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The thermal conductivity of argon in the critical region

B. W. Tiesinga, E. P. Sakonidou, and H. R. van den Berg

Van der Waals-Zeeman Laboratory, University of Amsterdam, Valckenierstraat 67, 1018 XE Amsterdam, The Netherlands

J. Luettmmer-Strathmann and J. V. Sengers

Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

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We have measured the thermal conductivity of argon at temperatures from 302 K down to 150.8 K and at densities up to 25 mol L⁻¹. The data were obtained with a steady-state method and we employed a guarded parallel-plate apparatus designed especially for investigating the thermal conductivity of fluids in the critical region. To interpret the data in the critical region a scaled crossover equation of state for argon in the critical region has been constructed. Equations for the thermal conductivity and viscosity of argon as a function of density and temperature are presented.

I. INTRODUCTION

This paper is concerned with an experimental and theoretical study of the behavior of the thermal conductivity of a fluid in the critical region. Argon was selected for this study, since this monatomic fluid is often used experimentally as a reference fluid for calibration, while it also serves as a model system for molecular computer simulations. Although experimental measurements of the thermal conductivity of argon as a function of density and temperature have been reported by a number of investigators,¹⁻¹⁶ a re-examination of the thermal conductivity in the critical region is of interest in view of recent advances in the theoretical treatment of the effects of critical fluctuations on the thermodynamic and transport properties of fluids.

Most of the early thermal-conductivity data have been obtained with a steady-state method in which the fluid, subjected to a stationary temperature gradient is located between two vertical concentric cylinders.²⁻⁵ More recently, the transient hot-wire method has become the preferred method for measuring the thermal conductivity of fluids including argon.⁶⁻¹⁰ In particular, Roder and collaborators have used the latter method to measure the thermal conductivity of argon in a wide range of densities and temperatures.¹¹⁻¹⁶

The thermal-conductivity data to be presented in this paper have been obtained with a parallel-plate apparatus as part of a Ph.D. project of one of the authors.¹⁷ The steady-state concentric-cylinder method and the transient hot-wire method are not suitable for measuring the thermal conductivity of fluids in the near-critical region because of the high probability of convective heat transfer.¹⁸ For the near-critical region a parallel-plate method, in which a thin horizontal fluid layer is subjected to a stationary temperature gradient imposed by heating the layer from above, is to be preferred.^{19,20} For this reason we have used a parallel-plate apparatus to measure the thermal conductivity of argon as a function of density and temperature. The primary purpose of this project was to obtain more detailed information on the behavior of the thermal conductivity of argon in the critical region. In addition, by including also measurements outside the near-critical region we have obtained a check on the ac-

curacy of the more popular transient hot-wire method for measuring the thermal conductivity of dense fluids.

II. EXPERIMENTAL METHOD

The thermal-conductivity apparatus employed in this research is shown in Fig. 1. The actual thermal-conductivity cell [(6)-(10)] is enclosed in a pressure vessel (1) which in turn is located inside a cryostat. This cylindrical cell contains an upper plate (6) and a lower plate (7) with surfaces that are polished flat and covered with a thin layer of gold. The plate surfaces are adjusted horizontally. The upper plate is surrounded by a guard plate (8). All sections of the upper plate, lower plate and guard plate are made of electrolytic copper. Heaters and thermometers, made of platinum, are located in grooves inside the plates and are electrically insulated from the copper sections by beads of beryllium oxide. The width $d = (154 \pm 2) \mu\text{m}$ of the gap (10) between the upper and lower plate is fixed by three glass spacers between the lower plate and the guard plate. The total height of the thermal-conductivity cell is 47 mm and its diameter is 67 mm. Heat is generated in the upper plate and transferred to the lower plate through the horizontal fluid layer in the gap between the plates.

The thermal conductivity λ is deduced from the equation

$$\lambda = \frac{dQ}{A\Delta T}, \quad (2.1)$$

where Q is the power generated in the upper plate to maintain a stationary temperature difference ΔT across the fluid layer between the upper and lower plate, while A (11.518 cm²) is the effective area of the upper plate. The ratio d/A in Eq. (2.1) is a cell constant which varies with temperature as

$$\frac{d}{A} = \left(\frac{d}{A} \right)_{293} [1 + 2.72 \times 10^{-5} (T/\text{K} - 293)], \quad (2.2)$$

where $(d/A)_{293} = (0.134 \pm 0.002) \text{ m}^{-1}$ is the value of the cell constant at a temperature $T = 293 \text{ K}$ and pressure $P = 0.1 \text{ MPa}$. Pressure effects on the cell constant are negligible. A small correction for radiative heat transfer is applied to the power Q .

FIG. 1. The pressure vessel and cryostat: (1) pressure vessel; (2) lid of the vessel; (3) coupling nut; (4) Bridgeman seal; (5) electrical feedthrough; (6) upper plate; (7) lower plate; (8) guard ring/plate; (9) insulation cap; (10) measuring gap with spacers; (11) mounting table; (12) telescopic tubes; (13) and (14) platinum resistance thermometers; (15) and (16) thermocouples; (17) main heater; (18) auxiliary heater; (19) disk for auxiliary heater; (20) copper cylinder; (21) lid of cryostat; (22) suspending rods for pressure vessel; (23) suspending rods for cryostat; (24) leveling screws; (25) filling capillary; (26) radiation shield; (A) and (B) connecting tubes.

To ensure that the power Q generated in the upper plate is dissipated through the fluid layer, the guard plate (8) is maintained at the same temperature as the upper plate (6). The guard plate in turn is surrounded by an insulation cap (9) made of kufalit, which is a composite material consisting of araldite and powdered magnesium silicate. This material is a good electrical as well as thermal insulator and it has a thermal-expansion coefficient comparable to that of copper. The latter property is important for the measurements at low temperatures (150 K) so as to ensure that no deformation of the cell and, hence, no change of the gap width will occur upon lowering the temperature.

The same thermal-conductivity apparatus was used to measure the thermal conductivity of ethane reported in a previous publication.²¹ For the measurements of the thermal conductivity of argon at cryogenic temperatures the cryostat, evacuated through tube A, was surrounded by liquid nitrogen contained in a big Dewar vessel. This is the main difference with the measurements of the thermal conductivity of ethane²¹ and of mixtures of carbon dioxide and ethane²² as far as the experimental setup is concerned. The temperature-regulation system is the same. A platinum resistance thermometer (13), located in the bottom of the pressure vessel, serves as temperature sensor and is incorporated in a Thomson bridge circuit. This bridge feeds a proportional-integrating regulation system for the current through two evenly wound manganin wires (17) at the outside of the pressure vessel. The cryostat consists of a copper cylinder (20), with a diameter of 203 mm, which is soldered to the lid (21) that is in turn suspended by means of three stainless-steel rods (23) from a plate. This system is provided with screws (24) to adjust the position of the cryostat so that the plates of the thermal-conductivity cell are exactly horizontal. Another feature for cryogenic measurements is that with the differential copper-constantan thermocouples (15) and (16) temperature differences can be detected between the nut (3) of the pressure vessel and its bottom. Any such temperature differences are eliminated with an auxiliary heating system (18) consisting of a 3 mm thick copper disk (19) which is mounted on the nut (3) and is provided with grooves in which a manganin resistor is located. Finally, tube B contains a copper radiation shield (26) that only at the top of this tube makes thermal contact so that no fluid will condense in the filling capillary (25) inside this tube.

For a more detailed description of the apparatus and of the experimental procedure the reader is referred to a previous publication.²³ Additional information including the application to argon can be found in the Ph.D. dissertation of one of the authors¹⁷ and also in an earlier report.²⁴

III. EXPERIMENTAL RESULTS

The argon gas used for the thermal-conductivity measurements was supplied by L'Air-Liquide and had a stated purity of 99.9997%. The thermal conductivity of argon in the critical region was measured at constant density as a function of temperature. Thermal-conductivity data were obtained at 15 isochores covering a density range from 0.07 to 24.55 mol L⁻¹. To obtain the value of the density ρ corresponding to each isochore the filling pressure was measured at a temperature of approximately 163 K which is about 12.5 K above the critical temperature. This density was then calculated from the observed pressure and temperature through equations of state as specified below. As additional checks on the operation of the thermal-conductivity apparatus the thermal conductivity was also measured isothermally as a function of pressure at two temperatures slightly above room temperature.

For the calculation of the densities associated with the experimental isochores, as well as for the interpretation of the thermal-conductivity measurements, we need an accurate

equation of state. Outside a range of temperatures and densities bounded by

$$148 \text{ K} \leq T \leq 180 \text{ K}$$

$$7.5 \text{ mol L}^{-1} \leq \rho \leq 20 \text{ mol L}^{-1}, \quad (3.1)$$

we used a global equation of state proposed by Stewart and Jacobsen.²⁵ The equation of state of Stewart and Jacobsen remains analytic at the critical point and, hence, it does not account for the known singular behavior of the thermodynamic properties near the critical point.²⁶ To remedy this problem we developed a new equation of state for argon in the critical region that includes the universal scaling-law behavior of the thermodynamic properties. For this purpose we adopted a crossover equation of state based on a six-term Landau expansion in a parametric form as proposed by Luettmmer-Strathmann *et al.*²⁷ and used it at temperatures and densities inside the region specified by Eq. (3.1). This crossover equation of state for argon in the critical region is specified in Appendix A. In developing this crossover equation of state care was taken to obtain consistency with the equation of state of Stewart and Jacobsen, at temperatures above the critical temperature where we measured the thermal conductivity.

For the critical temperature, pressure, and density of argon we have adopted the values

$$T_c = 150.663 \text{ K}, \quad P_c = 4.860 \text{ MPa},$$

$$\rho_c = 13.395 \text{ mol L}^{-1}. \quad (3.2)$$

The values quoted above for T_c and P_c are those recommended by Stewart and Jacobsen.²⁵ However, the value $\rho_c = 13.29 \text{ mol L}^{-1}$ quoted by Stewart and Jacobsen appears to be inconsistent with the isochoric specific-heat-capacity data of Anisimov *et al.*²⁸ which imply²⁹ $\rho_c = 13.395 \text{ mol L}^{-1}$. The global equation of state of Stewart and Jacobsen is based on temperatures in terms of IPTS-68. In this paper, therefore, we continue to express all temperatures in terms of IPTS-68 as well. The critical parameters used in this paper are close to the values $T_c = 150.673 \text{ K}$ and $\rho_c = 13.41 \text{ mol L}^{-1}$ very recently determined by Wagner and co-workers.³⁰

The experimental results obtained for the thermal conductivity of argon in the critical region are presented in Table I. For each measurement we give the average temperature T in the fluid layer between the two horizontal plates, the density ρ , the thermal-conductivity coefficient λ , and the temperature difference ΔT between the upper and lower plate used in the measurement. Moreover, for each isochore we show in the first line the filling pressure P and the density ρ calculated from the equation of state. There are some minor changes in the density of the isochores at densities and temperatures close to the critical point, because they have been corrected for the effect of gravity which induces a density profile³¹ along the 70 mm height of the pressure vessel that contains the thermal-conductivity cell. The measuring gap between the two horizontal plates is located 12 mm above the bottom of the pressure vessel. The maximum deviation of the calculated local density from the average filling density is +1.3%. Any temperature gradient over the interior of the pressure vessel would also affect the value of the local den-

sity. Such a temperature gradient was not observed so that no temperature corrections on the local density were applied. The average temperature of the fluid layer in the gas was obtained as $T_0 + \frac{1}{2}\Delta T + \frac{1}{3}\Delta T$, where T_0 is the temperature measured with the thermometer located at the position (14) in the bottom of the pressure vessel as indicated in Fig. 1; the contribution $(1/5)\Delta T$ to the average temperature accounts for the temperature increase of the lower plate due to the dissipation of heat received from the upper and guard plates. The temperatures T have actually been shifted by -0.12 K with respect to values published earlier^{17,24} in order to match the data with the critical temperature given in Eq. (3.2).

To avoid convection in the critical region it is important to apply small temperature differences ΔT . As can be seen from Table I for measurements very close to the critical point, the applied temperature difference was reduced to values less than 1 mK. As a check it was verified that the observed thermal conductivity λ remained independent of the applied temperature difference ΔT . These check measurements are included in Table I. Experimental results for the thermal conductivity of argon as a function of pressure at $T = 298.15 \text{ K}$ are presented in Table II.

The thermal-conductivity apparatus used for measuring the thermal conductivity of argon was subsequently used to measure the thermal conductivity of ethane²¹ and of mixtures of carbon dioxide and ethane^{22,32} in the critical region. After the experiments with the mixtures of carbon dioxide and ethane were completed, we installed an improved automated version for measuring the thermal conductivity as will be described in a future publication. As a check we used this automated version to measure the thermal conductivity of argon as a function of pressure at $T = 302 \text{ K}$. The results of these more recent measurements are presented in Table III. With the new automated setup different values of the temperature difference ΔT at a given pressure and temperature can be imposed readily. The temperature differences applied are also included in Table III. It was verified that the observed thermal conductivities are independent of ΔT with a standard deviation well below 0.2%.

In Fig. 2 we have plotted the thermal conductivity as a function of density along ten isotherms at average temperatures ranging from 150.79 to 168.13 K. In Fig. 3 we show the thermal conductivity along eight isochores in the critical region. In constructing these figures we applied minor corrections to the experimental thermal-conductivity values so that all data in Fig. 2 correspond to the same temperatures and those in Fig. 3 to the same densities. These small percentage corrections were calculated with the aid of the representative equation specified in Sec. IV.

The data shown in Figs. 2 and 3 demonstrate the pronounced enhancement of the thermal conductivity in the critical region as observed for many other fluids.^{19,21,33-35} The critical enhancement of the thermal conductivity of argon has been investigated previously by Bailey and Kellner^{3,36} and by Roder and co-workers.^{15,16} A detailed comparison of our results with those obtained by Bailey and Kellner and by Roder *et al.* will be presented in Sec. V. The previous studies yield information on the thermal conductivity of argon in the supercritical region down to a temperature

TABLE I. Experimental results for argon in the critical region along isochores.

P (MPa)	T (K)	ρ (mol L ⁻¹)	λ (mW m ⁻¹ K ⁻¹)	ΔT (mK)
0.093	163.03	0.0690		
	174.68	0.069	10.85	155.5
	163.14	0.069	10.15	159.6
	151.03	0.069	9.40	33.7
1.383	163.21	1.1057		
	163.12	1.106	11.33	142.2
2.572	163.19	2.2388		
	163.12	2.239	12.39	127.6
	159.16	2.239	12.39	127.9
	153.64	2.239	12.19	86.5
6.014	150.87	2.239	12.03	127.3
	163.04	8.1578		
	168.15	8.158	23.6	41.3
	168.14	8.158	23.6	27.3
	161.68	8.158	24.3	25.6
	155.18	8.158	26.1	22.9
	155.14	8.158	25.9	11.7
	153.64	8.158	26.9	22.0
	152.60	8.159	27.9	21.1
	151.81	8.159	28.2	20.8
	151.34	8.159	28.6	20.4
	151.08	8.159	28.6	20.4
6.801	150.81	8.159	28.5	20.4
	163.07	11.183		
	168.12	11.18	30.1	17.9
	163.05	11.18	31.3	16.7
	159.09	11.18	33.4	10.2
	159.09	11.18	33.6	10.2
	155.11	11.18	37.4	8.9
	153.59	11.19	40.6	8.1
	152.55	11.19	44.3	7.4
	151.52	11.19	51.2	3.78
	151.02	11.19	58.1	3.32
	150.91	11.19	60.8	3.17
	150.90	11.20	60.1	1.60
	150.79	11.20	63.4	1.52
7.061	163.09	12.394		
	168.12	12.39	31.6	17.1
	163.07	12.40	33.8	15.5
	159.09	12.40	36.3	9.4
	159.09	12.40	36.4	9.4
	155.11	12.40	41.5	8.0
	155.11	12.40	41.9	8.0
	153.59	12.40	45.7	7.2
	152.54	12.40	51.2	6.4
	151.51	12.41	64.3	3.01
	151.51	12.41	67.0	2.89
	151.01	12.43	84.9	2.27
	151.01	12.43	87.3	1.30
	151.01	12.43	86.5	2.22
	150.90	12.45	101.	0.75
	150.90	12.45	98.	0.49
	150.90	12.45	103.	0.33
	150.90	12.45	99.	1.15
	150.79	12.48	124.	0.61
	150.79	12.48	123.	0.92
7.165	163.05	12.922		
	152.54	12.93	53.5	1.8
	151.51	12.94	69.6	0.84
	151.46	12.94	68.5	1.41
	151.01	12.97	103.	0.93
	151.01	12.97	100.	0.96
	151.01	12.97	95.	1.02
	150.90	13.00	115.	0.84
	150.90	13.00	126.	0.40
	150.90	13.00	122.	0.79

TABLE I. (*Continued.*)

P (MPa)	T (K)	ρ (mol L ⁻¹)	λ (mW m ⁻¹ K ⁻¹)	ΔT (mK)
7.269	150.90	13.00	110.	0.88
	150.79	13.08	167.	0.30
	150.79	13.08	168.	0.30
	150.79	13.08	142.	0.35
	150.79	13.08	157.	0.17
	150.79	13.08	169.	0.30
	163.08	13.377		
	174.56	13.38	33.0	16.7
	168.23	13.38	33.8	16.0
	165.59	13.38	34.6	15.4
	163.06	13.38	35.7	14.7
	163.06	13.38	35.6	14.8
	160.90	13.38	36.9	14.1
	159.09	13.38	38.0	9.0
	155.11	13.38	43.4	7.7
	153.59	13.38	48.2	6.9
	152.55	13.38	53.9	3.6
	151.76	13.39	65.1	3.01
	151.29	13.40	80.1	2.38
	151.29	13.40	80.5	1.20
7.270	151.01	13.43	107.	0.47
	151.01	13.43	107.	0.57
	151.01	13.43	103.	0.60
	163.11	13.355		
	168.12	13.36	33.7	16.1
	164.67	13.36	35.7	21.9
	164.64	13.36	34.4	15.4
	163.08	13.36	35.2	14.9
	159.08	13.36	37.3	9.2
	155.11	13.36	43.3	7.7
	153.59	13.36	46.6	7.1
	152.54	13.36	53.7	6.1
	151.02	13.41	100.	0.97
	151.01	13.41	98.	0.99
	150.90	13.44	131.	0.38
	150.90	13.44	125.	0.41
	150.90	13.44	130.	0.43
	163.07	14.460		
7.519	168.12	14.46	36.0	15.0
	163.06	14.46	37.3	14.1
	159.09	14.46	38.8	8.8
	159.08	14.46	39.5	8.7
	155.11	14.46	44.4	7.5
	153.62	14.46	48.2	6.9
	153.60	14.46	48.0	6.9
	152.56	14.47	52.7	6.2
	151.53	14.47	63.6	3.04
	151.01	14.49	77.6	2.49
	151.01	14.49	77.1	1.48
	150.90	14.51	85.2	1.34
	150.78	14.54	91.2	1.25
	150.78	14.54	90.3	0.84
	163.08	15.646		
7.852	168.12	15.65	37.9	14.3
	163.06	15.65	39.0	13.3
	163.06	15.65	38.8	9.0
	158.71	15.65	40.7	12.6
	155.11	15.65	43.4	7.7
	155.11	15.65	44.8	5.6
	153.59	15.65	48.1	6.9
	152.55	15.65	49.8	6.6
	151.75	15.65	52.7	6.2
	151.28	15.65	55.9	5.8
	151.02	15.66	58.3	5.58
	151.02	15.66	58.5	3.31

TABLE I. (Continued.)

P (MPa)	T (K)	ρ (mol L ⁻¹)	λ (mW m ⁻¹ K ⁻¹)	ΔT (mK)
9.343	163.09	18.744		
	168.12	18.74	43.8	18.2
	168.12	18.74	44.0	21.7
	163.07	18.74	44.5	17.4
	158.15	18.74	45.0	11.4
	155.11	18.74	46.4	16.0
	153.59	18.74	46.3	10.8
	152.56	18.74	46.7	10.6
	152.56	18.74	46.5	15.8
	151.29	18.74	46.8	15.6
	150.80	18.74	48.0	10.2
	150.80	18.74	47.3	15.4
13.736	163.12	22.333		
	168.12	22.33	53.8	30.5
	168.12	22.33	53.8	30.2
	163.10	22.33	53.5	37.7
	163.09	22.33	53.4	25.2
	155.14	22.33	53.0	24.4
	155.13	22.33	53.3	19.4
	152.55	22.33	53.2	18.9
	151.05	22.33	53.5	28.6
	151.05	22.33	53.6	18.9
16.122	163.14	23.397		
	163.10	23.40	57.5	46.5
19.552	163.14	24.551		
	163.10	24.55	62.4	42.9

$T=157$ K which is more than 6 K above the critical temperature. As can be seen from Fig. 2, we have obtained the thermal conductivity at seven isotherms closer to the critical temperature.

After the measurements were completed we noticed that a certain amount of argon gas is absorbed by the kufalit which is the insulating material surrounding the guard plate. Absorption of gas into the kufalit cap can have, in principle, two effects: a change in the density of the fluid layer investigated and a possible change in the plate distance due to swelling of the kufalit cap. We therefore made a quantitative study of the effect by monitoring the absorption and desorption process over an extended period and by checking the reproducibility of the thermal-conductivity measurements after a substantial pressure change. We concluded that the errors in the density do not exceed 1%, while the observed

change of the distance between the plates reached a maximum of 2% due to temporary mechanical deformation of the cap and subsequently vanished slowly.

To estimate the accuracy of our thermal-conductivity measurements, a distinction must be made between the data far away and close to the critical point. The power Q generated in the upper plate was measured with an accuracy of 0.1%, the temperature difference ΔT could be determined with an accuracy about ± 0.1 mK and the area A was determined with an accuracy well within 0.01%. Outside the critical region the accuracy of the thermal-conductivity measure-

TABLE III. Recent experimental results for argon at 302 K as a function of pressure.

P (MPa)	T (K)	ρ (mol L ⁻¹)	λ (mW m ⁻¹ K ⁻¹)	ΔT (mK)
0.13	302.00	0.052	17.90	13.2; 104.3
1.247		0.500	18.30	26.4; 52.0
2.476		1.000	18.77	26.2; 51.7
4.896		2.000	19.81	26.4; 51.6
7.274		3.000	20.86	25.9; 51.5
9.628		4.000	22.01	51.5
11.976		5.000	23.22	25.9
14.334		5.999	24.54	25.9; 51.2
16.731		7.000	25.93	51.1
19.182		8.000	27.41	51.0
21.704		8.996	28.93	50.8
24.353		10.000	30.55	50.8
27.130		11.000	32.28	50.5
30.079		12.000	34.10	50.2

TABLE II. Experimental results for argon as a function of pressure at $T=298.15$ K.

P (MPa)	T (K)	ρ (mol L ⁻¹)	λ (mW m ⁻¹ K ⁻¹)	ΔT (mK)
0.284	298.15	0.115	17.66	117.7
5.202		2.160	19.62	106.6
10.470		4.432	22.19	94.1
20.825		8.812	28.59	73.3
26.119		10.834	32.07	65.7
33.695		13.361	36.83	57.1
34.310		13.547	37.20	56.5
42.429		15.755	41.92	50.3
52.549		17.973	48.23	43.8

FIG. 2. The thermal conductivity of argon in the critical region as a function of density along isotherms. The symbols indicate our experimental data. The solid curves represent values calculated from the equations presented in this paper.

ments is primarily dependent on the accuracy of the plate distance d . Due to the construction of the cell we could not determine this plate distance d *a priori* on an absolute basis to better than about 4%. For the first series of measurements

presented in Tables I and II, the last decimal in the value $d = 154 \mu\text{m}$ was determined by comparing our measurements with the thermal-conductivity values previously obtained in our laboratory at 298.15 K with a parallel-plate apparatus.^{1,37} The results of the more recent measurements presented in Table III are relative to a reference value for which we adopted the value $\lambda_0 = 17.86 \text{ mW m}^{-1} \text{ K}^{-1}$ of the thermal conductivity of argon at 302 K in the limit of zero density, as follows from the correlation to be presented in Sec. IV. The estimated accuracy of our thermal-conductivity measurements outside the critical region is 2%.

The uncertainty of the thermal-conductivity measurements becomes significantly larger in the near vicinity of the critical point, and will in practice depend on the distance from the critical point. This increased uncertainty is a consequence of the need for using very small values of the temperature difference ΔT . Furthermore, the thermal conductivity becomes increasingly sensitive to errors in the local density of the fluid layer between the upper and lower plate in the thermal-conductivity cell. It is difficult to give a precise estimate of the accuracy of the thermal-conductivity values in the near-critical region. We notice that at $T = 151.5 \text{ K}$ the thermal-conductivity data show a spread near ρ_c of 5% and at $T = 150.8 \text{ K}$, which is within 0.14 K from the critical temperature, the spread becomes as large as 15%.

IV. ANALYSIS

To interpret the behavior of the thermal conductivity λ in the critical region we define a critical thermal conductivity λ_{cr} such that

$$\lambda = \bar{\lambda} + \lambda_{cr}, \quad (4.1)$$

where $\bar{\lambda}$ is a regular or background thermal conductivity which one would expect in the absence of critical fluctuations.^{38,39} In practice we develop an equation for $\bar{\lambda}$

FIG. 3. The thermal conductivity of argon in the critical region as a function of the reduced temperature $T/T_c - 1$ along isochores. The symbols indicate our experimental data. The solid curves represent values calculated from the equations presented in this paper.

from experimental thermal-conductivity data outside the critical region.^{21,38} The viscosity η is decomposed similarly as

$$\eta = \bar{\eta} + \eta_{\text{cr}}. \quad (4.2)$$

The critical part λ_{cr} of the thermal conductivity diverges asymptotically close to the critical point as^{39–42}

$$\lambda_{\text{cr}} = \frac{RkT}{6\pi\eta\xi} \rho c_p, \quad (4.3)$$

where k is Boltzmann's constant, c_p the isobaric molar heat capacity, ξ the correlation length, and where $R=1.03$ is a universal amplitude.⁴³ The viscosity diverges as⁴²

$$\eta_{\text{cr}} = \bar{\eta}[(Q_0\xi)^z - 1], \quad (4.4)$$

where Q_0 is a system-dependent amplitude and where $z=0.063$ is a universal exponent.^{44–47}

The validity of the asymptotic equations (4.3) and (4.4) is restricted to a very small range of temperatures and densities near the critical point.³⁹ To interpret the actual behavior of the transport properties of fluids in the critical region one needs to include the nonasymptotic critical behavior of the transport properties. Equations that include the nonasymptotic critical behavior have been derived by Olchowy and Sengers^{48,49} from an approximate global solution of the mode-coupling equations for the effects of long-range fluctuations on the transport properties. As a result, the asymptotic equations (4.3) and (4.4) are generalized to^{21,50}

$$\lambda_{\text{cr}} = \frac{RkT}{6\pi\eta\xi} \rho c_p (\Omega - \Omega_0) \quad (4.5)$$

and

$$\eta_{\text{cr}} = \bar{\eta}(e^{zH} - 1), \quad (4.6)$$

where Ω , Ω_0 , and H are functions of temperature and density as specified in Appendix B. They depend on the specific heat capacities c_p and c_v , on the background transport properties $\bar{\lambda}$ and $\bar{\eta}$, and on the correlation length ξ . Equations for calculating ξ as a function of temperature and density are also included in Appendix B. In addition the functions Ω , Ω_0 , and H contain a system-dependent parameter q_D which represents a large cutoff of the wave numbers of the critical fluctuations. Equations (4.5) and (4.6) have been used to represent the critical enhancement of the transport properties of a number of fluids^{21,34,35,51–53} including argon.¹⁶

To apply Eq. (4.5) we need to specify the background transport properties $\bar{\lambda}$ and $\bar{\eta}$, which are decomposed as

$$\bar{\lambda} = \lambda_0(T) + \Delta\lambda, \quad (4.7)$$

$$\bar{\eta} = \eta_0(T) + \Delta\eta. \quad (4.8)$$

Here, $\lambda_0(T)$ and $\eta_0(T)$ are the values of the transport properties in the dilute-gas limit, which can be calculated from the kinetic theory of gases,⁵⁴ while $\Delta\lambda$ and $\Delta\eta$ are commonly referred to as excess thermal conductivity and excess viscosity.^{38,55} Recommended values for $\lambda_0(T)$ and $\eta_0(T)$ of argon are provided by a correlation of Kestin *et al.* based on extended corresponding states.⁵⁶ However, from an evaluation of various correlations for $\lambda_0(T)$ and $\eta_0(T)$ we have

TABLE IV. Coefficients in Eqs. (4.9)–(4.14) for the background transport properties $\bar{\lambda}$ and $\bar{\eta}$.^a

$\lambda_{00}=2.533\,41\times 10^{-1}$	$\eta_{00}=3.230\,54\times 10^{-1}$
$\lambda_{01}=4.718\,04\times 10^{-3}$	$\eta_{01}=6.071\,52\times 10^{-3}$
$\lambda_{02}=-1.006\,38\times 10^{-5}$	$\eta_{02}=-1.303\,02\times 10^{-5}$
$\lambda_{03}=1.120\,16\times 10^{-8}$	$\eta_{03}=1.455\,13\times 10^{-8}$
$\lambda_{04}=-4.940\,65\times 10^{-12}$	$\eta_{04}=-6.428\,92\times 10^{-12}$
$\lambda_{10}=1.026\,88$	$\eta_{10}=9.845\,74\times 10^{-2}$
$\lambda_{11}=-1.327\,91\times 10^{-5}$	$\eta_{11}=1.199\,90\times 10^{-3}$
$\lambda_{20}=-4.473\,80\times 10^{-2}$	$\eta_{20}=1.069\,76\times 10^{-1}$
$\lambda_{21}=3.193\,47\times 10^{-5}$	$\eta_{21}=-6.796\,21\times 10^{-5}$
$\lambda_3=1.799\,71\times 10^{-2}$	$\eta_3=-8.286\,56\times 10^{-3}$
$\lambda_4=-2.314\,64\times 10^{-3}$	$\eta_4=7.872\,79\times 10^{-4}$
$\lambda_5=1.630\,71\times 10^{-4}$	$\eta_5=-3.445\,62\times 10^{-5}$
$\lambda_6=-6.215\,32\times 10^{-6}$	$\eta_6=7.525\,82\times 10^{-7}$
$\lambda_7=1.231\,22\times 10^{-7}$	$\eta_7=-5.506\,80\times 10^{-9}$
$\lambda_8=-9.872\,33\times 10^{-10}$	

^a λ in $\text{mW m}^{-1} \text{K}^{-1}$, η in $\mu\text{Pa s}$, T in K, ρ in mol L^{-1} .

concluded, in accordance with the conclusion of Bich *et al.*^{57,58} that a better representation of the experimental data is obtained, if these transport coefficients are calculated from the collision integrals supplied by Aziz *et al.*^{59,60} for the HFD (Hartree–Fock dispersion)-B potential with the molecular parameters $\sigma=0.335\,28$ nm and $\epsilon/k=143.224$ K. We found that the resulting values for $\lambda_0(T)$ and $\eta_0(T)$ in the temperature range from 90 to 700 K can be represented to within 0.1% by simple equations of the form

$$\lambda_0(T) = (T/K)^{1/2} \sum_{i=0}^4 \lambda_{0i}(T/K)^i, \quad (4.9)$$

$$\eta_0(T) = (T/K)^{1/2} \sum_{i=0}^4 \eta_{0i}(T/K)^i \quad (4.10)$$

with coefficients λ_{0i} and η_{0i} presented in Table IV.

It turns out that the excess transport coefficients $\Delta\lambda$ and $\Delta\eta$ of simple fluids depend only weakly on temperature and they are often represented by polynomials in the density ρ with coefficients λ_i and η_i taken to be independent of temperature^{21,38,51–53}

$$\Delta\lambda = \sum_{i=1}^{n=8} \lambda_i(\rho/\text{mol L}^{-1})^i, \quad (4.11)$$

$$\Delta\eta = \sum_{i=1}^{n=7} \eta_i(\rho/\text{mol L}^{-1})^i, \quad (4.12)$$

as was also done by Le Neindre⁴ based on high-temperature concentric-cylinder data and more recently by Perkins *et al.*¹⁶ based on low-temperature transient-hot-wire data. It should be noticed that the values of the excess thermal conductivity calculated from the correlation of Le Neindre *et al.* are systematically about 4% (relative to the total thermal-conductivity value) higher than the corresponding values from Perkins *et al.* for the temperature and density ranges where both correlations overlap. Moreover, other thermal-conductivity data at temperatures above 300 K and densities above 15 mol L^{-1} (mostly derived from steady-state mea-

TABLE V. Data used for determination of the correlation for the excess thermal conductivity $\Delta\lambda$. P.P.=parallel plate, C.C.=concentric cylinder, T.H.W.=transient hot wire.

Author	Method	# of points	Temp. range (K)	Dens. range (mol L ⁻¹)
Sengers ^a	P.P.	84	273.15–348.15	0–30
Ikenberry ^b	C.C.	8	≈166–235	0–29
Bailey ^c	C.C.	28	≈160–298	0–30
Tufeu ^d	C.C.	81	≈302–607	0–23
Le Neindre ^e	C.C.	101	298.15–674.15	0–34
Kestin ^f	T.H.W.	32	300.65	0–14
Roder ^g	T.H.W.	130	157–324	0–31
This work	P.P.	13	≈151–175; 298.15	0–25
		477		

^aReference 37.

^eReferences 4, 5, and 65.

^bReference 2.

^fReference 6.

^cReference 3.

^gReference 15, 16, and 66.

^dReference 64.

measurements) appear also to be beyond the 2% limit of the correlation of Perkins *et al.*¹⁶ The assumption that the coefficients λ_i and η_i in Eqs. (4.11) and (4.12) can be treated as independent of the temperature is only valid approximately. There exists experimental⁶¹ and theoretical evidence^{62,63} that the leading coefficients λ_i and η_i do depend on temperature. Hence, in the present analysis we have allowed the coefficients of the first two terms in the expansions (4.11) and (4.12) to vary linearly with temperature

$$\lambda_i = \lambda_{i,0} + \lambda_{i,1}T/K, \quad (4.13)$$

$$(i = 1, 2)$$

$$\eta_i = \eta_{i,0} + \eta_{i,1}T/K. \quad (4.14)$$

To determine the coefficients in Eqs. (4.11) and (4.13) for the excess thermal conductivity $\Delta\lambda$ we considered the data sources listed in Table V. We omitted those data points for which the critical-enhancement contribution was estimated to be well above 1% and also a few points with an exceptional experimental error, leaving a total of 477 data. The corresponding densities were recalculated from the measured temperatures and pressures with the equations of state as specified in Sec. III. For the data reported by Roder *et al.*¹⁵ the appropriate temperatures, i.e., the average measuring temperatures, had to be rederived from the original data set.^{66,67} In Table V we have also indicated the experimental method, the number of data points retained from each individual author and the temperature and density range of the data. To reduce the effect of any systematic errors,⁵¹ we deduced values for the excess thermal conductivity by subtracting a dedicated zero-density value λ_0 , i.e., the particular value implied by the same individual data set. A comparison between these experimental values λ_0 measured by the various authors and the values calculated from our representative equation (4.9) is shown in Fig. 4. In Fig. 4 we have also included λ_0 values implied by the thermal-conductivity measurements at low densities obtained by Mardolcar *et al.*,⁹ by Millat *et al.*,¹⁰ and by Li *et al.*⁶⁸ with transient hot-wire methods.

FIG. 4. Percentage differences between experimental values for the thermal conductivity λ_0 of argon in the zero-density limit, measured by various authors, and the values calculated from the correlation, Eq. (4.9), as a function of temperature.

A fit with equal weights of the experimental excess thermal conductivities with an eighth degree polynomial in the density, Eq. (4.11), but with temperature-independent coefficients λ_i yielded a standard deviation $\sigma_\lambda = 1.2\%$ for $\Delta\lambda/\bar{\lambda}$. Introducing a linear temperature dependence of λ_1 yielded a substantial decrease of σ_λ by about 30% and a simultaneous linear temperature dependence of λ_1 and λ_2 yielded an additional decrease of σ_λ by about 20% to $\sigma_\lambda = 0.6\%$. However, a quadratic temperature dependence of λ_1 or an additional linear temperature dependence of λ_3 did not yield any significant decrease of σ_λ . Hence, we only retained a linear temperature dependence of λ_1 and λ_2 in accordance with Eq. (4.13). The values of the coefficients in Eqs. (4.11) and (4.13) are included in Table IV. From the values of the standard deviations σ_λ obtained for the different fits to the excess thermal conductivity and from the magnitude of the coefficients λ_{11} and λ_{21} the following conclusions can be drawn:

(i) The introduction of temperature-dependent coefficients λ_1 and λ_2 in Eq. (4.11) gives a significant improvement of the representation for the excess thermal-conductivity data.

(ii) The initial-density coefficient λ_1 shows a very weak temperature dependence, so that the temperature dependence of the excess thermal conductivity is practically completely accounted for by the temperature dependence of the coefficient λ_2 . For instance, due to the temperature dependence of the coefficients λ_1 and λ_2 , a temperature change of 200 K causes, at a density $\rho = 20$ mol L⁻¹, a change in the separate terms $\lambda_1\rho$ and $\lambda_2\rho^2$ of, respectively, 0.1% and 6% relative to the total excess thermal-conductivity value.

A comparison between the experimental excess thermal conductivities and the values calculated from Eqs. (4.11) and (4.13), relative to the total thermal conductivity λ , is shown in Fig. 5. It is seen that most of the experimental data, independent of the method by which the data were obtained, agree with the correlating equation within 1.5%. In Fig. 5 we have also displayed the results of our most recent measurements, obtained at 302 K (filled circles) and presented in

FIG. 5. Percentage differences between experimental values for the excess thermal conductivity $\Delta\lambda$ measured by various authors, and the values calculated from Eqs. (4.11) and (4.13) as a function of density.

Table III, as well as a representative selection of recent measurements obtained by Li *et al.*⁶⁸ We note that both data sets agree with the correlating equation within 0.5%, although these data were not included in developing the correlating equation. We estimate that Eqs. (4.11) and (4.13) represent the excess thermal conductivity of argon in a temperature and density range bounded by

$$150 \text{ K} \leq T \leq 650 \text{ K}, \quad 0 \text{ mol L}^{-1} \leq \rho \leq 35 \text{ mol L}^{-1}. \quad (4.15)$$

Rainwater and co-workers^{62,69} have proposed a theoretical procedure for calculating the coefficients λ_1 and η_1 of the first density correction in Eqs. (4.11) and (4.12), which has been further developed by Vogel and co-workers.^{63,70} In Fig. 6 we compare the coefficient λ_1 deduced from our fit, Eq. (4.13), to the experimental thermal-conductivity data with values of λ_1 calculated by Vogel *et al.* on the assumption that the molecular interaction of argon can be represented by a Lennard-Jones potential⁶³ with molecular parameters $\sigma = 0.341 \text{ nm}$ and $\epsilon/k = 125 \text{ K}$.

Since the calculated uncertainty of our experimental λ_1 is about 7%, it can be concluded that the experimental and theoretical results for λ_1 overlap within this range of uncertainty. However, this agreement is mainly accidental. First, the Lennard-Jones 12–6 potential that has been used in the theory is only approximate for monatomic gases. Secondly, the extraction of λ_1 from the excess thermal-conductivity correlation is not very reliable, since this correlation has been developed as a mathematical representation of excess thermal-conductivity data without giving special attention to the physical meaning of the various coefficients in the correlation. More reliable reference values for comparison with the theoretical result are obtained by the introduction of ex-

FIG. 6. The coefficient λ_1 of the first density correction to the thermal conductivity as a function of temperature. The line represents the values of λ_1 implied by our correlating equation. The two data points represent estimated experimental values of λ_1 at about 300 K. The dashed curve represents λ_1 calculated by Vogel and co-workers on the assumption that the argon molecular interaction can be represented by a Lennard-Jones potential.

perimental values for λ_1 which are determined in a more appropriate way, i.e., by direct determination from data sets along isotherms. The two individual points in Fig. 6 have been determined in this way from quadratic fits in the density range up to 12 mol L^{-1} to transient-hot-wire data measured along the isotherm at 300.65 K by Kestin *et al.*⁶ and to our data at 302 K (Table III; filled circles in Fig. 5). Both points fall clearly (about 20%) below the theoretical curve.

To determine the coefficients in Eqs. (4.12) and (4.14) for the excess viscosity $\Delta\eta$ we considered the data sources listed in Table VI from which we took a total of 346 data points. The values of the viscosity η_0 in the zero-density limit implied by these data sources are compared with our representative equation (4.10) in Fig. 7. In this figure we have also included data obtained by Reynes *et al.*,⁷⁷ although their viscosity measurements at higher densities have not been taken into account since they exhibit deviations up to 8% at $\rho = 17 \text{ mol L}^{-1}$.

To represent the experimental excess viscosities we have adopted a seventh degree polynomial in the density and

TABLE VI. Data used for the determination of the correlation for excess viscosity $\Delta\eta$. exc. n means n points are excluded for the determination of the final correlation; C.F.=capillary flow, O.D.=oscillating disk, T.C.=torsional crystal.

Author	Method	# of points	Temp. range (K)	Dens. range (mol L ⁻¹)
Michels ^a	C.F.	96	273.15–348.15	0–29
Flynn ^b	C.F.	27	194.65–373.15	0–17
Gracki ^c	C.F.	47 exc.2	173.15–298.15	0–21
Kestin ^d	O.D.	40	298.15	0–4
Vermesse ^e	C.F.	25	308.15	5–40
Haynes ^f	T.C.	117 exc.4	173–298	0–26
		352 exc.6		

^aReference 71.

^bReference 72.

^cReference 73.

^dReference 74.

^eReference 75.

^fReference 76.

FIG. 7. Percentage differences between experimental values for the viscosity η_0 of argon in the zero-density limit, measured by various authors, and the values calculated from the correlation, Eq. (4.10), as a function of temperature.

again applied equal weights to all data points. If all coefficients η_i in Eq. (4.12) are taken as constants independent of temperature, the equation yields a standard deviation σ_η for $\Delta\eta/\bar{\eta}$ of 0.9%. Introducing a linear temperature dependence of η_1 and η_2 in accordance with Eq. (4.14) reduces σ_η to 0.5%. The values of the coefficients in Eqs. (4.12) and (4.14) are included in Table IV.

A comparison between the experimental excess viscosities and the values calculated from Eqs. (4.12) and (4.14), relative to the total viscosity η , is shown in Fig. 8. It is seen that most of the experimental data agree with the correlating equation within 1.25%. We estimate that Eqs. (4.12) and (4.14) represent the excess viscosity of argon in a temperature and density range bounded by

$$150 \text{ K} \leq T \leq 400 \text{ K}, \quad 0 \text{ mol L}^{-1} \leq \rho \leq 40 \text{ mol L}^{-1}. \quad (4.16)$$

Having determined the background transport coefficients $\bar{\lambda}$ and $\bar{\eta}$ we are now in a position to compare our experimental thermal conductivity data for argon in the critical region with the theory of Olchowy and Sengers⁴⁸ represented by Eqs. (4.5) and (4.6). These equations contain one system-dependent parameter q_D as shown explicitly in Appendix B. From a fit to our 142 experimental thermal-conductivity data shown in Table I, with weights based on the estimated accuracies mentioned in Sec. III, we obtain

FIG. 8. Percentage differences between experimental values for the excess viscosity $\Delta\eta$, measured by various authors, and the values calculated from Eqs. (4.12) and (4.14) as a function of density.

FIG. 9. The thermal conductivity of argon along three supercritical isotherms as measured by Bailey and Kellner (Refs. 3 and 36) with a concentric-cylinder apparatus. The solid curves represent values calculated from the equations presented in this paper.

$$q_D^{-1} = 0.191 \text{ nm}, \quad (4.17)$$

which is close to the value $q_D^{-1} = 0.200 \text{ nm}$ deduced by Perkins *et al.*¹⁶ from a set of data points farther above the critical temperature.

The values calculated for the thermal conductivity $\lambda = \bar{\lambda} + \lambda_{cr}$ are represented by the solid curves in Figs. 2 and 3. The calculated behavior of the thermal conductivity in the critical region is in satisfactory agreement with the experimentally observed behavior at most supercritical isotherms as can be seen from Fig. 2. At temperatures within 0.4 K from the critical temperatures the deviations increase up to 15%. However, at these temperatures the experimental data exhibit an appreciable spread also. We conclude that the equations of Olchowy and Sengers for the critical thermal-conductivity enhancement are consistent with the experimentally observed behavior.

V. COMPARISON WITH RESULTS OF OTHER INVESTIGATORS

The enhancement of the thermal conductivity of argon in the critical region has been investigated previously by Bailey and Kellner^{3,36} with a concentric-cylinder method and by Roder *et al.*^{15,16} with a transient-hot-wire method. In Figs. 9 and 10 we show the thermal-conductivity data obtained by these authors in the critical region. The solid curves in these figures indicate the values calculated from the equations in the previous section for representing our thermal-conductivity data in the critical region. The data obtained by Bailey and Kellner at 169.27 and at 160.52 K are in good agreement with our data in the entire density range except at low densities. However, the thermal-conductivity values obtained by Bailey and Kellner at 154.62 K near the critical density are substantially larger, which is obviously a consequence of the difficulty of avoiding convection in a concentric-cylinder apparatus close to the critical point. The thermal-conductivity data obtained by Roder *et al.*^{15,16} in the critical region are in agreement with our data within the

FIG. 10. The thermal conductivity of argon along two supercritical isotherms as measured by Roder *et al.* (Refs. 15 and 16) with a transient hot-wire method. The solid curves represent values calculated from the equations presented in this paper.

combined accuracy of the measurements. To appreciate the magnitude of the critical thermal-conductivity enhancement it is interesting to compare the thermal-conductivity scale in Figs. 9 and 10 with that shown in Fig. 2.

Gumerov *et al.*⁷⁸ have reported measurements of the thermal diffusivity $D_T = \lambda / \rho c_p$ of argon in the supercritical region obtained with a transient interferometric method. The thermal diffusivity data obtained at four supercritical temperatures are shown in Fig. 11. The curves represent the values calculated from the equations in the preceding section with c_p from the equation of state in the critical region. The agreement is again quite satisfactory except for some deviations at the temperature closest to the critical temperature.

Finally, in Fig. 12 we show a deviation plot of the available thermal-conductivity data between 151 and 295 K. Most of these data were not included in the determination of the

FIG. 11. The thermal diffusivity $D_T = \lambda / \rho c_p$ of argon along four supercritical isotherms as measured by Gumerov *et al.* (Ref. 78) with a transient interferometric method. The solid curves represent values calculated from the equations presented in this paper. The asterisks correspond to our experimental data adjusted to 153.16 K.

FIG. 12. Percentage differences between experimental thermal-conductivity data in the temperature range 151–295 K and the values calculated from the equations presented in this paper.

equations for the excess thermal conductivity, since the critical enhancement is well above 1% and, with the exception of our own measurements, were not used for the determination of the parameter q_D . In this figure we have not included our data points along the three near-critical isochores, which are shown in Fig. 3.

As mentioned earlier, the data of Bailey and Kellner^{3,36} show some deviations at low densities. This may be connected with possible parasitic heat flow in a concentric-cylinder apparatus whose relative contribution becomes more important at low densities.⁷⁹ Of more interest is the comparison with the measurements of Roder *et al.*^{15,16} obtained with a transient-hot-wire method. These data show deviations of $\pm 3\%$ from the correlating equation for the thermal conductivity presented in this paper, of which the critical-enhancement part is based on our results obtained with a parallel-plate method. These deviations are within but not much smaller than the combined accuracies of the two methods.

VI. CONCLUSIONS

We have obtained a detailed set of experimental data for the thermal conductivity of argon in the critical region. Our data supplement previous information obtained for the enhancement of the thermal conductivity of argon in the critical region^{3,15,16,36} and are consistent with the behavior deduced from the mode-coupling theory for the effects of critical fluctuations on the thermal conductivity.⁴⁸ We have developed representative equations for the thermal conductivity and viscosity of argon as a function of temperature and density valid in the ranges specified by Eqs. (4.15) and (4.16), respectively. Values of the thermal conductivity at selected pressures and temperatures calculated from the equations are presented in Table VII.

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TABLE VII. Thermal conductivity of argon in $\text{mW m}^{-1} \text{K}^{-1}$.

T, K	P, MPa								
	0.1	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
151.0	9.6	9.9	10.4	11.0	11.8	12.6	13.8	15.4	17.7
151.5	9.6	10.0	10.5	11.1	11.8	12.6	13.8	15.3	17.5
152.0	9.6	10.0	10.5	11.1	11.8	12.6	13.7	15.2	17.4
153.0	9.7	10.0	10.5	11.1	11.8	12.6	13.7	15.1	17.1
154.0	9.8	10.1	10.6	11.2	11.8	12.7	13.7	15.0	16.8
155.0	9.8	10.2	10.6	11.2	11.9	12.7	13.6	14.9	16.6
160.0	10.1	10.4	10.9	11.4	12.0	12.7	13.6	14.6	15.9
165.0	10.4	10.7	11.2	11.6	12.2	12.8	13.6	14.4	15.5
170.0	10.7	11.0	11.4	11.9	12.4	13.0	13.6	14.4	15.3
175.0	11.0	11.3	11.7	12.1	12.6	13.1	13.7	14.4	15.2
180.0	11.3	11.6	12.0	12.4	12.8	13.3	13.8	14.5	15.1
185.0	11.6	11.9	12.2	12.6	13.0	13.5	14.0	14.5	15.2
190.0	11.9	12.1	12.5	12.9	13.3	13.7	14.2	14.7	15.2
195.0	12.2	12.4	12.8	13.1	13.5	13.9	14.3	14.8	15.3
200.0	12.5	12.7	13.0	13.4	13.7	14.1	14.5	15.0	15.4
210.0	13.0	13.3	13.6	13.9	14.2	14.6	14.9	15.3	15.7
220.0	13.6	13.8	14.1	14.4	14.7	15.0	15.4	15.7	16.1
230.0	14.1	14.4	14.6	14.9	15.2	15.5	15.8	16.1	16.5
240.0	14.7	14.9	15.1	15.4	15.7	16.0	16.2	16.5	16.8
250.0	15.2	15.4	15.7	15.9	16.2	16.4	16.7	17.0	17.3
260.0	15.8	15.9	16.2	16.4	16.7	16.9	17.2	17.4	17.7
270.0	16.3	16.5	16.7	16.9	17.1	17.4	17.6	17.9	18.1
280.0	16.8	17.0	17.2	17.4	17.6	17.9	18.1	18.3	18.5
290.0	17.3	17.5	17.7	17.9	18.1	18.3	18.5	18.8	19.0
300.0	17.8	18.0	18.2	18.4	18.6	18.8	19.0	19.2	19.4
310.0	18.3	18.5	18.7	18.8	19.0	19.2	19.4	19.6	19.8
320.0	18.8	18.9	19.1	19.3	19.5	19.7	19.9	20.1	20.3
330.0	19.3	19.4	19.6	19.8	20.0	20.1	20.3	20.5	20.7
340.0	19.7	19.9	20.1	20.2	20.4	20.6	20.8	21.0	21.1
350.0	20.2	20.3	20.5	20.7	20.9	21.0	21.2	21.4	21.6
360.0	20.7	20.8	21.0	21.1	21.3	21.5	21.6	21.8	22.0
370.0	21.1	21.2	21.4	21.6	21.7	21.9	22.1	22.2	22.4
380.0	21.6	21.7	21.9	22.0	22.2	22.3	22.5	22.6	22.8
390.0	22.0	22.1	22.3	22.4	22.6	22.8	22.9	23.1	23.2
400.0	22.4	22.6	22.7	22.9	23.0	23.2	23.3	23.5	23.6
420.0	23.3	23.4	23.6	23.7	23.9	24.0	24.1	24.3	24.4
440.0	24.1	24.3	24.4	24.5	24.7	24.8	24.9	25.1	25.2
460.0	25.0	25.1	25.2	25.3	25.5	25.6	25.7	25.9	26.0
480.0	25.8	25.9	26.0	26.1	26.3	26.4	26.5	26.6	26.8
500.0	26.6	26.7	26.8	26.9	27.0	27.2	27.3	27.4	27.5
520.0	27.4	27.5	27.6	27.7	27.8	27.9	28.0	28.2	28.3
540.0	28.1	28.2	28.3	28.5	28.6	28.7	28.8	28.9	29.0
560.0	28.9	29.0	29.1	29.2	29.3	29.4	29.5	29.6	29.7
580.0	29.7	29.7	29.9	30.0	30.1	30.2	30.3	30.4	30.5
600.0	30.4	30.5	30.6	30.7	30.8	30.9	31.0	31.1	31.2
T, K	P, MPa								
	4.5	5.0	6.0	7.0	8.0	9.0	10.0	15.0	20.0
151.0	22.3	48.7	49.5	52.5	55.1	57.3	59.3	67.1	73.2
151.5	21.7	56.4	48.7	51.9	54.5	56.7	58.7	66.7	72.8
152.0	21.1	35.1	48.1	51.2	53.9	56.2	58.2	66.2	72.3
153.0	20.2	27.8	46.5	49.8	52.6	55.0	57.1	65.3	71.5
154.0	19.6	25.0	45.1	48.5	51.4	53.9	56.0	64.4	70.7
155.0	19.1	23.4	43.7	47.1	50.1	52.7	55.0	63.5	69.9
160.0	17.5	19.8	28.0	39.8	43.9	47.0	49.6	59.1	65.9
165.0	16.7	18.3	22.9	30.1	37.3	41.3	44.3	54.9	62.1
170.0	16.3	17.5	20.7	25.2	30.9	35.9	39.5	50.9	58.5
175.0	16.0	17.1	19.5	22.8	26.8	31.2	35.1	47.2	55.1
180.0	15.9	16.8	18.8	21.4	24.4	27.9	31.3	43.8	51.9
185.0	15.8	16.6	18.4	20.5	22.9	25.7	28.6	40.7	49.0
190.0	15.8	16.5	18.0	19.9	21.9	24.2	26.7	38.0	46.3
195.0	15.9	16.5	17.9	19.4	21.2	23.2	25.3	35.8	43.9
200.0	16.0	16.5	17.7	19.1	20.7	22.5	24.3	33.8	41.8
210.0	16.2	16.6	17.7	18.8	20.1	21.5	23.0	30.9	38.2
220.0	16.5	16.9	17.8	18.7	19.8	21.0	22.2	28.9	35.4
230.0	16.8	17.2	17.9	18.8	19.7	20.7	21.8	27.5	33.4

TABLE VII. (*Continued.*)

T, K	P, MPa								
	4.5	5.0	6.0	7.0	8.0	9.0	10.0	15.0	20.0
240.0	17.2	17.5	18.2	19.0	19.8	20.6	21.5	26.6	31.8
250.0	17.6	17.9	18.5	19.2	19.9	20.7	21.5	25.9	30.7
260.0	18.0	18.2	18.8	19.4	20.1	20.8	21.5	25.5	29.8
270.0	18.4	18.6	19.2	19.7	20.3	21.0	21.6	25.3	29.2
280.0	18.8	19.0	19.5	20.1	20.6	21.2	21.8	25.1	28.7
290.0	19.2	19.4	19.9	20.4	20.9	21.5	22.0	25.1	28.4
300.0	19.6	19.8	20.3	20.8	21.2	21.7	22.2	25.0	28.1
310.0	20.0	20.3	20.7	21.1	21.6	22.0	22.5	25.1	27.9
320.0	20.5	20.7	21.1	21.5	21.9	22.4	22.8	25.3	27.9
330.0	20.9	21.1	21.5	21.9	22.3	22.7	23.1	25.5	28.0
340.0	21.3	21.5	21.9	22.3	22.7	23.1	23.5	25.7	28.1
350.0	21.7	21.9	22.3	22.6	23.0	23.4	23.8	25.9	28.2
360.0	22.2	22.3	22.7	23.0	23.4	23.8	24.1	26.2	28.3
370.0	22.6	22.7	23.1	23.4	23.8	24.1	24.5	26.4	28.5
380.0	23.0	23.1	23.5	23.8	24.1	24.5	24.8	26.7	28.7
390.0	23.4	23.5	23.8	24.2	24.5	24.8	25.2	27.0	28.9
400.0	23.8	23.9	24.2	24.5	24.9	25.2	25.5	27.2	29.1
420.0	24.6	24.7	25.0	25.3	25.6	25.9	26.2	27.8	29.5
440.0	25.4	25.5	25.8	26.0	26.3	26.6	26.9	28.4	30.0
460.0	26.1	26.3	26.5	26.8	27.1	27.3	27.6	29.0	30.5
480.0	26.9	27.0	27.3	27.5	27.8	28.0	28.3	29.6	31.1
500.0	27.6	27.8	28.0	28.2	28.5	28.7	29.0	30.3	31.6
520.0	28.4	28.5	28.7	29.0	29.2	29.4	29.7	30.9	32.2
540.0	29.1	29.2	29.5	29.7	29.9	30.1	30.4	31.5	32.8
560.0	29.9	30.0	30.2	30.4	30.6	30.8	31.0	32.2	33.3
580.0	30.6	30.7	30.9	31.1	31.3	31.5	31.7	32.8	33.9
600.0	31.3	31.4	31.6	31.8	32.0	32.2	32.4	33.4	34.5
T, K	P, MPa								
	30.0	40.0	50.0	75.0	100.0	200.0	300.0	400.0	
151.0	82.9	91.0	98.1						
151.5	82.5	90.6	97.7						
152.0	82.1	90.3	97.4						
153.0	81.4	89.5	96.6						
154.0	80.6	88.8	95.9						
155.0	79.9	88.1	95.2						
160.0	76.2	84.6	91.8						
165.0	72.8	81.3	88.6						
170.0	69.5	78.1	85.5						
175.0	66.4	75.2	82.6						
180.0	63.6	72.4	79.9	95.6					
185.0	60.9	69.8	77.3	93.0					
190.0	58.3	67.3	74.8	90.5					
195.0	56.0	65.0	72.5	88.2					
200.0	53.8	62.8	70.4	85.9	99.0				
210.0	49.9	58.9	66.4	81.8	94.8				
220.0	46.6	55.5	62.9	78.1	91.0				
230.0	43.8	52.5	59.8	74.8	87.5				
240.0	41.6	49.9	57.1	71.9	84.3				
250.0	39.7	47.7	54.7	69.2	81.4				
260.0	38.2	45.8	52.6	66.8	78.8				
270.0	37.0	44.2	50.7	64.6	76.4				
280.0	36.0	42.8	49.1	62.7	74.2				
290.0	35.1	41.6	47.6	60.9	72.2				
300.0	34.4	40.5	46.3	59.2	70.3	107.0			
310.0	33.8	39.6	45.2	57.7	68.6	104.7			
320.0	33.5	39.0	44.3	56.5	67.2	102.6			
330.0	33.2	38.5	43.6	55.3	65.8	100.6			
340.0	33.1	38.1	42.9	54.3	64.6	98.8			
350.0	32.9	37.7	42.4	53.4	63.4	97.1			
360.0	32.9	37.5	42.0	52.6	62.4	95.5			
370.0	32.9	37.2	41.6	51.9	61.5	94.0			
380.0	32.9	37.1	41.3	51.3	60.6	92.5			
390.0	32.9	37.0	41.0	50.7	59.8	91.2			
400.0	33.0	36.9	40.8	50.2	59.1	90.0	117.1		
420.0	33.1	36.8	40.5	49.4	57.8	87.7	114.2		

TABLE VII. (Continued.)

P, MPa										
T, K	30.0	40.0	50.0	75.0	100.0	200.0	300.0	400.0		
440.0	33.4	36.9	40.3	48.7	56.8	85.7	111.5			
460.0	33.7	37.0	40.2	48.2	56.0	84.0	109.1			
480.0	34.1	37.2	40.3	47.9	55.3	82.4	106.9			
500.0	34.5	37.4	40.4	47.6	54.7	81.0	104.9	127.5		
520.0	34.9	37.7	40.5	47.5	54.3	79.8	103.1	125.3		
540.0	35.3	38.0	40.7	47.4	54.0	78.7	101.4	123.2		
560.0	35.8	38.4	41.0	47.4	53.7	77.8	99.9	121.3		
580.0	36.3	38.7	41.2	47.4	53.5	76.9	98.6	119.6		
600.0	36.8	39.1	41.5	47.5	53.4	76.2	97.4	118.0		
P, MPa										
T, K	4.8	4.9	5.0	5.1	5.2	5.3	5.4	5.5	5.6	5.7
151.0	31.0	49.2	48.7	47.1	47.0	47.2	47.5	47.8	48.2	48.6
151.5	27.7	33.0	56.4	48.6	46.8	46.6	46.8	47.1	47.4	47.8
152.0	25.8	29.0	35.1	55.9	48.3	46.5	46.3	46.4	46.7	47.0
153.0	23.7	25.3	27.8	31.5	38.5	49.2	47.0	45.6	45.5	45.6
154.0	22.3	23.5	25.0	26.9	29.6	33.7	39.7	45.2	45.2	44.7
155.0	21.3	22.3	23.4	24.7	26.3	28.4	31.2	35.0	39.5	42.8
160.0	18.8	19.2	19.8	20.3	20.9	21.5	22.2	23.0	23.8	24.7
165.0	17.6	18.0	18.3	18.7	19.0	19.4	19.8	20.3	20.7	21.2
170.0	17.0	17.3	17.5	17.8	18.1	18.4	18.7	19.0	19.3	19.6
175.0	16.6	16.8	17.1	17.3	17.5	17.7	18.0	18.2	18.5	18.7
180.0	16.4	16.6	16.8	17.0	17.1	17.3	17.5	17.7	17.9	18.2

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APPENDIX A: EQUATION OF STATE FOR ARGON IN THE CRITICAL REGION

To specify the thermodynamic properties of argon in the critical region we have adopted a parametric crossover model proposed by Luettmer-Strathmann *et al.*²⁷ based on a renormalized six-term Landau expansion⁸⁰ for the Helmholtz free-energy density A/V . The equation of state is expressed in terms of reduced quantities

$$\tilde{\rho} = \frac{\rho}{\rho_c}, \quad \tilde{T} = -\frac{T}{T_c}, \quad \tilde{A} = \frac{T_c A}{P_c V T} \quad (\text{A1})$$

and

$$\Delta\tilde{\rho} = \tilde{\rho} - 1, \quad \Delta\tilde{T} = \tilde{T} + 1. \quad (\text{A2})$$

The reduced Helmholtz free-energy density $\tilde{A}$ is decomposed as

$$\tilde{A} = \Delta\tilde{A} + \rho\tilde{\mu}_0(\tilde{T}) + \tilde{A}_0(\tilde{T}), \quad (\text{A3}) \quad \text{with}$$

where $\mu_0(\tilde{T})$ and $\tilde{A}_0(\tilde{T})$ are analytic background functions represented by truncated Taylor expansions with adjustable coefficients

$$\tilde{\mu}_0(\tilde{T}) = \sum_{j=2}^5 \tilde{\mu}_j(\Delta\tilde{T})^j, \quad (\text{A4})$$

$$\tilde{A}_0(\tilde{T}) = -1 + \sum_{j=1}^4 \tilde{A}_j(\Delta\tilde{T})^j. \quad (\text{A5})$$

The term $\Delta\tilde{A}$ in Eq. (A3) contains the effects of the critical fluctuations. It is related to a renormalized $\Delta\tilde{A}_r$ for 3-dimensional Ising-like systems by a transformation of the form^{27,80}

$$t = c_t \Delta\tilde{T} + c \left(\frac{\partial \Delta\tilde{A}_r}{\partial M} \right)_t, \quad (\text{A6})$$

$$M = c_\rho (\Delta\tilde{\rho} - d_1 \Delta\tilde{T}) + c \left(\frac{\partial \Delta\tilde{A}_r}{\partial t} \right)_M, \quad (\text{A7})$$

$$\Delta\tilde{A} = \Delta\tilde{A}_r - c \left(\frac{\partial \Delta\tilde{A}_r}{\partial M} \right)_t \left(\frac{\partial \Delta\tilde{A}_r}{\partial t} \right)_M, \quad (\text{A8})$$

where c_t , c_ρ , c , and d_1 are system-dependent constants. To specify $\Delta\tilde{A}_r(t, M)$ the variables t and M are expressed in terms of two parametric variables r and Φ such that

$$t = r Z^{(1/\nu-2)/\omega} (1 - \frac{1}{2}\Phi^2), \quad (\text{A9})$$

$$M = (u^* \tilde{u} \Lambda)^{-1/2} (r^{2\nu} + \Lambda^2)^{(1-\omega)/4} r^\beta Z^{(\eta-\omega)/2\omega} \Phi, \quad (\text{A10})$$

TABLE VIII. Universal critical constants.

$u^*=0.472$
$\nu=0.630$
$\eta=0.0333$
$\omega\nu=0.51$
$\omega_a=2.1$

$$Z(r) = \frac{1}{(1-\bar{u})r^{\omega\nu} + \bar{u}(r^{2\nu} + \Lambda^2)^{\omega/2}}. \quad (\text{A11})$$

In terms of these parametric variables the expression for $\Delta\tilde{A}_r(r, \Phi)$ becomes

$$\Delta\tilde{A}_r = \sum_{i=1}^7 c_i F_i(\Phi) f_i(r). \quad (\text{A12})$$

with

$$\begin{aligned} c_1 &= \frac{1}{2\bar{u}u^*\Lambda}, & c_2 &= \frac{1}{24\bar{u}u^*\Lambda}, & c_3 &= -\frac{\nu}{2\alpha\bar{u}^{1/\omega}\Lambda}, \\ c_4 &= \frac{a_{05}\bar{u}}{120(\bar{u}u^*\Lambda)^{5/2}}, & c_5 &= \frac{a_{06}\bar{u}^{3/2}}{720(\bar{u}u^*\Lambda)^3}, \\ c_6 &= \frac{a_{14}\bar{u}^{1/2}}{24(\bar{u}u^*\Lambda)^2}, & c_7 &= \frac{a_{22}\bar{u}^{-1/2}}{4(\bar{u}u^*\Lambda)}. \end{aligned} \quad (\text{A13})$$

$$\begin{aligned} F_1(\Phi) &= \Phi^2 - \frac{1}{2}\Phi^4, & F_2(\Phi) &= \Phi^4, \\ F_3(\Phi) &= 1 - \Phi^2 + \frac{1}{4}\Phi^4, \\ F_4(\Phi) &= \Phi^5, & F_5(\Phi) &= \Phi^6, \end{aligned} \quad (\text{A14})$$

$$\begin{aligned} F_6(\Phi) &= \Phi^4 - \frac{1}{2}\Phi^6, & F_7(\Phi) &= \Phi^2 - \Phi^4 + \frac{1}{4}\Phi^6, \\ f_1(r) &= r^{3\nu}(r^{2\nu} + \Lambda^2)^{(1-\omega)/2} Z^{-1}(r), & f_2(r) &= f_1(r), \\ f_3(r) &= r^{3\nu} Z^{-1/\omega}(r) - r^2 Z^{-2(2-1/\nu)/\omega}(r), \\ f_4(r) &= r^{\nu(3+\omega a)}(r^{2\nu} + \Lambda^2)^{(1-\omega)3/4} \\ &\quad \times Z^{-(3/2+1/2\omega-\omega_a/\omega)}(r), \\ f_5(r) &= r^{9/2\nu}(r^{2\nu} + \Lambda^2)^{(1-\omega)3/4} Z^{-3/2}(r), \end{aligned}$$

$$f_6(r) = f_5(r), \quad f_7(r) = f_5(r). \quad (\text{A15})$$

Equations (A9)–(A15) contain system-dependent coefficients a_{ij} of a classical Landau expansion, a system-dependent reduced coupling constant $\bar{u}$ and a cutoff wave number Λ , whereas ν , η , $\alpha=2-3\nu$, $\beta=\nu(1+\eta)/2$, ω , and ω_a are universal critical exponents and u^* is a universal fixed-point coupling constant. The values of the universal constants are presented in Table VIII. Equations for calculating the various derivatives of $\Delta\tilde{A}$ can be found in the original publication.²⁷

To determine the values of the system-dependent constants we considered experimental P – ρ – T data reported by Michels *et al.*⁸¹ with temperatures converted to IPTS-68^{82,83} and isochoric specific heat-capacity data reported by Anisimov *et al.*²⁸ We restricted ourselves to temperatures between 148 and 205 K, in the density range between 6.75 and 17.5 mol L^{−1} with the additional constraint that the inverse reduced susceptibility, defined by

$$\tilde{\chi}^{-1} = \left(\frac{\partial^2 \tilde{A}}{\partial \rho^2} \right)_T = \rho^{-1} \left(\frac{\partial P}{\partial \rho} \right)_T \frac{\rho_c^2 T_c}{P_c T} \quad (\text{A16})$$

should not exceed a value larger than 2.2. To ensure a proper matching with the global equation of state of Stewart and Jacobsen²⁵ outside the critical region we supplemented the experimental data with values for the pressure P , isobaric specific heat capacity c_p and the isochoric specific heat capacity c_v from the equation of state of Stewart and Jacobsen at temperatures between 148 and 205 K and densities between 6.75 and 20 mol L^{−1}, excluding the near-critical region by omitting densities between 9 and 17.5 mol L^{−1} at temperatures below 160 K. Since there are systematic deviations between the pressure data of Michels *et al.*⁸¹ and those generated from the global classical equation at higher densities,²⁵ we excluded experimental P – ρ – T data at densities larger than 17.5 mol L^{−1}. The values of the system-dependent constants obtained from a fit to the crossover equation of state to the data specified above are presented in Table IX.

We recommend the crossover equation of state in the range of temperatures and densities as specified by Eq. (3.1).

TABLE IX. System-dependent constants in the crossover equation of state for argon.

Critical parameters			
$T_c=150.663$ K	$\rho_c=13.395$ mol L ⁻¹	$P_c=4.860$ MPa	
Crossover parameters			
$\bar{u}=0.33627$	$\Lambda=3.1682$		
Scaling-field parameters			
$c_t=1.8171$	$c_p=2.4786$	$c=-0.012\ 22$	
Classical parameters			
$a_{05}=-2.250$	$a_{06}=0.5041$	$a_{14}=0.089\ 44$	$a_{22}=-0.009\ 60$
Equation-of-state background parameters			
$\tilde{A}_1=-4.8890$	$\tilde{A}_2=2.7695$	$\tilde{A}_3=-2.195$	$\tilde{A}_4=4.300$
$d_1=-0.158\ 55$			
Caloric background parameters			
$\tilde{\mu}_2=-5.5667$	$\tilde{\mu}_3=-0.8167$	$\tilde{\mu}_4=-1.548$	$\tilde{\mu}_5=-7.67$
Molar mass			
$M=0.039\ 948$ kg mol ⁻¹

FIG. 13. Percentage differences between experimental c_v data obtained by Anisimov *et al.* (Ref. 28) between 152 and 200 K and the values calculated from the crossover equation of state.

At the boundary of this range at temperatures above T_c the pressures and densities calculated from the crossover equation and the global equation generally agree to within 0.1% and never differ by more than 0.2%; the c_v values at the boundary calculated from the two equations generally agree to within 1% and never differ by more than 2%. Since all our thermal-conductivity data were obtained at temperatures above 150 K, we tried to maximize the consistency between the two equations in the supercritical region and not along the phase boundary below T_c .

To elucidate the quality of the crossover equation of state we show in Figs. 13 and 14 a comparison between the iso-

FIG. 14. Percentage differences between experimental c_v data obtained by Anisimov *et al.* (Ref. 28) between 148 and 152 K and the values calculated from the crossover equation of state.

FIG. 15. The isochoric specific heat-capacity c_v of argon in the critical region as a function of temperatures along three isochores. The symbols indicate experimental values obtained by Anisimov *et al.* (Ref. 28). The solid curves represent values calculated from the crossover equation of state and the dashed curves represent values calculated from the analytic equation of state of Stewart and Jacobsen (Ref. 25).

choric specific-heat data reported by Anisimov *et al.*²⁸ and the values calculated from the crossover equation of state. The deviations are within 2% in most of the temperature range, while increasing slightly at temperatures very close to the critical temperature. As a further illustration we show in Fig. 15 the specific-heat data of Anisimov *et al.* at three isochores as a function of temperature along with the values calculated from the crossover equation and the equation of Stewart and Jacobsen. This figure confirms that the classical equation of state is not suitable for representing the specific heat capacity in the near-critical region.

In addition there exists a set of experimental sound-velocity data for argon in the critical region reported by Thoen *et al.*⁸⁴ which were not considered in the determination of the constants in the crossover equation of state. Our crossover equation of state gives a good representation of the sound-velocity data of Thoen *et al.* in the supercritical region as shown in Fig. 16. The sound velocity of the coexisting vapor and liquid phases is shown in Fig. 17. The crossover equation describes the experimental sound-velocity data much better on the liquid branch than on the vapor branch, where the deviations of the experimental from the calculated values are systematic at the lower temperatures. This is likely due to the fact that we did not use any caloric property data below 148 K to determine any constants in the crossover equation of state and it is an indication that care should be taken with any use of the crossover equation in the vapor phase below the critical temperature.

APPENDIX B: EQUATIONS FOR λ_{cr} AND η_{cr}

1. Auxiliary functions

$$y_D = \arctg(q_D \xi),$$

$$y_\delta = \frac{\arctg[q_D \xi / (1 + q_D^2 \xi^2)^{1/2}] - y_D}{(1 + q_D^2 \xi^2)^{1/2}},$$

FIG. 16. The sound velocity of argon at supercritical temperatures as a function of pressure. The symbols indicate experimental values obtained by Thoen *et al.* (Ref. 84) and the solid curves represent values calculated from the crossover equation of state.

$$y_\alpha = \rho k T / 8 \pi \bar{\eta}^2 \xi,$$

$$y_\beta = \bar{\lambda} / \bar{\eta} (c_p - c_v),$$

$$y_\gamma = c_v / (c_p - c_v),$$

$$y_\eta = (y_\delta + y_\beta / y_\alpha) / y_D,$$

$$y_\nu = y_\gamma y_\delta / y_D,$$

$$F(x, y_D) = \frac{1}{(1-x^2)^{1/2}} \ln \left[\frac{1+x+(1-x^2)^{1/2} \operatorname{tg}(y_D/2)}{1+x-(1-x^2)^{1/2} \operatorname{tg}(y_D/2)} \right].$$

FIG. 17. The sound velocity of argon in the coexisting vapor and liquid phases below the critical temperature. The symbols indicate experimental values obtained by Thoen *et al.* (Ref. 84) and the solid curves represent values calculated from the crossover equation of state.

2. Equations for the thermal conductivity

$$\lambda_{cr} = \frac{RkT}{6\pi\eta\xi} \rho c_p [\Omega(\{y_i\}) - \Omega_0],$$

$$\Omega(\{y_i\}) = \frac{2}{\pi} \frac{1}{1+y_\gamma} \times \left[y_D - \sum_{i=1}^4 \frac{(a_3 z_i^3 + a_2 z_i^2 + a_1 z_i + a_0)}{\prod_{j=1, j \neq i}^4 (z_i - z_j)} F(z_i, y_D) \right],$$

$$\Omega_0 = \frac{1 - \exp\{-(q_D \xi)^{-1} + (q_D \xi \rho_c / \rho)^2 / 3\}^{-1}}{\pi/2 [1 + y_\alpha (y_D + y_\delta) + y_\beta (1 + y_\gamma)^{-1}]},$$

$$\prod_{i=1}^4 (z + z_i) = z^4 + b_3 z^3 + b_2 z^2 + b_1 z + b_0 = 0,$$

$$a_0 = y_\gamma^2 - y_\alpha y_\gamma y_\delta, \quad b_0 = y_\alpha y_\gamma y_\delta,$$

$$a_1 = y_\alpha y_\gamma y_D, \quad b_1 = y_\alpha y_\gamma y_D,$$

$$a_2 = y_\gamma - y_\beta - y_\alpha y_\delta, \quad b_2 = y_\gamma + y_\beta + y_\alpha y_\delta,$$

$$a_3 = y_\alpha y_D, \quad b_3 = y_\alpha y_D.$$

3. Equations for the viscosity

$$\eta_{cr} = \bar{\eta} [e^{zH(\{y_i\})} - 1]$$

$$H(\{y_i\}) = h(\{y_i\}) + \sum_{i=1}^3 \frac{(c_2 v_i^2 + c_1 v_i + c_0)}{\prod_{j=1, j \neq i}^3 (v_i - v_j)} F(v_i, y_D),$$

$$h(\{y_i\}) = [3y_\gamma y_\eta + 3y_\eta/2 - y_\eta^3 - y_\nu]y_D + [y_\eta^2 - 2y_\gamma - 5/4]\sin y_D - y_\eta(\sin 2y_D)/4 + (\sin 3y_D)/12 + \frac{[y_\gamma(1+y_\gamma)]^{3/2}}{(y_\nu - y_\gamma y_\eta)} \operatorname{arctg}\{[y_\gamma/(1+y_\gamma)]^{1/2} \operatorname{tg} y_D\}.$$

$$\prod_{i=1}^3 (v + v_i) = v^3 + y_\eta v^2 + y_\gamma v + y_\nu = 0,$$

$$c_0 = y_\eta y_\nu (y_\eta^2 - 3y_\gamma - 2) + y_\nu^2 - y_\gamma y_\nu (1 + y_\gamma)^2 / (y_\nu - y_\gamma y_\eta),$$

$$c_1 = (y_\nu - y_\gamma y_\eta)(y_\eta^2 - 3y_\gamma - 2) + y_\gamma^2(1 + y_\gamma)^2 / (y_\nu - y_\gamma y_\eta),$$

$$c_2 = y_\eta^4 - 4y_\gamma y_\eta^2 - 2y_\eta^2 + 2y_\eta y_\nu + 3y_\gamma^2 + 4y_\gamma + 1.$$

4. Equations for the correlation length

$$\xi = \xi_0 \Gamma^{-\nu/\gamma} \left[\tilde{\chi}(T, \rho) - \tilde{\chi}(T_r, \rho) \right]^{1/\gamma} \frac{T_r}{T},$$

$$\gamma = \nu(2 - \eta), \quad T_r = 2T_c.$$

5. Constants in the equations for λ_{cr} and η_{cr}

Critical exponents: $z=0.063$, $\nu=0.630$, $\gamma=1.239$. Critical amplitudes: $R=1.03$, $\xi_0=1.64 \times 10^{-10}$ m, $\Gamma=0.0616$. Cut-off wave number: $q_D^{-1}=1.91 \times 10^{-10}$ m.

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