§25. Molecular Dynamics Study of Structure Formation of a Single Polymer Chain by Cooling

Fujiwara, S., Sato, T.

Computer simulation of structure formation of polymer chains has recently become the focus of attention in physics, chemistry, biology, and materials science. Since polymer chains show diverse static and dynamical structures, they have various mechanical and thermodynamical properties. Our purpose is to clarify the mechanisms of structure formation of polymer chains at the molecular level. In particular, our concern is to investigate the structure formation process of a single polymer chain by cooling. To this end, we carry out the molecular dynamics (MD) simulations of a single polymer chain and analyze the formation process of the orientationally ordered structure during gradual stepwise cooling and during quenching^{1)–3)}.

The model polymer chain consists of 500 methylene groups, which are treated as united atoms. The united atoms interact via bonded potentials (bond-stretching, bond-bending and torsional potentials) and a non-bonded potential (12-6 Lennard-Jones potential). The atomic force field used here is the DREIDING potential⁴⁾. We use the velocity Verlet algorithm and apply the Nosé-Hoover method in order to keep the temperature of the system constant. The total linear momentum and angular momentum are set to be zero in order to cancel overall translation and rotation of a polymer chain. The MD simulations are carried out as follows. At first, we provide a randomly distributed configuration of a single polymer chain at high temperature ($T = 800$ K). The system is then cooled to lower temperature by gradual stepwise cooling or quenching.

We show, in Fig. 1, the time dependence of the global orientational order parameter P_2 in the case of gradual stepwise cooling. We find from this figure that the global orientational order as a whole grows in a gradual manner in the case of gradual stepwise cooling.

In Fig. 2, we show the time evolution of P_2 in the case of quenching. Figure 2(a) indicates that, at $T = 500$ K, we can see the clear transition between the orientationally ordered state and the randomly oriented state. At $T = 300$ K [Fig. 2(b)], on the other hand, the global orientational order grows in a stepwise manner. This result can be interpreted in the following way. In the case of quenching, the system tends to be trapped in a metastable state which corresponds to less orientationally-ordered structure and stays in the

metastable state for some duration. Once the system finds out a path to another metastable state, it makes a sudden transition from the original state to another state through the path.

Fig. 1. The time evolution of the global orientational order parameter P_2 in the case of gradual stepwise cooling.

Fig. 2. The time evolution of the global orientational order parameter P_2 (a) at $T = 500$ K and (b) at $T = 300$ K in the case of quenching.

References

- 1) Fujiwara, S. and Sato, T., J. Chem. Phys. **107**, (1997) 613.
- 2) Fujiwara, S. and Sato, T., J. Chem. Phys. **114**, (2001) 6455.
- 3) Fujiwara, S. and Sato, T., Computer Physics Communications (in press).
- 4) Mayo, S.L. *et al.*, J. Phys. Chem. **94**, (1990) 8897.