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STRESS RELAXATIONS AT LOW FREQUENCIES IN FLUID-SATURATED ROCKS

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Abstract - A new laboratory apparatus measures the complex Young's modulus of rock samples at frequencies between 4 and 400 Hz and at strain amplitudes near $10^{-7}$. There is negligible attenuation and modulus dispersion in vacuum-dry rocks. In water-saturated samples of sandstone, limestone, and granite there are large attenuation peaks which are caused by stress relaxations. The attenuation and modulus data can be described by Cole-Cole distributions of relaxation times. The stress relaxations occur at low frequencies, have narrow distributions of characteristic times, are thermally activated, and have activation energies (16-22 kJ/mol) which are characteristic of hydrogen bonds. The modulus defect and peak attenuation are shown to vary with different pore fluids (water, ethanol, and n-decane). The results are explained in terms of the pore fluids lowering the surface free energy of the rock-forming minerals.

Introduction

An assumption is frequently made in geophysics that acoustic wave velocities and attenuations are nearly constant over a wide frequency range (1 Hz-1 MHz). A new apparatus was designed to measure Young's modulus and $Q^{-1}$ over a range of frequencies, including the frequencies used in seismic exploration, in order to look for frequency-dependent moduli and attenuation. Measurements were needed at strain amplitudes less than $10^{-6}$, where attenuation is linear and the results are relevant to wave propagation away from the seismic source. Earlier work by Gordon and Davis (3) and Tittmann et al. (6) had shown that trace amounts of water can dramatically increase the attenuation in rocks and lower their moduli. Identifying stress relaxations in fluid-saturated rocks answers longstanding questions concerning their anelasticity.

Experimental

The apparatus (Figure 1) directly measures the phase angle between stress and strain at selectable frequencies between 4 and 400 Hz and at strain amplitudes near $10^{-7}$. The rock sample (38 mm diameter and ~140 mm length) is epoxied between steel end plates. An electromagnetic shaker applies an axial force (<10 N) to the sample; a piezoelectric transducer (PCB 208A) measures the applied force while a capacitive displacement transducer (Ade 2101/2001K) monitors the sample deformation. The two signals are digitized and stacked in real-time in a Nicolet 1174 signal averager.
The resulting time series are transferred to an HP 9845B computer, which uses a Fourier series analysis to calculate the amplitude and phase of each signal. These data and instrument calibrations are used to calculate stress, strain, Young's modulus and $Q^{-1}$. See Spencer (5) for details.

The system is calibrated by measuring high-$Q$ materials (aluminum and high-density carbon). Phase angles are normally accurate and repeatable to $\pm 0.1^\circ$, corresponding to an accuracy of $\pm 0.002$ in $Q^{-1}$. The accuracy of Young's modulus, being limited primarily by the accuracy of the displacement measurement ($\pm 1\%$ or $\pm 3.10^{-10}$ m, whichever is larger), is $\pm 2\%$ in stiff materials like aluminum or igneous rocks and $\pm 1\%$ in most sedimentary rocks.

Results

Results are shown for Navajo sandstone, a clean, silica-cemented, quartzose sandstone with only traces of authigenic illite. The effects of clay minerals are minimized but not totally eliminated in this rock. The sample was dried in a vacuum (25 $\mu$m Hg) at 25°C, while being periodically flushed with argon. This gave a reproducible condition of dryness where there is essentially no physisorbed water. It was then vacuum- and pressure-saturated with different pore fluids. All measurements were made on a jacketed sample at atmospheric confining pressure.

Young's modulus is independent of frequency ($E = 38.4 \pm 0.2$ GPa) in dry Navajo sandstone (Figure 2), and there is negligible attenuation. There is a strong dispersion in Young's modulus and a large attenuation peak when the sample is water-saturated. The results can be described as a stress relaxation; the attenuation peak is narrow and the characteristic relaxation times are very long. A Cole-Cole distribution of relaxation times closely matches the attenuation and modulus data. The real and imaginary parts of Young's modulus are given by

$$E' = E_o + \frac{1}{2}(E_\infty - E_o) \left[ 1 - \frac{\sinh((1-\alpha)x)}{\cosh((1-\alpha)x) + \sin \frac{1}{2} \alpha \pi} \right]$$

$$E'' = \frac{1}{2}(E_\infty - E_o) \cos \frac{1}{2} \alpha \pi \frac{\cosh((1-\alpha)x) + \sin \frac{1}{2} \alpha \pi}{\cosh((1-\alpha)x) + \sin \frac{1}{2} \alpha \pi}$$

where $x = \ln \omega T_o$. The parameters for each relaxation are determined by best-fitting a Cole-Cole solution to the laboratory data. The relaxation parameters are compiled in Table 1.

When it was recognized that there is a stress relaxation in Navajo sandstone, the temperature was lowered from 25°C to 4°C in order to determine whether the relaxation is thermally activated. Lowering the temperature simply shifts the relaxation to a lower frequency. The activation energy ($16.3 \pm 2.5$ kJ/mol) is estimated using
the Arrhenius equation. This energy is very low and is characteristic of hydrogen bonds. The stress relaxation apparently involves a process in which hydrogen bonds are broken. The low activation energy precludes any process in which a significant number of solid-solid bonds are broken.

<table>
<thead>
<tr>
<th>Material</th>
<th>Saturant</th>
<th>T, °C</th>
<th>E₀, GPa</th>
<th>E∞, GPa</th>
<th>f₀, Hz</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Navajo sandstone</td>
<td>water</td>
<td>25</td>
<td>14.0 ± 0.1</td>
<td>28.5 ± 0.2</td>
<td>700 ± 25</td>
<td>0.22 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>25</td>
<td>14.0 ± 0.1</td>
<td>28.5 ± 0.5*</td>
<td>1150 ± 50</td>
<td>0.22 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>ethanol</td>
<td>25</td>
<td>26.75 ± 0.05</td>
<td>38.8 ± 0.6</td>
<td>1000 ± 100</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>n-decane</td>
<td>25</td>
<td>34.0 ± 0.05</td>
<td>34.6 ± 0.05</td>
<td>7 ± 2</td>
<td>0.03 ± 0.03</td>
</tr>
<tr>
<td>L.lgH₂O</td>
<td>25</td>
<td>14.8 ± 0.1</td>
<td>28.8 ± 0.2</td>
<td>6500 ± 200</td>
<td>0.54 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>

*Assumed from results at 4°C.

Clark et al. (2) showed that $Q_E$ is sharply reduced by the adsorption of a few monolayers of water or ethanol but that benzene or n-hexane has little effect until the partial pressure $P/P_0$ reaches 0.9. In order to examine the effects of different pore saturants, the Navajo sample was vacuum dried and then successively saturated with distilled water, anhydrous ethanol (0.06 wt% H₂O), and n-decane (<20 ppm H₂O). These fluids have similar densities and viscosities; so, other things remaining equal, the attenuation should be nearly the same if the dominant mechanism involves primarily inertial and/or viscous effects. However, they have very different chemical, electrochemical, and dielectric properties.

There is a stress relaxation with each pore fluid (Figure 3), the attenuation peaks are all narrow and have approximately the same center frequency, but the magnitudes of the relaxations and the attenuation peaks increase in the order n-decane < ethanol < water. The unrelaxed modulus in the decane- and ethanol-saturated conditions is the same as in the vacuum-dry condition. Saturation with water, however, reduces the high-frequency modulus below the value in the dry sample. There appears to be a weak relaxation near 7 Hz in the decane-saturated rock. These results cannot be explained in terms of fluid-mechanical models which include only the viscous or inertial effects of the pore fluid.

A simple experiment showed that a small amount of water, distributed throughout the rock, can reduce the stiffness nearly as much as full saturation does. The Navajo sandstone was initially vacuum-dried and then was allowed to equilibrate for 28 days in 100% relative humidity air. The sample imbibed only 1.10 gm H₂O, corresponding to less than 7% of the pore volume, but $E_0$ and $E_\infty$ are nearly the same as in the water-saturated condition (Figure 4). However, the center frequency is higher in the moistened rock, and there is a broader distribution of relaxation times.

I have observed stress relaxations near 2 kHz in four quartz-rich rocks (Navajo sandstone, Oklahoma granite, Berea sandstone and Massilon sandstone). There is a
suggestion that the similar relaxation frequencies are due to the commonality of the rock-forming minerals and the pore fluid, rather than any details of the rock fabric, pore geometry or permeability. I have also observed a stress relaxation near 17 Hz in Spergen (Indiana) limestone.

Discussion

The laboratory measurements show that there are stress relaxations in fluid-saturated rocks and that the relaxations have the following characteristics:

1. They occur slowly (0.5-100 ms) and with narrow distributions of relaxation times.
2. The relaxations are thermally activated and have low activation energies (16-22 kJ/mol).
3. The modulus defect is large with water, but relaxations occur even with non-polar fluids.
4. A small amount of water can reduce the stiffness as much as full saturation does, but the relaxation times are then shorter and more broadly distributed.

These observations severely limit possible interpretations, and I am unaware of any model in the literature which is consistent with all of them. I will now outline a process for the stress relaxations which is consistent with all the laboratory data. Further work is needed to clarify the mechanism and the details of the surface chemistry.

The results are explained in terms of the pore fluids lowering the surface free energy of the rock-forming minerals. A low-amplitude sinusoidal stress causes strain and generates infinitesimal increments of surface area throughout the rock sample. An insignificant number of solid-solid bonds are broken; otherwise the activation energy would be higher. Martin (4) determined an activation energy of 109 kJ/mol for water-assisted crack growth in quartz. The relaxation process involves the movement of adsorbed molecules to the active deformation sites. The molecules, by bonding to the surface, reduce the surface free energy and thus generate the frequency-dependent softening in the rock.

The relaxation data with different pore fluids (Figure 3) can be compared quantitatively with available thermodynamic data. Van Voorhis et al. (7) determined the reduction in surface free energy, $\gamma_{SO} - \gamma_{SL}$, when silica is immersed in water (139 mJ/m$^2$), ethanol (110 mJ/m$^2$), n-hexane (28 mJ/m$^2$), and n-heptane (29 mJ/m$^2$); n-decane is assumed to behave like n-hexane and n-heptane. The surface free energy of silica in vacuum, $\gamma_{SO}$, is taken as 280 mJ/m$^2$ [see Brunauer et al. (1)]. I have plotted (Figure 5) the fractional reduction in Young's modulus $(E_\infty - E_0)/E_\infty$ for the relaxations in Figure 3 versus the fractional reduction in surface energy $(\gamma_{SO} - \gamma_{SL})/\gamma_{SO}$.
when silica is immersed in the three fluids. The observed correlation suggests that the relaxation is intimately connected with the reduction in surface energy.

The other laboratory results are logical consequences of this process. A small amount of water, distributed by surface forces so as to minimize the surface free energy, should reduce the stiffness nearly as much as full saturation does. The distributions of relaxation times are narrow, suggesting that the relaxations are caused by fundamental, molecular interactions. The distributions would presumably be broader if geometrical factors like the pore size and shape were important. It is also reasonable that the relaxation times are so long. They are similar to the times for dielectric (Debye) relaxation of polar molecules in the first few monolayers. However, stress relaxations differ from dielectric relaxations. A typical Debye relaxation requires a polar molecule, while a stress relaxation does not. Also, the center frequencies of the two relaxations shift in opposite directions as the fluid film becomes thinner. The frequency of the Debye relaxation drops because the polar molecules are held more tightly to the surface. The fact that the stress relaxation shifts to a higher frequency suggests a different mechanism involving the movement of molecules.

Conclusions

Stress relaxations occur at low frequencies in fluid-saturated samples of sandstone, limestone and granite. The narrow relaxations cause attenuation and modulus dispersion, in agreement with the Kramers-Kronig integral relations. The relaxations probably occur primarily in the shear modulus. There can be multiple relaxations in a single sample. Stress relaxations occur with different pore fluids, and the relaxation process apparently involves the movement of adsorbed molecules. The molecules, by bonding to the surface, reduce the surface free energy and thus generate frequency-dependent softening in the rock. There is negligible attenuation and modulus dispersion in vacuum-dry rocks.

References

(1) S. Brunauer et al.: Can. J. Chem. 34, 1483, 1956
(2) V. A. Clark et al.: J. Geophys. Res. 85, 5190, 1980
(4) R. J. Martin: J. Geophys. Res. 77, 1406, 1972
(7) J. J. Van Voorhis et al.: J. Phys. Chem. 61, 1513, 1957
Fig. 1. Section through the laboratory apparatus. Indicated are the rock sample (A), force transducer (K), displacement transducer (C), electromechanical shaker (D), shaker table (E), load cell (B), load plate (I), clamping rings (K), fixture for the displacement transducer (L), and flexible rubber jacket (M).

Fig. 2. Young's modulus and \( \frac{1}{Q_E} \) in vacuum-dry and water-saturated Navajo sandstone. The stress relaxation in the water-saturated rock shifts with temperature.

Fig. 3. Stress relaxations in Navajo sandstone when the same sample is saturated with distilled water, ethanol, or n-decane.

Fig. 4. A small amount of water, distributed throughout the rock, reduces the stiffness of Navajo sandstone as much as full saturation does. The center frequency of the stress relaxation is higher in the moistened rock, and there is a broader distribution of relaxation times.

Fig. 5. The fractional reduction in Young's modulus, for the relaxations in Figure 3, versus the fractional reduction in surface free energy when silica is immersed in the three fluids. The relaxation process appears to involve the reduction in surface energy.