Fractional Calculus as a Tool for Applications in Soft Matter: Electrical Impedance Response of Liquid Crystals

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Main Objectives of the Work

- To use **impedance spectroscopy** to investigate **modulated phases of liquid crystals**;
- The focus is the **low-frequency limiting behavior**, which relies on **ionic motion**;
- The technique is useful to characterize the physical parameters of the material as well as **to understand how the natural modulation present in the media affects ionic diffusion**;
- The conceptual framework to analyze the data is the Poisson-Nernst-Planck (PNP) model, extended to the field of **fractional calculus** in order to account for **anomalous diffusion**.
- This is the **PNPA** ("A" for anomalous) model.

Anomalous Diffusion

Motivation

Such turmoil means that there are secret motions, out of sight, that lie concealed in matter.

Lucretius, *De rerum natura*.

- The mean square displacement

$$\langle (\Delta z)^2 \rangle = \langle z^2 \rangle - \langle z \rangle^2 \tag{1}$$

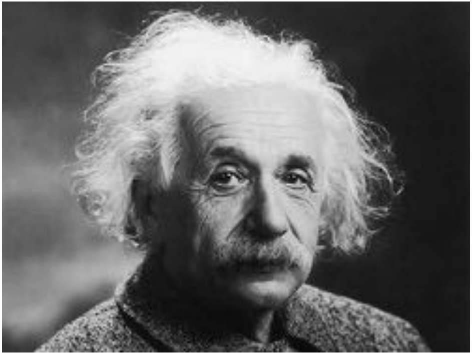
represents the smearing out of a substance by diffusion.

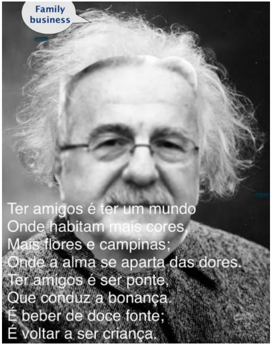
- The diffusive processes may be characterized in general as

$$\langle (\Delta z)^2 \rangle \propto t^\alpha, \tag{2}$$

with the case $\alpha = 1$ being the normal one, whereas the cases $\alpha < 1$ (subdiffusion) and $\alpha > 1$ (superdiffusion) characterize the **anomalous diffusive behavior**.

Diffusion as a family business





Uncle Albert (1879-1955), pioneer in the family business. Paper: On the motion of small particles suspended in a stationary liquid according to the molecular kinetic theory of heat. A. Einstein, *Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen*, Annalen der Physik **17**, 549 (1905).

Anomalous Diffusion: Basic Concepts

- The **Brownian motion** is characterized by a diffusion packet that is initially concentrated at a point and takes later the **Gaussian form**, whose width grow in time as $t^{1/2}$, characterizing what we called **normal diffusion**.
- If we look at the **diffusion equation** for a constant diffusion coefficient, that is

$$\frac{\partial \rho(z,t)}{\partial t} = D \frac{\partial^2 \rho(z,t)}{\partial z^2},$$

we may notice that the square of **the position scales linearly** with t and we may expect that

$$\langle z^2 \rangle \sim t.$$

Anomalous Diffusion and Fractional Calculus

- Similarly, if we look at a **space-time fractional equation** in the form
$$\frac{\partial^\gamma \rho(z,t)}{\partial t^\gamma} = D\frac{\partial^\alpha \rho(z,t)}{\partial z^\alpha},$$
we may expect that
$$\langle z^2 \rangle \sim t^{2\gamma/\alpha}.$$
- We may expect that for $2\gamma = \alpha$ we have to deal with a **normal diffusion**.
- When $2\gamma < \alpha$ the **subdiffusion processes** are relevant;
- For $2\gamma > \alpha$ the process under investigation is **superdiffusive**.
- **Fractional Calculus** is a powerful tool to handle with **anomalous diffusion processes**!

- **The mathematician cannot create things at will, any more than the geographer can; he can only discover what is there and give it a name.**

  Gottlob Frege

- **Clouds are not spheres, mountains are not cones, coastlines are not circles, and bark is not smooth, nor does lightning travel in a straight line.**

  Benoît Mandelbrot

- The term **fractional calculus** has been used (as a misnomer) for the theory of integrations and derivatives of **arbitrary order**.
- The question about the possible meaning of a derivative of **arbitrary order** was formulated by Guillaume François Antoine, **marquis of L'Hôpital** (1661-1704), by means of a letter addressed to the great mathematician and philosopher **Gottfried Wilhelm Leibniz** (1646-1716) — who gave a **positive and correct answer** to the instigating question.

- Since then fractional calculus was the object of analysis by great mathematicians, including Leonhard **Euler** (1707–1783), Pierre Simon **Laplace** (1749–1827), Jean-Baptiste Joseph **Fourier**(1768–1830), Niels Henrik **Abel** (1802–1829), Joseph **Liouville** (1809–1882), Georg Friedrich Bernhard **Riemann** (1826–1866), Nikolay Yakovlevich **Sonin** (1849–1915), Aleksey Vasilievich **Letnikov** (1837–1888), Paul Mathieu Hermann **Laurent** (1841–1908), among many others.

- It was briefly mentioned (perhaps for the first time as such) in 1819, in the book of **Sylvestre François Lacroix** (1765–1843);
- Let, for instance, $y = x^m$; when n is an integer, one has for any arbitrary $m \in \mathbb{N}$:

$$\begin{aligned} d^n y = d^n(x^m) &= m(m-1)\cdots(m-n+1)x^{m-n}dx^n \\ &= \frac{\Gamma(m+1)}{\Gamma(m-n+1)}x^{m-n}dx^n, \quad n \in \mathbb{N}. \end{aligned} \tag{3}$$

If we put $m = 2$ and $n = 1$, then we obtain $\boxed{d^1(x^2) = 2x\,dx}$, as expected. Now, we may consider $m = 1$ and $n = 1/2$ and try to answer to the original question. We obtain:

$$\boxed{d^{1/2}x = \frac{\Gamma(2)}{\Gamma(3/2)}x^{1/2}dx^{1/2} = \frac{2}{\sqrt{\pi}}\sqrt{x\,dx}}. \tag{4}$$

- The result obtained by Lacroix may be put in the usual form as:

$$\boxed{\frac{d^{1/2}x}{dx^{1/2}} = \frac{2\sqrt{x}}{\sqrt{\pi}}}. \tag{5}$$

Consider, now, $n = 1/2$ and $m = 0$, that is, $y = x^0 = 1$. In this case, Eq. (3) yields a **surprising result**:

$$\frac{d^{1/2}1}{dx^{1/2}} = \frac{\Gamma(1)}{\Gamma(1/2)}x^{-1/2} = \frac{1}{\sqrt{\pi x}} \neq 0. \tag{6}$$

The Lacroix derivative of a constant is not zero, as one expects if one tries to keep the usual meaning of the derivative.

- This “strange” result shows that **fractional derivatives have many special and ever counter-intuitive properties**.

Elements of Fractional Calculus

The Riemann-Liouville Operator

- Nowadays, **a well-established form for the derivative of arbitrary order is the so-called Riemann-Liouville operator**, although it is the result of several contributions (mainly by Liouville), which is defined as:

$$ {}_c\mathrm{D}_x^\alpha f(x) = \frac{1}{\Gamma(k-\alpha)} \frac{d^k}{dx^k} \left[\int_c^x \frac{f(t)}{(x-t)^{\alpha+1-k}} dt \right], \; x > c, \quad (7) $$

  with $k \in \mathbb{N} = \{1, 2, 3, \ldots\}$, for $0 < p = k - \alpha < 1$, where $\Gamma(k-\alpha)$ is the gamma function.

- We notice that k is the smallest integer greater than α, with ${}_c\mathrm{D}_x^k f(x) = d^k/dx^k f(x)$ being the usual derivative of $f(x)$.

- In 1967, Caputo introduced a new definition of a fractional derivative, which is connected with the **fractional Riemann-Liouville integral and differential** operators;
- In terms of this operator, the initial conditions can be formulated in the usual way, i.e., by stating them in terms of integer order operators.
- The **Caputo operator** is defined as

$$
\begin{aligned}
{}^{\mathrm{C}}_{c}\mathrm{D}^{\alpha}_{x} f(x) &= \frac{1}{\Gamma(p)} \int_{c}^{x} (x-t)^{p-1} f^{(n)}(t)\,dt \\
&= \frac{1}{\Gamma(n-\alpha)} \int_{c}^{x} \frac{f^{(n)}(t)}{(x-t)^{\alpha+1-n}}\,dt,
\end{aligned}
\tag{8}
$$

for $n-1<\alpha<n$, which permits us to interpret it as being equal to the **Riemann-Liouville integral** of the $n^{\mathrm{th}}-$derivative of the function $f(x)$.

Elements of Fractional Calculus

The Riemann-Liouville and Caputo Operators

- For physical applications, it is useful to put $c = -\infty$ in the Riemann-Liouville derivative; then, it becomes

$$
\begin{aligned}
{}_{-\infty}\mathrm{D}_x^{\alpha} f(x) &= \frac{d^m}{dx^m}\left[\frac{1}{\Gamma(m-\alpha)}\int_{-\infty}^{x}\frac{f(t)}{(x-t)^{\alpha+1-m}}dt\right] \\
&= \frac{1}{\Gamma(m-\alpha)}\int_{-\infty}^{x}\frac{f^{(m)}(t)}{(x-t)^{\alpha+1-m}}dt \\
&= {}_{-\infty}^{\mathrm{C}}\mathrm{D}_x^{\alpha} f(x), \qquad m-1<\alpha<m. \qquad (9)
\end{aligned}
$$

- In this limit, both definitions become equal provided that $f(x)$ and its derivatives have a reasonable behavior when $x \to \infty$, that is, $f^{(k)}(-\infty) \to 0$, for $k = 0, 1, \dots, n-1$, with $n = \lceil \alpha \rceil$.
- Useful to consider stationary processes is now permitted as, for instance, in the response of the fractional order dynamical systems to a periodic signal, **required in the impedance problems**, in the wave propagation in continuous media, etc.

PNP Model: Insulating medium containing ions

The Poisson-Nernst-Planck usual model

- In the presence of the external electric field $\mathbf{E}(\mathbf{r}, t)$, the charges move, giving rise to currents of **neutral** as well as of **positive** and **negative** charges.
- If we denote the bulk density of these particles, respectively with $n_n(\mathbf{r}, t)$ (**neutral**), $n_p(\mathbf{r}, t)$ (**positive**), and $n_m(\mathbf{r}, t)$ (**negative**) and, likewise, the current density as $\mathbf{j}_n(\mathbf{r}, t)$, $\mathbf{j}_p(\mathbf{r}, t)$, and $\mathbf{j}_m(\mathbf{r}, t)$, the continuity equations are

$$
\begin{aligned}
\frac{\partial}{\partial t} n_p(\mathbf{r}, t) &= -\nabla \cdot \mathbf{j}_p(\mathbf{r}, t) + S(\mathbf{r}, t), \\
\frac{\partial}{\partial t} n_m(\mathbf{r}, t) &= -\nabla \cdot \mathbf{j}_m(\mathbf{r}, t) + S(\mathbf{r}, t), \\
\frac{\partial}{\partial t} n_n(\mathbf{r}, t) &= -\nabla \cdot \mathbf{j}_n(\mathbf{r}, t) - S(\mathbf{r}, t), \qquad (10)
\end{aligned}
$$

The Poisson's Equation

- To obtain the set of the fundamental equations of the PNP model, we have to consider also the Poisson's equation, written as

$$\nabla \cdot \mathbf{E}(\mathbf{r}, t) = \frac{q}{\varepsilon} \left[n_p(\mathbf{r}, t) - n_m(\mathbf{r}, t) \right]. \tag{11}$$

- **This equation connects the bulk density of ions of positive and negative charges**, of absolute value q, **to the actual profile of the electric field across the sample**.
- The total electric current is formed by the **conduction** and the **displacement** currents:

$$\mathbf{j}(\mathbf{r}, t) = q \left[\mathbf{j}_p(\mathbf{r}, t) - \mathbf{j}_m(\mathbf{r}, t) \right] + \varepsilon \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t}. \tag{12}$$

The Total Current is Solenoidal

- If we now combine the first two of Eqs. (10) with Eq. (12), we conclude that

$$\nabla\cdot\mathbf{j} = -q\left\{\frac{\partial}{\partial t}\left[n_p(\mathbf{r},t) - n_m(\mathbf{r},t)\right]\right\} + \varepsilon\nabla\cdot\frac{\partial\mathbf{E}(\mathbf{r},t)}{\partial t} = 0, \quad (13)$$

when the equation of Poisson, Eq. (11), is used.

- Indeed, **the total density of current has to be solenoidal**, i.e,

$$\nabla\cdot\mathbf{j}(\mathbf{r},t) = \nabla\cdot\left\{q\left[\mathbf{j}_p(\mathbf{r},t) - \mathbf{j}_m(\mathbf{r},t)\right] + \varepsilon\frac{\partial\mathbf{E}(\mathbf{r},t)}{\partial t}\right\} = 0. \quad (14)$$

- Solenoidal? Why is this so important?

The Electrical Impedance

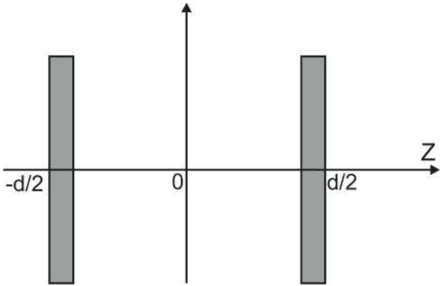


Figure: Typical 1D sample in the shape of a slab of thickness d. Two electrodes, of area S, placed a distance d apart. $V(t) = V_0 e^{i\omega t}$.

- The **electrical impedance** is defined as

$$\mathcal{Z} = \frac{V(d/2,t) - V(-d/2,t)}{I(t)} = \frac{\Delta V(t)}{I(t)}, \quad I(t) = j(t) \times S(= \text{area})$$

- In this case, for a one-dimensional problem, the current density $\mathbf{j}$ **has to be position independent**.

Continuity Equation (**Fractional**)

- We analyze an extension of the PNP model by expressing the continuity equation **in terms of the Caputo fractional time derivative**:

$$
\begin{aligned}
\tau^{\gamma-1}\frac{\partial^\gamma n_p(\mathbf{r},t)}{\partial t^\gamma} &= -\nabla\cdot\mathbf{j}_p(\mathbf{r},t)+S(\mathbf{r},t),\\
\tau^{\gamma-1}\frac{\partial^\gamma n_m(\mathbf{r},t)}{\partial t^\gamma} &= -\nabla\cdot\mathbf{j}_m(\mathbf{r},t)+S(\mathbf{r},t),\\
\tau^{\gamma-1}\frac{\partial^\gamma n_n(\mathbf{r},t)}{\partial t^\gamma} &= -\nabla\cdot\mathbf{j}_n(\mathbf{r},t)-S(\mathbf{r},t),
\end{aligned}
\tag{15}
$$

- If we now combine the new set of fundamental equations of the extended model, Eqs. (41) and (11), following the procedure used before, it is possibile to conclude that $\nabla\cdot\mathbf{j}(\mathbf{r},t)=0$, i.e., **the total current is solenoidal**:

$$
\nabla\cdot\left\{q\left[\mathbf{j}_p(\mathbf{r},t)-\mathbf{j}_m(\mathbf{r},t)\right]+\varepsilon\tau^{\gamma-1}\frac{\partial^\gamma}{\partial t^\gamma}\mathbf{E}(\mathbf{r},t)\right\}=0. \tag{16}
$$

Continuity Equation and **Distributed Order**

- We rewrite the fundamental equations by promoting the following modifications:

$$\frac{\partial^\gamma}{\partial t^\gamma} \to \int_0^1 d\gamma p(\gamma)\tau^{\gamma-1}\frac{\partial^\gamma}{\partial t^\gamma}(\cdots), \quad \boxed{\int_0^1 p(\gamma)d\gamma = 1}. \quad (17)$$

- The new set of fundamental equations of the extended PNP model will be now represented by the following continuity equations:

$$\begin{aligned}
\int_0^1 d\gamma p(\gamma)\tau^{\gamma-1}\frac{\partial^\gamma}{\partial t^\gamma}n_p(\mathbf{r},t) &= -\nabla\cdot\mathbf{j}_p(\mathbf{r},t)+S(\mathbf{r},t),\\
\int_0^1 d\gamma p(\gamma)\tau^{\gamma-1}\frac{\partial^\gamma}{\partial t^\gamma}n_m(\mathbf{r},t) &= -\nabla\cdot\mathbf{j}_m(\mathbf{r},t)+S(\mathbf{r},t),\\
\int_0^1 d\gamma p(\gamma)\tau^{\gamma-1}\frac{\partial^\gamma}{\partial t^\gamma}n_n(\mathbf{r},t) &= -\nabla\cdot\mathbf{j}_n(\mathbf{r},t)-S(\mathbf{r},t), \quad (18)
\end{aligned}$$

and the equation of Poisson, Eq. (11).

Anomalous PNP model – Slab

Full Dissociation: $S(\mathbf{r}, t) = 0$ and $\mathbf{j}_n(\mathbf{r}, t) = 0$.

- The equations to be solved are reduced to the two following:

$$\begin{aligned} \int_0^1 d\gamma p(\gamma)\tau^{\gamma-1}\frac{\partial^\gamma}{\partial t^\gamma} n_p(z,t) + \frac{\partial}{\partial z} j_p(z,t) &= 0, \\ \int_0^1 d\gamma p(\gamma)\tau^{\gamma-1}\frac{\partial^\gamma}{\partial t^\gamma} n_m(z,t) + \frac{\partial}{\partial z} j_m(z,t) &= 0. \end{aligned} \quad (19)$$

together with the equation of Poisson:

$$\frac{\partial^2 V(z,t)}{\partial z^2} = -\frac{q}{\varepsilon}\left[n_p(z,t) - n_m(z,t)\right]. \quad (20)$$

Anomalous PNP model – Impedance

- The current densities for **positive** ($p = +$) and **negative** ($n = -$) charges are defined as:

$$\begin{aligned} j_{\pm}(z,t) &= -D\frac{\partial}{\partial z}n_{\pm}(z,t) \mp \mu q n_{\pm}(z,t)\frac{\partial}{\partial z}V(z,t) \\ &\approx -D\frac{\partial}{\partial z}n_{\pm}(z,t) \mp \mu q N\frac{\partial}{\partial z}V(z,t) \end{aligned} \tag{21}$$

where D is the diffusion coefficient and μ is the mobility.

- The solutions (**for the linear regime**) are in the form:

$$n_p(z,t) = N + \eta_p(z)e^{i\omega t} \quad \text{and} \quad n_m(z,t) = N + \eta_m(z)e^{i\omega t} \tag{22}$$

with $N >> |\eta_p(z)|$ and $N >> |\eta_m(z)|$ and

$$V(z,t) = \phi(z)e^{i\omega t}.$$

- **Typical boundary conditions** that can be used are:

$$j_\alpha\left(z=\pm\frac{d}{2},t\right)=\pm\int_{-\infty}^{t}dt'K(t-t')\frac{d}{dt'}n_\alpha\left(z=\pm\frac{d}{2},t'\right), \tag{23}$$

  with $\alpha=+$ (**positive** ions) and $\alpha=-$ (**negative** ions).

- In Eqs. (23), we have introduced a kernel $K(t)$ to formulate the problem in more general terms.
- Indeed, if $K(t)=ke^{-t/\tau_a}$, where τ_a is an adsorption time, this current may be related to the **adsorption-desorption process at the interface, governed by a Langmuir-like balance equation**.

Anomalous PNP model – Impedance

Boundary Conditions

- Other choices for the functional form of $K(t)$ are **phenomenological ways** to introduce additional **memory effects** in the problem.
- This may be helpful because the presence of the fractional derivative in the bulk equation accounts **for memory-like effects in the bulk** behavior of the system.
- In contrast, the presence of $K(t)$ in the boundary conditions may be related to surface effects at the interface.
- This permits us to investigate how the surface governs the electrical response of the system.

Anomalous PNP model – Impedance

Boundary Conditions

- To complete the problem formulation, we have to state the boundary conditions used for the electric potential. They are:

$$V\left(z=\pm\frac{d}{2},t\right)=\pm\frac{V_0}{2}e^{i\omega t}, \tag{24}$$

  where the amplitude $V_0 \ll k_B T/q$, i.e., has to be small enough to represent a small ac signal problem (**linear response**);

- The quantity

$$\boxed{\lambda=\sqrt{\frac{\varepsilon k_B T}{2q^2 N}}}$$

  defines the **Debye screening length**.

Anomalous PNP model – Impedance

- Analytical calculations yield for the **electrical impedance**:

$$\boxed{Z(\omega) = \frac{2}{S\varepsilon\beta^2}\,\frac{[\tanh(\beta d/2)]\,/\,(\lambda^2\beta) + (d/2D)\,\mathcal{E}(i\omega)}{\Phi(i\omega) + \kappa(i\omega)\,(1 + \Phi(i\omega)\lambda^2/D)\tanh(\beta d/2)\,/(\lambda^2\beta)}} \tag{25}$$

in which

$$\mathcal{E}(i\omega) = \Phi(i\omega) + \kappa(i\omega)\beta\tanh\left(\frac{d\,\beta}{2}\right), \tag{26}$$

with

$$\beta = \sqrt{\frac{1}{\lambda^2} + \frac{\Phi(i\omega)}{D}}. \tag{27}$$

Anomalous PNP model – Impedance

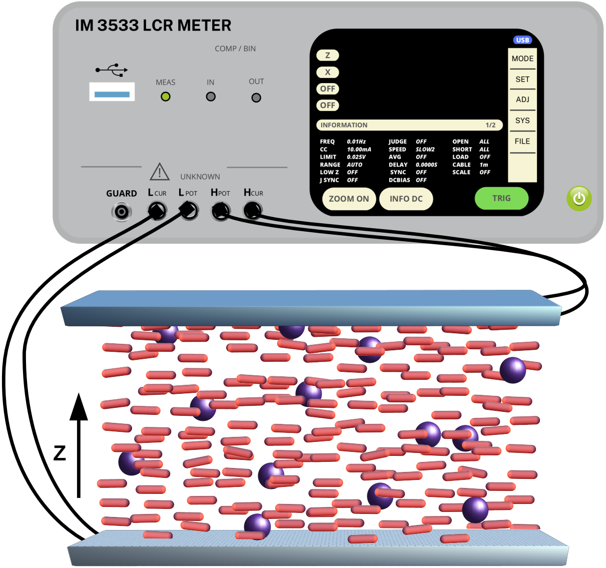
- Surface memory kernel:

$$
\begin{aligned}
\kappa(i\omega) &= e^{-i\omega t}\int_{-\infty}^{t} dt' K(t-t')e^{i\omega t'} \\
&= \underbrace{k_1(i\omega)^{\gamma_1} + k_2(i\omega)^{\gamma_2}}_{\text{This particular case}}, \qquad (28)
\end{aligned}
$$

- Distributed regime:

$$
\begin{aligned}
\Phi(i\omega) &= \frac{1}{\tau}\int_{0}^{1} d\gamma p(\gamma)(i\omega\tau)^{\gamma} \\
&= \underbrace{i\omega + \frac{(i\omega\tau)^{\gamma}}{\tau}}_{\text{This particular case}} . \qquad (29)
\end{aligned}
$$

Anomalous PNP model – PNPA: Experimental setup



Anomalous PNP model – Conductivity

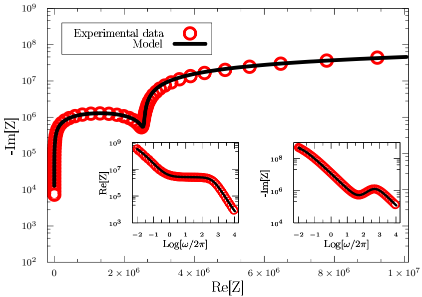


Figure: Complex-plane (or Nyquist diagram) for the impedance spectrum of E7 at 35°C. Components of the impedance are plotted in the bottom for the range of 0.01Hz to 200kHz. Open red circles represent experimental data. The **solid black** line corresponds to the predictions of the PNPA model with $\Phi(i\omega) = \tau^{\gamma-1}(i\omega)^{\gamma}$ and $\bar{\kappa}(i\omega) = \bar{\kappa}(i\omega)^{\delta}$, in which $D = 2.5 \times 10^{-11} m^2/s$, $\mathcal{S} = 5 \times 10^{-6} m^2$, $\varepsilon = 11.5\varepsilon_0$, $d = 9.99 \times 10^{-6} m$, $\bar{\kappa} = 2 \times 10^{-6}\ m/s^{1-\delta}$, $\gamma = 0.99$, $\delta = 0.65$, and $\lambda = 5.75 \times 10^{-8} m$.

Anomalous PNP model – Acetone

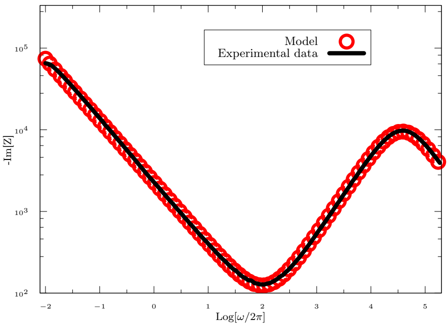


Figure: Imaginary part of the impedance versus the frequency of the acetone.

Anomalous PNP model – Acetone

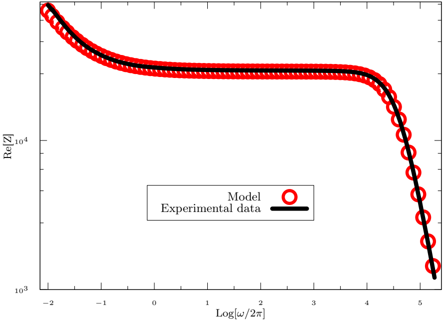


Figure: Real part of the impedance versus the frequency of the acetone.

Anomalous PNP model – Acetone

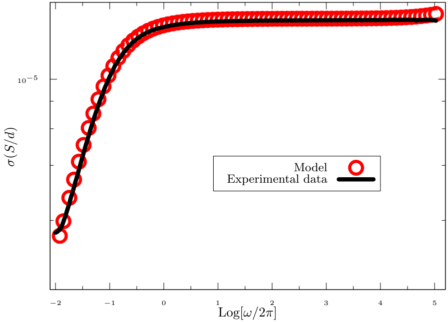
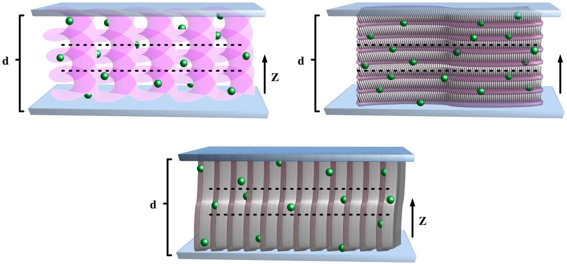


Figure: Conductivity *versus* frequency. The solid black line is related to experimental data and the open red circles correspond to the theoretical models.

PNPA Model: Applications to Liquid Crystals



Representation of the studied liquid crystalline phases: (a) Cholesteric with planar anchoring; Smectic-A with (b) homeotropic and (c) planar alignment. The green spheres illustrate the ions.

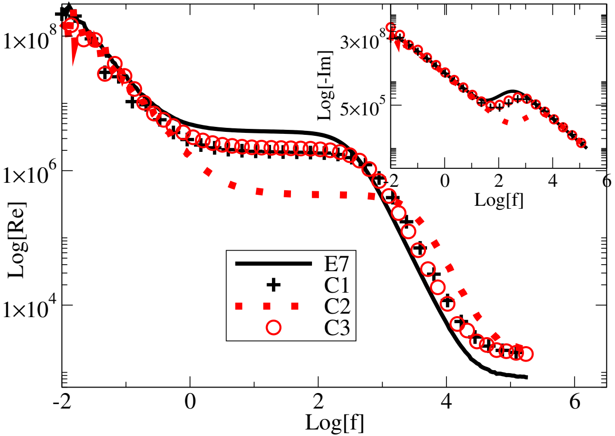
PNPA Model: Applications to Liquid Crystals

Samples of E7

1. Sample C1: E7 + 5.52% of R811 + 5.46% of S811 $\rightarrow$ Total: 10.98% of chiral dopant;
2. Sample C2: E7 + 3.74% of R811 + 8.18% of S811 $\rightarrow$ 11.98% of chiral dopant; Pitch $\approx 2.25\mu$m (for 4.44% of S811).
3. Sample C3: E7 + 1.48% of R811 + 9.59% of S811 $\rightarrow$ 11.07% of chiral dopant; Pitch $\approx 1.24\mu$m (for 8.11% of S811).

PNPA Model: Applications to Liquid Crystals

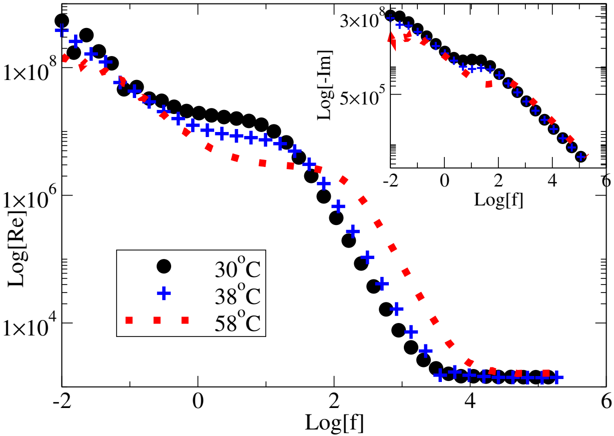
E7 Samples



The logarithm of Real and Imaginary parts *vs* the logarithm of the frequency for the following samples: pure E7 (solid black line), C1 (black cross), C2 (red squares), and C3 (open red circles).

PNPA Model: Applications to Liquid Crystals

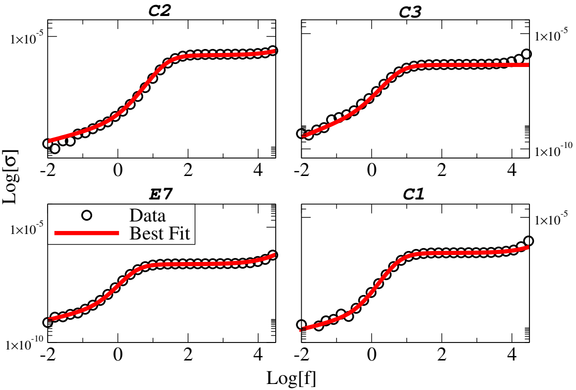
8CB Samples at different temperatures



The logarithm of Real and Imaginary parts *vs* the logarithm of the frequency for 8CB samples at 30°C (black circles), 38°C (blue cross), and 55°C (red squares) temperatures.

PNPA Model: Applications to Liquid Crystals

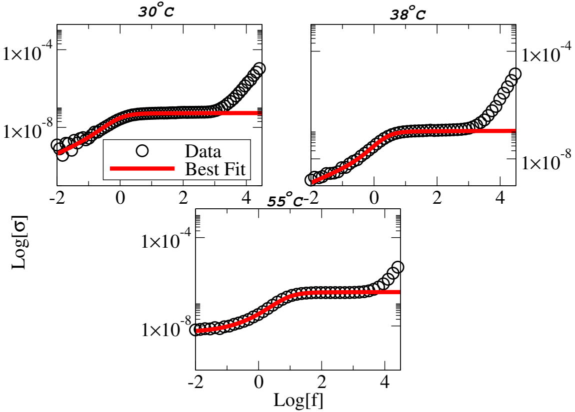
E7 Samples



The logarithm of conductivity *vs* the logarithm of the frequency for the following samples: pure $\mathrm{E7}$, $\mathrm{C1}$, $\mathrm{C2}$, $\mathrm{C3}$. The open black circles represent the experimental data, and the solid red line shows the best fit.

PNPA Model: Applications to Liquid Crystals

8CB Samples



The logarithm of conductivity *vs* the logarithm of the frequency for the 8CB samples at 30°C, 38°C, and 55°C temperatures. The open black circles represent the experimental data, and the solid red line shows the best fit.

Summary of exponents behavior/meaning

- Surface memory kernel:

$$\begin{aligned} \kappa(i\omega) &= e^{-i\omega t}\int_{-\infty}^{t} dt' K(t-t')e^{i\omega t'} \\ &= \underbrace{k_1(i\omega)^{\gamma_1} + k_2(i\omega)^{\gamma_2}}_{\text{adsorption-desorption}}, \end{aligned} \tag{30}$$

- k_i $(i = 1, 2)$ are phenomenologically connected with the range of the forces responsible for the adsorption/desorption phenomena;
- Conductivity:

$$\sigma = \frac{d\,\mathrm{Re}(Z)}{S|Z|^2} \quad \rightarrow \quad \sigma \sim t^{1-\alpha}$$

- The mean square displacement:

$$\langle(\Delta z)^2\rangle \sim t^{\alpha}$$

PNPA Model: Physical Parameters

E7 samples

Samples	Pure E_7	C1	C2	C3
ε	$12\varepsilon_0$	$12.5\varepsilon_0$	$15\varepsilon_0$	$16\varepsilon_0$
$D(m^2/s)$	1.4×10^{-11}	1.7×10^{-11}	6.9×10^{-11}	1.5×10^{-11}
$\lambda(m)$	5.4×10^{-8}	4.33×10^{-8}	4.7×10^{-8}	4.9×10^{-8}
$\tau^{\gamma-1}$	2.7	2.1	2.1	1.7
γ	0.99	0.99	0.97	0.99
γ_1	0.35	0.40	0.44	0.58
$\kappa_1(m/s)$	3.2×10^{-8}	1.3×10^{-8}	2.5×10^{-8}	2.4×10^{-8}
α	0.65	0.60	0.56	0.42

Parameters found by adjusting Eq. (25) to the measured data of samples $\mathrm{C1}$, $\mathrm{C2}$, $\mathrm{C3}$, and pure E7. Notice that α is the time exponent of the mean square displacement $\langle(\Delta z)^2\rangle$ while from the conductivity, we obtain $1-\alpha$.

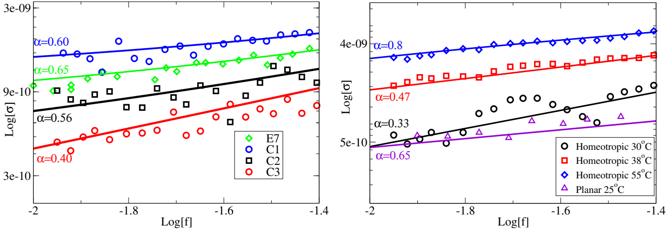
PNPA Model: Physical Parameters

8CB Samples

8CB	$25^\circ C$	$30^\circ C$	$38^\circ C$	$55^\circ C$
Anchoring	Planar	Homeotropic	Homeotropic	Homeotropic
ε	$9\varepsilon_0$	$11\varepsilon_0$	$13\varepsilon_0$	$10\varepsilon_0$
$D(m^2/s)$	4.4×10^{-12}	1.05×10^{-11}	2.2×10^{-11}	6.2×10^{-11}
$\lambda(m)$	4.22×10^{-8}	1.45×10^{-7}	1.58×10^{-7}	1.38×10^{-7}
γ_1	0.35	0.6	0.5	0.2
$\kappa_1(m/s)$	1×10^{-8}	3.8×10^{-7}	6.2×10^{-7}	1.0×10^{-6}
$\kappa_2(m/s)$	0.0	0.0	0.0	4.2×10^{-7}
γ	0.99	0.99	0.99	0.99
$\tau^{\gamma-1}$	2.6	5.3	4.0	3.6
α	0.65	0.4	0.5	0.80

Parameters found by adjusting Eq. (25) to the measured data of the samples with 8CB. Notice that α is the time exponent of the mean square displacement $\langle(\Delta z)^2\rangle$ while from the conductivity, we obtain $1 - \alpha$.

PNPA Model: Conductivity



Low-frequency behavior of the conductivity for all the chiral nematic (and pure E7) (left) and 8CB (right) samples. The solid lines show the fitted line ($f^{1-\alpha}$). Notice that α is the time exponent of the mean square displacement $\langle(\Delta z)^2\rangle$ while from the conductivity, we obtain $1-\alpha$. The samples with higher inclination (higher $1-\alpha$) correspond to the ones where ions have to permeate to diffuse, leading to considerable subdiffusive behavior.

Concluding Remarks

- The **chiral nematic samples** were made by keeping the amount of chiral dopant fixed, so **the significant difference among samples was the pitch**.
- In the case of the **Smectic sample**, we measured it in two different geometries.
- By changing temperature, we used the same sample to measure the spectrum in the Smectic-A, Nematic, and Isotropic mesophases.
- All the samples present a **subdiffusive behavior**, but **the samples with modulation have a much lower exponent** characterizing the diffusivity.

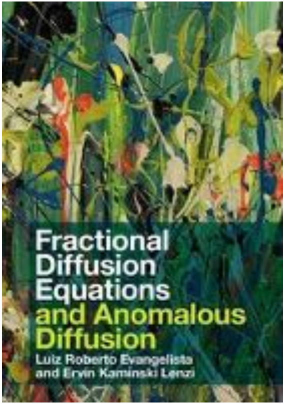
Concluding Remarks

- Such a phenomenon is directly related to **the morphology of the phase** and can be associated with a **cage-like diffusion**.
- **Impedance spectroscopy**, thus, is simple to measure and a non-destructive technique that can **probe the morphology of the material** besides acquiring many electric parameters.
- **Fractional Calculus and Anomalous Diffusion** can be combined to provide a **powerful tool** to analyze electrical impedance in complex fluid systems.

Recent Papers

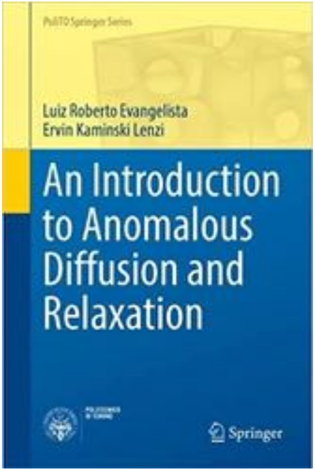
- **Time-fractional approach** to the electrochemical **impedance**: The displacement current, G. Barbero, E. K. Lenzi, and L. R. Evangelista, Journal of Electroanalytical Chemistry **920**, 116588 (2022);
- **Anomalous diffusion** and surface effects on the **electric response** of electrolytic cells, A. M. Scarfone, G. Barbero, L. R. Evangelista, and E. K. Lenzi, Physchem **2022**, 163–178;
- **Electrical impedance response** of liquid crystals and **anomalous diffusion**: A **fractional approach**, M. P. Rosseto, R. R. R. de Almeida, R. S. Zola, E. K. Lenzi, and L. R. Evangelista, Journal of the Electroanalytical Society **170**, 096504 (2023);
- Probing **modulated liquid crystals media** with **dielectric spectroscopy**, M. P. Rosseto, R. R. R. de Almeida, E. K. Lenzi, L. R. Evangelista, and R. S. Zola, Journal of Molecular Liquids **390**, Part A, 122943 (2023).

Publicity: Already arrived...



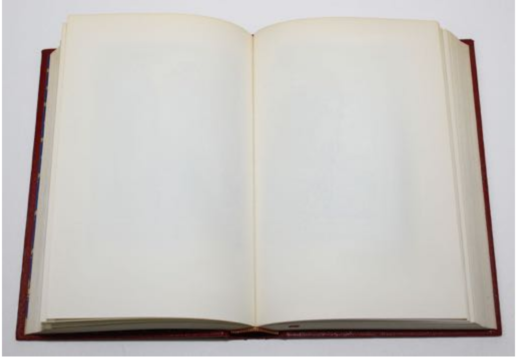
Published in 2018.

Publicity: Just arrived...



Available from January, 2023.

Publicity: Coming soon...



Buch ohne Worte. Available from ?

Thank you!

Grazie!

Appendix

PNPA: Anomalous PNP model

- Extensions can be obtained by considering the **continuous time random walk** (CTRW) approach based on a suitable choice of the probability density function, $P(\mathbf{r}, t)$.
- There are two ways to implement the extension:
  1. In the first one, **the displacement current remains unchanged whereas the conduction current is modified by the presence of the fractional derivative**;
  2. In the second one, **the conduction current remains unchanged whereas the displacement current is written in terms of time-fractional derivatives**.
- The first way implies **modifying phenomenological equations**;
- The second way would imply **modifying fundamental equations** $\rightarrow$ **Maxwell's equations**.

Anomalous PNP model: Time-Fractional Derivative

- In general, the diffusion equations are written as follows:

$$\frac{\partial}{\partial t}P(\mathbf{r},t) = -\,{}_{t_0}\mathrm{D}_t^{1-\gamma}\left[\nabla\cdot\mathcal{J}(\mathbf{r},t\,)\right], \tag{31}$$

or

$${}^{C}_{t_0}\mathrm{D}_t^{\gamma}P(\mathbf{r},t\,) = \frac{\partial^\gamma}{\partial t^\gamma}P(\mathbf{r},t\,) = -\nabla\cdot\mathcal{J}(\mathbf{r},t\,), \tag{32}$$

where

$$\mathcal{J}(\mathbf{r},t\,) = -\left\{D\nabla P(\mathbf{r},t) - \frac{D}{k_B T}\left[\mathbf{F}(\mathbf{r},t\,)P(\mathbf{r},t)\right]\right\}, \tag{33}$$

with $\mathbf{F}(\mathbf{r},t)$ being an external field acting on the system.

Anomalous PNP model: Time-Fractional Derivative

- In Eq. (31) ${}_{t_0}\mathrm{D}_t^{1-\gamma}(\cdots)$ is the fractional Riemann-Liouville operator, i.e.,

$$\boxed{{}_{t_0}\mathrm{D}_t^{\gamma} g(\mathbf{r}, t\,) = \frac{1}{\Gamma\,(k-\gamma)}\frac{d^k}{dt^k}\int_{t_0}^{t} d\bar{t}\,\frac{g(\mathbf{r}, \bar{t}\,)}{(t-\bar{t})^{\gamma+1-k}}}, \qquad (34)$$

where $k-1<\gamma<k$, with k an integer, and t_0 is related to the conditions initially imposed to the system.

- In Eq. (32), we introduced another fractional operator, i.e., the Caputo fractional time operator, defined as follows:

$$\boxed{{}_{t_0}^{C}\mathrm{D}_t^{\gamma} g(\mathbf{r}, t\,) = \frac{\partial^\gamma}{\partial t^\gamma} g(\mathbf{r}, t) = \frac{1}{\Gamma\,(k-\gamma)}\int_{t_0}^{t} \frac{d\bar{t}}{(t-\bar{t})^{\gamma+1-k}}\frac{\partial^k}{\partial \bar{t}^k} g(\mathbf{r}, \bar{t})}. \; (35)$$

- We underline that Eqs. (31) and (32) are equivalent when $0<\gamma<1$.

Anomalous PNP model: Time-Fractional Derivative

- Another interesting feature of Eqs. (31) and (32) concerns the possibility to rewrite them, respectively, as follows:

$$\begin{aligned} \frac{\partial}{\partial t} P(\mathbf{r}, t) &= - \nabla \cdot \mathbf{j}(\mathbf{r}, t) \quad \text{with} \\ \mathbf{j}(\mathbf{r}, t) &= {}_{t_0}\mathrm{D}_t^{1-\gamma} \mathcal{J}(\mathbf{r}, t) \end{aligned} \tag{36}$$

and

$$\begin{aligned} \frac{\partial^\gamma}{\partial t^\gamma} P(\mathbf{r}, t) &= - \nabla \cdot \mathbf{j}(\mathbf{r}, t) \quad \text{with} \\ \mathbf{j}(\mathbf{r}, t) &= \mathcal{J}(\mathbf{r}, t). \end{aligned} \tag{37}$$

- Equations (36) and (37), related to Eqs. (31) and (32), suggest TWO DIFFERENT POSSIBILITIES of extending the standard approach of the PNP model in order to incorporate time-fractional derivatives.

Anomalous PNP model: Two Different Implementations

- In the first case,

$$
\begin{aligned}
\frac{\partial}{\partial t} P(\mathbf{r}, t) &= - \quad \nabla \cdot \mathbf{j}(\mathbf{r}, t) \quad \text{with} \\
\mathbf{j}(\mathbf{r}, t) &= \quad {}_{t_0}\mathrm{D}_t^{1-\gamma} \mathcal{J}(\mathbf{r}, t\ ),
\end{aligned}
\tag{38}
$$

the **continuity equation is preserved**, with **an extension of the current density** in which time-fractional operators are present only acting on the term representing the **conduction current**;

- In the second case,

$$
\begin{aligned}
\frac{\partial^{\gamma}}{\partial t^{\gamma}} P(\mathbf{r}, t) &= - \quad \nabla \cdot \mathbf{j}(\mathbf{r}, t) \quad \text{with} \\
\mathbf{j}(\mathbf{r}, t) &= \quad \mathcal{J}(\mathbf{r}, t\ ).
\end{aligned}
\tag{39}
$$

the **continuity equation is extended** and the standard form of the current density is modified, but **the time-fractional derivative is present only in the term representing the displacement current**.

First Case: The Riemann-Lioville Time Derivative

- If we now combine the new set of fundamental equations of the extended model, it is mandatory to conclude that $\nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0$, i.e.,

$$\nabla \cdot \left\{ q\tau^{1-\gamma} \; {}_{-\infty}\mathrm{D}_t^{1-\gamma} \left[\mathbf{j}_p(\mathbf{r}, t) - \mathbf{j}_m(\mathbf{r}, t) \right] + \varepsilon \frac{\partial}{\partial t} \mathbf{E}(\mathbf{r}, t) \right\} = 0. \tag{40}$$

- This means that a physically sound extension of the PNP model using fractional derivatives requires an extended expression of the total current **in which the conduction current is defined in terms of a derivative of arbitrary order** whereas **the term of the displacement current keeps its original definition** in terms of a first-order partial time derivative of the electric field.

Second Case: Continuity Equation and Caputo Operator

- We analyze an extension of the PNP model by expressing the continuity equation in terms of the Caputo fractional time derivative:

$$
\begin{aligned}
\tau^{\gamma-1}\frac{\partial^{\gamma} n_p(\mathbf{r},t)}{\partial t^{\gamma}} &= -\nabla\cdot\mathbf{j}_p(\mathbf{r},t)+S(\mathbf{r},t),\\
\tau^{\gamma-1}\frac{\partial^{\gamma} n_m(\mathbf{r},t)}{\partial t^{\gamma}} &= -\nabla\cdot\mathbf{j}_m(\mathbf{r},t)+S(\mathbf{r},t),\\
\tau^{\gamma-1}\frac{\partial^{\gamma} n_n(\mathbf{r},t)}{\partial t^{\gamma}} &= -\nabla\cdot\mathbf{j}_n(\mathbf{r},t)-S(\mathbf{r},t), \qquad (41)
\end{aligned}
$$

- If we now combine the new set of fundamental equations of the extended model, following the procedure used before, it is possible to conclude that $\nabla\cdot\mathbf{j}(\mathbf{r},t)=0$, i.e.,

$$
\nabla\cdot\left\{q\left[\mathbf{j}_p(\mathbf{r},t)-\mathbf{j}_m(\mathbf{r},t)\right]+\varepsilon\tau^{\gamma-1}\frac{\partial^{\gamma}}{\partial t^{\gamma}}\mathbf{E}(\mathbf{r},t)\right\}=0. \qquad (42)
$$

Highlights

- Analysis of the connection between PNP model and displacement current.
- Electrical conductivity and **evidence of the anomalous diffusion**.
- Implications of **the fractional extension to the total current density.**
- Extensions of the PNP model and **connection with CPE elements**.

References

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