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Thermal Conductivity of Nitrogen at High Pressures

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The results of the measurements of the thermal conductivity coefficients of nitrogen at 298.15 K from atmospheric pressure up to 1 GPa are reported. The experimental values are used to test the Modified Enskog Theory and the corresponding state principle. The experimental values are also compared with the results of computer simulation of the thermal conductivity of a Lennard Jones fluid.

KEY WORDS: thermal conductivity; high pressure; nitrogen; computer simulation; modified Enskog theory.

1. INTRODUCTION

Recently, we extended thermal conductivity measurements of noble gases up to 1 GPa [1, 2]. The excess thermal conductivity

$$\Delta\lambda(\rho, T) = \lambda(\rho, T) - \lambda(0, T) \tag{1}$$

describes the difference between the thermal conductivity $\lambda(\rho, T)$ at density ρ and the value $\lambda(0, T)$ in the low density limit $\rho \longrightarrow 0$ at the same temperature. The comparison of experimental data with theoretical results shows that the excess thermal conductivity of heavier noble gases at room temperature can be reduced to one universal curve if we use parameters valid in gas, liquid, and solid phases as reduction parameters. Parameters of the Barker potential [3] were found appropriate for this reduction. For a molecular fluid like nitrogen, which does not have a spherical shape, the comparison, as we will see in this paper, is more complicated. In our laboratory, the thermal conductivity of nitrogen was measured previously up to 120 MPa and from room temperature up to 700°C [4, 5]. The excess thermal conductivity

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was also found temperature independent when plotted in terms of density. From a practical point of view, only one series of measurements along one isotherm and along one isobar permits the calculation of thermal conductivity in a wide range of liquid and gas phases, with the exception of the critical region.

2. EXPERIMENTAL DETERMINATION OF THE THERMAL CONDUCTIVITY OF N_2

Measurements were made in a coaxial cylindrical cell described in detail in previous papers [4–6]. A new cell has been designed to fit into the bore of a high pressure vessel used in the experiments up to 1 GPa [2]. The outer cylinder was 200 mm long with a 30 mm o.d., while the inner cylinder was 100 mm long with a 15 mm diameter. The gap between the cylinders was 0.2 mm. The inner cylinder was centered by five pins made of saphire. The temperature constancy was achieved by circulating temperature controlled water in the water-jacket of the high pressure vessel. The temperature stability of the cell was better than 0.01°C. The results are reported in Table I as a function of pressure P and density ρ. Their estimated total error is 1%. The density values were calculated from the data given in refs. [7] and [8]. These new results are in agreement with previous data obtained in the same type of a cell up to 0.1 GPa [4, 5].

Table I. Thermal Conductivity of N_2 at 298.15 K

P (MPa)	ρ (kg m^{-3})	λ (mW m^{-1}K^{-1})
0.1	1.15	26
50	414	57
100	573	85.5
150	662	109
200	724	131
300	812	170.5
400	876	204
500	927	234
600	971	261
700	1,008	285
800	1,041	308
900	1,071	329
1,000	1,098	350

Table II. Comparison Between Calculated Results by the MET Approximation and Experimental Data

P(MPa)	200	600	950
$\rho(\mathrm{kg\,m^{-3}})$	724	971	1,080
$(\lambda/\lambda_0)_{\mathrm{calc}}$	5.14	8.95	12.5
$(\lambda/\lambda_0)_{\mathrm{exp}}$	5.04	10.0	13.2

3. COMPARISON WITH STATISTICAL TRANSPORT THEORIES

Our comparison will be restricted to the Modified Enskog Theory (MET) [9, 10]. The usual Enskog theory applies to hard sphere molecules of diameter σ and mass m. The thermal conductivity, λ, is given by

$$\lambda = \lambda_0\, b\rho \left(\frac{1}{b\rho\chi} + 1.2 + 0.755\, b\rho\chi\right) \tag{2}$$

where λ_0 is the dilute gas thermal conductivity,

$$b = \frac{2}{3}\pi\frac{\sigma^3}{m} \tag{3}$$

and χ is the value of the equilibrium radial distribution function at a distance σ from the center of an individual molecule. In the MET approximation, the definitions of b and χ become

$$b = B(T) + T\frac{dB}{dT} \tag{4}$$

where B is the second virial coefficient for compressibility and

$$b\rho\chi = \frac{1}{R}\left(\frac{\partial PV}{\partial T}\right)_V - 1 \tag{5}$$

A comparison between experimental and calculated values is given in Table II.

4. SCALING OF THE EXCESS THERMAL CONDUCTIVITY

By analyzing dilute gas viscosity data, Kestin et al. [11] showed that if this property is reduced by a molecular length (σ) and energy (ϵ/k_B), the

Table III. Parameters of the L.-J. Potential for Argon and Nitrogen

	Ar	N_2	Units
σ	3.291	3.568	$10^{-10}\,m$
ϵ/k_B	153.61	113.07	K

reduced viscosity coefficients η^* of different fluids, including noble gases and N_2, fall on a single curve when plotted as a function of the reduced temperature T^*. The reduced quantities are defined as follows:

$$T^* = T(\epsilon/k_B)^{-1} \tag{6}$$

$$\rho^* = \rho\,\sigma^3/m \tag{7}$$

$$\eta^* = \eta\,\sigma^2\,m^{-1/2}\,\epsilon^{-1/2} \tag{8}$$

$$\lambda^* = \lambda\sigma^2\,m^{1/2}\,\epsilon^{-1/2}\,k_B{}^{-1/2} \tag{9}$$

This procedure does not require any particular shape for the intermolecular potential. If we consider the thermal conductivity coefficient of the dilute gas, scaling applies only to the part owing to the contribution of energy transfer by translation, and not to the total coefficient, which includes also a contribution of internal modes. However, we can check if the excess thermal conductivity is affected by internal modes by using these scaling parameters. For example, reduced excess thermal conductivity of Ar and N_2 can be compared. For these fluids, σ and ϵ/k_B are given in Table III [11]. Table IV shows that scaling of the dilute gas viscosity cannot be extended to the excess thermal conductivity of N_2, the ratio $\Delta\lambda_N^*/\Delta\lambda_A^*$ being different from unity.

5. COMPARISON WITH COMPUTER CALCULATION OF λ

Via nonequilibrium molecular dynamics, Ashurt [12] calculated the thermal conductivity coefficient of a Lennard-Jones fluid as a function of

Table IV. Scaling of Excess Thermal Conductivity of Argon and Nitrogen with the Use of L.-J. Potential

	Ar		N_2		
ρ^*	ρ_A (kg m^{-3})	$\Delta\lambda_A$ (mW m^{-1} K^{-1})	ρ_N (kg m^{-3})	$\Delta\lambda_N$ (mW m^{-1} K^{-1})	$\dfrac{\Delta\lambda_N^*}{\Delta\lambda_A^*}$
0.753	1,402	131	771	124	1.085
0.976	1,816	269.3	1,000	257	1.095

temperature and density. Combining experimental data and calculated values, Ashurt proposed the following equation to represent the reduced excess thermal conductivity:

$$\Delta\lambda^* = T^{*2/3} a(\exp bX - 1) \tag{10}$$

where

$$X = \rho^* T^{*-1/4} \tag{11}$$

with

$$a = 0.36 \text{ and } b = 3.76$$

To make a comparison between Ashurt's calculation and our experimental data, we have to define a Lennard-Jones potential for N_2 molecules, which are not spherical. This nonsphericity was taken into account by adding to the spherical interaction a quadrupole interaction [13]. Thus the intermolecular potential function becomes:

$$\phi(r) = 4\epsilon_0 \left\{ \left(\frac{\sigma_0}{r}\right)^{12} - \left(\frac{\sigma_0}{r}\right)^{6} \right\} + \frac{\Theta_1 \Theta_2}{r^5} F(\Phi, \Theta_1, \Theta_2) \tag{12}$$

From the dilute gas viscosity, where the effect of the quadrupolar interaction is small, and from the second virial coefficient $B(T)$, the following parameters for the spherical part of the potential were extracted:

$$\sigma_0 = 3.702 \times 10^{-10} \text{ m}$$

$$\epsilon_0 / k_B = 87.5 \text{ K}$$

We will use these parameters to reduce the experimental excess thermal conductivity of N_2 and make the comparison with calculated values. This comparison is presented graphically in Fig. 1. The agreement is surprisingly good. However, due to the poor precision of the calculated values and to the arbitrary choice of the Lennard-Jones potential parameters, it would be dangerous to assume the validity of this approach to predict the excess thermal conductivity of molecular fluids.

6. CONCLUSIONS

The comparison between experimental data and theoretical results shows that we cannot expect to predict, with a good accuracy, the thermal

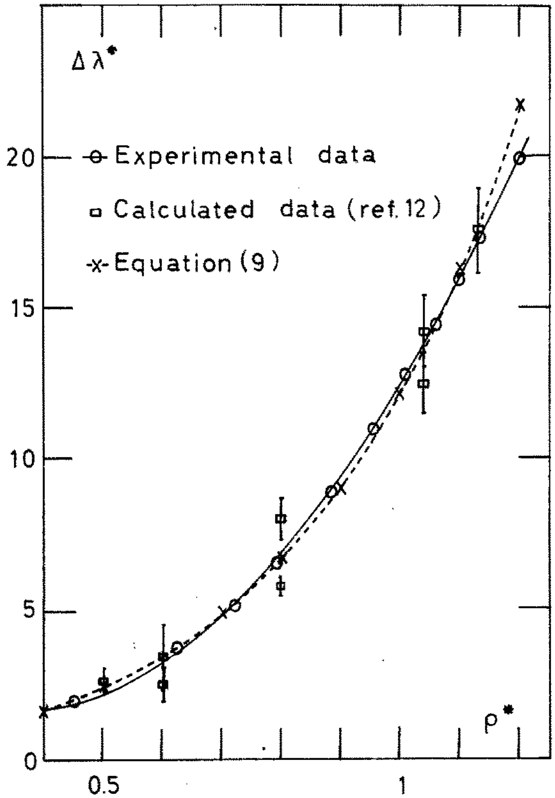

Fig. 1. Comparison between calculated and experimental thermal conductivity of N_2 at 25°C.

conductivity of high density molecular fluids from the Enskog theory or derived Enskog theories. We have shown previously that if we use parameters of the Lennard-Jones potential derived from the second virial coefficient to reduce transport properties, the corresponding states principle is verified for the heavier noble gases only at low or moderate densities (deviation less than 10%) [6, 14]. For nitrogen, which does not have a spherical molecule, the agreement cannot be expected to be better.

The agreement between the Ashurt equation and our experimental data may be considered as fortuitous. However, the Ashurt calculation and experimental data show that the excess thermal conductivity is almost temperature independent. Therefore, even if the thermal conductivity coefficient cannot be predicted with the existing theories, a good evaluation may be made by performing a set of measurements along one isobar and a set along one isotherm, provided that the equation of state of the fluid is known.

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