ELASTIC BEHAVIOUR OF MATTER UNDER VERY HIGH PRESSURES

Uniform Compression

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Received April 21, 1960

1. INTRODUCTION

THE elastic behaviour of substances, which are already in a highly strained state, is a subject of considerable importance, in its fundamental aspects as well as in its application to important questions like the constitution and stability of massive entities such as exist in the interior of the Earth. In a paper entitled 'Elasticity and Constitution of the Earth's Interior,' Birch (1952) has given a comprehensive account of this problem. Matter in the interior of the Earth is subjected to large stresses, resulting in an accumulation of great amounts of strain energy. It is known that periodical releases of the strain energy, thus accumulated, manifest themselves as earthquakes in various regions, although the exact causes thereof and the detailed mechanism of these energy releases, are still matters open for further study. It is also known that shear waves are not sustainable in the interior of the Earth below a depth of about 3,000 km., while up to that depth from the surface, compressional as well as shear waves are present. An explanation of these remarkable phenomena would necessarily involve a knowledge of the elastic behaviour of matter at the depths in question. Thus, the first step in this direction would be the evaluation of the elastic constants of substances, which are already under great strains, in terms of known parameters.

When considering such large strains, one has to have recourse to the finite or non-linear theory of elasticity, an exact development of which in matrix form has been given by Murnaghan (1951). When the strain components are large, the stress at a point is no longer a linear function of the strain components at that point, but includes quadratic terms as well, and the strain energy function ϕ has to be extended to include at least the cubic powers of the strain components. The coefficients of the quadratic terms have been called 'the Second Order Elastic Constants' and of the cubic terms, 'the Third Order Elastic Constants'. Birch (1947, 1952), Fumi

(1951), Hearmon (1953) and Bhagavantam (1949, 1957) have dealt with this problem and have derived the independent third order constants for the various crystal classes. In the present work, a reference to these investigations will become necessary as the strain energy includes second as well as third order elastic constants.

In studying the elastic response of a substance which is initially subjected to a finite strain, additional strains can always be visualized as infinitesimal in character, since the case of a finite strain superposed over another finite strain can be reanalyzed so as to correspond to an infinitesimal strain imposed on a finite one. As this additional strain is infinitesimal, its effect in the strain energy function will be limited to quadratic terms only, the coeffiicients of which will be the elastic constants appropriate to the substance in the prestressed state. We shall designate these as the 'effective elastic constants'. They completely specify the elastic response of a substance in a state of finite strain, when additional infinitesimal strains are superposed thereon. These effective constants will depend on the second and third order elastic constants of a stress-free state and also upon the state of initial stress.

Expressions for such effective elastic constants can be derived by noting that the elastic energy of the infinitesimal deformation must be equal, after multiplication by a suitable magnification factor and allowing for the work done by the external forces, to the difference in the total energy of the system when subjected, firstly to the finite strain, and secondly to the finite *plus* infinitesimal strain considered as a single composite state of strain. The magnification factor arises because the strain energy always refers to a unit initial volume and this volume is different according as whether we choose our initial state as the stress-free state or as a state of finite initial stress. It will be observed from the details given in the following that this method of evaluating the elastic constants from the use of the energy difference, adopted in the present paper, is much simpler than the method of evaluating them from the Stress Matrix—a procedure adopted by some earlier workers (Birch, 1947; Hughes and Kelly, 1953). There is a discrepancy between the values obtained by us in this paper and by Birch (1947) and a discussion of the same is also given.

It has to be mentioned here that Green and Zerna (1954) have considered the question of superposition of an infinitesimal deformation over a triaxial finite strain for an isotropic substance but their treatment does not explicitly bring in the third order elastic constants. We have explicitly considered these constants and studied in detail the case of cubic symmetry because such a case would pertain closely to substances which actually occur in nature. In the present paper we have also included, in a tentative and general way, the indications which the energy function would give regarding the anomalous behaviour of matter subjected to high pressures. Detailed discussions of this aspect involve the Theory of Dynamical Elasticity, a topic which we propose dealing with in a subsequent paper.

2. Finite Deformation Theory

We now proceed to give the formalism of the finite deformation theory to the extent required for our problem. By a deformation, we mean that the internal constituent points in a body have undergone displacements with respect to each other, so that their relative distances have altered. To specify such an alteration in the distance between a point P and every other point Q, R, S, etc., in its neighbourhood, we first note that the general expression for an infinitesimal length appears as a quadratic ($ds^2 = dx^2 + dy^2 + dz^2$). If therefore ds_0 is the length PQ before deformation and ds the same length after deformation, half the alteration in the square of the length, $(ds^2 - ds_0^2)/2$ is taken as a measure of the state of strain of the distance PQ in question. By assigning general positional co-ordinates to Q, the alteration in length not only of PQ but of every other length PR, PS, etc., in the neighbourhood of P is obtained, so that the state of strain around P is completely specified by the quadratic form $(ds^2 - ds_0^2)/2$. To derive an expression for this quantity, we note that, if as a result of the deformation, a point with initial co-ordinates (a, b, c) referred to any convenient space fixed Cartesian co-ordinate system moves over to a final position (x, y, z) referred, for convenience to the original frame, we can introduce a displacement vector with components (u, v, w) given by $x = a + u$, $y = b + v$, $z = c + w$, where u, v, w are functions of the initial positional co-ordinates (a, b, c). If the point P, with co-ordinates (a, b, c) moves over, as a result of deformation to P′ with co-ordinates $(x, y, z) = (a + u,\ b + v,\ c + w)$, the point Q in the infinitesimal neighbourhood of P with co-ordinates say $(a + da,\ b + db,\ c + dc)$ will move over to the position $(x + dx,\ y + dy,\ z + dz)$ where dx, dy, dz are given by the relations

$$dx = \left(1 + \frac{\partial u}{\partial a}\right) da + \frac{\partial u}{\partial b} \cdot db + \frac{\partial u}{\partial c} \cdot dc$$

$$dy = \frac{\partial v}{\partial a} \cdot da + \left(1 + \frac{\partial v}{\partial b}\right) db + \frac{\partial v}{\partial c} \cdot dc$$

$$dz = \frac{\partial w}{\partial a} \cdot da + \frac{\partial w}{\partial b} \cdot db + \left(1 + \frac{\partial w}{\partial c}\right) dc. \qquad (1)$$

The nine derivatives $\partial u/\partial a$, etc., completely specify the most general displacements, including rotations of the element as a whole, in which the relative distances of points within the element are not altered. There is therefore no room for play of the elastic forces within the element, and one could then remove the effect of rotations by the removal of the antisymmetric part in the equations by employing the usual methods. This will leave only 6 independent combinations of the displacement derivatives to be considered in the elastic deformation. If we take it that the rotations are zero, this will immediately require that $\partial u/\partial b = \partial v/\partial a$, etc., so that the matrix of the transformation is symmetric as it stands with six independent components. In the linear or infinitesimal theory of elasticity, the strain components are identified with these six independent displacement derivatives $\partial u/\partial a$, $\partial v/\partial b$, etc. In the finite or non-linear theory of elasticity, however, we work out $(ds^2 - ds_0^2)/2$ using relation (1) and noting that $ds^2 = dx^2 + dy^2 + dz^2$ = square of length PQ after deformation and $ds_0^2 = da^2 + db^2 + dc^2$ = square of length PQ before deformation. This quadratic form therefore appears as

$$\frac{ds^2 - ds_0^2}{2} = \eta_{11}da^2 + \eta_{22}db^2 + \eta_{33}dc^2 + 2\eta_{12}dadb + 2\eta_{23}dbdc + 2\eta_{31}dcda \tag{2}$$

where

$$\eta_{11} = \frac{\partial u}{\partial a} + \frac{1}{2}\left[\left(\frac{\partial u}{\partial a}\right)^2 + \left(\frac{\partial v}{\partial a}\right)^2 + \left(\frac{\partial w}{\partial a}\right)^2\right] \tag{3}$$

with similar equations for η_{22} and η_{33}, and

$$\eta_{12} = \eta_{21} = \frac{1}{2}\left(\frac{\partial v}{\partial a} + \frac{\partial u}{\partial b}\right) + \frac{1}{2}\left(\frac{\partial u}{\partial a}\cdot\frac{\partial u}{\partial b} + \frac{\partial v}{\partial a}\cdot\frac{\partial v}{\partial b} + \frac{\partial w}{\partial a}\cdot\frac{\partial w}{\partial b}\right) \tag{4}$$

with similar equations for η_{23}, η_{31}, etc.

The η's are thus coefficients in a certain quadratic form expressing the change in the squared length and they constitute the 9 entities of a (3, 3) matrix styled as the strain matrix. In view of the symmetry of this matrix, the 9 components reduce to 6 and a convenient representation of the strain matrix is

$$\eta = \begin{pmatrix} \eta_1 & \eta_6 & \eta_5 \\ \eta_6 & \eta_2 & \eta_4 \\ \eta_5 & \eta_4 & \eta_3 \end{pmatrix}. \tag{5}$$

It is evident from (3) and (4) that when the squares and products of the displacement derivatives $\partial u/\partial a$, etc., are neglected, the strain matrix of the finite theory becomes identical with the infinitesimal matrix. In view of the respective definitions, one can also say that in the infinitesimal theory, it is of no consequence whether the displacement derivatives are calculated at the initial or final positions of a point and the initial and final positions are thus interchangeable. In the finite theory, however, the distinction between the initial and final states has to be maintained.

The displacement of a point from an initial position (a, b, c) to the final position (x, y, z), as given in equation (1), is most conveniently represented by the transformation $x = Ja$, $(x = x, y, z)$, $(a = a, b, c)$ and J, the Jacobian of the transformation is given from (1) by

$$J = \begin{pmatrix} 1+\frac{\partial u}{\partial a} & \frac{\partial u}{\partial b} & \frac{\partial u}{\partial c} \\ \frac{\partial v}{\partial a} & 1+\frac{\partial v}{\partial b} & \frac{\partial v}{\partial c} \\ \frac{\partial w}{\partial a} & \frac{\partial w}{\partial b} & 1+\frac{\partial w}{\partial c} \end{pmatrix} = \begin{pmatrix} \frac{\partial x}{\partial a} & \frac{\partial x}{\partial b} & \frac{\partial x}{\partial c} \\ \frac{\partial y}{\partial a} & \frac{\partial y}{\partial b} & \frac{\partial y}{\partial c} \\ \frac{\partial z}{\partial a} & \frac{\partial z}{\partial b} & \frac{\partial z}{\partial c} \end{pmatrix}. \qquad (6)$$

Denoting by J^* the transpose of this matrix, it is evident that if we form the product matrix J^*J, subtract unity from each of the 3-diagonal elements and halve the result, we get the matrix of coefficients of the quadratic form (2) and this is the strain matrix (5). Murnaghan (1951) has employed this form as the definition of the strain matrix in the following way.

$$\eta = \tfrac{1}{2}(J^*J - E_3). \qquad (7)$$

In (7), E_3 is the unit matrix of dimension 3. We also note here that the subtraction of E_3 indicates that the original length is being subtracted from the new or altered length between two points, which means that in our treatment, we are excluding all such displacements which keep the relative distance between every two points within an element unaltered. Rotations are displacements of this type, and in the finite theory, the removal is effected from the product matrix J^*J and not from J itself as in the infinitesimal theory. J thus need not be a symmetric matrix, nor is it rendered so, in the finite theory. A simple shear given by

$$x = a + \eta b, \; y = b, \; z = c,$$

is an example of an unsymmetrical J. However the strain matrix formed from the same by the formula $\eta = \frac{1}{2}(J^*J - E_3)$ is symmetric. When formulating the most general displacement, we must therefore take J with 9 independent components (and not reduce to 6 by removal of the anti-symmetric part), so long as finite deformations are concerned. We shall have occasion to refer to this question again at a subsequent stage in this paper.

3. STRAIN ENERGY EXPRESSION IN THE FINITE THEORY, WITH AND WITHOUT AN INITIAL STRESS

The strain energy ϕ, measured per unit volume of the initial state, would be a function of the 6 strain components $\eta_1 \ldots \eta_6$, and can therefore be expanded as a power series in the η's.

$$\phi = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \ldots\ldots \tag{8}$$

The constant ϕ_0 has no significance for us, as we are interested only in the derivatives of ϕ. The first order term ϕ_1 will be a linear function of the η's of the form

$$\phi_1 = c_1\eta_1 + c_2\eta_2 + c_3\eta_3 + 2c_4\eta_4 + 2c_5\eta_5 + 2c_6\eta_6. \tag{9}$$

In the infinitesimal theory of elasticity, the 6 components of stress $T_1, T_2, \ldots T_6$ corresponding to the 6 independent elements in the (3, 3) symmetric stress matrix T_{ik} are obtained as the derivatives of ϕ with respect to the corresponding strain component

$$T_{ik} = \frac{\partial \phi}{\partial \eta_{ik}}. \tag{10}$$

Like the strain tensor, we use here the notation $T_{11} = T_1$, $T_{22} = T_2$, $T_{33} = T_3$, $T_{23} = T_{32} = T_4$, $T_{31} = T_{13} = T_5$, $T_{12} = T_{21} = T_6$. In the finite theory, the stresses are given, as shown by Murnaghan, as the elements in the matrix derived from the formula

$$T = \frac{\rho_x}{\rho_a} J \frac{\partial \phi}{\partial \eta} J^*. \tag{11}$$

Here ρ_x is the density of a volume element after deformation while ρ_a is its density before the deformation. If V_x and V_a be the corresponding volumes per unit mass of the substance, we have the relations

$$\frac{\rho_x}{\rho_a} = \frac{V_a}{V_x} = \frac{1}{\text{Determinant } J}. \tag{12}$$

To apply formula (11), we have to first write out the energy as a function of all the 9 strain components η_{ik}, *i.e.*, disregarding the symmetry relation $\eta_{ik} = \eta_{ki}$. Same procedure has to be adopted when applying (10) and (9) as well. From this the energy derivative matrix $\partial\phi/\partial\eta_{ik}$ has to be obtained and the product matrix of J, $\partial\phi/\partial\eta$ and J* be formed. This has to be finally multiplied by $\rho_x/\rho_a = (1/\text{det. J})$. Such calculations are in general laborious.

Whether the stress formula is regarded as based on (10) or (11), it is easy to see, on differentiating ϕ, that the first order coefficients $c_1, c_2 \cdots c_6$ must be equal to the initial stress components $T_1^0, T_2^0 \ldots T_6^0$ whenever such stresses are present. When we consider the superposition of strains $\delta\eta_1, \delta\eta_2 \cdots \delta\eta_6$ over finite strains $\eta_1^0, \eta_2^0 \cdots \eta_6^0$ caused by stresses $T_1^0, T_2^0 \cdots T^0_6$, the general form of ϕ_1 will be

$$\phi_1 = T_1^0\delta\eta_1 + T_2^0\delta\eta_2 + T_3^0\delta\eta_3 + 2T_4^0\delta\eta_4 + 2T_5^0\delta\eta_5 + 2T_6^0\delta\eta_6. \tag{13}$$

When the initial stress is a uniform hydrostatic pressure P, which is the case under consideration in the present paper,

$$\phi_1 = -P(\delta\eta_1 + \delta\eta_2 + \delta\eta_3) \tag{14}$$

$-P$ being used for the stress, since P is generally kept positive. This first order term in the energy will not occur whenever the energy is measured from an initial state of zero stress.

The second order energy ϕ_2, being a quadratic form in the η's, contains as coefficients the usual second order elastic constants, which correspond with the generalized Hooke's Law, while the third order term ϕ_3 contains the third order elastic constants as already mentioned, these coming into play when the strains are large. Following Birch (1947) and Hearmon (1953), we can write the full energy expression for a substance of cubic symmetry, when the strains are all measured from the state of zero strain, *i.e.*, a stress-free state, as

$$\begin{aligned}\phi &= \phi_2 + \phi_3 \\ &= \frac{c_{11}}{2}(\eta_1^2 + \eta_2^2 + \eta_3^2) + c_{12}(\eta_1\eta_2 + \eta_2\eta_3 + \eta_3\eta_1) \\ &\quad + 2c_{44}(\eta_4^2 + \eta_5^2 + \eta_6^2) + C_{111}(\eta_1^3 + \eta_2^3 + \eta_3^3) \\ &\quad + C_{112}\{\eta_1\eta_2(\eta_1 + \eta_2) + \eta_2\eta_3(\eta_2 + \eta_3) + \eta_3\eta_1(\eta_3 + \eta_1)\} \\ &\quad + C_{123}\eta_1\eta_2\eta_3 + C_{456}\eta_4\eta_5\eta_6 + C_{144}(\eta_1\eta_4^2 + \eta_2\eta_5^2 + \eta_3\eta_6^2) \\ &\quad + C_{155}\{\eta_1(\eta_5^2 + \eta_6^2) + \eta_2(\eta_4^2 + \eta_6^2) + \eta_3(\eta_4^2 + \eta_5^2)\}. \quad (1\,5\end{aligned}$$

This contains 3 second order constants and 6 third order constants. The general method followed in writing the third power terms is to expand ϕ_3 and write it as $\Sigma C_{pqr}\eta_p\eta_q\eta_r$, where p, q, r take any values 1 to 6 subject to the condition $p \leq q \leq r$.

When we consider the case of superposition of an infinitesimal deformation $\delta\eta$ over an initial state of finite strain η corresponding to an initial hydrostatic pressure P, the energy for the $\delta\eta$ deformation should be written, to be consistent with the above formulation, as

$$\phi' = \phi'(\delta\eta) = -\mathrm{P}(\delta\eta_1 + \delta\eta_2 + \delta\eta_3) + \frac{b_{11}}{2}(\delta\eta_1{}^2 + \delta\eta_2{}^2 + \delta\eta_3{}^2) + b_{12}(\delta\eta_1\delta\eta_2 + \delta\eta_2\delta\eta_3 + \delta\eta_3\delta\eta_1) + 2b_{44}(\delta\eta_4{}^2 + \delta\eta_5{}^2 + \delta\eta_6{}^2). \quad (16)$$

The higher powers are neglected as the deformation $\delta\eta$ is treated as infinitesimal. The $\delta\eta$ are measured from the η state and the energy is per unit volume of this η state.

4. EVALUATION OF THE STRAIN ENERGY FOR MATERIAL UNDER HYDROSTATIC PRESSURE

We now proceed to evaluate the Strain Energy function defined in (16) in terms of the constants c_{11}, C_{111}, etc., of the stress-free state, defined in (15). For this purpose, we first carry out the finite hydrostatic deformation of the medium by which a point (a, b, c) is moved over to a point (x_0, y_0, z_0) given by $x_0 = (1+\eta)\,a$, $y_0 = (1+\eta)\,b$, $z_0 = (1+\eta)\,c$ where

$$\eta = \frac{\partial u}{\partial a} = \frac{\partial v}{\partial b} = \frac{\partial w}{\partial c}$$

giving the magnitude of the compression as a change of length per unit initial length. The corresponding Jacobian is

$$\mathrm{J}_0 = \begin{pmatrix} 1+\eta & 0 & 0 \\ 0 & 1+\eta & 0 \\ 0 & 0 & 1+\eta \end{pmatrix}. \quad (17)$$

From the Murnaghan formulæ for strain and stress (7 and 11), we get the strain and stress matrices respectively as

$$\begin{pmatrix} \eta+\eta^2/2 & 0 & 0 \\ 0 & \eta+\eta^2/2 & 0 \\ 0 & 0 & \eta+\eta^2/2 \end{pmatrix} \quad (18)$$

$$\begin{pmatrix} \dfrac{\frac{\partial\phi}{\partial\eta_1}}{1+\eta} & 0 & 0 \\ 0 & \dfrac{\frac{\partial\phi}{\partial\eta_2}}{1+\eta} & 0 \\ 0 & 0 & \dfrac{\frac{\partial\phi}{\partial\eta_3}}{1+\eta} \end{pmatrix}. \tag{19}$$

Substitution of the strain matrix values (18) in the energy expression (15) gives us the energy due to the hydrostatic pressure alone. To obtain the energy for the initial strain *plus* the infinitesimal strain, we formulate the corresponding J. If as a result of this additional strain the point (x_0, y_0, z_0) moves over to (x, y, z), the most general relationship between them will be given by

$$\begin{aligned} x &= (1+\delta_1)\,x_0 + \delta_6 y_0 + \delta_5 z_0 \\ y &= \delta_6 x_0 + (1+\delta_2)\,y_0 + \delta_4 z_0 \\ z &= \delta_5 x_0 + \delta_4 y_0 + (1+\delta_3)\,z_0. \end{aligned} \tag{20}$$

The transformation $x_0 \rightarrow x$ being thus given by the Jacobian

$$J_\delta = \begin{pmatrix} 1+\delta_1 & \delta_6 & \delta_5 \\ \delta_6 & 1+\delta_2 & \delta_4 \\ \delta_5 & \delta_4 & 1+\delta_3 \end{pmatrix}. \tag{21}$$

In formulating J_δ in this form with 6 components, we have assumed that the rotations are removed beforehand. Special cases such as that of a simple shear, superposed over a finite strain, would require the consideration of an unsymmetrical J. We will not, however, consider such a case here for the sake of simplicity.

Now substituting the values of $x_0 = (1+\eta)\,a$, etc., we finally get the transformation from the initial position a, b, c to the final position x, y, z as

$$x = \mathrm{J}a$$

where

$$\mathrm{J} = (1+\eta)\,J_\delta. \tag{22}$$

Forming $\frac{1}{2}(\mathrm{J}^*\mathrm{J} - \mathrm{E}_3)$, we obtain the strain matrix for this entire deformation $\eta + \delta\eta$, as

$$\begin{pmatrix} R + q^2\delta\eta_1 & q^2\delta\eta_6 & q^2\delta\eta_5 \\ q^2\delta\eta_6 & R + q^2\delta\eta_2 & q^2\delta\eta_4 \\ q^2\delta\eta_5 & q^2\delta\eta_4 & R + q^2\delta\eta_3 \end{pmatrix} \tag{23}$$

where $R = \eta + \eta^2/2 =$ Initial strain, $q = 1 + \eta$

$$\delta\eta_1 = \delta_1 + \tfrac{1}{2}(\delta_1^2 + \delta_5^2 + \delta_6^2) \qquad \delta\eta_4 = \delta_4 + \tfrac{1}{2}(\delta_2\delta_4 + \delta_3\delta_4 + \delta_5\delta_6)$$
$$\delta\eta_2 = \delta_2 + \tfrac{1}{2}(\delta_2^2 + \delta_4^2 + \delta_6^2) \qquad \delta\eta_5 = \delta_5 + \tfrac{1}{2}(\delta_1\delta_5 + \delta_3\delta_5 + \delta_4\delta_6)$$
$$\delta\eta_3 = \delta_3 + \tfrac{1}{2}(\delta_3^2 + \delta_4^2 + \delta_5^2) \qquad \delta\eta_6 = \delta_6 + \tfrac{1}{2}(\delta_1\delta_6 + \delta_2\delta_6 + \delta_4\delta_5) \tag{24}$$

It should be noted here that we are maintaining the distinction between the δ matrix (21) which specifies the displacement, and the $\delta\eta$ matrix which is the strain matrix corresponding to the J_δ transformation. Further, while we have taken our additional deformation as infinitesimal, we are still keeping the square terms δ_1^2, etc., in the expression for $\delta\eta$. This is necessary because the energy of the infinitesimal deformation ϕ' will ultimately have terms up to squares and products of the displacement derivatives δ_1, δ_2, etc. If ϕ' contained only quadratic terms in the $\delta\eta$, it would have been wholly unnecessary to keep any square of the δ in the expression for $\delta\eta$. However, when an initial stress is present, ϕ' contains linear terms in the $\delta\eta$ which give rise to terms of the second degree in the δ's as is evident from (24). Hence we note the important point that, when an initial stress is present, even an infinitesimal strain thereon will have to be treated as a finite one only, no approximation being justifiable in the value for the strain element. After the energy expression is formed using the correct value of the strain component, terms higher than the second powers of the displacement derivatives could be neglected, to justify its classification as an infinitesimal deformation.

We can substitute the values of the strains from (23) to get the total energy. An equivalent, but somewhat simpler method would be to note that an increase of $\delta\eta$ from the 'η' state gives rise to an increase of $\Delta\eta = (1 + \eta)^2\,\delta\eta$ in all the elements of the strain matrix. Here $\Delta\eta$ is the increase in strain when the strain is measured with reference to the stress-free state, while $\delta\eta$ is measured from the state of finite strain η. As the energy expression (15) refers to the initial stress-free conditions, any increase of the energy due to an increment of $\Delta\eta$ in the strain, can be most simply got from the Taylor formula,

$$\phi(\eta + \Delta\eta) - \phi(\eta) = \sum \frac{\partial\phi}{\partial\eta_r}\cdot\Delta\eta_r + \frac{1}{2}\sum\sum \frac{\partial^2\phi}{\partial\eta_r\partial\eta_s}\Delta\eta_r\Delta\eta_s \tag{25}$$

neglecting higher powers of the $\Delta\eta$. This is the energy of the infinitesimal deformation when referred to a unit volume of the stress-free state. We multiply it by $1/\text{Det}\, J_0$ to refer it to a unit volume of the 'η' state [*see* equation (12) in this connection], *i.e.*, by a factor $(1+\eta)^{-3}$. According to the energy method explained earlier, we equate this quantity to ϕ' to get

$$(1+\eta)^{-3}\,[\{R\,(c_{11}+2c_{12})+R^2\,(3C_{111}+6C_{112}+C_{123})\}$$
$$\times\,(1+\eta)^2\,(\delta\eta_1+\delta\eta_2+\delta\eta_3)$$
$$+\tfrac{1}{2}\{c_{11}+R\,(6C_{111}+4C_{112})\}\,(1+\eta)^4\,(\delta\eta_1{}^2+\delta\eta_2{}^2+\delta\eta_3{}^2)$$
$$+\{c_{12}+R.C_{123}+R.4C_{112}\}\,(1+\eta)^4\,(\delta\eta_1\delta\eta_2+\delta\eta_2\delta\eta_3+\delta\eta_3\delta\eta_1)$$
$$+\tfrac{1}{2}\{4c_{44}+R\,(2C_{144}+4C_{155})\}\,(1+\eta)^4\,(\delta\eta_4{}^2+\delta\eta_5{}^2+\delta\eta_6{}^2)].$$

$$=\phi'=-P\,(\delta\eta_1+\delta\eta_2+\delta\eta_3)+\frac{b_{11}}{2}(\delta\eta_1{}^2+\delta\eta_2{}^2+\delta\eta_3{}^2)$$
$$+\,b_{12}\,(\delta\eta_1\delta\eta_2+\delta\eta_2\delta\eta_3+\delta\eta_3\delta\eta_1)$$
$$+\,2b_{44}\,(\delta\eta_4{}^2+\delta\eta_5{}^2+\delta\eta_6{}^2). \qquad (26)$$

Equating the coefficient of $\delta\eta_1$ on either side, we immediately get

$$-P=(c_{11}+2c_{12})\frac{\eta+\eta^2/2}{1+\eta}+\frac{(\eta+\eta^2/2)^2}{1+\eta}(3C_{111}+6C_{112}+C_{123})$$

which, on development in powers of η and retaining up to η^2, becomes

$$-P=\eta\,(c_{11}+2c_{12})+\eta^2\left(3C_{111}+6C_{112}+C_{123}-\frac{c_{11}}{2}-c_{12}\right). \qquad (27)$$

In the same manner by equating coefficients of $\delta\eta_1{}^2$, $\delta\eta_1\delta\eta_2$ and $\delta\eta_4{}^2$ we get

$$b_{11}=c_{11}+\eta\,(c_{11}+6C_{111}+4C_{112})+\eta^2\,(9C_{111}+6C_{112}) \qquad (28)$$

$$b_{12}=c_{12}+\eta\,(c_{12}+4C_{112}+C_{123})+\eta^2\left(6C_{112}+\frac{3}{2}C_{123}\right) \qquad (29)$$

$$b_{44}=c_{44}+\eta\left(c_{44}+\frac{C_{144}}{2}+C_{155}\right)+\eta^2\left(\frac{3}{4}C_{144}+\frac{3}{2}C_{155}\right). \qquad (30)$$

5. Effective Elastic Energy and Effective Elastic Constants

So far our task has been to derive an expression for the additional strain energy due to an infinitesimal deformation in powers of the strain components $\delta\eta$, each of which however involved not only terms linear in the δ_1, δ_2, etc., but quadratic terms in them as well. For further discussion on the elastic behaviour of the substance from the 'η' state, it will be necessary to express this energy in terms of $\delta_1 \cdots \delta_6$. Substituting from (24) in (16) and retaining terms up to the second power of δ's only, we get

$$\phi' = -\mathrm{P}(\delta_1 + \delta_2 + \delta_3) + \tfrac{1}{2}(b_{11} - \mathrm{P})(\delta_1^2 + \delta_2^2 + \delta_3^2)$$
$$+ b_{12}(\delta_1\delta_2 + \delta_2\delta_3 + \delta_3\delta_1) + (2b_{44} - \mathrm{P})(\delta_4^2 + \delta_5^2 + \delta_6^2). \tag{31}$$

The expression ϕ' refers to the total deformation energy which should be rendered available from external sources in order that the deformation η to $\eta + \delta\eta$ could be effected on a unit volume element in the η state. It has to be remembered however that an external force, namely the hydrostatic stress, is already present and there is the potential energy associated with this force. When displacements resulting in deformations δ_1, δ_2, δ_3 take place, an amount of energy $\Delta\mathrm{W} = -\mathrm{P}(\delta_1 + \delta_2 + \delta_3)$ is released from this external potential energy. In other words the work done by the existing external force in this displacement which is $\Delta\mathrm{W}$ can go in, as increase in internal energy, *i.e.*, the strain energy, and thus meet the part of the total requirement ϕ'. Hence the extra energy, that should be made available in order that the deformation η to $\eta + \delta\eta$ may take place, is given by $\phi_e = \phi' - \Delta\mathrm{W}$. ϕ_e, which is the effective elastic energy, represents the energy associated with an infinitesimal deformation which takes place from a state of finite strain, just as the usual elastic energy ϕ refers to a similar deformation of a state with zero initial strain. ϕ_e is thus obtained from ϕ' by the removal of the linear terms $-\mathrm{P}(\delta_1 + \delta_2 + \delta_3)$. We have

$$\phi_e = \phi' - \Delta\mathrm{W} = \phi' + \mathrm{P}(\delta_1 + \delta_2 + \delta_3) = \frac{c'_{11}}{2}(\delta_1^2 + \delta_2^2 + \delta_3^2)$$
$$+ c'_{12}(\delta_1\delta_2 + \delta_2\delta_3 + \delta_3\delta_1) + 2c'_{44}(\delta_4^2 + \delta_5^2 + \delta_6^2) \tag{32}$$

where

$$c'_{11} = b_{11} - \mathrm{P} = c_{11} + \eta(2c_{11} + 2c_{12} + 6\mathrm{C}_{111} + 4\mathrm{C}_{112})$$
$$+ \eta^2\left(12\mathrm{C}_{111} + 12\mathrm{C}_{112} + \mathrm{C}_{123} - \frac{c_{11}}{2} - c_{12}\right)$$

$$c'_{12} = b_{12} = c_{12} + \eta(c_{12} + 4\mathrm{C}_{112} + \mathrm{C}_{123}) + \eta^2\left(6\mathrm{C}_{112} + \frac{3}{2}\mathrm{C}_{123}\right)$$

$$c'_{44} = b_{44} - \frac{\mathrm{P}}{2} = c_{44} + \eta\left(\frac{c_{11}}{2} + c_{12} + c_{44} + \frac{\mathrm{C}_{144}}{2} + \mathrm{C}_{155}\right)$$
$$+ \eta^2\left(\frac{3}{2}\mathrm{C}_{111} + 3\mathrm{C}_{112} + \frac{\mathrm{C}_{123}}{2} + \frac{3}{4}\mathrm{C}_{144}\right.$$
$$\left. + \frac{3}{2}\mathrm{C}_{155} - \frac{c_{11}}{4} - \frac{c_{12}}{2}\right). \tag{33}$$

The new constants c'_{11}, c'_{12}, c'_{44} will be called the effective elastic constants. While ϕ_e could have been directly derived by substitution of relations such as $\delta\eta_1 = \delta_1 + \frac{1}{2}(\delta_1^2 + \delta_5^2 + \delta_6^2)$, in the function ϕ, the development of an intermediate function ϕ' as has been done in this paper helps us to retain $\delta\eta$ as it is, till a convenient stage is reached, whereafter ϕ_e could be easily deduced. This reduces the labour involved in a full substitution of $\delta\eta$ from the beginning itself.

The $\delta_1, \delta_2 \ldots \delta_6$ are the displacement derivatives. In the infinitesimal theory, they are directly identified with the infinitesimal strain components themselves. We can therefore get the stresses required for effecting the δ deformation by the usual processes of differentiating the appropriate strain energy function, which in this case is ϕ_e. We thus obtain for the additional strains $t_1, t_2 \cdots t_6$ the relations

$$t_1 = c'_{11}\delta_1 + c'_{12}(\delta_2 + \delta_3) \quad (34)$$

with similar equations for t_2 and t_3 and

$$t_4 = 2c'_{44}\delta_4 \quad (35)$$

with similar equations for t_5 and t_6. (34) and (35) are indicative of the linear relationships which connect the additional stresses with the additional strains through the effective elastic constants c'_{11}, c'_{12}, c'_{44}.

6. Derivation of Effective Elastic Constants from Stress Matrix Method

In the foregoing sections we have indicated the derivation of the effective elastic energy and the effective constants from the energy method. It is also possible to derive the same from the stress matrix and this method has been adopted by some workers (Birch, 1947; Hughes and Kelly, 1953). The method is not simpler, since in any case, the energy function has to be evaluated as an essential step for the derivation of the stress from the Murnaghan formula $T = (\rho_x/\rho_a) J (\partial\phi/\partial\eta) J^*$. We form the appropriate matrices for an $(\eta + \delta)$ transformation, and after the product matrix of all the three matrices J, $\partial\phi/\partial\eta$, J* is worked out and the same is multiplied by ρ_x/ρ_a, we retain only the constant and terms linear in the δ's. This gives the total stress appropriate to an $\eta + \delta$ deformation. From this, the extra stress appropriate to the infinitesimal deformation has to be found out. A direct subtraction like $T_{\eta+\delta} - T_\eta$ to obtain the extra stress is incorrect, since the stress, being referred to the final state, has different reference conditions for $T_{\eta+\delta}$ and T_η (which is really the pressure P in our present case). In this respect the position is more complicated than in the energy method. Whereas

$\phi(\eta + \delta) - \phi(\eta)$ employed in our energy method is an allowed subtraction as both refer to the common condition of a state of zero stress, $T_{\eta+\delta} - T_\eta$ in the stress matrix method is not an allowed subtraction in view of the difference in the reference frames. We have to refer $T_{\eta+\delta}$ and T_η to common reference conditions and then deduct the effect of the pressure. Birch calculated the total stress $T_{11} = T_1$ and equated it to an expression $-P + c'_{11}\delta_1 + c'_{12}(\delta_2 + \delta_3)$, wherein he identified c'_{11}, c'_{12}, etc., with the effective elastic constants. However, they would be so only if $T_{11} + P$ (it has to appear in this form as T_{11} is negative while P is kept positive) represents the extra pressure. But as pointed out earlier, the removal of the pressure term in this manner from T_{11} is not justified. Likewise he calculated T_{12} and on the basis that there is no initial shearing stress he identified T_{12} with $2c'_{44}\delta_6$. Here again, he has not taken into account the fact that a pressure P in an η state is equivalent to a stress tensor of a somewhat different type when referred to the $\eta + \delta$ state; the representation of the pressure in the $\eta + \delta$ state has in fact a component $-P\delta_6$ in the $T_6 = T_{12}$ term, and $-P(1 - \delta_2 - \delta_3)$ in the T_{11} term as will be shown in the next paragraph. So, as long as the Murnaghan formulæ for stress, which refer everything to the final state, are employed, the pressure should also be referred to those final conditions, and to obtain the excess stress we have to subtract $-P(1 - \delta_2 - \delta_3)$ from T_{11} and similarly subtract $-P\delta_6$ from T_{12}. As the correction does not involve δ_1, c'_{11} is unaffected and it follows that c'_{11} as derived by us should be identical with that obtained by Birch. As the δ_2 term in T_{11} now comes with an additional correction $-P\delta_2$, the value of c'_{12} obtained by Birch will have to be corrected by subtracting P. Likewise, c'_{44} obtained by him should be corrected by the addition of P/2. We give below the values obtained by Birch which were developed up to the first power of η along with our values up to the same power, although in the actual working given by us earlier, we have developed up to η^2.

Values of Birch	Values obtained by authors
$c'_{11} = c_{11}+\eta(2c_{11}+2c_{12}+6C_{111}+4C_{112})$	$c'_{11} = c_{11}+\eta(2c_{11}+2c_{12}+6C_{111}+4C_{112})$
$c'_{12} = c_{12}+\eta(C_{123}+4C_{112}-c_{11}-c_{12})$	$c'_{12} = c_{12}+\eta(C_{123}+4C_{112}+c_{12})$
$c_{44}' = c_{44} + \eta\left(c_{44} + c_{11} + 2c_{12} + \frac{C_{144}}{2} + C_{155}\right)$	$c'_{44} = c_{44} + \eta\left(\frac{c_{11}}{2} + c_{12} + c_{44} + \frac{C_{144}}{2} + C_{155}\right)$
$-P = \eta(c_{11} + 2c_{12})$	$-P = \eta(c_{11} + 2c_{12})$

The value of P when referred to the final $\eta + \delta$ conditions can also be obtained by using the formula given by Murnaghan $T^a dS^a = T dS^x$ where T^a is the stress in an initial frame with a surface area element given by dS^a, T the stress in the final state with an element of area dS^x. The relation between dS^x and dS^a is

$$dS^x = \frac{\rho_a}{\rho_x} (J^*)^{-1}\, dS^a. \tag{37}$$

Hence we get

$$T^a = \frac{\rho_a}{\rho_x} T\, (J^*)^{-1},$$

or

$$T = \frac{\rho_x}{\rho_a} T^a J^*. \tag{38}$$

In our case, the η state is the initial state and the $\eta + \delta$ state is the final state.

Hence

$$J = J^* = \begin{vmatrix} 1+\delta_1 & \delta_6 & \delta_5 \\ \delta_6 & 1+\delta_2 & \delta_4 \\ \delta_5 & \delta_4 & 1+\delta_3 \end{vmatrix}$$

and

$$\frac{\rho_x}{\rho_a} = \frac{1}{\det. J}\cdot$$

Substituting these values, we find that the stress $-$ P in the η state appears, in the $\eta + \delta$ state, as the stress given by the matrix

$$\begin{pmatrix} -P(1-\delta_2-\delta_3) & -P\delta_6 & -P\delta_5 \\ -P\delta_6 & -P(1-\delta_3-\delta_1) & -P\delta_4 \\ -P\delta_5 & -P\delta_4 & -P(1-\delta_1-\delta_2) \end{pmatrix}. \tag{39}$$

Hence these matrix elements have to be subtracted from T_{11}, T_{12}, etc., before the correct extra stress is obtained.

Instead of referring P to the final $\eta + \delta$ state and removing its effect from T_{11}, T_{12}, etc., one could also refer the total stresses T_{11}, T_{12}, etc., to the η state and then remove P directly. This will not involve any modification of the pressure, whereas the stresses, since they are referred to the η state as the initial state, can be deduced from the simpler formula $T^a =$

$J(\partial\phi/\partial\eta)$. Here T^a is what Murnaghan (1951) calls the modified stress matrix. It can be verified that results identical with the above are obtainable by such a procedure as well.

7. DISCUSSION OF RESULTS

Experimental data concerning the third order constants are very meagre. Whatever is available [Hearmon (1953), Hughes and Kelly (1953)] suggests that all these constants are negative and an order of magnitude larger than the second order constants. In the discussion given by Hearmon (1953), the data obtained by Lazarus (1949) concerning c'_{ik} in respect of the cubic crystals KCl, NaCl, CuZn, up to hydrostatic pressures of 10,000 bars were considered. Hearmon plotted the ratio c'_{ik}/c_{ik} against η and obtained a nearly straight line relationship. Using the values of the slopes of these lines, he derived values for the 3 third order combinations C_a, C_b, C_d given by

$$C_a = 6C_{111} + 4C_{112}; \quad C_b = C_{123} + 4C_{112}; \quad C_d = \tfrac{1}{2}C_{144} + C_{155}.$$

In NaCl, for example, C_a was -100, C_b was -14 and C_d was -11, in units of 10^{11} dynes per sq.cm. The corresponding values of the second order elastic constants are roughly $c_{11} = 4{\cdot}9$, $c_{12} = 1{\cdot}2$, $c_{44} = 1{\cdot}2$. In view of the method employed, Hearmon has cautioned that the accuracy of these values is not likely to be high. However, the order of magnitude of the third order constants suggested by these calculations seems to be correct, and further work of Hughes and Kelly (1953) supports this view.

As the readings were taken in a portion of the $(c'_{ik}/c_{ik}, \eta)$ graph which was nearly straight, it is clear that, in this region the η^2 term in the formulæ (33) could be neglected. For the same reason, there would not be any appreciable difference whether Birch's expressions of the effective elastic constants, or those derived by us from the energy expression method are used. When, however, we use the values of the third order constants as derived above for discussing the behaviour of the energy function for large η, the η^2 term, as also the effective elastic constants as derived by us from the energy function will have to be used.

Thus, neglecting the second order constants in comparison with the third order ones, we find from (33) that each of the effective elastic constants can be represented as,

$$c'_{ik} = c_{ik} + A\eta + B\eta^2 \tag{40}$$

where A equals C_a, C_b or C_d respectively as defined earlier, and B is nearly equal to 2A in case of c'_{11} and 3/2 A in case of c'_{12} and more than 3/2 A in case of c'_{44}. A is ordinarily negative and as η itself is negative for compression, the formula shows that the elastic constants should, as a rule, increase with increasing compression, so long as η is not too large. Such an increase is to be expected, since these elastic constants express the magnitude of energy required for deforming a substance which is already in a compressed state. As the compression increases, the energy required for compressing further should naturally increase indicating increasing resistance of the substance to further deformation. What is interesting, however, is that the formulæ (33) and (40) indicate the possibility that the elastic constants might increase up to a point only and then start decreasing. That this will happen, other factors remaining unchanged, when $1 + 3\eta = 0$ or $\eta = -0{\cdot}3$, in the case of c_{12} and when $\eta = -0{\cdot}25$ in the case of c_{11} and less than $-0{\cdot}3$ in the case of c'_{44} may be inferred by equating $(dc'_{ik}/d\eta)$ to zero. However $\eta = -0{\cdot}25$ to $-0{\cdot}3$ corresponds to a very large strain difficult of realisation in practice. Since a decrease of the elastic constants with increasing pressure is itself indicative of anomalous behaviour, we have to conclude that matter should be expected to behave in an abnormal manner when the magnitude of compression becomes as high as $0{\cdot}25$ to $0{\cdot}3$.

This of course is a purely qualitative conclusion, and the magnitude might well be somewhat different when we develop c'_{ik} to include η^3 terms also. Other physical conditions such as the temperature are bound to play an important part and these have not been considered.

8. Effective Elastic Energy in Normal Co-ordinates

We note that the function ϕ_e given by (32) is separable in the variables δ_4, δ_5, δ_6 but not in δ_1, δ_2, δ_3 because of cross-products. To discuss the behaviour of this function, it is necessary to make a 'normal co-ordinate transformation' so that each variable could be treated independently. We introduce new orthogonal variables given by

$$\theta_1 = \frac{1}{\sqrt{3}}(\delta_1 + \delta_2 + \delta_3)$$

$$\theta_2 = \frac{1}{\sqrt{2}}(\delta_1 - \delta_2)$$

$$\theta_3 = \frac{1}{\sqrt{6}}(\delta_1 + \delta_2 - 2\delta_3). \tag{41}$$

In terms of these, we rewrite (32) as

$$\phi_e = (c'_{11} + 2c'_{12})\frac{\theta_1^2}{2} + (c'_{11} - c'_{12})\frac{\theta_2^2 + \theta_3^2}{2} + 2c'_{44}(\delta_4^2 + \delta_5^2 + \delta_6^2). \tag{42}$$

The system will therefore become unstable when any of the coefficients $c'_{11} + 2c'_{12}$, $c'_{11} - c'_{12}$ or c'_{44} becomes negative. Of these, the first is only hypothetical, because c'_{11} and c'_{12} being initially positive, the term $c'_{11} - c'_{12}$ will, if at all, become negative long before $c_{11}' + 2c_{12}'$ does so and we may safely exclude the first case. As regards the other two coefficients $\frac{1}{2}(c'_{11} - c'_{12})$ and c'_{44}, we notice that both are identical in the isotropic case. For such a case, we may take the criterion that as soon as c'_{44} tends to assume negative values, instability sets in. With the present meagre available data, it is not possible to calculate the magnitude of the compression at which this phenomenon sets in for any particular case like the interior of the earth. However, the form of c'_{44} especially in its expression as $b_{44} - P/2$ suggests that with monotonously increasing pressure, the possibility of its becoming negative at some stage of the compression cannot be ruled out. This is especially so in substances in which c_{44} goes on decreasing with pressure such as in the case of KCl even from the very beginning (Hearmon, 1953). Even if c_{44} increases at first and decreases later due to the importance of the η^2 term, or decreases due to other causes such as the effect of temperature, a stage will be reached when c'_{44} becomes negative. It is obvious that the substance then becomes unstable under the action of shearing stresses and this may be interpreted by saying that it can no longer sustain shear waves.

A more detailed discussion of the instability problem, and the extension of the present work to include a finite initial stress of any type, will be taken up in subsequent papers.

9. SUMMARY

In order to study the elastic behaviour of matter when subjected to very large pressures, such as occur for example in the interior of the earth, and to provide an explanation for phenomena like earthquakes, it is essential to be able to calculate the values of the elastic constants of a substance under a state of large initial stress in terms of the elastic constants of a natural or stress-free state. An attempt has been made in this paper to derive expressions for these quantities for a substance of cubic symmetry on the basis of non-linear theory of elasticity and including up to cubic powers of the strain components in the strain energy function. A simple method of deriving them directly from the energy function itself has been indicated for any general case and the same has been applied to the case of hydrostatic compression. The notion of an effective elastic energy—the energy require to effect an infinitesimal deformation over a state of finite strain—has been introduced, the coefficients in this expression being the effective

elastic constants. A separation of this effective energy function into normal co-ordinates has been given for the particular case of cubic symmetry and it has been pointed out, that when any of such coefficients in this normal form becomes negative, elastic instability will set in, with associated release of energy.

ACKNOWLEDGEMENT

One of us (E. V. C.) is indebted to the Government of India in the Ministry of Communications and to the Director-General of Observatories, New Delhi, for kind grant of study leave, which has rendered it possible for him to take up the present work.

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