

Grüneisen,²⁴ Born,²⁵ and Fürth²⁶ corresponding to the Mie form for the potential energy U of an atom in the interatomic force field, given by

$$U = -A/r^{3(m-1)} + B/r^{3(n-1)}, \quad (10)$$

where r is the interatomic distance, and A and B are either interaction constants or lattice sums. In this case, the constants n and m are chosen either from theoretical considerations (e.g., to correspond to a Lennard-Jones potential) or from the requirement of a fit to thermodynamic parameters (such as the lattice energy) of the solid at normal pressure. To a large extent, these equations of state from lattice models have been supplanted for applications at high pressure by the forms discussed previously.

Some discussion of the relative merits of these various special forms of Eq. (1) is in order. Because of the generality of the underlying assumptions, one might expect Birch's equation of state to have a wide range of applicability, and such appears to be the case. The equation in the form (4) seems to reproduce the majority of Bridgman's experimental data on the isothermal equations of state of inorganic solids, within about the experimental uncertainty⁸ (exclusive of the occurrence of polymorphic phase transitions). In the case of the highly compressible alkali metals, for example, this statement appears true for normal temperature up to the limit of Bridgman's pressure measurements (about 10^5 bars, where, in the case of potassium, the fractional compression is about $\frac{1}{2}$). The fact that it contains only one disposable parameter, and fits such a wide range of data, makes Eq. (4) extremely useful.

On the other hand, use of Birch's equation entails some minor drawbacks at the lower pressures. For sufficiently low pressure, the equation of state of any solid can be described by the Bridgman equation

$$-(V - V_0)/V_0 = aP - bP^2, \quad (11)$$

where $a(=K_0^{-1})$ and b are constants.¹⁶ By means of the Lorentz-Slater relation^{15,22}

$$\gamma = -\frac{1}{2}(\partial \ln K / \partial \ln V)_T - \frac{1}{6} \quad (12)$$

for the Grüneisen constant as evaluated from compressibility parameters at fixed temperature T , one can obtain this constant for the solid at zero pressure as

$$\gamma = b/a^2 - \frac{2}{3}, \quad (13)$$

from the Bridgman equation. However, the Lorentz-Slater relation yields

$$\gamma = \frac{1}{2}(n + m - \frac{1}{3}), \quad (14)$$

²⁴ E. Grüneisen in *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1926), Vol. 10, pp. 1-59.

²⁵ M. Born, *J. Chem. Phys.* 7, 591 (1939). The equation of state contains a temperature-dependent term which can be omitted for purposes of the present discussion.

²⁶ R. Fürth, *Proc. Roy. Soc. (London)* A183, 87 (1944). The equation of state contains a temperature-dependent term which can be omitted for purposes of the present discussion.

from Eq. (1), which corresponds to $\gamma = 11/6$ for the Birch equation. Unless the Grüneisen constant of the solid in question has this particular value, which corresponds to $2b/a^2 = 5$ from²⁷ Eq. (13), the Birch equation fails to yield the correct curvature of the $P-V$ curve at zero pressure. For the alkali metals, specifically, the Birch values for the Grüneisen constant and the parameter $2b/a^2$ seem definitely high, and the constant values from Bardeen's equation of 4/3 and 4, respectively, are closer to corresponding averages over these metals obtained by means of Grüneisen's law.²⁸ On the other hand, it can be noted that the average value of the Grüneisen constant over most solids has closely the Birch value, since Slater²⁹ has estimated the average value of the ratio $2b/a^2$ over most materials as 5. Finally, one can observe that the modified Murnaghan equation, with n evaluated in terms of γ by Eq. (8), can be reduced exactly to the Bridgman equation by means of Eq. (13) when the pressure is small. Thus, the equation of Murnaghan as modified by the author is capable of yielding identically the correct curvature of the $P-V$ curve of a solid at zero pressure.

One sees that the equations of Birch, of Murnaghan, and of Bardeen are subsumed under the general equation of state represented by Eq. (1). Various equations (or special cases thereof) treated by Gombas fall into the general class of Eq. (1) also.²¹ The temperature dependence of all these special forms can be obtained by determining the proper temperature dependence of Eq. (1).

III. GENERAL TEMPERATURE-DEPENDENT EQUATION

The special forms of Eq. (1) which have been discussed yield reasonable approximations to the pressure at fixed temperature, when the constants K_0 and V_0 correspond to the temperature in question. For all these forms, it is consistent with experimental results to assume that the exponents n and m are constants, and that the entire volume dependence of the pressure is contained in the powers V^{-n} and V^{-m} appearing. The former assumption for the case of Murnaghan's equation will be examined in Sec. IV. To generalize Eq. (1) to arbitrary temperature, it will be postulated that the constants V_0 and K_0 are replaced by parameters \mathcal{V} and \mathcal{K} , respectively, which are functions only of temperature (aside from dependence on constants fixed by an initial state).⁸ The generalization of Eq. (1) becomes

$$P = (n-m)^{-1} \mathcal{K} [(\mathcal{V}/V)^n - (\mathcal{V}/V)^m], \quad (15)$$

and that of Eq. (2) is

$$K = (n-m)^{-1} \mathcal{K} [n(\mathcal{V}/V)^n - m(\mathcal{V}/V)^m]. \quad (16)$$

²⁷ Birch has shown (reference 4) that the value $2b/a^2 = 5$ follows directly from certain approximations in the theory of finite strain.

²⁸ J. J. Gilvarry, *J. Chem. Phys.* 23, 1925 (1955).

²⁹ J. C. Slater, *Phys. Rev.* 57, 744 (1940).