Abstract of Doctoral Dissertation

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Title of Doctoral Dissertation

On the study of a reaction-diffusion particle model for clustering of self-propelled oil droplets on a surfactant solution
(界面活性溶液上の自走油滴の集団運動に対する反応拡散-粒子モデルの研究)

A lot of clustering behaviors are commonly observed in various animate system, but it is difficult to provide experimental means because of the complexity of motions and the difficulty of controlling behavior of individual organisms. On the other hand, motions of chemical droplets such as repulsive, self-propelled, and clustering in inanimate system have been extensively studied. As they can be useful for controlling parameters as well as creating advanced system, inanimate systems are important for understanding the motions. Recently, we found that a closed environment where a glass cover is placed on the channel shown that ethyl salicylate droplets on the surface of sodium dodecyl sulfate solution exhibit transient oscillatory dynamics, leading to the formation of a single cluster via the merging of sub-clusters. When the glass cover is removed, oscillatory behavior resumes, and the cluster breaks up. In this study, we understand the mechanism of this clustering for droplets based on the mathematical model consisting of the reaction-diffusion equations considering the concentration of each chemical substance and a chemical system.

We used ethyl salicylate (ES) as an oil and sodium dodecyl sulfate (SDS) as a surfactant solution, and we set up a simpler geometry such as a narrow channel since the part of difficulty for understanding the mechanism lies in a variety of states the cluster can take in a two-dimensional system. In a chemical system, with a one-dimensional system where ES is placed on SDS, we consider two-dimensional systems of both the air region by a cover and the water region filled as SDS. Therefore, we set six assumptions:

- The water region is divided into the upper and lower phase.
- The ES molecules are distributed on the surface and exchanged between the air and the surface.
- The SDS-ES complex occurs on the surface and dissolved into water.
- The surface tension is decreased with an increase in the concentration of ES or SDS.
- The shape of the ES droplet does not change.
- Droplets interact with each other only by the excluded volume effect.

Based on the above assumptions, we formulated the mathematical model consisted of five components; the motion of the droplet depending on the surface tension difference, the concentration of ES on the surface, the diffusion of SDS and SDS-ES complex in the upper phase, and ES in the air region. Since the boundaries of two-dimensional systems play an important role, we assign the boundary conditions; representing the effect of the cover, reflecting the evaporation, the condensation, the complex formation on the surface, and implying the diffusion between the upper and the lower phase. In particular, we introduced the excluded volume effect because the lateral capillary attraction is not the reason for the clustering. Hence, we have neglected the lateral capillary force to show that the clustering is still possible.

In numerical calculation, as the initial condition, we set zero and unique variable, but it is important to choose a suitable value through simulation. To select a suitable value and parameters, we checked the phase diagram which implies the transition such as the stationary, the oscillatory, and the rotating droplet according to suitable value. By selected parameters set, the transition motion from the oscillation to the stationary of a single droplet is qualitatively reproduced, and we found that the ES concentration has an impact influence on the oscillatory motion. Likewise, our model reproduces experimentally observed clustering for 20 droplets, and we analyzed that the SDS concentration causes the droplets between the peaks to drive into the valley, resulting in the effective attractive force since a high SDS concentration mean a low surface tension. Also, we realized that the droplets reach the stationary state because the high ES concentration in the air disturbs the evaporation of ES molecules on the surface. For this reason, the oscillatory motion occurs because the absence of a cover induces the evaporation on the surface through the decrease of ES concentration in the air. Our model successfully reproduces transient oscillations and the characteristics of cluster formation, and the effect of the glass cover.

The upper and the air layer are assumed to be the place where relevant chemical processes in the water and the air phase occur, such as the supply of ES molecules, adsorption, complex formation, evaporation, and condensation. Ideally, these layers should be very small, we could obtain a two-layer system with the surface and the bulk water. In other words, the one-dimensional model could be derived from the two-dimensional model by making zero the depth of the upper phase and the height between the surface and the cover by additive assumption:

- The depth of the upper phase and the height between the surface and the cover are sufficiently small.

The equations related to the motion of the droplet and the concentration of ES equally coincide with the two-dimensional model because these equations are consisted of the one-dimensional system. The equations consisted of the two-dimensional system are combined with each boundary condition.

Similar to a two-dimensional model, we simulate to select suitable value parameters set, and find the phase diagram and three kinds of states showing a tendency similar to the numerical result of a two-dimensional model. The remarkable difference between the two models is that, under a closed cover, the droplet of a two-dimensional model quickly reaches the stationary state, whereas the oscillatory dynamics decreasing the amplitude according to time occurs in the one-dimensional model. As well, in the case of 20 droplets, the droplets actively oscillate in the beginning, but the clusters are not formed as a single cluster, unlike a two-dimensional model. Note that the clustering formation depends on the system size. Our main idea that the clustering dynamics can be explained by the SDS concentration is thoroughly confirmed in both models. Furthermore, additional analysis to verify that our model can explain the phenomenon well has been conducted experimentally and numerically. We compare the first clustering time, defined as the time to form a sub-cluster mostly consisted of two droplets starting from an initial configuration for 5, 6, 8, 10, 15, 20, 25, and 30 of droplets. For each number of droplets, we repeat the experiment three times and measured the average and the standard deviation of the first clustering time. Then we perform the corresponding numerical simulations with three different initial random configurations. We observe the same tendency in experiment and simulation for two models in that the first clustering time is a decreasing function of the number of droplets. In particular, in more than 20 droplets, droplets have been shown to fit well between experiment and simulations. However, discrepancies are noticeable as the number of droplets decreases, and the simulation results of two models confirm that the one-dimensional model is more consistent with the experiment than the two-dimensional model. Remarkable point is that, for 5 droplets, we could not observe the cluster formation in experiment and one-dimensional model, whereas two-dimensional model always produced clusters.

Finally, the study has experimentally shown spontaneous oscillatory dynamics and clustering of chemical droplets and developed two mathematical models to account for the experimental results. The effect of the cover has also considered, which has been confirmed to have a significant effect on the droplet dynamics at the surface and in the air phase. Our mathematical model successfully reproduces clustering when the cover is closed and the recovery of their movement when the cover is removed. The results of numerical simulations show that the concentration of SDS affects clustering dynamics. One important implication of our result is that clustering can be explained without considering attracting interactions due to the lateral capillary force. We also confirm that one-dimensional model can be explained phenomena better that two-dimensional model. Our model overestimates the tendency of forming sub-clusters for the smaller number of droplets. All these discrepancies would result from the fact that our model is a phenomenological model, where the parameter values in the model have not been validated by experimental measurements.