International Journal of Thermophysics, Vol. 7, No. 2, 1986

The Transport Coefficients of Polyatomic Liquids[1]

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The paper presents the results of a preliminary attempt to represent both the viscosity and the thermal conductivity of normal alkanes in the liquid phase by means of a mutually consistent scheme. The correlation method proposed is based upon the general results of the hard-sphere theory of dense fluids, although it does not make use of the detailed predictions of that model. It is shown that the viscosity of the alkanes, ethane, propane, *n*-butane, *n*-hexane, and *n*-octane may be represented by a single, universal function of reduced volume if each species is assigned a characteristic molar volume which is but weakly temperature dependent. Using the same values of molar volume the thermal conductivity of the same fluids can be represented by a further universal function of reduced volume by means of the choice of a second, temperature-independent parameter.

KEY WORDS: alkanes; hard-sphere theory; hydrocarbons; thermal conductivity; viscosity.

1. INTRODUCTION

The prediction of the properties of fluids is more reliable if the method adopted is founded on a realistic physical model combined with a suitable theory, even when neither the model nor the theory is exact. In the case of the transport properties of liquids the most successful method of this kind is based upon the application of the kinetic theory of a dense hard-sphere fluid to the van der Waals model of the liquid [1]. Dymond [1, 2–4],

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[1] Paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

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Woolf [5], and their collaborators have made extensive and successful use of this model in the interpretation and description of the viscosity and diffusion coefficient of fluids and fluid mixtures over a wide range of conditions. Independently, a more heuristic treatment based on the same model has been applied to the thermal conductivity of liquids [6, 7].

However, the independence of the treatments of the viscosity and diffusion coefficient, on the one hand, and the thermal conductivity, on the other, has led to a number of inconsistencies in the results reported. Moreover, until recently, there were very few fluids for which all three properties had been accurately measured in the same range of thermodynamic states so that the inconsistencies have not always been clearly revealed. The availability of new experimental data for the viscosity and thermal conductivity of a number of liquid normal alkanes over a wide range of conditions provides the opportunity to examine the question of consistency afresh and to refine the description of the transport properties of such fluids.

2. BASIS OF THE CORRELATION

2.1. Background

The van der Waals model of a dense fluid assumes that, at sufficiently high densities and temperatures, the true intermolecular pair potential for the molecules may be replaced by a rigid core repulsion surrounded by a uniform attractive potential [1]. When used together with the Enskog theory and the results of computer simulation [8, 9], the complete theory therefore leads to an explicit prediction of the density dependence of all of the transport properties of a hard-sphere fluid that, with a suitable interpretation, should be applicable to a real dense fluid of structureless particles. However, the systems of interest here, liquid alkanes, differ in at least two respects from those to which the hard-sphere theory is expected to be directly applicable. First, the molecules are not spherically symmetric and possess internal energy. Second, the densities considered are generally higher than those for which the hard-sphere model is appropriate. For these reasons we do not employ the detailed results of the hard-sphere theory in our analysis but rather we use the theory as a guide to the development of a description of the properties.

In the case of the viscosity of a hard-sphere fluid, it can be shown [1] that the dimensionless quantity, η^*, defined by the relationship

$$\eta^* = (16/5)(2N_A)^{\frac{1}{3}}(\pi/MRT)^{\frac{1}{2}}\eta V^{\frac{2}{3}} = 6.035 \times 10^8 \eta V^{\frac{2}{3}}/(MRT)^{\frac{1}{2}} \qquad (1)$$

(where all quantities are measured in SI units) is a function only of the ratio of the molar volume, V, of the system to a characteristic molar volume V_0. That is,

$$\eta^*_{\mathrm{SHS}} = F_\eta(V/V_0) \tag{2}$$

where the function F_η has been given elsewhere [1]. In these expressions η is the fluid viscosity, M the molecular mass of the fluid, T the temperature, and R the universal gas constant. It has been shown [10] that the available data for monatomic fluids conform to the result of Eq. (2) provided that the characteristic volume, V_0, is allowed to be temperature dependent.

In order to describe the same property for dense polyatomic systems, while retaining the essential features of a rigid-body model, the rough hard-sphere model has been employed [1, 11]. For this system, at sufficiently high densities and temperatures, the reduced viscosity, η^*, is just proportional to the smooth hard-sphere value, so that

$$\eta^*_{\mathrm{RHS}} = C\eta^*_{\mathrm{SHS}} \tag{3}$$

Here C, the translation–rotation coupling factor, is independent of density and is usually assumed to be independent of temperature. Equation (3) has been tested against experimental data for a number of polyatomic fluids and found to be satisfactory. In the particular case of the lower normal alkanes it was found that the coupling factor C could be taken to have the value unity [12].

In the case of the thermal conductivity of the hard-sphere theory an analogous definition of a reduced thermal conductivity leads to the result that [1]

$$\lambda^* = (64/75)[\pi^{\frac{1}{2}}(2N_A)^{\frac{1}{3}}/R]\,\lambda V^{\frac{2}{3}}(RT/M)^{\frac{1}{2}} = 1.936 \times 10^7 \lambda V^{\frac{2}{3}}(RT/M)^{\frac{1}{2}} \tag{4}$$

with all quantities in SI units, and that

$$\lambda^*_{\mathrm{SHS}} = F_\lambda(V/V_0) \tag{5}$$

Again the available data for the monatomic gases confirm the validity of Eq. (5) and the values of V_0 for them derived from an analysis of viscosity [through Eq. (2)] or thermal conductivity [through Eq. (5)] are mutually consistent [1, 13].

For polyatomic fluids the situation is rather more complicated than for the viscosity because the internal energy is very much more important for the thermal conductivity. Attempts to account for the effect of internal energy have begun from an equation of the form [6, 7, 14–16]

$$\lambda^* = BF_\lambda(V/V_0) \tag{6}$$

In the first attempt [6] B was evaluated from an approximate dilute gas theory, while F_λ was determined empirically. In a second attempt [7] the rough hard-sphere theory of Dahler and his collaborators [15, 16] was employed to evaluate both B and F_λ [7, 14]. Both of these analyses proved successful in correlating the thermal conductivity of the liquids. However, in both approaches, the derived values of the characteristic volume were not entirely consistent with those obtained from independent treatments of viscosity. The inconsistency between the values of V_0 arising from these studies may be shown to be directly attributable to the nonuniqueness in the selection of V_0 for the thermal conductivity when the properties are analyzed independently.

2.2. The New Representation

The advantage that accrues from the consistent representation of the viscosity and thermal conductivity for polyatomic fluids is just that which pertains for monatomic fluids. That is, it becomes possible to generate values of one property from measurements of the other. Furthermore, a representation of either property individually, according to equations of the form of (2) and (5), permits the prediction of data over a wider range of thermodynamic states than are covered by experiment. In order to maintain these advantages in the development of a new representation we retain the notions of Eqs. (2) and (5) which derive from the rigid-sphere model, although we abandon the rigid-sphere functions themselves.

Thus we write

$$\eta^* = f_\eta(V/V_0) \tag{7}$$

and

$$\lambda^* = Bf_\lambda(V/V_0) \tag{8}$$

where the functions f_η and f_λ are now to be determined from experimental data. Further, guided by the success of previous, similar analyses [6, 7, 12, 14], we hypothesize that the function f_η and f_λ are universal among the homologous series of normal alkanes and that the species dependence is contained entirely in the quantities V_0 and B. However, in contrast to previous analyses, we ensure consistency of the characteristic volumes V_0 by imposing the constraint that they should be so and, subsequently, determine the values of the parameter B which achieve this identity. The parameter B represents the scaling of the thermal conductivity owing to the presence of different amounts of internal energy in the various normal alkanes to be considered. In the preliminary analysis presented here it is assumed that the parameter B is temperature independent.

3. THE CORRELATION

3.1. Experimental Data

Since the earlier analyses of transport coefficient data for liquid normal alkanes were performed, new measurements over a wider range of thermodynamic states have been reported. Diller and his collaborators [17–19] have measured the viscosity of ethane, propane, and *n*-butane in the temperature range 90–300 K at pressures up to 30 MPa, while Dymond, Isdale, and their co-workers [4, 20] have reported data on *n*-hexane and *n*-octane in the temperature range 300–400 K at pressures up to 500 MPa. Both sets of measurements have an estimated uncertainty of ±1–2%. In the case of thermal conductivity Roder and his co-workers [21, 22] have reported results for ethane and propane in the temperature range 110–300 K at pressures up to 70 MPa. Le Neindre and his group [23] have reported data for liquid *n*-butane in the temperature range 300–413 K at pressures up to 70 MPa. The accuracy of these results is estimated to be in the range ±1–2%. Finally, Li et al. [24] have reported thermal conductivity data for *n*-hexane and *n*-octane in the temperature range 300–400 K and pressures up to 700 MPa with an associated uncertainty of ±0.3%.

3.2. The Viscosity Correlation

In order to develop a correlation of the form of Eq. (7) for the viscosity of the normal alkanes, Eq. (1) has first been employed to evaluate η^* for the data for ethane and propane along each isotherm studied by Diller et al. [17, 19]. This procedure is used to construct a series of curves in (η^*, log V) space. According to Eq. (7) it should be possible to form one single curve from these segments by linear translation along the log V axis only. Because the line segments do not generally overlap, this superposition has been accomplished by a combination of graphical and numerical methods and leads to the plot shown in Figs. 1 and 2 for the extreme ranges of V/V_0. The intermediate range of V/V_0 reveals similar behavior and is omitted for brevity. In preparing these figures a value for V_0 for ethane at 290 K has been deduced by fitting the line η^* against log V for it to the smooth hard-sphere result. The desired values of V_0 for the remaining isotherms of ethane as well as for propane are given in Table I. Figures 1 and 2 confirm the two elements of the hypothesis of Eq. (7), namely, that for one fluid the quantity η^* is a function only of (V/V_0) and that the function is the same for ethane and propane. The maximum deviation of any datum from a common curve amounts to only ±2%. Given the function f_η^* in Figs. 1 and 2 it is now possible to determine the

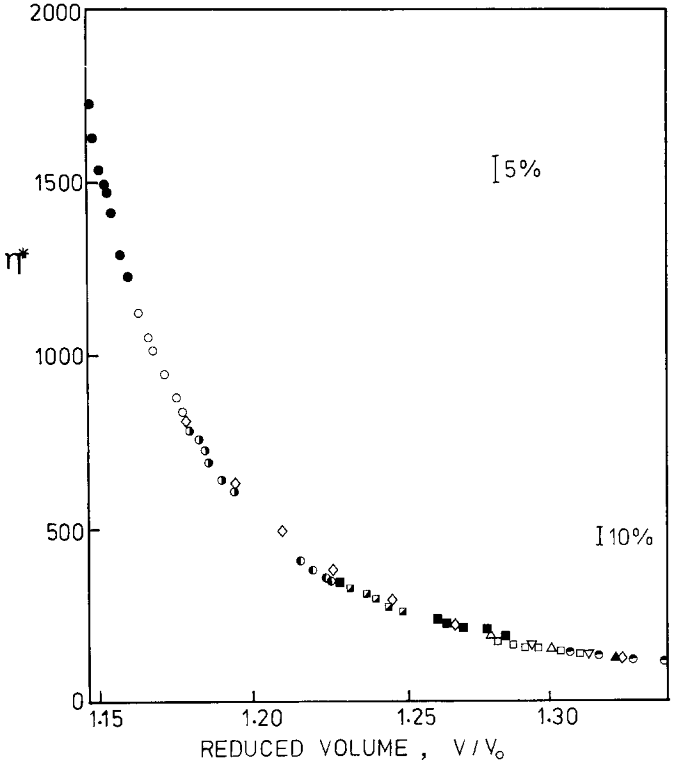

Fig. 1. The reduced viscosity of *n*-alkanes as a function of reduced volume for low reduced volumes. Propane [17]: (●) 90 K; (○) 95 K; (◑) 100 K; (◐) 110 K; (◓) 140 K. *n*-Butane [18]: (◪) 140 K; (■) 150 K; (□) 160 K. *n*-Hexane [20]: (△) 298 K; (▽) 323 K; (▲) 348 K. *n*-Octane [4]: (◇) 298 K.

values of V_0 for the viscosity data for the remaining liquids by the superposition process. The derived values of V_0 are listed in Table I, while Figs. 1 and 2 include the data for *n*-butane, *n*-hexane, and *n*-octane. It can be seen that although the maximum deviation from a common curve now amounts exceptionally to $\pm 8\%$, the mean square deviation is about 1.5%. Considering the wide range of thermodynamic states involved in the plot (from 90 to 400 K and from 0.1 to 500 MPa) as well as the fact that the reduced viscosity changes by nearly three orders of magnitude over the range of V/V_0 examined, this degree of agreement is remarkable and amply confirms Eq. (7).

The ratio $V_0(T)/V_0$ $(T = 300\text{ K})$ for the fluids ethane to *n*-hexane exhibits a smooth temperature variation that is almost universal among the

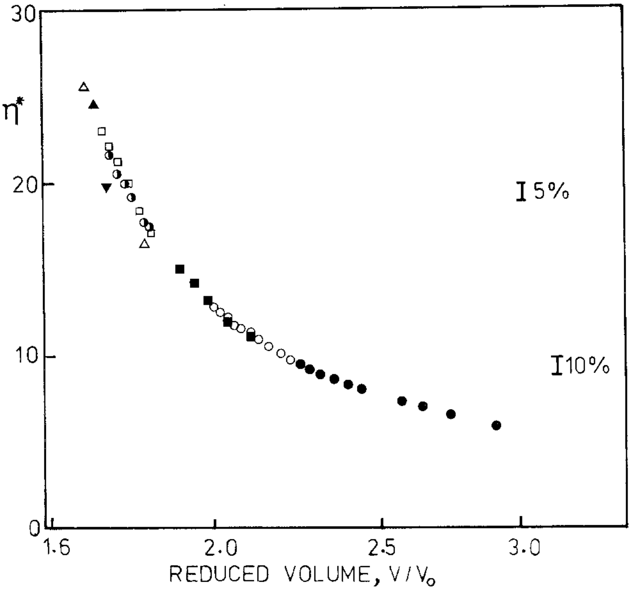

Fig. 2. The reduced viscosity of *n*-alkanes as a function of reduced volume for large reduced volumes. Ethane [19]: (●) 290 K; (○) 250 K; (◑) 200 K. Propane [17]: (■) 300 K. *n*-Butane [18]: (□) 300 K. *n*-Hexane [20]: (▲) 323 K; (▼) 348 K; (△) 373 K.

various hydrocarbons. Figures 1 and 2 alone provide a means of estimating the viscosity of the liquid hydrocarbons studied at densities beyond those examined experimentally for specific isotherms. When combined with a representation of $V_0(T)/V_0$ $(T = 300\ K)$, they certainly permit interpolation of data with respect to temperature and also a modest amount of extrapolation in the same variable.

It would be relatively straightforward at this stage to represent the data in Figs. 1 and 2 by a single equation. However, at present this would be premature since, ideally, the curve should be optimized with respect to all the data on *n*-alkanes which are not yet available in the form required.

3.3. The Thermal Conductivity Correlation

The essence of the new proposal for the correlation of the thermal conductivity is that the values of V_0 to be employed are those determined from the viscosity. Since the isotherms studied for the thermal conductivity are not identical to those examined for the viscosity, it is generally necessary to interpolate within the data in Table I. In the specific case of butane the

Table I. Values of the Characteristic Volume V_0 for n-Alkanes

	$10^6 V_0$ ($m^3 \cdot mol^{-1}$)				
T(K)	C_2H_6	C_3H_8	$n-C_4H_{10}$	$n-C_6H_{14}$	$n-C_8H_{18}$
90	—	52.11	—	—	—
95	—	51.72	—	—	—
100	35.77	51.35	—	—	—
110	35.23	50.69	—	—	—
120	34.70	—	—	—	—
130	34.32	—	—	—	—
140	—	48.75	63.60	—	—
150	33.65	—	62.85	—	—
160	—	—	62.23	—	—
180	—	—	61.13	—	—
200	31.42	—	60.41	—	—
250	30.38	—	58.13	—	—
290	29.42[a]	—	—	—	—
298	—	—	—	83.82	—
300	—	42.71	55.29	—	113.1
323	—	—	—	83.12	—
348	—	—	—	82.21	—
373	—	—	—	81.45	—

[a] Reference value.

determination of V_0 requires an extrapolation to higher temperatures than were studied for the viscosity. This process degrades the reliability of the values of V_0 so that the extrapolation is limited to 50 K, which includes the lowest two isotherms of the reported thermal conductivity data.

According to Eq. (8) values of λ^* derived from experimental thermal conductivity data and plotted as a function of (V/V_0) for the same fluid at different temperatures should lie on the same curve since B was presumed independent of temperature. Furthermore, it should be possible to superimpose lines of ln λ^* against (V/V_0) for different fluids upon one another by means of a vertical shift alone. Figures 3 and 4 show the result of this exercise for the same fluids as were studied earlier. The value of B for ethane has been arbitrarily assigned the value unity and the values for the remainder of the fluids determined by fitting the plot of λ^* vs (V/V_0) to this curve. Figures 3 and 4 reveal that the data for ethane lie on a single curve with a deviation of no more than $\pm 2\%$. The remaining alkanes studied conform to the same curve when an appropriate, temperature-independent value of the parameter B is selected. The worst fit occurs for n-butane at the highest

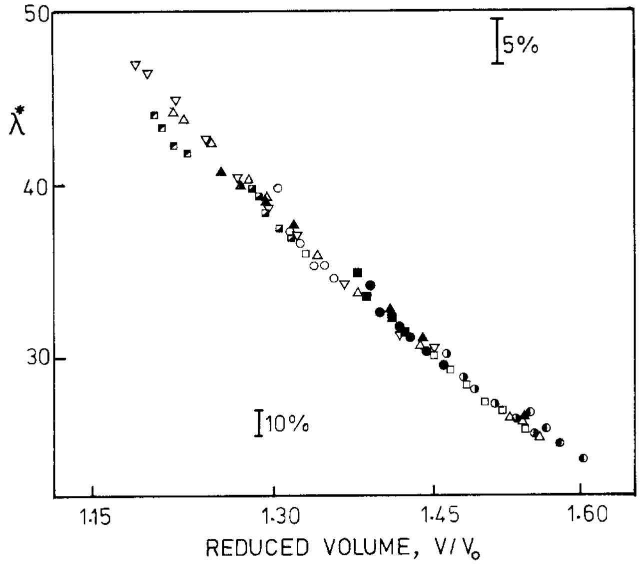

Fig. 3. The reduced thermal conductivity of *n*-alkanes as a function of reduced volume for small reduced volumes. Ethane [22]: (○) 110 K; (●) 135 K; (◑) 155 K; (◐) 175 K. Propane [21]: (□) 227 K; (■) 196 K; (◪) 169 K; (◩) 139 K. *n*-Hexane [24]: (△) 307 K; (▲) 321 K. *n*-Octane [24]: (▽) 307 K.

temperature, presumably owing to the need for extrapolation to determine V_0.

According to its method of introduction the parameter B should reflect the increasing contribution of internal energy to heat transport in the fluid as the number of degrees of freedom of the molecule increases. It might be expected therefore that the quantity should show a smooth variation with, for example, molecular mass. The values of B derived by the method described above do indeed confirm this expectation.

Just as for the correlation of the viscosity, the correlation of the thermal conductivity permits the generation of data over a wider range of temperature and density than that for which experimental data exist.

4. CONCLUSIONS

The present formulation, which uses as its foundation the results of the hard-sphere theory of fluids, permits the extension of a body of viscosity or thermal conductivity data for a normal alkane to a range of thermodynamic states outside of the region studied experimentally with only a

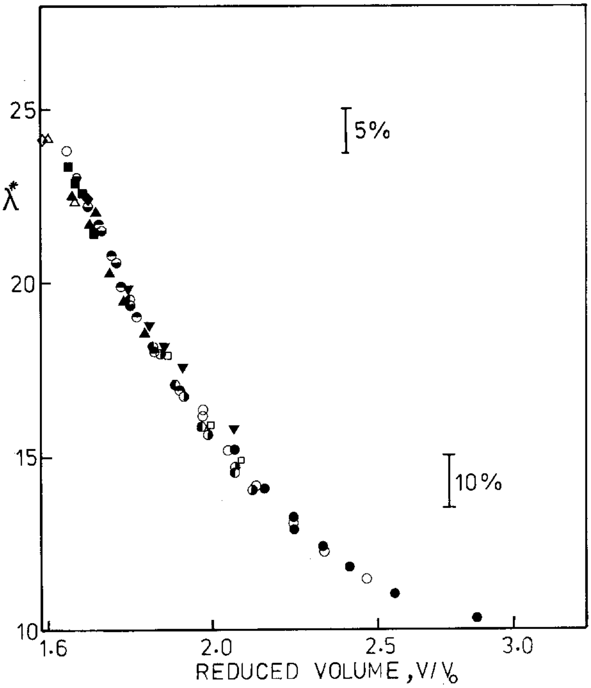

Fig. 4. The reduced thermal conductivity of *n*-alkanes as a function of reduced volume for large reduced volumes. Ethane [22]: (●) 295 K; (○) 275 K; (◑) 255 K; (◐) 235 K; (◓) 215 K; (◒) 195 K; (△) 175 K. Propane [21]: (□) 299 K; (■) 260 K. *n*-Butane [23]: (▲) 298 K; (▼) 358 K. *n*-Hexane [24]: (◇) 307 K; (◆) 321 K.

small loss of accuracy. In principle, the density dependence of the viscosity of an alkane along an isotherm may be predicted from just one datum at a particular density. A single datum for the thermal conductivity then enables this process to be carried through for the second property as well.

Evidently, if it were possible to relate the characteristic volume of the molecules to some other molecular parameter such as the mass it would also be possible to predict the viscosity of normal alkanes for which no measurements exist. Equally, if the parameter *B* could be identified explicitly in terms of known molecular characteristics, the thermal conductivity could be predicted. At the stage of development of the correlation presented here, these ideas must, however, remain speculative.

The results presented in this paper encourage the view that both the viscosity and the thermal conductivity of the liquid normal alkanes can be given consistent descriptions by the use of just two, species-dependent parameters. However, in the work described, the universality of the functions f_η^* and f_λ^* has been optimized independently and with respect to a subset of the fluids for which data exist. A more rigorous statistical treatment, in which the universality of the available experimental thermal conductivity and viscosity data for all normal alkanes is optimized simultaneously, is therefore necessary before definitive correlations are established. In addition, since V_0 has a well-established physical significance in terms of the hard-sphere model, it is desirable that the parameter B be given a similar pedigree by means of a model in which internal energy is accounted for explicitly. These represent the topics of our current and future work. Thus, whereas the present paper illustrates the potential of the correlation for the purpose of extending a model body of data to ranges of conditions not covered experimentally, there remains a significant effort to render the scheme quantitative.

ACKNOWLEDGMENTS

The work described in this paper has received financial support from the U.K. Science and Engineering Research Council and the Department of Trade and Industry.

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