

28j Investigation of the Role of Geometry and Fluid Structure in the Description of Depletion Forces Via Scaled Particle Theory-Based Integral Equations for Hard Sphere Fluids

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The ability of colloidal particles to self-organize suggests that colloids could be used as precursors for advanced materials via the generation of complex microstructures. The precise control of colloidal dispersions, however, rests upon our knowledge of the forces that arise between colloids and between colloids and various surfaces. An important class of interparticle forces known as depletion forces is induced by the presence of other colloids and arises solely as a result of entropic considerations. Passive structures etched into the walls of containers can create entropic potential fields of sufficient range and magnitude so that the motion and position of large colloids may be controlled.

Depletion forces are typically modeled with excluded volume arguments that arise from hard sphere-like behavior of colloidal particles. Colloids that behave similar to hard spheres are surrounded by an exclusion volume, or equivalent cavity, which cannot contain solvent particles. Based on the method of Asakura and Oosawa (J. Chem. Phys., 1954, 22, 1255), when the exclusion volume of a colloid intersects a surface or the exclusion volume of another colloid, the colloid will be attracted toward the surface or other colloid. These arguments, while providing a qualitative basis for the appearance of depletion forces, usually fail to quantitatively describe depletion forces and provide no mechanism for the appearance of repulsive entropic effects.

To gain further insight into the origin and nature of depletion forces, we examine the fluid structure of hard sphere colloids near surfaces via a newly derived integral equation based on the scaled particle theory of confined hard sphere fluids (Siderius and Corti, Phys. Rev. E, 2004, 71 036141 and 036142). Exact solution of the integral equation, along with simulation results, predicts the appearance of a local density enhancement near the colloid-surface interface. These results suggest that the excluded volume argument is not totally adequate for describing depletion forces and instead the geometry of and the fluid structure near the colloid-surface interface must be considered. Overall, the integral equation lends new insights into the nature of depletion forces and highlights the importance of fluid structure in the understanding of depletion interactions.