Beyond Brownian motion: Long-range correlation

—Pohang, 27th April 2023—

The founding fathers of diffusion theory: $\langle \mathbf{r}^2(t) \rangle \propto Kt$

Paul Langevin (1872-1946)
Albert Einstein (1879-1955)

Marian Smoluchowski
(1872-1917)

William Sutherland
(1859-1911)

Einstein's conditions on Brownian motion

Paul Lévy [Processus stochastiques & mouvement brownien (1948)]: ≪The stochastic process, that we will call linear Brownian motion, is a schematisation that well represents the properties of real Brownian motion, observable on a sufficiently small but not infinitely small scale, and which assumes that the same properties exist across the scales.≫

Einstein's postulate: a stochastic process describes normal diffusion if

(i) $\exists$ finite correlation time beyond which displacements are independent

(ii) displacements are identically distributed

(iii) displacements have a finite second moment

Main features: linear mean squared displacement & Gaussian probability density (CLT)

$$\langle \mathbf{r}^2(t)\rangle = 2dK_1 t, \quad P(\mathbf{r},t) = (4\pi K_1 t)^{-d/2} \exp\left(-\frac{\mathbf{r}^2}{4K_1 t}\right)$$

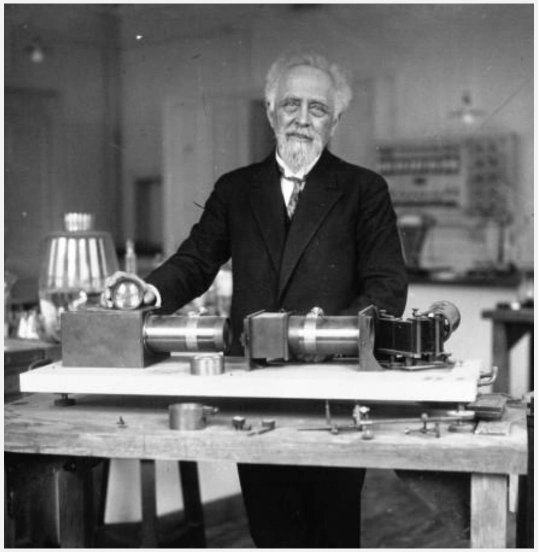
Confining potential $V(x)$: Boltzmannian equilibrium PDF: $P_{\mathrm{eq}}(x) = \mathscr{N} \exp\left(-\beta V(x)\right)$

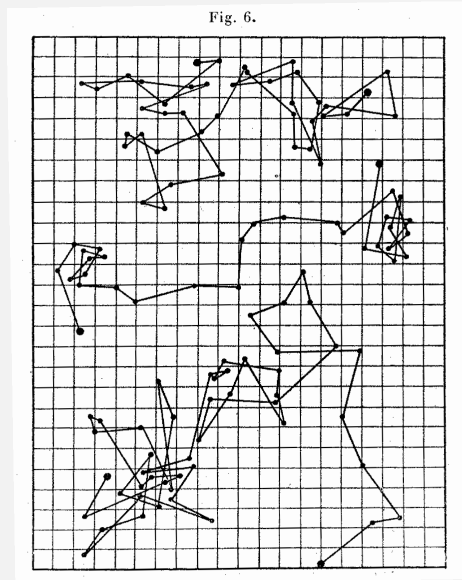
Ergodic in Birkhoff-Boltzmann-Khinchin sense (time average converges to ensemble)

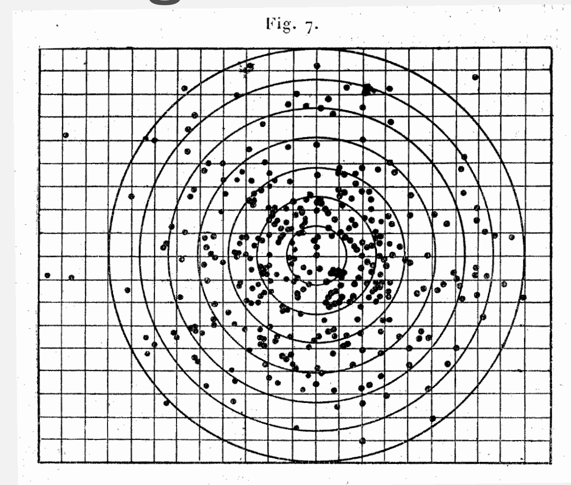
Violation of these conditions leads to anomalous diffusion with MSD $\langle \mathbf{r}^2(t)\rangle \simeq K_\alpha t^\alpha$ and/or non-Gaussian PDF $\rightsquigarrow$ Breakdown of universality

N van Kampen, Stochastic processes in physics & chemistry; J-P Bouchaud & A Georges, Phys Rep (1990)

Les atomes: Brownian motion and Avogadro's number

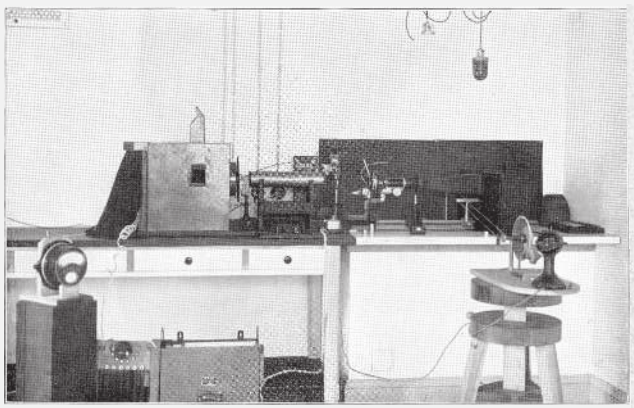


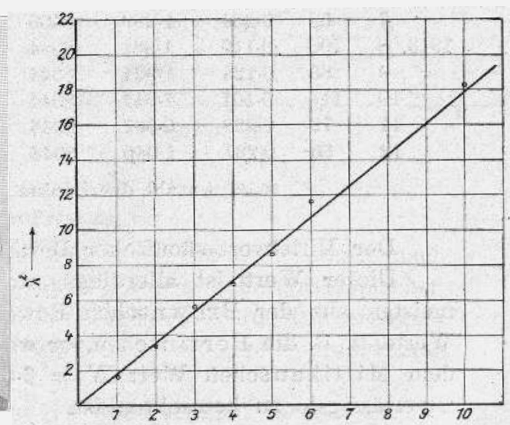


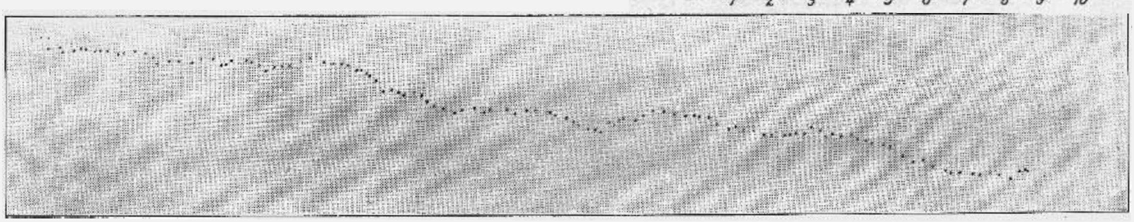


Δt=30 sec

$$K = \frac{k_B T}{m\eta} = \frac{(R/N_A)T}{m\eta}$$



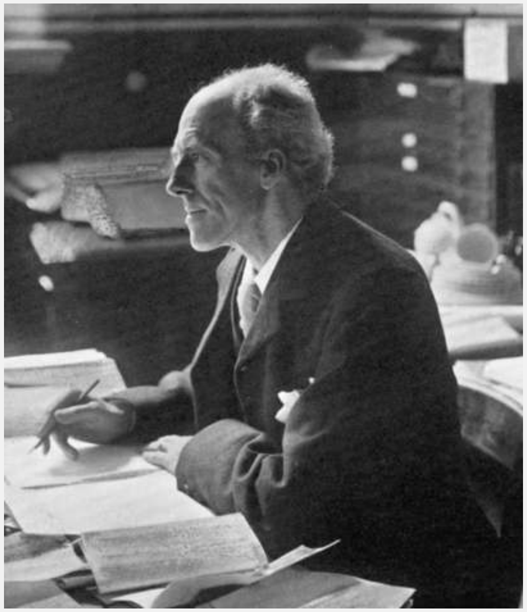




J Perrin, Comptes Rendus (Paris) 146 (1908) 967: $N_A = 70.5 \times 10^{22}$; I Nordlund, Z Physik (1914): $N_A = 5.91 \times 10^{23}$

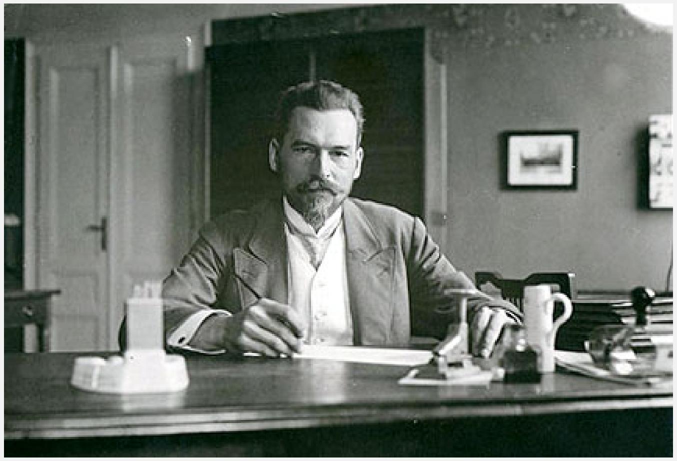
Brownian motion & random walks applied . . .

Louis Bachelier, 1900:
Brownian motion of
financial markets



Karl Pearson, 1905:
Spreading of mosquitoes
in rain forests

Marian v Smoluchowski, 1916:
Molecular reaction kinetics

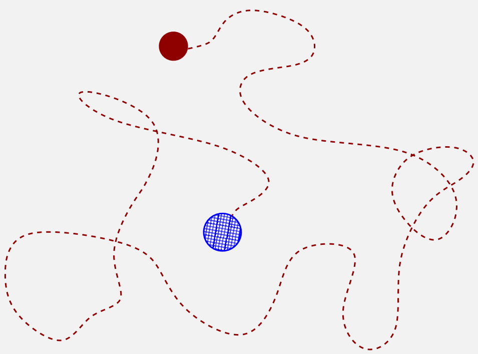


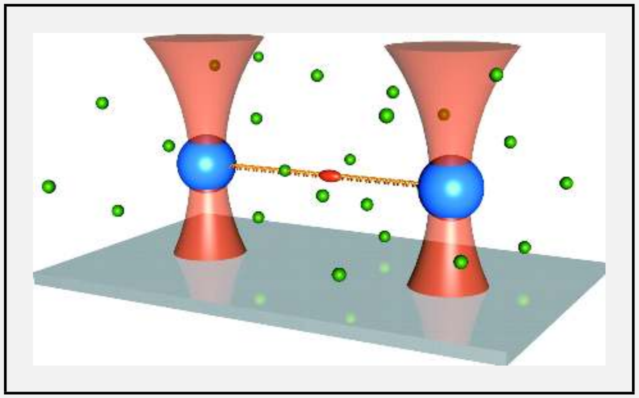
Elliott Montroll, 1943:
Manhattan project,
chain reaction of
neutrons

Molecular reaction times: macro vs micro

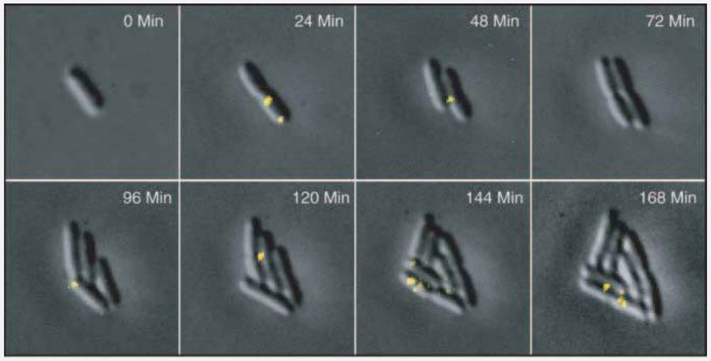
Search rate for particle with diffusivity $D_{3\mathrm{d}}$ to find an immobile target of radius a (assuming immediate binding):

$$k_{\mathrm{on}} = 4\pi D_{3\mathrm{d}} a$$





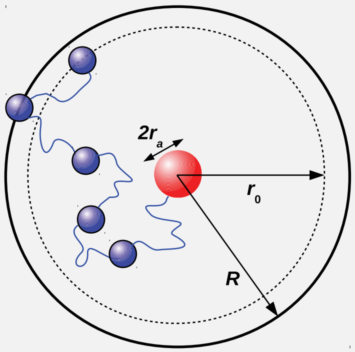
G Wuite, RM et al, PNAS (2008,2009)

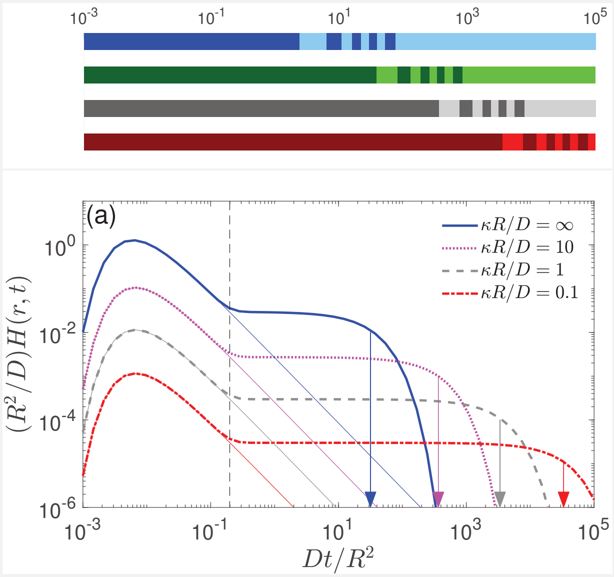


Yu et al, Science (2006)

Strong defocusing of reaction times

Geometry- vs reaction-control

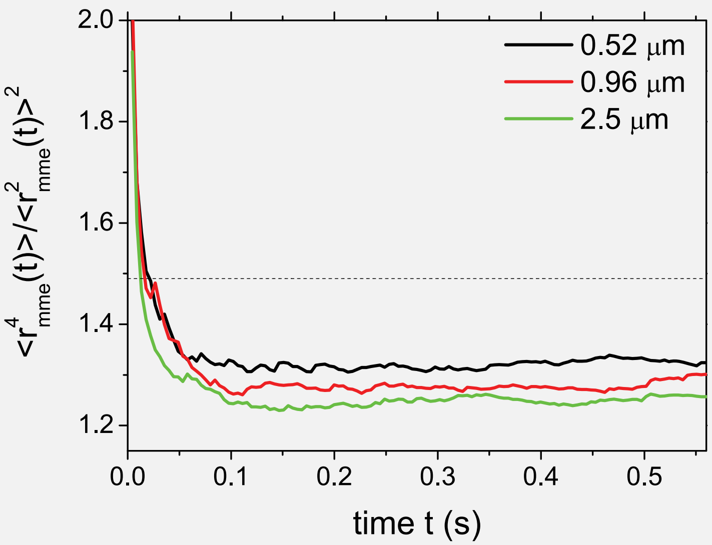


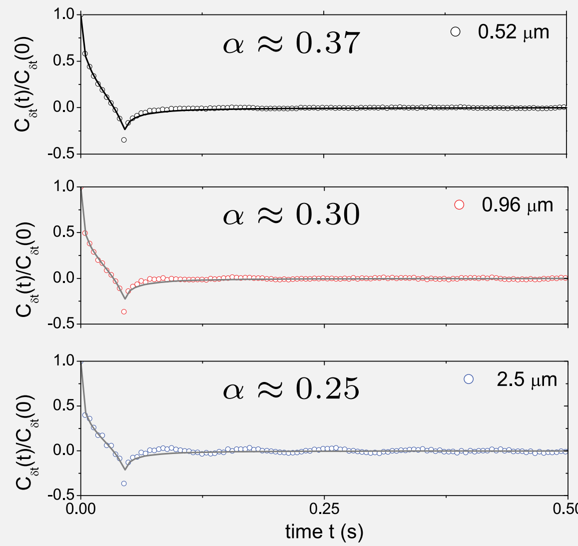


M v Smoluchowski, Physikal Zeitschr (1916)

A Godec & RM, PRX (2016); D Grebenkov, RM & G Oshanin (2018-)

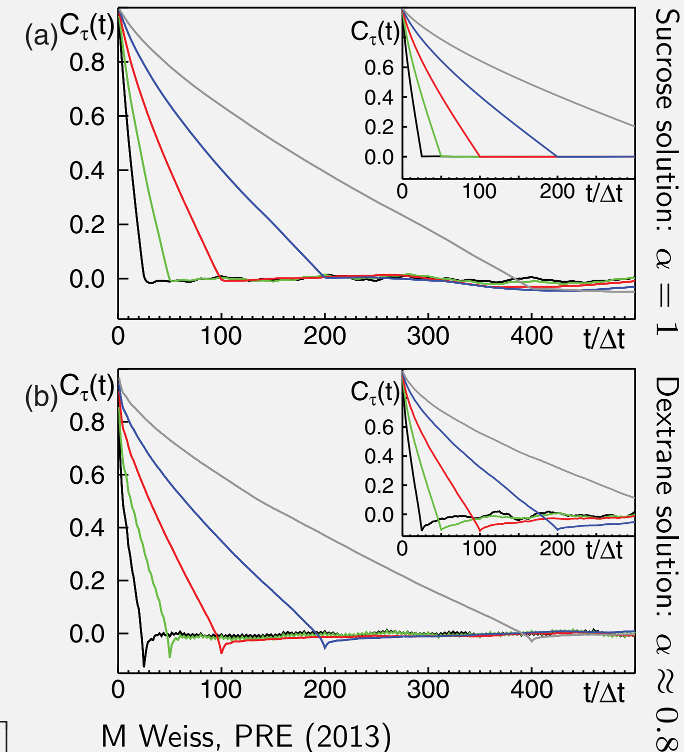
Passive motion of submicron tracers in cells is viscoelastic I



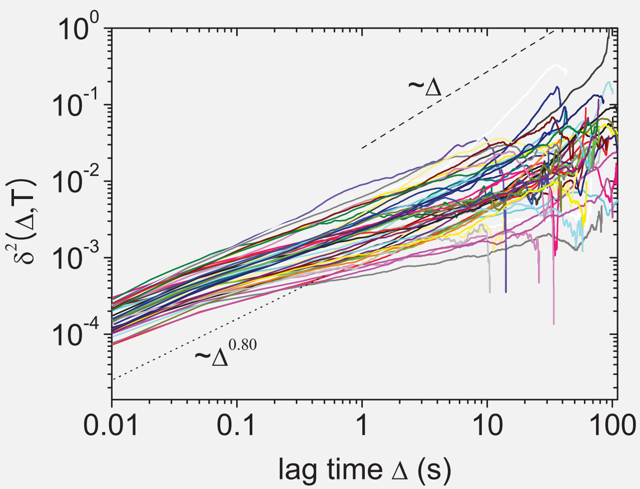


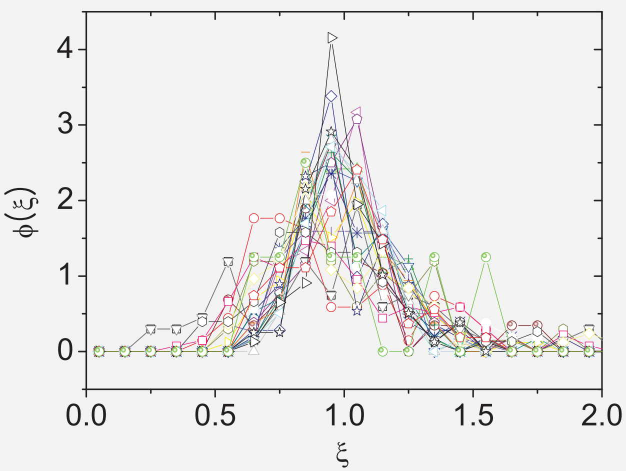
Beads in worm-like micellar solution

JH Jeon, N Leijnse, L Oddershede & RM, NJP (2013)



M Weiss, PRE (2013)



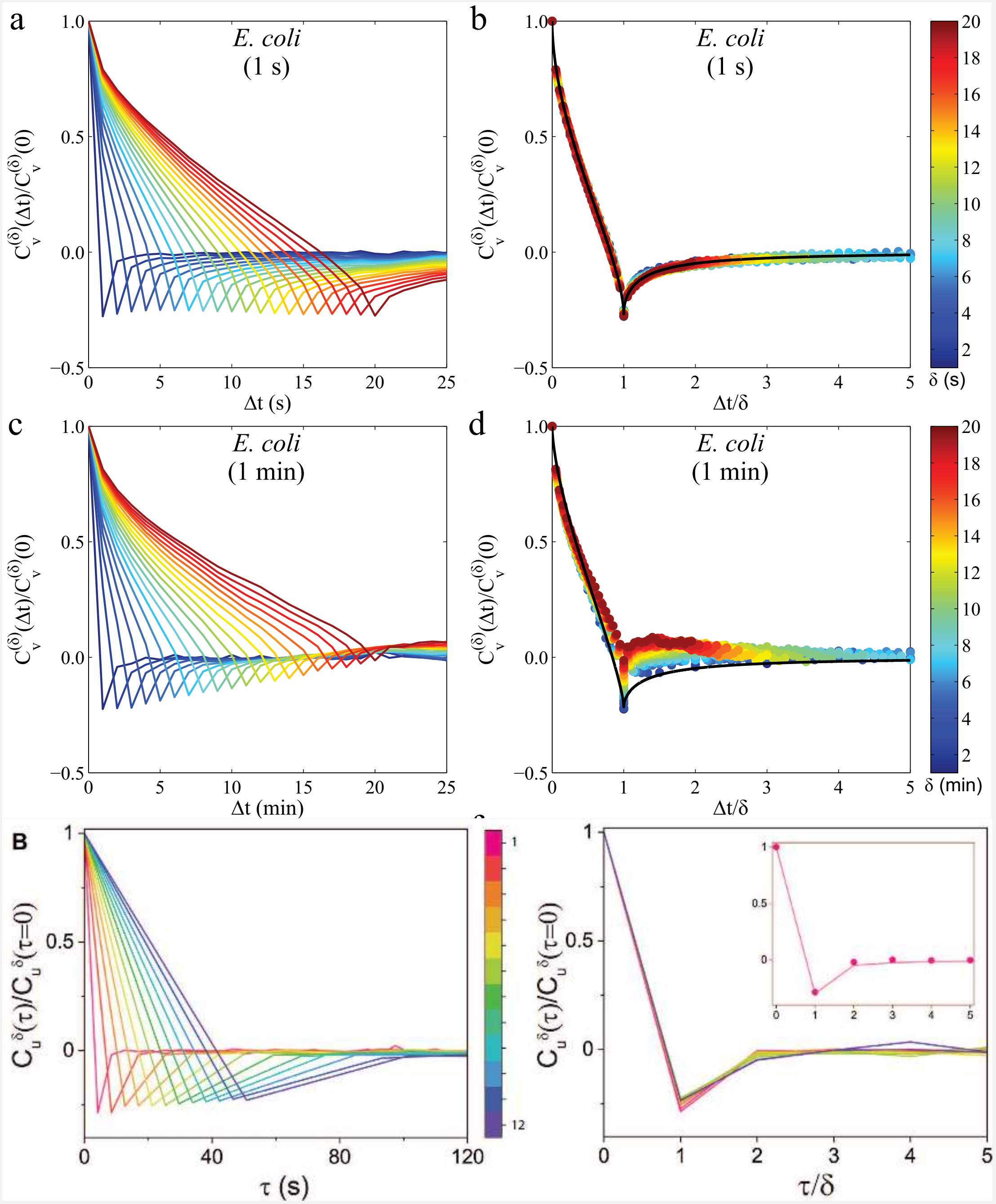


Endogeneous lipid granules

in living yeast cells

J-H Jeon, V Tejedor, S Burov, E Barkai, C Selhuber-Unkel, K Berg-Sørensen, L Oddershede & RM, PRL (2011)

Passive motion of submicron tracers in cells is viscoelastic II



RNA molecules in living E coli cells

TJ Lampo, S Stylianidou, MP Backlund, PA Wiggins & AJ Spakowitz, BPJ (2017)

AttB DNA-binding proteins in living bacillus subtilis cells

R Arbel-Goren, SA McKeithen-Mead, D Voglmaier, I Afremov, G Teza, AD Grossman & J Stavans, NAR (2023)

Fractional Brownian motion

FLE: fluctuation-dissipation $\rightsquigarrow$ asymptotic thermal equilibrium [books by Zwanzig, Kubo]

FBM: "external noise" for non-equilibrium systems or "open systems" [Klimontovich, Statistical physics of open systems] $\rightsquigarrow$ biological cells, animals, weather, finance

Mandelbrot-van Ness smoothed FBM [SIAM Rev (1968)]:

$$\frac{dx(t)}{dt} = \sqrt{2D(t)}\xi_H(t)$$

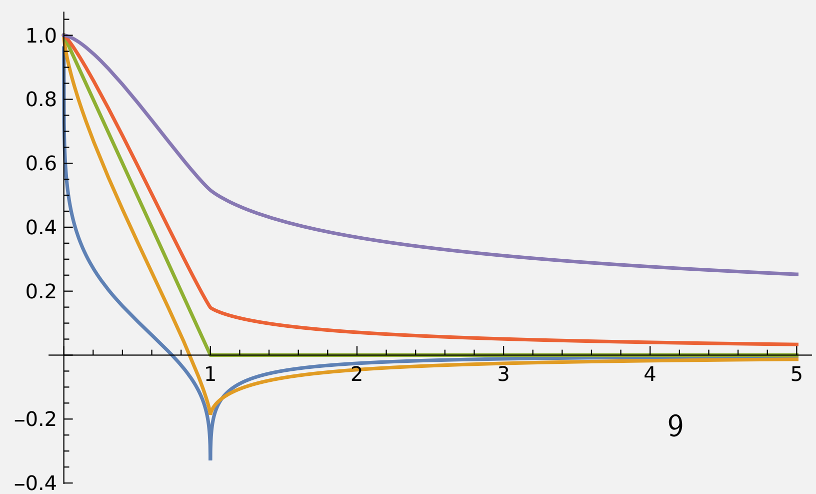
$\xi_H(t)$ is fractional Gaussian noise, understood as the derivative of smoothed FBM:

$$\langle \xi_H(t)\xi_H(t+\tau)\rangle = \frac{1}{2\delta}\left(|t+\delta|^{2H} - 2|\tau|^{2H} + |t-\delta|^{2H}\right) \sim H(2H-1)\tau^{2H-2}$$

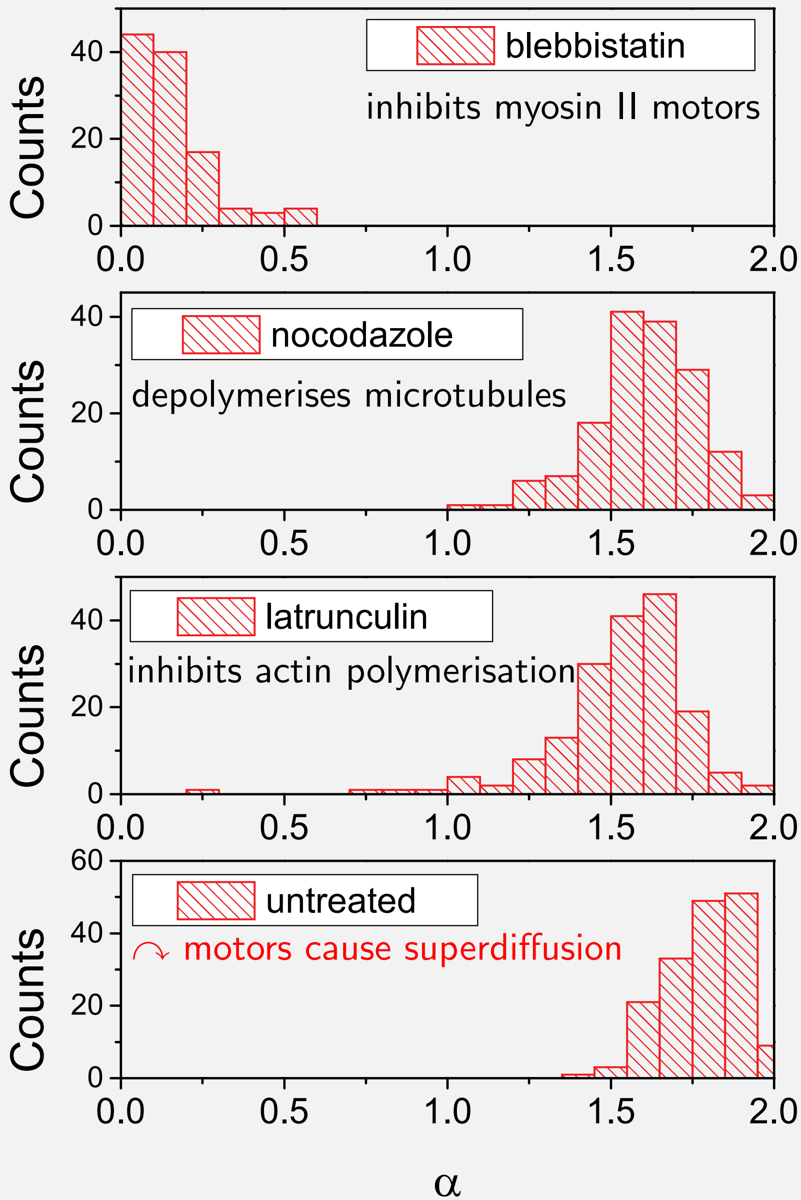
Displacement correlator:

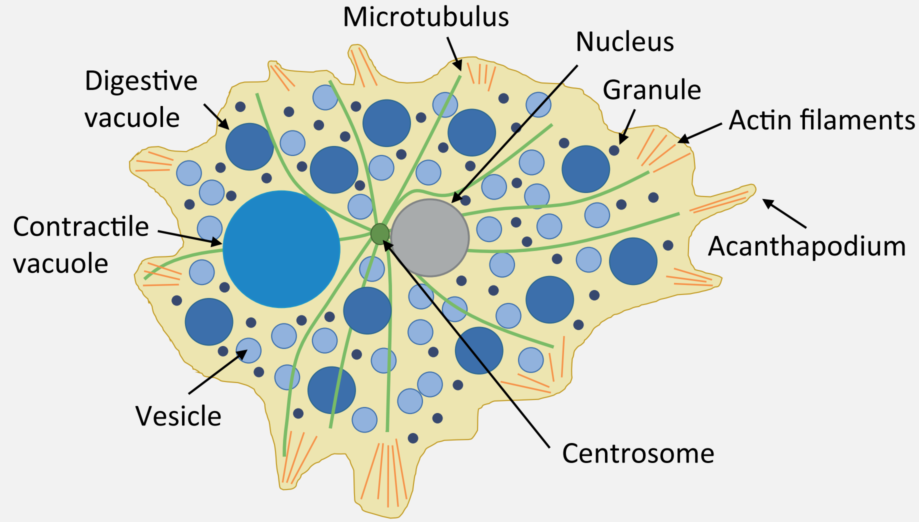
$$C_{\delta t}(t) = \frac{\langle [\mathbf{r}(t+\delta t) - \mathbf{r}(t)] \cdot \mathbf{r}(\delta t) - \mathbf{r}(0)]\rangle}{\delta t^2}$$

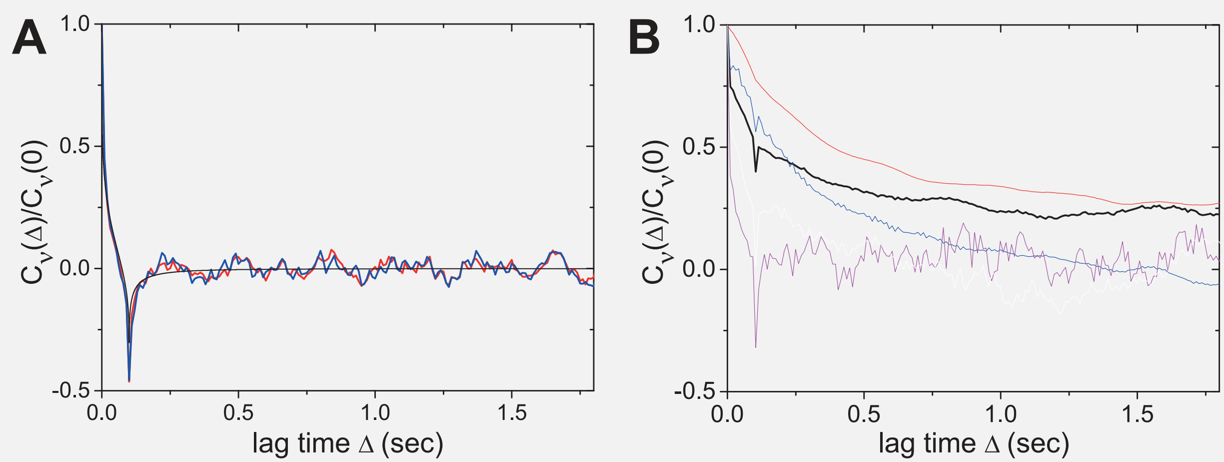
$$\frac{C_{\delta t}(t)}{C_{\delta t}(0)} = \frac{(t+\delta t)^{2H} - 2t^{2H} + |t-\delta t|^{2H}}{2\delta t^{2H}}$$



Superdiffusion in supercrowded Acanthamoeba castellani

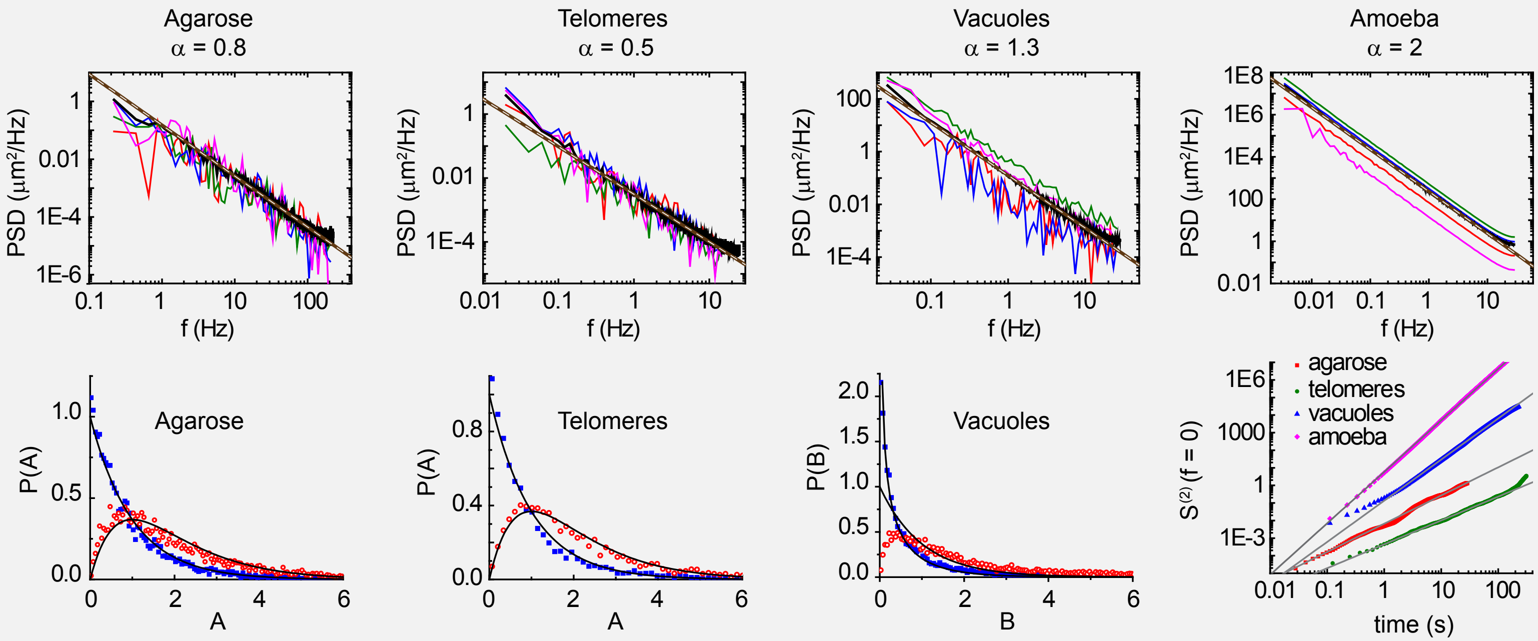


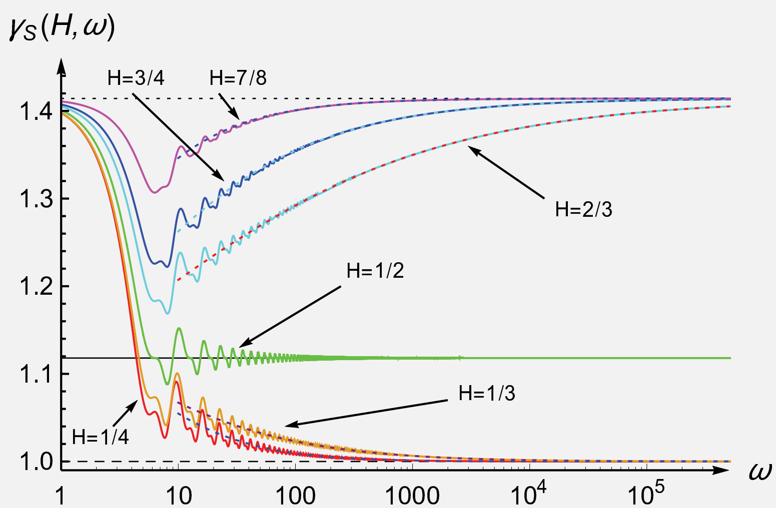




JF Reverey, J-H Jeon, H Bao, M Leippe, RM & C Selhuber-Unkel, Sci Rep (2015); S Thapa, N Lukat, C Selhuber-Unkel, A Cherstvy & RM, JCP (2019)

Power spectral density of a single FBM trajectory



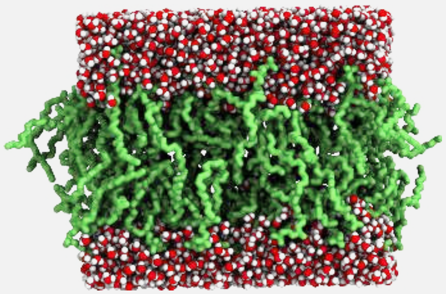


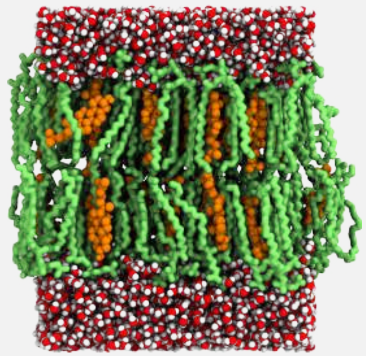
$$S(f,T) = \frac{1}{T}\left|\int_0^T \exp(ift)X_t dt\right|^2$$

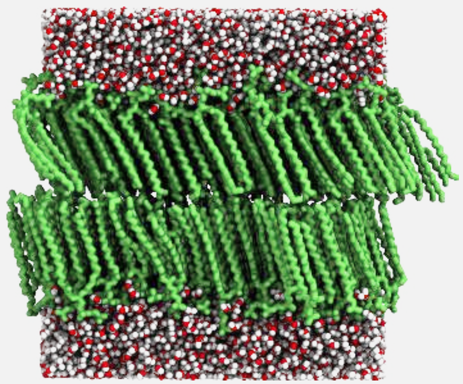
$$\gamma = \frac{\left(\langle S_T^2(f)\rangle - \langle S_T(f)\rangle^2\right)^{1/2}}{\langle S_T(f)\rangle}$$

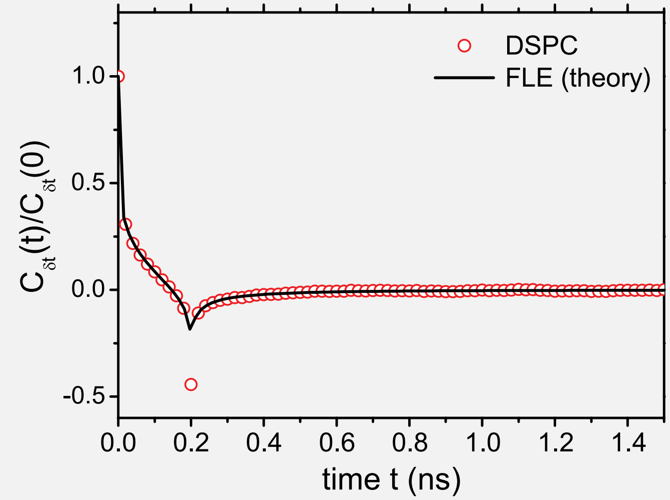
D Krapf, N Lukat, E Marinari, RM, G Oshanin, C Selhuber-Unkel, A Squarcini, L Stadler, M Weiss & X Xu, PRX (2019)

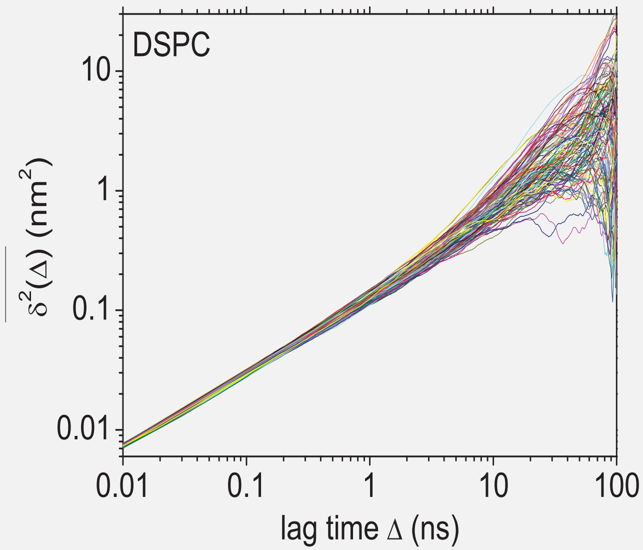
Single lipid motion in bilayer membranes

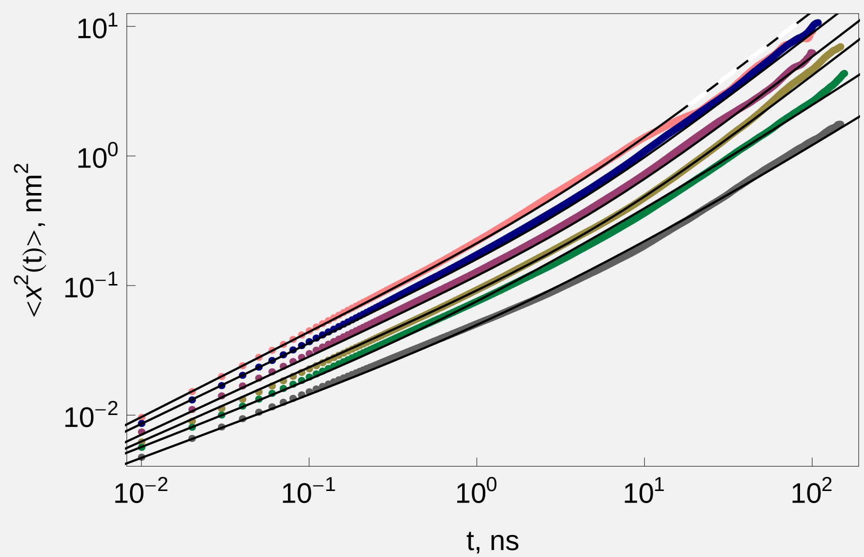












Pure bilayer:

$t^{2/3} \longrightarrow t^1$

/w cholesterol/gel:

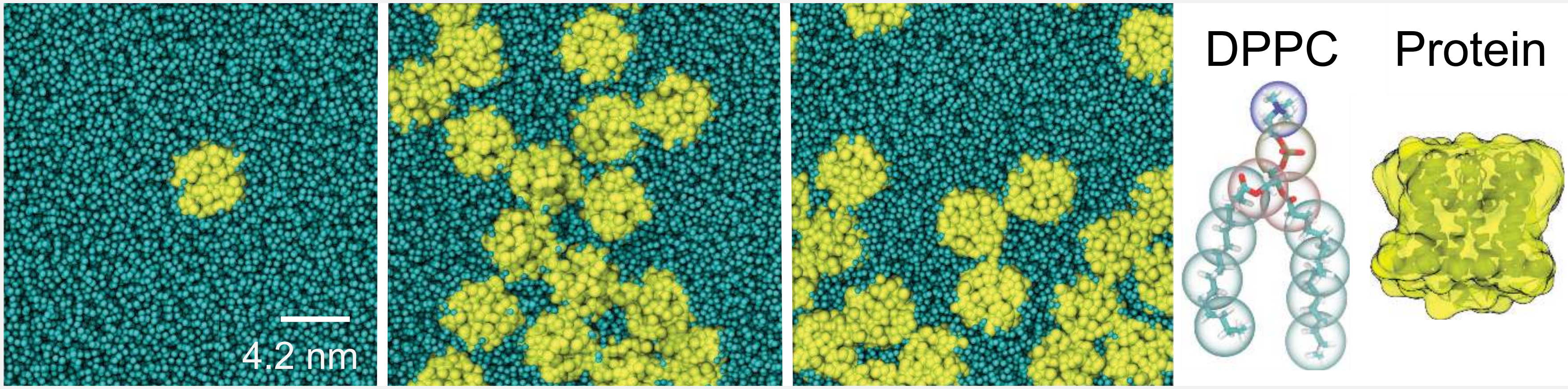
$t^\alpha \longrightarrow t^{\alpha'>\alpha}$

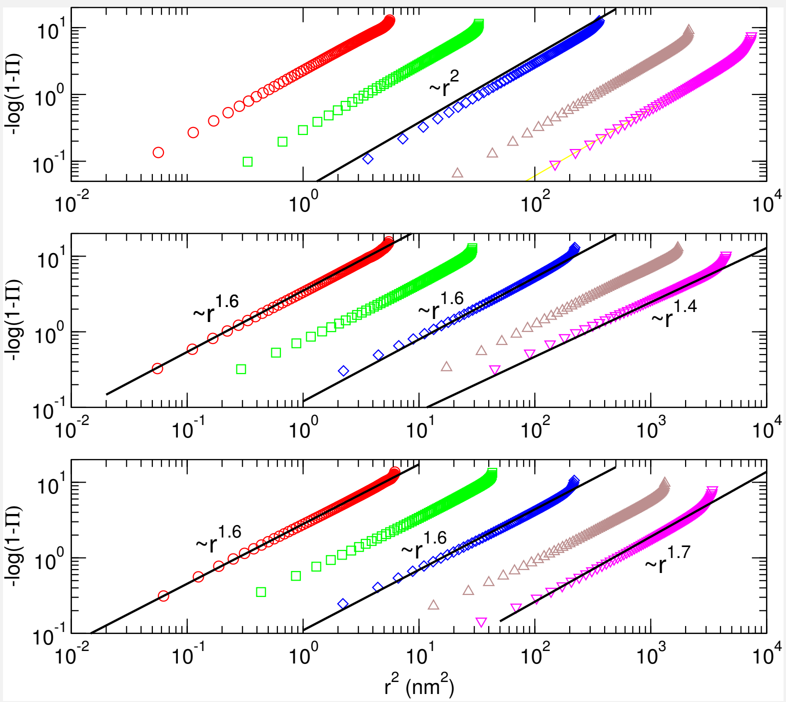
Tempered GLE

D Molina-Garcia, T Sandev, H Safdari, G Pagnini, AV Chechkin & RM, NJP (2018)

J-H Jeon, H Martinez-Seara Monne, M Javanainen & RM, PRL (2012)

Crowding in membranes: non-Gaussian lipid/protein diffusion

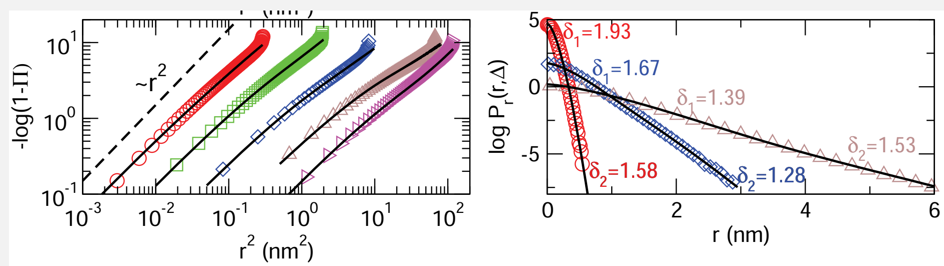




Dilute membrane: $P(r,t)$ Gauss

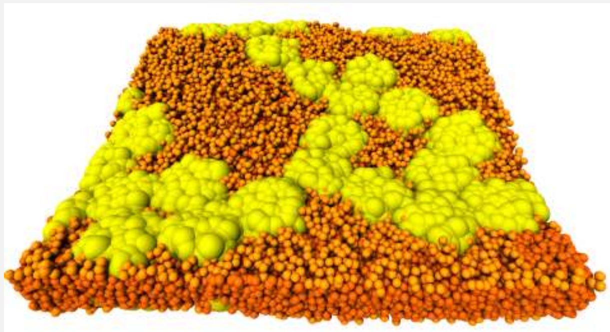
Crowded membrane ($\delta \approx 1.3 \ldots 1.7$):

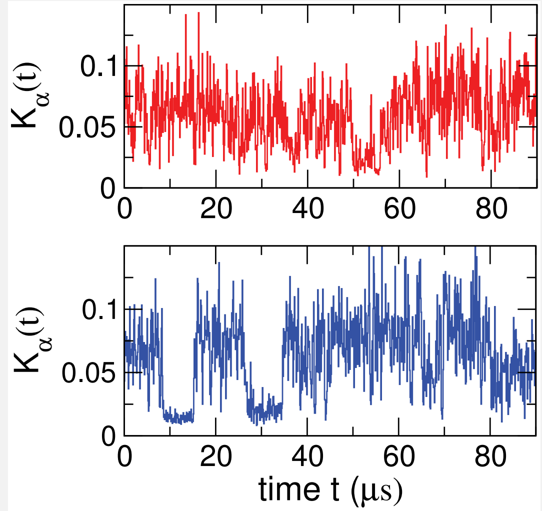
$$P(r,t) \propto \exp\left(-\left[\frac{r}{ct^{\alpha/2}}\right]^{\delta}\right)$$

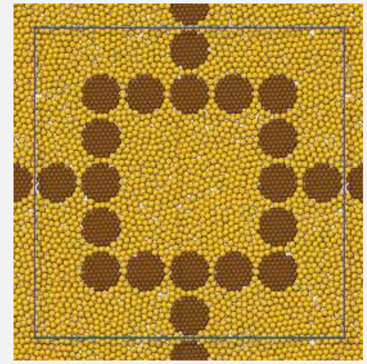


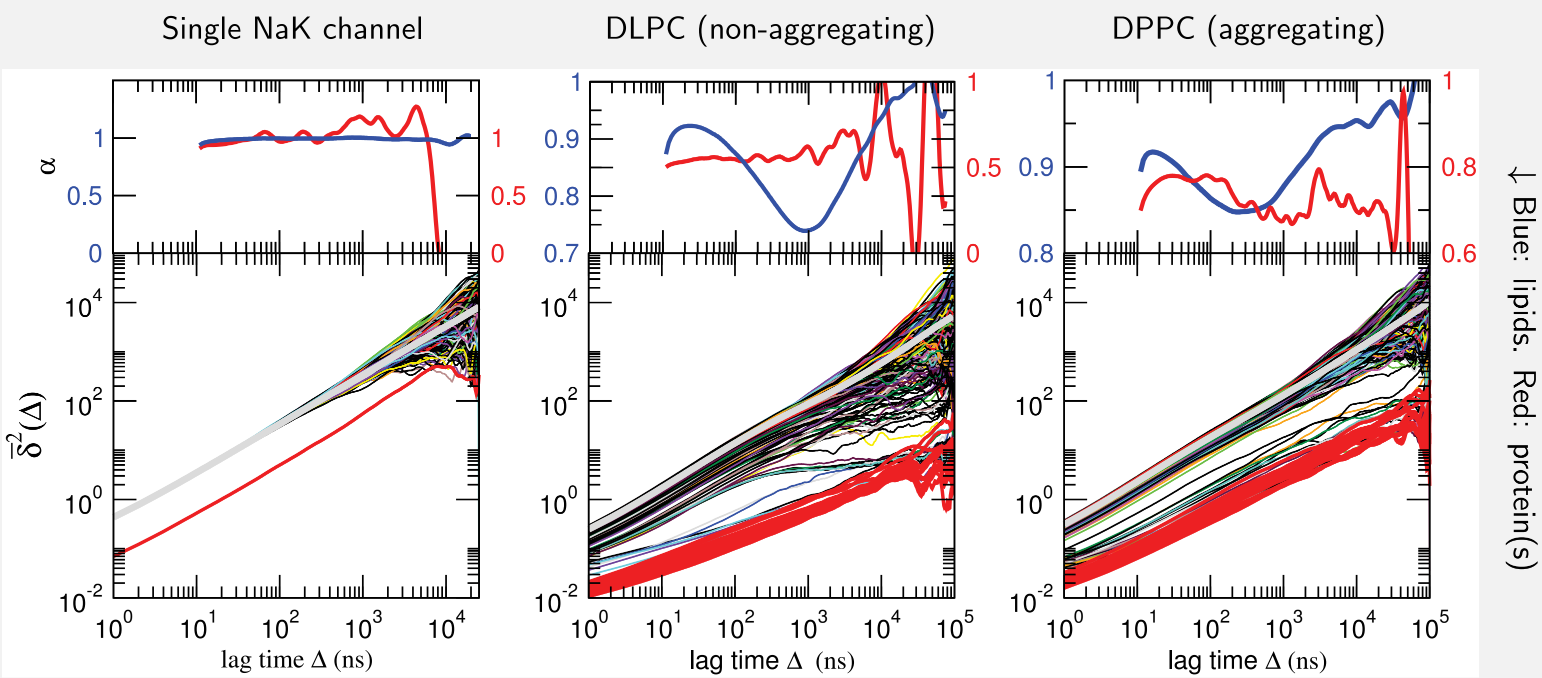
J-H Jeon, M Javanainen, H Martinez-Seara, RM & I Vattulainen, PRX (2016); compare Faraday Disc (2013) & PRL (2012)

Intermittent lipid diffusion in protein-crowded membranes



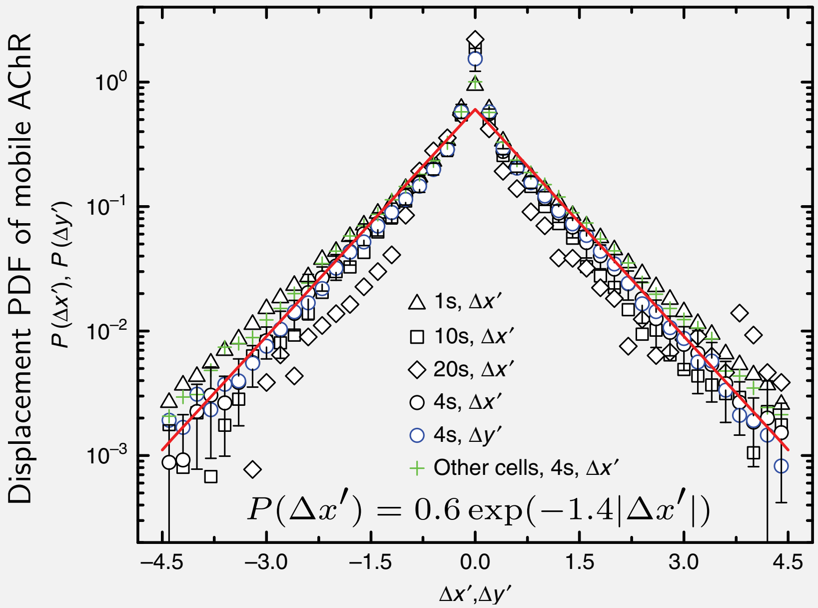


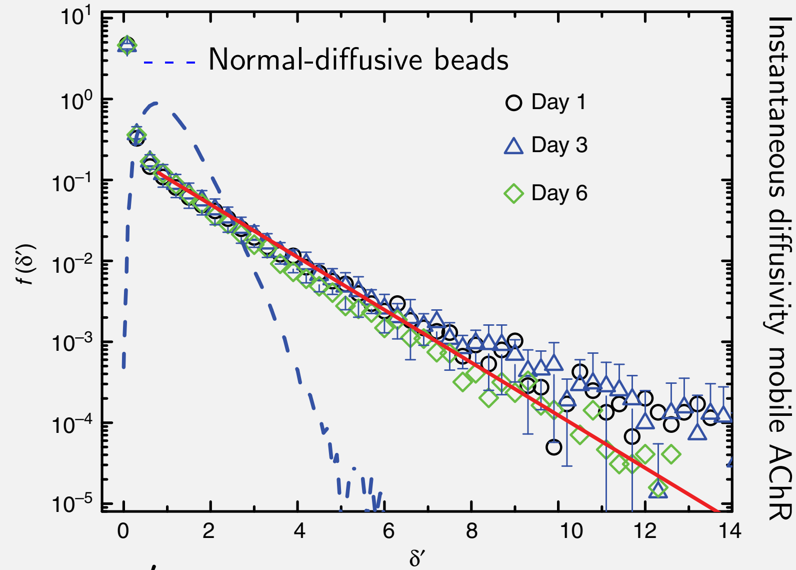




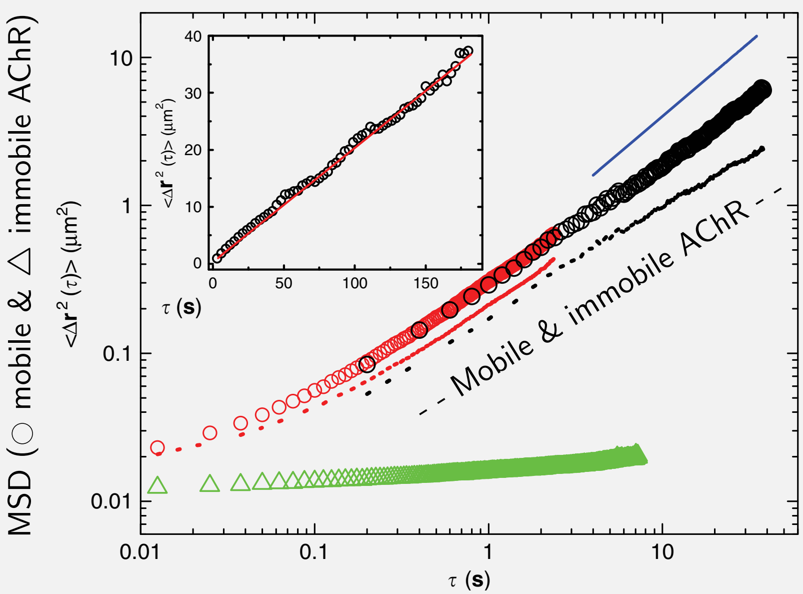
J-H Jeon, M Javanainen, H Martinez-Seara, RM & I Vattulainen, PRX (2016); compare Faraday Disc (2013)

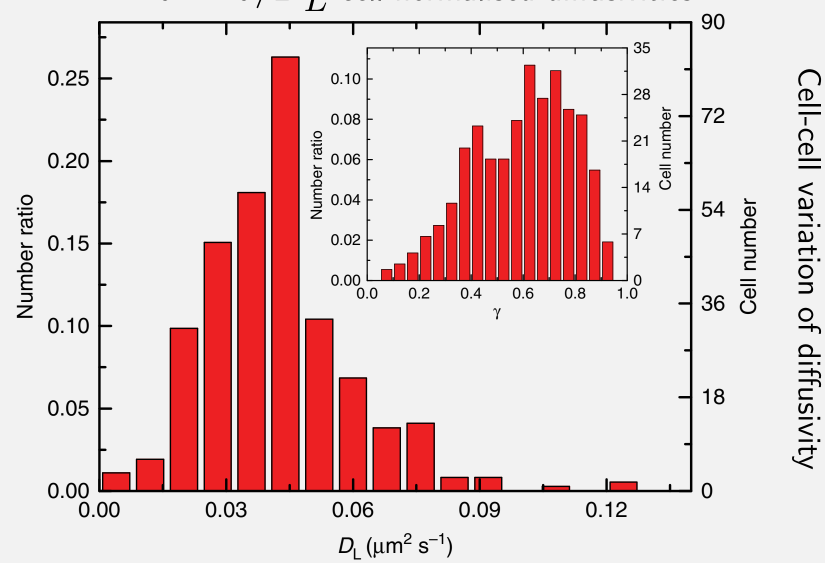
Non-Gaussianity of acetylcholine receptors in Xenopus cells





$\delta' = \delta / D_L$ cell-normalised diffusivities

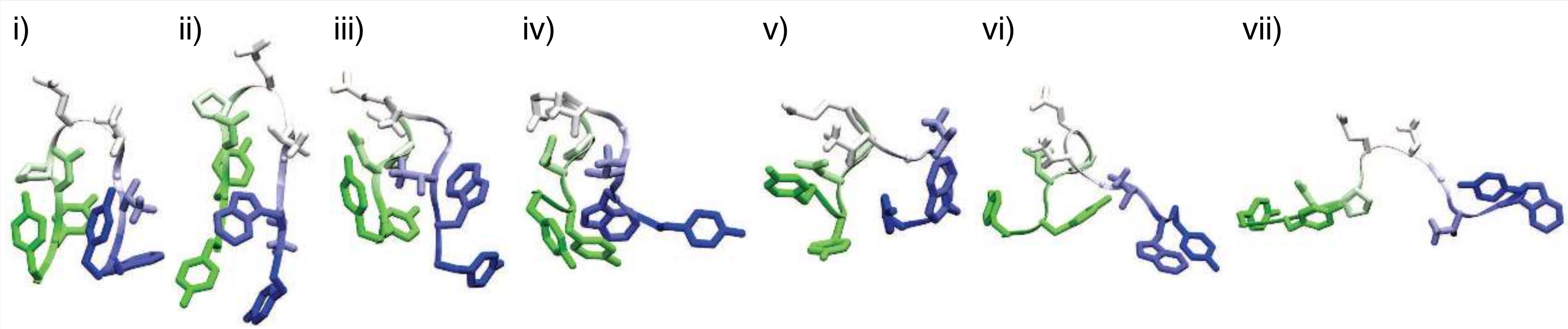


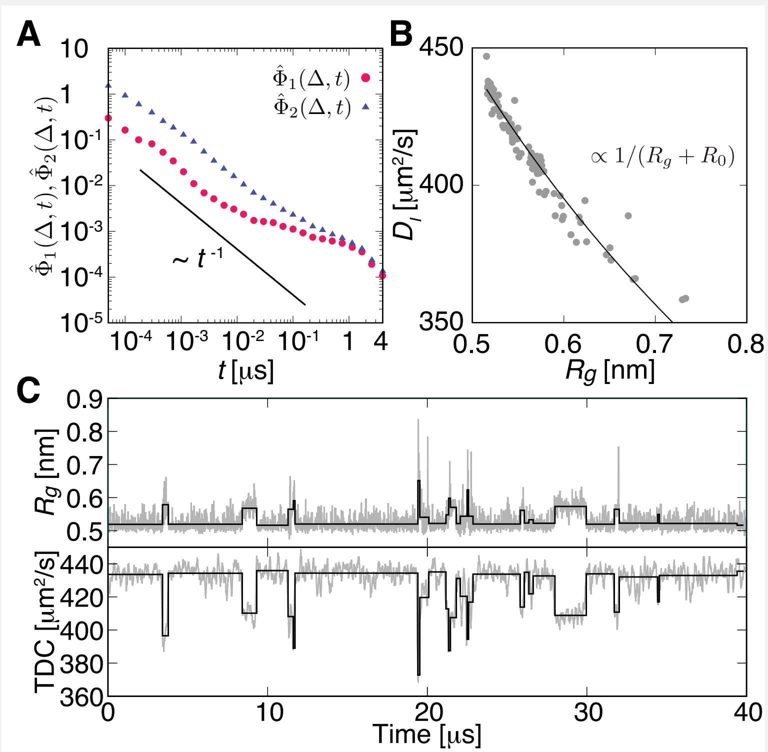


D_L from $\langle \mathbf{r}^2(\tau) \rangle = 2 D_L \tau$

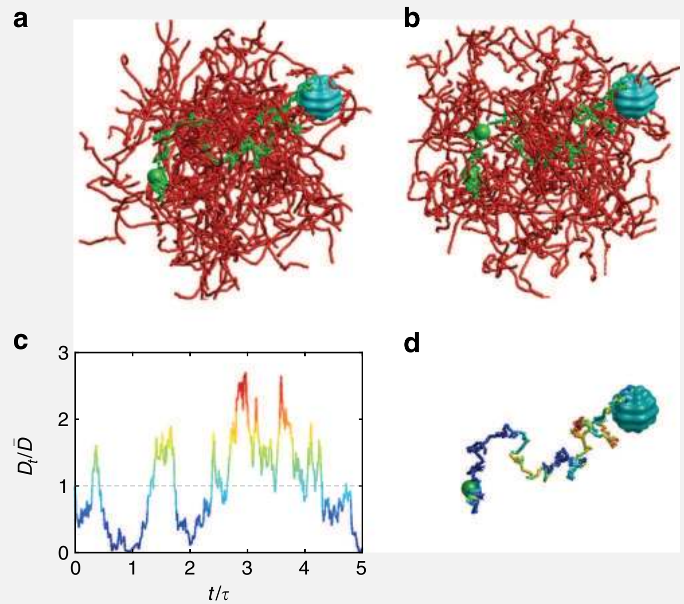
W He, H Song, Y Su, L Geng, BJ Ackerson, HB Peng & P Tong, Nat Comm (2016)

Instantaneous diffusivity of shape-fluctuating proteins





Annealed diffusing-diffusivity in rearranging heterogeneous environments



Y Lanoiselée, N Moutal, & D Grebenkov, Nat Comm (2018)

E Yamamoto, T Akimoto, A Mitsutake & RM, PRL (2021)

Viscoelastic diffusing-diffusivity model

DD model for Brownian yet non-Gaussian motion:

MV Chubinsky & G Slater, PRL (2014); R Jain & KL Sebastian, JPC B (2016), AV Chechkin, F Seno, RM & IM Sokolov, PRX (2017); V Sposini, AV Chechkin, G Pagnini, F Seno & RM, NJP (2018)

FBM-generalised diffusing-diffusivity model:

$$\frac{dx(t)}{dt} = \sqrt{2D(t)}\xi_H(t)$$

with $D(t)$ as squared Ornstein-Uhlenbeck process $Y(t)$:

$$D(t) = Y^2(t), \quad \frac{dY(t)}{dt} = -Y + \eta(t)$$

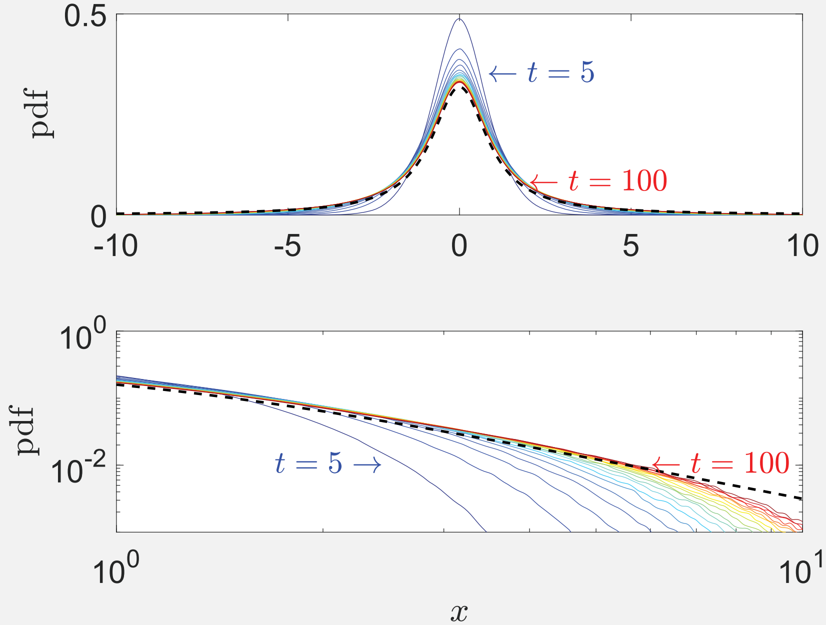
Here, $\eta(t)$ is white Gaussian noise with zero mean & unit variance

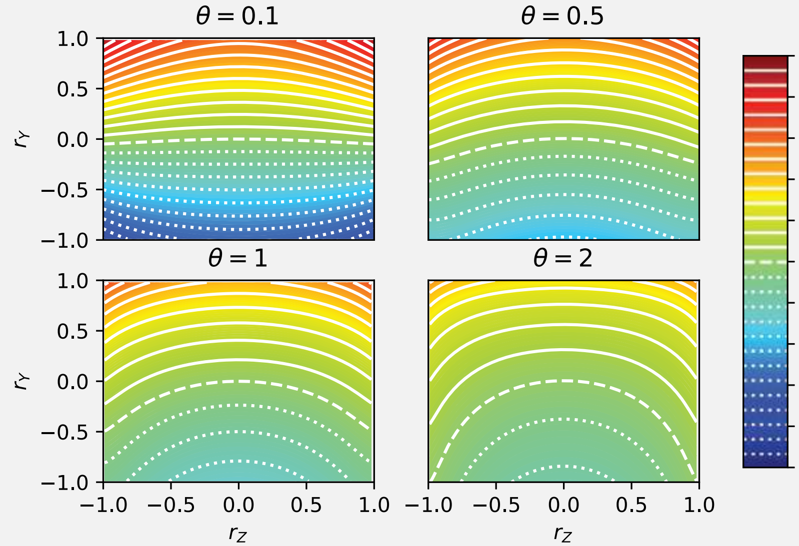
$\xi_H(t)$ is fractional Gaussian noise, understood as the derivative of the Mandelbrot-van Ness smoothed FBM [SIAM Rev (1968)]:

$$\langle \xi_H(t)\xi_H(t+\tau)\rangle = \frac{1}{2\delta}\Big(|t+\delta|^{2H} - 2|\tau|^{2H} + |t-\delta|^{2H}\Big) \sim H(2H-1)\tau^{2H-2}$$

W Wang, AV Chechkin, F Seno, IM Sokolov & RM, NJP (2020); W Wang, AG Cherstvy, AV Chechkin, S Thapa, F Seno, X Liu & RM, JPA (2020)

Non-Gaussian dynamics in the presence of correlated noise



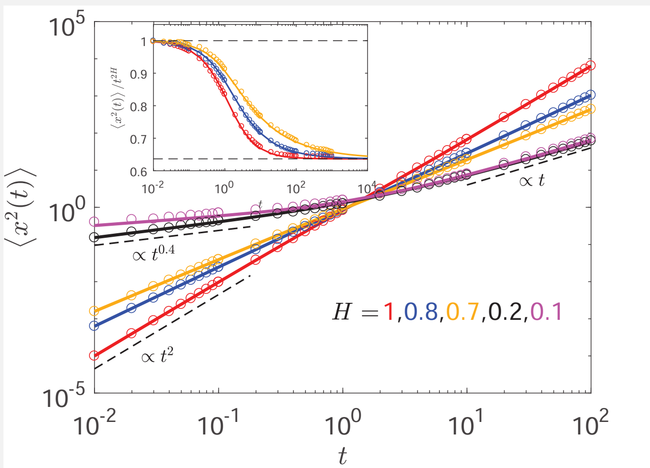


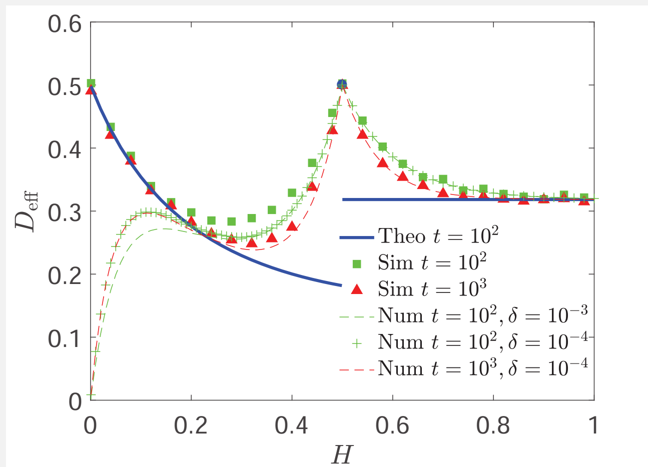
Codifference detects non-Gaussianity

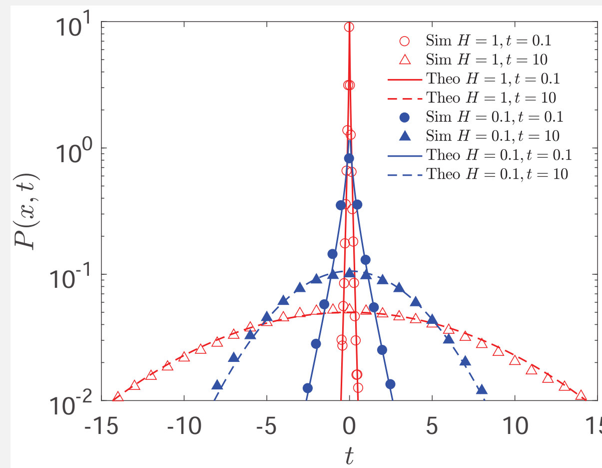
& non-ergodicity

Viscoelastic diffusing-diffusivity model

Prosecco-DD



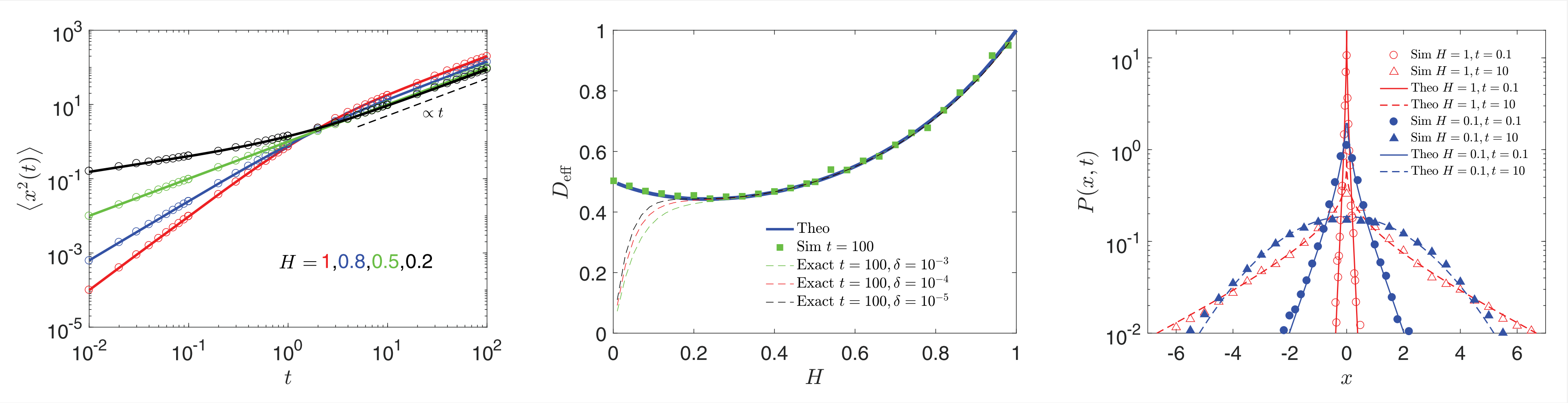




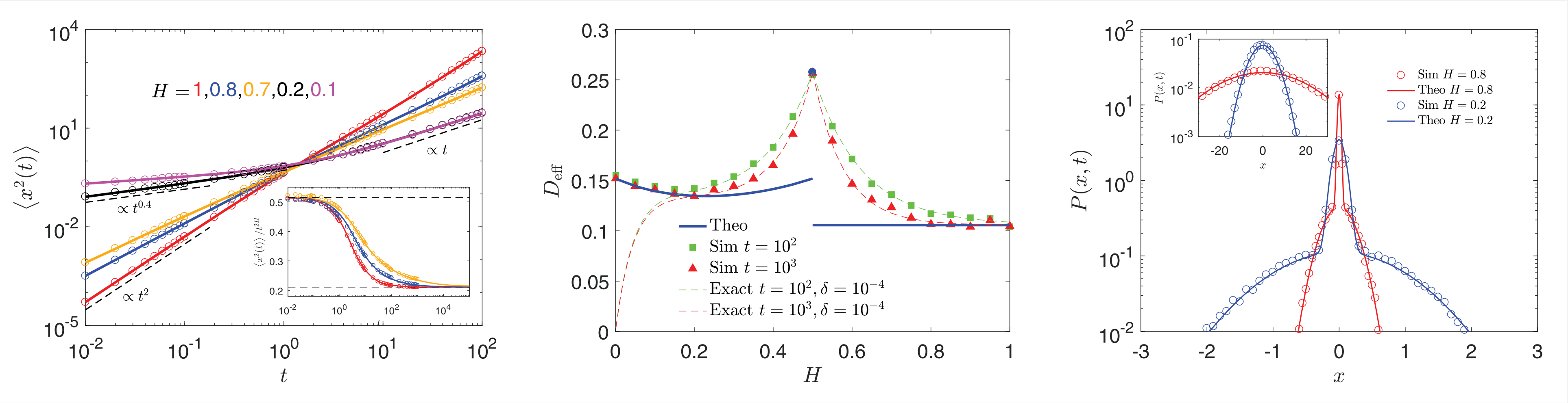
J Ślęzak, M Magdziarz & RM, NJP (2018), NJP (2019); W Wang, AV Chechkin, F Seno, IM Sokolov & RM, NJP (2020)

Viscoelastic diffusing-diffusivity model

Tyagi model



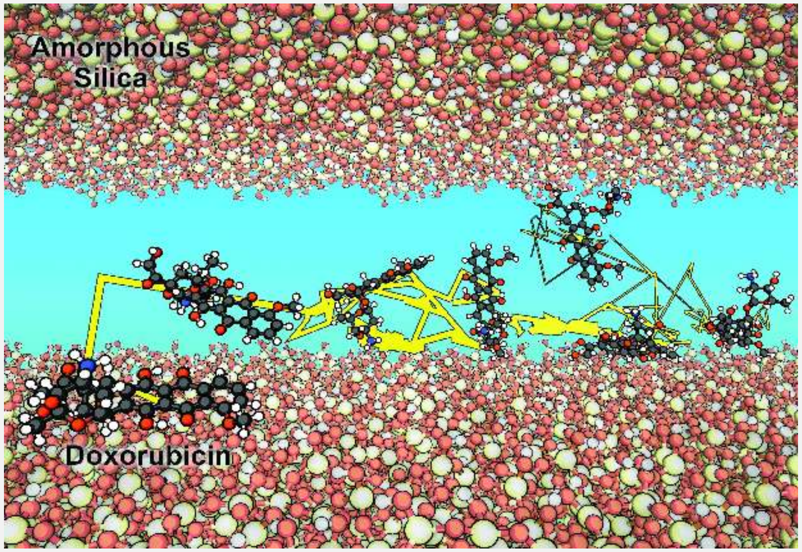
Switching model

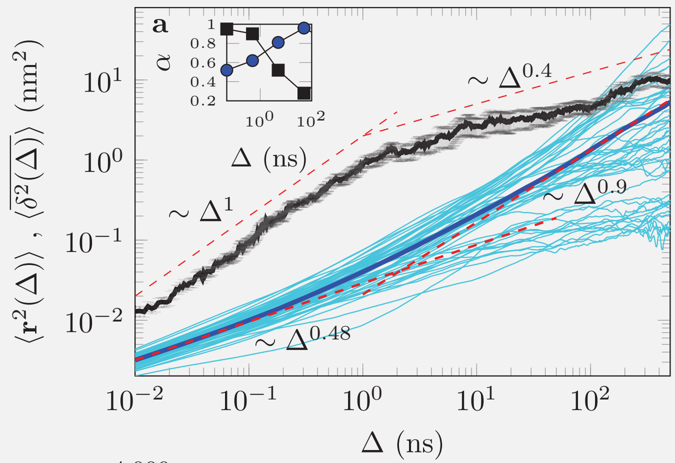


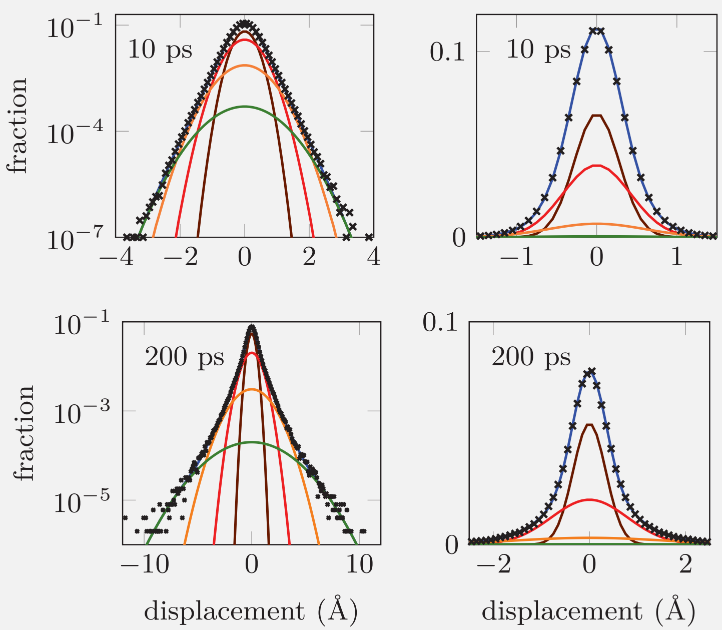
W Wang, AV Chechkin, F Seno, IM Sokolov & RM, NJP (2020)

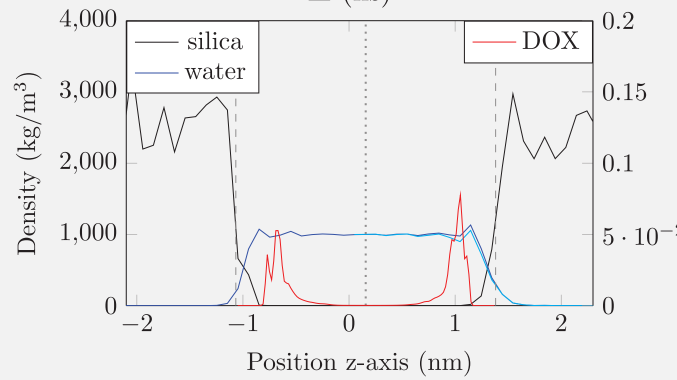
Doxorubicin drug molecule diffusion in silica nanochannels

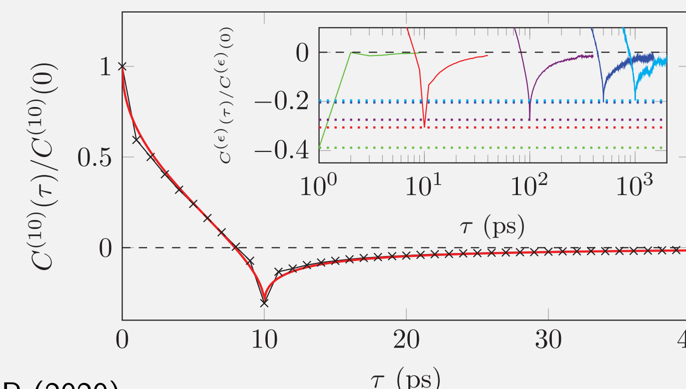
Anomalous diffusion of mixed origin











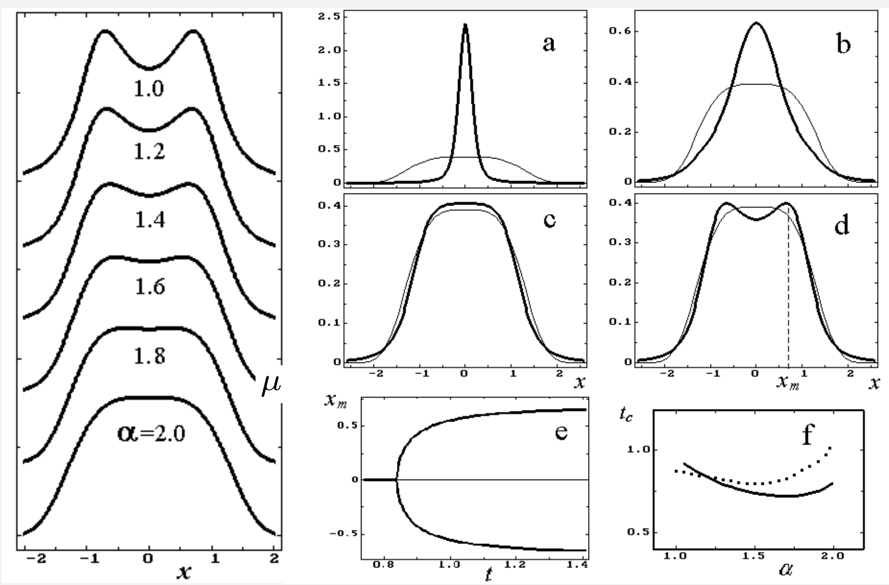
A Díez Fernández, P Charchar, AG Cherstvy, RM & MW Finnis, PCCP (2020)

Lévy flights ($\lambda(x) \simeq |x|^{-1-\mu}$) in superharmonic potentials

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial x}\frac{V'(x)}{m\eta}P(x,t) + K^{\mu}\frac{\partial^{\mu}}{\partial |x|^{\mu}}P(x,t), \quad V(x) \simeq |x|^{c}$$

Harmonic potential: $P_{\rm st}(x) = L_{\mu}(x)$ [S Jespersen, RM & HC Fogedby, PRE (1999)]

Quartic potential $V(x) = \frac{1}{4}x^4$



Box-like potentials: K Capała, A Padash, AV Chechkin, B Shokri, RM & B Dybiec, Chaos (2020)

Subharmonic potentials:
Convergence to stationary state only if:

$$c > 2 - \mu, \quad 0 < \mu \leq 2$$

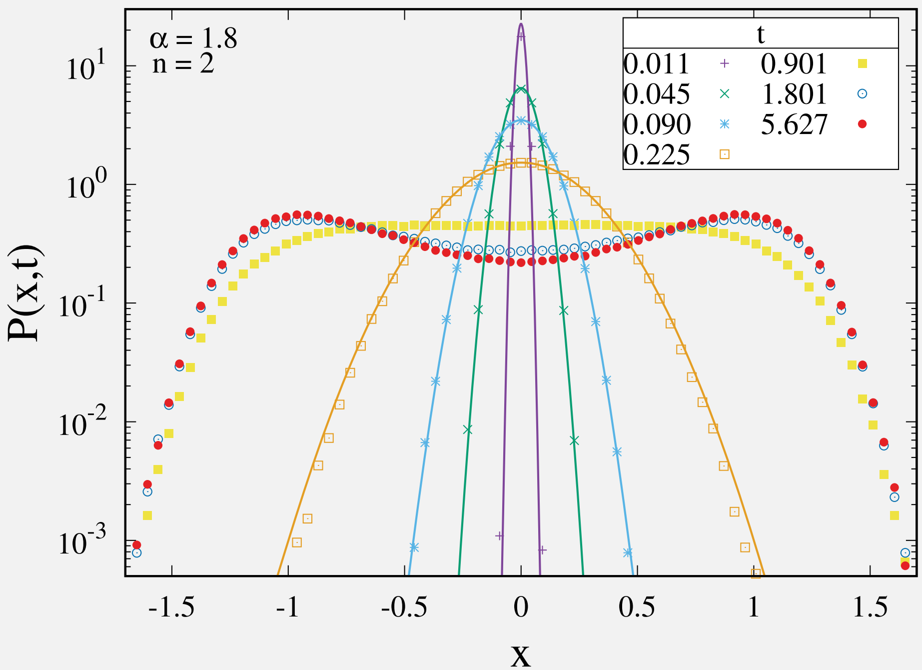
Otherwise motion is unconfined B Dybiec, AV Chechkin & IM Sokolov, JSTAT (2010)

AV Chechkin, VYu Gonchar, J Klafter, RM & LV Tanatarov, Chem Phys (2002); PRE (2003); JSP (2004)

Fractional BM in super- and subharmonic potentials

$$\frac{d}{dt}X(t) = -V'(x)X(t) + \xi_\alpha(t) \quad \therefore \quad \langle \xi_\alpha(t)\xi_\alpha(t+\tau)\rangle \sim \alpha(\alpha-1)K_\alpha \tau^{\alpha-2}$$

Quartic potential



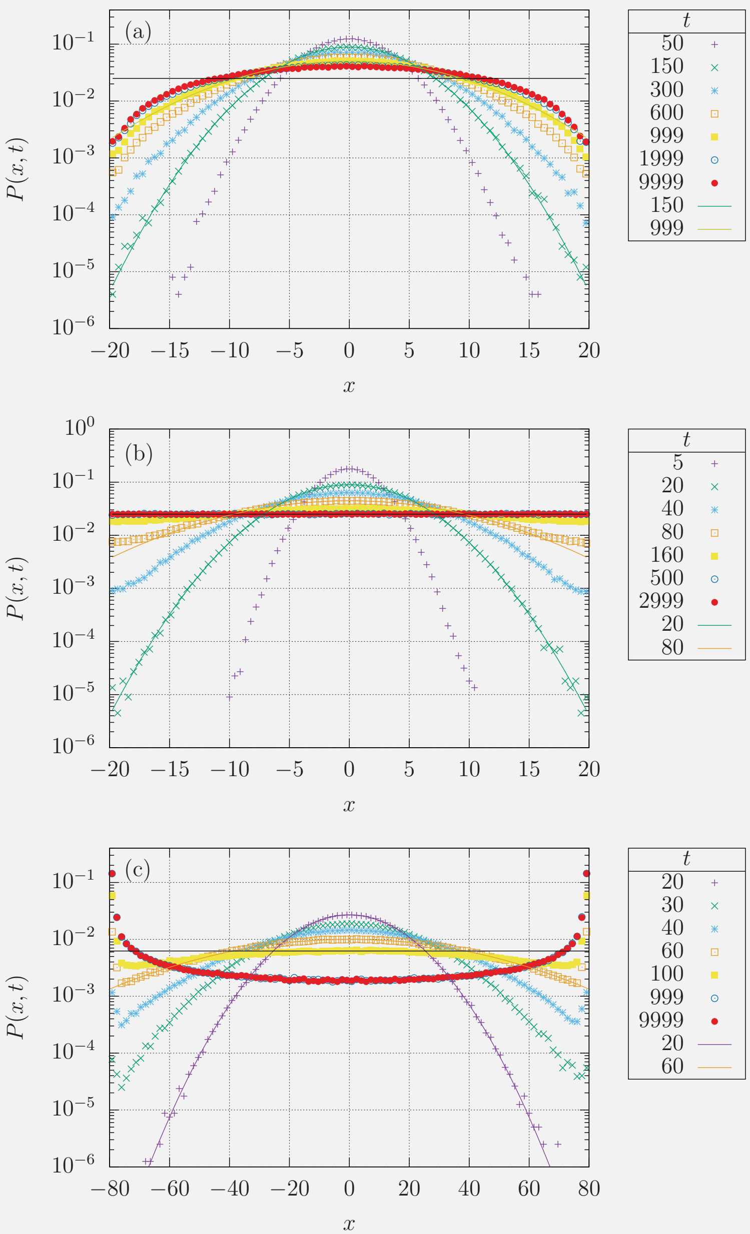
Convergence to stationarity only if (free motion $\langle x^2(t)\rangle_{\mathrm{FBM}} \simeq t^\alpha$, $\langle |x|^\delta(t)\rangle_{\mathrm{LF}}^{2/\delta} \simeq t^{2/\mu}$):

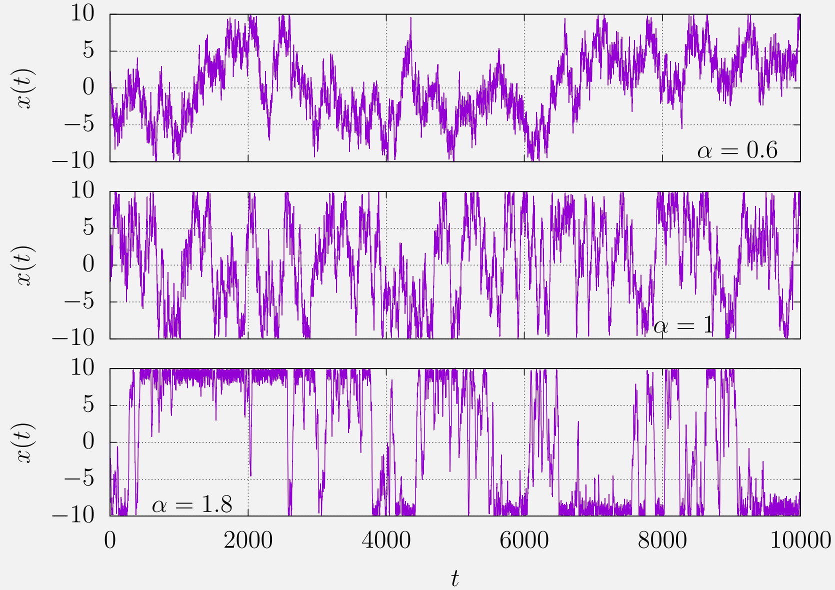
$c > 2 - \dfrac{2}{\alpha}$ self-similarity index $H = \dfrac{\alpha}{2}$

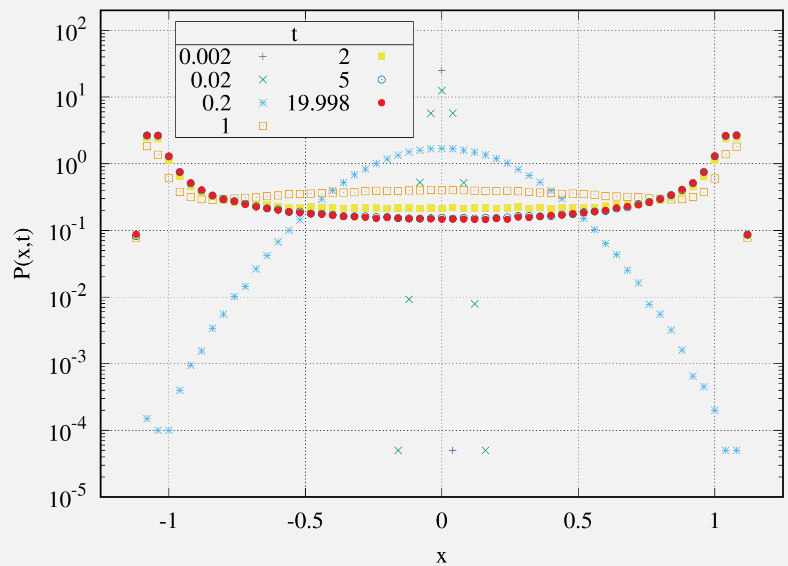
$c > 2 - 1/H$

For Lévy flight $H = 1/\mu \Rightarrow$ same criterion for existence for stationary states

FBM: accretion & depletion effects near hard boundaries



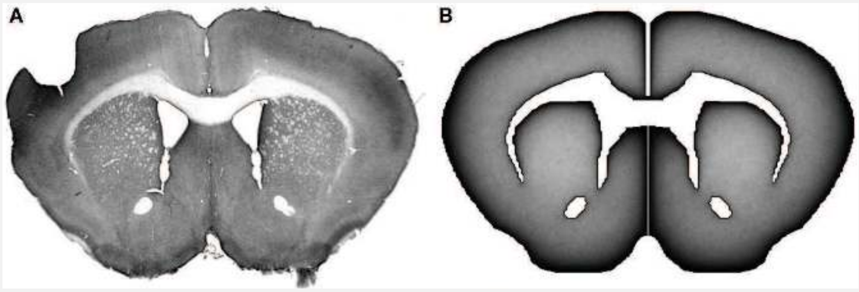


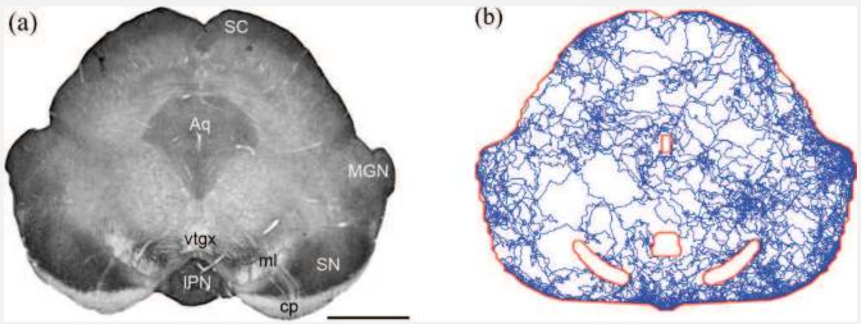


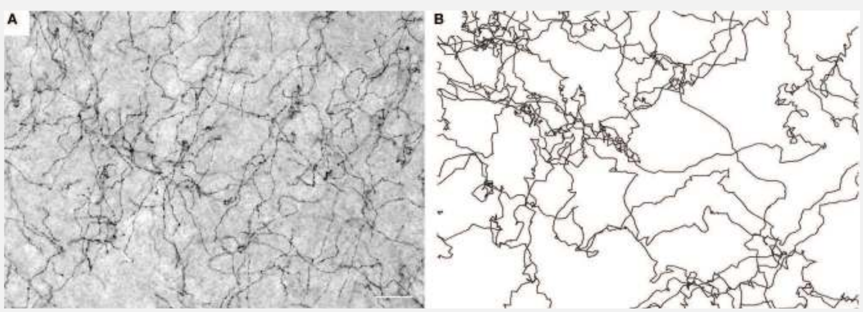
T Guggenberger, G Pagnini, T Vojta & RM, NJP (2019); AHO Wada & T Vojta, PRE (2018); T Vojta, S Skinner & RM, PRE (2019)

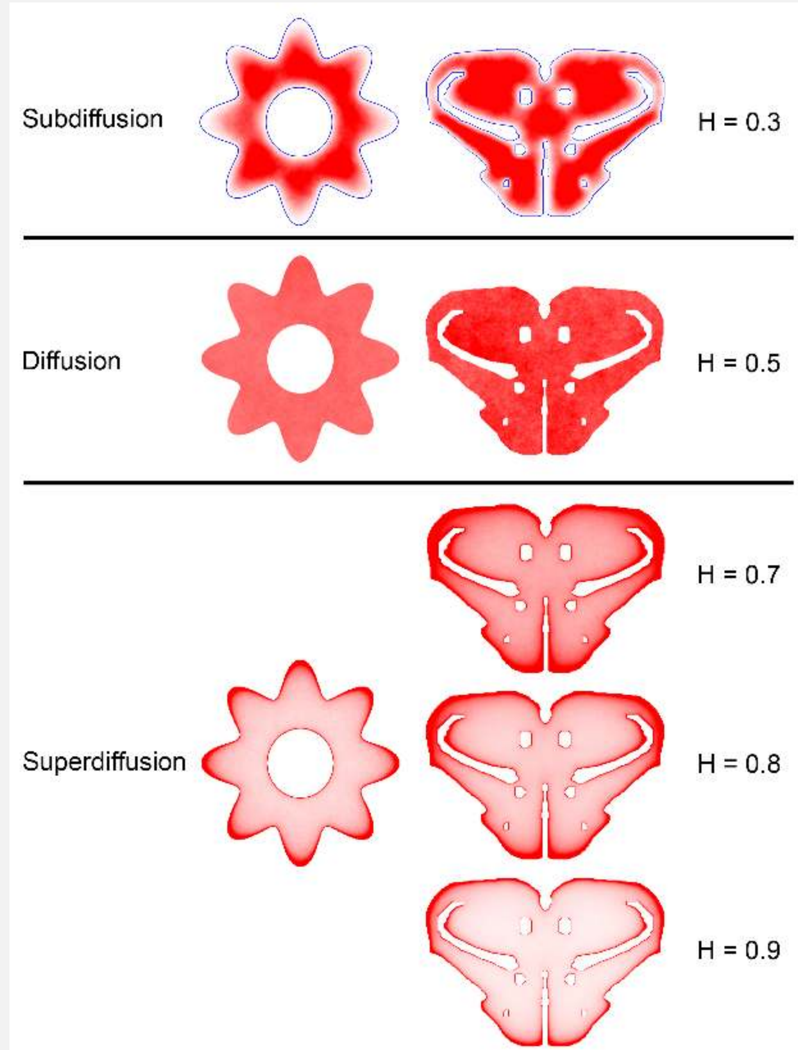
Brain serotonergic axons as FBM paths

Correlated fluctuations effect non-flat profile





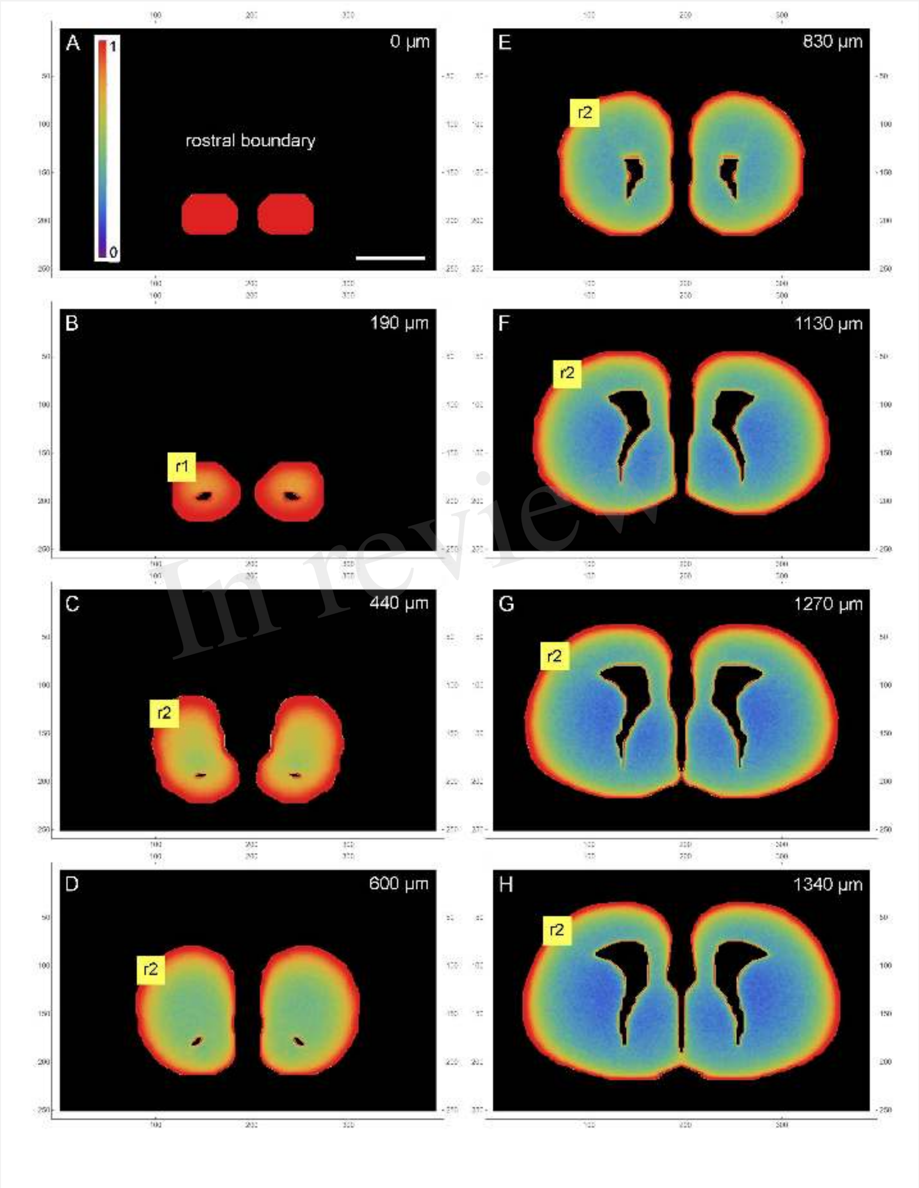




S Janušonis, N Detering, RM & T Vojta, Front Comp Neurosc (2020); T Guggenberger, T Vojta & RM, NJP (2019)

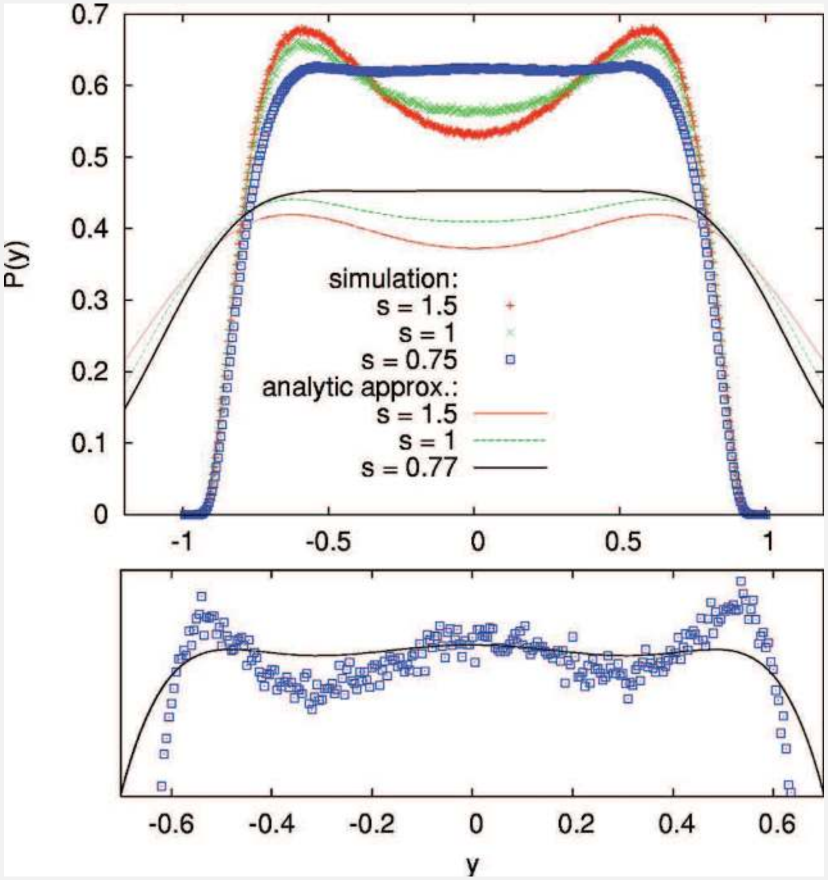
Brain serotonergic axons as FBM paths

Figure 2.TIF

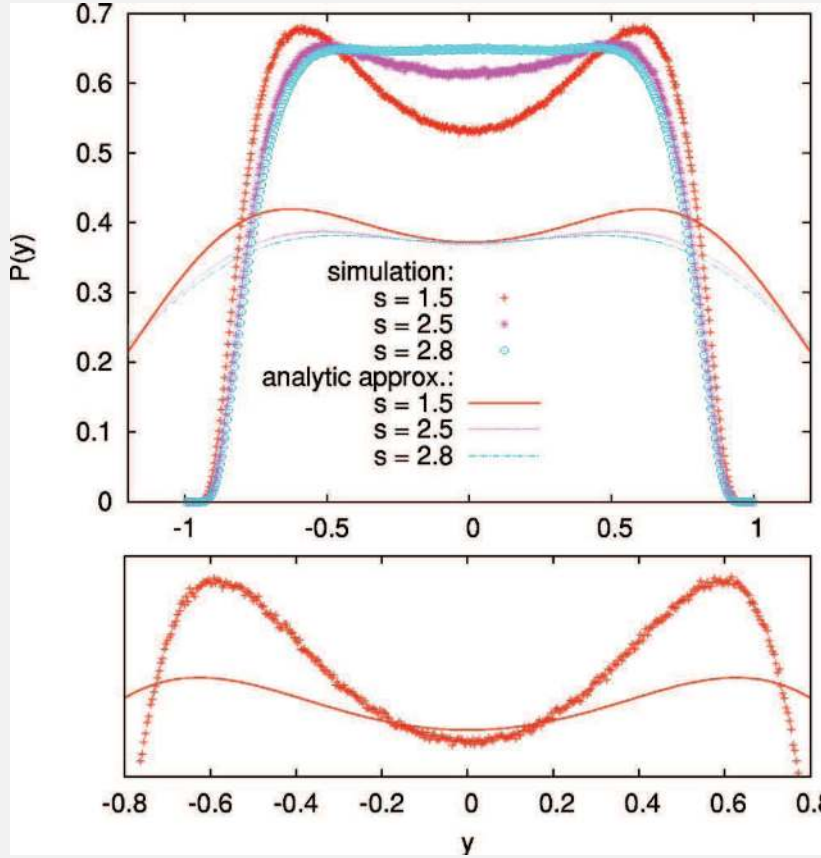


S Janušonis, JH Haiman, RM & T Vojta, Front Comp Neurosc (2022)

Bimodality in the transverse fluctuations of a grafted semiflexible polymer



$s = L/\ell_p$: stiff $\rightarrow$ semi-flexible



semi-flexible $\rightarrow$ flexible

Modelling in terms of worm-like chain model

P Benetatos, T Munk & E Frey, PRE (2005)

Doubly-stochastic processes

"Roughness" in, i.a., financial data, is modelled by subdiffusive, antipersistent FBM

Roughness changing over time is often modelled by doubly-stochastic models, e.g.,

$$X(t) = \sqrt{\alpha(t)} \int_0^t (t-s)^{(\alpha(t)-1)/2} dB(s),$$

in Paul Lévy's Riemann-Liouville formulation. $B(s)$ is the Wiener process $\rightsquigarrow$ locally varying roughness according to $\alpha(t)$ [e.g., A Ayache & J Lévy-Vehel (2000)]:

$$\langle X^2(t)\rangle \simeq t^{\alpha(t)}$$

$\rightsquigarrow$ where is the memory? $H(t)$, e.g., in cells during life cycle (density variation), in cooling membranes, in gel during cross-linking process etc.

Imagine a Brownian motion changing from K_1 to K_2 at $t=\tau$, described as

$$\tilde{B}(t) = \int_0^t \sqrt{K(s)} dB(s), \quad \rightsquigarrow \quad \langle X^2(t)\rangle = \begin{cases} 2Kt_1, & t \leq \tau \\ 2K_2(t-\tau) + 2K_1\tau, & t > \tau \end{cases}$$

whereas the above formulation would produce $\langle X^2(t)\rangle = 2K(t)t$

W Wang, M Balcerek, K Burnecki, AV Chechkin, S Janušonis, J Ślęzak, T Vojta, A Wyłomańska & RM (2023)

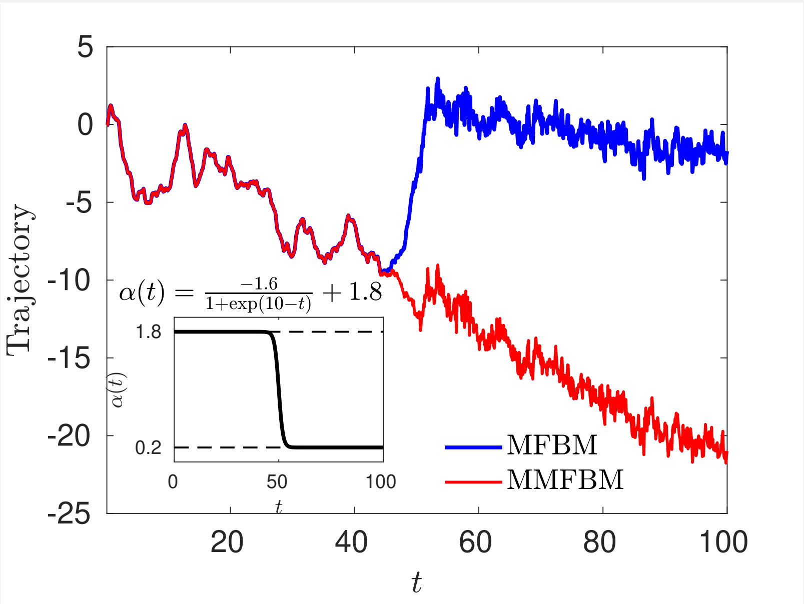
Doubly-stochastic processes

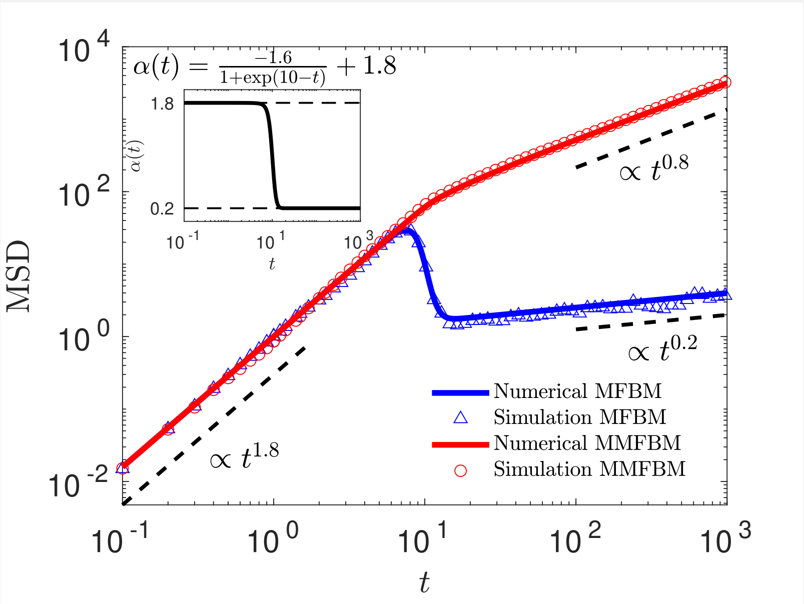
Solution is time-local scaling exponent (memory-multi-FBM):

$$X(t)=\int_0^t\sqrt{\alpha(s)}(t-s)^{(\alpha(s)-1)/2}dB(s),$$

Example of switching α, ($\alpha=\alpha_1$ for $t\leq\tau$, α_2 for $t>\tau$):

$$\langle X^2(t)\rangle=\begin{cases}t^{\alpha_1}, & t\leq\tau\\ t^{\alpha_1}-(t-\tau)^{\alpha_1}+(t-\tau)^{\alpha_2}, & t>\tau\end{cases}\sim(\alpha_1\tau)t^{\alpha_1-1}+t^{\alpha_2}$$





W Wang, M Balcerek, K Burnecki, AV Chechkin, S Janušonis, J Ślęzak, T Vojta, A Wyłomańska & RM (2023)

Doubly-stochastic processes

Response function. Define the increments $X^\delta(\tau) = X(\tau+\delta) - X(\tau)$

Then consider a short α-perturbation:

$$\alpha(t) = \begin{cases} 1, & t \leq \tau \\ \alpha \neq 1, & \tau < t \leq \tau + \delta \\ 1, & t > t + \delta \end{cases}$$

Response function:

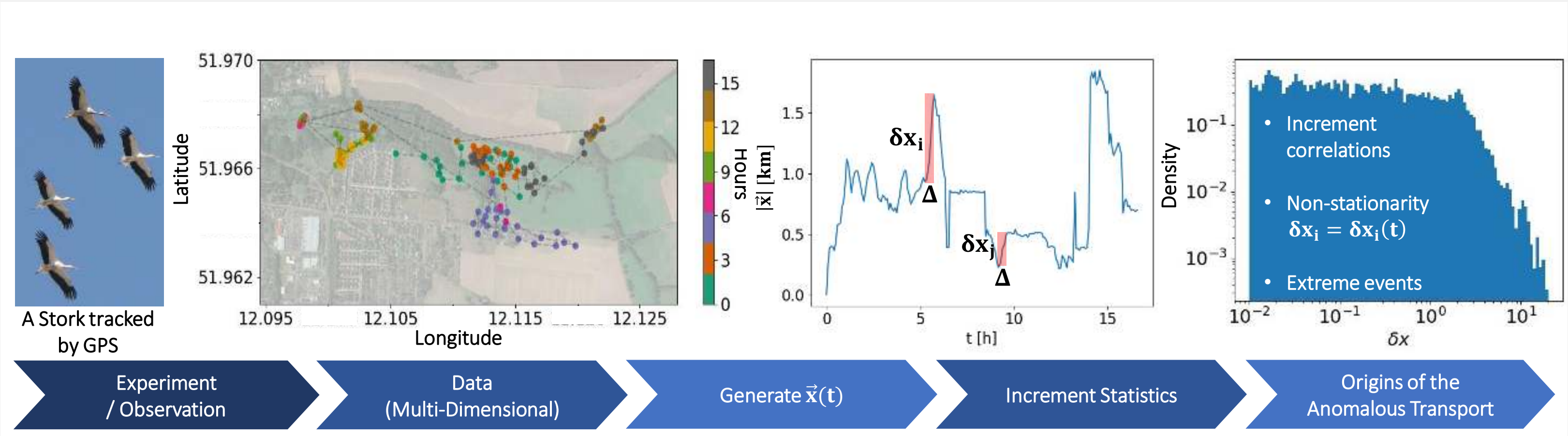
$$\langle X^\delta(\tau) X^\delta(\tau+T)\rangle = \alpha \frac{\alpha-1}{2T^{1-\alpha}} \delta \mathbb{B}\left(\frac{\delta}{T}; \frac{\alpha+1}{2}, 1-\alpha\right)$$

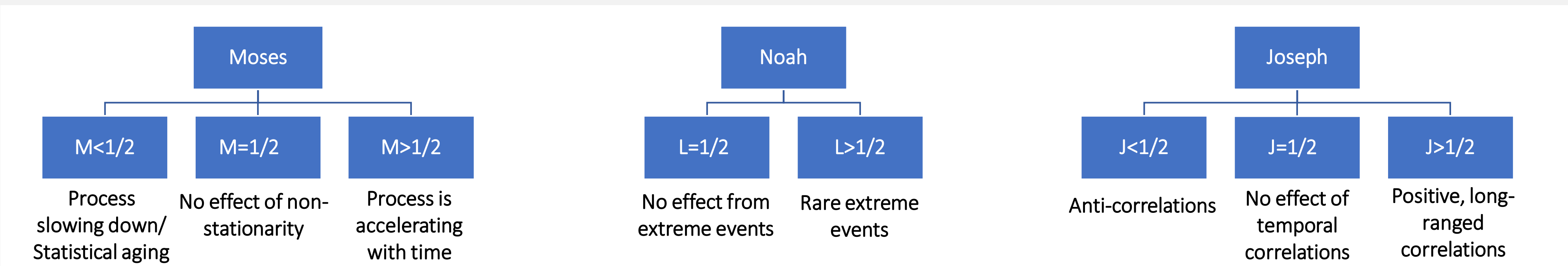
for $\delta \to 0$, at time T after τ. When $T \to \infty$

$$\langle X^\delta(\tau) X^\delta(\tau+T)\rangle \sim \alpha[(\alpha-1)/(\alpha+1)]\delta^{\alpha/2+3/2} T^{\alpha/2-3/2}.$$

Even after a long period T a short perturbation still influences the process, with a sign depending on whether $\alpha \gtrless 1$

Scaling analysis of anomalous diffusion: molecules → animals





O Vilk, E Aghion, T Avgar, C Beta, O Nagel, M Weiss, A Sabri, D Krapf, R Sarfati, DK Schwartz, RM, R Nathan & M Assaf, PRR (2022)

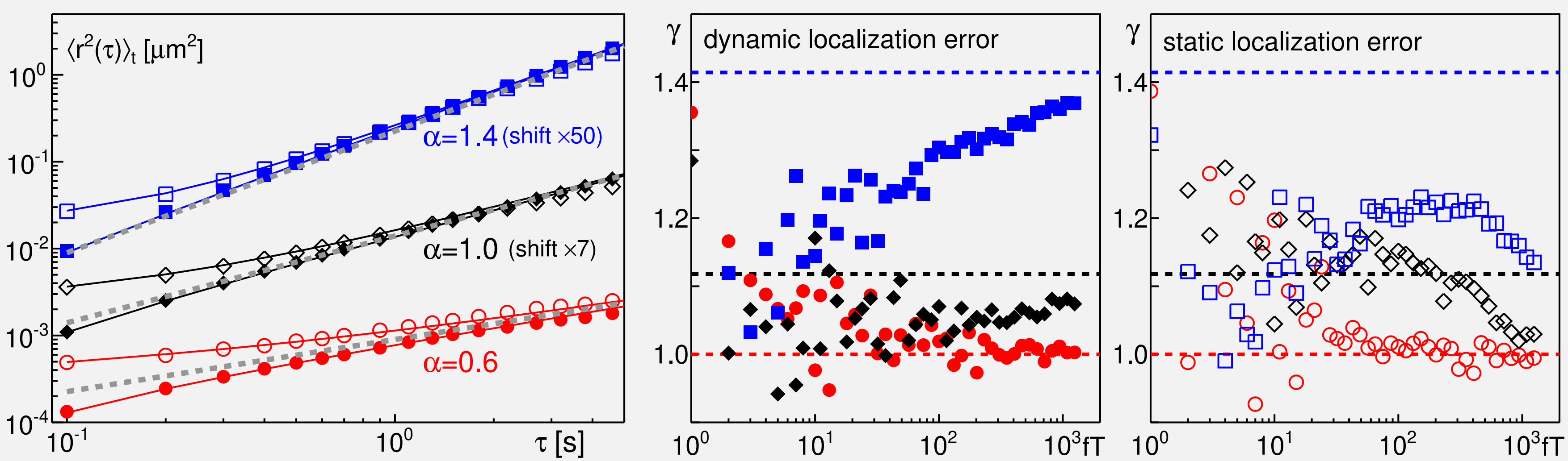
Robust criterion for anomalous diffusion

Two sources of noise: static (finite photon count, additive OU) & dynamic (finite measurement time). Static noise effect on γ:

$$H < 1/2: \qquad \gamma_Y^2(f,T) \sim 1; \qquad \sigma_e = 0 : 1$$

$$H = 1/2: \qquad \gamma_Y^2(f,T) \sim 1 + \frac{1}{4}\left(1 + \frac{\sigma_e^2}{2u^2 D} f^2\right)^{-2}; \qquad \sigma_e = 0 : \frac{\sqrt{5}}{2}$$

$$H > 1/2: \qquad \gamma_Y^2(f,T) \sim 1 + \left(1 + \frac{\sigma_e^2}{u^2 D} T^{1-2H} f^2\right)^{-2}; \qquad \sigma_e = 0 : \sqrt{2}$$



V Sposini, D Krapf, E Marinari, R Sunyer, F Ritort, F Taheri, C Selhuber-Unkel, R Benelly, M Weiss, RM & G Oshanin, Comm Phys (2022)

The ANomalous DIffusion challenge

nature COMMUNICATIONS

ARTICLE

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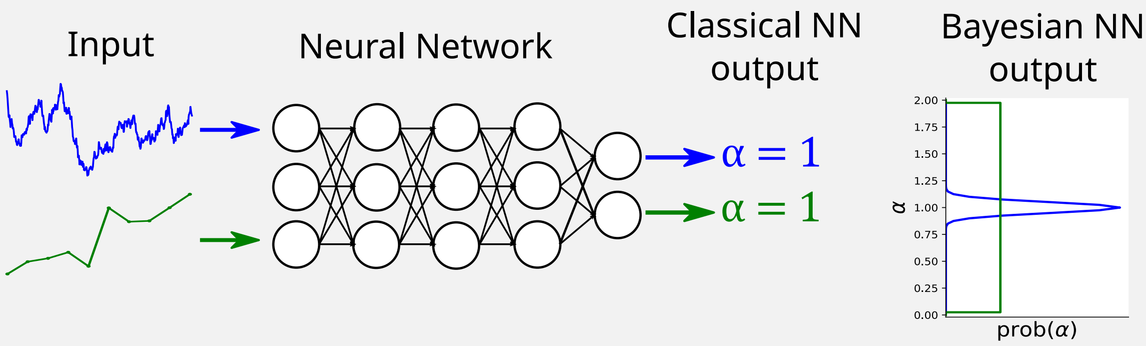
Check for updates

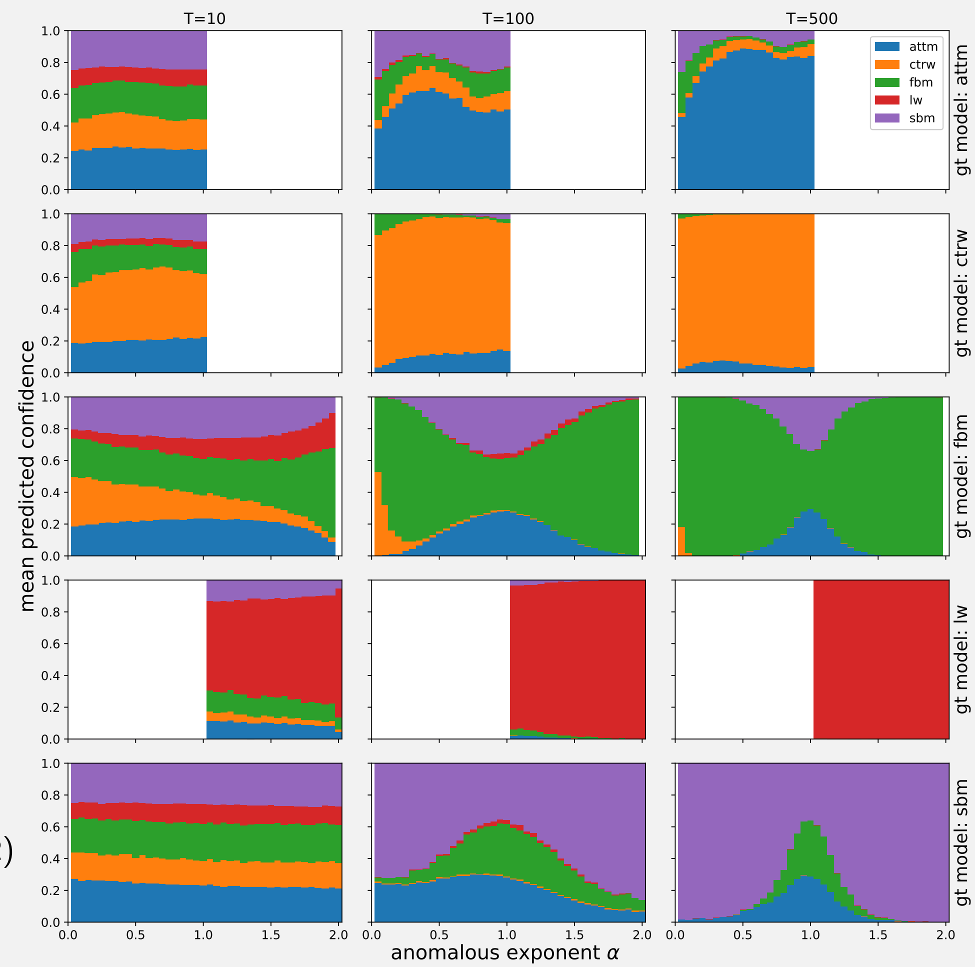
Objective comparison of methods to decode anomalous diffusion

Gorka Muñoz-Gil[1], Giovanni Volpe[2✉], Miguel Angel Garcia-March[3], Erez Aghion[4], Aykut Argun[2], Chang Beom Hong[5], Tom Bland[6], Stefano Bo[4], J. Alberto Conejero[3], Nicolás Firbas[3], Òscar Garibo i Orts[3], Alessia Gentili[7], Zihan Huang[8], Jae-Hyung Jeon[5], Hélène Kabbech[9], Yeongjin Kim[5], Patrycja Kowalek[10], Diego Krapf[11], Hanna Loch-Olszewska[10], Michael A. Lomholt[12], Jean-Baptiste Masson[13], Philipp G. Meyer[4], Seongyu Park[5], Borja Requena[1], Ihor Smal[9], Taegeun Song[5,14,15], Janusz Szwabiński[10], Samudrajit Thapa[16,17,18], Hippolyte Verdier[13], Giorgio Volpe[7], Artur Widera[19], Maciej Lewenstein[1,20], Ralf Metzler[16] & Carlo Manzo[1,21✉]

Bayesian-weighted deep learning model selection

“Beyond the Black Box problem”





H Seckler & RM, Nat Comm (2022)

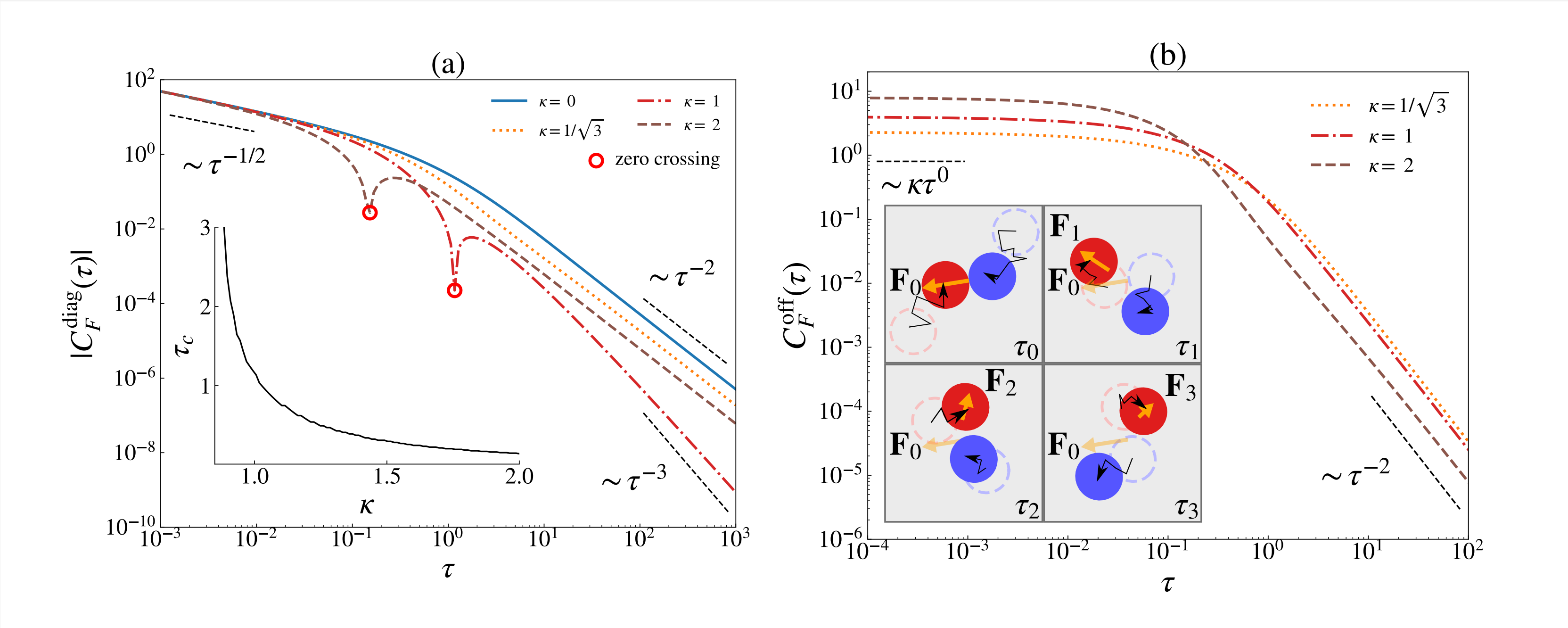
Odd-diffusive systems at equilibrium

Odd-diffusive system has diffusion tensor $\mathbf{D} = D_0(\mathbf{1} + \kappa\boldsymbol{\varepsilon})$: Lorentz force, skyrmions

$\boldsymbol{\varepsilon}$ Levi-Civita: $\varepsilon_{xy} = -\varepsilon_{yx} = 1; \varepsilon_{xx} = \varepsilon_{xy} = 0$

Force autocorrelation shows oscillations at equilibrium, contradicting claims that it should decay monotonically [M Caraglio & T Franosch, PRL (2022)]

Conjecture for tail of the correlation function $\simeq \tau^{-3/2}$ also violated



Summary

1. Single particle tracking & supercomputing provide access to unprecedented insight into microscopic dynamics of complex systems
2. Long-range correlated motion is revealed across scales, from drug molecules in silica slabs over intracellular motion to flying birds
3. Inhomogeneity of tracer ensemble and/or environment cause pronouncedly non-Gaussian displacement distributions
4. Long-range correlated processes defy mathematical analysis (e.g., first-passage) & show strange interactions with boundaries
5. Objective data analysis methods aid in identification of models & parameters: Bayesian-maximum likelihood, deep learning, & their combinations. Measurement error! AnDi challenge special issue of JPA & AnDi 2!

For slides or questions: write to rmetzler@uni-potsdam.de