

# ON THE MIE-GRÜNEISEN AND HILDEBRAND APPROXIMATIONS TO THE EQUATION OF STATE OF CUBIC SOLIDS\*

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**Abstract**—An analysis is made of the conditions under which the equation of state of a cubic solid under hydrostatic pressure takes the form given by either the Mie-Grüneisen or the Hildebrand approximation. The condition of validity of the vibrational or thermal formulation of the Mie-Grüneisen approximation is reduced to the existence of a purely volume-dependent characteristic temperature for the vibrational or thermal free energy of the solid. The analysis consists then in a search for temperature ranges where these restrictions on the functional form of the free energy, and the restrictions on the form of the internal energy imposed by the Hildebrand approximation, are satisfied for a non-metal in the quasi-harmonic approximation. The main results are as follows: (1) At temperatures somewhat above the Debye characteristic temperature for the (quasi-harmonic) high-temperature heat capacity at constant volume, it is appropriate to take as equation of state the vibrational Hildebrand equation; (2) at somewhat lower temperatures, this Hildebrand equation is generally more inaccurate than the corresponding Mie-Grüneisen equation; and (3) in the low-temperature  $T^3$  region of the heat capacity, the equation of state reduces to the thermal Mie-Grüneisen equation. The explicit forms of the vibrational and thermal Mie-Grüneisen equations of state, and of their volume derivatives at constant temperature, are reported together with the corresponding Hildebrand equations. Some corollary results are obtained, within the quasi-harmonic approximation, on the temperature variation at constant volume of the Grüneisen parameters relating the explicit volume and temperature dependence of the vibrational and thermal free energy and of the entropy of a cubic solid, and (in an Appendix) on the temperature variation of the Debye temperatures appropriate to the various thermodynamic functions of any non-metal. The available experimental and theoretical evidence on the anharmonic contributions to the thermodynamic functions of solids is briefly discussed, and points to the conclusion that their weight is quite small in the region of temperature of interest for our analysis.

## 1. INTRODUCTION

THE FORMULATION of the equation of state of a cubic solid under hydrostatic pressure which is commonly adopted to determine the volume dependence of the lattice energy of the solid from empirical data is based either on the Hildebrand approximation<sup>(2)</sup> or on the Mie-Grüneisen approximation.<sup>(3)</sup> In recent years, it has been tacitly assumed that the Mie-Grüneisen equation of state, which takes approximate account of the explicit volume dependence of the (vibrational or thermal) free energy of the solid, is a better formulation to

use than the Hildebrand equation of state, which neglects the explicit volume dependence of the (vibrational or thermal) internal energy of the solid. In effect, HUANG<sup>(4)</sup> took the Mie-Grüneisen equation of state as equation of reference in analyzing the validity of the Hildebrand equation. The same attitude is implicit also in some calculations of BORN and HUANG<sup>(5)</sup>, who have adopted the vibrational Mie-Grüneisen equation of state, and an approximation to its volume derivative at constant temperature, to recalculate the parameters entering the Born expression for the lattice energy of the alkali halides from empirical data at room temperature and atmospheric pressure. More recently RICE *et al.*<sup>(6)</sup> have derived the  $P$ - $V$  isotherm

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at 0°K for a number of metals from their shock-wave compression data by adopting the thermal Mie-Grüneisen equation of state, in an approximation proposed by DUGDALE and MACDONALD, as the equation of state appropriate above room temperature. BENEDEK<sup>(7)</sup> has used, instead, the vibrational Mie-Grüneisen equation of state, with the Grüneisen parameter  $\gamma$  taken as a constant, to deduce from those data the volume dependence of the lattice energy of some metals, neglecting the electronic contribution to the vibrational free energy at room temperature and zero pressure.

Here we will investigate systematically the conditions under which the equation of state of a cubic solid, subject only to hydrostatic pressure, reduces to the form given by either the Mie-Grüneisen or the Hildebrand approximation. General thermodynamic arguments, which extend previous work of BORN<sup>(8)</sup>, GRÜNEISEN<sup>(3)</sup> and DAVIES<sup>(9)</sup>, lead one quite easily to express the condition of validity of the vibrational or thermal formulation of the Mie-Grüneisen approximation as a restriction on the form of the vibrational or thermal free energy of the solid as a function of its volume and temperature. One can then show that the experimental observation, for a given solid, of a Grüneisen parameter  $\gamma$  which does not depend on temperature at constant volume in a certain range of temperature and volume does not ensure, in general, the validity in this range of either form of the Mie-Grüneisen equation of state. Thermodynamics does not allow one, instead, to establish whether the special functional form of the vibrational (or thermal) free energy, which expresses the Mie-Grüneisen approximation, is more or less restrictive than the special functional form of the vibrational (or thermal) energy, which expresses the Hildebrand approximation. Some general results on the validity of these various functional restrictions can be obtained within the quasi-harmonic approximation to the statistical mechanics of a non-metal, both at the low temperatures where only long-wave acoustic modes are thermally excited, and in the temperature range of convergence of the THIRRING-STERN<sup>(10)</sup> expansions for the thermodynamic functions, completing previous work of BORN<sup>(11)</sup> and BARRON<sup>(12,13)</sup>. Within this approximation, the vibrational Mie-Grüneisen equation of state and the corresponding Hildebrand equation are both strictly valid only at

temperatures where the heat capacity at constant volume has attained its classical value, but at somewhat lower temperatures the former can be expected to be less inaccurate than the latter. Furthermore, within the temperature range of convergence of the Thirring-Stern expansions, the independence of  $\gamma$  from temperature at constant volume does ensure the validity of the vibrational Mie-Grüneisen equation of state. The thermal Mie-Grüneisen equation, instead, is the appropriate equation of state for a non-metal in the  $T^3$  region of the heat capacity. At moderate and high temperatures, the thermal Mie-Grüneisen and Hildebrand equations are less accurate than the corresponding vibrational equations, and they become valid only if the zero-point energy of the solid becomes negligible compared to its thermal energy, so that the two formulations of each approximation coincide.

## 2. THERMODYNAMIC DISCUSSION OF THE MIE-GRÜNEISEN AND HILDEBRAND APPROXIMATIONS

The equation of state of a cubic solid subject only to hydrostatic pressure,  $P = -(\partial F/\partial V)_T$ , can be written alternatively in the so-called *vibrational* and *thermal* formulations (see, e.g., BENEDEK<sup>(7)</sup> and BARRON<sup>(12)</sup>). These correspond, respectively, to splitting the Helmholtz free energy of the solid  $F(V, T)$  into the energy of the static solid of volume  $V$  in its electronic ground state [the lattice energy  $W_L(V)$ ] plus a "vibrational" free energy  $F_{\text{vib}}(V, T)$ , or into the non-thermal energy [the cohesive energy  $W_C(V)$  of the solid of volume  $V$  at 0°K] plus a "thermal" free energy  $F_{\text{th}}(V, T)$ . The free energies  $F_{\text{vib}}(V, T)$ ,  $F_{\text{th}}(V, T)$  involve, of course, the vibrational and thermal energies of the solid  $W_{\text{vib}}(V, T)$  and  $W_{\text{th}}(V, T)$ , and the total entropy  $S(V, T)$ . We write the equation of state in these two completely equivalent formulations in a form which, though seemingly unduly elaborate, is particularly well suited for the subsequent thermodynamic discussion:

$$P + \frac{dW_L}{dV} = \gamma' \frac{W_{\text{vib}}}{V} \quad (1a)$$

$$\gamma'(V, T) = \frac{V}{T} \frac{[\partial(F_{\text{vib}}/T)/\partial V]_T}{[\partial(F_{\text{vib}}/T)/\partial T]_V} \quad (1b)$$