Statistical mechanics of two hard disks in a rectangular box

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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 $0 \leq x \leq l_x$ and $0 \leq y \leq l_y$, 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 $R = [(x_1 - x_2)^2 + (y_1 - y_2)^2]^{1/2} \geq d$ 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

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

It is convenient to divide the space $(l_x, l_y)$ into four regions, $l_x \geq d, l_y \geq d$ (region I), $l_x \geq d, l_y < d$ (region II), $l_x < d, l_y \geq d$ (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

$$f_d(x | l_x, l_y) = g(x | l_x, l_y), \quad f_{IV}(x | l_x, l_y) = g_{IV}(x | l_x, l_y).$$

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., $l_x \geq x > 0$, since two particles cannot change their left-right relationship in the course of time. Symmetry consideration tells us that

$$g_{II}(y | l_x, l_y) = f(y | l_x, l_y), \quad g_{IV}(y | l_x, l_y) = f_{IV}(y | l_x, l_y).$$

We start from region I. When $l_x \geq x \geq d$, the contribution to $f(x)$ from $f_{I}(x)$ and $f_{II}(y)$ is $l_x^2$ and from the relation $0 \leq x \leq l_x - x$, the contribution from $x_1$ integration is $(l_x - x)$. Thus we have

$$f(x) = l_x^2/l_x(x - x)/Z_c \quad (d \leq x \leq l_x).$$

When $0 \leq x \leq d$ and if we confine the contribution from $f(x)$ from the region $y_1 \leq y_2$, we have the factor $l_x - [y_1 + (d^2 - x^2)^{1/2}]$ from $y_2$ integration and this is first integrated from 0 to $l_x - (d^2 - x^2)^{1/2}$ 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 $y_1 \geq y_2$ gives precisely the same contribution as above to $f(x)$. Thus immediately we have

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

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
\[ Z_c(l_x, l_y) = l_x^2 l_y^2 - 12 l_x l_y + 21 l_x^2 l_y^2 - 4 l_x^3 l_y^2 \]
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

\[
p_x = (1 - W) p_{n\text{-con}} + W p_{\text{con}},
\]

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 \( p_{\text{con}} \) the pressure in this situation which is larger than \( p_{n\text{-con}} \) for the noncontact case. As \( l_x \) becomes small from \( l_x > d \), \( p_x \) increases due to the increase of both \( p_{n\text{-con}} \) and \( p_{\text{con}} \). Under further compression, \( p_x \) decreases first due to drastic decrease of \( W \) and \( W p_{\text{con}} \) and then increases due to increase of \( p_{n\text{-con}} \) (\( W \approx 0 \)), 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
two curves $C1,C2$ from $(d, l_y)$ 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 $l_y = l_y,e$, 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 $l_x>d$ 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 $l_x/l_d$ is larger than 1 and $l_y/l_d$ becomes gradually small and approaches 1.

In order for the particle located in the upper part to exchange positions with one in the lower part, the transition state, $y = y_2 - y_1 = 0$ must be crossed. If we put $l_x/l_d = 1 + \epsilon$ with $0<\epsilon<1$, it is readily obtained from Eqs. (1) and (4) that $g(y=0)$ approaches $\epsilon^2$, showing that it takes a long time of the order $\epsilon^{-2}$ 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 discussed in the near future.

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