The phase diagram of the step-function system by molecular simulations

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The pressure–volume–temperature (*pVT*) relations for intermolecular interactions described by a repulsive step-function are obtained by molecular dynamics (MD) and Monte Carlo (MC) simulations. The system is modeled as a cubic unit cell with periodic boundary condition, where the unit cell contains 108 molecules. The pressure is obtained by the virial equation, and the phase diagram is estimated by Maxwell construction. The self-diffusion coefficients are calculated by MD simulation and used to assign phases as solid or fluid. High- and low-density solid and fluid phases are identified at low temperatures, and negative expansion is observed in the fluid phase near the low-density solid.

Keywords: Step function; Phase diagram; Negative expansion; Monte Carlo simulation; Molecular dynamics simulation

1. Introduction

Interactions between spherical molecules have been described by various systems, including hard sphere, square-well and step-function systems [1], which are expressed respectively by:

$$u(r) = \infty \quad (r \leq \sigma),$$
$$u(r) = 0 \quad (r > \sigma),$$
(1)

$$u(r) = \infty \quad (r \leq \sigma),$$
$$u(r) = -\varepsilon \quad (\sigma < r \leq \lambda\sigma),$$
$$u(r) = 0 \quad (\lambda\sigma < r),$$
(2)

$$u(r) = \infty \quad (r \leq \sigma),$$
$$u(r) = \varepsilon \quad (\sigma < r \leq \lambda\sigma),$$
$$u(r) = 0 \quad (\lambda\sigma < r).$$
(3)

Figure 1 compares the characteristics of these three systems in terms of intermolecular distance *r*. The constant ($\varepsilon > 0$) has dimensions of energy and is used as the unit of energy in this paper. The unit of length is the constant σ, and the constant λ is fixed at 1.5 in this work. The properties of the molecular system governed by these three potential functions are summarized below.

1.1 Hard sphere system (N = 108)

In the hard sphere system, an order–disorder phase transition occurs with changes in density. This transition can be seen in the pressure–volume–temperature (*pVT*) relation obtained by standard Metropolis Monte Carlo (MC) simulation [1,2] with cubic periodic boundary condition (figure 2). The initial configuration for this system is a face-centered cubic lattice, and each MC step is defined as *N* trials in an *N*-molecule system (*N* = 108). After equilibration (5×10^6 MC steps), and equivalent length of simulation was performed to obtain thermal averages. The pressure at a given temperature and volume is calculated by the virial formula [1] as follows.

$$\frac{pV}{NkT} = 1 + \frac{2}{3}\pi\frac{N}{V}\sigma^3 g(\sigma_+),$$
$$g(\sigma_+) = g(\sigma + \delta), \delta \rightarrow 0, (\delta > 0).$$
(4)

Here, *k* is the Boltzmann constant and *g(r)* is the pair correlation function.

The unit of pressure employed hereafter is ε/σ^3, where the constant ε is an arbitrary energy unit. The phase transition volume is not dependent on temperature in this system, and is determined by free energy calculations [3]. Estimation of the phase transition volume by the conventional Maxwell contraction [4] (table 1) affords

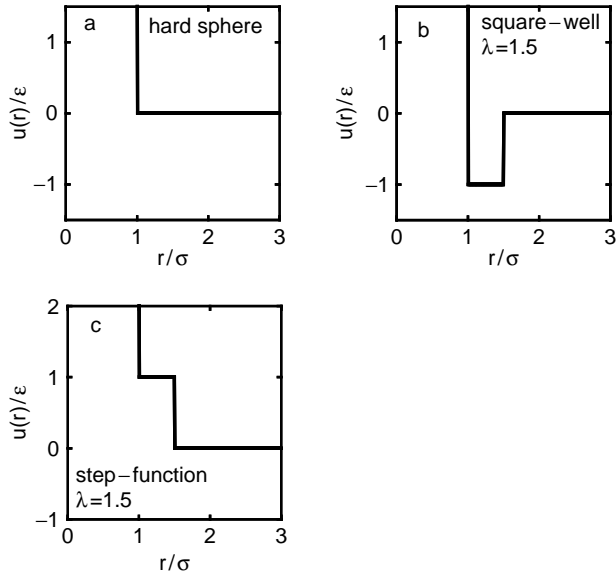*Corresponding author. Email: kataoka@k.hosei.ac.jp

Figure 1. Characteristics of (a) hard sphere, (b) square-well, and (c) step-function potential functions $u(r)$ with respect to intermolecular distance r.

Table 1. Phase transition volumes in the hard-sphere system.

Method	V_s/σ^3	V_f/σ^3	References
Free energy calculation	0.961	1.06	[3]
Maxwell construction	0.977	1.07	This work

where t is the total simulation time, N_c is the total number of collisions, m is molecule mass, and c and t_c are the number and time of each collision. The change in velocity at t_c is given by $\Delta v_{ij}(t_c)$ for the $i - j$ pair. The molecular distance between i and j in the collision is given by $r_{ij}(t_c)$.

The unit time τ for this simulation is given by:

$$\tau = \sigma\sqrt{\frac{m}{\varepsilon}}. \qquad (6)$$

The self-diffusion coefficient D is obtained from the plot of mean square displacement with respect to time, and is plotted in figure 4 against the volume per particle. Small values in figure 4 correspond to the high-density region (solid state). The transition volume obtained from this figure is comparable to that obtained from figure 2.

1.2 Square-well potential system (N = 108)

The pVT relation for the square-well system (figures 5 and 6), obtained by MC simulation with the conventional minimum image method, is very similar to that for the Lennard-Jones system [1] due to the attractive term in the potential function. The simulations conditions are the same as those adopted for MC simulations of the hard sphere system above. The pressure is obtained by the

results similar to those obtained by free energy calculations.

Figure 3 shows the pair correlation function $g(r)$. According to this function, the dense state $V/N = 0.90\sigma^3$ corresponds to the solid state, and the low-density state $V/N = 1.20\sigma^3$ denotes the fluid state.

Molecular dynamics (MD) simulations under the same conditions employed for MC simulations reveal the dynamic properties of the system. The pressure in the system is calculated by [5]

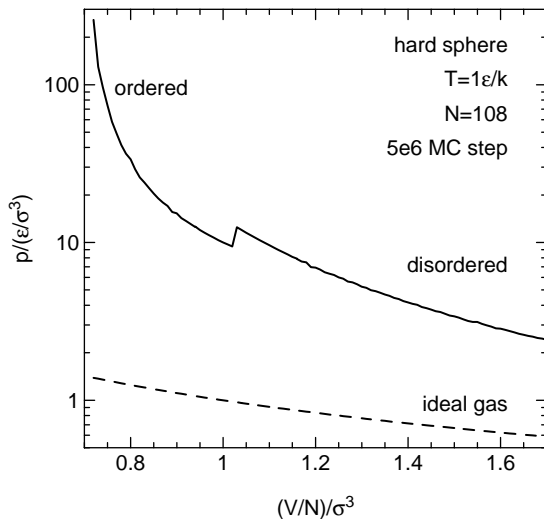$$\frac{pV}{NkT} = 1 + \frac{1}{3NkT}\frac{1}{t}\sum_{c=1}^{N_c} m\Delta v_{ij}(t_c)\cdot r_{ij}(t_c), \qquad (5)$$

Figure 2. Isotherm of pressure p with respect to volume per particle V/N for the hard-sphere system. Isotherm for ideal gas is shown for comparison.
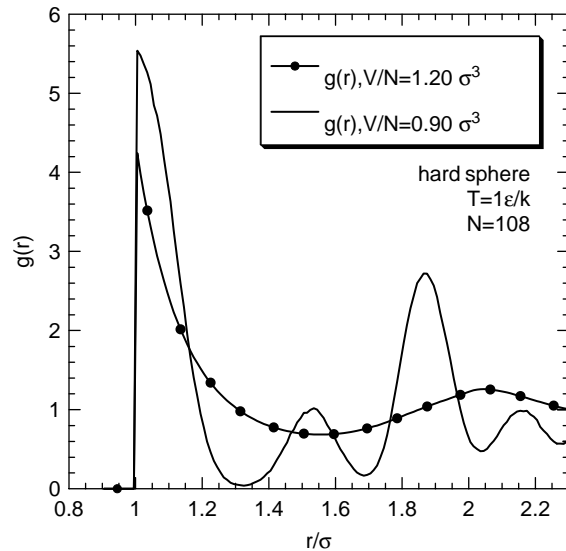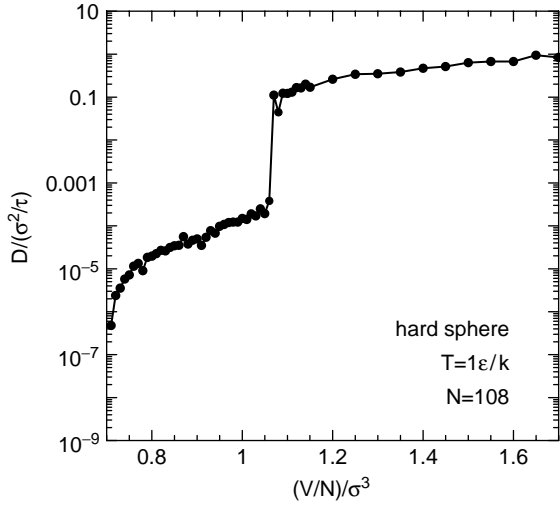

Figure 3. Pair correlation function $g(r)$ for the hard-sphere system.

Figure 4. Isotherm of self-diffusion coefficient *D* with respect to volume per particle *V/N* for the hard sphere system.

Figure 6. Low-pressure region of *pVT* relation for the square-well system.

following virial equation [6]:

$$\frac{pV}{NkT} = 1 + \frac{2}{3}\pi\frac{N}{V}\sigma^3$$
$$\times \left[g(\sigma_+) - g(\lambda\sigma_-)\big(1 - \exp\big(\beta u(\lambda\sigma_-)\big)\big)\lambda^3\right],$$
$$g(\sigma_+) = g(\sigma + \delta), \delta \to 0, (\delta > 0),$$
$$g(\lambda\sigma_-) = g(\lambda\sigma - \delta), \delta \to 0, (\delta > 0), \qquad (7)$$

where $\beta = 1/kT$.

The liquid–solid transition occurs near $V/N = 1\sigma^3$ at high pressure (figure 5), and the liquid–vapor transition is expected to occur at $T = 1\varepsilon/k$. The variation in average potential energy in the square-well system (figure 7) shows that the most stable state is realized at the highest densities, and that the two-phase region at $T = 1\varepsilon/k$ occurs near $V/N = 10\sigma^3$. From pair correlation function at
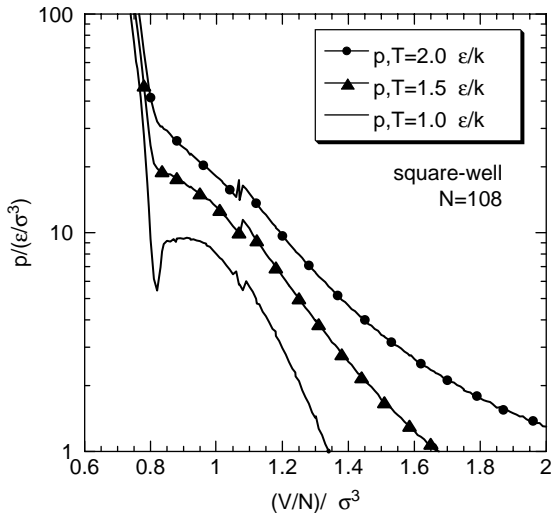
$T = 1\varepsilon/k$ (figure 8), the molecular system has a solid structure at $V/N = 0.80\sigma^3$, and a liquid structure at $V/N = 1.20\sigma^3$.

The variation in the self-diffusion coefficient of the square-well system with volume at $T = 1.4\varepsilon/k$ is shown in figure 9. A jump in *D* occurs near $V/N = 1\sigma^3$, separating the solid state (smaller *D*) from the liquid state (larger *D*). The *pVT* relation shows that this temperature is close to the critical temperature.

1.3 Step-function system (N = 2) in a spherical cell

In the step-function system, two types of solid structure are possible at low temperatures according whether the wall is defined as infinite or finite [7]. The high-density structure appears under high pressure, and the low-density solid is stable at low pressure. Negative thermal expansion
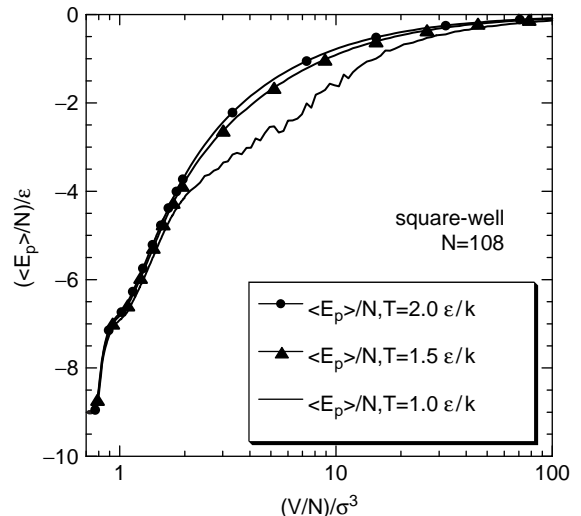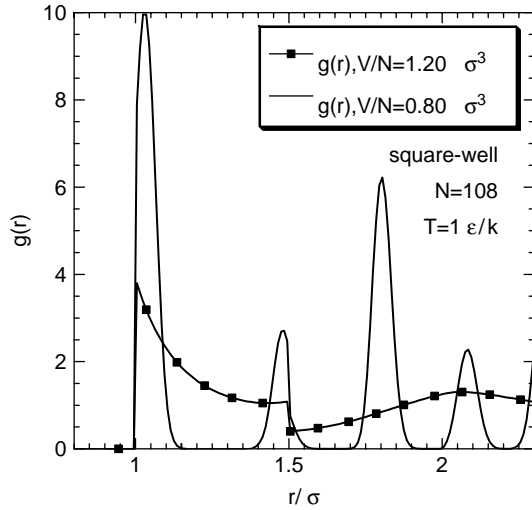

Figure 5. High-pressure region of *pVT* relation for the square-well system.

Figure 7. Change in average potential energy per particle $\langle E_p/N\rangle$ with respect to volume per particle *V/N* for the square-well system.

Figure 8. Pair correlation function $g(r)$ for the square-well system.

has also been reported for low-dimensional step-function systems [8]. A similar model has been used to study negative expansion in two dimensions [9].
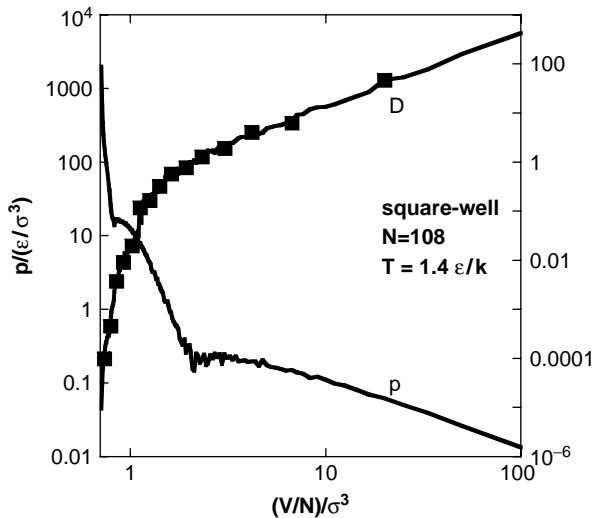
The thermodynamic properties are obtained by a canonical partition function Q for the two-molecule system in a spherical cell [10], given as the product of an ideal gas part Q_{id} and an interaction part Q_e [11]:

$$Q = Q_{id}Q_e,$$
$$Q_e = \frac{1}{V^2}\int_V\int_V \exp(-\beta u(r_{12}))d^3r_1 d^3r_2.$$

(8)

The following constants are employed in the equations below:

$$V_c = V = \frac{4\pi}{3}r_c^3, \quad V_1 = \frac{\pi}{6}\sigma^3, \quad V_2 = \frac{\pi}{6}(\lambda\sigma)^3. \quad (9)$$

Integration gives the partition function Q_e as [10]

$$Q_e = 0, \quad V \le V_1$$
$$Q_e = e^{-\beta\varepsilon}\left(1 - \frac{\sigma^3}{r_c^3} + \frac{9\sigma^4}{16r_c^4} - \frac{\sigma^6}{32r_c^6}\right), \quad V_1 < V \le V_2$$
$$Q_e = 1 - \frac{e^{-\beta\varepsilon}\sigma^3}{r_c^3} - \frac{\lambda^3\sigma^3}{r_c^3} + \frac{e^{-\beta\varepsilon}\lambda^3\sigma^3}{r_c^3}$$
$$+ \frac{9e^{-\beta\varepsilon}\sigma^4}{16r_c^4} + \frac{9\lambda^4\sigma^4}{16r_c^4} - \frac{9e^{-\beta\varepsilon}\lambda^4\sigma^4}{16r_c^4}$$
$$- \frac{e^{-\beta\varepsilon}\sigma^6}{32r_c^6} - \frac{\lambda^6\sigma^6}{32r_c^6} + \frac{e^{-\beta\varepsilon}\lambda^6\sigma^6}{32r_c^6}$$

(10)

where $V_2 < V$.

The Helmholtz free energy is written as

$$A = -kT\ln(Q) = A_{id} + A_e$$
$$= -kT\ln(Q_{id}) - kT\ln(Q_e). \quad (11)$$

The ideal gas term is defined as

$$A_{id} = -kT\ln(Q_{id}), \quad Q_{id} = \left(V_r T_r^{3/2}\right)^2,$$
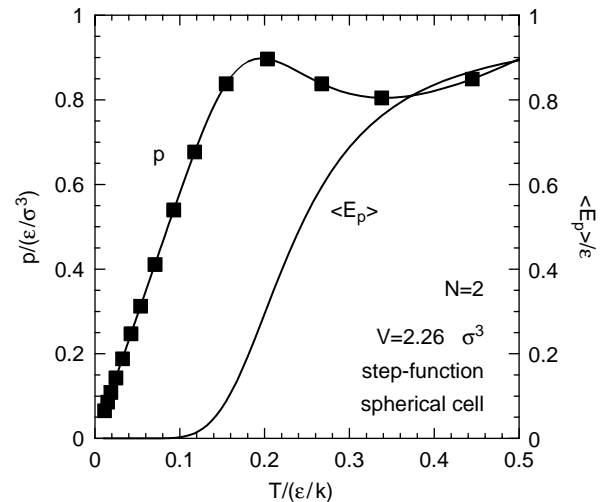$$T_r = \frac{kT}{\varepsilon}, \quad V_r = \frac{V}{\sigma^3}. \quad (12)$$

The pressure is given by

$$P = \frac{2kT}{V} + p_e. \quad p_e = kT\left(\frac{\partial\ln Q_e}{\partial V}\right)_T. \quad (13)$$

Other thermodynamic properties are calculated by standard approaches [4].

Some interesting properties of the step-function system are shown in figure 10, in which the pressure and average potential energy are plotted as functions of temperature at $V = 2.26\sigma^3$. The pressure exhibits a maximum and

Figure 9. Isotherm of self-diffusion coefficient D and pressure p with respect to volume per particle V/N for the square-well system.

Figure 10. Variation in theoretical pressure p and average potential energy $\langle E_p\rangle$ with respect to temperature T for the step-function system (spherical cell, $N = 2$).

minimum, which can be understood as follows. The energy changes from 0 to approximately 0.7ε near $T = 0.3\varepsilon/k$, allowing molecules at higher temperature to stay in the region $\sigma < r < 2r_c$, where r is the molecular distance in the cell and r_c is the radius of the cell (see equation (9)). At low temperature, on the other hand, the molecule is confined to the state $\lambda\sigma < r < 2r_c$. As a result of the effective volume, the pressure decreases near $T = 0.3\varepsilon/k$. The sign of the differential coefficient $(\partial V/\partial T)_V$ is closely connected to that of the expansion coefficient α:

$$\alpha = -\frac{1}{V}\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial p}\right)_T = \kappa_T \left(\frac{\partial p}{\partial T}\right)_V. \qquad (14)$$

The expansion coefficient and isothermal compressibility κ_T are plotted against temperature in figure 11 for a constant volume of $V = 2.26\sigma^3$.

1.4 Step-function system (N = 2) in a periodic cubic cell

The spherical cell above deals with two molecules. To extend the result to an infinite system, a cubic periodic boundary condition is introduced. When the unit cell includes two molecules and the potential is described by a step function, the canonical partition function [12] is obtained by the minimum image convention [1,2].

The temperature dependence of pressure and average potential energy are shown in figure 12 ($V = 6.6\sigma^3$). The $p - T$ curve has negative slope in this case. The corresponding isothermal compressibility and expansion coefficient are shown in figure 13. The expansion coefficient becomes negative near $T = 0.2\varepsilon/k$.

The volume of $6.6\sigma^3$ is much larger than that ($V = 2.26\sigma^3$) examined in the case of a spherical cell.
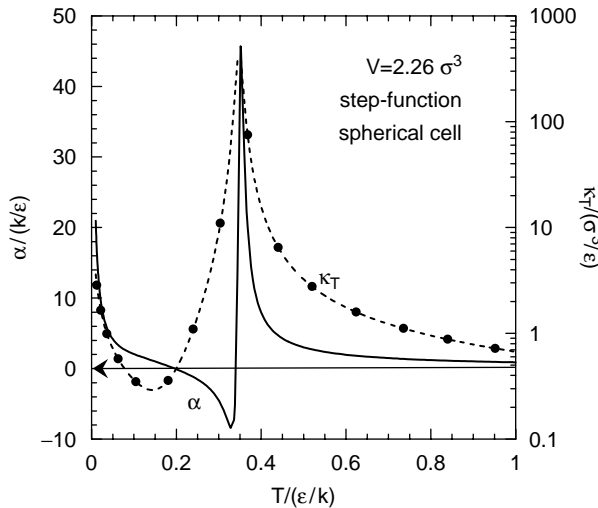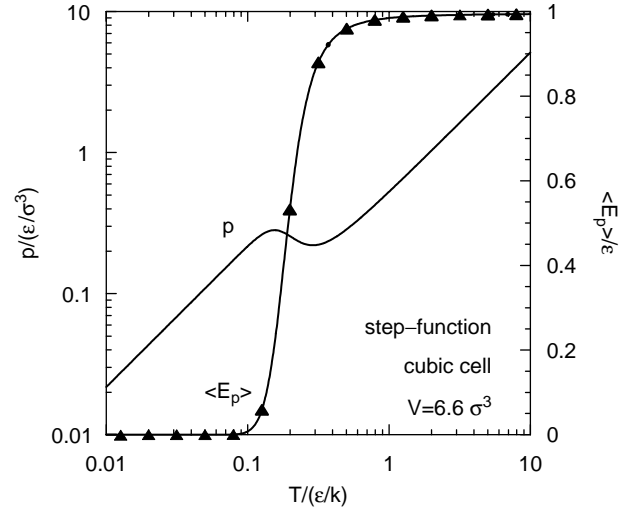

Figure 12. Variation in theoretical pressure p and average potential energy $\langle E_p \rangle$ with respect to temperature T for the step-function system (cubic boundary condition with minimum image convention, $N = 2$).

In a periodic system, the center of mass of a molecule is restricted to within the basic cell, while molecules interact with other molecules in the basic cell and in the imaginary cells given by the minimum image convention. In the case of the spherical cell, the center of mass of the molecule is restricted within the spherical cell, but there are no molecules in other cells with which to interact.

Both solid and fluid phases occur in the hard sphere system (figure 2) at any temperature, while solid, liquid and vapor phases are possible in the square-well system at low temperature (figure 6), and two types of solid phase are possible in the step-function system at low temperature
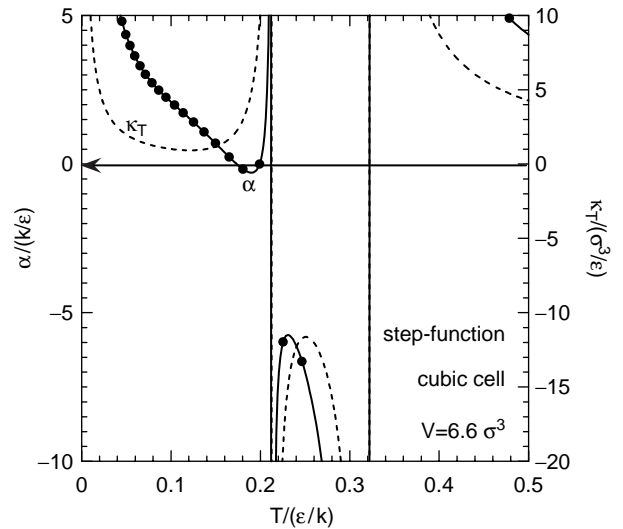

Figure 11. Variation in thermal expansion coefficient α with respect to temperature T for the step-function system (spherical cell, $N = 2$). Isothermal compressibility κ_T is shown for comparison.

Figure 13. Variation in expansion coefficient α and isothermal compressibility κ_T with respect to temperature T for the step-function system (cubic boundary condition with minimum image convention, $N = 2$).

(figure 1). A fluid phase is also expected in the three-dimensional periodic system.

These results show that the pressure in the hard-sphere system is a linear function of temperature (see equation (5)), whereas the pressure in the step-function system exhibits a maximum and minimum in a given volume (figures 10 and 12, $N = 2$).

2. Model and simulation method

The behavior of molecular interactions in a step-function system were examined using the above cubic unit cell model with periodic boundary condition and minimum image convention. The pair potential energy $u(r)$ is given as a function of the intermolecular distance r by equation (3). MC simulations were performed for $N = 108$ by the Metropolis method [1,2] with initial distorted fcc lattice configuration. The pressure is given by the virial equation (equation (7)), and the simulation was performed for 1×10^8 MC steps, where each step consists of N trials. MD simulations were performed under the assumption of binary collision [5] for numerical integration of the equation of motion. The MD simulations occasionally stopped prematurely due to simultaneous collision of more than two molecules. In such cases, the error state was skipped and the subsequent state was executed with larger volume or higher temperature. Pressure was calculated by equation (5). Simulations were conducted for a total of 1×10^5 collisions for equilibration, followed by an equivalent number of collisions for thermal averaging. The self-diffusion coefficient was obtained by the plot of mean square displacement with respect to time.

To obtain the *pVT* relation for the step-function system over a wide range of (*T,V*) space, the volume dependence of the pressure was studied at many constant temperatures
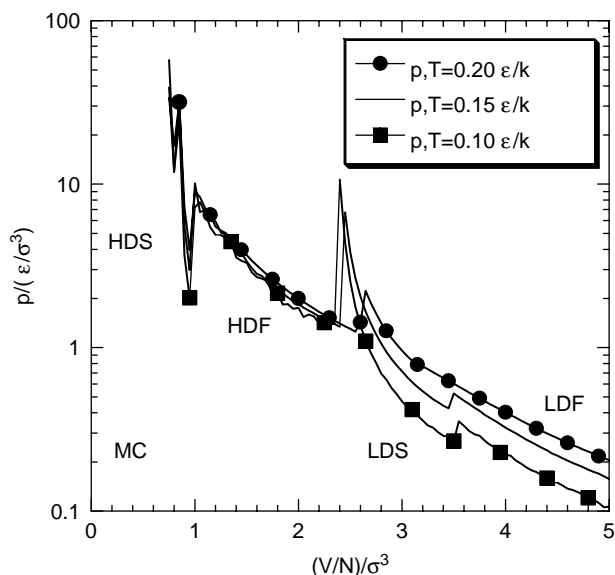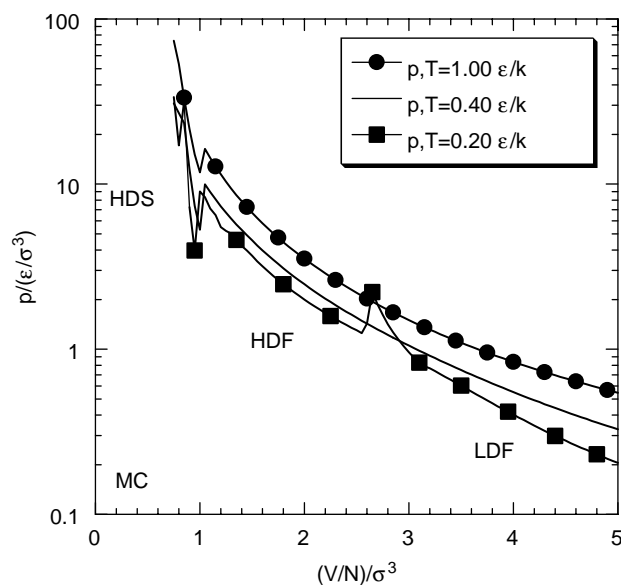

Figure 15. *pVT* relation for the step-function system at high temperature (MC simulation).

by MC simulation. The averaged pressure in MC simulations was found to be scattered at low temperature ($T < 0.1\varepsilon/k$), presumably due to the effect of the discrete potential function (figure 1). The pressure in the MD simulations, on the other hand, was stable even at low temperature ($T < 0.1\varepsilon/k$). The *pVT* relation calculated by MD simulation is therefore used for the low-temperature region.

3. Simulation results

The *pVT* relations obtained by MC simulations are shown in figures 14 and 15. In the low-temperature cases (figure 14,

Figure 14. *pVT* relation for the step-function system at low temperature (MC simulation).
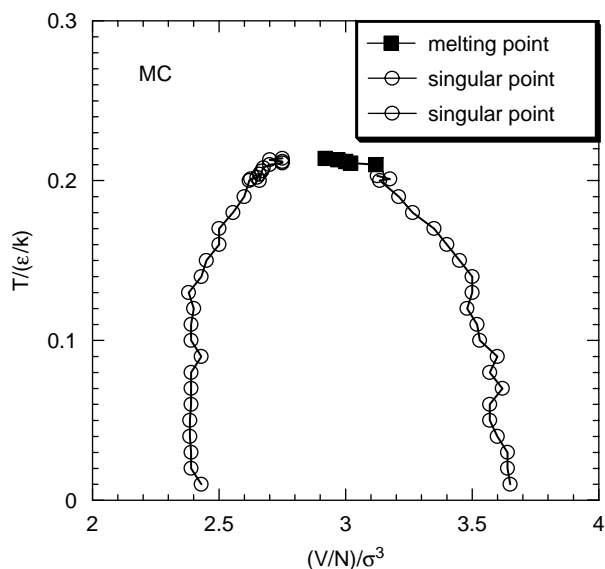

Figure 16. *V − T* phase diagram showing singular and melting points obtained from the *pVT* relation for the step-function system (MC simulation).
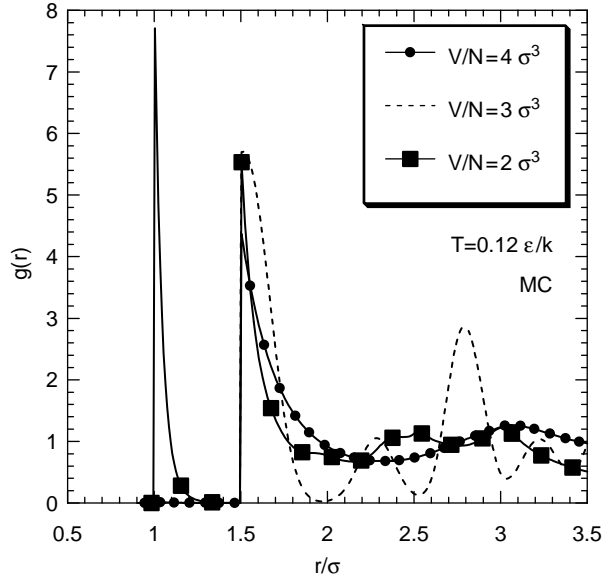
Figure 17. Pair correlation function $g(r)$ for the step-function system (MC simulation).

Figure 19. Variation in self-diffusion coefficient D with volume per particle V/N for the step-function system (MD simulation).

$T = 0.10 - 0.15\varepsilon/k$), three singular points can be seen in the $p - V$ plot near $V/N \approx 1.0$, 2.5 and $3.5\sigma^3$. Singular points in the highest-density region ($V/N < 1\sigma^3$), corresponding to phase transitions in the solid state, are not considered in this work. At $T = 0.20\varepsilon/k$, two singular points occur in the pVT relation, corresponding to the states with volumes $V/N \approx 1.0$ and $2.5\sigma^3$. Only one singular point occurs at higher temperatures ($T = 0.40$ and $1.00\varepsilon/k$), corresponding to $V/N \approx 1.0\sigma^3$. The states outside or between the singular points are tentatively assigned as low-density fluid (LDF), low-density solid (LDS), high-density fluid (HDF) or high-density solid (HDS) states. These states
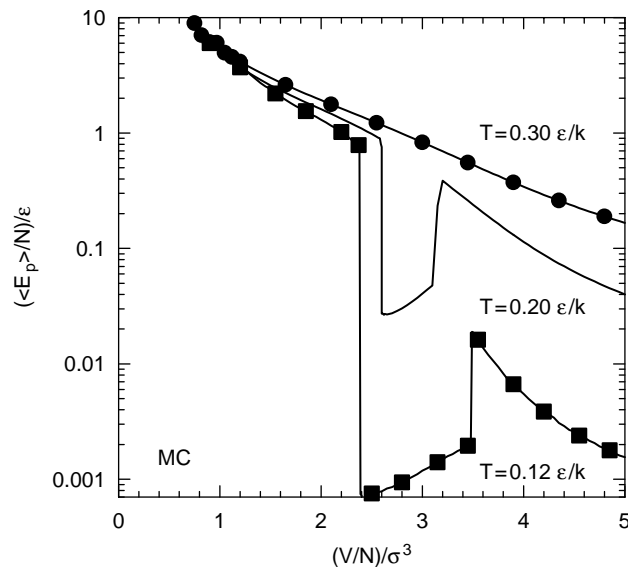
are confirmed below by the pair correlation function, the average potential energy, and the self-diffusion coefficient.

The singular points ($V/N > 2.0\sigma^3$) are plotted in figure 16. The corresponding pair correlation functions are shown in figure 17. The state at $V/N = 3\sigma^3$ is solid, whereas the states at $V/N = 2$ and $4\sigma^3$ are fluid. This assignment is confirmed by the average potential energy per particle $\langle E_p/N \rangle$ plot in figure 18. The $T = 0.12\varepsilon/k$ state in the figure is the well-defined solid state with a volume near $V/N = 3\sigma^3$, while the $T = 0.20\varepsilon/k$ state is near the melting point, as determined below.

The variation in the self-diffusion coefficient with volume and temperature is shown in figure 19. Jumps in D

Figure 18. Variation in average potential energy per particle $\langle E_p/N \rangle$ with volume per particle (V/N) for the step-function system (MC simulation).
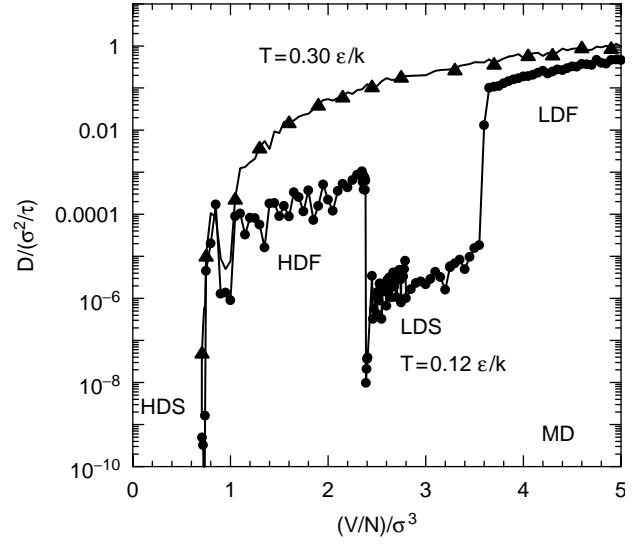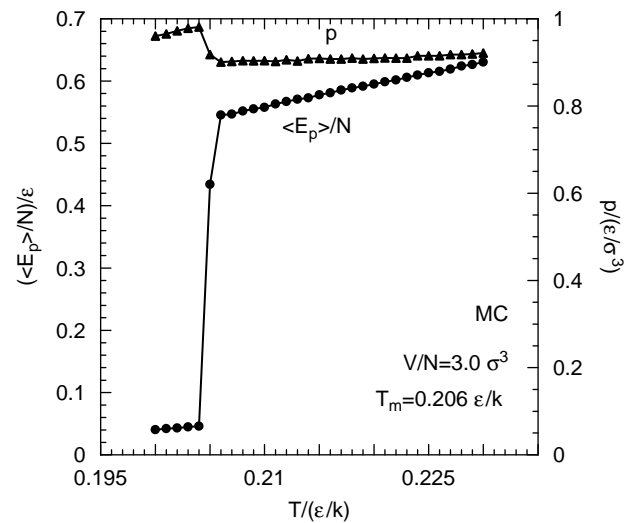

Figure 20. Plot of pressure p and average potential energy per particle $\langle E_p/N \rangle$ with respect to temperature T to illustrate melting of a low-density solid in the step-function system (MC simulation).
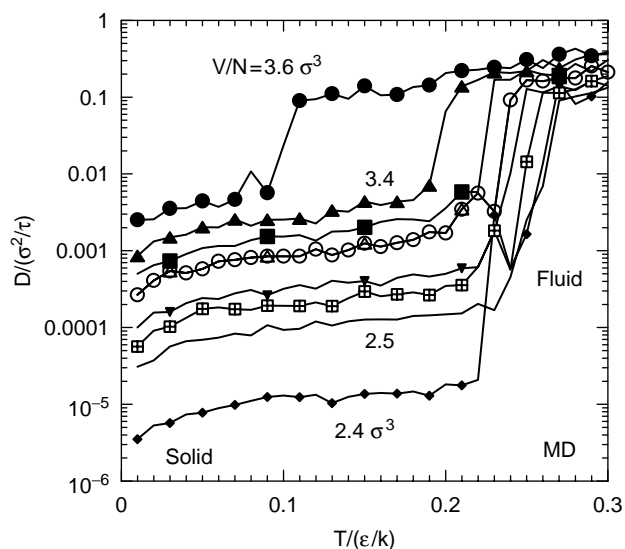
Figure 21. Variation in self-diffusion coefficient D with temperature T and volume per particles V/N for the step-function system (MD simulation).

Figure 23. Example of Maxwell construction.

occur near the volumes corresponding to the change of states. The change in D in figure 19 is many orders of magnitude in size.

The melting of the LDS state can be seen in the plot of pressure and average potential energy per particle with respect to temperature in figure 20. This figure is similar to figures 10 and 12 ($N = 2$). The melting points determined in this way are denoted by solid squares in figure 16. Figure 21 shows the melting behavior described by the self-diffusion coefficient determined by MD simulation. The obtained melting points are plotted in figure 22 for comparison with the values determined by MC simulation.
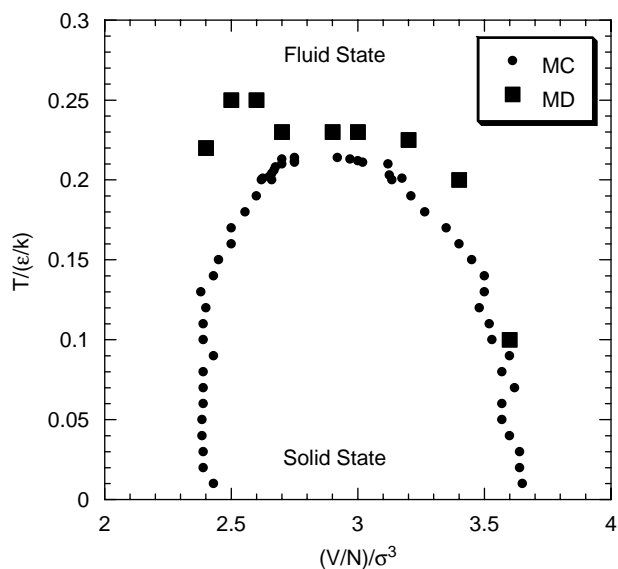
The figure reveals that there is some hysteresis in the melting behavior, and that the melting points determined by MD simulation are higher than those obtained by MC simulations.

4. Phase diagram

A Maxwell construction is used to estimate the phase boundary from the pVT relation. An example is shown in figure 23. The estimated phase diagram in (V, T) space is shown in figure 24. The two critical points thus determined are as follows:

Figure 22. Comparison of melting points determined from MD self-diffusion coefficients with those obtained from the singular points in the MC pVT relation for the step-function system.
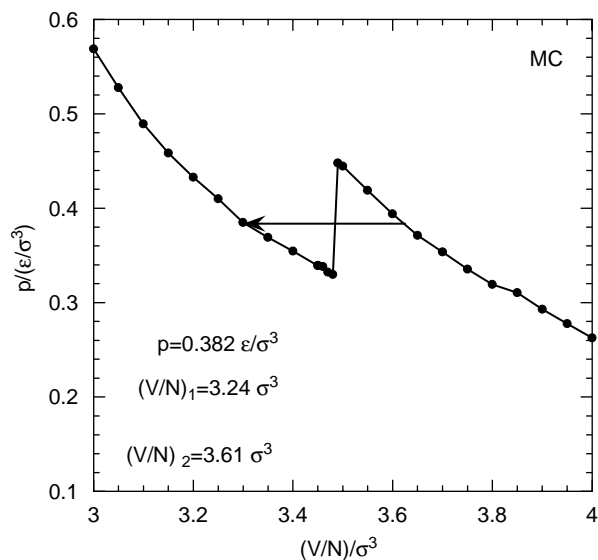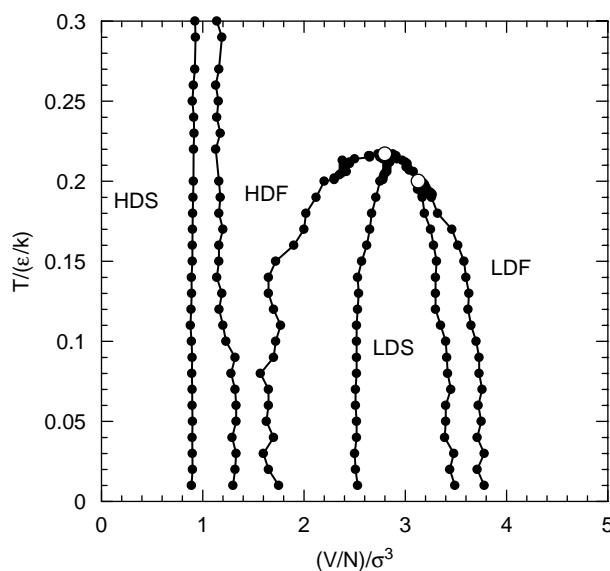

Figure 24. Estimated $V - T$ phase diagram for the step-function system. Critical points are denoted by open circles, and states are denoted by respective labels. Regions without state assignments are two-phase states.
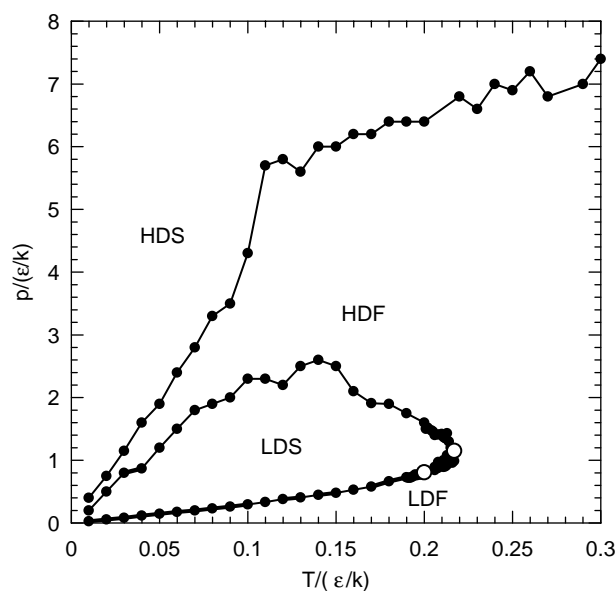
Figure 25. Estimated $T - p$ phase diagram for the step-function system. Critical points are denoted by open circles.
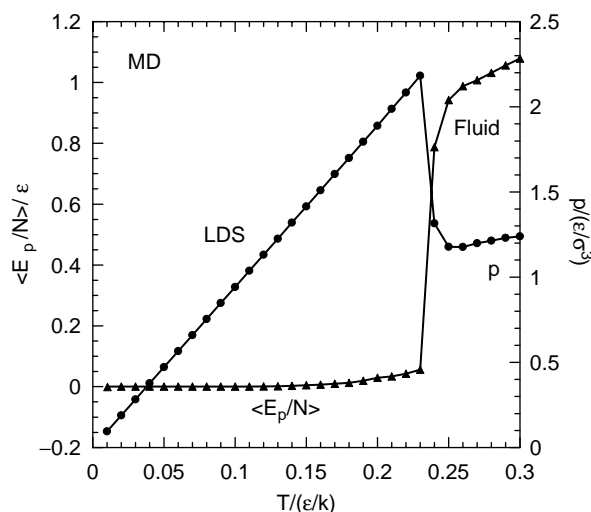

Figure 26. Example of $T - p$ curve ($V/N = 2.70\sigma^3$) for the step-function system (MD simulation). Average potential energy per particle $\langle E_p/N \rangle$ is shown for comparison.

(1) $T_c = 0.217\varepsilon/k$, $V_c/N = 2.80\sigma^3$, $p_c = 1.15\varepsilon/\sigma^3$

(2) $T_c = 0.200\varepsilon/k$, $V_c/N = 3.13\sigma^3$, $p_c = 0.81\varepsilon/\sigma^3$

The phase diagram in the (T, p) domain is shown in figure 25. This high-temperature region of this phase diagram resembles the $T > 0.1\varepsilon/k$ region for the two-dimensional step-function system reported by Young and Alder [7]. It is characteristic that there is no phase boundary between the LDS and HDS states in the (T,p) diagram (figure 25).

5. Negative expansion

Negative expansion is expected to occur in the fluid phase for such a phase boundary with negative slope ($\mathrm{d}p/\mathrm{d}T < 0$). An example is shown in figure 26 ($V/N = 2.70\sigma^3$). The temperature dependences of pressure and average potential energy are similar to those seen in figures 10 and 12 ($N = 2$). The physical reason for the occurrence of negative expansion in the step-function system is the same for the $N = 2$ system, and is consistent with previous work in lower-dimensional step-function systems [8,9].

Acknowledgements

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