Configuration of Nonspherical Amphiphilic Particles at a Fluid-Fluid Interface

Supplementary Information

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We validate the flat interface assumption (FIA) which enables us to rapidly calculate the attachment energy and find energy minima of nonspherical amphiphilic particles at an oil-water interface.

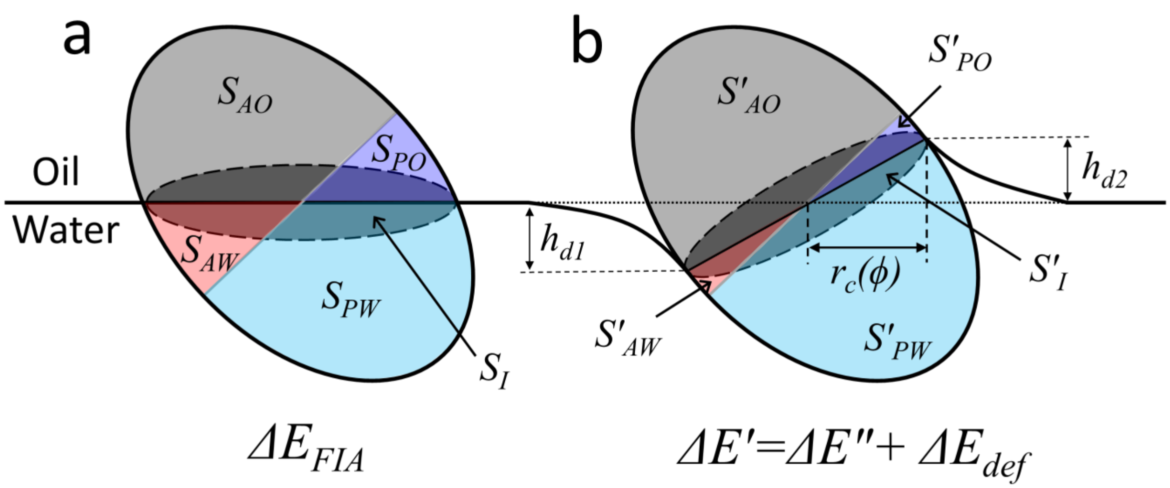

Fig. 1S Schematics of an amphiphilic ellipsoid with and without interface deformation. (a) A tilted orientation of the amphiphilic ellipsoid under the flat interface assumption (FIA). S_{ij} indicates that the surface area of *i* region of the particle in *j* fluid phase. The subscripts, *A*, *P*, *O*, and *W* denote apolar, polar, oil, and water, respectively. S_I is the area of the flat oil-water interface occupied by the particle. (b) Interface deformation caused by the wetting of each fluid on the preferred region of the particle. Similarly, S'_{ij} represents that the surface area of *i* region of the particle in *j* fluid phase without the FIA. S'_I is the area of the deformed oil-water interface occupied by the particle. The three-phase contact line on the ellipsoid is assumed to be an ellipse.

Attachment Energy Calculation without the flat interface assumption (FIA)

The interface deformation around an amphiphilic particle, which can be caused by the wetting of each fluid to its preferred region of amphiphilic particles (*i.e.*, oil on apolar surface and water on polar surface, respectively) or sometimes to its nonpreferred region may affect the equilibrium configuration (Fig. 1Sb). In this case, the attachment energy of the particle with the interface deformation ($\Delta E'$) can be divided into two separate contributions: 1) the energy contribution ($\Delta E''$) due to the particle surface area exposed to each fluid phase (S'_{AO}, S'_{PO}, S'_{AW}, and S'_{PW}) and S'_I, and 2) the energy contribution (ΔE_{def}) due to the deformed oil-water interface (Fig. 1Sb). Therefore, $\Delta E'$ can be expressed as,[1]

$$\Delta E' = \Delta E'' + \Delta E_{def} \,. \tag{S1}$$

$\Delta E''$ is an analogue of eqn 1 and 2 in the main text,

$$\Delta E''_{IW} = \Delta E'' = \gamma_{OW}\left(S'_{AO}\cos\theta_A + S'_{PO}\cos\theta_P - S'_I\right) \text{ from the water phase} \tag{S2}$$

$$\Delta E''_{IO} = -\gamma_{OW}\left(S'_{AW}\cos\theta_A + S'_{PW}\cos\theta_P + S'_I\right) \text{ from the oil phase.} \tag{S3}$$

Note that eqn S2 and S3 are identical to eqn 1 and 2 when the interface is flat (*i.e.*, $\Delta E_{def} = 0$). Similar to the case of the FIA, we use eqn S1 and S2 to determine the equilibrium configurations without the FIA ($\Delta E''_{IW} = \Delta E''$).

ΔE_{def} is the free energy change of the oil-water interface with and without the interface deformation, given by,

$$\Delta E_{def} = \gamma_{OW}\left(S_{def} - S_{flat}\right), \tag{S4}$$

where S_{def} and S_{flat} are the areas of the deformed and the flat oil-water interface, respectively. The deformed interface height can be estimated by solving the Laplace equation in polar coordinates,

$$h_d(r,\phi) = \frac{a_0}{2} + \sum_n \left(\frac{r_c(\phi)}{r}\right)^n \left(a_n \cos(n\phi) + b_n \sin(n\phi)\right), \tag{S5}$$

where $r_c(\phi)$ is the radial distance between the three-phase contact line and the center of S'_I in Fig. S1b, and r and ϕ are the radial distance from the three-phase contact line ($r \geq r_c$) and polar angle, respectively. The Fourier coefficients, a_0, a_n, and b_n are obtained from a given boundary condition (*i.e.*, the three-phase contact line), $h_d(r = r_c, \phi) = A_0 + \sum_n \left(A_n \cos(n\phi) + B_n \sin(n\phi)\right)$. In this calculation, we assume that the interface exhibits a dipolar deformation, as indicated by h_{d1} and h_{d2} in Fig. S1b. The deformed surface area (S_{def}) is numerically calculated by dividing the surface into a large number of triangles and integrating them.[1] It is important to note that a higher multipole deformation, such as quadrupoles has been observed; however, since such a deformation would not exert significant torque on the interface-trapped particles, the equilibrium orientation is unlikely to be affected significantly.

Equilibrium Configuration

Similar to the case of the FIA in the main text, we calculate the attachment energy ($\Delta E'$ (d_v, h_{d1}, h_{d2}, θ_r) in eqn S1 and S2) of an amphiphilic particle by varying the vertical position (d_v) as well as the height of interface deformation (h_{d1}, h_{d2} in Fig. S1b) at a constant value of $\theta_r = \Theta$ (*i.e.*, $\Delta E'(d_v, h_{d1}, h_{d2})\big|_{\theta_r=\Theta}$). The minimum attachment energy is then found ($\Delta E'_{min}$ ($\theta_r = \Theta$)) and the same procedure for different values of θ_r is repeated to obtain the global (or equilibrium) energy minimum ($\Delta E'_{eq}$). The corresponding equilibrium orientation and vertical displacement at this global energy minimum are $\theta'_{r,eq}$ and $d'_{v,eq}$, respectively.

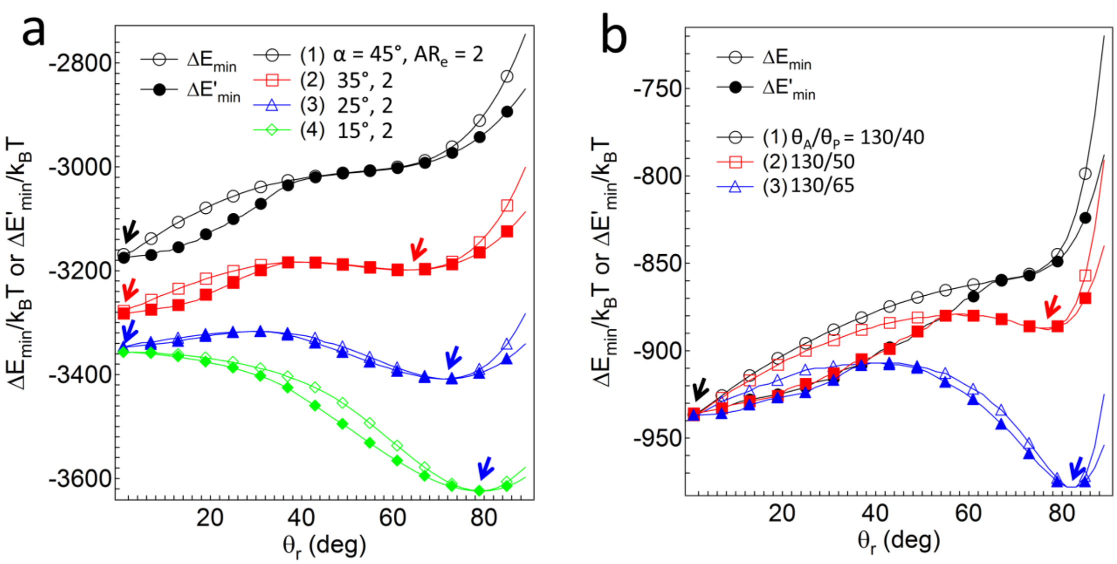

Fig. S2 Comparison of the minimum attachment energy profiles of amphiphilic ellipsoids with (ΔE_{min}) and without ($\Delta E'_{min}$) the FIA. (a) Ellipsoids with θ_A/θ_P = 120/60, c = 10 nm, AR_e = 2, and (1) α = 45°, (2) 35°, (3) 25°, (4) 15°. (b) Ellipsoids with AR_e = 5, α = 90°, c = 10 nm, and (1) θ_A/θ_P = 130/40, (2) 130/50, (3) 130/65. The plots with the FIA (open symbols) in panel a and b are identical to those in Fig. 2b and 3b in the main text, respectively. Arrows indicate the location of energy minima, suggesting that the both calculations with and without the FIA consistently find equilibrium and metastable orientations with negligible differences.

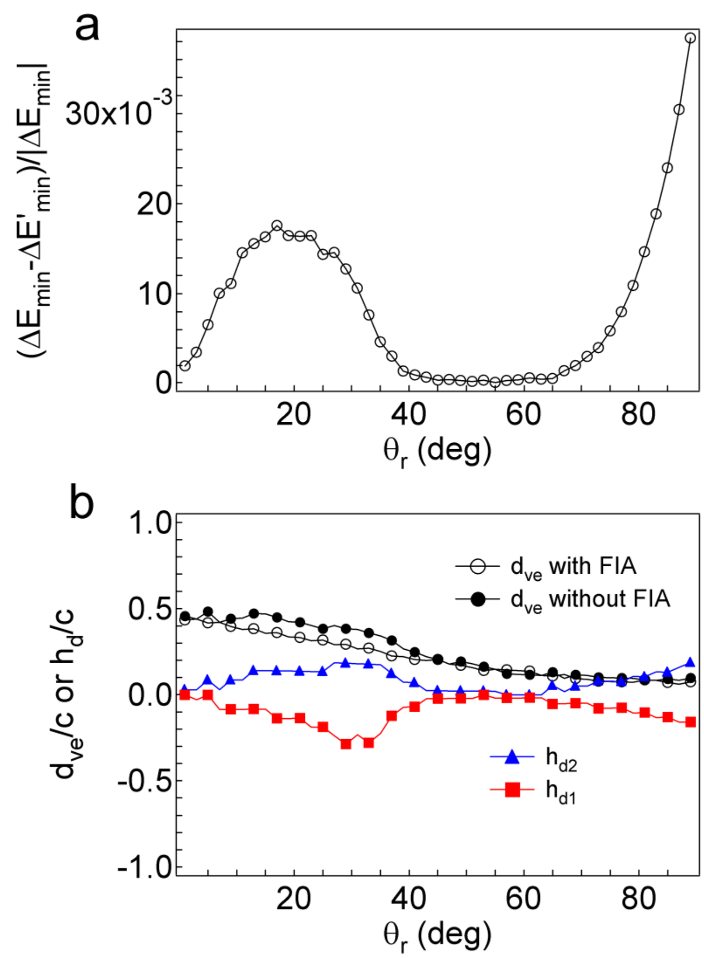

Fig. S3 (a) Normalized difference between ΔE_{min} and $\Delta E'_{min}$ for an amphiphilic ellipsoid with θ_A/θ_P = 120/60, c = 10 nm, α = 45°, and AR_e = 2. (b) The vertical displacement (d_{ve}) obtained from with and without the FIA, and the height of interface deformation (h_{d1} and h_{d2} in Fig. S2a).

The deviation between ΔE_{min} and $\Delta E'_{min}$ $\left(\frac{1}{N}\sum_{N}\frac{|\Delta E_{\min}-\Delta E'_{\min}|}{|\Delta E_{\min}|}\right.$, N is the number of data points) in Fig. S3a is less than 1.0% for θ_r between 0 and 90°, suggesting that the FIA can be used to rapidly and accurately determine the equilibrium configuration. The vertical displacement (d_{ve}) of the particle with respect to the oil-water interface obtained from the both methods is in good agreement with each other (black circles in Fig. S3b). Based on the calculation without the FIA (eqn S1, S2, S4 and S5), when the amphiphilic ellipsoid rotates from $\theta_r = 0$ to 90°, the surface wetting of apolar and polar surfaces of the particle on its preferred fluid phase (*i.e.*, oil and water, respectively) leads to the interface deformation, $h_{d1} \leq 0$ and $h_{d2} \geq 0$, as shown in Fig. S3b (see the geometry in Fig. S1b). Such interface deformation causes the minor deviation with the result *via* the FIA, as seen in Fig. S3a.

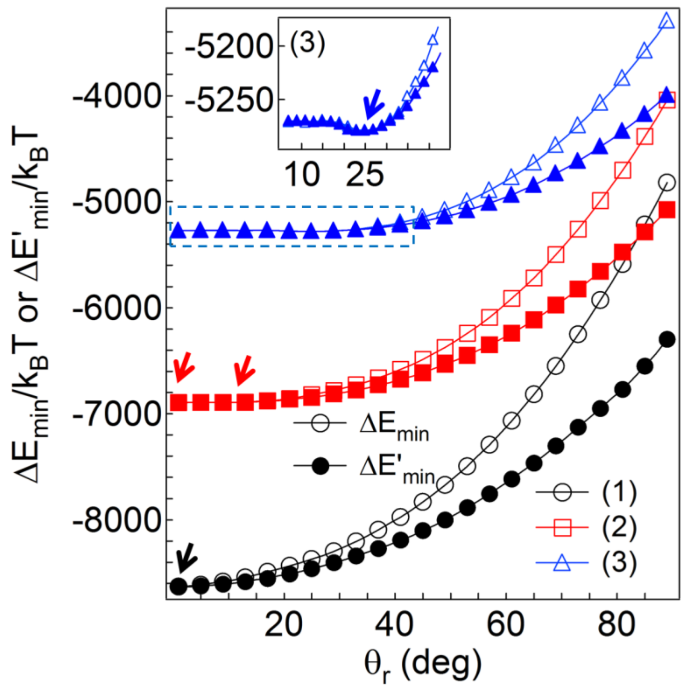

Fig. S4 The minimum attachment energy of symmetric amphiphilic dumbbells ($AR_d = 1.5$ and $R = 10$ nm) with (ΔE_{min}, open symbols) and without ($\Delta E'_{min}$, closed symbols) the FIA. Each color indicates different wettability, (1) $\theta_A/\theta_P = 120/40$, (2) 110/40, and (3) 100/40. The inset shows the magnified plot of (3) $\theta_A/\theta_P = 100/40$. Arrows indicate that the calculations with and without the FIA consistently show equilibrium orientations with negligible difference. The plots for the FIA (open symbols) are identical to those in Fig. 4b in the main text.

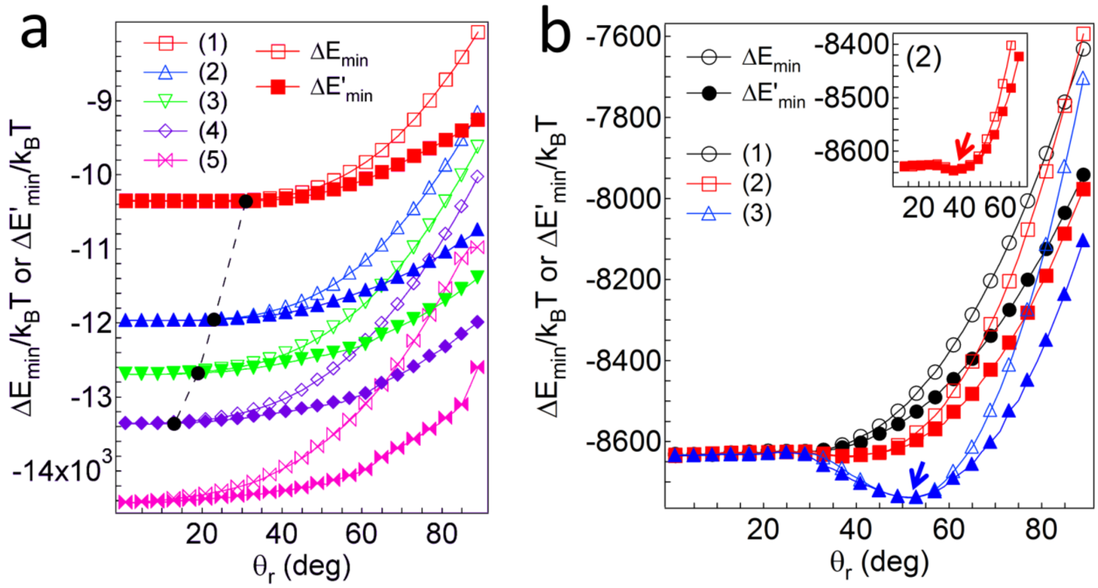

Fig. S5 Comparison of the minimum attachment energy profiles of asymmetric amphiphilic dumbbells with (ΔE_{min}, open symbols) and without ($\Delta E'_{min}$, closed symbols) the FIA. (a) Asymmetric dumbbells with AR_d = 1.8, R_A/R_P = 2 (R_A = 10 and R_P = 5 nm), and (1) θ_A/θ_P = 130/20, (2) 140/20, (3) 145/20, (4) 150/20, (5) 160/20. Black circles indicate $\theta_{r,int}$ for different values of θ_A/θ_P. (b) Asymmetric dumbbells with θ_A/θ_P = 120/60, R_A/R_P = 2 (R_A = 10 and R_P = 5 nm), and (1) AR_d = 1.5, (2) 1.65, (3) 1.8. The inset shows the magnified plot for the case of AR_d = 1.65. The results of the FIA (open symbols) in panel a and b are identical to those in Fig. 5b and 6b in the main text, respectively. Arrows in the cases of (2, 3) in panel b indicate that the two results with and without the FIA consistently show tilted equilibrium orientations with negligible differences.

1. B. J. Park, D. Lee, *ACS Nano* **2012**, *6*, 782.