

Simplified Model for the Critical Thermal-Conductivity Enhancement in Molecular Fluids

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Abstract This paper reviews the available information for the thermal-conductivity enhancement. This enhancement can be represented by a simplified solution of the mode-coupling theory of critical dynamics with two critical amplitudes and one cutoff wave number as fluid-specific parameters. Using corresponding states, these fluid-specific parameters are correlated in terms of their dependence on the acentric factor. A universal representation of the critical enhancement of the thermal conductivity for a large number of molecular fluids is presented.

Keywords Acentric factor · Correlation length · Corresponding states · Critical amplitudes · Critical dynamics · Mode-coupling theory · Thermal conductivity · Thermal diffusivity

1 Introduction

The thermal conductivity is known to exhibit a substantial increase for fluids in the vicinity of their vapor-liquid critical points. To account for this phenomenon, the total thermal conductivity λ is decomposed as the sum of an enhancement of the thermal conductivity, $\Delta_c\lambda$, caused by the presence of long-range critical fluctuations, and a background thermal conductivity, λ_b , which is the thermal conductivity to be expected in the absence of critical fluctuations [1]:

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$$\lambda = \Delta_c \lambda + \lambda_b. \quad (1)$$

The critical thermal-conductivity enhancement is significant over a substantial range of densities and temperatures around the critical point. This phenomenon is illustrated in Fig. 1, which shows the reduced ranges of density, temperature, and pressure where a critical enhancement of the thermal conductivity is observed for H₂O as an example [2]. It is seen that the enhancement is significant over the reduced density range $0.06 < \rho/\rho_c < 2.27$ and over the reduced temperature range $0.81 < T/T_c < 1.44$. The thermal conductivity exhibits an appreciable enhancement over similarly large ranges of density, temperature, and pressure in other fluids such as CO₂ [3]. Hence, this critical enhancement phenomenon is not only of scientific interest but must also be accounted for in practical applications, such as for power generation and refrigeration cycles, and should be incorporated in fluid-property packages such as REFPROP [4].

A theoretical description for the thermal-conductivity enhancement in the critical region of fluids has been developed by a number of authors [5–13]. These theoretical descriptions have been used as tools to represent experimental thermal-conductivity data for a variety of fluids. The purpose of the present paper is to assess the available information so as to obtain a general procedure for dealing with the critical thermal-conductivity enhancement in a large number of molecular fluids for practical

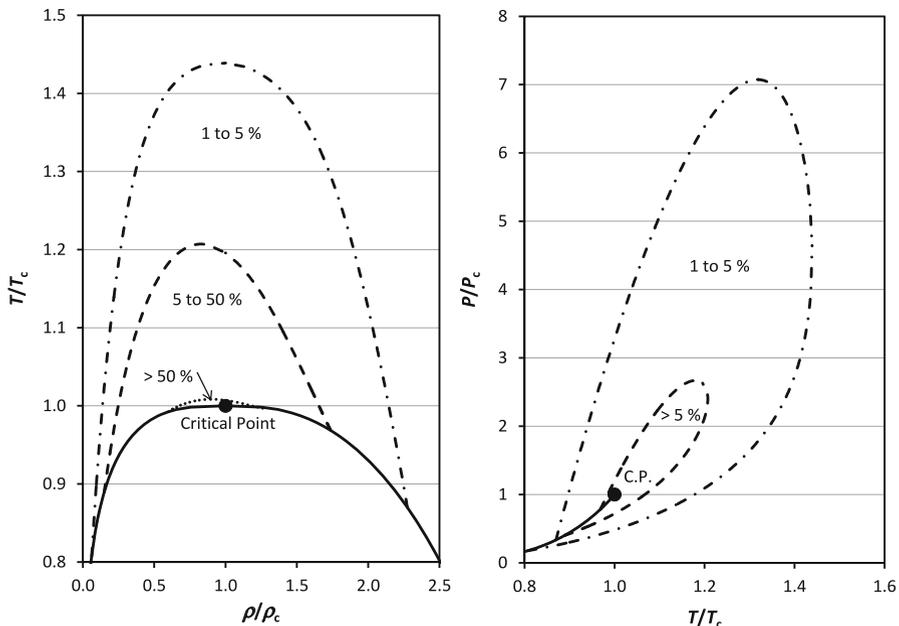


Fig. 1 Reduced ranges of density (ρ), temperature (T), and pressure (P), relative to their values ρ_c , T_c , P_c at the critical point, where the critical enhancement contribution to the thermal conductivity is larger than 1 % for H₂O [2]. The critical enhancement exceeds 50 % in the regions between dotted 50 % curves and the saturation curves (solid), while it ranges from 5 % to 50 % in the regions between the dashed 5 % curves and the dotted 50 % curves and it ranges from 1 % to 5 % in the regions between the dotted–dashed 1 % curves and the dashed 5 % curves

applications, including fluids for which only limited experimental information is available. We shall proceed as follows. In Sect. 2, we review results from the mode-coupling theory of critical dynamics for the transport properties of fluids in the critical region. Specifically, we consider a simplified solution, originally developed by Olchowy and Sengers [6], relating the thermal-conductivity enhancement to thermodynamic properties of the fluid, to a correlation length associated with the critical fluctuations, and to a fluid-specific cutoff wave number for the long-range critical fluctuations. In Sect. 3, we describe how in this solution the correlation length can be related to the isothermal compressibility of the fluid. In Sect. 4, we develop a procedure for estimating the relevant thermodynamic critical amplitudes and the length scale associated with the cutoff wave number for the critical fluctuations for a large number of molecular fluids by using an extended corresponding-states approach that includes a dependence of the critical amplitudes on the acentric factor. In Sect. 5, we then formulate a general method for representing the thermal-conductivity enhancement in a large number of molecular fluids with no adjustable parameters. In Sect. 6, we briefly compare our expression for the critical enhancement of the thermal conductivity with those proposed by other investigators. Finally, some concluding remarks are presented in Sect. 7. Our procedure can be used not only to correlate experimental thermal-conductivity data, but also to estimate the critical thermal-conductivity enhancement when limited experimental information is available.

2 Theory

The decay rate of the critical fluctuations in fluids near the vapor-liquid critical point is determined by the thermal diffusivity $D = \lambda/(\rho C_P)$, where ρ is the density and C_P is the isobaric heat capacity. In this paper, we identify ρ with the molar density and C_P with the molar isobaric heat capacity. The separation, Eq. 1, of the thermal conductivity into both critical and background contributions implies a corresponding separation of the thermal diffusivity D into a critical contribution $\Delta_c D = \Delta_c \lambda/(\rho C_P)$ and a background contribution $D_b = \lambda_b/(\rho C_P)$ [1]:

$$D = \Delta_c D + D_b. \quad (2)$$

At the critical point, both $\Delta_c D$ and D_b and, hence, D become zero, a phenomenon known as critical slowing down of the fluctuations. The background contribution D_b represents the classical contribution to the slowing down of the fluctuations in which the diffusivity would vanish in proportion to C_P^{-1} . In addition, the shear viscosity η also contains a critical enhancement contribution $\Delta_c \eta$ and a background contribution η_b :

$$\eta = \Delta_c \eta + \eta_b. \quad (3)$$

In contrast to the critical thermal-conductivity enhancement $\Delta_c \lambda$, the critical viscosity enhancement $\Delta_c \eta$ is small and restricted to a very narrow range of temperatures near the critical point [14].

The mode-coupling theory of critical dynamics [15, 16] yields a set of coupled integral equations for the critical contributions to the thermal diffusivity and the shear viscosity. Because of the long-range nature of the critical fluctuations, one needs to account for the dependence of $\Delta_c D(q)$ and $\Delta_c \eta(q)$ on the wave number q of the fluctuations. One then obtains [9]

$$\Delta_c D(q) = \frac{\Delta_c \lambda(q)}{\rho C_P(q)} = \frac{k_B T}{(2\pi)^3 \rho} \int_0^{q_D} d\mathbf{k} \left[\frac{C_P(|\mathbf{q} - \mathbf{k}|)}{C_P(q)} \right] \frac{\sin^2 \theta}{k^2 \eta(k) / \rho + |\mathbf{q} - \mathbf{k}|^2 D(|\mathbf{q} - \mathbf{k}|)}, \tag{4}$$

$$\Delta_c \eta(q) = \frac{1}{2q^2} \frac{k_B T}{(2\pi)^3} \int_0^{q_D} d\mathbf{k} C_P(k) C_P(|\mathbf{q} - \mathbf{k}|) \left[\frac{1}{C_P(k)} - \frac{1}{C_P(|\mathbf{q} - \mathbf{k}|)} \right]^2 \frac{k^2 \sin^2 \theta \sin^2 \phi}{k^2 D(k) + |\mathbf{q} - \mathbf{k}|^2 D(|\mathbf{q} - \mathbf{k}|)}, \tag{5}$$

where k_B is Boltzmann’s constant and T is the temperature, and where θ and ϕ are, respectively, the polar and azimuthal angles of the wave vector \mathbf{k} with respect to the wave vector \mathbf{q} . The integrals are to be evaluated over all magnitudes $k = |\mathbf{k}|$ up to a maximum value q_D which corresponds to a length scale separating long-range critical fluctuations, where mode-coupling theory is applicable, and short-range fluctuations. In principle, the cutoff wave number q_D could be dependent on density and temperature, but is, in practice, approximated by a constant. Note that D , η , and C_P depend only on the magnitude of the wave vector of the critical fluctuations. To deduce the critical contributions to the actual thermal diffusivity, thermal conductivity, and shear viscosity, we need the solution of Eqs. 4 and 5 in the hydrodynamic limit $q \rightarrow 0$.

Asymptotically close to the critical point, $\Delta_c D$ approaches a Stokes–Einstein law of the form,

$$\Delta_c D = \Delta_c D(0) \approx \frac{R_D k_B T}{6\pi \eta \xi}, \tag{6}$$

where ξ is a correlation length and R_D is a universal dynamic amplitude ratio [17, 18]. An asymptotic evaluation of Eq. 4 yields $R_D \simeq 1$ [15, 16]. If account is made of a small frequency dependence of the viscosity in the mode-coupling integrals, one obtains $R_D \simeq 1.03$ [19]. Slightly larger theoretical values have been reported on the basis of a dynamic renormalization approach, namely, $R_D \approx 1.038$ [20, 21] and $R_D \approx 1.065$ [13].

Asymptotically close to the critical point, the viscosity η satisfies an equation of the form [22],

$$\eta \approx \eta_b (Q\xi)^z, \tag{7}$$

where z is a universal dynamic critical exponent, and Q is a system-specific coefficient. An asymptotic evaluation of Eq. 5 yields $z = 8/(15\pi^2) = 0.054$ [9]. The currently accepted value of the dynamic critical exponent is $z \simeq 0.068$ [23, 24].

The asymptotic Stokes–Einstein law in Eq. 6 is valid only in a very small region around the critical point [9]. Thus, to obtain a realistic description of the observed critical thermal-conductivity enhancement, one needs a nonasymptotic solution of the mode-coupling equations, Eqs. 4 and 5. A comprehensive nonasymptotic solution was obtained by Olchowy, Luettmmer-Strathmann, and Sengers [5,9]. An alternative solution has been presented by Kiselev and Kulikov [10,11]. The solution of Olchowy and coworkers [5,9] has been applied to represent the critical thermal-conductivity enhancement of carbon dioxide [9,25], ethane [7,9,26], nitrogen [8], argon [27,28], methane [29], propane [30], butane [31], isobutane [32], and of some refrigerants, namely, R134a [33,34] and R152a [35]. The alternative solution of Kiselev and Kulikov has been applied to carbon dioxide, ethane, and methane [11,12,36], and also to some refrigerants [37].

The comprehensive solution of Olchowy and coworkers [5,9] is rather complicated. Hence, for practical applications, Olchowy and Sengers [6] proposed a simplified approximate solution of Eq. 4. First, it is noted that the critical enhancement of the viscosity is sufficiently small and can be neglected in practical applications [38]. Hence, we approximate $\eta(k)$ in Eq. 4 by $\eta \simeq \eta_b$ independent of the wave number k . This approximation decouples the two mode-coupling integrals, and in the limit $q \rightarrow 0$, Eq. 4 then reduces to

$$\Delta_c D = \frac{\Delta_c \lambda}{\rho C_P} \simeq \frac{R_D k_B T}{(2\pi)^3 \eta} \int_0^{q_D} d\mathbf{k} \left[\frac{C_P(k)}{C_P(0)} \right] \frac{k^{-2} \sin^2 \theta}{1 + \rho D(k)/\eta}. \quad (8)$$

In Eq. 8, we entered the universal dynamic amplitude ratio R_D so that Eq. 8 will reproduce the asymptotic behavior in Eq. 6 near the critical point. In the near-critical region, the term $\rho D(k)/\eta$ in the integrand of Eq. 8 becomes small, since the thermal diffusivity D vanishes at the critical point. Away from the critical point, its value is positive. Hence, if we neglect this term, we overestimate the integral. However, this term never becomes really large, and one may try to compensate for the overestimation by integrating up to a lower cutoff wave number $\bar{q}_D < q_D$:

$$\Delta_c D = \frac{\Delta_c \lambda}{\rho C_P} \simeq \frac{R_D k_B T}{(2\pi)^3 \eta} \int_0^{\bar{q}_D} d\mathbf{k} \left[\frac{C_P(k)}{C_P(0)} \right] \frac{\sin^2 \theta}{k^2}. \quad (9)$$

It is interesting to note that Eq. 8 is identical to the simple mode-coupling integral originally considered by Kawasaki [15] and by Ferrell [39] except for the presence of a finite upper cutoff wave number \bar{q}_D . Retention of a finite upper cutoff number is an essential and necessary feature for getting a physically realistic nonasymptotic representation for the critical thermal-conductivity enhancement. The wave-number dependence of the isobaric heat capacity C_P is related to the wave-number dependence of the isothermal susceptibility $\chi = \rho (\partial \rho / \partial P)_T$ through the thermodynamic relation,

$$C_P(k) = C_V(k) + \frac{T}{\rho^3} \left(\frac{\partial P}{\partial T} \right)_\rho^2 \chi(k) \simeq C_V + \frac{T}{\rho^3} \left(\frac{\partial P}{\partial T} \right)_\rho^2 \frac{\chi(0)}{1 + k^2 \xi^2}, \quad (10)$$

where P is the pressure and C_V is the isochoric molar heat capacity. The isochoric heat capacity C_V diverges only weakly at the critical point; thus, it depends only weakly on the wave number k , while the slope $(\partial P / \partial T)_\rho$ remains finite at the critical point. In the Ornstein-Zernike approximation, $\chi(k) = \chi(0) / (1 + k^2 \xi^2)$ [40].

Using these approximations, Olchowy and Sengers [6] arrived at a representation for the critical enhancement that can be written in the form [2],

$$\Delta_c \lambda = \rho C_P \Delta_c D \simeq \frac{\rho C_P R_D k_B T}{6\pi \eta \xi} Y(\bar{q}_D \xi). \quad (11)$$

In this equation, Y is a crossover function defined by

$$Y(y) \equiv \frac{2}{\pi} \left\{ \left[(1 - \kappa^{-1}) \arctan(y) + \kappa^{-1} y \right] - \left[1 - \exp\left(\frac{-1}{y^{-1} + y^2 \rho_c^2 / 3 \rho^2}\right) \right] \right\}, \quad (12)$$

where κ is the ratio of the isobaric and isochoric heat capacities:

$$\kappa = \frac{C_P}{C_V}. \quad (13)$$

In the limit $y = \bar{q}_D \xi \rightarrow \infty$, Eq. 11 reproduces the asymptotic critical behavior in accordance with Eq. 6. The mode-coupling integrals in Eqs. 4 and 8 do not vanish far away from the critical point, since mode coupling also accounts for the presence of the so-called long-time-tail contributions to the transport properties far away from the critical point [41, 42], which are contained in the background thermal conductivity λ_b . The second term in Eq. 12 subtracts a residual contribution so as to ensure that the critical thermal-conductivity enhancement will vanish in the limit $y = \bar{q}_D \xi \rightarrow 0$ far away from the critical point [5, 9].

We note that the expression for the critical thermal-conductivity enhancement in Eqs. 11–13 depends on the heat capacities C_P and C_V , the shear viscosity η , the correlation length ξ , and a system-specific cutoff parameter \bar{q}_D . A procedure for estimating the correlation length will be described in the subsequent section. The correlating equation for the critical thermal-conductivity enhancement requires an equation of state that yields reliable values for the compressibility and the heat capacities in the critical region. In addition, it assumes that an equation for the viscosity is available. However, information about the small critical enhancement of the viscosity is not necessary.

3 Critical Amplitudes and Correlation Length

In the theory of critical phenomena, it is convenient to express all thermodynamic properties in dimensionless form. One procedure, to be referred to as option I, is to

express the temperature T in terms of the critical temperature T_c , the density ρ in terms of the critical density ρ_c , and the chemical potential μ per mole in terms of RT_c , where R is the molar gas constant. One thus defines [43]

$$\bar{T} = \frac{T}{T_c}, \quad \bar{\rho} = \frac{\rho}{\rho_c}, \quad \bar{P} = \frac{P}{\rho_c RT_c}, \quad \bar{\mu} = \frac{\mu}{RT_c}, \quad \bar{C}_V = \frac{\rho C_V}{\rho_c R}, \quad \bar{\chi} = \frac{RT_c}{\rho_c} \chi, \tag{14}$$

where $\chi = (\partial\rho/\partial\mu)_T = \rho(\partial\rho/\partial P)_T$ is the susceptibility. Note that the proper isomorphous heat capacity in the theory of critical phenomena is not the molar heat capacity C_V , but the heat-capacity density ρC_V [44]. In addition, one defines the difference functions,

$$\Delta\bar{T} = \frac{T - T_c}{T_c}, \quad \Delta\bar{\rho} = \frac{\rho - \rho_c}{\rho_c}. \tag{15}$$

Asymptotically close to the critical point, the isochoric heat capacity and the susceptibility diverge as a function of temperature in the one-phase region ($\Delta\bar{T} \geq 0$) along the critical isochore $\rho = \rho_c$ as

$$\bar{C}_V \approx \bar{A}_0 (\Delta\bar{T})^{-\alpha}, \tag{16}$$

$$\bar{\chi} \approx \bar{\Gamma}_0 (\Delta\bar{T})^{-\gamma}. \tag{17}$$

The coexistence density $\rho = \rho_{cxc}$ on either side of the phase boundary below the critical temperature ($\Delta\bar{T} \leq 0$) depends on the temperature asymptotically close to the critical point as

$$\Delta\bar{\rho}_{cxc} \approx \pm \bar{B}_0 |\Delta\bar{T}|^\beta. \tag{18}$$

In these power laws α, β , and γ are universal critical exponents such that $\gamma = 2 - \alpha - 2\beta$. Currently accepted values are [45,46]

$$\alpha \simeq 0.110, \quad \beta \simeq 0.326, \quad \gamma \simeq 1.239. \tag{19}$$

The critical amplitudes $\bar{A}_0, \bar{B}_0, \bar{\Gamma}_0$ satisfy a universal relation [18,45,47],

$$\frac{\alpha \bar{A}_0 \bar{\Gamma}_0}{\bar{B}_0^2} = 0.058 \pm 0.001. \tag{20}$$

The asymptotic power law for the temperature dependence of the correlation length along the critical isochore in the one-phase region ($\Delta\bar{T} \geq 0$) reads [40]

$$\xi \approx \xi_0 (\Delta\bar{T})^{-\nu}, \tag{21}$$

with

$$\nu = (2 - \alpha) / 3 \simeq 0.630. \quad (22)$$

According to the principle of two-scale-factor universality [43,45,47,48],

$$\xi_0 (\alpha \bar{A}_0 N_A \rho_c)^{1/3} = 0.266 \pm 0.003, \quad (23)$$

where N_A is Avogadro's number. Equations 20 and 23 represent the currently accepted values of these universal amplitude relations [45,47]. Note that $N_A \rho_c$ is the inverse of the molecular volume, v_c , at the critical point.

An alternative procedure, often adopted in articles dealing with the thermodynamic behavior of fluids near the critical point and here referred to as option II, uses, instead of RT_c , the critical pressure P_c as a reduction parameter. One then defines [49]

$$T^* = \frac{T}{T_c}, \quad \rho^* = \frac{\rho}{\rho_c}, \quad P^* = \frac{P}{P_c}, \quad \mu^* = \mu \frac{\rho_c}{P_c}, \quad C_V^* = \rho C_V \frac{T_c}{P_c}, \quad \chi^* = \chi \frac{P_c}{\rho_c^2}. \quad (24)$$

In terms of this option, the asymptotic equations corresponding to the power laws given by Eqs. 16 and 17 are

$$C_V^* \approx A_0^* (\Delta T^*)^{-\alpha}, \quad \chi^* \approx \Gamma_0^* (\Delta T^*)^{-\gamma}, \quad (25)$$

where $\Delta T^* = \Delta \bar{T}$. The critical amplitudes are related to those in Eqs. 16 and 17 by $A_0^* = \bar{A}_0 Z_c^{-1}$, $\Gamma_0^* = \bar{\Gamma}_0 Z_c$, where $Z_c \equiv P_c / (\rho_c RT_c)$ is the value of the compressibility factor at the critical point. Although option II defined by Eq. 24 appears to be the one most frequently adopted, we prefer here to adopt option I defined by Eq. 14. The reason is that in the theory of critical phenomena, the ordering field is $\mu / (RT)$ and not $\mu \rho / P$, so that option I has a more physical foundation [50].

From Eqs. 17 and 21 we note that, asymptotically,

$$\xi = \xi_0 \left(\bar{\Gamma}_0^{-1} \bar{\chi} \right)^{\nu/\gamma}. \quad (26)$$

Equation 26 is valid only in the asymptotic critical limit on the critical isochore [44], but is used as an approximation for estimating the correlation length at all relevant densities and temperatures. Equation 26 provides an estimate for the actual correlation length that approaches a molecular scale far away from the critical point. On the other hand, ξ in Eq. 11 is to be identified with that part of the correlation length that is associated with the long-range critical fluctuations and, hence, should vanish far away from the critical point. This inconsistency is removed by subtracting from Eq. 26 a molecular-scale value implied by this equation far away from the critical point. Hence, Olchowy and Sengers [5,6] have proposed to modify Eq. 26 into

$$\xi = \xi_0 \left(\bar{\Gamma}_0^{-1} \Delta \bar{\chi} \right)^{\nu/\gamma}, \quad (27)$$

Table 1 Application of simplified Olchowy–Sengers model for critical thermal-conductivity enhancement

Fluid	R_D	\bar{T}_R	ν	γ	\bar{T}_0	ξ_0 (nm)	\bar{q}_D^{-1} (nm)
Argon [54]	1.01	2	0.63	1.2415	0.190	0.130	0.32
Nitrogen [54]	1.01	2	0.63	1.2415	0.190	0.170	0.4
Oxygen [54]	1.01	2	0.63	1.2415	0.191	0.240	0.51
Carbon dioxide [6]	1.01	2	0.63	1.2415	0.189	0.150	0.4
Carbon dioxide [25]	1.01	1.5	0.63	1.2415	0.189	0.150	0.4
Normal hydrogen [58]	1.01	1.5	0.63	1.2415	0.171	0.150	0.4
Parahydrogen [58]	1.01	1.5	0.63	1.2415	0.172	0.150	0.5
Water [2]	1.01	1.5	0.63	1.239	0.262	0.130	0.4
Methane [6]	1.01	2	0.63	1.2415	0.213	0.180	0.38
Ethane [6]	1.01	2	0.63	1.2415	0.201	0.190	0.29
Ethane [51]	1.01	2	0.63	1.242	0.201	0.190	0.545
Propane [30]	1.03	1.5	0.63	1.239	0.179	0.194	0.717
Butane [31]	1.03	1.5	0.63	1.239	0.181	0.194	0.875
Isobutane [32]	1.03	1.5	0.63	1.239	0.180	0.194	0.658
<i>n</i> -Octane [55]	1.03	1.5	0.63	1.239	0.193	0.194	0.686
<i>n</i> -Nonane [55]	1.03	1.5	0.63	1.239	0.195	0.194	1.04
<i>n</i> -Decane [55]	1.03	1.5	0.63	1.239	0.199	0.194	0.709
R125 [56]	1.03	1.5	0.63	1.239	0.185	0.194	0.5835
R134a [52]	1.03	2	0.63	1.239	0.191	0.194	0.529
R125 [53]	1.03	1.5	0.63	1.239	0.185	0.194	0.748
Methylcyclohexane [57]	1.03	1.5	0.63	1.2415	0.193	0.150	0.624
Sulfur hexafluoride [59]	1.01	1.5	0.63	1.2415	0.187	0.190	0.35
Toluene [60]	1.02	1.5	0.63	1.239	0.189	0.220	0.62

where

$$\Delta\bar{\chi} = \bar{\chi}(\bar{T}, \bar{\rho}) - \bar{\chi}(\bar{T}_R, \bar{\rho}) \left(\frac{\bar{T}_R}{\bar{T}} \right), \quad (28)$$

with the additional condition that ξ should be set equal to zero when $\Delta\bar{\chi} \leq 0$. In Eq. 28 \bar{T}_R corresponds to a reference temperature where the critical thermal-conductivity enhancement will be negligibly small. In practice, values for \bar{T}_R varying from 1.5 to 2.5 have been used.

Equations 11 and 27 completely specify the simplified Olchowy–Sengers model for the critical thermal-conductivity enhancement. This simplified model has been used to represent the thermal conductivity of many fluids, as shown in Table 1 [2, 6, 25, 30–32, 51–60]. In Table 1, we have listed the values used for the dynamic amplitude ratio R_D , the reference temperature ratio \bar{T}_R , the inverse cutoff wave number \bar{q}_D^{-1} , the critical exponents ν and γ , the susceptibility amplitude \bar{T}_0 (converted from Γ_0^*), and the correlation-length amplitude ξ_0 . The critical exponents ν and γ and the dynamic

amplitudes ratio R_D should be universal. We also expect that one should be able to assign in practice the same value for the reference-temperature ratio \bar{T}_R . On the other hand, the critical amplitudes ξ_0 and \bar{T}_0 , and also the cutoff wave number \bar{q}_D^{-1} , are fluid-specific parameters. However, accurate information for the critical amplitudes is not available for all fluids, and estimates have been made. In addition, the cutoff parameter \bar{q}_D^{-1} is commonly determined from a fit of Eq. 11 to experimental thermal-conductivity data. The question arises whether we can develop a procedure for obtaining consistent values for these fluid-specific parameters. For this purpose, we consider a generalized corresponding-states approach including a dependence on the acentric factor often used in correlating thermodynamic properties of fluids [61].

4 A Generalized Corresponding-States Approach

In Table 2, we present a survey of the critical amplitudes that we have deduced from a review of the literature [11, 28, 29, 34, 35, 62–94]. The values for the critical amplitudes in the literature have either been determined from an asymptotic analysis of experimental data [49, 63, 65–67, 70–72, 74, 82, 86, 87] or from a fit to experimental heat capacity and P - ρ - T data in terms of a crossover equation of state [28, 29, 35, 62, 64, 68, 69, 73, 75–81, 83–85, 88–94]. The critical amplitudes found in Refs. [75, 85] for methane and ethane are very different from those found in Refs. [49, 77, 80, 81] and have been discarded. In some cases, we found that the value for the heat-capacity amplitude strongly depends on the temperature range used in fitting the asymptotic power law. In the case of n -pentane and n -hexane, we reinterpreted the information in Refs. [86, 90] by determining an effective value for A_0 as a function of ΔT and extrapolating these values to $\Delta T \rightarrow 0$. In the case of toluene, there is a large discrepancy between the amplitudes in Refs. [83, 85]; we adopted the heat-capacity amplitude from a fit to a crossover equation [83] and determined \bar{B}_0 from a re-analysis of coexistence-curve data [85]. We used a similar procedure for deducing \bar{A}_0 and \bar{B}_0 for n -hexane from Ref. [88].

The values for \bar{A}_0 , \bar{B}_0 , and \bar{T}_0 for the fluids listed in Table 2 are plotted as a function of the acentric factor ω in Figs. 2, 3, and 4, respectively. The acentric factor is defined in terms of the vapor pressure of the liquid at a reduced temperature $\bar{T} = 0.7$ and is nearly zero for monatomic gases, such as argon [95]. The acentric factor ranges from negative values for monatomic gases to larger positive values for large polyatomic and polar molecules. For this purpose we used the values for the acentric factor ω provided by the REFPROP package [4], with some additional values from the book of Reid et al. [95]. The critical amplitudes depend not only on the values adopted for the critical exponents in the analysis, but also on the temperature range of the analysis and how an account has been made for the presence of nonasymptotic corrections to the asymptotic power laws. Hence, the uncertainty in the values reported for critical exponents cannot be assessed from standard deviations of least-squares fits to experimental data. From the spread in reported critical-amplitude values in the literature that were obtained by different authors for the same fluids, it appears that the uncertainties may be of the order of 15 % for \bar{A}_0 , 10 % for \bar{B}_0 , and 20 % for \bar{T}_0 . In view of these considerations, we submit that a linear dependence of the critical amplitudes, \bar{A}_0 and \bar{B}_0 , on the acentric

Table 2 Critical amplitudes for a number of fluids

Fluid	T_c (K)	ρ_c (kmol · m ⁻³)	P_c (MPa)	\bar{A}_0	\bar{B}_0	$\bar{\Gamma}_0$	ξ_0 (nm)	Refs.
³ He	3.310	13.7	0.114	1.09	1.07	0.50	0.26	[62]
Ne	44.48	24.0	2.720	5.86	1.42	0.18	0.13	[49,63]
Ar	150.73	13.4	4.865	5.28	1.42	0.20	0.14	[49]
Ar	150.66	13.4	4.860	5.02	1.50	0.21	0.16	[28]
Ar	150.69	13.4	4.863	5.31	1.48	0.19		[64]
Ar	150.69	13.4	4.863	5.18				[65]
Kr	209.29	10.8	5.493	5.30	1.42	0.20	0.17	[49]
Xe	289.73	8.50	5.840	5.13	1.42	0.20	0.19	[49,66,67]
HD	35.96	15.9	1.484	4.55	1.28	0.18	0.16	[49]
N ₂	126.21	11.2	3.398	6.82	1.48	0.16	0.15	[49,63]
H ₂ O	647.10	17.9	22.064	7.25	1.97	0.25	0.13	[68,69]
H ₂ O	647.10	17.7	22.064	7.64	1.95	0.25	0.13	[70]
D ₂ O	643.85	17.8	21.671	7.20	1.97	0.25	0.13	[68,69]
D ₂ O	643.85	17.8	21.671	7.97	2.02	0.27	0.13	[70]
CO ₂	304.11	10.6	7.372	7.62	1.68	0.22	0.15	[71]
CO ₂	304.13	10.6	7.372	7.95	1.64	0.18	0.15	[72]
CO ₂	304.14	10.6	7.377	7.37	1.71	0.20	0.15	[11]
SF ₆	318.72	5.08	3.755	8.34	1.71	0.18	0.19	[73,74]
NH ₃	405.04	13.7	11.277	6.61	1.82	0.26		[75]
NH ₃	405.37	13.8	11.336	7.56	1.77	0.22	0.14	[76]
CH ₄	190.56	10.1	4.599	4.92	1.46	0.22	0.18	[29,77]
C ₂ H ₄	282.35	7.63	5.040	5.88	1.55	0.21	0.18	[49,78]
C ₂ H ₄	282.35	7.64	5.042	5.98	1.59	0.20		[79]
C ₂ H ₆	305.32	6.87	4.872	6.24	1.60	0.19	0.19	[80]
C ₂ H ₆	305.32	6.87	4.872	5.81	1.57	0.22		[77]
C ₂ H ₆	305.32	6.87	4.872	6.17	1.60	0.20		[81]
C ₂ H ₆	305.32	6.87	4.872	6.09				[82]
C ₃ H ₈	369.85	5.00	4.248	6.84	1.67	0.21		[75]
C ₇ H ₈	591.89	2.91	4.126	8.79	1.83	0.20		[83,84]
<i>n</i> -C ₄ H ₁₀	425.16	3.93	3.796	6.40	1.67	0.21		[85]
<i>i</i> -C ₄ H ₁₀	407.84	3.89	3.629	7.02	1.64	0.20	0.22	[49]
<i>n</i> -C ₅ H ₁₂	469.70	3.22	3.370	9.02	1.90			[86]
<i>n</i> -C ₅ H ₁₂	469.62	3.20	3.372	9.88	1.78			[87]
<i>n</i> -C ₆ H ₁₄	507.79	2.69	3.088	9.27	1.81	0.18		[88]
<i>n</i> -C ₆ H ₁₄	507.20	2.71	3.028	8.71	1.69	0.16		[89]
<i>n</i> -C ₇ H ₁₆	539.86	2.32	2.727	8.20	1.85			[90]
R134a	374.27	5.05	4.065	8.00	1.70	0.19	0.19	[34,91,92]
R134a	374.27	5.05	4.065	8.21	1.81	0.20		[93]
R152a	386.41	5.57	4.520	7.85	1.69	0.19	0.19	[35,94]
R32	351.35	8.21	5.795	7.02	1.82	0.24		[93]

factor yields a reasonable estimate for these critical amplitudes of molecular fluids. The critical amplitudes reported for ^3He [62] have not been included in these figures, since they appear to be affected by quantum effects and cannot be expected to obey the proposed correlation. The amplitudes, \bar{A}_0 and \bar{B}_0 , are directly related to experimental heat-capacity and coexistence-curve data, and we prefer to use these amplitudes as our primary information for developing a practical correlation:

$$\bar{A}_0 = 5.58 + 7.94\omega, \quad (29)$$

$$\bar{B}_0 = 1.45 + 1.21\omega. \quad (30)$$

The relative standard deviations between the data and the fits of Eqs. 29 and 30 are 10 % and 3.5 % respectively, which is comparable to the estimated uncertainties in the critical-amplitude values themselves. The susceptibility amplitude \bar{T}_0 can then be calculated in accordance with Eq. 20:

$$\bar{T}_0 = \frac{0.058\bar{B}_0^2}{\alpha\bar{A}_0}. \quad (31)$$

Gerasimov has proposed a correlation for the thermodynamic properties of *n*-alkanes and some aromatic hydrocarbons in the critical region also in terms of the acentric factor [96]. Rather than considering the critical amplitudes directly, Gerasimov introduced a linear dependence on the acentric factor of the fluid-specific coefficients in the crossover model developed by Chen et al. [97]. From this correlation, one can readily calculate the critical amplitudes A_0^* , $B_0^* = \bar{B}_0$, and Γ_0^* . We have converted A_0^* and Γ_0^* to the values for \bar{A}_0 and \bar{T}_0 by using a linear fit of Z_c of the fluids given in Table 2 in terms of the acentric factor ω :

$$Z_c = 0.2925 - 0.1222\omega. \quad (32)$$

The values for the critical amplitudes resulting from the correlation of Gerasimov are represented by dashed curves in Figs. 2 and 3. From Figs. 2 and 3, we see that both correlations are consistent with the available information, except that our correlation also includes fluids with a negative acentric factor.

The amplitude \bar{T}_0 is more difficult to determine than the amplitudes \bar{A}_0 and \bar{B}_0 , since it has to be deduced from differentiation of the P - ρ - T surface. As can be seen from Fig. 4, there is a considerable spread among the values of \bar{T}_0 from the literature. The values for \bar{T}_0 estimated from Eqs. 29–31 are represented by the solid curve in Fig. 4. Values for \bar{T}_0 estimated from the correlation of Gerasimov [96] are represented by the dashed curve in Fig. 4. The slope of the correlation of Gerasimov [96] disagrees with both the data and the present correlation since it includes helium (not shown in Fig. 4), which we excluded from our analysis due to large quantum effects. The amplitude \bar{T}_0 shows very little dependence on the acentric factor, as can also be seen from the values listed in Table 1. While Eqs. 29–31 are used in this paper,

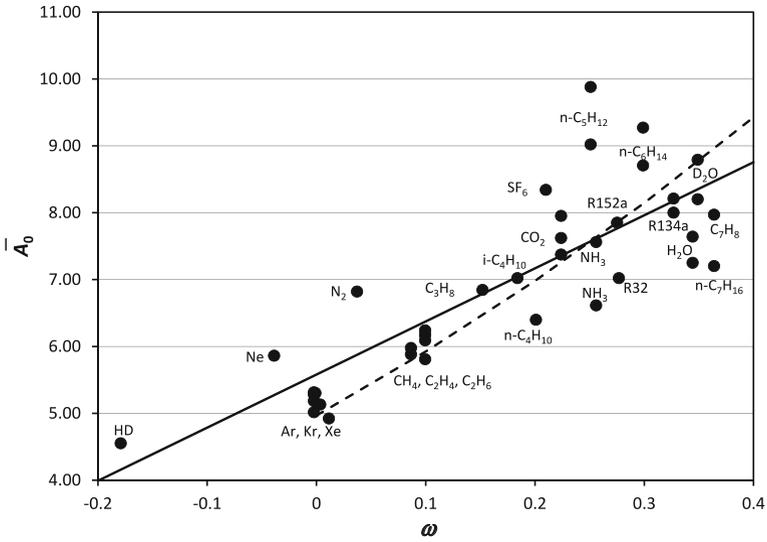


Fig. 2 Heat-capacity amplitude \bar{A}_0 as a function of the acentric factor ω . The *symbols* indicate values deduced from the literature in Table 2. The *solid line* represents values calculated from the correlating Eq. 29. The *dashed curve* represents values calculated from the correlation of Gerasimov [96]

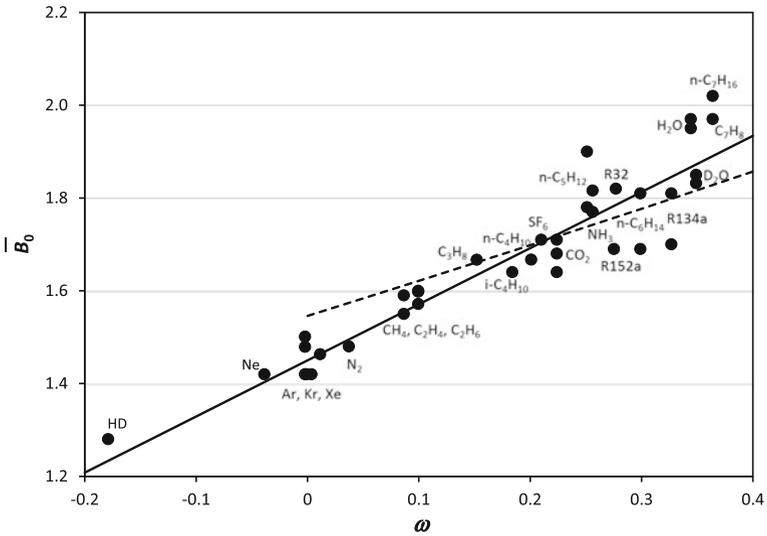


Fig. 3 Coexistence-curve amplitude \bar{B}_0 as a function of the acentric factor ω . The *symbols* indicate values deduced from the literature in Table 2. The *solid line* represents values calculated from the correlating Eq. 30. The *dashed curve* represents values calculated from the correlation of Gerasimov [96]

a reasonable alternative would be to identify \bar{T}_0 with its average value (with a two standard-deviation uncertainty) of

$$\bar{T}_0 \simeq 0.206 \pm 0.051. \tag{33}$$

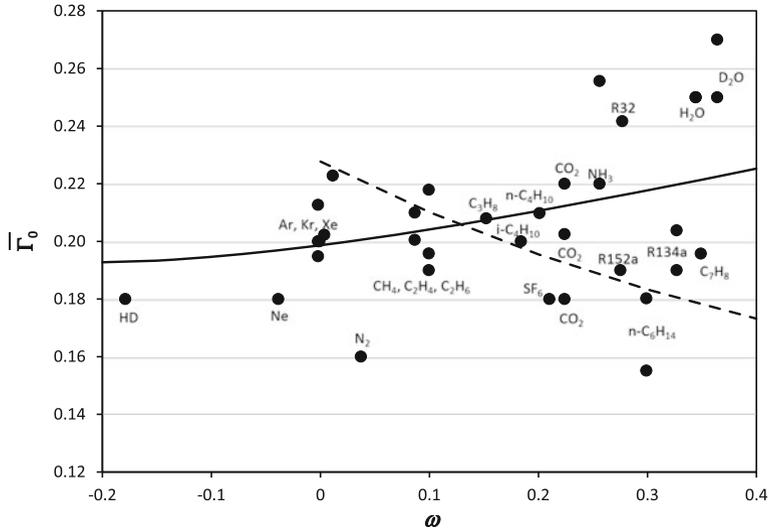


Fig. 4 Susceptibility amplitude $\bar{\Gamma}_0$ as a function of the acentric factor ω . The symbols indicate values deduced from the literature in Table 2. The solid curve represents values calculated from the correlating Eq. 31. The dashed curve represents values calculated from the correlation of Gerasimov [96]

Having obtained a correlation, Eq. 29, for the heat-capacity amplitude \bar{A}_0 , we can now estimate the correlation-length amplitude ξ_0 from Eq. 23:

$$\xi_0 = 0.266 \left(\frac{v_c}{\alpha \bar{A}_0} \right)^{1/3}, \tag{34}$$

where $v_c = (N_A \rho_c)^{-1}$ is the molecular volume at the critical point. A comparison with the correlation-length amplitudes estimated from Eq. 34 with the experimentally derived correlation-length amplitudes listed in Table 2 is shown in Fig. 5. It is seen that Eq. 34 provides good estimates for the correlation-length amplitude. We note that ξ_0 depends not only on $v_c^{1/3}$, but also on the acentric factor ω through Eq. 23 for \bar{A}_0 .

In order to represent the critical thermal-conductivity enhancement, we also need an estimate for the cutoff parameter \bar{q}_D in Eq. 11. In Fig. 6, we show the values for \bar{q}_D^{-1} listed in Table 1 as a function of the cube root of the critical volume, $v_c^{1/3}$. The actual values for \bar{q}_D^{-1} are somewhat sensitive to the equation adopted for the background thermal conductivity λ_b . We conclude that \bar{q}_D^{-1} correlates with the cube root of the critical volume, $v_c^{1/3}$, within the accuracy with which this cutoff parameter can be determined:

$$\bar{q}_D^{-1} = -0.0240 + 0.863 v_c^{1/3}, \tag{35}$$

with both \bar{q}_D^{-1} and $v_c^{1/3}$ expressed in nanometers.

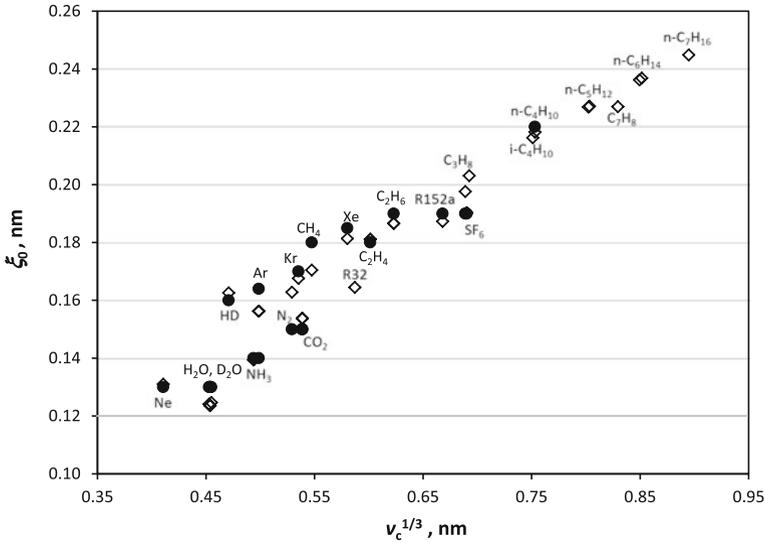


Fig. 5 Correlation-length amplitude ξ_0 as a function of the cubic root of the molecular volume v_c . The closed symbols indicate the values deduced from the literature in Table 2. The open symbols indicate values calculated from the correlating Eq. 34. Note that ξ_0 depends not only on $v_c^{1/3}$ but also on the acentric factor through \bar{A}_0 in Eq. 34

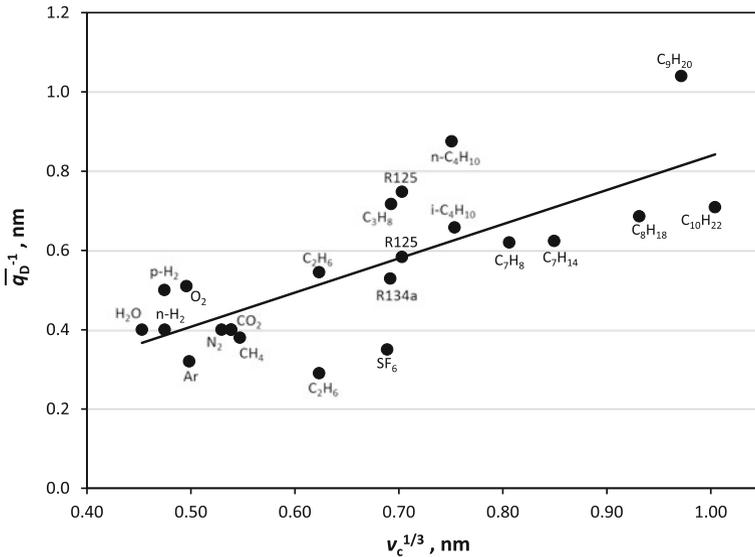


Fig. 6 Cutoff parameter \bar{q}_D^{-1} as a function of $v_c^{1/3}$. The symbols indicate the values of \bar{q}_D^{-1} from Table 1. The solid curve represents values calculated from the correlating Eq. 35

5 Universal Representation of the Critical Thermal-Conductivity Enhancement

From the information provided in the previous sections, we conclude that for practical applications the critical thermal-conductivity enhancement $\Delta_c\lambda$ can be represented by Eq. 11 with the following recommended universal parameters:

$$R_D = 1.02, \quad \bar{T}_R = 1.5, \quad \nu = 0.630, \quad \gamma = 1.239, \quad (36)$$

with $\alpha = 2 - 3\nu = 0.110$ in accordance with Eq. 22. The susceptibility amplitude \bar{T}_0 is to be calculated from Eq. 31 with the amplitudes \bar{A}_0 and \bar{B}_0 given by Eqs. 29 and 30, or one can use the value given by Eq. 33 as an estimate. The correlation-length amplitude ξ_0 is to be calculated from Eq. 34 with the amplitude \bar{A}_0 again to be calculated from Eq. 29. Finally, the cutoff parameter \bar{q}_D^{-1} is to be calculated from Eq. 35. This procedure yields a practical representation of the thermal-conductivity enhancement without any adjustable parameters and enables one to calculate $\Delta_c\lambda$ from a fundamental equation for the thermodynamic properties, provided that equations for the background viscosity and background thermal conductivity are available. We show in Figs. 7–9 the thermal conductivity calculated with this procedure relative to data for H₂O [98], R125 [56], and isobutane [99] in the critical region, as examples. As mentioned earlier, the actual values of the cutoff parameter \bar{q}_D^{-1} are somewhat sensitive to the equation adopted for the background thermal conductivity λ_b . For this reason, the cutoff parameter \bar{q}_D^{-1} is often determined by simultaneously optimizing the equation for the critical enhancement $\Delta_c\lambda$ and an equation for the background thermal conductivity λ_b . In applying the theory for fluids where adequate experimental information for the thermal conductivity in the critical region is available, one could continue to fit for an effective \bar{q}_D^{-1} . However, we expect that such a fit will hardly be necessary. Instead, one could use the universal representation for $\Delta_c\lambda$, and just develop an equation for the background thermal conductivity λ_b . Moreover, in the absence of experimental thermal-conductivity data in the critical region, the proposed universal representation will yield a realistic estimate for the magnitude of the critical thermal-conductivity enhancement as a function of temperature and density.

6 Comparison with Work of Other Investigators

As can be seen from Eqs. 6 and 11, asymptotically close to the critical point, the critical thermal-conductivity enhancement becomes

$$\Delta_c\lambda \approx \frac{\rho c_P R_D k_B T}{6\pi\eta\xi}. \quad (37)$$

The expressions proposed for $\Delta_c\lambda$ by Olchow, Luettemer-Strathmann, and Sengers in Refs. [5, 9] and the one by Kiselev and Kulikov [10, 11] all incorporate the asymptotic Stokes–Einstein limit, given by Eq. 37, but they contain more comprehensive expressions for the crossover function $Y(\bar{q}_D\xi)$ in Eq. 11. The solution of the mode-coupling

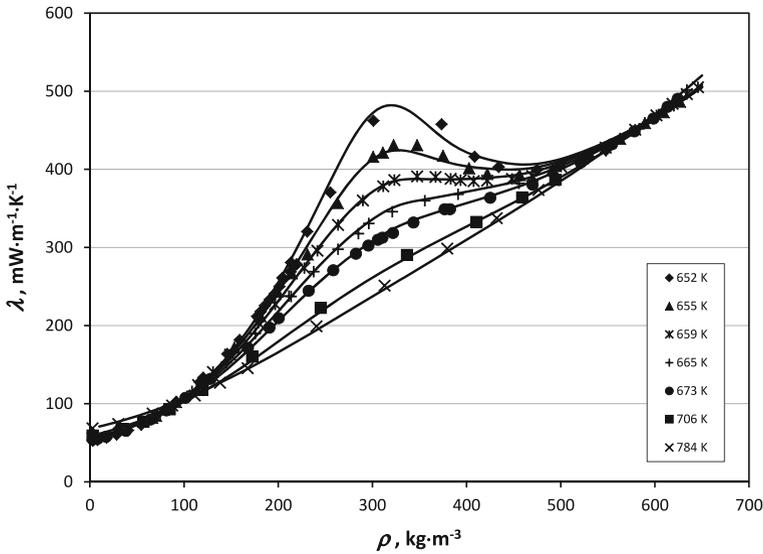


Fig. 7 Thermal conductivity of H₂O in the critical region. The *symbols* indicate experimental thermal-conductivity data reported by Tufeu and LeNeindre [98]. The *curves* represent values calculated with the universal representation for $\Delta_c\lambda$ and with an equation for the background thermal conductivity λ_b developed by Huber et al. [2]

Eqs. 4 and 5 obtained by Olchowy and coworkers in [5,9] has the form,

$$Y(y) = \frac{2}{\pi} (1 - \kappa^{-1}) \arctan(y) + \dots, \tag{38}$$

so that the first correction to the asymptotic Stokes–Einstein limit is identical to the one in Eq. 12. However, it contains many additional terms, which we have approximated by $(2/\pi)\kappa^{-1}y$. The expression adopted for the subtracted term in Eq. 12 for $Y(y)$ is a simplified version of the ones adopted in [5] and [9]. As we have done in the present paper, Kiselev and Kulikov [10,11] also decouple Eq. 4 from Eq. 5 by neglecting any wave-number dependence of the viscosity η . However, they retain an approximate expression for the k -dependent thermal diffusivity in the denominator in the integrand of Eq. 8. Thus our crossover equation, given by Eq. 12, is actually an approximation to the more comprehensive solutions of both Olchowy and coworkers [5,9] and of Kiselev and Kulikov [10,11], except that Kiselev and Kulikov assume that κ^{-1} in Eq. 12 is negligibly small.

A very simple practical empirical estimate for the critical thermal-conductivity enhancement has been proposed by Mathias et al. [100]:

$$\Delta_c\lambda = a \left(\frac{RT}{\rho} \chi \right)^b, \tag{39}$$

where a and b are two fluid-specific parameters to be determined from a fit to experimental thermal-conductivity data. Hence, in this approximation, $\Delta_c\lambda$ will diverge

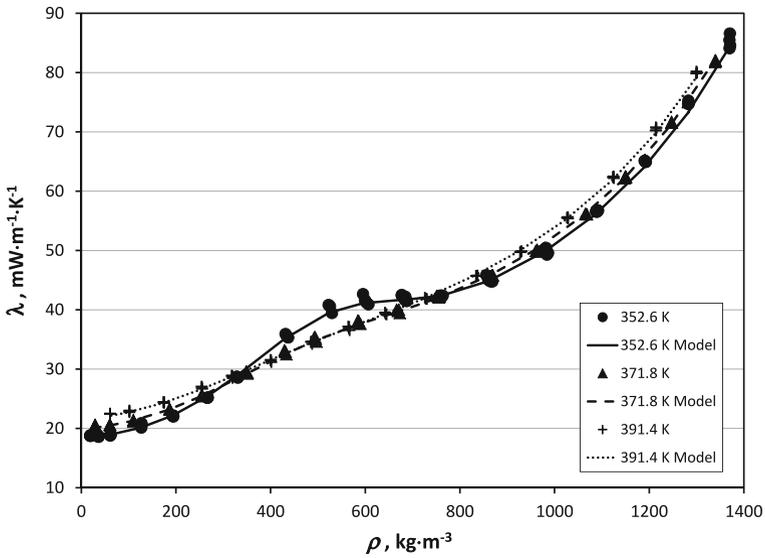


Fig. 8 Thermal conductivity of R125 in the critical region. The *symbols* indicate experimental thermal-conductivity data reported by Perkins and Huber [56]. The *curves* represent values calculated with the universal representation for $\Delta_c\lambda$ and with an equation for the background thermal conductivity λ_b adopted by Perkins and Huber [56]

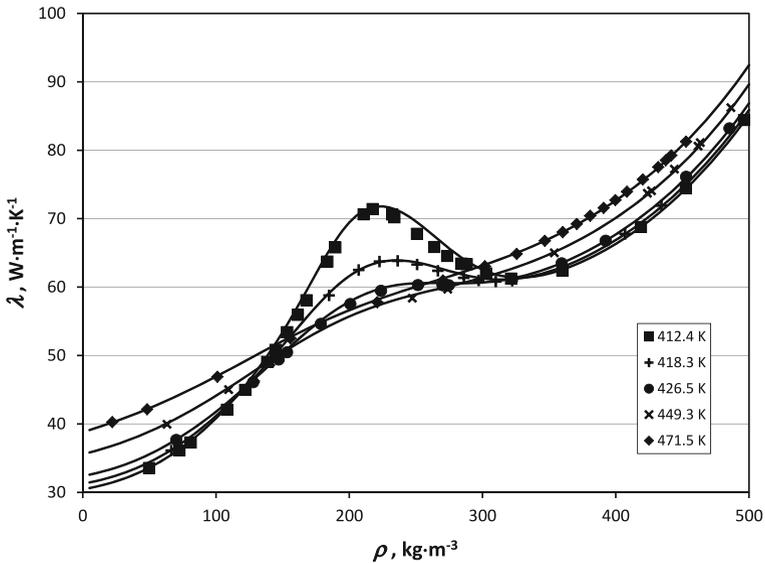


Fig. 9 Thermal conductivity of isobutane in the critical region. The *symbols* indicate experimental thermal-conductivity data reported by Nieuwoudt et al. [99]. The *curves* represent values calculated with the universal representation for $\Delta_c\lambda$ and with an equation for the background thermal conductivity λ_b adopted by Perkins [32]

asymptotically as χ^b . It is interesting to compare this asymptotic behavior with the asymptotic behavior of Eq. 37 predicted by the mode-coupling theory of critical dynamics. From Eq. 10 we see that $\rho C_P = \rho C_P(0)$ will diverge as χ , while the correlation length ξ according to Eq. 27 will diverge as $\chi^{v/\gamma}$. If we approximate the viscosity η by the non-divergent background viscosity, as we have done in the present paper, we conclude from Eq. 37 that $\Delta_c \lambda$ should diverge as $\chi^{1-v/\gamma}$. Hence, in principle, the exponent b in Eq. 39 should not be a fluid-specific parameter, but should have the universal value,

$$b = 1 - v/\gamma \simeq 0.49. \quad (40)$$

The fluid-specific values found by Mathias et al. [100] for b differ significantly from this universal value. In this connection, we note that Mathias et al. [100] use a Peng-Robinson equation of state to estimate the susceptibility. We have found that use of a Peng-Robinson equation of state is not consistent with the more theoretically based Eq. 11 for the critical enhancement due to incorrect behavior of both the susceptibility and heat capacity in the critical region. Equation 39 does not vanish far away from the critical point, but this minor deficiency could be remedied by subtracting a term from χ similar to Eq. 27.

7 Discussion

We have confirmed that the crossover model given by Eq. 11, together with Eqs. 12, 13, and 36, yields a good practical representation of the critical enhancement of the thermal conductivity of many fluids. Use of this equation requires an equation of state for the thermodynamic properties and an equation for the viscosity of the fluid. The equation of state must provide reasonable values for the compressibility and specific-heat capacities of the fluid in the critical region. Systematic errors in the fluid compressibility and specific heat from an equation of state will translate to systematic errors in the critical enhancement of the thermal conductivity. In this regard, we recommend that cubic equations of state, such as the Peng-Robinson equation, not be used with this model in the critical region. In addition, the representation requires two fluid-specific critical amplitudes and one fluid-specific cutoff wave number \bar{q}_D . When reliable values for the critical amplitudes are not available, they can be estimated by the procedure described in Sect. 4. When experimental thermal-conductivity data are available in the critical region, the cutoff wave number \bar{q}_D can, in principle, be determined from a fit to the crossover model. However, in practice, it can be equally well estimated from Eq. 35. Hence, the procedure described in this paper can be used to obtain quantitative estimates for the critical enhancement of the thermal conductivity of many molecular fluids, even in the absence of experimental thermal-conductivity data in the critical region. An assessment of an extension of the theory to describe the critical enhancement of the thermal conductivity in fluid mixtures [11, 101] will require additional research.

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