



Dielectric relaxation under pressure in granular dielectrics containing water: Compensation rule for the activation parameters

A.N. Papathanassiou*, I. Sakellis, J. Grammatikakis

University of Athens, Physics Department, Section of Solid State Physics, Panepistimiopolis, GR 15684 Zografos, Athens, Greece

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ABSTRACT

The dielectric relaxation of water-filled granular dielectrics under hydrostatic compression is investigated in the frequency domain. The activation volume and activation enthalpy governing a dominant relaxation mechanism of sandstone partially saturated with water are determined experimentally for the first time. The present results combined with recently published results for various wetted porous dielectrics indicate that, despite the complexity of this class of matter, such as heterogeneity of composition and micro-structural landscape and their disordered environment, a compensation rule between the absolute value of the activation volume and enthalpy is likely to be valid. The proportionality constant is determined by the isothermal bulk modulus and its pressure derivative, according to an earlier thermodynamic elastic model.

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1. Introduction

The dielectric properties of porous matter (fully or partially) filled with fluids (such as water or solutions) has been the subject of fundamental and applied research during the last decades. Intense polarization phenomena inducing huge values of the dielectric constant were detected through broadband complex impedance spectroscopy [1–4] and high-resolution thermally stimulated current (TSC) spectroscopy [5,6]. The dielectric constant of these systems is very different from the values of the individual phases, respectively. Theoretical approaches emphasize the electrochemical interaction between the solid and liquid phase, and on the double-layer polarization [7]. While pure research efforts focus on understanding the correlations in complex heterogeneous systems, there is considerable interest in diverging fields of applied science: For example, large dielectric constant materials are highly desirable in materials science for microelectronic applications, wetting and hydration determine the efficiency of industrial sensors or catalysts for chemical reactions. Moreover, in the field of geophysics, the knowledge of the dielectric properties of rocks saturated with water can provide valuable information toward understanding electric signals emitted in the earth's crust, in oil exploration [8].

Recently, experimental research was carried out investigating the effect of hydrostatic pressure on the dielectric relaxation of water-saturated granular dielectrics. By varying the pressure, novel information is gained on the dynamics of complex systems [9]. It was found that some

water-filled rocks exhibit dielectric relaxation mechanisms that are characterized by negative values of the activation volume. At the same time there is no physical restriction on the sign of the activation volume [10,11]. As it will be clarified in the next section the activation volume is actually a dynamic volume (or fluctuation volume) and may either have positive or negative sign. Negative activation volumes are very rarely found in the solid state. To the best of our knowledge, negative activation volume for dielectric relaxation has been found in β -PbF₂ crystals doped with impurities [12], in semi-conducting polypyrrole [13,14] and for ionic conductivity in β -AgI (B4-phase) under pressure [15,16]. In the present work we report novel results on the dielectric relaxation of sandstone saturated with water at various temperatures and pressures, which is a prototype granular silicate granular dielectric. Natural or artificially synthesized sandstone is a typical porous material used very often for experimental work [1,2,5,6,17–20]. The present results, together with some results of our laboratory that were recently published probably suggest a universal compensation rule interconnecting the activation volume with the activation enthalpy in water filled granular materials. The proportionality constant is established by the thermodynamic elastic model proposed by Varotsos and Alexopoulos [10].

2. Theoretical concepts

Dielectric relaxation is characterized by the dielectric relaxation time τ , which is a phenomenological quantity. Adopting the rate theory, the relaxation time is linked to microscopic quantities according to the next equation:

$$\tau(P, T) = (\lambda\nu)^{-1} \exp\left(g^{act}/k_B T\right) \quad (1)$$

* Corresponding author. Tel./fax: +30 2107276729.

E-mail addresses: antpapa@phys.uoa.gr (A.N. Papathanassiou), e_sakel@phys.uoa.gr (I. Sakellis).

where ν is the vibration frequency of the relaxing charge carrier, λ is a geometrical constant, g^{act} is the Gibbs activation energy for relaxation, T denotes the absolute temperature and k_B is the Boltzmann's constant. Note that all thermodynamic quantities appearing in this paper are related to relaxation or, alternatively, to the localized motion of the electric charge entities that form the relaxing 'dipoles'. Taking the thermodynamic definition $g^{act} = h^{act} - Ts^{act}$, where h^{act} and s^{act} are the activation enthalpy and entropy, respectively, and differentiating Eq. (1) with respect to $(k_B T)^{-1}$, at constant pressure, we get:

$$(\partial \ln \tau / \partial (1/k_B T))_P = h^{act} \quad (2)$$

provided that the term $\ln(\lambda \nu) + (s^{act}/k_B)$ is practically constant; the later constrain indicates that the empirical Arrhenius law describes the temperature dependence of the relaxation time. Alternatively, by differentiating the above equation with respect to pressure at constant temperature, we get:

$$(\partial \ln \tau / \partial P)_T = -\frac{\gamma}{B} + \frac{v^{act}}{k_B T} \quad (3)$$

where $\gamma \equiv -(\partial \ln \nu / \partial \ln V)_T$ is the Grüneisen constant (V denotes the volume), $B \equiv -(\partial P / \partial \ln V)_T$ is the isothermal bulk modulus and $v^{act} \equiv (\partial g^{act} / \partial P)_T$ is the activation volume.

Relaxation processes can be studied in the frequency domain through a proper dielectric function such as the tangent loss angle function $\tan \delta \equiv \text{Im}(\epsilon) / \text{Re}(\epsilon)$, where $\text{Im}(\epsilon)$ and $\text{Re}(\epsilon)$ are the imaginary and the real part of the (relative) complex permittivity ϵ (reduced to its value of free space). For a Debye relaxation, the latter dielectric function exhibits a maximum at frequency $f_{\max, \tan \delta} = \sqrt{\epsilon_s / \epsilon_\infty} / (2\pi\tau)$, where τ the relaxation time (Eq. (1)), ϵ_s and ϵ_∞ denote the static and high-frequency (relative) permittivity, respectively. The partial derivatives of the natural logarithm of the last relation with respect to reciprocal temperature and pressure, respectively, gives:

$$(\partial \ln \tau / \partial (1/k_B T))_P = \frac{1}{2} (\partial \ln(\epsilon_\infty / \epsilon_s) / \partial (1/k_B T))_P - (\partial \ln f_{\max, \tan \delta} / \partial (1/k_B T))_P \quad (4a)$$

$$(\partial \ln \tau / \partial P)_T = \frac{1}{2} (\partial \ln(\epsilon_\infty / \epsilon_s) / \partial P)_T - (\partial \ln f_{\max, \tan \delta} / \partial P)_T \quad (4b)$$

Eqs. (2) and (4a), as well as Eqs. (3) and (4b) direct to:

$$h^{act} = \frac{1}{2} (\partial \ln(\epsilon_\infty / \epsilon_s) / \partial (1/k_B T))_P - (\partial \ln f_{\max, \tan \delta} / \partial (1/k_B T))_P \quad (5a)$$

$$v^{act} = k_B T \left\{ \frac{\gamma}{B} + \frac{1}{2} (\partial \ln(\epsilon_\infty / \epsilon_s) / \partial P)_T - (\partial \ln f_{\max, \tan \delta} / \partial P)_T \right\} \quad (5b)$$

We stress that Eqs. (4b) and (5b) presume an Arrhenius temperature dependence of τ [21].

Dispersions broader than the Debye one can be described by various empirical functions. The connection of $f_{\max, \tan \delta}$ with the dielectric relaxation time τ is given by $f_{\max, \tan \delta} = \frac{(\epsilon_s / \epsilon_\infty)^{\frac{1}{2x}}}{2\pi\tau}$, where x coincides with 1, α , β or γ for the Debye, Cole–Cole (CC), Kohlrausch–Williams–Watts (KWW) and Cole–Davidson (CD) cases, respectively [22,23]. h^{act} and v^{act} are obtained through Eqs. (5a) and (5b), provided that $1/2$ is replaced with $1/2x$.

3. Experimental details

Sandstone of known composition and porosity, which was earlier studied in a previous work through TSC spectroscopy [5], was employed in the present study. The composition of the sandstone is: 40 wt.% quartz, 10 wt.% amphibolite and pyroxene, 6 wt.% glimmer

mica, 16 wt.% feldspars, and 26 wt.% calcite. The porosity, obtained by optical microscopy on thin sections, was about 0.11. Samples of thickness ranging from 1 to 2 mm and parallel surfaces of about 1–2 cm² were placed inside the pressure vessel, which uses silicone oil as the pressure transmitting fluid, of a Novocontrol (Germany) high pressure apparatus operating from ambient pressure to 0.3 GPa and thermostated at the desired temperature, from room temperature to 373 K. Silver paste (Granville) was placed on the parallel opposite surfaces of the specimen to achieve good contact between the metallic electrodes and the sample. A very thin insulating layer of epoxy covered the specimen to prevent contamination from the pressure transmitting fluid [13,24–27]. Note that the manufacturer of the pressure vessel suggested independently the use of epoxy layer in order to jacket the sample. The pressure system was connected with an HP impedance analyzer operating from 10⁻² to 10⁶ Hz. Measurements in the frequency domain were monitored by a computer. The samples were immersed and kept in distilled water at 363 K for one week. Continuous weighting during the water-saturation process shows that saturation was achieved in two days. The advantage of water-saturation at elevated temperature is the expansion of the specimen and the subsequent dilation of the pore cavities which assists diffusion of water molecules. By weighting the sample before and after the wetting process we found that the hydrated rock accommodates about 0.24 wt.% water.

4. Results and discussion

Typical isothermal plots $\tan \delta$ as a function of frequency f at various pressure values are depicted in Fig. 1. A well-defined relaxation peak shifts toward lower frequency on compression, indicating that pressure reduces the relaxation time. The variation of $\ln f_{\max, \tan \delta}$ upon P (inset of Fig. 1) seems to obey a linear law. The low and high frequency limits of $\text{Re}(\epsilon)$ at various pressures (having typical values of $\epsilon_s \approx 2 \times 10^5$ and $\epsilon_\infty \approx 38$ at $T = 313$ K and $P = 300$ MPa) give $(\partial \ln(\epsilon_\infty / \epsilon_s) / \partial P)_T \approx 0.86 \text{ GPa}^{-1}$. A linear fit to the datum points

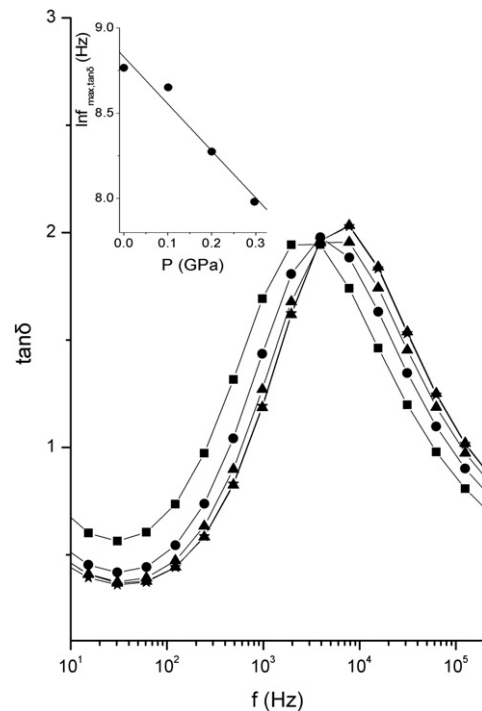


Fig. 1. Isotherms ($T = 277$ K) of $\tan \delta$ vs frequency of water-filled sandstone at various pressures: 0.1 MPa (stars), 100 MPa (triangles), 200 MPa (circles) and 300 MPa (squares). Inset: Variation of $f_{\max, \tan \delta}$ upon P . The straight line is the best fit to the datum points.

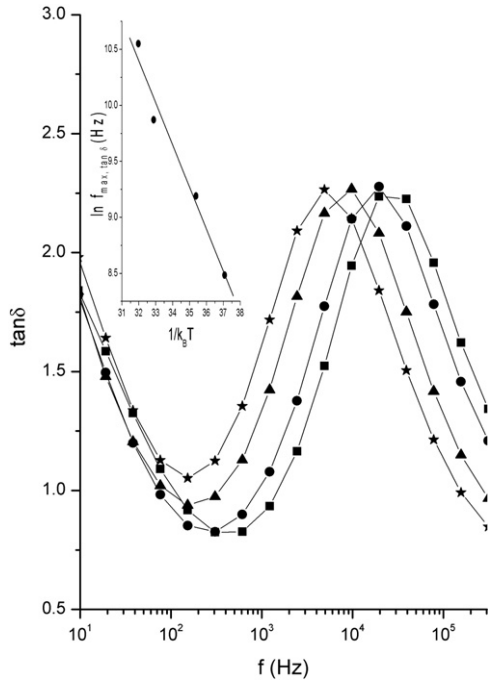


Fig. 2. Temperature dependence of $\tan \delta$ vs frequency plots: 313 K (stars), 328 K (triangles), 353 K (circles) and 363 K (squares). Inset: variation of $f_{\max, \tan \delta}$ upon $1/k_B T$. The straight line is the best fit to the datum points.

shown in the inset of Fig. 1 gives $(\partial \ln f_{\max, \tan \delta} / \partial P)_T = (2.3 \pm 0.6) \text{ GPa}^{-1}$. Eq. (5b) yields $v^{act} = (7 \pm 1) \text{ cm}^3/\text{mol}$. As mentioned in Section 2, the extraction of the activation volume presumes an Arrhenius temperature dependence of the relaxation time, which is true because in Fig. 2, where $\tan \delta(f)$ isobars collected at various temperatures are presented. We see that the relaxation peak shifts to higher frequency on increasing the temperature. The variation of $\ln f_{\max, \tan \delta}$ vs reciprocal temperature (inset of Fig. 2) is approximately linear and actually provides a constant value for $(\partial \ln f_{\max, \tan \delta} / \partial (1/k_B T))_P = -(0.37 \pm 0.04) \text{ eV}$ and an intercept $\ln f_{\max, \tan \delta}(T \rightarrow \infty) = (22 \pm 1)$. On the other hand, the low and high frequency limits of $\text{Re}(\epsilon)$ vs frequency at various temperatures gives $(\partial \ln(\epsilon_\infty/\epsilon_s) / \partial (1/k_B T))_P \approx 0.004 \text{ eV}$. Hence, Eq. (5a) yields the thermodynamic quantity of the activation enthalpy $h^{act} = (0.37 \pm 0.04) \text{ eV}$. Defining $f_{\max, \tan \delta}(T \rightarrow \infty) \equiv (2\pi\tau_{0, \tan \delta})^{-1}$ and using the intercept value given above, we get $\tau_{0, \tan \delta} = 0.3 \pm 0.5 \text{ ns}$, which provides an estimate for the pre-exponential factor of an Arrhenius-dependent dielectric relaxation time $\tau_0 \approx 10^{-12} \text{ s}$.

We note that the values of v^{act} and h^{act} were estimated by Eqs. (5a) and (5b) respectively, which refer to a Debye relaxation. Actually, the recorded peaks are somewhat broader than the Debye ones: for instance, the Kohlrausch–Williams–Watts (KWW) gives

$\beta \approx 0.8$. If someone reasonably assumes that both the dielectric relaxation time and the effective $\tan \delta$ relaxation time are described by a common KWW function and a corresponding common value β , and uses the modified equations suggested at the last paragraph of Section 2, the correction to v^{act} and h^{act} is within the experimental errors and it is therefore practically negligible.

The complexity of the system makes it difficult to identify the relaxation mechanism in water-saturated sandstone. It is meaningless to attribute it solely to dipole relaxation, interfacial or grain boundary relaxation etc. The dynamics are collectively taking place in a highly disordered heterogeneous environment; different co-operative relaxing components constitute an effective dynamic system.

A question that arises is whether thermodynamic quantities (i.e., the activation volume and activation enthalpy for relaxation) controlling the dynamic properties (such as the dielectric relaxation time) of the granular heterogeneous (concerning their microstructure or their composition or both) materials are correlated in a unified manner. For example, do v^{act} and h^{act} values for different porous dielectrics saturated with water obey a compensation rule of the form $v^{act} = Fh^{act}$, where the proportionality constant F is a function of the materials' physical quantities. We adopt a thermodynamic elastic model introduced by Varotsos and Alexopoulos (cB Ω model) [10,28–31], which states that:

$$g^{act} = cB\Omega \quad (6)$$

where B is the isothermal bulk modulus, Ω is a mean atomic (or molar) volume and c is a parameter that does not change with temperature or pressure. Moving entities draw enthalpy from the heat bath of phonons, which is used for elastic work associated with diffusion and it is assumed that the elastic work is associated with bulk modulus of the elastic host matrix. In other words, the elasticity of the solid controls the dynamic processes taking place. Eq. (6) has successfully described formation, migration and activation processes. The latter usually has a static component referring to formation of defects and a term for migration. While activation enthalpy is positive, formation, migration and activation volumes induced can be positive, negative or null. The elastic work required to expand an elastic sphere by increasing its radius by Δr equals that required to suppress the sphere by reducing its radius by Δr . In both cases, the elastic energy is proportional to the same elastic constant and the same 'energy' $|g^{act}| = |cB\Omega|$, if B is a dominant elastic parameter for this process. The partial pressure derivative of this formula tells us the size of the activation volume $|v^{act}| \equiv |(\partial g^{act} / \partial P)_T|$, but its sign is determined by the correlation between the dynamic process with the relaxation of the environment and the dynamic re-arrangement of the structural (atomic or molecular) units when the relaxing atom is in its 'excited' state in relation to the configuration of the structural units in the 'ground' state. In practice, the experiment establishes the sign of the activation volume. Alternatively, the elastic work accompanying any process to deform an elastic medium either outwards (positive activation volume) or inwards (negative activation

Table 1

Activation volumes and activation enthalpies obtained from dielectric relaxation experiments in wetted rocks. The isothermal bulk modulus and its pressure derivative are enlisted to estimate (in the last column) the predicted value of the activation volume according to Eq. (7).

Material	v^{act} (cm^3/mol)	h^{act} (eV)	B (GPa)	$(\partial B / \partial P)_T$	$B^{-1}((\partial B / \partial P)_T - 1)$ (GPa^{-1})	$B^{-1}((\partial B / \partial P)_T - 1)h^{act}$ (cm^3/mol)
Sandstone	7 ± 1^a	0.37 ± 0.04^a	23–26 ^e	4–5 ^e	0.16–0.22	6.8 ± 0.9
Limestone (CaCO_3)	3.0 ± 0.4^b	$\approx 0.6^c$	55 ± 2^f	$\approx 4^f$	0.055	3.2 ± 0.8
Granodiorite	-9 ± 2^d	0.48 ± 0.08^d	49 ± 1^g	$\approx 10^g$	0.17	8 ± 3

All materials were saturated with water. The elastic data correspond to ambient pressure: B was estimated from linear extrapolation of the high pressure $B(P)$ data to 0.1 MPa (ambient pressure). The same high-pressure region yields $(\partial B / \partial P)_T$ (see the discussion in the text).

^a Present work.

^b Low frequency mechanism Ref. [9].

^c Ref. [40].

^d Ref. [41].

^e Data from Ref. [42] for sandstones with porosity around 0.1.

^f Data from Ref. [43] for water-saturated limestone.

^g Data from Ref. [44] for granodiorite filled with tap water.

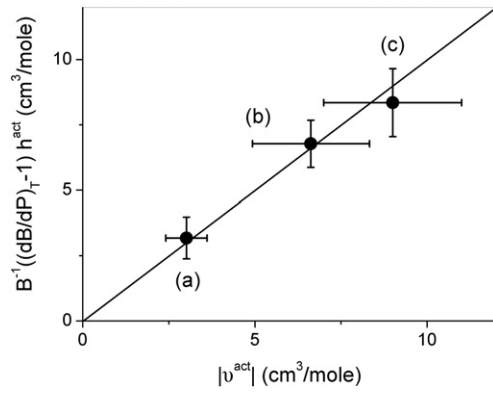


Fig. 3. The quantity $B^{-1}((\partial B/\partial P)_T - 1)h^{act}$ vs the absolute value of v^{act} for dielectric relaxation in water-saturated specimens of: (a): limestone, (b): sandstone (b), and (c): granodiorite. The solid line is the prediction of the $cB\Omega$ model.

volume) is proportional to $B\Omega$. Differentiating Eq. (6) with respect to pressure at constant temperature, Varotsos and Alexopoulos obtained $v^{act} = B^{-1}((\partial B/\partial P)_T - 1)g^{act}$. The entropic term Ts^{act} is usually much smaller than h^{act} , thus, it is not far-stretched to consider $g^{act} \cong h^{act}$, hence, Eq. (8) is rewritten [10]:

$$v^{act} \cong B^{-1} \left[\left(\frac{\partial B}{\partial P} \right)_T - 1 \right] h^{act} \quad (7)$$

We stress that Eq. (7) actually provides the net (absolute) value of v^{act} . We note that Eq. (7) reveals a compensating rule between v^{act} and h^{act} . Eq. (2) was checked at ambient pressure in a wide range of solids extending from silver halides [32] to rare gas solids [33], in ionic crystals under gradually increasing uni-axial stress [34] in which electric signals are emitted before fracture (such as the signals detected before earthquakes [35–37]), as well as in disordered polycrystalline materials [38]. Using experimental values for B (at ambient pressure) and $(\partial B/\partial P)_T$ and v^{act} and h^{act} data obtained from dielectric relaxation experiments under pressure and temperature, respectively, for different granular hydrated dielectrics, one can examine if datum points in a v^{act} vs $B^{-1}((\partial B/\partial P)_T - 1)h^{act}$ diagram collapse on a master straight line with slope 1.

The isothermal compressibility (i.e., the inverse of B) of granular matter has – to a first approximation – two components: the compressibility of the empty pore space and the compressibility of the bulk grains [38,39]. In a partially saturated porous media, one component is the compressibility of the empty pore space and the other is an effective compressibility of the solid grains and the confined fluid (in this case, bulk refers to solid grains plus the confined water. It was clarified earlier that the measured B values at low pressure are governed by the closing of the porosity (more precisely, the portion of the porosity that is not filled with water); therefore, information for the true (bulk) B and $(\partial B/\partial P)_T$ is obtained by working in the high pressure region of a $B(P)$ diagram, where datum points are described by a straight line. The extrapolation of this straight line to ambient pressure provides the true values of B and $(\partial B/\partial P)_T$ of the bulk matrix. In Table 1 we provide dielectric relaxation results from our laboratory, elastic data from the literature and estimates of the quantity $B^{-1}((\partial B/\partial P)_T - 1)h^{act}$ for three different granular dielectrics partially saturated with water. In Fig. 3, $B^{-1}((\partial B/\partial P)_T - 1)h^{act}$ vs the absolute value of the activation volume v^{act} is depicted. We observe that the datum points lie, within the experimental uncertainty, on a straight line with slope one, which is the prediction of the $cB\Omega$ model (Eq. (7)).

5. Conclusion

Novel experimental work on the dielectric relaxation of granular dielectrics partially filled with water, which constitute a class of materials of importance in engineering and geophysics, under hydrostatic compression at various temperatures provides experimental values of the activation enthalpy and volume. Despite the diversity and complexity of the systems, the thermodynamic parameters combined with the materials' elastic quantities can lead to a compensation rule. This result is explained within the frame of the elastic thermodynamic model suggested previously by Varotsos and Alexopoulos.

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