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Slow Variations of Mechanical and Electrical Properties of Dielectrics and Nonlinear Phenomena at Ultrasonic Irradiation[1]

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Abstract—The interconnection between variations of elasticity and dielectric permittivity of mesoscopic solid systems under exposure to ultrasound is experimentally observed. A phenomenological theory generalizing Debye's approach for polar fluids is developed to explain the measured data. The substitution of acoustic measurements by dielectric ones not only simplifies the procedure, but also offers new possibilities to remotely evaluate the mechanical properties of materials and natural media.

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Mesoscopic solids like polycrystals, granular media, defective materials, soils and rocks are widespread in nature, science and engineering. They display unusual properties. For example, their acoustic nonlinearity can be 2–4 order higher than "physical" or "geometrical" nonlinearity of perfect media [1]. The huge nonlinearity is caused by several effects, namely, by Hertzian contact between grains [2] and micro-asperities of rough grain surfaces [3], by cracks inside specimen, or by weak bonds between rigid sections of medium [4]. For fractured solids the measurement of higher harmonics or combination frequencies of ultrasonic waves evaluates internal damage and, consequently, the mechanical strength of the medium or manufactured products [1].

A second phenomenon is "slow dynamics" [5, 6]. "Slow" denotes that after a disturbance of the thermodynamic state of the material—for example by ultrasonic irradiation, temperature shifts, or mechanical impacts—the mechanical properties vary during seconds, minutes, hours, or even days. The softening of the materials and decrease in sound velocity is typical. "Fast" means a temporal scale on the order of a period of ultrasonic vibration. Many mesoscopic solids contain weak bonds whose amplitude of strain vibration caused by acoustic wave is much higher than the amplitude for rigid grains. As a result, strong local heating weakens these bonds, and the total elasticity of the medium decreases [7, 8].

Measurements have been performed mostly in rods or in core samples serving as acoustic resonators (Fig. 1). The resonant frequency slowly decreases with increase in acoustic amplitude. At the same time, a distortion of the frequency response is observed (Fig. 2), typical for nonlinear media. Almost always the nonlinear distortion and the slow dynamics phenomena take place simultaneously [9]. It has earlier been shown the possibility to separate the nonlinear distortion and slow dynamic phenomena using constant strain frequency sweep [10]. Hysteretic phenomena are observed—the mechanical properties depend on the history of irradiation [11, 12]. Of earlier results on dielectrics coupled to mechanical effects can be mentioned that the conductivity of dipole composite electrolytes had a peak at a mechanical elongation of 10% [13]. Shear mechanical and dielectric frequency sweep measurements were performed on glass forming liquids where the loss spectra and their peaks were measured [14]. Theory and experiments of the dielectric dependence of frequency in granular material can be found in [15].

Large volumes of experimental data have been obtained up to now relating to the evolution of parameters of structured materials subjected to acoustic irradiation. Among them the rock materials must be listed first, such as granite, sandstone, limestone, a variety of grainy media, as well as glasses, plastics, and other materials with complicated molecular structure.

Most acoustically studied media are polar dielectrics. Their molecules or domains are known to attribute a dipole moment even at absence of an external electric field. The polarization mechanism for such dielectric is in the alignment interaction of molecules with the electric field. The orientation is the main mechanism for gases and liquids, as well as for crystals in which dipoles can rotate. With the decrease in elasticity after ultrasonic treatment the mechanical resistance to rotation of dipoles decreases as well, and the dielectric permittivity increases. Therefore the change in mechanical properties is accompanied by a

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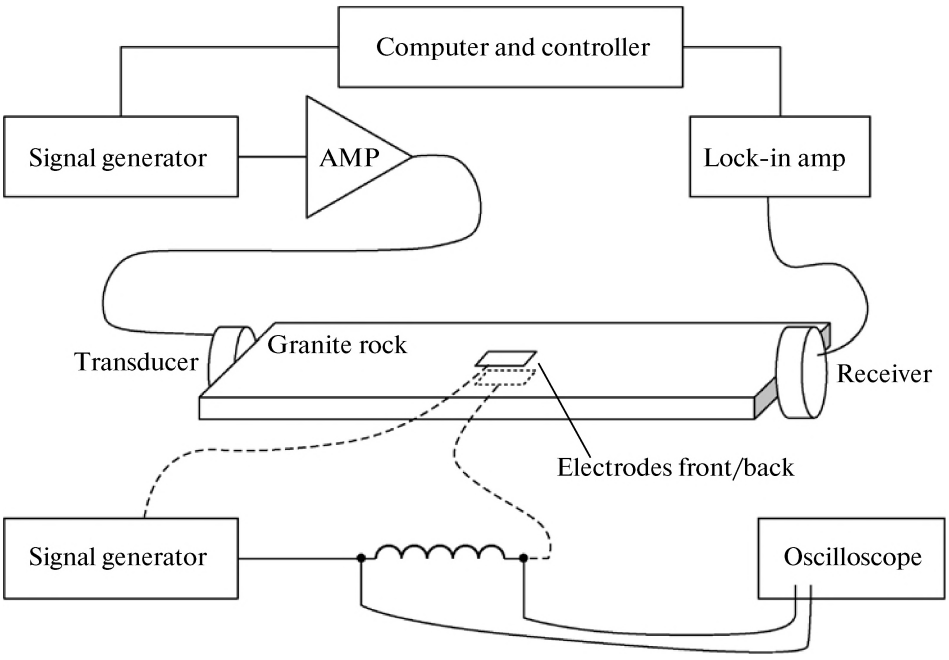

Fig. 1. Scheme of experimental set-up.

change in electrical parameters such as permittivity and dielectric susceptibility. This connection opens up possibilities to observe slow dynamics by means of accurate electrical measurements. In this way a new method of acoustic-electric diagnostics can be realized.

Measurements were carried out using rods of rectangular cross-section made of granite and plexiglass. Both materials displayed similar behavior, and only the results for granite are discussed below. The experimental scheme is shown in Fig. 1.

An acoustic wave was excited by a piezoelectric transducer placed at one end of the rod. A standing wave was created. The resonance frequency decreased with increase of the AC voltage amplitude applied to the transducer (see dashed line in Fig. 2). The nonlinear frequency shift is caused by the softening of weak bonds between grains and increases with increase in amplitude of ultrasonic vibration. This phenomenon is an effect of cubic acoustic nonlinearity [16, 17]. Simultaneously the capacitance was measured by two metallic film electrodes which were glued to opposite sides of the rod forming an electric capacitor. The magnitude of its capacitance was measured by a resonant method. Namely, the resonance frequency of electric vibration was recorded for a swept electric signal. The measured dependence of the electric capacitance (proportional to the dielectric permittivity) on amplitude is shown by the solid line in Fig. 2.

The theory explaining the connection between the acoustic resonance frequency shift and the electric capacitance will now be derived. It modifies the Debye approach based on orientation of polar molecules of fluids in the electric field and their disorder by thermal fluctuations. The equation for the rotating motion of a molecule is [18]:

$$I_{ik}\frac{d\Omega_k}{dt} = K_i. \quad (1)$$

Here I_{ik} is the inertia tensor, Ω_k is the angular velocity, and K_i is the moment of acting forces. To describe the motion in the plane containing both the axis of the molecule (its dipole moment **d**), and the electric-field vector **E**, Eq. (1) is rewritten as

$$I\frac{d\Omega}{dt} = [\mathbf{d}\times\mathbf{E}]_\Omega = -dE\sin\theta. \quad (2)$$

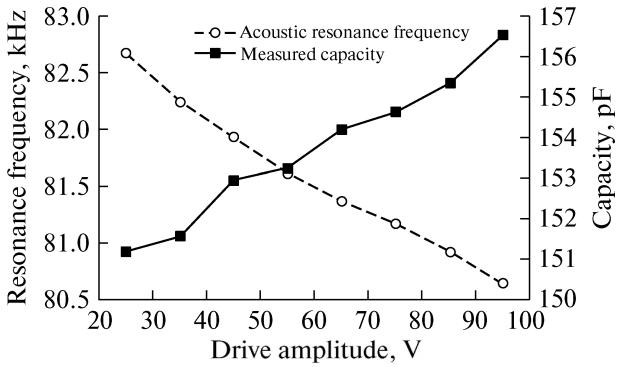

Fig. 2. Measured dependence of ultrasonic resonance frequency (dashed), and measured capacitance (solid), on acoustical amplitude for the granite rod.

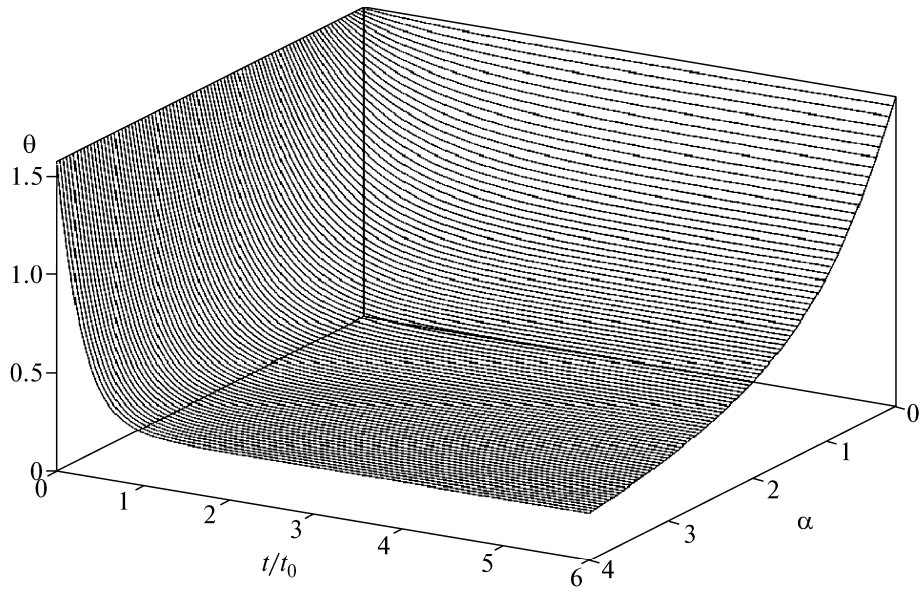

Fig. 3. Transient process of electric orientation of a dipole at elastic resistance of surrounding medium.

Here θ is the angle between the vectors of electric field and dipole moment. The cross-product is projected onto the angular velocity vector which is orthogonal to the plane. Adding to Eq. (2) moments of both the friction force acting on the molecule at its rotation and the force of elastic resistance of the surrounding medium, a nonlinear equation is derived

$$I\frac{d^2\theta}{dt^2} + \nu\frac{d\theta}{dt} + dE\sin\theta + \beta R^2\sin(\theta - \theta_0) = 0. \quad (3)$$

Here ν is the effective viscosity, β is the elasticity, R is the typical length of a dipole, and θ_0 is the value of the angle θ when the electric field is switched off.

Evidently, the dipole is "damped" for low (ultrasonic) frequencies; it cannot perform a high-Q vibration. In this case the second temporal derivative in Eq. (3) can be eliminated. The solution to the corresponding simplified nonlinear first-order equation has the following form:

$$\cos(\theta - \theta_{st}) = \frac{\tanh(t/t_*) + \cos(\theta_0 - \theta_{st})}{1 + \tanh(t/t_*)\cos(\theta_0 - \theta_{st})}. \quad (4)$$

Solution (4) describes the turning of a molecule from its initial position (at $t = 0$), characterized by the angle θ_0, to the final steady-state position (at $t \longrightarrow \infty$) for which the angle θ reaches the stationary value θ_{st}, defined by the relation

$$\tan\theta_{st} = \frac{\beta R^2\sin\theta_0}{dE + \beta R^2\cos\theta_0}. \quad (5)$$

In all cases the inequality $\theta_{st} < \theta_0$ is valid, and the angle between the vectors of the electric field and the dipole decreases with time. The typical time of this transient process is

$$t_* = \frac{t_0}{\sqrt{1 + 2\alpha\cos\theta_0 + \alpha^2}}, \quad t_0 = \frac{\nu}{\beta R^2}, \quad \alpha = \frac{dE}{\beta R^2}. \quad (6)$$

The time (6) decreases with increase in both field intensity and mechanical elasticity of the medium. In very strong fields, at field magnitudes $E \longrightarrow \infty$, the steady-state angle $\theta_{st} \longrightarrow 0$, and the dipole moment is directed along the field. In weak electric fields the angle differs slightly from its initial value $\theta \approx \theta_0$.

The process of how the angle between dipole and electric field approaches the steady-state value (5) is shown in Fig. 3 as a function of two variables: normalized time t/t_0 and the parameter α (6). The initial value of this angle (at $t/t_0 = 0$) is $\theta_0 = \pi/2$ for all curves.

The dependence of t_* on the strength of the electric and the elastic field indicates the nonlinear character of frequency dispersion of permittivity in strong fields. The dependence of permittivity on dE/kT is given by the well-known Langevin function. However, electric nonlinearity is neglected hereafter; only terms linear in E are considered.

The potential of the applied forces, in accordance with Eq. (3), is

$$U - U_0 = -dE\cos\theta - \beta R^2\cos(\theta - \theta_0). \quad (7)$$

When the electric field is switched off, the dipole axes are oriented chaotically and have no preferred orientation. The initial angle θ_0 has a uniform statistical distribution over the spatial angle in spherical coordinates.

The dipole moment per unit volume (or polarization of a medium) is a sum of the projections onto **E** of the dipole moments of all N molecules in this volume. The thermal motion of molecules leads to fluctuation of angles θ, and the polarization equals

$$P = Nd\langle\cos\theta\rangle. \tag{8}$$

In this formula angle brackets denote double averaging over angles θ_0 and over energies using the Boltzmann statistical distribution. It is necessary to calculate the integral

$$\langle\cos\theta\rangle = C\int_0^\pi \sin\theta_0 d\theta_0 \times \int_0^\pi \cos\theta\exp\left(-\frac{U(\theta,\theta_0)}{kT}\right)\sin\theta d\theta. \tag{9}$$

Here C is the normalization constant, and U is defined by formula (7). Only weak electric fields are of interest here, and nonlinear polarization phenomena are insignificant. Therefore the exponent in the integrand (9) is expanded in powers of **E** keeping only linear terms. After this expansion and a complicated calculation of the integral (9) it takes the form

$$\langle\cos\theta\rangle = \frac{dE}{3kT}F\left(b = \frac{\pi}{4}\frac{\beta R^2}{kT}\right),$$
$$F(b) = \frac{1+\frac{3kT}{\beta R^2}I_1^2\left(\frac{\pi}{4}\frac{\beta R^2}{kT}\right)}{1+\frac{\pi}{2}I_0\left(\frac{\pi}{4}\frac{\beta R^2}{kT}\right)I_1\left(\frac{\pi}{4}\frac{\beta R^2}{kT}\right)}. \tag{10}$$

Here I_0 and I_1 are modified Bessel functions. The function F is the factor accounting for elastic resistance. For fluids $b = 0$ and $F = 1$, and the simple Debye formula follows from (10). At small values of parameter b the result

$$F \approx \left(1-\frac{\pi}{16}b\right), \quad \langle\cos\theta\rangle = \frac{dE}{3kT}\left(1-\frac{\pi^2}{64}\frac{\beta R^2}{kT}\right) \tag{11}$$

is obtained from formula (10), and at large b the asymptotic dependence $\sim 1/2b$ is valid.

After calculating the polarization one can derive the equation for permittivity:

$$\varepsilon = 1+\frac{4\pi Nd^2}{3kT}F\left(\frac{\pi}{4}\frac{\beta R^2}{kT}\right). \tag{12}$$

To obtain the result (12), formulas (8), (10) are used, as well as the well-known connection between electric field, electric induction and polarization: $\dot{D} = \varepsilon\dot{E} = \dot{E} + 4\pi\dot{P}$. Because $F(b)$ is a decreasing function of b, the increase in elasticity of a medium is accompanied by a decrease of its permittivity (12).

To be able to compare theory and experiment formula (12) is rewritten in a more convenient form:

$$\frac{d}{dI}\ln(\varepsilon-1) = \frac{d}{dI}\ln\left[\frac{1}{kT}F\left(\frac{\pi}{4}\frac{\beta R^2}{kT}\right)\right]. \tag{13}$$

Here the logarithmic derivative on the sound intensity I is taken of both sides of the Eq. (12). Now two physical parameters are excluded from the formula (13), the dipole moment d of one molecule, and the number N of dipoles in a unit volume; as it is difficult to evaluate these parameters for media of complicated mesoscopic structure.

At temperatures below the melting point one can put $b \gg 1$ and use the corresponding asymptotic of the function F. The explicit dependence on temperature disappears here and only the dependence through the elastic module $\beta = \beta(T)$ remains. In turn, the temperature increases at increase of the ultrasonic intensity $T = T(I)$, and therefore

$$\frac{d}{dI}\ln(\varepsilon-1) = -\frac{d}{dI}\ln\beta(T(I)).$$

It is not necessary to give the explicit equations $\beta = \beta(T)$, $T = T(I)$ in order to provide an explanation of experimental results. Instead, by paying attention to the measured resonance frequency shift, which is proportional to the sound velocity c, which in turn is proportional to the square of elastic module, the formula takes the form:

$$\frac{1}{(\varepsilon-1)}\frac{d\varepsilon}{dI} = -\frac{2}{c}\frac{dc}{dI}.$$

Finally, take into account that the intensity is proportional to the square of the amplitude of vibration, and that both resonance frequency and dielectric permittivity during the experimental measurement varied weakly in comparison with their initial magnitudes. It means that

$$\varepsilon = \varepsilon_0 + \varepsilon', \quad f_{\text{res}} = f_0 - f'.$$

Small additions to equilibrium quantities (subscript "zero") are marked by strokes. By considering all of the above remarks, a formula can be derived

$$\frac{d\varepsilon'}{dA} = \frac{2}{f_0}(\varepsilon_0-1)\frac{df'}{dA}. \tag{14}$$

Here A is the amplitude of the acoustic vibration in the material. Through Eq. (14), the capacitance variation $C' \sim \varepsilon'$ can be obtained theoretically from the experimentally measured variation in frequency f'. The result, with the dielectric permittivity ε_0 of granite at given humidity taken from literature [19], is shown by the dashed line in Fig. 4 together with the measured capacitance from Fig. 2 (solid line). The difference in slope between the measured and the theoretical curves is fairly small.

The dependence of dielectric properties of materials on their mesoscopic structure gives the possibility to conclude if there are internal defects or second

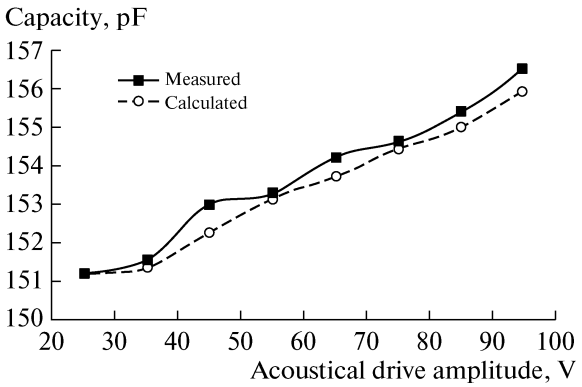

Fig. 4. The measured electric capacitance (solid); and the theoretical electric capacitance (dashed) as functions of the acoustical drive voltage.

phase inclusions, or to evaluate the material strength or other mechanical properties. From the viewpoint of physical applications it is interesting to use these methods for studying the relaxation and hysteretic dynamics, as well as the kinetics of phase transitions. In particular, unusual behaviors of the dielectric properties of ice and frozen sand were observed recently [20]. In accordance with the theory (12), the dielectric permittivity decreased abruptly at freezing. The hysteretic loop observed at the cyclic freezing-melting process is connected with a meta-stable state of ice-water mixture existing in the presence of impurities. However, the dielectric measurements [20] were not accompanied by mechanical ones. Still, it is just the mechanical properties of frozen soil that are of prime interest for construction of roads, buildings and pipelines in the north, and these data may be obtained by processing of electrical data. The use of microwaves at satellite measurements of permittivity of ground requires the non-steady state theory, which describes the frequency dispersion indicated above (see (3), (4) and Fig. 3).

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