

Wetting-Induced Aggregation of Colloids

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More than two decades ago, in a seminal paper John Cahn proposed scaling arguments for the possibility of a wetting transition in two coexisting fluid phases near the critical point. Since then, Cahn's model has been tested in many fluid systems and further refined by including the real interactions between the fluid and the solid wall. A fascinating consequence of the existence of a wetting transition is the possibility for a transition from weak to strong adsorption in the homogeneous phase. The situation is further enriched in nonstandard geometries having special geometrical constraints. The subject of this review concerns one such situation, where charge-stabilized colloidal particles are suspended in the homogeneous region of a binary liquid mixture. In this case, the preferential adsorption of one of the liquid components on to the colloid surface completely modifies the stability of the particles leading to an aggregation process. Although the exact mechanism underlying the adsorption phenomenon is still debated, it is closely related to the wetting transition. Recent experimental developments concerning the static and dynamic aspects of this phenomenon are reviewed. In addition, the main findings of a theoretical model based on the adsorption-modified electrostatic interactions between the colloidal particles are discussed.

KEY WORDS: Adsorption; aggregation; colloids; interfaces; wetting.

1. INTRODUCTION

The interest in the wetting behavior of fluids near the critical point was first recognized by Cahn in a seminal paper published more than two decades ago.⁽¹⁾ Since then the phenomenon of transition from partial to complete wetting has been widely studied for a fluid in contact with a planar substrate.⁽²⁻⁴⁾ Additional features appear in non-planar geometries, such as in

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spherical or cylindrical geometries.^(5,6) However, an interface bound to a spherical or cylindrical substrate cannot grow infinitely because the resulting increase in the surface area leads to a diverging positive contribution to the surface free energy of the system.⁽⁴⁾ This means that the complete wetting as depicted in the original model of Cahn⁽¹⁾ does not occur in spherical or cylindrical geometries and it is replaced by a transition from a weak to strong adsorption reminiscent of prewetting transition for a planar substrate.⁽⁶⁾ In curved geometries, further complications arise due to capillary condensation—the unfavorable growth in the surface area can be reduced by the formation of a liquid bridge between the neighboring substrates.^(7,8)

2. FIRST OBSERVATION

Spherical colloidal particles suspended in a binary liquid mixture are an interesting candidate for wetting in curved geometry.⁽⁹⁾ Here the colloids are stabilized by an electric double layer emanating from the ionizable surface groups. Two new features can arise in this case. Unlike for the planar substrate, the walls themselves are movable in this case, hence a fluid bridge can be formed between the particles as they approach each other by brownian motion.⁽⁸⁾ The adsorbed fluid layer can modify the electrostatic forces stabilizing the suspension.⁽⁹⁾ This scenario was first

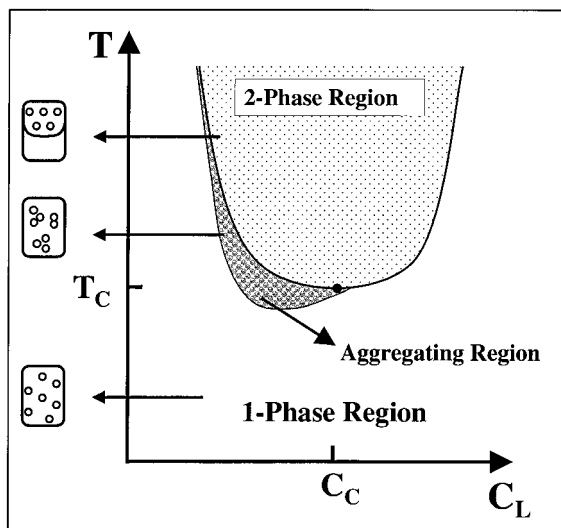


Fig. 1. The schematic phase diagram of 2,6-lutidine and water mixture containing small amounts of silica colloids. Here C_L is the bulk lutidine concentration (weight fraction), with $C_c \approx 0.29$ and $T_c \approx 34^\circ\text{C}$.

investigated by Beysens and Estève for Stöber silica colloids suspended in the binary mixture of 2,6-lutidine (L) and water (W).⁽¹⁰⁾ They observed an aggregation of colloidal particles as the temperature is varied towards the coexistence temperature (T_{CX}) of the host mixture in the homogeneous phase. This aggregation occurs at a well defined temperature (T_A) and is reversible. It is preceded by a strong increase in L-adsorption as measured by light scattering (turbidity).^(10, 11) In the phase diagram as depicted in Fig. 1, the aggregating region which lies on the W-rich branch is demarcated by a line of T_A 's beneath the two-phase region. A similar behavior was noticed when quartz powder was used instead of silica colloids.⁽¹¹⁾ However, in this case the aggregation occurs on the L-rich side of the phase diagram.

Subsequent investigations have confirmed that this aggregation is a consequence of a preferential adsorption of one of the liquid components on to the colloid surface.⁽¹¹⁾ Figure 2 shows the increase of sample turbidity (τ) as the bulk coexistence region is approached. For a given bulk lutidine concentration (C_L), prior to particle aggregation, τ varies with the adsorbed layer thickness (l), $\tau \sim 1 + 6(l/a)$, where a is the radius of bare particles.⁽¹⁰⁾ Figure 3 displays a macroscopic manifestation of L adsorption on to silica particles. This preference can be varied, for instance L is preferentially adsorbed on to silica colloids while the trend is exactly opposite for quartz powder where W is preferentially adsorbed. A similar effect was noticed by

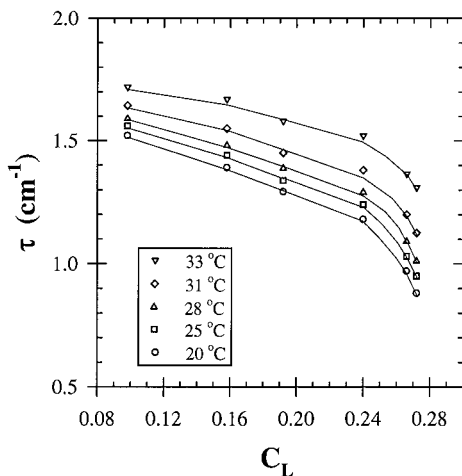


Fig. 2. The behavior of adsorbed 2,6-lutidine (L) layer on Stöber colloids (SiO_2) immersed in a mixture of lutidine and water at various temperatures for different bulk L concentrations (weight fractions), C_L 's.

Van Duijneveldt and Beysens, when a small amount of $\text{Mg}(\text{NO}_3)_2$ was added to the dilute silica colloidal suspension in LW.⁽¹²⁾ The added Mg^{2+} ions suppressed L-adsorption and eventually reverted to W-adsorption. Gallagher *et al.*⁽¹³⁾ noticed an analogous behavior using polystyrene latex particles in LW mixture. For high surface charge densities, the aggregation occurred on the L-rich side of the phase diagram corresponding to W adsorption. In contrast, the aggregation took place on the W rich side when latex particles of relatively low surface charge density were used. At coexistence, the particles nearly partition to the preferred phase below a wetting temperature (T_w) for the dispersed particles.⁽¹³⁾

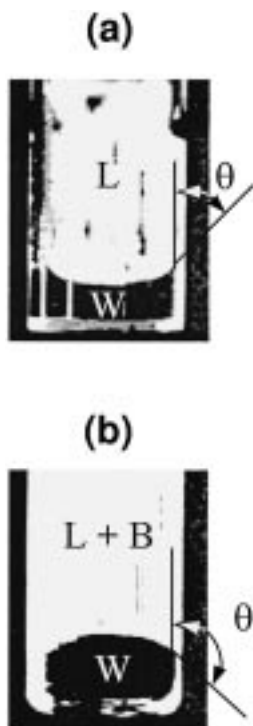


Fig. 3. Macroscopic manifestation of the 2,6-lutidine (L) adsorption on to Stöber silica colloids immersed in a 2,6-lutidine and water (W) mixture (LW). (a) Glass tube filled with LW mixture above the bulk coexistence (L weight fraction, $C_L = 0.40$, and $T = 40^\circ\text{C}$). The W-rich phase is at the bottom and it wets the tube wall as indicated by the meniscus directed upwards. (b) After Stöber silica colloids (B) were suspended, the meniscus inverts and becomes directed downwards, because the L-rich phase wets the colloids which are stuck on to the wall.

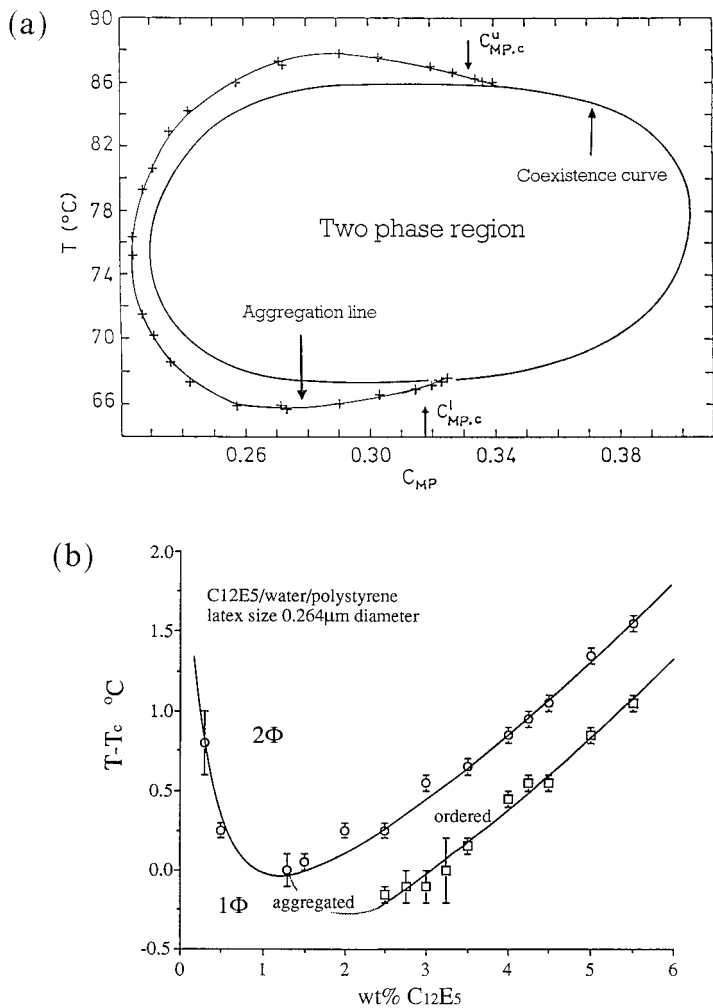


Fig. 4. Examples of flocculation curves for (a) Stöber silica colloids suspended in 3-methyl pyridine (MP), water (W) and heavy water (HW) mixtures.⁽¹⁴⁾ Here C_{MP} is the bulk MP concentration by weight. (b) Polystyrene latex particles in mixtures of non-ionic surfactant $\text{C}_{12}\text{E}_{15}$ and water⁽¹⁸⁾ (reproduced with permission). Regions marked by 1 Φ and 2 Φ correspond to respectively the homogeneous and coexisting phases of the binary mixture, and in the ordered region colloidal aggregates form a polycrystalline phase.

3. GENERALITY OF THE DESTABILIZATION PHENOMENON

Further experiments spanned over the last decade have revealed that this aggregation phenomenon is a general feature among many binary liquid mixtures and different colloids (Figs. 4a and b). For small concentrations, silica colloids aggregate in a similar way as in LW mixture for a variety of binary systems; isobutyric acid + water,⁽¹³⁾ reentrant ternary mixture of 3-methylpyridine, water and heavy water,⁽¹⁴⁾ surfactant 2-butoxyethanol (C_4E_1) and water,⁽¹⁵⁻¹⁷⁾ etc. Nearly identical behavior has also been noticed using polystyrene latex particles.^(13, 18)

More recently, the behavior at high colloid concentrations has been interpreted as a ternary phase separation.^(15, 16) In this picture, the aggregation phenomenon has been termed as a gas-liquid transition for colloids. On this basis equilibrium phase boundaries and critical lines have been constructed.

4. THE FLOCCULATED PHASE

There have been several attempts to characterize the flocculated phase. Gurfein *et al.*⁽¹¹⁾ deduced the average distance between particles to be 3 times the average particle radius. This revealed that the particles do not come in direct contact during the aggregation. In addition, they noticed that the flocculated phase is iridescent when viewed by white light suggesting that this phase consists of randomly oriented colloidal crystallites. Koehler and Kaler⁽¹⁸⁾ studied this aspect in detail in the C_4E_1 and water system with polystyrene latex spheres. They noticed an angle dependent colors (with a polychromatic light) typical of diffraction from colloidal crystals. The color pattern is determined by the size of the colloidal particles (which determines the lattice parameter). As expected, the rate of crystallization increased with colloid concentration. The crystalline diffraction is marked by a peak in the scattered light intensity. The crystallization kinetics was followed by monitoring the time dependence of the peak position, though a clear distinction between FCC or BCC type structure could not be discerned.

5. AGGREGATION AND FRAGMENTATION KINETICS

The kinetics of aggregation⁽¹⁹⁾ and the reverse process of fragmentation⁽²⁰⁾ have been studied in the dilute system of silica colloids in LW mixture. The structure factor as measured by light scattering has a squared lorentzian form with the scattered intensity $I(q)$,

$$I(q) = \frac{I_0}{(1 + q^2 R^2 / 10)^2} \quad (1)$$

where $I_0 \propto \bar{M}$, the average cluster mass) is the intensity at scattering wave vector (q) = 0 and R is the average cluster radius. The time evolution of \bar{M} and R have the form, $\bar{M} \sim t$ and $R \sim t^{1/3}$ (Fig. 5), which is in accordance with the diffusion limited aggregation.⁽¹⁹⁾ However, the measured aggregation rates were much larger than that possible by purely diffusive motions of the colloids indicating strong attractive interactions between the particles. In addition, the measured structure factor showed Porod behavior ($S(q) \sim q^{-4}$) which corresponds to a compact morphology of the aggregates. This observation further strengthened the argument that within an aggregate, the colloids are embedded in an index matched matrix of L. The dynamics of fragmentation⁽²⁰⁾ is determined by the limiting processes of particle diffusion and L desorption. When the system is relatively close to T_A , the L desorption is the rate limiting factor. In the desorption limited case, $I(q)$ has the same form as in Eq. (1), with $\bar{M} \sim 1/t$ and $R \sim 1/t^{1/3}$ (Fig. 6). When the system is quenched sufficiently below T_A , the desorption

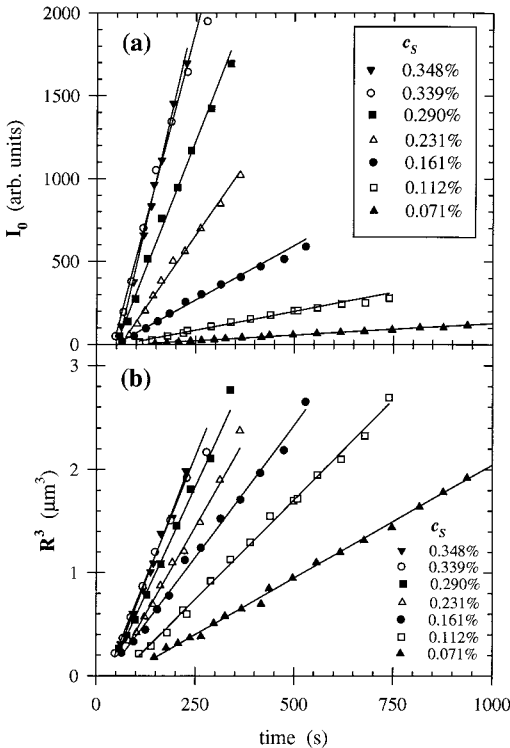


Fig. 5. Aggregation kinetics: time evolution of (a) I_0 and (b) mean radius (R) of aggregates for different colloid concentrations, c_s (weight %).

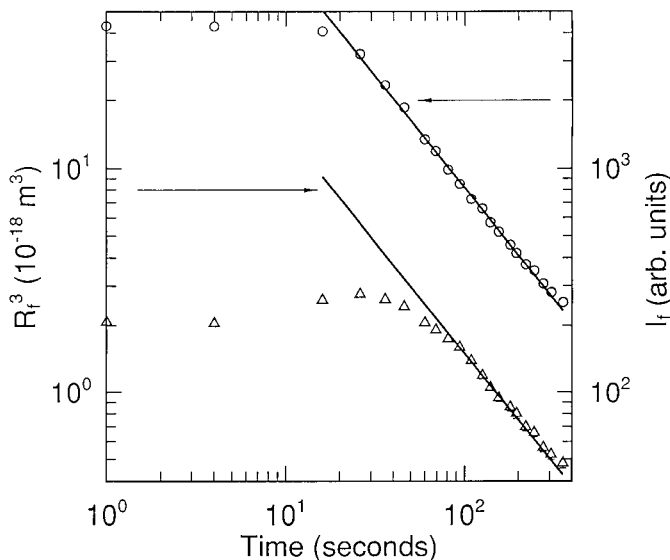


Fig. 6. Fragmentation kinetics: time variation of average fragment mass, I_f (\circ) and radius of gyration, R_f (Δ), near T_A .

is instantaneous and the remaining kinetics is governed by particle redispersion by repulsion and diffusion. This is marked by a correlation signal in the static structure factor,⁽²⁰⁾ and the resulting $I(q)$ has the form,

$$I(q) = \frac{I_f}{(1 + q^2 R_F^2 / 10)^2} + I_p \exp(-R_p^2 q^2) \quad (2)$$

where $I_f \propto \bar{M}$, $R_f \propto R$, I_p is an amplitude (in arbitrary units) proportional to the magnitude of correlation and R_p is the characteristic range of correlation. The kinetics in this case has an exponential behavior.

6. PARTICLE INTERACTIONS

There have been several attempts to measure the particle interactions prior to aggregation.^(9, 11, 15, 21) Gurfein *et al.* noticed an increase in the scattered light intensity at small angles as T_A is approached.⁽¹¹⁾ This increase was interpreted in terms of a divergence in the adsorbed layer thickness. The behavior of turbidity^(9, 10) was also found to be consistent with this argument. Small angle neutron scattering measurements performed in the stable region of C_4E_1 —water system demonstrated a change from repulsive hard-sphere to sticky hard-sphere behavior as the C_4E_1 concentration was increased from zero.⁽¹⁵⁾ However, in this work, T_A was not

approached in any systematic manner. Kurnaz and Maher⁽²¹⁾ measured the second virial coefficient (B_2) in dilute suspensions of polystyrene latex in LW mixtures both critical and off-critical using static light scattering. The measured B_2 changed from positive (repulsive) to negative (attractive) as the temperature T_A is reached. The magnitude of B_2 in the unaggregated region suggested the existence of long-ranged repulsive interactions (non DLVO).

7. THEORETICAL ATTEMPTS

There have been numerous theoretical attempts to provide a quantitative explanation for this phenomenon of reversible aggregation. In the original report of Beysens and Estève,⁽¹⁰⁾ the observed aggregation was tentatively interpreted as the manifestation of a *prewetting* transition.^(3, 4) However, such a transition in a spherical geometry has to be considerably weak in comparison to that near a planar substrate.^(5, 6) An alternate approach was to consider the aggregation as a phase separation in a three component system.⁽²²⁾ This approach has received a renewed interest⁽²³⁻²⁵⁾ and three-component phase prisms have been constructed.^(16, 18) In this scheme, the main role of colloids is to couple to the host degrees of freedom by preferring one of the host liquid species and thereby decreasing the local interaction strength.^(23, 24) In the interface potential approach, Yeomans and coworkers⁽⁶⁻⁸⁾ considered the capillary condensation and consequent bridging between the spheres as a possible mechanism for the wetting induced colloidal aggregation. Very recently, more accurate density functional theory has been used to study the wetting behavior of one-component fluids on spheres and cylinders.⁽²⁶⁾

Due to the enhancement of order parameter fluctuations near the critical point, the local perturbation caused by a particle is not screened completely within a few atomic layers but influences the system over appreciable distances. This can give rise to a long-ranged interaction between the particles. This effect has been examined by Fisher and de Gennes,⁽²⁷⁾ and it scales with the bulk correlation length. Recently, this force has been termed as critical Casimir force in analogy with the Casimir effect due to confinement of quantum fluctuations of the electromagnetic field.⁽²⁸⁾ This fluctuation induced interaction which scales as inverse of distance, exceeds $k_B T$ when the particle separation becomes smaller than the correlation length of critical fluctuations. However, this force can be dominant only in critical systems and much of the systems studied here are off-critical where the bulk correlation length has its normal value.

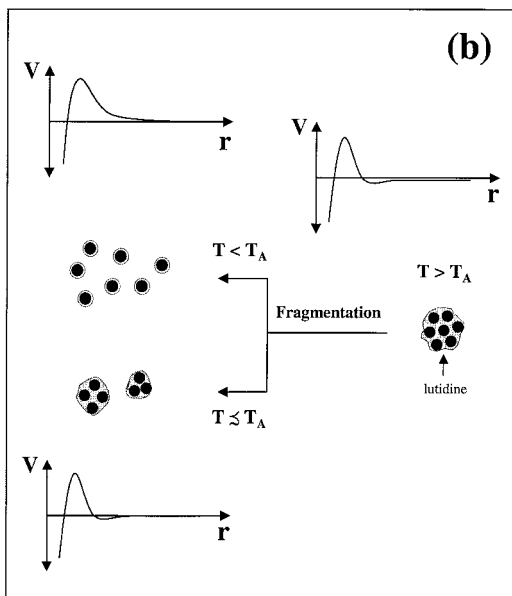
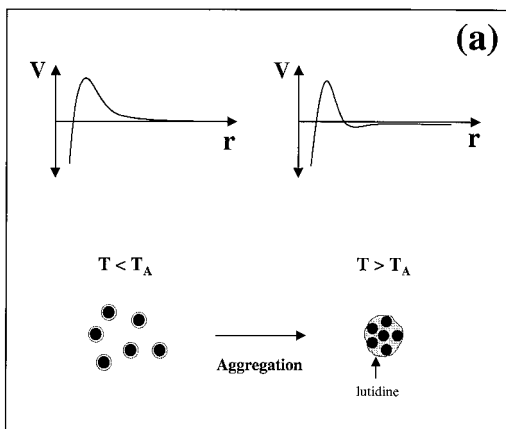


Fig. 7. Schematics of (a) aggregation and (b) fragmentation processes according to the model based on an adsorption-modified interparticle potential.

An interaction potential approach has been used recently^(29, 30) in order to elucidate many experimental features of this aggregation phenomenon. The underlying spirit is to estimate the changes in the two body potential $V(r)$ in the presence of an adsorbed wetting layer.

The initial interactions in the stable suspension were modeled in terms of an improved DLVO potential⁽²⁹⁾ with the attractive dispersion interactions described by the Dzyaloshinskii–Lifshitz–Pitaevskii (DLP) potential.⁽³¹⁾

$$V(r) = V_{n=0}^{\text{DLP}} + V_{n>0}^{\text{DLP}} + V^{\text{elec}} \quad (3)$$

where $V_{n=0}^{\text{DLP}}$ and $V_{n>0}^{\text{DLP}}$ are the zero-frequency and finite frequency DLP dispersion interactions, respectively, and V^{elec} is the screened electrostatic potential. Changes in the attractive and repulsive contributions to the DLVO potential in the presence of an adsorbed layer were calculated. This work revealed that the primary factor that modifies colloidal stability in the presence of an adsorbed wetting layer is the Debye screening length within the layer which is different from that in the bulk. This screening length progressively weakens the repulsive contribution to the DLVO potential as the adsorption thickness increases. For a typical dilute suspension of Stöber silica in LW, the onset of aggregation corresponds to an adsorbed layer thickness of about 12 nm.^(29, 30) Once the adsorbed layers associated to two particles coalesce, the inter-particle medium essentially becomes pure L and the resulting interaction potential has a high repulsive barrier which prevents the particles coming in direct contact.⁽³⁰⁾ The competing effects of this repulsive barrier and the coalescence energy (which tries to bind the particles together) gives rise to a shallow secondary minimum in the interaction potential. The line of T_A 's calculated by this model resembled the measured curves. These authors⁽³⁰⁾ further uncovered many global aspects of the adsorption-induced aggregation including the aggregation kinetics (Fig. 7) and second virial coefficient. However, possible limitations of this approach stem from the existence of non-DLP interactions in the reference system which is the unaggregated charged colloidal systems in LW.

8. CONCLUSION

The existence of a wetting transition in the coexisting liquid phases is primarily responsible for the strong adsorption phenomenon in the vicinity of the phase coexistence curve. When colloids are suspended in such a mixture, an adsorbed layer is formed over the particles as a function of temperature and/or concentration of the host mixture. The resulting

modifications in the interparticle interaction potential lead to the reversible destabilization of the colloidal suspension.

The phenomenon is quite general and can be applied to a broad range of systems. Since the destabilization occurs at moderate temperatures, biological systems are possible candidates. Further efforts are needed in order to more directly measure the particle interactions at the onset of aggregation, and to elucidate the fine structure of aggregates.

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