



*Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary*

THEORY AND SIMULATION OF TRANSPORT PROPERTIES FOR PENETRABLE-SPHERE MODEL SYSTEMS: II. SHEAR VISCOSITY

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Molecular dynamics simulations have been carried out to investigate the collective transport properties of shear viscosity coefficients in the penetrable-sphere model fluid. A qualitative agreement is found between simulation results and an empirical Enskog-like approximation proposed in this present work. However, the mismatching tendencies are gradually growing with increasing both densities and repulsive energy parameters due to the cluster-forming structure and the phase transition from the fluid-like to the solid-like state. In addition, relevant historical background on viscosity is addressed to sketch the traditional kinetic theory of gases and simulation-based computational approaches.

INTRODUCTION

This series of two papers, dedicated to Professor Ionel Haiduc, is concerned with theoretical and simulation studies to investigate the dynamic transport properties of penetrable-sphere (PS) model systems by using the molecular dynamics (MD) simulation method: the former article for the self-diffusion and this one for the shear viscosity. From a theoretical point of view, likely the hard-sphere (HS) interaction to hard condensed matter, the PS potential model has a character of the idealized reference system in soft condensed matter. In this way, the PS system can be used as a stringent benchmark to test various computational and statistical mechanical approaches¹⁻¹¹ in soft condensed systems such as colloids, polymers, liquid crystals, and a number of biological materials.

As mentioned briefly in the introductory part of the previous paper, the most spectacular increase in science and engineering capabilities has been demonstrated in high-performance computing related with technical advances in both hardware and software. This has enabled the development of computational modeling and simulations with great speed and accuracy. As an intermediate between theory and experiment, simulation approaches solve the fundamental physicochemical equations with incorporating the efficient computational algorithm.¹² Computer simulations have accelerated progress in scientific understanding to design new materials and chemistries with predictive power, namely, *in silico* (via computer simulation) research.

There are in general two classes of *classical* simulation approaches: stochastic Monte Carlo (MC) and deterministic molecular dynamics (MD) methods.¹³ The MC method generates a sequence

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of independent configurations randomly according to the ensemble concept of Gibbs, while the MD method, based on the time-averaging concept of Maxwell and Boltzmann, solves the Newtonian equations of motion in many-body systems. The MC method is suitable for calculating only static equilibrium properties, but can be cast in a variety of different ensembles. The MD method treats real time motion and can be used to obtain both thermodynamic and time-dependent properties.

To the best of our knowledge, MD results for the shear viscosity coefficient in the PS model system have not been reported elsewhere in the literature. In the present work, we have proposed a simple heuristic Enskog-like approximation for the shear viscosity, and, for the comparison purpose, we have revisited the PS model system via the equilibrium MD method over a wide range of densities and repulsive energy parameters. Together with the existing approximations in Boltzmann and Enskog kinetic equations, our MD simulation results can be used directly to compare against various kinetic theory predictions and statistical mechanical approximations. In this role computer simulations are often referred to as machine experiment, in which essentially *exact* experimental data can be evaluated for precisely defined model systems.

HISTORICAL BACKGROUND ON VISCOSITY

Before embarking our research details, relevant historical background on viscosity will be described in this section to sketch the development of early kinetic theory of gases and simulation-based computational approaches. Very recently, an excellent review article¹⁴ in this topic has been electronically published in arXiv.org, in which more references are cited.

Maxwell¹⁵ was the first scientist who introduced the idea of random motion of atoms with the equilibrium statistical velocity distribution. In 1860, he established a relation between the shear viscosity and the mean free path. In his kinetic theory Maxwell demonstrated that viscosity could be proportional to the density, the mean free path, and the mean molecular velocity. On the other hand, the mean free path is inversely proportional to the density, and Maxwell's viscosity equation indicated that an increase of pressure does not result in any change of the viscosity coefficient of gases. Maxwell believed

that his predictions were absurd and therefore that the kinetic theory was wrong, or at least inadequate.

Boltzmann¹⁶ extended Maxwell's treatment of gas kinetic theories and proposed a probabilistic explanation. In 1872, Boltzmann attempted to establish the fundamental governing equation describing the changes in one-particle distribution function resulted from collisions between molecules, namely, the conservation of the probability density under its time evolution. The resulting integro-differential equation played a key role in determining the Boltzmann shear viscosity in the kinetic theory. In principle, the Boltzmann equation completely describes the dynamics of gas particles with appropriate boundary conditions. He also showed in his famous *Boltzmann's H-theorem* that, whatever the initial distribution function, the collisions always push toward the equilibrium Maxwell distribution.

In 1917, although the derivation known today is that of Enskog, the improved predictions were obtained from the kinetic transport theory independently by Chapman and Enskog.¹⁷ Interestingly, Chapman started from Maxwell's transport theory whereas the Enskog's derivation was based on Boltzmann's. Although it is a simple generation of the Boltzmann equation, the Enskog theory provides much accurate approximation to the transport phenomena, particularly in dense gases. Moreover, the analytical expressions for the transport coefficients in the kinetic theory can be adjustable for any given interaction potential. In the case of the hard-sphere potential in the dilute limit, the viscosity formula is now called as the Boltzmann viscosity, which confirms the temperature-dependence and the absence of density-dependence as predicted by the earlier Maxwell's kinetic theories.

As mentioned above, Maxwell showed in his kinetic theory that the viscosity coefficient is independent of the density. However, even in moderately dense gases, it appears that this property can no longer be observed experimentally. Enskog proposed an extension of his method predicting the density dependence. Considering a hard-sphere system, he assumed that the collision rate in a dense gas would be changed by a certain degree of structural factor, which is directly related with the equation of state. In hard-sphere systems, the Enskog factor is the same as the contact value in the radial distribution function. This argument leads to obtain the density dependent expression in

the kinetic theory of viscosity. Obviously, the Enskog factor reduces to unity only in the dilute gas limit.

In 1960's, Cohen,¹⁸ who is the Boltzmann medal laureate in 2004, proved that transport coefficients, in particular the viscosity coefficient, cannot be expressed in a power-series in terms of the density (analogous to the virial-expansion of the pressure in terms of the density). It was also shown that velocity correlations between molecules were observed over long distances, larger than the range of the intermolecular interaction. Although his contribution to the discovery of long-distance correlations may be great in the modern kinetic theories, these contributions do not seem to be significant in the viscosity of hard-sphere gases. Nevertheless, the Enskog prediction is still employed successfully in predicting numerical and experimental results.

In 1950's, a time-correlation function theory was first developed by Green¹⁹ and Kubo,²⁰ independently. They provided that, known as the Green-Kubo formulas, the transport properties can be expressed by the time-dependent velocity autocorrelations. It implies importantly that for all densities the transport coefficients can be calculated by the integral of time autocorrelation functions. In the case of dilute gases, this expression simply reduces to the Chapman-Enskog results. Soon after in the early 1960's, Helfand²¹ derived an alternative Einstein-like formula related to the variance of the so-called Helfand moments. For the time-dependent transport coefficients, the Green-Kubo expressions are related with the so-called Einstein relations, *i.e.*, the slope of mean-square displacement curve in the long time limit. Both the Green-Kubo formulas and the Einstein relations are valid at any density and temperature condition, whereas the kinetic theory has only been successfully applied to low or moderate density states of gases.

In 1970, the first MD calculation for viscosity properties in the systems of hard-disks and hard-spheres was developed by Alder et al.²² In this pioneering simulation work for the discontinuous potential, they proposed an algorithm based on the generalized Einstein relations derived from the Green-Kubo formulas. The first MD application of the Green-Kubo method for the continuous Lennard-Jones 12-6 potential has been performed by Levesque et al.²³ in 1973. We do not intend here to survey all possible theoretical approaches for viscosity in the literature, except for one important

implementation made by Viscardy and his coworkers.²⁴⁻²⁵ In 2003, Viscardy's research group has first applied the Helfand method to calculate viscosity coefficients for both continuous and discontinuous potentials during MD calculations. As proposed in their work, the Helfand-moment should be modified in order to satisfy the conventional periodic boundary conditions, and this can be expressed as an Einstein-like relation in terms of the variance of the Helfand moment. For the discontinuous HS system, their Helfand-moment approach is equivalent to the generalized Einstein relations proposed by Alder et al.²²

THEORETICAL APPROACH FOR SHEAR VISCOSITY

The so-called penetrable-sphere model potential is defined as

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

where σ is the diameter of penetrable spheres, and ε (>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 in the low-temperature limit ($T^* \equiv kT/\varepsilon \rightarrow 0$, or $\varepsilon^* \equiv \varepsilon/kT \rightarrow \infty$, where k is the Boltzmann constant, and T the temperature), while the PS system become a collisionless ideal gas in the high-temperature limit ($T^* \rightarrow \infty$, or $\varepsilon^* \rightarrow 0$). 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 method¹⁷ to the well-know Boltzmann equation. By using the first Sonine approximation, the shear viscosity coefficient obtained from the Boltzmann equation for the PS model is given by²⁶

$$\eta_0^{\text{PS}} = \frac{5}{16} \frac{\sqrt{mkT/\pi}}{\sigma^2} \frac{1}{\Omega_{22}^*} \quad (2)$$

where

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

with

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

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

$$\eta_o^{\text{HS}} = \frac{5}{16} \frac{\sqrt{mkT/\pi}}{\sigma^2} \quad (5)$$

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 ($\phi \rightarrow 0$). 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.¹⁷ The Enskog correction for the shear viscosity coefficient in the HS system can be written as

$$\eta_E^{\text{HS}} = \eta_o^{\text{HS}} \left[\frac{(1+8/5\phi\chi^{\text{HS}})^2}{\chi^{\text{HS}}} + \frac{768}{25\pi} \phi^2 \chi^{\text{HS}} \right] \quad (6)$$

where the Enskog factor is directly related to the contact value of the radial distribution function in the HS system, i.e., χ^{HS} . Theoretically in the HS model, an excellent approximation for χ^{HS} within the stable fluid region (can be provided by the Carnahan-Starling formula²²

$$\chi^{\text{HS}} \left(\equiv g^{\text{HS}}(\sigma^+) \right) = \frac{1-\phi/2}{(1-\phi)^3} \quad (7)$$

The HS Enskog formula for the sphere viscosity, as given in Eq. (6), can be represented by the different expression, i.e.,

$$\eta_E^{\text{HS}} = \eta_o^{\text{HS}} \left[\frac{1.016}{\chi^{\text{HS}}} + 0.8bn + 0.7737\chi^{\text{HS}}(bn)^2 \right] \quad (8)$$

where $b \left(\equiv (2\pi/3)\sigma^3 \right)$ is the second virial coefficient of the HS fluid. The three terms in the bracket of Eq. (8) are related to the kinetic, cross and collisional components, respectively. At liquid-like high density the last collisional term is the dominant component.

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 $Z \left(\equiv PV/NkT \right)$. For the HS system, one may have

$$Z^{\text{HS}} = 1 + 4\phi\chi^{\text{HS}} \quad (9)$$

and, similarly, for the PS fluid system,

$$Z^{\text{PS}} = 1 + 4\phi x \chi^{\text{PS}} \quad (10)$$

with

$$x = 1 - e^{-\varepsilon^*} \quad (11)$$

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 shear viscosity coefficient. From extensive MD computations with an efficient MD algorithm dealing with up to 32,000 HS particles, the following analytical fit to MD data was reported by Sigurgeirsson and Heyes²⁷

$$\eta_{\text{MD}}^{\text{HS}} = \eta_o^{\text{HS}} / \left[1 - \left(\frac{\phi}{\phi_1} \right) \right]^m \quad (12)$$

with the two fitting parameters of $m = 1.92$ and $\phi_1 = 0.58$. This equation reproduces MD shear viscosity data quite well within the equilibrium HS fluid range $0 < \phi < 0.493$. However, there is a rapid rise in the shear viscosity coefficient in the metastable density regime of $\phi \geq 0.5$. One must exercise caution carefully for the curve fitting in the metastable density range.

Based on Eq. (6), we propose an empirical Enskog-like approximation for the shear viscosity in the PS model system. It is made of three steps: (i) replace the Boltzmann viscosity by η_o^{PS} , as given by Eqs. (2)-(4); (ii) replace χ^{HS} by χ^{PS} ; (iii) replace ϕ by the product ϕx . Steps (i) and (ii) are quite evident, while step (iii) is inspired by Eqs. (8) and (9) and by the fact that in the limit $\varepsilon^* \gg 1$ the product ϕx is the relevant parameter combining density and temperature.⁴ In summary, an empirical Enskog-like approximation for the PS shear viscosity proposed in this work can be written as

$$\eta_E^{\text{PS}} = \eta_o^{\text{PS}} \left[\frac{(1+8/5\phi x \chi^{\text{PS}})^2}{\chi^{\text{PS}}} + \frac{768}{25\pi} \phi^2 x^2 \chi^{\text{PS}} \right] \quad (13)$$

In this equation, the Enskog factor can be given either from in Eq. (10), or from , 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 σ , a unit particle mass m , and a unit thermal energy kT . In these system units the reduced shear viscosity coefficient is expressed as . The resulting MD data for the shear viscosity coefficients are calculated by using the generalized Einstein relations developed by Alder et al.²²

In our MD investigations, the initial configurations with 864 penetrable spheres were generated by randomly inserting PS particles with velocities drawn from the Maxwell-Boltzmann distribution. The initial configurations were aged, or equilibrated, for 510^6 collisions before accumulating the final simulation results. Additional ensemble averages were evaluated from a total number of 510^8 collisions. Our MD algorithm has been tested in a number of ways. MD simulations for a few selected runs were compared with MC calculations reported in the literature.⁵ An excellent agreement with previous MC data again confirmed the validity of the MD method employed in this work. When the repulsive energy parameter was assigned to large values

(typically, $\varepsilon^* > 3$) in lower density regimes (typically, $\phi < 0.2$), the shear viscosity coefficients obtained from our MD simulations faithfully reproduced those of the pure HS system.^{22,27}

By using a semilogarithmic scale in Fig. 1(a) and the original scale in Fig. 1(b) and (c), we have illustrated the reduced shear viscosity coefficient as a function of the packing fraction ϕ . Larger statistical uncertainties are observed in calculating the shear viscosity coefficients from MD simulations. The shear viscosity is related with the fundamental mechanism of momentum dissipation under the influence of velocity gradients. At the microscopic level, viscosity arises because of a transfer of momentum between fluid layers moving at different velocities, as explained by Maxwell and Boltzmann kinetic theory. Following this argument, the shear viscosity can be measured from the *collective* time-dependent behavior of many particles. In contrast, the self-diffusion behavior is a *single* particle property and is determined from the motion of each particle, i.e., the average over N -particles, resulting in better statistics for the self-diffusion than the shear viscosity under the same simulation condition.

The detailed dynamic properties involved in the PS model systems has been already explained in the first series of papers, and we will summarize here only important findings for the shear viscosity properties displayed in Fig. 1.

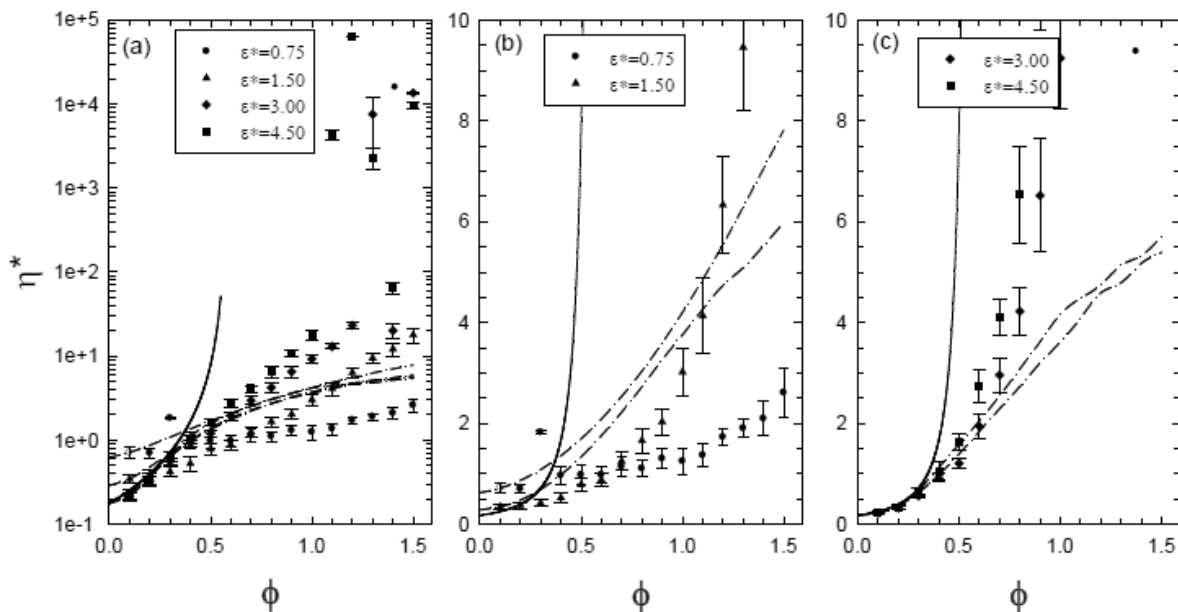


Fig. 1 – The reduced shear viscosity η^* as a function of the packing fraction ϕ in the semilogarithmic scale in (a) and the original scale in (b) and (c). The symbols denote MD simulation data for the PS system; the dotted and the solid line, respectively, correspond to the Enskog prediction in Eq. (6) and to the empirical MD data in Eq. (12) for the HS system; the chain-dotted lines represent an empirical Enskog-like approximation in Eq. (13), complimented with the MD-values of η^* .

(i) The HS shear viscosity coefficients of the Enskog HS equation is close to those of MD values within the narrow range of densities $\varphi \leq 0.3$, and the deviations between them are getting larger with increasing the densities, for instance, 4 at $\varphi = 0.555$. 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.

(ii) As observed in Fig. 1(a), MD results for the shear viscosity displays the linearly increasing tendency in the semilogarithmic scale. Furthermore, there is a transition tendency from a nearly independent (or, slightly increasing) function in lower repulsive systems, where the soft-type collisions are dominant, to a relatively rapid increasing function in higher repulsive system, where most particle collisions are the hard-type reflections due to the low-penetrability effects.

(iii) In contrast to the self-diffusion coefficients, a better prediction is achieved in higher repulsive systems (Fig. 1(c)) than lower repulsive ones (Fig. 1(b)). As expected, the mismatching tendencies are gradually growing with increasing densities.

(iv) In the two highly repulsive cases of $\varepsilon^* = 3.0$ and 4.5 (Fig. 1(c)), the shear viscosity coefficients from MD simulations are close to those of HS predictions over the density regime up to $\varphi \sim 0.4$. The phase transition from the fluid-like to the solid-like state is indicated for the dense systems of $\varphi > 1.2$ ($\varepsilon^* = 3.0$), and $\varphi > 1.1$ ($\varepsilon^* = 4.5$) as shown in Fig. 1(a). The Enskog-like theory strongly underestimates the values of the shear viscosity due to the cluster-forming structure, and, in this case, the collision contributions are more dominant than the kinetic contributions to the shear viscosity.

Before concluding this section, it is of interest to return to one of the observations made earlier to explain some relevant shortcomings involved in the Boltzmann theoretical approximation. The failure of the Boltzmann kinetic approximation for the PS model fluid becomes more important as the density increases. This is not surprising: one may recall that the Boltzmann kinetic theory is based on the high-dilution limit. A key element related to this kinetic theory is the molecular chaos assumption, known as “*Stosszahlansatz*”, in which the precollision velocities of two colliding particles are assumed to be totally uncorrelated. In addition, regardless of a given model potential, the Boltzmann kinetic theory deals with only binary

collision effects by totally neglecting multiple collisions. As observed in MD simulations for the PS model potential in this work, the deviation between our MD results and the Boltzmann predictions can be largely due to the neglect of such spatiotemporal correlations in the PS collision dynamics, particularly in dense system with cluster-forming structures.

CONCLUSIONS

In this series of two papers, we have carried out molecular dynamics simulations to investigate the time-dependent transport properties of the PS fluid over a wide range of the packing fractions and the repulsive energy parameters. Our MD results for the shear viscosity are compared directly with various theoretical approximations available in the literature including an empirical Enskog-like approximation proposed in this work. Similarly to the diffusion behavior, the deviations from MD data against our heuristic 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. In this case, the collision contributions become more dominant than the kinetic contributions to the shear viscosity. Reliable predictions, particularly for the systems of higher densities and higher repulsive energy barriers, may or may not be obtained from modified approximations by considering the structural effects (e.g., the effective packing correction, etc.) together with the energy effects (e.g., the mean-field energy correction, etc.). We are currently examining to extend our empirical Enskog-like predictions to the two limiting cases of high- and low-penetrability approximations in the PS model system. Further results will be reported with relevant MD data in the near future.

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