



# Thermodynamics of histories: application to systems with glassy dynamics

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Barcelona - 5th October 2006

# Outline

## 1 Motivations

- glassy systems
- a thermodynamic phase transition?

## 2 Thermodynamics of histories

- historical background
- **histories** versus configurations

## 3 A picture of phase coexistence

- kinetically constrained models
- dynamical free-energy

# Glassy systems: a picture

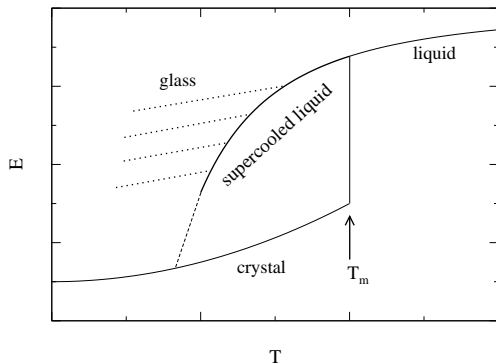


Fig.1 from Ritort and Sollich, *Adv. in Phys.* **52** 219 (2003)

# Glassy systems: experimental characterisation

## Real systems

- glasses obtained from supercooled liquids
- colloids
- magnetic spin glasses
- polydisperse gases of hard spheres

## Dramatic slow-down of the dynamics

- viscosity strongly depends on temperature
- large relaxation times  $\tau$  , heuristic fits:

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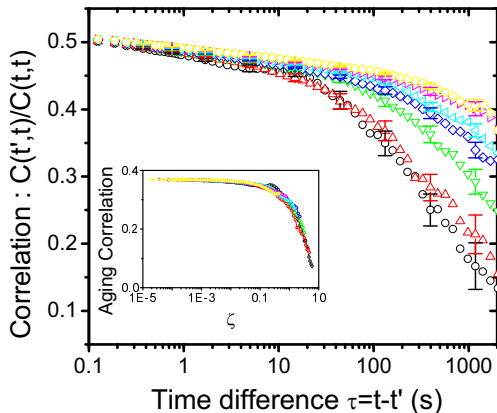
## Dramatic slow-down of the dynamics

- viscosity strongly depends on temperature
- large relaxation times  $\tau$  , heuristic fits:

$$\tau \sim \exp\left(\frac{A}{T - T_0}\right) \quad \text{or} \quad \tau \sim \exp\left(\frac{A}{T^b}\right) \quad \text{or} \dots$$

# Anomalous decay of correlation function: aging

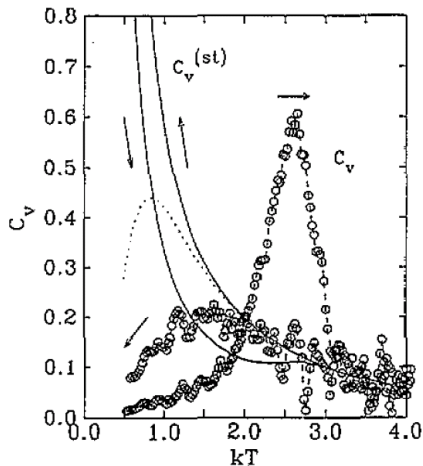
experimental data  
(magnetic spin glass)



from Hérissson and Ocio, *PRL* **88** 257202 (2002)

# Hysteresis

specific heat in a kinetically  
constrained model



from Graham, Piché and Grant, *J. Phys. Cond. Matt.*, **5** L349 (1993)

# Diverging length

## Direct Experimental Evidence of a Growing Length Scale Accompanying the Glass Transition

L. Berthier,<sup>1\*</sup> G. Biroli,<sup>2</sup> J.-P. Bouchaud,<sup>3,4</sup> L. Cipelletti,<sup>1</sup>  
D. El Masri,<sup>1</sup> D. L'Hôte,<sup>4</sup> F. Ladieu,<sup>4</sup> M. Pierno<sup>1</sup>

Understanding glass formation is a challenge, because the existence of a true glass state, distinct from liquid and solid, remains elusive: Glasses are liquids that have become too viscous to flow. An old idea, as yet unproven experimentally, is that the dynamics becomes sluggish as the glass transition approaches, because increasingly larger regions of the material have to move simultaneously to allow flow. We introduce new multipoint dynamical susceptibilities to estimate quantitatively the size of these regions and provide direct experimental evidence that the glass formation of molecular liquids and colloidal suspensions is accompanied by growing dynamic correlation length scales.

Berthier *et al.*, *Science* **310** 1797 (2005)

$(n \geq 4)$ -point correlator



# BUT...

## Absence of thermodynamic phase transition in a model glass former

Ludger Santen & Werner Krauth

CNRS-Laboratoire de Physique Statistique, Ecole Normale Supérieure,  
24 rue Lhomond, 75231 Paris Cedex 05, France

.....

The glass transition can be viewed simply as the point at which the viscosity of a structurally disordered liquid reaches a universal threshold value<sup>1</sup>. But this is an operational definition that circumvents fundamental issues, such as whether the glass transition is a purely dynamical phenomenon<sup>2</sup>. If so, ergodicity gets broken (the system becomes confined to some part of its phase space), but the thermodynamic properties of the liquid remain unchanged across the transition, provided they are determined as thermodynamic equilibrium averages over the whole phase space. The opposite view<sup>3-6</sup> claims that an underlying thermodynamic phase transition is responsible for the pronounced slow-down in the dynamics at the liquid-glass boundary.

Santen and Krauth, *Nature* **405** 550 (2000)

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# Thermodynamic of histories for glassy systems

## Chaotic Properties of Systems with Markov Dynamics

VL, Appert-Rolland and van Wijland, *PRL* **91** 010601 (2005)

### Space-time thermodynamics of the glass transition

Mauro Merolle<sup>†</sup>, Juan P. Garrahan<sup>‡</sup>, and David Chandler<sup>†§</sup>

<sup>†</sup>Department of Chemistry, University of California, Berkeley, CA 94720-1460; and <sup>‡</sup>School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom

Contributed by David Chandler, June 15, 2005

We consider the probability distribution for fluctuations in dynamical action and similar quantities related to dynamic heterogeneity. We argue that the so-called “glass transition” is a manifestation of low action tails in these distributions where the entropy of trajectory space is subextensive in time. These low action tails are a consequence of dynamic heterogeneity and an indication of phase coexistence in trajectory space. The glass transition, where the system falls out of equilibrium, is then an order–disorder phenomenon in space–time occurring at a temperature  $T_g$ , which is a weak function of measurement time. We illustrate our perspective ideas with facilitated lattice models and note how these ideas apply more generally.

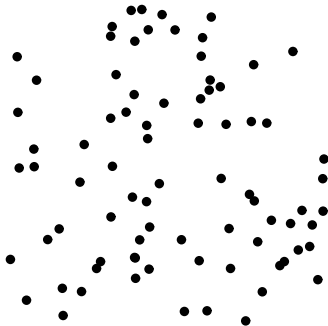
dynamic heterogeneity | entropy | phase transition | supercooled liquids

**A** glass transition, where a supercooled fluid falls out of equilibrium, is irreversible and a consequence of experimental protocols, such as the time scale over which the system is prepared and the time scale over which its properties are observed (for reviews, see refs. 1–3). It is thus not a transition in

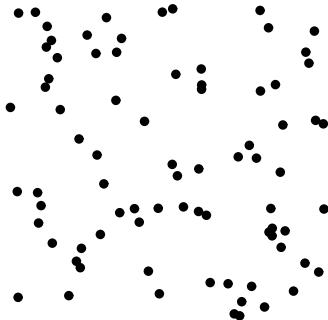
22). In both cases, there is an energy function  $J\sum_i n_i$ , where  $J > 0$  sets the equilibrium temperature scale,  $n_i$  is either 1 or 0, indicating whether lattice site  $i$  is excited or not, and the sum over  $i$  extends over lattice sites. The system moves stochastically from one microstate to another through a sequence of single-cell moves. In the FA model, the state of cell  $i$  at time slice  $t + 1$ ,  $n_{i,t+1}$ , can differ from that at time slice  $t$ ,  $n_{i,t}$ , only if at least one of two nearest neighbors,  $i \pm 1$ , is excited at time  $t$ . In the East model the condition is that  $n_{i+1,t}$  must be excited. These dynamic constraints affect the metric of motion, confining the space–time volume available for trajectories (23). This mimics the effects of complicated intermolecular potentials in a dense nearly jammed material. Excitations in this picture are regions of space–time where molecules are unjammed and exhibit mobility. As such, we refer to  $n_{i,t}$  as the mobility field. For both models, the dynamics is time-reversal symmetric and obeys detailed balance. The equilibrium concentration of excitations,  $c \equiv \langle n \rangle = 1/(1 + e^{J/T})$ , is the relevant control parameter. The average distance between excitations sets the characteristic length scale for relaxation,  $\ell \approx$

Merolle, Garrahan and Chandler, *PNAS* **102** 10837 (2005)

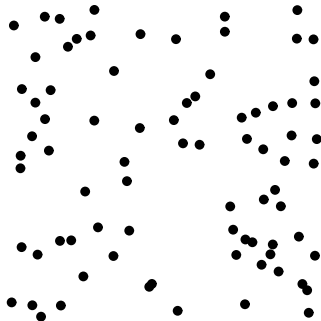
# Histories vs configurations



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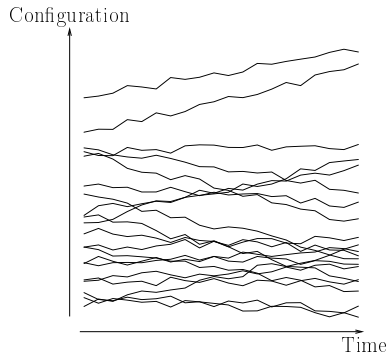


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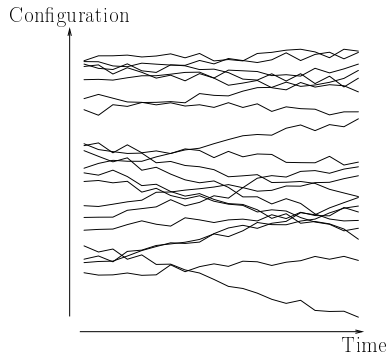




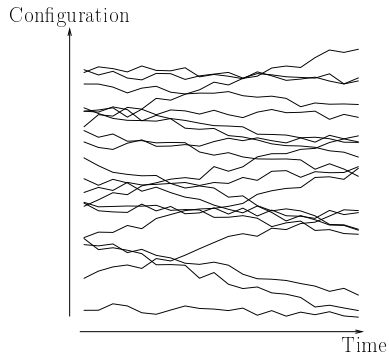
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# Histories vs configurations



# Historical perspective

## Historical background in mathematics

- Ruelle's thermodynamic formalism: **deterministic** dynamics
- work of Kolmogorov, Sinai, Shannon

## In physics

- Gaspard: *discrete* time **stochastic** dynamics
- our contribution: *continuous* time **stochastic** dynamics

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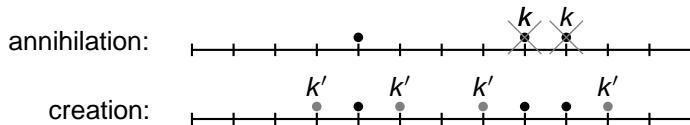
## In physics

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# Kinetically Constrained Models (KCM)

## Fredrickson Andersen model in 1D

- $L$  sites  $\mathbf{n} = \{n_i\}$  with  $n_i = 1$  or  $0$  in **one dimension**
- Constraint: **at least one neighbor is alive** to allow an event
- Transition rates:
  - annihilation with rate  $W(1_i \rightarrow 0_i) = k$
  - creation with rate  $W(0_i \rightarrow 1_i) = k'$



# Outline

Classification of histories using **time-extensive** parameters on  $[0, t]$

- number of *configuration change*:  $K$
- “*dynamical complexity*”:  $Q_+$

$$Q_+[history] = \ln \text{Prob}[history]$$

$$= \sum_{k=1}^K \ln \frac{W(\mathbf{n}_k \rightarrow \mathbf{n}_{k+1})}{r(\mathbf{n}_k)} \quad \text{with } r(\mathbf{n}) = \sum_{\mathbf{n}' \neq \mathbf{n}} W(\mathbf{n} \rightarrow \mathbf{n}')$$

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Probing the space of histories: density  $\rho(K)$ ,  $\rho(Q_+)$

$$\rho(K) = \sum_{\substack{\text{histories} \\ \text{from } 0 \text{ to } t}} \delta(K - K[hist]) \rho(t)$$



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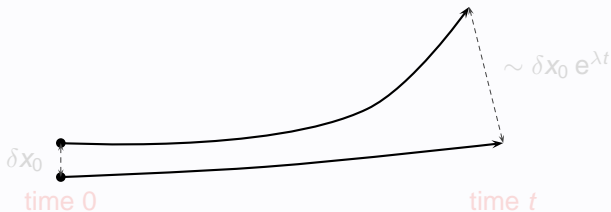
$$\rho(Q_+) = \sum_{\substack{\text{histories} \\ \text{from } 0 \text{ to } t}} \delta(Q_+ - Q_+[hist]) \rho(t)$$

# Dynamical entropy

## Kolmogorov Sinai entropy

$$h_{\text{KS}} = - \lim_{t \rightarrow \infty} \frac{1}{t} \sum_{\text{histories}} \text{Prob}\{\text{history}\} \ln \text{Prob}\{\text{history}\} = - \lim_{t \rightarrow \infty} \frac{1}{t} \langle Q_+ \rangle$$

## Lyapunov exponents for deterministic dynamics

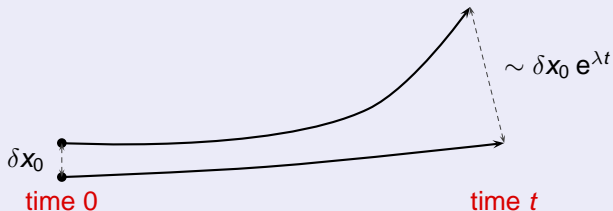


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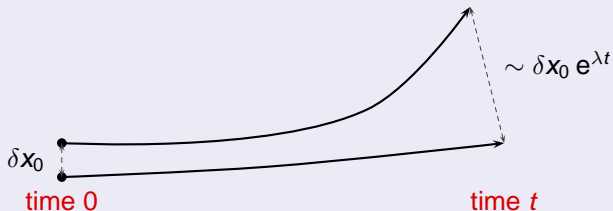


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## Lyapunov exponents for deterministic dynamics



Pesin theorem:

$$h_{\text{KS}} = \sum_{\lambda_i > 0} \lambda_i$$

# Dynamical partition function

## Probing fluctuations (1): the micro-canonical way

- Thermodynamics of configurations

$$Z(E, N) = \sum_{\mathbf{n}} \delta(E - \mathcal{H}(\mathbf{n})) \quad (\text{large } N)$$

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- Thermodynamics of histories [Ruelle]

$$Z_{\text{dyn}}(Q_+, t) = \sum_{\substack{\text{histories} \\ \text{from } 0 \text{ to } t}} \delta(Q_+ - Q_+[history]) \quad (\text{large } t)$$

# Dynamical partition function

## Probing fluctuations (2): the canonical way

- Thermodynamics of configurations

$$Z(\beta, N) = \sum_n e^{-\beta \mathcal{H}(n)} = e^{-N f(\beta)} \quad (\text{large } N)$$

- Thermodynamics of histories [Ruelle]

$$Z_{\text{dyn}}(s, t) = \sum_{\substack{\text{histories} \\ \text{from } 0 \text{ to } t}} \text{Prob}\{\text{history}\}^{1-s} = e^{-t f_{\text{dyn}}(s)} \quad (\text{large } t)$$

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## Canonical (dynamical) ensemble

- $\beta$  conjugated to energy
- $s$  conjugated to dynamical complexity  $Q_+$



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$$\rho_+(s) = \frac{1}{Z_{\text{dyn}}(s, t)} \sum_{Q_+} e^{-s Q_+} \rho(Q_+)$$

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## Canonical (dynamical) ensemble

$$\rho_K(s) = \frac{1}{Z_K(s, t)} \sum_K e^{-s K} \rho(K)$$

# Results

## Explicit expression

$$\begin{aligned}
 Z_{\text{dyn}}(s, t | \mathcal{C}_0, t_0) &= \sum_{K=0}^{+\infty} \sum_{\mathcal{C}_1, \dots, \mathcal{C}_K} \int_{t_0}^t dt_1 \, r(\mathcal{C}_0) e^{-(t_1 - t_0)r(\mathcal{C}_0)} \dots \\
 &\quad \int_{t_{K-1}}^t dt_K \, r(\mathcal{C}_{K-1}) e^{-(t_K - t_{K-1})r(\mathcal{C}_{K-1})} \\
 &\quad e^{-(t - t_K)r(\mathcal{C}_K)} \left[ \prod_{n=1}^K \frac{W(\mathcal{C}_{n-1} \rightarrow \mathcal{C}_n)}{r(\mathcal{C}_{n-1})} \right]^{1-s} \\
 &= \left\langle e^{-s Q_+} \right\rangle
 \end{aligned}$$

# Results

## Canonical (dynamical) **s-state**

- **micro-canonical**: fixed value of  $Q_+$
- **canonical**: fixed value of  $s$
- $s > 0$  : more active state ("high"  $Q_+$ )
- $s = 0$  : steady state
- $s < 0$  : less active state ("low"  $Q_+$ )

## Of practical interest

- $f_{\text{dyn}}(s)$  = smallest eigenvalue of some operator
  - corresponding eigenvector = **s-state**
- exact results, numerical approach

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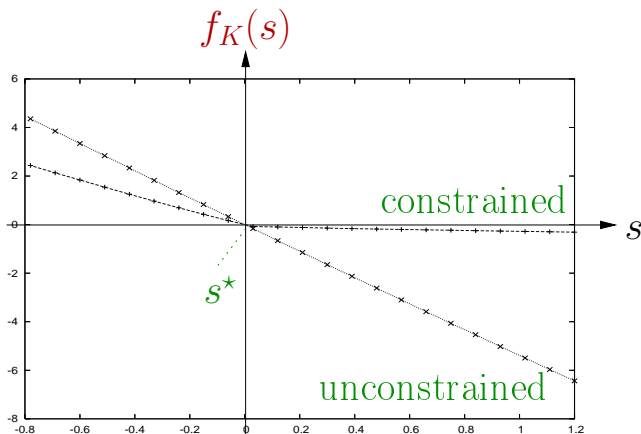
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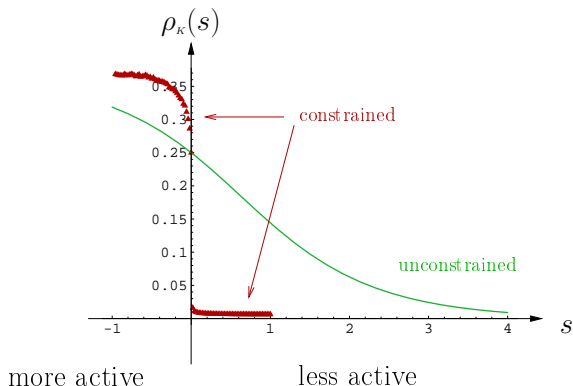
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# Dynamical phase transition



Comparison between constrained and unconstrained model

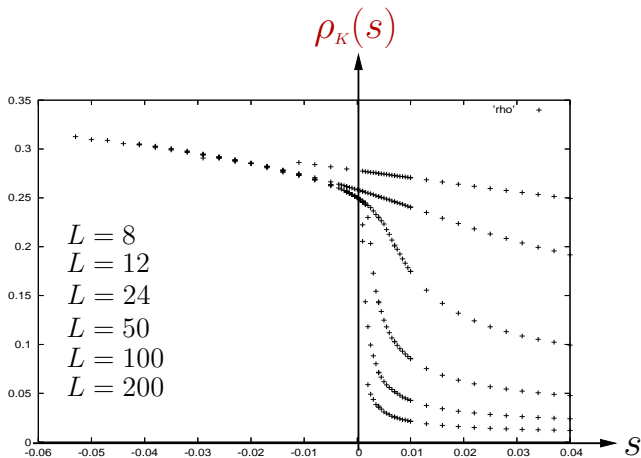
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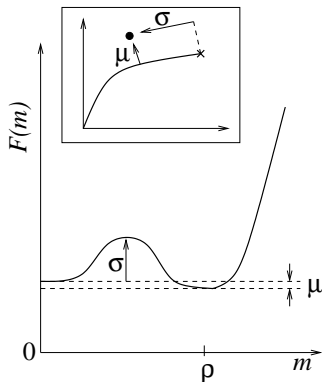


# Dynamical phase transition



Large size scaling

# Dynamical free energy picture (1)



From Jack, Garrahan and Chandler, [cond-mat/0604068]

## Dynamical free energy picture (2)

Mean-field version of FA model:

$$f_{\text{dyn}}(s) = \min_{\rho} \mathcal{F}(\rho, s)$$

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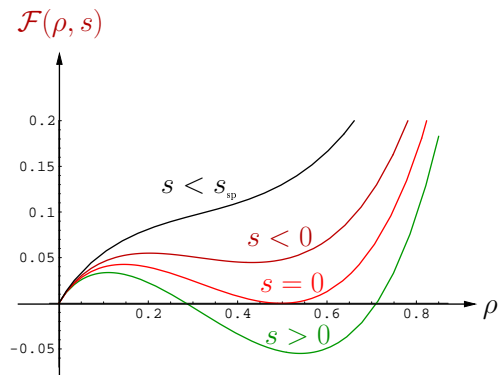
$$\begin{aligned} f_{\text{dyn}}(\mathbf{s}) &= \min_{\rho} \mathcal{F}(\rho, \mathbf{s}) \\ &= \mathcal{F}(\rho(\mathbf{s}), \mathbf{s}) \end{aligned}$$

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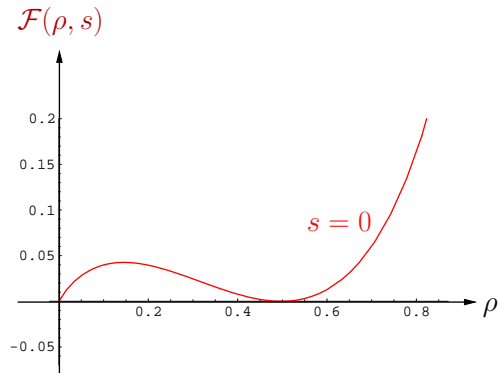
$$= \mathcal{F}(\rho(s), s)$$



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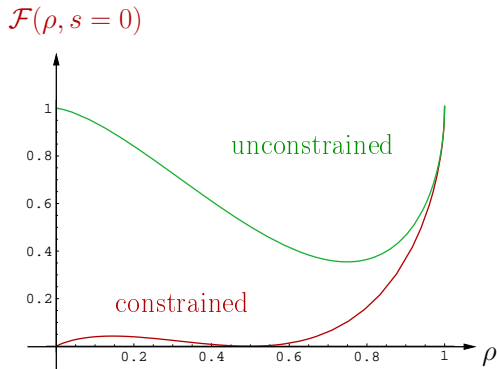
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# Conclusions

## Framework

- Unified picture
- Criticality in a “hidden” **dynamical** direction

## Main results

- **s-states**  $\equiv$  probe of dynamical aspects of the steady state
- Efficient tools to find **dynamical phase transition** in physical models
- **glassiness in KCM's**  $\leftrightarrow$   **$s = 0$  is a critical point**



# Conclusions

## Perspectives – Open questions

- Relations between  $\langle K^2 \rangle_c$  and  $(n \geq 4)$ -correlators?
- Measurement of the  $h_{KS}$  entropy jump at  $s = 0$ ?
- Non-equivalence of ensemble, non-convex free-energy?
- Quantitative behaviour of time relaxation?
- Experimental predictions?
- Experimental realization of  $s$ -states?

## References:

- *PRL* **91** 010601 (2005)
- `cond-mat/0606211`