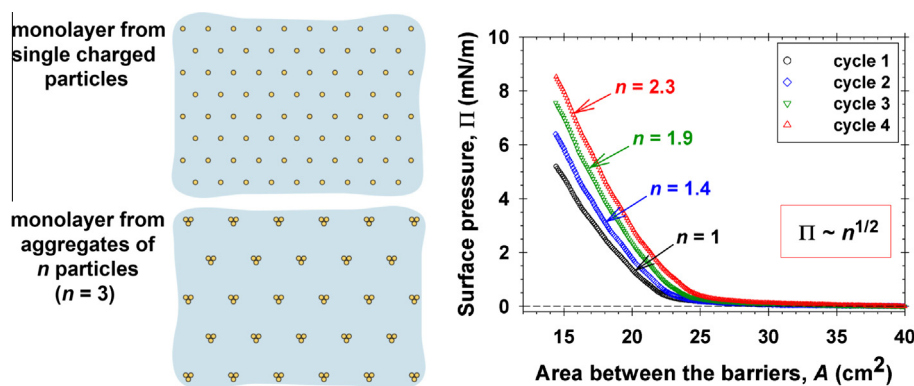# Monolayers of charged particles in a Langmuir trough: Could particle aggregation increase the surface pressure?

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GRAPHICAL ABSTRACT

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ABSTRACT

The effect of aggregation on the surface pressure, Π, of monolayers from charged micrometer-sized colloidal particles on the air/water interface is investigated. Π is completely due to the long-range electrostatic repulsion between the particles mediated by their electrostatic field in the air. The most probable origin of particle aggregation is the attraction between capillary quadrupoles due to undulated contact lines on particle surfaces. Aggregates have higher charge and repel each other stronger than single particles. The data analysis by means of a theoretical model implies that Π linearly increases with $n^{1/2}$; n is the mean aggregation number, which can be determined from the experimental Π vs. area curves. The presence of electrolyte promotes aggregation, which tends to increase Π, but simultaneously reduces the surface charge that leads to lower Π. For our system, the first effect prevails and apparently paradoxical behavior is observed: the addition of salt in water enhances the electrostatic surface pressure. The data indicate limited aggregation: the rise of the electrostatic barrier prevents the further coalescence of aggregates if they have become sufficiently large. The results contribute for a better understanding of the factors that control the interactions in monolayers of charged particles at liquid interfaces.

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1. Introduction

Non-densely packed monolayers from charged micron-sized particles on a liquid interface [1–3] have been investigated in view of their potential use for producing micro-patterned surfaces with applications for antireflective and superhydrophobic coatings [4–8], micro-lens arrays [9,10], structures in biosensing and bio-engineering [11,12], and in relation to their importance for the interactions in Pickering emulsions [13–18], and for the phase-transfer catalysis [19,20]. The surface pressure isotherms for monolayers from charged particles have been studied

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experimentally and theoretically for colloidal spheres at oil/water [3,21,22] and air/water [2,23] interfaces. Because the interparticle distances in such monolayers are of the order of several micrometers, i.e. much larger than the Debye length in the aqueous phase, the electrostatic interaction between the particles happens across the nonpolar fluid (air, oil). This interaction can be due to charges located at both the particle/water [24–29] and particle/nonpolar-fluid [3,13,15,30–38] interfaces. One possible origin of the electric charge at the particle/nonpolar-fluid interface can be the preferential adsorption of H^+ or OH^- ions from dissociated H_2O molecules in the atmospheric air [38–41] during the procedure of particle hydrophobization.

In experiments with optical tweezers, it was established that the effect of different hydrated counterions, Na^+, Rb^+ and Mg^{2+}, on the electrostatic repulsion between two particles at the oil/water interface is relatively weak [29,42]. Particle aggregation in monolayers of charged particles has been also observed and investigated [3,15,21,31]. Surface pressure isotherms with charged microgel particles at the oil/water interface have been measured, and it was concluded that the results are affected by the different shape and size of the microgel particles in their charged and uncharged states at the interface [43]. The effect of external uniform electrostatic field on uncharged [44] and charged [45] dielectric particles at a liquid interface was theoretically investigated.

From theoretical viewpoint, a particle of uniformly distributed surface charges, which is attached to a water/nonpolar-fluid interface, creates electric field that has a dipolar asymptotics. The force of electrostatic repulsion between two such particles (parallel dipoles) is [3,24–26]:

$$F_{ER} = \frac{3p_d^2}{2\varepsilon_n L^4} \quad (L \gg r_c, \kappa^{-1}), \tag{1}$$

where L is the center-to-center distance between the two particles; r_c is the radius of their contact lines; κ is the Debye screening parameter; ε_n is the dielectric constant of the nonpolar fluid

(air, oil); p_d is an effective dipole moment. The factor 2 in the denominator of Eq. (1) accounts for the fact that the dipolar field occupies only the upper half-space (the nonpolar fluid), whereas the electric field in the aqueous phase is screened by the ions in water.

If the charges are located at the *particle/nonpolar-fluid* interface (Fig. 1a), then the effective dipole moment p_d is [33]:

$$p_d = 4\pi\sigma \, D(\alpha_c, \varepsilon_{pn})R_p^3 \sin^3 \alpha_c \tag{2}$$

R_p is the particle radius, α_c is a central angle ($\sin\alpha_c = r_c/R_p$; for small deformations in the liquid interface created by the floating particle, we have $\alpha_c \approx \theta$, where θ is the contact angle); σ is the electric charge density at the particle/nonpolar-fluid interface; $D = D(\alpha_c, \varepsilon_{pn})$ is a known dimensionless function, which can be calculated by means of Table 1 and Eq. (D.1) in Ref. [33]; $\varepsilon_{pn} \equiv \varepsilon_p/\varepsilon_n$ is the ratio of the dielectric constants of the particle and nonpolar fluid.

If charges are located at the *particle/water* interface (Fig. 1b), then the effective dipole moment p_d can be estimated from the expression [25,26,28,29]:

$$p_d = \frac{4\pi\varepsilon_n \sigma_{pw}R_p^2(1 + \cos\alpha_c)}{\varepsilon_w \kappa}, \tag{3}$$

where ε_w is the dielectric constant of water; σ_{pw} is the electric charge density at the particle/water interface, and κ is the Debye screening parameter. Correspondingly, p_d given by Eq. (3) decreases upon the addition of electrolyte in the aqueous phase, whereas p_d expressed by Eq. (2) should be insensitive to the concentration of electrolyte in the water. Experimentally, this was observed with 1 μm sized silica particles at the octane/water interface – salt concentrations up to 1 M NaCl in the aqueous phase did not alter the interparticle distances [13]. In general, p_d might be a superposition of the contributions expressed by Eqs. (2) and (3). This superposition could be a sum or difference depending on whether the aforementioned two dipole moments have parallel or antiparallel orientation.
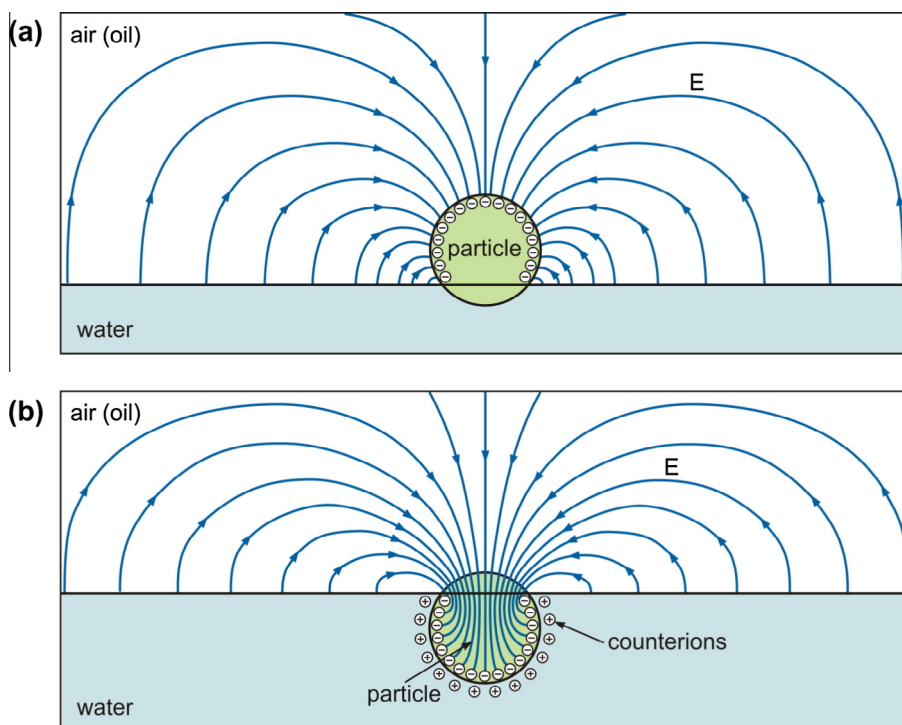

Fig. 1. Possible sources of the electric field in the nonpolar fluid (air, oil): (a) charges at the particle/nonpolar-fluid interface; (b) charges at the particle/water interface; their field can be weakened because of the effect of counterions in the aqueous phase.