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Theory of dielectric relaxation in non-crystalline solids: from a set of micromotions to the averaged collective motion in the mesoscale region

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Abstract

Based on the rather general decoupling procedure that reduces a set of micromotions to the averaged collective motion in the mesoscale region, a consistent and general theory of dielectric relaxation describing a wide set of dielectric spectroscopy (DS) data measured in a certain frequency/temperature range can be developed. The new theory explains and generalizes the Vogel–Fulcher–Tamman (VFT) equation and leads to the new type of kinetic equation, containing non-integer operators of differentiation and integration combined in the specific triads. Each triad combines three operators: the first non-integer operator has a real exponent, the other two form a pair of non-integer operators having the complex conjugate power-law exponents. This approach explains naturally the 'universal response' (UR) phenomenon discovered by Jonscher in a wide class of heterogeneous materials and confirms the justified data-curve fitting approach developed previously as a phenomenological tool for the analysis of raw complex permittivity data. It explains and generalizes some well-established experimental facts and contains also new predictions that can be verified in the experiment. This general approach helps to find the proper place for the DS as a science studying the different types of the 'reduced' collective motions and their various interactions with each other in the mesoscale region. This new theory explains also the fact *why* kinetic equations containing non-integer operators are realized in reality. They are necessary for description of slow collective motions which are probably realized in the intermediate range of scales not only in DS. Reology and mechanical relaxation represent also interesting and not well-understood phenomena, where the 'fractional' kinetics will find its proper place.

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1. Introduction

Despite substantial progress in experimental measurements in dielectric spectroscopy (DS) [1] the modern state of the theory of dielectric relaxation remains unsatisfactory. At present (as before) a number of empirical relationships exist in order to fit the broadband dielectric spectra of a wide class of heterogeneous materials. The most popular empirical expression which is used to describe the generalized broadened asymmetric relaxation loss peak is the Havriliak–Negami (HN) expression [2]

$$\varepsilon^*_{\mathrm{HN}}(\mathrm{j}\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + (\mathrm{j}\omega\tau)^{\nu})^{\beta}}. \quad (1)$$

Here, $\varepsilon^*_{\mathrm{HN}}(\mathrm{j}\omega)$ is the HN complex permittivity with real and imaginary components $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$, respectively. Traditionally, the measured permittivity-frequency data are interpreted and analyzed quantitatively using expression (1) or its linear combinations. However, in this description the fitting parameters ν and β are empirical and the desired relationship with structural or microscopic motion parameters of the material considered is *not* known.

Other approaches such as the mode-coupling theory [3] and the concentration fluctuation model [4] allow one to understand qualitatively only a part of the dielectric spectra of glass-forming systems and at present they cannot be used for the description of the measured complex permittivity in a wide frequency/temperature range for other heterogeneous materials.

In our opinion, any new theory providing a description of the given dielectric spectrum in a broad frequency range should satisfy the following conditions:

1. It should explain *how* the numerous microscopic motions observed in disordered materials may be reduced to a few power-law exponents occurring in analytical expressions for the complex permittivity chosen for the fitting of the measured data.
2. It should explain the empirical Vogel–Fulcher–Tamman (VFT) equation, which is observed in a wide class of glass-forming systems and other non-crystalline materials.
3. It should explain *why* empirical expressions suggested previously by Cole and Cole or Cole and Davidson [2] chosen for the analytical description of complex permittivity fit closely certain DS data.
4. It should explain the 'universal' response phenomenon discovered by Jonscher [5] and observed in a wide class of heterogeneous materials.
5. This theory should describe the measured complex permittivity of numerous heterogeneous materials in a wide frequency/temperature range.
6. The suggested theory should not contradict the basic principles of the existing theory of non-equilibrium processes.

Only if these points are satisfied, the new theory can be valid for the treatment of experimental data and practical applications in the modern broadband dielectric spectroscopy.

Thus, the construction of such a theory (which should be derived from the first principles) is the basic problem of the DS.

The main object of this paper is to develop a new theory of dielectric relaxation satisfying the requirements mentioned above. Our consideration is based on the Mori–Zwanzig formalism [6]; however, the decoupling procedure for the memory function is new and original. It uses a hypothesis connecting the self-similar cluster structure of a medium and is valid for some intermediate (mesoscale) region located between $\omega_{\min n}$ and ω_{Mxx} frequencies, respectively. One can prove mathematically that summation over partly correlated self-similar clusters constructing a possible structure for a heterogeneous medium, where microprocesses of relaxation/exchange (they will be specified below) with thermostat occur, leads in the frequency domain to the generalized element coinciding with the memory function and having the following analytical expression:

$$K_1(\mathrm{j}\omega) = K_0 + C_0(\mathrm{j}\omega)^{\pm\nu} + C_1(\mathrm{j}\omega)^{\pm\nu+\mathrm{j}\langle\Omega\rangle} + C_1^*(\mathrm{j}\omega)^{\pm\nu-\mathrm{j}\langle\Omega\rangle}. \quad (2)$$

It is natural to define this function as the *generalized* (when $\langle\Omega\rangle \neq 0$) impedance function describing