Colloidal Aggregation in Microgravity by Critical Casimir Forces

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By using the critical Casimir force, we study the attractive strength dependent aggregation of colloids with and without gravity by means of near field scattering. Significant differences were seen between microgravity and ground experiments, both in the structure of the formed fractal aggregates as well as in the kinetics of growth. In microgravity purely diffusive aggregation is observed. By using the continuously variable particle interaction potential we can for the first time experimentally relate the strength of attraction between the particles and the structure of the aggregates.

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Colloidal aggregation is important in a wide range of applications. Nevertheless, there are many fundamental questions still unresolved. There are many theoretical models that describe aggregation depending on one of two limiting steps: the transport of particles towards the aggregate or the sticking of the particles at the aggregate surface. Diffusion limited aggregation (DLA), for instance, describes the formation of structures by which the building blocks move by diffusion alone and stick as soon as they touch [1]. On the other hand, reaction limited aggregation was simulated by incorporating a sticking probability to account for an activation barrier in the sticking of the particles [2]. This was also studied experimentally by systematically changing the activation barrier in a system containing charged colloids [3]. In most experimental cases, however, it is diffusion and reaction limited cluster aggregation that is observed [4]. Pure DLA is not seen in colloidal systems because convection caused by gravity prevents it. Even so, diffusion limited aggregation and reaction limited aggregation are the simplest models available and are the extremes of the possible mechanisms for aggregation. In nature, however, the strength of sticking can have a profound influence on aggregation, as will be shown by the research presented here.

The critical Casimir effect [5–10] in this case offers an experimentally convenient way to control interactions between colloidal particles, namely, just by adjusting the temperature [6,7]. In the quantum Casimir effect, an attraction between two dielectric plates in vacuum arises due to the confinement of zero-point fluctuations of the electromagnetic field [11]. Fisher and de Gennes were the first to realize that this phenomenon could also occur in classical systems [12]. They showed that a force arises between objects (e.g., colloids) in a dielectric medium due to the confinement of bulk fluctuations. This effect becomes significant near the solvent critical point, where the correlation length becomes of the order of the separation between objects; hence, the term critical Casimir effect. By making use of a simple model for charge stabilized colloids in a binary mixture, the experimentally observed temperature dependent aggregation could even be accounted for [7]. The great advantage of this technique over more traditional means, such as depletion interactions or salt induced flocculation, is that the interaction is continuously tunable, reversible, and accurate. Moreover, the critical Casimir force adjusts itself by a change in temperature on a molecular time scale resulting in an effective potential. This renders the interaction comparable to atomic systems.

Here, we report on the first experimental study of the relation between the well depth of the particle interaction potential and the structures formed in the aggregation process, i.e., a relation between attractive strength and fractal dimension. In order to measure this, two conditions had to be met: absence of gravity and a continuously variable attractive force. The first condition could be met on board the International Space Station (ISS). The second is guaranteed by the nature of the critical Casimir force, which is a function of the correlation length of the suspending fluid. In microgravity, we always found fractal structures formed by diffusion limited aggregation with a fractal dimension that decreases continuously with increasing attraction. Surprisingly, experiments conducted simultaneously on the ground on the same samples showed only one type of aggregate with a constant fractal dimension, formed by a reaction limited process.

The microgravity experiment operated on board the Columbus module of the ISS in the Microgravity Science Glovebox. The experiment could be controlled remotely from the European Space Agency's Spanish User Support and Operations Center in Madrid. We used charge stabilized fluorinated latex particles with a radius of 200 nm, density of 1.6 g/mL, and refractive index of $n = 1.37$, closely matched by that of the solvent mixture, with

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$n = 1.40$. This "binary" mixture consists of 3-methyl pyridine (3MP) in water and heavy water with a 3MP weight fraction of $X_{3MP} = 0.39$ and a D_2O/H_2O weight fraction of $X_{hw} = 0.63$. This mixture has a lower critical solution temperature of 49 °C [13]. The fluorinated particles consist of a PFA (tetrafluoroethylene copolymerized with perfluoroalkyl-vinyl ether) core and a fluorinated latex shell added through seeded growth as described in Ref. [14]. These particles were the best available choice taking into account the solvent density, refractive index, and chemical stability with respect to 3MP. Before addition of the colloids, the solvent mixture was purified by distillation under vacuum. Four different dispersions were prepared while contact with oxygen was avoided. Each sample contained the same colloid volume fraction of $\sim 10^{-4}$ and four different salt concentrations of 0.31, 0.79, 1.5, and 2.7 mmol/L sodium chloride (NaCl). From these dispersions, duplicate sets of samples were taken for microgravity and ground experiments. The aggregation of the colloids was studied by means of near field scattering (NFS) [15]. The samples were illuminated by a collimated laser beam 8 mm in diameter with a wavelength of 930 nm. The interference between the transmitted beam and the scattered light was recorded behind the sample at a distance of 2.9 mm. A 20× microscope objective imaged this plane onto a CCD with a pixel size of 10 μm. Data analysis has been performed following the methods described in Ref. [15]. The data were corrected for a Talbot related effect according to Ref. [16]. For each sample, the aggregation temperature T_{agg} was determined. We then investigated the aggregation with temperature jumps from below T_{agg} to T_{agg}, $T_{agg} + 0.1$, $+0.2$, $+0.3$, and $+0.4°$, increasing the attractive strength with each jump. For each temperature, the aggregation process was followed for 1 h by acquiring NFS images with a frame rate of 1 s^{-1}. The sample was then cooled to a temperature far below T_{agg}, followed by stirring for at least 3 h before a new measurement was started.

The growth of aggregates is reflected in the time evolution of the normalized variance of the scattered intensity (NVI) (inset of Fig. 1). This curve is the result of changes in the number density of scatterers and their cross sections. The start of aggregation is marked by an increase in the NVI, which is mainly due to the increase of the cross section. For small particles this depends strongly on the scatterer radius. The NVI was used to detect both the start and the time scale of the aggregation process. A typical measured NVI curve shows a small bump, followed by a strong linear increase (inset of Fig. 1). The start of aggregation t_0 was determined by extrapolation of the linear regime to zero NVI. The initial bump was not taken into account because the temperature inside the cell was not yet constant. Although differences in t_0 were observed for measurements at different temperatures, for repetitions at the same temperature no significant differences were seen.

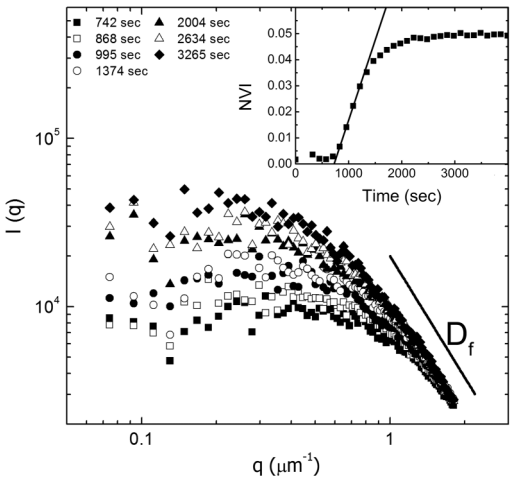

FIG. 1. Typical light scattering result of the aggregation of colloids in microgravity. Different curves represent different points in time during the aggregation process. Inset: Normalized variance of the scattering intensity (NVI) in time (sample: 0.31 mmol/L NaCl at T_{agg}).

The NFS data allow us to elucidate the structure and average length scale of the aggregates as they grow. This is reflected in the angle dependent scattering intensity as shown in Fig. 1. Here, the scattering intensity is given as a function of the scattering wave vector q [$q = (4\pi/\lambda) \times \sin(\theta/2)$, in which λ is the wavelength of the radiation used and θ is the scattering angle]. The different symbols represent different times of growth with the overall scattering intensity increasing as the aggregates grow. For each sample a similar series of scattering curves was recorded at different temperature jumps above T_{agg}.

At high q, all distributions superimpose onto the same asymptotic curve, which follows a power law behavior. This behavior is characteristic for scattering by fractal structures [17]. In Fig. 1 the intensity distributions are given on a log-log scale, converting the power law dependence into a linear form of which the slope equals the fractal dimension D_f. The fractal dimension is a measure for the internal structure of the aggregates and relates the radius of gyration (R_g) to the number of particles (N) by $R_g \propto N^{1/D_f}$. For a closed packed structure, D_f would be close to 3.

We found that in microgravity the fractal dimension varied systematically with temperature controlling the attractive interactions (Table I). D_f decreases as the temperature increases: from 2.4 at low temperatures, close to the theoretical DLA limit of 2.5, to about 1.8 at high temperatures [2]. The structures become more open as the attractive strength is increased. D_f was constant throughout the measurement for the reported temperatures. Almost no dependence on salt concentration was seen. The observed differences were all within experimental error. On the ground there was no effect of the temperature on D_f

TABLE I. Fractal dimensions as measured at different temperatures under microgravity. On the ground, there was no dependence on temperature; hence, an average value is given.

Salt concentration (mmol/L)	T_{agg} D_f	T_{agg} +0.1 D_f	T_{agg} +0.2 D_f	T_{agg} +0.3 D_f	T_{agg} +0.4 D_f	Ground average D_f
0.31	2.4	2.0	2.0	1.9	1.8	1.6
0.79	2.35	2.1	2.1	2.0	1.95	1.7
1.5	2.3	1.9	1.95	1.8	2.05	1.7
2.7	2.4	2.1	2.1	1.8	2.0	1.8

(Table I). The determined average D_f was close to the highest temperature measurement in microgravity for the same sample.

Despite the difference in attractive strength, the growth of aggregates at different temperatures does show similar behavior. As shown in Fig. 2 for two measurements in microgravity, the intensity distributions of the growing aggregates can be reduced to a single form using the measured D_f:

$$S(q, q_{red}) = q_{red}^{-D_f} F(q/q_{red}), \quad (1)$$

This kind of collapse is characteristic for a type of spinodal decomposition process [18]. In regular spinodal decomposition the intensity distributions are scaled by using q_{red}^{-D}, with D being the system's dimensionality. The similar collapse of the measured intensity distributions suggests a possible common mechanism in the dynamics of this aggregation process [19]. Experiments on the gelation of colloidal particles by means of depletion forces suggest that diffusion limited aggregation is a deeply quenched limit of spinodal decomposition [20], a limit which is reached as soon as the interaction strength becomes much larger than the thermal energy. The critical Casimir force increases rapidly with increasing temperature, and it quickly becomes larger than the thermal energy of the system [5,7]. Our results therefore substantiate this point of view.

The directly adjustable potential depth of our critical Casimir system allows us to observe differences between the growth of aggregates at different attractive strengths. At $T_{agg} + 0.4°$, the highest measured attractive strength, a clear peak can be distinguished, while at the lowest attractive strength at T_{agg}, the maximum is not very pronounced (Fig. 2). Scattering curves for spinodal decomposition contain a peak which moves towards lower q in time indicating the growth of a characteristic length scale in the system. A decrease in scattering intensity at low q is characteristic for a region around the aggregate depleted of colloids [19]. We find that the peak and subsequent decrease are more pronounced at higher temperature. This indicates that when the interaction strength between the particles increases, so does the depletion region around the aggregates.

The kinetics and the rate of growth of the aggregates offers insight into the underlying mechanism controlling the aggregate growth. A characteristic length scale of the system is given by $q_{red}^{-1} \propto R_g \propto N^{1/D_f}$, as determined by Eq. (1). The evolution of q_{red}^{-1} in time for both the microgravity and ground experiments, corrected for the starting time t_0, is given in Fig. 3.

It is immediately evident that the speed of growth of the aggregates in microgravity is significantly lower and follows a different dependence than for the same experiments on the ground. In microgravity, the aggregate size increases steadily in time. This differs from what is seen for hard-sphere colloids where microgravity experiments revealed a two-step process in the rate of growth of crystallites [21]. In our case, within the uncertainty of the determined t_0, the growth rate agrees with a power law with the exponent $1/D_f$ for all temperatures. This result is valid for all samples measured in microgravity, regardless of the salt

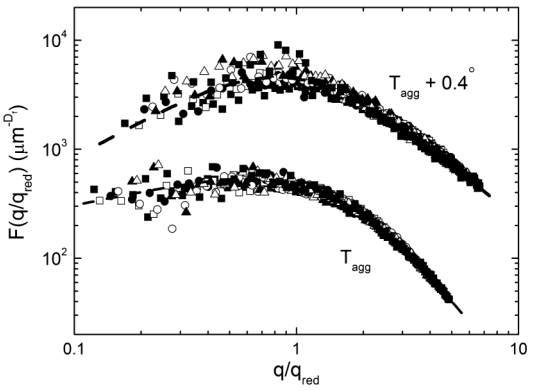

FIG. 2. Collapse of scattering curves in microgravity. Rescaled scattering intensity as a function of rescaled wave vector q (sample: 0.31 mmol/L NaCl). Lines are drawn as a guide to the eye to demonstrate the decrease at low q.

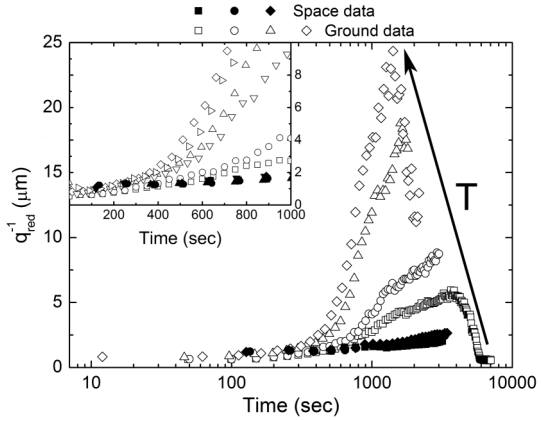

FIG. 3. Growth of structures in time at different temperatures. Results from both microgravity (closed symbols) and ground experiments (open symbols) are shown (sample: 1.5 mmol/L NaCl). Inset: Enlargement of the start of the aggregation process.

concentration. This power law behavior is characteristic for diffusion limited models [1,22].

In microgravity, two aspects of the relation between growth rate and potential become apparent. First, the repulsive part of the potential does not influence the growth rate. The salt concentration only determines the aggregation temperature where the correlation length becomes of the order of magnitude of the Debye screening length [7]. The most surprising result, however, is that DLA is always observed even at the lowest interaction strength, namely, at the aggregation temperature. Theory in this case implies a sticking probability of one. We observe that the structure of the aggregates changes from compact objects ($D_f = 2.5$) at aggregation to more open structures (lower D_f) as the temperature is increased beyond aggregation. Experiment implies that at aggregation with a well depth of $\sim kT$, restructuring takes place into a more compact object. At higher temperatures, and larger well depths, restructuring gradually stops and the resulting structure is more open, exhibiting the same fractal dimension as under gravity.

In pure DLA, aggregates grow by addition of single particles only. Under microgravity conditions diffusion is the only dynamical degree of freedom available. When aggregation starts, aggregates are formed everywhere in the system and grow by the addition of single particles. As soon as the aggregates grow, their diffusive motion slows down. As a result, at later stages immobile aggregates grow only by capturing the faster moving single particles. Eventual growth by cluster-cluster aggregation takes place on a time scale far beyond the observation time of the experiment. Thus, the observed decrease in the fractal dimension with increasing temperature cannot be explained by this mechanism. Despite the change in fractal dimension, the underlying dynamical process remained the same: DLA.

On the ground the growth of aggregates is markedly different. The dynamics of the aggregates is strongly influenced by convection of the suspending fluid and settling in gravity. Because of this, aggregates not only capture more single particles but also coalesce with each other. At early stages the growth rate follows the purely diffusive case as is seen in microgravity (inset of Fig. 3). However, cluster-cluster aggregation sets in fast and results in a sharp increase in the speed of growth after about 200–500 s. The growth rate then follows a more exponential form which points to reaction limited aggregation and it depends strongly on the attractive strength. Aggregates grow faster at higher temperature jumps. The sudden drop at later times shows the massive settling of the aggregates. Here, the largest aggregates are removed from the field of view.

In summary, using critical Casimir forces in microgravity and on the ground, we have investigated the attractive strength dependent nature of aggregation and of the structures formed. Ground measurements are severely affected by sedimentation, resulting in reaction limited behavior. The growth rate of aggregates strongly depends on the attractive strength. In microgravity, a purely diffusive behavior is seen reflected both in the measured fractal dimensions for the aggregates as well as the power law behavior in the rate of growth. Formed aggregates become more open as the attractive strength increases. The structure of the colloidal aggregates can thus be altered simply by changing the temperature.

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