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Anomalous relaxation and dielectric response

Igor Goychuk
Institute of Physics, University of Augsburg, Universitätsstraße 1, D-86135 Augsburg, Germany
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It is shown that all the known experimental (quasi)*stationary* dielectric response functions of glassy media can be derived from a standard generalized Langevin description of overdamped torsional dipole oscillators in trapping potentials with random orientations under some minimal assumptions. The *non-Markovian* theory obeys the fluctuation-dissipation theorem and the Onsager regression theorem. Moreover, it displays no aging on the time scale of the dielectric response, all in assumption of local thermal (quasi)equilibrium. Aging might come from jumping among metastable traps. It occurs on a quite different time scale which is not related to the *principal* dielectric response. We put the old phenomenological theory of Cole and Cole, Davidson and Cole, and others on a firm basis within a stochastic, thermodynamically consistent approach.

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It is well known that glassylike media are not at global thermodynamical equilibrium. This implies such phenomena as nonstationarity and aging, which are accompanied by long-range memory effects and $1/f$ noise dielectric fluctuations. However, on the typical time scale of the dielectric response in spectroscopy experiments these disordered media can be considered yet as quasistationary, being local, at thermal equilibrium. The purpose of this Rapid Communication is to show how all the known *quasistationary* anomalous dielectric response functions emerge from a simple and meaningful theoretical model.

Let us consider an ensemble of electrical dipoles $\mu_i=\mu$ with (disordered) orientations $\phi_i^{(0)}$ [two-dimensional (2D) model is assumed for simplicity]. Dipoles have the inertia moments J and can dynamically reorient, $\phi_i(t)=\phi_i^{(0)}+\delta\phi_i(t)$, sitting in orientational trapping potentials $U(\delta\phi)=\kappa(\delta\phi)^2/2$ (harmonic approximation is assumed). The dipoles are subjected to the periodic electrical field $\mathcal{E}(t)=\mathcal{E}_0\cos(\Omega t)$ and to random stochastic perturbations of the environment. The latter can be described within the standard model of bilinear coupling to thermal bath of harmonic oscillators. The interaction of the ith dipole with the field is $H_{int}(t)=-\mu\cos(\phi_i(t)-\alpha)\mathcal{E}(t)\approx-\mu\cos(\phi_i^{(0)}-\alpha)\mathcal{E}(t)+\mu\sin(\phi_i^{(0)}-\alpha)\delta\phi_i(t)\mathcal{E}(t)$ in the linear approximation (α is the field orientation). Mutual dipole-dipole interaction is included in the local trapping potentials in a mean-field manner. Under the model assumptions the stochastic dynamics of individual dipole (subindex i is omitted) is described by the generalized Langevin equation (GLE) [1–4]

$$J\delta\ddot{\phi}(t)+\int_0^t\eta(t-t')\delta\dot{\phi}(t')dt'+\kappa\delta\phi(t)=\xi(t)+\gamma\mathcal{E}(t), \tag{1}$$

where $\gamma=\mu\sin(\alpha-\phi_i^{(0)})$ and $\xi(t)$ is a Gaussian random force with the autocorrelation function $\langle\xi(t)\xi(t')\rangle$ related to the frictional kernel $\eta(t)$ by the fluctuation-dissipation relation

$$\langle\xi(t)\xi(t')\rangle=k_BT\eta(|t-t'|). \tag{2}$$

The dipole-environmental interaction is fully captured by $\eta(|t-t'|)$, which can be derived from a detailed microscopic model or can alternatively be considered as a phenomenological function to be determined experimentally from the spectroscopic experiments. The popular model of Ohmic thermal bath yields $\eta(t)=2\eta\delta(t)$, where η is the Stokes viscous friction coefficient. This corresponds to a standard model of torsional dipole oscillators [5], which is Markovian. Any other choice implies non-Markovian memory effects. We assume in the following the dipole dynamics to be heavily overdamped ($J\to0$). Then, the first inertial term can be neglected. In the Markovian limit this yields the Debye model. The solution of Eq. (1) can be found with the help of the Laplace transform $\tilde{f}(s)=\int_0^\infty\exp(-st)f(t)dt$. It formally reads

$$\widetilde{\delta\phi}(s)=\tilde{\theta}(s)\delta\phi(0)+\frac{\tilde{\theta}(s)}{\tilde{\eta}(s)}\tilde{\xi}(s)+\frac{1}{2}\gamma\mathcal{E}_0\left(\frac{1}{s-i\Omega}+\frac{1}{s+i\Omega}\right)\frac{\tilde{\theta}(s)}{\tilde{\eta}(s)}, \tag{3}$$

where

$$\tilde{\theta}(s)=\frac{\tilde{\eta}(s)}{\kappa+s\eta(s)} \tag{4}$$

is the Laplace-transformed relaxation function describing the noise-averaged, $\langle\xi(t)\rangle=\langle\tilde{\xi}(s)\rangle=0$, relaxation of an angle fluctuation $\delta\phi(0)$,

$$\langle\delta\phi(t)\rangle=\theta(t)\delta\phi(0), \tag{5}$$

in the absence of external fields. The last term in Eq. (3) yields the asymptotic ($t\to\infty$), noise-averaged response to a cosinusoidal periodic field:

$$\langle\delta\phi(t)\rangle=\frac{1}{2}\tilde{\chi}(\Omega)\gamma\mathcal{E}_0e^{-i\Omega t}+\text{c.c.}, \tag{6}$$

with the complex linear response function reading in the frequency domain

$$\tilde{\chi}(\Omega)=\frac{\tilde{\theta}(-i\Omega)}{\tilde{\eta}(-i\Omega)}. \tag{7}$$

Next, Eq. (3) yields for the noise-averaged, double-Laplace-transformed autocorrelation function

$$\langle \widetilde{\delta\phi(s)}\,\widetilde{\delta\phi(s')}\rangle = \tilde{\theta}(s)\tilde{\theta}(s')[\delta\phi(0)]^2 + \gamma\mathcal{E}_0\delta\phi(0)\tilde{\theta}(s)\tilde{\theta}(s') \times\left[\frac{s}{\eta(s)(s^2+\Omega^2)} + \frac{s'}{\eta(s')(s'^2+\Omega^2)}\right] + \frac{\tilde{\theta}(s)}{\tilde{\eta}(s)}\frac{\tilde{\theta}(s')}{\tilde{\eta}(s')}\langle\xi(s)\xi(s')\rangle + \overline{\langle\widetilde{\delta\phi(s)}\rangle}\;\overline{\langle\widetilde{\delta\phi(s')}\rangle}, \tag{8}$$

where the symbol $\overline{(\cdots)}$ in the last term denotes the thermal *ensemble* average over the fluctuations $\delta\phi(0)$ taken with the Boltzmann distribution at temperature T. This yields $\overline{\delta\phi(0)}=0$ and $\overline{[\delta\phi(0)]^2}=k_BT/\kappa$.

As is shown in Ref. [6], the double Laplace transform of a function $f(t,t')$, which depends only on the absolute value of the difference of two time arguments, reads (here, for the noise autocorrelation function)

$$\langle\xi(s)\xi(s')\rangle = k_BT\frac{\tilde{\eta}(s)+\tilde{\eta}(s')}{s+s'}. \tag{9}$$

Using this relation and Eq. (4), Eq. (8) can identically be transformed as

$$\langle \widetilde{\delta\phi(s)}\,\widetilde{\delta\phi(s')}\rangle = \left([\delta\phi(0)]^2 - \frac{k_BT}{\kappa}\right)\tilde{\theta}(s)\tilde{\theta}(s') + \gamma\mathcal{E}_0\delta\phi(0)\tilde{\theta}(s)\tilde{\theta}(s') \times\left[\frac{s}{\eta(s)(s^2+\Omega^2)} + \frac{s'}{\eta(s')(s'^2+\Omega^2)}\right] + \frac{k_BT}{\kappa}\frac{\tilde{\theta}(s)+\tilde{\theta}(s')}{s+s'} + \overline{\langle\widetilde{\delta\phi(s)}\rangle}\;\overline{\langle\widetilde{\delta\phi(s')}\rangle}. \tag{10}$$

Even in the absence of a periodic field, the *single*-dipole autocorrelation function obtained from Eq. (10) by inversion to the time domain depends on both time arguments exhibiting seemingly an *aging* phenomenon as described by the first term in Eq. (10). This nonstationarity appears, however, also in the Markovian limit. The structure of Eq. (10) makes it quite obvious that such "aging" lasts for the time of $\theta(t)$ decay—quite in the spirit of the regression hypothesis. Moreover, an additional equilibrium *ensemble averaging* in Eq. (10) removes this nonstationarity caused by the initial preparations,

$$\overline{\langle\widetilde{\delta\phi(s)}\,\widetilde{\delta\phi(s')}\rangle} = \frac{k_BT}{\kappa}\frac{\tilde{\theta}(s)+\tilde{\theta}(s')}{s+s'} + \overline{\langle\widetilde{\delta\phi}(s)\rangle}\;\overline{\langle\widetilde{\delta\phi}(s')\rangle}. \tag{11}$$

This has two important consequences. First, the equilibrium autocorrelation function in the absence of field is

$$\overline{\langle\delta\phi(t)\,\delta\phi(t')\rangle} = \frac{k_BT}{\kappa}\theta(|t-t'|), \tag{12}$$

manifesting that the decay of equilibrium autocorrelations follows to the relaxation of fluctuations—i.e. *proving* rigorously the Onsager regression theorem for this model. It is by no means trivial in the non-Markovian case [7,8], especially for a particular case of the fractional Gaussian noise,

$$\langle\xi(t)\xi(0)\rangle = \frac{k_BT\eta_\alpha}{\Gamma(1-\alpha)}\frac{1}{|t|^\alpha}, \quad 0<\alpha<1. \tag{13}$$

It corresponds to *subdiffusion*, or fractional Brownian motion [9] in a parabolic potential—i.e., to an overdamped fractional Brownian oscillator [10]

$$\eta_\alpha D_*^\alpha\delta\phi(t) + \kappa\delta\phi(t) = \xi(t) + \gamma\mathcal{E}(t), \tag{14}$$

where

$$D_*^\alpha f(t) = \frac{1}{\Gamma(1-\alpha)}\int_0^t dt'\frac{1}{(t-t')^\alpha}\frac{\partial}{\partial t'}f(t')$$

is the operator of the fractional Caputo derivative [11,12]. At the same time, it corresponds also to the sub-Ohmic model of coupling to the thermal bath oscillators (with the spectral density $J(\omega)\propto\eta_\alpha\omega^\alpha$ [4]) or to a fracton thermal bath [13]. Within a purely phenomenological description, such fractional derivatives were first used in the theory of relaxation processes by Gemant [14,15] to account for a frequency-dependent viscoelastic friction corresponding exactly to the model considered (see in [16], p. 351). Presently, such fractional derivatives are routinely used in the theory of anomalous diffusion based on the continuous-time random walk (CTRW) approach and the related fractional Fokker-Planck equation methodology [12]. Within the Langevin equation methodology, such a phenomenological frequency-dependent friction must be complemented by a random force with the autocorrelation function obeying the fluctuation-dissipation relation (2) at temperature T. The relaxation function in this particular case is

$$\theta(t) = E_\alpha[-(t/\tau_D)^\alpha], \tag{15}$$

with $\tau_D=(\eta_\alpha/\kappa)^{1/\alpha}$, where $E_\alpha(z)$ is the Mittag-Leffler function $E_\alpha(z)=\Sigma_{n=0}^\infty z^n/\Gamma(\alpha n+1)$ and $E_1(z)=\exp(z)$ [11]. Such a relaxation function corresponds to the Cole-Cole model of glassy dielectric media [16,17], as we will see shortly. Indeed, the second profound consequence of Eq. (11) and the regression property is the fluctuation-dissipation theorem (FDT)

$$\tilde{\chi}(\Omega) = \frac{\overline{[\delta\phi(0)]^2}}{k_BT}[1+i\Omega\tilde{\theta}(-i\Omega)], \tag{16}$$

which relates the spectrum of equilibrium fluctuations $[\mathrm{Re}\,\tilde{k}(i\Omega)]$ and the linear susceptibility [or the absorption of electromagnetic energy related to $\mathrm{Im}\,\tilde{\chi}(\Omega)$] in the frequency domain [18] or the linear response function and the relaxation function in the time domain [1]:

$$\chi(t) = -\frac{\mathrm{H}(t)\overline{[\delta\phi(0)]^2}}{k_B T}\frac{d\theta(t)}{dt}. \tag{17}$$

Here, $\mathrm{H}(t)$ is the Heaviside step function. Equation (16) yields for the considered subdiffusion model the Cole-Cole susceptibility

$$\tilde{\chi}(\Omega) = \chi_\infty + \frac{\chi_0 - \chi_\infty}{1 + (-i\Omega\tau_D)^\alpha}, \tag{18}$$

where $\chi_0 = 1/\kappa$ is the static susceptibility per one dipole torsional oscillator and $\chi_\infty = 0$ is the high-frequency limiting value, which is zero within the model considered (nonzero χ_∞ is mainly due to the electronic response, which is not considered here). Vice versa, for any experimental, "glassy" $\tilde{\chi}(\Omega)$ the corresponding Laplace-transformed GLE kernel can be readily found (after setting formally $\chi_\infty \to 0$) as

$$\tilde{\eta}(s) = \frac{1}{s}\left(\frac{1}{\tilde{\chi}(is)} - \frac{1}{\chi_0}\right). \tag{19}$$

The connection between the Cole-Cole dielectric response function and the Mittag-Leffler relaxation based on subdiffusion was uncovered first [17,19] within the CTRW approach [20] assuming *ad hoc* the validity of the FDT [21]. It must be emphasized, however, that within the CTRW theory, the validity of the FDT in time-dependent fields requires (i) thermal equilibrium and (ii) finiteness of the mean residence times [8,22]. The latter requirement excludes, however, strict subdiffusion which—within the CTRW approach——fails to respond stationary to time-periodic fields [23–26]. This circumstance makes the dielectric response theories based on the CTRW *subdiffusion* and FDT out of base—the residence time distributions can have infinite second moment [8], but the first moments (mean residence times) must be finite [8,22]. Otherwise, (i) there is no thermal FDT (apart from the zero-frequency, static force limit), (ii) aging is principal, and (iii) nonergodicity starts to rule the physics of relaxation processes [27]. It must be emphasized that subdiffusion in a parabolic potential within the GLE approach does not display any such anomaly. "Aging" in a trapping parabolic potential is at most a transient phenomenon. It is worth noting in this respect that experimental τ_D lies typically in the range of 10^{-11}–10^{-3} s; i.e., it is not a macroscopic time scale [16]. This does not exclude, however, a true aging in the case of multistable—e.g., bistable potentials. Such a true aging occurs but on a quite different time scale of the escape from the trap (transition between wells) [28]. It does not define the quasistationary dielectric response, but is rather superimposed on it, creating an aging time-framework if, e.g., a macroscopically nonequilibrium dipole polarization was created by a strong pulse of electric field.

The Cole-Cole dielectrical response implying a strict subdiffusion presents an extreme case. Less anomalous is the Davidson-Cole response function [17,29]

$$\tilde{\chi}(\Omega) = \frac{\chi_0}{(1 - i\Omega\tau_D)^\alpha}. \tag{20}$$

For this model, Eq. (19) yields

$$\tilde{\eta}(s) = \frac{\kappa}{s}[(1 + s\tau_D)^\alpha - 1]. \tag{21}$$

Note that this case does not correspond to a strict subdiffusion since the integral of memory kernel $\int_0^\infty \eta(t)dt = \lim_{s\to 0}\tilde{\eta}(s)$ is finite and equal to $\kappa\alpha\tau_D$. More precisely, the subdiffusion regime is restricted by the initial time scale $t \ll \tau_D$. For $t \gg \tau_D$, it turns over into the normal diffusion. Inversion of Eq. (21) to the time domain yields

$$\eta(t) = \kappa\tau_D \frac{\sin(\pi\alpha)}{\pi}\Gamma(1+\alpha)\Gamma(-\alpha, t/\tau_D), \tag{22}$$

where $\Gamma(-\alpha, t)$ is an incomplete gamma function. Asymptotics are $\eta(t) \sim t^{-\alpha}$ for $t \ll \tau_D$ and $\eta(t) \sim t^{-\alpha-1}\exp(-t/\tau_D)$ for $t \gg \tau_D$. The corresponding relaxation function can be obtained by inversion of Eq. (4) and reads [17,29]

$$\theta(t) = \Gamma(\alpha, t/\tau_D)/\Gamma(\alpha). \tag{23}$$

It decays exponentially as $\theta(t) \propto \exp(-t/\tau_D)/t^{1-\alpha}$ for $t \gg \tau_D$. The initial relaxation is, however, strongly nonexponential.

A generalization of the Cole-Cole and Davidson-Cole dielectric response functions is due to Havriliak and Negami [30]:

$$\tilde{\chi}(\Omega) = \frac{\chi_0}{[1 + (-i\Omega\tau_D)^\alpha]^\beta}, \tag{24}$$

where $0 < \beta < 1$. It also corresponds to a strict subdiffusion. The corresponding relaxation function $\theta(t)$ can be expressed in terms of the Fox's H function; cf. Ref. [17]. This can be done also for the corresponding memory kernel $\eta(t)$. We note that for any other experimental form of linear susceptibility the underlying GLE description can be given via the corresponding Laplace transforms. The considered basic model is flexible enough to incorporate, e.g., two different τ_D's (two different kind of dipoles, or trapping potentials) or any other spectrum of anomalous relaxation times, etc.

In particular, many realistic viscoelastic memory kernels $\eta(t)$ can be approximated by a (possibly infinite) sum of exponentials, $\eta(t) = \Sigma_i \eta_i \nu_i \exp(-\nu_i t)$. The Laplace transform of such an infinite expansion can be remoulded as a continued fraction (Mori representation [5]). The simplest model of viscoelasticity corresponds then to an exponentially decaying memory kernel (the continued fraction is broken at the first convergent term in the Laplace domain). In the absence of the inertia term, the corresponding relaxation function $\theta(t)$ has, however, a singular feature—it starts from a jump at $t = 0$. A more realistic model of the viscoelasticity, which is free of this pathology in the overdamped case, corresponds to the memory friction, which is the sum of a δ function (viscous friction) and an exponentially decaying term. In this case, the relaxation function $\theta(t)$ is the sum of two exponentials, providing thus the simplest non-Debye model of solvents.

In fact, this paper puts a very successful phenomenological theory by Gemant, Cole and Cole, Davidson and Cole, and others on a firm basis within a stochastic theory that incorporates random fluctuations in a thermodynamically consistent manner. A generalization to incorporate *nonlinear*

dynamics (in particular, reorientation in multistable potentials) is, however, much more difficult. Such extremely sluggish large-amplitude reorientations will entail aging superimposed on the main time course of the dielectric response. The resulting physical picture is, nevertheless, simple: The small-amplitude motions of torsional dipole oscillators in trapping orientational potentials are responding to perturbing time-dependent electrical fields. Namely, they are responsible for the observed anomalous dielectric response. The physical reason is viscoelasticity as it was understood already by Gemant [14]. The CTRW processes with infinite mean residence times, which can be used to model large-amplitude jumping from trap to trap, *do not respond stationary* to time-periodic fields, as was rigorously proven recently [25,26]. This latter mathematically intricate fact can be easily understood due to the following reasoning: a CTRW-based subdiffusion can be obtained formally from a normal diffusion in a discrete time measured by some periodic process—a clock—upon the so-called subordination—i.e., upon introducing a random operational time, which in the case of subdiffusion possesses no mean value [31]. This means, however, that any external field varying in the *real* physical time with no matter how small but *finite* frequency is looking *infinitely fast* in the realm governed by such a randomized clock. As is commonly known, the response strength is always inversely proportional to the field frequency (possibly in some noninteger power) which is, within the operational time framework, virtually infinite. This is the reason why the *nonergodic* CTRW subdiffusion principally fails to respond stationary to time-periodic fields [26]. The GLE description associated with a viscoelastic friction for the torsional dipole oscillators is fundamentally different in this respect, providing a reliable, conceptually appealing, and physically correct framework for the anomalous dielectrical response theory.

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