

**PROGRESS TOWARD NEW REFERENCE CORRELATIONS FOR THE TRANSPORT PROPERTIES  
OF CARBON DIOXIDE**

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**ABSTRACT**

While the thermodynamic properties of CO<sub>2</sub> are available with excellent accuracy from the reference-quality equation of state of Span and Wagner, the current reference correlations for transport properties (thermal conductivity and viscosity) are relatively old and have significant room for improvement. We describe current work at NIST to improve the data situation for both transport properties. For the viscosity, new theoretical results for the dilute vapor and a semitheoretical scaling approach for the liquid allow us to produce an improved correlation. In the case of the thermal conductivity, we measured new data with a transient hot-wire instrument. These measurements cover temperatures from 219 K to 751 K at pressures up to 69 MPa, with uncertainties near 0.5 % for the liquid and compressed gas, increasing to 3 % for low-pressure gases and conditions very near the critical point. This improves the uncertainty at most conditions by more than a factor of two compared to previous measurements. These new data, in combination with literature data and theoretical results for the dilute gas, are being employed to produce a new standard correlation for the thermal conductivity as a function of temperature and density. The new correlation will employ state-of-the-art theory to incorporate the near-critical enhancement of the thermal conductivity that is significant in a sizable region around the critical point.

## INTRODUCTION

The thermophysical properties of the working fluid are essential for design, analysis, and optimization of any power cycle. While the thermodynamic properties (vapor pressure, enthalpy, density, etc.) are usually the most important, the transport properties (thermal conductivity and viscosity) are also important for understanding the heat-transfer and fluid-flow aspects of the system.

In the case of carbon dioxide (CO<sub>2</sub>), the existing reference correlations for transport properties, as used for example in NIST's REFPROP software (Lemmon et al., 2013), are based on work that is now about 25 years old (Vesovic et al., 1990) and that has significant room for improvement. NIST therefore undertook a project to produce state-of-the-art correlations for the thermal conductivity and viscosity of CO<sub>2</sub>. In the case of the thermal conductivity, this also involved measuring new experimental data over a wide range of subcritical and supercritical conditions.

In this paper, we first review the state of the art for the thermodynamic properties of CO<sub>2</sub>, which also play a role in the transport correlations. We then describe our new thermal conductivity measurements, progress toward a new thermal conductivity correlation, and progress toward a new viscosity correlation.

## THERMODYNAMIC PROPERTIES

Thermodynamic properties of fluids are typically described with an equation of state (EOS). While in the last century it was common to use simple pressure-explicit cubic EOS such as the van der Waals or Peng-Robinson equations, these forms are inadequate for highly accurate description of fluid properties. Modern EOS are typically written in the form of a fundamental equation for the Helmholtz energy as a function of temperature and density. Differentiation and other straightforward manipulations allow calculation of all thermodynamic properties (vapor pressure, enthalpy, density, heat capacity, sound speed, etc.) in a mutually consistent manner. While modern Helmholtz EOS are subject to some theoretical constraints, they typically include many parameters that are adjusted to experimental data. For well-studied fluids like CO<sub>2</sub>, sufficient data exist to produce an EOS that, while more complicated than simple cubic EOS, represents the fluid properties with much greater accuracy.

The thermodynamic properties are important not only in their own right, but also for their role in transport properties. For both theoretical and practical reasons, transport properties are correlated as a function of temperature and density. Since experimental data are almost always measured as a function of temperature and pressure, an EOS is needed to obtain the density corresponding to each point; any error in the EOS will distort the correlation. In addition, the transport properties (especially the thermal conductivity) exhibit divergence near the critical point. Correct description of this region requires some thermodynamic quantities (such as the heat capacity and the isothermal compressibility) for calculation of the critical enhancement.

The existing reference correlations for CO<sub>2</sub> transport properties were developed with the EOS of Ely et al. (1987). While this EOS was fairly accurate, a significant improvement was achieved with the EOS of Span and Wagner (1996). Span and Wagner used an approach that optimized the functional form of the EOS while fitting to the data, achieving uncertainties similar to those of the best experimental data. Comparison with data shows that, depending on the property and region considered, the Span-Wagner EOS is more accurate than the EOS of Ely et al. by up to a factor of 10; it also represents properties near the critical point much more accurately. This greatly improved accuracy is another reason to revisit the CO<sub>2</sub> transport property correlations in order to produce new correlations that are consistent with the Span-Wagner EOS.

The EOS of Span and Wagner (1996) is recommended at pressures up to 800 MPa (approximately 116 000 psia) and temperatures up to 1100 K (1520 °F). It was designed to extrapolate in a physically reasonable manner to both higher temperatures and pressures, so it should provide benchmark values for any conditions that would be encountered in supercritical CO<sub>2</sub> power cycles.

Because of its many terms, the Span-Wagner EOS may not be convenient to use for computationally intensive applications, such as computational fluid dynamics. In such cases, the best approach may be to use a spline-based table lookup method with splines pre-calculated on an appropriate grid from the EOS. Such an approach has recently been developed for water and steam (Kunick et al., 2014).

## THERMAL CONDUCTIVITY

The thermal conductivity of CO<sub>2</sub> has been measured with a variety of transient and steady-state techniques. The thermal conductivity,  $\lambda$ , can also be estimated from measurements of thermal diffusivity,  $a$ , at temperatures and pressures where the density,  $\rho$ , and isobaric specific heat,  $C_p$ , are well known, through the expression  $\lambda = a\rho C_p$ . A thorough analysis of the thermal conductivity data of CO<sub>2</sub> was given by Vesovic et al. (1990), who assessed the reliability of each data source and designated the most reliable data sets as primary; these sets were used during the development of their thermal conductivity correlation. The less reliable data sets were designated as secondary; these data sets provided useful comparisons with the correlation at conditions where more reliable primary data sets were not available. The thermal conductivity was correlated as a function of temperature,  $T$ , and density,  $\rho$ , which is typically calculated with an accurate EOS at the temperature and pressure,  $p$ , of the measured thermal conductivity. The 1990 work used the EOS of Ely et al. (1987) for this purpose.

Vesovic et al. (1990) designated 10 data sets as primary for the thermal conductivity of the dilute gas. Only six of these primary data sets had an uncertainty of 1 % or less, covering a temperature region from 285 K to 470 K. The low-temperature region from 186 K to 285 K was covered by four primary data sets with an uncertainty of 5 %. Theoretical predictions supplemented the available primary data with uncertainties of 5 %. At higher densities, Vesovic et al. designated five data sets as primary with uncertainties of 1.5 % or less that covered the temperature region from 298 K to 470 K with pressures up to 30 MPa and also included an additional data set with 5 % uncertainty that covered the high-temperature region up to 724 K with pressures up to 100 MPa. Thus, the uncertainty of the data sets used in the 1990 correlation is 5 % at temperatures below 285 K and above 470 K. At pressures above 30 MPa, the uncertainty again increases to 5 %, even at temperatures from 285 K to 470 K. Since this 1990 assessment, there have been a few additional measurements of the thermal conductivity and thermal diffusivity of CO<sub>2</sub>. However, the limitations due to the increased uncertainty of the data at low temperatures and at high temperatures remain.

The measurements reported in the present work cover the liquid, vapor and supercritical phase regions of CO<sub>2</sub> at temperatures from 219 K (-65 °F), near the triple point, to 751 K (892 °F) and at pressures up to 70 MPa (10 150 psia) with reduced uncertainty compared to available data. These measurements, along with other information available since 1990, are used to produce an improved reference correlation for the thermal conductivity of CO<sub>2</sub>.

### Thermal Conductivity Measurements

The measurements of the thermal conductivity of CO<sub>2</sub> were obtained with two transient hot-wire instruments that have previously been described in detail. The low-temperature apparatus (Roder, 1981) covers the temperature region from 60 K to 340 K, while the high-temperature apparatus (Perkins et al., 1991) covers the temperature range from 300 K to 750 K. Both apparatus can measure in the liquid, vapor and compressed gas phases at pressures up to 70 MPa. Each measurement cell consists of a pair of hot wires of differing length operating in a differential arrangement to eliminate errors due to axial conduction. The outer cavities around the two hot wires have a diameter of 9 mm and the cavities for both hot wires are enclosed by a pressure vessel that is capable of operation at pressures up to 70 MPa. The low-temperature pressure vessel is copper and is enclosed in an isothermal shield in a cryostat cooled with liquid nitrogen (Roder, 1981). The high-temperature pressure vessel is 316-alloy stainless steel and is enclosed in an isothermal shield in a furnace (Perkins et al., 1991). Initial cell temperatures,  $T_i$ , are determined with a reference platinum resistance thermometer with an uncertainty of 0.005 K, and pressures,  $p_e$ , are determined with a pressure transducer with an uncertainty of 7 kPa. The measurements for this work were made with bare platinum hot wires with a diameter of 12.7  $\mu\text{m}$ . All reported uncertainties are for a coverage factor of  $k = 2$ , approximately corresponding to a 95 % confidence interval. During an experiment, a current is passed through the wires starting at time zero; the wires function as both electrical heat sources and resistance thermometers to measure the temperature rise.

The basic theory that describes the operation of the transient hot-wire instrument is given by Healy et al. (1976). The hot-wire cell was designed to approximate a transient line source as closely as possible, and

deviations from this model are treated as corrections to the experimental temperature rise. The ideal temperature rise  $\Delta T_{id}$  is given by

$$\Delta T_{id} = \frac{q}{4\pi\lambda} \left[ \ln(t) + \ln\left(\frac{4a}{r_0^2 C}\right) \right] = \Delta T_w + \sum_{i=1}^{10} \delta T_i, \quad (1)$$

where  $q$  is the power applied per unit length,  $\lambda$  is the thermal conductivity of the fluid,  $t$  is the elapsed time,  $a = \lambda/(\rho C_p)$  is the thermal diffusivity of the fluid,  $\rho$  is the density of the fluid,  $C_p$  is the isobaric specific heat capacity of the fluid,  $r_0$  is the radius of the hot wire,  $C = 1.781\dots$  is the exponential of Euler's constant,  $\Delta T_w$  is the measured temperature rise of the wire, and  $\delta T_i$  are corrections to account for deviations from ideal line-source conduction. During analysis, a line is fit to a linear section of the  $\Delta T_{id}$  versus  $\ln(t)$  data and the thermal conductivity is obtained from the slope of this line. Both thermal conductivity and thermal diffusivity can be determined with the transient hot-wire technique as shown in Eq. (1), but only the thermal conductivity results are considered here. The experiment temperature,  $T_e$ , associated with the thermal conductivity is the average temperature at the wire's surface over the period that was fitted to obtain the thermal conductivity.

For gas-phase measurements, two corrections must be carefully considered (Healy et al., 1976; Assael et al., 1992; Taxis and Stephan, 1994; Li et al., 1993; Li et al., 1994). First, since the thermal diffusivity of the gas is much different from that of the wire, the correction for the wire's finite radius becomes very significant. Second, the thermal diffusivity of the dilute gas varies inversely with the pressure, so it is possible for the transient thermal wave to penetrate to the outer boundary of the gas region during an experiment at low pressure. The present transient hot-wire wires require careful correction for the wire's finite radius during such dilute-gas measurements. Measurement times must be selected to minimize the correction for penetration to the outer boundary due to the relatively small diameter of the concentric fluid region around each hot wire. The full heat-capacity correction (Healy et al., 1976) was applied to the present measurements. For a few of the measurements at the lowest pressures, the outer boundary was encountered during the usual one-second duration of the experiment, so the experiment time was reduced to minimize the magnitude of this correction. Transient experiments are generally limited to 1 s in duration, with 250 measurements of temperature rise taken as a function of elapsed time relative to the onset of wire heating. Fluid convection is normally not a problem, except in the critical region.

At very low pressures, the transient hot-wire system described above can be operated in a steady-state mode, which requires smaller corrections (Roder et al., 2000). The working equation for the steady-state mode is based on a different solution of Fourier's law, but the geometry is still that of concentric cylinders. This equation can be solved for the thermal conductivity of the fluid,

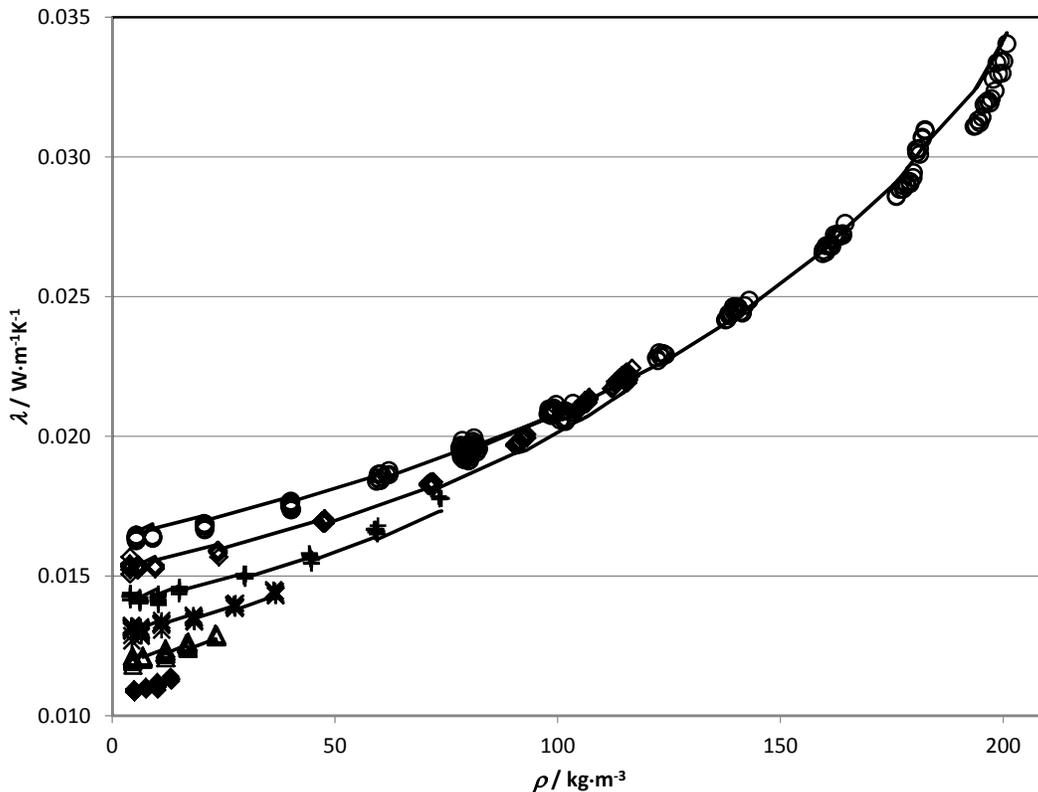
$$\lambda = \frac{q \ln(r_2/r_1)}{2\pi(T_1 - T_2)}, \quad (2)$$

where  $q$  is the applied power per unit length,  $r_2$  is the internal radius of the outer cylinder,  $r_1$  is the external radius of the inner cylinder (hot wire), and  $(T_1 - T_2)$  is the measured temperature difference between the hot wire and its surrounding cavity.

For the concentric-cylinder geometry described above, the total radial heat flow per unit length,  $q$ , remains constant and is not a function of the radial position. Assuming that the thermal conductivity of the fluid is a linear function of temperature, such that  $\lambda = \lambda_0(1 + b_\lambda T)$ , it can be shown that the measured thermal conductivity is given by  $\lambda = \lambda_0(1 + b_\lambda(T_1 + T_2)/2)$ . Thus, the temperature assigned to the measured thermal conductivity corresponds to the mean temperature of the inner and outer cylinders,  $T_m = (T_1 + T_2)/2$ . This assumption of linear temperature dependence for the thermal conductivity is valid for experiments with small temperature differences. The density assigned to the measured thermal conductivity is calculated from an equation of state at  $T_m$  and the measured pressure. An assessment of corrections during steady-state hot-wire measurements is available (Roder et al., 2000).

We performed measurements on a pure (99.994 %) sample of carbon dioxide with the low-temperature hot-wire apparatus at temperatures from 220 K to 340 K and the high-temperature hot-wire apparatus at temperatures from 310 K to 750 K. These measurements were made along subcritical vapor isotherms at

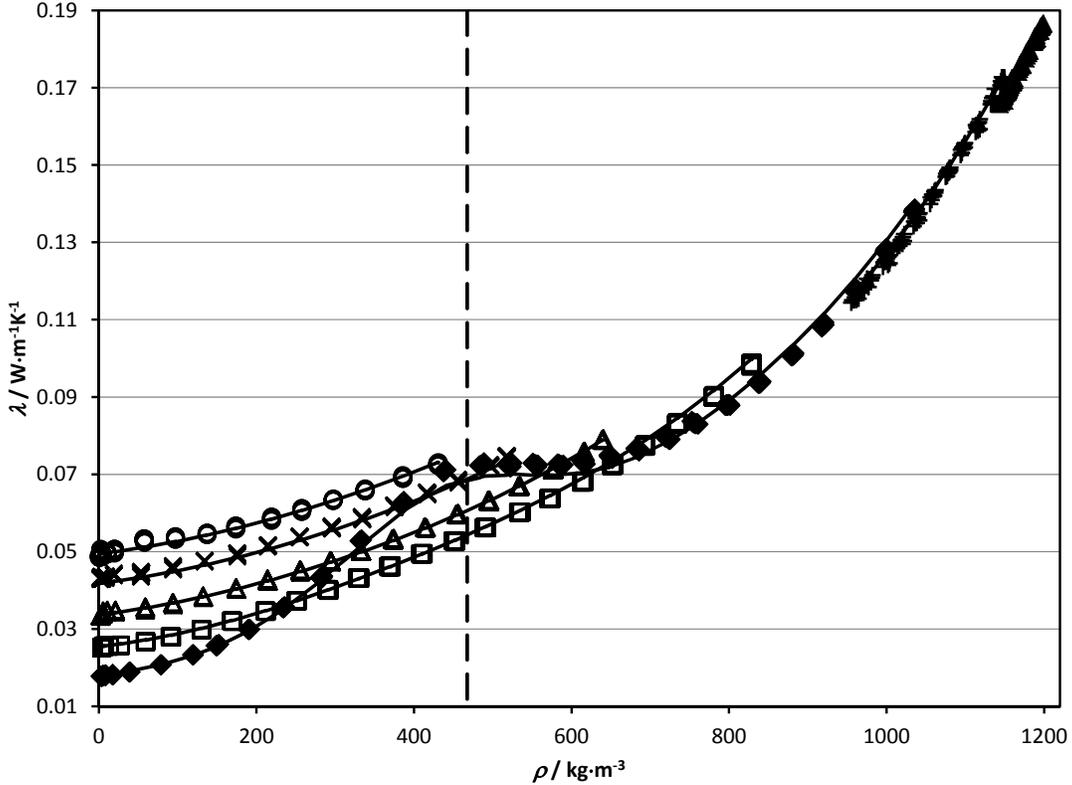
temperatures of 219, 237, 252, 267, 282, 296 K, liquid isotherms at temperatures of 225, 228, 238, 253, 268, 283, 297 K, and along supercritical isotherms at temperatures of 312, 315, 327, 342, 370, 403, 453, 503, 553, 604, 651, 702, and 751 K. The transient-hot-wire apparatus was operated in the steady-state mode at pressures below 0.5 MPa with subcritical vapor and supercritical gas. The transient mode was used at pressures from 0.5 MPa up to the saturation line for subcritical-vapor isotherms and up to 68 MPa for supercritical gas. The transient mode was also used for the liquid phase at pressures from the saturation line up to 68 MPa. A significant critical enhancement, centered near the critical density, was observed along the supercritical isotherms. Measurements were made at up to 10 different applied power levels (10 different temperature rises) to verify that natural convection was not a problem during the measurements. Thermal conductivity data for CO<sub>2</sub> in the subcritical vapor phase are shown in Fig. 1. The vapor isotherms near the critical temperature begin to cross each other at the highest densities (near saturation) due to the critical enhancement. The measurements at different applied powers and temperature rises are clearly separated and visible at the highest densities along the isotherm at 296 K. Selected thermal conductivity data for CO<sub>2</sub> in the subcritical liquid and supercritical phases are shown in Fig. 2. The supercritical isotherm at 315 K is seen to cross over isotherms up to 604 K near the critical density of CO<sub>2</sub> due to the critical enhancement.



**Figure 1. Thermal conductivity data for the subcritical vapor phase of carbon dioxide along isotherms:  $\blacklozenge$ , 219 K;  $\triangle$ , 237 K;  $*$ , 252 K;  $+$ , 267 K;  $\diamond$ , 282 K; and  $\circ$ , 296 K. The lines are calculated with the NIST REFPROP program (Lemmon et al., 2013) based on the correlation of Vesovic et al. (1990) with the equation of state of Span and Wagner (1996).**

The final analysis of all the measurements has been completed. The data have been compared extensively with existing data relative to the best available correlations for the thermal conductivity of carbon dioxide. The present data are in good agreement with other reliable data in the critical region. At temperatures above 651 K, indications of corrosion of welds and electrical leakage between the hot wires and ground were observed during the initial measurements. The high-temperature hot-wire cell was rebuilt and the isotherms at 651 K, 702 K, and 751 K have since been repeated with improved results and reduced uncertainty. The isotherm at 651 K was re-measured before and after the highest-temperature

isotherm at 750 K to verify that any corrosion at the highest temperatures did not alter the results. In addition, argon gas was measured at 651 K and 751 K after the CO<sub>2</sub> measurements to verify proper performance of the rebuilt hot-wire cell. We have confidence in the thermal conductivity measurements and analysis over the entire temperature region from 219 K to 751 K. The uncertainties of the present measurements are 0.5 % for liquid and compressed gas, increasing to 3 % for gas below 1 MPa and in the critical region. These new data enable a new correlation to be developed with reduced uncertainty in regions where the current correlation (Vesovic et al., 1990) has relatively large uncertainty, near 5 %, due to the uncertainty of the available data for the thermal conductivity of CO<sub>2</sub>.



**Figure 2. Selected thermal conductivity data for CO<sub>2</sub> in the subcritical liquid and supercritical phases along isotherms: ▲, 225 K; +, 268 K; ◆, 315 K; □, 403 K; △, 503 K; ×, 604 K and ○, 702 K. The lines are calculated with the NIST REFPROP program (Lemmon et al., 2013) based on the correlation of Vesovic et al. (1990) with the equation of state of Span and Wagner (1996). The dashed line indicates the critical density.**

### Thermal Conductivity Correlation

The thermal conductivity  $\lambda$  can be expressed as the sum of three independent contributions, as

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T), \quad (3)$$

where  $\rho$  is the density,  $T$  is the temperature, and the first term,  $\lambda_0(T) = \lambda(0, T)$ , is the contribution to the thermal conductivity in the dilute-gas limit, where only two-body molecular interactions occur. The residual term,  $\Delta\lambda(\rho, T)$ , represents the contribution of other effects to the thermal conductivity of the fluid at elevated densities including many-body collisions, molecular-velocity correlations, and collisional transfer. 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.

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  $\lambda_0(T)$  and  $\Delta\lambda_c(\rho, T)$

theoretically. In addition, it is possible to derive information about  $\lambda_0(T)$  from experiment. In contrast, there is almost no theoretical guidance concerning the residual contribution,  $\Delta\lambda(\rho, T)$ , so its evaluation is based entirely on experimentally obtained data.

To develop the zero-density correlation, we followed the procedure used in the development of a standard reference formulation for the thermal conductivity of water (Huber et al., 2012), which uses the concept of Key Comparison Reference Values (Cox, 2002) to consider the uncertainties from different data sources. We identified from the literature a primary set of experimental data, and restricted the density to less than  $50 \text{ kg}\cdot\text{m}^{-3}$ . We then included the new experimental data obtained in this study from both the low- and high-temperature apparatus operated in both steady-state mode and transient mode at densities less than the cutoff of  $50 \text{ kg}\cdot\text{m}^{-3}$ . We did not include transient data for temperatures above 505 K. For transient hot-wire measurements, the correction for the finite outer boundary containing the gas becomes increasingly large, due to the increasing thermal diffusivity of the gas, as the pressure of the gas decreases. This correction becomes even more significant as the temperature increases and for outer boundaries less than 1 cm diameter, and this is why we did not include in the primary data the low-density measurements made above 505 K. Steady-state hot-wire measurements of the dilute gas require much smaller corrections and have lower uncertainty than such transient hot-wire measurements with relatively large corrections for the finite outer boundary, and all steady-state low-density measurements were included in the primary set.

All low-density, primary data points were then arranged into bins encompassing a temperature range of 8 K or less, with at least 4 data points in each bin. Points that were already extrapolated to zero density by the original authors were not put into bins and were treated as separate isotherms. The new data from this study were also treated as separate isotherms. It was not possible to classify all points into bins, since some exceeded the 8 K limit or failed to have at least 4 points.

The nominal temperature of an isotherm “bin” was computed as the average temperature of all points in a bin. The thermal conductivity of each point was then corrected to the nominal temperature,  $T_{\text{nom}}$ , by

$$\lambda_{\text{corr}}(T_{\text{nom}}, \rho) = \lambda_{\text{exp}}(T_{\text{exp}}, \rho) + [\lambda(T_{\text{nom}}, \rho) - \lambda(T_{\text{exp}}, \rho)]_{\text{calc}}, \quad (4)$$

where the calculated values were obtained from the Vesovic et al. (1990) thermal conductivity formulation. The resulting set of bins were obtained considering 1299 points from 21 sources, obtained with a variety of experimental techniques and with a range of uncertainties. The data covered nominal temperatures from 219 K to 751 K with an average bin size of less than 3 K.

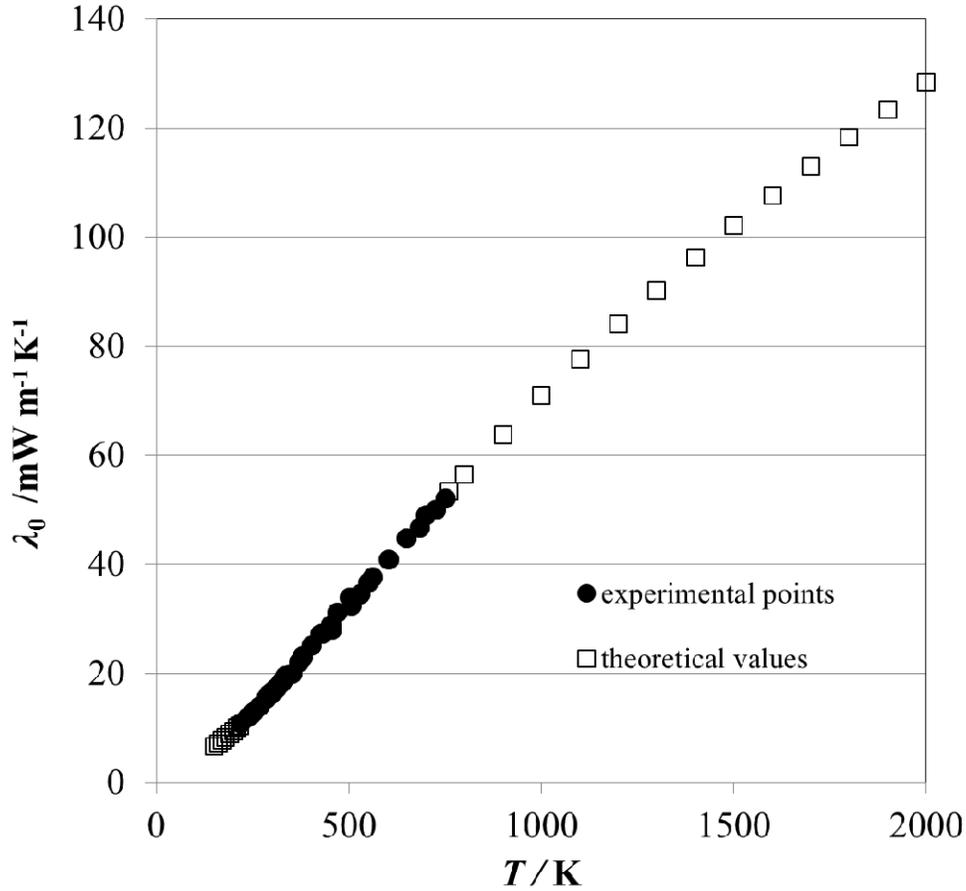
Weighted linear regression was then used to extrapolate the nominal isotherms in order to obtain the value at zero density,  $\lambda_0$ . Points were weighted with a factor equal to the inverse of the square of the estimated relative uncertainty. 95% confidence intervals were constructed from the regression statistics. Isotherms with large inconsistencies in the underlying data were rejected from further consideration. This procedure resulted in 45 zero-density points from 219 K to 751 K.

In order to supplement the experimental data set at very low and at high temperatures where data are unavailable or sparse, we incorporated selected theoretical points from the recent work of Hellmann (2014), who used a new four-dimensional rigid-rotor potential energy surface and the classical trajectory method. We first adjusted the theoretical values by multiplying them by a factor of 1.011, as recommended by Hellmann (2014) based on his comparison with reliable experimental values, and ascribed to the theoretical values an uncertainty, namely 1 % for points between 300 K and 700 K, increasing to 2 % at 150 K and 2000 K. We included 8 points from 150 K to 215 K, and 14 points from 760 K to 2000 K, so that the final set of zero-density values range from 150 K to 2000 K.

The zero-density values were fit using orthogonal distance regression to the equation form used in the IAPWS water formulation (Huber et al, 2012) for the thermal conductivity in the limit of zero density,

$$\lambda_0(T_r) = \frac{\sqrt{T_r}}{\sum_{k=0}^J \frac{L_k}{T_r^k}}, \quad (5)$$

where  $T_r = T/T_c$  is a reduced temperature and the  $L_k$  are fitted parameters. We used the critical temperature from the Span and Wagner (1996) equation of state,  $T_c = 304.182$  K. The final set of  $\lambda_0$  values contained 67 data points from 150 K to 2000 K and is shown in Fig. 3. Four terms were needed, and the weights were equal to the inverse of the square of the estimated uncertainty.



**Figure 3. Dataset for  $\lambda_0$  used in the regression.**

Figure 4 shows the relative deviation between the  $\lambda_0$  data and Eq. (5). Also shown are deviations with respect to the correlation of Vesovic et al. (1990) and with the theoretical calculations of Hellmann (2014). The values of Hellmann have been scaled upward by a factor of 1.011 as mentioned earlier. The correlation of Vesovic was designed to be used only over the range 200 K to 1000 K, and it is obvious that at low temperatures it does not extrapolate well. At high temperatures, the Vesovic correlation extrapolates in a reasonable manner because theoretical considerations were included in its high-temperature behavior. The present work uses the theoretical calculations of Hellmann (2014) to guide both the low- ( $150 < T/K < 215$ ) and high-temperature ( $760 < T/K < 2000$ ) behavior of the correlation outside of the range of the best experimental data. Equation (5) may be extrapolated safely to 2000 K, the limit of the theoretical data included in the fit, although it does not take into account partial dissociation of  $\text{CO}_2$  at very high temperatures. The present work agrees with the experimental points to within about 2 %, and to within 1 % with the theoretical calculations of Hellmann. The correlation of Vesovic et al. (1990) relied heavily on data from Millat et al. (1987) and Johns et al. (1986), particularly in the region 330 K to 470 K; the present work considered additional data (primarily from this work) that tended to be lower than the data of Millat et al. and Johns et al. and that are in closer agreement with the theoretical calculations of Hellmann (2014). To assess the uncertainty of the dilute-gas correlation, we consider the comparisons with the scaled theoretical values of Hellmann, which have an estimated uncertainty of 1 % between 300 K and 700 K, increasing to 2 % at both 150 K and 2000 K, and we will adopt those same values for our uncertainty estimate for Eq. (5).

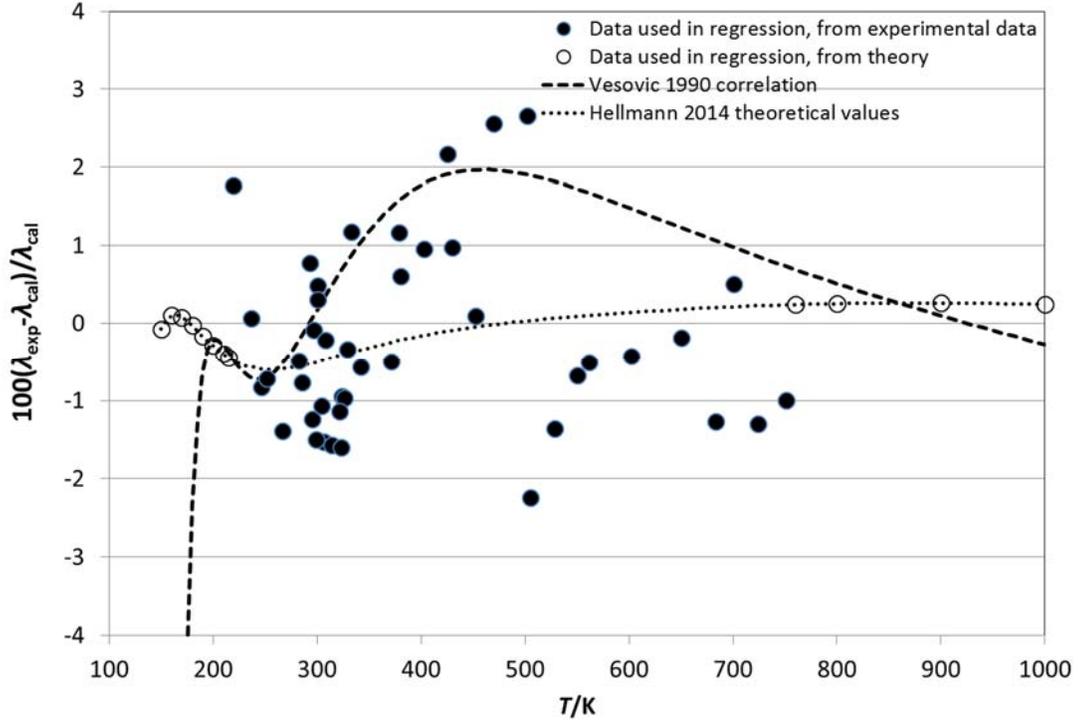


Figure 4. Comparison of  $\lambda_0$  correlation with the regressed data.

After  $\lambda_0$  is determined, the other two terms in Eq. (3) can be addressed. 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. We use a simplified crossover model proposed by Olchowy and Sengers (1989) to represent the critical enhancement. Recently, Perkins et al (2013) proposed a generalized form of this model that requires only one parameter, and we will adopt this approach, fitting only the inverse cutoff wavenumber.

For the residual contribution, we propose a simple polynomial function of temperature and density,

$$\Delta\lambda(\rho, T) = \sum_{i=1}^5 (B_{1,i} + B_{2,i}(T/T_c)) (\rho/\rho_c)^i. \quad (6)$$

The procedure will be to fit all the primary data simultaneously to obtain the coefficients  $B_{1,i}$  and  $B_{2,i}$  of the residual thermal conductivity, Eq. (6), and the single cutoff wavenumber parameter for the critical enhancement, while maintaining the values of the dilute-gas thermal-conductivity obtained by Eq. (5). This work is currently in progress.

## VISCOSITY

Viscosity measurements of  $\text{CO}_2$  have been carried out since 1846, but until now have not been assembled in one comprehensive database. In this work, references from six previous correlations of the viscosity of  $\text{CO}_2$ , as well as those included in the current versions of the AIChE DIPPR database, the NIST ThermoData Engine, and the Landolt-Börnstein compilations were retrieved. It turned out that all compilations and databases were incomplete. Thus, the compilation in this project comprises for the first time all known literature data for the viscosity of  $\text{CO}_2$  in one single repository.

The analysis of Vesovic et al. (1990) prompted new viscosity measurements of  $\text{CO}_2$  to resolve discrepancies between some data sets in the compressed liquid region. These measurements were carried out by

van der Gulik (1997) and formed the basis for the revised viscosity correlation of Fenghour et al. (1998). Since then, a number of experimental and computational data sets have been published for the viscosity of CO<sub>2</sub>, yet only two have expanded the temperature and pressure range. The measurements of Estrada-Alexanders and Hurly (2008) covered the vapor and gas region between 220 K and 370 K up to the vapor pressure or 3.15 MPa, whichever is lower. Abramson (2009) measured in a diamond anvil cell at temperatures from 308 K to 670 K with pressures from 480 MPa to 7960 MPa. In the dilute gas region, Vogel (2014) recalculated the results of Vogel and Barkow (1986) and of Hendl et al. (1993), using for calibration a highly accurate first-principles value for the viscosity of helium at room temperature. Figure 5 shows how the selected experimental data cover the fluid region of CO<sub>2</sub> relative to the melting curve, the vapor-pressure curve, and the sublimation curve. Also included in Fig. 5 is the Frenkel line connecting the loci of viscosity minima  $(\partial\eta/\partial T)_\rho = 0$ , where the transition from liquid-like to gas-like interaction mechanisms occurs. A large gap is seen from 0.5 MPa to about 700 MPa at 550 K and above where only 24 data points were measured by Golubev et al. (1971). Viscometric capabilities in that range are rare.

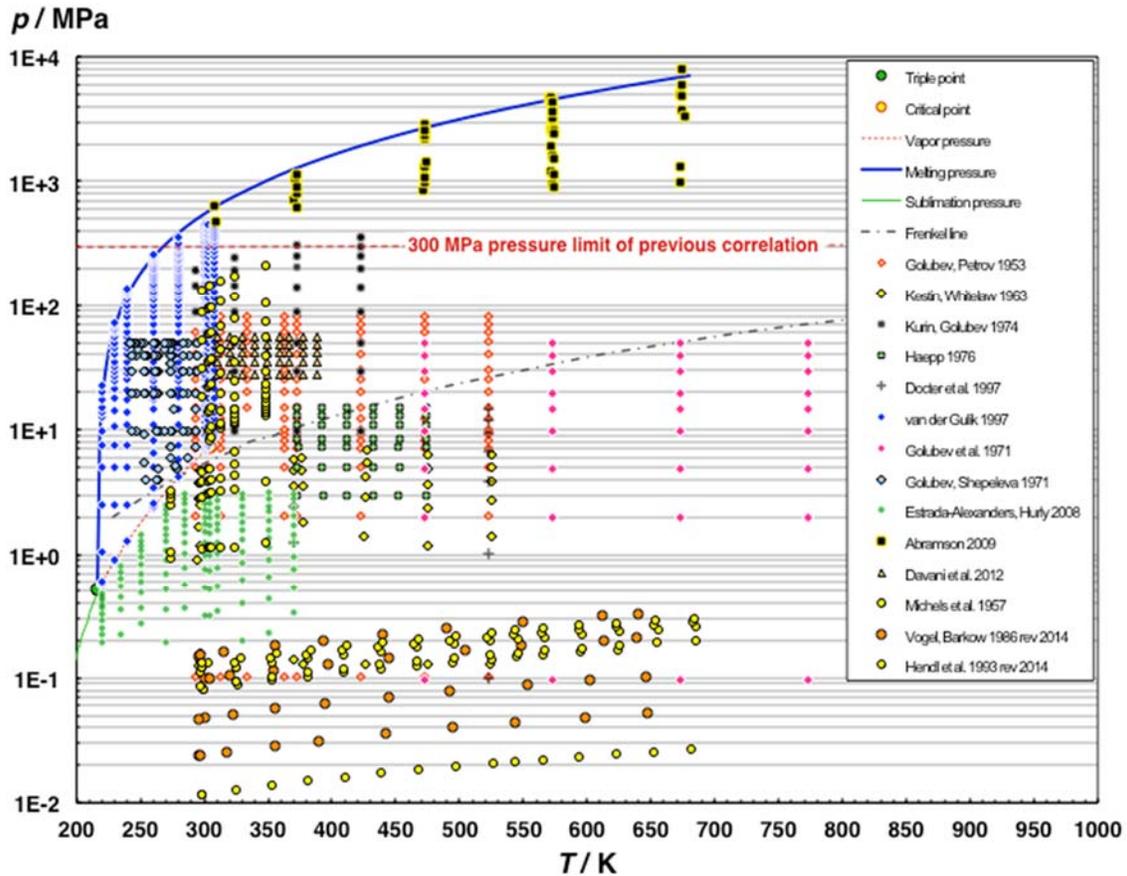


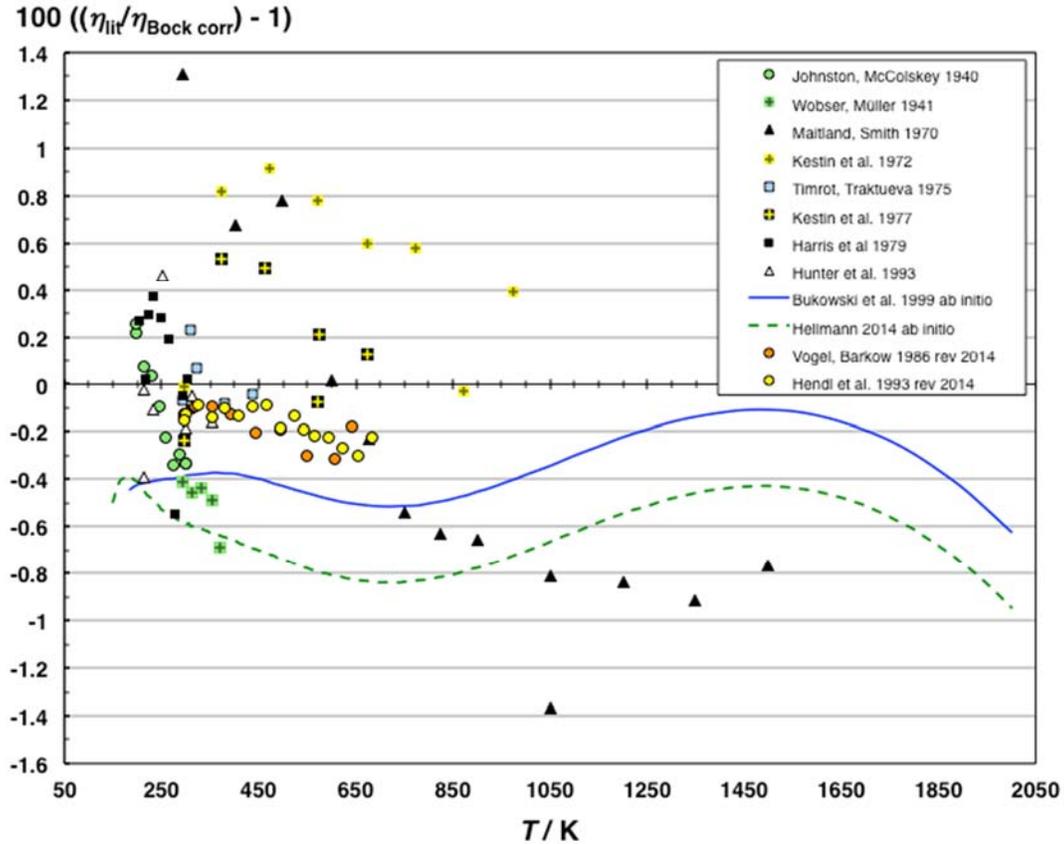
Figure 5. Distribution of selected viscosity data of CO<sub>2</sub>.

In a manner similar to Eq. (3), the viscosity can be correlated in terms of temperature  $T$  and density  $\rho$  by

$$\eta(T, \rho) = \eta_0(T) + \Delta\eta(T, \rho) + \Delta\eta_c(T, \rho), \quad (7)$$

where  $\eta_0(T)$  is the viscosity in the limit of zero density,  $\Delta\eta(T, \rho)$  is the residual part, and  $\Delta\eta_c(T, \rho)$  is the critical enhancement of the viscosity due to its singularity at the critical point. CO<sub>2</sub> is one of the few compounds whose critical viscosity enhancement has been measured with high precision. However, the near-critical results of Berg and Moldover (1990) were not considered in the correlations of Vesovic et al. (1990) or Fenghour et al. (1998). Consequently, there is a lack of awareness and an incomplete understanding of the critical viscosity enhancement of CO<sub>2</sub>; this work is expected to correct that deficiency.

The most recent correlation of  $\eta_0(T)$ , the viscosity in the limit of zero density, was by Bock et al. (2002). Relative deviations of selected experimental data and values calculated from first principles are shown in Fig. 6. The deviations of the experimental data are increasingly positive with decreasing temperature. The values calculated from first principles by Bukowski et al. (1999) and Hellmann (2014) are systematically lower than the experimental data and exhibit a different temperature dependence. Assessment of the deviations is continuing and no final conclusion has been reached.



**Figure 6. Deviations of experimental viscosity data in the limit of zero density and values calculated from first principles relative to the correlation of Bock et al. (2002).**

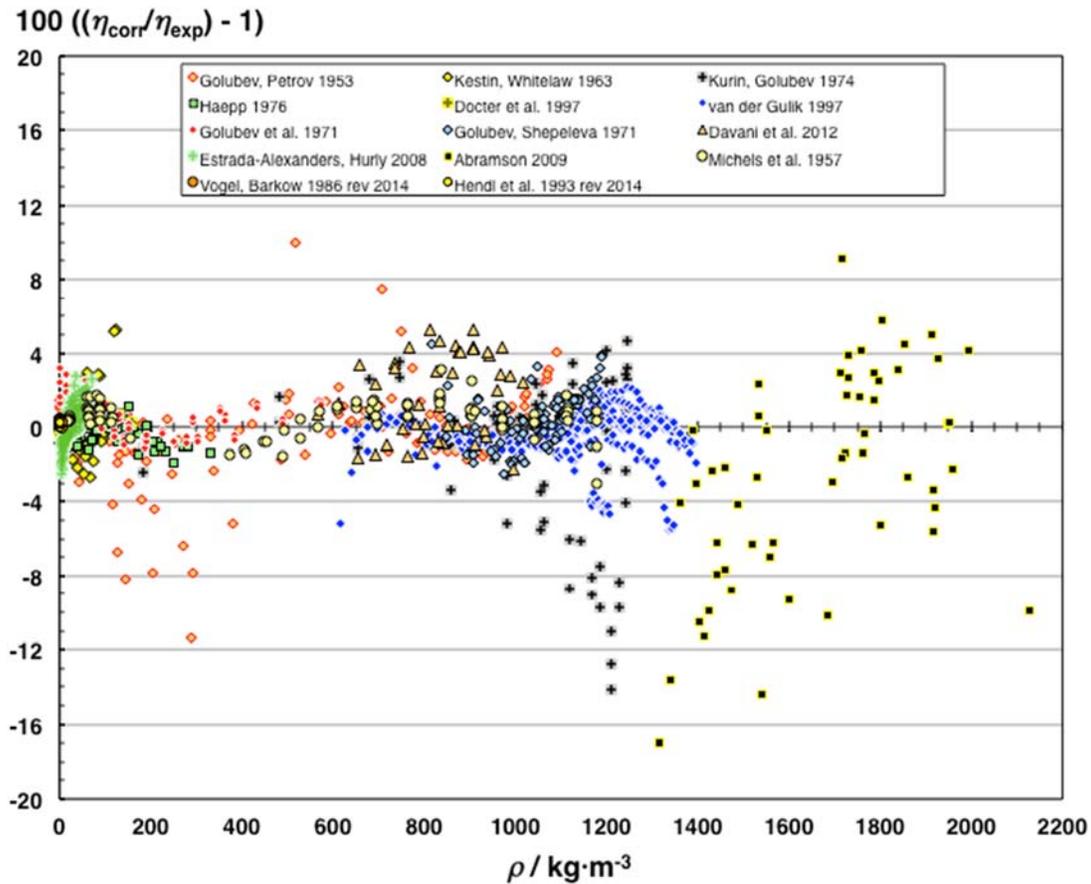
The extremely wide range of the viscosity data for CO<sub>2</sub> poses a formidable challenge to formulate the residual term  $\Delta\eta(T, \rho)$ . As explained by Muzny et al. (2013), symbolic regression was applied to identify functional terms that represent the data with the least sum-of-squares deviation and with a limited number of adjustable parameters. So far, the best representation has been achieved with the expression

$$\Delta\eta(T, \rho) = \eta_{\text{IL}} \left[ a_1 \rho_r + a_2 \rho_r^{a_3} + (a_4 \rho_r)^{a_5} / T_r \right], \quad (8)$$

where the viscosity reduction constant

$$\eta_{\text{IL}} = \frac{\rho_{\text{IL}}^{2/3} \sqrt{RT_t}}{M^{1/6} N_A^{1/3}} \quad (9)$$

is formed with the density  $\rho_{\text{IL}}$  of the saturated liquid at the triple-point temperature  $T_t = 216.592$  K,  $M$  is the molar mass of CO<sub>2</sub> (44.0095 kg·kmol<sup>-1</sup>),  $N_A$  the Avogadro constant, and  $R$  the universal gas constant.  $\rho_r$  and  $T_r$  are density and temperature reduced with the triple-point values,  $\rho_r = \rho/\rho_{\text{IL}}$  and  $T_r = T/T_t$ . The three density terms contain only five adjustable parameters,  $a_1$  to  $a_5$ . More important, they relate to theoretical concepts for the gas-like and the liquid-like viscosity characteristics. The first two terms in the bracket arise similarly from kinetic theory, while the third term represents thermodynamic scaling.



**Figure 7. Percent deviations of selected experimental data from the preliminary viscosity correlation for CO<sub>2</sub>.**

Relative deviations of the preliminary correlation relative to the experimental data are shown in Fig. 7 as a function of density for the entire fitted data set. The revised low-density data of Vogel and collaborators are represented within their experimental uncertainty. Deviations in excess of 4 % are observed for the data of Golubev and Petrov (1953). Closer inspection showed that such deviations also occurred with the previous correlation by Fenghour et al. (1998) and the corresponding data points are all in the near-critical region. Due to the high compressibility of fluids in this region, the flow of CO<sub>2</sub> in the capillary viscometer of Golubev and Petrov was not described correctly by the working theory of such instruments at that time. An extended working theory for compressible flows in capillary viscometers was not developed until 40 years later. The systematically deviating data of Golubev and Petrov (1953) will be omitted from the fit data set in future regressions.

Of interest is the representation of the data of Estrada-Alexanders and Hurly (2008). The deviations are small, but range systematically within  $\pm 3$  %. This exceeds their estimated experimental uncertainty of 0.6 %. At the lowest densities, the data are lower than those of Vogel and collaborators, which are represented within their lower experimental uncertainty of 0.2 %. This may be caused by an inadequate temperature dependence of the present formulation at the low temperatures of the data of Estrada-Alexanders and Hurly.

Deviations exceeding 4 % are observed for the high-density data of Kurin and Golubev (1974) and for the low-density data of Abramson (2009). These occur at temperatures where the two data sets overlap. Deviations of similar magnitude occurred for the data of Kurin and Golubev in the correlation of Fenghour et al. (1998) when the data of Abramson (2009) were not yet available. Thus, the deviations of the data of Kurin and Golubev may be due to a systematic inconsistency of their results with those of van der Gulik (1997) and Abramson (2009). It is also possible that the three-term formulation of Eq. (8) may be too

limited to represent the viscosity of CO<sub>2</sub> at high pressures due to term interferences. The next step of this work will aim to alleviate these term interferences by combining gas-like and liquid-like terms with a transition function instead of simple addition.

## CONCLUSIONS

We have taken new experimental data, covering a wide range of conditions, for the thermal conductivity of carbon dioxide. These data, along with other recent data and improved theoretical understanding, are being used to produce a reference correlation for the thermal conductivity of CO<sub>2</sub> that is expected to significantly reduce the uncertainty in that property. Similarly, additional literature data and theoretical results are being used to produce an improved reference correlation for the viscosity of CO<sub>2</sub>. It is expected that both correlations will be completed in early 2015.

## REFERENCES

- Abramson, E.H., 2009, "Viscosity of carbon dioxide measured to a pressure of 8 GPa and temperature of 673 K," *Phys. Rev. E* **80**, 021201.
- Assael, M.J., Karagiannidis, L., Richardson, S.M., Wakeham, W.A., 1992, "Compression Work Using the Transient Hot-Wire Method," *Int. J. Thermophys.* **13**, 223.
- Berg, R.F., Moldover, M.R., 1990, "Critical exponent for the viscosity of carbon dioxide and xenon," *J. Chem. Phys.* **93**, 1926.
- Bock, S., Bich, E., Vogel, E., Dickinson, A.S., Vesovic, V., 2002, "Calculation of the transport properties of carbon dioxide. I. Shear viscosity, viscomagnetic effects, and self-diffusion," *J. Chem. Phys.* **117**, 2151.
- Bukowski, R., Sadlej, J., Jeziorski, B., Jankowski, P., Szalewicz, K., Kucharski, S.A., Williams, H.L., Rice, B.M., 1999, "Intermolecular potential of carbon dioxide dimer from symmetry-adapted perturbation theory," *J. Chem. Phys.* **110**, 3785.
- Cox, M.G., 2002, "The evaluation of key comparison data," *Metrologia* **39**, 589.
- Ely, J.F., Magee, J.W., Haynes, W.M., 1987, *Thermophysical Properties for Special High CO<sub>2</sub> Content Mixtures*, GPA Research Report RR-110 (Gas Processors Association, Tulsa, OK).
- Estrada-Alexanders, A.F., Hurly, J.J., 2008, "Kinematic viscosity and speed of sound in gaseous CO, CO<sub>2</sub>, SiF<sub>4</sub>, SF<sub>6</sub>, C<sub>4</sub>F<sub>8</sub>, and NH<sub>3</sub> from 220 K to 375 K and pressures up to 3.4 MPa," *J. Chem. Thermodyn.* **40**, 193.
- Fenghour, A., Wakeham, W.A., Vesovic, V., 1998, "The Viscosity of Carbon Dioxide," *J. Phys. Chem. Ref. Data* **27**, 31.
- Golubev, I.F., Petrov, V.A., 1953, "The Viscosity of Gases and Gas Mixtures," *Trudy GIAP*, 5.
- Golubev, I.F., Gnezdilov, N.E., Brodskoya, G.V. 1971, "The Viscosity of Air and Carbon Dioxide at Various Temperatures and Pressures," *Kimiya i tekhnol. organ. sinteza, ONTI, GIAP, part 8*, 48.
- Healy, J., DeGroot, J.J., Kestin, J., 1976, "The Theory of the Transient Hot-Wire Method for Measuring the Thermal Conductivity," *Physica* **C82**, 392.
- Hellmann, R., 2014, "Ab Initio Potential Energy Surface for the Carbon Dioxide Molecule Pair and Thermophysical Properties of Dilute Carbon Dioxide Gas," *Chem. Phys. Lett.*, in press.
- Hendl, S., Neumann, A.-K., Vogel, E., 1993, "The viscosity of carbon dioxide and its initial density dependence," *High Temp. - High Press.* **25**, 503.
- Huber, M.L., Perkins, R.A., Friend, D.G., Sengers, J.V., Assael, M.J., Metaxa, I.N., Miyagawa, K., Hellmann, R., Vogel, E., 2012, "New International Formulation for the Thermal Conductivity of H<sub>2</sub>O," *J. Phys. Chem. Ref. Data* **41**, 033102.
- Johns, A.I., Rashid, S., Watson, J.T.R., 1986, "Thermal Conductivity of Argon, Nitrogen, and Carbon Dioxide at Elevated Temperatures and Pressures," *J. Chem. Soc., Faraday Trans. 1* **82**, 2235.

Kunick, M., Kretschmar, H.-J., Gampe, U., di Mare, F., Hrubý, J., Duška, M., Vinš, V., Singh, A., Miyagawa, K., Weber, I., Pawellek, R., Novi, A., Blangetti, F., 2014, "Fast Calculation of Steam and Water Properties in Computational Fluid Dynamics with the Spline-Based Table Look-Up Method (SBTL)," *J. Eng. Gas Turbines & Power*, in preparation.

Kurin, V.I., Golubev, I.F., 1974, "The Viscosity of Argon, Air and Carbon Dioxide at Pressures up to 4000 kg/cm<sup>2</sup> and at Different Temperatures," *Therm. Eng.* **21**, 125.

Lemmon, E.W., Huber, M.L., McLinden, M.O., 2013, *REFPROP: Reference Fluid Thermodynamic and Transport Properties*, NIST Standard Reference Database 23, Version 9.1 (Standard Reference Data, National Institute of Standards and Technology, Gaithersburg, MD).

Li, S.F.Y., Papadaki, M., Wakeham, W.A., 1993, "The Measurement of the Thermal Conductivity of Gases at Low Density by the Transient Hot-Wire Technique," *High Temp. High Press.* **25**, 451.

Li, S.F.Y., Papadaki, M., Wakeham, W.A., 1994, "Thermal Conductivity of Low-Density Polyatomic Gases," in *Thermal Conductivity 22*, T.W. Tong, Ed. (Technomic Publishing: Lancaster, PA), p. 531.

Millat, J., Mustafa, M., Ross, M., Wakeham, W.A., Zalaf, M., 1987, "The Thermal Conductivity of Argon, Carbon Dioxide and Nitrous Oxide," *Physica A* **145**, 461.

Muzny, C.D., Huber, M.L., Kazakov, A.F., 2013, "Correlation for the Viscosity of Normal Hydrogen Obtained from Symbolic Regression," *J. Chem. Eng. Data* **58**, 969.

Olchow, G.A., Sengers, J.V., 1989, "A Simplified Representation for the Thermal Conductivity of the Critical Region," *Int. J. Thermophys.* **10**, 417.

Perkins, R.A., Roder, H.M., Nieto de Castro, C.A., 1991, "A High-Temperature Transient Hot-Wire Thermal Conductivity Apparatus for Fluids," *J. Res. NIST* **96**, 247.

Perkins, R.A., Sengers, J.V., Abdulagatov, I.M., Huber, M.L., 2013, "Simplified Model for the Critical Thermal-Conductivity Enhancement in Molecular Fluids," *Int. J. Thermophys.* **34**, 191.

Roder, H.M., 1981, "A Transient Hot Wire Thermal Conductivity Apparatus for Fluids," *J. Res. Natl. Bur. Stand.* **86**, 457.

Roder, H.M., Perkins, R.A., Laesecke, A., Nieto de Castro, C.A., 2000, "Absolute Steady-State Thermal Conductivity Measurements by Use of a Transient Hot-Wire System," *J. Res. NIST* **105**, 221.

Span, R., Wagner, W., 1996, "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa," *J. Phys. Chem. Ref. Data* **25**, 1509.

Taxis, B., Stephan, K., 1994, "The Measurement of the Thermal Conductivity of Gases at Low Density by the Transient Hot-Wire Technique," *Int. J. Thermophys.* **15**, 141.

van der Gulik, P.S., 1997, "Viscosity of Carbon Dioxide in the Liquid Phase," *Physica A* **238**, 81.

Vesovic, V., Wakeham, W.A., Olchow, G.A., Sengers, J.V., Watson, J.T.R., Millat, J., 1990, "The Transport Properties of Carbon Dioxide," *J. Phys. Chem. Ref. Data* **19**, 763.

Vogel, E., 2014, personal communication.

Vogel, E., Barkow, L., 1986, "Precision Measurements of the Viscosity Coefficient of Carbon Dioxide between Room Temperature and 650 K," *Z. phys. Chem. (Leipzig)* **267**, 1038.

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