§18. Molecular Dynamics Simulation of Melting Process in *n*-Nonane Ultrathin Films

Fujiwara, S., Maruyama, R., Itoh, T., Hashimoto, M. (Kyoto Inst. Tech.),
Horiuchi, R.

It is known that n-alkane shows the anomalous structure at a few degrees above the melting temperature. In this structure, a solid monolayer forms at the surface of an isotropic n-alkane liquid above its bulk melting temperature[1),2)]. This phenomenon, which is called surface freezing, occurs only for carbon numbers $14 < n \leq 50$. In this study, we investigate the melting process of n-nonane (n-C_9H_{20}) 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 - 9 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-nonane ultrathin films with 3 - 9 layers at 50 K and then heat the systems stepwise.

In the case of n-nonane with 6 layers, the system melts at 272K. We show, in Fig. 1, snapshots of n-nonane ultrathin films with 6 layers at 272 K in the course of melting. It is found from this figure that melting occurs layer by layer from the surface. This type of melting, surface melting, is observed for all other n-nonane ultrathin films with different numbers of layers. It is thus concluded that n-nonane ultrathin films exhibits surface melting.

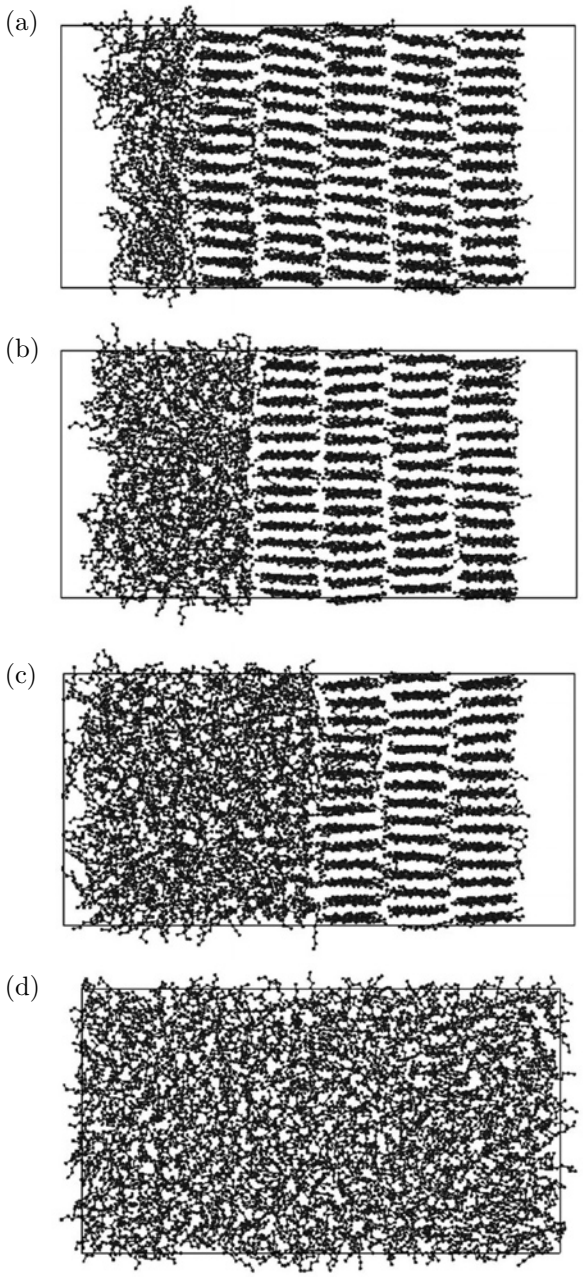

Fig. 1. Snapshots of n-nonane ultrathin films with 6 layers at 272 K in the course of melting: (a) $t = 18.6$ ns, (b) 20.5 ns, (c) 22.0 ns and (d) 22.4 ns.

1) Earnshaw, J.C. and Hughes, C.J.: Phys. Rev. A, **46** (1992) R4494.
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/.