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Liquid-solid phase transition of a system with two particles in a rectangular box

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We study the statistical properties of two hard spheres in a two-dimensional rectangular box. In this system, a relation similar to the van der Waals equation is obtained between the width of the box and the pressure working on the sidewalls. The autocorrelation function of each particle's position is calculated numerically. This calculation shows that, near the critical width, the time at which the correlation becomes zero gets longer as the height of the box increases. Moreover, fast and slow relaxation processes such as the α and β relaxations in supercooled liquids are observed when the height of the box is sufficiently large. These relaxation processes are discussed with reference to the probability distribution of the relative positions of the two particles.

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The liquid-solid phase transition is a very familiar phenomenon. This transition in a system with so many degrees of freedom has been studied through many kinds of analytical and numerical models [1]. Numerically, the liquid-solid phase transition is studied in a system containing 10–10^4 hard or soft core particles by Monte Carlo and molecular dynamics simulations [2–6]. The motions of individual particles (molecules) are different in the liquid phase and the solid phase: In the liquid phase, particles can exchange positions with each other, and each particle can move all around the system. On the other hand, in the solid phase, particles cannot exchange positions, and they move only in restricted small areas.

Now we consider a rectangular box containing two hard spheres with the same diameter d. The height of the box is larger than $2d$. When the width of the box is larger than $2d$, these spheres can exchange positions [Fig. 1(a)]. However, these particles cannot exchange their positions when the width of the box is smaller than $2d$ [Fig. 1(b)]. Thus we regard these as the simplest forms of, respectively, the liquid state and the solid state. Then, a problem arises: In such a simple system near the critical width $(=2d)$ of the box, can we find characteristic phenomena like the Alder transition [3,4,6] of a system with many hard spheres? In this paper, we focus on statistical and dynamical properties of the spheres near the critical width of the box to understand this problem.

The system under consideration consists of two-dimensional hard sphere particles with unit mass and unit radius which are confined in a two-dimensional rectangular box. Here, the width and the height of the box are, respectively, a and b, and all the walls are rigid (Fig. 1). Interactions between two particles or between a particle and a wall occur only through hard core collisions. These collisions are implemented in the following manner: the tangential velocities to the collision plane are preserved, while the normal component of the relative velocity Δv_n changes to $-\Delta v_n$. The total energy of the system is given as 1. Because this system consists of rigid spheres and rigid walls, the qualitative behaviors are independent of the total energy. We set $b>4$ for most of our discussion which means these two particles can exchange their positions in the horizontal direction. Note that in this paper the state with $a>4$ is regarded as the liquid state and the state with $a<4$ is regarded as the solid state.

Figures 2(a) and 2(b) are typical relationships between the width a and the pressure P_a on the sidewalls for heights $b=4.3$–6.7. Here, P_a is defined as the time average of the impulses caused by the bouncing of particles on the sidewalls per unit length per unit time. In these figures, a region of a in which the volume compressibility is negative appears for small b around the critical width $a^*=4.0$. These curves are similar to the van der Waals loop [1] or the loop of the Alder transition [3,4,6] which includes the liquid-solid coexistence region. This negative volume compressibility seems to indicate the appearance of a phase transition around the critical width $a^*=4.0$ that distinguishes the solid state from the liquid state. If b becomes larger than a critical value $b^* \sim 6.0$, however, this curvature is reduced, and the compressibility becomes positive for all a. In this case, we cannot observe the distinction between the liquid and solid states. Figures 2(c) and 2(d) are the typical relationships between the width a and the pressure on the upper and lower walls P_b for heights $b=4.3$–6.7. Here, P_b is defined as the time average of the impulses caused by the bouncing of particles on the upper and lower walls per unit length per unit time. Unlike the relation of P_a and a, P_b decrease monotonically with increase of a. Such anisotropy seems to be one of the char-

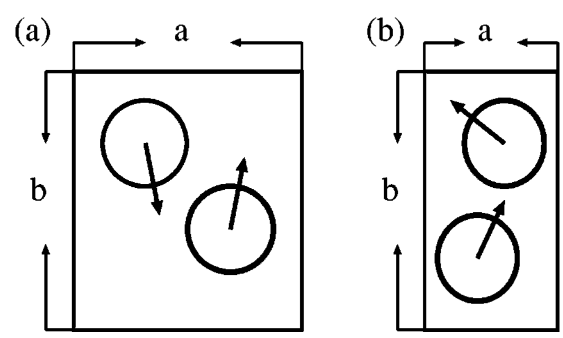

FIG. 1. Illustration of two-particle system in rectangular box. (a) Width of box is larger than the sum of two diameters (liquid state), and (b) width of box is smaller than the sum of two diameters (solid state).

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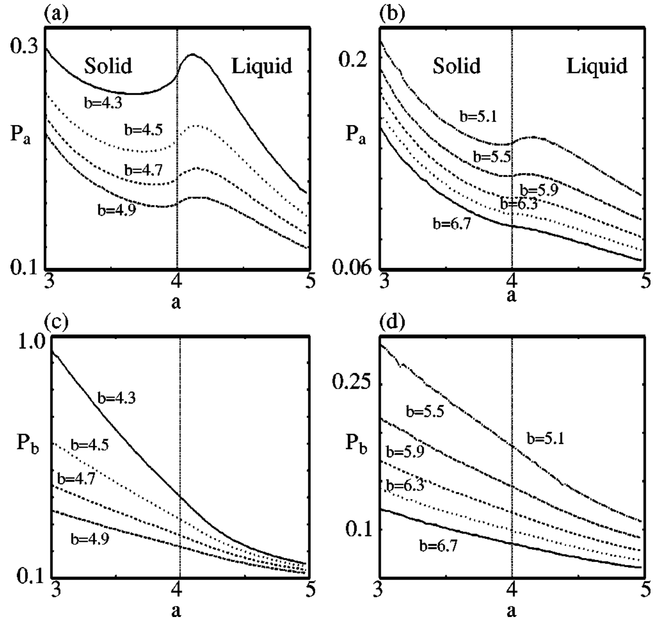

FIG. 2. Relationships between the width a and the pressure P_a with (a) $b=4.3,4.5,4.7,4.9$, (b) $b=5.1,5.5,5.9,6.3,6.7$ in descending order, and that between the width a and the pressure P_b with (c) $b=4.3,4.5,4.7,4.9$, (d) $b=5.1,5.5,5.9,6.3,6.7$.

acteristic features of this system, which does not appear in a system with many hard spheres. If we focus only on the a-P_a relation, however, this system can be regarded as one of the simplest models to imitate the phenomena of the liquid-solid phase transition. Here, a and P_a correspond, respectively, to the volume and pressure of a system with many particles.

Now, we consider the counterpart of b above in a system with many hard spheres or in more general systems with many degrees of freedom. Figure 3(a) shows typical autocorrelation functions for the position of each particle $C(t)$

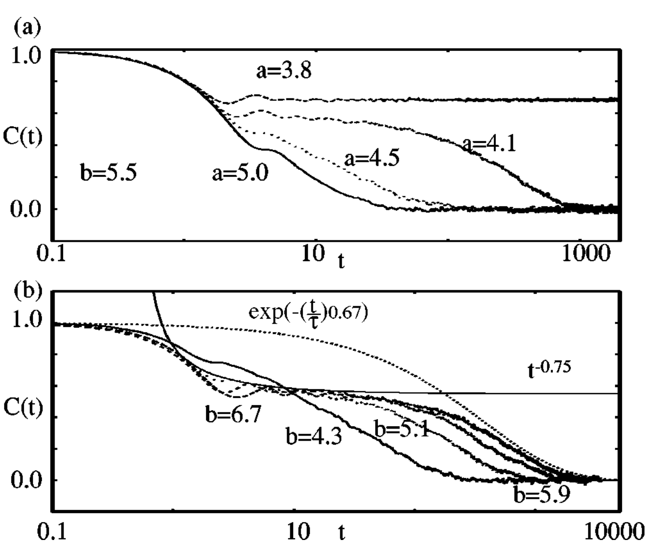

FIG. 3. Autocorrelation function of each particle's position $C(t)$; (a) $a=3.8,4.1,4.5,5.0$ with $b=5.5$, and (b) $b=4.3,5.1,5.9,6.7$ with $a=4.1$. Fitting lines are $C(t)=t^{-0.75}$ and $C(t)=\exp(-(t/\tau)^{0.67})$.

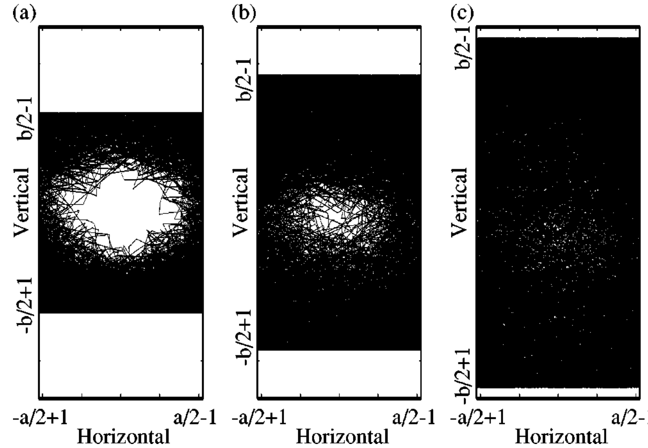

FIG. 4. Typical trajectories of particles (a) $b=4.7$, (b) $b=5.7$, and (c) $b=6.7$ with $a=4.1$.

$=\langle \mathbf{x}(0)\mathbf{x}(t)\rangle / \langle \mathbf{x}(0)\mathbf{x}(0)\rangle$ in the solid state ($a=3.8$) and in liquid states ($a=4.1$, $a=4.5$, and $a=5.0$ with $b=5.5$). Here, $\mathbf{x}(t)$ is the position of a particle. In the liquid state, the relaxation process becomes slower as the width comes closer to the critical value. In the solid state ($a=3.8$), the correlation function has a finite value for $t\to\infty$ because two particles cannot exchange their positions. Figure 3(b) shows autocorrelation functions for $b=4.3,5.1,5.9,6.7$ near the critical width a^* ($a=4.1$). These curves indicate that each relaxation process contains both fast and slow processes for a little above the critical width. These fast and slow relaxations can be fitted with functions, respectively, $t^{-\beta}$ ($\beta\sim 0.75$) and $\exp(-(t/\tau)^{\alpha})$ ($\alpha\sim 0.67$, τ=const.). On increasing b, the form of $C(t)$ changes as follows. (i) The time at which the correlation becomes zero gets longer. (ii) When b is larger than a critical value $b^{**}\sim 5.0$, the fast relaxation and the slow relaxation are clearly separated by the appearance of plateau. These relaxations are similar to the β and α relaxations of the density fluctuations in a supercooled liquid [7]. A system that includes nonuniform molecules tends to become a supercooled liquid when it is cooled or compressed [7]. Moreover, the liquid-solid coexistence region disappears in a system with many hard spheres when the size polydispersity of the spheres is larger than a critical value [6]. From these facts, we conclude that the present two-particle system imitates the phase transition in a system that consists of many nonuniform elements. Here, the quantity b corresponds to the dispersion of particles characters like the size polydispersity in a system with many particles. In order to discuss the mechanism producing the above simulation results, we focus on the statistical properties of each particle's trajectory for each b near the width a^*.

Figures 4(a), 4(b), and 4(c) are typical trajectories of the centers of particles for, respectively, $b=4.7$, $b=5.7$, and $b=6.7$ with $a=4.1$. If the volume of the box is large enough and we can ignore the particle volume, these trajectories fill the rectangular region that is enclosed by the points $([a-d]/2,[b-d]/2)$, $([a-d]/2,-[b-d]/2)$, $(-[a-d]/2,[b-d]/2)$, and $(-[a-d]/2,-[b-d]/2)$ [Fig. 4(c)]. Here, d is the diameter of each particle, which is set as 2 in our discussion. This means particles wander all around the box

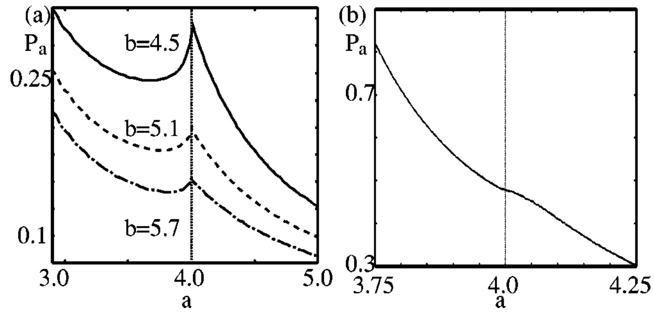

FIG. 5. (a) a-P_a relations of the rectangular Sinai billiard with $b=4.5,5.1$, and 5.7, and (b) a-P_a relation of two particles in a square box.

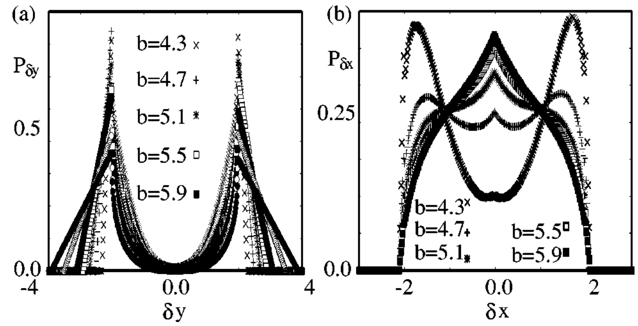

FIG. 6. Probability distributions (a) $P_{\delta y}$ of vertical component of relative position vector δy, and (b) $P_{\delta x}$ of horizontal component of relative position vector δx between two particles with $a=4.1$. $b=4.3,4.7,5.1,5.5$, and 5.9 from the bottom [near $\delta x=0.0$ in (b)].

as in ideal gas systems. When the size of the box becomes small, however, the finite volume effect of the particles becomes evident. In particular, if the relation

$$(a-d)^2+(b-d)^2<(2d)^2 \tag{1}$$

is satisfied, a region appears around the central part of the box that the particles' centers cannot enter. When $b<2+2\sqrt{3}$, the above equation is satisfied around $a=a^*=4$ and the trajectory of the centers of the particles is shown in Fig. 4(a). For $a<a^*=4$ the trajectory of the centers of the particles is given like Fig. 4(b) for $2+2\sqrt{3}<b<b^*=6$. In these cases, the trajectory of the center of a particle is similar to what is observed in a Sinai billiard [8]. Thus, in order to discuss these situations, we consider an $(a-d)\times(b-d)$ rectangular Sinai billiard which includes a hard sphere with diameter d ($d=2$). Using the equipartition rule, we can calculate the a-P_a relation of the Sinai billiard analytically as in the correlated cell model [9]. For each particle in the Sinai billiard, the entropy S is obtained by using the phase space volume $S=\ln[A_r(a,b)A_v]$ and the free energy F is given by $F=U-S$. (The Boltzmann constant k_B and temperature T are set as 1.) Here, $A_r(a,b)$ and A_v are the phase space volumes of, respectively, the real space part and the velocity space part, and the internal energy U is constant because this system consists of hard walls and a hard sphere.

$A_r(a,b)$ is given by

$$A_r=\begin{cases}(a-d)(b-d)-\dfrac{\pi}{4}d^2 \quad (a>4) & (2)\\[2ex] (a-d)(b-d)-(a-d)\dfrac{d}{2}\cos\theta-\dfrac{d^2}{2}\theta \quad (a\leqslant 4), & (3)\end{cases}$$

where $\sin\theta=(a-d)/d$ and $d=2$. Using the above relations with $P_a b=-\partial F/\partial a$, the a-P_a relation of the system for $b<6$ is obtained, and we can observe a liquid-solid phase transition as in Fig. 5(a). In this case, the width $a=a^*=4$ is a singular point and this point gives the maximal pressure independent of b. On the other hand, however, the a-P_a relations in the simulation results [Figs. 2(a) and 2(b)] have an inflection point near the critical width $a=a_*=4$, and the form of each curve is smooth. In addition, we consider a square box system in which a and b are varied with $a=b$. This system satisfies $b<2+2\sqrt{3}$ around $a\sim a^*$. Following the calculation for the rectangular Sinai billiard above, the a-P_a relation of the $(a-d)\times(a-d)$ square Sinai billiard can be obtained analytically. The profile of the a-P_a relation for the square Sinai billiard obtained in this calculation is almost the one as the result for the rectangular billiard. However, it is remarkable that P_a $(=P_b)$ decreases monotonically with increasing $a(=b)$ in the simulation of two particles in a square box [Fig. 5(b)] [10].

Finally, we discuss the mechanism of the appearance of the plateau in $C(t)$, the autocorrelation function of each particle's position, near the width $a=a^*$ by considering statistical properties of the particle trajectories. Now, we define $P_{\delta x}$ and $P_{\delta y}$ as the probability distributions of δx and δy. Here, δx is the horizontal component and δy is the vertical component of the relative position vector between the centers of two particles. Figures 6(a) and 6(b) are, respectively, δy-$P_{\delta y}$ relations and δx-$P_{\delta x}$ relations for $b=4.3,4.7,5.1,5.5,5.9$ with $a=4.1$. In Fig. 6(a), the maximum points of $P_{\delta y}$ are always far from the point $\delta y=0$. In Fig. 6(b), however, the position of the maximum point of $P_{\delta x}$ depends on b. When b is small, the maximum points of $P_{\delta x}$ are far from the point $\delta x=0$. This means that two particles tend to face each other on a diagonal line of the box. Because of this tendency, it is rather easy for these two particles to exchange their positions in both vertical and horizontal directions. Hence, the time at which $C(t)$ becomes 0 is relatively short. On the other hand, only one maximum point of

$P_{\delta x}$ appears at $\delta x = 0$ when b is larger than the critical value $b^{**} \sim 5.0$. In this case, the height of the box is large enough for the particles to change positions almost freely but only in the horizontal direction. This is considered to be the origin of the fast relaxation in the simulation. This situation also means that statistically two particles tend to line up vertically. In this case, the exchange of two particles' positions in the vertical direction is strongly hindered. This is the origin of the plateau in $C(t)$, after which the slow relaxation starts.

In this paper, the liquid-solid phase transition and the long time correlation of two hard spheres confined in a two-dimensional rectangular box are studied. Between the width of the box and the pressure at the sidewalls, a relation like the van der Waals equation is obtained. However, the range of the box width in which the volume compressibility is negative goes to zero when the height of this box passes through a critical value. The autocorrelation function of each particle's position is calculated near the critical width. As the height of the box increases, the time at which this correlation becomes zero gets longer. Moreover, a fast relaxation and a slow relaxation are clearly separated by the appearance of a plateau when the height of this box is sufficiently large. These relaxation processes are discussed by considering the form of the probability distribution of the relative positions of two particles. As a conclusion, this system is considered to be one of the simplest systems that imitates the liquid-solid phase transition of a system with many nonuniform elements. Still, in the relation between the width of the box and the pressure at the sidewalls, some discrepancies appear between the analytical and simulation results. Thus further consideration is required of dynamical properties like the long time correlation, which forbids equipartition. These topics seem to have a close relation with the slow dynamics in Hamilton dynamical systems [11]. In addition, the pressure on the walls is anisotropic in our system, while the pressure of a system with many particles is usually uniform. This also is a problem to be solved. Moreover, the understanding of the glass transition or other nonequilibrium systems [12] through our simple model is a future issue.

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