Exact results in linear thermomechanics of fluid-saturated porous media

James G. Berryman
Lawrence Livermore National Laboratory
P. O. Box 808 L-202
Livermore, CA 94551-9900

and

Graeme W. Milton
Courant Institute of Mathematical Sciences
New York University
251 Mercer Street
New York, NY 10012

Abstract

Exact results are derived relating the various bulk moduli (frame, unjacketed, and pore) and heat capacity of inhomogeneous fluid-saturated porous media to the pertinent thermal expansion coefficients and component moduli when only two porous solid constituents are present. The porous solids need not be space filling or in perfect welded contact, so these results apply to materials containing some voids or cracks interspersed between the two constituents in addition to the interior voids associated with their pores. The key ratio of fluid pressure to temperature change producing uniform expansion or contraction is shown to be independent of porosity.

Using arguments similar to those used by Cribb¹ and Schulgasser² for thermoelasticity, Berryman and Milton³ have recently shown that exact relations may be obtained for a porous material composed of only two porous constituents that completely fill the volume of the composite (except for the pore space within themselves). Although these results dramatically improve our modeling capability compared to that of Gassmann's equation⁴ (derived assuming only a single solid constituent is present), the assumption that the two porous components must be volume filling is very restrictive and precludes using this analysis for the common situation in rocks and other porous materials where other voids and cracks are present. It is the purpose of this paper to point out that, by introducing another field (temperature), we can obtain exact results for two constituents plus voids, thus eliminating this unpleasant restriction imposed by the previous approach. This idea is similar to Schulgasser's approach to analyzing three component polycrystalline composites.²

For isotropic materials and hydrostatic pressure variations, the three independent variables in linear thermomechanics of porous media are the confining (external) pressure p_c , the fluid (pore) pressure p_f , and the temperature θ . The differential pressure $p_d \equiv p_c - p_f$ is often used to eliminate the confining pressure. The equations of the fundamental dilatations are

$$-\frac{\delta V}{V} = \frac{\delta p_d}{K} + \frac{\delta p_f}{K_s} - 3\alpha \delta \theta \tag{1}$$

for the total volume V,

$$-\frac{\delta V_{\phi}}{V_{\phi}} = \frac{\delta p_d}{K_p} + \frac{\delta p_f}{K_{\phi}} - 3\alpha_{\phi}\delta\theta \tag{2}$$

for the pore volume V_{ϕ} , and

$$-\frac{\delta V_f}{V_f} = \frac{\delta p_f}{K_f} - 3\alpha_f \delta\theta \tag{3}$$

for the fluid volume V_f . Equation (1) serves to define the various constants of the porous solid, such as the drained frame bulk modulus K, the unjacketed bulk modulus K_s , and the coefficient of linear thermal expansion α for the composite frame. Similarly, (3) defines the bulk modulus K_f and linear thermal expansion coefficient α_f of the pore fluid. Although reciprocity⁵ shows that $K_p = \phi K/(1 - K/K_s)$ where ϕ is the porosity, the remaining bulk modulus K_{ϕ} in (2) is independent of the others and (with rare exceptions⁶) has seldom been estimated and never been measured for composite porous materials such as rocks. The thermal expansion coefficient α_{ϕ} for the pore space has been introduced previously by McTigue⁷, but no measured values of this coefficient are available.

Treating δp_c , δp_f , and $\delta \theta$ as the independent variables in our thermomechanical theory, we define the dependent variables $\delta e \equiv \delta V/V$, $\delta \zeta = (\delta V_\phi - \delta V_f)/V$, and δs , which are respectively the total volume dilatation, the increment of fluid content, and the increment of entropy. Introducing the combination of moduli $\sigma = 1 - K/K_s$, we find the general relations may be expressed by

$$\begin{pmatrix} \delta e \\ -\delta \zeta \\ \delta s \end{pmatrix} = \begin{pmatrix} 1/K & -\sigma/K & 3\alpha \\ -\sigma/K & 1/M + \sigma^2/K & 3\phi(\alpha_f - \alpha_\phi) \\ 3\alpha & 3\phi(\alpha_f - \alpha_\phi) & [\phi c_p^{(f)} + (1 - \phi)c_p]/\theta_0 \end{pmatrix} \begin{pmatrix} -\delta p_c \\ -\delta p_f \\ \delta \theta \end{pmatrix}. \tag{4}$$

The constant M is related to the other moduli by

$$\frac{1}{M} = \frac{\sigma}{K_s} + \phi \left(\frac{1}{K_f} - \frac{1}{K_\phi} \right). \tag{5}$$

The heat capacity at constant pressure for the fluid is $c_p^{(f)}$ and for the composite frame is c_p , while the ambient temperature is θ_0 . The first equation in (4) is just a restatement of (1). The second equation follows immediately from (2) and (3). The third equation follows from the definition of the entropy^{8,9} and reciprocity, since the matrix in (4) must be both symmetric and nonnegative.

Now the unjacketed modulus can be related to the thermal expansion coefficient and the constituents' properties. Suppose a composite porous medium is composed of two types of porous solid (A,B) occupying volume fractions $v_A = V^{(A)}/V$ and $v_B = V^{(B)}/V$, respectively. The porosities of these two constituents are $\phi^{(A)}$ and $\phi^{(B)}$, at least one of which must be nonzero and composed of connected pores. The drained frame moduli of the constituents are $K^{(A)}$ and $K^{(B)}$, while the material (or grain) moduli are $K^{(A)}_m$ and $K^{(B)}_m$. The thermal expansion coefficients of the constituent grains (and therefore also of the frames and pores) are $\alpha^{(A)}$ and $\alpha^{(B)}$. The heat capacities at constant pressure for the constituents are $c_p^{(A)}$ and $c_p^{(B)}$. These two constituents may not fill up the entire volume, so the volume fraction of cracks or voids is given by $v_C = 1 - v_A - v_B$. Consider the gedanken experiment in the unjacketed, nonisothermal configuration ($\delta p_d \equiv 0, \delta \theta \neq 0$) such that the relative change in the volumes $V^{(A)}, V^{(B)}$ of the constituents are the same and therefore also equal³ to that of the total volume V. Then, we have the set of equalities

$$-\frac{\delta V}{V} = \frac{\delta p_f}{K_s} - 3\alpha \delta \theta$$

$$= \frac{\delta p_f}{K_m^{(A)}} - 3\alpha^{(A)} \delta \theta$$

$$= \frac{\delta p_f}{K_m^{(B)}} - 3\alpha^{(B)} \delta \theta.$$
(6)

It follows that these equalities are satisfied if the changes of these fields have the ratio

$$3\frac{\delta\theta}{\delta p_f} = \frac{1/K_m^{(A)} - 1/K_m^{(B)}}{\alpha^{(A)} - \alpha^{(B)}} = \frac{1/K_s - 1/K_m^{(B)}}{\alpha - \alpha^{(B)}}$$
$$= \frac{1/K_m^{(A)} - 1/K_s}{\alpha^{(A)} - \alpha}.$$
 (7)

These relations determine K_s in terms of α together with the constituents' moduli $K_m^{(A)}, K_m^{(B)}$ and thermal expansion coefficients $\alpha^{(A)}, \alpha^{(B)}$. If the bulk moduli of the constituents are the same so $K_m^{(A)} = K_m^{(B)}$, then clearly the unjacketed modulus satisfies $K_s = K_m^{(A)}$ regardless of the values of the thermal expansion coefficients.

For the combination of δp_f and $\delta \theta$ given by (7), the porosity of the composite does not change. In fact, changes in p_f and θ do not induce changes in porosity for either constituent

and, since the overall deformation takes the form of uniform swelling or shrinking, ϕ is constant. Thus,

$$-\frac{\delta\phi}{\phi} = \left(\frac{1}{K_{\phi}} - \frac{1}{K_{s}}\right) \delta p_{f} - 3\left(\alpha_{\phi} - \alpha\right) \delta\theta \equiv 0. \tag{8}$$

Combining the result (7) with (8), we find

$$\frac{1}{K_{\phi}} = \frac{1}{K_s} + (\alpha_{\phi} - \alpha) \left(\frac{1/K_m^{(A)} - 1/K_m^{(B)}}{\alpha^{(A)} - \alpha^{(B)}} \right). \tag{9}$$

In the limit of equal constituent bulk moduli, it is again clear that $K_{\phi} = K_s = K_m^{(A)} = K_m^{(B)}$ regardless of the values of the α s. The result (9) could also have been obtained by noting that $\delta \zeta$ in (4) equals the volume average of the fluid increments in the three types of constituents. Although instructive, this approach is much less efficient at producing the desired result (9) than the derivation presented here.

The increment of entropy δs may also be computed as the average of the constituent entropies. Using this approach, we find that the effective heat capacity c_p of the porous frame is determined by

$$c_p = \langle c_p \rangle_s + 9\theta_0 \left[(\alpha - \phi \alpha_\phi) / (1 - \phi) - \langle \alpha \rangle_s \right] \left(\frac{\alpha^{(A)} - \alpha^{(B)}}{1/K_m^{(A)} - 1/K_m^{(B)}} \right), \tag{10}$$

where the average $\langle \cdot \rangle_s$ is over the solid volume so, for example,

$$\langle c_p \rangle_s = \left[v_A (1 - \phi^{(A)}) c_p^{(A)} + v_B (1 - \phi^{(B)}) c_p^{(B)} \right] / (1 - \phi).$$
 (11)

Note that (10) reduces correctly to the result of Rosen and Hashin¹⁰ when the porosity $\phi \to 0$. Various other exact results may be obtained using standard arguments from thermodynamics. For example, consider the limit of constant total volume ($\delta e = 0$) when the porous frame is drained of fluid. Then, it is easy to show that the heat capacity at constant volume is given by $c_v = c_p - 9\alpha^2 K\theta_0/(1-\phi)$, reducing to the standard result when $\phi \to 0$. This expression and the equivalent results for the constituent heat capacities $c_v^{(A)}$ and $c_v^{(B)}$ may be used to eliminate the c_p s in (11), thereby producing an exact expression for c_v in terms of constituent properties. Similarly, considering the adiabatic ($\delta s = 0$) limit when the frame is drained of fluid, shows that the adiabatic bulk modulus of the porous frame is $K_a = Kc_p/c_v$. Once exact results are available for all these constants, then the Grüneisen parameter $\gamma = 3\alpha K/c_v$ may also be computed for the composite porous medium.

Two other results may be obtained in the undrained (and confined $\delta\zeta = 0$), isothermal $(\delta\theta = 0)$ limit. The undrained bulk modulus⁴ is easily shown to be $K_u = K/(1 - \sigma B)$ and the undrained thermal expansion coefficient⁷ is $\alpha_u = \alpha + \phi(\alpha_f - \alpha_\phi)B$, where the factor B, given by $B = \sigma M/(K + \sigma^2 M)$, is known as Skempton's coefficient.¹¹

Using data from Refs. 12–14, some examples of typical values of the bulk moduli and thermal expansion coefficients of minerals and metals are presented in Tables I and II. These values are used to evaluate the inverse of the ratio in (7) for some pairs of minerals in Table III. We see that this factor can have either sign. Recalling that $1 \text{ GPa} = 1 \text{ kJ/cm}^3$ and assuming that the

difference $(\alpha_{\phi} - \alpha) \simeq \pm 5 \times 10^{-7} \, {}^{\circ}K^{-1}$, the correction to the pore bulk modulus $(1/K_{\phi} - 1/K_s)$ can be negligible or it can be of the same order of magnitude as the unjacketed compressibility $1/K_s$. Thus, the importance of this correction term is strongly problem dependent. On the other hand, the correction to the specific heat $(c_p - \langle c_p \rangle_s)$ is of about the same order as the difference $(c_p - c_v)$ and therefore generally negligible.

It is difficult to make any further quantitative progress until some of the remaining unknowns in the equations such as α, α_{ϕ} , or K_{ϕ} have been measured.

The results (7), (9), and (10) apply generally to two- component composite porous media with or without additional voids or cracks present. The authors' earlier exact results³ for K_s and K_{ϕ} in terms of the frame and grain moduli of the components are valid only when these constituents are volume filling, so no additional voids or cracks were allowed. Thus, both sets of formulas are valid in the absence of extra voids and cracks and, therefore, additional relations between the various bulk moduli and the thermal expansion coefficients follow easily from the results presented here in this special case.

Another advantage of the new formulas is that the key ratio found in (7) depends only on material constants K_m and α (that are commonly tabulated for minerals, metals, etc.) and – most importantly – have no dependence on the porosity. By contrast, the earlier formulas³ depend on the frame moduli of the porous constituents, which depend implicitly on the porosities and therefore are more difficult to tabulate.

We thank H. F. Wang for comments that suggested initiation of this work. Berryman's work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48 and supported specifically by the Geosciences Research Program of the DOE Office of Energy Research within the Office of Basic Energy Sciences, Division of Engineering and Geosciences. Milton's work was performed with support from the Air Force Office of Scientific Research through grant AFOSR 90-0090, from the Army Research Office through grant DAAL 03-89-K-0039, and from a Packard Fellowship.

References

- [1] J. L. Cribb, Nature **220**, 576 (1968).
- [2] K. Schulgasser, J. Material Sci. Lett. 8, 228 (1989).
- [3] J. G. Berryman and G. W. Milton, Geophysics 56, 1950 (1991).
- [4] F. Gassmann, Veirteljahrsschrift der Naturforschenden Gesellschaft in Zürich 96, 1 (1951).
- [5] R. J. S. Brown and J. Korringa, Geophysics 40, 608 (1975).
- [6] D. H. Green and H. F. Wang, Geophysics 51, 948 (1986).
- [7] D. F. McTigue, J. Geophys. Res. 91, 9533 (1986).
- [8] M. A. Biot, J. Appl. Phys. 27, 240 (1956).
- [9] R. M. Christensen, Mechanics of Composite Materials (Wiley, New York, 1979), Chapter IX, pp. 311-339.
- [10] B. W. Rosen and Z. Hashin, Int. J. Engng. Sci. 8, 157 (1970).
- [11] A. W. Skempton, Geotechnique 4, 143 (1954).
- [12] Y. Sumino and O. L. Anderson, in *CRC Handbook of Physical Properties of Rocks*, Vol. III, R. S. Carmichael (ed.), CRC Press, Boca Raton, Florida, 1982, Chapter 2, pp. 39–137.
- [13] R. A. Robie, B. S. Hemingway, and J. R. Fisher, Thermodynamic Properties of Minerals and Related Substances at 298.25 K and 1 Bar (10⁵ Pascals) Pressure and at Higher Temperatures, Geological Survey Bulletin 1452, Washington, 1978, pp. 1-456.
- [14] N. F. Mott and H. Jones, The Theory of the Properties of Metals and Alloys (Dover, New York, 1956), pp. 318-319.

Table I. Density, isothermal bulk moduli, linear thermal expansion coefficients, and heat capacities of various minerals at 20°C. Data from refs. 12 and 13.

Mineral	Formula	$\rho \; (\mathrm{g/cm^3})$	K_m (GPa)	$\alpha \ (^{\circ}\mathrm{K}^{-1})$	$c_p (\mathrm{J/g^\circ K})$
				$\times 10^{-6}$	
Corundum	${ m Al_2O_3}$	3.987	263.2	5.4	0.775
Lime	${f CaO}$	3.345	113.6	12.7	0.751
Microcline	$\mathrm{KAlSi_3O_8}$	2.560	52.1	5.3	0.727
lpha-Quartz	${ m SiO}_2$	2.648	37.1	11.7	0.742

Table II. Density, isothermal bulk moduli, linear thermal expansion coefficients, and specific heats of various metals at 25°C and a pressure of 100 kPa. Data from refs. 13 and 14.

Metal	Formula	$\rho \; (\mathrm{g/cm^3})$	K_m (GPa)	$\alpha \ (^{\circ} \mathrm{K}^{-1})$	$c_p \ (\mathrm{J/g^\circ K})$
				$\times 10^{-6}$	
Iron	${ m Fe}$	7.87	166.7	11.8	0.449
Nickel	m Ni	8.91	185.2	13.4	0.444
Copper	$\mathrm{C}\mathbf{u}$	8.93	133.3	16.5	0.385
Silver	Ag	10.50	99.0	18.9	0.235

Table III. Ratios of fluid pressure and temperature change [see Eq. (7)] resulting in uniform expansion or contraction for various pairs of minerals. Values used are those displayed in Tables I and II.

Mineral Pairs	$rac{1}{3}\delta p_f/\delta heta \ (\mathrm{J/cm}^3\cdot \mathrm{^\circ K})$
$\mathrm{SiO}_2/\mathrm{Al}_2\mathrm{O}_3$	0.272
$\mathrm{SiO}_2/\mathrm{CaO}$	- 0.055
$\mathrm{SiO}_{2}/\mathrm{KAlSi}_{3}\mathrm{O}_{8}$	0.825
Cu/Ag	- 0.923
Fe/Ni	- 2.592
Ni/Cu	1.475