



Detection of collective motions in dielectric spectra and the meaning of the generalized Vogel–Fulcher–Tamman equation

Raoul R. Nigmatullin*

Theoretical Physics Department, Physical Faculty, Kazan State University, Kremlevskaya str., 18, 420008 Kazan, Tatarstan, Russian Federation

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ABSTRACT

Based on the reduction property of dielectric spectra associated with the power-law function $[\sim(j\omega\tau)^{\pm\nu}]$ that appears in the frequency domain, one can develop an effective procedure for detection of different reduced motions (described by the corresponding power-law exponents) in temperature domain. If the power-law exponent ν is related to characteristic relaxation time τ by the relationship $\nu = \nu_0 \ln(\tau/\tau_s) / \ln(\tau/\tau_0)$ (here τ_s, τ_0 are the characteristic times characterizing a movement over fractal cluster that is defined in Ref. [Ya.E. Ryabov, Yu. Feldman, J. Chem. Phys. 116 (2002) 8610]) and the simple temperature dependence of $\tau(T) = \tau_A \exp(E/T)$ obeys the traditional Arrhenius relationship, then one can prove that any extreme point figuring in the complex permittivity $\varepsilon(j\omega)$ spectra (characterized by the values $[\omega_m, y(\omega_m)]$) obeys the generalized Vogel–Fulcher–Tamman (VFT) equation. This important statement confirms the existence of the 'universal' response (UR) (discovered and classified by Jonscher in frequency domain) and opens new possibilities in the detection of the 'hidden' collective motions in temperature region for self-similar (heterogeneous) systems. It gives also the extended interpretation of the VFT equation and allows one to differentiate collective motions passing through an extreme point. This differentiation, in turn, allows one to select the proper fitting function containing one or two (at least) relaxation times for the fitting of the complex permittivity function $\varepsilon(j\omega)$ in the limited frequency domain. This conclusion can allow for the classification of dielectric spectroscopy as the spectroscopy of the reduced (*collective*) motions, which are described by different power-law exponents on the mesoscale region. The verification of this approach on available DS data (poly(ethylene glycol)-based-single-ion conductors) completely confirms the basic statements of this theory and opens new possibilities in general classification of different motions that can be detected in the analysis of the different dielectric permittivity spectra.

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1. Introduction and the formulation of the problem

For many years, dielectric spectroscopy (DS) related to measurements of complex permittivity $\varepsilon(j\omega)$ and impedance $Z(j\omega)$ was considered as *empirical* science in comparison with possibilities of the EPR (NMR) magnetic measurements and thereby was ignored by many serious researches. But nowadays, thanks to the development of the fractal geometry and to the establishing of definite relationships of the fractal geometry with the fractional calculus [2,3], there are new possibilities of understanding of the proper (correct) place of DS. Now the interest of many scientists working in the field of dielectric spectroscopy is on the analysis of different polymers, glass-forming systems, complex (heterogeneous and fractal) systems and materials having different types of conductivity. If one reads attentively the recent materials related to achievements in the field of dielectric spectroscopy [4] one can notice that substantial

progress has been made in experimental measurements and lack of general theories that are confirmed experimentally and relate the parameters of dielectric relaxation with structural parameters of the material considered. As a certain theoretical achievement, one can notice the recent paper of Coffey et al. [5], where inertial effects in anomalous relaxation are considered, and the report of Ngai in Ref. [4], where the recent progress of dielectric relaxation of the glass-forming systems has been outlined. It is necessary to remark also the papers of Dyre and coworkers [6,7] related to analysis and construction of the theory of conductivity for a wide class of heterogeneous materials. But unfortunately, to date the progress in construction of the general and reliable theory of dielectric relaxation remains unsatisfactory. The author wants to show the importance of DS as a spectroscopy of the reduced (*collective*) motions in the region of mesoscale. Under the mesoscale region the author understands the region, where the structural properties of the matter are self-similar (fractal) and characterized presumably by two scales ($\lambda < \eta < A$). Usually, the minimal-scale λ is associated with a size of a small group of atoms or molecule, the large-scale A is identified with an 'elementary physical volume' that is accepted as a point in the mathematical

* Tel.: +7 843 236 06123.

E-mail address: nigmat@knet.ru