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Molecular Dynamics Studies of Two Hard-Disk Particles in a Rectangular Box I. Thermodynamic Properties and Position Autocorrelation Functions

Soong-Hyuck Suh†, Jae-Wook Lee*, Hee Moon and James M. D. MacElroy*****

Department of Chemical Engineering, Keimyung University, Daegu 704-701, Korea
*Department of Chemical Engineering, Seonam University, Namwon 590-711, Korea
**Faculty of Applied Chemistry, Chonnam National University, Gwangju 500-757, Korea
***Centre for Synthesis and Chemical Biology, the Conway Institute of Biomolecular and Biomedical Research, Department of Chemical Engineering, University College Dublin, Belfield, Dublin 4, Ireland
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Abstract−Molecular dynamics simulations have been carried out for the simple few-body systems of two hard-disk particles confined within a 2-dimensional rectangular box. Wall pressures, the collision frequencies, density profiles, two-particle probability distributions, and position autocorrelation functions were computed to examine the thermodynamic, structural and time-dependent properties of such systems. Excellent agreement was found between simulation results and theoretical predictions recently proposed by Munakata and Hu. Detailed dynamic effects are also discussed to describe configurational particle trajectories including fast/slow relaxation processes observed in the position autocorrelation functions.

Key words: Molecular Dynamics Simulations, Finite Few-Body Systems, Thermodynamic Properties, Position Autocorrelation Functions

INTRODUCTION

With the declaration of initiatives and the proposal of an implementation plan in the field of nanotechnology [Roco et al., 2000], recent research areas in chemical engineering have placed increasing emphasis on molecular-based applications, where nanoscaled-level approaches could be employed for tailoring and design of nanomaterials for specific use. Professor Hyun-Koo Rhee and his collaborators were among the first to recognize the importance of this perspective in engineering science and emphasized the requirement of coordinated work in fundamental research, its application and its ultimate development [Park et al., 2000; Oh et al., 2001; Lee and Rhee, 2002; Suh and Rhee, 2003].

This article, dedicated to Professor H.-K. Rhee, is concerned with molecular simulation studies to investigate the thermodynamic, structural and time-dependent properties of two hard-disk particles confined in a 2-dimensional rectangular box. In the field of theory, modeling and simulation, the most significant advances applicable to nanotechnologies have been associated with the advent of more powerful computers and relevant theoretical approaches in statistical mechanics. Molecular simulation by means of either Monte Carlo (MC) or molecular dynamics (MD) calculations have been accepted as the most satisfactory basis for a better understanding and interpretation of molecular systems [Allen and Tildesley, 1993]. In fact, the results obtained from molecular simulations have provided the thermodynamic and transport properties of nanoscaled materials for performing leading edge research at the atomic or molecular level [MacElroy and Suh, 2001; MacElroy et al., 2001].

In the usual many-body systems, statistical mechanical definitions are related to the so-called thermodynamic limit, where the system volume and the number of particles tend to infinity while the number density is kept fixed in the thermodynamic sense. In more recent years, considerable attention has focussed on the study of finite, few-body, systems, and more rigorous treatments are possible by means of analytical considerations and computer simulations. Quite different effects emerge in finite systems, which are not observed in the infinite bulk behavior. For instance, in a system of finite hard disks confined within a circular cavity, Nemeth and Lowen [1998] have reported a transition from ergodic to non-ergodic behavior referred to as ergodicity breaking with a concomitant dynamical crossover from hydrodynamic relaxation to particle exchange hopping. In the theoretical and MC simulation studies of Kegel et al. [1999], the grand distribution function of small systems of hard spheres was calculated by applying an exact relation between the available volume and the partition function. Interestingly, at a certain point, it was found that the available volume increased with increasing number of particles, and the steep increase for small systems indicated the signature of a first-order freezing transition.

As one of the simplest finite few-body systems, Awazu [2001] has investigated the thermodynamic properties and the position autocorrelation functions for a system composed of two hard disks in a 2-dimensional rectangular box using the MD computational method. In this simulation work, a relation similar to the van der Waals instability detected from the negative compressibility was observed between the width of the box and the pressure at the sidewalls. More recently, the corresponding phase transition, mainly due to ergodic/non-ergodic structural changes of confined particles, was analyzed theoretically based on the exact partition function and its related

†To whom correspondence should be addressed.
E-mail: shsuh@kmu.ac.kr
‡This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

equilibrium distribution functions [Munakata and Hu, 2002].

For comparison purpose with theory and simulations, we have revisited this model system via the MD simulation method. It turns out that there are rich structural and correlation properties in space and time in such a simple system. The model employed in this work, together with the MD computational details, is introduced in the next section. In this section a brief description of the theoretical approach proposed by Munakata and Hu [2002] is also included. We present our MD results in the following section, where various statistical and dynamic properties are calculated over a wide range of box sizes. Simulation results for the wall pressure and the probability distribution functions are directly compared to test the applicability of the corresponding theoretical predictions. The correlation functions of colliding particles in space and time are also determined for the position autocorrelation functions. Such time-dependent properties are of particular interest because they can provide specific details for particle motions in the confined geometry.

THEORY AND COMPUTATIONS

We consider a simple system consisting of two hard-disk particles, having the same particle diameter d, confined within a 2-dimensional rectangular box. Here, the four walls of the rectangular box are assumed to be rigid, and the box width and the height are denoted as L_x and L_y, respectively.

As mentioned in the previous section, such a 2-dimensional model system has been investigated analytically by Munakata and Hu [2002] based on the configurational partition function and its related equilibrium distribution functions. In their statistical mechanical approach, the partition function Z_c can be characterized by the two parameters of the effective box size, $l_x(\equiv L_x-d)$ and $l_x(\equiv L_y-d)$. The final results for Z_c in their analysis are summarized as follows:

$$Z_c(l_x\ge d, l_y\ge d) = l_x^2 l_y^2 - \pi l_x l_y d^2 + \frac{4(l_x+l_y)d^3}{3} - \frac{d^4}{2}, \tag{1}$$

$$Z_c(l_x\ge d, l_y< d) = \frac{l_x^2 l_y^2}{2} - \frac{l_y^4}{12} + \frac{2l_x d^3}{3} + \frac{l_x^2 d^2}{2} - l_x l_y d^2 \sin^{-1}\left(\frac{l_y}{d}\right) - \frac{l_x(l_y^2+2d^2)\sqrt{d^2-l_y^2}}{3}, \tag{2}$$

$$Z_c(l_x< d, l_y< d) = \frac{l_x^2 l_y^2}{4} - \frac{l_x^4+l_y^4}{24} + \frac{(l_x^2+l_y^2)d^2}{4} + \frac{d^4}{8} + \frac{l_x l_y d^2}{2}\left(\frac{\pi}{2} - \sin^{-1}\left(\frac{l_x}{d}\right) - \sin^{-1}\left(\frac{l_y}{d}\right)\right) - \sqrt{d^2-l_y^2}\left(\frac{l_x d^2}{3} + \frac{l_x l_y^2}{6}\right) - \sqrt{d^2-l_x^2}\left(\frac{l_y d^2}{3} + \frac{l_x^2 l_y}{6}\right). \tag{3}$$

For Eq. (2) with the relationship of symmetry, one may remark that

$$Z_c(l_x< d, l_y\ge d) = Z_c(l_y\ge d, l_x< d). \tag{4}$$

It is also worth noting from Eq. (1) to Eq. (3) that

$$Z_c(l_x> d, l_y = d^+) = 2Z_c(l_x\ge d, l_y< d^-). \tag{5}$$

and

$$Z_c(l_x = d^+, l_y< d) = 2Z_c(l_x = d^-, l_y< d). \tag{6}$$

For the conditions expressed in Eqs. (5) and (6), the confined geometry itself reflects the ergodic/non-ergodic transition at l_x=d for a fixed l_y, or at l_y=d for a fixed l_x.

Statistical thermodynamic properties can be obtained starting from the partition function with the aid of fundamental thermodynamic relationships. For example, the configurational part of the entropy S can be expressed as

$$S(l_x, l_y) = k_B \ln Z_c(l_x, l_y), \tag{7}$$

where k_B represents the Boltzmann constant, and the wall pressure, P_x and P_y, at the given temperature T, can be written as

$$P_i(l_x, l_y) = T\frac{\partial S(l_x, l_y)}{\partial l_i} = k_B T\frac{(\partial Z_c)/(\partial l_i)}{Z_c} \quad (i=x, y). \tag{8}$$

We note that, in contrast to the functional behavior of the configurational partition function in Eqs. (5) and (6), there is no discontinuity at l_x=d or at l_y=d for the resulting pressure equation because the discontinuity factor is cancelled out between the numerator and the denominator terms in Eq. (8).

Theoretical results determined from Eq. (8) can be compared directly with the *exact* machine-experimental data obtained from either MC or MD simulations for such a precisely defined model system. To this end together with more detailed statistical investigations in space and time, we have carried out MD simulations in a manner similar to that originally proposed by Alder and Wainwright for hard-core systems [Alder and Wainwright, 1959]. The hard-wall collisions with the boundaries of the box were treated by the rule of elastic specular scattering, in which the tangential component of velocities to the collision plane was preserved but the normal component of velocities was changed. Post-collisional velocities for colliding particles were also assigned according to specular collision dynamics. The MD computational algorithm employed in this work is described elsewhere in our earlier studies for hard-sphere fluids in cylindrical [Suh and MacElroy, 1986; MacElroy and Suh, 1987] and spherical pore systems [Suh et al., 1998; Kim and Suh, 2000].

Thermodynamic, structural and time-dependent properties were evaluated during our MD simulations, including wall pressures, collision frequencies, density profiles, two-particle probability distributions, and the position autocorrelation functions. Each simulation run was, at a given condition, conducted for a total of 20 million collisional events. The MD results reported in the next section were all scaled to reduced dimensionless quantities, by using the unit hard-disk diameter d, the unit particle mass m, and the unit thermal energy k_BT. In this system of units, the translational kinetic energy of the particles in *total* is scaled to 2, which should be conserved during the MD simulations regardless of the system input parameters for the box size.

RESULTS AND DISCUSSION

In Fig. 1, MD results for the wall pressure are presented as a function of L_x at a given condition of L_y. The wall pressure was evaluated from the time average of the instantaneous momentum changes arising during each particle collision with the walls of the box per unit length per unit time. For the side-wall (left and right) pressure P_x, as displayed in Fig. 1(a), exhibits sharp local maxima near L_x~2.0-2.1 with decreasing box length L_y. For systems of smaller L_y-values, it is found that there are more pronounced unstable regions where the volume compressibility becomes negative. This anisotropic pres-

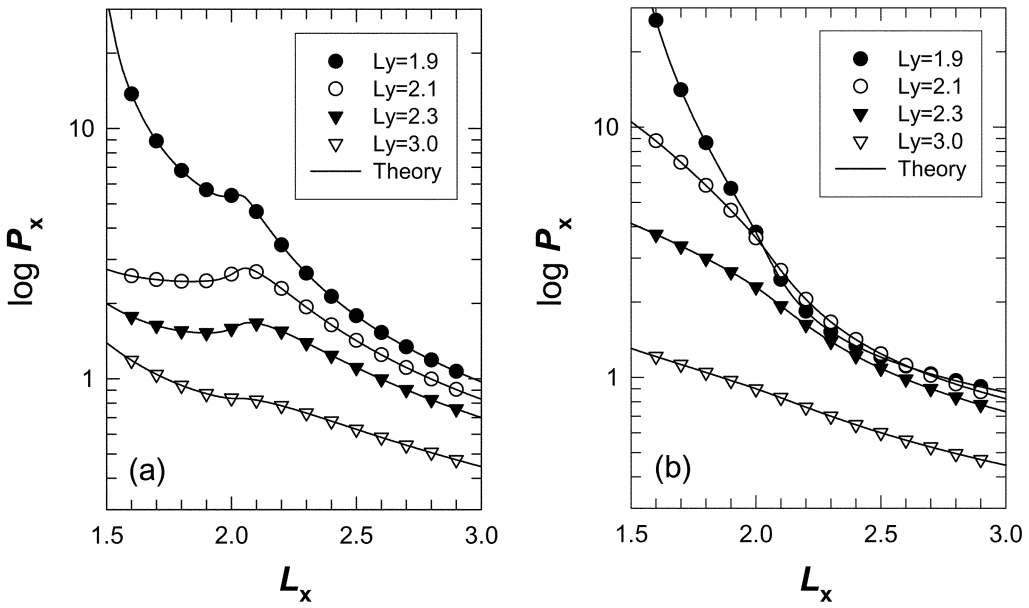

Fig. 1. (a) The x-wall (left and right) pressures P_x and (b) the y-wall (upper and lower) pressures P_y as a function of L_x. The solid lines correspond to theoretical predictions by Munakata and Hu [2002].

sure behavior in the L_x vs. P_x curves is indicative of the ergodic/non-ergodic phase transition, which is dominated by the purely geometric constraint in the hard-wall system. This pressure curve (or, the equation of state) is similar to the van der Waals loop of a liquid/vapor transition or the Alder loop of a solid/fluid transition at high densities for bulk hard-sphere systems. In contrast to the L_x-P_x relationship, the L_x vs. P_y curves decrease monotonically with increasing L_x-values, as can be seen in Fig. 1(b) for the wall pressure on the upper and lower walls. We note here that such pressure behavior arises from the system responses of P_x and P_y to the variations in L_x. It is obvious that, with variations in L_y the P_y curve will display a pressure instability, which (at fixed L_x) is absent in the P_x curve.

Also shown as the solid curves in Fig. 1 are theoretical predictions evaluated from the configurational partition function and its pressure relationship proposed by Munakata and Hu [2002]. Theoretical results for the wall pressure P_x and P_y through Eq. (1) to Eq. (8) are shown to be in excellent agreement with the MD simulation results. Such an exact expression can only be derived for systems containing only a few particles, particularly in the case of N= 2. For N>2, possible configurations become more complex, even in the simple hard-disk system, and massive computations are required to evaluate the corresponding thermodynamic partition function for large N. In the previous work of Awazu [2001], the rectangular Sinai model was employed to calculate the wall pressure analytically based on the correlated cell approximation [Alder et al., 1963; Dellago and Posch, 1996]. For this Sinai model, P_x has a maximum value independent of L_y, and there is one singular point exactly at L_x=2.0. This model approximation may explain the wall pressure behavior only qualitatively, but not quantitatively.

In Fig. 2, collision frequencies per unit time determined during our MD simulations are illustrated for the x-wall collisions, ω_{wx}, [Fig. 2(a)], the y-wall collisions, ω_{wy}, [Fig. 2(b)], and the particle/particle collisions, ω_p, [Fig. 2(c)]. The excluded volume effect on colliding particles becomes evident when the size of the box size is small, and the resulting characteristics of the wall collision frequencies in Figs. 2(a) and 2(b) are shown to be very similar to those of the matching wall pressures in Figs. 1(a) and 1(b). For the x-wall collision frequencies, as also observed in the wall pressure behavior, locally developed maxima are gradually reduced when the box height L_y is decreased, and nearly disappear for the system L_y=3.0. The y-wall collision frequencies do not indicate such inhomogeneous behavior but decay monotonically with increasing box width L_x.

One interesting observation from Figs. 1(b) and 2(b) is that, in the region of $2.1 \le L_x \le 2.6$, the y-wall collision frequencies and relevant wall pressures for the case L_y=1.9 are smaller than those for L_y=2.1 (Note that the frequencies and the pressures displayed in Figs. 1 and 2 are scaled in logarithmic units.). This, at first sight, appears to be a counterintuitive result and implies that, during a fixed time interval, the smaller the system the smaller the collision probability against the wall. This behavior can be explained from both geometric and dynamic points of view. When the sum of two hard-disk diameters is equal to or less than the box height ($L_y \le 2.0$), confined particles in the box cannot change their positions in the horizontal x-direction. On the other hand, in systems of less stringent confinement ($L_y > 2.0$), two particles may move freely, exchanging their spatial positions with each other along the x-direction. In addition to this geometric effect, more frequent collisions with the wall can arise during position overtaking processes, particularly when the box length is slightly larger than two particle diameters. These phenomena are not limited to the finite few-body system, and a similar observation, namely the dynamic chattering effect, was also made in previous MD studies of hard-sphere fluids and mixtures in cylindrical microcapillaries [Suh and MacElroy, 1986; MacElroy and Suh, 1987]. Such dynamic chattering effects between two colliding particles could explain, at least qualitatively, restricted or hindered diffusion processes when the size of confined particles approaches that of the effective pore radius in nanoporous systems.

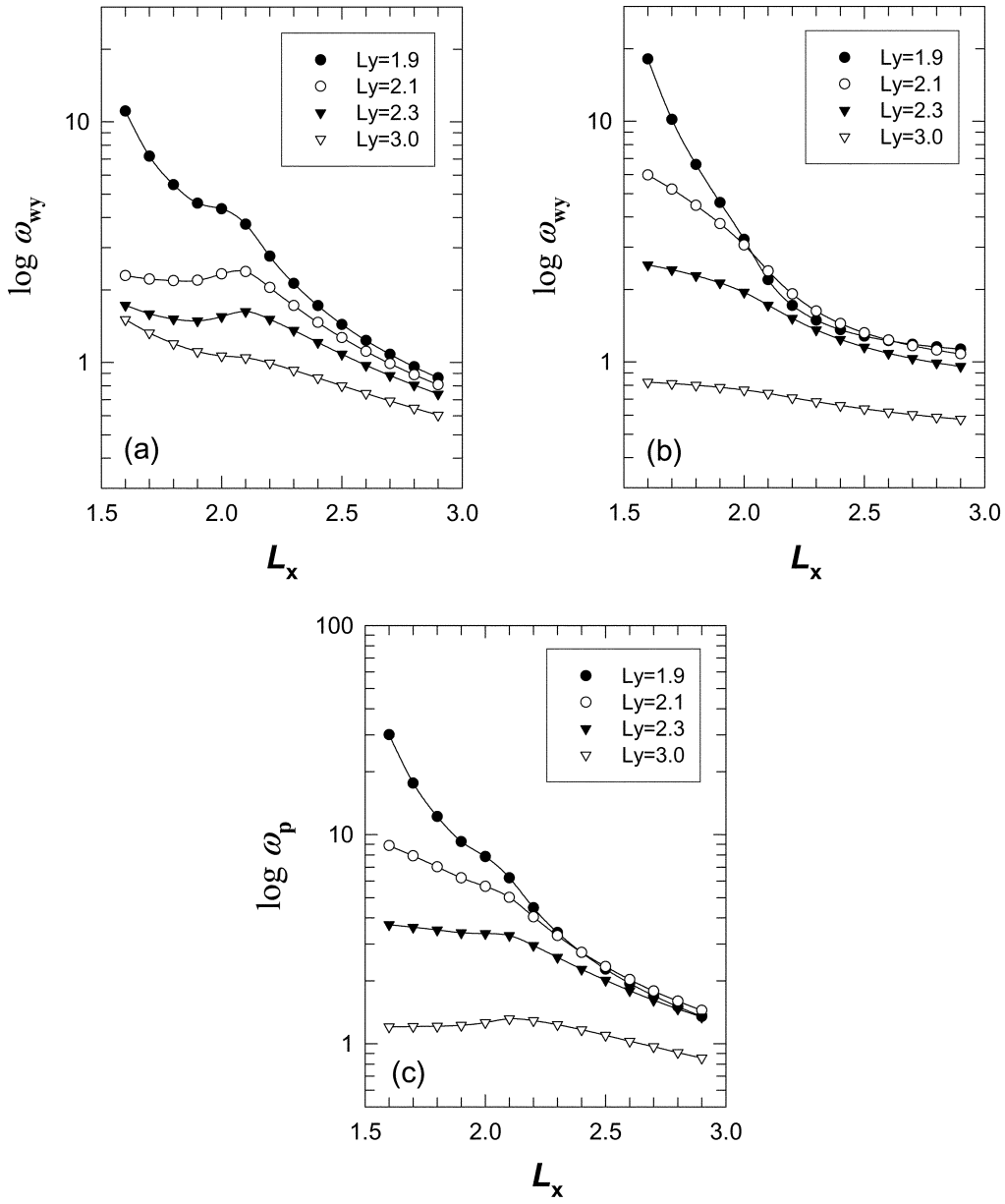

Fig. 2. (a) The x-wall collision frequencies ω_{wx}, (b) the y-wall collision frequencies ω_{wy} and (c) the particle/particle collision frequencies ω_p as a function of L_x. The solid lines are only a guide to the eye.

In statistical thermodynamics, it is easily shown that, as in bulk systems, the wall pressure is directly related to the wall contact value of the equilibrium one-particle density profile

$$P_i = k_B T n_i\left(\frac{L_i - d}{2}\right) \quad (i=x, y) \tag{9}$$

Here, $n_x(x)$ is the density profile in the x-direction, which satisfies

$$L_y \int_{L_x/2}^{L_x/2} n_x(x)dx = N, \tag{10}$$

and, for the density profile in the y-direction, $n_y(y)$,

$$L_x \int_{L_y/2}^{L_y/2} n_y(y)dy = N. \tag{11}$$

Furthermore, we consider the equilibrium two-particle probability distributions $\rho_x(x)$ and $\rho_y(y)$ for the relative coordinates $x \equiv x_1 - x_2$ and $y \equiv y_1 - y_2$. These probability functions can be also numerically obtained from MD computations by sorting the relative distance between the centers of two hard-disk particles. The required conditions for such probability distributions are

$$\int_{-L_x}^{L_x} \rho_x(x)dx = 1, \tag{12}$$

and

$$\int_{-L_y}^{L_y} \rho_y(y)dy = 1. \tag{13}$$

The density profiles and probability distribution functions in Eqs. (10) to (13) are all even functions, and, in Figs. 3 and 4, we have illustrated them only in the half-interval.

For the system L_y=2.3, we plot one-particle density profiles $n_x(x)$

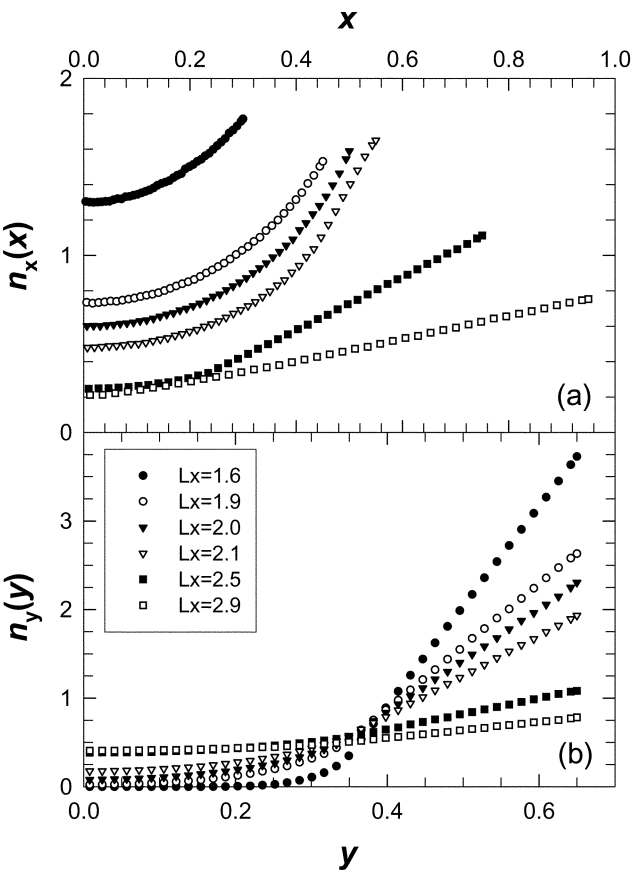

Fig. 3. (a) The density profiles $n_x(x)$ as a function of x and (b) the density profiles $n_y(y)$ as a function of y for the system L_y= 2.3.

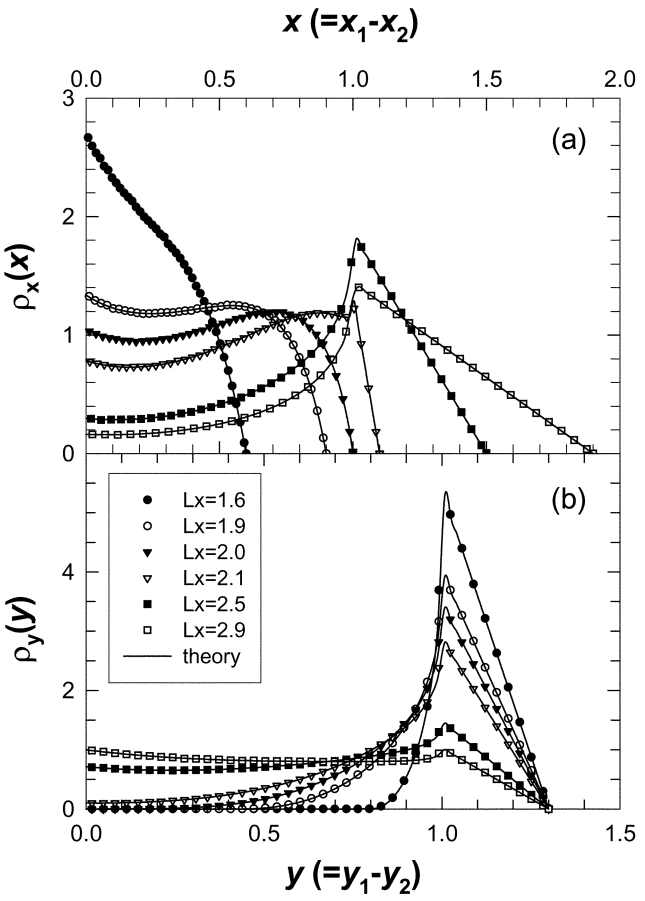

Fig. 4. (a) The two-particle probability distributions $\rho_x(x)$ as a function of $x \equiv x_1 - x_2$ and (b) the two-particle probability distributions $\rho_y(y)$ as a function of $y \equiv y_1 - y_2$ for the system L_y= 2.3. The solid lines correspond to theoretical predictions by Munakata and Hu [2002].

in Fig. 3(a) and $n_y(y)$ in Fig. 3(b), respectively. It is observed that, for smaller (or, more compact) systems, the central part of the box (x, y=0) is less populated and more particles are located near the wall. The variations in the contact density at the wall in this figure are found to be closely matched with the variations in the wall pressures (see, Fig. 1). We have independently measured the wall pressure value, as expressed in Eq. (9), from the contact value extrapolated to the wall, and compared the resulting MC-type wall pressures with MD wall pressures obtained from the time average of momentum exchanges in the wall collisions. There were, depending on the curvature of density profiles, some marginal errors of approximately 3-5% mainly due to the difficulties involved in the extrapolation to the fluid/wall contact point [Allen and Tildesley, 1987].

The corresponding two-particle probability distributions, $\rho_x(x)$ and $\rho_y(y)$, are illustrated in Fig. 4 for the same system L_y=2.3 as in Fig. 3. Also shown in this figure as the solid curves are the theoretical predictions by Munakata and Hu [2002]. Again, as in the case of the wall pressure in Fig. 1, excellent agreement with the MD simulations confirms the high quality of their analytical approach. The peak maxima in $\rho_x(x)$ are shown to be dependent on L_x, while the local maxima in $\rho_y(y)$ are seen to be independently located near y≈ 1.0. For L_x=1.6, the probability distributions are larger near x≈0 [Fig. 4(a)] and y≈1 [Fig. 4(b)], indicative of a favorable layering configuration. As the L_x-values increase, the vertically favored configuration is changed to a diagonally favored one. For the case L_x= 2.5 and beyond this range, $\rho_x(x)$ and $\rho_y(y)$ exhibit wide uniform distributions, and the particle trajectories for larger L_x- and L_y-values can be regarded as random 2-dimensional motions.

The relaxation of fluctuations described by correlation functions in space and time can lead to important insights into the collision dynamics in confined systems of different geometries [Murthy and Singer, 1987]. During our MD simulations we have computed the position autocorrelation function (PACF), $C_{rr}(t)$, expressed as

$$C_{rr}(t) = \left\langle \frac{1}{N}\left(\sum_{i=1}^{N} \mathbf{r}_i(t) \cdot \mathbf{r}_i(0) \right) \right\rangle, \tag{14}$$

where the symbol <...> denotes the ensemble average over the time origin t=0. Three kinds of PACFs were computed and these are defined with respect to correlations in the x-coordinate, $C_{xx}(t)$, the y-coordinate, $C_{yy}(t)$, and both coordinates, $C_{rr}(t)$ as explicitly written in Eq. (14).

In Figs. 5 and 6, we have illustrated the various PACFs as functions of t for the systems L_y=2.1 and L_y=2.3, respectively (note that these autocorrelation functions are presented as the normalized forms calculated by dividing the original correlation functions by their

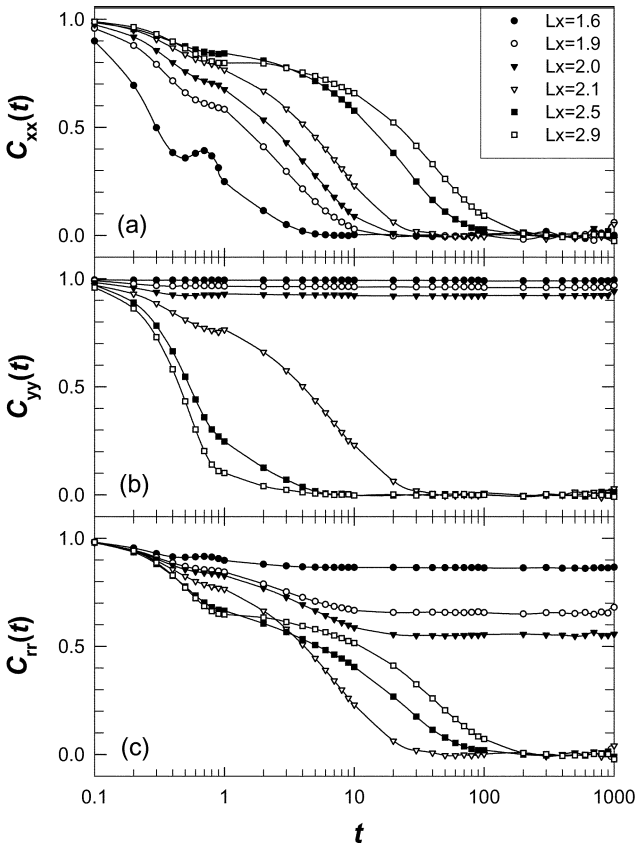

Fig. 5. (a) The x-coordinate position autocorrelation functions $C_{xx}(t)$, (b) the y-coordinate position autocorrelation functions $C_{yy}(t)$, and (c) the total position autocorrelation functions $C_{rr}(t)$ as functions of t for the system L_y=2.1. The solid lines are only a guide to the eye.

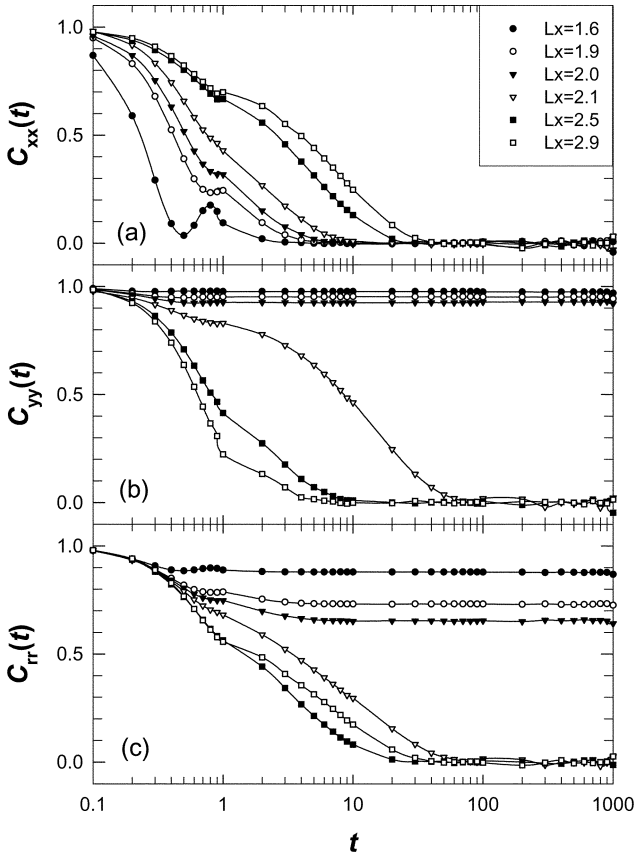

Fig. 6. The same as in Fig. 5 but for the system L_y=2.3.

zero time values). From these figures we observe the following: (i) In the solid-like state, the PACFs have a finite positive value because two hard-disk particles cannot exchange their positions, (ii) the PACFs drop off rapidly in the fluid-like state where particle positions are available over all configurational space, and (iii) In the intermediate range between the solid/fluid states, the PACFs exhibit a plateau due to relaxation processes resulting from the collisions between the two hard disk particles. One of the most striking features displayed in both Figs. 5(a) and 6(a) is the appearance of local maxima for systems with $L_x \leq 2.0$. A relatively large local maximum is clearly observed in $C_{xx}(t)$, for example, near t=0.7 for L_x= 1.6 and L_y=2.1, and near t=0.8 for L_x=1.6 and L_y=2.3. This indicates frequent discontinuous jumping motions (or, hopping-like motions) horizontally in the x-direction. As the box width increases towards L_x=2.0, this maximum is reduced in size and shifts towards slightly longer times. Such hopping-like motions in the vertical y-direction are not detected in $C_{yy}(t)$ [Fig. 5(b) and Fig. 6(b)] because the L_y-values in both cases are greater than 2.0.

One last interesting point is also observed in $C_{rr}(t)$ in Fig. 5(c) and Fig. 6(c), which is related to fast/slow relaxation processes within the confined system. Comparing the cases L_x=2.1 and L_x=2.5 for L_y=2.1 in Fig. 5(c), the PACF for L_x=2.1 exhibits a slower relaxation in the short time region than that for L_x=2.5. However, after approximately t≈3, the PACF for L_x=2.1 starts to relax faster than that for L_x=2.5. A corresponding relaxation transition process is not observed for the system L_y=2.3 shown in Fig. 6(c). This suggests that, at a certain condition, configurational positions in larger systems are more strongly correlated than in smaller systems. Under these conditions the overtaking processes decrease with increasing box size within a given time period which is longer than the mean time between particle collisions. Such fast/slow relaxation processes can be one of the characteristic features observed in finite few-body system, which may not appear in infinite, many-body systems.

CONCLUSION

In the present work we have investigated one of the simplest few-body systems consisting of two hard-disk particles, confined within a 2-dimensional rectangular box, by means of molecular dynamics simulations. A range of thermodynamic, structural and time-dependent properties were calculated during the MD simulations, including wall pressures, collision frequencies, density profiles, two-particle probability distributions, and position autocorrelation functions. The MD simulation results are also compared with theoretical predictions, recently proposed by Munakata and Hu [2002], based on the configurational partition function and its related equilibrium distribution functions. Excellent agreement with the MD results for the wall pressures and related structural properties confirms the accuracy of their predictions both qualitatively and quantitatively. Even for such a simple finite few-body system, the structural and correlation properties exhibit a complex and rich physical behavior in

both space and time. The density at the wall, which is structured through a complicated packing of hard-disk particles in a small rectangular box, is the main factor influencing the van der Waals instability observed in the corresponding wall pressure. In addition to this structural effect, the greater frequency of collisions with the wall, which ultimately results in dynamic chattering effects, enhances the local peak maxima in the wall pressure curve. Detailed dynamical effects are also discussed relating to fast/slow relaxation processes of colliding hard-disk particles as observed in the position autocorrelation functions. We are currently investigating similar properties for more realistic interaction systems, and the results of these studies will be reported in future work.

REFERENCES

Alder, B. J. and Wainwright, T. E., "Studies in Molecular Dynamics. I. General Method," *J. Chem. Phys*., **31**, 459 (1959).

Alder, B. J., Hoover W. G. and Wainwright, T. E., "Cooperative Motion of Hard Disks Leading to Melting," *Phys. Rev. Lett.*, **11**, 241 (1963).

Allen, M. P. and Tildesley, D. J., "Computer Simulation of Liquids," Clarendon Press, Oxford (1987).

Allen, M. P. and Tildesley, D. J. (eds.), "Computer Simulation in Chemical Physics," Kluwer Academic Publishers (1993).

Awazu, A., "Liquid-Solid Phase Transition of a System with Two Particles in a Rectangular Box," *Phys. Rev. E*, **63**, 032102 (2001).

Dellago, Ch. and Posch, H. A., "Lyapunov Instability, Local Curvature, and the Fluid-Solid Phase Transition in Two-Dimensional Particle Systems," *Physica A*, **230**, 364 (1996)

Kegel, W. K., Reiss, H. and Lekkerkerker, H. N. W., "Freezing Transition in Very Small Systems of Hard Spheres," *Phys. Rev. Lett.*, **83**, 5298 (1999).

Kim, S.-C. and Suh, S.-H., "Adsorption of Multi-Component Hard Sphere Fluids in Micropores," *Mol. Phys*., **99**, 81 (2001).

Lee, H.-T. and Rhee, H.-K., "Steam Tolerance of Fe/ZSM-5 Catalyst for the Selective Catalytic Reduction of NO_x," *Korean J. Chem. Eng*., **19**, 574 (2002).

MacElroy, J. M. D. and Suh, S.-H., "Computer Simulation of Moderately Dense Hard-Sphere Fluids and Mixtures in Microcapillaries," *Mol. Phys.*, **60**, 475 (1987).

MacElroy, J. M. D. and Suh, S.-H., "Equilibrium and Nonequilibrium Molecular Dynamics Studies of Diffusion in Model One Dimensional Micropores," *Microporous and Mesoporous Mat*., **48**, 195 (2001).

MacElroy, J. M. D., Pozhar, L. A. and Suh, S.-H., "Self-Diffusion in a Fluid Confined within a Model Nanopore Structure," *Colloids and Surf. A*, **187**, 493 (2001).

Munakata, T. and Hu, G., "Statistical Mechanics of Two Hard Disks in a Rectangular Box," *Phys. Rev. E*, **65**, 066104 (2002).

Murthy, C. S. and Singer, K., "Description of the Molecular Trajectories in Simple Liquids," *J. Phys. Chem*., **91**, 21 (1987).

Nemeth, Z. T. and Lowen, H., "Freezing in Finite Systems: Hard Discs in Circular Cavities," *J. Phys.: Condens. Matter*, **10**, 6189 (1998).

Oh, H.-S., Kang, K.-K., Kim, M.-H. and Rhee, H.-K., "Synthesis of MFI-Type Zeolites Under Atmospheric Pressure," *Korean J. Chem. Eng*., **18**, 113 (2001).

Park, S.-H., Lee, J.-H. and Rhee, H.-K., "Disproportionation of 1,2,4-Trimethylbenzene over Zeolite NU-87," *Korean J. Chem. Eng*., **17**, 198 (2000).

Roco, M. C., Williams, R. S. and Alivisatos, P. (eds.), "Nanotechnology Research Directions," Kluwer Academic Publishers (2000); also on website http://itri.loyola.edu/nano/IWGN.Research.Directions/

Suh, S.-H. and MacElroy, J. M. D., "Molecular Dynamics Simulation of Hindered Diffusion in Microcapillaries," *Mol. Phys*., **58**, 445 (1986).

Suh, S.-H., Heo, N.-H. and Nicholson, D., "Knudsen Diffusion in the Sequentially Linked Spherical Pores," *J. Chem. Eng. Japan*, **31**, 644 (1998).

Suh, Y.-W. and Rhee, H.-K., "Synthesis of Stable Mesostructured Zirconia: Tween Surfactant and Controlled Template Removal," *Korean J. Chem. Eng*., **20**, 65 (2003).