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宇宙実験に向けた荷電コロイド粒子の静電吸着と会合体形成の研究

A Study on Electrostatic Adsorption and Clustering of Charged Colloidal Particles for Space Experiments

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1. Introduction

Oppositely charged colloidal particles associate in their aqueous dispersions and form clusters under appropriate conditions (**Fig. 1**). A tetrahedral colloidal cluster, where four particles are attached to a central particle, has been studied as a building block of diamond lattice structures [1] (**Fig. 2**). The diamond lattices of colloidal crystals have attracted a considerable attention as novel photonic materials having a complete photonic band gap.

To fabricate diamond lattices having good structural uniformity, the tetrahedral clusters should have a good structural symmetry. For clusters of charged colloidal particles, the structural symmetry appears to significantly depend on the magnitude of the electrostatic repulsion between attached particles. The stronger repulsion should result in more ordered structural arrangement of the attached particles, i.e., better symmetry of the tetrahedral clusters. This is similar to the crystallization of charged colloids. In aqueous dispersion, charged colloidal particles are regularly arranged in the face centered or body centered cubic lattices, because of long range electrostatic repulsion. In this sense, the clustering of charged particles may be regarded as crystallization of colloidal particles on a spherical surface.

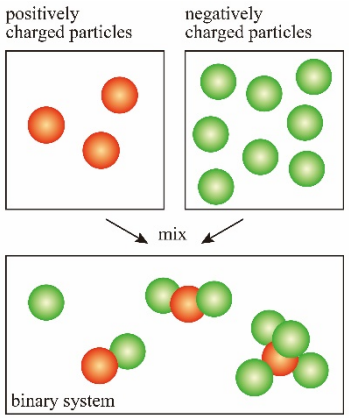

Fig. 1 A schematic diagram of association in binary colloidal system.

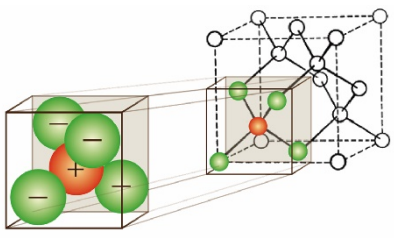

Fig. 2 An illustration of a tetrahedral cluster in a diamond lattice.

In the present study, we investigated resemblance between the electrostatic adsorption of charged colloidal particles on oppositely charged plate, and the cluster formation (**Fig. 3**). Here, we focused on an influence of added salt on the particle adsorption, and its relevance with the formation of

the tetrahedral clusters. We used colloidal silica (SiO_2) particles for the present experiments.

For the photonic application, the colloidal particles having high refractive indexes (n_r) are sometimes desired; for example, the perfect photonic band of the diamond lattices are formed when n_r is larger than approximately 2. However, materials having high refractive index usually have large values of specific gravity ρ at the same time. Thus, microgravity environment, where an effect of gravitational sedimentation is negligibly small, would be ideal for the structure formation of colloidal particles having high n_r values. We have been preparing a space experiment on clustering of various colloidal particles, including silica (n_r = 1.45; ρ = 2.1) and titania (TiO_2, n_r = 2.5; ρ = 4). The experiments were performed in July 2020, and the samples are going to return to the Earth in 2021.[2] We will briefly describe the sample preparation for the space experiment.

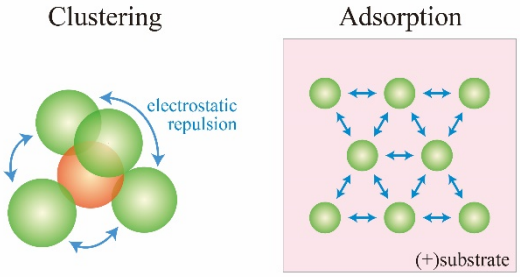

Fig. 3 Both systems have a regular arrangement due to sufficiently strong electrostatic repulsion between negatively charged colloidal particles.

2. Experimental Section

2.1 Preparation of the Positively Charged Silica Particles

The positively charged, rhodamine-labeled silica particles were prepared by modifying silica particles with poly(ethyleneimine) by the following manner.

Silica dispersions : 1.04 g of silica particles (KE-P100, Japan Catalyst, Tokyo, Japan) was dispersed in 100 mL ethanol, by ultra-sonification. The colloidal dispersion was then centrifuged and the sediment were dispersed in 10 mL ethanol.

RITC-APTES : 2.5 mg of rhodamine isothiocyanate (RITC, Sigma-Aldrich, St. Louis, U.S.A.) was dissolved in 2 mL ethanol and 10 μLs of 3-aminopropyltriethoxysilane (APTES, Shin-Etsu Chemical, Tokyo, Japan) was slowly added. The samples were stirred for 24 hours. RITC were bound to APTES because of coupling reaction between amine and isothiocyanate groups.

Rhodamine-dyed silica particles : 100 μLs of the resulted RITC-APTES and 430 μLs of tetraethoxysilane (TEOS, Shin-Etsu Chemical) were dissolved to 13 mLs ethanol and 4.3 mLs Milli-Q water (Millipore, Massachusetts, U.S.A). 620 μLs of 28 wt% ammonia/water (Wako, Tokyo, Japan) and 10 mLs of the KE-P100 silica dispersion were then added to the solution, and stirred for 24 hours. The resulted silica dispersions were washed with ethanol for three times by centrifuge.

Poly(ethyleneimine)-modified rhodamine-dyed silica particles : 1.5 mLs of trimethoxysilylpropyl-poly(ethyleneimine) (50 wt% solution in isopropanol, Gelest, Morrisville, U.S.A.) was dissolved to 13 mLs ethanol and 4.3 mLs Milli-Q water and stirred for 5 min. 620 μLs of 28 wt% ammonia/water and 10 mL of the dispersion of rhodamine-dyed silica particles were mixed, added dropwise to the reaction solution, and stirred for 24 hours. The solution was then purified by centrifuge in water for three times.

2.2 Preparation of the Negatively Charged Silica Particles

The negatively charged, sodium poly(styrenesulfonate)-modified silica particles were synthesized by a similar manner to that for the rhodamine-dyed positively charged particles. Fluorescein isothiocyanate, (FITC, Wako) was used as fluorescent dye molecules. The poly(styrenesulfonate) were introduced to provide negative charges by a following manner.

Introduction of vinyl groups on the particle surface: 30 mLs of the fluorescein-dyed silica particles, 350 μLs of tetrapropyltrimethoxysilane (TPM, Shin-Etsu Chemical), 850 μLs of 28 wt% ammonia/water were introduced in a 200 mL flask. After 20 mLs of ethanol was added, the dispersion medium was reduced to 40 mLs by using a rotary evaporator under reduced pressure at 45℃ for 40 min. The samples were then washed with ethanol by centrifuges for three times, and redispersed in 70 wt% EG/water.

Modification of the silica particles by poly(styrenesulfonate) : 60 mLs of 70 wt% EG/water, 1.0 g of *p*-styrenesulfonic acid sodium salt (Wako), and 30 mLs of the dispersion of the vinyl-modified, fluorescein-labeled silica particles were

introduced in a 200 mL flask, and bubbled by nitrogen gas for 15 min in an oil bath maintained at 75℃. 35 mg of photoinduced polymerization initiator, VA-086 (Wako), was dissolved in 10 mLs of 70 wt% EG/water, and bubbled with a nitrogen gas. These two solutions were mixed and stirred for 24 hours at 75℃. The resulted particles were washed with Milli-Q water by centrifuge for three times and dispersed in 20 mLs of Milli-Q water.

2.3 Preparation of the Positively Charged Glass Substrate

The positively charged glass substrates were prepared by modifying glass substrates with poly(ethyleneimine) by the following manner. Coverslips (24 mm × 60 mm, thickness = 0.17 mm, Matsunami, Tokyo, Japan) were cleaned by immersing in sulfuric acid for more than 1 day and were washed well with Milli-Q water. Then the coverslips were immersed in a mixture of 26 mLs ethanol, 8.6 mLs Milli-Q water and 3.0 mLs of trimethoxysilylpropyl-poly(ethyleneimine). After 1.24 mLs of 28 wt% ammonia solution was added, the reaction solution was maintained for 24 hours. The substrate was washed well with Milli-Q water before used.

2.4 Adsorption of Negatively Charged Colloidal Particles on Positively Charged Plate

We observed adsorption of colloidal particles onto glass surfaces by an inverted optical microscope (ECLIPSE 80i, Nikon). The area fraction φ_A was calculated from the number of the adsorbed particles in a viewing field. The spatial regularity of the adsorbed particle was evaluated based on 2D radial distribution function g(r).

2.5 Clustering of Oppositely Charged Colloidal Particles

Aqueous dispersions of positively and negatively charged particles were mixed to form clusters. In order to minimize the gravitational sedimentation, the samples were rotated at 3 rpm using an automatic rotator. Distribution of the association number was determined from optical micrographs. We determined the bond order parameter q_{tetra}, which was a measure of symmetry of tetrahedral cluster (**Fig. 4**), by using a confocal laser scanning microscope (LSM, ECLIPSE Ti+C2, Nikon).

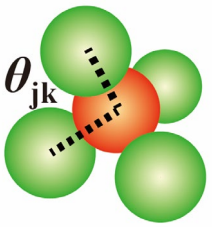

Fig. 4 Angle indicating tetrahedral symmetry.

3. Results and Discussion

3.1 Adsorption Experiment

We examined the adsorption of the negatively charged particles onto the positively charged substrate at various NaCl concentrations, C_s. **Fig. 5** shows an example of the g(r) – r plot. From the plot, we determined the height of the first peak h_1, which is a measure of the spatial regularity of the adsorbed particles. In **Fig. 6**, h_1 - C_s plot and φ_A – C_s plot are presented by green and red symbols. Both plots showed a maximum at around C_s = 50 μM. The repulsion between the

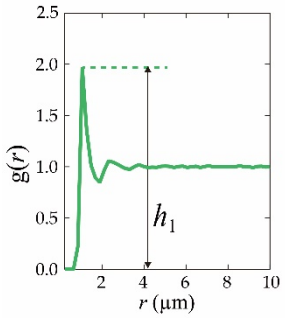

Fig. 5 The g(r) *vs.* interparticle distance r.

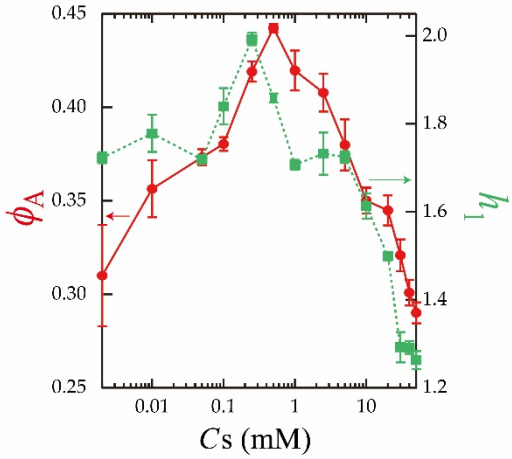

Fig. 6 Area fraction φ_A of the adsorbed particles on the PEI-modified glasses and the g(r) value at the first peak h_1 at various values of NaCl concentration, C_s.

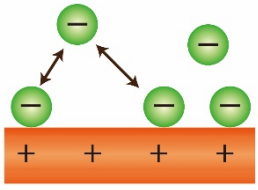

Fig. 7 An illustration of the electrostatic repulsion between free and adsorbed particles.

free and adsorbed particles was stronger at lower C_s (**Fig. 7**), while the attraction between the particles and substrate was weaker at higher C_s. The observed maximum appears to be due to combination of these two effects.

3.2 Clustering Experiment

We estimated an averaged value of q_{tetra} of the clusters at various values of C_s. We also determined a distribution of the association number of clusters, and obtained the proportion of tetrahedral clusters, p_4. **Fig. 8** is the p_4 and the value of q_{tetra} at various values of C_s. At higher values of p_4, the clusters having the better structural symmetry were obtained. As shown in **Fig. 9**, the repulsion between the free particles and cluster is stronger at lower C_s, and clustering of oppositely charged colloidal particles is weaker at higher C_s. The observed maximum appears to be due to an interplay of these two factors.

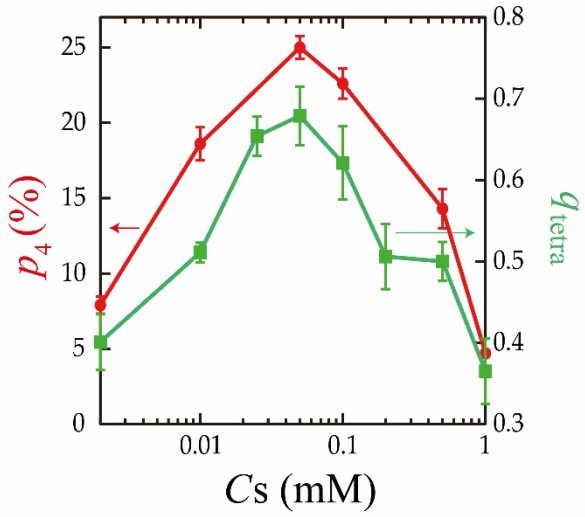

Fig. 8 Population of tetrahedral cluster p_4 and the value of q_{tetra} at various C_ss.

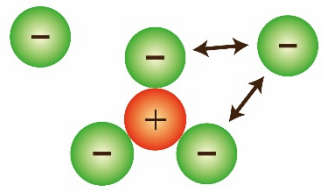

Fig. 9 An illustration of the electrostatic repulsion between free particles and cluster.

3.3 Comparison of Adsorption and Clustering Systems

We compared the abovementioned results obtained in the two systems in terms of the interaction potential between the negatively charged particles and positively charged particles or plate. Here we summed an electrostatic potential having a Yukawa form, and van der Waals potential (**Fig. 10**). **Fig. 11** shows plots of h_1 and q_{tetra} against a magnitude of

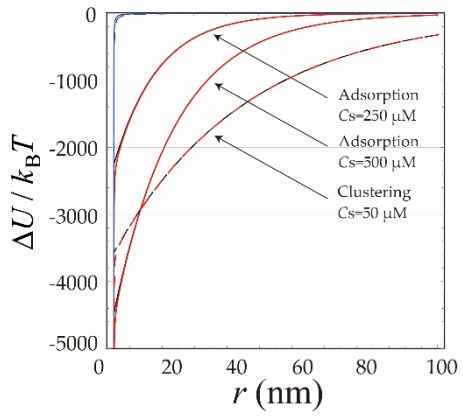

Fig. 10 Potential curves for electrostatic (black curves), vdW (blue curves) and total (red curves) interaction between particle and plate (solid curves), binary particle systems (dashed curves).

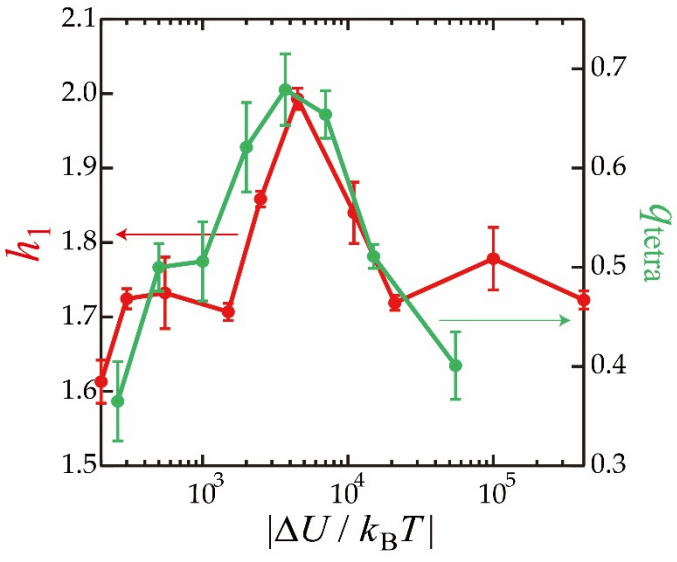

Fig. 11 Values of h_1 and q_{tetra} plotted against magnitude of the interaction potential.

particle/plate and particle/particle attraction. The q_{tetra} and h_1 exhibited similar trend when plotted by using the interaction magnitude. Thus, the cluster and electrostatic adsorption showed a good correspondence.

3.4 Application to Space Experiment

We observed that the optimum condition for formation of the tetrahedral clusters were around C_s = 50 μM. Based on the present results, we chose the salt concentrations of the samples for the space experiments at C_s = 0, 50, 100, and 200 μM. The concentration of positively charged particles was determined to be 0.048 vol% and the negatively charged particles was determined to be 0.002 vol%, respectively, and the particles were sealed in two separated tetra bags, mixed in space, and kept for 2 days. UV curable gelation reagents were mixed to the samples to fix the sample under UV illumination after the clusters will be formed.

4. Conclusion and Outlook

In this study, we investigated a relation between the electrostatic adsorption of particles on charged plate and the cluster formation. Both the $\varphi_A - C_s$ plots and p_4 - C_s plots had a maximum at around C_s = 50 μM. The maximum could be explained for in terms of an interplay of the electrostatic repulsion between like charged particles and the electrostatic attraction between oppositely charged particles (or particle/plate). The spatial regularity of the adsorbed particle, determined in terms of h_1 and q_{tetra}, were largest at C_s around the maximum. We could compare behavior of the two systems based on the interaction magnitude.

The sample of the space experiments is going to return in 2021. We plan to compare the results obtained in this study with the space experiments, and investigate a change in the distribution of the association number under microgravity.

References

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2) JAXA website: https://iss.jaxa.jp/kiboexp/news/180830_colloid.html

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