

and

$$P + \frac{dW_c}{dV} = \gamma'' \frac{W_{th}}{V} \quad (2a)$$

$$\gamma''(V, T) = \frac{V}{T} \frac{[\partial(F_{th}/T)/\partial V]_T}{[\partial(F_{th}/T)/\partial T]_V} \quad (2b)$$

The Grüneisen parameters γ' and γ'' differ, in general, from the parameter γ defined by the Grüneisen relation:

$$\gamma(V, T) = \frac{V}{T} \frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V} = \frac{V\beta}{C_V K} \quad (3)$$

where β , K and C_V are the coefficient of volume thermal expansion, the isothermal compressibility and the heat capacity at constant volume of the solid.

The vibrational formulation consists in replacing γ' in equation (1a) by γ . Similarly, the thermal formulation of the Mie-Grüneisen approximation replaces γ'' in equation (2a) of the Mie-Grüneisen approximation by γ . This is permissible in a certain range of temperature and volume when and only when γ' , or γ'' , does not depend explicitly on temperature in such a range, as is apparent from the equations

$$\left(\frac{\partial \gamma'}{\partial T}\right)_V = \frac{C_V}{W_{vib}} (\gamma - \gamma') \quad (4)$$

$$\left(\frac{\partial \gamma''}{\partial T}\right)_V = \frac{C_V}{W_{th}} (\gamma - \gamma'') \quad (5)$$

which re-express the temperature derivative of the equation of state at constant volume by means of the thermodynamic identity $(\partial P/\partial T)_V = \beta/K$. This leads at once to the thermodynamic expression of the two formulations of the Mie-Grüneisen approximation, namely to the restrictions on the functional form of the thermodynamic functions of the solid which represent necessary and sufficient conditions for the validity of these formulations in a given range of temperature and volume. Indeed, the integration of equations (1b) or (2b) under the condition that γ' , or γ'' , be a function only of the volume of the crystal in a certain temperature range leads to the following functional form for

the vibrational free energy of the solid:

$$F_{vib}(V, T) = Tf(T/\Theta'(V)) \quad (6a)$$

or for its thermal free energy

$$F_{th}(V, T) = Tf(T/\Theta''(V)). \quad (7a)$$

Here f denotes an arbitrary function, while $\Theta'(V)$ and $\Theta''(V)$ are general characteristic temperatures, subject only to the restrictions

$$\gamma'(V) = -\frac{d \ln \Theta'}{d \ln V} \quad (6b)$$

$$\gamma''(V) = -\frac{d \ln \Theta''}{d \ln V}. \quad (7b)$$

The conditions (6a) and (7a) are clearly less restrictive than the Debye model. It should also be stressed that the restrictions (6) and (7) are not, in general, thermodynamically equivalent, and thus the vibrational and thermal Mie-Grüneisen equations of state are not alternative formulations of the same equation, contrary to equations (1) and (2). BORN⁽⁸⁾ had already shown, by a different procedure, that for an Einstein solid with frequency ν the validity of the vibrational Mie-Grüneisen equation of state implies that the vibrational free energy has the form $Tf[T/\nu(V)]$, while GRÜNEISEN⁽³⁾ had pointed out that this equation follows from the assumption that the vibrational free energy has the form (6a).

The thermodynamic expression of the condition that γ be a purely volume-dependent function in a certain range of temperature is similarly obtained by integrating equation (3). This leads to the following functional form for the entropy of the solid:

$$S(V, T) = S(T/\Theta(V)) \quad (8a)$$

$$\gamma(V) = -\frac{d \ln \Theta}{d \ln V} \quad (8b)$$

implying that whenever γ does not depend on temperature at constant volume, it measures the logarithmic derivative of a purely volume-dependent characteristic temperature for the entropy. Condition (8a) is less restrictive than conditions (6a) and (7a), since when the vibrational or thermal free energy is of the form (6a) or (7a) in a certain

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