

Calculation and algebraic approximation of the diffusion and viscosity coefficients for polar gases as functions of temperature and parameters of the Stockmayer potential

V.P. Kochanov and V.I. Starikov

*Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk*

Received August 8, 2001

The gas kinetics collision integrals describing the diffusion and viscosity are calculated as functions of dimensionless temperature and energy of dipole-dipole interactions. The algebraic approximations for viscosity and diffusion coefficients of polar gases are constructed with the mean accuracy of 0.5%. Based on experimental data on the temperature dependence of the water vapor viscosity coefficient, parameters of the Lennard-Jones (12-6) potential are determined for H₂O-H₂O interaction.

Introduction

In Ref. 1, Monchick and Mason proposed a scheme and calculated the transport coefficients for polar (and nonpolar, as a particular case) gases from classical calculations of scattering cross sections based on the Lennard-Jones intermolecular interaction potential supplemented with the dipole-dipole interaction (Stockmayer potential). The model of Ref. 1 provides for a good quantitative description of experimental data, and its main advantage is the possibility of determining the parameters of Lennard-Jones potential from the experimental dependence of the viscosity and diffusion coefficients on the gas temperature. The tables of collision integrals of the Boltzmann kinetic theory that determine the transport coefficients were calculated in Ref. 1 and then those were used in Refs. 2 and 3. At the same time, the tabular representation of the dependence of collision integrals on the reduced temperature and the dipole moment is inconvenient from the viewpoint of solution of the inverse problem on reconstruction of the potential. Thus, Monchick and Mason¹ used a heuristic graphical method for this purpose, and minimization with the use of the least squares method was made likely by interpolating the tables.

The aim of this work is to reconstruct the calculations of Ref. 1 in a wider range of values of the reduced dipole moment and to approximate algebraically the dependence of the calculated diffusion and viscosity coefficients on the reduced temperature and the reduced dipole moment, since such an approximation is more convenient in reconstructing the potential than tables.

1. Computational scheme

According to the kinetic theory of gases,¹⁻³ the viscosity η and self-diffusion D_{11} coefficients can be expressed through the collision integrals $\Omega^{(l,s)*}$ as:

$$\eta = \frac{5}{16} \sqrt{\frac{mkT}{\pi}} \frac{f_{\eta}}{\sigma_0^2} \left\langle \Omega^{(2,2)*} \right\rangle, \quad (1)$$

$$D_{11} = \frac{3}{8n} \sqrt{\frac{kT}{\pi m}} \frac{f_D}{\sigma_0^2} \left\langle \Omega^{(1,1)*} \right\rangle. \quad (2)$$

Here T and n are the gas temperature and the particle number density; m is the molecular mass; k is the Boltzmann constant; σ_0 is the parameter of the Lennard-Jones potential that denotes the distance, at which the potential is zero. The dimensionless parameters f_{η} and f_D are expressed through the collision integrals averaged over orientation $\langle \Omega^{(l,s)*} \rangle$:

$$f_{\eta} = 1 + 3 [8\langle E^* \rangle - 7]^2 / 196, \\ f_D = 1 + [6\langle C^* \rangle - 5]^2 [2\langle A^* \rangle + 5]^{-1} / 8; \quad (3)$$

$$\langle A^* \rangle = \langle \Omega^{(2,2)*} \rangle / \langle \Omega^{(1,1)*} \rangle, \quad \langle C^* \rangle = \langle \Omega^{(1,2)*} \rangle / \langle \Omega^{(1,1)*} \rangle; \\ \langle E^* \rangle = \langle \Omega^{(2,3)*} \rangle / \langle \Omega^{(2,2)*} \rangle.$$

The diffusion coefficient of a binary mixture D_{12} is connected with the self-diffusion coefficient as follows²:

$$D_{12} = \frac{\rho_1}{\rho_2} \left(\frac{\rho}{n} \right)^2 \frac{1}{m_1 m_2} D_{11}, \quad (4)$$

$$\rho_{1,2} = m_{1,2} n_{1,2}, \quad \rho = \rho_1 + \rho_2, \quad n = n_1 + n_2,$$

where $n_{1,2}$ and $m_{1,2}$ are the number densities and the molecular masses of gas mixture components; $\rho_{1,2}$ are mass densities of the components.

The collision integrals are calculated from the Stockmayer potential of intermolecular interactions:

$$V(r) = 4\epsilon_0 [(\sigma_0/r)^{12} - (\sigma_0/r)^6] - 2d_1 d_2 \delta / r^3, \quad (5)$$

where r is the separation between the centers of molecules, ϵ_0 is the minimum (depth of the potential well) of the Lennard-Jones potential represented by the first term in Eq. (5); $d_{1,2}$ are the constant dipole moments of molecules; δ is the angular shape factor (scattering phase function) of dipole-dipole interaction:

$$\delta = \cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\varphi / 2. \quad (6)$$

Here $\theta_{1,2}$ are polar angles and φ is the angle of orientation of dipole moments about the axis z passing through the centers of molecules.

The order of calculations was as follows. First, the scattering angles were calculated in the system of the center of gravity by the classical equation⁴:

$$\chi = \pi - 2b \int_{r_0}^{\infty} \frac{dr}{r^2} / \sqrt{1 - b^2/r^2 - 4V(r)/(mv^2)}, \quad (7)$$

$$2m = m_1 + m_2,$$

where b is the impact parameter; v is the relative velocity of molecules in the system of the center of gravity; r_0 is the smallest possible separation between molecules, it is determined from the condition that the radicand in Eq. (7) equals zero.

Then the scattering cross sections were determined

$$Q^{(l)*} = \frac{2}{\sigma_0^2} \left[1 - \frac{1 + (-1)^l}{1 + l} \right]^{-1} \int_0^{\infty} (1 - \cos^l \chi) b db. \quad (8)$$

Averaging of the cross sections (8) over orientations and velocities of molecules yields the sought averaged collision integrals:

$$\langle Q^{(l)*} \rangle = \frac{1}{8\pi} \int_{-1}^1 d \cos \theta_1 \int_{-1}^1 d \cos \theta_2 \times \int_0^{2\pi} d\varphi Q^{(l)*} [\delta(\theta_1, \theta_2, \varphi)], \quad (9)$$

$$\langle \Omega^{(l,s)*} \rangle = [(s + 1)!]^{-1} \times \int_0^{\infty} \exp(-g^2) (g^2)^{s+1} \langle Q^{(l)*} \rangle dg^2, \quad (10)$$

$$g = v / \sqrt{2kT/m}.$$

According to Ref. 5, the triple integration in Eq. (9) can be replaced by a single one:

$$\langle Q^{(l)*} \rangle = \int_{-1}^1 w(\delta) Q^{(l)*}(\delta) d\delta; \quad (11)$$

$$w(\delta) = \begin{cases} (\operatorname{arcsinh} \sqrt{3}) / \sqrt{3} = 0.760346, & |\delta| \leq 1/2, \\ (\operatorname{arcsinh} \sqrt{3} - \operatorname{arcsinh} \sqrt{4\delta^2 - 1}) / \sqrt{3}, & 1/2 < |\delta| \leq 1, \end{cases}$$

where $\operatorname{arcsinh} x$ is the inverse hyperbolic sine.

All the computer codes used in calculations were written on Fortran and assumed doubled accuracy. Integration in Eqs. (7), (8), (10), and (11) was made with the use of the 7-point Newton–Cotes quadrature formula with the splitting of the complete intervals of integration into 1000–2500 parts. In calculations of the scattering angles (7), particular attention has been paid to the orbiting effect⁴ leading to the logarithmic divergence of angles for certain values of energies and impact parameters. The resulting error in calculation of angles that largely determines the error of collision integrals did not exceed 0.1% in orbiting regions and was 2 to 4 orders of magnitude less beyond these regions.

2. Calculated results and their approximation

The calculated values of averaged collision integrals $\langle \Omega^{(1,1)*} \rangle$ and $\langle \Omega^{(2,2)*} \rangle$ determining diffusion and

viscosity are shown in Figs. 1 and 2 as functions of the reduced temperature T^* and dimensionless parameter of dipole–dipole interaction δ_{\max} :

$$T^* = kT / \epsilon_0, \quad \delta_{\max} = d_1 d_2 / (2\epsilon_0 \sigma_0^3). \quad (12)$$

As is seen from Figs. 1 and 2, the dependences of the collision integrals $\langle \Omega^{(1,1)*} \rangle$ and $\langle \Omega^{(2,2)*} \rangle$ on T^* and δ_{\max} are qualitatively the same and quantitatively close. The mean discrepancy (variance) between the calculated collision integrals and tabulated values¹ is, respectively 0.8% for $\langle \Omega^{(1,1)*} \rangle$ and 0.6% for $\langle \Omega^{(2,2)*} \rangle$ as T^* varies from 0.1 to 100 and δ_{\max} varies from 0 to 2.5. The correction factors f_{η} and f_D in Eqs. (1) and (2) exceed unity by a value less than 0.8% in the entire ranges of T^* and δ_{\max} .

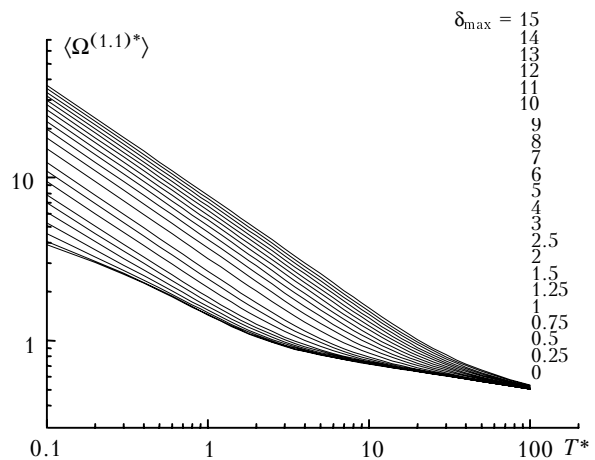


Fig. 1. Collision integral averaged over molecular orientations that determines diffusion of polar molecules as a function of reduced temperature for different values of the dipole–dipole interaction. The curves with larger values of δ_{\max} lie above the curves with smaller δ_{\max} .

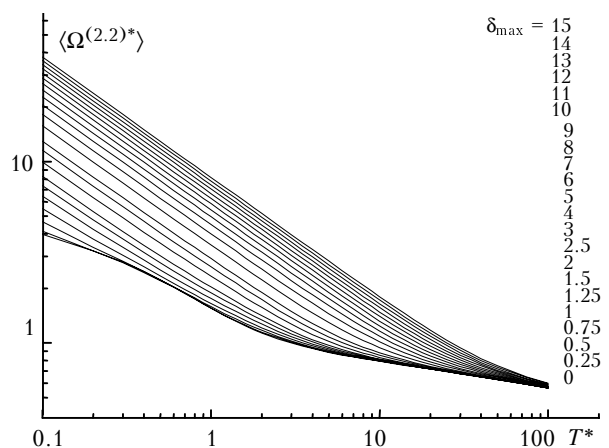


Fig. 2. Collision integral averaged over molecular orientations that determines viscosity of gas of polar molecules as a function of reduced temperature for different values of the parameter of dipole–dipole interaction. The curves with larger values of δ_{\max} lie above the curves with smaller δ_{\max} .

Based on the calculated results, we have constructed the following algebraic approximations of the viscosity and diffusion coefficients:

$$\eta = \sqrt{mkT} \eta_{\text{appr}}(T^*, \delta_{\text{max}}) / \sigma_0^2; \quad (13)$$

$$\log \eta_{\text{appr}} = \{a_1 \log T^* + b_1 + (a_2 \log T^* + b_2) (|\log T^*|/c)^n\} / [1 + (|\log T^*|/c)^n];$$

$$x \equiv \delta_{\text{max}},$$

$$a_1 = 0.7247422 - 5.655572 \cdot 10^{-3} x - 2.7576455 \cdot 10^{-3} x^2 + 6.0319724 \cdot 10^{-4} x^3 - 4.3094133 \cdot 10^{-5} x^4 + 1.0436741 \cdot 10^{-6} x^5 - 0.25886413 / [1 + (|x - 0.57363447| / 1.2445309)^{1.6227661}],$$

$$a_2 = 0.5267300 - 0.1085746 x + 0.0295374 x^2 - 2.744741 \cdot 10^{-3} x^3 + 9.083092 \cdot 10^{-5} x^4 - 3.141767 \cdot 10^{-7} x^5 - 0.3195205 / [1 + (x/0.7709013)^2];$$

$$b_1 = 0.9420289 \exp[-(x/9.016335)^{0.7853031}] + 0.2123226 x / [1 + (x/0.9221603)^{2.16481}] - 1.900440,$$

$$b_2 = -1.510562 + 1.59735 \cdot 10^{-2} x - 2.045292 \cdot 10^{-2} x^2 + 2.664993 \cdot 10^{-3} x^3 - 1.160109 \cdot 10^{-4} x^4 + 6.793047 \cdot 10^{-7} x^5 + 0.4415847 / [1 + (x/0.6668185)^{3.772842}];$$

$$c = 2.873601 - 1.8226866 \cdot 10^{-2} x - 1.1059057 / [1 + (x/0.61982071)^{2.1703422}] - 0.63683164 / [1 + (|x - 2.0519534| / 2.3517048)^{1.781408}] - 0.8709687 / [1 + (|x - 8.1070084| / 8.8435919)^{2.1515749}];$$

$$n = 1.885564332 + 0.7557933802 x - 0.2704320299 x^2 + 6.37128014 \cdot 10^{-2} x^3 - 5.86250287 \cdot 10^{-3} x^4 + 1.291786853 \cdot 10^{-4} x^5 + 8.517075478 \cdot 10^{-6} x^6 - 3.47866534 \cdot 10^{-7} x^7 + 1948.879525 x^{10} \exp[-(x/0.2675743746)^2].$$

$$D_{11} = \sqrt{kT/m} D_{\text{appr}}(T^*, \delta_{\text{max}}) / (\sigma_0^2 n); \quad (14)$$

$$\log D_{\text{appr}} = \{a_1 \log T^* + b_1 + (a_2 \log T^* + b_2) (|\log T^*|/c)^n\} / [1 + (|\log T^*|/c)^n];$$

$$a_1 = 0.5607221 - 0.1045448 / (1 + (|x - 0.5519868| / 0.8608552)^{2.105597}) + 0.0610949 x - 0.01133582 x^2 + 0.001028817 x^3 - 4.594191 \cdot 10^{-5} x^4 + 8.10626 \cdot 10^{-7} x^5,$$

$$a_2 = 0.36931455 - 0.04179245 x + 0.029561990 x^2 - 0.6602176 \cdot 10^{-2} x^3 + 7.1451886 \cdot 10^{-4} x^4 - 3.7876797 \cdot 10^{-5} x^5 + 7.8073647 \cdot 10^{-7} x^6 - 0.14027412 / (1 + (x/0.69408058)^2);$$

$$b_1 = 0.9558057 \exp[-(x/9.222500)^{0.8158828}] + 0.1589620 x / (1 + (x/1.105653)^{2.325833}) - 1.794677,$$

$$b_2 = -1.360751 - 0.0435378 x + 0.821021 \cdot 10^{-2} x^2 - 0.1315467 \cdot 10^{-2} x^3 + 1.202311 \cdot 10^{-4} x^4 - 3.682373 \cdot 10^{-6} x^5 + 0.3800890 / (1 + (x/0.7984236)^{3.056603});$$

$$c = 1.469084 + 0.1006964 x - 0.0444112 x^2 + 0.01196448 x^3 - 0.1459229 \cdot 10^{-2} x^4 + 8.005541 \cdot 10^{-5} x^5 - 1.630008 \cdot 10^{-6} x^6 - 0.3907924 / (1 + (x/0.6409462)^{3.198427});$$

$$n = 2.0804220 - 1.2180876 x + 0.99333563 x^2 - 0.26975727 x^3 + 0.03769358 x^4 - 0.28385368 \cdot 10^{-2} x^5 + 1.0982147 \cdot 10^{-4} x^6 - 1.720156 \cdot 10^{-6} x^7 + 1.3481912 x / (1 + (x/0.91679324)^2).$$

Approximations (13) and (14) are valid as T^* varies from 0.1 to 100 and δ_{max} varies from 0 to 15. Their standard deviations from the exact calculated values are 0.5%, and this discrepancy is sufficient for quantitative processing of data. At $\delta_{\text{max}} = 0$ Eqs. (13) and (14) describe viscosity and diffusion of nonpolar

gases based on the Lennard–Jones potential of intermolecular interaction.

Processing of experimental data⁶ using the temperature dependence of water vapor viscosity at atmospheric pressure [Eq. (13)] and the least squares method at the given dipole moment of the H₂O molecule

$d = 1.85 D$ yielded the following values for parameters of the Lennard–Jones potential: $\epsilon_0/k = 521.2$ K, $\sigma_0 = 2.551$ Å ($\delta_{\max} = 1.433$), which well agree with the results obtained by fitting¹ the same experimental data: $\epsilon_0/k = 506$ K, $\sigma_0 = 2.71$ Å ($\delta_{\max} = 1.2$).

References

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