Density of Sodium along the Liquid-Vapor Coexistence Curve, including the Critical Point

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Abstract. Sodium densities along the whole liquid-vapor coexistence curve are reanalyzed using the equation proposed by Apfelbaum and Vorob'ev [1]. The formulation has built-in the correct behavior for liquid and vapor densities, both at low temperature and in the near-critical region. Thus, it satisfactorily represents the available experimental data in the low and intermediate temperature range, while providing a sound density extrapolation to the critical point: in reduced units, the calculated values for sodium are consistent with those measured for rubidium and cesium [2], as require by the principle of Corresponding States. The enthalpy of vaporization, calculated via Clapeyron relation, is also correctly described.

The main differences between our results and those from the previous formulation by Fink and Leibowitz [3] are found in the high temperature region (2300 K $- T_c$), where the coexistence curve predicted by the latter exhibits an unusual shape.

Our results indicate that the value for the critical density (180 ± 10) kg/m^3 is 20% lower than the one recommended before (219 ± 20) kg/m^3.

Key Words: sodium density, coexistence curve, corresponding state, critical point.

1. Introduction

Due to properties such as high thermal conductivity, low vapor pressure, extended liquid range, low neutrons capture and good compatibility with fuel and structural materials, liquid sodium is considered as a potential coolant for Fast Reactors.

To design and operate a reactor or an experimental facility, thermodynamics and transports properties of sodium are needed in an extended range. Moreover, safety regulations demand the knowledge of the behavior far above operating conditions, even beyond the vapor-liquid critical point (critical temperature T_c = 2504 K). But due to the tough experimental conditions, no information is available above 1600 K. To cover the whole liquid range, properties of fluid sodium were estimated by extrapolation, using empirical equations of state with adjustable parameters, usually calculated by fitting them to the experimental data. For that purpose, the information most commonly used are the critical point coordinates, the enthalpy of vaporization and the density of the dense phase. Wrong values of the experimental data used to adjust the parameters will certainly lead to wrong values of extrapolated properties.

In this work, we apply an equation proposed recently [1], combined with precise experimental data of other alkali metals [2], to represent the density of sodium. The equation has the proper behaviour both at low temperatures and near the critical point, providing a fair representation of the densities of the fluid phases from the melting to the critical points. The enthalpy of vaporization and the coordinates of the critical point are also obtained.

2. Background

2.1   Previous Formulation

The most comprehensive description of the thermophysical properties of sodium is due to J. K. Fink and L. Leibowitz [3]. They represented the liquid phase density (ρ_L) from the melting temperature to the critical temperature (T_c) using a single equation:

$$\rho_L/(\text{kg/m}^3) = 219 + 511.58\,\tau^{0.5} + 275.32\,\tau \tag{1}$$

The variable τ in eq. (1) represents the reduced distance to the critical temperature, i.e. $\tau = 1- T/T_c$. The density of the vapor phase (ρ_V) was calculated through the Clapeyron equation, using the liquid density, the enthalpy of vaporization ($\Delta_{vap}H$) and the slope of the vapor pressure curve ($dp/dT)_\sigma$.

$$\rho_V^{-1} = \rho_L^{-1} + \Delta_{vap}H / \left(T\,\frac{dp}{dT}\Big|_\sigma \right) \tag{2}$$

The expression for $\Delta_{vap}H$ and $(dp/dT)_\sigma$ are given by these authors. In particular, the former was expressed in terms of τ as follows:

$$\Delta_{vap}H/(\text{kJ/kg}) = 4398.6\,\tau^{0.29302} + 393.37\,\tau \tag{3}$$

The values of T_c and ρ_c used by these authors were (2503.7 ± 12) K and (219 ± 20) kg/m^3, respectively [3].

The coexistence curve formulated by Fink and Leibowitz is depicted in *FIG. 1*; the inset amplifies the critical region. Clearly, the critical point location is abnormal. The pathology is obvious in the diameter, *i.e.* the mean value of the coexistence densities, as it changes abruptly from 185 kg/m^3 to 219 kg/m^3 in the last 0.2 K before T_c.
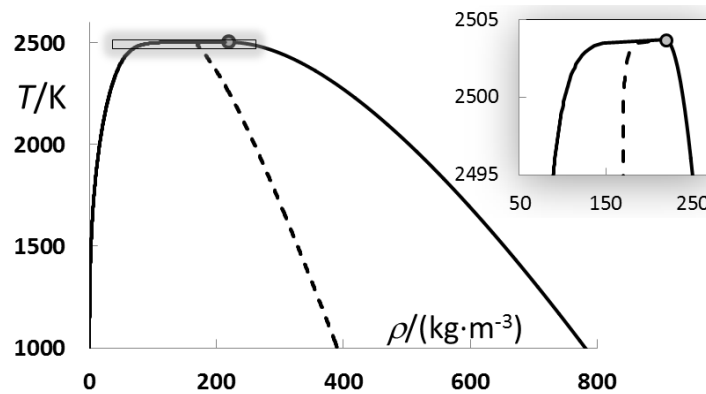

FIGURE 1: Coexistence curve and critical point of sodium, according reference [3]. Solid lines: liquid and vapor densities; dashed line: average densities. The circle shows the recommend critical point. The inset is a magnification of the shadowed area (last 9 K to T_c).

Evidently, the previous formulation is inappropriate to describe the critical region.

2.2 Critical Behavior

The description of thermodynamics properties using analytical equations fails near a critical point. According to Universality of the Critical Phenomena [4], the shape of the coexistence curve of sodium can be described using the following equation:

$$\rho_d = \frac{\rho_L + \rho_V}{2} = \rho_c\left(1 + D_1 \cdot \tau + D_{1-\alpha} \cdot \tau^{1-\alpha} + D_{2\beta} \cdot \tau^{2\beta} + \cdots\right) \qquad (4)$$

$$\frac{\rho_L - \rho_V}{2\rho_c} = B\,\tau^{\beta}(1 + B_1 \cdot \tau^{\Delta} + \cdots) \qquad (5)$$

In this equation, ρ_d, known as the *diameter*, is the average density between the vapor and the liquid phases. The constants D_i, B and B_1 are system-dependent amplitudes while α, β and Δ are universal critical exponents; for the Ising model, their values are $\alpha = 0.11$, $\beta = 0.326$ and $\Delta = 0.51$.

The first two terms in eq. (4) are known as regular terms; together they express the Law of Rectilinear Diameters [5]. The last terms are predicted by theory of critical phenomena.

Eq. (5) states that, near the critical point, both coexistence densities have almost *cubic* shape ($\beta = 0.326 \sim 1/3$), whereas sodium's previous formulation represents the liquid phase as *parabolic*, see eq. (1). On the contrary, the near critical behavior of the vapor phase of Fink and Leibowitz formulation is determined by the heat of vaporization, an almost cubic function of τ, see eq. (3). This is the reason for the unrealistic variation of the diameter of the previous formulation [3] in the critical region, see *FIG. 1*.

3.   The Fitting Equation and Procedure

The proposed formulation is based on the expression given by Apfelbaum and Vorob'ev [1]; a single equation for representing liquid and vapor branches of pure fluids, including metals.

$$\rho_{\pm} = \rho_d \left\{1 \pm \left[1 - \exp\left(-\frac{q\,\tau}{1-\tau}\right)\right]^{\beta}\right\} \qquad (6)$$

In this equation, ρ_+ and ρ_- represent the coexisting liquid and vapor densities, respectively, ρ_d is the diameter of the coexistence curve, β is the critical exponent describing the shape of the equilibrium curve, eq. (5), and q is a parameter related to the heat of vaporization.

Despite its simplicity, eq. (6) possesses the correct critical limits and it also describes the expected behavior of the vapor phase at low temperatures [1].

To reduce the number of fitting parameters, and based on the behavior reported for rubidium and cesium [2,6,7], only the $D_{1-\alpha} \cdot \tau^{1-\alpha}$ term shall be considered in the description of the diameter, eq. (4). The inclusion of the linear and/or the 2β terms did not improve substantially the fit [8].

To represent the density along the coexistence curve, we applied eq. (6) to both fluid phases with a temperature dependent q. We adopted the following expression:

$$q = \frac{q_c}{1 + q_1 \cdot \tau + q_2 \cdot \tau^2} \tag{7}$$

Coefficients ρ_c, $D_{1-\alpha}$, q_c, q_1 and q_2 were obtained by fitting equations eqs. (4), (6) and (7) to the available experimental information, minimizing the sum of the weighted residues. In order to compensate the lack of experimental information on sodium at high temperatures (*i.e.*, near the critical point), in the data set we included densities of rubidium [2], making use of the *Principle of Corresponding State* [9]: liquid and vapor density of rubidium were transformed to sodium [8], using the critical values of temperature and density (for rubidium: $T_c = 2017$ K; $\rho_c = 292$ kg/m^3).

4. Results and Discussion

The coefficients obtained by fitting equations eqs. (4), (6) and (7) to the data are given in Table I, together with the goodness of the fit χ.

Table I: Coefficients obtained from fitting eqs. (4), (6) and (7)

ρ_c/(kg m^{-3})	$D_{1-\alpha}$	q_c	q_1	q_2	χ
179	1.831	8.827	1.831	-1.017	3.0

The coexistence curves, both obtained from the previous formulation and calculated using these parameters, and all experimental data used in the fitting process, including those of *transformed* rubidium, are depicted in *FIG. 2*.

FIGURE 3 compares the coexistence curves, in reduced units, with the high-temperature density data of alkali metals rubidium and cesium (for cesium: $T_c = 1921$ K; $\rho_c = 379$ kg/m^3). The agreement observed in *FIG. 2* between the previous formulation and the experimental data or the present equation disappears in this reduced units representation, due to the large value of the critical density recommended by the previous formulation.
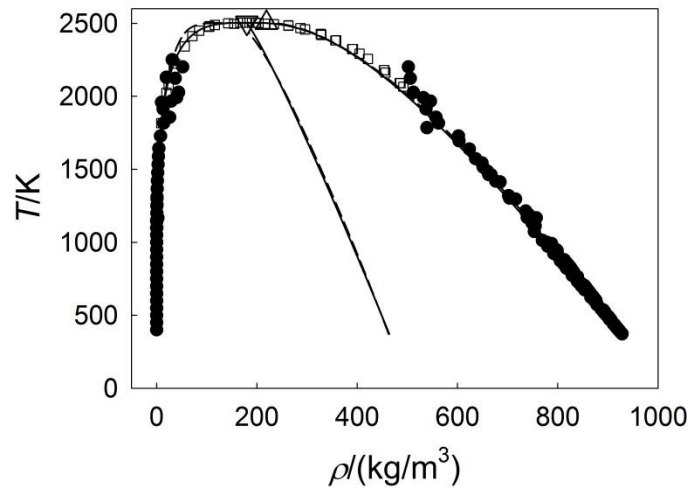
FIGURE 2: Full circles: sodium data set. Empty squares: transformed rubidium data. Lines: densities of liquid and vapor phases, and of the diameter, according to Fink and Leibowitz (dashed) and present work (solid). Critical point, as proposed by Fink and Leibowitz △ and by present work▽.
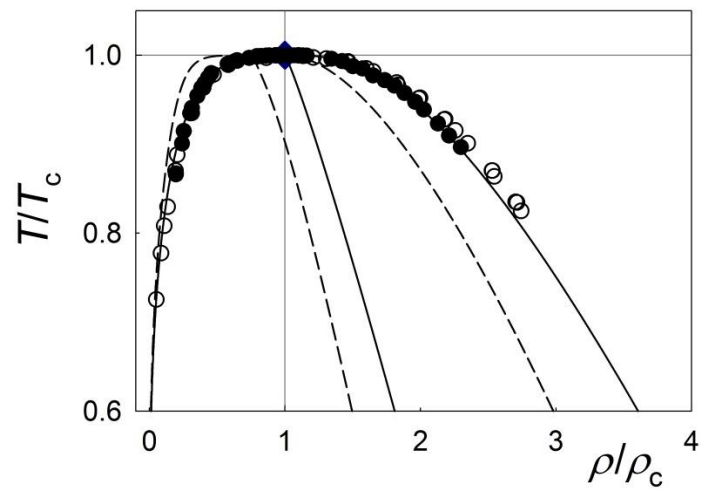

FIGURE 3: The coexistence curve of alkali metals Na, Rb and Cs in reduced units. Experimental data for Rb (open circles) and Cs (full circles). Densities of liquid and vapor phases, and of the diameter, according to equation proposed by Fink and Leibowitz (dashed) and present work (solid). The critical point at $\rho/\rho_c = 1$ and $T/T_c = 1$ is represented by a diamond.
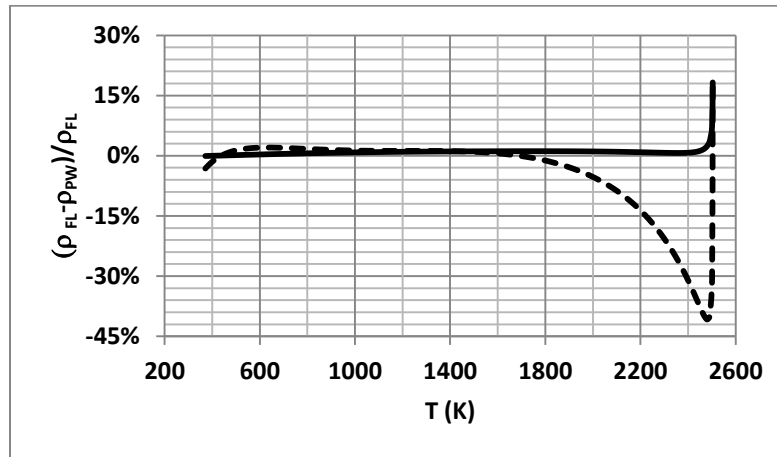
FIGURE 4: Percentage deviation between Fink and Leibowitz formulations and present work, $(\rho_{FL} - \rho_{PW})/\rho_{FL}$. Solid line: liquid phase. Dashed line: vapor phase.

FIGURE 4 shows the percentage deviation between Fink and Leibowitz's and present formulations. Deviations are not really significant for the liquid phase (less than 10% at $T = T_c - 5$ K, 20 % at $T = T_c$) but the vapor density is 34 to 40% underestimated by Fink and Leibowitz at 20 K from the critical temperature. The main failure of Fink and Leibowitz formulation is in requiring the differences of vapor and liquid phase to behave non-classically while imposing a classical behavior for the liquid one. The consequence, as illustrated in *FIG. 1*, is that the characteristic flatness of the coexistence curve displayed near the critical point is, in Fink and Leibowitz formulation, all on the vapor side, while the liquid branch is not flat but parabolic.

Properties related to the density will reflect the different values obtained by the previous and present formulations for the vapor phase. Here we show a comparison between some of these properties, according to the two formulations. The properties to be compared are the enthalpy of vaporization (obtained here using the Clapeyron equation), and the isothermal compressibility and the isobaric thermal expansion coefficient of vapor sodium.

The enthalpy of vaporization is depicted in *FIG. 5*. Our values are calculated using the Clapeyron equation, eq. (2), with Fink and Leibowitz's recommended values for $(dp/dT)_\sigma$. At low temperature, our results present an unrealistic small hook. At high temperature, they describe the expected behavior of this property.
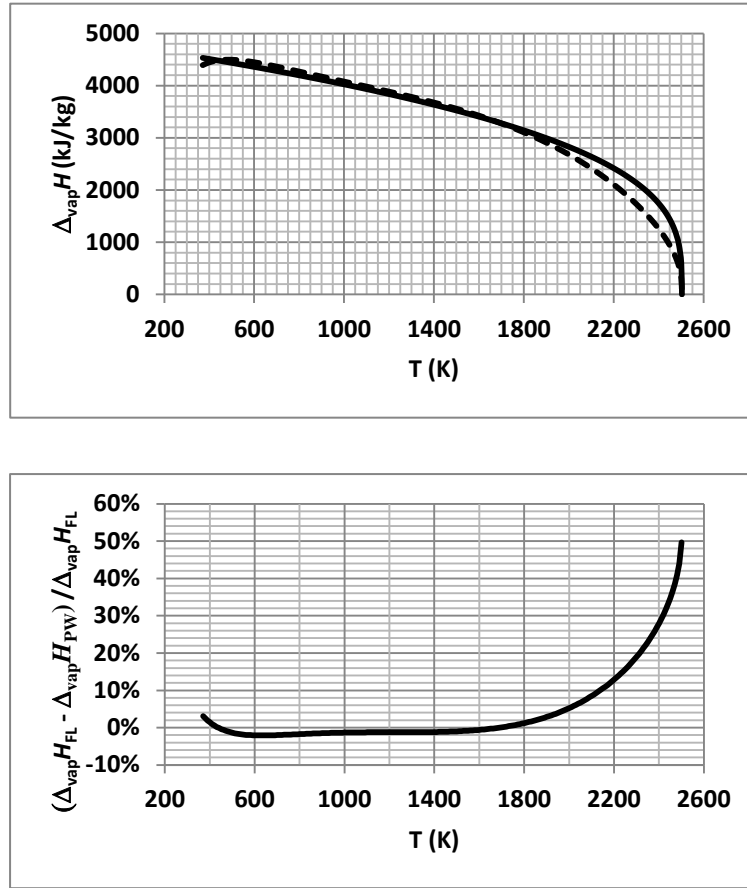
FIGURE 5: Upper panel: Enthalpy of vaporization calculated from Fink and Leibowitz formulation (solid line) and from present results (dashed line). Lower Panel: Percentage of deviation between Fink and Leibowitz's and present work. $(\Delta_{vap}H_{FL} - \Delta_{vap}H_{PW})/\Delta_{vap}H_{FL}$.

As was the case of the vapor density, the enthalpy of vaporization recommended previously tends to its critical value ($\Delta_{vap}H = 0$ for $T = T_c$) only very close to the critical point, therefore displaying a very steep temperature dependence. On the contrary, our calculated values show a more realistic behavior.

The isobaric thermal expansion coefficient $\alpha_P = V^{-1}(\partial V/\partial T)_p$ and the isothermal compressibility $\beta_T = -V^{-1}(\partial V/\partial p)_p$ of *sodium vapor* were calculated from the following exact thermodynamic relations [5]:

$$\alpha_P = \frac{\alpha_\sigma}{\left(1 - \frac{\gamma_\sigma}{\gamma_V}\right)} \qquad\qquad \beta_T = \frac{\alpha_P}{\gamma_V}$$

where α_σ, the relative ratio of volume change with temperature, but under liquid-vapor saturation conditions $\alpha_\sigma = V^{-1}(\partial V/\partial T)_\sigma$, is the experimentally accessible quantity. Coefficients $\gamma_V = (\partial p/\partial T)_V$ and $\gamma_\sigma = (\partial p/\partial T)_\sigma$, were taken from Fink-Leibowitz formulation [3], as they show no critical anomaly.
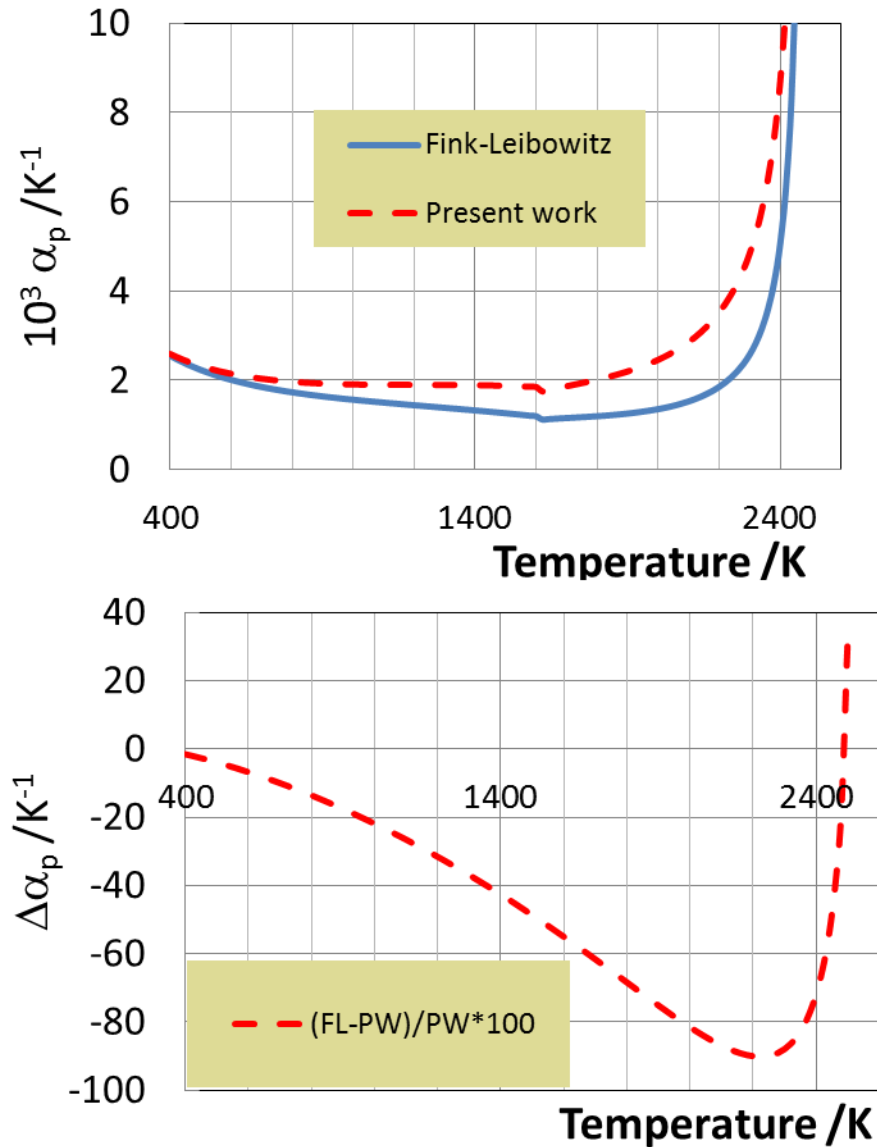
FIGURE 6: Upper Panel: Isobaric Thermal Expansion Coefficient of sodium vapor, according to Fink and Leibowitz (solid line) and our formulation (dashed line). Lower Panel: Percentage of deviation between Fink and Leibowitz's and present work for the thermal expansion coefficient.

As expected, deviations in the calculated thermal expansion coefficients of the vapor are large for temperatures above 2000 K: the values recommended by the previous formulation are up to 90 % lower than those obtained in this work, as depicted in *FIG. 6*.

The same is valid for the isothermal compressibility, shown in *FIG. 7*. At temperatures higher than 2000 K, the vapor phase of sodium is, for the previous formulation, less compressible than obtained in this work.
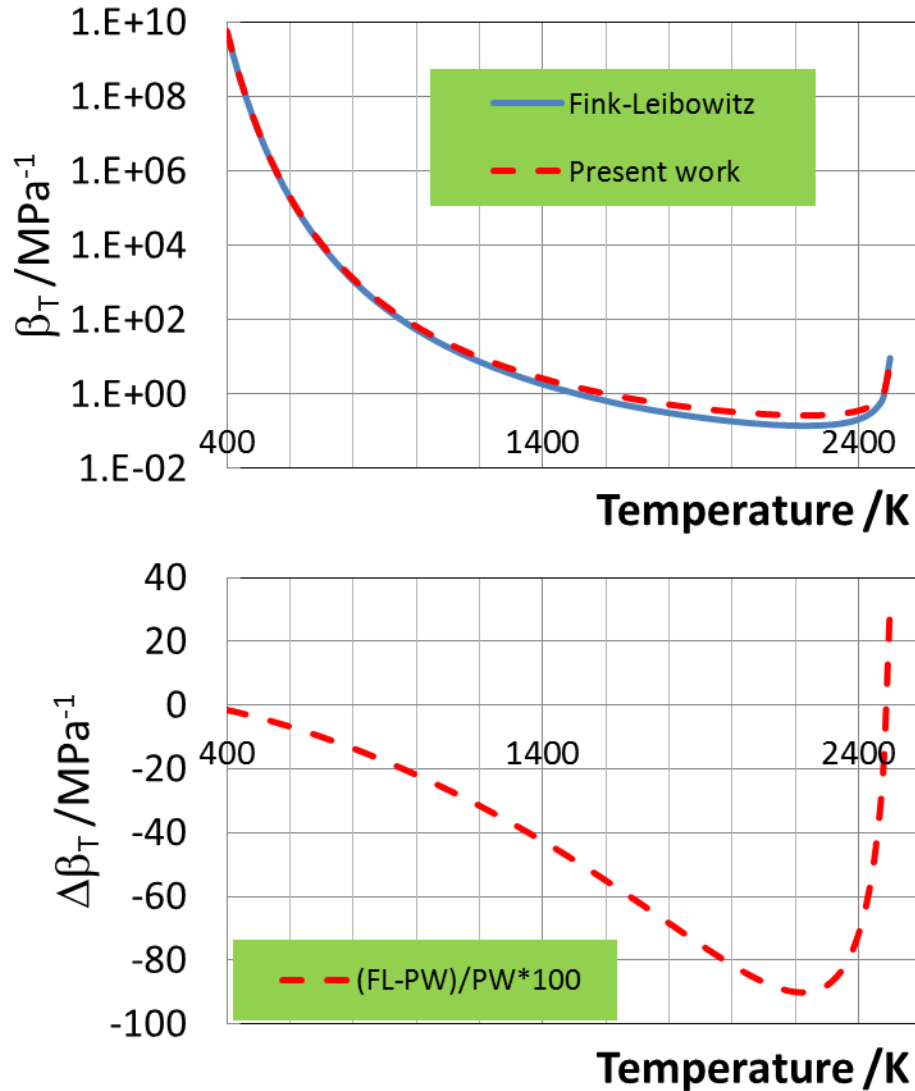
FIGURE 7: Upper Panel: Isothermal Compressibility of the vapor phase, according to Fink and Leibowitz (solid line) and present (dashed line) formulations. Lower Panel: Percentage of deviation between the isothermal compressibility of Fink and Leibowitz and our results.

5. Conclusions

With an adequate dependence of the diameter and the energy parameter q with temperature, the Apfelbaum and Vorob'ev equation correctly represents the coexistence curve of alkali metals considered (sodium, rubidium and cesium).

The critical density obtained in this work for sodium is consistent with the experimental data of rubidium and cesium, although 20 % lower than that generally recommended in the literature.

In our opinion, the difference arises from the inadequate extrapolation made earlier of the sodium data to the critical temperature. On the contrary, our formulation contains the correct information of the critical behavior.

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