A Generalized Soft-Sphere Model for Monte Carlo Simulation

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Abstract A new collision model, called the generalized soft-sphere (GSS) model, is introduced. It employs the same total cross section as the generalized hard-sphere (GHS) model, whereas the deflection angle is calculated by the soft-sphere scattering model. In virtue of a two-term formula given to fit the numerical solutions of collision integrals for the Lennard-Jones (6-12) potential and for the Stockmayer potential, the parameters of the GSS model are determined explicitly. Coefficients of viscosity, self-diffusion and diffusion predicted by the GSS model compare quite well with measured data for both polar and non-polar molecules over a wide temperature range.

INTRODUCTION

The direct simulation Monte Carlo (DSMC) method is a general numerical technique to analyze rarefied gas flows [1]. The strategy of DSMC is to track the molecular trajectory and status based on the collision mechanics of model molecules, and then obtain physical quantities of interest through statistical average. A physically realistic collision model is therefore critical for DSMC to predict various gas flows reliably and accurately. In actual gases the force between two molecules is repulsive at small distances, and more weakly attractive at larger distances. This behavior is most simply described by the Lennard-Jones (6-12) potential [2,3]

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (1)$$

The parameters ε and σ (which have dimensions of energy and length, respectively) are constants characteristic of the chemical species of the colliding molecules, and r is the inter-molecular separation. Systematic studies [2,3] showed that the potential (1) was adequate for many non-polar molecules such as air.

For polar molecules like ammonia and water vapor, however, strong electrostatic interaction leads to anomalous behavior with respect to the potential (1) [2,3]. This electrostatic contribution is proven proportional to the inverse third power of the intermolecular separation. Stockmayer combined such a term with the Lennard-Jones potential [2,3]

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 - \delta \left(\frac{\sigma}{r} \right)^3 \right]. \quad (2)$$

where δ is a dimensionless constant that measures the polarization of a substance. The potential (2), known as the Stockmayer potential, was successfully applied to many polar molecules [2,3].

An accurate procedure to calculate collision cross sections and scatter under the potentials (1) or (2) has been widely used in kinetic studies of transport properties [2,3]. Application of this procedure to DSMC, though straightforward in principle, is too computationally intensive in engineering context where millions and even

billions of molecular collisions have to be considered. Many efforts [4-9] have been paid to establish a collision model appropriate to the DSMC method. The variable hard-sphere (VHS) model proposed by Bird [4,5] assumes that the total cross section varies like

$$\sigma_T \propto c_r^{-2\omega}, \quad (3)$$

while the deflection angle in a collision follows the hard sphere scattering law, i.e. an isotropic scattering in the center of mass frame of reference, where c_r is the relative speed of the colliding molecules.

The total cross section (3) bears the same relation of coefficient of viscosity to temperature as the inverse-power-law (IPL) potential [1,4]

$$\mu \propto T^{\omega+1/2}. \quad (4)$$

It is known that IPL considers the repulsive force between molecules only and becomes poor at low temperatures where the attractive force dominates [2,3]. Therefore, it is desirable to establish a model based on potentials with both attraction and repulsion like (1). Under the hard-sphere scattering, the potential (1) has the following relation of coefficient of viscosity to temperature [9]

$$\mu \propto \frac{T^{1/6+1/2}}{1+c_o T^{-1/2}}, \quad (5)$$

where c_o is a constant. Clearly, the relations (4) and (5) are inconsistent. This led to the introduction by Hassan and Hash [9] of the GHS model that still employs the hard-sphere scattering law, but the total collision cross section is assumed as

$$\frac{\sigma_T}{\sigma^2} = \sum \beta_j \left(\frac{E_t}{\varepsilon} \right)^{-\ell_j}, \quad (6)$$

where $E_t = \frac{1}{2} m_r c_r^2$, m_r is the reduced mass of two colliding molecules, and β_j and ℓ_j are constants that depend on the interaction potential and the molecular species under consideration.

Koura and his co-workers [6,7] showed that the hard-sphere scattering led to an incorrect ratio of the momentum to viscosity cross-section. They suggested a soft-sphere scattering model to calculate the deflection angle [7]

$$\chi = 2 \arccos \left[(b/d)^{1/\alpha} \right], \quad (7)$$

where b is the miss-distance impact parameter, d is the collision diameter, and α is chosen to match the real ratio of the momentum to viscosity cross section.

Besides the computational efficiency, these models aimed at phenomenological reproduction of transport coefficients of real gases. They were to some extent successful, whereas certain important issues such as molecular polarization remain to be settled. Moreover, the parameters involved in the GHS model were not explicitly expressed, and had to be numerically solved through the least-square fitting of experimental data of viscosity coefficient for simple gases and of binary diffusion coefficient for gas mixtures [8,9]. This is somewhat inconvenient for practical use, and sometimes even infeasible because the measurement of the diffusion

coefficients is difficult to observe and experimental data are often not available [3,11].

In this paper, firstly, a universal collision model, named as generalized soft-sphere (GSS) model, is suggested that applies to both polar and non-polar molecules over a wide temperature range. Then, a fitting formula of the numerical solutions of the collision integrals for the potentials (1) and (2) is given, which is appropriate to determine the parameters of the GSS model explicitly. Next, transport coefficients predicted by GSS previous models are compared with experimental data.

GSS MODEL

The GSS model combines the advantages of the GHS and VSS models, in which the total cross section and the deflection angle are described by Eqs. (6) and (7), respectively. The main difficulty associated with this model is how to determine the involved parameters explicitly, which is essentially important for practical convenience.

It is known that the coefficients of viscosity and self-diffusion of a simple gas, to the first approximation, may be written as [2,3]

$$\mu = \frac{5}{16} \left(\frac{\sqrt{\pi m k T}}{\pi \sigma^2 \Omega^{(2,2)*}} \right), \quad (8)$$

$$D = \frac{3kT}{16p} \left(\frac{\sqrt{2\pi k T / m_r}}{\pi \sigma^2 \Omega^{(1,1)*}} \right), \quad (9)$$

with

$$\Omega^{(1,1)*} = \frac{1}{\pi \sigma^2} \int_0^\infty \exp(-\zeta^2) \zeta^5 \sigma_D d\zeta, \quad (10)$$

$$\Omega^{(2,2)*} = \frac{1}{2\pi \sigma^2} \int_0^\infty \exp(-\zeta^2) \zeta^7 \sigma_\mu d\zeta, \quad (11)$$

where $\zeta^2 = \frac{1}{2} m_r c_r^2 / kT$, σ_μ and σ_D are the viscosity and momentum cross sections, respectively, p and T are the gas pressure and temperature, m is the molecular mass, and k is the Boltzmann constant. For the soft-sphere scattering, we have [7]

$$\sigma_\mu = \frac{2S_\mu}{3} \sigma_T, \quad \sigma_D = S_D \sigma_T, \quad (12)$$

with

$$S_\mu = 6\alpha / [(\alpha + 1)(\alpha + 2)], \quad (13)$$

$$S_D = 2/(\alpha + 1). \quad (14)$$

Substituting of Eqs. (6) and (12-14) into (10) and (11) yields the self-diffusion and viscosity integrals for the GSS model

$$\Omega_{GSS}^{(1,1)*} = \frac{1}{\pi(\alpha^* + 1)} \sum \beta_j^* \Gamma(3 - \ell_j^*) T_*^{-\ell_j^*}, \quad (15)$$

$$\Omega_{GSS}^{(2,2)*} = \frac{\alpha^*}{\pi(\alpha^*+1)(\alpha^*+2)} \sum \beta_j^* \Gamma(4-\ell_j^*) T_*^{-\ell_j^*}, \quad (16)$$

where $T_* = kT/\varepsilon$, and $\Gamma(\dots)$ denotes the gamma function.

A simple means to determine the parameters of the GSS model is to compare the right-hand sides of Eqs. (15) and (16) against those of (10) and (11). However, the latter may be solved analytically only at special conditions such as IPL or the hard-sphere scattering law. For the Lennard-Jones (6-12) potential, there was only the numerical solution available, that was obtained by Hirschfelder, Curtiss and Bird and tabulated as functions of $T_* = kT/\varepsilon$ from 0.3 to 400 in Tables I-M, Ref. 3. The current paper suggests a two-term fitting formula

$$\Omega_{fit}^{(2,2)*} = a_1 T_*^{-c_1} + a_2 T_*^{-c_2}, \quad (17)$$

where $a_1 = 1.1$, $a_2 = 0.4$, $c_1 = 0.133$, and $c_2 = 1.25$. As shown in Fig.1a), there is a remarkable agreement between Eq. (17) and the data of Hirschfelder, et al.

The fitting formula (17) is also suitable to the Stockmayer potential. c_1 and c_2 do not change, whereas a_1 and a_2 need an additional term to include the polarization effect

$$a_1 = 1.1 - 0.044\delta, \quad a_2 = 0.4 + 0.76\delta. \quad (18)$$

In Fig. 1b), the formula (17), with a_1 and a_2 calculated by Eq. (18), compares well with the accurate solution obtained by Krieger [10] (also see Table IX, Ref. 3).

Equating the right hand sides of Eqs. (16) and (17) yields

$$\ell_1^* \equiv c_1 = 0.133, \quad (19)$$

$$\ell_2^* \equiv c_2 = 1.25, \quad (20)$$

Figure 1 Comparison of the fitting formula (17) with the accurate solutions [3,10].

Figure 2 Comparison of the self-diffusion integral (15) for the GSS model with the accurate solution [3].

$$\frac{\alpha^*}{\pi(\alpha^*+1)(\alpha^*+2)} \times \beta_1^* \Gamma(4 - \ell_1^*) \equiv a_1, \quad (21)$$

$$\frac{\alpha^*}{\pi(\alpha^*+1)(\alpha^*+2)} \times \beta_2^* \Gamma(4 - \ell_2^*) \equiv a_2, \quad (22)$$

and $\beta_j^* \equiv 0$ for $j > 2$. This indicates that the first two terms of the general form (6) are enough for either Lennard-Jones or Stockmayer potential.

Another relation to determine α^* , β_1^* and β_2^* may be provided by $\Omega_{GSS}^{(1,1)*}$ that is in satisfactory agreement with the numerical solution of $\Omega^{(1,1)*}$ for the Lennard-Jones (6-12) potential given in Table I-M of Ref. 3, when (Fig. 3)

$$\alpha^* = 1.5. \quad (23)$$

This value is reasonable since α^* generally lies between 1 and 2 (cf. Ref. 1, pp.42).

From Eqs. (21-23), β_1^* and β_2^* may be easily solved

$$\beta_1^* = 3.962 - 0.158\delta, \quad \beta_2^* = 4.558 + 8.660\delta. \quad (24)$$

ε , σ , and δ

The parameters ε , σ and δ in the potentials (1) and (2) for like molecules may be determined from experimental data of coefficient of viscosity. A procedure was described in detail in Ref. 3 that also provided the values of ε , σ and δ for many gases in Tables 8.4-1, 8.6-1 and I-A.

Force constants between unlike molecules, in principle, may be obtained from the binary diffusion coefficient at different temperatures. However, unlike the measurement of coefficients of viscosity that has been carried out accurately for a number of gases, few measurement of diffusion has been made [3,11]. It is customary

to make use of the combining laws to relate the force constants between unlike molecules to those between like molecules [3]. If both unlike molecules are non-polar or polar, the combining laws are simply as

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \quad \delta_{ij} = \sqrt{\delta_i \delta_j}. \quad (25)$$

The interaction between a polar molecule and a non-polar molecule obeys the same potential as that between two non-polar molecules, i.e. the Lennard-Jone (6-12) potential, whereas the combining laws to determine the force constants are a little different [3]

$$\sigma_{np} = \frac{1}{2}(\sigma_n + \sigma_p)\xi^{-1/6}, \quad \varepsilon_{np} = \sqrt{\varepsilon_n \varepsilon_p} \xi^2, \quad \xi = 1 + 0.5\alpha_n \sigma_n^{-3} \delta \sqrt{\varepsilon_p / \varepsilon_n}, \quad (26)$$

where σ_n, ε_n are Lennard-Jones potential parameters for the non-polar molecule, σ_p, ε_p are Stockmayer potential parameters for the polar molecule, and α_n is reduced polarizability of the non-polar molecule. The values of α_n for many gases were given in Table 13.2-3, Ref.3.

COMPARISON OF MODELS WITH EXPERIMENT

A number of experiments have been carried out to measure transport coefficients. The measured data obtained by different authors covered a wide temperature range, and were collected in Chapter 8, Ref. 3 and Table 6-177, Ref. 11. In the GSS model, the coefficients of viscosity, self-diffusion and diffusion are given by Eqs. (8), (9), (15) and (16), and the parameters involved are calculated by Eqs. (18-20), (23), and (24).

Figure 3a) compares the viscosity coefficient for argon given by the GSS model and experiment [3,11], which are in excellent agreement over the entire range of temperature. Also included is the profile given by the VSS model based on the IPL for which the VSS parameters are available (cf. Table I, [7], or Table A3, [1]). The VHS and GHS profiles, not shown in the figures, almost overlay with the VSS and GSS profiles, respectively. The differences between the VSS and experimental results at the low and high temperatures may be attributed to the attractive portion of molecular interaction neglected in IPL and a constant of ω used in VSS for convenience of engineering simulation. It is known that the attractive force becomes important at low temperature, and the real value of ω markedly varies with the range of temperatures (cf. [2], pp. 231).

Figure 3 Comparison of coefficients of viscosity given by the GSS model with measured data [3,11].

The coefficients of viscosity of water vapor given by GSS and experiment [11] show a satisfactory agreement in Fig. 3b. Because of a strong polar property ($\delta=2.333$), the IPL and Lennard-Jones potentials are not suitable to this kind of molecules [2,3], so are the VHS, VSS and GHS models based on them.

Table 1 compares the self-diffusion coefficients for four common gases (Ar, H₂, N₂, and CO₂) given by the models and experiment [3]. The GSS results agree quite nicely with the measured data, with the difference generally within 5%, except at an extremely low temperature of 20K for hydrogen where it is nearly 10%. The difference between the VSS model based on IPL and the experiment is about 10% at normal temperatures, but it becomes serious at the lower temperatures. Because of the hard-sphere scattering employed, the GHS and VHS results generally deviate more than 20-30% from the experimental data.

TABLE 1. Self-diffusion coefficients (cm²sec⁻¹) at 1 atm given by four models and experiment.

Gas	T (°K)	GSS	VSS	GHS	VHS	Experiment [3]
Ar	77.7	0.0130	0.0178	0.0104	0.0134	0.0134 ± 0.0002
	273.2	0.161	0.173	0.129	0.131	0.156 ± 0.002
	353.2	0.258	0.276	0.206	0.207	0.249 ± 0.003
H ₂	20.4	0.0100	0.0165	0.008	0.0140	0.00816 ± 0.0002
	85.	0.172	0.179	0.138	0.152	0.172 ± 0.008
	273.	1.327	1.255	1.062	1.067	1.285 ± 0.002
N ₂	77.7	0.0160	0.0205	0.0128	0.0164	0.0168 ± 0.0003
	273.2	0.181	0.183	0.145	0.146	0.185 ± 0.006
	353.2	0.287	0.286	0.230	0.228	0.287 ± 0.009
CO ₂	194.8	0.0478	0.0557	0.0382	0.0375	0.0516
	273.2	0.0938	0.1069	0.0750	0.0720	0.0970
	312.8	0.1218	0.1389	0.0974	0.0935	0.1248
	362.6	0.1614	0.1847	0.129	0.1244	0.1644

TABLE 2. Diffusion coefficients (cm²sec⁻¹) at 1 atm given by GSS,VSS and experiment.

Gas	T (°K)	GSS	VSS	Experiment [3]
N ₂ -H ₂	273.2	0.696	0.712	0.674
	288.2	0.764	0.783	0.743
	293.2	0.787	0.808	0.76
N ₂ -CO ₂	273.2	0.134	0.120	0.144
	288.2	0.148	0.131	0.158
	293.2	0.153	0.135	0.16
	298.2	0.157	0.139	0.165
H ₂ -CO ₂	273.2	0.571	0.526	0.550
	288.2	0.628	0.580	0.619
	293.2	0.648	0.599	0.60
	298.2	0.667	0.618	0.646

Tables 2 compares the coefficients of diffusion for non-polar molecules given by GSS, VSS and experiment [3], and Table 3 compares those for polar molecule H₂O and non-polar molecules given by GSS and experiment³. The GSS parameters ε , σ and δ are obtained using the combining laws (25) and (26), respectively. As can be seen, there is an excellent agreement between the GSS and experimental results.

TABLE 3. Coefficient of diffusion (cm²sec⁻¹) for H₂O and non-polar gases at 1 atm.

Gas	T (°K)	GSS	Experiment [3]
H ₂ O-H ₂	307.4	1.00	1.02
	328.5	1.13	1.12
	352.2	1.28	1.20
H ₂ O-CO ₂	307.4	0.198	0.202
	328.5	0.225	0.211
	352.2	0.258	0.241
H ₂ O-He	307.4	1.00	0.90
	328.5	1.12	1.01
	352.2	1.26	1.12
H ₂ O-N ₂	307.4	0.272	0.256
	328.5	0.309	0.303
	352.2	0.352	0.359

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