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Thermal Diffusivity and Thermal Conductivity of Steam in the Crossover Region

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In this paper, we present a comparison of the thermal diffusivity and thermal conductivity data of steam in the temperature range $0.02\,\mathrm{K} < T - T_c < 140\,\mathrm{K}$ with a recent formulation of crossover from singular to regular behavior of the transport properties of fluids. We have used two sets of experimental data previously obtained by the authors. The agreement between experimental and calculated data is good.

KEY WORDS: crossover region; steam; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Near the critical point, various thermodynamic and transport properties of pure fluids diverge. These divergences are asymptotically described by nonanalytic expressions which satisfy conditions of universality. Far away from the critical region, classical equations can be used. The crossover problem consists in deriving a global formulation of the thermodynamic and transport properties over large temperature and density ranges. There are few formulations which allow the determination of the thermal conductivity (or the thermal diffusivity) from the close vicinity of the critical point up to the range where it behaves "regularly." Up to date, some semiempirical functions were proposed for analyzing the experimental data [1]. In this work, we present the comparison of our experimental data with a new formulation proposed by Olchowy and Sengers [2] and derived from the mode-mode coupling theory. We have used the thermal conductivity data of

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steam obtained by Tufeu and Le Neindre [3] by a thermodynamic method and the values of the thermal diffusivity obtained by Desmarest et al. [4] by a technique of photon-correlation spectroscopy near the critical point.

2. EXPERIMENTAL DATA

2.1. Thermal Conductivity

The thermal conductivity of steam was measured by Tufeu and Le Neindre [3] by the coaxial cylinder method in the temperature range 250°C $< T <$ 510°C up to 950 MPa corresponding to about twice the critical density.

2.2. Thermal Diffusivity Along the Critical Isochore

The experimental thermal diffusivity along the critical isochore shown in Fig. 1 is obtained from the experimental generalized thermal diffusivity data measured by light scattering in the temperature range 0.02 K $<$ $T - T_c < 1$ K (T_c is the critical temperature) and from the thermal conduc-

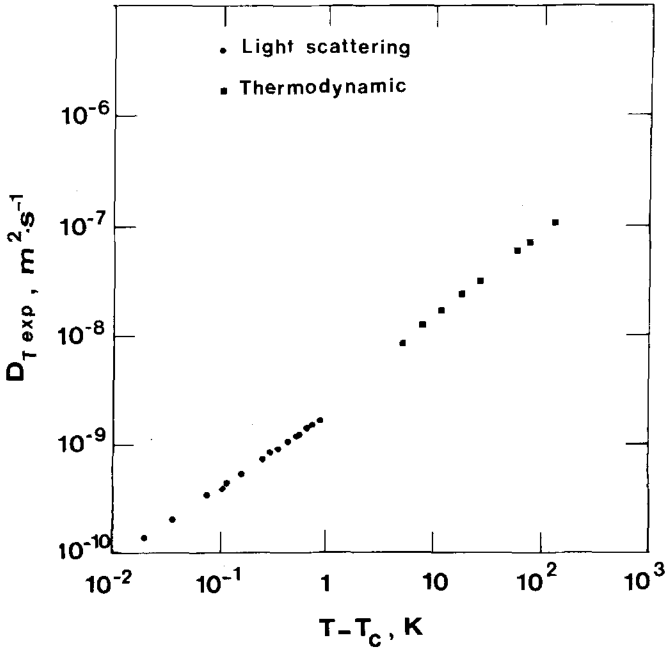

Fig. 1. Thermal diffusivity of H_2O along the critical isochore.

tivity data. The light scattering experiment allows the measurement of a generalized thermal diffusivity coefficient $D_T^*(q)$ (i.e., dependent on the wavenumber q of the scattered light) which is directly related to the decay rate of the critical fluctuations. So it is necessary to determine the corresponding experimental hydrodynamic thermal diffusivity D_T which can be analyzed altogether with the experimental thermal conductivity data.

2.2.2. Thermodynamic Data

The experimental thermal diffusivity is calculated by

$$D_T = \lambda/\rho C_p \tag{1}$$

where λ is the thermal conductivity at critical density ρ_c estimated from the data set obtained by Tufeu and Le Neindre [3] and C_p is the experimental specific heat at constant pressure measured by Sirota *et al.* [5].

2.2.2. Light Scattering Results

For the determination of the experimental hydrodynamic thermal diffusivity D_T in the temperature range $T - T_c < 0.9$ K, $D_T^*(q)$ is separated into critical and regular contributions $D_c^*(q)$ and $D_B^*(q)$, respectively:

$$D_T^*(q) = D_c^*(q) + D_B^*(q) \tag{2}$$

In the Ornstein–Zernike approximation, the regular part $D_B^*(q)$ is given by

$$D_B^*(q) = \frac{\lambda_B}{\rho C_p}(1 + q^2\xi^2) \equiv D_B(1 + q^2\xi^2) \tag{3}$$

where λ_B is the background term of the thermal conductivity, C_p is the specific heat at constant pressure, ξ is the correlation length, and D_B is the hydrodynamic regular contribution to the thermal diffusivity.

The critical part of the experimental generalized thermal conductivity $D_c^*(q)$ is given by

$$D_c^*(q) = D_T^*(q) - \frac{\lambda_B}{\rho C_p}(1 + q^2\xi^2) \tag{4}$$

If we assume that the q dependence of $D_c^*(q)$ is given by

$$D_c^*(q) = D_c \bar{\Omega}(q\xi) \tag{5}$$

where D_c is the hydrodynamic critical part of the thermal diffusivity and $\bar{\Omega}(q\xi)$ is a universal function of $q\xi$, the experimental hydrodynamic thermal diffusivity is obtained from the relation

$$D_T = D_c + D_B \tag{6}$$

In this procedure we have used the background term of the thermal conductivity λ_B determined by Tufeu et al. [6], the shear viscosity calculated by the equation proposed by Watson et al. [7], and the specific heat at constant pressure obtained from the scaled equation of state of Levelt-Sengers et al. [8]. We have chosen for the universal function $\bar{\Omega}(q\xi)$ the expression proposed by Paladin and Peliti [9]. The correlation length is calculated from the reduced isothermal susceptibility χ_T^* [10] by the following relation:

$$\xi = \xi_0^+ (\chi_T^*/\Gamma)^{\nu/\gamma} \tag{7}$$

with $\Gamma = 60.86 \times 10^{-3}$, $\gamma = 1.24$, and $\nu = 0.63$. χ_T^* is defined by the relation

$$\begin{aligned} \chi_T^* &= \chi_T P_c/\rho_c^2 \\ &= K_T P_c \rho^2/\rho_c^2 \end{aligned} \tag{8}$$

where χ_T is the isothermal susceptibility and K_T is the isothermal compressibility.

The amplitude ξ_0^+ has the value 1.21 Å as calculated previously by Garrabos [11] by using a transformation scale method.

The above procedure implies that using the crossover formulation in this temperature range gives the same thermal diffusivity values.

The dashed areas in Fig. 2 represent the uncertainties of the values of D_T. They correspond to the uncertainties of the experimentally determined values of D_T^* (3% at $0.02\text{ K} < T - T_c < 0.2\text{ K}$, increasing to 5% at $T - T_c \simeq 1$ K) and to the ±5-mK experimental uncertainties of $T - T_c$.

The experimental values of D_T are given in Table I. We observe a lack of experimental data in the temperature range $1\text{ K} < T - T_c < 5\text{ K}$. On the one hand, it was not possible with our experimental method to make measurements of the decay rate of critical fluctuations smaller than 1 μs by light scattering, which corresponds to $T - T_c \simeq 1$ K (90° observation); on the other hand, the thermodynamic measurements were limited to $T - T_c > 5$ K because of large heat transfer by convection closer to the critical point.

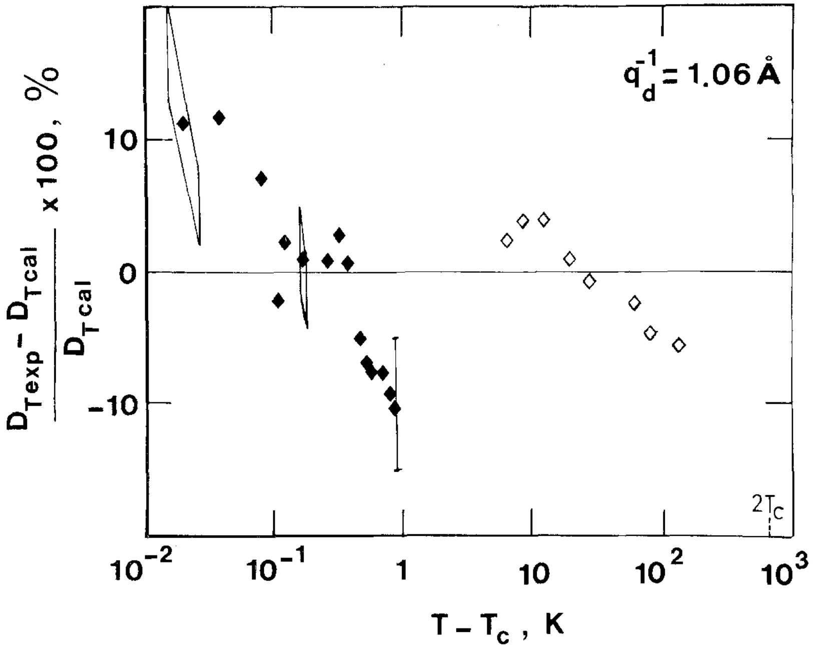

Fig. 2. Deviations between experimental and calculated values of the thermal diffusivity of steam along the critical isochore. ($q_d^{-1} = 1.06$ Å and λ_B from Ref. 6.)

3. ANALYSIS AND DISCUSSION

3.1. Crossover Formulation

We have compared our experimental data with the recent formulation of crossover proposed by Olchowy and Sengers [2] and derived from the mode-mode coupling theory. In this formulation the thermal diffusivity is again separated into two additive contributions. The critical part of the thermal diffusivity is calculated by

$$D_c = R \frac{k_B T}{6\pi\eta\xi} \Omega(\bar{y}, \rho^*) \tag{9}$$

where R is an universal amplitude ratio, k_B is the Boltzmann constant, η is the shear viscosity, and $\Omega(\bar{y}, \rho^*)$ is a crossover function. $\bar{y}$ Symbolizes a set of parameters which depend only on the thermodynamic properties C_P, C_v, and K_T, the background transport properties λ_B and η_B, and one fluid-dependent cutoff parameter q_d. This wavenumber is the only adjustable

Table I. Experimental Thermal Diffusivity of Steam Along the Critical Isochore

$T - T_c$ (K)	Method	D_T (exp) (10^{-10} m$^2 \cdot$s^{-1})
.02	L.S.[a]	1.50
.036	L.S.	2.25
.077	L.S.	3.66
.106	L.S.	4.23
.118	L.S.	4.73
.159	L.S.	5.79
.245	L.S.	7.91
.286	L.S.	9.03
.351	L.S.	10.29
.438	L.S.	11.46
.521	L.S.	12.85
.550	L.S.	13.28
.668	L.S.	15.39
.740	L.S.	16.37
.877	L.S.	18.43
5.23	Th.[b]	90.3
7.97	Th.	131.9
12.10	Th.	186.4
18.54	Th.	260
26.94	Th.	349
61.10	Th.	652
82.70	Th.	792
138	Th.	1127

[a] L.S. = light scattering method.
[b] Th. = thermodynamic method.

parameter in this analysis. $\rho^* = (\rho - \rho_c)/\rho_c$ is the reduced density and ρ_c is the critical density.

The correlation length is estimated from the "critical part" of the reduced isothermal susceptibility χ_T^* by the relation

$$\xi = \xi_0^+ (\Delta\chi_T^*/\Gamma)^{\nu/\gamma} \tag{10}$$

where $\Delta\chi_T^*$ is defined by

$$\Delta\chi_T^* = \chi^*(T, \rho) - \bar{\chi}^*(T, \rho) \tag{11}$$

where $\bar{\chi}^*(T, \rho) = \chi^*(T_r, \rho)\, T_r/T$ is the background susceptibility for a reference temperature $T_r = 1.5\ T_c$.

For this computation of the thermal diffusivity, we first assign a value to q_d^{-1}, then we calculate the shear viscosity. This last value being determined, we calculate the thermal diffusivity, which allows us a new estimation of q_d^{-1} to repeat a cycle. The wavenumber q_d is always estimated from the thermal diffusivity because of its strong critical anomaly which persists over a large temperature and density range around the critical point.

3.2. Comparison with Experimental Data

The thermodynamic data C_P, C_v, and K_T are calculated by the scaled equation of state of Levelt-Sengers et al. [8] in the temperature range $T - T_\mathrm{c} < 40$ K and the density range $200\ \mathrm{kg \cdot m^{-3}} < \rho < 420\ \mathrm{kg \cdot m^{-3}}$. Outside this region, these parameters are calculated by the classical equation given by Haar et al. [12]. η_B is taken from Ref. 13.

The correlation length ξ is obtained by the relation (10) with $\xi_0^+ = 1.21$ Å calculated by Garrabos [11].

We have chosen for the amplitude R the value 1.075, which has given together with $\xi_0^+ = 1.21$ Å the best agreement between calculated and

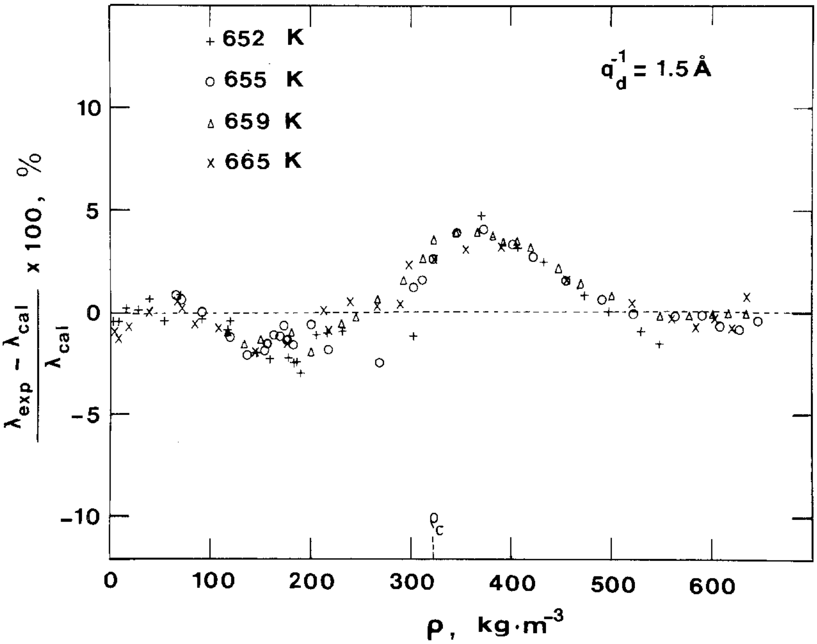

Fig. 3. Deviations between experimental and calculated values of the thermal conductivity of steam for quasi-isotherms $T = 652$, 655, 659, and 665 K. ($q_\mathrm{d}^{-1} = 1.5$ AA and λ_B from Ref. 6.)

experimental generalized thermal diffusivity close to the critical point [4]. This $R = 1.075$ value is larger than the expected universal amplitude $R = 1.01 \pm 0.04$ given in Ref. 14.

The thermal conductivity measurements do not extend to temperatures high enough to get data uncontaminated by critical effects. A first estimation of the thermal conductivity background λ_B was proposed by Tufeu et al. [6]. They assumed that $\Delta\lambda_c = 0$ for $\rho = 0$ and $\rho = 2\rho_c$. Moreover, a corresponding states approach allowed the estimation of $\Delta\lambda_c$ at $(T - T_c)/T_c \simeq 0.01$ [15].

The result of the fit of D_T is that we find a value for $q_d^{-1} = 1.06$ Å. The deviations are shown in Fig. 2. We note that the larger deviations between calculated and experimental thermal diffusivity values occur near the critical point.

The comparison of our thermal conductivity data with the crossover equation is shown in Figs. 3 and 4. Here, the best fit has been obtained for $q_d^{-1} = 1.5$ Å. Systematic deviations can be noted for $\rho \simeq 150\ \mathrm{kg \cdot m^{-3}}$ and at densities $280\ \mathrm{kg \cdot m^{-3}} < \rho < 480\ \mathrm{kg \cdot m^{-3}}$, the maximum deviations occurring at densities $\rho \simeq 1.15\,\rho_c$. The deviations at the densities close to

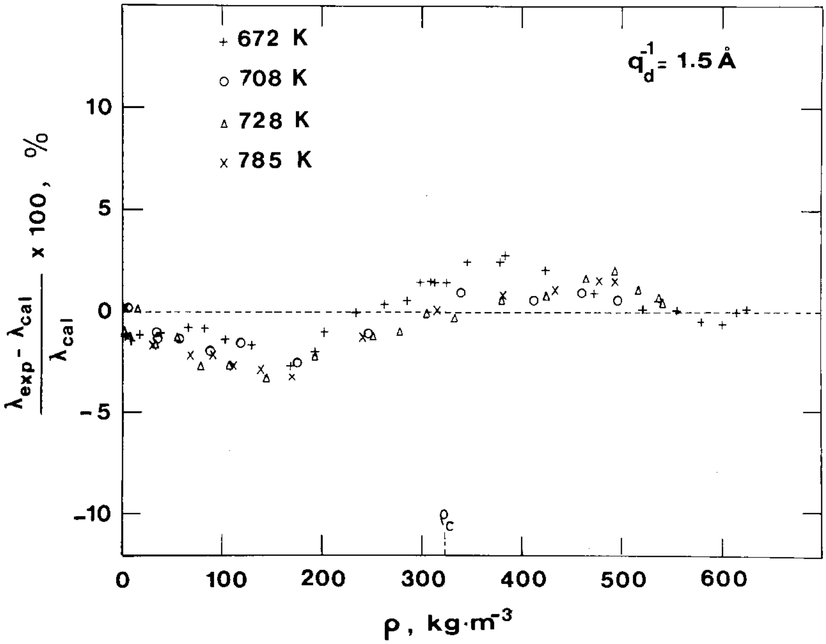

Fig. 4. Deviations between experimental and calculated values of the thermal conductivity of steam for quasi-isotherms $T = 672$, 708, 728, and 785 K. ($q_d^{-1} = 1.5$ Å and λ_B from Ref. 6.)

Table II. Coefficients a_i and b_i for $\lambda_0(T)$ and $\tilde{\lambda}_B(\rho)$

λ_0			$\tilde{\lambda}_B$		
$a_0 =$	8.9372	E-04	$b_1 =$	1.420	E-04
$a_1 =$	4.90018	E-05	$b_2 =$	1.41744	E-06
$a_2 =$	2.56541	E-08	$b_3 =$	−1.54583	E-09
$a_3 =$	4.127	E-11	$b_4 =$	1.02745	E-12
$a_4 =$	−8.73764	E-15			
$a_5 =$	−1.55286	E-17			
$a_6 =$	4.81493	E-21			

ρ_c can be due to an underestimation of the heat transfer by convection in the determination of λ.

A second fit was made with a new estimation of the background thermal conductivity λ_B represented by the equation

$$\lambda_B = \lambda_0(T) + \tilde{\lambda}_B(\rho) \tag{12}$$

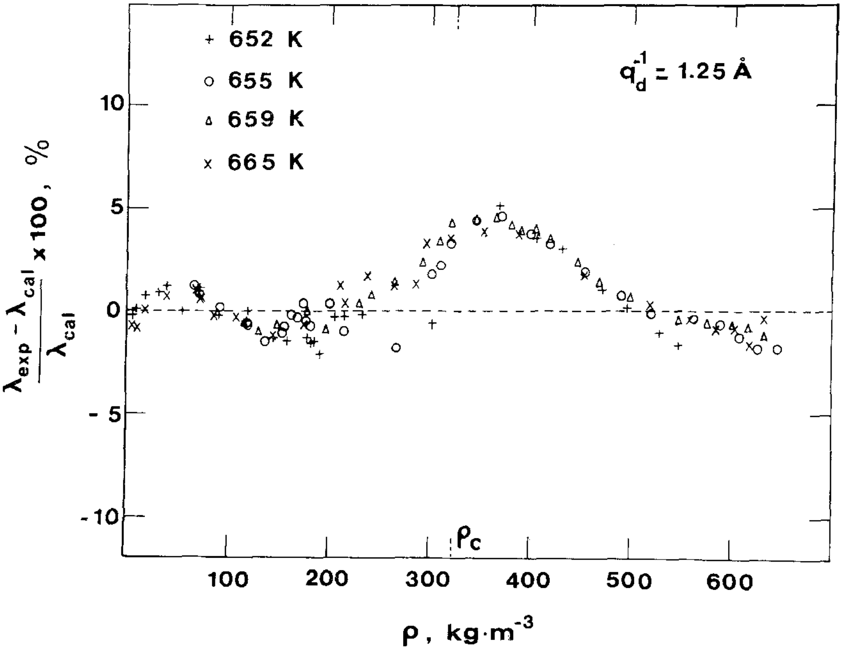

Fig. 5. Deviations between experimental and calculated values of the thermal conductivity of steam for quasi-isotherms $T = 652$, 655, 659, and 665 K. ($q_d^{-1} = 1.25$ Å and λ_B from Table II.)

λ_0 and $\bar{\lambda}_B$ are given by the expressions

$$\lambda_0 = \sum_{i=0}^{6} a_i T^i \tag{13}$$

$$\bar{\lambda}_B = \sum_{i=1}^{4} b_i \rho^i \tag{14}$$

The parameters of these equations are given in Table II. Using this background thermal conductivity, we find a value for $q_d^{-1} = 1.25$ Å. A better agreement is obtained at low density (Figs. 5 and 6) and there is no significant change in the vicinity of the critical density and at high density ($\rho > 200\ \mathrm{kg \cdot m^{-3}}$).

Using the new background thermal conductivity and $q_d^{-1} = 1.25$ Å to fit the thermal diffusivity along the critical isochore, the data obtained by using the thermodynamic method are systematically larger than the calculated values. The deviations reported in Fig. 7, which are larger than the ones observed for the thermal conductivity, are due to the high experimental thermal conductivity values near the critical density as already noted and to the fact that the experimental C_p measured by Sirota

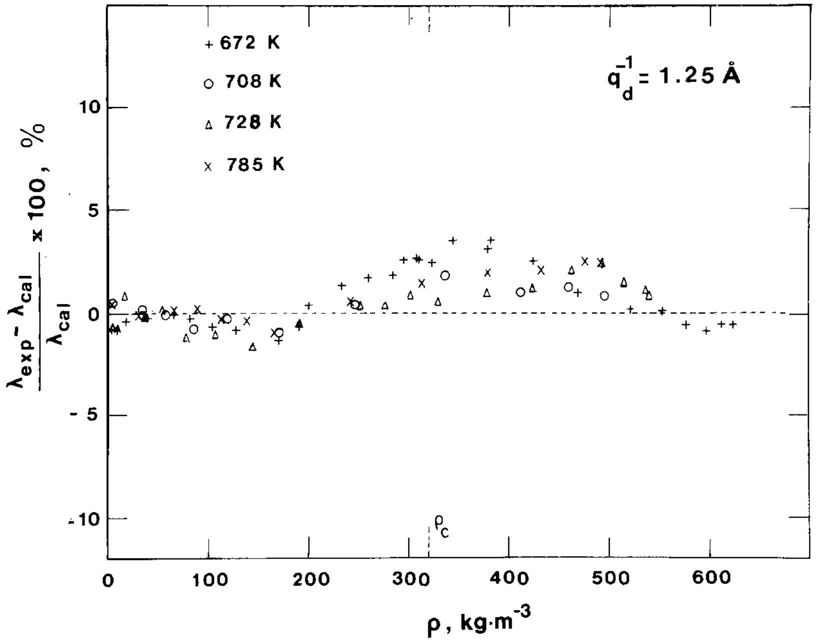

Fig. 6. Deviations between experimental and calculated values of the thermal conductivity of steam for quasi-isotherms $T = 672$, 708, 728, and 785 K. ($q_d^{-1} = 1.25$ Å and λ_B from Table II.)

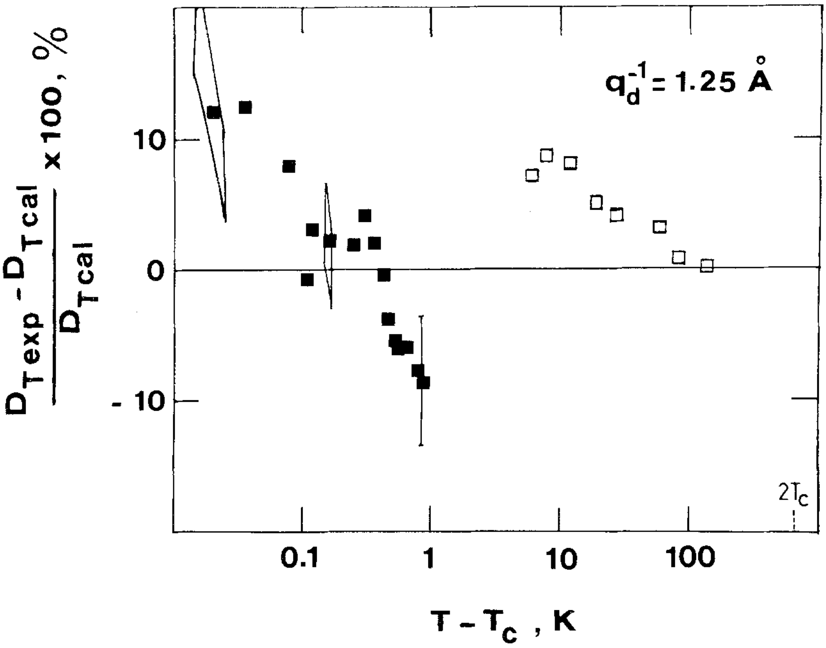

Fig. 7. Deviations between experimental and calculated values of the thermal diffusivity of steam along the critical isochore. ($q_d^{-1} = 1.25$ Å and λ_B from Table II.)

et al [5] are smaller than the values calculated by the scaled equation of state. The deviations between experimental and calculated D_T values for $T - T_c < 1$ K are not significantly modified when the new λ_B and q_d^{-1} are chosen.

Finally, it appears that our experimental data compare reasonably well with the crossover equation when the thermal conductivity background given in this paper and a value for $q_d^{-1} = 1.25$ Å are chosen.

Another set of data obtained by Sirota et al. [16] is also available for the termal conductivity of steam in the critical region. The deviations between the calculated (with the same λ_B, ξ_0^+, q_d^{-1}, R parameters) and the experimental values are larger than the deviations that we have obtained in the comparison with our own data set. The deviations amount to 25% for the 22.6-MPa isobar.

4. CONCLUSION

In spite of the theoretical questions concerning the application of the formulation and particularly the persistence of a critical excess for correlation length values lower than the cutoff parameter and lower than the intermolecular collision distance, the formulation of Olchowy and Sengers leads to a good description of the thermal diffusivity and of the thermal conductivity of steam obtained by the authors in a large temperature and density range.

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