Application of the perturbation theory for the calculation of thermodynamic and transport properties of hydrogen and its isotopes

Yu A Bogdanova, I V Maklashova, S A Gubin and U D Vagina
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)
Kashirskoye shosse 31, Moscow 115409, Russia
bogdanova.youlia@bk.ru

Abstract. In this paper, we analyzed the analytical relationships in the literature to calculate the viscosity coefficient obtained from the Chapman-Enskog kinetic theory using the Lennard-Jones pair interaction potential. In the proposed formulas for calculating the viscosity of individual substances, there are values of the radial distribution function and the hard-sphere diameter. These quantities were obtained using a technique developed previously by the authors based on the perturbation theory used to calculate the thermophysical properties of substances.

1. Introduction
Perturbation theory is a theory, which allows to make physically based calculations of the thermodynamic properties of fluids at high pressures. One of the best theories for finding equations of state (EOS) of fluids both at high pressures and temperatures, and at lower temperatures and densities, is the perturbation theory of Kang et.al. (KLRR) [1]. This theory reproduces the results of Monte Carlo calculations with good accuracy for different types of interaction potentials of molecules. Perturbation theory is applicable to any gaseous or condensed systems, whose interactions are described by the interatomic potential.

The main idea of any perturbation theory is to divide the potential \( \phi(r) \) of the studied system (i.e., the system for which it is necessary to calculate excess thermodynamic properties compared to an ideal gas) into two components: the dominant part \( \phi^{\text{ref}}(r) \), which is the interaction potential of molecules in some basic system, and a small perturbation \( \phi^{\text{pert}}(r) \). A hard sphere system, which is usually used to study dense fluids, is used as the basis system.

In [2, 3], an improved version of the EOS model of mixtures was successfully applied to calculate the thermodynamic properties of binary systems whose interaction is expressed by the Exp-6 and the Morse potentials.

Perturbation theory also allows to calculate the hard sphere diameter, the packing fraction coefficient, and the radial distribution function of hard spheres. Knowing these values makes it possible to determine the transport properties of a substance, such as viscosity, thermal conductivity, and diffusion.

In the present work, EOS [2] based on perturbation theory is used to calculate the thermodynamic properties of hydrogen isotopes both at normal conditions and in the area of high pressures.
The laws of the kinetic molecular theory of gases in the area of high pressures can not be applied as it seems unrealistic for calculation the transport properties of hydrogen isotopes, such as viscosity and diffusion. The analytical relations [4, 5] for calculating the transfer coefficients obtained from the Chapman – Enskog kinetic theory using the Lennard – Jones potential were analysed. In the proposed formulas [4, 5] for calculating the viscosity of individual substances, there are values of the radial distribution function and the diameter of the hard spheres, which can be obtained from the perturbation theory, which is used to calculate the thermophysical properties of substances.

2. The interatomic interaction potential
In the present research, the Lennard-Jones potential is used to describe interparticle interactions:

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

where \( \varepsilon \) is the well depth, \( \sigma \) is the finite distance at which the inter-particle potential is zero, \( r \) is the distance between the particles. The potential reaches its minimum at the distance \( r_{\text{min}} = 2^{\frac{1}{6}}\sigma \). When the distance between the centers of the particles is less than \( r_{\text{min}} \), the repulsive forces prevail over the attractive forces.

The optimum parameters of the Lennard-Jones potential for describing interactions between hydrogen isotope molecules in the present work are presented in Table 1.

| Molecule | \( T \leq 500 \text{ K} \) | \( T > 500 \text{ K} \) |
|----------|-----------------|-----------------|
|          | \( \varepsilon/k_B \), \( \text{K} \) | \( \sigma, \text{A} \) | \( \varepsilon/k_B \), \( \text{K} \) | \( \sigma, \text{A} \) |
| H\(_2\)  | 33.3            | 2.968           | 33.3            | 2.948           |
| D\(_2\)  | 34.9            | 2.948           | 34.9            | 2.938           |

3. The viscosity of hydrogen isotopes
The viscosity of a gas is determined by the collision of particles of which it is made of. Viscosity is described by the movement and interaction of molecules. In a gas, the distance between the molecules is significantly larger than the radius of action of molecular forces, at this point the viscosity of gases is determined mainly by molecular motion. There is a constant exchange of molecules between the layers of gas, which are moving relative to each other due to their continuous chaotic (thermal) motion. The transition of molecules from one layer to the next one, which moves at a different speed, leads to the transferring of a certain amount of motion from one layer to another. As a result, while slower layers accelerate, faster ones slow down. The work of an external force balancing the viscous resistance and supporting the steady flow completely transforms into heat.

The viscosity of a gas depends weakly on its density (pressure), since when the gas is compressed, the total number of molecules passing from layer to layer increases, but each molecule penetrates into the neighboring layer less deeply and transfers a smaller amount of motion (Maxwell's law). For the viscosity of ideal gases, the following relation is given in molecular kinetic theory [6]:

\[ \eta = \frac{1}{3} \rho \bar{v} \bar{l} \]  

(1)

\( \eta \) – viscosity, \( \rho \) – density of the fluid, \( \bar{v} \) — average speed of molecules, \( \bar{l} \) — average mean free path.

The viscosity of the gases increases proportionally with heating. For very rarefied gas the concept of viscosity loses its meaning.

This theory is not applicable for dense gas. The theory of viscosity of dense gases was proposed by Enskog [7], who supposed that the momentum in a gas is transferred from layer to layer not only by
molecules whose centres pass through the plane separating these layers, but also by molecules whose centres are located on both sides of imaginary partition plane.

Analytical dependences for viscosity were analyzed over a wide range of pressure and temperature, which were based on a literature review [4–14]. The transfer coefficients, such as viscosity, thermal conductivity, and diffusion for a pure gas, which are obtained from the rigorous Chapman-Enskog kinetic theory using the Lennard-Jones interaction model are the most reliable.

The following viscosity dependencies were chosen for verification. They give the most reliable results. The formula was obtained from the Boltzmann equation for hard spheres [4]:

\[
\eta_B = 1.0160 \cdot \frac{\sqrt{m}}{16d^2} \cdot \frac{k_B T}{\pi}
\]

\(d(T, P)\) - diameter of hard spheres, \(m\) – mass of the particle, \(k_B\) - Boltzmann constant

It was shown in [8] that expression (2) corresponds to coefficient for an ideal gas consisting of hard-sphere particles. That is why, this expression is applicable only in the area of low pressures close to atmospheric.

For the high pressure region, analytical expressions for calculating the viscosity of dense gas mixtures of hard spheres are presented in [5, 8, 9]. All of them are written in different variables, but they show the same results. In this work, the expression [5] was chosen:

\[
\eta = \frac{\eta_B}{g(T, P)} \left(1 + \frac{4}{15} \pi \rho d^2 g(T, P)\right)^2
\]

\(g(T, P)\) – radial distribution function at contact point, \(\rho\) – viscosity, \(d\) – diameter of hard spheres.

The values of the distribution function and the diameter of the hard spheres are determined according to the method [15], which is an essential part of the EOS model [2] based on the thermodynamic perturbation theory.

The verification of the chosen expressions (2) - (3) for calculating the viscosity of hydrogen isotopes (H\(_2\) and D\(_2\)) was carried out on the basis of experimental data at 1 atm [6, 13] and at elevated pressures [6, 10, 14].

The results of calculating the viscosity as a function of temperature at a pressure of 1 atm for hydrogen and deuterium are presented in Figures 1 and 2 respectively.

---

**Figure 1.** Viscosity of H\(_2\) depending on temperature at 1 atm. Lines - calculation results: 1 - by the formula (2), 2 - by the formula (3). Symbols - data [6, 13].

**Figure 2.** Viscosity of D\(_2\) depending on temperature at 1 atm. Lines - calculation results: 1 - by the formula (2), 2 – by the formula (3). Symbols - data [6, 13].
Tables 2–4 provide statistics on deviations of the results of calculating the viscosity of hydrogen and deuterium according to formulas (2) - (3) from the literature data [6, 10, 13, 14].

**Table 2.** Statistics of deviations of calculated viscosity of hydrogen H\(_2\) and deuterium D\(_2\) from data [6, 13] at 1 atm (average / maximum value, %).

| Formula | References | 198.15–1273.15 K [6] | 200–2000 K [13] |
|---------|------------|----------------------|------------------|
|         | Hydrogen H\(_2\) |                      |                  |
| 2       |            | 4.94/11.41           | 5.93/11.84       |
| 3       |            | 4.94/11.41           | 5.93/11.84       |
|         | Deuterium D\(_2\) |                      |                  |
| 2       |            | 5.28/11.4            | 7.65/13.36       |
| 3       |            | 5.28/11.4            | 7.65/13.36       |

**Table 3.** Statistics of deviations of calculated viscosity of hydrogen H\(_2\) from data [6, 10, 14] at high pressure (average / maximum value, %).

| Formula | References | 200–1000 K | 288.15–523.15 K | 323.15–423.15 K |
|---------|------------|------------|-----------------|-----------------|
|         |            | 0.1–100 MPa [14] | 0.1–81 MPa [6] | 2–192 MPa [10] |
| 2       |            | 5.25/35.9   | 4.61/16.22      | 5.62/18.08      |
| 3       |            | 3.82/13.09  | 3.72/6.48       | 4.35/8.65       |

**Table 4.** Statistics of deviations of calculated viscosity of deuterium D\(_2\) from data [10] at high pressure (average / maximum value, %).

| Formula | References | 298.15–348.15 K | 2–200 MPa [10] |
|---------|------------|-----------------|----------------|
| 2       |            | 13.06/41.25     | 7.14/17.07     |
| 3       |            |                  |                |

As can be seen from Figures 1-2, as well as statistical tables 2-4, expression (3) in the best way allows us to calculate the viscosity values in accordance with experimental data for hydrogen and deuterium both at normal pressure and in the range of elevated pressures and temperatures.

4. Conclusion
Based on the calculations of the viscosity coefficient for hydrogen isotopes, analytical formula (3) is recommended for calculating the transport properties of hydrogen in a wide range of pressures and temperatures.

The values of the radial distribution function and the diameter of the hard spheres included in the expression for calculating the viscosity can be determined on the basis of the technique [15].

Thus, the equation of state [2], based on perturbation theory, allows one to determine not only the thermophysical properties of hydrogen isotopes, but also transport properties, such as viscosity, diffusion, and thermal conductivity under normal conditions and in the high-pressure range in good agreement with experimental data.

**References**

[1] Kang H S, Lee C S, Ree T, Ree F H 1985 *J. Chem. Phys.* 82 414
[2] Bogdanova Yu A, Gubin S A, Victorov S B, Gubina T V 2015 *High Temperature* 53 481
[3] Bogdanova Yu A, Gubin S A, Viktorov S B, Shargatov V A, Lyubimov A V 2010 *Rus.Phys.J.* **53** 243
[4] Chapman S, Cowling T G 1991 *The Mathematical Theory of Non-Uniform Gases* (Cambridge: Cambridge University Press) p 446
[5] Montanero J M, Santos A 1996 *Phys. Rev. E.* **54** 438
[6] Golubev I F 1959 *Viscosity of Gases and Gas Mixtures. A Handbook* (Moscow: GIFML) p 375
[7] Enskog D 1922 *Kgl Svenska Vetenskapsakad Handl* **63** 1
[8] Marques Jr W, Kremer G M 1991 *Revista Brasileira de Fisica* 1991 **21** 402
[9] Protopapas P, Andersen H C, Parlee N A D 1975 *Chemical Physics* **8** 17
[10] Mitchels A, Shipper A, Rintoul W 1953 *Physica* **19** 1011
[11] Jakobsen Hugo A 2008 *Chemical Reactor Modeling. Multiphase Reactive Flows* (Springer-Verlag Berlin Heidelberg) 1244
[12] Viswanath D S, Ghosh T, Prasad D H L, Dutt N V K, Rani K Y 2007 *Viscosity of Liquids Theory, Estimation, Experiment and Data* (Springer Netherlands) p 662
[13] *Physical Values. Handbook* 1991 (Moscow: Energoatomizdat Publisher House) p 365
[14] Vargaftik N B 1972 *Handbook of the thermophysical properties of gases and liquids* (Moscow: Nauka) p 720
[15] Bogdanova Yu A, Gubin S A, Maklashova I V 2019 *Physics of Atomic Nuclei* **82** 1486