

THE CONTRIBUTIONS OF THE VAN DER WAALS LABORATORY
TO THE KNOWLEDGE OF TRANSPORT PROPERTIES¹

P.S. van der Gulik²

¹ Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25-30,

2000, Boulder, Colorado, U.S.A.

² Van der Waals-Zeeman Instituut, Universiteit van Amsterdam

Valckenierstraat 65-67, 1018 XE Amsterdam, The Netherlands

ABSTRACT

As early as 1931, Michels and Gibson showed that the hard-sphere Enskog Theory, published in 1922, did not agree with their measurements of the viscosity of nitrogen. In 1952 the same was shown by Michels and Botzen for their thermal conductivity measurements on nitrogen and the Modified Enskog Theory did not fit their experimental data either. Finally, in 1973 Trappeniers and Jan Michels showed that the same is true for the coefficient of self-diffusion of krypton and that the failure is due to the formation of clusters.

Measurements of the thermal conductivity of argon in 1955 motivated the study of the behavior of the transport phenomena 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. Offringa showed in 1978 that viscosity has a small critical anomaly. In 1991 Mostert and in 1996 Sakonidou showed that the anomaly in the thermal conductivity is absent 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. The comparison of the results with computer simulations showed that the Enskog theory is not valid in the highest one-third of the density range. In the middle one-third just above the critical density, a special version of the hard-sphere Enskog theory describes the measurements within the experimental accuracy. Using this result it appeared to be 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 to intracluster transport described by the hard-sphere Enskog theory.

KEYWORDS: Critical Enhancement, Enskog Theory, Theoretical Model, Transport Properties, Van der Waals Laboratory.

1. INTRODUCTION

The theory of the transport phenomena originates from the kinetic theory of gases which was introduced by Maxwell in 1859. For an exact solution Boltzmann's equation, published in 1872, had to be solved. In 1910 Hilbert proved the existence and uniqueness of a solution and thereupon, the Boltzmann equation was solved independently by Chapman and by Enskog 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 extended the theory to dense gases of hard spheres and this theory is known as the Enskog theory. In 1970 computer simulations of the viscosity of hard spheres by Alder, Gass and Wainwright proved that this theory is valid for hard spheres up to about twice the critical density, but that in the last third part of the fluid-density range up to the melting density the relative viscosity increases with the density up to nearly twice the Enskog value.

2. EARLY RESULTS CONCERNING THE ENSKOG THEORY

Already before the actual founding of the van der Waals Laboratory Michels and Gibson constructed the Van der Waals vertical-capillary viscometer and measured the viscosity of nitrogen up to 100 MPa at 298, 323 and 348 K. In a paper in 1931 [1] and in Gibson's thesis in 1933 [2] they showed that the hard-sphere Enskog theory is only in qualitative agreement with the experimental values of the viscosity. Twenty years later this conclusion could be confirmed by Schipper[3,4], who measured the viscosity of hydrogen and deuterium at temperatures from 298 up to 398 K and at pressures up to

200 MPa. Thereafter, this viscometer has been in use for similar measurements on argon[5], carbon dioxide[6], neon[7] and krypton[8].

Also twenty years later, in 1952, Michels and Botzen[9,10,11] showed that also their heat-conductivity measurements on nitrogen could not be described with the Enskog theory, nor in the normal version neither in the version now known as the Modified Enskog Theory. For this purpose the parallel-plate apparatus was constructed, suited for pressures up to 250 MPa and for temperatures from 298 up to 348 K. Afterwards, this apparatus was used for the measurements on argon[12], carbon dioxide[13,14], again argon[15] and neon[16].

In 1968 the same conclusion could be drawn for selfdiffusion by Oosting[17,18], who applied a proton spin-lattice relaxation-time method on methane at low temperatures down to 77 K and at pressures up to 300 MPa. The same method was used afterwards by Arends[19,20] on ethylene and by Peereboom[21] on xenon. Finally, J.Michels[22,23] showed by his analysis of the density dependence of the selfdiffusion coefficient of krypton, which he had measured by means of a tracer method, that this density dependence is influenced by the formation of dimers and larger clusters, and that it cannot be described with Enskog theory.

3. THE CRITICAL REGION

The measurements of the heat conductivity of argon by Michels, Botzen, Friedman and Sengers[12] gave rise to the special study of the critical region. Also the viscosity measurements on carbon dioxide by Michels, Botzen and Schuurman[6] showed an enhancement around the critical density. Later on both phenomena appeared to be artifacts due to convection and the working equations respectively. However, a careful improvement of the parallel-plate cell by Sengers[13,14] 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. The work of Sengers motivated the development of theory for the critical region. Afterwards, a new smaller parallel-plate cell was built, suited also for low temperatures, that was applied for measurements in the critical region of xenon[24] and argon [25,26]. A decennium later this apparatus was used to study the heat conductivity in the critical region of mixtures. Firstly, Mostert[27,28] showed that a critical enhancement in an ethane-carbon dioxide mixture is improbable and thereupon Sakonidou[29,30] definitively showed the non-existence of such an enhancement in the critical region of a 50-50 % mixture of methane and ethane. Meanwhile, Offringa[31] 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, afterwards used for measurements on sulfur hexafluoride[32]. This material is interesting because it is suited to study in the critical region under microgravity circumstances. This type of study was performed by de Bruijn[33], resulting in his thesis about heat transfer in a critical fluid under microgravity conditions, a spacelab experiment[34].

4. THE LOGARITHMIC TERM

In the meantime several efforts had been made to improve the theory. In analogy with the virial equation of state series expansions of the transport phenomena in the density were developed. In the sixties the existence of a logarithmic term in this series expansion was supposed. In order to check this possibility Snel[35,36] 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 to conclude to the existence or non-existence of a logarithmic term. It was Van den Berg[37,38] who succeeded by means of a thorough improvement of the vertical-capillary viscometer and its working equations[39] to measure the viscosity of krypton with the exceptional accuracy of 1 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 compressible flow taking into account the thermal effects in a compressible viscous flow in a capillary[40]. Later on 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. Afterwards, he guided the improvement of the parallel-plate heat-conductivity apparatus resulting in the excellent measurements of Sakonidou. Finally, he was involved in the microgravity experiments.

5. HIGH PRESSURE VISCOSITY MEASUREMENTS AND THE ENSKOG THEORY

The conclusion of J. Michels[22,23] about the influence of the formation of clusters on the density dependence of the transport phenomena was based too on his computer simulations of the transport properties of square-well molecules[41]. In this way he also confirmed the result of Alder, Gass and Wainwright that for the viscosity the Enskog theory for hard spheres is valid up to twice the critical density, but that in the remaining third part of the density range up to the melting density the relative viscosity increases to nearly twice the Enskog value[42]. The technical possibilities in the seventies enabled Van der Gulik to develop a vibrating-wire viscometer suited for pressures up to 1 GPa and for low temperatures down to liquid nitrogen temperature, so that it became possible to check this behavior of the viscosity for simple gases up to the melting density.

The comparison of the experimental results with these computer simulations[43,44,45] shows that the Enskog theory is indeed not valid in the highest one-third fluid-density range near the melting line. In this range the relaxation-time method introduced by Maxwell in his second paper about transport properties has to be applied[46]. In the second one-third fluid-density range just above the critical density, however, a special version of the hard-sphere Enskog theory describes the measurements within the experimental accuracy[47]. Using this result it appeared to be possible to describe the viscosity in the first one-third 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.

This is shown in the figure for measurements performed at the Van der Waals Laboratory. The filled symbols present the measured values, the solid curves the values

calculated with the model and the open symbols the deviations of the experimental values from the calculated ones in parts per thousand. The oldest measurements on argon[5], the diamonds, show deviations up to 5 parts per thousand, the neon data[7], the upwards-pointing triangles, only 2 per thousand, the older krypton data[8], the triangles pointing to the right-hand side, again 5 parts per thousand and the precision data of Van den Berg[37,38] at low density 0.5 parts per thousand. The unpublished xenon data, the triangles pointing down, show that the measurements were not always easy. They show a spread of a few percent and a false critical enhancement of 9 percent. 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 is only valid up to twice the critical density, at higher densities the deviations start to increase systematically.

It is now up to the scientific community to judge if it can be said that the problem of the theory of transport properties is solved in principle with this contribution of the Van der Waals Laboratory.

REFERENCES

1. A.Michels and R.O.Gibson, *Proc.Roy.Soc. [A]* **134**: 288 (1931)
2. R.O. Gibson, The viscosity of gases at high pressures.
Thesis, (University of Amsterdam, 1933)
3. A.Michels, A.C.J.Schipper and W.H.Rintoul, *Physica* **19**: 1011 (1953)
4. A.C.J. Schipper, The viscosity of compressed hydrogen and deuterium.
Thesis, (University of Amsterdam, 1954)
5. A.Michels, A.Botzen and W.Schuurman, *Physica* **20**: 1141 (1954)
6. A.Michels, A.Botzen and W.Schuurman, *Physica* **23**: 95 (1957)
7. N.J.Trappeniers, A.Botzen, H.R. van den Berg and J. van Oosten,
Physica **30**: 985 (1964)
8. N.J.Trappeniers, A.Botzen, J. van Oosten and H.R. van den Berg,
Physica **31**: 945 (1965)
9. A. Botzen, The thermal conductivity of gases at high pressures.
Thesis, (University of Amsterdam, 1952)
10. A.Michels and A.Botzen, *Physica* **18**: 605 (1952)
11. A.Michels and A.Botzen, *Physica* **19**: 585 (1953)
12. A.Michels, A.Botzen, A.S.Friedman and J.V.Sengers, *Physica* **22**: 121 (1955)
13. J.V. Sengers, Thermal conductivity measurements at elevated gas densities including the critical region. *Thesis*, (University of Amsterdam, 1962)
14. A.Michels, J.V.Sengers and P.S. van der Gulik,
I. *Physica* **28**: 1201, II. *Physica* **28**: 1216 (1962)
A.Michels and J.V. Sengers, III. *Physica* **28**: 1238 (1962)
15. A.Michels, J.V.Sengers and L.J.M. van de Klundert, *Physica* **29**: 149 (1963)

16. J.V.Sengers, W.T.Bolk and C.J.Stigter, *Physica* **30**: 1018 (1964)
17. P.H. Oosting, Zelfdiffusie en protonspin-roosterrelaxatie in methaan.
Thesis, (University of Amsterdam, 1968)
18. C.J.Gerritsma and N.J.Trappeniers, I *Physica* **51**: 365 (1971)
C.J.Gerritsma, P.H.Oosting and N.J.Trappeniers, II *Physica* **51**: 381 (1971)
P.H.Oosting and N.J.Trappeniers, III *Physica* **51**: 395, IV *Physica* **51**: 418 (1971)
19. B. Arends, A spin-echo investigation of selfdiffusion in liquid ethylene.
Thesis, (University of Amsterdam, 1979)
20. B.Arends, K.O.Prins and N.J.Trappeniers, *Physica A* **107**: 307 (1981)
21. P.W.E.Peereboom, H.Luigjes, K.O.Prins and N.J.Trappeniers,
Physica B **139-140**: 134 (1986), *Physica A* **156**: 260 (1989)
22. J.P.J. Michels, De dichtheidsafhankelijkheid van de zelfdiffusiecoëfficiënt van krypton. *Thesis*, (University of Amsterdam, 1973)
23. N.J.Trappeniers and J.P.J.Michels, *Chem.Phys.Lett.* **18**: 1 (1973)
24. J. van Oosten, De warmtegeleidingscoëfficiënt van xenon in het kritische gebied.
Thesis, (University of Amsterdam, 1974)
25. B.W. Tiesinga, De kritische anomalie in de warmtegeleidingscoëfficiënt van argon.
Thesis, (University of Amsterdam, 1980)
26. B.W.Tiesinga, E.P.Sakonidou, H.R. van den Berg, J.Luettmer-Strathmann
and J.V.Sengers, *J. Chem. Phys.* **101**: 6944 (1994)
27. R. Mostert, The thermal conductivity of ethane and of its mixtures
with carbon dioxide in the critical region.

- Thesis*, (University of Amsterdam, 1991)
28. R. Mostert, H.R. van den Berg, P.S. van der Gulik and J.V. Sengers,
High Temp.-High Press. **24**: 469 (1992)
R. Mostert and J.V. Sengers, *Fluid Phase Equilibria* **75**: 235 (1992)
29. E. Sakonidou, Thermal conductivity of fluids and fluid mixtures in the critical region.
Thesis, (University of Amsterdam, 1996)
30. E.P. Sakonidou, H.R. van den Berg, C.A. ten Seldam and J.V. Sengers
Phys. Rev. E **56**: 4943 (1997), *J. Chem. Phys.* **109**: 717 (1998)
31. J.C.A. Offringa, De viscositeitscoefficient van xenon in het kritische gebied.
Thesis, (University of Amsterdam, 1978)
32. J.H.B. Hoogland, H.R. van den Berg and N.J. Trappeniers, *Physica A* **134**: 169 (1985)
33. R. de Bruijn, R.J.J. van Diest, T.D. Karapantsios, A.C. Michels, W.A. Wakeham and J.P.M. Trusler, *Physica A* **242**: 119 (1997)
34. R. de Bruijn, Heat transfer in a critical fluid under microgravity conditions, a spacelab experiment. *Thesis*, (University of Amsterdam, 1999)
35. J.A.A. Snel, De dichtheidsontwikkeling van de warmtegeleidingscoefficient van kooldioxide en krypton. *Thesis*, (University of Amsterdam, 1973)
36. J.A.A. Snel, N.J. Trappeniers and A. Botzen,
I, II. *Proc. Kon. Ak. Amsterdam* **B82**: 303 (1979)
III. *Proc. Kon. Ak. Amsterdam* **B83**: 69 (1980)
37. H.R. van den Berg, Precisiemetingen aan de viscositeits-coefficient van krypton

en de logaritmische term in de dichtheidsontwikkeling.

Thesis, (University of Amsterdam, 1979)

38. H.R. van den Berg and N.J. Trappeniers, *Chem. Phys. Lett.* **58**: 12 (1978)
39. H.R. van den Berg, C.A. ten Seldam and P.S. van der Gulik,
Physica A **167**: 457 (1990)
40. H.R. van den Berg, C.A. ten Seldam and P.S. van der Gulik,
J. of Fluid Mech. **246**: 1 (1993), *Int. J. of Thermophys.* **14**: 865 (1993)
41. J.P.J. Michels and N.J. Trappeniers, *Chem. Phys. Lett.* **33**: 195 (1975),
Physica A **90**: 179 (1978)
42. J.P.J. Michels and N.J. Trappeniers, *Chem. Phys. Lett.* 66, 20 (1980)
I. *Physica A* **101**: 156 (1980), II. *Physica A* **104**: 243 (1980),
III. *Physica A* **107**: 158 (1981), IV. *Physica A* **107**: 299 (1981)
43. P.S. van der Gulik and N.J. Trappeniers, *Physica A* **135**: 1 (1986),
Physica A **156**: 921 (1989)
44. P.S. van der Gulik, R. Mostert and H.R. van den Berg,
Physica A **151**: 153 (1988), *Fluid Phase Equilibria* **79**: 301 (1992)
45. P.S. van der Gulik, *Physica A* **238**: 81 (1997)
46. P.S. van der Gulik, *Physica A* **256**: 39 (1998)
47. P.S. van der Gulik and N.J. Trappeniers, *Physica B* **139-140**: 137 (1986)

FIGURE CAPTION

Fig. 1.

The viscosity of noble gases, as measured at the Van der Waals Laboratory, as 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 in parts per thousand of the experimental values from the theoretical model.

