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Short Communication

Hartmann's equation of state for Materials at Extreme Compression

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Abstract

Hartmann's equations of state formulated for liquids, polymers and nanomaterials have been demonstrated in the present study to satisfy the thermodynamic constraints at extreme compressions. This reveals the applicability of Hartmann's equation for materials at very high pressures. We have also derived expressions for the pressure derivatives of bulk modulus up to third order. The expressions thus derived have been verified with the help of identities which are valid at extreme compressions. An application of the Hartmann equation has been presented here to predict the pressure-volume-temperature relationships for NaCl crystal and $CaSiO_3$ perovskite mineral. The results obtained in the present study are found to compare well with the experimental data.

Keywords

Introduction

An equation of state (EOS) formulation is an important tool for investigating the pressure P- volume V- temperature T relationship[1]. Volumes of a material at high pressures and high temperatures are needed for understanding its thermoelastic behaviour[2, 3]. The thermoelastic properties can be described in terms of pressure derivatives of the bulk modulus[4-6]. An equation of state must satisfy the boundary conditions at zero – pressure as well as in the limit of infinite pressure. The Grüneisen parameter provides a useful link between thermal and elastic properties of materials[2, 3, 6, 7]. There exists an equation of state due to Hartmann[8] which is based on the fundamental thermodynamic principles[9, 10]. This EOS is capable of predicting the changes in pressure as well as in temperature. An application of the Hartmann equation has been presented here to predict the pressure-volume-temperature relationships for NaCl crystal and $CaSiO_3$ perovskite mineral. The results obtained in the present study are found to compare well with the experimental data.

Material and Methods

The Hartmann EOS representing the relationship between P, V and T as follows[8]

$$\frac{P}{K_0}\left(\frac{V}{V_0}\right)^n = \left(\frac{T}{T_0}\right)^{3/2} - \ln\frac{V}{V_0} \qquad (1)$$

where K_0 is the bulk modulus at P=0. The exponent n is a material-dependent constant. T_0 is the temperature characteristic of the material. Equation (1) gives $V = V_0$ at P=0 and T=0. This is the boundary condition at initial values of P and T. At very high pressures in the limit of extreme compression, we have the volume V tends to be fulfilled by any EOS in order to be physically acceptable. In case of the Hartmann EOS, these conditions are satisfied.

An expression for the bulk modulus $K = -V(dP/dV)_T$ is obtained by differentiating Eq. (1) with respect to pressure at constant temperature. Thus we find

$$K = K_0\left(\frac{V}{V_0}\right)^{-n} + nP \qquad (2)$$

At P=0, $V = V_0$, we have $K = K_0$, the zero-pressure value of bulk modulus. With the increase in pressure P, the volume ratio V/V_0 decreases, and both the terms on right side of Eq. (2) increase rapidly, and become infinitely large. Thus the bulk modulus K tends to infinity in the limit of infinite pressure. At infinite pressure, Eq. (2) with the help of Eq. (1) gives

$$\left(\frac{P}{K}\right)_\infty = \frac{1}{n} \qquad (3)$$

Equation (2) gives the following expression for the pressure derivative of bulk modulus

$$K' = \frac{dK}{dP} = n + \frac{n}{K}(K - nP) \qquad (4)$$

At P=0, Eq. (4) yields

$$n = \frac{K_0'}{2} \qquad (5)$$

At infinite pressure, we use Eq. (3) in Eq. (4) to obtain

$$n = K_\infty' \qquad (6)$$

Equation (5) and (6) then yield

$$K_\infty' = \frac{K_0'}{2} \qquad (7)$$

Thus values of n and K'_∞ are different for different materials since K'_0 is a material-dependent parameter. This is consistent with the earlier findings due to Stacey[11, 12] who derived the following identity

$$\left(\frac{P}{K}\right)_\infty = \frac{1}{K'_\infty} \tag{8}$$

Equation (8) is satisfied by equations (3) and (6). Expressions for higher pressure derivatives of bulk modulus are obtained from eq (4) by differentiating it with respect to pressure

$$KK'' = -n^2(1 - K'P/K) \tag{9}$$

where $K'' = d^2K/dP^2$. We multiply K'' by K so that KK'' is dimensionless. Eq (9) reveals that KK'' is negative at zero-pressure and at finite pressures, and it becomes zero at extreme compression (V→0, and P→∞) because Eq (8) becomes valid. eq (9) on differentiating with respect to pressure yields

$$K^2K''' = KK''\left(n^2\frac{P}{K} - 2K'\right) \tag{10}$$

Where $K''' = d^3K/dP^3$. We multiply K''' by K^2 so that K^2K''' is dimensionless. At extreme compression K^2K''' tends to zero, since KK'' also tends to zero. But their ratio remains finite at extreme compression, as eq (10) gives

$$\left(\frac{K^2K'''}{KK''}\right)_\infty = -K'_\infty \tag{11}$$

At zero pressure KK'' and K^2K''' both are finite

$$K_0K''_0 = -\frac{K'^2_0}{4} \tag{12}$$

$$K_0^2K'''_0 = \frac{K'^3_0}{2} \tag{13}$$

The Grüneisen parameter γ provides useful link between thermal and elastic properties of materials. We have the following relationship

$$\gamma = \frac{1}{2}K' - \frac{1}{6} \tag{14}$$

so that, at infinite pressure we have

$$\gamma_\infty = \frac{1}{2}K'_\infty - \frac{1}{6} \tag{15}$$

According to the Hartmann EOS $K'_\infty = K'_0/2$, we have

$$\gamma_\infty = \frac{1}{4}K'_0 - \frac{1}{6} \tag{16}$$

Since K'_0 is always greater than one, γ_∞ is always greater than zero, i.e. the Grüneisen parameter γ remains positive and finite at extreme compression. There exists an identity between the pressure derivatives of bulk modulus at infinite pressure given as follows[13]

$$\left(\frac{K^2K'''}{KK''}\right)_\infty = -2K'_\infty - \frac{1}{K'_\infty}\left(\frac{KK''}{1 - K'P/K}\right)_\infty \tag{17}$$

Equation (9) based on the Hartmann EOS gives

$$\left(\frac{KK''}{1 - K'P/K}\right)_\infty = -K'^2_\infty \tag{18}$$

Equations (11) and (18) satisfy the identity given by Eq. (17). We have thus found that the Hartmann EOS[8-10, 14, 15] is consistent with the infinite pressure behaviour of materials[11-13].

Results and Discussion

The results for isothermal compressions derived from the Hartmann EOS are given in table 1 for $CaSiO_3$ and in Figure 1 for NaCl. In both the cases the experimental data[16,17] have been included in the Table as well as Figure for the sake of comparison. It is found that the results obtained in the present study using the Hartmann equation of state (EOS) are in good agreement for NaCl crystal as well as $CaSiO_3$ perovskite mineral. The pressure-volume-temperature relationships provide useful informations regarding various thermodynamic processes.

At constant temperature, i.e. isothermal conditions by studying pressure-volume relationships we can determine the isothermal bulk modulus $K = -V(dP/dV)_T$ of the materials. At constant pressure, i.e. isobaric conditions the volume-temperature relationships yield the relationship for the thermal expansivity $\alpha = -(1/V)(dV/dT)_P$.At constant volume, i.e. isochoric thermal conditions pressure-temperature relationships are useful for predicting the thermal pressures. In this case we make use of identity $(dP/\ dT)_V = \alpha K_T$.

Conclusion

We have found that the Hartmann equation of state which has been widely applicable for liquids, polymers and nanomaterials, is consistent with the infinite pressure behavior of solids. The Grüneisen parameter γ plays central role in explaining thermal and elastic properties of materials. The identity between the pressure derivatives of bulk modulus at infinite pressure used here satisfy by the Hartmann equation of state (EOS). The pressure-volume-temperature relationships, as discussed at length by Stacey and Davis, in the present study are found to compare well with the experimental data.

Table 1
Results for CaSiO3, volumes (Å3) calculated from the Hartmann EOS (eq. 1), and experimental values from Wang et al.[16]
δ_T = 4.8, K_0 = 232 GPa αK_T = 7.2 x 10^{-3} GPa K^{-1}

T(K)	P(GPa)	V(Å^3) Calculated	V(Å^3) Experimental
301	2.66	45.08	45.03
303	4.15	44.81	44.87
303	6.54	44.40	44.38
303	7.94	44.17	44.14
302	8.97	44.00	44.01
304	9.63	43.90	43.93
306	10.07	43.83	43.83
570	4.68	45.06	45.12
572	7.09	44.63	44.63
570	8.48	44.39	44.37
575	9.50	44.23	44.22
572	10.15	44.12	44.12
572	10.58	44.05	44.07
771	5.04	45.26	45.25
772	7.52	44.81	44.78
774	8.97	44.56	44.51
770	9.98	44.38	44.38
769	10.58	44.28	44.28
769	10.92	44.23	44.23
980	5.51	45.46	45.44
976	9.37	44.74	44.71
980	10.49	44.55	44.53
977	11.06	44.45	44.45
970	11.35	44.40	44.41
1172	11.69	44.59	44.54
1368	12.04	44.77	44.76

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