



Attachment and detachment of particles to and from fluid interfaces

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Abstract

In this topical review, we commemorate some of the outstanding contributions of Prof. Peter Kralchevsky in the field of colloid and interface science. In particular, we focus on his achievements on phenomena involving the attachment and detachment of colloidal particles to and from fluid interfaces, giving a personal perspective on how his work has inspired our own research and the activities of a thriving scientific community. We specifically concentrate our presentation on the issues of emulsion stability via particle adsorption and desorption, particle organization via capillary immersion forces and on the relevance of electrostatic barriers to spontaneous particle adsorption. This review takes the reader through numerous developments, from the early '90s to the present day, and reflects on the importance of the legacy of the work of Prof. Kralchevsky for the years to come.

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Introduction

When looking at the lifetime contributions of scientists of the caliber of Prof. Peter Kralchevsky, it is natural to be in awe of their achievements. However, it is when the crystalline clarity of their scientific discourse is accompanied by a warm and kind heart that they become a true source of inspiration for younger researchers. Coming into contact with the work of Prof. Kralchevsky, but, especially, for some of us, having the fortune to

collaborate with him has been an experience with profound influence on many aspects of our academic lives: from teaching capillarity to undergraduate students, through defining and refining some of our dearest research questions, to influencing ideas that led to a start-up company. In particular, the insights that Prof. Kralchevsky has provided on how colloidal particles attach and detach from fluid interfaces, and thereby spontaneously organize themselves into larger structures, have had the deepest impact on our work. Among those, here we wish to highlight three of them: (i) his contributions to rationalizing the causes influencing particle adsorption by developing a quantitative theory on the image charge interactions between charged spherical particles and a fluid interface; (ii) his work on the stability of Pickering emulsions from both an experimental and theoretical point of view; (iii) his understanding of the mechanism behind two-dimensional (2D) crystallization in convective assembly, which, together with previous theoretical works, identified the fundamental importance of lateral immersion forces in determining particle organization at fluid interfaces.

Much of the interest in adsorbing and detaching particles onto and from fluid interfaces arises from the multiple application perspectives they offer. Particles at fluid interfaces act as stabilizers and are therefore present in a variety of products and processes where emulsions and foams are involved, such as in foods, personal care or household products. Moreover, they are central to industrial processes, such as mineral recovery in froth flotation, where interfaces must be destabilized to recover the materials of interest [1,2]. In addition, harnessing particles at interfaces can be used to produce functional structures and complex materials, for example, masks for colloidal lithography, reversible plasmonic mirrors, coatings with specific wettability or reflection properties [3]. For this latter purpose, control not only over the adsorption but also over the assembly of particles at fluid interfaces is required.

In this topical review, far from providing an exhaustive report on these vast topics, we bring our personal perspective on them, focusing on the implications that the work of Prof. Kralchevsky has had, and still has, for our work, as well as for a thriving scientific community. We start by dwelling on phenomena involving particle

attachment and follow up with those connected to particle detachment from fluid interfaces. We conclude by reflecting on how the legacy left by Prof. Kralchevsky may continue to shape the development of novel exciting research directions.

Attachment

Thermodynamics and dynamics of the adsorption process

The propensity of solid micro and nano-particles to adsorb at fluid interfaces (e.g. air–liquid or liquid–liquid) has a thermodynamic basis; replacing part of the fluid interface with a solid particle causes a free energy reduction (ΔE) that is directly proportional to the cross-sectional area of the interface now occupied by the particle. The extent of this energy reduction, therefore, depends on the interfacial tension between the two fluids (γ_{12}), the particle size, and its wetting properties through its contact angle (θ). For ideal, smooth, and chemically uniform spherical particles with radius R_p , adsorbing from the fluid phase where their surface energy is lowest (i.e. water for hydrophilic particles or oil for hydrophobic ones), this leads to the following relation: [4,5].

$$\Delta E = \pi R_p^2 \gamma_{12} (1 \pm \cos(\theta))^2 \quad (1)$$

We remark that this simple equation holds in the case of negligible line tension contributions at the three-phase contact line, where the particle surface meets the two fluids, and that it implies the fact that the particle will take up an equilibrium position at the interface, which satisfies its wetting condition along the three-phase contact line without deforming the interface [6]. Any deviation from this equilibrium position and any interface deformation consequently lead to an energy increase and to a drive for the system to reach equilibrium: whether achieving equilibrium is kinetically possible is at the core of many of the phenomena we discuss here and it has been a central question in the work of Prof. Kralchevsky.

Equation (1) has some simple, but very important, implications. The contact angle defines how much of the particle protrudes into one of the two fluids. Conventionally, water is taken as the reference relative to which θ is measured. In this way, $\theta < 90^\circ$ corresponds to hydrophilic particles, which are mostly immersed in water, and $\theta > 90^\circ$ corresponds to hydrophobic particles, mostly immersed in oil or air. Following Young's law, θ at equilibrium is given by the interaction energies between the particle and the two fluids (γ_{1p} and γ_{2p}), and between the two fluids (γ_{12}), such that $\cos(\theta) = \frac{\gamma_{2p} - \gamma_{1p}}{\gamma_{12}}$. Correspondingly, for particles larger than few nanometers, and θ not too close to 0° or 180° , the values of ΔE greatly exceed the thermal energy $k_B T$, and thermal

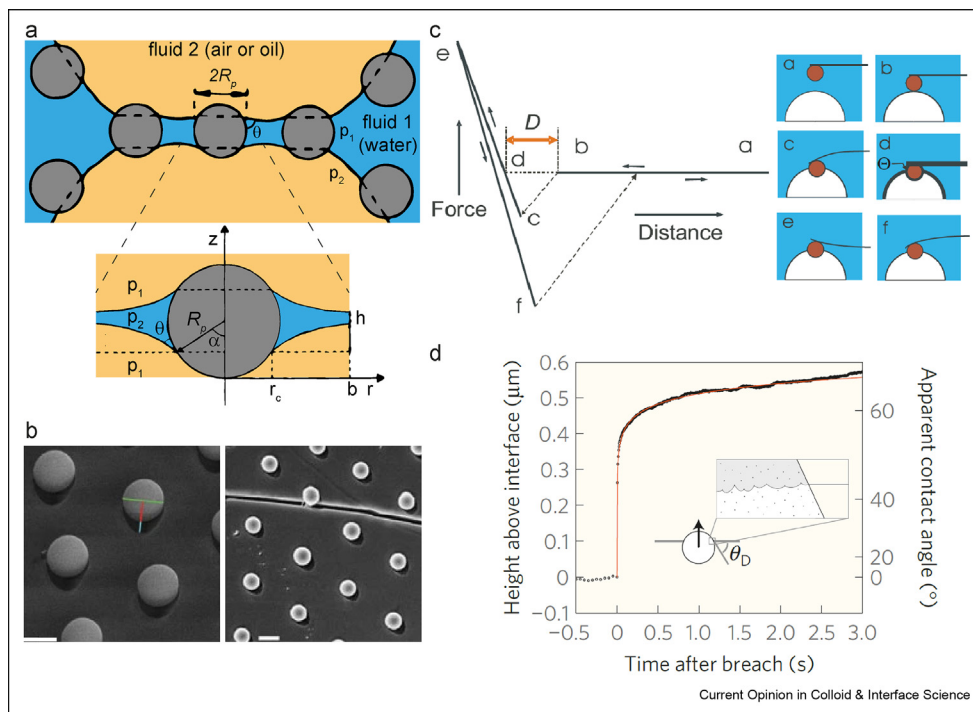
fluctuations cannot detach adsorbed particles from the interface, where they remain irreversibly attached.

The irreversible binding of solid particles at fluid interfaces is at the core of a class of materials called particle-stabilized, or alternatively Pickering or Pickering–Ramsden, emulsions and foams, where the impossibility to spontaneously desorb particles from an interface prevents the coalescence of particle-decorated droplets or bubbles upon reaching a critical surface coverage [7]. However, in addition to these purely energetic arguments, there are other factors that contribute to the stabilization of particle-covered droplets or bubbles. Focusing on emulsions, for two droplets to coalesce, the fluid film separating them must thin and eventually rupture upon coalescence.

In 1992, Denkov et al. [8] proposed a mechanism whereby the capillary pressure generated by a thinning particle-laden fluid film separating two emulsion droplets efficiently prevents film drainage and thus guarantees prolonged stability. In the situation described by Figure 1a, the capillary pressure p_c , that is, the difference between the pressure inside the droplet (p_2) and in the film (p_1), causes a deformation of the interface around the adsorbed particles, which is a function of particle contact angle, size, and separation between the particles. They found that smaller particles stabilize fluid interfaces more efficiently, that the maximum capillary pressure is higher for lower contact angle values and that it rapidly increases if particles are more densely packed together on the droplet's surface. Moreover, they investigated two modes of motion for the meniscus to migrate over the particle surface: (i) the case where the contact line freely slides allowing a constant contact angle, and (ii) the case where a contact angle hysteresis arises because of a discrepancy between an advancing and receding angle. The latter case is highly relevant for experimental studies since, in practical situations, any form of surface roughness or heterogeneity can give rise to such contact angle hysteresis. The impact of hysteresis is at the basis of many further research developments, including some of our own, that will be discussed later. In particular, reducing the value of the receding contact angle implies that additional work needs to be done by the capillary pressure to deform the interface before the three-phase contact line starts moving. This leads to the conclusion that 'the maximum capillary pressure p^* increases with increasing contact angle hysteresis, and hence, the film stability also increases' [8]. The calculations reported in this seminal article show that the theoretical values of the maximum capillary pressure for 1 micron particles can very easily exceed 10^4 Pa, supporting the conclusions about the enhanced stability of particle-coated droplets.

In the same article, the authors quantified the energy required to detach an adsorbed particle (eq. (1)) and

Figure 1



a) Schematic of a particle-laden fluid film separating two drops (or bubbles). The inset shows the case in which $p_c > 0$. θ is the particle contact angle, and α indicates the location of the three-phase contact line relative to the particle center. Adapted with permission from the study by Denkov *et al.* [8]. **(b)** Cryo-SEM images from FreSCa of 500 nm latex particles at a decane–water interface (left) and of 200 nm latex particles at a hexane–water interface. The presence of a shadow allows measuring the contact angle of individual particles immobilized at a vitrified water interface after metal deposition with a tilt angle of 30° . Scale bars: 300 nm. Adapted with permission from the study by Isa *et al.* [9]. **(c)** Diagram of a force–versus–distance curve in a model colloidal-probe AFM measurement. In the insets, the letters indicate the particle position with respect to a bubble–water interface, and the corresponding position in the force–versus–distance curve. Adapted with permission from the study by Gillies *et al.* [10]. **(d)** Vertical displacement of a particle breaching an oil–water interface and the corresponding apparent contact angle as measured by holographic microscopy. Adapted with permission from the study by Kaz *et al.* [11]. AFM, atomic force microscopy; SEM, scanning electron microscopy.

related the value of θ with the expected direction of particle expulsion, either toward phase 1 (water) for $\theta < 90^\circ$ or phase 2 (air or oil) for $\theta > 90^\circ$. Overall, these results allowed explaining several earlier experimental findings on emulsions stabilized by solid particles and lay the foundation of further works on particle-stabilized bubbles and drops.

A large number of experiments had also shown that, typically, oil-in-water (o/w) and water-in-oil (w/o) Pickering emulsions could be formed with hydrophilic and hydrophobic particles, respectively, at roughly equivalent volume fractions of the two phases [12]. Intuitively, this fact could be expected to follow from simple geometrical considerations related to the droplets' curvature. Remarkably, Kralchevsky *et al.* [13] used a thermodynamic argument to show that interface curvature is only a higher-order effect and that the type of emulsion is dominated by the sign of the work of emulsification. In particular, they proposed a thermodynamic criterion to predict the type of emulsion formed as a function of θ and the volume fractions of the

two fluids (ϕ). In their model, they computed the flexural and dilatational energies for curved interfaces covered by particles interacting via capillary forces and compared them to the emulsification work. Curvature, that is, bending effects, is only important for densely-packed particle layers where preferential wetting by the continuous phase stabilizes droplets of the opposite, disperse phase (e.g. hydrophilic particles stabilizing oil droplets in water). However, preferential wetting more strongly affects the total energy required to bring particles, initially dispersed into one phase, to their thermodynamic equilibrium position at the fluid interface. In particular, starting with particles initially dispersed in phase 1 (here: water); for $\phi_2 \leq \phi_1$, the model predicts that stable o/w or w/o emulsions are formed for $\theta < 90^\circ$ and $\theta > 90^\circ$, respectively. In addition, the model predicts a catastrophic phase inversion (i.e. a transition from o/w to w/o or *vice versa* at constant particle wetting angle) upon increasing ϕ_2 by using the same particles as stabilizers. Interestingly, this contradicts purely curvature-based arguments. For $\phi_2 > \phi_1$ (and particles in the aqueous phase 1), the model predicts that

flocculated w/o emulsions are formed with hydrophilic particles and that hydrophobic colloids give rise to o/w emulsions. Despite being an anomalous situation, this combination could be experimentally observed if kinetic effects additionally contribute to the emulsion stability. In their analysis, Kralchevsky et al. specifically defined several other factors, which may affect emulsion formation, type and stability going beyond purely thermodynamic arguments. These factors include the existence of a barrier for particle adsorption at the interface, the influence of the adsorption rate (which strongly depends on the hydrodynamic flows caused by mixing), and the presence of kinetically-trapped states for the contact line on the particle surface, which lead to metastable contact angle values. All these effects influence particle adsorption at fluid interfaces at various levels and have deeply impacted our own research.

Given the central role of the value of the single-particle contact angle to determine the fate of particle-stabilized interfaces, these predictions came ahead of their time. In fact, up until the early 2000s, only very few alternatives existed to measure the contact angle of individual particles adsorbed at fluid interfaces, and most conclusions were drawn based on macroscopic characterizations of the wetting of powders or particle-coated surfaces. However, the already-mentioned relevance of heterogeneity, hysteresis, and kinetic effects drove the flourishing of many new additional contact-angle measurement techniques, including our own [9], which strongly inspired us to verify some of the predictions by Kralchevsky et al. Among the numerous methodologies developed to measure the contact angle of individual particles [14,15], techniques that are based on the immobilization of particles at the fluid interface are probably the most suitable for single-particle analysis, for example, the gel trapping [16] and the freeze-fracture shadow-casting (FreSCa) cryo-scanning electron microscopy (SEM) techniques (Figure 1b) [9]. Such methods allow for visualizing the immobilized interfaces *ex-situ* by means of high-resolution microscopy techniques, such as SEM and atomic force microscopy (AFM), and are, therefore, applicable to colloids ranging from few nm to μm . In addition, they can be used for the measurement of contact angles of ensembles of individual particles at a time, allowing to collect statistically robust information on contact angle distributions and correlating surface properties to wetting. However, they do not provide detailed information on the dynamics of the adsorption process, in relation to the potential role of the kinetic factors described before.

Time-resolved information can be obtained by sacrificing statistics with alternative experimental techniques. As a first example, the development of colloidal probe AFM allowed the direct investigation of the particle-interface interactions during adsorption and desorption processes upon recording the deflection of the cantilever holding a

particle and converting it into a force [17,10]. In a model experiment (schematically shown in Figure 1c), a smooth and chemically homogeneous colloidal particle is glued onto an AFM cantilever and driven toward the fluid interface. Before touching the interface, no force is recorded (step 'a' in Figure 1c). Upon touching it, the particle 'jumps into contact' and gets drawn toward the interface by the capillary force (steps 'b' and 'c'), and the newly formed contact line moves onto the particle surface until it reaches an equilibrium position (step 'd'). At this stage, the measured force is zero. Upon further pushing of the particle into the second fluid (step 'e'), the curvature of the cantilever is reverted and the measured force increases. During retraction of the cantilever (step 'f'), particle detachment can be characterized. A close look at this process will be described in Section 3. A smooth force-versus-distance curve indicates that the contact line does not pin on the particle surface, and from the measured immersion depth of the particle it is also possible to calculate its contact angle. As analyzed in the following Section, contact line pinning can be imparted by surface roughness [18,19] or by sculpting the surface of the AFM probe [20]. By improving the time resolution of such experiments to the μs range, two separate wetting regimes have been detected: a first fast wetting ($\sim 0.1\text{ ms}$, independent on the particle wettability) attributed to the balanced effect of capillarity and inertia, and a second, much slower, relaxation of the contact angle toward equilibrium, which did not reach a stable position over the timescale of the experiment (6 s) [21].

Slow relaxation of contact angles following a breach of the interface was also observed by holographic microscopy (Figure 1d) [11,22]. As polystyrene particles approached an oil-water interface from the water side, a discontinuity in their position was evidenced. However, the resulting apparent contact angle was much lower than the expected one at equilibrium, and the particle protrusion continued to evolve logarithmically over long timescales (up to $\sim 10\text{ s}$). This relaxation could be rationalized considering thermally-activated de-pinning events where the contact line overcame nanoscale heterogeneities characterized by small pinning energies [11,23]. Studying of the adsorption kinetics of particles of different composition and surface functionalities showed that some particles, especially polymeric ones dispersed in water, display surface heterogeneities that can pin the contact line with energy barriers up to an order of magnitude greater than those of other particles (such as oil-dispersed PMMA and small silica particles) resulting in longer logarithmic relaxation times [22]. Notably, thermally activated fluctuation of the contact line is likely to happen also after the particles reach their equilibrium interfacial position and were proposed to be the cause of the unexpectedly slow lateral (2D) diffusion of adsorbed particles with respect to their (3D) diffusion in the bulk [24].

The relationship between contact angle hysteresis, surface heterogeneity, and emulsion stability postulated by Prof. Kralchevsky inspired some of us to design colloidal particles with tailored surfaces to explore new routes for Pickering stabilization of interfaces. In principle, the pinning of the contact line can be controlled at will by using particles with precisely designed surface roughness. For increasing roughness, a rugged surface ensures that pinning sites have an energy sufficiently high to arrest the particles at metastable positions during the adsorption process. We thus synthesized a library of silica ‘raspberry’ particles with controlled size and density of surface asperities and identical surface chemistry, and visualized their adsorption at oil-water interfaces by means of cryo-electron microscopy [25]. By functionalizing the surface of the silica particles with almost neutrally-wetting groups, the colloids could be dispersed both in the aqueous and the non-polar phase. However, for increasing surface roughness, their adsorption to the interface from either side was arrested earlier and earlier. Therefore, rougher particles adsorbed from the water phase became effectively more hydrophilic, while, if adsorbed from the oil side, the same particles became effectively more hydrophobic. This wetting hysteresis was exploited to use the same batch of rough particles as ‘universal emulsifiers’, able to stabilize both o/w and w/o emulsions depending on their initially dispersion phase (see Section 3), essentially verifying the earlier predictions of Kralchevsky *et al.*

Spontaneous adsorption and adsorption barriers

While thermodynamics explains why particles are so strongly held at fluid interfaces, and why ultimately their adsorption is energetically favorable, in typical experiments, where particles approach a fluid interface from the bulk, adsorption is not always a spontaneous process. Instead, in many cases, an adsorption barrier strongly hinders, or even prevents, the spontaneous adsorption of particles [26]. Often, particles dispersed in water are stabilized by electrostatics, and electrostatic interactions may determine if particle adsorption will spontaneously take place.

Early works on the aggregation of particles at the air–water interface as a function of the ionic strength of the solution already revealed the presence of an adsorption barrier. Williams and Berg [27], in particular, demonstrated that by increasing ionic strength, the adsorption rate of negatively charged polystyrene particles to the interface could be greatly increased, from almost no adsorption to substantial adsorption over the timescale of the experiment. The authors attributed this result to the increased screening of the long-range electrostatic repulsion between the particles and the air–water interface. Such an electrostatic repulsion arises from negative charges whose presence has been successively confirmed both at the air–water [28] and

oil-water [29] interface. As a consequence, in studies on foam formation, it was thus found that positively charged polystyrene particles readily adsorb at the air–water interface at pH values at which their surface remains positive, while negatively charged polystyrene particles did not form any noticeable foams (as sketched in Figure 2a) [30]. Similarly, anionic particles with pH-dependent surface groups were found to be good stabilizers only upon charge suppression or inversion (Figure 2b) [31].

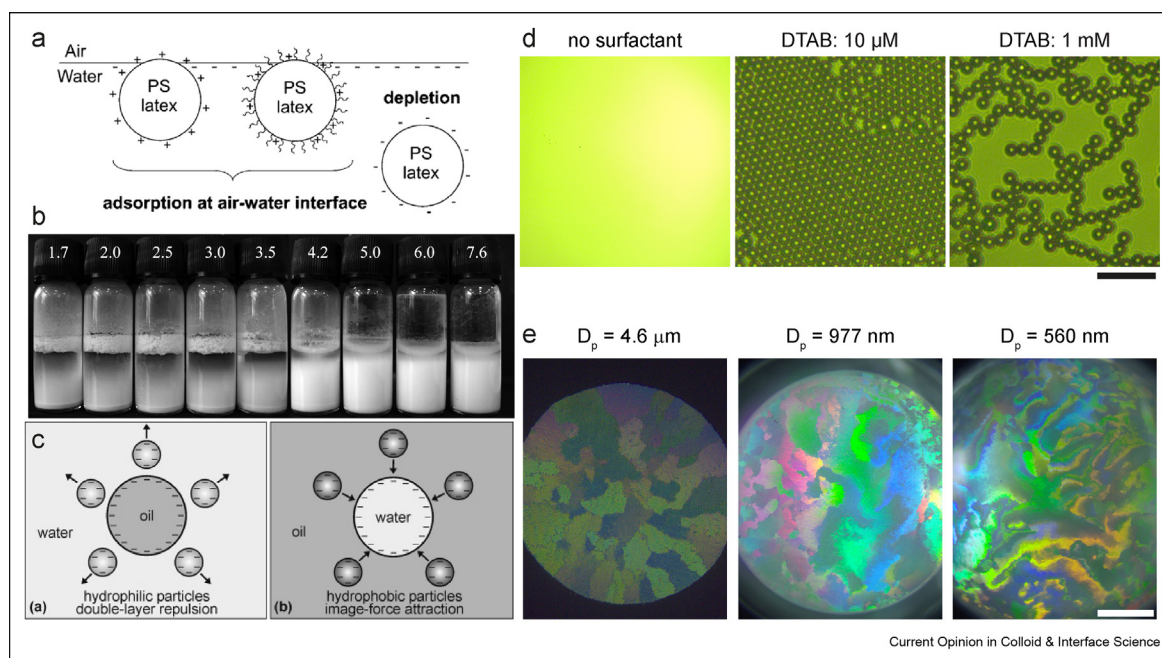
This concept was also demonstrated for oil-water interfaces by Golemanov *et al.* [32], who showed that stable emulsions with sulfate-stabilized polystyrene particles could be obtained upon the addition of 0.3–0.5 M of NaCl (the exact amount being dependent on the specific particles used). The authors noted that the threshold concentration of NaCl for particle adsorption was very close to that causing particle coagulation in suspension, therefore it was important to find the working NaCl concentration for each particle batch investigated that would not cause irreversible bulk aggregation. The link between particle coagulation and interfacial adsorption was further proved by varying the valence (Z) of the counterions, comparing NaCl with $MgCl_2$ and $AlCl_3$. The electrolyte concentration required for the formation of stable emulsions, and therefore extensive particle adsorption, followed the Schulze-Hardy rule for particle coagulation in bulk, which states that the critical coagulation concentration is proportional to $1/Z^6$ [32].

The interactions between charged particles and interfaces are not only due to Coulombic contributions. When the two fluids have a large difference in their dielectric constants, another type of electrostatic interaction arises, called imaged charge effect. An electric charge (q) near a discontinuity in permittivities (ϵ) perceives a force as if it interacts with an ‘image’ charge (q') placed at a distance $2d$ in the other phase (where d is the distance between the particle and the interface), of magnitude: [36].

$$q' = q \cdot \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \quad (2)$$

If charged particles are suspended in water (ϵ_1) near an interface with air or oil (ϵ_2), for which $\epsilon_1 > \epsilon_2$, then the image charge interaction is always repulsive, regardless of the sign of the particle charge, and as in the case of real charges, it can be screened adding electrolytes [36]. Instead, if the particles are dispersed in the oil phase, the sign of the image charge is opposite to that of the particle, and the resulting interaction is attractive. Danov *et al.* [33] developed a theoretical framework for calculating the interaction forces in such a case. In particular, the resulting expressions generalize the known theory of interactions between point charges to the case of particles that have a

Figure 2



(a) Schematic of the interactions between latex particles and the air–water interface: cationic particles adsorb at the interface, while anionic ones do not. Adapted with permission from the study by Kettlewell et al. [30] (b) Photographs of vials containing anionic particles in aqueous suspensions at different pH values, after shaking the dispersion. Foams are produced only upon charge suppression or inversion (pH = 1.7–3.5). Adapted with permission from the study by Binks et al. [31] (c) Schematic drawing of the electrostatic repulsion between an oil drop and anionic particles in water, and of the image-charge attraction between a water drop and anionic particles in the oil. Adapted with permission from the study by Danov et al. [33] (d) Transmission micrographs of an air–water interface. In the absence of surfactant, anionic polystyrene particles dispersed in water do not adsorb at the interface. With 10 μM of the surfactant DTAB, a 2D crystal is obtained. With 1 mM, a gel-like structure is obtained. Scale bar: 25 μm. Adapted with permission from the study by Anyfantakis et al. [34] (e) Structural colors from 2D crystalline assemblies of silica particles having different diameters at the air–water interface, in the presence of 5–10 μM DTAB. Scale bar: 1 mm. Adapted with permission from the study by Anyfantakis et al. [34] and Vialetto et al. [35].

finite size and uniform surface charge densities. As a consequence, deviations from point charge interactions are found if the particle-interface distance is comparable to the particle size. Such a quantitative theory supports experimental findings of spontaneous particle accumulation at oil-water interfaces when charged particles are dispersed in the oil phase (see Figure 2c) and shows how this interaction is strong and long-ranged for $R_p > 30 \text{ nm}$ and common surface charge densities.

Understanding and rationalizing the effect of electrostatics in the attachment of particles at fluid interfaces also enables exploring alternative routes for promoting particle adsorption. Particularly, when this process is exploited for the controlled assembly of 2D ordered materials, a careful balance of decreasing electrostatic interactions between particles and the fluid surface, at the same time keeping the particle surface charge high enough to maintain dispersed particles, has to be considered. In many cases, the addition of hydrophilic salts, by screening the particle charge in solution, can cause unwanted particle aggregation; therefore, other additives have been explored to promote spontaneous

particle adsorption and further tune their interfacial organization [26].

One of the most commonly used additives for enhancing particle adsorption are surfactants added to the water phase. They offer several advantages over common salts, including their ability to accumulate at fluid interfaces, selectively bind onto suspended particles, and the possibility to incorporate stimulus-responsive moieties into their structures (as in light-responsive surfactants). In addition, they can modify both the wettability and charge of the particles by adsorbing onto their surfaces. However, at the relatively high surfactant concentration typically used, particle neutralization and hydrophobization induces aggregation and hinders a precise control over the 2D assemblies.

Taking inspiration from the works of Prof. Kralchevsky and others, some of us investigated conditions at which surfactants could be used to promote particle adsorption into controlled 2D structures. In a first article, Anyfantakis et al. [34] studied mixtures of anionic particles with minute amounts of surfactants of the

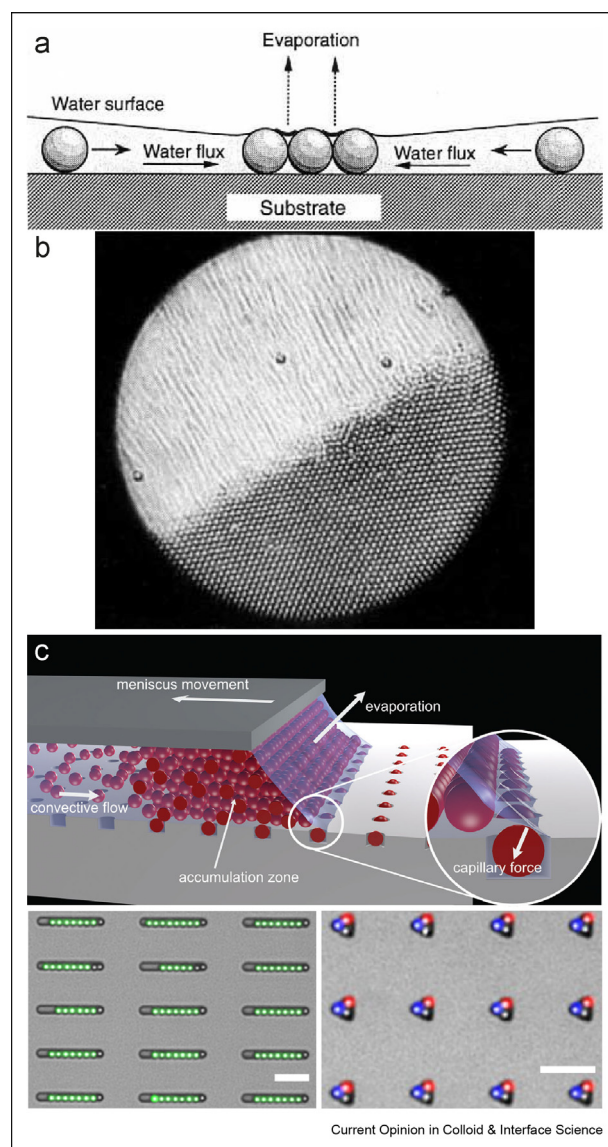
opposite charge (Figure 2d). It was found that at ultra-low surfactant concentrations ($10^2 - 10^4$ times below the CMC, critical micellar concentration), particles could adsorb at the air–water interface, reaching complete adsorption of all particles in suspension for a surfactant concentration of $\text{CMC} \cdot 10^{-3}$. In this regime, particles remained highly charged and thus prone to crystallization (Figure 2d, middle). These results indicate that substantial adsorption of surfactants onto the particles is not a requirement to promote complete particle adsorption to the fluid interface. The enhanced adsorption was instead attributed to shielding of the electrostatic repulsion between the water surface and like-charged particles by the accumulation of the cationic surfactants onto the fluid interface. Further increase in surfactant concentration allowed screening the particle repulsion and decreased the interparticle distance in ordered structures until the concentration threshold for particle neutralization and consequent aggregation into a percolating network was reached (Figure 2d, right). This methodology was then extended to a range of surfactants [37] and particles with different sizes (Figure 2e) and surface chemistry [35,38]. Notably, careful tuning of the interactions at play among interfacial particles also allowed achieving the light-controlled dynamic assembly of particles at an air–water interface, in the presence of the minute amount of a photo-responsive surfactant [37]. The desorption of surfactants from the fluid interface upon light irradiation (and fast re-adsorption upon stimulus removal) was engineered to reversibly switch the 2D assembly between a disordered (in dark) and a highly crystalline state (under light) upon on/off light cycles. Because the crystalline state could be kept only upon continuous energy supply by light irradiation, this system is an intriguing example of dissipative, out-of-equilibrium assembly.

Detachment

In the previous section, we have described some of the factors affecting the attachment of particles to fluid interfaces and introduced some of the consequences that these factors have on the properties of the resulting materials. Essentially, at the microscopic level, the process of particle attachment to an interface implies the motion of the three-phase contact line over the particle surface *toward* its equilibrium position. Conversely, the process of particle detachment involves the motion of the contact line *away* from its equilibrium position, either back toward the phase from which the particle reached the interface or past its equilibrium position into the other phase. Displacing particles from their equilibrium positions inevitably causes a deformation of the interface surrounding them, which correspondingly gives rise to capillary forces not only acting on the individual particles but also inducing interactions between neighboring adsorbed particles. The

receding motion of the contact line over the particle surface, and the resulting capillary forces, can be directly measured at the single-particle level using AFM [17,10,39], whereby particles are individually pulled through an interface. However, the direct manifestation of collective capillary interactions resulting from particle detachment emerges already in the drying of a colloidal monolayer, where particles deposited over a substrate

Figure 3



a) Sketch of the mechanism for convective deposition. (b) Photograph of the growth of a two-dimensional crystal of particles upon water evaporation on a solid substrate. Adapted with permission from Ref. [41] (c) Top: Schematic of the process of capillary assembly over a topographical template. Bottom: examples of geometrically and compositionally asymmetric colloidal clusters produced by sequential capillarity-assisted particle assembly (sCAPA). Scale bars: 5 μm . Adapted with permission from Refs. [46,47].

see a moving contact line over their surfaces as the fluid evaporates.

Controlled particle deposition from the fluid interface

The latter principle was elegantly exploited in 1992 by Denkov et al. [40,41], who developed a technique to pattern highly ordered 2D particle assemblies onto solid substrates from drying drops (Figure 3a and b). A drop of the particle suspension was placed on a glass substrate and enclosed by a Teflon ring. The hydrophobic walls ensured a slightly concave shape of the air–water surface. Because of water evaporation, the liquid layer thinned until, in the center of the substrate, its height was comparable to the particle size. When this happened, the particles freely moving in the bulk liquid pierced the water surface and remained trapped between the fluid interface and the solid substrate (Figure 3a). Trapped particles then arranged themselves into a hexagonal assembly creating the nucleus of the 2D crystal on the glass substrate. Following water evaporation, particles from the bulk of the droplet moved toward the ordered assembly and were incorporated in the growing crystal (Figure 3b). This process continued until the whole suspension dried, leaving a highly ordered crystalline layer. The mechanism responsible for particle assembly proposed by the authors largely relied on previous theoretical works by Kralchevsky et al. [42,44] and Paunov et al. [43]. When the particles remain trapped at the air–water interface, the liquid forms a receding contact angle on the particle surface, which gives rise to a deformation of the surrounding fluid interface. The overlap of these deformations between approaching particles induces a strong long-ranged attraction, successively termed lateral immersion force, which, together with hydrodynamic drag forces caused by water evaporation, drives the particle assembly and is the main cohesive force holding the forming 2D crystal.

This was a fundamental result, of great relevance in understanding and rationalizing the interactions between particles adsorbed at fluid interfaces and with strong implications for applications in surface patterning of micro-structured materials. Before this insight, lateral capillary forces were considered to be relevant only for large floating objects, whose weight was enough to deform the fluid interface. Instead, Kralchevsky and Nagayama [45] established both theoretically and experimentally that lateral capillary (immersion) forces exist between small ($R_p < 5 \mu\text{m}$) adsorbed particles and contribute to the total interaction potential between them, in many cases directing the final assembled structures.

The mechanism of particle assembly from thin evaporating films of their suspensions was successively called

‘convective deposition’ and finds numerous applications for the production of highly ordered particle assemblies [48]. An extension of this technique was later developed by Prevo and Velev [49], which described a setup to drag at a constant speed, a liquid meniscus of the particle suspension on the targeted substrate to ensure rapid coating of large substrate areas. By precise control of the deposition parameters (such as evaporation rate, dragging speed and particle concentration), large crystalline layers could be deposited with controlled thickness and packing symmetry. Nowadays, convective deposition, and closely-related methods based on the capillarity-induced deposition of particles over topographical templates [50,47], are routinely used for patterning colloidal particles into highly-controlled structures, of possible use for the fabrication of high-performance devices for applications in electronic, optics, and life science. Recently, some of us have further extended capillarity-assisted particle assembly to a sequential process ([46], Figure 3c) as a way to synthesize compositionally and geometrically anisotropic particle clusters as new versatile and functional microswimmers [51,52].

Detachment from smooth to rough particles

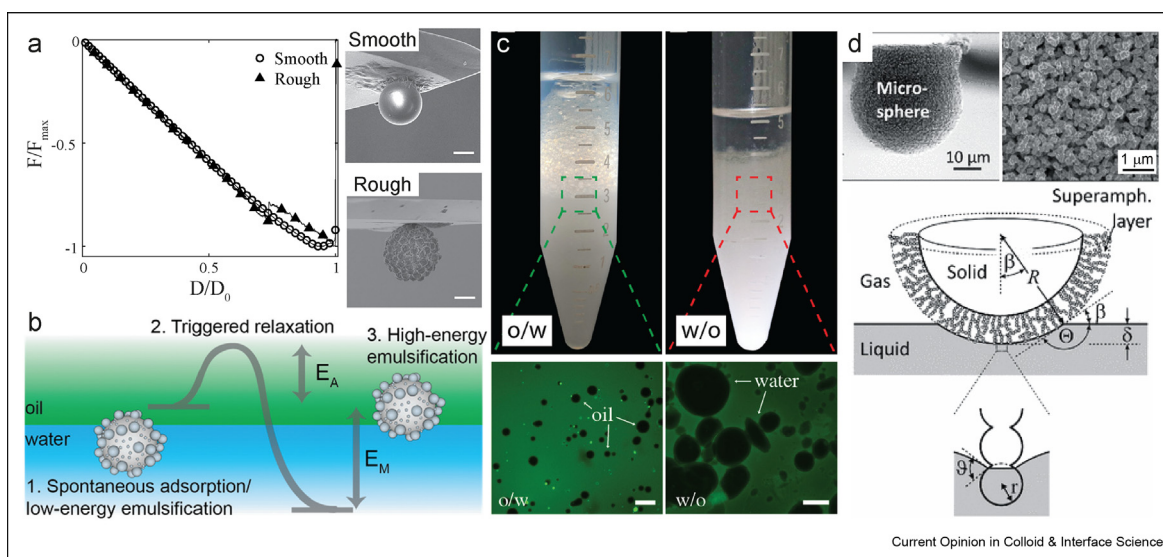
In addition to influencing the way in which we have developed new particle assembly strategies, some of us have directly worked together with Prof. Kralchevsky to extend a theory, originally developed by Scheludko et al. [53], and later expanded by Pitois and Chateau [54] and Chateau and Pitois [55] to fully quantify the detachment of spherical particles from fluid interfaces. In a first publication [39], we developed a detailed theoretical model to interpret the experimental data from colloidal-probe AFM to directly extract (i) the maximal capillary force upon detachment; (ii) the detachment distance, corresponding to the particle displacement relative to equilibrium at the moment when the particle leaves the interface; and (iii) the work for quasistatic detachment. These parameters all relate to the value of the three-phase contact angle θ and its hysteresis, which we measured independently using methods complementary to AFM. In particular, we devised a very accurate closed-form expression for the work for quasistatic detachment for the case of contact-line sliding. Our formulation improves those derived by Pitois and Chateau [54] and Chateau and Pitois [55] in describing the portion of the force–versus–distance curve during the last stages of particle detachment, that is, after the maximal capillary force is overcome and the contact rapidly slides over the particle surface. Our model was experimentally validated by calculating the theoretical force–versus–distance curves without using any adjustable parameters and demonstrating that they closely coincide with the experimental data for a wide range of contact angles.

In a second publication [19], we investigated the detachment of rough particles from oil–water interfaces, singling out the role of surface roughness, and surface chemistry on the nature of desorption. Figure 4a reports typical retraction curves from AFM experiments using a smooth or rough probe detaching from a fluid interface. In general, we observed that for hydrophobic particles, increasing the surface roughness changes the type of detachment mechanism from contact-line sliding to contact-line pinning. The pinning of the contact line induces a change in the shape of the force–versus–distance curve close to the detachment point, where an abrupt detachment takes place upon overcoming the maximal capillary force. Moreover, the presence of surface asperities introduces multiple pinning sites, causing a broad distribution of detachment forces and distances among similar particles. The maximal capillary force correlates with the number of asperities wetted and pinned by the contact line before detaching, as also shown by Ye et al. [18]. Finally, the presence of noise in the force signal during the retraction demonstrates that the contact line does not undergo a single-step detachment but that the particle is dewetted in

several steps, corresponding to the depinning of the contact line from the different surface asperities.

As previously observed [25], rough colloidal probes approaching the interface from the apolar phase are rendered effectively more hydrophobic. These insights have direct implications on the design of colloidal particles with tailored surfaces to control the stabilization and destabilization of Pickering emulsions and foams. In fact, as described in Section 2, the detachment energy of a particle from the interface depends on its cross-sectional area at the interface. Particles presenting surface heterogeneities, that is, topographical or chemical pinning points, may adsorb in metastable positions, different from their equilibrium one, such that an effective protrusion height, and correspondingly a cross-sectional area at the interface, becomes a function of the adsorption conditions. In particular, as we observed using colloidal-probe AFM, the detachment force becomes a function of the force that was applied onto the particle when it adsorbed at the interface. In fact, greater forces may be able to ‘push a particle into the interface’ overcoming contact-line pinning barriers of

Figure 4



a) Normalized force–versus–distance (F – D) retraction curves from colloidal-probe AFM measurements where a smooth (open circles) or a rough silica particle (filled triangles) is pulled away from a hexadecane–water interface. F_{max} is the maximal capillary force during detachment, and D_0 is the detachment distance, that is, the distance at which the particle no longer touches the interface. For the smooth case, contact-line sliding implies that F_{max} is reached before D_0 . In the rough case, contact-line pinning leads to an abrupt detachment at D_0 accompanied by earlier, smaller force jumps associated with partial dewetting. Right: SEM images of the colloidal probes used. Scale bars: $3 \mu\text{m}$. Adapted with permission from the study by Zanini et al. [19]. **(b)** Schematic of the principle for mechanical phase inversion process of Pickering emulsions stabilized by rough particles. E_a is the amplitude of the energy barrier that a pinned contact line must overcome to reach the thermodynamic minimum energy E_m . **(c)** The transition from o/w to w/o emulsions as a function of emulsification energy is obtained using effectively hydrophilic ($\theta \approx 75^\circ$) rough polystyrene particles. Upon stronger agitation, the same emulsion undergoes a catastrophic phase inversion. Scale bars: $20 \mu\text{m}$ left, $100 \mu\text{m}$ right. **(b)**, **(c)** Adapted with permission from the study by Zanini et al. [56]. **(d)** Top: SEM image of a colloid coated with a superamphiphobic layer and corresponding zoomed-in view of the layer’s microstructure. Bottom: schematic of the interaction of a superamphiphobically coated colloid with a fluid interface, showing the contact angle of the nanoparticles in the layer (ϑ) and the macroscopic contact angle (θ). Adapted with permission from the study by Ye et al. [18].

lower magnitude. Translating this concept into processing parameters, higher energy inputs during an emulsification process may bring a higher number of asperities in contact with the interface, thus leading to greater detachment forces, and hence to the improved stability of the resulting emulsion. Conversely, in applications such as oil separation and particle recovery, low detachment forces, which could be achieved by low emulsification energies or tailored surface roughness, would instead be preferred.

Some of us exploited these ideas even further and designed particle surfaces and emulsification processes such that, by controlling the metastability of an effective particle contact angle at the interface, a mechanical phase inversion could be achieved [56] or prevented [57]. For example, by starting with mildly hydrophobic and rough particles dispersed in an aqueous phase and using low emulsification energy, the particles could already be trapped in metastable positions at the interface during the early stages of adsorption (left particle in the scheme of Figure 4b) [56]. Consequently, they only showed little protrusion into the oil, which made them effectively hydrophilic and thus enabled the stabilization of o/w emulsions, contrary to the expectations based on their surface chemistry (Figure 4c, left). At a later stage, a stronger agitation applied to the same emulsion enabled overcoming contact-line pinning (schematically represented by the energy barrier E_A in Figure 4b) and allowed the particles to reach their equilibrium, hydrophobic contact angle, causing an *in situ*, mechanically-driven phase inversion to a w/o emulsion without changing the system composition (Figure 4c, right). Similar *in situ* phase inversion from w/o to o/w was also demonstrated with rough, mildly hydrophilic particles initially dispersed in oil.

Beyond emulsion stabilization, contact-line pinning and the formation of metastable effective contact angles also influences the interaction of surfaces coated with superhydrophobic and superamphiphobic layers with fluid interfaces, being therefore of high relevance for the production of coatings with desired wettabilities. These, typically, are layers composed of aggregated nanoparticles forming a 3D structured surface with characteristic pore sizes. By keeping liquids in a metastable position with air trapped underneath, these layers are used for producing liquid-repellent surfaces. For example, Ye et al. [18] investigated the attachment and detachment of microparticles coated with a superamphiphobic layer to both air–water and air–oil interfaces (Figure 4d). When a liquid wets such a structured surface, it starts by forming a contact line with the outermost nanoparticles and capillary bridges among the nanoparticles are created. These coated colloids are characterized by the material's contact angle (ϑ) of the nanoparticles in the layer and a macroscopic contact angle (θ) of the entire object. For smooth

surfaces, these two values coincide, $\vartheta = \theta$. Instead, on coated surfaces, the formation of microscopic contact angles precludes further contact between the liquid and the colloid, resulting in very high apparent contact angles. Interestingly, in the case of interactions with interfaces having very low γ , such as air–oil, the liquid can enter in between the nanoparticles, wetting the coating, and precluding its superamphiphobic properties. This happens when the capillary pressure exerted by the liquid overcome the critical depinning pressure (which depends on the distance between the surface asperities) and therefore wets the internal nanoparticles [18].

Conclusions

With this topical review, we have attempted to highlight and emphasize the importance of some of the achievements by Prof. Kralchevsky. In addition to their role in contributing to shape a broad research field from the early 90s to date, these results have implications for potential future developments. Here, we describe some of them, which we personally find particularly exciting.

Bijels (or bicontinuous interfacially jammed emulsion gels) [58] are a special class of Pickering emulsions, where the phase separation between two liquids undergoing a spinodal decomposition is arrested by particle adsorption onto the growing fluid interface. These materials are particularly promising as catalytic supports encompassing a very large surface area and would moreover allow continuous feeding and exchange between the liquid phases. Since their conception more than a decade ago, bijels typically suffered from limited mechanical stability and required a delicate balance of the particle and fluid properties to be realized. Central to their performance is in fact the capability of colloidal particles to stabilize liquid–liquid interfaces with a very broad range of curvatures (both positive and negative) and control the kinetics of the stabilization to obtain materials with uniform structure and, therefore, properties. An exciting recent development by Haase et al. [59] has shown that, through controlled solvent extraction from a ternary mixture and using silica particles modified *in-situ* by the adsorption of an oppositely charged surfactant, large-scale, mechanically robust bijels with a high degree of structural control can be produced in a continuous fashion. This approach opens up new opportunities, such as efficient catalysis and reactive separation for chemical reactions [60], where we expect to see rapid progress in the near future. We remark that harnessing particle attachment/detachment and tuning electrostatic adsorption barriers are the key steps to enable these processes.

The last two decades have also seen the development of more 'exotic' objects originating from the covering of liquid interfaces with particles, such as liquid marbles [61]: liquid drops coated by solvophobic particles. Such

objects allow the encapsulation of various solutions into drops in a perfectly non-wetting state, with a dramatically reduced adhesion to solid or liquid surfaces. This permits their transport with much lower forces than the one required to transport wetting liquids [62]. They have been extensively studied for their intriguing physical properties, as easily programmable micro-reactors for chemical synthesis, and for the fabrication of novel materials [63–65]. Controlling particle adsorption and surface coverage is of fundamental importance when producing liquid marbles because it both governs the interaction between the drops and their surroundings, and it affects their lifetime and ability to exchange material with neighboring marbles or the surrounding fluid through the voids between the adsorbed particles.

Capillarity-driven assembly has recently seen a resurgence in interest for a broad research community working in the field of micro and nano-patterning, especially in relation to the top-down integration of multiple materials in controlled structures [47]. The strength of this approach lies in exploiting capillary forces generated by particle detachment to drive the assembly of multi-material structures without the need for chemical specificity. Very recent developments have shown that even soft hydrogel particles can be successfully co-assembled with mechanically rigid organic or inorganic colloids by capillarity [52]. This offers exciting opportunities to fabricate complex, responsive microstructured materials for a tantalizing range of applications revolving around the transport and manipulation of matter at small length scales using external stimuli, with the vision of downscaling soft robotic systems to the colloidal scale.

As the last example, controlling the pinning of solid particles at fluid interfaces can be used as an effective way to arrest coalescence and engineer the rheological properties of complex interfaces, as elegantly shown for the case of particle-stabilized bubbles [66]. Given that many naturally occurring particles have highly irregular and heterogeneous surfaces, it seems to us that a vast range of opportunities exists to engineer or even just select, systems that fulfill generic criteria leading to a desired stabilization effect. In particular, inspired by the findings of Prof. Kralchevsky *et al.*, we hypothesize that the combined effect of a broad range of different surface heterogeneity characteristics, such as, roughness, topography, chemical heterogeneities, and so on, could be grouped together by a single parameter, that is, the energy pinning the contact line. This will help rationalize new strategies for the fabrication and optimization of interface-dominated materials fabrication, as in the case of emulsions and foams. Here, identifying generic design principles may lead to a simplification of the formulations used for a broad range of products and processes, toward more sustainable use of particle systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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