

Predicted Thermodynamic and Physical Boundary of the Superheated and Stretched Water by some EOS and the Fluctuation Theory of Relaxation

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ABSTRACT

In the present work, we have predicted the thermodynamic (mechanical) and physical (kinetic) boundary in superheated and stretched water using several equations of state (EOS), some accurate and other less accurate ones but closer to physical models. The position and the curvature of the SP have been determined using IAPWS-97, Speedy and others EOS.

The maximum negative pressure that a stretched liquid can sustain without cavitation (nucleation and growth of a vapor bubble) is its tensile strength. Previous theoretical estimation of the tensile strength for the superheated water has been approximated from 270 to 6000 bar while experimental data yielded values from 1 to 277 bar. New coefficients have been obtained by regressing some of the previous EOS according to the existing experimental data of the stretched and superheated water, a new location of the SP has been determined and a more realistic description of the maximum density temperature (TMD) is succeeded.

The kinetic SP lies above the SP, qualitatively reproduces its shape and represents the boundary beyond which no equilibrium thermodynamic state can exist. Starting from the critical point, the kinetic SP first traces the physical boundary of the metastable states in superheated water, and then passes through negative pressures defining the limit of stability in stretched water. In order to calculate the kinetic SP in superheated and stretched water, we apply the fluctuation theory of relaxation taking into account the curvature effect on the surface tension.

The parameters of the kinetic SP according to fluctuation theory of relaxation are given in analytic forms with the aid of a modified van der Waals EOS with coefficients functions of the temperature. The kinetic SP is expressed by a new equation in terms of the temperature and the density calculated. A new form for the parameter g of the kinetic equation is proposed, that is very accurate from the triple point up to temperatures close to the critical point.

An analytic form in terms of the temperature and the density expresses the TMD line. The resulting estimate for the TMD is plotted and is verified that this curve intersects the SP at the minimum that occurs at a temperature 328 K and a pressure -183 MPa. The expected extension of the TMD line from the minimum up to the liquid ice III phase transition: is plotted and the intersection with the Melting Line of ice III, occurs at a temperature 254.4 K and a pressure 265 MPa. From the other side of the minima, the TMD line reentrant into the stable area of SP with positive slope.

KEYWORDS: Metastable liquid, superheated and stretched water, mechanical SP, kinetic SP, bimodal, fluctuation theory of relaxation.

INTRODUCTION

Superheated water exists in a state of precarious equilibrium. However, experiments show that a condition is eventually reached in which boiling can no longer be prevented and a new phase appears suddenly. This is because extraneous impurities merely facilitate what spontaneous molecular motion can also accomplish. The possibility of superheating a liquid above its boiling point is not limited to water. All liquids and their mixtures can be brought to a condition whereby minor external disturbances trigger the sudden appearance of one or more new phases, including, in the case of some liquid mixtures, another liquid phase of different composition. Such a condition of precarious equilibrium is called metastable equilibrium. Superheated liquids are said to be metastable. Much of what we know about metastable liquids derives from careful experiments on small, high-purity samples [1].

The limit of superheat of a liquid is the maximum temperature that a liquid can attain before it spontaneously vaporizes. This upper limit on the metastable, superheated state depends on the ambient pressure that the liquid experiences. Mechanical stability considerations of classical thermodynamics permit the calculation of the thermodynamics limit of superheated. This limit is the locus minima in the liquid isotherms, i.e. the SP curve of the liquid, which satisfies the

equations $\left[\frac{\partial p}{\partial v}\right]_T = 0$ and $\left[\frac{\partial^2 p}{\partial v^2}\right]_T > 0$. The SP curve separates the metastable region, which

satisfies the mechanical stability condition $\left[\frac{\partial p}{\partial v}\right]_T < 0$, from the unstable region, for which

$$\left[\frac{\partial p}{\partial v}\right]_T > 0.$$

The volume of the liquid decreases and the rate of heating increases determine the bubble nucleation flux, the probability for a bubble nucleus growing beyond the critical size in a given time decreases and the limit of superheat which can be achieved increases [2].

Thermodynamic, mechanical stability considerations place an upper limit on the domain of metastable fluid. For an approximation of this limit, the so-called Spinodal (SP), an accurate EOS is needed. To demonstrate the effect of the used equation, the SP has been determined from several equations of state. The position and the curvature of the SP depend on the EOS used for computation. It is well known that a fluid can be supersaturated without the occurrence of a phase transition even though its state is such that it lies within the two-phase region. This supersaturation is a metastable state, which many persist for a considerable length of time. Being responsible for many phenomena, which appear during phase transition the metastable state, has a significant effect on transient processes and heat transfer.

It is well established that the microscopic origin of the anomalies is related to increase hydrogen bonding between water molecules as the temperature is lowered. However, the thermodynamic properties that result from the microscopic behavior, dictated by the hydrogen bonding interactions, are not well established. Specifically, there are two different thermodynamic scenarios that have been proposed for the metastable behavior of water, which invoke distinct thermodynamic mechanisms for an explanation of anomalous behavior:

- 1) **Retracing SP scenario.** Speedy [3] showed that the Temperature of Maximum Density (TDM), which at ambient conditions is negatively sloped in the (p, T) plane, remains

negatively sloped at negative pressures. The inevitable intersection of the TDM and the liquid-gas SP results in a retracing of the SP as a consequence of thermodynamic consistency alone. However, there is no clear argument necessitating such a retracing SP to reach positive pressures.

- 2) **Critical-point scenario.** Poole et al [4] attempted to calculate the location of the liquid-gas SP in computer simulations of water with commonly used model potentials. They failed to observe the retracing of the SP. The slope of TMD does not remain negative, but changes sign at negative pressures, thus removing the thermodynamic requirement for the SP to retrace.

MECHANICAL SPINODAL

Wan der Waals Equation of State (EOS) :

EOS have been very valuable tools both in producing predictive calculations of the (p, v, T) behavior of fluid phases as well as interpreting and rationalizing that behavior even as a molecular level. It was van der Waals who first tackled this problem successfully in the late nineteenth century (1873). His well-known equation of state:

$$\left(p_r + \frac{3}{v_r^2} \right) \cdot \left(v_r - \frac{1}{3} \right) = \frac{8}{3} \cdot T_r \quad (1)$$

where a and b are parameters, the first related to the intensity of the molecular attractive forces, the second expressing the core molecular volume of the spaces, constitutes the simplest example of a cubic EOS capable of explaining the liquid-gas equilibrium, the critical behavior and fluids' metastability as well. We will focus our attention in the later case. For a quantitative description of fluids' behavior there are currently much more rigorous equations of state than the van der Waals one, although their usefulness comes at the cost of lesser physical insight. Therefore, for sake of clarity and simplicity, we will use the van der Waals equation of state and in the second part of present work revised vdW EOS is proposed.

The thermodynamic limit of metastability, the SP line, will in fact never be reached, since homogeneous nucleation can be triggered by local density fluctuations. These fluctuations account for the appearance of gaseous microcavities, which increase considerably in number and size as the SP line is approached.

At sufficiently low temperatures note that this isotherm extends to the absolute negative pressure region on the "liquid side", but not on the "gas side". This is the natural corollary of the fact that a liquid can be stretched while neither a gas nor the state of equilibrium between and liquid can. A liquid can be called superheated either if its temperature is higher than corresponding boiling temperature at a given pressure or if its pressure is lower than the corresponding vapor pressure at a given temperature. In any case it is always stretched (or under tension) in comparison to the liquid phase at the liquid-gas equilibrium, a situation in which it will relax under the constraints of constant volume and temperature. At sufficiently strong tensions the liquid can be at absolute negative pressures [5].

As van der Waals EOS numerous other empirical relations have been proposed for describing the p-v-T behavior of gases and liquids, each of which is designed for a particular application. Some of these equations are quite accurate over a small range of temperature and density;

others apply to the properties in the gaseous and liquid phases. Firstly is given two two-constant EOS - those of van der Waals and Berthelot. These equations are handy because of their simple analytic form. Of more cumbersome form, but considerably more useful for accurate work, are the equations of Hipman (with arbitrary constants) and Eberhart (with three arbitrary constants). All these equations of state with the arbitrary constants for water are followed [6].

Berthelot EOS:

$$\left(p_r + \frac{3}{T_r \cdot v_r^2} \right) \cdot \left(v_r - \frac{1}{3} \right) = \frac{8}{3} \cdot T_r \quad (2)$$

Hipman EOS:

$$\left(p_r + \frac{a}{(v_r - b) \cdot (T_r \cdot v_r - c)} \right) \cdot (v_r - d) = s \cdot T_r \quad (3)$$

Constants for water:

a = 10.3347, b = 0.2523, c = -1.7750, d = 0.2927 and s = 4.230

Eberhart EOS:

$$\left(p_r + \frac{(n+1)}{(n-1) \cdot T_r^m \cdot v_r^n} \right) \cdot \left(v_r - \frac{n-1}{n+1} \right) = z \cdot T_r \quad (4)$$

Constants for water:

n = 1.574, m = 0.62 and z = 4.264

IAPWS release

For industrial use, the proof of the thermodynamic properties of water and steam is the International Association for the Properties of Water and Steam (IAPWS) latest release called "IAPWS Industrial Formulation 1997", which replaces the previous industrial formulation "The 1967 IFC-Formulation for Industrial Use" [7]. The IAPWS Industrial Formulation 1997 consists of a set of equations covering the following range of validity:

(273.15K ≤ T ≤ 1073.15K, p ≤ 100Mpa) and (1073.15K ≤ T ≤ 2273.15K, p ≤ 10Mpa).

The metastable vapor region is a subregion of the region 2 and it is obtained the same equation but with different numerical values for coefficients. For the subregion of metastable liquid the properties in the stable single-phase liquid region (region 1) also yields reasonable values.

Experimental results

In the region of superheated liquid there is a study with experimental data for water by Chukanov and Skripov (1970) and plotted many isotherms in the temperature range 139.1 to 213.0°C, with a deep penetration into the metastable region [8]. The experimental apparatus used in the experiments with water consists of a glass piezometer (pressure gage), a thermostat, a pressure chamber and a system for varying the pressure.

Although the experimental data defer a lot with the calculated values, which are obtained by the above empirical equation of state, the difference between the theoretical obtained by IAPWS 1997 and experimental specific volumes never exceeded 0.03% not only for the stable but also for the metastable states. More certain as it seems on the Table 3 of the Appendix the experimental values tend to be equal to these given by IAPWS 1997.

In principle the limit of stability maybe located directly by extrapolating experimental values of $\left(\frac{\partial p}{\partial v}\right)_T$ along an isotherm to find the pressure $p_s(T)$ at which $\left(\frac{\partial p}{\partial v}\right)_T \rightarrow 0$ or by extrapolating along an isobar at p to find the temperature $T_s(p)$ at which $\left(\frac{\partial p}{\partial v}\right)_T \rightarrow 0$. In practice several thermodynamically equivalent extrapolation methods have been used in the region p-T space near the critical point.

The SP of the van der Waals and Eberhart EOS are shown on Fig 1 in comparison with experimental results by Skripov [9]. Both EOS represent the SP line only qualitatively. The saturation line is calculated by IAPWS 1992 relative release [10]. In the Fig. 2 are shown SP of the Berthelot and Hipman EOS in comparison with experimental data of Skripov [9]. As it is clearly shown the SP of these EOS are close enough to the exp. SP.

Two scenarios

Henderson and Speedy extended the measurements precise of pressure-temperature isochores to -15.8 MPa and into the doubly metastable region. In order to perform the long extrapolation of the precise pVT data which is available on water in the range of 0-100°C and 0-100 MPa, it is introduced a reliable EOS by Speedy [3, 11], which has some theoretical justification.

$$p = p_s + \sum_{n=1} \left[\frac{1}{n!} \cdot \left(\frac{\partial^n p}{\partial \rho^n} \right)_{T, p_s} \cdot (\rho - \rho_s)^n \right] \quad (5)$$

To obtain a useful equation of state, it is necessary to make assumptions and one of these is that the series in Eq. 5 converges rapidly. When terms $n \geq 3$ are dropped from Eq. 5, it can be written in the simple form:

$$1 - \frac{p}{p_s} = B \cdot \left(\frac{v_s}{v} - 1 \right)^2 \quad (6)$$

where:

$$B = - \left(\frac{\partial^2 p}{\partial \rho^2} \right)_{T, p_s} \cdot \frac{1}{2 \cdot p_s \cdot v_s^2} \quad (7)$$

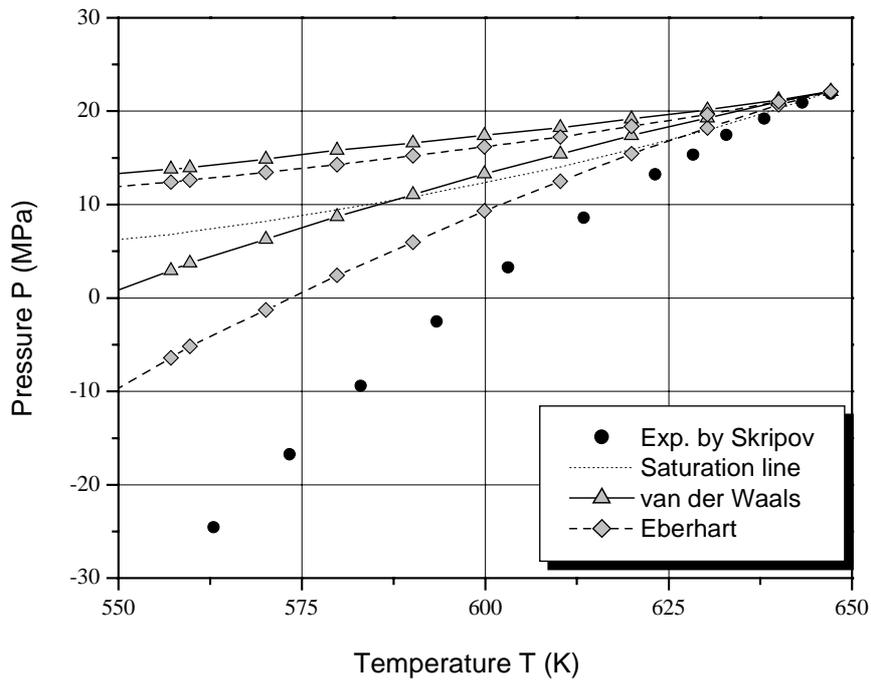


Fig. 1 SP computed by EOS of Van der Waals and Eberhart in comparison with exp. results by Skripov.

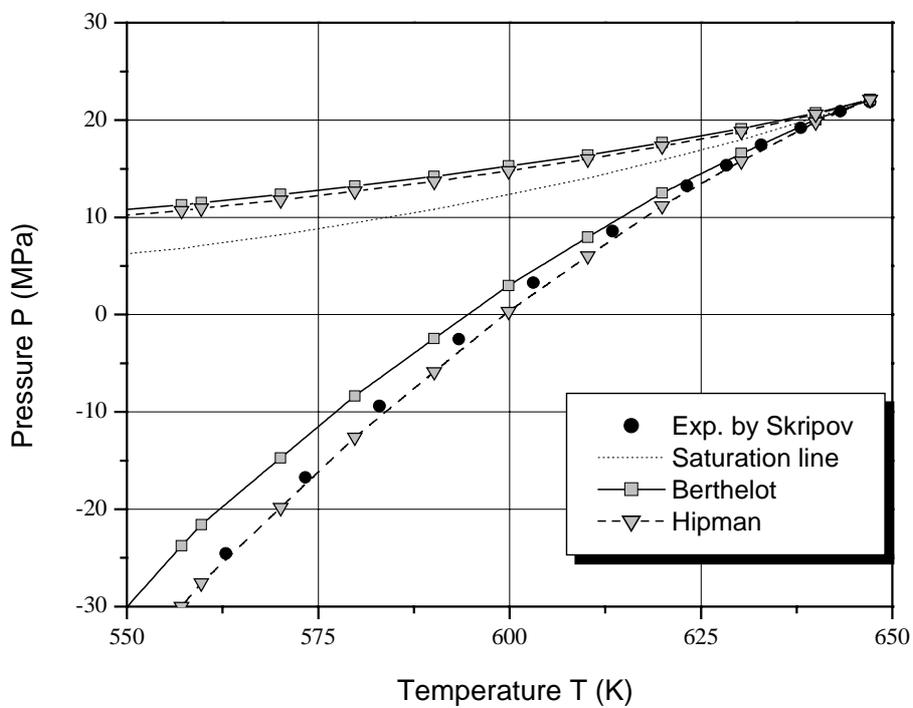


Fig. 2 SP computed by EOS of Berthelot and Hipman in comparison with exp. results by Skripov.

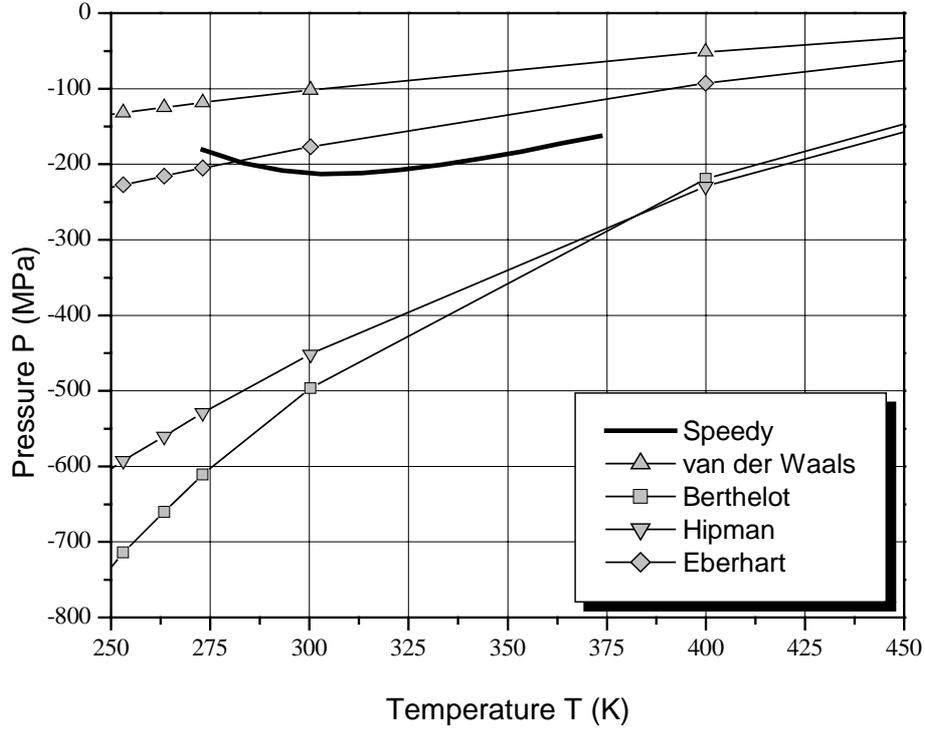


Fig. 3 SP computed by different EOS and computed results extrapolating by the proposed equation for stretched water by Speedy.

As it shown in Fig. 3 the curve of the p-T diagram retraces at values of relative pressure under zero, in opposite with the applying EOS. The first derivative of the appearing equations of state $\frac{\partial p}{\partial T}$ is always positive and as a result there is no retracing. In this way are proposed two different scenarios obtained by the bibliography.

According the first scenario thermodynamic analysis is based on two assumptions: i) the liquid under investigation has somewhere in the (p, T) plane a Temperature of Maximum Density (TMD) line with a negative slope, and ii) the liquid-gas SP is not retracing. It is considered the general behavior of the TMD and Temperature of Extremal Compressibility TEC lines, knowing that in a finite window of the (p, T) plane the TMD locus in negatively sloped and that the liquid-gas SP is not retracing. It is also assumed in this scenario that the TMD line lies in the liquid region, i.e., that all the temperatures, at which the TMD line is observed, are less than the liquid-gas critical point.

On the other hand there is the scenario that introduced by Srikanth Sastry et al. [12], which is the simplest one that consistent with experimental observations. The significance of their work is not to have proved a particular scenario, but rather to provide a simpler explanation of experimental observations than those recently emphasized. In the point of the retracing of SP that this scenario proposes, agrees the equation of Speedy, which is described above. According to the stability limit conjecture, water has a continue SP curve bounding the superheated, supercooled and stretched metastable states.

KINETIC SPINODAL

Kinetic boundary of metastable liquids according to fluctuation theory of relaxation.

In the present paper have been adopted the kinetic theory of relaxation of metastable state developed by Patashinskii and Shumilo [13, 14] and the studies based on this theory for the kinetic boundary of metastable water by Kiselev [15].

According to the transitions phase theory of thermodynamics, the limit of fluid metastable states is the SP, the locus of the states of infinite compressibility [16]. Nevertheless, long before reaching the SP state, the metastable cycle shrinks physically [17,18]. The classical theory of homogenous nucleation determines the cycle of the metastable state, as the mean time of formulation of a critical nucleus of the stable phase t_M , depending on the thermodynamic as well as the transport properties of the fluid. According to this theory, as metastable phase is defined the metastable fluid's short-lived state, which remains a thermodynamic one. Patashinskii and Shumilo [13,14] established in their fluctuation theory of relaxation of metastable states, the physical limits of metastable states in the form of a locus with a shortened mean time of the critical nucleus formation of the stable phase t_M , in relation to the characteristic time of alternation of fluctuations to local equilibrium t_R . In case that $t_M < t_R$, the whole theory of homogenous state becomes no longer valid and due to the fluctuations, the initially homogeneous state becomes no longer valid and, due to the fluctuations, the initially homogeneous state swifts, in time $t_M = t_R$, to an heterogeneous state [19].

Both times, t_M and t_R , depend on the kinetic properties of the liquid, but the ratio t_M/t_R depends only on the thermodynamic properties. Therefore, the physical boundary of the metastable state, or kinetic SP, is completely determined by the equation [15]:

$$\left(\frac{u_2}{u_3^{4/3}} \right)_{KS} = \frac{1}{g} \cdot \left(\frac{k_B \cdot T}{W_{\min}} \right)^{2/3} \quad (8)$$

where k_B is Boltzmann's constant and W_{\min} the nucleation barrier for the spherical vapor bubble in the metastable liquid and the parameters u_2 , u_3 , and g of the effective Hamiltonian are related to the thermodynamic parameters of a real physical system.

$$\frac{u_2}{k_B \cdot T \cdot \rho} = \bar{\mu}_{\rho}(T, \rho) = \frac{1}{R \cdot T} \cdot \left(\frac{\partial P}{\partial \rho} \right)_T \quad (9)$$

and

$$\frac{u_3}{\frac{1}{2} \cdot k_B \cdot T \cdot \rho} = \bar{\mu}_{\rho\rho}(T, \rho) = \frac{1}{R \cdot T} \cdot \left[- \left(\frac{\partial P}{\partial \rho} \right)_T + \rho \cdot \left(\frac{\partial^2 P}{\partial \rho^2} \right)_T \right] \quad (10)$$

$$\frac{2^{4/3}}{(k_B \cdot T \cdot \rho)^{1/3}} \left(\frac{u_2}{u_3^{4/3}} \right)_{KS} = \frac{\bar{\mu}_{\rho}(T, \rho)}{\bar{\mu}_{\rho\rho}(T, \rho)} = r_{\mu}(T, \rho) \quad (11)$$

$$r_{\mu}(T, \rho) = \frac{k_B \cdot T \cdot \rho^{\frac{1}{3}}}{2^{\frac{4}{3}} \cdot g} \cdot \frac{1}{W_{\min}^{\frac{2}{3}}} \quad (12)$$

Kiselev [15] proposes as a good approximation of the parameter g in Eq (12) the relation:

$$g = k_B \cdot T \cdot \rho_c^{\frac{1}{3}} \quad (13)$$

where ρ_c is a critical density.

The critical radius and the nucleation barrier for the spherical vapor bubble in the metastable liquid are [15]:

$$r_c = \frac{2 \cdot \sigma}{P^*} \cdot \left[\exp\left(\frac{v_L^* \cdot (P - P^*)}{R \cdot T}\right) - \frac{P}{P^*} \right]^{-1} \quad (14)$$

$$W_{\min}(r_c) = \frac{16\pi}{3} \cdot \sigma \cdot \left(\frac{\sigma}{P^*}\right)^2 \cdot \left[\exp\left(\frac{v_L^* \cdot (P - P^*)}{R \cdot T}\right) - \frac{P}{P^*} \right]^{-2} \quad (15)$$

where superscript * denotes the parameters on the coexistence curve.

Application using a modified Van der Waals equation

Kiselev [15] has been shown that the van der Waals equation only qualitatively reproduces the form of the kinetic SP that lies above the thermodynamic SP ($P_S < P_{KS} < 0$).

In this part of the paper the coefficients a and b of the van der Waals equation for the water are calculated in terms of the temperature fitting the data coming from analytic equation of Saul and Wagner [20] along the binodal and SP.

Then the van der Waals equation reads:

$$P = \frac{R \cdot T}{(1 - b(T) \cdot \rho)} - a(T) \cdot \rho^2 \quad (16)$$

The correlations for $a(T)$ and $b(T)$ have been written in the forms:

$$a(T) = \sum_{n=0}^5 v a_n \cdot T^n \quad (17)$$

$$b(T) = \frac{1}{10^4} \cdot \sum_{n=0}^5 v b_n \cdot T^n \quad (18)$$

Table 1 gives the values of the coefficients va_n and $vb_n, n = 0 \dots 5$. Table 2 gives the values of the pressure P_c , the temperature T_c and the density ρ_c of the water at the critical point and the corresponding values for the coefficients a_{vdw} and b_{vdw} of classical Van der Waals equation. The ratio $\frac{a(T)}{a_{vdw}}$ and $\frac{b(T)}{b_{vdw}}$ are illustrated in the diagrams of Figs. 4 and 5, respectively.

Table 1 The coefficients va_n and $vb_n, n = 0 \dots 5$ of Eqs. 17 and 18 respectively.

va_0	-14332.201	vb_0	-157.78179
va_1	175.44681	vb_1	2.0656409
va_2	-0.82527341	vb_2	-0.010121029
va_3	0.001965147	vb_3	2.4406219E-5
va_4	-2.344612E-6	vb_4	-2.8948671E-8
va_5	1.1126847E-9	vb_5	1.3513366E-11

Table 2 The pressure P_c , the temperature T_c and the density ρ_c of the water at the critical point and the corresponding values for the coefficients a_{vdw} and b_{vdw} of classical vdW EOS.

$P_c = 22.064 \text{ MPa}$	$T_c = 647.096 \text{ K}$	$\rho_c = 322 \text{ Kg/m}^3$	$R = 461.89 \frac{\text{J}}{\text{Kg} \cdot \text{K}}$
$a_{vdw} = \frac{9}{8} \frac{R \cdot T_c}{r_c} = 1044.246 \frac{\text{N} \cdot \text{m}^4}{\text{Kg}^2}$		$b_{vdw} = \frac{1}{3 \cdot \rho_c} = 1.035197\text{E-}3 \frac{\text{m}^3}{\text{Kg}}$	

The Mechanical SP Line

As first suggested by Speedy and Angell [21] for the SP line for water in the p-T plane, starting from the critical point the pressure decreases with decreasing T reaching a minima. From this point SP is reentrant and the pressure increases with decreasing T further and passes back to positive pressures. This SP line in the mean field approach is very well.

Illustrated by the modified van der Waals equation following the equations obtained from the

condition $\left(\frac{\partial P}{\partial \rho}\right)_T = 0$:

$$T = 2 \cdot a(T) \cdot \frac{\rho}{R} \cdot (1 - b(T) \cdot \rho)^2 \quad (19)$$

$$P = a(T) \cdot \rho^2 \cdot (1 - 2 \cdot b(T) \cdot \rho)^2 \quad (20)$$

Figure 6 shows the density of liquid water along the binodal/ Eq (16) and SP as a function of temperature calculated with the Eq (19). The resulting estimate for the P-T, SP line is plotted in Fig. 7.

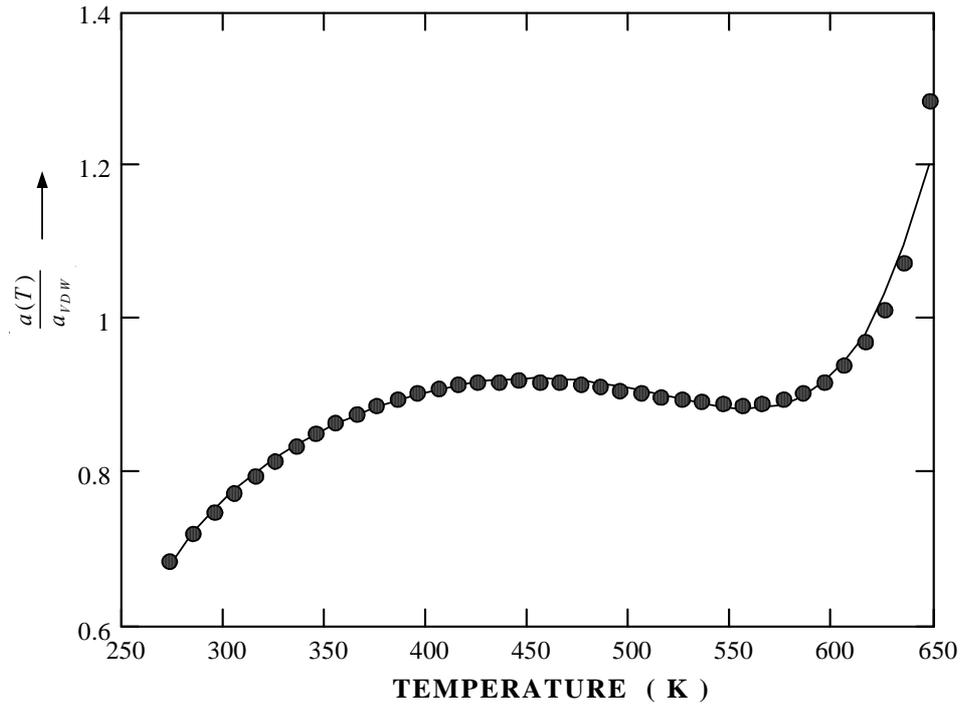


Fig. 4 The ratio $\frac{a(T)}{a_{vdw}}$ of the proposed in this work Van der Waals EOS /Eq. 16. The graphical representation of Eq.17 (correlation) corresponds to the solid line and the calculated points correspond to the solid circle symbols.

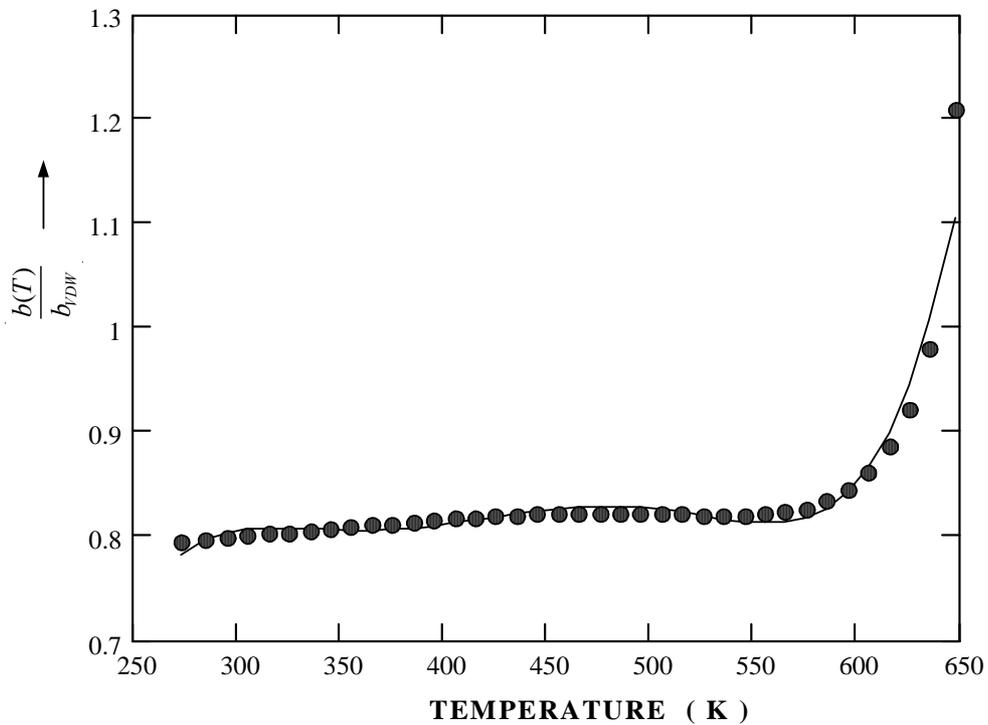


Fig. 5 The ratio $\frac{b(T)}{b_{vdw}}$ of the proposed in this work Van der Waals EOS /Eq. 16. The graphical representation of Eq.17 (correlation) corresponds to the solid line and the calculated points correspond to the solid circle symbols.

The Kinetic SP Line (KS)

Applying Eq. 9 and 10 with Van der Waals EOS in the form of Eq. 20, it is obtained:

$$\bar{\mu}_\rho(T, \rho) = \frac{1}{R \cdot T} \cdot \left(\frac{\partial P}{\partial \rho} \right)_T = \frac{1}{(1-b(T) \cdot \rho)^2} - \frac{2 \cdot \rho \cdot a(T)}{R \cdot T} \quad (21)$$

$$\bar{\mu}_{\rho\rho}(T, \rho) = \frac{1}{R \cdot T} \cdot \left(\frac{\partial^2 P}{\partial \rho^2} \right)_T = \frac{2 \cdot b(T)}{(1-b(T) \cdot \rho)^3} - \frac{2 \cdot a(T)}{R \cdot T} \quad (22)$$

and

$$r_\mu(T, \rho) = \frac{\bar{\mu}_\rho(T, \rho)}{\bar{\mu}_{\rho\rho}(T, \rho)^{\frac{4}{3}}} \quad (23)$$

According to the Eq. 12 and 15, it is obtained:

$$r_\mu(T, \rho) = \frac{k_B \cdot T \cdot \rho^{\frac{1}{3}}}{2^{\frac{4}{3}} \cdot g} \cdot \frac{1}{\left(\frac{16\pi}{3} \right)^{\frac{2}{3}} \sigma(T)^2} \cdot \frac{P^*(T)^{\frac{4}{3}}}{\sigma(T)^2} \cdot \left[\exp\left(\frac{v_L^* \cdot (P - P^*)}{R \cdot T} \right) - \frac{P}{P^*} \right]^{\frac{4}{3}} \quad (24)$$

Using smoothed the experimental data obtained by Zheng et al [22, 23] for the density in the nucleation limit of stretched water and the corresponding pressure values calculated with the Saul and Wagner equation [20], the surface tension from the Vargaftic et al and the vapor pressure from Wagner, it has been devised the following function:

$$F(T, \rho) = \frac{1.188}{10^7} \cdot \frac{T^2 \cdot \rho^{\frac{1}{3}}}{r_\mu(T, \rho)} \cdot \frac{P^*(T)^{\frac{4}{3}}}{\sigma(T)^2} \cdot \left[\exp\left(\frac{v_L^* \cdot (P - P^*)}{R \cdot T} \right) - \frac{P}{P^*} \right]^{\frac{4}{3}} \quad (25)$$

As shown on Fig. 8, the function $F(T, \rho)$ that has a constant value equal to the unit in the entire temperature range except some points near the critical point.

Comparison of Eq. 24 and 25 gives:

$$\frac{k_B \cdot T}{2^{\frac{4}{3}} \cdot g} \cdot \frac{1}{\left(\frac{16\pi}{3} \right)^{\frac{2}{3}}} = \frac{1.188}{10^7} \cdot T^2 \quad (26)$$

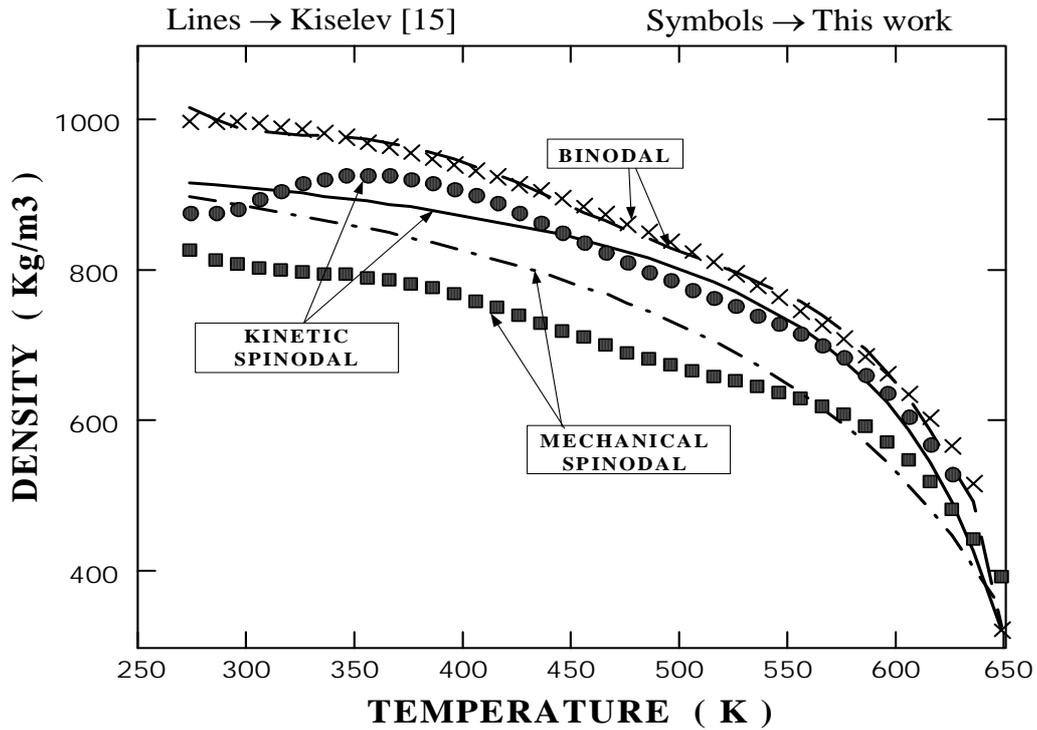


Fig. 6 The density of the Binodal, the Mechanical and Kinetic SP according to Kiselev [15], (dash, solid and dash-dot lines respectively) and the results of the present work (x, circle and square symbols respectively).

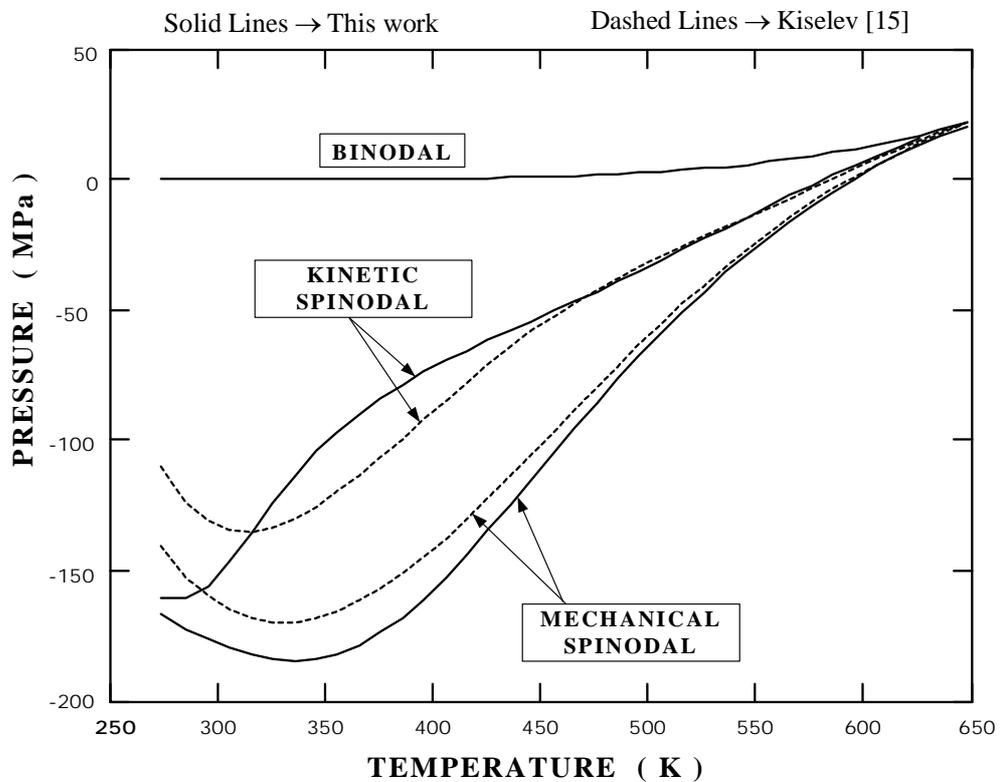


Fig. 7 The Mechanical and Kinetic SP according to Kiselev [15], (dot lines) and the results of the present work (solid lines).

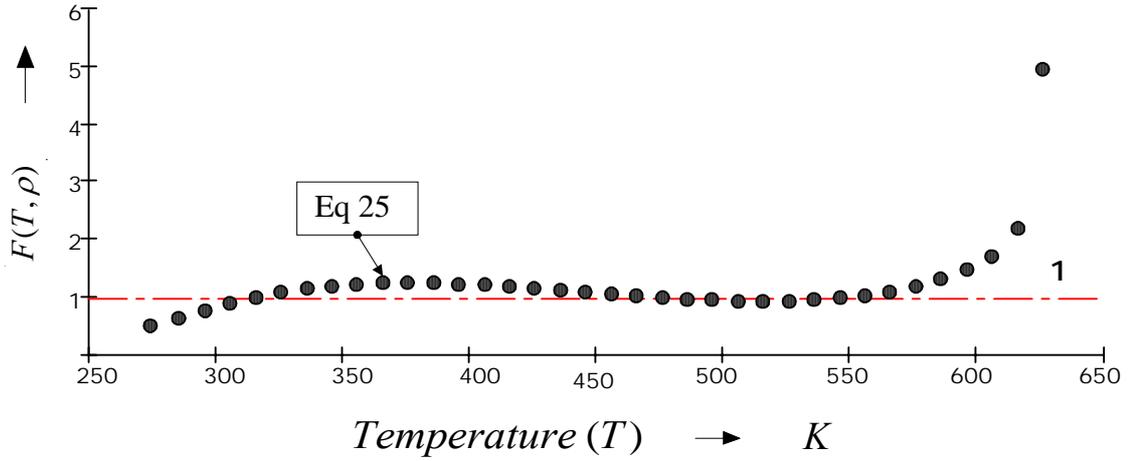


Fig. 8 For the entire temperature range is valid $F(T, \rho) \approx 1$ except some points close to the critical temperature.

So the proposed approximation for the parameter g by Kiselev [15], $g = k_B \cdot T \cdot \rho_c^{\frac{1}{3}}$, maybe substituted by the more accurate dimensionless form \bar{g} as follows:

$$\bar{g} = \frac{g}{k_B \cdot T_c \cdot \rho_c^{\frac{1}{3}}} = \frac{115.025}{T} \quad (27)$$

From the kinetic SP Eq. 24 of the superheated stretched water and Eq. 21, 22 and 20, it is obtained an equation for the kinetic density in terms of the temperature.

The resulting estimate for the density and the pressure of the kinetic SP line are plotted in Fig. 6 and 7 respectively. On the same figures are shown the Kiselev calculated density and pressure kinetic SP lines [15].

The Temperature of Maximum Density Line (TMD)

The SP line for water in the p-T plane is strongly related to the existence of a line along which the density of liquid water is a maximum: The Temperature of Maximum Density Line (TMD). Using vdW EOS/ Eq. 16 the experimental $P-T$ data of the TMD line coming from the literature Henderson and Speedy [25], Chen et al [26], Meyer et al [27] are converted to $\rho-T$ data and the following correlation it is obtained:

$$\rho_{TMD} = dm_0 + dm_1 \cdot T + dm_2 \cdot T^2 \quad (28)$$

where $198 \text{ K} \leq T \leq 336 \text{ K}$ and Table 2 gives the values of the coefficients dm_n , $n = 0 \dots 3$.

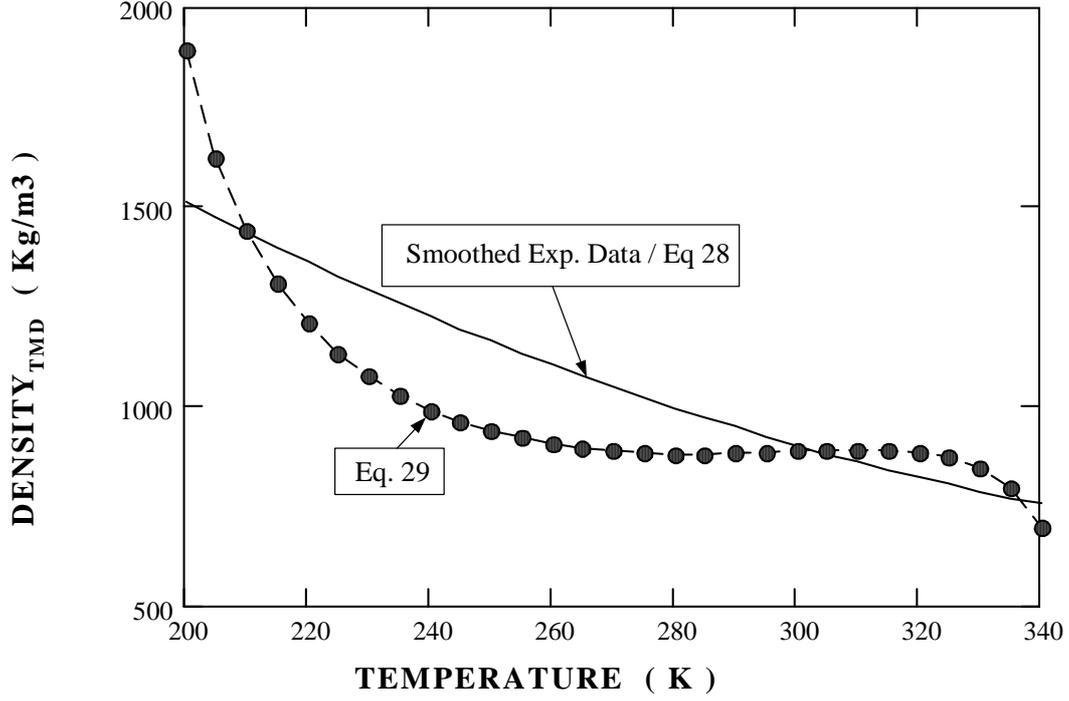


Fig. 9 The deviation of the calculated maximum density according to Eq. 29 (dash line with circle symbol) in comparison with the smoothed exp. Data/ Eq. 28 (solid line).

Table 2 The coefficients dm_n , $n = 0 \dots 3$ of Eq. 28

dm_0	dm_1	dm_2
3766.8258	-14.727996	0.01726039

It has been shown on the basis of thermodynamic arguments by Debenedetti et al [1] that the most physically plausible way for the TMD line to terminate is at an intersection with the SP line. Furthermore it has been by Speedy [3, 11] that an intersection in the P-T plane of a negative sloped TMD line with a positively sloped SP requires that SP has a minimum at the intersection point. Verification for the intersection of the TMD line with SP is succeeded with modified VDW EOS as follows:

From the definition on the TMD is valid: $\left(\frac{\partial \rho}{\partial T}\right)_p = 0$ and $\left(\frac{\partial P}{\partial T}\right)_\rho = 0$. Applying the last constraint for the modified van der Waals equation, it is obtained the equation:

$$R \cdot \left(\frac{1}{\rho} - b(T) + T \cdot \frac{\partial b(T)}{\partial T} \right) - \frac{\partial a(T)}{\partial T} \cdot (1 - b(T) \cdot \rho)^2 = 0 \quad (29)$$

Figure 9 shows the deviation of the calculated maximum density according to Eq. 29 (dash line with circle symbol) in comparison with the smoothed exp. Data/ Eq. 28 (solid line).

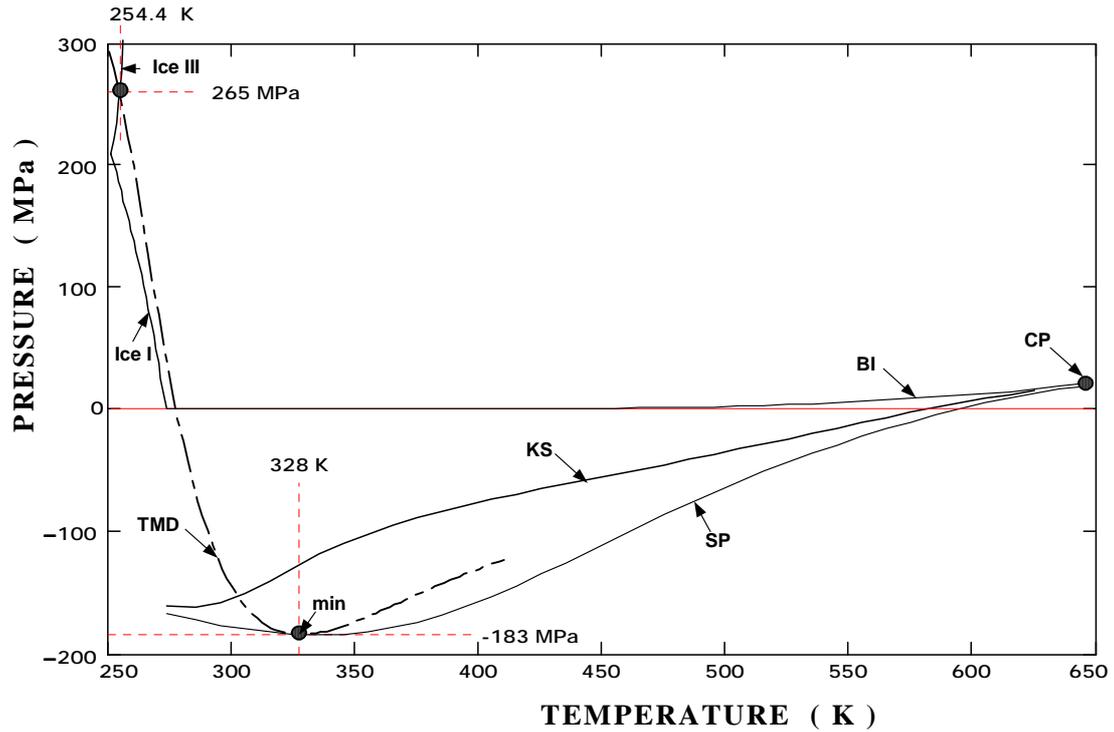


Fig. 10 The TMD line calculated with maximum density values coming from Eq. 29 and the vdW EOS/Eq. 16. (dash dot line). On the same figure are shown BI, KS, SP and the melting lines of ice I and ice III.

The resulting estimate for the TMD line is plotted in Fig. 10. The minimum occurs at a temperature 328 K and the minimum pressure -183 Mpa. The same TMD line can be considered as a minimum in $P_{\rho}(T)$, an isochore of P as a function of T . On the same figure, it is shown the expected extension of the TMD line from the minimum up to the liquid ice III phase transition: the TMD line intersects the Melting Line of ice III, IAPWS Release [28], at a temperature 254.4 K and a pressure 265 MPa. From the other side of the minima, the TMD line reenters into the stable area of SP with positive slope. Note that the appearance of a TDM line with positive slope is thermodynamically possible, and has been observed in simulations of a simple pair potential, Pool et al [4].

CONCLUSIONS

- Empirical equations of state have been proposed for describing the p - v - T behavior of gases and liquids in metastable region, each of which is designed for a particular application. Some of these equations are quite accurate over a small range of temperature and density; others apply to the properties in the gaseous and liquid phases. Another point that separates them is the number of adjustable constants they have, something that makes them easier or not to be applied.
- According to fig. 1 it is shown that the experimental data are included between the curves given by Berthelot and Hipman, something that shows clearly that these EOS give more realistic results in this section - isotherms close to the critical point - of metastable region.
- As it is shown on the tables, the smaller divergences between the empirical EOS and the experimental data obtained by Chukanov and Skripov are these of the EOS of Berthelot and Hipman, with maximum divergence at 10.5% and 16.9% respectively.

- The IAPWS industrial formulation seems to accurate quite good these experimental data, as the maximum divergence is only 0.047%. For the above comparison it is used the EOS of the first region that proposed at IAPWS.
- Fitting accurate data along the binodal and SP, the coefficients of the van der Waals EOS for the water are expressed in terms of the temperature (Eq. 17 and 18 for $a(T)$ and $b(T)$ respectively). Then the parameters of the kinetic SP according to fluctuation theory of relaxation are given in analytic forms.
- The mechanical and kinetic SP calculated with the modified vdW EOS are very close to the results given by Kiselev [15]. The kinetic equation (Eq 24) is expressed in terms of the temperature and the density. A new form for the parameter g of the kinetic equation is proposed, that is very accurate from the triple point up to temperatures close to the critical point.
- An analytic form in terms of the temperature and the density expresses the TMD line. The resulting estimate for the TMD is plotted and is verified that this curve intersects the SP at the minimum that occurs at a temperature 328 K and a pressure -183 MPa .The expected extension of the TMD line from the minimum up to the liquid ice III phase transition: is plotted and the intersection with the Melting Line of ice III, occurs at a temperature 254.4 K and a pressure 265 MPa. From the other side of the minima, the TMD line reentrant into the stable area of SP with positive slope.

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APPENDIX

Table 3 Comparison of IAPWS 97 with Chukanov experimental data.

T (C)	Ps (bar)								
463.15	12.55	473.35	15.62	482.55	18.85	492.65	22.98	504.15	28.50
p	$\frac{dv}{v}$								
bar		bar		bar		bar		bar	
40.00	0.0018	25.00	-0.0026	40.00	0.0128	40.10	0.0101	40.20	0.0339
30.10	-0.0070	20.30	-0.0043	30.10	0.0128	30.30	0.0042	30.20	0.0446
20.20	-0.0061	16.60	0.0026	20.30	0.0034	24.30	-0.0008	28.20	0.0430
14.40	-0.0114	15.40	0.0043	18.40	0.0043	22.30	0.0034	26.30	0.0405
12.50	-0.0131	14.10	-0.0017	16.40	-0.0017	20.30	-0.0008	24.30	0.0396
10.50	-0.0149	12.90	0.0000	14.50	-0.0009	18.40	0.0025	22.30	0.0471
9.53	-0.0158	11.60	-0.0052	12.60	-0.0077	16.50	-0.0025	20.40	0.0281
8.54	-0.0158	10.60	-0.0052	10.60	-0.0060	14.60	-0.0076	18.50	0.0264
7.53	-0.0166	9.57	-0.0043	9.58	-0.0043	12.60	-0.0034	16.50	0.0256
6.55	-0.0175	8.58	-0.0043	8.59	-0.0034	10.60	-0.0076	14.60	0.0239
5.58	-0.0184	7.57	-0.0043	7.58	-0.0102	9.64	-0.0059	12.70	0.0132
4.61	-0.0193	6.60	-0.0043	6.60	-0.0094	8.65	-0.0118	10.70	0.0206
3.63	-0.0193	5.62	-0.0043	5.63	-0.0085	7.64	-0.0092	9.68	0.0165
2.64	-0.0201	4.65	-0.0130	4.66	-0.0077	6.65	-0.0076	8.69	0.0124
1.65	-0.0210	3.67	-0.0121	3.69	-0.0068	5.69	-0.0134	7.68	0.0082
0.65	-0.0219	2.68	-0.0121	2.70	-0.0145	4.71	-0.0117	6.70	0.0033
		1.69	-0.0121	1.71	-0.0136	3.74	-0.0092	5.73	-0.0016
		0.69	-0.0121	0.71	-0.0119	2.76	-0.0076	4.76	0.0025
						1.76	-0.0134	3.78	-0.0025
						0.76	-0.0109		

NOMENCLATURE

c_p	specific heat at constant pressure
J	nucleation rate
k	Boltzmann's constant
KS	kinetic spinodal
K_T	isothermal compressibility
K_B	Boltzmann's constant
p	pressure
r	radius of vapor bubble
SP	mechanical spinodal
T	temperature
TMD	Temperature of Maximum Density
t_M	life time of metastable state
t_R	relaxation time
v	specific volume
W_{\min}	nucleation barrier

Subscripts

c	critical
L	liquid
M	mean
r	relative
s	saturation

v	vapor
vdW	van der Waals

Greek letters

α_p	coefficient of thermal expansion
δ	correction factor
ρ	density
σ	surface tension