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Editorial overview

Depletion forces in single phase and multi-phase complex fluids

This special issue is devoted to an ambivalent paradigm: the general concept of depletion forces, first investigated as a unified general view of the indirect effect of a non-absorbing solute, on the interaction potential between two colloids, and proposed by Asakura and Oosawa (AO) [1], and discussed in a Faraday-type author meeting discussion [2].

The simplicity of the AO-result, its generality and quantitative link with solvent activity and osmotic pressure explain the success of the concept, and its usage in quantitative studies on colloidal stability of complex fluids. It was soon realised that steric stabilisation could be treated as negative depletion [3]. If the colloid becomes larger than the diameter of the non-adsorbing solutes, very simple analytic predictions, such as the sticky sphere model initially developed by Baxter [4] in the seventies and the subsequent attempts to predict phase diagram, were very successful. Due to the absence of generic way to treat complex shapes [5], the extension to nonspherical objects and solutes went on difficulties.

Strange enough, while the generality of hydration forces as discovered by Parsegian and coworkers was easily recognized, see e.g. Ref. [6], the fact that the concept of depletion forces is of the same level of generality was very recently recognized to be one of the four cardinal forces driving colloidal fluids in the "nanoscience" [2,7], as shown in Fig. 1. Most textbooks still consider the electrostatic/van der Waals competition as the source of stability and phase transition of most colloidal systems.

The present issue deals with recent progresses in predictive modelling of depletion forces. 60 years after the pioneering paper by Asakura and Oosawa [1], the new developments in this field are in the following research directions:

(i) Generalizations from mere hard core interactions between the smaller and larger particles [1], to other kinds of *repulsive and attractive interparticle forces* have been presented [8]. The invited review by Harries and Sapir [9] disentangles the deep link between enthalpy/entropy compensation and depletion, along with the approach well detailed by Dill and Bromberg in their classical and extremely pedagogic textbook [10]. The effects of soft electrostatic particle/particle and particle/wall interactions on the depletion force have been investigated both experimentally and theoretically [11]. Image-charge effects and salting-out phenomena have been studied by Curtis and Lue [12]. As demonstrated by Moncho-Jordá and Odriozola [13], the effective wall–wall interactions are notably influenced by the nature of the particle–particle and particle–wall interactions.

(ii) Extension of the theory to *higher concentrations* of the smaller particles (the depletant), at which the interaction force oscillates with the surface-to-surface distance, so that the depletion force is identified with the first minimum of the oscillatory structural force at small distances [11,14]. A general analytical expression for calculating the structural and depletion forces at various concentrations of hard spheres has been derived by Trokhymchuk and Henderson [14]. The thin liquid film balance invented by Scheludko in Sofia [15] is a very sensitive technique for measuring osmotic pressure of thin films of colloids. This approach allows a very detailed analysis of surface layering of nonionic and charged micelles. Quantitative check of prediction of the effect of depletion force on the disjoining pressure can be obtained, and last but not least, counting of the micelles present per unit area for different thicknesses of a thin liquid film gives a clever and independent measurement of aggregation numbers, once the cmc is known, as shown by K. Danov and coauthors [11].

(iii) New aspects of the depletion surface force related to mixed dispersions of *two and multiple depletants* are reviewed by Ji and Walz [16]. It is demonstrated that if two species of particles form dimers, the depletion attraction can be stronger than the simple superposition of the two separate depletion effects. Next, experimental examples for such synergistic depletion effects are given for binary mixtures of surfactant + polymer, and nanoparticles + polymer. Finally, a ternary mixture of large, middle-size and small particles are considered, and the effect of "condensation" of the middle-size particles on the surfaces of the large particles driven by the depletion effect of the small particles (the halo effect) is considered [16].

(iv) The effect of the *geometrical shape of depletant particles* (spheres, prolate and oblate ellipsoids, disks, needles) has been investigated by Piech and Walz [17] and reviewed by Briscoe [18]. Thus, for needles and disks the depletion energy is much higher than that for spheres, i.e. they are effective depletants. For the same aspect ratio, the depletion energy mediated by oblate spheroids is greater than that by prolate spheroids under constant number density due to their comparatively larger volume. The effect of the *internal architecture* (degrees of freedom) of the particles for the case of polymers and similar kind of soft colloids has been also investigated [13,19].

(v) Another research direction is the role of *depletion forces in biological systems*. Indeed, 20–30% of the cellular volume is occupied by soluble proteins and macromolecules. Depletion forces due to the proteins in such a crowded environment are conjectured to contribute to vesicular traffic/clustering, membrane fusion, actin bundling and amyloid fibril formation. Given the noncovalent nature of depletion forces, they are highly adaptable to dynamic cellular processes [18]. The DNA molecules are compacted in the central part of the cell owing to the depletion effect of proteins and ribosomes. The DNAs are so tightly confined that they have been observed to explode out of the cell and could expand up to 100 times in volume in its liberated

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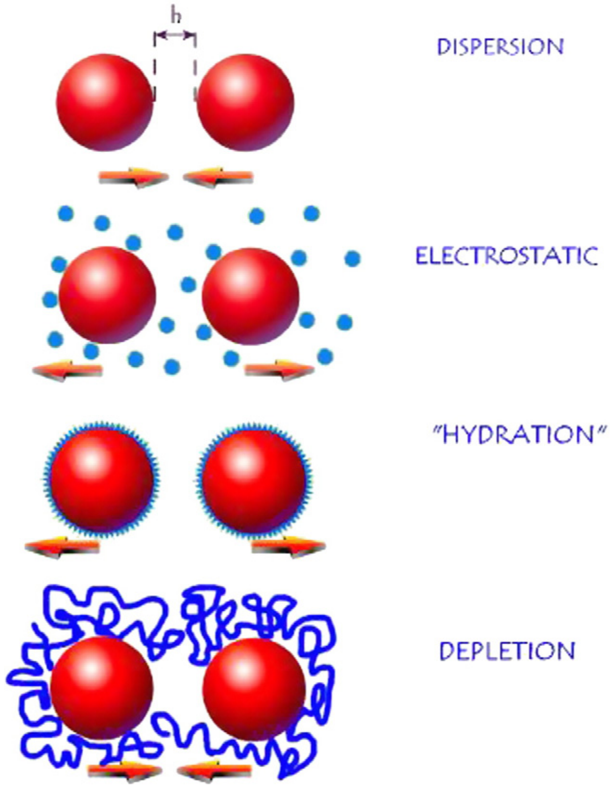

Fig. 1. The four cardinal forces governing complex fluids. At molecular scale, dispersion is favoured by entropy. Entropic effects can also be considered as a molecular driving force [2].

nucleoid state [20]. The compaction of double-stranded DNA by negatively charged proteins and colloids, and the single-molecule DNA conformational dynamics has been investigated by Yoshikawa and coworkers [21].

(vi) The role of *depletion forces in dynamic processes* represents an additional research area. The effect of polymer-induced depletion attraction on the diffusion and sedimentation of colloidal particles, and on the suspension rheology is reviewed by Remco Tuinier et al. [22].

(vii) Finally, the depletion force drives *the formation water-in-oil agglomerates* in non-aqueous media — from weak aggregates to reverse micelles, as supposed by H.-F. Eicke [23] in the seventies. However, the importance of the third component as a structuring nucleating species could not be demonstrated at that time. Progress in small angle scattering of weakly scattering systems, as well as the molecular dynamics could demonstrate this in the case of weak aggregates that are the intermediary form between organometallic complexes and more classical "reverse micelles" containing hundred molecules or more per micelle. These weak reverse aggregates of 10–20 molecules seem to occur frequently [24]. In the case of ionic aggregates containing 10–30 ions, such as the DOLLOP discovered by Gebauer and Cölfen in 2008 [25], or even the surfactant-free microemulsions [26], and for which the structural unambiguous proof of existence has been available only recently [27]. The recognition of weak aggregation, with a diffuse interfacial film that can be understood as an interphase [28].

Thus hydration force combined to depletion effects and steric stabilisation, opposed to the entropy favouring always dispersion as molecular fluids, seems to be a consequence of the interplay between van der Waals and electrostatic forces as in DLVO, which is limited to the two top interaction mechanisms in Fig. 1. The same weak non-covalent interactions have to be considered together with curvature and packing in molecular tectonics [29,30]. The influence of "weaker" forces triggers the formation of weaker thermodynamically stable structured aggregates, which will be the topic of next special issue of current opinion, to appear in 2016.

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