Correlation of the Thermal Conductivity of Normal and Parahydrogen from the Triple Point to 1000 K and up to 100 MPa[a]

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This paper contains new, representative equations for the thermal conductivity of normal and parahydrogen. The equations are based in part upon a body of experimental data that has been critically assessed for internal consistency and for agreement with theory whenever possible. Although there are sufficient data at normal temperatures, data at very low or very high temperatures as well as near the critical region are scarce. In the case of the dilute-gas thermal conductivity, a new theoretically based correlation was adopted, as it agreed very well with the existing data. Moreover, in the critical region, the experimentally observed enhancement of the thermal conductivity is well represented by theoretically based equations containing just one adjustable parameter. The correlations are applicable for the temperature range from the triple point to 1000 K and pressures up to 100 MPa for both normal hydrogen and parahydrogen. *© 2011 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved.* [doi:10.1063/1.3606499]

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1. Introduction

The study of the thermal conductivity of hydrogen began near the end of the 19th century. In the 1960s and 1970s, there was a major emphasis on researching the thermophysical properties of hydrogen to provide support for NASA and the U.S. space program. More recently, interest in hydrogen has reemerged due to the potential use of hydrogen as an energy carrier that can be produced from diverse resources in an environmentally sound manner. In 2007, two papers were published, which summarized the status of experimental data for equilibrium[1] and transport[2] properties of hydrogen. Jacobsen *et al.*[1] identified the need for a revised equation of state, and subsequently new equations of state were developed for normal and parahydrogen.[3] Most recently, Sakoda and co-workers[4] reviewed the thermodynamic properties and the existing equations of state, concluding that the equation of state of Leachman *et al.*[3] was presently the most appropriate to use for an accurate representation of the thermodynamic properties of hydrogen and parahydrogen. In this work, we develop new, wide-ranging correlations for the thermal conductivity of hydrogen and parahydrogen, which incorporate densities from the new equations of state,[3] and also consider new experimental[5,6] and theoretical[7] data that allow the range of validity of the correlation to extend to higher temperatures than previous correlations, as recommended in Ref. 2.

There are several publications in the literature that present correlations or tables of recommended values for the thermal conductivity of hydrogen and parahydrogen.[6,8–12] McCarty and Weber[12] presented tables for the thermal conductivity of parahydrogen valid over the temperature range from the freezing line to 2778 K (5000 °R) and pressures to 68.9 MPa (10 000 psia). For temperatures below 100 K, the values are based on the experimental data of Roder and Diller.[13] For temperatures greater than 100 K, the thermal conductivity was calculated based on a modified Enskog theory.[14] Later, in 1984, Roder[15–17] made extensive measurements on normal, para and mixtures of ortho and parahydrogen and presented correlating equations valid to 70 MPa. In 1990, McCarty[18] extended the correlations to pressures up to 120 MPa, and these coefficients were used in the NIST12 (MIPROPS) database[19] and later incorporated directly into the REFPROP database[20] (and also the NIST Chemistry Webbook[21]) that currently provide recommended values for the thermal conductivity of hydrogen and parahydrogen. Most recently, Moroe *et al.*[6] provided a new correlation that is applicable up to 100 MPa and 773 K. However, it is not recommended for temperatures below 78 K; therefore, in this work we will compare our results to the wide-ranging correlations developed by McCarty[18,19] that have been incorporated into REFPROP.[20]

It should finally be noted that "normal" hydrogen is 75% orthohydrogen with 25% parahydrogen and is the equilibrium composition at room temperature and above. The equilibrium composition changes as the temperature is decreased, becoming nearly pure parahydrogen at the normal boiling temperature.[3]

2. Methodology

The thermal conductivity λ is expressed as the sum of three independent contributions as

$$\lambda(\rho, T) = \lambda_o(T) + \Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T), \qquad (1)$$

where ρ is the density, T is the temperature, and the first term, $\lambda_o(T) = \lambda(0, T)$, is the contribution to the thermal conductivity in the dilute-gas limit, where only two-body molecular interactions occur. The final term, $\Delta\lambda_c(\rho, T)$, the critical enhancement, arises from the long-range density fluctuations that occur in a fluid near its critical point, which contribute to divergence of the thermal conductivity at that singular point. Finally, the term $\Delta\lambda(\rho, T)$, the excess property, represents the contribution of all other effects to the thermal conductivity of the fluid at elevated densities including many-body collisions, molecular-velocity correlations, and collisional transfer.

The identification of these three separate contributions to the thermal conductivity and to a transport property in general is useful because it is possible, to some extent, to treat both $\lambda_o(T)$ and $\Delta\lambda_c(\rho, T)$ theoretically. In addition, it is possible to derive information about $\lambda_o(T)$ from experiment. In contrast, there is almost no theoretical guidance concerning the excess contribution, $\Delta\lambda(\rho, T)$, so its evaluation is based entirely on experimentally obtained data.

It is obvious that the analysis described above must be applied to the best available experimental data for the thermal conductivity. Thus, a prerequisite to the analysis is a critical assessment of the experimental data. For this purpose, two categories of experimental data are defined: primary data employed in the development of the correlation and secondary data used simply for comparison purposes. According to the recommendation adopted by the Subcommittee of Transport Properties (now known as The International Association for Transport Properties) of the International Union of Pure and Applied Chemistry, the primary data are identified by the following criteria:[22]

(i)   Measurements must have been made with a primary experimental apparatus, i.e., one for which a complete working equation is available.

(ii) The form of the working equation should be such that sensitivity of the property measured to the principal variables does not magnify the random errors of measurement.

(iii) All principal variables should be measurable to a high degree of precision.

(iv) The published work should include some description of purification methods and a guarantee of the purity of the sample.

(v)   The data reported must be unsmoothed data. While graphs and fitted equations are useful summaries for the reader, they are not sufficient for standardization purposes.

(vi) The lack of accepted values of the thermal conductivity of standard reference materials implies that only absolute and not relative measurement results can be considered.

(vii) Explicit quantitative estimates of the uncertainty of reported values should be given, taking into account the precision of experimental measurements and possible systematic errors.

(viii) Owing to the desire to produce low-uncertainty reference values, limits must be imposed on the uncertainty of the primary data sets. These limits are determined after critical evaluation of the existing data sets.

These criteria have been successfully employed to establish standard reference values for the viscosity and thermal conductivity of fluids over wide ranges of conditions, with uncertainties in the range of 1%. However, in many cases in practice, such a narrow definition would limit the range of the data representation unacceptably. Consequently, within the primary data set, it is also necessary to include results that extend over a wide range of conditions, albeit with a poorer accuracy, provided they are consistent with other more accurate data or with theory. In all cases, the accuracy claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

In the following sections, we treat the individual contributions to the thermal conductivity of each fluid separately, in each case subjecting all of the relevant available experimental data to critical scrutiny in order to compile the primary data set, and derive a global correlation of $\lambda(\rho, T)$. The thermal conductivity correlation for normal hydrogen will be presented first and then the correlation for parahydrogen.

3. The Normal Hydrogen Correlation

Table 1 summarizes, to the best of our knowledge, experimental measurements of the thermal conductivity of normal hydrogen reported in the literature. References that present only graphical results or a correlating equation are not included in this summary. Thirteen sets were considered as primary data. The transient hot-wire measurements of Perkins,[5] Mustafa et al.,[23] Roder,[17] Assael and Wakeham,[24] Clifford and Platts,[25] and Clifford et al.[26,27] were all performed in an absolute way, exhibited very low uncertainty, and fulfill the aforementioned criteria for primary data. The recent measurements of Moroe et al.[6] were performed in a calibrated transient short wire, but as they extend to higher temperatures and pressures and were performed in a very precise and well-described manner, they were also considered as primary data. The remaining sets were performed in steady-state instruments that could also be considered as primary. Hence the measurements of Perkins[5] performed with a steady-state hot-wire, the measurements of Clerc et al.[28] and Le Neindre[29] performed in concentric-cylinder instruments, and the measurements of Hemminger[30] performed in a guarded hot-plate instrument were also considered as primary data. Finally, the measurements of Roder and Diller[13] performed in a guarded hot-plate instrument were also

TABLE 1. Thermal conductivity measurements of normal hydrogen.

First author	Year publ.	Technique employed[a]	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
Primary data							
Moroe[6]	2011	THW	99.99	2.0	198	323–772	0.2–100
Perkins[5]	2011	HW	99.999	2.0	279	301–601	0.3–19
Perkins[5]	2011	THW	99.999	1.5	525	301–601	0.3–70
Hemminger[30]	1987	GHP	99.999	0.8	6	313–463	0.1
Mustafa[23]	1987	THW	99.999	0.5	51	307–428	2.5–10
Roder[17]	1984	THW	99.999	1.5	1135	103–301	0.6–69.7
Assael[24]	1981	THW	99.9998	0.2	12	307–308	2–9
Clifford[25]	1981	THW	99.999	0.2	41	310–385	1.9–23.5
Clifford[26]	1980	THW	99.9995	0.2	30	299–301	2–36
Clerc[28]	1977	CC	99.995	1.0	16	298–373	0.1–60
Clifford[27]	1975	THW	99.95	2.6	2	78–283	0.1
LeNeindre[29]	1972	CC	na	2.5	28	273–873	0.1–80
Roder[13]	1970	GHP	na	3.0	112	17–198	0.1–11.8
Secondary data							
Carey[31]	1974	AR	na	1.0	18	295–299	0.15–11
Saxena[32]	1971	HW	99.95	2.0	10	313–450	0.001–0.1
Saxena[33]	1970	HW	99.95	2.0	32	373–1273	0.1–0.2
Saxena[34]	1970	HW	99.95	2.0	3	313–366	0.1
Timrot[35]	1969	HW	na	na	17	400–2000	0.1
vanDael[36]	1968	CTGC	99.5	na	1	297	0.1
Mukhopadhyay[37]	1967	HW	99.95	1.0	7	258–473	0.1
Hamrin[38]	1966	CC	na	2.5	58	275–348	0.1–67
Sherif[39]	1965	HW	na	na	8	92–280	0.1
Golubev[40]	1964	CB	99.998	na	195	78–298	0.1–49
Geier[41]	1961	HW	na	1.0–2.0	13	273–1473	0.1
Blais[42]	1960	HW	na	4.0	11	1200–2100	0.08
Chaikin[43]	1958	HW	na	5.0	5	293–503	0.1
Srivistava[44]	1959	HW	na	na	1	95	0.03
Salceanu[45]	1956	HW	na	na	1	303	0.1
Powers[46]	1954	PP	na	2.0	12	17–24	0.03–0.3
Keyes[47]	1954	CTGC	na	na	10	358–523	0.1–14.7
Lenoir[48]	1951	HW	99.7	1.5–3.0	8	316	0.1–21
Stolyarov[49]	1950	CC	99	3.0	23	291–575	0.1–49
Ubbink[50]	1948	PP	na	na	14	15–274	0.1
Johnston[51]	1946	HW	99.99	0.5	19	80–380	0.1
Ubbink[52]	1943	PP	na	na	4	19–273	0.003–0.1
Archer[53]	1938	HW	na	0.2	1	273	0.01
Spencer-Gregory[54]	1938	HW	na	na	11	95–280	0.09–0.1
Vargaftik[55]	1938	HW	na	na	8	319–710	0.1
Nothdurft[56]	1937	HW	na	na	1	273	0.1
Gregory[57]	1935	HW	na	na	9	295–593	0.1
Dickins[58]	1934	HW	na	0.4	2	273–282	0.08
Kannuluik[59]	1934	HW	na	0.5	11	274	0.003–0.8
Kornfeld[60]	1931	HW	na	na	1	298	0.1
Ibbs[61]	1929	K	na	na	1	273	0.1
Schneider[62]	1926	HW	na	1.0	10	280–315	0.002–0.06
Weber[63]	1917	HW	na	na	1	273	0.1
Eucken[64]	1913	HW	na	na	4	21–273	0.1
Eucken[65]	1911	HW	na	na	5	80–373	0.1
Wassiljewa[66]	1904	HW	na	na	1	295	0.1
Schleiermacher[67]	1888	HW	na	na	2	273–373	0.1

[a]AR, acoustic resonator; CB, cylindrical bicalorimeter; CC, coaxial cylinder; GHP, guarded hot-plate; CTGC, constant-temperature gradient cell; HW, hot-wire; K, katharometer; na, not available; PP, parallel plate; THW, transient hot-wire.
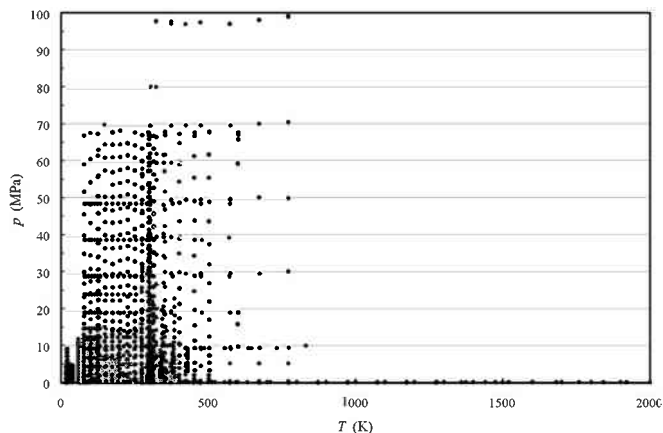
Fɪɢ. 1. Temperature and pressure ranges of the experimental thermal conductivity data for normal hydrogen.

included as primary data, since they are the only reliable measurements that are performed at temperatures below the critical, and also include some points near the critical region. The remaining measurements in Table 1 did not fulfill the criteria for primary data, and hence they were considered as secondary data.

Figure 1 shows the temperature and pressure range of the measurements outlined in Table 1. Temperatures for all data were converted to the ITS-90 temperature scale.[68] The development of the correlation requires densities; the equation of state of Leachman et al.[3] was used to provide the density for each experimental state point from the experimental temperature and pressure. We also adopt the values for the critical point and triple point from this equation of state; the critical temperature, T_c, the critical pressure, p_c, and the critical density, ρ_c, were taken to be equal to 33.145 K, 1.2964 MPa, and 31.262 kg m^{-3}, respectively.[3] The triple-point temperature is 13.957 K.[3] It should be noted that, for this equation of state, the uncertainty in density from an input of temperature and pressure was reported to be 0.1% at temperatures from the triple point to 250 K and at pressures up to 40 MPa, except in the critical region, where an uncertainty of 0.2% in pressure is generally attained. Furthermore, in the region between 250 K and 450 K and at pressures to 300 MPa, the uncertainty in density was stated as 0.04%, while at temperatures between 450 K and 1000 K, the uncertainty in density increases to 1%. We also note that the estimated uncertainty for the heat capacities is 1.0%.[3]

3.1. The dilute-gas limit

Assael and coworkers[69] published a correlation for the thermal conductivity of normal hydrogen in the dilute-gas limit that was developed by critically evaluating experimental data available through 1985. Due to limitations of the experimental data, the correlation is recommended only over the restricted temperature range of 100–400 K. Since that time, there have been significant advances in theoretically based calculations for dilute-gas thermal conductivity that we utilize here to extend the range of validity. In a recent pa-

per, Mehl et al.[7] employed the spherical version of the hydrogen intermolecular potential determined in *ab initio* calculations by Patkowski et al.[70] to calculate the viscosity and thermal conductivity of normal and parahydrogen by use of a full quantum-mechanical formalism. To supplement the tables in Mehl et al.,[7] we obtained more detailed tables of values of the dilute-gas thermal conductivity (ranging from 10 K to 2000 K in 1 K intervals) from Mehl,[71] and used data from 10 K to 2000 K to develop the correlation presented here. Mehl et al.[7] reported that the average fractional difference between the theoretically calculated values and experimental data was (0.1 ± 1.1) % in the temperature range 10–384 K, while at higher temperatures (600–2000 K) ranged from 4% to 10%. We fit these tabular values for the dilute-gas thermal conductivity of normal hydrogen to the following functional form:

$$\lambda_o(T) = \frac{\sum_{i=0}^{m} A_{1,i}(T/T_c)^i}{\sum_{i=0}^{n} A_{2,i}(T/T_c)^i} . \qquad (2)$$

The coefficients $A_{1,i}$ and $A_{2,i}$ for normal hydrogen ($m = 6$, $n = 3$) are given in Table 2. The correlation agrees with the tabulated values of Mehl et al.[7,71] to within 0.6% at temperatures above 20 K, with a maximum deviation of 2% at 12 K.

Figure 2 shows the percentage deviations of dilute-gas primary experimental data and the theoretical values of Mehl et al.[7,71] from the values calculated by Eq. (2). With the exception of a few experimental points (of slightly higher uncertainty), the values calculated by Eq. (2) represent the data within $\pm 2\%$. In addition to the primary data, two additional correlations are shown:

(a) The correlation attributed to McCarty[18] as implemented in REFPROP (Ref. 20) that is based on modified Enskog theory at high temperatures, and has an uncertainty of up to 10% (Ref. 14);

(b) The correlation of Assael et al.,[69] published in 1986, is based upon the semiclassical kinetic theory of

Tᴀʙʟᴇ 2. Coefficients of Eqs. (2) and (3) for normal hydrogen.

i	$A_{1,i}$ (W m^{-1} K^{-1})	$A_{2,i}$ (−)
0	$-3.409\,76 \times 10^{-1}$	$1.384\,97 \times 10^{2}$
1	$4.588\,20 \times 10^{0}$	$-2.218\,78 \times 10^{1}$
2	$-1.450\,80 \times 10^{0}$	$4.571\,51 \times 10^{0}$
3	$3.263\,94 \times 10^{-1}$	$1.000\,00 \times 10^{0}$
4	$3.169\,39 \times 10^{-3}$	
5	$1.905\,92 \times 10^{-4}$	
6	$-1.139\,00 \times 10^{-6}$	

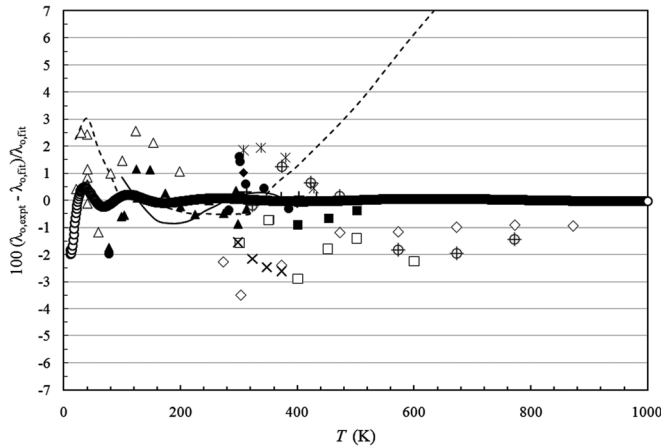| i	$B_{1,i}$ (W m^{-1} K^{-1})	$B_{2,i}$ (W m^{-1} K^{-1})
1	$3.630\,81 \times 10^{-2}$	$1.833\,70 \times 10^{-3}$
2	$-2.076\,29 \times 10^{-2}$	$-8.867\,16 \times 10^{-3}$
3	$3.148\,10 \times 10^{-2}$	$1.582\,60 \times 10^{-2}$
4	$-1.430\,97 \times 10^{-2}$	$-1.062\,83 \times 10^{-2}$
5	$1.749\,80 \times 10^{-3}$	$2.806\,73 \times 10^{-3}$

FIG. 2. Percentage deviations of dilute-gas primary experimental data of normal hydrogen from the values calculated by Eq. (2). Perkins-THW[5] (■), Perkins-HW[5] (□), Mustafa *et al.*[23] (✳), Hemminger[30] (+), Roder[17] (▲), Roder and Diller[13] (△), Assael and Wakeham[24] (◆), Clifford[25–27] (●), Clerc *et al.*[28] (x), Le Neindre[29] (◇), Moroe *et al.*[6] (⊕), McCarty[18] (--), Assael *et al.*[69] (—), and Mehl *et al.*[7,71] (○).

polyatomic gases and a body of critically evaluated experimental data. The correlation is limited to the range of 100–400 K. Above room temperature, the uncertainty is no more than ±0.5%, but below room temperature it rises to ±1.5% (Ref. 69) and is not recommended for use below 100 K.

Both these correlations agree with the values proposed by Eq. (2), well within the mutual uncertainties.

3.2. The excess thermal conductivity

The thermal conductivities of pure fluids exhibit an enhancement over a large range of densities and temperatures around the critical point and become infinite at the critical point. This behavior can be described by models that produce a smooth crossover from the singular behavior of the thermal conductivity asymptotically close to the critical point to the nonsingular background values far away from the critical point.[72–74] The density-dependent terms for thermal conductivity can be grouped according to Eq. (1) as $[\Delta\lambda(\rho,T) + \Delta\lambda_c(\rho,T)]$. To assess the critical enhancement either theoretically or empirically, we need to evaluate, in addition to the dilute-gas thermal conductivity, the excess thermal conductivity contribution. The procedure adopted during this analysis used ODRPACK (Ref. 75) to fit all the primary data simultaneously to the excess thermal conductivity and the critical enhancement, while maintaining the parameters already obtained from the fit of the dilute-gas thermal-conductivity data. The density values employed were obtained by the Helmholtz equation of state of Leachman *et al.*[3]

The excess thermal conductivity was represented with a polynomial in temperature and density,

$$\Delta\lambda(\rho,T) = \sum_{i=1}^{5} \left(B_{1,i} + B_{2,i}(T/T_c) \right)(\rho/\rho_c)^i. \quad (3)$$

The coefficients $B_{1,i}$ and $B_{2,i}$ are shown in Table 2.

3.3. The critical enhancement

3.3.1. Simplified crossover model

The theoretically based crossover model proposed by Olchowy and Sengers[72–74] is complex and requires solution of a quartic system of equations in terms of complex variables. A simplified crossover model has also been proposed by Olchowy and Sengers.[76] The critical enhancement of the thermal conductivity is given by

$$\Delta\lambda_c = \frac{\rho C_p R_D k_B T}{6\pi\bar{\eta}\xi}\left(\bar{\Omega} - \bar{\Omega}_0\right), \quad (4)$$

with

$$\bar{\Omega} = \frac{2}{\pi}\left[\left(\frac{C_p - C_V}{C_p}\right)\arctan(\bar{q}_D\xi) + \frac{C_V}{C_p}\bar{q}_D\xi\right] \quad (5)$$

and

$$\bar{\Omega}_0 = \frac{2}{\pi}\left[1 - \exp\left(-\frac{1}{(\bar{q}_D\xi)^{-1} + (\bar{q}_D\xi\rho_c/\rho)^2/3}\right)\right]. \quad (6)$$

In Eqs. (4)–(6), k_B is Boltzmann's constant, $\bar{\eta}$ is the background viscosity that we obtained from the recommended correlation in the REFPROP (Refs. 18 and 20) database, C_p and C_v are the isobaric and isochoric specific heat obtained from the equation of state,[3] and $\bar{q}_D$ is the effective wavenumber cutoff determined by fitting thermal conductivity data in the critical region; we found that $\bar{q}_D^{-1} = 4.0 \times 10^{-10}$ m. The correlation length ξ is given by

$$\xi = \xi_0\left(\frac{p_c\rho}{\Gamma\rho_c^2}\right)^{\nu/\gamma}\left[\left.\frac{\partial\rho(T,\rho)}{\partial p}\right|_T - \left(\frac{T_{ref}}{T}\right)\left.\frac{\partial\rho(T_{ref},\rho)}{\partial p}\right|_T\right]^{\nu/\gamma}. \quad (7)$$

As already mentioned, the coefficients of Eq. (2) were fixed, while the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. (3) and $\bar{q}_D$ in Eqs. (4)–(7) were fitted with ODRPACK (Ref. 75) to the primary data for the thermal conductivity of hydrogen. This crossover model requires the universal constants[76] $R_D = 1.01$, $\nu = 0.63$, and $\gamma = 1.2415$, and system-dependent amplitudes Γ and ξ_0. For this work, we adopted the values $\Gamma = 0.052$ and $\xi_0 = 1.5 \times 10^{-10}$ m as given by Olchowy and Sengers[76] for CO_2, and a reference temperature far above the critical temperature where the critical enhancement is negligible, $T_{ref} = {}^3/_2 T_c$,[77] which for normal hydrogen is 49.7175 K.

Table 3 summarizes comparisons of the primary data with the correlation, and also with the correlation of McCarty.[18–20] Here, we define the percent deviation as PCTDEV = $100(\lambda_{exp} - \lambda_{fit})/\lambda_{fit}$, where λ_{exp} is the experimental value of the thermal conductivity and λ_{fit} is the value calculated from the correlation. The average absolute percent deviation (AAD) is found with the expression AAD = $(\sum|PCTDEV|)/n$, where the summation is over all n points and the standard deviation is

TABLE 3. Evaluation of the normal hydrogen correlation for the primary data.

First author	Year publ.	Present AAD (%)	Present STDEV (%)	McCarty[18–20] AAD (%)	McCarty STDEV (%)
Moroe[6]	2011	1.320	1.142	5.693	6.472
Perkins[5] (steady state)	2011	1.816	0.921	3.134	2.502
Perkins[5] (transient)	2011	1.330	0.687	3.567	2.498
Hemminger[30]	1987	0.143	0.073	1.114	1.063
Mustafa[23]	1987	0.836	0.443	1.268	1.082
Roder[17]	1984	1.121	1.526	0.735	1.010
Assael[24]	1981	0.140	0.163	1.191	0.100
Clifford[25,26]	1981	0.350	0.443	0.700	0.738
Clerc[28]	1977	3.096	0.716	3.475	1.183
Clifford[27]	1975	1.456	1.119	0.700	0.738
LeNeindre[29]	1972	1.591	0.803	4.901	3.759
Roder[13]	1970	2.894	3.413	2.670	2.938
Total		1.348	1.745		

FIG. 4. Percentage deviations of primary experimental data of normal hydrogen from the values calculated by the present model as a function of the density. Perkins-THW[5] (■), Perkins-HW[5] (□), Mustafa et al.[23] (✳), Hemminger[30] (✛), Roder[17] (▲), Roder and Diller[13] (△), Assael and Wakeham[24] (◆), Le Neindre[29] (◇), Clifford[25–27] (●), Clerc et al.[28] (x), and Moroe et al.[6] (⊕).

$$STDEV = ([n\sum PCTDEV^2 - (\sum PCTDEV)^2]/n^2)^{1/2}.$$ Note that the new correlation performs significantly better than the McCarty correlation[18–20] for the data set of Moroe et al.,[6] especially at high temperatures and high pressures, as indicated in Figs. 3(a) and 3(b). This is not surprising, since the Moroe et al.[6] data were not available at the time the McCarty correlation[18–20] was developed.

Figure 4 shows the percentage deviations of all primary thermal conductivity data from the values calculated by Eqs. (1)–(7), as a function of the density, while Fig. 5 shows the same deviations but as a function of the temperature. For supercritical hydrogen, the correlation represents the data to within 4% (at a coverage factor of 2) at pressures up to 100 MPa. The representation of the liquid-phase data is 8%, again at a 95% confidence level. This is considered acceptable based on inconsistencies between several liquid isotherms that may be due to ortho-para conversion during the measurements.[17] Ortho-para conversion would be most
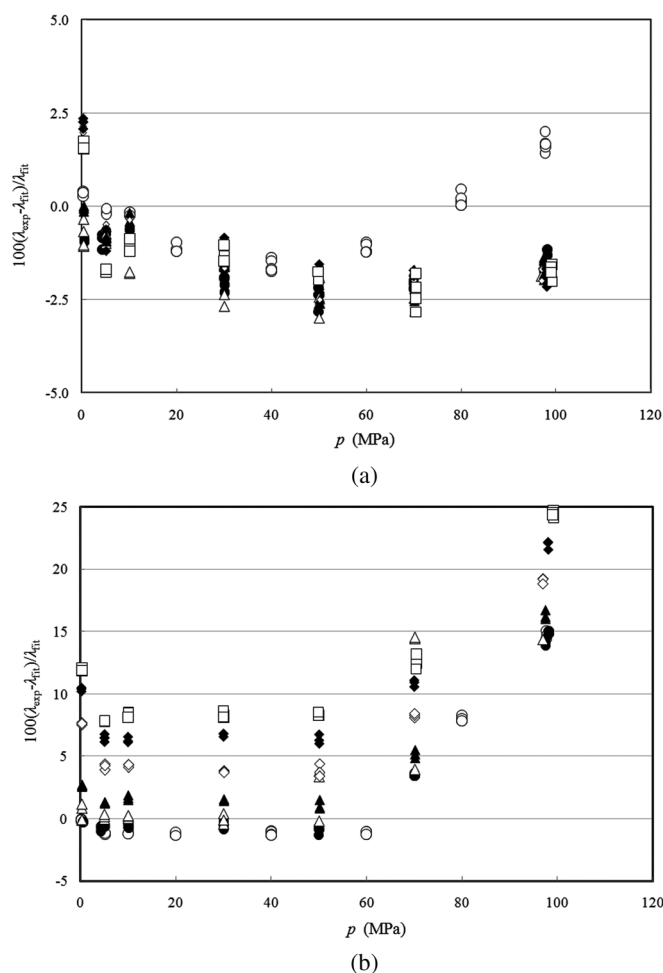

(a)

(b)

FIG. 3 (a) Percentage deviations of the data of Moroe et al.[6] for the thermal conductivity of normal hydrogen as a function of pressure from the values calculated by the present model. (1). 323 K (○), 373 K (●), 423 K (△), 473 K (▲), 573 K (◇), 673 K (◆), and 772 K (□). (b) Percentage deviations of the data of Moroe et al.[6] for the thermal conductivity of normal hydrogen as a function of pressure from the values calculated by the correlation of McCarty.[18–20] 323 K (○), 373 K (●), 423 K (△), 473 K (▲), 573 K (◇), 673 K (◆), and 772 K (□).
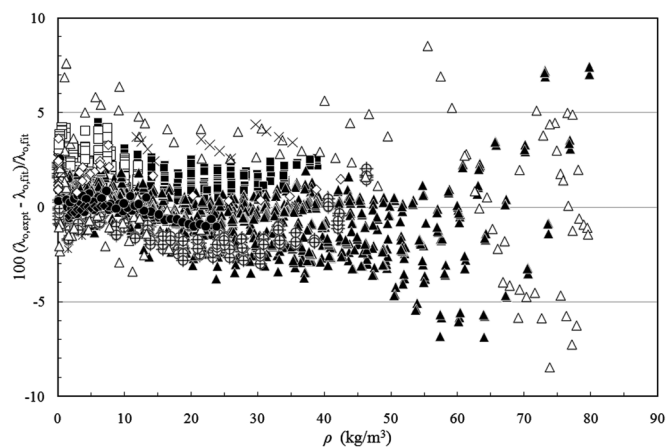

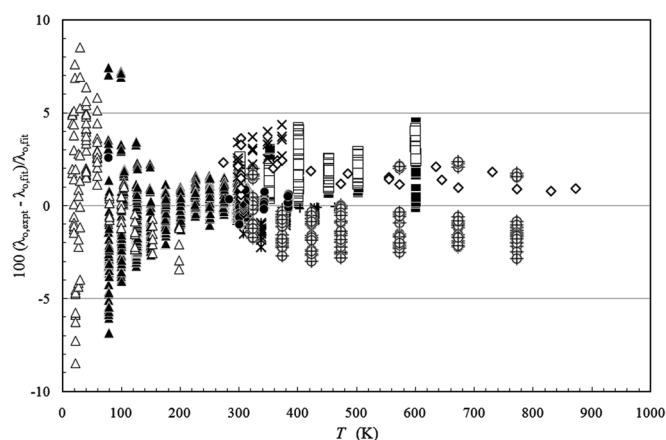FIG. 5. Percentage deviations of primary experimental data of normal hydrogen from the values calculated by the present model as a function of the temperature. Perkins-THW[5] (■), Perkins-HW[5] (□), Mustafa et al.[23] (✳), Hemminger[30] (✛), Roder[17] (▲), Roder and Diller[13] (△), Assael and Wakeham[24] (◆), Le Neindre[29] (◇), Clifford[25–27] (●), Clerc et al.[28] (x), and Moroe et al.[6] (⊕).

FIG. 6. Percentage deviations of secondary experimental data of normal hydrogen from the values calculated by the present model as a function of the density. Archer[53] (◆), Blais and Mann[42] (⬙), Carey *et al.*[31] (◆), Chaikin and Markevitch[43] (◆), Dickins[58] (◆), Eucken[64,65] (△), Geier and Shafer[41] (▲), Golubev and Kaltzsina[40] (▲), Gregory[57] (▲), Hamrin and Thodos[38] (○), Ibbs and Hirst[61] (Φ), Johnston and Grilly[51] (◑), Kannuluik and Martin[59] (◐), Keys[47] (⬭), Kornfeld and Hilferding[60] (⬬), Lenoir and Commings[48] (⊞), Mukhopadhyay *et al.*[37] (⊞), Northdruft[56] (⊟), Powers *et al.*[46] (⬛), Salceanu and Bojin[45] (▣), Saxena[32–34] (●), Schneider[62] (⊖), Sherif[39] (◆), Spencer-Gregory and Dock[54] (■), Srivistava and Srivistava[44] (⊕), Stolyarov *et al.*[49] (△), Timrot *et al.*[35] (◇), Ubbink[50,52] (□), van Dael and Cauwenbergh[36] (x), Vargaftik and Parfenov[55] (✳), Wassilewa[66] (-), and Weber[63] (+).

pronounced for the lowest temperatures during measurements on normal hydrogen.

In Figs. 6 and 7, the percentage deviations of the secondary thermal conductivity data from the values calculated by Eqs. (1)–(7) are shown as a function of the density and the temperature, respectively. As expected, the spread of the
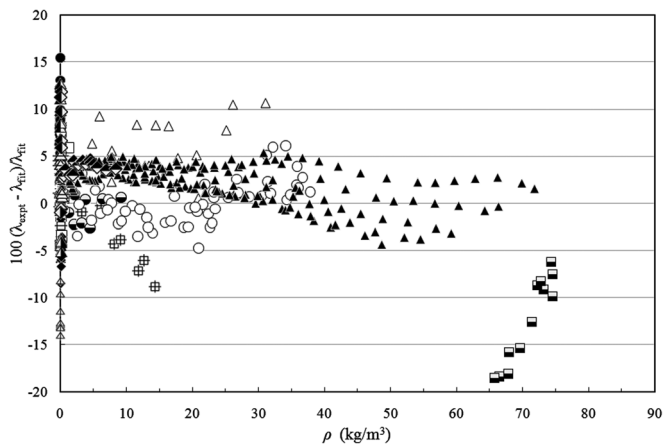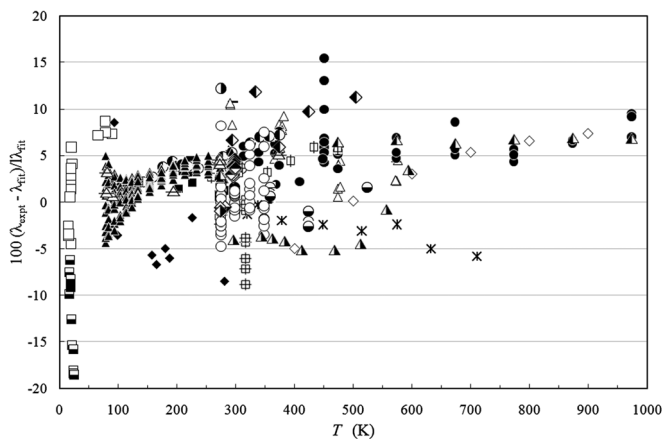

FIG. 7. Percentage deviations of secondary experimental data of normal hydrogen from the values calculated by the present model as a function of the temperature. Archer[53] (◆), Blais and Mann[42] (⬙), Carey *et al.*[31] (◆), Chaikin and Markevitch[43] (◆), Dickins[58] (◆), Eucken[64,65] (△), Geier and Shafer[41] (▲), Golubev and Kaltzsina[40] (▲), Gregory[57] (▲), Hamrin and Thodos[38] (○), Ibbs and Hirst[61] (Φ), Johnston and Grilly[51] (◑), Kannuluik and Martin[59] (◐), Keys[47] (⬭), Kornfeld and Hilferding[60] (⬬), Lenoir and Commings[48] (⊞), Mukhopadhyay *et al.*[37] (⊞), Northdruft[56] (⊟), Powers *et al.*[46] (⬛), Salceanu and Bojin[45] (▣), Saxena[32–34] (●), Schneider[62] (⊖), Sherif[39] (◆), Spencer-Gregory and Dock[54] (■), Srivistava and Srivistava[44] (⊕), Stolyarov *et al.*[49] (△), Timrot *et al.*[35] (◇), Ubbink[50,52] (□), van Dael and Cauwenbergh[36] (x), Vargaftik and Parfenov[55] (✳), Wassilewa[66] (-), and Weber[63] (+).
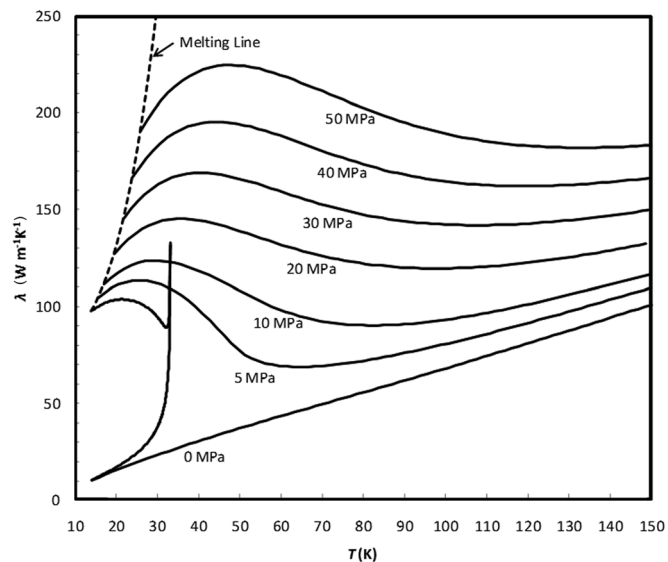
FIG. 8. Thermal conductivity of normal hydrogen as a function of the temperature for different pressures.

deviations is now much wider. Finally, Fig. 8 shows a plot of the thermal conductivity values calculated by Eqs. (1)–(7) for the temperature range 14–150 K for pressures between 0 MPa and 50 MPa.

3.3.2. Empirical critical enhancement

For applications at state points that are relatively distant from the critical point (about 10–15 K from the critical temperature), the critical enhancement is adequately represented by the following empirical expression:

$$\Delta\lambda_c(\rho, T) = \frac{C_1}{C_2 + |\Delta T_c|} \exp\left[-(C_3\Delta\rho_c)^2\right], \quad (8)$$

where $\Delta T_c = (T/T_c) - 1$ and $\Delta\rho_c = (\rho/\rho_c) - 1$. This equation does not require accurate information on the compressibility, specific heat, and viscosity of normal hydrogen in the critical region, as does the theory of Olchowy and Sengers.[72–74,76] The coefficients of Eqs. (2) and (3) were fixed while the coefficients of Eq. (8) were fitted to the primary data. The values obtained were $C_1 = 6.24 \times 10^{-4}$ W m^{-1} K^{-1}, $C_2 = -2.58 \times 10^{-7}$, and $C_3 = 0.837$. Figure 9 shows the percentage deviations between the primary data and the values calculated by Eqs. (2), (3), and (8), as a function of the temperature. By comparing Figs. 5 and 9, it can be seen that employing Eq. (8) results in very little deterioration in the representation of the data; the deviations for the Roder and Diller data from Eq. (8) range from −8% to +15%, while those for the simplified Olchowy-Sengers enhancement vary from −9% to +9%.

4. The Parahydrogen Correlation

Table 4 summarizes existing measurements of the thermal conductivity of parahydrogen reported in the literature, to
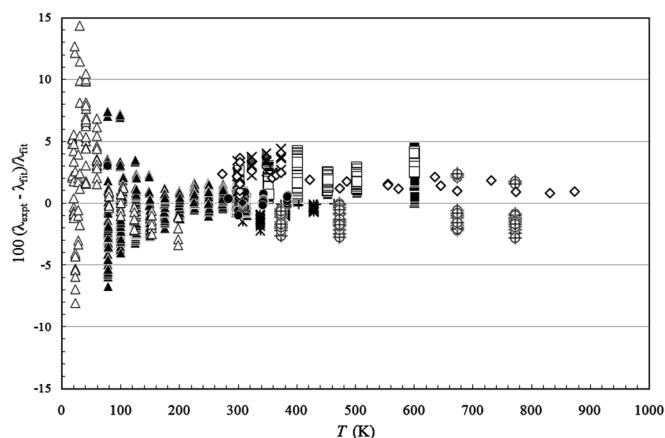
FIG. 9. Percentage deviations of primary experimental data of normal hydrogen from the values calculated by Eqs. (2), (3), and (8) as a function of the temperature. Perkins-THW[5] (■), Perkins-HW[5] (□), Mustafa et al.[23] (✳), Hemminger[30] (✛), Roder[17] (▲), Roder and Diller[13] (△), Assael and Wakeham[24] (◆), Le Neindre[29] (◇), Clifford[25–27] (●), Clerc et al.[28] (x), and Moroe et al.[6] (⊕).

FIG. 10. Temperature and pressure ranges of the experimental thermal conductivity data of parahydrogen.

the best of our knowledge. It can be seen that the number of measurements is hardly sufficient for a good correlation. Furthermore, only the transient hot-wire measurements of Roder[15] and the steady-state hot-wire measurements of Roder and Diller[13] can be considered as primary data. In addition, the data of Powers et al.,[46] in this case, deviated very much from the above two sets making them unusable, while the uncertainty of the data of Dwyer et al.[78] makes that set unsuitable for this work. Figure 10 shows the temperature and pressure range of the primary measurements outlined in Table 4. Temperatures for all data were converted to the ITS-90 temperature scale.[68] The parahydrogen equation of state of Leachman et al.[3] was used to provide the density for each experimental state point using the experimental temperature and pressure. The critical point associated with this equation of state is $T_c = 32.938$ K, $p_c = 1.2858$ MPa, and $\rho_c = 31.323$ kg m^{-3} and the triple point temperature is 13.8033 K.[3] The uncertainties for density and heat capacity for this equation of state are identical to those for the normal hydrogen equation of state by Leachman et al.[3]
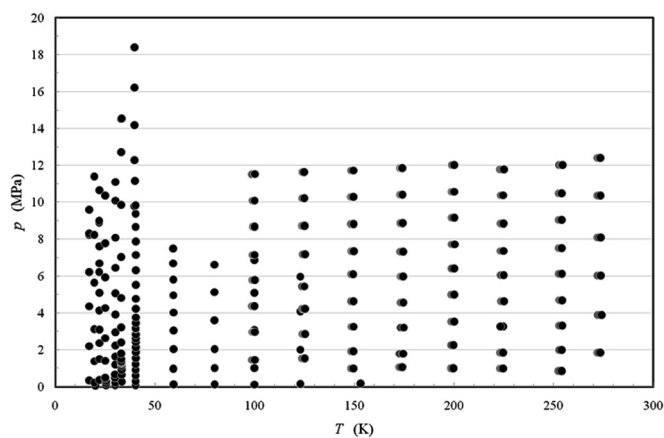
4.1. The dilute-gas limit

As discussed in the case of normal hydrogen, it was preferred to base the dilute-gas thermal conductivity correlation on the work of Mehl et al.[7] To supplement the tables in Ref. 7, we obtained more detailed tables of values of the dilute-gas thermal conductivity (ranging from 10 K to 2000 K in 1 K intervals) from Mehl[71] and used data from 10 K to 2000 K to develop the correlation presented here. The average fractional difference between the theoretically calculated values and the experimental data was reported as (-0.7 ± 1.2) % in the temperature range 10–275 K, while at higher temperatures (600–2000 K) it was estimated to be from 4% to 10%. We again fit the functional form of Eq. (2) to the tabulated values of Mehl. Table 5 shows the coefficients $A_{1,i}$ and $A_{2,i}$ found for parahydrogen.

Figure 11 shows the percentage deviations of dilute-gas primary experimental data and the theoretical values of Mehl et al.[7,71] from the values calculated by Eq. (2) at temperatures from 10 K to 2000 K. The values calculated by Eq. (2) represent the data within approximately 1% to as low as 12 K. In addition to the primary data, the correlation attributed to McCarty,[18,19] as implemented in REFPROP,[20] is also shown as a solid line. The McCarty correlation agrees with the

TABLE 4. Thermal conductivity measurements of parahydrogen.

First author	Year publ.	Technique employed[a]	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
Primary data							
Roder[15]	1984	THW	na	1.5	269	99–274	0.9–13
Roder[13]	1970	HW	99.8	na	136	17–153	0.02–19
Secondary data							
Dwyer[78]	1966	GME	99.0	50.0	9	15–22	0.02–22
Powers[46]	1954	PP	na	2.0	7	16–23	0.1

[a]GME, gradient measurement enclosure; HW, hot-wire; PP, parallel plate; THW, transient hot-wire.

TABLE 5. Coefficients of Eqs. (2) and (3) for parahydrogen.

i	$A_{1,i}$ (W m^{-1} K^{-1})	$A_{2,i}$ (−)
0	$-1.245\,00 \times 10^{0}$	$1.423\,04 \times 10^{4}$
1	$3.102\,12 \times 10^{2}$	$-1.939\,22 \times 10^{4}$
2	$-3.310\,04 \times 10^{2}$	$1.583\,79 \times 10^{4}$
3	$2.460\,16 \times 10^{2}$	$-4.818\,12 \times 10^{3}$
4	$-6.578\,10 \times 10^{1}$	$7.286\,39 \times 10^{2}$
5	$1.082\,60 \times 10^{1}$	$-3.573\,65 \times 10^{1}$
6	$-5.196\,59 \times 10^{-1}$	$1.000\,00 \times 10^{0}$
7	$1.439\,79 \times 10^{-2}$	

i	$B_{1,i}$ (W m^{-1} K^{-1})	$B_{2,i}$ (W m^{-1} K^{-1})
1	$2.659\,75 \times 10^{-2}$	$-1.217\,27 \times 10^{-3}$
2	$-1.338\,26 \times 10^{-3}$	$3.666\,63 \times 10^{-3}$
3	$1.302\,19 \times 10^{-2}$	$3.887\,15 \times 10^{-3}$
4	$-5.676\,78 \times 10^{-3}$	$-9.210\,55 \times 10^{-3}$
5	$-9.233\,80 \times 10^{-5}$	$4.007\,23 \times 10^{-3}$

experimental data to within about 3% at temperatures below 600 K, with increasing deviations at higher temperatures.

4.2. Excess thermal conductivity and critical enhancement

4.2.1. Simplified crossover model

As in the case of normal hydrogen, the coefficients of Eq. (2) were fixed, while the coefficients of Eqs. (3)–(7) were fit with ODRPACK (Ref. 75) to the primary transient[15] and steady-state[13] data for the thermal conductivity of parahydrogen. We used the same values for the universal constants and amplitudes for parahydrogen as were used for normal hydrogen, and a reference temperature where the critical enhancement is negligible $T_{\mathrm{ref}} = ^3/_2 T_{\mathrm{c}} = 49.407$ K. In this case, it was found that $\bar{q}_{\mathrm{D}}^{-1} = 5.0 \times 10^{-10}$ m.

Table 6 summarizes comparisons of the primary data with the correlation, and also with the correlation of McCarty,[18–20]
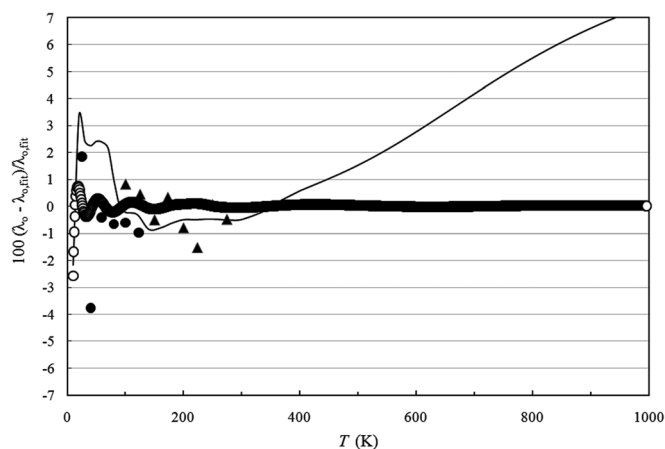
TABLE 6. Evaluation of the parahydrogen correlation for the primary thermal conductivity data.

First author	Year publ.	Present AAD (%)	Present STDEV (%)	McCarty[18,20] AAD (%)	McCarty STDEV (%)
Roder[15]	1984	0.247	0.316	0.500	0.533
Roder[13]	1970	1.467[a]	1.833[a]	2.214[a]	2.208[a]
Total		0.634	1.067		

[a]Excludes points at 32.98–33.05 K in the critical region.

while Fig. 12 graphically depicts the percentage deviations of the primary thermal conductivity data from the values calculated by Eqs. (1)–(7), as a function of the density, and Fig. 13 shows the same deviations but as a function of the temperature. With the exception of some data very near the critical point (points of Roder and Diller[13] at temperatures 32.98–33.05 K), the remaining data seem to be well within ±4% of the present work. Figure 14 shows the thermal conductivity as a function of density for two isotherms that exhibit critical enhancement. The model is shown with and without the critical enhancement term. The experimental data of Roder and Diller[13] are plotted at nominal isotherms of 33 K and 40 K using the experimental values of temperature and density. The model has difficulty matching the extremely steep rise of thermal conductivity seen for the 33 K isotherm, but captures the general behavior. At conditions farther removed from critical, but where there still is a significant critical enhancement, the model represents the data very well as indicated by the 40 K isotherm in the figure.

4.2.2. Empirical critical enhancement

Equation (8) was also employed for parahydrogen to correlate the critical enhancement at state points that are relatively distant from the critical point (about 5–10 K from the

FIG. 11. Percentage deviations of dilute-gas primary experimental data of parahydrogen from the values calculated by Eq. (2). Roder[17] (▲), Roder and Diller[13] (●), McCarty[18] (—-), and Mehl *et al.*[7,71] (○).

FIG. 12. Percentage deviations of primary experimental data of parahydrogen from the values calculated by the present model as a function of the density. Roder[17] (●) and Roder and Diller[13] (○).
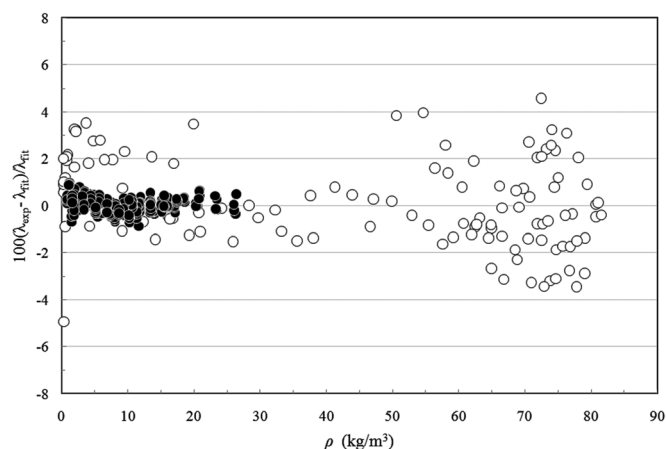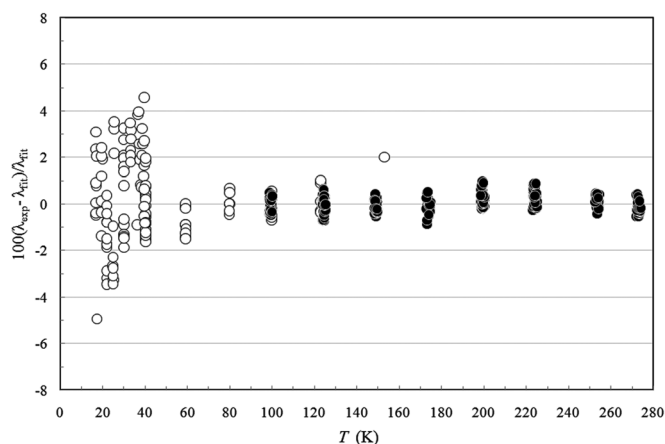
FIG. 13. Percentage deviations of primary experimental data of parahydrogen from the values calculated by the present model as a function of the temperature. Roder[17] (●) and Roder and Diller[13] (○).

critical temperature). The coefficients of Eqs. (2) and (3) were fixed, while the coefficients of Eq. (8) were fitted to the primary data. The values obtained were $C_1 = 3.57 \times 10^{-4}$ W m^{-1} K^{-1}, $C_2 = -2.46 \times 10^{-2}$, and $C_3 = 0.2$. Employing Eq. (8) results in very little deterioration in the representation of the data, as was seen earlier with normal hydrogen.

5. Computer-Program Verification

Table 7 is provided to assist the user in computer-program verification. The thermal conductivity calculations are based on the tabulated temperatures and densities.
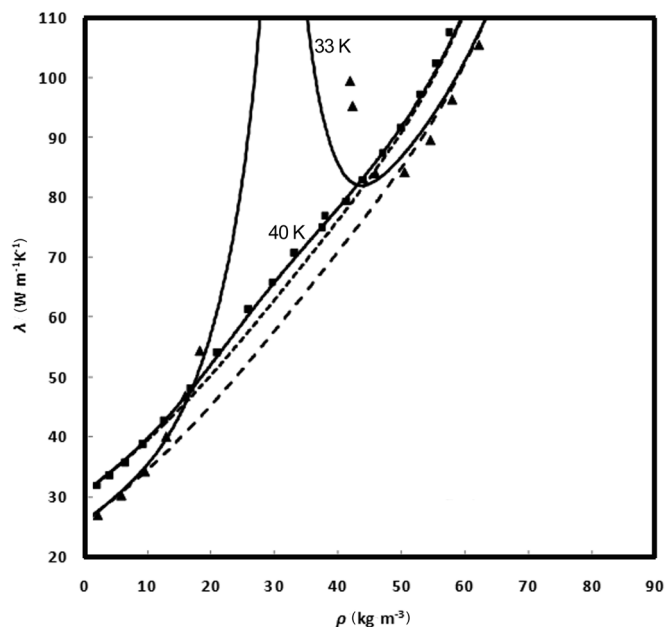

FIG. 14. Thermal conductivity of parahydrogen as a function of density, for 33 K and 40 K isotherms. At 33 K: present model (—), no enhancement (– –), Roder and Diller[13] (▲); At 40 K: present model (—), no enhancement (- - -), Roder and Diller[13] (■).

TABLE 7. Sample points for computer verification of the correlating equations.

		λ (mW m^{-1} K^{-1})	
T (K)	ρ (kg m^{-3})	Normal hydrogen	Parahydrogen
298.150	0.00000	185.67	192.38
298.150	0.80844	186.97	192.81
298.150	14.4813	201.35	207.85
35.0000	0.00000	26.988	27.222
35.0000	30.0000	75.594[a]	70.335[a]
35.0000	30.0000	71.854[b]	68.611[b]
18.0000	0.00000	13.875	13.643
18.0000	75.0000	104.48	100.52

[a]Computed with modified Olchowy–Sengers critical enhancement.
[b]Computed with empirical critical enhancement.

6. Range of Validity and Uncertainty Estimates

The primary data for normal hydrogen listed in Table 1 cover a wide range of conditions and extend to 100 MPa. In addition, we made comparisons with the recommended values given in the handbook by Vargaftik *et al.*[10] that are presented in Table 8. The densities in Table 8 are obtained from the equation of state of Leachman *et al.*[3] evaluated at the

TABLE 8. Comparison of extrapolated values λ_{fit} of present correlation with values from tables in Ref. 10.

T (K)	p (MPa)	ρ (kg m^{-3})	λ_{fit} (mW m^{-1} K^{-1})	$\lambda_{\text{Vargaftik}}$ (mW m^{-1} K^{-1})	100 ($\lambda_{\text{fit}}/\lambda_{\text{Vargaftik}}$ - 1)
Normal hydrogen					
400	30	15.879	248.6	249.1	−0.2
600	30	11.036	322.0	319.8	0.7
800	30	8.471	395.3	388.3	1.8
1000	30	6.877	471.2	457.7	2.9
400	60	28.155	269.8	268.0	0.7
600	60	20.287	334.0	331.7	0.7
800	60	15.886	402.7	397.0	1.4
1000	60	13.062	476.3	464.7	2.5
400	100	40.872	305.7	295.1	3.6
600	100	30.599	359.0	349.4	2.7
800	100	24.496	420.1	409.7	2.5
1000	100	20.434	488.3	474.5	2.9
Parahydrogen					
400	30	15.875	250.4	246.2	1.7
600	30	11.032	320.0	316.4	1.1
800	30	8.468	390.1	384.5	1.5
1000	30	6.875	463.6	453.0	2.3
400	60	28.140	272.6	267.8	1.8
600	60	20.272	339.7	329.7	3.0
800	60	15.874	406.5	393.5	3.3
1000	60	13.053	476.9	459.5	3.8
400	100	40.846	297.3	296.7	0.2
600	100	30.565	360.7	349.9	3.1
800	100	24.466	428.7	408.3	5.0
1000	100	20.411	498.8	470.8	5.9

given values of *T* and *p*. Based on comparisons with the primary data and the comparisons with Vargaftik's recommended data,[10] we ascribe an uncertainty of less than 4% (considered to be estimates of a combined expanded uncertainty with a coverage factor of 2) for the correlation at temperatures from 100 K to 1000 K at pressures to 100 MPa. For temperatures from the triple point to 100 K, at pressures to 12 MPa, we estimate the uncertainty to be 7%, except near the critical point. The model behaves in a physically reasonable manner for extrapolations to pressures above 12 MPa at temperatures below 100 K, but will be subject to larger uncertainties.

The experimental primary data set is more limited for parahydrogen; the primary data extend only to 20 MPa. For the region where there are experimental data, from the triple point to 300 K at pressures to 20 MPa, we estimate an uncertainty of 4%, with the exception of the critical region. We use the recommended values of Vargaftik in Table 8 to assist in assigning an uncertainty for higher pressures. Based on comparisons with these data, we estimate the uncertainty to be 6% for temperatures from 400 K to 1000 K and pressures to 100 MPa. The correlation behaves in a physically reasonable manner for extrapolations to higher pressures at temperatures below 400 K, but will be subject to larger uncertainties. In addition, the uncertainty in the critical region is much larger, since the thermal conductivity at the critical point diverges and accurate measurements in this area are extremely difficult.

7. Conclusion

New wide-ranging correlations for the thermal conductivity of normal and parahydrogen were developed based on critically evaluated experimental data and recent theoretical results of Mehl *et al.*[7] Incorporation of the recent new high-pressure, high-temperature measurements of Moroe *et al.*[6] extended the range of the correlation to higher temperatures and pressures than the earlier work of McCarty.[18–20] There is still a need for high-pressure data at temperatures less than 320 K, and for more liquid-phase data and data in the critical region. The correlations are valid from the triple point to 1000 K and at pressures up to 100 MPa. The correlations are expressed in terms of temperature and density, and the densities were obtained from the equations of state of Leachman *et al.*[3]

Acknowledgments

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