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THERMAL CONDUCTIVITY AND VISCOSITY OF SIMPLE FLUIDS†

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Abstract—The behavior of the thermal conductivity and viscosity coefficient of simple fluids as a function of pressure, density and temperature is surveyed. Particular attention is given to the behavior of the transport coefficients in the critical region. In a previous paper [1] it was shown that the thermal conductivity coefficient exhibits a pronounced maximum in the critical region. Additional information confirming the existence of such a maximum is presented.

Theoretical predictions of the transport coefficients in dense systems are often based on the theory of Enskog. A survey is presented showing to what extent the theory of Enskog describes the density dependence of the transport coefficients in monatomic fluids. Finally, the transport mechanism leading to the anomalous rise of the thermal conductivity in the critical region is indicated.

NOMENCLATURE

B,	second virial coefficient;
$b = 2\pi\sigma^3/3m$,	covolume of rigid spherical molecules;
c_p,	specific heat at constant pressure;
c_v,	specific heat at constant density;
k,	Boltzmann's constant;
m,	mass of a molecule;
p,	pressure;
p_c,	critical pressure;
R,	molar gas constant;
T,	temperature in °K;
T_c,	critical temperature in °K;
t,	temperature in °C;
t_c,	critical temperature in °C;
V,	molar volume.

Greek symbols

η,	shear viscosity coefficient;
η_0,	viscosity coefficient at low density;
λ,	thermal conductivity coefficient;
λ_0,	thermal conductivity coefficient at low density;
λ',	contribution to λ from translational degrees of freedom of the molecules;
λ_0',	λ' at low density;
λ'',	contribution to λ from internal degrees of freedom of the molecules;
ρ,	density in amagat units;
ρ_c,	critical density;
$\rho^* = b\rho$,	reduced density;
σ,	diameter of a rigid spherical molecule;
χ,	value of the equilibrium radial distribution function at a separation σ from the center of an individual molecule;
$\lambda/\rho c_p$,	thermal diffusivity.

1. INTRODUCTION

IN RECENT YEARS more data have become available for the thermal conductivity coefficient and viscosity coefficient of fluids at elevated pressures or densities. These data include measurements for simple fluids like monatomic fluids. Information for relatively simple fluids is highly desirable as these substances disclose the effect of the basic molecular mechanisms involved in the transport of energy and momentum without too many complications. Data for relatively simple fluids provide the best test for the adequacy of theories of transport of the gaseous and liquid state.

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Also a few investigations have been devoted to a study of the behavior of the transport coefficients in the critical region. In particular these studies have revealed the existence of a thermal conductivity anomaly in the critical region analogous to the well known specific heat anomaly, a phenomenon which was not well recognized previously.

In view of these developments it seems valuable to review the dependence of the transport coefficients on pressure, density and temperature. The dependence of the viscosity coefficient and thermal conductivity coefficient on pressure, density and temperature at temperatures high relative to the critical temperature is considered in section 2. Then particular attention is devoted to the behavior of these transport coefficients in the critical region in section 3. Many calculations and correlations of the transport coefficients at elevated densities are based on the theory of Enskog for a dense gas of rigid spherical molecules. In view of the new data available for simple fluids in section 4 a survey is given to what extent the density dependence of the transport coefficients is described by the Enskog theory.

2. THE VISCOSITY AND THERMAL CONDUCTIVITY AT TEMPERATURES HIGH RELATIVE TO THE CRITICAL TEMPERATURE

The dependence of the viscosity and the thermal conductivity on pressure and density at temperatures high relative to the critical temperature is illustrated using the data for argon as an example.

The viscosity coefficient of argon at three different temperatures, namely at 75°C, 25°C [2] and at −50°C [3], is shown as a function of pressure in Fig. 1. As is well known the isotherms intersect as a function of pressure. At low pressure $(\partial\eta/\partial T)_p$ is positive. In a dilute system the transport of momentum and energy is primarily effected by the free kinetic motion of the molecules. As the temperature increases the mean velocity increases and therefore also the associated transport of momentum and energy. At higher pressures $(\partial\eta/\partial T)_p$ is negative as is also the case in the liquid state. In a dense system the transport of momentum and energy is mainly effected directly through the intermolecular forces when the molecules move in their mutual interaction field. This contribution is often classified as collisional transfer. As a result the transport coefficients depend sensitively on the density. An increase of temperature at constant pressure corresponds to a decrease in density and consequently to a decrease in viscosity and thermal conductivity. The intersection between two adjacent viscosity isotherms occurs at a lower pressure the lower the temperature.

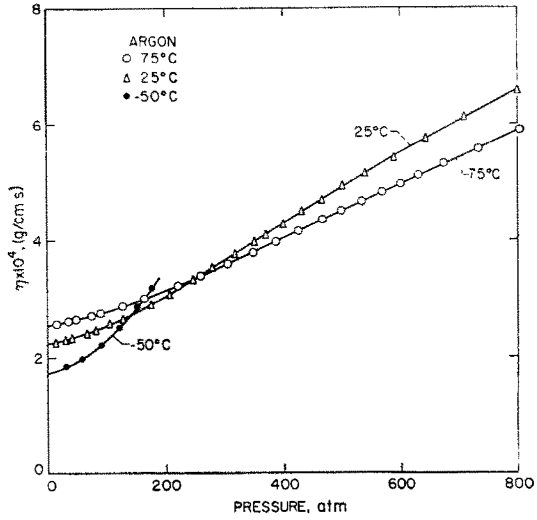

FIG. 1. The viscosity of argon as a function of pressure. (Data at 75°C and 25°C from [2]; at −50°C from [3].)

The viscosity of argon at the same temperatures is plotted as a function of density in Fig. 2. Throughout this paper densities are expressed in amagat units; one amagat unit is the density of the substance at 0°C and one atmosphere. For argon a density of 640 amagat at 75°C corresponds to a pressure of 2000 atmospheres.

The viscosity increases monotonically both with density and temperature. At lower densities the viscosity isotherms are nearly parallel as was particularly emphasized by Ross *et al.* [3]. This indicates that the initial slope $(\partial\eta/\partial\rho)_T$ varies only slightly with temperature. The property that the excess viscosity $\eta - \eta_0$, where η_0 is the viscosity of the system in the dilute state, is mainly dependent on the density alone is used in many correlations [4].

Contrary to $(\partial\eta/\partial T)_p$, $(\partial\eta/\partial T)_\rho$ remains posi-

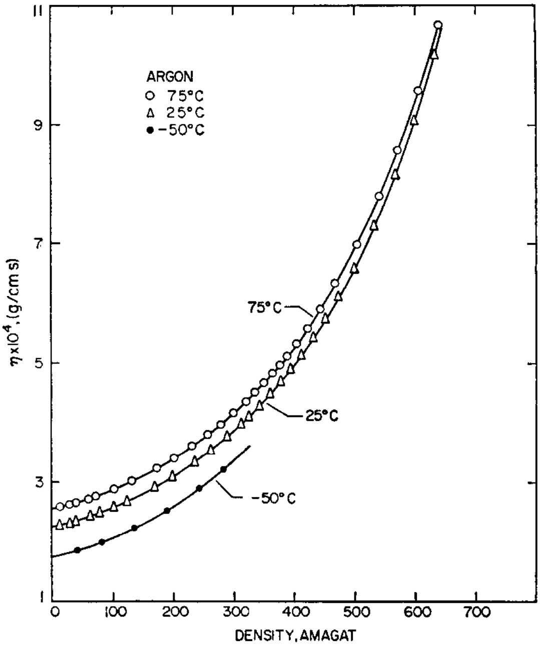

FIG. 2. The viscosity of argon as a function of density. (Data at 75°C and 25°C from [2]; at −50°C from [3].)

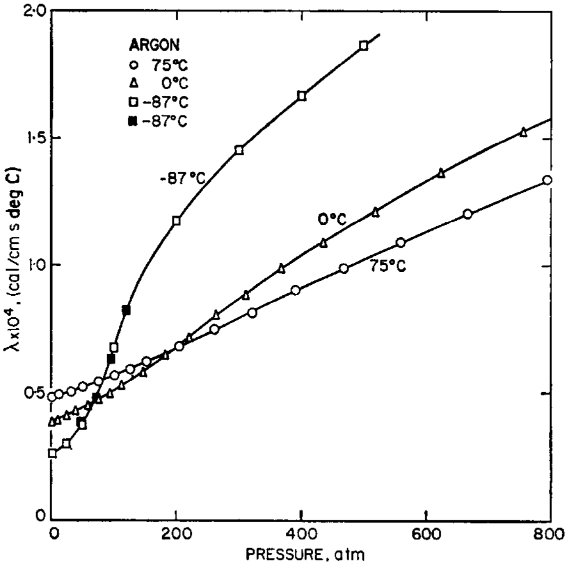

FIG. 3. The thermal conductivity of argon as a function of pressure. (Data at 75°C and 0°C from [10], data at −87°C ■ from [11] and □ from [12].)

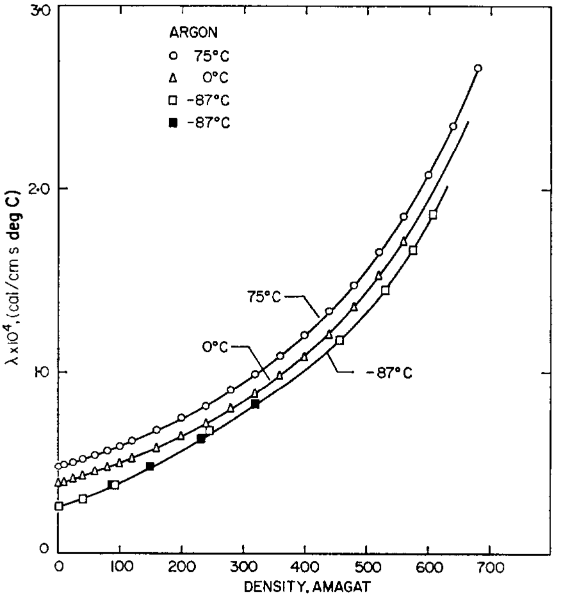

FIG. 4. The thermal conductivity of argon as a function of density. (Data at 75°C and 0°C from [10], data at −87°C ■ from [11] and □ from [12].)

tive in the density range shown. This was very recently confirmed for argon also at temperatures lower than the critical temperature [5]. At the Van der Waals Laboratory of the University of Amsterdam a similar behavior was found for N_2 (measured up to 450 amagat [6]), for H_2 and D_2 (measured up to 800 amagat [7]), and for neon (measured up to 770 amagat [8]). The characteristic variable is the density, which determines the average distance between the molecules, rather than the pressure. As mentioned above the large negative value of $(\partial\eta/\partial T)_p$ is related to the associated change in density. At very high densities also $(\partial\eta/\partial T)\rho$ becomes negative as has been observed for CO_2 [9].

The behavior of the thermal conductivity coefficient is at first sight very similar to that of the viscosity. The thermal conductivity coefficient of argon at 75°C, 0°C [10] and at −87°C [11, 12] is shown as a function of pressure in Fig. 3 and as a function of density in Fig. 4. Close inspection of the thermal conductivity isotherm at −87°C as a function of density shows a slight extra increase of λ in the neighborhood of 300 amagat, the origin of which phenomenon will be discussed in the subsequent section. Apart from this detail the curves have the same features as those for η. It may be remarked that for all the substances investigated at the Van der Waals Laboratory (N_2 up to 600 amagat [13], argon up to 680 amagat [10], neon up to 1000 amagat [14], CO_2 up to 600 amagat [1]) $(\partial\lambda/\partial T)_\rho$ is positive at high densities.

3. THE VISCOSITY AND THERMAL CONDUCTIVITY IN THE REGION NEAR THE CRITICAL POINT

The few investigations dealing with the behavior of the transport coefficients in the critical region were mainly carried out for CO_2 because of its conveniently accessible critical temperature.

The first detailed study of the viscosity of CO_2 in the critical region was carried out by Naldrett and Maass [15] using an oscillating disk method. Plotted as a function of density a small extra increase of the viscosity coefficient near the critical density and temperature was found (see Fig. 5). On the other hand data obtained at the Van der Waals Laboratory using a capillary flow method [9] indicated a much larger anomalous increase of the viscosity in the critical region. However, it was realized that only little precision could be ascribed to these viscosity data near the critical point because the experimental method, which required a pressure difference along the capillary, was not particularly appropriate for the critical region. In order to resolve the discrepancy between these results and the previous results of Naldrett and Maass new experiments for CO_2 were recently carried out by Kestin, Whitelaw and Zien using an oscillating disk [16]. They essentially confirmed the results of Naldrett and Maass and concluded that there is only a small effect of the presence of the critical point. The results are shown in Fig. 5. Data obtained by Michels, Botzen and Schuurman [9] outside the critical region, where the data are accurate, are included in the figure. Data obtained in the critical region for ethane, propane and n-butane [17], although not analyzed as a function of density, also indicate that any anomalous effect of the presence of the critical point on the viscosity should be small.

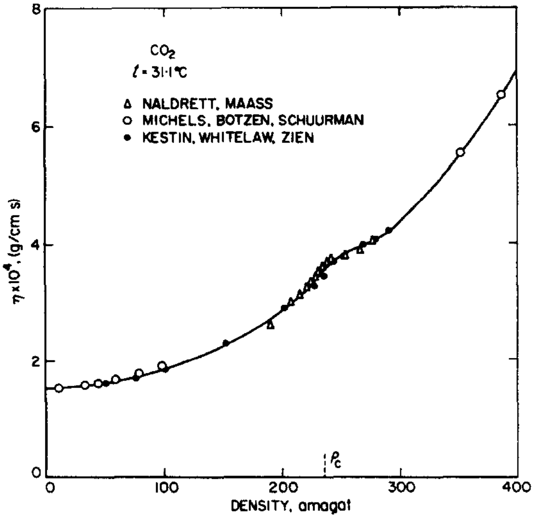

FIG. 5. The viscosity of CO_2 near the critical temperature as a function of density.

In the case of the thermal conductivity a real pronounced increase of this coefficient has been observed as the critical point is approached. It should be pointed out that this phenomenon has sometimes been overlooked in the literature. Two features tend to obscure the information:

1. In the critical region the tendency for convection as a result of a temperature gradient becomes very large [18]. The contribution of convection to the heat transfer observed is proportional to, among others, the expansion coefficient and the specific heat at constant pressure, both of which quantities become infinite at the critical point. As a result any observed increase of the heat transfer in the critical region is likely to be attributed to the onset of convection and it is difficult to detect a residual effect resulting from an increase of the heat conductivity coefficient itself.

2. The thermal conductivity coefficient is often considered either as a function of pressure at constant temperature or as a function of temperature at constant pressure, sometimes even including the critical pressure. As both $(\partial\rho/\partial p)_T$ and $(\partial\rho/\partial T_p)$ become infinite at the critical point, (*i*) a very small pressure increment at a constant temperature is equivalent to a large density change around the critical density and (*ii*)

measurements at the critical pressure are not equivalent to measurements near the critical density unless the temperature is exactly equal to the critical temperature to within a few tenths of a degree. Consideration of the dependence of the density on pressure and temperature is essential in order to study phenomena in the critical region.

Guildner made a critical study of the behavior of the thermal conductivity of CO_2 in the critical region and observed a pronounced anomalous increase of the heat conductivity using a heat conductivity cell consisting of two concentric cylinders [19]. Unfortunately he had to correct his experimental data for convection which diminishes the accuracy of the data. A detailed study of the thermal conductivity of CO_2 was carried out at the Van der Waals Laboratory with a parallel plate apparatus where convection could be avoided up to close to the critical point [1, 18, 20]. The thermal conductivity of CO_2 is shown as a function of density in Fig. 6 up to 600 amagat, corresponding to pressures up to 2000 atm. In contrast to the behavior at high temperatures the thermal conductivity isotherms intersect as a function of density and show an anomalous increase the more pronounced the closer to the critical point. (The critical parameters of CO_2 are: $t_c = 31{\cdot}04$°C, $\rho_c = 236$ amagat, $p_c = 72{\cdot}85$ atm [21].) The phenomenon closely resembles the anomaly in the specific heat at constant density c_v [1].

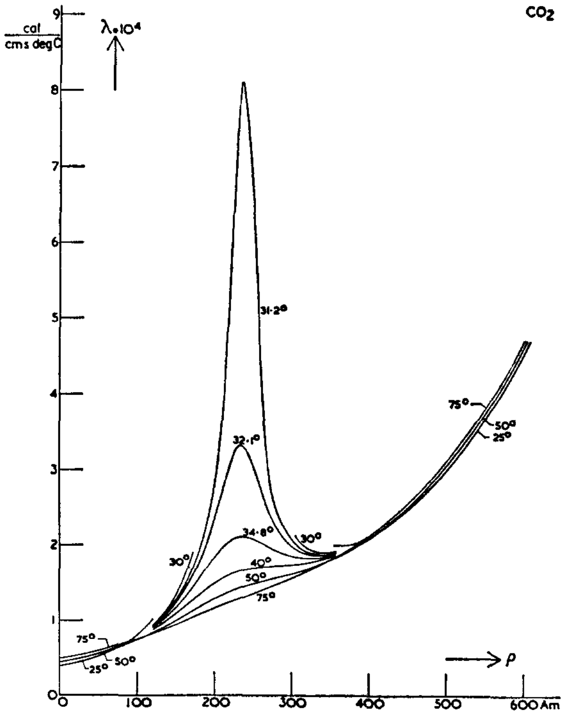

Fig. 6. The thermal conductivity of CO_2 as a function of density.

In Fig. 7 the thermal conductivity coefficient of CO_2 is plotted as a function of pressure from 1 to 200 atmospheres. The figure illustrates that for each isotherm the effect of the critical region is restricted to a small pressure interval. At higher temperatures, e.g. at 50°C, the influence of the critical region is easily noticed when considered as a function of density (Fig. 6), but hardly as a function of pressure (Fig. 7).

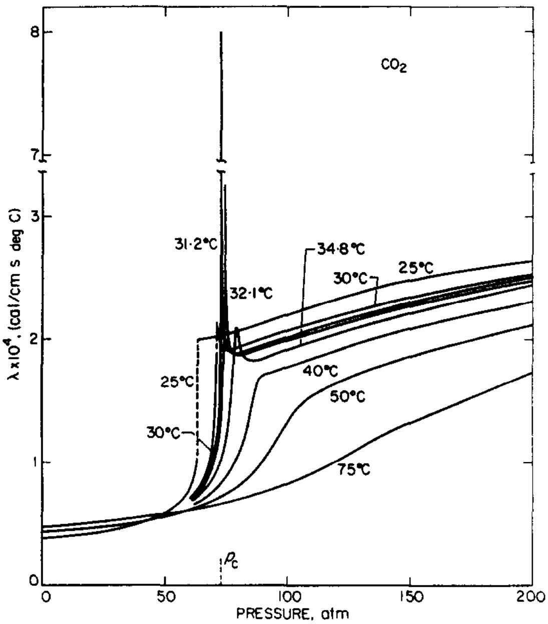

Fig. 7. The thermal conductivity of CO_2 as a function of pressure from 1 to 200 atm.

An interesting quantity is the thermal diffusivity $\lambda/\rho c_p$ which is the leading term in the time decay of fluctuations. This quantity is shown in Fig. 8. For the computation of the thermal

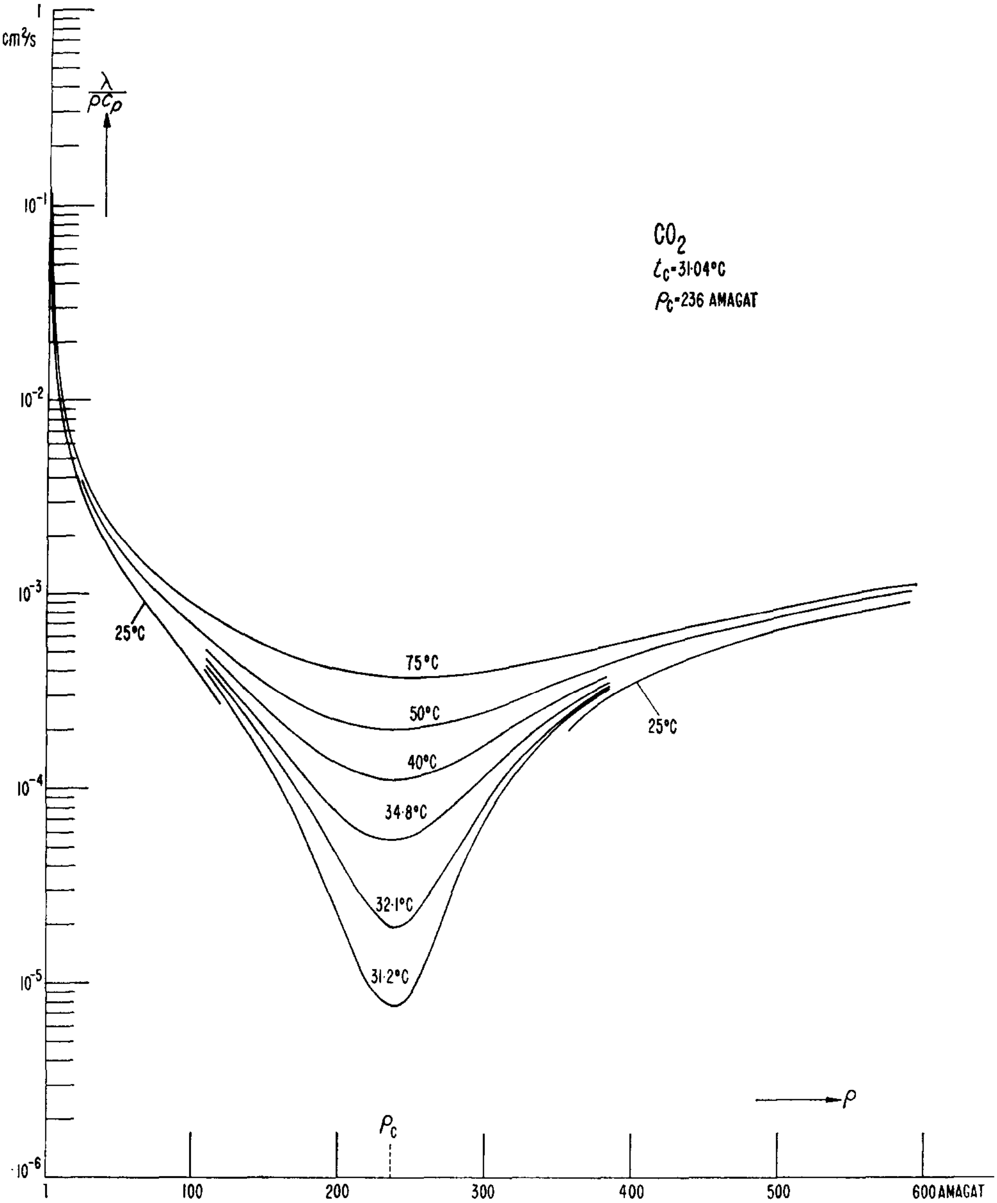

FIG. 8. The thermal diffusivity $\lambda/\rho c_p$ of CO_2.

diffusivity outside the critical region c_p values calculated from the p–V–T data were used [22]; in the critical region only $c_p - c_v$ was calculated from the compressibility isotherms and added to the experimental data for c_v [23]. As the specific heat at constant pressure c_p increases much more rapidly than λ, $\lambda/\rho c_p$ decreases in the critical region indicating the increase of the life time of fluctuations.

From the data given in Fig. 6 it is evident that if the thermal conductivity is analyzed as a function of density, the first indication of the existence of the thermal conductivity anomaly can already be noticed at temperatures higher than the critical temperature from the occurrence of intersections in the thermal conductivity isotherms as a function of density. Careful analysis of existing data for other gases as a function of density confirms the generality of the behavior shown for the thermal conductivity of CO_2.

As an example we consider the thermal conductivity of argon again. Measurements at constant pressures at a number of temperatures were presented by Ziebland and Burton [11] and by Ikenberry and Rice [12]. Using the compressibility isotherms the pressure dependence was reduced to a density dependence. Two thermal conductivity isotherms, namely at 166°K and 186°K, and a part of the isotherm at 149·6°K thus obtained as a function of density are presented in Fig. 9. Although as a result of the widely spaced pressure intervals used no data near the critical point are included, the isotherms do intersect and at 166°K, which is 15° above the critical temperature, an anomalous increase of already 25 per cent in the thermal conductivity can be noticed. Also at 149·6°K, which is 1° below the critical temperature, the thermal conductivity shows an anomalous increase when the coexistence line is approached from the liquid side. (The critical parameters of argon are: $T_c = 150{\cdot}86°\text{K}$, $\rho_c = 300{\cdot}4$ amagat.)

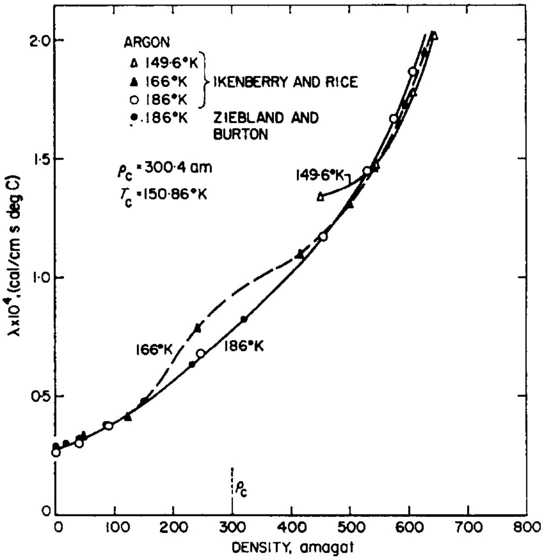

FIG. 9. The thermal conductivity of argon at 149·6°K, 166°K and 186°K as a function of density.

A similar analysis was carried out for the thermal conductivity of nitrogen. For the data obtained by Ziebland and Burton [11] at constant pressures the corresponding densities were calculated; the experimental data were then interpolated to equal temperatures. Two thermal conductivity isotherms, thus obtained as a function of density, at −125°C and −140°C, are shown in Fig. 10. (The critical parameters of N_2 are: $t_c = -147°\text{C}$, $\rho_c = 248{\cdot}7$ amagat.) At −140°C, which is 7° above the critical temperature, a pronounced increase in the thermal conductivity can be noticed. Although this conclusion is only based on a few experimental points, the effect is certainly real since (*i*) the anomalous increase of 35 per cent is much larger than the experimental error and (*ii*) the crucial experimental points were obtained with two different values of the temperature difference across the gas layer. The fact that the thermal

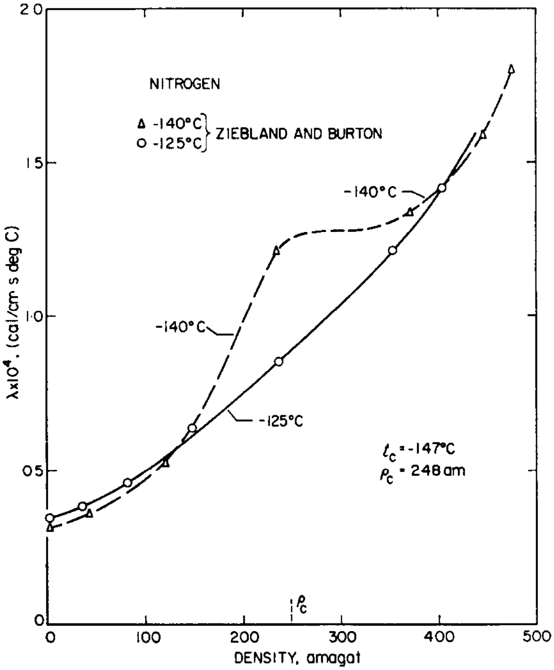

FIG. 10. The thermal conductivity of nitrogen at −125°C and −140°C as a function of density.

conductivity coefficient measured was independent of the value of the temperature difference guarantees that the increase observed is not due to convection.

Very recently Ziebland and Needham [24] measured the thermal conductivity of ammonia at two supercritical isotherms, namely at 138·8°C and 157·1°C which is respectively 6·4° and 24·7° above the critical temperature, covering the range around the critical density. They also observed a pronounced anomalous increase of the thermal conductivity leading to the existence of a maximum at the isotherm of 138·8°C.

These results question the applicability of a reduction of the thermal conductivity coefficient of fluids with the aid of its value at the critical point, a procedure widely used in reduced state correlations of the thermal conductivity [4, 25]. Two remarks should be made:

1. In these procedures "critical" values of the thermal conductivity coefficient are obtained either by interpolation as a function of temperature at constant pressure or as a function of pressure at constant temperature. In these procedures, as mentioned before, the whole density range around the critical is easily overlooked. Although "critical thermal conductivity values" thus obtained may be useful in correlating the thermal conductivity outside the critical region, it must be kept in mind that these parameters do not represent the thermal conductivity near the critical point at all.

2. Moreover, the interpolation procedure to obtain these parameters becomes less defined the more data become available as is apparent from Figs. 6 and 7. Therefore the use of a better defined reduction parameter is badly needed.

4. THE DENSITY DEPENDENCE OF THE VISCOSITY AND THERMAL CONDUCTIVITY COMPARED WITH THE THEORY OF ENSKOG

Many calculations of the transport coefficients at elevated densities are based on the theory of Enskog for a dense gas of rigid spherical molecules. Two aspects of the Enskog theory have contributed to its important role:

1. The theory of Enskog seems to describe the transport coefficients reasonably well for at least one idealized model, namely rigid spheres. It was shown in a previous paper [26] that the theory of Enskog can be obtained from first principles under the so-called assumption of molecular chaos. Although this assumption is certainly not rigorous, numerical calculations for rigid spheres indicate that the assumption is reasonably fulfilled in the dense state of a rigid sphere gas [27].

2. Application of the theory of Enskog requires adjustment of a few parameters only, e.g. the diameter of the spheres, while other approximate theories often involve a number of unknown parameters. A recent review of existing approximate theories of transport for the dense state was made by McLaughlin [28].

According to the theory of Enskog the viscosity coefficient η and the thermal conductivity coefficient λ for a gas of rigid spheres are represented by [29, 30]:

$$\eta = \eta_0\, b\rho \left(\frac{1}{b\rho\chi} + 0{\cdot}800 + 0{\cdot}761\, b\rho\chi\right) \tag{1}$$

$$\lambda = \lambda_0\, b\rho \left(\frac{1}{b\rho\chi} + 1{\cdot}200 + 0{\cdot}755\, b\rho\chi\right) \tag{2}$$

while the equation of state is given by:

$$pV = RT(1 + b\rho\chi) \tag{3}$$

Here $b = 2\pi\sigma^3/3m$ is the covolume with σ the diameter and m the mass of a molecule. η_0 and λ_0 are the values of the transport coefficients in the diluted state:

$$\eta_0 = \frac{5{\cdot}08}{16\sigma^2}\left(\frac{mkT}{\pi}\right)^{\frac{1}{2}}, \quad \lambda_0 = 2{\cdot}522\, \eta_0 \frac{3k}{2m} \tag{4}$$

χ is the value of the equilibrium radial distribution function at a distance σ from the center of an individual molecule, for which a number of coefficients in its virial expansion are known:

$$\chi = 1 + 0{\cdot}6250\, b\rho + 0{\cdot}2869\, (b\rho)^2 + 0{\cdot}115\, (b\rho)^3 + 0{\cdot}109\, (b\rho)^4 + \dots \tag{5}$$

The density dependence of the transport coefficients of a real gas can be compared with the density dependence for a gas of rigid spheres that would have the same values η_0 and λ_0 in the diluted state. This is achieved by calculating an effective diameter σ, and consequently an effective value of the covolume b, from the experimental η_0 and λ_0 with (4); χ can then be obtained from its expansion (5) It is remarked that the theory of Enskog predicts a uniform behavior of η/η_0 and λ/λ_0 as a function of the reduced density $\rho^* = b\rho$.

This procedure was carried out for the noble gases. Comparison of the behavior thus predicted with the experimental data is presented in Figs. 11 and 12. The drawn curve represents the prediction of Enskog's theory. It is seen that the data follow the behavior predicted reasonably well up to a density of $b\rho = 0{\cdot}4$. This density $b\rho = 0{\cdot}4$ corresponds for helium to a density of about 650 amagat units, for neon to about 400 amagat, for argon to about 160 amagat and for xenon to 65 amagat. It is concluded that the theory of Enskog accounts for the principal contributions to the density dependence observed for η and λ at moderate densities. At higher densities, however, the increase predicted is much too steep.

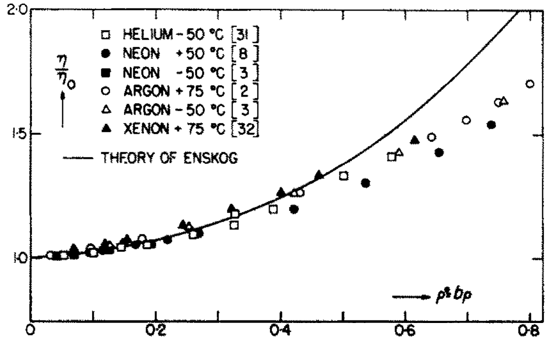

FIG. 11. Density dependence of the viscosity of helium, neon, argon and xenon compared with the theory of Enskog.

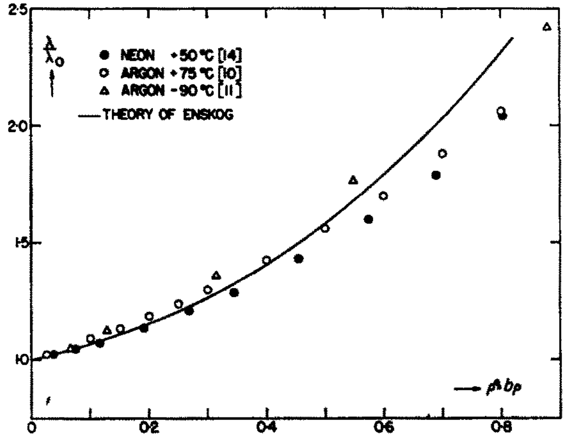

FIG. 12. Density dependence of the thermal conductivity of neon and argon compared with the theory of Enskog.

As already suggested by Enskog [29] an attempt can be made to represent the transport coefficients of a real gas by equations (1) and (2) over a larger density range by attributing effective values to the parameters b and χ deduced from the compressibility isotherms of of the substance. In this way one can also partially account for the influence of attractive forces between the molecules. The procedure most commonly used is the one introduced by Michels and Gibson [6]. In this procedure effective values of $b\rho\chi$ are calculated by requiring that the pressure p in the equation of state for rigid spheres (3) is to be identified with the thermal pressure $T(\partial p/\partial T)_V$ of the real gas:

$$b\rho\chi = \frac{1}{R}\left(\frac{\partial pV}{\partial T}\right)_V - 1 \tag{6}$$

In order that the modified Boltzmann equation introduced by Enskog reduces to the ordinary Boltzmann equation at low densities, one should still require

$$\lim_{\rho\to 0} \chi = 1 \tag{7}$$

so that [30]:

$$b = B + T\frac{\mathrm{d}B}{\mathrm{d}T} \tag{8}$$

where B is the second virial coefficient. It is remarked that some care is needed in the calculation of $b\rho\chi$ from (6) at low densities. Near one atmosphere the experimental value of the right-hand side of equation (6) becomes inaccurate and for consistency one should check explicitly that condition (7) is satisfied.

This procedure was also used to calculate η and λ for the noble gases. The experimental data for the viscosity of helium, neon, argon and xenon are compared with the behavior thus predicted in Figs. 13(a, b, c, d). A comparison with the thermal conductivity of neon and argon is made in Fig. 14(a, b). The difference between the theoretical and experimental values is tabulated in Table 1. The theory of Enskog

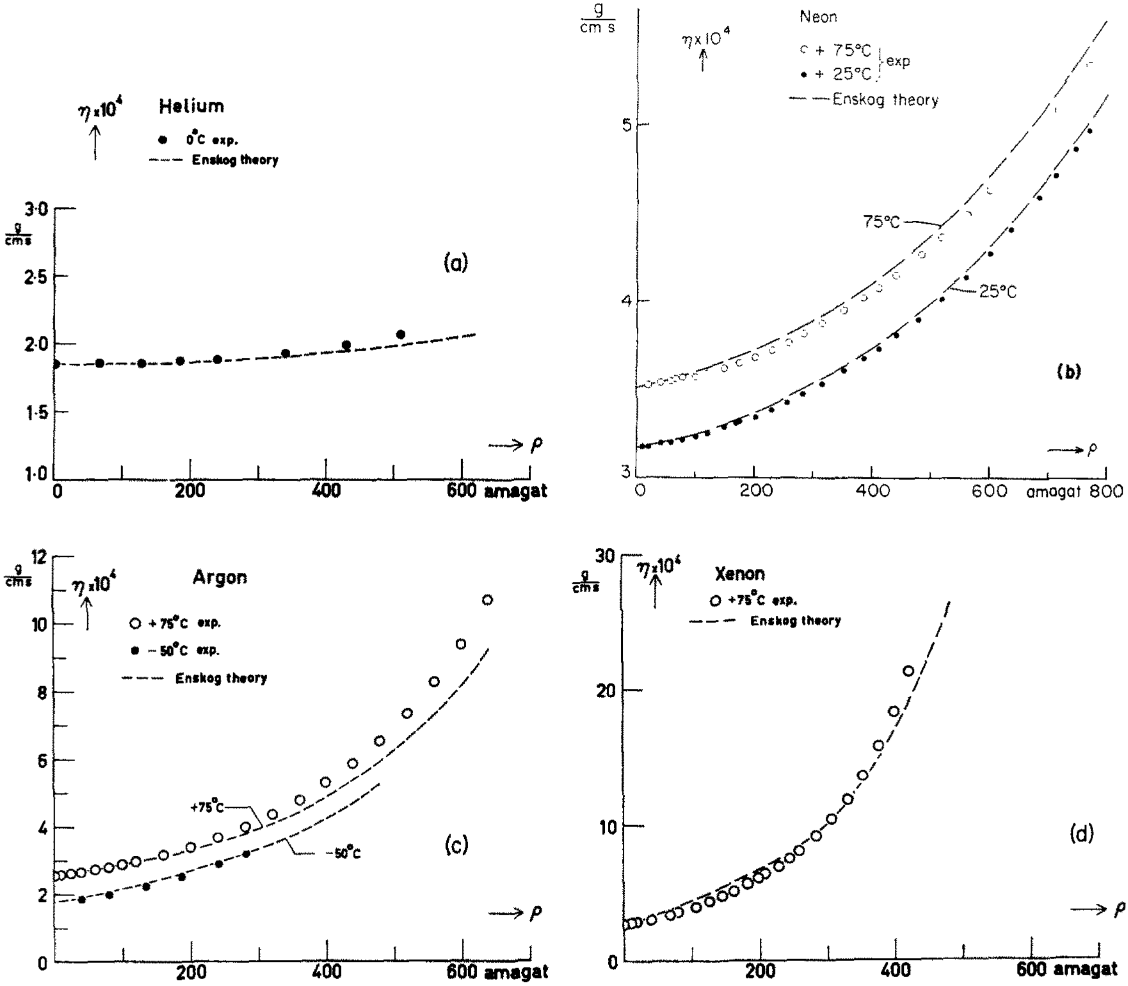

FIG. 13. Density dependence of the viscosity of the noble gases compared with the empirical modification of the theory of Enskog. (Sources of experimental data: helium [31], neon [8], argon [2, 3], xenon [32].)

describes the main trend of the density dependence fairly well over a large density range.

A similar comparison was carried out for the viscosity of hydrogen and nitrogen, shown in Figs. 15(a, b). The maximum difference between calculated and experimental data is 7 per cent for H_2 (ρ up to 800 amagat) and 4 per cent for N_2 (ρ up to 400 amagat).

The theory of Enskog only describes the density dependence of the thermal conductivity resulting from the translational degrees of freedom. The contribution from internal degrees of freedom will vary much less with increasing density. Therefore a modified procedure should be used to apply the theory of Enskog to the thermal conductivity of polyatomic gases. Hirschfelder, Curtiss and Bird [30] proposed for the influence of the internal degrees of freedom a correction to be added to the expression for the thermal conductivity resulting from the translational degrees of freedom as given by Enskog:

$$\lambda = \lambda' + \lambda'' \qquad (9)$$

Table 1. Comparison of the viscosity and the thermal conductivity of the noble gases with the empirical modification of the theory of Enskog

$$\frac{\eta_{\text{calc}} - \eta_{\text{exp}}}{\eta_{\text{exp}}}$$

ρ (amagat)	100	200	300	400	500	600	700
helium 0°C	0%	0%	−1%	−2%	−4%		
neon +75°C	+1%	+1%	+1%	+1%	+1%	+1%	+1%
neon +25°C	+1%	+1%	+1%	+1%	+1%	+2%	+2%
argon +75°C	0%	−3%	−5%	−8%	−10%	−12%	
argon −50°C	+5%	+5%	0%				
xenon +75°C	+14%	+10%	0%	−7%			

$$\frac{\lambda_{\text{calc}} - \lambda_{\text{exp}}}{\lambda_{\text{exp}}}$$

ρ (amagat)	100	200	300	400	500	600	700
neon +75°C	0%	0%	0%	−1%	−2%	−2%	−2%
neon +25°C	0%	−1%	−2%	−2%	−3%	−4%	−4%
argon +75°C	−3%	−7%	−11%	−12%	−13%	−15%	
argon −90°C	+1%	−4%	−8%	−6%	−4%		

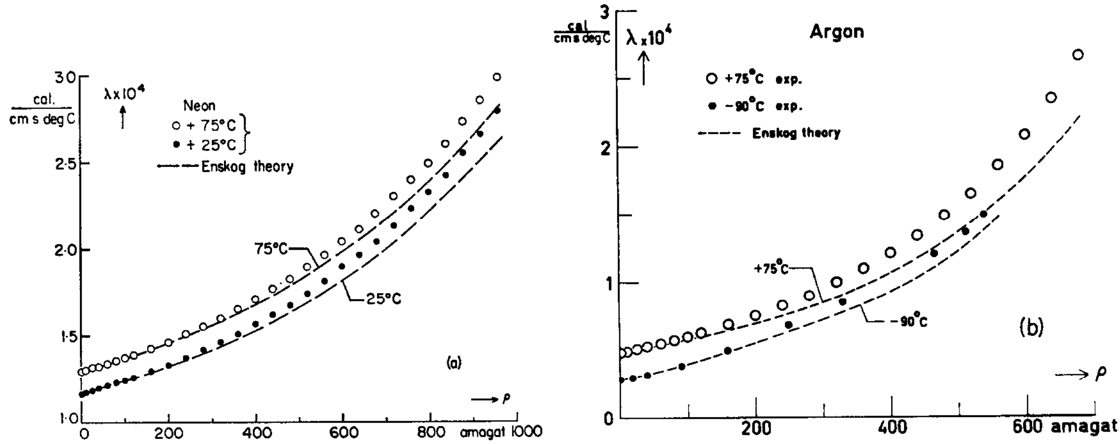

FIG. 14. Density dependence of the thermal conductivity of neon and argon compared with the empirical modification of the theory of Enskog. (Sources of experimental data: neon [14], argon [10, 11].)

where

$$\lambda' = \lambda_0' b\rho \left(\frac{1}{b\rho\chi} + 1{\cdot}200 + 0{\cdot}755\, b\rho\chi\right) \quad (10)$$

represents the contribution of the translational degrees of freedom only, and

$$\lambda'' = \frac{\lambda_0 - \lambda_0'}{\chi} \quad (11)$$

the additional contribution of the internal degrees of freedom. The thermal conductivity coefficient thus calculated for nitrogen at 75°C

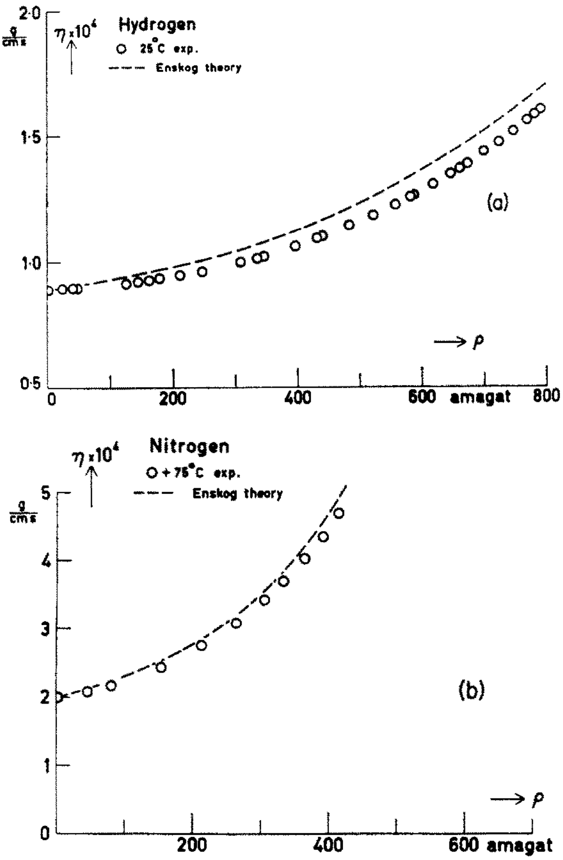

FIG. 15. Density dependence of the viscosity of H_2 and N_2 compared with the empirical modification of the theory of Enskog. (Sources of experimental data: H_2 [7], N_2 [6].)

is compared with the experimental data in Fig. 16. The maximum deviation is 16 per cent (ρ up to 600 amagat).

For more complicated gases the theory of Enskog may lead to larger deviations from the experimental data. For instance, for CO_2 the viscosity and thermal conductivity coefficient can only be represented by the Enskog formulae (1) and (2) over a large density range, if different values of the covolume b are used for η and λ [20, 29].

However, at least for the simpler fluids the theory of Enskog does contain the essential transport mechanisms for a dilute as well as for a strongly compressed gas and, given the proper values of b and χ to be used, away from the critical point does account for the main trend of the density dependence of viscosity and thermal conductivity.

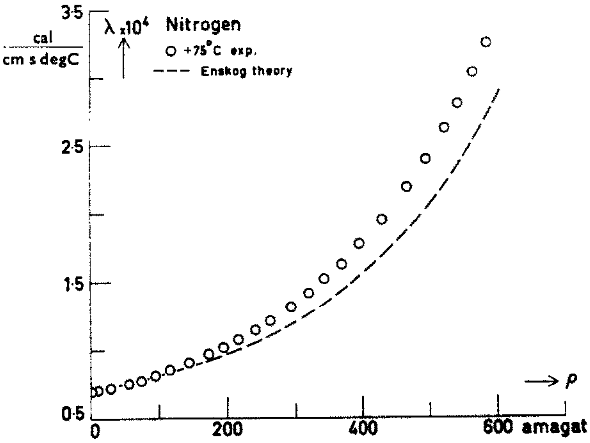

FIG. 16. Density dependence of the thermal conductivity of N_2 compared with the empirical modification of the theory of Enskog. (Experimental data from [33].)

It is remarked that the temperature dependence of η and λ cannot well be studied with the theory of Enskog. For instance Kim and Ross have remarked that according to the theory of Enskog the initial slope $(\partial\eta/\partial\rho)_T$ is proportional to η_0 and therefore to $\sqrt{T}$, which does not seem the case at high temperatures [34].

The theory of Enskog, as can be expected, does not account at all for the thermal conductivity anomaly in the critical region [20]. As mentioned before in the molecular transport of momentum and energy a kinetic contribution associated with the free motion of the molecules and a potential contribution accounting for the exchange of momentum and energy during the relative motion of the molecules in their mutual interaction field can be distinguished. The theory of Enskog presents an estimate for both contributions. However, in the case of the thermal conductivity also a third mechanism must be considered, namely the transport of potential energy associated with the motion of the center of gravity of interacting particles. This contribution may be very important in the critical region, where the molecules tend to form clusters containing a large amount of internal energy. This contribution does not occur in the

Enskog theory. Also the fact that a similar contribution is not present in the viscosity may be connected with the absence of an appreciable anomaly in the viscosity in the critical region.

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Résumé—Le comportement de la conductivité thermique et de la viscosité de fluides simples en fonction de la pression, de la densité et de la température est examiné en détail. On a prêté particulièrement attention au comportement des coefficients de transport dans la région critique. Dans un article antérieur [1], on a montré que le coefficient de conductibilité thermique passe par un maximum prononcé dans la région critique. Des renseignements complémentaires confirmant l'existence d'un tel maximum sont présentés.

Les prévisions théoriques des coefficients de transport dans les systèmes denses sont souvent basés sur la théorie de Enskog. Une vue d'ensemble est présentée montrant dans quelle mesure la théorie de Enskog décrit la dépendance des coefficients de transport en fonction de la densité dans des fluides monoatomiques. Enfin, le mécanisme de transport conduisant à l'augmentation anormale de la conductivité thermique dans la région critique est indiqué.

Zusammenfassung—Das Verhalten der Wärmeleitfähigkeit und der Viskosität einfacher Flüssigkeiten wird als Funktion von Druck, Dichte und Temperatur betrachtet. Besondere Beachtung erfährt das Verhalten der Transportgrössen im kritischen Gebiet. In einer früheren Arbeit [1] wurde gezeigt, dass die Wärmeleitfähigkeit im kritischen Gebiet ein ausgeprägtes Maximum aufweist. Zusätzliche Informationen, welche die Existenz eines solchen Maximums bestätigen, werden mitgeteilt.

Theoretische Vorhersagen der Transportgrössen in festen Systemen basieren oft auf der Theorie von Enskog. In einer Übersicht wird angegeben, wie weit die Theorie Enskogs die Dichteabhängigkeit der Transportgrössen in einatomigen Flüssigkeiten beschreibt. Schliesslich wird auf den Transportmechanismus, der zu dem anomalen Anstieg des Wärmeleitvermögens im kritischen Gebiet führt, hingewiesen.

Аннотация—Рассматривается поведение коэффициентов теплопроводности и вязкости простых жидкостей как функция давления, плотности и температуры. Особое внимание уделяется поведению коэффициентов переноса в критической области. В предыдущей статье [1] показано, что коэффициент теплопроводности имеет ярко выраженный максимум в критической области. Приводятся дополнительные сведения, подтверждающие существование такого максимума.

Теоретическое определение коэффициентов переноса в плотных системах часто основывается на теории Энского. Представленный обзор показывает до какой степени теория Энского описывает зависимость коэффициентов переноса от плотности в одноатомных жидкостях. В заключении, отмечен механизм переноса, ведущий к аномальному росту коэффициента теплопроводности в критической области.