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THE THERMAL CONDUCTIVITY OF LIQUID ARGON

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The thermal conductivity of liquid argon has been measured along isotherms at 107, 113, 118, 124 and 130 K and pressures up to 10 MPa using the transient hot-wire technique. The instrument is capable of measuring the thermal conductivity of fluids with an accuracy of ±0.5 percent in thermodynamic states far from the critical region.

The experimental data have been employed in conjunction with ideas based upon the hard-sphere theory of dense fluids to develop a reliable procedure for interpolation and extrapolation of the thermal conductivity of liquid argon.

1. Introduction

The thermal conductivity of liquid argon has been measured by several authors in the temperature range between the triple and critical points and pressures up to 10 MPa. All these measurements have been performed by steady state methods[1–4]) and the results have an accuracy of not better than 3 to 4 percent. Furthermore, the lack of a suitable equation of state for liquid argon at the time made the theoretical study of the dependence of the thermal conductivity on density impossible.

Recently we have developed in Lisbon an instrument to measure the thermal conductivity of fluids in the temperature range 77 K to 477 K and pressures up to 20 MPa using the transient hot-wire technique[5]). The use of the same instrument in the measurement of the thermal conductivity of gaseous argon has already allowed us to establish its accuracy on the order of ±0.5 percent[6]).

The high accuracy of the results obtained with this instrument can be used to

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test, with confidence, the ideas involved in one of the most successful theories of transport phenomena in the liquid state, the hard-sphere theory. This theory, based on the Enskog dense gas solution of the Boltzmann equation for hard spheres, has been applied to monatomic liquids and to pseudo-spherical molecules. It has achieved some success in the description of the viscosity and self diffusion coefficient[7]), as well as in the correlation of the mutual diffusion coefficient in binary liquid mixtures[8,9]).

The Enskog theory alone is insufficient to represent the behavior of even a hard-sphere fluid because it neglects correlations of the molecular velocities. Generally, the corrections to the theory for these effects are taken from the results of molecular dynamics calculations for a hard-sphere system[10]). The thermal conductivity data reported in this paper refer to relatively low temperatures at which the hard-sphere theory is not expected to apply. Nevertheless, an analysis of the data carried out in a manner suggested by the theory shows that the same procedure can form the basis of a reliable scheme for interpolation and extrapolation:

2. Experimental

The transient hot-wire instrument used in the present work has been fully described elsewhere[5]) and the characteristics of the hot wire cells were the same as those employed in our previous work[6]). The argon used for the measurements has a stated purity in excess of 99.999 percent. The density of liquid argon required for the reduction of the experimental data on the λ, ρ diagram was calculated from the equation of state recently developed by Stewart et al.[11]). The values obtained with this equation for the 107 K isotherm are consistent with the values published by the present authors[6]) using the IUPAC equation of state[12]). The heat capacity of liquid argon was taken from the compilation of Vargaftik[13]).

The transient hot-wire method is recognized today as the method of highest accuracy for the measurement of the thermal conductivity of liquids far from the critical region proper; the data obtained with this type of instrument has been recently proposed as the basis for standard reference data in thermal conductivity of liquids near the saturation line[14]).

A complete theory of the transient hot-wire instrument has been provided elsewhere[15–18]). For the present purpose it is necessary only to establish that the instrument operates in accordance with its theory. A necessary condition for this conclusion is that a suitably corrected transient temperature rise of the hot wire (typically 3 K) should be a linear function of the logarithm of time, t, which has elapsed following the initiation of heating.

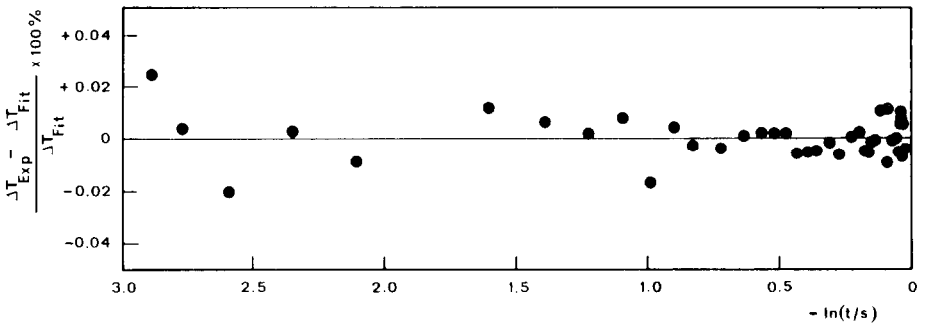

Fig. 1. Deviations of experimental data from linearity for a complete set of measurements.

Accordingly, fig. 1 contains a plot of the deviations of the corrected, measured temperature rise, ΔT_{exp}, from a linear fit in $\ln t$, for a typical run at $T = 124$ K and $P = 7.47$ MPa in argon. The deviation plot reveals no systematic trends and, on the basis of this and other suitable procedures described elsewhere[5,6,17]), we conclude that the instrument conforms to its model. A similar analysis leads to an estimated precision in the thermal conductivity measurements of ±0.2 percent, but the accuracy of the results is slightly degraded to one of ±0.5 percent because of the uncertainty in a number of instrument constants[5,6]).

3. Results

Tables I to V contain the experimental data for the five isotherms studied at 107, 113, 118, 124 and 130 K. The tables include the thermal conductivity at the reference state $\lambda(T_r, \rho_r)$ and the thermal conductivity adjusted to a nominal temperature T_{nom}. The correction was applied in the form

$$\lambda(T_{nom}, \rho_r) = \lambda(T_r, \rho_r) + \left(\frac{\partial \lambda}{\partial T}\right)_{\rho_r} (T_{nom} - T_r), \tag{1}$$

with $(\partial\lambda/\partial T)_{\rho_r}$ estimated from the wide ranging correlation developed by Younglove and Hanley[19]). In no case did the adjustments amount to more than ±0.1 percent, so that the contribution of any uncertainties derived from them to the error in the reported thermal conductivity is negligible.

The results for the isotherm at 107 K have already been presented in a previous publication[6]), but they are included here for the sake of completeness and also because a different equation of state has been used in this work.

There has been some discussion on the dependence of the excess thermal

Table I
Thermal conductivity of liquid argon at $T_{nom} = 107$ K.

P (MPa)	T_r (K)	ρ_r (kg m^{-3})	$\lambda(T_r, \rho_r)$ (mW m^{-1} K^{-1})	$\lambda(T_{nom}, \rho_r)$ (mW m^{-1} K^{-1})
0.791	107.14	1263	100.1	100.1
0.791	107.07	1263	100.9	101.0
1.659	107.50	1265	101.3	101.4
2.410	107.40	1269	101.9	101.9
3.133	107.43	1274	102.5	102.6
3.781	107.50	1275	103.3	103.4
4.408	107.18	1280	103.8	103.8
5.199	107.94	1278	104.3	104.4
5.820	107.37	1285	105.1	105.2
6.660	107.21	1290	105.6	105.6
8.025	107.82	1292	106.5	106.6

Table II
Thermal conductivity of liquid argon at $T_{nom} = 113$ K.

P (MPa)	T_r (K)	ρ_r (kg m^{-3})	$\lambda(T_r, \rho_r)$ (mW m^{-1} K^{-1})	$\lambda(T_{nom}, \rho_r)$ (mW m^{-1} K^{-1})
1.065	113.74	1213	92.05	92.09
1.479	113.81	1215	92.46	92.51
2.030	113.73	1219	92.91	92.95
2.512	113.44	1224	93.57	93.59
3.132	113.35	1229	93.98	94.00
3.821	113.57	1231	94.71	94.74
4.510	113.58	1235	95.30	95.33
5.337	113.75	1238	96.05	96.09
6.232	113.82	1242	96.92	96.96
7.128	113.60	1249	97.72	97.75
8.024	113.68	1253	98.41	98.44
9.402	113.50	1260	99.66	99.68

conductivity of liquids on the temperature[20]). This quantity, defined as

$$\Delta\lambda(\rho, T) = \lambda(\rho, T) - \lambda(0, T) \tag{2}$$

is plotted in fig. 2. The value of the dilute gas value $\lambda(0, T)$ (values are listed in table VII) was taken from ref. 19. This figure shows that all the points conform to a single curve within ±1 percent and this result supports the idea that the excess thermal conductivity in the liquid state is a function of density alone, for small density changes. A quadratic fit with respect to density was selected to

Table III
Thermal conductivity of liquid argon at $T_{nom} = 118$ K.

P (MPa)	T_r (K)	ρ_r (kg m^{-3})	$\lambda(T_r, \rho)$ (mW m^{-1} K^{-1})	$\lambda(T_{nom}, \rho_r)$ (mW m^{-1} K^{-1})
1.685	118.20	1180	87.10	87.11
2.167	118.68	1180	87.62	87.64
2.925	118.60	1185	88.41	88.43
3.579	118.61	1190	89.60	89.62
4.165	118.65	1194	90.27	90.29
4.785	118.51	1199	91.00	91.01
5.405	118.44	1204	91.50	91.51
6.026	118.57	1207	92.06	92.07
6.956	118.59	1212	93.18	93.19
7.679	118.46	1217	93.75	93.76
8.575	118.38	1223	94.58	94.59
9.195	118.34	1226	94.76	94.77
10.45	118.30	1233	95.85	95.85

Table IV
Thermal conductivity of liquid argon at $T_{nom} = 124$ K.

P (MPa)	T_r (K)	ρ_r (kg m^{-3})	$\lambda(T_r, \rho_r)$ (mW m^{-1} K^{-1})	$\lambda(T_{nom}, \rho_r)$ (mW m^{-1} K^{-1})
2.995	123.99	1139	81.29	81.29
3.546	123.88	1145	81.99	81.99
4.235	123.90	1151	82.82	82.82
4.786	123.97	1155	83.51	83.51
5.337	123.81	1160	84.08	84.08
6.026	123.78	1166	84.95	84.95
6.508	123.93	1168	85.42	85.42
6.922	123.69	1173	85.80	85.80
7.473	123.67	1177	85.99	85.99
7.852	123.84	1178	86.82	86.82
8.300	123.60	1183	87.30	87.30
8.713	123.91	1184	87.73	87.73
9.092	123.55	1189	88.08	88.08
9.402	123.86	1188	88.45	88.45

describe the dependence of the excess with this state variable,

$$\Delta\lambda/\text{mW m}^{-1}\text{ K}^{-1} = 84.16 - 1.699 \times 10^{-1}\rho + 1.407 \times 10^{-4}\rho^2 , \quad (3)$$

where the density is expressed in kg m^{-3}.

The standard deviation of the fit was found to be 0.55 mW m^{-1} K^{-1} corresponding to 0.85 percent at the lowest density and 0.55 percent at the highest.

Table V
Thermal conductivity of liquid argon at $T_{nom} = 130$ K.

P (MPa)	T_r (K)	ρ_r (kg m^{-3})	$\lambda(T_r, \rho_r)$ (mW m^{-1} K^{-1})	$\lambda(T_{nom}, \rho_r)$ (mW m^{-1} K^{-1})
2.374	130.02	1071	71.04	71.04
3.132	130.75	1073	72.55	72.54
3.580	131.10	1075	73.13	73.12
4.097	130.43	1088	74.08	74.07
4.579	130.50	1093	74.74	74.73
5.062	130.30	1100	75.24	75.23
5.613	129.96	1109	76.13	76.13
6.164	129.82	1115	76.95	76.95
6.715	130.45	1115	77.75	77.74
7.266	130.39	1121	78.34	78.33
7.818	130.14	1128	79.00	79.00
8.472	130.08	1134	79.74	79.74
9.092	130.18	1138	80.54	80.54
9.609	130.26	1141	81.36	81.36
10.09	129.30	1152	81.74	81.75

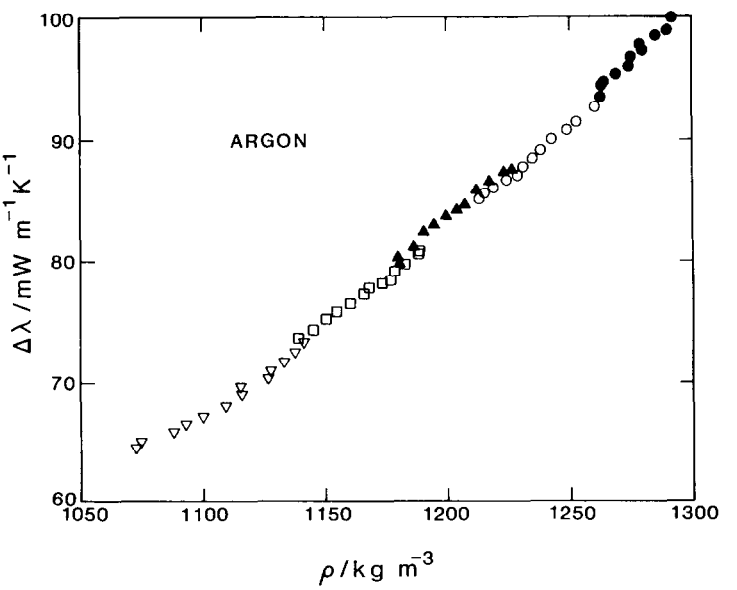

Fig. 2. The excess thermal conductivity of liquid argon as a function of density. ●$T \simeq 107$ K; ○$T \simeq 113$ K; ▲$T \simeq 118$ K; □$T \simeq 124$ K; ▽$T \simeq 130$ K.

The use of eq. (3) with $\lambda(0, T)$ from ref. 19 enables the calculation of the thermal conductivity of liquid argon at any density between 1000 and 1300 kg m^{-3} with an accuracy better than 1 percent.

The comparison of the present data with data obtained by other authors is rather difficult because they refer to different thermodynamic states. Ref. 2 reports only three points for each isotherm that overlaps with our work, but at temperatures that differ by 2 to 4 K from ours. The data of Bailey and Kellner[4]) for the liquid state are more comprehensive, although isobaric. The representation of these data has been achieved with a functional form similar to that used by Roder and Friend for methane–ethane mixtures[21]) that will be discussed in more detail in a future paper[22]). Here it is sufficient to report that the present data depart from this correlation by no more than ±2 percent, which is within the uncertainty of the experimental data of Bailey and Kellner of ±3 percent.

4. Discussion

The present experimental data are analyzed in light of the most successful theory of molecular transport in the liquid phase based on the van der Waals model of the liquid[23]). This model represents a real fluid by a rigid sphere system with a weakly temperature dependent core size, V_0. It is expected to be most applicable to real fluids at high temperatures and low densities where the attractive forces have least effect. The use of the rigid sphere model allows the dominant effects in transport phenomena in dense fluids to be analyzed with the aid of the Enskog theory. But, this theory neglects correlations in velocity space so that it cannot describe even a rigid sphere system completely. Dymond[23]) employed the results of molecular dynamic simulations of hard sphere fluids to derive corrections to the Enskog theory for the velocity correlations. The net result is that a suitably defined, reduced thermal conductivity is a function only of the ratio of the molar volume for the fluid to the characteristic core size, V_0. That is,

$$\lambda^* = \frac{\lambda}{\lambda_0}\left(\frac{V}{V_0}\right)^{2/3} = F_\lambda\left(\frac{V}{V_0}\right), \tag{4}$$

where V is the molar volume of the fluid, $V_0 = N\sigma^3/\sqrt{2}$, λ_0 the dilute gas hard-sphere thermal conductivity coefficient given by

$$\lambda_0 = \frac{25C_V}{32\pi\sigma^2}\left(\frac{\pi kT}{m}\right)^{1/2}, \tag{5}$$

with C_V the molecular heat capacity at constant volume, equal to $3k/2$ for a monatomic fluid, k is the Boltzmann constant, m the molecule mass, σ its diameter, and N the Avagadro number. The function $F_\lambda(V/V_0)$ may also be written as

$$F_\lambda\left(\frac{V}{V_0}\right) = \left(\frac{\lambda}{\lambda_E}\right)\left(\frac{\lambda_E}{\lambda_0}\right)\left(\frac{V}{V_0}\right)^{2/3}, \tag{6}$$

where λ_E/λ_0 is the ratio of the thermal conductivity of a dense hard sphere system to that of a dilute gas of hard spheres. According to the Enskog theory this ratio is given by

$$\frac{\lambda_E}{\lambda_0} = \frac{1}{g(\sigma)} + 1.2\left(\frac{b}{V}\right) + 0.755 g(\sigma)\left(\frac{b}{V}\right)^2, \tag{7}$$

where $b = 2\pi N\sigma^3/3$. In this equation $g(\sigma)$ is the radial distribution function at contact of spheres of diameter σ, given by the Carnahan–Starling equation[24])

$$g(\sigma) = \frac{(1 - 0.5y)}{(1 - y)^3}, \tag{8}$$

where $y = b/4V$.

The Enskog theory is based on the molecular chaos approximation. However, molecular dynamics calculations[25,26]) have demonstrated that hard-sphere systems have correlated motions at intermediate and high densities. Alder et al.[27]) have computed the corrections to the Enskog transport coefficients for systems of 108 and 500 particles and their values can be expressed by the relation[28])

$$\frac{\lambda}{\lambda_E} = 1.02 + 0.1\left[\left(\frac{V_0}{V}\right) - 0.3\right], \tag{9}$$

for $V/V_0 > 1.33$.

Eqs. (6) to (9) can be arranged in a single form as a function of $x = V_0/V$ given by

$$F_\lambda\left(\frac{V}{V_0}\right) = [1.02 + 0.1(x - 0.3)]\left\{\frac{(1 - 0.7405x)^3}{(1 - 0.3702x)} + 3.554x + 6.624x^2\left[\frac{1 - 0.3702x}{(1 - 0.7405x)^3}\right]\right\} x^{-2/3}. \tag{10}$$

If the hard-sphere model represents the present experimental data it should

be possible to superimpose experimental values of λ^* defined in ref. 7 as

$$\lambda^* = 1.610 \times 10^8 \lambda V^{2/3} \left(\frac{M}{R^3 T} \right)^{1/2}, \tag{11}$$

where M is the molecular mass of argon, in kg mol^{-1}, on a plot of λ^* as a function of ln V, merely by a choice of V_0 for each isotherm. The values of V_0 selected by a least-squares criterium for each isotherm are presented in table VI.

This table also shows that the largest standard deviation among the five isotherms is 1.2 mV m^{-1} K^{-1}, about 1.2 percent. However, if the deviation between the theoretical and the experimental values are plotted as a function of V/V_0 (fig. 3), a systematic departure becomes apparent. The functional deviation varies linearly with V/V_0, with a slope that is approximately temperature independent.

These results support the statement that F_λ is a function of V/V_0 alone for liquid argon, but that the functional form given by eq. (10) is not quite correct.

The present data are most conveniently represented by a function $F'_\lambda(V/V'_0)$, written in terms of a correction to eq. (10), in the form

$$F'_\lambda \left(\frac{V}{V'_0} \right) = F_\lambda \left(\frac{V}{V'_0} \right) \left[A + B \left(\frac{V}{V'_0} \right) \right]. \tag{12}$$

Here, A and B are temperature-independent coefficients within the present range of thermodynamic states. The change in the representational function requires adjustment of the values of the characteristic volumes V'_0 that secure the optimum agreement for each isotherm. The new values are listed in table VI for the optimum values of the coefficients $A = 0.40$ and $B = 0.28$. With this set of parameters the standard deviation along any isotherm does not exceed ± 0.4 mW m^{-1} K^{-1} which is consistent with the estimated accuracy of the experimental data.

The comparison between the theoretical values evaluated with the corrected

Table VI
Hard-core volumes for argon from hard-sphere theory.

T (K)	$10^6 V_0$ (m^3 mol^{-1})	σ (mW m^{-1} K^{-1})	$10^6 V'_0$ (m^3 mol^{-1})	σ (mW m^{-1} K^{-1})
107	16.18	0.59	16.77	0.38
113	16.12	0.84	16.50	0.27
118	16.06	1.2	16.40	0.37
124	16.00	0.73	16.01	0.21
130	15.94	1.09	15.52	0.39

function $F_\lambda(V/V_0')$ and the experimental data is shown in fig. 4 as a deviation plot, and there is now no systematic departure between theory and experiment.

The success of the correlation of eqs. (1) and (12) in representing the thermal conductivity of argon allows us to perform reliable interpolation and extrapolation of the experimental data. For example, we can use the represen-

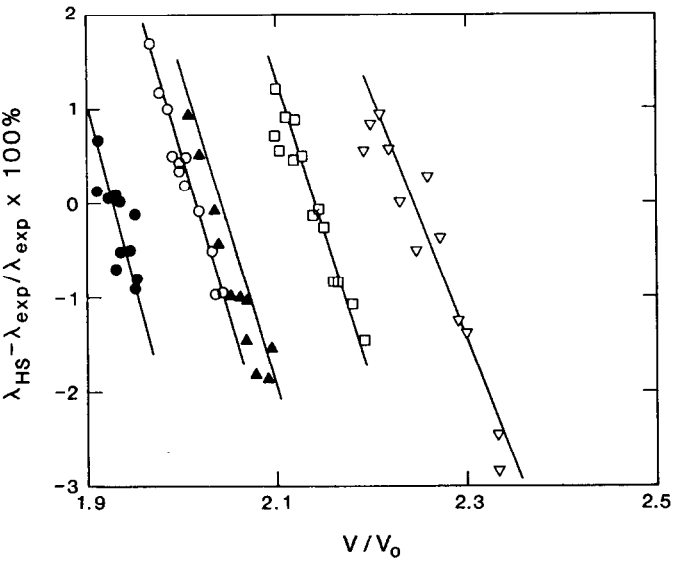

Fig. 3. Deviations between the hard-sphere values and the experimental data as a function of V/V_0. Symbols are the same as in fig. 2.

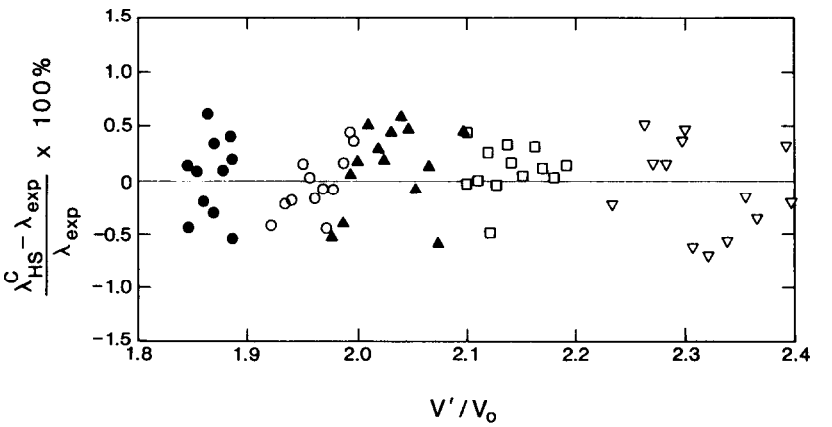

Fig. 4. Deviations between the corrected hard-sphere values and the experimental ones as a function of V'/V_0. Symbols are the same as in fig. 2.

Table VII
Thermal conductivity values of argon extrapolated to the saturation line, $mW\,m^{-1}\,K^{-1}$.

		Eq. (3)	Corrected hard spheres model	Ref. 19	
T (K)	ρ_{sat} ($kg\,m^{-3}$)	λ_{sat}	λ_{sat}	λ_0	λ_{sat}
107	1262	100.6	100.5	6.82	100.7
113	1217	92.96	92.34	7.19	93.10
118	1176	86.57	87.04	7.50	86.83
124	1124	78.88	79.25	7.87	79.28
130	1065	71.09	71.91	8.24	71.57

tation to obtain an estimate of the thermal conductivity of liquid argon on the saturation line, which is impossible to measure directly with the present method. An estimate of the same quantity can also be made by the extrapolation of eq. (3) to saturation conditions.

Table VII compares the results obtained by both extrapolations and the correlation of ref. 19. It can be seen that the extrapolation procedures used agree within ±1 percent, being almost coincident at the lowest temperature. However, and because the correlation has some theoretical basis, we prefer to consider the values obtained with the corrected hard sphere theory as more reliable. Table VII also shows that the correlation of ref. 19 yields a reasonably correct behavior of the thermal conductivity of argon along the saturation line.

5. Conclusion

New experimental data of the thermal conductivity of liquid argon were obtained with a transient hot-wire instrument, having an estimated accuracy better than 0.5 percent. It was found that the excess thermal conductivity is a function of density alone in the range of thermodynamic states covered.

The hard-sphere theory of the dense fluid state, while not strictly applicable to the low-temperature high-density state does seem to form the basis of a reliable correlation scheme capable of accurate extrapolation. An empirical adaptation of the theory is able to represent the experimental data with a standard deviation of ±0.3 percent and a maximum deviation of ±0.7 percent.

These results seem to suggest the measurement of the thermal conductivity of argon in a much wider density range, as well as of krypton and xenon, in order to confirm the proposed corrections to the smooth hard-sphere theory. We hope to report the results of such research in the near future.

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