

Supporting Information

“Steric Interaction in Colloidal Deposition”

(1) Brush Model

Derivation of

- force expression for sphere-plate interaction $F_{sp}(H)$
- energy expression for plate-plate interaction $V_{pp}(H)$
- energy expression for sphere-plate interaction $V_{sp}(H)$

from the force expression $F(H)$ based on a brush model {deGennes:1987ec} for plate-plate interaction between two polymer layers

$$\frac{F(h)}{k_B T} = \frac{1}{s^3} \left[\left(\frac{h_c}{h} \right)^{\frac{9}{4}} - \left(\frac{h}{h_c} \right)^{\frac{3}{4}} \right] \quad (\text{Brush Model})$$

$$\begin{aligned} \frac{v_{pp}(h)}{k_B T} &= \int_{\infty}^h \frac{-F(x)}{k_B T} dx \\ &= -\frac{1}{s^3} \int_{\infty}^h \left[\left(\frac{h_c}{x} \right)^{\frac{9}{4}} - \left(\frac{x}{h_c} \right)^{\frac{3}{4}} \right] dx = -\frac{1}{s^3} \int_{h_c}^h \left[\left(\frac{h_c}{x} \right)^{\frac{9}{4}} - \left(\frac{x}{h_c} \right)^{\frac{3}{4}} \right] dx \\ &= -\frac{1}{s^3} \left[\frac{48}{35} h_c - \frac{4}{5} h \left(\frac{h_c}{h} \right)^{9/4} - \frac{4}{7} h \left(\frac{h}{h_c} \right)^{3/4} \right] \end{aligned}$$

$$\begin{aligned} \frac{V_{sp}(H)}{k_B T} &= 2\pi a \int_H^{\infty} \frac{v_{pp}(h)}{k_B T} dh = 2\pi a \int_H^{h_c} \frac{v_{pp}(h)}{k_B T} dh \\ &= \frac{2\pi a}{s^3} \int_H^{h_c} \left[\frac{48}{35} h_c - \frac{4}{5} h \left(\frac{h_c}{h} \right)^{9/4} - \frac{4}{7} h \left(\frac{h}{h_c} \right)^{3/4} \right] dh \\ &= -\frac{8\pi a}{35s^3} h_c \left[12h + 28h \left(\frac{h_c}{h} \right)^{5/4} - \frac{20}{11} h \left(\frac{h}{h_c} \right)^{7/4} \right]_H^{h_c} \\ &\approx \frac{8\pi a}{35s^3} h_c^2 \left[-38.2 + 12 \left(\frac{H}{h_c} \right) + 28 \left(\frac{H}{h_c} \right)^{-1/4} - \frac{20}{11} \left(\frac{H}{h_c} \right)^{11/4} \right] \end{aligned}$$

$$\frac{F_{sp}(H)}{k_B T} = -\frac{1}{k_B T} \frac{dV_{sp}(H)}{dH} = -\frac{8a}{35s^3} h_c \left[12 - 7 \left(\frac{H}{h_c} \right)^{\frac{5}{4}} - 5 \left(\frac{H}{h_c} \right)^{\frac{7}{4}} \right]$$

with $h_c = 2\delta$

$$\frac{V_{sp}(H)}{k_B T} \approx \frac{32\pi a}{35s^3} \delta^2 \left[-38.2 + 6\tilde{H} + 33.3\tilde{H}^{-1/4} - 0.27\tilde{H}^{11/4} \right]$$

$$\approx \frac{32\pi a}{35s^3} \delta^2 \left[\tilde{H} + 5.55\tilde{H}^{-1/4} - 0.045\tilde{H}^{11/4} - 6.36 \right]$$

$$\approx 17.23 \frac{a\delta^2}{s^3} \left[\tilde{H} + 5.55\tilde{H}^{-1/4} - 0.045\tilde{H}^{11/4} - 6.36 \right]$$

$$\frac{F_{sp}(H)}{k_B T} = 17.28 \frac{a\delta}{s^3} \left[-1 + 1.39\tilde{H}^{-\frac{5}{4}} + 0.12\tilde{H}^{\frac{7}{4}} \right]$$

(2) Mushroom Model

Derivation of

- force expression for sphere-plate interaction $F_{sp}(H)$
- energy expression for plate-plate interaction $V_{pp}(H)$
- energy expression for sphere-plate interaction $V_{sp}(H)$

from the force expression $F(H)$ based on a mushroom model {deGennes:1987ec} for plate-plate interaction between two polymer layers

$$\frac{F_{pp}(h)}{k_B T} = \frac{1}{s^2 h_c} \left(\frac{h_c}{h} \right)^{\frac{8}{3}} \quad (\text{Mushroom Model})$$

$$\begin{aligned} \frac{V_{pp}(h)}{k_B T} &= - \int_{\infty}^h \frac{F(x)}{k_B T} dx \\ &= - \frac{1}{s^2 h_c} \int_{\infty}^h \left(\frac{h_c}{x} \right)^{\frac{8}{3}} dx = - \frac{1}{s^2 h_c} \int_{h_c}^h \left(\frac{h_c}{x} \right)^{\frac{8}{3}} dx \\ &= \frac{3}{5s^2 h_c} \left[x \left(\frac{h_c}{x} \right)^{\frac{8}{3}} \right]_{h_c}^h = \frac{3}{5s^2 h_c} \left(h \left(\frac{h_c}{h} \right)^{\frac{8}{3}} - h_c \right) \end{aligned}$$

$$\begin{aligned}
\frac{V_{sp}(H)}{k_B T} &= 2\pi a \int_H^\infty \frac{v_{pp}(h)}{k_B T} dh = 2\pi a \int_H^{h_c} \frac{v_{pp}(h)}{k_B T} dh \\
&= \frac{6\pi a}{5s^2 h_c} \int_H^{h_c} \left(h \left(\frac{h_c}{h} \right)^{8/3} - h_c \right) dh \\
&= -\frac{3\pi a}{5s^2} \left(3h_c \left(\frac{h_c}{h} \right)^{2/3} + 2h \right) \Bigg|_H^{h_c} \\
&= \frac{3\pi a}{5s^2} \left(3h_c \left(\frac{h_c}{H} \right)^{2/3} + 2H - 5h_c \right)
\end{aligned}$$

With $h_c = 2\delta$

$$\begin{aligned}
\frac{V_{sp}(H)}{k_B T} &\approx 3.77 \frac{a\delta}{s^2} \left(\tilde{H} + 4.75\tilde{H}^{-2/3} - 5 \right) \\
\frac{F_{sp}(H)}{k_B T} &\approx 3.77 \frac{a}{s^2} \left(-1 + 3.17\tilde{H}^{-5/3} \right)
\end{aligned}$$