Thermal conductivity of a moderately dense gas

Carlos A. Nieto de Castro

Departamento de Quimica, Faculdade de Ciencias, Universidade de Lisboa, 1700 Lisbon, Portugal

Daniel G. Friend [1], Richard A. Perkins and James C. Rainwater

Thermophysics Division, National Institute of Standards and Technology [2], Boulder, CO 80303, USA

Recent extensive measurements of the thermal conductivity of argon and nitrogen have enabled us to evaluate the first density correction as a function of temperature and to compare it with a theoretical prediction. The prediction follows from a previously published microscopically based theory, which includes effects due to collisional transfer, collisions among three molecules, and monomer–dimer collisions. The first density correction was evaluated for a Lennard-Jones interaction potential. An ad hoc modification of the theory accounts for contributions to the thermal conductivity from internal degrees of freedom. The comparison shows good agreement over a wide range of temperatures.

1. Introduction

Several years ago, Rainwater and Friend [1,2] developed a theory of the leading density corrections to transport properties of gases and successfully applied the theory to data available at that time. The theory later yielded good agreement [3] with more recent viscosity data for benzene and methanol vapors at low reduced temperature [4]. The initial comparison for thermal conductivity was primarily limited to monatomic gases because of the difficulty in treating energy transfer associated with internal degrees of freedom.

New measurements of the thermal conductivity of argon and nitrogen by Nieto de Castro, Perkins, and co-workers [5–8] have included sufficient and accurate data in the low density and moderately dense gas regions to allow a determination of the first density coefficient for the thermal conductivity. In the current work, we compare the theory with these new measurements. We include the data for polyatomic molecules by using an Enskog hard-sphere model to calculate the internal contribution to the first density

correction as a diffusive process. We also express the theoretical results for the transport virial coefficients, previously reported graphically [2] and tabulated for certain values of the reduced temperature [3], in simple correlations.

A density expansion for the thermal conductivity can be written as

$$\lambda(\rho, T) = \lambda_0(T) + \lambda_1(T)\rho + \dots, \tag{1}$$

where the series may contain nonanalytic terms such as $\rho^2 \ln \rho$ [9]; these are of higher order than the linear term and are outside our immediate concern. Eq. (1) can also be written in a virial format, which is the basis for our calculations and comparisons, as

$$\lambda = \lambda_0(T)[1 + B_\lambda(T)\rho + \dots], \tag{2}$$

where the temperature dependences of both λ_0 and B_λ are of central importance. Experimental determinations of B_λ are made by examining the region where the isothermal thermal conductivity data are linear in density and evaluating the slope and intercept. Comparisons have been based on a dimensionless form of the second thermal conductivity virial coefficient,

$$b_\lambda = 3B_\lambda/2\pi N_A \sigma^3, \tag{3}$$

where N_A is the Avogadro constant, σ is the Lennard-Jones distance parameter, and the density in eqs. (1) and (2) should be in moles per unit volume.

2. Experimental data

The experimental thermal conductivities of argon and nitrogen were obtained with a transient hot-wire technique over a broad range of temperatures and pressures from 80 to 425 K and from 0.1 to 70 MPa. The data obtained at NIST in Boulder for both fluids are tabulated in ref. [8]. A discussion of the results for gaseous argon is given in ref. [5]. An additional correction for the compression work contribution to the energy transport has been made; this affects the experimental thermal conductivity values of argon at low densities. The corrected results for λ_0 and B_λ are given in table 1; these supersede the values tabulated in table 3 of ref. [5], and values for λ_0 differ by up to 6%. Table 1 includes the standard deviation of the regression fit used to evaluate the zero-density thermal conductivity and the maximum density used in the linear regression. Additional data for argon, obtained on the hot-wire apparatus at the University of Lisbon, have been discussed in ref. [6]. The nitrogen data are discussed in ref. [7]. The general accuracy of all the data is better than 1% even in the region of low density measurements.

Although the measured experimental parameters are temperature and pressure, it is the density dependence which is important for our discussion. For argon in ref. [5], the equation of state of Younglove [10] was used to analyze the data and to convert from pressure to density dependence. The data of ref. [6] were analyzed with the IUPAC equation of state [11]. Differences between the two representations of the argon thermodynamic surface are insignificant in the density range of interest, so re-analysis of the earlier data is not warranted. The equation of state by Jacobsen et al. [12] was used to study the nitrogen data of ref. [7].

In addition, isothermal data are required to determine both λ_0 and B_λ. The experimental method, which produces varying temperature rises from about 2 to 4 K in the experimental cell, gives data corresponding to the average temperature which occurs during the heating cycle (less than 1 s). Replicate measurements, corresponding to different temperature rises (or power input to the hot wire), serve to confirm the absence of convection and the precision of the data. The data are not precisely along isotherms because of the varying temperature rises. To obtain isothermal data, corrections based on the correlations presented in refs. [5,7] were applied to the data. These corrections amounted to no more than 0.2% of the experimental thermal conductivity.

The low density isothermal data for argon are shown in fig. 1. The temperature ranges from 103 to 324 K. Several problems are associated with the ex-

Table 1
Low density thermal conductivity coefficients for argon

T (K)	λ_0 (mW m^{-1} K^{-1})	σ_s [a] (mW m^{-1} K^{-1})	B_λ (ℓ mol^{-1})	ρ_{max} (mol ℓ^{-1})
103.00	6.42	0.05	0.155	0.340
113.00	7.00	0.03	0.147	0.525
123.00	7.57	0.05	0.143	0.952
133.00	8.18	0.04	0.133	1.523
142.00	8.69	0.06	0.127	1.909
157.00	9.56	0.11	0.110	1.478
173.00	10.63	0.07	0.0997	2.517
203.00	12.39	0.06	0.0856	3.339
223.00	13.43	0.08	0.0804	3.475
273.00	16.41	0.09	0.0609	3.489
302.00	17.70	0.10	0.0599	3.988
324.00	18.89	0.13	0.0561	4.351

[a] σ_s is the root mean square deviation in λ_0 as determined from the linear regression.
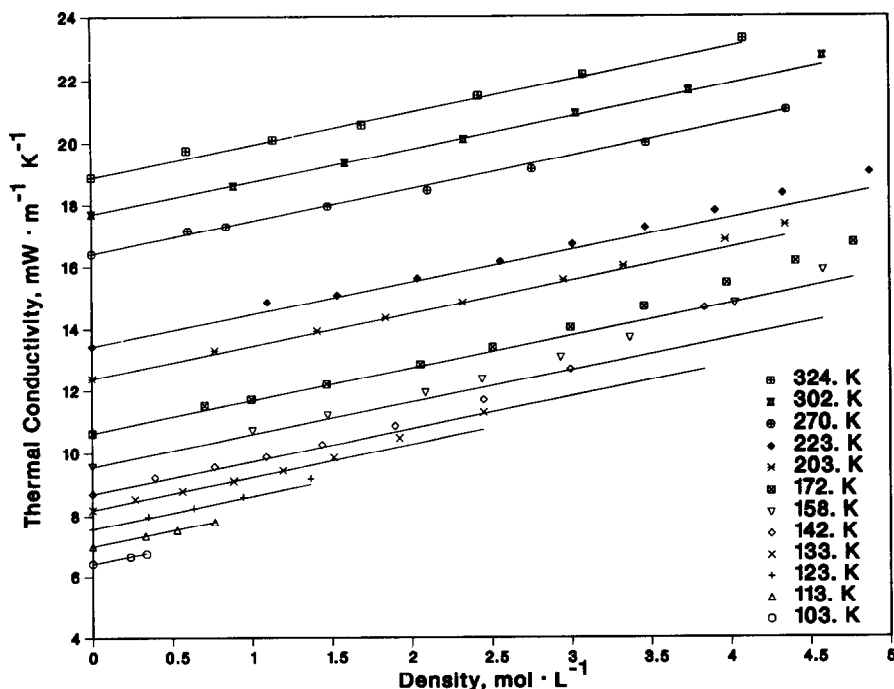
Fig. 1. Low density thermal conductivity of argon adjusted to lie along isotherms as shown. The lines represent the theoretical first density correction.

traction of the transport second virial coefficients from experimental data. First, the accuracy of data usually decreases as the density decreases; for instance, in ref. [5] we have estimated the error associated with the measurements as 0.6% at low densities but 0.2% in the liquid. Because the vapor pressure and the density of the saturated vapor are small at low temperatures, in this region it is difficult to obtain the quantity of reliable data necessary to obtain an accurate first density correction. There is not very much density variation between the dilute gas and the phase boundary, so that we cannot easily implement regression schemes which seek to establish the range over which the thermal conductivity is linear in density. Finally, isotherms near the critical temperature exhibit curvature at relatively low densities; this is evidently due to the fluctuation-induced critical enhancement. For argon, with a critical temperature of 150.86 K, this curvature is quite noticeable in the isotherms between 123 and 172 K. In this region, the maximum density considered in the regression was limited as shown in table 1. It is currently not possi-

ble to separate unambiguously the critical enhancement from the background thermal conductivity; however, we believe that the contribution from the enhancement is quite small in our restricted range of density. In the theoretical approach we are examining here, we have not attempted to quantify the enhancement contribution.

From data such as that shown in fig. 1 and an analogous plot for nitrogen in ref. [7], it is possible to estimate both the dilute gas thermal conductivity and the first density correction. We have estimated the linear range of each isotherm, and have obtained the slope and intercept of the isotherm using linear regression. In table 1, we report values of these quantities for argon, and a similar table for nitrogen was presented in ref. [7].

3. Theory

The theory of the initial density dependence of viscosity and thermal conductivity was outlined in ref.

[2]. In this section, we will summarize the theoretical approach and describe the modification which accounts for contributions to the thermal conductivity from internal degrees of freedom. The transport virials were divided into three contributions according to

$$B_\mu = B_\mu^{(2)} + B_\mu^{(3)} + B_\mu^{(M-D)} . \qquad (4)$$

This treatment excludes contributions from internal modes. In eq. (4), the subscript μ indicates the property being considered; both thermal conductivity and viscosity were discussed in refs. [2,3]. (Extension of the theory to self-diffusion will be discussed very briefly below.) The superscripts indicate contributions from collisions which occur in the fluid between two molecular constituents (monomers), among three monomers, and between a single monomer and a (stable or metastable) dimer.

The terms $B_\mu^{(2)}$ were evaluated from kinetic theory by using a truncation of the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy with a Bogoliubov hypothesis [13]; the approach includes both collisional transfer (nonlocality) and direct kinetic contributions. This approach has extended the theory pioneered by Curtiss and co-workers [14–17], and uses the dynamics of particles with realistic potentials (for example, Lennard-Jones), in contrast to approaches such as the modified Enskog theory (MET) [18] that are based on hard-sphere dynamics. The transport virial coefficients depend on collision integrals that are similar to, but more complex than, the collision integrals in the Chapman–Enskog solution for dilute gas transport properties [19].

An essential innovation in the work of Rainwater and Friend [2,3] was the realization that the operator formalism, which projects a collisional trajectory to a distant precollisional past of uncorrelated particles, does not affect the subspace of phase space for which the two particles are (stably or metastably) bound. This led to a re-evaluation of $B_\mu^{(2)}$ with modified contributions from terms previously dependent upon the ordinary (pressure) virial coefficients [1,20]. The numerical results of this analysis, based on the Lennard-Jones 12-6 interaction potential, have been tabulated in ref. [3].

The contribution from $B_\mu^{(3)}$ is equivalent to that introduced by Hoffman and Curtiss [15]. As in the Enskog theory for hard spheres [21], an approximate distribution function is introduced into a collision integral to account for the change in frequency of two-body collisions caused by the presence of a third molecule. Values for this quantity, which incidentally has the same value for both the thermal conductivity and viscosity, are also tabulated in ref. [3]; there is substantial agreement between these values and the values reported in ref. [16] in the region of overlap.

Finally the quantities $B_\mu^{(M-D)}$ were evaluated in a manner similar to an approach of Stogryn and Hirschfelder [22]. Because the population of dimers is proportional to the density, the contribution of the monomer–dimer collisions to the first density correction can be calculated from the dilute gas (Chapman–Enskog) kinetic theory [19] of binary mixtures. The only adjustable parameters of the theory occur in this part of the calculation. The Lennard-Jones 12-6 interparticle potential gives reasonable results for many thermophysical properties of many systems; this interparticle potential has been well studied, and tabulated values of the two parameters, ϵ/k and σ, are readily available [23]. The reduced well depth is represented by ϵ/k, where k is the Boltzmann constant, and the interparticle separation corresponding to zero potential is given by σ. However, the intermolecular potential between the dimer (associated with the Lennard-Jones potential) and the monomer, and especially an adequate effective spherical representation of it, is not well known. We have chosen to retain the Lennard-Jones 12-6 potential for this interaction and have estimated an effective well depth and distance parameter by optimizing the fit of transport property data to the theory. The values $\epsilon_{MD}/\epsilon = 1.15$ and $\sigma_{MD}/\sigma = 1.02$ were obtained in ref. [2], using both viscosity and thermal conductivity data, and were used in ref. [3], where the results were tabulated; these values may not represent the best approximation of the potential on physical grounds [4], but have been retained here.

In this work, we introduce a correction to the theory which accounts for the contributions of internal degrees of freedom present in the thermal conductivity of polyatomic molecules. As in typical treatments of the dilute gas [19,23], we separate the contributions according to

$$\lambda = \lambda' + \lambda'' , \qquad (5)$$

where singly primed quantities represent collisional contributions, as previously discussed, and doubly primed quantites represent contributions from the intramolecular modes. We have assumed that the density expansions of each of these contributions can be considered separately, and we proceed in a manner similar to that used in refs. [18,24].

The contribution of the internal degrees of freedom to the dilute gas thermal conductivity is typically modelled as a diffusive process according to [25]

$$\lambda_0 = \tfrac{5}{2}\eta_0 C'_V/m + \rho M D_0 C''_V/m , \qquad (6)$$

where C_V is the isochoric heat capacity per molecule, m is the molecular mass, M is the molar mass, and D_0 is the dilute gas value of the self-diffusion coefficient (which is inversely proportional to density). The first term is the kinetic contribution λ'_0, and the kinetic portion of the heat capacity, C'_V, is approximated as $\tfrac{3}{2}k$; thus

$$\lambda'_0 = \tfrac{15}{4}\eta_0 k/m . \qquad (7)$$

The second term is the contribution from internal modes and depends on the self-diffusion coefficient as well as the internal contribution to the isochoric heat capacity. We assume, as in refs. [18,24], that the lowest-order density dependence of the internal contribution, which is defined by

$$\lambda'' = \rho M D C''_V/m , \qquad (8)$$

stems entirely from the leading density correction to the self-diffusion coefficient D.

In principle, the density dependence of the diffusion constant could be evaluated directly from the kinetic theory which we have presented. Bennett and Curtiss [17] attempted this sort of calculation; in that study, however, the operator formalism mentioned above was applied to the entire phase space, including regions where dimerization occurs, and the monomer–dimer collision contributions did not appear explicitly. Furthermore, agreement with viscosity and thermal conductivity data at low reduced temperature was poor. Although the results of ref. [17] were used for the density-dependent diffusion with some success by Olmsted et al. [26], we believe that those results cannot be used with confidence.

We have not, thus far, extended our work in kinetic theory to analyze the modifications necessary to cal-culate the self-diffusion coefficient. There are special problems with the diffusion calculation, including the need to consider (at least) binary mixtures, the presence of three types of dimers, and the possible importance of higher-order Sonine corrections. In the absence of such a theory, we have adopted the density expansion of the self-diffusion coefficient directly from the hard-sphere Enskog theory [19,21]. This approach differs slightly from refs. [18,24] which used modifications of the Enskog theory. Using the known third (pressure) virial coefficient for hard spheres, we can write

$$D = D_0(1 - 0.625\rho^* + ...) , \qquad (9)$$

where $\rho^* = 2\pi N_A \sigma^3 \rho/3$, so that $b''_\lambda = -0.625$. We retain the Lennard-Jones distance parameter σ rather than introducing a separate hard-sphere diameter when reducing the densities in eq. (9) and elsewhere; in ref. [24], the use of a corresponding states distance parameter in the analogous equations was denoted MET-II.

From the expression

$$\lambda = \lambda'_0(1 + b'_\lambda \rho^* + ...) + \lambda''_0(1 + b''_\lambda \rho^*...) , \qquad (10)$$

we can now write

$$b'_\lambda = b_\lambda(\lambda_0/\lambda'_0) + 0.625(\lambda_0/\lambda'_0 - 1) . \qquad (11)$$

In eq. (11), b'_λ is related to the quantity B^*_λ of ref. [2] by a factor $3/2\pi$, b_λ is the reduced experimental slope, λ_0 is the experimental dilute gas thermal conductivity, and λ'_0 is obtained from eq. (7).

4. Comparisons between theory and experiment

In fig. 2, we show a comparison between theoretical values of b'_λ and values calculated from experimental data. In addition to the data for argon and nitrogen, as discussed above, we have plotted data from the compilation of Ross et al. [24]. In all cases, values for the Lennard-Jones parameters, σ and ϵ/k, have been obtained from the tables of Reid et al. [23].

The theoretical curve in fig. 2 has been obtained by correlating the tabulated values of the second thermal conductivity virial coefficients of Rainwater and Friend [3] using

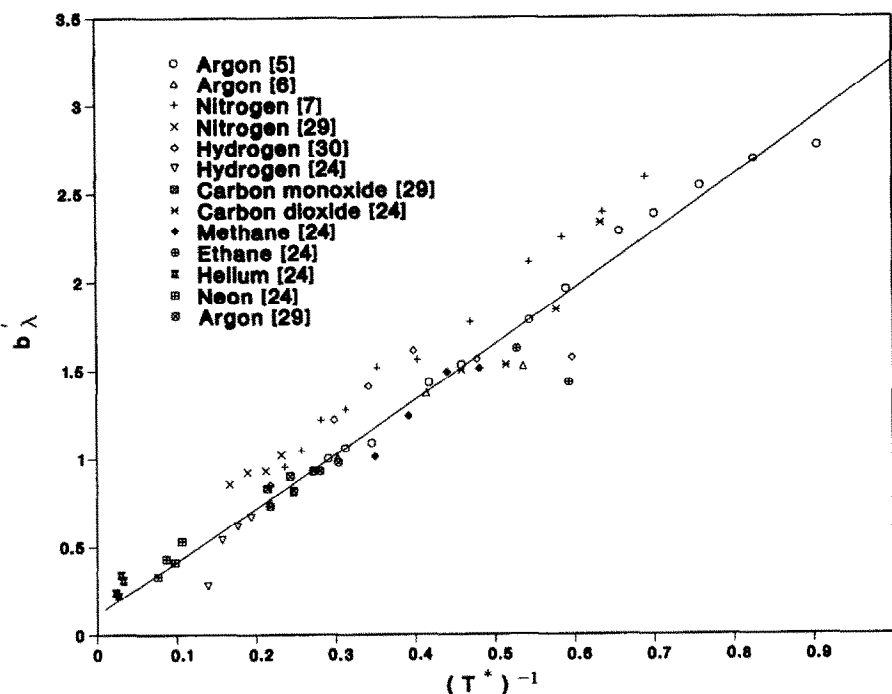$$b'_\lambda = (a_1 + a_2 T^*)/(a_3 + T^*) . \qquad (12)$$

Fig. 2. Comparison between theory and experiment for second (kinetic) thermal conductivity virial coefficient b_λ'. Line is from eq. (12) and experimental quantities have been derived from data in refs. [5–8] and compilation in ref. [24] as described in text and legend.

The tabulation in ref. [3] was based on numerical integrations of generalized collision integrals for the Lennard-Jones interaction potential. In eq. (12), the reduced temperature T^* is defined by $T^* = kT/\epsilon$, and the fitted coefficients were found to have values of $a_1 = 2.9749$, $a_2 = 0.1140$, and $a_3 = -0.04953$. The average absolute deviation of the fit from the eleven points tabulated in ref. [3] which have reduced temperature between 0.8 and 30 was 0.2%; the maximum absolute deviation in b_λ' for this temperature range is 0.4%.

We have also fitted the theoretical values for b_η from ref. [3] to a polynomial in inverse temperature; the shape of this curve is much more difficult to represent in a simple algebraic expression. Because momentum cannot be stored in internal degrees of freedom, the tabulated second viscosity virial coefficients represent the entire (appropriately reduced) experimental quantity. For reduced temperatures between 0.8 and 30 we can write

$$b_\eta = b_1 + b_2/T^* + b_3/T^{*2} + b_4/T^{*3} \qquad (13)$$

with $b_1 = -0.09413$, $b_2 = 1.5709$, $b_3 = -0.2189$, and $b_4 = -1.3174$. For the eleven viscosity points, the average absolute deviation of eq. (13) is 2%, and the maximum deviation is 5.5% for the very small value of b_η (0.09) at $T^* = 30$. Unlike the thermal conductivity virial coefficient, the viscosity virial coefficient twice changes sign [3], and a correlation will inevitably show large percent deviations in the vicinity of the sign changes.

We have discussed, in section 2, the method of extracting B_λ and λ_0 from the new experimental data for argon and nitrogen. For argon, $B_\lambda(T)$ can be reduced using eq. (3), with the needed Lennard-Jones parameters for eq. (3) and the temperature reduction from ref. [23], and used directly in fig. 2 for comparison with the theoretical curve. The data for the diatomic nitrogen fluid have been adjusted according to eq. (11) for use in fig. 2; values for λ_0 were taken directly from the experimental isothermal data and λ_0' was computed from eq. (7) using the NIST MIPROPS correlation [27] to evaluate η_0. The contribution of internal modes to the total B_λ amounts to

about 7% at the lowest temperature and 27% at the highest temperature. Thus, uncertainties of 10% in the first density correction of the self-diffusion coefficient, stemming from the use of the hard-sphere approximation of eq. (9) rather than a more rigorous kinetic theory or an ad hoc modification of the Enskog theory [18,24], result in uncertainties of less than 4% in the total thermal conductivity virial coefficient; these correspond to uncertainties of less than 5% in the value of b'_λ computed from eq. (11) and used in the comparison of fig. 2.

The complete set of thermal conductivity virial coefficients tabulated in ref. [24], omitting only N_2O for which the reference is unclear, is also included in fig. 2. For the monatomic species, the values directly from ref. [24] (with original data in refs. [24,28,29]), with reduction using the Lennard-Jones parameters from ref. [23], were used in fig. 2. For the polyatomic fluids (with original data in refs. [24,29,30]), we adjusted for internal degrees of freedom as in eq. (11). Values for λ_0 and η_0 were obtained from the experimental papers if they were tabulated, or from correlations or tabulations in refs. [27,31–33] as appropriate. The agreement between theory and experiment as seen in fig. 2 is generally excellent for the noble gases. For the polyatomic gases, such as nitrogen, the larger deviations are probably due to our approximate treatment of internal degrees of freedom.

As a final comparison between the theory of the second thermal conductivity virial coefficient and experimental data, we have included a deviation plot for the low density argon data as fig. 3. The dilute gas contribution λ_0 has been taken as the experimental value from the intercept of the isotherms. The density dependence is from the expression of eq. (10) (with $\lambda_0 = \lambda'_0$ for argon) with the theoretical value of b'_λ from eq. (12). The agreement is again seen to be excellent, except at the higher densities for isotherms with temperatures within about 20 K of the critical temperature. The single term in the density expansion gives good results up to about 3 mol ℓ^{-1} except for isotherms in the range 133–158 K, around the critical temperature of 150.86 K of argon.
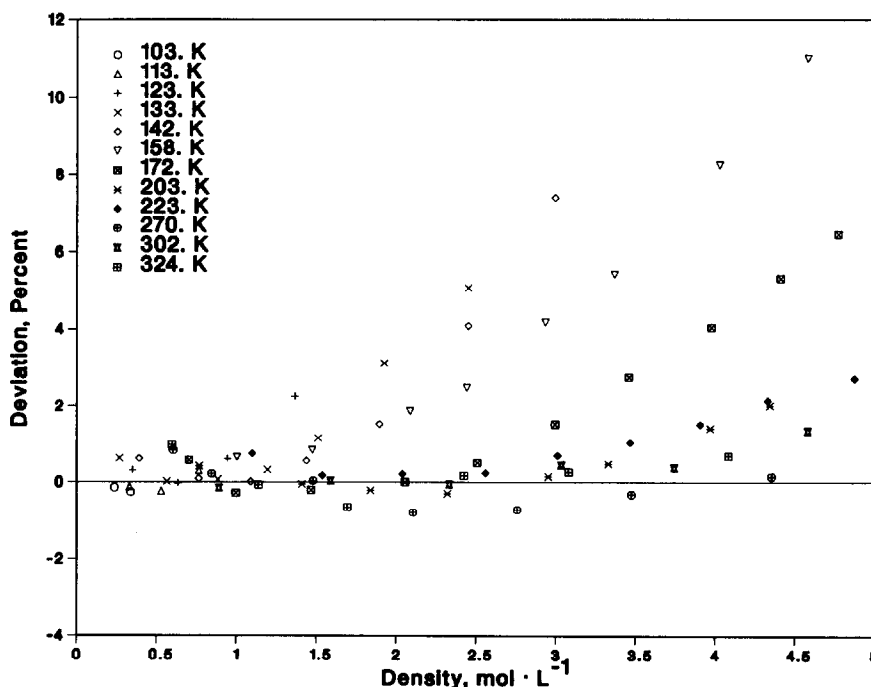

Fig. 3. Deviation plot for argon thermal conductivity data at low densities. Base line represents eq. (2) through linear order in density with λ_0 from experiment (fig. 1).

The strong temperature dependence of the thermal conductivity virial coefficient indicated in fig. 2, and the excellent agreement between theory and experiment shown in figs. 2 and 3, is not as readily apparent when examining the isothermal slope, λ_1 of eq. (1). Theory indicates that this quantity for argon should decrease by about 10% over the range from 103 to 324 K of table 1. The data for argon indicate an uncertainty in this quantity of nearly 10%, and no systematic temperature trend is discernible.

The comparisons shown here give increased confidence in the utility of this theoretical approach for both prediction and correlation of transport properties of gases at moderate densities. The simple correlations of eqs. (12) and (13) should serve well in these capacities. The simple, though ad hoc, extension of the theory to polyatomic gases is seen to be adequate to describe the existing experimental data. The nature of the temperature dependence of the second thermal conductivity virial coefficient now seems firmly established.

References

[1] J.C. Rainwater, J. Chem. Phys. 81 (1984) 495.

[2] D.G. Friend and J.C. Rainwater, Chem. Phys. Letters 107 (1984) 590.

[3] J.C. Rainwater and D.G. Friend, Phys. Rev. A 36 (1987) 4062.

[4] E. Vogel, E. Bich and R. Nimz, Physica A 139 (1986) 188.

[5] H.M. Roder, R.A. Perkins and C.A. Nieto de Castro, Intern. J. Thermophys. 10 (1989) 1141.

[6] U.V. Mardolcar, C.A. Nieto de Castro and W.A. Wakeham, Intern. J. Thermophys. 7 (1986) 259.

[7] R.A. Perkins, H.M. Roder, D.G. Friend and C.A. Nieto de Castro, to be published.

[8] H.M. Roder, R.A. Perkins and C.A. Nieto de Castro, Natl. Inst. Stds. Tech. (US), Internal Report IR 88-3902 (1988).

[9] B. Kamgar-Parsi and J.V. Sengers, Phys. Rev. Letters 51 (1983) 2163.

[10] B.A. Younglove, J. Phys. Chem. Ref. Data 11 Suppl. 1 (1982).

[11] S. Angus and B. Armstrong, International Thermodynamic Tables of the Fluid State – Argon (Butterworths, London, 1971).

[12] R.T. Jacobsen, R.B. Stewart and M. Jahangiri, J. Phys. Chem. Ref. Data 15 (1986) 735.

[13] N. Bogoliubov, J. Phys. (USSR) 10 (1946) 265.

[14] R.F. Snider and C.F. Curtiss, Phys. Fluids 1 (1958) 122.

[15] D.K. Hoffman and C.F. Curtiss, Phys. Fluids 7 (1964) 1887; 8 (1965) 667, 890.

[16] C.F. Curtiss, M.B. McElroy and D.K. Hoffman, Intern. J. Eng. Sci. 3 (1965) 269.

[17] D.E. Bennett and C.F. Curtiss, J. Chem. Phys. 51 (1969) 2811.

[18] H.J.M. Hanley, R.D. McCarty and E.G.D. Cohen, Physica 60 (1972) 322.

[19] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1954).

[20] D.G. Friend, J. Chem. Phys. 82 (1985) 967.

[21] D. Enskog, Kgl. Svenska Vetenkapsakad. Handl. 63 (1922) No. 4.

[22] D.E. Stogryn and J.O. Hirschfelder, J. Chem. Phys. 31 (1959) 1545.

[23] R.C. Reid, J.M. Prausnitz and B.E. Poling, The Properties of Gases and Liquids, 4th Ed. (McGraw-Hill, New York, 1987).

[24] M. Ross, R. Szczepanski, R.D. Trengove and W.A. Wakeham, The Initial Density Dependence of the Transport Properties of Gases, presented at AIChE Annual Winter Meeting, Miami 1986.

[25] E.A. Mason and L.J. Monchick, J. Chem. Phys. 36 (1962) 1622.

[26] R.D. Olmsted, G.R. Staker, R.D. Trengove and P.J. Dunlop, Chem. Phys. Letters 87 (1982) 274.

[27] R.D. McCarty, Natl. Bur. Stds. (US) Technical Note TN 1097 (1986).

[28] M.J. Assael, M. Dix, A. Lucas and W.A. Wakeham, J. Chem. Soc. Faraday Trans. I 77 (1981) 439.

[29] E.N. Haran, G.C. Maitland, M. Mustafa and W.A. Wakeham, Ber. Bunsenges. Physik. Chem. 87 (1983) 657.

[30] H.M. Roder, Intern. J. Thermophys. 5 (1984) 323.

[31] A. Boushehri, J. Bzowski, J. Kestin and E.A. Mason, J. Phys. Chem. Ref. Data 16 (1987) 445.

[32] R.D. McCarty, J. Hord and H.M. Roder, Natl. Bur. Stds. (US) Monograph 168 (1981).

[33] G.J. Sherman, J.W. Magee and J.F. Ely, Intern. J. Thermophys. 10 (1989) 47.