Theoretical study of thermal conductivities of various gas mixtures through the generalized Lennard-Jones interaction potential for application in gas-discharge lasers

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Abstract. Thermal conductivities of helium, neon, bromine, and hydrogen are calculated on the basis of the \((12-6)\) Lennard-Jones interaction approximation. Where necessary for a more precise approximation, a generalized \((n-m)\) Lennard-Jones interaction potential is used. Thermal conductivities of binary gas systems are calculated and compared through two different empirical methods for the case of gas discharges in He, Ne, and Ne-He mixtures with small admixtures of bromine and hydrogen. A new simple method is proposed for the thermal conductivity determination for the 3- and 4-component gas mixtures of our interest.

1. Introduction

Scientists often require reliable values of the physical properties of gases essential to the design of many kinds of scientific and industrial equipment. Handbooks provide convenient data sources. In spite of the enormous amount of data collected and correlated over the years [1-4] and the impressive developments in molecular theory and thermodynamics as well [3, 4], the rapid advance of technology into new fields seems always to maintain a significant gap between demand and availability, i.e. the scientist frequently finds a need for physical properties which have not been measured and which cannot be calculated using the existing theory.

One of the problems in the physics of gaseous discharges, gas-discharge lasers, and plasma in general is the determination of the thermophysical properties of gases and gas mixtures, namely, thermal conductivity, diffusion coefficient, etc. In particular, in gas-discharge laser physics thermal conductivity thoroughly determines the gas temperature distribution, and hence, the heavy-particle processes, thermal mode, stability of the laser operation, active particle concentration, etc., as we demonstrated in [5].

The elementary “hard-sphere” gas model assumed all atoms or molecules to be noninteracting rigid spheres of certain diameter and mass moving randomly at a mean velocity. Deviation from the hard-sphere kinetic theory led to studies on the interaction of atoms or molecules based on the realization that molecules attract at intermediate separation and repel when they come very close. The semiempirical \((12-6)\) interaction potential function of Lennard-Jones describes attraction and repulsion in an approximate quantitative fashion. Though this potential function is based upon rather tenuous...
theoretical grounds and has been widely criticized, it has been extensively used and modified. Where necessary, a generalized \((n-m)\) Lennard-Jones (L-J) interaction potential has been used. For some gases, a simplified modification \((n-6)\) L-J interaction potential has been employed for the first time in [6].

In view of the enormous prospect for application of several high-power metal atom and ion lasers in precise material processing and characterization of different materials, including soft and hard biological tissues, a detailed theoretical study on the thermal conductivity of various gases, both pure and mixtures, is carried out under gas-discharge conditions that are optimal for laser operation on the corresponding metal atom and ion transition. In order to reduce the operating temperature, metal halides are used instead of the elemental metal.

Thermal conductivities of helium, neon, bromine, and hydrogen are calculated on the basis of \((12-6)\) L-J interaction potential. Varying the repulsive parameter \(n\), a new modified \((7.5-6)\) L-J interaction potential (M L-J) is used for the first time to calculate the thermal conductivity of helium. Thermal conductivities of binary gas systems are calculated through the empirical method of Brokaw and, where possible, are compared for the first time with ones estimated via the combining (mixing) rules for the case of various gas mixtures. Due to the complex character of the existing formulae for the thermal conductivity of a \(k\)-component mixture, for example ones based on the Wassiljeva’s equation and its modifications, a new simple method is proposed for the thermal conductivity determination for the 3- and 4-component gas mixtures of our interest.

2. Results and discussion

Following [3] the thermal conductivity \(k_{\text{L-J}}\) for \((12-6)\) L-J approximation is expressed as follows:

\[
k_{\text{L-J}} = 0.083264 \frac{T_g^{0.5}}{\mu^2 \cdot \sigma^2 \cdot \Omega_v \left( \frac{k_b T_g}{\varepsilon_0} \right)},
\]

where \(\mu\) is the particle mass in amu, \(T_g\) is the gas temperature in K, \(\sigma\) is the inter-particle distance in Å,

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Thermal conductivities as a function of gas temperature for He, considering fit of experimental data. L-J and M L-J approximations.
at which the potential energy is zero, $\omega_0$ is the potential well depth, $\Omega_V$ is collision integral, which depends on the interaction potential, $k_b$ is the Boltzmann constant. $\Omega_V$ for the L-J potential the following expression is used [3]: $1/\Omega_V = 0.697 \left[ 1 + 0.323 \ln \left( k_b T_c / \epsilon_0 \right) \right]$. It is well known that the (12-6) L-J interaction potential function is not suited for quantum gases, namely He, H$_2$ and D$_2$. Using the (n-6) M L-J interaction potential and varying the repulsive parameter $n$ from 6.5 to 30 with a step of 0.5, it is found that a (7.5-6) M L-J interaction potential provides the best approximation of the existing experimental data for the thermal conductivity of helium. In figure 1, the thermal conductivities are shown as a function of the gas temperature for helium, considering allometric fit of the experimental data taken from [1], (12-6) L-J and (7.5-6) M L-J approximations.

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To use L-J or M L-J interaction potentials, reliable values are required of the two potential parameters ($\sigma$ and $\omega_0$), which are experimentally determined or theoretically through well-known empirical relations with the critical volume ($V_c$) and the critical ($T_c$) or boiling ($T_b$) temperature. In the all-too-frequent situation, in which no experimental or theoretical values of the needed constants ($\sigma$, $\omega_0$, $V_c$, $T_c$ and $T_b$) are at hand, rigid (hard) sphere (R Sph) approximation must be used for thermal conductivity estimation. For this approximation, $\sigma$ is the R Sph diameter (sum of atomic radii of the interacting particles) in Å and $\Omega_V$ is unity in (1).

![Figure 2. Thermal conductivities as a function of the gas temperature for atomic and molecular bromine.](image)

Figure 2 presents the thermal conductivities as a function of the gas temperature for atomic and molecular bromine. Reliable experimentally determined values of the two potential parameters and critical constants exist only for molecular (Br$_2$) bromine. In this figure our results for the thermal conductivity obtained with (12-6) L-J interaction potential are also compared with the one obtained
with the \((17.5-6)\) M L-J interaction potential used in [6]. The discrepancy is negligible. The two potential parameters, which have been experimentally determined [3] and are used in our research, do not require modification of the \((12-6)\) L-J interaction potential. From the viewpoint of chemistry, the dissociation of \(\text{Br}_2\) molecules to Br atoms is a reversible reaction with rate constants for direct (dissociation of \(\text{Br}_2\) molecules) and reverse (recombination of Br atoms) reactions, which mainly depend on the gas temperature. The pressure starts influencing the thermal conductivity at values higher than 1 atm (0.1 MPa). Unfortunately, from the viewpoint of plasmachemistry, the electron-molecule impacts lead to the dissociation prevailing over the recombination under the gas-discharge conditions characterized by an electron temperature of about one order of magnitude higher than the gas temperature. Both temperatures are defined through mean energy or velocity values of the Maxwellian distribution function for the respective particles, i.e. electrons or heavy particles. Using spectroscopic extinction measurements, a detailed study on the \(\text{Br}_2\) and Br atom concentration and pressure in the discharge zone has been carried in [7]. In figure 3, the thermal conductivities of the binary gas system \(\text{Br}-\text{Br}_2\) are plotted as calculated on the basis of the empirical method of Brokaw [3]. Applying the Brokaw’s method for binary systems two or three times, the thermal conductivities of 3- and 4-component gas mixtures are obtained. In figure 3, the thermal conductivities are also given for Ne, considering allometric fit of the experimental data taken from [1], and for Ne-Br-Br\(_2\) as well.

Thermal conductivities of gases containing \(\text{H}_2\) molecules and H atoms are shown in figure 4 with two different allometric fitting functions, as is made in [5]. This is because of the dissociation of hydrogen molecules, which increases rapidly at gas temperatures above 1600 K, resulting in the intensification of heat extraction from the discharge zone. Thermal conductivities of Ne-H\(_2\)-Br-Br\(_2\) and Ne-H-Br-Br\(_2\) are also presented in this figure.

![Figure 3](image-url)

**Figure 3.** Thermal conductivity as a function of the gas temperature for Ne, considering fit of experimental data, Br-Br\(_2\), Ne-Br-Br\(_2\) gas mixtures.

Sometimes certain amount of Ne is added to the buffer-gas He for additional gas-discharge heating, i.e. an additional increase in the gas temperature. Figure 5 presents thermal conductivities of He, Ne, and several Ne-He mixtures, namely, 5 Torr–40 Torr, 10 Torr–35 Torr, and 15 Torr–30 Torr, as a function of the gas temperature using Brokaw’s method for binary gas mixtures and the method of combining rules (Ne-He L-J and Ne-He M L-J). Allometric fit of the experimental data, \((12-6)\) L-J and \((7.5-6)\) M L-J approximations are used for pure He thermal conductivity. A modification of the \((12-6)\) L-J interaction potential is not required for pure Ne.
Thermal conductivities of gas mixtures between Br-Br$_2$ and He(10 Torr), Ne(16.7 Torr), He(45 Torr), and the abovementioned Ne-He mixtures are shown in figure 6.

![Graph showing thermal conductivities of gases and mixtures.](image)

**Figure 4.** Thermal conductivities of H$_2$, H, Ne-H$_2$-Br-Br$_2$, and Ne-H-Br-Br$_2$ gases and mixtures.

![Graph showing thermal conductivities of He, considering fit of experimental data, L-J and M L-J approximations, Ne, and Ne-He mixtures.](image)

**Figure 5.** Thermal conductivities of He, considering fit of experimental data, L-J and M L-J approximations, Ne, and Ne-He mixtures.
Figure 6. Thermal conductivities of gas mixtures between Br-Br$_2$ and He, Ne, and Ne-He mixtures.

3. Conclusions
The thermal conductivity of helium, calculated by the new (7.5-6) M L-J interaction potential, is a better approximation than the (12-6) L-J and R Sph approximations. The empirical method of Brokaw is widely used for binary systems, because it is not dependent on the way of thermal conductivity determination for pure components, namely experimental, (M) L-J, R Sph, etc. Combining rules show promise when one of the pure components is at low pressure in comparison to the other one.

Applying two or three times the empirical method of Brokaw for binary systems, a new simple method is developed for calculation of thermal conductivities of various 3- and 4-component gas mixtures used as active media of several metal atom and ion lasers. Utilization of Wassiljewa’s equation for calculation of thermal conductivity of $k$-component mixture is in progress.

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