

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 is 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.