Supporting information

Separation-dependence evolution of inter-particle interaction in the oriented-attachment growth of nanorods: A case for hexagonal nanocrystals

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Derivation of vdW and CI between elongated hexagonal NR and hexagonal precursor NC

The energy of vdW attractive interaction between two small particles is given by Eq. 1.

$$E = -\int_{V_1} dv_1 \int_{V_2} dv_2 \frac{q^2\lambda}{r^6} \tag{1}$$

For solving this volume integral, we utilize the surface integral to simplify this integral. Hence, the expression of hemisphere in Cartesian coordinate is depicted in Eq. 2.

$$z = \sqrt{r^2 - x^2 - y^2} \tag{2}$$

Due to symmetry, this curved surface of hexagon is separated into 12 equivalent parts. And the area of curved surface inside the hexagonal NR can be given by Eq. 3.

$$[surface] = 12\iint_{D_{xy}} \sqrt{1 + z_x^2(x,y) + z_y^2(x,y)}dxdy \tag{3}$$

The procedure of solving this double integral is exhibited in Eq. 4.

$$\begin{aligned}
[surface] &= 12\iint_{D_{xy}} -\frac{r}{\sqrt{r^2 - x^2 - y^2}}dxdy \\
&= 12\int_0^{\frac{\sqrt{3}}{2}R} dx \int_0^{\frac{x}{\sqrt{3}}} -\frac{r}{\sqrt{r^2 - x^2 - y^2}}dy \\
&= 12\int_0^{\frac{\sqrt{3}}{2}R} r\arctan(\frac{x}{\sqrt{3r^2 - 4x^2}})dx \\
&= 12\left[r^2\arctan(\frac{\sqrt{3r^2 - 3R^2}}{r}) + \frac{\sqrt{3}}{2}rR\arctan(\frac{R}{2\sqrt{r^2 - R^2}}) - \frac{1}{3}\pi r^2\right]
\end{aligned} \tag{4}$$

Assuming that the separation between elongated hexagonal NR and hexagonal precursor NC is much larger than the size of the precursor, we can then view the curved surface as a plane and obtain the expression of vdW interaction between hexagonal NR and an atom, as shown in Eq. 5

$$E_p = -\int_{C-\frac{1}{2}L_1}^{C+\frac{1}{2}L_1} \frac{q_1 \lambda}{r^6}[surface]dr \tag{5}$$

We integrate q_2E_p in the whole domain of the precursor, and then obtain the expression of vdW between hexagonal NR and hexagonal precursor NC, as described in Eq. 6.

$$E = -\int_{D-\frac{1}{2}L_2}^{D+\frac{1}{2}L_2} q_2 E_p \left[surface\big|_{r=C}\right]dC \tag{6}$$

Substituting E_p into Eq. 6, we obtain Eq. 7.

$$E = -q_1 q_2 \lambda \int_{D-\frac{1}{2}L_2}^{D+\frac{1}{2}L_2} \left[surface\big|_{r=C}\right]dC \int_{C-\frac{1}{2}L_1}^{C+\frac{1}{2}L_1} [surface]\frac{1}{r^6}dr \tag{7}$$

By replacing the entire coefficients with Hamaker constant ($A=\pi^2 q^2 \lambda$), we get Eq. 8.

$$E = -\frac{A}{\pi^2}\int_{D-\frac{1}{2}L_2}^{D+\frac{1}{2}L_2} \left[surface\big|_{r=C}\right]dC \int_{C-\frac{1}{2}L_1}^{C+\frac{1}{2}L_1} [surface]\frac{1}{r^6}dr \tag{8}$$

Furthermore, by substituting [surface] into Eq. 8, the expression of vdW between elongated hexagonal NR and hexagonal precursor NC can then be expressed in Eq. 9.

$$\begin{aligned} E = -\frac{144}{\pi^2} A \int_{D-\frac{1}{2}L_2}^{D+\frac{1}{2}L_2} & \left[C^2 \arctan\left(\frac{\sqrt{3C^2-3R^2}}{C}\right) + \frac{\sqrt{3}}{2} CR \arctan\left(\frac{R}{2\sqrt{C^2-R^2}}\right) - \frac{1}{3}\pi C^2\right]dC \\ \int_{C-\frac{1}{2}L_1}^{C+\frac{1}{2}L_1} \frac{1}{r^6} & \left[r^2 \arctan\left(\frac{\sqrt{3r^2-3R^2}}{r}\right) + \frac{\sqrt{3}}{2} rR \arctan\left(\frac{R}{2\sqrt{r^2-R^2}}\right) - \frac{1}{3}\pi r^2\right]dr \end{aligned} \tag{9}$$

CI between two arbitrary points can be described in Eq. 10.

$$E = \frac{1}{4\pi\varepsilon}\frac{Q_1 Q_2}{r} \tag{10}$$

For obtaining CI, we first calculate CI between the eight sides of the hexagonal NR and a point charge at (x_0, y_0). For bottom surface of the hexagonal NR which is closed to hexagonal precursor, we divide hexagonal surface into three areas and get CI in Eq. 11.

$$\begin{aligned} E_{pI} = & \int_{-R}^{-\frac{1}{2}R} dx \int_{-\sqrt{3}(x+R)}^{\sqrt{3}(x+R)} \frac{\sigma_1}{\sqrt{(x-x_0)^2+(y-y_0)^2+s^2}}dy + \int_{-\frac{1}{2}R}^{\frac{1}{2}R} dx \int_{-\frac{\sqrt{3}}{2}R}^{\frac{\sqrt{3}}{2}R} \frac{\sigma_1}{\sqrt{(x-x_0)^2+(y-y_0)^2+s^2}}dy \\ & + \int_{\frac{1}{2}R}^{R} dx \int_{\sqrt{3}(x-R)}^{-\sqrt{3}(x-R)} \frac{\sigma_1}{\sqrt{(x-x_0)^2+(y-y_0)^2+s^2}}dy \end{aligned} \tag{11}$$

For bottom surface of hexagonal NR, which is far from hexagonal precursor CI, we substitute s with $s+L_1$ in E_{pI} and get E_{pII}.

In addition, for six sides of hexagonal NR, the expressions are similar and thus we present them together as follows. CI between the point charge and one side is shown in Eq. 12,

$$E_{p1} = \int_{-R}^{-\frac{1}{2}R} 2dx \int_0^{L_1} \frac{\sigma_1}{4\pi\varepsilon\sqrt{R^2+(z+s)^2}}dz \tag{12}$$

where $R^2 = (x - x_0)^2 + (y - y_0)^2$ and $y = -\sqrt{3}(x + R)$.
We substitute $y = -\sqrt{3}(x + R)$ in E_{p1} with $y = \sqrt{3}(x + R)$ and get E_{p2}.

CI between point charge and the third side is shown in Eq. 13,

$$E_{p3} = \int_{-\frac{1}{2}R}^{\frac{1}{2}R} dx \int_0^{L_1} \frac{\sigma_1}{4\pi\varepsilon\sqrt{R^2 + (z+s)^2}} dz \tag{13}$$

where $R^2 = (y + \frac{\sqrt{3}}{2})^2$.

By substituting $R^2 = (y + \frac{\sqrt{3}}{2})^2$ in E_{p3} for $R^2 = (y - \frac{\sqrt{3}}{2})^2$, we get E_{p4}. CI between point charge and the fifth side is shown in Eq. 14,

$$E_{p5} = \int_{\frac{1}{2}R}^{R} 2dx \int_0^{L_1} \frac{\sigma_1}{4\pi\varepsilon\sqrt{R^2 + (z+s)^2}} dz \tag{14}$$

where $R^2 = (x - x_0)^2 + (y - y_0)^2$ and $y = -\sqrt{3}(x - R)$. By substituting $y = -\sqrt{3}(x - R)$ in E_{p5} with $y = \sqrt{3}(x - R)$, we get E_{p6}. We then get the expression of CI between hexagonal NR and point charge by adding these eight parts together, as shown in Eq. 15.

$$E_p = E_{pI} + E_{pII} + \sum_{i=1}^{6} E_{pi} \tag{15}$$

Similarly, for the bottom surface of the hexagonal precursor NC, which is close to hexagonal NR,

$$E_I = \int_{-R}^{-\frac{1}{2}R} dx_0 \int_{-\sqrt{3}(x+R)}^{\sqrt{3}(x+R)} \sigma_2 E_p dy_0 + \int_{-\frac{1}{2}R}^{\frac{1}{2}R} dx_0 \int_{-\frac{\sqrt{3}}{2}R}^{\frac{\sqrt{3}}{2}R} \sigma_2 E_p dy_0 + \int_{\frac{1}{2}R}^{R} dx_0 \int_{\sqrt{3}(x-R)}^{-\sqrt{3}(x-R)} \sigma_2 E_p dy_0 \tag{16}$$

where $s = d$.

For the bottom surface of the hexagonal precursor NC, which is far from hexagonal NR, we substitute $s = d$ in E_I with $s = d + L_2$ and get E_{II}.

Due to symmetry, the six sides of the hexagonal precursor NC have the same values of CI, which can be marked as E_s,

$$E_s = 6\int_{-\frac{1}{2}R}^{\frac{1}{2}R} dx_1 \int_d^{d+L_2} \sigma_2 E_p ds \tag{17}$$

where $y_0 = \frac{\sqrt{3}}{2}R$.

Therefore, the CI between the elongated hexagonal NR and the short hexagonal precursor NC is given in Eq. 18.

$$E = E_I + E_{II} + E_s \tag{18}$$

The integration of vdW and CI are too complex and thus we choose to solve the integration by numerical evaluation *via* adaptive Simpson quadrature.

Therefore, the total potential energy associated with the OA growth of the hexagonal NR can be shown in Eq. 19.

$$E_{tot} = E_{vdW} + E_{CI} \tag{19}$$