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The Thermal Conductivity of Ethane in the Critical Region[1]

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The thermal conductivity of ethane in the critical region has been measured isochorically at densities up to 1.76 times the critical density and at temperatures down to 0.13 K above the critical temperature. The measurements were performed with a thermal conductivity apparatus based on the parallel-plate method. The experimental accuracy was 0.5 to 5%, depending on the distance to the critical point. The experimental results agree well with a recently developed crossover theory for the thermal diffusivity of fluids in the critical region.

KEY WORDS: critical region; ethane; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Most methods for measuring the thermal conductivity in fluids fail in the vicinity of the gas–liquid critical point, because, in that region, convection is very difficult to avoid and because the application of a temperature gradient causes uncertainty in the thermodynamic state of the fluid. The parallel-plate method, in which a horizontal layer of the fluid is heated from above, is a configuration in which these effects can be avoided, even very close to the critical point, by choosing a small temperature difference and a small plate separation. It is, therefore, not surprising that the most accurate data for the thermal conductivity in the neighborhood of the critical point have been measured with such a device.

With the present apparatus a strong critical anomaly of the thermal conductivity of xenon [1] and argon [2] has been measured at tem-

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peratures down to 0.13 K above the critical temperature. The results were analyzed in terms of a revised mode–mode coupling theory [2, 3]. The aim of the present series of measurements is the study of the thermal conductivity of the binary mixture carbon dioxide–ethane near the mixture critical point. Therefore, reliable measurements close to the critical point of the pure substances are necessary. For the thermal conductivity of carbon dioxide, the well-known measurements of Sengers et al. [4–7] are available. The present study provides measurements of a comparable accuracy and extent for ethane, which has, according to Douslin and Harrison [8], a critical pressure P_c of 4.87176 MPa, a critical temperature T_c of 305.33 K, and a critical density ρ_c of 6.870 $\mathrm{mol \cdot dm^{-3}}$.

The theory for the transport properties of the pure components has recently been extended to a complete description of the critical enhancement of the viscosity and the thermal conductivity in the entire region where a critical enhancement is observed [9–11]. This crossover formalism contains only one adjustable parameter which has the physical meaning of a finite cutoff wave number for the long-range critical fluctuations.

2. EXPERIMENTAL

The thermal conductivity cell, which is mounted in a pressure vessel, is shown in Fig. 1. The fluid surrounds the cell and fills the gaps between the guard ring, upper plate, and lower plate. The cell is based on the guarded hot plate principle. Heat supplied by the upper plate heater is transported from the upper plate to the lower plate across the gap of thickness $d = 155\ \mu m$ through the sample fluid. The two plates are separated by thin glass spacers. The heat generated in the heaters in the guard ring serves to eliminate net heat transport from the upper plate to its surroundings. The guard ring, upper plate, and lower plate are composed of several sections of electrolytic copper. All heater and thermometer wires in the plates and guard ring lie in grooves and are electrically insulated from the copper parts by strings of numerous beads of beryllium oxide, which is a good thermal conductor. Furthermore, an isolation cap made of kufaleyt is placed around the guard ring. A good room temperature stabilization system was used which kept this temperature constant to within 0.1 K, because part of the electrical bridge circuit was, inevitably, outside the pressure vessel.

The thermal conductivity of the fluid can be deduced from the relation

$$\lambda = Qd/(A\,\Delta T) \tag{1}$$

where Q is the power developed in the upper plate heater, A is the effective area of the upper plate, d is the distance between the plates, and ΔT is the

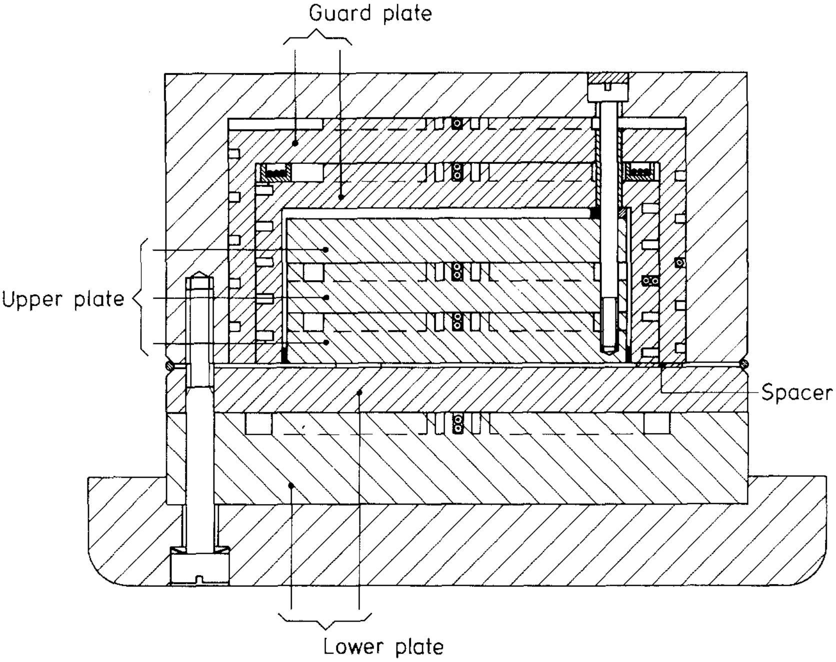

Fig. 1. The parallel-plate thermal conductivity cell.

temperature difference across the fluid layer measured by means of potentiometry. Due to the high sensitivity of this method, temperature differences ΔT as small as 1 mK can be employed, and furthermore, an accurate equalization of the temperatures of the upper plate and guard ring can be realized to within 20 μK. Some small corrections of a few percent have to be applied, first, to the value of the power Q as a consequence of radiation and the temperature distribution within the cell and, second, to the value of the measured temperature difference ΔT because of the thermal resistance of the copper between the thermometers and the gap.

The gas used was research-grade ethane supplied by Matheson, which has, according to the manufacturer, a purity of at least 99.97%. Because the fraction of the fluid at room temperature was very small in the present experimental setup, it was possible to measure the thermal conductivity along isochores, which allows a better definition of the thermodynamic state of the sample fluid close to the critical point. For each isochore, the pressure vessel was filled at 333 K, which is 28 K above the critical temperature. After each filling procedure or temperature change the system was left for 10 to 60 h to equilibrate.

The bath temperature was measured on the IPTS-68 with a platinum resistance thermometer to within 1 mK. The pressure was measured with a conventional deadweight pressure gauge with an accuracy of 0.01 %. The density of the sample gas was calculated from the measured pressure and temperature. Outside the critical region the equation of state of Friend et al. [12] was applied, and inside the critical region the scaled fundamental equation of Olchowy and Sengers [11].

3. RESULTS AND DISCUSSION

A few thermal conductivity measurements were made with nitrogen at a temperature of 298.562 K and at pressures of 0.246 and 1.095 MPa to check the performance of the apparatus. Nitrogen was chosen because a large number of accurate experimental data, obtained with the concentric-cylinder and hot-wire methods, are available [13–16]. At the lower pressure, where a small correction for accommodation had to be made [17, 18], the result was 25.82 $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$, while the literature values range from 25.82 to 26.06 $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$. At the higher pressure these values are 26.31 and 26.28 to 26.43 $\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$, respectively.

The thermal conductivity of ethane was measured at eight temperatures along 10 isochores. The accuracy of the measurements is estimated to be 0.5 to 5 %, depending on the distance to the critical point. At the lowest density, about 0.7 $\mathrm{mol \cdot dm^{-3}}$, the measured values are in agreement with previously published data, especially with those of Roder et al. [19, 20], Prasad et al. [21], Le Neindre et al. [22], and Desmarest et al. [23] within the combined experimental error.

On approaching the critical point, the temperature differences across the gap were chosen successively smaller in order to avoid convection. The absence of convection was checked experimentally by repeating measurements regularly with various temperature differences across the gap. The values of the thermal conductivity obtained in this way were independent of the experimental temperature difference between the plates.

In Fig. 2 the experimental data, measured in 10 isochores at eight different temperatures, are plotted in terms of the thermal diffusivity $D_T = \lambda/\rho c_p$ against the density ρ of the fluid. The value of the isobaric specific heat c_p is calculated from the equations of state mentioned above. The corresponding complete isotherms calculated with the crossover theory of Olchowy and Sengers [11] are drawn as solid lines. In this calculation the value of the reciprocal wavenumber q_D is taken as $q_D^{-1} = 1.7\ 10^{-10}$ m [11]. The theoretical isotherms have small discontinuities at the densities 4.8 and 9.2 $\mathrm{mol \cdot dm^{-3}}$, which reflects the use of two different equations of state, inside and outside the critical region, without the application of a blending

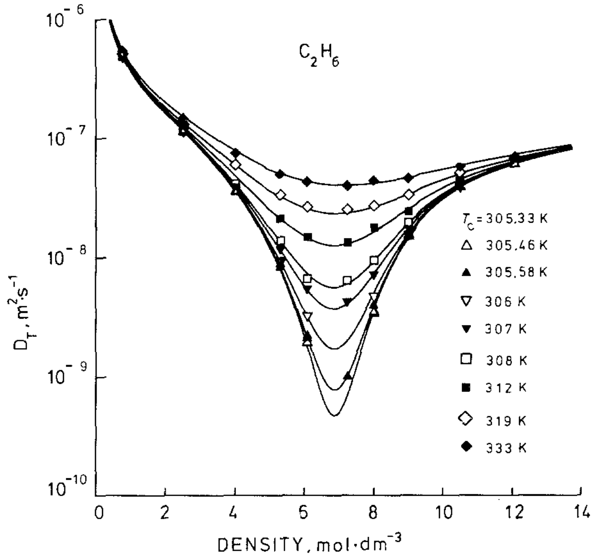

Fig. 2. The thermal diffusivity of ethane in the critical region versus the density. The solid lines indicate the isotherms calculated from the crossover theory [11].

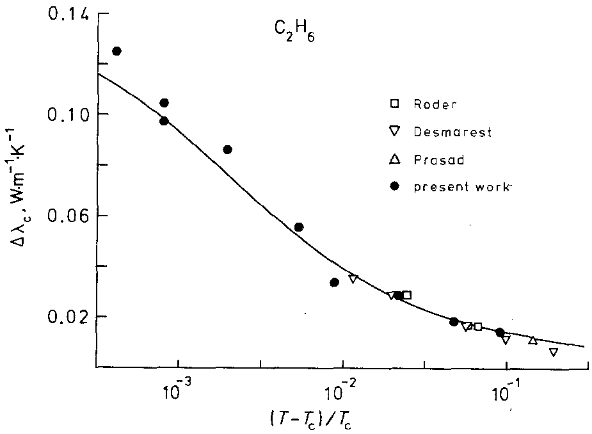

Fig. 3. The critical enhancement of the thermal conductivity of ethane at 6.094 mol · dm^{-3} versus the reduced temperature. The solid line indicates the isochore calculated from the crossover theory [11].

function. Like other substances such as xenon, argon, and carbon dioxide, the thermal diffusivity of ethane shows a pronounced minimum corresponding to a maximum in the thermal conductivity. At the lowest temperature employed, 0.13 K above the critical temperature, the highest critical enhancement of the thermal conductivity which was measured is about 3.5 times larger than the background value.

Figure 3 shows the critical enhancement $\Delta\lambda_c$ of the thermal conductivity, which is obtained by subtracting the preliminary background values [11] against the reduced temperature $\varepsilon = (T - T_c)/T_c$ for the present experimental data along the isochore with a density of about 90% of the critical density. The theoretical isochore is shown as a solid line. Moreover, the available literature data [19, 21, 23] are displayed corrected to the given density. Figure 3 illustrates that the present measurements extend the experimental range of reduced temperatures by more than one decade. The present experimental results for this isochore are also given in Table I.

The standard deviations of our measurements with respect to the crossover theory of Sengers and Olchowy are in agreement with the estimated experimental accuracies. Along each isochore the standard deviation of our measurements with respect to the crossover theory of Sengers and Olchowy is about equal to or slightly less than the estimated experimental accuracy, which ranges from 0.5% far from the critical point to 5% close to the critical point. We therefore conclude from our measurements of the thermal conductivity of ethane in the critical region that the agreement between the experimental results and those calculated by the crossover theory of Sengers and Olchowy is very satisfactory over the entire experimental range, which extends down to 0.13 K above the critical temperature and up to 1.76 times the critical density.

Table I. The Thermal Conductivity, λ, of Ethane at 6.094 $\text{mol} \cdot \text{dm}^{-3}$

P (MPa)	T (K)	λ ($\text{mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)
4.883	305.455	161.98
4.894	305.574	141.59
4.894	305.575	134.30
4.927	305.922	123.10
5.024	306.961	92.632
5.123	308.022	70.913
5.488	311.992	66.106
6.216	319.948	56.916
7.413	333.103	54.732

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REFERENCES

1. J. van Oosten, Ph.D. thesis (University of Amsterdam, Amsterdam, 1974).
2. B. W. Tiesinga, Ph.D. thesis (University of Amsterdam, Amsterdam, 1980).
3. N. J. Trappeniers, in *Proceedings of the 8th Symposium on Thermophysical Properties*, J. V. Sengers, ed. (American Society of Mechanical Engineers, New York, 1982), Vol. I, p. 232.
4. J. V. Sengers, Ph.D. thesis (University of Amsterdam, Amsterdam, 1962).
5. A. Michels, J. V. Sengers, and P. S. van der Gulik, *Physica* **28**:1201 (1962).
6. A. Michels, J. V. Sengers, and P. S. van der Gulik, *Physica* **28**:1216 (1962).
7. A. Michels and J. V. Sengers, *Physica* **28**:1238 (1962).
8. D. R. Douslin and R. H. Harrison, *J. Chem. Thermodyn.* **5**:491 (1973).
9. G. A. Olchowy and J. V. Sengers, *Technical Report BN 1052* (Institute for Physical Science and Technology, University of Maryland, College Park, 1986).
10. G. A. Olchowy and J. V. Sengers, *Phys. Rev. Lett.* **61**:15 (1988).
11. G. A. Olchowy and J. V. Sengers (in press).
12. D. G. Friend et al. (in press).
13. B. Le Neindre, *Int. J. Heat Mass Transfer* **15**:1 (1972).
14. E. N. Haran, G. C. Maitland, and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **87**:657 (1983).
15. A. A. Clifford, J. Kestin, and W. A. Wakeham, *Physica* **A97**:287 (1981).
16. M. J. Assael and W. A. Wakeham, *J. Chem. Soc. Faraday Trans. I* **77**:697 (1981).
17. P. Welander, *Ark. Fys.* **7**:507 (1953).
18. H. S. Taylor, *A Treatise on Physical Chemistry* (Van Nostrand, Toronto, 1951), Vol. 2, p. 131.
19. H. M. Roder, *Experimental Thermal Conductivity Values for Hydrogen, Methane, Ethane and Propane, NBSIR 84-3006* (National Bureau of Standards, Boulder, Colo., 1984).
20. H. M. Roder and C. A. Nieto de Castro, *High Temp. High Press.* **17**:453 (1985).
21. R. C. Prasad and J. E. S. Venart, *Int. J. Thermophys.* **5**:367 (1984).
22. B. Le Neindre, R. Tufeu, P. Bury, P. Johannin, and B. Vodar, in *Thermal Conductivity. Proceedings of the Eight Conference*, C. Y. Ho and R. E. Taylor, eds. (Plenum, New York, 1969), p. 229.
23. P. Desmarest and R. Tufeu, *Int. J. Thermophys.* **8**:293 (1987).