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First Pressure Derivative of Bulk Modulus for Porous Materials*

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Two equations are derived giving the effect of porosity in the form of spherical pores upon the pressure derivative dK/dp of bulk modulus. In the first equation, dK/dp is expressed in terms of porosity and the second-order elastic constants for the solid material, whereas in the second equation, the third-order constants are needed as well. The expressions are evaluated for thirteen materials, showing that dK/dp for porous material may be either larger or smaller than the value for the solid matrix.

INTRODUCTION

Accurate measurements of both bulk modulus K_0 and the rate of change dK_0/dp of bulk modulus with pressure are necessary when values obtained at low pressure must be extrapolated to higher pressures. These second- and third-order constants are important parameters in the high pressure equations of state now being applied to studies[1] of the Earth's interior, for example. Clearly, when measurements are made on porous samples, the values must be corrected before being used to predict the behavior of material deep in the earth, which undoubtedly is pore free. This correction is a matter of increasing concern as attention turns to minerals which are not available in dense polycrystalline form or as single crystals of sufficiently large size.

Typically, porosity is encountered when samples are prepared by hot-pressing minerals which are available only in the form of fine powders. Samples can be sintered completely only with difficulty, and often pores remain at the interstices of adjacent grains. The pores thus have more or less equant dimensions and can be adequately approximated as spherical cavities. Porosity may be as high as 25%, although values of a few percent or less are more common.[2]

Bulk modulus K can be corrected using the formula first derived by Mackenzie[3] for solids containing a small amount of porosity η in the form of spherical cavities. Mackenzie's equation may be written in the form

$$(1-\eta)/K=1/K_0+3\eta/4\mu_0, \tag{1}$$

where K and μ are bulk modulus and rigidity, and subscript zero refers to the solid material. Although (1) is strictly applicable only to samples with low porosity, the formula has been shown to be valid also when the porosity is very high ($\eta\approx 1$)[4]; Hashin[5] found that (1) was valid over the entire range of porosity for spherical pores distributed in a special way; and bulk modulus measured in static tests on glass with spherical pores agreed to reasonable accuracy with values predicted by (1) for porosities up to 0.7.[4] Thus, Mackenzie's formula provides an effective method for correcting bulk modulus when porosity is in the form of spherical pores. As shown by Hashin and Shtrikman,[6] (1) is also the upper bound on bulk modulus when pore configuration is arbitrary, so the effect of nonsphericity and interaction between pores is to reduce the bulk modulus to a value less than that calculated from (1).

The success of Mackenzie's formula for predicting the bulk modulus of porous samples suggests that the same approach should be used in deriving the analogous expression for dK/dp. Mackenzie developed his theory using linear elasticity, in which K_0 and μ_0 are independent of stress. Therefore, one cannot simply differentiate Mackenzie's expression to find dK/dp in terms of dK_0/dp and $d\mu_0/dp$, the second-order constants, and porosity, as has been suggested.[2,7] Nonlinear theory must be used. Two approaches (called here the first- and second-order approximations) based on Murnaghan's[8] nonlinear theory of elasticity and following Mackenzie's analysis where applicable, are described below.

FIRST-ORDER APPROXIMATION

Birch,[9] using Murnaghan's[10] analysis of the finite deformation of an elastic solid, derived an expression relating bulk modulus $K_0(p)$ of a nonporous solid at some pressure p to the value $K_0(0)$ at zero pressure:

$$K_0(p)=K_0(0)+4p. \tag{2}$$

Birch's expression is a first-order approximation in that it does not contain any elastic constants other than those appearing in the linear theory. Let us assume, as an approximation, that (2) is valid for porous material as well as the nonporous material for which it was derived; i.e.,

$$K(p)=K(0)+4p. \tag{3}$$

Mackenzie's expression, Eq. (1), may be substituted for $K(0)$, giving

$$K(p)=K_0(1-\eta)[1+(3K_0/4\mu_0)\eta]^{-1}+4p. \tag{4}$$

Differentiating (4) with respect to p [note that only η on the right-hand side of (4) depends on p] and evaluating at zero pressures gives

$$dK/dp=4-K_0(1+3K_0/4\mu_0)\,d\eta/dp. \tag{5}$$

Previous linear elastic analysis[11] shows that $d\eta/dp$ is $-3\eta/4\mu_0$ when pores are spherically shaped. After some

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reduction, (5) for $\eta \ll 1$ becomes simply

$$dK/dp = 4 + \eta a(1+a), \tag{6}$$

where $a = 3K_0/4\mu_0$.

SECOND-ORDER APPROXIMATION

A better approximation may be obtained by retaining only Mackenzie's basic assumption that the bulk modulus of a sample with spherical pores is equal to the apparent bulk modulus of a hollow sphere with the same porosity. The radial displacement Δ of a sphere having initial radius R resulting from pressure p is related to dK/dp by the identity

$$3dK/dp = 9K^2(d^2\Delta/Rdp^2) - 1. \tag{7}$$

Thus, dK/dp can be found by deriving an expression for the radial displacement of a hollow sphere under external pressure, retaining terms of $O(p^2)$. Fortunately, Murnaghan[12] has carried out much of the analysis required. One finds, following Murnaghan, that the radial displacement Δ of a hollow sphere of external radius R is

$$\frac{\Delta}{R} = -(1-\eta)^{-1}\left(\frac{p}{3K_0}\right)\left(1+\eta\frac{3K_0}{4\mu_0}\right) + \left(\frac{1}{1-\eta}\right)^2\left(\frac{p}{3K_0}\right)^2 \times\left(\frac{1}{2} - \frac{9l_0+n_0}{3K_0}\right) + \eta\left(\frac{1}{1-\eta}\right)^2\left(\frac{p}{4\mu_0}\right)^2\left(-\frac{9}{4} + \frac{4\mu_0}{3K_0} + \frac{n_0-6m_0}{K_0} + \frac{n_0}{4\mu_0} + \tfrac{1}{4}\eta(11+\tfrac{1}{4}n_0)\right), \tag{8}$$

where l_0, m_0, and n_0 are the third-order constants for the solid material in Murnaghan's notation. Differentiating (8) twice and substituting the resulting expression into (7), one finds that

$$dK/dp = dK_0/dp + \eta a^2[5/2 + 1/a - 2(dK_0/dp)(a)^{-1} + 4d\mu_0/dp + n_0/6\mu_0], \tag{9}$$

where terms of $O(\eta^2)$ have been neglected. Two of Murnaghan's third-order constants have been replaced in (9) by the more convenient parameters dK_0/dp and $d\mu_0/dp$ by means of the following relations[13]:

$$n_0 - 6m_0 = 6K_0(d\mu_0/dp + \mu_0/3K_0 + 1)$$
$$2(9l_0+n_0) = -9K_0(dK_0/dp). \tag{10}$$

DISCUSSION

As described above, expressions are derived relating dK/dp for a material with spherical pores to porosity η and the elastic parameters for the solid material. In the first-order approximation [Eq. (6)] only the porosity and the second-order constants K_0 and μ_0 for the solid material are needed. The second-order approximation [Eq. (9)] requires knowing the three third-order constants—dK_0/dp, $d\mu_0/dp$, and Murnaghan's n_0—as well.

For the purpose of discussion, the expressions for dK/dp can be written as

$$dK/dp = dK_0/dp(1+\alpha\eta), \tag{11}$$

where in the first-order approximation

$$\alpha_1 = a(1+a)(dK_0/dp)^{-1} \tag{12}$$

and in the second-order approximation

$$\alpha_2 = a^2[2.5 + 1/a - 2(dK_0/dp)/a + 4d\mu_0/dp + n_0/6\mu_0](dK_0/dp)^{-1}. \tag{13}$$

Thus, α in (11) is a measure of the sensitivity of dK/dp to porosity.

The second- and third-order elastic constants needed for evaluating α have been calculated using the Voigt–Reuss–Hill approximation from measurements on single crystals for twelve materials with cubic symmetry by Barsch.[14] Measurements from different sources differ in value, so Barsch presents more than one set of constants for some materials. The values of α calculated from data in Barsch's list and for vitreous silica from measurements by Bogardus[15] are given in Table I. Data has been converted from the modified Voigt notation used by Barsch and Bogardus to the Murnaghan notation used here by means of the following relations:

$$2l_0 = c_{123} + 2c_{144}$$
$$m_0 = c_{144} + 2c_{456}$$
$$n_0 = 4c_{456}. \tag{14}$$

These relations were derived by comparing expressions from Seeger and Buck[13] with corresponding ones from Toupin and Bernstein.[16]

Note in Table I that generally the value of α_1 does not equal, even approximately, the value of α_2 for the same compound. One value may be several times larger than the other, and differences in sign are common. The value of α_2, being based on more exact analysis, is presumably the more reliable, so we conclude that the first-order approximation is not adequate. The difficulty probably lies in the initial assumption that Birch's expression [Eq. (2)] is valid for porous material. Birch derived his expression for material under pure hydrostatic pressure, whereas the stresses in a porous body are not homogeneous.

The magnitude of α_2 in Table I varies over a range of about two orders of magnitude, and both positive and negative values are present. Thus, until the second- and third-order constants have been measured, one cannot be sure whether the effect of porosity will be large or small or whether it will raise or lower the bulk modulus. A rough rule of thumb may be advanced on the basis of data in Table I: α_2 is greater than 3.0 when a is greater than 2.0. This rule is tentative, however, and may not hold up when data on other materials is available.

TABLE I. Parameters α_1 and α_2 defined by (12) and (13) and third-order constants.

Material[a]	a	dK_0/dp	$d\mu_0/dp$	$n_0/6\mu_0$	α_1	α_2
Cu	2.15	5.13	1.54	−0.96	1.32	3.05
Ag	2.56	4.00	1.76	−0.83	2.27	9.75
Au	4.77	4.95	1.01	−2.05	5.55	12.05
LiF	1.07	4.29	2.02	−1.10	0.52	0.63
NaCl-1	1.28	5.17	1.66	−1.27	0.56	0.18
NaCl-2	1.28	3.11	1.59	−1.40	0.94	1.79
NaCl-3	1.28	5.03	1.69	−1.26	0.58	0.31
NaCl-4	1.26	4.69	1.58	−1.25	0.61	0.32
KCl-1	1.45	4.90	1.00	−0.97	0.73	−0.22
KCl-2	1.45	5.14	0.93	−1.06	0.69	−0.49
MgO	0.93	3.83	2.55	−1.84	0.47	0.84
Si-1	1.10	4.15	0.49	−0.721	0.56	−0.84
Si-2	1.10	3.69	0.46	−0.73	0.63	−0.71
Ge-1	1.03	4.55	0.90	−0.65	0.46	−0.56
Ge-2	1.03	4.27	0.88	−0.78	0.49	−0.51
GaAs-1	1.21	4.49	0.62	−0.67	0.60	−0.75
GaAs-2	1.21	4.54	1.11	−0.61	0.59	−0.11
InSb	1.52	3.99	0.15	−0.46	0.96	−1.13
YIG[b]	1.55	3.02	−0.21	−0.09	1.31	−1.32
SiO_2[c]	2.38	−2.31	−1.90	−0.23	−3.48	7.23

[a] Data used in preparing this table is from Barsch (see Ref. 14) except for vitreous silica data from Bogardus (see Ref. 15). Data on same material from different sources is denoted by number following compound, such as NaCl-1.

[b] Yttrium iron garnet.

[c] Vitreous silica.

Additional uncertainty in estimating the effect of porosity arises because of the difficulty in obtaining accurate values of the third-order constants. This is shown by the four entries for NaCl in Table I, where experimental uncertainties in measurements of elastic constants introduces an uncertainty in α_2 of an order-of-magnitude.

Usually one is interested in estimating the value of dK_0/dp for nonporous material from measurements on porous samples rather than the other way around. Unfortunately, the result based on the second-order approximation cannot be inverted to give dK_0/dp in terms of parameters measured on porous samples: Although μ_0 and K_0 in the expression for α_2 in (13) can be estimated from measurements on porous material using Mackenzie's expressions, we have no way for finding $d\mu_0/dp$ and n_0. The effect of porosity on these two third-order constants can be found by analyzing the deformation resulting from small nonhydrostatic stresses on a hollow sphere under external hydrostatic pressure. The required solutions are apparently not available however.

Estimating dK_0/dp from measurements on porous material on the basis of the first-order approximation is trivial: as shown by Birch [Eq. (2) above], the value is 4.0 independent of the values of the second-order constants. Recently Birch[17] derived to the same order of approximation expressions for the pressure derivatives of V_p and V_s. He used these formulas and Mackenzie's expressions for the effect of porosity on second-order constants to estimate the pressure coefficients of velocities in forsterite with 6% porosity. The predicted value of $\partial(\ln V_p)/\partial p$ showed good agreement, whereas $\partial(\ln V_s)/\partial p$ showed poor agreement with the measured values.

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