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THE DENSITY DEPENDENCE OF THE THERMAL CONDUCTIVITY OF TOLUENE

The paper describes a new interpretation of the density dependence of the thermal conductivity of liquid toluene in terms of an equation based upon the van der Waals model of a dense fluid. The new analysis is carried out on accurate thermal conductivity data reported previously with the aid of results for the density of toluene published more recently. A simple correlation, based on the van der Waals model, is found to relate the thermal conductivity to the molar volume of the liquid with an accuracy commensurate with the uncertainty in the former.

1 — INTRODUCTION

In an earlier publication [1] we reported measurements of the thermal conductivity of liquid toluene over the pressure range 0.1 to 585 MPa, and in the temperature range 35–87°C. The estimated accuracy of the reported experimental data is one of $\pm 0.3\%$. However, at the time of publication there were no available density data for the liquid with a comparable accuracy over the same range of conditions. It was therefore not possible to analyse the density dependence of the thermal conductivity in the manner which has proved successful for many other liquids [2]. Furthermore, it was not possible to deduce from the measurements thermal conductivities on the saturation line of toluene which have been proposed as standard reference values for liquid thermal conductivity. This is because only an extrapolation of the thermal conductivity to the saturation line which is carried out using density as the independent variable has a secure foundation [3]. The availability of new, accurate values of the density of toluene over a range of temperatures and pressures [4,5] has now made it possible to re-analyse the thermal conductivity data in order to fulfil both of the objectives set out above.

2 — DENSITY DEPENDENCE OF THE THERMAL CONDUCTIVITY

Accurate density measurements for liquid toluene have recently been reported independently by Kashiwagi *et al.* [4], and Easteal and Woolf [5]. The experiments of the former authors extend over the pressure range up to 250 MPa and the temperature range 0 to 100°C, and have a claimed accuracy of $\pm 0.1\%$. The results of the latter authors cover the more limited temperature range 5–50°C and extend to pressures as high as 500 MPa. The estimated accuracy of this second set of data is also $\pm 0.1\%$. The most accurate thermal conductivity

data [1] extend along five isotherms in the range 35-87°C and up to 585 MPa. Consequently, the combination of the two new sets of experimental densities allow us to prepare a table of thermal conductivity as a function of density over at least part of the complete range of thermodynamic states. In preparing this table, which comprises Table I, we have combined the representations of density as a function of pressure along several isotherms given by Kashiwagi *et al.* [4] and Eastal and Woolf [5]. For each experimental pressure employed in the thermal conductivity measurements the density at the temperature of interest has then been obtained by interpolation using a procedure described elsewhere [6]. When the densities obtained from the two independent sources are compared in an overlapping range of thermodynamic states the values never differ by more than $\pm 0.2\%$, and usually by much less. This value is taken as an upper limit to the uncertainty in the densities quoted in Table I. The corresponding uncertainty in the thermal conductivity is one of $\pm 0.3\%$.

3 — REPRESENTATION OF THE DATA

An analysis of the thermal conductivity of a dense fluid, [7,8] based on the rough hard-sphere model of the fluid suggests that to a good approximation the quantity

$$\lambda^* = \frac{\lambda}{(\lambda_{tr,0})} \left(\frac{V}{V_0} \right)^{2/3} = F(V/V_0) \quad (1)$$

should be a function of (V/V_0) alone. Here, λ is the thermal conductivity of the dense fluid at a molar volume V . The quantity $\lambda_{tr,0}$ is the translational contribution to the thermal conductivity of the gas in the limit of zero-density and V_0 is the close-packed volume of the hard-sphere system [7, 8]. Owing to the fact that the real molecules have repulsive potential wells that are not infinitely steep, V_0 will possess a weak temperature dependence.

Table I
The thermal conductivity of toluene as a function of density

T = 308.15 K			T = 320.15 K			T = 330.15 K			T = 345.15 K			T = 360.15 K		
ρ	λ		ρ	λ		ρ	λ		ρ	λ		ρ	λ	
kg m ⁻³	mW m ⁻¹ K ⁻¹		kg m ⁻³	mW m ⁻¹ K ⁻¹		kg m ⁻³	mW m ⁻¹ K ⁻¹		kg m ⁻³	mW m ⁻¹ K ⁻¹		kg m ⁻³	mW m ⁻¹ K ⁻¹	
854.7	128.9		843.2	125.2		838.9	124.4		821.3	118.4		806.6	113.4	
855.2	129.1		844.3	126.6		842.6	125.2		821.4	118.7		829.6	123.2	
856.5	129.6		861.6	133.7		849.7	128.3		832.0	122.1		848.1	131.1	
862.6	132.4		867.7	135.6		860.5	132.8		840.3	126.5		849.1	130.2	
866.9	134.6		884.9	143.7		862.9	135.1		862.0	136.0		865.3	139.5	
878.3	139.6		899.4	150.6		872.2	138.1		891.6	150.0		882.2	146.6	
889.7	145.5		911.5	156.3		888.6	146.1		904.1	155.8		893.7	152.1	
892.3	146.3		921.9	161.8		901.1	152.1		915.4	161.4		905.0	158.0	
897.1	148.6		924.5	168.3		912.9	158.4		924.5	166.0		925.5	168.1	
898.2	149.1		948.5	175.4		924.3	163.9		934.8	171.0				
928.7	163.8					933.6	169.0							
938.1	168.1					942.5	173.1							
955.8	177.6													

In order to test the hypothesis of equation (1) for toluene it is sufficient to demonstrate that the lines of λ^* against $\ln V$ for each isotherm can be superimposed upon each other by shifts along the $\ln V$ axis. The shift necessary along this axis for two isotherms represents the change in V_0 between the two temperatures. For this purpose experimental values of λ^* may be evaluated from the equation [7, 8].

$$\lambda^* = 1.936 \times 10^7 \lambda V^{2/3} (M/RT)^{1/2} \quad (2)$$

wherein M is the molecular weight of the fluid, R the universal gas constant and T the absolute temperature. For definiteness we adopt a value for V_0 at 308 K deduced from viscosity measurements made by Kashiwagi and Makita [9]. Figure 1 then shows the

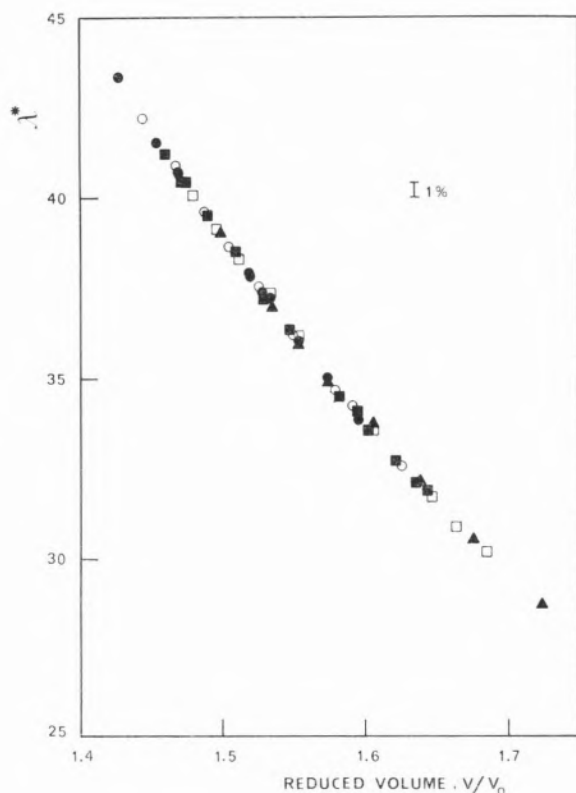


Figure 1

The reduced thermal conductivity, λ^* , for toluene as a function of V/V_0 .

●: 308.15 K; ○: 320.15 K; ■: 330.15 K;
□: 345.15 K; ▲: 360.15 K.

result of the superposition of the remaining thermal conductivity isotherms on the reference line at 308 K by shifts along the $\ln V$ axis. It can be seen that the agreement between the various isotherms is remarkable which confirms the hypothesis of equation (1). The values of V_0 which secure this agreement are listed in Table II.

Table II

The temperature dependence of the core volume V_0 for toluene

T/K	$10^6 V_0 / \text{m}^3 \text{ mol}^{-1}$
308.15	67.51
320.15	67.18
330.15	66.86
345.15	66.59
360.15	66.25

It follows from this discussion that the experimental data for the thermal conductivity along all isotherms may be represented by a single equation for which the simple form

$$\ln \lambda^* = 4.5540 - 2.1989 \ln (V/V_0) \quad (3)$$

is found to be an optimum by least squares regression. Figure 2 shows deviations of the original thermal conductivity data [1] from the correlation together with the recent results of other workers [4]. The data on which the correlation is based depart by no more than $\pm 1\%$ from the universal equation and have a standard deviation of only $\pm 0.3\%$. Furthermore, although the data of Kashiwagi *et al.* [4] depart by as much as 1.5% from the correlation at the highest temperatures and pressures, the deviation is usually much less and is within the mutual uncertainty of the data and the correlation.

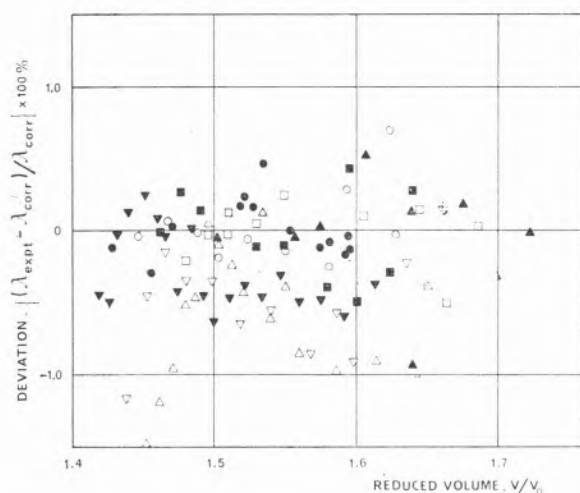


Figure 2

Deviations of experimental thermal conductivity data from the correlation of equations (1) and (2) and Table II.

Present work — ●: 308.15 K; ○: 320.15 K; ■: 330.15 K; □: 345.15 K; ▲: 360.15 K. Kashiwagi *et al.* [4] — ▲: 313.15 K; ▽: 323.15 K; △: 348.15 K.

4 — THE THERMAL CONDUCTIVITY ALONG THE SATURATION LINE

The desirability of establishing standard reference values for the thermal conductivity of liquids is vividly illustrated by the wide range of values reported for almost any liquid [10]. Toluene itself has often been proposed as a suitable reference material. The accuracy of the thermal conductivity data discussed in this paper makes them suitable for inclusion in the establishment of such standard reference values. However, since the normal reference conditions pertain to the saturation line or to 0.1 MPa the data considered require extrapolation in order to be used in this fashion. The preceding section has illustrated that an extrapolation based on the dependence of the thermal conductivity on density is both reliable and simple. Accordingly, we have fitted an equation of the form of equation (2) to the thermal conductivity data for each isotherm and used the fit to derive the thermal conductivity at saturation. The values are listed in Table III. Inevitably this extrapolation degrades the accuracy of the original experimental data to

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Table III

The thermal conductivity of toluene along the saturation line

T/K	$\lambda/\text{mW m}^{-1} \text{K}^{-1}$
308.15	128.5
320.15	124.9
330.15	121.0
345.15	116.9
360.15	112.0

some extent, but the extrapolation is not large and it is estimated that the reported saturation line values should not be in error by more than $\pm 1\%$.

ACKNOWLEDGEMENTS

The authors are grateful to the United Kingdom Department of Trade and Industry, the United Kingdom Science and Engineering Research Council and the Instituto Nacional de Investigação Científica, Portugal for financial support of this work. They also wish to express their thanks to Drs. A. J. Eastal and L. Woolf for performing the high pressure density measurements and allowing them to use the data prior to publication.

(received, 5th July 1985;
in revised form, 31st December 1985)

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RESUMO

A dependência da densidade na condutibilidade térmica do tolueno

Este trabalho descreve uma nova interpretação da dependência da densidade da condutibilidade térmica do tolueno em termos de uma equação baseada no modelo de van der Waals para um fluido denso. A nova análise é baseada em valores precisos da condutibilidade térmica anteriormente publicados e de valores de densidade do tolueno publicados recentemente. Verifica-se que, existe uma correlação simples baseada no modelo de van der Waals, entre a condutibilidade térmica e o volume molar do líquido, com uma exactidão compatível com a incerteza dos dados experimentais.