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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.

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 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 $\boldsymbol{\sigma}$ and a representation of strain $\mathbf{E}$. 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 $\boldsymbol{\xi}$ to a current state described by coordinates $\mathbf{x}$. The relation between the states is provided by the deformation gradient tensor $\mathbf{F} = \partial \mathbf{x}/\partial \boldsymbol{\xi}$, and $J = \det \mathbf{F} = V/V_0$ 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

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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

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

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

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

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 $K' = (\partial K/\partial p)_T = x(\partial K/\partial p)/K$.

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

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

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

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

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

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

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

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