§18. Simulation Study of the Structural Formation of Short Polymer Chains

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Computer simulation of the structural formation in complex liquids has recently become the focus of attention in chemical physics. We aim at understanding the mechanisms of the structural formation of a polymer chain system, which is typical of complex liquids, at the molecular level. With a view to investigating the structural formation at the molecular level, we carry out molecular dynamics simulations of 100 short polymer chains, each of which consists of 20 CH\textsubscript{2} groups, and analyze the formation process of the orientationally ordered structure.

The united CH\textsubscript{2} groups interact via the bonded potentials (bond-stretching, bond-bending and torsional potential) and the non-bonded potential (12-6 Lennard-Jones potential) [1,2]. We use the velocity version of the Verlet algorithm and apply the Nose-Hoover method in order to keep the temperature of the system constant.

At first, we prepare random configuration of short polymer chains at high temperature ($T = 700$ K) and then it is quenched to $T = 400$ K.

Figure 1 shows the snapshots of the chain configurations for $T = 400$ K at $t = 1, 200$ and 2000 ps. From Fig. 1(a), we find that the polymer chains form random structures at $t = 1$ ps. Figures 1(b) and 1(c) indicate that the local orientationally-ordered regions (clusters) grow in several positions with time and at last they coalesce into a large cluster. It is also found from Fig. 1(c) that, in the orientationally ordered structure, almost all the bonds are in the trans state and the gauche states are located exclusively in the chain ends. From detailed analyses of clusters, we find the following formation process of the orientationally ordered structure: (1) At the initial stage ($t < 120$ ps), only small clusters, whose sizes are less than 10, are formed. (2) At the second stage ($120 < t < 210$ ps), small clusters grow and several middle-sized clusters, whose sizes are between 10 and 40, are formed. (3) At the third stage ($210 < t < 300$ ps), middle-sized clusters coalesce into a large cluster. (4) After that ($t > 300$ ps), the cluster gradually grows larger.

Fig. 1. The chain configurations of short polymer chains for $T = 400$ K (a) at $t = 1$ ps, (b) at $t = 200$ ps and (c) at $t = 2000$ ps.

References