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Construction and investigation of a hard-sphere crystal-melt interface by a molecular dynamics simulation

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The hard-sphere crystal-melt interfaces, which had been regarded as difficult to construct in computer simulations, were realized by the molecular dynamics (MD) simulation according to the algorithm by Alder and Wainwright [J. Chem. Phys. **31**, 459 (1959)]. The fcc (100), (110), and (111) interfaces were studied. At first, an MD simulation was done for a system which consisted of two blocks; identical heavy particles were laid in the crystal block and identical light ones in the melt block. The crystal block was the fcc with the density of the crystal phase, whereas in the melt block particles in the fcc arrangement were put in its central part with the average density being consistent with the melt phase. After the melt block reached the melt state, masses of the whole system were brought to be identical. Continuing the MD simulation farther, we obtained the equilibrium configuration with the hard-sphere crystal-melt interface. The trajectories and the density profiles were investigated.

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Since the first molecular dynamics (MD) simulation for the hard-core system [1] was carried out, no one could successfully perform the MD simulation of the crystal-melt coexistence in the three-dimensional hard-sphere (3DHS) systems. Neither the crystallization from the fluid phase nor the coexistence with the plane interfaces has succeeded in the 3DHS system, whereas the coexistence in a two-dimensional system was obtained early by the MD simulation [2]. Following Alder and Wainwright [3], one may reason that the failures in the simulations of the crystallization in the 3DHS system are due to the small system sizes and the short total run times suppressing the fluctuation necessary to yield crystalline nuclei. Note that in the Alder and Wainwright (AW) algorithm [4,5] the time evolution is accomplished by the collision-by-collision approach, while for the soft-potential system the time is evoluted by the step-by-step algorithm [5]; therefore the AW method usually requires a longer computation time as compared with the ordinary one. On the other hand, for the nonexistence of any simulations of the 3DHS crystal-melt interfaces, one may speculate by using crude lattice models such as Temkin's [6] that the absence of the attractive force does not stabilize the hard-sphere crystal-melt interfaces or that the hard-sphere crystal-melt interfaces are too diffuse to construct. These speculations are, however, not precise. A molecular theoretical approach to the above crude model was given by Nakano [7] and is being developed by Mori *et al.* [8], In addition, it should be noted that the MD simulations of the crystal-melt interfaces have been carried out for the soft-sphere systems [9–11], which are also comprised of pure repulsion. Hence, we expect to observe the equilibrium crystal-melt interfaces in a 3DHS system as well and carry out a computer simulation with large system size.

To construct a crystal-melt interface, we divided the system with the periodic boundary condition into two parts, melt and crystal blocks. At first, we put identical hard spheres in each block. Masses of particles in the crystal block were set to be 1000 times heavier than those in the melt block. The crystal block was filled with particles in the fcc arrangement with a lattice constant consistent with the density of the crystal phase (0.545 in volume fraction obtained by a single-occupancy cell method [12]), whereas in the melt block, particles in a close-packed fcc arrangement were put in its central part and the number of particles there was determined so that the total melt density was consistent with that from Ref. [12] (0.494 in volume fraction). In order to get a quite high collision rate in the melt block, the close-packed arrangement was adopted. Orientations of the fcc lattice in both blocks were the same and the configurations for the (100), (110), and (111) interfaces were investigated. For respective orientations, the crystal blocks consisted of 33, 45, and 33 layers and the total numbers of particles were 3888, 3787, and 4230. Figure 1 shows the initial configuration for the (110) interface. Due to the periodic boundary condition, both ends of the picture are identical, i.e., the numeral "0" on the bottom side indicates the central layer in the crystal block.

We carried out the MD simulations according to the AW algorithm [4,5]. For nonidentical hard-sphere systems, the velocity change of a particle i with mass m_i, diameter σ_i, and velocity $\boldsymbol{v}_i$, due to the collision with a particle j with mass m_j, diameter σ_j and velocity $\boldsymbol{v}_j$, is given by

$$\Delta \boldsymbol{v}_i = -\frac{2m_j}{m_i+m_j}\frac{b_{ij}}{\sigma_{ij}}\boldsymbol{r}_{ij}, \quad b_{ij}=\boldsymbol{v}_{ij}\cdot\boldsymbol{r}_{ij}, \tag{1}$$

where $\boldsymbol{v}_{ij}=\boldsymbol{v}_i-\boldsymbol{v}_j$, $\boldsymbol{r}_{ij}=\boldsymbol{r}_i-\boldsymbol{r}_j$, and $\sigma_{ij}=(\sigma_i+\sigma_j)/2$. In the case in which the diameters are identical, $\sigma_i=\sigma$ for all i. Heavy particles scarcely moved, while light ones moved well. After about 500 000 total collisions in the melt blocks,

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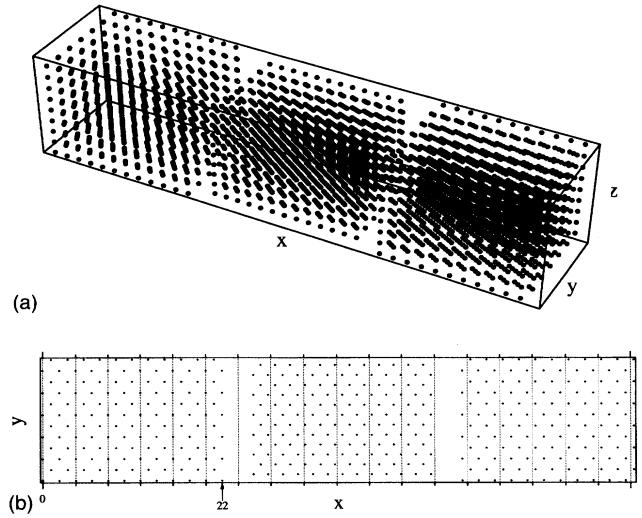

FIG. 1. Presentation for the crystal and melt blocks. (a) A 3D picture of the fcc (110) interface. (b) The projection onto the xy plane. Due to the periodic boundary condition, both ends of the side of the frame are identical. Thus the numeral "0" on the bottom of Fig. 1(b) corresponds to the central layer of the crystal block. In the crystal block, there is a fcc crystal with a volume fraction of 0.545, while in the remainder, the total volume fraction is 0.494. The numeral "22" on the bottom indicates that the right end layer of the crystal block is the 22nd layer from the 0th layer.

the particles there became disordered as shown in Fig. 2(a). Then we set the masses of all particles identical and began the MD simulations again until the systems were regarded as in equilibrium. We saw, for respective orientations, no significant difference in the density profiles at around the 1 000 000th and 2 000 000th collisions. Figure 2(b) shows the trajectories of an identical-particle system after the

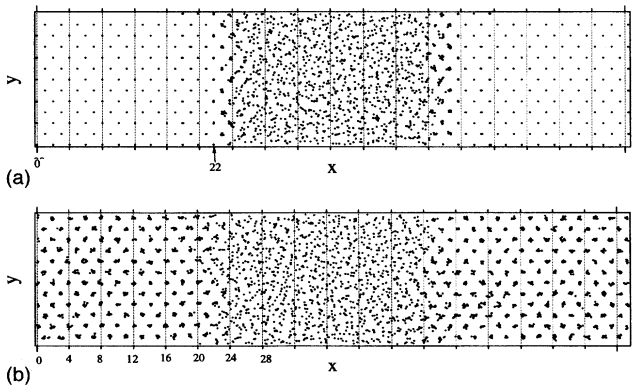

FIG. 2. (a) A snapshot after 500 000 total collisions in the melt block for the fcc (110) interface. The melt block has been melted. On the bottom the initial positions of the right end and the central layers of the crystal block are indicated. (b) Trajectories of the identical-particle system for the fcc (110) interface during 70 collisions per particle at the equilibrium state. The particles in the upper two layers are picked up for drawing. The numerals on the bottom of the picture are the labels of the layers assigned sequentially from the center to the right.

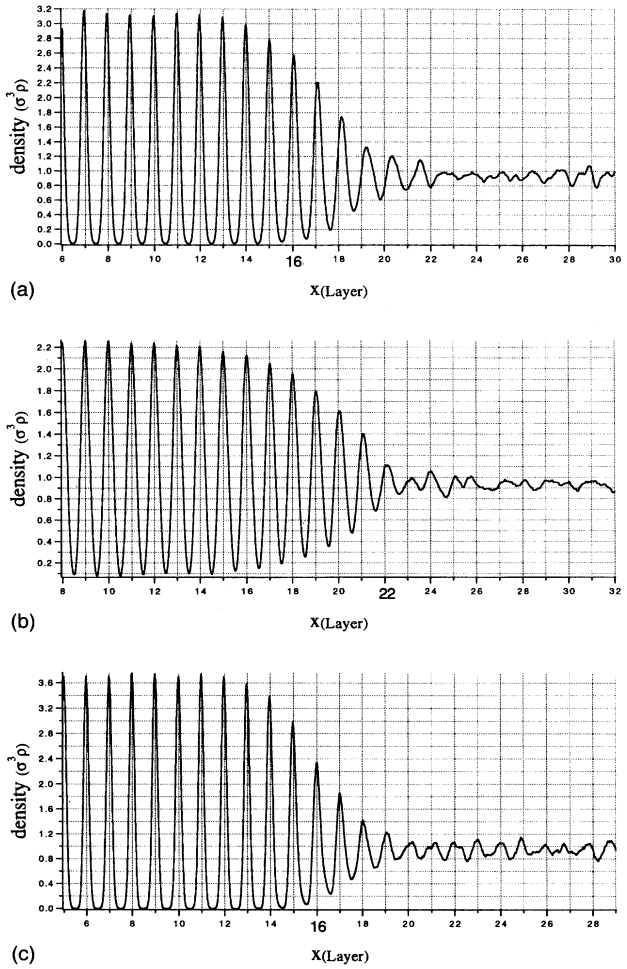

FIG. 3. The density profiles for the fcc (100), (110), and (111) interfaces. (a), (b), and (c) show the interfaces with (100), (110), and (111) orientations, respectively. The labels of the layers are shown on the bottom in the same manner as in Fig. 2(b) and the initial positions of the right end layers of the crystal blocks are emphasized, respectively. We see that the interfacial regions in which the density profiles differ from those in the crystal and the melt phases are extended in eight or nine layers in all the orientations. It is clearly seen in (a) and (c) that the order is created within the regions which have been disordered.

2 000 000 collisions in total. The density profiles at the equilibrium state are shown in Fig. 3. In spite of the absence of the attractive force, apparent layered structures are observed in the interfaces. In Fig. 3(a) and 3(c), we see that the layered structures were created within the regions which had been disordered. Figure 3 shows that the interfacial regions with density profiles different from those in the crystal and the melt phases are extended over eight or nine layers in each orientation. Analysis of the intralayer orderings, calculation of the radial distribution functions and the diffusion coefficients, and so on are in progress.

In the conventional lattice models of the crystal-melt interface [6,13] we neglect the density change due to melting or crystallization because the volume change there is only about 10%. The present success for the hard-sphere crystal-

melt interface in equilibrium shows the necessity of the theory in which the contribution of density difference is incorporated. In the usual expression of the chemical potential difference,

$$\Delta\mu = \Delta\epsilon - T\Delta s + p\Delta v, \tag{2}$$

it is not obvious, in general, whether the term $p\Delta v$ is negligible or not in comparison with the first two terms. In the hard-core case, $\Delta\epsilon = 0$ is exactly satisfied. Accordingly, incorporation of the terms $T\Delta s$ and $p\Delta v$ is essential in the case such as the hard-core system.

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