Molecular dynamics simulation for the morphological change of water-in-oil microemulsion droplets induced by addition of polymer chains

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1. Chain conformations in water particle solvent and in oil particle solvent.

In this study we used a simple chain model having the bond potential only, *i. e.* no angle-bending and torsion potentials. Then we investigated the behavior of the chain composed of 75 monomers in water particles. They were located in the simulation box under a periodic boundary condition. The temperature and the pressure were kept constant at 1.0, respectively. In Fig. S1, we showed the time variation of the end-to-end distance (R_F) of the chain in water at T = 1.0, where the chain had no angle-bending and torsion potentials. For reference, we showed the typical snapshots of the chain in water in Fig. S2(a). The chain conformation fluctuated between the elongated and collapsed states, which is a characteristic behavior of a random coil state. In addition, we investigated the degree of polymerization (N) dependence of R_F . As a result, we obtained $R_F \propto N^{-0.6}$, indicating that the chain behaves as a random coil.

For comparison, we also showed the time variation of the end-to-end distance of the chain in oil particles in Fig. S1 with the typical snapshots in Fig. S2(b). The other simulation conditions were fixed. In oil, the chain collapsed due to its hydrophilicity. Therefore, we concluded that the chain model used in this study behaves as a random coil in water at T = 1.0.



Fig. S1. Time variations of the end-to-end distance (R_F) of the chain in water (black line) and oil (red line) particle solvent, respectively.

(a) Water particle solvent



Fig. S2. Typical snapshots of the chain conformations in water particle solvent (a) and in oil particle solvent (b).

2. Constant temperature and constant pressure conditions

We carried out a simulation at constant *NPT* in order to investigate the formation of water-in-oil droplets. In Fig. S3, the time variations of the temperature and the pressure were shown during the simulation in Fig. 2. Both the temperature and the pressure were fluctuating around 1.0, and they were controlled very well.



Fig. S3. Time variation of the temperature (black line) and the pressure (red line) during the formation of the water-in-oil droplets in Fig. 2.

3. Equilibrium nature of water-in-oil droplets

We carried out a simulation at constant *NPT*, then it is important to show the equilibrium nature of our simulation. In Fig. S4, we showed the time variation of the total number density, ρ , and the simulation box size, *L*, during the formation of the spherical droplets in Fig. 2. After three droplets were formed at $t = 1,500\tau$, ρ and *L* kept almost constant.



Fig. S4. Time variation of the total number density (black line) and the simulation box size (red line) for Fig. 2.

Fig. S5 shows the time variation of the total non-bonded energy. With the lapse of time, a decrease in the total non-bonded energy was observed because of the growth of the spherical droplets. After $t = 1,500\tau$, the total non-bonded energy fluctuated around a constant value. Figs. S4 and S5 indicate that the final stages obtained in this simulation are the equilibrium states.



Fig. S5. Time variation of the total non-bonded energy during the formation of the droplets in Fig. 2.

4. Equilibrium nature of droplets containing chains

Fig. S6 showed the time variations of the total non-bonded energy for (ε_{HC} , N_{C}) = (3.0, 6) and (3.8, 6) in Fig. 4. The total non-bonded energy for (ε_{HC} , N_{C}) = (3.8, 6) was lower than that for (3.0, 6) due to the difference of ε_{HC} . With the growth of the droplets by coalescence, the total non-bonded energy decreased. For (ε_{HC} , N_{C}) = (3.0, 6), no significant change in the total non-bonded energy was observed after $t = 450\tau$. For (ε_{HC} , N_{C}) = (3.8, 6), a decrease in the total non-bonded energy was observed, and the decrease between 2000 τ and 2500 τ corresponds to the coalescence of the droplets containing the chains in Fig. 4(b). After the coalescence of the droplets containing the chains, the total non-bonded energy just fluctuated around a constant value. These results indicate that the final states obtained in our simulations are the equilibrium states.



Fig. S6. Time variations of the total non-bonded energy during the formation of the droplets for $\varepsilon_{\rm HC} = 3.0$ and $N_{\rm C} = 6$ in Fig. 4(a) (black line) and for $\varepsilon_{\rm HC} = 3.8$ and $N_{\rm C} = 6$ in Fig. 4(b) (red line).