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Highly accurate transport properties of helium-4, helium-3, and their binary mixtures by *ab initio* potential

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ABSTRACT

A helium–helium interatomic potential determined from quantum–mechanical *ab initio* calculations by Przybytek et al. has been used in the framework of the classical kinetic theory to calculate the transport properties of helium. The viscosity, thermal conductivity, diffusion coefficient, and thermal diffusion factor were calculated for helium-4, helium-3, and their binary mixtures at low density between 100 and 10,000 K. The predicted results of this work are listed in the Appendix, which are more accurate than the corresponding measured quantities over a wide temperature range.

1. Introduction

Traditionally, accurate experimental transport property data were used to extract information about intermolecular interactions between molecules. The development of increasingly accurate *ab initio* potentials made possible the theoretical predictions of properties of helium with accuracy exceeding experimental values. From 1995 to 2007, the National Institute of Standards and Technology (NIST) described the application of the kinetic theory of gases to calculate the *ab initio* thermophysical properties of helium [1–3]. More recently, the group of Vogel at the University of Rostock reported an accurate *ab initio* potential of helium, together with the derived thermophysical properties [4,5]. Most recently, Przybytek and his co-workers computed the most accurate potential available to date for helium by including adiabatic, relativistic, and quantum electrodynamics contributions [6]. Later, in 2012, this new pair potential has been utilized in calculating the thermophysical properties of helium, that is, the second pressure virial coefficient and second acoustic virial coefficient for ^{4}He, ^{3}He, and ^{4}He–^{3}He mixtures and the viscosity and thermal conductivity for ^{4}He and ^{3}He [7].

The field of metrology and calibration can benefit from the reduced uncertainties in the transport properties of helium at low density. For example, the theoretical results of thermal conductivity will facilitate the redetermination of the Boltzmann constant and the development of a new, helium-based, pressure standard. The reliable instruments for viscosity measurements usually include the capillary-flow viscometer, the oscillating-disk viscometer, the rotating-cylinder viscometer, and the vibrating-wire viscometer, which are all operated in a relative manner. The accuracy of the viscosity of more complex molecular gases will be improved with the help of viscometers calibrated with the helium values. Acoustic resonators might also require the accurate viscosity results of helium for primary acoustic thermometry and for measuring the speed of sound in diverse gases.

In this work, the *ab initio* potential of Przybytek et al. [6] was used to study the transport properties of helium-4, helium-3, and their binary mixtures by the classical kinetic theory of gases. Highly accurate values of the viscosity, thermal conductivity, diffusion coefficient, and thermal diffusion factor were provided in the dilute-gas limit for the temperature range from 100 to 10,000 K. It should be mentioned that the classical calculations are valid at the considered temperatures where the ratio of the thermal de Broglie wavelength $h/\sqrt{2\pi mkT}$ to atomic diameter σ is much less than 1.

2. Model and methods

To classically evaluate the transport properties by means of the kinetic theory of dilute gases, the following procedure has been employed.

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2.1. Cross section

First, a large number of the energy-dependent cross sections $Q^{(l)}(E)$ are determined over wide ranges of collision energy E [8],

$$Q^{(l)}(E) = 2\pi\left[1 - \frac{1+(-1)^l}{2(1+l)}\right]^{-1} \int_0^\infty (1-\cos^l\theta) b\,db \tag{1}$$

in which l represents the weighting factor for molecular collisions and b the impact parameter. The scattering angles θ are governed by the two-body collisions between molecules and can be written as,

$$\theta(E,b) = \pi - 2b\int_{r_0}^\infty \frac{dr/r^2}{\sqrt{1-b^2/r^2 - V(r)/E}} \tag{2}$$

where $V(r)$ is the intermolecular potential and r is the separation between molecules. The distance r_0 shows the closest approach in a molecular collision, which can be solved from the formula,

$$1 - b^2/r_0^2 - V(r_0)/E = 0 \tag{3}$$

An analytical function was adopted to represent the helium–helium interaction potential [6],

$$V(r) = e^{-ar}\sum_{i=0}^{2} P_i r^i + e^{-br}\sum_{i=0}^{1} Q_i r^i - \sum_{n=3}^{16} f_n(\delta r)\frac{C_n}{r^n} \tag{4}$$

Here a, b, P_i, Q_i, and δ are adjustable parameters fitted to the computed values of $V(r)$ and C_n are fixed. The dispersion coefficients C_7 and C_9 were neglected. $f_n(x)$ is the Tang–Toennies damping function [9],

$$f_n(x) = 1 - e^{-x}(1 + x + x^2/2! + \cdots + x^n/n!) \tag{5}$$

Table 1 lists the fitted parameters of the potential, wherein ε/k and σ are the well depth and the location of the zero of the potential, respectively [6]. All parameters of the pair interaction potential were expressed in the atomic units.

2.2. Collision integral

Integrations of the transport cross sections $Q^{(l)}(E)$ are performed to yield the temperature-dependent collision integrals $\Omega^{(l,s)}(T)$, which are necessary to derive the transport properties under consideration,

$$\Omega^{(l,s)}(T) = [(s+1)!(kT)^{s+2}]^{-1}\int_0^\infty Q^{(l)}(E)e^{-E/kT}E^{s+1}\,dE \tag{6}$$

Table 1
Parameters of the analytical representation of the intermolecular potentials $V(r)$ for the helium systems.

Parameter	Value	Unit
a	3.64890303652830	bohr^{-1}
b	2.36824871743591	bohr^{-1}
P_0	−25.4701669416621	hartree
P_1	269.244425630616	hartree.bohr^{-1}
P_2	−56.3879970402079	hartree.bohr^{-2}
Q_0	38.7957487310071	hartree
Q_1	−2.76577136772754	hartree.bohr^{-1}
δ	4.09423805117871	bohr^{-1}
C_3	0.000000577235	hartree.bohr^3
C_4	−0.000035322	hartree.bohr^4
C_5	0.000001377841	hartree.bohr^5
C_6	1.461830	hartree.bohr^6
C_8	14.12350	hartree.bohr^8
C_{10}	183.7497	hartree.bohr^{10}
C_{11}	$-0.7674\cdot10^2$	hartree.bohr^{11}
C_{12}	$0.3372\cdot10^4$	hartree.bohr^{12}
C_{13}	$-0.3806\cdot10^4$	hartree.bohr^{13}
C_{14}	$0.8534\cdot10^5$	hartree.bohr^{14}
C_{15}	$-0.1707\cdot10^6$	hartree.bohr^{15}
C_{16}	$0.286\cdot10^7$	hartree.bohr^{16}
ε/k	$3.482245\cdot10^{-5}$	hartree
σ	4.996160	bohr

2.3. Transport property

Finally, the low-density transport properties are obtained by combining the different collision integrals $\Omega^{(l,s)}(T)$. For a pure species at temperature T with molecular mass m [10],

$$\eta = \frac{5}{16}(\pi mkT)^{1/2}\frac{f_\eta}{\Omega^{(2,2)}} \tag{7}$$

$$\lambda = \frac{75}{64}(\pi k^3T/m)^{1/2}\frac{f_\lambda}{\Omega^{(2,2)}} \tag{8}$$

$$D = \frac{3}{8}(\pi k^3T^3/m)^{1/2}\frac{f_D}{P\Omega^{(1,1)}} \tag{9}$$

$$\alpha_T = \frac{15}{2}\frac{(6C^*-5)(2A^*+5)}{A^*(16A^*-12B^*+55)}(1+\kappa_0) \tag{10}$$

in which η is the viscosity, λ the thermal conductivity, D the diffusion coefficient, α_T the thermal diffusion factor, P the pressure of one atmosphere (101.3 kPa), and k the Boltzmann constant (1.380658×10^{-23} J K^{-1}). Exact calculations of transport properties require higher-order approximations of the kinetic theory. The factor f_η and f_λ up to the fifth-order approximations were adopted for the viscosity and thermal conductivity (see the Appendix of [11] for the expressions), whereas f_D and κ_0 represent the second-order corrections to the diffusion coefficient and thermal diffusion factor [10],

$$f_D = 1 + \frac{1}{8}(6C^*-5)^2(2A^*+5)^{-1} \tag{11}$$

$$\kappa_0 = \frac{1}{9}(7-8E^*)\left[\frac{2A^*}{35/4+7A^*+4F^*}\left\{H^* + \frac{[A*(7-8E^*)-7(6C^*-5)][35/8+28A^*-6F^*]}{42A^*(2A^*+5)}\right\} - \frac{5}{7}\left\{H^* + \frac{7}{5}\frac{(6C^*-5)}{(2A^*+5)} - \frac{3}{10}(7-8E^*)\right\}\right] \tag{12}$$

The quantities A^*–F^* are evaluated by the ratios of the collision integrals $\Omega^{(l,s)}(T)$,

$$A^* = \Omega^{(2,2)}/\Omega^{(1,1)} \tag{13}$$

$$B^* = (5\Omega^{(1,2)} - 4\Omega^{(1,3)})/\Omega^{(1,1)} \tag{14}$$

$$C^* = \Omega^{(1,2)}/\Omega^{(1,1)} \tag{15}$$

$$E^* = \Omega^{(2,3)}/\Omega^{(2,2)} \tag{16}$$

$$F^* = \Omega^{(3,3)}/\Omega^{(1,1)} \tag{17}$$

$$H^* = (3B^* + 6C^* - 35/4)/(6C^*-5) \tag{18}$$

For a binary mixture of species 1 and 2, the transport properties are calculated according to [10],

$$\eta_{mix} = \frac{1+Z_\eta}{X_\eta + Y_\eta} \tag{19}$$

$$\lambda_{mix} = \frac{1+Z_\lambda}{X_\lambda + Y_\lambda} \tag{20}$$