Weak Ergodicity Breaking

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A. Rebenshtok, G. Margolin, S. Burov, G. Bel, Y. He

PRL (2008) (with R. Metzler)
PRL 99 208302 (2007)
PRL 98 250601 (2007)
JSP 123 883 (2006)
PRL 94, 080601 (2005)
PRL 94, 240602 (2005)
• Blinking Quantum Dots, Sub-Diffusion in Polymer Networks and of mRNA in the cell.

• Anomalous Diffusion, power law waiting times

• Distribution of Time Averages for Weak Ergodicity Breaking (Bouchaud).

• Possible generalization of Boltzmann--Gibbs statistics.
Main Result: DISTRIBUTION of TIME AVERAGES

- Let $\mathcal{O}$ be a physical observable, and $\bar{\mathcal{O}}$ its time average,

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

- Weak Ergodicity Breaking is related to Anomalous Diffusion

$$\langle x^2 \rangle \sim t^\alpha \quad 0 < \alpha < 1.$$

- Ergodic case $\alpha = 1$

$$f_1 \left( \bar{\mathcal{O}} \right) = \delta \left( \bar{\mathcal{O}} - \langle \mathcal{O} \rangle \right).$$

Rebenshtok, Barkai PRL 99 210601 (2007)
Nano Crystals also called Quantum Dots


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Non-ergodic Intensity Correlation Functions


Averaged time in States On and Off is infinite.

If $I(t) < I_{\text{thresh}}$ process is in state off.

Power law waiting time $\psi(\tau) \propto \tau^{-(1+\alpha_{\text{off}})}$. 

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Power Law Sojourn Times Lead To Ergodicity Breaking and Non-Stationarity

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Continuous Time Random Walk (CTRW)

Average Waiting Time is $\infty$. Diffusion is anomalous $\langle r^2 \rangle \propto t^\alpha$.
Golding and Cox *PRL* (2006)

He Burov Metzler EB *PRL* (2008)
Einstein $D = \sigma^2/2\langle \tau \rangle$. 
If $\langle x^2 \rangle \sim t^\alpha$ then $D = 0$ and $\langle \tau \rangle = \infty$. 
Condition for ergodicity $t \gg \langle \tau \rangle$ is never met.

In single particle experiments the problem of ensemble averaging is removed.

Time averages are not identical to ensemble averages, when the average waiting time is infinite.

What theory replaces ergodic statistical mechanics for such systems?

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• **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

$$\psi(t) \propto t^{-1-\alpha} \quad 0 < \alpha < 1$$
Time Averages

- Occupation fraction
  \[ \bar{p}_x = \frac{t_x}{t}. \]

- Time average:
  \[ \bar{O} = \sum_{x=-L,L} O_x \bar{p}_x. \]

- For example
  \[ \bar{X} = \sum_{x=-L}^{L} x \bar{p}_x. \]
Trajectory Unbiased RW $q = 1/2 \; \alpha = 1/2$
Non-Ergodic Phase

$\alpha = 0.5$

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Prob. that a member of an ensemble occupies lattice point $x$ is $P_{x}^{eq}$.

For an ergodic process $\bar{p}_x = P_{x}^{eq}$.

$$\langle O \rangle = \sum P_{x}^{eq} O_x = \overline{O}$$

For $0 < \alpha < 1$ what is the pdf of $\overline{O}$?
\[ P_x(n + 1) = q_{x+1} P_{x+1} (n) + (1 - q_{x-1}) P_{x-1} (n). \]

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

\[ f(t_x) = l_{\alpha, A\alpha} P_x^{eq} n(t_x) \]

- Use

\[ \overline{P}_x = \frac{t_x}{\sum_{x=-L}^{L} t_x} \]
Multidimensional PDF of $\overline{p}_1, \cdots, \overline{p}_L$

$$P_L(\overline{p}_1, \cdots, \overline{p}_L) = \delta \left(1 - \sum_{x=1}^{L} \overline{p}_x\right) \int_0^\infty dy y^{L-1} \prod_{x=1}^{L} l_{\alpha, P_x^{eq}}(y \overline{p}_x)$$

Independent of $n$, details of $\psi(t)$.

Depends on $\alpha$ and $P_x^{eq}$.

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The PDF of TIME AVERAGES

Using \( \overline{O} = \sum_x P_x O_x \) and the multi-dimensional joint PDF

\[
f_\alpha (\overline{O}) = -\frac{1}{\pi} \lim_{\epsilon \to 0} \text{Im} \frac{\sum_{x=1}^{L} P^e_x (\overline{O} - O_x + i\epsilon)^{\alpha-1}}{\sum_{x=1}^{L} P^e_x (\overline{O} - O_x + i\epsilon)^\alpha}.
\]

**Ergodicity if** \( \alpha \to 1 \)

\[
f_{\alpha=1} (\overline{O}) = \delta (\overline{O} - \langle O \rangle).
\]

**Localization when** \( \alpha \to 0 \)

\[
\lim_{\alpha \to 0} f_\alpha (\overline{O}) = \sum_{x=1}^{L} P^e_x \delta (\overline{O} - O_x).
\]

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PDF of $\bar{X}$ BIASED CTRW

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Directions

Blinking QDs.

Stochastic Models: CTRW, fractional Fokker-Planck equations.

Deterministic models, relation with weak chaos.

Random systems.

Distribution of Diffusion and Transport Coefficients.

Transition from single particle to the ensemble.
Blinking Nano Crystals

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<table>
<thead>
<tr>
<th>Group</th>
<th>Material</th>
<th>Nu.</th>
<th>Radii</th>
<th>$T$</th>
<th>$\alpha_{on}$</th>
<th>$\alpha_{off}$</th>
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<tbody>
<tr>
<td>Dahan</td>
<td>CdSe-ZnS</td>
<td>215</td>
<td>1.8nm</td>
<td>300 K</td>
<td>0.58(0.17)</td>
<td>0.48(0.15)</td>
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<td>Orrit</td>
<td>CdS</td>
<td>2.85</td>
<td>1.2</td>
<td>EXP</td>
<td></td>
<td>0.65(0.2)</td>
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<tr>
<td>Bawendi</td>
<td>CdTe...</td>
<td>200</td>
<td>1.5</td>
<td>10 – 300</td>
<td>0.5(1.0)</td>
<td>0.5(1.0)</td>
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<tr>
<td>Kuno</td>
<td>CdSe-ZnS</td>
<td>300</td>
<td>2.7</td>
<td>300</td>
<td>0.8 – 1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Cichos</td>
<td>Si</td>
<td></td>
<td></td>
<td>300</td>
<td>0.8 – 1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Ha</td>
<td>CdSe(coat)</td>
<td></td>
<td></td>
<td>300</td>
<td>Exp?</td>
<td>1</td>
</tr>
</tbody>
</table>
Efros, Orrit, Onsager, Hong-Noolandi

\[ r_{Ons} = \frac{e^2}{k_b T \epsilon} \simeq 7 \text{nm} \]  (1)
Distribution of time averaged intensity $\overline{I}$

A particle undergoing a random walk in a random energy landscape in one dimension.

Traps on a lattice have a depth $-E_x \ x = 0, \ldots, L$.

$\{E_x\}$ are IID random variables whose PDF is

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

In addition a deterministic potential field $U_x^{det}$ is acting on the particle. The total potential energy

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

The system temperature is $T$. It is responsible for the activation of the particle from one trap to the other.

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Dynamics and Occupation Fraction

The dynamics are described by the master equation

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

\[
\tau_i = \exp\left(\frac{E_x}{T}\right).
\]

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.

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

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

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.
Our main result valid in a continuum limit, for \( T/T_g < 1 \)

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

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

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

The deterministic part of the Hamiltonian and 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

\[
    f (\bar{p}) \sim \delta (\bar{p} - P_B).
\]
PDF of occupation fraction $\alpha = T/T_g = 3$

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

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

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

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PDF of occupation fraction $\alpha = T/T_g = 0.3$
The Averaged Occupation Fraction $U^{det}(x) = x$

![Graph showing the averaged occupation fraction as a function of $T/T_g$ with comparison between simulation and theory.](image-url)
Generality of Result for Quenched Disorder

\[ \bar{p} = \frac{t_x}{t} \sim \frac{Z^{Obs}}{Z} \]

If \( Z \) is Lévy distributed then WEB holds.

\( Z \) is Lévy distributed for models of anomalous diffusion in disordered systems.

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\[
\delta^2(\Delta, t) = \frac{\int_{0}^{t-\Delta} [x(t' + \Delta) - x(t')]^2 \, dt'}{t - \Delta}
\]

He Burov Metzler EB PRL (2008)
\[ \overline{\delta^2} \sim N \]

\[ \xi = \frac{\overline{\delta^2}}{\langle \overline{\delta^2} \rangle} \]

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

<table>
<thead>
<tr>
<th>Boltzmann--Gibbs</th>
<th>WEB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha = 1$</td>
<td>$\alpha &lt; 1$</td>
</tr>
<tr>
<td>normal diffusion</td>
<td>anomalous diffusion $\langle r^2 \rangle \sim t^{\alpha}$</td>
</tr>
<tr>
<td>Gaussian</td>
<td>Levy -- Lamperti</td>
</tr>
</tbody>
</table>

| $f_1 (\mathcal{O}) = \delta [\mathcal{O} - \langle \mathcal{O} \rangle]$ | $f_\alpha (\mathcal{O}) = -\frac{1}{\pi} \lim_{\epsilon \to 0} \text{Im} \sum_{x=1}^{L} P_{x}^{eq} (\mathcal{O} - \mathcal{O}_x + i\epsilon)^{\alpha-1} / \sum_{x=1}^{L} P_{x}^{eq} (\mathcal{O} - \mathcal{O}_x + i\epsilon)^{\alpha}$ |
| $\overline{\delta^2} = \langle x^2 \rangle$ | Transport Coefficients Random |

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