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Review

Colloids at Fluid Interfaces

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Abstract: Over the last two decades, understanding of the attachment of colloids to fluid interfaces has attracted the interest of researchers from different fields. This is explained by considering the ubiquity of colloidal and interfacial systems in nature and technology. However, to date, the control and tuning of the assembly of colloids at fluid interfaces remain a challenge. This review discusses some of the most fundamental aspects governing the organization of colloidal objects at fluid interfaces, paying special attention to spherical particles. This requires a description of different physicochemical aspects, from the driving force involved in the assembly to its thermodynamic description, and from the interactions involved in the assembly to the dynamics and rheological behavior of particle-laden interfaces.

Keywords: particles; interfaces; rheology; colloids; dynamics; surface tension; contact angle

1. Introduction

Many dietary products, such as mayonnaise or milk, are good examples of emulsions, which consist of dispersions of liquid droplets in a continuous phase formed by an immiscible liquid. The adsorption of surface-active molecules at the droplet-continuous phase interface is essential for the stabilization of these systems. Similarly, the stability of foams appearing in some beverages, such as beer, is crucial to preventing the fast evaporation of carbon dioxide from the beer in the glass. In general, liquid foams consist of a dispersion of air bubbles in a continuous aqueous phase [1–4]. Indeed, their stability is only possible as a result of the adsorption of surface-active molecules at the bubble-aqueous phase. Foams and emulsions are also present in pharmaceutical formulations, as well as in shampoos and bath creams, affecting the sensorial perception associated with the use of the products (softness, creaminess, etc.), as well as the feeling of cleanliness [5–8].

Considering the above examples, it is easily to conclude that the adsorption and assembly of surface-active molecules (e.g., surfactant, (bio)polymers, and micro- and nanoparticles) at fluid interfaces provide the basic building blocks for the creation of emulsions and foams [9], remarkably important in different areas with scientific and technological impacts [10–14]. In particular, the interaction of colloidal particles with interfaces plays a central role in many processes with an industrial interest, including metal recovery by flotation, tertiary oil recovery, interfacial biocatalysis, gas storage, and biomass conversion [14–17]. Furthermore, biomedical processes, such as the inhalation and transport of colloidal particles through the respiratory tract, involve the interactions of colloidal systems and fluid interfaces [18,19].

In addition, the symmetry breaking and the dimensional confinement appearing from the presence of an interface provides a versatile platform for designing and manufacturing nanomaterials (e.g., materials based in quasi-two-dimensional (quasi-2d) colloidal arrays, where the interfaces are templates or scaffolds for the assembly of colloidal systems). The combination of this geometrical restriction with

the prospect of tuning and controlling the assembly of colloidal objects has very recently opened a new avenue for building new functional materials with potential applications for chemical synthesis, separation of chemical compounds, and reconfigurable devices.

On the basis of the above discussion, the understanding of the most fundamental aspects involved in the fabrication and control of colloids assembled at fluid interfaces is of paramount importance to improving their use in the design of new technological systems [20–22]. Future developments of the colloidal confinement could enable fabrication of biomimetic and active materials, which could respond to an external perturbation, and even alter their environment. This requires an understanding of the physicochemical bases underlying the behavior of such complex interfaces, which requires a deeper understanding of the physicochemical bases governing the assembly of quasi-2D materials, as well as on the dynamic and equilibrium properties of the assembled systems [3,19,23–36].

In summary, this review presents a general perspective of the most fundamental aspects related to the attachment of colloids at the fluid interface, and the physicochemical properties of the assembled systems, paying special attention to the understanding of the behavior of spherical particles confined at fluid interfaces. In addition, some specific aspect related to the behavior of other colloidal systems at fluid interfaces are briefly discussed.

2. Driving the Assembly: Interfacial Tension and Contact Angle

2.1. Interfacial Tension

The driving force responsible for the adsorption of molecules at a fluid interface is associated with a decrease of the interfacial tension, and therefore the free energy associated with the formation of the interface [7,8,10–13]. Therefore, the adsorption of amphiphilic molecules (e.g., from surfactants to (bio)polymers) and colloidal particles (including the ones with two regions presenting a different chemical nature, the so-called Janus particles [37–39]) at fluid interfaces is driven by the minimization of the Gibbs free energy owing to a decrease of the contact area between the two fluids. This can be explained on the basis of a decrease of the interfacial tension, γ, which may be defined as (i) the force per unit of length acting tangentially at the interface along the contact line between the two phases, or (ii) the energy cost, G_γ, associated with the generation of one unit of contact area, A, between two immiscible fluids at constant values of pressure (p) and temperature (T), i.e., $\gamma = \left(\frac{\partial G_\gamma}{\partial A}\right)_{T,p}$.

It is worth mentioning that the adsorption of colloidal particles at fluid interfaces does not lead to a decrease of the interfacial tension between the two fluid phases, $\gamma_{f_1 f_2}$, at the microscopic level as occurs when traditional surfactants are involved. However, a change of this property at the macroscopic level is generally found. This decrease can be understood considering the appearance of a 2D lateral pressure (Π) within the interface due to the entrapment of particles. This lateral pressure is opposed to the tendency of the interface to contract and minimize its area. Therefore, it is possible to assume that the increase of the interfacial packing leads to a measurable decrease of the interfacial tension [40–49]. Thus, the different origins found for the surface tensions of conventional surfactants and particles at fluid interfaces have limited the development of accurate thermodynamics models describing the behavior of particle-laden interfaces.

The application of conventional state equations (for example, Langmuir, Frumkin, etc. adsorption isotherms) for a thermodynamics description of the interfaces coated by amphiphiles is a mature field of research [50,51]. However, the description of the behavior of colloidal particles trapped at fluid interfaces has been more elusive, mainly due to the differences existing between the sizes of the colloids and the solvent molecules. This makes it necessary to develop a new thermodynamics framework which enables a correct description of particle-laden interfaces. There have been several attempts to provide an accurate thermodynamics description of particle-laden interfaces. The first one was provided by Binks [4] combining the Volmer equation, which accounts for the absence of lateral interactions between particles at low packing density, with the van der Waals equation, which enables describing the lateral interactions between the particles occurring at high packing density. This model

was based on the following two main assumptions: (i) each particle behaves as a surfactant molecule and (ii) the area of each particle is finite and similar to its geometrical area. However, this description failed because it only provided a correct prediction for the surface tension at high interfacial densities when the role of the interparticle interactions was important. Experimental findings showed that even at long interparticle distances the interactions play a central role for controlling the interfacial properties which differs from the behavior found for surfactant monolayers. Thus, the differences between particles and surfactant molecules, and the role of the interparticle interactions resulted in failure of the model.

An improved description was provided by Miller's group [52,53]. They developed a model based on those previously used for describing the adsorption of proteins at fluid interfaces [54], including specific features to account for the behavior of the particle-laden interfaces. Thus, they defined the surface pressure ($\Pi = \gamma_0 - \gamma$, with γ_0 and γ being the surfaces tension for the bare interface and the interface after the adsorption of colloidal particles, respectively) for a particle-laden interface as follows:

$$\Pi = \frac{k_B T}{\omega_0}\left[ln\left(1 - \frac{\omega}{A}\right) + \left(\frac{\omega}{A}\right)\right] - \Pi_{coh}, \quad (1)$$

where $\frac{\omega}{A}$ provides information related to the interfacial coverage and ω_0 gives information of the particle area, with Π_{coh} being the so-called cohesion pressure, which gives information about the interactions occurring along the interface, and k_B and T the Boltzmann constant and the absolute temperature, respectively. This model provides a good description of the behavior of particles trapped at a fluid interface far from a close-packed state, independently of the size of the particles and their chemical nature.

An alternative description of the thermodynamic behavior of particles at fluid interfaces was proposed by Groot and Stoyanov [55]. This considered a dependence of the interactions with the interfacial packing, resulting in the following expression:

$$\Pi = \frac{4k_B T}{\pi d^2}\left[\frac{byZ}{\lambda} - b_2 y^2\right], \quad (2)$$

where d is the distance within which the long-range interactions occurs, and Z is the compressibility factor [56]. $\sqrt{\lambda}$ and y represent the effective diameter of the particles and the interfacial coverage, respectively, with b and b_2 being interactions parameters related to the interaction potential. This model was successfully tested by Deshmukh et al. [57]. The development of more refined models describing the thermodynamics behavior of particle-laden interfaces requires a detailed consideration of the interparticle interactions, as well as the wettability of the particles. Furthermore, the inclusion of morphological and structural aspects is expected to help with an accurate description.

2.2. Contact Angle and Wetting

The energy associated with the entrapment of colloidal particles at fluid interfaces (trapping energy ΔE_p) frequently exceeds the thermal energy, $k_B T$, which is the opposite to what usually happens when surfactant molecules are concerned [58]. Thus, assuming the simplest case, the adsorption of a chemically homogeneous spherical particle (without any significant roughness) at an interface between two immiscible fluids, it is possible to define the energy for trapping a particle at the interface, ΔE_p, as the difference between the energy of the particle dispersed in one of the phases, and the energy of the same particle at the fluid interface.

$$\Delta E_p = -\pi R^2 \gamma_{f_1 f_2}(1 \pm cos\theta)^2, \quad (3)$$

where R is the radius of the particle and $\gamma_{f_1 f_2}$ indicates the interfacial tension between the two fluid phases. The sign ± is associated with the relative position of the particles with respect to the interface, with + and − signs giving an indication that particles are placed above (hydrophobic particles) or

below (hydrophilic particles) the interfacial plane. Equation (3) introduces the parameter θ, which is the contact angle of the colloidal particles attached at the fluid interface, giving a measurement of the particle wettability for each phase, according to Figure 1. This is clear considering an interface between water and an apolar fluid, in which particles with $\theta < 90°$ are assumed to be hydrophilic, whereas those with $\theta > 90°$ are defined as hydrophobic. It is worth mentioning that the preferential partition of particles between the two phases plays a central role in the relaxation mechanisms appearing in particle-laden interfaces, and as matter of fact in their potential technological applications [59,60].

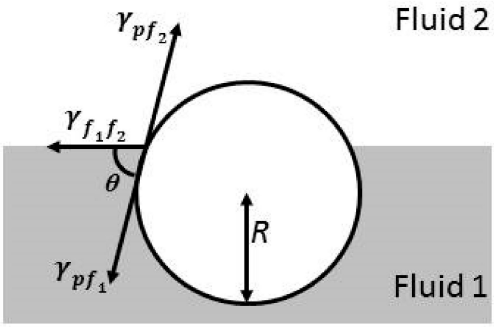

Figure 1. Scheme of a typical situation for the trapping of a particle at an arbitrary fluid interface, where θ represents the contact angle or relative wettability of the particle by the interface, R is the particle radius, and $\gamma_{f_1f_2}$, γ_{pf_1}, and γ_{pf_2} are the interfacial tensions corresponding to the fluid-fluid interface and the two fluid-solid (and fluid-particle) interfaces, respectively.

On the basis of the scheme shown in Figure 1, and assuming that Young's law is fulfilled, Equation (4), i.e., there is mechanical equilibrium, it is possible to define the contact angle

$$0 = \gamma_{pf_2} - \gamma_{pf_1} - \gamma_{f_1f_2} cos\theta_{f_1}, \tag{4}$$

$$\theta_{f_2} = \pi - \theta_{f_1}, \tag{5}$$

$$\cos\left(\theta_{f_1}\right) = \frac{\gamma_{pf_2} - \gamma_{pf_1}}{\gamma_{f_1f_2}}, \tag{6}$$

$$\cos\left(\theta_{f_2}\right) = \frac{\gamma_{pf_1} - \gamma_{pf_2}}{\gamma_{f_1f_2}}, \tag{7}$$

where θ_{f_1} and θ_{f_2} represent the contact angles of the particles with the polar and apolar phases, respectively; and γ_{pf_1}, y, γ_{pf_2} are referred to the interfacial tensions corresponding to the two fluid-solid interfaces. The relative position of a colloidal particle with respect to the interfacial plane is always defined by its contact angle. Equation (6) is a generalization giving a description of the attachment of spherical particles at the interface between two fluids. However, it is possible to make different modifications on such an equation to include the role of particle geometry and roughness, its surface chemical heterogeneity, and even the effect of the line tension, particularly when nanoparticles are considered [31,61,62]. Thus, Equation (6) is considered as a simple model enabling the evaluation of the assembly process of colloidal objects at fluid interfaces, depending on the following three experimentally accessible parameters: contact angle, interfacial tension between the fluid phases, and particle dimensions.

On the basis of Equation (5), it is possible to assume that microparticles adsorb at fluid interfaces irreversibly, with entrapment energy exceeding many times the thermal energy. However, when colloidal nano-objects are concerned, the reversibility or irreversibility are strongly dependent on the interfacial tension between the fluids, and an adsorption-desorption equilibrium, similar to that found in common surfactants, could possibly appear. Despite the importance of the contact angle, its experimental determination is far from trivial. Nowadays, there are different available techniques

enabling its determination., which are extensively discussed in recent reviews by Maestro et al. [31] and Zanini and Isa [63].

There are several approaches for tuning the wettability of colloidal particles, which are based on the modification of the surface nature of the particles through chemical or physical procedures [27]. The former frequently consider the irreversible attachment of ligands onto the particle surface through a selective chemical reaction enabling the formation of covalent bonds, e.g., thiols onto gold surfaces or silanes onto SiO_2 surfaces [64–66]. The modification of particle wettability through physical procedures relies on the interaction (through electrostatic, van der Waals, or hydrogen bonding interactions) of particles with surface-active molecules, generally surfactants or polymers [44–46], but in some cases low molecular weight compounds, such as alcohols, allow modifying the wettability of the particles [47,67].

The above discussion demonstrates that both the wettability of colloidal objects and the decrease of the interfacial tension play a central role in controlling the assembly of particles at the fluid interfaces. However, a complete description of the assembly process also requires including the role of the interactions between particles at the interface [24,27,33,68]. This is because the interactions involved in the assembly process, which can present different origins, for example, electrostatic, van der Waals, hydrogen bonds, and covalent bonds, controls the structure and dynamics within the interface, impacting, as matter of fact, in the physicochemical properties of the assembled systems, and consequently in their potential applications.

2.3. Organization of Colloids at Interfaces

The wettability of the colloidal particles and the interactions appearing within the interface [30,69,70] govern the structure and equilibrium properties of particle-laden interfaces. Several studies have shown that the hydrophobicity of the particles presents a strong impact on both the interfacial coverage and the position of the particles within the interfacial plane [44,71,72]. For example, Santini et al. [45] studied the adsorption of monolayers of silica nanoparticles decorated with palmitic acid at the water-vapor interface. Their results showed an enhanced interfacial coverage with particles hydrophobicity. On one hand, particles with the lowest hydrophobicity have been found to form isolated particle rafts at the interface, and on the other hand, the increase of the hydrophobicity of the particles has yielded the formation of close-packed films. The increase of hydrophobicity was clearly related to a sharp decrease of the interfacial tension and an increase of the layer thickness and the surface concentration of particles at the interface. Therefore, it is possible to assume that an increase of the hydrophobicity of the particles is the driving force for the transition between layers with a lost packing to close-packed particle-laden interfaces [42,43,73–75].

Finally, a direct visualization of single microparticles at the interface is possible. Currently, it is routine to analyze their individual positions using video microscopy. Following this approach, it has been possible to analyze the densification process of particle-laden interfaces, revealing the existence of transitions between different phases as the interfacial coverage is increased, similar to the scenario found in the corresponding three-dimensional (3D) counterparts. Furthermore, such phase transitions appear independently of the particles size, with the latter slightly shifting the threshold interfacial densities in which the phase transition occurs [69,70,76].

3. Interactions between Colloids Trapped at Fluid Interfaces

From a fundamental point of view, the interactions occurring between colloidal particles trapped at a fluid interface are different from those expected on the corresponding 3D counterpart systems. This is associated with the role of the interface as a confining environment. Thus, a colloidal particle trapped at a fluid interface is considered as an object attached to a fluctuating surface that separates two different phases, with the physicochemical properties (e.g., density, dielectric permittivity, and ionic strength) of such phases being, in general, significantly different. Furthermore, the properties of such discontinuity can be modified by factors such as the size and shape of the assembled objects, their charge, their wettability, and their surface chemistry [27,33,45,68,77–79]. These factors can have

a combined effect on the behavior of the interface, making it difficult to introduce a quantitative description of the interactions involved in systems formed by colloids trapped at fluid interfaces. Here, a brief description of the main forces driving the assembly of colloidal particles is presented. From a broad view, it is possible to classify the forces into the following two groups: (i) direct interactions, which are intrinsically related to the nature of colloidal objects (size, shape, surface chemistry, charge, and roughness) and (ii) external interactions, associated with the presence of external fields, which act on individual objects or sets of them.

3.1. Direct Interactions

A description of the interactions occurring in colloids assembled at fluid interfaces is difficult due to the complex balance that exists between different types of repulsive and attractive interactions, which involved many objects (an example of the different types of interactions is schematized in Figure 2).

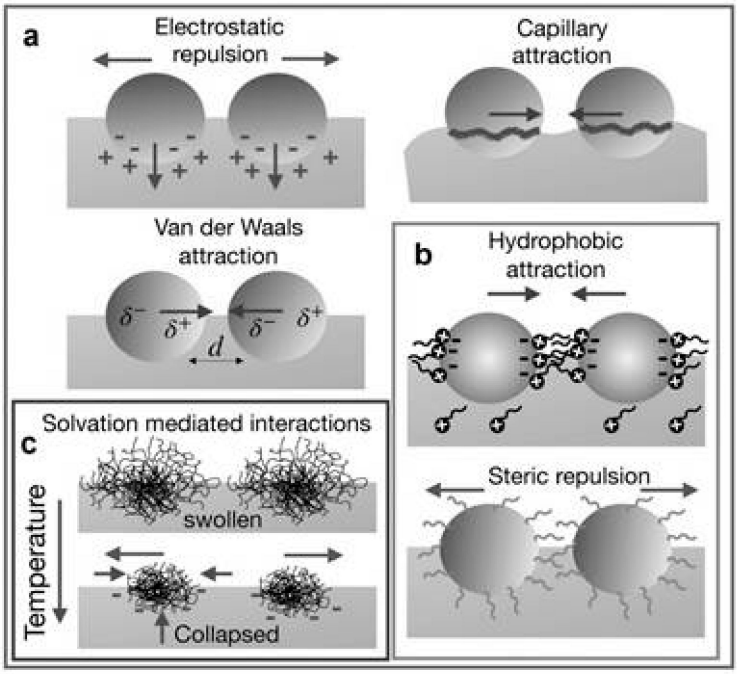

Figure 2. Different types of interactions occurring between colloidal particles at a fluid interface: (**a**) Total electrostatic repulsions by combining dipolar and Coulomb interaction counterbalanced by van der Waals and capillary attractive forces, (**b**) ligand-mediated interactions, attractive hydrophobic forces and steric repulsions, and (**c**) solvation-mediated interactions that appear in particular cases due to changes in the environment. Adapted from Maestro [33], Copyright (2019), with permission from Elsevier.

The repulsive contribution is the result of a combination between a screened repulsive Coulombic interaction, which operates at short distances, and the long-range dipole–dipole interactions resulting from the asymmetric distribution of charges. This is associated with the different dissociation degree of the dissociable groups present at the colloid surface as a result of their immersion in fluids with different dipolar constants [80–83]. The role of the repulsive interaction is reinforced by steric contributions due to the presence of a shell surrounding the particle, which presents, in most of the cases, a polymeric nature. Thus, the overlapping of the shells of different particles leads to the emergence of an osmotic pressure that prevents the particles aggregation, avoiding the unfavorable decrease of the system entropy associated with the shell compression [84–86]. Considering the attractive interactions, it is necessary to mention the role of the van der Waals interaction. The impact of these interactions for colloids trapped at fluid interfaces is strongly influenced by the size, shape, and wettability of the objects [42,77]. Furthermore, the presence of hydrophobic interactions should not be neglected. These

are the consequence of the requirement of minimization free energy as a result of the unfavorable nature of the contact between colloidal objects, with hydrophilic nature, and the solvent [87].

The last type of direct interactions which should be considered, when colloidal matter trapped at fluid interfaces is concerned, are the capillary forces. These can present both attractive and repulsive characteristics which appear from the interfacial deformation associated with the entrapment of the particles at the interface. This leads to the appearance of a meniscus which leads to the emergence of long-range interactions between colloids, even larger than the size of a single colloidal particle, to ensure the area minimization. The appearance of a meniscus around an isotropic colloid at a flat interface makes it necessary that the colloids exert a force in the direction perpendicular to the interface. This can occur when the densities of the colloidal particles and the fluid are similar, or when the colloids and the interface present charges [69,70,76,88–91]. In contrast, the role of capillary interactions can be considered negligible for small colloids, or when electrostatic interactions are weak. The appearance of a nonuniform wetting of the colloids for the interface can also lead to the appearance of a force in the direction perpendicular to the interface, distorting the contact line and enhancing the importance of the capillary interactions [92]. It is worth mentioning the important role of the interfacial heterogeneity in the interactions occurring within the interface. Particular cases of this are found when glass transitions appear in mixtures of particles with different sizes, or in the emergence of attractive interactions between colloids with charges that are equal are concerned. This can be explained by considering the asymmetric distribution of charge within the interface [37,76,93–96].

3.2. External Interactions

External fields have been revealed as a very effective way to tune the assembly of colloidal objects at interfaces, enabling control over the mechanical, optical, and electronic properties of these assembled systems [97,98]. The confinement of particles at fluid interfaces is associated with a restriction of their vertical motion, which is governed mainly by the wettability of the particles. It is expected that once the colloids are placed in their equilibrium positions, only small fluctuations appear around their equilibrium positions in relation to the interfacial place. However, when the motion within the interfacial plane is considered, particles can diffuse freely within such a plane [99]. This 2D diffusion can be manipulated by the mechanical deformation of the interface, by changing the interfacial area (dilatational deformations) or its shape (shear deformations), tuning the characteristic of the interfacial assembly which can even induce 2D phase transitions [100–102]. Similar effects can also be induced using external fields, e.g., magnetic or electric one [88,103].

Moreover, the change of the environmental conditions (pH, temperature, and ionic strength) can also be used to modify the interactions and the organization of particles at the fluid interface. Furthermore, this can also be exploited to tune the assembly of the particles at the interface, which has been explored mainly in the assembly of microgel particles [57,85,104].

The understanding of the interactions involving multiple bodies has special relevance because they can have a significant influence on the transport phenomena occurring within the confinement plane. Therefore, the modification of the energy landscape and the physicochemical properties of the interfaces have a critical impact on the development of new interface-based materials.

4. Dynamics of Colloids Trapped at Fluid Interfaces

The analysis of the dynamics of adsorbed colloid at the fluid interface needs to take into consideration the interactions involving several particles, as well as the interactions between the particles and the two adjacent fluids. Therefore, the motion of colloids trapped at the interface is strongly influenced by the existence of fluid phases, which controls, in many cases, the time scales [30,105].

The motion, in short time limits, for particles trapped at fluid-like monolayers which present compressible behavior, results in density fluctuations similar to that expected for a sound wave. This presents a characteristic time given by $t_s = R/c_s$, where R and c_s are the radius of the particle and the speed of sound, respectively. These dynamics processes occur at extremely short times

(~0.1 ns). Furthermore, a second dynamic defined by a characteristic time, t_h, appears associated with the hydrodynamic interactions. This latter process is coupled with the velocity field generated by the colloidal motion, which induces a drag force between the particles, appearing in a time scale close to 10 ns. This time scale is similar to the time needed for the displacement of the transverse moment generated by the particle motion, which is a distance similar to the interparticle distance. The hydrodynamics interactions can appear coupled to some additional processes associated with the initial velocity of the colloids, resulting from a time-dependent velocity field due to the particle motion. This type of motion presents a characteristic time associated with the transverse diffusion coefficient [30,106,107].

It is worth mentioning that the motion of the colloids depends on the diffusion coefficient $D_0 = k_B T/g$, with g being the Stokes friction coefficient. The characteristic time for colloidal motion at the interface can span from 1 ms to 1 s, which clearly shows evidence of the separation between the colloidal dynamics and other interfacial processes. Thus, it is possible to assume that the motion of a colloid can be described as a diffusion process affected for the interactions with neighboring colloids. Information about the dynamics of trapped particles can be obtained by analyzing the trajectories of colloids at the interface, which gives information on the mean square displacement (MSD, $\langle \Delta r^2(t) \rangle$), which is related to the diffusion coefficient, D, and the characteristic length of the translational motion [30,89,90,107,108],

$$\langle \Delta r^2(t) \rangle = 2dDt^{\alpha}, \tag{8}$$

where α is a scale exponent and d represent the number of dimensions. Considering a low interfacial coverage, linear dependence of the MSD would be expected on time, with the diffusion coefficient obtained from the slope of the representation defined by Equation (9) [30,107]. The increase of the coverage leads the system to a more complex dynamic, with the following two clear thresholds: (i) short times and (ii) long times. The existence of two regimes is characterized by a change of the time dependence of the MSD with the increase of the time, with such change being associated with the restriction of the diffusion region. At short times, the dynamics is limited to short distances (neighboring colloids), which leads to the appearance of the self-diffusion coefficient at short times,

$$D_0 = \lim_{t \to 0} \frac{\langle \Delta r^2(t) \rangle}{4t}, \tag{9}$$

The diffusion coefficient in the short time limit decreases with an increase of the interfacial coverage, ϑ, as a result of the interactions. Thus, $D_s = \alpha D_0(1 - \mu\vartheta)$, with μ being a parameter considering the interactions [109]. In the long time limit, the collective motions of the particles start being important for the interfacial dynamics, leading to a diffusion coefficient defined as

$$D_m = \lim_{t \to \infty} \frac{\langle \Delta r^2(t) \rangle}{4t}, \tag{10}$$

Considering the long time limit, the motion of a particle can be described in terms of the escaping of the particle from a box, which is defined by its close neighbors, i.e., the α-relaxation [110]. At high interfacial coverages, the interparticle repulsion arrests the dynamics within the experimental window [90]. Therefore, the motion of the particles must be considered in terms of an harmonic Brownian oscillator (BHO), with the Langevin equation including a restoring elastic force accounting for the behavior of the particles [111]

$$m\frac{dv}{dt} = -gv + F(t) - kx, \tag{11}$$

where m and v correspond to the mass and velocity of one particle, respectively, and k is the force constant, with $F(t)$ being a random force. Assuming the overdamped limit and neglecting the role of the inertia, the following solution is obtained [112]:

$$\langle \Delta r^2(t) \rangle \; = \; 2d\delta^2\left[1 - e^{-D_0 t/\delta^2}\right], \tag{12}$$

where $\delta^2 \; = \; k_B T/k$. The characteristic time is defined as $t_{BHO} = \delta^2/D_0 = g/k$. A better description of the dynamics of Brownian particles when interactions are involved makes it necessary to introduce ad hoc corrections to Equation (13). This can be done considering the non-exponential character of the relaxation [113].

$$\langle \Delta r^2(t) \rangle \; = \; 2d\delta^2\left[1 \; - \; e^{-(D_0 t/\delta^2)^c}\right]\left(1 + \frac{D_0 t}{\delta^2}\right), \tag{13}$$

where c is a stretching exponent, assuming values below 1 and providing information about the width of the relaxation time spectrum. In Equation (14), a term giving information about the long time dynamics of particles is included. This term assumes the escaping dynamics of particles from their groups, resulting in the appearance of a linear dependence with time. For solid-like monolayers, it is necessary to introduce the overdamped bead-spring model (OBS) accounting for the dynamics when the coverage is high [114]

$$m\frac{dv_i}{dt} \; = \; -gv_i \; + \; F_i(t) \; - \; k\sum_j^{nn}\left(u_j(t) \; - \; u_i(t)\right), \tag{14}$$

where $u_i(t)$ accounts for the displacement of a particle i in a time t, with n being the number of closest neighbors to i. The high interfacial coverage existing in solid-like monolayers makes impossible the appearance of escaping dynamics, leading to the disappearance of the linear dependence of the MSD when long times are concerned. Thus, the solution reads as follows:

$$m\langle \Delta r^2(t) \rangle \; = \; \frac{2dk_B T}{kN}\sum_b \frac{1}{L(q_b)}\left[1 \; - \; e^{-kL(q_b)t/b}\right], \tag{15}$$

Equation (15) only considers the interaction with the closest neighbors, where $L(q_b) \; = \; \sum_j^{nn} \frac{1}{L(q_b)}\left[1 \; - \; \cos\left(q_x n_j\right)\right]$ represents the net factor and q_b is the b-order wave-vector, whereas i represents a vector going from the particle i to the particle j. This model is reduced to the BHO one in the initial stages and tends to the following limit at long times:

$$\lim_{t\to\infty}\langle \Delta r^2(t) \rangle \; = \; \frac{2dk_B T}{kN}\sum_b \frac{1}{L(q_b)}, \tag{16}$$

where the threshold value depends on the strength of the harmonic force and the net factor.

5. Rheological Behavior of Particles Attached at Fluid Interfaces

Rheology studies the deformation and flow of materials as a response to the application of a mechanical disturbance. This can lead to a change in the material size (dilation) or in its shape (shear). The understanding of the relaxation processes as a result of mechanical deformation is of central importance for describing the mechanical behavior of materials, and their potential use in the fabrication of systems with technological interest [51,115–118]. This has stimulated extensive research activity aimed to shed light on the behavior of colloidal particles confined in 2D, which is of particular interest to the understanding of biological processes involving self-assembled systems operating under continuous mechanical perturbations.

Therefore, the understanding of the interfacial response against mechanical perturbations transcends the field of physicochemical, and should be considered a challenge with a marked multidisciplinary nature [119–130]. Figure 3 schematized the different deformation modes that can undergo a fluid interface, including those occurring within the plane (dilation and shear) and those occurring out the plane (bending and splaying). In the following, some of the main aspects associated with the response of particle-laden interface against in-plane mechanical perturbations, either dilational or shear one, are analyzed.

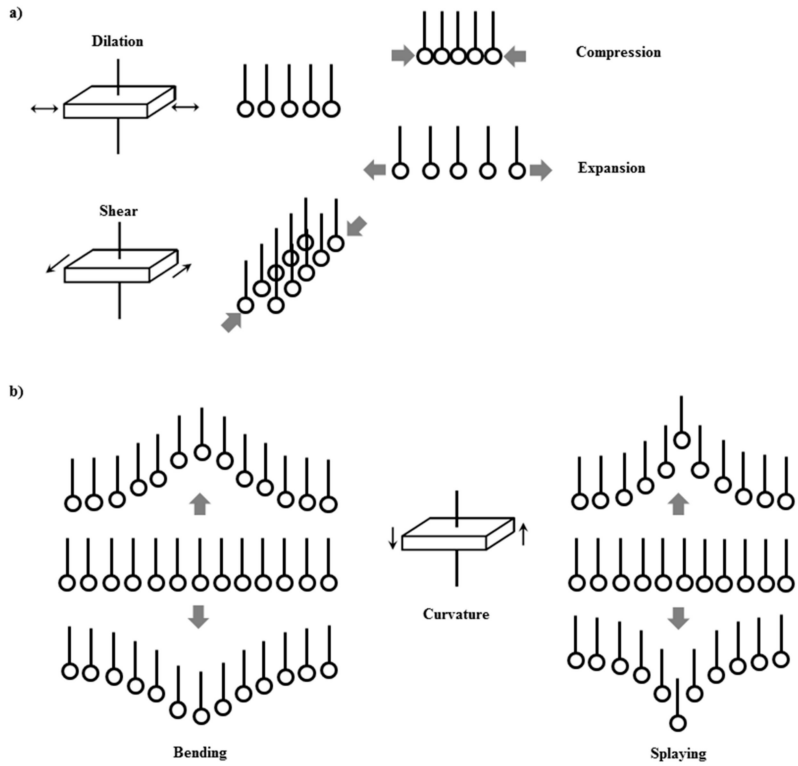

Figure 3. Sketch of the different dynamic modes appearing for fluid interfaces: (**a**) In-plane modes (dilation and shear) and (**b**) out-of-plane modes (bending and splaying).

5.1. Dilational Rheology

The dilational rheology of interfaces gives information related to changes in surface tension as result of changes in the interfacial are, or what is the same in the interfacial coverage. Therefore, a time-dependent infinitesimal change of the interfacial, $\delta A(t)$, due to an uniaxial deformation, produces a change in surface pressure, $\delta\Pi(t)$, defined as [131,132]:

$$\delta\Pi(t) = \Pi(t) - \Pi_0 = \frac{\partial\Pi}{\partial A}\delta A = \varepsilon(t)u(t), \tag{17}$$

where $\varepsilon(t) = -A_0(\partial\Pi/\partial A)_T$ represents the time-dependent viscoelastic modulus. Equation (17) gives a generic definition considering a surface pressure change $\delta\Pi$ associated with the modification of the surface area $u(t) = \delta A/A_0$. Under equilibrium conditions, the dynamics modulus assumes a value similar to that corresponding to the Gibbs elasticity ε_0

$$\varepsilon(t) \to \varepsilon_0 = \Gamma\left(\frac{\partial\Pi}{\partial\Gamma}\right)_{eq} \tag{18}$$

where $\Gamma = 1/A$ represents the surface excess. Assuming a small amplitude deformation with a characteristic frequency ω, the complex modulus is defined as,

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\omega\kappa(\omega) \tag{19}$$

where $\varepsilon'(\omega)$ is the storage modulus, the imaginary part the loss modulus is $\varepsilon''(\omega) = \omega\kappa(\omega)$, and $\kappa(\omega)$ represents the dilational interfacial viscosity. From the above presented definition of the dilatational viscoelastic modulus, it is expected that such a parameter can be changed either from the adsorption of colloids at the interface or from the modification of the available interfacial areas, which results in interfacial relaxation processes occurring in different time scales [46]. Despite the many efforts made to understand the behavior of particle monolayers against dilational deformations, there are several aspects that still remain unclear, especially those related to the theoretical description of the experimental results [52,53,133,134]. The first theoretical description of the mechanical response of interfaces with particles was given by the Miller group [52,53], who followed a similar procedure to that used in the description of proteins, and mixtures of proteins and surfactants [54,135], at fluid interfaces, gave a description of the mechanical response of particle-laden interfaces. However, such description is merely theoretical, without any development of its practical application.

It has been mentioned that the adsorption of particles at fluid interfaces is strongly influenced by its wettability, and thus some effect of this property can be expected in the mechanical performance of the interface, as was demonstrated by Safouane et al. [136]. Thus, the increase of the hydrophobicity of the particles favors their incorporation at the interface, resulting in layers with higher values of the storage modulus than that corresponding to the loss one. This behavior is in turn related to an increase in the interactions between particles at the interface [137]. Analyzing the characteristic relaxation process, it was found that particles undergo a reorganization process within the interface (~10^{-3} s). Such relaxation was slowed down by the increase of the hydrophobicity of the particles due to the increase of the steric hindrance at the interface [138].

Polymeric particles present a behavior slightly different to that discussed above as a result of their partially deformable character, with both the storage and the loss moduli increasing with the interfacial coverage. However, above a threshold value of the interfacial coverage, a steep decrease of the viscoelastic moduli occurs due to the possible distortion of the quasi-2D layer, appearing as the buckling of the monolayer. Such systems present a transition between a fluid-like behavior to a solid-like behaviour with the densification of the interface [69,139,140]. Therefore, we assume that the dilational rheological response is strongly dependent on the specific region of the phase diagram under study [73]. For polymeric particles, the storage modulus was higher than the loss modulus within the entire interfacial coverage range, with this behavior being independent on the stain rate [139]. For low interfacial densities, the elastic component increases with the interfacial coverage due to the presence of repulsive interactions. When such repulsions are screened, an increase of both storage and loss moduli was found with the interfacial coverage until the formation of a close-packed monolayer [73]. For the highest interfacial densities, values of the storage modulus in the range of 350–600 mN/m were found.

5.2. Shear Rheology

For deformations in the interfacial plane, the shear elasticity can be defined as a constant of proportionality between the applied stress, u_{xy}, and the resulting deformation, σ_{xy}. For a solid monolayer, such proportionality can be expressed in terms of Hook's Law, $\sigma_{xy} = Gu_{xy}$. However, when fluid-like monolayers are concerned, it is the viscosity that defines the behavior, $\sigma_{xy} = \eta(du_{xy}/dt)$, where η represents the interfacial viscosity and (du_{xy}/dt) the strain rate. For oscillatory deformations, the complex viscoelastic modulus can be defined as,

$$G(\omega) = G'(\omega) + iG''(\omega) = G'(\omega) + i\omega\eta(\omega), \tag{20}$$

where $G'(\omega)$ and $G''(\omega)$ are the storage and loss moduli, respectively. The first study focused on the response against shear deformations of particle-laden interfaces was performed by Cicuta et al. [141]. They found that the reduced deformability of the particles leads to a behavior controlled by the loss modulus (viscous behavior) which contrasts with the elastic response found when deformable molecules are concerned. Furthermore, a sharp increase of the viscoelastic modulus was found by the interfacial coverage. Thus, the behavior of quasi-2D systems against shear deformations appears significantly to that found for their respective 3D counter-parts, as was also independently stated by Trappe et al. [142]. Further developments of the studies related to the shear response of particle-laden interfaces evidence the critical role of the interfacial organization of the particles in the interfacial shear response, with behavior for systems in which aggregation appears similar that that found in 3D systems. This is explained by the influence of the interactions in the rheological response of interfaces [143].

For asymmetric particles, it was found that the anisotropic reorganization of particles at the interface plays a central role on the shear response, with a behavior reminiscent of a 2D-plasticized system when the coverage is low. The increase of the coverage leads to a perfect elastic interfacial behavior which differs from the scenario found for spherical particles [144]. Barman and Cristopher [145] found that the increase of the interfacial coverage drives a transition between shear-thinning to yielding one as a result of the differences in the stresses dissipation appearing for asymmetric particles. Furthermore, the linearity of the response disappears with the increase of the interfacial density, with the viscoelastic modulus presenting a power-law dependence on the surface coverage [142]. Madivala et al. [146] found that the strength of the electrostatic interactions between asymmetric particles defines the shear response of the particle-laden interface, with the interfacial organization controlling the interfacial properties. The role of the morphology of the particles was confirmed using non-spherical particles with different aspect ratio, which showed shear-thickening response. Furthermore, the increase of the particles asymmetry decreases the interfacial density in which jamming occurs [147].

The particle roughness also plays an important role in the rheological response of particle-laden interface, presenting effect that depends on the interfacial coverage. For low interfacial coverage, the roughness reduces the shear viscosity, with the opposite being true when the interfacial density increases. This is the result of the decrease of the interparticle friction which influences the role of particles in emulsion stabilization [147,148].

It is expected that the contact angle of particles trapped at the fluid interface also influences the rheological response. Safouane et al. [136] found that an increase in particle hydrophobicity leads to the increase of storage and loss moduli, with the monolayers of particles presenting the lowest hydrophobicity having a mainly elastic behavior. The increase of the hydrophobicity leads to an increase of the viscous character, with particles presenting a contact angle around 90° having a gel-like behavior ($G' = G''$)

6. Conclusions

This review reports some of the most relevant physicochemical bases underlying the attachment of colloidal systems to fluid interfaces. The prospects of tuning and controlling the assembly of colloids at interfaces following different approaches, such as modifying particle's wettability, intermolecular interactions and interfacial flows, make them potential candidates to create complex and hierarchical structures that have many potential technological applications. There are to date many experimental and theoretical efforts to unravel the complex physics involved in the interfacial assembly of colloidal particles. However, to obtain a complete framework describing the behavior of particle-laden interfaces is still a challenge. This is due to the existence of many parameters (shape and size of the particles, chemical nature, wettability, etc.) affecting the interfacial morphology and response against mechanical deformations, which can influence in the future applications of particle-laden interfaces.

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