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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 rodlike) 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.

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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 (PE) 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 [1,2], latex particles with various oppositely charged polyelectrolytes [3], or hematite particles with polyacrylic acid [4].

In such solutions, each sphere adsorbs many Z-ions. They strongly repel each other at the surface of the sphere and form a strongly correlated two-dimensional liquid reminiscent of a 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 [5] in addition to what mean field theories predict. Therefore, when the 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 [6]. In Fig. 1 the "neutrality" line $c_0(s)$ is shown in plane (s,c) together with two signs of Q^* that 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 [7]. This energy gain results in an attraction between spheres that, together with the traditionally discussed van der Waals forces, leads to 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 [1,2].

Because colloidal solutions are stable due to the Coulomb repulsion between particles, coagulation is usually 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

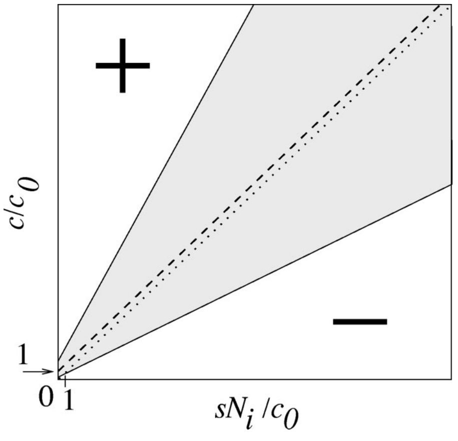

FIG. 1. Phase diagram of a solution of negative spheres with compact Z-ions in the plane of their concentrations (s,c). The dotted line corresponds to the isoelectric composition $c=sN_i$, where $N_i=Q/Z$ is the number of Z-ions needed to neutralize one sphere. The dashed line corresponds to the concentration of Z-ions $c=c_0(s)$, where the net charge of a sphere with adsorbed Z-ions crosses zero. The two solid lines define the external boundary of domain where spheres coagulate. The plus and minus are the signs of the net charge of free spheres above and below the dashed curve.

so weak that the free energy is gained when spheres touch each other. Thus when, say, the concentration of Z-ions, c, 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 earlier paper [6], we derived expressions for $c_c(s)$ and $c_d(s)$. These curves are plotted in Fig. 1. Remarkably, phase diagrams of this type were discovered experimentally more than half a century ago for complexes of strongly oppositely charged proteins [8]. However, in Ref. [8] only the charge of large aggregates of macroions (coacervate droplets) was measured and the net charge of a single macroion was not discussed. No explanation was proposed for charge inversion of aggregates. In Ref. [6] we suggested an equilibrium theory of the phase diagram of Fig. 1 and showed that aggregates of spheres and isolated spheres change sign of their net charge at the same line $c_0(s)$.

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 above 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

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

where the critical concentration

$$c_0(s)=c_0+sN_i\,. \tag{2}$$

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 [5] $c_s\exp(\mu_{SCL}/k_BT)$, where c_s is the three-dimensional concentration of the surface layer of the SCL of Z-ions and μ_{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. [6], the net charge of the sphere was shown to be proportional to U near the neutrality line,

$$Q^*=CU, \tag{3}$$

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 ε is dielectric constant of water. Because U depends on the correlation chemical potential μ_{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). Detailed derivation of Eq. (3) can be found in Sec. II of Ref. [6] [See Eq. (26) of this reference].

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

$$V_{max}=\alpha CU^2, \tag{4}$$

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

$$\nu(U)=\nu_0\exp(-\alpha CU^2/k_BT). \tag{5}$$

The exponential factor of Eq. (5) is, of course, the probability of activation above the Coulomb barrier between two macroions.

Equation (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,

$$\mathcal{R}(t)\simeq\mathcal{R}_1\ln(t/t_1), \tag{6}$$

where the size and time constant $\mathcal{R}_1$ and t_1, respectively, will be given in Sec. III.

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 that desorb from smaller 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 [1] or other oppositely charged polyelectrolytes [3], or hematite particles complexed with polyacrylic acid [4]. In all these experiments, the authors 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 undercharged or overcharged and the Coulomb barrier exponentially diminishes their sticking probability. The results of Refs. [1,3] are in qualitative agreement with Eq. (5). However, the authors of Ref. [4] observed a plateau in the aggregation rate around the neutrality point $U=0$, instead of $\ln[\nu(U)]\propto U^2$. 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 rodlike shape at a given *Z*-ion concentration. In Sec. 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 (or to reaction limited 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 μ_{SCL}) and, therefore, is constant for a given *c* and sphere surface charge density σ. 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,

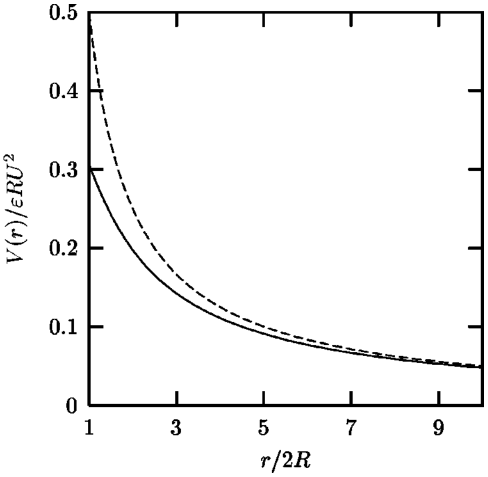

FIG. 2. The Coulomb potential barrier between two spheres (the solid line). For comparison, the Coulomb potential barrier for two spheres with fixed charge is plotted (the dashed line). Note that, although not plotted, at distances very close to $r/2R=1$, the interaction energy drops below zero due to the short range electrostatic correlation attraction between *Z*-ions and the van der Waals attraction between spheres.

$$-V(r)=\frac{C_{11}(r)+2C_{12}(r)+C_{22}(r)}{2}U^2-\varepsilon RU^2, \tag{7}$$

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 is εR.

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

$$F(r)=V(r)-\sum_{i,j=1}^{2}C_{ij}(r)U^2=-V(r). \tag{8}$$

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

The capacitance is C_{11}, C_{22}, and C_{12} have been calculated for two spherical conductors [9]:

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

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

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

Substituting Eqs. (9) and (10) into Eq. (7), 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. 2. For comparison, the potential barrier for the case when the spheres keep their charge $q^*=C(\infty)U=\varepsilon RU$ fixed when approaching each other 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

$$V_{max}\simeq 0.3\varepsilon RU^2. \tag{11}$$

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).

One should bear in mind that in writing down Eq. (11), the maximum of the potential is assumed to be at the contact distance $r=2R$ between two spheres. Due to the electrostatic correlation attraction and the van der Waals attraction between spheres, the maximum of the potential is actually located at some distance δr away from contact. However, both of these forces are of very short range nature. Therefore, unless the system is in the very vicinity of the neutral composition $(U\simeq 0)$, δr is much smaller than R and the potential energy $V(r)$ drops steeply near $r=2R$. Indeed, the van der Waals force between two spheres near contact is $HR/\delta r^2$, where H is the Hamaker constant ($\sim 10k_BT$ at room temperature). Equating this force with the Coulomb force εU^2, one has $\delta r/R\sim\sqrt{H/\varepsilon RU^2}\ll 1$. The electrostatic correlation attraction force has the range of the average distance between Z-ions on the sphere surface that is also much smaller than R. Thus, we have $\delta r\ll R$ for both forces. Therefore, the correction to V_{max} is very small and one can use Eq. (11) for the kinetic potential barrier between two spheres.

In the above calculation, it is also assumed that 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

$$V_{max}=\varepsilon RU^2 \quad (R\gg r_s). \tag{12}$$

Comparing this result with Eq. (11), one sees that, besides 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 preceding 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 $\mathcal{R}(t)$ [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 is small, so that at small enough U (close to the neutrality line) the Coulomb barrier between aggregates is smaller than k_BT. 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 [12]:

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

where $\tau_{\rm diff}\sim\eta/k_BTs$, s is the initial concentration of free macroions, and η 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_BT. Using Eq. (11), one sees that this regime is reached when the typical size equals

$$\mathcal{R}_1\simeq k_BT/\varepsilon U^2. \tag{14}$$

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 $(\mathcal{R}/R)^{d_f}$, the time at which $\mathcal{R}_1$ is reached is

$$t_1=\tau_{\rm diff}(k_BT/\varepsilon U^2R)^{d_f}. \tag{15}$$

When $t > t_1$, the Coulomb barrier $V_{max} \simeq \varepsilon \mathcal{R} U^2$ 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 [12]

$$\frac{dN(t)}{dt} = -\kappa D \mathcal{R}^2 N^2 \exp(-V_{max}/k_B T), \qquad (16)$$

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

$$\mathcal{R} = \mathcal{R}_1 (N_1/N)^{1/d_f}, \qquad (17)$$

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

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

where $N_1 = N(t_1)$. Equation (6) 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 $\mathcal{R}(t)$. 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 $\exp(-V_{max}/k_BT)$] becomes very small and a different and faster aggregate growth mechanism, namely, the LS one, comes into play. In this mechanism, the large aggregates do not collide with each other and the primary mechanism for aggregate growth is no longer due to real space diffusion of a large cluster. Instead, smaller aggregates shrink and eventually dissolve by releasing spheres. These spheres are adsorbed by larger aggregates leading to their growth. This process of releasing and adsorbing of individual spheres (coalescence) has much smaller kinetic barriers than the barrier for direct collision of large aggregates. This is because the latter grows with aggregate size [Eqs. (11) and (12)], while both the binding energy E_b of a sphere in a large aggregate (due to the short range van der Waals attraction between spheres and the short range attraction caused by the electrostatic correlation of Z-ions at the place of contact between spheres) and the Coulomb barrier between a large aggregate and a sphere are finite and very weakly depend on the aggregate size. It should be noted here that, although this binding energy E_b saturates when the aggregate size grows to infinity, it is the small difference between E_b of smaller aggregates and of larger aggregates (caused by the smaller surface energy per sphere of the larger ones) that is responsible for the flux of released spheres being directed toward larger aggregates. One can find extensive discussion of this mechanism for neutral particles in Ref. [11]. It is found that the concentration of typical size aggregates in this mechanism decreases as inverse of time [11]:

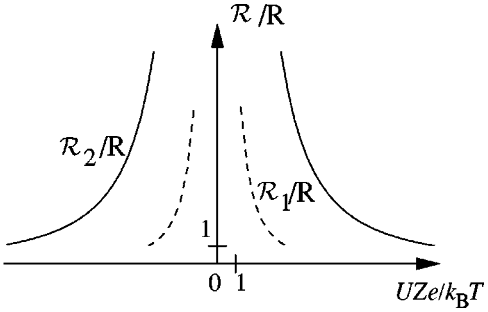

FIG. 3. The typical aggregate sizes $\mathcal{R}_1$ and $\mathcal{R}_2$ at which aggregate growth mechanism crosses over from the diffusion limited regime to the "self-regulated" regime and then to the Lifshitz-Slezov regime a function of the dimensionless parameter UZe/k_BT.

$$N(t) \propto \tau_{\mathrm{LS}}/t, \qquad (19)$$

where the time constant τ_{LS} exponentially depends on the activation energy needed to detach a sphere from an aggregate which, for neutral spheres, is the same as the magnitude of the binding energy, $\tau_{\mathrm{LS}} \propto \exp(|E_b|/k_BT)$.

In our system, there is a finite Coulomb barrier between a sphere and a large aggregate, which is of the order of the electrostatic self-energy of the sphere, $0.5\varepsilon R U^2$. Thus, the activation energy E of coagulation is larger than the magnitude of the binding energy,

$$E = |E_b| + 0.5\varepsilon R U^2, \qquad (20)$$

and the time constant τ_{LS} is given as

$$\tau_{\mathrm{LS}} \propto \exp(E/k_B T). \qquad (21)$$

One can easily find the size of the typical aggregate at which LS mechanism is important by comparing the detaching time τ_{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 $\exp(-\varepsilon \mathcal{R} U^2/k_BT)$. This gives

$$\varepsilon \mathcal{R} U^2 = E. \qquad (22)$$

Thus, the typical size at which LS regime starts is,

$$\mathcal{R}_2 = E/\varepsilon U^2. \qquad (23)$$

A phase diagram of different regimes of coagulation is shown in Fig. 3. With increasing time, $\mathcal{R}$ grows along a vertical line starting from $\mathcal{R} = R$. Below the dotted line that represents $\mathcal{R}_1(U)$, the coagulation is diffusion limited and the aggregate mass increases with time, linearly as t/τ_{diff}. Above the solid line that represents $\mathcal{R}_2$, the coagulation process is of LS nature and the aggregate mass also increases linearly with time t/τ_{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 ($r_s > \mathcal{R}_2$). For smaller screening length, when the typical aggregate size reaches r_s, due to the fractal nature of aggregates, the Coulomb barrier stops increasing [15]. 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).

Denoted by t_s the time at which the typical aggregate size reaches r_s [from Eq. (6), $t_s \simeq t_1 \exp(\varepsilon r_s U^2/k_B T)$]. At $t > t_s$, the exponential factor in Eq. (16) becomes constant, $\exp(-\varepsilon r_s U^2/kBT)$, and so does the factor κ. The solution of this equation shows a fast decrease in the concentration of typical aggregates with time,

$$N(t) = N(t_s)\left[1 + \frac{t - t_s}{\tau_{\mathrm{react}}}\frac{d_f - 1}{d_f}\right]^{d_f/(1-d_f)}, \qquad (24)$$

where τ_{react} is an exponentially long time constant,

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

In a typical situation $d_f \simeq 2$ 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 [13,14]. We currently do not have a clear understanding of the origin of this theoretical result.

At even smaller screening length $r_s < \mathcal{R}_1$ the Coulomb barrier between two aggregates never becomes larger than $k_B T$ 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 $r_s < \mathcal{R}_2$.

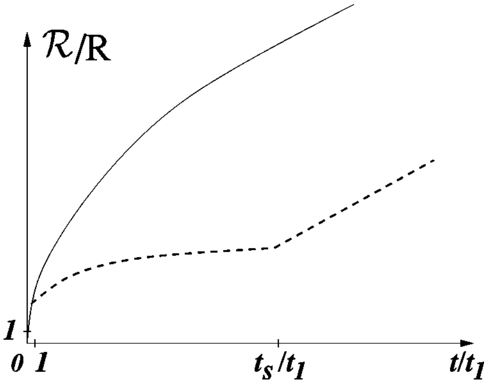

FIG. 4. Sketch of the dependence of the size $\mathcal{R}$ of typical aggregates as function of time t. The solid line corresponds to the case of very strong screening $r_s < \mathcal{R}_1$, where the Coulomb barrier is smaller than $k_B T$ and aggregation is diffusion limited ($\mathcal{R} \propto \sqrt{t/\tau_{\mathrm{diff}}}$). The dashed line corresponds to intermediate screening $\mathcal{R}_1 < r_s < \mathcal{R}_2$, where one goes from diffusion limited aggregation to self-regulated aggregation [$\mathcal{R} \propto \ln(t/t_1)$] and to irreversible reaction limited aggregation ($\mathcal{R} \propto t/\tau_{\mathrm{react}}$).

IV. AGGREGATIONS OF RODLIKE 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 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 are a number of different paths of aggregation of rods.

The authors of Ref. [10] 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. 5(a)]. 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 weak. 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. 5(b)]. One can easily see that, in this way, charges of the rods are kept farther from each other than in Fig. 5(a). Thus for the path of Fig. 5(b), 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 rod 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 ($L \gg r_s \gg a$). Thus the change in the capacitance of the system when the ends of the two rods start touching each other is $\Delta C \simeq \varepsilon L/\ln^2(L/a)$ for the weak screening case, and is $\Delta C \simeq \varepsilon r_s/\ln^2(r_s/a)$ for stronger screening.

As the rods start to overlap, the short range attraction between the rods come into play, which partially compensates the increases in Coulomb repulsion and the reduced

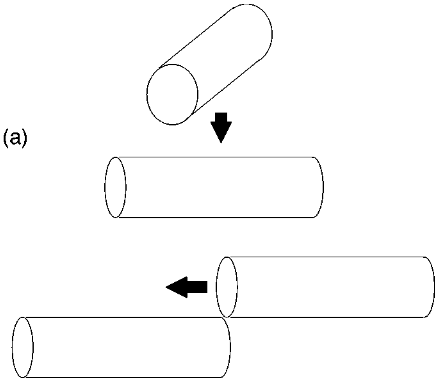

FIG. 5. Different paths of coagulation for two rigid rods. (a) The path studied in Ref. [10]. (b) The path, which according to our paper, has lower kinetic barrier.

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 $-\Delta C(x)U^2 - x\epsilon$, which is $x[\varepsilon LU^2/\ln(L/a) - \epsilon]$ for the weak screening case and is $x[\varepsilon LU^2/\ln(r_s/a) - \epsilon]$ 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, $\epsilon > \varepsilon LU^2/\ln(r_s/a)$, one easily sees that when the rods start to overlap, total energy start to decrease. Thus, the maximum of the potential barrier is at about the distance at which the rods start to overlap,

$$V_{max} \simeq \begin{cases} \varepsilon LU^2/\ln^2(L/a) & \text{for } r_s > L, \\ \varepsilon r_s U^2/\ln^2(r_s/a) & \text{for } r_s < L. \end{cases} \tag{25}$$

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 $\varepsilon LU^2/\ln(L/a)$ for $r_s > L$, and $\varepsilon LU^2/\ln(r_s/a)$ 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. (3) 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 kinetics. 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 stops 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 cannot even reach the reaction limited aggregation regime and always stays in the regime of diffusion limited aggregations.

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[15] If the aggregates are perfectly spherical, their Coulomb barrier would have to continue to grow with their size regardless of the screening length [See Eq. (12)]. However, due to their fractal nature, the aggregate surface where they touch each other has the same curvature as that of an aggregate with size r_s. Thus, the Coulomb barrier for two aggregates with size $\mathcal{R} > r_s$ remains the same as the Coulomb barrier between two aggregates with size r_s, which is equal $\varepsilon r_s U^2$.