

On the Validity of the Equations of State of Water in the Metastable Region at High Pressures

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Numerical procedure is applied that permits to find the limits of applicability of IAPWS-95 formulation in the metastable region. The domain of validity of IAPWS-95 on P - T diagram of water substance is determined. In the ranges of temperature 240–300 K and pressure 0–1 GPa, the P - V - T equation of state of Nagornov and Chizhov (Tchijov) [*J. Appl. Mech. Techn. Phys.*, **31**, 378 (1990)] can be a reasonable alternative to IAPWS-95 in the phase-change problems in which the preference should be given to computational efficiency. We show that on ice VII–water melting curve at very high pressures the only reliable equation of state of water is IAPWS-95.

1. Introduction

Modern multiparameter equations of state (EOS) of liquids are presented by the specific Helmholtz free energy f as a function of temperature T and density ρ : $f = f(T, \rho)$ [1]. For liquid water, the most widely used EOS of this type are those of Saul and Wagner (SW EOS) [2], Pitzer and Sterner (PS EOS) [3], and Wagner and Pruß (IAPWS-95) [4], the last one being the EOS recommended for general and scientific use by the International Association for the Properties of Water and Steam. These equations, valid in very wide ranges of pressure P and temperature T , have been developed to accurately reproduce thermodynamic properties of water in the region of its thermodynamic stability.

Quasi-static experiments [5-7] show that liquid water may exist in the metastable state well inside the regions of stability of solid-ice phases, at temperatures as low as 181.15 K at $P = 0.2$ GPa [8]. On the other hand, shock compression of water ice to stresses up to 4.5 GPa [9-11] and dynamic compression of liquid water under shock wave reverberation experiments (peak pressures between 1–5 GPa) [12] indicate that for P - T conditions expected in those experiments water should be in the ice region of the equilibrium phase diagram. The models of non-equilibrium phase transitions in ice-water systems induced by shock compression [13-16] require, therefore, that EOS of water be

valid in the metastable region at high pressures (at least up to 5 GPa). Problems related to metastable water also arise in the models of the processes of high-pressure-shift freezing of food [17, 18].

Equations of state developed specifically for supercooled water have been proposed by Jeffery and Austin [19] and Kiselev and Ely [20]. Both EOS are valid at relatively low pressures (less than 0.3 GPa and 0.19 GPa, respectively). Nagornov and Chizhov (Tchijov) [21] derived a simple P - V - T equation of state (NC EOS) valid for $240 \leq T$ (K) ≤ 300 and $P \leq 1$ GPa. For higher pressures, it is necessary to study the properties of the universal EOS [1-3] at T lower than the corresponding ice–water transition temperatures.

The extrapolation behavior of SW EOS and PS EOS in the metastable region at high pressures was recently investigated by Tchijov [22]. In that study, a numerical algorithm has been proposed that permitted to determine the domain of validity of SW EOS on the P - T diagram of water substance.

In the present paper, we apply the algorithm [22] to IAPWS-95 and find the limits of its applicability in the ice region of the equilibrium phase diagram. This is particularly important since IAPWS-95 now replaces SW EOS in scientific and engineering applications. Then we demonstrate that simple and computationally efficient NC EOS [21] reproduces with sufficient accuracy the values of the specific volume of supercooled water calculated by using IAPWS-95 in the region $240 \leq T$ (K) ≤ 300 , $0 \leq P$

(GPa) ≤ 1 . Finally, we compare the behavior of SW EOS, PS EOS, and IAPWS-95 along ice VI–water and ice VII–water transition lines at pressures up to 20 GPa.

2. EOS of Water in the Metastable Region at High Pressures

2.1. Domain of validity of IAPWS-95 in the metastable region IAPWS-95 is the fundamental equation for the specific Helmholtz free energy f expressed as

$$\frac{f(\rho, T)}{RT} = \Phi^0(\delta, \tau) + \Phi^r(\delta, \tau) \quad (1)$$

where $\delta = \rho/\rho_c$, $\tau = T_c/T$, Φ^0 y Φ^r are the ideal-gas part and the residual part of f , respectively, T_c and ρ_c are the temperature and the density at the critical point, and R is the specific gas constant. IAPWS-95 is valid in the water region of the P - T diagram from the melting curve to 1273 K [23]; for basic properties such as pressure and enthalpy, IAPWS-95 can be extrapolated to extremely high pressures and temperatures. Thermodynamic properties of water can be derived from (1) by differentiation. In particular, pressure P is calculated as

$$P = \rho RT \left(1 + \delta \frac{\partial \Phi^r}{\partial \delta} \right). \quad (2)$$

Equation (2) is the P - V - T EOS of water in which pressure P is the function of independent variables temperature T and density ρ .

In the applications in which phase changes in ice-water systems come into play, a natural pair of independent thermodynamic parameters is P and T . In this case, non-linear algebraic equation (2) must be resolved with respect to ρ by using a numerical iterative solver.

In order to find the domain of validity of IAPWS-95 in the metastable region of P - T diagram, we apply a numerical algorithm previously used by Tchijov [22] to study the extrapolation properties of SW EOS and PS EOS. For a given value of P_* ($0 \leq P_*$ (GPa) ≤ 20), we calculate the value of ρ inside the region of thermodynamic stability of water. Then we move along the isobar $P = P_*$ into the region of supercooled water, using a small temperature decrement dT . At each step, we apply a Newton-Raphson method using as initial

approximation the value of ρ found at the previous step. The procedure is repeated until one of the following occurs: (i) the convergence of the method fails; (ii) the iterations converge to physically meaningless values (negative or very small positive densities). For each P_* , we find the value T_* of the temperature at the last point on the isobar $P = P_*$ where the Newton-Raphson iterations were successful. The results of calculations for $0 \leq P_*$ (GPa) ≤ 5 are presented in Fig. 1. Thick dashed line is the locus of the points (T_*, P_*) which is considered a boundary of the domain of validity of the IAPWS-95 in the metastable water region. For comparison, the boundary of the domain of validity of SW EOS is also presented (thin dashed line in Fig. 1). One can see that IAPWS-95 can be extrapolated to substantially lower temperatures than SW EOS. The density of water along the isobars is depicted in Fig. 2. The dashed line in Fig. 2 consists of the points (T, ρ) that correspond to the boundary between the stable and the metastable water regions (solid line in Fig. 1). The extrapolated values of density exhibit reasonable behavior in the whole domain of validity of IAPWS-95 in the metastable region except for the proximity of IAPWS-95 limit.

2.2. IAPWS-95 and NC EOS at $240 \leq T$ (K) ≤ 300 and $0 \leq P$ (GPa) ≤ 1

One of the problems that arise in the application of fundamental EOS of water [2-4] to modeling of phase-change processes is the necessity to resolve equation (2) by numerical iterations each time the density ρ or the specific volume $V = 1/\rho$ of water is required as function of P and T . The iteration procedure is time-consuming and reduces the efficiency of EOS, especially in computationally demanding applications. For example, Kowalczyk et al. [24] performed numerical simulation of convection driven high pressure induced ice-water phase changes. To calculate the specific heat of water they used SW EOS-based formula, but to compute the density of water they used NC EOS. Referring to SW EOS, the authors of [24] note: “The density of water can also be calculated with this equation of state but the time of the computation is much longer due to the more complicated form of equation than the equation of Nagornov and Chizhov.”

NC EOS [21] represents specific volume V of water as a function of P and T :

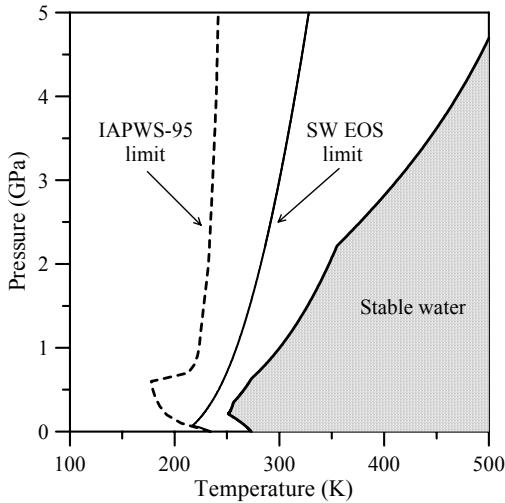


Fig. 1. The P - T diagram of water substance. Thick dashed line is the left boundary of the domain of validity of IAPWS-95.

$$V = \frac{V_0(T)}{[1 + m\beta_0(T)P]^{1/m}}, \quad (3)$$

where $V_0(T)$ and $\beta_0(T)$ are specific volume and coefficient of isothermal compressibility at $P_0 = 1$ bar ($=10^5$ Pa), and m is a constant. $V_0(T)$ is a rational function and $\beta_0(T)$ is a fifth-order polynomial of T ; the explicit expressions for these functions can be found in [21]. Equation (3) is simple and computationally efficient. It has been successfully used to study equilibrium phase transitions in ice-water systems to pressures up to 1 GPa [21, 25].

In Fig.3, the relative differences between the values of specific volume of water calculated by using NC EOS and IAPWS-95 are presented. In the ranges of temperature $240 \leq T(K) \leq 280$ and pressure $0 \leq P(\text{GPa}) \leq 1$ that correspond to the domain of validity of NC EOS, the relative differences do not exceed 0.7%. In the above-mentioned ranges of T and P the NC EOS may be a reasonable substitute for IAPWS-95 in the phase-change problems in which high accuracy of IAPWS-95 may be sacrificed in favor of computational efficiency of NC EOS.

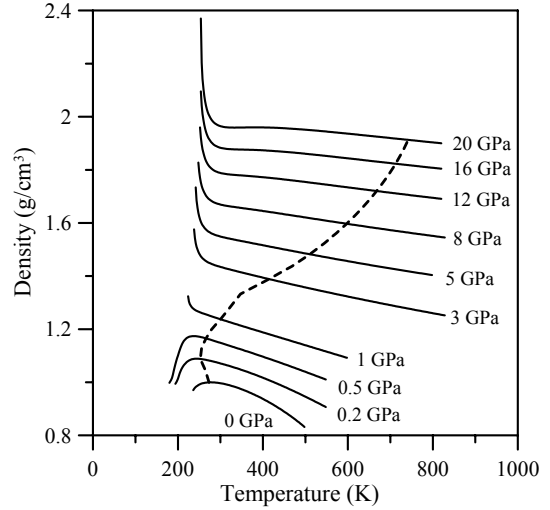


Fig. 2. The isobars of water computed by using IAPWS-95 (solid lines). Dashed line is the boundary between the stable and the metastable water regions.

3. EOS of Water on the Phase Transition Lines at High Pressures

A problem related to the extrapolation properties of the equations of state of water [2-4] in the metastable region is the behavior of these EOS on the liquid-solid transition lines at high pressures. Tchijov et al. [26] studied the equilibrium phase transitions water-ices Ih, III, V, and VI at pressures up to 2 GPa. SW EOS was used in [26] to calculate thermodynamic properties of water.

In this section, we compare the density of water computed by using PS EOS, SW EOS, and IAPWS-95, with the density of corresponding ices on the melting curves ice VI-water and ice VII-water, at pressures up to 20 GPa. The equations of the lines of phase transition are taken from the contribution of Wagner et al. [27]. The densities of ices VI and VII are calculated by using the relationships from the works of Tchijov et al. [26] and Yingwei Fei et al. [27], respectively. The results are presented in Fig. 4. One can see that PS EOS returns too small values of density at pressures below 3 GPa. Therefore, it is not reliable in the low-pressure region. At pressures above 14 GPa (SW EOS) and 17 GPa (PS EOS), the computed densities of water exceed the density of ice VII, which is physically incorrect. By contrast, IAPWS-95 exhibits quite reasonable behavior on the ice VI-water and ice VII-water transition lines in the

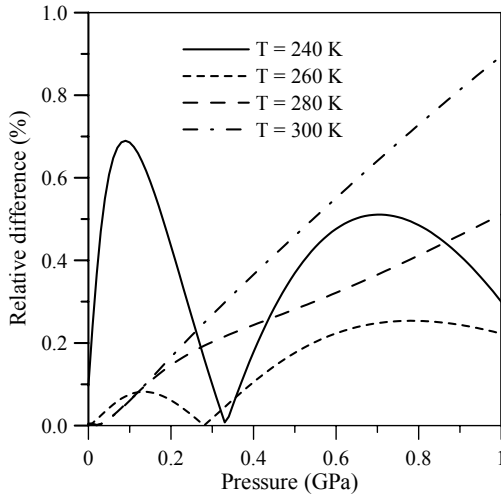


Fig. 3. Relative difference $100|V_1 - V_2|/V_1$. V_1 and V_2 are the values of specific volume of water calculated by using NC EOS and IAPWS-95, respectively.

pressure range 0.6324 GPa (the pressure at the triple point ice V – ice VI – water) to 20 GPa. For this reason, IAPWS-95 is the only EOS of water among the considered equations of state that can be used on the lines of phase transitions both at low and at high pressures.

4. Conclusions

The domain of validity of IAPWS-95 in the metastable region of the phase diagram of water substance is determined. This domain extends to significantly lower temperatures than that of SW EOS.

In the rectangular area $240 \leq T(K) \leq 280$, $0 \leq P(\text{GPa}) \leq 1$ of the P - T diagram of water, NC EOS can be a reasonable alternative to IAPWS-95 in the ice-water phase-change problems in which preference should be given to computational efficiency.

On the melting curves ice VI–water and ice VII–water which cover the range of pressures 0.6324–20 GPa, the only valid EOS of water is IAPWS-95. The values of density of water at very high pressures calculated by using other equations of state (PS EOS and SW EOS) are in contradiction with the density of ice VII on the ice VII–water transition line.

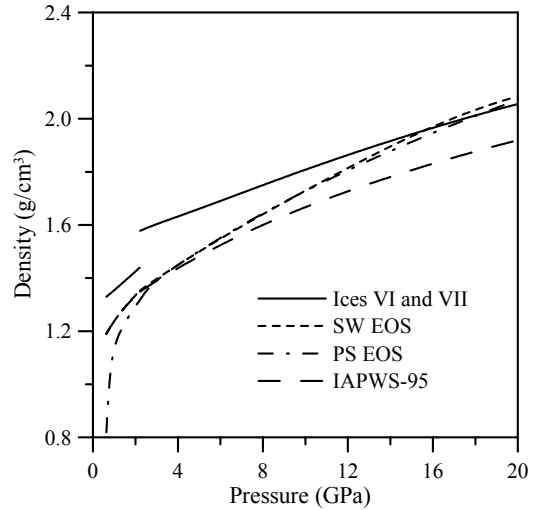


Fig. 4. Density of water and ices VI and VII on the ice VI–water and ice VII–water melting curves.

Acknowledgements

The authors are grateful to National University of Mexico for financial support of this work by the PAPIIT Grant No. IN100405.

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