

A Modified Enskog-Like Equation of Self-Diffusion Coefficients for Penetrable-Sphere Model Fluids

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Molecular dynamics simulations have been performed to investigate the transport properties of self-diffusion coefficients in the penetrable-sphere model system. The resulting simulation data for the product of the packing fraction and the self-diffusion coefficient exhibit a transition from an increasing 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. A modified Enskog-like equation implemented by the effective packing fraction with the mean-field energy correction is also proposed, and this heuristic approximation yields a reasonably good result even in systems of high densities and high repulsive energy barriers.

Key Words : Molecular dynamics simulation, Self-diffusion, Modified Enskog-like approximation

Introduction

During the last couple of decades much progress has been made in our understanding of the static and dynamic properties of soft-condensed matter including colloids, polymers, foams, gels, granular materials, and a number of biological materials. The effective model potentials can be of various nature,¹ and the different minimal model has to be considered accounting for the boundness of repulsive interactions in such soft-condensed systems.² One of the simplest model systems in this approach is the so-called penetrable-sphere (PS) fluids, in which two overlapping spheres can penetrate each other with the finite repulsive energy parameter. This bounded PS potential has been the subject of several theoretical and simulation studies.³⁻¹²

Suh and his co-workers¹³ has investigated two different theoretical predictions, based on the fundamental-measure theory proposed by Schmidt⁵ and the bridge density-functional approximation proposed by Zhou and Ruckenstein,¹⁴ to the inhomogeneous structure of PS model fluids confined within the spherical pore system. It is also reported in his group¹⁵ 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 Ghosh⁸ has been extended to PS fluid mixtures. Very recently, in addition to the thermodynamic and structural properties of PS systems, molecular dynamics simulation studies for dynamic transport properties have been carried out to add useful insights into the cluster-formation and related thermophysical properties of PS systems.¹⁶

There are in general two classes of computer simulation

approaches: stochastic Monte Carlo (MC) and deterministic molecular dynamics (MD) methods. In MD calculations, the actual trajectories of atoms or molecules are evaluated by the numerical integration of Newton's equations of motion, in which time-dependent transport properties can be determined. Up to date, almost all simulations for the PS model fluid have been carried out using the MC method. To our best knowledge, except for our previous simulation work cited above,¹⁶ MD results for the PS interaction potential have not been presented in the literature. Computationally, a better statistics can be achieved in MD simulations for systems with discontinuous potentials. For instance, in order to calculate the virial route to the equation of state for hard-core systems, MC computations require an accurate estimation of the radial distribution function. In many cases the radial distribution function may change rapidly near the contact distance for the systems of ionic solutions, highly charged colloids, aligned liquid crystals, etc. Under these circumstances the extrapolation to the contact value may lead to larger uncertainties. For this reason, the pressure determined by MC calculations, particularly in the discontinuous interaction system, is known to be less accurate than that by MD simulations.^{17,18}

As a continuation of theoretical and simulation approaches along this direction, one of the main motivations in this work is to develop the statistical mechanical-based heuristic approximation, namely, a modified Enskog-like equation of self-diffusion coefficients, in order to investigate the diffusion behavior involved in the PS system. By obtaining the essentially *exact* machine data for precisely defined model systems, MD simulation studies can be used to assess the applicability of our proposed diffusion equations. Such simulation approaches at the atomic or molecular level can also be used to improve theoretical/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.

Model and Theoretical Approaches

With the finite and bounded core-repulsion the penetrable-sphere pair potential is described as

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

where $\varepsilon (> 0)$ is the strength of the repulsive energy barrier between two overlapping spheres with the diameter σ when they penetrate each other. The PS model is simply reduced to the classical hard-sphere (HS) system when $\varepsilon^* (\equiv \varepsilon/k_B T) \rightarrow \infty$ (where T is the temperature and k_B is the Boltzmann constant). This is equivalent to the zero-temperature limit $T^* (\equiv k_B T/\varepsilon) \rightarrow 0$. In the opposite high-temperature limit or in the high-penetrability limit ($T^* \rightarrow \infty$, $\varepsilon^* \rightarrow 0$), the PS system becomes a collisionless ideal gas.

In the PS system the overlapping penetrability allows one in principle to consider any value of the nominal packing fraction, $\phi (\equiv (\pi/6)\rho^*)$, where $\rho^* (\equiv N\sigma^3/V)$ is the reduced particle number density, N , the number of particles, and V , the system volume. Note that the maximum packing fraction in the pure HS system is $\sqrt{2}\pi/6 (\cong 0.7405)$ from the face-centered cubic structure.

In the low-density regime $\phi \rightarrow 0$ the transport properties of a gas made of particles interacting via a given potential can be derived by the application of the Chapman-Enskog method to the well-known Boltzmann kinetic equation.¹⁹ For the PS model fluid, Santos²⁰ reported the self-diffusion coefficient D_0^{PS} obtained from the Boltzmann equation in the first Sonine approximation,

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

where

$$\Omega_{11}^* = 1 - \int_0^\infty dy e^{-y} y^2 R_1(y/\varepsilon^*), \quad (3)$$

with

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

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

$$D_0^{HS} = \frac{1}{16\sqrt{\pi}} \frac{\pi k_B T \sigma}{m} \phi, \quad (5)$$

Eqs. (2) and (5) are derived from the Boltzmann kinetic equation in the first Sonine approximation, and thus they are well justified in the high dilution limit $\phi \rightarrow 0$. On the other

hand, they do not account properly for finite-density effects with increasing densities. To correct this deficiency, several empirical or semiempirical expressions have been proposed in the case of the HS system. Among them, the most basic one is provided by the Enskog kinetic theory.^{19,21} From taking account of the effective number of collisions in the moderately dense or the dense gas, the Enskog correction for the self-diffusion coefficient in the HS model is represented as

$$D_E^{HS} = \frac{D_0^{HS}}{g^{HS}(\sigma^+)}, \quad (6)$$

where the Enskog factor $g^{HS}(\sigma^+)$ is the contact value of the radial distribution function of the HS fluid.

There are also a number of empirical formulas for D^{HS} . For systems of 500 HS particles or slightly fewer, the following analytical fit to MD data was reported by Speedy²²

$$D_{MD}^{HS} = D_0^{HS} \left(1 - \frac{\phi}{\phi_g}\right) \left[1 + c_1 \left(\frac{\phi}{\phi_g}\right)^2 - c_2 \left(\frac{\phi}{\phi_g}\right)^4\right]. \quad (7)$$

Here, $\phi_g = 0.57$ is the packing fraction at the HS glass transition and Speedy's values are $c_1 = 0.48$ and $c_2 = 1.17$. Recently, much more extensive MD computations were performed by Sigurgeirsson and Heyes,²³ and they refined the values of the fitting coefficients $c_1 = 0.4740$ and $c_2 = 1.1657$ with an efficient MD algorithm dealing with up to 32,000 HS particles. The MD-based empirical form in Eq. (7) takes account of the crowding effects in the first bracket term and the hydrodynamic backflow effects at intermediate densities in the second bracket term.

In the case of the PS system, the task of extending the Boltzmann result in Eq. (2) for a finite density to evaluate the self-diffusion coefficient D^{PS} is much more difficult than in the HS case. For instance, the ratio D^{PS}/D_0^{PS} is not only a function of density as in the HS case but also a function of temperature or, equivalently, of ε^* .

In our previous MD studies,¹⁶ similar to the Enskog approximation in the HS fluid as given in Eq. (6), a following simple Enskog-like expression for the PS fluid was proposed

$$D_E^{PS} = \frac{D_0^{PS}}{g^{PS}(\sigma^+)}. \quad (8)$$

This simple expression for predicting self-diffusion coefficients was found to be in a reasonable agreement in the dilute system by comparing against MD simulation data. However, for the dense PS system especially with higher repulsive energy parameters, the noticeable discrepancies were observed due to the locally inhomogeneous cluster-forming structure as well as the collective dynamic motion in collision processes involved in the PS fluid. Based on such observations in our simulation studies, we propose a kind of the heuristic equation for the self-diffusion properties, adjusted by the effective volume with mean-field energy corrections, namely, the modified Enskog-like equation

$$D_{mE}^{PS} = \frac{D_0^{PS}}{g^{PS}(\sigma^+) \phi(\varepsilon^* \rightarrow 0)} \frac{\phi_{eff}}{\phi} \exp\left[\left(\frac{6}{\pi}\right) \Delta \phi_{eff} \varepsilon^*\right], \quad (9)$$

where

$$\Delta\phi_{eff} = \phi_{eff} - \phi(\varepsilon^* \rightarrow 0). \quad (10)$$

For $\phi(\varepsilon^* \rightarrow 0)$, the corresponding particle configuration becomes that of a totally unbiased random structure, and, at a given packing fraction ϕ in the limit ($\varepsilon^* \rightarrow 0$), this leads statistically to

$$\phi(\varepsilon^* \rightarrow 0) = 1 - e^{-\phi}. \quad (11)$$

In the limit $\varepsilon^* \rightarrow 0$ and $\phi \rightarrow 0$, our modified Enskog-like expression expressed in Eqs. (9) through (11) reduces to a simple HS-type Enskog approximation in Eq. (8).

In our heuristic diffusion equation above, the effective particle volume fraction ϕ_{eff} is defined as the average effective total volume occupied by PS particles divided by the system volume. The second term in Eq. (9) represents the effective volume correction relative to the fully penetrating PS structure $\phi(\varepsilon^* \rightarrow 0)$. The last exponential term is related to the energy barrier effects, in which the factor $6/\pi$ is used to convert the total energy difference from the volume-based scale into the number-based one, i.e., the reduced number density (cf. $\Delta\rho_{eff}^* = (6/\pi)\Delta\phi_{eff}$). This latter argument can be supported by the fact that the total configurational energy is related to the number of interacting pair-particles, but not to the effective system volume occupied by particles.

Results and Discussion

All MD results reported in this work are scaled to dimensionless quantities by using a unit particle diameter σ , a unit particle mass m , and a unit thermal energy $k_B T$. In these system units the reduced self-diffusion coefficient is expressed as $D^* = D/\sigma\sqrt{k_B T/m}$.

In Table 1, system characteristics employed in this work and MD simulation results for the reduced self-diffusion coefficient are presented. Also listed in this table are the contact value of the radial distribution function $g(\sigma^+)$ and the effective packing fraction ϕ_{eff} measured during MD simulation runs. The self-diffusion coefficient was calculated from mean-square displacement curve using the Einstein formula. The value of $g(\sigma^+)$ was carefully evaluated from the 5-points

extrapolation of $g(\sigma)$ vs. r/σ near the contact distance.

We determined ϕ_{eff} by the conventional hit-and-miss method using a uniform ($10 \times 10 \times 10$) grid over approximately half a million equilibrium configurations during our MD computations. For the systems with $\varepsilon^* = 0.2, 0.5, \text{ and } 1.0$, the resulting MD values of ϕ_{eff} in Table 1 are very close to the theoretical predictions for randomly distributed configurations as in Eq. (11). In the case $\varepsilon^* = 3.0$, is ϕ_{eff}/ϕ close to unity up to $\phi \leq 3$, which indicates HS-like configurations, and at $\phi = 0.6$ it crosses the random distribution expectation. As we increase densities further, PS particles are much overlapped in the case $\varepsilon^* = 3.0$. For instance, about 54% of the available volume is effectively occupied at $\phi = 1.0$; in contrast, at the same density for $\varepsilon^* = 0.2, 0.5, \text{ and } 1.0$, particles occupy about 65% of the total volume, indicating a less degree of particle clustering effects.

By using a semilogarithmic scale in Figure 1, we have illustrated the product ϕD^* as a function of the packing fraction ϕ . As one may expect, the self-diffusion coefficient (but, not the product of ϕD^* 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) $D^{PS} > D^{HS}$ for all sets of ε^* -values, (ii) $D_0^{PS} > D_E^{PS}$ (or, D_{mE}^{PS}) for all sets of ϕ -values at a given ε^* , and (iii) $D_{MD}^{PS} > D_E^{PS}$ (or, D_{mE}^{PS}) for all sets of ϕ -values at $\varepsilon^* = 0.2, 0.5, \text{ and } 1.0$, but this is not always true in the case of $\varepsilon^* = 3.0$.

Case (i) can be easily understood in terms of the energy barrier effects as explained above. In this case, the reduced PS collisional integral Ω_{11}^* , calculated from Eqs. (3) and (4), is always less than unity. In the dilute regime $\phi \rightarrow 0$, as can be seen in Figure 1 by the extrapolation of MD diffusion data to $\phi = 0$, a remarkably good agreement with D_0^{PS} can be found for all sets of ε^* -values. This confirms the validity of PS kinetic approaches, recently developed by Santos,²⁰ in the context of the Chapman-Enskog method for the Boltzmann equation of dilute gases. In case (ii), D_0^{PS} and D_E^{PS} , as

Table 1. System characteristics and MD simulation results for the penetrable-sphere model system

ϕ	$\varepsilon^* = 0.2$			$\varepsilon^* = 0.5$			$\varepsilon^* = 1.0$			$\varepsilon^* = 3.0$		
	D^*	$g(\sigma^+)$	ϕ_{eff}									
0.1	41.49	1.006	0.0959	9.579	1.032	0.0968	3.549	1.087	0.0978	1.149	1.241	0.0996
0.2	21.15	1.012	0.1839	4.936	1.057	0.1865	1.800	1.154	0.1896	0.513	1.521	0.1968
0.3	14.38	1.018	0.2643	3.379	1.077	0.2689	1.196	1.203	0.2737	0.303	1.744	0.2861
0.4	10.95	1.022	0.3374	2.560	1.092	0.3436	0.882	1.236	0.3493	0.194	1.834	0.3599
0.5	8.889	1.026	0.4038	2.044	1.105	0.4111	0.690	1.257	0.4161	0.130	1.827	0.4167
0.6	7.508	1.030	0.4639	1.726	1.113	0.4717	0.548	1.273	0.4745	0.0841	1.810	0.4590
0.7	6.473	1.033	0.5181	1.455	1.121	0.5258	0.459	1.279	0.5252	0.0548	1.764	0.4891
0.8	5.753	1.036	0.5672	1.269	1.127	0.5740	0.364	1.287	0.5683	0.0355	1.711	0.5104
0.9	5.104	1.038	0.6113	1.117	1.131	0.6168	0.299	1.288	0.6047	0.0240	1.648	0.5271
1.0	4.656	1.040	0.6509	1.003	1.134	0.6549	0.257	1.280	0.6353	0.0155	1.610	0.5407

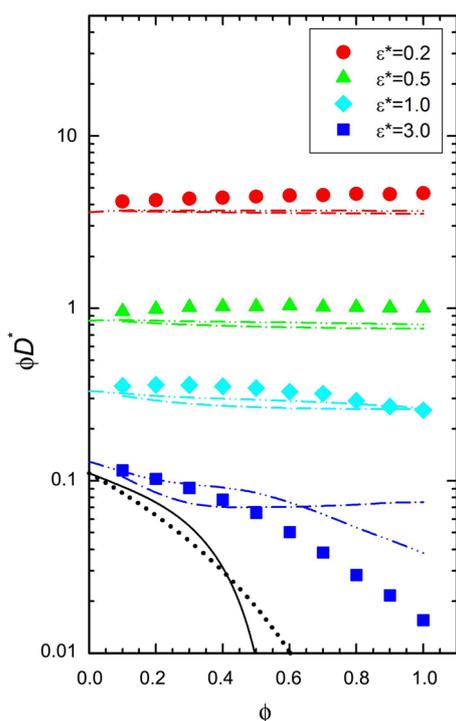


Figure 1. The product of the packing fraction ϕ and the reduced self-diffusion coefficient D^* as a function of the packing fraction ϕ for the PS system. The symbols are MD simulation data for the PS fluid; the dotted and the solid lines, respectively, correspond to the Enskog prediction in Eq. (6) and to the empirical MD data in Eq. (7) for the HS system; the chain-dotted lines represent a simple Enskog-like approximation in Eq. (8), complimented with the MD-values for $g(\sigma^+)$; the chain-dot-dotted lines denote the modified Enskog-like approximation in Eq. (9), complimented with the MD-values for $g(\sigma^+)$ and ϕ_{eff} .

represented in Eq. (8), are simply related to the contact value of radial distribution functions. The corresponding $g^{PS}(\sigma^+)$ becomes larger values with increasing the packing fraction due to the particle crowding effects near the contact distance, and thus $D_0^{PS} > D_E^{PS}$. 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-type and the 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.

One of the striking features clearly displayed in the PS system, which cannot be observed in the HS system, is that MD data for the product ϕD^* exhibit a transition from an increasing function of density ($\epsilon^* = 0.2$), where the soft-type collisions are dominant, to a decreasing function ($\epsilon^* = 3.0$), where most particle collisions are the hard-type reflections due to the low-penetrability effects. (Although not shown in this work, the similar diffusion behavior was observed for

higher repulsive systems of $\epsilon^* \geq 3.0$) For the cases of $\epsilon^* = 0.2, 0.5$ and 1.0 , both a simple HS-type Enskog prediction in Eq. (8) and a modified Enskog-like prediction in Eq. (9) show a reasonably good agreement with MD diffusion results, even though the discrepancies in both two approximations are gradually increased with increasing the system densities except for $\epsilon^* = 1.0$ and $\phi \geq 0.8$. As we increase the repulsive energy parameters, a qualitatively better agreement is observed in a modified Enskog-like approximation than in a simple HS-type Enskog equation.

For the pure HS fluid, it has been reported^{22,23} 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. (7) (a solid line) with Enskog theoretical approximations in Eq. (6) (a dotted line). In the present studies, the Carnahan-Starling formula²⁴ was employed to evaluate the contact value of the HS system, i.e., $g^{HS}(\sigma^+) = (1-\phi/2)/(1-\phi)^3$, which is known to be very accurate for the HS system. Although not possible for direct measurements in Figure 1, where the resulting curves are drawn for the ϕD^* -values, but not for the D^* -values solely, 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 particles²³), followed by a rapid fall as the HS crystallization is approached.

For the PS systems of $\epsilon^* = 3.0$, the qualitatively similar trend with the HS fluid is observed from a simple Enskog-like prediction in Eq. (8) complimented with the MD contact values in Table 1. MD data for $\phi \leq 0.2$ are very close to this theoretical equation, and, at the intermediate density of $0.2 \leq \phi \leq 0.4$, only marginal errors are exhibited. However, beyond this density range, the deviation starts to be noticeable with increasing ϕ . In contrast to larger reductions for MD self-diffusion coefficients, the product of ϕD^* slightly increase with increasing densities in Eq. (8) for the PS system. This opposed diffusion behavior deduced from a simple Enskog-like equation is not correct. In fact, as listed in Table 1, the $g(\sigma^+)$ -values are getting decreasing, but ϕ_{eff} -values are still increasing for the systems of $\phi > 0.4$ with $\epsilon^* = 3.0$, indicating the development of locally inhomogeneous clustering-formations in the PS fluid.

For the same condition of $\epsilon^* = 3.0$, the modified Enskog-like equation proposed in this work, using the MD contact values and the effective packing fractions in Table 1, gives a remarkably good result for $\phi \leq 0.4$. More reliable PS self-diffusion coefficients can also be extended up to $\phi < 0.5-0.6$. Above this density range, by comparing MD simulation data, it is found that the resulting self-diffusion coefficients from our proposed diffusion equation are seemingly over-estimated. On the other hand, more importantly, the modified diffusion approximation in this work does correctly describe the diffusion behavior for systems of $\phi > 0.5-0.6$, in which a simple Enskog-like equation does not predict the correct diffusion behaviors in the PS fluid.

Before concluding this section, it will be of interest to

describe some relevant shortcomings for a modified Enskog-like approximation proposed in this work. It is worthwhile recalling that this heuristic diffusion equation, originally formulated from the Boltzmann kinetic theory with the Enskog correction factor, is implemented only by a certain equilibrium structural property, i.e., the effective packing fraction. Moreover, regardless of a given model potential, the Boltzmann kinetic theory deals with only binary collision effects by totally neglecting multiple collisions with the molecular chaos assumption, known as ‘*Stosszahlansatz*’. Under those conditions, particularly in densely colliding systems, the deviation from our modified Enskog-like approximation can be largely due to the structure-based phase transition together with the neglect of such dynamic correlation effects in the PS collision dynamics.

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 fraction ϕ and the reduced repulsive energy parameter ε^* to investigate the transport properties of self-diffusion coefficients in the PS fluid. In the zero-density regime $\phi \rightarrow 0$, 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 interestingly observed in our MD computations for the PS fluid that the resulting simulation data for the product of the packing fraction and the self-diffusion coefficients exhibit a transition from an increasing 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-penetration effects.

As expected, the deviations from MD data with theoretical approximations become more profoundly exhibited with increasing densities. For higher repulsive systems, a simple Enskog-like approximations can be applicable only with the narrow range of densities of $\phi < 0.2$. The possibilities of obtaining more reliable self-diffusion coefficients are made from a modified Enskog-like equation, adjusted by the effective packing fraction with the mean-field energy correction. This heuristic approximation proposed in this work yields a reasonably good result even in systems of high densities and high repulsive energy barriers. For other transport properties

of the shear viscosity and the thermal conductivity, we are currently examining to extend our modified Enskog-like predictions to the two limiting cases of high- and low-penetration approximations in the PS model system. Further statistical mechanical approaches will be reported with relevant MD simulation results in the near future.

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