

truncated two terms earlier than the static contribution.

The analogous equations in terms of η and E are

$$P(\eta, T) = -\frac{(1+2\eta)^{-1/2}}{3V_0} (b_0 + b_1\eta + b_2\eta^2 + b_3\eta^3 + \dots), \quad (32)$$

$$b_0 = \left(\frac{d\bar{\phi}}{d\eta}\right)_0 + \frac{1}{2}gU_q^0, \quad (32a)$$

$$b_1 = \left(\frac{d^2\bar{\phi}}{d\eta^2}\right)_0 + \frac{1}{4}(2h' - g^2)U_q^0 - \frac{1}{4}g^2TC_q^0, \quad (32b)$$

$$b_2 = \frac{1}{2}\left(\frac{d^3\bar{\phi}}{d\eta^3}\right)_0 + \dots, \quad (32c)$$

$$b_3 = \frac{1}{6}\left(\frac{d^4\bar{\phi}}{d\eta^4}\right)_0 + \dots, \quad (32d)$$

and

$$P(E, T) = -\frac{(1-2E)^{5/2}}{3V_0} (c_0 + c_1E + c_2E^2 + c_3E^3 + \dots), \quad (33)$$

where c_0 , c_1 , etc. are defined analogously. Again, the thermal contributions are truncated two terms earlier than the static contributions.

Before some further remarks about these equations are made, in the next section, the parameters entering these equations will be related to quantities which are commonly (or potentially) determined experimentally. By successive differentiation of equation (31), the isothermal bulk modulus $K_T = -V(\partial P/\partial V)_T$, and its isothermal pressure derivatives, $K'_T = (\partial K_T/\partial P)_T$, etc., can be obtained in terms of the a 's. Evaluating these and equation (31) at $e = 0$, we can solve for the a 's in terms of P_0 , K_0 , etc., where the subscript '0' denotes evaluation at $e = 0$ and the subscript 'T' is dropped for now, obtaining

$$a_0 = -3V_0P_0, \quad (34a)$$

$$a_1 = -3V_0(-3K_0 + 2P_0), \quad (34b)$$

$$a_2 = -3V_0\left(\frac{9}{2}K_0K'_0 - \frac{9}{2}K_0 + P_0\right), \quad (34c)$$

$$a_3 = -3V_0\left[-\frac{9}{2}K_0^2K''_0 - \frac{9}{2}K_0K'_0(K'_0 - 1) - K_0\right]. \quad (34d)$$

Similarly, from equations (32) and (33),

$$b_0 = -3V_0P_0, \quad (35a)$$

$$b_1 = -3V_0(-3K_0 + 3P_0), \quad (35b)$$

$$b_2 = -3V_0\left(\frac{9}{2}K_0K'_0 - \frac{7}{2}P_0\right), \quad (35c)$$

$$b_3 = -3V_0\left[-\frac{9}{2}K_0^2K''_0 - \frac{9}{2}K_0K'_0(K'_0 + 1) + \frac{1}{2}K_0 + \frac{19}{2}P_0\right], \quad (35d)$$

$$c_0 = -3V_0P_0, \quad (36a)$$

$$c_1 = -3V_0(-3K_0 + 5P_0), \quad (36b)$$

$$c_2 = -3V_0\left(\frac{9}{2}K_0K'_0 - 18K_0 + \frac{35}{2}P_0\right), \quad (36c)$$

$$c_3 = -3V_0\left[-\frac{9}{2}K_0^2K''_0 - \frac{9}{2}K_0K'_0(K'_0 - 7) - \frac{143}{2}K_0 + \frac{105}{2}P_0\right]. \quad (36d)$$

To obtain g and h , we first differentiate equation (24) for γ and solve for g and h , obtaining

$$g = -6\gamma_0, \quad (37)$$

$$h = g\left[3\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_{0T} + g - 1\right]. \quad (38)$$

γ_0 can be obtained from the thermodynamic identity

$$\gamma = \frac{V\alpha K_T}{C_V}, \quad (39)$$

and the volume derivative of γ is given by the identity [12]

$$\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T = 1 + \delta_T - K'_T - \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T, \quad (40)$$

where

$$\delta_T = -\frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T}\right). \quad (41)$$

In these equations, C_V is the specific heat at constant volume and $\alpha = (\partial V / \partial T)_P / V$ is the volume coefficient of thermal expansion.

Equations (34) to (41) determine the six equation of state parameters V_0 , a_1 , a_2 , a_3 , g and h in terms of the six laboratory quantities V_0 , K_0 , K'_0 , K''_0 , and $(\partial K / \partial T)_P$. P_0 and a_0 are determined by V_0 and g through (31a) and (34a).

The procedure for determining the parameters is as follows. Assuming that V_0 , K_0 , K'_0 , K''_0 , α and $(\partial K / \partial T)_P$ are known at some temperature T_0 and zero pressure, then g and h (which are temperature independent) and a_1 , a_2 and a_3 can be evaluated, using (34–41), at T_0 . This serves to define the reference state as $P = 0$, $T = T_0$, $V = V_0$. Then $P_0(T_0) = 0 = a_0(T_0)$. Finally, a_0 and a_1 , which include the temperature dependence of the equation of state (31), can be evaluated at any temperature T using (31a) and (31b):

$$a_0(T) = a_0(T_0) + \frac{1}{2}g[U_q^0(T) - U_q^0(T_0)], \quad (42a)$$

$$\begin{aligned} a_1(T) = & a_1(T_0) + \frac{1}{4}(2h - g^2) \\ & \times [U_q^0(T) - U_q^0(T_0)] \\ & - \frac{1}{4}g^2[TC_q^0(T) - T_0C_q^0(T_0)]. \end{aligned} \quad (42b)$$

Of course, in this procedure, U_q^0 and C_q^0 must be known or estimated as functions of temperature. For many applications, the Debye or Einstein models can be used to estimate these. These require the empirical input of the characteristic temperature of the

solid. If more extensive empirical input of U_q^0 and C_q^0 is desired, the specifically anharmonic contribution to the U and C_v must be subtracted before such data are used [3, Part VII].

Illustrative numerical applications of the equations derived in this section are given in a later section and in another paper [13].

4. FURTHER DISCUSSION OF THE THEORY

Firstly, some further comments on the approximations used in the derivation of these equations will be made.

Equations (31), (32) and (33) are all derived from fourth-order expansions (in terms of the appropriate strain) of the free energy. According to the discussion of the previous section, however, these expansions can, in general, be taken to any order. For example if the 'Eulerian' equation is truncated after the third-order term, and P_0 is assumed to be zero, the well known 'Birch–Murnaghan' equation [5, 11] results. The contribution of the present theory is to give, approximately, the explicit temperature dependence of such finite strain equations.

The 'Mie–Grüneisen approximation' was invoked at several points in this derivation. Strictly, such a strong assumption is not necessary. If we were to follow the procedure used in deriving the Mie–Grüneisen form (17) of the equation of state, then we would define, in (30), another mean of the derivatives of the ω_j , and the corresponding summations could thus be replaced. In general, however, these means bear no simple relation to each other. In the Mie–Grüneisen approximation, all of the quantities being averaged are identical and this difficulty is removed. An alternative, weaker assumption, discussed by Leibfried and Ludwig [3] is to replace the means of these derivatives with the derivatives of the mean of the ω_j^2 , which can be fairly easily calculated from lattice models. Evidently, this approximation may be reasonable at very low or very high temperatures (relative to the Debye temperature), but will be poorer at inter-