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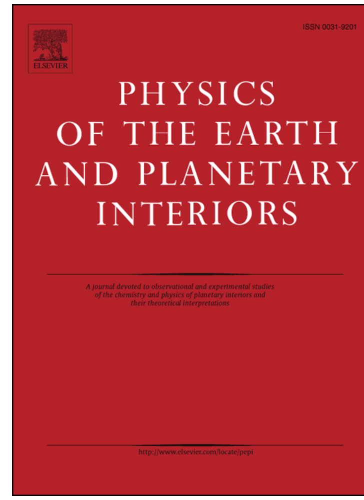

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Towards constitutive equations for the deep Earth

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Abstract

A new formulation of constitutive equations for states of high compression is introduced for isotropic media, exploiting a separation between hydrostatic and deviatoric components in strain energy. The strain energy is represented as functions of strain invariants, with one purely volumetric component and the other which vanishes for purely hydrostatic deformation. This approach preserves the form of familiar equations of state through the volumetric component, but allows the addition of volume and pressure dependence of the shear modulus from the deviatoric term. A suitable shear modulus representation to accompany a Keane equation of state is demonstrated.

Keywords: Constitutive equations, Equations of State, Bulk Modulus, Shear Modulus, Deep Earth

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1. Introduction

The pressures and temperatures in the Earth's lower mantle are already high enough that properties of materials differ substantially from the ambient state. Experimental and *ab initio* computational methods have steadily improved, so that there is now substantial information available on the behaviour of the bulk modulus (K) at large compression. Recently the shear modulus (G) has also been probed for many materials of importance in the deep Earth.

The dominant representation of material behaviour for high-pressure

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studies is the use of the Birch-Murnaghan formulation coupled with a Mie-Grüneisen-Debye treatment of thermal effects. A systematic anisotropic formulation was provided by Stixrude and Lithgow-Bertollini (2005) from which bulk and shear moduli can be readily extracted.

However, many experimental studies at high compression have favoured rather different representations of bulk modulus behaviour. Thus Sakai et al. (2016) in a study of the post-perovskite phase have preferred the Keane equation of state (EOS), having tested a range of parameterisations. Yet, except for Birch-Murnaghan, there is no corresponding development for the shear modulus.

In this study we demonstrate that it is possible to develop an isotropic formulation of the constitutive equation between stress and strain that allows the retention of familiar equations of state for the bulk modulus, whilst including shear effects via a deviatoric component. This representation enlarges the repertoire of available ways of describing material behaviour under high pressure and temperature.

2. Constitutive Equations

A constitutive equation provides a specification of the relation between the stress tensor σ and a representation of strain E. We will initially consider states solely under compression, and briefly introduce thermal effects in Section 3. We will follow the continuum mechanics approach and notation of Kennett and Bunge (2008), making a development in terms of strain energy W.

We consider a deformation from a reference state (unstressed) described by coordinates ξ to a current state described by coordinates x. The relation between the states is provided by the deformation gradient tensor $\mathsf{F} = \partial x/\partial \xi$, and $J = \det \mathsf{F} = V/V_0$ is then the ratio of a volume element in the current state (V) to that in the reference state (V_0). We also introduce the displacement gradient tensor $\mathbf{A} =$

$\mathbf{F} - \mathbf{I}$, which provides a measure of the distortion introduced by the deformation.

In terms of $\mathbf{F}$ and the Green strain $\mathbf{E} = \frac{1}{2}(\mathbf{F}^T\mathbf{F} - \mathbf{I})$, the components of the stress tensor $\boldsymbol{\sigma}$ are given by

$$J\sigma_{ij} = F_{ik}\frac{\partial W}{\partial F_{jk}} = F_{ik}F_{jl}\frac{\partial W}{\partial E_{kl}}, \tag{1}$$

where we use the Einstein summation convention of summation over repeated suffices.

The nature of the strain energy W thus determines the relationship between stress and strain. For an elastic material, W can be equated to the specific Helmholtz free energy $\mathcal{F}/\rho$, where ρ is density. In terms of specific quantities the thermodynamic relations are

$$\rho dW = -\rho S dT + \rho_0 \sigma_{ij} dA_{ij}, \tag{2}$$

in terms of the displacement gradient $\mathbf{A}$, specific entropy $\mathcal{S}$ and temperature T. The stress tensor σ_{ij} can be derived from $\mathcal{F}$ as

$$\sigma_{ij} = \frac{\rho}{\rho_0}\frac{\partial \mathcal{F}}{\partial A_{ij}} \tag{3}$$

since the volume ratio J can also be written as $J = \rho_0/\rho$.

The most complete current formulation of such a constitutive equation is that by Stixrude and Lithgow-Bertelloni (2005), based on the earlier work of Birch and Murnaghan. This employs a Taylor series expansion of the Helmholtz free energy about the reference state in terms of the Eulerian strain tensor $e = \frac{1}{2}(\mathbf{I} - [\mathbf{F}\mathbf{F}^T]^{-1})$. The volume transformation

$$\left(\frac{\rho}{\rho_0}\right)^2 = J^{-2} = \det[2\boldsymbol{e} - \mathbf{I}]. \tag{4}$$

The Helmholtz Free energy is then written as a power series in the Eulerian strain

$$\mathcal{F} = V_0 \sum_i B_i \boldsymbol{e}^i, \tag{5}$$

this Birch-Murnaghan formulation is commonly taken to 3 or 4 terms.

By examining local perturbations from a stressed state the elastic moduli K, G can be extracted. The choice of Eulerian strain markedly reduces the influence of the third-order term in strain in (5). The third-order representation does not involve any second derivatives of moduli. When coupled with a representation of thermal pressures with a Debye-Mie-Grüneisen form this provides a complete system for characterising states with moderate pressure (as in Section 3).

The disadvantage of this approach is that it essentially extrapolates from low pressure to higher pressures, depending strongly on the gradients of the moduli (K_0', G_0') in the reference state. The situation is improved if high-pressure information is available for a material, but even then differences can arise from the way in which the inversion for the set of mechanical and thermal parameters is conducted. Kennett and Jackson (2009) have demonstrated that a full nonlinear inversion can be effective, and provide both uncertainty estimates and information about cross-coupling between parameters.

2.1. Equations of State

In many situations a reduced form of the constitutive equation is employed relating volume V, pressure p and temperature T. Such *equations of state* (EOS) can only describe the behaviour of the bulk modulus (K). A number of different formulations have been used to fit experimental data on material properties at high pressure, and can be written in terms of the density ratio $x = \rho/\rho_0 = V_0/V = J^{-1}$.

The 'cold' part of equations of state provides a specification of the pressure p as a function of volume $p(V)$ or, equivalently, density ratio $p(x)$. The bulk modulus K can be extracted from the expressions for the pressure in the EOS from $K = -V(\partial p/\partial V)_T = x(\partial p/\partial x)$. A further differentiation extracts the pressure derivative $K' = (\partial K/\partial p)_T = x(\partial K/\partial p)/K$.

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The Vinet-Rydberg-Morse EOS (Vinet et al., 1987) is based on an atomic force model, with pressure represented as

$$p = 3K_0 x^{2/3}[1 - x^{-1/3}] \exp\{\tfrac{3}{2}(K_0' - 1)[1 - x^{-1/3}]\}, \tag{6}$$

where K_0 is the bulk-modulus at ambient conditions, and $K_0' = [\partial K/\partial p]_0$ is its pressure derivative. The bulk modulus as a function of the density ratio x is then

$$K = K_0 x^{2/3}\left[2 + (\zeta - 1)x^{-1/3} - \zeta x^{-2/3}\right] \exp\{\zeta[1 - x^{-1/3}]\}, \tag{7}$$

where $\zeta = \frac{3}{2}(K_0' - 1)$.

Poirier and Tarantola (1998) used a similar development to the Birch-Murnaghan approach, but employed logarithmic strain, which gives a more rapid convergence. To second order, the pressure is

$$p = K_0 x\left[\ln x + \tfrac{1}{2}(K_0' - 2)(\ln x)^2\right]. \tag{8}$$

Although originally derived using logarithmic strain, the Poirier-Tarantola EOS (8) can be recognised as simply a function of the strain invariant $x = 1/J$. The associated representation of the bulk modulus is

$$K = K_0 x\left[1 + (K_0' - 1)\ln x + \tfrac{1}{2}(K_0' - 2)(\ln x)^2\right]. \tag{9}$$

Stacey and Davis (2004) advocate the use of the Keane (1954) EOS for deep Earth studies because it links to properties at (nominal) infinite pressure:

$$p = K_0\left[\frac{K_0'}{K_\infty'^2}[x^{K_\infty'} - 1] - \left(\frac{K_0'}{K_\infty'} - 1\right)\ln x\right]. \tag{10}$$

Thermodynamic arguments suggest a lower bound on K_∞' of 5/3. The Keane EOS can be regarded as an interpolant rather than just an extrapolant, though the high pressure limit enters as a parameter in fitting. The Keane representation of the bulk modulus has a rather simple form,

$$K = K_0\left[1 + \frac{K_0'}{K_\infty'}\left(x^{K_\infty'} - 1\right)\right]. \tag{11}$$

Each EOS should be regarded as a parametric representation of behaviour, and thus when different expressions are used to fit the same experimental data the values obtained for K_0, K_0' will be similar but not identical (see, e.g., Sakai et al. 2016).

None of these equations of state have any associated shear moduli. Further, unlike the Birch-Murnaghan expansion, none has any obvious extensions to tensor form that would allow extraction of shear properties.

2.2. Isotropic Constitutive Equations

If we concentrate attention on just the bulk modulus (K) and shear modulus (G) we can describe behaviour in terms of isotropic constitutive equations. The important materials in the deep Earth, e.g. bridgmanite and ferro-periclase, are intrinsically anisotropic at the crystal level. Nevertheless, the properties of aggregates can be adequately described in isotropic terms, as is commonly used.

For an isotropic medium, the strain energy W can be represented as a function of invariants of the strain measures (Spencer, 1980). An extensive development has been made for large deformation in rubber-like materials in tension, whereas we need results for strong compression.

The deformation gradient $\mathbf{F}$ can be written in terms of a stretching component and a rotation in two ways

$$\mathbf{F} = \mathbf{R}\mathbf{U} = \mathbf{V}\mathbf{R} \tag{12}$$

where $\mathbf{U}^2 = \mathbf{F}^T\mathbf{F}$ and $\mathbf{V}^2 = \mathbf{F}\mathbf{F}^T$. $\mathbf{U}$, $\mathbf{V}$ have the same eigenvalues, the principal stretches $\lambda_1, \lambda_2, \lambda_3$, but the principal axes vary in orientation by the rotation $\mathbf{R}$. The useful invariants of $\mathbf{U}$, $\mathbf{V}$ are

$$J^2 = \lambda_1^2\lambda_2^2\lambda_3^2 = \det \mathbf{U}^2, \tag{13}$$

a purely hydrostatic term, representing changes in volume, and

$$L = J^{-2/3}[\lambda_1^2 + \lambda_2^2 + \lambda_3^2] = J^{-2/3}\mathrm{tr}\,\mathbf{\Lambda}^2 = J^{-2/3}\mathrm{tr}\,\mathbf{U}^2. \tag{14}$$

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which concentrates on the deviatoric aspects of deformation.

In such an isotropic medium the principal axes of the stress tensor $\boldsymbol{\sigma}$ align with those of V (the Eulerian triad), whereas the principal axes of U and E are rotated by R (the Lagrangian triad). In terms of the principal stretches we can recast (1) in the form of an expression for the rth principal stress

$$\sigma_r = \frac{1}{J}\lambda_r \frac{\partial W}{\partial \lambda_r}, \qquad \text{no sum on } r, \tag{15}$$

whilst recognising the rotation between the principal directions of the elements on the left- and right-hand sides of the equation (15).

Now consider a strain energy function W as a function of the stretch invariants J, L with two independent volume terms $\Phi(J)$ and $\Psi(J)$:

$$W = \Phi(J) + \{L - 3\}\Psi(J); \tag{16}$$

incorporating a direct volume dependence in $\Phi(J)$ and a deviatoric component in the second term. For *purely hydrostatic compression* $\lambda_1 = \lambda_2 = \lambda_3 = \bar{\lambda}$, $J = \bar{\lambda}^3$ and $\{L - 3\} = \bar{\lambda}^{-2} 3\bar{\lambda}^2 - 3 = 0$, so that the deviatoric term $\{L - 3\}\Psi(J) = 0$.

As detailed in Appendix A1, the rth principal stress derived from the strain energy form (16) is

$$\sigma_r = \frac{\partial \Phi}{\partial J} + \frac{2}{J^{5/3}}\left[\lambda_r^2 - \tfrac{1}{3}\mathrm{tr}\,\boldsymbol{\Lambda}^2\right]\Psi(J) + \{L - 3\}\frac{\partial \Psi}{\partial J}. \tag{17}$$

For a hydrostatic state, when $L - 3 = 0$, the dependence on $\Psi(J)$ vanishes and so

$$\sigma_r = -p = \frac{\partial \Phi}{\partial J}, \tag{18}$$

i.e., isotropic stress independent of the form of $\Psi(J)$. Each of the equation of state expressions in (6), (8) and (10) correspond to a specification of $\partial\Phi/\partial J$, even though the original derivations did not explicitly use the strain invariant.

The full stress tensor

$$\boldsymbol{\sigma} = \mathsf{R}\left\{\left(\frac{\partial \Phi}{\partial J} + \{L - 3\}\frac{\partial \Psi}{\partial J}\right)\mathbf{I} + \frac{2}{J^{5/3}}\left[\mathsf{U}^2 - \tfrac{1}{3}\mathrm{tr}(\mathsf{U}^2)\mathbf{I}\right]\Psi(J)\right\}\mathsf{R}^{\mathsf{T}}, \tag{19}$$

with strong simplification in the hydrostatic case when $\{L-3\}=0$ and the term in Ψ vanishes to:

$$-p\mathbf{I}=\frac{\partial\Phi}{\partial J}\mathbf{I}. \tag{20}$$

The representation (16) with a separation of hydrostatic and deviatoric parts was suggested by neo-Hookean equations for rubbers, but now includes a volume (density) modulation of $\{L-3\}$ through $\Psi(J)$ to allow for strong compression.

The elastic moduli as a function of density (and hence pressure) can be extracted from the stress tensor in the form (19) by making a first order expansion about a hydrostatic compressed state with $\lambda_r=\bar{\lambda}(1+e_r)$. Then, e.g., $J=\bar{\lambda}^3(1+\mathrm{tr}\{\boldsymbol{e}\})+O(e^2)$.

The details of the first order expansion about the hydrostatic state are presented in Appendix A2. The rth principal stress in terms of $\boldsymbol{e}$ reduces to:

$$\sigma_r=-p+J\frac{\partial^2\Phi}{\partial J^2}\mathrm{tr}\{\boldsymbol{e}\}+\frac{2}{J}\Psi(J)[e_r-\tfrac{1}{3}\mathrm{tr}\{\boldsymbol{e}\}]. \tag{21}$$

We can recognise the elastic moduli by comparison with the standard form for isotropic media

$$\sigma_r=-p+K\mathrm{tr}\{\boldsymbol{e}\}+G[e_r-\tfrac{1}{3}\mathrm{tr}\{\boldsymbol{e}\}] \tag{22}$$

so that we have:

$$\begin{aligned}&\text{Bulk Modulus} && K=J\partial^2\Phi(J)/\partial J^2,\\ &\text{Shear Modulus} && G=2\Psi(J)/J.\end{aligned} \tag{23}$$

We have thus demonstrated that it is possible to retain existing EOS representations of the bulk modulus K with a suitable specification of $\Phi(J)$, but to attach shear dependence through a new function of volume (density) $\Psi(J)$. In terms of the density ratio x the shear modulus G and shear wavespeed β take the form:

$$G=\frac{2}{J}\Psi(J)=2x\Psi(x), \qquad \beta^2=\frac{G}{\rho}=2\rho_0\Psi(x). \tag{24}$$

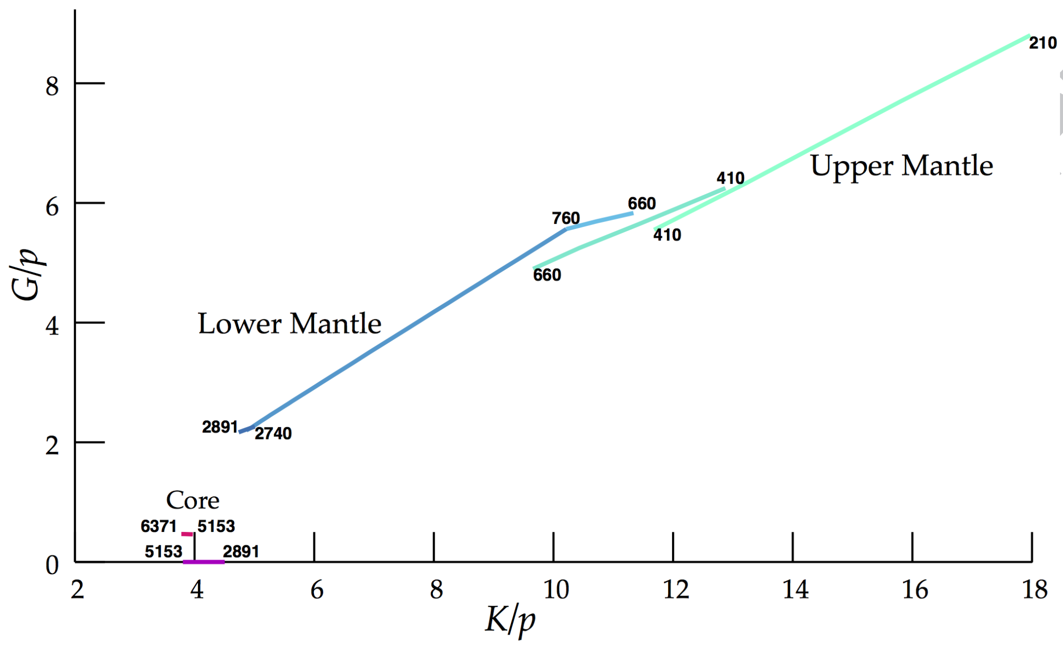

Figure 1: Multiple linear segments for the relation between G/p and K/p for different parts of the *ak135* Earth model (Kennett et al., 1995). The depths for each segment are indicated. Multiple depths indicate the presence of major discontinuities.

It is thus possible to capture the volume dependence of the shear modulus in a simple form. But, since the pressure equation relates only to K, the pressure derivative G' will be coupled to K, K'.

2.3. Building constitutive equations

The treatment of Section 2.2 demonstrates that we can specify pressure and bulk modulus behaviour as a function of compression through a strain energy contribution $\Phi(J)$, with the description of the shear modulus to be assigned through a separate function $\Psi(J)$.

The group of equations of state considered in Section 2.1 already provide different representations of pressure and bulk modulus, and can thus be used directly. But, how then should we link in shear properties?

For current Earth Models, empirical relations of the form

$$G = aK - bp, \tag{25}$$

provide good piecewise fits to segments of radial Earth structure (Figure 1), such as the entire lower mantle. Different coefficients a, b describe the behaviour of the various segments, indicated by different tones in Figure 1. At major discontinuities such as the '410 km' and '660 km' discontinuities or the inner-core boundary, the moduli K, G show discontinuous increases with depth at constant pressure so that segments can overlap.

The empirical relation (25) suggests that we should seek functional forms for the representation of $G(x)$ that incorporate the dependencies on density ratio of both bulk modulus and pressure for any particular equation of state. Thus the functional form of $\Psi(J)$ combines elements from $\Phi'(J)$, $\Phi''(J)$.

Although the Vinet-Rydberg-Morse equation of state is frequently effective in representing bulk modulus behaviour, it is based on a central potential model that does not readily relate to shear. We therefore demonstrate how a shear counterpart to the Keane EOS can be constructed. We combine the suite of functional dependencies from (10) and (11) to suggest a representation

$$G(x) = G_0 \left(A \ln x + B x^{K'_\infty} + (1 - B) \right), \tag{26}$$

with pressure derivative

$$G'(x) = \frac{\partial G}{\partial p} = \frac{x}{K}\frac{\partial G}{\partial x} = \frac{G_0}{K(x)} \left(A + B K'_\infty x^{K'_\infty} \right), \tag{27}$$

where $K(x)$ is given by (11). The constant A is unconstrained by the initial condition on the modulus, but can be extracted from G'_0 as

$$A = G'_0 \left(\frac{K_0}{G_0} \right) - B K'_\infty. \tag{28}$$

The expression for the shear modulus is thus strongly linked to that of the bulk modulus, but has three independent parameters G_0, G'_0 and B. In a similar way

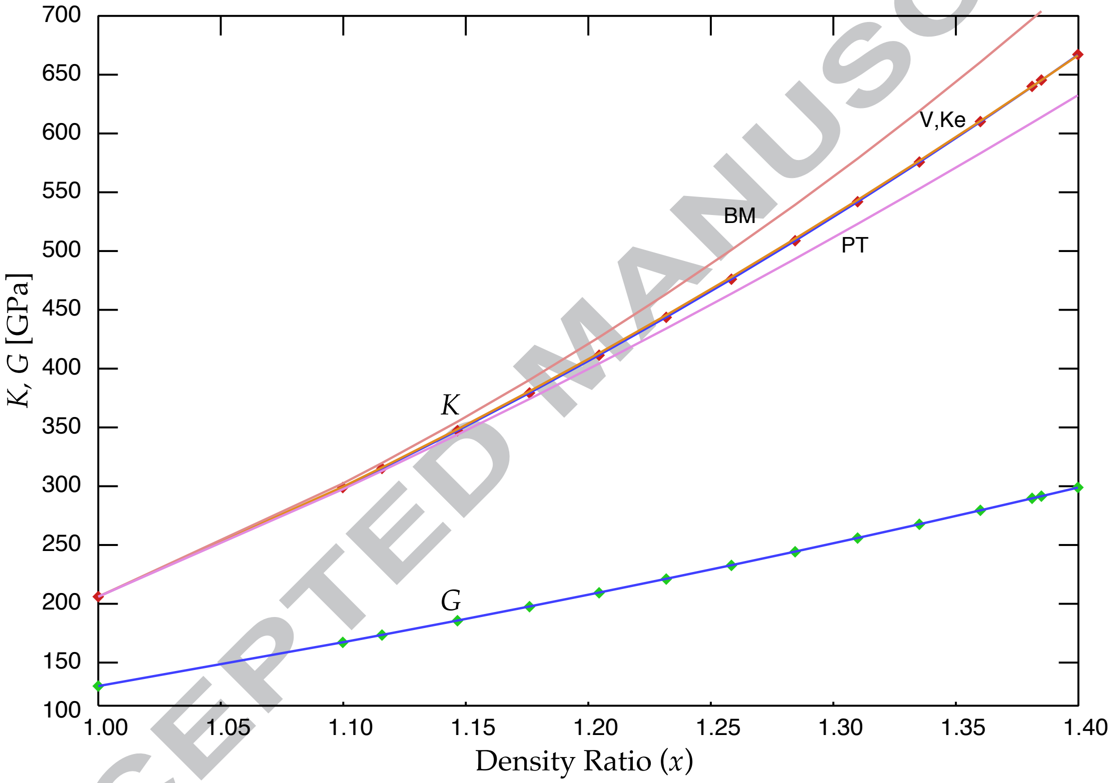

Figure 2: Bulk and shear modulus for the lower mantle as a function of the density ratio x, with EOS fits using the same values of K_0, K'_0 and a fit to the shear modulus using (26). BM: Birch-Murnaghan; PT: Poirier-Tarantola; V: Vinet-Rydberg-Morse, Ke, Keane.

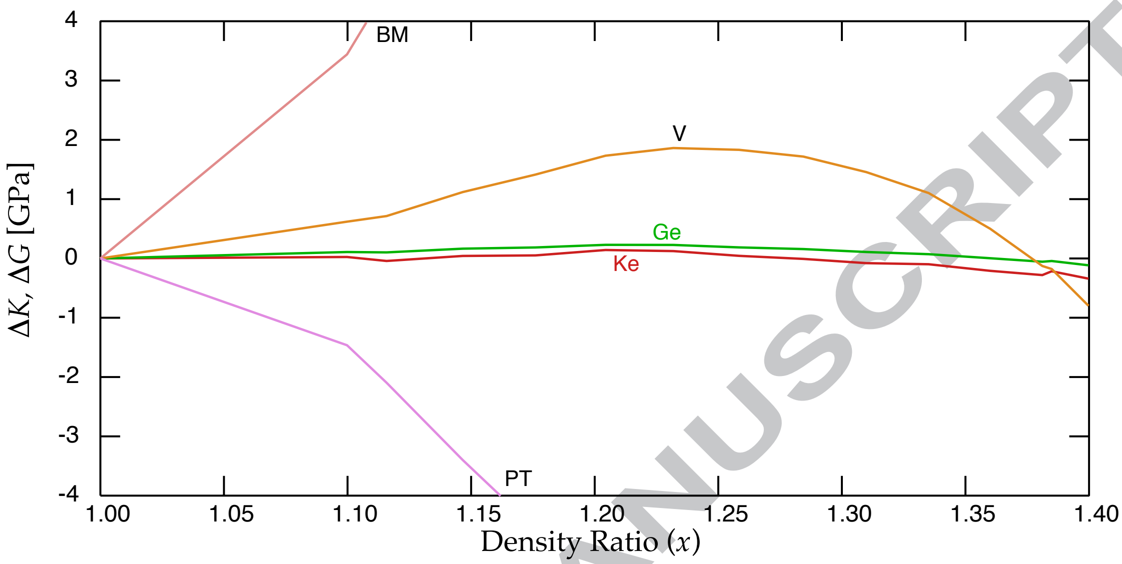

Figure 3: Deviations of fits to Bulk and shear modulus for the lower mantle as a function of the density ratio x. BM: Birch-Murnaghan; PT: Poirier-Tarantola; V: Vinet-Rydberg-Morse, Ke, Keane; Ge: fit to the shear modulus using (26).

to the three parameter fit for the bulk modulus (K_0, K_0', K_∞') this triad of shear parameters provides considerable flexibility in fitting data.

The differences between the various styles of representation of dependence on compression x only become evident for conditions corresponding to the lower mantle and deeper. We use the K, G values from Table 1 of Stacey and Davis (2004), ignoring temperature effects, as a sample with a wide span of density ratios (Figure 2). We compare the suite of equations of state with the same nominal K_0 value (206.06) and K_0' (4.2), and show how we can use the shear equation (26), linked to the Keane EOS, to fit the G distribution.

For density ratios up to 1.10 there is essentially no difference in the values from the third-order Birch-Murnaghan form or any of the other EOS. As compression increase the results diverge. The Vinet-Rydberg-Morse and Keane results fit the data points well, but the Birch-Murnaghan and Poirier-Trantola forms deviate significantly for larger x. In each case, adjustment of the values of K_0' can improve the fit, though not over the full range of compression.

The Vinet-Rydberg-Morse results provide a good two-parameter fit to the specified $K(x)$ values with deviations less than 2 GPa (~0.4%), as can be seen in Figure 3 that compares the deviations from the specified values. The three-parameter fit with the Keane EOS (K_∞' = 2.575) is even better (<0.05%). With this same set of specified K_0, K_0', and K_∞', the shear representation (26) is readily tuned to match the $G(x)$ exceptionally well (G_0=130.02, G_0'=1.745, B = 0.72), as can be seen in Figure 3.

This example demonstrates that linked bulk and shear modulus representations can be satisfactorily developed exploiting the functional dependencies suggested by the empirical relation (25). The need is strongest for high compression, and shear information is beginning to become available in this regime as experimental techniques improve.

3. Mie-Grüneisen-Debye thermal contribution

In order to construct a full constitutive equation we need to include thermal effects as well as those associated with deformation. This can readily be done by including an additional contribution to the specific Helmholtz Free Energy:

$$\mathcal{F}(V,T) = \mathcal{F}_C(V,0) + \mathcal{F}_D(V,T), \tag{29}$$

combining a 'cold' part $\mathcal{F}_C(V,0)$ and a 'warm' part $\mathcal{F}_D(V,T)$ as in Stixrude and Lithgow-Bertelloni (2005). Then the contributions to the *elastic moduli* can be thought of in terms of trajectories in an $M,\ T,\ p$ space (Figure 4).

The contribution from lattice vibrations can be well represented by the Debye form

$$E_D(T) = 9nRT\left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} d\xi \frac{\xi^3}{\exp(\xi)-1}, \tag{30}$$

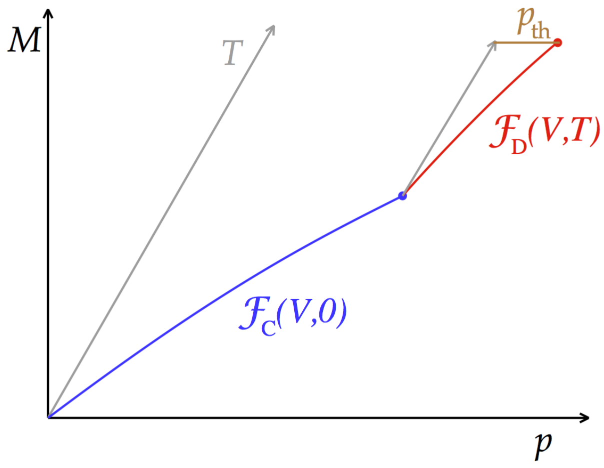

Figure 4: Inclusion of thermal stress as an additional component in M, T, p space.

where n is the number of atoms in the unit cell, R is the gas constant. This simple form is effective since the net thermal effect is not sensitive to the details of the electron distribution (Stixrude and Lithgow-Bertelloni, 2005). The lattice vibrations add an additional thermal component to the pressure

$$p(V,T) = p_C(V,0) + \frac{\gamma_D}{V} E_D(V,T) \tag{31}$$

where γ_D is the Grüneisen parameter.

The temperature dependence of pressure is given by

$$\left[\frac{\partial p}{\partial T}\right]_V = \alpha K_T(V,T) = \gamma_D \frac{C_V}{V} \tag{32}$$

in terms of the isothermal bulk modulus $K_T = -V[\partial p/\partial V]_T$ and the thermal expansion coefficient $\alpha = (1/V)(\partial V/\partial T)_P$. The other thermal parameters are based on the quasi-harmonic approximation

$$\gamma = -\frac{d \ln \nu}{d \ln V} = \gamma_D, \qquad q = \frac{d \ln \gamma}{d \ln V}. \tag{33}$$

with also η_s as the shear strain derivative of the Grüneisen parameter γ. The adiabatic bulk modulus K_S is then given by

$$K_S = K_T(1 + \alpha\gamma T), \qquad \left[\frac{\partial p}{\partial T}\right]_S = \frac{K_S}{\gamma T}, \tag{34}$$

Stixrude and Lithgow-Bertelloni (2005) provide convenient forms for the strain dependence of the Grüneisen parameter γ and η_s. Alternative representations such as that due to Al'tshuler et al (1987) can also be employed.

4. Discussion and Conclusions

By casting the strain energy function W for an isotropic medium as a function of strain invariants in a form that allows complete separation between hydrostatic and deviatoric components, we have been able to retain familiar forms for equations of state with the addition of a full description of shear. The functional form of the shear modulus as a function of volume does not depend on the bulk modulus, but the representations are coupled through pressure dependence and pressure derivatives.

The current approach thus provides a functional alternative to the use of the Birch-Murnaghan finite-strain formulation for shear, with considerable flexibility available in the description of shear behaviour. Further we do not need to impose adiabatic corrections to the shear modulus. The linear dependence between K/p and G/p for current Earth models, suggests that the elements included in the volume dependence of the shear modulus should be similar to those used for the bulk modulus and pressure. We have shown that a shear counterpart to the Keane EOS can be constructed exploiting these dependencies, exploiting the constraints from bulk-modulus fitting. There are no shear analogues of the thermodynamic constraints on the properties of the bulk modulus at extreme compression.

For many materials the range of conditions accessible to experiment is still limited, and so properties at high compression will commonly require extrapolation. It is just in this high compression regime that, as noted by Poirier and Tarantola (1998), the differences in constitutive relations become important (Figures 2, 3). By bringing in constraints from very high pressures the problem is converted to a more suitable interpolation, even though this also involves parameter fitting. With the addition of linked shear representations we can expect to improve the description of very high pressure phases, and hopefully understand the complex variations of shear wavespeed in seismic images of the lowermost mantle.

The approach we have employed to link in a shear component to the constitutive equation is specific to the isotropic situation, and there is no immediate generalisation to the fully anisotropic case. Yet, the functional form of the constitutive equation (19) suggests that there may be merit in seeking anisotropic tensor forms in which stress depends on multiple measures of strain

such as those proposed by Hill (1968). The family of Seth-Hill tensors have the same first order expansion, but different dependence on finite strain that may be exploited to produce suitable general constitutive relations.

Appendix A. Appendix: mathematical derivations

Appendix A.1. Principal stress relations

For the strain energy

$$W = \Phi(J) + \{L-3\}\Psi(J), \text{ with } \{L-3\} = \left\{ \frac{1}{J^{-2/3}}(\lambda_1^2+\lambda_2^2+\lambda_3^2) - 3 \right\}, \quad \text{(A.1)}$$

the σ_r principal stress takes the form

$$\sigma_r = \frac{1}{J}\lambda_r \frac{\partial W}{\partial \lambda_r} = \frac{\lambda_r}{J}\frac{\partial J}{\partial \lambda_r}\frac{\partial \Phi}{\partial J} + \frac{\lambda_r}{J}\left[\frac{\partial}{\partial \lambda_r}\{L-3\}\Psi(J) + \{L-3\}\frac{\partial J}{\partial \lambda_r}\frac{\partial \Psi}{\partial J}\right]. \quad \text{(A.2)}$$

Now

$$\begin{aligned} \frac{\lambda_r}{J}\frac{\partial J}{\partial \lambda_r} &= 1, && \text{(A.3)} \\ \frac{\lambda_r}{J}\frac{\partial}{\partial \lambda_r}\{L-3\} &= \frac{1}{2J^{-2/3}}\left(2\lambda_r^2 - \tfrac{2}{3}(\lambda_1^2+\lambda_2^2+\lambda_3^2)\right). && \text{(A.4)} \end{aligned}$$

Thus the σ_r principal stress takes the form

$$\sigma_r = \frac{\partial \Phi}{\partial J} + \frac{2}{J^{-5/3}}\left[\lambda_r^2 - \tfrac{1}{3}\mathrm{tr}\boldsymbol{\Lambda}^2\right] + \{L-3\}\frac{\partial \Psi}{\partial J}. \tag{A.5}$$

For an isotropic medium the principal stress align with the Eulerian triad, and the principal stretches with the Eulerian triad so that the full stress tensor takes the form

$$\boldsymbol{\sigma} = \mathbf{R}\left\{\left(\frac{\partial \Phi}{\partial J} + \{L-3\}\frac{\partial \Psi}{\partial J}\right)\mathbf{I} + \frac{2}{J^{5/3}}\left[\mathbf{U}^2 - \tfrac{1}{3}\mathrm{tr}(\mathbf{U}^2)\mathbf{I}\right]\Psi(J)\right\}\mathbf{R}^T, \tag{A.6}$$

with rotation by $\mathbf{R}$.

For a hydrostatic deformation the stretches are equal, $\lambda_1 = \lambda_2 = \lambda_3 = \bar{\lambda}$ and so $J = \bar{\lambda}^3$, $\lambda_1^2 - \frac{1}{3}\mathrm{tr}\boldsymbol{\Lambda}^2 = 0$ and $L - 3 = 0$. The isotropic stress then reduces to

$$-p\mathbf{I} = \frac{\partial \Phi}{\partial J}\mathbf{I} \tag{A.7}$$

in terms of pressure p.

Appendix A.2. Derivation of moduli

Consider making a first order perturbation about a hydrostatic compressed state with $\lambda_r = \bar{\lambda}(1 + e_r)$, so that $J = \bar{\lambda}^3(1 + \mathrm{tr}\{\boldsymbol{e}\}) + O(e^2)$. Then the σ_r principal stress from (A.4) takes the form

$$\begin{aligned}\sigma_r \;=\; & \frac{\partial \Phi}{\partial J} + \mathrm{tr}\{e\}J\frac{\partial^2 \Phi}{\partial J^2} + \frac{2\bar{\lambda}^2}{J^{5/3}}\left(e_r - \tfrac{1}{3}\mathrm{tr}\{\boldsymbol{e}\}\right)\Psi(J) \\ & + \frac{2}{J^{5/3}}\left[\lambda_r^2 - \tfrac{1}{3}\mathrm{tr}\boldsymbol{\Lambda}^2\right]\Psi(J) + \frac{2}{J^{5/3}}\left[\lambda_r^2 - \tfrac{1}{3}\mathrm{tr}\boldsymbol{\Lambda}^2\right]\mathrm{tr}\{\boldsymbol{e}\}\,J\frac{\partial \Psi}{\partial J} \\ & + [L-3]\left\{\frac{\partial \Psi}{\partial J} + \mathrm{tr}\{\boldsymbol{e}\}\,J\frac{\partial^2 \Psi}{\partial J^2}\right\} + \frac{\bar{\lambda}^2}{J^{2/3}}\left[3 + 2\mathrm{tr}\{\boldsymbol{e}\} - 3 - 2\mathrm{tr}\{\boldsymbol{e}\}\right]\frac{\partial \Psi}{\partial J}.\end{aligned} \tag{A.8}$$

For the hydrostatic base state all the terms in square brackets in the last two lines of (A.8) vanish, and so (A.8) reduces to

$$\sigma_1 = -p + J\frac{\partial^2 \Phi}{\partial J^2}\mathrm{tr}\{e\} + \frac{2}{J}\Psi(J)\left(e_1 - \tfrac{1}{3}\mathrm{tr}\{\boldsymbol{e}\}\right), \tag{A.9}$$

since $-p = \partial\Phi/\partial J$, and $\bar{\lambda}^2 = J^{2/3}$.

The representation of the principal stress in terms of the bulk modulus K and shear modulus G is

$$\sigma_r = -p + K\mathrm{tr}\{\boldsymbol{e}\} + G\left(e_r - \tfrac{1}{3}\mathrm{tr}\{\boldsymbol{e}\}\right), \tag{A.10}$$

and thus we identify

$$K = J\frac{\partial^2\Phi(J)}{\partial J^2}, \qquad G = \frac{2}{J}\Psi(J). \tag{A.11}$$

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Highlights

- New formulation of constitutive equations for deep Earth studies
- Separation of hydrostatic and deviatoric components
- Allows use of existing equations of state but with a shear modulus attached.