



Depletion forces in bulk and in confined domains: From Asakura–Oosawa to recent statistical physics advances



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ABSTRACT

This article summarizes recent theoretical research concerned understanding depletion forces. These forces appear when small colloidal particles, polymers or other entities, usually called depletants, are driven out from the gap or film between two macroparticles. Applying the modern tools of statistical mechanics and in agreement with experimental measurements it is shown that depletion attraction is only a part of more general medium-mediated interaction forces in colloidal dispersions known as structural forces. Finally, it highlights the important role that long-range structural forces could play in various applications relying on effecting particle dispersion, foam and emulsion stability, as well as wetting behavior of colloidal fluids on solid.

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1. Introduction

Numerous colloid-based products, such as emulsions, foams, gels, polymer latexes, paints, inks, and coatings, widely known as colloidal dispersions, have one important common feature – their constituents are characterized by extremely different size dimensions (see Fig. 1 for visualization). These could be air bubbles or liquid droplets that are extremely large when compared to the nanosized latex or micellar colloidal particles as well as nanosized colloids themselves are large enough when compared to the species of molecular solvents in which they are dispersed. In all these cases, the surfaces of the larger particles serve as a spatial confinement for the suspending medium of smaller species, altering properties of this medium that culminates in medium-induced (effective) interaction forces between larger particles. It is evident, that understanding the forces acting between macroparticles (or surfaces) becomes an important problem for basic as well as for applied science, since interaction forces govern the physical properties of the entire system, affecting both the quality of colloidal products as well as the quality of processes that involve colloidal particles, such as coagulation, flocculation, sedimentation and lubrication.

In the case of an athermal suspending medium, such interaction forces are essentially entropic, as was demonstrated first by Asakura

and Oosawa [1], who suggested the mechanism of effective interaction between two large solutes immersed in a fluid of non-adsorbing polymers: when the separation distance between solute macrosurfaces is less than the size of suspending fluid species the latter are expelled (depleted) from the gap between the macrosurfaces leading to an anisotropy of the local pressure. The so-called Asakura–Oosawa (AO) depletion interaction is always attractive, if the separations between the two macrosurfaces are less than the diameter of depletant species, and become zero otherwise.

A suspending medium in the AO approach is modeled by a mutually noninteracting (penetrable, or ideal) polymer particle that significantly reduces the effects of the depletant fluid structure. This seems to be justified for colloid–polymer mixtures where the AO depletion mechanism has been verified by analyzing the phase separation behavior and flocculation of colloids with added non-adsorbing polymers as well as by direct measurement in a variety of colloid–polymer mixtures [2,3]. However, in general, a more appropriate model for the depletant medium is a fluid of hard-core or hard-sphere particles [4–6]. The effective forces between the macrospheres dispersed in a hard-sphere solvent have been studied by means of modern tools of statistical physics such as integral equation theory [7–9], density functional theory [10–14], and computer simulations [9,15–19]. The results of these studies have shown that taking into account the hard-core repulsion between particles of suspending medium emphasizes the importance of interparticle correlations, i.e. depletant structure, and brings new features to the depletant-mediated interaction. The most intriguing of

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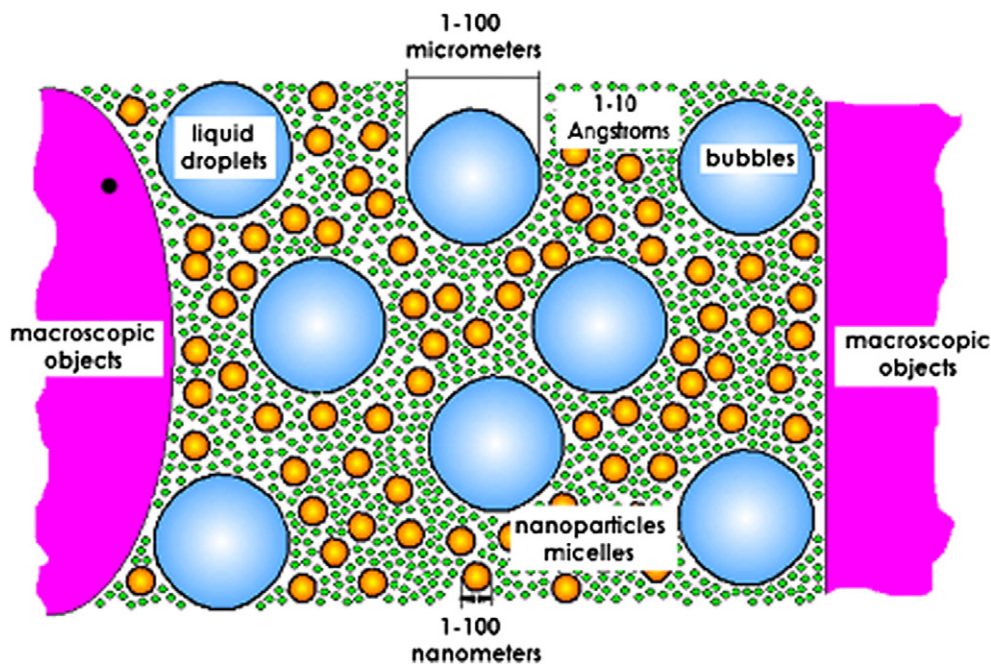


Fig. 1. Different scales of colloidal dispersions: a molecular scale (a few angstroms) of the primary suspending medium due to water, some organic solvents and electrolyte ions; a sub-microscopic scale (1 nm to 100 nm) that encompasses nanoparticles or surfactant aggregates called micelles; a microscopic scale (1 μm to 100 μm) that characterizes the size of liquid droplets or bubbles in emulsions or foam systems; and a macroscopic scale.

these is a repulsive energy barrier, located in front of the attractive depletion well, and followed by the energy oscillations extended up to several depletant particle diameters.

Experimentally oscillatory effective interactions were found to arise when two macrosurfaces are immersed in supramolecular solutions such as colloidal and biocolloidal suspensions [20–26] and micellar solutions [27,28] as well as have been observed also in pure molecular (aqueous and organic) solvents [29]. The latter is an important observation that indicates that the interaction induced between a pair of macrosurfaces resolves the discrete structure of suspending medium at length scales as small as that of the molecular solvent. Moreover, surprisingly it has been found that a hard-sphere fluid that is a rather crude model of a molecular medium, reproduces remarkably well the main features (oscillations and exponential damping) of experimentally measured forces [29].

In what follows, first, we outline the Ornstein–Zernike integral equation approach within statistical mechanics and show that, indeed, the depletion interaction forces are only a part of more general medium-mediated interaction forces in colloidal dispersions known as the structural forces [30]. Secondly, we will present a simple calculation of structural and depletion forces in bulk colloidal suspensions as well as in colloidal films. Finally, this highlights the important role that the long-ranged structural forces could play in various applications relying on effecting particle dispersion, foam and emulsion stability, as well as wetting behavior of colloidal fluids on solid.

2. Integral equation approach to solvent-mediated interactions in colloidal dispersions

The microscopic properties of a discrete depletant medium near macrosurfaces, that are the route to solvent-mediated interactions in colloidal dispersions, can be obtained within statistical mechanics either by computer simulation (also called a computer experiment) or by means of semi-analytical approaches such as the density functional theory (DFT) or integral equation theory.

2.1. Ornstein–Zernike equation

An important ingredient for all theoretical approaches is the Ornstein–Zernike (OZ) equation [31]

$$h_{ij}(R_{12}) = c_{ij}(R_{12}) + \sum_{k=1}^3 \rho_k \int h_{ik}(R_{13}) c_{kj}(R_{32}) dr_3, \quad (1)$$

where subscripts i, j , and k run over all the depletant medium components 1 and 2, as well as the macroparticles G (component 3 is equivalent to G that is the abbreviation of giant), ρ_i is the number density of the particles of component i while r_i is the position of any particle 1 and $R_{12} = |r_1 - r_2|$ is the distance between particle 1 and particle 2.

The functions $h_{ij}(R) = g_{ij}(R) - 1$ are called the total correlation functions for a pair of particles of species i and j that are separated by the distance R . The functions $g_{ij}(R)$ are the pair or radial distribution functions. The functions $c_{ij}(R)$ are the direct correlation functions that specify the direct correlations between two particles. The convolution integral in right-hand-side of Eq. (1) is the indirect part of the total correlation function.

Many model systems consist of particles with a hard core

$$u_{ij}(R) = \begin{cases} \infty, & R < d_{ij} \\ 0, & R \geq d_{ij}, \end{cases} \quad (2)$$

where $d_{ij} = (d_i + d_j)/2$ and d_1, d_2 are the diameters of suspending fluid species while $d_3 \equiv d_G = D$ is the diameter of the large solute. The infinity for $R < d_{ij}$ reflects the mutual impenetrability of the pair of interacting particles due to the presence of a hard core. Of course, real particles do not have a hard core. However, the repulsive part of the pair potential is steep so that approximating this repulsive part by a hard core is not unreasonable. A closure that is extremely useful for hard-core systems is the mean spherical approximation (MSA) [32],

$$h_{ij}(R) = -1, \quad R < d_{ij}, \quad (3)$$

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