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Contributions of the Van der Waals Laboratory to the Knowledge of Transport Properties of Fluids[1]

P. S. van der Gulik[2]

After the presentation of Enskog's theory of the transport phenomena at high densities in 1922, one of the aims of the Van der Waals Laboratory was to check this theory with accurate experimental results. As early as 1931, Michels and Gibson published data on the viscosity of nitrogen taken by means of the Van der Waals vertical-capillary viscometer. In 1952, Michels and Botzen presented thermal-conductivity measurements on nitrogen taken by means of the parallel-plate heat-conductivity apparatus. Finally, in 1968 Trappeniers and Oosting presented data on the self-diffusion coefficient of methane obtained with a nuclear magnetic resonance spin-echo spectrometer. In all of these cases agreement with either the Enskog theory or the modified Enskog theory was not obtained. In 1973 Trappeniers and J. Michels showed that the self-diffusion coefficient of krypton obtained with a tracer method deviates from Enskog theory due to the formation of clusters. Measurements of the thermal conductivity of argon in 1955 motivated a study of transport phenomena of fluids in the critical region. This resulted, in 1962, in the first proof of the existence of a rather strong divergence in the thermal conductivity of carbon dioxide, by Michels, Sengers, and Van der Gulik. In 1978 Offringa showed that the viscosity has only a small critical anomaly, while Oosting showed as early as 1968 that, for self-diffusion, such an anomaly could not be detected. In 1991 Mostert, and in 1996 Sakonidou, showed that the anomaly in the thermal conductivity is finite in mixtures near the vapor–liquid critical line. In the 1970s a vibrating-wire viscometer suited for measuring the viscosity near the melting line of simple gases was developed to check predictions by computer simulations of the viscosity of hard spheres. From the comparisons, it could be concluded that in the density range from the critical density up to twice this density, a special version of the hard-sphere Enskog theory describes the measurements within the experimental accuracy. With this result it was possible to describe the viscosity in the low-density range, up to the critical density, by a model of a gradual transition from intercluster transport described by the Chapman–Enskog theory

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[2] Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, Valckenierstraat 65-67, 1018 XE Amsterdam, The Netherlands. E-mail: gulik@science.uva.nl

to intracluster transport described by the hard-sphere Enskog theory, a model inspired by J. Michels' conclusion that the formation of clusters influences the transport properties.

KEY WORDS: critical enhancement; Enskog theory; theoretical model; transport properties; Van der Waals Laboratory.

1. INTRODUCTION

The theory of transport phenomena originates from the kinetic theory of gases which was introduced by Maxwell in 1859 [1]. For an exact solution, Boltzmann's equation, published in 1872 [2], had to be solved. In 1910 Hilbert [3] proved the existence and uniqueness of a solution and, thereupon, the Boltzmann equation was solved independently by Chapman [4] and by Enskog [5] in 1917. This solution is known as the Chapman–Enskog theory and is valid for rarefied hard spheres and, in an adjusted version, also for rarefied real gases. Finally, in 1922, Enskog [6] extended the theory to dense gases of hard spheres and this theory is known as the Enskog theory. From the beginning, the Van der Waals Laboratory aimed to check this theory by accurate measurements of the transport properties of fluids at high densities. For this purpose a vertical-capillary viscometer was developed as early as the 1920s, and two decades later, a parallel-plate heat-conductivity apparatus was built. Measurements of the self-diffusion were undertaken when, again two decades later, the technical possibilities became available.

In Section 2 a general review of the methods and results is given; Section 3 is devoted to the critical region, and Section 4 to the experimental test of the existence of a logarithmic term in the density expansion. In 1970, computer simulations of the viscosity of hard spheres by Alder et al. [7] proved that the Enskog theory is valid for hard spheres up to about twice the critical density but that in the last third of the fluid-density range up to the melting density the relative viscosity increases with density up to nearly twice the Enskog value. In Section 5 the contributions of the Van der Waals Laboratory to such simulations are discussed, and Section 6 describes the construction of a vibrating-wire viscometer suited for pressures up to 1 GPa and low temperatures, to check these simulation predictions, which led to a different interpretation of the Enskog theory.

In the appendices, listings are given of theses and publications of the Van der Waals Laboratory on transport properties. Therefore, references to these are indicated by the letter and number under which they are listed in the appendix concerned. As far as is reasonable, the historical order is maintained.

2. CLASSICAL MEASUREMENTS, APPARATUSES, AND RESULTS

2.1. Viscosity

Already before the actual founding of the van der Waals Laboratory, Michels and Gibson constructed the Van der Waals vertical-capillary viscometer [A1, B1]. The goal was accurate, absolute measurements at high pressures to check theory. At that time the transpiration and rotational methods were the only methods for which an exact mathematical treatment was developed, but the lack of knowledge of the effect of pressure on the elastic constants was reason to reject the rotational method. The drawback of the transpiration method, that the capillary had to withstand the internal pressure, and that its distortion was not readily calculable, was removed by inserting the glass apparatus in a steel vessel, so that the capillary, of known compressibility, was submitted to hydrostatic pressure. The use of a mercury piston made possible the application of small pressure differences (maximum of 50 kPa) compared to the total pressure; its position was detected by means of platinum contacts. Figure 1 shows a schematic view of the apparatus, as given in the thesis of Schipper [A3]. In 1931 the first results for the viscosity of nitrogen up to 100 MPa at 298, 323, and 348 K were published by Michels and Gibson [A1, B1]. They concluded that the hard-sphere Enskog theory is in only qualitative agreement with the experimental values of the viscosity. Two decades later Schipper [A3, B3] presented measurements on the viscosity of hydrogen and deuterium at temperatures from 298 to 398 K and at pressures up to 200 MPa with the same conclusion. Thereafter, this viscometer has been used for similar measurements on argon [B4], carbon dioxide [B5], neon [B6], and krypton [B7].

2.2. Heat Conduction

Two decades later, in 1952, Michels and Botzen [A2, C1, C2] published heat-conductivity measurements on nitrogen at pressures up to 250 MPa. For this purpose a parallel-plate apparatus was constructed, suitable for pressures up to 250 MPa and for temperatures from 273 to 348 K. This method was preferred over the hot-wire method because of the absence of convection, end effects, and a temperature drop at the surface of the wire. Convection was avoided by heating a horizontal gas layer from above, a guard ring prevented end effects, and the small isotropic temperature gradient over a large surface made the temperature drop negligibly small at pressures larger than 1 MPa. Figure 2 shows a diagram of the apparatus as given in the thesis of Botzen [A2]. The authors drew the conclusion

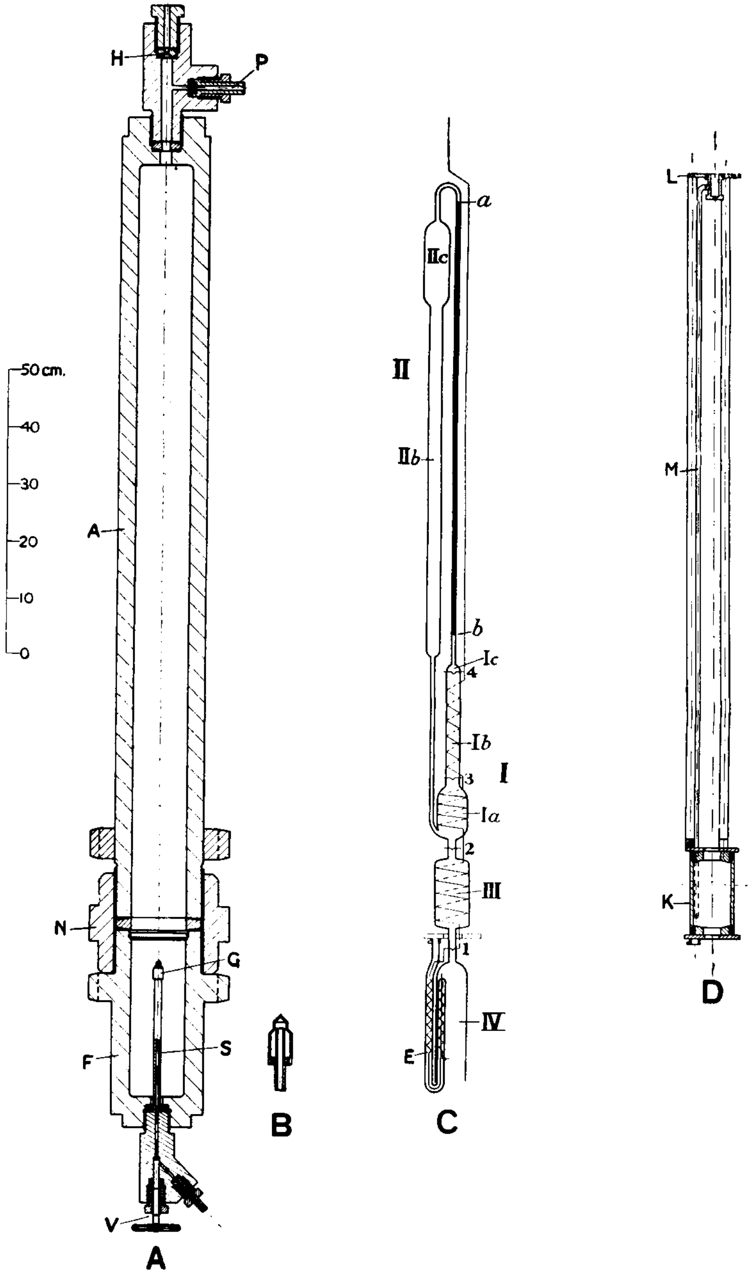

Fig. 1. Schematic view of the Van der Waals vertical-capillary viscometer, as given in the thesis of Schipper [A3].

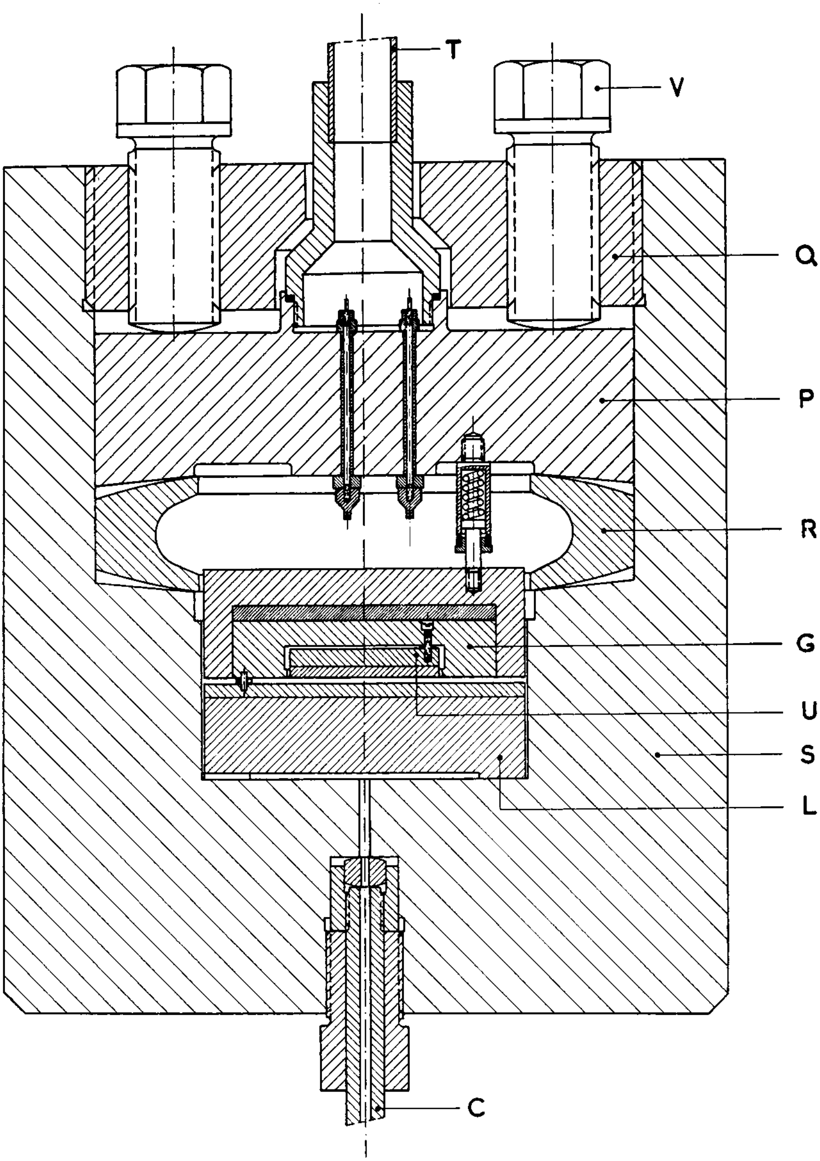

Fig. 2. Diagram of the parallel-plate heat-conductivity apparatus, as given in the thesis of Botzen [A2].

that the heat conductivity could not be described by the Enskog theory, either in the normal version or in the version now known as the modified Enskog theory. Afterward, this apparatus was used for measurements on argon [C3], carbon dioxide [A4, C4–C6], again argon [C7], and neon [C8].

2.3. Self-Diffusion

In the 1960s, under the directorship of N. J. Trappeniers, nuclear magnetic resonance measurements were set up. Within that framework an rf pulse- or spin-echo spectrometer was developed by Gerritsma [D3] for measurements of the spin-lattice relaxation time T_1. The same apparatus was used by Oosting [A5, D1–D6] to measure the self-diffusion coefficient of methane at low temperatures down to 77 K and at pressures up to 230 MPa by means of the proton spin-lattice relaxation-time method. In 1968, he published measurements along three isotherms at 194.8, 273.15, and 298.15 K up to a density of 400 $\mathrm{kg \cdot m^{-3}}$, along five isochores at 35, 54, 77, 90, and 168 $\mathrm{kg \cdot m^{-3}}$ and along the coexistence line. The same method was used afterward by Harris [D8] for liquid methane, by Arends [A11, D9] for ethylene, and by Peereboom [D10, D11] for xenon and ethene.

J. Michels [A7, D7] determined very accurately the density dependence of the self-diffusion coefficient of krypton at 297.97 K up to densities of 640 $\mathrm{kg \cdot m^{-3}}$ by means of a tracer method. He showed that this density dependence is influenced by the formation of dimers and larger clusters and that it cannot be described by the usual Enskog theory.

3. THE CRITICAL REGION

The measurements of the heat conductivity of argon in 1955 by Michels, Botzen, Friedman, and Sengers [C3] gave rise to the special study of the critical region. The viscosity measurements on carbon dioxide in 1957, by Michels, Botzen, and Schuurman [B5], showed an enhancement around the critical density as well. Later on, both phenomena appeared to be artifacts, due to convection in the first case, and due to the absence of the influence of compressibility in the working equations in the second case. However, careful improvement of the parallel-plate cell by Sengers [A4, C4–C6] made it possible to measure the heat conductivity in the critical region of carbon dioxide accurately. The result was the proof of the existence of the critical enhancement in 1962. The work of Sengers motivated the development of theory for the critical region.

Afterward, a new smaller parallel-plate cell was built [C12, C13, C22], suitable also for low temperatures, that was used for measurements in the critical region of xenon by Van Oosten [A8] in 1974 and of argon by

Tiesinga [A12, C17] in 1980. A decade later this apparatus was used to study the heat conductivity in the critical region of mixtures. First, Mostert [A13, C11, C14–C16] showed in 1991 that an infinite critical enhancement in an ethane–carbon dioxide mixture is improbable, and thereupon, Sakonidou [A14, C18, C19, C21] in 1996 definitively showed that the enhancement in the critical region of a 50–50% mixture of methane and ethane is finite.

Meanwhile, in 1978, Offringa [A9] studied the viscosity of xenon in the critical region and showed that for viscosity the critical enhancement is very small. For this purpose a special horizontal-capillary viscometer was constructed, used afterward for measurements on sulfur hexafluoride [B11]. SF_6 is an interesting material because the value of its critical temperature, 318.74 K, makes it very suitable for study in the critical region under microgravity conditions. Such a study was performed by de Bruijn [C20], resulting in his 1999 thesis, *Heat Transfer in a Critical Fluid Under Microgravity Conditions, a Spacelab Experiment* [A15]. Finally, Oosting [A5, D1–D6] showed as early as 1968 that the critical enhancement of the self-diffusion in methane is negligible.

4. THE LOGARITHMIC TERM

In the meantime several efforts had been made to improve the theory. In analogy with the virial equation of state, power series expansions of the transport phenomena in the density were developed. In the 1960s the existence of a logarithmic term in this series expansion was theoretically predicted [8, 9]. To check this possibility, Snel [A6, C9, C10] developed a hot-wire method for the accurate determination of the thermal conductivity of carbon dioxide and krypton in a limited density range. However, this range and the accuracy of the measurements did not allow a conclusion on the existence or nonexistence of a logarithmic term. Likewise, in 1973, J. Michels came to the conclusion that with his measurements of the self-diffusion coefficient the necessity of a logarithmic term could not be demonstrated. It was Van den Berg [A10, B9] who succeeded by means of a thorough improvement of the vertical-capillary viscometer and its working equations [B17] to measure the viscosity of krypton with an exceptional accuracy of 1 part in 10,000 and to show that, if a logarithmic term exists, the corresponding coefficient is so small that the term can be neglected.

For this purpose he extended the theory of capillary viscometers to non-steady-state compressible flow, taking into account the thermal effects in a compressible viscous flow in a capillary [B20, B21]. However, the necessity to check the dimensions of the viscometer, in particular the diameter and the roundness of the capillary, meant the end of this viscometer.

Later Van den Berg also improved the horizontal-capillary viscometer. His measurements of the viscosity of sulfur hexafluoride are now in the process of being published. Afterward, he guided the improvement of the parallel-plate heat-conductivity apparatus, resulting in the excellent measurements of Sakonidou [C19, C21]. Finally, he was involved in the microgravity experiments.

5. SIMULATIONS

The conclusion of J. Michels [A7, D7] about the influence of the formation of clusters on the density dependence of the transport phenomena was based not only on his experimental work but also on computer simulations of self-diffusion [E1, E2]. With Ten Seldam, the Van der Waals Laboratory had a computer programming specialist of the earliest hour, and around 1970 the first laboratory computer was installed. This facility, in the first place, enabled much more involved calculations. For instance, the computation of the working equations for the capillary viscometers, taking into account the compressibility of the fluid, as developed by Van den Berg [B17, B20, B21], could not be performed without the use of a computer. Before this facility became available, measurements of the viscosity in the critical region could not be evaluated. In the second place, computers were applied for measurement automation, such as for the horizontal-capillary viscometer. Finally, J. Michels started molecular dynamics simulations of transport properties by means of large computers. By the simulation of transport properties of square-well molecules [E3–E7], he confirmed the result of Alder and co-workers [7] that for viscosity the Enskog theory for hard spheres is valid up to twice the critical density, but that in the remaining third of the density range up to the melting density, the relative viscosity increases to nearly twice the Enskog value.

6. HIGH-PRESSURE VISCOSITY MEASUREMENTS

Technical advances in the 1970s enabled Van der Gulik to develop a vibrating-wire viscometer suitable for pressures up to 1 GPa and for temperatures down to liquid nitrogen temperature, so that it became possible to check the density dependence of the viscosity for simple gases up to the melting line. A comparison of experimental results for argon [B10, B12, B13] with the computer simulations showed that the Enskog theory is indeed not valid in the highest one-third of the fluid-density range near the melting line. In this range the relaxation-time method introduced by Maxwell [10] in his second paper about transport properties has to be applied [B26]. In the second one-third of the fluid-density range just above the critical density, however, a special version of the hard-sphere Enskog theory with different diameters for the collision cross section and for the temperature-dependent excluded volume describes the measurements within the experimental accuracy [B12]. Using this result it was possible to describe the viscosity in the first one-third of the fluid-density range up to the critical density within the experimental accuracy with a model of a gradual transition of two momentum-transport mechanisms, intracluster transport described by hard-sphere Enskog theory and intercluster transport described by the Chapman–Enskog theory [4, 5]. This model is based on the conclusion of J. Michels that dimers and clusters play a role already at low densities.

Figure 3 shows the result for measurements on noble gases at 298 K performed at the Van der Waals Laboratory: the filled symbols present the

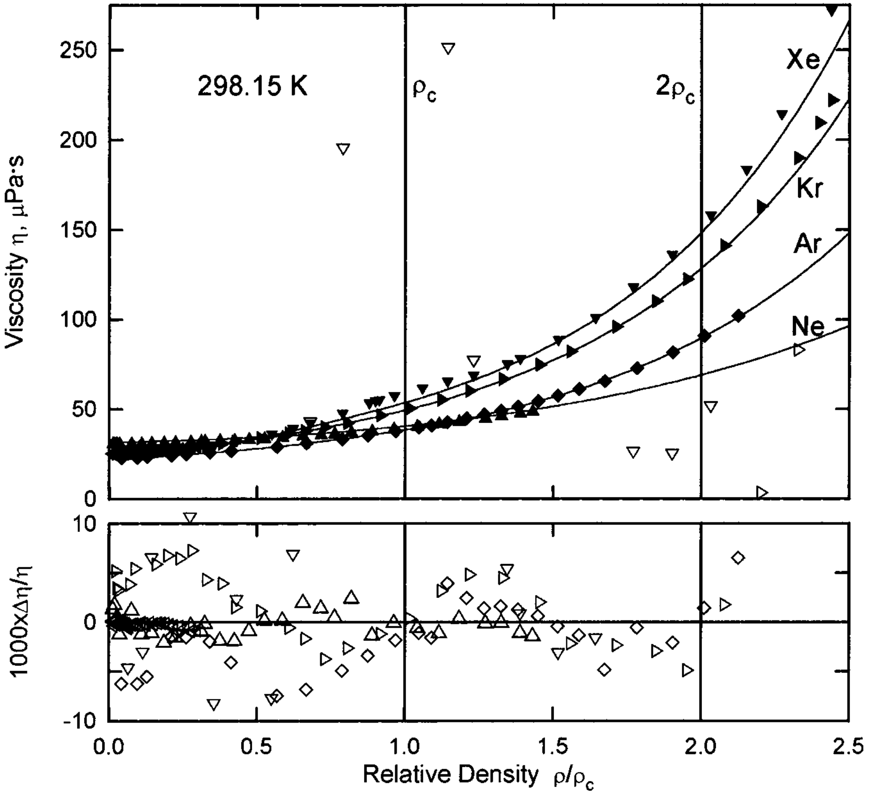

Fig. 3. Viscosity of noble gases, as measured at the Van der Waals Laboratory, as a function of the relative density ρ/ρ_c. The filled symbols represent the experimental data; the solid curves, the values calculated according to the model; and the open symbols, the deviations of the experimental values from the theoretical model (in parts per thousand).

measured values, the solid curves the values calculated with the model, and the open symbols the deviations of the experimental values from the calculated values in parts per thousand. The oldest measurements on argon [B4], the diamonds, show deviations of up to 5 parts per thousand; the neon data [B6], the upward-pointing triangles, only 2 parts per thousand; the krypton data [B7], the rightward-pointing triangles, again 5 parts per thousand; and the precision data of Van den Berg [A10, B9] at low density, 0.5 part per thousand. The unpublished xenon data, the downward-pointing triangles, show that the measurements were not always easy. They show a spread of a few percent and a false critical enhancement of 9%. The latter phenomenon can now be avoided by applying the new working equations developed by Van den Berg. Furthermore, it is clearly seen that the model has still to be extended to densities higher than twice the critical density: at higher densities, the deviations start to increase systematically. Nevertheless, the contributions of the Van der Waals Laboratory to the knowledge of the transport properties of fluids have led to great advances in the theoretical understanding.

APPENDIX A: THESES, UNIVERSITY OF AMSTERDAM

Michels Period

A1 (1933) R. O. Gibson, *The Viscosity of Gases at High Pressures.*
A2 (1952) A. Botzen, *The Thermal Conductivity of Gases at High Pressures.*
A3 (1954) A. C. J. Schipper, *De Viscositeit van Gecomprimeerde Waterstof en Deuterium.*
A4 (1962) J. V. Sengers, *Thermal Conductivity Measurements at Elevated Gas Densities Including the Critical Region.*

Trappeniers Period

A5 (1968) P. H. Oosting, *Zelfdiffusie en Protonspin-Roosterrelaxatie in Methaan.*
A6 (1973) J. A. A. Snel, *De Dichtheidsontwikkeling van de Warmtegeleidingscoefficient van Kooldioxide en Krypton.*
A7 (1973) J. P. J. Michels, *De Dichtheidsafhankelijkheid van de Zelfdiffusiecoefficient van Krypton.*
A8 (1974) J. van Oosten, *De Warmtegeleidingscoefficient van Xenon in het Kritische Gebied.*
A9 (1978) J. C. A. Offringa, *De Viscositeitscoefficient van Xenon in het Kritische Gebied.*

A10 (1979) H. R. van den Berg, *Precisiemetingen aan de Viscositeits-Coefficient van Krypton en de Logarithmische Term in de Dichtheidsontwikkeling.*

A11 (1979) B. Arends, *A Spin-Echo Investigation of Self-Diffusion in Liquid Ethylene.*

A12 (1980) B. W. Tiesinga, *De Kritische Anomalie in de Warmtegeleidingscoefficient van Argon.*

Last Period

A13 (1991) R. Mostert, *The Thermal Conductivity of Ethane and of Its Mixtures with Carbon Dioxide in the Critical Region.*

A14 (1996) E. Sakonidou, *Thermal Conductivity of Fluids and Fluid Mixtures in the Critical Region.*

A15 (1999) R. de Bruijn, *Heat Transfer in a Critical Fluid Under Microgravity Conditions, a Spacelab Experiment.*

APPENDIX B: ARTICLES ABOUT VISCOSITY

Michels Period

B1 (1931) A. Michels and R. O. Gibson, The measurement of the viscosity of gases at high pressures. The viscosity of nitrogen to 1000 atms. *Proc. Roy. Soc. [A]* **134**:288 (1931).

B2 (1936) J. Versluys, A. Michels, and J. Gerver, A method for the measurement of the viscosity of saturated methane-oil solutions under pressure. *Physica* **3**:1093 (1936).

B3 (1953) A. Michels, A. C. J. Schipper, and W. H. Rintoul, The viscosity of hydrogen and deuterium at pressures up to 2000 atmospheres. *Physica* **19**:1011 (1953).

B4 (1954) A. Michels, A. Botzen, and W. Schuurman, The viscosity of argon at pressures up to 2000 atmospheres. *Physica* **20**:1141 (1954).

B5 (1957) A. Michels, A. Botzen, and W. Schuurman, The viscosity of carbon dioxide between 0°C and 75°C and at pressures up to 2000 atmospheres. *Physica* **23**:95 (1957).

Trappeniers Period

B6 (1964) N. J. Trappeniers, A. Botzen, H. R. van den Berg, and J. van Oosten, The viscosity of neon between 25°C and 75°C at pressures up to 1800 atm. Corresponding states for the viscosity of the noble gases up to high densities. *Physica* **30**:985 (1964).

B7 (1965) N. J. Trappeniers, A. Botzen, J. van Oosten, and H. R. van den Berg, The viscosity of krypton between 25°C and 75°C and at pressures up to 2000 atm. *Physica* **31**:945 (1965).

B8 (1965) N. J. Trappeniers, A. Botzen, C. A. ten Seldam, H. R. van den Berg, and J. van Oosten, Corresponding states for the viscosity of the noble gases up to high densities. *Physica* **31**:1681 (1965).

B9 (1978) H. R. van den Berg and N. J. Trappeniers, Experimental determination of the logarithmic term in the density expansion of the viscosity coefficient of krypton at 25°C. *Chem. Phys. Lett.* **58**:12 (1978).

B10 (1980) N. J. Trappeniers, P. S. van der Gulik, and H. van den Hooff, The viscosity of argon at very high pressure, up to the melting line. *Chem. Phys. Lett.* **70**:438 (1980).

B11 (1985) J. H. B. Hoogland, H. R. van den Berg, and N. J. Trappeniers, Measurements of the viscosity of sulfur hexafluoride up to 100 bar by a capillary-flow viscometer. *Physica A* **134**:169 (1985).

B12 (1986) P. S. van der Gulik and N. J. Trappeniers, Application of Enskog theory on the viscosity of argon. *Physica B* **139/140**:137 (1986).

B13 (1986) P. S. van der Gulik and N. J. Trappeniers, The viscosity of argon at high densities. *Physica A* **135**:1 (1986).

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B14 (1988) P. S. van der Gulik, R. Mostert, and H. R. van den Berg, The viscosity of methane at 25°C up to 10 kbar. *Physica A* **151**:153 (1988).

B15 (1989) R. Mostert, P. S. van der Gulik, and H. R. van den Berg, The working equations of a vibrating wire viscometer. *Physica A* **156**:909 (1989).

B16 (1989) R. Mostert, P. S. van der Gulik, and H. R. van den Berg, Comment on the experimental viscosity of argon at high densities. *Physica A* **156**:921 (1989).

B17 (1990) H. R. van den Berg, C. A. ten Seldam, and P. S. van der Gulik, Working equation for a capillary viscometer with non-steady compressible flow. *Physica A* **167**:457 (1990).

B18 (1991) P. S. van der Gulik, R. Mostert, and H. R. van den Berg, The viscosity of carbon dioxide up to 450 MPa. *High Temp. High Press.* **23**:87 (1991).

B19 (1992) P. S. van der Gulik, R. Mostert, and H. R. van den Berg, The viscosity of methane at 273 K up to 1 GPa. *Fluid Phase Equil.* **79**:301 (1992).

B20 (1993) H. R. van den Berg, C. A. ten Seldam, and P. S. van der Gulik, Compressible laminar flow in a capillary. *J. Fluid Mech.* **246**:1 (1993).
B21 (1993) H. R. van den Berg, C. A. ten Seldam, and P. S. van der Gulik, Thermal effects in compressible viscous flow in a capillary. *Int. J. Thermophys.* **14**:865 (1993).
B22 (1993) P. S. van der Gulik, The viscosity of the refrigerant 1,1-difluoroethane along the saturation line. *Int. J. Thermophys.* **14**:851 (1993).
B23 (1995) P. S. van der Gulik and M. El Kharraz, The viscosity of liquid carbon dioxide. *Int. J. Thermophys.* **16**:145 (1995).
B24 (1995) P. S. van der Gulik, Viscosity of saturated R152a measured with a vibrating wire viscometer. *Int. J. Thermophys.* **16**:867 (1995).
B25 (1997) P. S. van der Gulik, Viscosity of carbon dioxide in the liquid phase. *Physica A* **238**:81 (1997).
B26 (1998) P. S. van der Gulik, The linear pressure dependence of the viscosity at high densities. *Physica A* **256**:39 (1998).

APPENDIX C: ARTICLES ABOUT HEAT CONDUCTION

Michels Period

C1 (1952) A. Michels and A. Botzen, A method for the determination of the thermal conductivity of gases at high pressures. *Physica* **18**:605 (1952).
C2 (1953) A. Michels and A. Botzen, The thermal conductivity of nitrogen at pressures up to 2500 atmospheres. *Physica* **19**:585 (1953).
C3 (1955) A. Michels, A. Botzen, A. S. Friedman, and J. V. Sengers, The thermal conductivity of argon between 0°C and 75°C at pressures up to 2500 atmospheres. *Physica* **22**:121 (1955).
C4 (1962) A. Michels, J. V. Sengers, and P. S. van der Gulik, The thermal conductivity of carbon dioxide in the critical region. I. The thermal conductivity apparatus. *Physica* **28**:1201 (1962).
C5 (1962) A. Michels, J. V. Sengers, and P. S. van der Gulik, The thermal conductivity of carbon dioxide in the critical region. II. Measurements and conclusions. *Physica* **28**:1216 (1962).
C6 (1962) A. Michels and J. V. Sengers, The thermal conductivity of carbon dioxide in the critical region. III. Verification of the absence of convection. *Physica* **28**:1238 (1962).
C7 (1963) A. Michels, J. V. Sengers, and L. J. M. van de Klundert, The thermal conductivity of argon at elevated densities. *Physica* **29**:149 (1963).

C8 (1964) J. V. Sengers, W. T. Bolk, and C. J. Stigter, The thermal conductivity of neon between 25°C and 75°C at pressures up to 2600 atm. *Physica* **30**:1018 (1964).

Trappeniers Period

C9 (1979) J. A. A. Snel, N. J. Trappeniers, and A. Botzen, Experimental studies in thermal conductivity of fluids. A hot wire method for the determination of the thermal conductivity of carbon dioxide and krypton at elevated densities. *Proc. Kon. Ak. Amsterdam* **B82**:303 (1979).

C10 (1980) J. A. A. Snel, N. J. Trappeniers, and A. Botzen, Experimental studies in thermal conductivity of fluids. The theory of convection for the model of two vertical coaxial cylinders. *Proc. Kon. Ak. Amsterdam* **B83**:69 (1980).

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C11 (1989) R. Mostert, H. R. van den Berg, and P. S. van der Gulik, The thermal conductivity of ethane in the critical region. *Int. J. Thermophys.* **10**:409 (1989).

C12 (1989) R. Mostert, H. R. van den Berg, and P. S. van der Gulik, A guarded parallel-plate instrument for measuring the thermal conductivity of fluids in the critical region. *Rev. Sci. Instrum.* **60**:3466 (1989).

C13 (1990) R. Mostert, H. R. van den Berg, and P. S. van der Gulik, Measurements of the thermal conductivity of nitrogen with a parallel-plate instrument. *Int. J. Thermophys.* **11**:597 (1990).

C14 (1990) R. Mostert, H. R. van den Berg, P. S. van der Gulik, and J. V. Sengers, The thermal conductivity of ethane in the critical region. *J. Chem. Phys.* **92**:5454 (1990).

C15 (1992) R. Mostert, H. R. van den Berg, P. S. van der Gulik, and J. V. Sengers, The thermal conductivity of carbon dioxide-ethane mixtures in the critical region. *High Temp. High Press.* **24**:469 (1992).

C16 (1992) R. Mostert and J. V. Sengers, Asymptotic behavior of the thermal conductivity of a binary fluid near the plait point. *Fluid Phase Equil.* **75**:235 (1992).

C17 (1994) B. W. Tiesinga, E. P. Sakonidou, H. R. van den Berg, J. Luettmer-Strathmann, and J. V. Sengers, The thermal conductivity of argon in the critical region. *J. Chem. Phys.* **101**:6944 (1994).

C18 (1996) E. P. Sakonidou, H. R. van den Berg, C. A. ten Seldam, and J. V. Sengers, The thermal conductivity of methane in the critical region. *J. Chem. Phys.* **105**:10535 (1996).

C19 (1997) E. P. Sakonidou, H. R. van den Berg, C. A. ten Seldam, and J. V. Sengers, Finite thermal conductivity at the vapor-liquid critical line of a binary fluid mixture. *Phys. Rev. E* **56**:4943 (1997).

C20 (1997) R. de Bruijn, R. J. J. van Diest, T. D. Karapantsios, A. C. Michels, W. A. Wakeham, and J. P. M. Trusler, Heat transfer in pure critical fluids surrounded by finitely conducting boundaries in micro-gravity. *Physica A* **242**:119 (1997).

C21 (1998) E. P. Sakonidou, H. R. van den Berg, C. A. ten Seldam, and J. V. Sengers, The thermal conductivity of an equimolar methane-ethane mixture in the critical region. *J. Chem. Phys.* **109**:717 (1998).

C22 (1999) E. P. Sakonidou, H. R. van den Berg, C. A. ten Seldam, and J. V. Sengers, An improved guarded parallel-plate method for measuring the thermal conductivity of fluids in the critical region. *Int. J. Thermophys.* **20**:1339 (1999).

APPENDIX D: ARTICLES ABOUT SELF-DIFFUSION

Trappeniers Period

D1 (1965) N. J. Trappeniers, C. J. Gerritsma, and P. H. Oosting, The self-diffusion coefficient of water, at 25°C, by means of spin echo technique. *Phys. Lett.* **18**:256 (1965).

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APPENDIX E: ARTICLES ABOUT COMPUTER SIMULATIONS

Trappeniers Period

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