THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

MOLECULAR DYNAMICS SIMULATION OF THE ORIENTED ATTACHMENT
OF SILVER NANOPLATES IN PRESENCE OF POLYVINYLPYRROLIDONE

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Abstract

In the experimental synthesis of silver nanoplates, the solution consists of small triangular Ag plate, Polyvinylpyrrolidone (PVP) and Polyethylene glycol (PEG) as solvent. The scope of this paper only focus on the interactions between Ag plate and PVP, where we investigated the Ag plate and PVP system in three different set ups of MD simulations. First is the MD simulations of single-plate, aiming to look at PVP chain length effects as well as Ag plate configuration effects. Second is the unbiased MD simulations of two-plates, which is to investigate how two Ag plates will interact with each other in the presence of PVP. Third is the biased MD simulations that pull two plates together to form attachment, then Umbrella Sampling was used to calculate the Potential Mean Force (PMF) of plate attachment with the presence of PVP. Each set up of the simulations gave different collective insights to aid the knowledge about the Oriented Attachment mechanism.

From single plate equilibration simulations, the system with the least binding preference was the short PVP 5-mer chains on type A plate with slanted side. System that displayed highest binding preferences towards the plate flat faces over the plate sides was the system with long polymer chains (PVP 100-mer) on type B plate with HCP sides. The PVP chains preferred to bind on the flat surface because there is a larger number of possible conformations and the chains have larger degree of freedom or entropy. This way, the plate sides are less crowded and can be approached by another plate and undergo Oriented Attachment.

From unbiased two-plates MD simulations, there were no successful attachments in any of the 8 systems run with PVP 100-mer even at ramped up temperature from T = 900 K to T = 1200 K.

Insights from pull simulations and umbrella sampling showed that Major-Minor side attachment systems (similar to Oriented attachment) required smaller force constant of 1400 eV/Å. While the plate face-face attachment used larger force constant of 1500 eV/Å. The PMF calculated the energy barrier to be 57.0 ± 1.8 kcal/mol for Major-Minor side attachment system and 70.2 ± 3.0 kcal/mol for parallel face-face attachment. Confirming that Major-Minor side attachment or Oriented Attachment has lower energy barrier and is the more likely mechanism. The PMF for both systems showed energy local minima before the energy barriers. This could explain why the two-plates system unbiased runs were less successful because the systems were stuck at the local energy minimum.

Possible future work include doing umbrella sampling and analysis for systems at T = 1200 K. To further study PVP binding behavior onto surface and examine how a single PVP 100-mer chain lay itself onto the plate can help predict the binding preferences. Also, PEG can be added to investigate solvent effects. Plate-PVP-PEG system is more similar to experimental system and therefore will describe the system more accurately. In a far future where the system is more well understood, it is possible to switch the force field to reactive force fields, which are more representative of experimental systems.
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Chapter 1

Introduction
In a broad view, nanocrystals have many unique electrical, optical and magnetic properties leading to wide applications in various fields such as catalyst, solar energy and sensing[1]. These applications depend upon the nanocrystal shape therefore the synthesis process must be extremely precise. That is why research in shape-controlled synthesis of metal nanocrystals became a very important field. Surface Plasmon Resonance (SPR) is one of Silver nanoplate’s unique characteristics that researchers are most interested in. SPR is a phenomenon caused by the excitation of surface plasma waves (SPW) leading to anomalous diffraction on diffraction gratings. It is a charge-density oscillation, which can exist between two material with dielectric constants of opposite signs[2]. Surface Enhanced Raman Spectroscopy (SERS) and Surface Enhanced Fluorescence (SEF) are spectroscopic techniques that utilize metal nanocrystals, where their operations are very highly dependent on the nanomaterial’s SPR and in-plane dipole resonance[3][4]. Optical sensors like these two applications are comprised of optical domain, chemical domain and data processing component that takes the information from the optical domain. The optical data input can then be processed to quantify the change in the nanocrystal’s refractive index, in which can be used to characterize the sample on the metal sensor. And therefore the size of nanoplates that are used must be controlled well to be able to produce high quality spectroscopy. If we can understand all the factors that control the size and shape of the nanocrystals, then the production of nanostructures for industrial application can be more efficient and effective.

Solution-phase method is one of the most popular ways of synthesizing nanocrystals to form certain shapes. The mechanisms of nucleation and growth of these structures are still not well known due to the mechanism’s extremely high complexity. Particular molecules can be added to a solution and they would direct the growth of metal nanocrystals into specific shapes. These molecules are called Structure-Directing Agents (SDAs), in which different SDAs can be added to a solution and different nanostructures would form. SDAs are very important in shape-controlled synthesis of metal nanocrystals and experimental results have convincingly shown that SDAs are crucial in controlling the final nanostructure in synthesis. However, the role of SDA at the molecular level is still unclear and the facet-selectivity mechanisms they undergo are not well understood.
The common hypothesis is that SDA embodies strong binding selectivity, binding onto one crystal facet very strongly compared to other surfaces. Therefore, that surface continues to grow because molecules are constantly added onto the facets that are less hindered by the SDAs [5]. Al-Saidi et al. have investigated the root of the selectivity [6]. In this referenced work, they focused on PVP surface-selective binding on Ag surfaces by using DFT calculations. They were able to find that PVP binds more favorably onto Ag {100} than Ag {111} facet. In the same way, we will predict the results of our simulations by following the SDA’s strong facet binding selectivity hypothesis leading to directed attachment.

In our study, we will focus on silver nanoplate systems. The Ag nanoplate synthesis process can be outlined as follows. During initial nucleation, Ag\(^+\) ions come from AgNO\(_3\) dissolved in a water-PEG mixture with the presence of PVP. Where PVP serves as the SDA for this particular system. After the seeds are formed, initial plate formation happens in solution with Ag seeds, PEG and PVP. Furthermore, the plate growth is accelerated through the Oriented Attachment mechanism[7]. We will study the Ag plate system after nucleation. In experimental systems, the solution consists of small triangular Ag plate, PVP and PEG as solvent. The scope of this paper will only focus on the interactions between Ag plate and PVP. The goal is to gain preliminary knowledge into the Ag nanoplate Oriented Attachment system, especially PVP’s SDA effects. Once sufficient information about Ag plate and PVP system is acquired in this study, investigation of PEG solvent effects is definitely an important possible future work.

Oriented Attachment is a mechanism in which smaller units of established nanostructures act as building blocks for more complex structures. Preferred crystal face reactivity and nanocrystals dipole moments are thought to be possible driving force for the oriented assembly process. The assembly usually lead to the elimination of high-energy facet. Aherne et al. used Molecular Dynamics to study the energy preferences in solvent binding [4]. They were able to find that the sides/edges of Ag nanoplates are very thermodynamically unstable compared to the faces. An interesting effect observed in that study was when two nanocrystals approach each other, they would reach a free-energy minimum while there were still one or two layers of solvent between their
surfaces. This is called a mesocrystal configuration. It is also found that mesocrystal configuration between the smallest facets have the lowest energy barrier for aggregation[8]. This gave us some vision of why growth through side-side Oriented Attachment is more likely to happen than through face-face attachment. From this referenced study, the solvent and nanocrystal interactions were described by Lennard-Jones potentials. While this method gave very meaningful insight into solvent-nanocrystal interactions, they did not develop a case specific study. In our work, we are able to use a more specific force field that was developed for Ag, PVP, EG and (Polyethylene oxide)PEO system[1]. As our system will focus on PVP effects on Ag nanoplate, our MD system will use the case specific force field, allowing us to investigate PVP as our explicit SDA in the system.

In this paper, we will investigate the Ag plate and PVP system in three set ups of MD simulations. First set up is single-plate MD simulations, aiming to look at PVP chain length effects as well as Ag plate configuration effects. Second set up is unbiased two-plates MD simulations, which is to investigate how two Ag plates will interact with each other in the presence of PVP. Third set up is using Umbrella Sampling technique to calculate the Potential Mean Force(PMF) of plate attachment with the presence of PVP.
Chapter 2

Computational Methods
2.1 Molecular Dynamics Background

Molecular Dynamics (MD) simulations system were set up to imitate the Ag plate and PVP system in the molecular scale under the NVT ensemble. NVT or canonical ensemble is an ensemble with fixed number of atoms (N), fixed volume (V) and is in a heat bath with fixed temperature (T). Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is the program used to run all MD in the work presented in this paper. The systems were simulated in different ways with the attempt to elucidate the mechanism of Oriented Attachment between two Ag nanoplates in the presence of PVP as the explicit SDA. Although in synthesis experiments, PEG was the solvent used, for the scope of this paper all of the systems are in vacuum and solvent is not explicitly included in our system. Different lengths of PVP oligomers were used to investigate chain length effects.

2.1.1 Molecules in the System

There are two different configurations of how the Ag plates were structurally built, they were used in this work at different parts in the process. First, referred to as Ag nanoplate type A are triangular plates with a total of 9 layers of Ag atoms shown in Figure 2.1. The two exposing flat faces of the plates are \{111\} facets. Two sides of the plates are \{110\} facets and the one remaining side is \{111\}.

![Figure 2.1: Triangular Silver Nanoplate Type A](image)

Figure 2.1: Triangular Silver Nanoplate Type A (a) left side of the plate with \{110\} facet (b) front face of the plate with \{111\} facet (c) bottom side of the plate with \{111\} facet (d) right side of the plate with \{110\} facet
Secondly, Ag nanoplate type B were modeled as twinned triangular plates with a total of 9 layers of Ag atoms. Two sides of the plates are \{110\} facets that twin outward, therefore, are referred to as the major sides or major groove. One side is \{111\} facet that twins inward, and is called the minor side or minor groove of the plates. This type of plate has Hexagonal Closed-Packed (HCP) packing structure inside[9]. The triangular Ag plate used in the MD simulation is shown in Figure 2.2.

Figure 2.2: Triangular Silver Nanoplate Type B (a) left side of the plate with \{110\} facet that twins outward (major groove) (b) front face of the plate with \{111\} facet (c) right side of the plate with \{110\} facet that twins outward (major groove) (c) top side of the plate (d) bottom side of the plate with \{111\} facet that twins inward (minor groove)

The plates used in simulations have an edge-length to thickness ratio of 4:1 to match with the experimental geometric ratio. [7] Both types of plates have edge lengths of 80.90 Å and thickness of 21.24 Å. Both type A and type B plates were used to observe PVP chain interactions with the plate face and sides. While only type B plates were used in two-plate systems where attachment is expected, because the major and minor grooves represent the plate in experimental systems where Oriented Attachment was observed.
2.1.2 Velocity-Verlet Algorithm

All of our MD simulations use the Velocity-Verlet Algorithm for time step integration. In 1960s, Loup Verlet developed the popular basic integration scheme. It was based on a higher-order method used 60 years earlier to integrate electron trajectories[10]. Single Time Step algorithms like Verlet’s are preferred over MTS (Multiple Time Step) algorithms because of the computational simplicity. This was done by truncating the equations of motions to 3rd order Taylor-expansion to find the velocity. Computation for simulators have to go through many iterative calculations and codes. The Verlet scheme offers stability and simplicity which provides ease in simulation calculations. Not only that, due to this simplicity it is easier to implement variations in the basic methods (e.g. constrained dynamics, extensions to various statistical ensembles).

Position found by Verlet algorithm is accurate to the 4th order as shown in Eq. 2.1. Taylor expansion is applied around $X(t)$, describing terms both forward and backward in time.

$$X(t + \Delta t) + X(t - \Delta t) =$$

$$X(t) + \Delta t V(t) + \frac{\Delta t^2}{2} \ddot{F}(X(t)) + \frac{\Delta t^3}{6} \dot{V}(t) + O(\Delta t^4)$$

$$+ X(t) - \Delta t V(t) + \frac{\Delta t^2}{2} \ddot{F}(X(t)) - \frac{\Delta t^3}{6} \dot{V}(t) + O(\Delta t^4)$$

$$= 2X(t) + \Delta t^2 \ddot{F}(X(t)) + O(\Delta t^4)$$

(2.1)

There are three popular variants of Verlet: Leapfrog, Velocity and Position Verlet. The differences between them are the time interval used in the integration. The propagation triplet of velocity Verlet is shown in Eq. 2.2

$$V^{n+1/2} = V^n + \frac{\Delta t}{2} \ddot{F}^n$$

$$X^{n+1/2} = X^n + \Delta t V^{n+1/2}$$

$$V^{n+1/2} = V^{n+1/2} + \frac{\Delta t}{2} \ddot{F}^n$$

(2.2)
Velocity Verlet is preferred even in some MTS schemes. Forces are calculated at the end of the time interval and is convenient to do force splitting. Additionally, in one iteration cycle Velocity Verlet only requires one constrained-dynamics rather than two like needed in Position Verlet. Position Verlet has lower accuracy in terms of velocity estimation. [11] However, it is said that Position Verlet is recommended for methods with large time step. The case discussed in this work uses a timestep of 1 femtosecond, therefore Velocity Verlet is more suitable and selected.

### 2.2 Force Fields

The Force Field used in this work is the Metal-Organic Many-Body (MOMB) force field description for the Ag-EG-PVP system. This force field description was developed by Zhou et al. [1] Dispersion-corrected Density Functional Theory (DFT) was the calculation method that resulted in values that coincide with experimental data. The force field was described through different methods to represent the interactions between different types of atoms/molecules as discussed below.

The Embedded-Atom Method (EAM) is a way to describe the interactions between molecules inside a simulation environment. EAM works best when describing purely metallic bonding, where there is no directional bonding within the lattice.[12] Metallic bond between Ag-Ag atoms in our system were described by EAM. There is only metallic bonding in our nanoplate system, as the plate only consists of Ag atoms. The method does not work with covalency, significant charge transfer nor Fermi-surface effects. Despite that, our system still fits within the working scope of EAM.

CHARMM force fields are developed to be used especially in the biological fields in response to rapid growth in computational biochemistry and biophysics field. The database of forcefields for different systems has been continuously improved and the applications have been rapidly expanding in computational sciences field for the past 30 years. [13] In our system, CHARMM force fields were used to describe the organic-organic molecules interactions. Mostly PVP oligomers interactions, and when applicable, PEG chains[1]. More specifically, the force field parameters were
used to describe bond stretching, bending and most of the bond angles and torsions[14]. Values were obtained from both literature and from DFT calculations to formulate the force field.

The form of CHARMM dihedral potential is displayed in Eq. 2.3.

\[ E_{dihedral} = K_\chi \left[ 1 + \cos(n \chi - \delta) \right] \]  

\[ \chi = \text{dihedral or torsion angle} \]
\[ K_\chi = \text{dihedral angle force constant} \]
\[ n = \text{periodicity or multiplicity} \]
\[ \delta = \text{phase} \]

The form of bond-angle bending potential is displayed in Eq. 2.4.

\[ E_{angle} = K_\theta (\theta - \theta_0)^2 \]  

\[ K_\theta = \text{force constant} \]
\[ \theta = \text{bond angle} \]
\[ \theta_0 = \text{equilibrium bond angle value} \]

Morse potentials coupled with Grimme’s vdW method were used to describe the interactions between Ag and organic atoms within the system. The force field developed were mainly used to represent long-range vdW attraction and short-range Pauli repulsion. Where vdW are the most dominant interaction in the organic molecules adsorption to Ag surfaces. [6] Binding of the organic molecules with Ag nanostructures mostly happens through the O atom. [5] Therefore, a one-way electron-density function was utilized and allow O atoms to influence the Ag electron density. The Ag-Ag and Ag-organic interaction potentials are represented in the form displayed in Eq. 2.5, where the mathematical form can be found in Zhou et al [1].
\[ E = \sum_{i}^{Ag} F_{Ag} \left( \sum_{j \neq i} \rho_{Ag-Ag}(r_{ij}) + \sum_{j \neq i} \rho_{O-Ag}(r_{ij}) \right) + \frac{1}{2} \left[ \sum_{i \neq j}^{Ag-Ag} \phi_{Ag-Ag}(r_{ij}) + \sum_{i \neq j}^{Ag-M} \phi_{Ag-M}(r_{ij}) \right] \] (2.5)

### 2.3 Single-Plate MD Simulations

Our hypothesis about PVP-plate affinity is that PVP has stronger attraction to the \{111\} Ag face over the \{110\} side on the Ag nanoplate. However, there is not yet an MD investigation that was done to directly compare that in the case of Ag nanoplates. In our work, we created single-plate systems with PVP chains. Both plate types and different chain lengths of PVP were experimented to investigate the affinity of PVP towards the plate facets. In other words, this was used to investigate the plate size and chain length effects. The systems were then run on LAMMPS to equilibrate and density profiles of PVP molecules were plotted to compare the density between different sides. The simulations were run by freezing the Ag atoms inside the plates completely and letting PVP molecules move around at a temperature of 900K. The summary of systems is shown in Table 2.1. Density profiles were plotted in the form of histogram profiles. 2D histograms were generated by segmenting dimensions within the system into hexagonal bins. The color of each bin tells us the density of oxygen PVP in each bin. As mentioned in the previous section, oxygen is the binding atom between PVP and the Ag Plate. Therefore, the sum of the number of oxygen atoms in PVP molecules in each bin was counted to find the density of PVP.

### 2.4 Unbiased Two-Plates MD Simulations

Two-Plates and PVP systems were created from equilibrated system number 7 from Table 2.1 consisting of type B Plate and PVP 100-mer. The PVP-covered plates were duplicated and arranged into different initial configurations by using Moltemplate. Moreover, those systems were run to
<table>
<thead>
<tr>
<th>System number</th>
<th>Plate type</th>
<th>PVP chain Length</th>
<th>Number of PVP chains</th>
<th>Equilibration Time (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>PVP5-mer</td>
<td>78</td>
<td>22.7</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>PVP5-mer</td>
<td>156</td>
<td>21.4</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>PVP10-mer</td>
<td>78</td>
<td>23.5</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>PVP5-mer</td>
<td>72</td>
<td>22.5</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>PVP5-mer</td>
<td>156</td>
<td>24.4</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>PVP10-mer</td>
<td>78</td>
<td>19.7</td>
</tr>
<tr>
<td>7</td>
<td>B</td>
<td>PVP 100-mer</td>
<td>10</td>
<td>27.8*</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of Single Ag Plate Systems Equilibration at T=900K. *System 7 underwent simulated annealing to 1200K and back to 900K. The system were run at 1200K for around 5 ns.

investigate how PVP and plates behave when the plates are arranged differently. The two-plates simulations are run in the NVT ensemble with temperature being at T = 900 K, while for some of the systems temperature was ramped up to T = 1200 K to observe different results. The predictions include: first, major-minor grooves can come together, and the mechanism of Oriented Attachment can be observed. Second, parallel configurations of the plates will result in PVP clumping in between the plates, and the flat plate faces will not attach to each other. This can support the experimentally observed results that Oriented Attachment happens. In our MD system, without any solvent, PVP chains bind more strongly onto the Ag surfaces in vacuum. Therefore, we offset this overbinding by running our simulations at elevated temperatures. This allows the PVP’s mobility to be more representative. Additionally, raising temperature allow us to obtain better sampling results over a short period of time, as we are limited by the computational expenses.

### 2.5 Umbrella Sampling

#### 2.5.1 Pull Biased MD Simulations

There are preliminary steps before Umbrella Sampling can be executed. The initial trajectories of the desired Umbrella Sampling simulations have to be generated by using LAMMPS.
this case, the desired trajectory is when two plates are “pulled” towards each other and finally form attachment. In order to prepare the initial trajectories, successful “biased runs” have to be accomplished. The biased runs are based upon constricting the collective variables within the system. The 3 collective variables controlled in our biased system are called ZPULL, FIXSLIDE and FIXROTATE. For every collective variable, a force is used for the constricting to a target value. The strength of the force is defined by the spring constant and the difference between the target value and the current value.

The main collective variable in the system is ZPULL, the distance between two plates, as the plates are pulled towards each other. The target distance is progressively reduced after every set number of timesteps, force of a hypothetical spring pulls the plates towards the target distance. Lower and upper boundaries of the collective variable must be provided, in this case is 0 to 80 Å. The starting target distance is “centers”, which is set at the original distance between plates, in this case, is 66.5 Å. The final target distance or “targetCenters” is 2.5 Å, which is at the attachment distance between the center of mass of the selected molecules on the plates. The atom selection for the main and reference group is done by taking atoms near the edge of the each plates where attachment happens, an example is shown in Fig 2.3. The atoms are found by obtaining the atom numbers of all Ag atoms that are inside the set interval within the x direction, trying to make the selected atoms as close to a monolayer as possible. This type of selection is done rather than using the mass of the whole Ag plate to prevent plates from sliding over each other to reduce the distance. This also provide better control and focus the center of mass at the right point.
Figure 2.3: Highlighted in green are the atoms selected on one plate for side-to-side attachment pulling simulation.

“ForceConstant” is the spring constant (k) used to control the collective variable, a larger force constant represents a stronger force used to hold plates at the target value of the collective variable. “TargetNumStages” represent how many times the target distance changes, less number of stages means movement will be more abrupt while more number of stages means the movement of plates will be more gradual. “TargetNumSteps” is the number of timesteps the simulation will run per stage. The longer number of steps means the plates have more time to equilibrate at the distance set for that stage.

```
colvarsTrajFrequency 1000
colvar {
    name ZPULL
    width 1.0
    UpperBoundary 80.0
    LowerBoundary 0.0
    distanceZ {
        main { atomNumbers ... }
        ref { atomNumbers ... }
        axis (1.0,0.0,0.0)
    }
}

harmonic {
    colvars ZPULL
```
The second collective variable used in the system is \textit{FIXSLIDE}. The purpose of this variable is the second-step prevention to stop plates from sliding over each other. It is done by fixing the plates relative position on the z plane. From example below, as “centers” is set at 0, means the attaching sides of the plates held not move over or under each other by a force with spring constant value of 100 eV/Å². Only the “centers” value was set but not “targetCenters” because this value is to be kept fixed throughout the simulation. The atom selection for this collective variable is the same as in \textit{ZPULL}.

```plaintext
colvar {
  name FIXSLIDE
  width 1.0
  UpperBoundary 20.0
  LowerBoundary 0.0
  distanceXY {
    main { atomNumbers ... }
    ref { atomNumbers ... }
    axis (1.0,0.0,0.0)
  }
}
harmonic {
  colvars FIXSLIDE
  forceConstant 100.0
  centers 0
}
```

Another collective variable used is \textit{FIXROTATE}. It is used to restrict plate rotation, and is done by fixing dihedral angle between the plate corners as illustrated in Figure 2.4. The value of the dihedral angle is set to 0° means that the plate edges should stay parallel to each other, and is being held by spring constant of 100 eV/Å².
Figure 2.4: Highlighted in green are the atoms selected on plate corners for side-to-side attachment pulling simulation. (a) X-direction view looking straight onto the side of one plate. (b) Angled view seeing the selected atoms in relative to the other plate. (c) Z-direction view to see the selected atoms on both plates, where all 4 atoms should lie on the same plane.

```plaintext
colvar {
  name FIXROTATE
  width 1.0
  UpperBoundary 10
  LowerBoundary 0
  dihedral {
    group1 {
      atomNumbers 29192
    }
    group2 {
      atomNumbers 21682
    }
    group3 {
      atomNumbers 11106
    }
    group4 {
      atomNumbers 8851
    }
  }
}
```

2.5.2 Umbrella sampling

Once successful biased simulation initial trajectories are accomplished, umbrella sampling provides the ability to simultaneously run sampling simulations. First, the initial trajectories must be
divided into windows where plates are at different distance away from each other. This is done by putting LAMMPS command to output a set number of windows from the start to the attachment, the greater number of windows, the smaller the increment of the plate distance between each window.

After that, the restart files are used as initial configurations for umbrella sampling simulations. In these sampling simulations, the plates are fixed to the distance at that restart by a small ZPULL force. If the plates attraction force is very strong, the ZPULL force will not be able to hold the plates to their original position and will move closer together. Similarly, if the repulsion force is too strong, plates will move further apart. Inside the sampling simulations, this will result in the plates spending more time in a energetically favorable distance. Once the results from all runs are compiled, Umbrella Integration is used to find the Potential of Mean Force (PMF) of the trajectories. Umbrella Integration uses the probability distribution of distance, force constant and temperature to generate PMF profile, as more accurately described in Eq. 2.6.

\[
A_i(\xi) = -\frac{1}{\beta} \ln P_i^b(\xi) - \omega_i(\xi) + F_i
\]  

(2.6)

\[\xi = \text{reaction coordinate (distance in this case)}\]

\[A_i(\xi) = \text{Potential of Mean Force}\]

\[\beta = \frac{1}{k_BT}\]

\[P_i^b(\xi) = \text{Biased Probability Distribution of } \xi\]

\[\omega_i(\xi) = \text{Harmonic bias Potential}\]

\[F_i = \text{Additive Constant to be found by algorithm}\]

In order to obtain a complete PMF Profile, the probability distribution histogram must be complete. In other words, every point between the starting and ending values must be sampled at least once, and there can not be a gap in the distribution histogram. To achieve this, the challenge comes to selecting the appropriate force constant, number of sampling windows and sampling time. As previously discussed, the probability distribution is influenced by the tendency of system to move
in a particular direction and the force constant. When force constant is too weak, plates will follow system forces and only the favorable distance will be sampled. And when force constant is too strong, system will not move from the starting position of that sampling window. An appropriate force constant is one that allows the system to move gradually from the starting point towards the favored distance. That way, the compiled results from all simulation windows will have distribution for the complete spectrum.
Chapter 3

Results and Discussion
3.1 Single-Plate MD Simulations

In this section, the discussion will mainly involve investigation of PVP chain-length effects and Ag plate atom configuration effects (with type A and type B plates). In the density plot diagrams, there is a color spectrum next to every diagram for convenience in comparing the color on the tiny hexagonal windows to the normalized color scale. The density plots represented are normalized per system, in a sense that, the color spectrum on the side of each diagram can not be compared to the diagram from another system with different number of PVP chains or different plate configurations. \( V_{\text{max}} \) noted on the top of the diagrams are the maximum count of Oxygen atoms in one bin for the trajectories analyzed for that system.

In the first system, type A plate is surrounded by 78 molecules of PVP 5-mer and the simulation ran for 22.7 ns at \( T = 900 \) K. In Figure 3.1(a), there is an even distribution of PVP on the face of the plate. On the \{110\} side shown in Figure 3.1(b), there is less PVP density in comparison to the two \{111\} sides. In Figure 3.1(c) and (d), yellow lines are visible along the length of the sides, which shows that there is a geometrical ordering of the PVP oxgen’s atom along the crystal lattice of the \{111\} side facet.

![Figure 3.1](image)

Figure 3.1: Plots of PVP’s Oxygen density histogram for type A plate PVP 5-mer system. (a) Top face of plate (b) Bottom side of plate \{110\} (c) Right side of plate \{111\} (d) Left side of plate \{111\}

The next system has the same set up as the previous, with a type A plate for system number 2. However, the amount of PVP 5-mer were doubled to 156 molecules and was run for 21.4 ns at \( T = 900 \) K. The purpose of this system was to see if having excess PVP will affect the distribution along the Ag plate surface. From the results as shown in Figure 3.2, the density plot has a similar
trend to original system. While probability density in Figure 3.2(a) the center of the face is denser than near the sides. PVP 5-mer chains seem to aggregate onto the \{111\} sides more than \{110\} sides.

![Figure 3.2](image)

Figure 3.2: Plots of PVP’s Oxygen density histogram for type A plate PVP 5-mer system with double number of PVP. (a) Top face of plate (b) Bottom side of plate \{110\} (c) Right side of plate \{111\} (d) (b) Left side of plate \{111\}

We then investigated the chain length effect by increasing PVP chain length to 10 monomers chains in system number 3. The number of PVP was kept at 78 molecules surrounding a type A plate and was equilibrated for 23.5 ns at T = 900 K. Results are shown in Figure 3.3, longer chain in this case did not have significant effect on PVP density preference on the plate surfaces. In relative to the size of the plate, the length of the PVP chain is still quite small. For a single PVP 10-mer chain, it can still stretch out fully when attached onto either the face and the side of the plate, this is why there is no conformational driving force for a chain to stick onto one over the other.

![Figure 3.3](image)

Figure 3.3: Plots of PVP’s Oxygen density histogram for type A plate PVP 10-mer system. (a) Top face of plate (b) Bottom side of plate \{110\} (c) Right side of plate \{111\} (d) (b) Left side of plate \{111\}

In system number 4, type B plate is surrounded by 78 molecules of PVP 5-mer and the simulation ran for 22.5 ns at T = 900 K. In Figure 3.4(a), density profile shows a fairly even distribution
of PVP across the plate. With a different type of plate configuration, there is slightly more PVP on
the face than on the \{111\} sides. Higher density was observed along the length of the \{110\} side
as there is a yellow line running along the top part of the side in Figure 3.4(c). This preference
is opposite from what was seen in type A plate systems. This might be because PVP 5-mer fits
slightly better on the minor groove of the plate. Overall, the difference is not significant enough
to say there is a strong preference for PVP binding locations on the plate. Shorter PVP chains are
more freely to move around on the surface, that is why the molecules do not prefer one surface
over another.

Figure 3.4: Plots of PVP’s Oxygen density histogram for type B plate PVP 5-mer system. (a) Top
face of plate (b) Bottom side of plate \{111\} (c) Right side of plate \{110\} (d) (b) Left side of plate
\{111\}

For a type B plate in system number 5 with double amount of PVP 5-mer (156 number of
molecules), the equilibration was run for 24.4 ns at T = 900 K. The results is displayed in Figure
3.5. The general PVP-binding trend is the same, with small preference of face over the side.
The PVP density are fairly even between the sides in this system, still showing small preferences
between faces and sides.

Figure 3.5: Plots of PVP’s Oxygen density histogram for type B plate PVP 5-mer system with
double number of PVP. (a) Top face of plate (b) Bottom side of plate \{111\} (c) Right side of plate
\{110\} (d) (b) Left side of plate \{111\}
In system 6, a type B plate is surrounded by 78 molecules of PVP 10-mer. Equilibration time was 19.7 ns, the system temperature was set to \( T = 900 \) K. The density plot in Figure 3.6(a) displays brighter highlight around the center of the face, additionally the density plot for the sides have lower values. Result from this system started to show that PVP 10-mer prefers to interact and bind to the face of the plate rather than the sides. This selectivity is more obvious in this system than in system 3 even though the PVP 10-mer chain length is the same. The structural differences in the plate types may help to explain the different results. Type A and type B plates have the same length and thickness dimensions, the difference is the sides in type A are slanted and flat, while in type B there is twinning into major and minor groove as described in earlier sections. PVP chains are more able to relax and bind naturally on flat surfaces, explaining why the surface characteristics of the two plate types are significant for PVP binding preference. System 6 also pinpoints the chain length effect because binding preferences started to emerge, in comparison to PVP 5-mer in system 4 which did not show binding preferences.

In system 7, 10 molecules of long PVP 100-mer chains were added to a type B plate. In total, the simulation was run for 27.8 ns, it was run at \( T = 900 \) K for around 22 ns then further equilibrated at \( T = 1200 \) K for around 5 ns. Figure 3.7 shows the density plot of PVP 100-mer after the 1200 K equilibration. In system 7, due to very long PVP chain is used, the chain length effect is very evident. As seen in Figure 3.7(a), the highest density are at the center of the face and there is very low densities around all the sides of the plate. Extremely strong preference of face over side is observed. As discussed earlier, PVP chains would prefer to relax on the larger flat surface.
rather than on a small side, especially for long chains. The thermodynamic argument is that a PVP chain has larger number of possible conformations on the plate face, in other words, it has larger entropy than on the sides. Therefore, the chains have much higher affinity towards the face of the plate. Because PVP 100-mer is more similar to chain length used in real plate synthesis, this result supports the prediction of Oriented Attachment that can happen spontaneously in synthesis systems.

![Figure 3.7](image.png)

Figure 3.7: Plots of PVP’s Oxygen density histogram for type B plate PVP 100-mer system. (a) Top face of plate (b) Bottom side of plate {111} (c) Right side of plate {110} (d) Left side of plate {111}

From the collection of results in this section, the differences between type A and type B plates were seen beginning at PVP 10-mer systems. Type B plates allowed PVP chains to have selectivity towards binding with plate faces than the twinning sides, while in type A no preference was seen. The chain length effects could be very strongly observed when moving from shorter chain to longer chains, where PVP 5-mer systems did not show preferences but PVP 100-mer system showed very strong preference towards face of the plate than the sides.

### 3.2 Unbiased Two-Plates MD Simulations

Many two-plates systems with different initial configurations were run by taking the equilibrated system 7 plate, duplicating the plate to form the two-plates system by using Moltemplate. For each initial configuration, the system first start at $T = 900$ K but some systems were ramped up to $T = 1200$ K to find alternative behavior of the system. In these PVP 100-mer systems no Oriented Attachments were observed even though the two-plates system were run for even over
10 ns. After running for a certain length of time, in many systems the plates seem to stop moving towards each other. A certain layer of PVPs are in between the two plates, forming a film that seem to prevent the attachment between the nanoplates. This is very similar to the mesocrystal configuration observed with Ag nanocrystals and solvents in a referenced study[4]. This happened with both systems with side-side initial configuration and face-face initial configuration.

![Image](image.png)

Figure 3.8: (a) Minor-Minor side initial configuration for Two-Plates systems (b) Close-up initial configuration (c) Results after 6.12 ns of simulation at T = 900 K (d) Results after 4.08 additional ns from diagram (c) simulation at T = 900 K (e) Results after 3.98 additional ns from diagram (c) simulation at T = 1200 K

In Figure 3.9 shows a system that used plate from equilibrated system 6, which consisted of twin plates with PVP 10-mer. This temperature in this system was ramped up to T = 1200 K and was only run for 1.5 ns. This was the only unbiased system where plate attachment was observed. At such a high temperature of 1200 K, PVP 10-mer chains do not bind very strongly to the plates. Without the hindrance from PVP, the two plates could come together quite in a very short time. However, since the SDA effect is not the real driving force for attachment in this case, this does not fall into the category of Oriented Attachment.

![Image](image.png)

Figure 3.9: Plates attachment in unbiased two-plates system with PVP 10-mer at T = 1200 K (a) Major-Minor side initial configuration for Two-Plates systems (b) snapshot at 0.3 ns (c) snapshot at 0.7 ns (d) snapshot at 1.1 ns where plates were attached
3.3 Pull Biased MD Simulations

There are possibilities for attachment with unbiased systems like in experimental Ag nanoplate synthesis, however, brute force approach was applied and success rate was very low. In order to obtain more information about Oriented Attachment mechanism, Umbrella Sampling method was applied to compute a Potential of Mean Force for the system. The preliminary steps to Umbrella Sampling is generating initial trajectories for the attachment through biased MD simulations pulling the plates towards each other. There are certain challenges regarding to these “pull” simulations, for the three collective variables defined in the Computational Methods section: \textit{ZPULL}, \textit{FIXSLIDE} and \textit{FIXROTATE}. \textit{FIXSLIDE} and \textit{FIXROTATE} collective variables are constant throughout the pull simulations, therefore the “ForceConstant” and “Centers” values are fixed and easier to set value of. While for \textit{ZPULL} collective variable, there are many factors that influence the success of the pull simulations. Those factors include the “ForceConstant”, “TargetNumStages” and “TargetNumSteps”. These three factors have to come together as a good combination to have a successful attachment. Setting large number of stages means the change is more gradual, and the system must have enough time to equilibrate at each stage to be able to move on to the next stage without lagging. Ideally, very large “TargetNumStages” and “TargetNumSteps” are preferred, however, they need to stay within the computational limit to be efficient. Regarding to the force constant, if force constant is too small, although the final “TargetCenters” is at attachment point, there is not enough force to push through the steric hindrance of PVP chains. The stronger force constant means that the plates are pulled to the set distance more forcefully. However, if the force constant is too strong, PVP chains will not have a chance to move out of the way and become constantly squished in between the attaching plate.

In this section, two pull simulations were run. The first one is the Major-Minor side attachment or what we expect to happen. The second system is the Parallel face-face attachment. The hypothesis concerning two these systems is that parallel configuration will require more force to obtain successful attachment than the major-minor side attachment. This hypothesis is based on
earlier results from the single plate system where PVP chains choose to aggregate on the face of the plates. In order to have parallel face-face attachment, all of those PVP chains must move out to the side. Having to force so many more PVP molecules to move away from their preferred binding surface will require much larger force compared to the major-minor side attachment system. For the Major-Minor side attachment simulation, successful combination of factors were $k = 1400 \text{ eV/Å}$, 155 number of stages with 10,000 timesteps per stage. While for Parallel face-face attachment $k = 1500 \text{ eV/Å}$, 100 number of stages and 10,000 timesteps per stage were used.

### 3.4 Umbrella Sampling

In Umbrella Sampling section, the trajectories generated from the pull simulations are divided into small windows to run samples simultaneously. As outlined in the Computational Methods section, the key part in the sampling process is an appropriate sampling force constant have to be chosen in order to obtain a good PMF graph. Usually the new force constant value is much smaller than the value used in the pull simulations. Then, data from all the windows are integrated using Umbrella Integration equation.

In the Major-Minor side attachment system, trajectories were split into 100 windows, where each window ran for 2.5 ns. Window number 1 is the window where plates are the furthest apart, and window number 100 is where two plates are entirely attached. From window 1-94 and 99-100, the force constant ($k$) was set at 2 eV/Å, and between window 96-98 $k$ was set to be 10. According to the PMF from the in Figure 3.10, The output PMF displayed the energy barrier to be $57.0 \pm 1.8 \text{ kcal/mol}$. The windows that required high value of $k$ are the windows surrounding the energy barrier peak. The energy is high and unfavorable, so the plate would want to move to a distance with lower energy. Therefore $k$ of 2 is not strong enough to keep the distance near the set point needed for the histogram. By changing $k$ to 10 for that set of windows, all distance were sampled as there is no zero value on the histogram shown in Figure 3.11. At distance $z$ is at around 25 Å apart, there is a local energy minimum, this is the distance where PVP chains from both plates start
to associate with each other. It is suspected that most unbiased simulation runs from the previous section were stuck at similar energy minimum along the energy surface. This is could be a similar phenomenon to a mesocrystal configuration[4]. Therefore this can explain why the success rate of unbiased runs were low. In real synthesis systems where Oriented Attachment is observed, the mixture consist of triangular nanoplates, PVP and PEG as solvent. The unbiased simulations that were run in this study would have followed this PMF profile. In this study, solvent effects are still not considered, in which we expect that PVP system in vacuum have a larger local minimum and higher energy barrier relative to a solvated environment. With the presence of solvent, it is possible that the PMF profile will be changed.

Figure 3.10: Potential of Mean Force Plot for Major-Minor side attachment system where $z$ is the distance between two plates
Figure 3.11: Umbrella Sampling Histogram for Major-Minor side attachment system where $z$ is the distance between two plates

Figure 3.12 displays the PMF of Parallel face-face attachment system while Figure 3.13 displays the complete histogram of the system. The trajectories were divided into 100 windows while each window was run for 2 ns. All windows were run with force constant equal to 2 eV/Å, except for window 95-98 where $k$ value was set to 220 eV/Å. The energy barrier for this system has a value of $70.2 \pm 3.0$ kcal/kmol which is larger than the barrier of Major-Minor side attachment system. The actual energy barrier peak has a long tail up to around 32 Å, which is relatively wider than the Major-Minor side attachment. The local minimum being further distance away from the maximum makes it even more difficult for the system to reach attachment. This further supports the hypothesis of Oriented Attachment mechanism, prefers to attach between the plate sides and not the faces[4].
Figure 3.12: Potential of Mean Force Plot for Major-Minor side attachment system where $z$ is the distance between two plates

Figure 3.13: Umbrella Sampling Histogram for Major-Minor side attachment system where $z$ is the distance between two plates
Chapter 4

Conclusion and Future Work
4.1 Conclusion

Looking at the big picture, each part of the simulations gave different collective insights to aid the knowledge about Oriented Attachment mechanism. From single plate equilibration simulations, the system with the least binding preference was the short PVP 5-mer chains on type A plate with slanted side. System that displayed best binding preferences was the one with long polymer chains (PVP 100-mer) on type B plate with HCP sides. The PVP chains preferred to bind on the flat surface because there is a larger number of possible conformations and the chains have larger entropy or degree of freedom. This way, the plate sides are less crowded and can be approached by another plate and form oriented attachment. From unbiased two-plates MD simulations, there were no successful attachments in any of the 8 systems run with PVP 100-mer even at ramped up temperature from $T = 900$ K to $T = 1200$ K. There was one successful attachment with PVP 10-mer system ramped up to $T = 1200$ K. However, since PVP molecules were not strongly bound to any surface due to high temperature, therefore the trajectories do not count as Oriented Attachment. Insights from pull simulations and umbrella sampling showed that Major-Minor side attachment systems (similar to Oriented attachment) required smaller force constant of 1400 eV/Å. While the plate-plate face attachment used larger force constant of 1500 eV/Å. The output PMF displayed the energy barrier to be $57.0 \pm 1.8$ kcal/mol for Major-Minor side attachment system and $70.2 \pm 3.0$ kcal/mol for parallel face-face attachment. Confirming that Major-Minor side attachment or Oriented Attachment has lower energy barrier and is the more likely mechanism. The PMF for both systems showed energy local minima before the energy barriers predicted to be when PVP chains from both plates started interacting, similar to a mesocrystal configuration. This could be an explanation for why the two-plates system unbiased runs were less successful because the systems were stuck at the local energy minimum.
4.2 Future Work

The possible future work that can be done to find more about the system is to do umbrella sampling for systems at $T = 1200$ K, then the PMF of the attachment can be seen for that temperature. More comparison can be made to see the likelihood of Oriented Attachment Mechanism. Additionally, to further study PVP binding behavior onto surface, examining how a single PVP 100-mer chain lay itself onto the plate can help predict the binding preferences. This can be done in VMD to only show single chain at a time. Moreover, in our work, solvent effects were not taken into account. Therefore, once enough information and computational systems are for the current systems are ready, poly ethylene glycol system can be added. In plate-PVP-PEG system, polymer chain-length effects on single plates, umbrella sampling and even two-plates unbiased simulations can be done to better describe the system. In a far future where the system is more well understood, it is possible to switch the force field to ReaxFF, which is a more realistic force field that also take into account any reactions, bond forming/breaking or ion formation to describe the system even more realistically.
Bibliography


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Education
The Pennsylvania State University Graduation: May 2017
Bachelor of Science in Chemical Engineering (CH E)
Schreyer Honors College
Dean’s List
Fall 2013 – Fall 2016

Skills
- Python, Mathematica, MATLAB, Linux OS, Solidworks, HYSYS
- Fluent in Thai and English

Engineering Experiences
- **Facilities Engineer Intern** - *Chevron Thailand Exploration and Production Ltd. (CTEP)* 2016
  - Evaluated project’s feasibility of Glycol Dehydration skid verification for possible higher gas production
  - Applied course knowledge to identify and evaluate important design factors using HYSYS simulation
  - Delivered feasible project methodology as well as analysis and results in both an interim presentation to the department and a final presentation to a panel of senior engineers
  - Received a 50,000 THB (~$1,500) scholarship for excellent project and presentation
- **Teaching Assistant for Fluid Dynamics Course** - *Penn State Chemical Engineering Department* 2016-present
  - Lead a few lectures for a class of 168 students and perform relevant real world demonstrations through laboratory work
  - Deliver supplemental help sessions aimed at clarifying course concepts
  - Grade conceptual and computational final and midterm exams
- **Molecular Dynamics Simulation Research Assistant** - *Dr. Kristen Fichthorn Research Lab* 2015-present
  - Elucidate the Oriented Attachment (OA) growth mechanism of Silver nanoparticles in the presence of PVP
  - Utilize LAMMPS to simulate and test the hypothesized mechanism, then utilize Python and VMD to produce visualizations such as density profiles and molecule trajectories
  - Facilitate weekly meetings and advise on plausible direction to proceed with experiment methodology (i.e. factor/variables, experiment focus) based on theoretical knowledge
- **Trainee** - *Thai Nondestructive Testing Public Ltd (TNDT)* 2014
  - Acquired knowledge on processes of different nondestructive-testing inspections performed at TNDT

Academic Engineering Projects
- **MDEA Absorption Design Engineer** Mass Transfer Course Project 2016
  - Developed an iterative process on Mathematica to maximize profit by identifying best combination of three absorption tower mass transfer parameters for an Enhanced Oil Recovery methane/carbon dioxide mixture.
  - Calculated the max annual profit of $6.37 million
  - Formulated graphical and completed detailed report of design process
- **The Best Engineered Designed Award** Sustainability Innovation Project Sponsored by *Alcoa* 2013
  - Led a team of 5 to design an environmentally sustainable bike sharing center using aluminum
  - Researched, advised, and devised an implementation plan to develop a prototype of the bike sharing center to encourage students to utilize the center, reducing gas-fueled transportation

Leadership & Involvement
- **President**, Thai Student Association at Penn State University (ThSA) 2016-present
  - Organized and delegated responsibilities for the annual Thai Night event for 216 audiences
  - Planned all aspects of the 2016 Fall Welcome Social, attended by 50 Thai students
  - Reach out and initiate joint events with over 5 other student organizations.
  - Provide bi-annual financial activity reports to the Royal Thai Embassy in Washington, D.C.
- **Publicity Chair**, Penn State Chapter of the American Institute of Chemical Engineers (AIChE) 2016-present
  - Oversaw all aspects of social media of the club
  - Create posters and promote AIChE events e.g. company info sessions, general body meetings, tailgates
- **Orientation Leader**, International Student Orientation University Office of Global Programs 2016
  - Interacted closely with 2 groups of 20 incoming international students, aiding their transition to Penn State
  - Follow up and continue communication after the orientation (current)
- **Distinguished Member**, UNICEF at Penn state 2016
  - Conducted fundraisers and awareness events and participated in new meeting topics discussions every week
- **Selected Participant**, Global Engagement and Leadership Experience Conference (GELE) 2015
  - Selected through competitive application process to learn about all aspects to become a global leader through cultural discussions, engaging activities and practical scenario simulations
- **Mentor**, Engineering Orientation Network 2015
  - Provided academic guidance and worked closely with a group of 10 incoming chemical engineering students to assist them to familiarize with college life