Description of the anomalous dielectric relaxation in disordered systems in the frame of the Mori-Zwanzig formalism

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Abstract. In the frame of Mori-Zwanzig formalism the empirical Navriliak-Negami expression for the complex dielectric permittivity has been derived. The derivation is based on construction of kinetic equations for relaxation and memory functions accordingly. They contain integro-differential operators of non-integer order.

1. Introduction
One of the most striking features of the dielectric relaxation phenomenon in different disordered materials such as glass-forming liquids and amorphous polymers is the failure of the Debye theory [1]. This simple theory of dielectric relaxation cannot describe properly the low-frequency spectrum, where the real relaxation behavior can deviate essentially from the conventional exponential Debye's pattern and actually it is characterized by a broad distribution of relaxation times. Such behavior is reflected in the title anomalous dielectric relaxation and in the first time was suggested empirically in the pioneer paper [2] of the Cole's brothers in 1941 year for description of dielectric relaxation in polar liquids. These and subsequent investigators have proposed [3, 4] various empirical formulas describing the departure from the Debye behavior. In specific terms, the normal Debye relaxation process is characterized by a normalized complex dielectric permittivity (NCDP) function

\[ \hat{\varepsilon}(i\omega) = \frac{\varepsilon(i\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau}, \]  

where \( \varepsilon(i\omega) \) determines the complex dielectric permittivity (CDP), \( \varepsilon_0 \) and \( \varepsilon_\infty \) are low-frequency and high-frequency limits of the CDP \( \varepsilon(i\omega) \), correspondingly, \( \tau \) is a characteristic relaxation time defined in the present context as the Debye relaxation time. Equation (1) adequately describes the low frequency behavior of the observed complex susceptibility of many simple polar liquids.

A significant amount of experimental data on disordered systems supports the following empirical expressions for dielectric loss spectra, namely, the Cole-Cole equation [5]

\[ \hat{\varepsilon}(i\omega) = \left(1 + (i\omega\tau)^\alpha\right)^{-1}, \quad 0 < \alpha \leq 1, \]  

the Cole-Davidson equation.
and the Havriliak-Negami equation

\[ \hat{\varepsilon}(i\omega) = \left(1 + (i\omega\tau)^\alpha\right)^\beta, \quad 0 < \alpha, \beta \leq 1, \]

which is a combination of the Cole-Cole and Cole-Davidson equations.

As for physical mechanism determining the grounds of the Cole-Cole expression we see it in the hierarchical subordination of the dielectric relaxation process in many disordered systems [6,7], which, in turn, is related with a loss of ergodicity of the system considered. The hierarchical subordination is expressed in formation of clusters of relaxing dipoles having a self-similar structure. In paper [8] we formulated a model of anomalous dielectric relaxation based on hierarchical subordination of dynamic degrees of freedom. In the frame of this model it is possible to derive the Cole-Cole expression for the CDP and give the physical interpretation of the stretching power-law exponent \( \alpha \). In this paper, based on the results obtained in [8] we give a semi-phenomenological derivation for the Cole-Davidson and Havriliak-Negami expression for the CDP in the frame of the Mori-Zwanzig formalism.

2. Kinetic equations of the anomalous dielectric relaxation. General grounds

In this section we want to demonstrate the general approach of derivation of the desired kinetic equations for relaxation function. Their solutions lead (in frequency region) to the empirical expressions for the CDP reminded above. The relaxation function \( \phi(t) \) is defined as

\[ \phi(t) = \begin{cases} P(t) / P(0), & t \geq 0, \\ 0, & t < 0, \end{cases} \]

where \( P(t) \) determines an experimental relaxation function (the electric polarization), \( P(0) = \varepsilon_0 - \varepsilon_\infty \). The relaxation function \( \phi(t) \) is associated with the NCDP \( \hat{\varepsilon}(i\omega) \) by known relationship [5]

\[ \hat{\varepsilon}(i\omega) = \hat{L}[\phi(t);i\omega] = 1 - i\omega\hat{L}[\phi(t);i\omega], \]

where \( \hat{L}[\phi(t);i\omega] \) is the Laplace transform of the relaxation function \( \phi(t) \). Let us present the empirical expression for the NCDP \( \hat{\varepsilon}(i\omega) \) in the following form

\[ \hat{\varepsilon}(i\omega) = \left(1 + \hat{R}^{-1}(i\omega)\right)^{-1}, \]

where \( \hat{R}(i\omega) = (\hat{\varepsilon}^{-1}(i\omega) - 1)^{-1} \) we determine as the Laplace image of some function \( R(t) \):

\[ \hat{R}(i\omega) = \hat{L}[R(t);i\omega]. \]

Then for the functions NCDP mentioned above the functions \( \hat{R}(i\omega) \) and \( R(t) \) has the following forms:

Debye:

\[ \hat{R}_D(i\omega) = (i\omega\tau)^{-1}, \quad R_D(t) = \tau^{-1}; \]

Cole-Cole:

\[ \hat{R}_C(i\omega) = (i\omega\tau)^{-\alpha}, \quad R_C(t) = (\Gamma(\alpha))^{-1} \tau^{-\alpha} t^{-\alpha}; \]

Cole-Davidson:

\[ \hat{R}_{CD}(i\omega) = \sum_{k=0}^{\infty} (1 + i\omega\tau)^{-\beta(k+1)}, \quad R_{CD}(t) = e^{-\tau^{-1} \beta^{-1} E_{\rho,\beta}[\tau^{-\beta} t^{\beta}]} \]

where \( E_{\rho,\beta}[z] = \sum_{n=0}^{\infty} z^n / \Gamma(\rho n + \mu) \) determines two-parametric Mittag-Leffler function.
Havriliak-Negami:

\[ \hat{R}_{HN}(i\omega) = \frac{1}{1 + (i\omega\tau)^\alpha} - 1 = \sum_{k=0}^{\infty} (1 + (i\omega\tau)^\alpha)^{-\beta(k+1)}, \]

\[ R_{HN}(t) = \sum_{k=0}^{\infty} \tau^{-\alpha(k+1)}t^{\alpha(k+1)-1}E_{\alpha,\alpha(k+1)}^{\beta(k+1)}[-\tau^{-\alpha}t^\alpha] = \tau^{-\alpha\beta} \exp\left(-\alpha^{-1}\tau^{-\alpha}D_{t}^{1-\alpha}t\right)t^{\alpha-1}E_{\alpha,0}^{\beta}[\tau^{-\alpha}t^\alpha], \]

where \( E_{\rho,\nu}^{\gamma}[z] = \sum_{n=0}^{\infty} (\tau)_n z^n / n! \Gamma(\rho n + \mu) \) determines the generalized Mittag-Leffler function, \( \alpha D_{t}^{-\alpha} \) determines the fractional derivative in the Riemann-Liouville form and expression

\[ \alpha D_{t}^{-\alpha} \phi(t) = \Gamma^{-1}(\alpha) \int_0^t (t-t')^{\alpha-1} \phi(t')dt', \]

where \( \phi(t) = \int_0^t R(t-t')\phi(t')dt' \) determines the convolution of \( R(t) \) and \( \phi(t) \). The substitution of expressions for \( R(t) \) (8)-(11) into equation (14) immediately leads us to the desired kinetic equations that corresponds to empirical expressions mentioned above, viz., Debye, Cole-Cole, Cole-Davidson and Havriliak-Negami, correspondingly

\[ \frac{d\phi(t)}{dt} + \tau^{-\alpha}D_{t}^{-\alpha}\phi(t) = 0, \]

\[ \frac{d\phi(t)}{dt} + \tau^{-\alpha}\phi(t) = 0, \]

\[ \frac{d\phi(t)}{dt} + \tau^{-\beta}D_{t}^{-\beta}\phi(t) = 0, \]

\[ \frac{d\phi(t)}{dt} + \tau^{-\alpha\beta}\sum_{k=0}^{\infty} \tau^{-\alpha(k+1)}D_{t}^{-\alpha\beta}\phi(t) = 0. \]

Here we use the determination of the following integral operator \[ \[ E_{\rho;\nu,\alpha;\beta}^{\gamma} f(t) = \int_0^t (t-t')^{\nu-1}E_{\rho,\nu}^{\gamma}[\alpha(t-t')^{\alpha}]f(t')dt' = \sum_{m=0}^{\infty} \left( (\gamma)_m \alpha^m / m! \right) D_{t}^{-\nu-\alpha}f(t). \]

So, we proved that for the NCDP expressions corresponding to anomalous dielectric relaxation (including also the Debye's relaxation as a partial case) one can write the kinetic equations for the corresponding relaxation functions. The distinct feature of these kinetic equations is the presence of differential operators of non-integer order.
3. The Mori-Zwanzig formalism and memory function phenomenon

In the previous section we formulated an alternative approach to solution of the problem of the anomalous dielectric relaxation. It is based on derivation of kinetic equations for relaxation function that differs from the conventional Debye's relaxation function. We demonstrated the general approach of derivation of these kinetic equations that leads to the well-known empirical expressions for the CDP. Then in order to make next step it is necessary to construct a theory which can give a physical justification of these empirical expressions suggested earlier. Among known semi-phenomenological approaches (as far as we know) related to derivation of kinetic equations and associated with anomalous dielectric relaxation that similar to our approach we want to mark the follows. In paper [11] the kinetic equation corresponding to the Havriliak-Negami expression for the NCDP is derived by means of generalization of the noninertial Fokker-Plank equation for Brownian motion. In paper [12] the authors suggest an approach to analysis of the non-Debye's dielectric relaxation based on the Mori-Zwanzig formalism. The last approach from our point of view is the most acceptable for the purpose of derivation the kinetic equations of anomalous dielectric relaxation. This conclusion is based on the following reasons. Firstly, the projection operator method introduced by Mori-Zwanzig for construction of kinetic equations for temporal correlation functions is based on the first principles and actually can be considered as exact. Secondly, this method naturally introduces the memory function conception that is convenient in interpretation of physical results.

Equation for the temporal correlation function \( \psi(t) \) obtained in the frame of Mori-Zwanzig formalism can be written in the form [13]

\[
\frac{d\psi(t)}{dt} = -\int_0^t K(t-t')\psi(t')dt',
\]

where \( K(t) \) determines the memory function (MF).

In the frame of the linear response approximation, the fluctuations of polarization caused by thermal motion are the same as for the macroscopic reconstruction induced by the electric field [14]. Thus, one can equate the relaxation function and the macroscopic dipole correlation function (DCF) \( \psi(t) \) as follows

\[
\phi(t) \equiv \psi(t) = \frac{<M(t)M(0)>}{<M(0)M(0)>},
\]

where \( M(t) \) is the macroscopic fluctuating dipole moment of the sample volume unit, which is equaled to the vector sum of all entering in it molecular dipoles. So, the relaxation function \( \phi(t) \) satisfies to the same equation with memory (20). If one introduces the integral memory function (IMF) \( M(t) = \int_0^t K(t')dt' \) then the equation for the relaxation function (20) accepts the following form

\[
\frac{d\phi(t)}{dt} = -\frac{d}{dt}\int_0^t M(t-t')\phi(t')dt' = -\frac{d}{dt} M(t) * \phi(t),
\]

which mathematically coincides with equation (14). So the function \( R(t) \) in (14) can be interpreted as the IMF that is \( R(t) = M(t) \). So, comparing equation (22) with equations (15)-(18) we obtain the following expressions for the IMF that correspond to empirical expressions discussed earlier

Debye:

\[
M_D(t) = \tau^{-1},
\]

Cole-Cole:

\[
M_{CC}(t;\alpha) = \tau^{-\alpha}t^{\alpha-1}/\Gamma(\alpha),
\]

Cole-Devidson:

\[
M_{CD}(t;\beta) = e^{-t/\tau} \sum_{k=0}^{\infty} M_{CC}(t;\beta(k+1)) = e^{-t/\tau} \tau^{\beta-1}E_{\beta}[\tau^{-\beta}],
\]

\[
M_{CD}(t;\beta) = e^{-t/\tau} \sum_{k=0}^{\infty} M_{CC}(t;\beta(k+1)) = e^{-t/\tau} \tau^{\beta-1}E_{\beta}[\tau^{-\beta}],
\]

SPMCS 2012 IOP Publishing
Journal of Physics: Conference Series 394 (2012) 012013 doi:10.1088/1742-6596/394/1/012013
Havriliak-Negami: 

$$M_{HN}(t; \alpha, \beta) = \exp\left(-\alpha^{-1} \tau_0^{D_1-\alpha} t_1^{\alpha} \right) e^{D_{C1}^{1-\alpha} t} E_{\alpha\beta}[\tau^{1-\alpha} t].$$  \hspace{1cm} (26)  

Now it is necessary to develop a method for derivation of expressions for the IMF. We note that the Debye's expression for the IMF (23) corresponds to the absence of memory (Markovian process) and for this case we have $K_D(t) = \tau^{-\alpha} \delta(t)$. Non-Debye's expressions for IMF correspond to cases of the presence of a memory in the system considered.

4. Derivation of the Havriliak-Negami expression for the IMF

For derivation of the IMF (25) and (26) that correspond to Cole-Davidson and havriliak-Negami expressions it is necessary to construct the corresponding integro-differential (kinetic) equations. The Mori-Zwanzig formalism implies to calculate the memory function $K(t)$ from the following engaging system of integro-differential equations [15]

$$\frac{dK_n(t)}{dt} = -\int_0^t K_{n+1}(t-t')K_n(t')dt', \quad n = 1, 2, 3,...,  \hspace{1cm} (27)$$

where a set of $K_n(t)$ determines the so-called memory functions of the $n$th order and $K_1(t) \equiv K(t)$. For further conveniences we write these equations for the corresponding IMF

$$M_n(t) = tK_n(0) - \int_0^t K_n(t-t')M_n(t')dt', \quad n = 1, 2, 3,...,  \hspace{1cm} (28)$$

where $M_n(t) = \int_0^t K_n(t')dt'$. Let us analyze the equation for $M_1(t)$

$$M_1(t) = tK_1(0) - \int_0^t K_1(t-t')M_1(t')dt'. \hspace{1cm} (29)$$

If $K_1(0) = 0$, and $M_2(t) = M_{Cc}(t; \alpha) = \Gamma^{-1}(\alpha)\tau^{\alpha} \tau^{\alpha-1}$ then the last equation accepts the form

$$M_1(t) = -\tau^{\alpha-1} D_{t}^{\alpha} M_1(t) \Rightarrow \frac{dM_1(t)}{dt} = -\tau^{\alpha-1} D_{t}^{\alpha} M_1(t). \hspace{1cm} (30)$$

Let us suppose that $M_1(t)$ contains two parts: $M_1(t) = M_1^{(1)}(t) + M_1^{(2)}(t)$, where $M_1^{(2)}(t)$ is determined by equation (29) at $K_1(0) = 0$. At these conditions we obtain the following basic equation for $M_1(t)$:

$$M_1(t) = M_1^{(1)}(t) - \int_0^t M_2(t-t')M_1(t')dt'. \hspace{1cm} (31)$$

Let us suppose that this relaxation process considered in subsystems is superimposed on the second relaxation process that takes place between systems. The temporal evolution of the second process we determine by the second temporal argument $t'$ in the corresponding IMF as $M_1(t,t')$. Let us suppose that the second relaxation process obeys to kinetic equation (30)

$$dM_1(t,t')/dt' = -\tau^{\alpha-1} D_{t}^{\alpha} M_1(t,t'). \hspace{1cm} (32)$$

The solution of this equation can be written as

$$M_1(t,t') = \exp\left(-\tau^{\alpha-1} D_{t}^{\alpha} t'\right) M_1(t). \hspace{1cm} (33)$$

To the Havriliak-Negami expression for the IMF the following relaxation mechanism described above is realized: $M_1^{(1)}(t) = M_{Cc}(t; \alpha, \beta)$. Then as it follows from (31) the corresponding equations for the IMF describing the relaxation inside the systems accepts the form
\[ M_1(t) = \tau^{-\alpha_1} t^{\alpha_1-1} / \Gamma(\alpha_1) + \tau^{-\alpha_2} D_t^{-\alpha_2} M_1(t). \] (34)

The solution of this equation is known [10]
\[ M_1(t) = \tau^{-\alpha_1} t^{\alpha_1-1} E_{\alpha_1,\alpha_1} \left[ \tau^{-\alpha_1} t^{\alpha_1} \right]. \] (35)

The IMF for the combined relaxation process is determined from (33) at \( t' \to t \) and accepts the form
\[ M_1(t,t') = M_{\text{ENV}}(t;\alpha,\beta) = \exp \left( -\alpha^{-1} \tau^{-\alpha} D_t^{-\alpha} t \right) \tau^{-\alpha} t^{\alpha-1} E_{\alpha_1,\alpha_1} \left[ \tau^{-\alpha} t^{\alpha} \right], \] (36)

where \( \alpha = \tau_{\alpha}^a / \tau^a \). The Cole-Davidson expression for IMF is realized at \( \alpha=1 \). In this case the relaxation process between systems (as it follows from (32)) is described by Debye equation.

5. Conclusions

In this paper the authors suggest a method of description of the anomalous dielectric relaxation based on construction of kinetic equations containing non-integer differentiation/integration operators. For the derivation of the desired kinetic equations we use the Mori-Zwanzig formalism for correlation functions. This formalism determines also the important characteristics as memory function. Finally the problem of justification of empirical expressions for CDP is reduced to the derivation of the corresponding to them the desired IMF. For justification of the Havriliak-Negami empirical expression the following relaxation model is suggested. In this model relaxation in the system considered unifies the relaxation in dipole clusters and relaxation of dipole clusters themselves. In accordance with suggested relaxation model the scheme of the calculation of the desired IMF is suggested. It implies the construction of the corresponding kinetic equations for calculation of the desired IMF including each component of the relaxation process. The kinetic equations for the IMF are derived also in the frame of the Mori-Zwanzig formalism and based on utilization of the second order memory functions.

Acknowledgements

The work was done in the frame of the research plan "Dielectric spectroscopy and kinetics of complex systems" (Number: 12-18 02 0210 021000018) that has been accepted by the KFU for 2012 year.

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