

The Empirical Enskog-Like Approximation of Shear Viscosity in the Penetrable-Sphere Model

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The so-called penetrable-sphere (PS) interaction potential is defined as

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

where σ is the diameter penetrable sphere, and $\varepsilon (> 0)$ is the strength of the repulsive energy barrier between two overlapping spheres when they penetrate each other. The PS system simply reduces to the hard-sphere (HS) model in the zero-temperature limit, *i.e.*, $T^* (\equiv k_B T / \varepsilon) \rightarrow 0$, or $\varepsilon^* (\equiv \varepsilon / k_B T) \rightarrow \infty$, where k_B is the Boltzmann constant, and T the temperature. In the opposite high-temperature limit $T^* \rightarrow \infty$, or the high-penetrability limit $\varepsilon^* \rightarrow 0$, the PS system becomes a collisionless ideal gas. For the PS system, in principle, the overlapping penetrability allows any possible value of the nominal packing fraction $\phi (\equiv (\pi/6)\rho^*)$, where $\rho^* (\equiv N\sigma^3/V)$ is the reduced number density. 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.

The PS potential has been the subject of several theoretical and simulation studies.¹⁻³ Among them, one (SHS) of the authors has investigated two different theoretical predictions,^{2(a)} based on the fundamental-measure theory proposed by Schmidt^{1(b)} and the bridge density-functional approximation proposed by Zhou and Ruckenstein,^{1(c)} to the inhomogeneous structure of PS model fluids confined within the spherical pore system. It is also reported^{2(b)} 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^{1(g)} has been extended to PS fluid mixtures. Recently, in addition to the thermodynamic and structural properties of PS systems,² molecular dynamics (MD) simulation studies for dynamic transport properties³ have been carried out to add useful insights into the cluster-formation and related thermophysical properties of PS systems.

In this Note, as a continuation of theoretical and simu-

lation studies along this direction, the main motivation in this work is to develop the empirical approximation of shear viscosity coefficients for the PS model fluid. In order to assess the applicabilities of our proposed heuristic approximation, the essentially *exact* data of shear viscosity coefficients in the PS model system are obtained from the equilibrium MD method. Such simulation approaches employed in this work will be helpful to construct a fundamental basis of theoretical and practical predictions in interpreting real experimental data.

Shear Viscosity Theory

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.⁴ By using the first Sonine approximation, Santos⁵ has reported the shear viscosity coefficient obtained from the Boltzmann equation in the PS model, *i.e.*,

$$\eta_0^{PS} = \frac{5}{16\sqrt{\pi}} \frac{\sqrt{mk_B T}}{\sigma^2} \frac{1}{\Omega_{22}^*}, \quad (2)$$

where

$$\Omega_{22}^* = 1 - \frac{1}{2} \int_{\varepsilon^*}^{\infty} dy e^{-y} R_2(y/\varepsilon^*) \quad (3)$$

with

$$R_2(y) = \frac{(y-1)(3y^2+4y-12)}{15y^3} + \frac{8y^4-16y^3+58y^2-50y+15}{60y^{5/2}(y-1)^{3/2}} + \frac{(2y-1)(2y^2-2y+1)}{8y^3(y-1)^2} \ln(2y-2\sqrt{y(y-1)}-1). \quad (4)$$

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

$$\eta_0^{HS} = \frac{5}{16\sqrt{\pi}} \frac{\sqrt{mk_B T}}{\sigma^2}. \quad (5)$$

As noted above, Eq. (2) is derived from the Boltzmann kinetic equation in the first Sonine approximation, and thus they are well justified only in the high dilution limit $\phi \rightarrow 0$. On the other hand, they do not account properly for finite density effects upon increasing densities. To correct this deficiency, the Enskog kinetic theory⁴ has taken account into the fact that the collision frequency is increased by a factor associated with the spatial correlations between the two colliding particles. This *ad hoc* Enskog factor is equivalent to the contact value of the radial distribution function, *i.e.*, $\chi \equiv g(\sigma^+)$.

In statistical thermodynamic relations the Enskog factor χ is also related to the corresponding equation of state in terms of the compressibility factor $Z^{\text{HS}} (\equiv p/\rho k_B T)$.⁶ For the HS system, one may have

$$Z^{\text{HS}} = 1 + 4\phi\chi^{\text{HS}}, \quad (6)$$

and, similarly, for the PS system,

$$Z^{\text{PS}} = 1 + 4\phi x \chi^{\text{PS}} \quad (7)$$

with

$$x = 1 - e^{-\varepsilon^*}. \quad (8)$$

The parameter x in Eq. (8) denotes 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.

By using the Chapman-Enskog approach, the Enskog correction for the shear viscosity coefficient in the HS model is expressed as

$$\frac{\eta_E^{\text{HS}}}{\eta_0^{\text{HS}}} = \left[\frac{(1 + 8/5\phi\chi^{\text{HS}})^2}{\chi^{\text{HS}}} + \frac{768}{25\pi}\phi^2\chi^{\text{HS}} \right], \quad (9-a)$$

or, in terms of the compressibility factor,

$$\frac{\eta_E^{\text{HS}}}{\eta_0^{\text{HS}}} = \frac{4\phi}{Z^{\text{HS}} - 1} \left[\left(1 + \frac{2}{5}(Z^{\text{HS}} - 1) \right)^2 + \frac{48}{25\pi}(Z^{\text{HS}} - 1)^2 \right] \quad (9-b)$$

The first and second terms inside the square bracket of above equations are, respectively, the nonsingular and singular part, as can be measured from the shear stress autocorrelation function. With increasing densities, the second term, which is related with the collisional contribution, is getting more dominant than the first kinetic-related one.

There are also a number of empirical formulas for the HS transport properties in the framework of theoretical or simulation approaches. Among them, an empirical analytical fit for the HS shear viscosity has been reported by Sigurgeirsson and Heyes⁷ from extensive MD computations with an efficient MD algorithm dealing with up to 32,000 HS particles,

$$\frac{\eta_{\text{MD}}^{\text{HS}}}{\eta_0^{\text{HS}}} = \frac{1}{[1 - (\phi/\phi_1)]^m} \quad (10)$$

where the two fitting parameters are $m = 1.92$ and $\phi_1 = 0.58$. This empirical equation is known to reproduce MD data

reasonably well up to the equilibrium HS fluid range ($\phi \leq 0.493$). However, there is a rapid rise for the shear viscosity coefficient in the metastable density regime. One must exercise caution for the curve fitting in the density range above $\phi \cong 0.55$.

Based on the Enskog correction for the HS system, as appeared in Eqs. (9a) and (9b), we propose here the empirical Enskog-like approximation for the shear viscosity coefficient in the PS model

$$\frac{\eta_E^{\text{PS}}}{\eta_0^{\text{PS}}} = \left[\frac{(1 + 8/5\phi x \chi^{\text{PS}})^2}{\chi^{\text{PS}}} + \frac{768}{25\pi}\phi^2 x^2 \chi^{\text{PS}} \right], \quad (11-a)$$

or, in terms of the compressibility factor,

$$\frac{\eta_E^{\text{PS}}}{\eta_0^{\text{PS}}} = \frac{4\phi x}{Z^{\text{PS}} - 1} \left[\left(1 + \frac{2}{5}(Z^{\text{PS}} - 1) \right)^2 + \frac{48}{25\pi}(Z^{\text{PS}} - 1)^2 \right]. \quad (11-b)$$

In these equations the PS shear viscosity in the zero-density limit η_0^{PS} can be determined originally from the Boltzmann kinetic equation, as given in Eqs. (2) through (4). The PS compressibility factor Z^{PS} at a given density ϕ can be evaluated from either theoretical or numerical calculations.

Results and Discussion

For the comparison purpose with the empirical Enskog-like approximation for the shear viscosity proposed in this work, we have carried out equilibrium MD simulations for the three sets of PS fluids ($\varepsilon^* = 0.2, 1.0, \text{ and } 3.0$) over a wide range of density conditions ($0 < \phi \leq 1.5$). The detailed MD method is described elsewhere in our previous work.³ The PS shear viscosity coefficients were calculated during MD runs by means of the generalized Einstein relation, which was first developed by Alder *et al.*⁸ for the discontinuous potential system. All MD data reported here 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 those system units the reduced shear viscosity coefficient is expressed as $\eta^* = \eta/(\sqrt{mk_B T}/\sigma^2)$.

By using a semilogarithmic scale in Figure 1(a) and the original scale in Figure 1(b) through 1(d), we have illustrated the reduced shear viscosity coefficient η^* as a function of the packing fraction ϕ . Together with the resulting MD data for the PS system (the solid symbol), also illustrated in this figure includes the Enskog HS prediction (the dotted line) in Eqs. (9-a) or (9-b), the empirical HS formula fitted to MD calculations (the solid line) in Eq. (10), and our proposed Enskog-like PS approximation (the chain-dotted line) in Eqs. (11-a) or (11-b).

It is worthy noting here that for the Enskog HS prediction in Eq. (9-b) the numerical values of Z^{HS} at a given ϕ -value are evaluated by the Carnahan-Starling equation of state,⁹ *i.e.*, $Z^{\text{HS}} = (1 + \phi + \phi^2 - \phi^3)/(1 - \phi)^3$, which is known to be very accurate over almost the entire density range of the HS system. However, in statistical thermodynamic approaches for the PS model, only reliable values for χ^{PS} or Z^{PS} are limited to the dilute density regime. For this reason, the

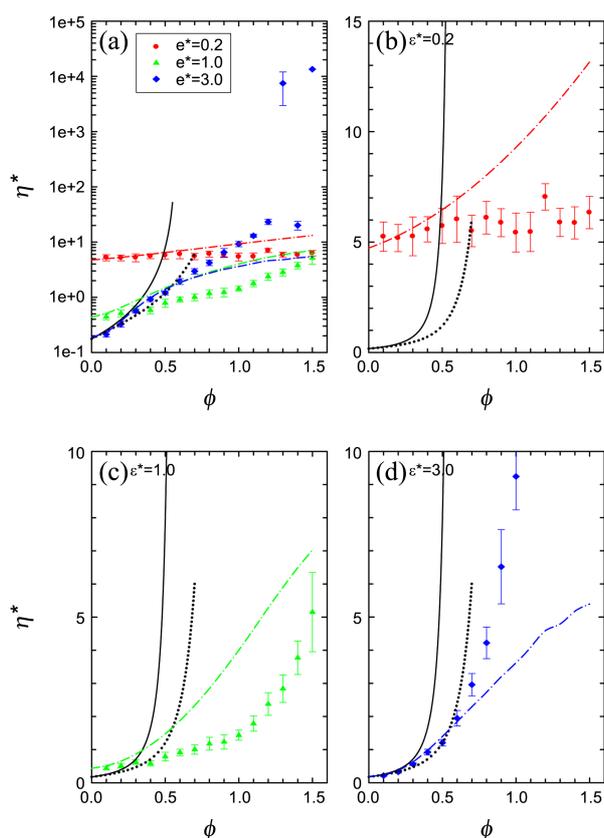


Figure 1. The reduced shear viscosity coefficient η^* as a function of the packing fraction ϕ in the semilogarithmic scale in (a) and the original scale in (b) to (d). The symbols denote MD simulation results for the PS fluid; the dotted and the solid lines, respectively, correspond to the Enskog prediction in Eqs. (9-a) or (9-b) and to the empirical MD data in Eq. (10) for the HS system; the chain-dotted lines represent the empirical Enskog-like approximation in Eqs. (11-a) or (11-b), complemented with the MD-values for Z^{PS} .

resulting MD data are directly incorporated into Eq. (11-b) for Z^{PS} values in the Enskog-like approximation.

Larger statistical uncertainties are observed in the shear viscosity by comparing with previous MD data for the self-diffusion coefficients.^{3(a),(c)} At the microscopic level, viscosity arises because of a transfer of momentum between fluid layers moving at different velocities. In this way, the shear viscosity can be evaluated by the *collective* time-dependent properties. In contrast, the self-diffusion process is a *single* particle property, implying the ensemble average over N -particles independently, which should lead to much better statistical results for the self-diffusion compared with the collective properties of the shear viscosity.

As expected, the HS shear viscosity coefficients of theoretical Enskog HS equation are close to those of MD values within the narrow range of densities $\phi \leq 0.2$, and the deviations between them are getting larger with increasing the HS densities, for instance, $\eta_{MD}^{HS}/\eta_E^{HS} \approx 4$ at $\phi = 0.555$. By extrapolating MD data to the zero-density limit, an excellent agreement is found with the Boltzmann kinetic equation for all sets of ε^* -values. As observed in Figure 1(a), MD results for the shear viscosity displays the linearly increasing

tendency in the semilogarithmic scale. Furthermore, there is a transition from a nearly independent (or, only slightly increasing) function in lower repulsive systems ($\varepsilon^* = 0.2$), where the soft-type collisions are dominant, to a rapidly increasing function in higher repulsive systems ($\varepsilon^* = 3.0$), where most particle collisions are the hard-type reflections due to the low-penetrability effects.

In the low density regime of the PS fluid, the heuristic Enskog-like approximation in conjunction with MD-measured Z^{PS} values agrees reasonable well with MD simulation data for the shear viscosity. The PS dynamic properties of $\varepsilon^* = 3.0$ (Figure 1(d)) are in many aspects similar to the HS fluid, yielding closer shear viscosity coefficients up to $\phi \approx 0.3$ with the HS predictions. The MD data are seen to be in a good agreement with the Enskog-like approximation in the density ranges $\phi \leq 0.5$. Beyond this range, deviations are more profoundly observed, particularly in the metastable or unstable phase transition for the density condition larger than $\phi \approx 1.3$, where the sudden jump is detected in the MD shear viscosity as displayed in Figure 1(a). In the PS model, even though there is the absence of attractive interactions between particles, the fluid/solid transition possibly occurs, likely the HS system. Moreover, the PS system exhibits the highly unconventional phase transition with the formation of multiple occupancy crystal-like structures, coupled with possible reentrant melting as further increasing of system densities.

In summary, for the comparison purpose with various theoretical approximations available in the literature, MD simulations for the shear viscosity in the PS fluid have been carried out over a wide range of the packing fraction ϕ . 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. A reasonable agreement is observed between MD data and the empirical Enskog-like approximation proposed in this work, except for the highly repulsive case with high densities due to the complex structures of clustering formation. We are currently examining to extend our heuristic Enskog-like predictions to the two limiting cases of high- and low-penetrability approximations in the PS model system, and our further statistical mechanical approaches will be reported with relevant MD results in the near future.

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