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Thermal Diffusivity of H_2O Near the Critical Point

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Abstract The asymptotic critical behavior of the thermal diffusivity of H_2O, deduced from dynamic light-scattering measurements, is shown to be in good agreement with the mode-coupling theory for critical dynamics in fluids. Consistency of the thermal-diffusivity measurements with the critical enhancement of the viscosity of H_2O is also demonstrated.

Keywords Critical phenomena · H_2O · Light scattering · Steam ·
Thermal conductivity · Thermal diffusivity · Viscosity · Water

1 Introduction

One of the goals of the International Association for the Properties of Water and Steam (IAWPS) is to recommend state-of-the-art procedures for calculating thermodynamic and transport properties of H_2O over a large range of temperatures and pressures. The recommended procedure for calculating the thermodynamic properties of H_2O is

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provided by the IAPWS Formulation for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use adopted in 1996 (IAPWS-95) [1–3]. Subsequently, IAPWS has embarked on a research effort, in collaboration with the International Association for Transport Properties (IATP), to develop new formulations for the transport properties of H_2O. As part of this effort, it became necessary to re-evaluate the divergent behavior of the transport properties near the critical point. An evaluation of the critical behavior of the viscosity of H_2O has been presented in a previous publication [4]. The resulting updated equation for the critical enhancement of the viscosity has been incorporated in the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance [5,6]. The present article is concerned with an evaluation of the asymptotic critical behavior of the thermal diffusivity, which is related to the divergent critical behavior of thermal conductivity. Reliable thermal-diffusivity data are available much closer to the critical point than are reliable thermal-conductivity data for H_2O, so it is important to demonstrate that they can be represented by theory with thermodynamic properties and viscosity calculated from the current IAPWS formulations [1–6].

2 Theory

For a theoretical description of the behavior of the thermodynamic and transport properties near the critical point, it is convenient to make the temperature T, the density ρ, and the pressure p dimensionless with the aid of their values T_c, ρ_c, p_c at the critical point:

$$\overline{T} = T/T_c, \quad \overline{\rho} = \rho/\rho_c, \quad \overline{p} = p/p_c. \tag{1}$$

2.1 Critical Fluctuations and Thermodynamics

In the vicinity of a critical point, fluids exhibit large fluctuations in the order parameter associated with the phase transition. For fluids near the vapor–liquid critical point, the order parameter can be asymptotically identified with the density, and the corresponding ordering field with the chemical potential. These fluctuations cause singular behavior of the thermodynamic and transport properties near the critical point. Asymptotically close to the critical point, this singular behavior can be characterized by power laws with universal critical exponents [7].

A susceptibility χ associated with the critical phase transition is defined as the derivative of the order parameter with respect to the ordering field. For fluids near the vapor–liquid critical point, this susceptibility is related to the isothermal compressibility such that in terms of dimensionless variables, $\overline{\chi} = \overline{\rho}(\partial\overline{\rho}/\partial\overline{p})_{\overline{T}}$ [8]. The spatial extent of the fluctuations is characterized by a correlation length ξ [9]. Along the critical isochore $\overline{\rho} = 1$ at $\overline{T} \geq 1$, the correlation length ξ and the susceptibility $\overline{\chi}$ diverge as a function of $t = (\overline{T} - 1)/\overline{T}$ according to power laws of the form

$$\xi \approx \xi_0 t^{-\nu} \quad \text{and} \quad \overline{\chi} \approx \Gamma_0 t^{-\gamma}, \tag{2}$$

where ξ_0 and Γ_0 are system-dependent amplitudes and ν and γ are universal critical exponents. In this article, we use the symbol $\approx$ to designate equality asymptotically close to the critical point. Fluids belong to the universality class of Ising-like systems for which [7,10]

$$\nu \simeq 0.630 \quad \text{and} \quad \gamma \simeq 1.239. \tag{3}$$

2.2 Viscosity

The shear viscosity μ is predicted to diverge asymptotically [11,12] as

$$\mu \approx \mu_b (Q_0 \xi)^{x_\mu}, \tag{4}$$

where Q_0 is a system-dependent wave number, while x_μ is a universal dynamic critical exponent, for which we have adopted the most recent theoretical value [13],

$$x_\mu \simeq 0.068. \tag{5}$$

In Eq. 4, μ_b is a so-called background viscosity, i.e., the viscosity in the absence of any critical fluctuations.

Because of the small value of the exponent x_μ, the critical enhancement of the viscosity is weak, and nonasymptotic contributions may appear rather close to the critical temperature [14]. This problem has been solved by generalizing Eq. 4 into a more complete nonasymptotic equation of the form [15],

$$\mu = \mu_b \exp(x_\mu Y). \tag{6}$$

In this equation,

$$Y = Y\,(q_C \xi, q_D \xi) \tag{7}$$

is a crossover function, in terms of two system-dependent wave numbers q_C and q_D, whose explicit mathematical expression is available elsewhere [4–6]. The function Y has the properties such that in the limit $\xi \to \infty$, Eq. 6 reduces to Eq. 4, while in the limit $\xi \to 0$, the function Y vanishes, so that sufficiently far away from the critical point, Eq. 6 reduces to $\mu = \mu_b$ [4–6,15].

2.3 Thermal Conductivity and Thermal Diffusivity

The thermal conductivity λ is decomposed as the sum of an enhancement of thermal-conductivity $\Delta_c\lambda$ due to the presence of critical fluctuations and a background thermal conductivity λ_b that is the thermal conductivity to be expected in the absence of critical fluctuations [16]:

$$\lambda = \Delta_c\lambda + \lambda_b. \tag{8}$$

This decomposition was originally suggested from an analysis of experimental thermal-conductivity data [17], and corresponds to a separation of the transport properties into a singular part and a bare part in the mode-coupling theory of critical dynamics [18,19]. There are two major differences between the critical enhancement of the viscosity and the critical enhancement of the thermal conductivity. First, the critical viscosity enhancement is weak and affects the viscosity only at temperatures and densities rather close to the critical point, while the critical thermal-conductivity enhancement is strong and affects the thermal conductivity in a large range of temperatures and densities around the critical point [16]. Second, the critical viscosity enhancement is a so-called multiplicative enhancement, that is, the amplitude of the enhancement is proportional to the background viscosity μ_b [12,15], as can be seen from Eq. 4, while the thermal conductivity exhibits an additive critical enhancement.

The decay rate of the critical fluctuations is determined by the thermal diffusivity $D = \lambda/(\rho c_p)$, where c_p is the isobaric specific heat capacity [20,21]. The separation, Eq. 8, of the thermal conductivity into a critical and a background contribution implies a corresponding separation of the thermal diffusivity D into a critical contribution $\Delta_\mathrm{c} D = \Delta_\mathrm{c}\lambda/\rho c_p$ and a background contribution $D_\mathrm{b} = \lambda_\mathrm{b}/(\rho c_p)$ [16,22]:

$$D = \Delta_\mathrm{c} D + D_\mathrm{b}. \tag{9}$$

The background contribution D_b represents the classical contribution to the slowing of the fluctuations in which the diffusion coefficient would vanish in proportion to c_p^{-1}. The mode-coupling theory of critical dynamics predicts that, asymptotically close to the critical point, $\Delta_\mathrm{c} D$ should satisfy an equation of the form,

$$\Delta_\mathrm{c} D = \frac{R_\mathrm{D} k_\mathrm{B} T}{6\pi\mu\xi}, \tag{10}$$

where k_B is Boltzmann's constant and R_D is a universal dynamic amplitude ratio close to unity [11]. Equation 10 can be interpreted as an Einstein relation $k_\mathrm{B}T/\zeta$ with a Stokes-law friction coefficient $\zeta = 6\pi\mu\xi$ of a cluster with radius ξ. Recently, it has been argued that it would be more proper to refer to the Stokes–Einstein relation, Eq. 10, as the Stokes–Einstein–Sutherland relation [23,24]. The diffusivity D vanishes at the critical point, causing the well-known phenomenon of critical slowing of the fluctuations. From Eqs. 4 and 10, it follows that $\Delta_\mathrm{c} D$ will vanish as $\xi^{-(1+x_\mu)} \propto t^{0.67}$. Since c_p diverges asymptotically as χ, D_b will vanish as $t^{1.239}$ and, hence, much faster than the critical part $\Delta_\mathrm{c} D$. From Eq. 10 it follows that the thermal conductivity will diverge as

$$\Delta_\mathrm{c}\lambda \approx \frac{R_\mathrm{D} k_\mathrm{B} T c_p}{6\pi\mu\xi} \propto t^{-0.57}. \tag{11}$$

3 Universal Dynamic Amplitude Ratio R_D

An interesting question is: what is the value of the universal dynamic amplitude ratio R_D? The theoretical predictions for R_D have varied from 0.8 to 1.2 as reviewed by

Privman et al. [25] and Folk and Moser [26]. The most reliable predictions obtained from dynamic renormalization-group theory seem to be the values $R_{\mathrm{D}} = 1.038$ found by Paladin and Peliti [27,28] and $R_{\mathrm{D}} = 1.063$ found by Folk and Moser [26]. The mode-coupling theory yields in first approximation $R_{\mathrm{D}} = 1.00$ [18,19], but when memory and nonlocal effects are included, one obtains an improved estimate of $R_{\mathrm{D}} = 1.03$ [12]. Here we follow Luettmer–Strathmann et al. [29], Kostko et al. [30], and Das et al. [31] by adopting as the most probable theoretical estimate,

$$R_{\mathrm{D}} = 1.05 \pm 0.03, \tag{12}$$

representing a compromise between the mode-coupling prediction of 1.03 and the most recent dynamic renormalization prediction of 1.065 from Folk and Moser.

Experimental determinations of the universal dynamic ratio have been reviewed by Sengers [16] and Privman et al. [25]. Most attempts to deduce an experimental value for R_{D} have been made for liquid mixtures near the critical consolute point, where D is to be identified with the mass diffusivity, which determines the decay rate of the concentration fluctuations. Some early experiments seemed to support the higher value of 1.2 for R_{D} [25]. However, for a reliable determination of R_{D}, one needs accurate values not only for the diffusivity but also for the correlation length and the shear viscosity, and uncertainty in these various properties leads to significant uncertainty in R_{D}. Moreover, it makes a difference whether or not one includes the critical viscosity enhancement in Eq. 10 for deducing R_{D} from dynamic light-scattering measurements of the diffusivity D. Subsequent, more reliable, determinations of R_{D} for liquid mixtures, are, within their experimental accuracy, generally consistent with the theoretical estimate in Eq. 12, as reviewed by Sengers [16] and by Privman et al. [25]. Recently, it has been shown that molecular dynamics simulations of critical dynamics in liquid mixtures are also consistent with a theoretical estimate of $R_{\mathrm{D}} \simeq 1.05$ [24,31].

Experimental determinations for R_{D} of one-component fluids near the vapor–liquid critical point have been reported for helium [32] and for xenon [33–35]. Agosta et al. [32] have deduced a value $R_{\mathrm{D}} = 1.05 \pm 0.10$ from their experimental data for helium and Wilkinson et al. [35] have arrived at an experimental value $R_{\mathrm{D}} = 1.00 \pm 0.04$ for xenon. The experimental information for H_2O will be evaluated in the next section.

In principle, it would be possible to deduce R_{D} for one-component fluids not only from dynamic light-scattering measurements of the thermal diffusivity D, but also from measurements of the thermal conductivity λ. However, there are some problems with that alternate procedure. First, one then needs not only accurate data for λ, μ, and ξ, but also for the strongly divergent isobaric specific heat capacity c_p. Second, it is very difficult to obtain accurate thermal-conductivity measurements close to the critical point, because of the need of a finite temperature difference in the experiments and the high probability of convection [36]. Hence, at the actual temperatures where the thermal conductivity has been measured, nonasymptotic corrections to the asymptotic prediction, Eq. 11, often need to be considered [29,37–39]. The best one can say is that experimental thermal-conductivity data are not inconsistent with Eq. 12 [29,40–42].

4 Application to H_2O

The recommended values for the critical parameters of H_2O are [1,8,43]

$$T_c = 647.096\,\mathrm{K}, \quad \rho_c = 322\,\mathrm{kg \cdot m^{-3}}, \quad p_c = 22.064\,\mathrm{MPa}. \tag{13}$$

These recommended values are based on an evaluation of the available experimental information by Levelt Sengers et al. [44].

4.1 Correlation Length

The available experimental information for the critical amplitudes of H_2O has been evaluated by Anisimov et al. [45] and by Kostrowicka Wyczalkowska et al. [46]. Based on these evaluations, we have adopted the values [4–6],

$$\xi_0 = 0.13\ \mathrm{nm}, \quad \Gamma_0 = 0.060. \tag{14}$$

From Eq. 3, it follows that

$$\xi \approx \xi_0(\overline{\chi}/\Gamma_0)^{\nu/\gamma}. \tag{15}$$

Although Eq. 15 is strictly valid only for $\rho = \rho_c$, it is also used as an approximation for $\rho \neq \rho_c$ [47]. However, in the present article we shall use Eq. 15 only for $\rho = \rho_c$.

In the theory of critical phenomena the correlation length ξ is to be interpreted as the correlation length associated only with the long-range critical fluctuations. Hence, this correlation length should vanish far away from the critical point, where the critical fluctuations become negligible. This goal can be accomplished by subtracting from the susceptibility a background contribution. Specifically, we follow a procedure proposed by Olchowy and Sengers [48] by generalizing Eq. 15 to

$$\xi = \xi_0 \left(\frac{\Delta\overline{\chi}}{\Gamma_0}\right)^{\nu/\gamma}, \tag{16}$$

where

$$\Delta\overline{\chi} = \overline{\chi}(\overline{T}, \bar{\rho}) - \overline{\chi}(\overline{T}_R, \bar{\rho})\frac{\overline{T}_R}{\overline{T}}. \tag{17}$$

In Eq. 17 $\overline{T}_R$ is a reference temperature, sufficiently high above the critical temperature, where the critical fluctuations can be assumed to be small. In practice, one may select $\overline{T}_R = 1.5$ [29,42,48]. Furthermore, $\Delta\overline{\chi}$ is taken to be zero, when the right-hand term in Eq. 17 becomes negative. This procedure assures that the correlation length from Eq. 17 will vanish far away from the critical point. Equations 16 and 17 are presented here for the sake of completeness. For the temperatures close to the critical temperature considered in this article, the difference between Eqs. 15 and 16 is insignificant.

4.2 Viscosity

The background viscosity in Eq. 6 is represented by an equation of the form [5,6],

$$\frac{\mu_\mathrm{b}}{\mu^*} = \overline{\mu}_0(\overline{T}) \times \overline{\mu}_1(\overline{T}, \overline{\rho}), \tag{18}$$

where the reducing parameter $\mu^* = 1\,\mu\mathrm{Pa}\cdot\mathrm{s}$. The dimensionless function for the viscosity of the dilute gas $\overline{\mu}_0(\overline{T})$ is given by

$$\overline{\mu}_0(\overline{T}) = \frac{100\sqrt{\overline{T}}}{\sum_{i=0}^{3} \frac{H_i}{\overline{T}^i}}, \tag{19}$$

and the dimensionless function for the excess contribution to viscosity $\overline{\mu}_0(\overline{T}, \overline{\rho})$ by

$$\overline{\mu}_1\left(\overline{T}, \overline{\rho}\right) = \exp\left[\overline{\rho}\sum_{i=0}^{5}\left(\frac{1}{\overline{T}} - 1\right)^i \sum_{j=0}^{6} H_{ij}\left(\overline{\rho} - 1\right)^j\right]. \tag{20}$$

The values of the coefficients H_i and H_{ij} are given in previous IAPWS publications [5,6].

From Eq. 6, we can define a critical viscosity-enhancement factor as

$$\mu/\mu_\mathrm{b} = \exp(x_\mu Y). \tag{21}$$

For H_2O, the two system-dependent wave numbers q_C and q_D in Eq. 7 for the crossover function $Y(q_\mathrm{C}\xi, q_\mathrm{D}\xi)$ are [4–6]

$$q_\mathrm{C}^{-1} \simeq 1.9\,\mathrm{nm}, \quad q_\mathrm{D}^{-1} \simeq 1.1\,\mathrm{nm}. \tag{22}$$

A comparison of Eq. 6 with experimental viscosity data for H_2O in the critical region has been presented in previous publications [4,6].

4.3 Thermal Diffusivity

The current recommended interpolating equation for the thermal conductivity of H_2O [49] is based on experimental and theoretical information that was available prior to 1977 [50]. At that time an attempt was made to determine the dynamic amplitude ratio for H_2O by fitting experimental thermal-conductivity data with Eq. 11 with R_D as an adjustable parameter. Since the experimental thermal conductivities were not sufficiently close to the critical point for Eq. 11 to be valid, the equation was modified by an empirical correction factor to account for nonasymptotic critical behavior of the thermal conductivity. This procedure yielded $R_\mathrm{D} \simeq 1.20$ [50,51]. On comparing with Eq. 12, we must now conclude that the amplitude of the asymptotic divergence of the critical thermal-conductivity enhancement implied by the recommended interpolating equation is about 15 % too large. Since the thermal diffusivity is related to the thermal conductivity by $D = \lambda/\rho c_p$, this problem can be addressed with the dynamic light-scattering measurements obtained by Desmarest and coworkers [52–54]. Unlike the thermal-conductivity measurements [54,55], these light-scattering measurements correspond to temperatures very close to the critical temperature and enable us to test the validity of Eq. 10 for H_2O without the need for nonasymptotic correction terms.

Dynamic light scattering yields the thermal diffusivity $D(q)$ at a finite wave number q, while Eq. 10 is valid for the thermal diffusivity $D = D(0)$ in the macroscopic long-wavelength limit $q \to 0$ [53,54]. Here we present a re-evaluation of the dynamic light-scattering data using an accurate equation for the wave-number dependence of the thermal diffusivity and currently available information for the thermodynamic properties of H_2O.

Just as in Eq. 9, $D(q)$ is to be separated into a critical part $\Delta_c D(q)$ and a background D_b:

$$D(q) = \Delta_c D(q) + D_b(q). \tag{23}$$

According to the principle of scaling [11], $\Delta_c D(q)$ depends on the wave number q through the product $q\xi$, such that

$$\Delta_c D(q) = \Delta_c D(0)\Psi(q\xi), \tag{24}$$

where $\Psi(z)$ is a universal dynamic scaling function that satisfies the boundary conditions,

$$\lim_{z\to 0} \Psi(z) = 1 \tag{25}$$

and

$$\lim_{z\to\infty} \Psi(z) \propto z^{1+x_\mu}. \tag{26}$$

An explicit expression for the dynamic scaling function $\Psi(z)$ has been proposed by Burstyn et al. [12]:

$$\Psi(z) = K(z)\left[1 + \left(\frac{z}{2}\right)^2\right]^{x_\mu}, \tag{27}$$

where $K(z)$ is the so-called Kawasaki function [18,19]:

$$K(z) = \frac{3}{4z^2}\left[1 + z^2 + \left(z^3 - z^{-1}\right)\right]\arctan(z). \tag{28}$$

In the analysis of the dynamic light-scattering data, Desmarest and coworkers [53, 54] used an alternative expression for $\Psi(z)$ proposed by Paladin and Peliti [27,28].

Both approximants for $\Psi(z)$ satisfy the boundary conditions, Eqs. 25 and 26, but with different amplitudes of the limiting power-law dependence, Eq. 26, for large values of z [12]. We prefer to use Eq. 27, because its accuracy has been validated by light-scattering experiments including its limiting behavior for large z [12]. However, as noted by Tufeu et al. [53], the differences between the two approximants are small in the actual range of $q\xi$ values probed in the experiment. The background contribution $D_b(q)$ in the so-called Ornstein–Zernike approximation is given by [22]

$$D_\text{b}(q) = \frac{\lambda_\text{b}}{\rho c_p}\left(1 + q^2\xi^2\right). \tag{29}$$

The original experimental values for $D(q)$ on the critical isochore $\rho = \rho_\text{c}$ as a function of $\Delta T = T - T_\text{c}$, reported at the 11th International Conference on the Properties of Water and Steam [56], are listed in Table 1. The data were obtained at $q = 1.549 \times 10^7\ \text{m}^{-1}$, and the corresponding values of $z = q\xi$ are also given in this table, where ξ is calculated from Eqs. 14 and 16 with properties from IAPWS-95 [1–3]. This value of q is based on the refractive index of water of 1.103 near the critical point for the laser with a wavelength of 632.8 nm [3,57]. Many investigators have approximated the dynamical scaling function as $\Psi(z) \simeq K(z)$. However, this approximation neglects any critical viscosity enhancement in the evaluation of the mode-coupling integral for $\Delta_\text{c}D(q)$ [18,19]. Table 1 also shows the critical viscosity-enhancement factor μ/μ_b calculated from Eq. 21. This factor is larger than unity at all experimental temperatures, and clearly the critical enhancement of the viscosity cannot be neglected in the interpretation of the dynamic light-scattering measurements.

We note in this article that the susceptibility χ and, hence, the correlation length ξ, as well as the isobaric specific heat capacity c_p, are always calculated from the IAPWS-95 Formulation [1–3]. The thermodynamic properties from the IAPWS-95 Formulation exhibit some deviations from the theoretically predicted power-law behavior for these thermodynamic properties at the temperatures where the thermal-diffusivity measurements have been obtained [8,46]. Nevertheless, we continue to use the IAPWS-95 Formulation to maintain consistency with the equations for the thermodynamic properties and for the viscosity recommended by IAPWS.

To evaluate the background contribution $D(q)$, we need an estimate for the background thermal conductivity λ_b. Because we have earlier concluded that the critical thermal-conductivity enhancement in the IAPWS Formulation for the thermal conductivity [49] is probably too large, the background thermal-conductivity values implied by this formulation have also become less reliable. Instead we have adopted an estimate for the background thermal conductivity λ_b proposed by Le Neindre et al. [58]:

$$\lambda_\text{b} = \lambda_0(T) + \sum_{i=1}^{4} \lambda^{(i)}\rho^i, \tag{30}$$

with values of the coefficients $\lambda^{(i)}$ also given in [58]. In Eq. 30, $\lambda_0(T)$ is the thermal conductivity of H_2O in the dilute-gas limit that can indeed be calculated from the IAPWS Formulation for the thermal conductivity [49].

Table 1 Thermal diffusivity $D(q)$ measured at $q = 1.549 \times 10^7\ \mathrm{m}^{-1}$ by Desmarest et al. [56] and the corresponding $D(q = 0)$ and R_D as a function of $\Delta T = T - T_\mathrm{c}$ and $q\xi$

ΔT (K)	$q\xi$	$D(q)(\mathrm{m}^2 \cdot \mathrm{s}^{-1})$	$D(q = 0)(\mathrm{m}^2 \cdot \mathrm{s}^{-1})$	R_D	μ/μ_b
0.020	0.964	2.79×10^{-10}	1.85×10^{-10}	1.08	1.18
0.036	0.713	3.28×10^{-10}	2.53×10^{-10}	1.05	1.16
0.077	0.481	4.36×10^{-10}	3.81×10^{-10}	1.02	1.13
0.106	0.408	4.79×10^{-10}	4.33×10^{-10}	0.95	1.12
0.118	0.385	5.28×10^{-10}	4.82×10^{-10}	0.99	1.12
0.159	0.330	6.26×10^{-10}	5.85×10^{-10}	1.01	1.11
0.245	0.262	8.29×10^{-10}	7.93×10^{-10}	1.05	1.09
0.286	0.241	9.39×10^{-10}	9.04×10^{-10}	1.09	1.09
0.351	0.216	10.61×10^{-10}	10.29×10^{-10}	1.09	1.08
0.438	0.191	11.73×10^{-10}	11.44×10^{-10}	1.04	1.07
0.522	0.174	13.10×10^{-10}	12.83×10^{-10}	1.03	1.07
0.550	0.169	13.52×10^{-10}	13.26×10^{-10}	1.03	1.07
0.668	0.151	15.61×10^{-10}	15.37×10^{-10}	1.05	1.06
0.740	0.143	16.58×10^{-10}	16.35×10^{-10}	1.04	1.06
0.877	0.130	18.62×10^{-10}	18.40×10^{-10}	1.03	1.05

From the above equations, it follows that the critical part $\Delta_\mathrm{c}D = \Delta_\mathrm{c}D(0)$ of the thermal diffusivity $D = D(0)$ is related to $D(q)$ as

$$D = \frac{D(q) - \left(\lambda_\mathrm{b}/\rho c_p\right)\left(1 + q^2\xi^2\right)}{\Psi(q\xi)} + \frac{\lambda_\mathrm{b}}{\rho c_p}. \tag{31}$$

The values of D, thus deduced from the experimental data in the limit $q \to 0$, are also included in Table 1. From Eqs. 9 and 10, it follows that the dynamic amplitude ratio R_D is related to D by

$$R_\mathrm{D} = \frac{6\pi\mu\xi}{k_\mathrm{B}T}\left[D - \frac{\lambda_\mathrm{b}}{\rho c_p}\right]. \tag{32}$$

The resulting "experimental" values for R_D of H_2O, obtained from Eq. 32 with the viscosity calculated from Eq. 6, are listed in Table 1 and are plotted as a function of $\Delta T = T - T_\mathrm{c}$ in Fig. 1. There is some spread in these experimental values at temperatures within 0.3 K of the critical temperature. However, as noted by the authors of [55], at temperatures within 0.1 K, the measurements may be affected by inhomogeneities associated with the very large compressibility. Although the effects of multiple scattering are known to be much smaller in dynamic light-scattering experiments than in static light-scattering experiments [59], some multiple scattering effects cannot be excluded very close to the critical temperature. If we average the values for R_D deduced

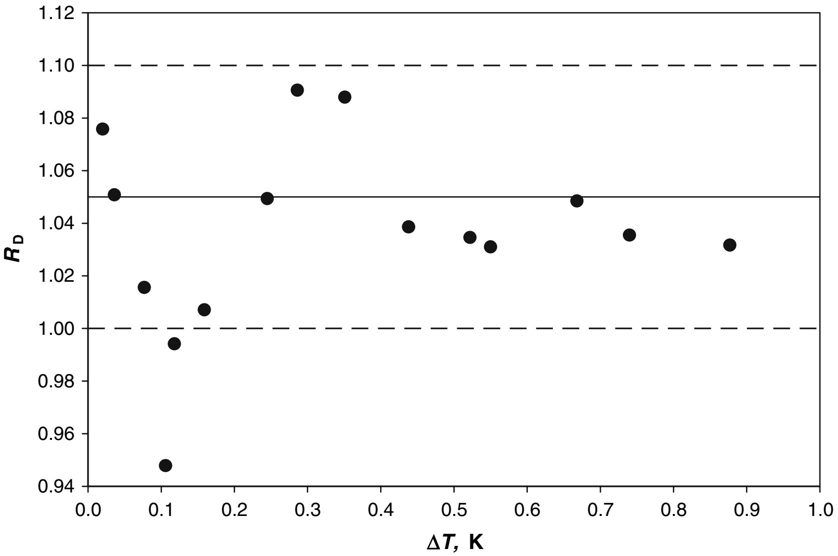

Fig. 1 Dynamic amplitude ratio R_D deduced from the light-scattering data of Desmarest et al. [56] as a function of $\Delta T = T - T_c$. *Solid line* indicates the mean value of 1.05 and *dashed lines* the two-standard-deviation limits of ±0.05

from the light-scattering measurements, we find $R_D = 1.04 \pm 0.05$; if we average the more accurate values for $\Delta T \geq 0.2$ K, we find

$$R_D = 1.05 \pm 0.05 \tag{33}$$

in good agreement with the theoretical prediction, given by Eq. 12. It is important to note that this good agreement depends upon accounting for the critical viscosity enhancement in the evaluation of Eq. 32.

5 Conclusions

As noted earlier we have used the IAPWS-95 Formulation [1–3] to calculate both the susceptibility χ in Eq. 16 for the correlation length ξ and the isobaric specific heat capacity c_p in Eq. 31 for converting the experimental wave-number-dependent diffusivity $D(q)$ into $D(q = 0)$. However, the IAPWS-95 Formulation does not satisfy the theoretical power-law behavior of these properties asymptotically close to the critical point accurately [8,46]. Specifically, at temperatures within 0.3 K, deviations of the IAPWS-95 Formulation from the theoretically predicted power laws for χ and c_p become substantial. Nevertheless we can conclude that equations of the mode-coupling theory for viscosity, diffusivity, and thermal conductivity do yield a consistent representation of these transport properties within the framework of the IAPWS equations. This mode-coupling theory will be used in future IAPWS work to develop an accurate formulation for the thermal conductivity and thermal diffusivity of H_2O over a wide range of conditions, including the critical region.

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