



*Dedicated to Professor Ionel Haiduc  
on the occasion of his 75<sup>th</sup> anniversary*

## THEORY AND SIMULATION OF TRANSPORT PROPERTIES FOR PENETRABLE-SPHERE MODEL SYSTEMS: I. SELF-DIFFUSION

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Molecular dynamics simulations have been performed to investigate the transport properties of self-diffusion coefficients in the penetrable-sphere model fluid. With increasing system densities, simulation results for the product of the packing fraction and the self-diffusion coefficient exhibit the transitional behavior: from a nearly independent function of density in lower repulsive systems, where the soft-type collisions are dominant, to a rapidly decreasing function in higher repulsive systems, where most particle collisions are the hard-type reflections due to the low-penetrability effects. In the systems of highly repulsive energy barriers, a poor agreement with theoretical and empirical predictions is observed even at moderate densities due to the cluster-forming structure and the phase transition from the fluid-like to the solid-like state.

### INTRODUCTION

When Professor Ionel Haiduc visited Korea in 2009 for *Korea/Romania Joint Workshop on Molecular Science and Engineering*, gave a special lecture on the subject of molecular and supramolecular chemistry.<sup>1</sup> A current progress in this research area, although not directly addressed in his lecture, has been associated with computer-based molecular simulations. In this way, new supramolecular materials, based on computer modeling and simulation techniques, can be fabricated with specific molecular structures in the processes of molecular recognition and supramolecular organization. Other simulation topics were also discussed with Professor Haiduc for further science and engineering applications demonstrated in the KISTI Supercomputing Center, Korea.

Apart from some initial system parameters, only an input requirement is the model interaction

potential in order to perform the standard *classical* computational method including Monte Carlo, Brownian dynamics, and molecular dynamics calculations.<sup>2</sup> For hard condensed matter, the steeply repulsive short-ranged potential rarely allows the overlapping configuration between two colliding particles, e.g., the hard-sphere and the Lennard-Jones potential. However, as observed even at the room temperature in the systems of molecular aggregates such as micelles and polymer chains in solution, the center of mass of two constitutive molecules can penetrate each other due to the weak interactions among structural elements and the delicate balance between the entropic and the enthalpic contributions to the free energy. In such soft condensed matter systems,<sup>3</sup> it is often represented by the ultrasoft bounded potential, *i.e.*, the *effective* interaction parameter.

For theoretical and simulation investigations in soft condensed matter, one of the simplest and com-

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monly used intermolecular pair-potentials is represented by the so-called penetrable-sphere (PS) model with the constant repulsive energy barrier. In late 1980's, as a simple theoretical approach to the micelle in a solvent, Marquest and Witten<sup>4</sup> have first suggested the qualitatively similar step-like interaction function in the explanation of their experimentally observed crystallization of copolymer mesophases, where a simple cubic solid phase coexisted with the disordered suspension. The PS model system has been the subject of several theoretical and simulation studies.<sup>5-8</sup> An excellent review in this area up to 2001 can be found elsewhere in the literature.<sup>9</sup>

One of the authors (SHS)<sup>10</sup> has investigated two different theoretical predictions, based on the fundamental-measure theory proposed by Schmidt<sup>11</sup> and the bridge density-functional approximation proposed by Zhou and Ruckenstein,<sup>12</sup> to the inhomogeneous structure of PS model fluids confined within the spherical pore system. It is also reported in his group<sup>13</sup> that the modified density-functional theory, based on both the bridge density functional and the contact-value theorem, has been applied to the structural properties of PS fluids near a slit hard wall, and that the Verlet-modified bridge function for one-component systems proposed by Choudhury and Ghosh<sup>14</sup> has been extended to PS fluid mixtures. More recently, together with the thermodynamic and structural properties of PS fluids,<sup>15-17</sup> molecular dynamics (MD) simulation studies for dynamic transport properties have been carried out to add useful insights into the cluster-formation and relevant thermophysical properties in the PS model system.<sup>18-19</sup>

As a continuation of theoretical and simulation approaches along this direction, the main motivation in the present work is to undertake the MD simulation study for the time-dependent transport properties of self-diffusion coefficients over wider ranges of densities and repulsive energy parameters. As an intermediate between theory and experiment, simulation studies are most challenging to prove into a better understanding of detailed diffusion processes in such model systems. The great advantage of simulation studies over experimental investigations lies in the possibilities of obtaining the detailed molecular motion and configurations in a phase space, which may be difficult to realize in the real laboratory. MD

simulation data for the self-diffusion coefficient obtained in this work can be used to assess the applicability of various theoretical and empirical equations available in the literature. Our simulation studies can also be used to improve theoretical and empirical approximations for soft-condensed matter, which in turn will be helpful to construct a fundamental basis of theoretical and practical predictions in interpreting real experimental data.

## THEORETICAL APPROACH FOR SELF-DIFFUSION

The pair-interaction between two penetrable spheres is defined as

$$u^{PS}(r) = \begin{cases} \varepsilon, & r < \sigma \\ 0, & r > \sigma \end{cases} \quad (1)$$

where  $\sigma$  is the diameter of penetrable spheres, and  $\varepsilon (>0)$  the strength of the repulsive energy barrier between two overlapping spheres when they penetrate each other. The penetrable-sphere model reduces to the hard-sphere (HS) system when  $\varepsilon^* \equiv \varepsilon/kT \rightarrow \infty$  (where  $k$  is the Boltzmann constant, and  $T$  the temperature). This is equivalent to the zero-temperature limit  $T^* \equiv kT/\varepsilon \rightarrow 0$ . In the opposite high-temperature or high-penetrability limit ( $T^* \rightarrow \infty$ , or  $\varepsilon^* \rightarrow 0$ ), the PS system become a collisionless ideal gas. Except in the HS case, penetrability allows one in principle to consider systems with any value of the nominal packing fraction  $\phi \equiv (\pi/6)n\sigma^3$ , where  $n$  ( $\equiv N/V$ ) is the number density.

In the low density regime ( $\phi \rightarrow 0$ ), the transport coefficients of a gas made of particles interacting via a given potential can be derived by the application of the Chapman-Enskog method<sup>20</sup> to the well-know Boltzmann equation. By using the first Sonine approximation, the self-diffusion coefficient obtained from the Boltzmann equation for the PS model is given by<sup>21</sup>

$$D_0^{PS} = \frac{1}{16} \sqrt{\frac{\pi kT}{m}} \frac{\sigma}{\Omega_{11}^*} \quad (2)$$

where

$$\Omega_{11}^* = 1 - \int_{\sigma^*}^{\infty} dy e^{-y} y^2 R_1(y/\sigma^*) \quad (3)$$

with

$$R_1(y) = \frac{(y-1)(y+2)}{6y^2} + \frac{4y^2-4y+3}{12y^{3/2}(y-1)^{3/2}} + \frac{2y-1}{8y^2(y-1)} \ln [2y - 2\sqrt{y(y-1)} - 1] \quad (4)$$

Obviously, in the low-penetrability limit ( $\varepsilon^* \rightarrow 0$ ), the self-diffusion coefficient for the PS model in Eq. (2) reduces to that of the HS model, namely,

$$D_0^{\text{HS}} = \frac{1}{16} \sqrt{\frac{\pi kT}{m}} \frac{\sigma}{\varphi} \quad (5)$$

As noted above, Eqs. (2) and (3) are derived from the Boltzmann equation in the first Sonine approximation, and thus they are well justified in the high-dilution limit ( $\varphi \rightarrow 0$ ). On the other hand, they do not account for finite-density effects. To correct this deficiency, several empirical or semiempirical expressions have been proposed in the case of the HS model. Among them, the most basic one is provided by the Enskog kinetic theory.<sup>20</sup> The Enskog correction for the self-diffusion coefficient in the HS system can be written as

$$D_E^{\text{HS}} = \frac{D_0^{\text{HS}}}{\chi^{\text{HS}}} \quad (6)$$

where the Enskog factor  $\chi^{\text{HS}}$  is directly related to the contact value of the radial distribution function in the HS system, *i.e.*,  $g^{\text{HS}}(\sigma^+)$ .

Eq. (6) takes into account that the effective number of collisions in a dense gas is increased by a factor  $\chi^{\text{HS}}$ , *i.e.*,  $g^{\text{HS}}(\sigma^+)$ . Consequently, the self-diffusion coefficient is decreased by the same factor, relative to the Boltzmann prediction at the same density. Theoretically in the HS model, an excellent approximation for  $\chi^{\text{HS}}$  within the stable fluid region ( $0 \leq \varphi \leq 0.494$ ) can be provided by the Carnahan-Starling formula<sup>22</sup>

$$\chi^{\text{HS}} \left( \equiv g^{\text{HS}}(\sigma^+) \right) = \frac{1-\varphi/2}{(1-\varphi)^2} \quad (7)$$

In statistical thermodynamic relations the Enskog factor in Eq. (6) can also be associated with the corresponding equation of state in terms of the compressibility factor  $Z$  ( $\equiv PV/NkT$ ). For the HS system, one may have

$$Z^{\text{HS}} = 1 + 4\varphi \chi^{\text{HS}} \quad (8)$$

and, similarly, for the PS fluid system,

$$Z^{\text{PS}} = 1 + 4\varphi x \chi^{\text{PS}} \quad (9)$$

with

$$x = 1 - e^{-2\varepsilon^*} \quad (10)$$

The parameter  $x$  shown above represents the degree of penetrability of the PS particles ranging from  $x = 0$  in the free-penetrability limit to  $x = 1$  in the HS impenetrability limit.

There are also a number of empirical formulas for the HS self-diffusion coefficient. For the systems of 500 particles or slightly fewer, the following analytical fit to MD data was reported by Speedy<sup>23</sup>

$$D_{\text{MD}}^{\text{HS}} = D_0^{\text{HS}} \left( 1 - \frac{\varphi}{\varphi_{\text{E}}} \right) \left[ 1 + c_1 \left( \frac{\varphi}{\varphi_{\text{E}}} \right)^2 - c_2 \left( \frac{\varphi}{\varphi_{\text{E}}} \right)^4 \right] \quad (11)$$

Here,  $\varphi_{\text{E}} \cong 0.57$  is the packing fraction at the HS glass transition and Speedy's values are  $c_1 = 0.48$  and  $c_2 = 1.17$ . Recently, more extensive MD computations were performed by Sigurgeirsson and Heyes<sup>24</sup> with an efficient MD algorithm dealing with up to 32,000 HS particles. They refined the values of the fitting coefficients  $c_1$  and  $c_2$  in Eq. (11) as  $c_1 = 0.4740$  and  $c_2 = 1.1657$ . This empirical form takes into account the crowding effects in the first bracket term and the hydrodynamic backflow effects at the intermediate densities in the second bracket term. Both the Enskog formula in Eq. (6) and the empirical expression in Eq. (11) have in common the fact that, as expected on physical grounds,  $D_E^{\text{HS}} < D_0^{\text{HS}}$ , *i.e.*, the self-diffusion coefficient decays more rapidly than hyperbolically with increasing density.

Based on the Enskog result in Eq. (6), it seems natural to propose the following Enskog-like expression

$$D_E^{\text{PS}} = \frac{D_0^{\text{PS}}}{\chi^{\text{PS}}} \quad (12)$$

where  $D_0^{\text{PS}}$  is given by Eq. (2) through Eq. (4). In this simple heuristic equation, the Enskog factor  $\chi^{\text{PS}}$  can be given either from  $Z^{\text{PS}}$  in Eq. (9), or from  $g^{\text{PS}}(\sigma^+)$ , *i.e.*, the contact value of the radial distribution function in the PS model.

## RESULTS AND DISCUSSION

All MD results reported in this work are scaled to dimensionless quantities by using a unit particle diameter  $\sigma$ , a unit particle mass  $m$ , and a unit thermal energy  $kT$ . In these system units the reduced self-diffusion coefficient is expressed as  $D^* = D/\sigma\sqrt{kT/m}$ . The resulting MD data for the self-diffusion coefficients are measured by the temporal integration of the velocity autocorrelation function using the Green-Kubo formula, and also by the slope of the mean-square displacement versus time using the Einstein relation. In our MD

simulations those two methods have produced consistent results, typically less than 3% differences.

By using a semilogarithmic scale in Fig. 1, we have illustrated the product  $\varphi D^*$  as a function of the packing fraction  $\varphi$ . As one may expect, the self-diffusion coefficient (not the product of  $\varphi D^*$  as displayed in this figure) tends to decrease with increasing PS densities. For the repulsive energy barrier effects, the similar trend is detected: lower repulsive systems tend to promote larger diffusivities in PS particles. This behavior is not counterintuitive. To add more repulsive interactions will enlarge the effective hard-collision diameter between two colliding particles, leading to impede the diffusion process in the PS system. In addition, there are also several interesting diffusion behaviors observed in this figure: (i)  $D_{\text{O}}^{\text{PS}} > D_{\text{H}}^{\text{PS}}$  for all sets of  $\varepsilon^*$ -values, (ii)  $D_{\text{O}}^{\text{PS}} > D_{\text{MD}}^{\text{PS}}$  for all sets of  $\varphi$ -values at a given  $\varepsilon^*$ -value, and (iii)  $D_{\text{MD}}^{\text{PS}} > D_{\text{E}}^{\text{PS}}$  for the lower density regime, while  $D_{\text{MD}}^{\text{PS}} < D_{\text{E}}^{\text{PS}}$  for the higher density regime for all sets of  $\varepsilon^*$ -values.

Case (i) can be easily understood in terms of the energy barrier effects as explained above. In this case, the reduced PS collision integral  $\Omega_{11}^-$  calculated from Eqs. (2) and (3) is always less than unity. In the dilute regime ( $\varphi \rightarrow 0$ ), as can be deduced from Fig. 1 by the extrapolation of MD diffusion data up to  $\varphi = 0.0$ , a remarkably good agreement with  $D_{\text{O}}^{\text{PS}}$  can be found for all sets of  $\varepsilon^*$ -values. This confirms the validity of PS kinetic approaches, recently developed by Santos,<sup>21</sup> in the context of the Chapman-Enskog method for the Boltzmann equation of dilute gases. In case (ii),  $D_{\text{O}}^{\text{PS}}$  and  $D_{\text{E}}^{\text{PS}}$ , as appeared in Eq. (12), are simply related to the contact value of radial distribution functions. The corresponding  $g^{\text{PS}}(\sigma^+)$  becomes larger values with increasing the packing fraction due to the particle crowding effects near the contact distance, and thus  $D_{\text{O}}^{\text{PS}} > D_{\text{E}}^{\text{PS}}$ , and, similarly,  $D_{\text{O}}^{\text{PS}} > D_{\text{MD}}^{\text{PS}}$ .

As regards for case (iii), this self-diffusion behavior may be interpreted from the two types of collision events occurring between the two colliding PS particles, namely, the *soft*- and *hard*-type collisions. Soft-type encounters give rise to the primary external collision at  $r = \sigma^+$ , followed by the secondary internal collision at  $r = \sigma^-$ . In contrast to the hard-type reflection, the soft-type

collision does not interrupt too much about PS particle trajectories along the scattering direction. Consequently, the soft-type collisions contribute to the enhancement of self-diffusion coefficients, whereas the hard-type collisions to the retardation of particle diffusion processes. In this diffusion behavior, the hard-type collisions are gradually dominant with increasing  $\varepsilon^*$ -values. In the two cases of  $\varepsilon^* = 3.0$  and 4.5, as increase system densities, such repulsive barrier effects are more dominant with the structural changes and the phase transition from fluid-like to solid-like states. Moreover, in higher density regimes, the cluster formation among PS particles significantly retard the particle diffusion behavior, as can be seen in Fig. 1 (e.g.,  $\varphi > 1.3$  for  $\varepsilon^* = 3.0$ , and  $\varphi > 1.1$  for  $\varepsilon^* = 4.5$ ).

In the semiempirical Enskog theory, as proposed in Eq. (12), many-body clustering effects are totally ignored in PS structural complexities. However, in predicting the self-diffusion coefficient from the simple heuristic theory, only two-body (or pairwise) structural correlations are considered by using the PS radial distribution function. Although not displayed in this figure, noticeable discrepancies are found in evaluating the PS Enskog factor between the compressibility route in Eq. (8) and the direct measurement of  $\chi^{\text{PS}}$  from  $g^{\text{PS}}(\sigma^+)$  in Eq. (12), particularly in the case of  $\varepsilon^* > 3.0$ . As reported in previous simulation studies,<sup>15</sup> such discrepancies are likely due to the appearance of cluster-forming structures in the PS system, implicitly indicating that the configurational states reached are not in the strict thermodynamic equilibrium due to long-lived metastable solid-like states in our MD simulations. One of the interesting features clearly displayed in the PS system, which cannot be observed in the HS system, is that MD data for the product  $\varphi D^*$  exhibit a transition from a nearly independent function of density ( $\varepsilon^* = 0.75$ ), where the soft-type collisions are dominant, to a rapidly decreasing function ( $\varepsilon^* = 4.5$ ), where most particle collisions are the hard-type reflections due to the low-penetrability effects. For the case of  $\varepsilon^* = 0.75$ , a simple HS-type Enskog prediction in Eq. (12) shows a reasonably good agreement with MD diffusion results.

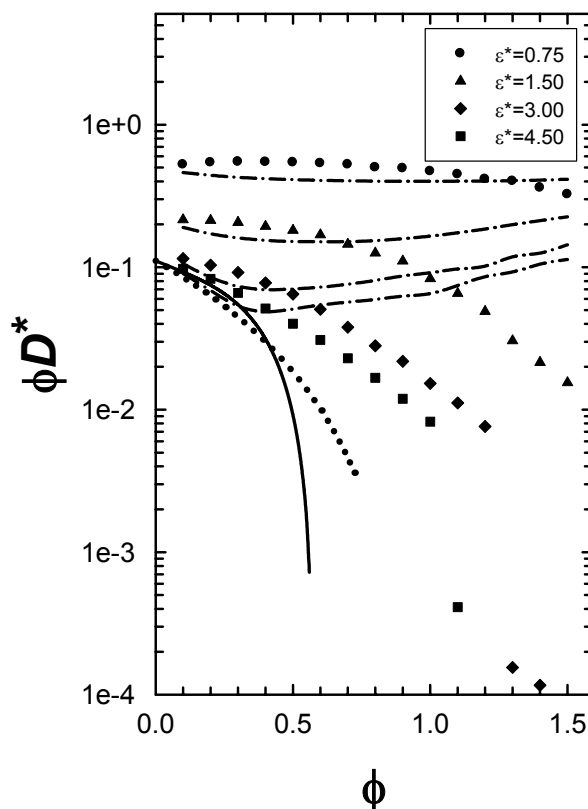


Fig. 1 – The product of the packing fraction  $\phi$  and the reduced self-diffusion coefficient  $D^*$  as a function of the packing fraction  $\phi$  for the PS model system. The symbols denote MD simulation results for the PS system; the dotted and the solid lines, respectively, correspond to the Enskog prediction in Eq. (6) and the empirical MD data in Eq. (11) for the HS system; the chain-dotted lines represent a simple Enskog-like approximation in Eq. (12), complimented with the MD-values of  $\phi^{PS}(\sigma^*)$ . The statistical errors for MD results are smaller than the symbol size.

For the pure HS fluid, it has been reported<sup>23,24</sup> that reliable self-diffusion data can be obtained from the Enskog kinetic equation over the range of equilibrium stable fluids ( $\phi < 0.494$ ). One may see this argument by comparing MD-fitting diffusion data in Eq. (11) (the solid line) with Enskog theoretical approximations in Eq. (6) (the dotted line). In the present studies, the Carnahan-Starling formula in Eq. (10) was employed to evaluate the contact value of the HS system, which is known to be very accurate for the HS system. Although not shown quantitatively in Fig. 1 (the resulting curves are drawn for the  $\phi D^*$ -values, but not for the  $D^*$ -values), MD-fitting data for the self-diffusion coefficient in the HS fluid indicate slightly larger values than the Enskog predictions at the intermediate densities (at most 5% differences in the systems of 32,000 HS particles<sup>24</sup>), followed by a rapid fall when the HS crystallization is approached. For the PS systems of  $\epsilon^* = 4.5$ , a similar trend with the HS fluid is observed from a simple Enskog-like prediction in Eq. (12) complimented with the MD contact values (the chain-dotted line). For this highest repulsive

condition, MD data for  $\phi < 0.2$  are very close to this theoretical equation, and, at the intermediate density of  $0.2 < \phi < 0.4$ , only marginal errors are exhibited. Beyond this density range, the deviation starts to be noticeable with increasing  $\phi$ -values.

## CONCLUSIONS

In the present work, for the comparison purpose with various theoretical approximations available in the literature, molecular dynamics simulations have been carried out over a wide range of the packing fractions and the repulsive energy parameters to investigate self-diffusion properties in the PS fluid. In the zero-density regime, an excellent agreement is found with the Boltzmann kinetic equation in the first Sonine approximation for the PS fluid. In contrast to the HS system, it is observed for the PS fluid that the resulting MD data for the product of the packing fraction and the self-diffusion coefficients exhibit a transition from a nearly independent function of density in lower repulsive systems, where the soft-type collisions

are dominant, to a decreasing function in higher repulsive systems, where most particle collisions are the hard-type reflections due to the low-penetrability effects. The deviations from MD data against a simple Enskog-like approximation becomes more profoundly exhibited with increasing densities due to the cluster-forming structures and the phase transition from fluid-like to solid-like states. For the high repulsive system of  $\epsilon^* = 4.5$ , for instance, a simple Enskog-like approximations can be applicable only with the narrow range of densities of  $\phi < 0.4$ .

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## REFERENCES

- I. Haiduc and F. T. Edelmann, "Supramolecular Organometallic Chemistry", Wiley-VCH, New York, 1999.
- M. P. Allen and D. J. Tildesley, "Computer Simulation of Liquids", Clarendon, Oxford, 1987.
- R. A. L. Jones, "Soft Condensed Matter", Oxford Univ. Press, Oxford, 2002.
- C. Marquest and T. A. Witten, *J. Phys. (France)*, **1989**, 50, 1267.
- C. N. Likos, M. Watzlawek and H. Löwen, *Phys. Rev. E*, **1998**, 58, 3135.
- M. J. Fernaund, E. Lomba and L. L. Lee, *J. Chem. Phys.*, **2000**, 112, 810.
- M. Schmidt and M. Fuchs, *J. Chem. Phys.*, **2002**, 117, 6308.
- A. Santos and A. Malijevský, *Phys. Rev. E*, **2007**, 75, 021201; **2007**, 75, 049901(E).
- C. N. Likos, *Phys. Rep.*, **2001**, 348, 267.
- S.-C. Kim and S.-H. Suh, *J. Chem. Phys.*, **2002**, 117, 9880.
- M. Schmidt, *J. Phys.: Condens. Matter*, **1999**, 11, 10163.
- S. Zhou and E. Ruckenstein, *J. Chem. Phys.*, **2000**, 112, 8079.
- S.-C. Kim, B.-S. Seong and S.-H. Suh, *J. Chem. Phys.*, **2009**, 131, 134701.
- N. Choudhury and S. K. Ghosh, *J. Chem. Phys.*, **2003**, 119, 4827.
- V. Chihaiia, J. M. Calderon-Moreno, N. Stanica, V. Parvulescu, M. Gartner and S.-H. Suh, *Rev. Roum. Chim.*, **2011**, 56, 1115.
- C.-H. Kim and S.-H. Suh, *Polymer(Korea)*, **2011**, 35, 325.
- C.-H. Kim and S.-H. Suh, *Polymer(Korea)*, **2011**, 35, 513.
- S.-H. Suh, C.-H. Kim, S.-C. Kim and A. Santos, *Phys. Rev. E*, **2010**, 82, 051202.
- S.-H. Suh and H. L. Liu, *Bull. Korean Chem. Soc.*, **2011**, 32, 1336.
- S. Chapman and T. G. Cowling, "The Mathematical Theory of Nonuniform Gases", Cambridge Univ. Press, Cambridge, 1970.
- A. Santos, "Kinetic Theory of Soft Matter. The Penetrable-Sphere Model", M. Capitelli, ed., AIP Conference Proc. Vol. 762, Melville, NY, 2005.
- N. F. Carnahan and K. E. Starling, *J. Chem. Phys.*, **1969**, 51, 635.
- R. J. Speedy, *Mol. Phys.*, **1987**, 62, 509.
- H. Sigurgeirsson and D. M. Heyes, *Mol. Phys.*, **2003**, 101, 469.