# Scaled equation of state for supercooled water in the mean-field approximation

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## Abstract

In this technical report we show that the assumption of thermodynamic liquid-liquid critical behavior in supercooled water already in the mean-field approximation yields a physically plausible explanation for the anomalous temperature dependence observed experimentally for the isochoric heat capacity, the isothermal compressibility, and the thermal expansivity of supercooled water.

## 1 Introduction

It has now been well established that the thermodynamic properties of $H_2O$ exhibit anomalous behavior upon supercooling [1-9]. A variety of explanations for the anomalous thermodynamic behavior of supercooled water have been proposed [10]. In this report we consider the existence of a liquid-liquid critical point [11-30] and its possible effects on the temperature dependence of the heat capacity, the isothermal compressibility, and the thermal expansivity of supercooled water.

The thermodynamic behavior of fluids near a critical point can be characterized in terms of two independent scaling fields, a "strong" field $h_1$ (ordering field) and a "weak" scaling field $h_2$, and one dependent scaling field $h_3$ [31]. These scaling fields in turn are related to the physical fields like temperature, pressure, and chemical potential. The specific details of the relationships between the scaling fields and the physical fields determine the actual nature of the thermodynamic behavior observed near critical points [32]. The thermodynamic property $\phi_1$ conjugate to the ordering field is called the order parameter of the critical phase transition. Near the vapor-liquid critical point this order parameter is related to the density. Near the liquid-liquid critical point in supercooled water the order parameter is related to the entropy, as first pointed out by Fuentevilla and Anisimov [33]. The applicability of scaled equations of state with the entropy as the order parameter for representing the anomalous thermodynamic behavior of supercooled water has been further investigated by Bertrand and Anisimov [34]. In this report we consider a scaled equation of state for supercooled water in the mean-field approximation, which neglects the effects of critical fluctuations on the thermodynamic behavior. The limitation is that a mean-field approximation cannot properly account for the actual singular asymptotic power-law behavior of thermodynamic properties with Ising-like critical exponents. However, mean-field equations for critical thermodynamic behavior of fluids are very simple and can be easily programmed. Moreover, mean-field theories may yield a qualitative physical representation of the thermodynamic behavior not asymptotically close to a critical point [35,36]. Actually, a complete thermodynamic theory is expected to require a crossover description from asymptotic singular critical behavior to non-asymptotic mean-field critical behavior [35,36]. Hence, it is of interest to investigate to which extent a mean-field approximation can account for the observed anomalous increase of heat capacity, compressibility and thermal expansivity in supercooled water.

This report is organized as follows. In Section 2 we formulate a thermodynamic model based on the assumption of the presence of a liquid-liquid critical point in supercooled water. Specifically, in Section 2.1 we introduce the concepts of scaling fields, scaling densities, and scaling susceptibilities. In Section 2.2 we show how these concepts can be applied to supercooled water. In Section 2.3 we implement the theoretical model in the so-called mean-field approximation. In Section 3 we provide a comparison of the theoretical model with experimental data for the isochoric heat capacity, the isothermal compressibility, and the thermal expansivity. We conclude that an equation of state based on the existence of a liquid-liquid critical point already yields in the mean-field approximation a plausible explanation for the anomalous temperature dependence of the heat capacity, compressibility, and expansivity of supercooled water.

## 2 Thermodynamic model

### 2.1 Scaling fields, scaling densities, and scaling susceptibilities

Near the critical point the dependent scaling field $h_3\left(h_1,h_2\right)$ becomes a generalized homogeneous function of the two independent scaling fields $h_1$ and $h_2$ [31]:

$$h_3(h_1,h_2) \approx |h_2|^{2-\alpha}\ f^{\pm}\left(\frac{h_1}{|h_2|^{2-\alpha-\beta}}\right), \tag{1}$$

where $\alpha = 0.110$ and $\beta = 0.236$ are universal critical exponents [37,38] and $f^{\pm}$, with the superscripts ± referring to $h_2 > 0$ and $h_2 < 0$, is a universal scaling function except for two system-dependent amplitudes. At the critical point

$$h_1 = h_2 = h_3\,. \tag{2}$$

Associated with the two independent scaling fields are two scaling densities: a strongly fluctuating density $\phi_1$ (order parameter) and a weakly fluctuating density $\phi_2$, such that

$$dh_3 = \phi_1 dh_1 + \phi_2 dh_2 \tag{4}$$

with

$$\phi_1 = \left(\frac{\partial h_3}{\partial h_1}\right)_{h_2}, \quad \phi_2 = \left(\frac{\partial h_3}{\partial h_2}\right)_{h_1}. \tag{5}$$

In addition we define scaling susceptibilities: a "strong" susceptibility $\chi_1$, a "weak" susceptibility $\chi_2$, and a "cross" susceptibility $\chi_{12}$:

$$\chi_1 = \left(\frac{\partial \phi_1}{\partial h_1}\right)_{h_2}, \quad \chi_2 = \left(\frac{\partial \phi_2}{\partial h_2}\right)_{h_1}, \quad \chi_{12} = \left(\frac{\partial \phi_1}{\partial h_2}\right)_{h_1} = \left(\frac{\partial \phi_2}{\partial h_1}\right)_{h_2}. \tag{6}$$

### 2.2 Application to supercooled water

In a fluid the physical fields are the temperature $T$, the pressure $P$, and the chemical potential $\mu$ (Gibbs energy per mole). To satisfy condition (2) one introduces $\Delta T = T - T_\mathrm{c}$, $\Delta P = P - P_\mathrm{c}$, and $\Delta\mu = \mu - \mu_\mathrm{c}$. In this report we adopt the usual convention that a subscript c refers to the value of the property at the critical point. To implement a scaled thermodynamic representation it is convenient to make all thermodynamic properties dimensionless in terms of the temperature $T_\mathrm{c}$ and the molar volume $V_\mathrm{c}$ at the critical point:

$$\hat{T} = \frac{T}{T_\mathrm{c}}, \quad \hat{\mu} = \frac{\mu}{RT_\mathrm{c}}, \quad \hat{P} = \frac{PV_\mathrm{c}}{RT_\mathrm{c}}, \tag{7}$$

where $R$ is the molar gas constant. As dimensionless physical densities we define

$$\hat{V} = \frac{V}{V_\mathrm{c}}, \quad \hat{S} = \frac{S}{R}, \quad \hat{C}_P = \frac{C_P}{R}, \tag{8}$$

where $V$ is the molar volume, $S$ the molar entropy, and $C_P$ the isobaric molar heat capacity. The corresponding dimensionless isobaric compressibility $\hat{\kappa}_T$ and coefficient of thermal expansion or expansivity coefficient $\hat{\alpha}_V$ are

$$\hat{\kappa}_T = -\frac{1}{\hat{V}}\left(\frac{\partial \hat{V}}{\partial \hat{P}}\right)_T, \quad \hat{\alpha}_V = \frac{1}{\hat{V}}\left(\frac{\partial \hat{V}}{\partial \hat{T}}\right)_P. \tag{9}$$

According to the principle of complete scaling, the scaling fields, $h_1$, $h_2$, and $h_3$, are analytic functions of $\Delta\hat{T}, \Delta\hat{P}$ and $\Delta\hat{\mu}$ [39-41]. Thus in first approximation $h_1$, $h_2$, and $h_3$ can be expressed as linear combinations of $\Delta\hat{T}, \Delta\hat{P}$ and $\Delta\hat{\mu}$ [39,42] with system-dependent coefficients. However, as shown by Anisimov and Wang [42,43], the number of system-dependent coefficients in the relationships between scaling fields and physical fields can be reduced to only a few by proper normalization of the scaling fields. For the relationships between the scaling fields and the physical fields near the liquid-liquid critical point in supercooled water we adopt:

$$h_1 = \Delta\hat{T} + a_1\,\Delta\hat{P} + a_2\left(\Delta\hat{P}\right)^2 , \tag{10}$$

$$h_2 = -\Delta\hat{P} + b_1\Delta\hat{T} , \tag{11}$$

$$h_3 = -\Delta\hat{\mu} + \Delta\hat{P} - \hat{S}_\mathrm{c}\,\Delta\hat{T} . \tag{12}$$

In Eqs. (10) and (11) we have neglected a contribution from the additional physical field $\Delta\hat{\mu}$ to $h_1$ and $h_2$, since such contributions only become significant in highly asymmetric systems [42,43]. In the relations above, $a_1$, $a_2$, and $b_1$ are system-dependent coefficients. The coefficients $a_1$ and $a_2$ represent the limiting slope and curvature of the phase-coexistence or Widom line $h_1 = 0$. The coefficient $b_1$ is a so-called mixing coefficient in the revised scaling approximation [43]. While near the vapor-liquid critical point the leading term in the expansion of the ordering field $h_1$ is $\Delta\hat{\mu}$ [43,44], the leading term in the expansion of $h_1$ near the liquid-liquid critical point in supercooled water is $\Delta\hat{T}$, since the entropy yields now the major contribution to the order parameter and not the density. Equations (10) - (12) differ from the model of Bertrand and Anisimov [34] for supercooled water in two aspects. First, following Fuentevilla and Anisimov [33] we have added a quadratic pressure contribution in the expansion for $h_1$ to accommodate a curvature of the phase-coexistence line $h_1 = 0$ as a function of pressure. Second, we prefer to formulate the scaling laws in terms of the physical potential $\mu(T,P)$, rather than in terms of $P(T,\mu)$ as was done by Bertrand and Anisimov, because it leads to simpler expressions for some thermodynamic properties. Equation (12) can be further simplified by taking $S_\mathrm{c} = 0$. From Eqs. (10) - (12) and using the thermodynamic differential relation

$$d\hat{\mu} = \hat{V}\,d\hat{P} - \hat{S}\,d\hat{T} \tag{13}$$

one finds for the volume $\hat{V}$ and the entropy $\hat{S}$

$$\hat{V} = 1 - a_{1,\mathrm{eff}}\phi_1 + \phi_2 , \tag{14}$$

$$\hat{S} = \hat{S}_\mathrm{c} + \phi_1 + b_1\phi_2 , \tag{15}$$

with

$$a_{1,\mathrm{eff}} = a_1 + 2a_2\Delta P . \tag{16}$$

The theoretical model only applies to critical parts of the various thermodynamic properties. Hence, to investigate whether the theory can account for the anomalous temperature dependence of the response functions we separate the isobaric heat capacity $\hat{C}_P$ , the isothermal compressibility $\hat{\kappa}_T$ , and the thermal expansivity $\hat{\alpha}_V$ into a critical part and a noncritical background part [34]:

$$\hat{C}_P = \hat{C}_{P,\mathrm{cr}} + \hat{C}_{P,\mathrm{b}} \ , \tag{17}$$

$$\hat{\kappa}_T = \hat{\kappa}_{T,\mathrm{cr}} + \hat{\kappa}_{T,\mathrm{b}} \ , \tag{18}$$

$$\hat{\alpha}_V = \hat{\alpha}_{V,\mathrm{cr}} + \hat{\alpha}_{V,\mathrm{b}} \ . \tag{19}$$

The theoretical model only yields expressions for the critical parts of these response functions:

$$\hat{C}_{P,\mathrm{cr}} = \hat{T}\left[\chi_1 + 2b_1\chi_{12} + b_1{}^2\chi_2\right], \tag{20}$$

$$\hat{\kappa}_{T,\mathrm{cr}} = \frac{1}{\hat{V}}\left[a^2{}_{1,\mathrm{eff}}\,\chi_1 - 2a_{1,\mathrm{eff}}\,\chi_{12} + \chi_2 + 2a_2\phi_1\right], \tag{21}$$

$$\hat{\alpha}_{V,\mathrm{cr}} = \frac{1}{\hat{V}}\left[\left(-a_{1,\mathrm{eff}}\,\chi_1\right) + \left(1 - a_{1,\mathrm{eff}}\,b_1\right)\chi_{12} + b_1\chi_2\right]. \tag{22}$$

### 2.3 Mean-field approximation

In the mean-field approximation ($\alpha = 0$, $\beta = ½$) the field $h_3$ can be represented by an asymptotic Landau expansion [45-47]

$$-h_3 = \frac{1}{2}a_0h_2\phi_1^2 + \frac{1}{4}u_0\phi_1^4 - h_1\phi_1, \tag{23}$$

where $a_0$ and $u_0$ are two system-dependent coefficients. Minimization of the potential as a function of $\phi_1$ at constant $h_1$ yields the condition

$$u_0\phi_1^3 + a_0h_2\phi_1 - h_1 = 0, \tag{24}$$

from which one can derive expressions for the scaling density $\phi_2$ and for the scaling susceptibilities in terms of the order parameter $\phi_1$:

$$\phi_2 = -\frac{1}{2}a_0\phi_1^2, \tag{25}$$

$$\chi_1 = \frac{1}{3u_0\phi_1^2 + a_0 h_2}, \tag{26}$$

$$\chi_2 = a_0^2\phi_1^2\chi_1, \tag{27}$$

$$\chi_{12} = -a_0\phi_1\chi_1. \tag{28}$$

## 3 Comparison with experimental data

We have compared the theoretical model for liquid-liquid critical behavior in the mean-field approximation with experimental data for the isobaric heat capacity, the isothermal compressibility and the thermal expansivity of supercooled water. The background contributions in Eqs. (17) - (19) should be smooth analytic functions of temperature and pressure and should not display any singular behavior as a function of temperature or pressure [48]. In this report we have tried the simplest background representation possible, namely a linear function of temperature for each experimental isobar:

$$\hat{C}_{P,\mathrm{b}} = A + B\hat{T}, \tag{29}$$

$$\hat{\kappa}_{T,\mathrm{b}} = C + D\hat{T}, \tag{30}$$

$$\hat{\alpha}_{V,\mathrm{b}} = E + F\hat{T}, \tag{31}$$

where *A*, *B*, *C*, *D*, *E*, *F* are adjustable constants that depend parametrically on the pressure.

The coefficients $a_1$ and $a_2$ in Eq. (10) have been calculated from a fit to the data for the Widom line as specified by Mishima [49]:

$$h_1 = \Delta\hat{T} + a_1\Delta\hat{P} + a_2\left(\Delta\hat{P}\right)^2 = 0. \tag{32}$$

We found the coefficient $b_1$ in Eq. (11) to be very small indicating little asymmetry in the liquid-liquid critical behavior of supercooled water. Hence, in the final fit the coefficient $b_1$ was set equal to zero. The experimental data for the response functions have been obtained as a function of temperature and pressure. At each $T$ and $P$ the scaling fields, $h_1$ and $h_2$, are calculated from Eqs. (10) and (11) and then the order parameter $\phi_1$ from Eq. (24). The molecular volumes in Eqs. (21) and (22) were estimated from an extrapolation of the IAPWS-1995 Formulation for the Thermodynamic Properties of Ordinary Water

Substance for General and Scientific Use [50]. Following Fuentevilla and Anisimov [33] we have neglected the small contribution from the term $2a_2\phi_1$ in Eq. (21).

The coefficients $a_0$ and $u_0$ in the classical Landau expansion (23) and the coefficients of the linear temperature dependence of the non-critical background contributions, given by Eqs. (30) – (32), were determined from fits to the experimental data. The critical parameters were also treated as adjustable constants but subject to the condition that they must be located on the Widom line as given by Eq. (32). The resulting values for the coefficients of the scaled equation of state are presented in Table 1. For the critical parameters we found $P_c = 17$ MPa and $T_c = 229$ K. However, the chi-square of the fit depends relatively weakly on the values chosen for the critical parameters $P_c$ and $T_c$, so that they could not be determined accurately from the fits.

A comparison of our mean-field thermodynamic model with experimental data for the heat capacity is shown in Fig. 1, with experimental data for the isothermal compressibility in Fig. 2, and with experimental data for the thermal expansivity data in Fig. 3. These figures confirm that the assumption of liquid-liquid critical behavior of supercooled water already in a mean-field approximation yields a physically realistic explanation of the anomalous temperature dependence of the isobaric heat capacity, the isothermal compressibility, and the thermal expansivity observed experimentally in supercooled water. Of course, a mean-field approximation cannot account for the divergence of these properties exactly, nor can it deal with weakly divergent properties or nondivergent properties, like the temperature and pressure dependence of volume or entropy, accurately. To obtain a thermodynamic representation of the thermodynamic properties within experimental accuracy it is necessary to apply a nonclassical implementation of the thermodynamic model given by Eq. (1). This is considered in a separate technical report [54].

Table 1: Coefficients of scaled mean-field thermodynamic model.

| | |
|---|---|
| $a_0$ | 0.017 |
| $u_0$ | 0.98 |
| $a_1$ | 0.0734 |
| $a_2$ | 0.0165 |
| $b_1$ | 0 |
| $P_\mathrm{c}$ | 17 MPa |
| $T_\mathrm{c}$ | 229 K |
| $\hat{C}_{P,\mathrm{b}} = A + B\hat{T}$ | $\hat{C}_{P,\mathrm{b}} = 7.161 + 0.615\hat{T}$ |
| $\hat{\alpha}_{V,\mathrm{b}} = E + F\hat{T}$ $P$ = 0.1 MPa | $\hat{\alpha}_{v,\mathrm{b}} = -1.273 + 1.102\hat{T}$ |
| $P$ = 40 MPa | $\hat{\alpha}_{V,\mathrm{b}} = -0.549 + 0.550\hat{T}$ |
| $P$ = 70 MPa | $\hat{\alpha}_{V,\mathrm{b}} = -0.0755 + 0.162\hat{T}$ |
| $P$ = 100 MPa | $\hat{\alpha}_{V,\mathrm{b}} = 0.362 - 0.199\hat{T}$ |
| $\hat{\kappa}_{T,\mathrm{b}} = C + D\hat{T}$ $P$ = 0.1 MPa | $\hat{\kappa}_{T,\mathrm{b}} = 0.163 - 0.0942\hat{T}$ |
| $P$ = 10 MPa | $\hat{\kappa}_{T,\mathrm{b}} = 0.151 - 0.0866\hat{T}$ |
| $P$ = 50 MPa | $\hat{\kappa}_{T,\mathrm{b}} = 0.120 - 0.0665\hat{T}$ |
| $P$ = 100 MPa | $\hat{\kappa}_{T,\mathrm{b}} = 0.0738 - 0.0339\hat{T}$ |

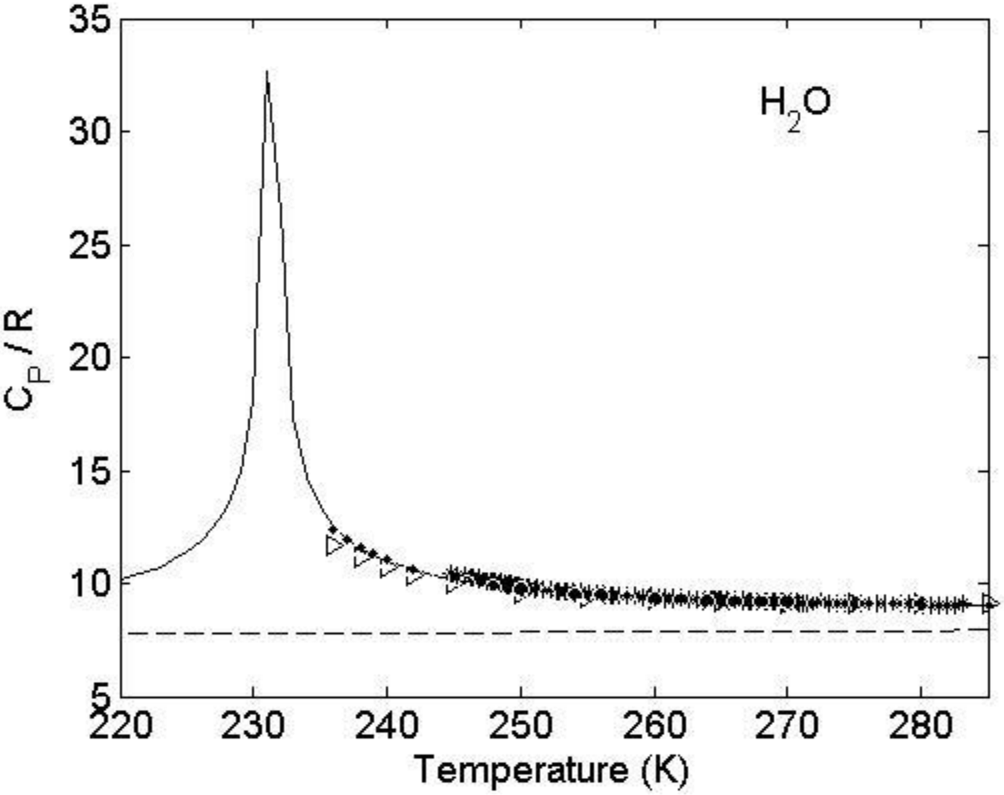

Fig. 1a). Comparison of mean-field equation of state with experimental data for the isobaric heat capacity at ambient pressure as a function of temperature. The curves represent values calculated from the equations presented in this report. The symbols indicate experimental data (diamonds [7], triangles [51], stars [52]). The estimated noncritical background contribution is plotted as a dashed line.

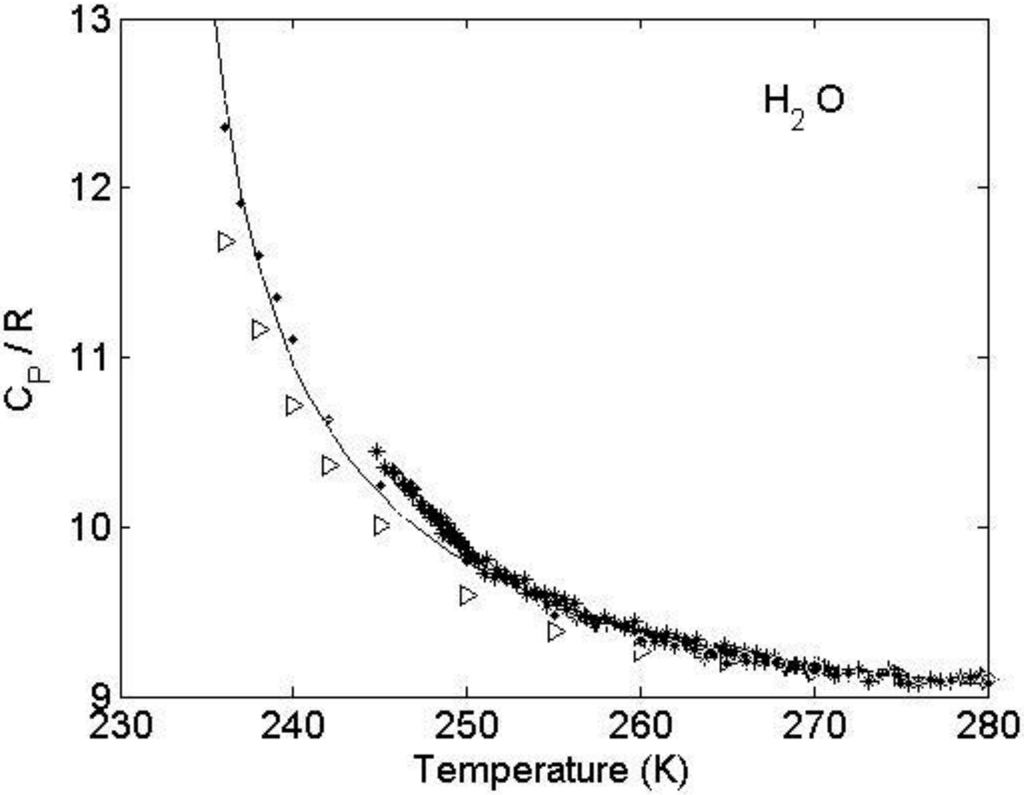

Fig. 1b). Comparison of mean-field equation of state with experimental data for the isobaric heat capacity at ambient pressure as a function of temperature in more detail.

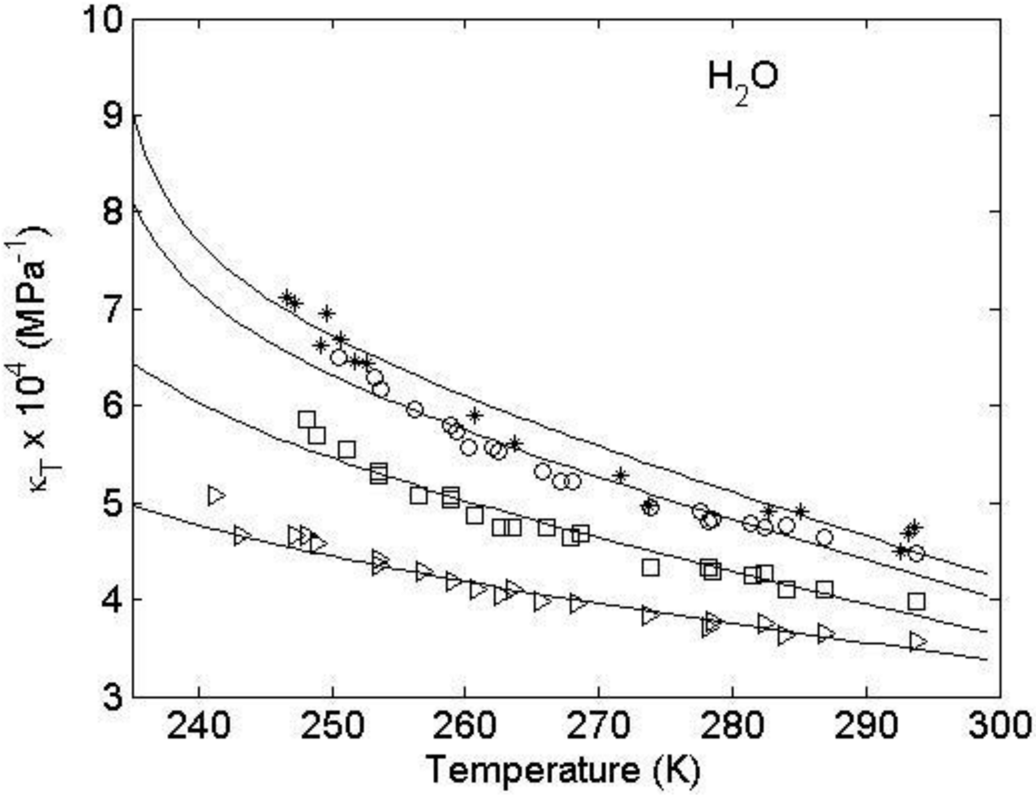

Fig. 2. Comparison of mean-field equation of state with experimental data for the isochoric compressibility along isobars as a function of temperature. The curves represent values calculated from the equations presented in this report. The symbols indicate experimental data (stars 0.1 MPa [4], open circles 10 MPa [5], squares 50 MPa [5], triangles 100 MPa [5]).

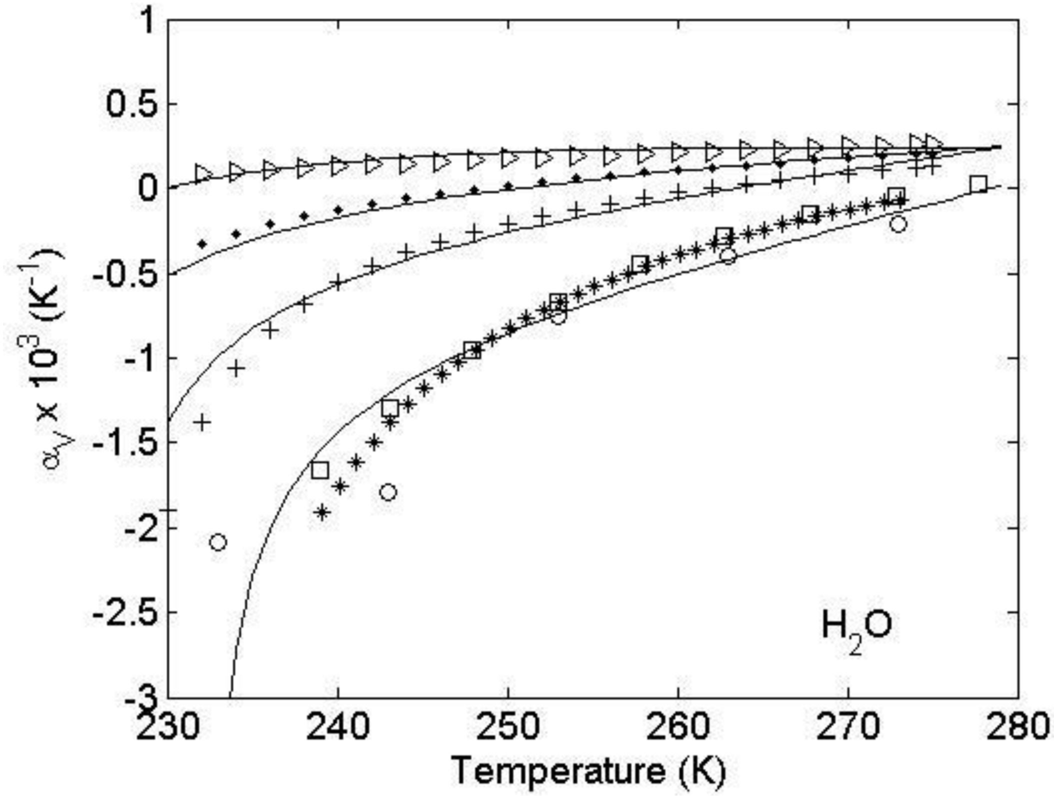

Fig. 3. Comparison of mean-field equation of state with experimental data for the thermal expansivity along isobars as a function of temperature. The curves represent values calculated from the equations presented in this report. The symbols indicate experimental data (squares 0.1 MPa [8], stars 0.1 MPa [9], open circles 0.1 MPa [52], plus 40 MPa [49], diamonds 70 MPa [49], triangles 100 MPa [49]).

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