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Molecular Dynamics Studies of Two Particles in a Rectangular Box: Hard-Sphere and Square-Well Interactions

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Abstract. Molecular dynamics simulations have been carried out for the simple few-body systems of two particles confined within a 2-dimensional rectangular box. The two different sets of interaction potentials between the colliding particles were employed in these studies: hard-sphere and square-well interactions. Wall pressures, the wall/particle and the particle/particle collision frequencies, and the position autocorrelation functions were computed to examine the thermodynamic, structural and time-dependent properties of such systems. Detailed dynamic effects are discussed to describe configurational particle trajectories including fast/slow relaxation processes observed in the position autocorrelation functions.

Keywords: molecular dynamics simulation, finite few-body system, hard-sphere, square-well

1. Introduction

Whether it is solid-like or fluid-like, the behavior of particles, or molecules, confined within a given structural system is often of significant importance in science and engineering applications, e.g., nanoporous and microporous materials such as carbon nanotubes, zeolites, and porous metal oxide compounds for heterogeneous catalysts and separation processes. From a simple structural point of view, the behavior will be solid-like if the particle center-of-mass positions are restricted to sub-nanometer spatial fluctuations and they cannot exchange their positions with neighboring particles. In a fluid-like phase, particles are subject to less stringent confinement and may move freely, exchanging their positions with each other.

In the usual many-body systems, the statistical mechanical definition is 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 to be fixed in the thermodynamic sense. In recent years, it has been gathered considerable attention to study the finite few-body systems, and more rigorous treatments are possible by means of analytical considerations and computer simulations (Nemeth and Lowen, 1998; Gonzalez et al., 1998; Roman et al.,

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1999, 2003; Cao et al., 2004). There have been observed quite different effects in the finite few-body systems, which are not emerged in the infinite bulk behavior. For instances, in the system of the finite hard disks in a circular cavity, Nemeth and Lowen (1998) have reported the transition from ergodic to non-ergodic behavior called the ergodicity breaking, and the dynamical crossover from hydrodynamic relaxation to particle exchange hopping.

As one of the simplest finite few-body systems, Awazu (2001) has studied the thermodynamic, structural and time-dependent properties for a system composed of two hard disks in the two-dimensional rectangular box using the molecular dynamics (MD) computational method. In his simulation work, it was observed a relation similar to the van der Waals instability detected from the negative compressibility between the width of the box and the pressure at the sidewalls. More recently, the corresponding phase transition was analyzed theoretically based on the exact partition function and its related equilibrium distribution function (Munakata and Hu, 2002). In the present work we have investigated this model system for both hard-sphere and square-well particles via the MD simulation method. In such a simple system, MD results can provide details for molecular motions in the confined geometry. The finite few-body MD results obtained in this work would be interest to compare with previous simulation studies for many particle systems at very low densities (Papadopoulos et al., 1999).

2. Computational Method

We consider the simple system of two particles in a two-dimensional rectangular box. Here, the four walls of the box are assumed to be rigid, and the box width and the height are L_x and L_y in units of the hard-sphere diameter σ, respectively. Two different sets of interaction potentials between the colliding particles were employed: hard-sphere (HS) and square-well (SW) interactions. The SW potential of differing both the well depth ε and the well width λ can cover a wide range of systems from sticky hard spheres (very narrow and deep wells) to the van der Walls limit (very wide and shallow wells). For our SW systems, we have chosen a fixed λ-value of 1.5 σ for the well width, and two conditions for the well depth ($\varepsilon/k_BT = -0.8$ for the attractive SW system and $\varepsilon/k_BT = +0.8$ for the repulsive SW system). Here k_B and T denotes the Boltzmann constant and the system temperature, respectively.

Molecular dynamics (MD) simulations were conducted in a manner similar to that described originally by Alder and Wainwright for hard-core systems (1959). The hard wall collisions with the boundaries of the box were treated via the normal rules of elastic specular scattering. The MD computational algorithm employed in this work is described elsewhere in our earlier simulation work for confined fluids in the cylindrical (Suh and MacElroy, 1986; MacElroy and Suh, 1987) and the spherical pore systems (Suh et al., 1998; Kim and Suh, 2001). For the purpose of direct comparison between the HS and the SW systems, the SW results were scaled to the same HS temperature by adjusting the averaged kinetic energy of the SW systems to that of the HS systems. The trajectories for each of simulation runs were 20 million collision steps in total. Our MD results reported in the next section were scaled to all reduced dimensionless quantities, using the unit hard-disk diameter σ, the unit particle mass m, and the unit thermal energy k_BT. Under this unit system, the total system energy is scaled to 2, which should be conserved during MD simulations regardless of system input parameters for the box size.

3. Results and Discussion

In Fig. 1(a) and (b), MD results for the wall pressure are illustrated as a function of L_x at a given condition of L_y for the x-wall (left and right) pressure P_x and the y-wall (upper and lower) pressure P_y, respectively. 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.

The HS simulation results for both P_x and P_y are found to be in excellent agreement with theoretical predictions evaluated from the configurational partition function and its thermodynamic relationship (Munakata and Hu, 2002). For the side-wall pressure P_x, as displayed in Fig. 1(a), sharp local maxima develop near $L_x \sim 2.0$ with decreasing the box length L_y. For the systems of smaller L_y-values, it is shown that there are larger unstable regions where the volume compressibility becomes negative. This anisotropic pressure behavior in the L_x vs. P_x curves indicates the ergodic/non-ergodic phase transition, which is dominated by the geometric constraint in the confined system. The pressure curve (or, the equation of

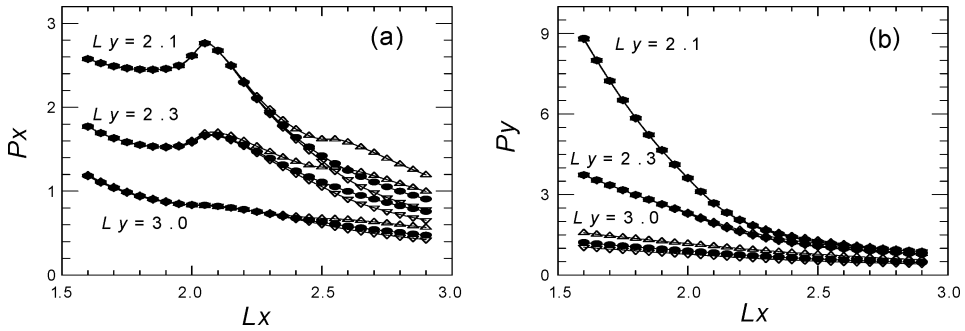

Figure 1. (a) The x-wall (left and right) pressures P_x, and (b) The y-wall (upper and lower) pressures P_y as a function of L_x. The symbol of solid circles, lower triangles, and upper triangles correspond to the hard-sphere, the attractive square-well and the epulsive square-well systems, respectively.

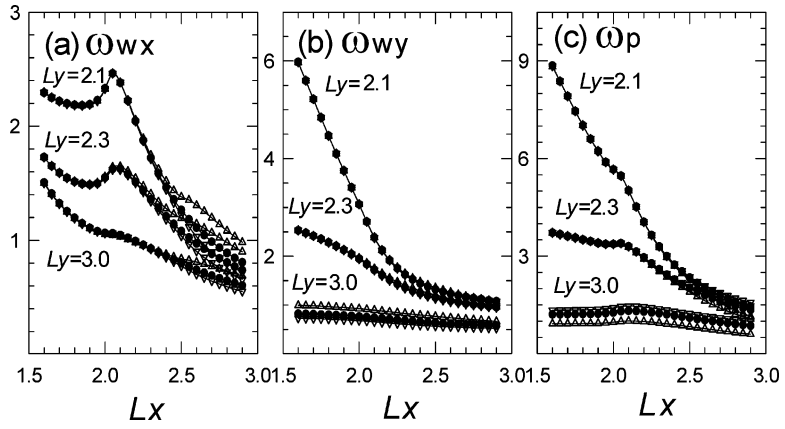

Figure 2. (a) The x-wall collision frequencies ω_{wx}, (b) The y-wall collision frequencies ω_{wy}, and (c) the particle/particle collision frequencies ω_p as a function of L_x. The symbols are as defined in Fig. 1.

state) in Fig. 1(a) is similar to the van der Waals loop of liquid/vapor transition or the Alder loop of solid/fluid transition for bulk hard-sphere systems at high densities near the random close packing. In the repulsive SW system, the weak secondary peak is also observed near $L_x \sim 2.5$ for the systems of $L_y = 2.1$, which indicates a structural change due to the repulsive collisions between the SW particles. This peak reduces in importance with increasing L_y-values, and eventually disappears as the box length L_y approaches a value of 3.0.

In contrast to the L_x-P_x relationship, as can be seen in Fig. 1(b), the L_x vs. P_y curves decrease monotonically with increasing the L_x-values. For the smaller systems of $L_y = 2.1$ and $L_y = 2.3$, it is observed that the y-wall pressure for both repulsive and attractive SW systems are similar with that of the HS system and their behaviors are close each other, particularly when the box size is small. For the larger systems of $L_y = 3.0$, however, the repulsive SW particles promote wall collisions while the attractive SW interactions enhance more frequent collisions between the particles rather than with the wall. This leads to lower wall pressures for the attractive SW system and higher wall pressures for the repulsive SW system. We note here that such pressure behaviors come from the system responses of P_x and P_y to the variations of L_x. It is obvious that, under the variations of L_y but a fixed value of L_x, the P_y curve will display the pressure instability behavior, but not for the P_x curve.

In Fig. 2, collision frequencies per unit time determined during our MD simulations are displayed 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)), respectively. The exclusion volume effect on colliding particles becomes evident when the box size is small, and the resulting characteristics of the wall collision frequencies in Figs. 2(a) and (b) are shown to be very similar to those of the matching wall pressures in Figs. 1(a) and (b). For the x-wall collision frequencies, as also observed in the wall pressure behavior in Fig. 1(a), the locally developed maxima are gradually reduced when the box height L_y is getting smaller, and nearly disappeared at the systems of $L_y = 3.0$. The y-wall collision frequencies in Fig. 2(b) do not indicate such inhomogeneous behaviors but decay monotonically with increasing the box width L_x. As can be deduced from the particle/particle collision frequencies in Fig. 2(c), the hard-core collision dynamics are dominant for the small system, whereas the soft-core collision dynamics are getting more significant with increasing the system size. This tendency is clearly illustrated in the case of $L_y = 3.0$.

During our MD simulations we have computed the normalized position autocorrelation function (PACF), which is defined as $\text{PACF}(t) = \langle \mathbf{r}(t).\mathbf{r}(0)\rangle / \langle \mathbf{r}(0).\mathbf{r}(0)\rangle$ where $\mathbf{r}(t)$ represents the particle position vector at a given time t and the symbol $\langle \ldots \rangle$ denotes the ensemble average over the time origin $t = 0$. We present several PACFs as a function of t for the systems of $L_y = 3.0$ in Fig. 3(a) and $L_x = 2.05$ in Fig. 3(b), respectively. The following remarks emerge from these figures: (i) In the solid-like state, PACFs have a finite positive value because two hard-disk particles cannot exchange their positions, (ii) PACFs drop off rapidly in the fluid-like state where particle positions are available over all configurational space, and (iii) In the intermediate between the solid/fluid states, PACFs have the signals of the plateau due to the relaxation process between two colliding particles. It can be regarded as a solid-like state for $L_x = 2.0$ and $L_y = 3.0$, and a fluid-like state for $L_x = 2.5$ and $L_y = 3.0$ in Fig. 3(a). For the systems of $L_x = 2.1$ in Fig. 3(a) and $L_x = 2.05$ in Fig. 3(b) the relaxation process is apparent where the overtaking motion between the colliding particles are sterically hindered. In the case of $L_y = 3.0$ in Fig. 3(b) the PACFs display a fast relaxation in the short time region, after which a slow relaxation starts. As we increase L_y-values, the PACFs tend to decay more rapidly during the particle collision time, and subsequently the trajectories of the moving particles are more correlated. This implies that the overtaking probabilities are becoming progressively smaller with increasing L_y-values.

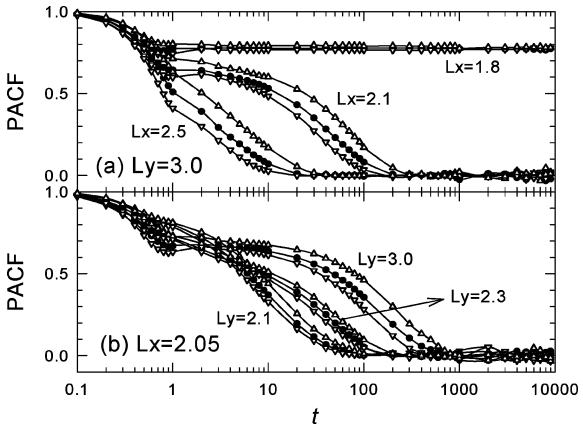

Figure 3. The position autocorrelation functions as a function of t. The symbols are as defined in Fig. 1.

In Fig. 4 we illustrate the typical trajectories of the center of one particle for the few selected runs in the case of $L_y = 3.0$. The particle trajectories displayed in this figure are plotted during 2,000 collision events. When the sum of two particle diameters is equal or less than the box width ($L_x \leq 2.0$), confined particles in the box cannot change their positions in the horizontal x-direction (HS with $L_x = 1.8$ in Fig. 4(a)). On the other hand, in the systems of less stringent confinement ($L_x > 2.0$), two particles may move freely, exchanging their spatial positions with each other along the x-direction (attractive SW with $L_x = 2.5$ in Fig. 4(b)). Under those conditions more frequent collisions among particles could be occurred during the position overtaking processes, particularly when the box length is slightly larger than two particle diameters. This effect is also indicated evidently in Fig. 2(c), where the particle/particle collision frequencies tend to increase near $L_x = 2.0$ for the system of $L_y = 3.0$. In addition to this geometric effect, the particle trajectories can be dominated by collision dynamics, depending on the nature of system interactions (repulsive SW with $L_x = 2.05$ in Fig. 4(c)). In this case the fast/slow relaxation processes are largely related to discontinuous jumping motions, or hopping-like motions. These phenomena is not limited to the finite few-body system, and a similar observation, namely the dynamic chattering effect, was also made in our previous MD studies of the hard-sphere fluids and mixtures in the cylindrical microcapillaries (Suh and MacElroy, 1986; MacElroy and Suh, 1987) and model one-dimensional nanopores (MacElroy and Suh, 2001; MacElroy et al., 2001). Such

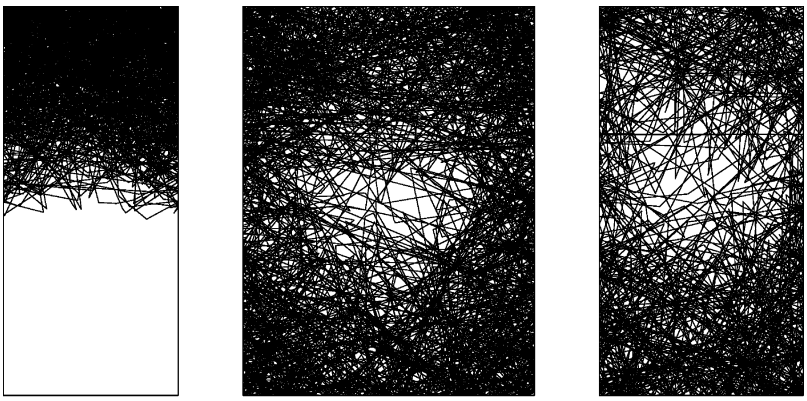

Figure 4. Typical trajectories of the center of one particle during 2,000 collision events for $L_y = 3.0$. (a) hard-sphere with $L_x = 1.8$, (b) attractive square-well with $L_x = 2.5$, and (c) repulsive square-well with $L_x = 2.05$.

dynamic chattering effects between two colliding particles could explain, at least qualitatively, the restricted or hindered diffusion processes when the size of confined particles approaches to that of the effective pore radius in nanoporous systems.

4. Conclusion

In the present work we have investigated one of the simplest few-body systems consisting of two confined particles within a two-dimensional rectangular box by means of molecular dynamics simulations. In such a simple finite few-body system, it turns out to have rich structural and correlation properties in space and time. For the small system the wall pressure shows the anisotropic behavior due to the ergodic/non-ergodic transition, which is similar with the van der Waals instability loop. The weak secondary peak is observed for the system of repulsive SW interactions. It is found that the addition of repulsive interactions between particles gives rise to the negative van der Waals instability, which is originated from the packing. The hard-core collision dynamics are dominant for the small system, whereas the soft-core collision dynamics are getting more significant with increasing the system size. In addition to the structural effect, more frequent dynamic collisions with the wall, namely dynamic chattering effects, could enhance the local maxima peak in the wall pressure curve. Detailed dynamic effects are also discussed with fast/slow relaxation processes of colliding particles as observed in the position autocorrelation functions.

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