THE OBSERVATION OF THE FRACTIONAL KINETICS IN DIELECTRIC RELAXATION: NEW INDICATORS OF THE COLLECTIVE MOTIONS

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Abstract: The author presented undoubted evidences that the fractional kinetics described by equations with non-integer integrals and derivatives containing real and complex-conjugated power-law exponents is observed experimentally in dielectric relaxation on the region of mesoscale. Besides, the author found the generalization of the well-known Vogel-Fulcher-Tamman empirical equation and showed that it divides one collective motion from another one in temperature region if dielectric spectra presented in the frequency domain. This important observation means that dielectric spectroscopy can be determined as the spectroscopy of the reduced collective motions on mesoscale region. The experimental confirmations of the last statement at analysis of complex dielectric spectra in conductive polymers have been found. *Copyright © 2002 IFAC*

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1. FORMULATION OF THE PROBLEM

In papers [Nigmatullin, 2005, 2006] a new theory of dielectric relaxation based on the fractional kinetics has been developed. The basic result that follows from the new theory can be formulated as follows: a group of self-similar microscopic motions described by expression

$$\sum_{n=-(N-1)}^{N-1} b^n f(z\xi^n) \Rightarrow A_\nu z^{\pm\nu} + B_\nu, \qquad z_{\min} < |z| < z_{\max} \tag{1}$$

is reduced to some collective motion appearing in the mesoscale, which, in turn, is described by one power-law exponent ν. In expression (1) b is a *spatial* scaling parameter related to the transfer/relaxation process in a weakly-correlated system, $z = j\omega\tau$ is a dimensionless complex variable of the Fourier transform, $f(z)$ is the Fourier image of a microscopic function, describing the relaxation/transfer process in the chosen fractal cluster. The characteristic relaxation time τ is associated to some diffusion/transfer process and related to the *dynamic* scaling parameter ξ. The power-law exponent ν entering in (1) and reflecting a possible temperature dependence is given by expression [Nigmatullin, 2005]

$$\nu = \frac{\ln(b)}{\ln(\xi)} \tag{2}$$

Below we omit possible complex-conjugated corrections in Eqn. (1) and do not show the limits of applicability of the right-hand expression for the complex variable z. These limits are given in Table of paper [Nigmatullin, 2005]. From expression (2) one can derive the generalization of this formula, initially obtained in [Ryabov and Feldman, 2002]. It relates the power-law exponent ν with one characteristic relaxation time τ associated with one type of collective motion as

$$\nu = \nu_0 \frac{\ln(\tau/\tau_s)}{\ln(\tau/\tau_0)},\ \nu_0 = \frac{\theta d_f}{2},\ \tau_s = \left[\frac{R_0 D_\theta^{-2}}{G^{1/d_f}}\right]^{\frac{2}{\theta}} \tag{3a}$$

where

$$\xi = \frac{\tau}{\tau_0},\ b = G\left(\frac{R}{R_0}\right)^{d_f},\ R^2 = D_\theta \tau^\theta, \tag{3b}$$

are supplementary expressions providing "a bridge" between Eqns. (2) and (3a). The value τ_0 denotes the cutoff scaling time related to the collective motion, D_θ defines the generalized diffusion coefficient and R_0 determines the mean cutoff size of a spherically-symmetric cluster in the 3D-space associated to the movement of electric dipoles over the given self-similar structure. We suppose [Nigmatullin, *et al.*, 2003] also that a possible connection between mean

relaxation time τ and external temperature T is given by the conventional Arrhenius relationship

$$\tau(T) = \tau_A \exp(E/T) \quad (4)$$

The general expression for the complex susceptibility that was derived from the kinetic equations containing non-integer integrals and derivatives is written in the form [Nigmatullin, 2005, 2006]

$$\varepsilon(j\omega) = \varepsilon_\infty + \frac{\sigma_0}{j\omega} + \frac{1}{(j\omega\tau_d)^\kappa} + \frac{\Delta\varepsilon}{1+R(j\omega)}$$

$$\equiv \varepsilon_s + \frac{\sigma_0}{j\omega} + \frac{1}{(j\omega\tau_d)^\kappa} - \frac{\Delta\varepsilon}{1+R^{-1}(j\omega)},$$

$$R(j\omega) = \left[(j\omega\tau_1)^{\pm\nu_1} + (j\omega\tau_2)^{\pm\nu_2} + \ldots\right]^{\pm 1},\ \Delta\varepsilon \equiv \varepsilon_s - \varepsilon_\infty, \quad (5)$$

where the Fourier image of the memory function $R(j\omega)$ includes a linear combination of power-law exponents and each independent power-law term can be associated with one type of collective motion. The first two terms in (5) take into account a possible contribution of conductive $\sim 1/(j\omega)$ and the low-frequency dispersion (LFD) $\sim 1/(j\omega\tau_d)^\kappa$ terms, correspondingly. The general problem that we are going to solve can be formulated as:

How to detect possible collective motions described by some power law exponents, if expressions (3), (4) and (5) keep their validity for different dielectric spectra?

In other words, we want to prove the following assertion: If expressions (3) and (4) are valid for *any* collective motion described by the function $y(\omega)$ belonging to the chosen part of dielectric spectra in admissible frequency/temperature range then *any* extreme point characterized by the transition frequency ω_m between two collective motions and its value $y(\omega_m)$ satisfies at certain conditions to the generalized Vogel-Fulcher-Tamman (VFT) equation. The generalized VFT equation for the first time was derived in paper [Nigmatullin, *et al*., 2003] and will be written here as

$$x_m \equiv \ln\omega_m = \ln(\tilde{\omega}_0) + \frac{e_0}{T} + \frac{\alpha_1}{T-p_1} + \frac{\alpha_2}{T-p_2}, \quad (6a)$$

$$2\ln\left(\frac{y_c(x_m)}{2}\right) = 2\ln(\tilde{y}_0) + \frac{w_0}{T} + \frac{\beta_1}{T-T_1} + \frac{\beta_2}{T-T_2}. \quad (6b)$$

Here the fitting parameters entering into last expressions $\tilde{\omega}_0, \tilde{y}_0, e_0, w_0, p_{1,2}, T_{1,2}, \alpha_{1,2}, \beta_{1,2}$ by nontrivial way depend on the initial parameters entering in relationships (3) and (4). They can be evaluated independently by means of the fitting procedure, if the left-hand sides of expressions (6) are known from experimental measurements.

2. RESULTS AND DISCUSSION

Omitting the mathematical and numerical details proving and verifying this statement one can definitely say the following:

1. Dielectric spectroscopy is the spectroscopy of collective motions that are appeared because of reduction procedure on mesoscale region.
2. The kinetic equations associated with these reduced motions contain a set of non-integer derivatives and integrals with real and complex conjugated exponents and describe a dissipative process of dielectric relaxation.
3. The generalized VFT equation (6) serves a specific "label" showing a transition of one collective motion to another one in temperature region.
4. These theoretical conclusions received recently definite experimental confirmations. The fractional kinetics described by equations with complex-conjugated exponents are observed in polymerization reaction of the polyvinylpyrrolidone (PVP) (Nigmatullin, *et.al*., 2007) and at dielectric study of neutral and charged hydrogels in swelling process (Yilmaz, *et.al*., 2007) The importance of the generalized VFT equation in detection of the different collective motions in complex dielectric spectra has been confirmed experimentally at analysis of conductive polymers (PolyEthylene Glycol doped by Li^+ ions).
5. This definite success in application of the fractional kinetics in dielectric spectroscopy should serve as an encouraging stimulus for other researches in detection of the fractional kinetics in reology, mechanical relaxation and other phenomena related with description of the strongly-interacting collective motions on the region of mesoscale (where a fractal structure of the clusters participating in dissipative processes plays an important role).

REFERENCES

Nigmatullin R.R., Osokin S.I., and Smith J (2003). New approach in the description of dielectric relaxation phenomenon: correct deduction and interpretation of the Vogel-Fulcher-Tamman equation. *Phys. C (Cond. Matt.) 15 pp. 3481-3503.*

Nigmatullin R.R. (2005). Theory of Dielectric Relaxation in Non-Crystalline Solids: From a Set of Micromotions to the Averaged Collective Motion in the Mesoscale Region. *Physica B: Physics of Condensed Matter, v.358, pp 201-215.*

Nigmatullin R.R. (2006). Fractional" kinetic equations and "universal" decoupling of a memory function in mesoscale region. *Physica A, v. 363 pp. 282-298.*

Nigmatullin R. R., Arbuzov A.A., Salehli F., Gis A., Bayrak I., and Catalgil-Giz H (2007). The first experimental confirmation of the fractional kinetics containing the complex power-law exponents: dielectric measurements of polymerization reaction. *Physica B: Physics of Condensed Matter v. 388 pp. 418-434*.

Ryabov Ya. E. and Feldman Yu. (2002). Novel approach to the analysis of the non-Debye dielectric spectrum broadening. *Physica A, v. 314, pp. 370-378.*

Yalmaz Y., Gelir A., Salehli F., Nigmatullin R.R. and Arbuzov A.A (2006). Dielectric study of neutral and charged hydrogels during the swelling

process. *Journal of Chemical Physics v. 125 N-234705.*