Hard and soft colloids at fluid interfaces: Adsorption, interactions, assembly & rheology

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ABSTRACT

Soft microgel particles inherently possess qualities of both polymers as well as particles. We review the similarities and differences between soft microgel particles and stiff colloids at fluid–fluid interfaces. We compare two fundamental aspects of particle-laden interfaces namely the adsorption kinetics and the interactions between adsorbed particles. Although it is well established that the transport of both hard particles and microgels to the interface is driven by diffusion, the analysis of the adsorption kinetics needs reconsideration and a proper equation of state relating the surface pressure to the adsorbed mass should be used. We review the theoretical and experimental investigations into the interactions of particles at the interface. The rheology of the interfacial layers is intimately related to the interactions, and the differences between hard particles and microgels become pronounced. The assembly of particles into the layer is another distinguishing factor that separates hard particles from soft microgel particles. Microgels deform substantially upon adsorption and the stability of a microgel-stabilized emulsion depends on the conformational changes triggered by external stimuli.

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Contents

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1. Introduction

While coarse emulsions have widespread applications ranging from food products, pharmaceuticals and cosmetics to oil recovery [1,2], they also share the property of thermodynamic metastability. In most cases the tendency of the droplets to assemble into a large volume of fluid is detrimental to the application (e.g. in many food products), while in other cases this proclivity is exploited to break the emulsion (e.g. in oil recovery). Clearly in both scenarios the thermodynamic properties of the emulsion are of utmost importance, and a thorough understanding of how the system is (thermodynamically or kinetically) stabilized is needed. Even though emulsions are known for a very long time, their stability is still an active area of research, in which new formulations and new theoretical descriptions are being explored [3–7].

Emulsion instability arises from the high energy associated to a liquid/liquid interface. Coalescence (film rupture) and Ostwald Ripening (due to differences in Laplace pressure of the drops) are the most important processes involved in destabilization. A classical way to eliminate (or at least counteract) these processes is to add amphiphilic molecules, i.e. surfactants. Alternatively, also colloidal particles can be used. Such particle-stabilized emulsions are known as (Ramsden)-Pickering emulsions [8–10]. Conventional Pickering stabilizers include rigid micro- or nano-sized particles of highly cross-linked polymers like PolyMethylMethacrylate (PMMA), Poly-styrene (PS) or amorphous solids like silica [11,12]. Since recently, also softer (i.e. deformable) particles like polymers or proteins have been used effectively for stabilizing emulsions and foams [13–15].

The efficiency of colloidal particles in stabilizing emulsions originates from the thermodynamics of their adsorption. The energy required to desorb a spherical particle from a fluid interface is given by:

$$E = \pi R^2 \gamma (1 \pm \cos \theta)^2 \qquad (1)$$

where R is the radius of the particle, γ is the interfacial tension and θ is the contact angle at the interface. The sign inside the brackets is positive or negative depending on whether the particle is being desorbed into air/oil phase or water phase. Already for particles with a size of a few tens of nanometers, this energy takes values of the order of 10^3 k_BT for contact angles that are not close to 0° or 180° [16]. For bigger colloids this energy becomes even larger and hence the adsorption can be considered as irreversible. This situation is in strong contrast to that of amphiphilic molecules which, due to their small desorption energies of the order of 10^0–10^1 k_BT, can desorb on a relatively short timescale, and hence cannot always completely preclude instability events.

While adsorption at a fluid interface is thus always thermodynamically favoured for particles, the process can be significantly slowed down in practice, which points at the possible presence of an adsorption barrier [17]. Sometimes this energy barrier is so high that Pickering emulsions can only be made by vigorous mechanical shaking, or a spreading solvent has to be used to deposit particles at an interface [18–20].

To understand the stability of a Pickering emulsion, one clearly has to consider much more than the adsorption alone. Eventually the reason why particle-coated droplets can maintain their integrity is that the particle layers on the encountering droplets repel each other strongly enough [10]. This first of all requires the particles to be present at sufficiently high (local) surface density, and secondly it requires a mechanism for the interparticle repulsion.

This aspect of particle interactions is where the complexity of Pickering emulsions becomes manifest. The interaction of an adsorbed particle with another particle in the same layer is fundamentally different from that between two particles that are adsorbed on different droplets (and thus interact through the continuous phase), while both contribute to the stability of the emulsion droplets. In the simplest case, the particles would be rigid spheres interacting only via their excluded volume; stability would then require a sufficiently high packing density (to be

achieved before the droplets encounter each other). In practice, electrostatic forces due to surface charges often play a role as well, and in a complex way, since the counterion distributions are different in the two phases [21–23] and also the volume distribution of the adsorbed particle over the two phases must be considered as a degree of freedom. Curvature of the droplet adds another dimension to the problem [24,25]. It is therefore not surprising that a variety of particle layer structures has been observed, and that different particle interactions were proposed to explain the different cases [21,26,27].

In the last decade, also a new class of particles, namely microgels, has generated interest as potential Pickering emulsion stabilizers. Microgel particles are made from a chemically cross-linked polymer that can be swollen by a solvent. The degree of swelling depends on the solvent quality and cross-link density [28,29]. Microgel particles made from thermo-sensitive polymers such as poly N-isopropyl acrylamide (PNIPAM) undergo reversible swelling/shrinking transitions at temperatures around the body temperature, and therefore are considered as promising particles for thermo-stimulated control of drug delivery [30,31]. The particle chemistry can also be varied, e.g., by incorporating charged co-monomers like acrylic or methacrylic acid to make them pH-responsive [32]. Also their hybrid physical character makes them interesting: the fact that they are particles makes them adsorb very strongly to the interface. On the other hand, their polymeric character strongly facilitates their attachment from solutions onto fluid interfaces. This combination of properties makes microgel particles ideal candidates for preparing emulsions with tunable stability [33]. Schmidt et al. [34] have coined the term "Mickering emulsions" for emulsions stabilized by microgel particles to highlight the fact that although these are conceptually similar to conventional Pickering emulsions stabilized by hard particles, the underlying mechanisms responsible for stabilization of these emulsions are drastically different.

Owing to these attractive properties, in particular PNIPAM (based) particles at fluid interfaces were intensively studied in the past few years. Several insightful studies were performed [35–39] and the suitability of PNIPAM as an emulsifier was demonstrated [34,37]. However, and remarkably, the kinetics of adsorption and thermodynamics of the interactions between microgel particles adsorbed in the same layer were addressed only in a few studies up till now [35].

Since excellent books and review papers have been written on Pickering emulsions (e.g. [16] and references therein) and on (PNIPAM) microgels [28–34], we will refer to these sources for further details. The specific focus of this review will be the state-of-the-art in understanding the behaviour of PNIPAM microgels at fluid interfaces, with a special emphasis on the kinetics of adsorption and the thermodynamic interactions between particles in the same layer. Comparisons with the behaviour of hard (spherical) particles at interfaces will serve as a reference case to highlight the similarities and differences with soft microgels.

One method that is particularly well suited to study both the interfacial adsorption kinetics and the subsequent interaction between colloidal particles is interfacial rheology. Also for this topic an excellent review book is available [40]. Therefore in this article we will shortly explain the concepts, and then more elaborately discuss the most recent developments in this field.

2. Adsorption dynamics

Although several experimental studies into particles adsorbing at fluid–fluid interfaces have been performed, most of them with stiff colloids [41–45] and a few with soft microgel particles [35,46], the processes controlling the kinetics of adsorption are generally complex and at present not clearly understood.

For the adsorption of colloidal particles, electrostatic interactions between the interface and the particle must play a role. This is most strongly evidenced by experiments in which no mechanical energy is supplied in order to assist the adsorption. It is experimentally established that air–water or oil–water interface is negatively charged,