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Pressure dependence of the isothermal bulk modulus of solids

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Abstract . Expressions for the isothermal bulk modulus B_t and its pressure derivatives for solids with analytical forms for their lattice potentials can be derived assuming the Helmholtz free energy to equal the lattice potential It has been observed in the past that the first pressure derivative of B_t and the ratio B_T/P reach a common limiting value as the solid is subjected to extremely high pressures ($P \to \infty$) We have reinvestigated this high pressure limiting behaviour with some interesting results In particular, the power law of the short-range potential yields a single common limit and not two distinct ones as reported elsewhere and the exponential law does not yield any limiting values at all

Keywords . Bulk modulus, power and exponential laws, high pressure limits

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1. Introduction

Expressions for the pressure P, the isothermal bulk modulus B_T and its pressure derivatives B'_T and B''_T can be derived from the lattice potential directly. These expressions can be used to study the high pressure behaviour of B_T/P and B'_T. It has been observed that for some potential energy functions, B_T/P and B'_T asymptotically approach finite limiting values. Shanker *et al* [1] have recently shown that the inverse power form of the lattice potential yields two distinct limits for these quantities. We show in this brief report that one of the two limits so found is spurious. We have also investigated other short range potentials and conclude that perhaps the common asymptotic limit of the two functions is a feature of potentials with an inverse power factor of the lattice parameter.

The analysis

The analysis is straightforward and well known. The essentials are being given here only to establish our point. Let us start with the Mie-Grueneisen lattice potential

$$u(r) = a / r^n + b / r^m. \tag{1}$$

a, b, n and m ($m > n$) are constants and r is the inter-atomic separation. From eq. (1), neglecting thermal effects, one obtains for the product of pressure P and volume $V = kr^3$, where k is a structure dependent constant

$$3PV = (mb / r^m)\left\{1 - (r/r_0)^{m-n}\right\}, \tag{2}$$

a subscript zero will invariably indicate value at zero pressure. Differentiation of eq. (2) yields

$$3B_T - 3P = (mb / 3Vr^m)\left\{m - n(r/r_0)^{m-n}\right\}. \tag{3}$$

Here, P is the pressure and B_T is the isothermal bulk modulus. We can therefore write

$$B_T / P = 1 + \left\{m - n(r/r_0)^{m-n}\right\} / 3\left\{1 - (r/r_0)^{m-n}\right\}. \tag{4}$$

In the extremely high pressure limit, even for $r/r_0 \sim 0.5$ instead of zero, $(r/r_0)^{m-n}$ should become negligible and we shall obtain

$$(B_T / P)_\infty = 1 + m/3. \tag{5}$$

The subscript ∞ indicates value at high pressure. Now, the pressure derivative of the isothermal bulk modulus B_T can be reduced to the form

$$B'_T = 1 + (P/9B_T)\left[\left\{m(m+3) - n(n+3)(r/r_0)^{m-n}\right\} / \left\{1 - (r/r_0)^{m-n}\right\}\right]. \tag{6}$$

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From eq. (6), we directly obtain

$$B'_{T0} = (m+n+6)/3, \quad (7)$$

(where B'_{T0} is the pressure derivative of the isothermal bulk modulus at zero pressure), a relation reported by Ledbetter [2] and used quite often in similar studies. Eq. (6) also yields

$$B'_{T\infty} = 1 + m/3 \quad (8)$$

which is obviously equal to $(B_T/P)_\infty$. Thus in the high pressure limit, both $(B_T/P)_\infty$ and $B'_{T\infty}$ asymptotically reach a common limiting value. Shanker *et al* [1] have used the short range force parameter

$$A = (1/3)\left\{d^2\phi/dr^2 - (2/r)d\phi/dr\right\}, \quad (9)$$

where ϕ is the short range potential They have obtained expressions for B_T and B'_T which can be put in the forms

$$B_T/P - 4/3 = A/3k\Pr, \quad (10)$$

$$B'_T = \{(4/3)P/B_T - 1\}\{(V/A)dA/dV - 1/3\} + 4/3. \quad (11)$$

Using the high pressure limit property

$$B'_{T\infty} = (B_T/P)_\infty, \quad (12)$$

the authors obtain a quadratic equation for $B'_{T\infty}$

$$9B'^2_{T\infty} - 9B'_{T0}B'_{T\infty} + 12(B'_{T0} - 4/3) = 0. \quad (13)$$

This equation in addition to the root expressed by eq. (8), yields another root in the case of ionic solids ($n = 1$) equal to 4/3 This is the value to which eqs (4) and (6) lead on wrongly accepting $(r/r_0)^{n-m}$ equal to zero. Clearly this second root is spurious. This is also obvious from eq (11) according to which $B'_T = 4/3$, if $B_T/P = 4/3$ This later result however, is not always true as can be verified through eq. (10). In particular, for the power law. short range potential or for the short range force constant, the right side of eq (10) does not lead to the required limit zero as P goes to infinity.

If we replace the second term on the right side of eq. (1) by the exponential form b.exp $(-r/\rho)$ of the short range repulsive potentials, we can obtain expressions for $(B_T/P)_\infty$ and $B'_{T\infty}$ exactly along the same lines as above. Strangely enough these expressions give in the limit r going to zero

$$(B_T/P)_\infty = B'_{T\infty} = 4/3. \quad (14)$$

This value is however, entirely unacceptable in view of the fact that the lattice energy $u(r)$ with this short range term reaches a maximum at a value of r in the case of NaCl more than hundred times smaller than r_0 and the lattice collapses as one crosses to lower r values. The values indicated in eq. (14) are obviously spurious. Analysis for the form (b/r) exp $(-r/\rho)$ does give a single limiting value 4/3 for ionic solids. This potential is clearly of the screened Coulomb potential form and its use in ionic solids, with the Coulomb potential as the basic binding interaction, can not be justified. Some other forms with the function A expressed as function of V/V_0 investigated by Shanker *et al* [1] also lead to asymptotic limits for $(B_T/P)_\infty$ and $B'_{T\infty}$ equal to 4/3 in addition to other values. It would however, appear from the analysis given above that this value should not be accepted without further checks on its validity.

3. Discussion

The analysis presented above obviously applies to the solids with potentials like those given by Born or by Lenard – Jones For ionic solids the high pressure limit of $B'_{T\infty}$ is given by

$$B'_{T\infty} = 1 + m/3 = B'_{T0} - 4/3, \quad (15)$$

where we have used eq. (7) to express 'm' in terms of B'_{T0}. B'_{T0} for NaCl has a value ~ 5.3 which gives for the parameter 'm' of the short range potential an acceptable value ~ 9. However, for many substances for example MgS, MgO etc, one uses a value B'_{T0} ~ 4 (see *e.g.* Jaiprakash and Shanker [3], Kushwah and Shanker [4]). This choice yields a value for $B'_{T\infty}$ nearly 2.75 which is pretty close to the value suggested by the isotherms for MgO, given in Figure 21 of Anderson [5]. These isotherms seem to approach the same value ~ 2.8 irrespective of the temperature of the isotherm. However, the value of m in this case, turns out to be ~ 5 which is too small for a short-range repulsive potential. For NaCl, the limiting value $B'_{T\infty}$ is obtained as $B'_{T\infty}$ ~ 4 which is much higher than the value suggested by extrapolation of data produced by Birch [6] and carried out by Shanker *et al* [1]. One concludes that the limiting values $B'_{T\infty}$ obtained from quadratic equations may often lead to a spurious root 4/3 and that the power law potential is not capable of accurate predictions of high pressure properties of ionic solids. In the case of Lenard-Jones solids, the value of $B'_{T\infty}$ will turn out to be $(m = 12)$ $B'_{T\infty} = 5$.

It has been stated in the past that the exponential form of the repulsive potential is not suited for high pressure studies in so far as it remains finite at P going of infinity, assuming that the lattice parameter goes to zero. It is easy to show that the total lattice potential with the exponential form of the repulsive energy reaches a maximum at a lattice parameter more than a hundred times smaller than its zero pressure equilibrium value Compressions of this order are much beyond the values ordinarily under consideration.

References

[1] J Shanker, S S Kushwah and P Kumar *Physica* **B239** 337 (1997)

[2] H Ledbetter *Phys. Stat. Sol. (b)* **181** 81 (1994)

[3] R Jaiprakash and J Shanker *Indian J Phys.* **70A** 633 (1996)

[4] S S Kushwah and J Shanker *Physica* **B225** 283 (1996)

[5] O L Anderson *J. Phys Chem. Solids* **58** 335 (1997)

[6] F Birch *J. Geophys Res.* **91** 4949 (1986)