EXTENDED AND GENERALIZED RYDBERG-VINET EQUATION OF STATE

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Abstract

The equation of state due to Rydberg and Vinet has been extended and generalized so as to make it applicable for different types of solids up to very high pressures. Various types of applications are presented and discussed.

Keywords: Equation of state, potential energy functions, phase transitions, Thomas Fermi energy.

INTRODUCTION

One of the tests of an equation of state fit is the accuracy with which it reproduces known zero pressure parameters. To this end, high – pressure static compression data can be compared with low-pressure elasticity measurements, including data from ultrasonic experiments, Brillouin scattering, or in some cases high precision static compression data. Useful low-pressure static compression data exist for hydrogen because of its very high compressibility. Swenson and Anderson [1] reported $K_{T_0} = 0.17 \pm 0.06$ GPa for n-H_2 from volumetric strain measurements to 2.5 GPa at 4.2 K. The results are in excellent agreement with those of Wanner and Mayer [2], who obtained K_{so} = 0.174 ± 0.010 GPa for single-crystal n-H_2 at 4.2K using ultrasonic methods. The latter number provides the best comparison with the present analysis (e.g. for n-H_2). These results are also close to zero-pressure Brillouin scattering results obtained at T = 4K for p-H_2 by Thomas et al. [3], the latter obtained KSO = 0.173 ± 0.001, with $K_{T_0} = 0.162$ GPa (corrected for isothermal conditions). Udovidchenko and Manzhelli [4] performed accurate static compression (volumetric) measurements on p-H_2 form 0 to 18MPa (down to 6K) and obtained $K_{T_0} = 0.186 \pm 0.006$ GPa. The neutron diffraction study of p-H_2 to 2.5 GPa by Ishmaev et al. [5] gave $K_{T_0} = 0.186 \pm 0.03$ and $K'_{T_0} = 6.33 \pm 0.2$. The Rydberg – Vinet K_0 is close to that determined directly, but the Birch and Holzapfel K_0 values are way too high. The deviation in K_{T_0} with the Rydberg-Vinet equation may be due to being thrown off by the equation of state glitch at 40 GPa, or may be due to insufficient flexibility in the Rydberg-Vinet equation over this large compression range. To examine this possibility, Cohen considered the extended Rydberg – Vinet equation given by Moriarty [6] and Vinet et al. [7].

$$P = 3K_0(1-x)x^{-2}\exp\left[\frac{3}{2}(K'_0-1)(1-x)+\beta(1-x)^2+\gamma(1-x)^3\right] \qquad (1)$$

where $\beta = \frac{1}{24}\left[36K_0K_0'' + 9K_0'^2 + 18K_0' - 19\right]$ (2)

When $\beta = 0$ and also $\gamma = 0$, then the extended Rydberg- Vinet equation (3) is reduced to the simple Rydberg–Vinet EOS (3). The Rydberg – Vinet EOS has been modified by Holzapfel [8] and by Hama and Suito [10] in order to remove its shortcomings.

The Holzapfel EOS is given below

$$P(x) = 3K_0x^{-5}(1-x)\exp[(cx + c_0)(1-x)] \quad (3)$$

and Hama and Suito EOS is written as follows

$$P(x) = 3K_0x^{-5}(1-x)\exp\left[\frac{3}{2}(K_0' - 3)(1-x)\right] \quad (4)$$

Holzapfel [8, 9] and Hama and Suito [10] modified the Rydberg formula to give $K'_\infty = 5/3$, but this is not going for enough. K'_∞ is an important, useful parameter, but it cannot be estimated in this way and, as Keane [11] observed, it has different values for different materials, all of them greater than 5/3. Parameters for the Thomas – Fermi state have no relevance to normal materials, and K'_∞ for a material in its observed state is not related to properties of something that it does not in the least resemble.

Extrapolation of an equation of state to infinite pressure merits a cautionary note. Infinite pressure properties are simply equation of state parameters, not observables in any direct sense, even in principle, because if any conventional solid were to approach infinite compression it would undergo dramatic phase transitions to exotic forms and equations of state do not carry through phase transitions. However parameters such as K'_∞ are just as legitimate as physical entities as are zero pressure properties, ρ_0 and K_0, for high pressure materials that do not survive decompression to P = 0. Stacey [12, 13] emphasized that an equation of state must satisfy basic physical laws, in particular thermodynamic relationships, even outside the pressure ranges over which the materials that it describes can exist. The thermodynamic identities retain their validity as $P \to \infty$.

Elsasser [14] first suggested the use of extrapolation to extreme pressure to constrain the form of an equation of state. He argued that at sufficient pressure all materials would be converted to a state described by Thomas – Fermi theory, effectively a free electron gas with embedded positive ions (nuclei). His idea was that equations of state should extrapolate smoothly to coincide with Thomas – Fermi theory at extreme compression. This suggestion misses the point that conversion to a Thomas – Fermi state would not be smooth and that any equation of state would be punctuated by discontinuities at phase transitions. The use of such an extrapolation to constrain K'_∞ has no validity and was rejected by Keane [11] but Knopoff [15] and Holzapfel [8] reintroduced Elsasser's idea, requiring equations of state to be adjusted to give $K'_\infty = 5/3$, to match the Thomas – Fermi condition. This idea has been accepted by others e.g. Hama and Suito [10] but must be rejected. Parameters for the Thomas-Fermi state have no relevance normal materials and K'_∞ for a material in its observed state is not related to properties of something that it does not in the least resemble. K'_∞ is an important, useful parameter, but it cannot be estimated in this way and, as Keane [11] observed, it has different values for different materials, all of them greater than 5/3.

Rydberg-Vinet EOS derived from the Rydberg potential, which has been extended by Moriarty [6] and Vinet et al. [7]. We have generalized the Eq. (1) as follows

$$P = a_1(1-x)x^{-n} \exp\left[a_2(1-x) + a_3(1-x)^2\right] \quad (5)$$

where

$$a_1 = 3K_0 \quad (6)$$

$$a_2 = \frac{1}{2}\left[\frac{9K_0K'_0}{a_1} - 2n + 1\right] \quad (7)$$

and $$a_3 = \frac{1}{6}\left[9K_0K''_0 + n^2 - n + 2na_2 + 2a_2 + a_2^2\right] \quad (8)$$

Here K_0, K'_0 and K''_0 are the pressure derivatives of bulk modulus at zero pressure. Where a_1 a_2 and a_3 depending up the value of K_0, K'_0 and $K_0K''_0$. These values are material depending i.e. changed only when the material changed. Since K_0, K'_0 and $K_0K''_0$ are also temperature dependent, a_1, a_2 and a_3 will changed accordingly.

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