*_1\) and \(\mathbf{a}^*_2\) (dashed). b) The first few \((m,n)\) points in the reciprocal lattice generated from the reciprocal lattice vectors \(\mathbf{a}^*_1\) and \(\mathbf{a}^*_2\). Only one half of the lattice is shown.
COMPREHENSIVE LIST OF REFERENCES


