1 INTRODUCTION

Granular materials play a major role in a large number of technological applications. The size of grains used depends on the application, ranging from large particles with diameters of several centimeters down to nanoparticles. However, the physical properties of powders change drastically when reaching the size of nanoparticles. While in ordinary dry granular materials contacts between the particles cannot sustain tensile loads, in the case of ultra-fine powders van der Waals forces lead to aggregation which is essentially irreversible. In contrast to volume forces such as gravity, which decrease with decreasing particle radius \( a \) like \( a^3 \), van der Waals forces are proportional to \( a \) and thus dominate all other forces in the case of sufficiently small particles. On the other hand, van der Waals forces are only short ranged, diverging like \( h^{-2} \) with increasing distance \( h \) between the surface of particles (T. van de Ven 1989). Thus, the van der Waals force can be approximated as an irreversible sticking force, which has no influence on particles separated from each other, but causes them to stick together irreversibly, as soon as they touch each other.

A promising strategy to reduce agglomeration of particles is to charge them electrically. If one manages to charge all particles with the same polarity, the mutual Coulomb repulsion delays or even suppresses the aggregation process. It has been shown that such a charge distribution can be established for particles suspended in a non-polar liquid (J.H. Werth et al. 2003; M. Linsenbühler et al. 2005). In the first part of this paper we investigate to what extent charges can be used to enhance the stability of a suspension against agglomeration. We present some results obtained from a rate equation investigation, recently published in (S.M. Dammer & D.E. Wolf 2004).

In the second part of the paper, we present an application which makes use of Coulomb forces: the coating of charged particles with sizes on the micrometer scale by oppositely charged nanoparticles. As shown in (M. Linsenbühler & K.-E. Wirth 2004), such a coating may enhance the flowability of a powder dramatically, since the nanoparticles on the particle surfaces act as spacers between the micrometer sized particles, thus reducing their mutual van der Waals forces. The aggregation process of oppositely charged particles has been studied in detail (J.H. Werth et al. 2005).

2 STABILIZATION AGAINST AGGLOMERATION

Let us consider a very fine suspended powder. The size of the particles shall be a few \( \mu \)m or below. We assume the particles to be all of the same insulating material, each carrying an electric charge of the same sign. The charged particles are subjected to Coulomb and van der Waals forces as well as Brownian motion and Stokes friction. As already pointed out in
the introduction, van der Waals forces will only dominate over Coulomb forces for particles very close to each other. Thus we assume that the van der Waals force has no effect except when particles collide and stick together irreversibly. The motion of the particles is then composed of a stochastic part due to Brownian motion and a deterministic part determined by the balance of repelling Coulomb forces and Stokes friction (S.M. Dammer et al. 2004). It may happen that particles (or agglomerates of particles) come into contact due to Brownian motion, thus forming a new agglomerate (Brownian coagulation). In the following we will investigate this aggregation process in further detail in terms of a rate equation approach.

We assume that initially the suspension consists of two primary particles, all of the same mass $m^*$, and carrying the same charge $q^*$. As particles collide they form clusters with increasing mass and charge. Since for the chosen initial conditions mass and charge of the clusters are proportional to each other, it is sufficient to describe them by a single index $i$ according to

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

(1)

Here $n_i(t)$ denotes the number density of clusters with mass $n_i=im^*$ and radius $a_i=i^\alpha a^*$ at time $t$. Each of them carrying the charge $q_i=iq^*$, where $1/\alpha$ denotes the fractal dimension of the aggregates (e.g. $\alpha=1/3$ for spherical particles). As initial condition we choose $n_i(t=0)=1$, $n_j(t=0)=0$ for $i>1$. The matrix $R_{ij}$ in the rate equation is called coagulation kernel and describes at which rate two clusters with indices $i$ and $j$ merge into a single one. For Brownian coagulation of charged particles one has

$$R_{ij} = \frac{(i^{\alpha} + j^{\alpha})(i^{-\alpha} + j^{-\alpha})}{i^{\alpha} + j^{\alpha}} \frac{\kappa_{ij}}{\exp(\kappa_{ij}) - 1},$$

(2)

$$\kappa_{ij} = \frac{k^2 q^2}{(4\pi \varepsilon_0 e^2 a^{*3} k_B T)} \quad \text{and} \quad 2k_B T/3\eta=1$$

(S.M. Dammer & D.E. Wolf 2004). Here $\kappa_{ij}$ is proportional to the Coulomb energy of two clusters being in contact, divided by the thermal energy. This Coulomb energy is necessary to bring two particles into contact from infinite separation. If the suspension contains countercharges so that a double layer forms, the Coulomb repulsion at short distances is combined with attractive forces at intermediate distances. In this case the activation energy for a particle collision can be enhanced, i.e. the collision rate can be reduced compared to Eq. (2).

If the system is initially unstable, i.e. $k^2 \ll 1$, it behaves essentially as if it was uncharged and aggregation occurs frequently. In this regime, the average aggregate mass increases linearly in time (M.H. Ernst 1986). However, as soon as particles with $\kappa_{ij} \approx 1$ become important, further aggregation is suppressed exponentially. Asymptotically, in this regime the average aggregate mass increases sub-logarithmically slow in time (S.M. Dammer & D.E. Wolf 2004). The crossover between these two regimes happens at a characteristic time $t_c$ and mass $M_c$ given by

$$t_c \approx k \cdot \frac{m^*}{\kappa_{ij}} \quad \text{and} \quad M_c \approx k \cdot \frac{m^*}{\kappa_{ij}},$$

(4)

where $t^*$ is the appropriate time unit, given by $t^* = 3\eta/n2k_BT$. $n$ is the initial number density of primary particles. Fig. 1 shows the temporal evolution of the average aggregate mass, obtained from a numerical solution of the rate equations (1). As an example, for an experimental situations with values like $\eta=10^{-4}\text{Pa s}$, $T=300\text{K}$, $a=1\mu\text{m}$ and $\kappa \approx 2 \cdot 10^3 \text{mm}^{-3}$ one finds $t^* \approx 150$s. Assuming $\varepsilon_r \approx 1$, charging with a single elementary charge on each primary particle corresponds to a value $k \approx 0.2$. For these parameters one finds with the dimensionless results of Fig. 1 that the crossover to slow aggregation occurs within hours.

For times larger than $t_c$ the suspension is usually called stable. However, note that aggregation still proceeds slowly. A consequence of this is that the mass distribution evolves towards a universal scaling form and that the relative width $\sigma_r$ of the distribution falls off to a universal value $\sigma_r^{\approx 0.207}$ that is much smaller than in the uncharged case (with $\sigma_r \approx 1$) (S.M. Dammer & D.E. Wolf 2004). Hence, for an initially narrow mass distribution $\sigma_r$, first grows similarly to the uncharged situation until time $t_c$, when it starts decreasing again (induced by the exponential
suppression of further aggregation) which is denoted as self-focusing. With the values of the example discussed above, this self-focusing effect occurs within an experimentally accessible time.

3 COATING OF PARTICLES WITH NANOPARTICLES

In this section we present an application which makes use of charged granular particles in suspension, namely the coating of powder particles with nanoparticles. As shown by experiments (M. Linsenbühler & K.-E. Wirth 2004), such a coating of powder particles, even by a small amount of nanoparticles, leads to a strong increase in flowability and fluidizability of powders.

A detailed description of the coating process can be found in (J.H. Werth et al. 2003). Therefore, we want to give only a brief description. During the process, both the powder particles and the nanoparticles are charged triboelectrically by stirring the suspension with a high speed stirring device. By choosing different, electrically insulating materials for the powder particles and the nanoparticles it is possible to charge both fractions oppositely in a single process. After the charging process is stopped, the suspension is left untouched and the particles may agglomerate with each other. Due to Coulomb forces, agglomeration of oppositely charged particles (i.e. powder particles and nanoparticles) is preferred, while agglomeration of equally charged particles is suppressed. Eventually, a dry powder of coated particles can be achieved by evaporation of the liquid nitrogen.

An interesting question is, to what extent the charges influence the deposition of the nanoparticles on the larger powder grains. To this end, we expect the nanoparticles to usually carry only one single elementary charge, while the larger powder particles may carry several elementary charges. Since the used materials are electric insulators, the elementary charges are immobilized at distinct positions on the particle surfaces. If a nanoparticle now approaches the surface of a larger particle, two situations may arise: it may touch the particle exactly at the position of a charge, thereby compensating this charge, or it may just touch on a random position on the surface, leaving a dipole moment interacting with more charged nanoparticles in the suspension. The second case may occur due to Brownian motion of the particles.

To answer the question, which situation is more likely and to what extent surface charges of powder particles are compensated by charged nanoparticles, we study a simplified model: point-like particles, each carrying one negative elementary charge, are continuously inserted far away from one infinitely large particle, represented by a flat wall and carrying one or several positive elementary charges. The point-like particles are subjected to Coulomb forces by interaction with the charges on the wall, to Brownian motion and to Stokes friction by the surrounding fluid. Coulomb interaction of equally charged particles among each other is not regarded. As soon as a particle touches the wall, it is removed from the system. Our aim is to compute the probability distribution \( \rho(\vec{r}) \) for the particles to touch the wall at position \( \vec{r} \).

The answer to this problem is given in detail in (J.H. Werth et al. 2005). Therefore, here we only motivate the according equations and present some results. The probability distribution \( P(\vec{r},t) \) to find a particle at point \( \vec{r} \) and time \( t \) can be described by a Fokker-Planck (FP) equation. It has the form

\[
\frac{\partial}{\partial t} P(\vec{r}, t) = -\nabla \cdot \vec{j}(\vec{r}, t),
\]

where

\[
\vec{j}(\vec{r}, t) = -D\nabla P(\vec{r}, t) + \vec{v}(\vec{r}) P(\vec{r}, t)
\]

is the probability current, \( D \) the diffusion constant, and

\[
\vec{v}(\vec{r}) = -\frac{q^2\vec{r}}{24\pi^2 \varepsilon_0 \eta r^3} = -\frac{Q}{\pi^2 r^2}\vec{r}
\]

is the particle velocity in the overdamped limit.

Measuring space in units of \( Q/D \) and time in units of \( Q^2/D^3 \) we obtain the parameter-free dimensionless equation

\[
\frac{\partial}{\partial t} P = \nabla^2 P - \nabla P \cdot \vec{u} - P (\nabla \cdot \vec{u})
\]

where \( \vec{u} = -\vec{r}/r^3 \).

We are only interested in the distribution \( \rho(\vec{r}) \) of incoming particles at the wall. This allows us to use a time independent FP equation. We arrive at the stationary FP equation

\[
\nabla^2 P - \nabla P \cdot \vec{u} - P (\nabla \cdot \vec{u}) = 0.
\]

Equation (9) can be solved analytically in the case of one single charge fixed at the wall. The analytical solution as well as an in-depth derivation of (9) and a numerical treatment of the according Langevin equation can be found in (J.H. Werth et al. 2005).

First we want to concentrate on the analytically solvable case of one single surface charge at the wall. The density distribution \( \rho(r) \) of particles reaching the wall in a distance \( r \) to the fixed charge is given by

\[
\rho(r) = 1 + \frac{1}{2r} + \frac{\pi}{2} \delta(r),
\]

where the density of nanoparticles far away from the wall is set to unity. There are three terms contributing to the density distribution: Firstly, there is a certain fraction of point particles which exactly reaches
Coulomb force acting on it, for all charges. If we denote the position along the
the particle. Gaussian noise corresponding to Brownian motion of
finitely, there is a concentration of particles around the
the surface charge, represented by the term \( \frac{C}{r} \). Secondly, there is a concentration of particles around the
the density of particles far away from the wall. Solution (10) provides no intrinsic length scale.

Moving from one single fixed charge to several charges distributed at the wall, there is no analytical solution of equation (9) until now. Especially, the sum of solutions of type (10) for several charges at different positions is not a solution of the multi-charge Fokker-Planck equation. However, as we will see, at least for only a few charges, adding up the single charge solutions can be a first approximation for the real problem.

Since analytical solutions are not tangible, the direct numerical simulation of a multi-charge Langevin equation can be used to obtain results. The Langevin equation describing the movement of a nanoparticle is given by

\[
\frac{\partial}{\partial t} \vec{r} = \frac{\vec{F}_C(\vec{r})}{6\pi \eta a} + \vec{\xi}(t) \tag{11}
\]

where \( \vec{r} \) is the position of the particle, \( \vec{F}_C(\vec{r}) \) is the Coulomb force acting on it, \( \eta \) is the dynamic viscosity of the fluid, \( a \) the particle radius and \( \vec{\xi}(t) \) is a white Gaussian noise corresponding to Brownian motion of the particle.

Fig. 2 shows densities of particle influx at the wall obtained numerically. In the simulations corresponding to Figures 2 (a)-(d), up to four charges are arranged in a line, separated by a distance of \( 2Q/D \). The bold curves show the density of particles touching the wall along this line. The light curves are obtained by adding up the \( 1/2r \)-shoelers from the single charge solution (10) for all charges. If we denote the position along the line of charges by \( y \), the light curves are given by

\[
\rho(y) = 1 + \sum_{i=1}^{n} \frac{1}{2|y - y_i|}. \tag{12}
\]

where \( n \) is the number of charges fixed at the wall. This approximation agrees nicely with simulations, although in the case of three and four charges the numerical data lie slightly below the light curves.

4 CONCLUSION

We discussed suspensions of monopolarly and bipolarly charged particles. In the former case, accumulation of charges leads to a crossover from fast to slow aggregation, followed by a self-focusing of the mass distribution towards a universal scaling form. In the latter case, we showed that bipolar charging may enhance the coating of powder particles with nanoparticles.

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