Self-Focussing Dynamics in Monopolarly Charged Suspensions

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The Smoluchowski equation for irreversible aggregation in suspensions of equally charged particles is studied. Accumulation of charges during the aggregation process leads to a crossover from power law to sub-logarithmic cluster growth at a characteristic time and cluster size. For larger times the suspension is usually called stable, although aggregation still proceeds slowly. In this regime the size distribution evolves towards a universal scaling form, independent of any parameter included in the theory. The relative width falls off to a universal value \( \sigma_t^\infty \approx 0.2017 \) that is much smaller than in the uncharged case. We conjecture that \( \sigma_t^\infty \) is a lower bound for the asymptotic relative width for all physical systems with irreversible aggregation.

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In many fields of science irreversible aggregation (or coagulation, agglomeration, clustering) phenomena are important. Examples include aerosol coalescence, polymerization or gelation (see, e.g., \[1\]–\[6\] and references therein). Such systems have been described using Smoluchowski’s coagulation equation and extensive analytical and numerical studies have been carried out for uncharged systems \[1\]–\[3\]. In spite of the fact that charges are present in a lot of aggregating systems, much less is known for the charged case. In this Letter we investigate the influence of charges on the aggregation process. In contrast to previous work which studied aggregation between oppositely charged particles \[3\] we investigate the aggregation dynamics of equally charged particles with the focus on suspensions. A practical example is given in \[3\], where coating of medical drug particles with nanoparticles is investigated, in order to make them inhalable.

As an intermediate step it is desirable to keep each powder component in suspension separately, controlling its aggregation by charging the particles equally. They collide due to Brownian motion, and strong van der Waals forces result in irreversible aggregation (Brownian coagulation). However, the results we derive are valid for more general systems, as well. Asymptotically neither the solvent nor the diffusion properties are important, as long as particles may have high kinetic energy, albeit as rare events, and charges accumulate in the aggregation process.

Usually a suspension is regarded as stable with respect to the aggregation of equally charged particles, if the particle diameter \( d \) is small compared to the Bjerrum length \( \ell_B=q^2/4\pi\varepsilon_0 k_B T \), where \( q \) is the charge of the particles, \( T \) and \( \varepsilon_r \) are the temperature and the relative dielectric constant of the carrying fluid, \( k_B \) is Boltzmann’s constant and \( \varepsilon_0 \) is the dielectric constant of vacuum. The reason is that for \( d<\ell_B \) the energy barrier for bringing two particles into contact is larger than the thermal energy.

Consider the case, where a suspension is initially unstable (as in \[4\]), which means that initially aggregation events are frequent. We are going to show that charge accumulation eventually leads to a crossover to slow aggregation at characteristic values of time \( t_c \) and cluster size \( s_c \). Above \( t_c \) the Bjerrum length becomes larger than the aggregate diameter, so that one would regard the suspension as stable for later times. However, the cluster size distribution keeps evolving slowly and approaches a universal self-similar form which is independent of any parameter included in the theory. A particular important consequence of this is that the relative width of the cluster size distribution \( \sigma_t \) starts decreasing at \( t_c \) and asymptotically reaches a universal value \( \sigma_t^\infty \approx 0.2017 \). In this sense, the cluster size distribution becomes narrower and we refer to this effect as charge-induced self-focussing. For Brownian coagulation the value \( \sigma_t^\infty \approx 0.2017 \) must be compared to \( \sigma_t \approx 1 \) for the uncharged case. We conjecture that \( \sigma_t^\infty \) is a lower bound for the asymptotic value of \( \sigma_t \) for all physical systems with irreversible aggregation. Our results are valid as long as aggregation events occur frequently compared to dissociation of clusters (neglected in the following).

We investigate Smoluchowski’s coagulation equation for monodisperse initial conditions, i.e. initially all particles have the same mass \( m^* \) and radius \( a^* \) and carry the same charge \( q^* \). As mass and charge of aggregates are proportional to each other in this case, one index \( i \) is sufficient in the coagulation equation

\[
\frac{dn_i(t)}{dt} = \frac{1}{2} \sum_{j+k=i} R_{jk} n_j(t)n_k(t) - n_i(t) \sum_{j=1}^{\infty} R_{ij} n_j(t). \tag{1}
\]

\( n_i(t) \) denotes the number density at time \( t \) of clusters of mass \( m_i = i m^* \), charge \( q_i = i q^* \) and radius \( a_i = i a^* \). \( 1/\alpha \) is the fractal dimension of the aggregates. If they are spherical (e.g., coagulating droplets) one has \( \alpha = 1/3 \). More generally one may assume that \( 1 > \alpha > 1/3 \) for fluffier aggregates. The initial conditions are \( n_i(t=0) = 1 \) and \( n_i(t=0) = 0 \) for \( i > 1 \). \( R_{ij} \) is the rate coefficient (coagulation kernel) for mergers between clusters with indices \( i \) and \( j \). Eq. (1) neglects spatial fluctuations and correlations. In this sense it is a mean field equation. We checked, that a Brownian dynamics simulation of aggre-
gating charged spheres in three dimensions is in accordance with the mean field description 7.

The rate coefficients \( R_{ij} \) depend on the particular physical system under consideration. In suspensions clusters of mass \( m_i \) diffuse with diffusion constant \( D_i \). Usually the van der Waals interaction is represented as a sticky contact force, leading to irreversible aggregation. Therefore, aggregation with a cluster of mass \( m_j \) occurs when the distance between the clusters equals \( a_i + a_j \) (Brownian coagulation). A finite range of the van der Waals interaction would basically increase this 'contact distance' by a constant, which becomes less and less important for growing clusters. For Brownian coagulation \( R_{ij} \) can be calculated by solving the diffusion equation in the presence of an absorbing sphere 4, 5 leading to
\[
R_{ij} = 4\pi(a_i + a_j)(D_i + D_j) r_{ij}.
\]
If Einstein's formula applies, one can insert \( D_j = \kappa B T / 6 \pi \eta a_i \), with the viscosity \( \eta \) of the carrying fluid. This leads to
\[
r_{ij} = \frac{2 \kappa B T}{3 \eta} (i^{\alpha} + j^{\alpha})(i^{-\alpha} + j^{-\alpha}). \tag{2}
\]

For most uncharged coagulating systems discussed in the literature the coagulation kernels are homogeneous functions of degree \( \lambda \), i.e. \( R_{bi bj} = b^\lambda R_{ij} \), with \( \lambda \leq 2 \) 1, 4. Eq. (2), for instance, corresponds to \( \lambda = 0 \). It turns out that \( \lambda \) is the most important parameter for the uncharged case. Depending on its value, the solutions of the coagulation equation are qualitatively different. For \( \lambda \leq 1 \) the cluster size distribution decays exponentially for large sizes at all times. In the scaling limit the solutions are self-similar and (for \( \lambda < 1 \)) have the form
\[
n_i(t) = s(t)^{-2} \phi(i/s(t)) \text{we have } s(t) \sim t^{1 - \lambda}. \tag{3}
\]
The scaling function \( \phi \) depends on the details of the underlying coagulation kernels. The average size \( s(t) \) is a measure for the average number of primary particles per cluster. For \( 2 \geq \lambda > 1 \) the cluster size distribution develops a power-law tail in finite time \( t \) at large sizes that violates mass conservation 1, 7 (runaway growth), which is associated with the occurrence of a gelation transition.

A derivation similar to the uncharged case leads to the coagulation kernel for Brownian coagulation of charged clusters 2,
\[
R_{ij} = W_{ij} r_{ij}, \quad W_{ij} = \kappa_{ij} / \left[ \exp(\kappa_{ij}) - 1 \right], \quad \kappa_{ij} = q_i q_j / [4 \pi \sigma_i \sigma_j (a_i + a_j) \kappa B T]
\]
where \( r_{ij} \) is the coagulation kernel for uncharged clusters, Eq. (2). It was assumed that at contact of the clusters the charges are separated by a distance \( a_i + a_j \).

The important feature of \( W_{ij} \) is that collisions of strongly charged particles (\( \kappa_{ij} \gg 1 \)) are exponentially suppressed. We are going to show that \( W_{ij} = \exp(-\kappa_{ij}) \) (which is found in charged granular gases 2) leads to the same asymptotic results.

The purpose of this Letter is to study the behavior of Eq. (2), depending on the parameters \( \lambda, \alpha \) and \( k = \sqrt{q^2 / (4 \pi \sigma_0 \epsilon r a^2 \kappa B T)} \), for rate coefficients that obey
\[
R_{ij} = (i^\alpha + j^\alpha)(i^{-\alpha} + j^{-\alpha}) \frac{\kappa_{ij}}{\exp(\kappa_{ij}) - 1} \tag{5}
\]
or
\[
R_{ij} = (i^\lambda j^\lambda) / \exp(-\kappa_{ij}) \tag{6}
\]
with
\[
\kappa_{ij} = \frac{k^2 i j}{(i^\alpha + j^\alpha)}. \tag{7}
\]

These expressions are motivated by the observations presented above. \( \kappa_{ij} \) is proportional to the Coulomb energy at contact of the clusters divided by a temperature-like variable. Eq. (5) is the dimensionless coagulation kernel for Brownian coagulation of charged clusters, Eq. (4), with \( 2 \kappa B T / 3 \eta = 1 \). Whereas this corresponds to \( \lambda = 0 \) as was pointed out above, we investigate the influence of \( \lambda > 0 \) using the general rate coefficient Eq. (6).

Let the system initially be unstable \((k^2 < 1)\) which means that in the beginning the exponential terms in Eqs. (5,6) are close to unity. The system basically behaves as if it was uncharged. This changes as soon as values of \( \kappa_{ij} \approx 1 \) become important so that the exponential terms must be taken into account. Then further aggregation is exponentially suppressed and cluster growth becomes very slow. This happens when the average cluster size \( s \) approaches a characteristic value \( s_c \) given by \( n_{sc} \approx \lambda \approx 1 \). Note that even systems which in the uncharged case exhibit runaway growth, i.e. \( 1 < \lambda \leq 2 \), eventually cross over to slow aggregation. According to Eq. (6) the crossover time \( t_c \) is given by \( s_c \sim t_c \) for \( \lambda < 1 \), leading to
\[
s_c \approx k^{\frac{1}{2 - 2\lambda}} \quad , \quad t_c \approx k^{\frac{2 - 2\lambda}{2 - \lambda}} \quad \text{for } \lambda < 1 , \tag{8}
\]
where \( t^* \) is the appropriate time unit. Note that the expression for \( s_c \) is also valid for \( \lambda > 1 \). Though similar arguments may be applied for \( t_c \) and \( \lambda > 1 \) we do not discuss this case here.

The rate equations (2) were solved numerically for various choices of the coagulation kernels \( R_{ij} \) and different values of \( k \). Fig. 1 shows data for Brownian coagulation of charged spheres (Eq. (5) with \( \alpha = 1/3 \)). The average size \( s(t) \) was calculated as \( s = M_1 / M_0 \) with the moments defined as \( M_n = \sum_i \hat{t}^n n_i \). \( M_1 \) is proportional to the constant total mass of the system and was chosen equal 1. \( s_c \) and \( t_c \) were determined according to Eq. (8). Fig. II clearly shows the crossover from fast power-law cluster growth to slow aggregation. Moreover, Eq. (8) is confirmed by the data collapse. In addition, we checked rate coefficients obeying Eq. (5) with different values of \( \lambda \) and \( \alpha \) and found in all cases agreement with Eq. (8), as well.

Comparison of the dimensionless rate (5) with Eq. (2) shows that the time unit is \( t^* = 3 \eta / 2 \kappa B T \), where \( \eta \) is the initial number density of primary particles. As an example, we compute the physical time scale \( t^* \) for possible realistic parameters. With \( \eta = 10^{-4} \text{Pa s}, T = 300 \text{K},\)
\(a^*=1\mu m\) and volume fraction \(\nu=10^{-3}\) (\(\tilde{n}\approx2\cdot10^5\text{mm}^{-3}\)) one obtains \(t^*\approx150s\). Assuming \(\epsilon_c\approx1\), charging with a single elementary charge on each primary particle corresponds to a value \(k=0.2\). For these parameters one finds with the dimensionless results of Fig. 1 that the crossover to slow aggregation occurs within hours.

In the unstable regime the system behaves basically as in the uncharged case and the cluster size distribution is approximately given by Eq. (3). Fig. 2 displays a double logarithmic plot of the scaled size distribution in the stable regime for three different times and two different choices of the rate coefficients. The coagulation kernel for the dashed lines obeys Eq. (4) with \(k=0.1\) and \(\alpha=1/3\) (Brownian coagulation of charged spheres). Solid lines correspond to Eq. (5) with \(k=0.05\), \(\alpha=0\) and \(\lambda=-2\). The inset shows the latter data unscaled (\(t_1<t_2<t_3\)). The parameter \(\alpha=0\) corresponds to the limiting case, where the Coulomb repulsion of large clusters becomes independent of the cluster radius. For comparison the dot-dashed line shows a decay \(\sim x^{-2}\). The labels \(a, b, \phi(a)\) and \(\phi(b)\) mark analytical expressions for the asymptotic edges of the distribution and the corresponding heights, which will be derived in the following. It can be seen that for monopolarly charged systems the cluster size distribution asymptotically converges to a self-similar solution analogous to Eq. (3). Furthermore, Fig. 2 strongly supports the claim that \(\phi(x)\) is independent of the details of the underlying coagulation kernel. The data suggest that the scaling function \(\phi(x)\) decays as \(\phi(x)\sim x^{-2}\) between sharp edges and is zero outside. As can be observed in the inset of Fig. 2, a consequence of this is that \(n_i\) is independent of the average size \(s\) between the edges of the size distribution. Based on the numerical data we assume

\[\phi(x) = \begin{cases} \phi_0 x^{-2} & \text{for } x \in [a, b] \\ 0 & \text{for } x \notin [a, b] \end{cases} \]  

(9)

Applying Eq. (9) one finds \(M_0=(\phi_0/s)(1/a-1/b)\) and \(M_1=1=\phi_0 \ln(b/a)\), together with \(s=M_1/M_0\) leading to

\[\ln(b/a) = [1/a - 1/b].\]  

(10)

The characteristic feature of the coagulation rates for monopolarly charged systems is that (in the stable regime) coagulation is exponentially suppressed with increasing cluster sizes. This feature does not depend on \(\lambda, k, \) and \(\alpha\) or whether one applies Eq. (3) or Eq. (4). The exponential suppression causes the rates for coagulation of clusters located at the left edge of the size distribution to be much larger than rates for any other coagulation events. Thus, clusters at the left edge with index \(i \in [as, as+\Delta i]\) coagulate, and mass conservation requires that this leads to an increase of the number of clusters with \(i \in [2as, 2as+2\Delta i]\). Hence, we expect that asymptotically \(b=2a\). Between the left and the right edge of the size distribution \(n_i\) is essentially not changed. The scaling function Eq. (4) is the only possibility to guarantee such a behavior. Inserting \(b=2a\) into Eq. (11) leads to

\[a=\frac{1}{2 \ln 2}, \quad b=\frac{1}{\ln 2}, \quad \phi_0=\frac{1}{\ln 2}.\]  

(11)

in good agreement with the numerical data, Fig. 2.

An important consequence of the universal form Eqs. (9-11) is that the relative width of the cluster size distribution \(\sigma_r=\sqrt{(M_2/M_0)/M_1^2}-1\) approaches a universal value \(\sigma_r^\infty\) with

\[\sigma_r \to \sigma_r^\infty = \sqrt{1/[2(\ln 2)^2]} - 1 \approx 0.2017.\]  

(12)
Fig. 3 shows numerical data for $\lambda=-(0,-2,-4)$ for monopolarly charged particles (solid lines) in comparison to the corresponding uncharged cases (dashed lines). $\sigma_{c}^{\infty}$ is considerably smaller than the relative width for any physical system we found in the literature.

For an initially narrow cluster size distribution the relative width first grows similar to the uncharged situation until time $t_{c}$, when it starts decreasing again, induced by the exponential suppression of further aggregation. We refer to this as self-focussing. The example discussed above, with $t^{*}\approx 150 s$, shows that this self-focussing effect can occur within an experimentally accessible time.

In the following, we specify what kind of time dependence the average size $s$ exhibits in the stable regime. For this purpose we calculate the time derivative $\frac{ds}{dt} M_{0} = \sum_{i} \frac{d}{dt} n_{i}(t)$. According to the previous results, in the stable regime $\frac{d}{dt} M_{0}$ reduces to a transfer from the left edge of the size distribution ($i=as$) to the right edge ($i=2as$). This behavior together with Eq. (9) leads to $\frac{ds}{dt} M_{0} = -\frac{1}{2} R_{ass} \phi_{0} \phi_{0}/(a s)^{4}$. In the stable regime the coagulation kernels asymptotically obey $R_{y,y} \approx \exp(-k^{2} y^{2-\alpha})$. Using $s = M_{1}/M_{0}$ we arrive at

$$\frac{ds(t)}{dt} \sim \frac{1}{s(t)^{2}} e^{-K s(t)^{2-\alpha}} \text{ with } K = k^{2} a^{2-\alpha}. \quad (13)$$

This results in the time interval $t_{2} - t_{1} \approx I(s_{2}) - I(s_{1})$ in which the average cluster size increases from $s_{1}$ to $s_{2}$, with $I(y) = \int_{1}^{y} dx x^{a} \exp(K x^{2-\alpha})$. Application of $I(y) \approx y^{\gamma} \exp(K y^{2-\alpha})$ for large $y \gg 1$, with the exponent $\gamma$ depending on $\alpha$, leads to $s(t) \sim (\ln t - \gamma \ln s(t))^{2-\alpha}$. Thus, we can conclude that asymptotically

$$s(t) \sim (\ln t)^{\frac{1}{2-\alpha}}. \quad (14)$$

A similar long-time behavior was observed in \[9,10,11\].

In conclusion, we investigated Smoluchowski’s coagulation equation for monopolarly charged particles. Charge accumulation leads to a crossover from power-law to sub-logarithmic cluster growth. Asymptotically the cluster size distribution approaches a universal scaling form, independent of any parameter included. This implies a self-focussing of the relative width of the distribution. A first experimental check is encouraging \[12\].

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