Charge-induced gelation of microparticles

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Abstract. A highly efficient coagulation process of microparticles was discovered during experiments that were carried out on the International Space Station. Charged microspheres injected into a low pressure neutral gas environment form mm-sized aggregates, provided the initial number density is high enough. The coagulation occurred at a rate $\sim 10^4$–$10^5$ times faster than that usually observed with uncharged grains. Theoretical estimates show that this process is so fast that it cannot even be explained by a coagulation process with charge enhanced cross-section. The observations can, however, be described by a ‘gelation phase transition’. We summarize the salient measurements, outline the theoretical description and show their compatibility.
1. Introduction

Coagulation—the growth of conglomerates by collisional adhesion of grains—is a ubiquitous process in planet formation, environmental science, combustion, air pollution, sedimentation, filter technology and many other fields such as flat screens and chip production. Experimental investigations have always been hampered by the fact that large aggregates cannot be easily levitated under gravity conditions, making controlled studies very difficult. Some microgravity experiments have been performed [1]—but many questions have been left unanswered, in particular the role of particle charging, which may prevent coagulation or enhance it, depending on the circumstances.

In this paper, we summarize the results of a number of experiments carried out in the last few years under microgravity conditions on the International Space Station. In particular, we find that the coagulation is distinctly different when the initial particle density is low or high. We discuss the data in terms of different coagulation models and identify the physics leading to the ‘runaway coagulation’ or ‘gelation transition’ observed when the initial particle density is high.

2. Experiment description

The Plasma Kristall experiment (PKE-Nefedov) [2] on the International Space Station was designed to investigate complex plasmas [3, 4] under microgravity conditions. It has been in operation since March 3, 2001. Apart from research into plasmas, it is also possible to investigate the physics of particle interactions in a neutral gas under microgravity conditions. This feature was used for the coagulation experiments discussed here.

The heart of the PKE experiment, described in detail in [2], consists of a plasma vessel, where a radio frequency (rf), low pressure argon discharge can be established between two parallel plate electrodes (figure 1). The separation between the 42 mm diameter electrodes is set to 30 mm. In addition to the rf-voltage, which is not used in these experiments, a low frequency (f < 100 Hz) bias voltage variation can be applied independently. The latter is used here to excite oscillatory motion on charged agglomerates, so that their charge-to-mass ratio can be determined. Particle dispensers mounted centrally in the electrodes are used to inject monodisperse...
Figure 1. Experimental setup. Particles are injected into the chamber by electrically operated ‘dust-dispensers’ through a sieve, which only allows the passage of single grains. Particles are viewed via an overview camera (see field of view LR) and a (high resolution) detailed camera (see HR).

The salient observations are the following: particles coagulate and form clusters of various masses (sizes). The mass spectrum of the clusters, \( n(m) \), can be deduced from figure 3, which shows...
Figure 2. (a) Image of a typical particle cloud during the injection into the neutral (argon) gas. About a few million particles are injected during the (2 s) injection cycle. The injected particles form a diverging plume which becomes flattened when frictional drag slows down their forward motion. The (single) image shows the central vertical cross-section through the cloud. Particles appear as elongated lines because the velocities are quite high at this stage. The horizontal ‘lines’ are an artefact of the interlace image recording. (b) Overlayed time series showing the oscillatory motion of the particles after the injection. Particles drift is mainly due to thermophoretic forces caused by small temperature differences in the experiment chamber (of order 1°).

Table 1. Particle properties and experiment conditions.

|                     | Experiment-1 | Experiment-2 |
|---------------------|--------------|--------------|
| Experiment date     | May 2001     | Jan 2003     |
| Gas                 | Ar           |              |
| ρ (mbar)            | 0.7          | 1.7          |
| a₀                  |              |              |
| m (kg)              | 3.1×10⁻¹⁴    |              |
| Nₑ (cm⁻³)           | 6×10⁸        | 4×10⁶        |
| V_HF (cm s⁻¹)       | 5–10         |              |

the number of clusters versus the reflected light intensity, I, measured just after the injection cycle. In experiment series 1 (figure 3(a)) the intensity spectrum decays with a single power law, \( \propto I^{-2.7} \), at the high-mass end without any apparent cut-off. In each experiment also a single, very large (runaway) aggregate was observed to form here. Figure 4 shows some of these aggregates. Using images obtained with the high resolution camera, we estimate that these aggregates have accumulated up to \( \sim 10^5 \) microparticles, which is a considerable fraction of the whole injected cloud. The large aggregates were observed immediately after the injection cycle, which means that they were formed during the injection period. Of course, no aggregate was introduced by
Figure 3. Intensity spectrum of clusters deduced by image analysis from images taken shortly after the injection cycle. (a) The reflected light intensity, $I$, of about $1.7 \times 10^5$ identified, coagulated particle clusters (averaged over $\approx 750$ frames and normalized to a single frame), yielding a power law ‘intensity distribution function’. Data were taken from an experiment in the first series (high-initial injected particle density). The intensity $I$ is assumed to be proportional to the cluster projection area, $\sigma$, which in turn is proportional to the squared average cluster radius, $A^2$. Considering clusters as fractal aggregates with the scaling law (3), the high-mass part of the mass spectrum can be retrieved from the intensity distribution ($I \propto m^{2/Df}$). The ‘runaway’ aggregates that are formed during these experiments are ‘detached’ from the smooth spectrum of clusters shown here and contain up to $\sim 10^5$ microparticles. Their loose fluffy structure resembles the numerical simulations of CCA. (b) The corresponding intensity histogram from experiment series 2 with low-initial injected particle density. The intensities $I$ of about $7 \times 10^4$ particle clusters (averaged over 519 frames and normalized to a single frame) are used here. The intensity values have been corrected to represent the same camera recording conditions (gain, background intensity) as used for (a).
the dispenser since the particles had to pass through the dispenser mesh. After the injection cycle the cluster mass (size) distribution remained practically unchanged. In experiment series 2 (figure 3(b)) the coagulation was significantly different, exhibiting a clear size cut-off and no single (runaway) particle was observed.

For each experiment, we identified two separate stages, the ‘high temperature stage’ and the ‘low temperature stage’. The ‘high temperature stage’ is the injection cycle, when the particle (cluster) velocities are dominated by the (15–20 Hz) gas pulsations produced by the operating dispenser. The average relative particle velocities are of the order of the velocity of the gas pulsations. This is because the period of the pulsations in our experiments (~10 ms) is of the same order as the gas–dust frictional coupling time $\gamma^{-1}$ (~3 ms for microparticles and slowly increases with cluster size), where $\gamma \approx 280 \text{ s}^{-1}$ is the neutral gas friction coefficient [5, 6]. The average velocity is estimated to be $V_{HT} \sim 5–10 \text{ cm s}^{-1}$ for microparticles and decreases with cluster size. For single particles this represents a temperature of $T_H \sim 500–2000 \text{ eV}$. Microparticles and small clusters should ‘Maxwellize’ quite rapidly at this stage due to frequent (~30–100 s$^{-1}$), mutual collisions in the cloud (particles/clusters are charged, see below). The ‘low temperature stage’ starts when the injection cycle is over and the particle motion is slowed down to the neutral gas ‘thermal level’ $V_{TL} \sim \sqrt{T_g/M}$ determined by the (room) temperature of the ambient gas, $T_g \sim 0.02 \text{ eV}$. For a microparticle, $V_{TL} \sim 0.03 \text{ cm s}^{-1}$.

The microparticles—although injected into a neutral gas—should be charged due to triboelectric effects or aggregate fractionation in local electric fields [7]. To identify possible charges on microparticles, a sinusoidally varying electric field with frequency $f = 4.7 \text{ Hz}$ and amplitude $26 \text{ V}$ was applied across the electrodes. Most of the microparticles responded to this field and performed oscillatory motions shown in figures 2(b) and 5 proving that these particles were indeed charged. From the relative phases, we know that both positively and negatively charged particles were present. Measuring the oscillation amplitude, $H$, we obtain the charge $Q$ for each individual particle, using the formula $H = QE/(2\pi f\gamma m)$ (where $E \approx 9 \text{ V cm}^{-1}$ is the
Figure 5. Individual particle trajectories. The actual particle motion is a superposition of a systematic drift and modulation by a sinusoidal electric field. The drift was subtracted in order to emphasize the oscillatory motion. Out-of-phase oscillations are a signature of opposite charges.

amplitude of the electric-field variation, $\gamma \approx 280 \text{ s}^{-1}$ is the neutral gas friction coefficient and $m$ is the particle mass). $m$ is estimated here using the reflected light intensity of the small agglomerate in relation to the light scattered by a single particle whose mass is known. (Single particle measurements are easily obtained by performing an experiment with identical conditions—except under ‘plasma on’ conditions. In this way, we can calibrate single particle light reflection properties throughout the chamber). Statistical analysis of the charge measurements shows that the mean charge of the entire cloud was too small to be detected (i.e., the particle cloud is presumably overall charge neutral) whereas the dispersion of the particle charge distribution is remarkably high, $\sqrt{\langle Q^2 \rangle} \sim 5000 \text{ e}$. Thus, on average, the clusters are significantly charged, either positively or negatively.

Summarizing the observation: we inject single particles into a neutral gas, the particles become charged, if the density exceeds a certain threshold a runaway coagulation (or gelation) ensues producing a single large conglomerate and a power law size distribution. Below the threshold the coagulation is clearly inhibited, the mass distribution exhibits a cut-off at a certain size and no single large particle is formed.

Obviously, coagulation is affected by electrostatic interactions. This is well known from many studies of atmospheric phenomena, for instance. What has not been observed so far is the type of ‘runaway coagulation’ as documented in figures 3 and 4.
4. Coagulation mechanisms

To understand the unusual observations of ‘runaway growth’, we first discuss the kinetics, and then the mechanisms of aggregation. Comparing the fractal structure of large aggregates with numerical simulations [8] suggests that cluster–cluster aggregation (CCA) is important. Then the simplest approach is to assume that the coagulation kinetics is mostly determined by CCA. The mass spectrum should be relatively narrow in this case with the major part of the spectrum located around a certain (average) cluster mass. Then the zero order moment of the mean-field (Smoluchowski) coagulation equation [9, 10] yields

\[ \frac{dN}{dt} = -\alpha N^2, \]

(1)

where \( N = \int n(m) dm \) is the number density of clusters, and \( \alpha(N) \) is the coagulation rate which is generally a function of the average cluster mass, \( M \). Equation (1) is exact, if the coagulation rate is mass-independent. The first mass moment of the coagulation equation gives overall mass conservation, irrespective of the aggregation process,

\[ MN = \text{const}, \]

(2)

where the average cluster mass is \( M = \int mn(m) dm / N \). The coagulation rate of clusters can be written as [9] \( \alpha = 4\pi\eta A^2 \delta V \), where \( \pi A^2 \sim \sigma \) is the average geometrical cross-section which is proportional to the cluster projection area, \( \sigma \) (i.e., \( A \) is the average cluster radius), \( \delta V \) is the average relative velocity, and \( \eta \) is a (possible) cross-section enhancement factor, which is determined by the particular mechanism of coagulation. The cluster size is related to the mass via the appropriate fractal scaling law [11],

\[ M \propto A^{D_f}, \]

(3)

with the fractal dimension usually varying in the range \( D_f \approx 1.6–2 \) [8].

We examine three possible coagulation mechanisms, starting from the ‘simplest case’ scenario, proceeding to higher levels of complexity.

4.1. Geometrical coagulation

Since the corresponding coagulation rate is proportional to the relative velocity, this mechanism should be most efficient at the ‘high temperature stage’—during the first 2 s of injection. In principle this agrees with the observations—the formation of a (single) large agglomerate during the injection cycle. However, there is no quantitative agreement: solution of equations (1) and (3) with \( \delta V = V_{HT} \) and \( \eta = 1 \) yields an upper limit for the number of coagulated microparticles per cluster of \( \sim 10 \), but not \( \sim 10^5 \) as observed.

4.2. Coagulation with charge–charge interaction

The enhancement coefficient for two clusters of opposite charges is given by [12, 13] \( \eta \approx 1 + Q^2 / (2AE_{\text{kin}}) \), where \( Q \) is the cluster charge and \( E_{\text{kin}} \) is the kinetic energy of the relative motion. The magnitude of \( Q \) can be estimated from the experimentally measured charge dispersion, i.e., \( Q \sim \pm \sqrt{\langle Q^2 \rangle} \). Electrostatic attraction increases as the particles slow down.
At the ‘low temperature stage’, when $E_{\text{kin}} \sim T_g$, the possible enhancement could be a few orders of magnitude, but during the injection cycle we have $Q^2/a_0 E_{\text{kin}} \ll 1$ even for microparticles and therefore $\eta \sim 1$. This implies that in the framework of the CCA model charge–charge interaction, whilst undoubtedly important in the ‘low temperature stage’, cannot be responsible for the observed coagulation during the (high temperature) injection stage.

### 4.3. Coagulation with charge–dipole interaction

The second mechanism of charge-induced enhancement is due to charge–dipole interaction, with dipoles induced by the field of neighbouring particles. This interaction is always attractive, irrespective of the charge sign, with the merger energy usually higher than that of the charge–charge interaction [13]. The charge–dipole attraction is dominant when $Q^2/a_0 E_{\text{kin}} \lesssim 1$—i.e., during the injection cycle. However, calculations show that the coagulation rate is still much too low—of the same order as the purely geometrical aggregation.

All higher order terms in the multipole expansion of the cluster–cluster interaction should have smaller magnitude than the dipole term and therefore are not considered here.

The conclusion is: the simplified CCA approach cannot identify the essential process leading to the observed aggregation, it falls short by 4–5 orders of magnitude when compared to the experiments. New physics is needed.

### 5. Runaway coagulation

In order to identify the process(es) leading to the observed rapid coagulation that we observed when the initial particle density is relatively high, we focus on the most curious feature of the observed coagulation—the formation of a single large aggregate which accumulates a significant (up to $\sim 10\%$) fraction of all injected particles. This aggregate is ‘detached’ from the smooth mass spectrum of clusters shown in figure 3(a)).

The very fact that so much mass ends up in a single aggregate suggests that some instability has occurred (and has been observed repeatedly, see figure 4). A possible candidate is the process called ‘gelation’ or ‘runaway growth’ [10, 14]. Physically, this process is triggered because the interaction between the clusters (namely, the coagulation rate) increases so rapidly with their size (mass), that, instead of a homogeneous coagulation throughout the volume, the whole ensemble becomes unstable against a ‘condensation’ into a single ‘droplet’.

Mathematical condition of the gelation is the divergence of the mass dispersion—the second moment of the mass spectrum [10, 14]. For our case, the mass dispersion can be derived from the generalized coagulation equation which takes into account not only the mass, but also the charge spectrum kinetics [13]. The generalized theory shows that the charge–dipole interaction can enhance gelation dramatically, provided the fractal dimension of clusters in the smooth spectrum is below the critical value $D_f = 2$ (assuming a Maxwellian velocity distribution). Recent numerical simulations [15] confirm these results. The gelation occurs at the ‘gelation time’ $t_{\text{gel}}$, when the distribution function is no longer bounded exponentially at the high-mass end, but behaves algebraically, $n(m, t_{\text{gel}}) \propto m^{-\tau}$, with $2 < \tau < 3$. Formally then, the total mass of the ‘finite size’ clusters is not conserved—there is a non-zero ‘mass flux’ at $m \to \infty$, which causes the formation of the ‘infinite’ gel particle.
Our measurements (experiment series 1) exhibit all the features peculiar to gelation: along with the formation of a single large (‘infinite’) aggregate observed for large amounts of injected particles, the spectrum of smaller (‘finite’) clusters in those cases is not bounded at the high-mass end, but has a power law tail. From figure 3(a), we get the slope of the mass spectrum $\tau \approx 2.5$–2.8 (assuming a fractal dimension $D_t \approx 1.6$–2), which is within the range necessary for runaway growth.

The gelation time—at which a massive runaway aggregate is formed—is of the order $t_{\text{gel}} \sim \left(\frac{Q^2/a_0 E_{\text{kin}}}{4\pi a_0^2 N_0 \delta V}\right)^{-1}$, i.e., it is determined by the charge–dipole correction of the initial geometrical coagulation rate. Assuming $1.6 \leq D_t \leq 1.9$ and $\delta V = V_{\text{HT}}$ (i.e., $Q^2/a_0 E_{\text{kin}} \sim 1$), we obtain the gelation time due to charge–dipole interaction $t_{\text{gel}} \sim 0.1$ s for large amounts of injected particles (experiment series 1) and $t_{\text{gel}} \sim 10$ s for small amounts of injected particles (experiment series 2), respectively. In other words, in the first case the gelation time is shorter and in the second case it is longer than the injection cycle used in all our experiments. Hence, all the measurements are compatible with the charge–dipole attraction being the driving mechanism of the observed runaway growth. Note that the magnitude of the induced dipole increases rapidly as two charged clusters approach each other. For instance, for a charge $Q$ located at a distance $r$ from a particle of (effective) radius $A$, the dipole moment is

$$d(r) \simeq -\alpha_d A^3 Q r^2 - A^2,$$

where $\alpha_d$ is the coefficient of the dipole interaction (for a sphere of dielectric permittivity $\epsilon$ the coefficient $\alpha_d = (\epsilon - 1)/(\epsilon + 2)$).

For purely geometrical interactions the runaway growth is possible only for unlikely low values of the fractal dimension $D_t \leq 4/3$ (see [13]). This is because the coagulation rates for this type of aggregation does not increase sufficiently steeply with cluster size (which is the necessary condition for the gelation [10, 14]).

6. Conclusion

We have observed a new rapid coagulation process which forms giant aggregate particles (of $\sim 10^5$ constituent microparticles) in seconds or less. We have identified a new phase transition—charge-induced gelation triggered by the dipole attraction between charged clusters—as the responsible mechanism: the main feature of the observed coagulation—the formation of single large aggregate—is a natural consequence of the gelation. Furthermore, the measured power law mass spectrum of smaller aggregates, $n(m) \propto m^{-\tau}$, with the slope $2 < \tau < 3$ and without apparent cut-off at the high-mass end is peculiar to the gelation onset as well. And finally, the gelation time for the experimental conditions is of the order of a second, provided the initial density of injected particles is high enough. In experiments with significantly lower particle injection the gelation transition was not found.

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