Potential of mean force for two nanocrystals: Core geometry and size, hydrocarbon unsaturation, and universality with respect to the force field

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Disciplines
Biological and Chemical Physics | Materials Chemistry | Materials Science and Engineering | Nanoscience and Nanotechnology
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Potential of mean force for two nanocrystals: Core geometry and size, hydrocarbon unsaturation, and universality with respect to the force field

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We present a detailed analysis of the interaction between two nanocrystals capped with ligands consisting of hydrocarbon chains by united atom molecular dynamics simulations. We analyze large cores (up to 10 nm in diameter) and ligands with unsaturated carbon bonds (oleic acid) and we investigate the accuracy of the computed potential of mean force by comparing different force fields. We also analyze the vortices that determine the bonding, including the case of asymmetric nanocrystals, and discuss effects related to the intrinsic anisotropy of the core. Overall our results are in agreement with the predictions of the recently proposed orbifold topological model. Published by AIP Publishing. https://doi.org/10.1063/1.5039495

I. INTRODUCTION

Nanocrystals (NCs) are nanometer scale crystalline inorganic cores functionalized by capping ligands. While successful assembly of structures with long range order has been reported for ligands such as DNA1,2 or water soluble polymers,3–5 this paper is focused on hydrocarbon ligands that have led to a fascinating number of single component6 and binary7–18 superlattices.

In our previous paper,19 we have presented a detailed study of the binding mechanism for two NCs to form a “diatomic” molecule. It was shown that vortices of ligands, see Fig. 1, play the same role as electronic orbitals in the covalent bonding of atoms or molecules. Precise calculations of the Potential of Mean Force (PMF) allowed us to quantify the binding free energy, which is of the order of several hundreds of $k_B T$s.

There are, however, a number of very important questions that needed further investigation. Experiments18 show successful self-assembly in NCs with core sizes of 10 nm or even bigger, while the largest cores included in previous20–23 work are at most of the order of two nms. This regime of large cores is also relevant as their shapes are polyhedra rather than perfect spheres, see Fig. 2, and as the relative size of the core to the ligand increases, anisotropic effects, those that arise from the non-sphericity of the core, may come into play. Furthermore, oleic acid, which includes a double bond at C9, is one of the most common ligands used in experiments,24 but no studies are available on the role of double bonds on ligand conformations. Finally, given the large magnitude of the binding free energies, the obvious question is how dependent are the results of the PMF on the particular force field. It is therefore urgent to settle and understand all these questions.

Early attempts to describe NC interactions with hard spheres,24,25 flexible potentials,26,27 or other coarse-grained models28 were qualitative in nature and could not correctly predict lattice density, packing fractions, and other observables.29 The Orbifold Topological Model (OTM)29 provided, for the first time, a rigorous quantitative description of the structural properties of Binary Nanoparticle Superlattices (BNSLS), as demonstrated by the successful parameter-free description of more than 160 experiments.30 The existence of vortices was one of the key OTM predictions that our simulations has recently confirmed.19 The investigations we report in this paper are also motivated at establishing the range of applicability for the OTM.

The organization of the paper is as follows: First, we describe the model and notations and then present PMF calculations and vortex configurations for simple hydrocarbons, large cores, and oleic acid and a comparison of the two force fields. Then we present a discussion of the results and some conclusions.

II. RESULTS

A. Model parameters

We consider NCs whose crystalline cores consist of gold atoms and whose ligands are saturated hydrocarbon chains or hydrocarbon chains having one degree of unsaturation, denoted by the formula Au_n(SC_m−C_9H_2m+1)_i, where n refers to the number Au atoms, x refers to the position of the first carbon in the double bond, and i is the number of grafted hydrocarbon chains. For clarity, we will eliminate hydrogens from our naming convention, instead denoting each one of the CH, CH2, or CH3 united atoms in our model as C. We studied 6 core sizes Au_{40}(SC_m)_2, Au_{201}(SC_m)_80, Au_{1205}(SC_m)_{258}, Au_{4032}(SC_m)_{332}, AuShell_{2300}(SC_m)_{750}, and AuShell_{3050}(SC_m)_{913}, considering distinct chain lengths of

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m = 4, 6, 9, 12, 17, and 18 carbons. The shapes of the cores follow truncated octahedral or cuboctahedral geometries, resulting in the [111] and [001] families of planes as the exposed surfaces of the fcc crystalline cores; see Fig. 2.

We determine the sulfur binding sites by projecting a unit sphere containing a given number of evenly distributed points on the surface of the core. These binding sites were grouped into three types: hollow, bridge, and on-top, as described in the work of Tachibana et al.,\textsuperscript{31} based on the relative location of the site to the close packed spheres of Au that comprise the core surface. The final positions of the bound sulfur atoms were determined by adding a distance normal to the plane of the core surface. The distance is dependent on the type of binding site.\textsuperscript{31} The resulting sulfur binding configuration on each NC core is shown in Fig. 3.

Because the NC core is not spherical, the precise definition of the diameter requires some assumptions. We define it by $D_i$ as twice the radius of gyration of the sulfur atoms, with an additional term of 0.24 Å added due to relative lengths of the S–C and C–C bonds. We define grafting densities as per molecular areas of grafting sites. We also measure the effective “atom.” Our force field follows Hautman and Klein\textsuperscript{32} and Ref. 33 for unsaturated chains; see the supplementary material for further details.

Following previous studies,\textsuperscript{19,21,34} we define the parameter $\lambda$ and $\tau$ from

$$
\lambda_i = \frac{L_i}{R_i}, \quad \tau_i = \frac{\tilde{r}_m}{R_i} \equiv \tau(\lambda_i, R_i),
$$

where $L_i$ is the extended length of the ligand, $\tilde{r}_m$ is half the NC separation, and $R_i$ is the core radius. There is an equation of state $\tau(\lambda_i, R_i)$, so $\tau$ is fixed by $\lambda$ and $R$. Common expressions are the Optimal Packing Model (OPM) formula\textsuperscript{34}

$$
\tau_{OPM} = (1 + 3\lambda_i\xi_i)^{1/3}
$$

and the Overlap Cone Model (OCM) formula\textsuperscript{21}

$$
\tau_{OCM} = \frac{\frac{1}{2} + \lambda_i}{\left(-1 + \sqrt{1 + \frac{8(1 + 3\lambda_i\xi_i)}{(1 + \lambda_i)^3}}\right)}.
$$

where $\xi_i = A_0/A$ is the ratio between the actual molecular area $A$ (that is, the area of the NC surface divided by the total number of grafted chains) to the minimum possible $A_0 \approx 20$ Å$^2$.

B. Configuration characteristics

1. Potential of mean force

We discuss the PMF in dry conditions, i.e., in the absence of a solvent. This is because in all experiments, the final result is a system where all the solvent is completely evaporated. Consideration of solvent effects are relevant to fully understand the dynamics of self-assembly, but should not affect

![FIG. 2. NC cores AuShell$_{1050}$ (SC$_{m-Cux}$)$_{913}$ (left), AuShell$_{1200}$ (SC$_{m-Cux}$)$_{750}$ (bottom center), and Au4032(SC$_{m-Cux}$)$_{432}$ (top center) with Au atoms shown in yellow and S atoms shown in red. Hydrocarbon chains are not drawn. The Au–Au distance is ∼2.8 Å. The geometry of the cores expose [001] and [111] planes. HC chains are attached at the sulfur sites, described by maximum length $L_0$ and having $n = m - 2$ defined dihedral angles where $m$ is the number of carbons in the chain. Unsaturated chains contain a cis double bond, located between carbons $x$ and $x + 1$.](image)
the final equilibrium state. The cases considered are listed in Table II. Note that this implies a range of \( \lambda \), see Eq. (1), over an interval \([0.27, 2.66]\). The PMF was calculated by the Weighted Histogram Analysis Method (WHAM) method, as discussed in our previous paper,\(^{19}\) and we provide a brief description in Sec. V. Four representative cases are shown in Fig. 4, see the supplementary material for the remaining cases, illustrating a competition between van der Waals attractions and entropically driven chain repulsions. The hydrodynamic radius \( r_H \) is the radius of the free (unperturbed) NC.

![Diagram of binding sites](image)

**FIG. 3.** The binding sites are determined by first projecting a unit sphere on the surface of the core (top left). These sites are categorized as hollow, bridge, or on-top, each having a certain distance perpendicular to the exposed plane (right) as described in the work of Tachibana et al.\(^{31}\) This approach is used for nanocrystal cores AuShell\(_{3050}(SC_m)_{913}\), AuShell\(_{2200}(SC_m)_{750}\), and Au\(_{4032}(SC_m)_{432}\) (bottom left).

<table>
<thead>
<tr>
<th>NC ( R_i ) (Å)</th>
<th>( \xi )</th>
<th>( L )</th>
<th>( \lambda )</th>
<th>( r_H ) (Å)</th>
<th>( 2\tilde{r}_m )</th>
<th>( \tau_H )</th>
<th>( \tau_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(_{201}) (SC(<em>4))(</em>{80})</td>
<td>10.15</td>
<td>1</td>
<td>7.09</td>
<td>0.70</td>
<td>14.5</td>
<td>27.5</td>
<td>1.43</td>
</tr>
<tr>
<td>Au(_{201}) (SC(<em>6))(</em>{80})</td>
<td>10.15</td>
<td>1</td>
<td>9.62</td>
<td>0.95</td>
<td>16.3</td>
<td>28.2</td>
<td>1.61</td>
</tr>
<tr>
<td>Au(<em>{40})(SC(</em>{17\text{Cis}8}))(_{62})</td>
<td>9.285</td>
<td>1</td>
<td>23.40</td>
<td>2.31</td>
<td>22.2</td>
<td>25.2</td>
<td>2.23</td>
</tr>
<tr>
<td>Au(<em>{40})(SC(</em>{16\text{Cis}9}))(_{62})</td>
<td>9.285</td>
<td>1</td>
<td>24.66</td>
<td>2.66</td>
<td>21.0</td>
<td>25.2</td>
<td>2.26</td>
</tr>
<tr>
<td>Au(<em>{201}) (SC(</em>{17\text{Cis}8}))(_{80})</td>
<td>10.15</td>
<td>1</td>
<td>23.40</td>
<td>2.31</td>
<td>22.2</td>
<td>28.2</td>
<td>2.23</td>
</tr>
<tr>
<td>Au(<em>{201}) (SC(</em>{16\text{Cis}9}))(_{80})</td>
<td>10.15</td>
<td>1</td>
<td>24.66</td>
<td>2.43</td>
<td>22.6</td>
<td>28.2</td>
<td>2.23</td>
</tr>
<tr>
<td>Au(<em>{1289})(SC(</em>{17\text{Cis}8}))(_{258})</td>
<td>18.23</td>
<td>1</td>
<td>23.40</td>
<td>1.28</td>
<td>32.7</td>
<td>51.5</td>
<td>1.79</td>
</tr>
<tr>
<td>Au(<em>{1289})(SC(</em>{18\text{Cis}9}))(_{258})</td>
<td>18.23</td>
<td>1</td>
<td>24.66</td>
<td>1.35</td>
<td>33.2</td>
<td>51.2</td>
<td>1.82</td>
</tr>
<tr>
<td>Au(_{40})(SC(<em>3))(</em>{432})</td>
<td>25.65</td>
<td>1</td>
<td>13.42</td>
<td>0.52</td>
<td>34.9</td>
<td>64.5</td>
<td>1.36</td>
</tr>
<tr>
<td>Au(<em>{40})(SC(</em>{12\text{Cis}3}))(_{432})</td>
<td>25.65</td>
<td>1</td>
<td>17.22</td>
<td>0.67</td>
<td>37.2</td>
<td>64.4</td>
<td>1.45</td>
</tr>
<tr>
<td>Au(<em>{40})(SC(</em>{18\text{Cis}3}))(_{432})</td>
<td>25.65</td>
<td>1</td>
<td>24.66</td>
<td>0.97</td>
<td>41.1</td>
<td>63.7</td>
<td>1.60</td>
</tr>
<tr>
<td>Au(<em>{40})(SC(</em>{18\text{Cis}9}))(_{432})</td>
<td>25.65</td>
<td>1</td>
<td>24.66</td>
<td>0.96</td>
<td>41.0</td>
<td>66.1</td>
<td>1.60</td>
</tr>
<tr>
<td>AuShell(<em>{2200}(SC_9)</em>{750})</td>
<td>40.21</td>
<td>0.741</td>
<td>13.42</td>
<td>0.33</td>
<td>48.2</td>
<td>92.7</td>
<td>1.20</td>
</tr>
<tr>
<td>AuShell(<em>{2200}(SC</em>{12})_{750})</td>
<td>40.21</td>
<td>0.741</td>
<td>17.22</td>
<td>0.43</td>
<td>50.5</td>
<td>91.7</td>
<td>1.25</td>
</tr>
<tr>
<td>AuShell(<em>{2200}(SC</em>{18})_{750})</td>
<td>40.21</td>
<td>0.741</td>
<td>24.66</td>
<td>0.62</td>
<td>54.2</td>
<td>93.7</td>
<td>1.35</td>
</tr>
<tr>
<td>AuShell(<em>{2200}(SC</em>{18\text{Cis}9})_{750})</td>
<td>40.21</td>
<td>0.741</td>
<td>24.66</td>
<td>0.61</td>
<td>54.0</td>
<td>95.3</td>
<td>1.34</td>
</tr>
<tr>
<td>AuShell(<em>{3050}(SC_9)</em>{913})</td>
<td>48.94</td>
<td>0.606</td>
<td>13.42</td>
<td>0.27</td>
<td>56.2</td>
<td>110</td>
<td>1.15</td>
</tr>
</tbody>
</table>

| TABLE I. Core diameters and grafting densities; see the main text for description. |
|----------------|---------|---------|---------|-------|---------|---------|
| \( 2R_i = D'_i \) (Å) | \( \sigma'_i \) (Å\(^2\)) | \( 2R_{[001]} = D'_{[001]} \) (Å) | \( \sigma'_{[001]} \) (Å\(^2\)) | \( 2R_{[111]} = D'_{[111]} \) (Å) | \( \sigma'_{[111]} \) (Å\(^2\)) |
| Au\(_{201}\) (SC\(_m\))\(_{913}\) | 51.31  | 19.15   | 51.6    | 17.6  | 45.4    | 17.6    |
| AuShell\(_{2200}(SC_m)_{750}\) | 80.42  | 27.09   | 81.4    | 20.0  | 71.2    | 27.0    |
| AuShell\(_{3050}(SC_m)_{913}\) | 97.88  | 32.97   | 99.0    | 30.0  | 86.6    | 29.9    |
to which we associate the variable \( \tau_H = r_H/R_i \). At distances \( \rho \approx 2r_H \), there is already a significant attraction between NCs, driven by the chains stretching toward each other. Binding free energies are very strong, in the range of several hundreds of \( k_BT \), in some cases larger than 300 \( k_BT \). Note that in all the cases, the free energy is about a factor of 5 smaller than the energy, which results from a significant energy entropy cancellation.

As noted previously,\(^{19}\) stronger bonding occurs for increasing core radius and increasing hydrocarbon lengths, but as shown in Fig. 4, keeping the core the same and increasing the ligand length lead to a much stronger bonding than increasing the core radius and keeping the ligand length constant. Relatively large isolated NCs (diameter of 5 nm) still remain spherical, which when interacting, display ligand vortices;\(^{29}\) see Fig. 5. For larger NCs, anisotropic effects resulting from the polyhedral shape of the core gradually emerge, eventually affecting the actual vortex structure, as we discuss further below.

### 2. Oleic acid

Typical ligand conformations for cores grafted with oleic and 1-octadecanethiol are displayed in Fig. 6. The unsaturated \( C_9 \) introduces significant rigidity, which limits the extension of the chains. The percentage of trans bonds as a function of NC separation for the first dihedral, the one closest to the core, shown in the bottom Fig. 6, reveals an initially more stretched configuration for the saturated case, as some gauche conformations are necessary to accommodate the double bond. Gradually, however, both distributions converge, and at the minimum of the PMF, the unsaturated chains remain with a higher trans percentage, showing that the double bond leads to more rigidity and hampers the motion of the saturated bonds.

Examples of PMF are shown in Fig. 7, where it is quite clear that the free energy minima are higher than those in the saturated case. In Table III, we provide a quantitative description of the effect of the double bond: It pushes apart
the NCs about 2 Å, see also Fig. 6, and decreases the bond strength by a hefty $\approx 70 \ k_B T$.

3. OPLS force field

In Fig. 8, we compare the force field used so far in our studies with the Optimized Potential for Liquid Simulations (OPLS). There is a perfect agreement for both the PMF, the energy, and the entropy for the Au$_{1289}$(SC$_{9}$)$_{258}$ and Au$_{201}$(SC$_{12}$)$_{80}$. For the Au$_{1289}$(SC$_{19}$)$_{258}$ case, the agreement is excellent for the free energy, while for the energy and entropy it occurs at sufficiently close separations. The observed difference in the energy is due to a slight hysteresis that occurs at sufficient high separations, as reported elsewhere. Given the difference in the structure of both force fields and the different coefficients of the non-bonded interactions, this close agreement is reassuring in that the quoted bonding free energies (minimum of the PMF) are very robust.

4. Anisotropic effects

As the NC cores become larger, significant anisotropic effects become apparent. This is the case of Au$_{4032}$(SC$_{9}$)$_{432}$ NC grafted with nonane, shown in Fig. 9, where the chains clearly exhibit a non-spherical distribution reflecting the polyhedral nature of the core. We therefore compute the PMF for configurations aligned along the [111] and the [001] faces. For the largest NC studied, the [111] face almost becomes to a planar interface and as a result, chains are strongly stretched and short chains (nonane) do not have room to develop vortices, as illustrated in Fig. 9.

The PMF is shown in Fig. 10 and demonstrates a small but significant difference that favors orientations along the [111] direction. More noticeable is the fact that bonding along the [111] direction has higher entropy but lower energy than the one along [001]. This is because the chains have a much lower number of configurations available in the latter case.
If we pick a fixed but otherwise arbitrary sulfur atom and define its orientation by a vector $\vec{n}$ normalized to one, the orientation of the NC is parameterized by a time series in ($\theta, \phi$), as shown in Fig. 11 for the two NCs involved in the calculation of the PMF. At sufficiently large separations, both orientations deviate from each other, while when they get close, around the minimum, both time series remain highly correlated showing that, within available time, the orientations are essentially locked and anisotropic effects remain.

### C. Asymmetric nanocrystals

There are two parameters relevant for NCs with different radii $r_A, r_B$, where, by definition, $r_B < r_A$. Here $r_A, r_B$ are the equivalent HS radius, which are given by the OPM formula Eq. (2). The fact that the OPM formula described the HS radius is discussed extensively in Ref. 29. The parameter
FIG. 10. Potential of mean force plots showing the effects of core orientation on the \( \text{Au}_{4032}(SC_9)_{32} \). The top left shows the PMF for the cores aligned on the [111] faces and the minimum as predicted by OPM Eq. (2) using the effective [111] diameter, \( D'_{[111]} \). The top right shows the PMF for cores aligned on the [001] faces with OCM Eq. (3) and OPM Eq. (2) shown. The bottom plots them together showing that the OPM result on the [111] face alignment has a smaller separation distance and a deeper well than [001] aligned faces.

\[
\gamma = \frac{r_B}{r_A} < 1 \quad \text{(4)}
\]

is used in mapping BNSLs to hard sphere parameters.\textsuperscript{26,27,29,30}

The softness asymmetry\textsuperscript{27} is defined as

\[
S_{AB} = \frac{L_B}{L_A} \quad \text{(5)}
\]

A summary of all the cases considered is given in Table IV showing that our study explores \( \gamma \) values 0.524 and 0.638 and \( S_{AB} \) values between [0.658, 2.13].

FIG. 11. Plots of the \( \theta \) and \( \phi \) angles, see definition in Fig. 2, as a function of time. The results are at 64 Å, which is approximately \( F_{\text{min}} \); the orientations of the NCs are strongly correlated, so their orientations ([001] or [111]) relative to each other are not changing over the course of the simulation.
### Table IV. Parameters describing the asymmetric cases analyzed in this study. The parameters are $\gamma$, Eq. (4), and softness asymmetry Eq. (5). The distance at the minimum of the PMF is $d_m$.

<table>
<thead>
<tr>
<th>Asymmetric pair</th>
<th>$\gamma$</th>
<th>$S_{AB}$</th>
<th>$d_m$ (Å)</th>
<th>$\tilde{r}_{A,m}$ (Å)</th>
<th>$\tilde{r}_{B,m}$ (Å)</th>
<th>$d_m / \tilde{r}_{A,m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuShell$<em>{2200}$(SC$</em>{18}$)$<em>{920}$–Au$</em>{4032}$(SC$<em>{9}$)$</em>{432}$</td>
<td>0.638</td>
<td>0.658</td>
<td>78.8</td>
<td>46.8</td>
<td>32.25</td>
<td>1.004</td>
</tr>
<tr>
<td>AuShell$<em>{2200}$(SC$</em>{18}$)$<em>{913}$–Au$</em>{4032}$(SC$<em>{9}$)$</em>{432}$</td>
<td>0.638</td>
<td>0.673</td>
<td>79.1</td>
<td>47.65</td>
<td>32.25</td>
<td>0.990</td>
</tr>
<tr>
<td>AuShell$<em>{3050}$(SC$</em>{9}$)$<em>{913}$–Au$</em>{4032}$(SC$<em>{18}$)$</em>{432}$</td>
<td>0.524</td>
<td>2.13</td>
<td>87.2</td>
<td>31.8</td>
<td>55.0</td>
<td>1.005</td>
</tr>
<tr>
<td>AuShell$<em>{3050}$(SC$</em>{9}$)$<em>{913}$–Au$</em>{4032}$(SC$<em>{18}$)$</em>{432}$</td>
<td>0.524</td>
<td>2.10</td>
<td>88.3</td>
<td>33.1</td>
<td>55.0</td>
<td>1.002</td>
</tr>
</tbody>
</table>

Two representative examples of the PMF for asymmetric NCs are provided in Fig. 12, with the remaining cases shown in the supplementary material. Because there is very little interdigitation, the location of the interaction plane, defined such that the average conformation of all chains on one side of the plane is grafted to the NC on the same side of the plane, may be defined. This is obtained as the mean $\mu$ of the chain distribution, following Ref. 19. The standard deviation $\sigma$ gives an idea of the plane roughness or curvature.

Overall, similarly as found in Ref. 19, the equilibrium separation between NC is given by $2\tilde{r}_{AB} = \tilde{r}_A + \tilde{r}_B$, but the location of the midplane $\mu$ is not just given as $\tilde{r}_A$, but rather is dependent on the softness asymmetry $S_{AB}$. It is interesting to note that the mid-formula is also obeyed by NCs with oleic acid as the capping ligand; see Fig. 12.

### III. DISCUSSION

#### A. General considerations

The location of the minima of the PMF, $2\tilde{r}_m$ for symmetric NCs, is expected to be described by the OCM formula,\(^{21}\) but as shown in Fig. 13 and pointed in Ref. 19, a clear breakdown is observed, more noticeable for large curvature $\lambda > 1$. Interestingly, the equilibrium separation is very sensitive to the nanocore radius $R$, but quite insensitive to the chain length $L$. In Ref. 19, we discussed a modified formula. Here, we propose

$$\tau_{A-OCM} \approx \tau_{OPM}(n = 4), \quad (6)$$

where $\tau_{OPM}(n = 4)$ is the OPM value of $\tau$ corresponding to 1-butanthiol ligands. It should be noted, however, that this formula gives, in some cases, an overestimate of the distance separation of about 10%.

For asymmetric NCs, the minimum of the PMF $d_m$ is well predicted by the simple formula

$$d_m = \tilde{r}_A + \tilde{r}_B, \quad (7)$$

as clear from Table IV. Note, however, that the location of the interacting plane is not a function of the radius, but rather, is a function of the softness asymmetry. We propose a mechanism that drives the plane location change, shown in Fig. 14, based on solving for a plane of interaction with equal contributed area from each NC. This is an indication of the system’s preference for the symmetric case, supported by the free energy information in Table V.

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**FIG. 12.** PMFs of asymmetric pairs AuShell$_{2200}$(SC$_{18}$)$_{920}$–Au$_{4032}$(SC$_{9}$)$_{432}$ and AuShell$_{3050}$(SC$_{9}$)$_{913}$–Au$_{4032}$(SC$_{18}$)$_{432}$. Calculated PMFs show good agreement with the symmetric sum prediction\(^{19}\) regardless of chain saturation.

**FIG. 13.** $\lambda$, $\tau$ plot for the nine symmetric cases considered; see Table II. Also shown are the OPM Eq. (2) and OCM Eq. (3) predictions. A clear breakdown of the OCM result is observed for $\lambda > 1$. Those points are described by the A-OCM as described in the text.
IV. CONCLUSIONS

We have provided a detailed analysis of the PMF and the effects of the core size and geometry, unsaturation, and dependence on the force field. We have shown that NCs show anisotropic effects at sufficiently low values of $\lambda \approx 0.5$; see Fig. 11. We have quantified the role of ligand unsaturation, i.e., double bonds, and shown that although do not modify equilibrium distances by much, about 2 Å, they have a very significant effect on the bonding energies, about 70 $k_B T$ higher than compared to the saturated case; see Table III. Comparison with the OPLS force field shows remarkable agreement, thus providing a very stringent cross-check that the calculated bond energies are independent of the details of the force field. Our results show that for sufficiently large cores and short ligands (small $\lambda$ values), significant anisotropic effects, consisting of orientations along certain faces of the core, become significant. Whether these orientations may play an important role in determining the structure of some BNSLs is an important question that will be investigated elsewhere.

The binding free energies are very strong, of the order of several hundreds of $k_B T$ with a significant energy-entropy cancellation. The study presented here confirms the predictions of the OTM$^{29,30}$ as the binding of two NCs is determined by vortices of ligands. In extending these results to BNSLs, the OTM predicts that equilibrium distances are dependent on the coordination on the environment. Therefore, the binding energy of two NCs within a superlattice will generally be lower than that for two isolated ones, but still of the order of several hundred $k_B T$; see Fig. 4. More coarse-grained models, such as the ones reported in Ref. 36, will be necessary to address many of these issues, as united atom models are very costly.
SUPPLEMENTARY MATERIAL

See supplementary material for the description of the force field and other simulation details and all calculated PMF plots.

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