Kinetics of macroion coagulation induced by multivalent counterions

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Due to the strong correlations between multivalent counterions condensed on a macroion, the net macroion charge changes sign at some critical counterion concentration. This effect is known as the charge inversion. Near this critical concentration the macroion net charge is small. Therefore, short range attractive forces between macroions dominate Coulomb repulsion and lead to their coagulation. The kinetics of macroion coagulation in this range of counterion concentrations is studied. We calculate the Coulomb barrier between two approaching like charged macroions at a given counterion concentration. Two different macroion shapes (spherical and rod-like) are considered. A new “self-regulated” regime of coagulation is found. As the size of aggregates increases, their charge and Coulomb barrier also grow and diminish the sticking probability of aggregates. This leads to a slow, logarithmic increase of the aggregate size with time.

I. INTRODUCTION

Water solutions of strongly charged particles (macroions) with multivalent counterions with large charge \( Z \) (\( Z \)-ions) are important in physics, chemistry, biology, chemical engineering and environmental science. Colloidal particles, charged membranes, double helix DNA, actin and other polyelectrolytes are examples of different macroions. Multivalent metallic ions, dendrimers, charged micelles, short DNA helices or other short PE can play the role of \( Z \)-ions.

We concentrate here on strongly asymmetric solutions in which size and charge of macroions are much larger than those of \( Z \)-ions. As the simplest example, we consider macroions as negatively charged rigid spheres with charge \(-Q\) and radius \( R \) in solution with compact positive \( Z \)-ions with the size \( a \ll R \) and charge \( 1 \ll Z \ll Q \). This can be a solution of positive latex particles with very short DNA helices or hematite particles with polyacrylic acid.

In such solutions, each adsorbs many \( Z \)-ions. They strongly repel each other at the surface of the sphere and form a strongly correlated two-dimensional liquid reminding Wigner crystal. When a new \( Z \)-ion approaches this liquid, it repels nearest \( Z \)-ions, creates a correlation hole or an oppositely charged image, which provides attraction of \( Z \)-ion to the surface in addition to what mean field theories predict. Therefore, when concentration of \( Z \)-ions, \( c \), reaches some critical value \( c_0(s) \), (which depends on concentration of macroions particles \( s \)) the net charge of each macroion, \( Q^* \), (which includes all adsorbed \( Z \)-ions) flips its sign. On Fig. 1 the “neutrality” line \( c_0(s) \) is shown in plane \((s, c)\) together with two signs of \( Q^* \) which it separates.

Correlations between \( Z \)-ions on the sphere surface also lead to another interesting effect. The correlation energy per \( Z \)-ion is lower at higher \( Z \)-ion concentration. This means when two spheres touch each other, at the place of contact where the \( Z \)-ion concentration doubles, correlation energy is gained. This energy gain leads to an attraction between spheres which is stronger than van der Waals forces and makes possible their coagulation. Coagulation is a key part of many industrial processes such as paper production, extraction of minerals, proteins and other macroions from solutions, or treatment of waste waters. On the other hand, there are many other cases where coagulation should be avoided. Delivery of short modified DNA molecules DNA adsorbed on the surface of positively charged latex particles is a good example.

Because colloidal solutions are stable due to the Coulomb repulsion between particles, coagulation is usu-
ally achieved by a large concentration of monovalent salt, which screens out these charges. When the concentration of salt grows beyond the coagulation threshold nothing new happens and macroions stay coagulated. If, instead of monovalent salt, we deal with Z-ions (add Z:1 salt) then charge inversion changes this situation. Coagulation happens only in the range of concentrations, which is close to the neutrality line (shown by gray in Fig. 1), so that the Coulomb repulsion is so weak that the free energy is gained when spheres touch each other. Thus when, say, the concentration of Z-ions, $c_i$ grows at fixed $s$, coagulation happens at some critical concentration, $c_c$, while at a larger concentration, $c_d$, aggregates of spheres dissolve, because spheres acquire large positive net charge. In our previous paper, we derived expressions for $c_c(s)$ and $c_d(s)$. These curves are plotted on Fig. 1. Remarkably, phase diagrams of this type were discovered experimentally more than half a century ago for complexes of strongly oppositely charged proteins. However, in Ref. 5 only the charge of large aggregates of macroions (coacervate droplets) was measured and the net charge of a single macroion was not discussed.

In this paper we go beyond equilibrium statistical physics and study kinetics for different domains of the phase diagram. There are two main slow processes in the problem: charge inversion and coagulation. The first one is slow in the upper left area of the phase diagram when free macroions are strongly overcharged. In this case, the growth rate of the macroion positive charge is limited by a large repulsive Coulomb barrier for new Z-ions. Activation over this barrier is necessary for a Z-ion to come close enough to macroion in order to feel attraction to its image in the strongly correlated liquid (SCL) of already adsorbed Z-ions.

In the coagulation domain surrounding the neutrality line charges of macroions are relatively small so that charge inversion is a fast process. On the other hand, coagulation of macroions can be very slow and take hours. Suppose we mix latex spheres with Z-ions in such concentrations that the corresponding point is in the gray area of the phase diagram and watch how the mass of aggregates grows as a function of time. Although the net charge $Q^*$ in the gray area is smaller than the bare charge $Q$, its absolute value can be much larger than $Z$ and the Coulomb barrier of repulsion of two macroions can be much larger than the barrier for charge inversion, which is created by the Coulomb interaction of a Z-ion with the macroion net charge $Q^*$. Therefore, in this paper, we assume Z-ions are always in equilibrium and study the kinetics of macroion coagulation only.

We first concentrate on the short time kinetics in which doublets of macroions appear. We calculate the Coulomb barrier between two approaching macroions as a function of the distance from the neutrality line. We measure this distance by the variable

$$U = \frac{k_BT}{Ze} \ln \left[ 1 + \frac{c - c_0(s)}{c_0} \right],$$

where the critical concentration

$$c_0(s) = c_0 + sN_i.$$  

Here $N_i$ is the number of Z-ions needed to neutralize one sphere. The concentration $c_0$ is the concentration of free Z-ions which is in equilibrium with neutralized spheres. It is equal to $c_0 \exp(\mu_{SCL}/k_BT)$, where $c_0$ is the three dimensional concentration of the surface layer of the SCL of Z-ions and $\mu_{SCL}$ is the chemical potential of Z-ions in SCL. It is negative and $|\mu_{SCL}| \gg k_BT$ so that $c_0$ is very small.

In Ref. 5, the net charge of the sphere was shown to be proportional to $U$ near the neutrality line:

$$Q^* = C U,$$

where $C$ is the capacitance of the macroion coated by the "metallic film" of SCL of Z-ions. For a sphere $C = \varepsilon R$, where $\varepsilon$ is dielectric constant of water. Because $U$ depends on the correlation chemical potential $\mu_{SCL}$ of Z-ions in the SCL, we call it the correlation voltage. From Eq. (1), one sees that if $c > c_0(s)$ spheres are overcharged (positive), while in the opposite case $c < c_0(s)$ they are undercharged (negative). Detail derivation of Eq. (3) can be found in Sec. II of Ref. 5 (See Eq. (26) of this reference).

Our main result is that the height of the Coulomb barrier between two spheres is

$$V_{max} = -\alpha CU^2,$$

where $\alpha$ is a numerical factor of the order of unity (at weak screening, $\alpha = 0.3$, at very strong screening, $\alpha = 1$). Thus the rate $\nu$ at which doublets appear has the form

$$\nu(U) = \nu_0 \exp(-\alpha CU^2/k_BT).$$

Exponential factor of Eq. (4) is, of course, the probability of activation above the Coulomb barrier between two macroions.

Eq. (4) suggests that the Coulomb barrier between aggregates increases as their size grows. This leads to the decreasing sticking probability between two aggregates as their size increases. This, in turn, leads to the slowing down of the growth of the aggregate size with time. We call this the "self-regulated" aggregation and show that in this case an aggregate size increases only as a logarithmic function of time

$$R(t) \simeq R_1 \ln(t/t_1),$$

where the size and time constant $R_1$ and $t_1$ will be given in Sec. III. To the best of our knowledge, this logarithmic behaviour is reported for the first time.
However, “self-regulated” aggregation cannot continue forever. When aggregates are so large that their time of activation above the Coulomb barrier is longer than the time for one macroion to desorb from an aggregate, one enters a Lifshitz-Slezov (LS) regime of coagulation where the aggregate size increases linearly with time with a very long time constant. In this regime, aggregates gain size by adsorbing free spheres which desorb from other aggregates.

Screening can diminish the Coulomb barrier substantially. At strong screening, the LS regime may never be reached. Instead the height of Coulomb barrier saturates when the aggregate size reaches the screening length \( r_s \). In this case, the “self-regulated” aggregation is followed by the reaction limited aggregation where Coulomb barrier is constant for any aggregates with size greater than \( r_s \) and the average aggregate size increases roughly quadratically in time.

There have been various experiments studying the kinetic of macroion coagulation induced by Z-ions, such as latex particles complexed with short DNA segments or hematite particles complexed with polyacrylic acid. In both experiments, the author observed an exponential increase in the rate of coagulation when the neutrality line is approached. At the same time, as the Z-ions concentration increases across this line, the electrophoretic mobility of the macroions changes sign suggesting a charge inversion effect. When Z-ions concentration are much larger or smaller than the neutrality composition, macroions are under- or overcharged and the Coulomb barrier exponentially diminishes their sticking probability. These results are in qualitative agreement with Eq. (1). However, instead of \( \ln[\nu(U)] \propto U^2 \), the authors of Ref. 3 observed a plateau in the aggregation rate around the neutrality point \( U = 0 \). This may be due to the limited time resolution of the experiment at the initial fast stage of coagulation.

The paper is organized as following. In Secs. II and IV, we study the kinetic barrier for two approaching macroion with spherical shape and rod-like shape at a given Z-ion concentration. In section III, we discuss different stages of macroion coagulation, namely how the coagulation rate crossovers from a diffusion limited regime to the new “self-regulated” regime and finally to LS regime. In the conclusion, we summarize our results.

II. COULOMB POTENTIAL BARRIER BETWEEN TWO APPROACHING SPHERES

Let us start by calculating the Coulomb barrier between two approaching spheres. Because the charge of each sphere is not fixed but self-adjusts (by releasing or absorbing Z-ions) according to their positions, one has to calculate self-consistently the Coulomb repulsion between spheres and their charges at a given separation. The capacitor charging picture of Eq. (3) offers a very convenient way of doing this. Indeed, the voltage \( U \) depends only on the concentration of bulk Z-ions and the surface charge density of the spheres (through the chemical potential \( \mu_{\text{SCL}} \)) and, therefore, is constant for a given \( c \) and sphere surface charge density \( \sigma \). Because the SCL of Z-ions on the macroion surface behaves as a metal, one can view the system of spheres and their aggregates as a system of conductors under a constant charging potential \( U \). Thus, one can calculate the net charge of not only spheres but also their aggregate of any size by using the appropriate capacitance \( C_{\text{aggregate}} \) instead of \( C \).

In the same way, the kinetic Coulomb potential barrier between any two aggregates can also be calculated.

Because, Z-ions are much more mobile than spheres, the process of charging up the spheres is much faster than coagulation and at any instance during the coagulation process, the Z-ions distribution is in equilibrium. With this assumption, one can write the Coulomb interaction energy between two spheres when they are at distance \( r \) from each other as:

\[
V(r) = \frac{C_{11}(r) + 2C_{12}(r) + C_{22}(r)}{2} U^2 - \varepsilon R U^2 ,
\]

where \( C_{11}(r) \), \( C_{22}(r) \) and \( C_{12}(r) \) are, respectively, the self capacitances of the spheres 1 and 2 and their mutual capacitance. The capacitance of an isolated sphere of is \( \varepsilon R \).

When dealing with a system under constant charging potential, the free energy \( F(r) \) of the system must include the work of the source (in our case, the population of free Z-ions) to maintain this potential

\[
F(r) = V(r) - \sum_{i,j=1}^{2} C_{ij}(r) U^2 = -V(r) .
\]

It is the lowering in the free energy compared to the reference system of two completely neutralized spheres with the rest of Z-ions free.

The capacitance \( C_{11}, C_{22} \) and \( C_{12} \) has been calculated for two spherical conductors:

\[
C_{11}(r) = C_{22}(r) = \varepsilon R \sinh \beta \sum_{n=1}^{\infty} \sinh^{-1} [ (2n-1) \beta] , \quad (9)
\]

\[
C_{12}(r) = -\varepsilon R \sinh \beta \sum_{n=1}^{\infty} \sinh^{-1} (2n \beta) , \quad (10)
\]

where \( \beta > 0 \) satisfies \( \cosh \beta = r/2R \).

Substituting Eqs. (10) into Eq. (5), one can easily find the cost in the free energy \( -V(r) \) in moving two spheres from infinity to the distance \( r \). The result is plotted by the solid line in Fig. 1. For comparison, the potential barrier for the case when the spheres keep their charge \( q^* = C(\infty)U = \varepsilon R U \) fixed when approaching each others is also plotted. The maximum of the potential barrier is located very close to the distance \( r = 2R \) where two spheres touch each other and is equal to

\[
V_{\text{max}} \approx 0.3 \varepsilon R U^2 . \quad (11)
\]
As one can see, at the maximum of the potential barrier, the self-adjustment of the sphere charge reduces this barrier height by about 40% compared to the barrier of $0.5\varepsilon RU^2$. One would get if the sphere charges were kept fixed upon approaching.

Due to this Coulomb barrier, the expression for the rate at which spheres come to each other to form doublets contains an exponential factor related to the probability of activation above this barrier as shown in Eq. (5).

In the above calculation, it is assumed the Coulomb potential is unscreened. In reality, there is always a finite concentration of monovalent salt in water solution, which leads to the screening of Coulomb interaction at distance larger than the Debye-Hückel screening length $r_s$. If $r_s$ is larger than the averaged distance between $Z$-ions at the surface of an aggregate, the correlation between $Z$-ions remains unscreened. Therefore, the concentration $c_0$, and correspondingly, the charging potential $U$ remain constant. Thus, in this regime, screening influences the process of coagulation only through the change in the capacitance of each sphere.

When the radius of the aggregate is smaller than the screening radius, $R < r_s$, the Coulomb interaction is not screened when the aggregates touch each other, therefore the above result remains valid. In the opposite case, when $R > r_s$, the capacitance of each isolated aggregate is that of a plane capacitor with thickness $r_s$ and area $4\pi R^2$, $C_{1,2}(\infty) = \varepsilon R^2 / r_s$. Using this planar capacitor approximation, it is not difficult to estimate the change in the total capacitance of the system when the two aggregates touch each other. Indeed, simple geometric calculation gives the reduction in the area of the planar capacitor when the two spherical aggregates touch each other is $4\pi Rr_s$. Thus, the change in the capacitance of the system is $\Delta C = C_{11} + 2C_{12} + C_{22} - C_1(\infty) - C_2(\infty) = \varepsilon R$. Thus, in this case the maximum of the potential barrier is

$$V_{\text{max}} = \varepsilon RU^2, \quad (R >> r_s). \quad (12)$$

Comparing this results with Eq. (11), one sees that, beside a numerical factor, screening does not affect the height of the potential barrier between two approaching spheres as long as $r_s$ is larger than the average distance between $Z$-ions on the spheres.

III. LATER STAGES OF COAGULATION

In previous sections, we discussed the kinetic barrier when two macroions approach each other to form a doublet. This fast process happens at the initial stage of coagulation where the concentration of free macroions is large. Doublets coagulate with free macroions or other doublets to form bigger macroions aggregates. This section deals with later stages of coagulation.

The problem of coagulation is generally complicated and can be solved exactly only in special cases. However, the main physics can be captured if one works with the dominant aggregate size $R(t)$ (with concentration $N(t)$) at a given time assuming this typical aggregates carry all the mass of the macroions.

Let us start from the initial stage of coagulation when the aggregate size are small, so that at small enough $U$ (close to the neutrality line) the Coulomb barrier between aggregates is smaller than $k_B T$. In this case, the Coulomb barrier of Eq. (11) has little effect and the probability of sticking for two aggregates is of the order of unity. This is the regime of the well-known diffusion limited aggregation. The concentration of the typical size aggregates decreases as inverse of time $t$,

$$N(t) = \frac{s}{1 + t/\tau_{\text{diff}}} \approx s \frac{\tau_{\text{diff}}}{t} \quad \text{for} \quad t \gg \tau_{\text{diff}}, \quad (13)$$

where $\tau_{\text{diff}} \sim \eta / k_B T s$, $s$ is the initial concentration of free macroions and $\eta$ is the viscosity of water. Thus, the rate of coagulation in this early stage is relatively constant independent of $U$ and equal to the rate of coagulation at the neutrality line where the charging potential $U$ is exactly zero and there is no Coulomb barrier.

The regime of diffusion limited aggregation stops when the typical size of the macroion aggregates reaches such a size that the Coulomb barrier is larger than $k_B T$. Using Eq. (11), one sees that this regime is reached when the typical size equal

$$R_1 \simeq k_B T / \varepsilon U^2. \quad (14)$$

Assuming an aggregate has a fractal dimension $d_f$ (in practical situation, $d_f \simeq 2$) so that the number of spheres in it is $(R/R)^{d_f}$, the time at which $R_1$ is reached is

$$t_1 = \tau_{\text{diff}} (k_B T / \varepsilon U^2 R)^{d_f}. \quad (15)$$
When \( t > t_1 \), the Coulomb barrier \( V_{\text{max}} \approx \epsilon RU^2 \) has to be taken into account. In this regime, the dominant contribution to the rate of coagulation comes from the tunneling of aggregates through the Coulomb barrier. The change in the concentration of typical aggregates obeys the equation:

\[
\frac{dN(t)}{dt} = -\kappa DR^2 N^2 \exp(-V_{\text{max}}/k_B T) \tag{16}
\]

where the numerical factor has been dropped on the right hand side and the factor \( \kappa \) satisfies \( \kappa^2 = -(d^2 V(r)/dr^2)_{\text{max}}/2k_B T \). Since the typical width of the Coulomb barrier is \( R \), \( \kappa \approx \sqrt{V_{\text{max}}/k_B T} \). Using the Stoke formula, \( D \approx k_B T/\eta R \), one can solve Eq. (16) assuming that the typical size aggregates consume all the mass of the macroions:

\[
R = R_1(N_1/N)^{1/d_f}, \tag{17}
\]

where \( N_1 = N(t_1) \). The concentration of typical size aggregates in this regime decreases logarithmically with time:

\[
N(t) \approx N_1 \left[ \ln \left( \frac{t - t_1}{t_1 d_f} + e \right) \right]^{-d_f}, \tag{18}
\]

where \( N_1 = N(t_1) \). Eq. (16) for the size of the typical aggregates can be obtained easily using the relationship (17).

As of our knowledge, this slow logarithmic kinetics was never reported in literature. It is the result of the increase in Coulomb barrier when aggregate size grows. This diminishes their sticking probability, which in turn slows down the kinetics from the linear size increase to a logarithmic one. We thus call this regime “self-regulated” aggregation.

In the regimes we considered so far, the increase in the aggregate mass is caused by a collision between two aggregates of size \( R(t) \). When the typical aggregate size becomes very large, the Coulomb barrier between two approaching aggregates becomes so high that the corresponding coagulation rate (which is proportional to \( \exp(-V_{\text{max}}/k_B T) \)) becomes very small, and a different and faster aggregate growth mechanism, namely the Lifshitz-Slezov (LS) one, comes into play. In this mechanism, the large aggregates do not collide into each other and the primary mechanism for aggregate growth is no longer due to real space diffusion. Instead, the change in their size is provided by the releasing and adsorbing of spheres which have much smaller kinetic barriers. This mechanism provides a faster coagulation process because the binding energy of a sphere in a very large aggregate and the Coulomb barrier between a very large aggregate and a sphere are finite and do not depend on the aggregate size. One can think of LS mechanism as a diffusion in size space. Interestingly, the concentration of typical size aggregates in this mechanism also decreases as inverse of time:

\[
N(t) \propto \tau_{\text{LS}}/t, \tag{19}
\]

where the time constant \( \tau_{\text{LS}} \) is much longer than \( \tau_{\text{diff}} \) because it is proportional to the concentration of free macroions in solution

\[
\tau_{\text{LS}} \propto \exp(-E/k_B T) \tag{20}
\]

Here \( E \) is the binding energy of a sphere in an aggregate which does not depend on the aggregate size.

One can easily find the size of the typical aggregate at which LS mechanism is important by comparing the detaching time \( \tau_{\text{LS}} \) of a small macroion from the aggregates with the activation time for two aggregates to go through the Coulomb barrier which is of the order \( \exp(-\epsilon RU^2/k_B T) \). This gives

\[
\epsilon RU^2 = E. \tag{21}
\]

Thus the typical size at which LS regime starts is:

\[
R_2 = E/\epsilon U^2. \tag{22}
\]

A phase diagram of different regimes of coagulation is shown in Fig. 3. With increasing time, \( R \) grows along a vertical line starting from \( R = R_2 \). Below the solid line which represents \( R_1(U) \), the coagulation is diffusion limited and the aggregate mass increases with time linearly as \( t/\tau_{\text{diff}} \). Above the solid line which represents \( R_2 \), the coagulation process is of LS nature and the aggregate mass also increases linearly with time \( t/\tau_{\text{LS}} \). In between these two lines is regime of “self-regulated” aggregation. In this regime, the aggregate size increases logarithmically.

Above, we dealt with the unscreened Coulomb potential between two aggregates. This is valid if the screening length of the solution is very large \( (r_s > R_2) \). For smaller screening length, when the typical aggregate size reaches \( r_s \), due to the fractal nature of aggregates, the Coulomb barrier stops increasing. In this case, LS regime cannot be reached. One goes from the “self regulated” regime to the regime of reaction limited aggregation with constant.
Coulomb barrier and almost zero probability of macroion detaching from the aggregates. One can calculate the change in the concentration $N$ in this regime using the Eq. (16).

Denote by $t_s$ the time at which the typical aggregate size reaches $r_s$ (from Eq. (16)), $t_s \approx t_1 \exp(\varepsilon r_s U^2/k_BT)$. At $t > t_s$, the exponential factor in Eq. (16) becomes constant, $\exp(-\varepsilon r_s U^2/k_BT)$, and so does the factor $\kappa$. The solution of this equation shows a fast decrease in the concentration of typical aggregates with time:

$$N(t) = N(t_s) \left[1 + \frac{t - t_s}{\tau_{\text{react}}} \right]^{d_f/(1-d_f)},$$

where $\tau_{\text{react}}$ is an exponentially long time constant:

$$\tau_{\text{react}} = \frac{\eta}{k_BT N(t_s)} \exp(\varepsilon r_s U^2/k_BT) \sqrt{\varepsilon r_s U^2/k_BT}.$$

In a typical situation, $d_f \approx 2$, the number of spheres in the typical aggregates (which is inversely proportional to $N$) increases as $t^2$. Although this is a very fast kinetic, it is still slower than an exponential growth of the cluster size suggested recently. We currently do not have a clear understanding of the origin of this theoretical result.

At even smaller screening length, $r_s < R_1$, the Coulomb barrier between two aggregates never becomes larger than $k_BT$ and one always stays in the regime of diffusion limited aggregation.

The evolution of the typical aggregate size as a function of time is plotted in Fig. 4 for $r_s < R_2$.

**IV. AGGREGATIONS OF ROD-LIKE POLYMERS**

In this section, we would like to discuss the kinetic barrier for the coagulation process when the role of macroion is played by a rigid polyelectrolyte (PE), such as DNA. We assume the length of PE molecules is smaller than its persistence length so that each can be considered as rigid rod. Due to the anisotropy of this problem, there is a number of different paths of aggregation of rods.

The authors of Ref. 3 studied the kinetic barrier between two approaching rods as a function of their orientation when the rods approach each other in the direction perpendicular to their bodies (Fig. 5a). We believe the kinetic barrier associated with this way of approaching is too large because of their large electrostatic repulsion when placed side by side, especially when the screening of solution is week. In this section, we propose another path of approaching of two rigid rods which has a lower kinetic barrier. Namely, the two rods approach in such a way that their centers of mass lie on a line parallel to their longer axes (See Fig. 5b). One can easily see that, in this way, charges of the rods are kept further from each other than in Fig. 5a. Thus for the paths of Fig. 5b, the kinetic barrier between the rods is lower.

We can calculate the Coulomb barrier between two approaching rods as in Sec. II, starting from the idea that both rods are under constant charging voltage $U$. The capacitance of a metallic rods of length $L$ and radius $a$ is $C = \varepsilon L/2 \ln(L/a)$ for a weakly screening solution ($r_s \gg L$) and is $C = \varepsilon L/2 \ln(r_s/a)$ for stronger screening ($L >> r_s >> a$). Thus the change in the capacitance of the system when the two rods ends start touching other is $\Delta C \approx \varepsilon L/\ln^2(L/a)$ for the weak screening case, and $\Delta C \approx \varepsilon r_s/\ln^2(r_s/a)$ for stronger screening.

As the rods start to overlap, the short range attraction between the rods starts to come into play, which partially compensates the increases in Coulomb repulsion and reduced the kinetic barrier. If the length of the overlap...
segment is \( x \) and if the attraction energy is \( -\epsilon \) per unit length, the free energy of the system can be written as \( -\Delta C(x)U^2 - \epsilon x \), which is \( x(\epsilon LU^2/\ln(L/a) - \epsilon) \) for the weak screening case and is \( x(\epsilon LU^2/\ln(r_s/a) - \epsilon) \) for the strong screening case. Because, in the final stage when the two rods lie parallel to each other, the attraction energy is assumed to win over their Coulomb repulsion, \( \epsilon > \epsilon LU^2/\ln(r_s/a) \), one easily sees that when the rods start to overlap, total energy start to decrease. Thus the maximum of the potential barrier is at the distance at which the rods start to overlap.

\[
V_{\text{max}} \simeq \begin{cases} 
\frac{\epsilon LU^2}{\ln^2(L/a)} & \text{for } r_s > L \\
\frac{\epsilon r_s U^2}{\ln^2(r_s/a)} & \text{for } r_s < L.
\end{cases}
\] (24)

Obviously, this potential barrier is much smaller than that in the case the rods approach each other in the direction perpendicular to their length. In the latter case, the maximum of the potential barrier is at the distance where they touch each other side by side and is equal to \( \epsilon LU^2/\ln(L/a) \) for \( r_s > L \), and \( \epsilon LU^2/\ln(r_s/a) \) for \( r_s < L \).

At later stages of aggregation, collinear approaches should dominate as well. This can explain why in many real and numerical experiments, very elongated structures are seen.

V. CONCLUSION

In this paper, we provide a general framework for calculation of the Coulomb potential between two macroions in solution of multivalent counterions and study various stages in the coagulation of macroions. The capacitance interpretation of Eq. (24) proves to be very useful in calculating the net charge of any macroions and aggregates of any shape. It also helps to easily calculate the Coulomb barrier between two approaching macroions. Using this equation, we are able to calculate and compare different paths of coagulation for rod-like macroions.

We discuss several stages of coagulation in time. In low salt, the coagulation process goes from a diffusion limited regime to a “self-regulated” regime and finally to the regime Lifshitz-Slezov kinetic. In the “self-regulated” regime, as the aggregate size increases, their Coulomb barrier increases diminishing their sticking probability and slowing down the kinetic. As a result, the aggregate size increases as a slow logarithmic function of time instead of the standard linear relationship. At higher salt concentration, Coulomb barrier is screened and stop increasing after the aggregates reach a certain size (of the order of the screening length \( r_s \)). In this case, Lifshitz-Slezov regime cannot be reached. Instead, one reaches a reaction limited regime where the Coulomb barrier is constant and the aggregate size increases quadratically in time. At very high salt concentration, one even cannot reach the reaction limited aggregation regime and always stays in the regime of diffusion limited aggregations.

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