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Manuscript Number:

Title: Formation of stable clusters in colloidal suspensions

Article Type: Special Issue: Brian Vincent

Section/Category:

Keywords: clusters, reversible coagulation, colloidal interactions

Corresponding Author: Dr. (Currently Unavailable) Victor Starov,

Corresponding Author's Institution:

First Author: (Currently Unavailable) Victor Starov

Order of Authors: (Currently Unavailable) Victor Starov

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Dr. habil. Reinhard Miller  
Max-Planck-Institut fuer Kolloid- und Grenzflaechenforschung  
Max-Planck-Campus, Haus 2  
Am Muehlenberg 2  
D-14476 Golm/Potsdam

Phone: +49 331 5679252  
Fax : +49 331 5679202  
e-mail: [miller@mpikg.mpg.de](mailto:miller@mpikg.mpg.de)

Direct Line:+44 (0)1509 222508  
Fax: +44 (0)1509 223923  
E-mail: [V.M.Starov@Lboro.ac.uk](mailto:V.M.Starov@Lboro.ac.uk)  
<http://www.lboro.ac.uk/departments/cg/staff/cgvms.htm>

3 July, 2008

Dear Professor Miller,  
We submit our review for a publication in the Special Issue of “Advances in Colloid and Interface Science” to selebrate the carrer of prof Bryan Vincent

## **Formation of stable clusters in colloidal suspensions**

Nina Kovalchuk<sup>1,2</sup>, Victor Starov<sup>1f</sup>, Paul Langston<sup>3</sup>, Nidal Hilal<sup>3</sup>

<sup>1</sup> *Department of Chemical Engineering, Loughborough University, Loughborough, LE11 3TU (UK)*

<sup>2</sup> *Institute of Biocolloid Chemistry, 03142 Kiev, Ukraine*

<sup>3</sup> *School of Chemical, and Environmental Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD (UK)*

Regards,

Victor Starov,

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<sup>f</sup> Corresponding author: [V.M.Starov@lboro.ac.uk](mailto:V.M.Starov@lboro.ac.uk)

## Formation of stable clusters in colloidal suspensions

Nina Kovalchuk<sup>1,2</sup>, Victor Starov<sup>1f</sup>, Paul Langston<sup>3</sup>, Nidal Hilal<sup>3</sup>

<sup>1</sup> *Department of Chemical Engineering, Loughborough University, Loughborough, LE11 3TU (UK)*

<sup>2</sup> *Institute of Biocolloid Chemistry, 03142 Kiev, Ukraine*

<sup>3</sup> *School of Chemical, and Environmental Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD (UK)*

### Abstract

The experimental evidences and available theoretical explanations on formation of stable clusters in colloidal suspensions are reviewed. The clusters form in the parameters range intermediate between that corresponds to a stable suspension built up by singlets and that causing the irreversible coagulation of the suspension. The stable clusters can appear as a result of a competition between a short range attraction and a long range repulsion between colloidal particles or due to reversible flocculation in the shallow secondary potential well.

*Key words:* clusters, reversible coagulation, colloidal interactions.

**Key words:** colloidal suspensions, colloidal forces, Brownian forces, clusters

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<sup>f</sup> Corresponding author: [V.M.Starov@lboro.ac.uk](mailto:V.M.Starov@lboro.ac.uk)

## **Introduction**

Colloidal suspensions and emulsions are nowadays an important part of our everyday life. Prediction and control of their properties is crucial for performance optimization in mining, oil, food, pharmaceutical industries, etc [1-3].

Stability is one of the most important characteristic of colloidal systems. It is determined by the balance of attractive and repulsive forces acting between colloidal particles. Usually colloidal interactions are considered in the frames of DLVO theory, which takes into account dispersion and electrostatic forces. Often structural forces and depletion attraction are considered as well [4,5]. If a suspension is composed of identical particles then dispersion forces always result in attraction and in absence of other forces cause coagulation of the suspension. The electrostatic forces between identical particles are always repulsive. The structural forces are caused by water dipoles orientation [5]. The electrostatic and structural repulsion stabilises the suspension kinetically due to appearance of the potential barrier preventing particles from coagulation [1-5]. Electrostatically stabilised suspension can be easily destabilised if potential barrier is considerably lowered (slow coagulation, reaction limited coagulation kinetics) or even fully disappears (rapid coagulation, diffusion limited coagulation kinetics) due to change of pH of dispersion medium which results in lowering of the surface charge/potential or by increase of the electrolyte (salt) concentration in the dispersion medium, which results in the decrease of the thickness of electrical double layer.

Therefore, any colloidal system, suspension or emulsion, is generally considered as being stable (i.e. composed of single particles) or as being unstable (i.e. undergoing irreversible coagulation). However, there is also third possible intermediate state of colloidal dispersion, the state of dynamic equilibrium between relatively small clusters of particles and single particles [6].

The possibility of controlled formation of stable cluster phase is of great scientific and practical interest as promising direction for creating of new materials with prescribed and controllable properties. On the other hand the possibility of formation of stable cluster phase should be always taken into account. A suspension containing clusters is often considered as stable one, but its properties could be quite different from the properties of suspension composed of single particles. It is known, for example, that viscosity of a bimodal and especially of a multimodal suspension differs considerably from the viscosity of a suspension composed by monodisperse

particles at the same volume fraction [7-9]. That means, that viscosity can change drastically also at formation of small clusters, what was confirmed theoretically as well as experimentally in Ref [10]. The cluster size and therefore properties of the suspension can change considerably due to the shear stress imposed [11,12].

The formation of stable clusters is especially important in biological systems, as aggregation here can result in severe diseases. It is known that Alzheimer's and Parkinson's diseases are induced by protein aggregation [13]. However, small clusters are hardly detectable by methods generally employed in medical practice. According to [13] solutions of  $\beta_2$ -microglobulin in physiological conditions contain a small fraction of aggregates about 100 nm in size which can be precursors for formation of larger aggregates at an unfavourable change of conditions. The aggregates are stable in size and concentration and after separation they reappears again after few days.

Thus, study of clustering in colloidal systems is of great importance for explaining, correct prediction and control of properties of colloidal suspensions as well as biological liquids. A brief survey of experimental and theoretical investigations of formation of stable cluster phase in colloidal suspensions is presented below. Below we mostly consider the perikinetic aggregation, where the cluster formation and breakage is not affected by the shear stress imposed.

## **Experimental**

The first experimental studies on formation of small clusters in dynamic equilibrium with single particles were inspired by Verwey and Overbeek [14,15], who showed theoretically the possibility of reversible aggregation of colloidal particles in the secondary potential well. Srivastava and Haydon [16] studied microscopically the aggregation of paraffin wax suspension depending on electrolyte concentration. Without electrolyte added suspension was stable and composed of single particles for a period of several weeks due to electrostatic repulsion (high negative zeta-potential) . After addition of 0.01 M KCl suspension became less stable, but still had half-life time of order of one week. Therefore, aggregation was studied at concentration of KCl of 0.02 M as well as in the presence of 0.01 M KCl + small concentrations 2:1 electrolyte. The aggregation (mainly doublets formation) was observed during a few hours whereupon the system proceeded to quasi-equilibrium state, where the number of monomers remained nearly constant.

Long, Osmond and Vincent [17] studied aggregation in suspensions of 6 different polystyrene lattices particles, sterically stabilised by alkyl polyethylene oxide ( $C_{12}E_6$ ) providing the moderate depth of potential well (1-20  $kT$ ,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature) as well as electrostatically stabilised. Aggregation was initiated by addition of  $BaCl_2$  electrolyte at 0.1 M concentration. This concentration exceeded the flocculation concentration for lattices in the absence of the stabilising surfactant. The equilibrium degree of flocculation was estimated microscopically and by turbidity measurements. After addition of the salt the samples were rotated slowly during 48 hours to reach the equilibrium. It was found that there exists a critical solid volume fraction above which the flocculation begins. The critical solid volume fraction decreases with an increase of the particles size. At the equilibrium in weakly aggregated suspension clusters coexisted with singlets according to the microscopy observations. It was observed that the singlets occasionally join the aggregates as well as breaks off them. A dilution of the aggregated sample below critical solid volume fraction resulted in a spontaneous breakage aggregates into singlets. By further increase of the solid volume fraction above threshold the ratio of the number of aggregates to the number of singlets remained practically constant whereas the size of aggregates increased. The study of aggregation in sterically stabilised polystyrene latex suspensions was continued in [18-20]. It was shown that at certain temperature and certain solid volume fraction there is a range of non-adsorbing polymer concentrations (depending on the molecular mass), where the aggregates coexisted with singlets.

A microscopy study of time evolution of suspensions composed of monodisperse particles of polystyrene latex was performed in [21]. The experiments were run in a glass cell with rectangular cross-section  $1 \cdot 0.5 \text{ mm}^2$  at temperature  $25^\circ\text{C}$  with particles which differ in diameters (0.915, 2 and  $3.75 \mu\text{m}$ ) and surface properties: zeta-potential at  $\text{pH}=6$  varied between -21 and  $-80 \mu\text{V}$  depending on the type of particles and the salt concentration ( $\text{NaCl}$ ). It was found that at low salt concentrations ( $10^{-5} \text{ M}$ ) the only single particles were present in the suspension during more than 6 hours of observations. At the higher salt concentration,  $3 \cdot 10^{-3} \text{ M}$ , the number of singlets in the system went down during about 15 minutes due to cluster formation whereupon remained unchanged. The number of clusters at the equilibrium was rather small in this case and they were mostly doublets. An increase of the salt concentration

up to  $10^{-2}$  M resulted in a further increase of the number of particles aggregated in clusters. The time required to reach the equilibrium in the system reached about 30 min for that salt concentration but the rate of the decrease of the number of singlets was higher than that at concentration  $3 \cdot 10^{-3}$  M. At still larger salt concentrations,  $6 \cdot 10^{-2}$  M and  $3 \cdot 10^{-1}$  M, singlets disappeared more and more quickly. At concentration  $3 \cdot 10^{-1}$  M, which was close to the critical coagulation concentration (CCC) there remained practically no singlets in the system after two hours of observations. For all the salt concentrations which were well below the CCC the number of particles in cluster was in most cases less than five. A motion of particles inside clusters was also observed. The latter results in both a change of the cluster shape, and a disconnection of particles from the cluster. The last observation confirms that in this case a reversible flocculation take place in the system and the equilibrium is indeed the dynamic equilibrium. At salt concentration  $3 \cdot 10^{-1}$  M a tendency to form chain-like structures rather than more uniform clusters was observed [21]. At that salt concentration the mobility of particles inside clusters was much slower and was observed mainly at the initial stage of flocculation.

The cluster formation in suspensions composed of monodisperse polystyrene latex particles depending on NaCl concentration was also studied in [22]. Two types of particles with diameters 5.1 and 2.6  $\mu\text{m}$  and titrable charge 0.6 and 2.5  $\mu\text{C}/\text{cm}^2$ , correspondingly, were used in this study. The formation of small clusters in dynamical equilibrium with single particles was found at salt concentration less than 0.1 M. The particles inside the clusters had considerable mobility. Triplets were always formed as open chains, usually not straight. However, after certain time they could change their shape to become the closed triangles. Reverse transformations were also observed. Aggregates dissociated only by breaking the only one interparticle bond. The decrease of the salt concentration resulted in the decrease of clusters lifetime and in the increase of the particles mobility inside clusters. Mobility in clusters formed by smaller particles was higher than in clusters formed by larger particles.

The aggregates of finite size were found in suspensions of polystyrene latex and graphitised carbon in  $10^{-2}$  M  $\text{KNO}_3$  solution [23]. The aggregation constant depended on the temperature, volume fraction of the solid and presence of non-interacting particles in the suspension. The influence of small shear stresses due to



slow rotation of the container with suspension preventing sedimentation is discussed thoroughly in [23].

The reversible aggregation of silica suspensions with mean size of particles of 0.4  $\mu\text{m}$  was studied using the flow ultramicroscopy at pH 2.0 (iso-electric point), 3.1 and 6.2 and in the range of KCl concentration of 0.01-0.8 M [24,25]. The rate and the degree of coagulation in those systems increased with increase of salt concentration at all pH, but there always was certain equilibrium degree of aggregation which did not exceeded 5. Structural forces seems to be important for the formation of equilibrium clusters in this case.

Plate-like crystals of the sodium montmorillonite clay Cloisite with a diameter of a few hundred nano-meters and a thickness of 1 nm were also found to form clusters in aqueous dispersions at small volume fractions of solids (less than 2 wt %) at NaCl concentration of  $10^{-3}$ - $10^{-4}$  M [26]. The clusters were much more compact in comparison to those formed by spherical particles, their fractal dimension was about 2.6. The radius of gyration was estimated as 400-600 nm at  $10^{-4}$  M NaCl and increased to about 3  $\mu\text{m}$  at  $10^{-3}$  M NaCl. The above results were obtained after suspension was kept under an unchanged conditions during 3 months. Small-angle light scattering confirmed no evolution in time after 2 months. Note, dynamically arrested solid-like states were observed in suspensions at the same solid volume fraction but at the salt concentrations of  $10^{-5}$  M and  $10^{-2}$  M. A further increase of the salt concentration above  $10^{-2}$  M resulted in the coagulation of the suspension.

The structure of equilibrium clusters formed in suspension of octadecyl-coated silica particles with radius 42.5 nm in decalin was studied in [27] by ultra-small angle X-ray scattering. Depletion attractions between the particles in this suspension was induced by addition of non-adsorbing polystyrene with radius of gyration 3.6 nm. The clustering was observed at polymer concentrations giving the contact attraction energy between 2 kT and 15 kT. At lower polymer concentrations suspension was composed of single particles, at larger polymer concentrations the gel transition occurred. The formation of dense clusters with size about 2  $\mu\text{m}$  was found in [27] with cluster structure practically independent of the polymer concentration and solid volume fraction. Surprisingly, it was also found that cluster size to a first approximation is also independent of polymer concentration.

The formation of stable clusters in suspension of iron oxyhydroxide ( $\alpha$ -FeOOH) spherical nano-particles with diameters of about 6 nm in aqueous solution of

NaNO<sub>3</sub> (0.001-0.1 M) was reported in [28]. According to the potentiometric titrations the iso-electric point for the iron oxyhydroxide nano-particles in aqueous dispersions was found at pH=8.65. The small-angle X-ray scattering and the dynamic light scattering was used to study the aggregation processes in the suspensions with volume fraction of solids 0.001-0.0015. It was found in [28] that below pH=5 the suspension was composed of single particles, above pH=6.6 the suspension coagulated forming large-scale fractal aggregates, whereas at pH 5-6.6 the formation of stable nano-clusters was observed. In contrast to [21,22] the single particles at equilibrium with cluster phase were not observed in [28], but the authors of [28] suppose that it can be difficult to detect the single particles in the presence of large clusters. The equilibrium cluster size increased with the pH increase, but even at pH=6.6 it remained in sub-micron range. At the same time there was not detectable dependence of cluster size on the concentration of suspension in the studied concentration range. The fractal dimension of the nano-clusters was estimated as 1.1-1.2, what indicate the preferable formation of single contiguous objects similar to chain-like structures, observed also in [21]. The monitoring of a dimension of clusters formed at pH=5-6 during 4 months confirmed their stability.

At still smaller length scale the formation of equilibrium clusters with a size about 1 nm was observed in aqueous solutions of silver iodide [29] with aggregation number depending on the concentration of iodide ions in the dispersion medium. Clusters (particles) of magnetite with a size 1.5-12.5 nm depending on the pH and the salt concentration were precipitated from aqueous solutions [30]. It was assumed in [30] that those clusters were thermodynamically stable. The size of thermodynamically stable gold nano-clusters in the range 1.5-20 nm was controlled by thiol concentration [31].

The most detailed study of the formation of stable clusters of colloidal particles was performed in [6,32-35] for suspensions of monodispersed spherical particles of polymethylmethacrylate, which were marked with fluorescent rhodamine and sterically stabilized by chemically grafted poly-12-hydroxystearic acid. The particles of different sizes were used in those studies, however, in all cases the thickness of steric layer was about 10 nm. The particles were suspended in a mixture 22:78 % by weight of cis-decalin and cycloheptyl bromide. The matching of densities allowed neglecting the gravity influence: according to [32] there was not any observable settling of the particles after centrifuging at 6000 g for 15 hours. The

particles were positively charged in the dispersion medium providing long range electrostatic repulsion. Screening Debye length for those suspensions as estimated in [33,35] was about 1  $\mu\text{m}$ , that is much larger in comparison to suspensions in aqueous media. Non-adsorbing linear polymer polystyrene added to the dispersion medium provided the short range depletion attraction in the system with strength controlled by the polymer concentration and the polymer size or the radius of gyration. The range of attraction interaction is close to the radius of the polymer gyration, which in [6, 32-35] was less than 100 nm, i.e. the attraction acts in that system on a much smaller length scale, than the repulsion.

At a very low polymer concentration the suspension was composed only of single particles. The presence of clusters at equilibrium with single particles was observed at intermediate polymer concentrations. An increase of both the polymer concentration and the solid volume fractions resulted in an increase of the cluster size and finally in a formation of gel-like structures [6, 32-35]. The percentage of monomers in the suspension decreased with an increase of the volume fraction of solids [6,35]. Using the confocal microscopy allowed a clear visualisation of the clustering and a direct determination of the number of particles in the cluster as well as the cluster shape. According to [6] in a suspension with particles of radius 660 nm at the polymer concentration 3g/l (molecular mass 212.4 kDa, radius of gyration 13.2 nm) the energy of attraction between two particles was about 5 kT. The latter resulted in the increase of the equilibrium cluster aggregation number from about 3 at the solid volume fraction 0.025 to more than 20 at the solid volume fraction 0.15. The number of particles in the largest observed cluster increased from 37 to 2340 at the increase of the solid volume fraction in the suspension from 0.011 to 0.086 [35].

A direct observation performed in [33] showed that the smallest clusters formed at low volume fractions in suspensions are nearly spherical. The clusters became more chain-like with relatively uniform thickness as the volume fraction in suspensions increased and the clusters grew. The formation of chain-like clusters is reported also in [35], where spherical clusters were not detected at all but it was found that a sphericity factor (0 for sphere and 1 for rod-like shape) even decreased with increase of the cluster size. A direct observation performed in [35] showed that the small clusters formed one-dimensional chains of particles, while large clusters remain anisotropic but already formed three dimensional structures. The difference in the

shape of small clusters reported in [33] and [35] most probably is due to different particles size and polymer concentration used in those studies.

According to [33] large anisotropic clusters are built up by face-sharing tetrahedral units where each particle is connected to six neighbours. A gel-network, which appears at even larger volume fraction of colloidal particles, consists of linked chain-like clusters [33]. The gelation due to interconnecting of the clusters is reported also in [34,35]. It is found in [35] that the average number of neighbours increases from about 2.5 for small cluster to about 6 for large clusters near the percolation threshold and remains unchanged after the gel transition.

The reversibility of cluster formation was proven in [32]. The clusters melted, as the polymer concentration was lowered by a gentle dilution using a filter membrane. At the same time the clusters break up or a dissociation of particles from the clusters was not observed in [32], in contrast to [21,22], and as it could be expected due to a reversibility of the aggregation process. Later however, visual observations performed in [35] revealed slow but continuous exchange by particles between clusters in suspension studied in [6,32-35].

The clustering kinetics at early stages (till 300 s) was studied in [32]. It was found that the average number of particles per a cluster increased approximately linearly with time. The characteristic time of the aggregation was found between 100 and 1000 s depending on the sample characteristics. On the whole the aggregation kinetics was determined in [32] as the intermediate between the diffusion limited and the reaction limited. According to [32] in a suspension with particles of 350 nm size, the potential well depth 5.1-5.5 kT and the solid volume fraction 0.03 the cluster formation was completed during 5 hours of observations and after that there was no further growth of the average cluster size for at least 21 hours.

The investigations discussed above were extended in [36] where the comparison of the clustering behaviour was performed for the three suspensions of sterically stabilised polymethylmethacrylate colloidal particles interacting through the depletion attraction caused by an addition of polystyrene. The positive charge of the polymethylmethacrylate colloidal particles in the suspension considered above was due to the presence of cycloheptyl bromide in the dispersion medium. Therefore in the second of the systems considered in [36] the pure cis-decalin was used as a dispersion medium. The particles remain uncharged in the latter case and the only colloidal force acting in the system was the depletion attraction. However, this suspension was under

the strong gravitational effects due to the density mismatch about  $0.3 \text{ g/sm}^3$  [36]. In the third suspension considered in [36] the tetrabutylammonium chloride (3.6 mM) was added to the suspension to screen the electrostatic interaction, providing the Debye length about 1.1 nm. The density remained matched in that case. The most important result of comparative study performed in [36] is the observation of a formation of equilibrium clusters in all three considered suspensions, even in those, where the electrostatic interaction was absent or screened by an electrolyte addition.

A suspension of sterically stabilised polymethylmethacrylate colloidal particles with the depletion attraction and the screened electrostatic repulsion was studied in [37]. This study confirmed results obtained in [36] that the phase of stable clusters at equilibrium with single particles exist even in the absence of a long-range electrostatic repulsion. The morphology of the clusters depended on the range of inter-particle attraction but not on the volume fraction of particles. The cluster formation began at polymer concentrations corresponding to the interaction potential about 1-2 kT in a suspension with a relatively long range attractive force. These clusters were rather compact: fractal dimension 2.4-2.6 and the most probable number of nearest neighbours 10-12. The clustering due the short range attraction began at polymer concentration providing the interaction energy about 10 kT. Clusters in that case had more branched structure: fractal dimension 1.7-1.8, the most probable number of nearest neighbours 3-5 [37].

Formation of equilibrium clusters in a suspension of amphiphilic colloidal particles was reported in [38]. One hemisphere of polystyrene particles with diameter of  $1 \mu\text{m}$  was hydrophobised by octadecanethiol in that suspension. Polystyrene hemispheres were then subjected to electrostatic repulsion whereas attraction forces were acting between hydrophobised hemispheres. Clustering in this suspension was studied by epifluorescence microscopy, depending on the salt concentration screening the electrostatic repulsion. Suspensions prepared without salt addition were composed of single particles. The small compact clusters were formed in suspensions with 1mM  $\text{KNO}_3$  added. Observed attachment and detachment of single particles as well as a rearrangements of the cluster shape pointed out the dynamic character of the equilibrium. At larger salt concentration (5 mM) small clusters joined into large branched, wormlike objects.

The cluster formation was observed also in the absence of a long-range electrostatic repulsion but due to repulsive structural forces. In [39] the attraction to

repulsion ratio for DNA-capped colloidal particles was regulated by the ratio complementary and non-complementary DNA used. An increase of the steric repulsion energy above a certain threshold value resulted in an appearance of quasi-stable clusters, which size decreased with a further increase of the repulsion. Qualitatively similar results were obtained for a suspension of micro particles (polystyrene, diameter 1.9  $\mu\text{m}$ ) and a suspension of nano particles (gold, diameter 9.6 nm).

Formation of equilibrium clusters was observed in many biological nano-colloidal systems. An example is given in [40], where the liposomes made of phosphatidylcholine revealed the reversible flocculation at the condition of zero zeta-potential at the shallow potential minimum due to the hydration force. A reversible aggregation of influenza viruses was observed at iso-electric point as well as at non-zero zeta-potentials [41]. The degree of aggregation in this case still depended on the NaCl concentration in the dispersion medium.

The equilibrium clusters were also discovered in solutions of the globular proteins, which can be considered as colloidal suspensions with very small, few nanometers, particles size. The clustering of a secretory enzyme lysozyme, which has a radius about 1.7 nm, molecular mass 14.4 kDa and net charge depending on dispersant pH was studied in [6,42,43]. The clustering was found to be the reversible process. The cluster size increased with an increase of salt concentration as well as with a decrease of the temperature and the aggregation number was proportional to the protein concentration. In [6] the aggregation number of lysozyme was estimated to be equal about 3 at 20  $^{\circ}\text{C}$  without a salt addition and to be equal about 5 at temperature 5  $^{\circ}\text{C}$  without a salt or in 50 mM NaCl solution at 20  $^{\circ}\text{C}$ . An irreversible aggregation of protein was observed in 50 mM NaCl solution at temperatures below 15  $^{\circ}\text{C}$ .

The equilibrium large polyelectrolyte-lipid complexes formed by the clustering of individual liposomes were found in [43]. Liposomes in clusters kept their nearly spherical shape, being only slightly deformed. The clusters with maximum radius formed always near iso-electric point and on average was tenfold larger than the liposome radius. The smaller clusters were approximately spherical, but large had more elongated shape.

## Theory

The main question about the stable cluster phase in colloidal suspensions is the nature of the stability. The first possibility is the thermodynamic equilibrium due to competition between the interaction energy and entropy contributions to the system free energy [18-20]. Such equilibrium is possible if the aggregation occurs in the shallow potential well with the depth comparable to the thermal energy. Inter-particle bonds in this case can be broken due to thermal motion of particles, i.e. the coagulation in the shallow potential well is reversible [18,45], and the clusters can be easily destroyed due to increase of temperature (an increase of the energy of the thermal motion) or due to a decrease of the salt concentration (a decrease of the depth of the secondary potential well) [45,46], what is not the case for coagulation in the deep primary potential well.

If the interaction energy between colloidal particles is much larger than  $kT$  and entropic effects can be neglected, formation of stable clusters is explained as a result of a competition between a short range attraction (van der Waals or depletion forces) and a long range repulsion (usually of the electrostatic origin) [47-52]. If the difference in the ranges of the attraction and the repulsion is large enough, then usually there is no secondary potential well on the curve representing the interaction energy between two particles. In this case there is only a potential barrier in front of the primary potential well. A similar shape of the potential energy curve is characteristic for the interaction of nanometre-sized particles.

In [47,48] a theoretical treatment of the problem of cluster formation in colloidal suspensions with colloidal particles interacting via a short range attraction and a long range repulsion is based on capillarity approximation, where the clusters are treated as uniform droplets. The energy of clusters is considered as the sum of two terms dependent on the number of particles in the cluster: one responsible for the dispersion attraction and another responsible for the repulsion due to the charge of the cluster. The driving force for the cluster growth according to this approach is the decrease of the surface energy of the cluster whereas the stabilising factor is the Columbic repulsion. The equilibrium cluster size minimizing the energy per a unit volume was found inversely proportional to the square of the charge of the colloidal particle and proportional to the cubic root of the solid volume fraction.

It is emphasised in [47,48] that the clustering of particles bearing the large enough charge can be accompanied by the condensation of counter-ions on the particles surfaces resulting in a decrease of their charge. This process destabilize the

suspension causing an increase of the equilibrium cluster size and can eventually lead to the irreversible coagulation of the colloidal suspension.

In [49-51] the dependence of a ground-state energy per a particle on the number of particles in a cluster was found from the Monte-Carlo simulations. An attractive part of the interaction potential was modelled by the Lenard-Jones potential

$$U_A(r) = 4u \left[ \left( \frac{\sigma}{r} \right)^{2\alpha} - \left( \frac{\sigma}{r} \right)^\alpha \right], \quad (1)$$

where  $u$  is the depth of the potential well,  $\sigma$  is the hardcore diameter of colloidal particle and  $r$  is the distance between the particles. The simulations were performed for the standard value  $\alpha=6$  as well as for  $\alpha=18$  and  $100$ . The last case corresponds to rather narrow potential well typical for narrow-range depletion attraction.

The screened electrostatic repulsion was modelled in [49] by Yukawa potential:

$$U_R(r) = A \frac{\exp(-r/\xi)}{r/\xi}, \quad (2)$$

where  $\xi$  is the screening length.

It was shown in [49] that in the absence of a repulsion the ground state energy decreases with an increase of the number of particles in the cluster, indicating the irreversible coagulation. When the repulsive term is added, the system behaviour depends on a relation between coefficients in Eq. (1) and (2). If the electrostatic repulsion is weak enough ( $A \ll u$ ), the ground state energy still decreases with an increase of the number of particles in the cluster. The increase of the amplitude of the repulsive potential makes the dependence of the ground-state energy on the cluster size considerably flat in the region of large clusters (with number of particles more than about 40). A further increase of  $A$  and a simultaneous increase of the screening length results in the appearance of a minimum in the ground-state energy per a particle, indicating that the clusters containing the larger number of particles are thermodynamically unstable. Typical values of parameters producing such a minimum are  $A=0.2u$ ,  $\xi=2\sigma$ . The larger the amplitude of the repulsion and the larger the screening length the smaller is the equilibrium cluster size. It is emphasised in [49] that the thermal motion of particles should result in a decrease of the equilibrium cluster size if the potential well depth is comparable to  $kT$ .



According to [50] the cluster formation is possible only if the amplitude of the attractive potential is large enough in comparison to the energy of the thermal motion ( $u > 5kT$  by  $A=0.2u$ ,  $\zeta=2\sigma$  in the model considered). The clusters will be destroyed by the thermal motion of particles at smaller amplitude of the attractive potential. Clusters formed in a suspension can move freely composing a fluid of clusters or can undergo a glass transition, when they are trapped in a cages due to the long range repulsion depending on the temperature and the solid volume fraction.

The existence of the optimal cluster size is explained in [49] in the following way. If a particle joins the cluster then the attractive interaction of the particle with the particles in the cluster results in a decrease of the system energy whereas the repulsive interaction contributes to an increase of the system energy. The attractive interaction is a short ranged, therefore the particle interacts in this way only with the nearest neighbours in the cluster. A repulsive interaction is a long ranged, therefore more distant particles in the cluster are involved in that interaction. Hence, if the cluster is big enough the increase of the system energy due to the repulsive interaction exceeds the decrease of energy due to the attraction.

The simulations performed in [49] allowed also determining the optimal shape of clusters. In the absence of the repulsion the spherical shape is preferable. The increase of the repulsive force results in a formation of more elongated to almost one-dimensional clusters. An increase of the cluster size results also in a structural changes from dense to more linear arrangement of particles inside clusters. Rather similar results, predicting appearance of small circular domains at small solid volume fraction and stripe-like arrays at large volume fraction were obtained in [52] (both by Monte Carlo simulations and experimentally) for 2D ensemble of nano-particles interacting by a short range attraction and a long range repulsion. In the case of a relatively small screening length (of the order of the particle radius) considered in [51] the preferable cluster shape was determined as a Bernal spiral composed of a face sharing tetrahedral, where each particle has six neighbours. Clusters may evolve to the branched structure and eventually to the percolating network indicating transition to a gel phase. Formation of linear clusters evolving to branched structures was predicted also in [53].

The molecular dynamic simulations of clustering and gelation in colloidal suspensions was performed in [54-58]. The formation of equilibrium clusters at volume fraction of particles below the gel transition was predicted [54-58] for

particles interacting via short range van der Waals attraction modelled by Lennard-Jones type of potential in the following form:

$$U_A(r) = \left( a_1 \left( \frac{\sigma}{r} \right)^{36} - a_2 \left( \frac{\sigma}{r} \right)^6 \right), \quad (3)$$

and long range electrostatic repulsion modelled by Yukawa potential:

$$U_R(r) = a_3 \exp\left(-\lambda \left( \frac{r}{\sigma} - 1 \right)\right), \quad (4)$$

where  $\lambda$ ,  $a_1$ ,  $a_2$  and  $a_3$ , which were chosen as  $\lambda=2.5$ ,  $a_1=2.3kT$ ,  $a_2=6kT$ ,  $a_3=3.5kT$ . At small volume fraction of particles the compact clusters with the average number of particles about 8-10 formed. By increasing the volume fraction of particles the tube-like structures containing up to 60 particles were found.

In [58] colloidal forces were modelled in the similar way, but parameters were fitted by comparison with the experimental results on the SAXS for lysozyme, globular protein with average diameter about 3.4 nm. The potential curve in this case has electrostatic repulsion barrier about 2 kT in front of a shallow primary minimum about 4 kT depth. Formation of a cluster phase was predicted for small volume fraction of particles with the maximum cluster size increasing with the increase of the volume fraction. At volume fractions above 0.148 clusters formed the percolated network.

In [59] the possibility of cluster formation in colloidal suspension with short range attraction and long range repulsion was considered using two-Yukawa potential in the following form:

$$U(r) = -K_1 \frac{\exp(-Z_1(r/\sigma - 1))}{r/\sigma} - K_2 \frac{\exp(-Z_2(r/\sigma - 1))}{r/\sigma}, \quad (5)$$

where the first term with  $K_1 > 0$  was selected for the inter-particles attraction whereas the second term with  $K_2 < 1$  used for the repulsion.  $Z_1$  and  $Z_2$  determine the attraction and the repulsion range. The appearance of a peak in the structure factor of clusters was found using Ornstein–Zernike equation. The structure factor was analysed varying the parameters in Eq. (5) as well as the volume fraction of particles.

It was found in [59] that the cluster phase appears only if attraction is strong enough. At weak attraction the system is composed by singlets. Clusters do not appear in the absence of the repulsion. In this case the irreversible coagulation is expected in the system. The number of clusters in the system and their size increase with the

increase of the strength of the attraction and its range. Clusters appear in the system already in the presence of a very weak repulsion. The increase of the repulsion strength as well as decrease of the repulsion range results in a decrease of the number of clusters and their size. These results are in line with those obtained in [49,50]. According to [59] there is the optimal solid volume fraction providing the maximum intensity of the cluster peak.

The reversible coagulation in the shallow potential well was considered in [18-20] using an analogy with simple liquids as a phase transition from gaseous phase of singlets to a liquid of clusters. At the equilibrium the volume fraction of clusters and singlets should obey the Boltzmann equation

$$\varphi_s = \varphi_c \exp\left(-\frac{E}{kT}\right), \quad (6)$$

where  $\varphi_s$  is the volume fraction of singlets,  $\varphi_c$  is the volume fraction of clusters, and  $E$  is the energy required to remove the particle from the cluster. The latter can be estimated as  $E=\beta U_0$ , where  $U_0$  is the potential well depth and  $\beta$  is the average of coordination number of a surface particle in the cluster. The depth of the potential well estimated in [17] using Eq (6) was in a reasonable agreement with those obtained by the direct calculation.

This approach was developed further in [60-65] employing the statistical thermodynamic methods in the framework of mean field method [60,61] and thermodynamic perturbation theory with a hard sphere system serving as a reference state [62-65] for calculation of the Helmholtz free energy of the suspension. Based on that the spinodal and coexistence curves as well as critical point location were predicted. The particle interaction was considered as a sum of the van der Waals attraction and the electrostatic repulsion. The latter was calculated either according to DLVO theory [60-63] or according to Belloni model (Yukawa potential) [64,65].

It was shown in [60-65] that at the reasonable values of physical parameters (temperature, solid volume fraction, particles size, zeta-potential, Hamaker constant) there exist an interval of salt concentrations below the critical coagulation concentration (depending on Hamaker constant) providing the coexistence of singlets and aggregates due to flocculation in the secondary potential well. Stable clusters appears only at large enough values of Hamaker constant [64]. According to [62,64,65] for electrostatically stabilized colloids at a fixed zeta-potential the particles size should exceed certain critical value to make possible such coexistence. Only the

irreversible coagulation in the primary potential well is expected for smaller particles. It was estimated in [62] that for aqueous suspension at room temperature and zeta-potential about 25 mV, the critical diameter of particles should be about 400 nm. The similar estimations performed in [64] give the critical diameter about 500 nm, whereas according to [65] this value is about 300 nm. Note, the same conclusion was obtained in one of the earliest experimental studies on coagulation of polystyrene latex [66]: the large particles (above 700 nm) are undergoing the reversible flocculation in the secondary potential well, whereas small particles (below 500 nm) coagulates irreversibly in the primary potential well was made.

In the case of reversible aggregation one can expect the formation of stable clusters in a suspension at the values of controlling parameters which fall in between of those corresponding to a fully dispersed state and those corresponding to a coagulated state. The cluster size in this case is determined by the ratio of the aggregation and the fragmentation rates and can be controlled by varying the system parameters. For example, an increase of the solid volume fraction results in the increase of the number of collisions in the system, i.e. in an increase of the aggregation rate. Therefore, the cluster size should increase with an increase of the solid volume fraction, observed experimentally [6,17,32-36]. As the bond energy between particles at the reversible aggregation is relatively small, particles inside the cluster can possess certain mobility. The latter was also observed in experiments [21,22,35,38]. The mobility of particles should be higher at the aggregation in the secondary potential well because the distance between the particles in the cluster is much larger than that at the coagulation in the primary potential well.

Note, the type of aggregation in the presence of both the primary and secondary minima depends essentially on the height of the potential barrier dividing primary and secondary potential well. If the barrier is not high enough, the gradual transition from the reversible to the irreversible aggregation is expected in the system [45]. At early stages of aggregation the particles flocculate in the secondary potential well and at this stage the suspension can be redispersed again in the way described above. But over the time the particles pass through the barrier to the primary potential well and the coagulation becomes irreversible.

Numerical simulations are widely used to study cluster formation caused by the reversible aggregation. In [67] the Brownian dynamic simulation was used to estimate the life-time of doublets and triplets reversibly flocculated in the secondary

potential well. The mathematical model proposed in [68] was used for direct numerical simulations. In this model the motion of colloidal particles is governed by hydrodynamic, colloidal and Brownian forces. Colloidal forces were modelled in the frames of DLVO theory as a sum of the van der Waals attraction and the electrostatic repulsion. The energy of repulsion was calculated as

$$U_R(r) = \pi \varepsilon_0 \varepsilon \sigma \psi_0^2 \ln(1 + \exp(-\kappa h)), \quad (7)$$

where  $\psi_0$  is the zeta-potential,  $\varepsilon$  is the relative dielectric constant of the dispersion medium,  $\varepsilon_0$  is the dielectric permittivity of vacuum,  $\kappa^{-1}$  is the Debye length,  $h=r-\sigma$  is the surface to surface separation. The energy of attraction was described by an empirical formula

$$U_A(r) = -\frac{A_H \sigma}{24h(1+1.77p)},$$

where  $A_H$  is the effective Hamaker constant,  $p=2\pi h/\lambda_L$ ,  $\lambda_L$  is the London wavelength.

The hydrodynamic mobility tensors were calculated according to Batchelor approach [69]. More simple expression, underestimating the hydrodynamic resistance at small separations was used for the comparison.

Calculations were performed for three different potential curves (with different depths of the potential well) for doublets and three other potential curves for triplets. Initially particles were placed at the distances corresponding to the bottom of the potential well. The time evolution of doublets or triplets was monitored until the distance between particles exceed the prescribed value, where the energy of interaction between particles was less than a few percent of kT. Repeated calculations were performed with different sets of random numbers modelling Brownian forces and then an averaged value was accepted as the life-time of the aggregate. The doublet life time was estimated as 0.25 s for the potential well depth of  $U_0=0.87$  kT, 1.4 s for  $U_0=4.68$  kT, and about 20 s for  $U_0=10.67$  kT (the last value is based on just 2 dissociations events). The importance of hydrodynamic interaction for aggregates life time is shown. Using a simplified model for the hydrodynamic interactions, which underestimates the hydrodynamic resistance at small separations, the life times were found much smaller that those obtained using more precise hydrodynamic model. It is emphasised that particle dissociation corresponding to the life time calculated can not be considered as a final one, as the particles remain at the close separation and can

after some time be aggregated again. That is why the values of the life-time obtained in those computer simulations are difficult to compare with the experimental data.

In [70] the average life-time of doublet formed by colloidal particles aggregated in the secondary potential well was estimated using the Smoluchowski approach for two particles diffusing in the field of hydrodynamic and colloidal forces [71]. The life-time was determined as a time when a separation between particles exceeds the certain prescribed value. The life-time was found by integration of the evolution equation, where the hydrodynamic interaction was modelled according to Brenner [72]. To compare the latter results with those obtained in [67] calculations were performed for two models of the van der Waals interaction, one of them the same as used in [67]. Good agreement was found for the potential well depths of 0.87 kT and 4.68 kT, but the life-time for  $U=10.67$  kT was found about 164 s. The possible discrepancy in the results can be explain by not enough statistical data for this case in [67] (only two simulations).

In [73] the life-time of doublets obtained using the Smoluchowski approach [71]. The calculated life-time was compared with results obtained using Brownian dynamic simulations. The latter was carried out according to two mathematical models: (i) proposed in [68], which is refereed below as “a diffusion model”, and (ii) based on the full Langevin equation taking into account inertia of particle. The lubrication approximation proposed in [74] was used to describe the hydrodynamic interaction between particles at small separations. To model the colloidal interaction between particles, the simplest possible presentation was accepted for the disjoining pressure  $\Pi(h)$ :

$$\Pi = \frac{2U_{\min}}{\pi a R} \frac{h_1 - h}{h_1 - h_0}, \quad 0 < h < h_0, \quad (9a)$$

$$\Pi = \frac{2U_{\min}}{\pi a R} \frac{h_2 - h}{h_2 - h_0}, \quad h_0 < h < h_2, \quad (9b)$$

where  $h_1$  and  $h_2$  are the closest distances between particle surfaces corresponding to the zeros of disjoining pressure,  $h_0$  is the distance corresponding to the minimum of disjoining pressure,  $U_{\min}$  is the depth of the potential well,  $R$  is the parameter depending on  $h_0$ ,  $h_1$  and  $h_2$ . The simplest form (9a)-(9b) retains however the most important features of the real disjoining pressure: presence of both repulsion and attraction as well as the presence of a potential well.

The mathematical model based on the full Langevin equation demands using the much smaller time step during the simulation. However, this model allows instead obtaining physically correct values of the instantaneous and average kinetic energy for each colloidal particle. The average kinetic energy of the particles was used as the system control parameter indicating that no artificial energy is created or dissipated in the system and therefore one can expect the correct description of the particle behaviour in the potential well.

The mean life-time of doublet time was calculated in [73] as average over 20 simulations for each potential well depth for the model based on full Langevin equation and from 40 simulations for the diffusion model [68]. Table 1 shows a good agreement between three sets of results obtained in [73].

Table 1. Comparison of doublet life-time [73].

The potential well depth, kT	1	3	5	7
The mean residence time calculated according to the Smoluchowski approach, s	0.044	0.12	0.50	2.7
The mean residence time obtained by simulations based on full Langevin equations, s	0.024	0.11	0.46	2.4
The mean residence time obtained by simulations according to the diffusion model [68], s	0.048	0.11	0.55	2.8

The computer simulations based on the model proposed in [73] were further performed for ensembles of 170 colloidal particles with two initial configurations – random and uniform distribution over 2D computational domain [75]. The solid volume fraction of the suspensions was about 30 %. The behaviour of the suspensions was studied for three values of the depth of the potential well: 3, 6 and 20 kT. The simulations enabled the monitoring a formation and a breakage of clusters in the suspension caused by competing colloidal interactions and thermal motion of particles. It was shown in [75] that at small depth of potential well (3 kT) the average cluster size is less than 2, i.e. in this case small clusters coexist with singlets. An increase of the depth of the potential well results in the increase of the cluster size. The clusters growth slows down with time as the singlets concentration in suspension decreases and time necessary to singlet to join the clusters increases. When this time becomes comparable with the life-time of particle in the cluster, the system reaches its

dynamic equilibrium state and the average cluster size remains constant, fluctuating around its equilibrium value.

In [76] numerical simulations were carried out for an ensemble of randomly diffusing particles. If after the diffusional step particles or clusters occupied neighbouring sites in the lattice they were aggregated and after that diffused as a single cluster. It was assumed that the diffusion coefficient is reversely proportional to the cluster radius, and the bonds between particles in the cluster can be broken with a probability depending on the bond energy and number of bonds per particle. Under those assumption the simulations enabled the prediction of the dynamics of the cluster growth and their structure at different values of the bond energy and the volume fraction of particles in the suspension. It was shown, that at the bond energy smaller than a certain threshold value, which depends on the solid volume fraction, the aggregation leads to a formation of sol of clusters without gelation. The similar approach but based on the population balance equation, which allows to follow the aggregation kinetics, was proposed in [77,78]. It was found that the equilibrium cluster size increases with the increase of the average bond life-time, i.e. with the increase of the potential well depth.

The fluid particle dynamic method is proposed in [79]. According to this method the suspension is treated as a mixture of two liquids with different viscosities: large one for particles and smaller one for dispersion medium. Each particle is represented by its concentration field. The viscosity of such complex fluid and the field of colloidal forces were obtained by the weightening over the concentration field. The dynamic of a suspension according to this method is governed by Navier-Stokes equations with co-ordinate dependent viscosity and volume forces. Simulation of aggregation in colloidal suspension with Lenard-Jones attraction potential was performed using this method and using the Brownian dynamic method without hydrodynamic interaction but with constant hydrodynamic friction coefficient. Comparison of the results has shown, that in the absence of the hydrodynamic interaction compact clusters were formed, whereas accounting for the hydrodynamic interaction resulted in a formation of chain-like clusters with an open structure.

## **Conclusions**

The equilibrium clusters were observed experimentally in diverse colloidal suspensions composed of polystyrene lattices, polymethylmethacrilate, graphitised



carbon, silica, clay, iron oxyhydroxide, gold, silver iodide as well as biological objects. The initial size of particles ranged from less than nanometre to some microns and number of particles in cluster varied from 2 to thousands depending on the experimental conditions.

The main forces involved in the cluster formation were dispersion and/or depletion attraction and electrostatic and/or structural repulsion. The main feature of all systems showing the formation of stable clusters is the limited strength of inter-particle attraction.

As a rule the cluster size increases with an increase of the potential well depth as well as with an increase of the solid volume fraction. Clusters have preferably chain-like shape but formation of small clusters of spherical shape was also reported. Most often clusters were observed in a dynamical equilibrium with singlets and particles inside the clusters retained their mobility.

Available theoretical analysis as well as numerical simulations allowed distinguishing two mechanisms of cluster formation: (i) stabilisation of cluster size due to the competition between the short range attraction-the long range repulsion and (ii) the reversible flocculation in the secondary potential well. A combination of both mechanisms is possible depending on the experimental conditions.

Despite of considerable progress in both experimental and theoretical studies of formation of stable clusters in colloidal suspensions the further comprehensive investigation of this phenomena, especially its kinetic aspects is required, to predict and control the suspension properties and provide the controllable formation of desired meso- and micro-sized self-assembled structures.

### **Acknowledgement**

The authors would like to acknowledge the support from The Engineering and Physical Sciences Research Council, UK (Grant [EP/C528557/1](#)).

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\* Suggested Reviewers

Professor Stanislav Dukhin [sdukhin@bestweb.net](mailto:sdukhin@bestweb.net)  
Professor Roque Hidalgo-Alvarez [rhidalgo@ugr.es](mailto:rhidalgo@ugr.es)  
Professor David Heyes [D.Heyes@surrey.ac.uk](mailto:D.Heyes@surrey.ac.uk)  
Professor Eric Dickinson [E.Dickinson@leeds.ac.uk](mailto:E.Dickinson@leeds.ac.uk)  
Professor Peter Kralchevsky [pk@lcpe.uni-sofia.bg](mailto:pk@lcpe.uni-sofia.bg)