

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

range of temperature and volume, the entropy is of the form (8a) with $\Theta(V) = \Theta'(V)$ or $\Theta(V) = \Theta''(V)$ [and the heat capacity at constant volume depends only on the ratio $T/\Theta(V)$], but the converse is not necessarily true. This implies that *the independence of γ from temperature at constant volume for a given solid in a certain range of temperature and volume, established by means of measurements of β , C_V and K , does not guarantee, in general, the validity in the same range of either formulation of the Mie-Grüneisen approximation.* However, if the entropy has the form (8a) in a temperature range from 0°K upwards, or if the heat capacity at constant volume has the form $C_V(V, T) = C_V(T/\Theta(V))$ in such a range and the entropy of the solid at 0°K is a constant, the thermal free energy has the form (7a) in the same range, with $\Theta''(V) = \Theta(V)$. DAVIES⁽⁹⁾ had already pointed out that if the heat capacity at constant volume has a purely volume-dependent characteristic temperature in a temperature range including the absolute zero, and Nernst's theorem applies, γ and γ'' are both given by the logarithmic derivative of this characteristic temperature.

The vibrational and thermal formulations of the Hildebrand approximation are traditionally expressed through the restrictions that they impose on the functional form of the internal energy W of the solid: these read

$$W(V, T) = W_L(V) + W_{\text{vib}}(T) \quad (9)$$

and

$$W(V, T) = W_C(V) + W_{\text{th}}(T) \quad (10)$$

respectively. These restrictions are completely equivalent to assuming that γ' and γ'' are related to γ by the equations

$$W_{\text{vib}}\gamma'(V, T) = TC_V\gamma(V, T) \quad (11)$$

$$W_{\text{th}}\gamma''(V, T) = TC_V\gamma(V, T) \quad (12)$$

The vibrational and thermal Hildebrand equations of state, obtained from equations (1a) and (2a) by using equations (11) and (12), respectively, are not alternative formulations of the same equation, since the restrictions (9) and (10) are not, in general, thermodynamically equivalent.

Thermodynamically, the validity of the Hildebrand restrictions on the vibrational or thermal energy of a solid in a certain range of temperature and volume does not ensure the validity in the same range of the Mie-Grüneisen restrictions on the corresponding free energies, nor vice versa. In particular, the validity of equation (9) in a range from $T_0(V)$ to a running T implies only that $F_{\text{vib}}(V, T)/T$ is the sum of a function of the temperature and a function of the volume, while the validity of equation (6) implies only that $W_{\text{vib}}(V, T) = Tg(T/\Theta'(V))$ with $g(x) = -x(df/dx)$. Thus, *in general, one has no thermodynamic reason to prefer either the Mie-Grüneisen or the Hildebrand approximation.* One can, on the other hand, establish thermodynamically the equivalence of the two approximations in a range of temperature and volume where the vibrational or thermal energy of the solid depends only on temperature, and in a linear way, and the vibrational or thermal free energy has the functional form $T \ln(T/\Theta(V))$, since either restriction follows from the other.

3. THERMODYNAMIC FUNCTIONS AND GRÜNEISEN PARAMETERS OF A CUBIC NON-METAL IN THE QUASI-HARMONIC APPROXIMATION

To discuss the validity of the functional restrictions on the thermodynamic functions of a cubic solid under hydrostatic pressure which express the Mie-Grüneisen and Hildebrand approximations, one must resort to the statistical mechanics of the solid. We restrict ourselves to cubic non-metals, for which it is plausible to adopt the adiabatic approximation and to neglect the electronic contributions to the vibrational parts of the thermodynamic functions. In addition, we treat the lattice contributions by the quasi-harmonic approximation: namely, we assume that these contributions, taking the (constant) entropy of the solid at 0°K as the zero for the entropy, are given by the thermodynamic functions of an assembly of uncoupled harmonic oscillators, whose frequencies depend only on the volume of the solid. The quasi-harmonic approximation has been used quite commonly in recent years in studies of thermodynamic properties of solids (see, e.g. Refs. 12-18), and, for our purposes, it has the merit of allowing a general analysis of the functional forms of the thermodynamic functions without the adoption of particular force models.