THE VOLTERRA TYPE EQUATION RELATED TO THE NON-DEBYE RELAXATION

Katarzyna Górska
Institute of Nuclear Physics (INP),
Polish Academy of Sciences (PAS)
Kraków, Poland

In collaboration with:

- Andrzej Horzela, INP PAS, Kraków, Poland
- Tibor K. Pogany, Obuda Univ., Budapest, Hungary
- Giuseppe Dattoli, ENEA, Frascati, Italy

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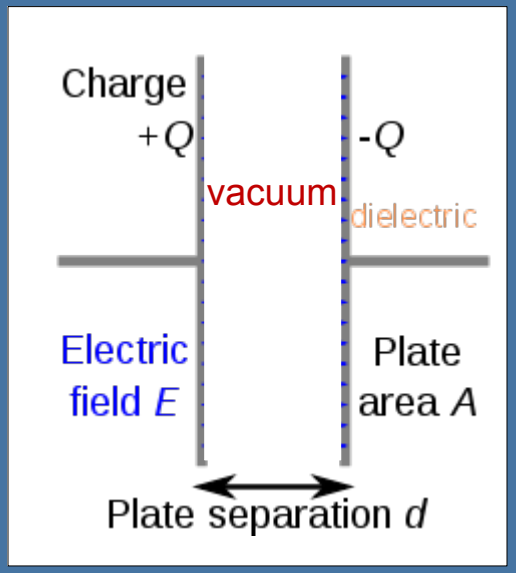
In physics, and in other natural sciences, under relaxation phenomena we usually mean processes describing the return of a perturbed system into *equilibrium*. Each relaxation can be categorized by a relaxation time τ. The simplest description of relaxation as a function of time f(t) is the Debye (called also *exponential*) law

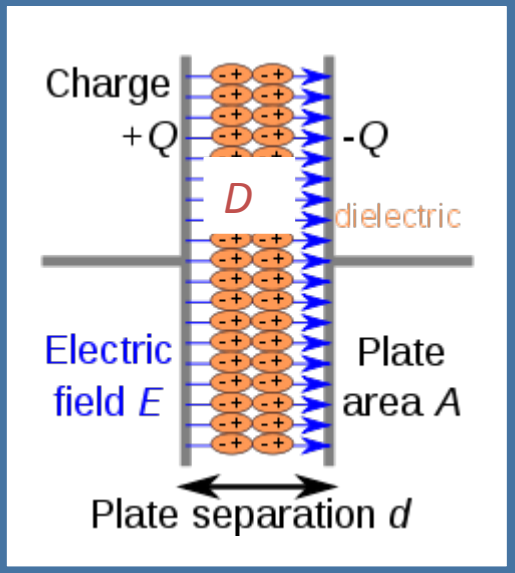
$$f(t) \sim \exp(-t/\tau).$$

Relaxations observed in complex systems usually are effects which cumulate more elementary processes, each of them being characterized by its own relaxation time.

Well known physical examples: decay of excited states, stress relaxation in viscoelastic media, relaxation of nuclear spin magnetic moments (NMR), luminescence phenomena, depolarization of dielectrics (dielectric relaxation).

Dielectric relaxation – a piece of school physics





The electric field inside the capacitor, which we name the electric induction and denote by D, differs from the external electric field but for the static case only by an universal multiplicative constant

$$D = \varepsilon_0 E$$

If the plates are separated by a dielectric then, because of polarization effects the electric field inside the capacitor, i.e. D, is reduced with respect to the external field E. Difference of these fields is called polarization P = D - E and depends on properties of the material filling the capacitor.

Description complicates for the time dependent case

$$D(t) = E(t) + P(t)$$

What's going on if the external field depends on time?

For many physical systems polarization can not follow the external field immediately and the system approaches its equilibrium only after some time. Return to equilibrium may be very fast, almost immediate, for conducting materials (e.g. metals) in which electric carriers are free (or almost free) but dielectrics need time to match new conditions up. Different time dependence of *E(t)* and *D(t)* is usually written down as the so-called constitutive relations

$$D(t) = \varepsilon_\infty E(t) + \int_{t_0}^{t} \kappa(t - t') E(t') \mathrm{d}t'$$

which take into account, in a way characteristic for a specific material (or even for a sample), „memory effects".

The basis formula is $D(t)=\varepsilon_\infty E(t)+\int_{t_0}^{t}\kappa(t-t')E(t')\mathrm{d}t'$ but for experiments it is more convenient to pass to the frequency domain, i.e. to the Fourier/Laplace transformed picture in which

$$\tilde{D}(\omega)=\varepsilon^*(\omega)\tilde{E}(\omega) \qquad \varepsilon^*(\omega)=\varepsilon_\infty+\tilde{\kappa}(\omega)$$

FORMS OF INTEGRAL KERNEL κ(t):

- The time domain response function $\phi(t)$ informs us about the current flowing through the experimental setup under the action of step function - like electric field.
  Its Fourier transform (spectral function) is complex

$$\tilde{\phi}(\mathrm{i}\omega)=\phi'(\mathrm{i}\omega)-\mathrm{i}\phi''(\mathrm{i}\omega)$$

$$\tilde{\phi}(\mathrm{i}\omega)=\int_0^\infty \mathrm{e}^{-\mathrm{i}t\omega}\phi(t)\mathrm{d}t=L[\phi(t);\mathrm{i}\omega]=\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_{static}-\varepsilon_\infty}$$

$\tilde{\phi}(\mathrm{i}\omega)$ must satisfy some conditions – namely be analytic in the upper half-plane which guarantees the Kronig-Kramers rule (Sochocki-Plemelj th.)

Experimental data for $\tilde{\phi}(i\omega)$ may be (quite well) described by phenomenological models having similar functional shape depending on 2 +1 parameters characterizing the material):

$$\tilde{\phi}(i\omega)=\left[1+(i\omega\tau)^{\alpha}\right]^{-\gamma}$$

τ is some time parameter

$$D(ebye):\alpha=\gamma=1$$

$$C(ole)C(ole):0<\alpha\le 1,\gamma=1$$

$$C(ole)D(avidson):\alpha=1,0<\gamma\le 1$$

$$H(avriliak)N(egami):$$

$$0<\alpha\le 1,0<\gamma\le 1$$

For solids there is no „primary" rule which model and which choice of parameters optimally fit the experimental data .

- The relaxation function $f(t)=-\phi'(t)$ which for the Havriliak-Negami relaxation is given by the Prabhakar function $f(t)=1-e^{\gamma}_{\alpha,1+\alpha\gamma}(t,-\tau^{-\alpha}).$

For $\gamma = 1$ it gives the relaxation function of the Cole-Cole model, i.e.

$$f(t)=E_{\alpha}[-(t/\tau)^{\alpha}].$$

What does the Prabhakar function $e^{\gamma}_{\alpha,\nu}(x,a)$ means?

$$e^{\gamma}_{\alpha,\nu}(x,a) = x^{\nu-1} E^{\gamma}_{\alpha,\nu}(ax^{\alpha}), \qquad a, x \in R$$

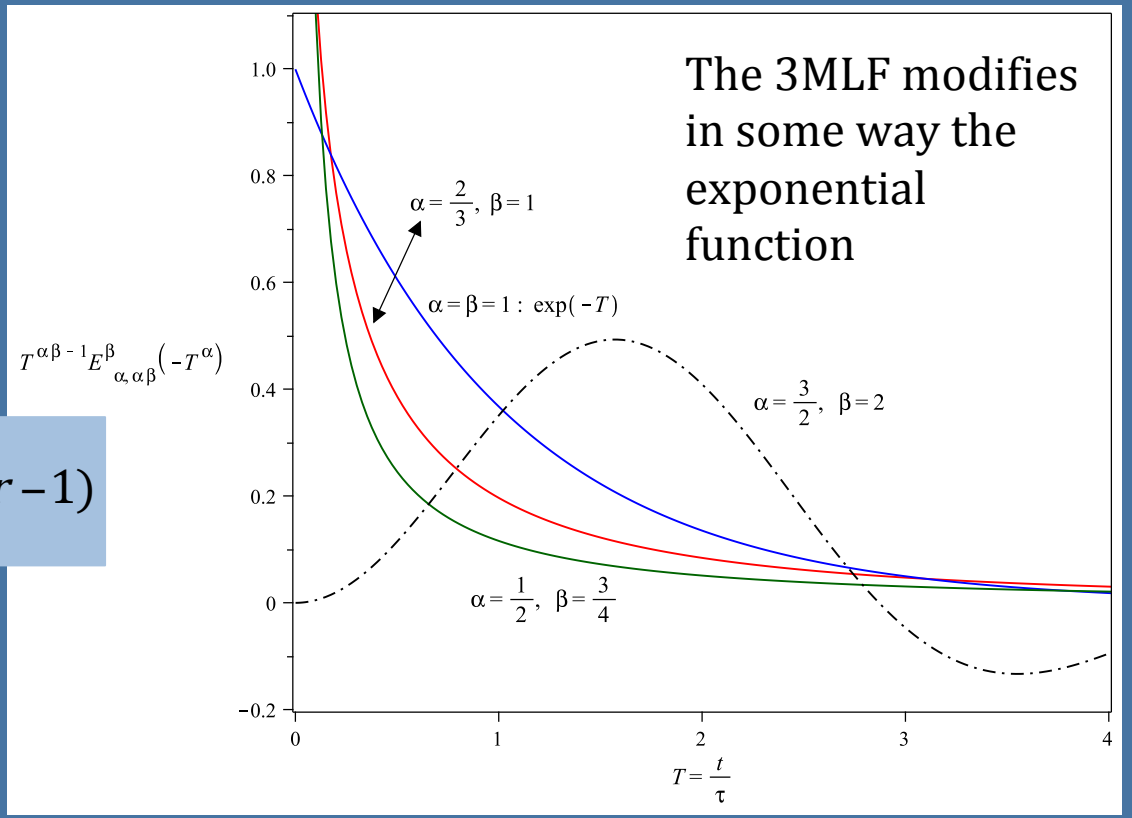
The series definition of the 3-parameters Mittag-Leffler function (3MLF) $E^{\gamma}_{\alpha,\nu}(ax^{\alpha})$ is equal to

$$E^{\gamma}_{\alpha,\nu}(y) = \sum_{r=0}^{\infty} \frac{(\gamma)_r \, y^r}{r!\,\Gamma(\beta+\alpha r)},$$

where

$$(\gamma)_r = \frac{\Gamma(\gamma+r)}{\Gamma(\gamma)} = \gamma(\gamma+1)(\gamma+2)\ldots(\gamma+r-1)$$

is the Pochhamer (raising) symbol.



The Prabhakar function is presented in the evolution equation of HN relaxation in the pseudo-operator ${}^{C}({}_0D_t^{\alpha}+a)^{\gamma}$

HANYGA (1999) GARRA, GORENFLO, POLITO, TOMOVSKI (2014), MAINARDI, GARRAPPA (2016, 2017)

What is this pseudo-operator ?

What form has the evolution equation?

${}^{C}({}_0D_t^{\alpha}+a)^{\gamma} f(t)$ is the regularized version of the pseudo-operator $({}_0D_t^{\alpha}+a)^{\gamma} f(t)$ Riemann-Liouville sense. It means that the regularization enable us to cancel the term with function *f(t)* at the initial moment.

Thus, the pseudo-operator ${}^{C}({}_0D_t^{\alpha}+a)^{\gamma} f(t)$ can be presented as the regularized series

$$ {}^{C}({}_0D_t^{\alpha}+a)^{\gamma} f(t) = {}^{C}\left[\sum_{r\geq 0} \frac{\Gamma(1+\gamma)}{r!\Gamma(1+\gamma-r)} a^{r}\ {}_0D_t^{\alpha(\gamma-r)} f(t)\right] $$

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Making the numerical calculation we have to truncate the series – it is not clear when the series must be truncated in order to obtain a prescribed accuracy.

We treat the pseudo-operator ${}^{C}({}_0D_t^{\alpha}+a)^{\gamma}$ as the following composition (integral)

$$
\begin{aligned}
{}^{C}({}_0D_t^{\alpha}+a)^{\gamma}\, g(t) &\equiv e^{-\gamma}_{\alpha,1-\alpha\gamma}(t;-a) * \frac{\mathrm{d}}{\mathrm{d}t} g(t) \\
&= \int_0^t e^{-\gamma}_{\alpha,1-\alpha\gamma}(t-u;-a)\, g'(u)\,\mathrm{d}u
\end{aligned}
$$

$0 < \alpha, \gamma \leq 1$

the Prabhakar function

$$e^{\mu}_{\alpha,\gamma}(t;a) = t^{\gamma-1} E^{\mu}_{\alpha,\gamma}(at^{\alpha})$$

$$L[e^{\mu}_{\alpha,\gamma}(t;a);s] = s^{\alpha\mu-\gamma}(s^{\alpha}-a)^{-\mu}$$

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integro-differential operator

the Prabhakar function

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$$ L[e^{\mu}_{\alpha,\gamma}(t;a);s] = s^{\alpha\mu-\gamma}(s^{\alpha}-a)^{-\mu} $$

$0 < \alpha, \gamma \leq 1$

In the literatures devoted to the theoretical study of relaxation processes can be found the **evolution equation** for HN model of relaxation in the form:

$$ {}^{C}({}_0D_t^{\alpha}+a)^{\gamma}\, P(t) = -\tau^{\alpha\gamma} E(t) $$

polarization electric field

MAINARDI, GARRAPPA (2016, 2017)

We can distinguish the following pseudo-operators called the *"generalized fractional derivative"*

$$({}_0^{?}D_t^{\alpha} g)(t) = \int_0^t k(t-\xi)\frac{\mathrm{d}}{\mathrm{d}\xi} g(\xi)\,\mathrm{d}\xi$$

which depend on the explicit form of the integral kernel *k(t):*

- (C)aputo derivative: $k(t) = t^{-\alpha} / \Gamma(1-\alpha)$
- (C)aputo-(F)abrizio derivative: $k(t) \propto e^{-\alpha t/(1-\alpha)}$
- (A)tangana-(B)aleanu derivative: $k(t) \propto E_{\alpha}[-\alpha t^{\alpha} / (1-\alpha)]$
- (P)rabhakar derivative: $k(t) \propto e^{-\gamma}_{\alpha,1-\alpha\gamma}(t,a)$

For $a = 0$ and $\gamma = 1$ we have the Caputo derivative

Their Laplace transforms are denoted as $K(\alpha; s)$.

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which depend on the explicit form of the integral kernel *k(t):*

- (C)aputo derivative: $k(t) = t^{-\alpha}/\Gamma(1-\alpha)$ $\quad K(\alpha;s) = s^{-1+\alpha}$
- (C)aputo-(F)abrizio derivative: $k(t) \propto e^{-\alpha t/(1-\alpha)}$ $\quad K(\alpha;s) = [\alpha + (1-\alpha)s]^{-1}$
- (A)tangana-(B)aleanu derivative: $k(t) \propto E_{\alpha}[-\alpha t^{\alpha}/(1-\alpha)]$

  $K(\alpha;s) \propto [\alpha s^{1-\alpha} + (1-\alpha)s]^{-1}$
- (P)rabhakar derivative:

  $k(t) \propto e^{-\gamma}_{\alpha,1-\alpha\gamma}(t,a)$ $\quad K(\alpha;s) \propto s^{-1}(s^{\alpha} - a)^{\gamma}$

Their Laplace transforms are denoted as *K(α; s)*.

Let us consider the integro-differential equation

$$\int_0^t k(t-\xi)\frac{\mathrm{d}}{\mathrm{d}\xi}f(\xi)\mathrm{d}\xi = -\Lambda(\tau,\alpha)f(t),$$

whose formal solution can be written as

$$f(\alpha,\Lambda;t) = L^{-1}\left[\frac{K(\alpha;s)}{s\,K(\alpha;s)+\Lambda(\tau,\alpha)}f(0);\ t\right]$$

inverse Laplace transform — initial condition

The solvability of the above equation is governed by the conditions:

$$K(\alpha;s)\to\infty, \quad sK(\alpha;s)\to 0, \quad \text{for} \quad s\to 0,$$
$$K(\alpha;s)\to 0, \quad sK(\alpha;s)\to\infty, \quad \text{for} \quad s\to\infty,$$

KOCHUBEI, 2011

For Prabhakar derivative with $\gamma = 1$ the Laplace transform of the integral kernel (memory) is equal to $K(\alpha; s) = s^{-1}(s^{\alpha} - a)$. Thus, the formal solution is given by

$$f(\alpha,\Lambda;t) = L^{-1}\left[\frac{s^{\alpha-1}}{s^{\alpha}+(\Lambda-a)}f(0);t\right] + L^{-1}\left[\frac{s^{-1}}{s^{\alpha}+(\Lambda-a)}f(0);t\right]$$

Because of $L[e^{\gamma}_{\alpha,\nu}(t;a);s]=s^{\alpha\gamma-\nu}(s^{\alpha}-a)^{-\gamma}$ and involving the property of the Mittag-Leffler function the solution $f(\alpha, \Lambda; t)$ reads

$$f(\alpha,\Lambda;t)=\frac{\Lambda}{\Lambda-a}E_{\alpha}[-(\Lambda-a)t^{\alpha}]f(0)-\frac{a}{\Lambda-a}f(0).$$

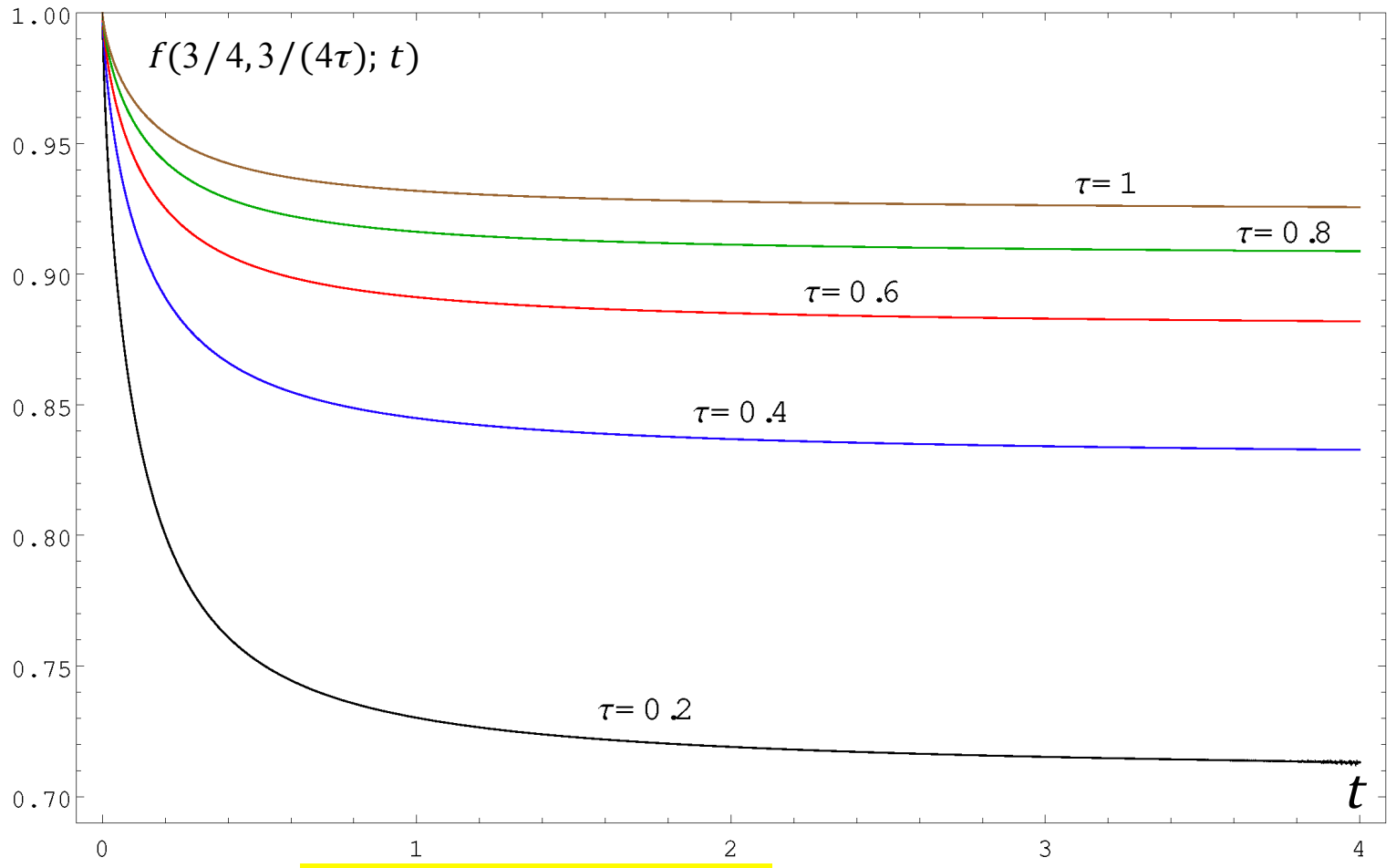
It is known that the above solution solves also the equation

$${}^{C}D^{\alpha}_{t}f(\alpha,\Lambda;t)=-(\Lambda-a)f(\alpha,\Lambda;t)-af(0)$$

NONNENMACHER, METZLER, 1995; WEST, 2010; GÓRSKA, PENSON, DATTOLI, 2011

known as the generalization of a relaxation (Cole-Cole) equation with a constant force term *a*. We shouldn't be surprised this result because of the integral kernel in the Prabhakar derivative $e^{-1}_{\alpha,1-\alpha}(t,a)$ is equal to

$$e^{-1}_{\alpha,1-\alpha}(t,a)=[t^{\alpha}\,\Gamma(1-\alpha)]^{-1}-a$$



For $t \to \infty$ it tents to

$$f(3/4,3/(4\tau);\, t) \to -\frac{a}{\Lambda - a} f(0) = \frac{4\tau}{1 + 4\tau}$$

For $a=0$ and $t\to\infty$ we have that

* $f(\alpha,\Lambda;t)\to 0$

* ${}^{C}D_t^{\alpha} f(\alpha,\Lambda;t) = -\Lambda f(\alpha,\Lambda;t)$

The integro-differential equation for the Mittag-Leffler function and the relaxation function of the Cole-Cole model.

Can we in this way obtain the equation governing the Havriliak-Negami relaxation? Let us consider

$$\int_0^t \underbrace{e^{-\gamma}_{\alpha,1-\alpha\gamma}(t-\xi)}_{k(t-\xi)} \frac{\mathrm{d}}{\mathrm{d}\xi} f(\xi)\mathrm{d}\xi = -\underbrace{\tau^{-\alpha}}_{\Lambda(\tau,\alpha)} f(t)$$

whose formal solution is given by

$$f(\alpha,\gamma,\tau^{-\alpha};t) = f(0) + \int_0^{\infty} e^{-a\xi} e^{1}_{\gamma,0}(-\tau^{-\alpha},\xi)\,\Phi_{\alpha}(\xi,t)d\xi\, f(0)$$

$$\Phi_{\alpha}(\xi,t) = L^{-1}[s^{-1}e^{-\xi s^{\alpha}};t]$$ known

If the solution $f(\alpha,\tau^{-\alpha};t)=E_{\alpha}[-(t/\tau)^{\alpha}]$ is related to the relaxation function of Cole-Cole relaxation then

$$f(\alpha,\gamma,\tau^{-\alpha};t)=f(0)+\int_0^{\infty}e^{-a\xi}e^{1}_{\gamma,0}(-\tau^{-\alpha},\xi)\,\Phi_{\alpha}(\xi,t)d\xi\,f(0)$$

under some conditions (we should find them) will give the relaxation function of the Havriliak-Negami model, i.e.

$$f(t)=1-e^{\gamma}_{\alpha,1+\alpha\gamma}[-(t/\tau)^{\alpha}].$$

THANK YOU FOR YOUR ATTENTION!!!