

論文の内容の要旨

論文題目

Confocal microscopy observation of the gelation process of colloidal suspensions

(コロイド分散系のゲル化過程の共焦点顕微鏡観察)

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< Introduction >

A gel is a space-spanning network and its dynamics is macroscopically arrested. Thus a gel has static elasticity and is widely used in our daily life. A gel has attracted considerable attention from the fundamental viewpoint because of its intriguing non-equilibrium and non-ergodic nature.

Among model gel systems, colloidal gels have been widely used because they provide a single particle resolution and tunability of inter-colloid attraction. Colloidal gels are formed by short-range attraction between colloids, and colloid-polymer mixtures have been often used. In a colloid-polymer mixture, colloids attract each other to increase the configurational entropy of polymers. We can control the attraction strength by the polymer concentration and its interaction range by the molecular weight of the polymers. Previous works have focused on both the phase diagram and the formation process of colloidal gels.

The phase diagram of colloidal gels is determined by two physical parameters: the colloid volume fraction and the polymer concentration which plays a role of the effective temperature (or the attraction strength). Experimentally a gel is formed as the attraction strength becomes strong enough to cause spinodal decomposition. Previous works have focused on the relation between gelation and spinodal decomposition. For example, Lu et al. measured the gelation boundary precisely and showed that it indeed coincides with the boundary of spinodal decomposition [Lu et al., Nature, 2008].

The mechanism of the gelation process is still controversial and simulation works suggest that hydrodynamic interactions play key roles in network formation. In Brownian dynamic simulations, systems form droplet structures in moderate strengths of attraction and gelation is induced only when we introduce attraction much stronger than the corresponding experimental value. In Brownian dynamic simulations only thermal fluctuations and short-range attraction are considered and the effects of hydrodynamic interactions are completely ignored. To study the effects of hydrodynamic interactions on gelation, Araki and Tanaka have developed the new simulation method for colloidal suspensions that can properly incorporate many-body hydrodynamic interactions and reported that hydrodynamic interactions strongly enhances network formation [Araki and Tanaka, PRL, 2000].

However, there has been little experimental evidence for the roles of hydrodynamic interactions in gelation processes because previous experiments could not access the early stage of gelation process. Here, we develop a new experimental method which allows us to directly follow the whole process of gelation with a single particle resolution and study the mechanism of gelation using it.

< Materials and methods >

Previous experimental works have focused on the 'final structures' of colloidal gels. In the previous method, all components are mixed in a sample bottle, incubated into a glass cell, and then observed by a microscope. This method has two fundamental problems for direct observation of the gelation process. First, gelation already starts in the sample bottle, which prevents the observation of

the early stage of the gelation. Second, the process of inserting the sample to the glass cell causes strong convective flow and strongly perturbs colloid motion. Therefore, the previous method is not suitable for direct observation of the kinetics of gelation.

This thesis focuses on the gelation process and its mechanism. So, we developed a new method. Gelation requires three components: colloids, polymers for inducing short-range attraction between colloids, and salt for screening the surface charges of colloids. Without salt, colloids are well dispersed by long-range electrostatic repulsions. Addition of salt reduces electrostatic repulsions and initiates aggregation of the colloids under the action of polymer-induced short-range attractions. In our method, a sample is initially prepared without salt and incubated into an observation cell attached with a membrane filter. After observation is started, a salt-reservoir is contacted with the observation cell. Then salt diffuses into the observation cell through the membrane filter, which initiates gelation. Our method allows us to observe the entire process of the gelation from the very early stage to the late stage without suffering from convective flow.

We synthesized sterically stabilized poly-methyl-methacrylate colloids with their radii of about 1.4 μm . Colloids were fluorescently labeled and observed three-dimensionally by a laser-scanning confocal microscope. We calculated the center positions of all colloids from the three-dimensional images with a help of a computer and analyze the structure and dynamics of the colloidal suspension.

< Cluster aggregation >

In results and discussions, we focus on four subjects: cluster aggregation, gelation in a dilute system, gelation in a dense system, and dynamical arrest. Cluster aggregation occurs in the early stage of all gel samples and each cluster forms a 'building block' in the gel networks. Therefore, understanding cluster aggregation is the basis for the gelation mechanism.

Previous simulation works have shown the effects of hydrodynamic interactions on cluster aggregation. Furukawa and Tanaka have prepared 13 colloids in an isosahedral configuration and let them aggregate. They have compared results of Brownian dynamics (without hydrodynamic interactions) with those of Fluid Particle Dynamics (with hydrodynamic interactions) [Furukawa and Tanaka, PRL, 2010]. In Brownian dynamics simulations, the colloids aggregate and form a compact cluster within a Brownian time of a colloid. In Fluid Particle Dynamics simulations, on the other hand, the fluid between the colloids must be squeezed out, which slows down cluster compaction by more than 10 times. This is a consequence of the incompressible nature of the solvent. Therefore, we focus on compaction dynamics of small clusters experimentally to elucidate the effects of hydrodynamic interactions.

We prepared a sample of the colloid volume fraction of 5 % and the polymer concentration of 1.0 mg/ml. As aggregation proceeds, the averaged cluster size and number of nearest neighbors (coordination number) monotonically increase. We successfully observed that three colloids are first connected linearly and then gradually form a compact cluster. All clusters with three colloids are identified and tracked with a high time resolution. From the measurements of the temporal change in the radius gyration of each cluster, we found that the process of cluster compaction takes more than 10 times of the Brownian time. The clusters composed of four and five colloids also show similar results. These results strongly suggest that hydrodynamic interactions severely retard cluster compaction and lead to long-lived linear open clusters.

To understand aggregation of the clusters that have more than five colloids, we evaluate the cluster structures by calculating the fractal dimension d_f . In the early stage of aggregation, d_f is

around 1.4. As aggregation proceeds, d_f increases to 1.8. Therefore, the clusters form chain-like structures ($d_f = 1$) in the early stage and gradually form compact structures ($d_f = 3$). The clusters of $d_f = 3$ are energetically favored, whereas the clusters of $d_f = 1$ is kinetically formed due to hydrodynamic interactions. Thus, we may say that hydrodynamic interactions compete with local energy minimization in each cluster.

Our results suggest that hydrodynamic interactions dominate the early stage of cluster aggregation, namely, the kinetic pathway is selected by momentum conservation.

< Gelation in a dilute system >

To study gelation in a dilute system, the colloid volume fractions are fixed at 7 % and only the polymer concentrations are changed. In each gel sample, both cluster size and coordination number increase as gelation proceeds. The radius gyration of the largest cluster increases to the system length, which leads to percolation. The fractal dimension increases from 1.4 in the early stage of gelation to 1.8 in the late stage. These results are consistent with the above results of cluster aggregation.

The question here is how a dilute gel is able to form an open space-spanning network. In our system, open clusters are connected with each other and finally form a space-spanning network. Because d_f is lower than three and increases as gelation proceeds, the colloid volume fraction itself has little importance. Instead, we calculate the 'effective' volume fraction by replacing each cluster to the effective sphere whose radius is equal to the radius gyration of the cluster. In all gel samples, the effective volume fractions sharply increase to approximately 60 %, which leads to percolation.

Our results reasonably explain the mechanism of percolation in a dilute gel. Hydrodynamic interactions decrease the fractal dimension of clusters down to 1.4 - 1.8. Thus the effective volume fraction can increase up to 60 %, which leads to percolation. If there were no hydrodynamic interactions, the fractal dimension would become close to three, the effective volume fraction could not increase, and the system would form droplet structures instead of a space-spanning network. Our finding suggests that hydrodynamic interactions play a key role in the percolation in a dilute gel.

< Gelation in a dense system >

To study gelation in a dense system, the colloid volume fractions are fixed at 15 % and 30 % and the polymer concentrations are changed. In all samples, the percolation processes are accomplished in a few minutes and then the networks slowly coarsen over several hours. The percolation process hardly depends on the polymer concentration while the coarsening process strongly does.

When the system percolates, the coordination number is approximately three and the bond-bond angle is approximately 100 deg. Thus, the percolated network has chain-like structures. Our results of cluster aggregation suggest that hydrodynamic interactions dominate the system in the early stage and facilitate the formation of linear open clusters. Because the system has a high colloid volume fraction, the linear clusters connect each other before they transform into compact structures. Therefore, the clusters form a chain-like network. This scenario is consistent with the process predicted by Fluid Particle Dynamics simulations. Our results suggest that hydrodynamic interactions also play key roles in the percolation in a dense gel.

In contrast, the coarsening process depends on the polymer concentration. As the polymer concentration decreases, the coordination number increases more rapidly. These results suggest that local energy landscape plays key roles in the coarsening process. With lower polymer concentration (or weaker attraction), the energy barrier for motion of each colloid is shallower and colloids more easily move to minimize the free energy. As the coordination number increases, energy barriers become higher and finally trap colloids. Furthermore, we directly observe the elementary processes of network coarsening. Chain-like rings in a percolated network gradually shrink and form compact domains with a help of thermal fluctuations of each colloid. In some cases, tension accumulated in the network leads to disconnection of weak chains. These continuous and discrete processes of network coarsening provide direct information on how the system lowers the free energy in the coarsening process.

< Dynamical arrest >

Dynamics of colloids is arrested in a gel. Previous works studied the structures and dynamics of colloidal gels and suggested that local condensation causes dynamical arrest. However, the 'process' of dynamical arrest has been poorly understood. Here, we directly investigate the relation between local condensation and dynamical arrest in gel samples with the colloid volume fraction of 7, 15, and 30 %. Even when the systems accomplish percolation, results of the analysis of the mean square displacements show that colloids are still mobile. Over several hours after percolation, the coordination numbers slowly increase, which leads to the decrease in the mean square displacements. Therefore, our results directly show a causal link between local condensation and dynamical arrest in a gel.

< Conclusion >

Gelation processes have been poorly understood experimentally. Here, we develop the new method and directly observe the entire processes of the gelation with a single particle resolution. Our results suggest that coupling of hydrodynamic interactions and local energy minimization plays a crucial role in gelation and ageing. Hydrodynamic interactions disturb compaction of colloids, enhance the open nature of the cluster structure, and help percolation. On the other hand, local energy minimization is a driving force of local compaction, which plays key roles in the coarsening process and dynamical arrest.

Our study sheds new light on the aggregation mechanism of not only colloidal suspensions but also similar complex fluids made of dynamically asymmetric components, such as polymer solutions and protein solutions.