The influence of type of the intermolecular interaction potential on transport properties of helium

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Abstract. A method for calculating the transport properties of helium based on the results of thermodynamic modeling using a theoretically equation of state obtained using perturbation theory is presented. The influence of the type of interparticle interaction potential on the accuracy of calculating the helium’s viscosity and thermal conductivity is shown in comparison with the known experimental data.

1. Introduction

Based on the perturbation theory, it is possible to physically reasonably calculate the thermodynamic properties of fluids at high pressures. One of the best theories to obtain the equation of state (EOS) of fluids both at high pressures and temperatures, and at lower temperatures and densities, is the perturbation theory KLRR [1, 2]. 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 in which there are interactions described by the interatomic potential.

Along with thermodynamic parameters, perturbation theory allows one to calculate the particle diameter in the approximation of hard spheres, the packing fraction coefficient, and the radial distribution function of hard spheres. Knowledge of these values makes it possible to determine the transport properties of a substance, such as viscosity, thermal conductivity, and diffusion.

However, the form of the interaction potential between the molecules of the substance under study significantly affects not only the thermodynamic parameters, but also the accuracy of the calculated transport properties.

In this paper, we studied the influence of the form of the interatomic interaction potential on the accuracy of the calculated values of the coefficient of viscosity and thermal conductivity using EOS based on the thermodynamic perturbation theory using helium as an example.

2. The interatomic interaction potential

To ensure the reliability of thermodynamic modeling, it is necessary to use potentials that realistically describe the nature of intermolecular forces in the pressure and temperature region of interest. Therefore, to analyze the influence of the potential of interparticle interaction on the accuracy of calculating the transport properties of helium, three types of pairwise spherically symmetric potentials
most applicable for describing the interaction of particles were chosen: Lennard-Jones, Morse, and Buckingham (Exp-6). The widespread two-parameter Lennard-Jones potential has the form:

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

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 $$r_{\text{min}} = 2^{1/6} \sigma$$. When the distance between the centers of the particles is less than $$r_{\text{min}}$$, the repulsive forces prevail over the attractive forces.

The three-parameter Morse potential is often used to describe the interaction of atoms and molecules of fluids and condensed matter, including metals, and has a simple form:

$$\varphi(r) = \varepsilon \left[ e^{-2\alpha(r-r_m)} - 2e^{-\alpha(r-r_m)} \right]$$  \hspace{1cm} (2)

At high pressures and temperatures, which are characteristic of shock waves and detonation, repulsive forces play an important role in the interactions of molecules. Therefore, in the field of extreme energy densities, the Buckingham Exp-6 potential has been substantiated to describe the intermolecular interaction of the components of the fluid mixture:

$$\varphi(r) = \frac{\varepsilon}{a-6} \left[ 6 \exp \left( \frac{\alpha}{r_m} \right) - \alpha \left( \frac{r_m}{r} \right)^6 \right], r \geq c$$  \hspace{1cm} (3)

where $$\varepsilon > 0$$ is the depth of the potential well ($$\min[\varphi(r)] = -\varepsilon$$); $$r_m$$ is the distance between the centers of the molecules at which the potential energy is minimal ($$\varphi(r_m) = -\varepsilon$$); $$\alpha$$ is a parameter that determines the stiffness of repulsion of molecules.

The potential parameters (1-3) for helium used in this work are presented in table 1.

Table 1. Sets of potential parameters of helium He - He

| Potential type | $$\varepsilon/k_B$$ | $$K$$ | $$r_m$$, Å | $$A$$, 1/Å |
|---------------|----------------------|-------|-------------|-------------|
| LJ           | 10.8                 | 2.57  | -           |
| Morse        | 12.6                 | 2.92  | 2.197       |
| Exp-6        | 13.0                 | 2.97  | 10.7        |

3. Calculation of transport properties of helium

An analysis of the analytical relationships available in the literature for calculating viscosity over a wide range of pressure and temperature changes is outside the scope of this work. The most reliable are the transfer coefficients, such as viscosity, thermal conductivity, and diffusion for pure gas, obtained from the rigorous Chapman-Enskog kinetic theory [3].

As a result of verification studies, a viscosity dependence was selected that gives the most reliable results. In the field of elevated pressures, the expression [5] is used in this work:

$$\eta = \frac{\eta_B}{g(T, P)} \left( 1 + \frac{4}{15} \pi \rho d^3 g(T, P) \right)^2 + \frac{3}{5} \zeta(\rho, T)$$  \hspace{1cm} (4)

where $$\eta_B = 1.0160 \cdot \frac{5}{16d^2} \cdot \sqrt{\frac{m}{\pi k_B T}}$$ is the viscosity obtained from the Boltzmann equation for hard spheres [4], $$m$$ is the particle mass, $$k_B$$ is the Boltzmann constant, $$g(T, p)$$ is the radial distribution function of hard spheres at the contact point, $$\rho$$ is the density, $$d$$ is the diameter of the hard spheres.

The second term in (4) is described by the equation:
\[ \zeta : (\rho, T) = \frac{4}{5} \rho^2 d^4 g(T, P)(\pi m k_B T)^2 \]

The values of thermal conductivity were calculated by the analytical formula [5]:

\[ \lambda = \frac{\lambda_B}{g(T, P)} \left( 1 + \frac{2}{5} \pi \rho d^3 g(T, P) \right)^2 + \frac{3 k_B}{2 m} \zeta (\rho, T) \]  \hspace{1cm} (5)

The values of the distribution function \( g(T, p) \) and the diameter \( d \) of hard spheres included in expressions (4) - (5) are determined according to the procedure [9], which is an integral part of the EOS model [2] based on the thermodynamic perturbation theory.

First, on the basis of EOS [2] using various types of interaction potentials (1) - (3), we calculated the thermodynamic parameters of helium at 1 atm in the temperature range 270–2000 K for comparison with reference data [6-8]. Using expressions (4) - (5) and the method of calculating the function distribution and diameter of hard spheres [9], the viscosity and thermal conductivity of helium were calculated under these conditions. The calculation results are presented graphically in Figure 1 in the form of the dependence of helium viscosity on temperature (Figure 1a) and the dependence of thermal conductivity on temperature (Figure 1b) in comparison with reference data [6–8].

Table 2 presents the statistics of deviations in the results of calculating the viscosity of helium using various types of interparticle interaction potentials (1) - (3) from reference data [6–8].

As can be seen from Figure 1, in the temperature range up to 1000 K, all potentials considered realistically describe the interaction of helium atoms, which allows one to calculate with good accuracy the viscosity and thermal conductivity of helium at atmospheric pressure. However, with increasing temperature, the results of calculations of both viscosity and thermal conductivity using the Exp-6 potential (3) show better agreement with the reference data. This conclusion is confirmed by table 2.
Table 2. Statistics of deviations of calculated values of helium viscosity and thermal conductivity from data [6–8] at 1 atm in a different temperature range (average / maximum value, %)

| Potential Type | Viscosity | Thermal conductivity |
|----------------|-----------|----------------------|
|                | 14.4–2273.15 K [6] | 53.15–1273.15 K [7] | 60–2200 K [8] | 70–2000 K [6] |
| LJ (1)         | 7.57/21.07 | 3.56/11.62           | 5.31/8.45     | 6.72/15.43    |
| Morse (2)      | 3.49/4.67  | 3.61/4.78            | 3.49/5.95     | 2.85/6.31     |
| Exp-6 (3)      | 1.28/4.02  | 1.32/2.63            | 1.72/4.31     | 2.81/6.56     |

Next, thermodynamic calculations were carried out at various pressures from 1 to 500 bar and temperatures from 150 K to 1500 K. The calculation results are presented in Figure 2 as separate isotherms of the dependences of helium viscosity (Figure 2a) and thermal conductivity (Figure 2b) of helium on pressure. Statistics of deviations of the calculated values of viscosity and thermal conductivity from the reference data [6] at elevated pressures and temperatures are presented in table 3.

Figure 2a. Viscosity of He depending on pressure at isotherms. Lines - calculation results with different interaction potential: 1 - by the LJ (1), 2 - by the Morse (2), 3 – by the Exp-6 (3). Symbols - data [6].

Figure 2b. Thermal conductivity of He depending on temperature at isotherms. Lines - calculation results with different interaction potential: 1 - by the LJ (1), 2 - by the Morse (2), 3 – by the Exp-6 (3). Symbols - data [6].

Table 3. Statistics of deviations of calculated values of viscosity and thermal conductivity of helium from data [6] at elevated pressures in various temperature ranges (average / maximum value, %)

| Potential Type | Viscosity | Thermal conductivity |
|----------------|-----------|----------------------|
|                | 77 K<T<473 K | 500 K<T<1273 K | 270 K<T<450 K | 500 K<T<1500 K |
| LJ (1)         | 3.75/10.01 | 5.11/6.92          | 3.47/7.81     | 5.01/9.48     |
| Morse (2)      | 2.82/7.44  | 4.08/4.65          | 1.35/5.35     | 4.11/6.15     |
| Exp-6 (3)      | 2.65/10.38 | 0.45/1.17          | 3.18/8.29     | 0.65/1.98     |
As can be seen from Figure 2, as well as statistical table 2, in the moderate temperature range, all the studied potentials satisfactorily describe the interaction of helium particles, which allows a satisfactory description of the transport properties of helium in this pressure and temperature range. Calculations of transport properties based on the considered interparticle potentials are in good agreement with reference data over the entire pressure range (1-500 bar). However, in the region of elevated temperatures (from 500 K), the Buckingham Exp-6 potential in the best way allows us to calculate the values of helium viscosity and thermal conductivity in accordance with the published data.

4. Conclusion
Based on the developed EOS [2] using various types of spherically symmetric potentials of interparticle interaction, the viscosity and thermal conductivity of helium were calculated 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 and thermal conductivity can be determined based on the methodology [9]. In the moderate temperature range, all three potentials considered allow satisfactory calculation of the transport properties of helium. It is shown that the description of the interaction of helium atoms using the three-parameter Exp-6 potential allows one to calculate with high accuracy the viscosity and thermal conductivity of helium in the region of elevated temperatures and pressures.

Thus, the equation of state [2] based on the perturbation theory using the Exp-6 interaction potential allows us to determine not only the thermophysical properties of helium, but also the transport properties, such as viscosity, and thermal conductivity under normal conditions and in the region of high pressures and temperatures in good agreement with experimental data.

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