Aging, ergodicity breaking and universal fluctuations in continuous time random walks: Theory and (possible) experimental manifestations
Outline

1. Normal Diffusion and random walks
2. Anomalous diffusion
3. Continuous-time random walk schemes
4. Aging and death of linear response
5. Nonergodicity
6. Universal fluctuations
The diffusion equation (1855)

Continuity
\[
\frac{\partial}{\partial t} n(x,t) = -\text{div}\, \mathbf{j}(x,t)
\]
+ linear response
\[
\mathbf{j} = -K \text{ grad}\, n(x,t)
\]

the diffusion equation
\[
\frac{\partial}{\partial t} n(x,t) = K \Delta n(x,t)
\]
Emergence of normal diffusion

Einstein (1905)

Postulates:
0) \(n(x,t) \rightarrow P(x,t)\)

i) \(\exists\) time interval \(\tau < \infty\), so that the particle’s motion during the two consequent intervals is independent.

ii) The displacements \(s\) during subsequent \(\tau\)-intervals are identically distributed.

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

iii) The second moment of \(s\) exists

\[ \lambda^2 = \int_{-\infty}^{\infty} s^2 \phi(s) ds < \infty \]
"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 $O$".

K. Pearson, 1905
Motion as a sum of small independent increments: \( x(t) = \sum_{i=1}^{N} s_i \)

\[
\lambda = \left\langle s_i^2 \right\rangle^{1/2}
\]
\[
0 < \lambda < \infty
\]

\[
\tau \propto \lambda / \left\langle v^2 \right\rangle^{1/2}
\]
\[
0 < \tau < \infty
\]

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

the central limit theorem

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

with \( K \propto \left\langle v^2 \right\rangle \tau \equiv \lambda^2 / \tau \)
Anomalous diffusion spreads its wings

Joseph Klafter and Igor M Sokolov

As all of us are no doubt aware, this year has been declared “world year of physics” to celebrate the three remarkable breakthroughs made by Albert Einstein in 1905. However, it is not so well known that Einstein’s work on Brownian motion – the random motion of tiny particles first observed and investigated by the botanist Robert Brown in 1827 – has been cited more times in the scientific literature than his more famous papers on special relativity and the quantum nature of light. In a series of publications that included his doctoral thesis, Einstein derived an equation for Brownian motion from microscopic principles – a feat of his work on Brownian motion. He did this by assuming...
The typical trajectories of spider monkeys in the forest of the Mexican Yucatan peninsula display steps with variable lengths, which correspond to a diffusive process that is faster than that of normal diffusion. An example of such a trajectory is shown on the left. A magnified part of it is shown on the right; this image looks qualitatively similar to the larger-scale trajectory, which is an important property of Lévy walks. Similar behaviour is found in the foraging habits of other animals, and could mean that anomalous diffusion offers a better search strategy than that of normal diffusion.

R Fernandez et al. 2004 Lévy walk patterns in the foraging movements of spider monkeys (Ateles geoffroyi); Behav. Ecol. Sociol. 55 223–230
An old story: In disordered solids...

The sum of slopes is always 2

H. Scher and E. Montroll, 1975
Explanation: Multiple trapping and CTRW

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!

Mean density of steps $M(t) = \frac{dN}{dt} \propto t^{\alpha-1}$

Mean squared displacement $\langle x^2(t) \rangle \propto t^\alpha$ with $\alpha < 1$
more subdiffusion…

J.W. Kirchner, X. Feng & C. Neal, Nature 403, 524 (2000),

K Ritchie et al., Biophys. J. 88 2266 (2005)
Experiments on protein relaxation

• Anomalous is normal
• Happy families are all alike; every unhappy family is unhappy in its own way:

Possible sources of anomalous subdiffusion:

1. CTRW with power-law waiting times as arising from random potential models (energetic disorder)
2. Diffusion on fractal structures, e.g. on the percolation cluster (geometrical disorder)
3. Temporal correlations due to slow modes.

The three cases correspond to different models and are described using different theoretical instruments.
An old story: In disordered solids...

Mean field model for a rugged potential landscape (trap model)

The sum of slopes is always 2

H. Scher and E. Montroll, 1975
The Subordination

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

\[
P(x,t) = \sum_{n=0}^{\infty} W(x,n) \chi_n(t)
\]

Probability to make exactly \( n \) steps up to the time \( t \)

Transition to continuum:

\[
P(x,t) = \int_{0}^{\infty} W(x,\tau)T(\tau,t)d\tau
\]
Short way to the result:

- Independent steps \( \Rightarrow \quad \langle x^2(t) \rangle = a^2 \langle n(t) \rangle \)
- Steps follow inhomogeneously in the physical time \( t \).
- The number of steps up to the time \( t \) may be calculated using the renewal approach:

  no steps up to time \( t \): \( \chi_0(t) = 1 - \int_0^t \psi(t')dt' \)

  1 step up to time \( t \): \( \chi_1(t) = \int_0^t \psi(t')\chi_0(t - t')dt' \)

  \( n \) steps up to time \( t \): \( \chi_n(t) = \int_0^t \psi(t')\chi_{n-1}(t - t')dt' \)

\[
\langle n(t) \rangle = \sum_{n=0}^{\infty} n\chi_n(t) = ?
\]
After Laplace-transform: \[ \tilde{\chi}_n(u) = \frac{1 - \tilde{\psi}(u)}{u} \tilde{\psi}^n(u) \]

\[
\langle \tilde{n}(u) \rangle = \frac{1 - \tilde{\psi}(u)}{u} \sum_{n=0}^\infty n \tilde{\psi}^n(u) = \frac{1 - \tilde{\psi}(u)}{u} \sum_{n=0}^\infty \tilde{\psi}(u) \frac{d}{d\tilde{\psi}} \tilde{\psi}^n(u)
\]

\[
= \frac{1 - \tilde{\psi}(u)}{u} \tilde{\psi}(u) \frac{d}{d\tilde{\psi}} \sum_{n=0}^\infty \tilde{\psi}^n(u) = \frac{\tilde{\psi}(u)}{u[1 - \tilde{\psi}(u)]}. 
\]

\[
\psi(t) \propto t^{-1-\alpha} \quad \Rightarrow \quad \tilde{\psi}(u) \simeq 1 - cu^\alpha + ...
\]

\[
\langle n(t) \rangle \propto t^{\alpha} \quad \Rightarrow \quad \langle \tilde{n}(u) \rangle \simeq c^{-1}u^{-1-\alpha}
\]
Nonstationarity

In normal diffusion:  \[ \langle [x(t_2) - x(t_1)]^2 \rangle = \langle x^2 (t_1 - t_2) \rangle = 2D(t_1 - t_2) \]

Explanation: Since  \[ \langle n(t) \rangle = t / \tau, \langle n(t_2) \rangle - \langle n(t_1) \rangle = \langle n(t_2 - t_1) \rangle \]

In all other cases  \[ \langle [x(t_2) - x(t_1)]^2 \rangle \propto \langle n \rangle = \langle n(t_2) \rangle - \langle n(t_1) \rangle \]

\[ \propto t_2^\alpha - t_1^\alpha \]

The process *ages*.

- Anomalous diffusion at long times
- Normal diffusion at short times
E.g.: Death of linear response

Field off → Field on

\[ m_1(t) = a \langle n(t) \rangle \]
\[ = a [\langle N(t) \rangle - \langle N(t_1) \rangle] \]
\[ = \text{const} \cdot (t^\gamma - t_1^\gamma) \]

\( a = \mu f \)
Fractional subdiffusion (CTRW)

Model:
\[ w_-(x) = \frac{1 - \varepsilon f(x)}{2} \quad w_+(x) = \frac{1 + \varepsilon f(x)}{2} \]

Waiting time pdf:
\[ \psi(t) \propto t^{-1-\alpha} \text{ with } 0 < \alpha < 1 \]
A master equation: probability balance

- Local balance \( \dot{p}_i(t) = J_i^+ - J_i^- \)

- Balance during transitions
  \[ J_i^+ (t) = w_{i-1,i} (t) J_{i-1}^- (t) + w_{i+1,i} (t) J_{i+1}^- (t) \]

- Linear response to bias
  \[
  w_{i-1,i} (t) = \frac{1}{2} + \frac{\epsilon}{2} f(t)
  \]
  \[
  w_{i+1,i} (t) = \frac{1}{2} - \frac{\epsilon}{2} f(t)
  \]

- Balance equation
  \[
  \dot{p}_i (t) = w_{i-1,i} (t) J_{i-1}^- (t) + w_{i+1,i} (t) J_{i+1}^- (t) - J_i^- (t)
  \]
Memory function

• Jump probability per unit time at time $t$:

$$J_i^-(t) = \psi(t)p_i(0) + \int_0^t \psi(t-t')J_i^+(t')dt'$$

no jumps arrival at $t = t'$

• Express $J_i^+$ through $\dot{p}_i(t) = J_i^+ - J_i^-$

$$J_i^-(t) = \psi(t)p_i(0) + \int_0^t \psi(t-t')[\dot{p}_i(t') + J_i^-(t')]dt'$$

in Laplace domain

$$\tilde{J}_i^-(u) = \tilde{\psi}(u)p_i(0) + \tilde{\psi}(u)[u\tilde{p}_i(u) - p_i(0) + \tilde{J}_i^-(u)]$$

• In Laplace domain

$$\tilde{J}_i^-(u) = u \frac{\tilde{\psi}(u)}{1-\tilde{\psi}(u)} \tilde{p}_i(u)$$

• In time domain

$$J_i^-(t) = \dot{\Phi}p(t) = \frac{d}{dt} \int_0^t M(t-t')p_i(t')dt'$$
Generalized master equation

General balance equation
\[ \dot{p}_i(t) = w_{i-1,i}(t)J_{i-1}^-(t) + w_{i+1,i}(t)J_{i+1}^-(t) - J_i^-(t); \]

+ memory kernel
\[ J_i^-(t) = \hat{\Phi} p(t) = \frac{d}{dt} \int_0^t M(t-t')p_i(t')dt'; \]

= generalized master equation
\[ \frac{dp_i(t)}{dt} = w_{i-1,i}(t)\hat{\Phi} p_{i-1}(t') + w_{i+1,i}(t)\hat{\Phi} p_{i+1}(t') - \hat{\Phi} p_i(t) \]

For power-law waiting time densities \( \psi(t) \propto t^{-1-\alpha} \) one has \( \hat{\Phi} \propto_0 D_t^{1-\alpha} \).

Continuum limit:
\[ \frac{\partial}{\partial t} p(x,t) = [K\Delta - \nabla (\mu f(x,t) \cdot \nabla)]_0 D_t^{1-\alpha} p(x,t) \cdot L_{FP} \]
Aging and death of linear response

\[ m_1(t) = \mu f_0 \int_0^t dt' \sin \omega t' M(t') \]

\[ \tilde{m}_1(u) = \mu f_0 \frac{\tilde{M}(u - i\omega) - \tilde{M}(u + i\omega)}{2iu} \]

Trick: \( \sin \omega t = \frac{e^{i\omega t} - e^{-i\omega t}}{2i} \)

+ shift theorem in Laplace domain

For \( t \to \infty \) linear response stagnates:

\[ m_1(t) \to -\mu f_0 \text{Im} M(-i\omega) \]


Exp.: “Experimental quenching of harmonic stimuli …” by P. Allegrini et al.

Numerics: M.-C. Néel, A. Zoia and M. Joelson, “Mass transport subject to time-dependent flow with nonuniform sorption in porous media”, PRE 80, 056301 (2009)
Experimental Quenching of Harmonic Stimuli: Universality of Linear Response Theory

Paolo Allegrini,1 Mauro Bologna,2,3 Leone Fronzoni,1 Paolo Grigolini,1,2,4 and Ludovico Silvestri1,5
1Dipartimento di Fisica “E. Fermi,” Università di Pisa and INFM CRS-SOFT, Largo Pontecorvo 3, 56127 Pisa, Italy
2Center for Nonlinear Science, University of North Texas, P.O. Box 311427, Denton, Texas 76203, USA
3Instituto de Alta Investigación, Universidad de Tarapacá-Casilla 6-D Arica, Chile
4Istituto dei Processi Chimici Fisici del CNR Area della Ricerca di Pisa, Via G. Moruzzi 1, 56124 Pisa, Italy
5L.E.N.S., University of Florence, via Nello Carrara 1, 50019 Sesto Fiorentino (FI), Italy
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We show that liquid crystals in the weak turbulence electroconvective regime respond to harmonic perturbations with oscillations whose intensity decay with an inverse power law of time. We use the results of this experiment to prove that this effect is the manifestation of a form of linear response theory (LRT).

FIG. 3 (color online). $\Lambda^{-}(t)/\epsilon$ with $\omega/2\pi = 0.07$ Hz and $\epsilon = 0.025, 0.031, 0.037, 0.044, 0.050$. 
We argue that this theory is a universal property, which is not confined to physical processes such as turbulent or excitable media, and that it holds true in all possible conditions, and for all possible systems, including complex networks, thereby establishing a bridge between statistical physics and all the fields of research in complexity.
Single molecule tracking


• In most experiments on subdiffusion, say in disordered semiconductors, the ensemble average is implied by the multiparticle nature of the problem.

• In single particle tracking experiments moving time average is a typical procedure used to obtain the diffusion coefficient.

Normal diffusion:

\[ \langle x^2(t) \rangle = 2Kt \]

Normal diffusion is an ergodic process: The ensemble average gives the same result as a time-moving average

\[ \langle x^2(t) \rangle_T = \frac{1}{T-t} \int_0^{T-t} [x(t'+t) - x(t')]^2 dt' \]

for a single long trajectory.
• Although the discrimination between normal diffusion and subdiffusion according to
  \[ \langle x^2(t) \rangle = 2Kt \]
  and
  \[ \langle x^2(t) \rangle = \frac{2K_\alpha}{\Gamma(1+\alpha)} t^\alpha \]
  seems simple, in practice, however, the situation is quite involved.

• The question of what is the “correct” averaging procedure in the anomalous case has seldom been discussed.
Model simulations

Single particle trajectories calculated from a CTRW with $\psi(t) \sim t^{-3/2}$

Some numerical results for the case $\psi(t) \sim t^{-1.8}$.
Nonergodicity mimicks inhomogeneity…

The distribution $p(K)$ of diffusion coefficients obtained from time averaged single trajectories for the case of $T=2\cdot10^6$, and $t=500$.

A. Lubelski, I.M.Sokolov and J. Klafter, PRL 100, 250602 (2008)
Explanation of the result for $\left< x^2(t) \right>_T$ \text{ens}

\begin{align*}
\langle n(t) \rangle_{\text{ens}} &\approx At^\alpha \\
\langle x^2(t) \rangle &\approx a^2 \langle n(t) \rangle_{\text{ens}}
\end{align*}

\begin{align*}
\langle [x(t_2) - x(t_1)]^2 \rangle_{\text{ens}} &= a^2 \left[ \langle n(t_2) \rangle_{\text{ens}} - \langle n(t_1) \rangle_{\text{ens}} \right]
\end{align*}

• Interchanging the sequence of averaging

\begin{align*}
\langle [x(t_2) - x(t_1)]^2 \rangle_{\text{ens}} &= a^2 \left[ \langle n(t_2) \rangle_{\text{ens}} - \langle n(t_1) \rangle_{\text{ens}} \right] \\
&= a^2 \frac{1}{T} \int_0^T \left[ \langle n(t'+t) \rangle_{\text{ens}} - \langle n(t') \rangle_{\text{ens}} \right] dt' = \frac{a^2 A}{T} \int_0^T \left[ (t'+t)^\alpha - t'^\alpha \right] dt'
\end{align*}

• For $t \ll T$ one gets: $\left< x^2(t) \right>_T = a^2 AT^{\alpha-1}t$

• Prediction: time dependent mean diffusion coefficient

$$K_{\text{eff}}(T) = a^2 AT^{\alpha-1} / 2$$
Numerical check for the prediction

Advice for experimentalists:
Check for the time-dependence of diffusion coefficient!
Absence of nonergodicity, and the subdiffusive behavior of the moving time averages is a witness against a whatever trap model of anomalous diffusion.


T. Neusius, I. M. Sokolov, J. C. Smith, PRE 80, 011109 (2009)
The fractal dimension of the main valley in the peptide’s potential landscape \( (d = 10^2 \div 10^3) \) is around \( d_f \approx 7 \).

Realistic rugged potential landscape in \( d = 3 \).
Elucidating the Origin of Anomalous Diffusion inCrowded Fluids

Jedrzej Szymanski and Matthias Weiss

Cellular Biophysics Group (BIOMS), German Cancer Research Center, Im Neuenheimer Feld 280, D-69120 Heidelberg, Germany
(Received 12 December 2008; published 15 July 2009)

FIG. 2. Mean square displacement $\langle r(t)^2 \rangle$ for obstructed diffusion (36% obstacle concentration), FBM, and CTRW (from top). Open symbols denote the ensemble-averaged MSD, and cross-like symbols denote the time-averaged MSD for a representative trajectory. While both approaches coincide for FBM and obstructed diffusion, the curves differ for the CTRW due to weak ergodicity breaking. For better visibility, MSD curves for FBM and obstructed diffusion have been shifted upwards (factor 50 and 250, respectively). Full lines scale as $\langle r(t)^2 \rangle \sim t^{0.82}$; the dashed line is linear in time.
Universal fluctuations

I.M. Sokolov, E. Heinsalu, P. Hänggi and I. Goychuk
Universal fluctuations in subdiffusive transport
EPL 86 (2009) 30009

M. Esposito, K. Lindenberg and I.M. Sokolov
On the relation between event-based and time-based current statistics,

Fig. 1: Two-level system embedded between a left (L) and a right (R) particle reservoir.
“normal” motion

\[ v(t) = v_0 + \delta v(t) \]

Two different means

\[ \bar{v}(t) = \langle v \rangle_t = \frac{\langle L(T) \rangle}{T} \]

and

\[ \bar{v}(L) = \langle v \rangle_L = L \left\langle \frac{1}{T(L)} \right\rangle \]

both converge to a sharp and the same limit for \( t \to \infty \) or \( L \to \infty \) (a property called self-averaging).

Although it is not quite correct, one often uses

\[ \bar{V}(L) = \frac{L}{\left\langle T(L) \right\rangle_{\text{ens}}} \]
“anomalous” motion (TOF)

Fig. 6.2. The effect of high barriers on the average mobility as perceived by J. Villain.

(stolen from Haus and Kehr)
Fixed-time and TOF setups

$\psi(t) \propto t^{-1 - \alpha}$

$\delta x \propto t^\alpha$

$n(t) \propto t^\alpha$

$v_\alpha = \Gamma(1 + \alpha) \left\langle \frac{\delta x}{t^\alpha} \right\rangle$

Units: Time in units of $\tau$

length in units of $<a>$

subvelocity in units of $\Gamma(1 + \alpha)\langle a \rangle / \tau^\alpha$

Directed RW
**Fixed-time velocity**

\[ \delta x = \langle a \rangle n(t) \quad (n >> 1) \]

\[ t = T \text{ fixed} \]

- no steps up to time \( t \):
  \[ p(0, t) = \chi_0(t) = 1 - \int_0^t \psi(t')dt' \]

- 1 step up to time \( t \):
  \[ p(1, t) = \chi_1(t) = \int_0^t \psi(t') p(0, t-t')dt' \]

- \( n \) steps up to time \( t \):
  \[ p(n, t) = \chi_n(t) = \int_0^t \psi(t') p(n-1, t-t')dt' \]

\[ p(n, u) = \frac{1 - \psi(u)}{u} [\psi(u)]^n \approx u^{\alpha-1} \exp[n \ln(1-u^{\alpha})] \approx u^{\alpha-1} \exp(-nu^{\alpha}) \]

\[ p(n, T) \approx \frac{1}{\alpha} \frac{T}{n^{1+1/\alpha}} L_\alpha \left( \frac{T}{n^{1/\alpha}} \right) \]

\[ \hat{L} \{ L_\alpha (x) \} = e^{-u^{\alpha}} \]
Universal fluctuations

Scaled velocity \( \xi_\alpha = v / v_0 \)

Distribution of scaled velocity:

\[
p(\xi_\alpha) = \frac{\Gamma(1+\alpha)^{1/\alpha}}{\alpha^{1+1/\alpha}} L_\alpha \left[ \left( \frac{\Gamma(1+\alpha)}{\xi_\alpha} \right)^{1/\alpha} \right]
\]

Moments of scaled velocity

\[
\overline{\xi_\alpha} = 1 \quad \text{Independent on } T
\]

\[
\overline{\xi_\alpha^2} = \frac{2\Gamma^2 (1+\alpha)}{\Gamma(1+2\alpha)} \Rightarrow \text{Universal fluctuations}
\]

Moments \textit{have to be} obtained by additional ensemble averaging!
TOF setup

$L$ fixed $\Rightarrow$ number of steps $n$ fixed

$$p(t) = n^{-1/\alpha} L_\alpha (n^{-1/\alpha} t)$$

Change of variables to $\xi = \Gamma(1+\alpha)L/t^\alpha$

$$\downarrow$$

$$p(\xi_\alpha) = \frac{\Gamma(1+\alpha)^{1/\alpha}}{\alpha \xi^{1+1/\alpha}} L_\alpha \left[ \left( \frac{\Gamma(1+\alpha)}{\xi_\alpha} \right)^{1/\alpha} \right]$$

the same as in the fixed time setup.

Note: mean velocity cannot be defined as $v = L/\langle t \rangle^\alpha$ since $\langle t \rangle$ diverges!!! *

$$\overline{\xi_\alpha} = 1$$

$$\overline{\xi^2_\alpha} = \frac{2\Gamma^2(1+\alpha)}{\Gamma(1+2\alpha)}$$
Same for periodic potential

\[ V(x) = V_0 \cos(2\pi x) - Fx \]

Dimensionless velocity is defined as

\[ \xi = \sqrt{v_{\alpha}(F)} \]

with

\[ v_{\alpha}(F) = \frac{K_{\alpha} \lambda [1 - \exp(-\beta F \lambda)]}{\int_0^\lambda dx \int_x^{x+\lambda} dy \exp[-\beta [U(x) - U(y)]]} \]

as following from the solution of FFPE
\[ p(\xi) = A(\alpha) \xi^{(\alpha-1/2)/(1-\alpha)} \exp[-B(\alpha)\xi^{1/(1-\alpha)}] \]

Large \( \xi \) - asymptotics

\( \alpha = 0.8 \) 
\( \alpha = 0.2 \)
Time-driven statistics  (analog fixed-time)

\[ \langle I^m \rangle_t = \frac{\langle k^m \rangle}{t^{\alpha m}} = \frac{1}{t^{\alpha m}} \sum_k k^m P_t(k) \]

Event-driven statistics  (analog TOF)

\[ \langle I^m \rangle_k = k^m \langle \frac{1}{t^{\alpha m}} \rangle = k^m \int dt \frac{P_k(t)}{t^{\alpha m}} \]

\[ \lim_{m \to \infty} \langle I^m \rangle_{\tau_0 + \tau_1} = \frac{\Gamma(m+1)}{\Gamma(\alpha m + 1)} \left( \frac{P_{10}^\nu - P_{01}^\nu}{\tau_0^\alpha + \tau_1^\alpha} \right)^m \]
Conclusions

• Anomalous is normal
• Happy families are all alike; every unhappy family is unhappy in its own way
• In subdiffusive systems governed by CTRW only ensemble averages attain sharp values, the time averages show universal fluctuations!
• If you want to get mean velocity or current, average velocity or current