Electronic Supplementary Information

General patchy ellipsoidal particle model for the aggregation behaviors of shape- and/or surface-anisotropic building blocks

Zhan-Wei Li,[†,‡] You-Liang Zhu,[*,†,‡] Zhong-Yuan Lu,[¶] and Zhao-Yan Sun[*,†,‡]

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China, University of Science and Technology of China, Hefei, 230026, China, and State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China

E-mail: youliangzhu@ciac.ac.cn; zysun@ciac.ac.cn

[*]To whom correspondence should be addressed
[†]Changchun Institute of Applied Chemistry
[‡]University of Science and Technology of China
[¶]Jilin University

Forces and torques

The force between two neighboring patchy ellipsoidal particles $\mathbf{F}_{ij}$ is given by the partial derivative of the anisotropic potential $U(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})$ with respect to $\mathbf{r}_{ij}$,

$$\begin{aligned}\mathbf{F}_{ij} &= -\frac{\partial U(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} \\ &= -\frac{\partial U_{GB}(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} - \frac{\partial U_{GB}(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} U_P(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij}) - \\ &\quad \frac{\partial U_P(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} U_{GB}(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij}).\end{aligned} \tag{1}$$

In Eq. (Eq. (1)), the partial derivative of $U_{GB}(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})$ is given by [1]

$$\begin{aligned}\frac{\partial U_{GB}(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} =& \frac{\partial U_r(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} \eta(\mathbf{A}_i, \mathbf{A}_j) \chi(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij}) + \\ & U_r(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij}) \eta(\mathbf{A}_i, \mathbf{A}_j) \frac{\partial \chi(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}},\end{aligned} \tag{2}$$

where

$$\frac{\partial U_r(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} = -\beta \hat{\mathbf{r}}_{ij} - \frac{\beta \sigma_{ij}^3(\mathbf{A}_i, \mathbf{A}_j, \hat{\mathbf{r}}_{ij})}{2 r_{ij}^2} \left[K - \left(K^T \cdot \hat{\mathbf{r}}_{ij}\right) \hat{\mathbf{r}}_{ij}\right], \tag{3}$$

with

$$\beta = \frac{24\varepsilon}{\sigma} \left[2 \left(\frac{\sigma}{h_{ij} + \gamma\sigma}\right)^{13} - \left(\frac{\sigma}{h_{ij} + \gamma\sigma}\right)^{7}\right] \quad \text{and} \quad K = \mathbf{G}_{ij}^{-1}(\mathbf{A}_i, \mathbf{A}_j) \cdot \mathbf{r}_{ij}, \tag{4}$$

and

$$\frac{\partial \chi(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} = \frac{4\mu}{r_{ij}^2} \left[I - \left(I^T \cdot \hat{\mathbf{r}}_{ij}\right) \hat{\mathbf{r}}_{ij}\right] \left[\chi(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})\right]^{(\mu-1)/\mu}, \tag{5}$$

with

$$I = \mathbf{B}_{ij}^{-1}(\mathbf{A}_i, \mathbf{A}_j) \cdot \mathbf{r}_{ij}. \tag{6}$$

In Eq. (Eq. (1)), the partial derivative of $U_P(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})$ is given by

$$\frac{\partial U_P(\mathbf{A}_i,\mathbf{A}_j,\mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} = -\sum_{\kappa=1}^{M_i}\sum_{\lambda=1}^{M_j}\Bigg[\gamma_\varepsilon \alpha f^{\alpha-1}\left(\mathbf{A}_i,\mathbf{A}_j,\mathbf{r}_{ij}\right)\Bigg(\frac{\pi}{2\theta_m^\kappa} \sin\frac{\pi\theta_i^\kappa}{2\theta_m^\kappa}\frac{\partial\theta_i^\kappa}{\partial\cos\theta_i^\kappa}\frac{\partial\cos\theta_i^\kappa}{\partial\mathbf{r}_{ij}}\cos\frac{\pi\theta_j^\lambda}{2\theta_m^\lambda}+ \frac{\pi}{2\theta_m^\lambda}\sin\frac{\pi\theta_j^\lambda}{2\theta_m^\lambda}\frac{\partial\theta_j^\lambda}{\partial\cos\theta_j^\lambda}\frac{\partial\cos\theta_j^\lambda}{\partial\mathbf{r}_{ij}}\cos\frac{\pi\theta_i^\kappa}{2\theta_m^\kappa}\Bigg)\Bigg], \tag{7}$$

where

$$\frac{\partial\theta_i^\kappa}{\partial\cos\theta_i^\kappa} = \begin{cases} 0 & \text{if } \cos^2\theta_i^\kappa = 1 \\ -\frac{1}{\sqrt{1-\cos^2\theta_i^\kappa}} & \text{otherwise,} \end{cases} \tag{8}$$

$$\frac{\partial\theta_j^\lambda}{\partial\cos\theta_j^\lambda} = \begin{cases} 0 & \text{if } \cos^2\theta_j^\lambda = 1 \\ -\frac{1}{\sqrt{1-\cos^2\theta_j^\lambda}} & \text{otherwise,} \end{cases} \tag{9}$$

$$\frac{\partial\cos\theta_i^\kappa}{\partial\mathbf{r}_{ij}} = -\left[\mathbf{A}_i^T\mathbf{n}_i^{\kappa b} - \left(\mathbf{A}_i^T\mathbf{n}_i^{\kappa b}\cdot\hat{\mathbf{r}}_{ij}\right)\hat{\mathbf{r}}_{ij}\right]/r_{ij}, \tag{10}$$

and

$$\frac{\partial\cos\theta_j^\lambda}{\partial\mathbf{r}_{ij}} = \left[\mathbf{A}_j^T\mathbf{n}_j^{\lambda b} - \left(\mathbf{A}_j^T\mathbf{n}_j^{\lambda b}\cdot\hat{\mathbf{r}}_{ij}\right)\hat{\mathbf{r}}_{ij}\right]/r_{ij}. \tag{11}$$

If $\mathbf{a}_{mi}$ denotes the mth row of the rotation matrix $\mathbf{A}_i$, then the torque τ_i acting on patchy ellipsoidal particle i due to its neighboring particle j is expressed as

$$\begin{aligned}
\tau_{ij} =& -\sum_m \mathbf{a}_{mi} \times \frac{\partial U(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{a}_{mi}} \\
=& -\sum_m \mathbf{a}_{mi} \times \frac{\partial U_{GB}(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{a}_{mi}} \left(1 + U_P(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})\right) - \\
& \sum_m \mathbf{a}_{mi} \times \frac{\partial U_P(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{a}_{mi}} U_{GB}(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij}) \\
=& \tau_{ij}^{GB} \left(1 + U_P(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})\right) + \tau_{ij}^{P} U_{GB}(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij}).
\end{aligned} \tag{12}$$

As given in Ref.,[1] τ_{ij}^{GB} can be written as

$$\tau_{ij}^{GB} = \tau_{ij}^{U_r} + \tau_{ij}^{\eta} + \tau_{ij}^{\chi}, \tag{13}$$

with

$$\tau_{ij}^{U_r} = -\eta(\mathbf{A}_i, \mathbf{A}_j)\chi(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij}) \frac{\beta \sigma_{ij}^3(\mathbf{A}_i, \mathbf{A}_j, \hat{\mathbf{r}}_{ij})}{2r_{ij}^2} \left(K^T \cdot \mathbf{A}_i^T \mathbf{S}_i^2 \mathbf{A}_i \times K\right), \tag{14}$$

$$\begin{aligned}
\tau_{ij}^{\chi} =& U_r(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})\eta(\mathbf{A}_i, \mathbf{A}_j) \frac{4\mu \left[\chi(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})\right]^{(\mu-1)/\mu}}{r_{ij}^2} \\
& \left(I^T \cdot \mathbf{A}_i^T \mathbf{E}_i \mathbf{A}_i \times I\right),
\end{aligned} \tag{15}$$

and

$$\tau_{ij}^{\eta} = -U_r(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})\chi(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij}) \sum_m \mathbf{a}_{mi} \times \mathbf{z}_{mi}, \tag{16}$$

where $\mathbf{z}_{mi}$ represents the mth row of the matrix $\mathbf{Z}_i$ given by

$$\mathbf{Z}_i = -\frac{1}{2} \left[\frac{2s_i s_j}{\det\left(\mathbf{G}_{ij}(\mathbf{A}_i, \mathbf{A}_j)\right)}\right]^{\nu/2} \frac{\nu}{\det\left(\mathbf{G}_{ij}(\mathbf{A}_i, \mathbf{A}_j)\right)} \mathbf{V}, \tag{17}$$

the matrix $\mathbf{V}$ is the derivative of the determinant of the matrix $\det\left(\mathbf{G}_{ij}(\mathbf{A}_i, \mathbf{A}_j)\right)$ with respect to the rotation matrix $\mathbf{A}_i$,

$$\mathbf{V} = [v_{my}] = \frac{\partial \det\left(\mathbf{G}_{ij}(\mathbf{A}_i, \mathbf{A}_j)\right)}{\partial \mathbf{a}_{mi}}, \tag{18}$$

and

$$[v_{my}] = \det\left(\mathbf{G}_{ij}(\mathbf{A}_i, \mathbf{A}_j)\right) \text{trace}\left[\mathbf{G}_{ij}(\mathbf{A}_i, \mathbf{A}_j) \cdot (\hat{\mathbf{e}}_y \otimes \mathbf{a}_{mi} + \mathbf{a}_{mi} \otimes \hat{\mathbf{e}}_y)\, s_{mi}^2\right]. \tag{19}$$

Here, $\hat{\mathbf{e}}_y$ is the unit vector of the coordinate axes in the body frame ($\hat{\mathbf{e}}_1 = [1,0,0]$, $\hat{\mathbf{e}}_2 = [0,1,0]$, and $\hat{\mathbf{e}}_3 = [0,0,1]$), s_{mi} is the mth semiaxis length of patchy ellipsoidal particle i, and $\otimes$ constructs a dyadic matrix from two vectors.

In Eq. (Eq. (12)), τ_{ij}^P is given by

$$\begin{aligned}
\tau_{ij}^P &= -\sum_m \mathbf{a}_{mi} \times \frac{\partial U_P(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial \mathbf{a}_{mi}} \\
&= -\sum_m \frac{\partial U_P(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij})}{\partial (\mathbf{A}_i^T \mathbf{n}_i^{\kappa b} \cdot \hat{\mathbf{r}}_{ij})} \left[\mathbf{a}_{mi} \times \frac{\partial (\mathbf{A}_i^T \mathbf{n}_i^{\kappa b} \cdot \hat{\mathbf{r}}_{ij})}{\partial \mathbf{a}_{mi}}\right] \\
&= -\sum_{\kappa=1}^{M_i} \sum_{\lambda=1}^{M_j} \frac{\pi \gamma_\varepsilon \alpha}{2\theta_m^\kappa} f^{\alpha-1}\left(\mathbf{A}_i, \mathbf{A}_j, \mathbf{r}_{ij}\right) \sin \frac{\pi \theta_i^\kappa}{2\theta_m^\kappa} \frac{\partial \theta_i^\kappa}{\partial \cos \theta_i^\kappa} \\
&\quad \cos \frac{\pi \theta_j^\lambda}{2\theta_m^\lambda} \left(\mathbf{A}_i^T \mathbf{n}_i^{\kappa b} \times \hat{\mathbf{r}}_{ij}\right).
\end{aligned} \tag{20}$$

Integration algorithms

The motion of patchy ellipsoidal particles is governed by Newtonian equations of motion.[2–6] In the space-fixed frame, the equations are expressed as

$$\dot{\mathbf{r}}_i = \mathbf{v}_i, \tag{21}$$

$$\dot{\mathbf{v}}_i = \frac{\mathbf{F}_i}{m_i}, \tag{22}$$

$$\dot{\mathbf{L}}_i = \tau_i, \tag{23}$$

$$\dot{\mathbf{q}}_i = \frac{1}{2}\mathbf{S}(\mathbf{q}_i)\, \omega_i, \tag{24}$$

where

$$\omega_i = (0, \omega_i^x, \omega_i^y, \omega_i^z) = \mathbf{A}(\mathbf{q}_i)(\mathbf{I}_i^b)^{-1}\mathbf{A}^T(\mathbf{q}_i)\mathbf{L}_i, \tag{25}$$

$$\mathbf{S}(\mathbf{q}_i) = \begin{pmatrix} q_{i,0} & -q_{i,1} & -q_{i,2} & -q_{i,3} \\ q_{i,1} & q_{i,0} & q_{i,3} & -q_{i,2} \\ q_{i,2} & -q_{i,3} & q_{i,0} & q_{i,1} \\ q_{i,3} & q_{i,2} & -q_{i,1} & q_{i,0} \end{pmatrix}, \tag{26}$$

and $\mathbf{F}_i = \sum_j \mathbf{F}_{ij}$ and $\tau_i = \sum_j \tau_{ij}$ are the force and torque acting on patchy ellipsoidal particle i due to all its direct neighbors, respectively.

The equations of motion in Eqs. (Eq. (21))-(Eq. (24)) are numerically integrated via a velocity-Verlet-like algorithm[2,4–6]

$$\mathbf{v}_i(t+\frac{1}{2}\delta t) = \mathbf{v}_i(t) + \frac{1}{2}\delta t\frac{\mathbf{F}_i(t)}{m_i}, \tag{27}$$

$$\mathbf{r}_i(t+\delta t) = \mathbf{r}_i(t) + \delta t\mathbf{v}_i(t+\frac{1}{2}\delta t), \tag{28}$$

$$\mathbf{L}_i(t+\frac{1}{2}\delta t) = \mathbf{L}_i(t) + \frac{1}{2}\delta t\tau_i(t), \tag{29}$$

$$\mathbf{q}_i(t+\delta t) = Q\left(\mathbf{q}_i(t), \delta t, \omega_i(t+\frac{1}{2}\delta t)\right), \tag{30}$$

$$\mathbf{v}_i(t+\delta t) = \mathbf{v}_i(t+\frac{1}{2}\delta t) + \frac{1}{2}\delta t\frac{\mathbf{F}_i(t+\delta t)}{m_i}, \tag{31}$$

$$\mathbf{L}_i(t+\delta t) = \mathbf{L}_i(t+\frac{1}{2}\delta t) + \frac{1}{2}\delta t\tau_i(t+\delta t). \tag{32}$$

The function Q in Eq. (Eq. (30)) is an application of the Richardson method to reduce the error in updating the quaternion $\mathbf{q}_i$. To preserve the constraint ${q_{i,0}}^2 + {q_{i,1}}^2 + {q_{i,2}}^2 + {q_{i,3}}^2 = 1$, $\mathbf{q}_i$ should be renormalized after being updated. Please refer to the Refs.[2,4–6] for more details about the Richardson method.

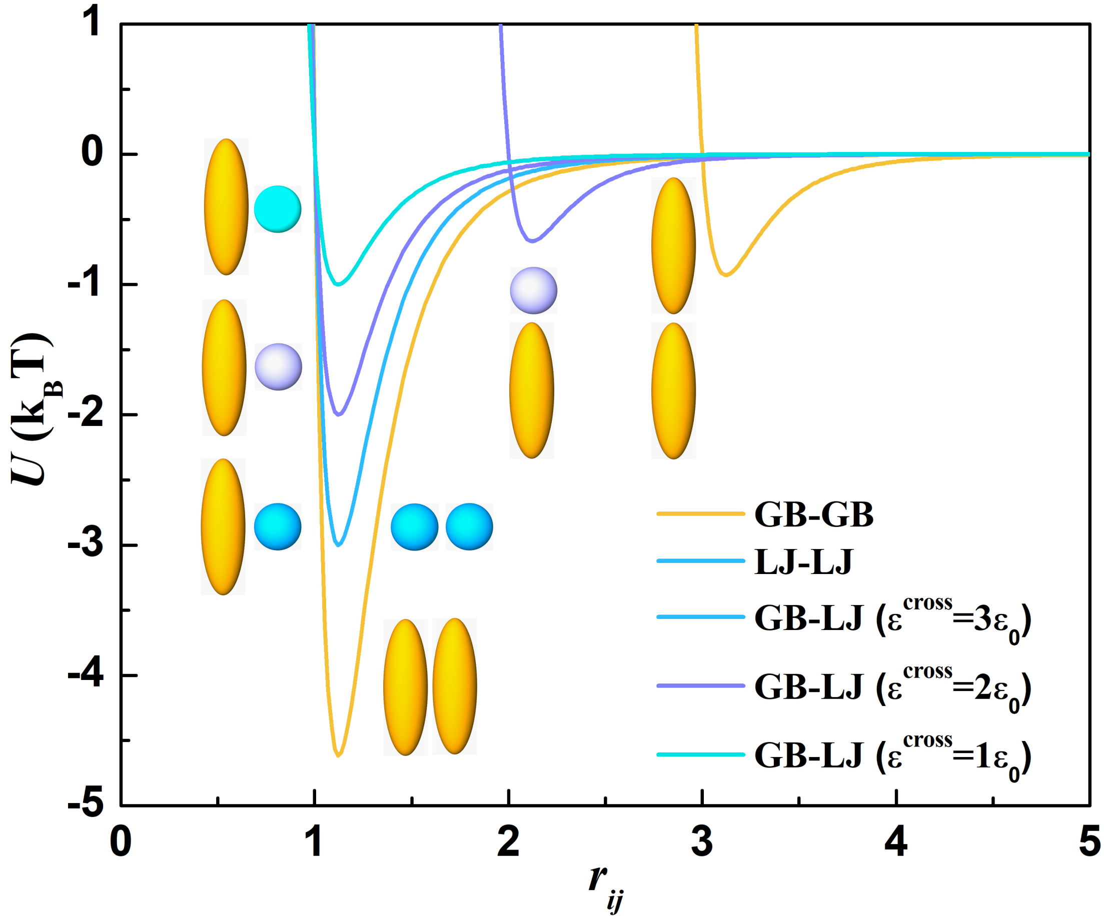

Figure S1: Representative potential profiles of solute-solute (GB-GB), solvent-solvent (LJ-LJ), and solute-solvent (GB-LJ) interactions. The LJ-LJ and GB-LJ with $\varepsilon^{cross} = 3\varepsilon_0$ curves are superimposed.

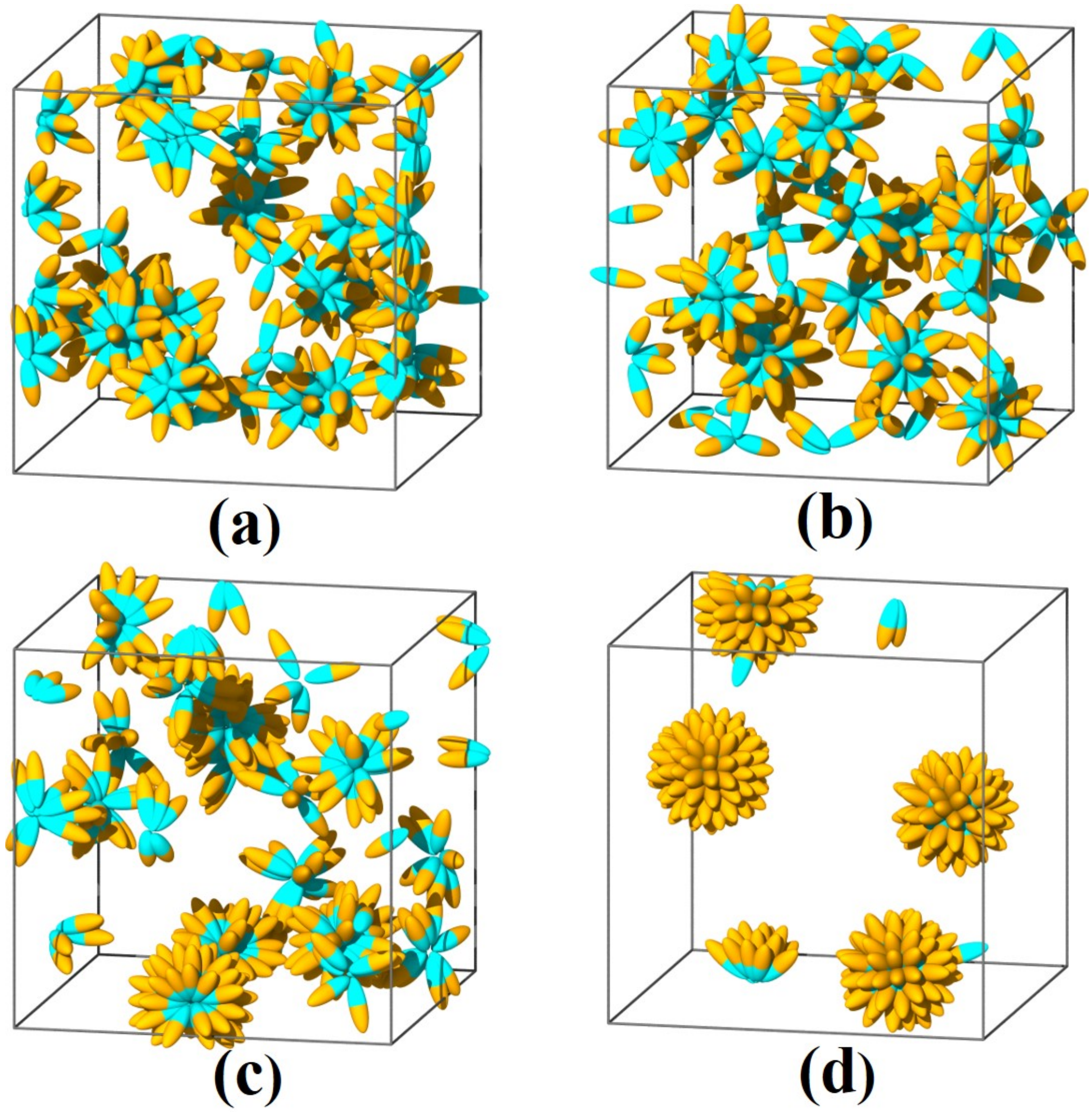

Figure S2: Typical ordered cluster structures self-assembled from Janus ellipsoids at different σ and ε^{cross}: (a) $\sigma = 1\sigma_0$ and $\varepsilon^{cross} = 3\varepsilon_0$, (b) $\sigma = 2\sigma_0$ and $\varepsilon^{cross} = 3\varepsilon_0$, (c) $\sigma = 3\sigma_0$ and $\varepsilon^{cross} = 3\varepsilon_0$, (d) $\sigma = 3\sigma_0$ and $\varepsilon^{cross} = 1\varepsilon_0$. For the sake of clarity, solvent is not shown.

References

1. Brown, W. M.; Petersen, M. K.; Plimpton, S. J.; Grest, G. S. *J. Chem. Phys.* **2009**, *130*, 044901.

2. Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press, Oxford, 1987.

3. Miller, T. F.; Eleftheriou, M.; Pattnaik, P.; Ndirango, A.; Newns, D.; Martyna, G. J. *J. Chem. Phys.* **2002**, *116*, 8649–8659.

4. Nguyen, T. D.; Phillips, C. L.; Anderson, J. A.; Glotzer, S. C. *Comput. Phys. Commun.* **2011**, *182*, 2307–2313.

5. Li, Z.-W.; Sun, Z.-Y.; Lu, Z.-Y. *Self-Assembling Systems: Theory and Simulation*; John Wiley & Sons, Ltd, 2017; pp 109–133.

6. Li, Z.-W.; Zhu, Y.-L.; Lu, Z.-Y.; Sun, Z.-Y. *Soft Matter* **2016**, *12*, 741–749.