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

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INTRODUCTION

Tetrahedral colloidal clusters of oppositely charged colloidal particles have been studied as building blocks of diamond lattice structures (**Fig.1**). To fabricate the diamond lattices, tetrahedral clusters having a good structural symmetry are required. For clusters of charged 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 (**Fig.2**). In this study, we focused on an influence of added salt on the particle adsorption, and its relevance with the formation of the tetrahedral clusters.

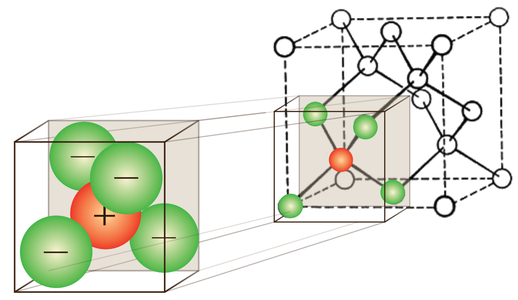


Fig.1 An illustration of a tetrahedral cluster in a diamond lattice.

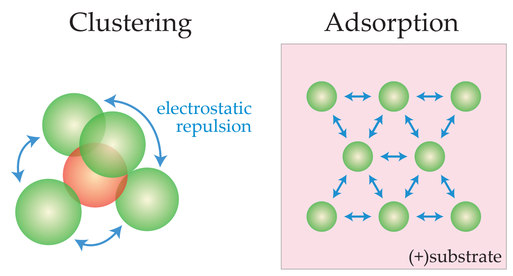


Fig.2 Regular particle arrangements are due to sufficiently strong electrostatic repulsion between negatively charged colloidal particles.

1) ADSORPTION EXPERIMENT

Glass substrate

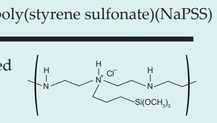
glass	coverslip	charge
PEIg	PEI-modified	positive

Cleaned by immersing in sulfuric acid for more than one day and washed well with purified water.

Colloidal particles

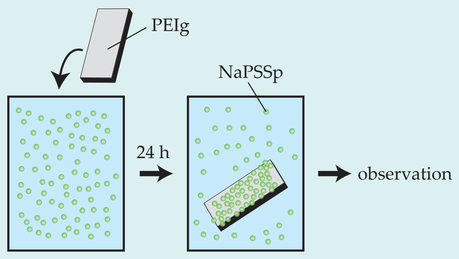
particles	diameter (nm)[a)]	ζ-potential (mV)[b)]	surface
PEIp*	1150	+60.8	trimethoxysilylpropyl modified polyethyleneimine(PEI)
NaPSSp**	1150	-49.6	sodium poly(styrene sulfonate)(NaPSS)

*red fluorescent labeled **green fluorescent labeled
a) by the SEM observation
b) by the microscopic electrophoresis measurement



Trimethoxysilylpropyl modified (polyethylenimine)

Adsorption of colloidal particles onto glass surfaces was observed by an inverted optical microscope (ECLIPSE 80i, Nikon) and a confocal laser scanning microscope (LSM, ECLIPSE Ti+C2, Nikon). The area fraction of adsorbed particles ϕ_A was calculated from the number of the adsorbed particles.



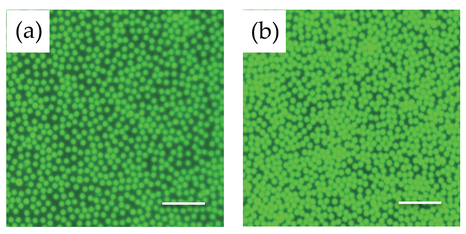


Fig.3 Optical micrographs showing electrostatic adsorption of the particles on a glass at (a) C_s = 2 μM (b) C_s = 500 μM. (scale bar : 10 μm)

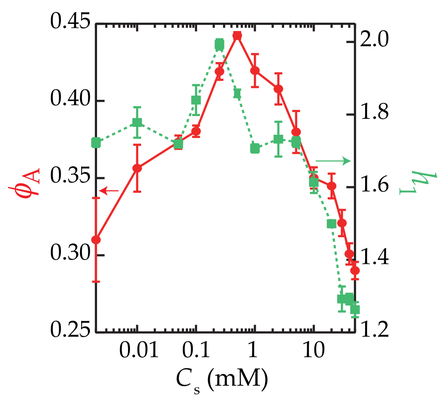
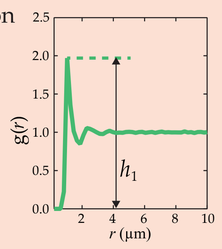


Fig.4 Area fraction ϕ_A of the adsorbed particles on the PEI-modified glasses and the g(r) value at the first peak h_1 at various values of NaCl concentration, C_s.

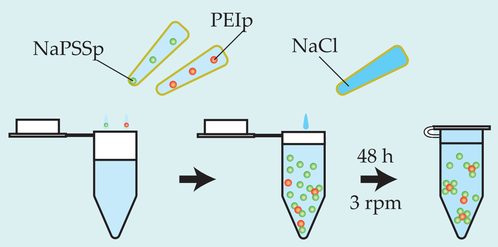
g(r) : radial distribution function

g(r) is the average density of other particles at a distance r from one particle. h_1 is the height of the first peak of the g(r).
As h_1 increases, the spatial regularity of the adsorbed particle becomes better.



Both the ϕ_A - C_s and h_1 - C_s plots had a maximum.

2) CLUSTERING EXPERIMENT



Oppositely charged particles were mixed to form clusters. Distribution of the association number was determined from optical micrographs. Bond order parameter q_{tetra} was estimated based on the LSM images. The population of tetrahedral clusters p_4 and the number of associated particles n was determined.

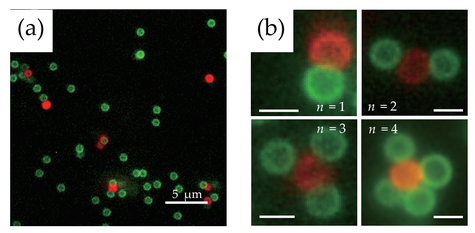


Fig.5 Optical micrographs of (a) colloidal dispersions containing clusters and (b) clusters of n = 1 to n = 4. (scale bar : 1 μm)

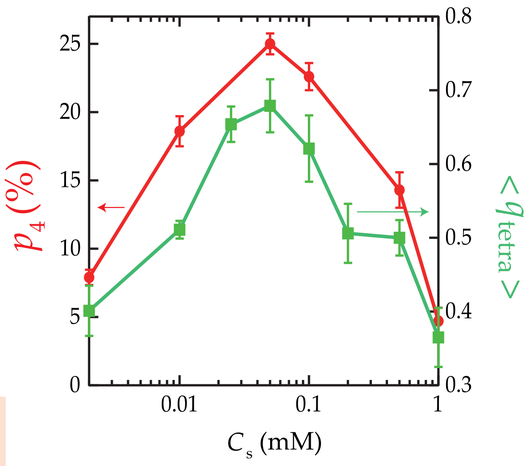


Fig.7 Population of tetrahedral cluster p_4 and the value of q_{tetra} at various C_Ss.

q_{tetra} : bond order parameter

q_{tetra} is an index as a measure of symmetry of the tetrahedron represented by equation (1).

$$q_{tetra} = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos\theta_{jk} + \frac{1}{3}\right)^2 \quad (1)$$

When the structure of the cluster is a regular tetrahedron, the value of q_{tetra} takes the maximum value 1.0. The values of θ_{jk} were measured from LSM images of the clusters.

Fig.6 The bond angle θ_{jk} is defined as the angle between two lines, which join the center particle and nearest neighbors j and k.

Both the p_4 - C_s and q_{tetra} - C_s plots had a maximum. It appears that the maximum was resulted from an interplay of the electrostatic repulsion between like charges and attraction between opposite charges.

3) COMPARISON of the TWO SYSTEMS

Interaction Potential

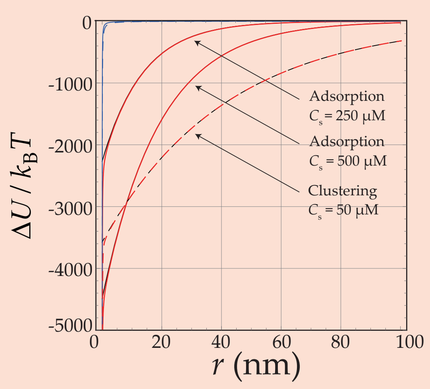


Fig.8 Interaction potential between particle and plate(solid curves), binary particle systems(dashed curves).

U_Y : Yukawa potential

$$U_Y(r) = \frac{\exp[\kappa(a_1+a_2)]}{(1+\kappa a_1)(1+\kappa a_2)}\frac{1}{4\pi\varepsilon_r\varepsilon_0}\frac{Z_1 Z_2 e_0^2}{r}\exp(-\kappa r)$$

a_i : particle radius
Z_i : charge number
κ^{-1} : Debye length
$\varepsilon_r\varepsilon_0$: permittivity
r : interparticle distance

U_{vdW} : van der Waals potential

$$U_{vdW}(r) = -\frac{A}{6}\left[\frac{2a_1a_2}{r^2-(a_1+a_2)^2} + \frac{2a_1a_2}{r^2-(a_1-a_2)^2} + \ln\frac{r^2-(a_1+a_2)^2}{r^2-(a_1-a_2)^2}\right]$$

A : Hamaker constant

U_{total} : total potential

$$U_{total}(r) = U_Y(r) + U_{vdW}(r)$$

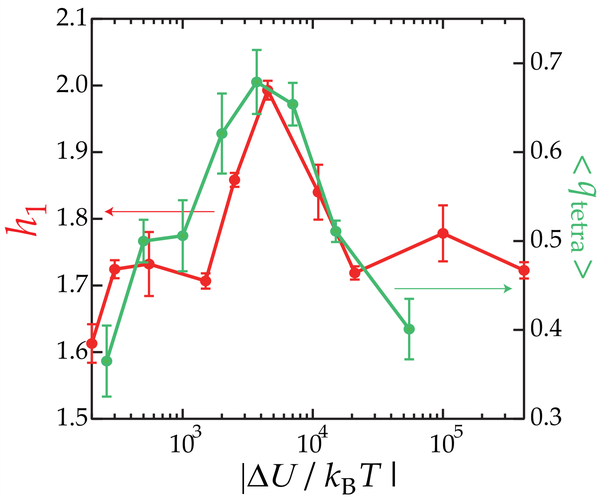


Fig.9 Values of h_1 and q_{tetra} plotted against magnitude of interaction potential.

The q_{tetra} and h_1 exhibited similar trend when plotted by using interaction magnitude $|\Delta U|$. This finding leads to universal understanding of the behavior of two systems.

4) SPACE EXPERIMENTS

We observed that the optimum condition for formation of the tetrahedral clusters was 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. A UV curable gelation reagents were mixed to the samples to fixed the sample under UV illumination after the clusters will be formed.

Fig.10 Images of space experiments. ©NASA/JAXA

CONCLUSIONS

- Both the ϕ_A – C_s and p_4 - C_s plots had a maximum at around C_s = 50 μM.
- The spatial regularity of the adsorbed particle, determined in terms of h_1 and q_{tetra}, was largest at C_s around the maximum.
- Behavior of the two systems were compared by using the interaction magnitude.