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Quantitative Prediction of Position and Orientation for Platonic Nanoparticles at Liquid/Liquid Interfaces

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ABSTRACT

Because of their intrinsic geometric structure of vertices, edges and facets, Platonic nanoparticles are promising materials in plasmonics and biosensing. Their position and orientation often play a crucial role in determining the resultant assembly structures at a liquid/liquid interface. Here, we numerically explored all possible orientations of three Platonic nanoparticles (tetrahedron, cube, and octahedron), and found that a specific orientation (vertex up, edge up, or facet up) is more preferred than random orientations. We also demonstrated their positions and orientations can be quantitatively predicted when the surface tensions dominate their total interaction energies. The line tensions may affect their positions and orientations only when total interaction energies are close to each other for more than one orientations. The molecular dynamics simulation results were in excellent agreement with our theoretical predictions. Our theory would advance our ability toward predicting the final structures of the Platonic nanoparticle assemblies at a liquid/liquid interface.

Table of Contents Image:

Large-area two-dimensional superlattices, obtained by interfacial assembly of shape-controlled nanoparticles, are emerging platforms with applications in all-absorptive surfaces, super resolution imaging, and smart transformation optical devices.¹⁻²¹ The polyhedral nanoparticle (NP) exhibits distinct anisotropic properties along different crystallographic directions,²² as well as its large curvatures along vertices and edges cause deep subwavelength confinement of electromagnetic fields.^{15-17, 23} Therefore, the structure of polyhedral nanoparticle's superlattice is vital to its nanoscale light-matter interactions in real applications.²⁴⁻²⁵ The Platonic solids are convex polyhedra with faces composed of identical convex regular polygons, including tetrahedron, cube, octahedron, dodecahedron, and icosahedron. Because of their vertices and regular planar facets, they can assemble into distinct superlattices with highly ordered resultant structure. It has been demonstrated that systematically tuning the surface wettability of a silver octahedron/cube leads to different orientations of the octahedron/cube, either vertex up, edge up, or facet up.²⁶ It has also been demonstrated that the Ag nanocubes functionalized with mixed surfactants can adopt edge up, vertex up, and facet up configurations by decreasing solvent polarity.²⁷ Moreover, the superlattice structural evolution from hexagonal close packing to open square structures has been observed.²⁸ However, a quantitative relationship between the configuration of a polyhedron and its interactions with solvents remains elusive. It is imperative to derive a reliable method to predict the position and orientation of a polyhedron at a liquid/liquid interface, which is a stepping stone for predicting the equilibrium structure of superlattices.

Predicting the equilibrium assembled structure of shape-controlled nanoparticle is a long-standing interest in experiment and theory. The position and orientation of polyhedral nanoparticles at an interface, which are determined by nanoparticle-liquid interactions, play fundamental roles in determining their resultant structure when the nanoparticle-nanoparticle

interaction is weak.^{25,28-31} The preponderance of previous work has focused on solids of revolution, such as sphere, ellipsoids, nanorods, and nanodiscs, whose equilibrium position at a liquid/liquid interface can be successfully obtained using free energy change theory.³²⁻⁵¹ However, it's very challenging to predict the equilibrium assembled structure of polyhedral nanoparticles because of their complex rotational degrees of freedom and their non-smooth surfaces. The truncated nanocubes can assemble into graphene like honeycomb and hexagonal lattices, possibly caused by the ligand adsorption and van der Waals forces.⁵² The capillary deformations have been introduced to predict the preferred orientation of cubes for several Young's contact angles value, and it has been found that capillary deformation may change the preferred orientation for an isolated cube when surface tension ratio R near 0 ($|R| < 0.3$).⁵³ In our previous work, the most stable position and the preferred orientation of an octahedron at a water/oil interface has been studied using free energy change theory under all the surface tension ratio R for two specific orientations: vertex up and facet up.⁵⁴ However, there are a large amount of possible orientations and positions for a polyhedron.⁵⁵⁻⁵⁶ Therefore, all the possible rotational degrees of freedom of polyhedral nanoparticles should be investigated systematically.

Here, we applied the free energy change theory to determine the interfacial position and orientation of a Platonic nanoparticle at a liquid/liquid interface. Tetrahedron, cube, and octahedron are chosen in our studies due to their unique geometry and their non-sphere shape among the Platonic solid family. Firstly, we obtained the interfacial free energy throughout a full range of positions and orientations under specific wettability for a Platonic solid at liquid/liquid interfaces. This approach can find the most stable position and preferred orientation among all the random orientations for a Platonic solid when surface interactions were dominant, and our results showed that the specific orientations (vertex up, edge up, and facet up orientations) were more

preferred than random orientations. Secondly, we derived the quantitative dependence of interfacial free energy on different positions under a full range of wettability (from extremely hydrophobic to extremely hydrophilic) for three specific orientations of tetrahedron, cube, and octahedron. Thus, the orientation and position of a given Platonic solid at a water/oil interface could be predicted from particle shape and surface tension ratio directly. Thirdly, the Molecular Dynamics (MD) simulations for a silver Platonic solid at the hexane/water interfaces were conducted to verify our predictions. We tuned the surface wettability (hydrophilic/hydrophobic ratio) of Ag Platonic solids by manipulating the amount of point charges on the surface Ag atoms while keeping the whole particle at charge neutral. This specific way was utilized to verify our theoretical predictions and we believe that other tuning methods could lead to the similar results.⁵⁷ The preferred orientation from our MD simulations was in excellent agreement with our extended free energy change theory, while the most stable position from MD simulations followed the predicted trend. Lastly, line tension was taken into account. The position and orientation can be affected by line tension near the boundary of regions, where the free energy of each orientation close to each other. Our theory bridges the gap between molecular-level interaction simulations and nanoparticle configuration experiments, where insights from nanoparticle surface wettability can be used to predict macroscopic superlattice formation in experiments in the future.

Thermodynamic Model for the Ag Platonic NP System with Random Orientations

In this part, we focus on the full range analysis of orientations for an isolated Platonic solid adsorbed at a water/oil interface. The orientation of a Platonic solid with respect to a fixed coordinate system can be characterized by the Euler angles, as shown in Figure 1. An arbitrary orientation can be expressed by composing three intrinsic elemental rotations: yaw, roll, and pitch, which can be described by Euler angles α , β , and γ , respectively.⁵⁸

In Figure 2, we illustrate three specific orientations for Platonic solids, namely vertex up, edge up, and face up orientation, together with a random orientation in the vicinity of a water/oil interface. The unit vector $\hat{z}$ is pointing up along z direction. The H is the half distance between the top plane to the bottom plane of the particle, where both planes are parallel to the water/oil interface. Therefore, for the Platonic particle, the highest point must be in the H plane (top plane), while the lowest point stays in the $-H$ plane (bottom plane). In some special orientations, these planes could contain a facet, a vertex, or an edge of the particle. For example, the total height ($2H$) of tetrahedron is solely the distance along the z direction between a vertex to the opposing facet in vertex up and facet up orientations; and is the distance between the two opposing edges in edge up orientation. For cube and octahedron, $2H$ is the distance between two opposing vertexes/edges/facets in vertex up/edge up/facet up orientations, respectively. The vector from the $H=0$ plane of Platonic solids to the water/oil interface is denoted by $h\hat{z}$. The height ratio v is defined as $v = h/H$, where $-1 < v < 1$ for all the orientations. From this definition, we can see that v is negative when the majority part of NP stays in oil, and it is positive when the majority part of NP stays in water. The cross point of $h\hat{z}$ and $H=0$ plane is denoted by O , which is also the center of mass for cubes and octahedrons, but not for tetrahedrons.

The Pieranski's free energy change theory can be extended to Platonic solids systems and normalized by total surface area A of Platonic solids and oil/water surface tension γ_{wo} as shown below:

$$F = F_{int}/A\gamma_{wo} = RA_{pw}/A - A_{st}/A + \tau L/A\gamma_{wo}, \text{ where } R = (\gamma_{pw} - \gamma_{po})/\gamma_{wo}. \quad (1)$$

In eq 1, F_{int} is the free energy change of a nanoparticle at an interface with height ratio v , referring to the free energy of the nanoparticle immersed in oil phases; γ_{pw} , γ_{po} , γ_{wo} and τ are the particle/water, particle/oil, water/oil surface tensions, and the three-phase line tension, respectively.

A_{pw} , A_{st} , and L are the particle/water interface area, oil/water interface area occupied by the nanoparticle, and the length of three-phase line, respectively. For a given system, the values of all surface tensions and the line tension are independent to the configuration of the Platonic solids, while only A_{pw} , A_{st} , and L are functions of the configuration. R is the surface tension ratio which is defined as $R = (\gamma_{pw} - \gamma_{po})/\gamma_{wo}$, and has the opposite sign compared to cosine of the contact angle where $\cos \theta = (\gamma_{po} - \gamma_{pw})/\gamma_{wo}$. This means that R is positive (negative) when the NP is hydrophobic (hydrophilic). Furthermore, the contribution from the line tension can be omitted because it is usually one order of magnitude smaller than surface tension.³⁵ With the line tension omitted, eq 1 can be rewritten as below:

$$F = F_{int}/A\gamma_{wo} = RA_{pw}/A - A_{st}/A, \text{ where } R = (\gamma_{pw} - \gamma_{po})/\gamma_{wo}. \quad (2)$$

Eq 2 can be applied to all orientations of a Platonic solid emerged at the water/oil interface, where the surface tensions are determined by the interactions between the Platonic solid and solvents. The numerical results of A_{pw} , and A_{st} can be obtained for all orientations. Three specific orientations, vertex up, edge up, and facet up orientations are picked up with extra attentions because the analytical expression of A_{pw} , and A_{st} can be obtained for these specific orientations, as described in Supporting Information S1-S7.

The Most Stable Position and Orientation for Random Orientated Platonic Solids

The results for three Platonic solids were discussed here separately. To find out the preferred orientation for a Platonic solid, the free energy change for every random orientation and position was calculated based on eq 2 with edge length $a=30$ nm for all the Platonic solids. For a given value of surface tension ratio R , all combinations of three dimensional (3D) rotations (yaw, roll, and pinch) were investigated and the orientation and position with the lowest free energy is the preferred interfacial configuration. The value of R chosen in this section is intentionally to have

the large free energy difference between the orientations so that the contribution from line tension can be ignored. The values of A_{wp} and A_{st} in eq 2 were obtained numerically by a method described in Supporting Information S7.

For a tetrahedron, we chose R has a value of positive and negative $1/3$. When R has the value of $1/3$, the minimum of free energy change is located at $\alpha = 7, \gamma = 1, \beta = 0$ degree, which is almost a vertex up orientation. For configurations slightly tilted from vertex up orientation, the free energy change is almost independent on yaw rotations (α) due to the symmetry. Therefore, we plot the contour graph of $R=1/3$ was plotted in Figure 3(a1) for β and γ change from 0 degree to 90 degrees with $\alpha = 7$ degrees. The lower energy configurations are concentrated in lower left corner suggesting near zero value of γ and β are preferred. Accordingly, the height ratio contour graph of same setup was plotted in Figure 3(b1), showing a minimal value of -1 for $\alpha = 7, \gamma = 1, \beta = 0$ degree. These results suggested that the vertex up orientation in the oil phase is preferred for a tetrahedron when $R = 1/3$.

For tetrahedron cases with $R = -1/3$, our results showed that the tetrahedron has the minimum free energy at $\alpha = 20, \gamma = 56, \beta = 55$ degrees, which is close to a facet up orientation. For the facet up orientation with small deviations, the yaw rotation does not nearly affect the free energy change due to symmetry again. Therefore, the free energy change contour graph was plotted in Figure 3(a2) for both γ and β from 0 degree to 90 degrees at $\alpha = 20$ degrees. The lowest energy point around $\gamma = 56, \beta = 55$ degree is the minimum of free energy. Similarly, the equilibrium height ratio was obtained from the height ratio contour graph in Figure 3(b2), which is 1. The tetrahedron stays in water with facet up orientation when $R = -1/3$.

It has been found that the interfacial evolution in water phase and that of in oil phase are mirror imaged⁴⁶ Therefore, we only discussed the region of $0 < R < 1$ in the following discussion for

cube and octahedron. The values of R were chosen to be 0.5 and 0.05 for a cube. The free energy change contour graph was calculated from eq 2 where the values of A_{wp} and A_{st} were obtained by the method described in Supporting Information S7. When $R = 0.5$, the cube has minimal free energy points around $\alpha = 42, \gamma = 45, \beta = 0$ degree, which is nearly a facet up orientation. As similar to what we did previously, the free energy change contour graph was plotted in Figure 3(a3) for both γ and β changing from 0 degree to 90 degrees, with α fixed at 42 degrees. The corresponding height ratio of -1 for $R=0.5$, which was from the height ratio contour graph in Figure 3(b3), indicates that the cube is staying in oil with facet up orientation. When $R = 0.05$, the cube has one minimal energy configuration at $\alpha = 16, \gamma = 52, \beta = 70$ degrees, and the corresponding height ratio is 0 as shown in Figure 3(a4) and (b4). This can be comprehended that the cube stays in right at the oil/water interface with an edge up orientation at equilibrium.

For an octahedron, the chosen R values are $\sqrt{3}/3$ and 0.05. The free energy change contour graph was plotted in Figure 3(a5) under the condition of $\alpha = 62$ for R equals to $\sqrt{3}/3$ case. The octahedron has a minimum free energy at $\gamma = 1, \beta = 55$ degrees, which is almost the facet up orientation. The height ratio of this configuration is -1, which is obtained from the height ratio contour graph in Figure 3(b5). This means that the octahedron is completely immersed in oil phase with one facet at the oil/water interface. When R has a value of 0.05, the same calculations and analysis were performed. Now the octahedron has minimal energy at the point of $\alpha = 12, \gamma = 0, \beta = 0$ degree and height ratio 0 at that equilibrium configuration, as shown in Figure 3(a6) and (b6). This time the octahedron is fixed at the interface with a vertex up orientation.

From all the data gathered above, for a given surface tension ratio R with the large free energy change difference, it is likely that the preferred free energy minimum orientations converge into the three specific types, which are vertex up, edge up, and facet up orientations. This is consistent

with previous work that hexagonal bipyramid and hexagonal bipyramid have minimum free energy with facet up orientation under specific wettability.²¹ Also, yaw rotations applied on these three specific orientations have nearly no effects on free energy change, only with some small deviation caused by rotational coordination converting during 3D rotation mathematic calculations. Therefore, we focused on these three specific orientations in the full range of surface tension ratio R .

The Most Stable Region for Platonic Solids in Three Specific Orientations

For every specific orientation of a Platonic solid, eq 2 was used to find its free energy change minimum since A_{pw} and A_{st} are functions of the height (h) for a given value of R . The analytical expressions for tetrahedron are listed below and the detailed information can be found in supporting information S1.

Vertex up orientation,

$$F = -\frac{3R+1}{16}v^2 + 2\left(\frac{3R+1}{16}\right)v + R - \frac{3R+1}{16}, -1 < v < 1 \quad (3)$$

Facet up orientation:

$$F = \frac{3R-1}{16}v^2 + 2\left(\frac{3R-1}{16}\right)v + \left(\frac{3R-1}{16}\right), -1 < v < 1 \quad (4)$$

Edge up orientation:

$$F = \frac{\sqrt{3}v^2}{12} + \frac{R}{2}v + \frac{R}{2} - \frac{\sqrt{3}}{12}, -1 < v < 1 \quad (5)$$

We plotted the free energy change minimum for three specific orientations for the full range of R in Figure 4. For a given value of R , the orientation with the lowest value in free energy change minimum is the most stable orientation. A Platonic solid may easily switch its orientation in the regions that two or three orientations have similar free energy change minimum. The absolute physical energy gap value depends on the nanoparticle size and the solvent-solvent interaction, which can be characterized by total surface area (A) and water oil surface tension (γ_{wo}).

For tetrahedron nanoparticles, the free energy change minimum F curves for full region of R values of the three specific orientations was shown in Figure 4a, and the results were also summarized in Table 1. In the region of $-1 < R < 0$, the free energy change minimum of facet up orientation always has smaller value than that of vertex up orientation and that of edge up orientation, which means the tetrahedral NP favors facet up orientation. In the region of $0 < R < 1$, the free energy change minimum of vertex up orientation has the smallest value, which means the tetrahedral NP favors vertex up orientation. So, it is likely that the vertex up orientation dominates when particle-water interaction is stronger than particle-oil interaction, and facet up orientation dominates in the opposite situation.

For cube nanoparticles, the result is a little bit more complicated despite of the simple cubic shape, as shown in Figure 4b. The analytical expressions for cube are listed below, where the detailed information can be found in supporting information S3.

Vertex up orientation:

$$F = \begin{cases} \left(\frac{9R-3\sqrt{3}}{16} \right) (1+v)^2, & a, -1 \leq v \leq -1/3 \\ \frac{3\sqrt{3}}{8} v^2 + \frac{3}{4} Rv + \frac{R}{2} - \frac{\sqrt{3}}{8}, & b, -1/3 < v < 1/3 \\ -\left(\frac{9R+3\sqrt{3}}{16} \right) (1-v)^2 + R, & c, 1/3 < v < 1 \end{cases} \quad (6)$$

Facet up orientation:

$$F = \frac{R}{3} v + \frac{R}{2} - \frac{1}{6}, -1 < v < 1 \quad (7)$$

Edge up orientation:

$$F = \begin{cases} \left(\frac{R}{6} v^2 + \left(\frac{2R}{3} - \frac{\sqrt{2}}{6} \right) v + \left(\frac{R}{2} - \frac{\sqrt{2}}{6} \right) \right), & a, -1 \leq v \leq 0 \\ \left(-\frac{R}{6} v^2 + \left(\frac{2R}{3} + \frac{\sqrt{2}}{6} \right) v + \left(\frac{R}{2} - \frac{\sqrt{2}}{6} \right) \right), & b, 0 \leq v \leq 1 \end{cases} \quad (8)$$

In the region of $-1 < R < (1 - \sqrt{2})/2$ and the region of $(\sqrt{2} - 1)/2 < R < 1$, the free energy change minimum of facet up orientation has the smallest value, which means the cube favors facet

up orientation. In the region of $(1 - \sqrt{2})/2 \leq R \leq (\sqrt{2} - 1)/2$, the free energy change minimum of edge up orientation is the smallest thus the cubic NP favors edge up orientation. These results are due to the fact that the cross-surface area A_{st} plays a key role in eq 2 to determine the free energy when R is close to 0. Therefore, the edge up orientation, which has the larger cross-surface area A_{st} , is more preferred than the other two orientations. The detailed derivations in three regions were provided in supporting information S4 and the main results were summarized in Table 2.

The octahedron nanoparticles were studied in our previous paper for vertex up and facet up orientations.⁵⁴ The edge up orientation data combined with previous work was shown in Figure 4c and summarized in Table 3. As a result, the edge up orientation is likely not the preferred orientation in any region. The facet up orientation dominates when R is in the region of $-1 < R < (3 - 4\sqrt{3})/9$ or the region of $(4\sqrt{3} - 3)/9 < R < 1$, and the vertex up orientation dominates when R is in the region of $(3 - 4\sqrt{3})/9 \leq R \leq (4\sqrt{3} - 3)/9$. Like the cube case, octahedron NP also has three distinct regions for R. Vertex up orientation is also the favored one in the central region near R=0. This is again due to the contributions from larger cross surface area A_{st} for vertex up orientation.

Furthermore, there are two notice-worthy details in this section. One is that there are always two mirrored regions where the NP will have one facet facing the oil/water interface when the absolute value of R is large. The other is that the range of the central region is widen from tetrahedron (zero central region) to cube and further into octahedron. This may be related to their geometry parameters. Based on the above discussion and Figure 4, R value could be manipulated to result in different energy gap profiles thus to control the orientations of Platonic solids.

Equilibrium Orientations from MD Simulations

As mentioned before, the most stable orientation and position of Platonic solids at a water/oil interface can be predicted by our analytical solutions from free energy change method primarily based on surface tensions. The information of equilibrium states can also be obtained from MD simulations, which take the following possible effects into consideration: line tension, interface fluctuation, and random distribution for surface ligands. Thus MD simulations can be a direct check for our analytical solutions. There is no restrictions on the position of nanoparticles in our simulations. Nanoparticles can completely immersed in oil (water) phase when their surface are sufficiently hydrophobic (or hydrophilic).

The values of R were calculated from γ_{pw} , γ_{po} , and γ_{wo} directly, which were obtained by MD simulation method introduced in supporting information S9. For the tetrahedron with the edge of 5.8 nm, all snapshots from MD simulations with R value ranging from nearly 0 to nearly 1 (Figure 5 a1-a4) clearly show obvious vertex up orientations as predicted by free energy change theory plotted in Figure 4a, even they are slightly tilted. To directly compare MD simulation results for $R = 0.38$, we plot the free energy change contour graph and the height ratio v for the same tetrahedron in Figure 5(c1) and Figure 5(d1), respectively. The difference of free energy change minimum between vertex up orientation and other two orientations (facet up and edge up) is about $139 k_B T$, which is much larger than the thermodynamic fluctuation. Thus the vertex up orientation is the most stable state, which is in excellent agreement with MD simulations. The tilting of tetrahedra may be due to the inhomogeneous distribution of point charge in our tetrahedral model, which we discussed in more details in the next session.

For a cube with edges of 3.9 nm, four sets of MD simulations were performed which have R values chosen in the region of $(1 - \sqrt{2})/2 \leq R \leq (\sqrt{2} - 1)/2$ or in the region of $(\sqrt{2} - 1)/2 < R < 1$. The orientations in the region of $-1 < R < (1 - \sqrt{2})/2$ are similar to those in the region

of $(\sqrt{2} - 1)/2 < R < 1$, thus we didn't show the redundant results here. The snapshots from four sets of MD simulations were shown from Figure 5(b1) to Figure 5(b4), where the values of R are equal to 0.99, 0.61, 0.23, and -0.04, respectively. Our theory predicts that a cube with $R = 0.61$ should have a facet up orientation at equilibrium configuration, and its free energy change contour plot and its height ratio v contour plot were plotted in Figure 5(c2) and in Figure 5(d2), respectively. It's obvious that the most stable orientation is around $\gamma = 45$ and $\beta = 0$ in Figure 5(c2), which is the facet up orientation. This result is in excellent agreement with MD result in Figure 5(b2) which shows a nearly perfect facet up orientation. The MD simulations show that a cube is in facet up orientation for $R = 0.99$, which is also in good agreement with our theory. A cube should have edge up orientation with R around 0 from our theory, where its free energy change contour graph and its height ratio v contour plot for $R = -0.04$ was plotted in Figure 5(c3) and in Figure 5(d3), respectively. There are two valleys in Figure 5(c3) because both edge up orientation and vertex up orientation have similar energy and both of them have smaller energy than facet up orientation. One valley is around $\gamma = 52$, $\beta = 70$ that is a perfect edge up orientation, and the other is around $\gamma = 5$, $\beta = 24$ that is close to a perfect vertex up orientation ($\gamma = 0$, $\beta = 0$). The valley with edge up orientation has about $0.55 k_B T$ lower energy than that with vertex up for this cube with edge of 3.9 nm. This energy difference increases dramatically with the particle size and is about $3.6 k_B T$ for a cube with edge of 10 nm. We observed edge up orientations in MD simulations, which was shown in Figure 5(b4), although the orientations of a cube in MD simulations is sensitive to the initial configurations of the cube. The situation of $R = 0.23$ is similar to that of $R = -0.04$, and the cube also prefers an edge up orientation.

For octahedron case, we included the edge up orientation and found the same conclusions as our previous work.⁵⁴ Therefore, we didn't compare and discuss MD simulations and analytical predictions again for octahedron here.

The Equilibrium Position Comparison from MD Simulations

The equilibrium heights of a tetrahedron at hexane/water interfaces with different wettability can be extracted from MD simulation trajectories. After the tetrahedron reaches its equilibrium position at a specific value of surface tension ration R , the value of height ratio v was extracted and averaged through 100ps, which were shown as triangles in Figure 6. Our theory predicts that the equilibrium heights is $h_e = -1$ for a tetrahedron when $0 \leq R < 1$, which was plotted as a red line in the Figure 6. When the value of R is closer to 1, the MD results were in excellent agreement with our prediction. However, the tetrahedron significantly moves toward water phase with the decrease of R value. With the same procedure, we obtained the values of height ratio for a cube at hexane/water interfaces from MD simulations, which were shown as squares in Figure 6. Our theory predicts that the equilibrium heights is $h_e = -1$ for a cube when $(\sqrt{2} - 1)/2 < R < 1$, which is the red line in the Figure 6. The cube significantly moves toward water phase when the R value is in this region. Our theory also predicts that the equilibrium heights is $h_e = 0$ for a cube when $0 < R < (\sqrt{2} - 1)/2$, which was plotted as the green line in the Figure 6. The cube significantly moves toward oil phase when the R value falls into this region.

For a tetrahedron, the prediction of equilibrium positions from our theory is only in excellent agreement with MD simulations when R value is close to 1. For a cube, our predictions are only in qualitative agreement with MD results. This mismatch may be due to the following reasons. 1) The thickness of water/oil interface slab is about 0.5 nm, which causes large fluctuation during the position calculation since our Platonic particles in MD simulations are a few nanometers in edge

length. Moreover, the tilting of orientation may also affect the position in MD simulations. 2) The surface charges are randomly distributed on surfaces of Platonic particles to mimic surfactants on the surfaces of nanoparticles. This random distribution of surface charges may lead to a non-uniform interaction with water molecules, which causes the deviations on surface interactions between MD simulations and our models. These interactions may also affect the configuration for Platonic solids at the interface, especially under high surface charge condition. 3) When R value is close to the boundaries between R regions, two or more orientations will have similar energy thus the position fluctuation becomes more significant or even less preferred orientations could appear. For example, $R=0.08$ case for a tetrahedron, near the boundary of $R = 0$; as well as $R=0.23$ case for a cube. 4) MD simulations include the contribution of line tensions while our models from eq 2 omit this effect. The contribution of the line tension could be significant when the R value is close the boundaries of R regions. For a tetrahedron, the line tension could greatly affect the equilibrium orientations when the R value is close to 0, which is discussed in details in the next section.

The Preferred Orientation for Platonic Solids with Line Tension

All predictions discussed in previous sessions are obtained assuming the contribution of the line tension is small thus can be ignored. When the energy difference between three orientations is small, the contribution of the line tension may play a more important role in determining the preferred orientation, such as leading to tilted orientations. For example, when R has a value of 0.9, the tetrahedron (cube/octahedron) is more hydrophobic and should have vertex (facet/facet) up orientation without tilt from the energy analysis based on our theory, which is shown in Figure 4, but the MD simulation results show tilted orientations, as shown in Figure 5. The mismatch of the MD simulations and the theory prediction from eq 2 may be caused by the neglect of the line

tension contribution. For a tetrahedron with edge length a , the length of three-phase line L equal to 0 , $2a$, and $3a$ for vertex up, edge up, and facet up orientations, respectively, as shown in supporting information S1. The facet up orientation has the longest three-phase line thus its energy change is affected mostly. It may just cause a tetrahedron tilted from perfect vertex up or facet up orientations when the line tension is small. However, if the energy difference is small enough and the line tension is large enough, a tetrahedron can even favor a facet up orientation instead of a vertex up orientation when the value of R is close to 1. The energy valley is around $\gamma = 65$, $\beta = 54$ in Figure 7a when $R = 0.9$ and $\tau = 0.5\gamma_{wo}L_0$ with $L_0 = 1\text{ m}$, which is a facet up orientation as shown in the inset of Figure 7a. Similarly, a tetrahedron can favor a tilted vertex up orientation instead of a facet up orientation when the value of R is close to -1, which was shown in Figure 7b.

For a cube with edge length a , the length of three-phase line L for vertex up, edge up, and facet up orientations are about 0 , $2a$, and $4a$ respectively, as shown in supporting information S3. Same as a tetrahedron, the facet up orientation also has the longest three-phase line for a cube thus its energy change is affected most. A cube prefers a tilted vertex up orientation instead of facet up orientation when $R = 0.9$ and $\tau = 2\gamma_{wo}L_0$, which was shown in Figure 7c. Recently, Roji *et. al.* has reported that a cube prefers vertex orientation at $R = 0$ and $R = 0.2$ as well as facet up orientation at $R = -0.3$,⁵³ which fall in region of $(1 - \sqrt{2})/2 < R < (\sqrt{2}) - 1/2$ and the region of $-1 < R < (1 - \sqrt{2})/2$ in our studies, respectively. Our results are consistent with their results in these specific regions. For an octahedron with edge length a , the length of three-phase line L for vertex up, edge up, and facet up orientations are about 0 , $2a$, and $3a$, respectively, as shown in supporting information S5. Same as a tetrahedron and a cube, the vertex up orientation also has the shortest three-phase line for an octahedron thus its energy change is affected least. An octahedron prefers

a tilted vertex up orientation instead of a facet up orientation when $R = 0.9$ and $\tau = 0.2\gamma_{wo}L_0$, which was shown in Figure 7d.

As discussed before, the absolute value of line tensions has different effects on the free energy change of Platonic solids. However, the value of line tensions is difficult to be accurately measured in experiment. For an ellipsoid, Bresme has discussed possible line tension value from 0 to $1.5\gamma_{wo}r_m$, where r_m is the radius while the ellipsoid close to sphere.⁴⁶ Thus, the line tension may only have noticeable effect when the R value is close to the boundaries. Normally, the line tension is one order of magnitude less than surface tension. So that it usually can be ignored.

In summary, we demonstrated that the extended free energy change theory can predict the equilibrium orientation of an isolated Platonic solid at a liquid/liquid interface. Our results revealed the quantitative relationship between the surface tension and the interfacial configuration for three Platonic nanoparticles: tetrahedron, cube, and octahedron. By exploring all possible orientations of Platonic nanoparticles including random orientation and the three specific orientations (vertex up, facet up, and edge up), we found that the most preferred orientation was one of three specific orientations instead of a random one. Therefore, the equilibrium configuration of a Platonic nanoparticle could be predicted by our free energy change theory. We also compared our predictions with the results from molecular dynamics simulations. In our MD simulations, increasing the wettability of Ag Platonic nanoparticle surface led the nanoparticle moving from the oil phase into the water phase with various orientations. The stable orientations from MD simulations were in excellent agreement with the results from our theoretical predictions. The position and orientation can be significantly affected by line tensions when the value of surface tension ratio is close to the boundary of regions. Since the position and orientation of Platonic nanoparticle in the vicinity of interface played a key role in the process of polyhedral nanoparticles

self-assembly, our findings would serve as a stepping stone in predicting a roadmap marking out the equilibrium structures of Platonic nanoparticle superlattice at a liquid/liquid interface.

ASSOCIATED CONTENT

Supporting Information

Supplementary information is available in the online version of the paper. **Reprints and permission** information is available online at <http://pubs.acs.org>. Correspondences and requests for materials should be addressed to S.L.

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Author Contributions

S.L. and W.X.S designed the research; W.X.S performed molecular dynamics simulations; W.X.S., Z. Z., and S.L. performed analyses; W.X.S., Z. Z., and S.L. wrote down the manuscript. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Figure 1. Sketch of Euler angles for Platonic solids rotation system: (a) tetrahedron, (b) cube, and (c) octahedron. Three intrinsic elemental rotations are yaw, roll, and pitch, which can be described by α , β , and γ in Euler angles, respectively. The mass center of Platonic solids are located at the origin of the Cartesian coordinates.

Figure 2. Sketch of Platonic solids in the vicinity of an oil/water interface: (a) tetrahedron, (b) cube, and (c) octahedron. The vertex up, facet up, edge up, and a random orientation are shown from left to the right. The unit vector $\hat{z}$ is pointing up along the z direction. The heights of solids is the distance between the highest and lowest planes, which containing the element of solids and paralleled to the oil/water interface. The H_V , H_F , and H_E are the half heights of solids in vertex up, facet up, and edge up orientations, respectively. The H is the half heights of nanoparticle with random orientations. The vector from the $H=0$ plane of solid to the interface is denoted by $h\hat{z}$. O is the cross point of the height line and $H=0$ plane, and is the mass center for cube and octahedron.

Figure 3. The free energy change contour surface ((a1, a2) tetrahedron, (a3, a4) cube, and (a5, a6) octahedron.) and the height ratio contour ((b1, b2) tetrahedron, (b3, b4) cube, and (b5, b6) octahedron.) for all the random orientations with Euler angle for 3D rotation with different surface tension ratio R at the vicinity of the oil/water interface. All particles have an edge length of 30 nm, and the γ_{wo} is 45.26 mN/m.

Figure 4. The relationship of R and the minimum of free energy change F for vertex up, edge up, and facet up orientation: (a) tetrahedron, (b) cube, and (c) octahedron. The values of R for five vertical lines are 0 (a), $(1 - \sqrt{2})/2$ left line of (b), $(\sqrt{2} - 1)/2$ right line of (b), $(3 - 4\sqrt{3})/9$ left line of (c), and $(4\sqrt{3} - 3)/9$ right line of (c), respectively.

Figure 5. a) Orientations and positions of Ag tetrahedron (a1-a4) in MD simulation with different R . b) Orientations and positions of Ag cube (b1-b4) in MD simulation with different R . c) Free energy change contour (c1-c3) for (a3), (b2), (b4), and d) height ratio v (d1-d3) for (a3), (b2), (b4) with different R obtained in MD simulation at the vicinity of the hexane/water interface. All particles have different edge lengths in MD simulation, and the γ_{wo} is 45.26 mN/m.

Figure 6. The relationship between the equilibrium height ratio h^e (h^e equals the v with the lowest free energy) and surface tension ratio R for tetrahedral and cubic Ag nanoparticle. The triangle symbols stand for tetrahedron' position obtained from MD, and the square symbols stand for cube's position obtained from MD, respectively. The green straight line is $h^e = 0$ in the region of $0 \leq R < (\sqrt{2} - 1)/2$, and the red straight lines is $h^e = -1$ in the regions of $(\sqrt{2} - 1)/2 < R < 1$, respectively.

Figure 7. The free energy change contour surface for all the orientation with Euler angle rotation with different R and line tension τ for (a, b) tetrahedron, (c) cube, and (d) octahedron, respectively. All particles have an edge length of 30 nm, and the γ_{wo} is 45.26 mN/m.

Table 1. The analytic solution for the minimum of free energy change F for vertex up, facet up and edge up tetrahedra.

	Region	Vertex up	Facet up	Edge up	Preferred Orientation	Preferred Position
1	$-1 < R < 0$	R	$\frac{3R-1}{4}$	$-\frac{\sqrt{3}}{4}R^2 + \frac{R}{2} - \frac{\sqrt{3}}{12}$	Facet up	$h_e = 1$, in water
2	$0 \leq R < 1$	$\frac{R-1}{4}$	0	$-\frac{\sqrt{3}}{4}R^2 + \frac{R}{2} - \frac{\sqrt{3}}{12}$	Vertex up	$h_e = -1$, in oil

Table 2. The analytic solution for the minimum of free energy change F for vertex up, edge up, and facet up cubes.

	Region	Vertex	Facet	Edge	Preferred Orientation	Preferred Position
1	$-1 < R < \frac{1-\sqrt{2}}{2}$	R	$\frac{5R-1}{6}$	$\frac{1}{12R} + \frac{7R}{6} + \frac{\sqrt{2}}{6}$	Facet up	$h_e = 1$, in water
2	$\frac{1-\sqrt{2}}{2} \leq R < \frac{\sqrt{2}-1}{2}$	$\frac{-\sqrt{3}R^2 + 4R - \sqrt{3}}{8}$	/	$\frac{R}{2} - \frac{\sqrt{2}}{6}$	Edge up	$h_e = 0$, half in oil, half in water
3	$\frac{\sqrt{2}-1}{2} \leq R < 1$	0	$\frac{R-1}{6}$	$-\frac{1}{12R} - \frac{R}{6} + \frac{\sqrt{2}}{6}$	Facet up	$h_e = -1$, in oil

Table 3. The analytic solution for the minimum of free energy change F for vertex up, edge up, and facet up octahedra.

	Region	Vertex up	Facet up	Preferred Orientation	h_e
1	$-1 < R < (3 - 4\sqrt{3})/9$	R	$(7R - 1)/8$	Facet up	$h_e = 1$, in water
2	$(3 - 4\sqrt{3})/9 \leq R \leq (4\sqrt{3} - 3)/9$	$(3R - \sqrt{3})/6$	$(-9R^2 + 8R - 3)/16$	Vertex up	$h_e = 0$, half oil, half water
3	$(4\sqrt{3} - 3)/9 < R < 1$	0	$(R - 1)/8$	Facet up	$h_e = -1$, in oil