

Consistency in the High-Temperature Equation of State of Solids¹

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Abstract. Four equations of state for solids are examined theoretically for mutual consistency in the high-temperature regime. It is found that neither the Birch-Murnaghan nor the Murnaghan equation can be shown to be consistent with either the Mie-Grüneisen or the Hildebrand equation. An expression is derived for the volume dependence of the Grüneisen parameter $\gamma(\rho)$. A recent theoretical treatment of NaCl, proposed for use as a pressure standard, is neither internally consistent, nor is it sufficiently precise for such a purpose.

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Introduction. In current use there appear several different equations of state for solids which differ in their derivations, in the quantities which they exhibit explicitly, and in the quantities which they leave as experimental parameters. It is the purpose of this paper to discuss together some of these equations, and to show to what extent their separate derivations are mutually consistent. Such consistency becomes important when two of these equations are used together in interpreting experimental data. For example, one [cf. Takeuchi and Kanamori, 1966] method/of reducing shock-wave data employs the Mie-Grüneisen equation to account for thermal effects in transforming the Hugoniot into an isotherm, which is then compared with the Birch-Murnaghan equation. Clearly, if this calculation is to have meaning, assumptions made in any one part of it must not be violated in another part. As another example, when a high-pressure experiment is calibrated using the equation of state of NaCl provided by Decker [1965], the resulting data are constrained by the assumptions of the Mie-Grüneisen equation of state, as used by Decker. If these data are then compared and extrapolated with the Birch-Murnaghan equation of state, the problem of consistency again must be faced.

Many equations of state can be classified into one of two broad classes: 'isothermal' equations which are concerned primarily with effects of compression at constant temperature, and 'thermal' equations which treat strictly thermal effects more precisely.

In this paper, we first give brief accounts of the derivations of some of these equations of state. Second, we develop a simple framework in which they can all be considered together. Next, we focus our attention on restrictions imposed upon the isothermal equations by the thermal equations. Then we consider the thermal equations from the isothermal viewpoint, and derive $\gamma(\rho)$ in terms of commonly measured crystal properties. Turning finally to recent work on NaCl, we find that internal consistency in the Mie-Gruneisen equation generates in this special case a $\gamma(\rho)$ from the microscopic lattice potential energy.

Isothermal equations of state. Prominent among this class is the Birch-Murnaghan equation

$$P(P, T) = \frac{3}{2} K_0(T) (Y^{1/3} - Y^{5/3}) [1 - \xi(T)(Y^{2/3} - 1)] \quad (1)$$

where

$$Y(P, T) = \frac{\rho}{\rho_0(T)} \quad (1a)$$

Here P is pressure, ρ density, T temperature, K the isothermal bulk modulus $\rho \left(\frac{\partial P}{\partial \rho} \right)_T$, and the subscript 0 refers to zero pressure. ξ is related to experimental quantities by

$$\xi(T) = - \frac{3}{4} [K'_0(T) - 4] \quad (2)$$

where K'_0 is $\left(\frac{\partial K}{\partial P} \right)_T$ as $P \rightarrow 0$. The B-M equation is derived [Murnaghan, 1937, Birch, 1938, 1947, 1952] from the theory of finite strain, in which it is proved that the strain is given by

$$\epsilon = \frac{-1}{2} (Y^{2/3} - 1) = \epsilon(P, T) \quad (3)$$

and it is assumed that a Taylor expansion, in the strain, of the Helmholtz free energy may be terminated at the cubic terms. Thus, in the present case of homogeneous isotropic compression

$$F(P, T) = \frac{9}{2} \frac{K_0(T)}{\rho_0(T)} \epsilon^2 + 6 \frac{K_0(T)}{\rho_0(T)} \xi(T) \epsilon^3 \quad (4)$$

The B-M equation then follows from

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (5)$$

where $V = \frac{1}{\rho}$ is the specific volume. We will return to the discussion of this equation shortly.

Another important member of this class is the equation of Murnaghan [1944]

$$P(P, T) = \frac{K_0(T)}{K_0'(T)} (y^{\beta_T} - 1) \quad (6)$$

where $\beta_T = K_0'(T)$. This follows from the assumption

$$K(P, T) = K_0(T) + K_0'(T)P$$

and is, experimentally, nearly indistinguishable from (1) over a considerable range of compression. This fact may be understood on the basis of the uniqueness of the Taylor expansion. Any two functions $f_1(y)$ and $f_2(y)$ that are constructed so as to satisfy the same boundary conditions

$$\left. \frac{d^n f_1}{d y^n} \right|_{y_0} = \left. \frac{d^n f_2}{d y^n} \right|_{y_0}$$

for $n = 0, 1 \dots M$ will have the same Taylor expansion about y_0 , through terms in y^M , and will differ only in the higher-order terms. The B-M and the Murnaghan equations represent two such functions, with $y_0 = 1$, and T not entering the problem. They are both 4-parameter equations for the free

energy F , with one of these parameters explicitly set to zero, leaving only ρ_0 , K_0 , and K'_0 apparent. Since the $M + 1 = 4$ term of the expansion in which they first begin to differ is

$$81 \frac{K_0}{\rho_0} \left[K_0 K_0'' + K_0'^2 - 7K_0' + \frac{14^3}{9} \right] \frac{\epsilon^4}{4!} \quad (7)$$

it is clear that the B-M assumption on K_0'' is

$$K_0'' = \frac{1}{K_0} \left(7K_0' - K_0'^2 - \frac{14^3}{9} \right) \quad (8)$$

The Murnaghan equation, of course, assumes

$$K_0'' = 0 \quad (9)$$

For a typical oxide, $K'_0 = 4$, $K_0 = 1000$ kb, and the RHS of (8) is $3.9 \times 10^{-3} \text{ kb}^{-1}$. This number is sufficiently close to zero to insure that the two forms agree closely over a wide range of y .

It is of interest to note that the RHS of (8) is not zero for any real K'_0 , and reaches its extremum at $K'_0 = 3.5$. It seems to be a remarkable coincidence that solids should have values of K'_0 so close to this extremum value. An examination of the derivation of equation 8 shows that this number, $7/2$, has its ultimate source in the fact that the number of dimensions in physical space is 3. We find it very interesting that / ^{typical} values of K'_0 are close to 3.5 and not some other number, like 10. In any case, this situation helps explain why it is that the series (4) is so quickly convergent.

Thermal equations of state. This class is most often motivated by considerations of the theory of lattice dynamics. In this theory, the lattice potential energy is expanded in a Taylor series about the equilibrium lattice configuration. Most, if not all, observed phenomena are explainable in principle if the series is terminated at the fourth-order terms:

$$\Phi = \Phi_0 + \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 \quad (10)$$

where

$$\Phi_k = \frac{1}{k!} \sum \underbrace{\phi_{\mu \dots \nu}^{m \dots n}}_{k \text{ terms}} q_{\mu}^{m \dots n} \dots q_{\nu}^{m \dots n}$$

and $\phi_{\mu \dots \nu}^{m \dots n}$ is the k th order coupling parameter, and $q_{\mu}^{m \dots n}$ is the i th component of the displacement from equilibrium of the atom in the μ th position of the unit cell which is located by the lattice vector $\tilde{m}$. The temperature is introduced with the assumption of thermal equilibrium, and the free energy can then be written down. It is

$$F(\rho, T) = \Phi_0(\rho) + \sum_{\substack{k, \lambda \\ \tilde{n}}} \left[\frac{1}{2} \hbar \omega_{\tilde{n}}(k, \lambda) + kT \ln (1 - e^{-\hbar \omega_{\tilde{n}}(k, \lambda)/kT}) \right] + F_3(T) + F_4(T) \quad (11)$$

Here, Φ_0 is the energy of assembling the (static) lattice to its equilibrium configuration. $\omega_{\tilde{n}}(k, \lambda)$ is a vibrational eigenfrequency, a function of the wave vector k and the polarization. F_3 and F_4 are ^{complicated} functions of temperature

only, which are given explicitly by Leibfried and Ludwig [1961]. At high temperature the energy enters the classical regime, and the equations simplify. We will content ourselves here with this restriction to temperatures greater than θ_D , the Debye temperature.

$$\begin{aligned}
 F = & \phi_0 + kT \sum \ln \frac{\hbar \omega(k, \lambda)}{kT} \\
 & - \frac{k^2 T^2}{16Ns} \sum_{\lambda} \sum_{\lambda'} \sum_{\lambda''} \frac{|\phi_{\lambda\lambda\lambda}^{kk'k''}|^2}{(\omega\omega'\omega'')^2} \left(\frac{2\omega - \omega''}{\omega + \omega' - \omega''} + \frac{\omega}{\omega + \omega' + \omega''} \right) \\
 & + \frac{k^2 T^2}{8Ns} \sum_{\lambda} \sum_{\lambda'} \frac{|\phi_{\lambda\lambda}^{4kk}|}{(\omega\omega')^2}
 \end{aligned} \tag{12}$$

This equation is the high-temperature form of equations 10.2 and 10.4 of Leibfried and Ludwig [1961]. N is the number of elementary cells; s is the number of atoms in a cell. $\phi_{\lambda\lambda\lambda}^{kk'k''}$ and $\phi_{\lambda\lambda}^{4kk}$ describe, respectively, the third- and fourth-order derivatives of the lattice potential energy, and are defined precisely by Leibfried and Ludwig. The frequencies ω depend on the lattice configuration through $\underline{k}$; insofar as this configuration can be described by the single parameter ρ , we can say that $\omega = \omega(\rho)$. However, the frequencies appearing in F_3 and F_4 of equation 11 and 12 must be evaluated at a fixed density because of the

presence of $\phi_{\lambda\lambda'\lambda''}^{kk'k''^2}$ and $\phi_{\lambda\lambda'}^{4kk'}$.

This situation can be briefly summarized by the statement that the anharmonic high T approximation is

$$F(\rho, T) = A(T) + B(\rho) + C(\rho)T + D(\rho)T^2 \quad (13)$$

In the harmonic approximation, ϕ_3 and ϕ_4 are zero, implying that $B(\rho)$ is quadratic in the strain, $C(\rho)$ is constant, and $D(\rho)$ is zero. In the fourth-order anharmonic approximation (which we shall call the anharmonic approximation) ϕ_3 and ϕ_4 are non-zero, but the next terms (ϕ_5 and ϕ_6) are zero, implying that $B(\rho)$ is quartic, $C(\rho)$ is quadratic, and $D(\rho) = D$ is constant.

The anharmonic equation of state is, from (5)

$$(P(\rho, T) = - \frac{d\phi_0}{dV} + \frac{1}{V} \sum_i \frac{d \ln \omega_i}{d \ln} h\omega_i \left[\frac{1}{2} + \frac{1}{e^{h\omega_i/kT} - 1} \right] \quad (14)$$

$$= - \frac{d\phi_0}{dV} + \frac{1}{V} \sum_i \gamma_i \epsilon_i \quad (14a)$$

where

$$\gamma_i = \frac{d \ln \omega_i}{d \ln \rho}$$

and

$$\epsilon_i = \hbar \omega_i \left[\frac{1}{2} + \frac{1}{e^{\hbar \omega_i / kT} - 1} \right]$$

are the Grüneisen parameter and the energy, respectively, of the i th normal mode of vibration.

The further assumption that all the γ_i are equal leads to the Mie-Grüneisen equation [Grüneisen, 1926].

$$P(\rho, T) = - \frac{d \phi_0}{dV} + \gamma \frac{E_{vib}}{V} \quad (14b)$$

where $E_{vib} = \sum \epsilon_i$.

The alternative assumption that E_{vib} is a function of T only yields the Hildebrand equation [Hildebrand, 1931]

$$P(\rho, T) = - \frac{d \phi_0}{dV} + \alpha KT \quad (14c)$$

where $\alpha = - \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$ is the thermal expansivity. These two equations were discussed by Fumi and Tosi [1962]. At high temperatures they converge together, as the first assumption becomes irrelevant, the second is automatically fulfilled, and the pressure becomes

$$\begin{aligned} P(\rho, T) &= - \frac{d \phi_0}{dV} + \frac{\sum \gamma_i}{V} kT \\ &= B'(\rho) + C'(\rho) T \end{aligned} \quad (14d)$$

with $C'(\rho) = \alpha K$. This equation is equivalent to

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_\rho = \left(\frac{\partial \alpha K}{\partial T} \right)_\rho = 0 \quad (15)$$

and this is a simple statement of the anharmonic high T approximation.

A coherent framework. In the present context, it is clear that the difference between the isothermal B-M equation (1) and the thermal equations (13) is merely one of viewpoint. We may expand $F(\rho, T)$ about a point ρ_0, θ corresponding to zero pressure and some finite temperature θ in many equivalent ways. If $t = T - \theta$

$$\begin{aligned} F(\rho, T) = & [F_{00} + F_{00}' t + F_{00}'' \frac{t^2}{2} + \dots] + g(t) \\ & + [F_{00}^* + F_{00}'^* t + F_{00}''^* \frac{t^2}{2} + \dots] \epsilon \\ & + [F_{00}^{**} + F_{00}'^{**} t + F_{00}''^{**} \frac{t^2}{2} + \dots] \frac{\epsilon^2}{2} \\ & + [F_{00}^{***} + F_{00}'^{***} t + F_{00}''^{***} \frac{t^2}{2} + \dots] \frac{\epsilon^3}{6} + \dots \end{aligned} \quad (16a)$$

$$\begin{aligned} = & [F_{00} + F_{00}'^* \epsilon + F_{00}''^{**} \frac{\epsilon^2}{2} + F_{00}'''^{***} \frac{\epsilon^3}{6} + \dots] \\ & + [F_{00}' + F_{00}'^* \epsilon + F_{00}''^{**} \frac{\epsilon^2}{2} + F_{00}'''^{***} \frac{\epsilon^3}{6} + \dots] t \quad (16b) \\ & + [F_{00}'' + F_{00}'^* \epsilon + F_{00}''^{**} \frac{\epsilon^2}{2} + F_{00}'''^{***} \frac{\epsilon^3}{6} + \dots] \frac{t^2}{2} + \dots \\ & + g(t) \end{aligned}$$

where the symbol $'$ means $(\frac{\partial}{\partial t})_\epsilon$, the superscript $*$ means

$(\frac{\partial}{\partial \epsilon})_t$, and the subscript 00 indicates evaluation at $P = \epsilon = 0$,

$t = 0$. The function $g(t)$ contains the nonpolynomial terms in t that are necessary to obtain the correct specific heat. The viewpoint in (16a) is clearly that of the B-M equation; the coefficient of ϵ will vanish when the boundary conditions at $P = 0$ are invoked, and the part independent of ϵ is one to which our attention need not be explicitly directed in the derivation of an isothermal equation of state.

But the viewpoint in (16b) is not that of the anharmonic theory. This is because the strains, as defined, are functions of T as well as ρ , and thus the coefficients of the various powers of t are not of the proper form. What is needed is a recognition of the fact that the free energy depends on the total strain from a fixed initial state. This strain, containing both isobaric and isothermal compression is clearly

$$e \equiv -\frac{1}{2} (X^{2/3} - 1) \quad (17)$$

where $x \equiv \frac{\rho}{\rho_{00}}$ and ρ_{00} is the density at $P = 0$, $t = 0$. Then we can expand F in terms of e and t in an equally valid and more instructive manner:

$$\begin{aligned} F(P, T) = & \left[F_{00} + \dot{F}_{00} t + \ddot{F}_{00} \frac{t^2}{2} + \dots \right] + g(t) \\ & + \left[F_{00}^{\dagger} + \dot{F}_{00}^{\dagger} t + \ddot{F}_{00}^{\dagger} \frac{t^2}{2} + \dots \right] e \\ & + \left[F_{00}^{\dagger\dagger} + \dot{F}_{00}^{\dagger\dagger} t + \ddot{F}_{00}^{\dagger\dagger} \frac{t^2}{2} + \dots \right] \frac{e^2}{2} \\ & + \left[F_{00}^{\dagger\dagger\dagger} + \dot{F}_{00}^{\dagger\dagger\dagger} t + \ddot{F}_{00}^{\dagger\dagger\dagger} \frac{t^2}{2} + \dots \right] \frac{e^3}{6} \\ & + \left[F_{00}^{\dagger\dagger\dagger\dagger} + \dots \right] \frac{e^4}{24} \end{aligned} \quad (18a)$$

$$\begin{aligned}
&= [F_{00} + \dot{F}_{00}^+ e + \ddot{F}_{00}^{++} \frac{e^2}{2} + \dddot{F}_{00}^{+++} \frac{e^3}{6} + \dots] \\
&+ [\dot{F}_{00} + \dot{F}_{00}^+ e + \ddot{F}_{00}^{++} \frac{e^2}{2} + \dddot{F}_{00}^{+++} \frac{e^3}{6} + \dots] t \quad (18b) \\
&+ [\ddot{F}_{00} + \ddot{F}_{00}^+ e + \dddot{F}_{00}^{++} \frac{e^2}{2} + \dots] \frac{t^2}{2} \\
&+ \dots + g(t)
\end{aligned}$$

where the superscript $\cdot$ means $(\frac{\partial}{\partial t})_\rho$, the superscript $+$ means $(\frac{\partial}{\partial e})_t$, and the subscript 00 indicates evaluation at $t = 0$, $e = 0$. The anharmonic theory is invoked to give the non-polynomial term in t ; from (12) it is clearly

$$g(t) = -3Ns k[(t + \theta) \ln(1 + \frac{t}{\theta}) - t] \quad (19a)$$

It is clearly possible to derive (18) from (16) by expanding ϵ in terms of e and t . But the degree of the expansion will be necessarily different for each term. In other words, each $y(\rho, T)$ appearing in (1) must be handled differently. We may conclude that the B-M equation, in the form of (1) and (4), is not consistent with the anharmonic theory, or with its results, equations 14. However, in the modified form implied by equation 17, it clearly is consistent, except for the term in e^4 . This term will contribute to the pressure at large strain, and it will contribute to $(\frac{\partial K}{\partial T})_{P, \Lambda}$ and $(\frac{\partial^2 K}{\partial P \partial T})$ at zero pressure. Its magnitude cannot be estimated with present experimental limits on K''_{00} .

The coefficients in (18) are defined experimentally by

$$F_{oo} = 0$$

$$\dot{F}_{oo} = 0$$

$$F_{oo}^{\dagger} = 0$$

$$F_{oo}^{\dagger\dagger} = 9 \frac{K_{oo}}{\rho_{oo}}$$

$$F_{oo}^{\dagger\dagger\dagger} = -27 \frac{K_{oo}}{\rho_{oo}} (K'_{oo} - 4)$$

$$F_{oo}^{\dagger\dagger\dagger\dagger} = -27 \frac{K_{oo}}{\rho_{oo}} (K''_{oo} K_{oo} + K'_{oo} - \frac{1}{9})$$

$$F_{oo}^{\dagger} = -3 \frac{\alpha_{oo} K_{oo}}{\rho_{oo}}$$

$$\dot{F}_{oo}^{++} = -9 \frac{\alpha_{oo} K_{oo}}{\rho_{oo}} \left[\delta_{oo} - K_{oo}' + \frac{5}{3} \right]$$

12.

(19b)

$$\dot{F}_{oo}^{++\ddagger} = -27 \frac{\alpha_{oo} K_{oo}}{\rho_{oo}} \left[\rho_{oo} - (\delta_{oo} - 3)(K_{oo}' - 4) \right]$$

$$\ddot{F}_{oo} = \frac{1}{\theta} \left[3 N_s k - C_{Voo} \right]$$

$$\ddot{F}_{oo}^{+} = -\frac{3}{\rho_{oo}} \left(\frac{\partial \alpha K}{\partial T} \right)_P = -3 \frac{\alpha_{oo}^2 K_{oo}}{\rho_{oo}} \left[K_{oo}' - 2\delta_{oo} + \beta_{oo} \right]$$

$$\ddot{F}_{oo}^{++} = -18 \frac{\alpha_{oo}^2 K_{oo}}{\rho_{oo}} \left[(K_{oo}' - 4) \left(\delta_{oo} + \frac{1}{2} \beta_{oo} - \frac{8}{3} \right) + \frac{7}{3} \left(\delta_{oo} - \frac{1}{2} \beta_{oo} \right) - \rho_{oo} - \frac{1}{2\alpha_{oo}^2 K_{oo}} \left(\frac{\partial^2 K}{\partial T^2} \right)_P - \frac{49}{18} \right]$$

$$\ddot{F}_{oo}^{++\ddagger} = -27 \frac{\alpha_{oo}^2 K_{oo}}{\rho_{oo}} \left[3(K_{oo}' - 4)(\beta_{oo} - 2\delta_{oo} + 3) - 2\rho_{oo}(\delta_{oo} - 3) + \frac{(K_{oo}' - 4)}{\alpha_{oo}^2 K_{oo}} \left(\frac{\partial^2 K}{\partial T^2} \right)_P + \frac{1}{\alpha_{oo}^2} \left(\frac{\partial^3 K(P, T)}{\partial T^2 \partial P} \right) \right]$$

where the derivatives are evaluated, of course, at the oo point. δ is the anharmonic parameter

$$\delta \equiv -\frac{1}{\alpha K} \left(\frac{\partial K}{\partial T} \right)_P$$

and

$$\beta \equiv \frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T} \right)_P$$

and

$$\zeta \equiv \frac{1}{\alpha} \frac{\partial^2 K(P, T)}{\partial P \partial T}$$

are introduced here to simplify the notation.

These coefficients are complicated for two reasons: the pressure is a volume derivative of the free energy rather than a strain derivative; and the values of K and α are such that in the laboratory we always measure $(\frac{\partial}{\partial T})_P$ instead of $(\frac{\partial}{\partial T})_p$. It is of interest to note that because of the sums in the last three equations of (19b), knowledge of $(\frac{\partial^2 K}{\partial T^2})_P$ is of limited usefulness without similar knowledge of $K(\frac{\partial \alpha}{\partial T})_P$ and $K \frac{\partial^3 K(P, T)}{\partial T^2 \partial P}$. All these terms are needed if the anharmonic theory is applied as in this context.

The anharmonic high T approximation is that terms in $\ddot{F}_{00}^{+++}$, $\ddot{F}_{00}^{++}$, $\ddot{F}_{00}^{+}$, $\ddot{F}_{00}^{++}$ are small compared to all other terms. For example,

$$| \ddot{F}_{00}^{+} \frac{t^2}{2} e | \ll | \ddot{F}_{00}^{+} t e | \quad (20)$$

or

$$| (K'_{00} - 2\delta_{00} + \beta_{00}) \frac{\alpha_{00} t}{2} | \ll 1$$

is actually an approximate statement of equation 15, evaluated at the 00 point. Of course, this will be true for small enough values of t , and despite the large uncertainties in $(\frac{\partial \alpha}{\partial T})_P$, it seems that this inequality will hold perhaps to $t \sim 1000^\circ$.

However, (20) is not sufficient to insure the adequacy of the ^{anharmonic high T} approximation. It must be shown that each term neglected is much smaller than each term retained, requiring, for example,

$$|\ddot{F}_{00}^+ e \frac{t^2}{2}| \ll |F_{00}^{++} t \frac{e^2}{2}| \quad (21a)$$

or

$$|(K'_{00} - \delta_{00} + \beta_{00}) \alpha_{00} t| \ll |3(K_{00} - \delta_{00} - \frac{5}{3})e| \quad (21b)$$

This inequality is not demonstrable, in general, except for very small values of e . We will return to this problem of the sufficiency of the ^{anharmonic high T} approximation in the final section.

Thermal restrictions on isothermal equations. While the demonstration of (20) and (21) is sufficient to establish the adequacy of the ^{anharmonic high T} approximation, it is for some purposes more convenient to consider the exact statement of the approximation

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_\rho = 0 \quad (15)$$

In this section, we consider (15) as a property of thermal equations in the ^{anharmonic high T} approximation that must be possessed by isothermal equations used in the same context. We discuss the conditions necessary for the inclusion of (15) in two

generalized isothermal forms of the equations of state.

Consider the form

$$P(p, T) = \sum_{i=1}^M c_i(T) y^{n_i} \quad (22)$$

of which (1) is an example. The c_i here are experimental quantities fixed by the boundary conditions at $y = 1$. The n_i are independent of T , and the only restriction on M is that it be finite. If such an equation is to meet the anharmonic high T condition (15), it must be that

$$\sum_i [c_i + (2\alpha_0 \dot{c}_i + \dot{\alpha}_0 c_i) n_i + c_i \alpha_0^2 n_i^2] y^{n_i} = 0 \quad (23)$$

Since ^{the} y^{n_i} are linearly independent, each bracket must equal zero independently, giving M algebraic equations which can be solved explicitly for the n_i in terms of c_i , α_0 , and their derivatives. It is obvious that any rational n_i (e.g., $n_1 = \frac{5}{3}$) can only meet this condition approximately, at least in macroscopic physics. This approximation is separate from, and additional to, the approximation in (21). But it is not possible, under present limitations, to state whether or not it is serious.

However, it is of interest to know whether the condition (15) can be met exactly by any equation of state. Consider the form

$$P(p, T) = K_0(T) f(y) \quad (24)$$

of which the Murnaghan equation (6) is an example, (providing K'_0 is independent of T). The second-order B-M equation (with $\xi = 0$) is another example. Some of the properties of this form are discussed by Birch [1968]. The only equation of the form (24) which meets the anharmonic high T condition is

$$P(P, T) = \frac{K_0}{n_1 - n_2} (Y^{n_1} - Y^{n_2}) \quad (25)$$

where

$$n_1 = \frac{K'_0}{2} [1 + \sqrt{1 - R_0(T)}]$$

$$n_2 = \frac{K'_0}{2} [1 - \sqrt{1 - R_0(T)}]$$

with

$$R_0(T) = \frac{4}{\alpha_0^2 K_0 (K'_0)^2} \frac{d^2 K_0}{dT^2}$$

The Murnaghan equation (6) is a special case of (25) corresponding to $R_0(T) = 0$. Therefore, one may use the M-G equation in conjunction with the Murnaghan equation only after demonstrating that $R_0 \ll 1$.

The demonstration is not generally possible. Soga and Anderson, 1967] measured K_S at zero pressure and high temperature for the polycrystalline oxides MgO , Al_2O_3 , and Mg_2SiO_4 . This can be converted from the adiabatic modulus to the isothermal modulus using

$$K = K_S / (1 + \tau \alpha \gamma)$$

It is then found that the curvature $\frac{d^2 K_0}{dT^2}$ is so small as to be unmeasurable, being equal to zero within a fourth of a standard deviation for all materials. However, if the standard deviation of $\frac{d^2 K_0}{dT^2}$ from its mean is taken as an upper bound for $\frac{d^2 K_0}{dT^2}$, then the quantity R_0 may, because of the factor $\frac{1}{K_0 \alpha_0^2}$, be quite large, and one therefore cannot conclude that $R_0 \ll 1$. Much more precise measurements of the temperature dependence of K_0 will be needed before it can be shown that $R_0 \ll 1$.

Thermal equations from the isothermal viewpoint. The expansion in (18) gives new insight into the quantities appearing in the thermal equations 14. The equation of state which follows from (18) via (15) is, in the anharmonic high T approximation,

$$\begin{aligned}
 P(P, T) = & \frac{3}{2} K_{00} (X^{7/3} - X^{5/3}) [1 - \xi(0)(X^{2/3} - 1)] \\
 & - \frac{1}{3V_{00}} X^{5/3} F_{00} \frac{e^3}{3!} \\
 & + \alpha_{00} K_{00} X^{5/3} [1 + 3e(\delta_{00} - K'_{00} + \frac{5}{3})] X
 \end{aligned} \tag{26}$$

Comparison with (13d) shows that arbitrariness in the choice of $\gamma(\rho)$ has been eliminated by this expansion. Essentially, the unknowns in γ have been expressed by the boundary conditions at the ∞ point. Hence,

$$\gamma(\rho) = \frac{1}{3Ns} \sum \gamma_i = \gamma_{\infty} (1 - 2e) \left\{ 1 + 3e \left[\delta_{\infty} - K'_{\infty} + \frac{5}{3} \right] \right\} \quad (27)$$

where $\gamma_{\infty} = \frac{\alpha_{\infty} K_{\infty} V_{\infty}}{3sR}$. Whenever the M-G equation of state is used with internal consistency, the function assumed for $\gamma(\rho)$ will converge to the form (27) in the high-temperature regime. This convergence must take place independently of assumptions on which modes of vibration contribute to γ , etc., since all modes are already contained in α .

Different materials exhibit a large variety of behavior of $\gamma(\rho)$. Some of the possibilities are illustrated in Figure 1 for several minerals of possible importance in the earth. It is seen that for some materials γ decreases rapidly, and goes through zero at compressions found in the lower mantle. This is remarkable behavior, and raises well-known problems with the thermal expansivity and the sign of the temperature changes accompanying adiabatic compression.

These problems notwithstanding, it is worth emphasizing here that the theoretical justification of (27) is similar in every respect to that leading to the Birch-Murnaghan equation of state.

Internal consistency in the Q-H approximation

In applying the Mie-Grüneisen equation of state, various assumptions are necessary, and it is important that these be made in a self-consistent way. In particular, we wish to discuss here the relations between γ and Φ_0 .

When the atomic interaction is unknown, then both γ and Φ_0 may be chosen independently. But where the interaction is known, both γ and Φ_0 are thereby determined. For example, Decker [196⁵~~X~~] in determining a numerical equation of state for NaCl assumes an interaction with Coulombic, dipole-dipole, dipole-quadrupole, and exponential repulsion terms. Since all these are central forces, he obtains an expression for Φ_0 (which he denotes by Φ) which involves only the lattice parameter r . He then assumes

$$\gamma = \gamma_0 + \lambda \frac{r-r_0}{r_0}$$

for the volume dependence of γ , where

$$\gamma_0 = \left(\frac{\alpha K}{\rho C_p} \right)_{P=0} = 1.59 \pm .16$$

and $r_0 = R(P=0)$. λ is empirically chosen to be 2.55.

However, γ is the logarithmic derivative of $\overline{\omega^2}$, and $\overline{\omega^2}$ is determined by the atomic interaction. From Leibfried and Ludwig [1961]

$$\overline{\omega^2} = \frac{1}{3sN} \sum_{k,\lambda} \omega^2(k,\lambda) = \frac{1}{3s} \sum_{\mu,1} \frac{1}{M_\mu} \Phi_{11}^{\mu\mu} = \frac{-1}{3s} \sum_{\mu,1} \frac{1}{M_\mu} \sum_{i,j} \Phi_{ij}^{\mu\nu} \frac{\partial}{\partial r_i} \frac{\partial}{\partial r_j} \quad (28)$$

where Σ' indicates summation over all lattice points except $\vec{h} = 0$, $\nu = \mu$. M_μ is the mass of atom μ .

Where the interaction depends only on the distance $R_{\vec{h}\nu}$ between atoms, the potential is

$$\Phi = \frac{1}{2} \Sigma \phi_{\mu\nu}(R_{\vec{h}\nu})$$

and (28) becomes

$$\frac{1}{\omega^2} = -\frac{1}{3s} \Sigma' \frac{1}{M_\nu} \nabla^2 \phi_{\mu\nu}(R_{\vec{h}\nu}) \quad (29)$$

where ∇^2 is the Laplacian operator. Grüneisen's parameter is

$$\gamma = \frac{1}{18s\omega^2} \Sigma' \frac{1}{M_\nu} R_{\vec{h}\nu} \frac{\partial}{\partial R_{\vec{h}\nu}} \nabla^2 \phi_{\mu\nu} \quad (30)$$

Where the interaction $\phi_{\mu\nu}$ is specified, it is easy to compute these functions. For the potential used by Decker [1965]

$$\begin{aligned} \frac{1}{\omega^2} = & -\frac{C^*}{6r^8} - \frac{D^*}{6r^{10}} \\ & + \frac{b}{\rho^2} \left(\frac{M_+ + M_-}{M_+ M_-} \right) \left(1 - 2 \frac{\rho}{r} \right) e^{-r/\rho} \\ & + \frac{2b_+}{\rho_+^2 M_+} \left(1 - 2 \frac{\rho_+}{r} \right) e^{-r\sqrt{2}/\rho_+} + \frac{2b_-}{\rho_-^2 M_-} \left(1 - 2 \frac{\rho_-}{r} \right) e^{-r\sqrt{2}/\rho_-} \end{aligned} \quad (31)$$

and

$$\begin{aligned}
 \gamma = \frac{-1}{36\omega^2} & \left[\frac{8C^*}{r^8} + \frac{10D^*}{r^{10}} + \frac{6b}{\rho^2} \frac{M_+ + M_-}{M_+ M_-} \left(2 + 2 \frac{\rho}{r} - \frac{r}{\rho} \right) e^{-r/\rho} \right. \\
 & + \frac{b_{+12}}{\rho_+^2 M_+} \left(2 + 2 \frac{\rho_+}{r\sqrt{2}} - \frac{r\sqrt{2}}{\rho_+} \right) e^{-r\sqrt{2}/\rho_+} \\
 & \left. + \frac{b_{-12}}{\rho_-^2 M_-} \left(2 + 2 \frac{\rho_-}{r\sqrt{2}} - \frac{r\sqrt{2}}{\rho_-} \right) e^{-r\sqrt{2}/\rho_-} \right] \quad (32)
 \end{aligned}$$

Here

$$C^* = 30 \left[\left(\frac{c_{--}}{M_-} + \frac{c_{++}}{M_+} \right) S_8'' + c_{+-} \left(\frac{1}{M_+} + \frac{1}{M_-} \right) S_8' \right]$$

$$D^* = 56 \left[\left(\frac{d_{--}}{M_-} + \frac{d_{++}}{M_+} \right) S_{10}'' + d_{+-} \left(\frac{1}{M_-} + \frac{1}{M_+} \right) S_{10}' \right]$$

and the c's, the d's, and the S's are defined by Mayer [1933]. Using the values for the constants found in Decker [1965] and in his reference, Mayer [1933], γ can be calculated numerically, and is shown in Figure 2. Also shown is the linear relation of Decker, and an arrow marking the maximum compression considered by him.

It is seen that, in the low-compression range, γ is nearly linear with $\frac{\Delta r}{r_0}$, with an initial value of 1.46, and an average slope of 1.70. Decker remarks that, for such behavior of γ , 'the fit to the experimental thermal expansion became quite poor.'

Decker's idea was that the equation of state of NaCl was sufficiently well understood theoretically that salt might be used as a pressure gauge in experiments on other materials. On the basis of the present remarks, it appears that the fourth-order anharmonic approximation,^{as} used by Decker, is not sufficient to accurately describe the behavior of NaCl. The application of the sixth-order anharmonic treatment, straightforward in this case, might be expected to yield better agreement.

However, a feature of the central force assumption implies that even this will not be sufficient, unless an atomic interaction which includes non-central forces is used. Leibfried and Ludwig show that, for central forces in cubic crystals, the inequalities

$$c_{12} < c_{44} \quad (33a)$$

and

$$\left(\frac{dc_{12}}{dT} \right)_V < \left(\frac{dc_{44}}{dT} \right)_V \quad (33b)$$

are implied for the adiabatic elastic constants c_{ij} . If these are not satisfied by the data, then non-central forces must be involved. Such is the case for NaCl [Barsch and Chang, 1964]. It thus appears that a theoretical basis for accurately describing the properties of NaCl must include non-central forces.

Summary. The conclusions reached here are of three sorts; those relating to mutual consistency, those relating to internal consistency, and those relating to adequacy of approximation. Of the first sort:

1. Because, in equation 1, each $y(T)$ must be treated differently, we conclude that the Birch-Murnaghan equation, in the form (1) and (4), is not consistent with lattice dynamics in the anharmonic high T approximation, nor with its results, the Mie-Grüneisen and Hildebrand equations.

2. However, with the modification implied by equation 17, the B-M equation becomes identical to the anharmonic high T equations, provided only that the term of (18) in e^4 can be shown to be negligible. The demonstration of this negligibility is beyond present experimental techniques.

3. The Murnaghan equation is consistent with the anharmonic high T equations, provided only that $R_0(T)$, equation 25, can be shown to be negligible compared to unity. The demonstration of this negligibility is beyond present experimental techniques.

4. Where two equations cannot be definitely proven consistent, they should not be used in the same calculation.

Of the second sort:

5. The Grüneisen parameter $\gamma(\rho)$ is defined in terms of boundary conditions by the expression in (27). Any other

assumption on $\gamma(\rho)$, such as that of Slater [1939] or of Dugdale and MacDonald [1953], must converge to this at high temperature.

6. Once an assumption has been made concerning the interaction between atoms in a crystal, then the lattice dynamics is completely determined, and only the degree of approximation remains to be chosen. In particular, in the fourth-order approximation, when the interaction is assumed, ϕ_0 , ω_1^2 and $\bar{\gamma}$ are all determined.

Of the third sort:

7. The data of NaCl are such as to require non-central forces for an adequate theoretical explanation.

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Table 1. Mineral Parameters

	Poly'xl Al ₂ O ₃	Single xl MgO	Poly'xl Mg ₂ SiO ₄
δ_{oo}	5.06*	3.54*	4.88 [†]
K'_{oo}	3.99 [†]	4.52 [‡]	4.9 [‡]
$\delta_{oo} - K'_{oo} + 1$	2.07	.02	.98
β_{oo}	2.24*	2.85*	3.49 [†]
γ_{oo}	1.27	1.46	.77
θ	1042°K	946°K	650°K

*Soga and Anderson [1966]

[†]Soga and Anderson [1967]

[‡]Anderson and Liebermann [1967]

FIGURE CAPTIONS

- Fig. 1 Grüneisen parameter as a function of strain, from equation 27, using the mineral parameters of Table 1.
- Fig. 2 Grüneisen parameter for the NaCl model of Decker [1965].

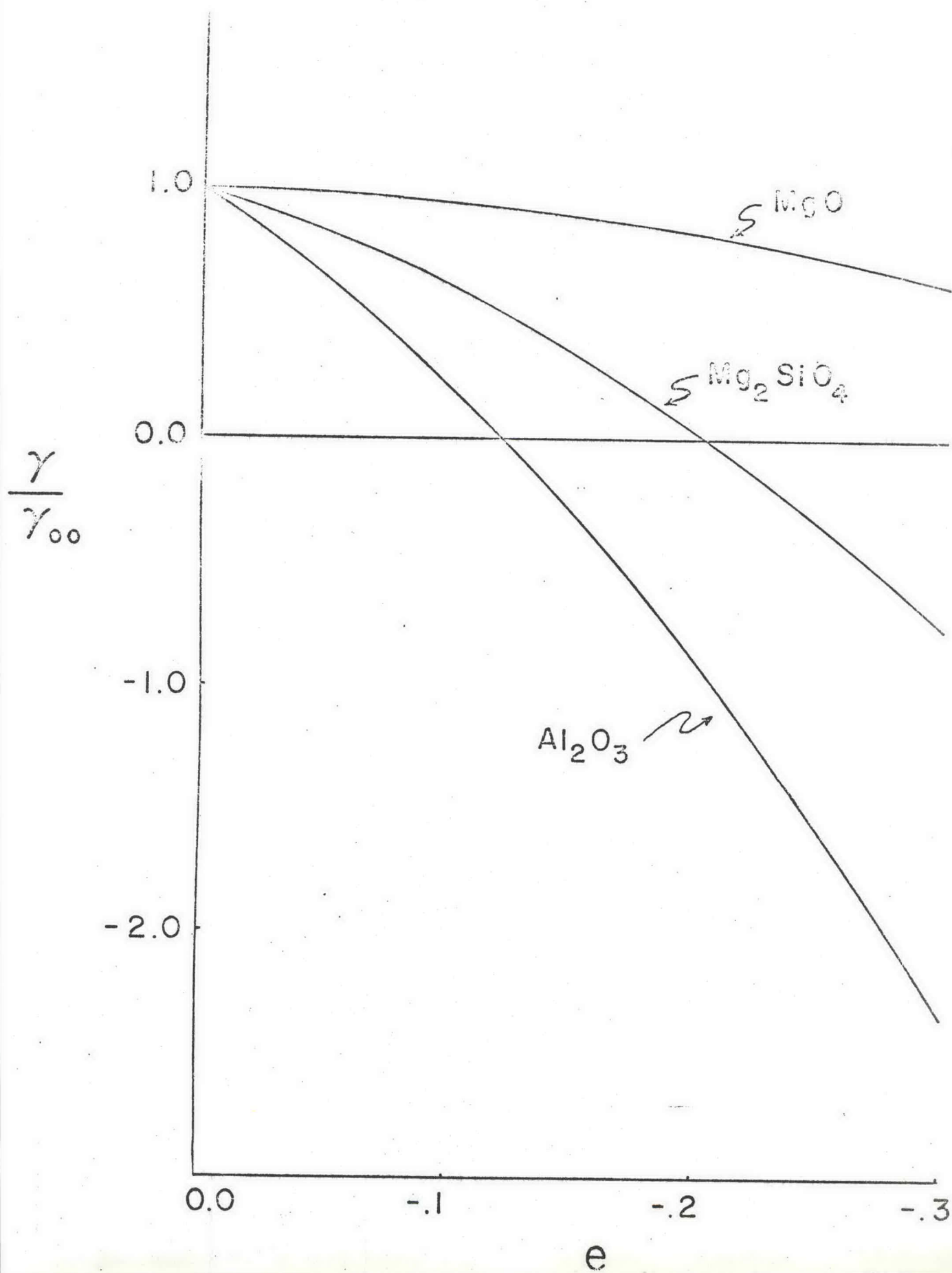


Fig. 2.

