Analysis of compatibility of the generalized Rydberg equation

B P Singh & S Gajendra
Department of Physics, Dr B R Ambedkar University, Institute of Basic Sciences, Khandari, Agra 282 002
E-mail: drbps.ibs@gmail.com

Received 20 January 2011; revised 4 May 2011; accepted 3 June 2011

An analysis of compatibility of the generalized Rydberg equation of state with the reciprocal K-primed equation of state has been presented. The method is based on the formulation for higher pressure derivatives of bulk modulus and the third-order Grüneisen parameter in the limit of extreme compression. It is found that the generalized Rydberg equation becomes consistent with the reciprocal K-primed EOS when a quadratic term in $P/K$ is included in the expression. This finding is consistent with the recent studies on the generalized Rydberg equation.

Keywords: Equation of state, Bulk modulus, Pressure derivatives, Extreme compression behaviour, Third-order Grüneisen parameter

1 Introduction

Stacey and Davis have emphasized that there are at least two conditions which should be satisfied by an equation of state (EOS) in order to be physically acceptable. These conditions are (i) $K'_\infty$, the pressure derivative of bulk modulus ($dK/dP$) in the limit of extreme compression ($V \to 0$ and $P \to \infty$) must be greater than 5/3, and (ii) real and reasonable values of properties should be obtained for the entire range of compressions. For example, negative pressure for any compression is disallowed.

Most of the equations of state proposed earlier do not satisfy one or both the conditions mentioned above. Stacey and Davis have found that the Keane K-primed EOS and the Stacey reciprocal K-primed EOS are two equations which satisfy these conditions very well. Either of them can be used equally satisfactorily according to the convenience and availability of the data.

In a subsequent study, Stacey generalized the EOS based on the Rydberg potential function. The generalized Rydberg EOS is free from the shortcomings of the original Rydberg-Vinet EOS, and it can be adjusted with different values of $K'_\infty$ for different materials satisfying the thermodynamic constraint $K'_\infty$ greater than 5/3. In the present study, we make an analysis for the compatibility of the generalized Rydberg EOS and the reciprocal K-primed EOS by determining higher pressure derivatives of bulk modulus and the third order Grüneisen parameter in the limit of extreme compression.

2 Method of Analysis

All the equations of state with $K'_\infty$ greater than zero satisfy the following identity in the limit of infinite pressure.

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

The pressure $P$ and bulk modulus $K$ both tend to infinity in the limit of extreme compression ($V \to 0$), but their ratio $P/K$ remains finite since $K'_\infty$ is positive and finite. The subscript $\infty$ represents the values at infinite pressure. Eq. (1) implies that (1$- K'_\infty P/K$), $(KK')$ and $(K^2K''')$ all become zero at infinite pressure. $K''$ and $K'''$ are $d^2K/dP^2$ and $d^3K/dP^3$, respectively. $K''$ is multiplied by $K$, and $K'''$ by $K^2$ so as to make the terms $KK''$ and $K^2K'''$ dimensionless. It has been found that the ratios given below remain finite, although numerators and denominators individually become zero at infinite pressure. The generalized Rydberg EOS gives:

$$\left( \frac{KK''}{1-K'_\infty P/K} \right)_\infty = -K_\infty \left( K_\infty - \frac{1}{3} \right)$$

$$\left( \frac{K^2K'''}{KK''} \right)_\infty = - \left( K_\infty + \frac{1}{3} \right)$$

and

$$\lambda_\infty = \frac{1}{3}$$
where $\lambda_\infty$ is the value of third-order Grüneisen parameter $\lambda$ at infinite pressure.

The Stacey reciprocal\textsuperscript{15} $K$-primed EOS gives:

$$\left( \frac{KK''}{1-K'P/K} \right)_\infty = -K''/K_0$$  \hspace{1cm} \text{(5)}$$

$$\left( \frac{K^2K''}{KK''} \right)_\infty = -\left( K''_K + K_0 \right)$$  \hspace{1cm} \text{(6)}$$

and

$$\lambda_\infty = \frac{K''_0}{K_0}$$  \hspace{1cm} \text{(7)}$$

It becomes clear that Eqs (2-4) based on the generalized Rydberg EOS are compatible with the corresponding Eqs (5-7) based on the Stacey reciprocal $K$-primed EOS, only if the following condition is satisfied:

$$K''_0 = \frac{1}{3}$$  \hspace{1cm} \text{(8)}$$

The seismic data reveal that for the Stacey reciprocal $K$-primed EOS, $K'_\infty = 3$ when $K'_0 = 5$ in case of the earth core, and $K'_\infty = 2.4$ when $K'_0 = 4.2$ in case of the earth lower mantle. These values of $K'_0$ and $K'_\infty$ do not satisfy Eq. (8) even approximately. In order to remove this discrepancy, we use the modified reciprocal $K$-primed EOS.

$$\frac{1}{K'} = A + B\left( \frac{P}{K} \right) + C\left( \frac{P}{K} \right)^2$$  \hspace{1cm} \text{(9)}$$

where $A = 1/K'_0$, $B = -K_0K''_0 / K'_0$, and

$$C = \frac{K'_0}{K_0} \left[ K'_0K''_0 + K'_0 \left( K'_0 - K'_\infty \right) \right]$$  \hspace{1cm} \text{(10)}$$

Eq. (9) gives:

$$\left( \frac{KK''}{1-K'P/K} \right)_\infty = -K'_0 \left( BK' + 2C \right)$$  \hspace{1cm} \text{(11)}$$

$$\left( \frac{K^2K''}{KK''} \right)_\infty = -2K'_0 + BK'_0 + 2C$$  \hspace{1cm} \text{(12)}$$

and

$$\lambda_\infty = (1-B)K'_0 - 2C$$  \hspace{1cm} \text{(13)}$$

It should be pointed out that Eqs (2-4) based on the generalized Rydberg EOS are compatible with the corresponding Eqs (11-13) based on Eq. (9) only if the following condition is satisfied.

$$\left( 1-B \right)K'_0 - 2C = \frac{1}{3}$$  \hspace{1cm} \text{(14)}$$

Substituting the values of $B$ and $C$ from Eq. (10) in Eq. (14) and eliminating $K_0K''_0$ in terms of $K'_0$ and $K'_\infty$ with the help of the following relation based on the generalized\textsuperscript{8} Rydberg EOS.

$$\frac{3}{2}K'_0 - 3K'_\infty + \frac{1}{2} = -3K'_0K''_0 - \frac{3}{4}K''_0 + \frac{1}{12}$$  \hspace{1cm} \text{(15)}$$

we get:

$$\left( 72K'_0 - 36 \right)K''_0 - \left( 27K'_0 - 18K'_\infty - 5 \right)K'_0 - 12K''_0 = 0$$  \hspace{1cm} \text{(16)}$$

Eq. (16) which is quadratic in $K'_\infty$ as well as $K'_0$ gives the condition for compatibility of the generalized Rydberg EOS and the modified reciprocal $K$-primed EOS in terms of $K'_0$ and $K'_\infty$.

3 Results and Discussion

Stacey and Davis\textsuperscript{1} have emphasized that the most critical test for an equation of state is in respect of the third order Grüneisen parameter $\lambda_\infty$ which is determined from the pressure derivatives of bulk modulus up to third order in the limit of extreme compression. In the present study, we have used this assertion to study the compatibility of the generalized Rydberg EOS with the reciprocal $K$-primed EOS. It has been found that the generalized Rydberg EOS becomes compatible with the modified reciprocal $K$-primed EOS having the $(P/K)$ and $(P/K)^2$ terms in the expression for $1/K'$ (Eq. 9). The compatibility condition yields a relationship between $K'_0$ and $K'_\infty$ [Eq.(16)]. Values of $K'_\infty$ corresponding to different values of $K'_0$ calculated from Eq. (16) are plotted in Fig. 1. Values of $K'_\infty$ are found to be different for different materials with different values of $K'_0$. Also the thermodynamic constraint $K'_0 > 5/3$ due to Stacey\textsuperscript{7} is satisfied for the materials with $K'_0 \geq 3.8$. For most solids, irrespective of the type of their chemical bonding, $K'_0$ is usually greater than 3.8. It may, thus, be concluded that the generalized Rydberg EOS is consistent with the modified reciprocal $K$-primed expression which is quadratic in $P/K$ (Eq. 9). It should also be mentioned that the
generalized Rydberg EOS fits the Earth lower mantle seismic data with $K'_0=4.2$ and $K'_\infty=1.78$, and also fits the Earth core seismic data with $K'_0=5.0$ and $K'_\infty=2.0$. These results reported by Stacey are in good agreement with the values given in Fig. 1.

Recent studies on equations of state have revealed that pressure-volume compression results obtained from the generalized Rydberg EOS with smaller values of $K'_\infty$ are in good agreement with the corresponding results obtained from the Stacey EOS with larger values of $K'_\infty$. This discrepancy in the values of $K'_\infty$ can be removed when we include a quadratic term, $(P/K)^2$, in the reciprocal $K$-primed equation. The results obtained in the present study with the help of the third-order derivatives also support the quadratic expression for the reciprocal $K$-prime.

Fig. 1 — Relationship between $K'_0$ and $K'_\infty$ based on Eq. (16)

References