

Universal compressibility behavior of dense phases

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We recently proposed an isothermal equation of state that was successfully applied to study the high-pressure behavior of molecular liquids. In this work we extend its applicability to liquid metals, polymers, molten salts, and solids. The possibility of considering this equation as an alternative to long-standing equations such as those of Tait and Birch-Murnaghan is emphasized. This suggestion is firmly supported by comparisons with experimental data up to pressures of several GPa. A new physical interpretation of the pressure coefficient of the Tait equation B_T is given. It can be identified to the divergence pressure along a pseudospinodal curve. We also compare the performance of our equation with the most successful equations of state used to represent isothermal data of solids, with excellent results. Our equation can be applied to systems with phase transitions. An interesting observation is that it seems that the different pseudospinodal curves obtained for the different phases can be put together into the same curve except for characteristic jumps occurring at the phase transitions.

I. BACKGROUND AND INTRODUCTION

Isothermal data at elevated pressures of liquids, polymers, and molten salts are widely represented by the following equation:^{1,2}

$$\rho(p) = \frac{\rho_0}{1 - C_T \ln\{(p + B_T)/(p_0 + B_T)\}}, \quad (1)$$

where p_0 is the atmospheric pressure, ρ_0 is the value of the density ρ measured at p_0 , and C_T and B_T are parameters to be determined. Equation (1) differs from the original equation used by Tait,³ which was originally derived to represent the compressibility of water. Many authors refer to it as the modified Tait equation but, for the sake of brevity, we simply call it the Tait equation from now on.

The analysis of high-pressure isothermal data of solids is commonly made in terms of the so-called Birch-Murnaghan equation^{4,5} which expresses the pressure p as a function of volume v in the following form:

$$p = (3/2)B_0 \left[\left[\frac{v_0}{v} \right]^{7/3} - \left[\frac{v_0}{v} \right]^{5/3} \right] \times \left\{ 1 - (3/4)(4 - B'_0) \left[\left[\frac{v_0}{v} \right]^{2/3} - 1 \right] \right\}, \quad (2)$$

where v_0 is the zero-pressure volume, B_0 is the isothermal bulk modulus at zero pressure, and B'_0 is its pressure derivative.

Very recently, Parsafar and Mason⁶ derived a universal equation of state valid for a wide variety of compressed solids. For a given temperature, the equation depends on four coefficients; one of them, v_0 , is some standard volume, which is often taken to be the molar volume at $p=0$, as in Eq. (2), but which can be quite arbitrary. Since the sum of the three other coefficients must be equal to the reference pressure, p_0 , at which v_0 is mea-

sured, only three independent coefficients describe each isotherm.

If v_0 is taken to be the zero-pressure molar volume, the equation can be expressed in terms of B_0 and B'_0 as follows:

$$p(v/v_0)^2 = (1/2)B_0 \left[(B'_0 - 7) - 2(B'_0 - 6)(v_0/v) + (B'_0 - 5)(v_0/v)^2 \right]. \quad (3)$$

Parsafar and Mason⁶ compared the results obtained with their equation with those from the equation proposed by Vinet *et al.*⁷ This second equation proved to give the best fit of the experimental data over the full range of compressions of solids experimentally available⁸ and can be written in the following form:⁷

$$p = 3B_0 \left[\frac{1-X}{X^2} \right] \exp[(3/2)(B'_0 - 1)(1-X)], \quad (4)$$

where $X = (v/v_0)^{1/3}$.

We recently confirmed that the pressure behavior of the isothermal compressibility κ_T of molecular liquids (including water) can be characterized by the following inverse power law:^{9,10}

$$\kappa_T(p) = \kappa^*(p - p_{sp})^{-\gamma}, \quad (5)$$

where κ^* is a proportionality constant and p_{sp} is the divergence pressure along a certain pseudospinodal curve at the considered temperature. We found that the value of the pseudocritical exponent γ was close to 0.85 (Refs. 9–11) and this value will be used here.

The integrated equation for the density which follows proved successful in representing isothermal data of several liquids as well^{11,12}

$$\rho = \rho_{sp} \exp \left\{ \left[\frac{\kappa^*}{(1-\gamma)} \right] (p - p_{sp})^{(1-\gamma)} \right\} \quad (6)$$

or

$$v = v_{\text{sp}} \exp \left\{ - \left[\frac{\kappa^*}{(1-\gamma)} \right] (p - p_{\text{sp}})^{(1-\gamma)} \right\},$$

where $\rho_{\text{sp}} (= 1/v_{\text{sp}})$ is the density (volume) of the liquid branch of the pseudospinodal curve at that temperature.

The equivalence established between Eqs. (5) and (6) and a universal superposition principle proposed by Sanchez, Cho, and Chen^{13,14} for compression data of liquids, polymers, and solutions suggested to us the possibility that our treatment would be of general application.⁹ It is the purpose of this work to extend the validity of the principle in which Eqs. (5) and (6) are based on liquid metals (mercury will be studied here), molten salts, polymers, and solids.

A striking feature of Eq. (6) is that it overcomes the well-known limitation of the Tait equation of requiring negative volumes at sufficiently high pressure.^{1,15} In addition, we shall introduce a new physical interpretation of the pressure coefficient of the Tait equation B_T , that is, to consider it as the negative value of the divergence pressure along a pseudospinodal curve p_{sp} . This equivalence allows us to obtain two other expressions relating the characteristic parameters of Eq. (6) to those of the Tait equation. Numerical comparisons are presented and discussed. The possibility of using Eq. (6) instead of the Tait equation to represent experimental data of liquids, polymers, and molten salts is emphasized. In addition, the results for solids are of a quality comparable to those obtained from the most successful equations recently proposed in the literature.

Finally, since Eq. (6) is applicable to both liquid and solid phases, the possibility of using a single pseudospinodal curve to describe high-pressure data for all condensed phases of a given substance is outlined.

II. EQUATION (6) VS TAIT, BIRCH-MURNAGHAN, AND OTHER EQUATIONS

The pressure parameter of the Tait equation B_T has received many theoretical and empirical interpretations, but most of them coincide in identifying the quantity $(p + B_T)$ as the difference between the thermal and attractive pressures of a liquid. Leyendekkers¹⁶ has recently compared B_T for water to the network stress or pressure derived from the application of the scaled particle theory.

We shall use a different physical interpretation of B_T here. Let us consider the expression that is derived from Eq. (1) for the isothermal compressibility, $\kappa_T = \rho^{-1}(\partial\rho/\partial p)_T$,

$$\kappa_T(p) = C_T(\rho/\rho_0)(p + B_T)^{-1}. \quad (7)$$

According to the definition of spinodal curve,¹⁷ where the isothermal compressibility diverges $[(\partial p/\partial\rho)_T = 0]$, B_T can be considered as the negative value of the divergence pressure along a spinodal curve [p_{sp} in Eqs. (1) and (6)], so let us write,

$$p_{\text{sp}} = -B_T. \quad (8)$$

Despite the simplicity of the equivalence established in Eq. (8), which is a direct consequence of Eq. (7), to the best of our knowledge, this explicit physical interpretation of the pressure coefficient of the Tait equation parameter is new. This prescription can be numerically confirmed by comparing the values of B_T for water given by Leyendekkers¹⁶ with those of p_{sp} reported by us in Ref. 9 obtained from the fitting of high-pressure data of Chen, Fine, and Millero¹⁸ to Eq. (6).

From Eqs. (5) and (7) at zero pressure one obtains the following expression which relates κ^* with the parameters of the Tait equation:

$$\kappa^* = C_T/B_T^{(1-\gamma)}. \quad (9)$$

On the other hand, from Eqs. (1) and (6) at zero pressure, the following expression relating ρ_{sp} and ρ_0 is obtained:

$$\rho_{\text{sp}} = \rho_0 \exp\{-C_T/(1-\gamma)\}. \quad (10)$$

A numerical confirmation of the validity of Eqs. (8) to (10) is given in Table I where the coefficients of Eq. (6) for carbon disulfide are compared with those calculated from the Tait coefficients previously reported by us.¹⁹

Although the coefficient C_T is usually taken as a constant for a given liquid, there is evidence that for liquids in general it is not a constant.² Its value for nonassociated liquids and polymers is commonly found to be between 0.08 and 0.10.¹ Values reported by Dymond and Malhotra² for some liquids confirm these limits. Some authors suggest to take it as a universal constant equal to 0.0894.²⁰ Nevertheless, an interesting consequence of Eq. (10) is that the ratio $(\rho_{\text{sp}}/\rho_0)$ should take a value about 0.50, which confirms the results of this quantity previously reported by us for liquids such as chloroform and *n*-hexane.⁹

Regarding Eqs. (2)–(4), as shown above, the behavior of solids at high pressures is generally described by the isothermal bulk modulus B_0 and its pressure derivatives B'_0 , B''_0 , etc., at zero pressure. For a given substance, the values of this parameters show considerable disagreement among different authors partly because they depend on the choice of the equation employed to describe the experimental data. Furthermore, the same equation usually leads to different values of the parameters depending on the experimental range of pressures considered.

TABLE I. Comparison of the characteristic parameters of Eq. (6) obtained from the fit of experimental densities (Ref. 19) with those calculated from the coefficients of the Tait equation reported in Ref. 19.

T/K	$\rho_{\text{sp}}/\text{mol dm}^{-3}$		$\kappa^*/\text{MPa}^{-0.15}$		p_{sp}/MPa	
	Eq. (6)	Tait	Eq. (6)	Tait	Eq. (6)	Tait
298.13	8.651	8.471	0.0482	0.0497	-104.9	-105.6
273.22	9.014	8.725	0.0462	0.0483	-123.2	-128.0
248.07	9.340	8.974	0.0447	0.0472	-142.8	-149.8
227.60	9.328	9.174	0.0449	0.0460	-175.8	-176.5
198.77	9.330	9.443	0.0454	0.0449	-217.9	-208.2

From Eqs. (5) and (6), the following expressions for B_0 , B'_0 , and v_0 are easily obtained as well

$$B_0 = (1/\kappa^*)(-p_{sp})^\gamma, \quad (11)$$

$$B'_0 = \gamma B_0 / (-p_{sp}), \quad (12)$$

$$v_0 = v_{sp} \exp\{\gamma / [(\gamma - 1)B'_0]\}. \quad (13)$$

The validity of these expressions will be shown in the following sections.

III. COMPARISON WITH EXPERIMENT

A. Liquid metals

Values of B_T for mercury were reported by Le Neindre and Osugi¹ by fitting the experimental pVT results of Bridgman²¹ between 243.15 and 293.15 K to Eq. (1). We fitted to Eq. (6) the experimental isotherms reported by Grindley and Lind²² for mercury of up to 800 MPa and found that, according to Eq. (8), the divergence pressures obtained were in excellent agreement with the smoothed values reported by Le Neindre and Osugi for $B_T(T)$. Furthermore, Eq. (6) fits the data within 0.0003 g cm^{-3} , being about 0.0014 g cm^{-3} the estimated uncertainty reported by the authors. Figure 1 shows the temperature dependence of our divergence pressures obtained from the fit and those B_T reported by Le Neindre and Osugi. Results of p_{sp} obtained at several temperatures from the experimental speed of sound measurements of Davis and Gordon²³ up to 1.3 GPa are also included in Fig. 1. Excellent agreement is found for these values as well, confirming an important feature of Eq. (6), namely, that, for a given temperature, its characteristic parameters are not too influenced either by the range of pressure con-

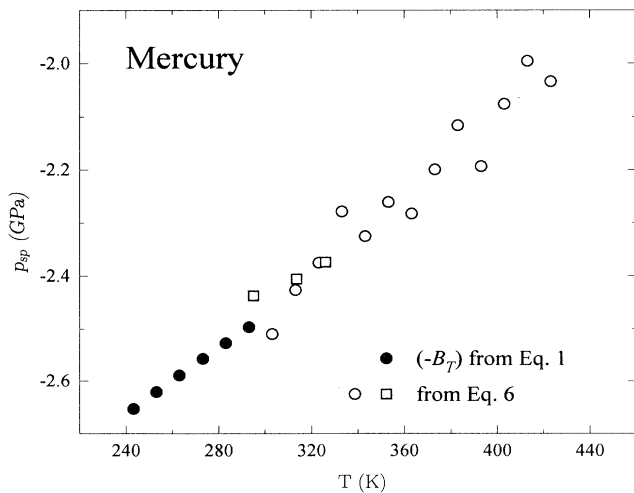


FIG. 1. Test of the validity of Eq. (8) for liquid mercury. We compare the results for the pressure parameter of the Tait equation B_T reported by Le Neindre and Osugi (Ref. 1) (●) with our results for the divergence pressures, p_{sp} , obtained from the fitting of the experimental isotherms of Grindley and Lind (Ref. 22) (○) and Davis and Gordon (Ref. 23) (□) to Eq. (6).

sidered in the correlation or by the different data sources consulted.

B. Polymers

In a recent review, Rodgers²⁰ reported the coefficients of the Tait equation for more than 50 polymers and experimental pVT data of four polymers up to 200 MPa. Although the values of the coefficients reported by this author are smoothed ones, they suffice for our purposes since we are mainly interested in evaluating the validity of the equivalence expressed by Eq. (8) and in the ability of Eq. (6) to represent experimental data at high pressures for different materials. We shall show here the results obtained for poly(ϵ -caprolactone) (PCL) only. We obtained similar results for polypropylene, poly(vinyl chloride), and poly(epichlorohydrin).

Thus, we fitted to Eq. (6) the specific volumes of PCL in the liquid state along five isotherms by fixing p_{sp} to the negative value of the smoothed values of $(B_T, \text{MPa}) = 189 \exp\{-0.003931(T - 273.15)\}$ reported by Rodgers. The parameters v_{sp} and κ^* obtained from the fit are plotted in Fig. 2 as functions of the temperature. Both quantities exhibit a simple linear dependence with temperature in this range of temperatures, which indicates that Eq. (6) would be useful to predict the high-pressure behavior of this kind of system at higher temperatures. Figure 3 shows the ability of Eq. (6) to represent the pVT of PCL using the parameters referred to above.

According to Eq. (9), our results of κ^* indicate that C_T should be about 0.084 rather than 0.0894 used by Rodgers. This difference leads to systematic differences between the corresponding parameters of Eqs. (1) and (6) according to Eqs. (9) and (10). It can be also confirmed by fitting the experimental data of Rodgers to Eq. (6) with the three parameters free; one finds that $(-p_{sp})$ is always greater than the B_T of Rodgers at the same temperature in about 20 MPa. A detailed analysis of Rodgers' results reveals that Eq. (1) is not flexible enough to fit the whole

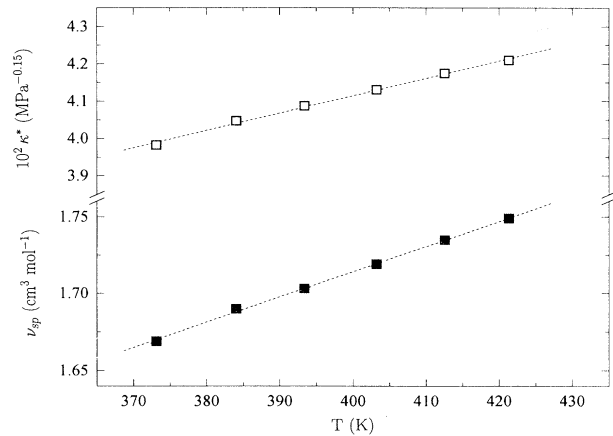


FIG. 2. Parameters v_{sp} (■) and κ^* (□) of Eq. (6) as functions of the temperature for poly(ϵ -caprolactone). Experimental specific volume results (Fig. 3) and those of $B_T(T)$ [equal to $-p_{sp}(T)$ according to Eq. (8)] taken from Ref. 20 (see text).

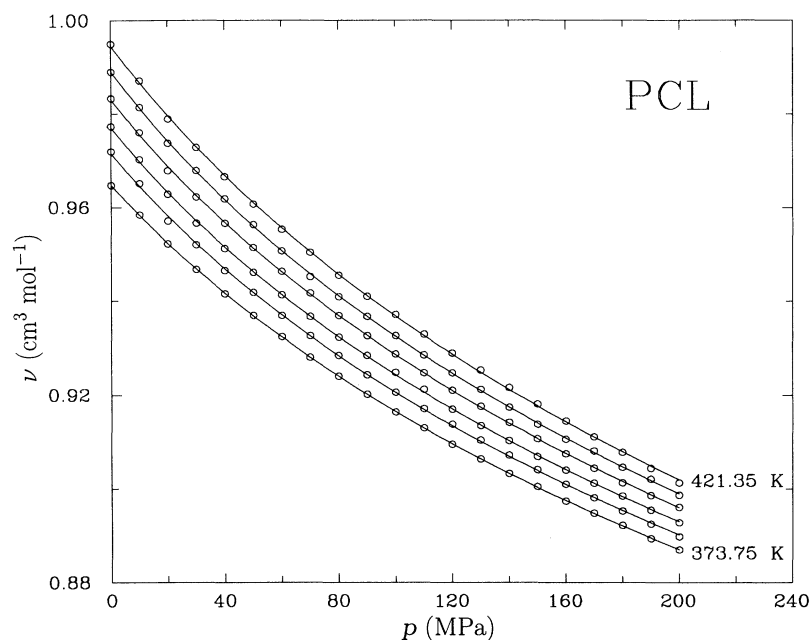


FIG. 3. Test of Eq. (6) (—) for experimental specific volume results of poly(ϵ -caprolactone) (PCL) (\circ) reported by Rodgers (Ref. 20). Isotherms are spaced about 10° apart ranging from 373 to 421 K.

pVT data using the functions described there. An alternative and suitable function to represent $p_{sp}(T)$,¹¹ and so $B_T(T)$, is the [1/1] Padé approximant proposed by Alba *et al.*²⁴ Supposing that the pseudospinodal curve in (p, T) variables is well described by this Padé, we have recently derived a complete equation of state based on Eq. (6).²⁵ The final expression represents accurately the thermodynamic properties of liquids up to very high pressures using only seven adjustable parameters, all of them with a clear physical meaning. Results of this section suggest the use of this equation of state in pVT correlations of polymers also.

C. Molten salts

Owens²⁶ reported densities of several molten alkali nitrates determined by the piston-cylinder method at pressures up to 9000 atm (1 atm = 0.101 325 MPa). The rough volume data were reported in the form $(v_1 - v)/v_0$, v_1 being the volume at 1000 atm and v_0 the zero-pressure volume. Figure 4 shows the test of Eq. (6) to represent the 377 K isotherm of KNO_3 . The characteristic parameters of Eq. (6) as obtained from the fit at this temperature are $v_{sp} = 5.5388 \text{ cm}^3 \text{ mol}^{-1}$; $\kappa^* = 0.009 761 \text{ atm}^{-0.15}$, and $p_{sp} = -9668 \text{ atm}$. Similar results were obtained for

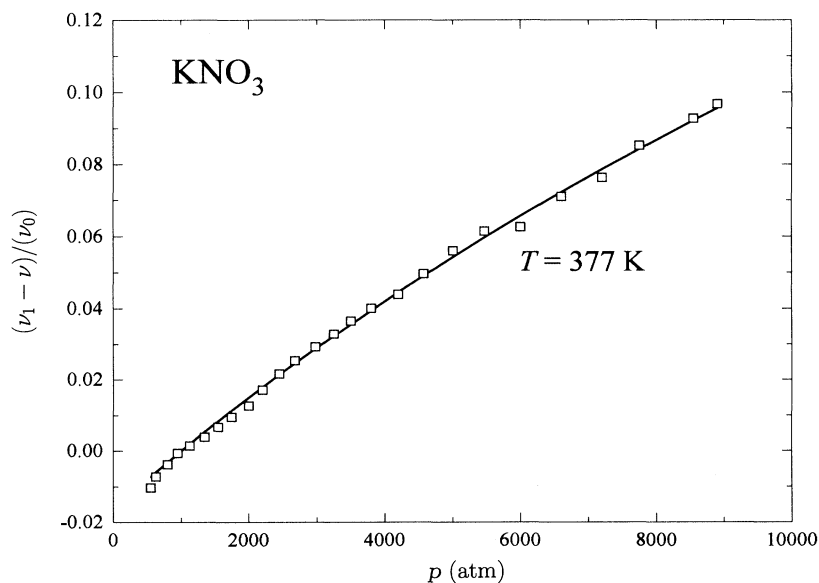


FIG. 4. Test of Eq. (6) for experimental specific volume results of molten KNO_3 at 377 K reported by Owens (Ref. 26) (\square). v_1 is the volume at 1000 atm and v_0 the zero-pressure volume.

all the isotherms of KNO_3 and other alkali molten salts, namely LiNO_3 , NaNO_3 , and RbNO_3 . In general, the results for κ_T at atmospheric pressure obtained by extrapolation of Eq. (5) agree well with those determined by ultrasonic measurements in molten salts.²⁶

D. Solids

We shall now analyze the literature data of some selected solids in order to test the prediction, representation and extrapolation capabilities of Eq. (6) in the study of these materials. We shall also compare the performance of Eq. (6) with those listed in Sec. I.

1. Normal hydrogen

Experimental data of normal hydrogen ($n\text{-H}_2$) are available in the literature for very high compressions at about 5 K,^{27,28} so this substance provides a severe test to any universal relation for solids. In this sense, Vinet *et al.*⁷ analyzed the experimental data of this substance in terms of their universal relation and found satisfactory agreement up to very high pressures using only zero-pressure data as input. The input values they used to determine the characteristic parameters of Eq. (4) are $B_0 = 1.7$ kbar and $B'_0 = 7.0$, which were taken from Ref. 27. We shall use these values here also, so according to Eqs. (11)–(13) the characteristic parameters of Eq. (6) are the following: $v_{\text{sp}} = 2.247v_0$; $\kappa^* = 0.1539$ kbar^{-0.15}, and $p_{\text{sp}} = -0.206$ kbar.

Figure 5 shows the comparison of the experimental relative compressions reported in Refs. 27 and 28 with those predicted from Eqs. (3), (4), and (6). As Vinet *et al.*⁷ already confirmed, the Murnaghan prediction deviates significantly at very high pressures so it is not included in

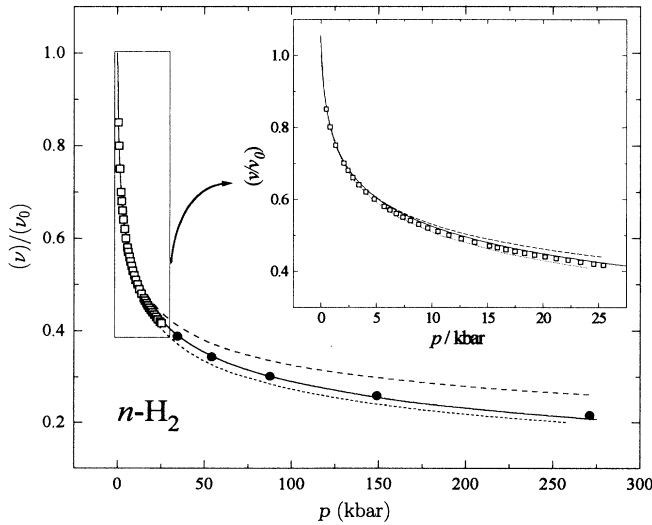


FIG. 5. Comparison of experimental relative compressions (v/v_0) for normal hydrogen (\square , Ref. 27; \bullet , Ref. 28) with several predictions using zero-pressure data as input (see text): [— — —, Eq. (3)], ($\cdot \cdot \cdot \cdot$, Eq. (4)], and [—, Eq. (6)]. The inset shows the low-pressure range with experimental data from Ref. 27 only.

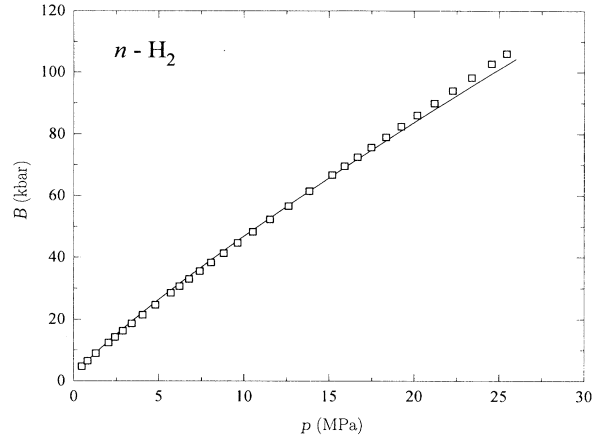


FIG. 6. Comparison of experimental bulk modulus B for normal hydrogen (\square , Ref. 27) with those predicted from Eq. (6) (continuous line).

the figure. It is observed that Eq. (6) yields the most accurate results over the whole pressure range.

Figure 6 compares data for the bulk modulus of $n\text{-H}_2$ reported by Anderson and Swenson²⁷ to those calculated from Eq. (5). Again, the agreement between calculated and experimental results is excellent.

2. Solid argon

The volumetric properties of solid argon were measured at room temperature by Ross *et al.*²⁹ up to 80 GPa using a diamond-window high-pressure cell. We have fitted their experimental volumes to Eq. (6). The characteristic parameters of the fit are the following: $v_{\text{sp}} = 51.726$ cm³ mol⁻¹; $\kappa^* = 0.1445$ GPa^{-0.15} and $p_{\text{sp}} = 0.28$ GPa. The results are plotted in the inset of Fig. 7. Ross *et al.*²⁹ reported Monte Carlo calculations for solid argon using an (exp-6) potential. They found a

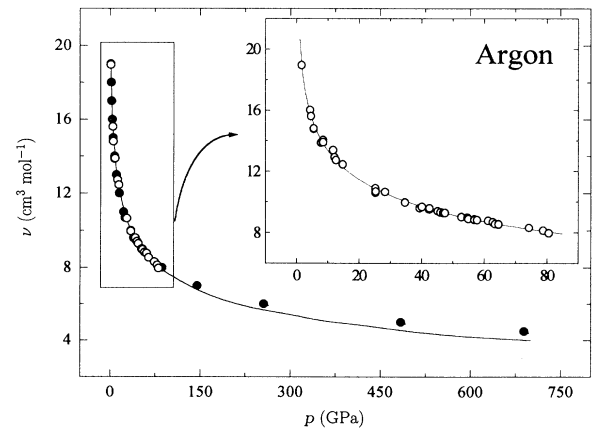


FIG. 7. Test of Eq. (6) for solid argon for experimental results of molar volume reported by Ross *et al.* (Ref. 29) (\circ) (see inserted figure). Comparison of molar volume results extrapolated with Eq. (6) up to 700 GPa (—) with those reported by Ross *et al.* (Ref. 29) from Monte-Carlo calculations using an (exp-6) potential.

good agreement between their calculated and experimental results up to 80 GPa and subsequently extended their calculations up to 700 GPa in order to compare their results with those determined from shock wave measurements. We have extrapolated our results using Eq. (6) up to 700 GPa. The comparison with the results of Ross *et al.* is plotted in Fig. 7. A fairly good agreement is found between both sets of data at the highest pressures, which confirms that, under the basis of some theoretical models also, Eq. (6) exhibits the correct trend up to extremely high pressures.

3. Ice VII

This is an allotropic form of ice with a body-centered-cubic unit cell and is the stable high-pressure phase at room temperature above 2.3 GPa.³⁰ Hemley *et al.*³¹ suggested that ice VII is a nonquenchable high-pressure phase. This issue makes ice VII a suitable phase for testing the fitting and extrapolation capabilities of Eq. (6) in solid water because of the absence of phase transitions.

Fei, Mao, and Hemley³⁰ measured the volumetric properties of ice VII up to 18 GPa using a diamond-anvil high-pressure cell. We fitted their results to Eq. (6) and found the following values for the characteristic constants: $v_{sp} = (1/\rho_{sp}) = 43.47 \text{ cm}^3 \text{ mol}^{-1}$, $\kappa^* = 0.1527 \text{ GPa}^{-0.15}$, and $p_{sp} = -4.02 \text{ GPa}$. Using these parameters we have calculated the volume of ice VII up to 130 GPa and found excellent agreement with the experimental results of Hemley *et al.*³¹ up to 128 GPa. The comparison is shown in Fig. 8.

We also fitted separately the experimental results of Fei, Mao, and Hemley³⁰ and Hemley *et al.*³¹ for ice VII to Eqs. (2), (3), (4), and (6) (explicit in the pressure). The characteristic parameters are recorded in Table II. The results are in good agreement with those reported by

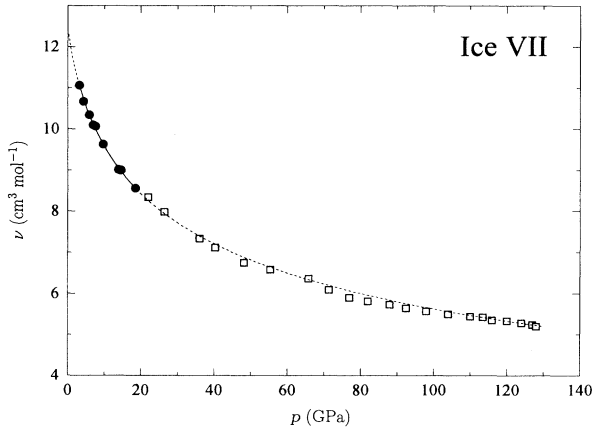


FIG. 8. Test of Eq. (6) for solid ice VII with experimental results of Fei, Mao, and Hemley (Ref. 30) (●) at room temperature. Only these results were used in the correlation (—). Comparison of molar volume results extrapolated with Eq. (6) up to 130 GPa (---) with those experimentally determined by Hemley *et al.* (Ref. 31) determined using a diamond-anvil cell (□) at the same temperature.

TABLE II. Comparison of the isothermal bulk modulus, B_0 , its pressure derivative, B'_0 , and the molar volume, v_0 , at zero pressure, for ice VII obtained from a weighted least-squares fit of the experimental molar volumes at 300 K: (a) up to 128 GPa (first row of each equation, 36 experimental points) (Ref. 31) and (b) up to 18 GPa (second row, ten experimental points) (Ref. 30). The chi square of the fit, χ^2 , is recorded in the last column.

	$v_0/\text{cm}^3 \text{ mol}^{-1}$	B_0/GPa	B'_0	χ^2/GPa^2
Eq. (2)	12.32±0.04	23.4±0.5	4.17±0.03	407
	12.4±0.2	21.7±4	4.5±0.6	4.48
Eq. (3)	12.54±0.05	18.9±0.6	5.12±0.05	341
	12.4±0.2	20.1±4	5.1±0.7	4.53
Eq. (4)	12.54±0.04	19.7±0.4	4.68±0.01	404
	12.4±0.2	21.0±4	4.7±0.4	4.50
Eq. (6)	12.40±0.05	21.6±0.7	4.38±0.05	399
	12.4±0.2	21.7±4	4.5±0.6	4.50

Hemley *et al.*³¹ using Eq. (2): $v_0 = (12.3 \pm 0.3) \text{ cm}^3 \text{ mol}^{-1}$, $B_0 = (23.7 \pm 0.9) \text{ GPa}$, and $B'_0 = (4.15 \pm 0.07)$. An important conclusion that can be extracted from Table II is that the parameters of Eq. (6) are not influenced too much by the range of pressures considered in the correlation; this feature of Eq. (6), already mentioned, is always desirable for any universal equation of state. It can be observed that unlike Eq. (2), Eqs. (3) and (4) meet also this condition.

4. Solid sodium chloride: Thermal expansion and temperature dependence of the parameters of Eq. (6)

Boehler and Kennedy³² reported accurate compression data of solid NaCl up to 3.5 GPa using a piston cylinder apparatus in which the length change of a single crystal of this substance is determined. We have calculated the ratio (v/v_0) from Eq. (6) using the values of B_0 and B'_0 obtained from ultrasonic experiments.⁷ Our computed values are in excellent agreement with experiment as shown in Table III.

The accuracy of the measurements of Boehler and

TABLE III. Molar volume ratio of NaCl (v/v_0) at 298.15 K predicted by Eq. (6) using the following parameters: $\kappa^* = 0.1304 \text{ GPa}^{-0.15}$ and $p_{sp} = -3.734 \text{ GPa}$, calculated from the experimental values of $B_0 = 23.5 \text{ GPa}$ and $B'_0 = 5.35$ given in Ref. 7.

p/GPa	Expt. (Ref. 32)	Eq. (6)
0.0	1.00 000	1.00 000
0.5	0.98 020	0.98 004
1.0	0.96 268	0.96 234
1.5	0.94 690	0.94 644
2.0	0.93 248	0.93 202
2.5	0.91 913	0.91 883
3.0	0.90 667	0.90 667
3.5	0.89 492	0.89 541

Kennedy allow them to determine, with relative accuracy, the pressure and temperature dependencies of the thermal-expansion coefficient α_p .

We think interesting to study this property for solids because Baonza, Cáceres, and Núñez³³ recently confirmed that the pressure behavior of α_p of molecular liquids is well represented by a power law identical in form to that expressed for κ_T in Eq. (5):

$$\alpha_p(p) = \alpha^*(p - p_{sp})^{-\gamma}, \quad (14)$$

where α^* is a proportionality constant and p_{sp} has the same meaning as that of Eqs. (5) and (6). For molecular liquids, the pseudocritical exponent γ of Eq. (14) was found to be close to 0.5 instead of close to 0.85 as found for κ_T .

An interesting observation found for molecular liquids was that Eqs. (5), (6), and (14) yielded the same pseudospinodal curve which, in addition, was consistent with other estimations.³⁴ This feature provided an excellent thermodynamic consistency test for these three equations. The question that arises now is whether this treatment would also be applicable to solids or not.

Thus, we correlated both the compression and thermal-expansion coefficient data of Boehler and Kennedy to Eqs. (6) and (14), respectively. A test of the fitting capabilities of Eqs. (6) and (14) is shown in Fig. 9.

The first interesting issue we found was that, unlike liquids, $\alpha_p(p)$ of solid NaCl can be well represented by Eq. (14) with a pseudocritical exponent equal to 0.85 as in the case of $\kappa_T(p)$. The characteristic coefficients of Eqs. (6) and (14) using $\gamma = 0.85$ are recorded in Table IV. It is noticeable that the divergence pressures obtained for both equations are almost identical for a given temperature. This observation indicates that the ratio (α_p/κ_T) , i.e., $(\partial p/\partial T)_v$, should be independent of the pressure at a given temperature, feature that would be useful for extrapolation. Experimental evidence of this observation is supported by the data reported by Yagi³⁵ for several alkali halides at high pressures. In fact, the assumption $(\partial p/\partial T)_v = \text{const}$ was used by Vinet *et al.*³⁶ to obtain the temperature dependence of the parameters of Eq. (4), and thereafter to predict the high-temperature behavior of Au, NaCl, and Xe, i.e., for temperatures above the Debye temperature θ_D , using the following expression:

$$p(v, T) = p(v, T_R) + \alpha_0(T_R)B_0(T_R)(T - T_R), \quad (15)$$

where T_R is a reference temperature and α_0 is the thermal-expansion coefficient at $p = 0$.

Parsafar and Mason⁶ have recently discussed Eq. (15). They stated that examination of pVT data for Au, NaCl, and Xe shows that $(\Delta p/\Delta T)$ at constant volume is only a weak function of T and v , and that Eq. (15) is quite successful for these systems. This feature for NaCl can be confirmed with the values of (α^*/κ^*) recorded in Table IV. However, many substances do not meet the criterion of $(\partial p/\partial T)_v = \text{const}$ and so would not be accurately described by Eq. (15).

Until now, we have not made any assumption about the temperature dependence of the characteristic parameters of Eq. (6) applied to solids. We have already men-

tioned that the Padé approximant given in Ref. 24 represents adequately liquid-vapor pseudospinodal curves of liquids and, as will be shown below, can be also used for solids.

v_{sp} (or ρ_{sp}) can be well described by any function able to represent the liquid branch of the vapor-liquid coexistence curve since both curves, pseudospinodal and coexistence, are related approximately only by a constant,^{9,17} in agreement with Eqs. (10) and (13). Therefore, it is necessary to study the temperature dependencies of both α^* and κ^* in order to confirm that Eq. (6) can be applied to any solid regardless of the temperature dependence of the ratio (α^*/κ^*) . For liquids it has been shown that κ^* is a smooth increasing function of temperature²⁵ and that α^* is a smooth decreasing function of temperature.¹¹ Results of Table IV for NaCl do not allow any conclusion for solids, but is obvious that the extent in which the two opposite behaviors are canceled clearly determines the variation of (α^*/κ^*) . So let us study this variation by an indirect, but quite general, method.

According to Skripov¹⁷ the spinodal curve can be considered as the envelope of the isochores of a given phase extrapolated well into the metastable region. Thus, although both κ_T and α_p are infinity at the spinodal, their

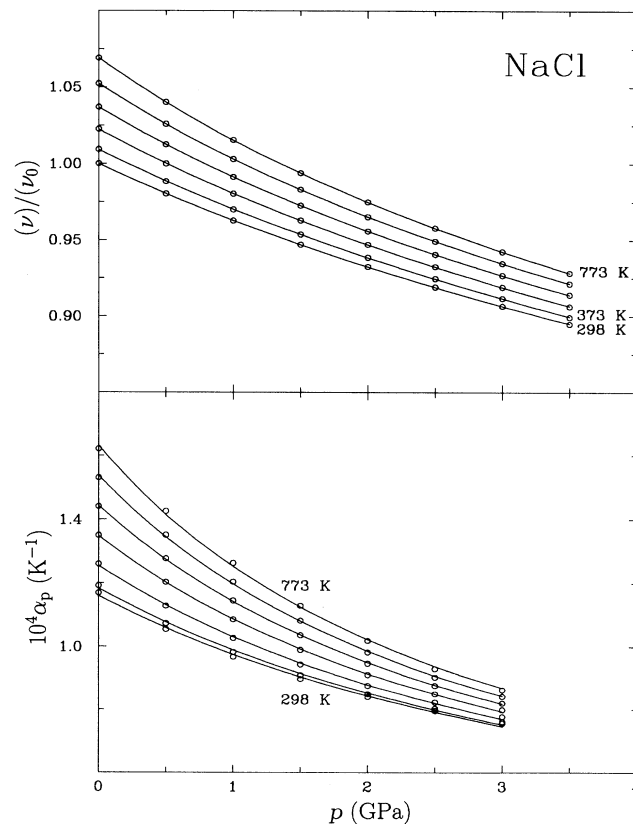


FIG. 9. Test of Eqs. (6) and (14) to represent compression and thermal expansion coefficient data of NaCl, respectively. Equations (6) and (14) are represented by continuous lines. The characteristic coefficients of both equations are recorded in Table IV. The experimental results (Ref. 32) of both quantities (\circ) are plotted at the following temperatures: 298, 373, 473, 573, 673, and 773 K.

TABLE IV. Characteristic coefficients of Eqs. (6) and (14) for NaCl obtained from the fit of experimental densities and thermal-expansion coefficient data reported in Ref. 32. Units are v_{sp} in $\text{cm}^3 \text{mol}^{-1}$; κ^* in $\text{GPa}^{-0.15}$; p_{sp} in GPa; α^* in $\text{K}^{-1} \text{GPa}^{0.85}$. σ_v and σ_α are the standard deviations of the volume and of α_p expressed in $\text{cm}^3 \text{mol}^{-1}$ and in K^{-1} , respectively.

T/K	Eq. (6)					Eq. (14)			
	v_{sp}	κ^*	p_{sp}	$10^4 \sigma_v$	$10^4 \alpha^*$	p_{sp}	$10^7 \sigma_\alpha$	$10^4 \alpha^*/\kappa^*$	$-0.85B_0/B'_0$
298	3.2482	0.1422	-4.27	1	4.050	-4.25	7	28.5	-4.06
373	3.3145	0.1442	-4.13	2	3.952	-3.86	5	27.4	-3.84
473	3.1292	0.1385	-3.59	1	3.875	-3.46	3	28.0	-3.42
573	2.9736	0.1333	-3.11	1	3.833	-3.15	3	28.8	-3.09
673	2.9735	0.1332	-2.84	1	3.822	-2.92	5	28.7	-2.81
773	3.0125	0.1346	-2.61	1	3.828	-2.72	9	28.4	-2.65

ratio is completely determined by the *shape* of the spinodal curve in (p, T) variables, which can be expressed in the following limiting form:

$$(\alpha_p/\kappa_T)_{sp} = (dp/dT)_{sp} = (dp_{sp}/dT), \quad (16)$$

which, according to Eqs. (5) and (14), can be written as

$$(dp_{sp}/dT) = \alpha^*/\kappa^*. \quad (17)$$

From Eq. (16) the only special feature expected for those solids with (α^*/κ^*) constant, or nearly constant, is that should exhibit quite straight pseudospinodals. This fact does not preclude the use of Eq. (6) for other solids exhibiting a moderate or strong variation of (α^*/κ^*) since they will only exhibit more strongly curved pseudospinodals. The problem for obtaining a universal equation applicable for all solids is translated to find a function flexible enough to represent the pseudospinodal curve. We have found that the Padé approximant referred to above is able to capture the form of the different pseudospinodals studied by us. We would like to mention that the limiting equivalence expressed by Eq. (16) has been used to develop a rather successful equation of state for liquids²⁵ and we think that is an interesting, and thermodynamically consistent, method to obtain a universal equation for solids as well. Preliminary results are quite encouraging.

Regarding the α_p data of solids and its representation by Eq. (14), it is interesting to note that Fei, Mao, and Hemley³⁰ used a quite similar equation to represent their α_p data of ice VII

$$\alpha_p(p) = \alpha_0 [(B'_0/B_0)p + 1]^{-\eta}, \quad (18)$$

where α_0 is the zero-pressure thermal-expansion coefficient, which is usually taken to be a linear function of the temperature, and η is an adjustable parameter, which can be related to the so-called Anderson-Grüneisen parameter.³⁷ Fei, Mao, and Hemley found η to be 0.9 for ice VII, a result quite close to the value used here for the pseudocritical exponent $\gamma=0.85$. Since Eqs. (14) and (18) can be identified term by term, the expression that relates the divergence pressure with other quantities is $p_{sp} = -(B_0/B'_0)$; a result which contrasts with that given in Eq. (12), although the difference can be easily explained as follows: as already pointed out by Fei, Mao, and Hemley,³⁰ Eq. (18) has the form of the Mur-naghan equation;⁵ according to Sanchez, Cho, and

Chen,¹⁴ the linear modulus approximation places a bound on the amount of isotropic tensile stress that the material can sustain in the value $-(B_0/B'_0)$. This is the mechanical limit for isothermal, isotropic dilation or stretching of the liquid or solid. Allowing for a negative curvature in the bulk modulus, which we have shown is equivalent to Eq. (5),⁹ reduces this bound by a factor of γ ,¹⁴ in agreement with Eq. (12). The validity of Eq. (12) can be confirmed from the last column of Table IV using the results of B_0 and B'_0 obtained by Boehler and Kennedy by fitting their experimental compression data on NaCl to Eq. (2).

IV. APPLICATION OF EQ. (6) TO SEVERAL PHASES OF A SINGLE SUBSTANCE

An important feature of Eq. (6) is that it can be applied to systems with phase transitions. Thus, the study of both liquid and solid phases of the same substance is

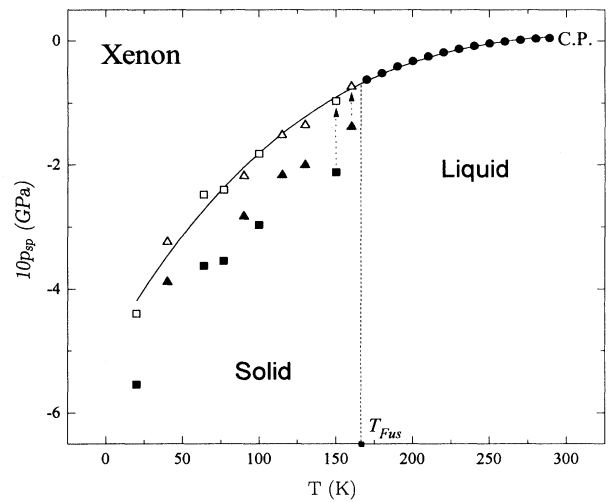


FIG. 10. Divergence pressures, p_{sp} , of liquid and solid xenon from Eq. (6). (○) obtained from experimental results of the liquid (Ref. 38). (■, ▲) obtained from experimental results of the solid (Ref. 39). (■, experimental runs L; ▲, experimental runs S). The arrows indicate that divergence pressures of the solid have been displaced accordingly to obtain a single pseudospinodal curve for both phases. The continuous line represents a simple third degree polynomial fit. C.P. denotes the critical point.

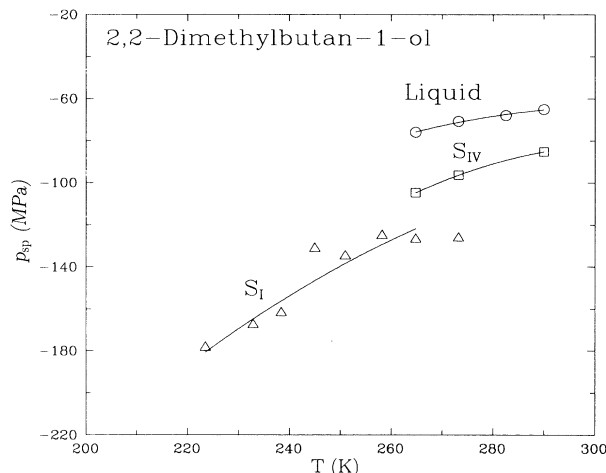


FIG. 11. Divergence pressures, p_{sp} , of liquid (\circ), solid IV (\square), and solid I (Δ) phases of 2,2-dimethylbutan-1-ol obtained by fitting the experimental results of Edelman, Bardelmeier, and Würflinger to Eq. (6).

quite interesting since it should provide us information about the trend exhibited by the pseudospinodal curves obtained using Eq. (6).

Accurate pVT results at high pressures are available in the literature for both liquid³⁸ and solid³⁹ xenon. We fitted the experimental isotherms of both phases to Eq. (6); the divergence pressures are plotted together in Fig. 10. Notice that both liquid-vapor and solid-liquid pseudospinodals⁴⁰ exhibit similar curvature, so it seems that both pseudospinodals can be put together into the same curve except for the jump occurring at the normal melting temperature.

Because the pressure ranges of liquid and solid densities found in the literature for Xe differ in two orders of magnitude, it is necessary to test that the jump in the value of the divergence pressures is independent of the pressure range considered in the correlation. Thus, we have fitted to Eq. (6) several isotherms of the liquid and the solid phases I and IV of 2,2-dimethylbutan-1-ol (Ref. 41) up to 300 MPa. The pseudospinodal curves obtained from the fit are plotted in Fig. 11. It seems that, as in the previous case, the different pseudospinodals follow similar trends but a characteristic jump in the divergence pressure is associated with each phase transition. Indeed, this is only an empirical observation and, at present, we are unable to relate these characteristic jumps to other characteristic quantities associated to the phase transition.

V. CONCLUSIONS

We have compared the ability of Eq. (6) to represent experimental isothermal data of several materials with perhaps the most well-known and long-standing used equations used to represent both liquid and solid phases, namely those of Tait and Birch-Murnaghan, respectively. It has been shown that Eq. (6) works equal to or better than both equations at moderate pressures and much better than extremely high pressures. Equation (6) has

been also compared to the most successful expressions available from literature, which have been analyzed here. The prediction and extrapolation capabilities of Eq. (6) have been also tested for several materials.

Although many alternative expressions to the Tait equation have been published in past years, none of them have succeeded in their challenge. Furthermore, many authors have pointed out that the simplicity and accuracy in reproducing experimental densities of the modified Tait equation will ensure its continued use well into the future.² Our own belief is that an utmost reason why the Tait equation is so well-established in the scientific community is that Tait coefficients are very frequently used in databases and reviews to represent experimental data for most materials. Maybe the possibility of obtaining the characteristic parameters of Eq. (6) through Eqs. (8)–(10) directly from Tait coefficients might ensure the use of Eq. (6) to represent the pVT surface of liquids, polymers, etc. In fact, if Eq. (8) is valid, Eqs. (9) and (10) are the simplest forms that can be obtained. Because of the different pressure dependence of Eqs. (1) and (6), slightly different values of the density are expected at high pressures. We have found that, if ρ_{sp} and κ^* are calculated from Eqs. (9) and (10), Eq. (6) yield lower values of the volume than Eq. (1) in about 0.5% at about 100 MPa. In practice, any value of the reference pressure can be chosen and, although escapes a bit from the scope of this work, we have found that experimental values are accurately reproduced using a reference pressure about 1.5–1.8 times B_T to calculate κ^* , so Eqs. (9) and (10) change a bit. Nevertheless, the important finding of the present work is that the procedure given here would definitively solve the problem of substituting the Tait equation from data correlation at high pressures.

Parsafar and Mason⁶ at the time of introducing the derivation of their universal equation for solids recovered the following statement of Macdonald:⁴² “It is extremely unlikely that there exists a universal equation of state, of useful degree of simplicity, best for all condensed materials.” Equation (6) is applicable to liquids, polymers, molten salts, and solids, and represents experimental pVT data with a quality comparable to the most widely used equations of state. It remains to be seen if Eq. (6) will be accepted by other scientists and researchers.

As a final comment, we would like to mention that while the liquid-vapor pseudospinodal curve obtained from the fit of experimental data of liquids to Eq. (6) lie very close to that calculated from $\alpha_p(p)$ measurements, that predicted from some equations of state³⁴ and that obtained from maximum superheat measurements in the metastable liquid region,⁹ it remains to be confirmed that the divergence pressures obtained through Eq. (6) from pVT data of the solid correspond to divergence pressures of a certain solid-liquid pseudospinodal curve obtained from other estimations.

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