Brownian motion & beyond

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— Oldenburg, 6th June 2019 —

190+ years after Brown: Microscopical observations

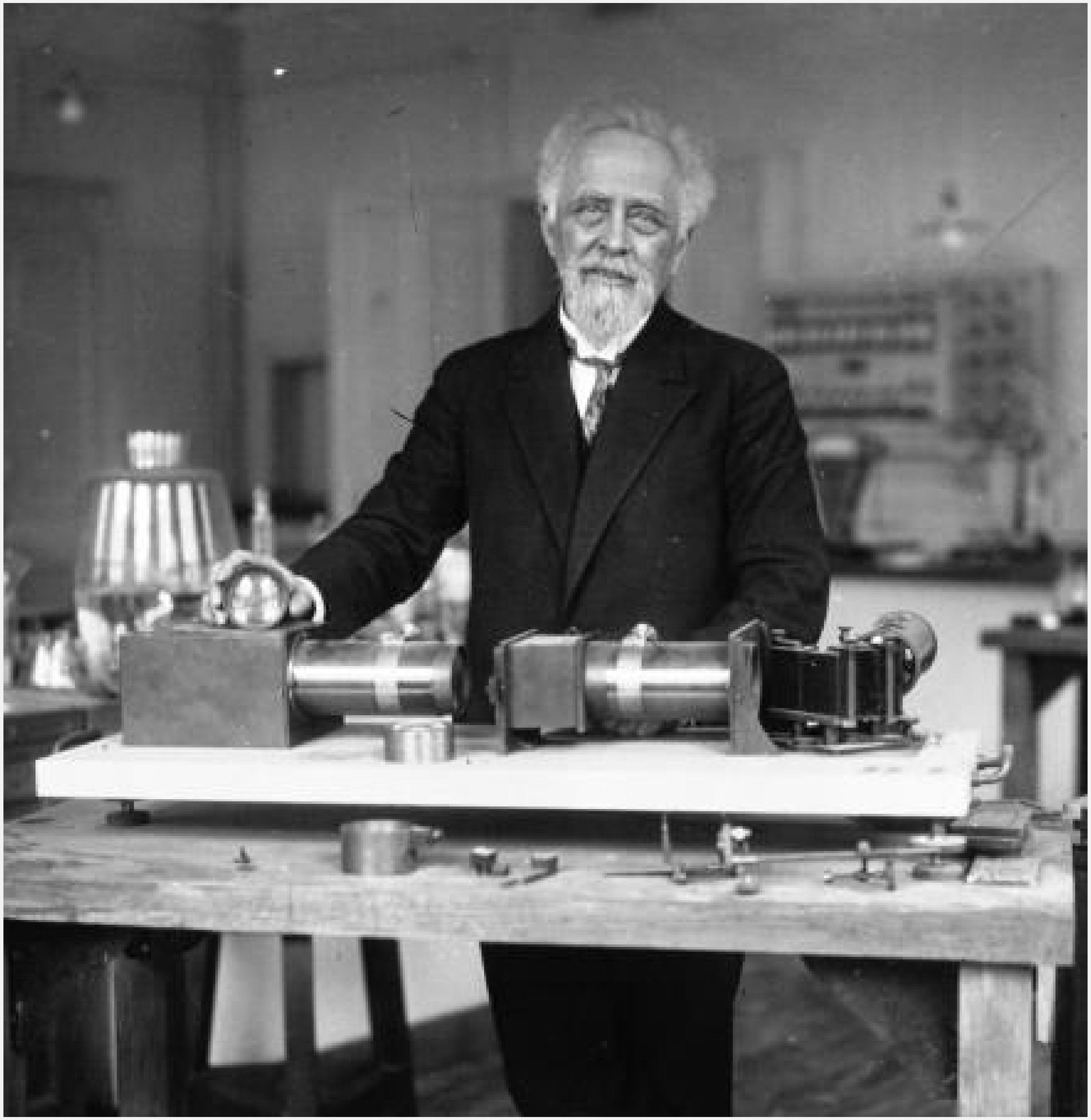
on the particles contained in the pollen of plants; and on the general existence of *active molecules* in organic and inorganic bodies

Grains of pollen, taken from Clarkia pulchella antherae fully grown but before bursting, were filled with particles or granules of unusually large size, varying from nearly 1/4000th to 1/5000th of an inch in length . . .

Rocks of all ages, including those in which organic remains have never been found, yielded the molecules in abundance. Their existence was ascertained in each of the constituent molecules of granite, a fragment of the Sphinx being one of the specimens examined.

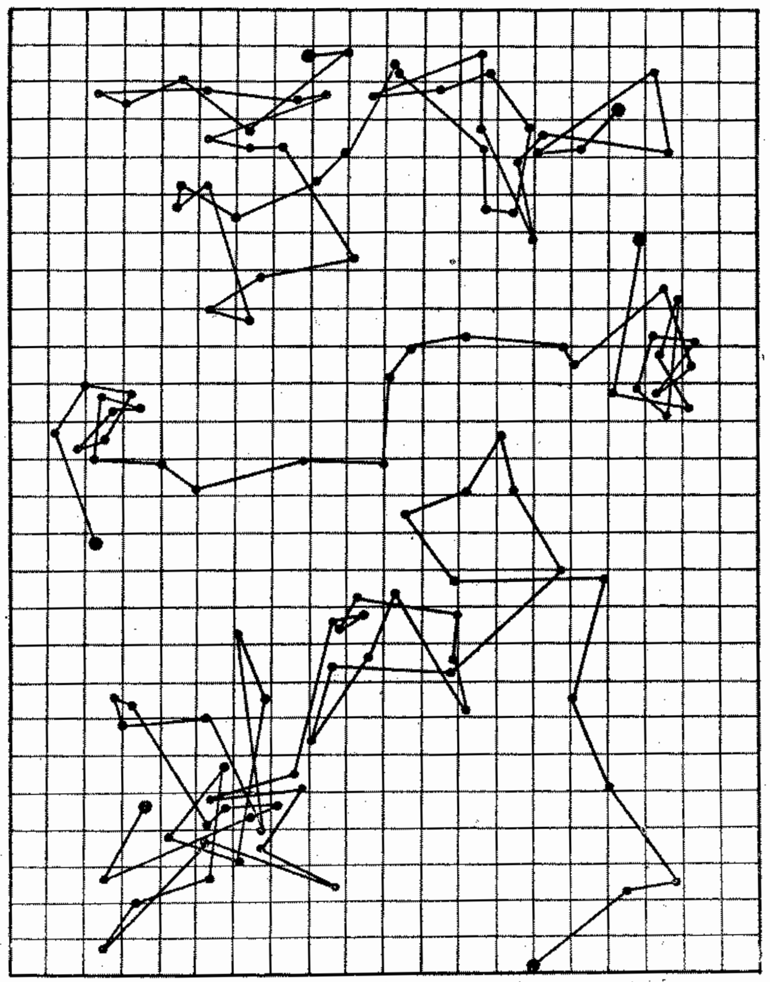
R Brown, Edinburgh new Philosophical Journal 358-371 (1828)

110+ years after Jean Perrin



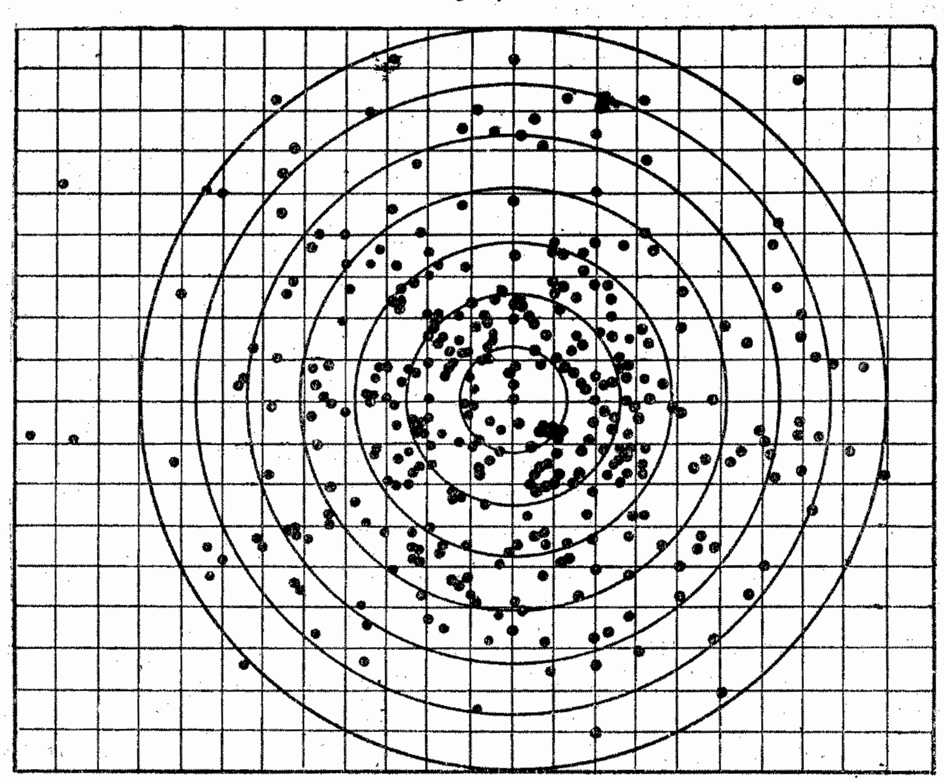
Brownian motion

Fig. 6.



Δt=30 sec

Fig. 7.



$$P(\mathbf{r}, \Delta t) = \frac{1}{(4\pi K \Delta t)^{d/2}} \exp\left(-\frac{r^2}{4K\Delta t}\right)$$

Einstein-Smoluchowski relation ($\langle \mathbf{r}^2(t) \rangle = 2dKt$):

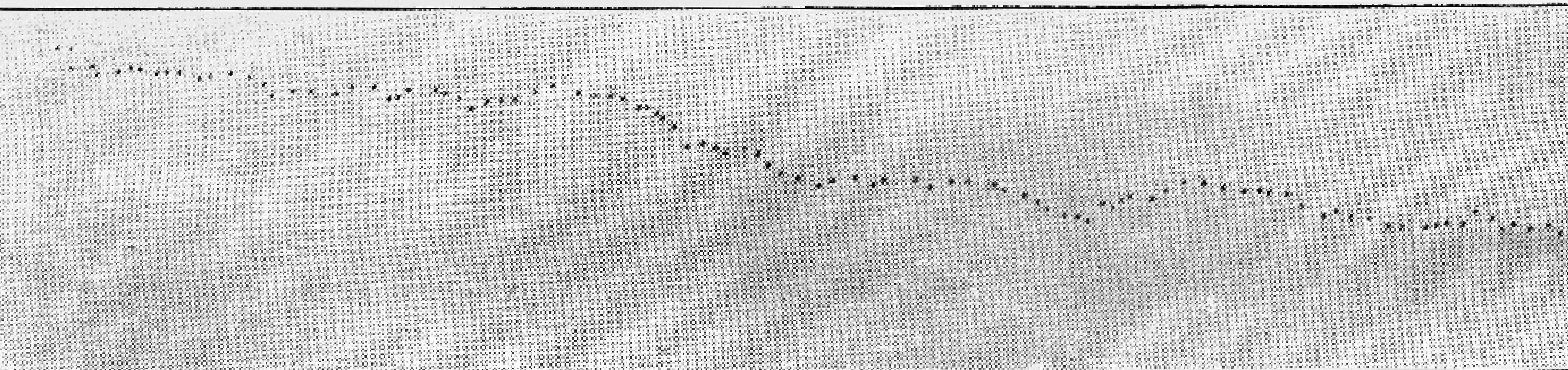
$$K = \frac{k_B T}{m\eta} = \frac{(R/N_A)T}{m\eta}$$

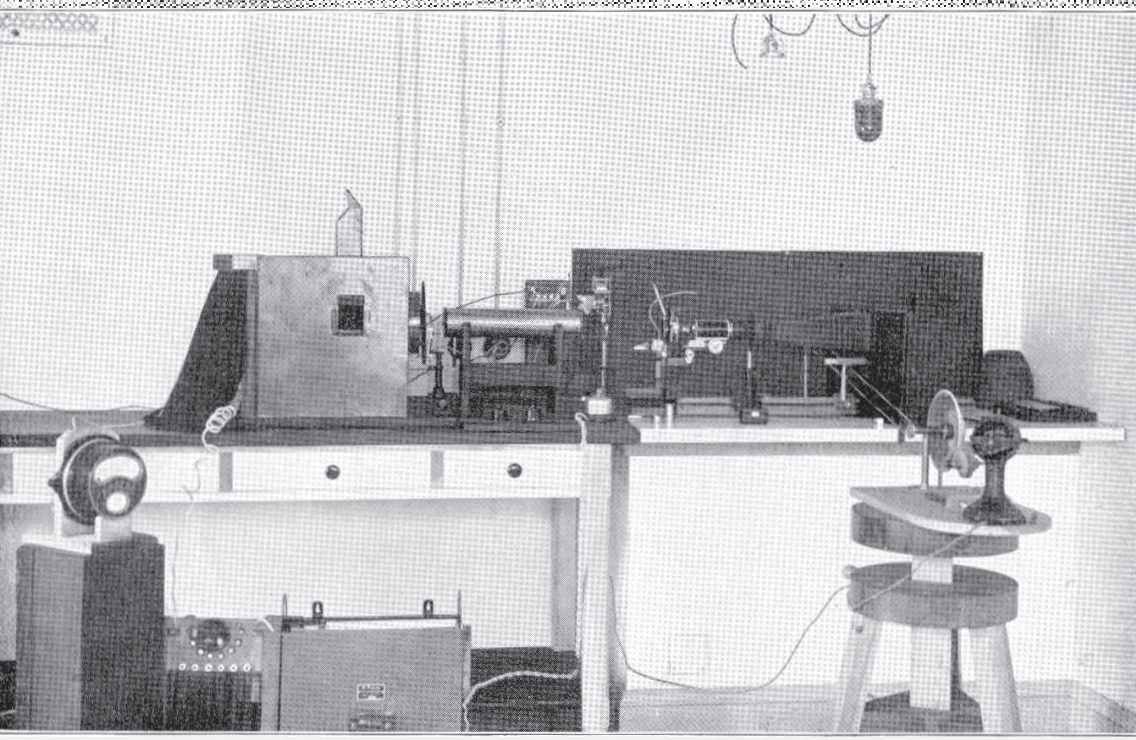
J Perrin, Comptes Rendus (Paris) 146 (1908) 967: $N_A = 70.5 \times 10^{22}$

Ivar Nordlund (1887-1918)

Verksam ved fysikalisk-kemiska institutionen vid Uppsala universitet. Arbetade även som amatörfotograf. Svåger till A Hamberg

Ivar Nordlund: 100+ years of SPT with time series analysis





I Nordlund, Z Physik (1914): $N_A = 5.91 \times 10^{23}$

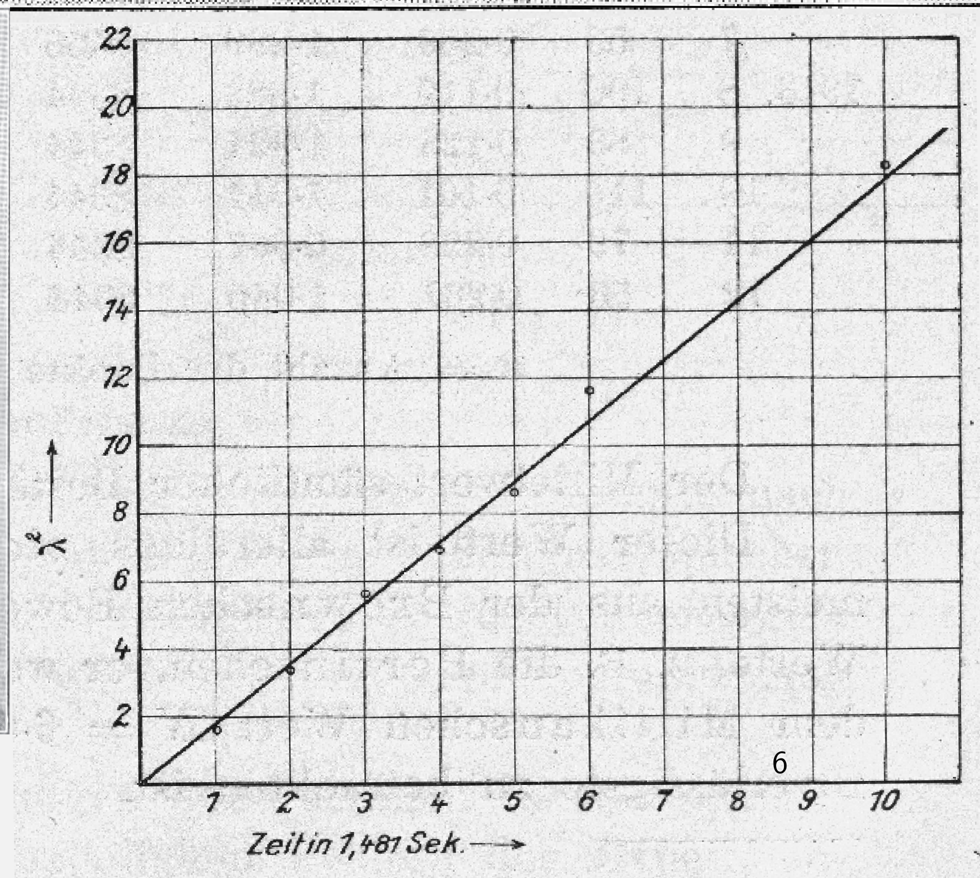
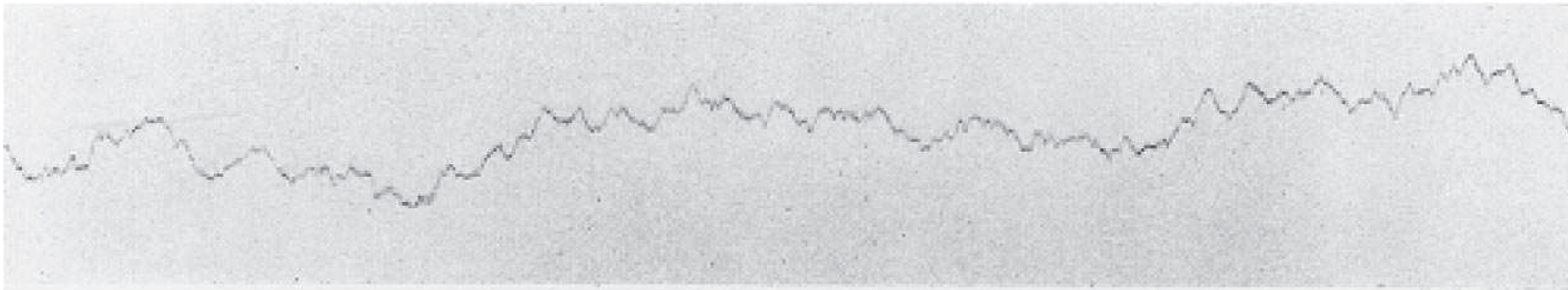


Fig. 11.

Eugen Kappler (1905-1977)

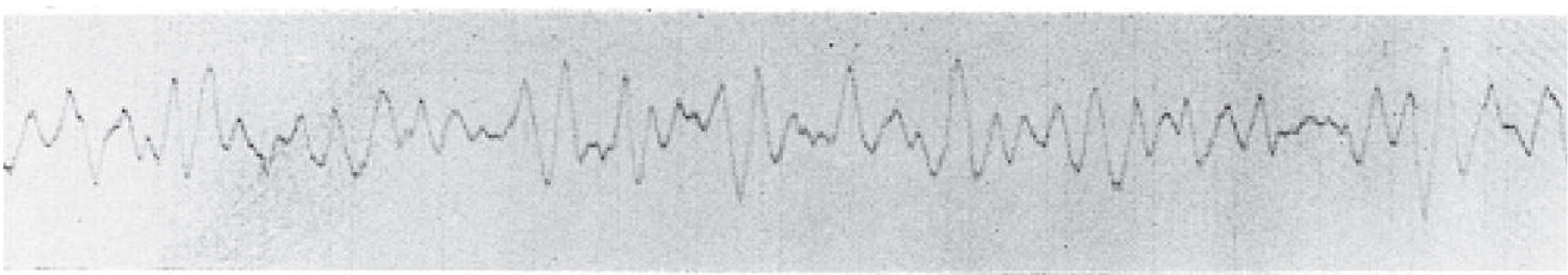
Obiturary by L Reimer, Physikalische Blätter Feb 1978 pp 86

Eugen Kappler: ultimate diffusion measurements



Registrieraufnahme der Brownschen Bewegung (natürliche Größe).
Direktionskraft $9{,}428 \cdot 10^{-9}$ abs. Einh. Trägheitsmoment: $1 \cdot 10^{-7}$ abs. Einh. Abstand Spiegel–Kamera: 72,1 cm.
Zeitmarke: 30 sec $dx = 1$ mm. a) Atmosphärendruck. Temperatur 13° C

Fig. 5a



Registrieraufnahme der Brownschen Bewegung (natürliche Größe).
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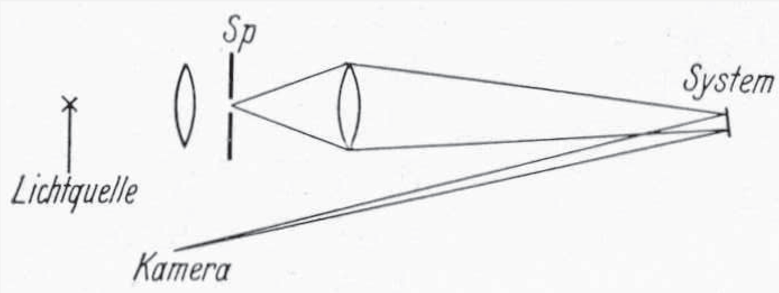
Zeitmarke: 30 sec $dx = 1$ mm. b) $1 \cdot 10^{-3}$ mm Hg. Temperatur 13° C

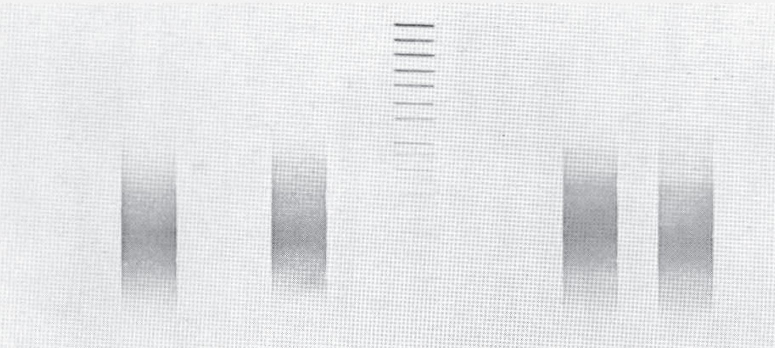
Fig. 5b

E Kappler, Ann d Physik (1931): $N_A = 60.59 \times 10^{22} \pm 1\%$

Kappler's diffusion measurements: mapping Boltzmann

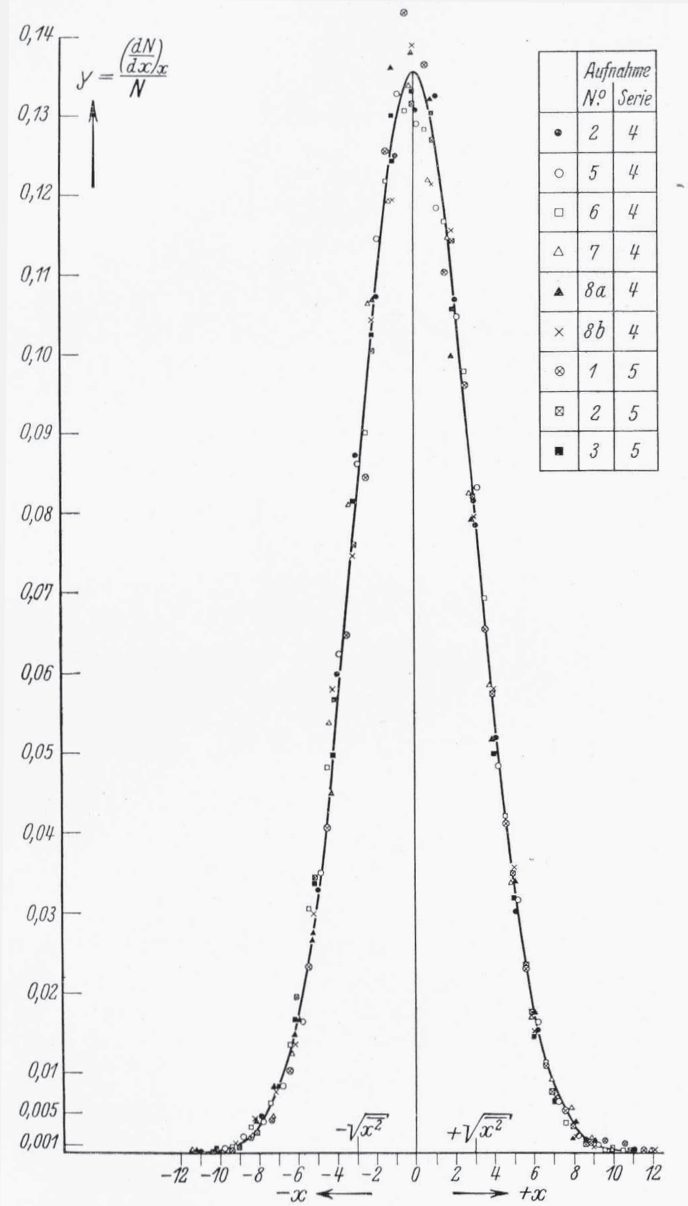


Schema der Meßanordnung
Fig. 1



Distribution @ fixed photographic plate

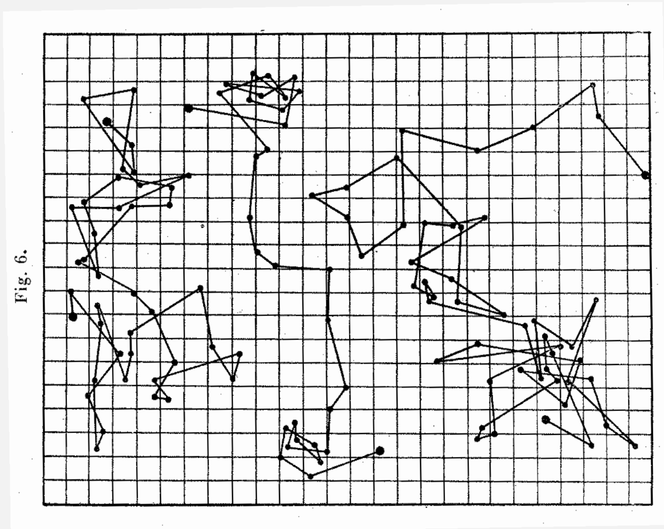
$$P_{\text{eq}}(x) = \mathscr{N} \exp\left(-\frac{\theta x^2}{k_B T}\right)$$

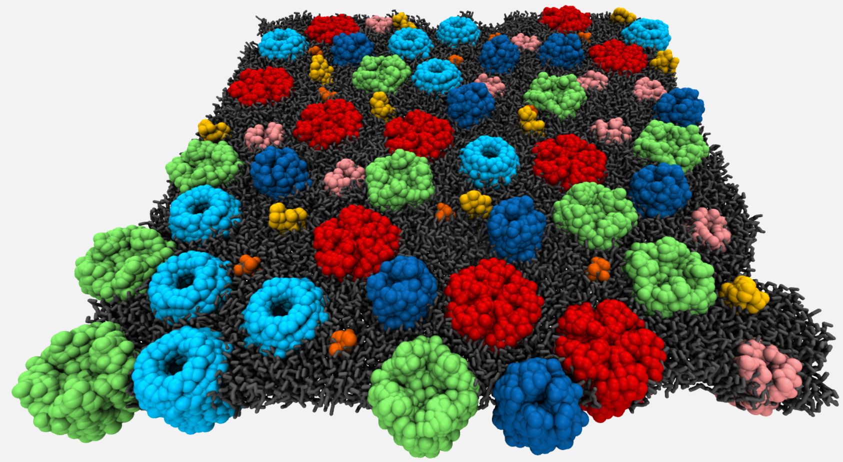


E Kappler, Ann d Physik (1931): $N_A = 60.59 \times 10^{22} \pm 1\%$

Stochastic processes in 2019: why should we care?

Jean Perrin (1908)





Courtesy Matti Javanainen

Novel insights from single particle tracking (e.g., superresolution microscopy, supercomputing)

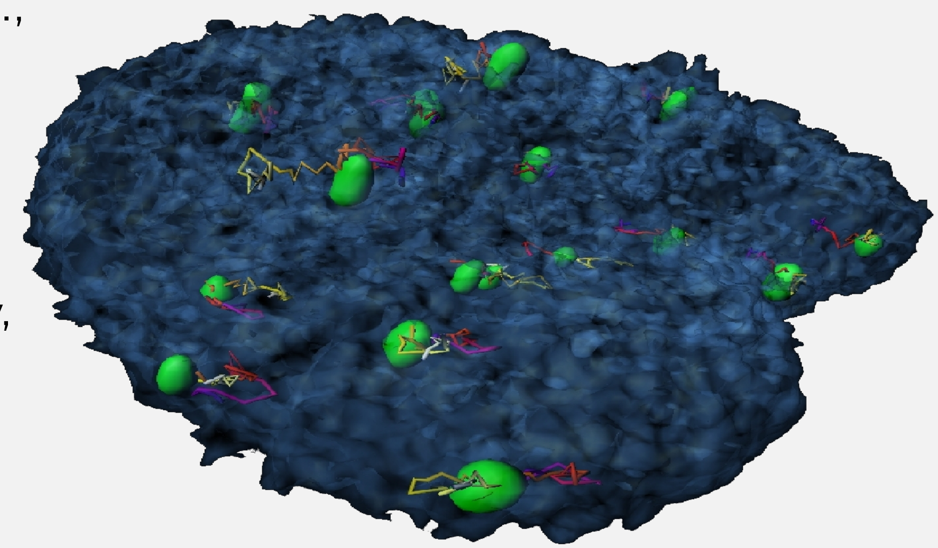
↷ Normal diffusion /w random parameters

↷ Anomalous diffusion of all sorts

↷ New physics: time averages, (non)ergodicity, ageing, non-Gaussianity

↷ Information from fluctuations

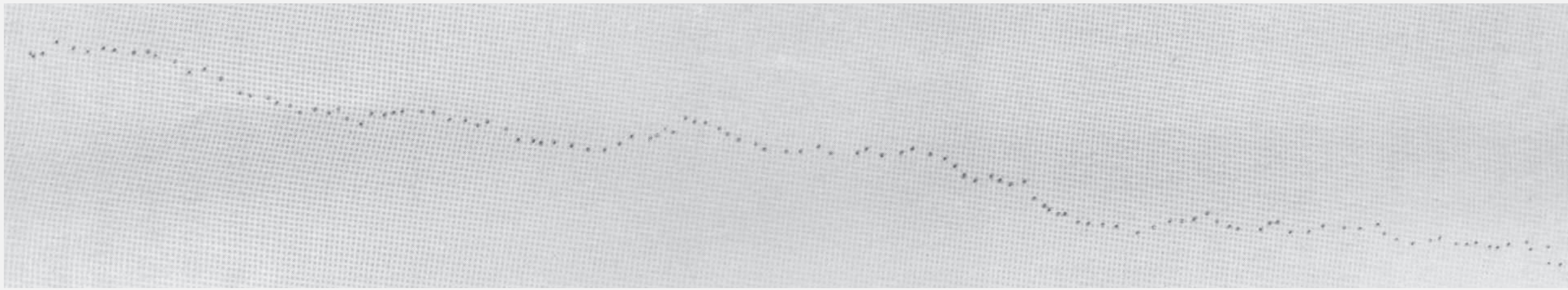
↷ Data analysis strategies



Courtesy Yuval Garini

E Barkai, Y Garini & RM, Phys Today (2012)

Extracting information from single Brownian trajectories



Ensemble averaged MSD for normal diffusion (on average # jumps $\sim$ elapsed time t):

$$\left\langle \mathbf{r}^2(t) \right\rangle = \int \mathbf{r}^2 P(\mathbf{r},t)d\mathbf{r} = 2dK_1 t \quad \left(= \langle \delta \mathbf{r}^2 \rangle \frac{t}{\tau}, \quad K_1 = \frac{\langle \delta \mathbf{r}^2 \rangle}{2d\tau} \right)$$

Single particle trajectory $\mathbf{r}(t)$, $t \in [0,T]$:

$$\overline{\delta^2(t)} = \frac{1}{T-t} \int_0^{T-t} \Big[\mathbf{r}(t'+t) - \mathbf{r}(t') \Big]^2 dt' = \frac{1}{T-t} \int_0^{T-t} \langle \delta \mathbf{r}^2 \rangle \frac{t}{\tau} dt'$$

Single trajectory information equals ensemble information (*Boltzmann-Khinchin*):

$$\lim_{T\to\infty} \overline{\delta^2(t)} = 2dK_1 t = \left\langle \mathbf{r}^2(t) \right\rangle$$

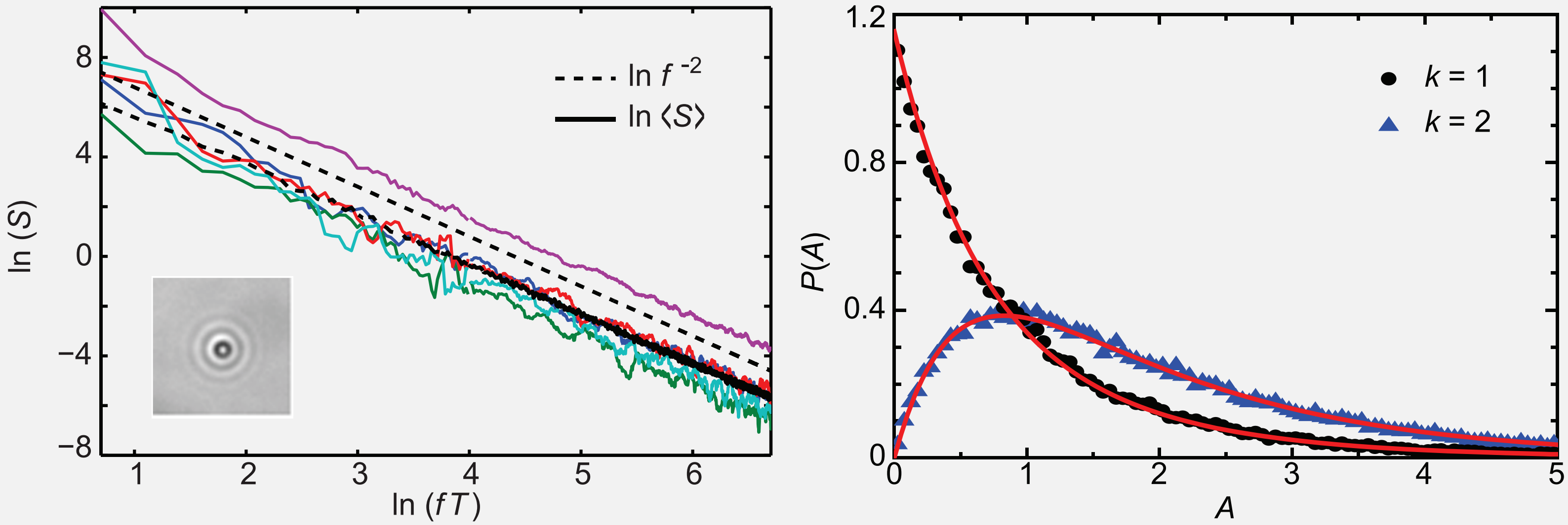
Anomalous diffusion is not always ergodic (weak or strong violoation):

$$\left\langle \mathbf{r}^2(t) \right\rangle \simeq K_\alpha t^\alpha \neq \overline{\delta^2(t)} \simeq t/T^{1-\alpha}$$

WEB: signature of non-stationarity of process. SEB: discontinuity of phase space

E Barkai, Y Garini & RM, Phys Today (2012); Y He, S Burov, RM & E Barkai, PRL (2008); S Burov, RM & E Barkai, PNAS (2010)

Power spectral density of a single Brownian trajectory



Standard ensemble-averaged power spectrum à la textbook definition:

$$\mu_S(f) = \lim_{T\to\infty} \left\langle S(f,T) \right\rangle$$

Single trajectory power spectrum suitable for finite-length & few trajectories:

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

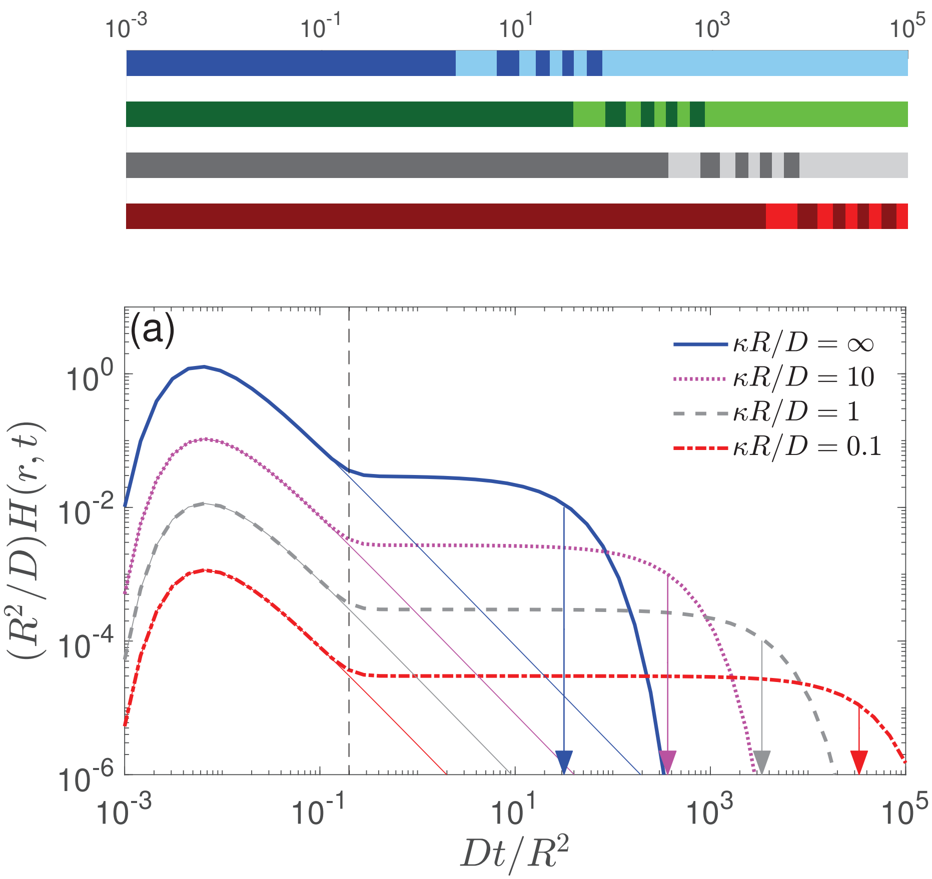
D Krapf, E Marinari, RM, G Oshanin, A Squarcini & X Xu, NJP (2018); Perspective: ND Schnellbächer & US Schwarz, NJP (2018)

Strongly defocused reaction times: geometry/reaction control

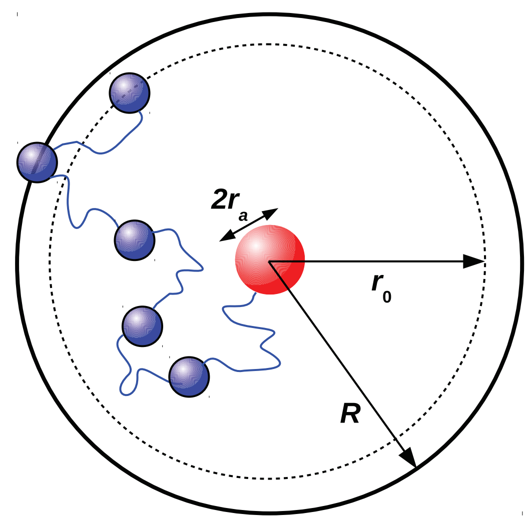
Mean/global mean first passage & cover times: O Bénichou, R Voituriez et al.: Nature (2007), Nature Phys (2008), Nature Chem (2010), Nature Phys (2015)

@ nM concentrations even on μm scale distance matters: O Pulkkinen & RM, PRL (2013)

Full first passage time density:



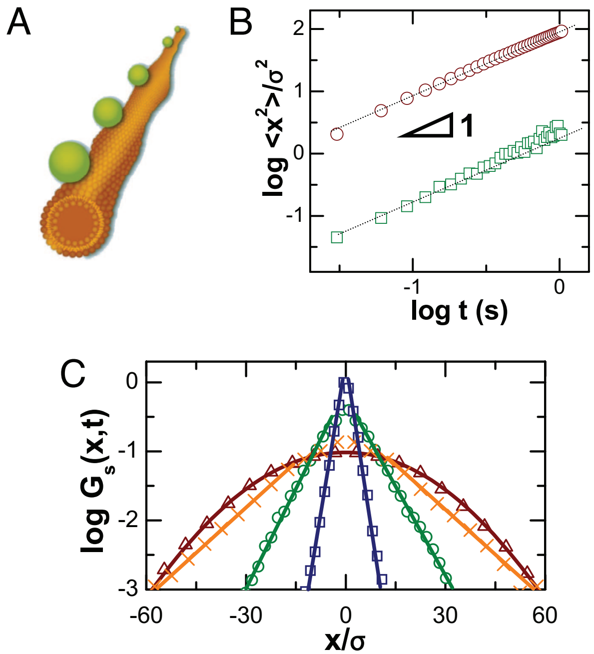
Direct vs indirect trajectories:



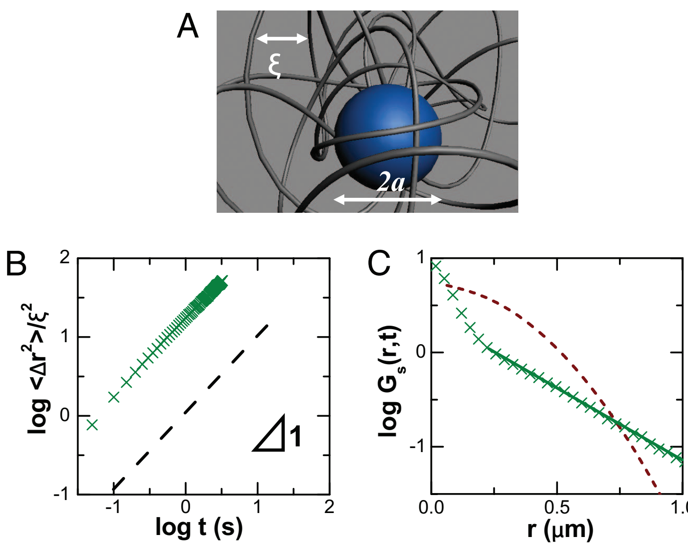
$$\langle t\rangle = \frac{(r_0 - r_a)(2R^3 - r_0 r_a[r_0 + r_a])}{6Dr_0 r_a} + \frac{R^3 - r_a^3}{3\kappa r_a}$$

D Grebenkov, RM & G Oshanin, Comm Chem (2019), PCCP (2018); A Godec & RM, PRX (2016), Sci Rep (2016)

When Brownian diffusion is not Gaussian

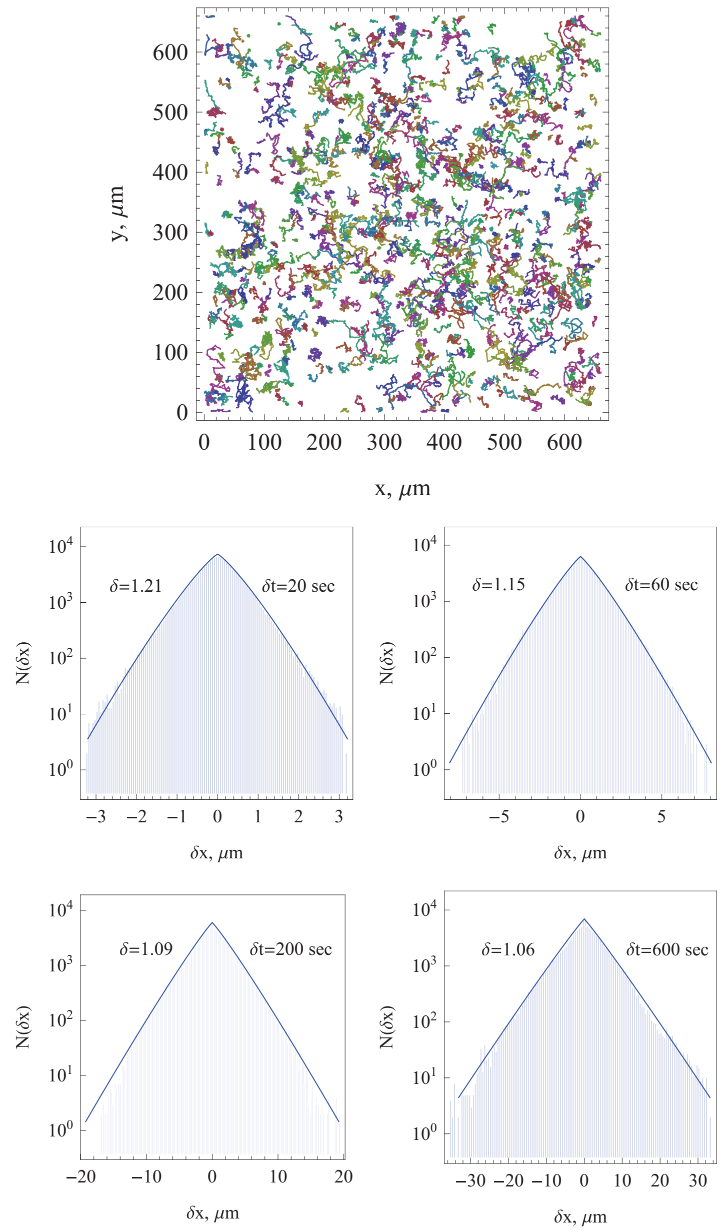


Colloidal beads on nanotubes



Nanospheres in entangled actin

Motion of dictyostelium cells



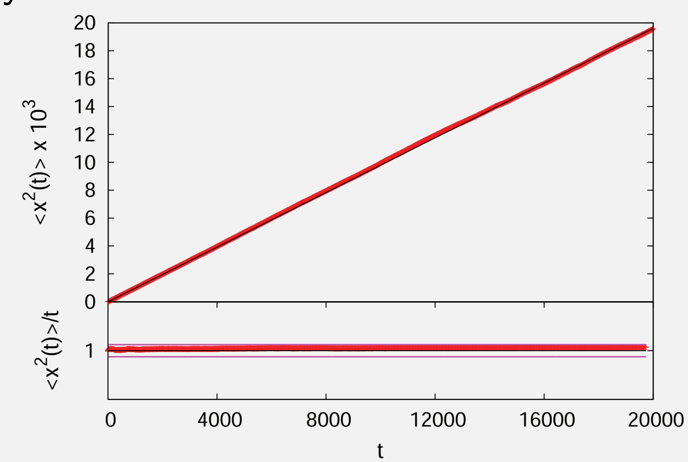
Wang et al, PNAS (2009); Nature Mat (2012)

AG Cherstvy, O Nagel, C Beta & RM, PCCP (2018)

Fickian, non-Gaussian diffusion with diffusing diffusivity

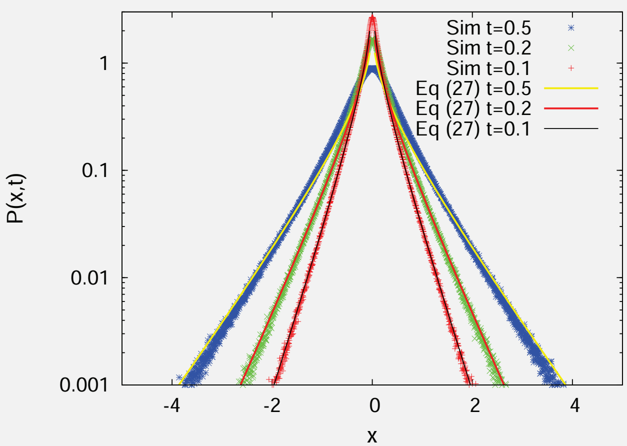
B Wang, J Kuo, SC Bae & S Granick, Nat Mat (2012): $\langle x^2(t)\rangle = 2K_1t$, yet $P(x,t)$ non-Gaussian. Superstatistical approach $P(x,t)=\int_0^\infty G(x,t|D)p(D)dD$
[C Beck & EDB Cohen, Physica A (2003); C Beck Prog Theor Phys Suppl (2006)]

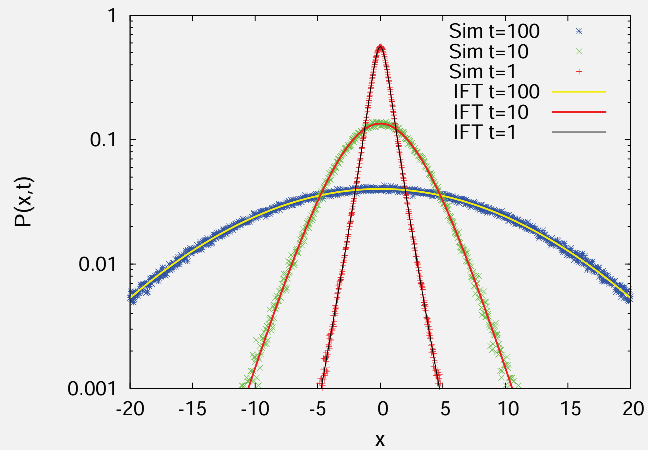
MV Chubinsky & G Slater, PRL (2014): diffusing diffusivity
[see also R Jain & KL Sebastian, JPC B (2016)]

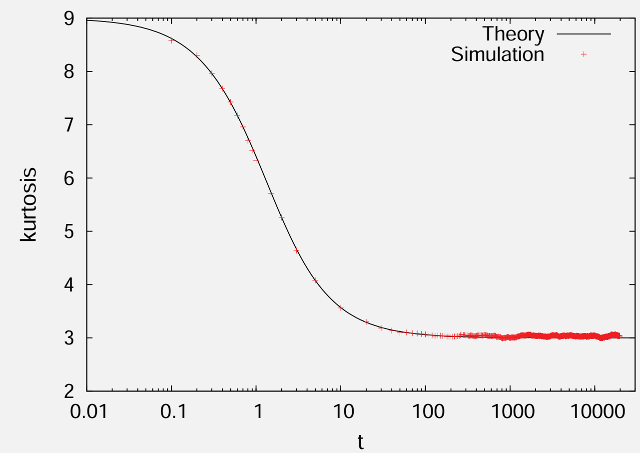


Our minimal model for diffusing diffusivity:

$$\dot{x}(t)=\sqrt{2D(t)}\xi(t)$$
$$D(t)=y^2(t)$$
$$\dot{y}(t)=-\tau^{-1}y+\sigma\eta(t)$$

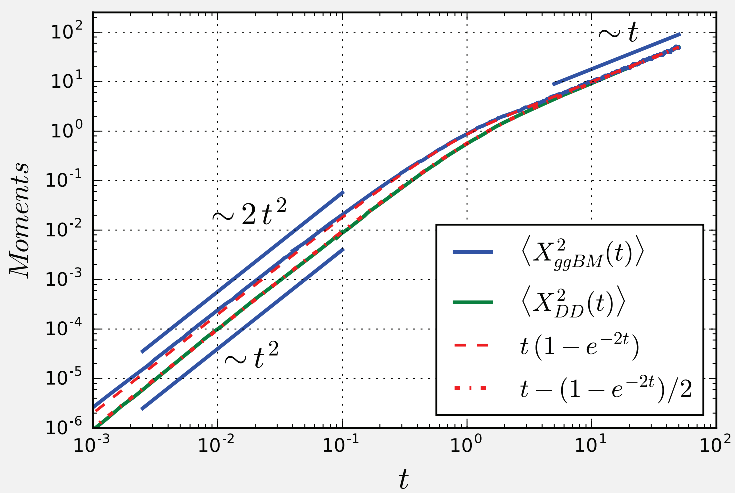


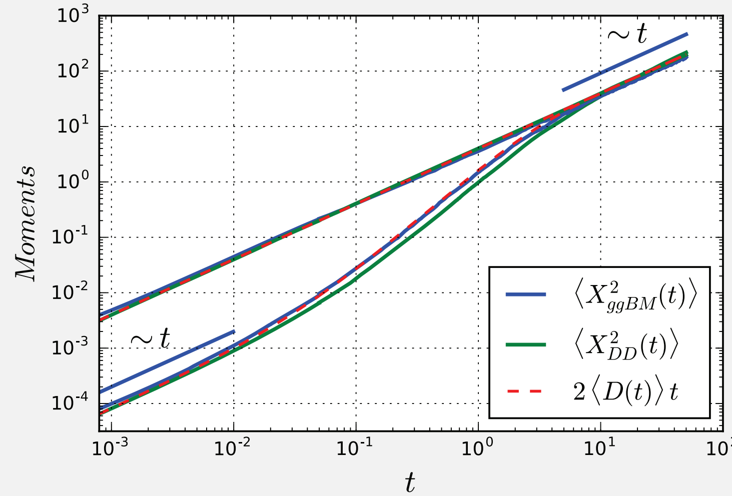




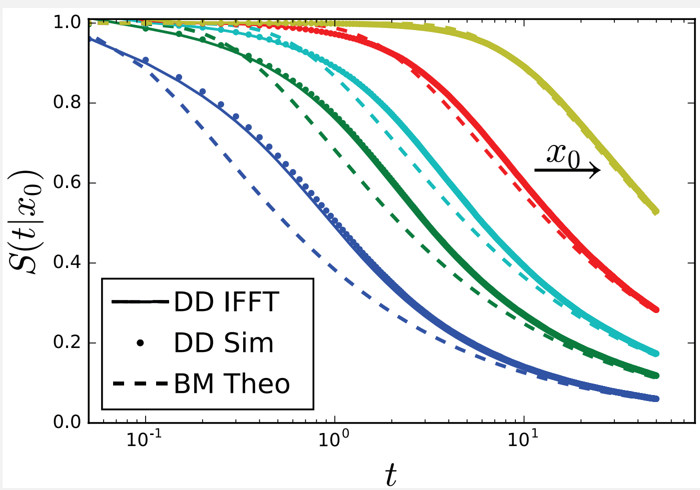
AV Chechkin, F Seno, RM & IM Sokolov, PRX (2017); generalised $\gamma(D)$: V Sposini, AV Chechkin, G Pagnini, F Seno & RM, NJP (2018)

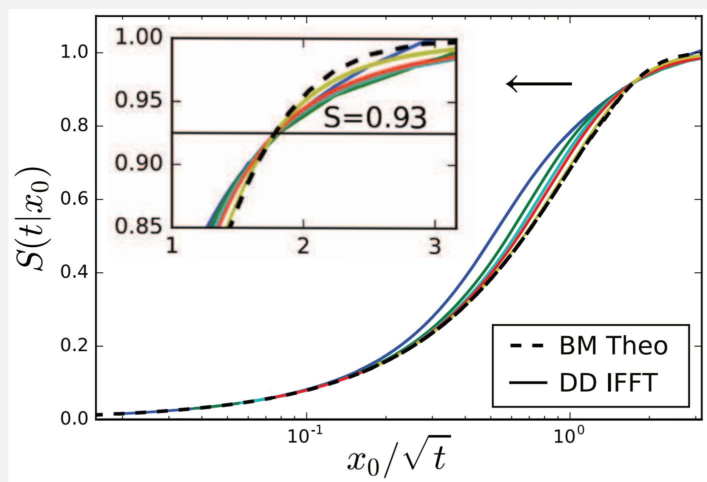
Non-equilibrium initial conditions for $D(t)$ dynamics





First passage statistics for diffusing diffusivity





[See also Y Lanoiselée, N Moutal & D Grebenkov, Nat Comm (2019)]

V Sposini, AV Chechkin, G Pagnini, F Seno & RM, NJP (2018); V Sposini, AV Chechkin & RM, JPA (2019)

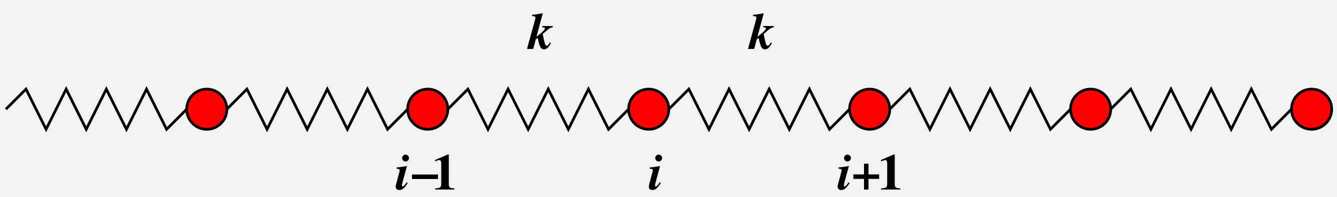
Fractional Langevin equations in viscoelastic systems

Coupled set of Markovian processes (e.g., Rouse model for polymers):

$$m_i\ddot{\mathbf{r}}_i(t) = k(\mathbf{r}_i - \mathbf{r}_{i+1}) + k(\mathbf{r}_{i-1} - \mathbf{r}_i) - \eta\dot{\mathbf{r}}_i + \sqrt{2\eta k_B T} \times \boldsymbol{\zeta}_i(t)$$

Integrating out all d.o.f. but one $\curvearrowright$ Generalised Langevin equation (GLE):

$$m\ddot{\mathbf{r}}(t) + \int_0^t \eta(t-t')\dot{\mathbf{r}}(t')dt' = \boldsymbol{\zeta}(t) \therefore \eta(t) = \sum_{i=1}^{N} a_i(k)e^{-\nu_i t} \to t^{-\alpha}$$



Kubo fluctuation dissipation theorem (in conti limit $\eta(t) \simeq t^{-\alpha}$ fractional Gaussian noise):

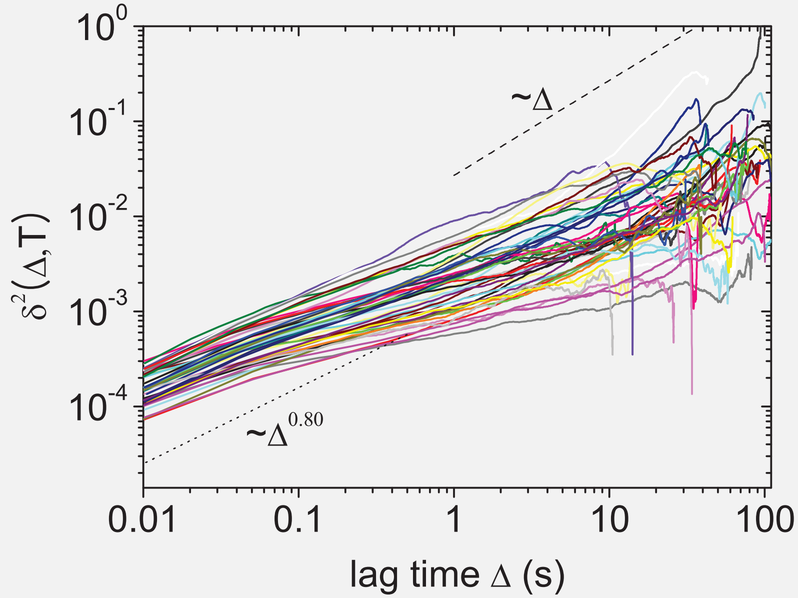
$$\langle \zeta_i(t)\zeta_j(t')\rangle = \delta_{ij}k_B T\eta(|t-t'|), \qquad p(\eta) \text{ Gauss}$$

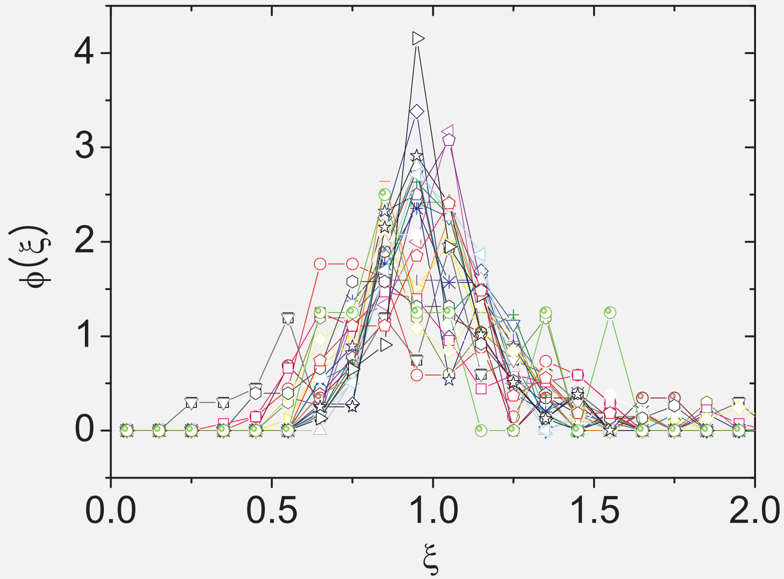
$\curvearrowright$ fractional Langevin equation & anomalous diffusion: $\langle \mathbf{r}^2(t)\rangle \simeq t^2 \ldots t^\alpha$

Quantum mechanics: Nakajima-Zwanzig equation using projection operators

Hydrodynamics: Basset force with $\eta(t) \simeq t^{-1/2}$ due to hydrodynamic backflow

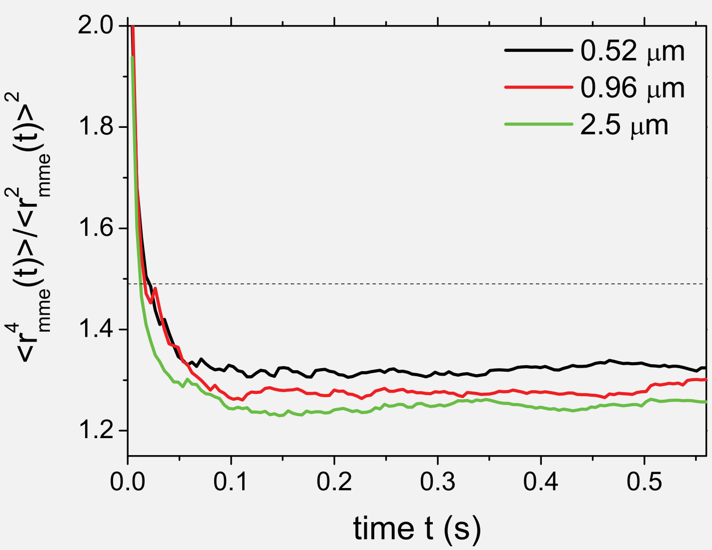
Passive motion of submicron tracers in cells is viscoelastic

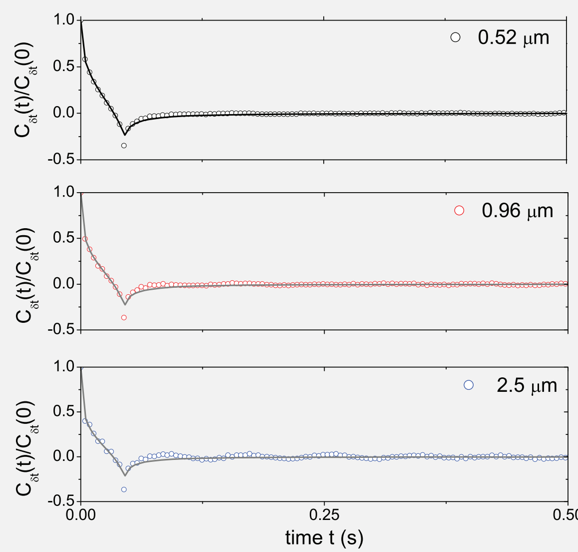


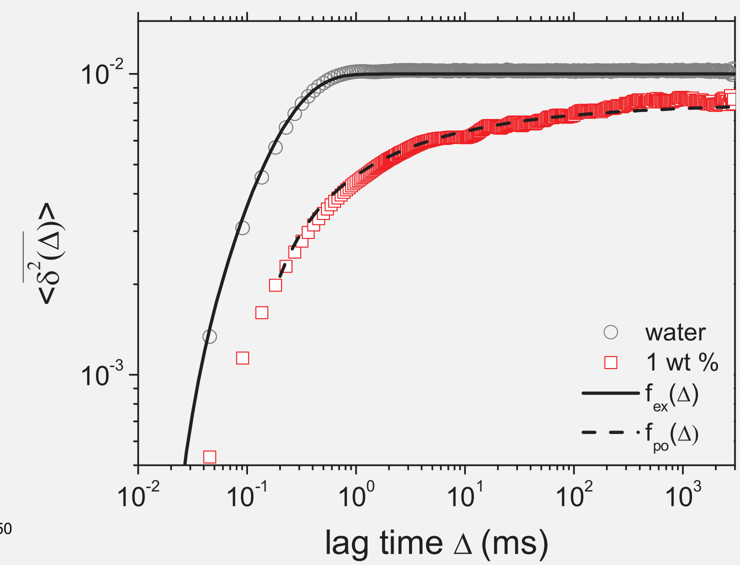


Lipid granules in living yeast cells ↓

Tracer beads in wormlike micellar solution ↓

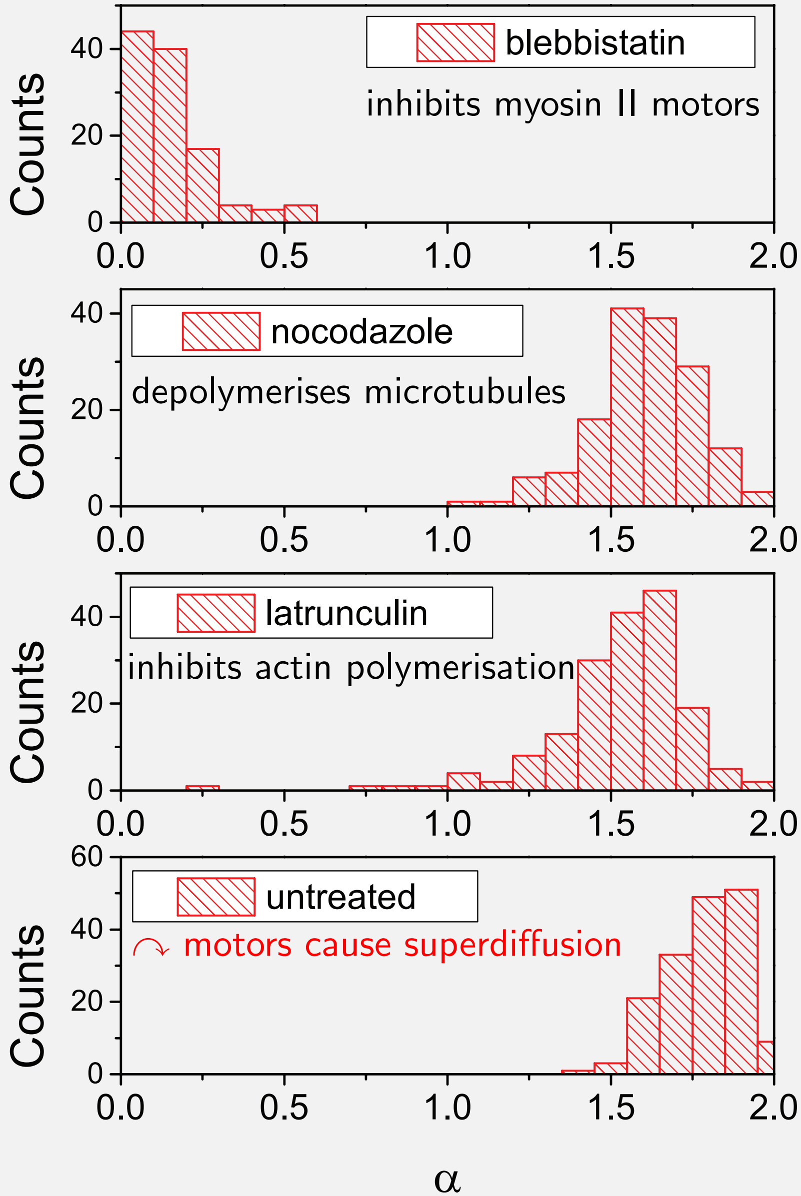


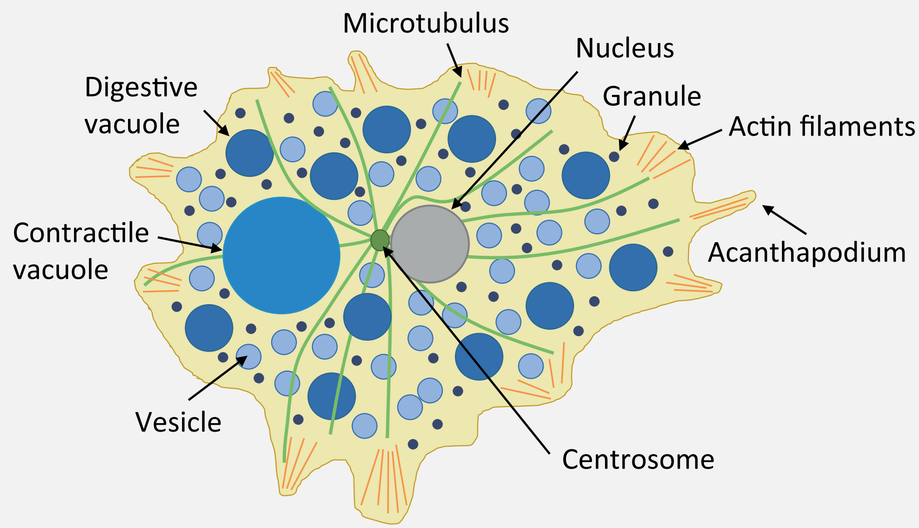


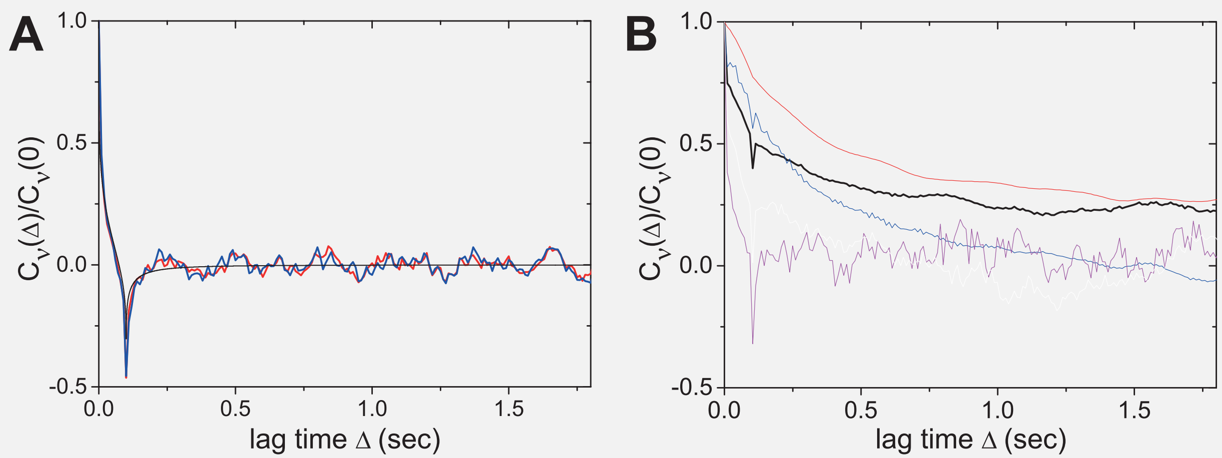


JH Jeon, . . . L Oddershede & RM, PRL (2011); JH Jeon, N Leijnse, L Oddershede & RM, NJP (2013)

Superdiffusion in supercrowded Acanthamoeba castellani

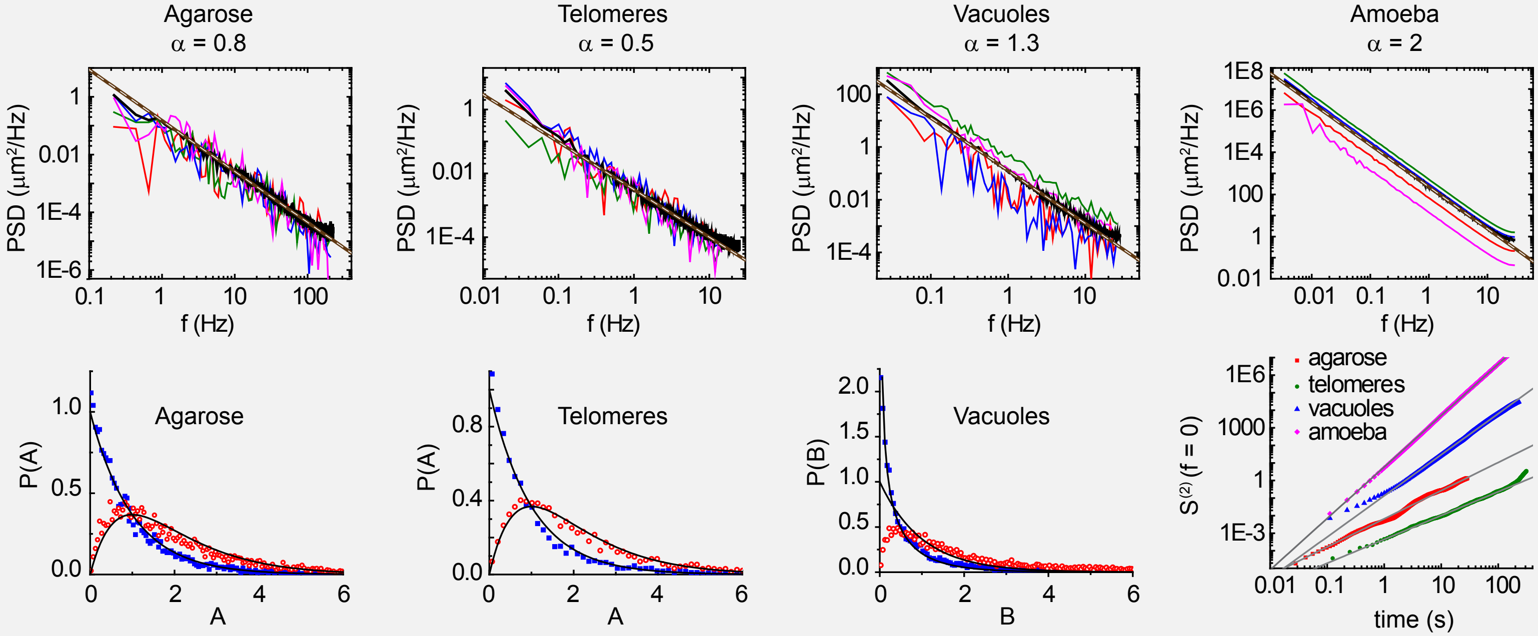


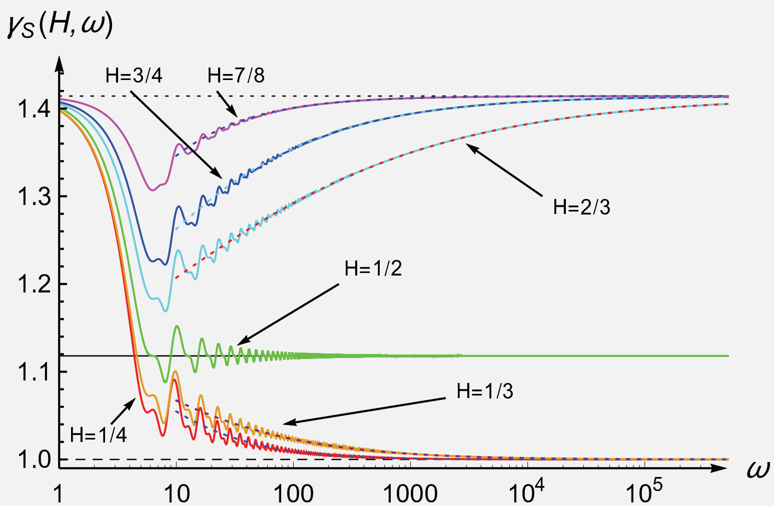




JF Reverey, J-H Jeon, H Bao, M Leippe, RM & C Selhuber-Unkel, Sci Rep (2015); see also S Thapa, . . . RM JCP (2019)

Power spectral density of a single FBM trajectory



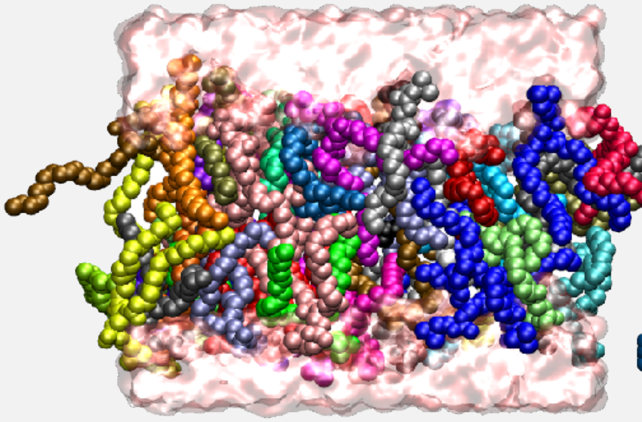


$$S(f,T) = \frac{1}{T}\left|\int_0^T \exp(ift)X_t dt\right|^2$$

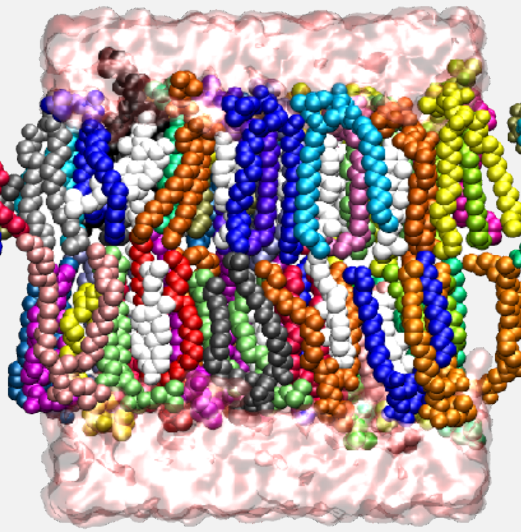
$$\gamma = \frac{\left(\langle S_T^2(f)\rangle - \langle S_T(f)\rangle^2\right)^{1/2}}{\langle S_T(f)\rangle}$$

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

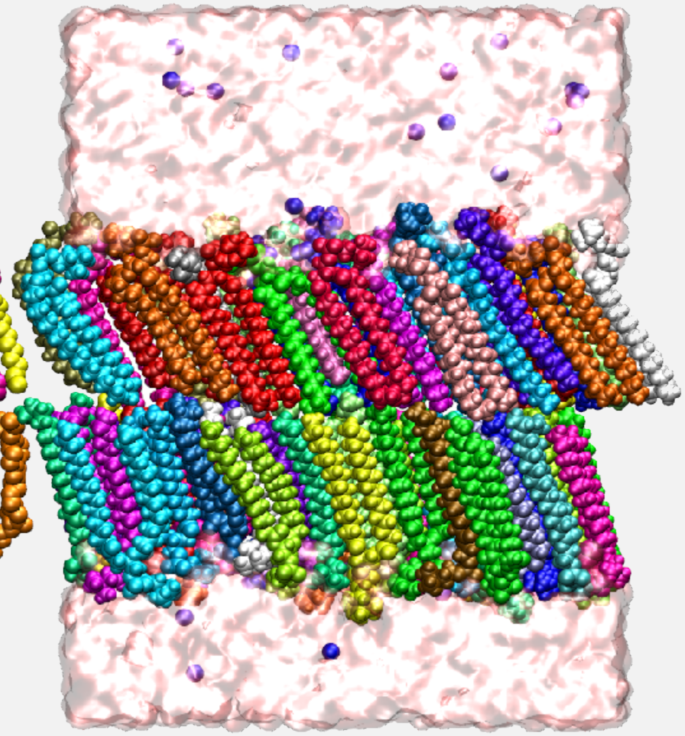
Single lipid motion in bilayer membrane MD simulations



Liquid disordered



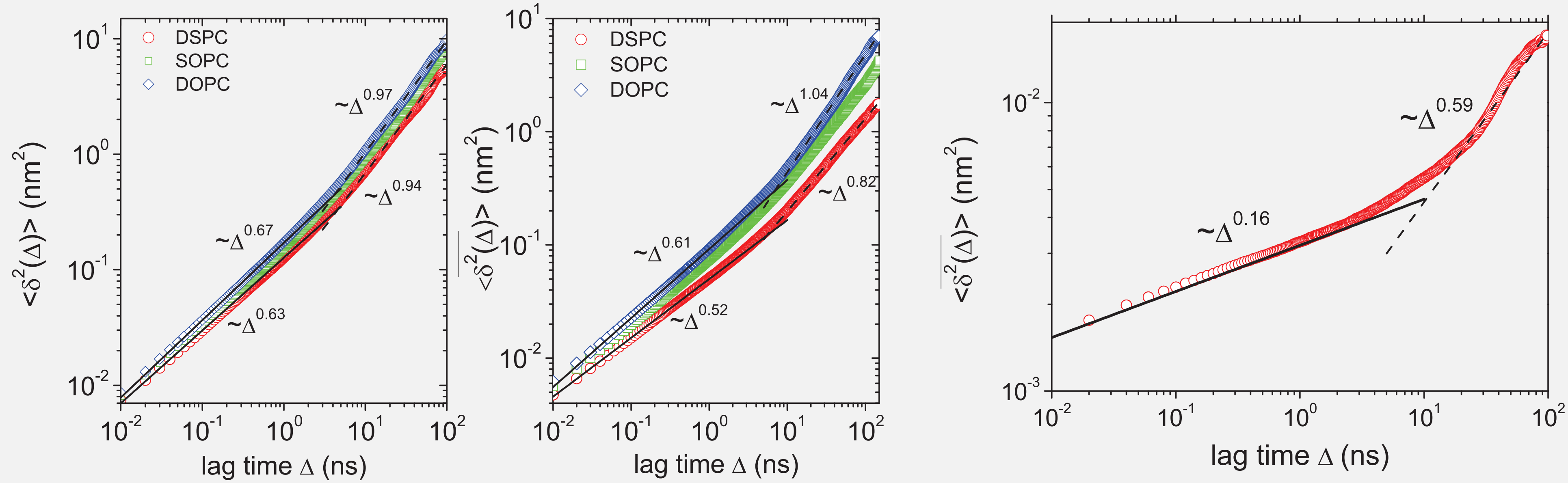
Liquid ordered



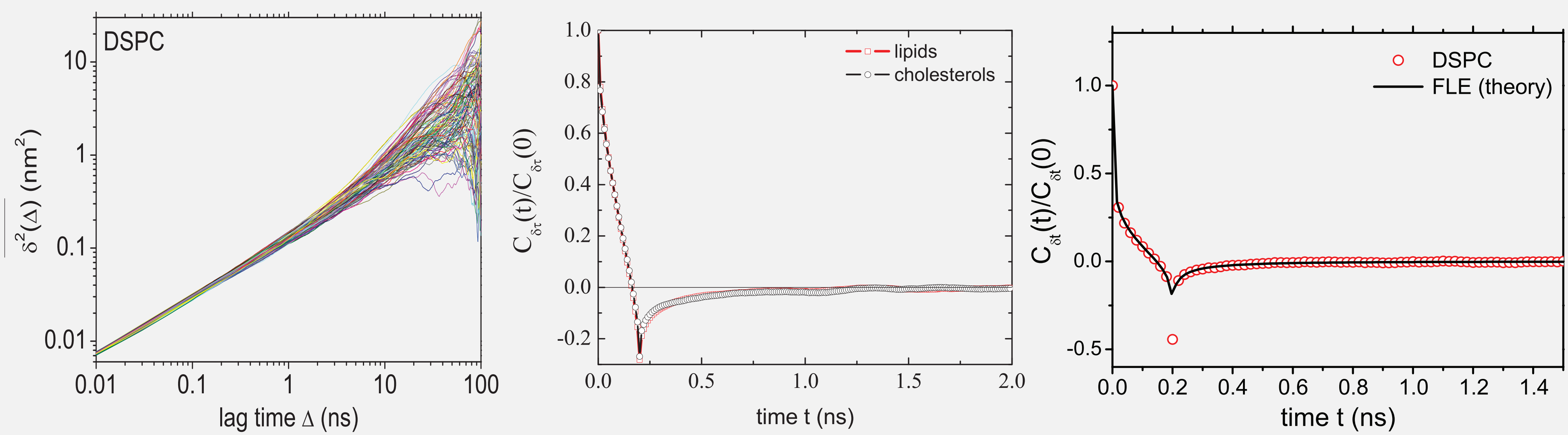
Gel phase

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

Liquid ordered/gel phases: extended anomalous diffusion



Reproducible TA MSD & antipersistent correlations

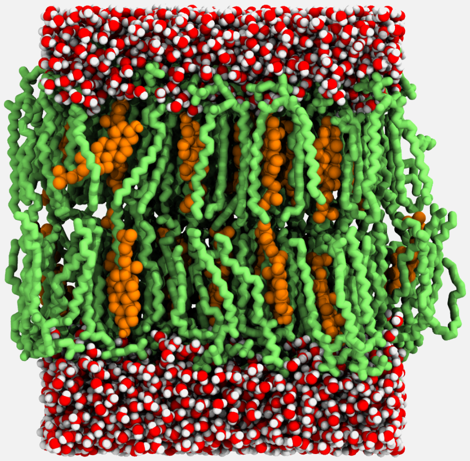


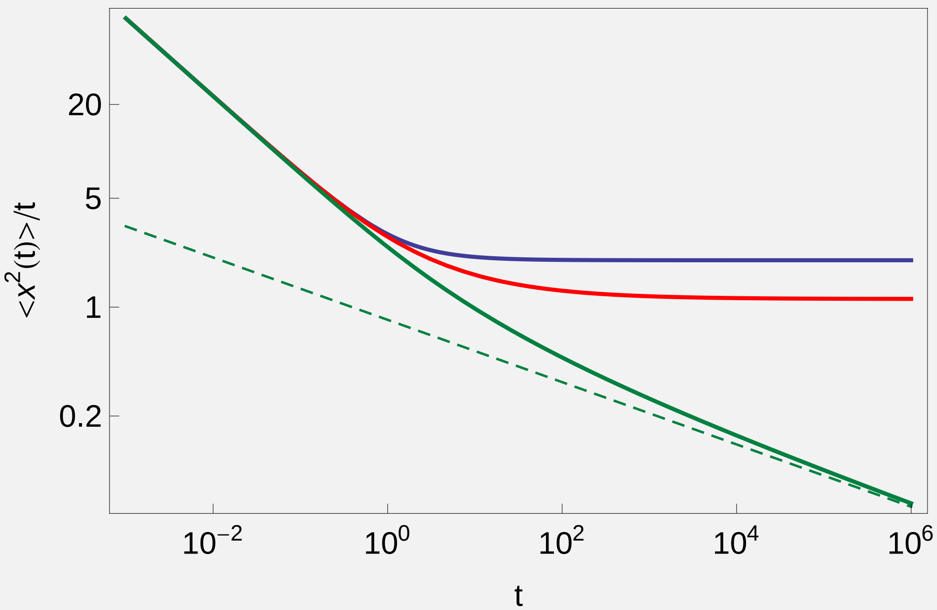
J-H Jeon, H Martinez-Seara Monne, M Javanainen & RM, PRL (2012)

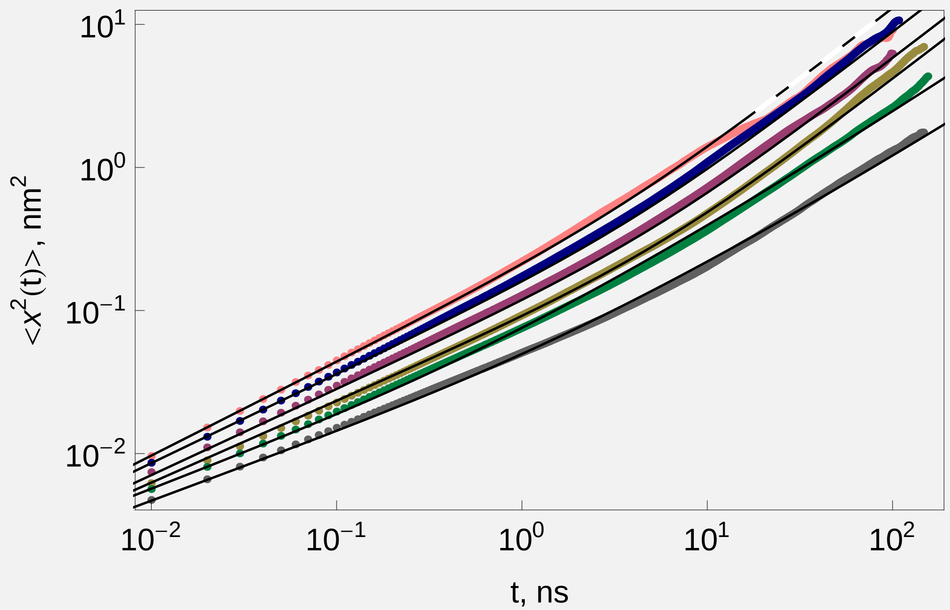
Tempered FLE motion: crossover to faster diffusion

Tempered fractional Gaussian noise:

$$\langle \xi(t)\xi(t+\tau)\rangle = \begin{cases} \dfrac{C}{\Gamma(2H-1)}\tau^{2H-2}e^{-\tau/\tau_\star} \\ \dfrac{C}{\Gamma(2H-1)}\tau^{2H-2}\left(1+\dfrac{\tau}{\tau_\star}\right)^{-\mu} \end{cases}$$

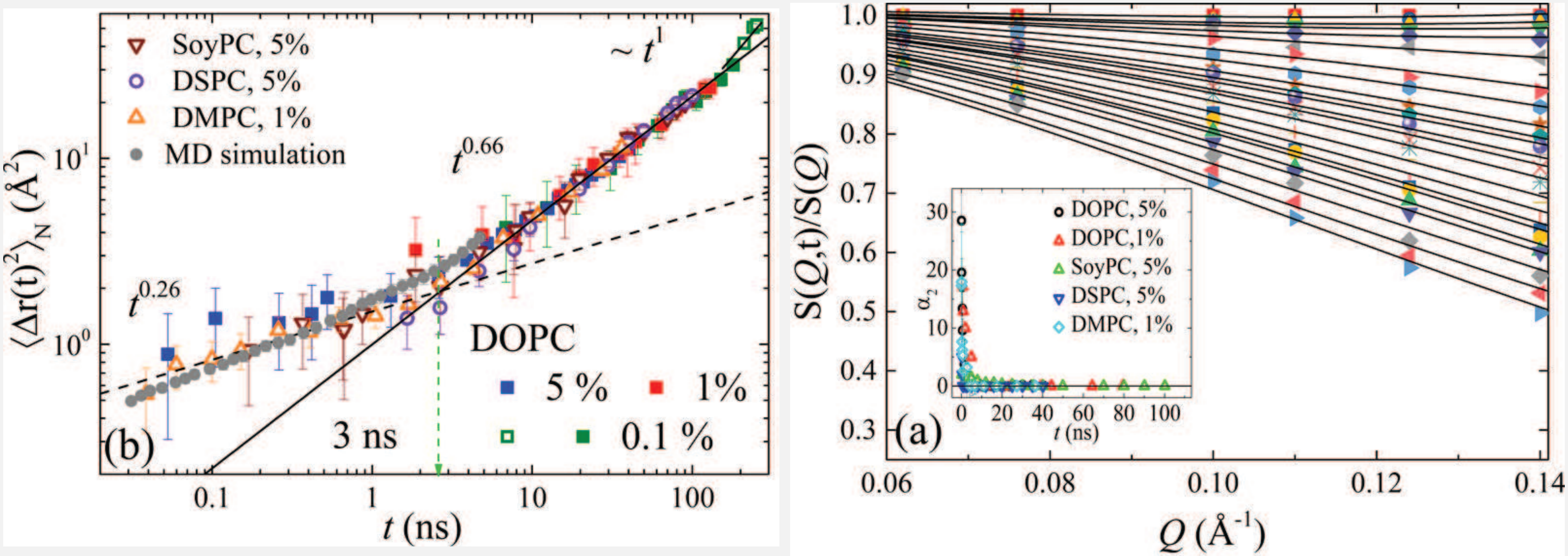






D Molina-Garcia, T Sandev, H Safdari, G Pagnini, AV Chechkin & RM, NJP (2018)

Extreme short time non-Gaussian subdiffusion

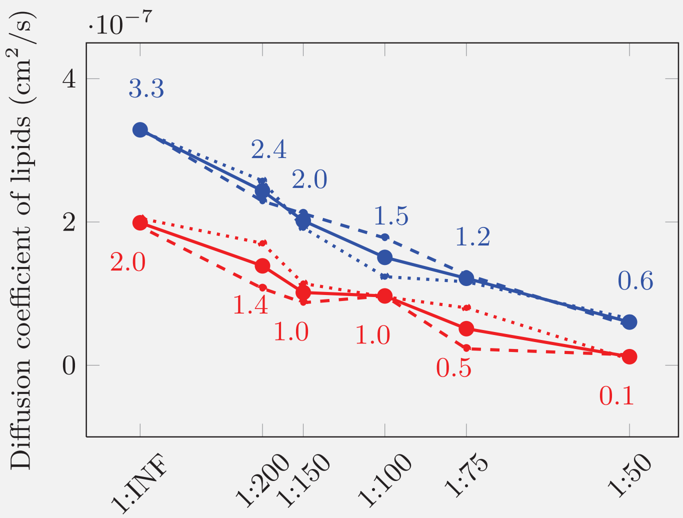


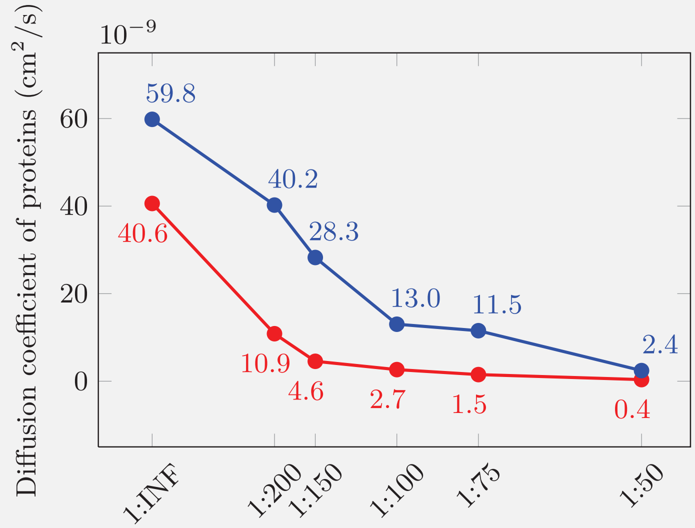
Authors suggest short time regime $\langle \mathbf{r}^2(t) \rangle \simeq t^{0.26}$
& transient trapping of lipids leading to non-Gaussian displacement distribution

[NB: Non-Gaussianity could also come from inhomogeneity]

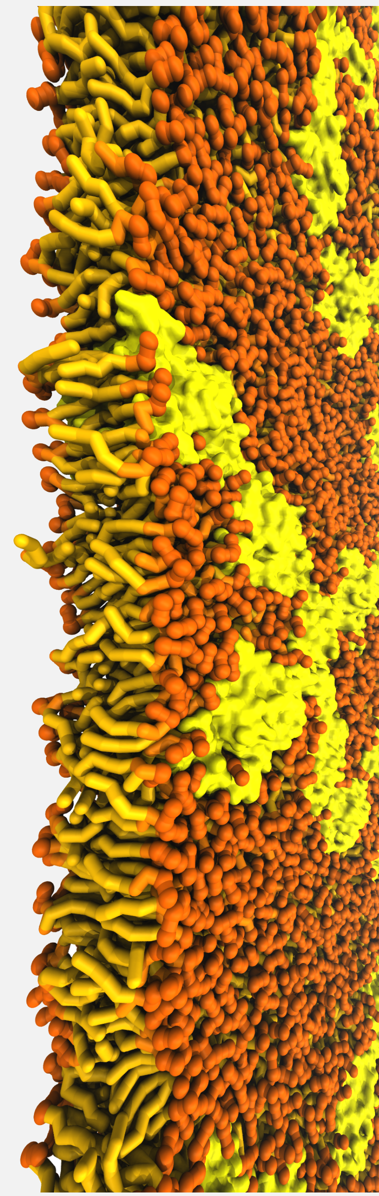
S Gupta, JU de Mel, RM Perera, P Zolnierczuk, M Bleuel, A Faraone & GJ Schneider, JPC Lett (2018)

Protein crowded membranes reduce effective mobility

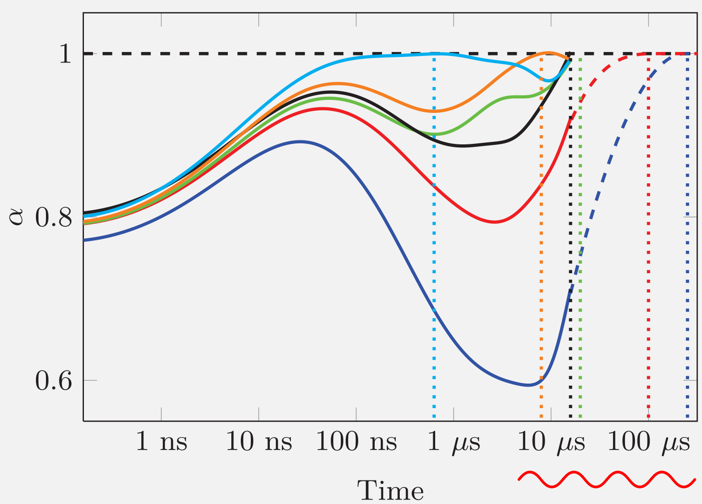


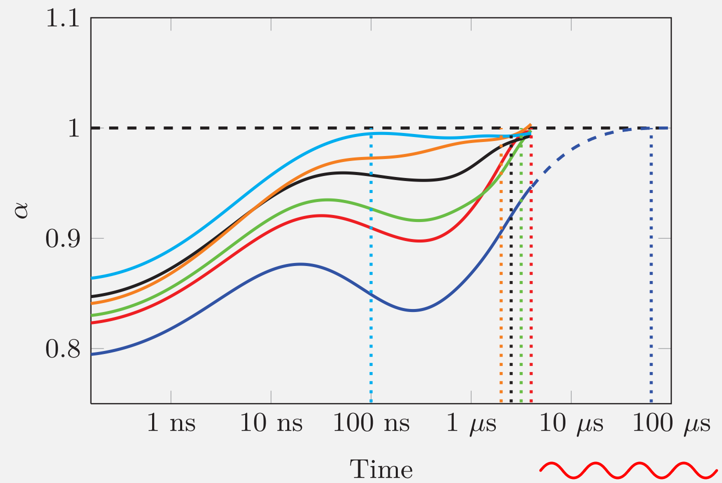


Blue: DLPC. Red: DPPC



Protein crowding effects anomalous lipid diffusion

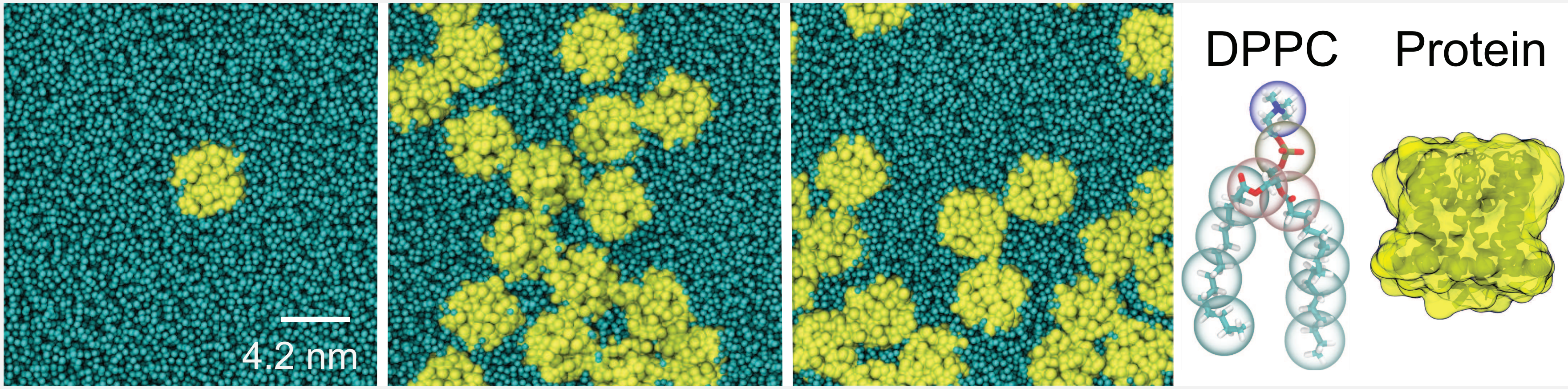


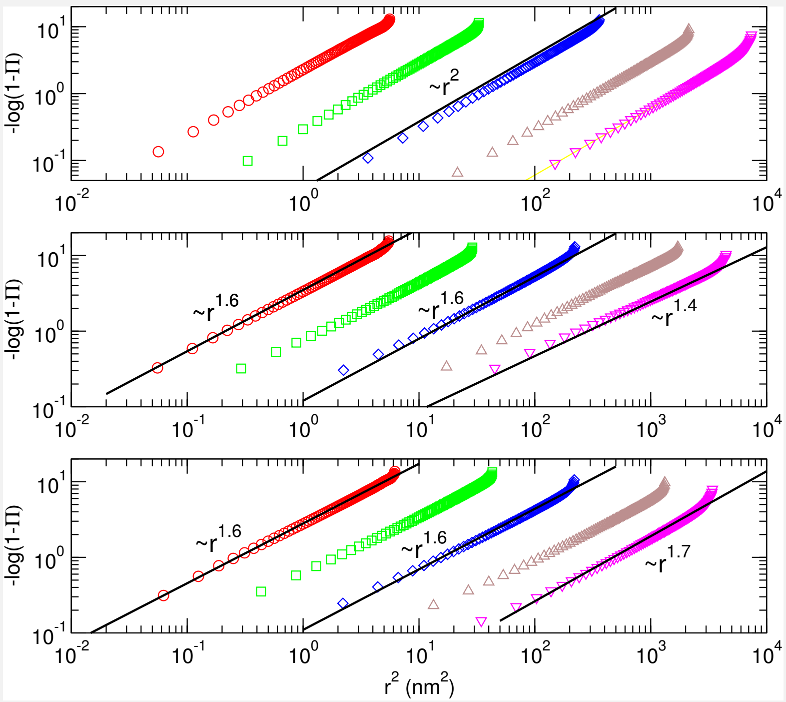


Left: DPPC (protein-aggregating) case. Right: DLPC protein non-aggregating case.

M Javanainen, H Hammaren, L Monticelli, JH Jeon, RM & I Vattulainen, Faraday Disc (2013)

Crowding in membranes: non-Gaussian lipid/protein diffusion

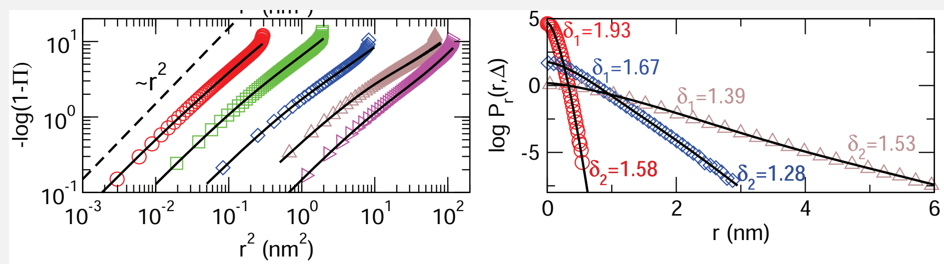




Dilute membrane: $P(r,t)$ Gauss

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

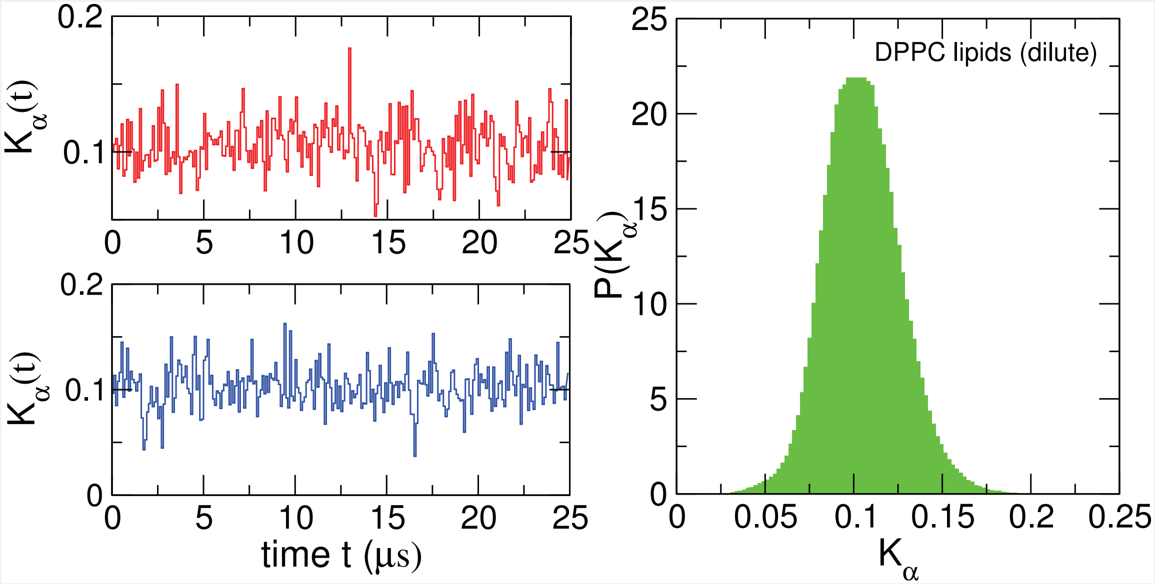
$$P(r,t) \propto \exp\left(-\left[\frac{r}{ct^{\alpha/2}}\right]^{\delta}\right)$$

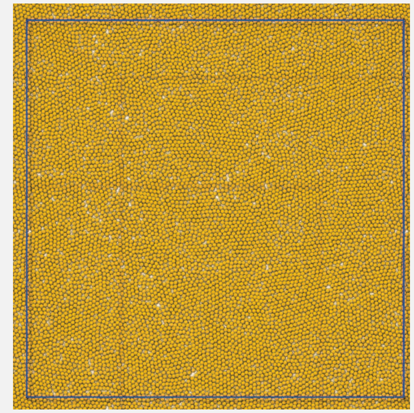


J-H Jeon, M Javanainen, H Martinez-Seara, RM & I Vattulainen, PRX (2016); see also Faraday Disc (2013)

Crowding in membranes increases dynamic heterogeneity

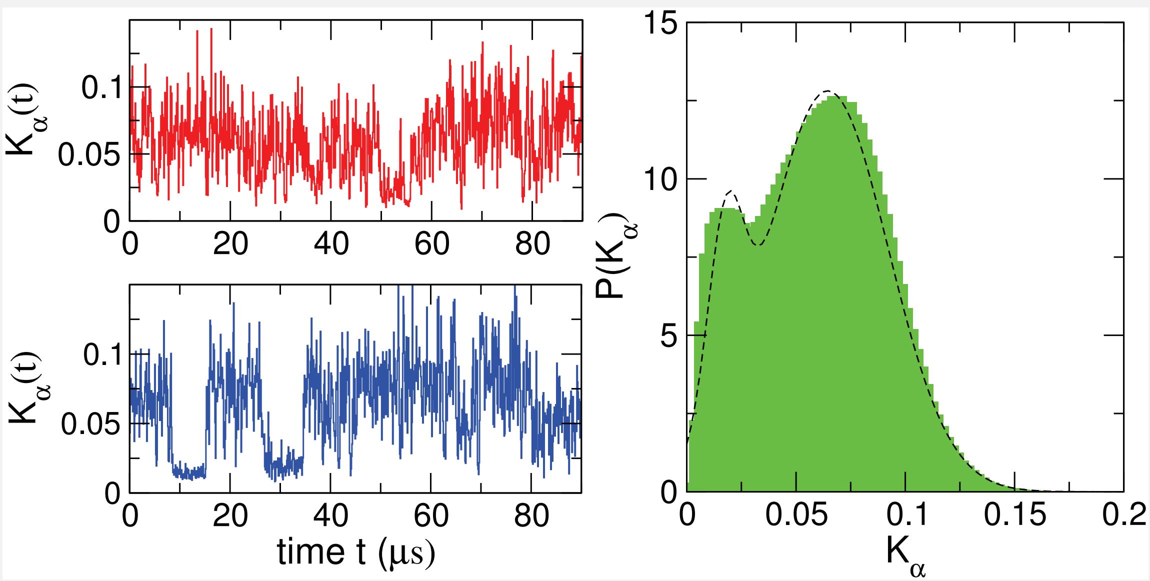
Diffusivity(t) for two lipids

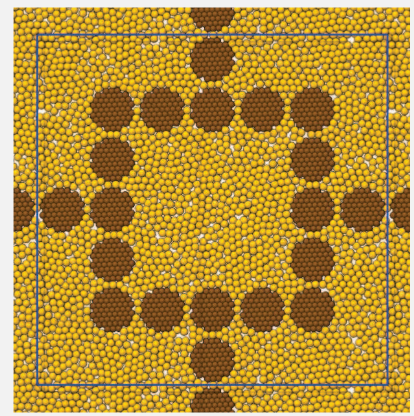




2D argon liquid

Lipid diffusivity, dilute membrane



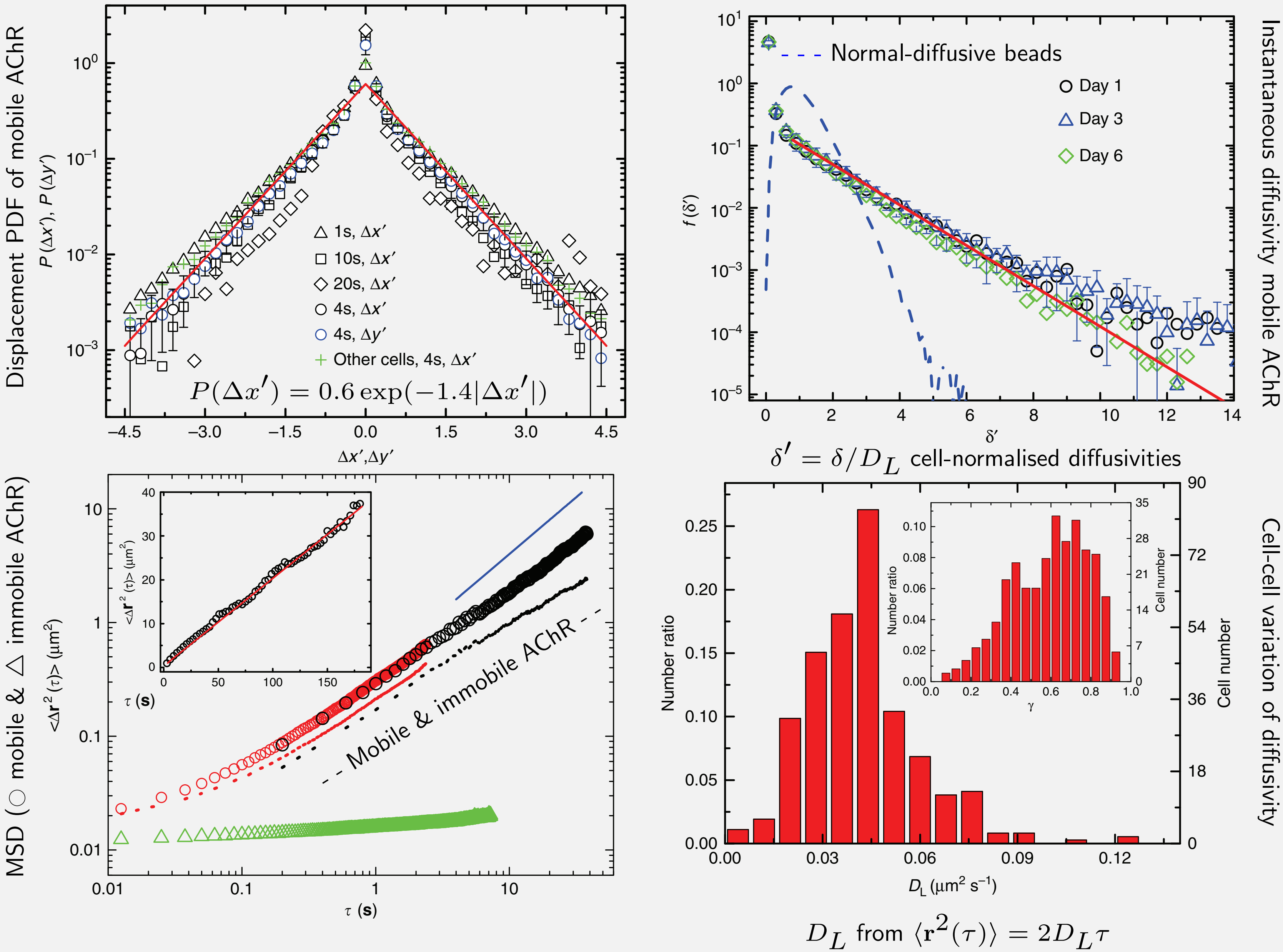


2D "blocked" argon

Lipid diffusivity, crowded membrane

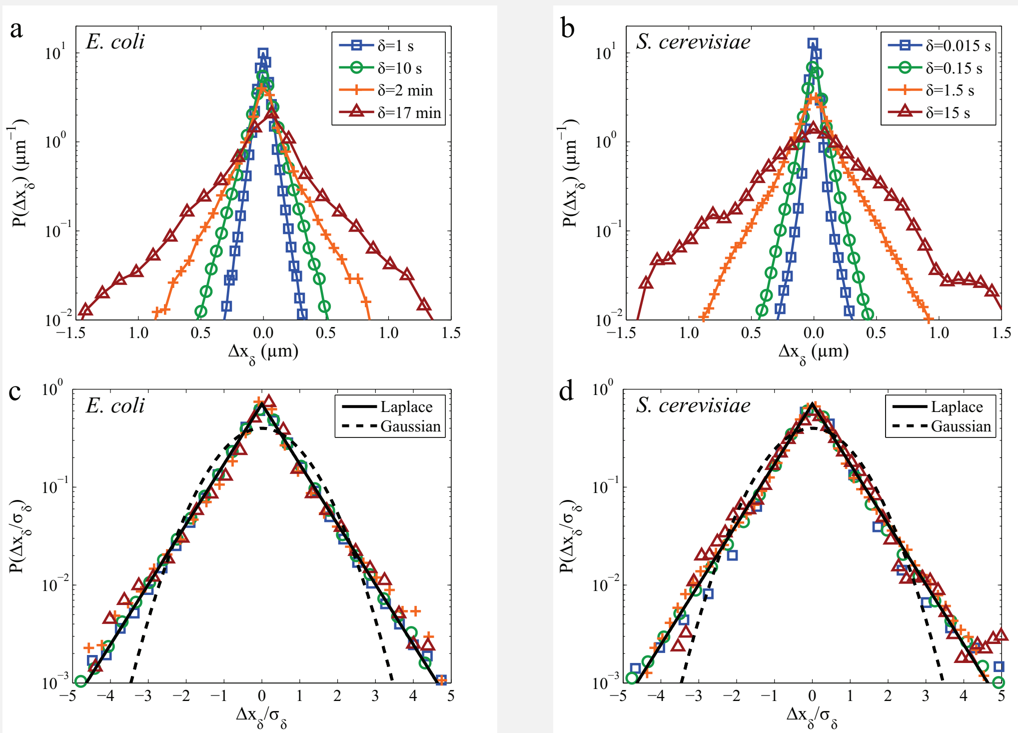
J-H Jeon, M Javanainen, H Seara Monne, RM & I Vattulainen, PRX (2016)

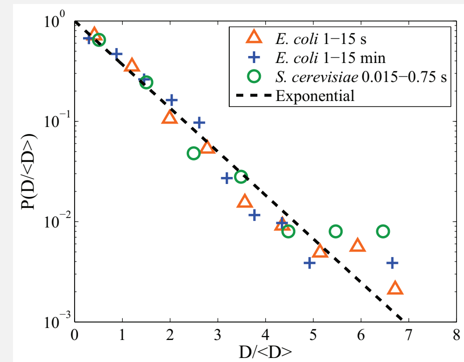
Non-Gaussianity of acetylcholine receptors in Xenopus cells

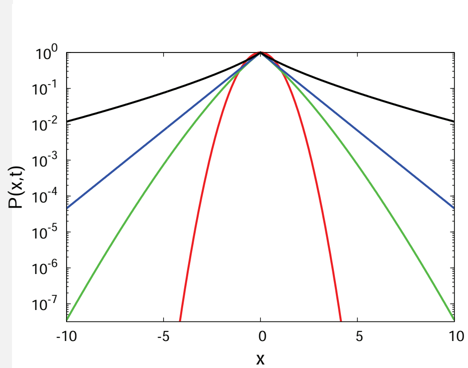


Non-Gaussian diffusion in viscoelastic systems

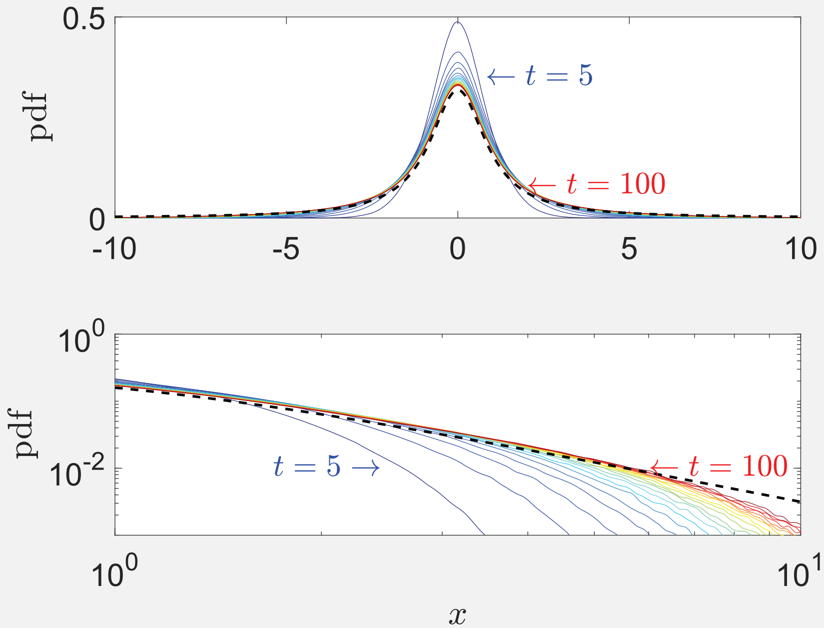
So far consensus: submicron tracer motion in cytoplasm is FBM-like, i.e., Gaussian
RNA-protein particles in E.coli & S.cerevisiae perform exponential anomalous diffusion:





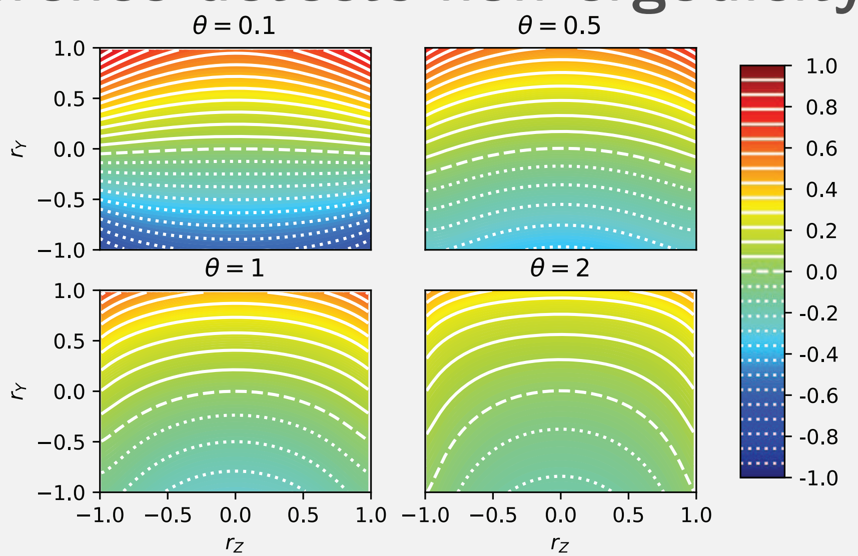


Superstatistical GLE: non-Gaussian viscoelastic diffusion



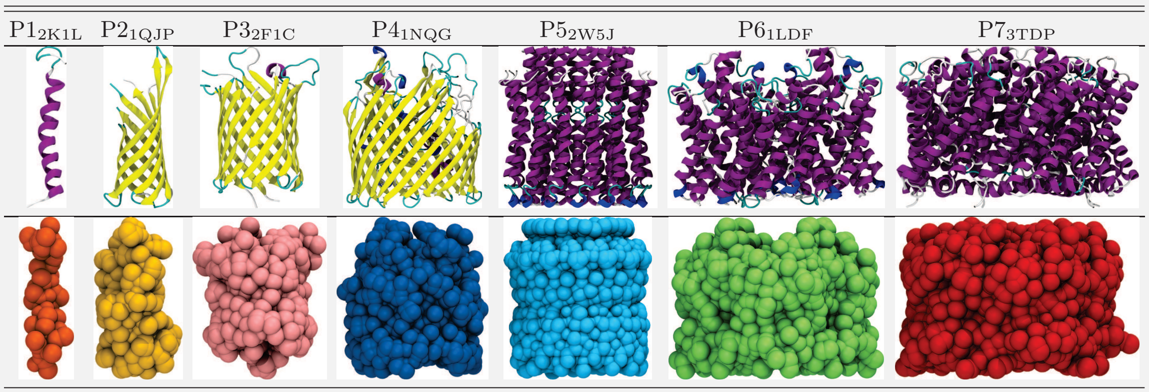
$$\langle \mathbf{r}^2(t) \rangle \simeq K_\alpha t^\alpha$$

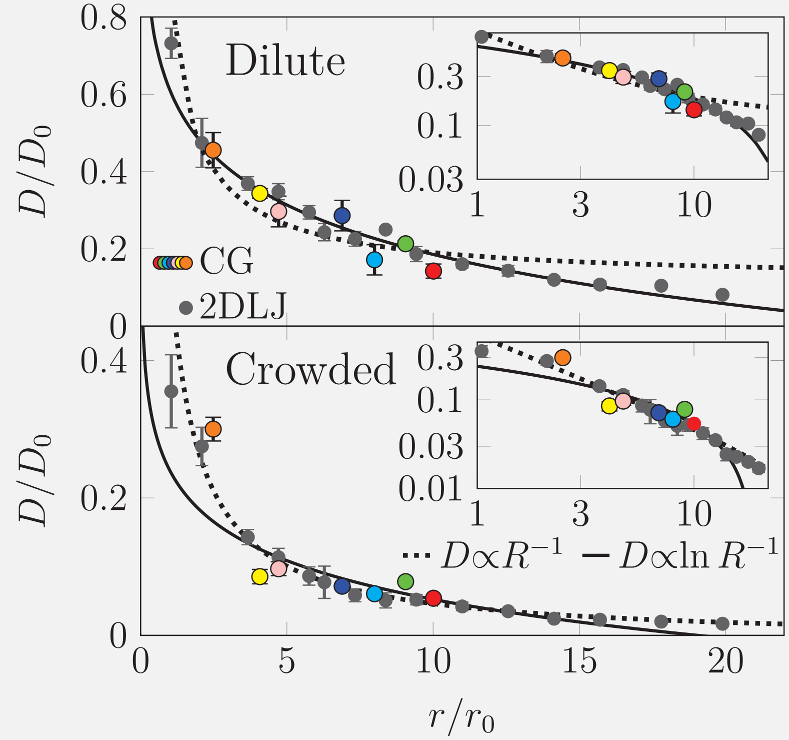
Codifference detects non-ergodicity & non-Gaussianity

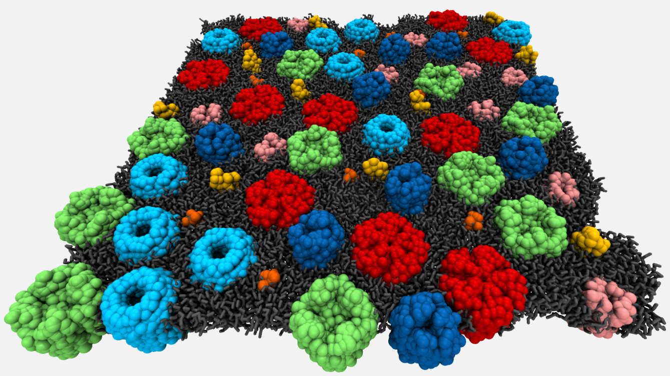


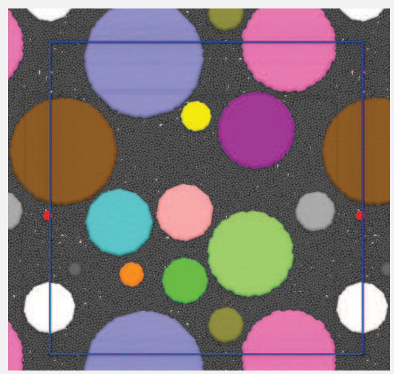
J Ślęzak, RM & M Magdziarz, NJP (2018), NJP (2019)

Geometry-induced violation of Saffman-Delbrück relation









Dilute system: Saffman-Delbrück law

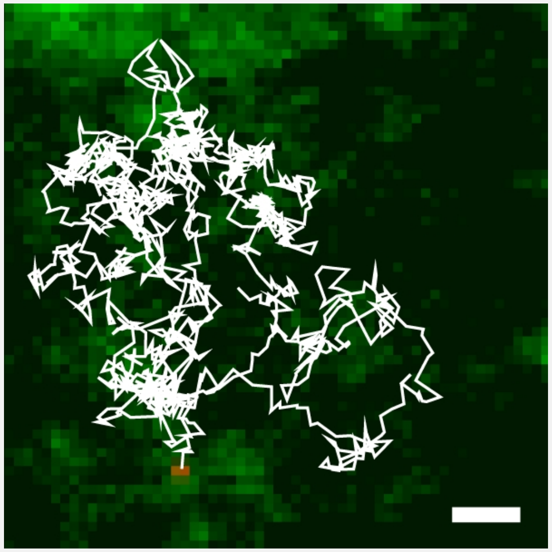
$$D(R) \simeq \log(1/R)$$

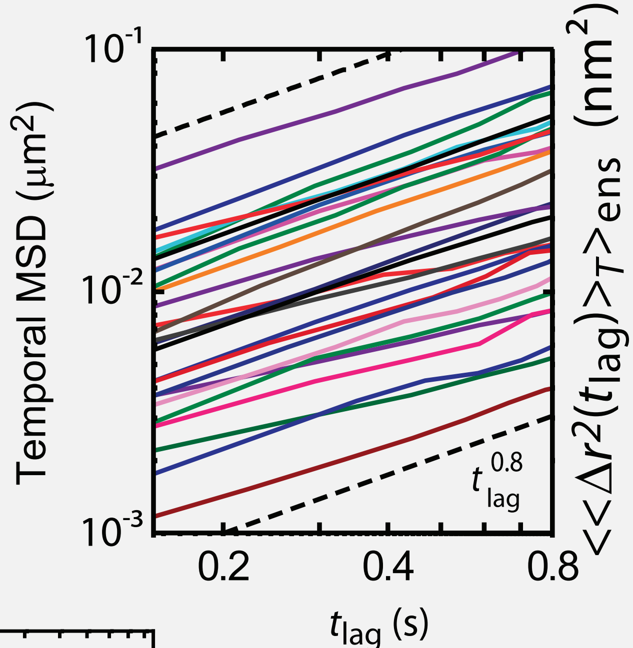
Crowded membrane & 2DLJ discs:

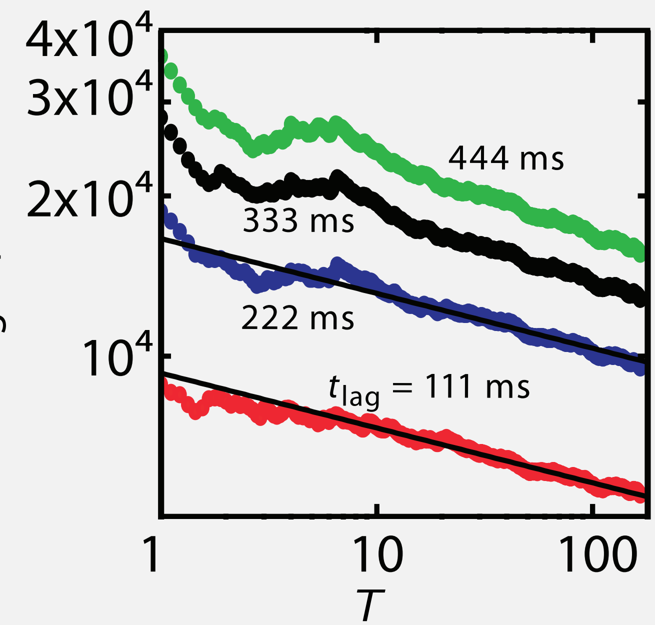
$$D(R) \simeq 1/R$$

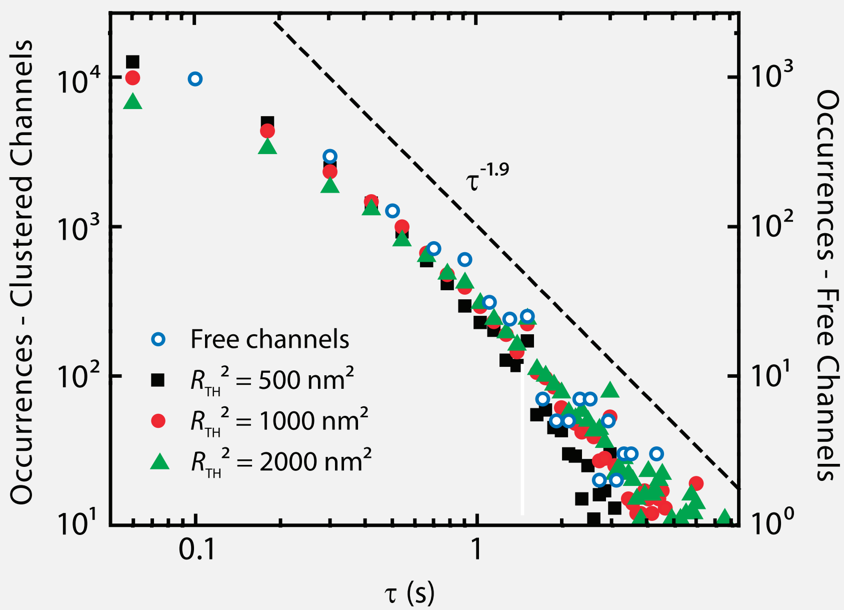
M Javanainen, H Seara Monne, RM & I Vattulainen, JPC Lett (2017)

CTRW-like motion of Ka channels in plasma membrane









$\psi(\tau) \simeq \tau^{-1-\alpha}$ scale free

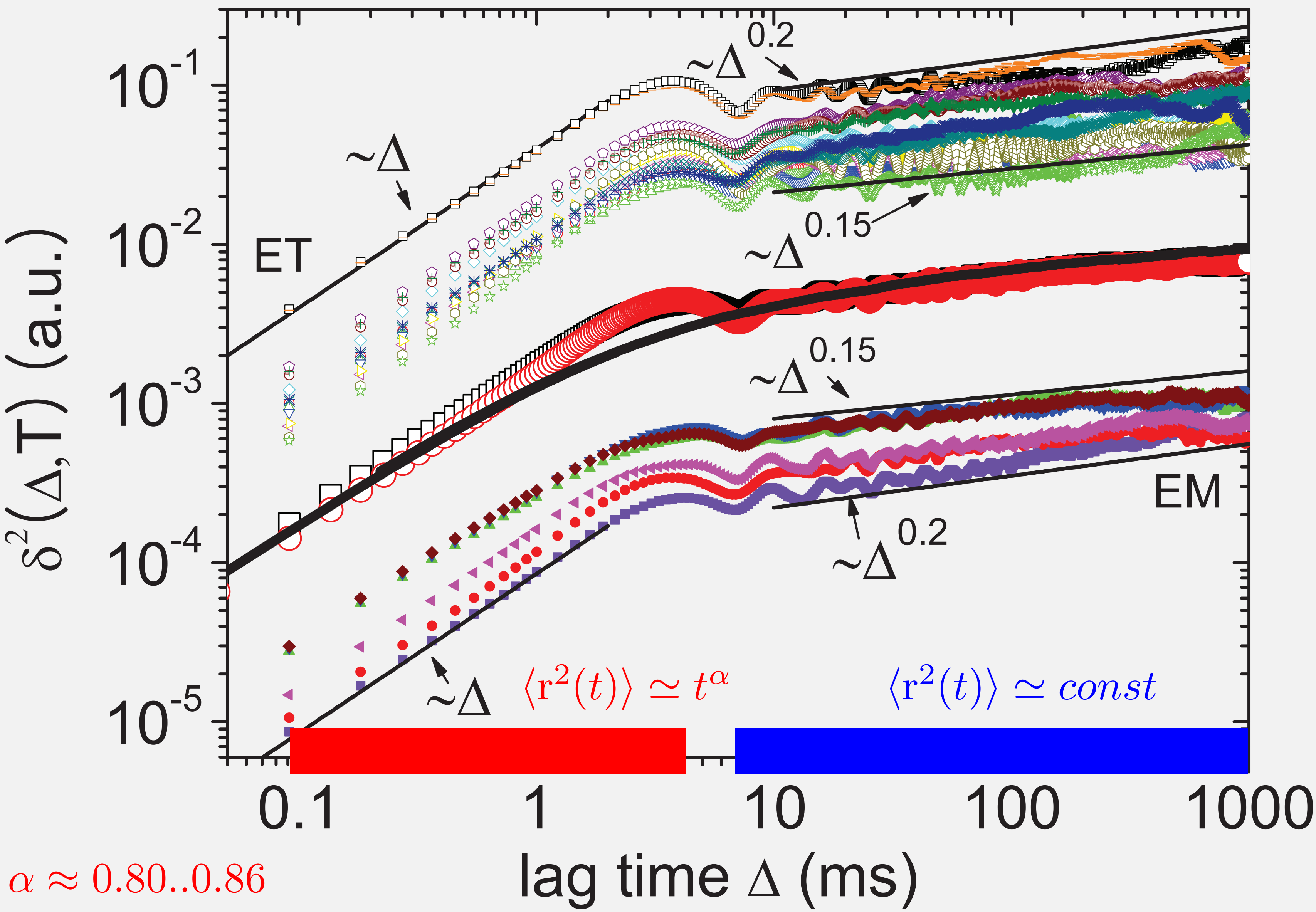
$\overline{\delta^2(\Delta)}$ apparently random

$$\Delta/T^{1-\alpha} \simeq \overline{\delta^2(\Delta)} \neq \langle \mathbf{r}^2(\Delta) \rangle \simeq \Delta^\alpha$$

$$P(\mathbf{r},t) \simeq \exp\left(-\beta r^{1/[1-\alpha/2]}\right)$$

AV Weigel, B Simon, MM Tamkun & D Krapf, PNAS (2011); theory: Y He, S Burov, RM & E Barkai, PRL (2008)

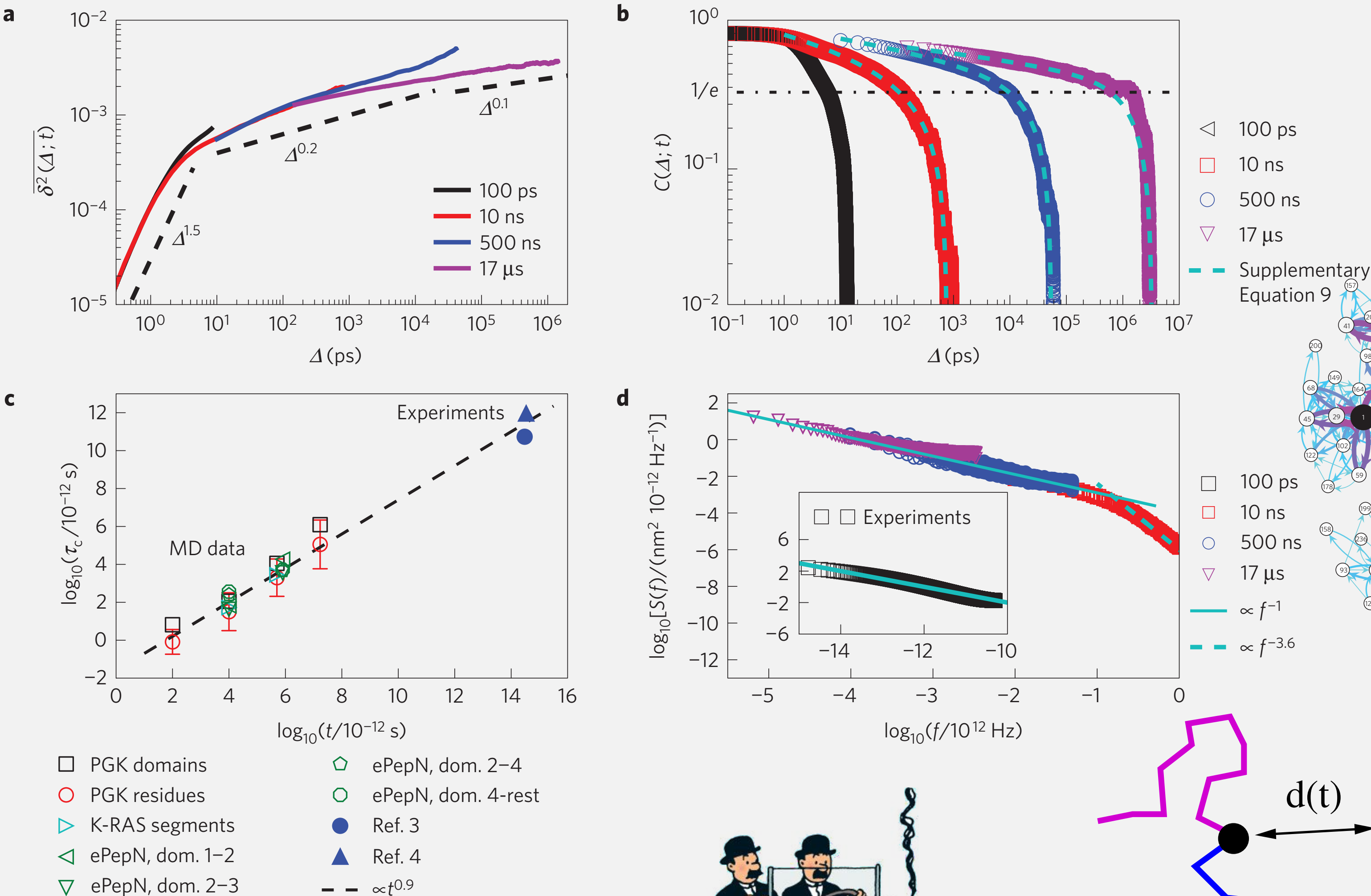
Granule subdiffusion in harmonic optical tweezer potential

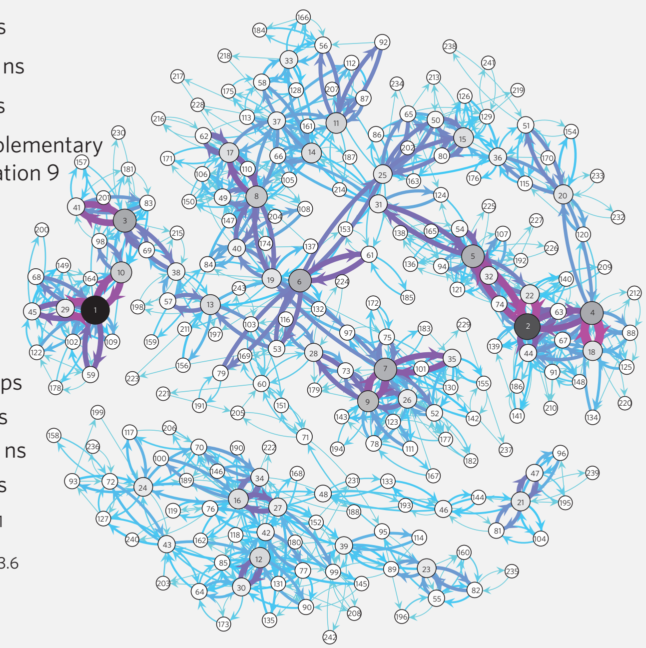


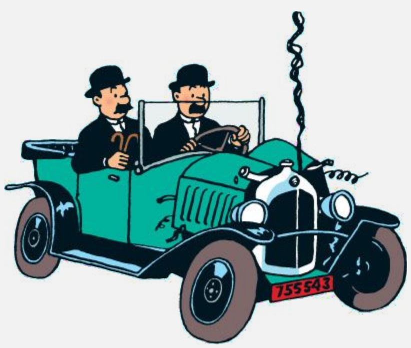
$\alpha \approx 0.80..0.86$

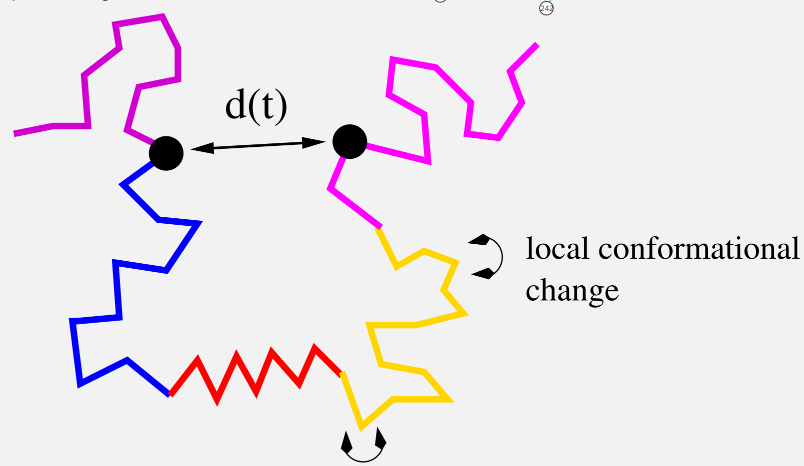
J-H Jeon, . . . , K Berg-Sørensen, L Oddershede & RM, PRL (2011); S Burov, RM, & E Barkai, PNAS (2010)

Self-similar internal protein dynamics: 13 decades of ageing



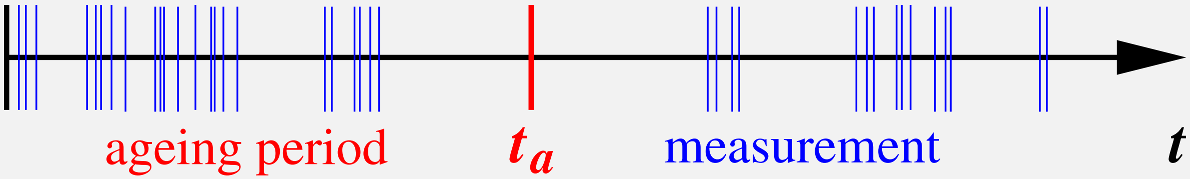






X Hu, L Hong, MD Smith, T Neusius, X Cheng & JC Smith, Nature Phys (2016); N&V RM Nature Phys (2016)

Ageing effects in single trajectory time averages

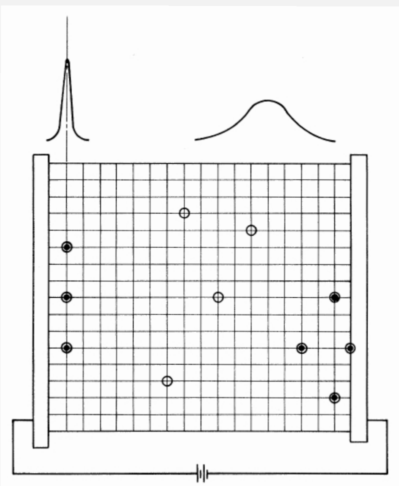


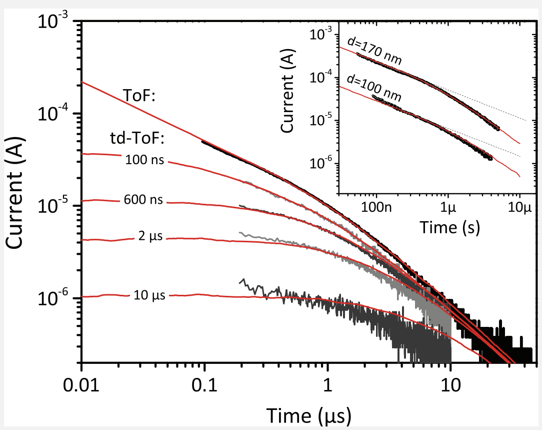
Ageing mean squared displacement ($\Lambda(z) = (1+z)^\alpha - z^\alpha$)

$$\left\langle\overline{\delta^2(\Delta)}\right\rangle_a = \frac{\Lambda_\alpha(t_a/T)}{\Gamma(1+\alpha)}\frac{g(\Delta)}{T^{1-\alpha}} \quad \not\Leftrightarrow \quad \langle x^2(t)\rangle_a \simeq \begin{cases} t^\alpha, & t_a \ll t \\ t_a^{\alpha-1}t, & t_a \gg t \end{cases}$$

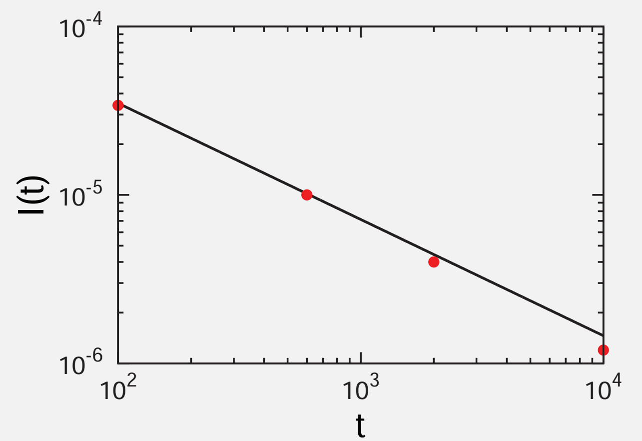
Probability to make at least one step during $[t_a, t_a + T]$: *population splitting*

$$m_\alpha(T/t_a) \simeq (T/t_a)^{1-\alpha}, \quad T \ll t_a$$





M Schubert, . . . & D Neher, Phys Rev B (2013)



H Krüsemann, R Schwarzl & RM, Transp Porous Media (2016), PRE (2015)

J Schulz, E Barkai & RM, PRL (2013), PRX (2014)

Summary

I Brownian yet non-Gaussian or non-Gaussian viscoelastic diffusion quite ubiquitously observed in heterogeneous media

II Excluded volume effects can explain basic features in 2D membranes

III Non-stationary processes such as CTRW are non-Gaussian by nature

IIII Non-ergodic, ageing dynamics on molecular scale

卌 Physics↔ARIMA time series analysis: J Ślęzak, RM, M Magdziarz, arXiv (2019)

卌I Bayes/max likelihood model determination: PCCP (2018), Soft Matter (2019)

- Membrane dynamics: RM, JH Jeon & AG Cherstvy, Biochimica et Biophysica Acta - Biomembranes **1858**, 2451 (2016)
- Single molecule experiments: C Nørregaard, RM, CM Ritter, K Berg-Sørensen & LB Oddershede, Chem Rev **117**, 4342 (2017)
- Anomalous diffusion models: RM, JH Jeon, AG Cherstvy & E Barkai, Phys Chem Chem Phys **16**, 24128 (2014)

Acknowledgements

Eli Barkai (Bar-Ilan U Ramat Gan)
Carsten Beta (U Potsdam)
Andrey Cherstvy, Aleksei Chechkin (U Potsdam)
Aljaz Godec (MPIBC Göttingen)
Denis Grebenkov (École Polytechnique)
Jae-Hyung Jeon (POSTECH Pohang)
Michael Lomholt (Syddansk U Odense)
Marcin Magdziarz (Politechnika Wrocławska)
Lene Oddershede (NBI Københavns U)
Gleb Oshanin (Sorbonne)
Gianni Pagnini (BCAM Bilbao)
Christine Selhuber-Unkel (U Kiel)
Flavio Seno (Universitá di Padova)
Igor Sokolov (Humboldt U Berlin)
Ilpo Vattulainen (Helsingin Yliopisto)
Matthias Weiss (U Bayreuth)
Agnieszka Wyłomańska (Politechnika Wrocławska)

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