

## The effect of the dipole-dipole repulsion on the size of the L-J particle aggregation

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### Summary

A Monte Carlo (MC) simulation is performed to study the effect of the dipole-dipole repulsion interaction to the size of Lennard-Jones (LJ) particle aggregation as an analogy of Liquid condensed (LC) domain formation of Zwitterionic surfactant, which contains the dipole moment, but neutral, at the air-water interface. The result shows the similar qualitative tendencies of changing characteristic aggregation size with the ratio of dipole-dipole repulsion to L-J potential, compared to the result from the simple calculation of the free energy to find the size of LC domains at equilibrium. In addition, we find that temperature effect on the aggregation size of particles with this potential is also well agreed with experimental observation.

### Background

During several decades, researchers have found that coexisting lipid monolayer phases (Liquid condensed and Liquid expanded) at the air-water interface possess interesting structures. Especially, this indicates that these interesting structures at the interface can be dramatically changed with several variables, such as temperature, composition of lipid, pressure, and interaction terms. Among these interesting variables, changing the interaction itself is very difficult to perform experimentally, and only simple free energy calculation has been available to identify this effect. Based on MC simulation for the simplified system, we can compare the effect of dipole-dipole repulsion term on the size of the domains at equilibrium with previously published results.

### Simulation method

In this research, we performed 2-dimensional MC-simulation because we are only interested in the structures at the 2-D interface. In addition, we neglect the effect of the solvent on the particle interactions, and thus, all particles in this system interact via L-J potential with dipole-dipole repulsion term. The details are listed below.

**N**, number of particles in the simulation box = 750     **$\rho$** , number density in simulation box = 0.15

**L**, length of simulation box = 70.71 X 70.71

**$r_{ij}^*$** , dimensionless length =  $\frac{r_{ij}}{\sigma}$  ,  **$T^*$** , dimensionless temperature =  $\frac{k_B T}{\epsilon}$

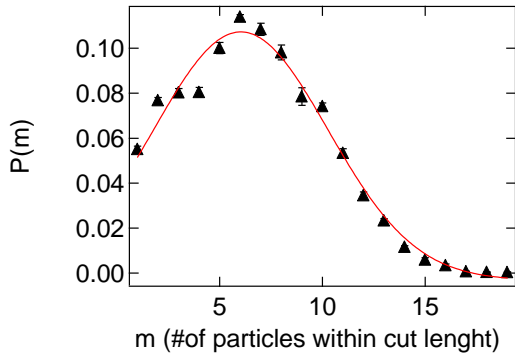
**ratio** = ratio between LJ potential and dipole-dipole repulsion.

$$U^*(r_{ij}^*) = 4 \left( \frac{1}{r_{ij}^{*12}} - \frac{1}{r_{ij}^{*6}} \right) + \text{ratio} * \frac{1}{r_{ij}^{*3}}$$

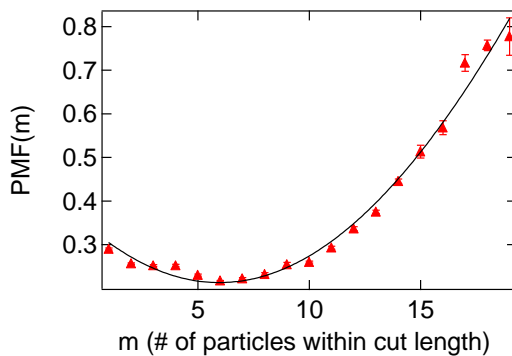
Here, to obtain faster simulation, we cut off above potential, where  $r_{ij}^* = 10$ .

Firstly, 750 particles are placed randomly in 2-D square lattice. We perform, then, the energy minimization process using conjugate gradient method. As a next step, to obtain equilibrium state, we perform MC-simulation with 480000 attempts (640 sweeps) with 50%  $\pm$  10% of acceptance ratio. Finally, we obtain the histogram to calculate the potential mean force (PMF) along the size of particle

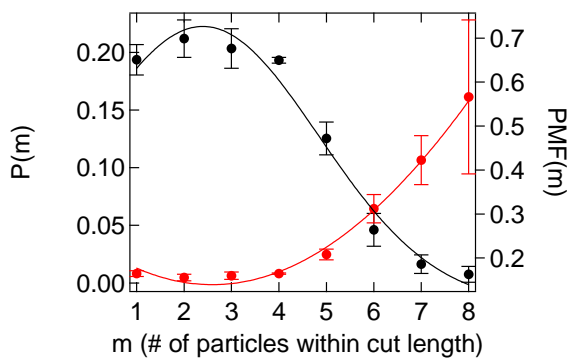
aggregation (or domain size). Here, to obtain better statistics, we run 5 independent production processes.



**Fig 1.**  $P(m)$  VS size of particle aggregation at  $T^* = 0.1$ , ratio = 0.025. This graph indicates Gaussian distribution of the domain size. To do the simpler simulation, we measure the number of particle within cut length ( $\sim 3$ ) around each particle, instead of measuring real size of domain, and this way, at least, provides the tendency of the size of domains with changing variables.



**Fig 2.**  $PMF(m)$  VS size of particle aggregation at  $T^* = 0.1$ , ratio = 0.025. Here, we calculate the PMF along the  $m$ ,  $PMF(m) = -T^* \times \ln(P(m))$ . Also, we fit the data with Gaussian function, and find the mean  $m$  value at minimum free energy.

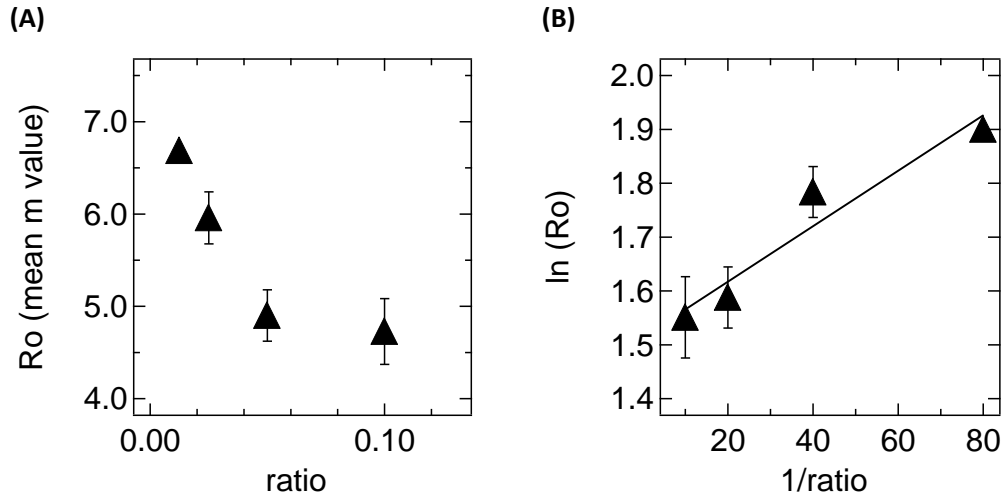


**Fig 3.**  $PMF(m)$  &  $P(m)$  VS size of particle aggregation at  $T^* = 0.1$ , ratio = 0.4. We change the ratio (or temperature) to obtain the tendency of the domain size with ratio (or temperature). We perform the exactly same way with above to obtain mean  $m$  value where the free energy is a minimum. In particular, the  $m$  values where  $P(m)$  is a maximum and where  $PMF(m)$  is a minimum are well agreed.

### Results and interpretation

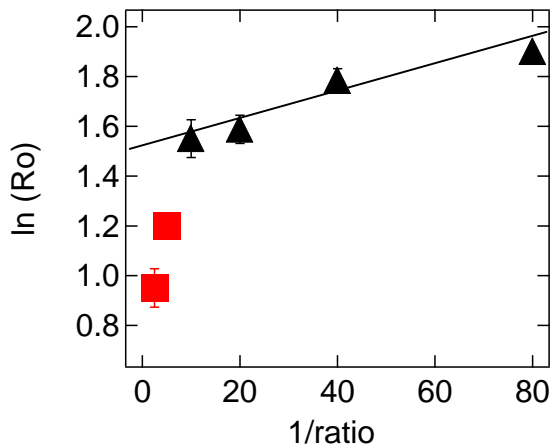
As a result of Fig.1, Fig.2 and Fig. 3, we investigate the relationship between  $R_0$  (mean  $m$  value) and the ratio of dipole-dipole repulsion to L-J potential. Intuitively, we can expect that  $R_0$  decreases with increasing ratio, shown in Fig 4(A). This means that increasing the repulsion term, which works in long range, would disturb the aggregation of the particles, and thus, we observe smaller size of particle aggregation. Previously, McConnell et al calculate the free energy of the domain of Zwitterionic surfactants at coexistence state which contains the line tension at the perimeter of domain and dipole-dipole repulsion within the domain, and thus, they showed that an equilibrium domain size is related to

the ratio of dipole-dipole repulsion to line tension with  $Ro \propto e^{1/ratio}$ . Here, shown in Fig 4 (B), we also identify that this relation is still working properly in our system even though our system is much simplified version, compared to the real system.



**Fig. 4. (A) Ro (mean m value) Vs ratio (B) ln Ro Vs 1/ratio at fixed  $T^*=0.1$ .** This graph shows that Ro decreases with ratio, and also well followed by the model, proposed based on the free energy calculation.

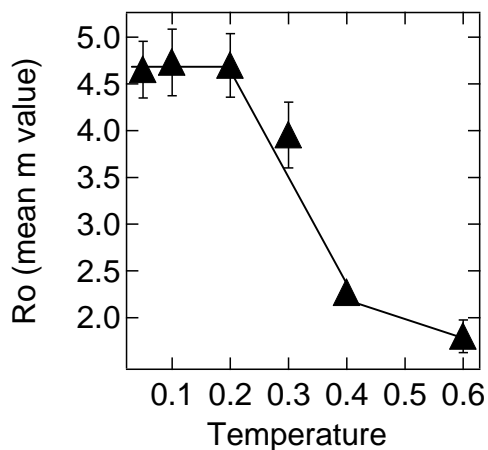
However, as increasing ratio value over 0.2, Ro is still decreasing with ratio, but its relation,  $Ro \propto e^{1/ratio}$ , starts to fail, shown in Fig 5. This possibly indicates that at high repulsion term, the balance between L-J potential and repulsion interaction may be broken, and repulsion interaction accelerates decreasing the size of particle aggregation.



**Fig. 5.** Two Ro values, where Ratio = 0.2 and 0.4, are added to Fig. 4(B). These two points are not agreed with previous model.

In addition, we also investigate the temperature effect on the size of particle aggregation. Here, we fix the ratio = 0.1, and vary the temperature from 0.05 to 0.6. As shown in Fig. 6, our simulation shows interesting tendency, not gradually decreases size with T. This interesting observation can be also explained by the behavior of real surfactant system. In case of Zwitterionic surfactants, they start to

nucleate to LC (Liquid condensed) domains at specific concentration of surfactants at fixed temperature. If temperature is increased, the specific concentration of surfactant where LC domain starts to nucleate is increased too. This strongly suggest that in our simulation set up ( $\rho = 0.15$ ), the aggregation of particles (or nucleation of domains) are available until 0.2 Temperature, but over this, they cannot have a nucleation process at this specific condition.



**Fig. 6.** Ro Vs Temperature at fixed ratio=0.1. Until  $T^*=0.2$ ,  $R_0$  is almost constant with varying temperature, but after this value  $R_0$  decreases drastically with temperature. The shape of this graph is similar to Heaviside step function.

In summary, we investigate  $R_0$ , mean  $m$  value, with the ratio of dipole-dipole repulsion to L-J potential and temperature. Interestingly, these two results are well agreed with the previous results from the real system of Zwitterionic surfactants at the air-water interface, and we show the possibility, which indicate that L-J particles with dipole-dipole repulsion is possibly useful for understanding the real 2-D structures of surfactants at the interface.

This model would be improved further by increasing the simulation size to make similar condition with the real system ( $10^7$  surfactants in the domain) and adding solvent effect to understand the PH-effect of sub-phase on the interface structure. More specified investigation of ratio value and temperature would also be interesting research.

#### Movie

finalP\_kyuhankim.avi

This video indicates the aggregation process of L-J particles with dipole-dipole repulsion during energy minimization and equilibration steps at  $T^* = 0.1$  and **ratio** between L-J potential and dipole-dipole repulsion = **0.1**.

#### Source code

finalP\_KyuHanKim.zip

#### Reference

1. Harden M. McConnell, 1991. 42:171-95, **Annu. Rev. Phys. Chem**