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Abstract
The spinodal is a locus in the $P-V$ diagram, which is the limit of metastability
of a substance with respect to a phase transition. In particular, it is the limit to
the negative (tensile) pressure exerted on a liquid, at which the liquid may still
be metastable with respect to the gas phase. By requiring that the Helmholtz
free energy should be analytic at the spinodal, it is possible to derive the limiting
behaviour of thermodynamic properties near the spinodal. In the present paper
we show how this analyticity requirement may be used to choose between
available equations of state (EOSs). In particular it is shown that the universal
equation of state (UEOS) proposed by Vinet *et al*, complies with the analyticity
requirement and may be used to locate the spinodal by extrapolation from
within the stable region. The Baonza or 'pseudospinodal' EOS, which is
apparently based on the functional form of thermodynamic properties near
the spinodal, actually contradicts the analyticity requirement and indeed yields
manifestly wrong results in locating the spinodal. However it is shown that
the Baonza equation may be viewed as an approximation to the UEOS in
states of compression. Its technical importance, which stems from its algebraic
simplicity, is also stressed in the present work.

1. Introduction

The equation of state (EOS) of compressed fluids has been studied extensively leading to
several well-known EOSs, e.g. Birch–Murnaghan and the universal equation of state (UEOS).
The EOS of expanded fluids has been less studied and the general form of the EOS is not
well established. The thermodynamic structure of expanded fluids contains several elements,
including the equilibrium between gas and liquid states culminating at the critical point, which
has been studied extensively, and the spinodal, which has not.

The spinodal is a locus in the $P-V$ diagram, which is the limit of metastability of a
substance with respect to a phase transition. For example there is a limit to the negative (tensile)

pressure exerted on a liquid, at which the liquid may still be metastable with respect to the gas phase (a state analogous to superheating). At this limiting pressure, the bulk modulus of the liquid tends to zero, thus removing any barrier to the phase transition. In principle, the spinodal can be detected by experiments in the metastable region, but in practice such experiments are extremely difficult. Instead, efforts have been made to locate the spinodal by extrapolation from the stable region of the phase diagram [1]. A spinodal determined by extrapolation is termed a 'pseudospinodal'. These attempts have not been as successful as might be hoped [2] due to the lack of data in the neighbourhood of the spinodal. Alternatively, it has been suggested that assumptions regarding the location of the spinodal and the behaviour of various properties near it, may help to interpret experimental results in the stable region. Recently, Baonza *et al* [3, 4] developed an EOS based on the behaviour of the compressibility in the vicinity of the pseudospinodal. This equation has proven to be very successful in describing the compression of many liquids and solids. However their treatment suffers from two difficulties:

(a) it contains an adjustable parameter, the value of which was found to be different from the theoretical prediction;
(b) it predicts unreasonable values for the locus of the pseudospinodal, i.e. it fails to describe the expanded fluid (as might be expected from other work [2]).

In the present work we try to resolve these difficulties by comparing the pseudospinodal EOS to the UEOS by Vinet *et al*. In the process we show that an important feature of a successful EOS of expanded fluids is the analyticity of the free energy near the spinodal, which we then apply as a constraint on the form of the EOS.

2. The thermodynamic behaviour near the spinodal

The thermodynamic properties near the spinodal can be determined through an expansion of the free energy in its vicinity [2, 5]. If the Helmholtz free energy is *analytic* near the spinodal, it can be expanded along an isotherm by a Taylor series in $V - V_{sp}(T)$, where $V_{sp}(T)$ is the volume of the substance at the meeting point of the isotherm and the spinodal. The result of such an expansion was shown by Speedy [5] to be:

$$F(V, T) = F(V_{sp}, T) - P_{sp}[V - V_{sp}(T)] + \frac{1}{2}\frac{B_{sp}}{V_{sp}}[V - V_{sp}(T)]^2 + O([V - V_{sp}(T)]^3) \quad (1)$$

where $P_{sp}(T)$ is the pressure at the spinodal and B_{sp} is the value of the bulk modulus there, which by definition is zero.

The consequence of this analysis is that along an isotherm, close enough to the spinodal

$$B \propto \alpha^{-1} \propto C_p^{-1} \propto (|P - P_{sp}(T)|)^\beta \quad (2)$$

where B is the bulk modulus, $P_{sp}(T)$ is the spinodal pressure, α is the thermal expansion coefficient, C_p is the specific heat and β is a 'pseudocritical' exponent. Following Compagner [6], Speedy [5] has shown that, if the analyticity condition is observed, the value of β should be 1/2. This result is obtained immediately by inspection of equation (1); the pressure near the spinodal is proportional to the second power in the expansion or equivalently the volume is proportional to the square root of the pressure. Since the bulk modulus is proportional to the first power in the volume expansion, it is also proportional to the square root of the pressure. Thus, analyticity of the EOS near the spinodal produces a well-defined type of behaviour that does not depend on the particular EOS.

3. A pseudospinodal equation of state

Baonza *et al* derived a pseudospinodal EOS by adopting expression (2) in the form

$$B = (1/\kappa^*)(P - P_{sp})^\beta \qquad (3)$$

where P is the pressure, P_{sp} and κ^* are temperature-dependent constants and β is a constant. They found that the experimental data for an impressive variety of liquids and solids fit equation (3) well. Moreover, the simple algebraic form of equation (3) makes the Baonza equation an excellent candidate for use in thermodynamic databases, as discussed in appendix B. However, this fit to the measured compression data can only be achieved for values of β of approximately 0.85. This value is in marked disagreement with the analysis and has no theoretical justification.

By substituting zero pressure in (3) Baonza *et al* were able to relate P_{sp} and κ^* to the bulk modulus B_0 and its pressure derivative B_0', both taken at zero pressure. Further, integration of (3) yields also an expression for volume–pressure dependence:

$$V = V_{sp} \exp\left[-\frac{\kappa^*}{(1-\beta)}(P - P_{sp})^{(1-\beta)}\right] \qquad (4)$$

where V_{sp} is the volume where $P = P_{sp}$, that is, the maximum volume to which the condensed phase can be expanded and still be metastable. By substituting $P = 0$, connections are found between the spinodal parameters V_{sp} and P_{sp} and parameters measurable at zero pressure

$$V_{sp} = V_0 \exp\left[\frac{\beta}{B_0'(1-\beta)}\right], \qquad (-P_{sp}) = \frac{\beta B_0}{B_0'} \qquad (5)$$

where V_0 is the volume taken at zero or ambient pressure. Baonza *et al* [4] noted that with $\beta = 0.85$, the values of the ratio V_{sp}/V_0 calculated from equation (5) are too high to be physically reasonable. For example, consider sodium, which has $B_0' = 4.125$ at 294 K [7], and its ambient-pressure volume $V_0(T = 294) = 23.743$ (cm^3 mol^{-1}). Equation (5) gives $V_{sp}/V_0 = 3.95$ and the calculated spinodal volume is $V_{sp}(T = 294) = 97.8$ (cm^3 mol^{-1}). This is an unreasonable value since it is larger even than the volume at the critical point which is $V_c = 76.67$ (cm^3 mol^{-1}) [8]. Another difficulty with the Baonza *et al* treatment lies in the fact that they found that the bulk modulus diverges near the spinodal with the exponent 0.85, while the thermal expansion coefficient diverges with the exponent of 0.5. The thermodynamic analysis predicts that α and B should be inversely proportional to each other near the spinodal [2] (equation (2)).

4. Comparison with the UEOS

We hope to resolve some of the difficulties encountered by Baonza *et al*, by comparing equation (3) to another successful EOS due to Vinet *et al* [9].

Vinet *et al* based their UEOS on an analysis of the scaling relations in the volume dependence of cohesive energy. They concluded that:

$$P = \frac{3B_0}{X^2}(1 - X)\exp[\eta_0(1 - X)] \qquad (6)$$

where $\eta_0 \equiv \frac{3}{2}(B_0' - 1)$, X is the linear compression $X \equiv (\frac{V}{V_0})^{1/3}$ and V is the actual volume at pressure P. Equation (6) was designed primarily for metallic and covalent materials. As shown in appendix A, the corrections due to ionization and Coulomb attraction are not large, so that the results of the present section should apply also to ionic solids.

It is possible to calculate V_{sp}/V_0 by equating the derivative dP/dV of equation (6) to zero, yielding

$$\frac{V_{sp}}{V_0} = \frac{1}{8\eta_0^3}\left[\eta_0 - 1 + \sqrt{\eta_0^2 + 6\eta_0 + 1}\right]^3 \tag{7}$$

which to first order of $(X - 1)$ is: $(X_{sp} - 1) \approx (\frac{1}{\eta_0+1})$.

The pseudospinodal pressure P_{sp} may also be calculated by substituting equation (7) in (6).

The values of V_{sp}/V_0 calculated by equation (7) are much lower than those calculated by the Baonza EOS (equation (5)) (e.g. for sodium, $V_{sp}/V_0 = 1.54$) therefore they are more realistic and closer to the experimentally determined values for metals [10].

Equation (6) is analytic for all positive volumes, including V_{sp}, adjacent to which it diverges with $\beta = 1/2$, in agreement with the thermodynamic analysis. In order to calculate the divergence exponent β not only near the spinodal, we generalize equation (3) by:

$$\beta = \left(\frac{\partial \ln(B)}{\partial \ln(P - P_{sp})}\right)_T. \tag{8}$$

Using the definitions $B = -V\frac{dP}{dV}$ and $B' = -\frac{V}{B}\frac{\partial B}{\partial V}$, expression (8) may be written as:

$$\beta = \frac{B'}{B}(P - P_{sp}). \tag{9}$$

By substituting equation (6) into (9) we get an expression for β as a function of compression X. This expression is quite cumbersome, but its features are revealed by graphical presentation. β was calculated from equation (9) for several values of B_0' and plotted against the compression in figure 1.

As seen in figure 1, for very large pressures, X tends to zero and β tends to 1. On the other hand, for zero pressure, $X = 1$ and

$$\beta(P = 0) = \frac{B_0'}{B_0}(-P_{sp}) = (2\eta_0 + 3)\frac{(X_{sp} - 1)}{X_{sp}^2}\exp[\eta_0(1 - X_{sp})]. \tag{10}$$

This $\beta(P = 0)$ falls around 0.7 for all values of B_0' between 3 and 15. Near the spinodal, i.e. for $X \to X_{sp}$ and $P \to P_{sp}$, $\beta \to \beta(P_{sp}) = 1/2$ as follows from compliance with the analyticity requirement.

As seen in figure 1, for moderate to high compression, the value of β is between 0.7 and 1. We must though consider that most of the data used by Baonza *et al* to determine their value of $\beta = 0.85$ was in the region of moderate to high compression, namely $1 > X > 0.6$. As seen in figure 1, this value of $\beta = 0.85$ is quite close to the values of the function $\beta(V)$ derived from the UEOS for this range of compression. Hence the UEOS gives nearly the same results as the Baonza equation in the compression region and yet avoids the difficulties encountered by Baonza near the spinodal. Thus, the Baonza equation may be viewed as an approximation to the UEOS. The value $\beta = 0.85$ makes the approximation particularly good for typical values of $5 < B_0' < 10$. Indeed, the same equation (4) was developed by Sanchez *et al* [11] as a mathematical approximation, without relying on the concept of a pseudospinodal. The Baonza EOS is nevertheless very useful, since it gives good predictions in states of compression, comparable to the UEOS, expressed in a simpler algebraic form. This makes the Baonza EOS a potential candidate for use in thermodynamic databases, as explained in appendix B.

5. The analyticity at the spinodal as a constraint on the equation of state

In the previous section it has been shown that, while the Baonza EOS, which does not comply with the analyticity requirement, yields wrong estimates of the spinodal, the UEOS, which
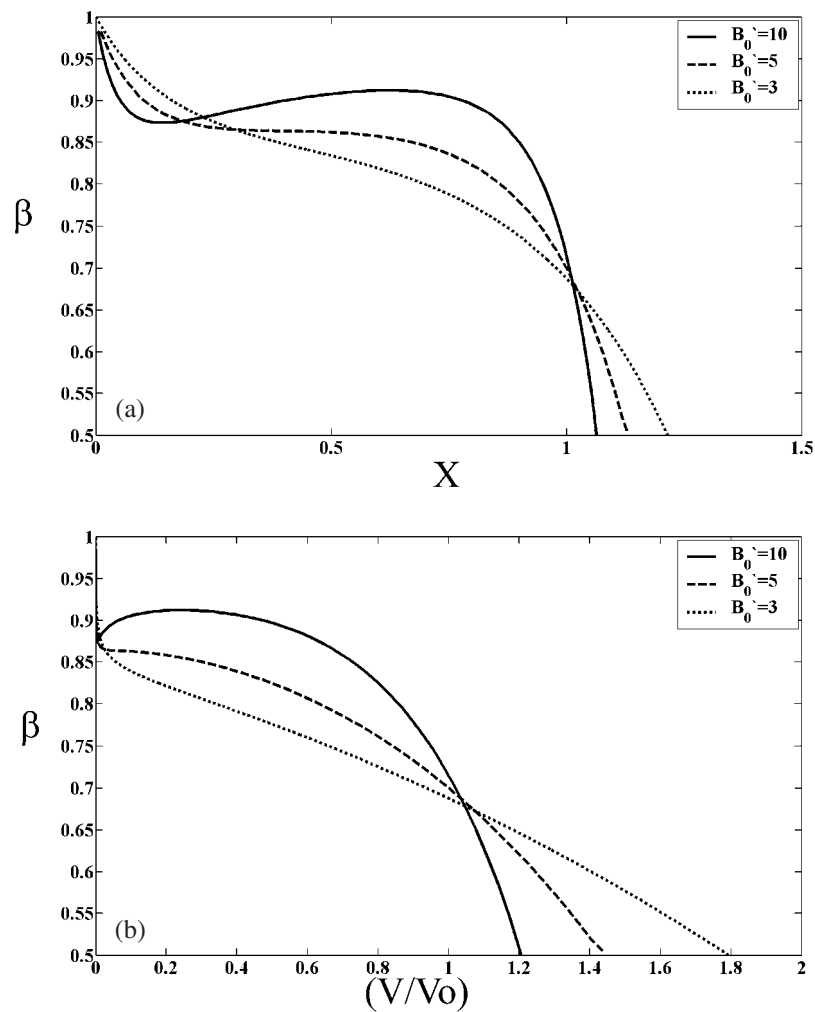
Figure 1. β as function of (a) the linear compression X (b) the relative volume, for several values of B_0'. It is seen that for the typical value of $B_0' = 5$, $\beta = 0.85$ is quite a good approximation to the UEOS for high compression.

does comply with the analyticity requirement, yields reasonable estimates for the spinodal locus. We suggest that in applications where the description of material behaviour in negative pressures is important, the analyticity assumption may serve as an aid for selecting a suitable EOS. Several EOSs, commonly used to describe condensed phases, are considered below.

5.1. The Murnaghan equation of state

The Murnaghan EOS has been popular because of its simplicity and because it may be integrated analytically [12, 13]. It is based on the assumption that the bulk modulus varies linearly with pressure

$$B = B_0 + B_0' P, \qquad B' = B_0'. \tag{11}$$

Integrating equation (11) yields:

$$V = V_0(1 + B_0'P/B_0)^{-\frac{1}{B_0'}}. \tag{12}$$

P_{sp} can be calculated by setting $B = 0$ in equation (11) giving $(-P_{sp}) = \frac{B_0}{B_0'}$. Substitution into equation (12) gives the manifestly wrong prediction $V_{sp} = 0$. By equation (9):

$$\beta = \frac{B'}{B}(P - P_{sp}) = \frac{B_0'}{(B_0 + B_0'P)}\left(P + \frac{B_0}{B_0'}\right) = 1. \tag{13}$$

Thus, the Murnaghan EOS does not comply with the analyticity requirement (section 1) and should not be used to describe matter in negative pressure.

5.2. The Birch–Murnaghan EOS

The Birch–Murnaghan EOS originated from finite-strain theory. However, it is very close to the UEOS in its predictions and also in its algebraic form, as shown by Jeanloz [14]. The Birch–Murnaghan EOS is given by:

$$P = \tfrac{3}{2}B_0(X^{-7} - X^{-5})[1 + \tfrac{3}{4}(B_0' - 4)(X^{-2} - 1)]. \tag{14}$$

The prediction for spinodal volume is:

$$\frac{V_{sp}}{V_0} = \left(\frac{21B_0' - 98 - 2\sqrt{9B_0'^2 - 84B_0' + 241}}{15B_0' - 80}\right)^{3/2}. \tag{15}$$

For sodium it gives the value $V_{sp}/V_0 = 1.64$, not far from the UEOS prediction as expected. As equation (14) is analytic everywhere except at $V = 0$, the Birch–Murnaghan EOS complies with the analyticity requirement.

5.3. The generalized Lennard-Jones potential and the Gilvarry EOS

The generalized Lennard-Jones cohesive energy relation can be written as [15]:

$$F = A(r)^{-m} - B(r)^{-n} \tag{16}$$

where r is the interatomic distance and A, B, m and n are constants. Common choices are $n = 6$ (for induced dipole interaction) and $m = 12$. After some manipulation, the constants A and B may be replaced by more physically meaningful parameters and (16) may be rewritten as:

$$F = \frac{F_0}{(m - n)}\left[n\left(\frac{V}{V_0}\right)^{-m/3} - m\left(\frac{V}{V_0}\right)^{-n/3}\right] \tag{17}$$

where F_0 is the binding free energy (which reduces to the binding energy U_0 at 0 K). Differentiating equation (17) with respect to the volume yields:

$$P = \frac{3B_0}{(m - n)}\left[\left(\frac{V}{V_0}\right)^{-(m/3+1)} - \left(\frac{V}{V_0}\right)^{-(n/3+1)}\right] \tag{18}$$

where B_0 is connected to the parameters of equation (17) by: $B_0 = \frac{F_0mn}{9V_0}$.

Equation (18) is the Gilvarry EOS [16]. Note that this EOS has one more adjustable parameter than the UEOS. Further differentiations yield:

$$B = \frac{3B_0}{(m - n)}\left[(m/3 + 1)\left(\frac{V}{V_0}\right)^{-(m/3+1)} - (n/3 + 1)\left(\frac{V}{V_0}\right)^{-(n/3+1)}\right] \tag{19}$$
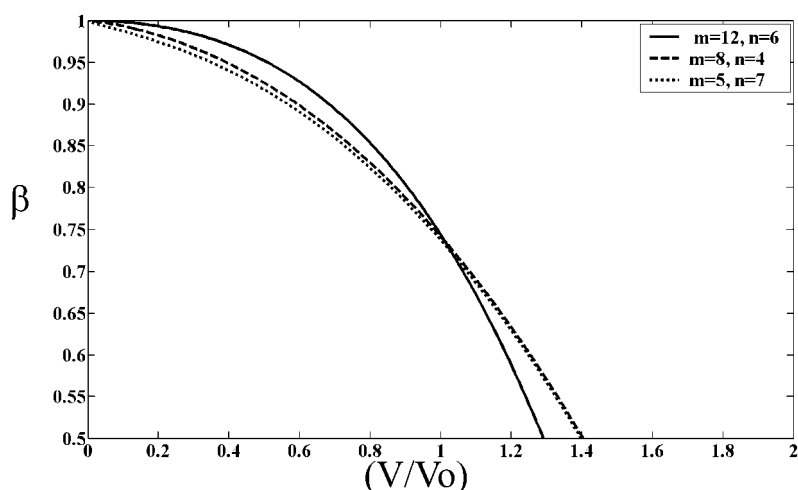
Figure 2. Calculation of the parameter β for several values of m, n in the Lennard-Jones potential.

and:

$$B' = \frac{\left[(n/3+1)^2\left(\frac{V}{V_0}\right)^{(m/3+1)} - (m/3+1)^2\left(\frac{V}{V_0}\right)^{(n/3+1)}\right]}{\left[(n/3+1)\left(\frac{V}{V_0}\right)^{(m/3+1)} - (m/3+1)\left(\frac{V}{V_0}\right)^{(n/3+1)}\right]}. \quad (20)$$

Setting $V = V_0$ in equation (20) yields $B'_0 = m/3 + n/3 + 2$.

V_{sp} is given by setting $B = 0$, giving

$$\frac{V_{sp}}{V_0} = \left(\frac{m+3}{n+3}\right)^{\frac{3}{(m-n)}}, \qquad \frac{-P_{sp}}{B_0} = \frac{3}{(m+3)}\left(\frac{m+3}{n+3}\right)^{\frac{-(n+3)}{(m-n)}} = \frac{3}{(m+3)}\left(\frac{V_{sp}}{V_0}\right)^{-(n/3+1)}. \quad (21)$$

Equation (17) may be expanded as a power series around V_{sp}. Now, β can be calculated by substituting equations (18)–(21) into (9). The results are presented in figure 2 and show that, at the spinodal, $\beta = 1/2$ (it is possible to give an explicit expression but it is too long for inclusion in the present text) as required i.e. Gilvarry EOS is suitable for describing the properties of expanded fluids.

5.4. The Lennard-Jones potential and molecular-based EOS

In the previous section, the Gilvarry EOS was deduced from a generalized Lennard-Jones potential by a simple algebraic manipulation. Such an approach may be justified at low temperature, where the thermal pressure is small relative to the zero-temperature binding energy, so that all temperature effects may be represented by temperature-dependent parameters in the potential. However, this is not rigorous, in the sense that if an ensemble of molecules is interacting via a Lennard-Jones potential (equation (16)), equation (18) may not be deduced from this theoretical setup by means of a statistical-mechanics analysis. Unfortunately, an exact analytical EOS, based on the Lennard-Jones potential, does not exist yet. This difficulty is overcome by the use of empirical EOSs, in which adjustable parameters are fitted to the results of computer simulations, and the development of semi-theoretical EOSs, based on the perturbation of some known EOS. An example of the second, more theoretical approach is the very accurate EOS due to Kolafa and Nezbeda [17] for the 12,6 Lennard-Jones potential. Another, particularly simple, EOS of this type was developed by Hess [18]. Hess started from

a modified hard-spheres approximation for a fluid of particles interacting only via the repulsive part of the Lennard-Jones potential, which he denoted WCA. The attractive part of the potential entered the EOS via the second virial coefficient. The resulting expressions are:

$$F = k_B T \left\{ \frac{\left(\frac{B^{WCA}}{V}\right)}{1 - \left(\frac{v_{eff}}{V}\right)} + \left[\frac{\left(\frac{v_{eff}}{V}\right)}{1 - \left(\frac{v_{eff}}{V}\right)} \right]^2 \right\} + \frac{k_B T}{V}(B^{LJ} - B^{WCA}) \qquad (22)$$

where k_B is the Boltzman constant, v_{eff} is an effective hard-sphere volume and B^{WCA} and B^{LJ} are the second virial coefficients of the WCA and Lennard-Jones potentials. v_{eff}, B^{WCA} and B^{LJ} are functions of the temperature.

Expression (22) for the free energy is analytical for $V > v_{eff}$. Thus, in principle, the Hess EOS may be used for locating the spinodal, although the spinodal volume cannot be evaluated analytically.

It should be noted that equation (22) may be used only for relatively high temperatures, since it does not include any 'cold' part.

6. Conclusions

The arguments leading to a power law behaviour of the bulk modulus near the spinodal are quite general. However, the extrapolation of such a power law from the stable region, in order to locate the spinodal, is probably wrong since it leads to unreasonable predictions of the spinodal volume. There is also an internal contradiction in such a procedure because, if a non-1/2 power law is used to fit experimental data in the stable region, then the assumption of analyticity on which the power law is based is violated. However, other commonly used EOSs comply with the analyticity assumption and it was shown that the use of such equations also leads to reasonable estimations of the spinodal locus. Therefore we propose that consistency with the analytical thermodynamic expansion be considered as a relevant constraint in constructing EOSs for expanded fluids.

With regard to the power law 'pseudospinodal' EOS of Baonza *et al*, it may be viewed as an approximation of other EOSs, such as the UEOS, for states of compression but it is not suitable for describing expanded fluids. Instead we propose that the main benefit of the Baonza equation is due to its simple algebraic form, which makes it potentially useful in thermodynamic databases, as discussed in appendix B.

Appendix A. Application of the UEOS to ionic solids

A pressure–volume relation (an EOS) is always based on a certain binding energy relation—a curve of energy plotted versus volume or atomic separation. The UEOS was originally derived by Vinet *et al* [9] from the 'universal binding energy relation' due to Rose *et al* [19]. Vinet *et al* noted from the start that, although the binding energy relation fits only metallic or covalent materials, the UEOS itself (the pressure–volume relation) is also suitable for ionic solids. An example of the applicability of (6) to ionic solids may be found in [9], where it is applied to NaCl.

In this appendix we evaluate the error in using the UEOS for ionic solids and show that it is small. This is done by comparing the UEOS to an EOS derived from a corrected binding energy relation, which provides a better fit for ionic materials. From the UEOS, we may derive a binding energy relation. The Helmholtz free energy is given by integration of (6)

$$F(T, V) - F(T, V_0) = \int_{V_0}^{V} P \, dV' = V_0 B_0 \frac{9}{\eta_0^2} \{[1 - \eta_0(1 - X)] \exp[\eta_0(1 - X)] - 1\}. \quad (23)$$

Setting a constraint

$$F(T, V_0) - F(T, \infty) = F_0, \tag{24}$$

where F_0 is the binding energy, yields the Rydberg function potential:

$$F(T, V) - F(T, \infty) = -F_0[1 + a]\exp[-a] \tag{25}$$

where $a = \sqrt{2\Delta}(X - 1)$ and Δ is the Sutherland parameter $\Delta = \frac{9V_0 B_0}{2F_0}$ [20]. This implies $\eta_0 = \sqrt{2\Delta}$. The Rydberg function agrees well with experimental results for metallic and covalent materials. Its agreement with experiment is not good for ionic or partially ionic materials. A similar problem occurs with other potentials in the analysis of diatomic molecules [21]. Therefore, it has even been suggested that the seemingly self-evident constraint (24) should be removed [21], so that, in the vicinity of the equilibrium atomic separation, the atomic dissociation energy F_0 should be replaced by some other effective binding energy. In fact, using the UEOS (6) with two adjustable parameters, B_0 and η_0, unbound by any relation to V_0 and F_0, is equivalent to dropping the constraint (24).

Smith *et al* [22] corrected the Rydberg function by adding a Coulomb attraction term. Kim *et al* [23] showed that the results might also be fitted by the Rydberg function, where the variable is scaled differently and another adjustable parameter is added, namely,

$$F(T, V) - F(T, V_\infty) = -F_0[1 + z]\exp[-z] \tag{26}$$

where $z \equiv a - ca^2$ and c is an adjustable parameter, related to the first coefficient in the Dunham expansion. Differentiating equation (26) with respect to the volume yields:

$$P = \frac{3B_0(1 - X)}{X^2}(1 - 3ca + 2c^2a^2)\exp(-z). \tag{27}$$

This is quite similar to the UEOS.

By further differentiating we can relate the constant c to measurable quantities:

$$\eta_0 \equiv \tfrac{3}{2}(B_0' - 1) = \sqrt{2\Delta}(1 + 3c). \tag{28}$$

Now, we examine the difference between equation (27) and the UEOS.

By division of (27) by (6) one obtains:

$$\frac{P_{Kim}}{P_{UEOS}} = (1 - 3ca + 2c^2a^2)\exp(3ac + ca^2) \approx 1 + (c - \tfrac{5}{2}c^2)a^2 - 3c^3a^3 + O(a^4). \tag{29}$$

Typically a_{sp} (at the spinodal) is 0.5 [23]. A typical value of c for alkali halides is 0.6. Thus the maximum correction in (29) is around 10%. In compression, the correction is even smaller because the Coulomb attraction term becomes less important at short distances.

In principle, we may use equation (27) to locate the spinodal by solving the equation: $\frac{dP}{dX} = 0$. However, this results in a 5th order polynomial equation, which does not have a closed form solution. Therefore, we use an approximation. We take the leading correction for the pressure and get:

$$\frac{P_{Kim}}{P_{UEOS}} \approx 1 + d\eta_0^2(X - 1)^2 \qquad \text{where } d = \frac{c(1 - \tfrac{5}{2}c)}{(1 + 3c)^2}. \tag{30}$$

The correction prefactor d is of order 0.1 with a maximum absolute value of 0.25. Now, equating $\frac{dP}{dX} = 0$ in (30), yields a polynomial equation:

$$[\eta_0 X^2 + (1 - \eta_0)X - 2] + d\eta_0^2[\eta_0 X^4 - (3\eta_0 + 1)X^3 + 3\eta_0 X^2 + (3 - \eta_0)X - 2] = 0. \tag{31}$$

The corrected X_{sp} may be evaluated by a single Newton–Raphson iteration, starting from X_{sp}^0 calculated for $d = 0$:

$$X_{sp} = X_{sp}^0 - \frac{d\eta_0^2[\eta_0 X_{sp}^{0\ 4} - (3\eta_0 + 1)X_{sp}^{0\ 3} + 3\eta_0 X_{sp}^{0\ 2} + (3 - \eta_0)X_{sp}^0 - 2]}{1 - \eta_0 + 2\eta_0 X_{sp}^0 + d\eta_0^2[4\eta_0 X_{sp}^{0\ 3} - 3(3\eta_0 + 1)X_{sp}^{0\ 2} + 6\eta_0 X_{sp}^0 + (3 - \eta_0)]}. \tag{32}$$

In order to evaluate the magnitude of the correction, it is enough to preserve only the leading term in powers of $(X_{sp}^0 - 1)$:

$$(X_{sp} - 1) = (X_{sp}^0 - 1)\left[1 + \frac{d\eta_0^2}{(1 + \eta_0)^2}\right]. \tag{33}$$

For the common values $c = 0.6$ and $B_0' = 5$, the relative correction to $(X_{sp} - 1)$ is around 3%. Hence, it may be concluded that although ionization and Coulomb attraction alter the shape of the binding energy curve, the effect on the EOS (6) is minor. Thus, it is safe to use equation (6) to describe ionic materials in compression and also for locating the spinodal.

Appendix B. Potential use of the Baonza EOS in thermodynamic databases

Current thermodynamic databases are used to calculate phase equilibria in various materials-engineering or geological applications, where pressure is sometimes an important factor. The thermodynamic properties of a substance are described in the database through the Gibbs free energy function, in the form:

$$G = G_{ambient}(T) + G_P(T, P) \tag{34}$$

where $G_{ambient}$ is the free energy at atmospheric pressure and G_P is the pressure component

$$G_P(T, P) = \int_{V_0}^{V} V' \, dP. \tag{35}$$

Up to now, the Murnaghan EOS was commonly used in thermodynamic databases to evaluate G_P because it may be integrated analytically [12, 13] while other EOSs, such as the UEOS or the Birch–Murnaghan EOS may not. However, the Murnaghan EOS is not suitable for pressures significantly larger in value than B_0. The Baonza EOS has proved successful at fitting experimental data even at such extreme pressures.

The Baonza EOS can also be integrated analytically if the exponent β is approximated by a rational number and the result is particularly simple if $\beta = 1 - 1/m$, where m is an integer. $m = 6$ or 7 provide a good approximation to the $\beta = 0.85$ value found by Baonza *et al*. With this approximation,

$$G_P(T, P) = B_0 V_0 \sum_{k=0}^{m-1} \frac{(m-2)!}{(m-1)^{(m-k-2)}k!} \left\{ B_0'^{(m-k-1)} \left[1 - Y^k \exp\left[-\frac{(m-1)(Y-1)}{B_0'}\right]\right]\right\}$$

$$Y \equiv \left(1 + \frac{m}{(m-1)} \frac{B_0' P}{B_0}\right)^{\frac{1}{m}}. \tag{36}$$

Thus, the Baonza EOS may be used in thermodynamic databases in the same way that the Murnaghan EOS is used today, but with an extended range of pressures. Similarly, the Baonza equation may be analytically integrated to give the Helmholtz free energy as a function of volume. This permits a relatively simple evaluation of properties such as sound velocities at extreme pressures.

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