LETTER TO THE EDITOR

Formation of meso-structures in colloidal monolayers

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Abstract. The spontaneous formation of loosely bound ordered aggregates has been observed in colloidal monolayers trapped at the air/water interface. The distance between particles in these meso-structures is of the order of the particle radius, implying that the colloidal interaction potential has a minimum at such distances. This is inconsistent with accepted theory. Possible connections with recent suggestions of hitherto unexpected attractive contributions to the pairwise interaction potential for bulk colloidal systems are discussed.

Colloidal systems have attracted much recent interest as models for diverse phenomena in condensed-matter physics [1]. In particular, monolayers of colloidal particles supported at a water/air interface have been used in many experimental studies of matter restricted to essentially two dimensions. These have included cluster–cluster aggregation [2–4], two-dimensional melting [5] and crystallite formation [6]. Very recently it has been reported that in some cases colloidal monolayers can spontaneously form loosely bonded, but ordered clusters and other structures [7]. These differ from the clearly crystalline arrays found by Onoda [6] in that there are spaces between the constituent particles and line tension is evident in the tendency to form circular arrays. We have independently observed similar phenomena, although our observations differ somewhat from the earlier report [7], as does our interpretation.

We believe that these observations support a quite separate current development [8, 9]: the challenge on several fronts to the accepted DLVO theory of colloidal interactions [10]. It has been suggested that relatively long-ranged attractive interactions may arise between like-charged colloids [9, 11]. In particular, several recent studies have inferred that when two colloidal particles are near to a solid object the inter-particle potential parallel to this 'wall' has a long-ranged attractive component which is absent when the particles are further from the wall [8, 12]. This is, we believe, indirectly relevant to our observations.

The colloidal particles used were polystyrene (sulphate) latex spheres of nominal diameters 0.949 ± 0.010, 2.836 ± 0.136 and 5.00 ± 0.15 μm (Polysciences Incorporated). The nominal surface charge density of these particles is $\sim$1 μC cm^{-2}. After thorough rinsing to remove water-soluble ions and adsorbed surfactants the particles were resuspended in methanol. Measured volumes of this suspension were slowly and carefully dispensed on to the surface of a 5 mm deep aqueous subphase (water from a Millipore Milli-Q system) contained in a rectangular glass trough, forming stable colloidal monolayers on the water surface.

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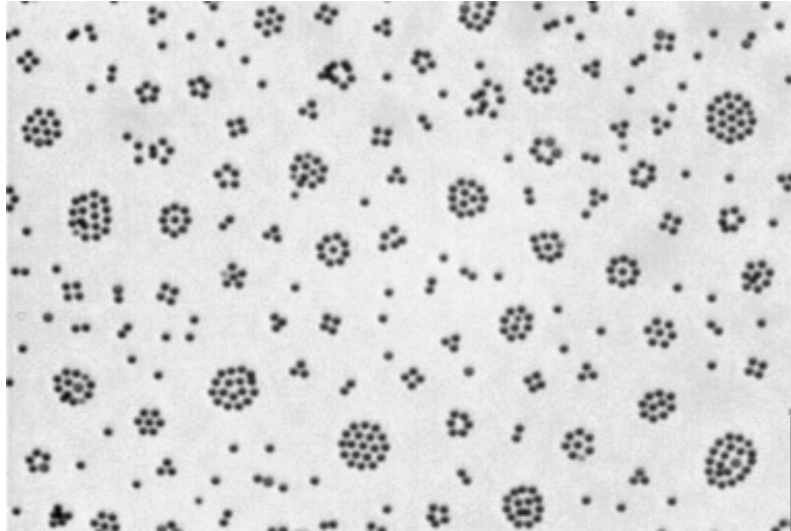
(a)
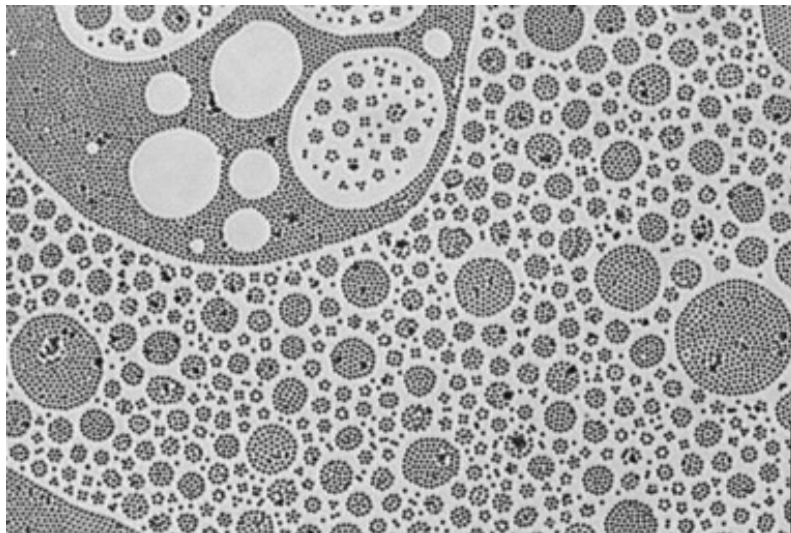
(b)

Figure 1. Two video-micrographs of monolayers of 3 μm colloidal particles containing spontaneously generated meso-structures: (a) clusters from dimers to examples containing of order 20 particles; (b) larger and more complex structures. The vertical bars in one corner of each micrograph indicate scale: 50 μm (a); 100 μm (b).

The glass trough, enclosed in a brass and perspex box to provide environmental isolation, was placed on the stage of an inverted microscope equipped with a video camera. Images could be directly grabbed for immediate analysis or recorded for subsequent playback.

In the only previous report [7] of phenomena such as those we find, it was reported that while fluorescent particles formed such structures, normal non-fluorescent particles did not. We have only used normal polystyrene particles, and find that ordered structures do occasionally form naturally, although their formation can be promoted by application
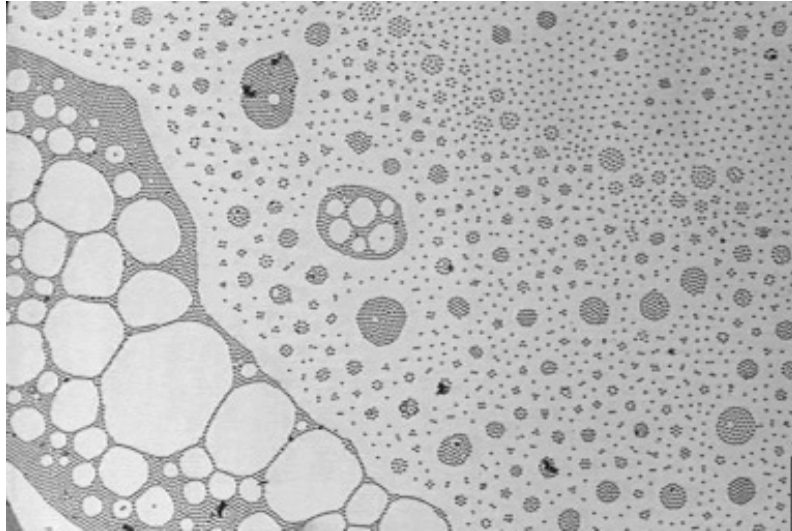
Figure 2. An example of more complex structure in a 3 μm particle monolayer, at lower magnification than in figure 1. The main meso-structure resembles the 'foam' structures previously reported [7]. The vertical bar in one corner of the micrograph indicates 100 μm.

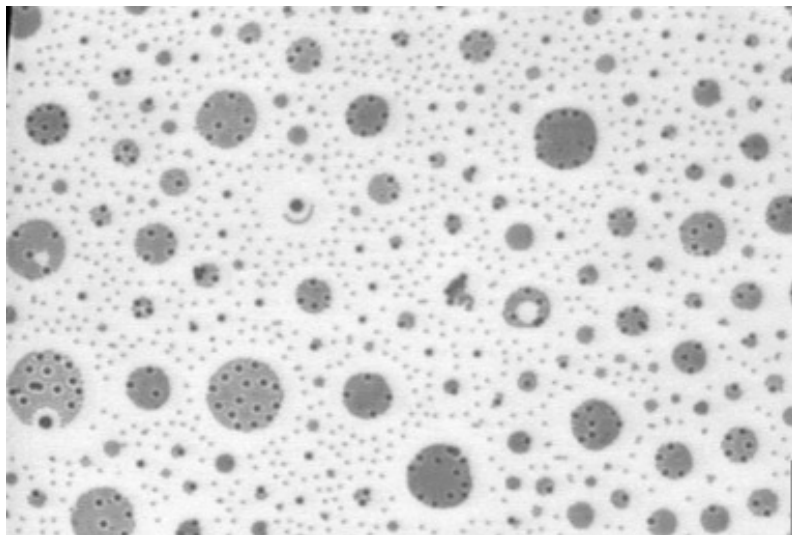**Figure 3.** An example of meso-structure formation in a mixed monolayer, comprising 1 μm particles with a smaller number of 3 μm and a very few 5 μm lattices. The grey areas are unresolved meso-structures of 1 μm particles, in which the inter-particle separation is $\sim 3R$. While this separation is not visible here, the depletion zones around the larger particles are readily apparent. The vertical bar in one corner of the micrograph indicates 50 μm.

of negative ions to the colloidal monolayer. We restrict ourselves here to those ordered structures which formed spontaneously as the monolayer was formed.

Figures 1 to 3 show typical examples of the types of structure which we observe, including ordered arrays of particles, as well as what may be described as 2D 'foam' [7].

To distinguish such ordered structures from the random, fractal objects formed in colloidal aggregation processes [2–4], commonly called clusters, we propose the name 'colloidal meso-structures' for them. In our experiments there are always a range of sizes present, from dimers to large structures. However they are formed, the meso-structures are at best metastable, dispersing over periods of the order of several hours to leave a homogeneous monolayer in a quasi-regular triangular array. This metastability implies a minimum in the inter-particle potential, deeper than kT, which is absent from conventional theory [10].

In our experiments colloidal meso-structures spontaneously form in monolayers of 2.8 μm polystyrene particles. In a very restricted set of trials this did not appear to be the case for 0.95 μm spheres. However, in monolayers comprising 0.95 μm particles with small admixtures of larger particles we do observe the formation of meso-structures, not all of which contain larger particles (figure 3). Larger particles in a meso-structure mainly comprising 0.95 μm particles are surrounded by a gap of width about the radius of the larger particles. These observations suggest that the underlying effect grows with particle size.

A feature which is common to all colloidal meso-structures is the significant separation between the constituent particles, typically about the particle radius R, which is also apparent in previous work [7]. The observations clearly indicate that there must be some comparatively long-ranged attraction acting between like-charged colloidal particles trapped at an air/water interface. It is the unbalanced excess of this attraction at the edges of the observed meso-structures which provides the necessary stabilizing line tension.
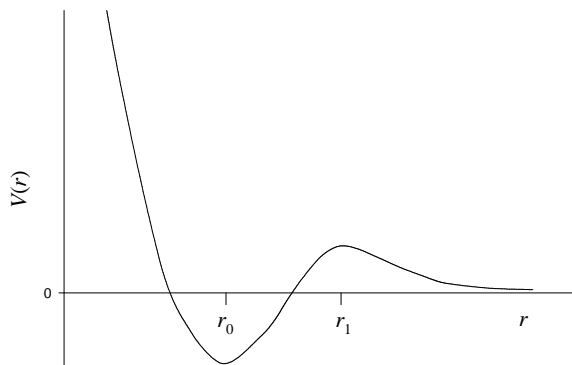

Figure 4. A schematic indication of the postulated form of the inter-particle potential for colloidal particles trapped at a water/air interface. The primary minimum is suppressed for simplicity. The secondary minimum occurs at $r_0 \sim 3R$.

The observations are consistent with an inter-particle potential (sketched in figure 4) which has a minimum at $r_0 \sim 3R$, some few kT lower than a maximum at r_1 ($>r_0$). In the final equilibrium state of the monolayer the particle separations r are greater than r_1 and the monolayer forms a relatively stable quasi-crystalline array, reflecting the long-range repulsion. The barrier at r_1 cannot be very high, as the metastable meso-structures disaggregate on timescales of the order of hours. The process of spreading the monolayer is quite turbulent, and the particles may be forced to approach each other quite closely, passing over the potential barrier to become temporarily trapped in the secondary minimum at r_0.

We consider the established pairwise interactions between colloidal particles of radii $R_{1,2}$ and (surface) charge $Z_{1,2}$, at a centre-to-centre separation r in the air/water interface.

They include attractive van der Waals and capillary forces, as well as repulsive electrostatic forces.

(1) The attractive van der Waals potential is well known [13] and can be approximated as

$$V_{\text{vdW}}(r) = -\frac{A}{6(r - R_1 - R_2)} \frac{R_1 R_2}{(R_1 + R_2)} \tag{1}$$

where A is the Hamaker constant. In computations an exact expression [13] was used rather than this approximation.

(2) The capillary attraction reflects the lowering of the gravitational potential as one particle descends the dimple in the liquid surface caused by a second particle:

$$V_{\text{cap}}(r) \propto -\gamma R_1^3 R_2^3 S(\theta_1) S(\theta_2) K_0(\lambda r) \tag{2}$$

where γ is the surface tension of the fluid, $\lambda = \sqrt{(\rho_l - \rho_v)g/\gamma}$ defines the capillary length λ^{-1} and $S(\theta)$ is a function of the water/air/latex contact angle [14]. $K_0(x)$ is a modified Bessel function. This capillary potential is rather long ranged, decaying over distances typified by λ^{-1}, which for water is ~ 2.7 mm.

(3) A charged particle at an interface and its (asymmetric) screening Debye cloud of counter-ions constitute an electric dipole [15]. Neighbouring dipoles interact through the water and also through the air, yielding a total electrostatic potential [15]

$$V_{\text{el}}(r) = \frac{2Z_1 Z_2 e^2}{4\pi \varepsilon_0 \varepsilon r} \left(\frac{\varepsilon^2}{\varepsilon^2 - 1} e^{-\kappa r} + \frac{1}{\varepsilon \kappa^2 r^2} \right) \tag{3}$$

where κ is the inverse of the Debye length. This expression is for a point charge, so the exponentially decaying portion, reflecting the screening of the charge on the particle, strictly requires correction for a particle of finite radius. However, at values of $r - R_1 - R_2$ significantly greater than κ^{-1} (~ 60 nm in our experiments, due to dissolution of CO_2 in water exposed to air [16, 17]) the second term in equation 3 ($\propto r^{-3}$) must be completely dominant.

The variations with particle size of these contributions to the total potential differ significantly. For two particles of like size, the van der Waals contribution is $\propto R$, the electrostatic potential is $\propto R^4$ and the capillary potential is $\propto R^6$.

Figure 5 shows the magnitudes of these three potentials, for the particular example of 3 μm particles of surface charge density 1 μC cm^{-2}, and using values of $3kT$ for the Hamaker constant [13] and 170° for the contact angle (which maximizes the capillary attraction). Note in particular that the van der Waals attraction never exceeds the electrostatic repulsion. For r just above $2R$ the electrostatic potential should actually be greater than is shown, due to the inappropriate first term of equation (3). However, the relevant point is the inability of the van der Waals and electrostatic potentials to yield a secondary minimum at an inter-particle separation of the order of $3R$. Similarly, any secondary minimum due to the capillary attraction would necessarily lie at very large r and be very small compared to kT.

We conclude that no combination of the accepted forces acting between colloidal particles trapped at a water surface can explain the present observations. This conclusion differs from that reached by Ruiz-Garcia *et al* [7], who implicated competition between van der Waals and electrostatic forces. A further argument against this conclusion is the size dependence of the present effects: the smaller the particles the harder it appears to be to form meso-structures (see above and [7]). This is exactly the opposite of what would be expected from competition between the van der Waals and electrostatic forces, as for
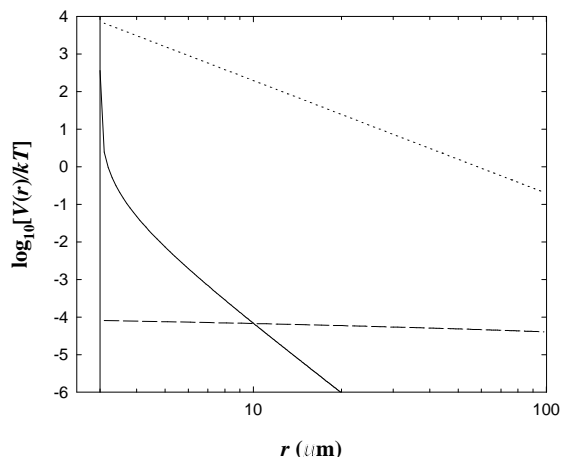
Figure 5. The absolute values of the van der Waals (solid), electrostatic (dotted) and capillary (dashed) potentials for 3 μm polystyrene spheres (the vertical line indicates $r = 2R$). The electrostatic force is repulsive, and the others are attractive. See the text for a discussion.

example when R is halved the electrostatic force is reduced relative to the van der Waals force by a factor of 8. These conclusions are based on pairwise interactions, ignoring any many-body effects. In practice such effects are unlikely to be significant, as increases of several orders of magnitude in the Hamaker constant or the capillary attraction would not provide the requisite long-ranged minimum in $V(r)$.

Colloidal meso-structures thus require an attractive contribution to the inter-particle potential which is longer ranged that the van der Waals force and stronger than the capillary interaction. It is helpful to briefly review several recent studies of three-dimensional colloidal suspensions [11, 8] in which essentially similar conclusions have been reached. It has been shown theoretically [9] that such attractions, with a minimum potential lying at some 3–6R, may arise in 3D from purely electrostatic effects, due to the periodicity of the arrangement of the colloidal particles and the counter-ions. This attraction increases with particle charge and suspension density, while it decreases with electrolyte concentration. Direct observations [8, 12] have shown that in the vicinity of a solid 'wall' the component of the inter-particle colloidal interaction parallel to the wall has an attractive component when the particles are within some 3 μm of the wall. This has been interpreted in terms of an electrostatic mechanism mediated by perturbation by the macro-ions of the atmosphere of counter-ions about the wall, the exact picture being rather uncertain, but perhaps somewhat as suggested by Chu and Wasan [9].

We believe that something similar underlies the present colloidal meso-structures. The water/air interface will have an associated cloud of ions, which will be perturbed by the latex particles, which here lie actually *in* the interface. This may well lead to attractive electrostatic effects, in the same fashion as suggested for the solid/liquid case [12, 8].

Fluorescent latex particles, which apparently form meso-structures more easily than normal ones [7], can have surface charge densities $\sim$100$\times$ greater than for normal particles (Molecular Probes, data sheets). In the mechanism sketched here, this would increase the perturbations of the counter-ions at the water surface, presumably increasing the magnitude of the attractive potential (cf. [9]). (The only other difference for fluorescent particles might be in the three-phase contact angle, affecting the capillary forces, but these are too weak to

be relevant.) The apparently greater effects that we observe for larger particles (apparent also in [7]) would be comprehensible in terms of the above mechanism.

In summary, we have independently observed the spontaneous formation of loosely bound, ordered aggregates of colloidal particles trapped at the air/water interface. While this confirms previous work [7], in our experiments such structures formed for normal, non-fluorescent particles. These observations appear to be inconsistent with the accepted theory of colloidal interactions [10], requiring a comparatively long-ranged attraction such as has recently been postulated [8, 9, 12].

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