GDR IDE
Workshop Les Houches
4th April 2023

On the relevance of shear transformations in the relaxation of supercooled liquids

M. Lerbinger[1], A. Barbot[1], D. Vandembroucq[1] and S. Patinet[1]

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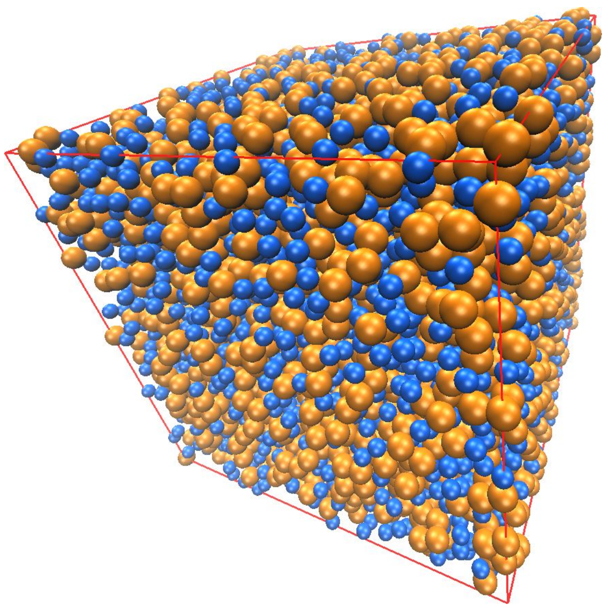
M. Lerbinger, A. Barbot, D. Vandembroucq and S. Patinet, Phys. Rev. Lett. **129**, 195501 (2022)

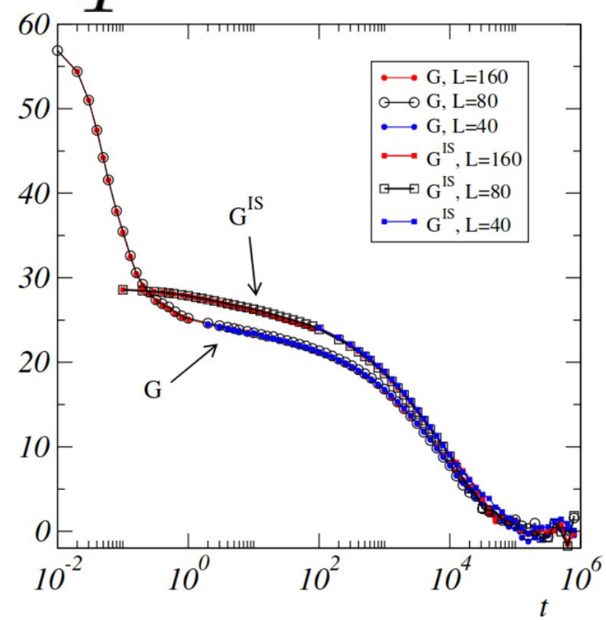
Point of view

Disorder



Elasticity

$$G(t) = \frac{L^2}{T}\langle \overline{\sigma}_{xy}(t_0)\overline{\sigma}_{xy}(t_0+t)\rangle$$



A. Lemaître, PRL **113**, 245702 (2014)

freeze

Viscous Liquids

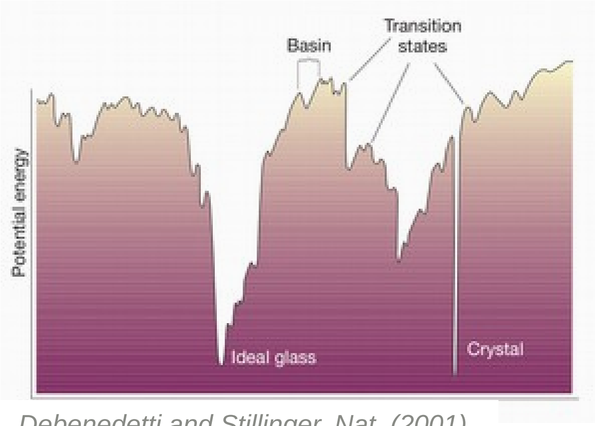
Amorphous Solids

flow

Plan

1) Relaxations in supercooled liquids

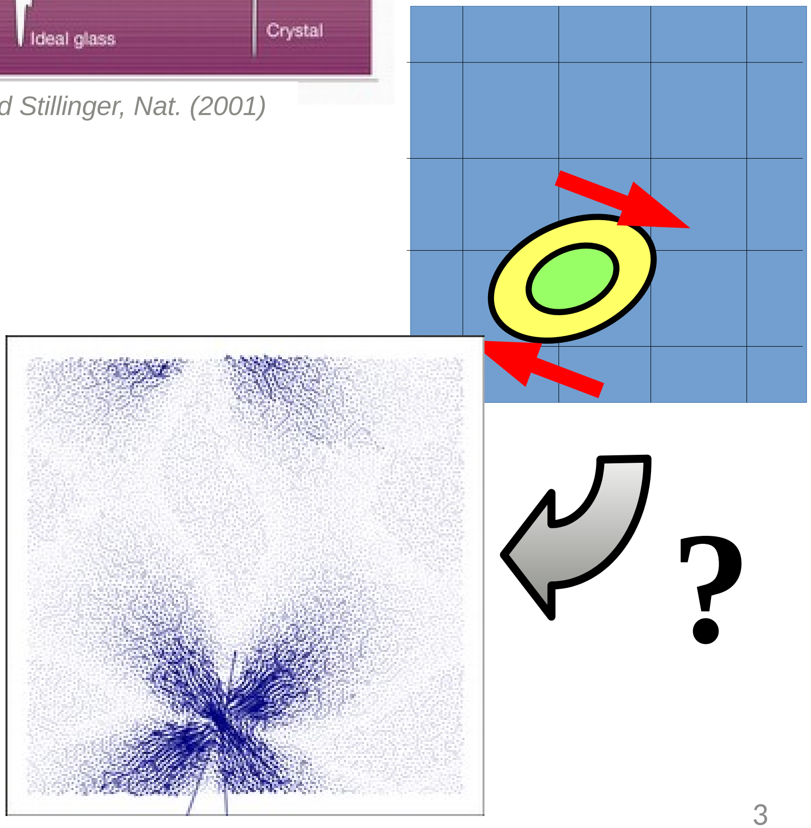
- Motivations and definitions
- Relaxation: nature, extension
- Inherent structure picture



Debenedetti and Stillinger, Nat. (2001)

2) Methods

- Dynamical observations
- Detection of relaxations
- Local yield stress method



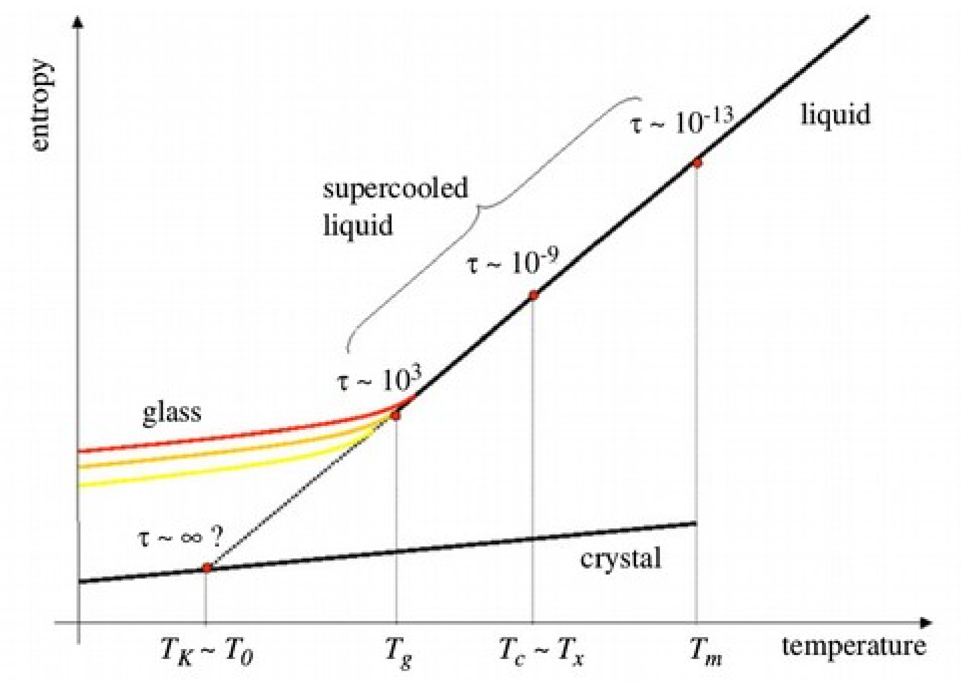
3) Results

- Correlations
- Real space interpretation of relaxations
- Reversibility of relaxations

Glass transition: phenomenology and questions

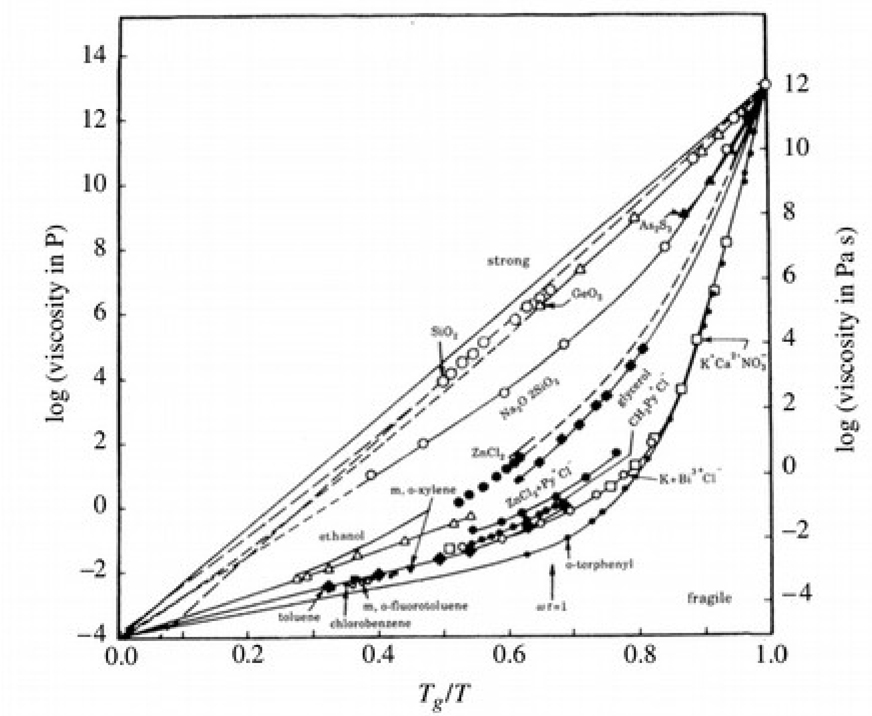
Motivation and definitions

The glass transition



A. Cavagna, Phys. Rep. 476, **51** (2009)

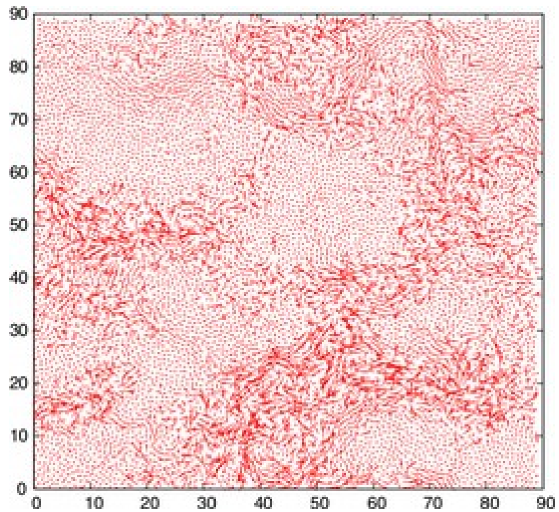
Divergence of the relaxation time



C. A. Angell, Nat. Tech. Inf. Serv., 1 (1985)

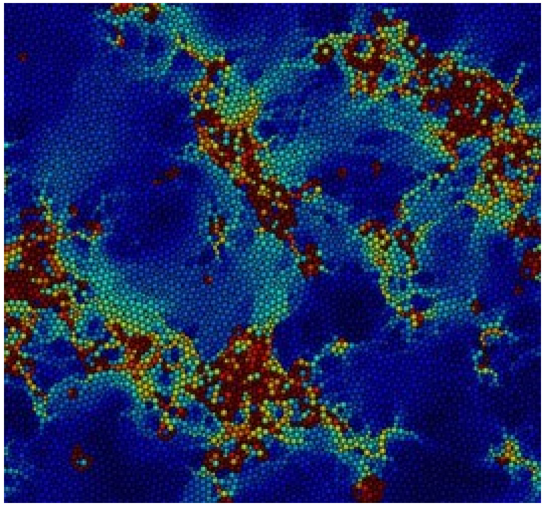
Glass transition: phenomenology and questions

Dynamical heterogeneities



L. Berthier and G. Biroli, Rev. Mod. Phys. **83** (2011)

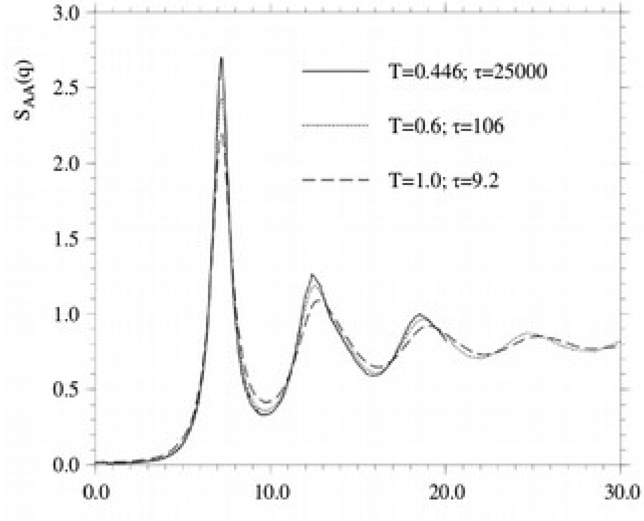
Hierarchical relaxations



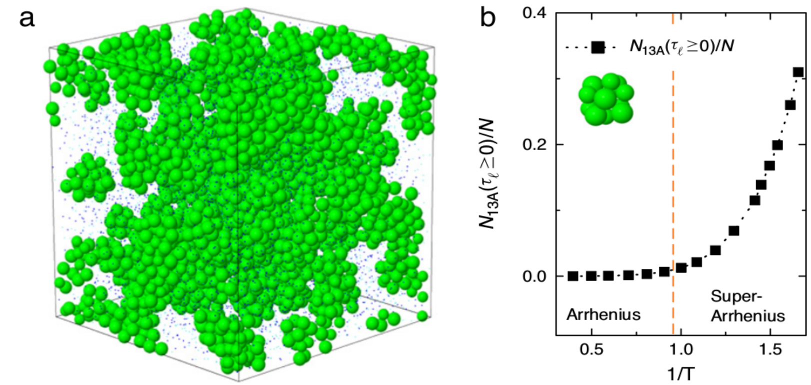
A. S. Keys et al., Phys. Rev. X, **1**, 021013 (2011)

Structural observables can hardly distinguish phases at a qualitative level

W. Kob, in: Supercooled Liquids, the Glass Transition and Computer Simulations, in: EDP Sciences, 199 (2003)

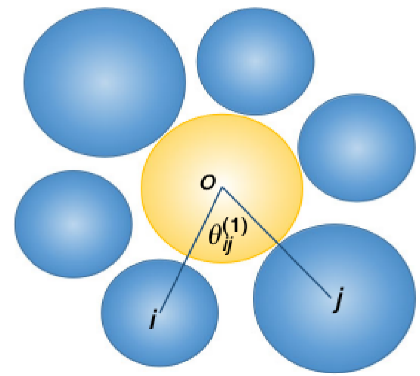


Attempts to relate structure and dynamics



Locally favored structures

A. Malins et al., J. Chem. Phys., **138** 12A535 (2013)



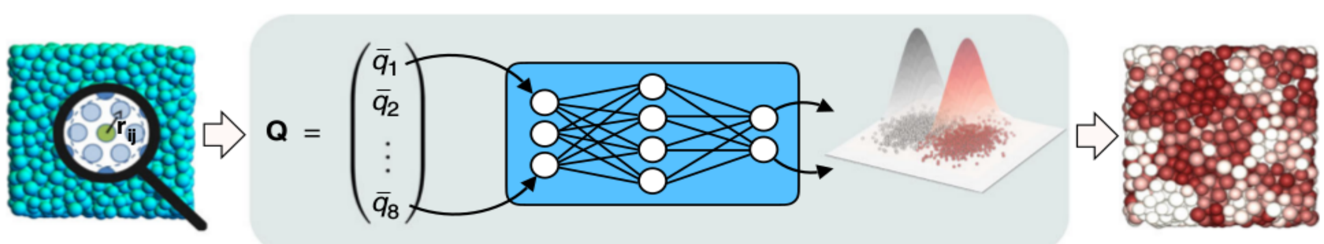
Multi-body order parameters

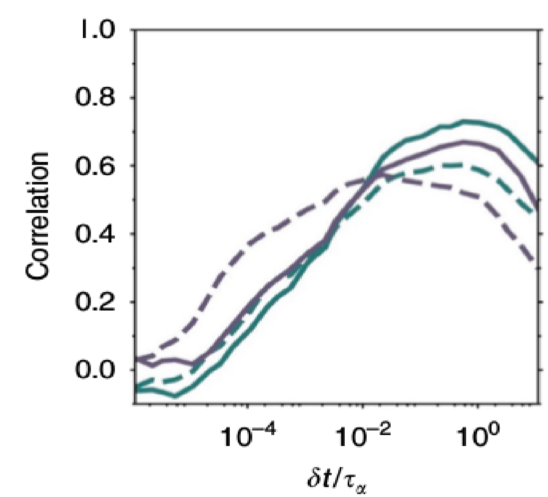
H. Tong and H. Tanaka, Phys. Rev. X, **8**, 011041 (2018)

H. Tong and H. Tanaka, Nat. Commun, **10**, 5596 (2019)

H. Tong and H. Tanaka, Phys. Rev. Lett., **124**, 225501 (2020)

Machine learning methods





E. Boattini et al., Nat. Comm., **11**, 5479 (2020)

V. Bapst et al., Nat. Phys, **16**, 448 (2020)

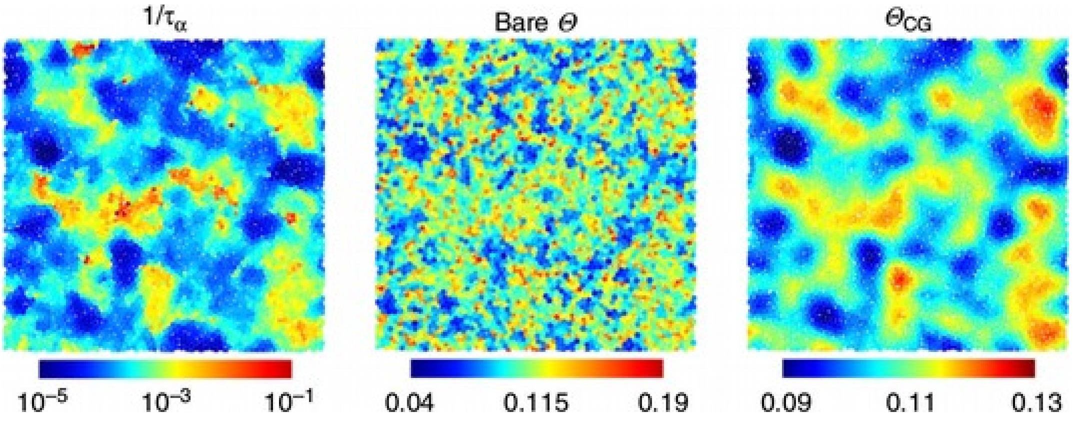
S. S. Schoenholz et al., Nat. Phys, **12**, 469 (2016)

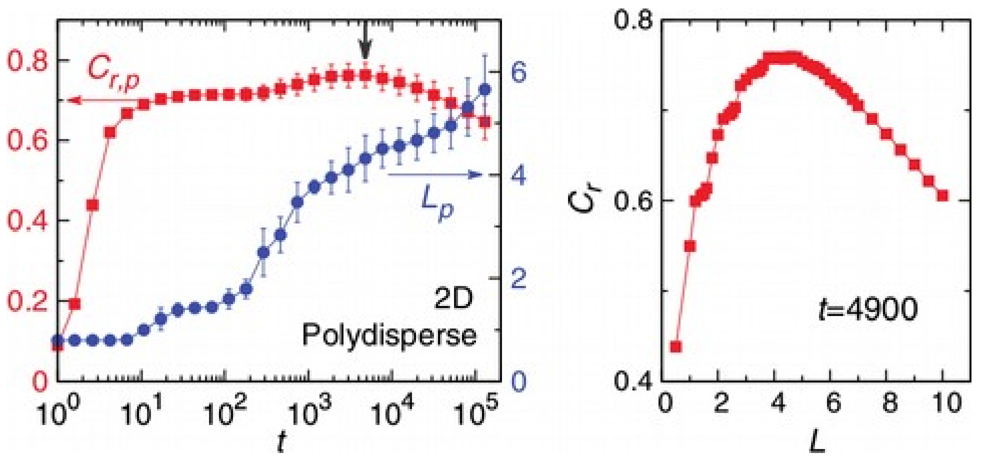
Necessity to employ coarse-grained description

Influence of structure on dynamics stronger on long length scales than on short ones

L. Berthier and R. L. Jack, Phys. Rev. E, **76**, 041509 (2007)

Multi-body order parameters





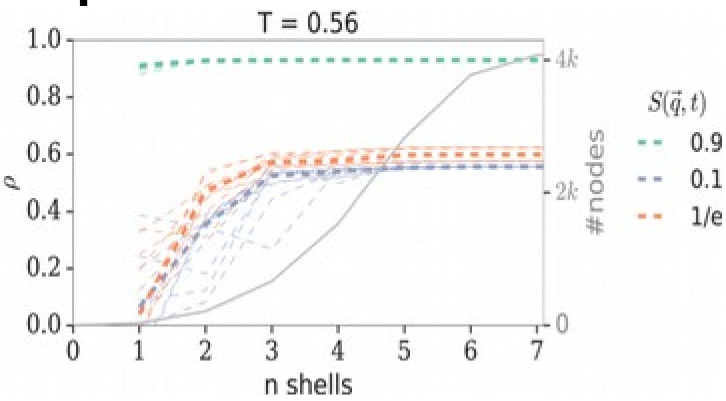
H. Tong and H. Tanaka, Nat. Commun, **10**, 5596 (2019)

Machine learning: Averaging local descriptors

E. Boattini et al., Phys. Rev. Lett., **127**, 088007 (2021)

Machine learning: shell

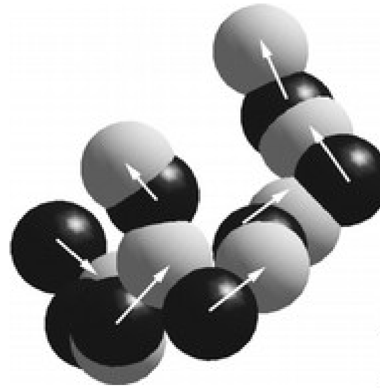
V. Bapst et al., Nat. Phys, **16**, 448 (2020)



Nature and spatial extension of the relaxations

Single atomic jump

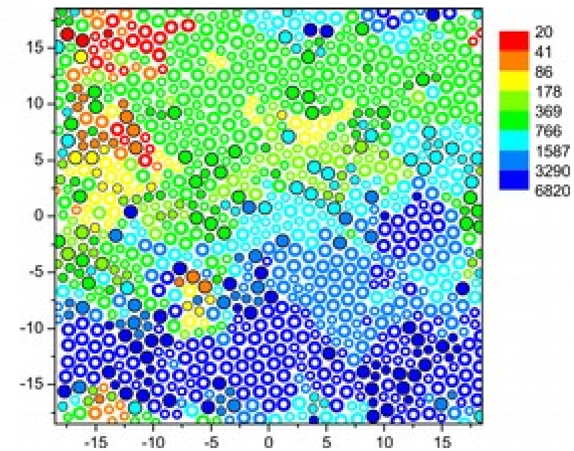
K. Vollmayr-Lee, J. Chem. Phys., **121**, 4781 (2004)



String-like motion

C. Donati et al., Phys. Rev. E, **60**, 3107 (1999)

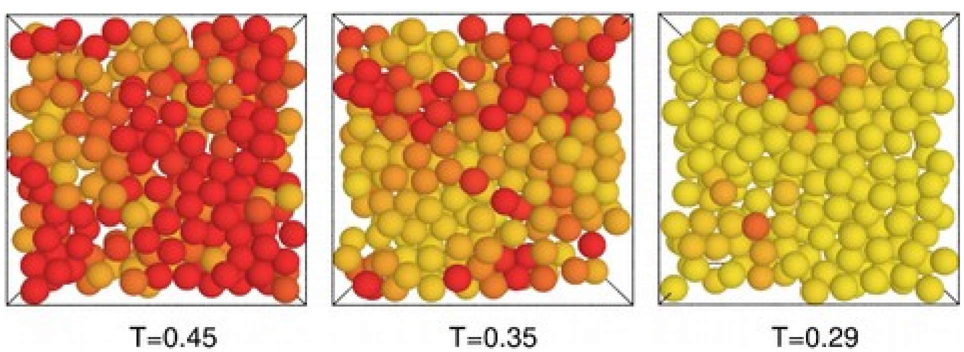
M. Vogel et al., J. Chem. Phys., **120**, 4404 (2004)

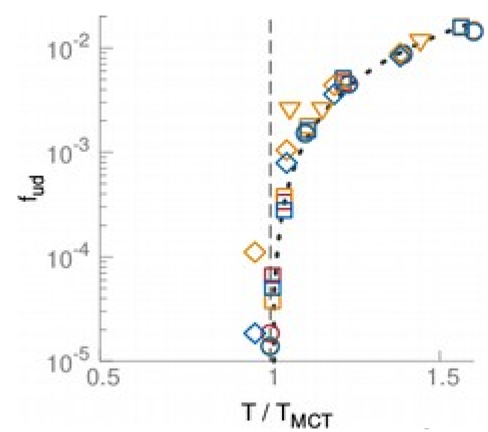


Local shear

A. Widmer-Cooper and P. Harrowell, Phys. Rev. E, **80**, 061501 (2009)

Relaxations tend to localize with the decrease in T





D. Coslovich, A. Ninarello, and L. Berthier, SciPost Physics, **7**, 77 (2019)

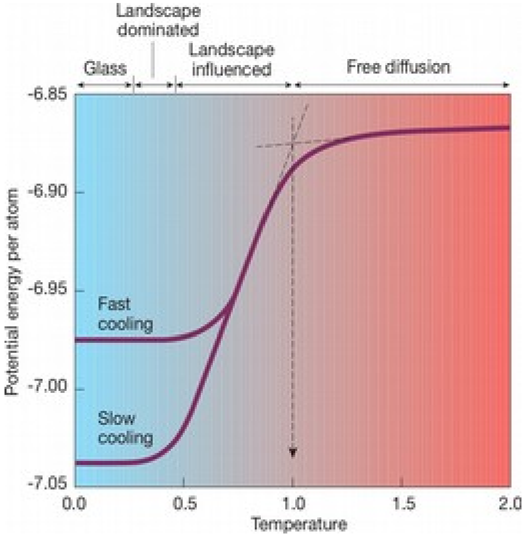
M. Shimada, D. Coslovich, H. Mizuno, and A. Ikeda, SciPost Phys., **10**, 001 (2021)

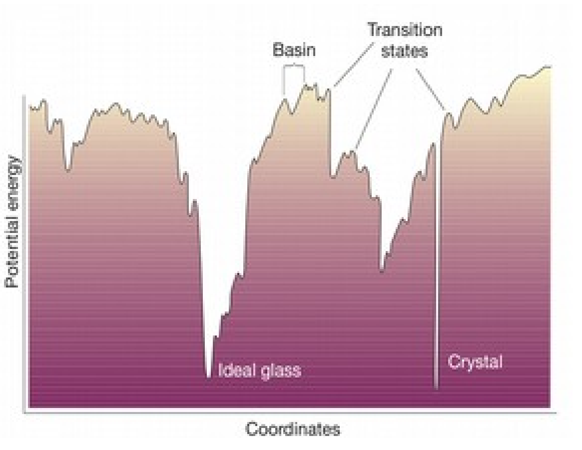
W. Ji, T. W. J. de Geus, E. Agoritsas, and M. Wyart, PRE, 102, 062110 (2020)

Liquids as flowing solids: role of the inherent states

Vibrations around potential energy minima, before quick jumps to other minima

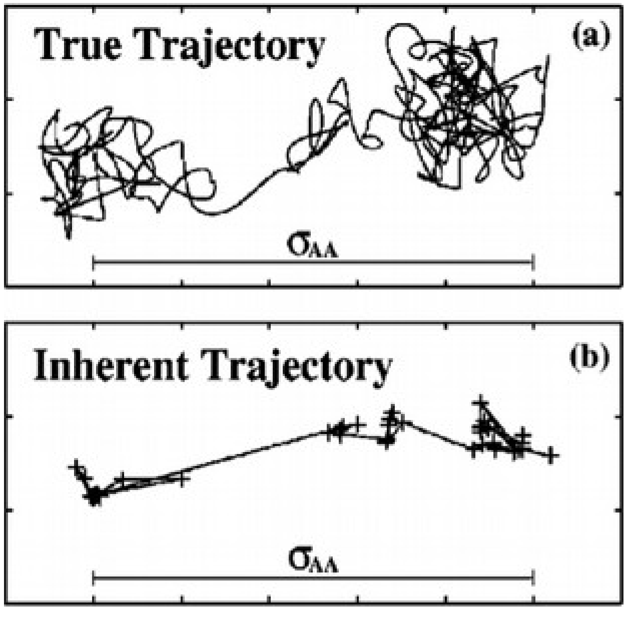
M. Goldstein, J. Chem. Phys., **51**, 3728 (1969)





This all the more approaching the glass transition

P. G. Debenedetti and F. H. Stillinger, Nat., **410**, 259 (2001)



Describe the dynamics by a succession of Inherent States

Schrøder T. B. et al., J. Chem. Phys. **112** 9834 (2000)

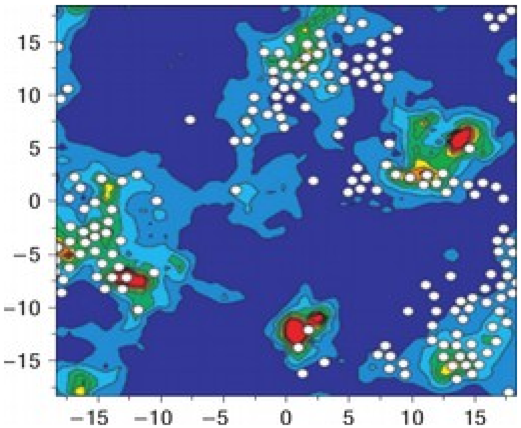
B. Doliwa and A. Heuer, Phys. Rev. Lett., **91**, 235501 (2003)

A. Heuer, J. Phys. Condens. Matter, **20**, 373101 (2008)

Evidences from the energy potential landscape perspective

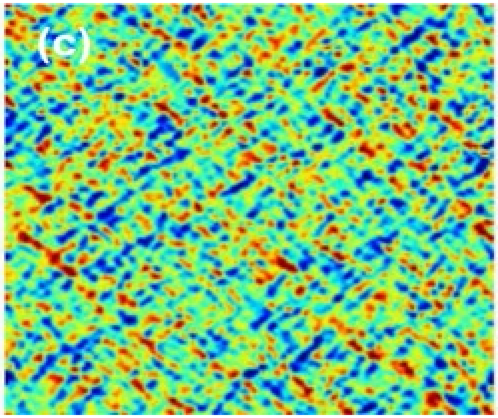
“Elastic” models (e.g. shoving)

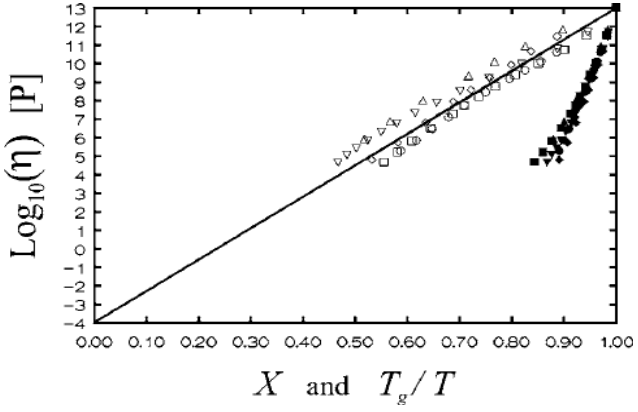
J. C. Dyre, Rev. Mod. Phys., **78**, 953 (2006)



Non-Arrhenian characteristic energy scale evidenced in fragile liquids

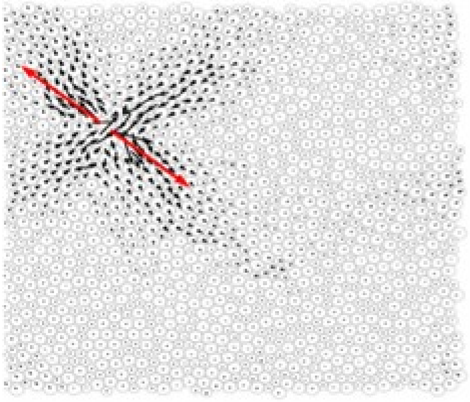
G. Kapteijns et al., J. Chem. Phys., **155**, 074502 (2021)





Soft vibrational modes linked to rearrangements

A. Widmer-Cooper et al., Nat. Phys, **4**, 711 (2008)



Local events (+ mechanical balance and material isotropy) imply long-ranged correlated stresses

A. Lemaître, Phys. Rev. Lett., **113**, 245702 (2014)

Summing up

Time scale and nature of relaxations in supercooled liquids?

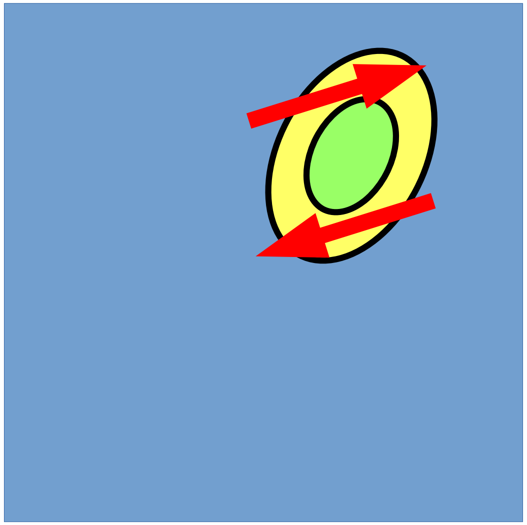
- Correlation (to some extent) between local structure and dynamics

- Need of coarse-grained quantities & relaxations localize as T is lowered

- Contrasting results about the nature of thermally activated excitations

- Mechanics of inherent structures (elasticity + shear) plays a crucial role

⇨ **<u>Proposal</u> : look at the local shear response of inherent structures**



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- Motivations and definitions
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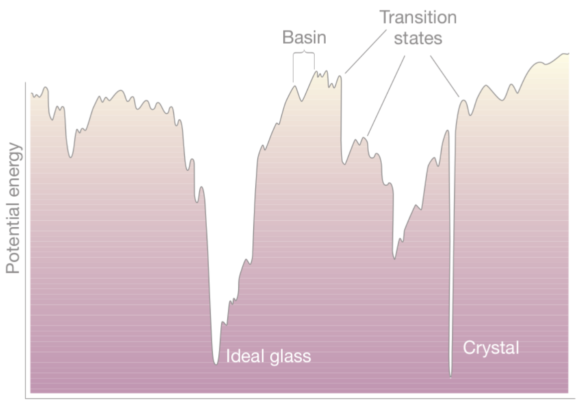
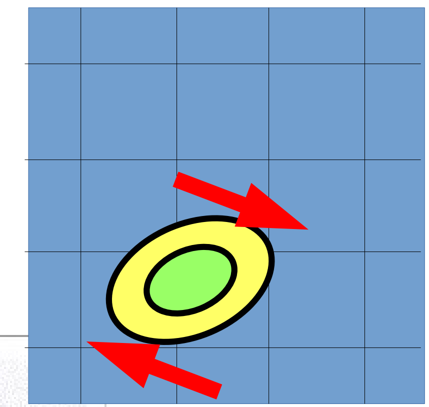
- Inherent structure picture

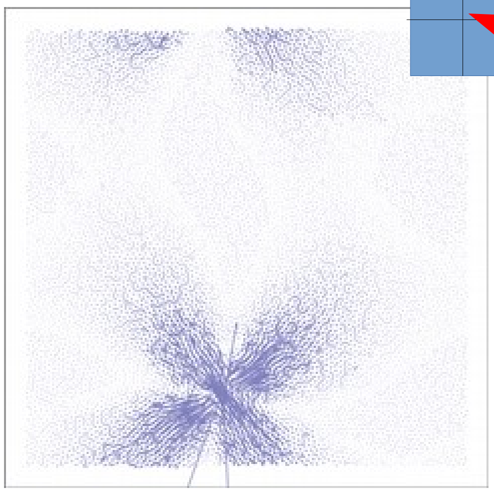


Debenedetti and Stillinger, Nat. (2001)

2) Methods

- **Dynamical observations**
- **Detection of relaxations**
- **Local yield stress method**





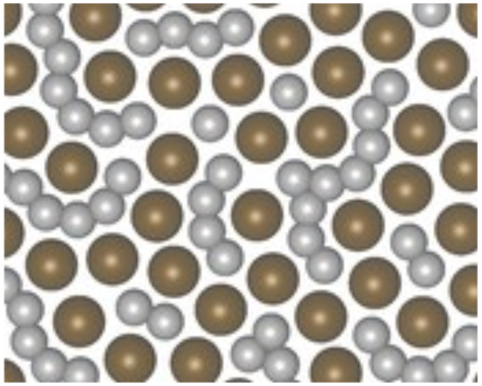
3) Results

- Correlations
- Real space interpretation of relaxations
- Reversibility of relaxations

System and simulation methods

System:

- Two-dimensional binary glass
- 10^4 atoms, ρ=1,024, PBC
- Lennard-Jones potentials *(+smoothing function)*



M. L. Falk, et al. *PRE* **57,** 7192 (1998)
A. Barbot, et al. PRE ***97****, 033001 (2018)*

$$U(r_{ij}) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + A, & \text{for } r_{ij} < R_{\text{in}} \\ \sum_{k=0}^{4} C_k (r_{ij} - R_{\text{in}})^k, & \text{for } R_{\text{in}} < r_{ij} < R_{\text{cut}} \\ 0, & \text{for } r_{ij} > R_{\text{cut}}, \end{cases}$$

- 20 samples, 100 replicas

Simulation methods:

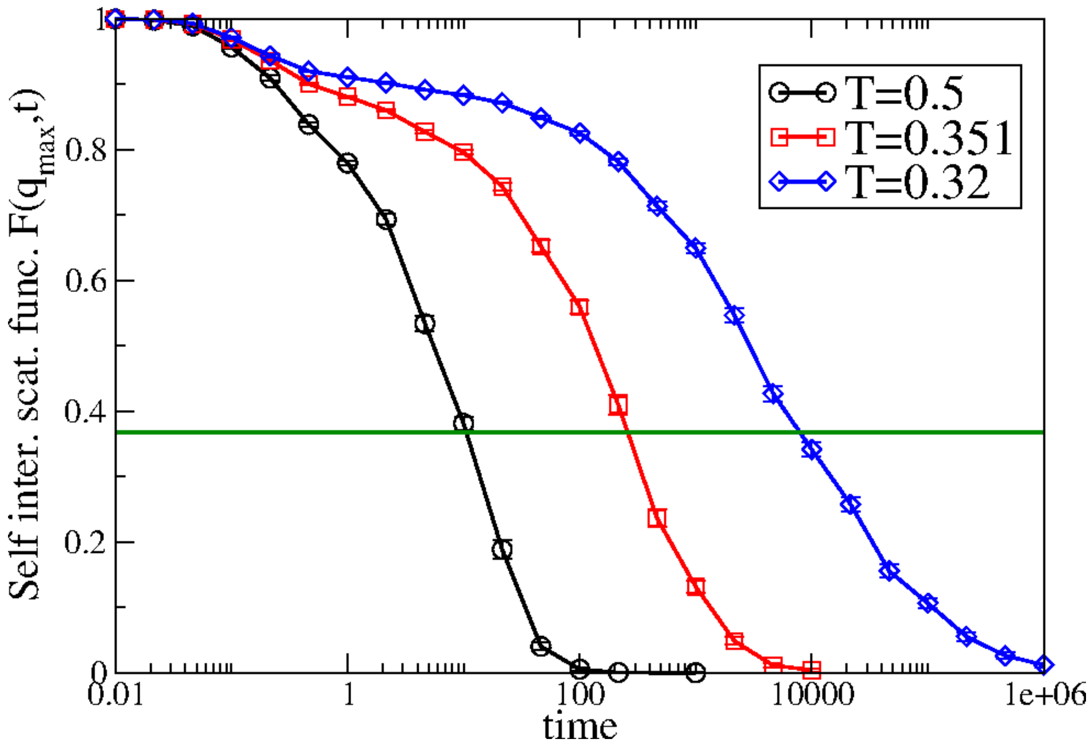
- NVT molecular dynamics
- Inherent structures from instantaneous quench
- Local loading: Athermal Quasi-Static shear

Codes:

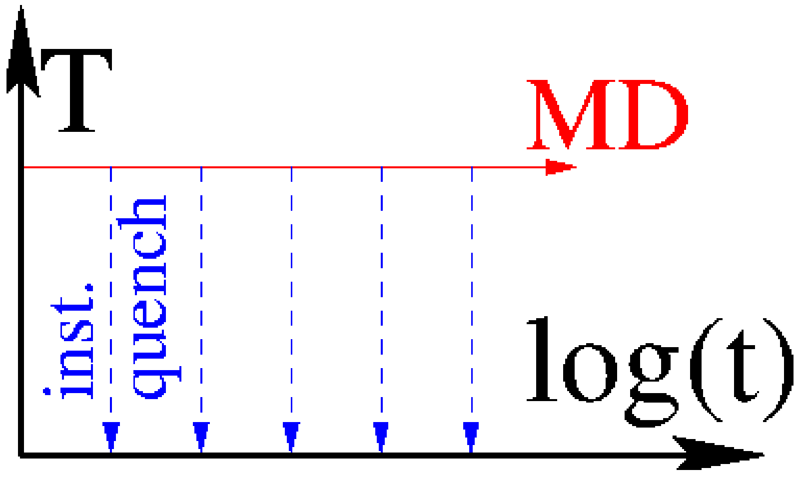
- Atomistic simulation: LAMMPS S. Plimpton, J. Comp. Phys., **117**, 1 (1995).

Methods: MD and inherent state generation

Equilibrium NVT simulations



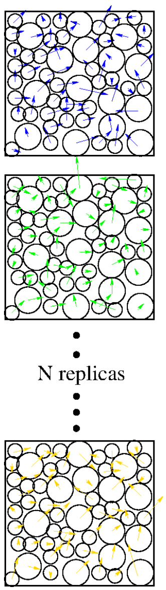
Instantaneous quench (v=0) at logarithmic increasing intervals + minimization (f=0)



2 maps: Dynamical variables and local properties

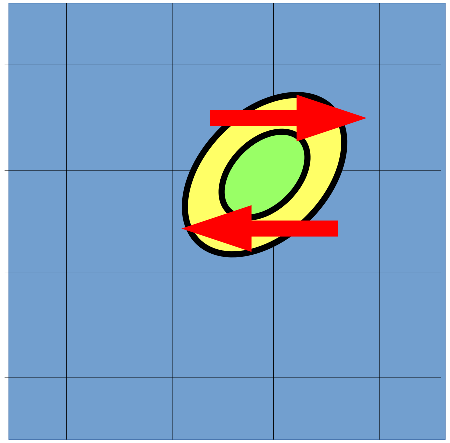
Dynamics ⟷ ? ⟷ **Initial IS structure**

Propensity



$$\langle \Delta r^2 \rangle$$

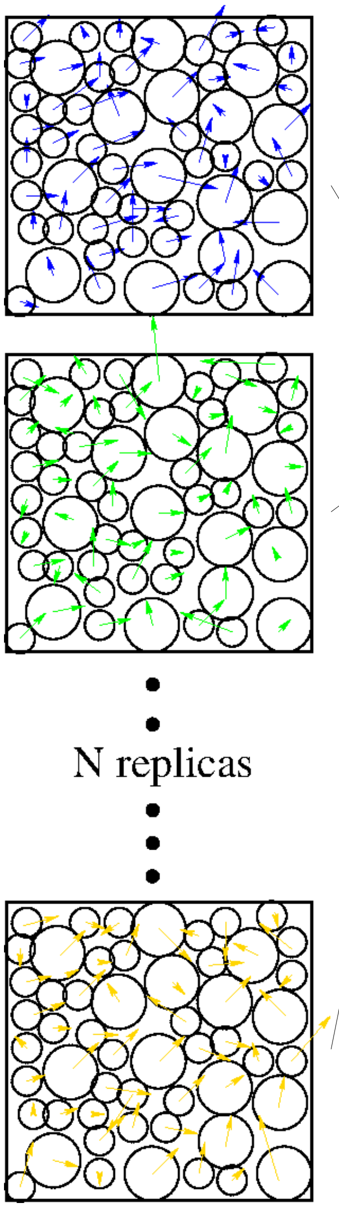
Local yield stress



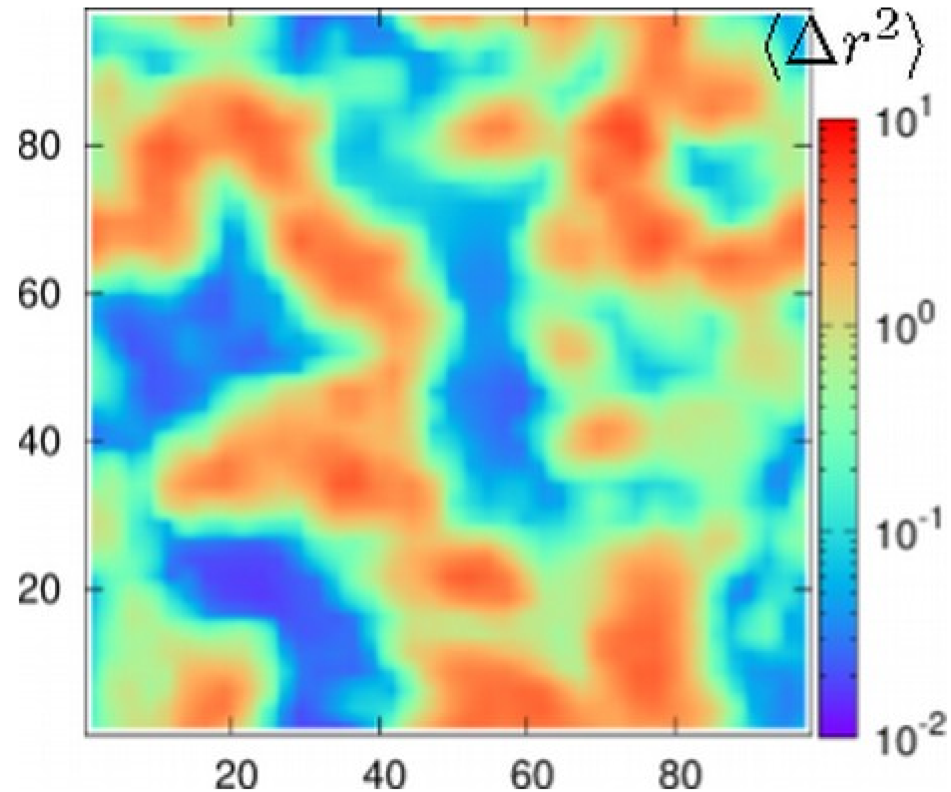
$$\Delta \tau^c_{min}$$

Methods: computation of propensity

100 replicas: Same initial structure + randomized velocities



$$\langle \Delta r^2(t) \rangle$$

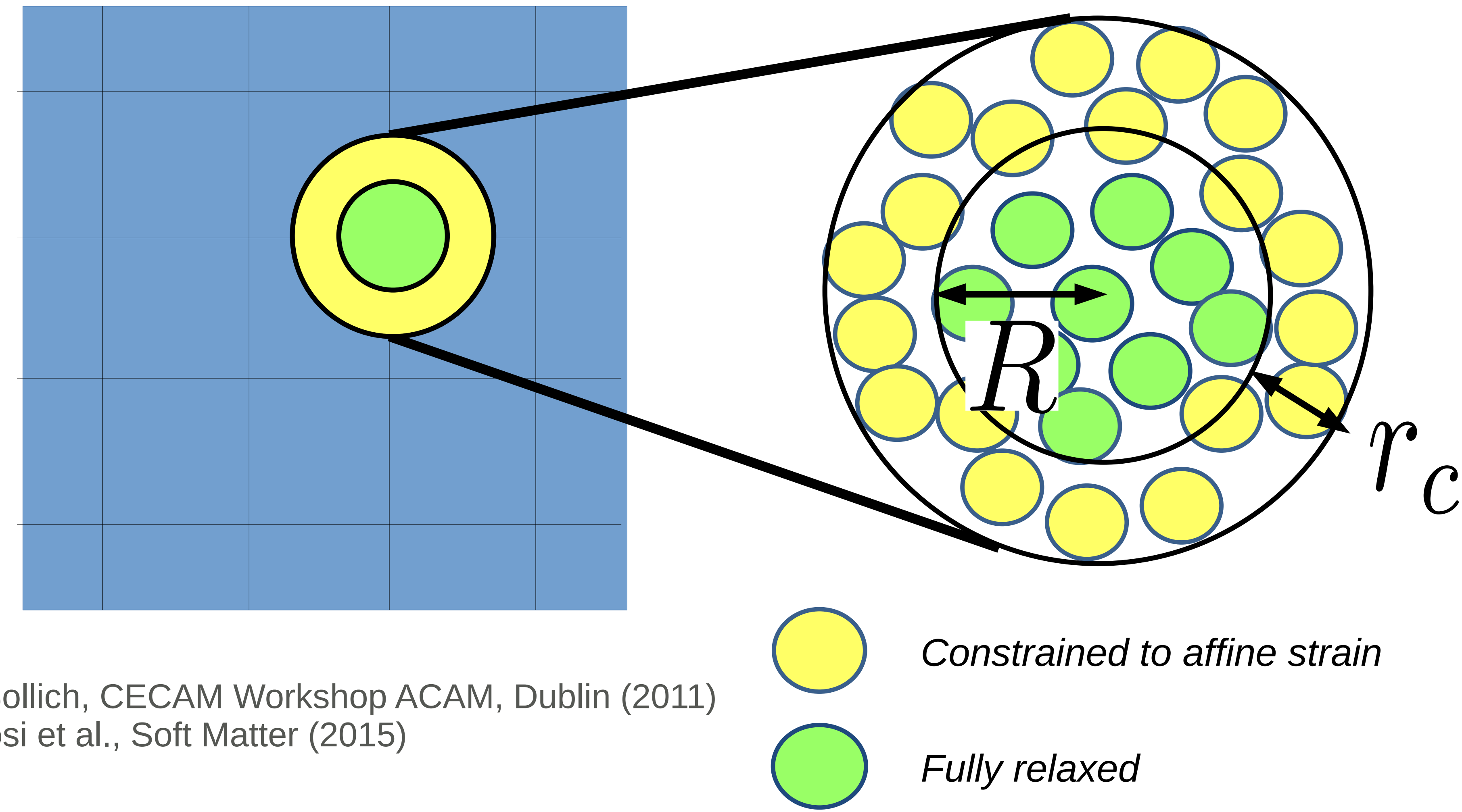


A. Widmer-Cooper et al. Phys. Rev. Lett., **93**, 135701 (2004)

⇒ Dynamical heterogeneities whose spatial fluctuations increase (at t ~ τ_α) as the temperature decreases

Method to probe the local yield stresses

Idea: Local loading with constrained boundary conditions



P. Sollich, CECAM Workshop ACAM, Dublin (2011)
Puosi et al., Soft Matter (2015)

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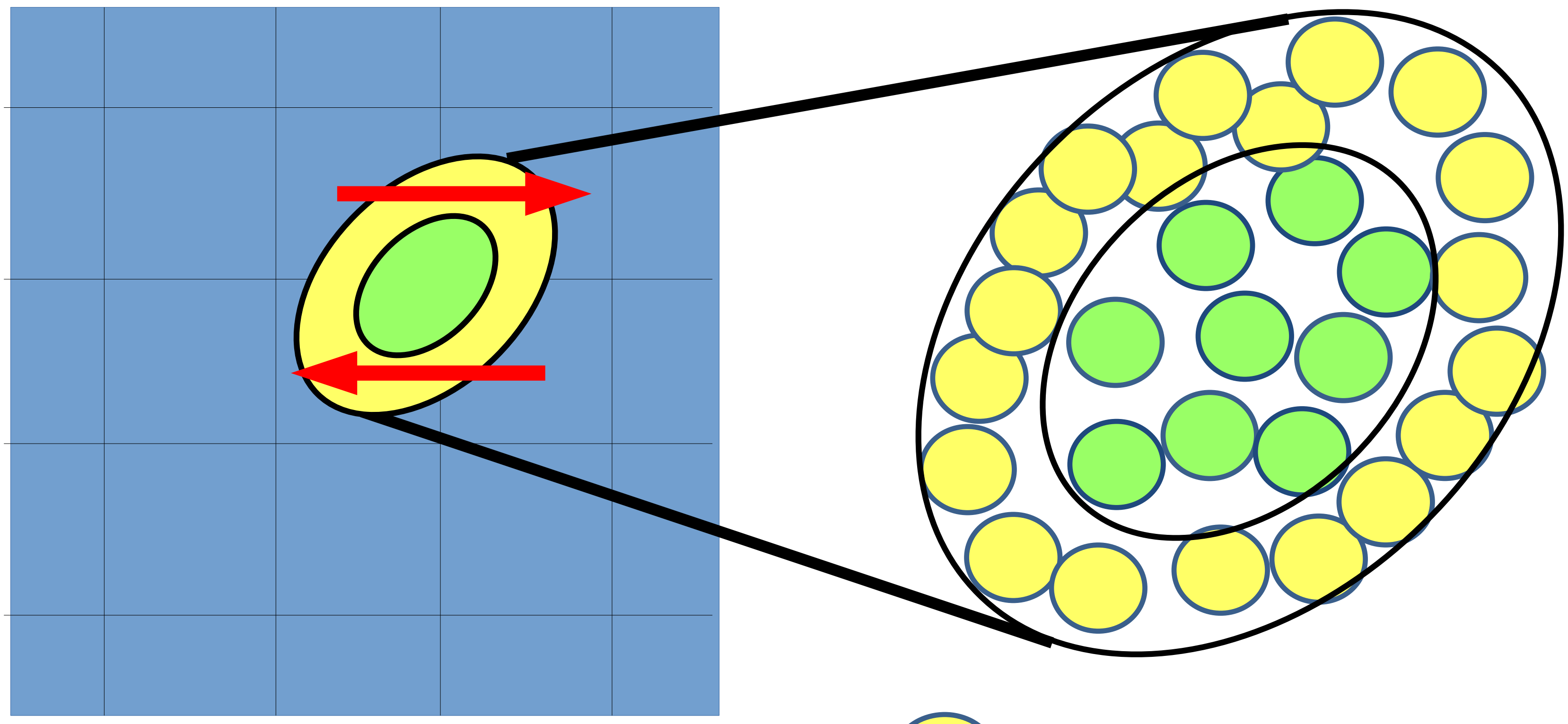

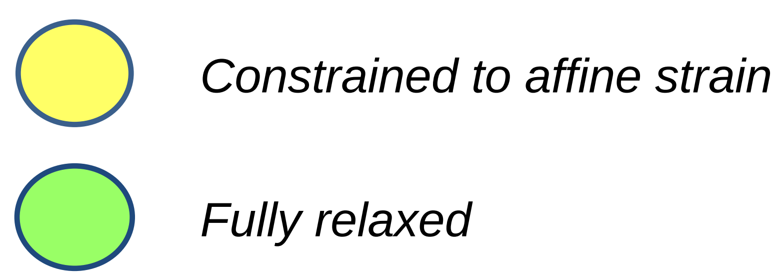

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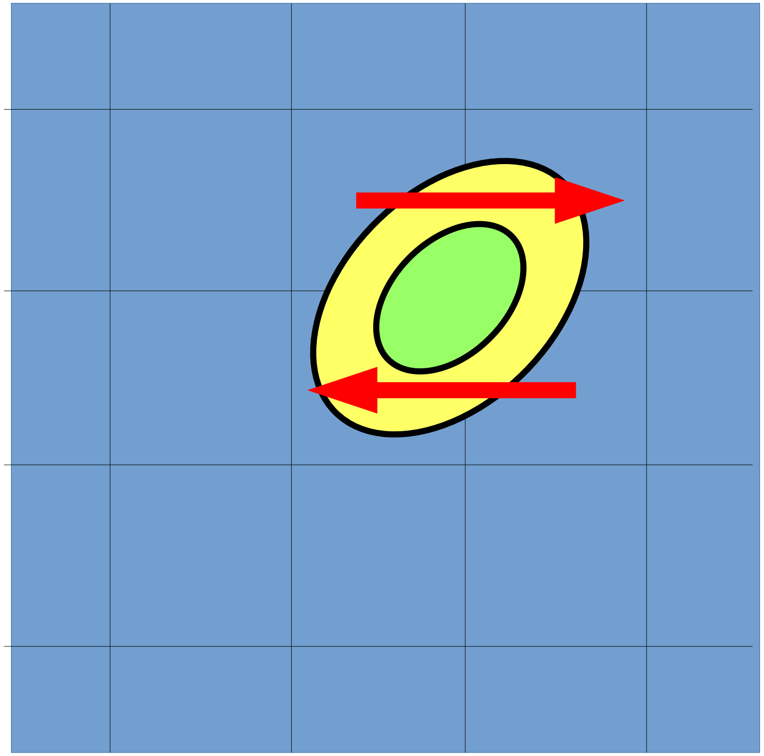
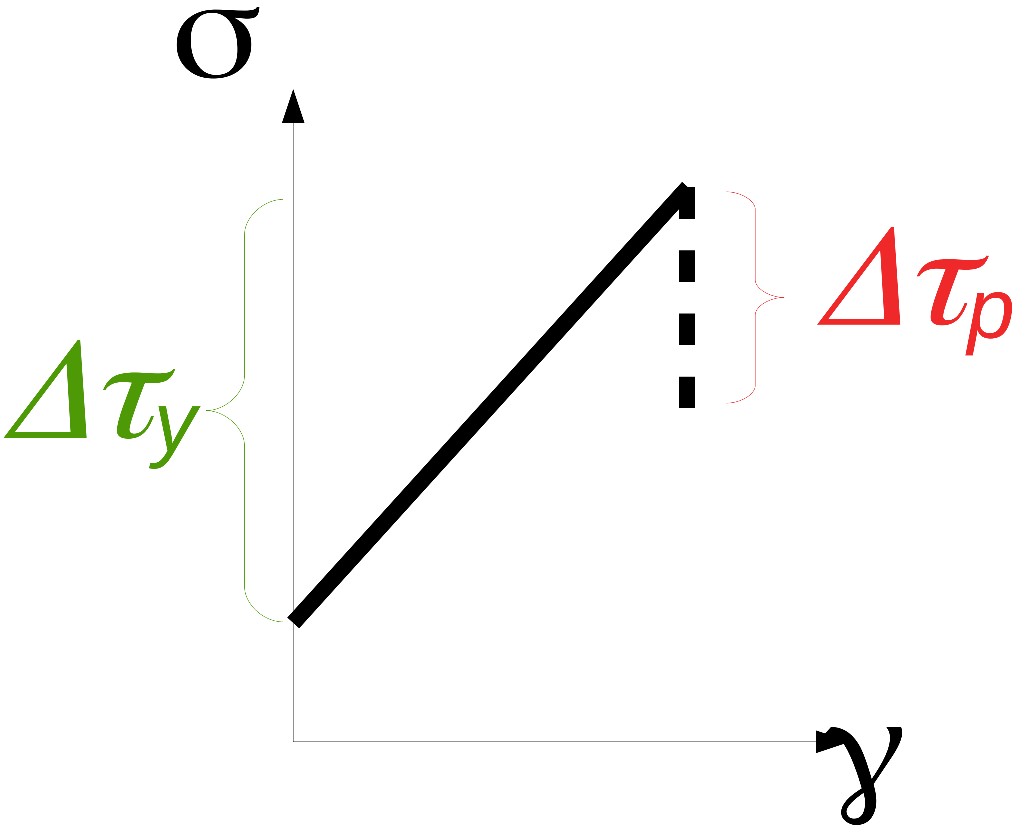
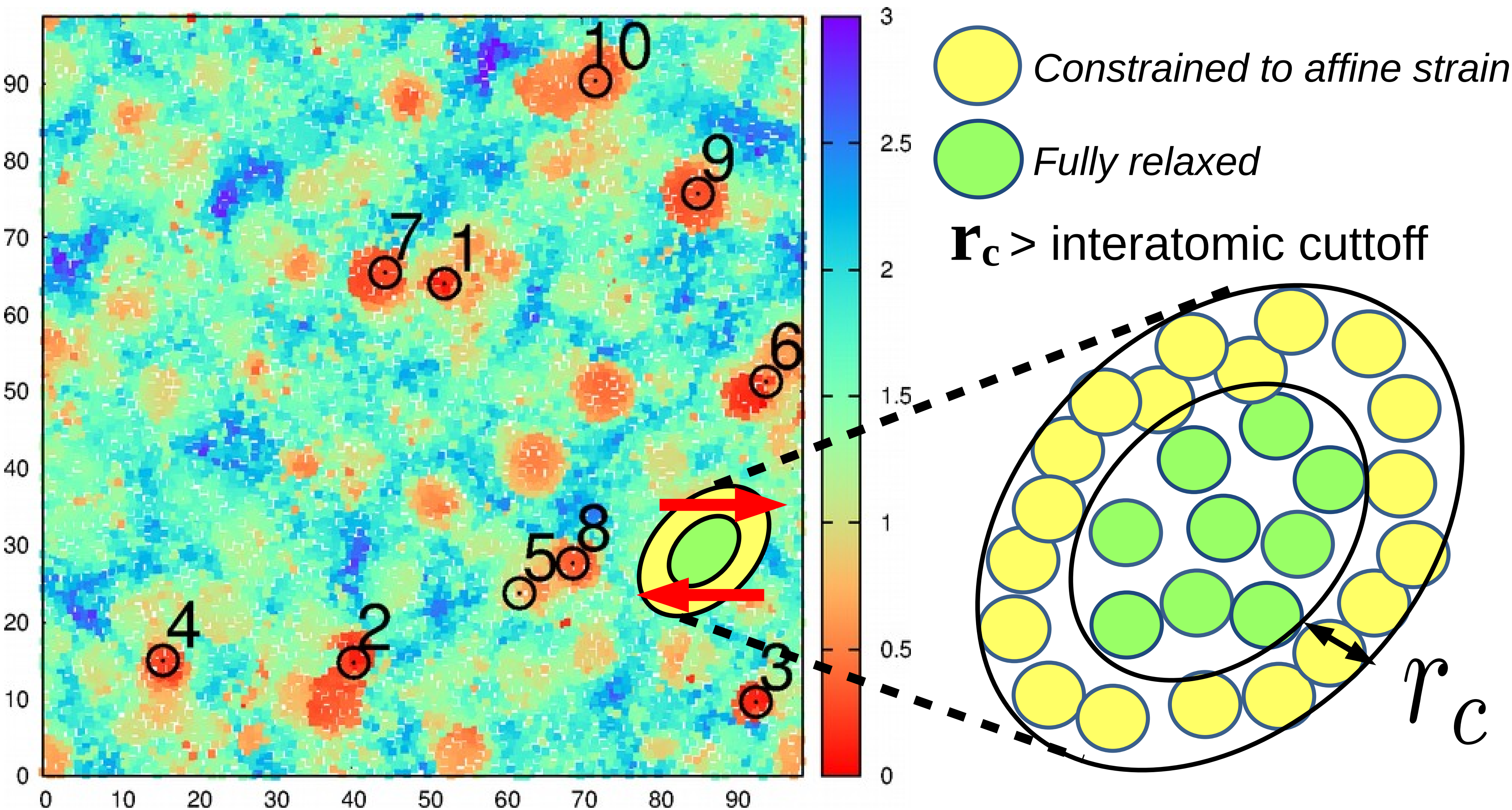




P. Sollich, CECAM Workshop ACAM, Dublin (2011)
Puosi et al., Soft Matter (2015)

S. Patinet, D. Vandembroucq and M. Falk, Phys. Rev. Lett. ***117****, 045501 (2016)*
A. Barbot, M. Lerbinger, A. Hernandez, R. García, M. Falk, D. Vandembroucq and S. Patinet, PRE ***97****, 033001 (2018)*

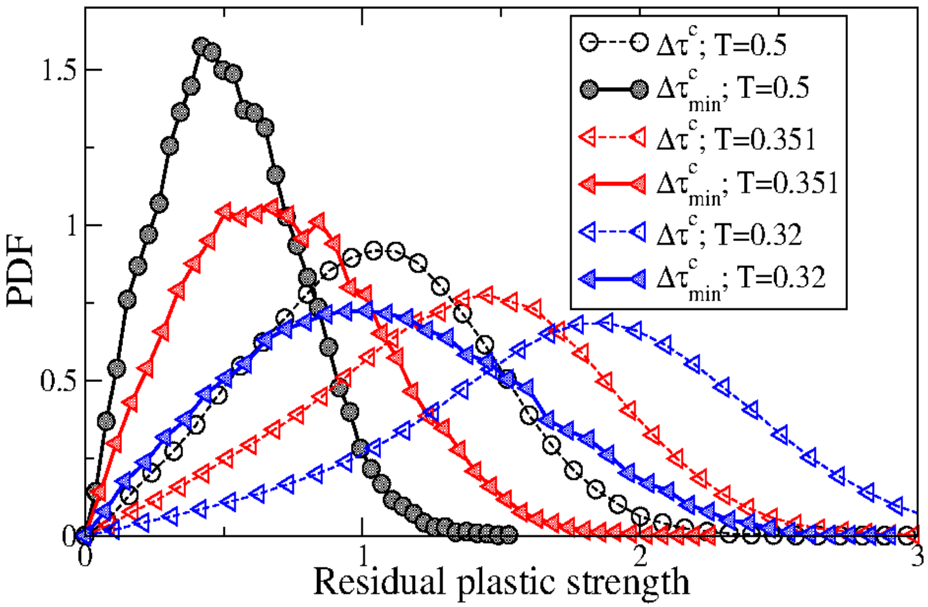
Local yield stress fields



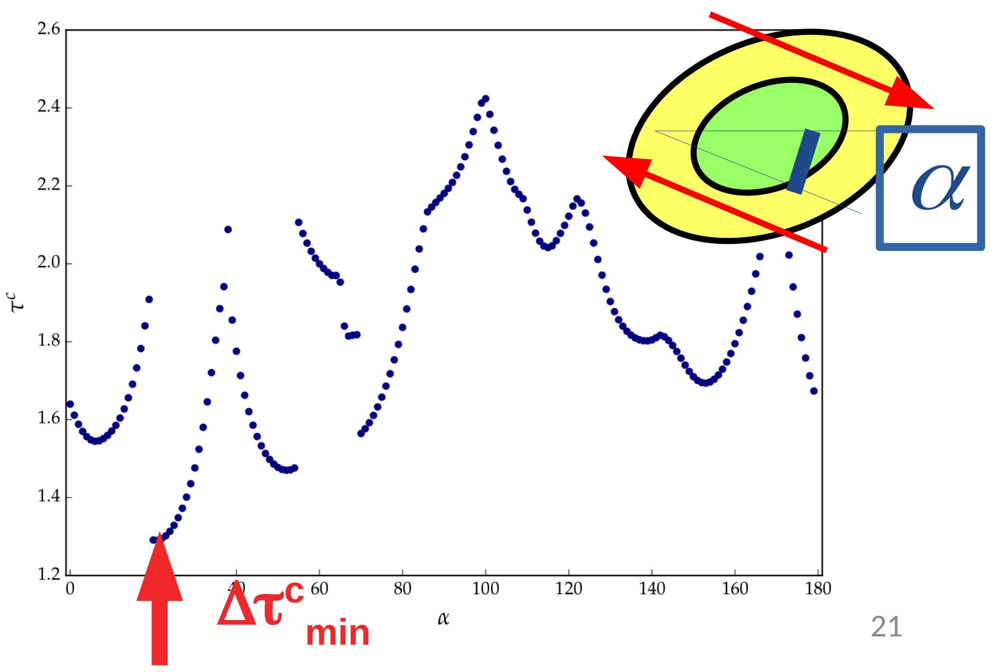
=> Method of **order ~ N** (can handle large system sizes) that measures of a slip threshold field with controlled ***spatial sampling*** and ***orientation***, which is ***non-perturbative*** and shows excellent ***correlation*** with plastic rearrangement locations (symbols numbered by order of appearance during remote loading).

Local yield stress statistics

Thresholds increase as the temperature is lowered



Consider the softest direction : $\Delta\tau^c_{min}$



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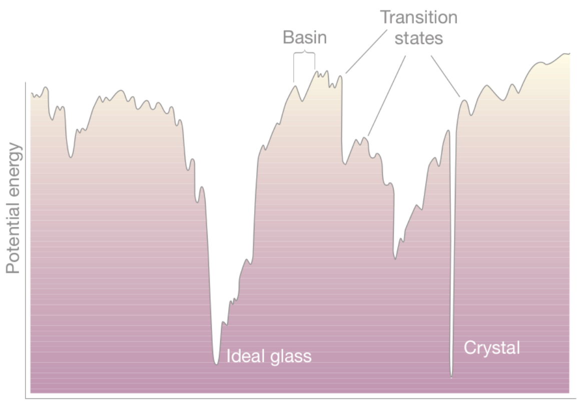

Debenedetti and Stillinger, Nat. (2001)

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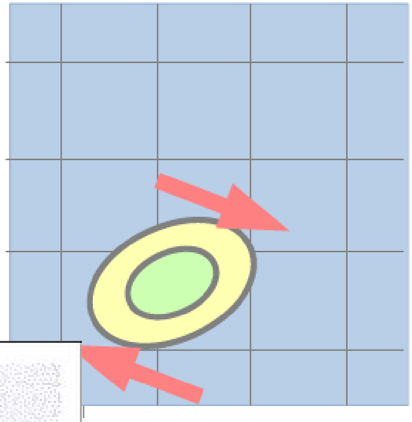

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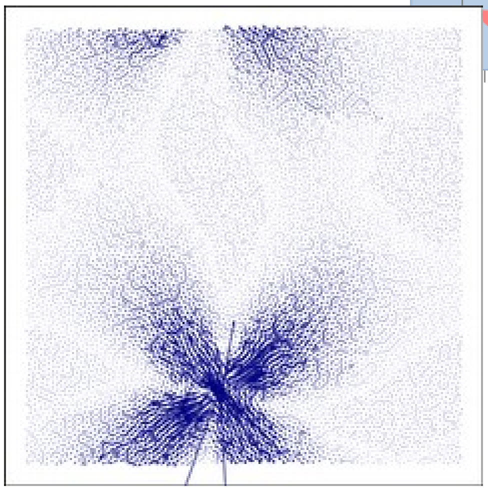
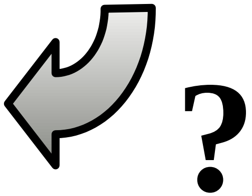
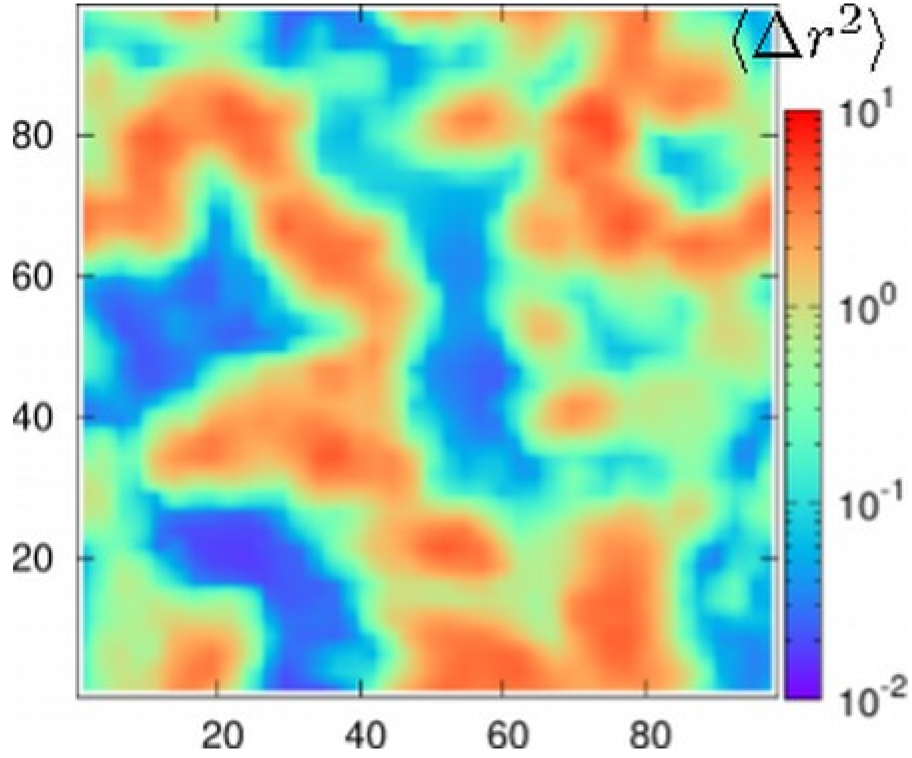


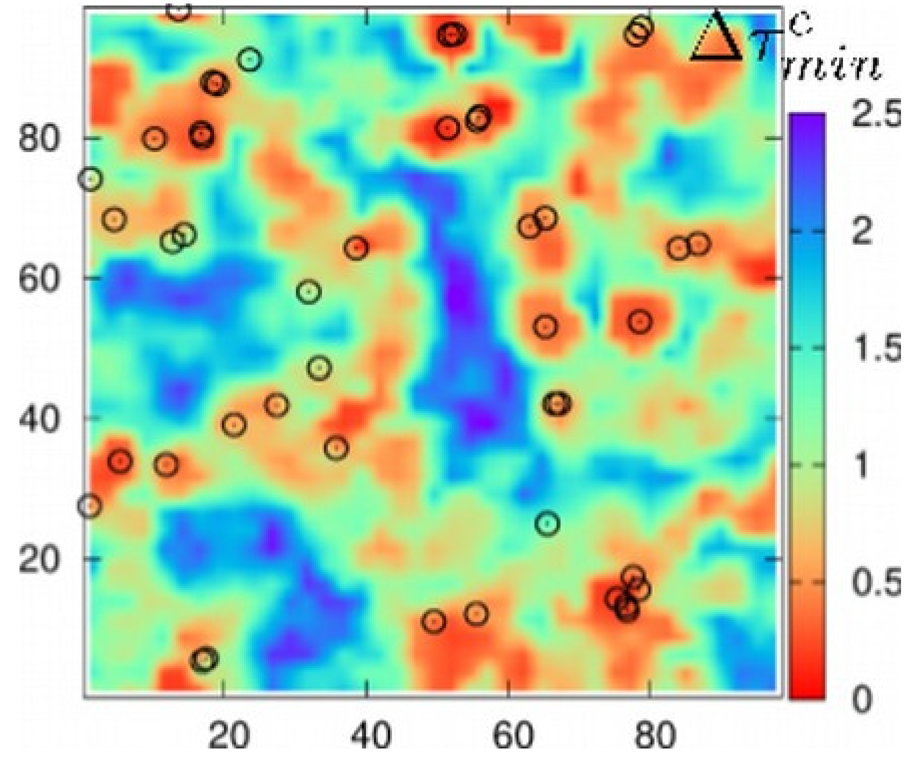


Correlation between propensity and $\Delta\tau^c_{min}$

Propensity at t ~ τ_α

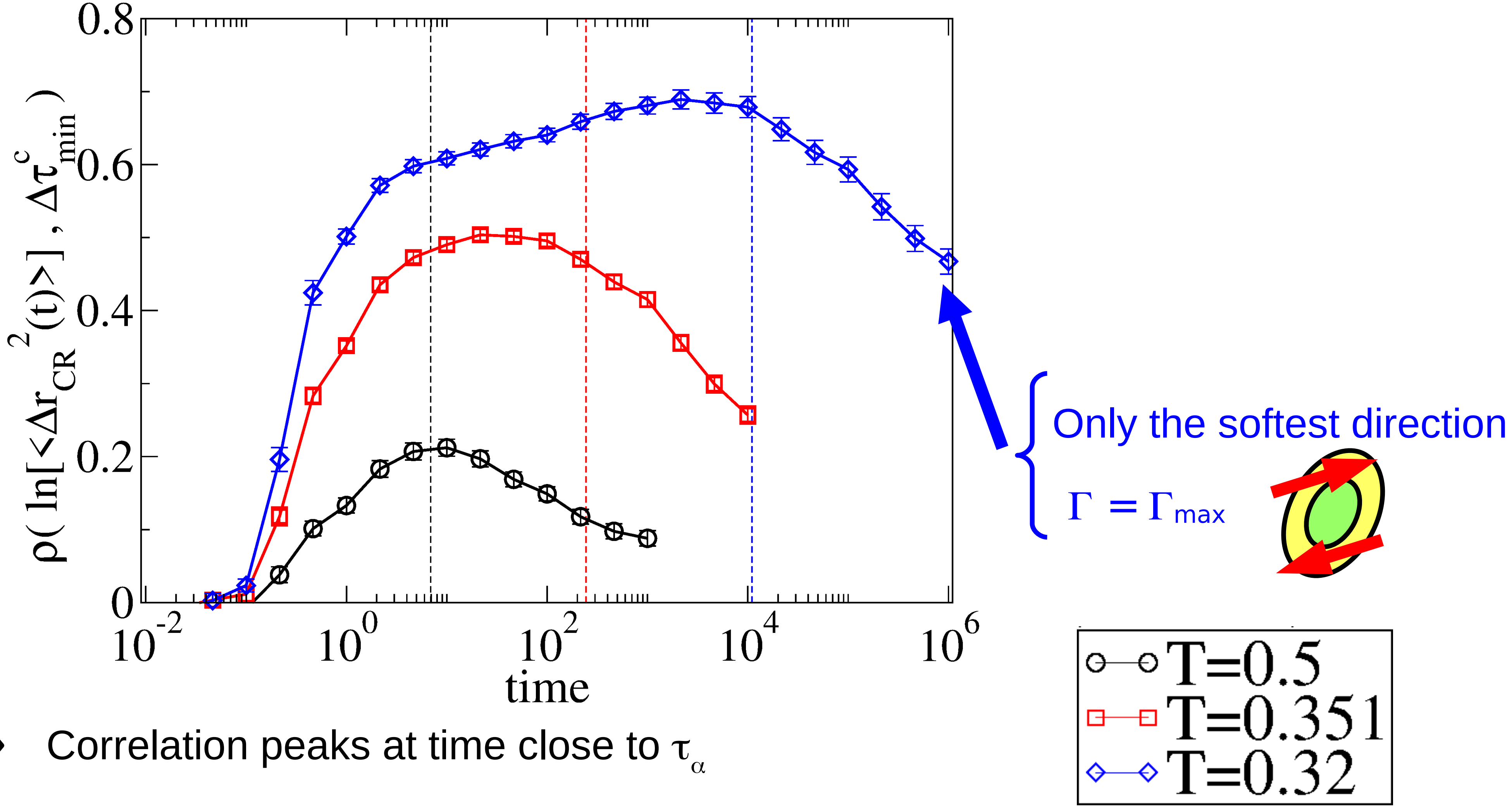


Local yield stress along the softest direction



Correlation between propensity and $\Delta\tau^{c}_{min}$

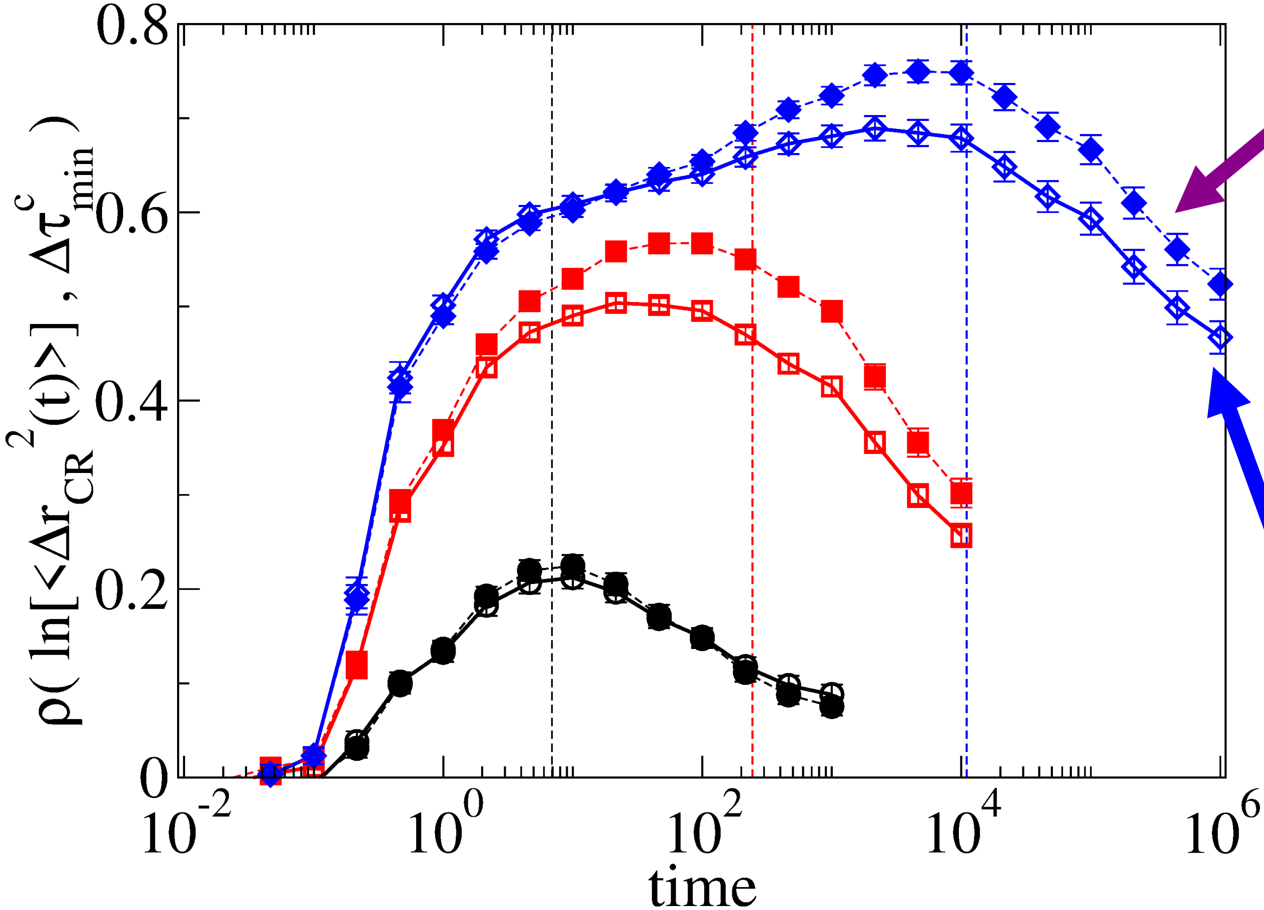
Pearson correlation



- Correlation peaks at time close to τ_{α}
- Correlation decreases with parent temperature

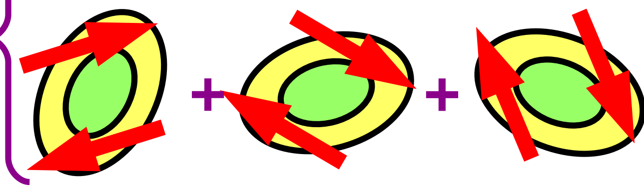
Correlation between propensity and $\Delta\tau^{c}_{min}$

Pearson correlation



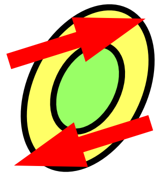
All soft directions

$\Gamma = \Sigma_i \Gamma_i$



Only the softest direction

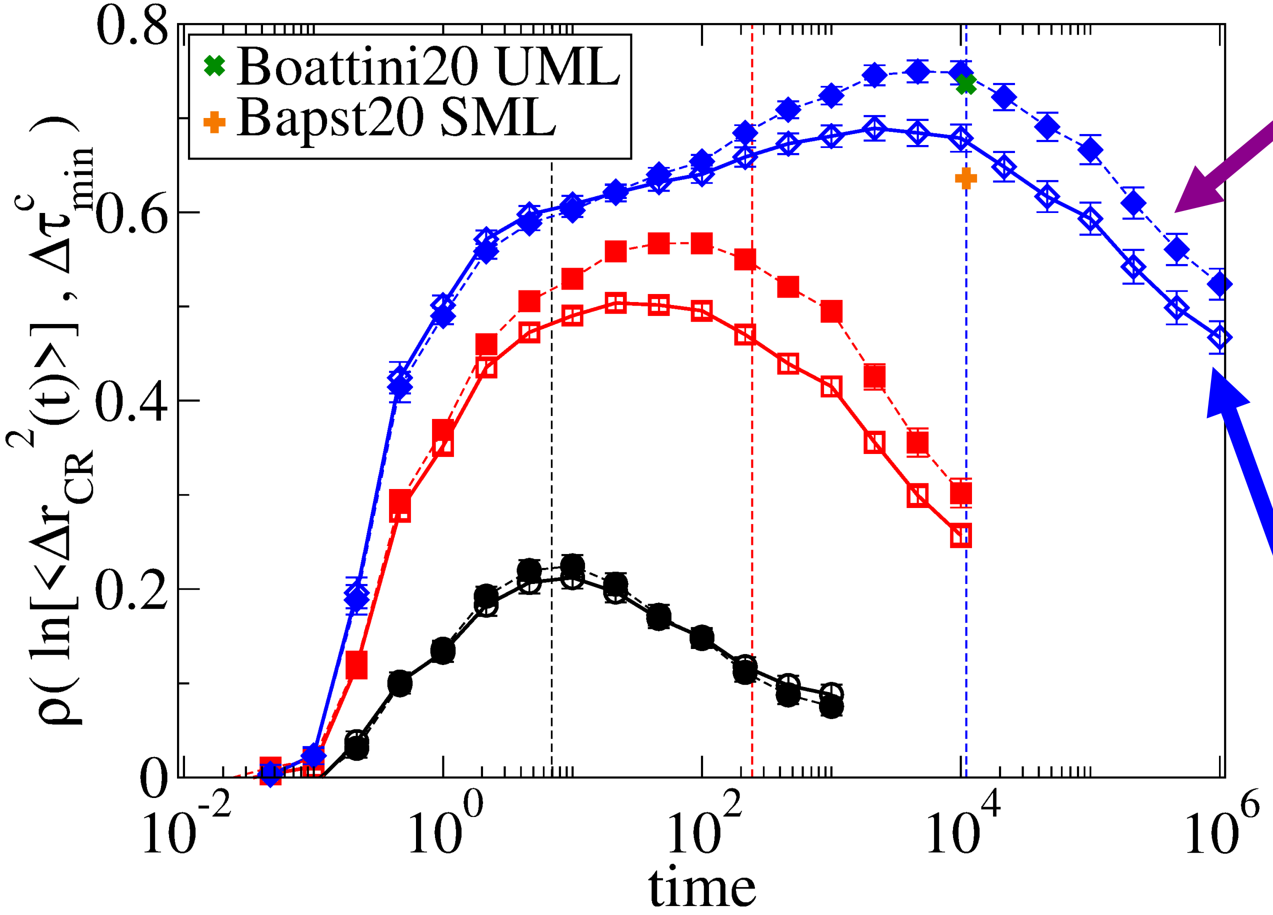
$\Gamma = \Gamma_{max}$

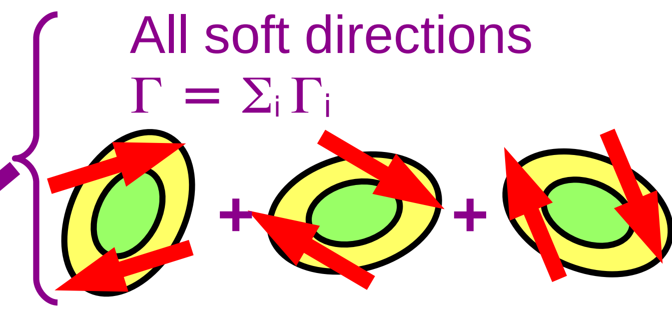


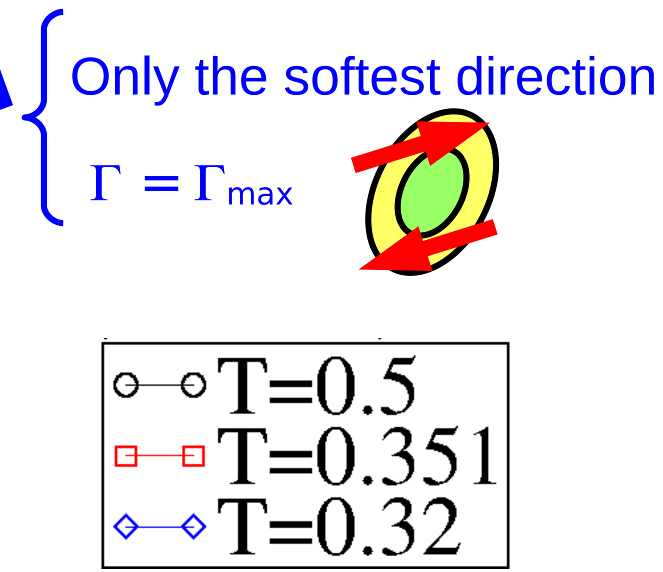
- Correlation peaks at time close to τ_α
- Correlation decreases with parent temperature

Correlation between propensity and $\Delta\tau^c_{min}$

Pearson correlation



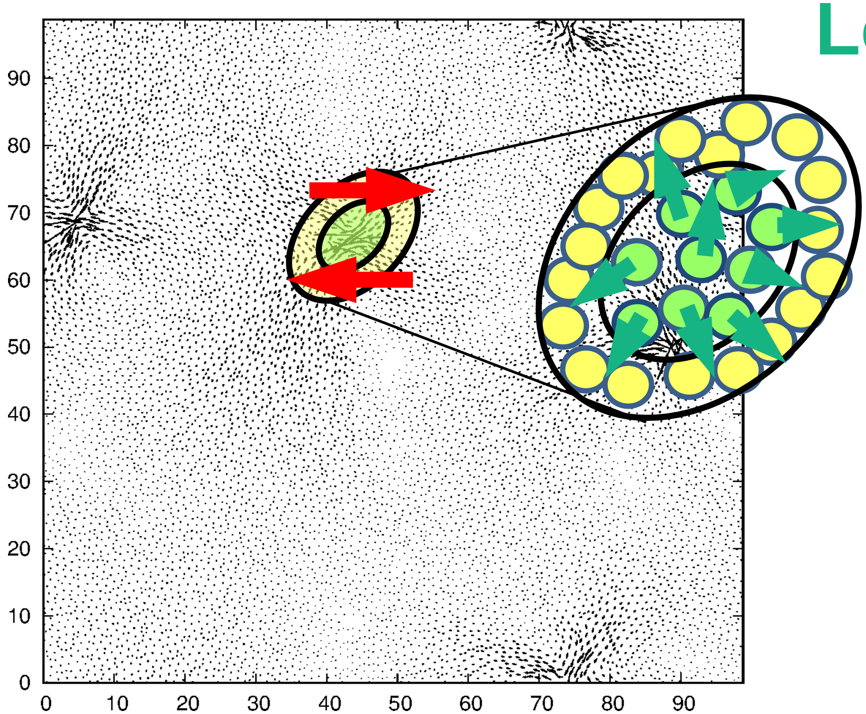




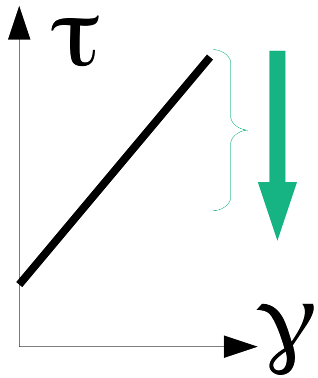
- Correlation peaks at time close to τ_α
- Correlation decreases with parent temperature
- Correlation maximum is comparable with state of the art ML

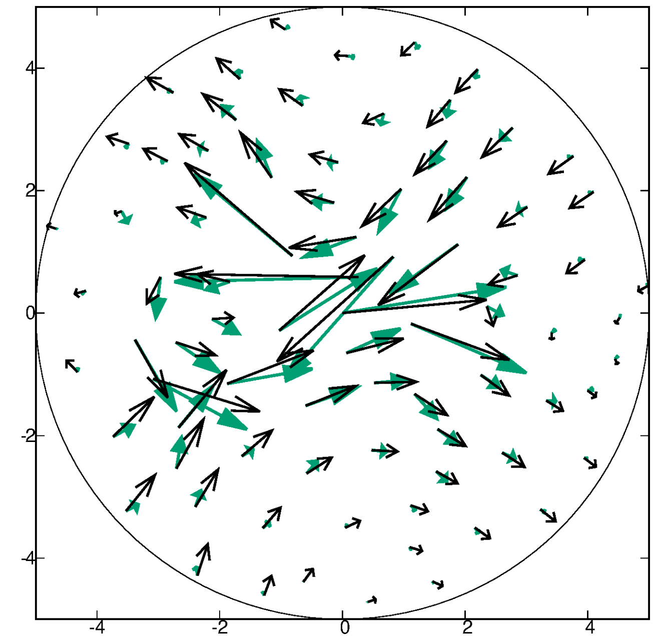
A real space view of core relaxations

Thermal rearrangement



Local shear test

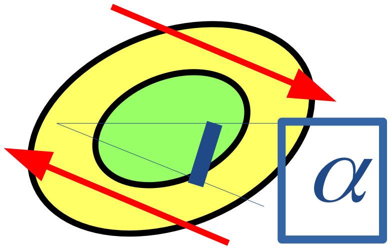


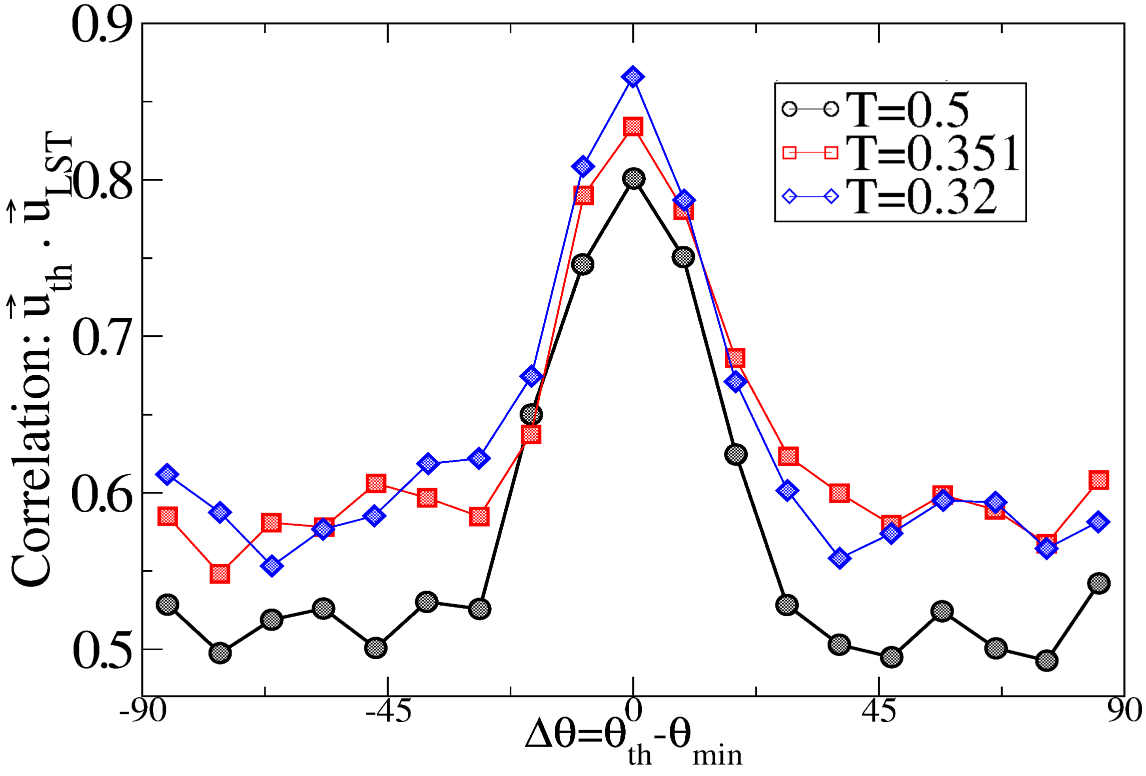


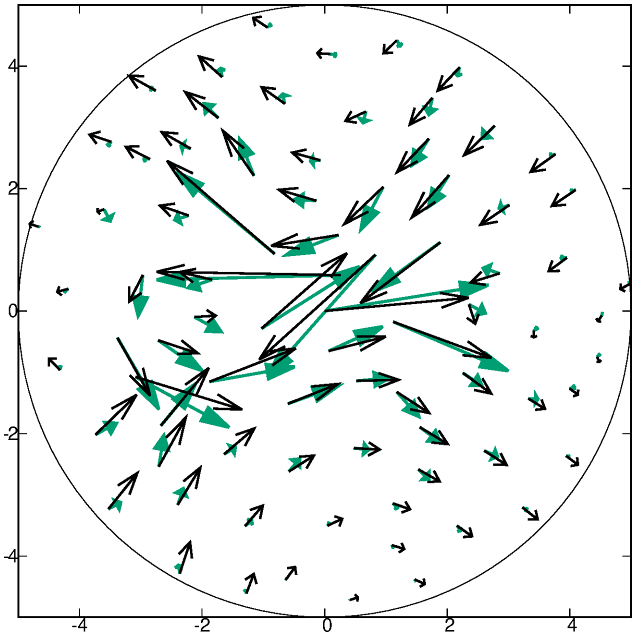
$\vec{u}_{TH}$ $\vec{u}_{LST}$

A real space view of core relaxations

Dot product correlation: $C = \vec{u}_{th} \cdot \vec{u}_{LST}$

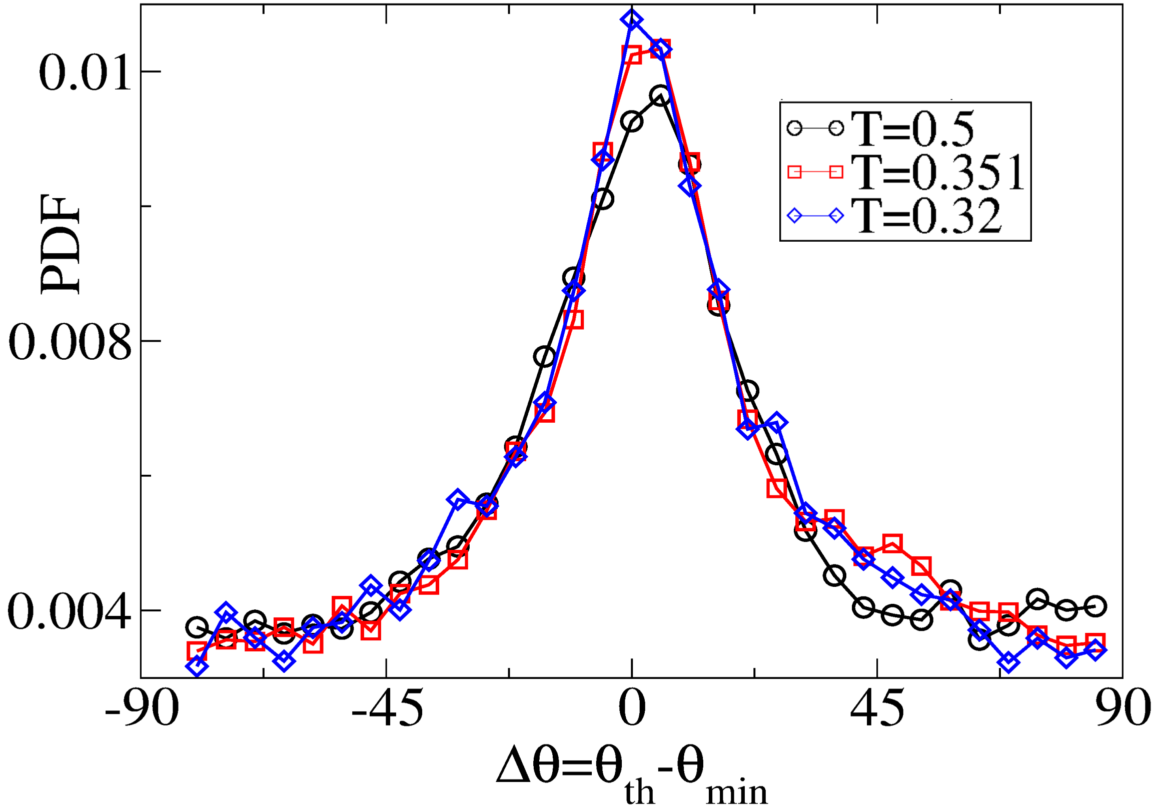


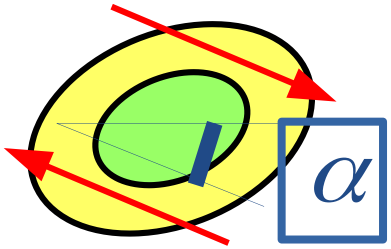


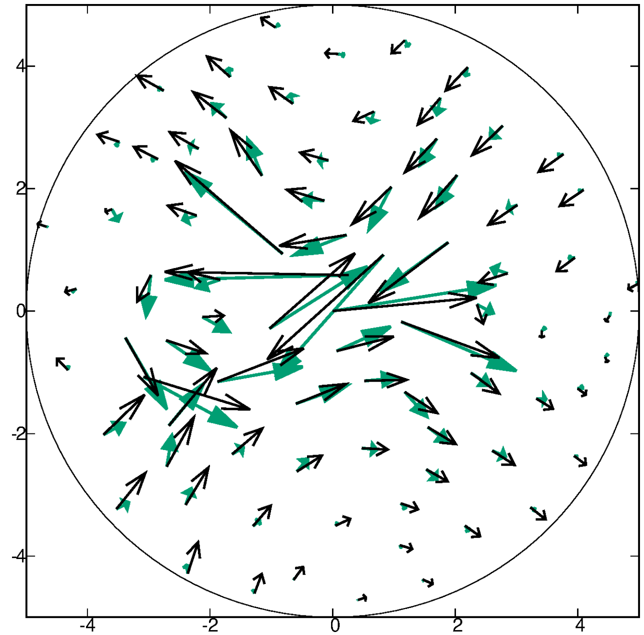


Correlation peaks in the vicinity of the softest shear direction

A real space view of core relaxations



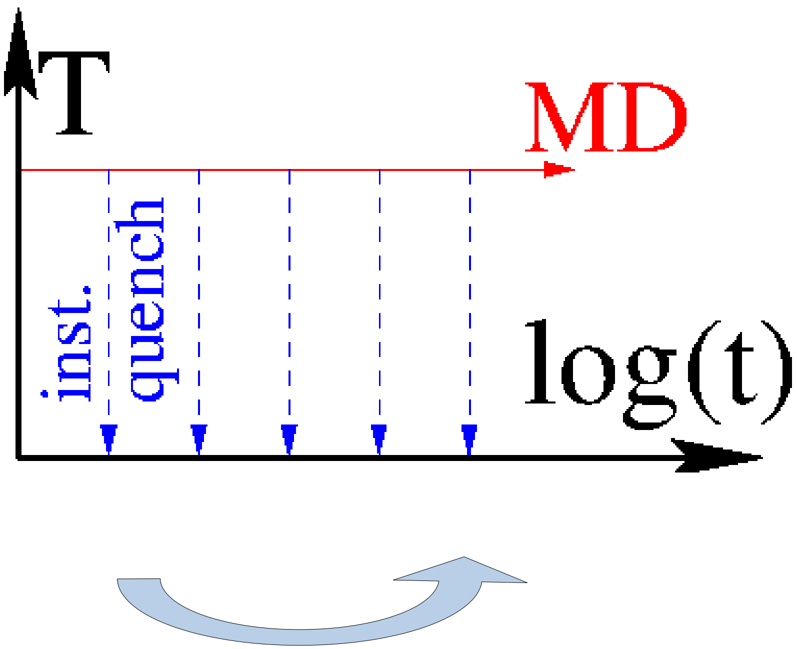




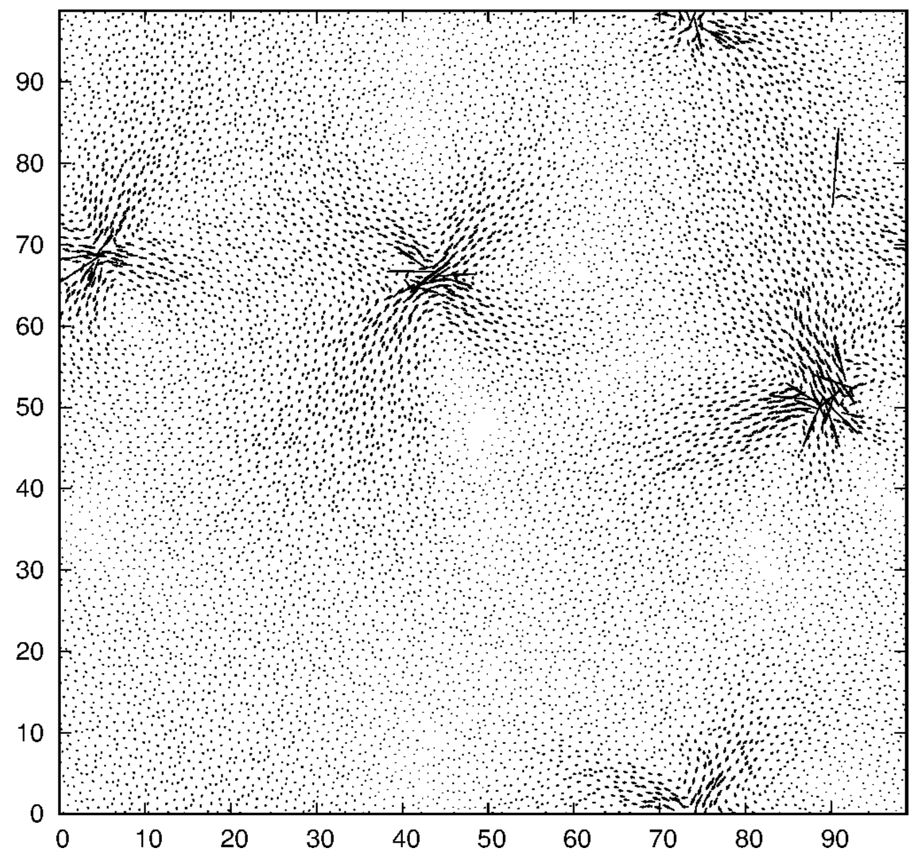
Correlation peaks in the vicinity of the softest shear direction

Rearrangements are more probable along this weak direction

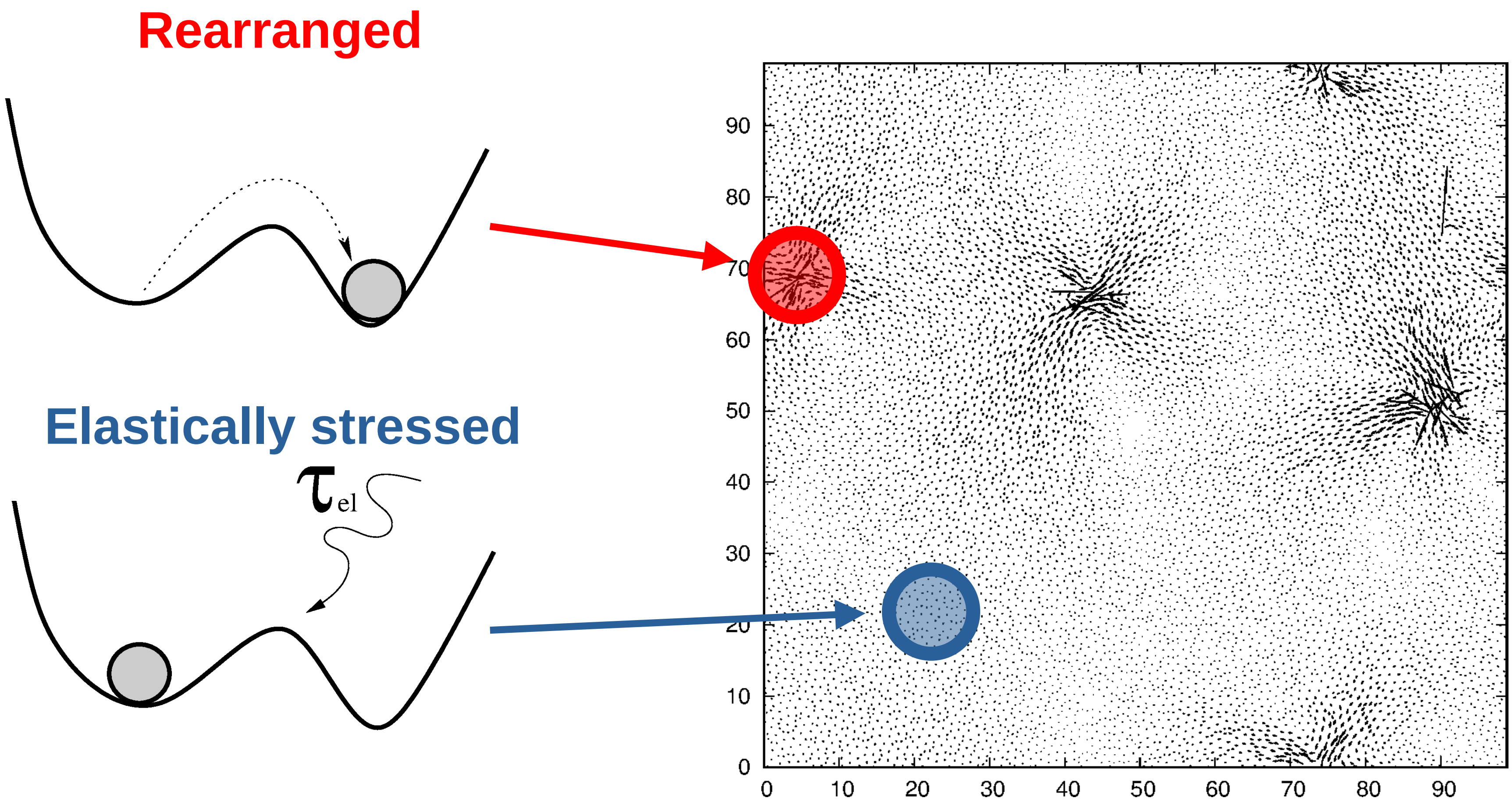
Methods: detection of local rearrangements



$$\overrightarrow{u}_{th}(t,t_0)$$

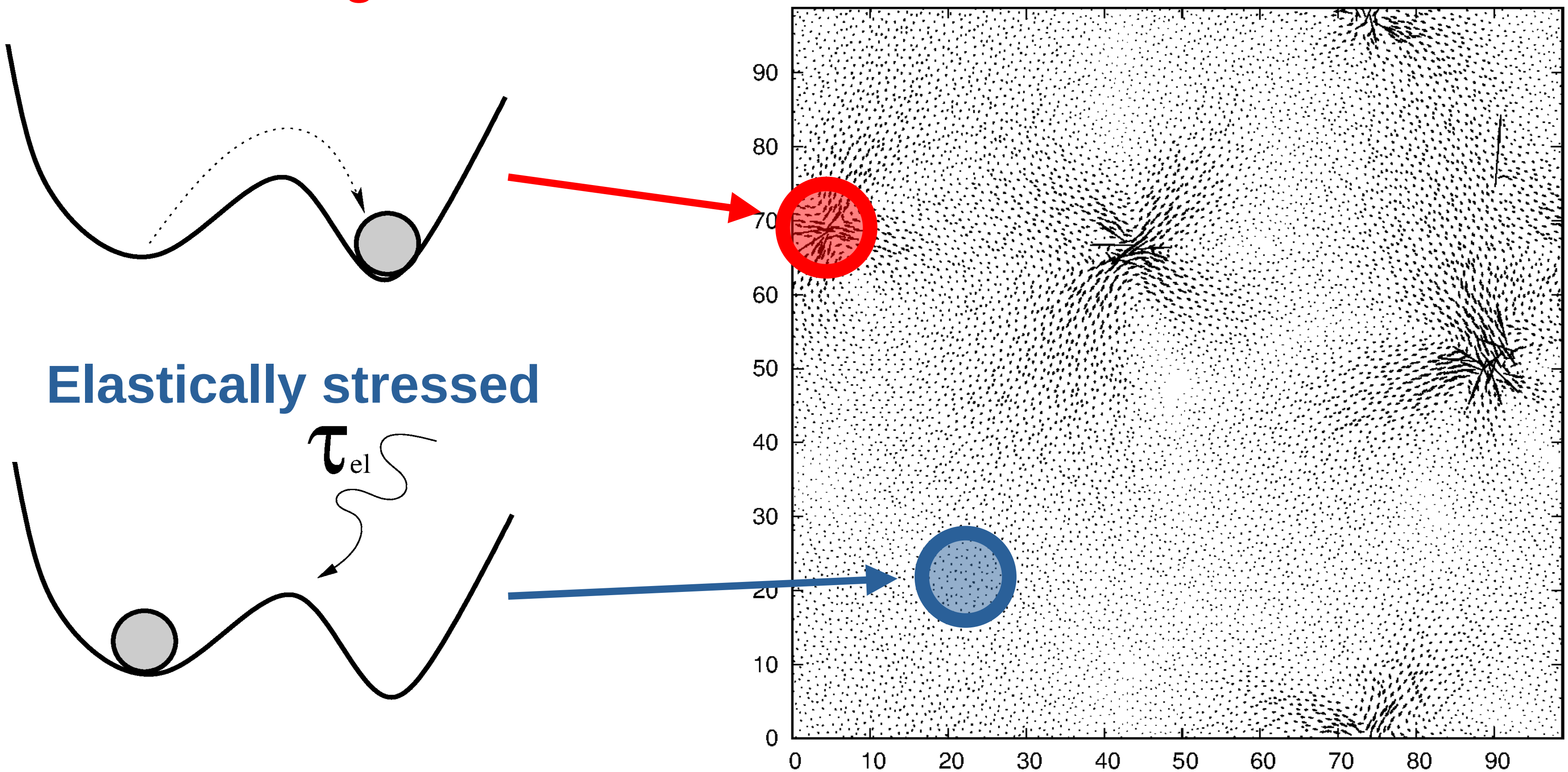


Methods: detection of local rearrangements



Methods: detection of local rearrangements

Rearranged



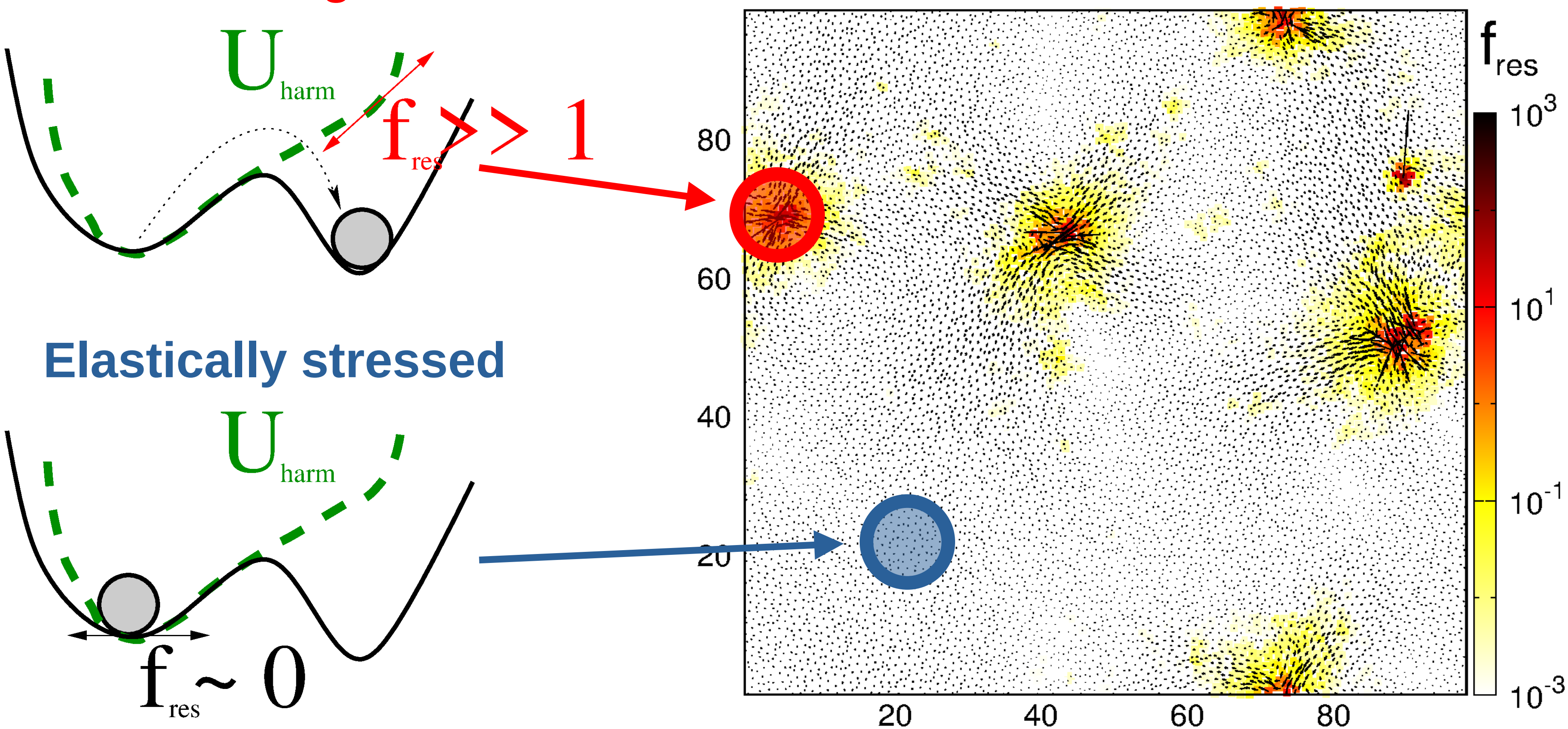
Linear response:

$$\overrightarrow{f}_{lin} = H_{t_0}\overrightarrow{u}_{th}(t, t_0)$$

A. Lemaître, Phys. Rev. Lett., **113**, 245702 (2014)

Methods: detection of local rearrangements

Rearranged



➡ Location of rearrangements

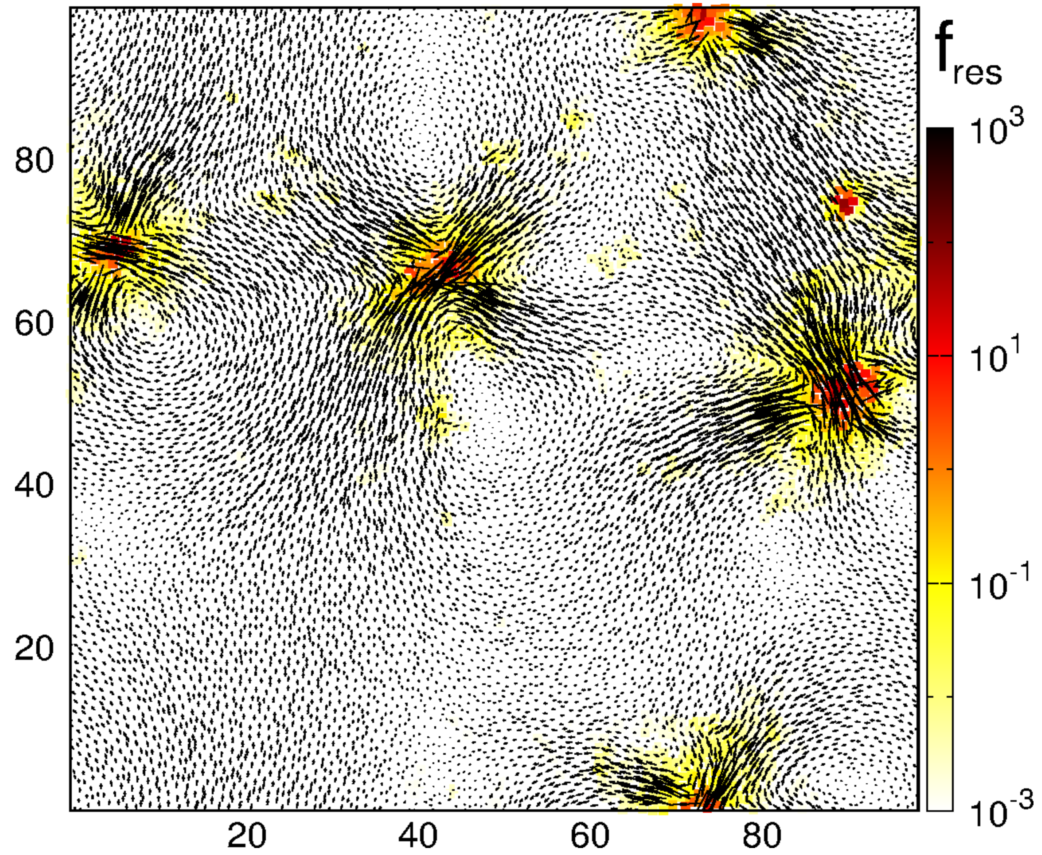
Linear response:

$$\overrightarrow{f}_{lin} = H_{t_0} \overrightarrow{u}_{th}(t, t_0)$$

A. Lemaître, Phys. Rev. Lett., **113**, 245702 (2014)

Methods: detection of local rearrangements

Displacement field of elastically stressed regions



Linear response:

$$\overrightarrow{f}_{lin} = H_{t_0} \overrightarrow{u}_{th}(t, t_0)$$

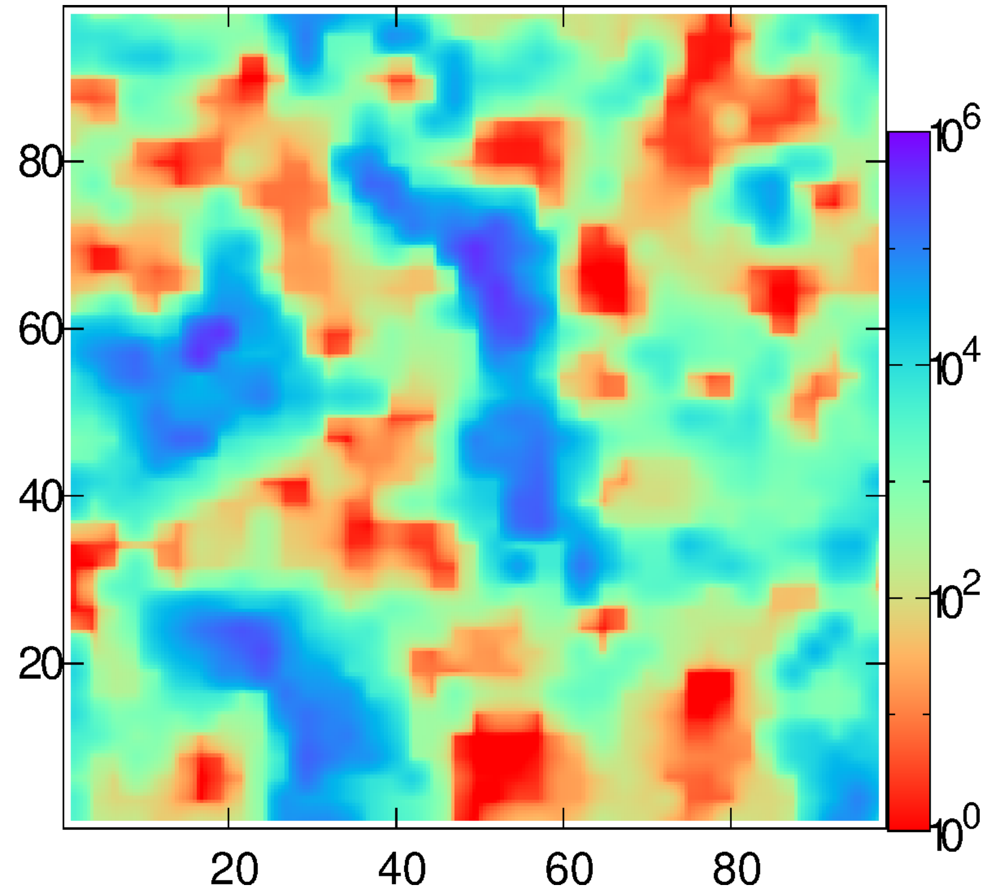
A. Lemaître, Phys. Rev. Lett., **113**, 245702 (2014)

➡ Location of rearrangements

➡ Long-range shear-like signature

Methods: detection of local rearrangements

$$\langle t_{FP} \rangle$$



- Location of rearrangements
- Long-range shear-like signature
- First passage time

Linear response:

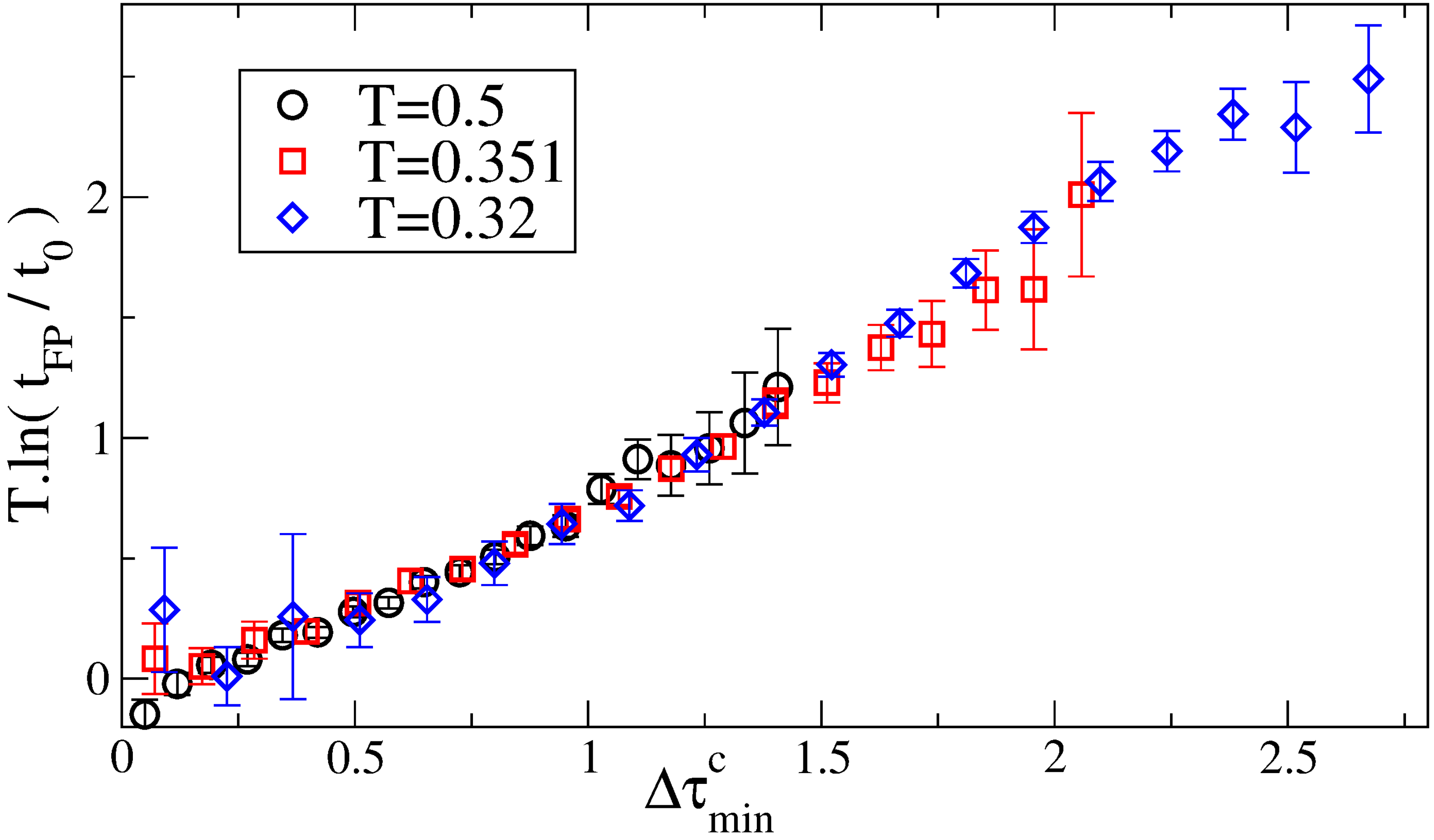
$$\overrightarrow{f}_{lin} = H_{t_0} \overrightarrow{u}_{th}(t, t_0)$$

A. Lemaître, Phys. Rev. Lett., **113**, 245702 (2014)

Scaling of energy barriers

Assuming a simple Arrhenius behavior:

$$t = t0.e^{\Delta U/kT} \quad \text{with } \Delta U = Cst.(\Delta\tau^{c}_{min})^{\delta}$$



Scaling of energy barriers

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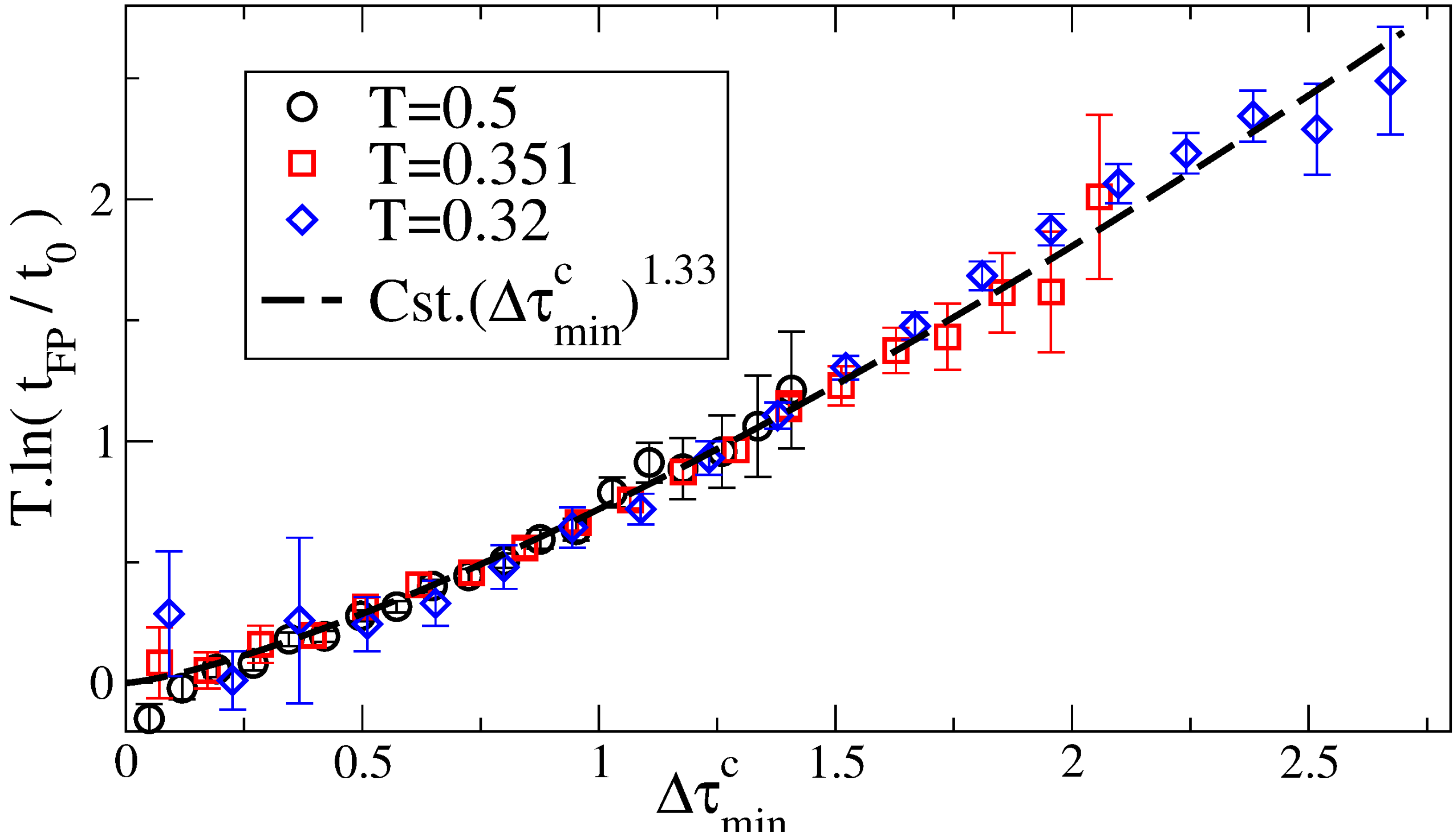
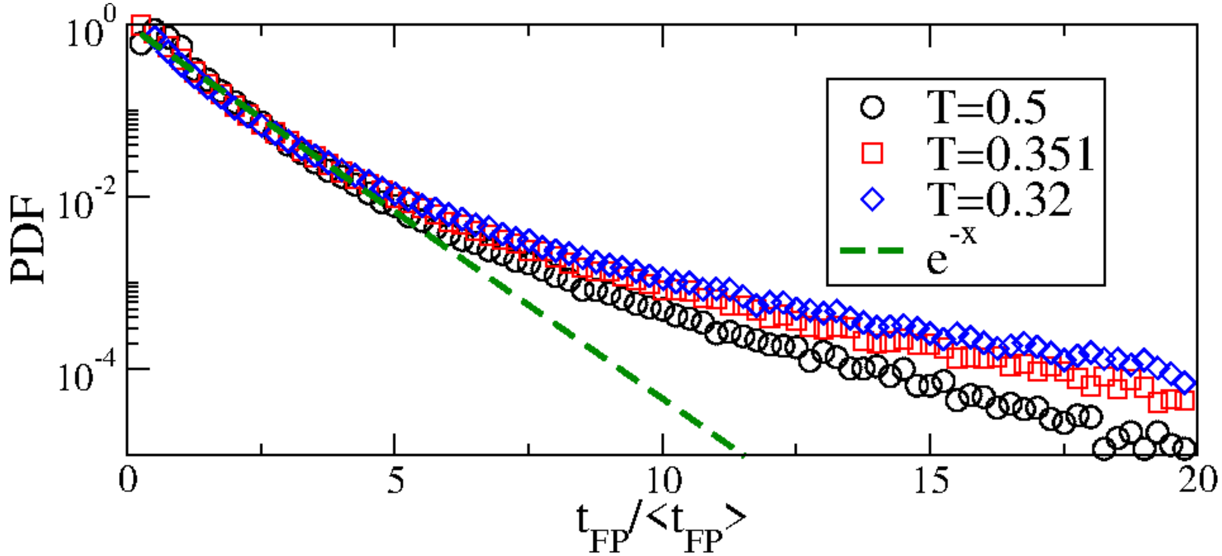


Compatible with the catastrophe theory scaling (δ = 3/2 = 1.5)
C. E. Maloney and D. J. Lacks, Phys. Rev. E, **73**, 061106 (2006)

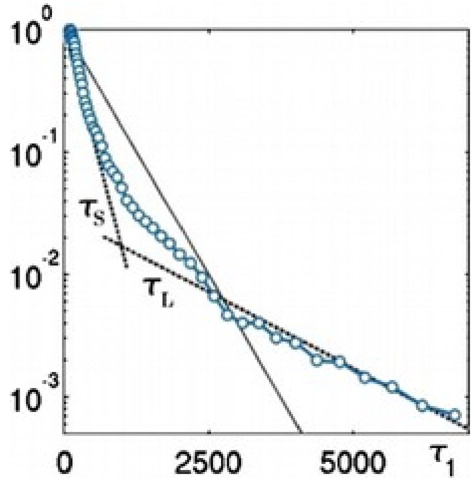
but much closer from nonlinear quasilocalized excitation scaling (δ = 4/3 = 1.33)
G. Kapteijns, D. Richard, and E. Lerner, Phys. Rev. E **101**, 032130 (2020)

First passage time statistics

Anomalous long tails

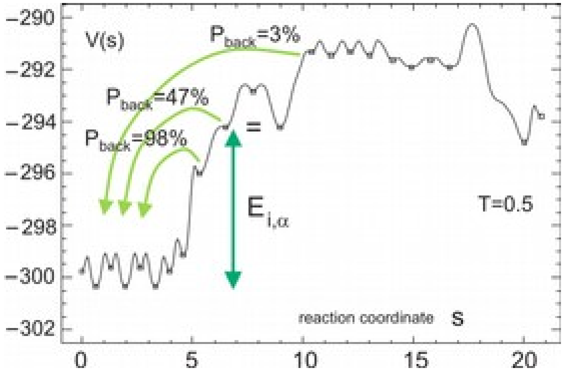


Resulting from aggregated jump clusters into avalanches?



R. Candelier et al., Phys. Rev. Lett. **105** (2010)

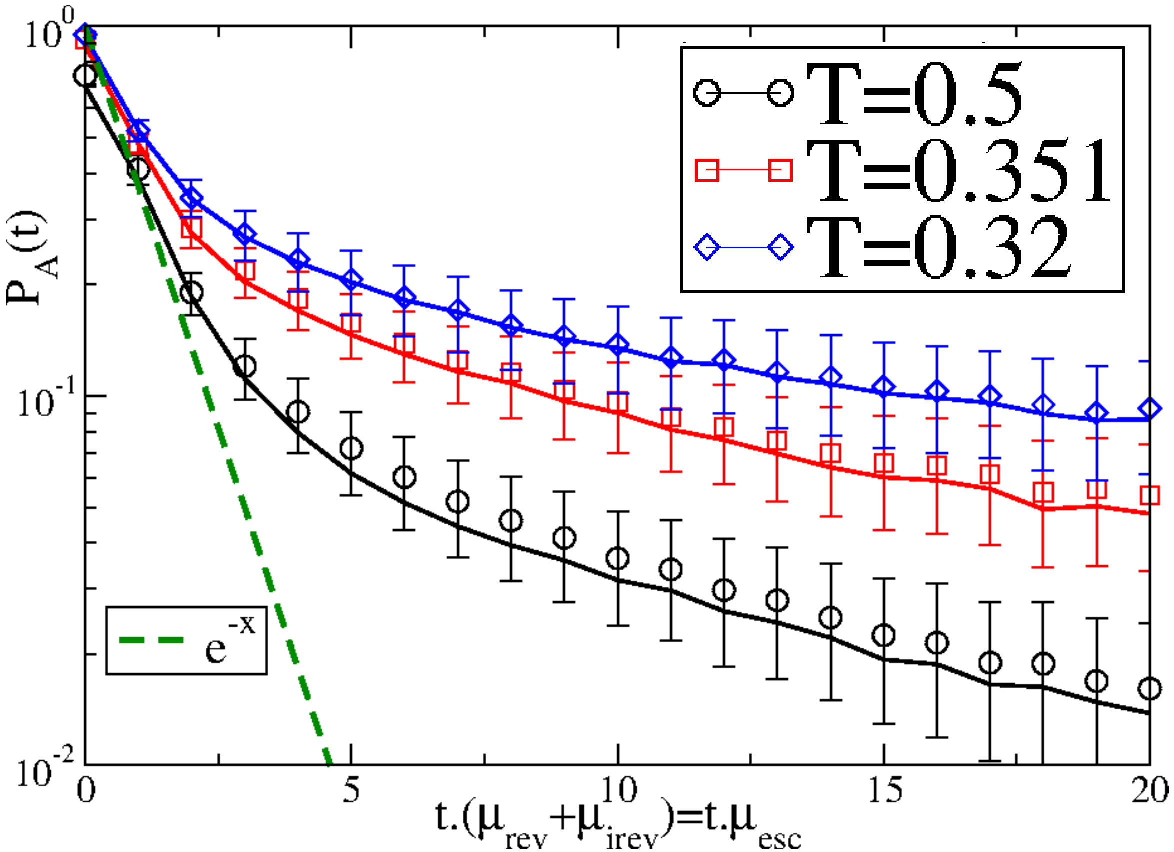
Escape processes of the meta basins correspond to complicated multiminima sequences?

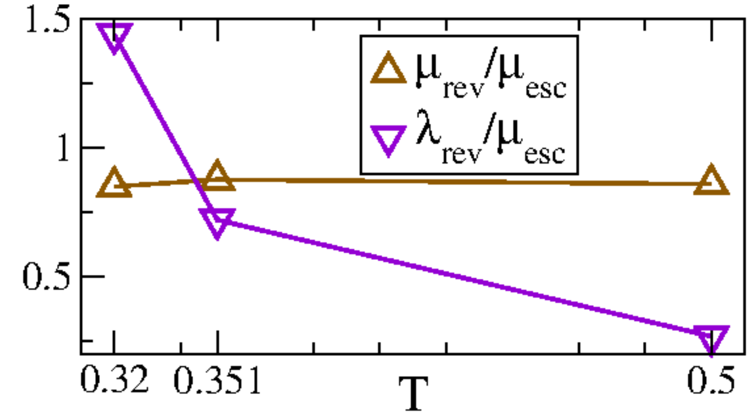


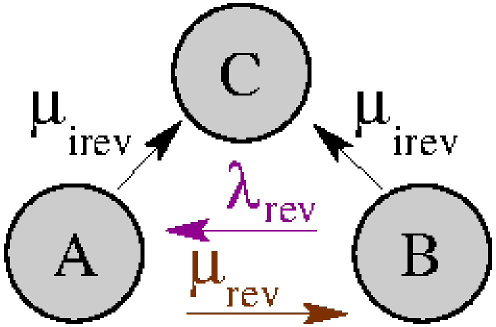
A. Heuer, J. Phys. Condens. Matter, **20**, 373101 (2008)

First passage time statistics

Probability to be in the initial state







$$P_A(t) = \frac{\lambda_{rev}(1-\phi_C)e^{-\mu_{irev}t}}{\mu_{rev}+\lambda_{rev}} + \frac{(\mu_{rev}-\phi_B(\lambda_{rev}+\mu_{rev})-\mu_{rev}\phi_C)e^{-(\mu_{irev}+\mu_{rev}+\lambda_{rev})t}}{\mu_{rev}+\lambda_{rev}}$$

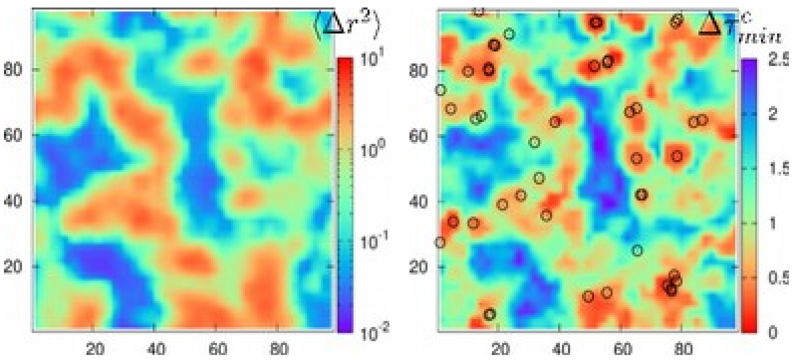
Back and forth motions modelled as a continuous 3-states Markov chain

➡ Reversible events relative rates which increase as the temperature is lowered

Conclusions

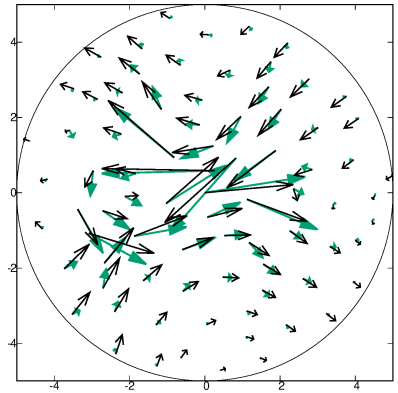
1) Correlations between dynamics and structure

- Correlation between propensity and $\Delta\tau^{c}_{min}$
- Maximum in the vicinity of τ_{α}
- Correlation comparable with ML



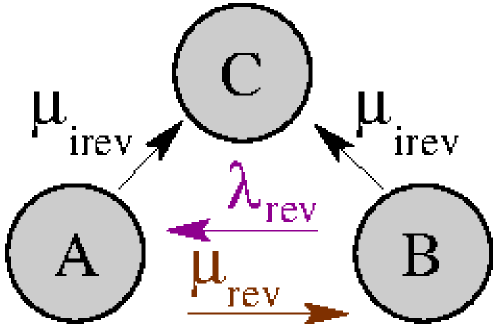
2) Real space picture of relaxations

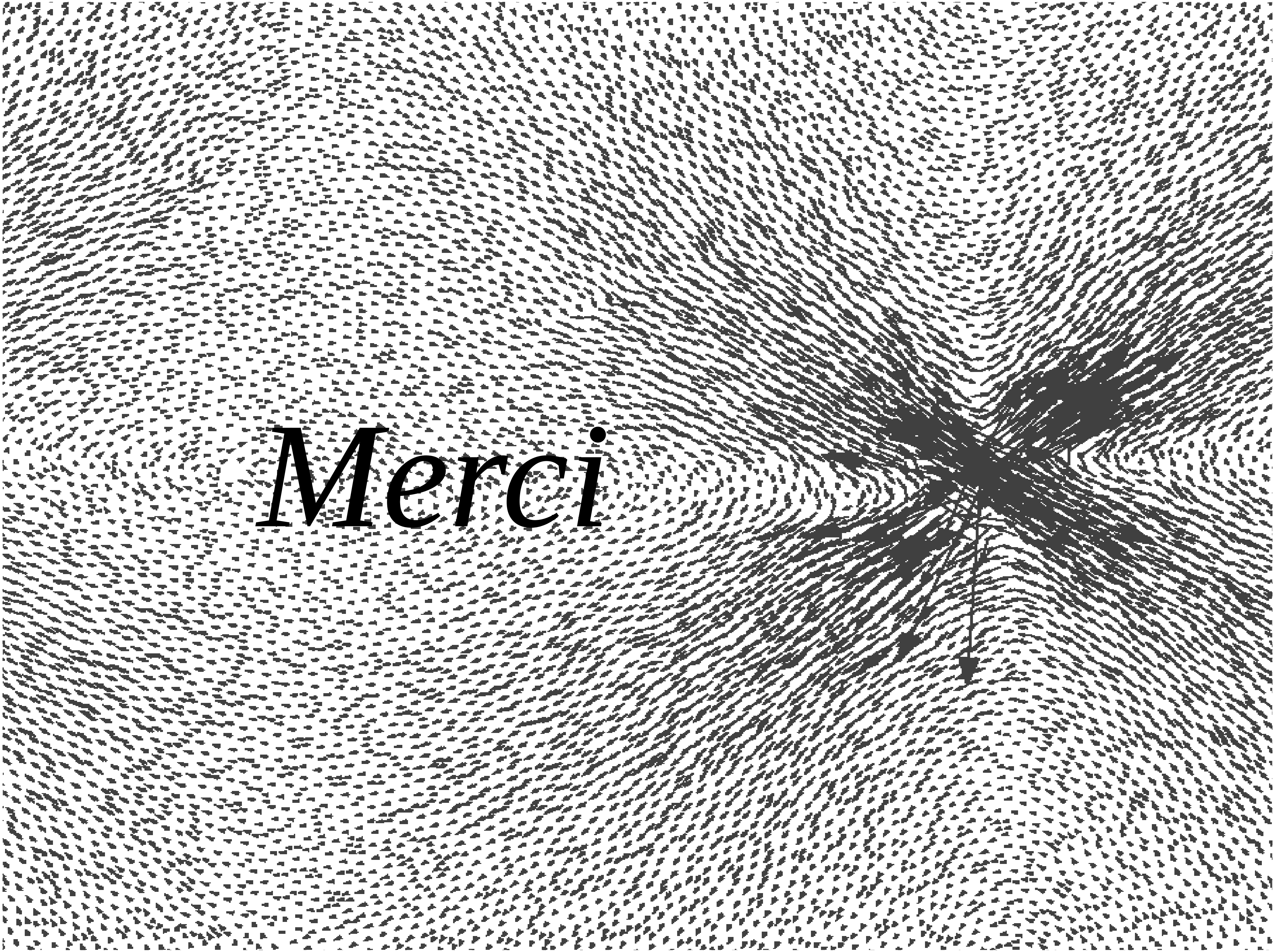
- Maximum correlation in the softest direction θ_{min}
- Rearrangements more probable in the vicinity of θ_{min}
- Effective ΔU scaling compatible with catastrophe theory but closer to NQE



3) First passage time statistics

- Anomalous long tail due to reversible rearrangements
- Reversibility increase as the temperature is lowered




Merci