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# Revisiting the thermostatistics of the Grüneisen parameters and applications to quasiharmonic solids

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ABSTRACT

We present an integrated thermostatistical study of the Grüneisen parameter and its application to a quasiharmonic solid. This analysis comprises two parts. The first part considers the connections between different thermodynamic formulations of the Grüneisen parameter, including those arising from the Mie-Grüneisen formula and related equations of state. We also establish the most general consequences of the so-called Grüneisen's rule. In the second part, Grüneisen's rule is used to establish the thermostatistics of a solid that obeys the quasiharmonic approximation. Both cases are relevant to the application of fundamental microscopic models of the heat capacity of solids.

## 1. Introduction

The Grüneisen parameter ($\gamma$) is a quantity with major theoretical and experimental importance in various fields, such as solid-state physics, geophysics, physical chemistry of materials, and high-pressure science. Thus, various formulations of $\gamma$ have been reported previously, which originate from diverse research fields. Some of these formulations are macroscopic and they involve thermodynamic quantities that need to be determined experimentally, whereas other formulations employ properties that are relevant to microscopic descriptions of behavior, particularly those that consider the vibrational properties of solids.

In recent years, the definitions and properties of Grüneisen parameters have been reviewed on several occasions and various attempts have been made to establish the relations between the $\gamma$ parameters that originate various research fields [1–3]. However, a survey of the most recent studies suggests that conceptual difficulties and challenges persist [4,5]. The main questions are related to the connections between the macroscopic definition of $\gamma$ and the $\gamma$ parameters involved in a key group of equations of state (EOS), beginning with the classical Mie-Grüneisen equation (MGE) [3,5–8]. There is also a need to establish the exact relations between the macroscopically defined $\gamma$ parameters and the microscopic description of the thermophysics of a solid provided by the quasiharmonic approximation (QHA) [1,2,9].

Various results that are relevant to both challenges have been considered in published reviews [1,2], but it is useful to develop a deductive conceptual framework that formulates consistent relations between these questions. In principle, this framework should start with the lowest possible number of definitions and proceed to establish the formal connections between the relevant quantities. In this manner, it should be possible to accurately distinguish definitions from necessary relations and both from the specific formulas [10,11] used in various application fields, particularly those based on the QHA [1,2]. The aim of the present study is to develop a conceptual framework that includes these characteristics using an integrated thermostatistical analysis.

The remainder of this study is organized as follows. In Section 2, a comparison of various macroscopic definitions is presented and the question of their compatibility [3] is addressed. In addition, a general expression of the MGE is presented, from which the various EOS found in previous studies may be deduced. In Section 3, the consequences of the so-called Grüneisen's rule ($\gamma = \gamma(V)$) for the thermodynamic behavior of a solid are explored. As a key application, an expression is presented that connects the macroscopic $\gamma$ with the phenomenological description of a solid that obeys the QHA. Section 4 considers the microscopic interpretation of $\gamma$ in the framework of the QHA. In particular, a thermostatistical treatment of a quasiharmonic solid is performed for two relevant cases, i.e., a solid with a single vibrational frequency and a solid with $n$ vibration modes. Section 5 provides a summary and some concluding remarks.

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## 2. Thermodynamic Grüneisen parameter

### 2.1. Definition and basic thermodynamic relation

Previous studies describe several quantities related to the Grüneisen parameter, which originate in various research fields. This has motivated a long standing discussion about the compatibility [3] among the various $\gamma$ parameters used in chemical physics [6], geophysics [7,12,13], crystallography, and high-pressure physics [1,14].

As the basis of the present study, we adopt the definition of the 'thermodynamic' Grüneisen parameter $\gamma_G$ traditionally [1,2], which is written as:

$$\gamma_G = V\left(\frac{\partial P}{\partial E}\right)_V = \frac{\alpha K_T V}{C_V}, \tag{1}$$

where $\alpha$ is the isobaric thermal expansion coefficient and $K_T$ is the isothermal bulk modulus. Using a Maxwell relation, Eq. (1) may be given the following alternative form.

$$\gamma_G = \frac{V}{C_V}\left(\frac{\partial S}{\partial V}\right)_T \tag{2}$$

### 2.2. Physical contributions to $\gamma_G$

The entropy of a solid may be expressed as the sum of the vibrational (vib), electronic (el), magnetic (mag), and other possible (other) contributions [1,2].

$$S = S_{vib} + S_{el} + S_{mag} + S_{other} \tag{3}$$

The derivation with respect to the logarithm of the volume and the application of Eq. (2) yields:

$$\left(\frac{\partial S}{\partial \ln V}\right)_T = \left(\frac{\partial S_{vib}}{\partial \ln V}\right)_T + \left(\frac{\partial S_{el}}{\partial \ln V}\right)_T + \left(\frac{\partial S_{mag}}{\partial \ln V}\right)_T + \left(\frac{\partial S_{other}}{\partial \ln V}\right)_T \tag{4}$$

and

$$C_V\gamma_G = C_{V,vib}\gamma_{G,vib} + C_{V,el}\gamma_{G,el} + C_{V,mag}\gamma_{G,mag} + C_{V,other}\gamma_{G,other}. \tag{5}$$

This result may be written in the following form.

$$\gamma_G = \frac{\sum_i C_{V,i}\gamma_{G,i}}{\sum_j C_{V,i}} \tag{6}$$

In Eq. (6), $C_{V,i}$ (with $i=$ vib, el, mag, other) represents the vibrational, electronic, magnetic, and other contributions to the heat capacity, and $\gamma_{G,i}$ represents the respective Grüneisen parameter. In general, these contributions depend on the volume and temperature, as does $\gamma_G$. The particular case where $\gamma_G$ is only a function of volume is discussed in Section 4.

## 3. Connection with the Mie-Grüneisen equation of state

To complete the analysis of the thermodynamically defined $\gamma$, we focus on the relation between $\gamma_G$ and the parameter $\gamma_{MGE}$, which is involved in the Mie-Grüneisen EOS. In the present section, we perform a thermodynamic analysis of the various contributions to the energy and the pressure of a solid.

### 3.1. "Thermal" and "cold" contributions to the E and F energy of a solid

The total energy ($E$) of a solid can be expressed as the sum of two terms. The first (the 'cold' contribution $E_c$) accounts for the contributions to the energy at $T=0$. The second (the 'thermal' $E_{th}$ contribution) accounts for the effects of temperature:

$$E(T,V) = E_c(0,V) + E_{th}(T,V) \tag{7}$$

where $E_{th}$ is given by

$$E_{th} = \int_0^T C_V\, dT. \tag{8}$$

In a similar manner, the Helmholtz energy ($F$) of a solid may be written as

$$F(T,V) = F_c(0,V) + F_{th}(T,V) = E_c(0,V) + F_{th}(T,V) \tag{9}$$

where $F_{th}$ is given by

$$F_{th} = -\int_0^T S\, dT. \tag{10}$$

An expression that includes the 'cold' ($P_C$) and 'thermal' ($P_{th}$) contributions to the equilibrium pressure of a solid may be obtained by combining Eqs. (9) and (10) with the identity

$$P = -(\partial F/\partial V)_T, \tag{11}$$

i.e.,

$$P = P_c(0,V) + P_{th}(T,V) \tag{12}$$

where

$$P_c = -\left(\frac{\partial E_c}{\partial V}\right)_T \tag{13}$$

$$P_{th} = \int_0^T \left(\frac{\partial S}{\partial V}\right)_T dT. \tag{14}$$

It should be emphasized that the current selection of contributions to $E$ (Eq. (7)), $F$ (Eq. (9)), and $P$ (Eq. (12)) is not the only possibility. An alternative description is provided in Section 3.3.

### 3.2. Exact relation between $\gamma_G$ and $\gamma_{MGE}$

Using the results presented in the previous subsection, it is possible to express $\gamma_G$ (Eq. (1)) in terms of "thermal" (th) quantities, as follows.

$$\gamma_G = V\left(\frac{\partial P_{th}}{\partial E_{th}}\right)_V \tag{15}$$

Equation (15) is used in the following to establish a general relation between the thermodynamic Grüneisen parameter and the parameter $\gamma_{MGE}$, which is involved in the Mie-Grüneisen EOS and is usually written as [5,14,15]

$$P = P_c + \frac{\gamma_{MGE}}{V}E_{th}, \tag{16}$$

i.e.,

$$\gamma_{MGE} = V\frac{P_{th}}{E_{th}}. \tag{17}$$

By integrating Eq. (15) at constant volume, we obtain

$$P_{th} = \frac{1}{V}\int_0^{E_{th}} \gamma_G\, dE_{th}, \tag{18}$$

which may be combined with Eq. (17) to obtain

$$\gamma_{MGE} = \frac{\int_0^{E_{th}} \gamma_G\, dE_{th}}{\int_0^{E_{th}} dE_{th}} = \langle\gamma_G\rangle. \tag{19}$$

Equation (19) gives the general relation between $\gamma_{MGE}$ and $\gamma_G$. In general, it is evident that these quantities are not identical but they are not incompatible, as suggested previously [16]. The former represents an energy weighted average of the latter over the corresponding energy range.

### 3.3. Generalizations

By integrating Eq. (1) between two energy states $E_0$ and $E$, we obtain

$$P(E,V)=P(E_0,V)+\int_{E_0}^{E}\gamma_G\,dE \tag{20}$$

and when applied to the same energy states with Eq. (19), this yields

$$P(E,V)=P(E_0,V)+\langle\gamma_G\rangle(E-E_0). \tag{21}$$

Equation (21) with different energy-weighted averages of $\gamma_G$ reproduces various alternative formulas related to the Mie-Grünesien EOS, which have been reported previously. In particular, making $E_0=0$ and $E=E_{th}$, yields Eq. (16). Alternatively, by identifying $E_0$ with the potential energy of the static lattice and $E-E_0$ with the total vibrational energy $E_{vib}$, we obtain

$$P=P_0+\frac{\gamma_{vib}}{V}E_{vib}. \tag{22}$$

Equation (22) was suggested previously in the fields of the physical chemistry of solids (e.g., Fumi and Tosi [6]) and geophysics (e.g., Mulargia and Boschi [3,12]). Indeed, this equation corresponds to the case where the only contribution to thermal energy (and to $\gamma$) is vibrational, i.e., it neglects all other contributions to $E_{th}$ and to $\gamma_G$ (Eq. (6)).

Finally, from Eq. (22), it is possible to derive an expression that is used in the calculation of the room-temperature (R) $P$ vs $V$ values from the so-called Hugoniot (H) data [8,15], which were obtained in shockwave (SW) experiments, i.e.,

$$P_R=P_H+\frac{\gamma_{SW}}{V}(E_R-E_H). \tag{23}$$

In summary, it may be stated that the parameters $\gamma_{MGE}$, $\gamma_{vib}$, and $\gamma_{SW}$ involved in various pressure-energy EOS are energy-weighted averages of $\gamma_G$ with different energy integration limits. Thus, these parameters should generally be considered as different quantities. This conclusion agrees with that of a previous study by one of the current authors (AFG) [8].

## 4. Grüneisen's rule and the thermodynamics of solids

### 4.1. A general consequence

It follows from Eqs. (19) and (21), that if $\gamma_G$ is only a function of volume (and not of energy), the various $\gamma$ parameters discussed in the previous section are identical, i.e.,

$$\gamma_{MGE}=\gamma_G=\gamma_{vib}=\gamma_{SW}. \tag{24}$$

The particular case where Eq. (24) holds is often referred to as Grüneisen's rule. In the following, we study the thermodynamics of a solid that satisfies Eq. (24) exactly. Therefore, we examine the consequences of the following condition.

$$\left(\frac{\partial\gamma_G}{\partial E_{th}}\right)_V=0 \tag{25}$$

The derivative in Eq. (25) may be expressed as

$$\gamma_G=V\left(\frac{\partial P_{th}}{\partial T}\right)_V\left(\frac{\partial T}{\partial E_{th}}\right)_V=\frac{V}{C_V}\left(\frac{\partial P_{th}}{\partial T}\right)_V, \tag{26}$$

which in combination with Eq. (25) yields

$$V\left[\frac{1}{C_V^2}\left(\frac{\partial^2 P_{th}}{\partial T^2}\right)_V-\frac{1}{C_V^3}\left(\frac{\partial C_V}{\partial T}\right)_V\left(\frac{\partial P_{th}}{\partial T}\right)_V\right]=0. \tag{27}$$

Finally, by introducing into Eq. (27), the identity

$$\left(\frac{\partial^2 P_{th}}{\partial T^2}\right)_V=\frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_T \tag{28}$$

we obtain the relation

$$\gamma_G=\frac{\left(\frac{\partial C_V}{\partial \ln V}\right)_T}{\left(\frac{\partial C_V}{\partial \ln T}\right)_V}. \tag{29}$$

Equation (29) may be considered the most general consequence of Grüneisen's rule. It is interesting to note that this relation was previously employed by Ahlers as a definition of a new $\gamma$ parameter that need to be evaluated based on experimental data [17]. Ahlers' parameter agrees with $\gamma_G$, where the latter is only a function of volume.

### 4.2. $\gamma_G$ for quasiharmonic lattice vibrations

As a key application of the general result given by Eq. (29), we will evaluate the $\gamma_G$ that corresponds to the case where there is only a vibrational contribution to $\gamma$. In particular, we assume a harmonic behavior, such as that represented by the Einstein or Debye model of solids with a characteristic temperature $\theta$, which is only a function of volume. In this case, which we refer to as the QHA [2], the temperature and volume dependency of the heat capacity of a solid may be described in terms of a single dimensionless variable

$$C_{V,vib}=\Phi[z] \tag{30}$$

where $z=T/\theta(V)$. In this case, we obtain

$$\left(\frac{\partial C_V}{\partial \ln V}\right)_T=-\frac{d\Phi}{d\ln z}\frac{d\ln\theta}{d\ln V} \tag{31}$$

$$\left(\frac{\partial C_V}{\partial \ln T}\right)_V=-\frac{d\Phi}{d\ln z}. \tag{32}$$

By introducing Eqs. (31) and (32) into Eq. (29), we obtain an expression that connects $\gamma_G$ for a solid in the QHA with the volume dependency of the characteristic temperature, i.e.,

$$\gamma_G=-\frac{d\ln\theta}{d\ln V}. \tag{33}$$

Equation (33) indicates that Grüneisen's rule holds exactly for a quasiharmonic solid. Conversely, a quantity defined as $-\frac{d\ln\theta}{d\ln V}$ [1] agrees with $\gamma_G$ only when the latter does not depend explicitly on temperature.

### 4.3. $\gamma_G$ for a linear electronic contribution

In general, the electronic contribution to the heat capacity of a solid is described as a linear function of temperature, i.e.,

$$C_{V,el}=\beta(V)T \tag{34}$$

where the coefficient $\beta(V)$ might be treated as dependent only on volume. By applying Eq. (29), we obtain:

$$\gamma_{G,el}=\frac{\partial\ln\beta}{\partial\ln V}. \tag{35}$$

Equation (35) may also be obtained by applying the definition (Eq. (2)) to the electronic contribution for the entropy involved in Eq. (3), i.e., $S_{el}=\beta(V)T$. Thus, we conclude that Grüneisen's rule holds exactly for a system where the only contribution to the heat capacity is given by Eq. (34). However, in the most general case of a quasiharmonic solid (Eq. (30)) with an electronic contribution (Eq. (34)), $\gamma_G$ will depend on both $V$ and $T$ (Section 2.2), thus Grüneisen's rule will not apply.

## 5. Microscopic interpretation of the Grüneisen parameters in the QHA

### 5.1. Solids with a single vibration frequency

The thermal contributions to the Helmholtz and the total energy of a harmonic solid with a single frequency $\omega(V)$ are given by Eqs. (36) and (37), respectively [18,19].

$$F_{th} = 3Nk_BT \ln\left[1 - \exp\left(-\frac{\hbar\omega(V)}{k_BT}\right)\right] \tag{36}$$

$$E_{th} = \frac{3N\hbar\omega}{\exp\left(\frac{\hbar\omega_j(V)}{k_BT}\right) - 1} \tag{37}$$

By combining Eqs. (36) and (37) with the identities $S = -(\partial F_{th}/\partial T)_V$ and $C_V = (\partial E_{th}/\partial T)_V$, and introducing the results in Eq. (2), we obtain

$$\gamma_G = -\frac{d\ln\omega(V)}{d\ln V}. \tag{38}$$

Equation (38), which is sometimes treated as a microscopic definition of $\gamma_G$ [4,9,14], may be obtained directly from Eq. (33) by making $\theta = \hbar\omega(V)/k_B$, which is the standard definition of $\theta$for a solid with a single vibration frequency [9,18,19].

The $\gamma_{MGE}$ parameter of this solid may then be calculated by combining the definition (Eq. (17)) with Eq. (11), i.e., from the relation

$$\gamma_{MGE} = -\left(\frac{\partial F_{th}}{\partial V}\right)_T \frac{V}{E_{th}}. \tag{39}$$

By introducing into Eq. (39), the expressions for $F_{th}$ (Eq. (36)) and $E_{th}$ (Eq. (37)), we obtain

$$\gamma_{MGE} = -\frac{d\ln\omega(V)}{d\ln V}. \tag{40}$$

Equations (38) and (40) indicate that for a quasiharmonic solid with a single vibration $\omega$, the $\gamma_G$ and $\gamma_{MGE}$ parameters are identical, as expected from Eq. (19) because $\gamma_G$ (Eq. (38)) and $\gamma_{MGE}$ (Eq. (40)) are only functions of volume.

### 5.2. Solids with “n” vibration modes

$F_{th}$ and $E_{th}$, respectively, for a solid with $n$ modes of vibration are given by the relations [18,19]

$$F_{th} = k_BT\sum_j^n \ln\left[1 - \exp\left(-\frac{\hbar\omega_j(V)}{k_BT}\right)\right] \tag{41}$$

$$E_{th} = \sum_j \frac{\hbar\omega_j(V)}{\exp\left(\frac{\hbar\omega_j(V)}{k_BT}\right) - 1}. \tag{42}$$

In a similar manner to the previous subsection, for $\gamma_G$, we obtain:

$$\gamma_G = \frac{\sum_j C_{V,j}\left(-\frac{\partial\ln\omega_j(V)}{\partial\ln V}\right)}{\sum_j C_{V,j}} = \frac{\sum_j C_{V,j}\gamma_{G,j}}{\sum_j C_{V,j}}. \tag{43}$$

In Eq. (43), which extends Eq. (38) to the case of $n$ modes of vibration, $C_{V,j}$ is the contribution of the mode $j$ to the $C_V$ of a solid. Previously, Eq. (43) was obtained by Barron [1] from vibrational entropy considerations.

Analogously, the $\gamma_{MGE}$ may be obtained by combining Eq. (39) with Eqs. (41) and (42), thus we obtain

$$\gamma_{MGE} = \frac{\sum_j E_{th,j}\left(-\frac{\partial\ln\omega_j(V)}{\partial\ln V}\right)}{\sum_j E_{th,j}} = \frac{\sum_j E_{th,j}\gamma_{G,j}}{\sum_j E_{th,j}}, \tag{44}$$

where $E_{th,j}$ is the contribution of the mode $j$ to $E_{th}$ of a solid.

In the QHA, the $\gamma_G$ and $\gamma_{MGE}$ parameters of a solid with $n$ modes of vibration may be interpreted as weighted averages of the $\gamma_{G,j}$ for a single vibration mode (Eq. (38)). However, for $\gamma_G$, the individual $\gamma_{G,j}$ parameters are weighted using the respective contribution $C_{V,j}$ to the specific heat, whereas $\gamma_{MGE}$ is an energy average of the $\gamma_{G,j}$ using weighting factors as the contributions $E_{th,j}$ to the thermal energy of a solid.

It should be emphasized that in a solid with $n$ vibration modes, both $\gamma_G$ (Eq. (43)) and $\gamma_{MGE}$ (Eq. (44)) are functions of $V$ and $T$. As a consequence, Grüneisen's rule does not hold so these two $\gamma$ parameters are not identical. To the best of our knowledge, Eq. (44) and its consequences for the relation between $\gamma_G$ and $\gamma_{MGE}$ have not been presented previously.

## 6. Conclusions

The Grüneisen parameter has been the subject of numerous studies. However, previous studies suggest two theoretical challenges to the understanding and appropriate application of this key thermophysical parameter. First, there are long-standing claims of an inconsistency among the definitions of $\gamma_G$ and $\gamma_{MGE}$. Second, there is a need for a formulation of the exact connections at the microscopic level between both parameters in the framework of the QHA.

With respect to the first problem, we showed that the definitions of $\gamma_G$ and $\gamma_{MGE}$ are not inconsistent. Indeed, $\gamma_G$ is the energetic average of $\gamma_{MGE}$. We also showed that the definitions are identical when $\gamma_G$ is only a function of the volume, i.e., when the so-called Grüneisen's rule holds.

With respect to the second problem, we showed that in the QHA, Grüneisen's rule leads to an expression for $\gamma_G$ and the volume dependency of the characteristic temperature $\theta$. This result was interpreted microscopically in detail for two fundamental cases: the case with a single oscillation frequency and that with $n$ oscillation modes. In both cases, we evaluated the relevant thermodynamic quantities $\gamma_G$ and $\gamma_{MGE}$. We found that for a solid with $n$ oscillation modes, the QHA leads to a $\gamma_G$, which is the average of each mode's contribution to the specific heat at constant volume, and to a $\gamma_{MGE}$, which is the average of each mode's contribution to the energy. We also showed that $\gamma_G$ and $\gamma_{MGE}$ are not identical in this case.

As a final remark, we suggest that this systematization of the thermodynamic relations and the microscopic interpretations that we present should be of importance for the formulation of the energetic equation of state and its application to the treatment of shockwave data, as well as its applications to geophysics and high-pressure physics, and to the systematization, critical analysis, and prediction of the thermodynamic properties of solids.

In future research, we will focus on the use of $\gamma_G$ in the formulation of the EOS for nanosystems.

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