Analysis of Grüneisen parameter and its volume derivatives for NaCl and hcp iron

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Several papers published in recent years on the Grüneisen parameter and its volume derivatives, are found to be inconsistent with the thermodynamic constraints developed by Stacey. The shortcomings have been rectified by using the Stacey formulations for the Grüneisen parameter. The results for the volume dependence of the Grüneisen parameter and its higher order derivatives have been presented up to very high pressures for NaCl and hcp iron.

Keywords: Grüneisen parameter, Thermodynamic constants, NaCl, hcp iron

1 Introduction
The Grüneisen parameter $\gamma$ and its volume derivatives provide fundamental basis for studying thermal and elastic properties of solids. Recently, Peng et al. have discussed the applications of three relationships for the volume dependence of $\gamma$ due to Fang, Nie and Cui. It has been shown by Peng et al. that the relations due to Fang and Cui are valid only at low pressures in the range 0-3 GPa for NaCl. They become physically inconsistent at higher pressures. The relationship due to Nie has been found to perform the best. However, in the present study, we discuss the main limitations of the formulations recently developed by these researchers by emphasizing that they are not consistent with the thermodynamic developments made by Stacey.

We make use of the formulations for $\gamma$ and its volume derivatives given by Stacey and Davis to obtain results in case of NaCl and hexagonal closed packed (hcp) iron.

2 Method of Analysis
The work of Peng et al. is based on an extension of the earlier work reported by Fang. The analysis presented by Fang was inadequate because of the two assumptions viz. (i) the validity of the Murnaghan’s approximation and (ii) the constancy of the second order Grüneisen parameter $q$, which is defined as:

$$ q = \left( \frac{\partial \ln \gamma}{\partial \ln V} \right)_T $$  

where $\gamma$ is the Grüneisen parameter defined as:

$$ \gamma = \frac{\alpha K_T V}{C_V} = \frac{\alpha K_S V}{C_P} $$  

where $\alpha$ is the thermal expansivity, $V$ the volume, $K_T$ the isothermal bulk modulus, $K_S$ the adiabatic bulk modulus and $C_V$, $C_P$ are the heat capacities at constant volume and pressure, respectively.

The Murnaghan’s approximation is written as:

$$ K = K_0 + K'_0 P $$

where $K$ is the bulk modulus, $K_0$ and $K'_0$ are the bulk modulus and its pressure derivative both at $P=0$. Thus, the Murnaghan approximation reveals that bulk modulus depends linearly on pressure. It is now well known that neither the Murnaghan approximation nor the constancy of $q$ is valid for materials at high pressures.

Nie has proposed an improvement in the earlier work by considering the volume dependence of $q$ as suggested by Jeanloz. The fact that $q \rightarrow 0$ at extreme compression $V \rightarrow 0$ suggested by Stacey and Isaak that the next derivative:

$$ \lambda = \left( \frac{\partial \ln q}{\partial \ln V} \right)_T $$

might be constant, at least to a useful approximation with constant $\lambda$, Eq. (4) then integrates to:

$$ q = q_0 \left( \frac{V}{V_0} \right)^\lambda $$
ln \left( \frac{\gamma}{\gamma_0} \right) = \frac{q_0}{\lambda} \left[ \left( \frac{V}{V_0} \right)^\lambda - 1 \right] \quad \ldots(6)

Eq. (6) given above coincides with Eq. (6) used by Nie\textsuperscript{6}. It has now become evident\textsuperscript{2,15,16} that the third-order Grüneisen parameter \( \lambda \) decreases significantly with the increase in pressure.

Cui and Chen\textsuperscript{7} have taken into account the volume dependence of \( q \) using an approximate thermodynamic relationship between \( q \) and the Anderson-Grüneisen parameter \( \delta_T \). The volume dependence of \( \delta_T \) was determined using the Chopelas-Boehler relationship\textsuperscript{17}. Cui and Yu\textsuperscript{8} have followed the similar procedure but they used the Anderson-Isaak\textsuperscript{18} formula for the volume dependence of \( \delta_T \). More recently Xing et al.\textsuperscript{9} have also used the Anderson-Isaak formula for the volume dependence of \( \delta_T \) in order to determine the dependence of \( \gamma \) on pressure, volume and temperature.

It should be mentioned that the Chopelas-Boehler relationship as well as the Anderson-Isaak formula are not consistent\textsuperscript{19} with the thermodynamic constraint\textsuperscript{10-12} according to which the thermal expansivity must approach to zero for a material in the limit of extreme compression \((V \rightarrow 0)\). As a consequence of this inconsistency, the expressions for the Grüneisen parameter obtained by these researchers\textsuperscript{7-9} yield either zero or infinity for the value of \( \gamma \) in the limit of extreme compression depending on whether the Anderson-Isaak formulation is used or the Chopelas-Boehler relationship is used. In fact, \( \gamma \) must approach to a positive finite value, greater than 2/3 for a material in the limit of extreme compression.

It should be emphasized that the relationship for \( \lambda \), \( q \) and \( \gamma \) obtained by Stacey and Davis are free from any criticism given above. Eqs \((103-105)\) of Ref. \((11)\) are given below:

\[
\lambda = \left( \frac{\partial \ln q}{\partial \ln V} \right)_T = \lambda_\infty + \left( \lambda_0 - \lambda_\infty \right) \frac{q}{q_0} \quad \ldots(7)
\]

\[
q = \frac{q_0}{\{ 1 + \left( \lambda_0 / \lambda_\infty \right) (V_0 / V)^\lambda - 1 \}} \quad \ldots(8)
\]

\[
\gamma = \gamma_0 \left[ \frac{\lambda_0}{\lambda_\infty} - \frac{\lambda_0}{\lambda_\infty} \frac{V}{V_0} \right]^{-q_0/\left( \lambda_0 - \lambda_\infty \right)} \quad \ldots(9)
\]

where the subscripts \( 0 \) and \( \infty \) stand for zero pressure and infinite pressure.

We make use of these equations to calculate values of \( \gamma \) for NaCl and hcp iron at different values of compression.

3 Results and Discussion

In the limit of extreme compressions, \( V \rightarrow 0 \), Eq. \((9)\) is reduced to the following form:\textsuperscript{10}

\[
\gamma_\infty = \gamma_0 \left[ \lambda_0 / \lambda_\infty \right]^{-q_0/\left( \lambda_0 - \lambda_\infty \right)} \quad \ldots(10)
\]

Eqs \((9)\) and \((10)\) yield:

\[
\gamma = \gamma_\infty \left[ 1 - \left( \lambda_\infty / \lambda_0 \right) \left( V / V_0 \right)^\lambda_\infty \right]^{-q_0/\left( \lambda_0 - \lambda_\infty \right)} \quad \ldots(11)
\]

It has been found that the Stacey reciprocal \( K \)-primed \( K \)-primed EOS is more suitable for describing thermal and elastic properties of solids than the pressure-volume relationships used by earlier researchers\textsuperscript{20,22}. The thermodynamic constraints\textsuperscript{2,11} yield the following relationships:

\[
\gamma_\infty = \frac{K'_\infty}{2} - \frac{1}{6} \quad \ldots(12)
\]

\[
\lambda_\infty = \frac{K'^2}{K'_0} \quad \ldots(13)
\]

Values of input parameters for NaCl and hcp iron are presented in Table 1. The pressure–volume results for NaCl are taken from Kushwah and Bharadwaj\textsuperscript{23} and for hcp iron from Shanker et al.\textsuperscript{24} and Vijay\textsuperscript{25}. These results are based on the Stacey reciprocal \( K \)-primed EOS which gives the following relationship:

\[
\ln \left( \frac{V}{V_0} \right) = \left( \frac{K'_0}{K'_\infty} - 1 \right) \left( \frac{P}{K} \right) + \frac{K'_0}{K'_\infty} \ln \left( 1 - \frac{K'_\infty}{K'_0} \frac{P}{K} \right) \quad \ldots(14)
\]

The values of the Grüneisen parameter \( \gamma \) as a function of volume have been determined for NaCl

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NaCl</th>
<th>hcp iron</th>
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<tbody>
<tr>
<td>( \gamma_0 )</td>
<td>1.63</td>
<td>1.83</td>
</tr>
<tr>
<td>( \gamma_\infty )</td>
<td>1.39</td>
<td>1.33</td>
</tr>
<tr>
<td>( q_0 )</td>
<td>0.8</td>
<td>1.18</td>
</tr>
<tr>
<td>( K'_0 )</td>
<td>5.2</td>
<td>5.0</td>
</tr>
<tr>
<td>( K'_\infty )</td>
<td>3.12</td>
<td>3.0</td>
</tr>
<tr>
<td>( \lambda_\infty )</td>
<td>1.87</td>
<td>1.8</td>
</tr>
<tr>
<td>( \lambda_0 )</td>
<td>10.5</td>
<td>6.6</td>
</tr>
</tbody>
</table>
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and hcp iron from Eq. (11) using the input data given in Table 1. The results for $\gamma$ at different pressures and corresponding volumes are reported in Tables 2 and 3. It is found that value of $\gamma$ decreases with the increase in pressure and remains between the values of $\gamma_0$ and $\gamma_\infty$. Values of second order Grüneisen parameter $q$ and third order Grüneisen parameter $\lambda$ have also been calculated using Eqs (7) and (8). Values of $q$ and $\lambda$

both decrease with the increase in pressure. The variations are quite significant. It should be emphasized that $\gamma_\infty$ and $\lambda_\infty$ both remain positive, whereas $q_\infty$ becomes zero. This is in accordance with the thermodynamics of solids in the limit of extreme compression. Of particular importance are the values of $\gamma$ and $q$ for hcp iron in the pressure range 155-337 GPa obtained in the present study. These values of $\gamma$ and $q$ are in close agreement with the corresponding value reported by Stacey and Davis\textsuperscript{11} for the core of the earth.

It should be mentioned here that Burakovsky and Preston\textsuperscript{26} have developed a model for the volume dependence of the Grüneisen parameter $\gamma$ according to which:

$$\gamma(V) = \gamma_\infty + c_1 V^{1/3} + c_2 V^n$$

\textit{...(15)}

where $c_1$, $c_2$ and $n$ are constants with $n>1$. These researchers\textsuperscript{26} have taken $\gamma_\infty = 1/2$ which is based on the Thomas-Fermi model. However, this model is not applicable for solids at extreme compression as discussed at length by Stacey and Davis\textsuperscript{11}. Al’tshuler et al.\textsuperscript{27} have presented the following relationship:

$$\gamma = \gamma_\infty + \left( \gamma_0 - \gamma_\infty \right) \left( \frac{V}{V_0} \right)^{\lambda_\infty}$$

\textit{...(16)}

Eq. (16) has been found\textsuperscript{3}, yields the variation of $\lambda$ with pressure which is not consistent with the seismic data\textsuperscript{11}.

4 Conclusions

In the present study, we have investigated the main limitations of the formulations recently developed by various researchers by emphasizing that they are not consistent with the thermodynamic developments made by Stacey. We make use of the formulations for Grüneisen parameter and its volume derivatives given by Stacey and Davis to obtain results in case of NaCl and hexagonal close packed (hcp) iron. The formulations used here satisfy the thermodynamic constraints in the extreme compression limit and yield results which are consistent with those based on the free-volume theory\textsuperscript{28,29}. The Grüneisen parameter and its volume derivatives are of central importance in the field of thermoelastic behavior and equations of state\textsuperscript{30-36} and equation of state\textsuperscript{30,31}.

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References