

# **Theoretical Techniques in Disordered Systems**

**Condensed Matter Physics Research Centre  
Indian Society for Non-Linear Analysts**

## **Ordering Disordered System by Fractional Calculus**

**18 -12-2009**

**Shantanu Das  
RRPS  
Reactor Control Division  
BARC**

# Prologue to Disorder Relaxation in Condense Matter & Fractional Calculus:

Fractional Calculus methods have been invoked (recently) to model relaxation processes in complex systems. This has lead to interesting discussions into nature of transport coefficients appropriately/equations to describe these complex materials. This observation is leading to thought to have ‘Universality’ of Disordered Material Relaxation” !!

Relaxation integral  $I_t^\phi$  where  $\phi$  characterizes ‘degree of intermittency’ in the relaxation process-and exact solutions of these integrals (may) describe relaxation in condense matter-’intermittency in relaxation’

Extension in this above model of relaxation , to include  $\beta$  ‘dynamic heterogeneity ‘ arising out from particle clustering (too may be included) which is ubiquitous in condense matter. With  $I_t^{\phi,\beta}$  intermittency plus heterogeneity.

$I_t^\phi f(t)$  Is Fractional Integration of arbitrary order.

$D_t^\phi f(t)$  Is Fractional Differentiation of arbitrary order

# Riemann Liouville (RL) fractional integration-antiderivative

Repeated n-fold integration generalization to arbitrary order

$$I_t^1 f(t) = d_t^{-1} f(t) = \int_0^t f(\tau) d\tau$$

$$I_t^2 f(t) = d_t^{-2} f(t) = \int_0^t \int_0^t f(\tau) d\tau d\tau = \int_0^t (t - \tau) f(\tau) d\tau$$

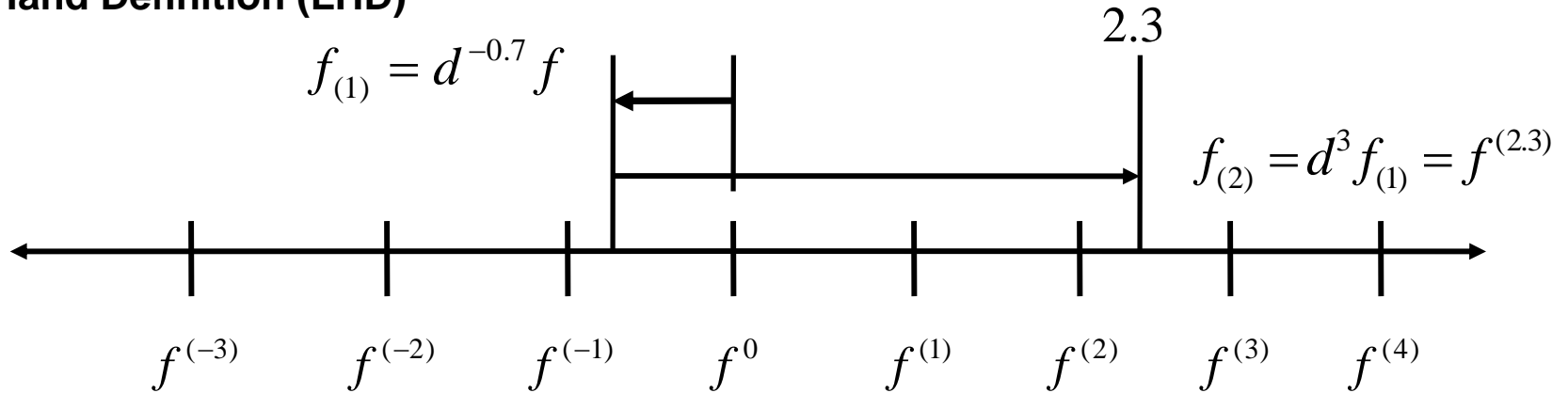
$$I_t^3 f(t) = d_t^{-3} f(t) = \int_0^t \int_0^t \int_0^t f(\tau) d\tau d\tau d\tau = \frac{1}{2} \int_0^t (t - \tau)^2 f(\tau) d\tau$$

$$I_t^n f(t) = d_t^{-n} f(t) = \underbrace{\int_0^t \int_0^t \dots \int_0^t}_{n} f(\tau) d\tau = \frac{1}{(n-1)!} \int_0^t (t - \tau)^{n-1} f(\tau) d\tau$$

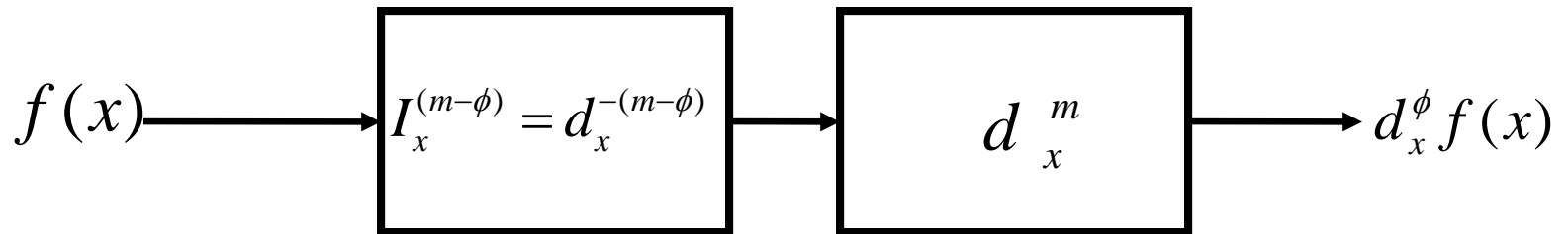
$$I_t^\phi f(t) = d_t^{-\phi} f(t) = \frac{1}{\Gamma(\phi)} \int_0^t (t - \tau)^{\phi-1} f(\tau) d\tau$$

# Riemann Liouville (RL) Fractional derivative

## Left Hand Definition (LHD)



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



$$d_x^\phi f(x) = d_x^m I_x^{m-\phi} f(x)$$

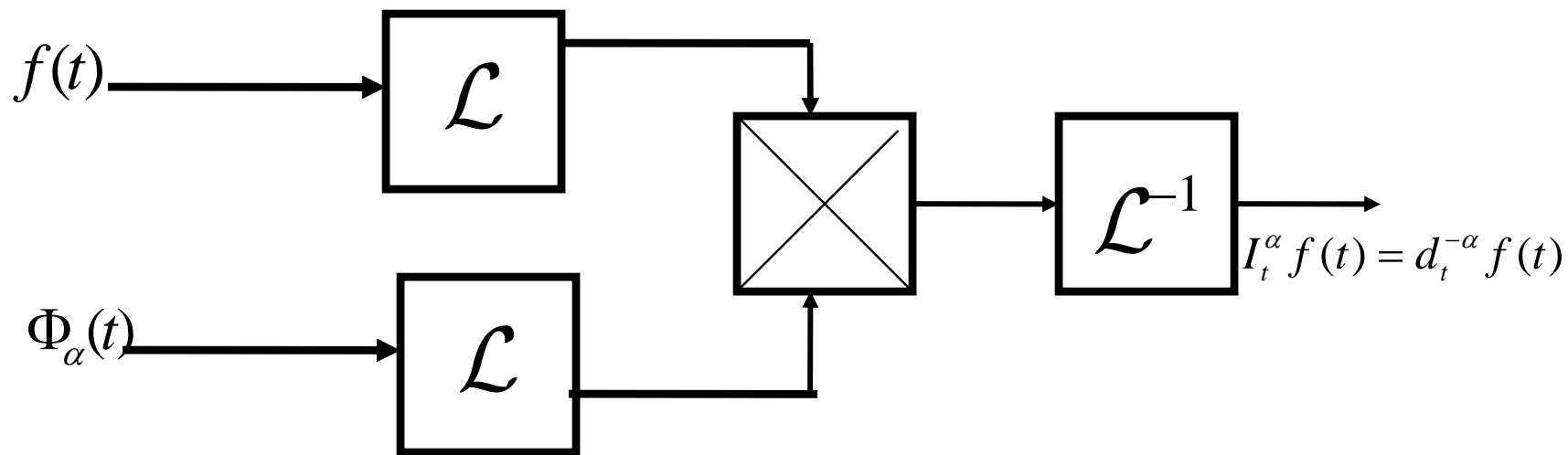
$$d_x^\phi f(x) = \frac{d^m}{dx^m} \left[ \frac{1}{\Gamma(m-\phi)} \int_0^x (x-\tau)^{-\phi-1+m} f(\tau) d\tau \right]$$

## Convolution with power function RL fractional integration:

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

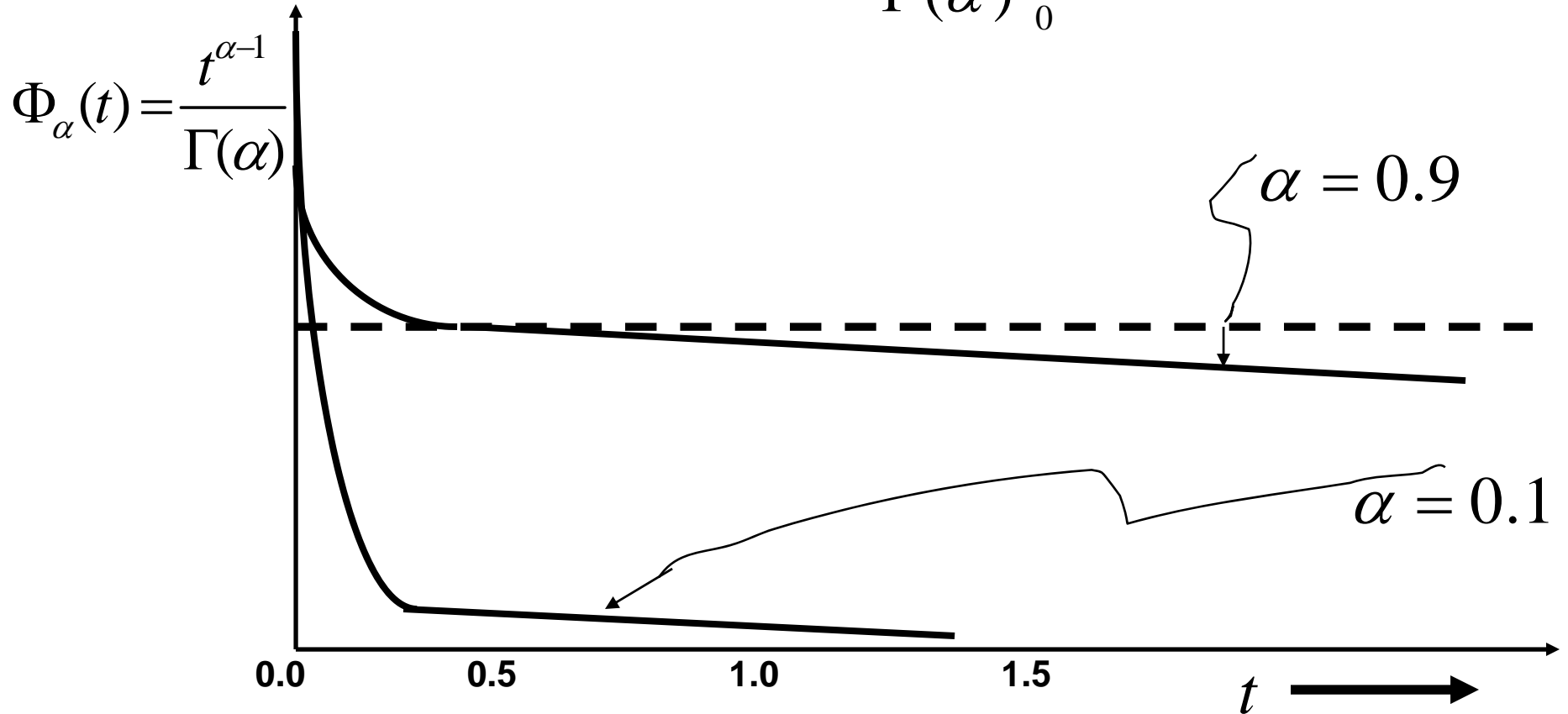
$$\Phi_\alpha(t) = \frac{t^{\alpha-1}}{\Gamma(\alpha)}; \mathcal{L}\{t^\mu\} = \frac{\Gamma(\mu+1)}{s^{\mu+1}}; \mathcal{L}\{\Phi_\alpha(t)\} = s^{-\alpha}$$

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



# Nature of Power Function in Fractional Differ-integration:

$$I_t^\alpha f(t) = d_t^{-\alpha} f(t) = \frac{1}{\Gamma(\alpha)} \int_0^t (t - \tau)^{\alpha-1} f(\tau) d\tau$$



$\lim_{\alpha \rightarrow 1} \Phi_\alpha(t) = H(t)$  Heaviside's Unit Step Function

$\lim_{\alpha \rightarrow 0} \Phi_\alpha(t) = \delta(t)$  Unit Delta Function

## Fractional derivative the Euler (1730) formula for monomial

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

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

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

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

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

**For positive index the process is differentiation**

**For negative index the process is integration**

## Ordered Relaxation: (Intense & Strong)

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

### Standard Maxwell Debye relaxation

Gives pure exponential solution with single relaxation time constant; this is strong relaxation (without-memory).

$$\frac{d}{dt} \Psi(t) + \lambda \Psi(t) = \delta(t)$$

$$\tau^{-1} = \lambda; \Psi(0) = 1; \Psi(0^-) = 0$$

$$\Psi(t) = e^{-t/\tau} = e^{-\lambda t}$$

## Disordered Relaxation: (Intermittent & weak)

For complex dissipating process we (may) have several time constants and let us have this 'disorder' in a power law representation so, the PDE is, this is weak relaxation

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

$$0 < \phi < 1$$

Power law is scale free with preferential 'statistics'



## Origination of Fractional Differential Equation in complex 'disordered' relaxation in condense matter:

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

The solution is

$$\Psi(\lambda, t) = e^{\left(-\lambda^{\{1/\phi\}} t\right)} \quad \text{'impulse response function'} \quad h(\lambda, t)$$

On integrating this  $h(\lambda, t)$  w.r.t.  $\lambda$  for all  $0, \infty$ , we obtain the function in time.

$$g(t) = \int_0^{\infty} h(\lambda, t) d\lambda = \int_0^{\infty} e^{\left\{-\lambda^{\{1/\phi\}} t\right\}} d\lambda$$

With change of variable and recasting with definition of Gamma function

as  $\Gamma(\alpha) = \int_0^{\infty} e^{-x} x^{\alpha-1} dx$  we get:

'Impulse response' of Linear Constant Coefficient System  
Starting from rest:

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

Observed is 'power-law' (long-tailed) decay (lingering memory!!)

## Response of relaxation to arbitrary forcing function-origin of $D_t^\phi f(t)$

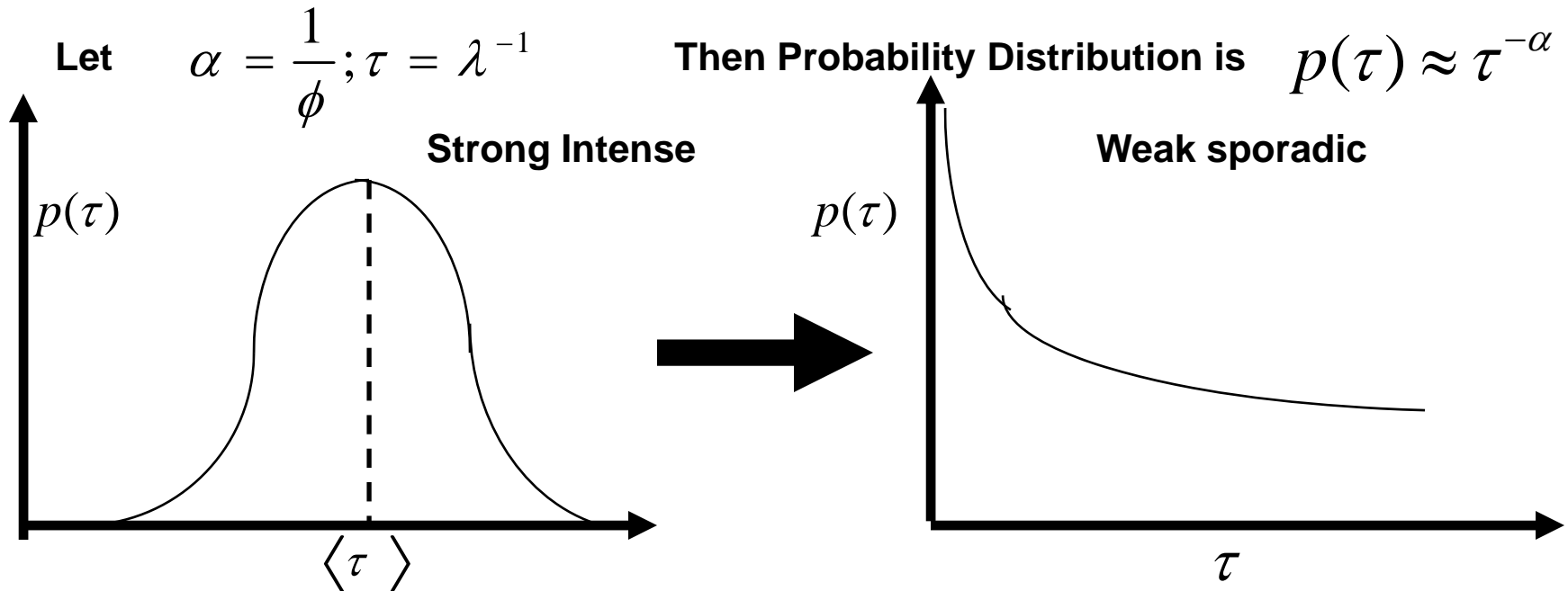
$$\frac{\partial}{\partial t} \Psi(\lambda, t) + (\lambda)^{1/\phi} \Psi(\lambda, t) = \dot{f}(t)$$
$$g(t) = \frac{\Gamma(1+\phi)}{t^\phi}$$

Response to the arbitrary forcing function is:

$$\begin{aligned} r(t) &= g(t) * \dot{f}(t) \\ &= \int_0^t d\tau g(t-\tau) \dot{f}(t) \quad \text{Here put the value of Green's function} \\ &= \Gamma(1+\phi) \int_0^t \frac{\dot{f}(t)}{(t-\tau)^\phi} d\tau = \Gamma(1+\phi) \int_0^t \frac{\dot{f}(t-\tau)}{\tau^\phi} d\tau \\ &= \Gamma(1+\phi) \Gamma(1-\phi) \int_0^t \frac{\tau^{-\phi}}{\Gamma(1-\phi)} \dot{f}(t-\tau) d\tau \\ &= \Gamma(1+\phi) \Gamma(1-\phi) I_t^{\phi-1} \{ \dot{f}(t) \} \\ &= \Gamma(1+\phi) \Gamma(1-\phi) D_t^\phi f(t) \end{aligned}$$

# Intermittency of relaxation random normal, and scale-free power law:

$$(\lambda)^{1/\phi} ; 0 < \phi < 1$$



A power law distribution  $p(x) \approx x^{-\alpha}$  implies that is asymptotically scale-Invariant. In general it is convenient to write from a minimum value as:

Moments of power law distribution

$$p(x) = \frac{\alpha - 1}{x_{\min}} \left( \frac{x}{x_{\min}} \right)^{-\alpha} ; \alpha > 1$$

$$\langle x^m \rangle = \int_{x_{\min}}^{\infty} x^m p(x) dx = \frac{\alpha - 1}{\alpha - 1 - m} x_{\min}^m$$

Which is well defined for  $m < \alpha - 1$  . That means for  $m \geq \alpha - 1$  all moments diverge.

Can have no defined average or variance!!

## Discharge (Strong & Intermittent-Weak)

### 1) Point Discharge:

$$v(t) = V_0 \exp\left(-t/RC\right) \quad \text{Strong}$$

Here the Capacitor discharges with constant time constant with constant farads and constant load resistance. If the RC circuit is point quantity then it is true as the relaxation Process will be uniform throughout the discharge process.

### 2) Distributed Discharge:

$$v(t) = V_0 \exp\left(-t/\{R(t)\}\{C(t)\}\right) \quad \text{Intermittent Weak}$$

Say the capacitor is spatially distributed, the discharge event may not be uniformly distributed in time. More so the capacitance farad may be function of time or even the farads may be having relation to the charge stored. This gives imperfect weak discharge with several time-constants in the discharge period!!

## **Discussion Normal Distribution vis-à-vis Power Law Distribution:**

- . Unlike the Normal-Distribution, in the Power Law Distribution ‘no meaningful average, that can be assumed to be representing unique relaxation time-constants; have several time constants of relaxation.**
  
- . Unlike the Normal-Distribution which mostly occur in static environment the Power-Law-Distribution occur when the following conditions are possibly met:**
  - 1. Variety.**
  - 2. Inequality.**
  - 3. Dependency.**
  - 4. Finite Resources.**

**The weak & intermittent relaxation meaning the initial state of the disturbed parameter decays to the equilibrium value weakly with sporadic weakening intensity (rate). The strong and intense relaxation has strong and intense rate.**

## Relaxation through several states (Variety of time constants)

$$\Psi(t) = [\Psi] = [\psi_1(t) \quad \psi_2(t) \quad \psi_3(t) \quad * \quad * \quad \psi_\infty(t)]$$

$$\begin{bmatrix} \psi_1(t) \\ \psi_2(t) \\ * \\ \psi_\infty(t) \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & * & a_{1\infty} \\ a_{21} & a_{22} & * & a_{2\infty} \\ * & * & * & * \\ a_{\infty 1} & a_{\infty 2} & * & a_{\infty\infty} \end{bmatrix} \begin{bmatrix} e^{-\lambda_1 t} \\ e^{-\lambda_2 t} \\ * \\ e^{-\lambda_\infty t} \end{bmatrix}$$

$$\Psi(t) = \|\Psi\| = \sqrt{[\Psi]^T [\Psi]}$$

## **Relaxation in complex process some comments:**

- . Sufficiently high micro structural disorder can lead statistically to macroscopic behavior well approximated by Fractional Calculus.**
- . Damping (relaxation) behavior of materials if modeled by Linear Differential Equations (LDE); with constant coefficient cannot include 'long-memory, that fractional order derivatives require.**
- . Rubber molecules (presumably) cannot remember past here (perhaps) LDE with constant coefficient can be involved. Such systems have 'exponential-decay'-system without memory. For large times the value goes to zero-(quickly).**
- . Many materials with 'complex' microscopic dissipative mechanisms may macroscopically show Fractional Order Differential Equation behavior. Damping (relaxation) models may involve relatively fewer fitted parameters compared to integer order complex models.**
- . Fractional Order behavior may be an artifact of many complex internal dissipative mechanisms-each of them with out memory.**

## General Decay Law of Equilibrium System:

Observable property of condense material  $A$  defined with  $\Psi(t)$  as autocorrelation function. Normalize  $A(t)$  so that it averages zero, then dimensionless auto-correlation function is:

$$\Psi(t) \equiv \frac{\langle A(t) A(0) \rangle}{\langle A^2(0) \rangle}$$

$A(t)$  Observable is physical quantity  
say stress, strain rate, voltage  
current , etc...

Obeys

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

Meaning the process evolution (relaxation) is wrapped up (convoluted) in the above integral expression with 'Memory-Kernel'. That is the value at present instant (or present state) is being influenced by all the states the system has been running from initial time (space)  $\tau = 0, 1, 2 \dots t$



## Memory Integrals review:

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

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

### 1. Memory breaks down (No-Memory)

-Exponential Relaxation

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

At large times the value is zero, and that is too quickly there is no relation to what happened to system in past! Ergodic.

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

$$\Psi(t) = \Psi_0 \exp\{-K_0 t\}$$

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

$$K(t) = K_0$$

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

$$\Psi(t) = \Psi_0 \cos(\sqrt{K_0} t)$$

## Memory Integral (Contd.)

3. Slowly varying Kernel which for small time behaves as power law gives FDE

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

$$\frac{d}{dt} \Psi(t) = -\frac{1}{\tau^q} {}_0 D_t^{1-q} \Psi(t)$$

$$\tau^q = [K_0 \Gamma(q-1)]^{-1}$$

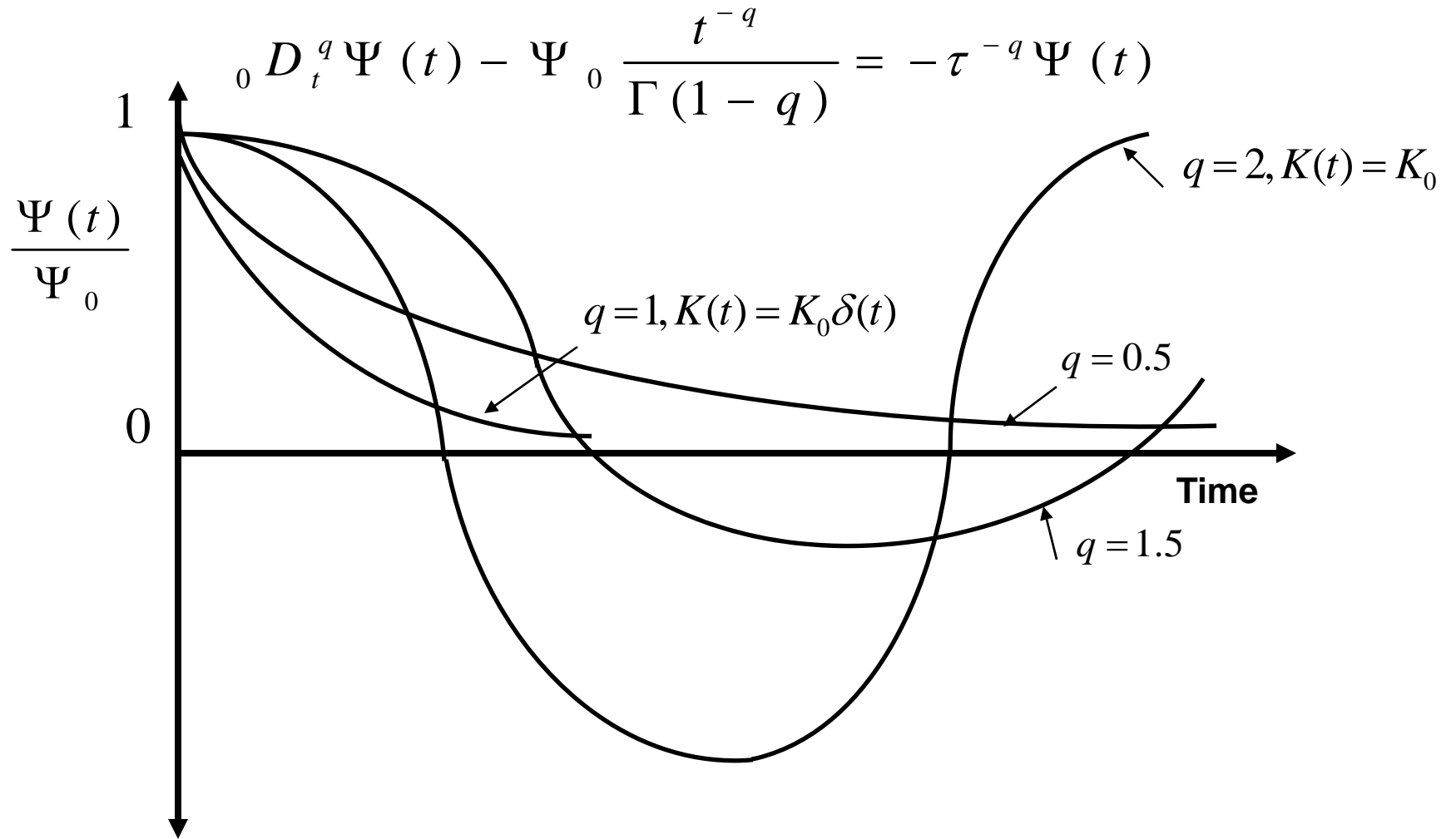
Apply  ${}_0 D_t^{-1}$  on both sides to get:

$$\Psi(t) - \Psi_0 = -\tau^{-q} {}_0 D_t^{-q} \Psi(t)$$

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

$${}_0 D_t^q \Psi(t) - \Psi_0 \frac{t^{-q}}{\Gamma(1-q)} = -\tau^{-q} \Psi(t)$$

# Memory Kernel & Fractional Differential Equation for Relaxation kinetics



## **Specifying the Memory Kernel in Relaxation Process:**

**The decay equation is generally describing the condense matter relaxation process, the specification of the memory kernel is difficult.**

**One way to ascribe this kernel as a representative particle in the material is subjected to fluctuating force exerted by its molecular environment and the time average of these fluctuating force is related to memory kernel, by 'fluctuating dissipating theorem' (Langevian-Brownian Motion)**

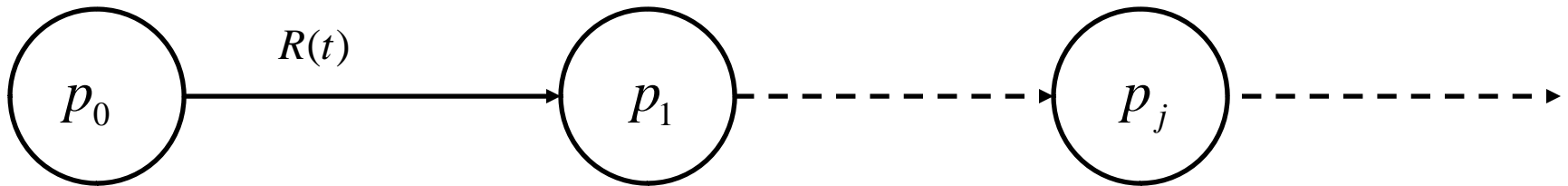
**Another way is 'return to equilibrium' in dynamic process governed by random evolution. This assumes that relaxation process occur as independent random variable in time. A heuristic physical motivation for describing the dynamical evolution of material composed of interacting particles as random-walk in phase-space. This random walk picture gives vivid conceptual picture of relaxation in many body system and occurrence of 'relaxation event times ( $\tau$ 's) after random (independent) time intervals. The intensity of these fluctuations has implications for character of the relaxation process and general 'universality class' of relaxation emerge from this approach. Relation between relaxing quantity may be related thus with 'renewal theory'-a generalization of Poisson's process with arbitrary hold times.**

# Generalized Poisson's process:

The system begins at state zero at initial time 0, and change its state at time T, where the T is to be randomly drawn from  $p(x) = \lambda e^{-\lambda x}$  What is the probability that system will be In state-1 at some arbitrary time:

$$P_1(t) = \int_0^t \lambda e^{-\lambda t} dt = 1 - e^{-\lambda t}$$

$$P_0(t) = e^{-\lambda t} \text{ Is the probability the system is at state-0 At the arbitrary time t.}$$



$$R(t) = \lambda; \frac{d}{dt} p_0(t) = -\lambda p_0; \frac{d}{dt} p_1(t) = -\lambda p_1(t) + \lambda p_0(t); \dots$$

Probability density for the 'first passage' time between the relaxation increment events: For a process with changing rate function is generalization of first passage equation of The Poisson's event is-

$$\frac{d}{dt} p_0(t) = -R(t) p_0(t) + \frac{d}{dt} R(t)$$

$$R(t) = p(t) + p(t) * R(t) = p(t) + \int_0^t d\tau p(t-\tau)R(\tau)$$

Feller's fluctuation theory

## Renewal Theory and Memory Kernel:

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

$$\Psi(0) = 1$$

Integrate both sides:

$$\Psi(t) - \Psi(0) = - \int_0^t d\tau \int_0^t d\tau K(t - \tau) \Psi(\tau)$$

$$\Psi(t) = 1 - \int_0^t d\tau R(t, \tau) \Psi(\tau)$$

$$R(t, \tau) = R(t - \tau) = \int_0^t d\tau K(t - \tau)$$

$$R(t) = \int_0^t d\tau K(\tau)$$

## Classes of relaxation:

$R(t)$  is the Renewal rate-Rate at which members drop out through death and where new members are added to keep total number of policy holder the same

$\Psi(t)$  is the decay in relative number of charter member of insurance group.

Here consider  $\Psi(t)$  as probability that initial state of the dynamic system's property  $A(0)$  persists (survives) up-to time 't'.

Continuum picture of Feller's fluctuating theory: 
$$R(t) = p(t) + \int_0^t d\tau p(t-\tau)R(t)$$

Where  $p(t)$  is the probability describing the time between relaxation increment events. The solution to this equation gives the rate kernel of the large-scale relaxation process.

The occurrence of 'universality' in  $\Psi(t)$  and  $R(t)$  in this model of condense matter relaxation from the observation that solution  $R(t)$  from above equation for large 't' depends on existence of moments of  $p(t)$

$$\langle t^n \rangle = \int_0^\infty d\tau (\tau)^n p(\tau)$$

1. Finite average and variance-Strong Relaxation
2. Infinite average and Infinite Variance-Strong Intermittent Relaxation
3. Finite average and Infinite Variance-More Intermittent Relaxation

## Strong Relaxation (Strong Mixing):

Relaxation event occurs with well defined average period  $\langle t \rangle < \infty$  with finite standard deviation (variance)  $\langle t^2 \rangle < \infty$

Relaxation with Poisson's probability distribution  $p(t) = \frac{1}{\tau_0} e^{-t/\tau_0}$  describing the time between relaxation increment events.

Then from:  $\frac{d}{dt} R(t) = \frac{d}{dt} p(t) + p(t)R(t)$  The rate is:  $R(t) = \frac{1}{\tau_0}$

Implying:  $\Psi(t) = e^{-t/\tau_0}$  Strongly decaying to zero.

Meaning, generally  $R(t)$  for any  $p(t)$  with finite  $\langle t \rangle$  and  $\langle t^2 \rangle$  has the asymptotic behavior dependence  $R(t) \approx \frac{1}{\tau_0} + \frac{C_1}{t}$ . That is rapidly approaching to constant rate.

Exponential decay (strong-relaxation/mixing) is commonly found in idealized medium, of condensed matter relaxation and more generally with one average time constant Having relaxation kernel with no memory.

$$R(t) = \int_0^t d\tau K(\tau) \quad K(t) = \frac{1}{\tau_0} \delta(t)$$

$$\Psi(t) = 1 - (\tau_0)^{-1} I_t^1 \Psi(t)$$

$$D_t^1 \Psi(t) = -(\tau_0)^{-1} \Psi(t)$$



## Weak relaxation-strongly intermittent relaxation:

Relaxation event with no average or standard deviation (power law)  $\langle t \rangle; \langle t^2 \rangle \rightarrow \infty$

$$R(t) \approx C_2 \frac{t^\phi}{t} = C_2 t^{\phi-1}$$

$0 < \phi < 1$  For large times  $t \rightarrow \infty$  implies highly intermittent relaxation

Indicates non-integral dimensions of time “Fractal Dimension” Hausdroff number a non-integer different from topological dimension. Gives degree of intermittency ‘fractal dimensions’ of time points at which relaxation process occurs.

‘Time is not flowing in uniform way perhaps has some power law in evolution’

A fractional integral/differential equation is required to have this relaxation:

$$\Psi(t) = 1 - (\tau_0)^{-1} I_t^1 \Psi(t)$$

$$D_t^1 \Psi(t) = -(\tau_0)^{-1} \Psi(t)$$



$$\Psi(t) = 1 - (\tau)^{-\phi} I_t^\phi \Psi(t)$$

$${}_0 D_t^\phi \Psi(t) - \frac{t^{-\phi}}{\Gamma(1-\phi)} = -\tau^{-\phi} \Psi(t)$$

## Rate increases with time

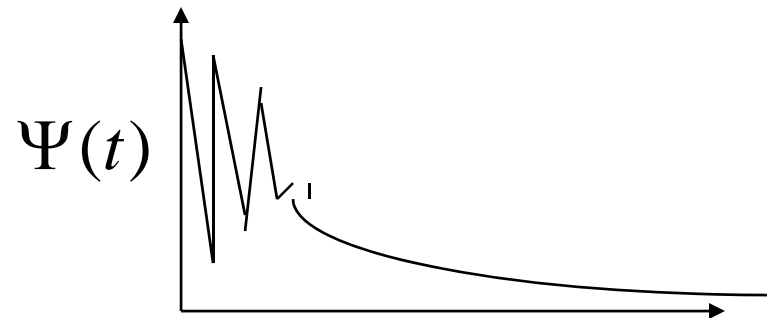
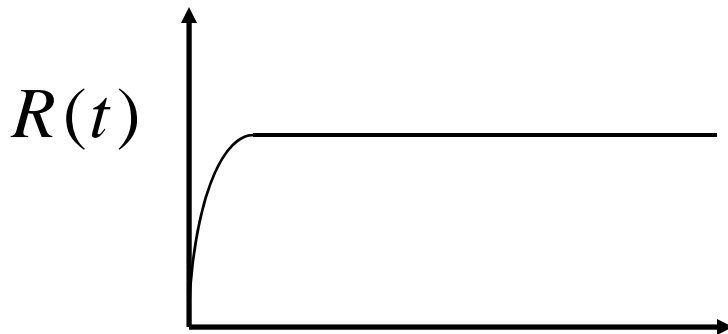
$$R(t) \approx t^{\phi - 1} \quad 1 < \phi \leq 2$$

As  $\phi \rightarrow 2$ , the fractal dimension approaches topological dimension,  
The kernel is approaching:

$$R(t) = \int_0^t d\tau K(\tau) \rightarrow \frac{t}{\tau_0} \text{ Rate is increases} \quad K(t) \rightarrow \frac{1}{\tau_0} \text{ Tends to constant memory}$$

$$\Psi(t) \approx \cos \frac{t}{\tau_0} \quad \text{Oscillatory relaxation}$$

Relaxation process occurring at small scales in condense matter. The situation may be significant for material systems far driven from equilibrium.



# Rate Generalization and Riemann-Liouville (Fractional) Differentials.

The classes of mixing can be generalized by rate with degree of intermittency as:

$$R_{\phi}(t) \approx \frac{\Omega_0}{\Gamma(\phi)} (t)^{\phi-1} \quad 0 < \phi \leq 1$$

$\Omega_0$  Is 'coupling-constant' governing the relaxation rate intensity  $\Gamma(\phi)$  is normalization factor

$$\lim_{\phi \rightarrow 1} R_{\phi}(t) \approx \Omega_0 = \frac{1}{\tau_0} \quad \text{Strong mixing with no intermittency}$$

Insertion of  $\phi$ , characterizing degree of intermittency or RL operator yields FDE

$$\Psi(t) = 1 - \int_0^t d\tau R(t, \tau) \Psi(t) = 1 - \Omega_0 I_t^{\phi} \Psi(t)$$

The relaxation process is described by Mittag-Leffler function (exact solution)

$$\Psi(t) = E_{\phi}(-\Delta_{\tau}) \quad \text{With} \quad \Delta_{\tau} = \left( \frac{t}{\tau_0} \right)^{\phi} \quad \& \quad \tau_0 = (\Omega_0)^{-1/\phi}$$

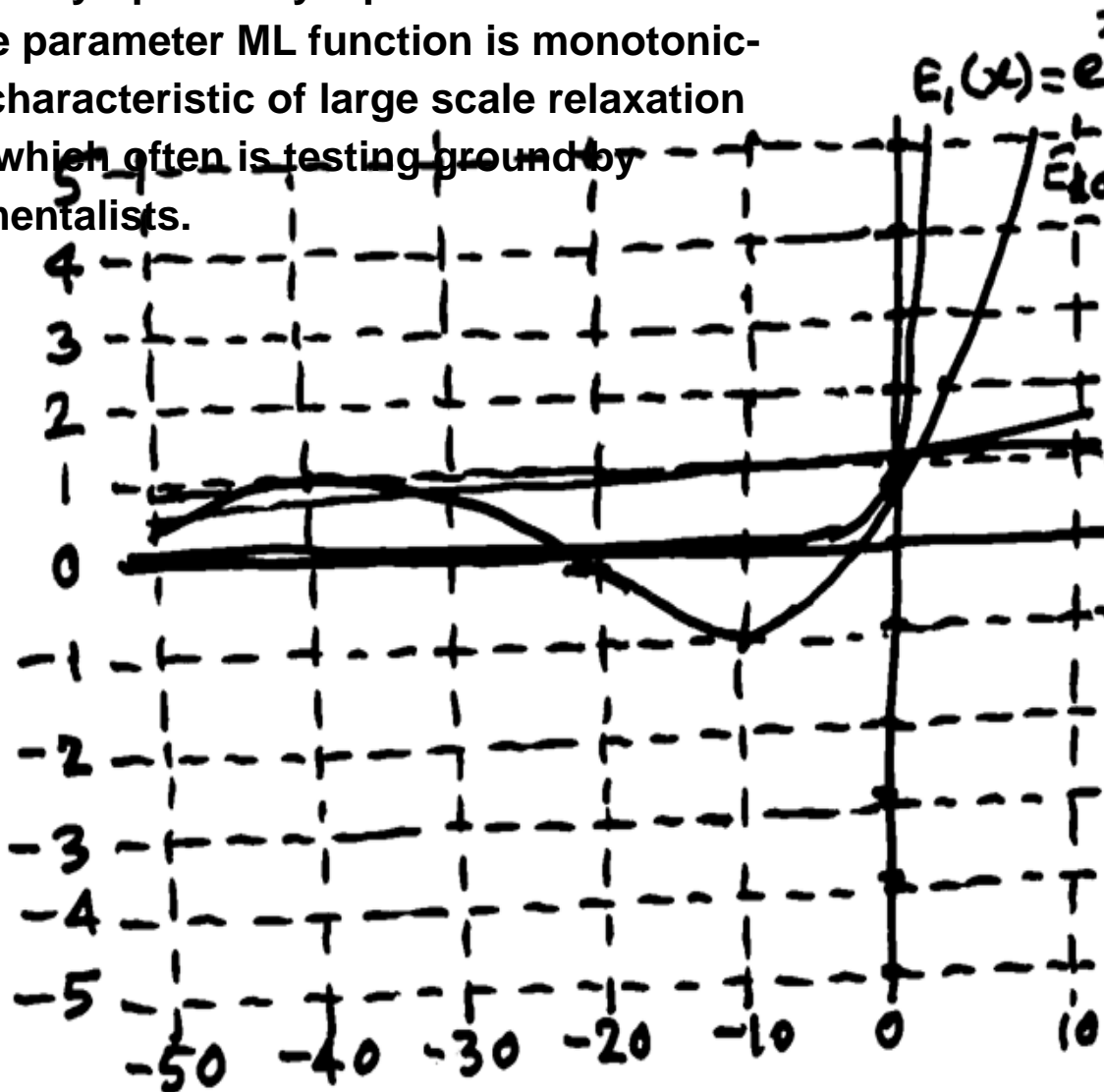
Asymptotically for weak relaxation (mixing)

$$\Psi(t, \phi) \approx \left( \frac{t}{\tau_0} \right)^{-\phi} \quad ; t \rightarrow \infty$$

# MITTAG-LEFFLER FUNCTION PLOT

Mittag-Leffler function is generalization of Exponential function ( which is observed in strong mixing) different 'arguments' of ML gives different rate and asymptotically a power function.

The one parameter ML function is monotonic- this is characteristic of large scale relaxation decay which often is testing ground by experimentalists.



$$E_{\alpha}(x) = \sum_{k=0}^{\infty} \frac{x^k}{\Gamma(\alpha k + 1)}$$

$$E_1(x) = e^x$$

## Series Solution

The FDE gives a series solution which closes down to Higher Transcendental Function. Mittag Leffler is one of them. The general class are Miller-Ross, Robotnov-Hartley, Agarwal, Srivastava, Fox Functions, are all generalizations of Transcendental Trigonometric Hyperbolic functions found in Integer Order Calculus.

$$\begin{aligned}
 E_{\phi}(-\Delta_{\tau}) &= \sum_{k=0}^{\infty} \frac{(-\Delta_{\tau})^k}{\Gamma(\phi k + 1)} = 1 - \frac{\Delta_{\tau}}{\Gamma(\phi + 1)} + \frac{\Delta_{\tau}^2}{\Gamma(2\phi + 1)} - \frac{\Delta_{\tau}^3}{\Gamma(3\phi + 1)} + \dots \\
 &= 1 - \frac{\left(\frac{t}{\tau_0}\right)}{\Gamma(\phi + 1)} + \frac{\left(\frac{t}{\tau_0}\right)^2}{\Gamma(2\phi + 1)} - \frac{\left(\frac{t}{\tau_0}\right)^3}{\Gamma(3\phi + 1)} + \dots \quad \tau_0 = (\Omega_0)^{-1/\phi}
 \end{aligned}$$

$$E_{\phi \rightarrow 1}(-\Delta_{\tau}) = e^{-\Delta_{\tau}} = e^{-\left(\frac{t}{\tau_0}\right)} \quad \text{Strong mixing without intermittency}$$

Changing temperature (and thus the magnitude of the coupling constant  $\Omega_0$ ) the functional form of relaxation function is invariant. Provided  $\phi$  does not change in the temperature interval. This time temperature invariant property is due to scale invariant memory kernel.

# Scale Invariant Memory Kernel from Power Law relaxation rate for weak mixing

$$\Psi(t; \phi) \approx \left( \frac{t}{\tau_0} \right)^{-\phi}$$

$$K(t, \phi) = \frac{d}{dt} R(t) = \frac{d}{dt} \frac{\Omega_0}{\Gamma(\phi)} t^{\phi-1} = \frac{\Omega_0}{\Gamma(\phi-1)} t^{\phi-2}$$

$$0 < \phi \leq 1$$

$$K(\mu t; \phi) = \mu^{\phi-2} K(t; \phi)$$

We may take a note that rate in strong relaxation is constant and its integral from zero to infinity is infinite, and the function  $\Psi(t)$  decays to zero very fast. For rate that decays fast with time (say exponentially) so that its integral from zero to infinity is 'finite' then the function  $\Psi(t)$  no longer decays to zero at large times.

This Non-Ergodic limiting behavior corresponds to material which is not in equilibrium-common in glassy materials.

Weak class of relaxation process involving fractional operator leads to breakdown of ergodicity as classically defined. This  $\phi$  may define 'degree of ergodicity' or 'quasi-mixing' or 'quasi-relaxation'.

## Sense for intermittency & fractional differential operator (comment)

The occurrence of weak mixing (relaxation) leads to non-trivial constitutive relations involving fractional operators. The Mittag-Leffler function

$$\Psi(t; \phi) \approx \left( \frac{t}{\tau_0} \right)^{-\phi}$$

Which can be good approximations over appreciable time scales (Scale-Invariance)-to Evaluate these weak relaxation processes in condense matter physics. For example if We introduce this approximation for shear relaxation, into the function relating stress & strain rate, in the limit of linear responses then we get equations for hybrids as in between pure Newtonian liquid  $\phi = 1$  and pure Hook's solid  $\phi = 0$  .

$$\sigma(t) \approx k I_t^{1-\phi} \dot{\varepsilon}(t) \quad \phi \in [0, 1]$$

Provides good approximation for 'polymer-gel' and is useful expression for understanding the 'internal' effect on the asymptotic frequency dependence of 'viscosity' of the small molecule liquids.

Note that usual definition of viscosity is not valid in this formulation; thus it becomes appropriate to define 'new type of transport coefficients'.

These fractional dynamic representations are also valid for electrical devices (Fractances) amalgamation of pure resistance pure capacitors and pure inductances. More-so the observed electrochemical process gives Warburg impedances in battery dynamics as half order element!!

$$v(t) \approx k D_t^{\phi} \dot{q}(t) \quad \phi \in [-1, 1]$$

## Spatial Clustering:

The previous discussed models for relaxations in condensed matter does not account for heterogeneity in matter which develop transiently through inter-particle interactions.

Cooled liquids develops large scale heterogeneity which modifies the relaxation process

This gives rise to 'stretched exponential' relaxation (mixing); even for systems which were locally 'strong-relaxing'.

$$\Psi(t) \approx \exp \left[ -\Omega_0 t^{1-\beta} / (1-\beta) \right]$$

$$\beta = 2/3 \quad \text{linear}$$

$$\beta = 1/2 \quad \text{sheet}$$

$$\beta = 2/5 \quad \text{clumps}$$

This denotes measure of fluid heterogeneity is related to geometry of cluster, can occur  
In clusters having fractal structures!!



## Memory Kernel for Stretched Exponential Relaxation:

$$\Psi(t) \approx \exp\left[-\Omega_0 t^{1-\beta} / (1-\beta)\right]$$

$$K(t, \tau) = \Omega_0 \tau^{-\beta} \delta(t - \tau)$$

$\beta = 0$  Strong relaxation without clustering heterogeneity.

$$\begin{aligned} \frac{d}{dt} \Psi(t) &= - \int_0^t d\tau K(t - \tau) \Psi(\tau) \\ &= - \int_0^t d\tau \Omega_0 \tau^{-\beta} \delta(t - \tau) \Psi(\tau) = -\Omega_0 \int_0^t d\tau \delta(t - \tau) \left\{ \tau^{-\beta} \Psi(\tau) \right\} \\ &= -\Omega_0 t^{-\beta} \Psi(t) \end{aligned}$$

$$\boxed{\frac{d\Psi(t)}{dt} = -\Omega_0 t^{-\beta} \Psi(t)}$$

## Relaxation with intermittency and cluster heterogeneity $\Psi(t, \phi, \beta)$ :

The relaxation process  $\Psi(t, \phi, \beta)$  will be Hybrid of Mittag-Leffler and Stretched Exponential  
With new Rate and Memory Kernel describing the process:

$$R_{\phi, \beta}(t, \tau) = \Omega_0 \tau^{-\beta} (t - \tau)^{\phi-1} / \Gamma(\phi) \quad \phi > 0 ; \beta \leq 1$$

$$\Psi(t; \phi, \beta) = 1 - \int_0^t d\tau R_{\phi, \beta}(t, \tau) \Psi(\tau; \phi, \beta)$$

$$\Psi(t; \phi, \beta) = 1 - \Omega_0 \int_0^t d\tau \left[ (t - \tau)^{\phi-1} \tau^{-\beta} / \Gamma(\phi) \right] \Psi(\tau; \phi, \beta)$$

**Erdelyi-Kober Fractional Operator:**

$$I_t^{p, q} f(t) = t^{-(p+q)} \int_0^t d\tau \left[ (t - \tau)^{q-1} \tau^p / \Gamma(q) \right] f(\tau)$$

**Relation to Riemann-Liouville Operator is:**

$$I_t^{p, q} f(t) = t^{-(p+q)} I_t^q \left[ t^p f(t) \right]$$

## Solution to Relaxation Equation with intermittency & clustering:

$$\Psi(t; \phi, \beta) = \sum_{k=0}^{\infty} a_k(\phi, \beta) [z_{\Omega}(\phi, \beta)]^k ; a_0(\phi, \beta) = 1$$

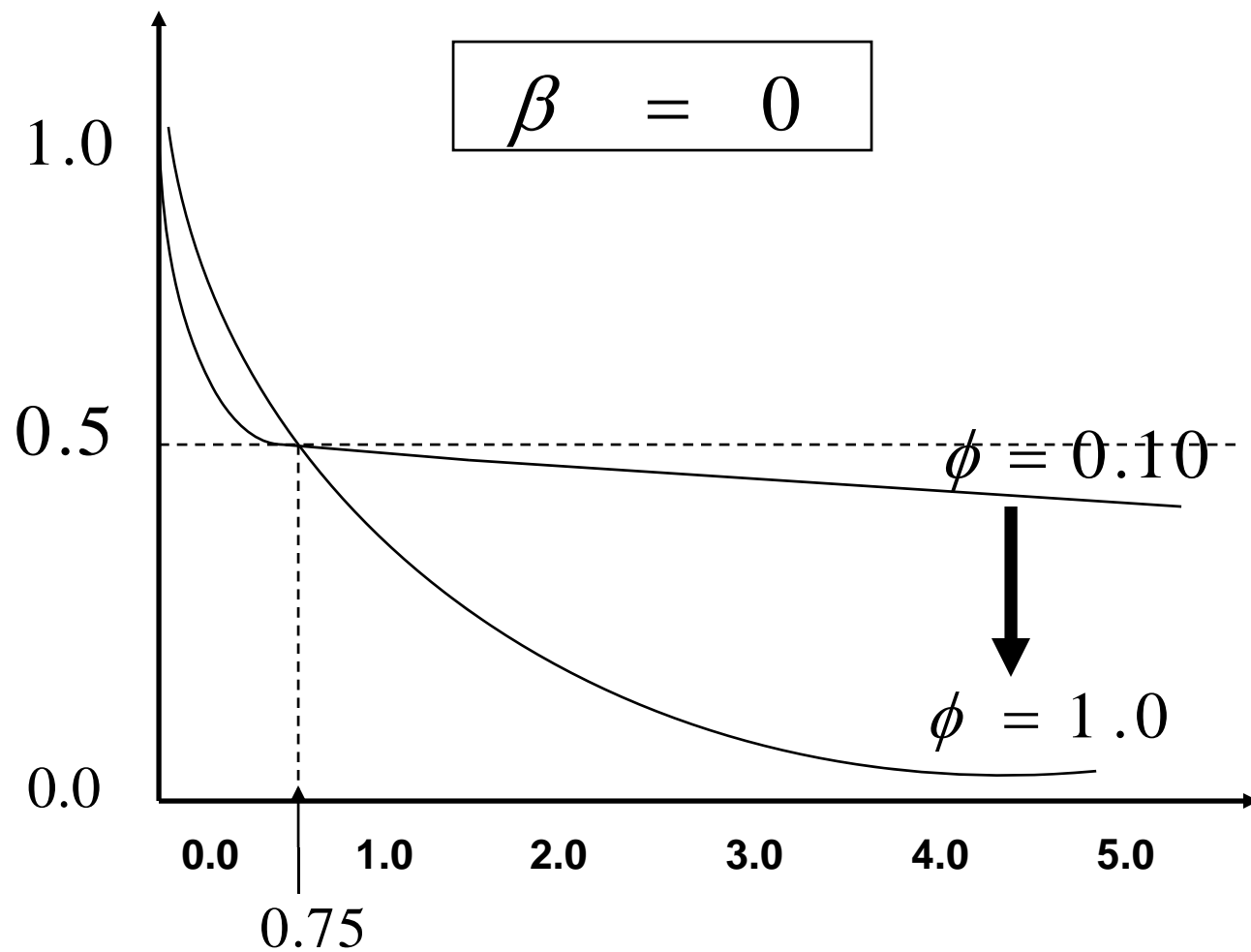
$$a_k(\phi, \beta) = \prod_{m=1}^k \frac{\Gamma(1 + m\hat{\phi} - \phi)}{\Gamma(1 + m\hat{\phi})}; k > 0$$

$$\hat{\phi} = \phi - \beta ; 0 < \hat{\phi}, \phi ; \beta \leq 1$$

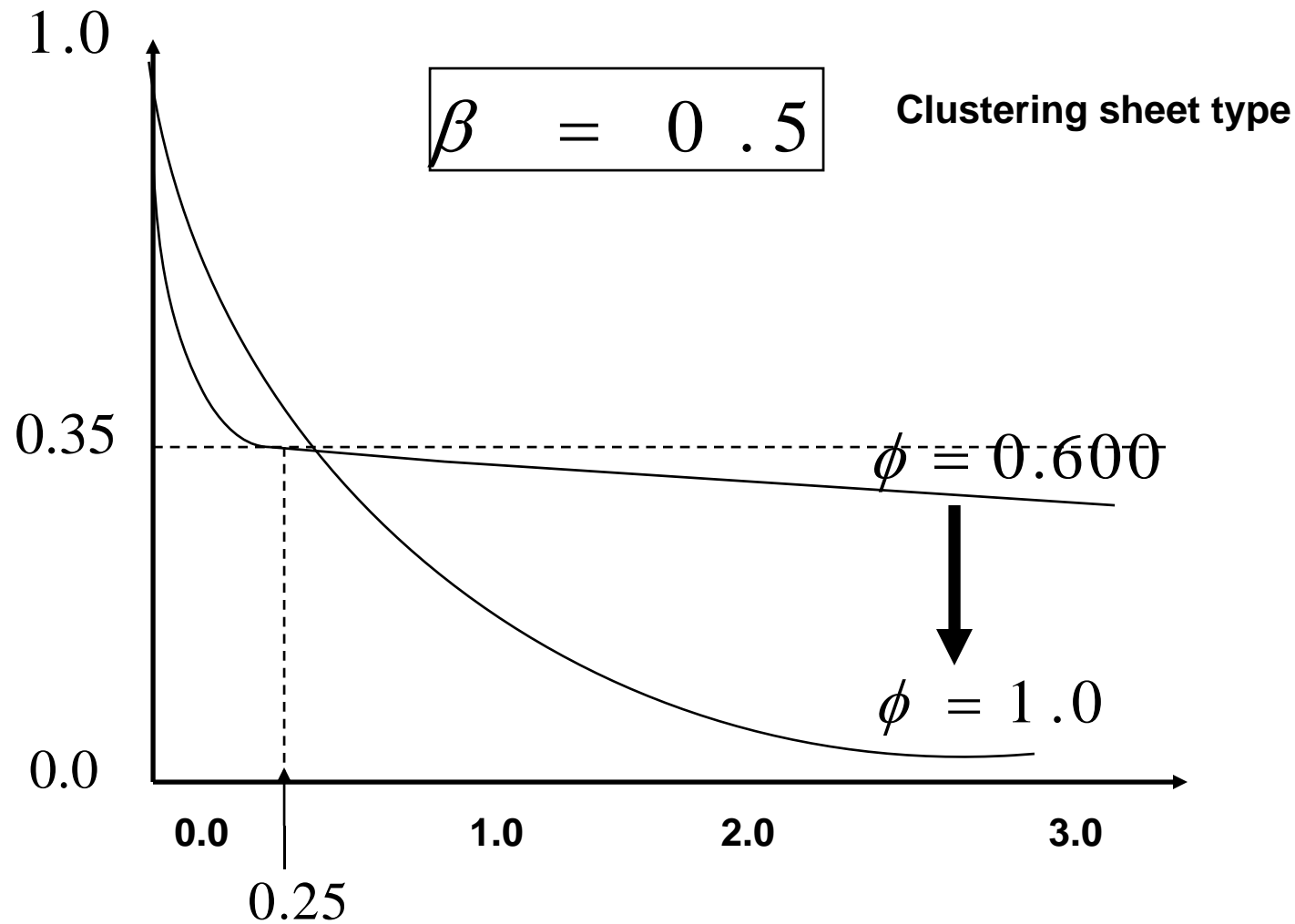
$$z_{\Omega}(\phi, \beta) = \Omega_0 \tau^{\hat{\phi}} = \left( \frac{t}{\tau^*} \right)^{\hat{\phi}} ; \tau^*(\phi, \beta) = \Omega_0^{-1/\hat{\phi}}$$

**Mittag-Leffler for  $\beta=0$  and stretched exponential for  $\phi=1$  otherwise hybrid of Mittag-Leffler & Stretched exponential.**

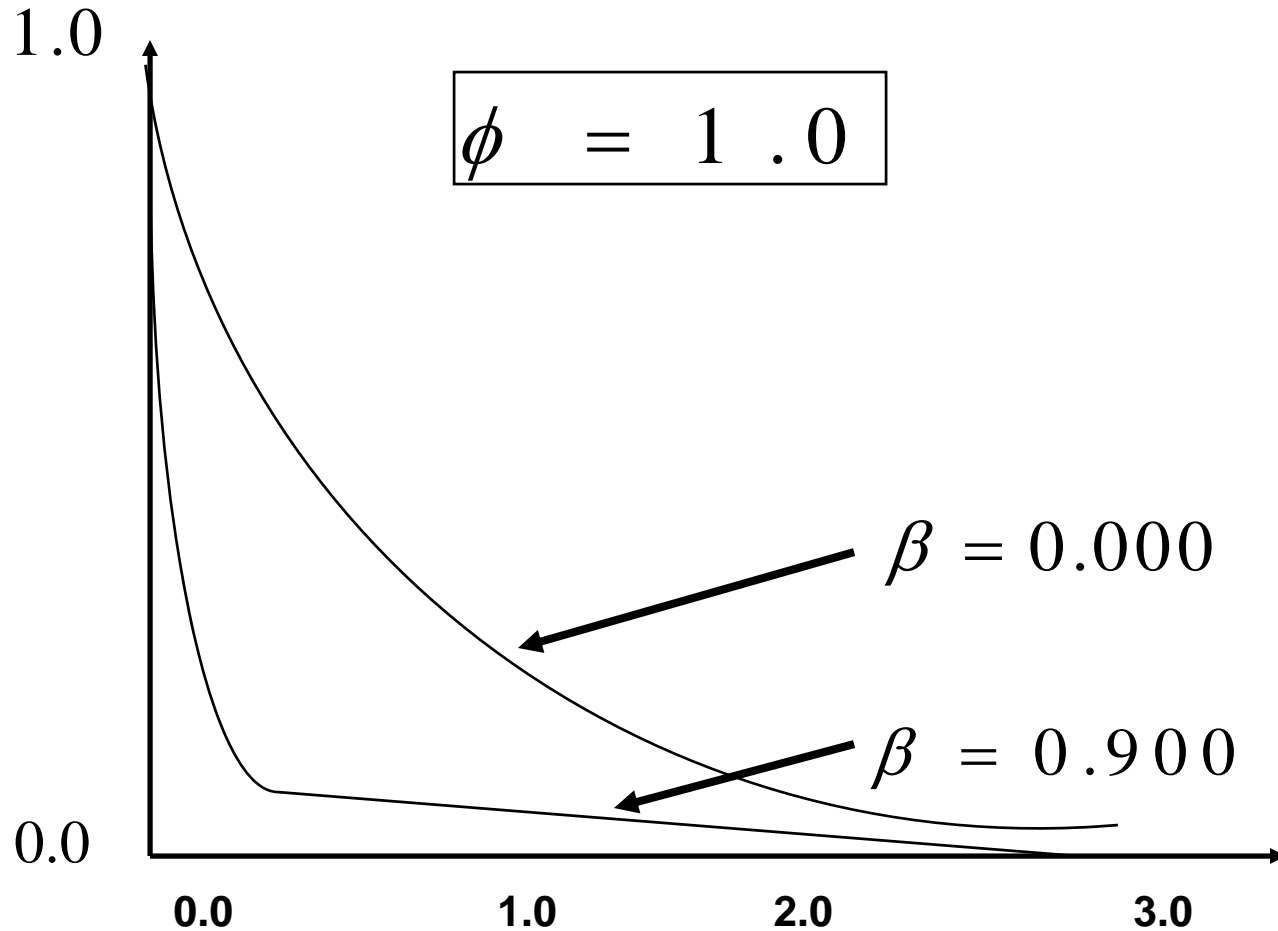
# Plots of relaxation curves weak relaxation without clustering (ML)



# Plots of relaxation curves Hybrids of ML & Stretched Exponential



## Plots of relaxation curves Strong Relaxation with Clustering:



$\Psi(t; \phi \rightarrow 1, \beta)$  Is stretched exponential relaxation Kohlrausch-William's Watts law  
Widely used to correlate relaxation data in complex liquids.

## Diffusion-classical

Fick's law of continuity (II law of diffusion)

Fick's constitutive equation (I law of diffusion  
like Fourier's law of heat conduction)

$$\frac{\partial}{\partial t} u(x, t) = - \frac{\partial}{\partial x} j(x, t)$$
$$j(x, t) = -\mathbb{D} \frac{\partial}{\partial x} u(x, t)$$

Relating diffusing quantity (temperature, charges, voltage, concentration etc.)  
and its flux

Combining the two we obtain Fick's law of diffusion as Diffusion Equation

$$\frac{\partial}{\partial t} u(x, t) = \mathbb{D} \frac{\partial^2}{\partial x^2} u(x, t)$$

With initial condition as delta function, and natural BC  $u(x, 0) = \delta(x); u(|x| \rightarrow \infty, t) = 0$   
we get Gaussian solution as:

$$u(x, t) = \frac{1}{\sqrt{4\pi\mathbb{D}t}} \exp\left(-\frac{x^2}{4\mathbb{D}t}\right)$$

For a very small time just at the start of diffusion process, there exist finite  
amount of diffusing quantity at very large distance, meaning diffusing elements  
posses infinite velocity!

## Diffusion Generalization:

The Fick's diffusion equation for vector form is thus: 
$$\frac{\partial}{\partial t} u(\bar{X}, t) = \mathbb{D} \nabla^2 u(\bar{X}, t)$$

For isotropic case 
$$\frac{\partial}{\partial t} u(r, t) = \mathbb{D} r^{1-d} \frac{\partial}{\partial r} r^{d-1} \frac{\partial}{\partial r} u(r, t)$$

$d$ -is Euclidian dimension of 1, 2, 3. The Laplacian operator is generalized  
1- is planar 2- cylindrical, and 3- spherical coordinates

One may too re-write the Laplacian operator with geometrical parameter  $g$  with  
0- for planar,  $\frac{1}{2}$  for cylindrical and 1-for spherical coordinate (geometry)

$$\frac{\partial}{\partial t} u(x, t) = \mathbb{D} \frac{\partial^2}{\partial r^2} u(x, t) + \frac{2g\mathbb{D}}{r} \frac{\partial}{\partial r} u(x, t)$$

These generalization of Laplacian operator give integer order diffusion equation. Can these number be arbitrary?. Well yes they can and then the Laplacian becomes fractional differential equation-giving fractional order diffusion equation. Well, if the diffusing species is moving in a matrix of well distributed obstacles or traps or attractors can they rate at fast or slow? There is thus possibility of this not following Gaussian or integer order law.



# Catteneo's Diffusion

**Catteneo diffusion: allows to have the diffusing flux 'relaxes' with some time constant , modifies the first law of Fickian diffusion as:**

$$j(x, t) + \tau \frac{\partial}{\partial t} j(x, t) = -\mathbb{D} \frac{\partial}{\partial x} u(x, t)$$

**Putting this new law in continuity equation (II law of Fick's) we get:**

$$\frac{\partial}{\partial t} u(x, t) + \tau \frac{\partial^2}{\partial t^2} u(x, t) = \mathbb{D} \frac{\partial^2}{\partial x^2} u(x, t)$$

**Catteneo diffusion equation (1948), it is like telegrapher's equation and has finite phase velocity of diffusing quantity,**

$$v_{ph} = \sqrt{\frac{\mathbb{D}}{\tau}}$$

**and not-infinite!**

**In a media with MEMORY the flux of diffusing quantity is related to previous history through relaxation function (Memory-Kernel)  $K(t)$**

$$j(x, t) = - \int_0^t K(t - t') \frac{\partial u(x, t')}{\partial x} dt'$$

**This convolution is also Boltzman's superposition law.**

# Catteneo's Diffusion & Memory Integral

Using this Memory Integral in the Catteneo's flux relaxation equation we get:

$$j(x,t) + \tau \frac{\partial}{\partial t} j(x,t) = - \left( \tau \frac{\partial}{\partial t} + 1 \right) \int_0^t K(t-t') \frac{\partial u(x,t')}{\partial x} dt' = -\mathbb{D} \frac{\partial u(x,t)}{\partial x}$$

By use of Leibniz's rule of differentiation of integral  $D[D^{-1}f] = D^{-1}[Df] + f(0)$  we get:

$$j(x,t) + \tau \frac{\partial}{\partial t} j(x,t) = -\tau K(0) \frac{\partial u(x,0)}{\partial x} - \int_0^t \left[ \tau \frac{\partial}{\partial t} K(t-t') + K(t-t') \right] \frac{\partial u(x,t')}{\partial x} dt' = -\mathbb{D} \frac{\partial u(x,t)}{\partial x}$$

We can take (from above)

$$\tau K(0) = \mathbb{D} \quad \text{and} \quad \tau \frac{\partial}{\partial t} K(t) + K(t) = 0$$

Solving for relaxation function or memory kernel we obtain:

$$K(t) = \frac{\mathbb{D}}{\tau} \exp\left(-\frac{t}{\tau}\right)$$

Making non-local (non-Markovian) theory of transport compatible with Catteneo equation!

## Generalized Catteneo's Equation:

A memory kernel of the form

$$K(s) = \frac{\mathbb{D}_M}{\tau^\nu} \frac{s^{-1}}{1 + \tau^{-1} s^{-\nu}} \quad \text{In Laplace form, or} \quad K(t) = \frac{\mathbb{D}_M}{\tau^\nu} E_{\nu,1} \left[ -\left(\frac{t}{\tau}\right)^\nu \right]$$

$0 < \nu < 1$

Gives fractional diffusion equation as:

$$\frac{\partial}{\partial t} u(x, t) + \tau^\nu \frac{\partial^{\nu-1}}{\partial t^{\nu-1}} \frac{\partial^2}{\partial t^2} u(x, t) = \mathbb{D}_M \frac{\partial^{\nu-1}}{\partial t^{\nu-1}} \frac{\partial^2}{\partial x^2} u(x, t)$$

And corresponding Generalized Catteneo Equation (GCE) is:

$$j(x, t) + \tau^\nu \frac{\partial^\nu}{\partial t^\nu} j(x, t) = -\mathbb{D}_M \frac{\partial^{\nu-1}}{\partial t^{\nu-1}} \frac{\partial}{\partial x} u(x, t)$$

A flux relaxation function (memory kernel) of Mittag-Leffler type which for a 'long time' as a power law behavior  $K(t) \approx t^{-\nu}$  can be associated with GCE Fractional Catteneo Equation or Fractional Diffusion Equation

## **Fractional Calculus**

**may have a different expression and is generalization of classical calculus**

**Perhaps can be utilized to express nature in exact way!!**

**to express happenings inside a**

**'Disordered-Media'**

**That is to**

**'Order the Disordered System'**

**Remember that 'Mathematical tools' go far beyond**

**our physical understanding**

**Several miles to go!!**