A model study of adlayer pattern formation of a linear molecule on square and triangular lattices

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A MODEL STUDY OF ADLAYER PATTERN FORMATION OF A LINEAR MOLECULE ON SQUARE AND TRIANGULAR LATTICES

BY

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THESIS

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................ iii
LIST OF TABLES .................................................................................................................. vi
LIST OF FIGURES ................................................................................................................ vii
ABSTRACT ............................................................................................................................ xiii

CHAPTER PAGE

1. INTRODUCTION .................................................................................................................. 1
2. LATTICE-MONOLAYER MODEL AND MINIMIZATION METHOD ......................................... 4
   2.1 Geometry ...................................................................................................................... 4
   2.2 Lattice Periodicity ...................................................................................................... 7
   2.3 Potential Energy .......................................................................................................... 9
   2.4 Energy Minimization .................................................................................................. 12
   2.5 Order Parameter ........................................................................................................ 14
   2.6 Radial Distribution Function .................................................................................... 16
3. RESULTS AND DISCUSSION FOR SQUARE LATTICE ...................................................... 18
   3.1 Introduction for Results on Square Lattice .................................................................. 18
   3.2 The Nearest-Neighbor Atom-Atom Distance, s .......................................................... 19
   3.3 Minimum NN Separation for Specified Ground State Geometries ............................. 22
   3.4 Adlayer Symmetry Notations .................................................................................... 26
   3.5 Contour Order Parameter Phase Diagrams, OPPD ..................................................... 28
   3.6 Contour Energy Parameter Phase Diagrams, VPPD .................................................... 30
   3.7 Analysis of Energy Parameter Phase Diagrams .......................................................... 32
      3.7.1 Small value of $r_e$ ($r_e=0.30$), Stripes and Square Pattern Geometries .......... 32
      3.7.2 Large value of $r_e$ ($r_e=0.74$), Herringbones and Perfect Herringbone .......... 39
      3.7.3 Large value of $r_e$ ($r_e=0.68$), Long Stripe .................................................. 42
      3.7.4 Intermediate value of $r_e$ ($r_e=0.60$), Herringbone and Irregular ................. 45
   3.8 Energy Parameter Phase Diagram Revisited ............................................................... 49
   3.9 Conclusions for Results on Square Lattice ................................................................. 50
4. RESULTS AND DISCUSSION FOR TRIANGULAR LATTICE ............................................ 52
   4.1 Introduction for Results on Triangular Lattice ............................................................ 52
   4.2 Adlayer Symmetry Labels and
      the Nearest-Neighbor Atom-Atom Distance, s ............................................................ 53
   4.3 Adlayer Symmetry Notations .................................................................................... 59
   4.4 Contour Parameter Phase Diagrams .......................................................................... 60
   4.5 Analysis of Energy Parameter Phase Diagrams .......................................................... 64
      4.5.1 Small value of $r_e$ ($r_e=0.40$), Sort Stripe, Honeycomb and
      Perfect Herringbone ................................................................................................. 64
      4.5.2 Intermediate value of $r_e$ ($r_e=0.60$), Long Stripe, Pinwheels and
      Triangular Geometries ............................................................................................... 70
      4.5.3 Large value of $r_e$ ($r_e=0.70$) ......................................................................... 74
   4.6 Conclusions for Results on Triangular Lattice ............................................................ 76
4.6.1 Small value of $r_e (r_e =0.40)$ ................................................................. 76
4.6.2 Intermediate value of $r_e (r_e =0.60)$ ......................................................... 78
4.6.3 Large value of $r_e (r_e =0.70)$ ................................................................. 79

5. CONCLUSION .......................................................................................................... 81

APPENDICES

APPENDIX A
  USAGE OF WALLPAPER GROUP SYMMETRY NOTATION ......................... 83

APPENDIX B
  CHARACTERIZATION OF ADLAYER PATTERN ON SQUARE LATTICE .. 86

APPENDIX C
  CHARACTERIZATION OF ADLAYER PATTERNS ON TRIANGULAR
  LATTICE................................................................................................................. 90

LIST OF REFERENCES ............................................................................................. 93
LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1 Closest nearest-neighbor (NN) atom-atom distance, ( s_1 ), for specified geometry as a function of ( \rho ). Also included in parentheses is the number of nearest-neighbor atoms, ( N_1 ). Note that there are two possible NN distances for the LS geometry, designated “tip-to-tip” and “side-by-side”. Those four and other curves were plotted in Figure 3.3.2.</td>
<td>21</td>
</tr>
<tr>
<td>3.3.1 Summarized adlayer patterns (found via global energy minimization calculations) on the square lattice.</td>
<td>25</td>
</tr>
<tr>
<td>3.4.1 Summary of characterized patterns on square lattice with the wallpaper group symmetry notations.</td>
<td>27</td>
</tr>
<tr>
<td>4.3.1 Summary of characterized patterns on triangular lattice with the wallpaper group symmetry notations.</td>
<td>59</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.1</td>
<td>Schematic representation of lattice sites with (a) square and (b) triangular symmetry.</td>
</tr>
<tr>
<td>2.1.2</td>
<td>Schematic representation of a two-dimensional (a) square and (b) triangular lattices. The lattice site-to-site length is shown as a multiple of (d). The (y) axis is rotated, 30(^\circ), (y)-axis that used as a reference axis for triangular lattice. Also shown the lattice site distance to the second nearest site for square and triangular lattices.</td>
</tr>
<tr>
<td>2.1.3</td>
<td>(a) This is schematic representation of molecules (i) and (j) which each carry homonuclear atoms (a) and (b), intermolecular “atom-atom” distances (r_{ij}^{aa}), (r_{ij}^{ab}), (r_{ij}^{ba}) and (r_{ij}^{bb}) and angles (\theta_i) and (\theta_j). (b) This panel is shows angle difference, (\Theta_{ij}), between molecules (i) and (j).</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Schematic representation of the PBC for (a) square and (b) triangular lattice symmetry; together with the four different orientation angles, (\Theta_i^{xy}), where (i = 1, \ldots, 4) in the primary cells.</td>
</tr>
<tr>
<td>2.2.2</td>
<td>(a) Schematic representation of the reference molecule, (\Theta_i^{xy}), in the primary cell surrounded by neighboring molecules, (\Theta_j^{xy}), where (i = 1, \ldots, 4) and (j = 1, \ldots, 8), for square lattice. (b) The reference molecule, (\Theta_i^{xy}), surrounded by neighboring molecules, (\Theta_j^{xy}), where (i = 1, \ldots, 4) and (j = 1, \ldots, 12), for triangular lattice.</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Schematic representation of the Morse potential as a function of atom-atom distance, (r). Note that (V_{Morse}(r) &gt; 0), for (r &lt; \sigma) and (V_{Morse}(r_e) = -D_e).</td>
</tr>
<tr>
<td>2.3.2</td>
<td>This is schematic representation of the (v(r)) plot for the Morse potential with three different Morse range parameters (\beta = 20, 10) and 6. The plot shows that “stiffness” of the Morse potential is dependent on the range parameter (\beta).</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Schematic representation of a global minimum search with repeated minimization processes at random initial points by the simplex algorithm. a. Global minimum of the potential energy. b. Minimization process to a local minimum. c. No energy barrier over passing is allowed.</td>
</tr>
<tr>
<td>2.5.1</td>
<td>Schematic representation of molecules (i) and (j) with calculated order parameter, (S_{ij}). In (a) molecules are parallel, (\theta_i = \theta_j) thus, (S_{ij} = 1). In (b) molecules are perpendicular, (</td>
</tr>
<tr>
<td>2.6.1</td>
<td>(a) Radial distribution function, RDF, of the short stripe geometry, (left (y)-axis) superimposed on the potential energy plot (right (y)-axis). Each frequency peak is the count of nearest-(next-nearest-, second-next-nearest-, etc.) neighbor per molecule, their bin width 0.03 and locations (this is, the NN (first left peak), NNN (second peak from the left) and etc.) are relative to (r_e). (b) Schematic representation of neighboring...</td>
</tr>
</tbody>
</table>
3.3.1.1 High-symmetry adlayer geometries found during the optimization. “Stripe” is used to designate the fact that all angles are the same. SS = “short stripe” denotes that all angles are equal to 0 (or $\pi/2$ or $\pi$). LS = “long stripe” denotes that all angles are $\pi/4$. SP denotes “square pattern”, where $\theta_1 = \theta_4 = 3\pi/4$, $\theta_2 = \theta_3 = \pi/4$. The “perfect herringbone” PHB denotes that the herringbone angles alternate between 0 and $\pi/2$. The “irregular” geometry, designated by irr, has no symmetry elements in the unit cell, has $(\theta_1, \theta_2, \theta_3, \theta_4) = (135^\circ, 152^\circ, 10^\circ, 102^\circ)$. These geometries are explained more fully in the text.

3.3.1.2 Low-symmetry adlayer geometries found during the optimization, and not described in Figure 3.3.1.1. DSP denotes a distorted SP, where $\theta_1 = \theta_4 \approx \pi/4$, $\theta_2 = \theta_3 \approx 3\pi/4$. The distortion angle is given by $\phi = \pi/4 - \theta_1 = 0.44$. HB-I denotes “herringbone” (of type I), where $\theta_1 = \theta_4$ and $\theta_2 = \theta_3$. The HB angle for the geometry shown is given by $\eta = |\theta_1 - \theta_2| = \pi/3$. The alternative form of “herringbone” (HB-II) has $\theta_1 = \theta_3$ and $\theta_2 = \theta_4$. DSS designates “distorted SS”. DSS-I has $\theta_3 = \theta_1$ and $\theta_2 = \theta_4$ and therefore possesses two mirror planes, and can be described by a “buckling” angle, $\theta_1$, here $20^\circ$. DSS-II has $\theta_3 = \pi - \theta_1$ and $\theta_2 = \pi - \theta_2$ and has one mirror plane, and can be described by two angles, here $(\theta_1, \theta_2) = (44^\circ, 155^\circ)$.

3.3.2 The minimum atom-atom separation distance, $s_i$, as a function of rigid molecule length, $\rho$, for chosen fixed geometries. The geometry labels SS, SP, LS, irr, PHB are explained in the caption to Figure 3.3.1.

3.5.1 Contour order parameter phase diagram as function of (distance) parameters ($\rho$, $r_e$) for several values of the Morse range parameters, $\beta$, on the square lattice. The key for the plot coloration is at the color bar (top panel). I and II used to designate regions DSS-I and DSS-II respectively, for clarity. See keys for all abbreviation labeling in Table 3.3.1.

3.6.1 Contour energy parameter phase diagrams as function of (distance) parameters ($\rho$, $r_e$) for several the Morse range parameters, $\beta$, on the square lattice. The key for the plot coloration is at the color bar (top panel). I and II used to designate regions DSS-I and DSS-II respectively, for clarity. See keys for all abbreviation labeling in Table 3.3.1.

3.7.1.1 The potential energy function $V(\rho)$ for the geometries described in Figure 3.3.1.1 for $r_e = 0.30$ and $\beta = 20, 10, 6$. The bold line is the potential energy of the GM obtained through the unbiased search. In the top panel, the cartoons illustrate the optimum geometry for several values of $\rho$. The red circles denote the radius $r_e$ about each atom, and are essentially the “soft spheres” associated with each atom.

3.7.1.2 Radial distribution function, showing the number of neighbor counts, $N$, as a function of atom-atom distance $s$, for various geometries for the case $r_e = 0.30$ and $\beta = 20$. SS and SP are labeled in Figure 3.3.1.1. DSS-I and DSS-II are described in Figure 3.3.1.2. Also shown is the Morse
potential energy function $v(s)$. The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.

3.7.1.3 Radial distribution function, showing the number of neighbor counts, $N$, as a function of atom-atom distance $s$, for various geometries for the case $r_e = 0.30$ and $\beta = 20$. LS and SP are labeled in Figure 3.3.1.1. DSP is described in Figure 3.3.1.2. The distortion angle of the DSP from the square is $\phi = 0.44$. Also shown is the Morse potential energy function $v(s)$. The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.

3.7.2.1 Potential energy $V_{\text{geometry}}(\rho)$ for the HB($15^\circ$, $75^\circ$) and PHB for the case $r_e = 0.74$, $\beta = 20$. The cartoons show the geometry at selected values of $\rho$. The circles around each atom have radius $r_e$.

3.7.3.1 The potential energy function $V(\rho)$ for the geometries described in Figure 3.3.1 for $r_e = 0.68$ and $\beta = 20$, 10, 6. The bold line is the potential energy of the GM obtained through the unbiased search. In the top panel, the cartoons illustrate the optimum geometry for a selected value of $\rho$. The GM potential energy is not shown in the bottom panel for clarity.

3.7.4.1 The potential energy function $V(\rho)$ for several geometries described in Figure 3.3.1 for $r_e = 0.60$ and $\beta = 20$. The bold line is the potential energy of the GM obtained through the unbiased search. At several values of $\rho$, the geometry is indicated by a letter. The corresponding labeled cartoons illustrate the optimum geometry for that value of $\rho$. $a$ denotes $\rho =0.60$; $b$ denotes $\rho =0.70$; $c$ denotes $\rho =0.86$; $d$ denotes $\rho =1.00$; $e$ denotes $\rho =1.15$. The interesting point is that the irr geometry manages to beat out the best two herringbones at point b, and it seems to be due to NNN. See following figure. HB-II becomes “crowded” as $\rho$ increases, ending up the way they look at point d.

3.7.4.2 Radial distribution function, for three geometries in the herringbone region, showing the number of counts, $N$, as a function of atom-atom distance $s$, for $\rho = 0.70$, 0.86, 1.00 corresponding to b,c,d on Figure 3.7.4.1. $r_e$ is fixed at 0.60, $\beta = 20$. Also shown is the Morse potential energy function $V(s)$. The potential energy of each geometry is indicated on the figure. The GM geometry is indicated with an asterisk. For $\rho = 0.70$, all three geometries have a NN count of four. However the HB-II geometry is beginning to experience repulsive strain. The HB-I is very similar to the distorted square geometry. It and the irr geometries are very similar as far as their NN are concerned. However, the irr has a slightly lower energy since it has one extra NNN at 0.75. For $\rho =0.86$, the HB-II geometry has 5 NN, making it the global minimum. For $\rho =1.00$, the HB-II is clearly strained. The HB-I has 4 NN; the irr has 5 NN, making it the global minimum.

4.2.1.1 Six high-symmetry ground state adlayer geometries found during optimization. “Stripe” is used to designate the fact that all angles are the same. SS (short stripe) geometry denotes that all angles are equal to
three degenerate forms: 0, π/3 or 2π/3. LS (long stripe) denotes that all angles are π/6 (or π/2 or 5π/6). HC (honeycomb) designates that θ₁ ≈ 5π/6 and θ₂ ≈ π/6, θ₃ = π/2 (or π/6 or 5π/6), θ₄ = π/2. The HC geometry is able to create several types of pinwheel (degraded HC) geometries (see Figure 4.2.1.3) by alternating primary cell angles within ± π/6. PHB (perfect herringbone) denotes that angles alternate between 0 and π/2. The irr (irregular) designates that θ₁ ≈ 30° and θ₂ ≈ 20°, θ₃ ≈ 40° and θ₄ = 120°. TR (triangular pattern) geometry has 3x3 primary cells and denotes that angles of the primary cell are alternating between 0, π/3 and 2π/3.

4.2.1.2 Ground state herringbone geometries are identified. The perfect herringbone (PHB) geometry discussed in Figure 4.2.1.1. HB denotes “herringbone”, where θ₁ = θ₃ and θ₂ = θ₄. The HB angle for the geometry shown is given by η = |θ₁ - θ₄| ≈ π/4. HB(DSS) denotes “herringbone” (distorted form of the short stripe, whose angles θₛₛ = 0 or π/3 or 2π/3), where θ₁ = θ₄ and θ₂ = θ₃. The HB(DSP) angle set for the geometry shown is given by {φ₁, φ₂}: {φ₁ = |θₛₛ - θ₂| = 20°, φ₂ = |θₛₛ - θ₃| = 13°}. HB(PHB) denotes “herringbone” (distorted form of the PHB), where θ₁ = θ₂ = 19° and θ₃ = θ₄ = 98°. These geometries are explained more fully in the text.

4.2.1.3 Ground state HC (honeycomb) geometries are identified. The high symmetry HC discussed in Figure 4.2.1.1. HC can be distorted (to form transitional pinwheel (PW) geometry) and this distorted form changes along increase of the parameter. PW-I geometry has (θ₁, θ₂, θ₃, θ₄) = (140°, 20°, 150°, 80°). PW-II geometry has (θ₁, θ₂, θ₃, θ₄) = (133°, 3°, 97°, 70°). PW-III geometry has (θ₁, θ₂, θ₃, θ₄) = (120°, 1°, 64°, 61°). These geometries are explained more fully in the text.

4.2.2 The minimum atom-atom separation distance, s₁, as a function of rigid molecule length, ρ, for chosen fixed geometries. The geometry labels SS/PHB, HC, PW-I, irr, LS, TR and HB are explained in the caption of Figures 4.2.1.

4.4.1 Contour order parameter phase diagram as function of (distance) parameters (ρ, rₑ) for several values of the Morse range parameters, β, on the triangular lattice. The key for the plot coloration is at the color bar (top panel). I and II used to designate regions HB(DSS) and HB(PHB) respectively, for clarity. Upper boundary of HC and LS distorts to PW-I and distorted LS as parameters are grow. PW-III region was swapped by the TR (explained further in the text) See keys for all abbreviation labeling in Figure 4.2.1.1.

4.4.2 Contour energy parameter phase diagram as function of (distance) parameters (ρ, rₑ) for several values of the Morse range parameters, β, on the triangular lattice. The key for the plot coloration is at the color bar (top panel), energy values were truncated at value -16 and swapped by -24 (see explanation in the text). I and II used to designate regions HB(DSS) and HB(PHB) respectively, for clarity. Upper boundary of HC and LS distorts to PW-I and distorted LS as parameters are grow.
PW-III region was swapped by the TR (explained further in the text).

See keys for all abbreviation labeling in Figure 4.2.1.

4.5.1.1 The potential energy function $V(\rho)$ for the geometries described in Figure 4.2.1 for $r_e = 0.40$ and $\beta = 20, 10, 6$. The bold line is the potential energy of the GM obtained through the unbiased search. At several values of $\rho$, the geometry is indicated by a letter. $a$ denotes $\rho = 0.68$; $b$ denotes $\rho = 0.72$; $c$ denotes $\rho = 0.74$; $d$ denotes $\rho = 0.80$; $e$ denotes $\rho = 1.00$. The red circles denote the radius $r_e$ about each atom, and are essentially the “soft spheres” associated with each atom.

4.5.1.2 Radial distribution function, showing the number of neighbor counts, $N$, as a function of atom-atom distance $s$, for various geometries for the case $r_e = 0.40$ and $\beta = 20$. HC is described in Figure 4.2.1.1. PW-I is described in Figure 4.2.1.3. HB(PHB) is described in Figure 4.2.1.2. Also shown is the Morse potential energy function $v(s)$. The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.

4.5.1.3 Radial distribution function, showing the number of neighbor counts, $N$, as a function of atom-atom distance $s$, for various geometries for the case $\rho = 0.60$, $r_e = 0.40$ and three different Morse range parameters $\beta = 20, 10, 6$. SS and PHB are labeled in Figure 4.2.1.1. Also shown is the Morse potential energy function $v(s)$. The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.

4.5.2.1 The potential energy function $V(\rho)$ for the geometries described in Figure 4.2.1 for $r_e = 0.60$ and $\beta = 20, 10, 6$. The bold line is the potential energy of the GM obtained through the unbiased search. At several values of $\rho$, the geometry is indicated by a letter. $a$ denotes distorted long stripe geometry at $\rho = 0.54$, $\beta = 20$; $b$ denotes $\rho = 0.66$, $\beta = 20$; $c$ denotes $\rho = 0.90$, $\beta = 20$; $d$ denotes $\rho = 0.64$, $\beta = 10$. The red circles denote the radius $r_e$ about each atom, and are essentially the “soft spheres” associated with each atom.

4.5.2.2 Radial distribution function, showing the number of neighbor counts, $N$, as a function of atom-atom distance $s$, for various geometries for the case $\rho = 0.64$, $r_e = 0.60$ and $\beta = 10$. PW-III is labeled in Figure 4.2.1.3, TR is labeled in Figure 4.2.1.1. Also shown is the Morse potential energy function $v(s)$. The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.

4.5.3.1 The potential energy function $V(\rho)$ for the geometries described in Figure 4.2.1 for $r_e = 0.60$ and $\beta = 20, 10, 6$. The bold line is the potential energy of the GM obtained through the unbiased search at several values of $\rho$. The geometry is indicated by a letter. $a$ denotes $\rho = 0.68$; $b$ denotes $\rho = 0.72$; $c$ denotes $\rho = 0.74$; $d$ denotes $\rho = 0.80$; $e$ denotes $\rho = 1.00$. The red circles denote the radius $r_e$ about each atom, and are essentially the “soft spheres” associated with each atom.
energy of the GM obtained through the unbiased search. At several values of \( p \), six restricted geometries were denoted.

A.1 Schematic representation of symmetry elements that used in the wallpaper group symmetry notation.

A.2 Schematic representation of the wallpaper group symmetry map used for adlayer geometry characterization. Each symmetry notation is a combination of symmetry elements (Figure A.1) that starts with letter: “p” (primitive cell) or “c” (face-centered cell). A number that goes after corresponds for lowest order rotation (type of rotation center) and the last, symmetry notation concludes by letter: “m” (mirror plane) and “g” (glide of reflection).

B.1 Adlayer geometries identified in this work. “Stripe” is used to designate the fact that all angles are the same. SS = ”short stripe” denotes that all angles are equal to 0 (or \( \pi/2 \) or \( \pi \)). LS = “long stripe” denotes that all angles are \( \pi/4 \). DSS designates “distorted SS”; DSS-I has two mirror planes; DSS-II has one mirror plane. SP denotes “square pattern”, where \( \theta_1 = \theta_3 = 3\pi/4, \theta_2 = \pi/4 \). DSP denotes a distorted SP, where \( \theta_1 = \theta_4 \approx 3\pi/4, \theta_2 = \theta_3 \approx \pi/4 \). HB denotes “herringbone”, where \( \theta_1 = \theta_3 \) and \( \theta_2 = \theta_4 \), and “perfect herringbone” PHB denotes that the herringbone angles alternate between 0 and \( \pi/2 \). The “irregular” geometry, designated by irr, has no symmetry elements in the unit cell, has \( \theta_1 \approx 20^\circ, \theta_2 \approx 57^\circ/6 \). This geometry is explained more fully in the text. Underneath each geometry we denoted symmetry notations explained in the text.

C.1 High-symmetry geometries identified in this work. SS is the “short stripe”, which denotes that all angles are equal to 0 (or \( \pi/3 \) or \( 2\pi/3 \) or \( \pi \)). HC (honeycomb) shows that \( \theta_1 = \pi/2 \) (or \( \pi/6 \) or \( 5\pi/6 \)), \( \theta_2 = \pi/2 \), \( \theta_3 = 5\pi/6 \), and \( \theta_4 = \pi/6 \). Degraded forms of the HC geometry are able to alternate four angles within ± \( \pi/6 \) (see Figure C.2). irr (irregular) designates that \( \theta_1 \approx \pi/6 \) and \( \theta_2 \approx 20^\circ \), \( \theta_3 \approx \pi/4 \) and \( \theta_4 = 2\pi/3 \). PHB (perfect HB) shows that the herringbone angles alternate between 0 and \( \pi/2 \). LS (long stripe) show that all angles are \( \pi/6 \) (or \( \pi/2 \) or \( 5\pi/6 \)). TR (triangular pattern) geometry has 3x3 primary cells and denotes that angles of the primary cell are alternating between 0, \( \pi/3 \) and \( 2\pi/3 \). Underneath each geometry we denoted symmetry notations explained in the text.

C.2 Herringbone geometries identified in this work. PHB denoted that the herringbone angles alternate between 0 and \( 5\pi/9 \). HB at high \( r_e \) contains set of two angles \( \theta_1 \approx 5\pi/9 \) and \( \theta_2 \approx \pi/9 \) where glide plane (that parallel to \( \tilde{y} \) axis of the triangular lattice) is a bisector with angle = \( \pi/3 \). Underneath each geometry we denoted symmetry notations explained in the text.

C.3 Adlayer geometries identified in this work. HC = “honeycomb” geometry designates that \( \theta_1 = \pi/2 \) (or \( \pi/6 \) or \( 5\pi/6 \)), \( \theta_2, \theta_3 \) and \( \theta_4 = \pi/2, 5\pi/6 \) and \( \pi/6 \), respectively. Remain degraded forms are able to alternate high-symmetry angles within ± \( \pi/6 \). Underneath each geometry we denoted symmetry notations explained in the text.
ABSTRACT

A MODEL STUDY OF ADLAYER PATTERN FORMATION OF A LINEAR MOLECULE ON SQUARE AND TRIANGULAR LATTICES

by

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University of New Hampshire, September, 2011

We have determined patterning and geometric properties of rigid-diatomic-molecular rotors, fixed on (square and triangular) the lattice site modeled by the Morse potential. Zero-K adlayer patterns were enhanced through the implementation of unconstrained multivariable function using derivative-free method (also known as simplex algorithm). Results have been obtained over wide geometry range for adlayer patterns composed of periodically repeated primary cell.

A primary focus of this work was the calculation of adlayer free energies and geometry at the ground state. Those were obtained from conformational search of the primary (2x2) cell to locate geometric configuration, which minimizes the total energy. The associated adlayer trends were interpreted in terms of nematic order parameters and characterized with the wallpaper group symmetry.
CHAPTER 1

INTRODUCTION

With the advent of STM as a tool to investigate thin layers of adsorbates on solid substrates, there has been considerable interest recently in understanding the structure and growth of these layers. The role played by such strong intermolecular interactions as hydrogen bonding has been investigated in a number of studies. However, relatively little work has been done in investigating the effect of systematic variations in the intermolecular on monolayer structure. We carry out here a study designed to elucidate some of these effects. We choose a diatomic molecule as the adsorbate, and consider a substrate lattice of square and triangular symmetries.

There have been several previous studies of the behavior of the two-dimensional monolayers formed by rigid diatomic molecules adsorbed on the lattice sites of square and triangular periodic substrates. Most of these studies have focused on the phase behavior of these monolayers as a function of temperature and density. However, there have been several studies, which have attempted to establish the ground state (zero K) structure of these monolayers -- or "adlayers", as we shall also refer to them in the remainder this work. Some workers have used this approach to determine the ground state of molecular adlayers, using a realistic intermolecular potential -- most frequently the quadrupole-quadrupole interaction between such species as H$_2$ or N$_2$.

A few authors have used a Lennard-Jones (6-12) potential between the constituent atoms to model the intermolecular interaction. But little in the way of systematic
understanding of adlayer geometries has appeared; by contrast, the theory of gas phase clusters is now well established. One advantage of this approach is that the parameters can be varied systematically and their effect on trends in the adlayer formation can be investigated. This is the approach we adopt here.

In the study of gas phase clusters, there has been extensive work carried out to determine the ground state geometry of atomic clusters using a wide variety of potential energy functions. The most frequently employed have been the Lennard-Jones and the Morse atom-atom potentials. A large literature exists in this area, and several concepts in this field are now well established: Cluster geometry can be predicted from these principles for a large range of cluster sizes. One advantage of the Morse potential is that it can incorporate the results of the Lennard-Jones potential as a special case by tuning the range parameter of the Morse potential. Several studies on gas phase Morse clusters have generated “phase diagrams”, which show the various structural packing motifs exhibited by the clusters as a function of cluster size and range parameter. Several reported structures were trended by periodic repetition of a primary cell, which never exceed size of (2 x 2) unit cell.

The goal of this work was to examine the structure of rigid diatomic molecules adsorbed on two different types of periodic lattices, square and triangular, using the Morse function to model the intermolecular potential energy. We employ techniques which have proven useful in illuminating the role of the intermolecular potential in gas-phase clusters. We utilize a Morse atom-atom potential, and search for the ground state structure, that is, the minimum of the potential energy (which will be the free energy minimum at zero K). We will also mention the APR – anisotropic plane rotor model.
Most of the more modern calculations have allowed the molecules to utilize the
dimension perpendicular to the surface.\textsuperscript{35} The APR literature (often utilizing much
simpler potential) is similar to our work in that all atoms are maintained in the adlayer
plane.\textsuperscript{36} We systematically investigate the role played by: (i) the size of the rotor; (ii) the
interaction length; (iii) the range parameter of the interaction potential. We characterize
planar geometry of adsorbed clusters by using the mathematics of wallpaper group
symmetry.\textsuperscript{37,38}

Our method and analysis elements are described in detail in Chapter 2. In Chapter
3, obtained results for ground state adlayers geometries on the square lattice were
analyzed and discussed in details. Results for the triangular lattice with subsequent
analysis and discussion are reported in Chapter 4. Conclusions are in Chapter 5.
CHAPTER 2

LATTICE-MONOLAYER MODEL AND MINIMIZATION METHOD

2.1 Geometry

A method has been developed to describe pattern formation of linear molecules adsorbed in a monolayer on a periodic lattice. Our goal is to determine the conditions under which the monolayer - “adlayer” - forms into different type of geometry patterns. The model involved in the study is as follows. The substrate is a symmetric two-dimensional lattice. We will use lattices that have square and triangular periodic symmetry:

![Diagram of lattice sites with square and triangular symmetry]

Figure 2.1.1 Schematic representation of lattice sites with (a) square and (b) triangular symmetry.

The lattice spacing is $d$. This is the distance between equivalent lattice sites. This is shown in Figure 2.1.1. All other distances are given as multiples of $d$. It is convenient
to use the following coordinates: \((x, y)\) for square and \((x, \tilde{y})\) for triangular lattices. The \(\tilde{y}\) axis is rotated 30° clockwise from the Cartesian \(y\)-axis (see Figure 2.1.2).

Figure 2.1.2 Schematic representation of a two-dimensional (a) square and (b) triangular lattices. The lattice site-to-site length is shown as a multiple of \(d\). The \(\tilde{y}\) axis is rotated, 30°, \(y\)-axis that used as a reference axis for triangular lattice. Also shown the lattice site distance to the second nearest site for square and triangular lattices.

A symmetric rigid linear rotor of length \(\rho\) occupies each lattice site of the lattice (Figure 2.1.3 panel (a)). Therefore, an interacting molecule system can be described in context as collection of rotors on a lattice whose centers of mass are separated from their nearest neighbor rotors by the lattice spacing. As a consequence of this description, their centers of mass are fixed. Therefore, the geometry of the lattice is fully defined by the set of rotor, or molecule angles.

At the tip of molecule is an atom-like species that interacts with the tips of other molecules. The atom-atom interaction energy is given by a potential energy function that depends only on the distance between the atoms. This is illustrated in Figure 2.1.3 (a) for
a pair of molecules, $i$ and $j$. The coordinates of each atom are given by the Cartesian coordinates in a lattice, the orientation angle, $\theta$, of each molecule with respect to fixed $x$-axis and the length of the molecule. For convenience, the two atoms of each molecule are labeled as $a$ or $b$ respectively, even though they have identical properties. It can be seen that between any two molecules, $i$ and $j$, four atom-atom interactions must be considered. Also, Figure 2.1.3 panel (b) illustrates the relative angle $\Theta_y$ between the molecules $i$ and $j$.

![Diagram](image)

**Figure 2.1.3** (a) This is schematic representation of molecules $i$ and $j$ which each carry homonuclear atoms $a$ and $b$, intermolecular “atom-atom” distances $r_{ij}^{aa}$, $r_{ij}^{ab}$, $r_{ij}^{ba}$ and $r_{ij}^{bb}$ and angles $\theta_i$ and $\theta_j$. (b) This panel shows angle difference, $\Theta_y$, between molecules $i$ and $j$. 
2.2 Lattice Periodicity

We utilize the periodic boundary conditions (PBC). This reduces the total configuration space from all possible values to a (2 x 2) primary cell. The PBC were applied in terms of an infinite replication (by rigid translation of the primary cell) along the (x, y) axes, (Figure 2.2.1). In our study we used a total of 9 primary unit cells to calculate molecule interactions. For each lattice symmetry, coordinates of (x, y) and (x, \( \tilde{y} \)) lattice sites were used to create plane containing as many as (6 x 6) sites, (Figure 2.2.1). A grid of 36 molecules is used to occupy those sites. We utilized a unit cell with 4 (randomly chosen) angles, \( \theta_i^{xy} \), (where \( i = 1, \ldots 4 \)) are shown in Figure 2.2.1.

![Diagram](image)

(a) (b)

**Figure 2.2.1** Schematic representation of the PBC for (a) square and (b) triangular lattice symmetry; together with the four different orientation angles, \( \theta_i^{xy} \), where \( i = 1, \ldots 4 \) in the primary cells.

In principle, the potential energy felt by each molecule in the primary cell can be calculated by summing over all other molecules. In practice, to avoid too many function
calls only molecules closest to the reference molecule are included in the sum (see Figure 2.2.2 (a)). For the square lattice, each molecule in the primary cell interacts with eight neighboring molecules. There are four potential calls per molecule pair. Thus, we need $4 \times 8 \times 4 = 128$ function calls to evaluate the potential energy for a single geometry.

For the triangular lattice (Figure 2.2.2 panel (b)), twelve neighboring molecules are needed, leading to a total of $4 \times 12 \times 4 = 192$ function calls per geometry. (We note that, had all 36 molecules been used, the number of function calls for both lattices would have been $(4 \times (36 - 1) \times 4 = 560$).

Figure 2.2.2 (a) Schematic representation of the reference molecule, $\theta_i^{xy}$, in the primary cell surrounded by neighboring molecules, $\theta_j^{xy}$, where $i = 1, \ldots, 4$ and $j = 1, \ldots, 8$, for square lattice. (b) The reference molecule, $\theta_i^{xy}$, surrounded by neighboring molecules, $\theta_j^{xy}$, where $i = 1, \ldots, 4$ and $j = 1, \ldots, 12$, for triangular lattice.
2.3 Potential Energy

The potential energy between \( i \) and \( j \) molecules is taken as the pairwise sum over all four atom-atom interactions (Figure 2.1.3 panel (a)). This interaction is given by the Morse potential as function of distance, \( r \):

\[
v(r) = V_{\text{Morse}}(r) / D_e = e^{-\beta(r-r_e)} \star (e^{-\beta(r-r_e)} - 2)
\]

(2.3.1)

where \( D_e \) is the dissociation energy of the atom-atom dimer (for convenience, all energy values will be reported in units of \( D_e \)). The Morse potential has two other parameters, \( r_e \) and \( \beta \). The interaction length \( r_e \) determines the location of the minimum of the pair potential. This minimum energy of the Morse is \( v(r) = V(r = r_e)/D_e = -1 \) as shown on this figure:

![Figure 2.3.1 Schematic representation of the Morse potential as a function of atom-atom distance, \( r \). Note that \( V_{\text{Morse}}(r) > 0 \), for \( r < \sigma \) and \( V_{\text{Morse}}(r_e) = -D_e \)](image)

where \( \beta \) is the Morse range parameter which determines the range of the atom-atom interaction. A small value of \( \beta \) means the potential is “softer” (that is, it will have a smaller force constant near \( r_e \)) than is a potential with a large value of \( \beta \), (see Figure 2.3.2).
Another quantity that can be defined from the Morse potential is $\sigma$, the distance at which $\nu(\sigma) = 0$. The value of $\sigma$ is given by:

$$\sigma(r_e, \beta) = r_e - \ln(2)/\beta \quad (2.3.2)$$

The Morse potential energy curve has two types of molecular “strain”. One is attractive strain, when the atom-atom separation distance $r > r_e$. Another is repulsive strain, when $\sigma < r < r_e$. Both types of strain will increase the minimum energy of the Morse potential from its optimal value. In order to avoid this, the system will tend to minimize strain by changing its geometry, $\theta$. 

**Figure 2.3.2** This is schematic representation of the $\nu(r)$ plot for the Morse potential with three different Morse range parameters $\beta = 20$, 10 and 6. The plot shows that “stiffness” of the Morse potential is dependent on the range parameter $\beta$.
Thus, the total potential energy between two molecules $i$ and $j$ is sum of the atom-atom pairwise interactions:

$$V_{ij} = v(r_{ij}^{aa}) + v(r_{ij}^{ab}) + v(r_{ij}^{ba}) + v(r_{ij}^{bb})$$

(2.3.3)

where $r_{ij}^{aa}$, $r_{ij}^{ab}$, $r_{ij}^{ba}$ and $r_{ij}^{bb}$ are the interatomic distances for molecules $i$ and $j$ (Figure 2.1.3 (a)). Thus, the potential energy experienced by the $i^{th}$ molecule due to all other molecules, $V_i$, is defined by:

$$V_i = \sum_{j\neq i} V_{ij}$$

(2.3.4)

Schematically this is shown in Figure 2.2.2. The total potential energy per molecule is computed as a sum of potentials divided by the number of molecules in the primary cell:

$$\bar{V} = \frac{1}{N_i} \sum_i V_i$$

(2.3.5)
2.4 Energy Minimization

The thermodynamic properties of the system are partly determined by the average potential energy value, \( \tilde{V} \), for zero \( K \), (see Equation 2.3.5). The most stable geometry configuration will be that which has the lowest \( \tilde{V} \) value on the potential energy "funnel" (Figure 2.4.1 label a.).

Thus, we search the configuration space for set of four angles \( (\theta_1, \theta_2, \theta_3, \theta_4) \) (0 \( \leq \theta_i \leq \pi \)) in the primary cell, Figure 2.2.1, to locate that configuration which minimizes \( \tilde{V} \),
which we call \( \bar{V}_{\text{min}} \). The minimum potential energy is obtained by the following procedure: for each parameter set, \( \{\rho, r_e, \beta\} \) (defined in Section 2.3), a random selection of angles is chosen using a flat random number on each of the angles. The potential energy at this point is obtained, and is further minimized (within 200 steps and angle variation threshold of 0.01° (1.74* 10^{-4} radians), (Figure 2.4.1 label b.)) by a derivative-free downhill slide (using the Matlab simplex routine)\(^{39}\) until no further improvement is achieved. Thus, in the process of minimization calculation will reject all uphill moves not allow them to overpass the energetic barrier (Figure 2.4.1 label c.) and lead to a local minimum energy, only. This is repeated for \( 10^3 \) starting points in sets of primary cell angles. The lowest energy obtained from all these initializations is reported as the best (presumably the global minimum, GM, \( \bar{V}_{\text{min}} \)) for that parameter set, and the geometry \( (\theta_1, \theta_2, \theta_3, \theta_4) \) is also reported.
2.5 Order Parameter

The order parameter, \( S \), is the tool used to analyze any geometric pattern systematically without the need for human interpretation.\(^{26,40,41} \) In principle, \( S \) is used for detection and characterization of the “liquid crystal” patterns.\(^{42,43} \) In our case, \( S \) was used for systematic characterization of any nematic, ground state adlayer pattern in terms of a degree of the order. The degree of order for any molecular pair, \( i \) and \( j \), is defined by:

\[
S_{ij} = \frac{3\cos^2\Theta_{ij} - 1}{2}
\]

(2.5.1)

where \( \Theta_{ij} = |\theta_i - \theta_j| \) is the relative angle between molecules \( i \) and \( j \) schematically represented in Figure 2.1.3(b). To get the average order parameter, \( S_i \), for any randomly-chosen molecule \( i \) surrounded by neighboring molecules \( j \) (Figure 2.2.2), we used:

\[
S_i = \frac{1}{N_j} \sum_{j \in N_i} S_{ij}
\]

(2.5.2)

where \( N_j \) is the number of interactive molecules around molecule \( i \). The averaged order parameter, \( \bar{S} \), over all \( i \) molecules in the primary cell and defined by:

\[
\bar{S} = \frac{1}{N_i} \sum_{i=1}^{N_i} S_i
\]

(2.5.3)

where \( N_i \) is the number of molecules in the primary cell.

In order to understand the order parameter, we will refer to the example in Figure 2.5.1. First figure panel is showing parallel \( i \) and \( j \) molecules. The value of \( S_{ij} \) is one, which corresponds to the highest-possible order parameter limit. All \( S_{ij} \) values were
calculated within the range from 1 to \(-1/2\), where on the second panel is shown the lowest-possible limit for \(S_{ij}\) (this is, if \(\Theta_{ij} = \pi/2\) then \(S_{ij} = -1/2\)).

(a) \hspace{1cm} (b)

\[ \theta_i \quad \theta_j \quad \theta_i \quad \theta_j \]

**Figure 2.5.1** Schematic representation of molecules \(i\) and \(j\) with calculated order parameter, \(S_{ij}\). In (a) molecules are parallel, \(\theta_i = \theta_j\) thus, \(S_{ij} = 1\). In (b) molecules are perpendicular, \(|\theta_i - \theta_j| = \pi/2\), thus, \(S_{ij} = -1/2\).

The degree of order for an adlayer pattern was obtained in form of averaged order parameter, \(\tilde{S}\), those values were used to plot the contour order parameter phase diagram (OPPD). Generally, averaged order parameter have served for systematic analyze of molecular adlayer pattern transitions extensively within the OPPD. Furthermore, the \(\tilde{S}\) will be combined with the contour energy parameter phase diagram, this will associate global potential energy with the ground state geometry (we will discuss this later in the text).
2.6 Radial Distribution Function

For any given geometry, atom-atom distances (involved in the interaction) are calculated as it discussed in Section 2.2. This gives a total of 128 and 192 distances per 4 molecules in the primary cell for square and triangular lattices, respectively. This all information has been used to make the radial distribution function, RDF, where frequency peaks were normalized to the number of nearest-neighbor interactions per molecule (Figure 2.6.1 panel a). Panel b is pictorially reflecting count of nearest-neighbor interacting atoms in the RDF. Note that panel b scheme is showing number of interactions per atom; we multiplied it by 2 to make this count per molecule. Utilizing the RDF provides a systematic visual method to understand (within a particular geometry) distribution of neighboring atoms and nearest-neighbor atom-atom distances, $s$, that are relative to $r_e$. Where the first peak (from left) designates presence of 2 nearest-neighbors atom-atom distances (that is, there are two NN interactions per molecule), at the $s_1 = r_e$ (for the short stripe geometry). Any frequency peak is located out of the attractive range of the potential energy curve, such peak has insignificant contribution to the global energy. In most cases less significant peaks were declined from the RDF.
Figure 2.6.1 (a) Radial distribution function, RDF, of the short stripe geometry, (left y-axis) superimposed on the potential energy plot (right y-axis). Each frequency peak is the count of nearest-(next-nearest-, second-next-nearest-, etc.) neighbor per molecule, their bin width 0.03 and locations (this is, the NN (first left peak), NNN (second peak from the left) and etc.) are relative to $r_e$. (b) Schematic representation of neighboring atoms per atom. Count was multiplied by 2 and reported as number of neighboring atoms per molecule.
3.1 Introduction for Results on Square Lattice

In this chapter we consider a linear molecule of length $\rho$ on the square lattice. We will compare our results to the results in the literature. Several ground state adlayer geometries on square lattice have been previously identified.\textsuperscript{16,44} In our work, we were able to identify several “new” minimum energy adlayer geometries. Those include geometries in which one or more molecules in the adlayer adopt a distortion with respect to the highly symmetric “parent” geometry. Along with covering results in our model (which is related to the anisotropic plane rotor model, APR) those geometries are excluded from introduction, but will be mentioned in the discussion, where appropriate. However, the following have been seen before: square pattern, various types of herringbone and stripe geometries.

In our work we use a wide range of potential energy. This allows us to report a wider range of adlayer geometries than has been seen by other workers.
3.2 The Nearest-Neighbor Atom-Atom Distance, $s$

Based on the $V_{\text{min}}$ (defined in Section 2.4), we can identify adlayer geometries at their ground state along with the nearest-neighbor atom-atom distance, $s$. Let it be the square lattice whose patterns were summarized in Figures 3.3.1. As will be shown later, the minimum atom-atom distance, $s_I$, will be significant in understanding the total potential energy. For some of the simpler geometries, the minimum atom-atom distance can be easily given in closed form. For instance, consider the square pattern, SP (Figure 3.3.1.1), which has 2 sets of angles in its primary cell: $\theta_1 = \theta_2 = \pi/4$ and $\theta_2 = \theta_3 = 3\pi/4$. The minimum nearest-neighbor (NN) atom-atom distance, $s_I$, is given by $s_I = s = 1 - \rho/\sqrt{2}$. By reviewing SP geometry and recalling the periodicity of the lattice, we note that there are $N_1 = 4$ (that is, there are four NN interactions per molecule). These are all between atoms on molecules whose centers lay one lattice spacing away from any reference molecule. The second- or next-nearest-neighbor (NNN) interaction occurs between atoms lie on molecules whose center of mass has separation distance of $\sqrt{2}$, and the NNN distance is therefore $s_2 = \sqrt{2} - \rho$. There are $N_2 = 2$ NNN interactions per molecule. So the potential energy (per molecule) for this geometry can be written:

$$V(\rho) = N_1v(s_1) + N_2v(s_2) + ...$$

(3.2.1)

where, $v$ already defined in Section 2.3 and as mentioned above atom-atom interaction count and minimum distances are $N_1 = 4$, $s_1 = 1 - \rho/\sqrt{2}$ and $N_2 = 2$, $s_2 = \sqrt{2} - \rho$ (for the SP geometry).
Now we consider the effect of \( \rho \) on the minimum distance and the NN interaction count. For \( \rho \to 0 \), molecules are capable of being completely relaxed in their 2D rotation (although we note that the \( \rho = 0 \) case itself is trivial, since it corresponds to molecules of zero length). However, if to take the square pattern, SP, with fixed angles within the unit cell and continuously decrease \( \rho \) length to zero, then \( s_I \to 1 \). Now, each atom lies on a lattice site, two atoms on four lattice sites are NN to two reference atoms and they separated as far as lattice spacing go. In addition, both atoms on each of the next-closest lattice sites (\( \sqrt{2} \)) are now next-nearest-neighbors (NNN) to considered two reference atoms. The potential energy per molecule is given by:

\[
V(\rho = 0) = N_1 v(s_1) + N_2 v(s_2) + ... \tag{3.2.2}
\]

where for \( \rho = 0 \) and \( s_1 = 1 \) and \( s_2 = \sqrt{2} \), now \( N_1 = N_2 = 16 \). The number of NN available for each adlayer geometry will be important in determining the minimum-energy geometry, and we shall emphasize this in what follows.

In addition, in the limiting case of high \( \beta \), \( |\nu(r > r_e)| \gg |\nu(r_e)| \). Therefore the pair potential will approach to zero for \( r > r_e \), meaning that only the nearest-neighbor interaction contributes to the total potential.

In addition, the potential will be greater than zero (repulsive) for \( r < \sigma = r_e - \ln(2) \beta \approx r_e \) for a large value of \( \beta \). Therefore, the high \( \beta \) case will usually be the starting point for discussions. The result and discussion section will use the concept of the minimum atom-atom distance together with a discussion of the range parameter \( \beta \).
The explicit equations of $s_i(p)$ for the simple geometry cases (Figure 3.3.1.1) that contributes most to the total potential are given in Table 3.2.2. Note that those $s_i$ equations can describe atom-atom separation in closed form, atom-atom separation for remaining geometries are shown as $s_i(p)$ curves in Figure 3.3.2.

Table 3.2.1 Closest nearest-neighbor (NN) atom-atom distance, $s_j$, for specified geometry as a function of $p$. Also included in parentheses is the number of nearest-neighbor atoms, $N_j$. Note that there are two possible NN distances for the LS geometry, designated “tip-to-tip” and “side-by-side”. Those four and other curves were plotted in Figure 3.3.2.

\[
SS: \quad s_i(p) = 1 - \rho; \quad N_i = 2
\]

\[
SP: \quad s_i(p) = 1 - \rho / \sqrt{2}; \quad N_i = 4
\]

\[
PHB: \quad s_i(p) = \sqrt{1 - \rho + \rho^2 / 2}; \quad N_i = 8
\]

\[
LS: \quad s_i(p) = \min(\sqrt{2} - \rho, \sqrt{1 + \rho^2 - \rho \sqrt{2}}); \quad N_i = (2,4)
\]
3.3 Minimum NN Separation for Specified Ground State Geometries

In order to explain the adlayer pattern formation on the square lattice, we focus our analysis on four simple high-symmetry adlayers, and one low-symmetry adlayer. The four high-symmetry geometries are: the short stripe (SS); the square pattern (SP); the long stripe (LS); the perfect herringbone (PHB) (See Figure 3.3.1.1). Note, that high-symmetry, ground state geometries (at certain parameter conditions) are able to degrade to its one or several distorted forms (we looked them as a transitional geometry forms). Distorted adlayer patterns are: the distorted SS – I and – II (DSS – I and DSS – II), the distorted SP (DSP) and herringbone (HB – I and HB – II) (See Figure 3.3.1.2). The basic principle of this is to designate pattern’s degradation from the high-symmetry. Where each degraded-geometry is connected to it’s high-symmetry parent, except for the one: the irregular (irr) ground state geometry. It has an irregular or low-symmetry geometry (this is, presence only of \( \pi \) rotation-center symmetry element, see Appendix A.2). In spite of the low-symmetry, the irr geometry was denoted for a great number of nearest-neighbors per molecule. Also, note that the main difference of the irr from the remaining adlayers is the primary cell, which has no similar angle repetition: \( \theta_1 \neq \theta_2 \neq \theta_3 \neq \theta_4 \).
Figure 3.3.1.1 High-symmetry adlayer geometries found during the optimization. “Stripe” is used to designate the fact that all angles are the same. SS = “short stripe” denotes that all angles are equal to 0 (or $\pi /2$ or $\pi$). LS = “long stripe” denotes that all angles are $\pi /4$. SP denotes “square pattern”, where $\theta_1 = \theta_4 = 3\pi /4$, $\theta_2 = \theta_3 = \pi /4$. The “perfect herringbone” PHB denotes that the herringbone angles alternate between 0 and $\pi /2$. The “irregular” geometry, designated by irr, has no symmetry elements in the unit cell, has $(\theta_1, \theta_2, \theta_3, \theta_4) = (135^\circ, 152^\circ, 10^\circ, 102^\circ)$. These geometries are explained more fully in the text.
Figure 3.3.1.2 Low-symmetry adlayer geometries found during the optimization, and not described in Figure 3.3.1.1. DSP denotes a distorted SP, where $\theta_i = \theta_4 \approx \pi / 4$, $\theta_2 = \theta_3 \approx 3\pi / 4$. The distortion angle is given by $\phi = \pi / 4 - \theta_1 = 0.44$. HB-I denotes "herringbone" (of type I), where $\theta_1 = \theta_2$ and $\theta_2 = \theta_3$. The HB angle for the geometry shown is given by $\eta = |\theta_1, \theta_3| \approx \pi / 3$. The alternative form of "herringbone" (HB-II) has $\theta_1 = \theta_2 = \theta_3$ and $\theta_2 = \theta_4$. DSS designates "distorted SS"; DSS-I has $\theta_1 = \theta_2 = \theta_3$ and therefore possesses two mirror planes, and can be described by a "buckling" angle, $\theta_1$, here 20°. DSS-II has $\theta_1 = \pi - \theta_1$, $\theta_2 = \pi - \theta_2$ and has one mirror plane, and can be described by two angles, here $(\theta_1, \theta_2) = (44°, 155°)$. 
Adlayer patterns and their abbreviation (mentioned in Figures 3.3.1) are summarized in the following table:

<table>
<thead>
<tr>
<th>Geometry Case</th>
<th>Adlayer Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-Symmetry Adlayer Case</td>
<td>Short Stripe (SS)</td>
</tr>
<tr>
<td></td>
<td>Long Stripe (LS)</td>
</tr>
<tr>
<td></td>
<td>Square Pattern (SP)</td>
</tr>
<tr>
<td></td>
<td>Perfect Herringbone (PHB)</td>
</tr>
<tr>
<td>Irregular, Low-Symmetry Adlayer Case</td>
<td>Irregular (irr)</td>
</tr>
<tr>
<td>Distorted (Transitional) Adlayer</td>
<td>Distorted Short Stripe – I (DSS – I)</td>
</tr>
<tr>
<td>Symmetry Case</td>
<td>Distorted Short Stripe – II (DSS – II)</td>
</tr>
<tr>
<td></td>
<td>Distorted Square Pattern (DSP)</td>
</tr>
<tr>
<td></td>
<td>Herringbone (HB)</td>
</tr>
</tbody>
</table>

The low-symmetry adlayer, irr (geometry shown in Figure 3.3.1.1.), was representative of a family of geometries with similar properties. It was chosen because when \( \rho = 1 \) this geometry has the higher NN count than does any of the high-symmetry geometries at the same value of \( \rho \). We note that at \( \rho = 1, r_e = 0.6 \) the \( N_1(\text{irr}) = 4 - 5 \) per molecule.

The curves \( s(\rho) \) for these six cases (SS, SP, LS, irr, PHB) with chosen fixed geometries are shown in Figure 3.3.2. (In the case of the LS, the discontinuity arises from the fact that \( s_I \) is the tip-to-tip interaction length at low \( \rho \), but later switches over to the side-by-side interaction).
Figure 3.3.2 The minimum atom-atom separation distance, $s_l$, as a function of rigid molecule length, $\rho$, for chosen fixed geometries. The geometry labels SS, SP, LS, irr, PHB are explained in the caption to Figure 3.3.1.
3.4 Adlayer Symmetry Notations

The wallpaper group symmetry notations were used to characterize adlayer patterns (mentioned in Figure 3.3.1). This mathematical classification technique of two-dimensional repetitive patterns is based on applying symmetry elements on a pattern of interest (for detailed descriptions of this selective method refer to Appendix A). For instance, on a plane, there are seventeen possible distinct symmetry notations (14 notations on the square lattice), denoted by the wallpaper group symmetry.\textsuperscript{37,45} In our work we were able identify seven adlayer symmetries. Patterns with symmetry elements and detailed description of the characterization process are reported in Figure B.1 (of Appendix B) and summarized in the following table:

Table. 3.4.1 Summary of characterized patterns on square lattice with the wallpaper group symmetry notations.

<table>
<thead>
<tr>
<th>Square Lattice</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short Stripe (SS)</td>
<td>p2mm</td>
</tr>
<tr>
<td>Distorted SS - I (DSS - I)</td>
<td>c2mm</td>
</tr>
<tr>
<td>Distorted SS - II (DSS - II)</td>
<td>c2mm</td>
</tr>
<tr>
<td>Square Pattern (SP)</td>
<td>p4mm</td>
</tr>
<tr>
<td>Distorted SP (DSP)</td>
<td>p4</td>
</tr>
<tr>
<td>Perfect Herringbone (PHB)</td>
<td>p4gm</td>
</tr>
<tr>
<td>Long Stripe (LS)</td>
<td>p2mm</td>
</tr>
<tr>
<td>irr</td>
<td>p211</td>
</tr>
<tr>
<td>Herringbone (HB)</td>
<td>p2gg</td>
</tr>
</tbody>
</table>
3.5 Contour Order Parameter Phase Diagrams, OPPD

In this section we will introduce the contour order parameter phase diagrams, OPPD, for values of the Morse range parameter, $\beta = 20$, 10 and 6. The averaged order parameter values $\tilde{S}$ (Equation 2.5.1) are plotted as function of distance parameters $(\rho, r_e; \beta)$. These are shown in Figure 3.5.1. Values in the color bar reflect the range of calculated order parameters, $1.0 \geq \tilde{S}(\rho, r_e; \beta) \geq -1/2$. In addition, that range corresponded to a coloration of the plots and used for visual comprehension of adlayer pattern distribution along (distance) parameters, $(\rho, r_e)$. For instance, the $\tilde{S}(\rho, r_e; \beta) = 1$, that shows that molecules lying in parallel, “stripe” geometry (with angle difference: $\Theta_{ij} = 0$). On the diagram, this is denoted with red color, Figure 3.5.1. It was fairly easy to assign borders for SS, DSS – I, irr, LS and HB patterns based on the contour. For the remaining regions, (DSS – II, SP, DSP and PHB) labels were assigned after visual inspection of the adlayer patterns at chosen points. Borders of each colored region were shown with a black line, which were used in the next section to interrelated distribution of the global energy with ground state geometries from Figure 3.3.1. All these regions are designated with an abbreviation and summarized in Table 3.3.1.
Figure 3.5.1 Contour order parameter phase diagram as function of (distance) parameters ($\rho$, $r_e$) for several values of the Morse range parameters, $\beta$, on the square lattice. The key for the plot coloration is at the color bar (top panel). I and II used to designate regions DSS-I and DSS-II respectively, for clarity. See keys for all abbreviation labeling in Table 3.3.1.
3.6 Contour Energy Parameter Phase Diagrams, VPPD

Contour energy parameter phase diagram, VPPD, \( \tilde{V}(\rho, r_e; \beta) \) is shown in Figure 3.6.1. Interrelated (OPPD and VPPD) diagrams are able to provide meaning for transition in between these adlayer regions at the OPPD.

Essentially, given VPPD will be used to analyze horizontal “cuts” (a lines, \( V(\rho, r_e(0.30, 0.60, 0.68); \beta (20, 10, 6)) \) through the potential energy function for various restricted geometries, (Figures 3.7.(1-3).1). When \( r_e = s(\rho) \) for a particular geometry, at least \( N_1 \) of the atom-atom distances are at their optimal value. Thus, we can estimate the potential energy for a given value of \( r_e \) (and large \( \beta \)) as being \(-N_1\) at that geometry. For instance, the line marked “SS” in Figure 3.3.2 gives the region of the \((\rho, r_e)\) parameter space where the SS geometry will be preferred. Furthermore, if we consider high (but not infinite) \( \beta \) we note that below and to the left of the SS line, the system will also tend to adopt the SS geometry (although there will be some “attractive” strain), since \( s > r_e \). For \( \rho \) values that lie to the right of this line, the SS geometry is now strained by repulsion, and becomes untenable. Further increase of \( \rho \) brings us to the SP line, where SP will be the most stable adlayer geometry.

In order to understand the energy parameter phase diagrams fully, we now examine each region in detail. To do this, we actually examine the full potential for each of the selected adlayer geometries as a function of \( \rho \). Plots are made at the three values of \( \beta \) used in Figure 3.7.(1-3).1, and for three fixed values of \( r_e \). These illustrative values of \( r_e \) are discussed in detail below.
Figure 3.6.1 Contour energy parameter phase diagrams as function of (distance) parameters ($\rho, r_e$) for several the Morse range parameters, $\beta$, on the square lattice. The key for the plot coloration is at the color bar (top panel). I and II used to designate regions DSS-I and DSS-II respectively, for clarity. See keys for all abbreviation labeling in Table 3.3.1.
3.7 Analysis of Energy Parameter Phase Diagrams

3.7.1 Small Value of $r_e (r_e = 0.30)$, Stripe and Square Pattern Geometries

In this section we will consider several plots of the potential energy, $V(\rho; r_e(0.30)$, $\beta(20, 10, 6))$ shown in Figure 3.7.1.1 for all ground state geometries from Figure 3.3.1.1. These energy plots will be correlated within the radial distribution function, RDF, (introduced in Section 2.6). The radial distribution functions, $N(s)$, were used for parameters: $r_e = 0.30; \rho = 0.70, 0.74, 0.88, 0.98$ and 1.10; $\beta = 20$ and shown in Figures 3.7.1.2 and 3.7.1.3. Thus, for small $r_e$ case we will consider six competing geometries (SS, DSS-I, DSS-II, SP, DSP and LS) that are preferred for different ranges of $\rho$.

We initially focus on the results for large $\beta$ (Figure 3.7.1.1, top panel), where the bold line is the potential energy of the global minimum, GM, obtained through the unbiased search. When $r_e$ is small, the molecules need to be fairly long to bring the atoms into contact with each other. For $\rho \leq 0.70$, the maximum attraction is obtained by the short stripe geometry, Figure 3.7.1.1.
Figure 3.7.1.1 The potential energy function $V(\rho)$ for the geometries described in Figure 3.3.1.1 for $r_e = 0.30$ and $\beta = 20, 10, 6$. The bold line is the potential energy of the GM obtained through the unbiased search. In the top panel, the cartoons illustrate the optimum geometry for several values of $\rho$. The red circles denote the radius $r_e$ about each atom, and are essentially the “soft spheres” associated with each atom.
The GM energy of the SS curve found to be \( V_{SS} = N_1 \nu(r_e) = -2 \) this is when \( s_j = r_e = 0.30 \) (where \( N_1 \) was obtained from the RDF as the first frequency peak, Figure 3.7.1.2, SS row, left panel). As \( \rho \) increases further the SS geometry becomes repulsively strained and cannot longed maintain the SS geometry. As \( \rho \) becomes larger, \( s_j \) for the SS geometry decreases, and will become less than \( \sigma (r_e, \beta) \), rendering the SS geometry repulsive.

However, the \( N_1=2 \) can be maintained by allowing the stripes to "buckle", with the geometry DSS-I (\( \theta_4 = \theta_1 \) and \( \theta_3 = \theta_2 \)), see Figure 3.7.1.1.

As \( \rho \) further increases towards 1.00, where the square pattern, SP (with \( N_1=4 \) and the GM potential energy is \( V_{SP} = N_1 \nu(r_e) = -4 \)), is the optimal geometry. But just before when the \( \rho=1.00 \), the DSS-I (\( \theta_4 = \theta_1 \) and \( \theta_3 = \theta_2 \)), geometry buckles further (to DSS-II, whose angles are \( \theta_3 = \pi - \theta_1 \) \( \theta_4 = \pi - \theta_2 \) trying to increase the NN count from 2 to 4, when the NNN frequency peak (second peak on the RDF) is approaching to the \( s_j \) (see Figure 3.7.1.2, DSS-I row, right panel). Especially, this is the case for the DSS-II, RDF shows an additional attraction contributed from the NNN, that maintain additional decrease of the GM energy, \( V_{DSS-II} \approx -3 \). We can describe these geometries as "transitional" or "degraded" forms of high-symmetry geometries.
Figure 3.7.1.2 Radial distribution function, showing the number of neighbor counts, \( N \), as a function of atom-atom distance \( s \), for various geometries for the case \( r_e = 0.30 \) and \( \beta = 20 \). SS and SP are labeled in Figure 3.3.1.1. DSS-I and DSS-II are described in Figure 3.3.1.2. Also shown is the Morse potential energy function \( v(s) \). The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.
We note that our simplistic analysis (Figure 3.3.2) predicts that the LS geometry will become significant near $\rho = 1.10$ and will have a GM potential energy $V_{LS} = -2$. By $\rho = 1.00$ (Figure 3.7.1.1), the system is now fully relaxed in the SP geometry. As $\rho$ increases beyond 1.00, more than can sustain the SP, the distorted SP (DSP) becomes the dominant geometry. Furthermore, from Figure 3.7.1.1, we see a competition between the favored DSP geometry and LS (at $\rho = 1.10$). The family of DSP has a lower potential energy since it maintains four NN. At $\rho = 1.10$ value, the LS will next be preferred and will have a potential energy $V_{LS} \approx -2$. See Figure 3.7.1.3
Figure 3.7.1.3 Radial distribution function, showing the number of neighbor counts, $N$, as a function of atom-atom distance $s$, for various geometries for the case $r_\alpha = 0.30$ and $\beta = 20$. LS and SP are labeled in Figure 3.3.1.1. DSP is described in Figure 3.3.1.2. The distortion angle of the DSP from the square is $\varphi = 0.44$. Also shown is the Morse potential energy function $v(s)$. The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.
The same general trend is very similar for the lower values of $\beta$ (Figure 3.7.1.1 middle and low panels). However, it should be noted that as the value of $\beta$ decreases, and the potential becomes “softer” and longer range, several new features come into play. In particular, since SP has both a larger values of $N_1$ and $N_2$ than does SS (Figure 3.7.1.2), the $\rho$ range over which SP is the dominant geometry increases at the expense of SS.

Turning now to the full contour VPPDs, we note that the above analysis using RDF histograms (with their frequency of each distance), Figure 3.3.2 together with the extra insight gained by studying the various plots of $V(\rho)$ helps explain the results of the full minimization for this value of $r_e$. 
3.7.2 Large Value of $r_e$ ($r_e = 0.74$), Herringbones and Perfect Herringbone

It is useful at this point to consider a large value of $r_e$, namely $r_e = 0.74$, since this introduces an important geometry family, the herringbone, and this $r_e$ is representative of this region. The herringbone is characterized by two independent angles, $(\theta_1, \theta_2)$. If $\theta_4 = \theta_1$ and $\theta_3 = \theta_2$ we label the geometry as HB-I; if $\theta_4 = \theta_2$ and $\theta_3 = \theta_1$ we label the structure as HB-II. The perfect herringbone (PHB) is clearly of type HB-I, and was described earlier. It has $\theta_1 = 0$ and $\theta_2 = \pi/2$. The values of $s_1$ and $N_1$ for the perfect herringbone are given in Table 3.2.1. An important HB-I geometry is shown in Figure 3.3.1.2. This is the HB-I $(15^\circ, 75^\circ)$, where the two angles differ by $60^\circ$. This geometry is important at large values of $\rho$, where the system can attain a geometry that is only very slightly distorted from hexagonal close-packing, in which the vectors between neighboring atoms would all be $60^\circ$. 
Figure 3.7.2.1 Potential energy $V_{\text{geometry}}(\rho)$ for the HB(15°, 75°) and PHB for the case $r_e = 0.74$, $\beta = 20$. The cartoons show the geometry at selected values of $\rho$. The circles around each atom have radius $r_e$.

In Figure 3.7.2.1, we plot the energy for the PHB and the HB-I (15°, 75°) as a function of $\rho$. It can be seen that (for this large value of $r_e$) the energy of the PHB decreases as $\rho$ increases from 0 to 0.74, at which value $s_I = r_e$, where $V_{\text{PHB}} = -8$. (This is why this $r_e$ was chosen.) The cartoon (Figure 3.7.2.1) illustrates that the PHB has 8 NN, whereas the HB-I shown here has about 4 NN by the $\rho$ value of 0.60.

By large values of $\rho$, however, say $\rho = 1.10$, the HB-I has a NN count of approximately 10. The reason for this is that for sufficiently large $\rho$, each atom behaves
approximately as a single atom, and the potential will be optimized by the other atoms
attaining hexagonal close-packing. On an isotropic surface, in a close-packed monolayer
of spherical species each atom would have 6 NN. Clearly, the rotor itself blocks one of
the close-packing atoms, leading to an \( N_1 \) for the rotor of about 10. This has already been
noted\(^{46}\) in a model study of bis-fullerenes on gold. By contrast, the atom-atom distances
for the more constrained PHB geometry are decreased below \( r_e \), and the system
experiences some repulsive strain.
3.7.3 Large Value of $r_e$ ($r_e = 0.68$), Long Stripe

In Figure 3.7.3.1, we plot the optimized potential energy $V(\rho; r_e(0.68); \beta (20, 10, 6))$ together with the potential energy $V_{\text{geometry}}(\rho)$ for the same geometries as described in Figure 3.3.1.1 (plus HB geometry).

Looking first at the $s_I(\rho)$ plot (Figure 3.3.2), we see that in this region, we expect the stripes and the square pattern to be stable at low $\rho$. At low $\rho$, the trends are similar to those observed at smaller values of $r_e$, but the range of values of $\rho$ for which SS, SP and irr are dominant is much smaller. Near $\rho = 0.50$, the preferred geometry is the distorted square, in common with our findings at previous $r_e$ values. However for $\rho >$ about 0.60, the LS geometry might be expected to be significant. See Figure 3.7.3.1.
Figure 3.7.3.1 The potential energy function $V(\rho)$ for the geometries described in Figure 3.3.1 for $r_e = 0.68$ and $\beta = 20, 10, 6$. The bold line is the potential energy of the GM obtained through the unbiased search. In the top panel, the cartoons illustrate the optimum geometry for a selected value of $\rho$. The GM potential energy is not shown in the bottom panel for clarity.
Where at $\rho = 0.75$, LS is shown as the most favored pattern with GM energy $V_{LS} = N_1 \nu(r_e) = -6$, since for this particular value of $\rho$ both the atom-atom and side-by-side NN distances are the same, which makes $N_1 = 6$. At this $r_e$ case, further increase of the $\rho$ will introduce the repulsive strain that split number of NN into $N_1 = 4$ (side-by-side interaction) and $N_2 = 2$ (atom-atom interaction). This is shown in cartoon of Figure 3.7.3.1 and note that the GM curve corresponds to that the LS is present for a short range of $\rho$.

In keeping with previous discussions of the effect of deceasing $\beta$, it would be expected that the “LS” region will be “swamped” by the HB-related regions, since these intrinsically possess more NN, and become broader in the $\rho$ space as $\beta$ decreases. Thus, the long stripe geometry (LS) is the global minimum only for the case of the most rugged potential energy surface explored here.
Finally, we consider a cut at constant $r_e = 0.60$. This value of $r_e$ was chosen since it corresponds with the region where an "irregular" geometry (see Figure 3.3.2) was detected as the global energy minimum for several points in the parameter space. This was a surprise to us, and we investigated it carefully. In Figure 3.7.4.1, we plot the global energy minimum $V(\rho; r_e(0.60); \beta(20))$, together with $V_{\text{geometry}}(\rho)$ for the square pattern, as well as for the herringbone systems mentioned earlier. As pointed out earlier, the selected irregular geometry (shown in Figure 3.3.1.1) has a NN count of about 4-5 near $\rho = 1.00$. It can be seen that both the herringbones (as well as all other higher-symmetry adlayer geometries) have energies higher than this near $\rho = 1.00$, and at several other values of $\rho$. 
Figure 3.7.4.1 The potential energy function $V(\rho)$ for several geometries described in Figure 3.3.1 for $r_e = 0.60$ and $\beta = 20$. The bold line is the potential energy of the GM obtained through the unbiased search. At several values of $\rho$, the geometry is indicated by a letter. The corresponding labeled cartoons illustrate the optimum geometry for that value of $\rho$. a denotes $\rho = 0.60$; b denotes $\rho = 0.70$; c denotes $\rho = 0.86$; d denotes $\rho = 1.00$; e denotes $\rho = 1.15$. The interesting point is that the irr geometry manages to beat out the best two, herringbones at point b, and it seems to be due to NNN. See following figure. HB-II becomes "crowded" as $\rho$ increases, ending up the way they look at point d.
At $\rho = 0.50$, for reasons explained earlier, the square pattern is the GM, and distorted square is preferred for slightly larger values of $\rho$, since it maintains the 4 NN count. It is clear from Figure 3.7.4.1 that HB-I is closely related to the distorted square, and retains its NN count (point a on Figure 3.7.4.1) and is the GM until point b. At this point, the three structures HB-I, HB-II and “irr” are all competitive. By examining the radial distribution function at this point (Figure 3.7.4.2) we see that the “irr” appears to be favored because of its number of NNN.

By point c, however, we see that the preferred pattern changes to HB-II, which has two different environments: one has NN 4; the other has NN 6. Thus, when $\rho$ is sufficiently large to allow this geometry, it will have an energy of approximately -5. This is lower than the $V_{HB-I} = -4$ and all the irregular geometries we located in this region were local (not global) minima.

As $\rho$ is further increased (towards point d), it can be seen that the HB-II geometry becomes repulsive, leaving a range of $\rho$ values (from 0.90 to 1.20) where the irregular geometry is once more the global minimum.

By point e, the HB-I is becoming similar to a close-packing environment, and has more than four nearest neighbors.

This alternation between the various forms or herringbone and irregular geometry can be seen in the parameter phase diagram in Figure 3.6.1.

We consider now the effect of reducing the range constant $\beta$ we note (from Figure 3.6.1) that the irregular region persists at large $\rho$ near the $r_e$ value of 0.60 as the potential is softened. However, in common with all the previous cases (see, for instance Figure
3.7.3.1), as the potential is softened, the energy spacing between the ground state and excited states becomes extremely small.

![Figure 3.7.4.2](image)

**Figure 3.7.4.2** Radial distribution function, for three geometries in the herringbone region, showing the number of counts, N, as a function of atom-atom distance s, for \( \rho = 0.70, 0.86, 1.00 \) corresponding to b,c,d on Figure 3.7.4.1. \( r_e \) is fixed at 0.60, \( \beta = 20 \). Also shown is the Morse potential energy function \( V(s) \). The potential energy of each geometry is indicated on the figure. The GM geometry is indicated with an asterisk. For \( \rho = 0.70 \), all three geometries have a NN count of four. However the HB-II geometry is beginning to experience repulsive strain. The HB-I is very similar to the distorted square geometry. It and the irr geometries are very similar as far as their NN are concerned. However, the irr has a slightly lower energy since it has one extra NNN at 0.75. For \( \rho = 0.86 \), the HB-II geometry has 5 NN, making it the global minimum. For \( \rho = 1.00 \), the HB-II is clearly strained. The HB-I has 4 NN; the irr has 5 NN, making it the global minimum.
3.8 Energy Parameter Phase Diagram Revisited

With the above results in place, we can now return to the contour VPPD with profit. As expected from the above, a slice through Figure 3.6.1 at low $r_e$ shows that the geometries predicted above are, indeed, the dominant ground state geometries founded from global minimum minimization search. However, we have found several transitional geometry forms (geometries lower in symmetry) between groups of high-symmetry geometries (shown in Figure 3.3.1.1).

At $r_e = 0.60$, we note the appearance and dominance of the irr pattern at large $\rho$, again, as predicted by NN count in fixed irr geometry in the radial distribution function (and recall that there is considerable “play” in the irr angles, so they can adjust to find the best potential).

At $r_e = 0.68$, we note that the structure is very sensitive to the value of the Morse parameter $\beta$. We have seen that for large $\beta$ the LS pattern (and its distorted variants, HB-II) appears near $\rho = 0.8$, and the HB-I variant of the PHB is dominant at large $\rho$. As $\beta$ is reduced, the different geometries become closer in energy, and the PHB (with its large number of NN contacts) becomes dominant.

At $r_e = 0.74$ and large $\rho$, we note that each atom of the HB-I structure is behaving as a single atom. The potential will be optimized by other atoms and attain formation of the hexagonal close-packing.
3.9 Conclusions for Results on Square Lattice

We have examined the putative global potential energy minimum ("ground state") for a system of homonuclear diatoms on a square lattice interacting through a pairwise additive atom-atom Morse potential. The use of the Morse potential allows us to control the range of the potential, which, in turn, controls the ruggedness of the potential landscape.

For the largest value of the $\beta$ (most rugged landscape) a large number of minimum-energy geometries have been identified. For small $r_e$ (that is, for cases where the interaction length is considerably smaller than the lattice spacing – a region that might be applicable for realistic molecules adsorbed on crystal lattices) we find a rich variety of adlayer geometry types. For small $\rho$ (small molecules) the dominant geometry is that of the short stripe (SS), in which the molecules try to optimize their NN interactions. As the size of the molecule is increased (keeping $r_e$ constant) we see a gradual transition to square pattern (SP) adlayers, and their close relations (such as distorted squares, DSP).

For $r_e = 0.50 - 0.70$, at large $\rho$, many of the preferred geometries are “irregular”, although long stripe (LS) are observed in some ranges of the parameters.

For large $r_e$ (that is, when the interaction range is on the same order of magnitude as is the lattice spacing) the dominant patterns are perfect herringbone (PHB, small $\rho$) and herringbones (HB, large $\rho$).

There are few published values for the minimum energy geometry for model (e.g. Lennard-Jones, LJ) potentials available. In a study of such a system$^{47}$ find a continuous order-disorder transition as the temperature is increased. Their LJ potential has $r_e \approx 0.98$, ...
\( \rho \approx 0.30 \) (in our units). From our work (see Figure 3.2.2) we note that this system has a 
PHB ground state (in agreement with their results). We also note (see for example, Figure 3.7.3.1) that the ground state is almost degenerate with all the excited state geometries. Therefore, since there is no distinct geometry for the first excited state, it is not 
unsurprising that this manifests itself as continues order-disorder transition. Comparable 
calculations carried out on a more rugged potential energy surface (such as with \( \beta = 20 \)) 
might be expected to show a sharper phase change.
CHAPTER 4

RESULTS AND DISCUSSION FOR TRIANGULAR LATTICE

4.1 Introduction for Results on Triangular Lattice

Several ground state adlayer geometries on triangular lattice have been previously identified by other workers. These include geometries in which one or more molecules in the adlayer adopt a perpendicular position with respect to the triangular lattice, or form a vacancy within the pattern network geometry (for same or different molecule types). In our work, we were able to identify “known” and several “new” minimum energy adlayer geometries. Along with covering results in our model (which is related to the anisotropic plane rotor model, APR) those geometries are excluded from introduction, but will be mentioned in the discussion, where appropriate. However, the following have been seen before: various types of herringbone and stripe and pinwheel geometries.

Again, in our work we use a wide range of potential energy. This allows us to report a wider range of adlayer geometries than has been seen by other workers.
4.2 Adlayer Symmetry Labels and the Nearest-Neighbor Atom-Atom Distance, s

In common with our work on the square lattice (discussed in Chapter 3), here we utilize the same methodology in order to found the total global minimum (GM) potential energy and several ground state geometries. These geometries (shown in Figures 4.2.1.1 - 4.2.1.3) are described below.

Figure 4.2.1.1. Six high-symmetry ground state adlayer geometries found during optimization. “Stripe” is used to designate the fact that all angles are the same. SS (short stripe) geometry denotes that all angles are equal to three degenerate forms: 0, π/3 or 2π/3. LS (long stripe) denotes that all angles are π/6 (or π/2 or 5π/6). HC (honeycomb) designates that θ₁ ≈ 5π/6 and θ₂ ≈ π/6, θ₁ ≈ π/2 (or π/6 or 5π/6), θ₃ = π/2. The HC geometry is able to create several types of pinwheel (degraded HC) geometries (see Figure 4.2.1.3) by alternating primary cell angles within ± π/6. PHB (perfect herringbone) denotes that angles alternate between 0 and π/2. The irr (irregular) designates that θ₁ ≈ 30° and θ₂ ≈ 20°, θ₃ ≈ 40° and θ₄ = 120°. TR (triangular pattern) geometry has 3x3 primary cells and denotes that angles of the primary cell are alternating between 0, π/3 and 2π/3.
Figure 4.2.1.2 Ground state herringbone geometries are identified. The perfect herringbone (PHB) geometry discussed in Figure 4.2.1.1. HB denotes “herringbone”, where $\theta_1 = \theta_3$ and $\theta_2 = \theta_4$. The HB angle for the geometry shown is given by $\eta = |\theta_1 - \theta_2| = \pi/4$. HB(DSS) denotes “herringbone” (distorted form of the short stripe, whose angles $\theta_{SS} = 0$ or $\pi/3$ or $2\pi/3$), where $\theta_1 = \theta_2$ and $\theta_3 = \theta_4$. The HB(DSP) angle set for the geometry shown is given by $\{\phi_1, \phi_2\} = \{\phi_1 = |\theta_{SS} - \theta| = 20^\circ, \phi_2 = |\theta_{SS} - \theta_2| = 13^\circ\}$. HB(PHB) denotes “herringbone” (distorted form of the PHB), where $\theta_1 = \theta_2 = 19^\circ$ and $\theta_3 = \theta_4 = 98^\circ$. These geometries are explained more fully in the text.
All found ground state geometries were classified under three cases. The first case includes adlayers with fixed (high-symmetry) geometry. These are short stripe (SS), long stripe (LS), honeycomb (HC), perfect herringbone (PHB), irr (irregular) and triangular pattern (TR) geometries. See Figure 4.2.1.1. Note the TR geometry cannot be described by the (2x2) unit cell, in fact it needs a (3x3) cell (whose primary cell angles alternate between 0, π/3 and 2π/3). The TR geometry has been seen before as well as our group was able to found this ground state geometry by using the Monte Carlo simulation. Here, we used the TR geometry to calculate single point energy (this is, for set of
parameters \( \{\rho, r_e, \beta\} \) in order to get (parameter dependent) energy and position on the contour energy and order parameter phase diagrams. We will discuss this in more details where appropriate.

The herringbone case is the most generic pattern identified. There are several varieties of herringbone (HB) patterns. These are PHB, HB, HB(DSS) and HB(PHB). See Figure 4.2.1.2. Note that two panel of HB geometries (in Figure 4.2.1.2, left and right panel of bottom row) are denoted as distorted forms of SS and PHB geometries, respectively. This was based on presence within the sublattice of two-fold rotation symmetry elements and p2 symmetry notation, Appendix C. Both geometries are really transitional (low-symmetry) forms of the SS and PHB (high-symmetry) geometries (further in the text this will be discussed in greater detail).

The very last case is the pinwheel (PW) geometry. This case starts from the honeycomb (high-symmetry) geometry. As distance parameters are proceeding to increase several pinwheel geometries were identified. See Figure 4.2.1.3.

The nearest-neighbor (NN) atom-atom distance, \( s \) (already mentioned in Section 3.2), will be significant in understanding the preferred adlayer geometry. Again, energy will be at its minimum, if the atom-atom minimum NN distance \( s_f = r_e \). For example, the minimum NN distance of SS geometry (recalling angles within the primary cell \( \theta_1=\theta_2=\theta_3=0, \) Figure 4.2.1.1), can be easily found and it given by formula \( s_f(\rho) = 1+\rho \) where \( \rho \) is a molecule length parameter. Recalling the periodicity of the lattice and inspecting geometry of SS, we note that \( N_i = 2 \), (that is, there are two atom-atom NN interactions per molecule), which has the potential energy (per rotor) \( V_{SS} = N_i v(r_e) = -2 \).
The curves for minimum atom-atom NN distance as a function of molecule length, \( s_1(\rho) \), (for SS and other geometries) are shown in Figure 4.2.2.

![Figure 4.2.2](image)

**Figure 4.2.2** The minimum atom-atom separation distance, \( s_1 \), as a function of rigid molecule length, \( \rho \), for chosen fixed geometries. The geometry labels SS/PHB, HC, PW-I, irr, LS, TR and HB are explained in the caption of Figures 4.2.1.

Note that the SS and PHB geometries have the same minimum NN distance distribution along change of \( \rho \) (both geometries shown by the single line, Figure 4.2.2), since both geometries are sharing one \( s_1 \) formula. This simplistic analysis (that is, a plot of \( s_1(\rho) = r_e \)) will be used in order to understand energy plots. We can estimate the global minimum, GM, potential energy for a given value of \( r_e \) (for a large \( \beta \)) as being \(-N_1\) at a certain geometry. For instance, the line (just not including the PHB) marked “SS” in Figure 4.2.2 gives the region of the \((\rho, r_e)\) parameter space where the SS geometry will be dominating. Furthermore, if we consider high (but not infinite) \( \beta \) and small \( r_e \) case, we
note that below and to the left of the SS line, the system will also tend to adopt the SS geometry (although there will be some "attractive" strain), since \( s_f > r_e \). For \( \rho \) values that lie to the right of this line, the SS geometry is now strained by repulsion, and becomes untenable. Further increase of \( \rho \) brings us to the HC line, where HC will be the most stable adlayer geometry. Beyond that, the next minimum reached (for sufficiently large \( \rho \)) is the PW-I. Thus, for the small \( r_e \) case we will consider competing geometries (SS, PHB, HC and PW-I) that preferred as \( \rho \) changes.

We also interested in the second-nearest-neighbor, NNN, distance, \( s_2 \). For the SS, this occurs between atoms that lie on parallel molecules (\( \sqrt{3}/2 \) distance apart) whose center of mass has value of lattice spacing. Thus, the NNN distance, \( s_2(\rho) = \sqrt{1 - \rho + \rho^2} \), further in the text we will report and compare both \( s_f \) and \( s_2 \) values in the radial distribution function (introduced in Section 2.6) for a specific geometry.

We also consider several adlayer geometries, which has two different symmetry environments. For instance, in the HC geometry (whose set of angles: \( \theta_1=5\pi/6 \), \( \theta_2=\pi/6 \) and \( \theta_3=\theta_4=\pi/2 \), see Figure 4.2.1.1), there are two types of sites: one has three-fold symmetry; the other two-fold. The diatoms at the 2-fold site are distant from NN (minimum NN distance is given by \( s_f=\sqrt{1 - \sqrt{3}\rho/2 + \rho^2} \)). These at the 3-fold site has \( s_f=1-\sqrt{3}\rho/2 \) and there are four atom-atom NN interactions per molecule, \( N_1=4 \). The average NN value used as \( \tilde{N}_1 \) =3 per three-center and \( v_{HC}= \tilde{N}_1 \nu(r_e) = -3 \).
4.3 Adlayer Symmetry Notations

As with adlayer geometries on square lattice, the wallpaper group symmetry notations were used to characterize geometries on triangular lattice (that is, discussed in Figure 4.2.1). Geometry characterization is fully discussed in Appendix C. We were able detect six adlayer symmetries from 14 possible on triangular lattice and summarized in the following table:

Table. 4.3.1 Summary of characterized patterns on triangular lattice with the wallpaper group symmetry notations.

<table>
<thead>
<tr>
<th>Triangular Lattice</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short Stripe (SS)</td>
<td>c2mm</td>
</tr>
<tr>
<td>Honeycomb (HC)</td>
<td>c2mm</td>
</tr>
<tr>
<td>irregular (irr)</td>
<td>p2mm</td>
</tr>
<tr>
<td>Perfect Herringbone (PHB)</td>
<td>p2mm</td>
</tr>
<tr>
<td>Long Stripe (LS)</td>
<td>c2mm</td>
</tr>
<tr>
<td>Herringbone: HB(DSS) &amp; HB(PHB)</td>
<td>p2</td>
</tr>
<tr>
<td>Herringbone (HB)</td>
<td>p2gg</td>
</tr>
<tr>
<td>Pinwheel (PW -I, -II, -III)</td>
<td>p2</td>
</tr>
<tr>
<td>Triangle (TR)</td>
<td>p3m1</td>
</tr>
</tbody>
</table>
4.4 Contour Parameter Phase Diagrams

In this section we will introduce the contour order parameter phase diagram, OPPD, (Figures 4.4.1) and the contour energy parameter phase diagram, VPPD, (Figures 4.4.2) for values of the Morse range parameter, $\beta = 20, 10$ and 6.

OPPD is the plot of averaged order parameter values $\tilde{S}$ (of nematic order parameter Equation 2.5.1) as a function of $(\rho, r_e; \beta)$. These are shown in Figure 4.4.1 for geometries in Figure 4.2.1. Values in the color bar reflect the range of calculated order parameters, $(1.0 \geq \tilde{S}(\rho, r_e; \beta) \geq 0)$. More detailed thoughts behind the order parameter and OPPD were explained in Sections 2.5 and 3.5.

In Figure 4.4.2, we plot the global minimum, GM, potential energy, $(\tilde{V}(\rho, r_e; \beta))$ to create VPPD. Interrelated (OPPD and VPPD) diagrams are able to provide meaning for transition in between these adlayer regions at the OPPD. More detailed thoughts behind the VPPD were explained in Sections 2.6.
Figure 4.4.1 Contour order parameter phase diagram as function of (distance) parameters ($\rho$, $r_e$) for several values of the Morse range parameters, $\beta$, on the triangular lattice. The key for the plot coloration is at the color bar (top panel). I and II used to designate regions HB(DSS) and HB(PHB) respectively, for clarity. Upper boundary of HC and LS distorts to PW-I and distorted LS as parameters are grow. PW-III region was swapped by the TR (explained further in the text). See keys for all abbreviation labeling in Figure 4.2.1.
Figure 4.4.2 Contour energy parameter phase diagram as function of (distance) parameters ($\rho$, $r_e$) for several values of the Morse range parameters, $\beta$, on the triangular lattice. The key for the plot coloration is at the color bar (top panel), energy values were truncated at value -16 and swapped by -24 (see explanation in the text). I and II used to designate regions HB(DSS) and HB(PHB) respectively, for clarity. Upper boundary of HC and LS distorts to PW-I and distorted LS as parameters are grow. PW-III region was swapped by the TR (explained further in the text) See keys for all abbreviation labeling in Figure 4.2.1.
Note that high-symmetry geometries, HC and LS, has tendency to distort due to the molecular strain (as parameters are increases). In result, PW-I and distorted LS are formed at upper boundary from both HC and LS, respectively.

Now, we will consider the lowest energy value of the top panel, Figure 4.4.2 (the blue region, where \( \rho \) is small). For \( \rho \to 0 \), molecules are capable of being completely relaxed in their 2D rotation. We also note that the \( \rho = 0 \) case itself is trivial, since it corresponds to molecules of zero length. Now, each atom lies on a lattice site, two atoms on six lattice sites are NN to two reference atoms and they separated as far as lattice spacing go. Thus, system has the lowest energy per molecule of \( V(\rho = 0) = N_1 v(s_l=r_e) = -24 \) (where \( N_1 = 6 \times 4 = 24 \)). However, all energy values lower than -16 were truncated and assumed to be -24 (as the lowest calculated energy). This is helped to differentiate coloration contrast of several regions with a small energy difference, Figure 4.4.2.
4.5 Analysis of Energy Parameter Phase Diagrams

4.5.1 Small value of \( r_e \) (\( r_e = 0.40 \)), Short Stripe, Honeycomb and Perfect Herringbone

In this section we will consider several plots of the potential energy, \( V(\rho; r_e(0.40), \beta(20, 10, 6)) \) shown in Figure 4.5.1.1 for all ground state geometries from Figure 4.2.1.1. These energy plots will be correlated within the radial distribution function, RDF, (introduced in Section 2.6), for understanding the contour energy parameter phase diagram (VPPD, Figure 4.4.2). The radial distribution functions, \( N(s) \), were used for parameters: \( r_e = 0.40; \rho = 0.60, 0.74, 0.68 \) and 0.72; \( \beta = 20 \) and shown in Figures 4.5.1.2 and 4.5.1.3. Thus, for small \( r_e \) case we will consider six competing geometries (SS, PHB, HC, PW - I, HB(PHB), PW – II and irr) that are preferred for different ranges of \( \rho \). As well for a simplistic analysis will use Figure 4.2.2 (that is, a plot of \( s_f(\rho) \), where \( s_f = r_e \)). Thus, we can estimate the global minimum, GM, potential energy for a given value of \( r_e \) (for a large \( \beta \)) as being \( -N_1 \) at certain geometry.

We initially focus on the results for large \( \beta \) (Figure 4.5.1.1, top panel), where the bold line is the potential energy of the global minimum, GM, obtained through the unbiased search. When \( r_e \) is small (\( r_e = 0.40 \)), the molecules need to be fairly long to bring the atoms into contact with each other. For \( \rho \leq 0.60 \), the maximum attraction is obtained by the short stripe geometry, Figure 4.4.2. We note that PHB is not a competitive geometry for this value of \( \beta \) (this we discuss further in the text).
Figure 4.5.1.1 The potential energy function $V(\rho)$ for the geometries described in Figure 4.2.1 for $r_e = 0.40$ and $\beta = 20, 10, 6$. The bold line is the potential energy of the GM obtained through the unbiased search. At several values of $\rho$, the geometry is indicated by a letter. a denotes $\rho = 0.68$; b denotes $\rho = 0.72$; c denotes $\rho = 0.74$; d denotes $\rho = 0.80$; e denotes $\rho = 1.00$. The red circles denote the radius $r_e$ about each atom, and are essentially the "soft spheres" associated with each atom.
The GM energy of the SS curve found to be $V_{SS} = N_1 \nu(r_e) = -2$ this is when $s_I = r_e = 0.40$ (recalling SS geometry (Figure 4.2.1.1), where $N_1 = 2$ per molecule). As $p$ increases further the SS geometry becomes repulsively strained and cannot longed maintain the SS geometry. As $p$ becomes larger, $s_I$ for the SS geometry decreases, and will become less than $\sigma (r_e, \beta)$, rendering the SS geometry repulsive. However, the $N_1 = 2$ can be maintained by allowing the stripes to “buckle”, with the geometry HB(DSS) ($\theta_2 = \theta_3$ and $\theta_3 = \theta_4$), see cartoons on Figure 4.5.1.1.

As $p$ further increases towards about 0.70, where the honeycomb, HC (with $N_1 = 3$ per three-center and the GM potential energy is $V_{HC} = \tilde{N}_1 \nu(r_e) = -3$), is the optimal geometry. This is happening when the HB(DSS) trying to increase the NN count from 2 to 3. As $p$ increases further, geometry of the HC distorts towards pinwheel - I, (PW - I) by twisting three molecules at the three-center (Figure 4.5.1.1, cartoons b and Figure 4.2.1.3). PW geometries are attempted to maintain the local HC of the atoms on the periphery of the wheel. Such (7-molecule) pinwheel structures have been observed previously in adlayers where the central molecule is oriented perpendicular to the surface, with its six (molecular) neighbors forming the pinwheel using three degenerate sublattices. Also it has been seen that six-molecular pinwheel (cluster of carbon monoxide molecules) forming a central vacancy for different molecule (argon molecules). This three-center twist is bringing an additional potential energy from the NNN atom-atom distance, which makes them be lower in energy than the high-symmetry HC geometry. The energy contribution from the second frequency peak is shown on the RDF, Figure 4.5.1.2, centered panel. Note, HB(PHB) geometry (for $p = 0.72$) is not
optimal since $s \neq r_e$, but HB(PHB) will be optimal as $\rho = 0.74$, Figure 4.5.1.2, right-bottom panel.

We suggest the current study is the first case reported where these PW adlayer geometries have been observed with the central molecule in the plane of the pinwheel. We suggest this occurs in our model because there is no obligation for the molecules to close-pack (indeed, there is no capability for the molecules to close-pack) since they are anchored to their lattice sites.

![Graphs](image)

**Figure 4.5.1.2** Radial distribution function, showing the number of neighbor counts, $N$, as a function of atom-atom distance $s$, for various geometries for the case $r_e = 0.40$ and $\beta = 20$. HC is described in Figure 4.2.1.1. PW-I described in Figure 4.2.1.3. HB(PHB) is described in Figure 4.2.1.2. Also shown is the Morse potential energy function $v(s)$. The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.
As $\rho$ further increases towards 0.80, PW-II is the optimal geometry. The HB(PHB) has become sufficiently energetically strained (as clearly shown in Figure 4.5.1.1 when GM curve is decreasing as $\rho$ increasing).

As $\rho$ continues to increase toward 1.00, the irregular, irr, optimal geometry is following after series of distorted HC geometries (pinwheels). irr has $N_1=4$ per molecule (Figure 4.5.1.3, right-bottom panel) and the GM energy of the irr curve found to be $V_{irr} = N_1v(r_e) = -4$.

![Figure 4.5.1.3](image)

**Figure 4.5.1.3** Radial distribution function, showing the number of neighbor counts, $N$, as a function of atom-atom distance $s$, for various geometries for the case $r_e = 0.40$ and $\beta = 20$. PW-II is described in Figure 4.2.1.3. PW-I described in Figure 4.2.1.1. Also shown is the Morse potential energy function $v(s)$. The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.

We note that our simplistic analysis (Figure 3.3.2) predicts that the high-symmetry LS and TR and HB geometries will become significant only after $r_e = 0.50$. We will discuss them in the following section.
The same general trend is very similar for the lower values of \( \beta \) (Figure 4.5.1.1 middle and low panels). However, it should be noted that as the value of \( \beta \) decreases, and the potential becomes "softer" and longer range, several new features come into play. In particular, the atom-atom NNN distances. In Figure 4.2.2, already was shown that \( s_I(\rho) \) is the same for both SS and PHB geometries. Also, PHB and SS both have the same number of NNN (\( N_2 = 4 \), shown on the radial distribution function as a second frequency peak, Figure 4.5.1.4). However, NNN of the PHB located closer to \( r_e \) than does NNN of the SS, Figure 4.5.1.4. Thus, as potential becomes "softer", NNN are providing a greater (additional) energy contribution to the GM energy, the \( \rho \) range over which PHB is the dominant geometry increases at the expense of SS.

For \( \rho = 0.60, r_e = 0.40 \)

![Graph showing radial distribution function](image)

**Figure 4.5.1.4** Radial distribution function, showing the number of neighbor counts, \( N \), as a function of atom-atom distance \( s \), for various geometries for the case \( \rho = 0.60, r_e = 0.40 \) and three different Morse range parameters \( \beta = 20, 10, 6 \). SS and PHB are labeled in Figure 4.2.1.1. Also shown is the Morse potential energy function \( v(s) \). The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.
4.5.2 Intermediate value of $r_e (r_e = 0.60)$, Long Stripe, Pinwheel and Triangular Geometries

In this section we will consider several plots of the potential energy, $V(\rho; r_e(0.60), \beta(20, 10, 6))$ shown in Figure 4.5.2.1 for all ground state geometries from Figure 4.2.1.1. In Figure 4.5.2.2, we show RDF (superimposed on the potential) for the cases $r_e=0.60$, $\rho=0.64$ for two different geometries. Thus, for this $r_e$ case we will consider competing geometries (SS, HC, LS, PW-III, TR and HB) that are preferred for different ranges of $\rho$.

In Figure 4.5.2.1, we plot the energy cuts for adlayer geometries: SS, HC, LS, PW-III, TR and HB. First we will discuss results for $\beta=20$. At $\rho=0.60$, (as for the section before) the SS is the preferred geometry. The HC geometry forms three-forming center and dominates over SS at $\rho=0.45$ (shown within the simplistic analysis plot, Figure 4.2.2), which become repulsively strained as $\rho$ increases beyond $\rho = 0.50$. For $\rho = 0.50$, the LS structure is a minimum, since its 4 NN “side-by-side” interactions are now feasible, allowing an energy of approximately $V_{LS} = N_1 v(r_e) = -4$, see cartoon of LS on Figure 4.5.2.1.
Figure 4.5.2.1 The potential energy function $V(\rho)$ for the geometries described in Figure 4.2.1 for $r_e = 0.60$ and $\beta = 20, 10, 6$. The bold line is the potential energy of the GM obtained through the unbiased search. At several values of $\rho$, the geometry is indicated by a letter. a denotes distorted long stripe geometry at $\rho = 0.54, \beta = 20$; b denotes $\rho = 0.66, \beta = 20$; c denotes $\rho = 0.90, \beta = 20$; d denotes $\rho = 0.64, \beta = 10$. The red circles denote the radius $r_e$ about each atom, and are essentially the “soft spheres” associated with each atom.

As $\rho$ is increased - to about 0.60 - the TR now becomes the most stable geometry with energy of approximately $V_{TR} = N_1v(r_e) = -5$, which contributed interactions from NN and NNN, Figure 4.5.2.1. The TR is characterized by a network of three-fold NN interactions.
TR geometry, too, becomes repulsively strained as ρ is further increased (that is, for β=20 TR will go to PW – III (cartoon b, Figure 4.5.2.1) and for β ≤ 10 it will go directly to herringbone geometry (for β = 10, Figure 4.5.2.1). The HB becomes the preferred pattern for ρ at about 0.75, Figure 4.5.2.1. HB has N₁ = 6 per molecule (cartoon c, Figure 4.5.2.1), with the followed GM energy at ρ=0.90 of \( V_{HB} = N_1 v(r_e) = -6 \) (that is lower energy of the TR geometry, Figure 4.5.2.1, top panel).

For Figure 4.5.2.1, β = 20, we consider several of “transitional forms”. In particular, as ρ increases geometries (such as LS and HC) undergo to distort. We observe a distorted LS (cartoon a, Figure 4.5.2.1) and pinwheel (Figure 4.2.1.3) geometries. For ρ= 0.54, the LS is (repulsively) strained, thus system can adopt distorted LS geometry to minimize its energy. This type of distortion is common for stripe pattern, as was found in SS undergo to HB(DSS) as ρ increases. Distorted LS holds until ρ becomes sufficiently large that the three-center attraction becomes sufficient in optimal geometries. (Again, any PW in general are not the high-symmetry geometry, they are honeycomb patter derivatives, Figure 4.2.1.3.) Patterns PW-II and –III are managed to maintain some of three-fold interactions of the TR, but PW-III is attempting to minimize repulsion by “twisting” (cartoon b, Figure 4.5.2.1).

The same general trend is very similar for the lower values of β (Figure 4.5.2.1 middle and low panels). However, it should be noted that as the value of β decreases, and the potential becomes “softer” and longer range, several new features come into play (such as NNN interactions). (For cartoons d of Figure 4.5.2.1, we have created the radial distribution function, Figure 4.5.2.2.) In Figure 4.5.2.1, we see that TR is energetically preferred over the PW-III, even if they both have the same number of NN distances per
molecule. This is clearly shown that TR has greater number of NNN per molecule (Figure 4.5.2.2). Thus, we see how NNN distances are playing an important role that makes TR be the optimal geometry. Furthermore, the potential energy curve of the TR is lower than calculate GM energy (we see this for high β, but at lower extent), for several PW geometries. We already discussed in Section 4.2 that TR geometry is a repetition of the (3x3) primary cell which energy was obtained from unrestricted minimization calculation. 51

Figure 4.5.2.2 Radial distribution function, showing the number of neighbor counts, N, as a function of atom-atom distance s, for various geometries for the case ρ=0.64, r_e = 0.60 and β = 10. PW – III is labeled in Figure 4.2.1.3, TR is labeled in Figure 4.2.1.1. Also shown is the Morse potential energy function v(s). The potential energy of certain geometries is indicated on the figure. The GM geometry is indicated with an asterisk.
4.5.3 Large value of $r_e (r_e = 0.70)$

In this section we will consider several plots of the potential energy, $V(\rho; r_e(0.70), \beta(20, 10, 6))$ shown in Figure 4.5.3.1 for all ground state geometries from Figure 4.2.1. For this $r_e$ case we will consider competing ground state geometries (SS, HC, LS, PW, TR and HB) that are preferred for different ranges of $\rho$.

As can be seen from $s(\rho)$, Figure 4.2.2, all the high-symmetry geometries (that is, those shown on Figure 4.2.1.1) now compete over a small range of $\rho$ values. The $V(\rho)$ plot confirms that the high-symmetry geometries are all essentially degenerate. The SS is following by the HC geometry (as was shown before). The next high-symmetry geometry is the LS with $N_1 = 4$ (Figure 4.5.3.2). The TR becomes repulsively strained by $\rho = 0.50$. The HB emerges as the least strained geometry at large $\rho$ and lowest energy $V_{HB}(\rho) = -6$. 
Figure 4.5.3.1 The potential energy function $V(\rho)$ for the geometries described in Figure 4.2.1 for $r_e = 0.70$ and $\beta = 20, 10, 6$. The bold line is the potential energy of the GM obtained through the unbiased search. At several values of $\rho$, six restricted geometries were denoted.
4.6 Conclusions for Results on Triangular Lattice

4.6.1 Small value of $r_e (r_e = 0.40)$

In this section we will discuss ground state geometries summarized on the contour energy parameter phase diagram, Figure 4.4.2. For small value of $r_e = 0.40$ and high $\beta = 20$ (Figure 4.5.1.1), we found SS is the optimal geometry, this result is similar to the square lattice (Figure 3.6.1). For both lattices, $\rho$ dependent energy decreased to its global minimum where $s=r_e$. As $\rho$ increases past 0.60 the SS geometry becomes repulsively strained and to maintain energy at -2 the SS has to distort. Such way to keep lowest possible energy is inherent to all types of stripes (sort and long stripes) placed on any lattice.

The next of the geometries to be preferred will be HC, with $V_{HC} = \tilde{N}_1 v(r_e) = -3$. (This geometry optimizes the number of three-center bonds. On the triangular lattice, this is possible, leaving the fourth rotor relatively distant from the three-center. This is to be contrasted with the SP in the square lattice, where every rotor can have four NN.) The “left out” central rotor has atoms rather distant from those in the main HC network (this also is shown by the radial distribution function that the second peak on the RDF (Figure 4.5.1.2) equals to (about) a potential energy of zero and distantly separated from $r_e$).

We note further, that in comparison to the square lattice, the LS is not a favorable geometry for low $r_e$, since the “tip-to-tip” distance will be larger in the triangular lattice. The overall trend of preferred geometries is well predicted by Figure 4.2.2. However, we need to point out that (at larger $\rho$) other geometries than the ones chosen for Figure 4.2.2
are possible. For instance, (as can be seen in Figure 4.2.1.2) the DSS (that is, herringbone type pattern for that \( r_e \) case) geometry avoids the repulsion of the SS geometry as \( \rho \) is increased, but retains \( N_1 \approx 2 \). At larger values of \( \rho \) than can sustain the HC, the distorted HC becomes the dominant geometry. These distortions of the HC are interesting, and have a geometry that we label PW for "pinwheel". (Also several others have seen and discussed 6-sublattice pinwheels.\textsuperscript{14} Here we see the center of the PW in the plane (as it is constrained to be.) Perhaps this is the first recorded case of PW where central atom remains in plane.) A typical sequence obtained by distorting a HC to a PW-III is shown in Figure 4.2.1.3, where “third” version of the PW geometry was recognized as a precursor to the TR geometry (we will discuss this in Section 4.6.2). As can be seen from the full contour VPPD, for large \( \rho \), these pinwheel structures are dominant for large \( \rho \), small \( r_e \).

We consider now the effect of reducing the range constant \( \beta \) in plots of \( V(\rho) \), Figure 4.5.1.1, middle and bottom panels. Now all geometries experience attractive interactions for much of the \( \beta \) range, and there are contributions from NN and NNN. The trend with which geometries become repulsive remains the same as for the large \( \beta \) case. However, we note now that the SS and PHB are almost energetically degenerate; they are both competing for the place on the contour VPPD. From the RDF (Figure 4.5.1.4), we see that competition concludes by losing of the SS geometry due to distal location of the NNN frequency peak relative to \( r_e \). Thus, for the “softer” potential, any NNN are playing a key role (this is, if they are in the range of the potential curve) in the potential energy determination. Even more to this, (referring to the contour VPPD), the SS will be
completely disfavored geometry as the Morse range parameter approaches to 5, SS geometry will be replaced by the PHB.

4.6.2 Intermediate value of $r_e (r_e = 0.60)$

For intermediate value of $r_e (r_e = 0.60)$, in Figure 4.5.2.1, we plot the potential energy $V(p; r_e(0.60), \beta(20, 10, 6))$ for all ground state geometries from Figure 4.2.1.1. As before, we focus first on the $\beta = 20$ case.

As for the $r_e = 0.40$ case, we see that the SS pattern is most attractive at low values of $\rho$. Next ($0.45 \leq \rho \leq 0.50$) the HC is favored (as it was at small $r_e$). However, for larger values of $\rho$, there is competition between LS and PW. This is seen in the energy cut, Figure 4.5.2.1.

From the very same energy plot we note appearance and dominance of the TR right in between LS and HB patterns, Figure 4.5.2.1. Following that, we see the TR region emerge ($0.58 \leq \rho \leq 0.72$), which is predicted by the fixed geometry $s_f(\rho)$ plot, Figure 4.2.2. The TR is an interesting geometry in that it is a “satisfied” PW (especially the PW-III pattern, since they both sharing the same three-center symmetry). This is precisely shown in the energy cut of Figure 4.5.2.1. As can be seen on the GM curve, we reveal presence of PW-III (that is, has (2x2) primary cell) transition pattern which can be “swapped” by the optimal TR geometry formed by (3x3) primary cell.
The fixed geometry which experiences the least repulsion is the HB (by which we mean HB with angle set of $\eta = |\theta_1 - \theta_2| \approx \pi/4$, and becomes the favored fixed geometry at high values of $\rho$. This is also common with the square lattice. As can be seen from the contour parameter phase diagram (Figure 3.5.1), the HB pattern is the primary pattern observed at large $\rho$ and $r_e$ and the pattern that helps to avoid (repulsive) strain in all types of molecular stripes (both lattices).

4.6.3 Large value of $r_e$ ($r_e = 0.70$)

For large value of $r_e = 0.70$, we found that the plot of constraint geometries used for simplistic analysis (Figure 4.2.2) was useful. In that it predicted that all the regular geometries occur within a very narrow span of $\rho$ values. The geometry with the largest $\rho$ is HB, and we see that this is the dominant structure at large $\rho$.

The $V(\rho)$ plot (Figure 4.5.3.1) confirms that the high-symmetry geometries are all essentially degenerate. Geometries occur within a very narrow width of $\rho$ values. In most cases when a molecular pattern formed via attraction rather than repulsion, we found that contribution to the total energy of both NN and NNN will be crucial. Looking at the constrained potential energy curves, we see lots of interesting results especially a quick transition to HB. Also north of the PW zone, because buried by LS and TR.

Also, plot of the $V(\rho)$ shows that HB is the only attractive region for $\rho$ greater than about 0.5. The HB geometry (similarly to the square lattice) is the most closely packed pattern that allows maintaining a maximum number of atom-atom NN distances per molecule.
Overall, we have note that a lattice type selection makes a huge difference in formation of adlayer geometries. For instance: patterns having three-fold symmetry in their geometry (HC, TR and PW) will never be a case on the square lattice (and vise versa regarding adlayers with four-fold symmetry (SP and DSP) on the triangular lattice).
CHAPTER 5

CONCLUSION

Used a wide range of potential energy allow us to report a wider range of adlayer geometries than has been seen by other workers. Role played by: rotor size, interaction length, range parameter of interaction potential were investigated. Large number of “ground-state” geometries has been successfully identified. Adlayer patterns were interpreted in terms of nematic order parameters and characterized with the wallpaper group symmetry. Overall, we have note that a lattice type selection makes a huge difference in formation of adlayer geometries this can be utilized in pattern prediction of self-assembled molecules on different substrates.
APPENDICES
APPENDIX A

USAGE OF WALLPAPER GROUP SYMMETRY NOTATION

Pattern characterization was done using the wallpaper group symmetry. This approach was based on the following symmetry elements: translation, center of rotation, reflection and glide mirror symmetry.

Center of rotation

- Order of six, $(2\pi/6)$
- Order of four, $(2\pi/4)$
- Order of three, $(2\pi/3)$
- Order of two, $(2\pi/2)$

Reflection plane

- Mirror plane
- Glide reflection

Figure A.1 Schematic representation of symmetry elements that used in the wallpaper group symmetry notation.

Translation symmetry is movement of every point of a unit cell by a constant distance in a specified direction. It is one of the rigid motions that can be performed within the two-dimensional plane of a lattice. Our interest will be primarily focused on two types of symmetry elements: rotation centers and reflection planes. A rotation is a rotational motion of an object after which its takes the initial geometry. A rotational center is a point about which this motion can be executed. An object may have more than
one rotational centers of symmetry; in other words this rigid motion might be degenerate to a certain degree. In our case we will discuss four different elements of rotation that adlayer pattern can exhibit. A mirror plane is symmetry with respect to reflection through that mirror plane. In a two-dimensional lattice such planes would be called an axis of symmetry. Glide reflection of symmetry is symmetry operation described by reflection in an axis of symmetry, followed by a translation parallel with the axis of symmetry. All mentioned symmetry elements were schematically proposed in Figure A.1.

Figure A.2 represents a map that can be used in the geometry characterization process. The search for any rotation symmetry elements (especially types of rotation centers) will be used as an initial step. Through that a “cluster” (collection of symmetry notations) whose lowest order rotation centers similar to pattern of interest will be defined. Then questions (if that geometry has any mirror planes, perpendicular mirror planes, or glide reflections) will be asked to eliminate notations that are unrelated to selected geometry. We will use this map to characterize geometries (Figure 3.2.1) in Appendix B.
<table>
<thead>
<tr>
<th>Lowest order rotation</th>
<th>Has mirror of reflection?</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YES</td>
</tr>
<tr>
<td>$2\pi/6$</td>
<td>p6mm</td>
</tr>
<tr>
<td>$2\pi/4$</td>
<td>Has mirrors at $\pi/4$</td>
</tr>
<tr>
<td></td>
<td>Yes: p4mm</td>
</tr>
<tr>
<td>$2\pi/3$</td>
<td>Has rot. centers off mirrors?</td>
</tr>
<tr>
<td></td>
<td>Yes: p31m</td>
</tr>
<tr>
<td>$2\pi/2$</td>
<td>Has perpendicular reflections?</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>Has rot. centers off mirrors?</td>
</tr>
<tr>
<td></td>
<td>Yes: c2mm</td>
</tr>
<tr>
<td>None</td>
<td>Has glide axis off mirrors?</td>
</tr>
<tr>
<td></td>
<td>Yes: c1m1</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure A.2** Schematic representation of the wallpaper group symmetry map used for adlayer geometry characterization. Each symmetry notation is a combination of symmetry elements (Figure A.1) that are starts with letter: “p” (primitive cell) or “c” (face-centered cell). A number that goes after corresponds for lowest order rotation (type of rotation center) and the last, symmetry notation concludes by letter: “m” (mirror plane) and “g” (glide of reflection).
APPENDIX B

CHARACTERIZATION OF ADLAYER PATTERN ON SQUARE LATTICE

Figure B.1 Adlayer geometries identified in this work. “Stripe” is used to designate the fact that all angles are the same. SS = “short stripe” denotes that all angles are equal to 0 (or π/2 or π). LS = “long stripe” denotes that all angles are π/4. DSS designates “distorted SS”; DSS-I has two mirror planes; DSS-II has one mirror plane. SP denotes “square pattern”, where \( \theta_1 = \theta_4 = 3\pi/4, \theta_2 = \theta_3 = \pi/4 \). DSP denotes a distorted SP, where \( \theta_1 = \theta_4 = 3\pi/4, \theta_2 = \theta_3 = \pi/4 \). HB denotes “herringbone”, where \( \theta_1 = \theta_3 \) and \( \theta_2 = \theta_4 \), and “perfect herringbone” PHB denotes that the herringbone angles alternate between 0 and π/2. The “irregular” geometry, designated by irr, has no symmetry elements in the unit cell, has \( \theta_1 \neq \theta_2 \neq \theta_3 \neq \theta_4 \). This geometry is explained more fully in the text. Underneath each geometry we denoted symmetry notation explained in the text.
Now, we focus on a group of patterns with symmetry elements that contain two-fold symmetry axes. In order to characterize patterns, we will use map (Figure A.2) that consider availability of mirror planes, located on or off (those mirror planes) centers of rotation and availability of glide of reflection. In Figure B.1 panel (a) shown the SS = “short stripe”. The primary cell of the SS has four equal angles: $\theta_1 = \theta_2 = \theta_3 = \theta_4$. Angles in the cell are degenerate; this denotes that all angles are equal to 0 (or $\pi/2$ or $\pi$). The SS adlayer pattern similarly to all others has translation symmetry. Since this symmetry is not playing a primary role in pattern characterization since its only a definition of repeated pattern, the translation symmetry will not be mentioned anymore in the text.

This SS geometry contains 4 centers of rotation order of two, which designated with differently colored rhombuses. This is also similar to LS = “long stripe”, whose all angles = $\pi/4$ and 2 centers of rotation (two-fold rotation) are located on the mirror planes, Figure B.1 (g). That denoted two-fold rotation (for SS and LS geometries) sets a cluster of 5 wallpaper group symmetry possibilities to choose from (c2mm, p2mm, p2mg, p2gg and p2). See Figure A.2. With SS geometry we see that all of 4 centers are located at intersections of 2 perpendicular reflection mirror axes (colored with blue color). Note, that presence of mirror plane splits cluster into 2 sets (c2mm, p2mm, p2mg) and (p2gg, p2), where first and second sets accounts for presence of mirror planes and glide planes, respectively. Presence of perpendicular mirrors eliminates the p2mg notation. As well, location of rotation centers on or off mirror plane determines if geometry has primitive (p2mm) or face-centered unit cell (c2mm). Thus, the SS and LS patterns could be characterized as $p2mm$ symmetry. In addition, there were found a 2 perpendicular glide
axis within geometry of LS (which is denoted as green, dotted line) and none in SS patterns.

The DSS is designated as “distorted SS”. Primary cell of patterns DSS - I and DSS - II denotes each a 2 sets of equal angles \( \theta_1 = \theta_4, \theta_2 = \theta_3 \) and \( \theta_1 = \theta_3, \theta_2 = \theta_4 \), respectively. DSS - I has 2 mirror planes and 3 two-fold centers of rotation; DSS - II has 1 mirror plane and 1 two-fold center of rotation. What really distinguishes them from the SS is the availability of the rotation centers off the mirror plane. Thus, both distorted versions of the SS are characterized as \( \text{c2mm} \). In addition, 2 perpendicular glide axis where found on the DSS - I and none on the DSS - II patterns. See Figure B.1 (b), (c).

Some adlayer pattern cases contain no mirror planes as symmetry elements. In this case patterns are examined for an availability of glide reflections. HB = “herringbone” and irr = “irregular” patterns belong to this category. Primary cell of HB pattern contains 2 sets of equal angles, \( \theta_1 = \theta_4, \theta_2 = \theta_3 \), 2 two-fold centers of symmetry and 1 reflection glide. The irr has no symmetry elements except for 1 two-fold center of symmetry, but the primary cell has no sets of equal angles. Thus, HB and irr patterns were characterized as \( \text{p2gg} \) and \( \text{p211} \), respectively. See Figure B.1 (h), (i).

Now, we focus on a group of patterns with symmetry elements, which possess four-fold symmetry axis. In order to characterize patterns, we will consider availability of mirror planes, mirror planes of \( \pi/4 \) and glide of reflection. The SP, DSP and PHB pattern denotes as “square pattern”, “distorted SP” and “perfect herringbone”, respectively. Where all three has 2 sets of equal angles, \( \theta_1 = \theta_4, \theta_2 = \theta_3 \), which are equal to \( 3\pi/4 \) and \( \pi/4 \), \( = 3\pi/4 \) and \( = \pi/4 \), and \( \pi/2 \) and 0 for SP, DSP and PHB, respectively. The SP has 2
four-fold and 1 two-fold centers of rotation, \( \pi/2 \) and \( \pi/4 \) mirror planes. Thus, we denote this pattern as \( p4mm \). Distorted version of the SP has 2 four-fold and 1 two-fold centers of rotation and no mirror planes. Thus, we characterized the DSP geometry as \( p4 \). Perfect version of the herringbone contains 2 two-fold rotation centers on 2 perpendicular reflection mirrors and 1 four-fold rotation center off the mirror plane. Because of the lack of a mirror plane of \( \pi/4 \) we denoted this pattern with \( p4gm \) notation. See Figure B.1 panels (d) - (f).
APPENDIX C

CHARACTERIZATION OF ADLAYER PATTERN ON TRIANGULAR LATTICE

Using already discussed pattern characterization method, we will focus on triangular lattice. Starting with the high-symmetry case, we will discuss symmetry notations for SS (short stripe), HC (honeycomb), PHB (perfect herringbone), LS (long stripe) and TR (triangular) patterns, they all mentioned in Figure C.1.

![Figure C.1](image-url)

**Figure C.1** High-symmetry geometries identified in this work. SS is the “short stripe”, which denotes that all angles are equal to 0 (or $\pi/3$ or $2\pi/3$ or $\pi$). HC (honeycomb) shows that $\theta_1 = \pi/2$ (or $\pi/6$ or $5\pi/6$), $\theta_2 = 5\pi/6$, and $\theta_4 = \pi/6$. Degraded forms of the HC geometry are able to alternate four angles within $\pm \pi/6$ (see Figure C.2). irr (irregular) designates that $\theta_1 = \pi/6$ and $\theta_2 \approx 20^\circ$, $\theta_3 \approx \pi/4$ and $\theta_4 \approx 2\pi/3$. PHB (perfect HB) shows that the herringbone angles alternate between 0 and $\pi/2$. LS (long stripe) show that all angles are $\pi/6$ (or $\pi/2$ or $5\pi/6$). TR (triangular pattern) geometry has 3x3 primary cells and denotes that angles of the primary cell are alternating between 0, $\pi/3$ and $2\pi/3$. Underneath each geometry we denoted symmetry notation explained in the text.
Consider the wallpaper group symmetry map (Figure A.2), the high-symmetry patterns were separated into two parts based on their center of rotation (two-fold (Figure C.1 panels (a)-(e)) and three-fold (panel (f)) rotation). The TR geometry designated with the \( p3m1 \) symmetry notation, since it composed of 3 mirror planes intercrossing at the three-fold center of rotation (no other rotation centers off mirror plane were found). The \( \text{irr} \) denotes 2 rotation centers located on intercrossed 4 mirror planes (at right angles to each other), and PHB geometries denotes 4 rotation centers located on intercrossed 4 mirror planes (at right angles to each other), thus both geometries designated with \( p2mm \) notation symmetry. Remaining geometries (SS, HC and LS) are designated with \( c2mm \) notation. They all have rotation center off perpendicular mirror planes (in this time availability of any glide plane in symmetry is not affecting assigned notations). See Figure C.1 for details.

Panels (a)-(d) (Figure C.2) show herringbone geometry with primitive unit cell and two-fold rotation:

![Figure C.2](image)

**Figure C.2** Herringbone geometries identified in this work. PHB denoted that the herringbone angles alternate between 0 and \( 5\pi/9 \). HB at high \( r_c \) contains set of two angles \( \theta_1 \approx 5\pi/9 \) and \( \theta_2 \approx \pi/9 \) where glide plane (that parallel to \( y \) axis of the triangular lattice) is a bisector with angle = \( \pi/3 \). Underneath each geometry we denoted symmetry notation explained in the text.
As was mentioned before, the PHB has \textbf{p2mm} symmetry notation. Degraded forms of the PHB are denoted with \textbf{p2} for low and middle part of the \( r_e \) (panels (b) and (c)) based on translation and two-fold rotation symmetry elements. Higher distance parameter, \( r_e \), contains a bisector (a line parallel to the \( \tilde{y} \) axis (Figure 2.1.2) with angle = \( \pi/3 \)) which plays a role of a glide plane (panel (d)). Thus, geometry of this pattern denoted with \textbf{p2gg} due to the presence of additional symmetry element (Figure C.2).

With the set of degraded PW (pinwheel) geometries (from high-symmetry HC (Figure C.3)), it is shown that there are no mirror and glide planes in panels (b)-(d) of Figure C.3.

![Figure C.3 Adlayer geometries identified in this work. HC = “honeycomb” geometry designates that \( \theta_1 = \pi/2 \) (or \( \pi/6 \) or \( 5\pi/6 \)), \( \theta_2 \), \( \theta_3 \) and \( \theta_4 = \pi/2 \), \( 5\pi/6 \) and \( \pi/6 \), respectively. Remain degraded forms are able to alternate high-symmetry angles within \( \pm \pi/6 \). Underneath each geometry we denoted symmetry notation explained in the text.](https://example.com/figure-c3)

Even more to that, a number of two-fold rotation centers has increased, which changed the unit cell form “center-faced” (HC) to “primitive” (PW). Thus, HC and PW geometries are denoted with \textbf{c2mm} and \textbf{p2} symmetry notations, respectively.
LIST OF REFERENCES


