

Density Dependence of the Viscosity of Some Noble Gases¹

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A theoretical model of the viscosity of gases at subcritical densities is presented. Up to now a suitable description of the viscosity of gases at these densities is missing, except for very rarefied gases. In the introduction a short description is given of what is already known about the viscosity of fluids, as far as needed to understand the following sections. Then a new theoretical model is proposed, based on conclusions drawn from the comparison of computer simulations and experimental data taken over a large density range. The value of the volume of close packing resulting from this comparison shows that at the critical density the distance between the molecules is nearly equal to the effective range of the intermolecular potential. Consequently, at subcritical densities the gas consists of a collection of clusters of molecules. The momentum is then transported by intracluster and intercluster transport. The theoretical model describes the gradual transition from intercluster transport to intracluster transport as a function of the density. The application of this model to some noble gas data shows that the viscosity is described within the experimental accuracy. From this application could be concluded that already at the lowest densities, clusters are usually present.

KEY WORDS: density dependence; Enskog theory; intercluster and intracluster momentum transport; noble gases; viscosity.

1. INTRODUCTION

Up to now the only suitable theory which is available to describe the viscosity at high densities is the hard-sphere Enskog theory published in 1922 [1]. In 1970 Alder et al. [2] proved by means of computer simulations that

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this theory is valid for hard spheres for densities up to twice the critical density. For higher densities the simulation values increase gradually up to nearly twice the theoretical value at the solidification density of the liquid. A similar investigation on square-well molecules reported by Michels and Trappeniers [3] confirmed this conclusion by extrapolation of the results. According to the hard-sphere Enskog theory, the viscosity coefficient η_{Enskog} is given by

$$\eta_{\text{Enskog}} = \eta_{\text{0hs}} \left\{ (1/\chi) + 0.8(b/V) + 0.7614(b/V)^2 \chi \right\} \quad (1)$$

where η_{0hs} stands for the hard-sphere Chapman–Enskog formula

$$\eta_{\text{0hs}} = (5/16)(\pi mkT)^{1/2}/\pi\sigma^2 \quad (2)$$

χ is the radial distribution function at contact taken from the Carnahan–Starling equation of state for hard spheres and expressed in b and V , b is the Van der Waals covolume given in terms of the molar volume of close packing V_0 , and V is the molar volume. The simulation data are given in terms of the viscosity coefficient relative to the theoretical hard-sphere Enskog value η_{Enskog} as a function of V_0/V .

For comparison with experimental data, the latter must also be given relative to η_{Enskog} and expressed in terms of the relative density V_0/V . V_0 is now an adjustable parameter to bring the real molecules and the hard spheres on the same measure. The value of V_0 can be chosen such that the high-density data fit to the simulation results in the density range near the solidification density and that the intermediate-density data deviate a constant value from them in the range between the critical density and twice the critical density [4–8].

This deviation with a constant factor indicates that the right theoretical description of the viscosity in this range can be obtained by a change in the density-independent part of η_{Enskog} [5]. Since in the constant factor η_{0hs} , Eq. (2), the mass m and the temperature T are well-known, the collision cross section

$$\pi\sigma^2 = \text{ccs} \quad (3)$$

is taken as a second adjustable parameter. This means that the effective values for the diameter of the molecules are taken different for the excluded volume expressed in V_0 and for the collision cross section. This theoretical description of the viscosity is called the special Enskog theory (SET). With these two adjustable parameters, V_0 and ccs , η_{SET} describes the experimental data in the intermediate-density range rather accurately [4–8]. However, η_{SET} does not describe the experimental viscosity at the subcritical densities.

At very low densities, the density-independent viscosity η_0 is usually described by the Chapman–Enskog formula

$$\eta_0 = (5/16)(\pi mkT)^{1/2}/(\text{ccs} \cdot \Omega^*) \quad (4)$$

where Ω^* is the reduced collision integral. With increasing density, up to the critical density, the viscosity shows an S-shaped deviation from η/η_{SET} [4–8]. Also, in the high-density range near the solidification density of the fluid, the results differ from η_{SET} . Recently van der Gulik [9] has shown that, in this density range, Maxwell's relaxation-time theory, given in his second viscosity paper [10], can be applied.

2. THE VISCOSITY AT SUBCRITICAL DENSITIES

The values for the molar volume of close packing V_0 , obtained by the fitting procedure mentioned above, are such that the molar volume at the critical density is about $5V_0$ [4–8]. This means that at the critical density the mean distance between the molecules is about 1.7 times the diameter of the molecules. This distance corresponds very nearly to the effective range of the intermolecular forces. At densities higher than the critical, the attractive spheres overlap, and the attractive forces on the molecules compensate each other; they act only as a background force and the molecules can be handled as soft spheres. Therefore, at these densities the viscosity can be described in terms of the special Enskog theory as mentioned above.

At densities somewhat lower than the critical, the mean distance between the molecules becomes larger than the effective range of the intermolecular potential and we have clusters of molecules held together by the intermolecular forces and empty spaces in between them. With decreases in the density, the clusters become smaller and smaller. Thus, at densities lower than the critical, a gas is mesoscopically homogeneous, but microscopically, on the level of atoms, inhomogeneous, a mixture of clusters and void.

For the viscosity this means that, at subcritical densities, we have to cope with two transport mechanisms, intracluster momentum transport inside the clusters and intercluster momentum transport over the empty spaces in between them. This two-mechanism model is an unavoidable consequence of the existence of clusters. The contribution of the intercluster transport decreases with increasing density, while the contribution of the intracluster transport increases with increasing density, since the clusters grow with the density.

According to modeling theory we have to look for the change in the density dependence of one of the contributions $F(V)$, say of the intracluster transport, $\partial F(V)/\partial(1/V)$. This contribution is determined by the amount

and magnitude of the clusters, and these change during collisions. Therefore, $\partial F(V)/\partial(1/V)$ is taken to be proportional to both the contribution $F(V)$ of the intracluster transport and the contribution $1-F(V)$ of intercluster transport

$$\partial F(V)/\partial(1/V) = rF(V)\{1-F(V)\} \quad (5)$$

where r is the rate of transition. The density is expressed in the molar volume V for convenience. This equation is known as the logistic equation. Its integration results in

$$F(V) = 1/\{1 + \exp(r\langle(V_0/V) - dh\rangle)\} \quad (6)$$

where dh is an integration constant, indicating the relative density, where $F = \frac{1}{2}$. V is reduced with V_0 for convenience.

The gradual transition from the mean-free path mechanism at very low density to the hard-sphere Enskog mechanism at the critical density is demonstrated by the S-shaped curves in Figs. 1–3. The temperature dependence reflects mainly the temperature dependence of the reduced collision integral Ω^* in the Chapman–Enskog part. Therefore, we assume that the momentum transport between the clusters is of the mean-free path

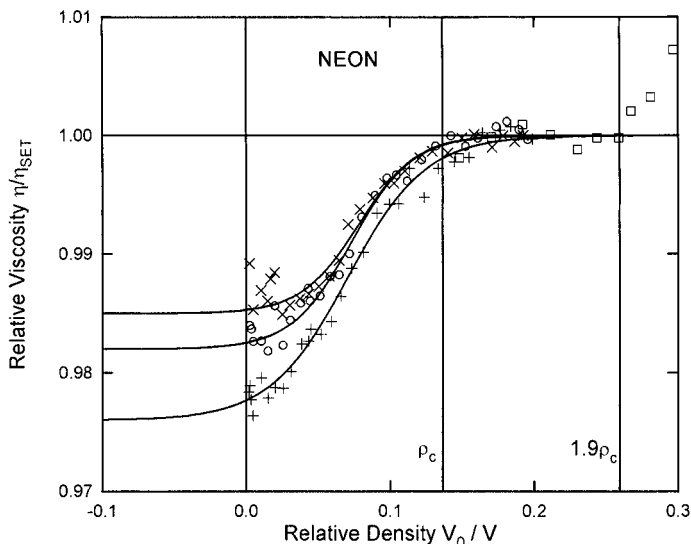


Fig. 1. Relative viscosity η/η_{SET} of neon as a function of the relative density V_0/V . Curves represent the theoretical model. Experimental data: (+) 298 K, (O) 323 K, (x) 348 K [11]; (□) 298 K [12].

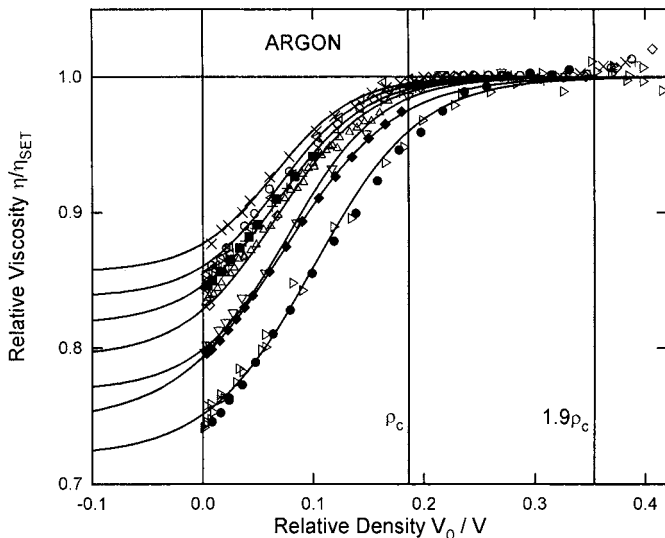


Fig. 2. Relative viscosity η/η_{SET} of argon as a function of the relative density V_0/V . Curves represent the theoretical model. Experimental data: (●) 173 K, (◆) 223 K, (■) 298 K [13]; (▷) 173 K, (▽) 223 K, (△) 270 K, (△) 298 K [14]; (◇) 273 K, (+) 298 K, (○) 323 K, (×) 348 K [15].

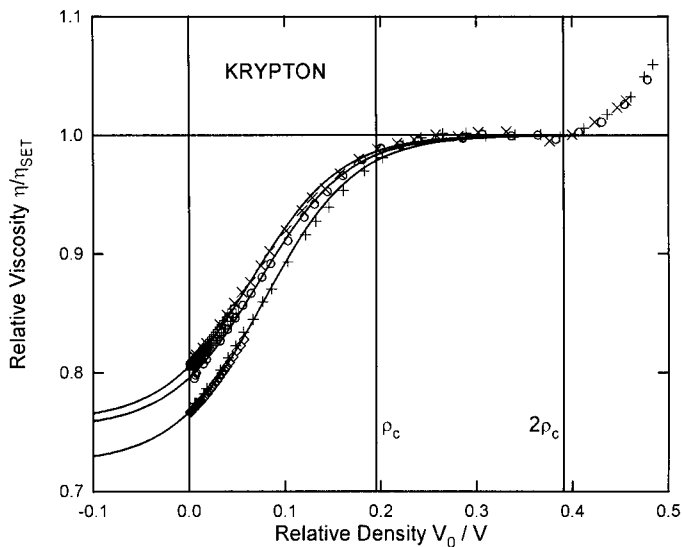


Fig. 3. Relative viscosity η/η_{SET} of krypton as a function of the relative density V_0/V . Curves represent the theoretical model. Experimental data: (+) 298 K, (○) 323 K, (×) 348 K [16]; (◇) 298 K, (□) 348 K [17].

type and is described by $\eta_{\text{SET}}/\Omega^*$. A good choice for the momentum transport within the clusters appears to be given by η_{SET} , so that

$$\eta = F(\eta_{\text{SET}}/\Omega^*) + (1 - F) \eta_{\text{SET}} \quad (7)$$

or

$$\eta = [(F/\Omega^*) + (1 - F)] \eta_{\text{SET}} \quad (8)$$

$$\eta = [1 + ((1/\Omega^*) - 1) F] \eta_{\text{SET}} \quad (9)$$

and

$$\eta = [1 - (1 - (1/\Omega^*)) / \{1 + \exp(r\langle(V_0/V) - dh\rangle)\}] \eta_{\text{SET}} \quad (10)$$

The term $[1 - (1/\Omega^*)]$ is the distance between the reduced Chapman–Enskog viscosity η_0/η_{SET} and $\eta_{\text{SET}}/\eta_{\text{SET}} = 1$, the amplitude A of the above mentioned S-shaped curve:

$$\eta = [1 - A / \{1 + \exp(r\langle(V_0/V) - dh\rangle)\}] \eta_{\text{SET}} \quad (11)$$

From a different point of view the logistic function describes the extinction of this amplitude $A = 1 - (1/\Omega^*)$ and therewith the extinction of the influence of the attractive forces with the density, with the rate r at relative density dh .

So we end up with a theoretical description of the viscosity for the density range up to nearly twice the critical density with five parameters, V_0 and ccs in η_{SET} and A , r , and dh in F .

3. APPLICATION TO SOME NOBLE GASES

This model is applied to the viscosity coefficients of neon [11, 12], argon [13–15], and krypton [16, 17], for which suitable data are available. For neon and argon the program is applied on data up to densities of 1.9 times the critical density and for krypton on data up to twice the critical density. The choice of the data has been somewhat arbitrary: sometimes data at the same temperature were combined, and sometimes data were taken separately because of systematical deviations. The data of van den Berg [17] have been given a higher weight than the corresponding data of Trappeniers et al. [16] because of their very high accuracy.

First, a five-parameter least-squares program was applied on these data. The results showed that the model describes the data amply within

the uncertainty of the data; however, the values of the parameters are not well defined, a range of values being possible within the limits set by the accuracy of the data. Therefore, the model was applied in two steps: first, V_0 and ccs were determined from the intermediate density data and then A , r , and dh were determined with a three-parameter least-squares program over the full density range. The result is presented in Table I. The standard deviation (SD) is the root of the mean square deviation in parts per thousand, and n is the number of data used. Also, the source of the data is indicated. The results show a decrease with temperature for the volume of close packing V_0 , the collision cross section ccs, and the amplitude A , and an increase with temperature for the rate r , while the integration constant dh is more or less constant.

Table II shows some results derived from these parameter values. With $A = 1 - (1/\Omega^*)$ the values of the reduced collision integral Ω^* are calculated. They are of the right magnitude and show the expected decrease with increasing temperature. Values for the diameter σ_{ccs} of the atoms are

Table I. Temperature-Dependent Model Parameters of Some Noble Gases

T (K)	V_0 ($\text{m}^3 \cdot \text{Mmol}^{-1}$)	ccs (10^{-20}m^2)	A	r	dh	SD	n
Neon							
298.15	5.785	20.38	0.0241	37.11	0.0712	0.9	37 30 [11], 7 [12]
323.15	5.69	20.22	0.0177	48.07	0.0734	0.8	28 [11]
348.15	5.60	20.04	0.0155	50.49	0.0771	0.7	25 [11]
Argon							
173.15	15.76	37.97	0.2720	21.71	0.1076	6.8	21 [13]
173.15	15.88	37.97	0.2795	20.86	0.1001	7.5	40 [14]
223.15	14.97	36.39	0.2539	19.94	0.0735	0.9	16 [13]
223.15	14.97	36.39	0.2315	24.14	0.0781	4.8	18 [14]
270.15	14.15	35.27	0.2151	20.58	0.0591	2.6	38 [14]
273.15	14.10	35.20	0.2064	23.81	0.0670	1.5	6 [15]
298.15	13.84	34.79	0.2116	20.51	0.0523	0.5	10 [13]
298.15	13.84	34.79	0.1767	27.86	0.0617	4.5	20 [14]
298.15	13.84	34.79	0.1821	24.90	0.0680	2.5	23 [15]
323.15	13.58	34.48	0.1621	26.74	0.0679	2.7	24 [15]
348.15	13.39	34.33	0.1435	27.58	0.0644	2.2	25 [15]
Krypton							
298.15	18.04	40.70	0.2764	21.30	0.0790	2.9	62 27 [16], 35 [17]
323.15	17.815	40.70	0.2466	21.54	0.0730	2.6	27 [16]
348.15	17.52	40.31	0.2405	21.74	0.0662	2.4	61 25 [16], 36 [17]

Table II. Values Derived from the Model Parameters of the Noble Gases

T (K)	Ω^*	σ_{ccs} (nm)	σ_{V_0} (nm)	Ratio
Neon				
298.15	1.025	0.255	0.239	1.067
323.15	1.018	0.254	0.237	1.069
348.15	1.016	0.253	0.236	1.070
Argon				
173.15	1.374	0.348	0.333	1.043 [13]
173.15	1.388	0.348	0.334	1.041 [14]
223.15	1.340	0.340	0.328	1.039 [13]
223.15	1.301	0.340	0.328	1.039 [14]
270.15	1.274	0.335	0.321	1.042 [14]
273.15	1.260	0.335	0.321	1.042 [15]
298.15	1.268	0.333	0.319	1.043 [13]
298.15	1.215	0.333	0.319	1.043 [14]
298.15	1.223	0.333	0.319	1.043 [15]
323.15	1.193	0.331	0.317	1.045 [15]
348.15	1.168	0.331	0.316	1.047 [15]
Krypton				
298.15	1.382	0.360	0.349	1.032
323.15	1.327	0.360	0.347	1.037
348.15	1.317	0.358	0.345	1.038

calculated from the collision cross section $\text{ccs} = \pi\sigma^2$ and for the effective excluded-volume diameters σ_{V_0} from the molar volumes of close packing $V_0 = N_A\sigma^3/\sqrt{2}$. The ratio of both radii and therefore a measure for the softness of the spheres are given in column 5 of Table II. In the case of argon the source of the data is also indicated.

Figures 1–3 show the viscosity reduced with the value of η_{SET} as a function of the reduced density V_0/V and also the theoretical curves calculated with the parameters presented in Table I. These curves are plotted down from the negative densities $V_0/V = -0.1$ to show their complete course. Figures 4–6 show the experimental data, the theoretical curves, and the deviations of these data from the theoretical values in parts per thousand. For neon (Fig. 4), the agreement is in general within 2 parts in thousand. For argon (Fig. 5), the agreement is mostly within 5 parts per 1000 with the exception of the data of Haynes [14]. The data taken at 173 K were worse; they have a spread of 15 parts per 1000 and are, therefore, omitted from the deviation plot. The deviations of the krypton data (Fig. 6) show the systematic difference between the data of Trappeniers et al. [16] and those

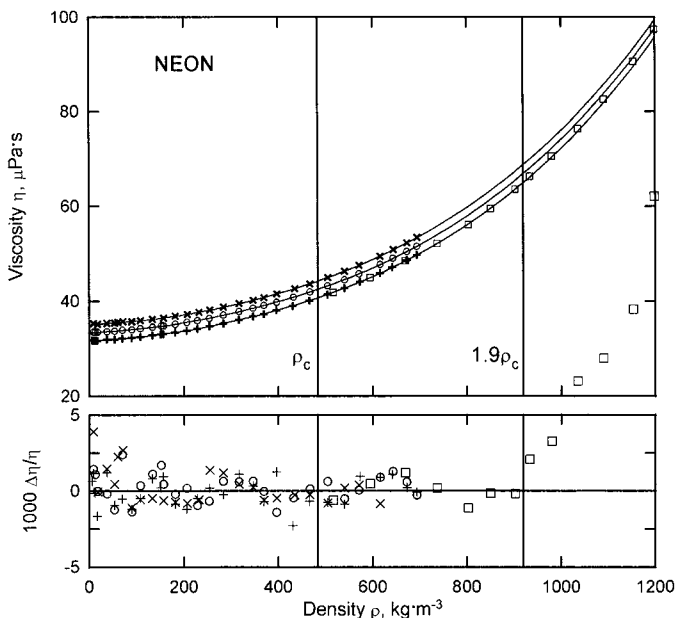


Fig. 4. Viscosity of neon as a function of density and deviations from the theoretical model in parts per thousand. Curves represent the theoretical model. Experimental data: (+) 298 K, (O) 323 K, (x) 348 K [11]; (□) 298 K [12].

of van den Berg [17]. For the data of Trappeniers et al. alone, a result like that of neon would be obtained.

4. INTERPRETATION AND CONCLUSIONS

The main conclusion from the application of this theoretical model to some noble gases is that the model describes the viscosity coefficient amply within the experimental uncertainty of the data, the agreement is mostly within a few parts per thousand. Consequently, many accurate data over a wide density range are needed to determine the values of the parameters accurately. A second conclusion, drawn from Figs. 1–3, is, that usually even at the lowest densities, clusters are present. Only at temperatures high above the critical temperature, as, for instance, for neon with a critical temperature of 44.4 K, the condition of the Chapman–Enskog theory that only binary collisions occur is more or less fulfilled, as Fig. 1 shows. This means that the rarefied-gas viscosity is not completely described by the Chapman–Enskog theory, which assumes single molecules, and that the

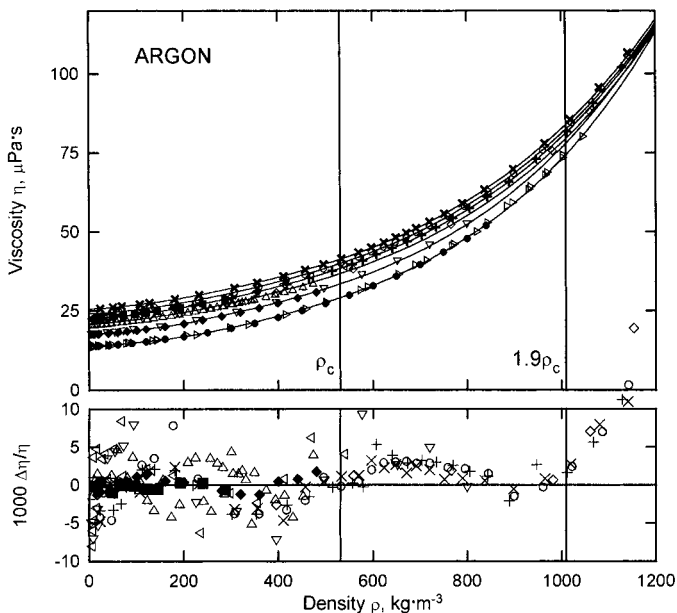


Fig. 5. Viscosity of argon as a function of density and deviations from the theoretical model in parts per thousand. Curves represent the theoretical model. Experimental data: (●) 173 K, (◆) 223 K, (■) 298 K [13]; (▷) 173 K, (▽) 223 K, (△) 270 K, (◁) 298 K [14]; (◇) 273 K, (+) 298 K, (○) 323 K, (×) 348 K [15].

values for Ω^* mentioned in Table II do not correspond to those derived from experimental values of η_0 but are a little bit larger. This can be important for the calculation of the intermolecular potential from low-density viscosity values. Also, the rarefied-gas viscosity is not independent of the density, as is also known from the Rainwater–Friend theory. A comparison should be made between this theory and the present model for very accurate data.

In contrast with what we have supposed in earlier publications, the collision cross section appears to decrease with the temperature also for noble gases, as for polyatomic molecules like methane [6, 7] and carbon dioxide [18], for which a temperature-dependent form factor is included in ccs. It must be stressed that ccs contains only the repulsive part of the intermolecular potential, the influence of the attractive forces is discounted in Ω^* . Also, the value of V_0 , and thereby of the excluded volume, decreases slightly with increasing temperature due to the fact that the molecules are not really hard; at high temperatures the molecules move faster, collide with greater impact, and penetrate each other further than at low temperatures.

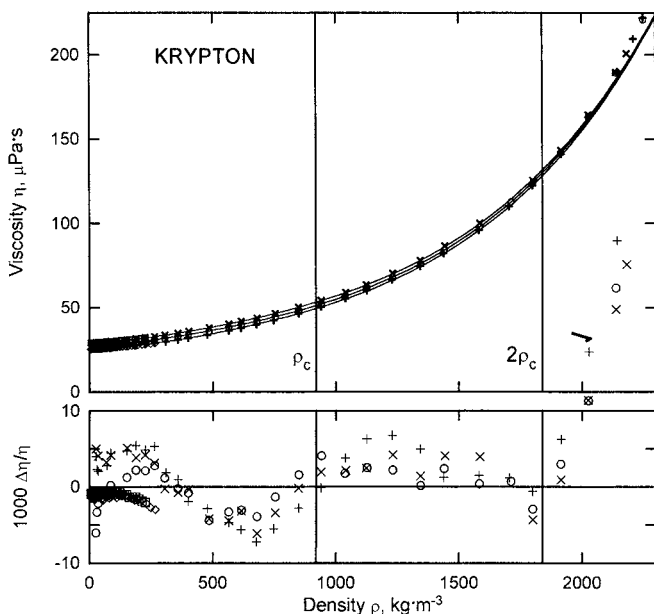


Fig. 6. Viscosity of krypton as a function of density and deviations from the theoretical model in parts per thousand. Curves represent the theoretical model. Experimental data: (+) 298 K, (○) 323 K, (×) 348 K [16]; (◇) 298 K, (□) 348 K [17].

Of course, also the corresponding diameter decreases smoothly with the temperature, as shown in Table II; in this respect the atoms behave as soft spheres. It can easily be understood that this excluded-volume diameter is a bit smaller than the collision cross-section diameter, since the “target” is hit or not and the corresponding diameter has nothing to do with penetration.

The fact that r increases with temperature includes that r eventually becomes negative at low temperatures. The result is a negative slope of η as function of the density, as is found experimentally for the viscosity of vapors far below the critical temperature. It means that the relative contribution of intercluster momentum transport increases with the density. This occurs when the magnitude of the vapor clusters is in equilibrium with the temperature and does not depend on the density. In that case with increasing density only the number of vapor clusters increases. As soon as the density becomes so high that the clusters tend to grow in magnitude, condensation occurs.

In general, the figures show that the theoretical model describes all experimental data within their experimental accuracy up to roughly twice

the critical density, while at higher densities the deviations increase very fast with the density, a very satisfactory result.

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