Statistical mechanics of two hard spheres in a box

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We investigate some statistical mechanical properties of a system consisting of two hard spheres in a D-dimensional rectangular box ($D=1,2,\ldots$). We give a theoretical method for computing a configurational partition function $Z_{c,D}$ of this system and compare the equation of state obtained from $Z_{c,D}$ with molecular dynamics simulations. Especially in $D=3$, we give a fully analytic expression for the pressure which turns out to have one or more negative compressibility regions when the box size is small.

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I. INTRODUCTION

Studies on dynamical and static (phase transitions) properties of (bulk) hard sphere fluids have a long history and are still gathering a lot of interest from many researchers [1–3]. On the other hand, recently considerable attention has been paid to statistical mechanical and dynamical properties of confined systems, which contain a few particles interacting mainly via hard disk or hard sphere potentials. These systems are of interest from the viewpoints of (a) foundation of statistical mechanics such as ergodicity, the equipartition law of energy, and theoretical (exact) calculations of partition functions, (b) statistical mechanical properties of small systems such as nanotubes and molecular size pores, and (c) some dynamical properties like diffusion or hopping which are related to the entropy barrier.

First we comment on the item (a). We have many studies of ergodicity from both theories [4–6] and numerical experiments [7–9]. Numerical investigations of ergodicity, which are indispensable since analytic approaches to ergodicity in many systems suffer from high barriers of mathematics, include interesting problems such as those of Fermi-Pasta-Ulam recurrence [10] and heat conduction [11].

For the system consisting of two or three hard disks in a rectangular box, exact calculations of the partition functions become possible because of the simplicity of interaction and few degrees of freedom [12,13]. In these systems, negative compressibility was first observed by Awazu [14] and then this was derived from the exact partition function [12]. This negative compressibility is similar to the one in a system consisting of many hard disks, where the isotherm as a function of density shows a van der Waals loop (Alder's transition) [15,16]. Now this phenomenon is observed for many confined systems and has some profound implications on real substances [17–19].

Now we turn to the item (b). For the system consisting of molecules confined by nanotubes or molecular size pores, we can observe many phenomena, for instance, capillary condensation, layering transitions, and so on [20]. Some properties of confined systems differ from those of bulk systems, e.g., the freezing temperature of porous systems shifts from that of bulk systems.

In the case of few-body adiabatic piston systems, where a rectangular box is separated by a piston and there are two hard disks in each box, the probability distribution of the piston's position which is computed from the configurational partition function of each box [21]. One can see that the probability distribution of the piston's position is changed from a unimodal shape to a multipeaked shape when the width of the box is changed. Although the motion of the piston is noisy in few-body adiabatic piston systems, one can observe a characteristic systematic motion of the adiabatic piston, i.e., the piston moves to a hotter region, by taking an ensemble average of the motion of the piston [22,23].

Finally we comment on the item (c). When one considers diffusion of a particle in a tube or Lorentz gas, the concept of the entropy barrier is useful [24–27]. Zwanzig derived a modified Fick-Jacobs equation containing the entropy barrier and a position-dependent effective diffusion coefficient for diffusion of a particle in a tube of varying section [24]. For the periodic Lorentz gas, it is possible to estimate the diffusion coefficient from the total phase space volume associated with a single trap by using the idea of a random walk between traps [28]. The entropy barrier plays an important role for other phenomena, for instance, slow relaxation of glasses, polymer translocation [29], protein folding [30], and so on. Some models which exhibit slow dynamics due to the entropy barrier have been proposed [31,32].

In all of these items, calculation of (exact) partition functions plays an important role and in this paper we present a theoretical method to calculate the partition function for two hard sphere systems in a box for arbitrary dimension D. We study the equation of state of this system using a configurational partition function $Z_{c,D}$. Moreover, we compare the equation of state with results of molecular dynamics simulations in order to investigate the ergodicity of this system numerically.

This paper is organized as follows. In Sec. II we give a method for computing $Z_{c,D}$ from $Z_{c,D-1}$. Since $Z_{c,1}$ is calculated easily, we are able to obtain a closed expression for $Z_{c,D}$. We explicitly calculate the exact $Z_{c,3}$ by using this relation. In Sec. III, we compare the theoretical results for $Z_{c,D}$ with results of molecular dynamics simulations. Moreover, other properties of this system such as the probability distributions of position and momentum of a hard sphere and the relaxation of temperature of particles are investigated. Section IV is a conclusion.

II. THEORY

We consider the system consisting of two hard spheres in a D-dimensional box. The diameter and mass of each hard sphere are d and m, respectively. The center and momentum of the ith hard sphere $(i=1,2)$ are denoted by $\boldsymbol{q}_i=(q_{i,1},\ldots,q_{i,D})$ and $\boldsymbol{p}_i=(p_{i,1},\ldots,p_{i,D})$, respectively. The size of a box in the jth direction $(j=1,2,\ldots,D)$ is L_j. The center of a hard sphere can move in a box whose length in the jth direction is $l_j\equiv L_j-d$ due to the repulsion between a hard sphere and a wall of the box.

The Hamiltonian of this system is given by

$$H=\sum_{i=1}^{2}\left(\frac{\boldsymbol{p}_i^2}{2m}+V_{\mathrm{ext}}(\boldsymbol{q}_i)\right)+V_{\mathrm{int}}(|\boldsymbol{q}_1-\boldsymbol{q}_2|), \tag{1}$$

where $V_{\mathrm{ext}}(\boldsymbol{q}_i)$ is a potential which confines hard spheres in a box,

$$V_{\mathrm{ext}}(\boldsymbol{q}_i)=\begin{cases}0, & 0\leqslant q_{i,j}\leqslant l_j, \quad j=1,\ldots,D,\\ \infty & \text{otherwise},\end{cases} \tag{2}$$

and $V_{\mathrm{int}}(|\boldsymbol{q}_1-\boldsymbol{q}_2|)$ is the interaction potential between two hard spheres,

$$V_{\mathrm{int}}(|\boldsymbol{q}_1-\boldsymbol{q}_2|)=\begin{cases}0, & |\boldsymbol{q}_1-\boldsymbol{q}_2|\geqslant d,\\ \infty, & |\boldsymbol{q}_1-\boldsymbol{q}_2|< d.\end{cases} \tag{3}$$

For the statistical mechanics of a few-body system, the entropy S is defined using the phase space volume bounded by the constant energy surface E, denoted by $\Gamma(E)$ [5,6,33,34],

$$\Gamma(E)=\int d\boldsymbol{q}_1\int d\boldsymbol{q}_2\int d\boldsymbol{p}_1\int d\boldsymbol{p}_2\Theta(E-H), \tag{4}$$

where $\Theta(x)$ is the Heaviside function,

$$\Theta(x)=\begin{cases}0, & x<0,\\ 1, & x\geqslant 0.\end{cases} \tag{5}$$

Since $|\boldsymbol{q}_1-\boldsymbol{q}_2|\geqslant d$ for our system, $\Gamma(E)$ is written as

$$\Gamma(E)=Z_{c,D}Z_{p,D}, \tag{6}$$

where $Z_{c,D}$ is the configurational partition function

$$Z_{c,D}=\int_0^{l_1}dq_{1,1}\int_0^{l_1}dq_{2,1}\cdots\int_0^{l_D}dq_{1,D}\int_0^{l_D}dq_{2,D} \times\Theta(|\boldsymbol{q}_1-\boldsymbol{q}_2|-d), \tag{7}$$

and $Z_{p,D}$ is the momentum partition function given by

$$Z_{p,D}=\int d\boldsymbol{p}_1\int d\boldsymbol{p}_2\Theta\left(E-\sum_{i=1}^{2}\frac{\boldsymbol{p}_i^2}{2m}\right). \tag{8}$$

For ergodic Hamiltonian systems, the entropy S is defined using $\Gamma(E)$ by [5,6,33,34]

$$S=\ln\Gamma(E)=\ln Z_{c,D}+\ln Z_{p,D}, \tag{9}$$

and the temperature T is obtained from S:

$$T=\left(\frac{\partial S}{\partial E}\right)^{-1}=\left(\frac{\partial \ln Z_{p,D}}{\partial E}\right)^{-1}, \tag{10}$$

where we set the Boltzmann constant to 1. T is determined by $Z_{p,D}$ only since $Z_{c,D}$ does not depend on E. At this point we note that one can use a microcanonical ensemble by replacing the Heaviside function in Eq. (4) by the Dirac δ function and by defining, at the same time, the temperature of the system by a microcanonical ensemble average $T=\langle p_{1,1}^2/m\rangle_{\mathrm{MC}}$. All the results below, both numerical and analytic, remain intact.

Moreover, the ensemble-averaged pressure on the wall perpendicular to the jth direction, $\langle P_j\rangle$, is obtained from S and T by

$$\langle P_j\rangle=T\left(\frac{\partial S}{\partial V}\right)_{L_{k(k\neq j)}}=\frac{1}{\prod_{k\neq j}L_k}\left(\frac{\partial \ln Z_{p,D}}{\partial E}\right)^{-1}\frac{\partial \ln Z_{c,D}}{\partial L_j}, \tag{11}$$

where $V=\prod_{k=1}^{D}L_k$.

$Z_{p,D}$ is the volume of a $2D$-dimensional sphere whose radius is $\sqrt{2mE}$, i.e., $Z_{p,D}\propto(2mE)^D$. Therefore we have $\ln Z_{p,D}=D\ln E+\text{const}$ and $T=E/D$. We give an analytic expression for $Z_{c,D}$ below. We show the parameter dependency of $Z_{c,D}$ explicitly as $Z_{c,D}(l_1,\ldots,l_D;d)$. Here we use $l_j=L_j-d$ instead of L_j for convenience.

A. One-dimensional case

First, we compute $Z_{c,1}$, i.e., the configurational partition function of the system consisting of two hard rods each with length d in a one-dimensional cylinder with length L_1. The centers of two hard rods are denoted by $q_{1,1}$ and $q_{2,1}$ (we assume $q_{1,1}<q_{2,1}$), respectively. Then the configurational partition function $Z_{c,1}(l_1;d)$ is given by [35]

$$\begin{aligned}Z_{c,1}(l_1;d)&=\int_0^{q_{2,1}}dq_{1,1}\int_0^{l_1}dq_{2,1}\Theta(q_{2,1}-q_{1,1}-d)\\&=\int_0^{q_{2,1}-d}dq_{1,1}\int_d^{l_1}dq_{2,1}\\&=\frac{(l_1-d)^2}{2}.\end{aligned} \tag{12}$$

Note that $q_{1,1}<q_{2,1}$ is retained in the dynamics, because hard rods cannot penetrate each other.

B. General case

Next, we turn to the method for computing $Z_{c,D}$. First, we consider the case where the configuration of hard spheres satisfies $q_{1,j}\leqslant q_{2,j}$ $(j=1,\ldots,D)$. The configurational partition function under this restriction, denoted by $\tilde{Z}_{c,D}$, is written as

$$\tilde{Z}_{c,D}(l_1,\ldots,l_D;d)=\int_0^{q_{2,1}}dq_{1,1}\int_0^{l_1}dq_{2,1}\cdots\int_0^{q_{2,D}}dq_{1,D}\times\int_0^{l_D}dq_{2,D}\Theta\left(\sqrt{\sum_{j=1}^{D}(q_{2,j}-q_{1,j})^2}-d\right). \tag{13}$$

We note that $\tilde{Z}_{c,D}(l_1,\ldots,l_D;d)=0$ if $\sqrt{\Sigma_{j=1}^{D}l_j^2}<d$. This is the case where the box cannot contain two hard spheres. We introduce the new variable $\boldsymbol{q}\equiv\boldsymbol{q}_2-\boldsymbol{q}_1$, and we can express Eq. (13) as

$$\tilde{Z}_{c,D}(l_1,\ldots,l_D;d)=\int_0^{l_1-q_1}dq_{1,1}\int_0^{l_1}dq_1\cdots\int_0^{l_D-q_D}dq_{1,D}\times\int_0^{l_D}dq_D\Theta\left(\sqrt{\sum_{j=1}^{D}q_j^2}-d\right), \tag{14}$$

where q_j is the jth component of $\boldsymbol{q}$. We note that the Heaviside function in Eq. (14) satisfies the relation

$$\Theta\left(\sqrt{\sum_{j=1}^{D}q_j^2}-d\right)=\begin{cases}\Theta\left(\sqrt{\sum_{j=1}^{D-1}q_j^2}-\sqrt{d^2-q_D^2}\right), & 0\leq q_D<d,\\ 1, & q_D\geq d.\end{cases} \tag{15}$$

We now perform the integrations in Eq. (14) over $\boldsymbol{q}_1$ and $\boldsymbol{q}$ except for q_D using Eq. (15), to obtain

$$\tilde{Z}_{c,D}(l_1,\ldots,l_D;d)=\int_0^{l_D}dq_D(l_D-q_D)\tilde{Z}_{c,D-1}\times(l_1,\ldots,l_{D-1};\sqrt{d^2-q_D^2}) \tag{16}$$

when $l_D<d$ and

$$\tilde{Z}_{c,D}(l_1,\ldots,l_D;d)=\int_0^{d}dq_D(l_D-q_D)\tilde{Z}_{c,D-1}\times(l_1,\ldots,l_{D-1};\sqrt{d^2-q_D^2})+\int_d^{l_D}dq_D(l_D-q_D)\prod_{j=1}^{D-1}\frac{l_j^2}{2} \tag{17}$$

when $l_D\geq d$. Since we know $Z_{c,1}$ ($=\tilde{Z}_{c,1}$), we can compute $\tilde{Z}_{c,D}$ from $Z_{c,1}$.

Here, we discuss the relation between $\tilde{Z}_{c,D}$ and $Z_{c,D}$. When two hard spheres can exchange their positions in the jth direction ($j=1,\ldots,D$), i.e., when it is possible that $q_{1,j}(t)>q_{2,j}(t)$ at a certain time t under the initial condition $q_{1,j}(t=0)\leq q_{2,j}(t=0)$, $\tilde{Z}_{c,D}$ is multiplied by 2, because the phase space volume is doubled. The condition for the two particles to be able to exchange their positions in the jth direction is expressed by

$$\sqrt{\sum_{k\neq j}l_k^2}\geq d. \tag{18}$$

Considering all j, we have

$$Z_{c,D}(l_1,\ldots,l_D;d)=K_D(l_1,\ldots,l_D;d)\tilde{Z}_{c,D}(l_1,\ldots,l_D;d), \tag{19}$$

where K_D satisfies

$$\log_2 K_D(l_1,\ldots,l_D;d)=\sum_{j=1}^{D}\Theta\left(\sqrt{\sum_{k\neq j}l_k^2}-d\right). \tag{20}$$

$Z_{c,2}$ was computed analytically before [12], and our result is consistent with this. Moreover we can calculate $Z_{c,3}$ explicitly; we show this calculation in Appendix A.

III. COMPARISON WITH NUMERICAL SIMULATIONS

A. Pressure

We compare the results obtained above with those from molecular dynamics simulations. We mainly consider the three-dimensional case $D=3$, in which the pressure on the wall perpendicular to the $j=1$ direction, P_1, is obtained statistical-mechanically from Eq. (11) as

$$\langle P_1\rangle=\frac{T}{L_2L_3}\frac{\partial\ln Z_{c,3}}{\partial L_1}=\frac{E}{3L_2L_3\tilde{Z}_{c,3}}\frac{\partial\tilde{Z}_{c,3}}{\partial l_1}. \tag{21}$$

We remark here that $\langle P_1\rangle$ has the physical meaning of pressure only if our system satisfies the ergodic assumption.

On the other hand, the pressure can be calculated also from molecular dynamics simulations, which we denote by $\bar{P}_1$, as the time average

$$\bar{P}_1(t)=\frac{1}{t}\frac{\sum_{n=1}^{N}2p_1[n]}{L_2L_3}. \tag{22}$$

Here t is the duration of the simulation, $2p_1[n]$ (>0) is the momentum transfer from a hard sphere to the wall on the right-hand side due to the nth collision, and N is the total number of collisions in time t. Hereafter, as units of length and mass we choose the diameter d and mass m of a hard sphere, respectively, and we set $E=D$; thus the temperature $T=1$ since the Boltzmann constant is set to 1.

We first investigate whether $\langle P_1\rangle=\bar{P}_1(t)$ when t is sufficiently large since we are interested in the ergodicity of our system. We always set $t=10^7$ and perform the simulations starting from 100 different initial conditions for each data point. As a result, statistical errors of all simulation results in this paper are less than half the point size. In Fig. 1, we show $\langle P_1\rangle$ and $\bar{P}_1$ for $L_2=5$ as a function of L_1 for several L_3. These are isotherms, since we consider the case with E, i.e., T, fixed. From Fig. 1, $\langle P_1\rangle=\bar{P}_1$ is confirmed and P_1 decreases monotonically as L_1 or L_2 increases.

In the case of $D=2$, a negative compressibility region in the (L_1,L_2) space near $L_1\simeq L_2\simeq 2$ was found [12,14]. It is

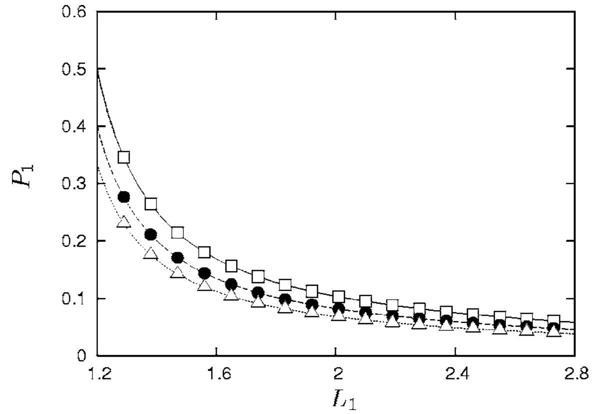

FIG. 1. P_1 as a function of L_1 for L_2=5.0. Curves are $\langle P_1\rangle$ with L_3=4.0 (solid), 5.0 (dashed), and 6.0 (dotted). Points are $\bar{P}_1$ with L_2=4.0 (open square), 5.0 (closed circle), and 6.0 (open triangle).

seen that when $L_1 < 2$ two hard disks at $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ cannot exchange their positions in the sense that $q_{1,2}(t) < q_{2,2}(t)$ for any t $(t>0)$ if $q_{1,2}(0) < q_{2,2}(0)$. As an example, we show P_1 as a function of L_1 for D=2 in Fig. 2. X_1 (Y_1) denotes a point where $\partial P_1/\partial L_1=0$ and $\partial^2 P_1/\partial L_1^2 > 0$ (<0). At the points X_1 and X_2, P_1 takes the same value, i.e., $P_1(X_1)=P_1(X_2)$. Similarly $P_1(Y_1)=P_1(Y_2)$.

Here we consider the situation where P_1 on the wall from the environment, which we denote by $P_{1,\mathrm{env}}$, is changed gradually from $P_1(Q)$ to $P_1(X_1)$ with L_1 allowed to instantaneously adjust its position to make $P_1=P_{1,\mathrm{env}}$. From Fig. 2, it is seen that L_1 increases continuously along the curve QX_1. If $P_{1,\mathrm{env}}$ decreases further below $P_1(X_1)$, L_1 jumps to $L_1(X_2)$ and increases thereafter continuously along the isotherms again. Coinversely, when $P_{1,\mathrm{env}}$ increases from $P_1(R)$ to $P_1(Q)$, L_1 decreases along the curve RY_1 and, after jumping to $L_1(Y_2)$, L_1 further decreases continuously to $L_1(Q)$. Therefore a system with L_1 in the range $L_1(X_1) < L_1 < L_1(Y_1)$ is not realized at equilibrium (negative compressibility region).

For the three-dimensional case, it would be worthwhile to study P_1 in the (L_1,L_2,L_3) space when L_2 and L_3 are small and the packing problem becomes important. Figure 3(a) shows $\langle P_1\rangle$ and $\bar{P}_1$, and a part of the dashed curve in Fig.

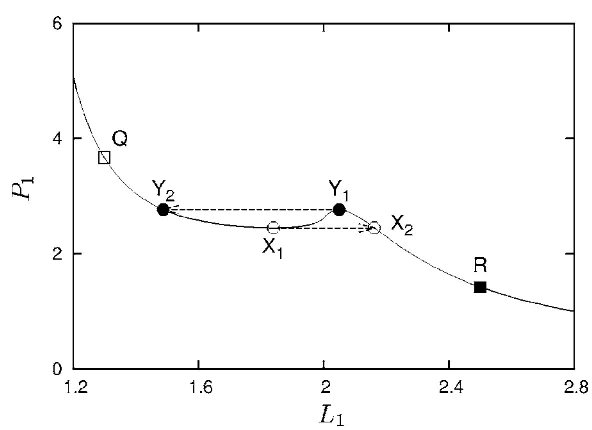

FIG. 2. P_1 as a function of L_1 for D=2. We set L_2=2.1.

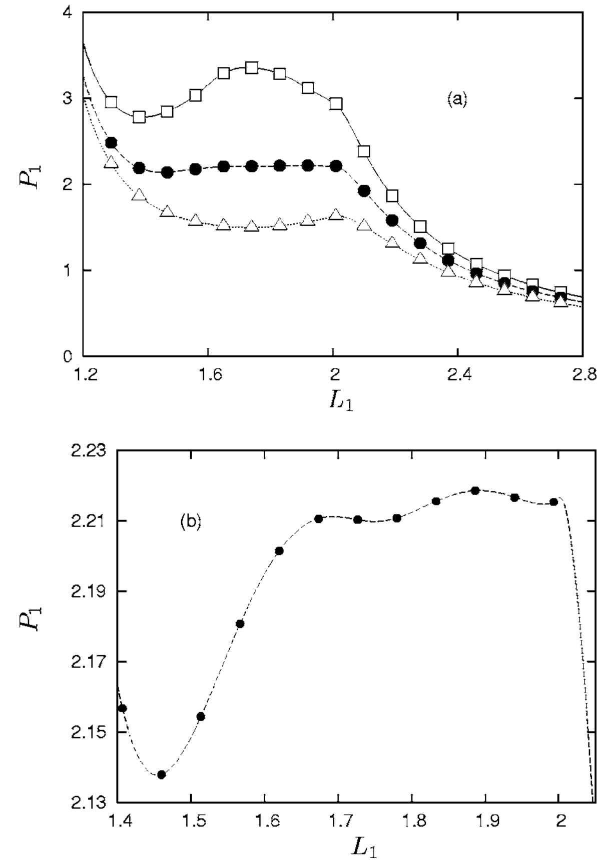

FIG. 3. P_1 as a function of L_1 with L_2=1.7. (a) Curves are $\langle P_1\rangle$ with L_3=1.85 (solid), 1.95 (dashed), and 2.05 (dotted). Points are $\bar{P}_1$ with L_3=1.85 (open square), 1.95 (closed circle), 2.05 (open triangle). (b) Enlarged in the case L_3=1.95.

3(a) (L_3=1.95) is enlarged in Fig. 3(b). From these figures it is observed that the section of negative compressibility depends on (L_1,L_2,L_3) rather sensitively. That is, when L_3 =1.85, the system shows negative compressibility for L_1 <1.7, while compressibility is negative at L_1=2 when L_3 =2.05. From Fig. 3(b), we notice that there are three negative compressibility sections on the L_1 axis for the case of L_3 =1.95.

From Fig. 3, one may infer that negative compressibility regions are distributed in a complicated way in the (L_1,L_2,L_3) space. Figure 4 shows a phase diagram of our system, i.e., curves on which $\partial P_1/\partial L_1=0$ are shown when L_2=1.7 (a), 1.9 (b), and 2.1 (c). In the regions enclosed by the curves, the compressibility is negative and physically the state is not realized.

For the case L_2=1.7, three negative compressibility regions exist in the (L_1,L_3) plane. Region A_1 may be regarded as a quasi-two-dimensional case since L_3 is rather small [12]. The line L_3=1.85 (L_3=2.05) intersects only the region A_2 (A_3). On the other hand, the line L_3=1.95 intersects both A_2 and A_3 regions. Moreover, the line cuts the A_3 region twice. Accordingly, three negative compressibility sections appear when L_3=1.95, and this is shown in Fig. 3(b).

For the case L_2=1.9, two negative compressibility regions exist in the (L_1,L_3) plane. Region B_1 which is regarded as a

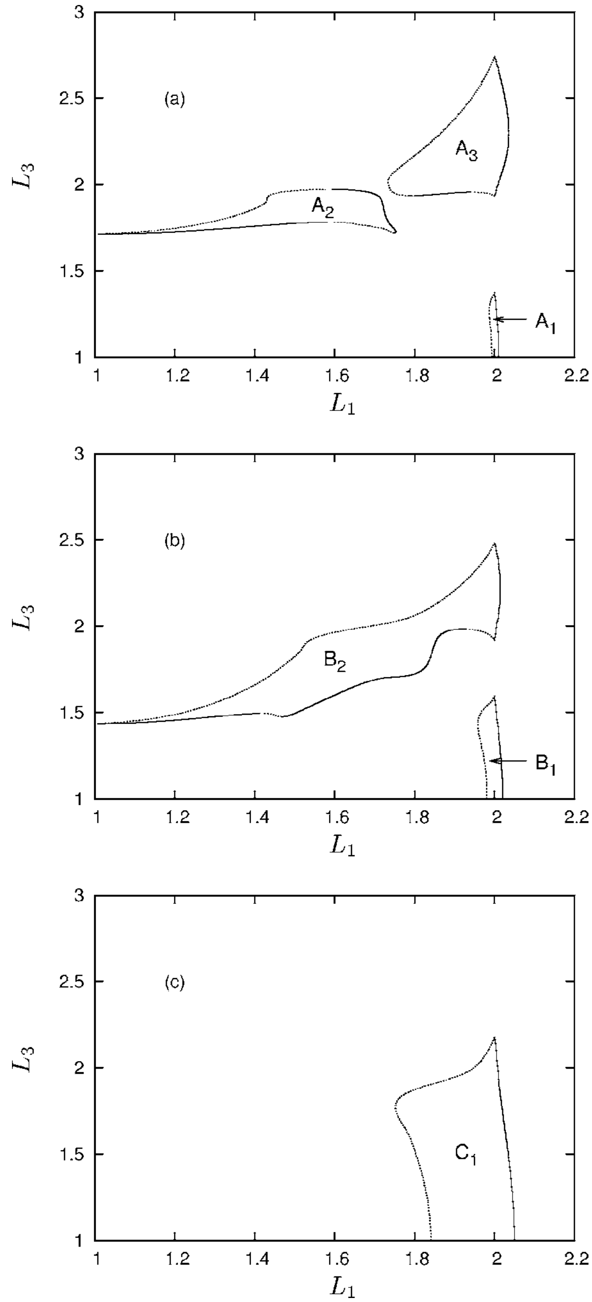

FIG. 4. Phase diagram in the (L_1,L_3) plane at $L_2=1.7$ (a), (b) 1.9, and (c) 2.1. Curves are $(\partial P_1/\partial L_1)=0$ with $(\partial^2 P_1/\partial L_1^2)>0$ (dotted) and $(\partial^2 P_1/\partial L_1^2)<0$ (solid).

quasi-two-dimensional case, is larger than region A_1. Region B_2 is formed by the merger of A_3 and A_2. For the case $L_2=2.1$, there is only one region C_1 where the compressibility is negative.

At this point we note first that it is rather difficult to make the physical origins of negative compressibility clear. As discussed in Ref. [12], ergodicity breaking and packing are the key factors. Second it is remarked that one cannot obtain the phase diagram shown in Fig. 4 if one has no analytic solution for P_1 since molecular dynamics calculations of P_1 are too time consuming.

In order to discuss the general case ($D=2$, 3, 4, and 5), we consider the case $L_1=\cdots=L_D=L$. Figure 5 shows the relation

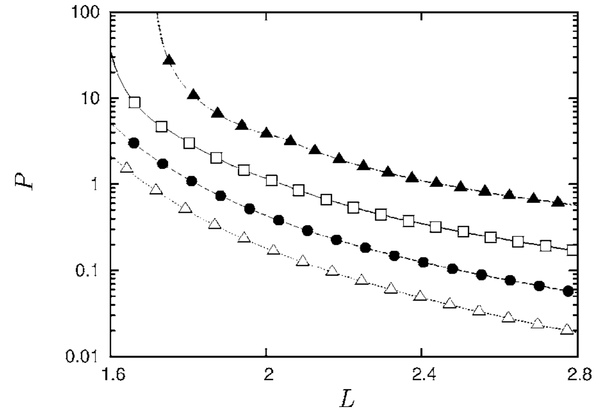

FIG. 5. Pressure of D-dimensional hard sphere in the box with $L_j=L$ $(j=1,\ldots,D)$ vs L. Curves are $\langle P\rangle$ with $D=2$ (dash-dotted), 3 (solid), 4 (dashed), and 5 (dotted). Points are $\bar{P}$ with $D=2$ (closed triangle), 3 (open square), 4 (closed circle), and 5 (open triangle).

between pressure and L. Here, the pressure on the wall, $\langle P\rangle$, is given by

$$\langle P\rangle = \frac{1}{DL^{D-1}}\left(\frac{\partial \ln Z_{p,D}}{\partial E}\right)^{-1}\frac{\partial \ln Z_{c,D}}{\partial l}, \tag{23}$$

where $l=L-d$. It is noted that we perform the integration Eq. (16) or Eq. (17) numerically for the case $D\geqslant 4$ in order to compute $Z_{c,D}$. In each D investigated here, the relation $\langle P\rangle=\bar{P}$ seems to be valid, which indicates that our system may be approximately ergodic.

B. Probability distributions of position and momentum

In a microcanonical ensemble, the probability distribution of momentum is not Maxwellian [36,37]. However the probability distribution of momentum approaches Maxwellian as the number of degrees of freedom of the system is increased.

The probability that $p_{1,1}$ is between p and $p+dp$ is denoted by $\rho_D(p)dp$, and $\rho_D(p)$ is given by

$$\rho_D(p) = \frac{\int d\boldsymbol{q}_1\int d\boldsymbol{q}_2\int d\boldsymbol{p}_1\int d\boldsymbol{p}_2\,\delta(H-E)\,\delta(p_{1,1}-p)}{\int d\boldsymbol{q}_1\int d\boldsymbol{q}_2\int d\boldsymbol{p}_1\int d\boldsymbol{p}_2\,\delta(H-E)} \propto (2mE-p^2)^{(2D-3)/2}, \tag{24}$$

with $\delta(x)$ is Dirac's delta function.

On the other hand the probability distribution of $q_{1,1}$, which we denote by $n_D(q)$, is given by

$$n_D(q) = \frac{\int d\boldsymbol{q}_1\int d\boldsymbol{q}_2\int d\boldsymbol{p}_1\int d\boldsymbol{p}_2\,\delta(H-E)\,\delta(q_{1,1}-q)}{\int d\boldsymbol{q}_1\int d\boldsymbol{q}_2\int d\boldsymbol{p}_1\int d\boldsymbol{p}_2\,\delta(H-E)}. \tag{25}$$

We can express $n_D(q)$ using a configurational partition function, and details are given in Appendix B.

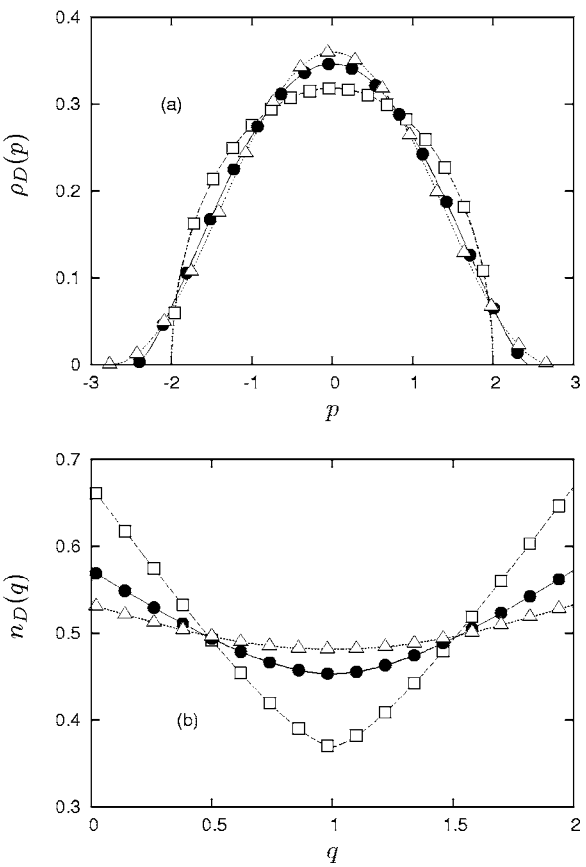

FIG. 6. Probability distribution functions $\rho_D(p)$ (a) and $n_D(q)$ (b) for the box with $L_j=3$ $(j=1,\ldots,D)$. Curves are results obtains theoretically in $D=2$ (dashed), 3 (solid), and 4 (dotted). Points are results obtained from molecular dynamics simulations in $D=2$ (open square), 3 (closed circle), and 4 (open triangle).

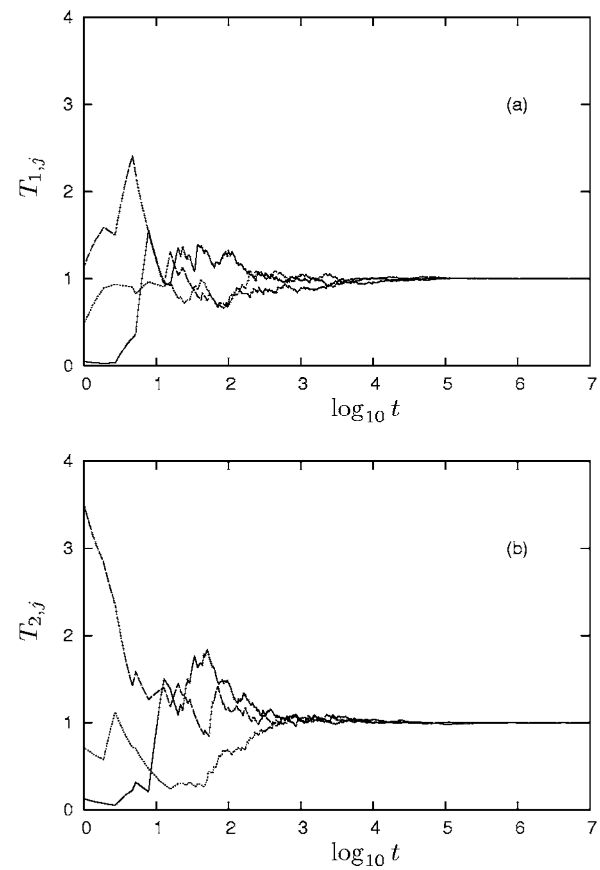

FIG. 7. Time evolution of $T_{1,j}$ (a) and $T_{2,j}$ (b) for $D=3$. We choose the parameters as $L_1=L_2=L_3=3$ and $E=3$. $j=1$, 2, and 3 are plotted by solid, dashed, and dotted curves, respectively.

In Fig. 6, we show $\rho_D(p)$ and $n_D(q)$ for $D=2$, 3, and 4 for the box with $L_1=\cdots=L_D=3$. Both $\rho_D(p)$ and $n_D(q)$ are in agreement with molecular dynamics simulations, i.e., we checked numerically the ergodicity for the probability distributions of $p_{1,1}$ and $q_{1,1}$.

From Fig. 6(a), one may expect that equipartition of energy, i.e., temperature, is satisfied for our system. To check this we define the temperature of the jth component of the ith sphere, $T_{i,j}(t)$, by

$$T_{i,j}(t)=\frac{1}{t}\int_0^t \frac{\{p_{i,j}(s)\}^2}{m}ds, \tag{26}$$

where $p_{i,j}(s)$ denotes $p_{i,j}$ at a time s. In Fig. 7, we show the time evolution of $T_{i,j}$ for the case $D=3$. We choose the parameters as $L_1=L_2=L_3=3$ and $E=3$, i.e., $T=1$. One can see that all $T_{i,j}$ converge to 1, which means that equipartition of temperature (i.e., energy) is satisfied.

IV. CONCLUSION

In this paper, we have investigated the system consisting of two D-dimensional hard spheres in a rectangular box. In particular, we have developed a method for computation of $Z_{c,D}$ from $Z_{c,D-1}$ and actually calculated the pressure and probability distributions of momentum and position under the assumption that our system is ergodic. The results obtained from the ergodic assumption have been confirmed to be in excellent agreement with molecular dynamics simulations. This indicates that our system is (quasi)ergodic.

In the case $D=3$, we have computed $Z_{c,3}$ analytically. Moreover, we have given a detailed phase diagram in which regions of negative compressibility are given in the space (L_1,L_2,L_3). From this we can see how points of negative compressibility are distributed in the space (L_1,L_2,L_3). This diagram was obtained with use of our analytic expression for $Z_{c,D}$. Conditions for occurrence of negative compressibility in a general D-dimensional system seem to be complicated compared with the case $D=2$ [12], and studying this condition in detail is left for future work.

APPENDIX A: ANALYTIC EXPRESSION FOR $D=3$

In this appendix, we compute $\widetilde{Z}_{c,3}$ by using results obtained in Sec. II. To compute $\widetilde{Z}_{c,3}$ we need $\widetilde{Z}_{c,2}$, which is given by [12]

$$\tilde{Z}_{c,2}(l_1,l_2;d)=\begin{cases} l_1^2l_2^2/4-\pi l_1l_2d^2/4+(l_1+l_2)d^3/3-d^4/8\equiv I_1(l_1,l_2;d), & l_1>d,l_2>d,\\ l_1^2l_2^2/4+l_1d^3/3+H(l_1,l_2;d)\equiv I_2(l_1,l_2;d), & l_1>d,l_2\leqslant d,\\ l_1^2l_2^2/4+l_2d^3/3+H(l_2,l_1;d)=I_2(l_2,l_1;d), & l_1\leqslant d,l_2>d,\\ l_1^2l_2^2/4+\pi l_1l_2d^2/4+d^4/8+H(l_1,l_2;d)+H(l_2,l_1;d)\equiv I_3(l_1,l_2;d), & l_1\leqslant d,l_2\leqslant d,\end{cases} \tag{A1}$$

where

$$H(l_1,l_2;d)\equiv-\frac{l_2^4}{24}+\frac{l_2^2d^2}{4}-\frac{(l_2^2+2d^2)l_1\sqrt{d^2-l_2^2}}{6}-\frac{l_1l_2d^2}{2}\arcsin\left(\frac{l_2}{d}\right). \tag{A2}$$

Below we can assume $l_1\geqslant l_2\geqslant l_3$ without loss of generality and $l_1^2+l_2^2+l_3^2\geqslant d^2$, i.e., the box is able to contain two hard spheres.

If $l_2>d$, $\tilde{Z}_{c,2}(l_1,l_2;\sqrt{d^2-q_3^2})=I_1(l_1,l_2;\sqrt{d^2-q_3^2})$ for any q_3 $(0\leqslant q_3\leqslant d)$. Hence, from Eqs. (16) and (17), $\tilde{Z}_{c,3}$ is given by

$$\tilde{Z}_{c,3}(l_1,l_2,l_3;d)=\int_0^d dq_3(l_3-q_3)I_1(l_1,l_2;\sqrt{d^2-q_3^2})+\frac{l_1^2l_2^2(l_3-d)^2}{8} \tag{A3}$$

when $l_3>d$ and

$$\tilde{Z}_{c,3}(l_1,l_2,l_3;d)=\int_0^{l_3} dq_3(l_3-q_3)I_1(l_1,l_2;\sqrt{d^2-q_3^2}) \tag{A4}$$

when $l_2>d\geqslant l_3$.

If $l_1>d\geqslant l_2$, we need to consider the relation between l_2 and $\sqrt{d^2-l_3^2}$, which is the minimum value of $\sqrt{d^2-q_3^2}$, since $\tilde{Z}_{c,2}(l_1,l_2;\sqrt{d^2-q_3^2})=I_1(l_1,l_2;\sqrt{d^2-q_3^2})$ when $l_2>\sqrt{d^2-q_3^2}$ and $\tilde{Z}_{c,2}(l_1,l_2;\sqrt{d^2-q_3^2})=I_2(l_1,l_2;\sqrt{d^2-q_3^2})$ when $l_2\leqslant\sqrt{d^2-q_3^2}$. In this case, $\tilde{Z}_{c,3}$ is given by

$$\tilde{Z}_{c,3}(l_1,l_2,l_3;d)=\int_0^{\sqrt{d^2-l_2^2}} dq_3(l_3-q_3)I_2(l_1,l_2;\sqrt{d^2-q_3^2})+\int_{\sqrt{d^2-l_2^2}}^{l_3} dq_3(l_3-q_3)I_1(l_1,l_2;\sqrt{d^2-q_3^2}) \tag{A5}$$

when $l_1>d\geqslant l_2>\sqrt{d^2-l_3^2}$, and

$$\tilde{Z}_{c,3}(l_1,l_2,l_3;d)=\int_0^{l_3} dq_3(l_3-q_3)I_2(l_1,l_2;\sqrt{d^2-q_3^2}) \tag{A6}$$

when $l_1>d>\sqrt{d^2-l_3^2}\geqslant l_2$.

If $d\geqslant l_1$, we need to consider the relation between l_1 as well as l_2 and $\sqrt{d^2-l_3^2}$. In this case, $\tilde{Z}_{c,3}$ is given by

$$\tilde{Z}_{c,3}(l_1,l_2,l_3;d)=\int_0^{\sqrt{d^2-l_1^2}} dq_3(l_3-q_3)I_3(l_1,l_2;\sqrt{d^2-q_3^2})+\int_{\sqrt{d^2-l_1^2}}^{\sqrt{d^2-l_2^2}} dq_3(l_3-q_3)I_2(l_1,l_2;\sqrt{d^2-q_3^2})+\int_{\sqrt{d^2-l_2^2}}^{l_3} dq_3(l_3-q_3)I_1(l_1,l_2;\sqrt{d^2-q_3^2}) \tag{A7}$$

when $d\geqslant l_1\geqslant l_2>\sqrt{d^2-l_3^2}$,

$$\tilde{Z}_{c,3}(l_1,l_2,l_3;d)=\int_0^{\sqrt{d^2-l_1^2}} dq_3(l_3-q_3)I_3(l_1,l_2;\sqrt{d^2-q_3^2})+\int_{\sqrt{d^2-l_1^2}}^{l_3} dq_3(l_3-q_3)I_2(l_1,l_2;\sqrt{d^2-q_3^2}) \tag{A8}$$

when $d\geqslant l_1>\sqrt{d^2-l_3^2}\geqslant l_2$, and

$$\tilde{Z}_{c,3}(l_1,l_2,l_3;d)=\int_\kappa^{l_3} dq_3(l_3-q_3)I_3(l_1,l_2;\sqrt{d^2-q_3^2}) \tag{A9}$$

when $\sqrt{d^2-l_3^2}\geqslant l_1\geqslant l_2$, where κ is defined by

$$\kappa=\begin{cases}0, & d^2<l_1^2+l_2^2,\\ \sqrt{d^2-l_1^2-l_2^2}, & d^2\geqslant l_1^2+l_2^2.\end{cases} \tag{A10}$$

From Eqs. (A3)–(A9), to show that $\tilde{Z}_{c,3}$ is obtained explicitly it is necessary to compute

$$J_i(u,v)\equiv\int_v^u dq_3(l_3-q_3)I_i(l_1,l_2;\sqrt{d^2-q_3^2})\quad(i=1,2,3). \tag{A11}$$

First J_1 is written as

$$J_1(u,v)=\sum_{k=0}^{5}a_{1,k}\int_v^u dq_3q_3^k+\sum_{k=0}^{3}b_{1,k}\int_v^u dq_3q_3^k\sqrt{d^2-q_3^2}=\sum_{k=0}^{5}a_{1,k}\{f_k(u)-f_k(v)\}+\sum_{k=0}^{3}b_{1,k}\{g_k(u;d)-g_k(v;d)\}, \tag{A12}$$

where $a_{1,k}$ and $b_{1,k}$ are given by

$$a_{1,1} = \frac{2\pi l_1 l_2 d^2 - 2l_1^2 l_2^2 + d^4}{8}, \quad a_{1,3} = -\frac{\pi l_1 l_2 + d^2}{4}, \quad a_{1,5} = \frac{1}{8},$$

$$a_{1,2i} = -l_3 a_{1,2i+1} \quad (i=0,1,2),$$

$$b_{1,1} = -\frac{(l_1+l_2)d^2}{3}, \quad b_{1,3} = \frac{l_1+l_2}{3},$$

$b_{1,2i}=-l_3 b_{1,2i+1}$ $(i=0,1)$,and we obtain f_k and g_k as

$$f_k(x) = \frac{x^{k+1}}{k+1}, \tag{A13}$$

$$g_0(x;s) = \frac{1}{2}\left[s^2 \arcsin\left(\frac{x}{s}\right) + x\sqrt{s^2-x^2}\right], \tag{A14}$$

$$g_1(x;s) = -\frac{(s^2-x^2)^{3/2}}{3}, \tag{A15}$$

$$g_2(x;s) = \frac{1}{8}\left[s^4 \arcsin\left(\frac{x}{s}\right) + (2x^2-s^2)x\sqrt{s^2-x^2}\right], \tag{A16}$$

$$g_3(x;s) = -\frac{(3x^2+2s^2)(s^2-x^2)^{3/2}}{15}. \tag{A17}$$

Note that we consider the case $s>0$, $x\geqslant 0$, and $\sqrt{s^2-x^2}\geqslant 0$ in this paper.

Second, J_2 is written as

$$J_2(u,v) = \sum_{k=0}^{1} a_{2,k}\{f_k(u)-f_k(v)\} + \sum_{k=0}^{3} b_{2,k}\{g_k(u;d)-g_k(v;d)\} + \int_v^u dq_3(l_3-q_3)H(l_1,l_2;\sqrt{d^2-q_3^2}), \tag{A18}$$

where $a_{2,k}$ and $b_{2,k}$ are given by

$$a_{2,0} = \frac{l_1^2 l_2^2 l_3}{4}, \quad a_{2,1} = -\frac{l_1^2 l_2^2}{4},$$

$$b_{2,1} = -\frac{l_1 d^2}{3}, \quad b_{2,3} = \frac{l_1}{3}, \quad b_{2,2i} = -l_3 b_{2,2i+1} \quad (i=0,1).$$

The last term of Eq. (A18) is written as

$$\int_v^u dq_3(l_3-q_3)H(l_1,l_2;\sqrt{d^2-q_3^2})$$
$$= \sum_{k=0}^{3}\left\{\alpha_k\int_v^u dq_3 q_3^k + \beta_k\int_v^u dq_3 q_3^k\sqrt{d^2-q_3^2} + \gamma_k\int_v^u dq_3 q_3^k \arcsin\left(\frac{l_2}{\sqrt{d^2-q_3^2}}\right)\right\}$$
$$= \sum_{k=0}^{3}[\alpha_k\{f_k(u)-f_k(v)\} + \beta_k\{g_k(u;\sqrt{d^2-l_2^2}) - g_k(v;\sqrt{d^2-l_2^2})\} + \gamma_k\{h_k(u;d,l_2)-h_k(v;d,l_2)\}], \tag{A19}$$

where α_k, β_k, and γ_k are given by

$$\alpha_1 = \frac{l_2^4 - 6l_2^2 d^2}{24}, \quad \alpha_3 = \frac{l_2^2}{4}, \quad \alpha_{2i} = -l_3\alpha_{2i+1} \quad (i=0,1),$$

$$\beta_1 = \frac{l_1(l_2^2+2d^2)}{6}, \quad \beta_3 = -\frac{l_1}{3}, \quad \beta_{2i} = -l_3\beta_{2i+1} \quad (i=0,1),$$

$$\gamma_1 = \frac{l_1 l_2 d^2}{2}, \quad \gamma_3 = -\frac{l_1 l_2}{2}, \quad \gamma_{2i} = -l_3\gamma_{2i+1} \quad (i=0,1).$$

h_k $(k=0,1,2,3)$ are obtained as

$$h_0(x;s_1,s_2) = x\arcsin\left(\frac{s_2}{\sqrt{s_1^2-x^2}}\right) + s_2\arcsin\left(\frac{x}{\sqrt{s_1^2-s_2^2}}\right) - \frac{s_1}{2}[\arcsin\{r_1(x;s_1,s_2)\} - \arcsin\{r_2(x;s_1,s_2)\}], \tag{A20}$$

$$h_1(x;s_1,s_2) = \frac{x^2}{2}\arcsin\left(\frac{s_2}{\sqrt{s_1^2-x^2}}\right) - \frac{s_2}{2}\sqrt{s_1^2-s_2^2-x^2} - \frac{s_1^2}{4} \times[-\arcsin\{r_1(x;s_1,s_2)\} - \arcsin\{r_2(x;s_1,s_2)\}], \tag{A21}$$

$$h_2(x;s_1,s_2) = \frac{x^3}{3}\arcsin\left(\frac{s_2}{\sqrt{s_1^2-x^2}}\right) - \frac{s_2(s_2^2-3s_1^2)}{6}\arcsin\left(\frac{x}{\sqrt{s_1^2-s_2^2}}\right) - \frac{s_2 x\sqrt{s_1^2-s_2^2-x^2}}{6} - \frac{s_1^3}{6}[\arcsin\{r_1(x;s_1,s_2)\} - \arcsin\{r_2(x;s_1,s_2)\}], \tag{A22}$$

$$h_3(x;s_1,s_2) = \frac{x^4}{4}\arcsin\left(\frac{s_2}{\sqrt{s_1^2-x^2}}\right) - \frac{s_2(x^2-2s_2^2+5s_1^2)}{12}\sqrt{s_1^2-s_2^2-x^2} - \frac{s_1^4}{8} \times[-\arcsin\{r_1(x;s_1,s_2)\} - \arcsin\{r_2(x;s_1,s_2)\}], \tag{A23}$$

and we define r_i $(i=1,2)$ in Eqs. (A20)–(A23) by

$$r_1(x;s_1,s_2) = \frac{s_1(x+s_1)-s_2^2}{\sqrt{s_1^2-s_2^2}|x+s_1|}, \quad r_2(x;s_1,s_2) = \frac{-s_1(x-s_1)-s_2^2}{\sqrt{s_1^2-s_2^2}|x-s_1|}. \tag{A24}$$

Note that we consider the case $s_1>0$, $s_2>0$, $x\geqslant 0$, and $s_1^2-s_2^2-x^2\geqslant 0$ in this paper.

Finally J_3 is written as

$$J_3(u,v) = \sum_{k=0}^{5} a_{3,k}\{f_k(u) - f_k(v)\} + \int_v^u dq_3(l_3 - q_3)H(l_1,l_2;\sqrt{d^2 - q_3^2}) + \int_v^u dq_3(l_3 - q_3)H(l_2,l_1;\sqrt{d^2 - q_3^2}), \quad \text{(A25)}$$

where $a_{3,k}$ are given by

$$a_{3,1} = -\frac{2l_1^2l_2^2 + 2\pi l_1 l_2 d^2 + d^4}{8}, \quad a_{3,3} = \frac{\pi l_1 l_2 + d^2}{4},$$

$$a_{3,5} = -\frac{1}{8}, \quad a_{3,2i} = -l_3 a_{3,2i+1} \quad (i = 0,1,2).$$

Each of the last two terms of Eq. (A25) is similar to Eq. (A19). Therefore, we can obtain Eq. (A11) explicitly, that is, it is possible to compute $\tilde{Z}_{c,3}$ from Eqs. (A3)–(A9) with Eqs. (A12), (A18), (A19), and (A25). Moreover $Z_{c,3}$ is easily obtained from $\tilde{Z}_{c,3}$ by using Eq. (19).

APPENDIX B: PROBABILITY DISTRIBUTION OF $q_{1,1}$

The probability distribution of $q_{1,1}$ is given by Eq. (25). Let us first consider the case $\sqrt{\Sigma_{j=2}^D l_j^2} < d$. If $q_{1,1} \leqslant q_{2,1}$ initially, $q_{1,1}(t) \leqslant q_{2,1}(t)$ for all $t>0$. In this case, we write Eq. (25) as

$$\begin{aligned} n_D(q) &= \frac{1}{\tilde{Z}_{c,D}(l_1,\ldots,l_D;d)} \int_0^{l_1} dq_{1,1} \int_0^{l_1-q_{1,1}} dq_1 \int_0^{l_2-q_2} dq_{1,2} \int_0^{l_2} dq_2 \cdots \int_0^{l_D-q_D} dq_{1,D} \int_0^{l_D} dq_D \Theta\left(\sqrt{\sum_{j=1}^{D} q_j^2} - d\right)\delta(q_{1,1}-q) \\ &= \frac{1}{\tilde{Z}_{c,D}(l_1,\ldots,l_D;d)} \int_0^{l_1-q} dq_1 G(q_1) \equiv F(q), \end{aligned} \quad \text{(B1)}$$

where $G(q_1)$ is given by

$$G(q_1) = \begin{cases} \tilde{Z}_{c,D-1}(l_2,\ldots,l_D;\sqrt{d^2-q_1^2}), & q_1 < d, \\ \prod_{j=2}^{D} (l_j^2/2), & q_1 \geqslant d. \end{cases} \quad \text{(B2)}$$

If $q_{1,1} > q_{2,1}$ initially, $q_{2,1}(t) \leqslant q_{1,1}(t)$ for all $t>0$ and we have naturally from a symmetry argument that

$$n_D(q) = F(l_1 - q). \quad \text{(B3)}$$

When $\sqrt{\Sigma_{j=2}^D l_j^2} \geqslant d$, both cases $q_{1,1}(t) \leqslant q_{2,1}(t)$ and $q_{1,1}(t) > q_{2,1}(t)$ are possible and we obtain $n_D(q)$ as

$$\begin{aligned} n_D(q) &= \frac{1}{2\tilde{Z}_{c,D}(l_1,\ldots,l_D;d)} \Bigg\{ \int_0^{l_1} dq_{1,1} \int_0^{l_1-q_{1,1}} dq_1 \int_0^{l_2-q_2} dq_{1,2} \int_0^{l_2} dq_2 \cdots \int_0^{l_D-q_D} dq_{1,D} \int_0^{l_D} dq_D \Theta\left(\sqrt{\sum_{j=1}^{D} q_j^2} - d\right)\delta(q_{1,1}-q) \\ &\quad + \int_0^{l_1} dq_{1,1} \int_{-q_{1,1}}^{0} dq_1 \int_0^{l_D-q_2} dq_{1,2} \int_0^{l_2} dq_2 \cdots \int_0^{l_D-q_D} dq_{1,D} \int_0^{l_D} dq_D \Theta\left(\sqrt{\sum_{j=1}^{D} q_j^2} - d\right)\delta(q_{1,1}-q) \Bigg\} \\ &= \frac{F(q) + F(l_1 - q)}{2}. \end{aligned} \quad \text{(B4)}$$

So we can express $n_D(q)$ from the configurational partition functions $Z_{c,D}$ and $Z_{c,D-1}$.

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