Chapter 24
An Application of Fractional Calculus to Dielectric Relaxation Processes

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1 Introduction

Fractional calculus, which is the field of mathematical analysis dealing with the investigation and applications of integrals and derivatives of arbitrary order, has attracted in recent years a considerable interest in many disciplines. It has been found that the behavior of many physical systems can be more properly defined by using the fractional theory. The flexibility of degrees of freedom, which is very easily obtained in the fractional theory, is one of the most important advantages of the fractional order modeling. Moreover, in recent years, the use of the fractional calculus in the analysis of the fractional diffusion equations has been a field of increasing interest [5, 11, 13–16, 21, 22].

1.1 The Fractional Integral and Riemann–Liouville Fractional Derivative

According to the Riemann–Liouville approach, the fractional integral of order $\alpha > 0$ is defined as,

$$ {}_aJ_t^{-\alpha}U(t) = \frac{1}{\Gamma(\alpha)} \int_a^t (t-\tau)^{\alpha-1} U(\tau) d\tau \tag{24.1} $$

$$ {}_aJ_t^{0}U(t) = U(t) \tag{24.2} $$

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Moreover, for $\alpha, \beta > 0, t > 0$, and $\upsilon > -1$ (24.1) has the following properties:

$$J_t^{-\alpha} J_t^{-\beta} U(t) = J_t^{-(\alpha+\beta)} U(t) \tag{24.3}$$

and

$$J_t^{-\alpha} t^{\upsilon} = \frac{\Gamma(\upsilon+1)}{\Gamma(\upsilon+1+\alpha)} t^{\upsilon+\alpha} \tag{24.4}$$

Also,

$${}_aD_t^p U(t) = \left(\frac{d}{dt}\right)^{m+1} \int_a^t (t-\tau)^{m-p} U(\tau) \mathrm{d}\tau. \tag{24.5}$$

The expression (24.5) is the most widely known definition of the fractional derivative and is usually called the Riemann–Liouville fractional derivative definition. The most important property of the Riemann–Liouville fractional approach is given by:

$${}_aD_t^{\alpha} \left({}_aJ_t^{-\alpha} U(t)\right) = U(t) \tag{24.6}$$

The Riemann–Liouville fractional differentiation operator is a left inverse to the Riemann–Liouville fractional integration operator of the same order α. The detailed properties of the operator J^{α} and D^p can be found in [17, 19, 20].

1.2 Adomian Decomposition Method

Adomian decomposition method (ADM) introduced by Adomian in 1980 has proved to be a very useful tool in the solution of nonlinear functional equations. The decomposition method consists of finding a solution in the form,

$$U(x,t) = \sum_{n=0}^{\infty} U_n(x,t), \tag{24.7}$$

where the components $U_n(x,t)$ will be determined recursively. More information about ADM can be found in [1].

2 Dielectric Relaxation Processes

Relaxation properties are generally expressed in terms of time-domain response function $f(t)$ or of the frequency-dependent real and imaginary components of its Fourier transform [23]:

$$\tilde{f}(i\omega) = \int_0^{\infty} e^{-i\omega t} f(t) \mathrm{d}t = \phi'(\omega) - i\phi''(\omega). \tag{24.8}$$

Classically, relaxation processes are described in terms of the exponential function:

$$\varphi(t) = \exp(-t/\tau), t \geq 0 \tag{24.9}$$

that is generally referred to as Maxwell–Debye relaxation. However, in many systems the dynamical behavior shows conspicuous deviations from the ideal exponential pattern. Therefore, in general the empirical expressions, involving adjustable parameters, have been widely used in the literature.

Commonly three general relaxation laws are encountered in the experimental studies of complex systems:

(i) Stretched exponential (KWW) function [24]

$$f(t) \approx \exp[-(t/\tau)^{\alpha}], 0 < \alpha < 1, t > \tau \tag{24.10}$$

(ii) Exponential–logarithmic function

$$f(t) \approx \exp[-B\ln^{\alpha}(t/\tau)] \tag{24.11}$$

(iii) Algebraic decay function

$$f(t) \approx (t/\tau)^{\alpha} \tag{24.12}$$

where α, τ, and B are the appropriate fitting parameters [18].

By definition, the normalized susceptibility, $\chi(\omega)$, is connected to the normalized relaxation function through the relation:

$$\chi(\omega) = \int_0^{\infty} e^{-i\omega t} \mathrm{d}(-\varphi(t)) = 1 - i\omega \int_0^{\infty} e^{-i\omega t} \varphi(t) \mathrm{d}t, \tag{24.13}$$

where $\varphi(t) = \Phi(t)/\varphi(0)$. A significant amount of experimental data on disordered systems supports the following empirical expressions for dielectric loss spectra, namely, the Cole–Cole equation [4],

$$\chi(\omega) = \frac{\chi_0}{1 + (i\omega\tau)^{\alpha}}, 0 < \alpha \leq 1 \tag{24.14}$$

the Cole–Davidson equation [6],

$$\chi(\omega) = \frac{\chi_0}{(1 + i\omega\tau)^{\beta}}, 0 < \beta \leq 1 \tag{24.15}$$

and the Havriliak–Negami equation [8] considered as a general expression for the universal relaxation law [10],

$$\chi(\omega) = \frac{\chi_0}{(1+(i\omega\tau)^{\alpha})^{\beta}}, 0 < \alpha \text{ and } \beta \leq 1. \tag{24.16}$$

Here, we should point out that the Havriliak–Negami equation is a combination of the Cole–Cole and Cole–Davidson equations.

3 The Ising Model and Fractional Relaxation

The spin–spin time correlation functions in a one-dimensional Ising model [9] with Glauber dynamics [7] was studied by Bozdemir [3], and later by Brey and Parados [2]. The main idea in those studies is the spin time autocorrelation function obtained in the one-dimensional Ising model with Glauber dynamics which is assumed to be identical with the dipole correlation function of a molecular chain. Based on this assumption, the system can be analyzed in the following way: The energy of the system in the one-dimensional Ising model for a spin configuration σ is

$$H(\sigma) = -J\sum_i \sigma_i \sigma_{i+1}, \tag{24.17}$$

where J is a positive coupling constant. The state of the system is specified by the spin vector $\sigma = \{\sigma_i\}$, where $\sigma_i = \pm 1$ is the spin at site i. The evolution of the system is described by a Markov process with Glauber dynamics. So, the conditional probability $P_{1/1}(\sigma, t/\sigma', t')$ of finding the system in the state σ at a time t, provided that it was given in the state σ' at a time t', obeys the master equation:

$$\frac{\partial P_{1/1}(\sigma,t/\sigma',t')}{\partial t} = \sum_{i=-\infty}^{\infty} \left[\omega_i(R_i\sigma)p_{1/1}(R_i\sigma,t/\sigma',t') - \omega_i(\sigma)p_{1/1}(\sigma,t/\sigma',t')\right], \tag{24.18}$$

where $R_i\sigma$ is the configuration obtained from σ by flipping the ith spin and $\omega_i(\sigma)$ is the transition rate for the flip. Following the above procedure, the spin–spin–time correlation function, in the low temperature limit, was found by Brey and Parados as the following differential equation,

$$\frac{\partial f_n}{\partial t} = -\alpha f_n(t) + \frac{\alpha\gamma}{2}[f_{n-1} + f_{n+1}], \tag{24.19}$$

where n is an integer in the range $-\infty < n < \infty$, α is a positive constant defining the time scale of the evolution of the system and γ is a function of temperature T of the heat bath given as:

$$\gamma = \tanh\frac{2J}{k_B T}, \tag{24.20}$$

where k_B is the Boltzmann's constant. Equation (24.19), which is a function of time and position, can be expressed as:

$$\frac{\partial f(x,t)}{\partial t} = -\alpha f(x,t) + \frac{\alpha\gamma}{2}\left[f(x-1,t) + f(x+1,t)\right]. \tag{24.21}$$

If one takes the Taylor expansion of Equation (24.21) and retains only terms up to second order, one obtains a diffusion type equation:

$$\frac{\partial f(x,\,t)}{\partial t} = (\alpha\gamma - \alpha)\, f(x,\,t) + \frac{\alpha\gamma}{2}\frac{\partial^2 f(x,\,t)}{\partial x^2} \tag{24.22}$$

If equation (24.22) is converted to fractional differential equation form, one gets

$$D_t^{\xi} f(x,t) = (\alpha\gamma - \alpha)\, f(x,t) + \frac{\alpha\gamma}{2}\frac{\partial^2 f(x,t)}{\partial x^2}, \tag{24.23}$$

where D_t^{ξ} is the Riemann–Liouville fractional differentiation operator, and the initial condition for $f(x,t)$ is

$$f(x,0) = \mathrm{e}^{-|x|}. \tag{24.24}$$

We adopt ADM for solving (24.23). According to this method we assume that

$$f(x,t) = \sum_{n=0}^{\infty} f_n(x,t). \tag{24.25}$$

Now, the fractional differential equation (24.25) can be written as, for $\upsilon + \zeta = 1$,

$$D_t^{\upsilon}\left(D_t^{\xi} f(x,t)\right) = (\alpha\gamma - \alpha) D_t^{\upsilon} f(x,t) + \frac{\alpha\gamma}{2} D_t^{\upsilon}\frac{\partial^2 f(x,t)}{\partial x^2}. \tag{24.26}$$

If we operate on both sides of this relation with integral operator Ω_t^{-1}, we reach to

$$\Omega_t^{-1} D_t^{\upsilon}\left(D_t^{\xi} f(x,t)\right) = (\alpha\gamma - \alpha)\Omega_t^{-1}\left(D_t^{\upsilon} f(x,t)\right) + \frac{\alpha\gamma}{2}\Omega_t^{-1}\left(D_t^{\upsilon}\frac{\partial^2 f(x,t)}{\partial x^2}\right) \tag{24.27a}$$

$$f(x,t) = (\alpha\gamma - \alpha)\Omega_t^{-1}\left(D_t^{\upsilon} f(x,t)\right) + \frac{\alpha\gamma}{2}\Omega_t^{-1}\left(D_t^{\upsilon}\frac{\partial^2 f(x,t)}{\partial x^2}\right). \tag{24.27b}$$

Moreover, the recursive relations related to the above equation are given in the following forms:

$$f(0) = f(x,0) = \mathrm{e}^{-|x|}$$

$$f(1) = (\alpha\gamma - \alpha) D_t^{-\xi} f(0) + \frac{\alpha\gamma}{2} D_t^{-\xi}\frac{\partial^2 f(0)}{\partial x^2} = \left(\alpha\gamma - \alpha + \frac{\alpha\gamma}{2}\right)\frac{\mathrm{e}^{-|x|} t^{\xi}}{\Gamma(\xi+1)}.$$

$$f(2) = (\alpha\gamma - \alpha)D_t^{-\xi} f(1) + \frac{\alpha\gamma}{2} D_t^{-\xi} \frac{\partial^2 f(1)}{\partial x^2} = \left(\alpha\gamma - \alpha + \frac{\alpha\gamma}{2}\right)^2 \frac{\mathrm{e}^{-|x|} t^{2\xi}}{\Gamma(2\xi+1)}.$$

$$f(3) = (\alpha\gamma - \alpha)D_t^{-\xi} f(2) + \frac{\alpha\gamma}{2} D_t^{-\xi} \frac{\partial^2 f(2)}{\partial x^2} = \left(\alpha\gamma - \alpha + \frac{\alpha\gamma}{2}\right)^3 \frac{\mathrm{e}^{-|x|} t^{3\xi}}{\Gamma(3\xi+1)}.$$

and so on. Therefore, the solution (24.27b) becomes:

$$\begin{aligned} f(x,t) &= \sum_{n=0}^{\infty} \left(\alpha\gamma - \alpha + \frac{\alpha\gamma}{2}\right)^n \frac{\mathrm{e}^{-|x|} t^{n\xi}}{\Gamma(n\xi+1)} \\ &= \mathrm{e}^{-|x|} E_\xi \left\{\alpha(-1+3\gamma/2)t^\xi\right\}, \quad 0 < \xi < 1, \end{aligned} \tag{24.28}$$

where $E_\xi\{\cdot\}$ is the Mittag–Leffler function given by:

$$E_\nu\{Z\} = \sum_{n=0}^{\infty} \frac{Z^n}{\Gamma(\nu n+1)}. \tag{24.29}$$

If we assume that the position of dipoles located between x and $x + x_0$ have a probability density given by:

$$f(x) = \frac{1}{x_0} \mathrm{e}^{(-x/x_0)}, \tag{24.30}$$

and substitute it into (24.30), integrate over all the space, we can obtain the time-dependent correlation function:

$$f(t) = \int_0^\infty \mathrm{e}^{(-x/x_0)} \mathrm{e}^{-|x|} E_\xi\{\alpha(-1+3\gamma/2)t^\xi\}\mathrm{d}x = \frac{E_\xi\{\alpha(-1+3\gamma/2)t^\xi\}}{1+x_0}, \tag{24.31}$$

where x_0 is the average value of x, and $1/2x_0$ is the average number of dipoles per unit length.

If equation (24.31) is substituted into (24.13), one obtains

$$\chi(\omega) = 1 - i\omega \int_0^\infty \mathrm{e}^{-i\omega t} \frac{E_\xi\{\alpha(-1+3\gamma/2)t^\xi\}}{1+x_0} \mathrm{d}t. \tag{24.32}$$

From this expression, in the frequency zone, the empiric Cole–Cole type equation is obtained as:

$$\chi(\omega) = \frac{x_0}{1 + (i\omega\tau)^\xi}, \quad 0 < \xi \leq 1, \tag{24.33}$$

where $\tau = [\alpha(-1+3\gamma/2)]^{-\xi}$, $\chi_0 = 1 + \lambda(i\omega\tau)^\xi$, and $\lambda = 1 - 1/(1+x_0)$.

Moreover, for sufficiently small times, (24.33), which is a Mittag–Leffter type function, exhibits the same behavior as with the stretched exponential function [12]:

$$f(t) \approx 1 - \frac{(t/\tau)^{\xi}}{\Gamma(\xi+1)} + \ldots \approx \exp\left[-\frac{(t/\tau)^{\xi}}{\Gamma(\xi+1)}\right], \quad 0 < t \ll 1, \tag{24.34}$$

which is known as Kolraush–William–Watts (KWW) function. Also, by using the asymptotic expansions it can be written as,

$$f(t) \approx \frac{\Gamma(\xi)\sin(\pi\xi)}{\pi}(t/\tau)^{-\xi}, \quad t \to \infty, \tag{24.35}$$

which has the same form with that of empirical algebraic decay function (24.12). When (24.19) is solved by using the eigenfunctions method with appropriate boundary conditions, which was done by [2],

$$\chi(\omega)\frac{\alpha(1-\eta^2)}{(1+\eta^2)\left[(i\omega+\alpha)^2-\alpha^2\gamma^2\right]}^{1/2} \tag{24.36}$$

is obtained, where $\eta = \tan J/K_{\mathrm{B}}T$. This expression, at low temperature, converts to a special case of the Cole–Davidson equation:

$$\chi(\omega) = \frac{1}{(1+i\omega\tau)^{1/2}}, \tag{24.37}$$

where τ is the relaxation time [2].

4 Conclusion

In this study, it is shown that fractional solution of the diffusion equation obtained from the stochastic Ising model, where we used the Adomian decomposition method for solving the fractional diffusion equation, gives a non-Debye type behavior which can also be represented by the Mittag–Leffler decay function. Furthermore, we may say that fractional dynamics in polar dielectric systems are a result of fractional dipole distribution in the medium. In the fractional approaches, the variable parameter α, especially used in the forming of the fractional order modeling, exhibits that the space of physical processes has a fractional form. Therefore, the irregularity (or chaos) in the nature compels us to use the fractional theory.

We have seen that the fractional order of the differential equations, which is compatible with most of the experimental results, is generally smaller than that of the integer order of differential equations. Likely, in the medium, the nearest neighbor interactions between dipoles or charged particles have not the same behaviors as that of the linear systems in terms of times and velocities, because the time (or energy) is fractionally changing in time. The local spaces of charged particles which have different time and energy intervals should lead to be resulted

to have fractional order differential equations. Moreover, it may be said that in the atomic levels (or electronic) the flow of the time is quantized. Therefore, the interactions between dipoles in questions may also be quantized in time domain. That is, quantization of the energy may be a result of the time quantization. As a result of these processes, the order of the differential equations should be changing during the interaction times.

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