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Classical Methods for Frequency-Based Equations of State

by Steven B. Segletes

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Classical methods for frequency-based equations of state

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Abstract

A review of recent work by the author in the area of classical equation-of-state development is presented. The scope of the review extends from equation-of-state stability constraints to a frequency-based, closed-form equation-of-state formulation incorporating the effects of non-nearest lattice neighbors.

Introduction

In recent decades, the development of classical frequency-based equation-of-state (EOS) methods [1–5] has fallen out of favor as more modern (*e.g.*, quantum) approaches have taken hold. Nonetheless, classical approaches continue to offer meaningful results

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that are straightforward to obtain for Grüneisen materials, wherein Γ , the Grüneisen function, is a function of volume only, such that $\Gamma = \Gamma(V)$.

Thermodynamic constraints

The use of classical thermodynamics, in and of itself, permits a great deal of knowledge to be ascertained about permissible EOS forms. Early work by the author in the area [6–8], for example, employed classical thermodynamics to ascertain interrelated constraints on the behavior of the Grüneisen function and Hugoniot. These constraint relations are typically the thermodynamic consequence of a mechanical constraint. As an illustration, the constraint of the post-normal-shock velocity to subsonic values (a well-known mechanical constraint) has a (less known) thermodynamic consequence [6] that $\Gamma(V) < 2V/(V_0 - V)$. That a number of production computer “wave-propagation” codes were found to be in violation of this and other constraints served only to highlight the importance of the functional coupling between a material’s mechanical (*i.e.*, cold pressure or p_c) behavior and its thermal behavior as epitomized by Γ .

Pursuing this macro-thermodynamic approach, the author [9] demonstrated the ability to compose thermomechanically coupled EOS forms in which, for example, the internal energy along the Hugoniot was given as a direct function of Γ . Formulations were based solely on the requirement that the EOS avoid various modes of thermodynamic instability, as these constraint violations were called. These EOS forms were not specific to a particular material, but were rather families of equations of state that were guaranteed to avoid various constraint violations.

Thermomechanical linkage

It is no accident that historical efforts to understand aspects of the EOS for crystalline solids settled upon the characteristic lattice frequency as the key variable [1–5, 10]. Excellent background of this topic is given by Slater [1]. On the thermal side of the problem, key variables are the Grüneisen function, $\Gamma(V)$, which relates changes in pressure p and energy E at constant volume V [eqn (1)], and specific heat, which relates changes in energy and temperature T at constant volume [eqn (2)]. Early work in specific heats by Born and von Karman [10], Einstein, and Debye established the link between specific heat and characteristic temperature Θ [eqn (3)] which, in turn, was shown proportional to a characteristic vibrational frequency of the lattice ω [eqn (4)]. The Grüneisen function, in turn, was also shown to be related to ω [eqn (5)].

Since the characteristic vibrational frequency is composed of an aggregation of many vibrational modes, the question arose as to the distribution of frequency modes that compose the aggregated spectrum. As with many good models, reasonable assumptions were made, some better than others. For modeling purposes, Einstein assumed all component ω_i were equal to the aggregate ω . While allowing for different component frequencies, Grüneisen assumed a similarity of behavior by way of $d\omega_i/dV = d\omega/dV$. Debye assumed a particular parabolic distribution on the frequency spectrum. It was, no doubt, the desire to better characterize the vibrational spectrum that has led researchers in the field to develop newer spectral methods. What is generally lost, however, with the added detail is the ability to capture results in closed form. Retaining the historical premise, then, that an aggregated vibrational frequency spectrum composed of only one or,

at most, several vibrational modes can adequately characterize the complete vibrational frequency spectrum of the lattice (and thus the thermal behavior), we turn to the mechanical side of the problem.

From vibration theory, the second derivative of the lattice energy potential, E_{pot} , with respect to a characteristic dimension, ξ , provides a measure of the bulk mechanical stiffness of the lattice. As with any mechanical stiffness, there is an associated frequency, which we herein call the volumetric frequency ω_{vol} , as it derives from the lattice potential, which characterizes the volumetric (*i.e.*, bulk) behavior of the lattice [eqn (6)].

Summarizing the relations that link the thermal to the mechanical side of the problem,

$$(dE/dp)_V = V/\Gamma \quad , \quad (1)$$

$$(dE/dT)_V = C_V \quad , \quad (2)$$

$$C_V = C_V(\Theta/T) \quad , \quad (3)$$

$$\Theta = h\omega/k \quad , \quad (4)$$

$$\Gamma = -(V/\omega) d\omega/dV \quad , \quad (5)$$

$$d^2 E_{\text{pot}}/d\xi^2 \sim (\omega_{\text{vol}}/\xi_\lambda)^2 \quad , \quad (6)$$

where h and k are Planck's and Boltzmann's constants, respectively. The ξ_λ , representing $d\xi/d\lambda$ in eqn (6), is a dimensional conversion metric necessary when the characteristic dimension ξ has units other than length (*e.g.*, Slater's theory [1]). The fundamental problem, constituting the classical approach to frequency-based equations of state, is this: (1) how to formulate the characteristic vibrational frequency ω ; and (2) how to relate the vibrational ω to the volumetric frequency ω_{vol} . In all of the historical models to be discussed [1–3], the volumetric frequency ω_{vol} is considered indistinguishable from, and thus equal to, the vibrational frequency ω . This point will be addressed in greater detail in a subsequent section, and represents a significant point of departure for the current work.

Slater [1] accomplished the calculation of the characteristic vibrational frequency ω by relating the elastic wave speed to both the characteristic frequency and the volumetric compressibility. In so doing, volume becomes the characteristic lattice dimension ξ by which ω_{vol} is calculated in eqn (6) (thus, $\xi_\lambda \sim V^{2/3}$). As a result, $\Gamma = -2/3 - (V/2)p_c''/p_c'$ was obtained by Slater, where the primes denote ordinary differentiation with respect to the specific volume, V .

Dugdale and MacDonald [2] differed with Slater's choice of V as the characteristic dimension ξ in eqn (6). They argued that the spring stiffness from which ω_{vol} derives must be based on a force-displacement and not a pressure-volume relationship. To prove the point, they showed how the hypothetical use of a harmonic lattice "spring" failed to produce the required $\Gamma = 0$ in the Slater model. Though deriving results in terms of pressure (not force), the crux of their modification, as has been shown [11], was the selection of the lattice spacing $\lambda \sim V^{1/3}$ as the characteristic dimension ξ governing the volumetric frequency (thus, $\xi_\lambda \sim 1$). By effecting this change alone, they obtained a form different from that of Slater, given by $\Gamma = -1/3 - (V/2)(p_c V^{2/3})''/(p_c V^{2/3})'$.

Pastine [3] attempted to extend the prior work. As before, volumetric and vibrational lattice frequencies were still assumed indistinguishable. However, he incorporated a 3-D lattice so as to combine three lattice vibrational modes (one longitudinal “*L*” and two transverse “*T*”) into the formulation of ω . For some reason, though, Pastine chose to aggregate the modal contributions by way of $\Gamma = \Gamma_L + 2\Gamma_T$, rather than by the accepted form of $3/\omega^3 = 1/\omega_L^3 + 2/\omega_T^3$, as given directly by Brillouin [12] or obtainable from Slater [1].

Plendl [5], while not developing an EOS directly, presents extensive and interesting methods of relating various material constants to the characteristic frequency of the lattice [essentially extending the ω -based equation set of eqns (1)–(6) to many additional material properties]. He shows how the characteristic frequency that matches vast experimental data for many materials is identical to the “frequency of the center of gravity” of the vibrational spectra, a concept he pioneered.

Solving the Grüneisen EOS [13]

The Grüneisen equation of state, which follows from the assumption that Γ is independent of temperature, may be expressed in a variety of ways, but amounts to

$$p - p_{\text{ref}} = (E - E_{\text{ref}})/\psi . \quad (7)$$

In this equation, ψ represents [7, 8] the convenient grouping V/Γ , while p and E are the pressure and specific internal energy, respectively. The reference functions (subscript “ref”) are states along some known reference curve of compression, such as an isotherm, isentrope, or Hugoniot, for example.

Since p_{ref} , E_{ref} , and ψ are functions of volume alone (whereas p and E are functions of volume and temperature), the mathematical solution to the Grüneisen EOS, eqn (7), requires, for a specified $G(V) = p_{\text{ref}}\psi - E_{\text{ref}}$ and ψ , the determination of p and E that satisfy

$$p\psi - E = G(V) . \quad (8)$$

Along the zero temperature (cold) isotherm, the dependent variables, p and E , are related by $p_c = -E'_c$, and so one obtains from eqn (8) an ordinary differential equation for E_c , in V :

$$\psi E'_c + E_c = -G(V) . \quad (9)$$

The solution to this differential equation would give the interatomic energy potential of the lattice. Without knowing, *a priori*, the G and ψ functions for a given material, the particular solution to eqn (9) cannot be obtained.

However, a complementary solution to this equation, corresponding to $G(V) = 0$, is obtainable, with the use of eqn (5), expressible in the current context as

$$\omega'/\omega = -1/\psi . \quad (10)$$

With this added equation, the complementary solution to the homogeneous Grüneisen cold-energy function, eqn (9) with $G=0$, was determined [13] as

$$E_c = A\omega , \quad (11)$$

where A is an integration constant. This solution is independent of the functional form for ψ (and thus independent of the form for Γ).

For the general case, where $G \neq 0$, the particular solution to the differential eqn (9) will, naturally, be more complicated. Even in the general case, however, the complementary solution to a differential equation is part of the particular solution, and will explicitly appear in the particular solution unless the boundary conditions to the problem are such that the coefficient associated with the complementary term is identically zero. On this basis, it was surmised [13] that ω might appear explicitly as a term in the zero-temperature energy potential for Grüneisen materials. Such a hypothesis was quite reasonable, when it was noted, from eqn (4), that ω is proportional to Θ , which constitutes, in totality, the zero-temperature energy potential in both the Einstein and Debye equations of state for crystalline solids (*i.e.*, E_c equals $3/2 Nk\Theta$ and $9/8 Nk\Theta$, respectively, where N is the number of atoms and k is Boltzmann's constant). Thus, the Einstein and Debye potentials are both complementary solutions to the Grüneisen EOS.

To make the jump from the exact complementary solution given by eqn (11) to an hypothesized particular solution, the author [13] considered the so-called universal EOS form of Rose *et al.* [14]. While not based on a vibrational approach, the universal EOS nonetheless exhibits a commonality shared over many materials, taking the form

$$E_{\text{pot}} = -E_b(1 + a + 0.05a^3)\exp(-a) \quad . \quad (12)$$

where E_{pot} , the energy potential of the lattice, equals the cold energy, E_c , shifted by a constant binding energy E_b , such that $E_{\text{pot}} = E_c - E_b$. The parameter a is a geometrical variable, linearly related to the lattice spacing through a parameter η by

$$a = \eta(\lambda/\lambda_0 - 1) \quad . \quad (13)$$

In hypothesizing a particular solution to eqn (9), the author [13] made two conjectures: (1) that the 0.05 term in the universal potential represented a correction for the fact that the a variable was defined to be linear with lattice spacing; and (2) that, given the complementary solution of eqn (11), ω would appear in the energy potential as an explicit term.

Thus, in accordance with the first conjecture, the following form was explored:

$$E_{\text{pot}} = -E_b(1 + f)\exp(-f) \quad , \quad (14)$$

where f would, unlike a , be some frequency- related variable that was nonlinear with lattice spacing. To satisfy the second conjecture, there are but three possibilities: either $\omega \sim \exp(-f)$, $\omega \sim f \exp(-f)$, or ω goes as the sum of these two. The second form is implausible, as it fails to meet necessary boundary conditions, and the third form essentially produces the complementary solution. For the remaining $\omega \sim \exp(-f)$ form then, the author determined a form for G , $G = D_1\omega - D_2$, that would, when solving eqn (9), yield the following result:

$$E_c = D_2 - A\omega(1 - D_1/A \ln \omega) \quad . \quad (15)$$

This solution to eqn (9), based on the possibility that $f = -\ln(\omega/\omega_0)$, can be expressed in

the modified universal form of eqn (14) with appropriate selection of constants A , D_1 , and D_2 .

In an effort, primarily to fit the data, but also to accommodate the “definite frequency” concept espoused by Plendl [4, 5], the author relaxed the fitting form to permit $f = -K \ln(\omega/\omega_0)$, where K is a material-based constant. With this generalization on f , the cold curve of eqn (15) took the form

$$E_c = E_b \{1 - (\omega/\omega_0)^K [1 - K \ln(\omega/\omega_0)]\} , \quad (16)$$

with the associated cold pressure as

$$p_c = \frac{E_b K^2}{\psi} (\omega/\omega_0)^K \ln(\omega/\omega_0) . \quad (17)$$

With these functions as the reference curve, the Mie-Grüneisen EOS, eqn (7), becomes

$$p\psi - E = E_b \{[(\omega/\omega_0)^K - 1] + K(K-1)(\omega/\omega_0)^K \ln(\omega/\omega_0)\} . \quad (18)$$

The parameter K , on the order of unity, is given by

$$K = \frac{C_0}{\Gamma_0 \sqrt{E_b}} , \quad (19)$$

where C_0 is the bulk sound speed of the material. K is defined so as to properly match the curvature of the potential at the ambient condition.

Implicit in the form of eqn (16), however, is the notion that the vibrational frequency of the lattice, ω , asymptotes to zero only as the lattice separation becomes infinite, whereupon the cold energy asymptotes to the binding energy of the lattice. In the absence of a lattice-vibration analysis, the flaw in this notion was not yet apparent to the author. Nonetheless, even with this flaw, and by assuming a simple linear relation in V for the ψ variable (shown to satisfy basic thermodynamic stability requirements [6]), experimental cold- and shock-compression data were well fit by the model for seven metals, out to several megabars of pressure.

Observations on the theory

Having met with this initial success, the author and a colleague began to explore the implications and consequences of the model. Segletes and Walters [15] made several intriguing analytical observations, merely by assuming a power-law behavior to the ψ function, $\psi = V^x$, in preference to the linear behavior previously assumed [13].

Primarily they found, by starting with eqn (17) and ignoring higher-order terms, that the model of Slater [1], Dugdale and MacDonald [2] or the free-volume theory of Vashchenko and Zubarev [16] could be recovered if the value of the exponent x were chosen as $4/9$, $2/3$, or $8/9$, respectively. Perhaps a better way of appreciating this similarity is to compare, without ignoring the higher-order terms, the governing equations for the historical models given by

$$\left[2 + \frac{4-3n}{3} (\psi/V) \right] \psi (p_c V^n)' + \psi^2 (p_c V^n)'' = 0 \quad (20)$$

to that of the current model (with power-law ψ function), which satisfies

$$K^2(p_c V^x) + [2K + x(\psi/V)]\psi(p_c V^x)' + \psi^2(p_c V^x)'' = 0 \quad (21)$$

Those three historical models [1, 2, 16] are given by eqn (20) when n takes on the values 0, 2/3, and 4/3, respectively. By comparison, the current model, eqn (21), for the case where $K=1$ and $x=2/3$, differs from the Dugdale-MacDonald theory [eqn (20) with $n=2/3$] by only the presence of the first term. Also noted are strong similarities to the other historical forms for alternate values of x .

Recall, at this stage, that the model given by eqns (16)–(19) was based on the complementary solution to the Grüneisen EOS, extended to encompass the functional behavior of the so-called universal potential [14]. Thus, the striking similarity between eqns (20) and (21) provided important additional support for the formulation of the particular solution embodied in eqn (16), itself based upon eqns (11) and (12).

This special case of the current model, in which $K=1$ and $\psi \sim V^{2/3}$, the author deemed the “quasi-harmonic” case, and proceeded to study in further detail [11]. The quasi-harmonic case was unique, in that the lattice potential, E , force, $dE/d\lambda$, and volumetric stiffness, $d^2E/d\lambda^2$, are all expressible solely in terms of the vibrational frequency, ω .

Denoting quasi-harmonic quantities as hatted ($\hat{}$) and treating, for consistency, λ as the specific lattice spacing, equal to the cube root of the specific volume, one may integrate the quasi-harmonic function, $\hat{\psi} = (\lambda_0/\hat{\Gamma}_0)V^{2/3}$, according to eqn (10), to obtain the quasi-harmonic vibrational frequency as

$$\hat{\omega}/\hat{\omega}_0 = \exp\{3\hat{\Gamma}_0[1 - \lambda/\lambda_0]\} \quad (22)$$

Though not at all apparent, the author was able to show that this frequency, inserted into the quasi-harmonic potential,

$$\hat{E}_c = \hat{E}_b \{1 - (\hat{\omega}/\hat{\omega}_0)[1 - \ln(\hat{\omega}/\hat{\omega}_0)]\} \quad (23)$$

actually produces a parabolic (*i.e.*, harmonic) potential well, \hat{E}_c , in the limit as $\hat{\Gamma}_0$ approaches zero (see Fig. 1). Harmonic limiting behavior was considered essential by Dugdale and MacDonald [2] and in that regard, the current work was shown as supportive of that tenet.

By contrast, however, the author explicitly showed [11] how the Dugdale-MacDonald relation relies on an assumed proportionality between volumetric stiffness associated with ω_{vol} , and the characteristic vibrational stiffness associated with the vibrational frequency, ω . The author recognized and inferred that the current model refutes this proportionality, explicitly stating that “the volumetric and vibrational stiffnesses... are not proportional.” [11]

But how could this distinction arise? The assumed proportionality between ω and ω_{vol} was not only an intrinsic facet of the early models [1–3], but was explicitly assumed by Brillouin [12] and more recently, as well, by Guinea *et al.* [17].

It was left to a subsequent transitional report [18] for the author to demonstrate this distinction between ω_{vol} and ω . As will be shown in the next section, the proportionality of ω_{vol} and ω is a direct consequence of lattice interactions confined to the nearest

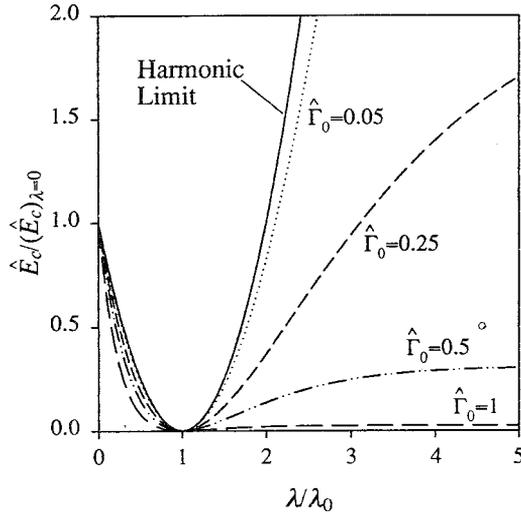


Figure 1. Normalized cold-compression energy vs. lattice spacing for the quasi-harmonic potential, with reference Grüneisen value as a parameter.

neighbors alone. And thus, any model which is constructed by way of nearest-neighbor-only interactions, going back to Slater [1], will as a consequence infer that $\omega_{\text{vol}} \sim \omega$.

Non-nearest neighbors

The key distinction between the author's model described by eqns (16)–(18) and the preponderance of prior classical frequency-based EOS work [1–3, 12, 17] concerns an assumed proportionality between the volumetric- and vibrational frequencies, ω_{vol} and ω , that is intrinsic to the cited prior work. While the author's model was originally derived through the use of thermodynamics and differential equations, and not through the use of lattice mechanics, the need arose to resort to elements of lattice mechanics in order to help refute this oft employed proportionality between ω_{vol} and ω .

This point was made [18] by the consideration of a simple 1-D lattice, such as that depicted in Fig. 2. Making the classical assumption that a given atom of interest (the test atom) interacts with every other atom in the lattice by way of a pairwise potential, the net force effect upon the test atom will arise from a summation of pairwise effects from every other atom in the lattice.

Consider then, two respective deviations from the equilibrium lattice, as depicted in Fig. 2: in one case, the deviation arising from an infinitesimal vibrational pulse of magnitude Δx that has just reached the test atom (a pulse implies, in this case, a fully cyclical event which leaves the lattice in its original configuration following the pulse's passage), and in the other case, an infinitesimal lattice expansion of amount $d\lambda$ brought about by an externally applied force increment ΔF . Denote the pairwise force interaction between the test atom and any other atom by f , where f will naturally be a function of the distance between the test atom and the other atom.

In the case of the vibrational pulse, the restoring force imparted to the displaced test

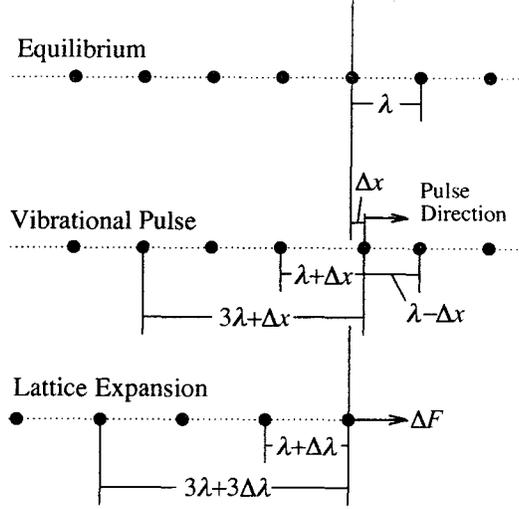


Figure 2. A 1-D lattice depicting the distinction between lattice vibration and expansion. As the test atom is momentarily displaced Δx during a vibrational wave-pulse, the distance from it to every other atom in the lattice is altered by Δx . In the case of lattice expansion by $\Delta \lambda$, the distance to the n 'th atom distant from the test atom is altered by a distance of $n \cdot d\lambda$.

atom that results from the pair of atoms located directly on either side will be $2(df/dx)_\lambda \cdot \Delta x$. The contribution from the pair located at a nominal distance of 2λ will be $2(df/dx)_{2\lambda} \cdot \Delta x$, and so on, such that the quotient of the net restoring force ΔF_{vib} to the Δx displacement of the test atom will be

$$\frac{\Delta F_{\text{vib}}}{\Delta x} = 2 \left[\left(\frac{df}{dx} \right)_\lambda + \left(\frac{df}{dx} \right)_{2\lambda} + \left(\frac{df}{dx} \right)_{3\lambda} + \dots \right]. \quad (24)$$

This ratio $\Delta F_{\text{vib}}/\Delta x$, taken in the limit as dF_{vib}/dx , represents the 1-D vibrational stiffness that resists the pulse disturbance described. We note and fully recognize the simplification of treating this vibrational pulse as indicative of the complete vibrational spectrum. To a simple order though, eqn (24) represents the stiffness associated with the vibrational frequency ω .

Turn now to the deviation engendered by the lattice expansion in Fig. 2, characterized by $\Delta \lambda$ and brought about by a uniform, externally-applied force increment ΔF . Unlike the vibrational pulse, which is a non-equilibrium event, the expanded lattice is in equilibrium with the external force increment ΔF . The test atom need not be on the lattice surface, since a free-body diagram may always be constructed in which the net equilibrium force to one side of the test atom is balanced by the pairwise contributions on the other side. While the change in the pairwise distance to the adjacent atom is $d\lambda$, the second atom from the test atom has been displaced by a distance of $2d\lambda$ with respect to the test atom, the third atom by $3d\lambda$, and so on. Thus, summing the net pairwise-force

changes resulting from the applied force increment dF , one obtains the force to extension quotient as

$$\frac{\Delta F}{\Delta \lambda} = 1 \left(\frac{df}{dx} \right)_{\lambda} + 2 \left(\frac{df}{dx} \right)_{2\lambda} + 3 \left(\frac{df}{dx} \right)_{3\lambda} + \dots \quad (25)$$

In the limit of an infinitesimal lattice extension, this ratio becomes $dF/d\lambda$ and represents the volumetric stiffness associated with the volumetric frequency ω_{vol} .

Comparing the forms of eqns (24) and (25) reveals that, if f is not linear in x (*i.e.*, not harmonic), the two stiffnesses and thus the two associated frequencies, can not be, in general, proportional to each other. This is a key result! If for the sake of simplicity, however, one were to confine the pairwise interactions to an atom's nearest neighbors only, then the stiffness associated with the restoring force from the vibrational pulse, equal to $2(df/dx)_{\lambda}$, would indeed be proportional to the stiffness associated with the lattice-extension (*i.e.*, volumetric) force, equal to $(df/dx)_{\lambda}$.

With this result, permitted now is the legitimate assertion of an EOS form in which the volumetric and vibrational stiffnesses (and associated frequencies) are not proportional. In the quasi-harmonic case, for example, the relationship turns out to be

$$\omega_{\text{vol}}^2 \sim \omega [1 + \ln(\omega/\omega_0)] \quad , \quad (26)$$

as displayed in Fig. 3 by way of the associated stiffnesses. Furthermore, it can be asserted that those historical models that have assumed a proportionality between ω_{vol} and ω have done so by making an explicit or implicit assumption that either the lattice is strictly harmonic or else the lattice interactions are confined to nearest neighbor interactions only. Interestingly, Fig. 3 reveals that, for small excursions about the '0' condition where $\omega = \omega_0$, an assumed proportionality between the vibrational and volumetric frequencies is

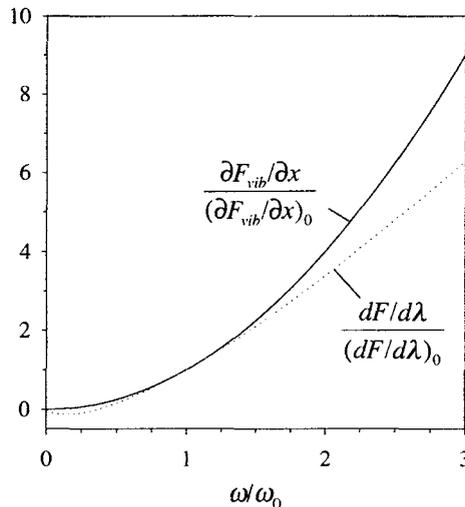


Figure 3. Comparison of vibrational and volumetric stiffnesses for quasi-harmonic potential.

a fair assumption, even for the quasi-harmonic potential where it is not strictly true.

With this understanding, the author proceeded to generalize this approach to the solution of 3-D lattices [19, 20].

Summation-form EOS

The author endeavored to pursue, for a 3-D lattice, the implications of the result in which the distinction between the volumetric and vibrational lattice stiffness was demonstrated [19, 20]. Rather than starting with a force-based analysis, as done in the preceding section to prove a point, energy was used as the starting basis, since the rules governing potential fields are clear and unambiguous.

Let the pairwise potential field between two like atoms be given, as a function of separation distance s , by $2\epsilon(s)$ such that a potential energy of magnitude ϵ may be associated with each atom of the pair. Define $\epsilon(s)$ relative to the infinite-separation condition, so that ϵ approaches zero at infinite separation. With an infinitely large number of these atoms, construct a hypothetical lattice with infinite interatomic separation, so that the lattice's potential energy is zero. Systematically bringing the atoms of this lattice together, while maintaining the relative proportions of interatomic separation, allows the lattice structure to be maintained while lowering the interatomic separation from an infinite value to an arbitrary finite value λ .

Consider one atom of this lattice as a "test atom" O , and define it at the Cartesian origin of a lattice-based coordinate system. The separation between atom O and another atom located at lattice position ijk having the coordinates $(x, y, z) = (\lambda i, \lambda j, \lambda k)$ is simply

$$s = \lambda(i^2 + j^2 + k^2)^{1/2} . \quad (27)$$

The potential energy associated with O , arising from its interactions with the rest of the lattice atoms, is given as a function of λ by

$$E_{\text{pot}}(\lambda) = \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \epsilon , \quad (28)$$

where we define $\epsilon(0) = 0$ to preclude an atom from contributing to its own potential. While eqn (28) references a simple cubic lattice for descriptive convenience, a sum involving the appropriate half-integers may be constructed to embody other lattices, such as face-centered-cubic (FCC) and body-centered-cubic (BCC) structures. E_{pot} represents the potential energy associated with atom O , in other words, the specific energy of compression, per unit atomic mass of the lattice.

In the ensuing discussion, let λ , for consistency, be defined as the *specific* lattice spacing, so that it may be set equal to the cube root of the specific volume, V . A lattice force F may be defined, consistent with the physical interpretation of pressure across a lattice face, as $F = p_c \lambda^2 = -(dE_{\text{pot}}/d\lambda)/3$. Eqn (28) may be differentiated to obtain the force as a sum of $d\epsilon/d\lambda$ terms, though the quantity $d\epsilon/d\lambda$ must be expressed via the chain rule as $d\epsilon/ds \cdot ds/d\lambda$. The first term in the chain is the negative of the pairwise force, $-f$, while the second term, obtained by differentiating eqn (27), varies proportionately to the distance of separation, in a manner wholly consistent with the discussion of the preceding section, such that

$$ds/d\lambda = s/\lambda = (i^2 + j^2 + k^2)^{1/2} . \quad (29)$$

The derivative of F with respect to λ may be taken after a similar fashion so as to obtain the volumetric stiffness of the lattice as

$$\frac{dF}{d\lambda} = \frac{1}{3} \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \frac{s^2}{\lambda^2} \cdot \frac{df}{ds} . \quad (30)$$

Note that the evaluation of eqn (30) relied on the fact that $d^2s/d\lambda^2$ is identically zero since, for a given ijk atom, s is linear with λ . Eqn (30), therefore, provides a function $dF/d\lambda$ that is proportional to ω_{vol}^2 . Using the terminology of eqn (6), $\xi = \lambda$ has been asserted here, so that $\xi_\lambda = 1$ follows directly.

In composing the vibrational stiffness, the author chose to employ one longitudinal and two transverse modes, combining them by way of $3/\omega^3 = 1/\omega_L^3 + 2/\omega_T^3$ [12]. In all cases though, the individual modes were derived from the highest frequency wave pulse, in which the stiffness resisting the pulse-displacement of a single plane of atoms was ascertained. This process is the 3-D analogy of the single-atom vibrational-pulse displacement described for the 1-D lattice in the preceding section. Note that, by considering the vibrational amplitudes as infinitesimal, the vibrational stiffness is modeled as a function of λ only; stiffness variations with vibrational amplitude are ignored (whereas a true anharmonic spring stiffness will vary as well with vibrational amplitude). This simplification is wholly consistent with a temperature-independent Grüneisen function, such that $\Gamma = \Gamma(V)$.

In the case of the longitudinal pulse, the stiffness is calculated that resists the pulsed motion of the $x = 0$ plane of atoms containing O by a displacement Δx in the $-x$ direction, allowing Δx to approach zero in the limit. In the case of the two modes involving a transverse (*i.e.*, shear) pulse, it is either the $y = 0$ or $z = 0$ plane of atoms which is vibrationally displaced by Δx in the $-x$ direction, for which the stiffness is calculated.

Again utilizing potential energy as the starting point, a vibrational restoration force may be evaluated by obtaining $\partial E_{pot}/\partial x$ as a summation of all the individual contributions of $\partial \epsilon/\partial x$. Like before, the chain rule is used to evaluate $\partial \epsilon/\partial x$ as $d\epsilon/ds \cdot \partial s/\partial x$. As in the volumetric analysis, $d\epsilon/ds$ is the negative of the pairwise force, $-f$. Whereas eqn (29), for $ds/d\lambda$, describes the motion relative to O from an incremental change in λ , $\partial s/\partial x$ in the present case describes the motion relative to O arising from the vibrational pulse of a plane of atoms containing O . It may be given as

$$\partial s/\partial x = x/s = \cos \gamma \quad (i \neq 0), \quad (31)$$

where γ is the direction cosine between the vector connecting O to the ijk position and the vector of relative atomic motion (the x -axis). Like s , the quantity γ will be unique for each ijk atom position. The $i \neq 0$ exclusion pertains to the longitudinal pulse, in particular, where the whole $i = 0$ plane of atoms is displaced and thus experiences zero displacement with respect to O . For the transverse pulses, the exclusion will be either $j \neq 0$ or $k \neq 0$ (which are actually identical cases because of lattice symmetry).

Unlike $d^2s/d\lambda^2$, which was identically zero in the calculation of the volumetric stiffness, $\partial^2 s/\partial x^2$ is not zero, since the distance from O to atom ijk does not vary linearly with the magnitude of the vibrational displacement Δx . In particular,

$$\partial^2 s / \partial x^2 = 1/s - x^2/s^3 = (\sin^2 \gamma) / s \quad (32)$$

With this knowledge, the modal vibrational stiffness $\partial F_m / \partial x$ (where m represents a particular vibrational mode), equal to $\partial^2 E / \partial x^2$ may be evaluated as

$$\frac{\partial F_m}{\partial x} = \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \left[\frac{df}{ds} \cos^2 \gamma + \frac{f}{s} \sin^2 \gamma \right], \quad (33)$$

where the $i \neq 0$ exclusion applies for the longitudinal-stiffness mode $\partial F_L / \partial x$, and the $j \neq 0$ restriction applies for the two (equal) transverse-stiffness modes $\partial F_T / \partial x$. The partial derivatives, here, connote that y and z are held constant during the x vibrational displacement.

Additionally, with γ unaffected by changes in λ , one may differentiate eqns (31) and (32) with respect to λ to obtain $d/d\lambda(\partial s / \partial x) = 0$ and

$$\frac{d}{d\lambda} \frac{\partial^2 s}{\partial x^2} = -\frac{\sin^2 \gamma}{s^2} \frac{ds}{d\lambda} = -\frac{\sin^2 \gamma}{s\lambda} \quad (34)$$

With the use of these relations, the quantities $d/d\lambda(\partial F_L / \partial x)$ and $d/d\lambda(\partial F_T / \partial x)$ may be obtained, by differentiating eqn (33), as

$$\frac{d}{d\lambda} \frac{\partial F_m}{\partial x} = \frac{1}{\lambda} \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \left[s \frac{d^2 f}{ds^2} \cos^2 \gamma + \left(\frac{df}{ds} - \frac{f}{s} \right) \sin^2 \gamma \right], \quad (35)$$

where the $i \neq 0$ restriction applies for the longitudinal ($m = L$) mode and the $j \neq 0$ restriction applies to the transverse ($m = T$) modes. Eqns (33) and (35) will be essential in the calculation of the Grüneisen function.

To this stage, the quantities E , F , $dF/d\lambda$, $\partial F_L / \partial x$, $\partial F_T / \partial x$, $d/d\lambda(\partial F_L / \partial x)$ and $d/d\lambda(\partial F_T / \partial x)$ may be obtained with the summations described. All the remaining quantities of interest are algebraically obtainable in closed form. For example, since ω_L and ω_T are proportional to the square root of the quantities $\partial F_L / \partial x$ and $\partial F_T / \partial x$ respectively, the aggregation relation $3/\omega^3 = 1/\omega_L^3 + 2/\omega_T^3$ may be cast in terms of vibrational stiffness to obtain

$$-\frac{\partial F_{\text{vib}}}{\partial x} = \left[\frac{3}{(-\partial F_L / \partial x)^{-3/2} + 2(-\partial F_T / \partial x)^{-3/2}} \right]^{2/3} \quad (36)$$

By differentiating eqn (36) with respect to λ , the following relation may be acquired, in terms of already calculated quantities:

$$\frac{d}{d\lambda} \frac{\partial F_{\text{vib}}}{\partial x} = \frac{1}{3} \left(\frac{\partial F_{\text{vib}} / \partial x}{\partial F_L / \partial x} \right)^{5/2} \frac{d}{d\lambda} \frac{\partial F_L}{\partial x} + \frac{2}{3} \left(\frac{\partial F_{\text{vib}} / \partial x}{\partial F_T / \partial x} \right)^{5/2} \frac{d}{d\lambda} \frac{\partial F_T}{\partial x} \quad (37)$$

Since the vibrational-stiffness $\partial F_{\text{vib}} / \partial x$ is proportional to ω^2 , it follows from eqn (5), (36), (37), and $V = \lambda^3$ that the Grüneisen function is obtainable as

$$\Gamma = \lambda^3 / V \psi = -\frac{\lambda}{6} \cdot \frac{d/d\lambda(\partial F_{\text{vib}} / \partial x)}{\partial F_{\text{vib}} / \partial x} \quad (38)$$

The author was able to show, for the special case of a harmonic pairwise potential, that Γ given by eqn (38) was identically zero as it should be [19]. Furthermore, one may ascertain directly from eqn (33) that, for the harmonic case where $df/ds = f/s = k_s$, the modal stiffness for the lattice is also a constant equal to $k_s n$, where n is the number of harmonic springs of stiffness k_s attached to atom O . The current model is thus seen to pass this common sense integrity test. For non-harmonic cases, a typical result is shown in Fig. 4.

A practical implementation of the method requires a specification of a pairwise potential, ε . To this end, the author opted to adapt the H02 potential of Schulte and Holzapfel [21]. Though not given as a pairwise potential, but rather expressed in (p, V) form, the H02 model can be re-expressed in force-distance rather than pressure-volume format as

$$f = -s_0 (df/ds)_0 x^{-3} (1-x) \exp[\alpha(1-x)] \quad , \quad (39)$$

where the variable x here represents s/s_0 , and the parameter α (constrained to $\alpha > 1$) governs the decay rate of the interaction. The energy potential, ε , can be obtained by integrating eqn (39) with respect to s , using either a packaged exponential-integral routine, or by way of a closed-form fit offered by the author [19, 22]. One way to picture the influence of the decay parameter α is as follows: when α is very large, the interatomic interactions decay rapidly over distance, so that the nearest neighbors' influence predominates. The larger α becomes, the closer to a nearest-neighbor paradigm the model becomes. By contrast, as α is decreased, approaching unity in the limit, the interactions decay more slowly over distance, and increasingly larger numbers of distant atoms interact in a mutual way.

In practice, the lattice summations can not be taken over an infinite lattice. As such,

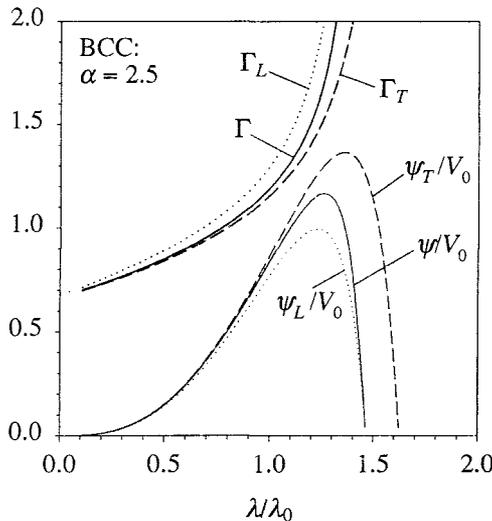


Figure 4. The ψ and corresponding Γ functions for a BCC lattice with $\alpha=2.5$, showing both L and T components as well as the aggregated function.

a suitably large radius s_{\max} is specified to guarantee convergence, so that terms are included in the summation if $s_{ijk} < s_{\max}$. Results indicate typical values for s_{\max} on the order of $8\times$ to $11\times$ the pairwise equilibrium distance s_0 , with the larger values corresponding to lower interaction-decay rates α . While the relative value of pairwise-to-lattice equilibrium spacing s_0/λ_0 was found to vary with decay parameter α and lattice structure, the trend was that, as α diminished towards its lower limit of unity, the value of s_0/λ_0 would monotonically increase significantly above unity. If one then considers such a lattice, evaluated under significant compression (*i.e.*, $\lambda_0/\lambda > 1$), the number of atoms in the summation convergence zone is observed to vary as $[(s_{\max}/s_0)(s_0/\lambda_0)(\lambda_0/\lambda)]^3$ ($\sim 4\pi/3 \cdot [10 \cdot 2 \cdot 2]^3$ for example), and represents a surprisingly large number of atoms (10^3 – 10^5) that can significantly affect the volumetric and vibrational response of the test atom O .

Other results were obtained, when exploring the parameter space of this summation-form EOS. It was observed that, while the summed lattice potential also followed, to a remarkable degree, the form of the H02 potential, a disparity was seen between the normalized lattice stiffness as compared to the corresponding pairwise stiffness. The lattice stiffness was always less than the corresponding pairwise stiffness, though the two stiffnesses approached each other as α grew large (*i.e.*, as the nearest-neighbor paradigm was approached).

As already shown with the equations, the summation results corroborate the distinction between the volumetric and vibrational stiffnesses, and thus the distinction between ω and ω_{vol} . By definition, the volumetric stiffness will experience its one and only zero at that value of $\lambda > \lambda_0$ where the lattice energy potential experiences an inflection change. The zero of the vibrational stiffness, in contrast, was always observed at a value of λ larger than that of the volumetric stiffness, regardless of lattice configuration.

Another result in the exploration of the summation EOS concerned the limiting behavior, for small λ , of Γ and Γ_{vol} , the latter needing a definition. In the manner directly analogous to eqn (5), a volumetric Grüneisen function may be defined as

$$\Gamma_{\text{vol}} = -(V/\omega_{\text{vol}}) d\omega_{\text{vol}}/dV . \quad (40)$$

As an aside, when ω_{vol}^2 is taken proportional to $d^2E/d\lambda^2$, as in the current approach, this quantity Γ_{vol} was shown [11] to exactly equal the Dugdale-MacDonald [2] definition of Γ . By contrast, the author showed [19] that the B' quantity frequently used by many authors in contemporary EOS work, equal to the pressure derivative of the bulk modulus, $B' = (\partial B/\partial p)_T$, is in fact related to the Slater [1] definition of Γ by $\Gamma_{\text{Slater}} = -1/6 + B'/2$.

Returning to the result of the summation-EOS model exploration, it was observed, with the H02 form as the pairwise potential in the summation EOS, that the lattice appears always, at large compression, to approach a limiting Γ value of $2/3$, even though the volumetric Γ_{vol} does not approach a common limit. This result was observed regardless of the decay parameter α . The same limit, however, is not produced when pairwise potential forms other than the H02 potential are tested in the model framework.

Finally, a few words are in order regarding the incompleteness of a frequency spectrum characterized by only three high-frequency modes. The hypothetical vibrational pulse utilized in this model (in which a single plane of atoms is vibrationally displaced) represents a waveform capturing only the highest frequency harmonic at which the lattice

is capable of oscillating. It is perhaps this incompleteness that is responsible for the Γ values of Fig. 4 appearing slightly lower than expected.

Another shortcoming of the current approach is the anisotropic bias of the vibrational stiffness. Because the vibrational stiffness is calculated for pulses aligned with very specific lattice-coordinate directions, the resulting stiffnesses inherently depict particular anisotropic biases, since they are not averaged over alternate lattice orientations.

These shortcomings are not debilitating, however. Historically, Einstein's specific heat work, for simplicity, actually assumed a single frequency at which the lattice oscillated. The work of Debye required the assumption of a particular vibrational spectrum. Grüneisen didn't need to assume a form on the spectrum, but required that the response of that spectrum to volumetric changes was similar for all frequencies. The assumptions of the current work place it, essentially, in this latter category. As long as the uncalculated frequencies respond to volumetric changes in a manner proportional to the response of the known mode, the calculation of the Grüneisen function, to which this work is directed, will be unaffected.

Though a more satisfying remedy was not computationally pursued [19], the author, in recognizing these shortcomings, proposed several remedies. The obvious choice to remedy the incomplete spectrum is to aggregate a characteristic frequency from additional modal components, specifically some low-frequency modes, in addition to the high-frequency components already obtained. For example, the lowest frequency response modes would arise from the stiffnesses that resist a uniaxial strain field (for the longitudinal mode) and a pure shear field (for the transverse modes).

Frequency-based EOS

There were two primary goals in developing the summation-form EOS of the preceding section. The first was to quantitatively demonstrate the distinction between the volumetric and vibrational stiffnesses in a 3-D lattice. The first goal has been amply demonstrated in the preceding chapter. The second goal was to see if a quantitative evaluation of that frequency distinction could provide ancillary support for the original EOS form derived by the author, given by eqns (16)–(19).

The pursuit of that second goal [19, 20] is the subject of this section's presentation. The approach adopted was to divide the problem into its mechanical (F) and thermal (Γ) parts, and to determine if the essence of the triple-summation EOS results of the preceding section could be captured in analytical formulations. In light of the desired goal of achieving a frequency-based EOS, fitting forms that were expressed in terms of frequency were examined.

Extremely good success was obtained with the following fit [19], over a wide range of stiffnesses (α) and lattice spacings (λ/λ_0):

$$\frac{F}{-\lambda_0(dF/d\lambda)_0} = \frac{(\omega/\omega_0)^\beta \ln(\omega/\omega_0)}{3\Gamma_0(\lambda/\lambda_0)^2} \quad (41)$$

The form, regardless of Γ_0 and parameter β , provides slope compatibility in the force at λ_0 . However, β may be selected to guarantee curvature compatibility in the lattice force, as

$$\beta = [\Gamma_{\text{vol}0} - 1/3 - 1/2 \cdot \Gamma_0(d\psi/dV)_0] / \Gamma_0 \quad (42)$$

An illustration of the quality of the eqn (41) fit is shown in Fig. 5. A larger $\alpha = 5$ value was selected for the figure to highlight the small, but noticeable, disparity between the summation form and eqn (41). As α is lowered, the quality of the fit to the summation form is improved, such that the model and fit curves become indistinguishable. All parameters in this fit are ambient-state material constants.

Turning to the thermal part of the problem, another frequency-based correlation was noted [19], that essentially relates Γ to ω :

$$\psi/\lambda^4 \sim \omega^\mu \quad , \quad (43)$$

where μ is a parameter that can be fitted for a given lattice configuration and interaction decay rate. Fig. 6 shows an example of the correlation. Invariably, μ is in the vicinity of 0.5, rising slightly for BCC lattices as α increases, and lowering slightly for FCC lattices.

Differentiating eqn (43) and dividing the result by eqn (43) itself allows for the elimination of ω , to obtain

$$\mu = 4/3 \cdot \psi/V - d\psi/dV \quad . \quad (44)$$

Eqn (44) serves two purposes. First, rather than requiring a fit of μ based on compression data, it provides the means to evaluate μ directly in terms of known material parameters, if evaluated at the V_0 state. Secondly, it allows for a more stringent test of the correlation, as it allows comparison, not of the terms of the correlation, but of their derivatives. Fig. 7 shows, for the lattice of Fig. 6, a comparison of the terms composing eqn (44). If the correlation of eqn (43) holds, then the $d\psi/dV$ curve should overlay the $4/3 \cdot \psi/V - \mu$ curve. The correlation is seen to hold over the compressive domain and only begins to diverge at larger lattice spacing, near and beyond the critical value of lattice spacing, call it λ_{stab} ,

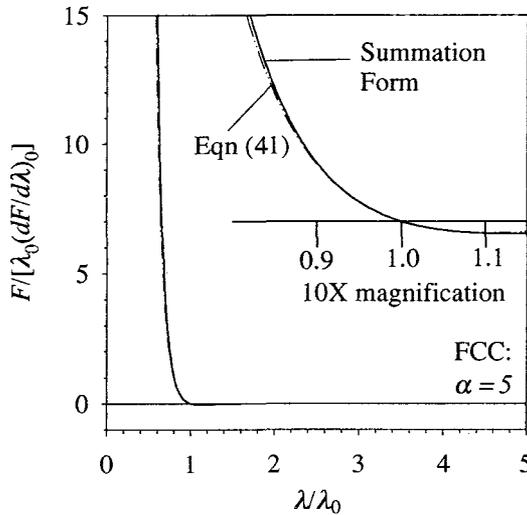


Figure 5. Comparison of summation-form EOS to eqn (41) for calculation of lattice force, F , for face-centered-cubic lattice with $\alpha = 5$.

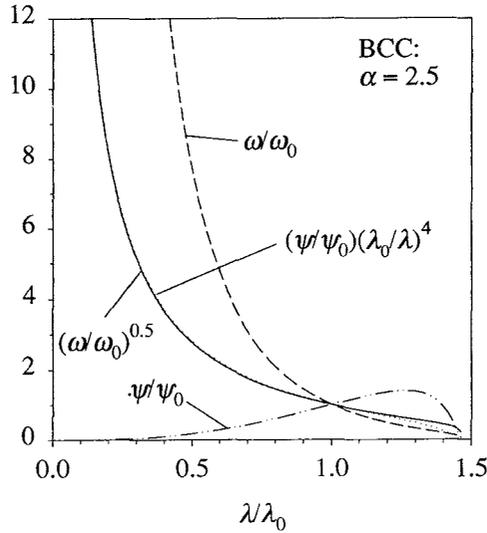


Figure 6. Correlation in summation-form EOS between ω^μ and ψ/λ^4 for body-centered-cubic lattice, with $\alpha = 2.5$ and $\mu = 0.5$.

where $d\psi/d\lambda$ changes sign. The use of eqn (44), evaluated at the V_0 state, as a means to obtain μ from extant material properties means, in terms of Fig. 7, that μ is selected such that the $d\psi/dV$ curve and the $4/3 \cdot \psi/V - \mu$ curve are forced to intersect at λ/λ_0 equal to unity. When such a technique is employed on the BCC $\alpha = 2.5$ lattice of Fig. 7, the resulting μ is not 0.5, but rather 0.538.

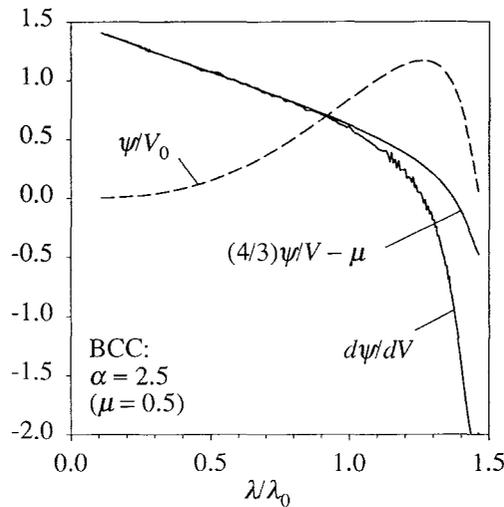


Figure 7. Comparison of terms comprising the derivative of the thermal correlation. Note that $d\psi/dV$ equals $(d\psi/d\lambda)/(3\lambda^2)$.

The differential equation, given by eqn (44), may be solved to yield the ψ (*i.e.*, the Γ) functional form corresponding to the empirical correlation form of eqn (43). It is

$$\psi/V_0 = 3\mu(V/V_0) - (3\mu - 1/\Gamma_0)(V/V_0)^{4/3} . \quad (45)$$

Eqn (45) approximates $d\psi/dV$ as linear in λ (compare with Fig. 7). As such, Γ varies as $1/(3\mu - b\lambda)$, where b is a constant. If, indeed, μ exactly equals 0.5, then the limiting high-compression value of Γ from the correlation would exactly equal 2/3, as already observed from the summation-form EOS.

Eqn (10) may be integrated, in light of eqn (45), to recover the functional form for the characteristic lattice frequency associated with the correlation form of eqn (43). The result is

$$\omega/\omega_0 = [3\Gamma_0\mu(\lambda_0/\lambda - 1) + 1]^{\mu} . \quad (46)$$

As a side note, the denoting of lattice spacing where $\psi' = 0$ by λ_{stab} makes reference back to earlier thermodynamic stability work of the author [8], in which it was shown that $\psi' > 0$ would be required to ensure that $(\partial E/\partial V)_p$ remain positive at elevated temperatures. Alternatively, $\psi' < 0$, while permitted, demands a phase change at elevated temperature, which is exactly the alternative expected for a highly expanded lattice state. A more immutable stability requirement, $\psi' > -1$, is required [7] to prevent a compressive shock from producing a net drop in pressure. Eqn (45) will always satisfy this requirement for positive ω , as long as $\mu < 1$.

The analytical fit of the mechanical behavior of the lattice, eqn (41) is a function of both frequency and lattice spacing. As such, it can not be integrated for the lattice potential without first specifying the manner in which ω is coupled to λ . However, by beginning with eqn (41) and substituting the correlation given by eqn (43) into it [in effect, multiplying by unity in the form of $(\omega/\omega_0)^\mu (\lambda/\lambda_0)^4 (\psi_0/\psi)$], one may obtain

$$\frac{3\Gamma_0^2 \cdot F}{-\lambda_0^2 (dF/d\lambda)_0} = \frac{\lambda^2}{\psi} (\omega/\omega_0)^{\mu+\beta} \ln(\omega/\omega_0) . \quad (47)$$

Recalling that F has been defined as $p_c \lambda^2$, a comparison of eqn (47) to the earlier derived eqn (17) reveals identical functional forms, with but one exception: in eqn (17), the exponent is K , whereas in eqn (47), it is $\mu + \beta$. Whereas K , evaluated by eqn (19), tended to fall in the 2/3 to 4/3 range for actual materials, values of $\mu + \beta$ tend to fall in the 4/3 to 5/3 range for the same materials. That two vastly different approaches to the same problem would yield nearly identical functional forms was both startling and reassuring.

A source of the discrepancy has already been alluded to. Namely, in the derivation of eqns (16)–(19), it had been implicitly assumed that ω would asymptote to zero only as the lattice spacing became infinite (*i.e.*, that E_c approaches E_b as ω approaches zero). Figs. 6 and 7, for example, serve to immediately discount that notion, as the rapid approach of ψ to zero (at λ equal to $1.463\lambda_0$ for the BCC lattice with α of 2.5) corresponds to a very non-asymptotic approach of ω to zero. Beyond this lattice spacing, the concept of “lattice” frequency makes no sense since, as the lattice stiffness changes sign, the restoring forces that keep the lattice intact becomes physically unstable. A highly expanded lattice beyond this point is a marginally stable academic construct that can not

exist in the real world. In the real world, the crystalline material would melt or otherwise change structure in order to reestablish a stable configuration.

If one: denotes the sum $\mu + \beta$ by κ ; employs the relation $F = p_c \lambda^2$; equivalently expresses the λ_0 lattice force gradient in terms of the bulk modulus as $-\lambda_0^2 (dF/d\lambda)_0 = 3B_0 V_0$; and references the energy zero to the equilibrium state of the lattice such that $E_c = E_{\text{pot}} + E_b$, then the lattice cold pressure may be expressed from eqn (47) and the cold energy (from the integration of $p_c \cdot dV$) as

$$p_c = \frac{B_0 V_0}{\Gamma_0^2 \psi} (\omega/\omega_0)^\kappa \ln(\omega/\omega_0) \quad , \quad (48)$$

$$E_c = -\frac{B_0 V_0}{(\Gamma_0 \kappa)^2} \{1 - (\omega/\omega_0)^\kappa [1 - \ln(\omega/\omega_0)^\kappa]\} \quad . \quad (49)$$

Lattice spacing, *per se*, has been eliminated as an independent variable! In these equations, the quantity $B_0 V_0$ may be replaced by the square of the bulk sound speed, C_0^2 , while κ , from eqns (42) and (44), is determined as

$$\kappa = [\Gamma_{\text{vol}0} + 1 - 3/2 \cdot \Gamma_0 (d\psi/dV)_0] / \Gamma_0 \quad . \quad (50)$$

The model, embodied in eqns (48) and (49), may be compared directly with the summation-form EOS. Rather than using fitted forms for ψ , such as eqns (45) and (46), the actual values for ψ and ω obtained from the summation-form EOS will be used directly in eqns (48) and (49) for the comparisons. In this manner, the accuracy of eqns (48) and (49) will be measured directly against the summation-form EOS, and not rely upon arbitrarily imposed fitting forms.

Figs. 8 and 9 show a representative comparison, for compressed and expanded states, for FCC lattices of decay parameter $\alpha = 2$ and 5, respectively. Excellent matches

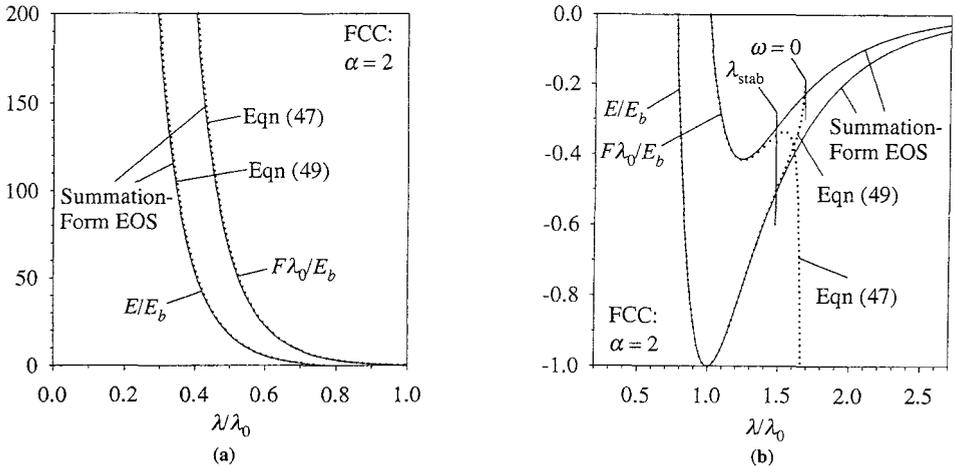


Figure 8. Comparison of lattice force and energy for the summation-form EOS and analytical forms, for an FCC lattice with $\alpha = 2$ decay parameter, (a) under compression, and (b) in expansion.

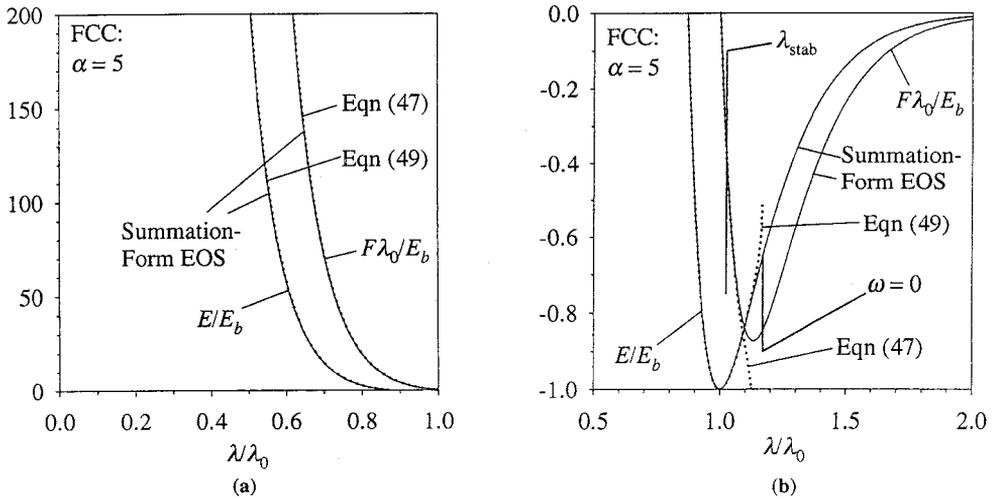


Figure 9. Comparison of lattice force and energy for the summation-form EOS and analytical forms, for an FCC lattice with $\alpha = 5$ decay parameter, (a) under compression, and (b) in expansion.

are obtained over a huge range of compression. In expansion, the match is excellent out to the value of lattice spacing denoted as λ_{stab} , corresponding to the maximum in ψ . As lattice spacing increases to the point where ω becomes zero, the analytical forms rapidly diverge from the summation-form of the EOS. Over a large practical domain of λ , however, the analytical form is indistinguishable from the summation-form EOS. This result holds for other cubic lattice structures as well (e.g., BCC).

Interestingly, the author found [19], from exploring the parameter space of the summation form EOS, that K of eqn (19) and κ of eqn (50) can, in fact, approach a common value of about 1.26, but only if the lattice interaction-decay coefficient α becomes very small (approaching unity). Since eqn (19) was predicated upon the generally false notion that ω approached zero only as the binding energy was reached (i.e., at large lattice spacing), one might infer, for those cases where K and κ are of similar magnitude, that λ_{stab} will occur at a large lattice spacing and that eqns (47) and (49) will continue to provide an excellent match to the summation-form EOS well beyond the minima in the energy and force curves. Fig. 10 validates this concept for the special case when α remains small (equal to 1.1 in this example). In this case, both λ_{stab} and $\omega = 0$ do not occur until beyond $\lambda/\lambda_0 > 7$.

Since the current modeling, in assuming the vibrational stiffness independent of vibrational amplitude, relies on $\Gamma = \Gamma(V)$, the results may be combined and cast in the Grüneisen-equation-of-state form of eqn (7). Using the cold-curve defined by eqns (48) and (49) as the reference curve gives the following equation of state [19, 20]:

$$p\psi - E = \left(\frac{C_0}{\Gamma_0 \kappa} \right)^2 \{ [(\omega/\omega_0)^\kappa - 1] + \kappa(\kappa - 1)(\omega/\omega_0)^\kappa \ln(\omega/\omega_0) \} \quad (51)$$

where κ is defined by eqn (50). If the constant κ were, instead, to take on the value K , eqn (51) would reduce identically to eqn (18), and for the reasons already discussed.

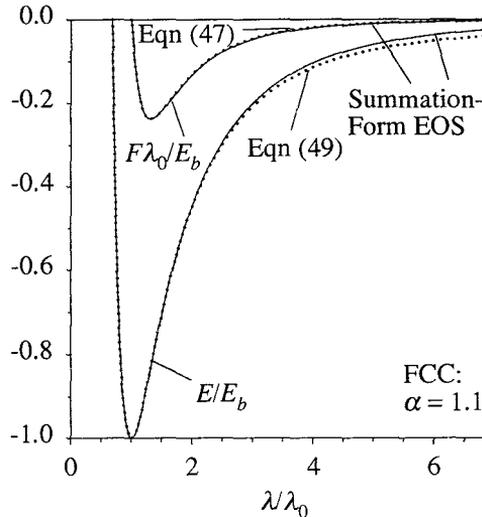


Figure 10. Comparison of lattice force and energy for the summation-form EOS and analytical forms, for an FCC lattice with $\alpha = 1.1$ decay parameter.

Comparison to data

It is desired to compare experimental data from various thermodynamic loading paths to the EOS model embodied in eqn (51). While the summation-form EOS requires only the specification of a pairwise potential in order to compute the lattice EOS, eqn (51) will require alternative data since the pairwise potential for an arbitrary crystalline solid is not known.

Since eqn (51) is not given as a function of λ or V (the variables by which experimental data are measured), the independent variable of the EOS, ω , must be related back to them to accomplish the experimental comparison. The simplest approach is to assume the validity of eqn (45), which amounts to assuming a functional form for Γ . The real behavior of ψ is undoubtedly more complicated, and one could expect an improved fit to data by customizing a fit to ψ for each given case. Nonetheless, rather than adopting a customized ψ function to “fit” compression data, the assumption of eqn (45) will provide immediate feedback as to whether the model is properly formulated.

Beyond this assumption, all required parameters are material constants which can, theoretically, be obtained from material data at the V_0 state. They include B_0 (or C_0), V_0 , Γ_0 , $\Gamma_{\text{vol}0}$, and $(d\psi/dV)_0$ [or $(d\Gamma/dV)_0$]. With these parameters, κ may be computed with eqn (50) and μ with eqn (44) [evaluated at the V_0 state as $4/(3\Gamma_0) - (d\psi/dV)_0$]. To be fair, however, it is difficult enough trying to obtain reliable material data for Γ , much less its derivative (akin to evaluating B''). Thus, the specification of $(d\psi/dV)_0$, in effect, amounts to a “fit” of the parameter μ . While the parameter $\Gamma_{\text{vol}0}$ may be estimated from B' data as $\Gamma_{\text{vol}0} = -1/2 + B_0'/2$, we choose instead to estimate it in the vicinity of $\eta/2.6$, where η is the anharmonicity parameter of Rose *et al.* [14] that appears in eqn (13), and is a measure of the curvature in the energy potential.

With all the parameters obtainable or estimable, the comparison of theory and data

may proceed. Available experimental data is generally of two varieties: cold compression and shock compression data. Cold-compression data may be compared directly with eqn (48), representing mechanical compression in the absence of significant thermal effects. The shock Hugoniot that results from shock compression, by contrast, is a function of both the mechanical and the thermal properties of the lattice. It may be obtained by eliminating E from eqn (51) by way of the Rankine-Hugoniot shock-energy relation:

$$E - E_0 = (p_0 + p)(V_0 - V)/2 \quad , \quad (52)$$

which governs the internal energy across a shock wave. For the reference Hugoniot originating from the equilibrium lattice condition, E_0 and p_0 are both zero.

The quality of the model/data match will test not only eqn (41), but also the observed correlation of eqn (43), both of which have fed into the formulation of eqns (48), (49) and, ultimately, (51). Comparisons to silver, aluminum, copper, and stainless steel are shown in Figs. 11–14, with the corresponding parameters given in Table 1.

The comparisons to both cold-compression and shock-Hugoniot data for these representative materials are very good to a number of megabars of compression.

Furthermore, the application of a more general form on ψ , as opposed to the assumed form of eqn (45), can further improve the correlation to data. The purpose, however, in retaining the simplified eqn (45) merely demonstrates the general utility of the method and approach. Further refinements, with the intent to improve correlation to data, would at this time serve only to obfuscate the simplicity of this static-atomic paradigm of lattice vibration.

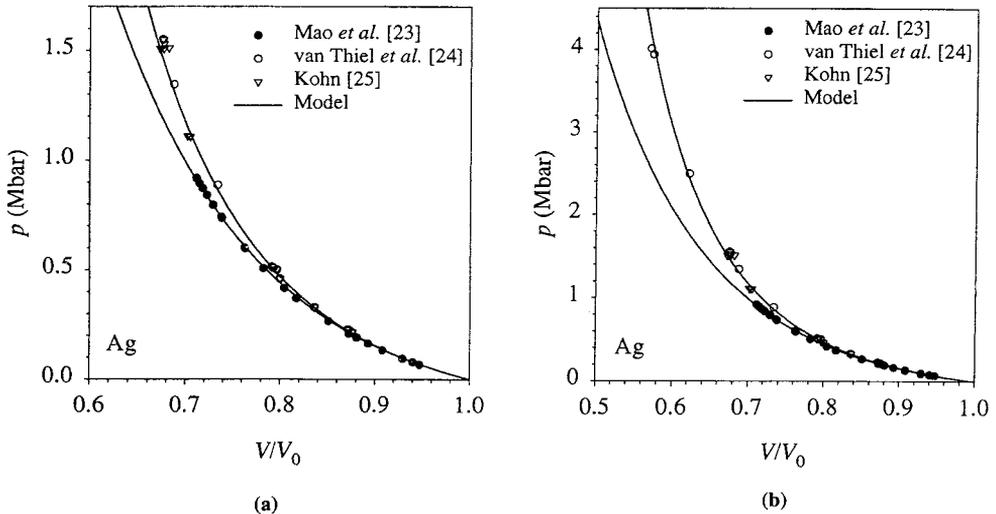


Figure 11. Cold-compression and shock-Hugoniot curves for silver (a) to 1.7 megabars; (b) to 4.5 megabars. Note that cold-compression data are filled symbols and Hugoniot data are open symbols.

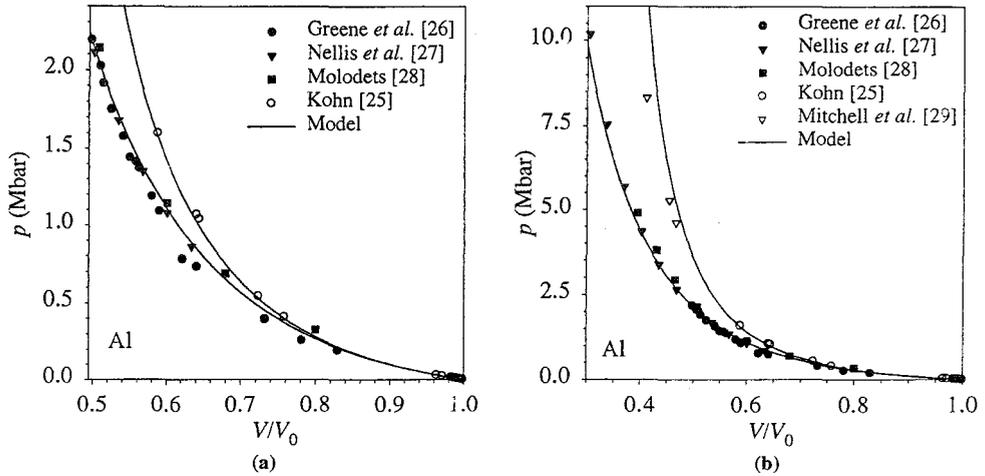


Figure 12. Cold-compression and shock-Hugoniot curves for aluminum (a) to 2.4 megabars; (b) to 11 megabars. Note that cold-compression data are filled symbols and Hugoniot data are open symbols.

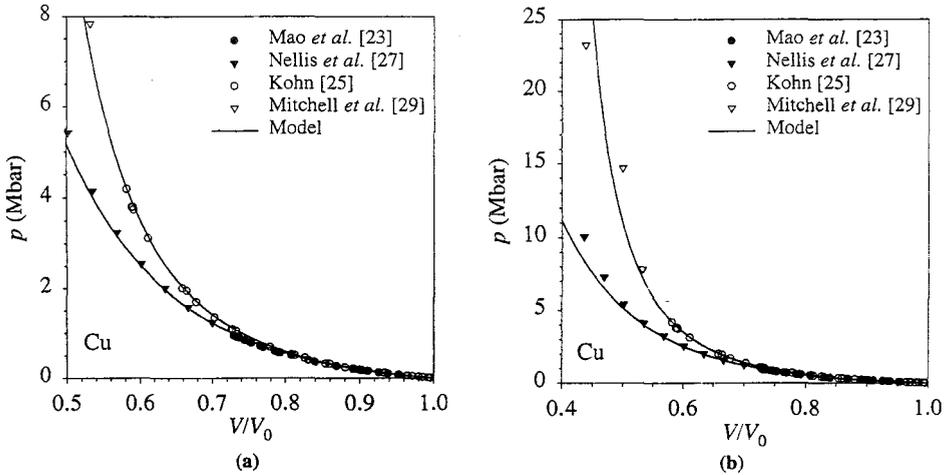


Figure 13. Cold-compression and shock-Hugoniot curves for copper (a) to 8 megabars; (b) to 25 megabars. Note that cold-compression data are filled symbols and Hugoniot data are open symbols.

Table 1. Material Parameters for Model Evaluation

	C_0 (m/s)	$1/V_0$ (kg/m ³)	Γ_0	Γ_{vol0}	$(d\psi/dV)_0$
Ag	3221	10490	2.22	2.29	0.10
Al	5189	2700	2.03	1.84	-0.06
Cu	3995	8930	2.02	2.10	0.14
St. Steel	4571	7896	1.81	2.00	0.19

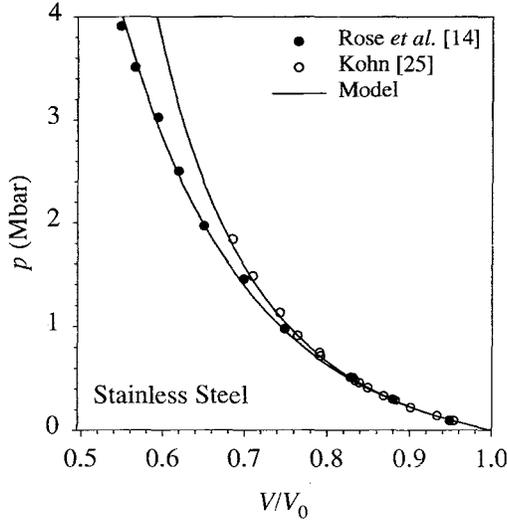


Figure 14. Cold-compression and shock-Hugoniot curves for stainless steel to 4 megabars. Note that cold-compression data are filled symbols and Hugoniot data are open symbols.

Conclusion

This article details a progression of work on classical equation-of-state methodology, that has occurred over the span of a decade. While the focus and the method of attack show significant breadth, results consistently point in a common direction. Namely, those results indicate: (a) that the mechanical and thermal components of material behavior are tightly coupled; (b) that a characteristic lattice frequency is the key thermomechanical linkage variable, fully consistent with historical work in the field; (c) that the frequency-based EOS currently offered, though derived by different means, is a natural outgrowth of the historical work of Slater [1], Dugdale and MacDonald [2] and others [3, 16]; (d) that the disparity between what the author calls “volumetric” and “vibrational” lattice stiffness arises naturally when non-nearest-neighbor interactions are accounted for; and finally, (e) that the frequency-based equation-of-state form, given by eqn (51) [and similarly by eqn (18)] can be arrived at using two completely different solution methodologies [13, 19].

The EOS of eqn (51) does not presuppose a functional form on the characteristic frequency, ω , in order to capture the behavior of the summation-form EOS. However, such a form is, to the first order, suggested by the correlation of eqn (43), noted from the application of the summation-form EOS. That correlation translates into an ω form given by eqn (46) and a corresponding model parameter κ given by eqn (50). With the use of the current EOS, eqn (51), and assuming the ω form of eqn (46), material (p - V - E) behavior is described with five measurable ambient-state material constants, as given in Table 1. Until such time, however, that the material parameter $(d\psi/dV)_0$ may be measured with greater accuracy, this parameter will remain something of a fitted constant.

Significantly, that both cold- and shock-compression data may be simultaneously fit is indicative of the general suitability of the model form. For it is impossible to vary a

model parameter to independently fit both of these curves. The model exhibits tightly coupled thermomechanical behavior, and any attempt to arbitrarily select a parameter value to fit the cold curve will alter the Grüneisen functional behavior (thus affecting the Hugoniot), and vice-versa.

The classical methods espoused in this work may seem quaint by comparison to modern quantum methods. While limited, perhaps, to EOS calculations in thermodynamic regimes where electronic effects do not exert overarching influence, the derivation of an analytical closed-form thermomechanically coupled equation of state for solids nonetheless represents an achievement of some utility.

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