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The Thermal Conductivity of Liquid Argon for Temperatures Between 110 and 140 K with Pressures to 70 MPa

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The paper presents new experimental measurements of the thermal conductivity of liquid argon for four temperatures between 110 and 140 K with pressures to 70 MPa and densities between 23 and 36 mol · L^{-1}. The measurements were made with a transient hot-wire apparatus. A curve fit of each isotherm allows comparison of the present results to those of others and to correlations. The results are sufficiently detailed to illustrate several features of the liquid thermal conductivity surface, for example, the dependence of its curvature on density and temperature. If these details are taken into account, the comparisons show the accuracy of the present results to be 1%. The present results, along with several other sets of data, are recommended for selection as standard thermal conductivity data along the saturated liquid line of argon, extending the standards into the cryogenic temperature range. The results cover a fairly wide range of densities, and we find that a hard-sphere model cannot represent the data within the estimated experimental accuracy.

KEY WORDS: argon (liquid); high pressures; low temperatures; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

The transient hot-wire method is recognized today as the method of highest accuracy for the measurement of the thermal conductivity of fluids for conditions removed from the critical region proper. For example, data obtained near the saturation lines of toluene and *n*-heptane with instruments of this type have been proposed recently as standard reference

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data for the thermal conductivity of liquids at temperatures near ambient [1].

New values for the thermal conductivity of liquid argon were presented in a companion paper [2] for a limited range of densities. There are several reasons why the present measurements were made. First, we wanted to extend the range of densities covered in the liquid. Second, we wanted to make a detailed comparison of measurements made at different laboratories using the same technique with different modes of operation to infer, if possible, the accuracies of the present apparatus. Third, we wanted to see if the combined set of results would allow a recommendation for standard reference data along the saturated liquid line of argon, thus extending the temperature range of standard reference data into the cryogenic range. Fourth, we wanted to examine the validity of the hard-sphere theory to predict the thermal conductivity of liquid argon with an extended range in density. Finally, the new results serve in part to fill a gap in the thermal conductivity data for argon, as discussed in Section 4.1.

The present study, which was carried out at temperatures below 140 K, significantly extends the range of available densities from 23 to 36 mol $\cdot$ L^{-1}. The new measurements were taken with density increments of roughly 0.5 mol $\cdot$ L^{-1} and are sufficiently close in temperature to describe the shape of the thermal conductivity surface in detail. In particular, the measurements show that the isotherms are curved, that this curvature increases as the isotherm approaches the saturated liquid boundary, that $(\partial\lambda/\partial T)_\rho$ is nonzero and about twice as large as $(d\lambda/dT)$ at zero density, and that the saturated liquid thermal conductivity rises as the temperature approaches critical.

2. METHOD AND APPARATUS

The measurements were made with a transient hot-wire thermal conductivity apparatus which has been fully described elsewhere [3]. This instrument has been used previously to measure the thermal conductivity surfaces in the liquid state for oxygen [4], propane [5], methane [6], ethane [7], and methane–ethane mixtures [8, 9]. It was tested on argon at 300.65 K [10].

Replicate measurements made at the same cell temperature and pressure but with different power levels verify the absence of convection. For any experimental point, the pressure, cell temperature, and applied power are measured directly. The experimental temperature and the thermal conductivity with their associated regression error are obtained through a data reduction program, while the density is calculated from an equation of state [11]. That the four or five different power levels used

result in slightly different experimental temperatures and densities and the temperatures at a given pressure level may differ by as much as 2 K. The experimental densities will differ also since they are calculated for the experimental temperature and the measured pressure from the equation of state.

The samples used were research grade argon stated by the supplier to be a minimum of 99.999 mol% argon. We used a small diaphragm compressor and observed normal precautions for high pressure and high vacuum.

3. RESULTS

To define the thermal conductivity surface of liquid argon, 214 points distributed among four isotherms, 110.485, 124.769, 138.775, and

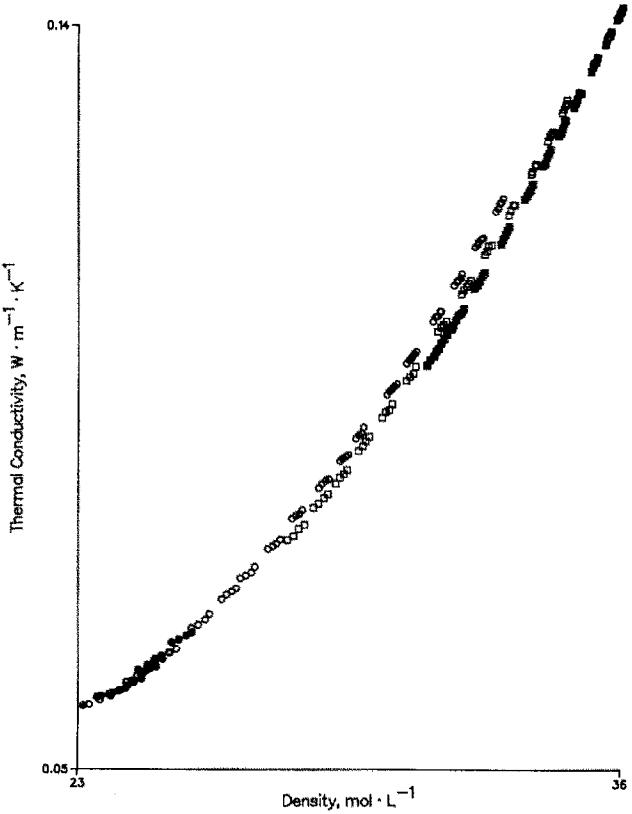

Fig. 1. Overview of the thermal conductivity measurements on liquid argon. (■) 110.485 K; (□) 124.769 K; (●) 138.775 K; (○) 140.132 K.

140.132 K, were obtained. An overview of the thermal conductivities is given in Fig. 1, which shows that the isotherms are curved and that this curvature increases as the isotherm approaches the saturated liquid boundary. Tables I through IV contain the experimental data, pressure, temperature, density, and thermal conductivity, for each isotherm. In much of the subsequent analysis it is desirable to have the thermal conductivities at the fixed values of temperature given above. Since the experimental temperatures may differ by as much as 2 K, the temperatures chosen above are simply the averages of all experimental temperatures along an isotherm. Each point is adjusted at constant density to the nominal temperature by a slight shift in temperature using an average $(\partial\lambda/\partial T)_\rho$ of 0.000136 $W \cdot m^{-1} \cdot K^{-2}$, which is discussed in detail below. The adjustments are no larger than 0.3% and the adjusted values of thermal conductivity are given in the last column in Tables I through IV.

4. DISCUSSION

The discussion is divided into several subsections, each covering a different topic. The first topic concerns the comparison of the present data to

Table I. The Thermal Conductivity of Liquid Argon at a Nominal Temperature of 110.485 K

Pressure (MPa)	Temperature (K)	Density ($mol \cdot L^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Adjusted to nominal T ($W \cdot m^{-1} \cdot K^{-1}$)
4.5750	111.222	31.352	0.09912	0.09902
4.5698	110.813	31.425	0.09974	0.09970
4.5640	110.300	31.515	0.10018	0.10021
4.5558	109.987	31.570	0.10077	0.10084
4.5494	109.667	31.626	0.10108	0.10119
7.1823	111.170	31.683	0.10176	0.10167
7.1791	110.731	31.757	0.10226	0.10223
7.1733	110.325	31.825	0.10281	0.10283
7.1676	109.969	31.884	0.10345	0.10352
7.1530	109.674	31.932	0.10346	0.10357
7.1859	109.658	31.939	0.10360	0.10371
10.1526	111.447	31.975	0.10394	0.10381
10.1479	111.011	32.045	0.10458	0.10451
10.1418	110.654	32.102	0.10516	0.10514
10.1291	110.215	32.171	0.10538	0.10542
10.1204	109.863	32.226	0.10589	0.10597
14.9996	111.330	32.493	0.10831	0.10820
14.9926	110.827	32.567	0.10871	0.10866

Table I *(Continued)*

Pressure (MPa)	Temperature (K)	Density ($mol \cdot L^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Adjusted to nominal T ($W \cdot m^{-1} \cdot K^{-1}$)
14.9865	110.531	32.611	0.10921	0.10920
14.9768	110.082	32.677	0.10981	0.10986
14.9694	109.737	32.728	0.11018	0.11028
21.6096	111.074	33.128	0.11365	0.11357
21.6039	110.711	33.177	0.11422	0.11419
21.5981	110.327	33.230	0.11478	0.11480
21.5903	110.010	33.273	0.11526	0.11532
21.5764	109.661	33.319	0.11568	0.11579
28.6855	111.058	33.692	0.11902	0.11894
28.6810	110.600	33.750	0.11943	0.11941
28.6706	110.252	33.794	0.11987	0.11990
28.6667	109.937	33.834	0.12012	0.12019
28.6948	109.581	33.882	0.12078	0.12090
35.3127	111.252	34.141	0.12306	0.12296
35.3124	110.870	34.187	0.12335	0.12330
35.3035	110.580	34.222	0.12412	0.12411
35.3006	110.179	34.270	0.12450	0.12454
35.2917	109.856	34.309	0.12497	0.12506
40.8582	111.168	34.515	0.12663	0.12654
40.8504	110.733	34.565	0.12700	0.12697
40.8569	110.448	34.599	0.12755	0.12756
40.8497	110.121	34.636	0.12831	0.12836
40.8497	109.903	34.662	0.12848	0.12856
47.2350	111.413	34.875	0.13004	0.12991
47.2265	111.060	34.915	0.13061	0.13053
47.2392	110.759	34.949	0.13105	0.13101
47.2414	110.427	34.986	0.13182	0.13183
47.2399	109.901	35.045	0.13175	0.13183
54.3577	111.352	35.285	0.13440	0.13428
54.3478	110.988	35.324	0.13496	0.13489
54.3442	110.809	35.343	0.13534	0.13530
54.3435	110.269	35.401	0.13555	0.13558
54.3315	109.965	35.433	0.13610	0.13617
60.5508	111.229	35.625	0.13770	0.13760
60.5480	110.935	35.656	0.13826	0.13820
60.5444	110.531	35.698	0.13864	0.13863
60.5429	110.162	35.736	0.13881	0.13885
60.5373	109.920	35.761	0.13927	0.13935
65.9322	111.189	35.899	0.14070	0.14060
65.9346	110.749	35.944	0.14096	0.14092
65.9350	110.455	35.973	0.14144	0.14144
65.9315	110.148	36.005	0.14164	0.14169
65.9315	109.807	36.039	0.14218	0.14227

the data of other authors, in particular, to the data of the companion paper [2]. The second topic covers the extrapolation of the present data to the saturation line and a proposal of standard reference data. The final topic presents an analysis of the application of the dense hard-sphere theory to the present data.

4.1. Comparison to the Data of Other Authors

Younglove and Hanley [12] recently reviewed viscosity and thermal conductivity for argon. This work pointed out a gap in accurate data for argon, particularly for thermal conductivity below room temperature. This gap is at least partially filled by the present results.

To analyze an isotherm or to compare results from different laboratories, we must shift the experimental results to a single temperature. Therefore, we must first answer the question: What is the correct value of $(\partial\lambda/\partial T)_\rho$ for this shift? We expect the $(\partial\lambda/\partial T)_\rho$ to depend slightly on both temperature and density. We could use a constant value of $0.00006\ \mathrm{W \cdot m^{-1} \cdot K^{-2}}$ derived at zero density from a recent correlation by Younglove and Hanley [12], or we could use the values calculated from this correlation for liquid densities. We could fit a low-order polynomial to each isotherm, as was done in the companion paper [2], and derive values for the $(\partial\lambda/\partial T)_\rho$ from the polynominals. These possibilities are plotted for two intermediate temperatures, 117.627 and 132.451 K, and the appropriate range of density overlap in Fig. 2. For the polynomials the $(\partial\lambda/\partial T)_\rho$ decreases with increasing density, while the opposite is true for

Table II. The Thermal Conductivity of Liquid Argon at a Nominal Temperature of 124.769 K

Pressure (MPa)	Temperature (K)	Density ($\mathrm{mol \cdot L^{-1}}$)	Thermal conductivity ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	Adjusted to nominal T ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)
1.9794	125.045	28.020	0.07800	0.07796
1.9634	124.467	28.160	0.07846	0.07850
1.9709	123.973	28.283	0.07933	0.07944
1.9862	123.379	28.430	0.07984	0.08003
5.5460	125.922	28.643	0.08190	0.08174
5.5431	125.351	28.765	0.08238	0.08230
5.5374	124.721	28.897	0.08307	0.08308
5.5332	124.282	28.988	0.08353	0.08360
8.0103	125.626	29.180	0.08481	0.08469
8.0068	125.133	29.275	0.08555	0.08550
8.0033	124.635	29.371	0.08598	0.08600

Table II *(Continued)*

Pressure (MPa)	Temperature (K)	Density ($mol \cdot L^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Adjusted to nominal T ($W \cdot m^{-1} \cdot K^{-1}$)
7.9983	124.190	29.455	0.08649	0.08657
11.3555	125.686	29.725	0.08881	0.08869
11.3541	125.130	29.824	0.08938	0.08933
11.3512	124.725	29.894	0.08996	0.08997
11.3491	124.249	29.978	0.09047	0.09054
15.1244	125.573	30.287	0.09281	0.09270
15.1194	125.079	30.367	0.09347	0.09343
15.1115	124.506	30.458	0.09372	0.09376
15.1054	124.122	30.519	0.09440	0.09449
20.1303	125.908	30.860	0.09726	0.09711
20.1275	125.336	30.944	0.09771	0.09763
20.1232	124.775	31.027	0.09806	0.09806
20.1182	124.420	31.079	0.09895	0.09900
26.8915	125.734	31.607	0.10314	0.10301
26.8865	125.180	31.681	0.10367	0.10361
26.8821	124.747	31.739	0.10400	0.10400
26.8765	124.220	31.809	0.10440	0.10447
33.3083	125.912	32.177	0.10764	0.10748
33.3047	125.489	32.229	0.10814	0.10804
33.2968	124.907	32.302	0.10854	0.10852
33.2883	124.597	32.340	0.10890	0.10892
33.3125	124.145	32.399	0.10926	0.10934
39.8519	125.731	32.736	0.11237	0.11224
39.8484	125.241	32.793	0.11280	0.11274
39.8470	125.005	32.821	0.11340	0.11337
39.8441	124.308	32.903	0.11351	0.11357
47.0679	125.293	33.315	0.11707	0.11700
47.0725	124.897	33.360	0.11766	0.11764
47.0686	124.362	33.419	0.11827	0.11833
47.0522	124.002	33.458	0.11829	0.11839
54.6185	124.963	33.850	0.12201	0.12198
54.6285	124.693	33.879	0.12233	0.12234
54.6313	124.150	33.937	0.12298	0.12306
54.6381	123.861	33.968	0.12323	0.12335
61.1645	124.972	34.246	0.12599	0.12596
61.1681	124.538	34.290	0.12655	0.12658
61.1638	124.145	34.330	0.12681	0.12689
61.1667	123.693	34.376	0.12710	0.12725
67.7589	125.245	34.591	0.12942	0.12936
67.7645	124.813	34.634	0.12984	0.12983
67.7671	124.417	34.673	0.13032	0.13037
67.7720	124.078	34.706	0.13091	0.13100
67.7457	123.980	34.714	0.13050	0.13061

Table III. The Thermal Conductivity of Liquid Argon at a Nominal Temperature of 138.775 K

Pressure (MPA)	Temperature (K)	Density ($mol \cdot L^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Adjusted to nominal T ($W \cdot m^{-1} \cdot K^{-1}$)
2.5655	139.839	23.122	0.05794	0.05780
2.5585	139.224	23.459	0.05899	0.05893
3.0826	139.952	23.554	0.05908	0.05892
2.5585	138.685	23.737	0.05928	0.05929
3.0816	139.370	23.832	0.05949	0.05941
2.5585	138.129	24.006	0.05976	0.05985
3.0805	138.692	24.136	0.06000	0.06001
2.5585	137.747	24.181	0.06031	0.06045
3.6846	139.298	24.287	0.06090	0.06083
3.0798	138.213	24.339	0.06075	0.06083
4.2734	139.820	24.445	0.06227	0.06213
3.6810	138.711	24.516	0.06175	0.06176
3.0781	137.754	24.526	0.06114	0.06128
4.2720	139.214	24.667	0.06284	0.06278
3.6785	138.128	24.736	0.06245	0.06254
4.2683	138.695	24.851	0.06360	0.06361
3.6753	137.730	24.881	0.06264	0.06278
4.2641	138.264	24.998	0.06396	0.06403
5.8207	139.740	25.247	0.06555	0.06542
5.8210	139.167	25.420	0.06590	0.06585
5.8203	138.562	25.599	0.06637	0.06640
5.8203	138.109	25.730	0.06675	0.06684

the correlation of Ref. 12. In addition, the values of $(\partial\lambda/\partial T)_\rho$ from the correlation for a large number of densities are less than the value of $d\lambda/dT$ at zero density, even to the extent of being negative. Departure plots show that neither of the two representations selected so far exhibits sufficient curvature to follow the isotherms over the entire range of density.

A glance at Fig. 1 reminds us that the experimental isotherms exhibit considerable curvature. Therefore, a third functional form, which involves an exponential and is known to work well for other liquids such as oxygen [4], is employed here:

$$\lambda(\rho, T) = \alpha\rho + \delta[e^{\beta\rho^\gamma} - 1.0] \tag{1}$$

where α, β, γ, and δ are adjustable parameters and λ is the thermal conductivity of the liquid at temperature T and density ρ. Equation (1) was fitted to the three long isotherms, and values of $(\partial\lambda/\partial T)_\rho$ for the two intermediate

Table IV. The Thermal Conductivity of Liquid Argon at a Nominal Temperature of 140.132 K

Pressure (MPa)	Temperature (K)	Density ($mol \cdot L^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Adjusted to nominal T ($W \cdot m^{-1} \cdot K^{-1}$)
3.0115	140.381	23.269	0.05805	0.05802
3.0100	139.887	23.524	0.05860	0.05863
3.0071	139.338	23.788	0.05910	0.05921
3.0040	138.944	23.968	0.05970	0.05986
3.8474	139.882	24.156	0.06076	0.06079
3.8446	139.211	24.421	0.06156	0.06169
3.8413	138.795	24.579	0.06195	0.06213
4.9692	140.324	24.650	0.06224	0.06221
4.9671	139.852	24.811	0.06319	0.06323
5.7816	140.947	24.851	0.06341	0.06330
4.9646	139.323	24.987	0.06369	0.06380
5.7759	140.375	25.030	0.06353	0.06350
5.7723	139.899	25.177	0.06433	0.06436
4.9617	138.644	25.207	0.06434	0.06454
5.7659	139.302	25.357	0.06478	0.06489
7.8423	140.879	25.719	0.06726	0.06716
7.8423	140.256	25.882	0.06765	0.06763
7.8386	139.607	26.048	0.06828	0.06835
7.8362	139.213	26.148	0.06895	0.06907
10.0357	140.788	26.440	0.07075	0.07066
10.0314	140.265	26.558	0.07130	0.07128
10.0275	139.667	26.692	0.07170	0.07176
10.0236	139.224	26.790	0.07205	0.07217
12.1974	141.364	26.890	0.07327	0.07310
12.1939	140.726	27.021	0.07360	0.07352
12.1903	140.078	27.153	0.07400	0.07401
12.1889	139.676	27.235	0.07467	0.07473
14.9220	141.154	27.549	0.07688	0.07674
14.9185	140.524	27.665	0.07721	0.07716
14.9156	140.022	27.757	0.07753	0.07754
14.9121	139.522	27.849	0.07803	0.07811
17.8274	141.026	28.131	0.08057	0.08045
17.8271	140.462	28.227	0.08092	0.08088
17.8246	139.993	28.307	0.08115	0.08117
17.8218	139.575	28.377	0.08158	0.08166
21.4942	140.803	28.775	0.08425	0.08416
21.4857	140.353	28.844	0.08472	0.08469
21.4850	139.751	28.937	0.08513	0.08518
21.4842	139.259	29.013	0.08532	0.08544

Table IV. *(Continued)*

Pressure (MPa)	Temperature (K)	Density ($mol \cdot L^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	Adjusted to nominal T ($W \cdot m^{-1} \cdot K^{-1}$)
24.7804	140.595	29.282	0.08752	0.08746
24.7772	140.183	29.341	0.08783	0.08782
24.7669	139.599	29.425	0.08808	0.08815
24.7554	139.191	29.483	0.08828	0.08841
28.1762	141.048	29.660	0.09026	0.09014
28.1769	140.484	29.738	0.09068	0.09063
28.1698	140.019	29.801	0.09087	0.09089
28.1679	139.692	29.846	0.09159	0.09165
34.9799	141.296	30.407	0.09552	0.09536
34.9746	140.861	30.461	0.09593	0.09583
34.9727	140.343	30.526	0.09624	0.09621
34.9652	139.922	30.578	0.09654	0.09657
34.9578	139.403	30.642	0.09681	0.09691
40.1198	141.719	30.871	0.09928	0.09906
40.1184	141.183	30.935	0.09968	0.09954
40.1184	140.734	30.988	0.09996	0.09988
40.1149	140.208	31.049	0.10040	0.10039
40.1031	139.735	31.104	0.10068	0.10073
46.9337	141.525	31.504	0.10430	0.10411
46.9366	141.034	31.559	0.10489	0.10477
46.9390	140.449	31.624	0.10498	0.10494
46.9387	140.022	31.671	0.10553	0.10554
46.9404	139.774	31.698	0.10552	0.10557
52.9978	141.350	32.010	0.10860	0.10843
52.9985	140.784	32.069	0.10907	0.10898
52.9953	140.435	32.106	0.10920	0.10916
52.9925	139.869	32.165	0.10950	0.10954
52.9950	139.567	32.197	0.10997	0.11005
59.7825	141.242	32.516	0.11324	0.11309
59.7714	140.656	32.574	0.11350	0.11343
59.7764	140.400	32.600	0.11385	0.11381
59.7711	139.773	32.663	0.11415	0.11420
59.7725	139.289	32.711	0.11431	0.11442
66.4015	140.628	33.018	0.11748	0.11741
66.4044	140.060	33.073	0.11780	0.11781
66.3980	139.637	33.113	0.11845	0.11852
66.4008	139.251	33.150	0.11858	0.11870
66.4022	138.882	33.186	0.11899	0.11916

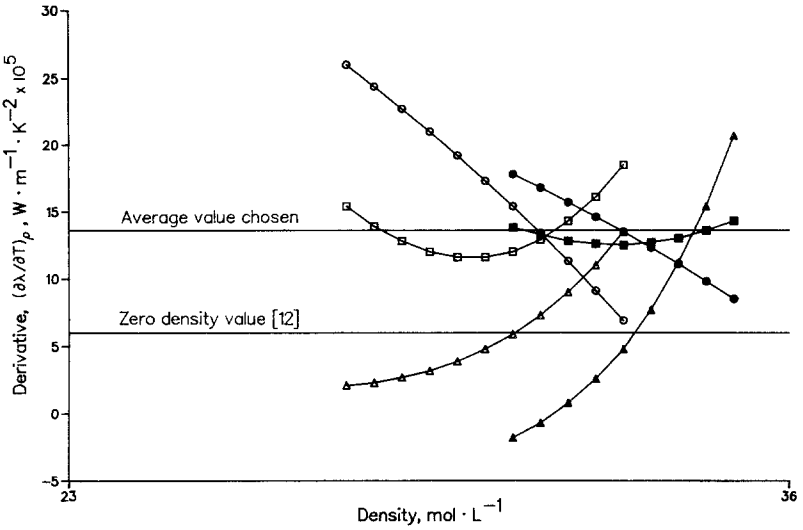

Fig. 2. Estimated values for the derivative $(\partial\lambda/\partial T)_\rho$ at two temperatures. 132.451 K: (□) Exponential fit; (○) parabolic fit; (△) correlation [12]. 117.627 K; (■) Exponential fit; (●) parabolic fit; (▲) correlation [12].

Table V. Thermal Conductivities Along the Saturated Liquid Line of Argon

Temperature (K)	Density, Ref. 11 ($mol \cdot L^{-1}$)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$) Ref. 2 and this paper	Eq. (4)	Deviation (%)
107.000	31.606	0.10060	0.10044	0.16
110.485	30.960	0.09574	0.09601	−0.29
113.000	30.478	0.09296	0.09282	0.15
118.000	29.472	0.08657	0.08648	0.10
124.000	28.160	0.07888	0.07887	0.01
124.769	27.982	0.07781	0.07789	−0.11
130.000	26.689	0.07109	0.07126	−0.23
138.775	24.049	0.05994	0.06013	−0.31
140.132	23.555	0.05871	0.05840	0.52

temperatures 117.627 and 132.451 K were derived and plotted in Fig. 2. The selection of $(\partial\lambda/\partial T)_\rho = 0.000136\ \mathrm{W \cdot m^{-1} \cdot K^{-2}}$ is made from Fig. 2 as an average value for the range of the liquid surface that is covered. In the first iteration of fitting Eq. (1) to the isotherms, the deviation patterns for the 124.769 and the 140.132 K isotherms showed systematic departures at the lower densities. We concluded that the curvature of the isotherms increases sharply as the isotherm approaches the saturation line, a sort of "hook." Values of the saturation densities can be found in Table V. A second set of curve fits for these temperatures was done by restricting the densities included in the fit to densities above 29.3 and 25.0 $\mathrm{mol \cdot L^{-1}}$, respectively.

We are now in a position to examine the precision of the present data and to compare the isotherms measured in this study to those measured in Lisbon by Calado et al. [2]. We adjusted all of the present data to the temperatures given above, namely, 110.485, 124.769, 138.775, and 140.132 K; i.e., we have used the last column in Tables I–IV. For the companion paper [2] we adjusted the 107 K isotherm to 110.485, the 124 K isotherm to 124.769 K, and the 130 K isotherm to 140.132 K. Figure 3 shows the

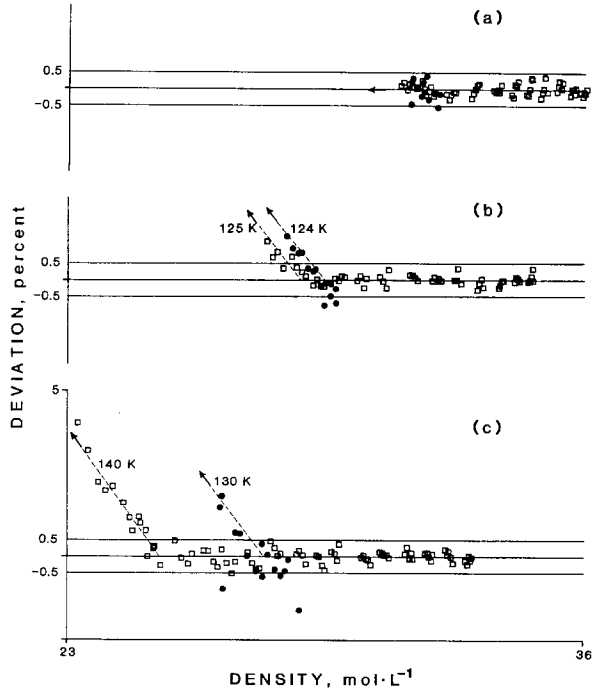

Fig. 3. Deviations. (a) 110.485 K; (b) 124.769 K; (c) 140.132 K. (□) This paper; (●) Ref. 2.

deviation plot for each of the isotherms, where the baseline is the curve fit of Eq. (1). We see in Fig. 3 that for 110.485 K the precision of the present data is better than 0.5% at the 2σ level, where σ is the standard deviation of the fit, Eq. (1). The precision of the companion paper is 0.4%, and the agreement between the two sources is within the 0.5% band. The extrapolation toward the saturation line should take place along the line of the arrow. For the 124.769 K isotherm we see the hook at densities below 29.3 mol $\cdot$ L^{-1} quite clearly. We were not able to include the hook into the baseline. However, if we consider the hooks as a systematic departure, then for 124.769 K we can assert that the precision of both the present data and those of the companion paper is 0.5% at the 2σ level and that the agreement between the two sets of data is within the 0.5% band. The extrapolation toward the saturation boundary should take place along the line of the hook as shown by the arrows in Fig. 3. For the 140.132 K isotherm, the hook at densities below 25.0 mol $\cdot$ L^{-1} is much larger than for the previous isotherm. In addition, the closest isotherm in the companion paper is at 130 K and had to be shifted by about 10 K for this comparison. We assert that the entire range of densities measured in the 130 K isotherm falls into the range of the "hook" for this isotherm. Taking the hooks into account we state that the precision of the present measurements is 0.5% at the 2σ level for the 140.132 K isotherm; it is somewhat more for the 130 K isotherm of Ref. 2. The agreement between the two sets of data for these temperatures is still within the 0.5% band but degraded to the 1σ level. Extrapolation of the saturated liquid line should take place along the lines of the arrows for either isotherm.

We conclude that the precision of the present measurements is 0.5% at the 2σ level. The accuracy of the present data is estimated to be better than 1% based on the following reasons: (a) the agreement for argon between the present data and those of the companion paper [2] of 0.5%; (b) a similar agreement of 0.5% between the liquid methane data measured in the present apparatus [6] and those measured in Lisbon for methane [13]; (c) an accuracy of 1% in the measurement of gaseous argon at 300.65 K in the present apparatus [10]; and (d) the extrapolation of the data presented in Ref. 10 which yields a zero-density kinetic theory Eucken factor within 0.3%.

Ziebland and Burton [14] measured the thermal conductivity of argon in temperature and pressure ranges that overlap the present data. Their data were compared with the present values and an agreement to within $\pm 2\%$ was found, which is commensurate with the mutual uncertainty of both data sets.

Bailey and Kellner [15] also measured the thermal conductivity of liquid argon in temperature and pressure ranges that overlap the present

work. However, their data were not obtained isothermally and thus cannot be compared directly. A functional form for the thermal conductivity surface of the type developed by Roder and Friend [8] for methane–ethane mixtures was fitted to their data, and a comparison was made with the present data. The agreement was found to be of the order of 2% at high densities, degrading slowly to about 3% at low densities. This result is commensurate with the estimated accuracy of the Bailey and Kellner data, 3%.

4.2. Thermal Conductivity of Liquid Argon Along the Saturation Boundary

Values for the thermal conductivity of saturated liquid argon can be obtained by the extrapolation procedure outlined in the previous section. The values are recorded in Table V and plotted in Fig. 4 for the isotherms measured in this paper and in the companion paper [2]. The saturation-line data vary linearly with temperature, a result that has been found for many liquids around room temperature, for temperatures not too close to critical.

The accuracy of the present data and those of Ref. 2 justifies a recommendation as standard reference data. Following the paper by Nieto de Castro et al. [1], we select the data presented herein and in Ref. 2 as primary data with an estimated accuracy of 1%, a sum of the experimental

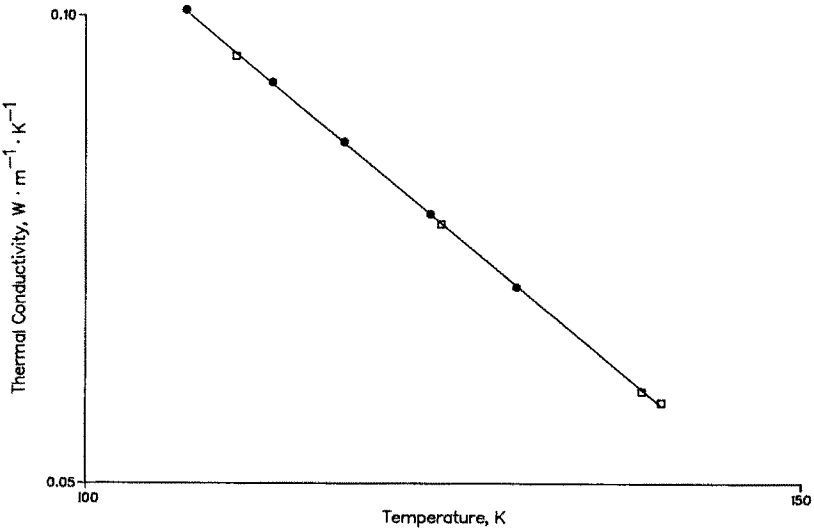

Fig. 4. The thermal conductivity along the saturated liquid line of argon. (□) This paper; (●) Ref. 2; (——) Eq. (5).

uncertainties and of the extrapolation procedure. Identical weight has been given to the data obtained in both laboratories.

A straight-line fit with a standard deviation of 0.00020 $W \cdot m^{-1} \cdot K^{-1}$ and a reference value of the thermal conductivity of liquid argon at 125 K was obtained for the saturation line with

$$\lambda(125.00\ K) = 0.07760 \pm 0.00020\ W \cdot m^{-1} \cdot K^{-1} \tag{2}$$

Following the suggestion presented in Ref. 1 we have expressed the correlation in dimensionless variables λ^* and T^*, defined as

$$T^* = T/125.00 \tag{3}$$

$$\lambda^*(T^*) = \lambda(T)/\lambda(125.00) \tag{4}$$

where $\lambda(125.00)$ is the adopted standard value for the thermal conductivity of liquid argon at 125.00 K. The correlation found was

$$\lambda^*(T^*) = 3.04350 - 2.04350\ T^*, \qquad \text{valid for } 107 < T < 140\ K \tag{5}$$

with a maximum deviation of 0.52% and a standard deviation of 0.00020 $W \cdot m^{-1} \cdot K^{-1}$. This correlation is also plotted in Fig. 4. Figure 5 shows a deviation plot from Eq. (5), including the data used as the basis

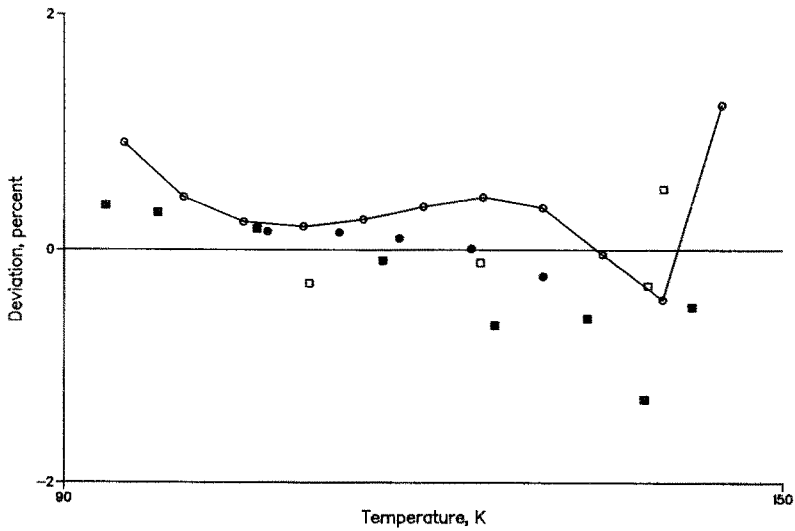

Fig. 5. Deviations from the proposed standard reference correlation for saturated liquid argon, Eq. (5), of the primary data sets [(□) this paper; (●) Ref. 2, of the secondary data set [(■) Ref. 14], and of the correlation (—⊖—) [12].

for the correlation and values for several temperatures calculated from the correlation presented by Younglove and Hanley [12].

Figure 5 also includes data obtained from the measurements of Ziebland and Burton [14], extrapolated to the saturation line. The procedure was as follows. The data are nearly isothermal and were adjusted to average temperatures by using $(\partial\lambda/\partial T)_\rho$ from Ref. 12. The data obtained for all isotherms were fitted to a quadratic in density, and this equation was used to extrapolate to the saturation-line density. For the isotherms above 133 K a graphical procedure was used, with an estimated error of 1%. The data of Ziebland and Burton, herein called secondary data, depart from Eq. (5) by no more than 1.5%.

Due to the overall uncertainty in the surface fitting and the problem of extrapolation to the saturation line, the data of Bailey and Kellner [15] are not included in Fig. 5.

Table V presents the values along the saturation line of argon from Ref. 2 and this paper, as well as proposed standard reference data at the same temperatures, from Eq. (4). The last column in this table shows the numerical deviations of the primary experimental data from the proposed correlation, well within 0.5%. For reference, we present in Table VI values of the thermal conductivity of liquid argon at saturation in 5 K increments.

We conclude that the present data and those of the companion paper confirm each other in the region of temperature overlap to better than 0.5%. These two sets of data are recommended for selection as standard thermal conductivity data along the saturated liquid line of argon and will extend the temperature range of thermal conductivity standards presented in Ref. 1 to cryogenic temperatures. These values confirm the correlation developed by Younglove and Hanley [12] under the auspices of the Sub-

Table VI. Recommended Values of the Thermal Conductivity of Liquid Argon Along the Saturation Line

Temperature (K)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
107	0.10044
110	0.09662
115	0.09029
120	0.08394
125	0.07760
130	0.07126
135	0.06491
140	0.05857

commitee on Transport Properties of Commission I.2 of IUPAC to better than 1% along the saturated liquid line. This agreement degrades to 5% at the higher densities.

4.3. Application of the van der Waals Model

The present experimental study covers a range of densities almost twice that covered by Ref. 2, so that an examination of how well the van der Waals model [16] represents the liquid data should be of interest. Furthermore, the new data can verify if the empirical corrections to the hard-sphere theory, obtained from liquid argon [2] and liquid methane [13] data for small density ranges, are applicable to much larger density ranges. The application of this model can be found in Refs. 2 and 13 and we do not enter into details here. We proceeded in three stages. In the first stage we tried to apply the van der Waals model in its original version [16], obtaining a value of $V_0(T)$, the hard-core volume, for each isotherm separately. The deviations found were systematic within 3% for the 110.485 and 124.769 K isotherms but increased to -10% for the 138.775 and 140.132 K isotherms, as the saturation density was approached. This result confirms the analysis in Ref. 2, that the van der Waals model functional does not have the correct curvature. In the second stage, the $V_0(T)$ values were changed slightly to make the isotherm deviation plots coalesce into a single, unique deviation curve which illustrates the difference in curvature between the experimental data and the theoretically predicted values.

Values chosen for $V_0(T)$ in the companion paper [2] and for both stages of the present results are shown in Fig. 6. All three of the functions of V_0 are seen to be very close to straight lines in temperature. The deviations between experimental and calculated values using the second-stage V_0's are plotted for the present results only in Fig. 7. The deviations are clearly systematic, they are not symmetrical about any particular value of V/V_0, and they show again the effect of the hooks in the experimental data. To represent the experimental data within the experimental precision requires a correction term which would have to be a function of V/V_0 or density.

Finally, in the third stage we have assumed the approach presented in Ref. 2 to be correct; thus the corrected van der Waals model was used, with the correction parameters A and B as determined in Ref. 2. It was possible to reproduce the 110.485 isotherm within 0.9%. However, deviations at the higher densities ran up to 4% for the 124.769 K isotherm and up to 16% for the 140.132 K isotherm. These results show that it is impossible to reproduce the curvature of the higher-temperature isotherms with parameters A and B independent of temperature, because the curvature of

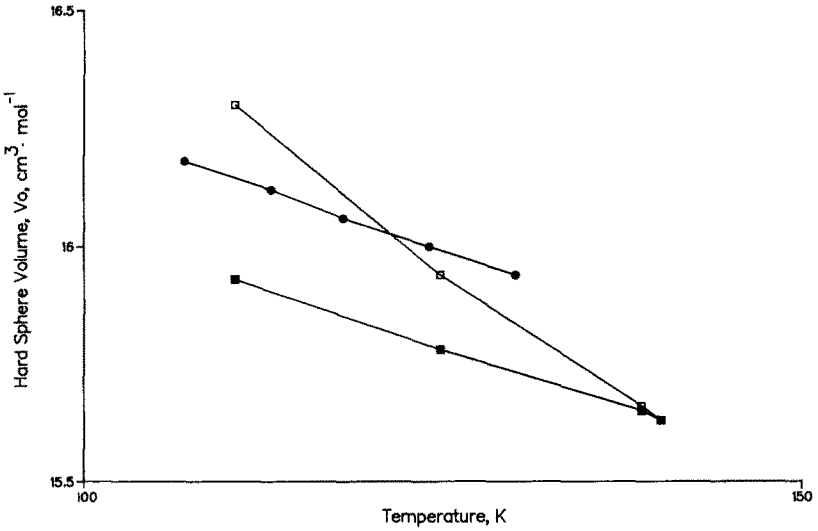

Fig. 6. Estimates of the close-packed hard-sphere volume vs temperature. (■) This paper, individual isotherms; (●) Ref. 2, individual isotherms; (□) this paper, combined isotherms.

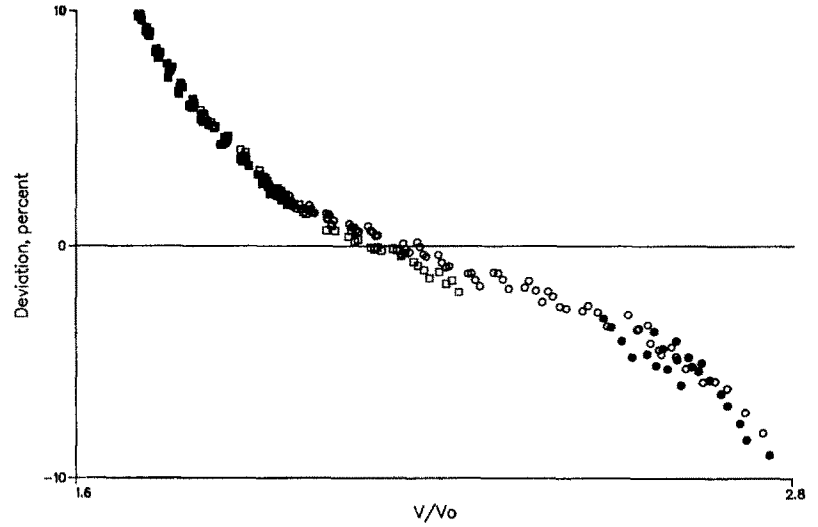

Fig. 7. Deviations between experimental points and the prediction of hard-sphere theory. (■) 110.485 K; (□) 124.769 K; (●) 138.775 K; (○) 140.132 K.

the isotherms extending to high densities becomes significant as the temperature approaches the critical temperature. We suggest that this effect arises from attractive intermolecular forces, an interpretation which violates the basic assumptions of the hard sphere theory.

This analysis demonstrates that the hard-sphere model cannot yield an accurate representation of the thermal conductivity of liquid argon over a wide range of densities, especially when the temperature approaches critical.

5. SUMMARY

New experimental data on the thermal conductivity of liquid argon were obtained with a transient hot-wire apparatus over a wide range of densities, 23 to 36 mol · L^{-1}. The new measurements describe the shape of the thermal conductivity surface in detail. In particular, the measurements show that the isotherms are curved, that this curvature increases as the isotherm approaches the saturated liquid boundary, that the $(\partial\lambda/\partial T)_\rho$ is nonzero and about twice as large as $d\lambda/dT$ at zero density, and that the value of the thermal conductivity on the saturated liquid line rises as the temperature approaches the critical temperature. A detailed comparison of these results with very recent results from another laboratory [2] shows that the precision of the present measurements is 0.5% at the 2σ level and that the accuracy of the present data is somewhat better than 1%. The agreement between the two sets of data is 0.5% at the 1σ level. The extrapolation of the present results to the saturated liquid line confirms those of the companion paper to better than 0.5% and those of the correlation developed under the auspices of IUPAC [12] to better than 1%. The two sets of data are recommended for selection as standard thermal conductivity data along the saturated liquid line of argon, and recommended values at 5 K intervals between 110 K and 140 K are presented. This selection will extend the temperature range of thermal conductivity standards to cryogenic temperatures. Finally, we conclude that the hard-sphere model cannot yield an accurate representation of the thermal conductivity of liquid argon over wide ranges of densities.

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