# Weak Ergodicity Breaking on the Nano-Scale

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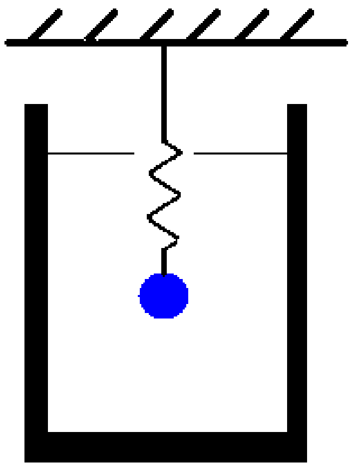
**Bel, Burov, Margolin, Metzler, Rebenshtok**

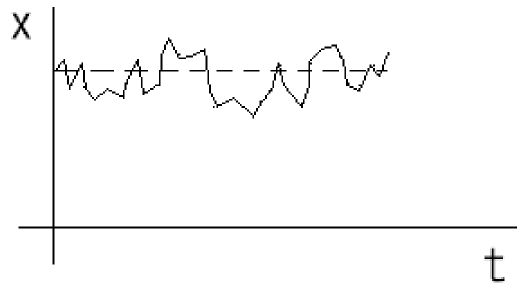
## Kyoto 2015

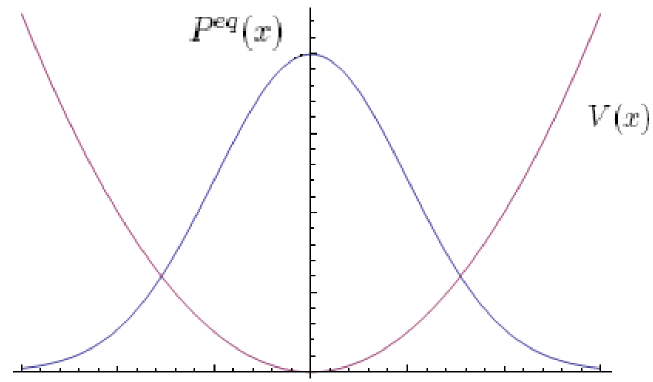
# Outline

- Single molecule experiments exhibit weak ergodicity breaking.
- Power law blinking quantum dots.
- sub-Diffusion of molecules in the live cell.

# Ergodicity





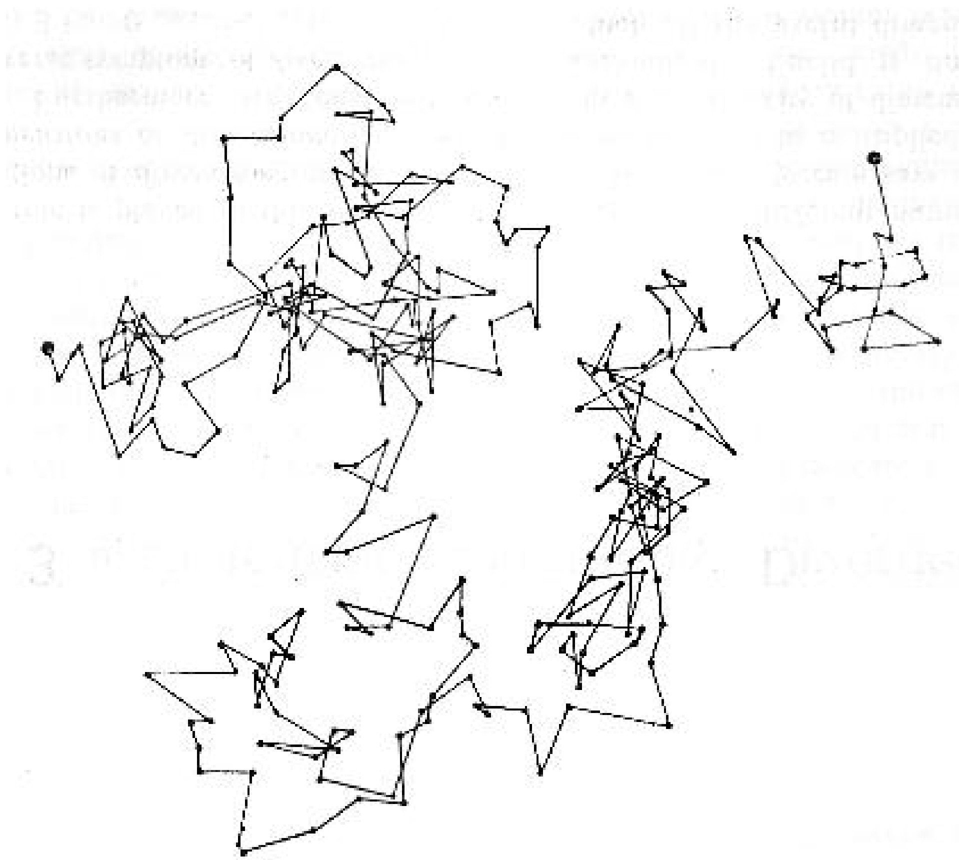

$$P^{eq}(x) = \frac{e^{-V(x)/k_B T}}{Z}$$

Ergodicity: time averages = ensemble averages.

$$\overline{x} = \lim_{t\to\infty} \frac{\int_0^t x(\tau) d\tau}{t}.$$

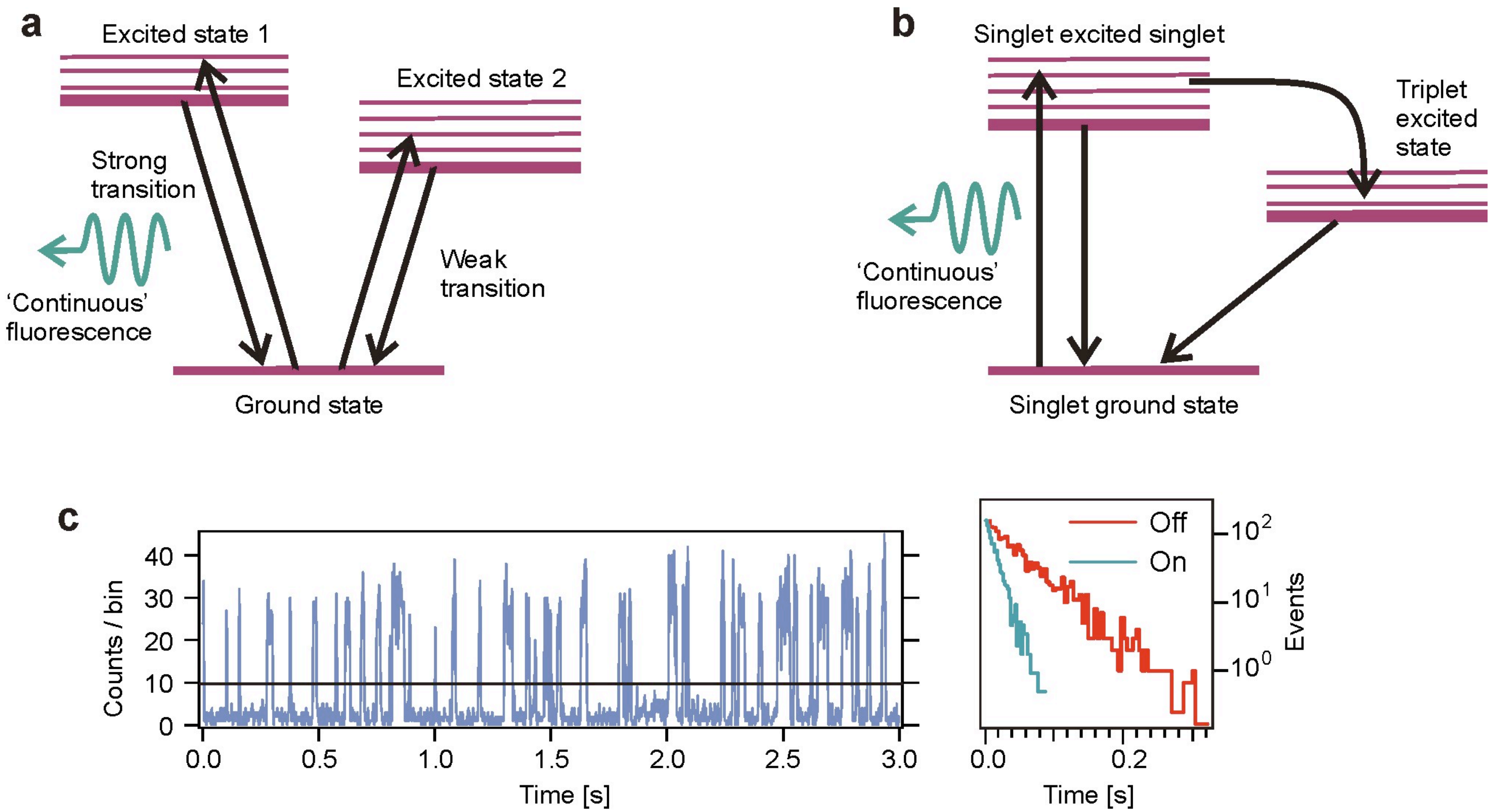
$$\langle x \rangle = \int_{-\infty}^{\infty} x P^{eq}(x) dx.$$

# Ergodicity out of equilibrium



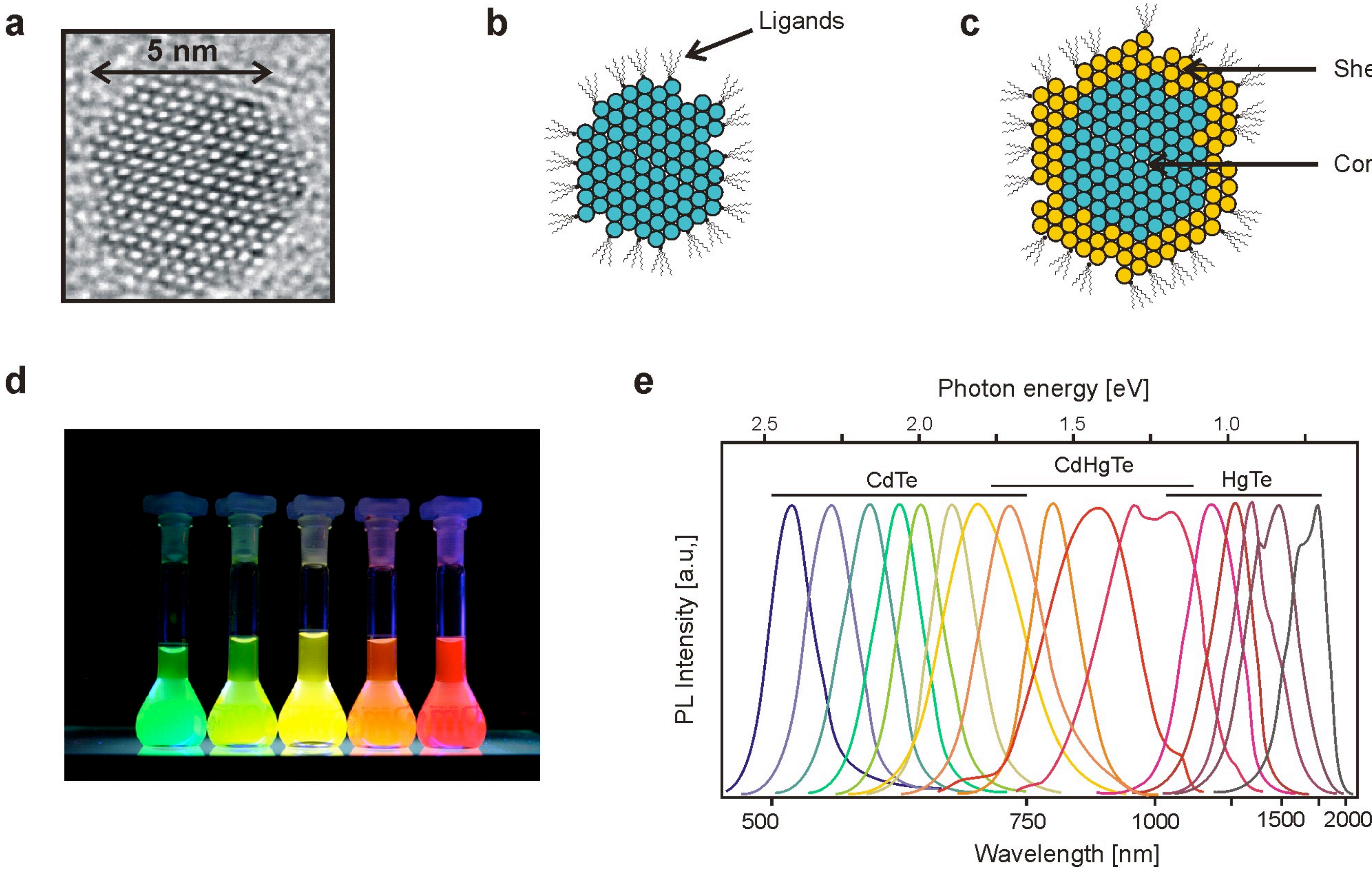
$$\overline{\delta^2}(\Delta, t) = \frac{\int_0^{t-\Delta} \left[x(t'+\Delta) - x(t')\right]^2 dt'}{t-\Delta} \to 2D\Delta$$

# Quantum Jumps: Atoms



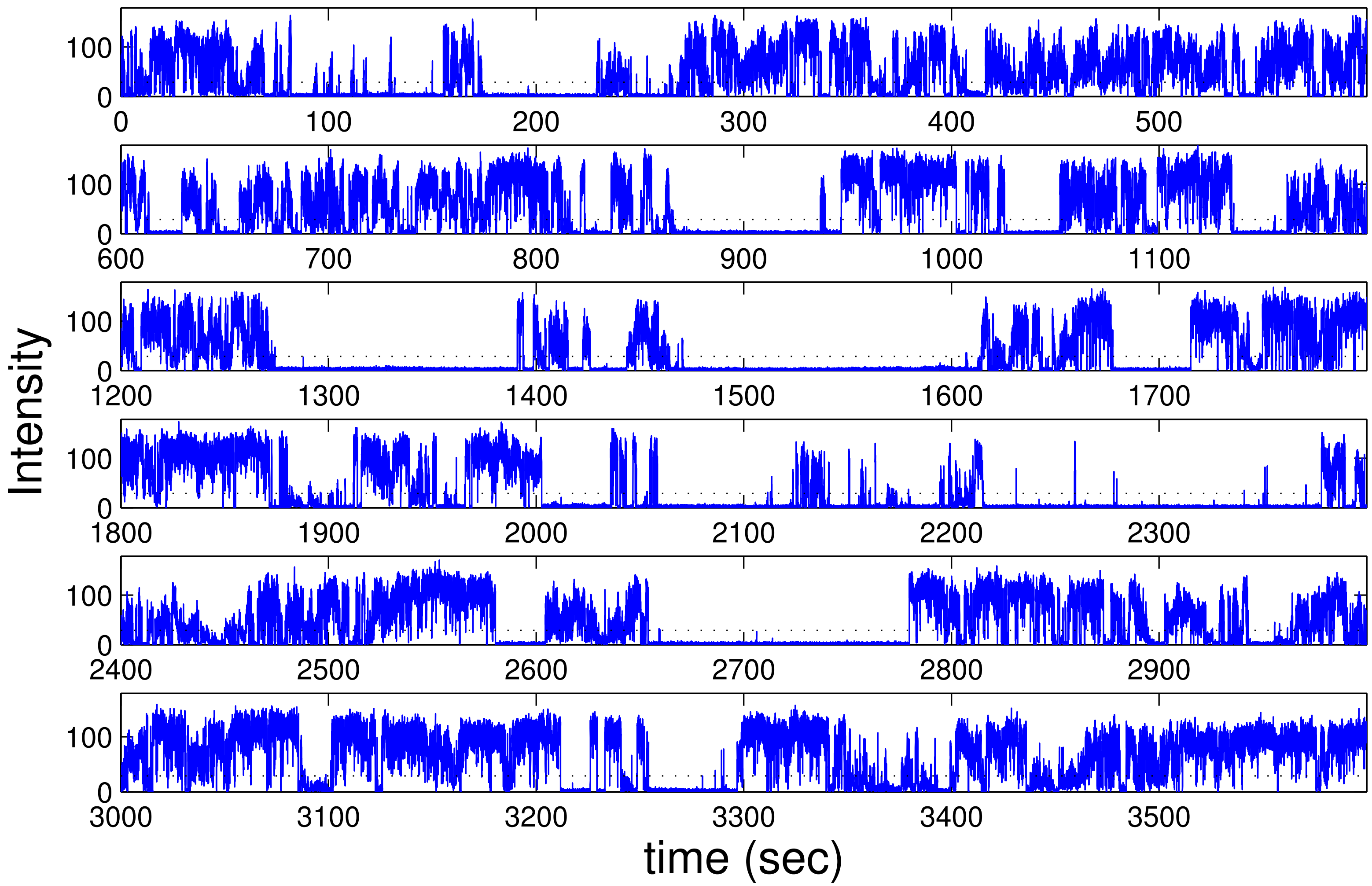

Stefani, Hoogenboom, Barkai Physics Today 62, 34 (2009).

# Quantum Dots

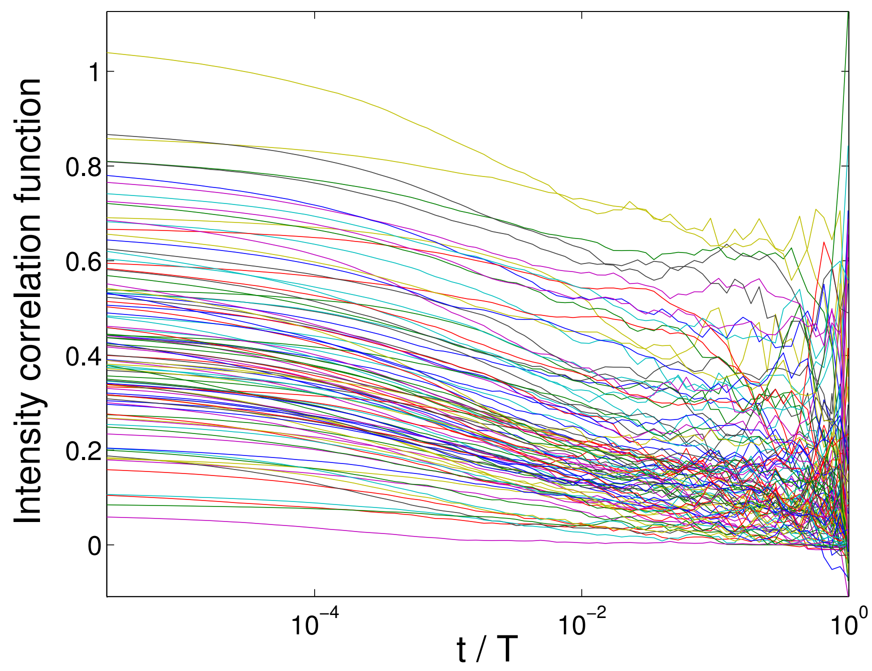



Stefani, Hoogenboom, Barkai **Physics Today** 62, 34 (2009).

# Blinking Nano Crystals (coated CdSe)



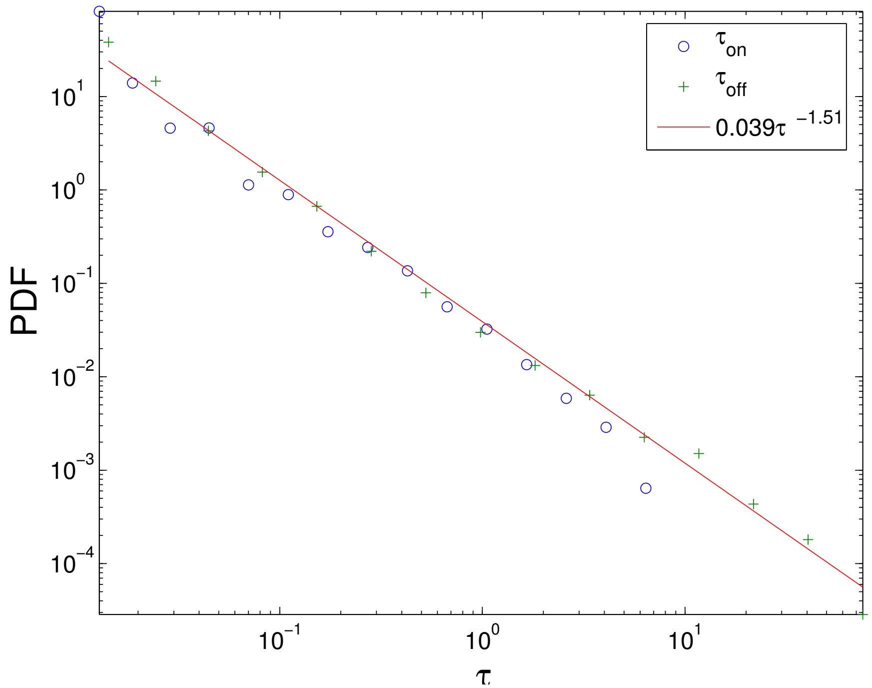
# Non-ergodic Intensity Correlation Functions




Experiment Brokmann, Dahan et al **Phys. Rev. Lett.** (2003).

Theory: Margolin, EB **Phys. Rev. Lett.** 90, 104101 (2005).

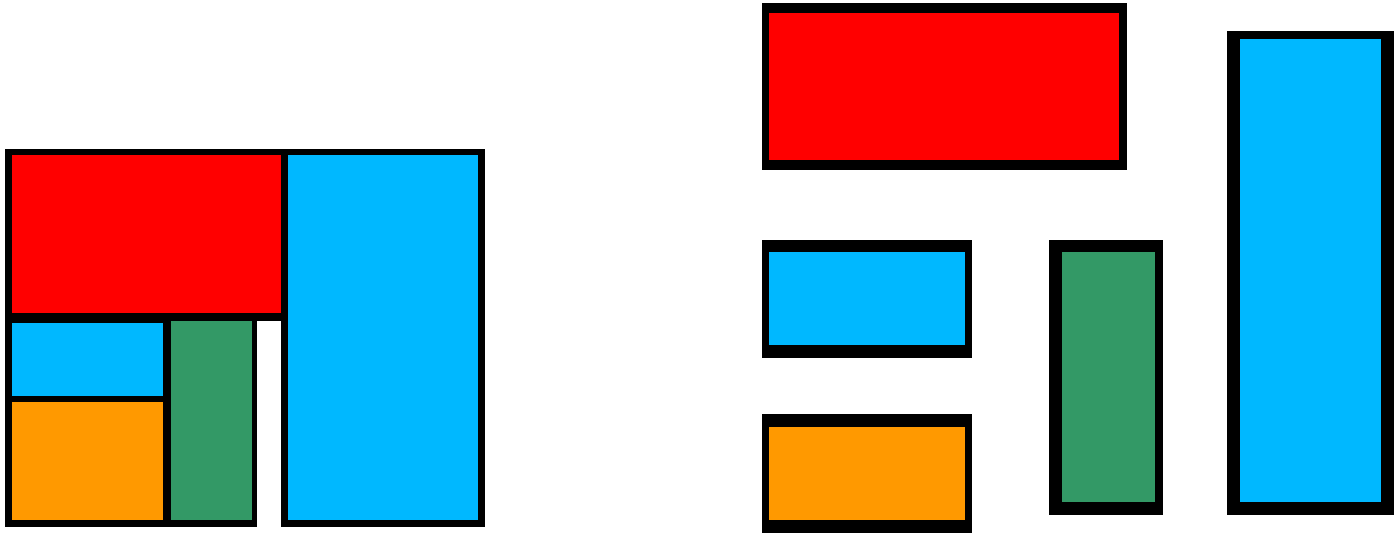
# Power Law Distribution of on and Off times




Power law waiting time $\psi(\tau) \sim \tau^{-\left(1+\alpha_{off}\right)}$.

Averaged time in States On and Off is infinite $\langle \tau \rangle = \infty$.

# Weak and strong Ergodicity Breaking



System is decomposed → strong ergodicity breaking.

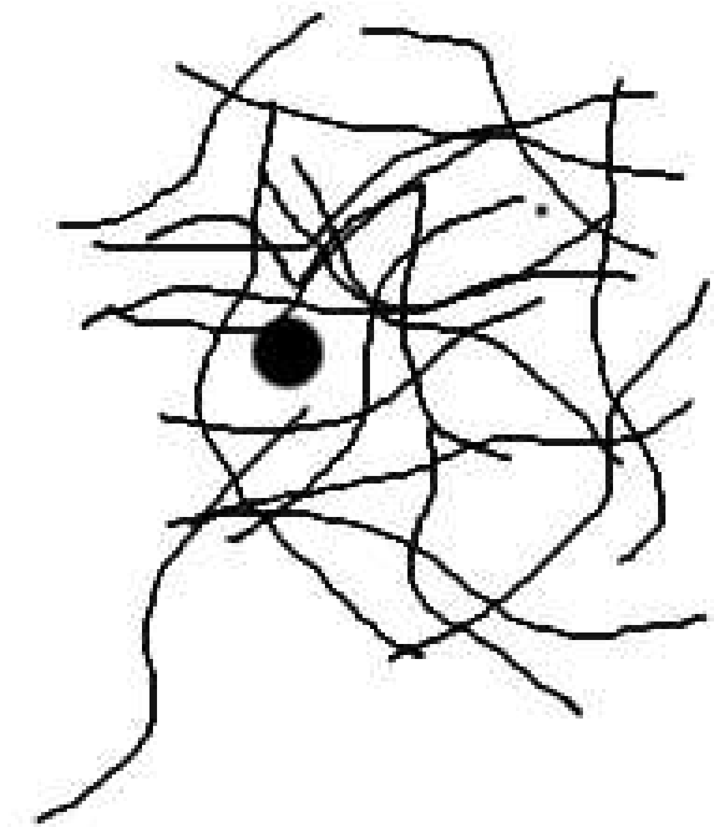
System's space explored → weak ergodicity breaking.

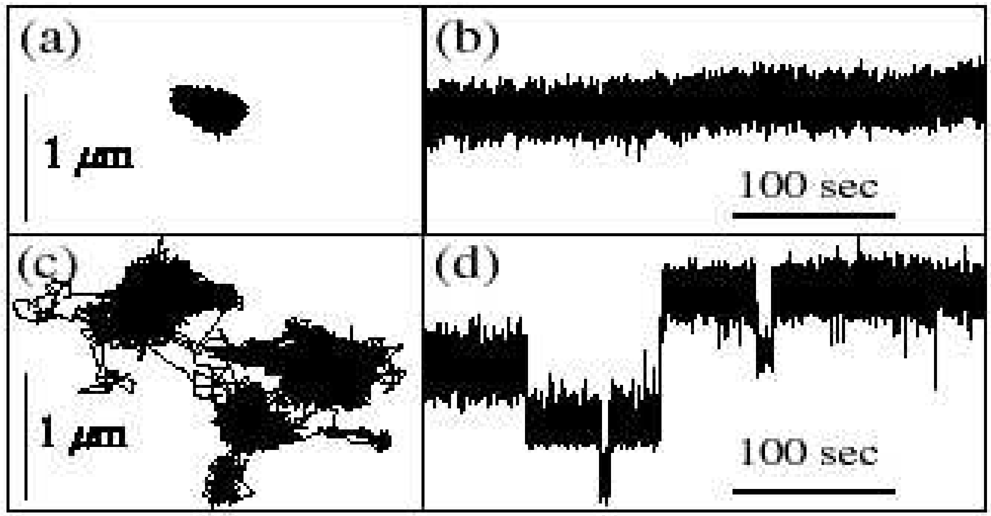
J. Bouchaud J. Phys. I France (1992).

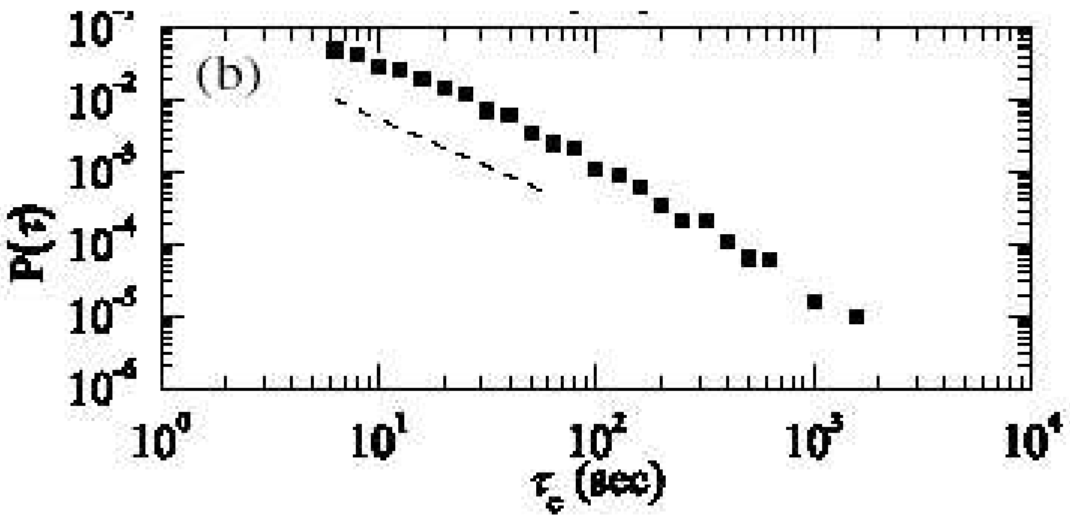
# Continuous Time Random Walk (CTRW)

Dispersive Transport in Amorphous Material Scher-Montroll (1975).

Bead Diffusing in Polymer Network Weitz (2004).

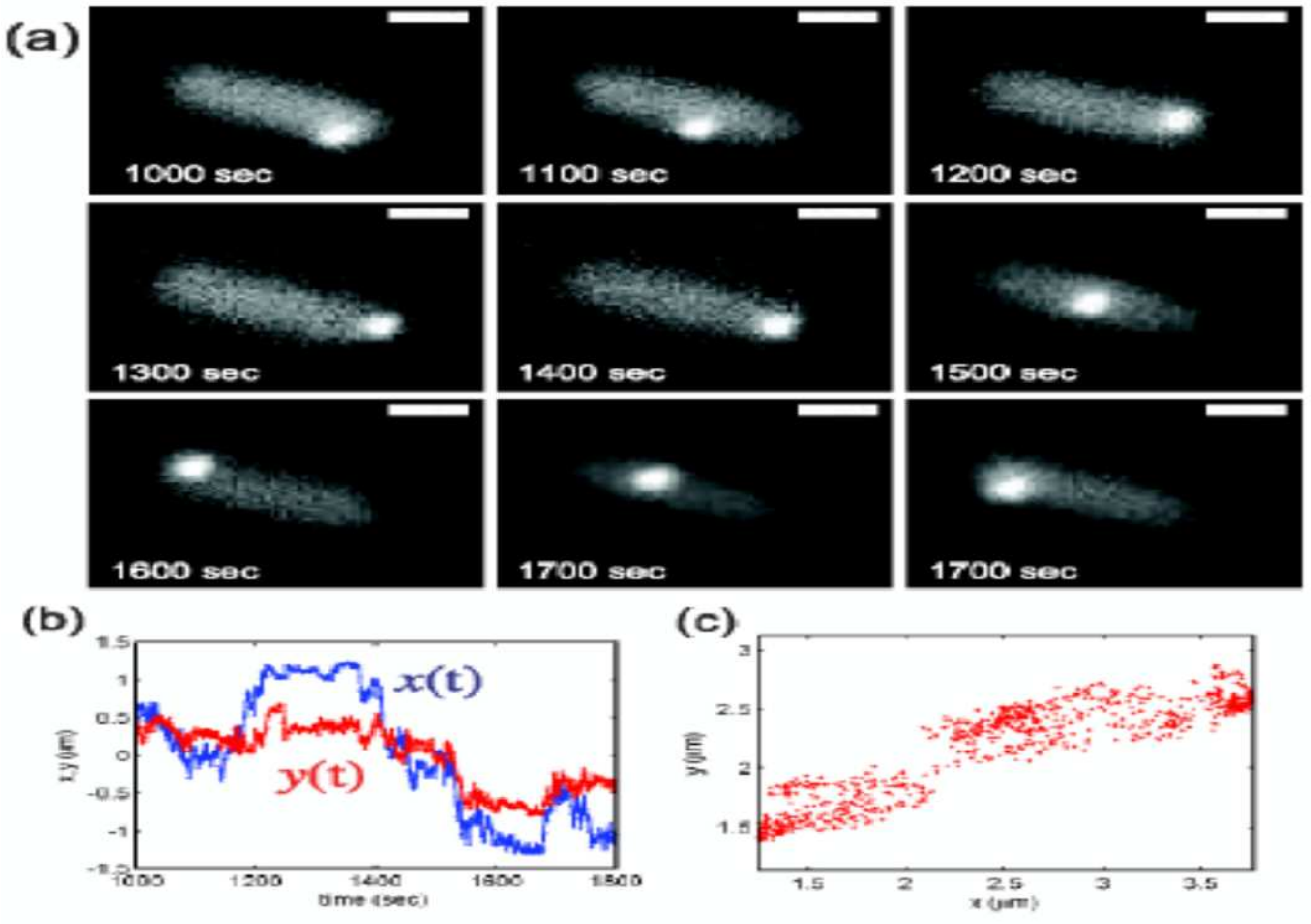


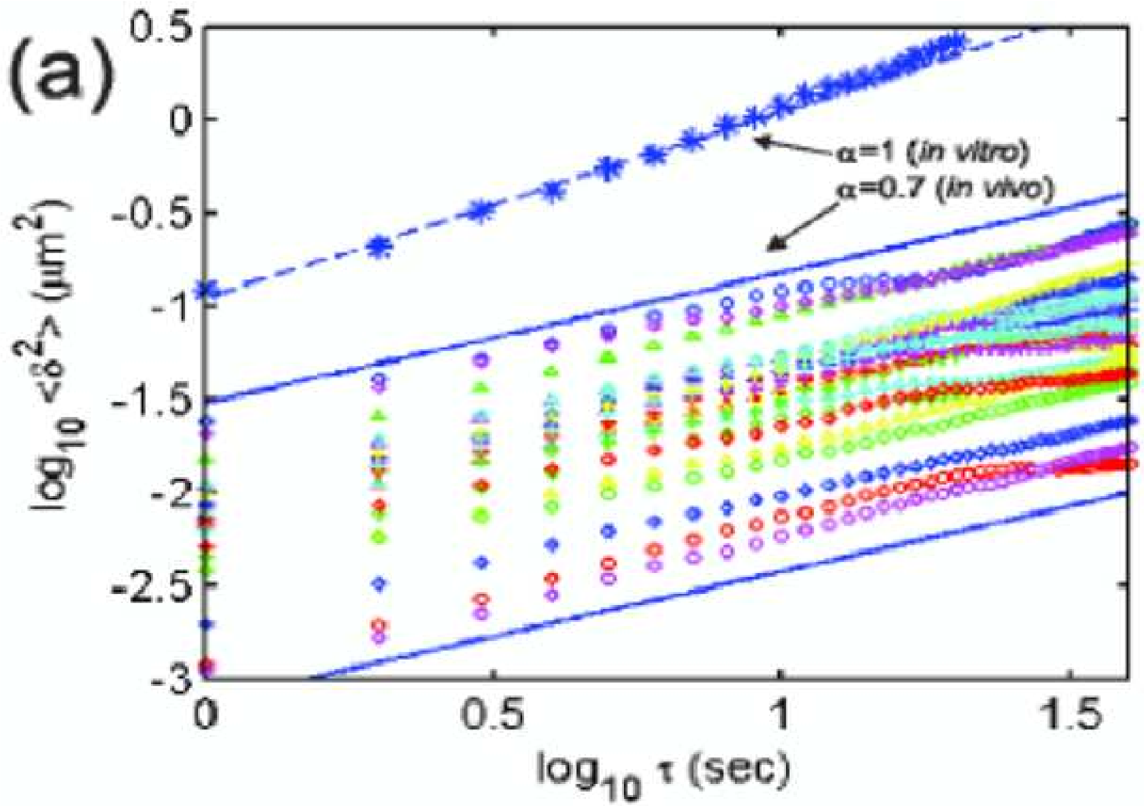



Average Waiting Time is $\infty$. Diffusion is anomalous $\langle r^2 \rangle \propto t^{\alpha}$.

# mRNA diffusing in a cell Golding and Cox






Golding and Cox **PRL** (2006)

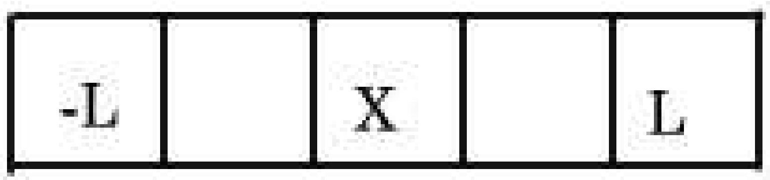
He Burov Metzler EB **PRL** (2008). Lubelski, Sokolov Klafter (ibid).

Kepten, .... EB, Garini **PRL** (2009).

# CTRW

- Renewal type of Random walk on lattice.
- Jumps to nearest neighbors only.
- $q_x$ $(1 - q_x)$ Prob. of jumping from $x$ to $x - 1$ $(x + 1)$.
- waiting times are i.i.d r.v with pdf

$$\psi(t) \propto t^{-1-\alpha} \qquad 0 < \alpha < 1$$



# Time Averages

- Occupation fraction

$$\overline{p}_x = \frac{t_x}{t}.$$

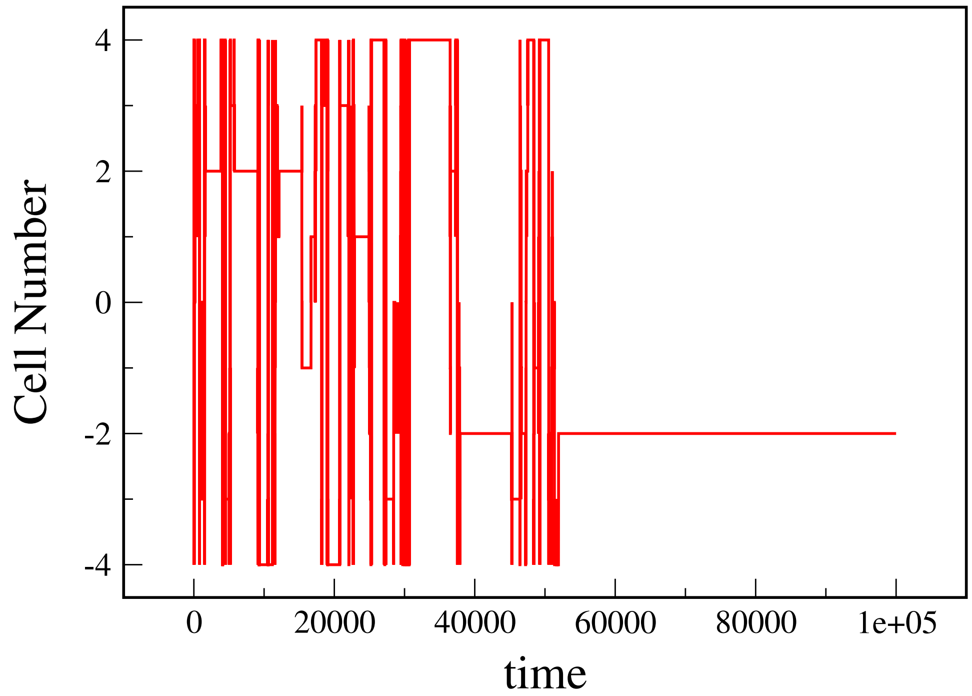
- Time average:

$$\overline{\mathcal{O}} = \sum_{x=-L,L} \mathcal{O}_x \overline{p}_x$$

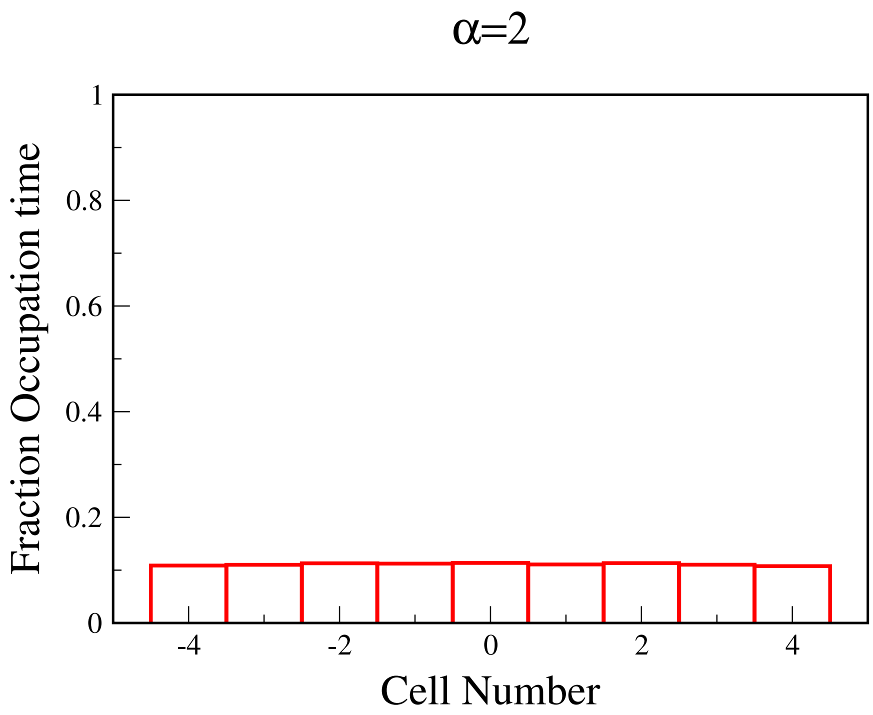
- For example

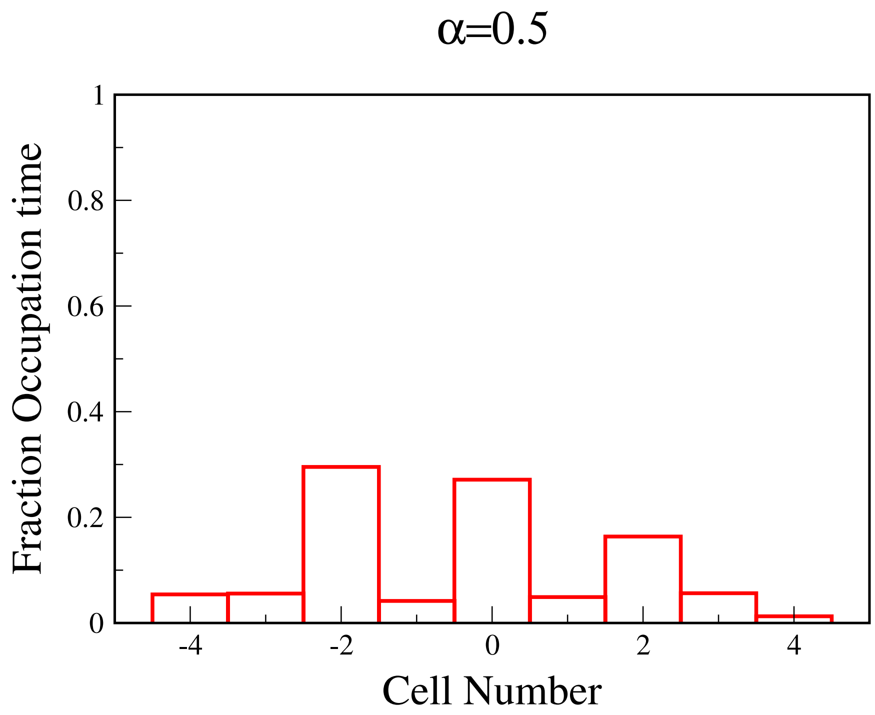
$$\overline{X} = \sum_{x=-L}^{L} x \overline{p}_x.$$

# Trajectory Unbiased RW $q = 1/2$ $\alpha = 1/2$



# Ergodic vs Non-ergodic Phases



# Population Dynamics in Step Number

$$P_x\left(n+1\right) = q_{x+1} P_{x+1}\left(n\right) + \left(1 - q_{x-1}\right) P_{x-1}\left(n\right).$$

When $n \to \infty$, an equilibrium is obtained $P_x^{eq}(n+1) = P_x^{eq}(n)$

# Levy Statistics

- $n_x$ number of times particle visits site $x$.
- When $n \to \infty$ $n_x/n = P_x^{eq}$
- $t_x$ total time spent in state $x$. Sum i.i.d r.v. whose mean is infinite.
- Apply Lévy's limit theorem

$$f\left(t_x\right) = l_{\alpha, A_\alpha P_x^{eq} n}\left(t_x\right).$$

- Use

$$\overline{p}_x = \frac{t_x}{\sum_{x=-L}^{L} t_x}$$

# The PDF of TIME AVERAGES

Using $\overline{\mathcal{O}} = \sum_x \overline{p}_x \mathcal{O}_x$

$$f_\alpha\left(\overline{\mathcal{O}}\right) = -\frac{1}{\pi} \lim_{\epsilon \to 0} \mathrm{Im} \frac{\sum_{x=1}^{L} P_x^{eq} \left(\overline{\mathcal{O}} - \mathcal{O}_x + i\epsilon\right)^{\alpha - 1}}{\sum_{x=1}^{L} P_x^{eq} \left(\overline{\mathcal{O}} - \mathcal{O}_x + i\epsilon\right)^{\alpha}}.$$

Ergodicity if $\alpha \to 1$

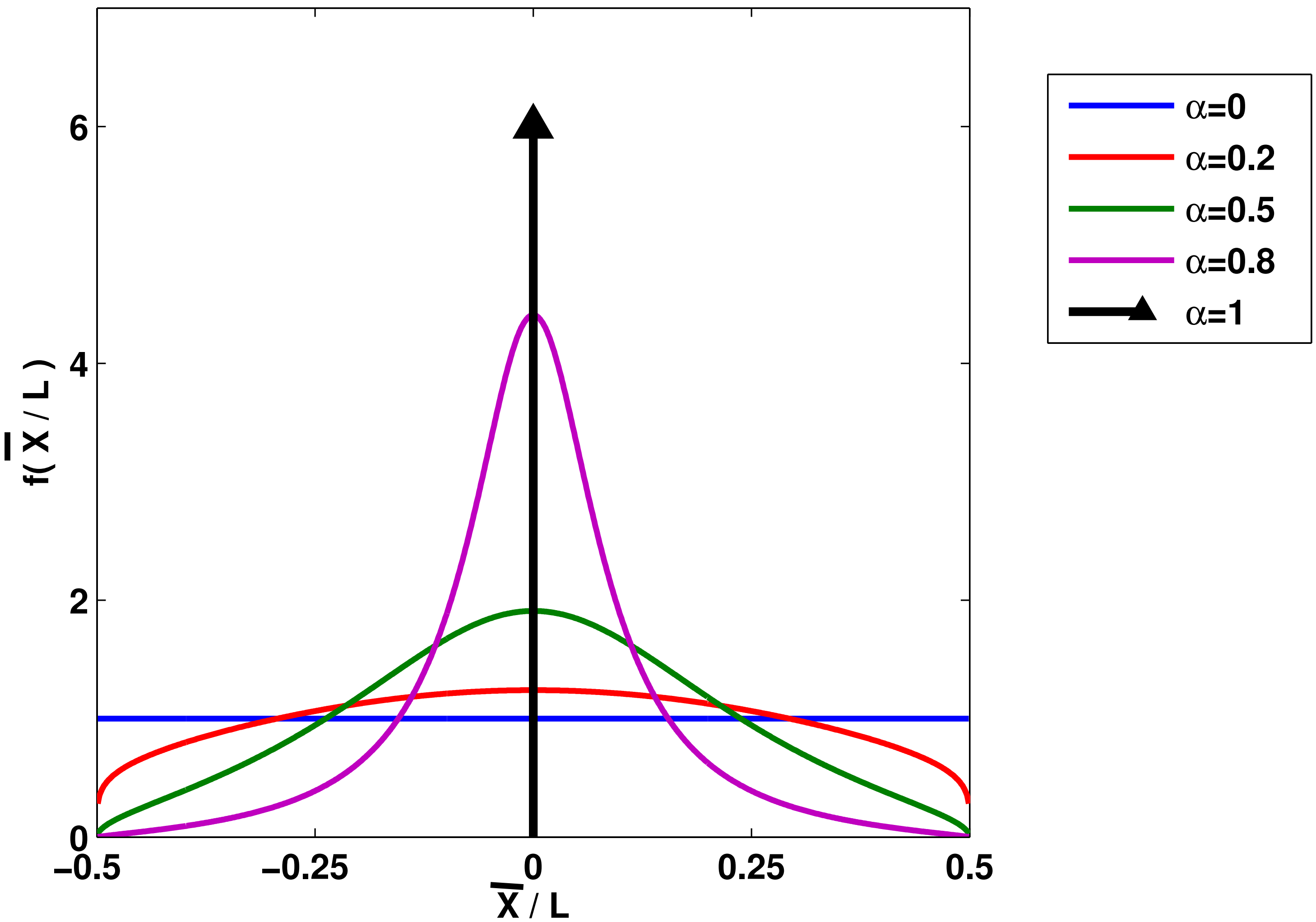
$$f_{\alpha=1}\left(\overline{\mathcal{O}}\right) = \delta\left(\overline{\mathcal{O}} - \langle \mathcal{O} \rangle\right).$$

Localization when $\alpha \to 0$

$$\lim_{\alpha \to 0} f_\alpha\left(\overline{\mathcal{O}}\right) = \sum_{x=1}^{L} P_x^{eq} \delta\left(\overline{\mathcal{O}} - \mathcal{O}_x\right).$$

Rebenshtok, Barkai **PRL 99 210601 (2007)**

# PDF of $\overline{X}$ UNBIASED CTRW



# Directions

Blinking QDs Margolin, Kuno.

$1/f$ noise Kantz, Niemann, Krapf, Leibovich.

Deterministic models, relation with weak chaos Bel, Korabel, Akimoto.

Disordered systems Burov.

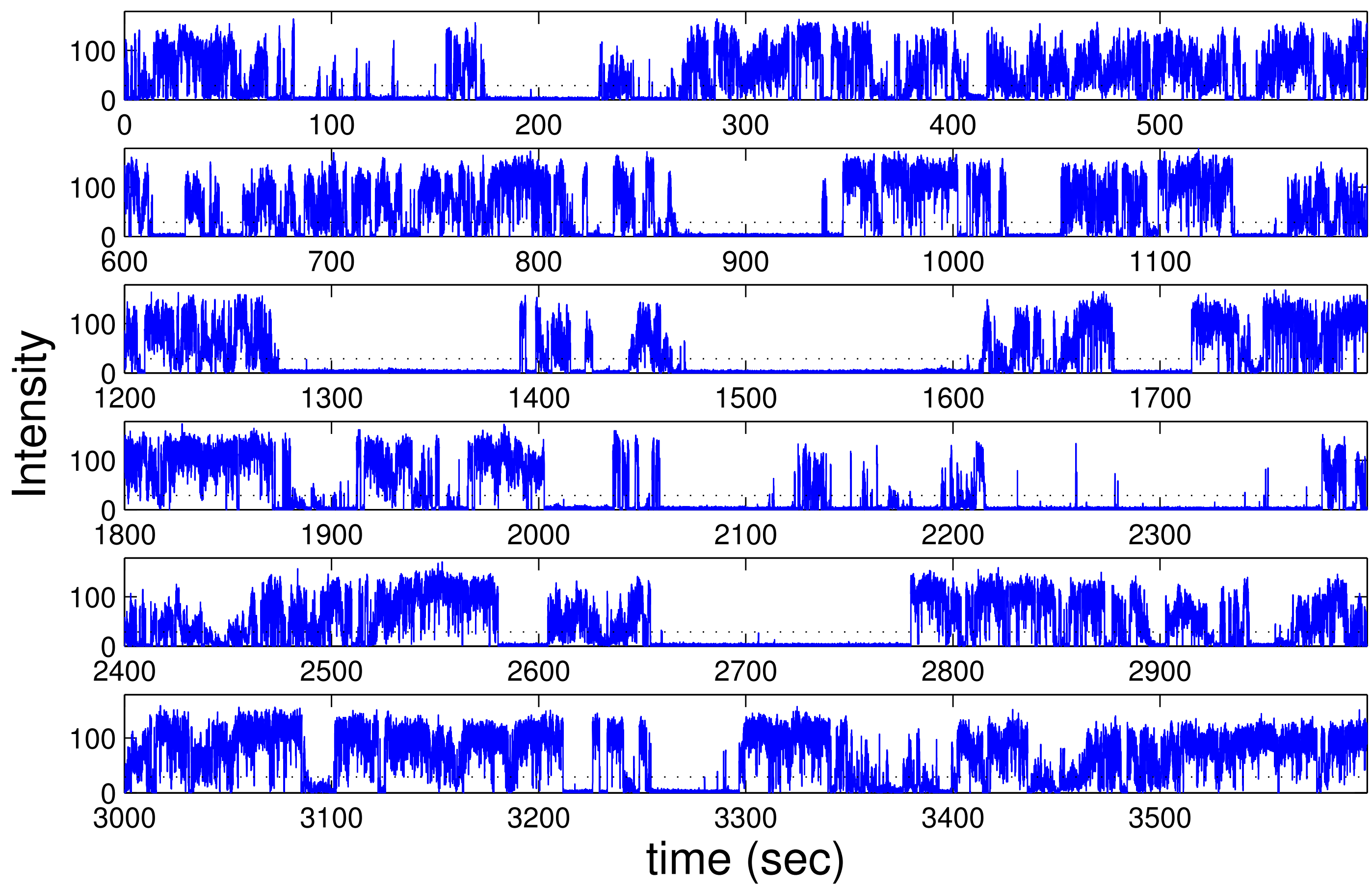
Distribution of Diffusion and Transport Coefficients Burov, Metzler.

fBM Deng Lévy walks CTRW Bel, Rebenshtok.

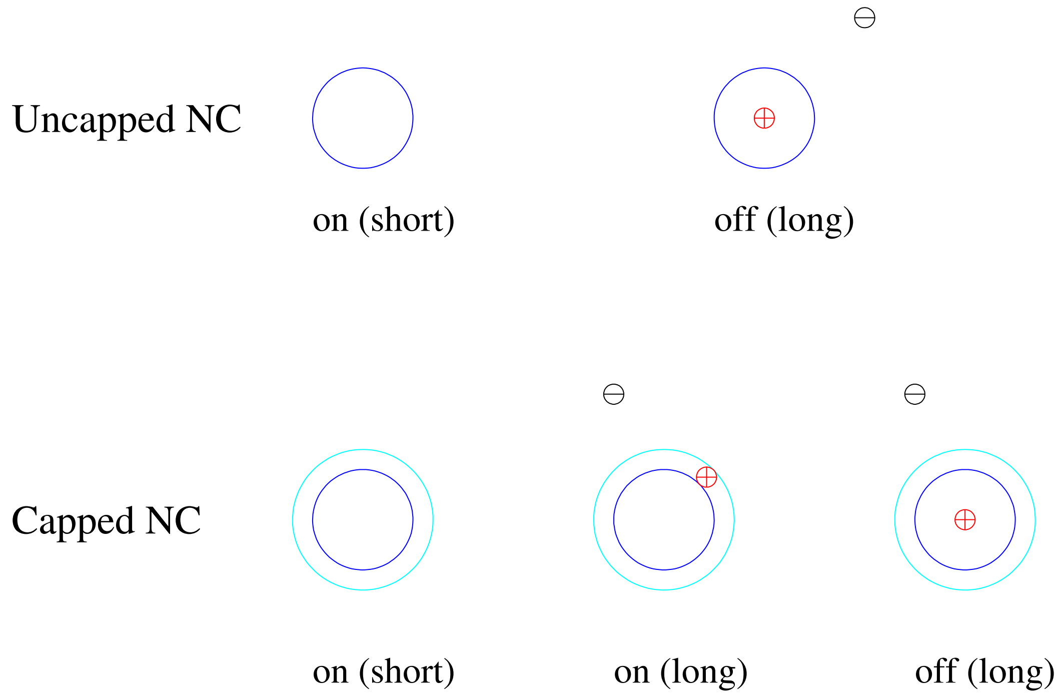
Fractional Feynman-Kac functionals Turgeman, Carmi.

Aging correlation functions Margolin, Leibovich.

Infinite Ergodic theory Korabel, Akimoto, Hanggi.


Intensity
100
0
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100
2200
2300
2400
2500
2600
2700
2800
2900
3000
3100
3200
3300
3400
3500
time (sec)

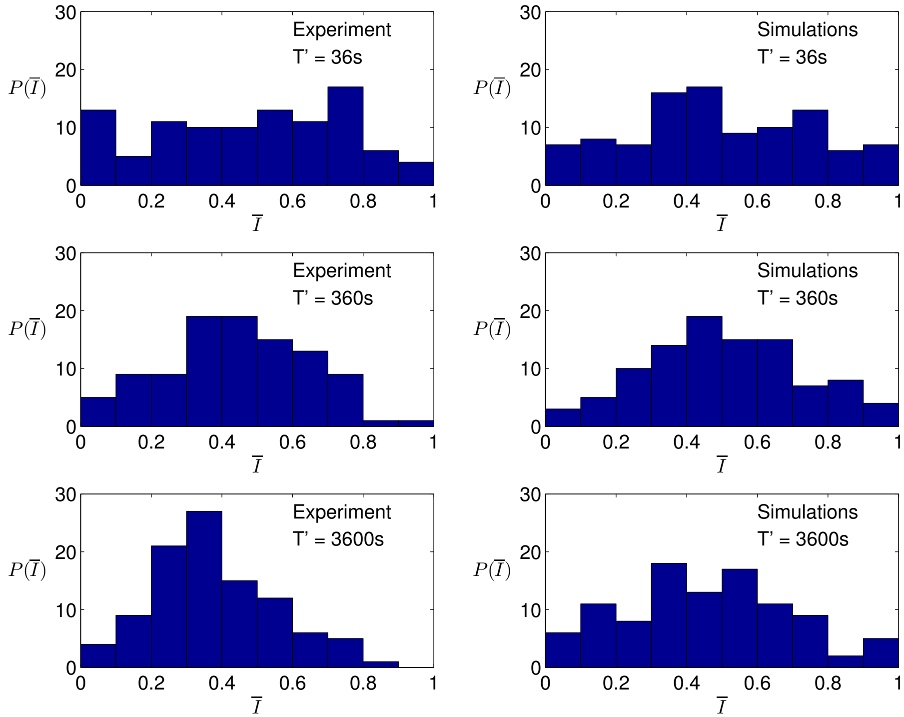
| Group | Material | Nu. | Radii | $T$ | $\alpha_{on}$ | $\alpha_{off}$ |
|---|---|---|---|---|---|---|
| Dahan | CdSe-ZnS | $215$ | $1.8$nm | $300$ K | $0.58(0.17)$ | $0.48(0.15)$ |
| Orrit | CdS | | $2.85$ | $1.2$ | EXP | $0.65(0.2)$ |
| Bawendi | CdTe.... | $200$ | $1.5$ | $10-300$ | $0.5(0.1)$ | $0.5(0.1)$ |
| Kuno | CdSe-ZnS | $300$ | $2.7$ | $300$ | $0.8-1.0$ | $0.5$ |
| Cichos | Si | | | $300$ | $0.8-1.0$ | $0.5$ |
| Ha | CdSe(coat) | | | $300$ | Exp? | $1$ |




Efros, Orrit, Onsager, Hong-Noolandi

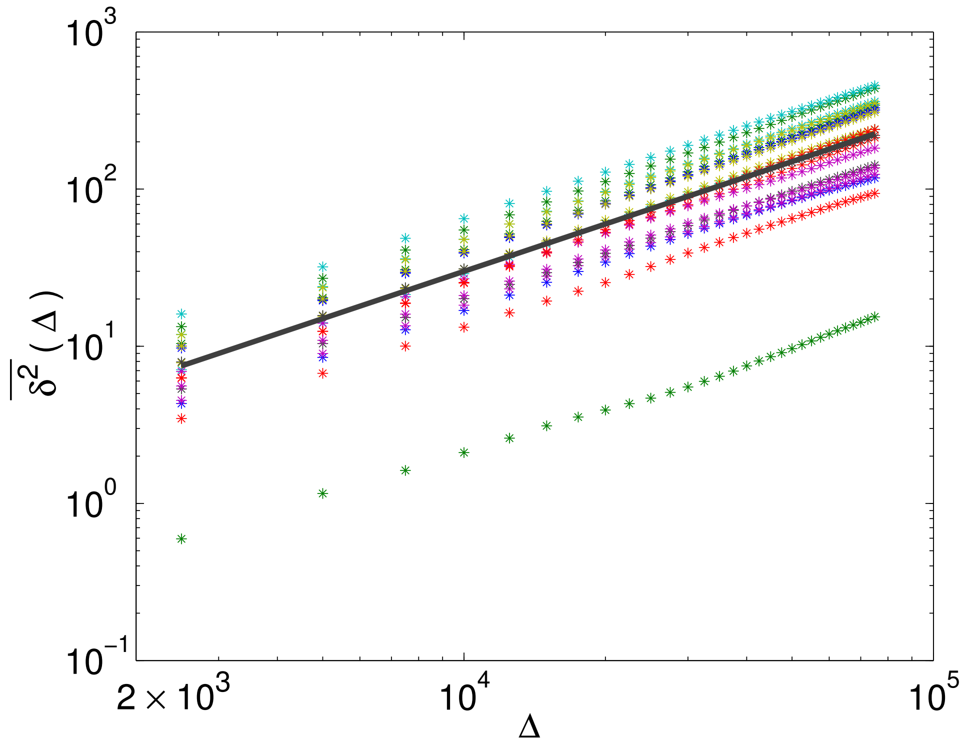
$$r_{Ons} = \frac{e^2}{k_b T \epsilon} \simeq 7\text{nm} \quad (1)$$

# Distribution of time averaged intensity $\overline{\mathcal{I}}$




CdSe-ZnS NC. Margolin, Kuno, Barkai (2006)

# Random Time-Scale Invariant Diffusion Constant




$$\overline{\delta^2}\,(\Delta, t) = \frac{\int_0^{t-\Delta} \left[x(t'+\Delta) - x(t')\right]^2 dt'}{t-\Delta}$$

He Burov Metzler EB PRL (2008)

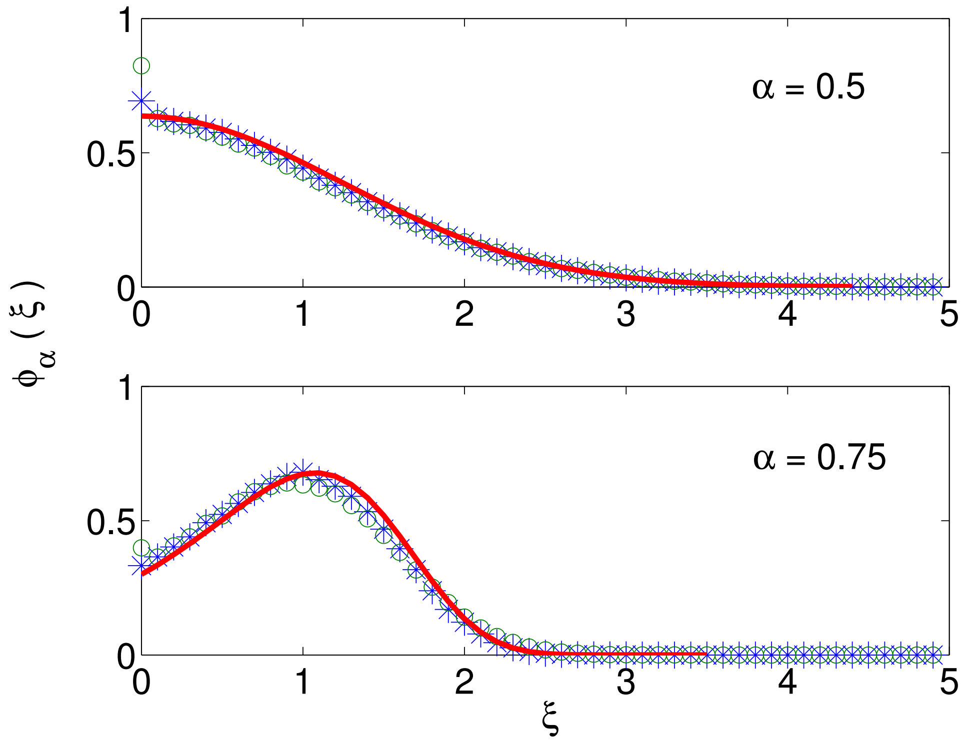
# Anomalous Seems Normal

$$\langle \overline{\delta^2} \rangle \sim \frac{2D_\alpha}{\Gamma(1+\alpha)} \frac{\Delta}{t^{1-\alpha}}$$

- A taste for this: if $\alpha = 1$ $\langle \overline{\delta^2} \rangle = 2D\Delta$.
  For anomalous diffusion $D(t) \sim d\langle x^2 \rangle / dt \sim t^{\alpha-1}$.
- We see aging effect $\langle \overline{\delta^2} \rangle$ decreases when measurement time increases.
- Anomalous diffusion seems normal $\langle \overline{\delta^2} \rangle \sim \Delta$.
- For closed system different behavior $\langle \overline{\delta^2} \rangle \sim \Delta^{1-\alpha}$ where $\Delta < t$.
- Burov, metzler, Barkai PNAS (2010)

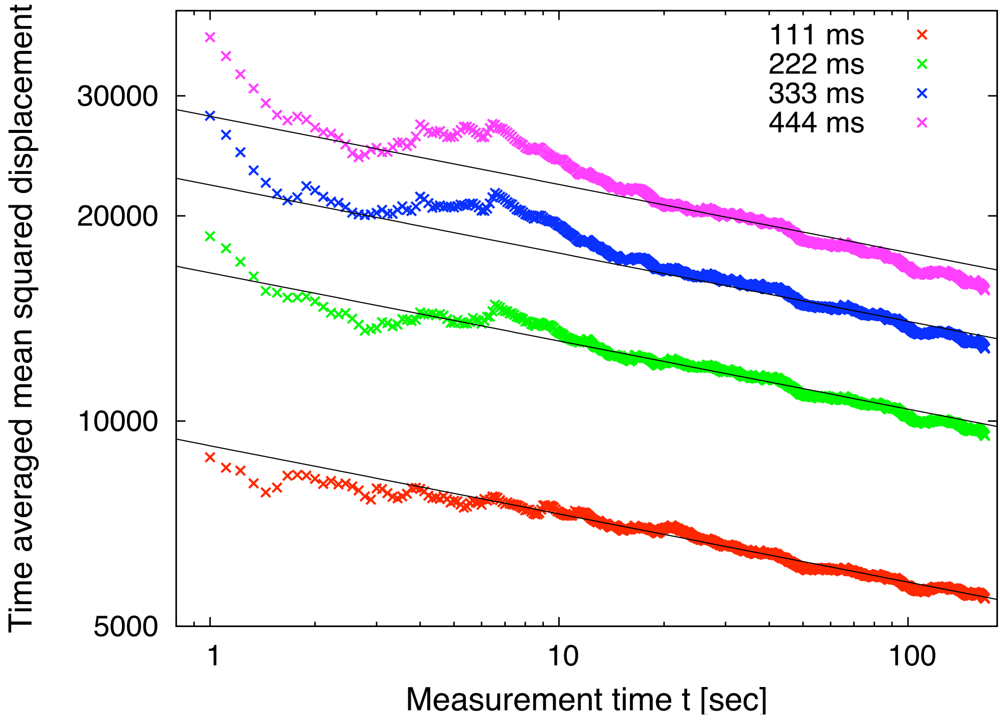
- $\overline{\delta^2} \sim N$. [Hint $[x(t'+\Delta) - x(t')]^2 = 0$ when particle is trapped].

- $\xi = \overline{\delta^2} / \langle \overline{\delta^2} \rangle$



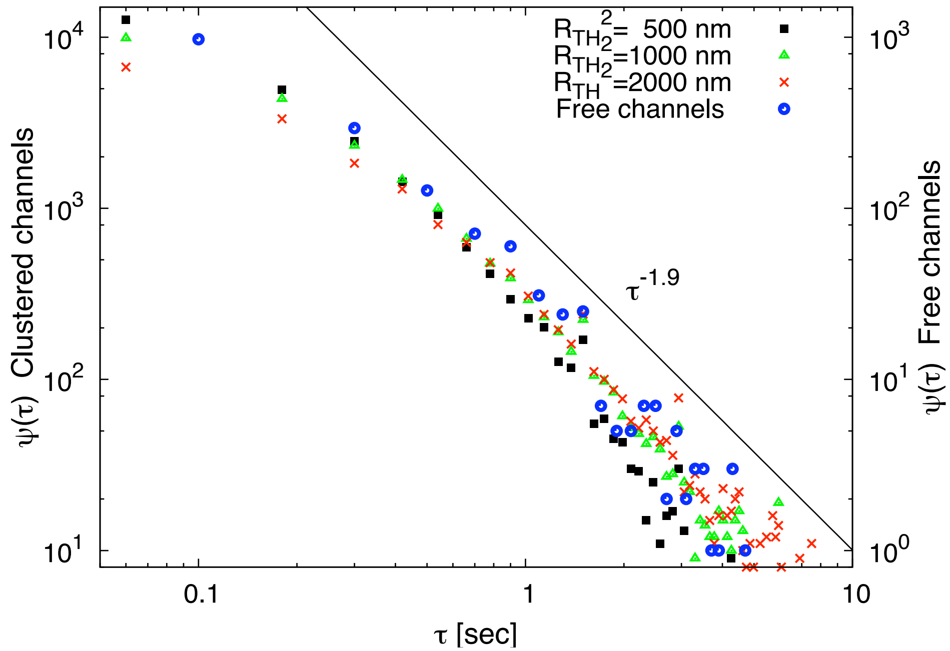

$$\lim_{t\to\infty} \phi_\alpha(\xi) = \frac{\Gamma^{1/\alpha}(1+\alpha)}{\alpha \xi^{1+1/\alpha}} l_\alpha \left[ \frac{\Gamma^{1/\alpha}(1+\alpha)}{\xi^{1/\alpha}} \right].$$

# Aging effect (Diego Krapf's experiment)




- The older you get the slower you are.
- Channel protein molecules on a membrane.
- Weigel · · · Krapf PNAS 2011

# Waiting time distribution (Krapf)




Power law waiting times lead to aging and weak ergodicity breaking
Barkai, Garini and Metzler **Physics Today** Aug. (2012).

| Boltzmann--Gibbs | WEB |
|---|---|
| normal diffusion | anomalous diffusion $\langle r^2 \rangle \sim t^\alpha$ |
| Gaussian | Lévy |
| $f_1\left(\overline{\mathcal{O}}\right) = \delta\left[\overline{\mathcal{O}} - \langle \mathcal{O} \rangle\right]$ | $f_\alpha\left(\overline{\mathcal{O}}\right) = -\frac{1}{\pi}\lim_{\epsilon\to 0} \text{Im} \frac{\sum_{x=1}^{L} P_x^{eq}\left(\overline{\mathcal{O}} - \mathcal{O}_x + i\epsilon\right)^{\alpha-1}}{\sum_{x=1}^{L} P_x^{eq}\left(\overline{\mathcal{O}} - \mathcal{O}_x + i\epsilon\right)^{\alpha}}.$ |
| Chaos | $\lambda = 0$, Infinite Invariant Density |
| $\overline{\delta^2} = \langle x^2 \rangle$ | Transport Coefficients Random |
| | |

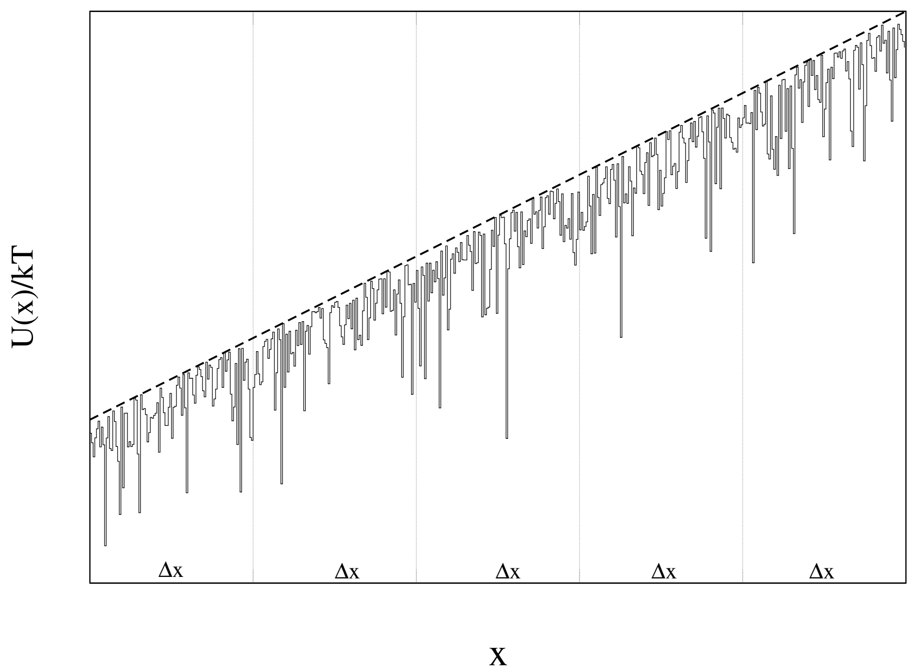
# Reviews

- Stefani, Hoogenboom, and Barkai *Beyond Quantum Jumps: Blinking Nano-scale Light Emitters* **Physics Today 62** nu. 2, p. 34 (February 2009).

- E. Barkai, Y. Garini and R. Metzler *Strange Kinetics of Single Molecules in the Cell* **Physics Today** 65(8), 29 (2012).

- R. Metzler, J, H. Jeon, A. G. Cherstvy, and E. Barkai *Anomalous diffusion models and their properties: non-stationarity, non-ergodicity and ageing at the centenary of single particle tracking* Phys. Chem. Chem. Phys. **16** (44), 24128 - 24164 (2014).

# Quenched Trap Model (Burov EB)




$$\rho(E) = \frac{1}{T_g} \exp(-\frac{E}{T_g}).$$

$$U_x = U_x^{det} - E_x.$$

# Dynamics and Occupation Fraction

The dynamics are described by the master equation

$$\frac{d}{dt}P_x(t) = -\frac{1}{\tau_x}P_x(t) + \frac{1}{2\tau_{x+1}}P_{x+1}(t) + \frac{1}{2\tau_{x-1}}P_{x-1}(t)$$

$$\tau_i = \exp(\frac{E_x}{T}).$$

Since $E_i$ are exponentially distributed

$$\psi(\tau) = \frac{T}{T_g}\tau^{-1-\frac{T}{T_g}}$$

When $T/T_g < 1$ the model exhibits anomalous diffusion.

# Occupation Fraction for the Quenched Trap Model

The occupation fraction in a domain $x_1 < x < x_2$

$$\overline{p} = \frac{t_x}{t} \sim \frac{Z^{Obs}}{Z} = \frac{\sum_{x=x_1}^{x_2} \exp\left(-\frac{U_x^{det} - E_x}{T}\right)}{Z}$$

where $Z$ is the normalizing partition function.

For a single realization of disorder, and for a finite system, the occupation fraction is given by Boltzmann statistics.

The occupation fraction is a random variable since $\{E_x\}$ are random variables.

# $T_g < T$ is the effective temperature of the system.

Our main result for $T/T_g < 1$

$$f\left(\overline{p}\right) \sim \delta_{T/T_g}\left[\mathcal{R}_x\left(T_g\right), \overline{p}\right]$$

$$\mathcal{R}_x(T_g) = \frac{P_B(T_g)}{1 - P_B(T_g)}$$

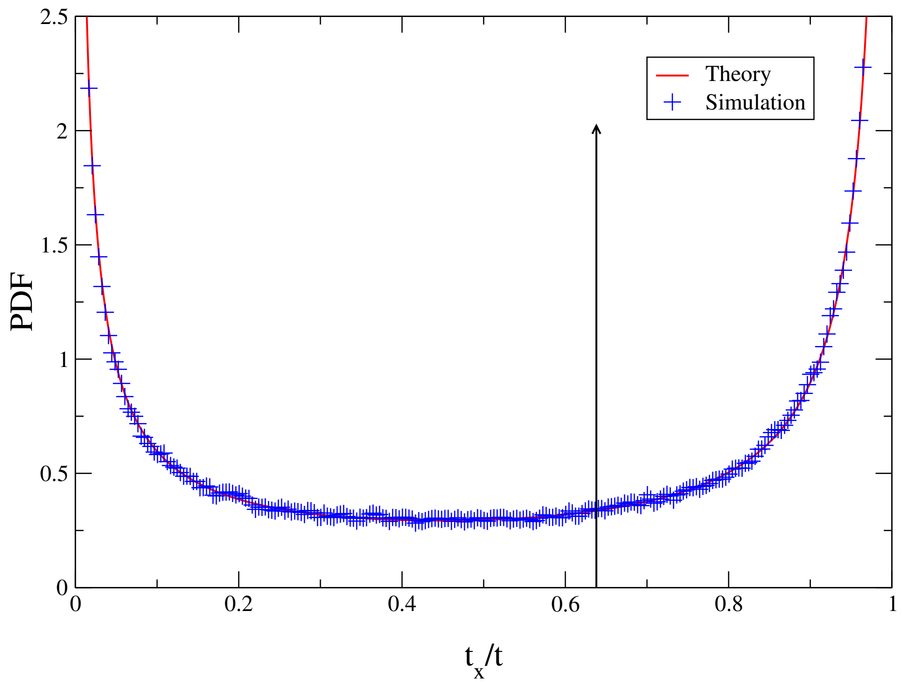
$$P_B(T_g) = \frac{\sum_{x=x_1}^{x_2} \exp\left(-\frac{U^{det}}{T_g}\right)}{Z}.$$

The temperature $T_g$ yield the statistical properties of the occupation fraction.

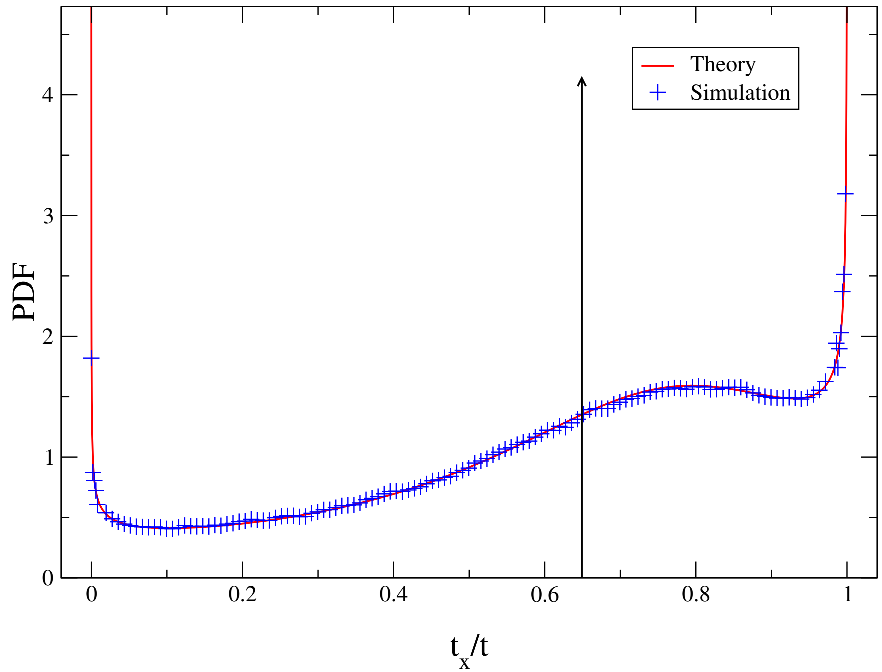
For $T > T_g$ standard Boltzmann Gibbs statistics is valid, even after averaging over disorder

$$f\left(\overline{p}\right) \sim \delta(\overline{p} - P_B).$$

# PDF of occupation fraction $\alpha = T/T_g = 0.3$

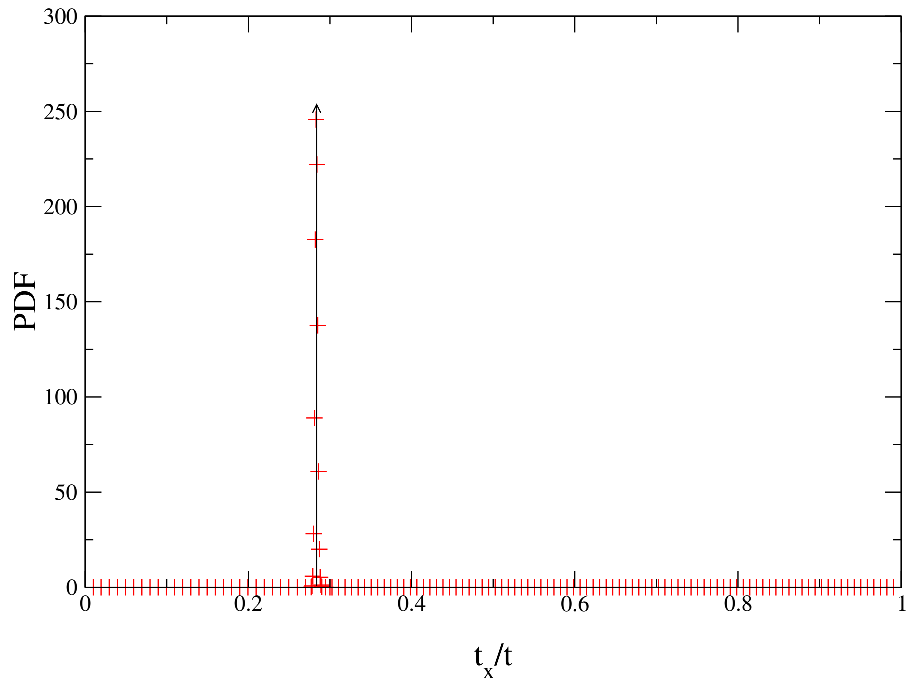


# PDF of occupation fraction $\alpha = T/T_g = 0.7$




$U(x) = x$, $T_g = 1$, observation domain $0 < x < 1$.

# PDF of occupation fraction $\alpha = T/T_g = 3$




$U(x) = x$, $T_g = 1$, observation domain $0 < x < 1$.

# Generality of Result for Quenched Disorder

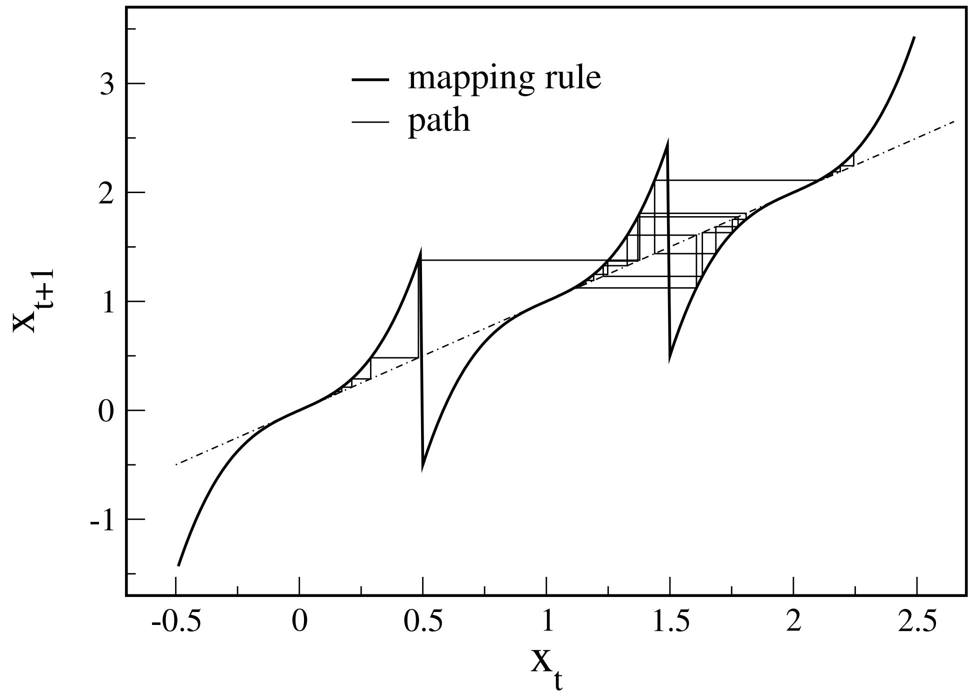
Quenched disorder: $\overline{p} = \frac{t_x}{t} \sim \frac{Z^{Obs}}{Z}$.

Weak Ergodicity Breaking: $\overline{p} = \frac{t_x}{t} = \frac{\sum_i \tau_i(x)}{t}$.

If $Z$ is Lévy distributed behavior similar to weak ergodicity is found.

Models of anomalous diffusion in disorder systems: $Z$ Lévy distributed.

# The Geisel Map




In a unit cell

$$x_{t+1} = x_t + a x^z, \qquad 0 < x < 0.5$$

# CTRW Dynamics

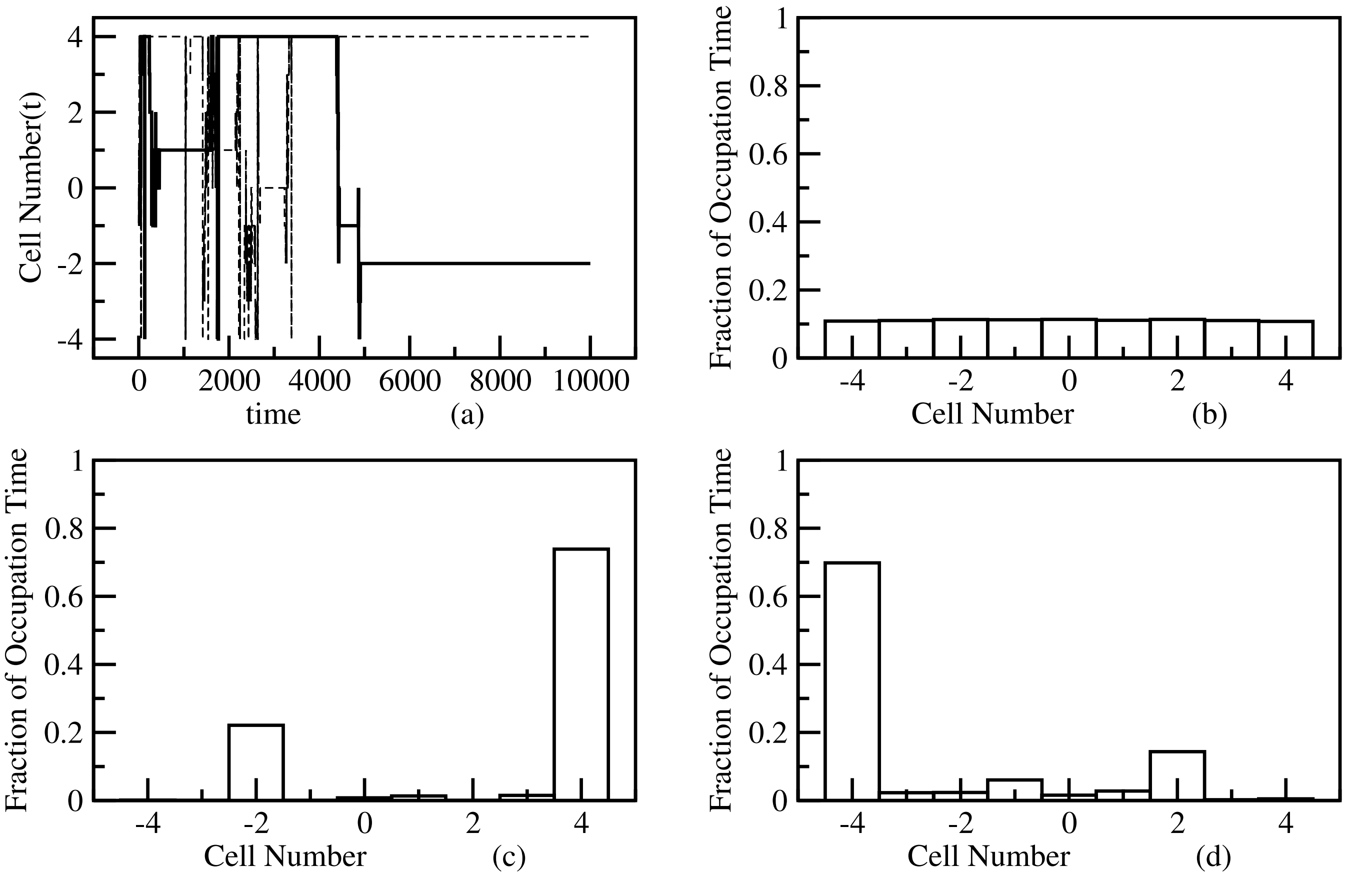
In vicinity of fixed point

$$\frac{dx}{dt} = ax^z$$

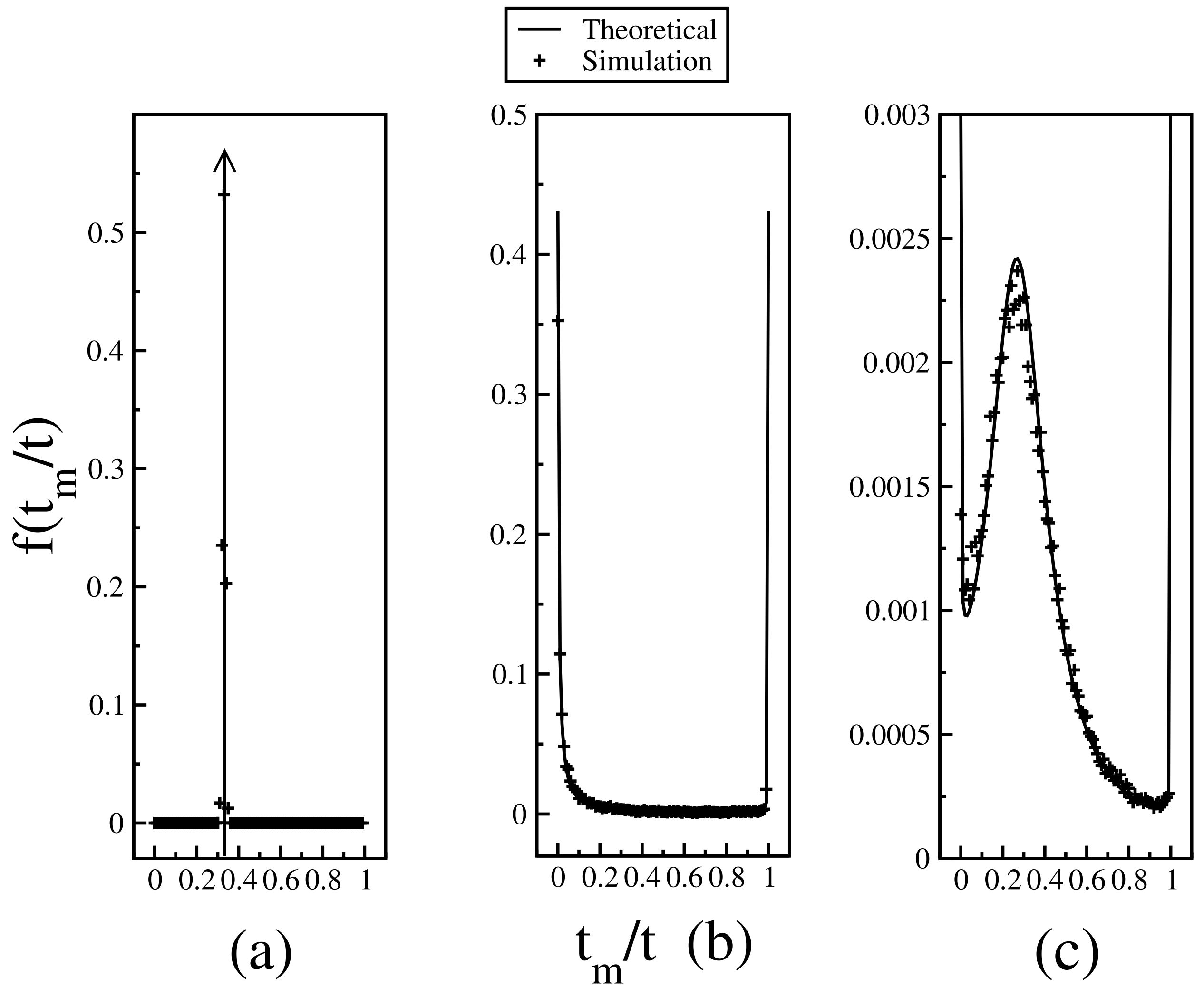
Smooth injection of trajectories

$$\psi(t) \propto t^{-(1+\alpha)}, \qquad \alpha = \frac{1}{z-1}.$$

# Random Occupation Times

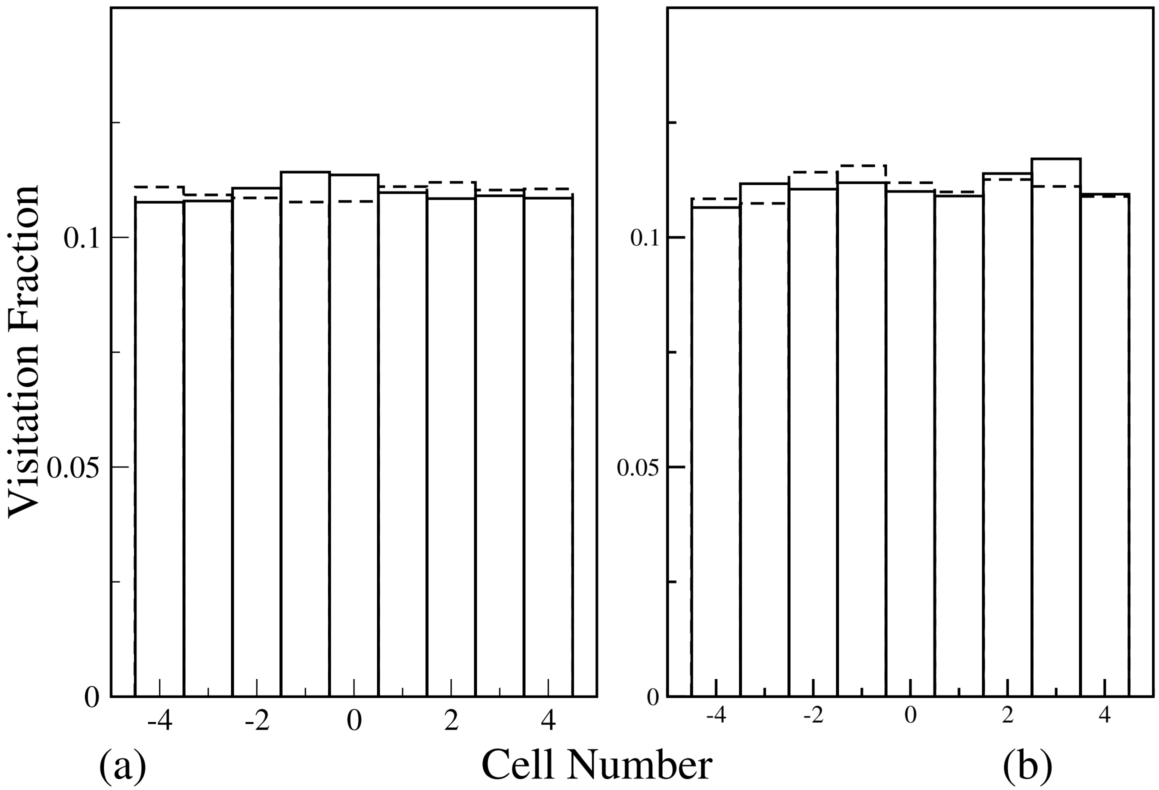


# Occupation Time Statistics




Bel, Barkai **Europhysics Letters 74** 15 (2006).

# Visitation Fraction




Visitation fraction is uniform, in and out of the ergodic phase, hence weak ergodicity breaking.

# Intermittency, Zero Lyapunov Exponent

Pesin identity $\lambda = h_{ks}$.

Intermittent dynamics: zero Lyapunov exponent $\lambda = 0$.

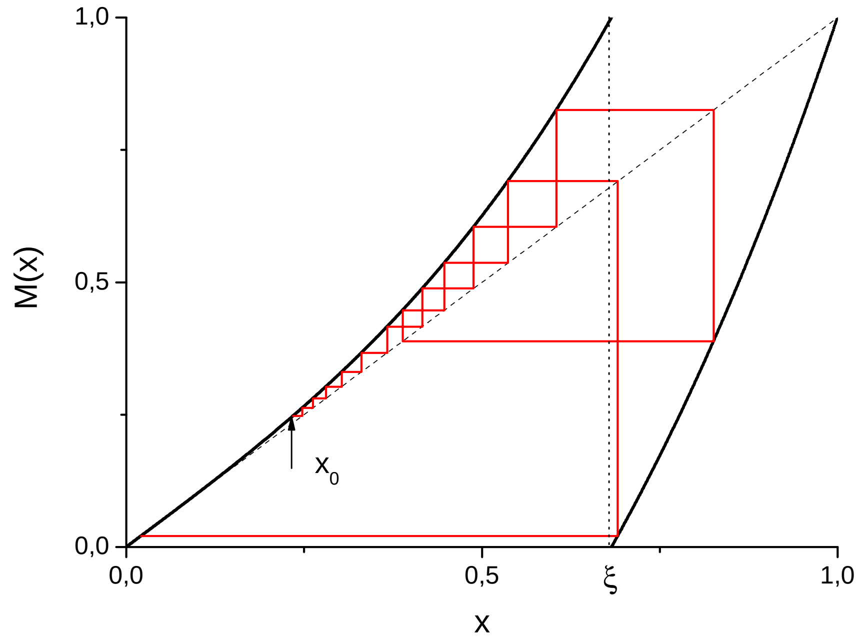
Stretched exponential separation of nearby trajectories:

$$\delta x = \delta x_0 \exp(\lambda_\alpha t^\alpha).$$

Our aim: Generalize Pesin Identity.

Take Away: Intermittency is related to Weak Ergodicity Breaking.

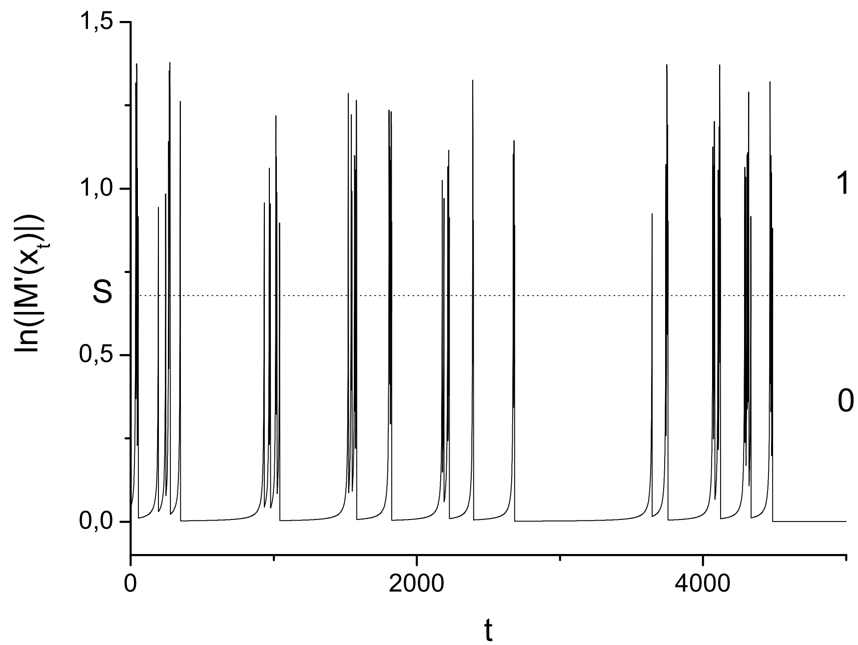
# Pomeau Manneville Map




$$x_{t+1} = M(x_t) \qquad\qquad M(x_t) \sim x_t + a(x_t)^z \qquad x_t \to 0$$

$$\lambda_\alpha = \frac{\sum_{t=0}^{t-1} \ln M'(x_t)}{t^\alpha}$$

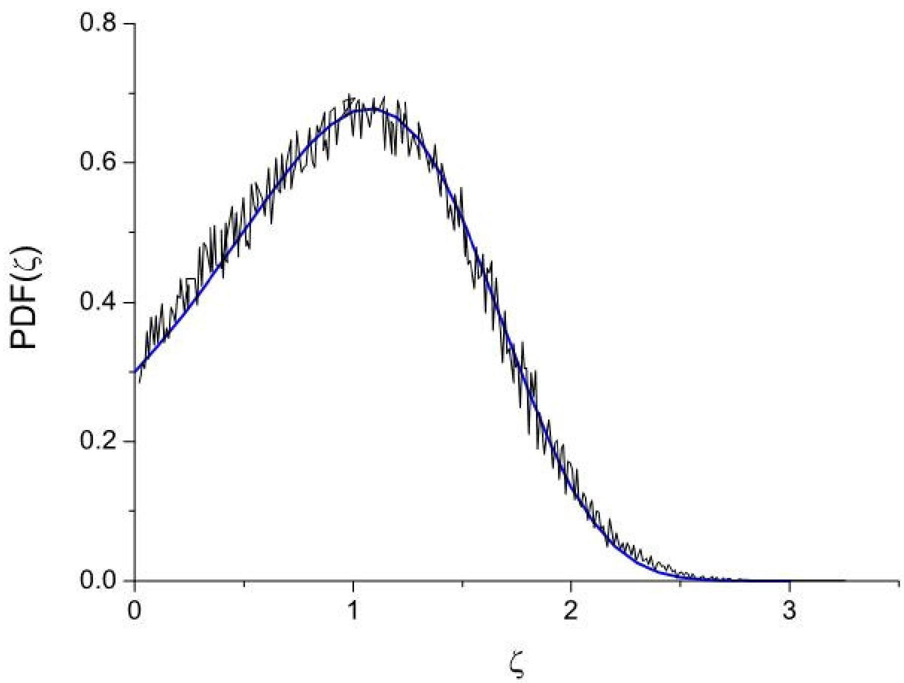
# Trajectory




$$\sum_{t=0}^{t-1} \ln M'(x_t) \propto t/\langle \tau \rangle \propto \frac{t}{\int^t t t^{-1-\alpha} dt} \propto t^{\alpha}$$

Distribution of number of renewals in $(0,t)$ yields distribution of $\lambda_\alpha$.

# Distribution of generalized Lyapunov Exp.

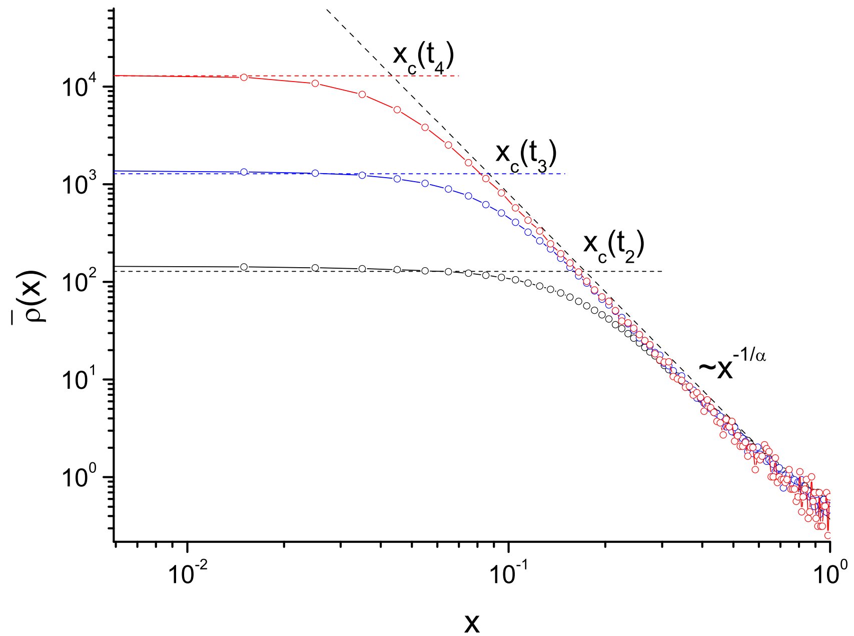



$\zeta = \lambda_\alpha / \langle \lambda_\alpha \rangle$

Renewal Theory: distribution of $\lambda_\alpha$ is Mittag-Leffler.

Korabel Barkai **Phys. Rev. Lett. 102**, 050601 (2009).

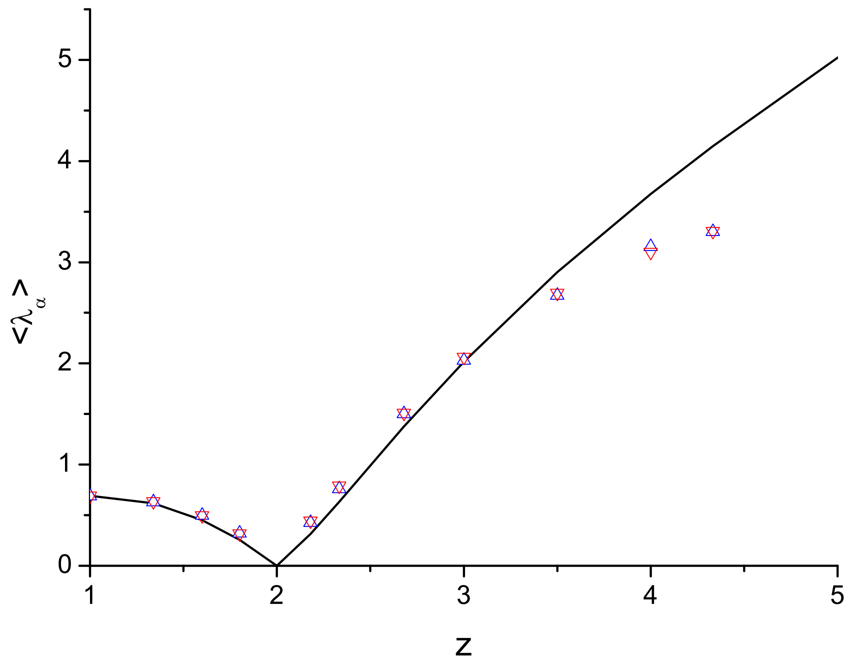
# Infinite Invariant Measure (Aaronson, Thaler, $\cdots$)




$$\bar{\rho}(x) = \frac{\rho(x,t)}{t^{\alpha-1}}$$

$\bar{\rho}(x) \propto x^{-1/\alpha}$ Non Normalizable.

# Generalized Lyapunov Exp.




$$\langle \lambda_\alpha \rangle = \int \ln |M'(x)| \bar{\rho}(x) dx$$

Even though $\bar{\rho}(x)$ non normalizable, it yields the average.

# Pesin Type of Identity

Krengel Entropy $h_\alpha$ is the Kolomogorov Sinai entropy of the first return map (Zweimüller, Thaler).

$s_t = 0$ left branch. $s_t = 1$ right branch.

$S = 00011110101 \cdots = (0)(00)(1)(11)(10)(101) \cdots$.

$n(t)$ number of words $(n(t) = 6)$.

$h_\alpha = \langle \frac{n \log_2 n}{t^\alpha} \rangle$

$$h_\alpha = \alpha \langle \lambda_\alpha \rangle.$$

A link between separation of trajectories and entropy.

| Boltzmann--Gibbs | WEB |
|---|---|
| normal diffusion | anomalous diffusion $\langle r^2 \rangle \sim t^\alpha$ |
| Gaussian | Lévy -- Lamperti |
| $f_1\left(\overline{\mathcal{O}}\right) = \delta\left[\overline{\mathcal{O}} - \langle \mathcal{O} \rangle\right]$ | $f_\alpha\left(\overline{\mathcal{O}}\right) = -\frac{1}{\pi}\lim_{\epsilon\to 0} \text{Im} \frac{\sum_{x=1}^{L} P_x^{eq}\left(\overline{\mathcal{O}} - \mathcal{O}_x + i\epsilon\right)^{\alpha-1}}{\sum_{x=1}^{L} P_x^{eq}\left(\overline{\mathcal{O}} - \mathcal{O}_x + i\epsilon\right)^{\alpha}}.$ |
| Chaos | $\lambda = 0$, Infinite Invariant Density |
| $\overline{\delta^2} = \langle x^2 \rangle$ | Transport Coefficients Random |
| | |

# Refs. and THANKS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