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**Anomalous diffusion and its electrical response in
impedance spectroscopy of polymer electrolytes-via-
generalized fractional calculus**

Shantanu Das

RCSDS

Reactor Control Division

B.A.R.C

Mumbai-400085

Adjunct Professor DIAT-Pune

UGC Visiting Fellow Dept. of Applied Mathematics, Univ. of Calcutta

shantanu@barc.gov.in

<http://scholar.google.co.uk/citations?user=9ix9YS8AAAAJ&hl=en>



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Department of Physics.

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**.....for integration mathematics of fractional calculus in several
experimental observations regarding impedance spectroscopy and
visco-elastic experiments plus other phenomena in condense matter physics**

**.....the present explanation of anomalous behavior in impedance
spectroscopy via fractional calculus to be communicated to PR journal.**



Observing anomalous impedance in polymers...how?

In the study prepare gelatin (biopolymer) based electrolyte with formaldehyde (0.25 g antifungal cross linking agent), 2 g Gelatin with different % wt. of plasticizer (Glycerol 0-40 %). No salts are added here.

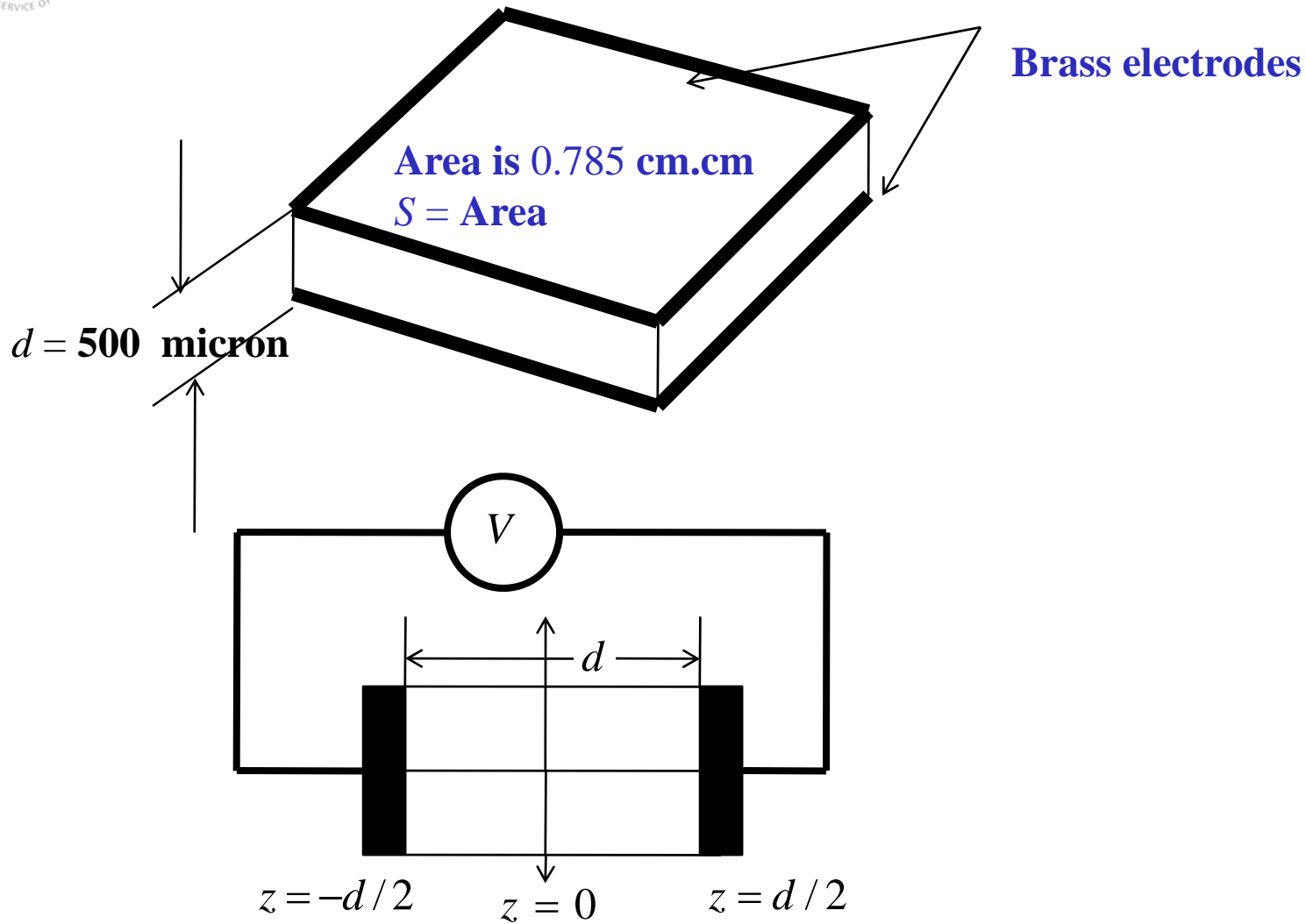
Here the conductivity is mainly due to H_3O^+ ions / OH^- ions, trapped in the polymer matrix and also due to impurities in the sample confirmed from EDAX data (P, S, C, As etc.).

The samples are prepared through solution cast method and what we get transparent film of thickness of about 300-500 micron.

The samples are characterized by Agilent LCR meter and real and imaginary parts of the impedance dispersion is recorded from 20 Hz- 2 M Hz.

The experimental data is compared with “modified” Poisson-Nernst-Planck (PNP) model, which is fractional counter part with fractional derivatives of original PNP theory-giving fractional diffusion-drift equation. Also we take non-blocking electrode boundary condition with memorized adsorption-desorption process. This new treatment helps to explain “anomalous” impedance observed at low frequency or large time-scales.

Sample geometry





Anomalous impedance dispersion elsewhere observed

The anomalous dispersion in impedance spectroscopy is observed in Liquid crystalline system (Nematic LC), and also at experiments with electrical response with ultra pure water (Milli-Q deionized water).

Lenzi EK, Riberio HV etal, Physical Review E 84, 041128 (2011), Santoro PA, Lenzi EK, etal, Mol. Cryst. Vol 576 , (2013)

The anomalous response is at low frequencies, where it is observed that the real part of the impedance increases with decrease in frequency.

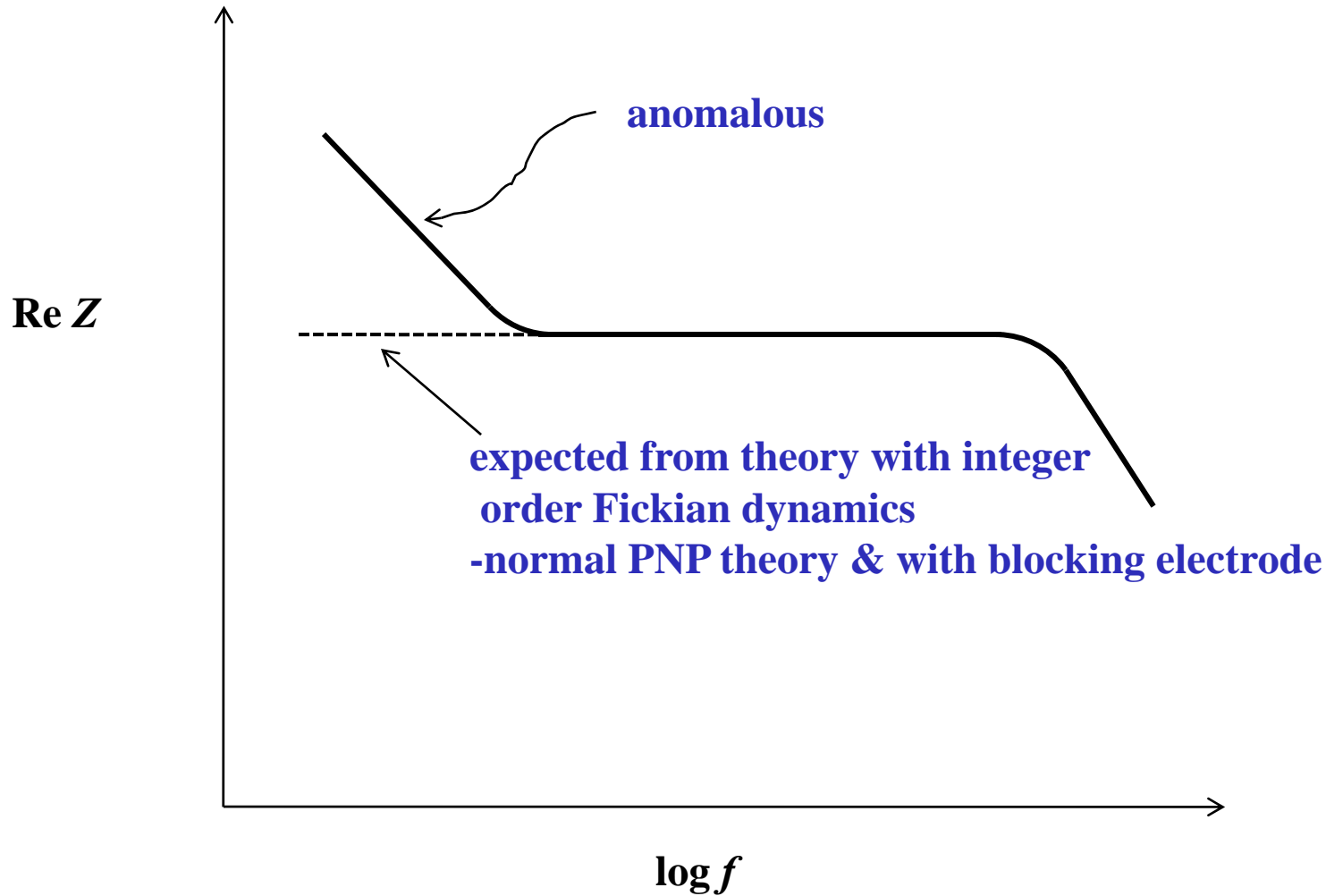
This phenomena does not get reflected by usual (integer order) Poisson-Nernst-Planck theory with boundary condition of blocking electrodes.

The PNP theory visualizes a constant and flat real impedance at low frequency, with a high frequency cut-off like a true low pass filter; fails to catch experimentally observed real part of impedance function rising with decrease of frequency.

The PNP is integer order differential equation theory-perhaps is inadequate to imbibe the complex mechanism if memorized relaxation, a non-Debye process, and complex adsorption-desorption processes at the surface (complex surface effects) are reckoned.



Anomalous impedance dispersion curve at low frequency





Anomalous explained by other means

Take different mobility for positive and negative ions or take different diffusion coefficient for them $D_+ = 10 D_-$

Lelidis I, Barbero G, Liquid Crystals (2005)

Introduce (Warburg like fractional impedance) $Z_i = C_a (i\omega)^{-a}$, $C_a > 0$, $0 < a < 1$ as metal-sample interfacial impedance. This interfacial impedance contributes to total resistance of cell with term $\text{Re}\{Z_i\} = \text{Re}\{C_a (i\omega)^{-a}\} = C_a \omega^{-a} \cos(a\pi/2)$, which is frequency dependent and particularly as $\omega \rightarrow 0$ it diverges, that is what is required. But the fractional order depends on the roughness of electrodes. There is though no correlation between roughness of brass electrodes here, as it is polished for each measurement! But for Super-Capacitors we do have rough electrodes and there is noticeable fractional order (a)

Bates JB, Chu YT, et al, Physical review Lett. 60, 627, (1988)

de Levie R, Electrochemical Acta 10, 113 (1965)

<http://pdfcast.org/pdf/fractional-calculus-and-application-in-engineering>

Shantanu Das, N C Pramaik, Int. J of Mathematics & Computation (IJMC) Vol. 20, Issue 3, pp 94-113 (2013)

Have integer order non blocking electrode as boundary condition (strong adsorption)

Murakami S, Naito H et al, J of Appl. Phys. 80 6396 (1996), and Japanese J of Appl. Phys. 36 2222 (1997)

Scott M et al, J of Colloidal Interface, 230 377 & 388 (2000)

Though the rising nature of Real part of Z is got, but difficult to match experiment data at low and high frequencies simultaneously!! Some other effects need be thus considered.



Constitutive equations with generalized calculus

Fractional continuity equation with distributed order where $n_\alpha(z, t)$ represents the bulk number density of diffusing and drifting species $\alpha = +$ for positive species and $\alpha = -$ for negative species, and $j_\alpha(z, t)$ is current flux

$$\int_0^1 dq (k(q)) \frac{\partial^q}{\partial t^q} n_\alpha(z, t) = - \frac{\partial}{\partial z} j_\alpha(z, t), \quad q \in (0, 1] \dots\dots\dots(1)$$

For normal case the fractional order distribution function is $k(q) = \delta(q - 1)$ thus we get

$$\int_0^1 dq (\delta(q - 1)) \frac{\partial^q}{\partial t^q} n_\alpha(z, t) = \frac{\partial}{\partial t} n_\alpha(z, t) = - \frac{\partial}{\partial z} j_\alpha(z, t)$$

A Fickian process

This is integer order continuity equation of normal PNP theory, a Fickian case!

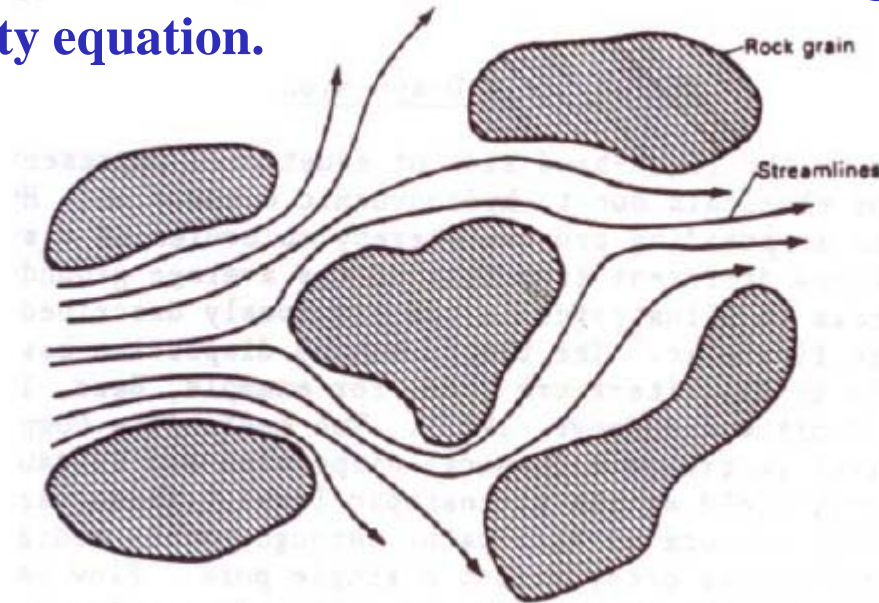
The current density is given by Diffusion-Drift equation as:

$$j_\alpha(z, t) = - \mathbb{D} \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha(z, t) \frac{dV}{dz} \dots\dots\dots(2)$$

- \mathbb{D} Diffusion constant V is cell excitation voltage T ambient temperature
- k_B Boltzmann constant q_e unit electronic charge

Transport in Disordered Media

True that ‘spatial heterogeneity’, roughness gives fractional order time derivative in the transport phenomena...is one of the reasons of having fractional time derivative in continuity equation.



From (1) and (2) we get fractional diffusion in the bulk electrolyte

$$\int_0^1 dq (k(q)) \frac{\partial^q}{\partial t^q} n_\alpha = - \frac{\partial}{\partial z} \left[-\mathbb{D} \frac{\partial n_\alpha}{\partial z} \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha \frac{dV}{dz} \right] = \mathbb{D} \frac{\partial^2 n_\alpha}{\partial z^2} \pm \frac{q_e \mathbb{D}}{k_B T} n_\alpha \frac{d^2 V}{dz^2}$$

Refer: Shantanu Das, Functional fractional Calculus, Springer-Verlag Germany

Shantanu Das, Formation of Fractional Derivative in Time due to Propagation of Free Green's Function in Spatial Stochastic Disorder Field for Transport Phenomena, Int J of Mathematics & Computation IJMC 2012.

Shantanu Das, "Evolution of Temporal Fractional Derivative due to Spatial Stochastic Disorder in Transport Phenomena", International Journal of Mathematics and Computation (IJMC), Vol. 17, Issue-4, pp. 1-20



Fractional derivative used is

Caputo's 1967 definition

$${}^C \frac{\partial^q}{\partial t^q} n_\alpha(z, t) \triangleq \frac{1}{\Gamma(k - q)} \int_{t_0}^t dt' (t - t')^{-q+k-1} n_\alpha^{(k)}(z, t) \dots\dots\dots(3)$$

$$k - 1 < q < k \quad q \in \mathfrak{R} \quad k \in \mathbb{Z}$$

$$n_\alpha^{(k)} = \frac{\partial^k}{\partial t^k} n_\alpha(z, t)$$

$$q = 0.5, \quad k = 1: \quad {}^C \frac{\partial^{0.5}}{\partial t^{0.5}} n_\alpha(z, t) = {}_{t_0}^C D_t^{0.5} = \frac{1}{\Gamma(0.5)} \int_{t_0}^t dt' (t - t')^{-0.5} \frac{\partial}{\partial t} n_\alpha(z, t)$$

$${}_{-\infty}^C D_t^q [e^{\beta t}] = \beta^q e^{\beta t} \quad {}_{t_0}^C D_t^q [N] = 0$$

$$\mathfrak{T} \left\{ {}_{-\infty}^C D_t^q n_\alpha(z, t) \right\} = (i\omega)^q \mathfrak{T} \left\{ n_\alpha(z, t) \right\} = (i\omega)^q \tilde{n}_\alpha(z, \omega)$$

The fractional derivative of $q = 0.5$ is having all past states weighted into it, while this is a non-local operator imbibing memory of the past states. The Caputo derivative requires differentiability condition, whereas classical Riemann-Liouville (RL) is operation of fractional integration of the function first then followed by integer differentiation (opposite of Caputo process), requires function to be continuous (need not be differentiable). RL derivative of a constant is not zero, but a decaying power function. Well if the process of differentiation is starting at start point minus infinity the RL derivative of constant is zero.

Read Annexure-1 for further details on fractional calculus, non-Markovian dynamics, non-Debye relaxation, memory etc.

Refer: Shantanu Das, Functional fractional Calculus, 2nd edition 2011 Springer-Verlag Germany



The order α of differ-integrals in D_t^α are

$\alpha \in \mathbb{Z}$	$\frac{df}{dt}$	$\frac{d^2 f}{dt^2}$	$\frac{d^{-1} f}{dt^{-1}}$	$\frac{d^{-2} f}{dt^{-2}} \dots$	Integer order differ-integrals
$\alpha \in \mathbb{Q}$	$\frac{d^{1/2} f}{dt^{1/2}}$	$\frac{d^{-3/4} f}{dt^{-3/4}}$	$\frac{d^{5/3} f}{dt^{5/3}} \dots$		Fractional (rational) order differ-integrals
$\alpha \in \mathbb{R}$	$\frac{d^{0.56} f}{dt^{0.56}}$	$\frac{d^\pi f}{dt^\pi}$	$\frac{d^{-1.333} f}{dt^{-1.333}} \dots$		Fractional (real) order differ-integrals
$\alpha \sim n\beta; \quad n \in \mathbb{N}$	$a_1 \frac{d^{0.55} f}{dt^{0.55}}$	$+ a_2 \frac{d^{2(0.55)} f}{dt^{2(0.55)}}$	$+ a_3 \frac{d^{3(0.55)} f}{dt^{3(0.55)}} \dots$		Fractional (sequential) order differ-integrals
$\alpha \in \mathbb{C}$	$\frac{d^{0.5+i0.65} f}{dt^{0.5+i0.65}}$	$\frac{d^{-1.33-i1.33} f}{dt^{-1.33-i1.33}} \dots$			Fractional (complex) order differ-integrals
$\alpha \sim a_k \sum_{k=0}^N q_k; \quad q \in \mathbb{R}$	$a_0 \frac{d^0 f}{dt^0}$	$+ a_1 \frac{d^{0.5} f}{dt^{0.5}}$	$+ a_2 \frac{d^{0.666} f}{dt^{0.666}}$	$+ a_3 \frac{d^{0.75} f}{dt^{0.75}} \dots$	Fractional (distributed) order differ-integrals
$\alpha \sim \int_{-\infty}^{+\infty} k(q) dq$	$\int_{-\infty}^{+\infty} dq k(q) \frac{d^q f}{dt^q}$				Fractional (continuous) order differ-integrals

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Refer: Shantanu Das, Functional fractional Calculus, 2nd edition 2011 Springer-Verlag Germany

Frequency and Time Domain Solution for Dynamic Systems having Differential Equations of Continuous Order", Shantanu Das, International Journal of Applied Mathematics & Statistics, Vol. 29, Issue No. 5, pp.6-16, [2012]

"Multiple Riemann Sheet Solution for Dynamic Systems with Fractional Differential Equations", Shantanu Das, International Journal of Applied Mathematics & Statistics. Vol. 28, Issue-4, pp83-89, [2012]



Unusual boundary condition

at the electrodes at $z = +/- d / 2$

$$j_{\alpha}(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t - \bar{t})) \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_{\alpha}(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}} ; \quad |\bar{q}| \in (0, 1] \quad \dots\dots\dots(4)$$

This is unusual process of dynamics of adsorption-desorption happening at the boundary, a very generalized way to write the process with generalized calculus.

For a blocking electrode case the memory kernel of the convolution at RHS $K_m(t) = 0$ gives B.C as $j_{\alpha}(z, t) \Big|_{z=\pm d/2} = 0$

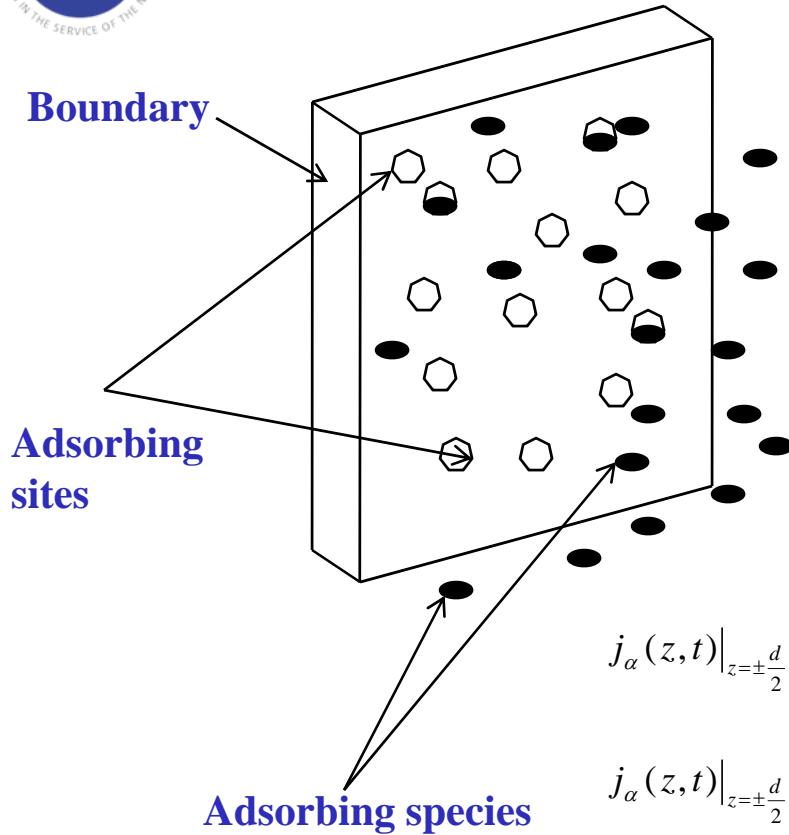
Taking $\bar{k}(\bar{q})$, the fractional order distribution function as $\delta(\bar{q} - 1)$ and the memory kernel as at RHS as delta function i.e. $K_m(t) = \delta(t)$, we return to a very simple case of adsorption-desorption at the boundary without any memory (Markovian-case), namely

$$j_{\alpha}(z, t) \Big|_{z=\pm d/2} = \pm \frac{\partial}{\partial t} n_{\alpha}(z, t) \Big|_{z=\pm d/2}$$

The surface effect given by above integer order differential equation is true if the process at the electrodes is taking place as if at all conditions the n_{α} 's (particles) ejecting or attaching to the surface uniformly, and with memory less dynamics-in homogeneous and smooth background!!

Refer: Shantanu Das, Functional fractional Calculus, 2nd edition 2011 Springer-Verlag Germany

Adsorption-a complex scene



In reality the adsorption (energy) of one site may not be independent of neighboring one's occupational state! Adsorption may also happen at inner layers!! The relaxation times of adsorption & desorption may not have any set average-may be diverging as power-law statistics!! This uncertain wait-time statistics may be cause of anomalous adsorption at the boundary. All adsorbing sites are may not be equivalent!!

$$j_{\alpha}(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \frac{dn_{\alpha}(z, t)}{dt} \Big|_{z=\pm \frac{d}{2}}$$

$$j_{\alpha}(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_{\alpha}(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}}; \quad |\bar{q}| \in (0, 1]$$

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Shantanu Das, Formation of Fractional Derivative in Time due to Propagation of Free Green's Function in Spatial Stochastic Disorder Field for Transport Phenomena, Int J of Mathematics & Computation IJMC 2012.

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Annexure-2 for Dynamics of Integer order Adsorption

Mechanism of Wave Dissipation via Memory Integral vis-a-vis Fractional Derivative", Shantanu Das, International Journal of Mathematics & Computation IJMC, Vol. 19, Issue No.2, pp72-83, [2013]



Actuality in surface effect- -a complex scene

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t - \bar{t})) \frac{\partial^{\bar{q}}}{\partial t^{\bar{q}}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}}$$

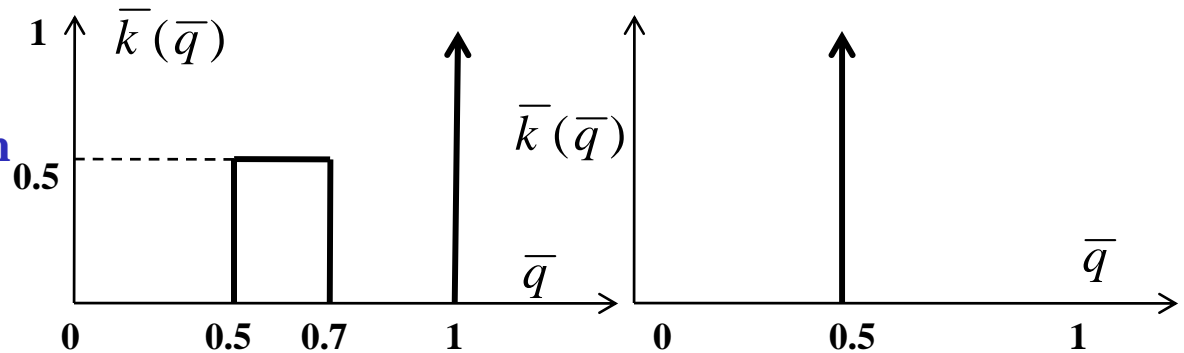
Fractional order distribution Function

1. Integer order delta function at order unity.

2. Fractional order delta function at say 0.5 gives half derivative in rate.

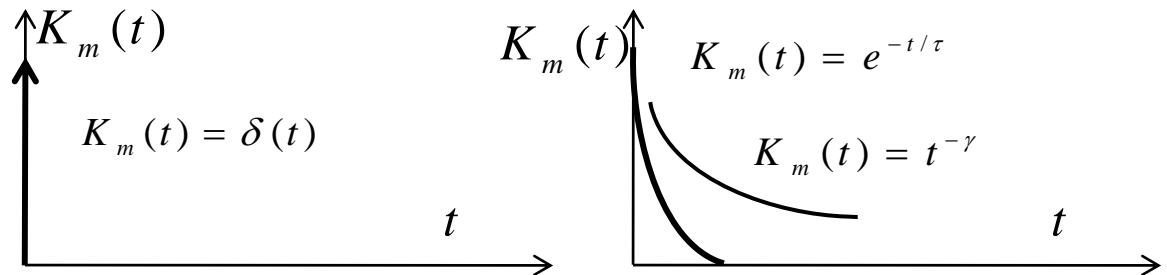
3. Continuous order i.e. between say 0.5-0.7 having infinite fractional orders of strength $1/2$.

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Refer: Shantanu Das, Functional fractional Calculus, 2nd edition 2011 Springer-Verlag Germany



Adsorption-desorption rate's memory kernel

1. Delta function, no memory
2. Exponential-Langmuir's kernel, short range correlation
3. Power law long temporal correlation





Several complex dynamics of adsorption & desorption by choosing memory kernel & order distribution function

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}}$$

.....generalized adsorption at boundary

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \frac{\partial}{\partial t} n_\alpha(z, t) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \delta(\bar{q} - 1), \quad K_m(t) = \delta(t)$$

.....simple adsorption

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \frac{\partial^{0.5}}{\partial t^{0.5}} n_\alpha(z, t) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \delta(\bar{q} - 0.5), \quad K_m(t) = \delta(t)$$

.....half-order adsorption

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_{-\infty}^t d\bar{t} \kappa_1 e^{-(t-\bar{t})/\tau_1} \frac{\partial}{\partial \bar{t}} n_\alpha(z, \bar{t}) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \delta(\bar{q} - 1), \quad K_m(t) = \kappa_1 e^{-t/\tau_1}$$

... integer order with Langmuir memory

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_{-\infty}^t d\bar{t} \kappa_2 e^{-(t-\bar{t})/\tau_2} \frac{\partial^{0.5}}{\partial \bar{t}^{0.5}} n_\alpha(z, \bar{t}) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \delta(\bar{q} - 0.5), \quad K_m(t) = \kappa_2 e^{-t/\tau_2}$$

...fractional order with Langmuir memory

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_{0.5}^{0.7} d\bar{q} \left(\frac{1}{2}\right) \times \int_{-\infty}^t d\bar{t} \kappa_3 (t-\bar{t})^{-\beta} \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_\alpha(z, \bar{t}) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \frac{1}{2}, \quad 0.5 \leq \bar{q} \leq 0.7, \quad K_m(t) = \kappa_3 t^{-\beta}$$

...continuous order with power law memory

...could be many more and also combinations of above even the \bar{q} could be negative



The Poisson's equation

The potential gradient is determined via Poisson's equation

$$\frac{\partial^2}{\partial z^2} V(z, t) = - \frac{q_e}{\epsilon} [n_+(z, t) - n_-(z, t)] \dots\dots\dots(5)$$

Let time dependent potential exciting the cell is $V(z, t) = \phi(z)e^{i\omega t}$ and at the boundary electrodes the potential is $V(d/2, t) = \pm (V_0/2)e^{i\omega t}$, with frequency $\omega = 2\pi f$

Let there be a small perturbation in number density by application of a small oscillating with voltage $n_\alpha(z, t) = N + \delta n_\alpha(z, t)$, with $\delta n_\alpha(z, t) \ll N$ is a good linear approx. with perturbed density varying as

$$\delta n_\alpha(z, t) = n_\alpha(z)e^{i\omega t}$$

Again let

$$\psi_+(z) = n_+(z) + n_-(z) \quad \& \quad \psi_-(z) = n_+(z) - n_-(z)$$

Now our aim is to find the impedance function $Z(\omega) = V(\omega) / I(\omega)$ from expressions (1)-(5); i.e. fractionally generalized PNP equations of impedance spectroscopy.



Assumptions in our fractional order modeling to get impedance

Assume sample slab is isotropic.

Assume that in thermodynamically equilibrium the sample contains a density N of ions of +ve and -ve, uniformly distributed.

The presence of external electric voltage produces a perturbation of the distribution of ions, in the sense that it remains globally neutral but now it is locally charged.

We suppose that the sample is subjected to a external voltage V_0 and frequency f . By indicating n_+ , and n_- respectively the density of positive and negative ions, we have $n_+(z, t) = n_-(z, t) = N$; for zero V_0 , and they are not equal for non-zero V_0 .

In this frame work, we assume mobility of +ve and -ve ion are same, and we consider mono-valent case

$$\mu_+ = \mu_-, \quad \mathbb{D}_+ = \mathbb{D}_- = \mathbb{D}$$

We also assume the $n_\alpha(z, t)$ is continuous and differentiable in z , and t .



Solution...

From (1) $\int_0^1 dq (k(q)) \frac{\partial^q}{\partial t^q} n_\alpha(z, t) = -\frac{\partial}{\partial z} j_\alpha(z, t)$ **& from (2)** $j_\alpha(z, t) = -\mathbb{D} \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha(z, t) \frac{dV}{dz}$

We get $\int_0^1 dq (k(q)) \frac{\partial^q}{\partial t^q} n_\alpha = -\frac{\partial}{\partial z} \left[-\mathbb{D} \frac{\partial n_\alpha}{\partial z} \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha \frac{dV}{dz} \right] = \mathbb{D} \frac{\partial^2 n_\alpha}{\partial z^2} \pm \frac{q_e \mathbb{D}}{k_B T} n_\alpha \frac{d^2 V}{dz^2}$

Substitute $n_\alpha(z, t) = N + \delta n_\alpha(z, t)$ **recognize** $\partial[n_\alpha(z, t)] / \partial t = \partial[\delta n_\alpha(z, t)] / \partial t$
and Caputo's derivative of ${}^c \partial^q N / \partial t^q = 0$

Put $n_\alpha(z, t) = N + \delta n_\alpha(z, t)$ **and the perturbed density as** $\delta n_\alpha(z, t) = n_\alpha(z) e^{i\omega t}$

$$\int_0^1 dq (k(q)) \frac{\partial^q [N + \delta n_\alpha(z, t)]}{\partial t^q} = \mathbb{D} \frac{\partial^2 [N + \delta n_\alpha(z, t)]}{\partial z^2} \pm \frac{q_e \mathbb{D}}{k_B T} [N + \delta n_\alpha(z, t)] \frac{d^2 V}{dz^2}$$

$$\int_0^1 dq (k(q)) \frac{\partial^q [\delta n_\alpha(z, t)]}{\partial t^q} = \mathbb{D} \frac{\partial^2 [\delta n_\alpha(z, t)]}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d^2 V}{dz^2} \pm \frac{q_e \mathbb{D} \delta n_\alpha(z, t)}{k_B T} \frac{d^2 V}{dz^2}$$

Put in above $\delta n_\alpha(z, t) = n_\alpha(z) e^{i\omega t}$ **and** $V(z, t) = \phi(z) e^{i\omega t}$ **to get the following**
by neglecting the last term of RHS, which is very small as $\delta n_\alpha(z, t) \ll N$ **, we get:**

$$\int_0^1 dq (k(q)) \frac{\partial^q n_\alpha(z) e^{i\omega t}}{\partial t^q} = \mathbb{D} \frac{\partial^2 n_\alpha(z) e^{i\omega t}}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d}{dz} \phi(z) e^{i\omega t} \quad \text{use } {}^c \frac{d^q}{dt^q} e^{i\omega t} \Big|_{-\infty}^t = (i\omega)^q e^{i\omega t}$$

Read Annexure -1 for further details on fractional calculus, non-Markovian dynamics, non-Debye relaxation, memory etc.

Refer: Shantanu Das, Functional fractional Calculus, 2nd edition 2011 Springer-Verlag Germany



Solution continued...1

$$\int_0^1 dq (k(q)) \frac{\partial^q n_\alpha(z) e^{i\omega t}}{\partial t^q} = \mathbb{D} \frac{\partial^2 n_\alpha(z) e^{i\omega t}}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d}{dz} \phi(z) e^{i\omega t}$$

Use ${}_{-\infty}^C D_t^q e^{i\omega t} = (i\omega)^q e^{i\omega t}$ to get the following

$$\int_0^1 dq (k(q)) (i\omega)^q n_\alpha(z) e^{i\omega t} = \mathbb{D} \frac{\partial^2 n_\alpha(z) e^{i\omega t}}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d^2}{dz^2} \phi(z) e^{i\omega t}$$

$$\int_0^1 dq (k(q)) (i\omega)^q n_\alpha(z) = \mathbb{D} \frac{\partial^2 n_\alpha(z)}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d^2}{dz^2} \phi(z)$$

We mention here that ${}_0^C D_t^q e^{\beta t} \neq \beta^q e^{\beta t}$, but ${}_{-\infty}^C D_t^q e^{\beta t} = \beta^q e^{\beta t}$ for $\beta > 0$; $0 < q < 1$

$$\int_0^1 dq (k(q)) \frac{\partial^q n_\alpha(z) e^{i\omega t}}{\partial t^q} = \int_0^1 dq (k(q)) \left\{ \frac{n_\alpha(z)}{\Gamma(1-q)} \int_{-\infty}^t dt' (t-t')^{-q} \frac{d}{dt} e^{i\omega t} \right\} = \int_0^1 dq (k(q)) n_\alpha(z) \left\{ {}_{-\infty}^C D_t^q e^{i\omega t} \right\}$$

In our study we are dealing with steady state response, thus the lower terminal in the integral transformed representation is at minus infinity. Also at the minus infinity the function $e^{\beta t}$ is zero.

In this study thus we aren't concerned with the initial conditions-at minus infinity all initial conditions related to differential equations are at rest (zero)

Read Annexure-1 for further details on fractional calculus, non-Markovian dynamics, non-Debye relaxation, memory etc.

Refer: Shantanu Das, Functional fractional Calculus, 2nd edition 2011 Springer-Verlag Germany

Frequency and Time Domain Solution for Dynamic Systems having Differential Equations of Continuous Order", Shantanu Das, International Journal of Applied Mathematics & Statistics, Vol. 29, Issue No. 5, pp.6-16, [2012]



Solution continued...2

We derived
$$\int_0^1 dq (k(q))(i\omega)^q n_\alpha(z) = \mathbb{D} \frac{\partial^2 n_\alpha(z)}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d^2}{dz^2} \phi(z) \dots(6)$$

Let us write the operator on LHS of above $\int_0^1 dq (k(q))(i\omega)^q \equiv \Lambda(i\omega)$, and write (6) as

$$\frac{\Lambda(i\omega)}{\mathbb{D}} n_\alpha(z) = \frac{\partial^2}{\partial z^2} n_\alpha(z) \pm \frac{q_e N}{k_B T} \frac{d^2 \phi(z)}{dz^2}$$

Use Poisson
$$\frac{\partial^2}{\partial z^2} V(z,t) = -\frac{q_e}{\epsilon} [n_+(z,t) - n_-(z,t)]$$

$$\frac{\partial^2}{\partial z^2} \phi(z) e^{i\omega t} = -\frac{q_e}{\epsilon} [n_+(z) e^{i\omega t} - n_-(z) e^{i\omega t}]$$

$$\frac{d^2 \phi(z)}{dz^2} = -\frac{q_e}{\epsilon} [n_+(z) - n_-(z)] \quad \text{substitute in (6) to get}$$

$$\frac{\Lambda(i\omega)}{\mathbb{D}} n_\alpha(z) = \frac{\partial^2 n_\alpha(z)}{\partial z^2} \mp \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \dots\dots\dots(7)$$

From (7) we segregate the equation for + and - charges as follows:

$$\frac{\Lambda(i\omega)}{\mathbb{D}} n_+(z) = \frac{\partial^2 n_+(z)}{\partial z^2} - \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)]$$

$$\frac{\Lambda(i\omega)}{\mathbb{D}} n_-(z) = \frac{\partial^2 n_-(z)}{\partial z^2} + \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)]$$



Solution continued...3

We derived

$$\frac{\Lambda(i\omega)}{\mathbb{D}} n_+(z) = \frac{\partial^2 n_+(z)}{\partial z^2} - \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)]$$

$$\frac{\Lambda(i\omega)}{\mathbb{D}} n_-(z) = \frac{\partial^2 n_-(z)}{\partial z^2} + \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)]$$

Rearranging above we get two differential equations

$$\frac{\partial^2 n_+(z)}{\partial z^2} = \frac{\Lambda(i\omega)}{\mathbb{D}} n_+(z) + \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \quad \dots\dots(8)$$

$$\frac{\partial^2 n_-(z)}{\partial z^2} = \frac{\Lambda(i\omega)}{\mathbb{D}} n_-(z) - \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \quad \dots\dots(9)$$

Adding (8) and (9) we have

$$\frac{\partial^2 [n_+(z) + n_-(z)]}{\partial z^2} = \frac{\Lambda(i\omega)}{\mathbb{D}} [n_+(z) + n_-(z)] \quad \dots\dots\dots(10)$$

Subtracting (9) from (8) we have

$$\frac{\partial^2 [n_+(z) - n_-(z)]}{\partial z^2} = \frac{\Lambda(i\omega)}{\mathbb{D}} [n_+(z) - n_-(z)] + \frac{2q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \quad \dots\dots(11)$$

Consolidating (10) and (11) we obtain 2nd order linear differential equation(not FDE)

$$\frac{d^2}{dz^2} \psi_{\pm} = \alpha_{\pm}^2 \psi_{\pm} \quad \dots\dots(12)$$

$$\alpha_-^2 = \frac{\Lambda(i\omega)}{\mathbb{D}} + \frac{1}{\lambda^2} \quad \dots\dots(13)$$

$$\alpha_+^2 = \frac{\Lambda(i\omega)}{\mathbb{D}} \quad \dots\dots(14)$$



Solution continued...4

We derived $\frac{d^2}{dz^2} \psi_{\pm}(z) = \alpha_{\pm}^2 \psi_{\pm}(z)$ $\alpha_{-}^2 = \frac{\Lambda(i\omega)}{\mathbb{D}} + \frac{1}{\lambda^2}$ $\alpha_{+}^2 = \frac{\Lambda(i\omega)}{\mathbb{D}}$

Remember $\lambda^2 = \frac{\epsilon k_B T}{2 q_e^2 N}$ gives Debye screening length λ . This is surface effect of bare sample, in contact with a substrate; where we have selective adsorbed charges on the surface screened by opposite charge giving a charge separation of a distance λ from the surface. This is basic phenomena of formation of Electric Double Layer Capacity ELDC. This bare screening length gets altered when we have potential in the electrolyte cell.

The solution of the ordinary differential equation is

$$\psi_{\pm}(z) = c_{\pm 1} e^{\alpha_{\pm} z} + c_{\pm 2} e^{-\alpha_{\pm} z}$$

We have symmetry in potential distribution about centre as $V(z, t) = -V(-z, t)$

$$\psi_{-}(z) = c_{-1} e^{\alpha_{-} z} + c_{-2} e^{-\alpha_{-} z} \quad \psi_{-}(-z) = c_{-1} e^{\alpha_{-}(-z)} + c_{-2} e^{-\alpha_{-}(-z)} \quad \psi_{-}(z) = -\psi_{-}(-z)$$

$$c_{-1} e^{\alpha_{-} z} + c_{-2} e^{-\alpha_{-} z} = -\left(c_{-1} e^{\alpha_{-}(-z)} + c_{-2} e^{-\alpha_{-}(-z)} \right) = -c_{-1} e^{\alpha_{-}(-z)} - c_{-2} e^{-\alpha_{-}(-z)}$$

$$(c_{-1} + c_{-2}) e^{\alpha_{-} z} = -(c_{-1} + c_{-2}) e^{\alpha_{-}(-z)} \quad (c_{-1} + c_{-2})(e^{\alpha_{-} z} + e^{-\alpha_{-} z}) = 0$$

Implying that

$$c_{-1} + c_{-2} = 0 \quad c_{-1} = -c_{-2} \quad \psi_{-}(z) = c_{-1} e^{\alpha_{-} z} - c_{-1} e^{-\alpha_{-} z} = c_{-1} (e^{\alpha_{-} z} - e^{-\alpha_{-} z})$$

$$\psi_{-}(z) = n_{+}(z) - n_{-}(z) = 2c_{-1} \left(\frac{e^{\alpha_{-} z} - e^{-\alpha_{-} z}}{2} \right) = 2c_{-1} \sinh(\alpha_{-} z) \dots\dots(15)$$



Potential solution ...(contd.)

From Poisson we have

$$\frac{d^2 V(z, t)}{dz^2} = -\frac{q_e}{\epsilon} [n_+(z, t) - n_-(z, t)] \quad V(z, t) = \phi(z) e^{i\omega t} \quad n_\alpha(z, t) = n_\alpha(z) e^{i\omega t}$$

$$\frac{d^2}{dz^2} \phi(z) = -\frac{q_e}{\epsilon} [n_+(z) - n_-(z)] = -\frac{q_e}{\epsilon} \psi_-(z) = -\frac{q_e}{\epsilon} [2c_{-1} \sinh(\alpha_- z)] \quad \dots\dots(16)$$

Integrating (16) we get gradient of potential i.e. proportional to electric field in the cell

$$\frac{d\phi(z)}{dz} = -\frac{q_e}{\epsilon \alpha_-} [2c_{-1} \cosh(\alpha_- z)] + c_1 \quad \dots\dots\dots(17)$$

Integrating (17) we get potential as a function in electrolyte cell

$$\phi(z) = -\frac{2q_e}{\epsilon \alpha_-^2} [c_{-1} \sinh(\alpha_- z)] + c_1 z + c_0$$

At origin the center of cell we have $\phi(z) \big|_{z=0} = \phi(0) = 0$ so from above $c_0 = 0$

$$\phi(z) = -\frac{2q_e}{\epsilon \alpha_-^2} [c_{-1} \sinh(\alpha_- z)] + c_1 z$$

Electric field & current function

The electric field is the negative gradient of potential function

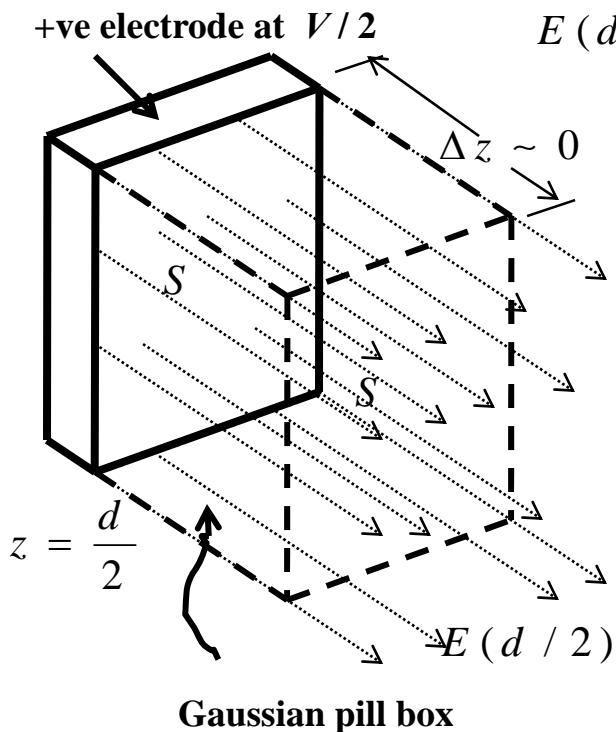
$$E(z, t) = -\frac{d}{dz}V(z, t) = -\frac{d}{dt}\phi(z)e^{i\omega t} = -\phi'(z)e^{i\omega t} \quad E\left(\frac{d}{2}, t\right) = -\phi'\left(\frac{d}{2}\right)e^{i\omega t}$$

We apply Gauss law at the electrode at $+d/2$ connected to potential $+V/2$. By this there will be preferential negative charges at the electrode adsorbed. The Gauss law states

$$\oiint_S E(d/2, t) \cdot dS = \frac{Q_{total}}{\epsilon} \quad \text{Where } Q_{total} \text{ is total charge enclosed in volume as } -\sigma_s \cdot S$$

LHS of Gauss law is flux through a closed surface of area S is $E(d/2, t) \cdot S$, therefore

$$E(d/2, t) = -\frac{\sigma_s}{\epsilon} \quad \text{where } -\sigma_s \text{ is total surface charge density}$$



Implying $\sigma_s = -\epsilon E\left(\frac{d}{2}, t\right) = \epsilon \phi'\left(z = \frac{d}{2}\right)e^{i\omega t}$

Therefore total charge at $d/2$ is

$$Q_{total} = \sigma_s S = \epsilon S \phi'(d/2)e^{i\omega t}$$

The current is

$$I(z, t) \Big|_{z=d/2} = \frac{d}{dt} Q_{total} = i\omega \epsilon S \phi'(d/2)e^{i\omega t}$$

Impedance is

$$Z = \frac{V}{I} \Big|_{z=d/2} = \frac{\phi(d/2)e^{i\omega t}}{i\omega \epsilon S \phi'(d/2)e^{i\omega t}} = \frac{\phi(d/2)}{i\omega \epsilon S \phi'(d/2)} \dots\dots(18)$$



The adsorption-desorption at boundary-its calculations

$$\begin{aligned}
 j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} &= \pm \int_0^1 d\bar{q} \left(\bar{k}(\bar{q}) \right) \times \int_{-\infty}^t d\bar{t} \left(K_m(t - \bar{t}) \right) \frac{\partial \bar{q}}{\partial \bar{t}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}} & n_\alpha(z, t) &= n_\alpha(z) e^{i\omega t} \\
 &= \pm \int_0^1 d\bar{q} \left(\bar{k}(\bar{q}) \right) \times \int_{-\infty}^t d\bar{t} \left(K_m(t - \bar{t}) \right) (i\omega)^{\bar{q}} e^{i\omega \bar{t}} n_\alpha(z) \Big|_{z=\pm \frac{d}{2}} & & \dots\dots(19) \\
 &= \pm \Phi(i\omega) n_\alpha(z) e^{i\omega t}
 \end{aligned}$$

Define boundary operator as $\Phi(i\omega) = \pm e^{-i\omega t} \int_0^1 d\bar{q} \left(\bar{k}(\bar{q}) \right) \times \int_{-\infty}^t d\bar{t} \left(K_m(t - \bar{t}) \right) (i\omega)^{\bar{q}} e^{i\omega \bar{t}}$

From (2) we have $j_\alpha(z, t) = -\mathbb{D} \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha(z, t) \frac{dV}{dz}$ **using this for above we get**

$$\begin{aligned}
 j_\alpha(z, t) &= -\mathbb{D} \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha(z, t) \frac{dV}{dz} & n_\alpha(z, t) &= N + n_\alpha(z) e^{i\omega t} & V &= \phi(z) e^{i\omega t} \\
 &= -\mathbb{D} \frac{d}{dz} n_\alpha(z) e^{i\omega t} \mp \frac{q_e \mathbb{D} N}{k_B T} \frac{d\phi(z)}{dz} e^{i\omega t} & n_\alpha(z) &\ll N
 \end{aligned}$$

$$-\mathbb{D} \frac{d}{dz} n_\alpha(z) e^{i\omega t} \mp \frac{q_e \mathbb{D} N}{k_B T} \frac{d\phi(z)}{dz} e^{i\omega t} \Big|_{z=\pm d/2} = \pm \Phi(i\omega) n_\alpha(z) e^{i\omega t} \Big|_{z=\pm d/2}$$

$$-\mathbb{D} \frac{d}{dz} n_\alpha(z) \mp \frac{q_e \mathbb{D} N}{k_B T} \frac{d\phi(z)}{dz} \Big|_{z=\pm d/2} = \pm \Phi(i\omega) n_\alpha(z) \Big|_{z=\pm d/2}$$



The adsorption-desorption at boundary-its calculations...1

$$-\mathbb{D} \frac{d}{dz} n_{\alpha}(z) \mp \frac{q_e \mathbb{D} N}{k_B T} \frac{d\phi(z)}{dz} \Big|_{z=\pm d/2} = \pm \Phi(i\omega) n_{\alpha}(z) \Big|_{z=\pm d/2}$$

As we segregated the +ve and -ve species earlier for Drift-Diffusion equation (1) and (2) and then adding and subtracting the obtained expression from above we can get;

$$\mathbb{D} \frac{d}{dz} \psi_{-}(z) + \frac{2q_e \mathbb{D} N}{k_B T} \frac{d\phi(z)}{dz} \Big|_{z=\pm d/2} = \mp \Phi(i\omega) \psi_{-}(z) \Big|_{z=\pm d/2} \quad \dots\dots(20)$$

$$\mathbb{D} \frac{d}{dz} \psi_{+}(z) \Big|_{z=\pm d/2} = \mp \Phi(i\omega) \psi_{+}(z) \Big|_{z=\pm d/2} \quad \dots\dots(21)$$

We have from (15) & (17) $\psi_{-}(z) = 2c_{-1} \sinh(\alpha_{-} z)$ and $\frac{d\phi(z)}{dz} = -\frac{q_e}{\epsilon \alpha_{-}} [2c_{-1} \cosh(\alpha_{-} z)] + c_1$ using them in (20) we get the following

$$2\mathbb{D}c_{-1} \cosh(\alpha_{-} z) + \frac{2q_e N \mathbb{D}}{k_B T} \left\{ -\frac{2q_e c_{-1} \alpha_{-} \cosh(\alpha_{-} z)}{\epsilon \alpha_{-}^2} + c_1 \right\} \Big|_{z=\pm \frac{d}{2}} = \mp \Phi(i\omega) 2c_{-1} \sinh(\alpha_{-} z) \Big|_{z=\pm \frac{d}{2}}$$

$$\left[\mathbb{D} \alpha_{-} \cosh(\alpha_{-} z) + \frac{q_e N \mathbb{D}}{k_B T} \left(-\frac{2q_e \alpha_{-}}{\epsilon \alpha_{-}^2} \right) \cosh(\alpha_{-} z) \pm \Phi(i\omega) \sinh(\alpha_{-} z) \right] c_{-1} + \frac{q_e N \mathbb{D}}{k_B T} c_1 \Big|_{z=\pm \frac{d}{2}} = 0$$

$$\left[\mathbb{D} \alpha_{-} \cosh(\alpha_{-} z) \left(1 - \frac{2q_e N}{k_B T \epsilon \alpha_{-}^2} \right) \pm \Phi(i\omega) \sinh(\alpha_{-} z) \right] c_{-1} + \frac{q_e N \mathbb{D}}{k_B T} c_1 \Big|_{z=\pm \frac{d}{2}} = 0$$



The adsorption-desorption at boundary-its calculations...2

$$\left[\mathbb{D} \alpha_- \cosh(\alpha_- z) \left(1 - \frac{2q_e N}{k_B T \varepsilon \alpha_-^2} \right) \pm \Phi(i\omega) \sinh(\alpha_- z) \right] c_{-1} + \frac{q_e N \mathbb{D}}{k_B T} c_1 \Big|_{z=\pm \frac{d}{2}} = 0$$

$$\left[\mathbb{D} \alpha_- \cosh(\alpha_- \{d/2\}) \left(1 - \frac{1}{\lambda^2 \alpha_-^2} \right) \pm \Phi(i\omega) \sinh(\alpha_- \{d/2\}) \right] c_{-1} + \frac{\varepsilon \mathbb{D}}{2 \lambda^2 q_e} c_1 = 0$$

The parameters are

$$\alpha_-^2 = \frac{\Lambda(i\omega)}{\mathbb{D}} + \frac{1}{\lambda^2} \quad \frac{1}{\lambda^2} = \alpha_-^2 - \frac{\Lambda(i\omega)}{\mathbb{D}}$$

Thus we get $1 - \frac{1}{\lambda^2 \alpha_-^2} = 1 - \left(\alpha_-^2 - \frac{\Lambda(i\omega)}{\mathbb{D}} \right) \frac{1}{\alpha_-^2} = \frac{\Lambda(i\omega)}{\mathbb{D} \alpha_-^2}$ using this in above

$$\left[\Lambda(i\omega) \frac{\cosh(\alpha_- \{d/2\})}{\alpha_-} \pm \Phi(i\omega) \sinh(\alpha_- \{d/2\}) \right] c_{-1} + \frac{\varepsilon \mathbb{D}}{2 \lambda^2 q_e} c_1 = 0$$

$$\frac{\cosh\left(\alpha_- \frac{d}{2}\right)}{\alpha_-} \left[\Lambda(i\omega) \pm \alpha_- \Phi(i\omega) \tanh\left(\alpha_- \frac{d}{2}\right) \right] c_{-1} + \frac{\varepsilon \mathbb{D}}{2 \lambda^2 q_e} c_1 = 0 \quad \dots\dots(22)$$

We define $\Lambda(i\omega) \pm \alpha_- \Phi(i\omega) \tanh\left(\alpha_- \frac{d}{2}\right) = E$ a new Fourier operator at $d/2$ using this E we get in (22)

$$\frac{E \cosh\left(\alpha_- \frac{d}{2}\right)}{\alpha_-} c_{-1} + \frac{\varepsilon \mathbb{D}}{2 \lambda^2 q_e} c_1 = 0 \quad \dots\dots(23)$$



The adsorption-desorption at boundary-its calculations...3

At $z = d/2$ we have $V = V_0/2$ and from (17) we have the potential function as

$$\phi(z) = -\frac{2q_e}{\varepsilon\alpha_-^2} [c_{-1} \sinh(\alpha_- z)] + c_1 z + c_0 \quad \frac{V_0}{2} = -\frac{2q_e}{\varepsilon\alpha_-^2} \left[\sinh\left(\alpha_- \frac{d}{2}\right) \right] c_{-1} + \left(\frac{d}{2}\right) c_1$$

From (23) we got
$$\frac{E \cosh\left(\alpha_- \frac{d}{2}\right)}{\alpha_-} c_{-1} + \frac{\varepsilon \mathbb{D}}{2\lambda^2 q_e} c_1 = 0$$

From these we can get the values of c_{-1} and c_1 to get the ratio of these two as:

$$\frac{c_1}{c_{-1}} = -\frac{\left[\frac{2\mathbb{D}}{\lambda^2 \alpha_-^2} \tanh\left(\alpha_- \frac{d}{2}\right) + \frac{E d}{\alpha_-} \right] E \cosh\left(\alpha_- \frac{d}{2}\right)}{\frac{\varepsilon \mathbb{D}}{2\lambda^2 q_e} \left[\frac{2\mathbb{D}}{\lambda^2 \alpha_-} \tanh\left(\alpha_- \frac{d}{2}\right) + E d \right]} = -\frac{2\lambda^2 q_e E}{\alpha_- \varepsilon \mathbb{D}} \cosh\left(\alpha_- \frac{d}{2}\right) \quad \text{.....(24)}$$

$$Z = \frac{\phi(z)}{i\omega\varepsilon S \frac{d\phi(z)}{dz}} = \frac{-\frac{2q_e}{\varepsilon\alpha_-^2} [c_{-1} \sinh(\alpha_- z)] + c_1 z}{i\omega\varepsilon S \left[-\frac{q_e}{\varepsilon\alpha_-} [2c_{-1} \cosh(\alpha_- z)] + c_1 \right]} = \frac{1}{i\omega\varepsilon S \alpha_-^2} \left[\frac{\sinh(\alpha_- z) - \frac{\alpha_-^2 \varepsilon z}{2q_e} \frac{c_1}{c_{-1}}}{\frac{1}{\alpha_-} \cosh(\alpha_- z) - \frac{\varepsilon}{2q_e} \frac{c_1}{c_{-1}}} \right] \quad \text{.....(25)}$$

The impedance dispersion

Putting the ratio of constants of integration obtained as in (24) into impedance relation of (25) we have

$$\begin{aligned}
 Z &= \frac{1}{i\omega \varepsilon S \alpha_-^2} \left[\frac{\sinh(\alpha_- z) - \frac{\alpha_-^2 \varepsilon z}{2q_e} \frac{c_1}{c_{-1}}}{\frac{1}{\alpha_-} \cosh(\alpha_- z) - \frac{\varepsilon}{2q_e} \frac{c_1}{c_{-1}}} \right] \\
 Z &= \frac{1}{i\omega \varepsilon S \alpha_-^2} \left[\frac{\sinh\left(\alpha_- \frac{d}{2}\right) - \frac{\alpha_-^2 \varepsilon \frac{d}{2}}{2q_e} \left(-\frac{2q_e \lambda^2 E}{\varepsilon \mathbb{D} \alpha_-}\right) \cosh\left(\alpha_- \frac{d}{2}\right)}{\frac{1}{\alpha_-} \cosh\left(\alpha_- \frac{d}{2}\right) - \frac{\varepsilon}{2q_e} \left(-\frac{2q_e \lambda^2 E}{\varepsilon \mathbb{D} \alpha_-}\right) \cosh\left(\alpha_- \frac{d}{2}\right)} \right] \\
 &= \frac{1}{i\omega \varepsilon S \alpha_-^2} \left[\frac{\sinh\left(\alpha_- \frac{d}{2}\right) + \frac{\alpha_- \frac{d}{2} \lambda^2 E}{\mathbb{D}} \cosh\left(\alpha_- \frac{d}{2}\right)}{\frac{1}{\alpha_-} \cosh\left(\alpha_- \frac{d}{2}\right) \left[1 + \frac{\lambda^2 E}{\mathbb{D}}\right]} \right] = \frac{1}{i\omega \varepsilon S \alpha_-^2} \left[\frac{\tanh\left(\alpha_- \frac{d}{2}\right) + \frac{\alpha_- \lambda^2 E}{\mathbb{D}} \frac{d}{2}}{\frac{1}{\alpha_-} \left[1 + \frac{\lambda^2 E}{\mathbb{D}}\right]} \right]
 \end{aligned}$$



The impedance dispersion in terms of basic derived operators

$$\begin{aligned}
 Z(i\omega) &= \frac{1}{i\omega \varepsilon S \alpha_-^2} \left[\frac{\tanh\left(\alpha_- \frac{d}{2}\right) + \frac{\alpha_- \lambda^2 E d}{\mathbb{D}}}{\frac{1}{\alpha_-} \left[1 + \frac{\lambda^2 E}{\mathbb{D}}\right]} \right] \quad \text{use} \quad E = \Lambda(i\omega) \pm \alpha_- \Phi(i\omega) \tanh\left(\alpha_- \frac{d}{2}\right) \\
 &= \frac{1}{i\omega \varepsilon S \alpha_-^2} \left[\frac{\frac{\tanh\left(\alpha_- \frac{d}{2}\right)}{\lambda^2 \alpha_-} + \frac{Ed}{2\mathbb{D}}}{\frac{1}{\lambda^2 \alpha_-^2} + \frac{\left(\alpha_-^2 - \frac{1}{\lambda^2}\right) \mathbb{D} \pm \alpha_- \Phi(i\omega) \tanh\left(\alpha_- \frac{d}{2}\right)}{\alpha_-^2 \mathbb{D}}} \right] \\
 &= \frac{1}{i\omega \varepsilon S \alpha_-^2} \left[\frac{\frac{\tanh\left(\alpha_- \frac{d}{2}\right)}{\lambda^2 \alpha_-} + \frac{Ed}{2\mathbb{D}}}{1 + \frac{\Phi(i\omega) \tanh\left(\alpha_- \frac{d}{2}\right)}{\alpha_- i\omega \lambda^2} \left(\frac{i\omega \lambda^2}{\mathbb{D}}\right)} \right] \quad \dots\dots\dots(26)
 \end{aligned}$$



The method utilized

We divide the process by assuming some species follow normal PNP and rest follow the anomalous PNP, denoted by fraction h and $1 - h$ respectively, through admittances Y_N and Y_A to get Z_{final} as

$$\frac{1}{Z_{final}} = h Y_N + (1 - h) Y_A = \frac{h}{Z_N} + \frac{1 - h}{Z_A} \quad \text{.....(27)}$$

$$Z_N = \frac{1}{i\omega S \epsilon \alpha_{N-}^2} \frac{\frac{\tanh(\alpha_{N-} d / 2)}{\lambda^2 \alpha_{N-}} + \frac{E_N d}{2 \mathbb{D}_N}}{1 + \frac{\Phi_N(i\omega) \tanh(\alpha_{N-} d / 2)}{\alpha_{N-} i\omega \lambda^2} \left(\frac{i\omega \lambda^2}{\mathbb{D}_N} \right)} \quad \text{.....(28)}$$

$$Z_A = \frac{1}{i\omega S \epsilon \alpha_{A-}^2} \frac{\frac{\tanh(\alpha_{A-} d / 2)}{\lambda^2 \alpha_{A-}} + \frac{E_A d}{2 \mathbb{D}_A}}{1 + \frac{\Phi_A(i\omega) \tanh(\alpha_{A-} d / 2)}{\alpha_{A-} i\omega \lambda^2} \left(\frac{i\omega \lambda^2}{\mathbb{D}_A} \right)} \quad \text{.....(29)}$$

\mathbb{D}_N is the normal diffusion coefficient \mathbb{D}_A is anomalous diffusion coefficient

$\int_0^1 dq (k(q)) (i\omega)^q \equiv \Lambda(i\omega)$ is generalized fractional order differential operator

$\Lambda_N(i\omega) = a(i\omega)$ is integer order operator corresponds to $a(\partial / \partial t)$

$\Lambda_A(i\omega) = b^q(i\omega)^q$ is fractional order operator corresponds to $b^q (\partial^q / \partial t^q)$, $0 < q < 1$



The other parameters are

The normal and anomalous impedance are

$$Z_N = \frac{1}{i\omega S \varepsilon \alpha_{N-}^2} \frac{\frac{\tanh(\alpha_{N-} d / 2)}{\lambda^2 \alpha_{N-}} + \frac{E_N d}{2 \mathbb{D}_N}}{1 + \frac{\Phi_N(i\omega) \tanh(\alpha_{N-} d / 2)}{\alpha_{N-} i\omega \lambda^2} \left(\frac{i\omega \lambda^2}{\mathbb{D}_N} \right)}$$

$$Z_A = \frac{1}{i\omega S \varepsilon \alpha_{A-}^2} \frac{\frac{\tanh(\alpha_{A-} d / 2)}{\lambda^2 \alpha_{A-}} + \frac{E_A d}{2 \mathbb{D}_A}}{1 + \frac{\Phi_A(i\omega) \tanh(\alpha_{A-} d / 2)}{\alpha_{A-} i\omega \lambda^2} \left(\frac{i\omega \lambda^2}{\mathbb{D}_A} \right)}$$

$$\alpha_{N-}^2 = \frac{\Lambda_N(i\omega)}{\mathbb{D}_N} + \frac{1}{\lambda^2} = \frac{a(i\omega)}{\mathbb{D}_N} + \frac{1}{\lambda^2} \quad \alpha_{A-}^2 = \frac{\Lambda_A(i\omega)}{\mathbb{D}_A} + \frac{1}{\lambda^2} = \frac{b^q(i\omega)^q}{\mathbb{D}_A} + \frac{1}{\lambda^2}$$

The operator E is

$$E_N = \Lambda_N(i\omega) + \alpha_{N-} \Phi_N(i\omega) \tanh(\alpha_{N-} d / 2) = a(i\omega) + \alpha_{N-} \Phi_N(i\omega) \tanh(\alpha_{N-} d / 2)$$

$$E_A = \Lambda_A(i\omega) + \alpha_{A-} \Phi_A(i\omega) \tanh(\alpha_{A-} d / 2) = b^q(i\omega)^q + \alpha_{A-} \Phi_A(i\omega) \tanh(\alpha_{A-} d / 2)$$



The boundary operator Φ

$$\Phi(i\omega) = \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) (i\omega)^{\bar{q}} e^{i\omega\bar{t}}$$

Take Langmuir kernel $K_m = \kappa e^{-t/\tau}$ **i.e.** $K_m(t-\bar{t}) = \kappa e^{-(t-\bar{t})/\tau}$ **& place it above**
carry out following steps.

$$\begin{aligned} \Phi(i\omega) &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (\kappa e^{-(t-\bar{t})/\tau}) (i\omega)^{\bar{q}} e^{i\omega\bar{t}} \\ &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \int_{-\infty}^t d\bar{t} \kappa e^{-\frac{t-\bar{t}}{\tau} + i\omega\bar{t}} = \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \int_{-\infty}^t d\bar{t} \kappa e^{\bar{t}\left(i\omega + \frac{1}{\tau}\right) - \frac{t}{\tau}} \end{aligned}$$

put $x = \bar{t}\left(i\omega + \frac{1}{\tau}\right) - \frac{t}{\tau}$ $\frac{dx}{d\bar{t}} = \left(i\omega + \frac{1}{\tau}\right)$ $d\bar{t} = \frac{dx}{\left(i\omega + \frac{1}{\tau}\right)}$ **to get the operator as following**

$$\begin{aligned} \Phi(i\omega) &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \int_{-\infty}^{i\omega t} dx \frac{\kappa e^x}{\left(i\omega + \frac{1}{\tau}\right)} \\ &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \frac{\kappa}{\left(i\omega + \frac{1}{\tau}\right)} e^x \Big|_{x=-\infty}^{x=i\omega t} = \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \frac{\kappa e^{i\omega t}}{\left(i\omega + \frac{1}{\tau}\right)} \\ &= \pm \kappa \tau \left(\frac{1}{1 + i\omega \tau} \right) \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \end{aligned}$$



The boundary operator Φ for normal & anomalous cases

$$\Phi(i\omega) = \pm \kappa \tau \left(\frac{1}{1 + i\omega \tau} \right) \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}}$$

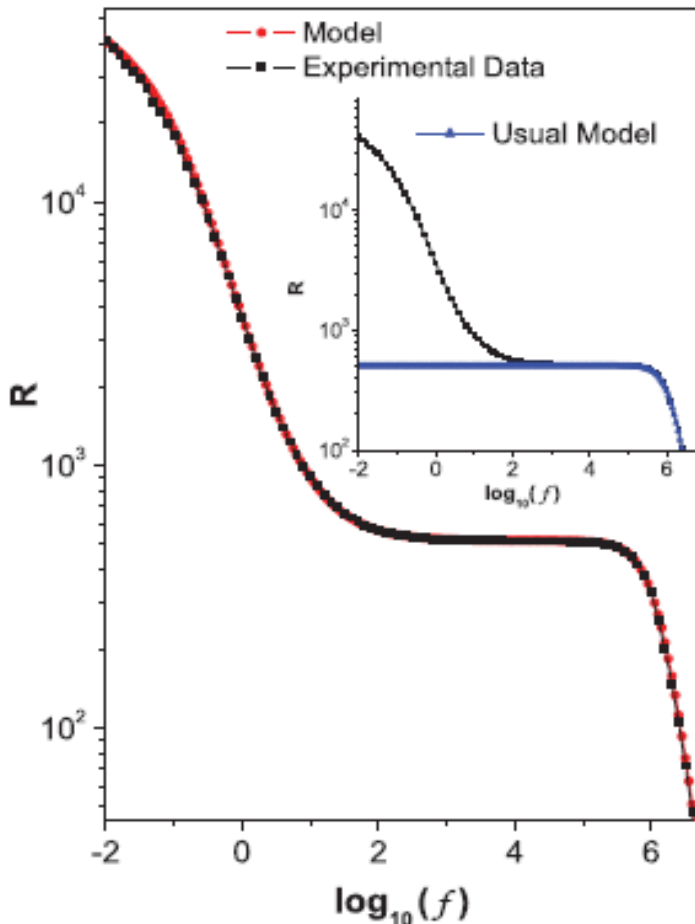
For normal case the order distribution function $\bar{k}(\bar{q}) = m \delta(\bar{q} - 1)$ with Langmuir kernel as $K_{mN} = \kappa_N e^{-t/\tau_N}$

$$\Phi_N(i\omega) = \pm \kappa_N \tau_N \left(m \frac{i\omega}{1 + i\omega \tau_N} \right)$$

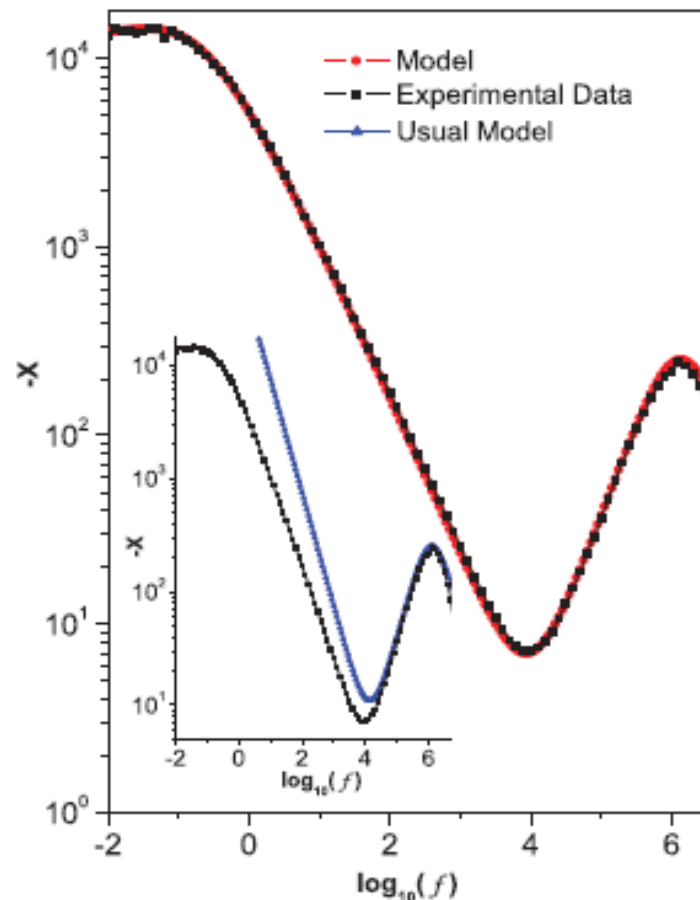
For anomalous case the order distribution function $\bar{k}(\bar{q}) = n \delta(\bar{q} - 1)$ $0 < \bar{q} < 1$ and Langmuir relaxation kernel as $K_{mA} = \kappa_A e^{-t/\tau_A}$

$$\Phi_A(i\omega) = \pm \kappa_{\bar{q}} \tau_{\bar{q}} \left(n \frac{(i\omega)^{\bar{q}}}{1 + i\omega \tau_{\bar{q}}} \right)$$

Experiment data fitted with new phenomenological expressions



Real part of impedance



Imaginary part of impedance



New phenomenological expressions are

The diffusion-drift:

$$\int_0^1 dq (k(q)) \frac{\partial^q}{\partial t^q} n_\alpha(z, t) = - \frac{\partial}{\partial z} j_\alpha(z, t), \quad q \in (0, 1]$$

$$h: \quad \frac{\partial n_\alpha(z, t)}{\partial t} = - \frac{\partial}{\partial z} j_\alpha(z, t) \quad (1-h) \quad \frac{\partial^q n_\alpha(z, t)}{\partial t^q} = - \frac{\partial}{\partial z} j_\alpha(z, t) \quad q \sim 0.8$$

$$h: \quad j_\alpha(z, t) = -\mathbb{D}_N \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}_N}{k_B T} n_\alpha(z, t) \frac{dV}{dz} \quad (1-h): \quad j_\alpha(z, t) = -\mathbb{D}_A \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}_A}{k_B T} n_\alpha(z, t) \frac{dV}{dz}$$

The boundary adsorption:

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}}; \quad \bar{q} \in (0, 1]$$

$$h: \quad j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \int_{-\infty}^t d\bar{t} \kappa_N e^{-(t-\bar{t})/\tau_N} \frac{\partial n_\alpha(z, \bar{t})}{\partial \bar{t}} \Big|_{z=\pm \frac{d}{2}} \quad (1-h): \quad j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \int_{-\infty}^t d\bar{t} \kappa_A e^{-(t-\bar{t})/\tau_A} \frac{\partial^{\bar{q}} n_\alpha(z, \bar{t})}{\partial \bar{t}^{\bar{q}}} \Big|_{z=\pm \frac{d}{2}}$$

$$\bar{q} \sim 0.6$$

The Poisson equation:

$$\frac{\partial^2}{\partial z^2} V(z, t) = - \frac{q_e}{\epsilon} [n_+(z, t) - n_-(z, t)]$$



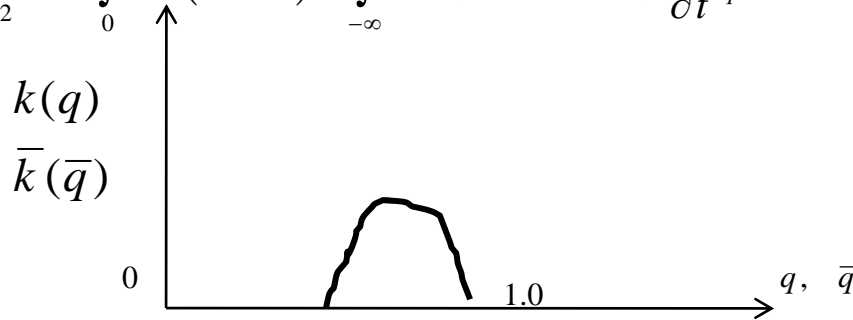
New phenomenological expressions further generalization

Planning for order distribution function, i.e. the fractional order is continuously distributed from one fractional number to one for

$$\int_0^1 d q (k(q)) \frac{\partial^q}{\partial t^q} n_\alpha(z, t) = - \frac{\partial}{\partial z} j_\alpha(z, t), \quad q \in (0, 1]$$

and

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}}; \quad \bar{q} \in (0, 1]$$



and use of power law memory kernel $K_m = t^{-\beta}; \quad 0 < \beta < 1$



Comment

The precise nature and the origin of anchoring and ‘anchoring energy’ at surface due to adsorption in these electrolyte cells of impedance spectroscopy are:

“Still subject of many fundamental and experimental studies and cannot be considered as solved problem”

Giovanni Barbero, Luiz Roberto Evangelista; Adsorption phenomena & anchoring energy in NLC-Taylor & Fransis (2006)



Conclusions

We obtained the anomalous impedance fitted via use of generalized calculus of non-integer order in continuity expression, and in the boundary where adsorption-desorption is taking place.

Apart from normal integer order PNP system, of continuity and drift-diffusion, the non-integer order calculus gives system dynamics with memory, and with non-Markovian assumption.

Therefore the complex dynamics of drift-diffusion and the adsorption-desorption process is the reality happening inside the electrolytic cell in contact with electrode.

The evidence of fractional calculus explaining the impedance spectroscopy of a Super-capacitor is too gaining prominence.

There are few new physical explanation yet to be developed on this new phenomenological expressions as to 'concept of penetration length' at boundary, the 'fractional diffusive lengths' at the bulk, the 'adsorption-desorption lengths'-rather continuous distributions of these parameters instead of single defined one!!

Many more new concepts are on anvil-this is yet to be communicated...

Some links on Fractional Calculus

<http://pdfcast.org/pdf/frontiers-of-mathematics-mathematical-science>

<http://pdfcast.org/pdf/theoretical-techniques-in-disordered-systems>

<http://pdfcast.org/pdf/essence-of-fractional-calculus-in-applied-sciences>

<http://pdfcast.org/pdf/national-work-shop-on-application-of-fractional-calculus-in-engineering>

<http://pdfcast.org/pdf/national-work-shop-on-application-of-fractional-calculus-in-engineering-physical-law-and-solving-ext>

<http://pdfcast.org/pdf/half-and-one-half-derivatives-in-physics>

<http://pdfcast.org/pdf/interdisciplinary-problems-in-non-linear-dynamics-1>

<http://pdfcast.org/pdf/generalized-fractional-calculus-appreciation>

<http://pdfcast.org/pdf/fractional-order-control-system-pi-d-1>

<http://pdfcast.org/pdf/national-work-shop-fractional-calculus-theory-application>

<http://pdfcast.org/pdf/fractional-calculus-and-application-in-engineering>

<http://pdfcast.org/pdf/negative-probability-with-a-half-coin-brownian-motion>

<http://www.dam.brown.edu/International%20Symposium/speakers.htm>

<http://www.springer.com/engineering/computational+intelligence+and+complexity/book/978-3-642-20544-6?detailsPage=reviews>



Thanking you all

I go home and again re-think what

is “ $d f (x) / d x$ ”

is?

as

**Mathematics goes far beyond
our physical understanding!!!**

Nature’s dynamics is in fractional derivative



Annexure-1

Regarding fractional calculus & relaxation dynamics, memory integral, continuous order system etc



Fractional differ-integrations are

...in between one full integration and one full differentiation

...generalization of normal differentiation and integration

...having causal, ${}_{-\infty}D_t^\alpha, {}_0D_t^\alpha$ non-causal structures ${}_tD_\infty^\alpha, {}_tD_b^\alpha$

...having past information contents-thus have memory for causal case, and future in non-causal case.

...having Riemann-Liouville (RL), Caputo types-the most popular ones. These two derivative are related via value of function at the start point. Well if the function value at the start point is zero then RL-Caputo are same; or if the start point of differ-integration is at time immemorial then also these RL-Caputo are same. Else they are different.

...having fractional order initial states for initializing the Laplace of RL-differ-integral; integer order initial states for initializing the Laplace of Caputo type

...having Fractional order Local Derivatives are derived from basic RL derivative -called KG-LFD; useful for getting fractional derivative of non differentiable points, fractional Taylor expansions, fractional differential geometry, fractal study etc.



Fractional integration-antiderivative

Repeated n -fold integration generalization to arbitrary order

$${}_0I_t^1 f(t) = {}_0d_t^{-1} f(t) = \int_0^t f(\tau) d\tau$$

$${}_0I_t^2 f(t) = {}_0d_t^{-2} f(t) = \int_0^t \int_0^t f(\tau) d\tau d\tau = \int_0^t (t - \tau) f(\tau) d\tau$$

$${}_0I_t^3 f(t) = {}_0d_t^{-3} f(t) = \int_0^t \int_0^t \int_0^t f(\tau) d\tau d\tau d\tau = \frac{1}{2} \int_0^t (t - \tau)^2 f(\tau) d\tau$$

$${}_0I_t^n f(t) = {}_0d_t^{-n} f(t) = \underbrace{\int_0^t \int_0^t \dots \int_0^t}_{n \text{ times}} f(\tau) d\tau = \frac{1}{(n-1)!} \int_0^t (t - \tau)^{n-1} f(\tau) d\tau \quad n \in \mathbb{Z}^+$$

Now replace factorial by Gamma function when n is non-integer

$${}_0d_t^{-\phi} f(t) = {}_0I_t^\phi f(t) = d_t^{-\phi} f(t) = \frac{1}{\Gamma(\phi)} \int_0^t (t - \tau)^{\phi-1} f(\tau) d\tau \quad \phi \in \mathbb{R}^+$$

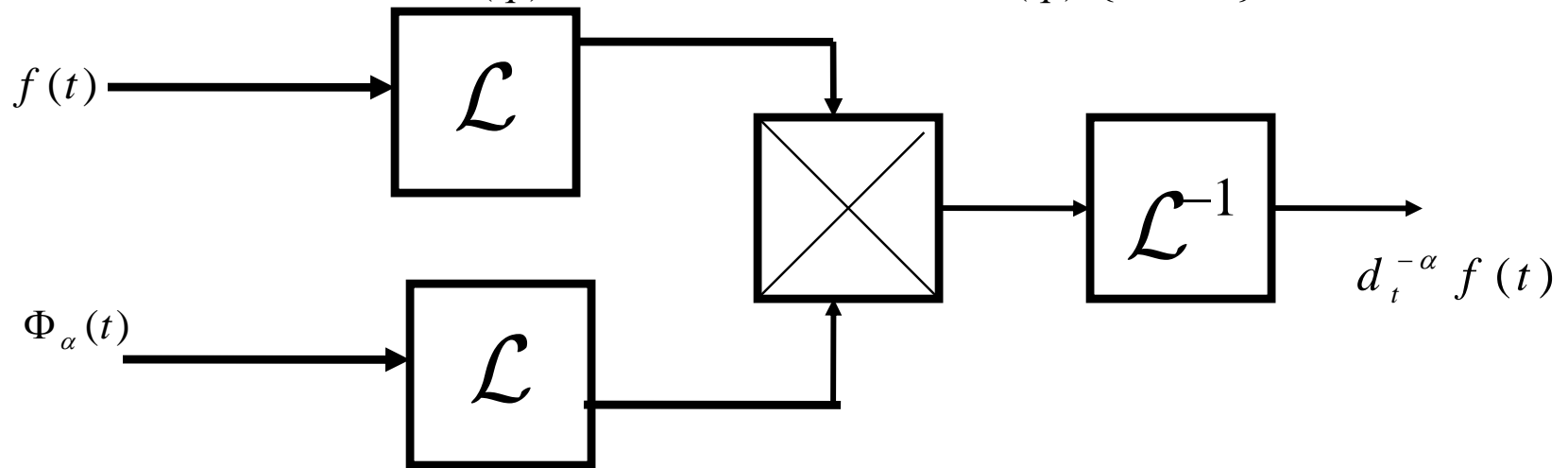
This is Riemann-Liouville fractional integration

Convolution with power function RL fractional integration:

$$d_t^{-\alpha} f(t) = \int_0^t \frac{(t-\tau)^{\alpha-1}}{\Gamma(\alpha)} f(\tau) d\tau = [f(t)] * \left(\frac{t^{\alpha-1}}{\Gamma(\alpha)} \right) = f(t) * \Phi_\alpha(t)$$

$$\Phi_\alpha(t) = \frac{t^{\alpha-1}}{\Gamma(\alpha)}; \mathcal{L}\{t^\mu\} = \frac{\Gamma(\mu+1)}{s^{\mu+1}}; \mathcal{L}\{\Phi_\alpha(t)\} = s^{-\alpha}$$

$$\mathcal{L}\{ {}_0 d_t^{-q} f(t) \} = \frac{1}{\Gamma(q)} \mathcal{L}\{t^{q-1}\} \mathcal{L}\{f(t)\} = \frac{1}{\Gamma(q)} \left\{ \frac{\Gamma(q)}{s^q} \right\} F(s) = s^{-q} F(s)$$





Fractional derivative

A very raw explanation Euler 1735

$$\frac{d^n f(x)}{dx^n} = \underbrace{\frac{d}{dx} \frac{d}{dx} \dots \frac{d}{dx}}_n f(x)$$

$$\frac{d^n}{dx^n} \{x^m\} = m(m-1)(m-2)\dots(m-n+1)x^{m-n}$$

$$\Gamma(m+1) = m(m-1)(m-2)\dots(m-n+1)\Gamma(m-n+1)$$

$$\frac{d^n}{dx^n} \{x^m\} = \frac{\Gamma(m+1)}{\Gamma(m-n+1)} x^{m-n}$$

$$\frac{d^{0.5}}{dx^{0.5}} \{x\} = \frac{\Gamma(1+1)}{\Gamma(1-0.5+1)} x^{1-0.5} = \frac{\sqrt{x}}{\Gamma(1+0.5)} = \frac{\sqrt{x}}{0.5\Gamma(0.5)} = \frac{2\sqrt{x}}{\sqrt{\pi}}$$

$$\frac{d^{0.5}}{dx^{0.5}} \{C\} \neq 0$$

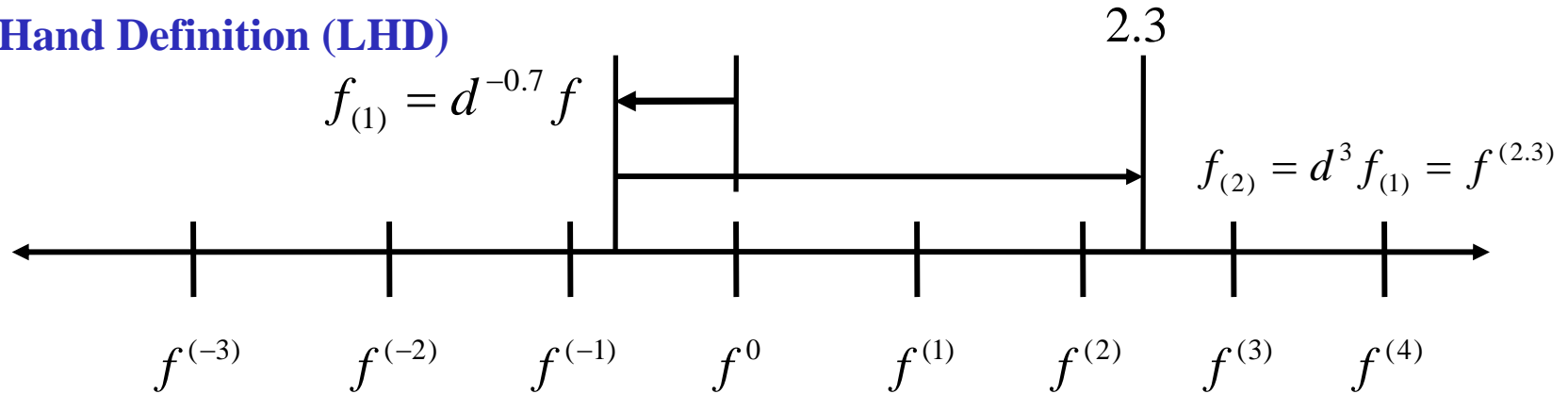
For positive index the process is differentiation

For negative index the process is integration

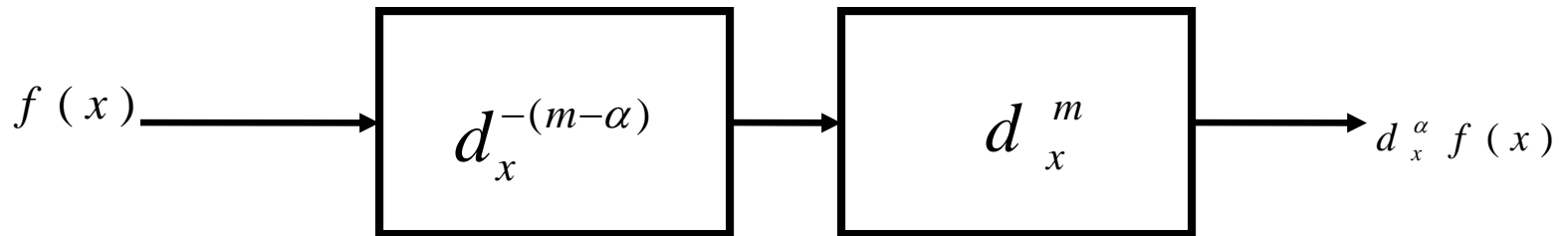
Fractional derivative of a constant is not zero!!

Reimann Liouveli (RL) Fractional derivative

Left Hand Definition (LHD)



Here 'm' is the integer just greater than fractional order of derivative



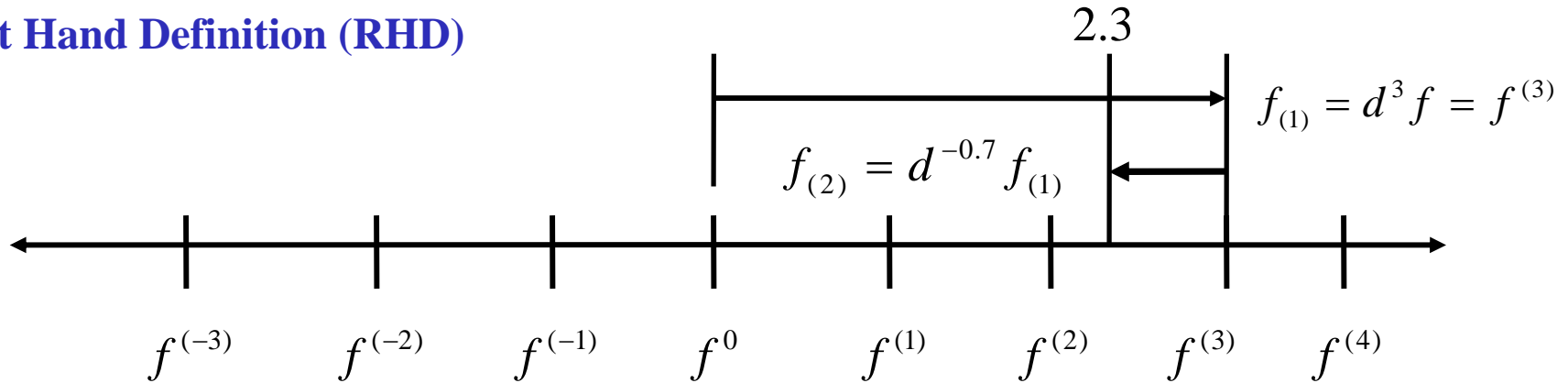
$$d_x^\alpha f(x) = \frac{d^m}{dx^m} \left[\frac{1}{\Gamma(m-\alpha)} \int_0^x (x-\tau)^{-\alpha-1+m} f(\tau) d\tau \right]$$

First do fractional integration then follow it up with integer order differentiation

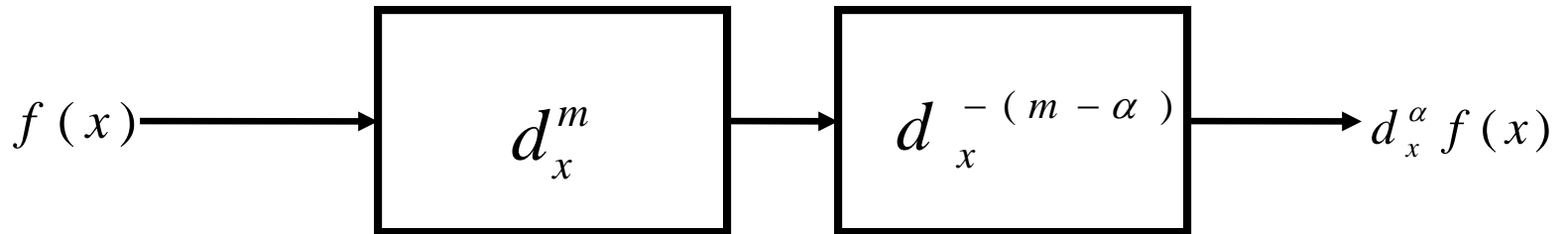


Caputo (1967) Fractional derivative

Right Hand Definition (RHD)



Here 'm' is the integer just greater than the fractional order derivative



$$d_x^\alpha f(x) = \left[\frac{1}{\Gamma(m-\alpha)} \int_0^x (x-\tau)^{-\alpha-1+m} \frac{d^m f(\tau)}{d\tau^m} d\tau \right]$$



First do integer order differentiation then follow it up with fractional order integration

Fractional Integration of exponential function & origin of Miller-Ross function & higher trigonometric functions:



$$f(t) = e^{at}$$

$$D^{-\nu} e^{at} = \frac{1}{\Gamma(\nu)} \int_0^t (t - \xi)^{\nu-1} e^{a\xi} d\xi$$

$$x = t - \xi$$

$$D^{-\nu} e^{at} = \frac{e^{at}}{\Gamma(\nu)} \int_0^t x^{\nu-1} e^{-ax} dx$$

Above is not elementary function, but is closely related to incomplete Gamma function

$$\gamma^*(\nu, t) = \frac{1}{t^\nu \Gamma(\nu)} \int_0^t \xi^{\nu-1} e^{-\xi} d\xi$$

$$D^{-\nu} e^{at} = t^\nu e^{at} \gamma^*(\nu, at) = E_t(\nu, a) \quad \text{Miller-Ross function}$$

Similarly the following are higher cosine and sine functions

$$D^{-\nu} \cos at = \frac{1}{\Gamma(\nu)} \int_0^t \xi^{\nu-1} \cos a(t - \xi) d\xi = C_t(\nu, a)$$

$$D^{-\nu} \sin at = \frac{1}{\Gamma(\nu)} \int_0^t \xi^{\nu-1} \sin a(t - \xi) d\xi = S_t(\nu, a)$$

Fractional differentiation of exponential Miller-Ross & trigonometric functions



$$f(t) = e^{at}$$

$$D^\mu e^{at} = D^m [D^{-\nu} e^{at}]; \mu = m - \nu$$

$$D^{-\nu} e^{at} = E_t(\nu, a)$$

$$D^m E_t(\nu, a) = E_t(\nu - m, a) = E_t(-\mu, a)$$

$$D^\mu e^{at} = E_t(-\mu, a)$$

Similarly, one can have $D^\mu \cos at = C_t(-\mu, a)$

$$D^\mu \sin at = S_t(-\mu, a)$$

$$f(t) = E_t(\lambda, a)$$

$$D^\mu E_t(\lambda, a) = D^m [D^{-\nu} E_t(\lambda, a)]; \mu = m - \nu$$

$$D^{-\nu} E_t(\lambda, a) = E_t(\lambda + \nu, a)$$

$$D^\mu E_t(\lambda, a) = E_t(\lambda - \mu, a)$$

Similarly, one can have

$$D^\mu C_t(\lambda, a) = C_t(\lambda - \mu, a)$$

$$D^\mu S_t(\lambda, a) = S_t(\lambda - \mu, a)$$

Table of fractional derivatives with lower terminal at zero of some functions

$${}_0d_t^q \{f(t)\}$$

Function $f(t)$	${}_0D_t^\alpha f(t)$. Fractional derivative
$H(t)$	$\frac{t^{-\alpha}}{\Gamma(1-\alpha)}$
$H(t-a)$	$\begin{cases} \frac{(t-a)^{-\alpha}}{\Gamma(1-\alpha)}, (t > a) \\ 0, (0 \leq t \leq a) \end{cases}$
$H(t-a)f(t)$	$\begin{cases} {}_aD_t^\alpha f(t), (t > a) \\ 0, (0 \leq t \leq a) \end{cases}$
$\delta(t)$	$\frac{t^{-\alpha-1}}{\Gamma(-\alpha)}$
$\delta^{(n)}(t)$	$\frac{t^{-\alpha-n-1}}{\Gamma(-\alpha-n)}$
$\delta^{(n)}(t-a)$	$\begin{cases} \frac{(t-a)^{-\alpha-n-1}}{\Gamma(-n-\alpha)}, (t > a) \\ 0, (0 \leq t \leq a) \end{cases}$
t^v	$\frac{\Gamma(v+1)}{\Gamma(v+1-\alpha)} t^{v+\alpha} \quad v > -1$
$e^{\lambda t}$	$t^{-\alpha} E_{1,1-\alpha}(\lambda t) = E_t(-\alpha, \lambda)$
$\cosh(\sqrt{\lambda t})$	$t^{-\alpha} E_{2,1-\alpha}(\lambda t^2)$
$\frac{\sinh(\sqrt{\lambda t})}{\sqrt{\lambda t}}$	$t^{1-\alpha} E_{2,2-\alpha}(\lambda t^2)$
$\ln(t)$	$\frac{t^{-\alpha}}{\Gamma(1-\alpha)} (\ln(t) + \psi(1) - \psi(1-\alpha))$
$t^{\beta-1} \ln(t)$	$\frac{\Gamma(\beta) t^{\beta-\alpha-1}}{\Gamma(\beta-\alpha)} (\ln(t) + \psi(\beta) - \psi(\beta-\alpha))$
$t^{\beta-1} E_{\mu,\beta}(\lambda t^\mu)$	$t^{\beta-\alpha-1} E_{\mu,\beta-\alpha}(\lambda t^\mu)$

Table of fractional derivatives with lower terminal at minus infinity of some functions

$${}_{-\infty}d_t^q \{f(t)\}$$

Table-2

RL derivative with lower terminal at $-\infty$ i.e. ${}_{-\infty}D_t^\alpha f(t)$,

Function $f(t)$	${}_{-\infty}D_t^\alpha f(t)$ Derivative
$H(t-a)$	$\begin{cases} \frac{(t-a)^{-\alpha}}{\Gamma(1-\alpha)}, (t > a) \\ 0, (t \leq a) \end{cases}$
$H(t-a)f(t)$	$\begin{cases} {}_aD_t^\alpha f(t), (t > a) \\ 0, (t \leq a) \end{cases}$
$e^{\lambda t}$	$\lambda^\alpha e^{\lambda t}$
$e^{\lambda t + \mu t}$	$\lambda^\alpha e^{\lambda t + \mu t}$
$\sin \lambda t$	$\lambda^\alpha \sin\left(\lambda t + \frac{\pi\alpha}{2}\right)$
$\cos \lambda t$	$\lambda^\alpha \cos\left(\lambda t + \frac{\pi\alpha}{2}\right)$
$e^{\lambda t} \sin \mu t$	$r^\alpha e^{\lambda t} \sin(\mu t + \alpha\varphi)$ $r = \sqrt{\lambda^2 + \mu^2} \quad \tan \varphi = \frac{\mu}{\lambda} \quad (\lambda, \mu > 0)$
$e^{\lambda t} \cos \mu t$	$r^\alpha e^{\lambda t} \cos(\mu t + \alpha\varphi)$ $r = \sqrt{\lambda^2 + \mu^2} \quad \tan \varphi = \frac{\mu}{\lambda} \quad (\lambda, \mu > 0)$



Some important functions relating to fractional calculus and their Laplace

Function	Time Expression $f(t)$	Laplace Transform $F(s)$
Mittag-Leffler	$E_q(at^q) = \sum_{n=0}^{\infty} \frac{a^n t^{nq}}{\Gamma(nq+1)}$	$\frac{s^q}{s(s^q - a)}$
Agarwal	$E_{\alpha,\beta}(t^\alpha) = \sum_{n=0}^{\infty} \frac{t^{\left(n+\frac{\beta-1}{\alpha}\right)\alpha}}{\Gamma(\alpha n + \beta)}$	$\frac{s^{\alpha-\beta}}{s^\alpha - 1}$
Erdelyi	$E_{\alpha,\beta}(t) = \sum_{n=0}^{\infty} \frac{t^n}{\Gamma(\alpha n + \beta)}$	$\sum_{n=0}^{\infty} \frac{\Gamma(m+1)}{\Gamma(\alpha m + \beta) s^{\alpha m+1}}$
Robotnov-Hartley	$F_q(a, t) = \sum_{n=0}^{\infty} \frac{a^n t^{(n+1)q-1}}{\Gamma(\{n+1\}q)}$	$\frac{1}{s^q - a}$
Miller-Ross	$E_t(v, a) = \sum_{k=0}^{\infty} \frac{a^k t^{k+v}}{\Gamma(v+k+1)}$	$\frac{s^{-v}}{s - a}$
Generalized Cosine	$C_t(v, a) = t^v \sum_{k=even}^{\infty} \frac{(-1)^{k/2} (at)^k}{\Gamma(v+k+1)}$	$\frac{s}{s^v(s^2 + a^2)}$, $\Re(v) > -1$
Generalized Sine	$S_t(v, a) = t^v \sum_{k=odd}^{\infty} \frac{(-1)^{\frac{k-1}{2}} (at)^k}{\Gamma(v+k+1)}$	$\frac{a}{s^v(s^2 + a^2)}$, $\Re(v) > -2$
Generalized R	$R_{q,v}(a, t) = \sum_{n=0}^{\infty} \frac{a^n t^{(n+1)q-1-v}}{\Gamma(\{n+1\}q - v)}$	$\frac{s^v}{s^q - a}$
Generalized G	$G_{q,v,r}(at) = \sum_{j=0}^{\infty} \frac{\{(-r)(-1-r)\dots(1-j-r)\}(-a)^j t^{(r+j)q-v-1}}{\Gamma(1+j)\Gamma(\{r+j\}q - v)}$	$\frac{s^v}{(s^q - a)^r}$



The fundamental theorem – is the relation between RL & Caputo!!

$$f(x) = f(a) + \int_a^x f'(t) dt$$

$$x \in [a, b] \quad f'(x) \in AC[a, b]$$

$$f(x) = D_x(I_x f(x)) = f(a) + \int_a^x f'(t) dt$$

$$f(x) = D(I_x f(x)) = f(a) + I(Df(x))$$

$$f(x) = D_x^n(I_x^n f(x)) = \sum_{k=0}^{n-1} \frac{f^{(k)}(a)}{k!} (x-a)^k + \frac{1}{(n-1)!} \int_a^x (x-t)^{n-1} f^{(n)}(t) dt$$

$$f(x) = D^n I^n f(x) = \sum_{k=0}^{n-1} \frac{f^{(k)}(a)}{\Gamma(k+1)} (x-a)^k + \frac{1}{\Gamma(n)} \int_a^x (x-t)^{n-1} f^{(n)}(t) dt$$

**Differentiation of integration is-constant(s) at start point plus integration of differentiation
This is also RL, Caputo fractional derivative; a very important generalization.**

$$D^n I^{n-\alpha} f(x) = \sum_{k=0}^{n-1} \frac{f^{(k)}(a)}{\Gamma(k+1-\alpha)} (x-a)^{k-\alpha} + \frac{1}{\Gamma(n-\alpha)} \int_a^x (x-t)^{n-\alpha-1} f^{(n)}(t) dt$$

$$D_x^\alpha f(x) = \sum_{k=0}^{n-1} \frac{f^{(k)}(a)}{\Gamma(k+1-\alpha)} (x-a)^{k-\alpha} + {}^C D_x^\alpha f(x)$$

$$0 < \alpha < 1 \quad D_x^\alpha f(x) = \frac{f(a)}{\Gamma(1-\alpha)} (x-a)^{-\alpha} + {}^C D_x^\alpha f(x)$$



Reviewing relaxation

Standard Maxwell Debye relaxation is

$$\tau \frac{d}{dt} \Phi(t) = -\Phi(t)$$

$$t > 0 ; \Phi(0) = \Phi_0$$

$$\Phi(t) = \Phi_0 e^{-t/\tau}$$

Gives pure exponential solution with single relaxation time constant

$$\Phi(t) - \Phi_0 = -\frac{1}{\tau} \frac{d^{-1}}{dt^{-1}} \Phi(t)$$

Also the Integral representation of Maxwell-Debye relaxation is:

$$\Phi(t) - \Phi_0 = -\frac{1}{\tau} \frac{d^{-1}}{dt^{-1}} \Phi(t)$$

The integral equation can be formally extended to Fractional Integral equation by replacing $\frac{1}{\tau} \frac{d^{-1}}{dt^{-1}}$ which leads to

$$\frac{1}{\tau} \frac{d^{-1}}{dt^{-1}} \rightarrow \frac{1}{\tau^\beta} \frac{d^{-\beta}}{dt^{-\beta}}$$

$$\Phi(t) - \Phi_0 = -\frac{1}{\tau^\beta} {}_0 D_t^{-\beta} \Phi(t)$$



Non Debye non-exponential relaxation process

Kohlraush Williams Watts (KWW) relaxation law:

$$\Phi(t) = \Phi_0 e^{\left\{ \left(-t/\tau \right)^\alpha \right\}}$$

Nutting Power Law relaxation:

$$\Phi(t) = \Phi_0 \left(1 + \frac{t}{\tau} \right)^{-n} ; 0 < n < 1$$

Observed in:

Dielectric relaxation, Stress Relaxation, Strain relaxation, NMR relaxation

Diffusion controlled relaxation, electrical circuits,.....; unlike normal relaxation

$$\Phi(t) = \Phi_0 e^{-t/\tau}$$



Memory vis-à-vis fractional calculus

1. **Non-exponential relaxation implies MEMORY i.e. the underlying fundamental relaxation process are NON-MARKOVIAN**
2. **Natural way to incorporate memory effect is fractional calculus via the involved Convolution integral in time (space). The present state is being influenced by all the states, the system has been running through at the times $t' = 0, 1, \dots, t$**
3. **The power-law Kernel defines the fractional expression represents a particular long memory.**

Fractional Integration is

$${}_0 D_t^{-\beta} f(t) = \frac{1}{\Gamma(\beta)} \int_0^t (t - \tau)^{\beta-1} f(\tau) d\tau = P_\beta(t) * f(t)$$

$$P_\beta(t) = \frac{t^{\beta-1}}{\Gamma(\beta)} \quad P_{\beta \rightarrow 1}(t) = H(t) \quad P_{\beta \rightarrow 0}(t) = \delta(t)$$



Memory integrals

$$\frac{d\Phi(t)}{dt} = - \int_0^t K(t-\tau)\Phi(\tau)d\tau = -K(t) * \Phi(t)$$

Represents Memory Integral i.e. all instances for $\tau = 0$ to $\tau = t$ contribute to situation at $\tau = t$

1. Memory breaks down i.e. Markovian Case:

$$K(t) = K_0\delta(t)$$

$$\frac{d}{dt}\Phi(t) = - \int_0^t K_0\delta(t-\tau)\Phi(\tau)d\tau = -K_0\Phi(t)$$

$$\Phi(t) = \Phi_0 \exp\{-K_0 t\}$$

$$\frac{d\Phi(t)}{dt} = - \frac{\Phi(t)}{t} = -K(t) * \Phi(t)$$

2. The opposite case Constant Memory i.e. leading to oscillatory case

$$K(t) = K_0$$

$$\frac{d^2}{dt^2}\Phi(t) = -K_0\Phi(t)$$

$$\Phi(t) = \Phi_0 \cos(\sqrt{K_0}t)$$



Slowly varying memory

3. Slowly varying Kernel which for small time behaves as power law gives KWW relaxation process

$$K(t) \approx K_0 t^\gamma \quad \Phi(t) = \Phi_0 \exp \left\{ -K_0 t^{\gamma+2} \right\}$$

4. Relaxation for Fractional Differential/Integral equation & its Memory Kernel

$$K(t) = K_0 t^{q-2}; 0 < q \leq 2$$

$$\frac{d}{dt} \Phi(t) = -\frac{1}{\tau^q} \left[{}_0 D_t^{1-q} \Phi(t) \right]; \quad \tau^q = [K_0 \Gamma(q-1)]^{-1}$$

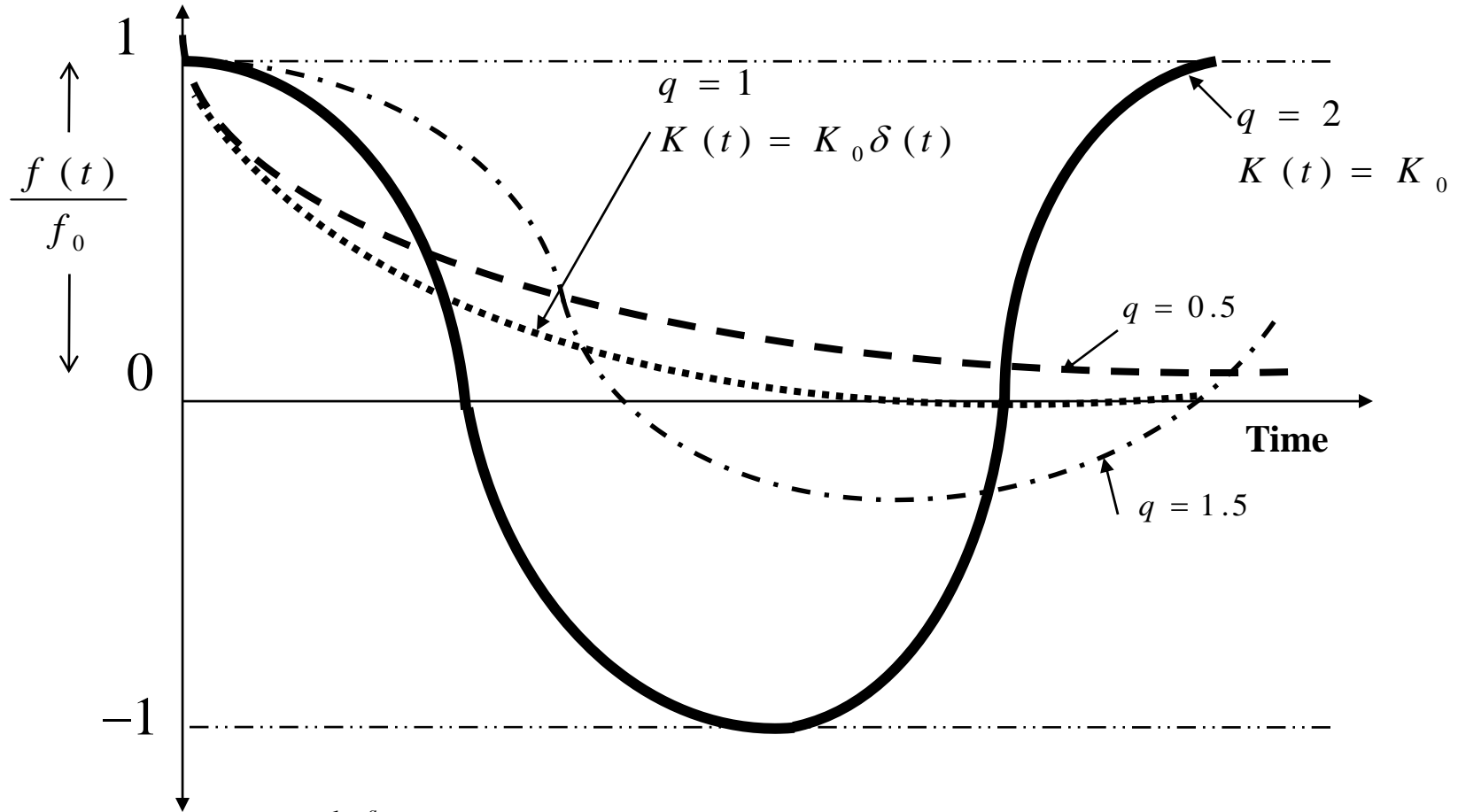
Apply ${}_0 D_t^{-1}$ on both sides to get: $\Phi(t) - \Phi_0 = -\tau^{-q} {}_0 D_t^{-q} \Phi(t)$

Apply ${}_0 D_t^q$ on both sides to get FDE

$${}_0 D_t^q \Phi(t) - \Phi_0 \frac{t^{-q}}{\Gamma(1-q)} = -\tau^{-q} \Phi(t)$$

Using Fractional Derivative of constant C as , non zero, that is $C t^{-q} / \Gamma(1-q)$ we get this

Memory Kernel & Fractional Differential Equation (FDE)



$$\frac{d^q}{d t^q} f(t) + \tau^{-q} f(t) = 0 ; \quad q \in \mathbb{R}^+$$

$$1 \leq q \leq 2$$

$$f(0) = f_0$$



Does 'd / dt' represent accumulation or loss always ?

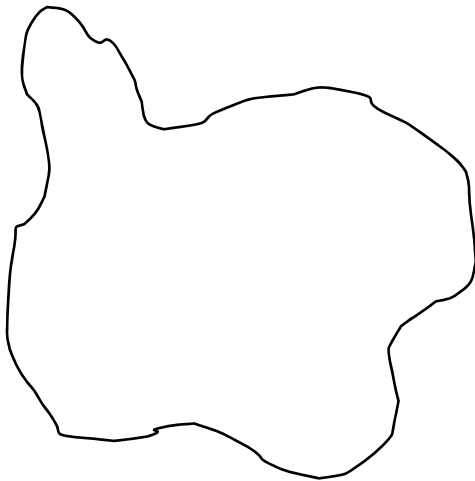
Well if there are temporary traps then?

Well if the boundary is partly reflecting?

Well if the elementary element (area, volume etc) be not a point quantity?

Well if mass of ball is not a point quantity?

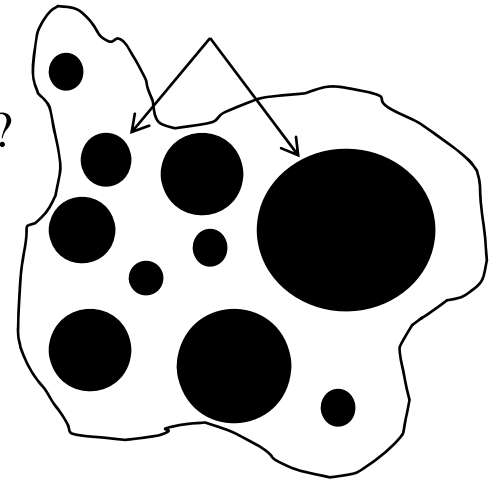
Well if spring is not mass-less?



$$\frac{d}{dt} \langle \phi \rangle = \text{GAIN} - \text{LOSS}?$$

$$\frac{d}{dt} \langle \phi \rangle = \text{GAIN} - \text{LOSS}?$$

Traps or Island (Forbidden zone)



Some are entraps temporarily indicating slow rate of change than d / dt

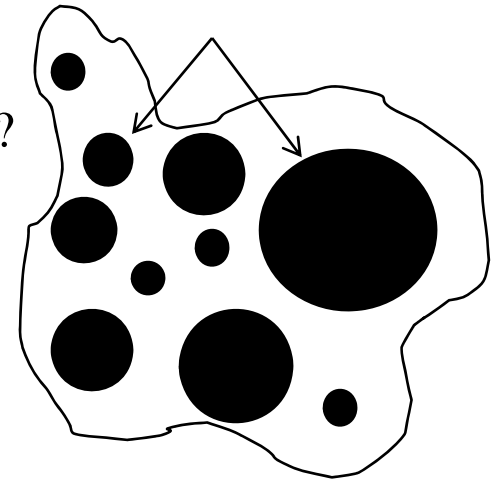
The particles cannot have the island paths indicating fast rate of change than d / dt



Spatial disorder heterogeneity giving fractional temporal derivative?

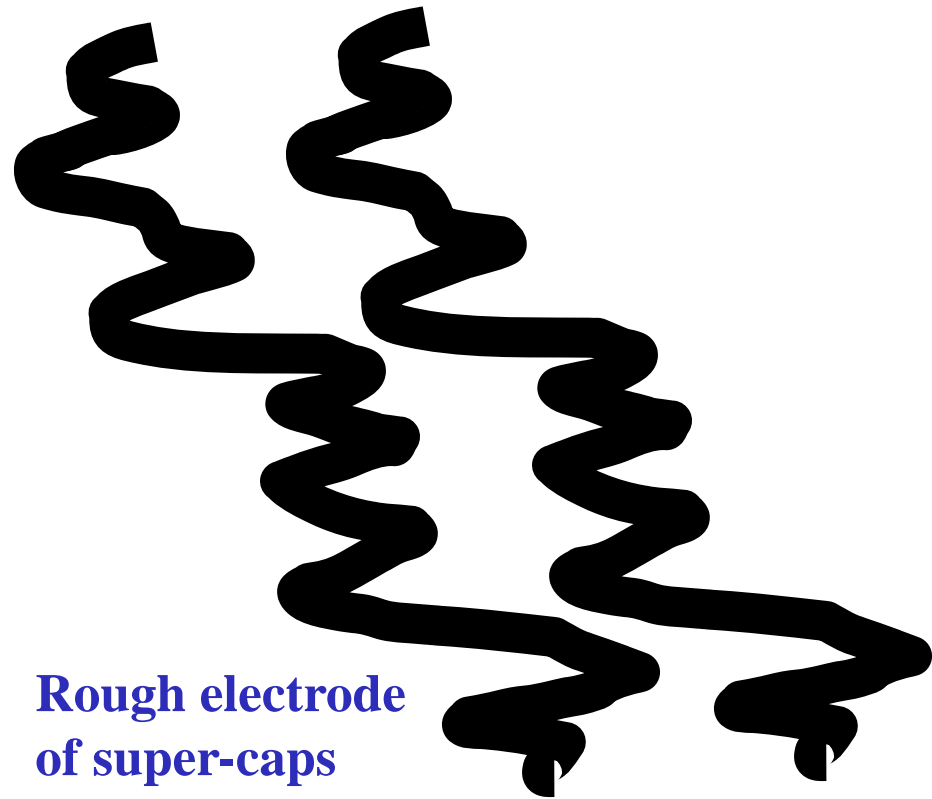
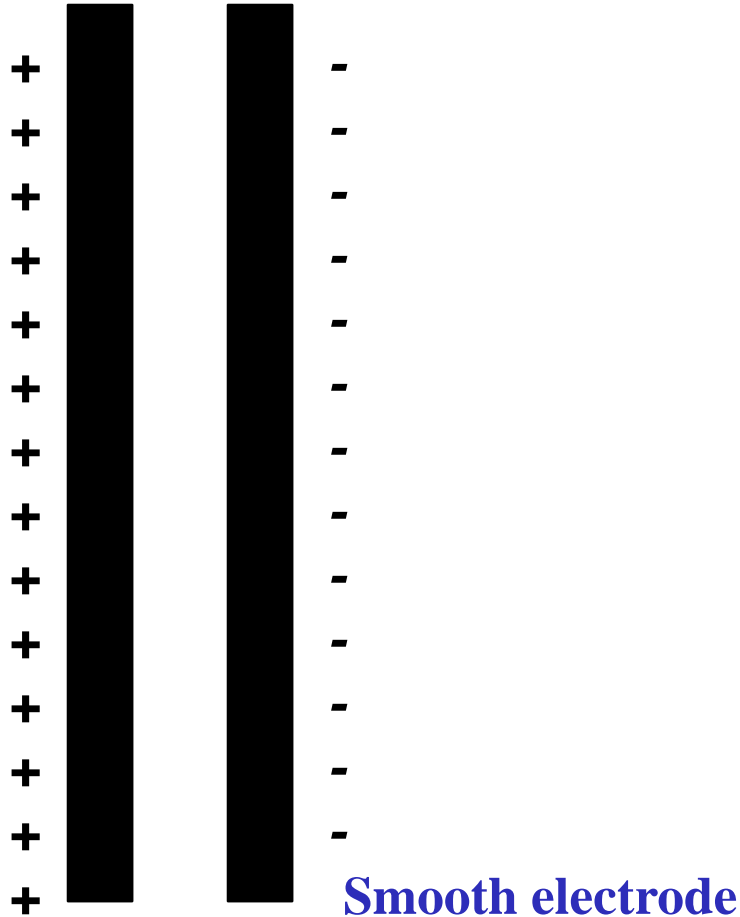
$$\frac{d}{dt}{}^{\alpha} \langle \phi \rangle = \text{GAIN} - \text{LOSS?}$$

Traps or Island (Forbidden zone)



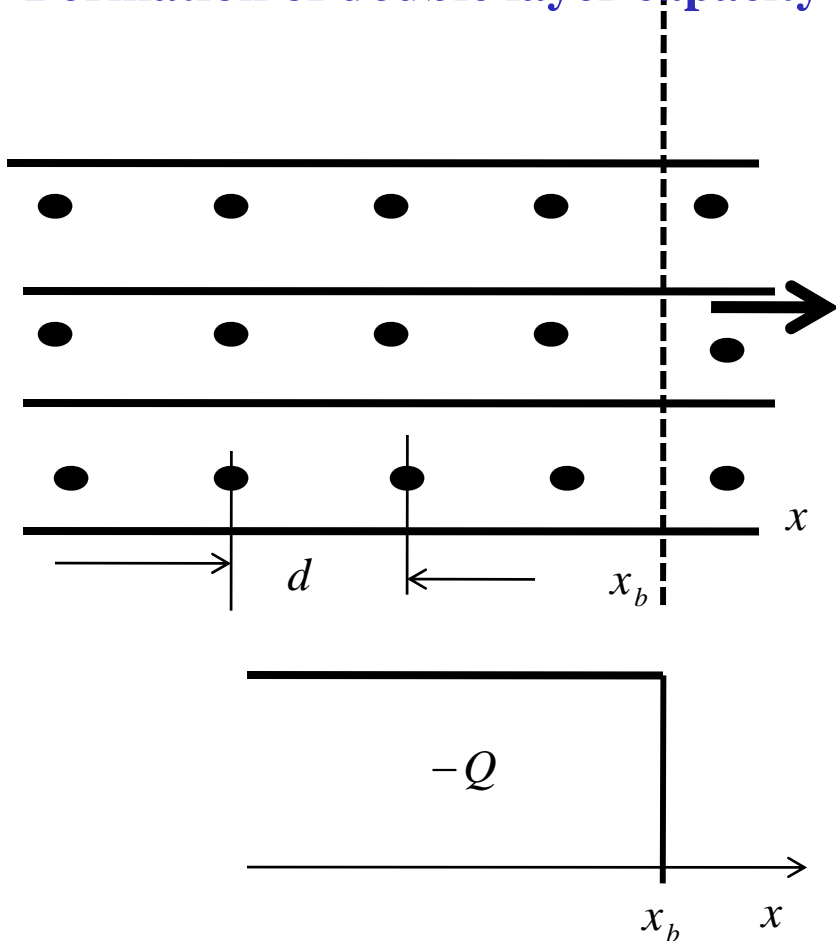
It is indeed true....

We take example of super-capacitor electrode is rough



Charge distribution at cleavage of electrode crystal

Formation of double layer capacity



Electrode material we consider as simple case made of positive nuclei on fixed 'regular' grid points inside a sea of homogeneous distribution of negative charge. By cleaving the electrode one obtains two halves which can be considered as electrodes; the cleaving is at x_b location, as depicted. Let us assume that cleavage has made interface of metal (electrode) and organic (electrolyte), and immediate picture of negative charge sea.

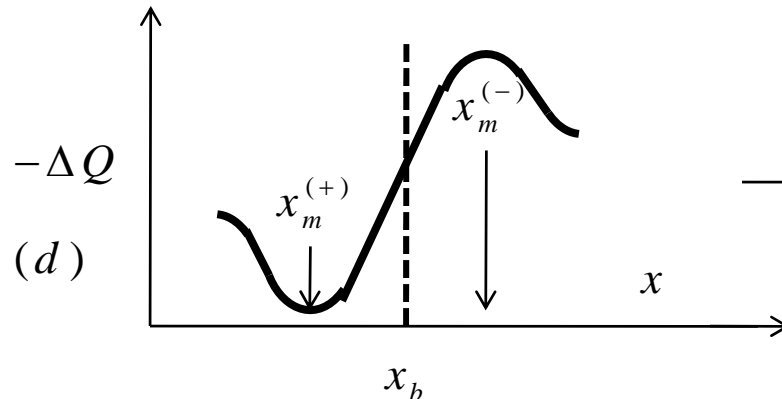
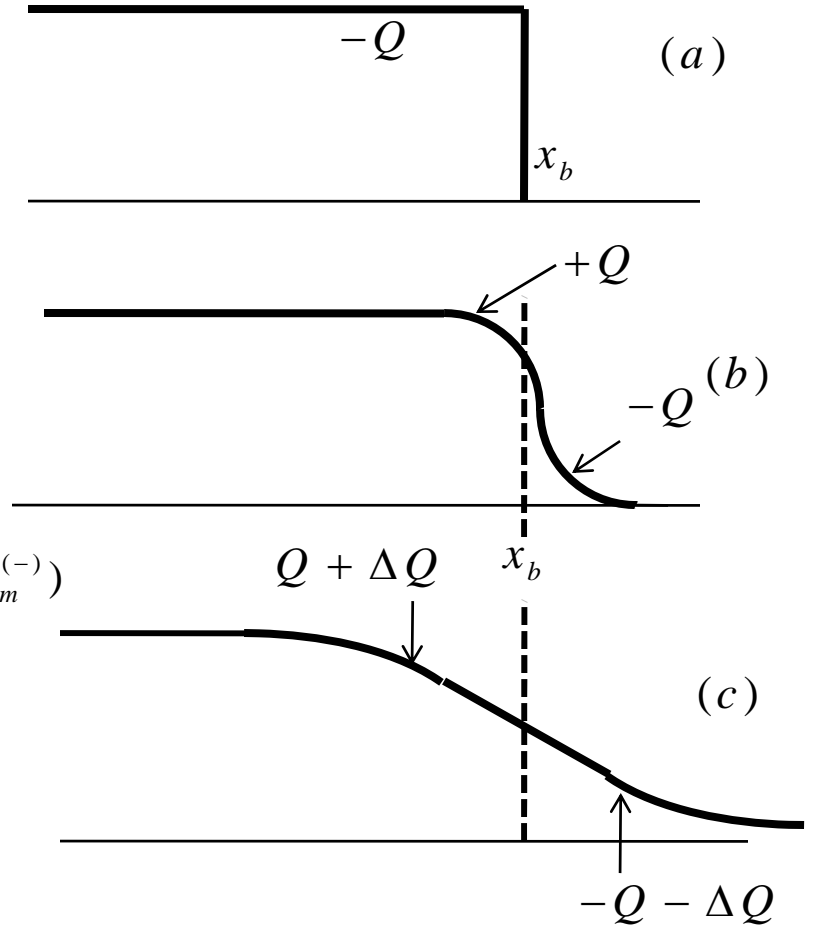
Double layer capacity

This special charge separation forms
 “capacity”; the metal-electrolyte
 capacity-and formation of double layer
 capacity C_m

$$x_m^{(+)} = \frac{\int_{-\infty}^{x_b} [\Delta Q(x)](x_b - x) dx}{\int_{-\infty}^{x_b} \Delta Q(x) dx}$$

$$x_m^{(-)} = \frac{\int_{x_b}^{\infty} [\Delta Q(x)](x - x_b) dx}{\int_{x_b}^{\infty} \Delta Q(x) dx}$$

$$C_m = \frac{1}{4\pi} (x_m^{(+)} - x_m^{(-)})$$



**Electric field
 Perpendicular to electrode**

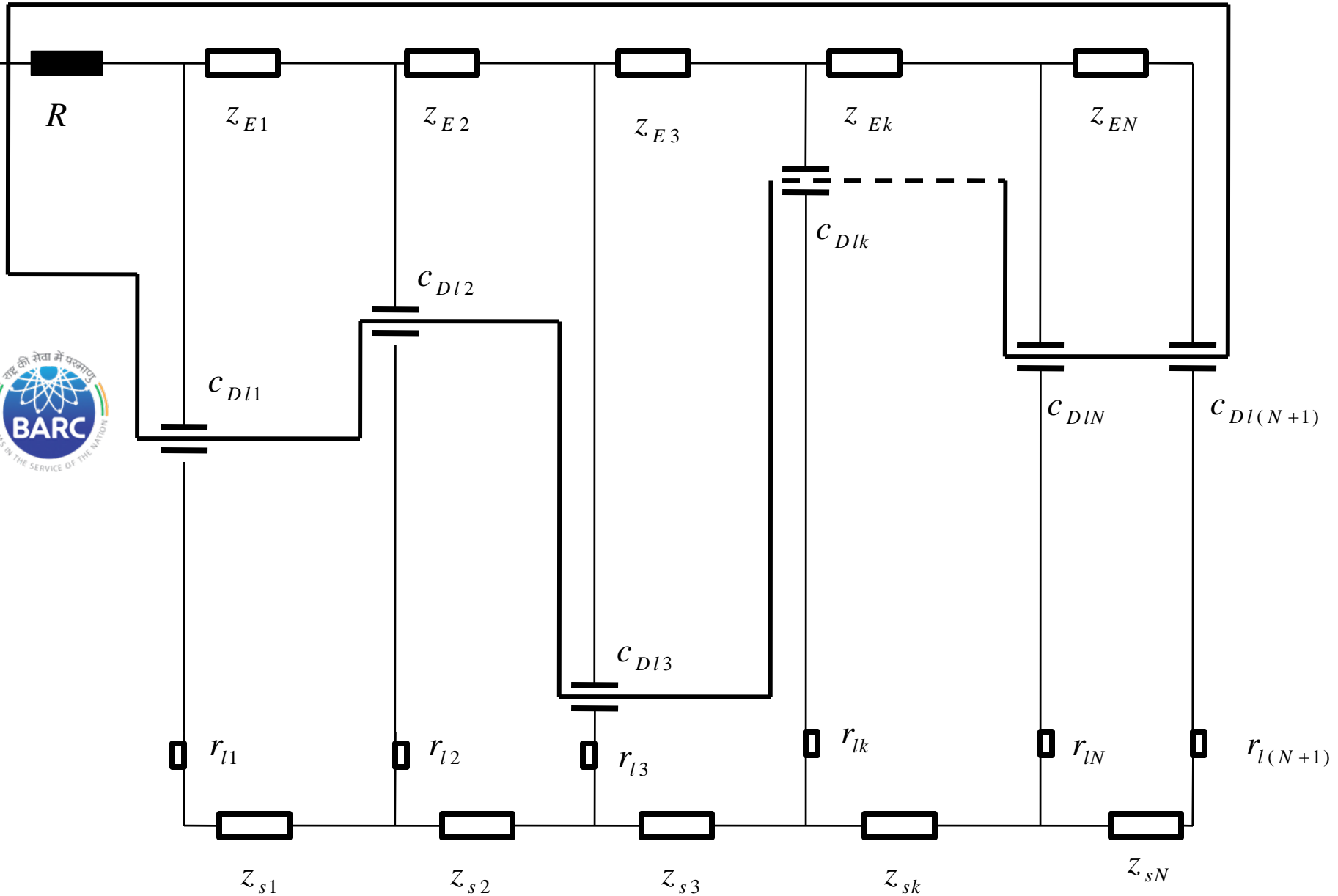


Disordered system

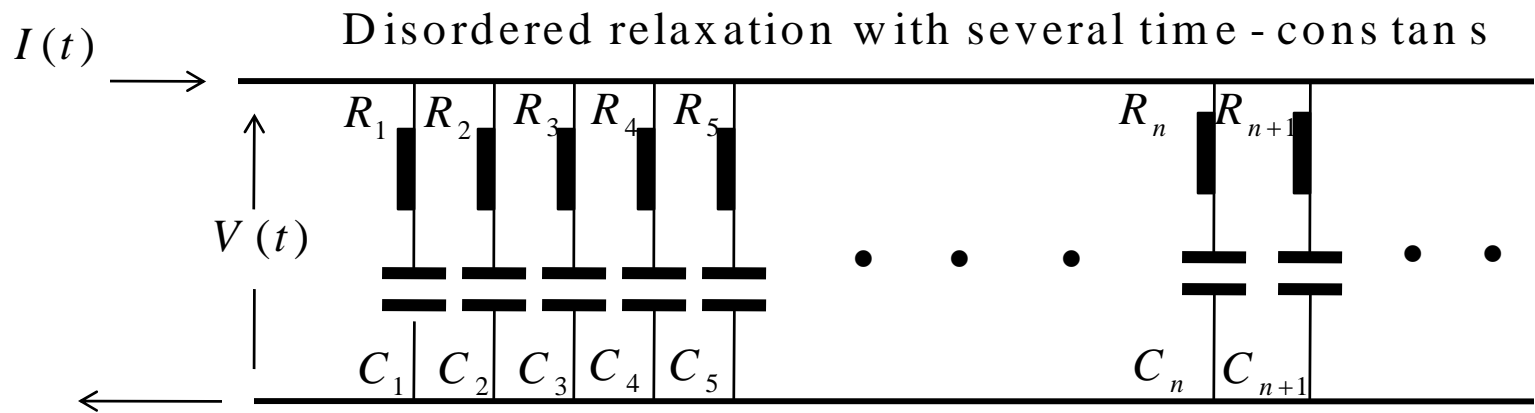
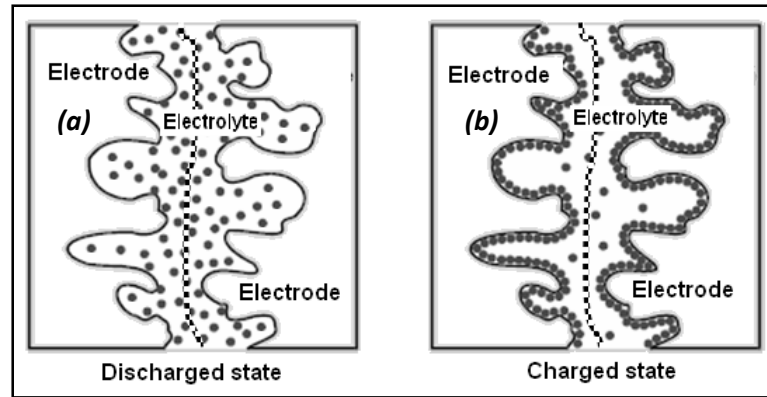
The distribution function is different for different cleavage. Some cleavage may be symmetrical, as ideal as shown some may have different nuclei distribution near cleavage, with different numbers as per crystal face cleavage of electrode. This distribution thus gives rise to several time-constant system, better described by fractional calculus, with unique disorder parameter .

Now if the above obtained capacity is same, assuming electrode surface is uniformly smooth, then we do not have problem to model; the capacitor system. However, due to rough nature the charge distribution function at each of the cleavage is different- the distribution does not and need not be a normal, Gaussian type. This fractal charge distribution can lead to a capacity of 'rough' electrode other than normal or Gaussian distribution-leading to power law distribution too! This is 'disordered' system.

Rough electrode circuitual representation of super-capacitor



Rough electrode carbon - aerogel



Fractional differential equation for rough electrodes

$$I(t) = K \frac{d^\gamma}{dt^\gamma} V(t)$$

Impedance of rough electrode

$$Z(s) = \frac{1}{Ks^\gamma}; \quad 0 < \gamma < 1$$



A several time-constant system-with no average-a disordered system

Consider a partial differential equation (PDE)

$$\frac{\partial}{\partial t} u(\lambda, t) + (\lambda)^{1/\alpha} u(\lambda, t) = \delta(t) \quad \alpha > 0$$

The above PDE is having free parameter λ

Now if for the free parameter $\alpha = 1$ then we have single time constant system $\lambda = \tau^{-1}$

with solution as $u(\lambda, t) = \exp(-\lambda t)$ with initial condition $u(\lambda, 0) = 1$

The several time constants (discharge rate) is taken as power law distribution as $(\lambda)^q$

$$q = 1 / \alpha \quad 0 < \alpha < 1$$

The strong-discharge or exponential discharge with one time constant follow a normal distribution with well defined average that represents average time constant or discharge rate, and that normal distribution has well defined standard deviation. Unlike the normal distribution the 'power-law' distribution has no defined average or moments (standard deviation); and is representation of system which has variety. The heterogeneity or the disordered system thus has varieties of ways by which dissipation mechanism takes place.



“Impulse response function” to “Impulse response” input-for disordered system

$$\frac{\partial}{\partial t} u(\lambda, t) + (\lambda)^{1/\alpha} u(\lambda, t) = \delta(t)$$

$$u(\lambda, t) = h(\lambda, t) = \exp\left(-\lambda^{1/\alpha} t\right)$$

$h(\lambda, t)$ denotes ‘impulse response function’. On integrating this ‘impulse response function’ for free variable we get the function of time and that is called ‘impulse response’ Green’s function

$$g(t) = \int_0^{\infty} h(\lambda, t) d\lambda = \int_0^{\infty} \exp\left(-\lambda^{1/\alpha} t\right) d\lambda = \frac{\Gamma(1 + \alpha)}{t^\alpha}$$

To get above substitute $\lambda^{1/\alpha} = x$ $\lambda = (x/t)^\alpha$ $d\lambda = \lambda^{1-(1/\alpha)} (\alpha/t) dx$

Steps are

$$g(t) = \int_0^{\infty} e^{-x} \left(\frac{\alpha}{t}\right) \lambda \lambda^{-(1/\alpha)} dx = \int_0^{\infty} e^{-x} \left(\frac{x}{t}\right)^\alpha \left(\frac{x}{t}\right)^{-1} dx$$

Using the Gamma definition

$$\Gamma(\alpha) \triangleq \int_0^{\infty} e^{-y} y^{\alpha-1} dy$$

$$\alpha \Gamma(\alpha) = \Gamma(1 + \alpha)$$

$$= \left(\frac{\alpha}{t}\right) \int_0^{\infty} e^{-x} \frac{x^{\alpha-1}}{t^{\alpha-1}} dx = \left(\frac{\alpha}{t^\alpha}\right) \int_0^{\infty} e^{-x} x^{\alpha-1} dx = \frac{\alpha \Gamma(\alpha)}{t^\alpha}$$

$$= \frac{\Gamma(1 + \alpha)}{t^\alpha}$$



Fractional derivative operator-in disordered system

$$\frac{\partial}{\partial t} u(\lambda, t) + (\lambda)^{1/\alpha} u(\lambda, t) = f'(t)$$

Then the response to this new excitation is convolution of Green's function obtained above with the forcing function that is:

$$r(t) = g(t) * f'(t) = \int_0^t g(\tau) f'(t - \tau) d\tau = \Gamma(1 + \alpha) \int_0^t \frac{f'(t - \tau)}{\tau^\alpha} d\tau \quad 0 < \alpha < 1$$

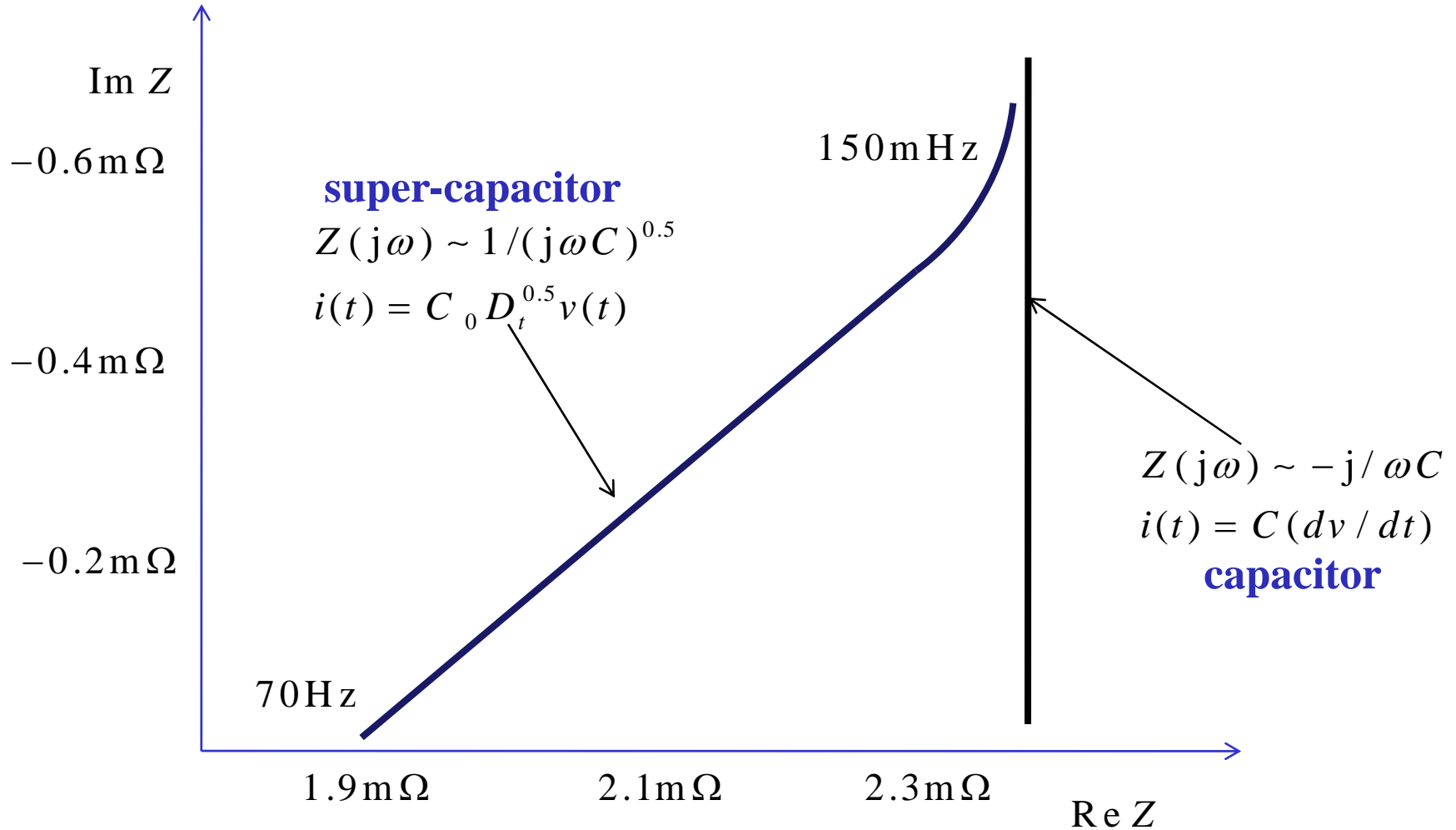
Multiplying and dividing the above expression with $\Gamma(1 - \alpha)$ Using fractional integral

$$\begin{aligned} r(t) &= \Gamma(1 + \alpha) \Gamma(1 - \alpha) \int_0^t \frac{(t - \tau)^{(-\alpha)}}{\Gamma(1 - \alpha)} f'(\tau) d\tau \\ &= \Gamma(1 + \alpha) \Gamma(1 - \alpha) D_t^{-(1-\alpha)} [f'(t)] \\ &= \Gamma(1 + \alpha) \Gamma(1 - \alpha) D_t^\alpha f(t) \end{aligned}$$

Implying the appearance of fractional derivative for cases where several time-constants define a relaxation process. Therefore a disordered relaxation (response) may well be formulated by fractional differential equation, the order giving the 'intermittency' of relaxation disordered process!



Impedance spectroscopy Nyquist plot of super-capacitor





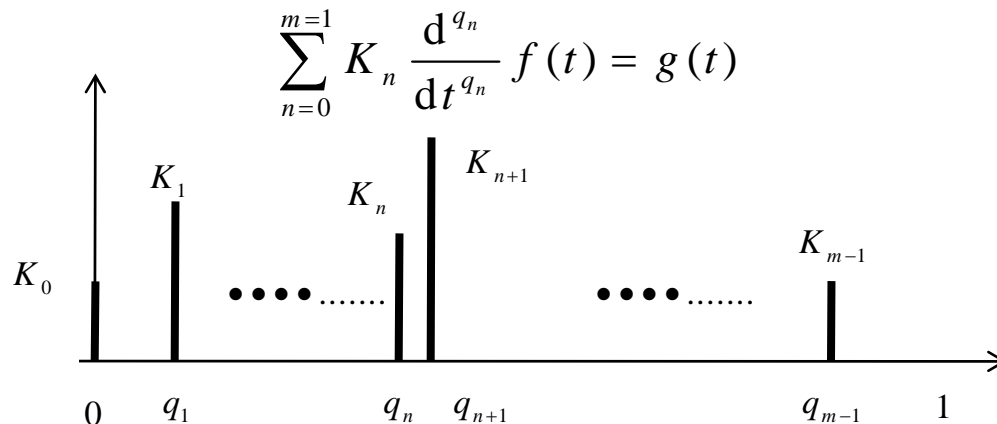
Continuous Order Differential Equation

A lumped system, spring dash pot, or RL circuit is ODE, system without memory!

$K_1 \frac{d}{dt} f(t) + K_0 f(t) = g(t)$ A fractional generalization gives a system with memory

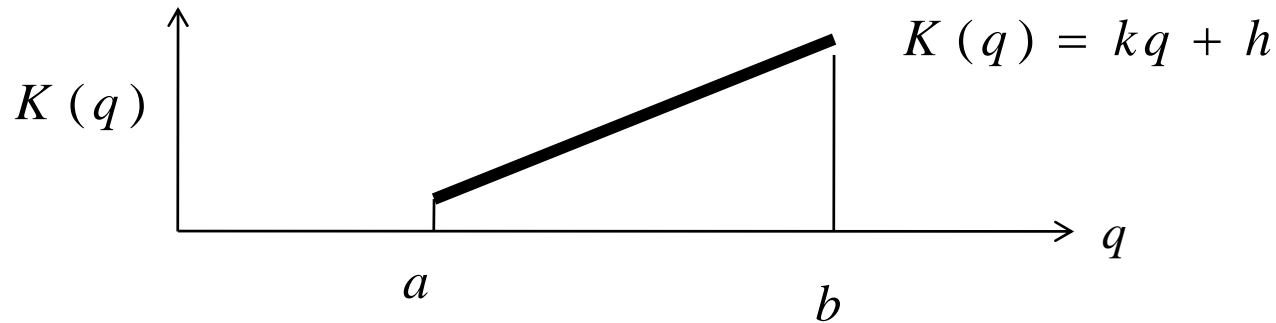
$$K_1 \frac{d^q}{dt^q} f(t) + K_0 f(t) = g(t)$$

A fractional order system with several fractionally damped element





Order is distributed continuously as linear function



$$\sum_{n=0}^{m=1} K_n \frac{d^{q_n}}{dt^{q_n}} f(t) = g(t) \quad \text{The summation } \Sigma \text{ is changed to } \int$$

**We get Continuous Order Differential Equation
(infinite memory types!!)**

$$\int_a^b \left(K(q) \frac{d^q}{dt^q} f(t) \right) dq = g(t)$$



Laplace Transforming the Continuous Order Differential equation

$$\int_a^b \left[K(q) \frac{d^{m+q}}{dt^{m+q}} f(t) \right] dq = \int_a^b \left[\frac{K(q)}{\Gamma(1-q)} dq \right] \left[\int_0^t \frac{f^{(m+1)}(u)}{(t-u)^q} du \right] = g(t)$$

Used definition of FD $\frac{d^{m+q}}{dt^{m+q}} f(t) = \frac{1}{\Gamma(1-q)} \int_0^t \frac{f^{(m+1)}(u)}{(t-u)^q} du \quad m < (m+q) < (m+1)$
 $m \in \mathbb{Z} \quad q \in \mathbb{R}$

Taking Laplace Transform

$$\int_a^b K(q) dq \left[s^{m+q} F(s) - s^q \sum_{n=0}^m s^{n-1} f^{(m-n)}(0) \right] = G(s)$$

For initial states zero the solution in Laplace domain is

$$F(s) = \frac{G(s)}{s^m \int_a^b K(q) s^q dq} = \frac{G(s)}{\Phi(s)}$$

$$\Phi(s) = s^m \int_a^b s^q K(q) dq$$



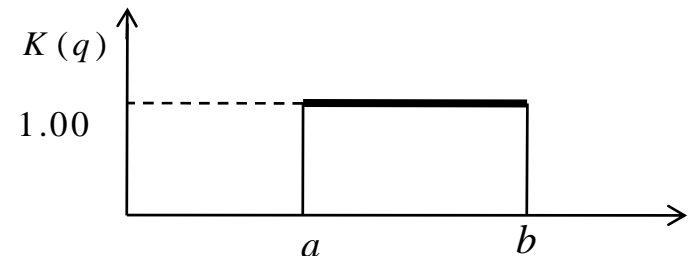
Frequency Response of Continuous order system

For a order distribution $K(q) = kq + h$ in the interval $[a, b]$ the transfer function looks like:

$$\begin{aligned}\Phi(s) &= s^m \int_a^b s^q K(q) dq \\ &= s^m \int_a^b s^q (kq + h) dq \\ &= s^m \frac{[(kb + h)s^b - (ka + h)s^a] - \frac{k(s^b - s^a)}{\ln s}}{\ln s}\end{aligned}$$

For a uniform order distribution case $k=0$; $h=1$ the transfer function is

$$\Phi(s) = \frac{(s^b - s^a) s^m}{\ln s}$$





The frequency response plot of continuous order transfer function

$$\Phi (s) = \frac{s^m (s^b - s^a)}{\ln s}$$

Putting $s = i\omega$ we will get Bode plot

$$\ln(i\omega) = \ln \left[|\omega| e^{i(\pi/2)} \right] = \ln |\omega| + i \left(\frac{\pi}{2} \right) \quad \text{giving} \quad |\ln s| = \sqrt{(\ln \omega)^2 + (\pi / 2)^2}$$

$$s^b = (i\omega)^b = |\omega|^b \angle (b\pi / 2) \quad s^a = (i\omega)^a = |\omega|^a \angle (a\pi / 2)$$

$$|A - B| = \sqrt{|A|^2 + |B|^2 - 2|A||B|\cos(\angle A - \angle B)}$$

$$|\Phi(i\omega)| = \frac{\sqrt{\omega^{2b} + \omega^{2a} - 2\omega^{a+b} \cos\left(\frac{\pi}{2}(b-a)\right)}}{\sqrt{(\ln \omega)^2 + (\pi / 2)^2}} (\omega)^m$$

Solution of continuous order differential equation in frequency domain is thus

$$|F(i\omega)| = \frac{|G(i\omega)|}{|\Phi(i\omega)|} = \frac{\sqrt{(\ln \omega)^2 + (\pi / 2)^2}}{\omega^m \sqrt{\omega^{2b} + \omega^{2a} - 2\omega^{a+b} \cos\left(\frac{\pi}{2}(b-a)\right)}}$$



The time domain solution of continuous order differential equation

$$\begin{aligned}
 f(t) &= \mathcal{L}^{-1}\{F(s)\} = \mathcal{L}^{-1} \frac{G(s)}{\Phi(s)} \\
 &= \mathcal{L}^{-1} \left\{ G(s) \frac{\ln s}{s^a (s^{b-a} - 1) s^m} \right\} \\
 &= g(t) \otimes \mathcal{L}^{-1} \left\{ \frac{\ln s}{s^a} \right\} \otimes \mathcal{L}^{-1} \left\{ \frac{1}{s^{b-a} - 1} \right\} \otimes \mathcal{L}^{-1} \left\{ \frac{1}{s^m} \right\} \\
 &= g(t) \otimes \mathcal{L}^{-1} \left\{ \frac{\ln s}{s^a} \right\} \otimes F_{(b-a)}(1, t) \otimes \frac{t^{m-1}}{\Gamma(m)}
 \end{aligned}$$

Robotnov Hartley function $F_q(a, t) = t^{(q-1)} \sum_{n=0}^{\infty} \frac{a^n t^{nq}}{\Gamma(nq + q)}$

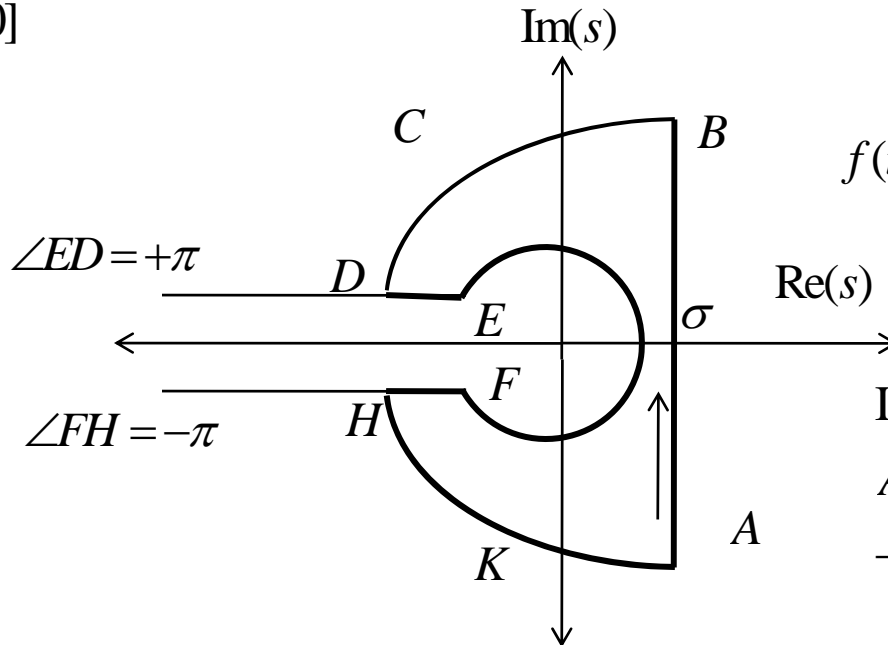
Laplace inverse of function with out poles in left half plane!!



Inverse Laplace of function with no roots in Left Half Plane

$$\bar{\Phi}(s) = \frac{s^b - s^a}{s \ln s} \quad 0 < a < b < 1 \quad G(s) = [\Phi(s) / s][sF(s)] = \bar{\Phi}(s)F'(s)$$

Why ? So as to make $\bar{\Phi}(s) \rightarrow 0$ at $s = \infty$. The inspection says that due to $\ln(s)$ there is no possibility of roots in negative plane! The logarithm is also multi-valued function, so as the power functions of non-integer orders; they have standard branch cut in complex plane that is $(-\infty, 0]$



$$f(t) = \mathcal{L}^{-1}\{F(s)\} = \frac{1}{2\pi i} \lim_{T \rightarrow \infty} \int_{\sigma - iT}^{\sigma + iT} e^{st} F(s) ds$$

Integration - contour

$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$
 $\rightarrow F \rightarrow H \rightarrow K \rightarrow A$



Apply residue theorem

Since the integration on large arc BCD and HKA is zero at large radius, and as the radius goes to zero the integration on the small arc EF is zero, we are left with:

$$\oint_{A,B,C,\dots,K,A} e^{st} \bar{\Phi}(s) ds = \int_A^B e^{st} \bar{\Phi}(s) ds + \int_D^E e^{st} \bar{\Phi}(s) ds + \int_F^H e^{st} \bar{\Phi}(s) ds = 2\pi i \sum \text{residue of poles}$$

Rearranging above and recognizing that contour does not enclose any poles we get

$$\frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} e^{st} \bar{\Phi}(s) ds + \frac{1}{2\pi i} \int_D^E e^{st} \bar{\Phi}(s) ds + \frac{1}{2\pi i} \int_F^H e^{st} \bar{\Phi}(s) ds = \frac{1}{2\pi i} \oint e^{st} \bar{\Phi}(s) ds = \sum \text{residues of poles} = 0$$

From above we have Laplace inverse as

$$\mathcal{L}^{-1} \{ \bar{\Phi}(s) \} = \frac{1}{2\pi i} \int_{\sigma-i\infty}^{\sigma+i\infty} e^{st} \bar{\Phi}(s) ds = - \frac{1}{2\pi i} \left[\int_D^E e^{st} \bar{\Phi}(s) ds + \int_F^H e^{st} \bar{\Phi}(s) ds \right]$$



The result in form of Bestimmte Integral

Use $s = re^{i\theta}$ on $\theta = \pm\pi$ we have $s = -r$ and $ds = -dr$

$$\begin{aligned} \mathcal{L}^{-1} \{ \bar{\Phi}(s) \} &= -\frac{1}{2\pi i} \left[\int_D^E e^{st} \bar{\Phi}(s) ds + \int_F^H e^{st} \bar{\Phi}(s) ds \right] \\ &= -\frac{1}{2\pi i} \left[-\int_{\infty}^0 e^{-rt} \bar{\Phi}(r, \theta = \pi) dr - \int_0^{\infty} e^{-rt} \bar{\Phi}(r, \theta = -\pi) dr \right] \\ &= \frac{1}{2\pi i} \left[\int_0^{\infty} e^{-rt} \left(\bar{\Phi}(r, \theta = \pi) - \bar{\Phi}(r, \theta = -\pi) \right) dr \right] \end{aligned}$$

Doing lot of algebra we obtain Laplace inverse of continuous order transfer function In form of Bestimmte integral; the Green's function is thus obtained for getting the time domain solution

$$\mathcal{L}^{-1} \{ \bar{\Phi}(s) \} = \frac{1}{\pi} \int_0^{\infty} e^{-rt} \frac{\left[r^{b-1} \{ -\ln r \sin(b\pi) + \pi \cos(b\pi) \} + r^{a-1} \{ \ln r \sin(a\pi) - \pi \cos(a\pi) \} \right]}{[(\ln r)^2 + \pi^2]} dr$$



List of few suggested reading

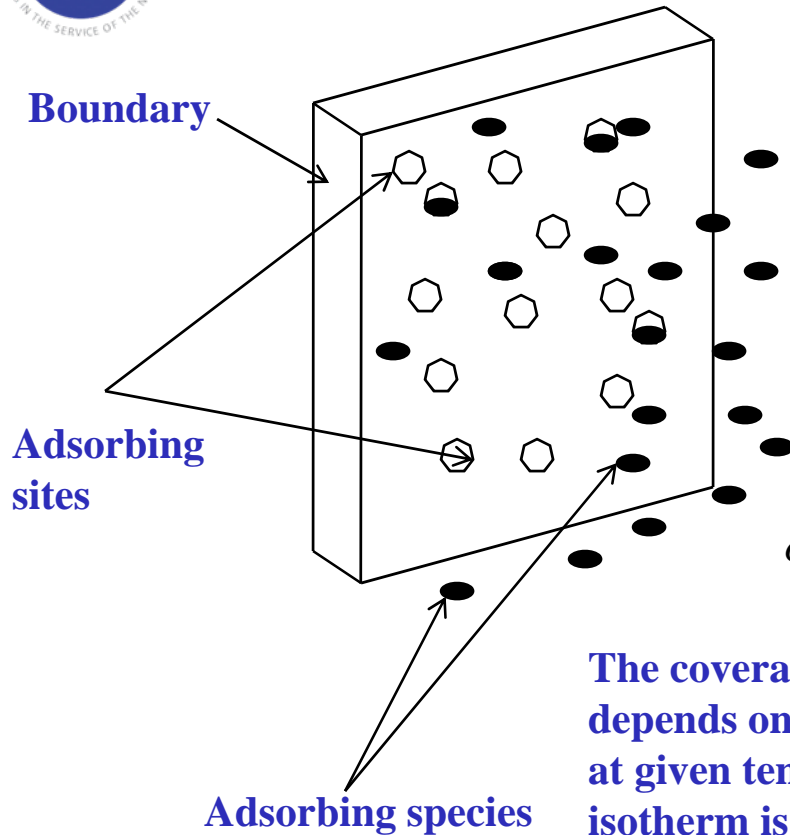
- "Micro-structural Roughness of Electrodes Manifesting as Temporal Fractional Order Differential Equation in Super-Capacitor Transfer Characteristics", Shantanu Das, Nimai Chand Pramanik (C-MET Thrissur), International Journal of Mathematics & Computation Vol 20, Issue No.3, pp 94-113, [2013]
- "Generalization of Fractional Calculus Operators With Applications: Developments", Shantanu Das, International Journal of Mathematics & Computations, Vol. 21, Issue 4, pp. 23-50, [2013]
- "Gramian for Control of Fractional Order Multivariate Dynamic System", Shantanu Das, International Journal of Applied Mathematics & Statistics IJAMAS, Vol 37. Issue No. 7, 2013; pp 71-96, [2013]
- "Geometrically Deriving Fractional Cross Product and Fractional Curl", Shantanu Das, International Journal of Mathematics and Computation IJMC, Vol. 20, Issue. 3, pp. 1-29, [2013]
- Mechanism of Wave Dissipation via Memory Integral vis-a-vis Fractional Derivative", Shantanu Das, International Journal of Mathematics & Computation IJMC, Vol. 19, Issue No.2, pp72-83, [2013]
- "Fractional order boundary controller enhancing stability of partial differential wave equation systems with delayed feedback", Shantanu Das, International Journal of Mathematics & Computation IJMC Vol. 19, Issue No. 2 Year 2013, pp 42-59, [2013]
- "Formation of Fractional Derivative in Time due to Propagation of Free Greens Function in Spatial Stochastic Disorder Field for Transport Phenomena", Shantanu Das, International Journal of Mathematics and Computation Vol. 17, Issue-4, pp 68-92, [2012]
- "Evolution of Temporal Fractional Derivative due to Spatial Stochastic Disorder in Transport Phenomena", Shantanu Das, International Journal of Mathematics and Computation (IJMC), Vol. 17, Issue-4, pp. 1-20, [2012]
- Frequency and Time Domain Solution for Dynamic Systems having Differential Equations of Continuous Order", Shantanu Das, International Journal of Applied Mathematics & Statistics, Vol. 29, Issue No. 5, pp.6-16, [2012]
- "Multiple Riemann Sheet Solution for Dynamic Systems with Fractional Differential Equations", Shantanu Das, International Journal of Applied Mathematics & Statistics. Vol. 28, Issue-4, pp83-89, [2012]
- "Functional Fractional Calculus (II-Edition)", Shantanu Das, Springer-Verlag Heidelberg Germany Book: ISBN-978-3-642-20544-6 Publication Date 01-06-2011, [2011]
- Fractional Stochastic Modeling for Random Dynamic Delays in Computer Control System", Shantanu Das, International Journal of Applied Mathematics & Statistics, 2011, Vol. 21, No. J11, pp131-140, [2011]
- "Solution of Extraordinary Differential Equation with Physical Reasoning by Obtaining Modal Reaction Series", Shantanu Das, Modelling and Simulation in Engineering, Hindawi Publishing Corp. Vol (2010), ID-739675, pp. 1-19 ,
- Generalized Dynamic System Solution by Decomposed Physical Reaction", Shantanu Das, International Journal of Applied Mathematics & Statistics, Vol-17(Special) No.J10,ISSN0973-1377(Print), ISSN0973-7545(On-line); pp45-77, [2010]
- "The Solution of Coupled Fractional Neutron Diffusion Equation with Delayed Neutron", T.Sardar*, S.Saha Ray*, R.K.Bera*, B.B.Biswas, Shantanu Das.(* Department of Mathematics Heritage Institute of Technology Kolkata), Int. J. of Nuclear Energy Science & Technology, Vol.5, No.2, pp105-113, [2010]
- "Fractional divergence for neutron flux profile in nuclear reactor", Shantanu Das, B B Biswas, Int. J. Nuclear Energy Science & Technology Vol.3 No.2 pp139-159, [2007]
- "Functional Fractional Calculus for system identification & controls ", Shantanu Das, Springer Verlag Berlin Book: ISBN-978-3-540-72702-6, (Publication date 16 October 2007),BARC library Book Section No.204472-(517.97:621.039.56-B08), [2007]



Annexure-2

Basics of Adsorption-desorption phenomena

Adsorption at surface & assumptions



We will consider physisorption, the species adsorbing retains its identity unlike chemisorption where bond is formed. Adsorption requires a particle to lose energy during collision with the surface. Some of the particles bombarding the surface will bounce back off the surface but at any particular density a certain fraction will remain giving rise to a coverage of the surface. The covering ratio or coverage is defined as:

$$\sigma_R = \frac{\text{Number of surface sites occupied}}{\text{Total number of surface sites}} = \frac{\sigma}{\sigma_0}$$

The coverage of the surface when dynamic equilibrium is reached depends on the density of phase. The variation of σ_R with density at given temperature is called adsorption isotherm. The simplest isotherm is Langmuir's isotherm, that gives the relation between the coverage of the first layer and the density at a particular temperature; with three basic assumption.

1. The adsorption occurs only on the first layer (monolayer coverage)
2. All adsorption sites are equivalent, and the adsorption process is uniform (it is perfectly flat at on a microscopic scale).
3. The adsorption energy of one site is independent of occupancy of neighboring sites.



Adsorption phenomena-Langmuir isotherm

The adsorbed particles are assumed to be in dynamic equilibrium with the molecules in the surroundings and the process can be treated as chemical reaction



The rate of adsorption is proportional to the density of A and the number of adsorbing sites at the surface i.e.

$$\frac{d\sigma}{dt} = k_a \rho (\sigma_0 - \sigma)$$

Where k_a is the rate constant for adsorption, ρ is the bulk density of adsorbate just in front of adsorbing surface, and $\sigma_0 - \sigma$ is the total number of the free sites. The rate of desorption is proportional to number of adsorbed species

$$\frac{d\sigma}{dt} = -k_d \sigma$$

Where the k_d is the rate constant for desorption. Introduce reduced quantities as $\sigma_R = \sigma / \sigma_0$ and $\rho_R = \rho / \rho_0$. At the equilibrium “net rate of adsorption” i.e. adsorption rate plus desorption rate is zero

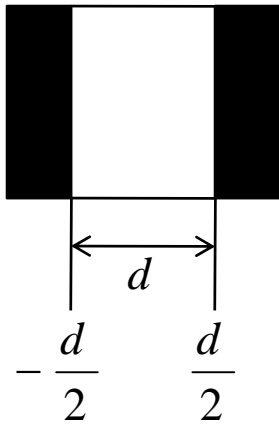
$$\text{Net rate of adsorption} = k_a \rho (\sigma_0 - \sigma) + (-k_d \sigma) = 0$$

From above we get Langmuir isotherm as: $\sigma_R = \frac{\alpha \rho_R}{1 + \alpha \rho_R}$ The α governs steady state and is $\alpha = \kappa \tau \rho_0 / \sigma_0$ and $\tau = 1 / k_d$, $\kappa = k_a \sigma_0$. The τ characteristic time constant for desorption and κ is associated with adsorption phenomena. Notice that $\kappa \tau$ has dimension of length. Also we have from the balance equation

$$\rho_R = \frac{1}{\alpha} \frac{\sigma_R}{1 - \sigma_R}$$

Equilibrium surface & bulk densities

We indicate $\rho(z, t)$ the density of the particles of the medium in the position z at a given time t , and $\sigma(t)$ is the surface density. The equilibrium values of these are



$$\lim_{t \rightarrow \infty} \rho(z, t) = \rho(z) = \rho \quad \lim_{t \rightarrow \infty} \sigma(t) = \sigma$$

The net rate of adsorption (adsorption rate + desorption rate) is

$$\frac{d\sigma}{dt} = k_a \rho (\sigma_0 - \sigma) - k_d \sigma$$

$$\frac{d\sigma}{dt} = \kappa \rho \left(1 - \frac{\sigma}{\sigma_0} \right) - \frac{1}{\tau} \sigma$$

$$\frac{d\sigma_R}{dt} = \kappa \frac{\rho_0}{\sigma_0} \rho_R (1 - \sigma_R) - \frac{1}{\tau} \sigma_R$$

At the equilibrium $d\sigma_R/dt = 0$, one gets the Langmuir isotherm, which can be shown to be thickness dependence. In fact, since $\rho_0 d$ is the initial number of particles per unit area, the conservation of number of particles at any time requires

$$2\sigma(t) + \int_{-d/2}^{d/2} \rho(z, t) dz = \rho_0 d$$

At the equilibrium $t \rightarrow \infty$ thus we have $2\sigma + \rho d = \rho_0 d$. From this equilibrium relation we obtain $\sigma_R + \alpha \delta (\rho_R - 1) = 0$; with $\delta = d / 2\kappa\tau$ as dimensionless thickness, where $\alpha = \kappa\tau\rho_0 / \sigma_0$



Dependence on sample thickness

Substitute $\sigma_R + \alpha \delta (\rho_R - 1) = 0$ **in** $\sigma_R = \frac{\alpha \rho_R}{1 + \alpha \rho_R}$ **to get**

$$\sigma_R^2 - [1 + (1 + \alpha) \delta] \sigma_R + \alpha \delta = 0$$

$$\sigma_R = \frac{1}{2} \left\{ 1 + (1 + \alpha) \delta - \sqrt{[1 + (1 + \alpha) \delta]^2 - 4 \alpha \delta} \right\}$$

Gives σ_R **as function of (normalized) thickness** δ

Similarly using $\rho_R = \frac{1}{\alpha} \frac{\sigma_R}{1 - \sigma_R}$ **we get** $\rho_R = \frac{-1 + (-1 + \alpha) \delta + \sqrt{[1 + (1 + \alpha) \delta]^2 - 4 \alpha \delta}}{2 \alpha \delta}$

For small d i.e. $\delta \rightarrow 0$ specifically $d \ll \kappa \tau$ we have

$$\begin{aligned} \sigma_R \Big|_{\delta \rightarrow 0} &= \lim_{\delta \rightarrow 0} \frac{1}{2} \left\{ 1 + (1 + \alpha) \delta - \sqrt{[1 + (1 + \alpha) \delta]^2 - 4 \alpha \delta} \right\} \\ &= \lim_{\delta \rightarrow 0} \frac{1}{2} \left\{ 1 + \delta + \alpha \delta - \sqrt{(1 + \delta + \alpha \delta)^2 - 4 \alpha \delta} \right\} \\ &= \frac{1}{2} \left\{ 1 + \delta + \alpha \delta - \sqrt{(1 + \delta)^2} \right\} \cong \alpha \delta \end{aligned}$$

$$\sigma_R = \frac{\sigma_{eq}}{\sigma_0} = \alpha \delta = \left(\frac{\kappa \tau \rho_0}{\sigma_0} \right) \left(\frac{d}{2 \kappa \tau} \right) = \frac{1}{2} \rho_0 d$$

For large d i.e. $d \gg \kappa \tau$

$$\sigma_R \approx \frac{\alpha}{1 + \alpha} - \frac{\alpha}{(1 + \alpha)^3} \frac{1}{\delta} + \mathcal{O}(\delta^{-2})$$

$$\rho_R \approx 1 - \frac{1}{1 + \alpha} \frac{1}{\delta} + \mathcal{O}(\delta^{-2})$$



Approximate dynamics expression for adsorption-and equilibrium values

We have dynamics as $\frac{d\sigma}{dt} = \kappa\rho \left(1 - \frac{\sigma}{\sigma_0}\right) - \frac{1}{\tau}\sigma$ in the limit in which $\sigma \ll \sigma_0$ we get the adsorption

$$\frac{d\sigma}{dt} = \kappa\rho - \frac{1}{\tau}\sigma$$

In dimensionless form it is written as $\frac{d\sigma_R}{dt} = \frac{\kappa\rho_0}{\sigma_0}\rho_R - \frac{1}{\tau}\sigma_R$

The steady state values of σ_R and ρ_R are such that $\rho_R = \frac{1}{\alpha}\sigma_R$

From the above relation of $\sigma_R = \alpha\rho_R$ and obtained expression $\sigma_R + \alpha\delta(\rho_R - 1) = 0$ we get

$$\sigma_R = \alpha \frac{\delta}{1 + \delta} \quad \& \quad \rho_R = \frac{\delta}{1 + \delta} = \frac{\sigma_R}{\alpha}$$

Instead obtained expressions

$$\sigma_R = \frac{1}{2} \left\{ 1 + (1 + \alpha)\delta - \sqrt{[1 + (1 + \alpha)\delta]^2 - 4\alpha\delta} \right\} \quad \& \quad \rho_R = \frac{-1 + (-1 + \alpha)\delta + \sqrt{[1 + (1 + \alpha)\delta]^2 - 4\alpha\delta}}{2\alpha\delta}$$



Poisson-Boltzmann equation

The solution (ions coming from impurities) is modelled as point ions embedded in a dielectric continuum representing the solvent (in our case the polymer). We suppose that the solution contains +ve and the -ve ions. Choose the coordinate system such that surface is situated in the plane $z = 0$. The Potential inside the plane is denoted by $V(z)$, given by Poisson's equation. Let $n_+(z)$ and $n_-(z)$ denote the density of the ions with charge $\pm q_e$, the dielectric constant is ϵ

$$\frac{d^2 V}{dz^2} = - \frac{\rho(z)}{\epsilon} \quad \rho(z) = q_e [n_+(z) - n_-(z)]$$

The density of ions depend on potential $V(z)$; and we choose $V(\infty) = 0$ as datum. According to Boltzmann's statistics $n_+(z) = n_0 \exp(-q_e V(z) / k_B T)$; $n_-(z) = n_0 \exp(q_e V(z) / k_B T)$ where n_0 is bulk density of ionic impurity of an infinite sample i.e. $z \rightarrow \infty, V(z) \rightarrow 0, n_{\pm}(z) = n_0$ Substituting this we get (along with Debye-Huckel approximation to get linear equation)

$$\frac{d^2 V(z)}{dz^2} = 2 \frac{q_e}{\epsilon} n_0 \sinh \left(\frac{q_e V(z)}{k_B T} \right) \cong \left(\frac{2 n_0 q_e^2}{\epsilon k_B T} \right) V(z) = \frac{1}{\lambda_0^2} V(z)$$

$$\lambda_0 = \sqrt{\frac{\epsilon k_B T}{2 n_0 q_e^2}} \quad \text{is Debye screening length}$$

Important feature of this Debye length is that it depends on the bulk density of ions.



Debye length

From the Poisson equation with Boltzmann ionic distribution & linearizing the same, we get

$$\frac{d}{dz} V(z) - \frac{1}{\lambda_0^2} V(z) = 0 \quad \lambda_0^2 = \left(\frac{\epsilon k_B T}{2 n_0 q_e^2} \right)$$

The solution is $V(z) = V_s e^{-z/\lambda_0}$, where V_s is fixed by charge conservation namely

$$\int_0^\infty \rho(z) dz = -\sigma \quad \text{where } \sigma \text{ is surface density of the substrate. With this we have potential}$$

$$V(z) = \frac{\sigma}{\epsilon} \lambda_0 e^{-z/\lambda_0}$$

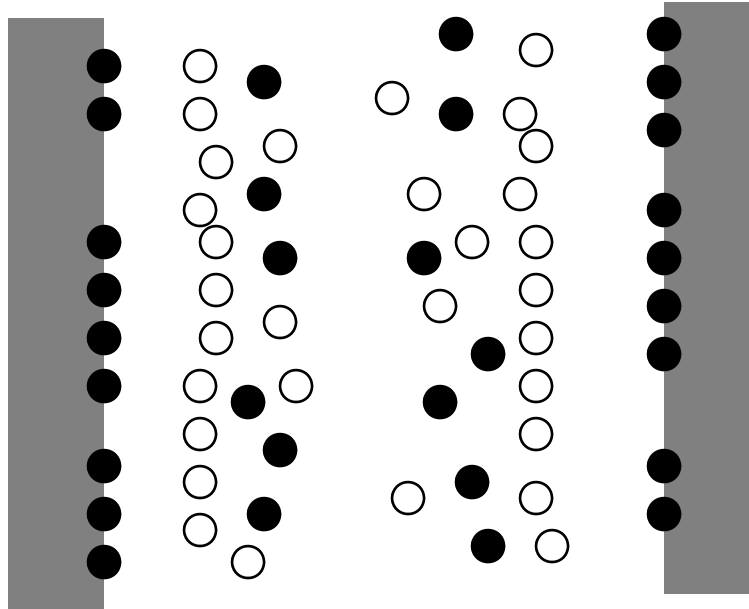
While the charge density we get from above Poisson equation as $\rho(z) = -\frac{\sigma}{\lambda_0} e^{-z/\lambda_0}$

In this manner, the excess charges on the surface is balanced by a 'space-charge' layer; which decays exponentially in the bulk solution. Consequently a double layer is formed near the surface.

The validity of the linear approximation works well when $q_e V / k_B T \ll 1$ implying that $V \ll k_B T / q_e \approx 25 \text{ mV}$ at the room temperature

Double layer capacity

Schematic representation of the Debye double layer showing the space-charge separation in the sample



The configuration of the charges shown above due to Debye screening has a 'capacity'
 The interfacial capacity per unit area is known as double-layer- capacity and can be approximated as

$$C = \frac{\epsilon}{\lambda_0}$$

It is the capacity of a parallel plate separation given by Debye screening length



End of Annexure