Modeling Thermoresponsive Microgels: Linking Internal Architecture to Collective Behavior

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We introduce a coarse-grained theoretical and computational framework to describe the compression and assembly of thermoresponsive core-shell microgels in good solvent conditions [1]. The approach explicitly accounts for internal morphological heterogeneity by decomposing the particle free energy into core and shell contributions, each governed by a Flory-Rehner-type description with distinct elastic and swelling characteristics. Mechanical equilibrium between these regions is imposed to obtain a self-consistent description of particle size and internal restructuring. Interparticle interactions are represented through a size-dependent multi-Hertzian pair potential that captures the differential compressibility and mechanical response of the core and corona. Model parameters are calibrated against dynamic light scattering measurements of PNIPAM microgels across temperatures spanning the lower critical solution temperature, enabling a quantitative description of thermally induced swelling and collapse, including variations in core size. Monte Carlo simulations based on these effective interactions are used to investigate concentrated suspensions under compression, focusing on structural and thermodynamic properties such as size distribution, effective packing fraction, spatial correlations, and phase behavior. Our results demonstrate that particle softness, responsiveness, and internal heterogeneity collectively govern the organization and state behavior of dense microgel systems, providing a direct link between single-particle properties and emergent collective phenomena.

Keywords:
Microgels, polymers, colloidal suspensions, Flory-Rehner theory, Monte Carlo simulation

References:

[1] A. Moncho et al., Macromolecules *58* , 19, 10659, **2025**

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