Linear Shear Elasticity and Osmotic Pressure of Concentrated Disordered Ionic Emulsions

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Abstract

We present a free energy model that describes two key thermodynamic properties, the osmotic pressure Π and the linear elastic shear modulus G'_p of a disordered system of concentrated deformable emulsion droplets stabilized by ionic surfactants over a range of volume fractions below, near, and above the random jamming point ϕ_c. The model unifies existing approaches[1,2,3] by considering entropic, electrostatic, and interfacial (EEI) contributions to a free energy, which depends on the droplet volume fraction ϕ and the applied shear strain γ. This EEI free energy is minimized with respect to an average deformation parameter that links these three contributions. This minimization reveals that the entropic term is dominant for ϕ well below ϕ_c, the electrostatic term is dominant for ϕ below ϕ_c, and the interfacial term is dominant for ϕ above ϕ_c. The predictions of the model describe measurements of $G'_p(\phi)$[4,5] for colloidal emulsions ranging from nanoscale to microscale, and also measurements of $\Pi(\phi)$ for microscale emulsions. Although emulsions stabilized by ionic surfactants that have been concentrated into disordered structures are technically out-of-equilibrium systems, this near-equilibrium minimization approach nevertheless reasonably predicts the constitutive properties of these systems.

References

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