Thermodynamics of histories
an application to systems with glassy dynamics

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[6]Department of Chemistry, University of California

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Motivations

Boltzmann-Gibbs thermodynamics

$$P(\mathcal{C}) = \mathrm{e}^{-\beta H(\mathcal{C})}$$

Before reaching equilibrium

- transient regime
- “glassy” dynamics

Non-equilibrium phenomena

- systems with a current (of particles, energy)
- dissipative dynamics (granular media)

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$\longrightarrow$ Need for a dynamical description

Outline

1. Motivations
   - statics vs dynamics

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2. Models of glass formers
   - example
   - thermodynamics of histories
   - results
   - dynamical phase coexistence

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3. Perspective

Glasses

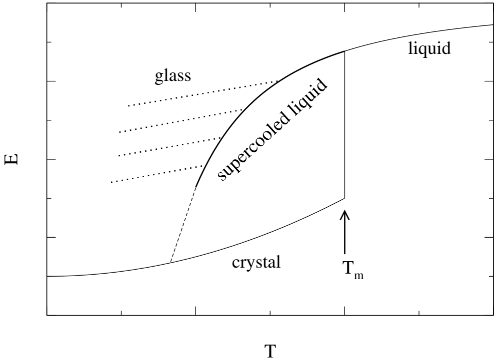
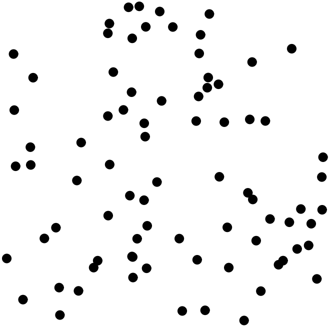


Fig.1 *in* Ritort and Sollich, *Adv. in Phys.* **52** 219 (2003)

From configurations to histories



fluctuations of configurations

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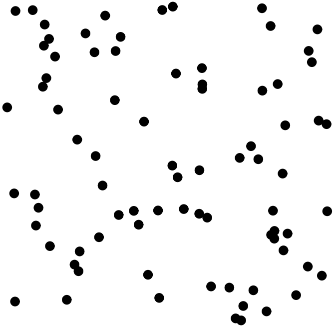

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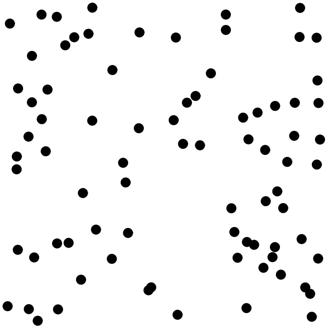

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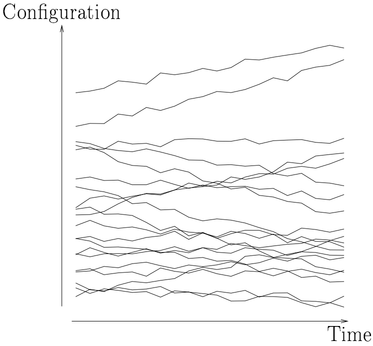

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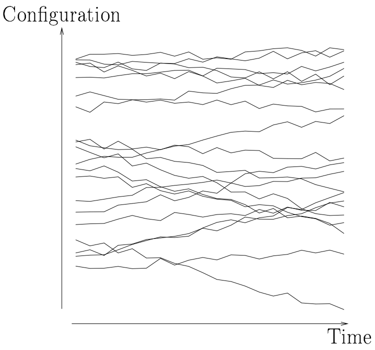

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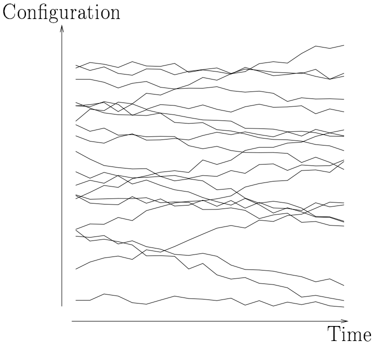

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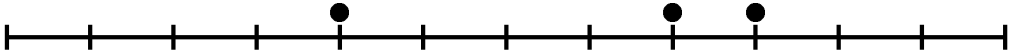
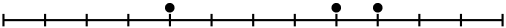


Independent particles

- L sites $\boldsymbol{n} = \{n_i\}$ with $\begin{cases} n_i = 0 & \text{inactive site} \\ n_i = 1 & \text{active site} \end{cases}$

Example



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  - activation with rate $W(0_i \to 1_i) = c$
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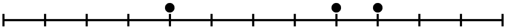

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Equilibrium distribution: $$P_{\text{eq}}(\boldsymbol{n}) = \prod_i c^{n_i}(1-c)^{1-n_i}$$

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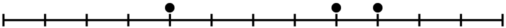

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Mean density of active sites: $$\langle n \rangle = \frac{1}{L}\sum_i \langle n_i \rangle = c$$

Kinetically constrained models (KCM)

Constrained dynamics: changes occur only around active sites.

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Fredrickson Andersen model in 1D

at least one neighbor of *i* must be active to allow *i* to change

inactivation:

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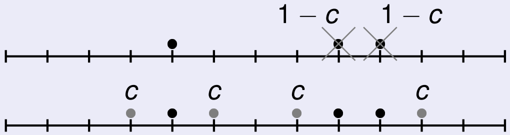

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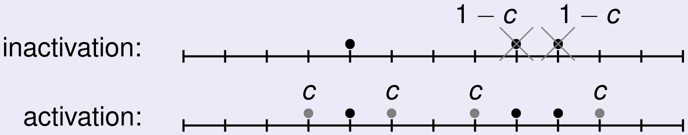

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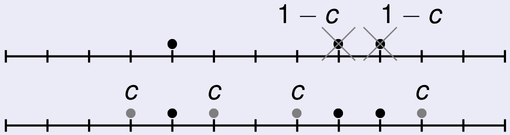

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Trajectories

$P_{\rm eq}(\boldsymbol{n})$ insufficient $\rightarrow$ analysis of histories

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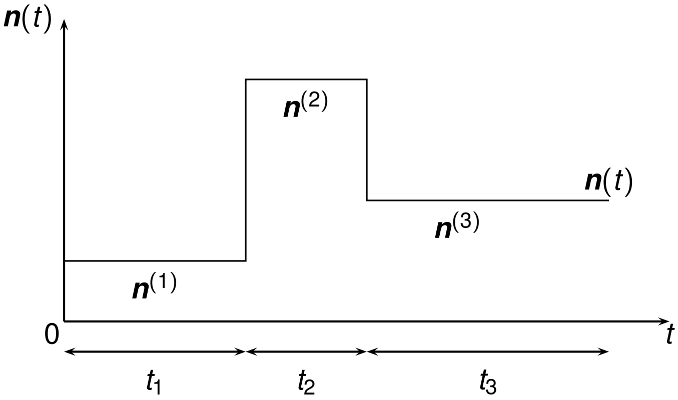

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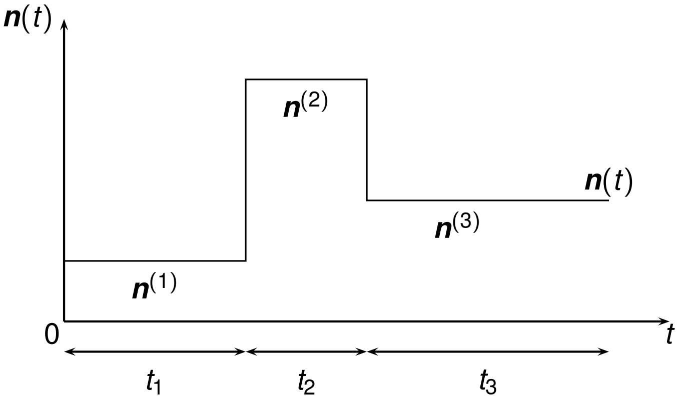

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Statistics over histories

Classification of histories according to a time extensive parameter

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$$\langle K \rangle = 2c^2(1-c)\,L\,t \qquad \text{(large } t\text{)}$$

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$\rho(K)$ gives information on non-typical histories

Dynamical partition function

Fluctuations (1): the micro-canonical way

- Thermodynamics of configurations

$$\Omega(E,L) = \left|\begin{array}{l}\text{number of configurations}\\ \text{with energy } E\end{array}\right. \qquad (\text{large } L)$$

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- Thermodynamics of histories [*à la* Ruelle]

$$\Omega_{dyn}(K, t) \; = \; \left| \begin{array}{l} \text{number of histories} \\ \text{with activity } K \text{ between 0 et } t \end{array} \right. \qquad \text{(grand } t\text{)}$$

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micro-canonical ensemble: technically painful

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Fluctuations (2): the canonical way

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(Dynamical) canonical ensemble

- β conjugated to energy
- s conjugated to activity K

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Fluctuations of K

$$\langle \mathrm{e}^{-sK} \rangle \sim \mathrm{e}^{-t\, L\, f_K(s)}$$

Dynamical free energy $f_K(s)$ $\leftrightarrow$ cumulant generating function of K.

s-state

s probes dynamical features

- average in the *s*-state of an observable $\mathcal{O}$:

$$\mathcal{O}(s) = \frac{\left\langle \mathcal{O}[\text{hist}]\, \mathrm{e}^{-sK} \right\rangle}{\left\langle \, \mathrm{e}^{-sK} \right\rangle}$$

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$s = 0$: equilibrium state
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2. Models of glass formers
   - example
   - thermodynamics of histories

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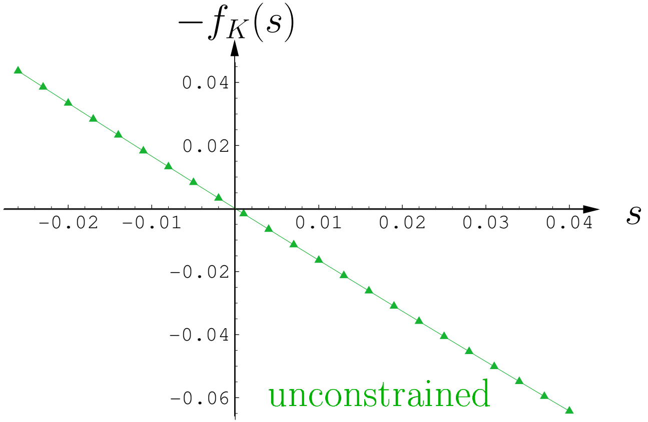
Dynamical phase transition: FA model (d=1)



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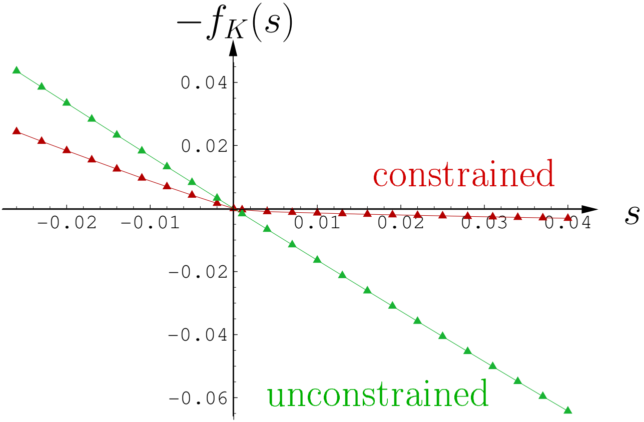

Comparison between constrained and unconstrained dynamics

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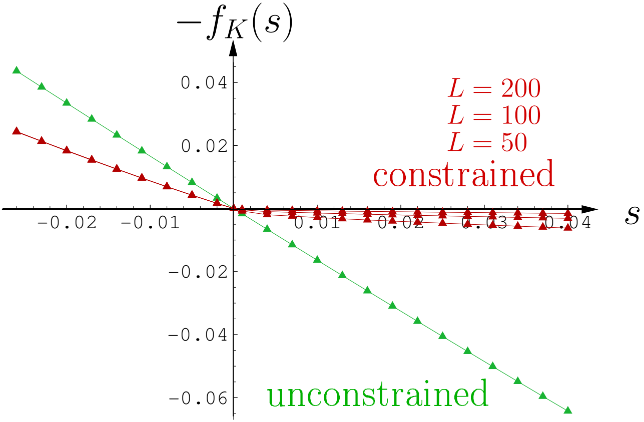

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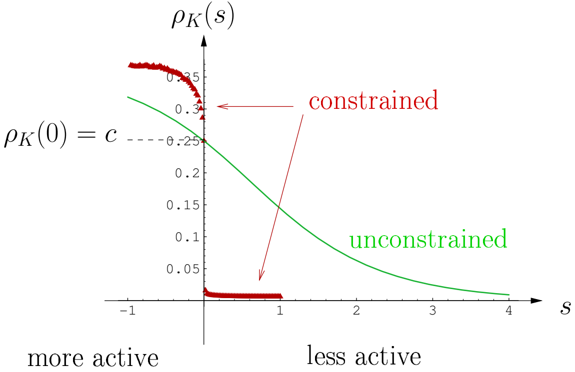

Comparison between constrained and unconstrained dynamics

Dynamical Landau free energy $\mathcal{F}(\rho, s)$

$$\left.\begin{array}{r}\text{Probability, in the } s\text{-state, to measure} \\ \text{a time-averaged density } \rho \text{ btw. 0 and } t\end{array}\right| \sim e^{-t\,L\,\mathcal{F}(\rho,s)}$$

Dynamical Landau free energy $\mathcal{F}(\rho, s)$

Probability, in the s-state, to measure
a time-averaged density ρ btw. 0 and t $\Big| \sim \mathrm{e}^{-t\,L\,\mathcal{F}(\rho,s)}$

$$\left\langle \mathrm{e}^{-sK} \delta\big(\langle n \rangle - L\rho\big) \right\rangle \Big| \sim \mathrm{e}^{-t\,L\,\mathcal{F}(\rho,s)}$$

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Extremalization procedure

$$f_K(s) = \min_{\rho} \mathcal{F}(\rho, s)$$

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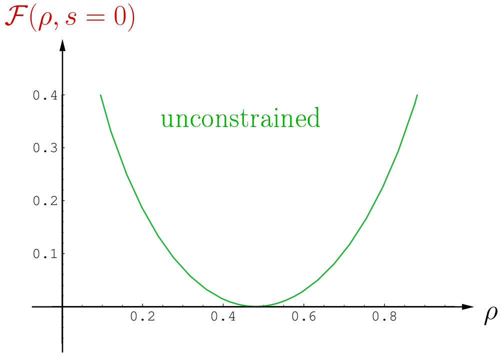
$$f_K(s) = \min_\rho \mathcal{F}(\rho, s)$$

Minimum reached at $\rho = \rho_K(s)$:

$$f_K(s) = \mathcal{F}(\rho_K(s), s)$$

Dynamical Landau free-energy landscape



$$\mathrm{Prob}_{[0,t]}(\rho) \sim \mathrm{e}^{-t\,L\,\mathcal{F}(\rho,s)}$$

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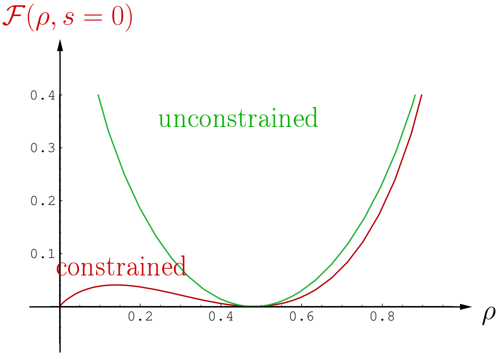

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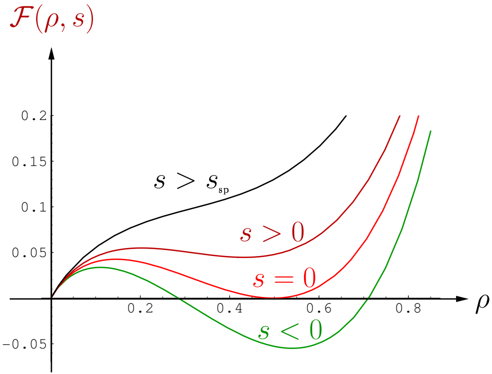

$$f_K(s) = \min_{\rho} \mathcal{F}(\rho, s) = \mathcal{F}(\rho_K(s), s)$$

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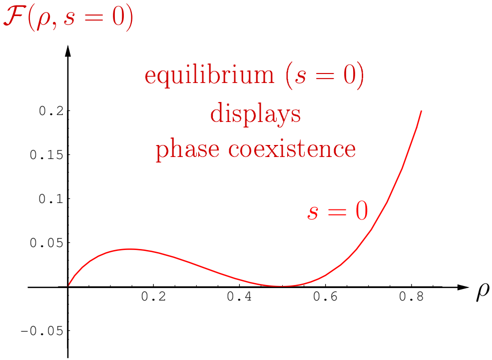

$$\text{Prob}_{[0,t]}(\rho) \sim \mathrm{e}^{-t\,L\,\mathcal{F}(\rho,s)}$$

Thermodynamics of histories: summary

Results

- *s*-states $\equiv$ tools to study dynamics
- Description of dynamical phase coexistence
  $\rightarrow$ Dynamical Landau free energy $\mathcal{F}(\rho, s)$ $\leftarrow$

Dynamical phase transition

- Criticality in a (dynamical) "hidden" dimension
- Dynamical heterogeneity

Perspective

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- Anomalous relaxation in the FA model.

References

- *PRL* **95** 010601 (2005)
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- Other glassy systems
  - *p*-spin models
  - structural glasses (Lennard-Jones)

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- Other glassy systems
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  - structural glasses (Lennard-Jones)
- Experimental realisation of $s(\simeq 0)$-states

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s-modified dynamics

- Markov processes:

$$\partial_t P(\mathcal{C},t) = \sum_{\mathcal{C}'} \Big\{ \underbrace{W(\mathcal{C}' \to \mathcal{C}) P(\mathcal{C}',t)}_{\text{gain term}} - \underbrace{W(\mathcal{C} \to \mathcal{C}') P(\mathcal{C},t)}_{\text{loss term}} \Big\}$$

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- More detailed dynamics for $P(\mathcal{C},K,t)$:

$$\partial_t P(\mathcal{C},K,t) = \sum_{\mathcal{C}'} \Big\{ W(\mathcal{C}'\to\mathcal{C})P(\mathcal{C}',K-1,t) - W(\mathcal{C}\to\mathcal{C}')P(\mathcal{C},K,t) \Big\}$$

s-modified dynamics

- Markov processes:

$$\partial_t P(\mathcal{C},t) = \sum_{\mathcal{C}'} \Big\{ \underbrace{W(\mathcal{C}' \to \mathcal{C}) P(\mathcal{C}',t)}_{\text{gain term}} - \underbrace{W(\mathcal{C} \to \mathcal{C}') P(\mathcal{C},t)}_{\text{loss term}} \Big\}$$

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- Canonical description: s conjugated to K

$$P(\mathcal{C},s,t) = \sum_K \mathrm{e}^{-sK} P(\mathcal{C},K,t)$$

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- Canonical description: s conjugated to K

$$P(\mathcal{C},s,t) = \sum_{K} \mathrm{e}^{-sK} P(\mathcal{C},K,t)$$

- s-modified dynamics [probability non-conserving]

$$\partial_t P(\mathcal{C},s,t) = \sum_{\mathcal{C}'} \Big\{ \mathrm{e}^{-sK} W(\mathcal{C}' \to \mathcal{C})P(\mathcal{C}',s,t) - W(\mathcal{C} \to \mathcal{C}')P(\mathcal{C},s,t) \Big\}$$

Numerical method (with J. Tailleur)

Evaluation of large deviation functions

$$Z(s,t) = \sum_{\mathcal{C}} P(\mathcal{C}, s, t) = \left\langle e^{-s\,K} \right\rangle \sim e^{-t f_K(s)}$$

- discrete time: Giardinà, Kurchan, Peliti [PRL **96**, 120603 (2006)]
- continuous time: Lecomte, Tailleur [JSTAT P03004 (2007)]

Cloning dynamics

$$\partial_t P(\mathcal{C}, s) = \underbrace{\sum_{\mathcal{C}'} W_s(\mathcal{C}' \to \mathcal{C}) P(\mathcal{C}', s) - r_s(\mathcal{C}) P(\mathcal{C}, s)}_{\text{modified dynamics}} + \underbrace{\delta r_s(\mathcal{C}) P(\mathcal{C}, s)}_{\text{cloning term}}$$

- $W_s(\mathcal{C}' \to \mathcal{C}) = e^{-s} W(\mathcal{C}' \to \mathcal{C})$
- $r_s(\mathcal{C}) = \sum_{\mathcal{C}' \neq \mathcal{C}} W_s(\mathcal{C} \to \mathcal{C}')$
- $\delta r_s(\mathcal{C}) = r_s(\mathcal{C}) - r(\mathcal{C})$

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