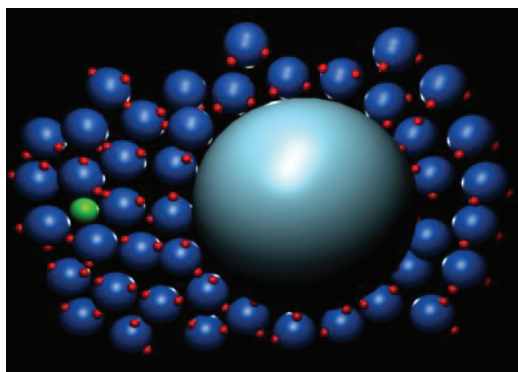


A Minimal Model of Nanoparticle Crystallization in Polar Solvents via Steric Effects

William Kung, Pedro Gonzalez-Mozuelos, Monica Olvera de la Cruz
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For nanoparticle systems, steric interactions among the ionic components originate from the structural organization of the polar solvent molecules surrounding these ions as molecular dipole moments. Such interactions may cooperatively enhance or counteract existing entropic depletion and electrostatic forces. In this work, we present a minimal analytical model illustrating that steric interactions can provide a *simple, generic mechanism* for *like-charge crystallization* in prototypical nanoparticle systems with counterions in polar solvents. Phenomenologically capturing these steric effects, we assume only the existence of a short-range pairwise Gaussian interaction for the nanoparticles characterized by steric-strength ratios labelled by w . Using an analytically obtained effective pairwise potential (EPP), we derive phase diagrams for nanoparticle systems and observe crystallization for a range of parameters. We further demonstrate that our minimal model is compatible with the phenomenon of *charge asymmetry*, whereby electrostatic effects are observed to act on positive and negative charge species asymmetrically beyond their sign difference.



TOP: Schematic illustration of our system: negatively-charged nanoparticle (ice blue), polar solvent molecules (water) with oxygen (blue) and hydrogen (red) atoms, as well as positively-charged counterion (green). **RIGHT:** Phase Diagram for a nano-particle system with nanoparticle charges $Z_M = \pm 10$ and counterion charges $Z_c = -/+1$, for the following short-range steric-strength ratios: [w_{\pm} denotes steric strength for positive (negative) charge species and $w = w_{++} = w_{--}$] (A) $w_{+}/w_{-} = 10$, (B) $w_{+}/w_{-} = 15$, and (C) $w_{+}/w_{-} = 20$. The nanoparticle-to-counterion size ratio R/a is plotted against the reduced particle number density n .

