



# Depletion forces between particles immersed in nanofluids



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## ABSTRACT

Understanding depletion forces between colloidal particles mediated by nanofluids, i.e. liquids containing hard or soft nanostructures, is immensely important in a number of industrial processes. We anticipate added complexities due to enhanced and multifactorial inter-depletant interactions associated with their size, shape, surface chemistry, and concentration. Here we briefly review recent efforts in direct measurement of depletion forces mediated by nanofluids, as well as a number of related studies on the phase transition in binary colloid mixtures with large size and shape asymmetry, a process in which depletion forces play an important role. We will also discuss the often under-appreciated importance of depletion forces mediated by proteo-nanofluids (liquids containing proteins) in facilitating cellular organisation. Some challenges and outstanding questions will emerge from the above discussions, as briefly summarised.

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## 1. Introduction

The depletion force is as subtle as it is complex [1]. Its magnitude and range, tuneable by the concentration and effective size of the depletant, compete and convolute with other colloidal interactions in operation (e.g. DLVO, hydration, hydrophobic, and steric forces) [2–4], and thus it is sometimes challenging to ascertain and quantify its contributions. Whilst its importance in industrial colloidal processes has long been recognised, its role in biological systems—quite prevalent indeed—to facilitate cellular organisation remains under-appreciated [5]. It is in this context that intensive research on depletion interactions has been undertaken in the past decades, which often focuses on polymers as depletants [6–8], due to their wide availability and industrial relevance, and refined theoretical descriptions accessible to model their behaviour and interactions [9].

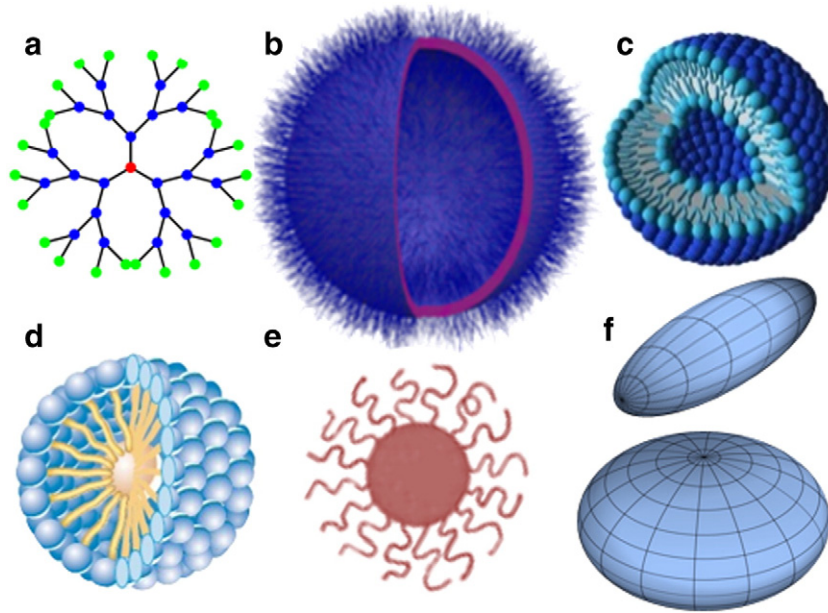
An increasing number of studies has recently been dedicated to depletion interactions between colloidal particles in *nanofluids*, i.e. here the size asymmetry between the interacting particles (often some  $\mu\text{m}$  in size) and the nano-sized depletants is significant. Nanofluids are liquid suspensions containing particles of different materials and shapes with at least one principle dimension in the range of a few nm to some hundreds of nm. The definition of nanofluids may be expanded so that the dispersed nanostructures may also broadly include soft constructs, e.g. micelles, dendrimers, polymersomes, liposomes, and polymer-decorated nanoparticles (Fig. 1) [10]. An important consideration here

is the shape anisotropy of the suspended nanostructures, a feature that can be fruitfully exploited but also presents challenges due to added complexities. It is well established that nanostructures with large aspect ratios tend to be effective depletants [1,11]; in addition, many biological nanostructures participating in depletion interactions (e.g. fibrinogens, *fd* virus [12] and tobacco mosaic virus (TMV)) possess large aspect ratios. This is represented schematically as ellipsoids in Fig. 1f, which can be generalised by varying the aspect ratio  $A = \alpha/\beta$  (Fig. 2(b)) [13,14] to describe needles and disks [11].

## 2. Phase separations in binary colloidal mixtures: implications to depletion attraction mediated by nanofluids

Cockbain in 1952 [15] observed “creaming” of ionic surfactant-stabilised oil-in-water emulsions at surfactant concentrations above their CMC. Fairhurst et al. revisited this instability in 1983 [16], reporting similar creaming effects when the non-ionic surfactant emulsifiers exceeded their CMC. The mechanism for this creaming effect only emerged in a study of SDS-stabilised silicon oil-in-water emulsions by Bibette et al. in 1990 [17], which attributed the fluid–solid phase transition to attractions due to depletion of SDS micelles between much larger,  $\mu\text{m}$ -sized emulsion droplets. Piazza and Pietro showed that the “solid” phase had a gel-like fractal structure [18]. Phase separations were later observed in binary mixtures of emulsion droplets of size  $\sim 260$ – $2,600$  nm, in which osmotic depletion was imparted by emulsion droplets themselves [19]. Similarly, a depletion flocculation mechanism was also suggested for the destabilisation of polystyrene latex particles of size  $\sim 300$ – $800$  nm in concentrated non-ionic Triton X-100 micellar solutions [20]. These are among the first experimental observations of depletion attractions between  $\sim \mu\text{m}$ -sized colloidal

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**Fig. 1.** The nanostructures in *nanofluids*, in addition to metal and inorganic nanoparticles, may also include a) polymeric dendrimers (a few nm in size); b) polymersomes (~50 nm to hundreds of nm) self-assembled from block-copolymers; c) liposomes (~100 nm); d) surfactant micelles (a few nm); e) polymer brush decorated particles; and f) prolate and oblate spheroids, which represent a wide range of particles with shape anisotropy, notably, elongated micelles, serum proteins and viruses.

emulsion droplets or latex particles mediated by nm-sized micelles. This talent of micelles has undergone somewhat of a renaissance recently in facilitating directed self-assembly to generate new nanomaterials [21,22] or assisting purification of nanoparticles [23].

Colloid scientists studying phase separations in binary mixtures of colloids with large size asymmetry (typically large and small spheres, of radius  $R$  and diameter  $\sigma$  respectively; cf. Fig. 1) and shape asymmetry (sphere–rod (diameter  $D \times$  length  $L$ ), rod–plate (diameter  $D_p \times$  thickness  $t$ ), or sphere–plate mixtures) are well versed with depletion in interpreting the observed phase separations. Notably, at least one of the colloidal component has at least one such dimension that it qualifies as a nanofluid. Sanyal et al. [24] and van Duijneveldt et al. [25] were among the first to observe the fluid–solid phase transition in binary *nearly-hard-sphere* colloids with the size ratio  $2R/\sigma > 5$ , attributing it to the depletion of smaller spheres between larger spheres, an observation later extended to using polymer-coated spheres or pNIPAM nanogels as *soft* depletants [26,27]. A more recent theoretical study considering binary mixtures of soft repulsive spheres however predicted stronger depletion, as compared to hard spheres, and also a metastable fluid–fluid phase transition, which is yet to be verified experimentally [28]. Kaplan et al. [29] and Dinsmore et al. [30] reported that the fluid–solid transition for the larger spheres was promoted at a hard flat wall, due to the enhanced excluded volume effects at the wall, pointing to the importance of geometry consideration. The effect of the depletant geometry is further demonstrated by plate- and rod-induced crystallisation in rod–sphere ( $R, L \gg D$ ) [31,32], rod–plate ( $L \gg D; D_p \gg t$ ) [33,34], and sphere–plate ( $D, R \gg t$ ) [35,36] mixtures.

Subtle and often weak between a particle pair, depletion effects are however amplified in such colloidal systems, which is assisted by careful experimental designs to minimise other forces that could otherwise mask the depletion force. These for instance include refractive index matching particles with the solvent to minimise the vdW force, or suppressing electric double layer force or using steric stabiliser to achieve an effective “hard sphere” depletant, simplifying the interpretation. It is no coincidence that these colloidal phase transition and crystallisation studies have yielded fruitful insights on *depletion attraction* in nanofluids, particularly the effect of depletant geometry on the strength of the depletion interaction.

### 3. Depletion attraction in dilute nanofluids: effect of depletant geometry

As outlined by Asakura and Oosawa [1,6,7,11], the origin of the depletion attraction is conceptually straightforward. It derives from the osmotic pressure imbalance due to the excluded volume  $V_m$  between two particles (of radius  $R$ ; Fig. 2(a)) in proximity expelling the nanofluids containing non-interacting small hard spheres (of diameter  $\sigma \ll R$ ) at a dilute number density  $\rho$  and volume fraction  $\phi = (1/2)\pi\sigma^3\rho$ . The depletion interaction energy (per unit area) at inter-surface separation  $h < \sigma$  can be expressed as

$$\frac{W_{\text{Sphere}}(h)}{k_B T} = -\rho V_m = -\frac{\pi}{2}\rho R\sigma^2 \left(1 - \frac{h}{\sigma}\right)^2 \quad (1)$$

At contact ( $h = 0$ ), the depletion adhesion energy is

$$\frac{W_{\text{Sphere}}(h = 0)}{k_B T} = -\frac{\pi}{2}\rho R\sigma^2. \quad (2)$$

Both the excluded volume  $V_m$  and the number density of  $\rho$  (or volume fraction  $\phi$ ) depend on the depletant geometry, a parameter readily accessible with nanofluids. Here we will follow an elegant treatment by Piech and Walz from a force balance approach [11] to illustrate the effect of ellipsoidal depletant shape on the adhesion depletion energy (i.e.  $h = 0$ ) between two particles of radius  $R (\gg \sigma, \alpha)$  immersed in a suspension of spheres or ellipsoids. As shown in Fig. 2(b), the aspect ratio  $A = \alpha/\beta$  can be varied to represent different shapes, e.g. needles ( $A \rightarrow \infty$  for the prolate spheroid) and disks/plates ( $A \rightarrow \infty$  for the oblate spheroid). Table 1 lists their depletion adhesion energy at  $h = 0$  as normalised with respect to that for spherical depletants (Eq. (2)), under two different conditions: constant number density  $\rho$  or constant volume fraction  $\phi$ , related to each other as

$$\phi_{\text{Prolate}} = \frac{4}{3}\pi\alpha\beta^2\rho \quad \phi_{\text{Oblate}} = \frac{4}{3}\pi\alpha^2\beta\rho. \quad (3)$$

Given  $A \geq 1$ , under constant  $\rho$ , depletion mediated by spheroids is always smaller than that by spheres. Physically, this arises from more

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