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**Electronic Supplementary Information for**

# Critical Review: Impacts of Macromolecular Coatings on Critical Physicochemical Processes Controlling Environmental Fate of Nanomaterials

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In this Electronic Supporting Information, we provide a brief overview of theory from colloid science describing interfacial forces for engineered nanomaterials (ENMs), with particular attention to macromolecular surface coatings. Reviews of these forces for uncoated particles in an environmental context have been provided elsewhere.[1-3] Briefly, Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is typically used to estimate the energy of interaction between a particle and another surface ($V_{DLVO}$) by summing the van der Waals ($V_{vdw}$) and electrostatic forces ($V_{el}$):

$$V_{DLVO} = V_{vdw} + V_{el} \tag{S1}$$

Expressions for the van der Waals and electrostatic energies for sphere-sphere interactions (e.g., aggregation) and sphere-plate interactions (e.g., deposition) for uncoated particles are provided elsewhere.[2, 4] The strength of these interactions will depend on the properties of the ENM (size, Hamaker constant, and surface charge or surface potential) and the dispersion medium (ionic strength and composition). Analytical expressions have also been developed for deposition interactions of nanoparticles where assumptions taken for larger colloids do not apply.[5]

Adsorbed macromolecules will change the DLVO forces and impart additional forces of interaction between two particles or between a particle and a surface. These "extended DLVO" forces have also been reviewed.[2] These forces include steric and electrosteric forces, Lewis acid-base interactions (including "hydrophilic" forces), and hydrophobic interactions.[4, 6] We focus on steric forces, which become important for thick macromolecular layers and have a strong impact on ENM stability against aggregation, particularly at higher ionic strengths (e.g., brackish and seawater) where purely electrostatic interactions are screened. Electrosteric forces can also be produced by charged polyelectrolyte coatings, for which the electrostatic and steric forces may not be independent or additive.[7, 8]

For the homoaggregation of two identical spherical particles with the assumption of a uniform adsorbed layer (i.e., uniform volume fraction of macromolecule around the particle), steric interactions can be incorporated into DLVO theory using the following equations by Vincent et al. (Equations S2 to S4)[9] or related expressions, e.g., those by Lozsán et al.[10] These expressions account for the entropy loss and osmotic pressure upon overlap or mixing of the adsorbed layers ($V_{s,mix}$) and the elastic repulsion when the layers are compressed between the particles ($V_{s,el}$). The particle and adsorbed layer properties required to calculate these forces are the particle radius ($a$) and the macromolecule's molecular weight ($M_2^{a}$), Flory-Huggins parameter ($\chi$), density ($\rho_2$), volume fraction ($\bar{\phi}_2^{a}$), and layer thickness ($\delta$).

$$V_{s,mix} = \frac{4\pi a k T}{v_1}\left(\bar{\phi}_2^{a}\right)^2\left(\frac{1}{2}-\chi\right)\left(\delta-\frac{h}{2}\right)^2 \; ; \qquad \delta < h < 2\delta \qquad \text{(S2)}$$

$$V_{s,mix} = \frac{4\pi a \delta^2 k T}{v_1}\left(\bar{\phi}_2^{a}\right)^2\left(\frac{1}{2}-\chi\right)\left(\frac{h}{2\delta}-\frac{1}{4}-\ln\frac{h}{\delta}\right) \; ; \qquad 0 < h < \delta \qquad \text{(S3)}$$

$$V_{s,el} = \frac{2\pi a k T \delta^2 \rho_2 \bar{\phi}_2^{a}}{M_2^{a}}\left\{\frac{h}{\delta}\ln\left[\frac{h}{\delta}\left(\frac{3-h/\delta}{2}\right)^2\right]-6\ln\left(\frac{3-h/\delta}{2}\right)+3\left(1-h/\delta\right)\right\}; \quad 0 < h < \delta \qquad \text{(S4)}$$

where $h$ is the separation distance between the hard particle surfaces, $k$ is the Boltzmann constant, $T$ is the temperature, and $v_1$ is the molar volume of the solvent. The magnitude of the steric force increases with the segment density or volume fraction ($\bar{\phi}_2^{a}$) of macromolecule around the particle surface. The layer thickness determines the volume of overlap of the adsorbed layers ($V_{lens}$ in Figure S1), as well as the extent of the repulsive interaction; coatings that are thick relative to the length scale of the attractive van der Waals interaction can prevent close approach and attachment of surfaces in the primary energy minimum. Finally, the solvency of the macromolecule in the dispersion medium of interest (e.g., water) will determine the sign and affect the magnitude of the energy of mixing for the overlapping adsorbed layers: layer overlap is unfavorable in "good" solvents for the macromolecule (i.e., $\chi < ½$) but favorable in "poor" solvents (i.e., $\chi > ½$).

In the interpenetration regime (Figure S1b), the polymer segment density increases. The consequences of this depend on the solvent quality. In a good solvent (Flory $\chi$ parameter < ½), increasing segment-segment contacts at the expense of decreasing segment-solvent contacts is energetically unfavorable, and the osmotic pressure in the interaction zone increases. This is manifested as a repulsive interaction, a force that would drive particles apart to relieve the local osmotic pressure gradient. This mechanism can fail if chains are weakly adsorbed and can respond to the increased osmotic pressure by desorbing. Since increasing solvent quality tends to decrease the adsorption energy, a balance must be struck between the stronger segment-segment repulsion and the weaker adsorption energy produced by better solvent quality. This relaxation route is not available for covalently anchored chains, and improving solvent quality improves stabilization without disadvantages.

In poor solvent conditions ($\chi > ½$), the opposite occurs. Segment-segment contacts are energetically preferred, and the system is driven to de-mix segments and solvents, producing a net attraction between the layers.

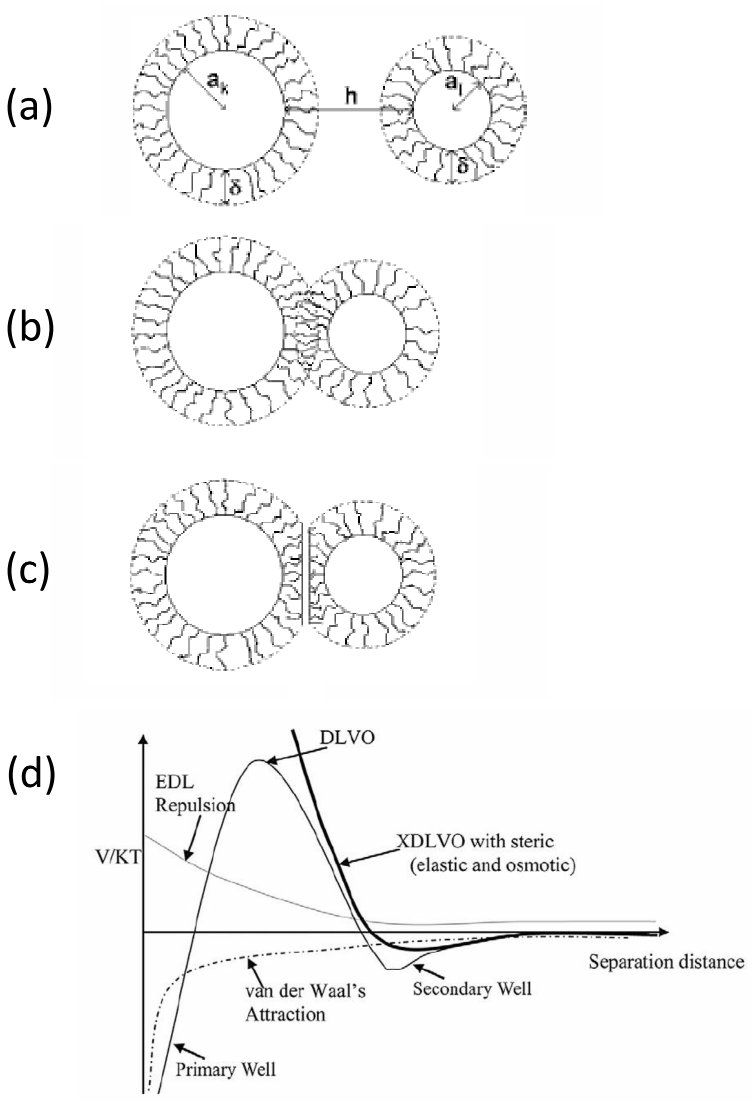

**Figure S1.** Distant interaction (a) and close approach with mixing (b) and compression (c) of adsorbed layers on macromolecule-coated particles, and the effect of steric interactions on the interaction energy between their surfaces (d), as can be described by Equations S2, S3, and S4, respectively, for particles of equal radius, i.e., $a_k = a_l$. Note cartoon drawings of particles and plot of interaction energy are not depicted at the same scale. Steric interactions, included in extended DLVO models, (d, "XDLVO" curve), can produce strong repulsive forces that exceed the attractive van der Waals forces. Therefore, the primary energy minimum that exists when only van der Waals and electrostatic forces are included (d, "DLVO" curve) may not exist when steric interactions are present. Figures (a) to (c) adapted from Lozsán et al.[10] copyright American Physical Society. Figure (d) reprinted from Hotze et al.[11] copyright Alliance of Crop, Soil, and Environmental Science Societies.

## Estimate of layer thickness required to provide stabilization against aggregation

The most important factor in successful steric stabilization is the solvent quality for the stabilizing polymer. When steric stabilization fails in the presence of thick layers, it normally is the result of poor solvent quality, rather than van der Waals attraction. The latter can be important when layers are thin. A rough guide to judge how thick a layer should be to render van der Waals attraction unimportant is to insist that when layers on opposing particle surfaces come into contact, the van der Waals attraction should be less than some cutoff value; -10 $kT$ would be reasonable. Thus, the minimum desirable layer thickness should be about half the separation distance where the van der Waals interaction equals -10 $kT$.

The van der Waals interaction energy between two spheres of radii $a_1$ and $a_2$, at a surface-to-surface separation distance $h$, is[12]

$$V(h) = -\frac{A\bar{a}}{12h}\left[\frac{1}{1+\dfrac{h}{2(a_1+a_2)}} + \frac{h/\bar{a}}{1+\dfrac{h}{\bar{a}}+\dfrac{h^2}{4a_1a_2}} + \frac{2h}{\bar{a}}\ln\left\{\frac{h}{\bar{a}}\left(\frac{1+\dfrac{h}{2(a_1+a_2)}}{1+\dfrac{h}{\bar{a}}+\dfrac{h^2}{4a_1a_2}}\right)\right\}\right]$$

where $\bar{a} = \dfrac{2a_1a_2}{a_1+a_2}$

Hamaker constants $A$ for typical metal oxide or organic particles interacting in water are on the order of $(1 - 10)\times10^{-20}$ J; metallic particles in water have Hamaker constants on the order of $30\times10^{-20}$ J. For equally sized particles of radius $a_1 = a_2 =$ 10 nm, the minimal layer thickness would only need to be about 0.1 nm to prevent the van der Waals energy from exceeding -10 *kT* for $A = 1\times10^{-20}$ J at 298K. For 100 nm radius, this would be approximately 1 nm. Almost any polymer would produce a layer at least as thick as these estimations, so the more important issues are whether or not the solvent quality for the polymer is good, whether or not the surface coverage is large enough to prevent bridging aggregation, and whether or not the strength of adsorption is large enough to prevent polymers from being squeezed out of the contact zone when particles collide. . These thicknesses increase to approximately 2 and 20 nm for 10 or 100 nm radii with $A = 30\times10^{-20}$ J. The desired layer thickness to ensure minimal vulnerability to van der Waals attraction would scale with the particle radius. Being able to produce a sufficiently thick layer can be an important issue for large metallic particles.

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