Reference Correlation of the Thermal Conductivity of Ethanol from the Triple Point to 600 K and up to 245 MPa

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Reference Correlation of the Thermal Conductivity of Ethanol from the Triple Point to 600 K and up to 245 MPa

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This paper contains new, representative reference equations for the thermal conductivity of ethanol. The equations are based in part upon a body of experimental data that have been critically assessed for internal consistency and for agreement with theory whenever possible. In the case of the dilute-gas thermal conductivity, a theoretically based correlation was adopted in order to extend the temperature range of the experimental 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 600 K and pressures up to 245 MPa. The overall uncertainty (at the 95% confidence level) of the proposed correlation is estimated to be less than 4.6%. *© 2013 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved.* [http://dx.doi.org/10.1063/1.4797368]

Key words: critical phenomena; ethanol; thermal conductivity; transport properties.

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1. Introduction

In a series of recent papers, new reference correlations for the thermal conductivity of normal and parahydrogen,[1] SF_6,[2] toluene,[3] benzene,[4] *n*-hexane,[5] and *n*-heptane,[6] covering a wide range of conditions of temperature and pressure, were reported. In this paper, the work is extended to the thermal conductivity of ethanol.

The goal of this work is to critically assess the available literature data, and provide a wide-ranging correlation for the thermal conductivity of ethanol that is valid over gas, liquid, and supercritical states, and that incorporates densities provided by the recent equation of state of Schroeder.[7]

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 the critical point. Finally, the term $\Delta\lambda(\rho, T)$, the residual 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 transport properties 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 residual contribution, $\Delta\lambda(\rho, T)$, so that its evaluation is based entirely on experimentally obtained data.

The analysis described above should 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 on 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 a well-established set of criteria.[8] 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, such a narrow definition unacceptably limits the range of the data representation. 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.

3. The Correlation

Table 1 summarizes, to the best of our knowledge, the experimental measurements[9–58] of the thermal conductivity of ethanol reported in the literature. Fifty sets are included in the table. From these sets, nine were considered as primary data.

The data of Assael *et al.*[10] were obtained in an absolute transient hot-wire instrument with an uncertainty of less than 0.5%, and this set was considered as primary data. Also in the primary data set, the measurements of Takizawa *et al.*,[12] Mukhamedzyanov and Usmanov,[14] and Jobst[17] performed in absolute transient hot-wire instruments with a slightly inferior uncertainty, up to 2%, were included. Four more hot-wire sets were considered as primary data: the measurements of Shashkov *et al.*,[11] Tarzimanov and Mashirov,[13] Brykov,[15] and Golubev and Vasilkov[16] with uncertainty of 1.5%, 1.5%, 2%, and 1.5%, respectively. Finally, the recent relative measurements of Tong and Li,[9] performed under pressure, were also included in the primary data set. Measurements under pressure were also reported by Popov and Malov,[29] but these were

Table 1. Thermal conductivity measurements of ethanol

First author	Year publ.	Technique employed[a]	Purity (%)	Uncertainty (%)	No. of data	Temperature range (K)	Pressure range (MPa)
Primary data							
Tong[9]	1995	ThRes-Rel	na	1	19	323–523	5.0–18
Assael[10]	1988	THW-Abs	99.70	0.5	10	306–335	0.1
Shashkov[11,b]	1983	SSHW	na	1.5	5	330–371	0.003
Takizawa[12]	1978	THW-Abs	na	1.5	11	191–323	0.1
Tarzimanov[13,b]	1974	HW	99.97	1.5	15	303–343	0.1
Mukhamedzyanov[14]	1971	THW-Abs	na	2	82	298–473	0.1–245
Brykov[15]	1970	HW	na	2	19	163–343	0.1
Golubev[16,b]	1969	HW	na	1.5	210	295–578	0.1–40
Jobst[17]	1964	THW-Abs	na	2	5	173–282	0.1
Secondary data							
Fujii[18]	1997	THW	na	2	2	297–298	0.1
QunFang[19]	1997	THW	99.80	0.7	6	253–303	0.1
Wang[20]	1995	Cal	99.70	1	1	298	0.1
Cai[21]	1993	HW	99.40	0.8	1	163–343	0.1
Wu[22]	1993	LITG	na	2	1	297	0.1
Yano[23]	1988	LITG	na	3	1	288	0.1
Baroncini[24]	1987	THW-Rel	na	2	6	298–348	0.1
Ogiwara[25]	1982	PP	99.90	2	8	293–328	0.1
Frurip[26]	1981	HW	na	1	149	329–419	0.01–0.23
Raal[27]	1981	THW	99.80	0.8	8	273–343	0.1
Mallan[28]	1972	THW	na	1.3	6	296–396	0.007–0.46
Popov[29]	1971	CC	99.70	2	56	299–557	0.1–29
Perry[30]	1968	HW	na	na	3	295–324	0.1
Venart[31]	1967	THW	na	0.5	13	290–350	0.1
Sale[32]	1966	HW	na	2	1	293	0.1
Tufeu[33]	1966	CC	na	1	8	273–343	0.1
Venart[34]	1964	RHF	na	2	1	327	0.1
Scheffy[35]	1961	CC	na	0.2	3	361–445	0.1
Abaszade[36,b]	1957	HW	na	na	26	273–513	0.0016–6
Hildenbrand[37]	1957	HW	na	na	1	303	0.1
Challoner[38]	1956	GHP-Abs	na	1	3	273–313	0.1
Tsederberg[39]	1956	HF	na	1.5	8	213–348	0.1
Sakiadis[40]	1955	SSPP	na	1.5	5	310–350	0.1
Filippov[41]	1954	HW	na	na	7	290–350	0.1
Mason[42]	1954	CC	na	5.1	11	293–333	0.1
Baxter[43]	1953	CC	na	2	2	303–313	0.1
Riedel[44]	1951	CC	na	na	6	233–333	0.1
Dittman[45]	1949	CC	na	2	3	301–322	0.1
Vargaftik[46]	1949	SSHW	na	2	2	303–343	0.1
Read[47]	1948	HW	na	na	1	293	0.1
Hutchinson[48]	1945	HW	na	3	1	291	0.1
Markwood[49]	1943	SSHW	na	na	3	273–348	0.1
Shushpanov[50]	1939	SSHW	na	na	12	326–401	0.03–0.53
Bates[51]	1938	HW	na	na	6	283–333	0.1
Daniloff[52]	1932	HW	99.8	0.5	1	303	0.1
Smith[53]	1930	CC	99.80	na	1	303	0.1
Bridgman[54]	1923	CC	na	4	13	303	0.1–1177
Goldschmidt[55]	1911	HW	na	na	2	194–303	0.1
Lees[56]	1898	PP	na	na	2	298–323	0.1
Henneberg[57]	1889	na	na	na	1	293.15	0.1
Weber[58]	1886	na	na	na	1	293	0.1

[a] Abs, absolute; Cal, calorimetry; CC, coaxial cylinder; GHP, guarded hot plate; HF, hot filament; HW, hot wire; na, not available; LITG, laser-induced transient grating; PP, parallel plate; Rel, relative; RHF, radial heat flow; SSHW, steady-state hot wire; SSPP, steady-state parallel plate; ThRes, thermal resistor; THW, transient hot wire.

[b] Includes vapor data employed to derive the dilute-gas thermal-conductivity correlation.

found to be inconsistent with all other data, and hence were not included in the primary data set.

Figure 1 shows the temperature and pressure range of the primary measurements outlined in Table 1. Temperatures for all data were converted to the ITS-90 temperature scale.[59] The development of the correlation requires densities; Schroeder[7] in 2011 reviewed the thermodynamic properties of ethanol and developed an accurate, wide-ranging equation of state valid for single-phase and saturation states from 160 to 650 K at pressures up to 280 MPa, with an uncertainty in density

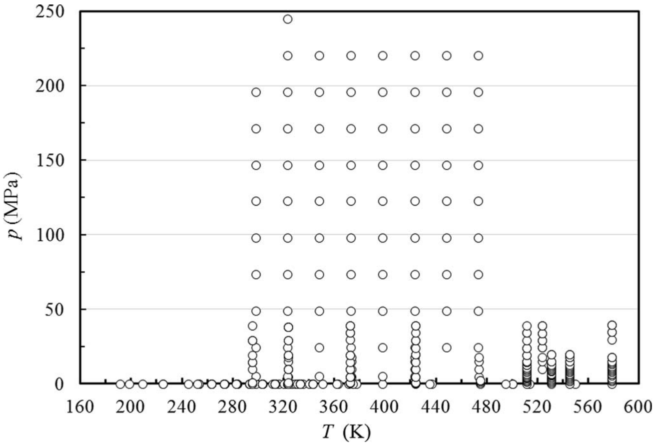

FIG. 1. Temperature and pressure ranges of the primary experimental thermal conductivity data for ethanol.

of 0.2%. These temperature and pressure limits also restrict the present thermal conductivity correlation. We also adopt the values for the critical point and triple point from his equation of state; the critical temperature, T_c, and the critical density, ρ_c, were taken to be equal to 514.71 K and 273.186 kg m^{-3}, respectively.[7] The triple-point temperature is 159.0 K.[7] Finally, the isobaric ideal-gas heat capacity up to 1500 K, proposed by Schroeder[7] with an uncertainty of 0.02%, was employed.

3.1. The dilute-gas limit

From the primary measurements shown in Table 1, three investigators[11,13,16] performed measurements near the dilute-gas limit. To increase the number of measurements, one more investigation,[36] initially classified as secondary data, was also included. The vapor measurements of Frurip *et al.*[26] were not included as they were presented only in a graphical form. No measurements are ever performed at zero pressure and the values of thermal conductivity are usually obtained by extrapolating the data along an isotherm to a dilute gas limit. Only Golubev and Vasilkov[16] studied the influence of pressure on thermal conductivity of ethanol in the vapor region, and examination of their data indicates that the variation is slight and rapidly decreases with increasing temperature. In this case we have extrapolated their data to zero density. All other investigators performed the measurements at sufficiently low pressures that the zero-pressure correction would be smaller than 0.5%, and hence we have used their quoted values as the dilute-gas thermal conductivity and marginally increased their claimed uncertainty. We should note, however, that we excluded the very high temperature data of Tarzimanov and Masirov[13] (>600 K), as according to the author dissociation of ethanol was observed.

In order to be able to extrapolate the temperature range of the aforementioned measurements (275–600 K), a theoretically based scheme was preferred in order to correlate the dilute-gas limit thermal conductivity, $\lambda_o(T)$, over a wide temperature range. In our previous work,[1–5] the scheme chosen was based on estimating the thermal conductivity, $\lambda_o(T)$, of the pure dilute gas, from its viscosity and ideal-gas heat capacity at constant volume, through a modified Eucken correlation.[60] This scheme worked quite successfully for small nonpolar spherical-like molecules, but started to produce larger deviations in longer hydrocarbons.[6] Thus, an alternative approach was adopted in this work.

The traditional kinetic approach for thermal conductivity results in an expression involving three generalized cross sections.[61,62] However, it is possible to derive an equivalent kinetic theory expression for thermal conductivity by making use of the Thijsse *et al.* approach,[63,64] where one considers expansion in terms of total energy, rather than separating translational from internal energy as is done traditionally. In this case, the dilute-gas limit thermal conductivity, $\lambda_o(T)$ (mW m^{-1} K^{-1}), of a polyatomic gas can be shown to be inversely proportional to a single generalized cross section,[61–64] $S(10E)$, as

$$\lambda_o(T) = 1000 \frac{5k_B^2(1+r^2)\,T}{2m\,\langle v\rangle_o\,S(10E)} f_\lambda, \tag{2}$$

where k_B is the Boltzmann constant, T (K) is the absolute temperature, f_λ (-) is the higher order correction factor, m (kg) is the molecular mass of ethanol (=0.04606844/6.02214 × 10^{23} kg), and $\langle v\rangle_o = 4\sqrt{k_B T/\pi m}$ (m/s) is the average relative thermal speed. The quantity r^2 is defined by $r^2 = 2C_{\mathrm{int}}^{\mathrm{o}}/5k_B$, where $C_{\mathrm{int}}^{\mathrm{o}}$ is the contribution of both the rotational, $C_{\mathrm{rot}}^{\mathrm{o}}$, and the vibrational, $C_{\mathrm{vib}}^{\mathrm{o}}$, degrees of freedom to the isochoric ideal heat capacity C_v^{o}.

The recent classical trajectory calculations[65–67] confirm that for most molecules studied, the higher order thermal conductivity correction factor is near unity. One can take advantage of this finding to define the effective generalized cross section S_λ (=$S(10E)/f_\lambda$) (nm^2), and rewrite Eq. (2) for the dilute-gas limit thermal conductivity of ethanol, $\lambda_o(T)$ (mW m^{-1} K^{-1}), as

$$\lambda_o(T) = 0.082189 \frac{(C_P^{\mathrm{o}}/k_B)\,\sqrt{T}}{S_\lambda}. \tag{3}$$

The ideal gas isobaric heat capacity of ethanol, C_P^{o} (=$C_{\mathrm{int}}^{\mathrm{o}} + 2.5k_B$) can be obtained from Schroeder,[7]

$$\begin{aligned}\frac{C_P^{\mathrm{o}}}{k_B} &= 4.43069 + 2.14326\frac{(420.4/T)^2 e^{420.4/T}}{(e^{420.4/T}-1)^2} \\ &\quad + 5.09206\frac{(1334/T)^2 e^{1334/T}}{(e^{1334/T}-1)^2} \\ &\quad + 6.60138\frac{(1958/T)^2 e^{1958/T}}{(e^{1958/T}-1)^2} \\ &\quad + 5.70777\frac{(4420/T)^2 e^{4420/T}}{(e^{4420/T}-1)^2}.\end{aligned} \tag{4}$$

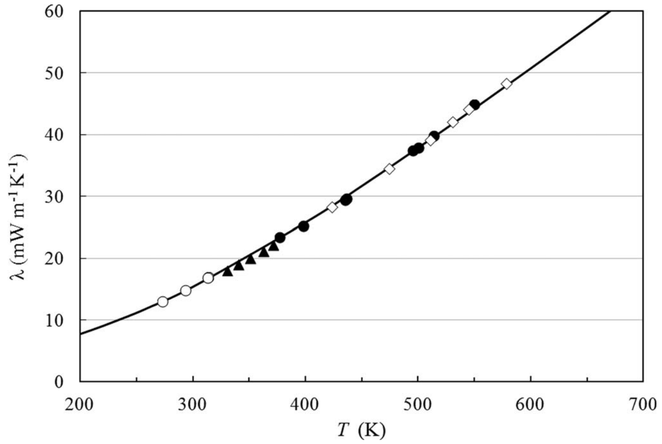

FIG. 2. Dilute-gas limit thermal conductivity as a function of temperature. Shashkov *et al.*[11] (▲), Tarzimanov and Mashirov[13] (●), Abaszade and Amiraslanov[36] (○), Golubev and Vasilkov[16] (◊), Eq. (6) (—).

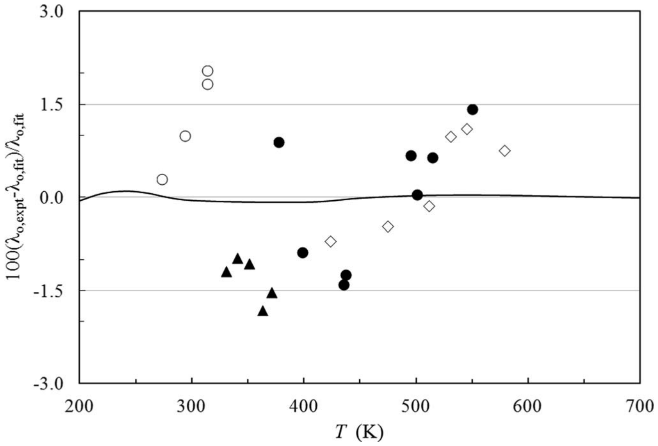

FIG. 3. Percentage deviations of primary experimental data for dilute-gas limit thermal conductivity of ethanol from the values calculated by Eqs. (2)–(5). Shashkov *et al.*[11] (▲), Tarzimanov and Mashirov[13] (●), Abaszade and Amiraslanov[36] (○), Golubev and Vasilkov[16] (◊), Eq. (6) (—).

It has been previously noted[64] and recently confirmed[61] for smaller molecules, that the cross section $S(10E)$ exhibits a nearly linear dependence on the inverse temperature.

In order to develop the correlation, we have fitted the effective cross section S_λ (nm^2), obtained from experimental data[11,13,16,36] by means of Eq. (3), to a polynomial in inverse temperature, resulting in the following expression:

$$S_\lambda = 0.3024 + 128.13/T. \tag{5}$$

Hence, Eqs. (3)–(5) form a consistent set of equations for the calculation of the dilute-gas limit thermal conductivity of ethanol. The experimental dilute-limit thermal-conductivity values, as well as the values calculated by Eqs. (3)–(5), are shown in Fig. 2, while Fig. 3 presents the percentage deviations of the dilute-gas experimental data from the values calculated by Eqs. (3)–(5). All the selected data are represented to within ±2%, which is commensurate with the uncertainty of the data. No obvious systematic trends are observed.

The values of the dilute-gas limit thermal conductivity, $\lambda_o(T)$, in mW m^{-1} K^{-1}, obtained by the scheme of Eqs. (3)–(5), were fitted as a function of the reduced temperature, $T_r = T/T_c$, for ease of use to the following equation:

$$\lambda_o(T) = \frac{-2.09575 + 19.9045\,T_r - 53.964\,T_r^2 + 82.1223\,T_r^3 - 1.98864\,T_r^4 - 0.495513\,T_r^5}{0.17223 - 0.078273\,T_r + T_r^2}. \tag{6}$$

Values calculated by Eq. (6) do not deviate from the values calculated by the scheme of Eqs. (3)–(5) by more than 0.1% over the temperature range 166–1000 K. This equation is hence employed in the calculations that will follow.

Finally, based upon the aforementioned discussion, Eqs. (3)–(5), or Eq. (6), represent the dilute-gas limit thermal conductivity to within 1.6% at the 95% confidence level.

3.2. The residual 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 residual values far away from the critical point.[68–70] 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 residual thermal-conductivity contribution. The procedure adopted during this analysis used ODRPACK (Ref. 71) to fit all the primary data simultaneously to the residual thermal conductivity and the critical enhancement, while maintaining the values of the dilute-gas thermal-conductivity data obtained by Eq. (6). The density values employed were obtained by the equation of state of Schroeder.[7]

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

$$\Delta\lambda(\rho, T) = \sum_{i=1}^{5} (B_{1,i} + B_{2,i}(T/T_c))(\rho/\rho_c)^i. \tag{7}$$

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

TABLE 2. Coefficients of Eq. (7) for the residual thermal conductivity of ethanol

i	$B_{1,i}$ (W m^{-1} K^{-1})	$B_{2,i}$ (W m^{-1} K^{-1})
1	$2.672\,22 \times 10^{-2}$	$1.771\,66 \times 10^{-2}$
2	$1.482\,79 \times 10^{-1}$	$-8.930\,88 \times 10^{-2}$
3	$-1.304\,29 \times 10^{-1}$	$6.846\,64 \times 10^{-2}$
4	$3.462\,32 \times 10^{-2}$	$-1.457\,02 \times 10^{-2}$
5	$-2.442\,93 \times 10^{-3}$	$8.091\,89 \times 10^{-4}$

3.3. The critical enhancement

3.3.1. Simplified crossover model

The theoretically based crossover model proposed by Olchowy and Sengers[68–70] 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.[72] The critical enhancement of the thermal conductivity from this simplified model is given by

$$\Delta\lambda_{\rm c} = \frac{\rho C_p R_{\rm D} k_{\rm B} T}{6\pi\overline{\eta}\xi}(\overline{\Omega} - \overline{\Omega}_0) \tag{8}$$

with

$$\overline{\Omega} = \frac{2}{\pi}\left[\left(\frac{C_p - C_v}{C_p}\right)\arctan(\overline{q}_{\rm D}\xi) + \frac{C_v}{C_p}\overline{q}_{\rm D}\xi\right] \tag{9}$$

and

$$\overline{\Omega}_0 = \frac{2}{\pi}\left[1 - \exp\left(-\frac{1}{(\overline{q}_{\rm D}\xi)^{-1} + (\overline{q}_{\rm D}\xi\rho_{\rm c}/\rho)^2/3}\right)\right]. \tag{10}$$

In Eqs. (8)–(10), $k_{\rm B}$ is Boltzmann's constant, $\overline{\eta}$ is the viscosity, and C_p and C_v are the isobaric and isochoric specific heat obtained from Schroeder.[7] To estimate the viscosity, the correlation of Kiselev *et al.*[73] implemented in the REFPROP (Ref. 74) program was employed. The correlation length ξ is given by

$$\xi = \xi_0\left(\frac{p_{\rm c}\rho}{\Gamma\rho_{\rm c}^2}\right)^{\nu/\gamma}\left[\left.\frac{\partial\rho(T,\rho)}{\partial p}\right|_T - \left(\frac{T_{\rm ref}}{T}\right)\left.\frac{\partial\rho(T_{\rm ref},\rho)}{\partial p}\right|_T\right]^{\nu/\gamma}. \tag{11}$$

As already mentioned, the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. (7) and $\overline{q}_{\rm D}$ in Eqs. (8)–(11) were fitted with ODRPACK (Ref. 71) to the primary data for the thermal conductivity of ethanol. This crossover model requires the universal constants[72] $R_{\rm D} = 1.02$, $\nu = 0.63$, and $\gamma = 1.239$, and system-dependent amplitudes Γ and ξ_0. For this work, we adopted the value $\Gamma = 0.05885$ and estimated $\xi_0 = 1.64296 \times 10^{-10}$ m, using the method presented by Perkins *et al.*[75] The effective cutoff wavelength $\overline{q}_{\rm D}^{-1}$ was found to be 5.3×10^{-10} m. The reference temperature $T_{\rm ref}$, far above the critical temperature where the critical enhancement is negligible, was calculated by $T_{\rm ref} = (^3/_2)T_{\rm c}$, which for ethanol is 772.06 K.

TABLE 3. Evaluation of the ethanol thermal-conductivity correlation for the primary data

First Author	Year publ.	AAD (%)	BIAS (%)
Tong[9]	1995	0.98	0.33
Assael[10]	1988	0.45	0.06
Shashkov[11]	1983	1.48	1.48
Takizawa[12]	1978	2.18	−1.96
Tarzimanov[13]	1974	2.71	−2.15
Mukhamedzyanov[14]	1971	1.17	0.05
Brykov[15]	1970	2.21	−2.21
Golubev[16]	1969	1.98	−0.50
Jobst[17]	1964	1.16	1.05
Entire data set		1.64	−0.53

Table 3 summarizes comparisons of the primary data with the correlation. We have defined the percent deviation as PCTDEV $= 100^*(\lambda_{\rm exp} - \lambda_{\rm fit})/\lambda_{\rm fit}$, where $\lambda_{\rm exp}$ is the experimental value of the thermal conductivity and $\lambda_{\rm fit}$ is the value calculated from the correlation. Thus, the average absolute percent deviation (AAD) is found with the expression AAD $= (\sum|\,\text{PCTDEV}\,|)/n$, where the summation is over all n points, and the bias percent is found with the expression BIAS $= (\sum\text{PCTDEV})/n$. The standard deviation of the overall fit is 2.3%.

Figure 4 shows the percentage deviations of all primary thermal-conductivity data from the values calculated by Eqs. (1) and (6)–(11), as a function of the density, while Figs. 5 and 6 show the same deviations but as a function of the temperature and pressure. The primary data for ethanol listed in Table 1 cover a wide range of conditions and extend to 245 MPa. Based on comparisons with the primary data, we calculate the uncertainty (at the 95% confidence level) for pressures less than 245 MPa and temperatures from 298 to 473 K to be less than 4.6%. At low temperatures (below 298 K), primary data are unavailable at pressures above atmospheric, so we cannot validate performance in that region against experimental data, but based on our experience with

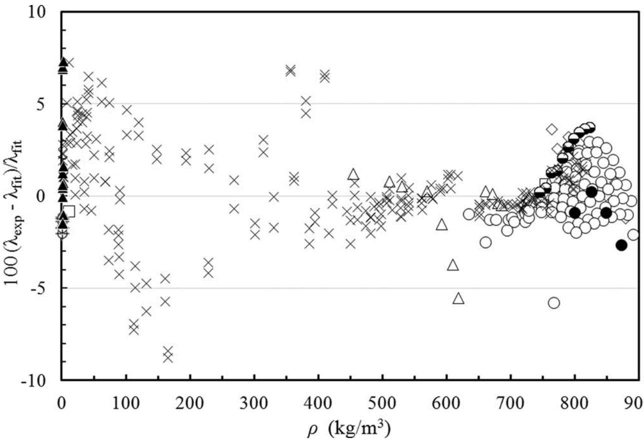

FIG. 4. Percentage deviations of primary experimental data of ethanol from the values calculated by the present model as a function of density. Tong and Li[9] (Δ), Assael *et al.*[10] (□), Shashkov *et al.*[11] (⊕), Takizawa *et al.*[12] (◊), Tarzimanov and Mashirov[13] (▲), Mukhamedzyanov and Usmanov[14] (○), Brykov[15] (◒), Golubev and Vasilkov[16] (×), Jobst[17] (●).

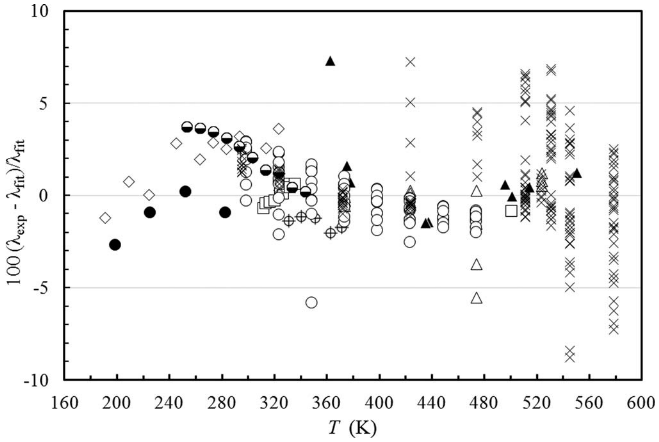

FIG. 5. Percentage deviations of primary experimental data of ethanol from the values calculated by the present model as a function of temperature. Tong and Li[9] (Δ), Assael *et al.*[10] (□), Shashkov *et al.*[11] (⊕), Takizawa *et al.*[12] (◊), Tarzimanov and Mashirov[13] (▲), Mukhamedzyanov and Usmanov[14] (○), Brykov[15] (◒), Golubev and Vasilkov[16] (×), Jobst[17] (●).

this model on other fluids, we expect similar performance. Similarly, for temperatures above 473 K the model can be validated with experimental data to 40 MPa, but we again estimate an uncertainty level of about 5% or slightly larger for the full pressure range. Uncertainties in the critical region are much larger, since the thermal conductivity approaches infinity at the critical point and is very sensitive to small changes in density.

Figures 7 and 8 show the percentage deviations of the secondary data from the values calculated by the proposed scheme. The majority of the deviations, except some very old sets, are within 5%–10% of the present correlation.

Finally, Fig. 9 shows a plot of the thermal conductivity of ethanol as a function of the temperature for different pressures.

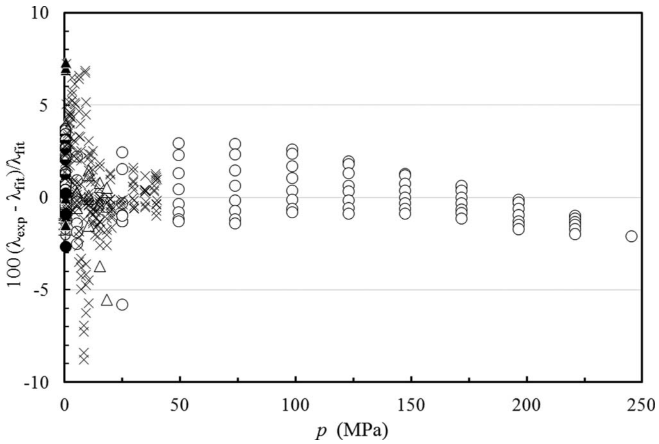

FIG. 6. Percentage deviations of primary experimental data of ethanol from the values calculated by the present model as a function of pressure. Tong and Li[9] (Δ), Assael *et al.*[10] (□), Shashkov *et al.*[11] (⊕), Takizawa *et al.*[12] (◊), Tarzimanov and Mashirov[13] (▲), Mukhamedzyanov and Usmanov[14] (○), Brykov[15] (◒), Golubev and Vasilkov[16] (×), Jobst[17] (●).

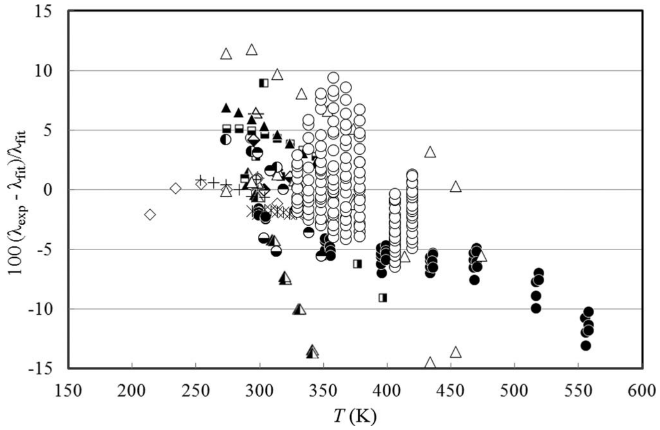

FIG. 7. Percentage deviations of secondary experimental data of ethanol from the values calculated by the present model as a function of temperature (period 1956–1998). Fujii *et al.*[18] (⊕), Qun-Fang *et al.*[19] (+), Wang and Yang[20] (△), Cai *et al.*[21] (⬘), Wu *et al.*[22] (△), Yano *et al.*[23] (⬒), Baroncini *et al.*[24] (◓), Ogiwara *et al.*[25] (⋇), Frurip *et al.*[26] (□), Raal and Rijsdijk[27] (⬓), Mallan *et al.*[28] (◨), Popov and Malov[29] (●), Perry and Jangda[30] (⬙), Venart and Krishnamurthy[31] (◭), Sale[32] (○), Tufeu *et al.*[33] (▲), Venart[34] (◭), Scheffy and Johnson[35] (■), Baxter *et al.*[43] (◒), Abaszade and Amiraslanov[36] (Δ), Hildenbrand and Happe[37] (◧), Challoner and Powell[38] (◐), Tsederberg[39] (◊).

3.3.2. Empirical critical enhancement

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

$$\Delta\lambda_c(\rho,T) = \frac{C_1}{C_2 + |\Delta T_c|}\exp[-(C_3\Delta\rho_c)^2], \qquad (12)$$

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 ethanol in the critical region, as

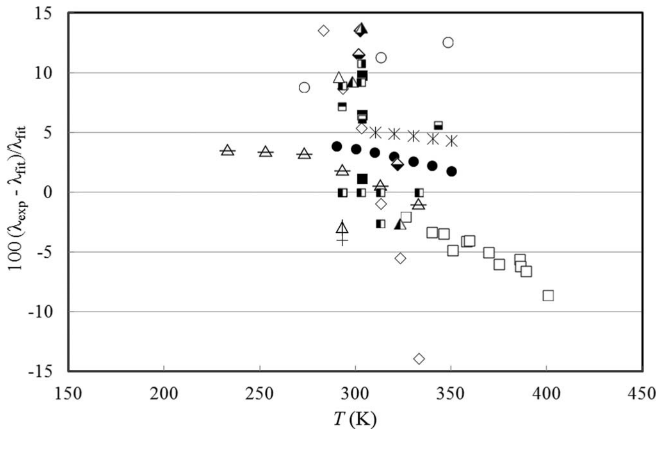

FIG. 8. Percentage deviations of secondary experimental data of ethanol from the values calculated by the present model as a function of temperature (period 1886–1955). Sakiadis and Coates[40] (⋇), Filippov[41] (●), Mason and Washington[42] (◧), Riedel[44] (△), Dittman and Winding[45] (⬙), Vargaftik[46] (⬓), Read and Lloyd[47] (△), Hutchinson[48] (Δ), Markwood and Benning[49] (○), Shushpanov[50] (□), Bates *et al.*[51] (◊), Danilof[52] (⊕), Smith[53] (◨), Bridgman[54] (■), Goldschmidt[55] (◭), Lees[56] (◭), Henneberg[57] (+), Weber[58] (⬒).

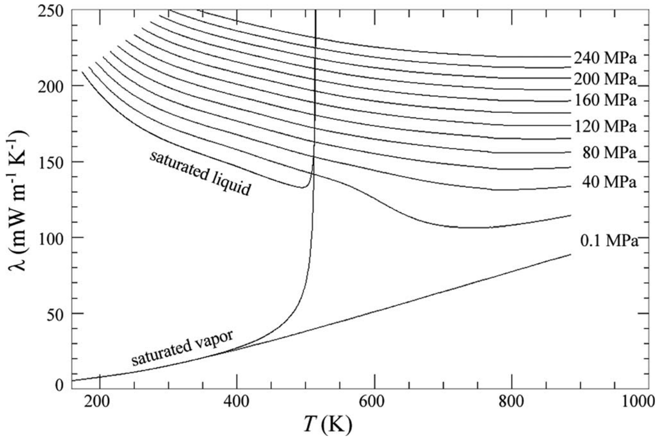

FIG. 9. Thermal conductivity of ethanol as a function of temperature for different pressures.

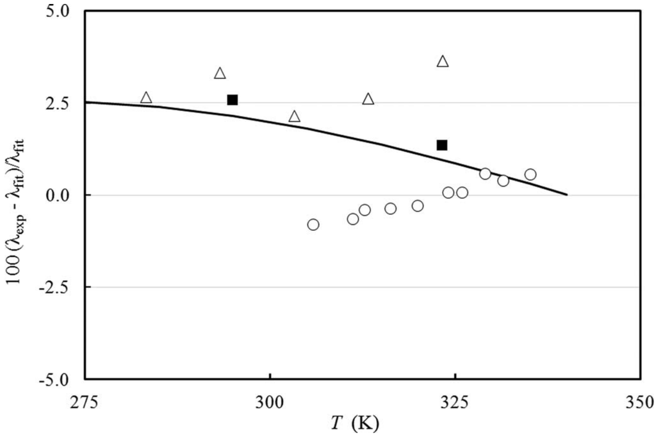

FIG. 11. Percentage deviations of selected primary experimental data of ethanol at 0.101 MPa from the values calculated by the proposed scheme of Eqs. (1) and (6)–(11). Assael *et al.*[10] (○), Takizawa *et al.*[12] (Δ), Golubev and Vasilkov[16] (■), values calculated by Eq. (13) (—).

does the theory of Olchowy and Sengers.[69] The coefficients of Eqs. (6) and (7) were fixed, while the coefficients of Eq. (12) were fitted to the primary data. The values obtained were $C_1 = 1.7 \times 10^{-3}$ W m^{-1} K^{-1}, $C_2 = 7.0 \times 10^{-2}$, and $C_3 = 1.7$. Figure 10 shows the percentage deviations between the primary data and the values calculated by Eqs. (1), (6), (7), and (12), as a function of the temperature. By comparing Figs. 5 and 10, it can be seen that employing Eq. (12) results in very little deterioration in the representation of the data.

3.4. The 0.101 MPa liquid line

From the primary data of Table 1, measured at or near 0.101 MPa, investigators that exhibited uncertainty higher than 1.5% were excluded. The remaining investigators are Assael *et al.*,[10] with quoted uncertainty of 0.5%, and Takizawa *et al.*[12] and Golubev and Vasilkov,[16] both with quoted uncertainties of 1.5%. The percentage deviations of these data from the values obtained by the proposed scheme of Eqs. (1) and (6)–(11) are shown in Fig. 11. These data were fitted to a linear equation for the thermal conductivity, $\lambda_{0.101\ \mathrm{MPa}}$ in mW m^{-1} K^{-1}, as a function of the absolute temperature, *T* in K, as

$$\lambda_{0.101\ \mathrm{MPa}} = 242.73 - 0.2545T. \tag{13}$$

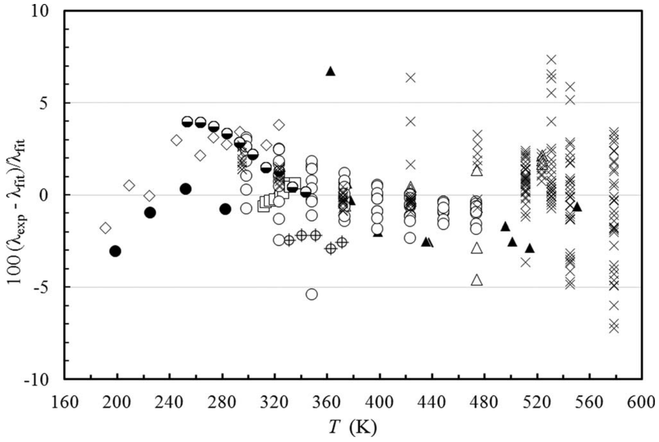

FIG. 10. Percentage deviations of primary experimental data of ethanol from the values calculated by Eqs. (1), (6), and (7) and the empirical enhancement of Eq. (12) as a function of temperature. Tong and Li[9] (Δ), Assael *et al.*[10] (□), Shashkov *et al.*[11] (⊕), Takizawa *et al.*[12] (◊), Tarzimanov and Mashirov[13] (▲), Mukhamedzyanov and Usmanov[14] (○), Brykov[15] (◒), Golubev and Vasilkov[16] (×), Jobst[17] (●).

This equation represents the selected primary data at 0.101 MPa, from 275 to 340 K with an uncertainty of 2.5% at the 95% confidence level. In Fig. 11, the percentage deviations of the values calculated by Eq. (13) from the values obtained by the proposed scheme of Eqs. (1) and (6)–(11) are also shown.

4. Computer-Program Verification

Table 4 is provided to assist the user in computer-program verification. The thermal-conductivity calculations are based on the tabulated temperatures and densities. Note that Eq. (6) was employed for the dilute-gas correlation.

TABLE 4. Sample points for computer verification of the correlating equations

T (K)	ρ (kg m^{-3})	λ (mW m^{-1} K^{-1})
300.00	850.00	209.68
400.00	2.00	26.108
400.00	690.00	149.21
500.00	10.00	39.594[a]
500.00	10.00	40.755[b]

[a] Computed with modified Olchowy-Sengers critical enhancement; the viscosity at this point for use in Eq. (8) was taken as $\eta = 14.840$ μPa s (see Sec. 3.3.1). Density values required for the enhancement term are from Schroeder.[7]

[b] Computed with empirical critical enhancement Eq. (12).

5. Conclusion

New wide-ranging correlations for the thermal conductivity of ethanol were developed based on critically evaluated experimental data. The correlations are valid from the triple point to 600 K, and at pressures up to 245 MPa. The correlations are expressed in terms of temperature and density, and the densities were obtained from the equation of state of Schroeder.[7] The overall uncertainty (at the 95% confidence level) of the proposed correlation is estimated to be less than 4.6% for the temperature range from 298 to 473 K at pressures up to 245 MPa. Primary experimental data are unavailable for comparisons at high pressures for both the low-temperature (below 298 K) and high-temperature (above 473 K) regions, and the uncertainties at high pressures for these temperatures may be slightly larger.

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