Statistical mechanics of two hard disks in a rectangular box

Toyonori Munakata
Department of Applied Mathematics and Physics, Kyoto University, Kyoto 606, Japan

Gang Hu
Department of Physics, Beijing Normal University, Beijing 100875, People's Republic of China

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A system of two hard disks in a rectangular box is studied based on the exact partition function and equilibrium distribution functions of particles. Box-size dependence of some quantities of interest, such as pressure and the particle distribution functions, is investigated and in particular the negative compressibility of the van der Waals type and the corresponding phase transition are analyzed in detail. This system turns out to have rich structures that are related to the ergode-nonergode transitions in this system.

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As is well known, chaos and ergodicity [1,2] serve as a bridge linking mechanics and statistics. This bridge is not limited to many-body systems, a main field for application of statistical mechanics. Currently, some few-body systems gather considerable attention in this regard and for few-body hard-core (or disk) systems, entropy [3], the thermodynamic second law [4], and a phase transition [5] are discussed to mention a few.

We consider a system composed of two identical hard disks put in a rectangular box, which was studied by Awazu [5] with a molecular dynamics (MD) method and a liquid-solid-like transition [6] with negative compressibility was observed to exist. It is noted, however, that without explicit analysis, the understanding of the mechanism underlying the interesting behavior is not complete and the purpose of this paper is to study the system by entirely analytical computation and understand the van der Waals features in the large density case statistical mechanically.

We denote the diameter of a hard disk by d and a horizontal (vertical) length of the rectangular box by $l_x+d(l_y+d)$. It is remarked that as l_x is decreased from above d to below d, the system naturally shows an ergode-nonergode transition, in which a particle occupying the upper part of the box is kept from going into the lower part when l_x becomes smaller than d. In order to take into account the particle-wall interaction, we introduce the coordinate system (x,y), in which x and y can take values in the range $0\leqslant x\leqslant l_x$ and $0\leqslant y\leqslant l_y$, respectively. With use of (x,y), the distribution function of the position coordinates $\{x_i,y_i(i=1,2)\}$ is simply given by $p(x_1,y_1;x_2,y_2)=1/Z_c$ for $R\equiv[(x_1-x_2)^2+(y_1-y_2)^2]^{1/2}\geqslant d$ and $p(x_1,y_1;x_2,y_2)=0$ for $R<d$. Here, the configurational partition function $Z_c(l_x,l_y)$ normalizes the probability distribution function by

$$\int dx_1dx_2dy_1dy_2p(x_1,y_1;x_2,y_2)=1.$$

Let us consider the probability distribution functions $f(x)$ and $g(y)$ for the relative coordinates $x=x_2-x_1$ and $y=y_2-y_1$, which were numerically obtained before [5]. For example, $f(x)$ is defined by

$$f(x)\equiv\int dx_1dx_2dy_1dy_2p(x_1,y_1;x_2,y_2)\,\delta(x-[x_2-x_1]).$$

It is convenient to divide the space (l_x,l_y) into four regions, $l_x\geqslant d,l_y\geqslant d$ (region I), $l_x\geqslant d,l_y<d$ (region II), $l_x<d,l_y\geqslant d$ (region III), and $l_x<d,l_y<d$ (region IV). Simple symmetry consideration reveals that in the region I and IV, $f(x)$ and $g(y)$ are even and we have

$$f_{\mathrm{I}}(x|l_x,l_y)=g_{\mathrm{I}}(x|l_y,l_x),\quad f_{\mathrm{IV}}(x|l_x,l_y)=g_{\mathrm{IV}}(x|l_y,l_x),\tag{1}$$

where size dependence of the functions f and g is shown explicitly. In regions II, $g(y)$ is even and $f(x)$ is to be treated only for, e.g., $l_x\geqslant x\geqslant 0$, since two particles cannot change their left-right relationship in the course of time. Symmetry consideration tells us that

$$g_{\mathrm{III}}(y|l_x,l_y)=f_{\mathrm{II}}(y|l_y,l_x),\quad g_{\mathrm{II}}(y|l_x,l_y)=f_{\mathrm{III}}(y|l_y,l_x).\tag{2}$$

We start from region I. When $l_x\geqslant x\geqslant d$, the contribution to $f(x)$ from $\int dy_1$ and $\int dy_2$ is l_y^2 and from the relation $0\leqslant x_1\leqslant l_x-x$, the contribution from x_1 integration is (l_x-x). Thus we have

$$f(x)=l_y^2(l_x-x)/Z_c\quad(d\leqslant x\leqslant l_x).\tag{3}$$

When $0\leqslant x\leqslant d$ and if we confine the contribution to $f(x)$ from the region $y_1\leqslant y_2$, we have the factor $l_y-[y_1+(d^2-x^2)^{1/2}]$ from y_2 integration and this is first integrated from 0 to $l_y-(d^2-x^2)^{1/2}$ over y_1 and then multiplied by l_x-x as the contribution from x_1 integration. Finally, this is to be multiplied by 2 since the region $y_1\geqslant y_2$ gives precisely the same contribution as above to $f(x)$. Thus immediately we have

$$f(x)=(l_x-x)[l_y-(d^2-x^2)^{1/2}]^2/Z_c\quad(0\leqslant x\leqslant d).\tag{4}$$

Noting that $f(x)$ is even in x, we obtain Z_c from the condition $\int_{-l_x}^{l_x}f(x)=1$ to be

$$Z_c(l_x,l_y)=l_y^2(l_x-d)^2+2\int_0^d[l_y-(d^2-y^2)^{1/2}]^2(l_x-y)dy$$
$$=l_x^2l_y^2-\pi d^2 l_x l_y+(4/3)(l_x+l_y)d^3-d^4/2. \quad (5)$$

In region II $f(x)$ is considered only in region $0\leqslant x\leqslant l_x$ as noted before. Note that x cannot be smaller than $x_{min}\equiv(d^2-l_y^2)^{1/2}$. In the region $d\leqslant x\leqslant l_x$, $f(x)$ is given as before by Eq. (3). When $x_{min}\leqslant x\leqslant d$, $f(x)$ is given by Eq. (4), that is,

$$f(x)=(l_x-x)[l_y-(d^2-x^2)^{1/2}]^2/Z_c \quad (x_{min}\leqslant x\leqslant d), \quad (6)$$

$$f(x)=0 \quad (0\leqslant x\leqslant x_{min}). \quad (7)$$

From the normalization condition $\int_0^{l_x}f(x)dx=1$, we have

$$Z_c(l_x,l_y)=l_y^2(l_x-d)^2/2+2\int_{\sqrt{d^2-l_y^2}}^d[l_y-(d^2-y^2)^{1/2}]^2\times(l_x-y)dy$$
$$=l_x^2l_y^2/2-l_y^4/12+2l_xd^3/3+l_y^2d^2/2-l_xl_yd^2\theta-l_x\times(l_y^2+2d^2)(d^2-l_y^2)^{1/2}/3, \quad (8)$$

where $\sin\theta=l_y/d$. As l_y approaches d from below d in Eq. (8) and from above d in Eq. (5), we notice that $Z_c(l_x,l_y\uparrow d)=Z_c(l_x,l_y\downarrow d)/2$, reflecting the nonergode-ergode transition at $l_y=d$. As to the probability distribution function of $y\equiv y_2-y_1$, it is easily obtained that

$$g(y)=(l_y-|y|)[l_x-(d^2-y^2)^{1/2}]^2/(2Z_c) \quad (0\leqslant|y|\leqslant l_y). \quad (9)$$

The results for region III are easily obtained from Eq. (2).

Finally, let us consider region IV. If $l_x^2+l_y^2\leqslant d^2$, the box can contain only one particle. For $l_x^2+l_y^2>d^2$, we have four ergodic components (if we regard two particles distinguishable), in each of which two particles are distributed along one of two diagonal lines of the box. The distribution function $f(x)$ of the relative coordinate x_2-x_1 (>0) is given by

$$f(x)=(l_x-x)[l_y-(d^2-x^2)^{1/2}]^2/(2Z_c) \quad [(d^2-l_y^2)^{1/2}\leqslant x\leqslant l_x], \quad (10)$$

$$f(x)=0 \quad [0\leqslant x\leqslant(d^2-l_y^2)^{1/2}]. \quad (11)$$

Z_c is calculated from $\int_0^{l_x}f(x)=1$ to have

$$Z_c(l_x,l_y)=(1/2)\int_{\sqrt{d^2-l_y^2}}^{l_x}[l_y-(d^2-y^2)^{1/2}]^2(l_x-y)dy$$
$$=l_x^2l_y^2/4-(l_x^4+l_y^4)/24+(l_x^2+l_y^2)d^2/4+l_xl_yd^2(\pi/2-\theta_1-\theta_2)/2-(d^2-l_y^2)^{1/2}[d^2l_x/3+l_xl_y^2/6]-(d^2-l_x^2)^{1/2}[d^2l_y/3+l_yl_x^2/6]+d^4/8, \quad (12)$$

where $\sin\theta_1=l_x/d$ and $\sin\theta_2=l_y/d$. It is easily confirmed that as l_x goes to d in Eq. (8); the Z_c is twice the Z_c obtained from Eq. (12) in the same limit. This is due to the ergode-nonergode transition additional to the one already mentioned just below in Eq. (8). It is noted, however, that there is no discontinuity in pressure, defined below by Eq. (14), as is readily seen from Z_c expressed by integral forms in Eqs. (5), (8), and (12).

Now we turn to the equation of state of our system. The configurational part of the entropy S_c is given by

$$S_c(l_x,l_y)=k_B\ln Z_c(l_x,l_y), \quad (13)$$

where k_B denotes the Boltzmann constant. Pressure on the wall is expressed by

$$p_x(l_x,l_y)=T\partial S_c/\partial l_x, \quad p_y(l_x,l_y)=T\partial S_c/\partial l_y, \quad (14)$$

with T the temperature of the system. For hard-disk systems T determines only a time scale and hereafter we put $k_B=1$, and $T=1$ for simplicity. It is remarked that our system is thermodynamically characterized by (l_x,l_y) and from symmetry $p_x(l_x,l_y)=p_y(l_y,l_x)$.

The unisotropic pressure obtained by MD experiments [5] in some part of (l_x,l_y) region $(l_y>d)$ was confirmed to be consistent with our analytic results of Eq. (14). As examples, some p_x for $l_y>d$ are shown in Fig. 1 as a function of l_x. We notice that the pressure p_x on the side (left or right) walls shows the van der Waals characteristics for $d<l_y<l_{y,c}$ where $l_{y,c}$ $(=2.106d)$ denotes the (upper) critical value of l_y to be discussed later. In contrast, p_y only monotonically decreases with l_x for $l_y>d$.

Usually the van der Waals behavior is ascribed to an interplay between the short-range repulsion and the long-range attraction in the interatomic potential [7]. The long-range attraction tends to reduce the pressure on the wall by means of a slight density increase inside the container of the gas. The hard-disk system shown in Fig. 1 is highly compressed and inhomogeneous. In Fig. 2, we plot, for $l_y/d=1.2$, the probability distribution function of x coordinate of a particle $n_x(x)$, defined by

$$n_x(x)\equiv\int dx_1dy_1dy_2p(x_1,y_1;x,y_2).$$

In this compact packing, generally particles are located near the wall and the central part of the box is less populated. As l_x/d decreases from 1.2 to 1.0, the n_x $(x=l_x)$, that is, the density at the side wall, first increases and then decreases, showing a (local) maximum around $l_x/d\simeq1.1$. This property of local density variation is in accord with the variation of pressure p_x shown in Fig. 1 $(l_y/d=1.2)$. Thus we consider that the density at a wall, which is determined through complicated packing of hard disks in a small rectangular box, is the main factor for the van der Waals behavior of p_x in Fig. 1. In contrast to n_x $(x=l_x)$, n_y $(y=l_y)$ turned out to increase monotonically as l_x/d is decreased from 1.2 to 1 for $l_y/d=1.2$. It is noted that whenever we observed the van der

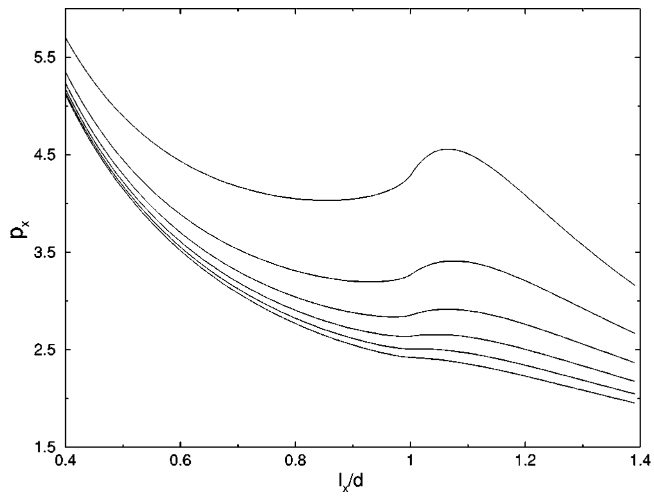

FIG. 1. Pressure on the vertical wall $p_x(l_x,l_y)$ for various l_y values as functions of l_x. From the upper curve, $l_y/d=1.2$, 1.4, 1.6, 1.8, 2.0, and 2.2. Temperature T and the Boltzmann constant are both set equal to one and the pressure is nondimensional.

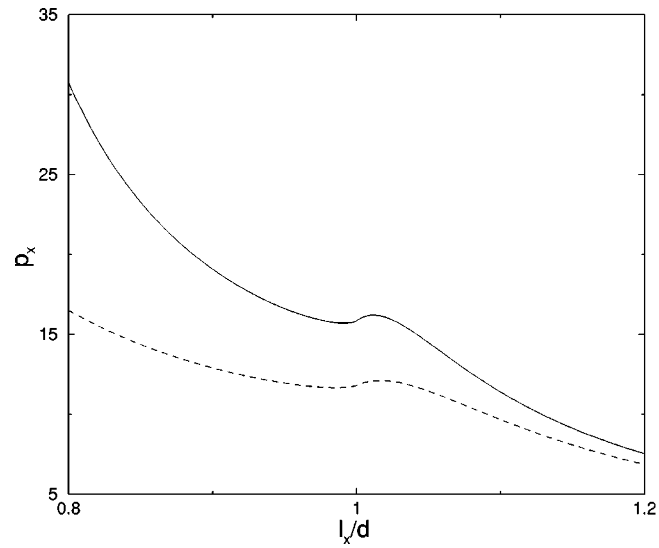

FIG. 3. l_x dependence of p_x for $l_y/d=0.75$ (full curve) and $l_y/d=0.85$ (dashed curve).

Waals behavior we simultaneously observed the similar nonmonotonic behavior of particle density at the wall.

Qualitatively we may understand this van der Waals behavior as follows: First let us express p_x as

$$p_x=(1-W)p_{n\text{-}con}+Wp_{con}, \tag{15}$$

where W denotes the probability of two particles being in contact with each other along the x axis, i.e., $|x_2-x_1|$ is around d, and p_{con} the pressure in this situation which is larger than $p_{n\text{-}con}$ for the noncontact case. As l_x becomes small from $l_x \gg d$, p_x increases due to the increase of both p_{n-con} and p_{con}. Under further compression, p_x decreases first due to drastic decrease of W and Wp_{con} and then increases due to increase of $p_{n\text{-}con}$ ($W \simeq 0$), resulting in the van der Waals behavior. A similar argument, if applied to the l_x dependence of p_y, can explain the monotonic behavior mentioned above.

We now proceed to the region $l_y<d$, which was not investigated before. Just as for the case $l_y>d$, we observed the van der Waals behavior for $p_x(l_x,l_y)$ as shown in Fig. 3. This is also qualitatively explained based on Eq. (15). That is, under a closely packed situation, the van der Waals behavior may result from the change in packing mechanism, which accompanies the ergode-nonergode transition. This is in sharp contrast with the many-body hard-core system for which there is no distinction between a gas and a liquid. In the region $l_y<d$, there is an unstable region, in which the compressibility from p_x becomes negative (see Fig. 3). As for p_y, we only observed a monotonous gaslike behavior for variation in l_x.

Collecting the results presented above for $p_x(l_x,l_y)$, we show in Fig. 4 the phase diagram in the (l_x,l_y) plane. The

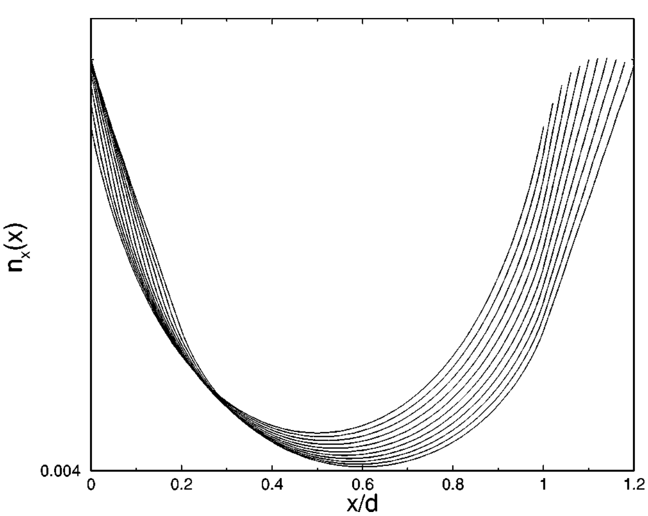

FIG. 2. Density profile $n_x(x)$ for $l_y/d=1.2$ and l_x in the range between 1.0 and 1.2 with the increment $\Delta l_x=0.02$. It is noted that x is in the range $0<x<l_x$.

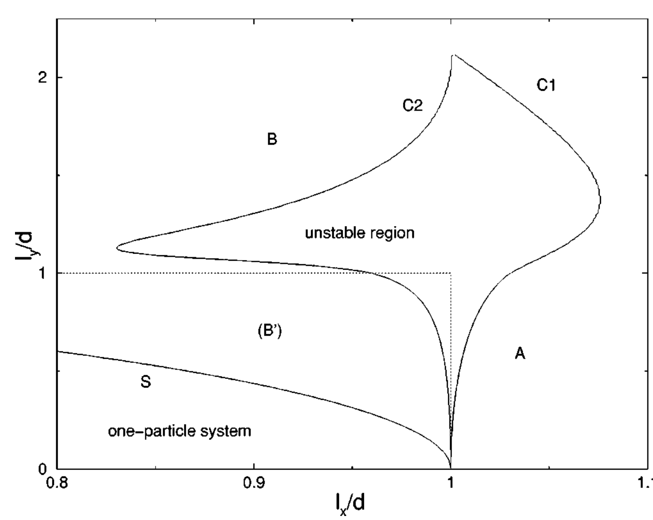

FIG. 4. Phase diagram in the (l_x,l_y) space.

two curves $C1$,$C2$ from $(d,\ l_{y,c})$ to $(d,0)$ determine the unstable region, in which the compressibility becomes negative. One may call the region *A*, which is either to the right of $C1$ or above the line $l_y = l_{y,c}$, a gas phase and the region *B*, which is left to $C2$, below the line $l_y = l_{y,c}$ and above *S*, a liquid phase. Inside the curve $S = (l_x, l_y)$: $l_x^2 + l_y^2 = d^2$, the system can contain only one particle. However in region *B*, if we distinguish a fully constrained region B': $l_x < d, l_y < d$ from the remaining half-constrained region $l_y > d$ in *B*, one may call the system in B' a solid phase and the transition below the line $l_y < d$ becomes the gas solid one. We note that this phase diagram comes from the system response, more explicitly, the response of p_x to l_x variation, p_y does not show any instability. If we study the response to l_y variation, then p_y shows instability and we only need to change the coordinates from the symmetry mentioned just below Eq. (14).

Finally, we comment on the probability distribution functions $f(x)$ and $g(y)$ for the relative positions. As a situation interesting from the viewpoint of application of the analytic expression for these functions, we consider that l_y/d is larger than 1 and l_x/d becomes gradually small and approaches 1. In order for the particle located in the upper part to exchange positions with the one in the lower part, the transition state, $y \equiv y_2 - y_1 = 0$ must be crossed. If we put $l_x/d = 1 + \epsilon$ with $0 < \epsilon \ll 1$, it is readily obtained from Eqs. (1) and (4) that $g(y=0)$ approaches ϵ^2, showing that it takes a long time of the order ϵ^{-2} for two particles to exchange their relative (upper-lower) positions and this results in the slow relaxation observed in Ref. [5].

In this paper we considered a system composed of two hard disks based on analytic expressions for the partition function and some probability distribution functions. A system of two particles, which shows ideal or low-density gas properties if put in a box with large volume or under the periodic boundary condition, behaves quite differently in a compressed situation and shows a gas-liquid or a liquid-solid-like transition. Packing is one of the most important factors controlling properties of dense liquids [8] and amorphous substances (glass) [9,10]. Thus, we believe that investigation of properties of a few-body system packed in a small box might give important insights on condensed matter physics. Along this line some properties of a three-disk system and a thin two-dimensional *N*-particle system will be dicussed in the near future.

[1] E. Ott, *Chaos in Dynamical Systems* (Cambridge University Press, Cambridge, 1993).

[2] L. E. Reichl, *The Transition to Chaos* (Springer-Verlag, Berlin, 1992).

[3] Z. Zheng, G. Hu, and J. Zhang, Phys. Rev. E **53**, 3246 (1996).

[4] Gang Hu, Zhigang Zheng, Li Yang, and Wei Kang, Phys. Rev. E **64**, 045102(R) (2001).

[5] A. Awazu, Phys. Rev. E **63**, 032102 (2001).

[6] This is best called a gas-liquid transition for reasons to be clarified later.

[7] L. E. Reichl, *A Modern Course in Statistical Physics* (University of Texas Press, Austin, 1980).

[8] J. P. Hansen and I. R. MacDonald, *Theory of Simple Liquids* (Academic Press, New York, 1986).

[9] *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1989).

[10] E. Donth, *The Glass Transition* (Springer-Verlag, Berlin, 2001).