SOME ASPECTS OF TRANSPORT .PROPERTIES AT HIGH PRESSURES

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We present a review of transport properties *i. e.*, self-diffusion, viscosity and thermal coductivity coefficients at high pressure. The pressure range of experimental results covered by this analysis will depend on the property or the effect which is studied. As the density is the relevant parameter, the density range includes moderately dense gases. dense gases, liquids, and solids. Particular attention is given to some regions of the phase diagram, as the liquid-solid transition or the critical region, where large variations of some of the transport properties are observed. Finally experimental data are compared with theoretical predictions based on Enskog's theory, modified Enskog's theory and computer simulations.

1. Introduction

The research in the field of transport properties is one of the most fundamental of the physics of dense materials and has important applications in high-pressure technology. This paper will be limited to a survey of some aspects of recent works on transport properties of compressed gases, liquids, and solids. However, the theoretical interpretation of transport properties is closely related to the progress in other fields of high-pressure physics as equilibrium or spectroscopic properties. For instance, density and temperature are more relevant parameters to fit excess transport properties than pressure and temperature. The thermal conductivity of polyatomic molecules depends on the transfer of momentum and energy through rotational and vibrational degrees of freedom.

The importance of high-pressure experiments is evident, even if there is not a fundamental difference between the behaviors of a liquid and a dense fluid. High-pressure studies enable one to extend the range of density and to separate density and temperature effects.

At low density, *i. e.*, atmospheric pressure for gases, transport mechanisms arise entirely from the kinetic transfer of momentum and energy of molecules. Both translational and internal transfer contribute to the kinetic energy of molecules. Transport coefficients which depend only on translational transfer (those from noble gases for instance) can be rigorously calculated through the Boltzmann equation if the intermolecular potential is known. On the contrary. as the viscosity of molecules is not sensitive to the internal transfer. viscosity coefficients were frequently used in the past to calculate parameters of intermoleclar potentials through Chapman-Enskog's theory.

At high density. *i. e.*. high pressure for gases or liquid density, in addition to the kinetic

transfer there is a collisional transfer. This collisional transfer is the main contribution to viscosity or thermal conductivity coefficients.

The self-diffusion coefficient of a fluid is a measure of the correlated translational motion of the fluid particles, and can be defined by

$$D = \frac{1}{3} \int_o^t <u_i(0).u_i(t)> dt \qquad (1)$$

where u_i are particles velocities at time 0 and t.   Theoretical predictions may be made of the particles velocities and the self-diffusion coefficient calculated when a suitable potential function is available.   Measurements of self-diffusion in dense fluids are mostly of recent origin.   Self-diffusion coefficients were measured through different experimental techniques as tracer diffusion, nuclear magnetic resonance, neutron diffraction.   Unfortunately the uncertainty is large (up to 15%).

The shear viscosity is the transport coefficient which was the most studied.   Experimental data cover a large range of temperatures and pressures and are generally very accurate (a fraction of a percent).   The first extensive studies of pressure on viscosity of liquids were carried out by Bridgman up to 30 kbar.[1]   This pressure range was increased recently.[2,3] The bulk or volume viscosity is obtained from measurements of the absorption of sound or the linewidth of Brillouin scattered line.   However in such measurements, the effects owing to shear viscosity and thermal conductivity are very large and a few experiments were carried out.

The thermal conductivity of dense substances was also studied in a large range of pressures and temperatures.   Generally measurements are not as accurate so shear viscosity measurements (1%).

The effects of pressure on transport properties are complex and were studied in thermo-dynamics of irreversible processes which take into account molecular motions and collisions.[4] Transport-property theories of dense fluids were significantly improved by Enskog[5] when he separated the effects of kinetic and collisional momentum and energy transfers.   When the density increases, the collisional frequency increases.   Sengers,[6] McLaughlin,[7] and Gubbins[8] have reviewed the theory of transport properties in dense fluids.   Theoretical methods to predict and to correlate transport coefficients of dense fluids were described by several authors.[9]   Recently theoretical informations were obtained from molecular dynamic simulations about the hydrodynamic aspect of transport phenomena by Evans and Streett.[10]   In molecular fluids, additional coefficients of viscosity were found: vortex viscosity and spin viscosity.

2. Definition of Transport Coefficients

The transport properties reported will be mainly restricted to those of pure substances, self-diffusion, shear viscosity and thermal conductivity.   We will not discuss bulk viscosity for which only few data are available.   The important subject of transport properties of mixtures which involves other properties such as mutual diffusion or thermodiffusion will be only

outlined.

Fluid transport of mass, momentum and energy are proportional, as a first approximation, to linear gradients of concentration, velocity and temperature. Fluids which obey these linear relations are known as Newtonian fluids. For simplicity we assume that each quantity varies in the x-direction. The self-diffusion coefficient D relates the current J to the gradient of concentration:

$$J = -D\frac{dc}{dx}. \tag{2}$$

The shear viscosity coefficient η relates the pressure P to the gradient of mean velocity of particles

$$P = -\eta\frac{dv}{dx}. \tag{3}$$

The thermal conductivity coefficient relates the heat flux Q to the temperature gradient

$$Q = -\lambda\frac{dT}{dx}. \tag{4}$$

Different corresponding state treatments of transport properties can be applied. If the intermolecular potential is known, the expressions for reduced coefficients of diffusion, viscosity and thermal conductivity are respectively

$$D^* = DM^{1/2}/\varepsilon^{1/2}\sigma, \tag{5}$$
$$\eta^* = \eta\sigma^2/(M\varepsilon)^{1/2}, \tag{6}$$
$$\lambda^* = (\lambda\sigma^2/k)(M/\varepsilon)^{1/2}, \tag{7}$$

where M is the molecular mass, k is the Boltzmann constant, and ε and σ are the parameters of energy and length of the intermolecular potential.

Transport coefficient can also be reduced in terms of critical constants T_c and ρ_c:

$$D_r = DM^{1/2}T_c^{-1/2}\rho_c^{1/3}, \tag{8}$$
$$\eta_r = \eta M^{-1/2}T_c^{-1/2}\rho_c^{-2/3}, \tag{9}$$
$$\lambda_r = \lambda M^{1/2}T_c^{-1/2}\rho_c^{-2/3}, \tag{10}$$
$$T_r = T/T_c, \tag{11}$$
$$\rho_r = \rho/\rho_c. \tag{12}$$

The hydrodynamic Stokes-Einstein equation relates the self-diffusion coefficient to shear viscosity

$$D = kT/C\pi\sigma\eta, \tag{13}$$

where σ is the hydrodynamic radius, k Boltzmann's constant. The constant C varies from 4 in the slipping boundary limit, whereas it is 6 for the stick boundary limit. The viscosity

is related to the thermal conductivity through the Prandtl ratio

$$Pr = \eta C_p / \lambda,$$
(14)

where C_p is the specific heat at constant pressure.

3. Transport Properties of Noble Gases

The transport properties of argon were probably the most studied and they can be used to look for the effects of pressure and temperature on a standard fluid.

Self-diffusion coefficients for compressed liquid argon were obtained by Naghizadeh and Rice.[11,12]

The viscosity of gaseous and liquid argon was reported by Haynes.[13] Recently the viscosity of argon was measured at three temperatures 223.15 K, 301.15 K and 323.15 K, up to the melting line by Trappeniers et al.[14] As was found previously by Vermesse and Vidal[15] within their range of pressure of 650 MPa, the results at room temperature can be represented by an almost linear relation between viscosity and pressure. In Fig. 1 we have plotted the excess viscosity of argon $\bar{\eta}(\rho, T)$ in function of the density.

$$\bar{\eta}(\rho, T) = \eta(\rho, T) - \eta(0, T),$$
(15)

where $\eta(\rho, T)$ is the measured viscosity and $\eta(0, T)$ the viscosity of the dilute gas. When the viscosity is written following Eq. (15) it has been observed that the excess function $\bar{\eta}$ is only weakly temperature dependent. However, as shown in Fig. 1, the temperature dependence increases, at high pressure, at the approach of the liquid-solid transition. Figure 1 shows that $\bar{\eta}$ decreases with increasing temperature along one isochore.

High-pressure thermal conductivity of argon was reported in large temperature ranges.[16-19] The thermal conductivity in liquid argon was measured by Bailey and Kellner.[20] In solid argon, White and Woods[21] and Pollack[22] reported the values of thermal conductivity near the triple point. In Fig. 2, we have plotted the excess thermal conductivity of argon *versus* density

$$\bar{\lambda}(\rho, T) = \lambda(\rho, T) - \lambda(0, T),$$
(16)

where $\lambda(\rho, T)$ is the measured thermal conductivity and $\lambda(0, T)$ the thermal conductivity of the dilute gas. In Fig. 2, where the density range is the same as in Fig. 1, any temperature effect is handly observed between low and high temperature measurements, even near the liquid-solid transition.

From the experimental data analysis of transport properties of argon near the liquid-solid transition it results that the excess viscosity is slightly temperature dependent and the excess thermal conductivity temperature independent.

We will show that this behavior is confirmed by the study of transport properties of noble gases in terms of correspondingstates. Accurate shear viscosity measurements were reported
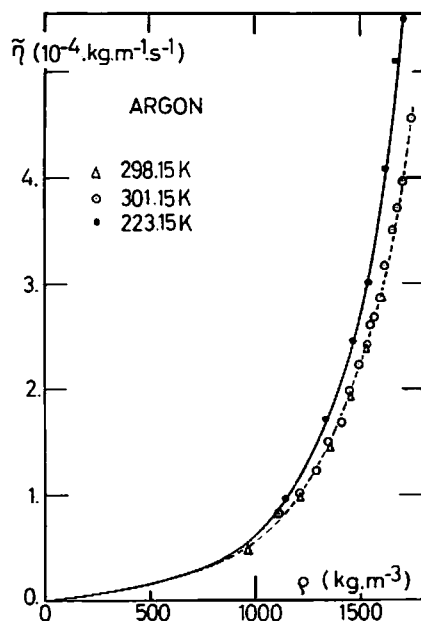
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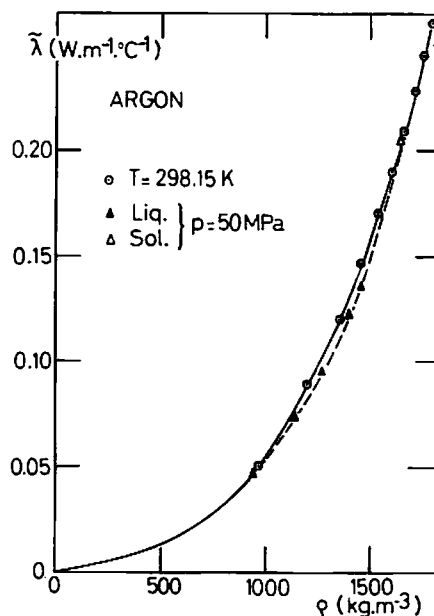Fig. 1. Excess viscosity of argon *versus* density.

Fig. 2. Excess thermal conductivity of argon *versus* density.

for noble gases: helium,[23] neon,[24] krypton[25] up to about 650 MPa by Vermesse and coworkers. Measurements of thermal conductivity of noble gases were carried out by Tufeu *et al.*[19,26] Following the corresponding state principle a specific property of substances belonging to the same class, is represented by a universal function when expressed as reduced quantity. If molecular parameters are used as reduction parameters, the law of corresponding states must be verified for all substances composed of spherical nonpolar molecules interacting through a potential $u(r) = \varepsilon\phi(r/\sigma)$ where $\phi(r/\sigma)$ is a universal function, ε is the minimum of the pair interaction potential energy, and σ the characteristic intermolecular distance. Moreover a corresponding state analysis is a suitable way to reduce transport properties for a comparison with theories.

The only reduction parameters which can be found in large number in the literature are those of the Lennard-Jones potential. The parameters of the Lennard-Jones potential lead to a correct description of state and transport properties of simple fluids in restricted temperature and density ranges as they are generally obtained from data at low density (second virial coefficient or viscosity of the dilute gas). Unfortunately this potential is no longer acceptable when contributions of many body interactions take place.[26] The critical constants are well known for numerous fluids, but a reduction in terms of critical constants does not lead to universal curves, as was verified for noble gases[27] and light hydrocarbons,[28] even if corrected critical constants by the acentric factor are used.[29]

The main goal of this new approach is to develop corresponding state relations which

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Table 1. Parameters of the Barker potential

Gas	ϵ/k (K)	σ (Å)	Reduced Temperatures
Helium	10. 4	2. 636	28. 7
Neon	42. 0	2. 764	7. 1
Argon	142. 1	3. 358	2. 17
Krypton	201. 9	3. 577	0. 983
Xenon	281. 0	3. 885	0. 76

enables one to predict the dependence of transport coefficients of dense gases in terms of the number of density n and in a large temperature range T. We have used parameters of the intermolecular potential proposed by Barker[30] as reduction parameters. These parameters (Table 1) were obtained from the analysis of numerous thermophysical data in different thermodynamic states.

We have plotted reduced excess of viscosity $\tilde{\eta}^*$ (Fig. 3) and thermal conductivity $\tilde{\lambda}^*$ (Fig. 4) against reduced density n^* for the five noble gases. Viscosity isotherms correspond to five reduced temperatures ranging from 0. 76 to 28. 7. We observe that a strong departure from one univeral curve takes place above a reduced density of 0. 6. As in the case of argon the temperature effect decreases when the reduced temperature increases.

Figure 4 shows a slight positive temperature effect up to $n^* = 0. 9$, but at higher reduced density, all data points are on the same curve. We have plotted the data obtained by different investigators for the liquid along the saturation line and the freezing line. If the anomalous
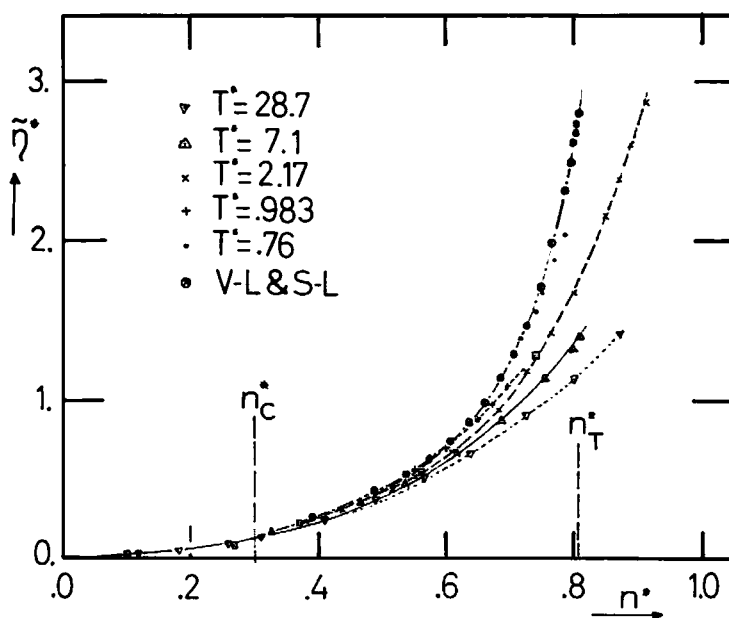
Fig. 3. Reduced excess viscosity of noble gases *versus* reduced density.

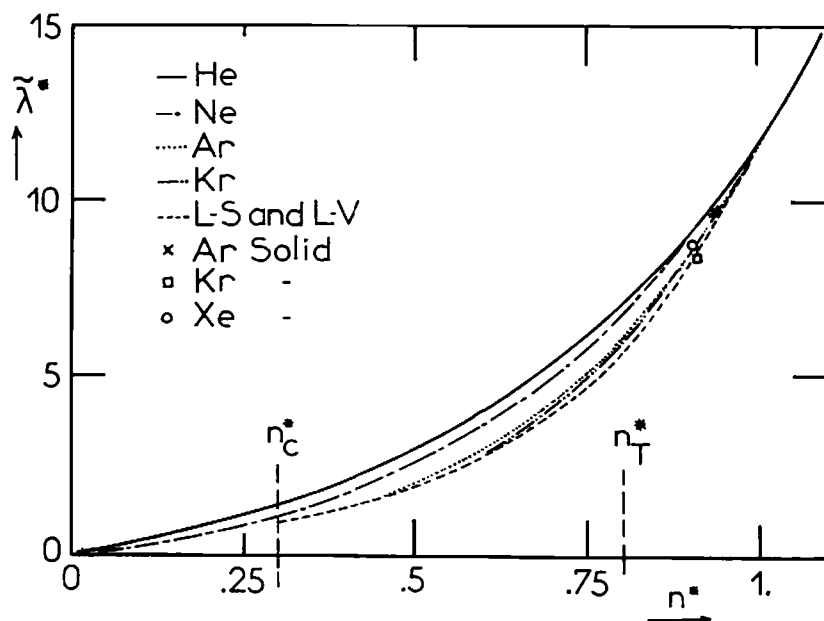42   B. le Neindre

Fig. 4. Reduced excess thermal conductivity of noble gases *versus* reduced density.

part of the thermal conductivity in the critical region is ignored, the variation of $\tilde{\lambda}^*$ *versus* n^* is a continuous curve.

In conclusion at the approach of the liquid-solid transition viscosity coefficients are temperature and density dependent and thermal conductivity coefficients only density dependent.

4. Transport Properties of Polyatomic Fluids

Compilations and extended reviews on thermophysical properties of polyatomic fluids in large temperature and pressure ranges have been reported by several authors.[31-33]

4-1. *Transport properties of molecular fluids*

Self-diffusion coefficients. Self-diffusion coefficients of methane were studied by several investigators. Dawson and coworkers[34] carried out an extensive study of self-diffusion coefficients D of methane. Below the critical density there is little effect of density ρ on the $D\rho$ product. and above that $D\rho$ product coefficients are decreasing significantly with reduced density. This fact was confirmed by other experimental self-diffusion data.[11,35-37]

Extensive measurements of self-diffusion coefficients of compressed liquids were carried out by Jonas and coworkers (Table 2). Their results are generally interpreted in terms of the rough sphere model which yields effective hard core diameters and a parameter that reflects the degree of coupling between the rotational and translational motions of molecules.

Table 2. Measurements of self-diffusion coefficients

Substances	References				Substances	References			
H_2	(39)	(40)			$(CH_3)_2CO$	(53)			
N_2	(41)				$C_6H_5NO_2$	(53)			
F_2	(42)				C_6H_5F	(50)			
CH_4	(34)	(35)	(37)		C_6H_5Cl	(50)	(53)		
CO	(43)				C_6H_5Br	(50)			
CO_2	(44)				C_6H_5I	(50)			
CS_2	(45)				CCl_4	(55)	(56)	(57)	
SF_6	(46)				$CF Cl_3$	(58)			
C_6H_6	(47)	(48)	(49)	(50)	C_4F_8	(59)			
C_6H_{12}	(38)				HF	(55)	(60)		
$CH_3-(CH_2)_5-CH_3$	(50)				HCl	(55)			
$CH_3-(CH_2)_8-CH_3$	(50)				$HCCl_3$	(55)			
$CH_3C_6H_{11}$	(51)				CH_3CCl_3	(61)			
C_5H_5N	(52)				NH_3	(55)	(62)	(63)	(64)
$Si(CH_3)_4$	(49)				H_2O	(55)	(65)		
CH_3OH	(53)	(54)			D_2O	(66)	(67)		
CH_3NO_2	(53)								

These authors measured also viscosities and densities in the same experimental conditions and checked up on the Stokes-Einstein relationship between D and η. Moreover they studied the solidification of some of these liquids forming the so-called plastic crystals. Thus, they measured[38] recently, self-diffusion coefficients of liquid cyclohexane as a function of temperature and pressure, over the density range $2.5 \leqslant \rho/\rho_c \leqslant 3.3$ and temperature range $0.5 \leqslant T/T_c \leqslant 0.7$. The degree of the coupling of the rotational and translational motions of the cyclohexane molecules was found to be close to that observed for liquid benzene.

In Table 2, we report a list of experimental data of self-diffusion coefficients in liquid or high pressure ranges.

Few success was achieved in corresponding states treatment of substances of similar molecular structure. Several relations to correlate self-diffusion coefficients in terms of reduced critical parameters have been proposed by Thodos et al..[68,69] Slattery and Bird[70] and Takahashi.[71]

Viscosity coefficients. Measurements of viscosity coefficients of molecular fluids were carried out in large temperature and pressure ranges. As we mentioned it, extensive measurements of viscosity of liquids at high pressures were reported by Bridgman.[1] Very accurate measurements of the viscosity of liquid fluorine[72] and liquid oxygen[73] were performed by Haynes in a lower pressure range (34 MPa). The viscosity of liquid nitrogen was measured by Grevendonk et al.[74] and gaseous nitrogen by Vermesse up to 650 MPa[75] and Golubev and Kurin up to 400 MPa.[76] The measurements of Michels and coworkers[77] and Trappeniers and coworkers[78] are generally limited up to 200 MPa. Several references on the viscosities of

molecular fluids were listed by Golubev[79] and Streett.[80] Outside the critical region, the viscosity of moleclar fluids can be written as for atomic fluids in a form of excess function. Far away from the liquid–solid transition, the excess viscosity is a slowly varying function which increases monotonically with density.[81,82] Several authors have shown the applicability of excess viscosity–density correlations.[83–85] The viscosity which is very sensitive to structural influences can be used to get information on the behavior of molecular fluids.[86–88]

Thermal conductivity coefficients. As for viscosity, the classical experiments of Bridgman[1] constitute almost all the available data of the pressure effect on liquid thermal conductivities. Recently we carried out a measurement of the thermal conductivity of nitrogen up to 1 GPa.[89] The thermal conductivity of a dilute gas composed of polyatomic molecules can be splitted into a translational part due to energy transfer by molecular motions and collisions and an internal part due to energy transfer associated with the internal degrees of freedom of the molecules. The thermal conductivity of a dense polyatomic fluid can be written as an excess thermal conductivity in function of density (Fig. 5). Then, it is more probable that rotations and vibrations modify the dilute gas value λ (0, T) but have small effects on the excess value. Some reviews on the thermal conductivity of liquids and dense gases were made by McLaughlin[90] and Tsederberg.[91]

Generalized equations were developed by Thodos *et al.*[92] to represent the excess thermal conductivity of nonpolar substances and were applied to dense gases.[93,94] Recently the correlations of the viscosity and thermal conductivity data of gaseous and liquid hydrocarbons: methane,[95] ethane[96] and propane[97] were evaluated by Hanley and coworkers.
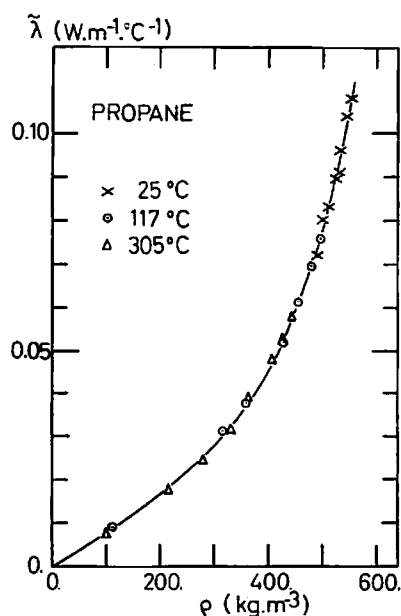

Fig. 5. Excess Thermal conductivity of propane *versus* density.

Isotopic effects on transport properties have been studied. Helium isotopes are the simplest system to study isotopic effects because if quantum effects are negligible only the masses of the two atoms ⁴He and ³He must be considered in transport mechanisms. This was verified for thermal conductivity.[98] On the contrary the theoretical analysis of transport properties of hydrogen and deuterium leads to different values of their potential parameters.[98-100]

4-2. Transport properties of polar fluids

The transport properties of polar fluids show some particular features. Among these polar fluids extended researches were performed on transport properties of water. At temperature below 30°C. an anomalous increase in the diffusion coefficients with pressure was observed.[65,101] This behavior has its origin in the tetrahedral open structure of water at low temperatures and is a consequence of significant distortion of the hydrogen bond network with compression. A similar behavior was observed for heavy water in the same temperature range.[66,67]

Stillinger and Rahman[102] in their molecular dynamics calculation of compressed liquid water predicted that the activation energies for self-diffusion and viscosity should decline with increasing pressure. This behavior was confirmed experimentally by Jonas et al.[101]

A review of viscosities and thermal conductivities of water was made by Kestin[103] and heavy water by Nagashima and Matsunaga.[104]

We recall that viscosities of water and heavy water show negative density coefficients below the critical temperature and that thermal conductivities of both liquids increase initially with
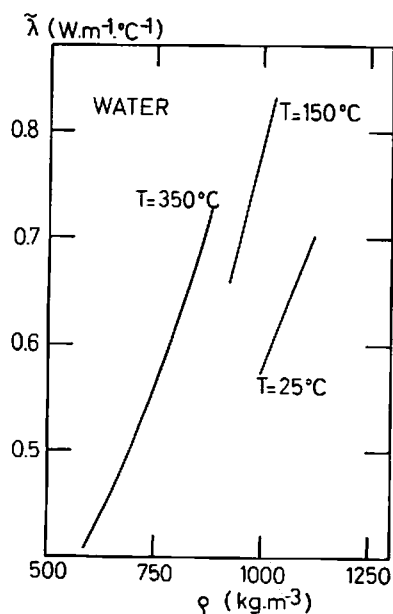

Fig. 6. Excess thermal conductivity of water versus density.

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temperatures. Simple excess functions cannot be used to fit experimental transport properties of water and the excess thermal conductivity is no longer temperature independent as it is shown in Fig. 6.

Methanol is another liquid which would exhibit a strong hydrogen bonding but lack the tetrahedral order typical for water. Data obtained for the self-diffusion coefficient of CH_3OH[54,105] show that the hydroxyl group is the governing factor on diffusion.

4-3. *Transport properties of melts*

Some experiments have been carried out to measure the viscosity of particular systems. The hydrostatic pressure effect on the viscosity of hydrous magmatic melts of different compositions (granite, albite, basalt) at constant H_2O content was studied by Persikov and Epelbaum[106] up to 400 MPa and Kushiro *et al.*[107,108] A correlative study of the viscosity, density and structure of GeO_2 melts has been carried out at high pressure.[109] The decrease in the viscosity of GeO_2 melts with increasing pressure was not attributed to a pressure-induced coordination change but to a systematic change in the nature of Ge–O bond with increasing pressure. Often such systems are non-Newtonian and the viscosity depends on the shear stress. The viscosity of a product like coal derived liquids was recently measured by Droege *et al.*[110]

5. Density Expansion of Transport Coefficients

One of the major trends of statistical mechanics applied to transport properties was to take into account progressively higher order collisions.[111-113]

The Navier-Stokes hydrodynamic equations with expressions for the transport coefficients were derived from the generalized Boltzmann equation. These theories lead to a virial expression for the effect of the number of density n on viscosity coefficient as

$$\eta(T, n) = \eta_0(T) + \eta_1(T) n + \eta_2(T) n^2 + \eta_3(T) n^3 + \dots \quad (17)$$

and thermal conductivity coefficient as

$$\lambda(T, n) = \lambda_0(T) + \lambda_1(T) n + \lambda_2(T) n^2 + \lambda_3(T) n^3 + \dots \quad (18)$$

5-1. *Low density limit*

In the low density limit transport properties $\eta_0(T)$ and $\lambda_0(T)$ are dominated by binary collisons. The Chapman-Enskog solution of the Boltzmann equation was used to obtain expressions for transport coefficients in excellent agreement with experimental data over a large temperature range.[5,114-117]

The temperature functions $\eta_0(T)$ or $\lambda_0(T)$ are calculated assuming a suitable form of the intermolecular potential or are used to define the linear and energy scaling factors by corresponding states.[118-121]

5-2. *First virial coefficients*

Refined theories to estimate the first terms of the density expansion $\eta_1(T)$ and $\lambda_1(T)$ were developed by Kim and Ross.[122,13] A systematic analysis of experimental transport coefficients yielding first density coefficient was carried out by Hanley and coworkers[63] and later on, by Kestin, Paykoç and Sengers[116] on viscosity and Tufeu and coworkers[18,124] on thermal conductivity. The coefficients η_1 and λ_1 of noble gases obey a law of corresponding states and can be reduced and plotted in terms of reduced temperature. Then η_1^* and λ_1^* are temperature insensitive in the temperature range $2 < T^* < 10$. The first virial coefficient of the viscosity of helium becomes negative at high reduced temperature as was predicted thoretically.[122] By contrast λ_1^* does not change sign and the experimental data are in better agreement with the theory of Stogryn and Hirschfelder[125] than the others.[123,126,127] Sengers *et al.*[128] have computed the first corrections to the Boltzmann equation results for transport coefficients of a gas of hard spheres, taking into account all the three-body dynamical events. The results are presented in Table 3.

Table 3. First virial coefficients of density expansions

Transport coefficient	Sengers *et al.*	Enskog's Theory
D_1 (self-diffusion)	-1.201 ± 0.002	$-\dfrac{5\pi}{12} \simeq -1.309$
η_1 (shear viscosity)	$+0.403 \pm 0.002$	$\dfrac{7\pi}{60} \simeq +0.367$
λ_1 (thermal conductivity)	$+1.252 \pm 0.001$	$\dfrac{23\pi}{60} \simeq +1.204$

5-3. *Prediction of a logarithmic term*

The other coefficients of virial expansions of transport coefficients are beset with difficulties, all of them are divergent. To account for the divergence, a logarithmic term was introduced in the density expansions, which are represented by series of the form

$$\eta(T, n) = \eta_0(T) + \eta_1(T) n + \eta_2'(T) n^2 \ln n + \eta_2(T) n^2 + \ldots \tag{19}$$

$$\lambda(T, n) = \lambda_0(T) + \lambda_1(T) n + \lambda_2'(T) n^2 \ln n + \lambda_2(T) n^2 + \ldots \tag{20}$$

A theoretical estimate of the first logarithmic term in the density expansions of the transport coefficients was carried out by Kan and Dorfman[129,130] and by Pomeau *et al.*[131,132] A number of attempts were made to experimentally detect the presence of $n^2 \ln n$ terms in the density expansion of transport coeffcients. A survey on the subject was published by Kan *et al.*[128] Recently, Codastefano and coworkers search for a logarithmic term in the density expansion of the diffusion coefficient of Kr in Xe.

The most notable analysis of viscosity was carried out by Kestin and coworkers[116,133] and Hanley and Haynes.[135] thermal conductivity by Tufeu.[18] both viscosity and thermal conduc-

tivity by Hanley and coworkers[83] and Kestin.[115] For the most part of experimental data the results are inconclusive. The data can be fitted equally well by a power series expansion in n or with $n^2 \ln n$ terms. In some cases, for instance, the viscosity of argon at low temperature is better fitted by adding an $n^2 \ln n$ term,[134] but in other cases, the reverse is true. For instance, the thermal conductivity of noble gases is better represented by a pure power series.[18] The $n^2 \ln n$ terms are second order corrections to the Boltzmann equation results and the n^2 terms must be accurately determined first. Actually, no theoretical value is available for these last coefficients. If theoretical estimates for the coefficients of logarithm terms are correct for real systems, then these terms are just at the limit of detectability.

6. Enskog Theory and Modified Enskog Theory

6-1. *Enskog theory*

Based on an approximate kinetic theory analysis, Enskog developed equations for the density dependence of transport properties of a hard sphere gas. As at low density, his theory considered the solution of the Boltzmann equation for binary collisions, but there are some important differences. Collisional transfer is included, the finite diameter σ of the hard sphere is taken into account, and the collisional frequency is that of the dense gas y is obtained from the hard sphere equation of state

$$y = \frac{P}{nRT} - 1. \tag{21}$$

The resulting transport coefficients are expressed in terms of their low density limit multiply by simple function of y

$$\frac{D}{D_0 bn} = \frac{1}{y}, \tag{22}$$

$$\frac{\eta}{\eta_0 bn} = \frac{1}{y} + 0.8 + 0.761 \, y, \tag{23}$$

$$\frac{\lambda}{\lambda_0 bn} = \frac{1}{y} + 1.2 + 0.755 \, y. \tag{24}$$

Here D_0, η_0 and λ_0 are the hard-sphere dilute gas transport coefficients according to the Chapman-Enskog theory,[5] n is the molecular number of density, $b = 2\pi\sigma^3/3m$ where σ is the molecular diameter and m the mass of the molecule, and $y = bn\chi$ where χ is the radial distribution function for hard spheres at contact.

6-2. *Modified Enskog theory (MET)*

For real fluids which are not of hard spheres, a modified Enskog theory (MET) was developed by Michels and Gibson.[136] In MET, y is determined by the thermal pressure T $(\partial p / \partial T)_v$ through

$$y = \frac{1}{R}\left(\frac{\partial pv}{\partial T}\right)_r - 1 \tag{25}$$

In their study of transport in simple dense gases Hanley and coworkers[137] found predictions of MET for the viscosity and thermal conductivity of argon, oxygen and hydrogen to within about 10-15%, for densities generally not exceeding twice the critical density. Experiments on the viscosity of F_2, on the saturated vapor pressure curve, showed agreement with previous MET predictions over most of the range studied.[72] Empirical modifications of the MET method was suggested by Sandler and Fizdom to obtain predictions of better accuracy.[138]

7. Comparison with Other Theories

There is no rigourous kinetic theory of transport in a dense gas composed of molecules of arbitrary intermolecular potential. A number of attemps were made to improve on MET in the high density range. The Rice-Allnatt theory[139] considers a more realistic potential, with a repulsive part using the Enskog theory and an attractive part using ideas from the theory of Brownian motion.

Several comparisons were tried with more elaborated theories. Tufeu and Kieffer[140] look at the main assumptions used in formulations of transport theories in dense fluids.[139],[141-146] trying to attach a precise physical meaning to these various assumptions. They concluded that the theoretical expectations, although acceptable, do not give a really satisfactory account for all the available experimental data and that further theoretical refinements are needed. A similar conclusion was drawn by Babb et al.[147-149] who compare the Rice-Allnatt and Prigogine, Nicolis and Misguich theories with the data of transport properties of dense gases.

Corrections to the approximate hard sphere dense fluid transport theory of Enskog, obtained by the method of molecular dynamics, have been introduced in the classical analytical expressions of transport coefficients by Dymond.[150] Furthermore, a method of correlation of liquid transport coefficients at different temperatures and pressures based upon the Van der Waals model of a fluid was described.[151,152] This model pictures a fluid as an assembly of molecules exerting strong repulsive forces with weak long-range attracting forces. Simple expressions for transport coefficients are obtained in terms of the hard sphere close-packed volume $V_0 = N\sigma^3/\sqrt{2}$ where N is the Avogadro number and σ is the molecular diameter. The density dependence of transport properties of rare gases at density greater than the critical density given by this model was shown to be in close agreement with the results of the exact hard sphere theory.

For polyatomic fluids, the exact smooth hard sphere theory has to be modified in order to account for nonspherical molecular shape and also for the possibility of coupling of translational and rotational motions. To apply the empirically modified hard sphere theory to the calculation of transport coefficients of polyatomic molecules, it is necessary to take into

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account the effects of exchange of angular momentum on collision in addition to linear momentum. and the possible coupling of translational and rotational motions. The latter effect on self diffusion was discussed by Chandler.[153] A method to correlate the viscosity data of dense polyatomic molecules was carried out by Dymond in function of reduced volumes (reduced in terms of the close-packed volume). Log-log plots were given for the viscosity of diatomic molecules F_2 and O_2, pseudo-spherical molecules : carbon tetrachloride and tetramethylsilane and larger aspherical polyatomic liquid spiro [4. 5] decane and perhydrochrysene.[151,152] The analytical expressions for the transport coefficients of liquids derived by Dymond. have been used by van Loef to determine self-diffusion coefficients for molecular liquids in function of density and temperature.[154,155]

As was shown by van Loef[154] the translational thermal conductivity λ_{trans}, for diatomic molecular liquids varies with density in the same way as the experimental thermal conductivity λ_{exp}. The agreement between λ_{trans} and λ_{exp} suggests that in the liquid state the translational contribution to the thermal conductivity represents the whole of the measured thermal conductivity and that contributions from internal degrees of freedom of diatomic molecules is negligible. The same results were obtained by Hanley et al.[137] who show that the internal contribution to the thermal conductivity. only slightly affects the MET results for the thermal conductivity of saturated liquid oxygen. However. it seems that for more complex molecular liquids, such as CO_2 or CS_2, internal contributions are important but decrease at the approach of the freezing curve.

Trappeniers et al.[14] compared the experimental results of viscosity coefficients of argon near the liquid-transition with the reduced expressions, in terms of the close pack volume V_0, given by Dymond. Strong discrepancies are found near the transition. In their studies of thermal conductivity of noble gases at high pressure, Tufeu et al.[26] found similar deviations reaching 13% at the density of 0. 6 V_0/V. Several relationships based on free-volume theory have been proposed to correlate transport properties of liquids. For instance. the Batschinski equation[156] modified by Hildebrand relates fluidity $(1/\eta)$ to the relative expansion from V_0.[157-159] The Doolittle equation describes accurately viscosities at atmospheric pressure.[160,161] Later Cohen and Turnbull derived a similar equation for a hard sphere fluid.[162] These equations have been used to fit the viscosity data for many liquids with a good accuracy when temperature dependent parameters are considered.[163,164]

We conclude that all presently availiable transport theories are unreliable at very high pressure and especially at the approach of the liquid-solid transition.

8. Computer Simulations

For the understanding of mechanisms of transport properties another alternative to experimental or theoretical studies is computer simulations. Over the last decade. this approach was developed through the method of molecular dynamics.[165] Two methods of simulation

were used equilibrium and non-equilibrium. Equlilbrium molecular dynamics has been used to calculate the average time correlation of fluctuations in equilibrium systems. using Green-Kubo explicit relationships for transport coefficients in terms of these time correlations.[166,167] Non-equilibrium systems were generated with desired flux by numerically simulating laboratory methods of transport measurements. Ashurst and Hoover described the simulation of Couette flow which determines the shear viscosity.[168,169] In these simulations. mainly two types of intermolecular potential were used : the hard sphere potential and the Lennard-Jones potential. The results of both simulations should be the same but differences arises from the finite number of particles and the duration of the calculation.

Alder, Gass and Wainwright[166] and Wood[170] have conducted extensive computer simulations of the molecular dynamics of hard sphere gases. They obtained the self-diffusion coefficient of a tagged hard sphere moving in a gas of mechanically identical hard spheres as a function of density. The computer simulation of the self-diffusion coefficient (Alder et al.) shows that two effects become important when the density is increased. At moderate densities dominates a hydrodynamic effect in which the vortices created by a moving sphere act back on its motion, leading to an increase in the diffusion coefficient. The second effect which appears at higher densities is a back scattering effect in which a particle bounces around in the cage formed by its neighbors, leading to a decrease in the diffusion coefficient.

The self-diffusion coefficient D of a monoatomic hard sphere fluid relative to the Enskog value D_E was obtained from molecular dynamics simulation.[158] At high density the decreasing of D/D_E was also related to a molecular caging effect. This effect was studied by Cukier and Mehaffey.[171] Van Loef[2] has compared the diffusion coefficients for argon obtained from several different techniques with the molecular dynamics data and found agreement within a few percent. A corresponding study of self-diffusion for the rare gas liquids near the coexistence curve shows agreement with L-J simulations within experimental error.[172] A good agreement was obtained by Hanley and Watts[173] between a simulation using a four parameter potential and experimental measurement of self-diffusion coefficients of CH_4. The temperature dependence $T^{0.9}$ is close to the linear dependence found in the molecular dynamics calculation of Levesque and Verlet. The self-diffusion coefficient of liquid nitrogen was measured by Powles et al.[41] They have compared the experimental data and a simulation using an anisotropic potential. The agreement is good. The molecular dynamics technique was extended by Evans and Street[16] to the calculations of time correlation functions occurring in the transport properties of dense fluids composed of rigid molecules. Specifically the calculations were carried out for liquid nitrogen modelled by a diatomic Lennard-Jones potential. A good agreement was found between calculated and experimental data.

The shear viscosity of a system of hard spheres through computer simulation was determined by Alder and coworkers.[166] they found viscosities two times higher than those predicted by Enskog's theory near freezing. Levesque et al.[167] simulated the shear viscosity of a

Lennard-Jones system corresponding to a state near the triple point of argon. They found a viscosity 2.5% higher than the experimental result but 1.5% smaller than the hard sphere result of Alder *et al.* The viscosity of dense krypton was computed by molecular dynamics, using Kubo's formula, by Vermesse and Levesque.[174] Three potentials were considered but none of them lead to an agreement with experimental values. Ashurt and Hoover[168,175] have calculated the viscosity of a Lennard-Jones system over a wide range of temperatures and densities. They found good agreement with experiments on argon within 5%. Vermesse and Vidal[176] compared their room temperature viscosity measurements of helium and neon with the simulation of Ashurt and Hoover. They found a very good agreement.

The equilibrium Lennard-Jones simulation of λ of Levesque was found in good agreement with experimental data at the triple point of argon and with the indirect nonequilibrium simulation of Ashurt and Hoover. These authors determine the ratio λ/η and η which give λ. From the energy dissipated by the shearing action and the resulting temperature distribution, Ashurt obtained the thermal conductivity. The precision of the calculated thermal conductivity is of the order of 10% at best. Tufeu *et al.*[26] using parameters of the Lennard-Jones potential have found a good agreement between the computed reduced excess thermal conductivity values $\tilde{\lambda}^*$, in the reduced temperature range $0.7 < T^* < 2$ and the experimental reduced excess thermal conductivities of argon, krypton, xenon in terms of the reduced density n^*. A good agreement was also found for nitrogen.[89]

The following relation was proposed by Ashurst and Hoover to fit experimental viscosities data:

$$\bar{\eta}\sigma^2(m\varepsilon)^{-1/2}(\varepsilon/kT)^{2/3} = 7.07x^4, \tag{26}$$

where

$$x = N\frac{\sigma^3}{V}\left(\frac{\varepsilon}{kT}\right)^{1/4}, \tag{27}$$

and V is the volume.
The fitting relation for thermal conductivity was

$$\bar{\lambda}\frac{\sigma^2}{k}(m/\varepsilon)^{1/2}(\varepsilon/kT)^{2/3} = a(\exp(bx) - 1), \tag{28}$$

where $a = 0.36$ and $b = 3.76$ for $kT > \varepsilon$,
$\quad\quad\quad a = 0.51$ and $b = 3.17$ for $kT < 3\varepsilon$.

These relations can be checked up on the experimental data, using parameters of the Lennard-Jones potential for σ and ε.

9. Transport Properties near the Liquid-Gas Critical Point

As the critical point is approached, the short range structure of the fluid does not

change but increasingly weak long-range correlations arise. The results are a divergence of transport coefficients. In the critical region the experimental results have shown no divergence of the self-diffusion coefficient. However the incertitude of these measurements is large. If we assume that the Stokes-Einstein's relation is still valid, D must have a weak divergence, as η^{-1}. In the critical region an other transport coefficient, the thermal diffusivity a, was recently obtained from Rayleigh scattering experiments. The decay rate of spontaneous thermal fluctuations in methane has been determined from Rayleigh scattering experiments by Ackerson and Straty.[177] Measurements were carried out around the critical point, along the coexistence curve, the critical isochore and an isotherm 0.8 K above the critical temperature.

A set of experiments was performed on ethane by Tufeu and co-workers, in order to obtain the thermal diffusivity behavior of this fluid along the critical isochore over a wide range of reduced temperatures. The following quantities were also measured: the thermal conductivity, the turbidity and the decay rate of thermal fluctuations (Fig 7).

The relation among the thermal diffusivity a, the thermal conductivity λ, the density ρ and the specific heat at constant pressure C_p,

$$a = \lambda(\rho C_p)^{-1} \tag{29}$$

is used to compare the measured thermal diffusivities with calculated ones. The Kawasaki's theory[179] predicts that the anomalous contribution to the thermal diffusivity Δa is given by
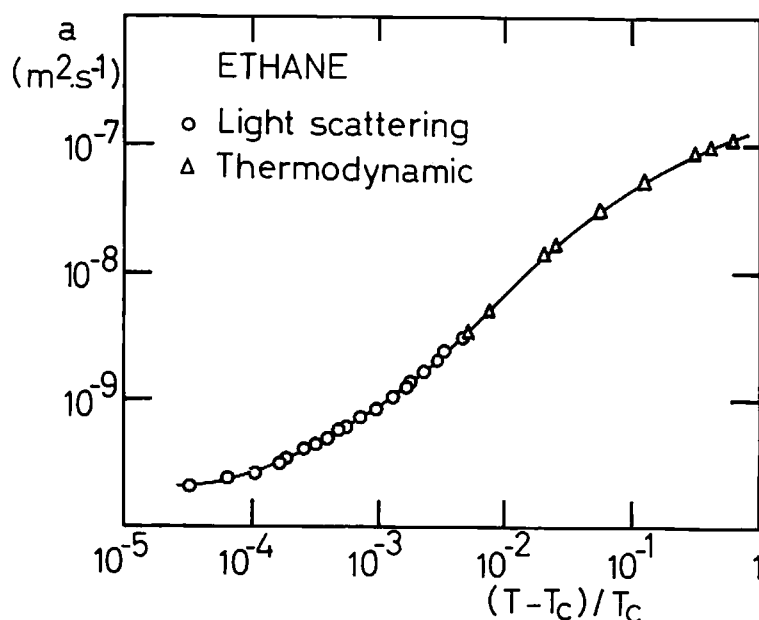
$$\Delta a = A \frac{kT}{6\pi\eta\xi}, \tag{30}$$

Fig. 7. Thermal diffusivity of ethane along the critical isochore.

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where A is a constant, k Boltzmann's constant, η the shear viscosity and ξ the correlation length. This result was interpreted as the anomalous contribution to the thermal diffusivity, owing to the diffusion of clusters with radius ξ and with a Stokes' law friction coefficient $6\pi\eta_i\xi$.

Theoretical and experimental evidences show that the shear viscosity diverges at the critical point. However, the critical enhancement of the viscosity of fluids is restricted to a narrow range of temperature. Measurements of the shear viscosity of fluids near the liquid-gas critical point are reported in Table 4. Basu and Sengers[189] have shown that the behavior of the viscosity of nitrogen as observed experimentally by Zozulya and Blagoi is consistent with current theoretical predictions. In order to describe the viscosity in the critical region, they seperate η into a background viscosity η_b and a critical enhancement $\Delta\eta(\rho, T)$.

$$\eta = \eta_b + \Delta\eta \tag{31}$$

Following simplified theoretical treatment, the relative critical enhancement $\Delta\eta/\eta_b$ diverges as[190-192]

$$\frac{\Delta\eta}{\eta_b} = \frac{8}{15\pi^2} \ln(q\xi)^\phi, \tag{32}$$

where q is the cut-off wave number integrating over the fluctuations with various wave numbers. More recent theoretical investigations[113,194] indicate that the relative viscosity exhibits a slightly more general power law divergence proportional to ξ^ϕ

$$\frac{\Delta\eta}{\eta_b} \simeq (q\xi)^\phi, \tag{33}$$

where ϕ is a universal exponent, independent of the nature of the fluid ($\phi = 8/15\pi^2 = 0.054$).

The thermal conductivity exhibits a critical enhancement in a large temperature range. The thermal conductivity varies significantly with small changes in pressure or temperature near the critical point. The critical enhancement exhibits large humps along an isotherm as the density is changed[195] as it is shown in Fig. 8. The experimental data (Table 5) have confirmed this strong divergence for all fluids. In recent years, equations were formulated to represent the critical enhancement of the thermal conductivity of fluids.[216-218] In the critical region the thermal conductivity λ is separated into a normal thermal conductivity λ_b and an anomalous thermal conductivity $\Delta\lambda(\rho, T)$:

Table 4. Viscosity measurements near the critical point

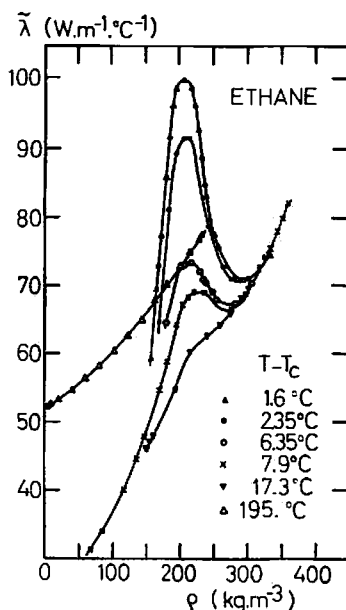| Fluids	References	Fluids	References
Xenon	180	Ethane	180
Nitrogen	181	Propane	186
Parahydrogen	182	n-Butane	186
Carbon dioxide	183, 184	Ethylene	187
Methane	185	Steam	188

Fig. 8. Thermal conductivity of ethane in the critical region.

Table 5. Survey of measurements of thermal conductivity in the critical region

Fluids	References	Fluids	References
Helium	196	Ethane	178
Argon	20	Propane	211
Xenon	197. 198	Isobutane	211
Parahydrogen	199	*n*-Hexane	212
Carbon dioxide	200. 208	Freon 13, (CF₃ Cl)	211. 213
Sulfur hexafluoride	209	Ammonia	214
Methane	210	Steam	215

$$\lambda = \lambda_b + \varDelta\lambda \tag{34}$$

Basu and Sengers[219] in their analysis of the thermal conductivity of steam connected the anomalous behavior in the vicinity of the critical point with the normal behavior of the thermal conductivity away from the critical point. The critical thermal conductivity enhancement is related to the anomalous behavior of the isothermal compressibility which in turn is represented by a scaled equation of state. Specifically, the critical enhancement was written by Sengers *et al.*[216,219] as

$$\varDelta\lambda = A \cdot \varDelta\lambda_c \cdot F(\varDelta T^*, \varDelta\rho^*), \tag{35}$$

where A is an adjustable constant. To definie $\varDelta\lambda_c$ they introduce a dimensionless temperature $T^* = T/T_c$, pressure $P^* = P/P_c$ and density $\rho^* = \rho/\rho_c$:

$$\varDelta\lambda_c = \frac{kP_c}{6\pi\eta_i\xi}\left(\frac{T^*}{\rho^*}\right)^2\left(\frac{\partial P^*}{\partial T^*}\right)^2\chi_T^*, \tag{36}$$

where χ_T^* is a symmetrized isothermal compressibility defined as

$$\chi_T^* = \rho^*(\partial\rho^*/\partial P^*)_T. \tag{37}$$

To a good approximation the correlation length is related to the isothermal compressibility by

$$\xi = \xi_0(\Gamma^{-1}\chi_T^*)^{\nu/(2-\eta)}. \tag{38}$$

where Γ^{-1} is the amplitude of the isothermal compressibility. Substitution of Eq. (38) into Eq. (36) yields

$$\Delta\lambda_c = \frac{kP_c\Gamma}{6\pi\eta\xi_0}\Big(\frac{T^*}{\rho^*}\Big)\Big(\frac{\partial P^*}{\partial T^*}\Big)^2(\Gamma^{-1}\chi_T)^{(1-\eta)/(2-\eta)}. \tag{39}$$

The function $F(\Delta T^*, \Delta\rho^*)$ is an empirical damping function which ensures the vanishing of $\Delta\lambda$ far away from the critical point. This approach was used also by Hanley *et al.* to estimate the critical enhancement of hydrocarbons.[95-97]

10. Transport Properties of Mixtures

Only a few experiments on transport properties of mixtures in large temperature and pressure ranges were carried out. This is due mainly to the time necessary to perform these experiments and some difficulties occurring at high pressure, in particular a possible separation of components by thermodiffusion in thermal conductivity experiments.

The pressure dependence of the mutual diffusion coefficients D_{AB} of some binary systems was measured recently up to 2 MPa by Dunlop and coworkers.[220-223] These results were used to calculate the first density correction for binary diffusion, in the form suggested by Bennet and Curtiss.[214] The results indicate that the first term of Thorne-Enskog's theory[225] for moderately dense gases is not adequate to describe binary diffusion. Islam and Stryland[226] reported the binary diffusion of argon-methane at 23°C from 2 to 15 MPa. Berry and Koeller[227] studied binary diffusion coefficients for three systems H_2-N_2, $CH_4-C_2H_6$ and $N_2-C_2H_6$, from 40 to 70°C, up to 100 MPa. For these mixtures the product $D_{AB}\rho$ decreases continuously with density. Search for size effects in the diffusion of Kr in CF_4 at various densities was carried out by Ricci and coworkers.[228]

The composition dependence of the viscosity of dense gas mixtures was reported by Di Pippo *et al.*[229] and Abe *et al.*[230] Thermal conductivity measurements of mixtures of monoatomic gases were carried out at room temperature[231] and up to 300°C.[232,233]

The Thorne-Enskog hard sphere, after a minor correction for consistency with the Onsager reciprocal relations of irreversible thermodynamics, was used as an interpolating formula between the end points.[234] A similar treatment was also reported by McElhannon and McLaughlin.[235]

Measurements of thermal conductivity of binary mixtures were extended at larger pressure by Naziev and Nurberdyev[236] and Zaporozhan and Geller.[237]

11. Transport Properties of Liquid Metals

Transport in liquid metals involves both electronic and core effects. It has been reviewed by Nachtrieb.[238]

The viscosity of mercury up to 100 MPa was reported by Barbero et al.[239] and later by Tippelskirch et al.[240] and Grouvel et al.[241]

Thermal conductivity and density measurements of liquid mercury were performed recently by Leycuras and Menexiadis[242] from 0 to 1200°C and 0 to 140 MPa corresponding to a density range from 13.6 to 10 g cm⁻³. Their main result is the appearance of a peak of low conductivity at 11.5 g cm⁻³.

Self-diffusion coefficients in liquid alkalis have been reviewed by Larsson et al.[243] Shear viscosity coefficients of the liquid alkali metals were reported by Hsu and Eyring.[244] Thermal conductivity experiments in solid and liquid Na have been carried out by Evangelisti and Isacchini.[245] Friedland collected data on thermal conductivity of liquid alkalis.[246]

In pure metals the heat transfer takes place mostly by free electrons. Wiedeman and Franz have shown that the ratio

$$\lambda/\sigma T = L = \text{constant}, \tag{40}$$

where σ is the electrical conductivity and T the absolute temperature. This relation indicates any change in the type of interaction which alters the relaxation times in the conduction of electron and heat. Moreover the thermal conductivity is not influenced by wall charge injection which is the case for electrical conductivity and can be measured more accurately.

A hard sphere model was applied to diffusion in liquid metals by Protopapas.[247] The self-diffusion and viscosity coefficients of expanded fluid mercury and cesium were calculated as a function of pressure and temperature up to their critical points with the aid of a modified Enskog theory by Tippelskirch.[248] Van Loef has shown that the electron transport properties in the liquid alkalis meet relationships with the molar volume, similar to those derived for atomic transport coefficients in hard sphere kinetic theory.[249,250]

12. Transport Properties of Solids

In a solid the self-diffusion coefficient is zero and the viscosity is not defined. The measurement of thermal conductivities of solids at high hydrostatic pressures are difficult owing to the pressure transmitting medium.

The thermal conductivity of dielectric or insulating material is related to the amount of heat transmitted by lattice vibrations (phonons) or lattice defects. Experimental and theoretical aspect of transport properties of rare gas solids were reviewed by Batchelder.[251] Thermal conductivities of solids under pressure were reviewed by Bolsaitis and Spain.[252] For non-metallic material the increase of thermal conductivity with pressure is approximately linear

with a slight decrease in slope at high pressures. The pressure effect $(\Delta\lambda/\lambda_0)/\Delta P$ is generally higher than for metallic solids and varies from 1.2×10^{-4} for teflon to 3.6×10^{-5} for NaCl, to 3.8×10^{-6} bar^{-1} for pyrex.

Lattice thermal conductivity is affected by crystal structure change. The effect on thermal conductivity of the structural aspect of molecular orientational disorder in a plastic crystal was investigated recently.[253-255]

Anderson and Backstrom[256-257] have shown that the pressure-dependence of the thermal conductivity of low and high density polyethylene is a sensitive function of the degree of crystallinity of the polymer.[258]

At a phase transition λ generally increases with phase density. However there are exceptions. For phase I of NH_4F and NH_4Cl and Ic of ice a negative pressure dependence of thermal conductivity $(\partial\lambda/\partial P)_T$ was found by Ross and Sandberg.[259-261] Such a negative value was found only for insulators having a hydrogen bond precisely tetrahedrally coordinated structure. In ice the hydrogen ordered phases were found to exhibit higher thermal conductivity than the disordered ones.

Thermal conductivity coefficients of ionic conductors KCl,[262] $NaCl$,[263] NaF[264] were investigated by Alm and Bäckström. The thermal conductivity of silver chloride which is used as high pressure-transmitting medium was studied up to 8.5 GPa by Vereschagin et al.[265] Recently, the pressure dependence of the thermal conductivity was obtained up to 2.5 GPa. for copper,[266] aluminium,[267] gold and silver,[268] and up to 0.8 GPa[269] for lead.

For metals, heat is transported mainly by electrons and the thermal conductivity λ is related to the electrical conductivity σ by the Wiedeman-Franz law. (Eq. 40) In the case of free electrons the theoretical value of the Lorentz number L is: 2.45×10^{-8} watt ohm/K^2. Experimental values of L range around the theoretical one. The effect of pressure on thermal conductivity can be interpreted on the basis of the Wiedeman-Franz ratio. The pressure derivative of the thermal conductivity $(\Delta\lambda/\lambda_0)/\Delta P$ vary from 17.3×10^{-6} bar^{-1} for Pb to 4.5×10^{-6} bar^{-1} for Ag and can be negative as for Bi $(-5.7\times10^{-6}$ bar$^{-1})$. Several equations were derived to estimate the thermal conductivity of solids and its pressure dependence.[270,271] However, these equations include parameters not always well defined and they are of doubtful applicability.

Pressure induced phase transformation may be accompanied by steep changes in thermal conductivity. This property was used by several investigators to study the variation of the specific heat near a phase transition.[272]

13. Conclusion

Results on the variation of transport properties with respect to the density and temperature can be summarized as follows. Far away from the critical region at constant temperature, D strongly decreases above the critical density and η and λ strongly increase at high density. At constant density η and follow the variation of the dilute gas. D increases strongly; η slightly

decreases and λ slightly increases with temperature.

More experimental measurements of transport properties at high pressure are needed at the approach of the liquid-solid transition where the viscosity varies strongly and the variation cannot be predicted theoretically.

In the critical region, the theory is well developed, but more measurements are needed to assess critical exponents.

Acknowledgments

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