

IUPAC Technical Report

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Reference correlations for the viscosity and thermal conductivity of fluids over an extended range of conditions: hexane in the vapor, liquid, and supercritical regions (IUPAC Technical Report)

Abstract: This article summarizes the correlation procedures developed for IUPAC Project 2012-040-1-100 [Reference correlations for the thermal conductivity and viscosity of fluids over extended range of conditions (vapor, liquid and supercritical regions)]. This project is focused on the development of wide-range reference correlations for the thermal conductivity and viscosity of fluids that incorporate as much theoretical knowledge of these properties as possible. The thermal conductivity and viscosity correlations developed here for pure fluids are functions of temperature and density. The best available equations of state for a given fluid are used to calculate the thermodynamic properties required for these correlations, often from measured temperatures and pressures. The correlation methodology developed during this project has been applied to hexane in this report but can be applied to any pure fluid with a reliable equation of state and reliable data for the thermal conductivity and viscosity over a significant range of temperatures and densities.

Keywords: correlation; critical evaluation; hexane; International Association for Transport Properties (IATP); IUPAC Physical and Biophysical Chemistry Division; thermal conductivity; transport properties; viscosity.

DOI 10.1515/pac-2014-0104

Received January 21, 2014; accepted November 12, 2014

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Article note: Sponsoring body: IUPAC Physical and Biophysical Chemistry Division and the International Association for Transport Properties (IATP).
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Preamble

This article summarizes the correlation procedures developed for IUPAC Project 2012-040-1-100 [Reference correlations for the thermal conductivity and viscosity of fluids over extended range of conditions (vapor, liquid and supercritical region)] chaired by Richard A. Perkins (National Institute of Standards and Technology, Boulder, CO, USA). Members of the project task group were Marcia L. Huber (National Institute of Standards and Technology, Boulder, CO, USA) and Marc J. Assael (Aristotle University, Thessaloniki, Greece). This project is focused on the development of wide-range reference correlations for the thermal conductivity and viscosity of fluids that incorporate as much theoretical knowledge of these properties as possible. The present paper focuses on the methodology for the development of wide-ranging correlations for the viscosity and thermal conductivity of fluids that has been developed during this project. This methodology can be applied to any pure fluid with reliable data for the thermal conductivity and viscosity that has a reliable equation of state available. It is best if the available viscosity and thermal conductivity data cover the entire range of temperatures and pressures of interest with low uncertainty.

This work is based on wide-range correlations from the literature and our own experience in the development of such correlations. In particular, the extensive work on the viscosity and thermal conductivity of carbon dioxide [1] and ethane [2, 3] by the IUPAC Subcommittee on Transport Properties [now known as the International Association for Transport Properties (IATP)] and on water [4–6] by the International Association for the Properties of Water and Steam (IAPWS) and IATP has influenced the present project.

In a series of recent papers, the project group has developed new reference correlations for the thermal conductivity of normal and para hydrogen [7], methylbenzene [8], SF₆ [9], benzene [10], hexane [11], heptane [12], ethanol [13], and methanol [14] covering a wide range of temperature and pressure. The project group has also reported its first viscosity correlation on hexane [15]. In the case of thermal conductivity, several alternative theoretical models have been used successfully for the dilute gas. This paper will demonstrate application of this correlation methodology to viscosity and thermal conductivity of hexane, with densities, specific heat, critical, and other thermodynamic properties provided by the equation of state of Span and Wagner [16].

1 Data selection and evaluation

The experimental data with lowest uncertainty must be identified for the property of interest. 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 recommendations adopted by the IUPAC Subcommittee on Transport Properties, the primary data are identified by the following criteria [17]:

- (i) Measurements must have been made with a primary experimental apparatus, i.e., one for which a complete working equation is available.
- (ii) The working equation for the apparatus 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 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) Data from absolute measurements are preferred. Data from absolute measurements do not depend on ambiguous data for the property of interest of one or more calibration fluids. Relative data may be considered if sufficient information is given in the original reference to adjust the reported values to account for changes in the accepted values for the properties of the reference fluids.
- (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 uncertainties 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 $\pm 1\%$. 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 data that extend over a wide range of conditions, albeit with a higher uncertainty, provided they are consistent with other data with reduced uncertainty or with theory. In all cases, the uncertainty claimed for the final recommended correlation must reflect the estimated uncertainty in the primary information.

2 Viscosity

The viscosity η can be expressed as the sum of four independent contributions [18], as

$$\eta(\rho, T) = \eta_0(T) + \eta_1(T)\rho + \Delta\eta(\rho, T) + \Delta\eta_c(\rho, T) \quad (1)$$

where ρ is the density, T is the absolute temperature, and the first term, $\eta_0(T) = \eta(0, T)$, is the contribution to the viscosity in the dilute-gas limit, where only two-body molecular interactions occur. The linear-in-density term, $\eta_1(T)\rho$, known as the initial density-dependence term, can be separately established with the development of the Rainwater–Friend theory [19–21] for the transport properties of moderately dense gases. The critical enhancement term, $\Delta\eta_c(\rho, T)$, arises from the long-range density fluctuations that occur in a fluid near its critical point, which contribute to divergence of the viscosity at the critical point. Finally, the term $\Delta\eta(\rho, T)$, the residual term, represents the contribution of all other effects to the viscosity of the fluid at elevated densities including many-body collisions, molecular-velocity correlations, and collision transfer.

The identification of these four separate contributions to the viscosity and to transport properties in general is useful because it is possible, to some extent, to treat $\eta_0(T)$, $\eta_1(T)$, and $\Delta\eta_c(\rho, T)$ theoretically. In addition, it is possible to derive information about both $\eta_0(T)$ and $\eta_1(T)$ from experiment. In contrast, there is little theoretical guidance concerning the residual contribution, $\Delta\eta(\rho, T)$, and therefore its evaluation is based entirely on experimentally obtained data.

An alternative expression that is a product of contributions has been used for the viscosity of water [4, 5]

$$\eta(\rho, T) = \eta_0(T) \times \eta_r(\rho, T) \times \eta_{cr}(\rho, T) \quad (2)$$

where $\eta_r(\rho, T)$ is the residual viscosity and $\eta_{cr}(\rho, T)$ is the critical enhancement contribution. In practice, correlations for the viscosity can be formulated as either a summation or a product of contribution terms. It is common to include the initial density dependence in the residual term and fit the initial density dependence along with the higher-order residual terms [1, 5]. It is also common to group the dilute-gas, first-density, and residual viscosity into the background viscosity [1] to isolate the critical enhancement contribution to the viscosity. For the purposes of this project, the summation expression of Eq. 1 is selected for the viscosity.

2.1 Viscosity of dilute gases

The dilute-gas limit viscosity, $\eta_0(T)$, can be analyzed independently of all other contributions in Eq. 1. For simple molecules, such as H_2 , N_2 , CO , CO_2 , H_2S , and H_2O [22], it is possible to calculate theoretical values for the viscosity and thermal conductivity from *ab initio* intermolecular potentials that agree well with the best available data. These theoretical values may be the best information available over some ranges of temperature; they may supplement primary data for these properties to provide better extrapolation to regions where reliable data are not available.

According to the kinetic theory, the viscosity of a pure polyatomic gas may be related to an effective collision cross-section, which contains all the dynamic and statistical information about the binary collision between molecules. The collision cross-section depends on the intermolecular potential of a molecule that requires, at a minimum, characteristic length and energy parameters. For practical purposes, the relation between viscosity and the collision cross-section is formally identical to that of monatomic gases and can be written as [23]

$$\frac{\eta_0(T)}{\mu\text{Pa}\cdot\text{s}} = \frac{0.021357 \sqrt{(M / \text{g}\cdot\text{mol}^{-1})(T / \text{K})}}{(\sigma / \text{nm})^2 S_\eta^*(T^*)} \quad (3)$$

where $S_\eta^* = S(2000) / (\pi \sigma^2 f_\eta)$ is a dimensionless reduced effective cross-section, M is the molar mass, σ is the length-scaling parameter, and f_η is a dimensionless higher-order correction factor according to Chapman and Cowling [24]. In the above equation, $S(2000)$ is a generalized cross-section that includes all of the information about the dynamics of the binary collisions that govern viscosity, which in turn are governed by the intermolecular potential energy surface of specific molecules [23]. The effective cross-section is usually expressed in the functional form

$$\ln S_\eta^*(T^*) = \sum_i \alpha_i (\ln T^*)^i \quad (4)$$

$$T^* = k_B T / \varepsilon \quad (5)$$

where T^* is the reduced temperature, ε/k_B is an energy-scaling parameter, and k_B is the Boltzmann constant. There are typically three or more dimensionless coefficients α_i in Eq. 4 that are fluid-specific and typically fit to data for the dilute-gas viscosity.

The temperature dependence of the linear-in-density coefficient of the viscosity, $\eta_1(T)$ in Eq. (1), is very large at subcritical temperatures and must be taken into account to obtain an accurate representation of the behavior of the viscosity in the vapor phase. It changes sign from positive to negative as the temperature decreases. Therefore, the viscosity along an isotherm should first decrease in the vapor phase and subsequently increase with increasing density [23]. Vogel et al. [25] have shown that fluids exhibit the same general behavior of the initial density dependence of viscosity, which can also be expressed by means of the second-viscosity-virial coefficient $B_\eta(T)$ as

$$B_\eta(T) = \frac{\eta_1(T)}{\eta_0(T)} \quad (6)$$

The second-viscosity-virial coefficient can be obtained in terms of a reduced second-viscosity-virial coefficient, $B_{\eta}^*(T^*)$, according to the theory of Rainwater and Friend [19, 20] for a Lennard-Jones fluid, as

$$B_{\eta}^*(T^*) = \frac{B_{\eta}(T)}{N_A \sigma^3} \quad (7)$$

where

$$B_{\eta}^*(T^*) = \sum_{i=0}^6 b_i (T^*)^{-0.25i} + b_7 (T^*)^{-2.5} + b_8 (T^*)^{-5.5} \quad (8)$$

In the above equations, N_A is Avogadro's constant, and the dimensionless coefficients b_i in Eq. 8 are given according to the fit of calculated theoretical values by Vogel et al. [23]. Since Eq. 8 is independent of the molecule, $\eta_1(T)$ only requires the fluid-specific parameters σ and ε/k_B . These same parameters are also used in the dilute-gas term.

Equations 3–8 present a consistent scheme for the correlation of the dilute-gas viscosity, $\eta_0(T)$, and the initial density-dependence term, $\eta_1(T)$. Five or more fluid-specific parameters can be fit to reliable (primary) experimental data that cover the dilute-gas region or to a combination of the primary experimental data with calculated values from intermolecular potential models that extend the range of validity for the resulting model. These parameters include the coefficients α_i in Eq. 4 and the scaling parameters σ and ε/k_B .

2.2 Residual viscosity

As already stated, the residual viscosity term $\Delta\eta(\rho, T)$ represents the contribution of all other effects to the viscosity of the fluid at elevated densities including many-body collisions, molecular-velocity correlations, and collision transfer. Because there is little theoretical guidance concerning this term, its evaluation is based entirely on experimentally obtained data. The residual viscosity is often represented by polynomial series in density (or reduced density) that may have temperature (or reduced temperature) dependent coefficients [1, 2].

The procedure adopted during this analysis used symbolic-regression software [26]¹ to fit all the primary data to the residual viscosity. Symbolic regression is a type of genetic programming that allows the exploration of arbitrary functional forms to regress data. The functional form is obtained by use of a set of operators, parameters, and variables as building blocks. Most recently this method has been used to obtain a correlation for the viscosity of hydrogen [27]. In the present work we restricted the operators to the set (+, −, *, /) and the operands (constant, T_r , ρ_r), with $T_r = T/T_c$ and $\rho_r = \rho/\rho_c$. Various choices of a scaling factor for density were tested, but the best results were obtained using the critical density. In addition, we found the best results when we adopted a form suggested from the hard-sphere model employed by Assael et al. [28], $\Delta\eta(\rho_r, T_r) = (\rho_r^{2/3} T_r^{1/2}) F(\rho_r, T_r)$, where the symbolic-regression method was used to determine the functional form for $F(\rho_r, T_r)$. For this task, the dilute-gas limit and the initial density-dependence terms were calculated for each experimental point (employing Eqs. 3–7) and subtracted from the experimental viscosity to obtain the residual term. The functional form for the residual term is expected to vary somewhat for different molecules.

2.3 Critical enhancement

The viscosity and thermal conductivity of pure fluids diverge at the critical point due to long-range fluctuations. The critical enhancement of viscosity can be described by the simplified theoretical crossover model

¹ Certain commercial equipment, instruments, or materials are identified in this report in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

of Bhattacharjee et al. [29] or the more rigorous crossover models of Olchoway and Sengers [30] and Luettmmer-Strathmann et al. [31]. The critical enhancement of thermal conductivity is significant over a wide region around the critical point and can be described by the simplified crossover model of Olchoway and Sengers [32] or by the more rigorous crossover models of Olchoway and Sengers [30] or Luettmmer-Strathmann et al. [31]. The more rigorous crossover models require matrix methods or complex variables for their evaluation.

Unlike the critical enhancement in thermal conductivity, the enhancement in viscosity is confined to a small region becoming relevant only at temperatures and densities very close to the critical point. For typical fluids, such as carbon dioxide [1], ethane [2], and water [5], the ratio $\Delta\eta_c(\rho, T)/\eta(\rho, T)$ exceeds 0.01 only within $\pm 1\%$ of the critical temperature of the fluid and near its critical density. In cases such as water [5], where there are reliable data for the viscosity very close to the critical point, the model of Bhattacharjee et al. [29] has been shown to work well and is recommended for such fluids.

There are no reliable data for the viscosity in the critical region of many industrial fluids such as hexane. When no reliable data on the viscosity critical enhancement are available, the contribution of the critical enhancement of viscosity is considered negligible; it is not further considered in the present paper. In practice, there are few industrial applications that require viscosity data this close to the gas–liquid critical point.

2.4 Viscosity correlation for hexane

The correlation for the viscosity of hexane [15] was developed from literature data that were selected and evaluated following the procedures discussed here. The primary data for the viscosity of hexane, selected according to the aforementioned criteria and shown in Table 1, were fit to the expression given in Eq. 1. There were no viscosity data available in the critical region, so the critical enhancement term $\Delta\eta_c(\rho, T)$ was set to zero. This assumption introduces an additional uncertainty that exceeds 1% within ± 8 K of the critical temperature near the critical density. The density values employed were obtained by the equation of state of Span and Wagner [16]. Among the primary data, the data of Vogel and Strehlow [38] were key to determination of the viscosity of the dilute gas. These data were measured with an absolute oscillating-disk viscometer on a high-purity sample of hexane and covered the temperature region from (298 to 631) K with pressures from 0.01 to 0.31 MPa. The data have an expanded uncertainty at a 95 % confidence level that ranges from $\pm 0.15\%$ to $\pm 0.30\%$. The functions for the viscosity of the dilute gas, Eqs. 3–8, have five or more fluid-dependent parameters that must be determined from these data. The ODRPACK [43] regression package was used to obtain optimum values for three coefficients α_i in Eq. 4 and the scaling parameters σ and ε/k_B . Equations 3–8

Table 1 Primary viscosity measurements and fit statistics for hexane [15]. The relative expanded uncertainty $u(\eta)$ of each data set is at 95 % confidence.

1 st author	Year	Technique ^a	x_{mass}	$u(\eta)/\%$	N	T_{min}/K	T_{max}/K	$P_{\text{min}}/\text{MPa}$	$P_{\text{max}}/\text{MPa}$	$A_{\Delta}/\%$	$B_{\Delta}/\%$
Oliveira [33]	1992	VBW-Abs	0.9999	0.5	38	303	348	0.1	150 ^b	0.83	−0.11
Assael [34]	1991	VBW-Abs	0.99	0.5	15	298	298	0.1	71	0.80	−0.79
Berstad [35]	1989	OCup-Abs	0.995	1.1	37	293	437	0.69	45	1.48	−1.48
Knapstad [36]	1989	OCup-Abs	0.99	0.5	7	288	327	0.1	0.1	0.78	−0.78
Grigor'ev [37]	1988	Cap	0.9929	0.9	53	178	323	0.1	59	0.61	−0.23
Vogel [38]	1988	OD-Abs	0.9993	0.3	82	298	631	0.01	0.31	0.10	0.02
Bauer [39]	1984	Cap	0.99	0.3	2	293	298	0.101	0.101	1.48	−1.48
Dymond [40]	1980	Cap	0.99	1.0	12	283	393	0.01	0.4	1.05	0.36
Dymond [41]	1980	FB	0.99	2.0	17	298	373	0.1	150 ^b	1.34	−1.18
Agaev [42]	1963	Cap	0.998	1–3	291	448	548 ^c	0.101	50 ^c	2.29	0.30
All Primary Data										1.56	−0.04

^aAbs, absolute; Cap, capillary; FB, falling body; OCup, oscillating cup; OD, oscillating disk; VBW, vibrating wire.

^bData restricted to 150 MPa.

^cData within 0.2 K of the critical temperature and within 0.1 MPa of the critical pressure were excluded.

fit the data of Vogel and Strehlow [38] with an expanded uncertainty of $\pm 0.3\%$ with these five fit parameters, given in Table 2. Figure 1 shows the data of Vogel and Strehlow [38] along with the correlation of Eqs. 3–8 that was fitted to these data.

The data of Vogel and Strehlow [38] were measured over a range of density, and experimental values for the second-virial-coefficient of viscosity can be determined from these data due to their low uncertainty. Figure 2 shows these experimental values for B_η with error bars, along with the theoretical curve from the theory of Rainwater and Friend [19, 20]. The change in the sign of B_η is clearly visible in both the experimental data and the theoretical curve [19, 20] over the temperature range from (350 to 650) K. There is good agreement between the experimental values for hexane and the theory, demonstrating that the theory of Rainwater and Friend [19, 20] can be used in the absence of reliable data to describe the second-density-virial coefficient of viscosity. With determination of the dilute-gas contribution to viscosity $\eta_0(T) + \eta_1(T)\rho$ and with $\Delta\eta_c(\rho, T) = 0$, only the residual contribution remains to be determined.

The entire set of primary data for the viscosity of hexane was considered after subtraction of the dilute-gas contributions, $\eta_0(T) + \eta_1(T)\rho$, to obtain experimental values for the residual viscosity. The final equation for the residual viscosity obtained from symbolic regression was

Table 2 Coefficients and parameters for the viscosity correlation of hexane [15].

Scaling parameters		
$(\varepsilon/k_{\text{B}})/K = 378.4$	$\sigma/\text{nm} = 0.6334$	
Coefficients α_i for Eq. 4 for the effective viscosity cross-section		
$\alpha_0 = 0.187\ 60$	$\alpha_1 = -0.484\ 30$	$\alpha_2 = 0.044\ 77$
Coefficients b_i for Eq. 8 from Vogel et al. [23]		
$b_0 = -19.572\ 881$	$b_1 = 219.73999$	$b_2 = -1015.322\ 6$
$b_3 = 2471.012\ 5$	$b_4 = -3375.1717$	$b_5 = 2491.659\ 7$
$b_6 = -787.260\ 86$	$b_7 = 14.085\ 455$	$b_8 = -0.346\ 641\ 58$
Coefficients c_i for Eq. 9 for the residual viscosity term		
$c_0/\mu\text{Pa}\cdot\text{s} = 2.534\ 023\ 35$	$c_1/\mu\text{Pa}\cdot\text{s} = -9.724\ 061\ 002$	$c_2 = 0.469\ 437\ 316$
$c_3 = 158.557\ 163\ 1$	$c_4/\mu\text{Pa}\cdot\text{s} = 72.429\ 168\ 56$	$c_5 = 10.607\ 512\ 53$
$c_6 = 8.628\ 373\ 915$	$c_7 = -6.613\ 464\ 41$	$c_8 = -2.212\ 724\ 566$

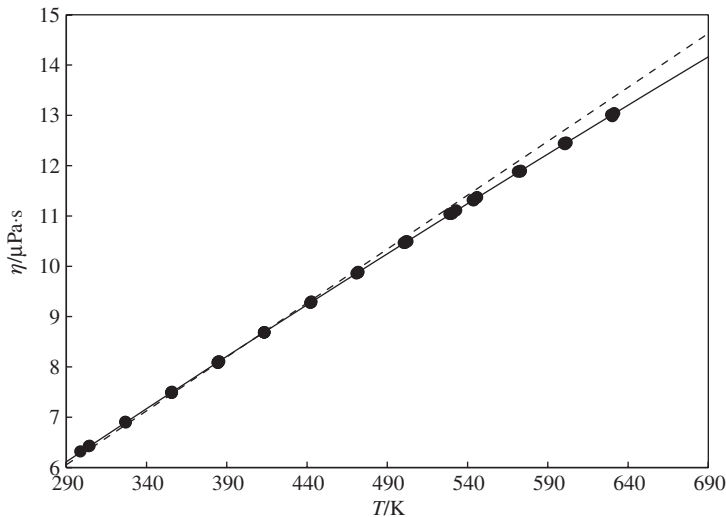


Fig. 1 Viscosity of hexane in the dilute-gas limit. ●, Vogel and Strehlow [38] Solid line Equations represents Eqs. 3–5 fitted to this viscosity data; dashed line represents Eqs. 21 and 22 with Lennard–Jones parameters σ and ε/k_B fitted to primary data for thermal conductivity.

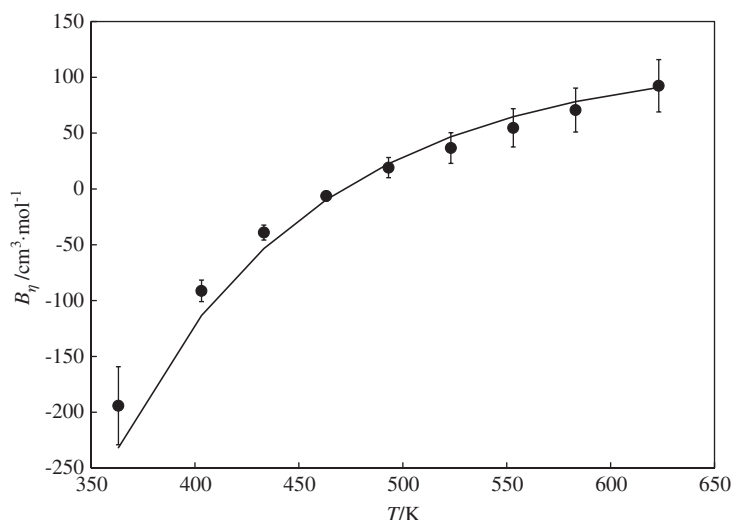


Fig. 2 Second virial coefficient for the viscosity of hexane. ●, Vogel and Strehlow [38]. Solid line represents the theory of Rainwater and Friend [19, 20], Eqs. 7 and 8.

$$\Delta\eta(\rho, T) = (\rho_r^{2/3} T_r^{1/2}) \left\{ \frac{c_0}{T_r} + \frac{c_1}{c_2 + T_r + c_3 \rho_r^2} + \frac{(c_4)(1 + \rho_r)}{c_5 + c_6 T_r + c_7 \rho_r + \rho_r^2 + c_8 \rho_r T_r} \right\} \quad (9)$$

Coefficients c_i for hexane are given in Table 2.

Table 1 also summarizes comparisons of the primary data with the correlation. We have defined the relative deviation from the fit in percent as $\Delta_r = 100 \cdot (\eta_{\text{exp}} - \eta_{\text{fit}}) / \eta_{\text{fit}}$, where η_{exp} is the experimental value of the viscosity and η_{fit} is the value calculated from the correlation. Thus, the average absolute percent deviation is found with the expression $A_\Delta = (\sum |\Delta_r|) / n$, where the summation is over all n points; the bias percent deviation is found with the expression $B_\Delta = (\sum \Delta_r) / n$. The average absolute percent deviation of the fit is 1.56, and its bias percent deviation is -0.04 . We estimate the uncertainty at a 95 % confidence level to be ± 2 % for the liquid phase at temperatures up to 450 K and pressures to 100 MPa. For the liquid at (450–600) K, the predominant measurements are those of Agaev and Golubev [42], which are of higher uncertainty and a larger degree of scatter than other primary data. In this region, we estimate the expanded uncertainty at the 95 % confidence level to be ± 6 %. As mentioned previously, we estimate the expanded uncertainty of the correlation at a 95 % confidence level for the low-density gas at temperatures from (298 to 631) K and pressures to 0.3 MPa to be ± 0.3 %.

In addition to Table 1, plots of percentage deviations of all primary viscosity data from the values calculated by Eq. 1 and Eqs. 3–9 are available in Michailidou et al. [15] as functions of density and temperature. With the exception of the data set of Agaev and Golubev [42], all primary data are represented to within ± 2 % over the temperature range (178–437) K at pressures to 100 MPa. As already discussed above, the data of Agaev and Golubev [42] display larger deviations. Figure 3 shows a plot of the viscosity of hexane as a function of the temperature for different pressures and for saturated liquid and vapor.

A previous reference correlation by Dymond and Øye [44] has been developed along the saturation line covering the temperature range (273–355) K. The Dymond and Øye [44] correlation has an uncertainty of ± 1 %, and is in agreement with the present correlation within this uncertainty. The correlation of Dymond and Øye [44] was heavily based on the measurements of Dymond [40] and the measurements of Oliveira and Wakeham [33] and Knapstad et al. [36]. The present correlation includes measurements of additional investigators (see Table 1). Full details of this correlation for the viscosity of hexane are available in Michailidou et al. [15], including a table of test values to verify computer coding of the correlation.

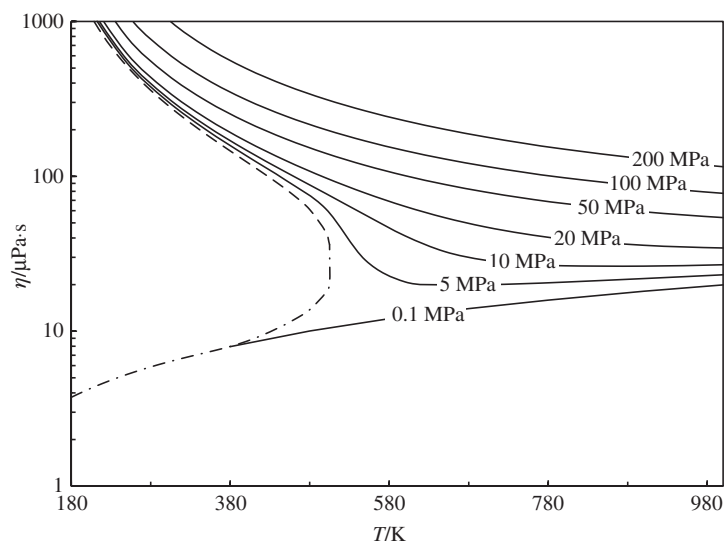


Fig. 3 Viscosity of hexane calculated from Eqs. 1 and 3–9 as a function of temperature for selected pressures and at saturation. Dashed line represents saturated liquid; dot-dashed line represents saturated vapor.

3 Thermal conductivity

The thermal conductivity λ can be expressed as the sum of three independent contributions, as

$$\lambda(\rho, T) = \lambda_o(T) + \Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T) \quad (10)$$

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 last term in Eq. 10 is the critical enhancement contribution to thermal conductivity, $\Delta\lambda_c(\rho, T)$, which arises from the long-range density fluctuations that occur in a fluid near its critical point that contribute to divergence of the thermal conductivity at that point. The remaining 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 collision transfer. This term includes the initial density dependence of thermal conductivity, which could be calculated from the Rainwater–Friend theory [19, 20] as with viscosity. This has been demonstrated for polyatomic molecules such as nitrogen [45]. In practice, the temperature dependence of the initial density term is small for thermal conductivity relative to that for viscosity, and it is more convenient to include it with the residual thermal conductivity.

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. It is also possible to derive information about $\lambda_o(T)$ from experiment. Theoretical knowledge of the dilute-gas thermal conductivity of polyatomic molecules is complicated by the rate of energy transfer between translational and internal energy modes (rotation, vibration, and electronic) that are observable by spectroscopic techniques. There is typically more empiricism in dilute-gas thermal conductivity theory relative to that for dilute-gas viscosity. 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.

3.1 Dilute-gas thermal conductivity

The dilute-gas limit viscosity, $\lambda_o(T)$, can be analyzed independently of all other contributions in Eq. 10. For simple molecules, such as H_2 , N_2 , CO , CO_2 , H_2S , and H_2O [22], it is possible to calculate theoretical values

for the viscosity and thermal conductivity from *ab initio* intermolecular potentials that agree well with the best available data. The calculations of thermal conductivity are more difficult and often less reliable due to energy transfer between internal energy modes. These theoretical values may be the best information available over some ranges of temperature; they may supplement primary data for these properties to provide better extrapolation to regions where reliable data are not available.

A reasonable estimate of the thermal conductivity, $\lambda_o(T)$, of a pure dilute gas may be obtained from the viscosity, $\eta_o(T)$, and ideal-gas heat capacity at constant volume, C_{v_o} , through the modified Eucken correlation [46],

$$f_{\text{Eu}} = \frac{\lambda_o(T)M}{\eta_o(T)C_{v_o}} = 1.32 + 1.77 \left(\frac{R}{C_{v_o}} \right) \quad (11)$$

In the above equation, M is the molar mass and R is the universal gas constant [47, 48]. To employ the equation, the dilute-gas viscosity (see above) and the ideal-gas heat capacity at constant volume from an equation of state are required. This approach has been used by our project group for methylbenzene [8], SF₆ [9], benzene [10], and hexane [11], but it becomes less effective for larger non-spherical molecules.

The traditional kinetic-theory approach for thermal conductivity results in an expression involving three generalized cross-sections [49, 50]. However, it is possible to derive an equivalent kinetic-theory expression for thermal conductivity by making use of the approach of Thijssse et al. [51, 52], 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 thermal conductivity, $\lambda_o(T)$, of a polyatomic gas can be shown to be inversely proportional to a single generalized cross-section [49–52], $S(10E)$, as

$$\lambda_o(T) = \frac{5k_B^2(1+r^2)T}{2m\langle v \rangle_o S(10E)} f_\lambda \quad (12)$$

where k_B is the Boltzmann constant [47, 48], T is the absolute temperature, f_λ is the dimensionless higher-order correction factor, m is the mass of the molecule, and $\langle v \rangle_o = 4\sqrt{k_B T / \pi m}$ is the average relative thermal speed. The quantity r^2 is defined by $r^2 = 2C_{\text{int}}^o / 5k_B$, where C_{int}^o is the contribution of both the rotational, C_{rot}^o , and the vibrational, C_{vib}^o , degrees of freedom to the isochoric ideal heat capacity C_v^o of the molecule.

The recent classical trajectory calculations [51–53] 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, $S_\lambda [= S(10E)/f_\lambda]$, and rewrite Eq. 12 for the dilute-gas thermal conductivity, $\lambda_o(T)$, as

$$\lambda_o(T) = \left(\frac{1}{4} \sqrt{\frac{\pi k_B^3}{m}} \right) \frac{C_p^o \sqrt{T}}{k_B S_\lambda} \quad (13)$$

It has been previously noted [51], and recently confirmed [49] for smaller molecules, that the cross-section S_λ exhibits a nearly linear dependence on the inverse temperature. The correlation is developed by fitting the effective cross-section S_λ , obtained from experimental data for the thermal conductivity of the dilute gas by means of Eq. 13, to a polynomial in inverse temperature, resulting in the following expression:

$$S_\lambda = d_o + d_{1/T} \quad (14)$$

The approach of Thijssse et al. [51, 52] requires information for the isobaric heat capacity of the molecule, C_p^o , usually from an equation of state, but is independent of the viscosity. Fitting the effective cross-section, Eq. 14 is preferred for larger, complex molecules and has been used by the project group for heptane [12], ethanol [13], and methanol [14].

3.2 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 [30, 45, 54]. The density-dependent terms for thermal conductivity can be grouped according to Eq. 10 as $[\Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T)]$. To assess the critical enhancement, we need to evaluate the residual thermal-conductivity contribution in addition to the dilute-gas thermal conductivity. The procedure adopted during this analysis used ODRPACK [43] to fit all the primary data to the residual thermal conductivity and the critical enhancement simultaneously while maintaining the parameters already obtained for the dilute-gas thermal-conductivity data. The critical constants, T_c and ρ_c , and the density values are obtained from a suitable equation of state.

The residual thermal conductivity is well represented with a polynomial of order n , in terms of reduced temperature and density:

$$\Delta\lambda(\rho, T) = \sum_{i=1}^n (B_{1,i} + B_{2,i}(T_r)) (\rho_r)^i \quad (16)$$

The order of the polynomial fit varies depending on the density range of the data and the nature of the molecule. The use of reduced temperature and density is preferred when fitting polynomial series since the coefficients of the higher-order terms remain of comparable magnitude to lower-order terms.

3.3 Critical enhancement

The theoretically-based crossover model proposed by Olchowky and Sengers [30, 45, 54] is complex and requires the solution of a quartic equation in terms of complex variables. A simplified crossover model has also been proposed by Olchowky and Sengers [32]. The critical enhancement of the thermal conductivity from this simplified model is given by

$$\Delta\lambda_c = \frac{\rho C_p R_D k_B T}{6\pi\eta\xi} (\bar{\Omega} - \bar{\Omega}_0) \quad (17)$$

with

$$\bar{\Omega} = \frac{2}{\pi} \left[\left(\frac{C_p - C_v}{C_p} \right) \arctan(\bar{q}_D \xi) + \frac{C_v}{C_p} \bar{q}_D \xi \right] \quad (18)$$

and

$$\bar{\Omega}_0 = \frac{2}{\pi} \left[1 - \exp \left(- \frac{1}{(\bar{q}_D \xi)^{-1} + (\bar{q}_D \xi \rho_c / \rho)^2 / 3} \right) \right] \quad (19)$$

In Eqs. 17–19, C_p and C_v are the isobaric and isochoric heat capacities, respectively, obtained from a suitable equation of state. Since the viscosity is required for the critical enhancement, and the modified Eucken correlation [46] approach for the dilute gas, it is preferable to correlate the viscosity of a given fluid prior to correlating the thermal conductivity. The correlation length ξ is given by

$$\xi = \xi_0 \left(\frac{p_c \rho}{\Gamma \rho_c^2} \right)^{\nu/\gamma} \left[\left. \frac{\partial \rho(T, \rho)}{\partial p} \right|_T - \left(\frac{T_{\text{ref}}}{T} \right) \left. \frac{\partial \rho(T_{\text{ref}}, \rho)}{\partial p} \right|_T \right]^{\nu/\gamma} \quad (20)$$

As already mentioned, the coefficients $B_{1,i}$ and $B_{2,i}$ in Eq. 16 and \bar{q}_D in Eqs. 17–19 were fit with ODRPACK [43] to the primary data for the thermal conductivity with the dilute-gas term subtracted. The crossover model requires the universal constants [32, 55] $R_D = 1.02$, $\nu = 0.63$, and $\gamma = 1.239$, and system-dependent amplitudes Γ and ξ_0 that are estimated using the method presented by Perkins et al. [55]. In Eq. 20, the reference temperature, $T_{\text{ref}} = 1.5 T_c$, was selected to be larger than the critical temperature where the critical enhancement is negligible as recommended by Perkins et al. [55].

3.4 Thermal-conductivity correlation for hexane

The correlation for the thermal conductivity of hexane [11] was developed from literature data that were selected and evaluated following the procedures discussed here. The primary data, selected according to the aforementioned criteria and shown in Table 3, were fitted to the expression given in Eq. 10. The density values employed were obtained with the equation of state of Span and Wagner [16].

As only two of the six primary data sets (Golubev and Naziev [63], and Naziev et al. [64]) extend to over 600 K, the modified Eucken correlation [46], Eq. 11, was used for the dilute gas to calculate the thermal conductivity in terms of the viscosity and isochoric specific heat. The modified Eucken approach assures that the thermal conductivity is consistent with the viscosity and specific heat, while maintaining good temperature extrapolation behavior beyond the region of reliable thermal-conductivity data. The same scheme was successfully adopted in the case of the dilute-gas thermal-conductivity correlations of methylbenzene [8], SF₆ [9], benzene [10], and hexane [11]. In these cases, the parameters for the viscosity correlation are optimized to represent the primary data for dilute-gas thermal conductivity. For hexane, the thermal conductivity correlation [11] was developed prior to the viscosity correlation [15] and the later viscosity correlation [15] will also give a reasonable, but more predictive representation of the thermal conductivity with Eq. 11.

The dilute-gas viscosity, η_o , can be written [46] as a function of the reduced collision integral $\Omega^*(T^*)$ as

$$\eta_o(T) = \frac{5}{16} \left[\frac{MRT}{\pi} \right]^{1/2} \frac{1}{\sigma^2 \Omega^*(T^*)} \quad (21)$$

where T is the absolute temperature and σ is the Lennard–Jones length parameter. The reduced collision integral can be calculated [65] as a function of the reduced temperature, $T^* = T(k_B/\epsilon)$, for the range $0.3 < T^* < 100$, as

$$\Omega^*(T^*) = 1.16145(T^*)^{-0.14874} + 0.52487 e^{-0.7732T^*} + 2.16178 e^{-2.43787T^*} - 6.435 \times 10^{-4} (T^*)^{0.14874} \sin[18.0323(T^*)^{-0.7683} - 7.27371] \quad (22)$$

where ϵ is the Lennard–Jones depth parameter and k_B is the Boltzmann constant.

The molar ideal-gas heat capacity at constant volume, C_v^o , can be obtained from the molar ideal-gas heat capacity at constant pressure, C_p^o , (as $C_v^o = C_p^o - R$), as this is given by [66]

$$\begin{aligned} \frac{C_p^o}{R} = & 4.0 + 11.6977 \left(\frac{182.326/(T/K)}{\sinh(182.326/(T/K))} \right)^2 + 26.8142 \left(\frac{859.207/(T/K)}{\cosh(859.207/(T/K))} \right)^2 \\ & + 38.6164 \left(\frac{1826.59/(T/K)}{\sinh(1826.59/(T/K))} \right)^2 \end{aligned} \quad (23)$$

Table 3 Primary thermal conductivity measurements and fit statistics for hexane [11]. The relative expanded uncertainty $u(\lambda)$ of each data set is at 95 % confidence.

1 st author	Year	Technique ^a	x_{mass}	$u(\lambda)/\%$	N	T_{min}/K	T_{max}/K	$P_{\text{min}}/\text{MPa}$	$P_{\text{max}}/\text{MPa}$	$A_{\Delta}/\%$	$B_{\Delta}/\%$
Watanabe [56]	2002	THW (Abs)	0.98	0.5	22	298	337	0.02	101	3.31	−3.31
Tanaka [57]	1988	THW (Abs)	0.99	1.0	45	283	373	0.1	250	4.02	−4.02
Assael [58]	1987	THW (Abs)	0.995	0.5	12	297	325	0.1	0.1	0.30	0.30
Li [59]	1984	THW (Abs)	0.999	0.3	77	307	360	1.8	643	0.56	−0.12
Kashiwagi [60]	1982	THW (Rel)	0.99	2.0	4	298	333	0.1	0.1	0.81	0.09
Naziev [61]	1981	CC (Abs)	na	1.5	78	196	473	0.10	50	1.88	−1.59
Mukhamedzyanov [62]	1971	THW (Abs)	0.9969	2.0	70	298	448	0.1	220	2.07	0.42
Golubev [63] ^b	1962	CC (Abs)	na	na	153	293	633	0.1	49	3.52	2.93
All Primary Data										2.46	−0.21

^aAbs, absolute; CC, coaxial cylinder; na, not available; Rel, relative; THW, transient hot wire.

^bIncludes vapor data employed to derive the dilute-gas thermal-conductivity correlation.

Equations 11 and 21–23 form a consistent scheme for the calculation of the dilute-limit thermal conductivity. It should be noted that the above equations assume that hexane behaves like a Lennard–Jones gas. In the above scheme, the only unknowns are the Lennard–Jones parameters, σ and ε/k_B . The seven sets of thermal conductivity measurements in the dilute limit were used to optimize these two parameters. The values obtained were $\sigma/\text{nm} = 0.550$ and $(\varepsilon/k_B)/\text{K} = 590$. These values also predict the viscosity values of Vogel and Strehlow [38] within $\pm 2.5\%$, as shown in Fig. 1. This dilute-gas viscosity fit has significantly higher uncertainty than the correlation developed subsequently for hexane [15], but is optimized for an accurate correlation for the thermal conductivity based on Eq. 11. The correlation, Eqs. 11 and 21–23, for the dilute gas is shown in Fig. 4 relative to the primary data.

For ease of use, the values of the dilute-gas thermal conductivity, $\lambda_o(T)$, obtained by Eqs. 11 and 21–23, were fit, as

$$\lambda_o(T) = A_0 + A_1 \cdot (T_r) + A_2 \cdot (T_r)^2 + A_3 \cdot (T_r)^3 \quad (24)$$

Values calculated by Eq. 24, with parameters given in Table 4, do not deviate from the values calculated by Eqs. 11 and 21–23 by more than $\pm 0.1\%$ over the temperature range 180–1000 K, and hence Eq. 24 was used for the dilute-gas thermal conductivity [11].

The primary data for the thermal conductivity of hexane were fit with the ODRPACK [43] regression package to Eqs. 16–20 after subtraction of Eq. 24 for the dilute-gas contribution. This resulted in 10 optimized A_{ji} coefficients and the optimized wave number cutoff q_D^{-1} that are summarized in Table 4. The fit statistics (defined above) for each of the primary data sets are given in Table 3. Plots available in Assael et al. [11] show the deviations between the primary data and the correlation of Eqs. 10–20 for the thermal conductivity in terms of temperature and density. Figure 5 shows the behavior of the thermal conductivity correlation along isotherms as a function of density, while Fig. 6 shows the behavior of the thermal conductivity correlation along isobars as a function of temperature. The critical enhancement is visible in Figs. 5 and 6 as a sharp increase in thermal conductivity near the critical point. The thermal conductivity is divergent as the critical point is approached.

New wide-ranging correlations for the thermal conductivity of hexane were developed based on critically evaluated experimental data. The correlations are valid from the triple point to 600 K, and at pressures up to 500 MPa. The correlations are expressed in terms of temperature and density, and the densities

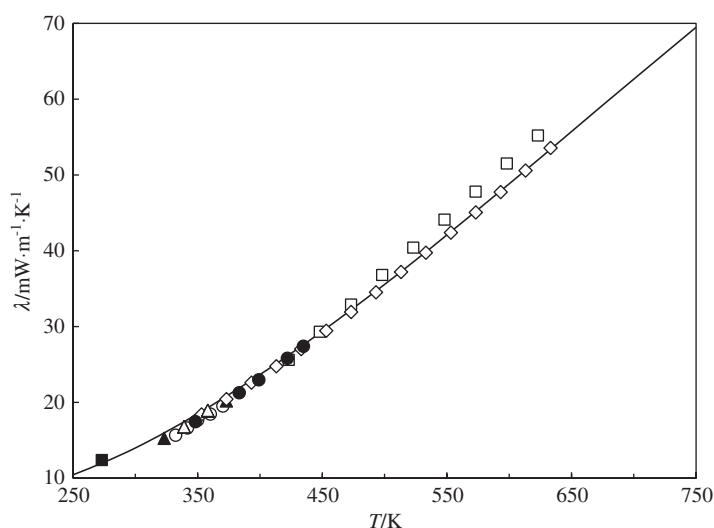


Fig. 4 Dilute-gas limit thermal conductivity as a function of temperature. \diamond , Golubev and Naziev [63]; \square , Naziev et al. [64]; \circ , Shashkov et al. [67]; \blacktriangle , Gray et al. [68]; \bullet , Vines and Bennett [69]; \triangle , Lambert et al. [70]; \blacksquare , Mann and Dickens [71]; solid line, Eq. 24.

Table 4 Coefficients of Eqs. 16–20 and 24 for the residual thermal conductivity of hexane [11].

Coefficients for A_i in Eq. 24 for the thermal conductivity of the dilute gas		
i	$A_i/\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	
0	6.6742×10^{-3}	
1	-23.7619×10^{-3}	
2	72.0155×10^{-3}	
3	-18.3714×10^{-3}	
Coefficients for B_{ji} in Eq. 16 for the residual thermal conductivity		
i	$B_{1,i}/\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$	$B_{2,i}/\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
1	$-3.014\,08 \times 10^{-2}$	$2.182\,08 \times 10^{-2}$
2	$1.679\,75 \times 10^{-1}$	$-1.008\,33 \times 10^{-1}$
3	$-1.297\,39 \times 10^{-1}$	$7.741\,80 \times 10^{-2}$
4	$3.828\,33 \times 10^{-2}$	$-2.159\,45 \times 10^{-2}$
5	$-3.702\,94 \times 10^{-3}$	$2.124\,87 \times 10^{-3}$
Fluid specific amplitudes for the critical enhancement, Eq. 20, following Perkins et al. [55]		
	$\xi_0/\text{nm} = 0.2364$	$\Gamma = 0.05803$
Cutoff wavenumber fit from primary data for the critical enhancement, Eqs. 17–19		
	$q_0^{-1}/\text{nm} = 0.737$	

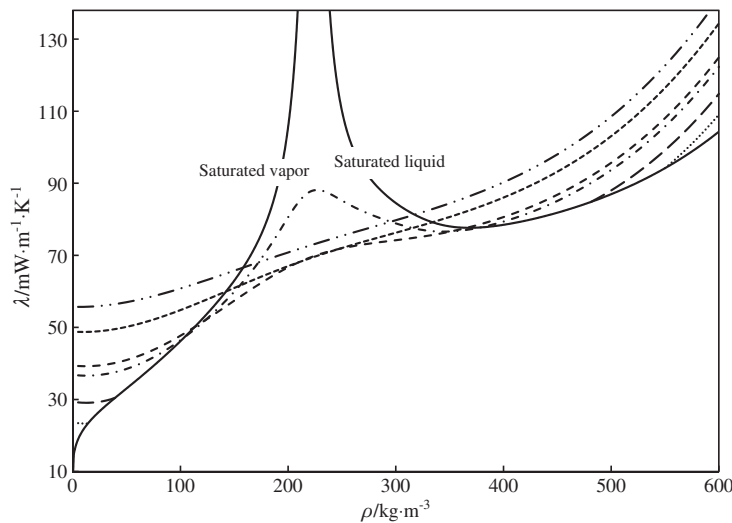


Fig. 5 Thermal conductivity calculated with Eqs. 10–20 as a function of density. A large critical enhancement is apparent near the critical density, 233.18 kg·m⁻³, for the saturated vapor and liquid, which are divergent at the critical point, and the isotherms closest to the critical temperature, 507.82 K. The isotherms are designated by the following: dotted line, 400 K; long-dashed line, 450 K; dot-dashed line, 510 K; medium-dashed line, 530 K; short-dashed line, 600 K; dot-dot-dashed line, 650 K.

were obtained from an equation of state of Span and Wagner [16]. The overall uncertainty (considered to be estimates of a combined expanded uncertainty with a coverage factor of two) of the proposed correlation is estimated, for pressures <500 MPa and temperatures <600 K, to be less than ±4.2 %. Full details of the correlation development for hexane are available in Assael et al. [11], including a table of test values to verify computer coding of the correlation.

4 Conclusions

This IUPAC project has made significant progress in developing correlation techniques that incorporate available theoretical knowledge on the viscosity and thermal conductivity of the dilute-gas, initial density

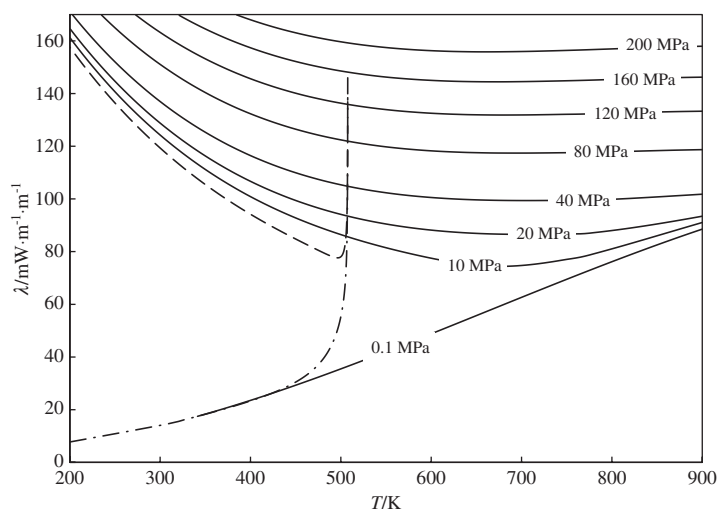


Fig. 6 Thermal conductivity of hexane calculated with Eqs. 10–20 as a function of temperature for different pressures and at saturation. Dotted line represents saturated liquid; the dot-dashed line represents saturated vapor.

dependence, hard-sphere liquids, and the critical region. This project is based on many years of work on these properties by the IUPAC Subcommittee on Transport Properties, continuing through the International Association for Transport Properties. The resulting correlations cover a wide range of temperatures, pressures, and densities. They can provide the viscosity and thermal conductivity for subcritical vapor and liquid, as well as supercritical fluid states. For hexane, considered here as the demonstration fluid, the correlations cover the temperature range from the triple point to 600 K, and are valid to pressures up to 100 MPa for viscosity and 500 MPa for thermal conductivity.

The correlation framework that is described in this paper can be applied to any pure fluid with adequate data for the viscosity and thermal conductivity provided that a suitable equation of state is available. The process begins with critical assessment of the available data sets in terms of the reliability of their measurement technique, uncertainty, and sample purity. The most reliable “primary” data sets are then fit, with the aid of a suitable equation of state, to functional forms discussed in this paper that incorporate key theoretical guidance that is available. Inclusion of theoretical guidance gives the resulting correlations much more reliable extrapolation behavior to conditions beyond the range of available data, such as very high pressures and temperatures, or very low temperatures where the low vapor pressure makes vapor measurements impossible.

The correlation framework requires an equation-of-state model that gives accurate values for the density, compressibility, and specific heat for the fluid over the range of temperatures and pressures of interest. For state points where the critical enhancement is insignificant, the correlation depends on knowledge of the density as a function of temperature and pressure – a less-severe test of an equation of state. In the critical region where the critical enhancement is significant, a very good equation of state is required, typically a multi-property Helmholtz free-energy model that has been fitted to reliable density and caloric data.

This correlation framework has already been applied to a number of industrially important fluids, including normal and para hydrogen [7], methylbenzene [8], SF_6 [9], benzene [10], hexane [11, 15], heptane [12], ethanol [13], and methanol [14], and it will be applied to additional fluids as this IUPAC project continues. This paper demonstrates application of this correlation framework to the specific example of hexane. Additional details for the resulting correlations for hexane are available in the literature for both the viscosity [15] and thermal conductivity [11]. The correlations for each fluid studied under this IUPAC project have been fully described in the literature and implemented in the National Institute of Standards and Technology (NIST) Standard Reference Database 23: REFPROP [72]. Thus, the resulting correlations are widely available to academic researchers and industry.

5 Membership of sponsoring bodies

The work described in this paper was carried out under the auspices of the International Association for Transport Properties (IATP) with partial financial support of the International Union of Pure and Applied Chemistry (IUPAC) Project 2012-040-1-100 [Reference correlations for the thermal conductivity and viscosity of fluids over extended range of conditions (vapor, liquid and supercritical region)]. Membership of the IUPAC Physical and Biophysical Chemistry Division Committee for the period 2014–2015 is as follows:

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This manuscript (PAC-REP-14-01-04) was prepared in the framework of IUPAC project 2012-040-1-100.

Acknowledgments: The authors gratefully acknowledge the guidance and valuable insight of V. Vesovic, W. A. Wakeham, J. V. Sengers, E. Vogel, R. Hellmann, and D. G. Friend.

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