§12. Molecular Dynamics Simulation for Melting Process of *n*-Nonadecane Ultrathin Films

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The n-alkanes are known to show the anomalous structures at a few degrees above the melting temperature. In this structure, a solid monolayer is formed at the surface of an isotropic n-alkane liquid above its bulk melting temperature[1),2)]. This phenomenon, which is known as *surface freezing*, occurs only for carbon numbers $14 < n_C \leq 50$. In this study, we investigate the melting process of n-nonadecane (n-$C_{19}H_{40}$) ultrathin films using molecular dynamics (MD) simulation and clarify its mechanism at the molecular level.

The computational model is the same as that used for n-alkane in Ref.[3]. Methyl and methylene groups are treated as united atoms. The united atoms interact via the bonded potentials (bond-stretching, bond-bending and torsional potentials) and the van der Waals nonbonded potential (12-6 Lennard-Jones(LJ) potential). The equations of motion for all particles are solved numerically using the velocity Verlet algorithm with a time step of $\Delta t = 2.05$ fs. We carry out the MD simulations by using the coarse-grained molecular dynamics simulator (COGNAC) in the OCTA system[4)]. We use the combination of a constant-temperature method (Nosé-Hoover method) and a constant-pressure method (Parrinello-Rahman method with unit cell angles fixed at 90°). The external pressure is set to 0.1 MPa, which corresponds to atmospheric pressure, and the cutoff distance for the LJ potential is 0.95 nm. As an initial configuration, the molecules are placed into 3 - 7 layers, each of which consists of 168 molecules. The molecular axis is parallel to the z direction, which is perpendicular to layers. The periodic boundary conditions are applied in the x, y, z directions with free space by two-molecule thickness in the z direction. We first prepare crystals of n-nonadecane ultrathin films with 3 - 7 layers at 50 K and then heat the systems stepwise.

We show, in Fig. 1, snapshots of n-nonadecane ultrathin films with 5 layers in the course of melting. This figure indicates that melting occurs layer by layer from the internal layers. It is also found that a temperature range exists where the internal layers are in the molten states and both surface layers remain in the crystalline state (Figs. 1(c) and 1(d))). This type of melting is observed for all other n-nonadecane ultrathin films with different numbers of layers. It is thus concluded that n-nonadecane ultrathin films exhibits surface freezing.

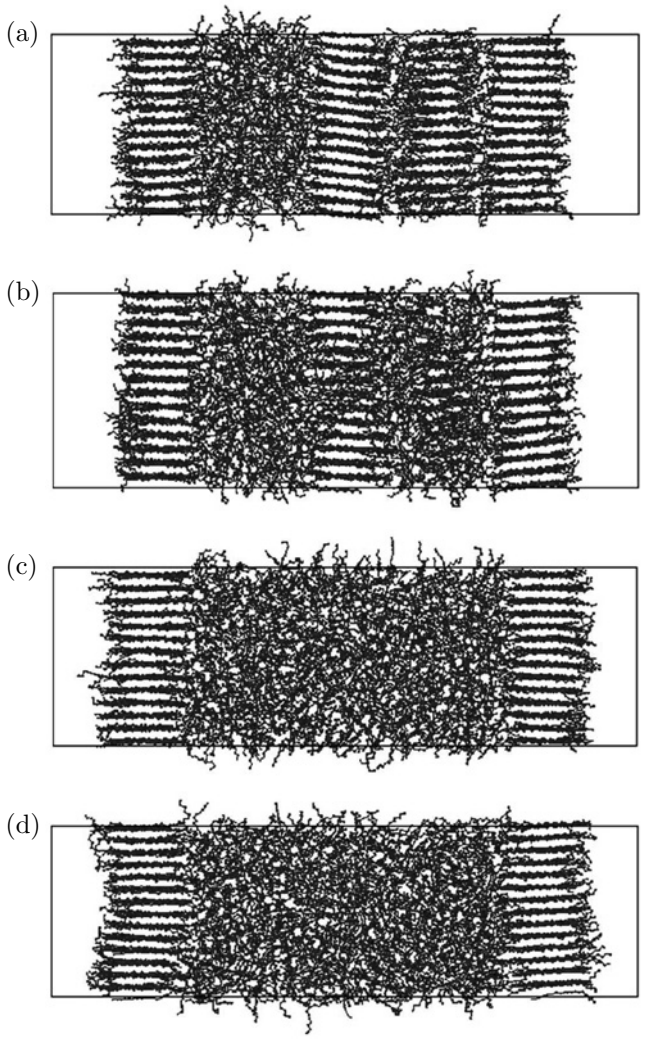

Fig. 1. Snapshots of n-nonadecane ultrathin films with 5 layers in the course of melting: (a) $T = 361$ K, (b) $T = 362$ K, (c) $T = 363$ K and (d) $T = 366$ K.

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2) Wu, X.Z., Shirota, E.B., Ocko, B.M. and Deutsh, M.: Phys. Rev. Lett. **70** (1993) 958.
3) Yamamoto, T., Nozaki, K., Yamaguchi, A. and Urakami, N.: J. Chem. Phys. **127** (2007) 154704.
4) http://octa.jp/.