

Structure Formation in a Short Chain-Molecule System: A Molecular Dynamics Study

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Abstract

The structure formation of 100 short chain molecules, each of which consists of 20 CH₂ groups, is investigated by means of a molecular dynamics simulation. The orientationally ordered structure is formed at a lower temperature by a sudden cooling from a random configuration at a higher temperature. It is also found that the growth of the local ordered clusters proceeds in a stepwise fashion.

Keywords:

molecular dynamics simulation, chain molecule, structure formation, orientational order

1. Introduction

Computer simulation of structure formation or self-organization has recently become the focus of attention in plasma physics and chemical physics. In plasma physics, structure formation in systems with long-range interactions, such as Coulombic interactions, has already been investigated. In contrast, in dusty plasmas and molecular systems, interactions between particles are short-ranged. The purpose of this paper is to clarify the mechanism of structure formation in systems with short-range interactions. To this end, we have carried out the molecular dynamics (MD) simulations of short chain molecules.

Some MD work has already been done on structure formation of short chain molecules. Esselink *et al.* carried out simulations of nucleation and melting of *n*-alkane systems [1] and Takeuchi studied structure formation of short chain molecules during the crystallization induction period [2]. Although several simulation studies of short chain molecules have been done on the structure formation, little is known about the growth process of orientational order during structure formation.

2. Model and Method

The present computational model is the same as the one used in the previous work on the structure formation of a single polymer chain [3]. The model chain molecules consist of a sequence of CH₂ groups, which are treated as united atoms. The mass of each CH₂ group is 14g/mol. 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 potential [4].

The numerical integrations of the equations of motion are performed using the velocity Verlet algorithm [5]. We apply the Nosé-Hoover method in order to keep the temperature of the system constant [6,7]. The integration time step and the relaxation constant for the heat bath variable are 1 fs and 0.1 ps, respectively. The cutoff distance for the Lennard-Jones potential is 10.5Å. The chain molecules are exposed to vacuum with no box to confine them. The total linear momentum and angular momentum are set to be zero in

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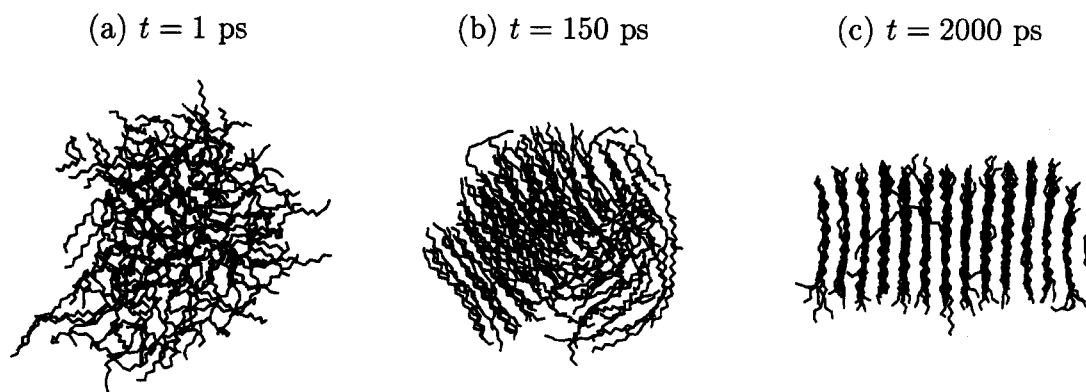


Fig. 1 The chain configurations of 100 short chain molecules at $T = 440\text{K}$ viewed along the b -axis. (a) $t = 1\text{ps}$, (b) $t = 150\text{ps}$ and (c) $t = 2000\text{ps}$.

order to cancel overall translation and rotation of chain molecules. The MD simulations are carried out as follows [8-10]. At first, we provide a randomly distributed configuration of 100 short chain molecules, each of which consists of 20 CH_2 groups, at high temperature ($T = 700\text{K}$). Note that there are no preferred directions in the system. The system is then quenched to several lower temperatures ($T = 300, 320, \dots, 460\text{K}$).

3. Simulation Results

3.1 Chain configuration

In Fig. 1, we show the chain configurations viewed along the b -axis at various times ($t = 1, 150$ and 2000ps) at $T = 440\text{K}$. The a , b , and c axes respectively correspond to the crystallographic a , b , and c axes in the orthorhombic system. From Figure 1, we find the following features: (i) At the early time ($t = 1\text{ps}$), the configuration of chain molecules is *random*. (ii) As time elapses ($t = 150\text{ps}$), growth of local orientationally-ordered clusters is observed in several positions. (iii) At last ($t = 2000\text{ps}$), several clusters coalesce into a large cluster and a highly ordered structure is formed. In the ordered structure, almost all the bonds are in the *trans* state.

3.2 Parallel ordering

In order to investigate the parallel ordering process, we need introduce the concept of a "*cluster*", which will physically mean a bunch of local orientationally-ordered chains which is formed through parallel ordering [1,8-10]. Our precise definition of a cluster is as follows. Two chain molecules belong to the same cluster if the following two conditions are satisfied: (i) $|\mathbf{r}_c^i - \mathbf{r}_c^j| < r_0$ and (ii) $\alpha_{ij} < \alpha_0$. \mathbf{r}_c^i is the position vector of the center

of mass of the i -th chain and α_{ij} is the angle between the principal axis with the smallest moment of inertia of the i -th chain and that of the j -th chain. It must also satisfy $0 \leq \alpha_{ij} \leq \pi/2$. In our calculations, we set $r_0 = 1.5\sigma$ ($\sigma = 0.36239\text{nm}$) and $\alpha_0 = 10^\circ$. In Fig. 2, we show the largest cluster size s as a function of time at several temperatures ($T = 340, 380, 400$ and 440K). It can be seen from this figure that the growth of the clusters is stepwise. This is a sensible result, since our analysis shows that the mechanism of cluster growth involves coalescence of smaller clusters into larger ones [8]. There is a similar stepwise behavior in the global orientational order parameter [8,10].

4. Summary and Discussion

By carrying out MD simulations of 100 short chain molecules, each consisting of 20 CH_2 groups, and analyzing the growth process of clusters, we have obtained the following results: (1) The orientationally ordered structure is formed at a lower temperature by quenching from a random configuration at a higher temperature. (2) The local orientationally-ordered clusters grow in a stepwise fashion.

The fact that the stepwise relaxation into a stable state takes place when the system is instantaneously changed into a nonequilibrium state is also observed in the process of self-organization in plasmas [11]. We therefore conclude that when a system is driven far from equilibrium, it will evolve to a minimum energy state in a stepwise fashion and this behavior is independent of the types of molecular interactions.

For the future work, we will carry out MD simulations of long chain molecules in order to investigate the effect of the entanglement on the

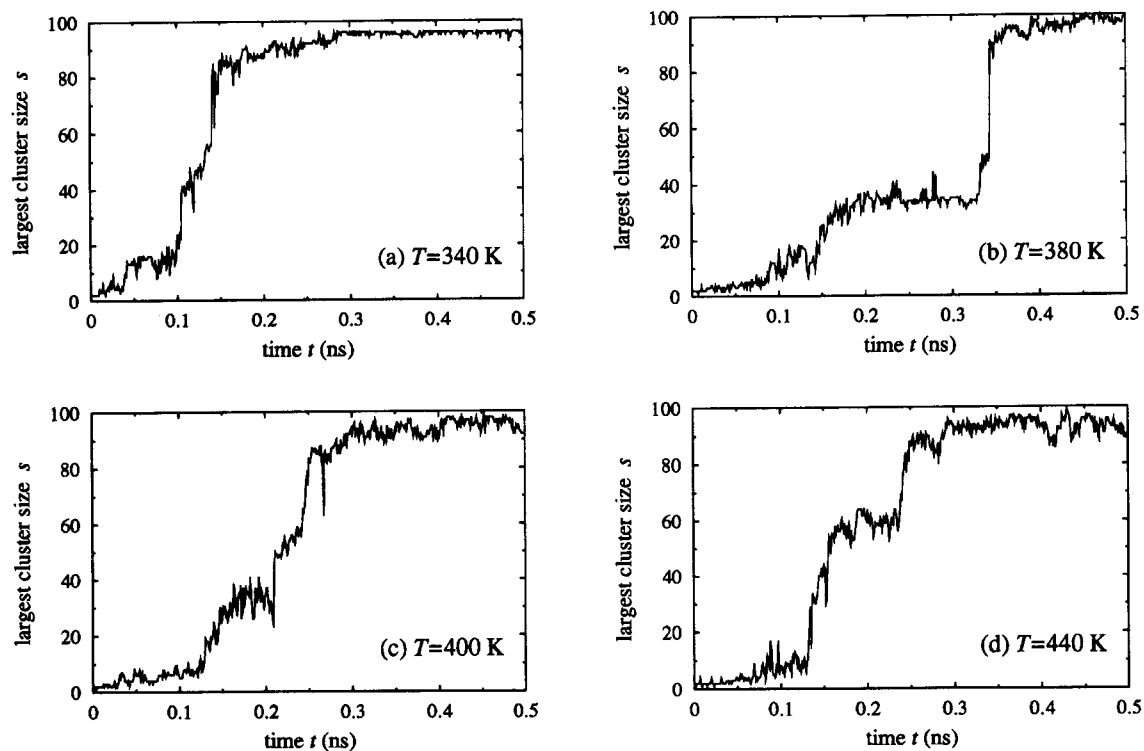


Fig. 2 The size of the largest cluster s versus time t , (a) at $T = 340\text{K}$, (b) at $T = 380\text{K}$, (c) at $T = 400\text{K}$ and (d) at $T = 440\text{K}$.

structure formation.

References

- [1] K. Esselink, P.A.J. Hilbers and B.W.H. van Beest, *J. Chem. Phys.* **101**, 9033 (1994).
- [2] H. Takeuchi, *J. Chem. Phys.* **109**, 5614 (1998).
- [3] S. Fujiwara and T. Sato, *J. Chem. Phys.* **107**, 613 (1997).
- [4] S.L. Mayo, B.D. Olafson and W.A. Goddard III, *J. Phys. Chem.* **94**, 8897 (1990).
- [5] W.C. Swope, H.C. Andersen, P.H. Berens and K.R. Wilson, *J. Chem. Phys.* **76**, 637 (1982).
- [6] S. Nosé, *J. Chem. Phys.* **81**, 511 (1984).
- [7] W.G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
- [8] S. Fujiwara and T. Sato, *Phys. Rev. Lett.* **80**, 991 (1998).
- [9] S. Fujiwara and T. Sato, *Molecular Simulation* **21**, 271 (1999).
- [10] S. Fujiwara and T. Sato, *J. Chem. Phys.* **110**, 9757 (1999).
- [11] S.P. Zhu, R. Horiuchi and T. Sato, *Phys. Rev. E* **51**, 6047 (1995).