From diffusion to anomalous diffusion: over a century after Einstein

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Outline

• From diffusion to anomalous diffusion

• Strange kinetics (subdiffusion)

• Strange kinetics: Levy flights and walks
The Diffusion Equation

\[ \frac{\partial}{\partial t} P(x,t) = K \frac{\partial^2}{\partial x^2} P(x,t) \]
The Diffusion Equation (1855)

Continuity

\[ \frac{\partial}{\partial t} n(\vec{x}, t) = -\text{div} \vec{j}(\vec{x}, t) \]

+ linear response

\[ \vec{j}(\vec{x}, t) = -K \text{grad} n(\vec{x}, t) \]

\[ \Rightarrow \text{the diffusion equation} \]

\[ \frac{\partial}{\partial t} n(\vec{x}, t) = K \Delta n(\vec{x}, t) \]

the Green’s function solution

\[ n(\vec{x}, t) = (4\pi Kt)^{-d/2} \exp \left( -\frac{\vec{x}^2}{4Kt} \right) \]

Essentially an equation for the pdf: \( n(\vec{x}, t) \rightarrow P(\vec{x}, t) \)
“The problem of the random walk”

“Can any of you readers refer me to a work wherein I should find a solution of the following problem, or failing the knowledge of any existing solution provide me with an original one? I should be extremely grateful for the aid in the matter. A man starts from the point O and walks l yards in a straight line; he then turns through any angle whatever and walks another l yards in a second straight line. He repeats this process n times. Inquire the probability that after n stretches he is at a distance between r and $r + \delta r$ from his starting point O”.

Karl Pearson

*Nature, 1905*
Pearson’s random walk
Brownian Motion
Emergence of Normal Diffusion

Einstein, 1905

Postulates:

i) Independent particles

ii) The particle’s motion during two consequent intervals is independent

iii) The displacement during t is s.

For unbiased diffusion: \( \phi(s) = \phi(-s) \)

Moreover, \( \lambda^2 = \int_{-\infty}^{\infty} s^2 \phi(s) ds < \infty \)

Essentially the Random Walk Model (1880, 1900, 1905×2)
Motion as a sum of small independent increments: \( x(t) = \sum_{i=1}^{N} s_i \)

mean free path
\[
\lambda = \langle s_i^2 \rangle^{1/2}
\]
\( 0 < \lambda < \infty \)

mean relaxation time
\[
\tau \propto \frac{\lambda}{\langle v^2 \rangle^{1/2}}
\]
\( 0 < \tau < \infty \)
\( N \equiv t / \tau \)

\[
\langle x^2(t) \rangle = \left( \sum_{i=1}^{N} s_i \right)^2 = N \langle s^2 \rangle + 2N \langle s_i s_j \rangle
\]

the central limit theorem
\[
P(x, t) = \left(4\pi K t\right)^{-1/2} \exp \left(-\frac{x^2}{4Kt}\right)
\]

with \( K \propto \langle v^2 \rangle \tau \equiv \frac{\lambda^2}{\tau} \)
Brownian motion (simple random walk)

\[ < r^2(t) > \sim Kt \quad ; \text{K is the diffusion coefficient} \]

Anomalous diffusion

(a) \[ < r^2(t) > \sim t^\alpha \]

\( \alpha < 1 \) Subdiffusion (dispersive)
\( \alpha > 1 \) Superdiffusion

(b) \[ < r^2(t) > \sim \log^\beta(t) \]

strong anomaly

Aim: creating framework for treating anomaly and strong anomaly in diffusion.
Physics of Disorder - Subdiffusion

H. Scher and E. Montroll, 1975

in crystalline solids

\[ I(t) = \frac{dP}{dt} = \frac{d}{dt} \int_0^L n(l, t) \, dl \]

**FIG. 10.** Normalized current trace \( I(t)/I(t_0) \) vs \( t/t_0 \), expected for a propagating Gaussian packet. Curve (1) corresponds to the longer \( t_0 \) and curve (2) corresponds to the shorter \( t_0 \). This figure illustrates the incompatibility of a Gaussian with the universality of \( I(0) \).
In disordered solids (no matter organic or inorganic...)

FIG. 7. A log$I$-log$t$ plot indicating the current $I(t)$ associated with a packet of carriers moving, in an electric field, with a hopping-time distribution function $\psi(t) \sim t^{-(1-\alpha)}$, $0 < \alpha < 1$, towards an absorbing barrier at the sample surface.
Subdiffusion

[Images showing subdiffusion phenomena with plots and graphs demonstrating diffusion characteristics and analysis.]
**Line C: Lipid granules, normally inside the cell (untreated)**
Diffusion of tracers in fluid flows.

Large scale structures (eddies, jets or convection rolls) dominate the transport. Example: Experiments in a rapidly rotating annulus (Swinney et al.).

Ordered flow: Levy diffusion (flights and traps)
Weakly turbulent flow: Gaussian diffusion
Superdiffusion
Classical scattering in an egg crate potential.

\[ \langle r^2(t) \rangle \approx t^{7/4} \]

Searching for Food
The scaling laws of human travel
The scaling laws of human travel

![Graph showing the scaling laws of human travel.](image)
Anomalous is Normal...
Frameworks for anomalous diffusion

1. Generalized diffusion equation
2. Fractional Brownian motion
3. Random velocity fields
4. Self avoiding walks
5. Fractional Fokker Planck Equation (FFPE)
6. Continuous Time Random Walk (CTRW)
7. Random walk on fractal structures
CTRW Frameworks

1. \( \psi(r,t) = \) Probability distribution to make a step \( r \) in time \( t \).  
   Single motion event

2. Jump Model

\[
P(r, t) = \text{p.d. of being at } r \text{ at time } t.
\]

\[
P(k, u) = \frac{\phi(u)}{1 - \psi(k, u)} \text{ Fourier-Laplace}
\]

3. \( \psi(r, t) = p(r)\psi(t) \), decoupling

4. Velocity model:

\[
P(r, t) = \int \eta(r - r', t - \tau) \widetilde{\Psi}(r', \tau) dr' d\tau
\]

\[
P(k, s) = \frac{\widetilde{\Psi}(k, s)}{1 - \psi(k, s)} \text{ Probability to move distance } r' \text{ at } \tau
\]
5. Possible generalizations:
   Distribution of velocities
   Coupled models
   Distance dependent velocities

6. \[ \tilde{\Psi}(r, t) \sim \delta(|r| - vt) \int_{t}^{\infty} \psi(t') dt' \]
1. Within the random walk framework:
   (a) Small changes in step length or time **not** enough
   (b) Need for processes on **all** scales;
   broad distribution
   no moments

2. \( < r^2(t) > \sim K t^\alpha \)
   Broad distributions
   Simple distributions

3. Long tailed distributions
   temporal (subdiffusion)
   spatial (superdiffusion)
Waiting Times

Continuous time random walk (CTRW) model.
Subdiffusion (dispersive transport)

\[ t^\alpha, \quad \alpha < 1 \]

1. Jump Model
   \( \psi(r, t) = p(r)\psi(t) \), decoupling
   
   \( p(r) \) well behaved
   
   \( \psi(t) \sim t^{-\alpha - 1}, \quad 0 < \alpha < 1 \)
   
   \( < t > = \infty \) no time scale

2. From CTRW:
   
   \( < r^2(t) > \sim t^\alpha, \quad 0 < \alpha < 1 \)
Explanation: The CTRW

\[ \rho(E_i) \propto \exp(-E_i / E_0) \]
\[ \tau_i = \tau_0 \exp(-E_i / k_B T) \]

The waiting-time distribution between the two jumps \( \psi(t) \propto t^{-1-\alpha} \)
with \( \alpha = k_B T / E_0 \)

Diffusion anomalies for \( 0 < \alpha < 1 \): the mean waiting time diverges!

Note: The CTRW processes with the power-law waiting times (with \( 0 < \alpha < 1 \)) are always nonstationary!
Gaussian, Exponential and Pareto Distributions
The Subordination

PDF of the particle’s position after $n$ steps (say, a Gaussian)

Probability to make exactly $n$ steps up to the time $t$

The limiting form of the characteristic function in Laplace representation

$$\psi (t) \propto t^{−1−\alpha} \Rightarrow \psi (u) \equiv 1 − Au^\alpha$$

The second moment $\langle x^2 (t) \rangle \propto t^\alpha$
1. Brownian motion

\[ P(r, t) \sim t^{-1/2} f(\xi) \]

\[ f(\xi) = \exp(-c \xi^2), \quad \xi = x / t^{1/2} \]

Gaussian \quad \langle x^2(t) \rangle \sim t

2. Subdiffusion

\[ P(r, t) \sim t^{-\alpha/2} f(\xi) \]

\[ \xi = r / t^{\alpha/2} \]

\[ f(\xi) \sim \begin{cases} 
\exp(-a_1 \xi - a_2 \xi^2) & \text{small } \xi \\
\exp(-b \xi^\delta), & \text{large } \xi, \quad \delta = 2/(2 - \alpha) 
\end{cases} \]

“Stretched” Gaussian \quad \langle x^2(t) \rangle \sim t^\alpha
Diffusion of tracers in fluid flows.

Large scale structures (eddies, jets or convection rolls) dominate the transport. Example: Experiments in a rapidly rotating annulus (Swinney et al.).

Ordered flow: Levy diffusion (flights and traps)
Weakly turbulent flow: Gaussian diffusion
Forms of stable distributions (Levy)

\[ P_\alpha(x \to \infty) \sim \frac{1}{|x|^{1+\alpha}} \]

\[ 0 < \alpha < 2 \]

\[ P_\alpha(x \to \infty) \sim \frac{1}{x^{1+\alpha}} \]

\[ 0 < \alpha < 1 \]
5. Possible generalizations:
   - Distribution of velocities
   - Coupled models
   - Distance dependent velocities

6. \[ \tilde{\Psi}(r, t) \sim \delta(|r| - vt) \int_{t}^{\infty} \psi(t') dt' \]
Normal vs. Anomalous Diffusion

Normal diffusion

Superdiffusion

Gauss
$n = 1000$

Cauchy
$n = 3000$
Levy-Pareto

- Self similarity (fractals)
  \[ \langle t \rangle = \infty \]
  or
  \[ \langle x^2(n) \rangle = \infty \]

- Modifying the 1905 assumptions
  \( \tau \to \infty \)
  \( \lambda \to \infty \)

- Memory or “Funicity” (after “Funes the memorious” by Jorge Luis Borges)
Coupled model

Possibility to include within the velocity model, interruptions by spatial localization (jump model)

\[
P(r,t) = \Psi(r,t) + \int_0^t \psi(r,t')\tilde{\Phi}(t-t')dt' + \int_{-\infty}^t \int_0^t \int_0^{t'} dt'' \psi(r',t'')\tilde{\psi}(t'-t'')\Psi(r-r',t-t') + \ldots
\]

\[
P(k,u) = \frac{\Psi(k,u) + \tilde{\Phi}(u)\psi(k,u)}{1 - \psi(k,u)\tilde{\psi}(u)}
\]
Conventional Wisdom

On renewal processes with non-exponential pausing times:

“It is hard to find practical examples besides the bus running without schedule along a circular route.” W. Feller

On Levy probability distributions with infinite moments:

“It is probable that the scope of applied problems in which they play an essential role will become in due course rather wide.” B. Gnedenko and A. Kolmogorov
"I used a waiting time distribution that had such a long time tail that the mean time of it did not exist. That was the step! Everything fell into place."

Harvey Scher
Derivation of the Continuous-Time Random-Walk Equation

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(Received 15 October 1979)

The transport of electrons or excitations on a lattice randomly occupied by guests is considered. The equation governing the transport in any configuration is assumed to be the master equation. A projection operator technique is used to derive the exact equation governing the transport averaged over all configurations, which can be written as either a generalized master equation or the continuous-time random-walk equations (CTRW), establishing the correctness of the CTRW for these problems.
Questions:

• Can Anomalous diffusion be described on the **same level** of description as simple diffusion?

• How does anomalous diffusion modify **reactions** and first passage times?

• Can we use a generalization of:

\[
\frac{\partial}{\partial t} P(x,t) = K \frac{\partial^2}{\partial x^2} P(x,t)
\]
Fractional Diffusion Equations

• Following scaling arguments one can postulate equations which are of non-integer order in time or in space, e.g.

\[ \frac{\partial^\alpha}{\partial t^\alpha} P(x,t) = K \frac{\partial^2}{\partial x^2} P(x,t) \]

or

\[ \frac{\partial}{\partial t} P(x,t) = K \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} \frac{\partial^2}{\partial x^2} P(x,t) \]

Such equations allow for:
• easier introduction of external forces
• introduction of boundary conditions
• using the methods of solutions known for “normal” PDEs
Fractional Derivatives

1695 Leibnitz - de l’Hospital

\[
\frac{d^n}{dt^n} t^m = \frac{m!}{(m-n)!} t^{m-n} \equiv \frac{\Gamma(1+m)}{\Gamma(1+m-n)} t^{m-n}
\]

Trivial generalization:

\[
\frac{d^\nu}{dt^\nu} t^\mu =_0 D^\nu_t t^\mu = \frac{\Gamma(1+\mu)}{\Gamma(1+\mu-\nu)} t^{\mu-\nu}
\]

Interesting:

\[
_0 D^\nu_t 1 = \frac{1}{\Gamma(1-\nu)} t^{-\nu}
\]

This definition is enough to handle the functions which can be expanded into Taylor series, but obscures the nature of the fractional differentiation operator.
All modern definitions are based on generalizations of the repeated integration formula:

\[ a D_x^{-n} f(x) = \int \int \cdots \int \frac{f(y_n)dy_n \cdots dy_1}{(n-1)!} \int_a^x (x-y)^{n-1} f(y)dy \]

Its generalization is: The fractional integral

\[ t_0 D_t^{-p} f(t) = \frac{1}{\Gamma(p)} \int_{t_0}^t \frac{f(t')}{(t-t')^{1-p}} dt' \quad (0 < p < 1) \]

Fractional derivatives may be defined through additional differentiation:

\[ t_0 D_t^q f(t) = \frac{d^n}{dt^n} t_0 D_t^{-(n-q)} f(t) \quad (n = \lceil q + 1 \rceil) \]

Fractional derivatives are nonlocal integral operators and are best suited for the description of nonlocalities in space (long jumps) or time (memory effects)
<table>
<thead>
<tr>
<th>Semi-integral</th>
<th>Function</th>
<th>Semi-derivative</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0D_x^{-1/2} f(x) = \frac{d^{-1/2}}{dx^{-1/2}} f(x)$</td>
<td>$f(x)$</td>
<td>$0D_x^{1/2} f(x) = \frac{d^{1/2}}{dx^{1/2}} f(x)$</td>
</tr>
<tr>
<td>$2C\sqrt{x}/\pi$</td>
<td>$C$, any constant</td>
<td>$C/\sqrt{\pi x}$</td>
</tr>
<tr>
<td>$\sqrt{\pi}$</td>
<td>$1/\sqrt{x}$</td>
<td>$0$</td>
</tr>
<tr>
<td>$x\sqrt{\pi}/2$</td>
<td>$\sqrt{x}$</td>
<td>$\sqrt{\pi}/2$</td>
</tr>
<tr>
<td>$4x^{3/2}/3\sqrt{\pi}$</td>
<td>$x$</td>
<td>$2\sqrt{x}/\pi$</td>
</tr>
<tr>
<td>$\frac{\Gamma(\mu+1)}{\Gamma(\mu+3/2)} x^{\mu+1/2}$</td>
<td>$x^\mu$, $\mu &gt; -1$</td>
<td>$\frac{\Gamma(\mu+1)}{\Gamma(\mu+1/2)} x^{\mu-1/2}$</td>
</tr>
<tr>
<td>$\exp(x) \text{erf}(\sqrt{x})$</td>
<td>$\exp(x)$</td>
<td>$1/\sqrt{\pi x} + \exp(x) \text{erf}(\sqrt{x})$</td>
</tr>
<tr>
<td>$2\sqrt{\pi/x} [\ln(4x) - 2]$</td>
<td>$\ln x$</td>
<td>$\ln(4x) / \sqrt{\pi x}$</td>
</tr>
</tbody>
</table>
\[ \frac{\partial}{\partial t} P(x,t) = \mathcal{D}_0^{1-\alpha} K \frac{\partial^2}{\partial x^2} P(x,t') \]

\[ \mathcal{D}_0^{1-\alpha} f(t) = \frac{\partial}{\partial t} \frac{1}{\Gamma(1-\alpha)} \int_0^t (t-t')^\alpha f(t') dt' \]
The Fractional Fokker-Planck Equation

\[ \dot{P}(x,t) = D_t^{1-\alpha} \left[ \frac{\partial}{\partial x} \frac{V'(x)}{m \eta_\alpha} + K_\alpha \frac{\partial^2}{\partial x^2} \right] P(x,t) \]

\[ [\eta_\alpha] = \sec^{\alpha-2} \]

- Force-free mean squared displacement
  \[ < x^2(t) >_0 = \frac{2K_\alpha}{\Gamma(1+\alpha)} t^\alpha \]

- Stationary solution
  \[ P_{st} \propto \exp \left( -\frac{V(x)}{k_B T} \right) \]

\[ K_\alpha = \frac{k_B T}{m \eta_\alpha} \quad \text{Generalized Einstein-Stokes relation} \]
Some Solutions

Ornstein-Uhlenbeck process: Diffusion in a harmonic potential

Free diffusion:
Left: Normal diffusion
Right: Subdiffusion with $\alpha = 1/2$

I.M. Sokolov, J. Klafter and A. Blumen, Fractional Kinetics, Physics Today, November 2002, p.48
Time-fractional Fokker-Planck equation for Lévy flights in time

\[
\frac{\partial^\beta f}{\partial t^\beta} = \frac{\partial}{\partial x}\left(\frac{dU}{dx} f\right) + D \frac{\partial^2 f}{\partial x^2}
\]

Weight function:

\[
\mathcal{W}(\tau) \frac{1}{\tau^{1+\beta}}, \quad 0 < \beta < 1, \quad \langle \tau \rangle = \infty
\]

Fractional Caputo derivative:

\[
\phi(t) \div \tilde{\phi}(s) = \int_0^\infty dt \phi(t) e^{-st} \Rightarrow \frac{\partial^\beta \phi}{\partial t^\beta} \div s^\beta \tilde{\phi}(s) - s^{\beta-1} \phi(0)
\]

Solution: separation of variables

\[
f_n(x, t) = T_n(t) \varphi_n(x)
\]

Time evolution: Mittag – Leffler relaxation

\[
T_n(t) = E_\beta \left( -\lambda_n t^\beta \right) \approx \begin{cases} 
\exp \left( -\frac{\lambda_n t^\beta}{\Gamma(1+\beta)} \right), & \lambda_n t^\beta \ll 1 \\
\lambda_n^{-1}\Gamma^{-1}(1-\beta)t^{-\beta}, & \lambda_n t^\beta >> 1
\end{cases}
\]

Stretched exponential law

Slow power law relaxation
Possible positions of derivatives:

<table>
<thead>
<tr>
<th>Normal forms:</th>
<th>Modified forms:</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\partial^\alpha}{\partial t^\alpha} P(x,t) = K \frac{\partial^2}{\partial x^2} P(x,t) )</td>
<td>( \frac{\partial}{\partial t} P(x,t) = \frac{\partial^{1-\alpha}}{\partial t^{1-\alpha}} K \frac{\partial^2}{\partial x^2} P(x,t) )</td>
</tr>
<tr>
<td>Caputo derivative on the “correct” side (l.h.s.)</td>
<td>Riemann-Liouville derivative on the “wrong” side (r.h.s.)</td>
</tr>
<tr>
<td>( \frac{\partial}{\partial t} P(x,t) = K \frac{\partial^{2\beta}}{\partial x^{2\beta}} P(x,t) )</td>
<td>( - \frac{\partial^{2-2\beta}}{\partial x^{2-2\beta} \partial t} P(x,t) = K \frac{\partial^2}{\partial x^2} P(x,t) )</td>
</tr>
<tr>
<td>Riesz-Weyl derivative on the “correct” side (r.h.s.)</td>
<td>Riesz-Weyl derivative on the “wrong” side (l.h.s.)</td>
</tr>
</tbody>
</table>
References:

“Beyond Brownian Motion”

“Strange Kinetics”

“The Random Walk Guide…”

“Fractional Kinetics”

“The Restaurant at the End of the Random Walk….”

“Anomalous Diffusion Spreads its Wings”
Physics World 18, 29 (2005)