The frustration-based theoretical approach of the glass transition

Gilles Tarjus
(LPTMC, Paris)

François Sausset, Pascal Viot,
Daniel and Steve Kivelson,
Zohar Nussinov

Diversity of views on the glass transition

What makes the problem interesting ?
What would it take to declare it solved ?

Atomic-level description & local relaxation mechanisms

versus

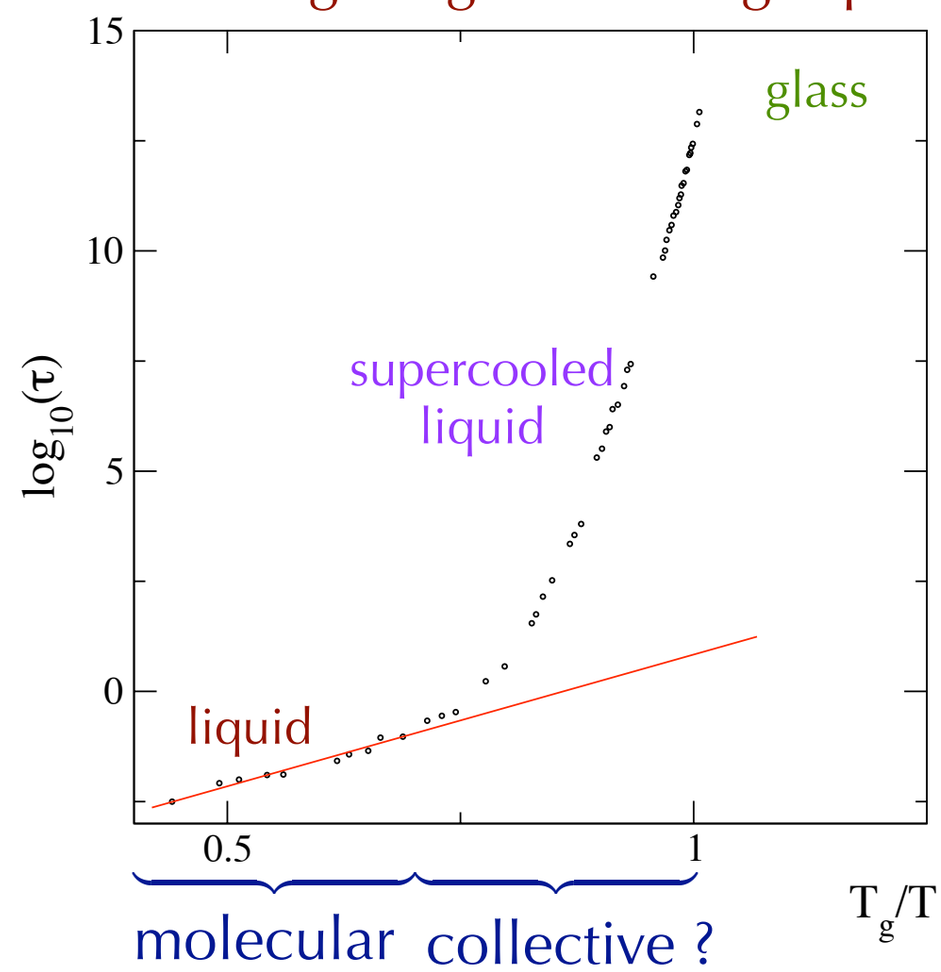
Coarse-graining, scaling & underlying critical points

- If critical point:
  - Dynamic vs static
  - Unattainable vs avoided

What is there to be explained about glass formation ?

- Phenomenon is universal and spectacular
- Dramatic temperature dependence of relaxation time and viscosity
- Slowing down faster than anticipated from high-T behavior

Arrhenius plot of relaxation time of a "fragile" glassforming liquid



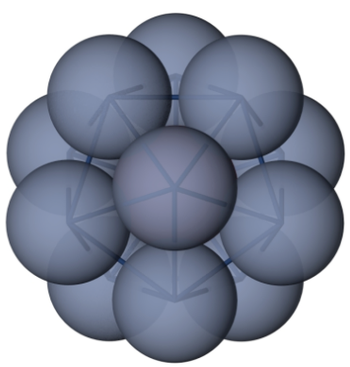
Tempting to look for detail-independent, collective explanation,
BUT: no observed singularity,
only modest supra-molecular length scale.

Frustration in liquids

"Frustration"= incompatibility between extension of the local order preferred in a liquid and tiling of the whole space

- Paradigm: frustrated icosahedral/polytetrahedral order in metallic glasses

Locally preferred structure in liquid

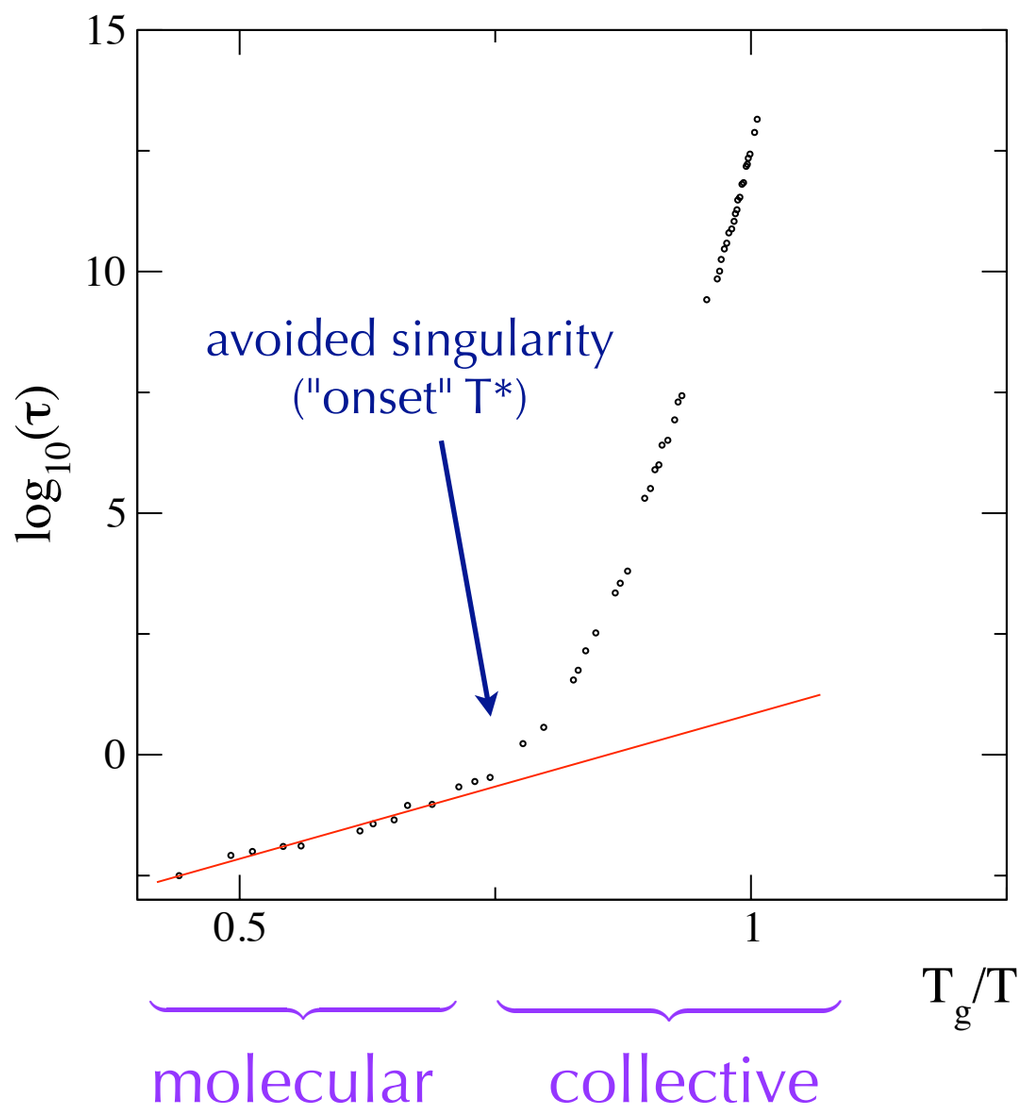


No global tiling
No icosahedral/polytetrahedral xtal
(instead: FCC/HCP xtal)

Frustration important for: - supercooling (*Frank, 1952, Charbonneau et al., 2009*)
- glasses (Curved-space approach: *Nelson, Sadoc-Mosseri, Sethna, 80's*)

Frustration based approach of glass formation

- Avoided singularity at T* → frustration-limited cooperative behavior



→ scaling below T* & some universality

D. & S. Kivelson , G.T., et al.
Review:
J.Phys.: Condens. Matter 17 (2005)

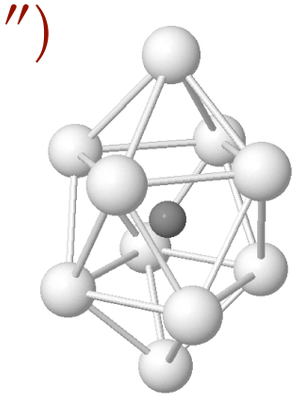
- Fragility goes <u>inversely</u> with frustration

Locally preferred structures (LPS) and fragility in 3D binary Lennard-Jones mixtures

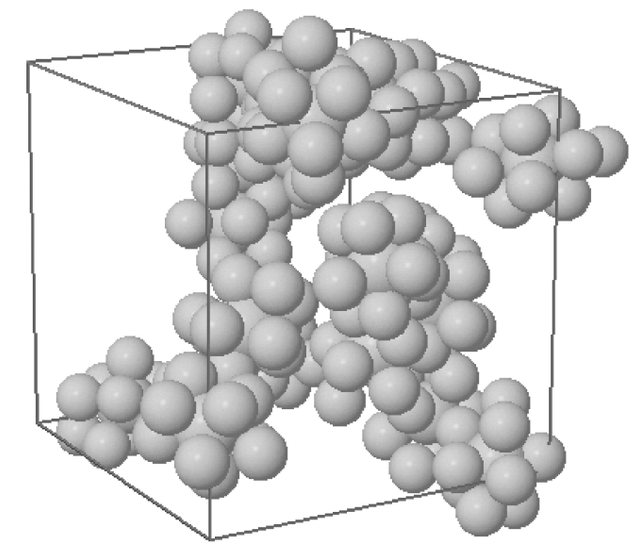
D. Coslovich & G. Pastore, J. Chem. Phys. **127**, *124504 (2007)*

- Kob-Andersen model ("BMLJ")

LPS:



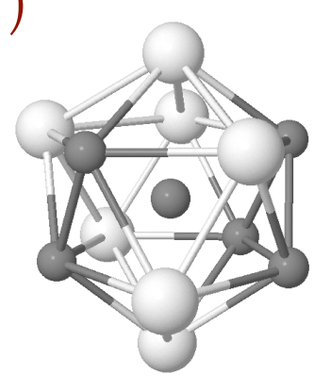
(a) (0,2,8)-polyhedron



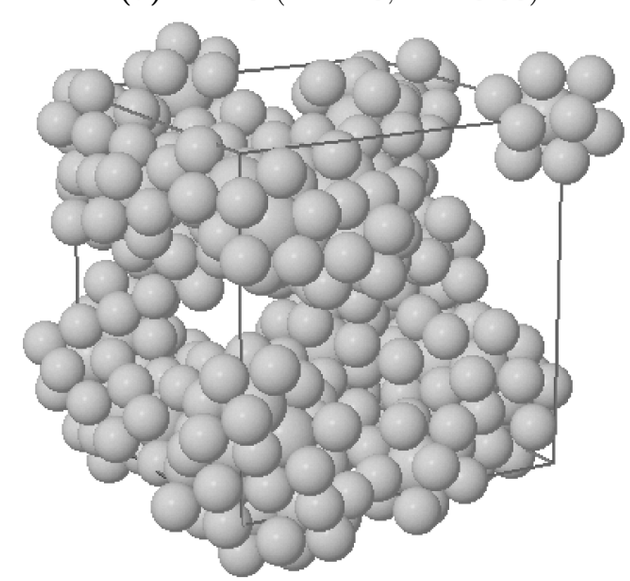
(a) BMLJ ($P = 10$, $T = 0.60$)

- Wahnstrom model ("WAHN")

LPS:



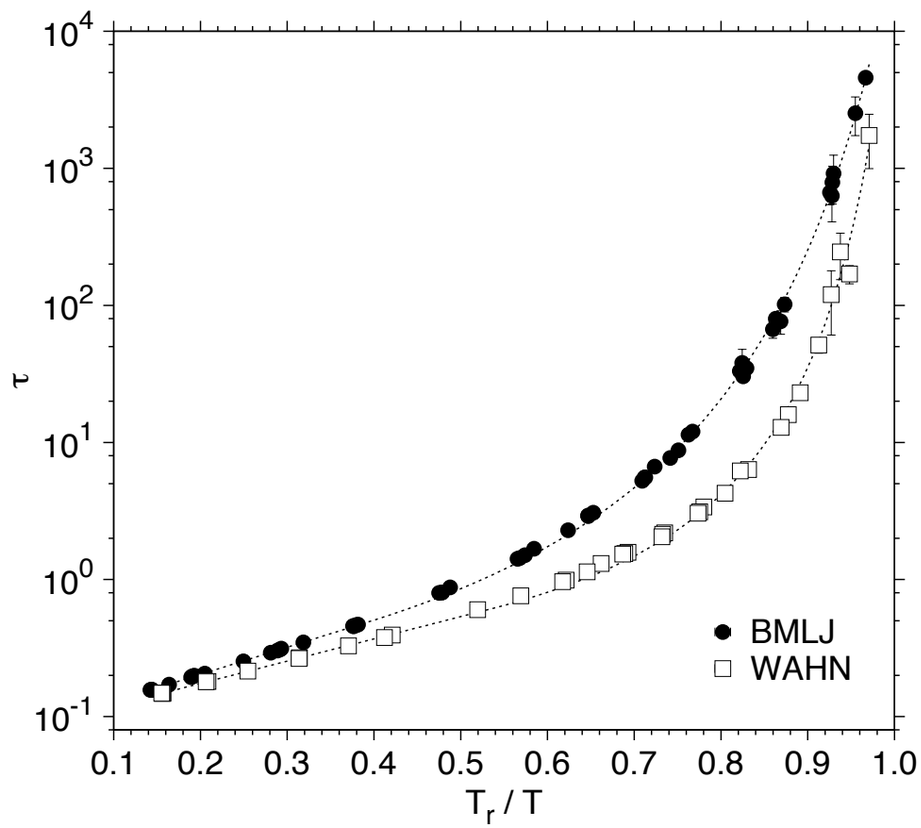
(c) (0,0,12)-polyhedron



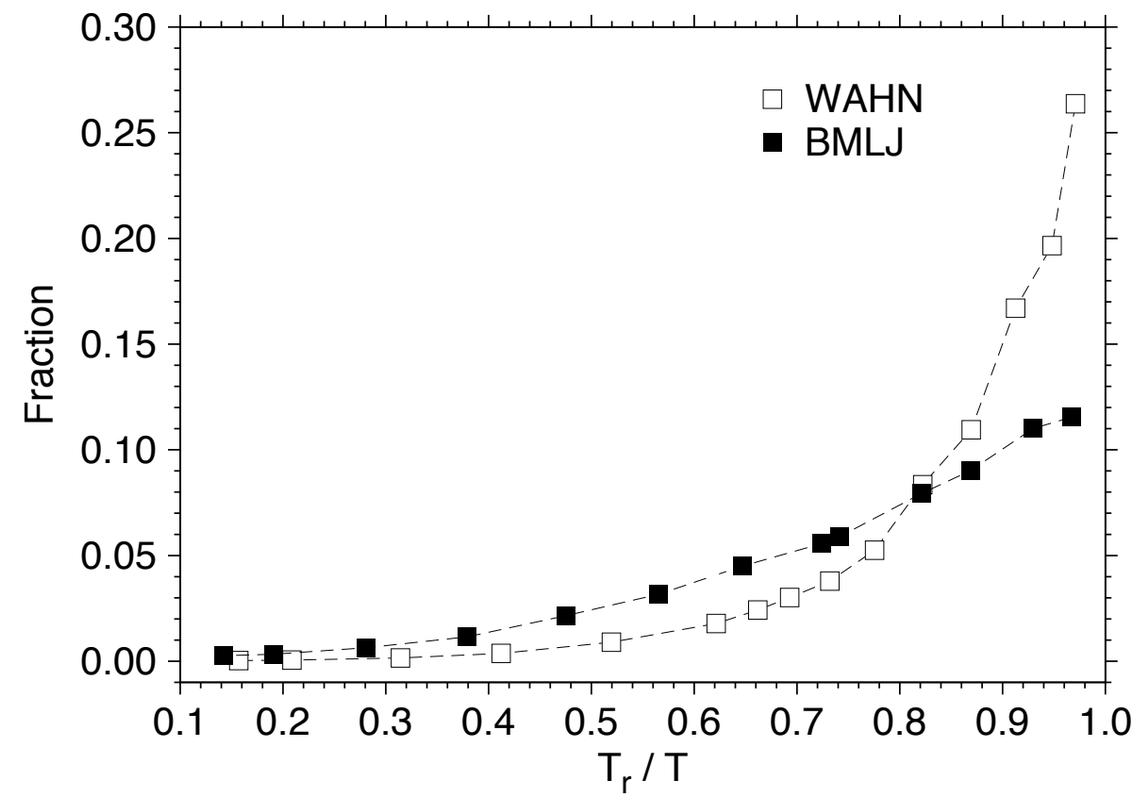
(b) WAHN ($P = 10$, $T = 0.645$)

LPS and fragility

D. Coslovich & G. Pastore, J. Chem. Phys. **127**, *124504 (2007)*



Arrhenius plot of relaxation time



Fraction of small atoms in LPS

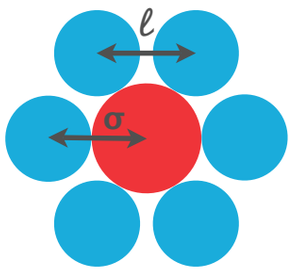
$(T_r =$ reference T at which $\tau = 4.10^4)$

Atomistic glassformer with tunable frustration:

Monodisperse Lennard-Jones liquid on the hyperbolic plane

- Known local order of liquid: hexatic/hexagonal

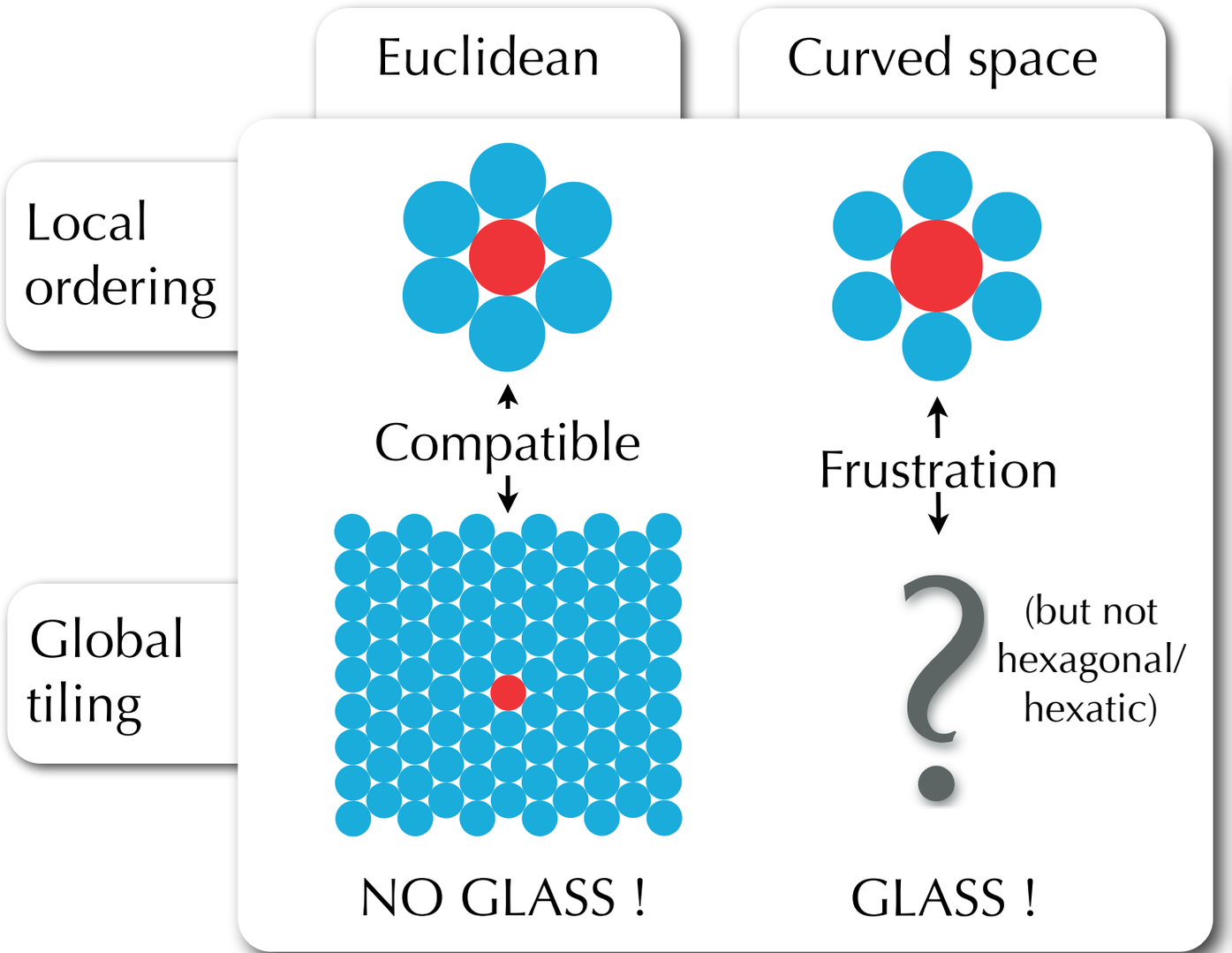
- Frustration (no crystal) due to negative curvature of space $-\kappa^2$



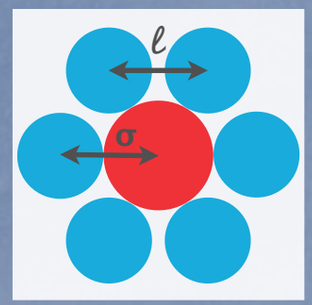
- MD simulation of 2D L-J model in hyperbolic geometry (NVE ensemble)

Why the hyperbolic plane ?

Monoatomic liquid in 2 dimensions

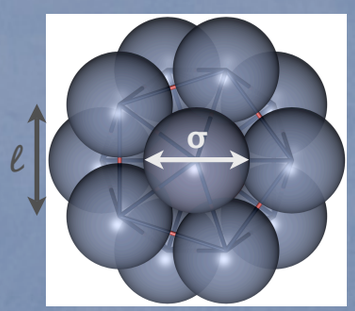


Frustrated hexagonal order in 2D curved space



$\sim$

Frustrated icosahedral order in 3D Euclidean space



- Negative curvature (hyperbolic) for an infinite space

Hyperbolic geometry

- Constant negative Gaussian curvature:

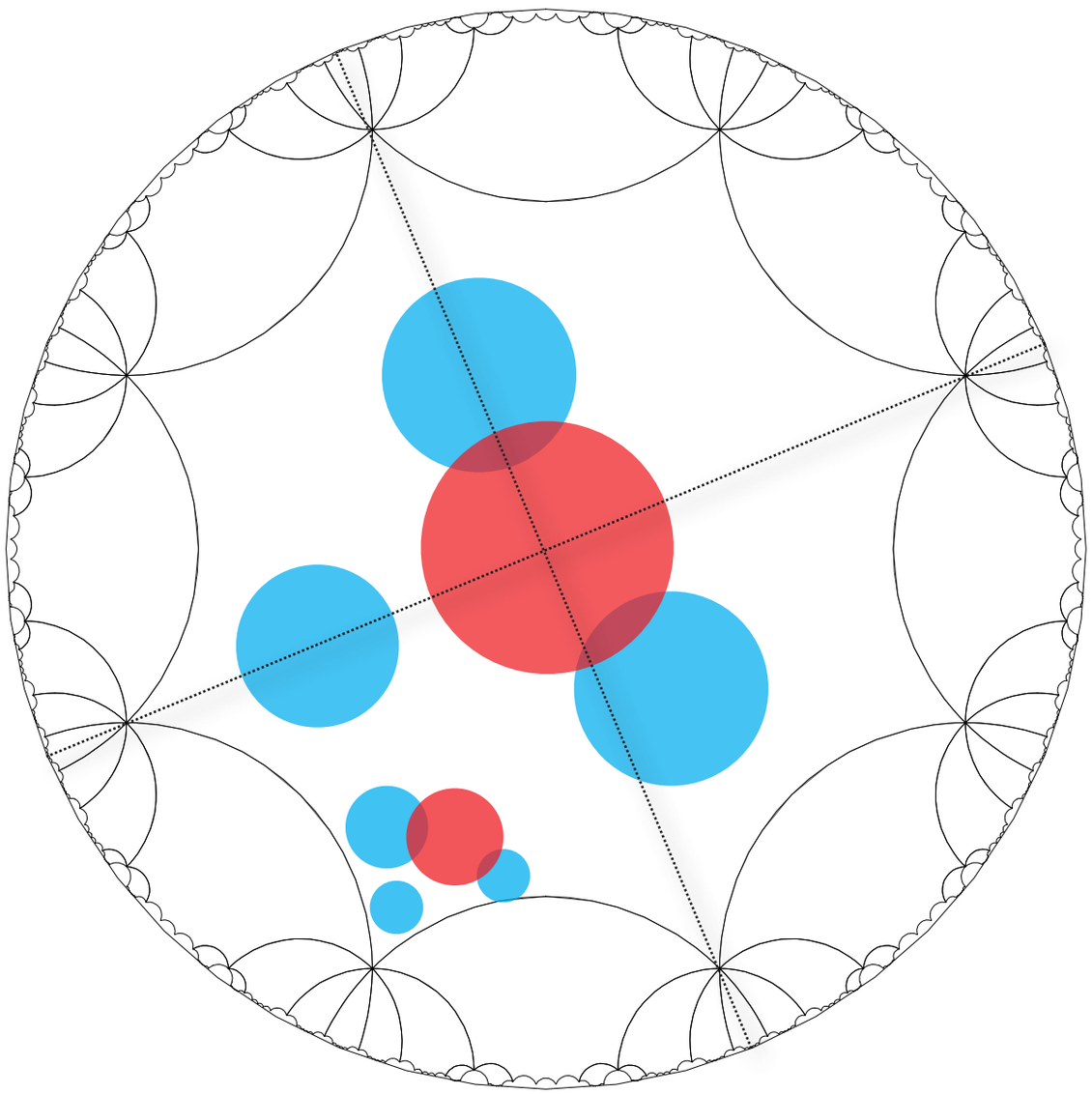
$$-\kappa^2$$

- Metric (polar coordinates):

$$\mathrm{d}s^2 = \mathrm{d}r^2 + \left(\frac{\sinh(\kappa r)}{\kappa}\right)^2 \mathrm{d}\theta^2$$

- Conformal representation:

$$r' = \tanh\left(\frac{\kappa r}{2}\right) \;\; ; \;\; \theta' = \theta$$



Poincaré disk model

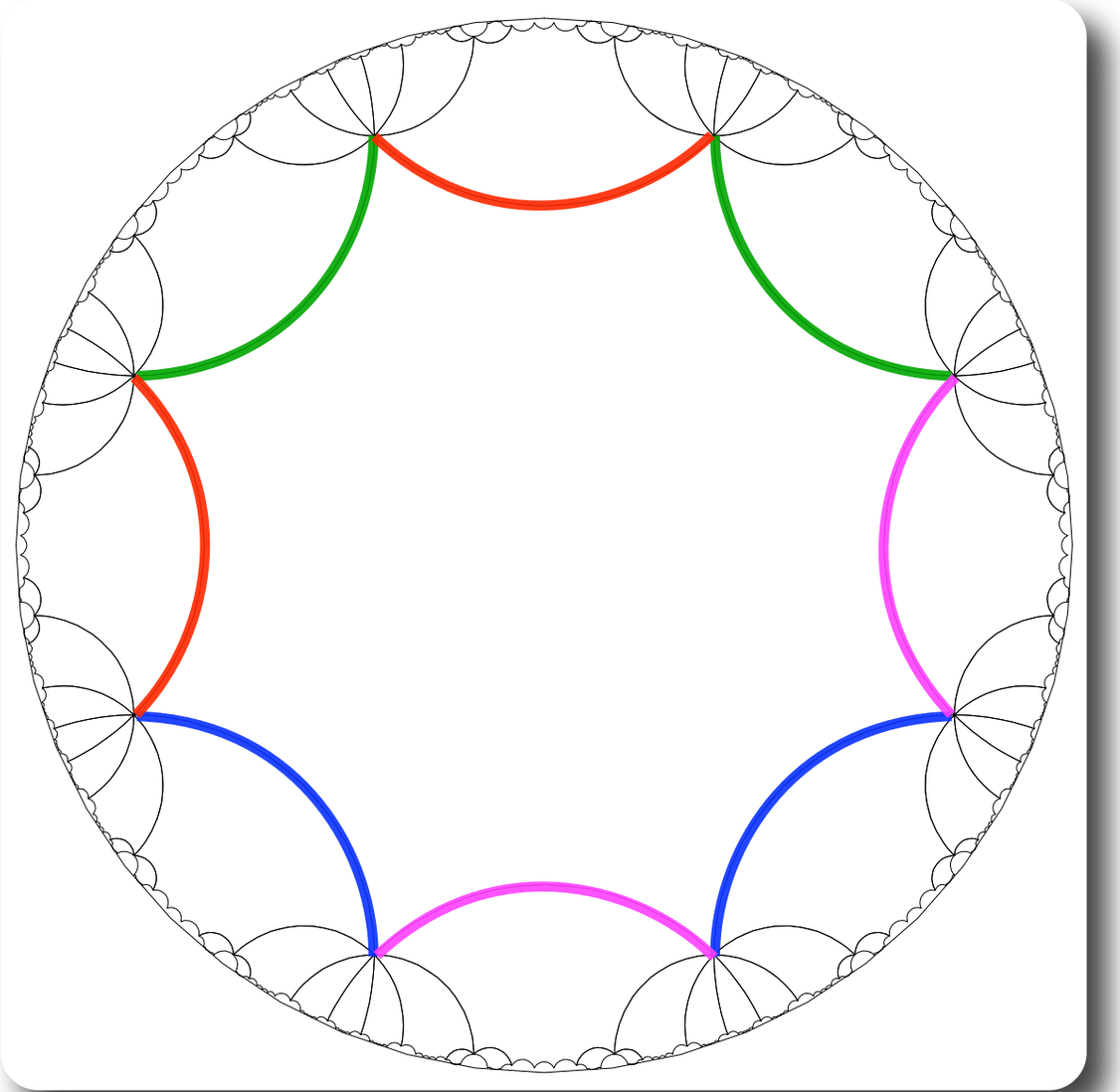
Molecular Dynamics simulation

- Usual one-component Lennard-Jones model on H^2

$$v(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^6)$$

- Newton's equations: generalized Verlet algorithm
- Periodic boundary conditions:
  - the simplest case : {8,8} tiling + special pairing of edges
  - infinite ways to build p.b.c.

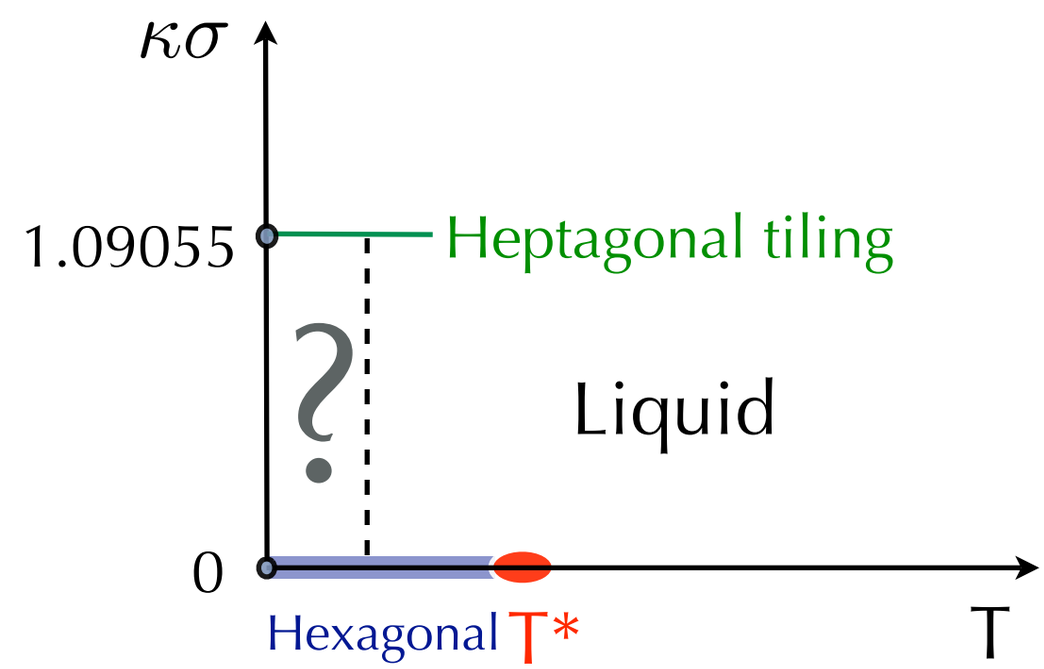
(F. Sausset,G.T., J. Phys. A: Math. Gen. (2007))



Parameters and dynamical observables

- Control parameters:
  - ✳ Frustration: $\kappa\sigma$
  - ✳ Density: $\rho\sigma^2$
  - ✳ Temperature: T
  - ✳ System's area: $4\pi\kappa^{-2}(g-1)$
    (Gauss-Bonnet)

g = genus of associated quotient space



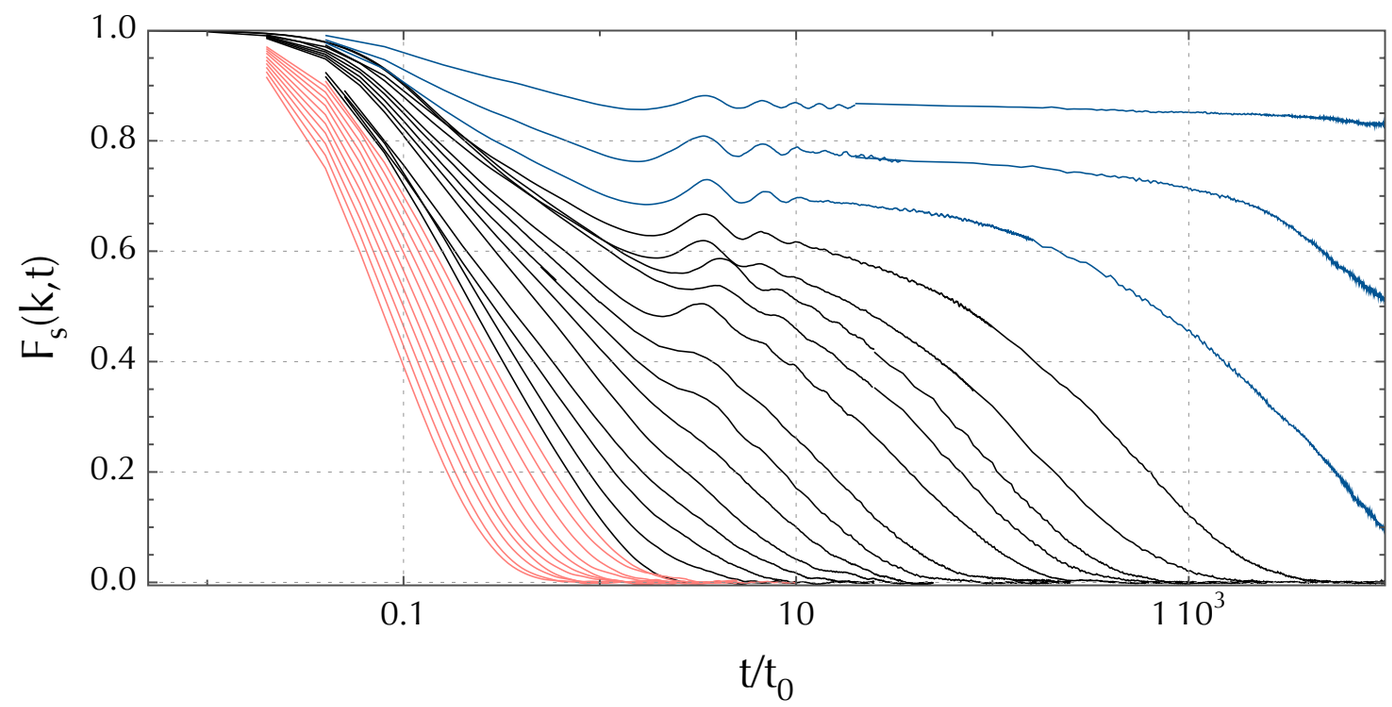
- Dynamical observable: self intermediate scattering function

$$F_s(k,t) = \frac{1}{N}\sum_{j=1}^{N}\left\langle P_{-\frac{1}{2}+i\frac{k}{\kappa}}\left(cosh(\kappa d_j(0,t))\right)\right\rangle$$

Observables

- Adjustable parameters:
  - ✳ Frustration : $\kappa\sigma$
  - ✳ Density : ρ
  - ✳ Temperature : T

Translational relaxation

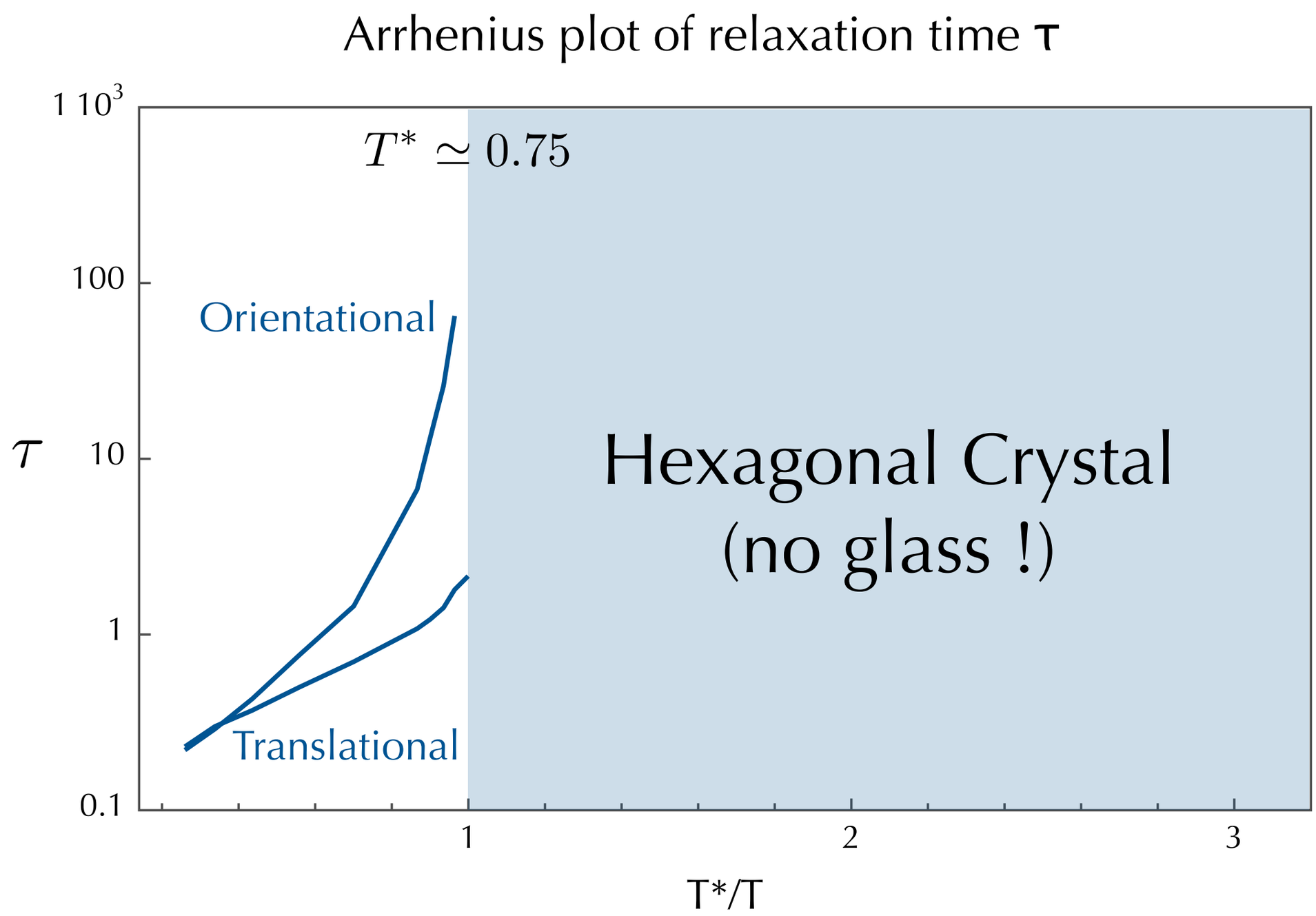


- Observables:
  - ✳ Diffusion : $\langle d(\tau) \rangle$
  - ✳ Incoherent intermediate scattering function :

$$F_s(k,t) = \frac{1}{N} \sum_{j=1}^{N} \langle P_{-\frac{1}{2}+i\frac{k}{\kappa}}(\cosh(\kappa d_j(0,t))) \rangle$$

  - ✳ Four-point dynamical susceptibility : $\chi_4^{NVE}(t)$
  - ✳ Bond-orientational correlation function : $G_6(r)_\Gamma = \langle \psi_6^*(r)\psi_6(0) \rangle_\Gamma / g(r)$

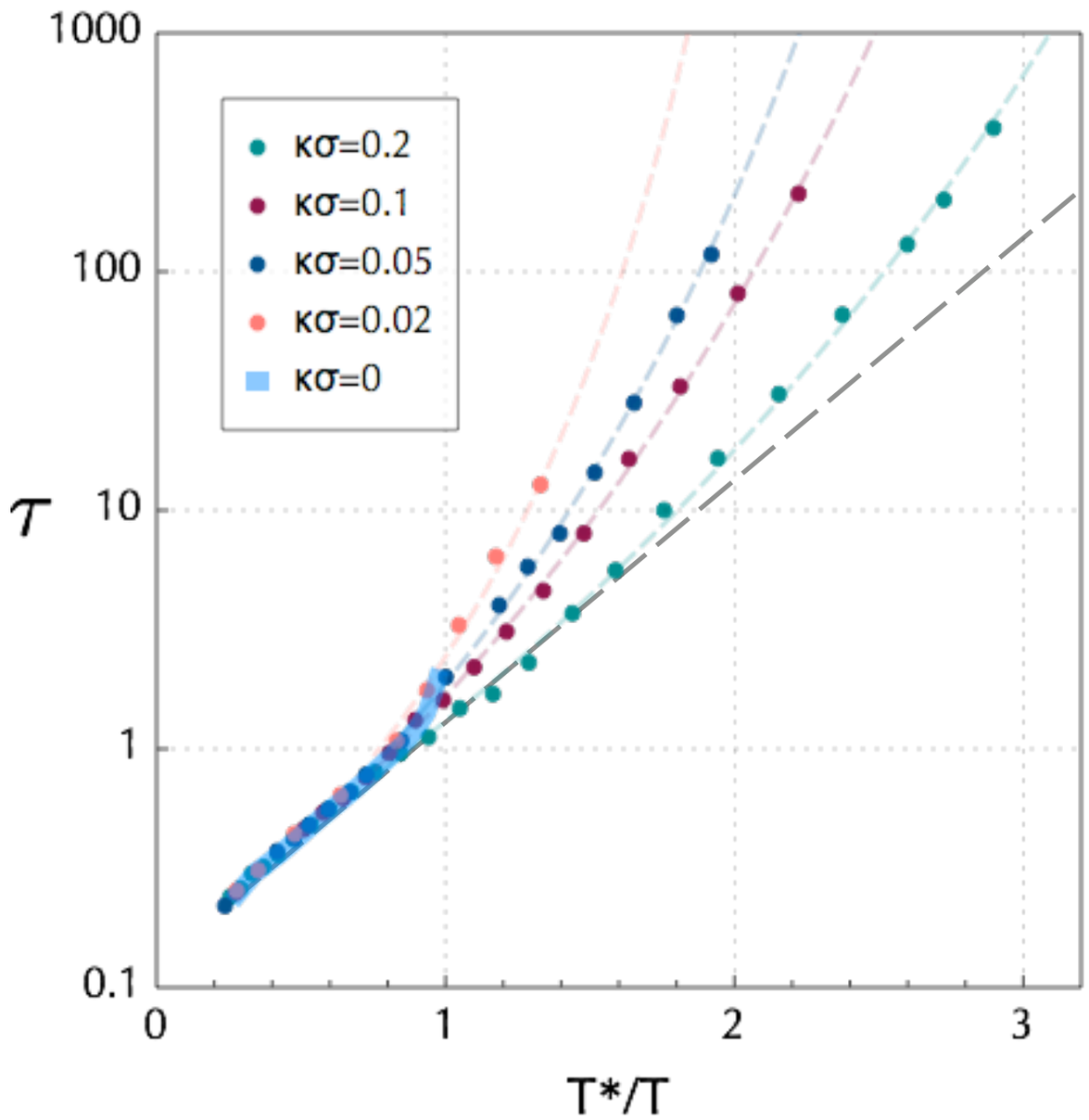
Euclidean plane ($\kappa = 0$)



Frustration and fragility

(frustration-induced avoided transition at T*)

Arrhenius plot of the translational relaxation time τ
[from $F_s(k,t)$]



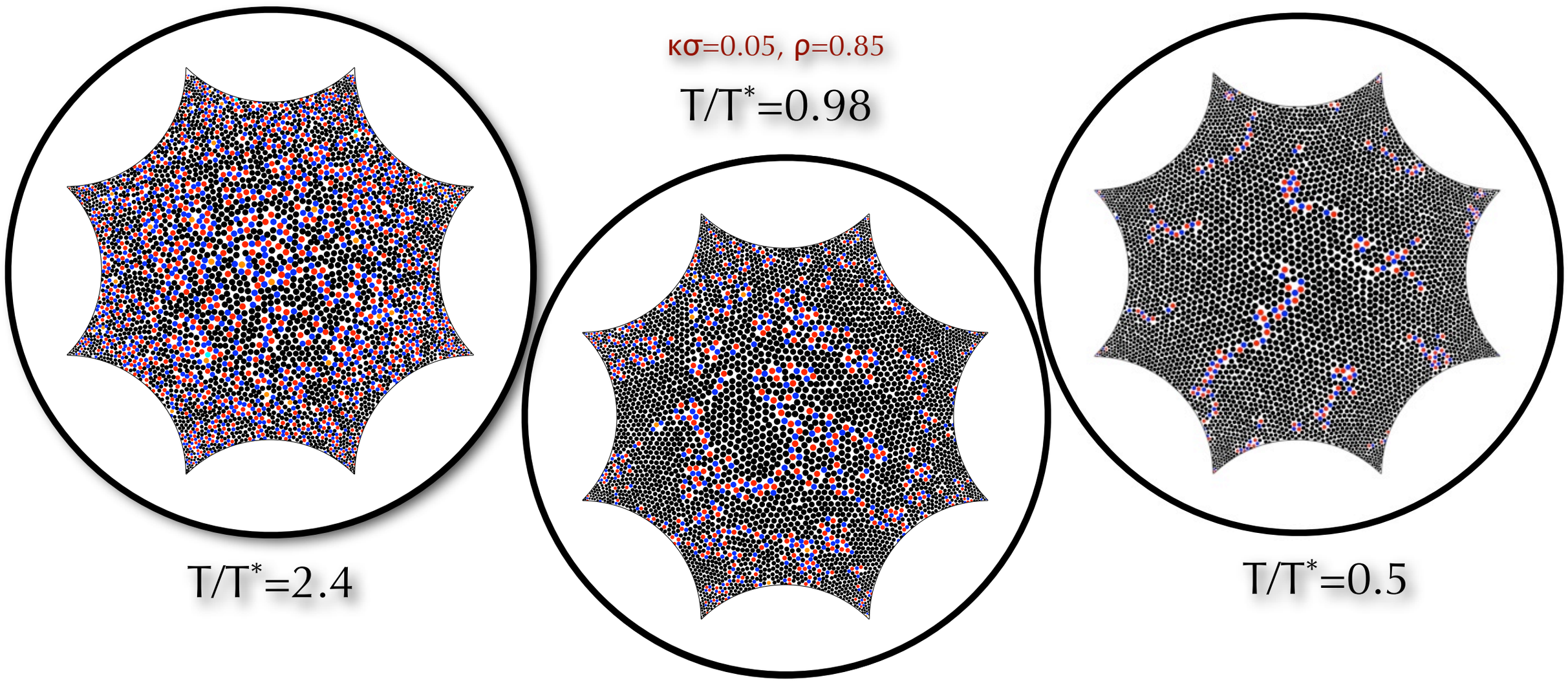
- Fragility increases with decreasing frustration and can be made as large as wanted (as $\kappa \to 0^+$)

- Onset temperature $\simeq T^*$

Growth of frustration-limited domains as T decreases

Topological defects in hexatic medium

- 7 neighbors (negative disclination)
- 5 neighbors (positive disclination)
- 6 neighbors

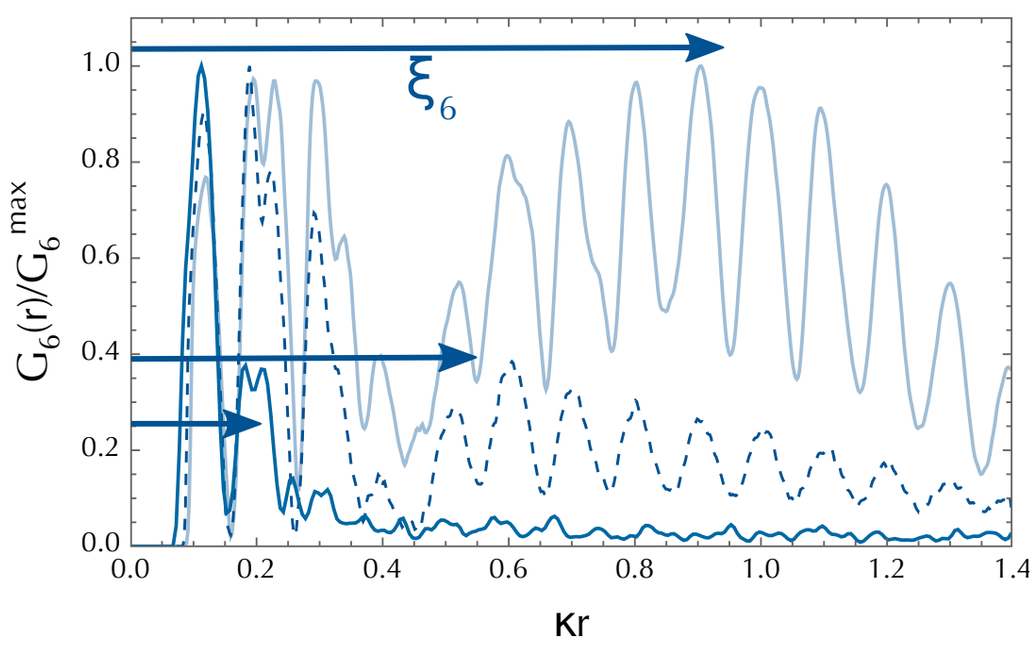


Poincaré disk representation

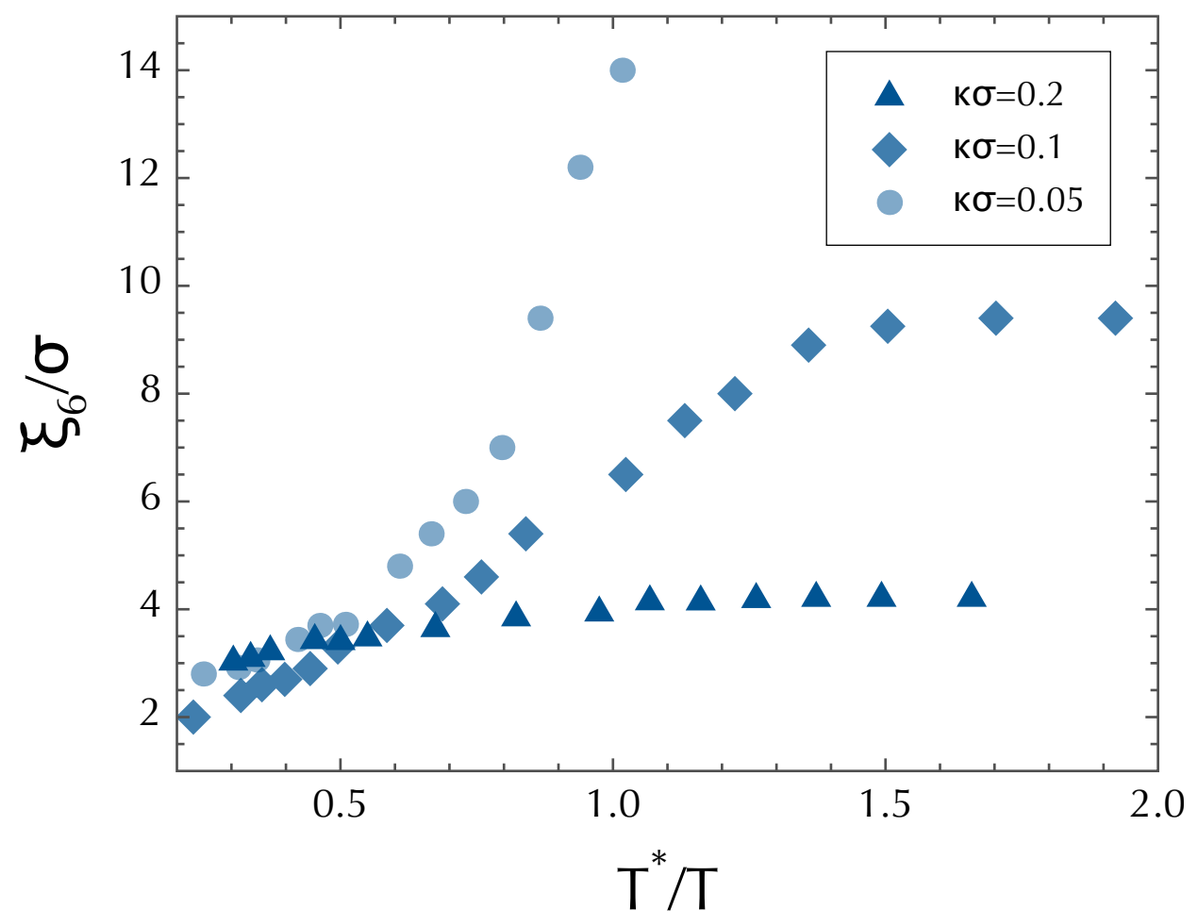
Structural length grows as T↓ and saturates at κ^{-1} due to frustration/curvature

From the bond-orientational correlation function:

$$G_6(r) = \langle \psi_6(r)\psi_6(0)* \rangle_\Gamma / g(r)$$



(Hexatic) structural length ξ_6



Link between relaxation & structure

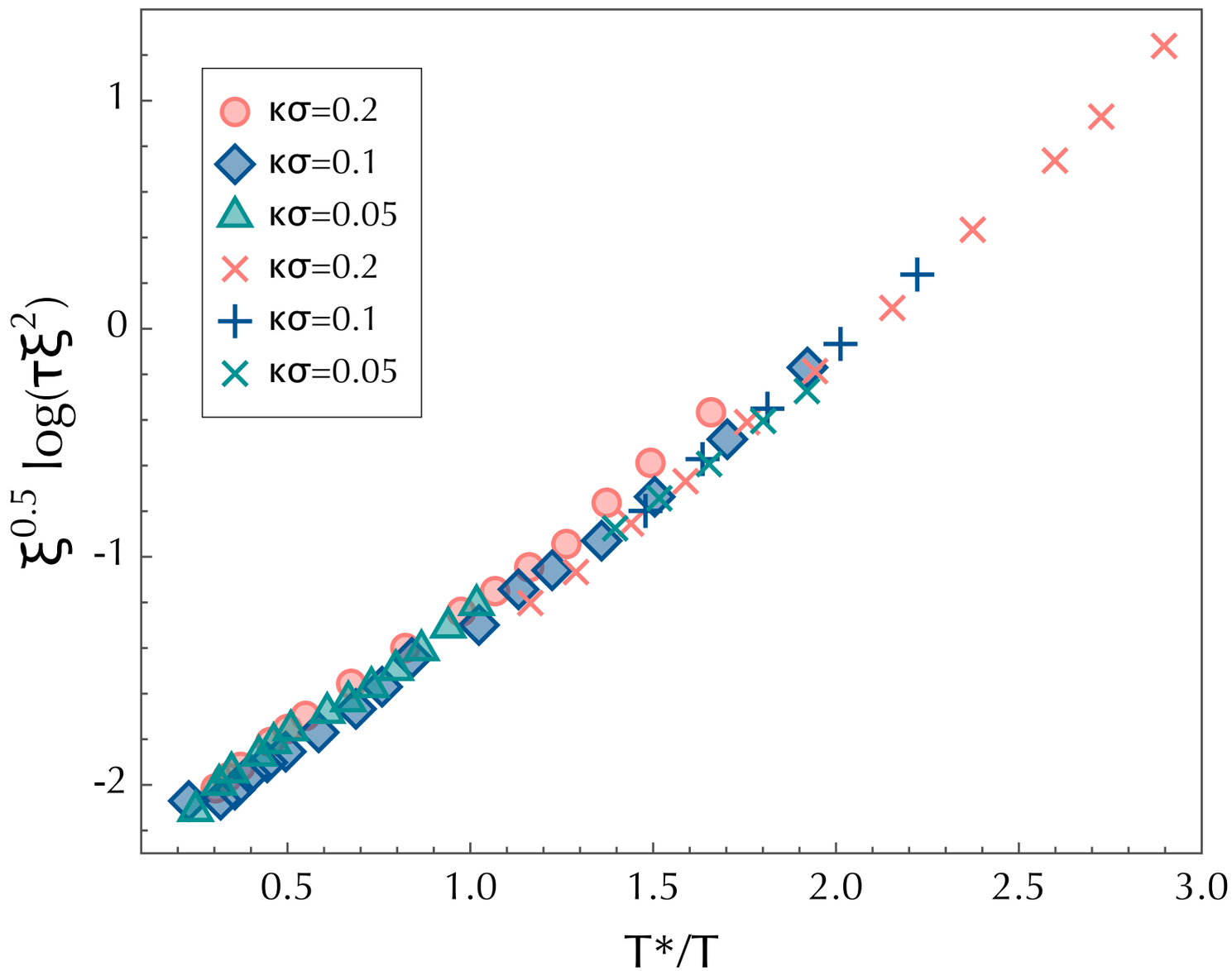
From defect diffusion
+ scaling hypothesis:

$$\tau \sim \xi_6^2 \exp[\frac{E(\xi_6)}{T}]$$

with $E(\xi_6) \sim \xi_6^{\psi}$

and find $\psi \simeq 0.5$

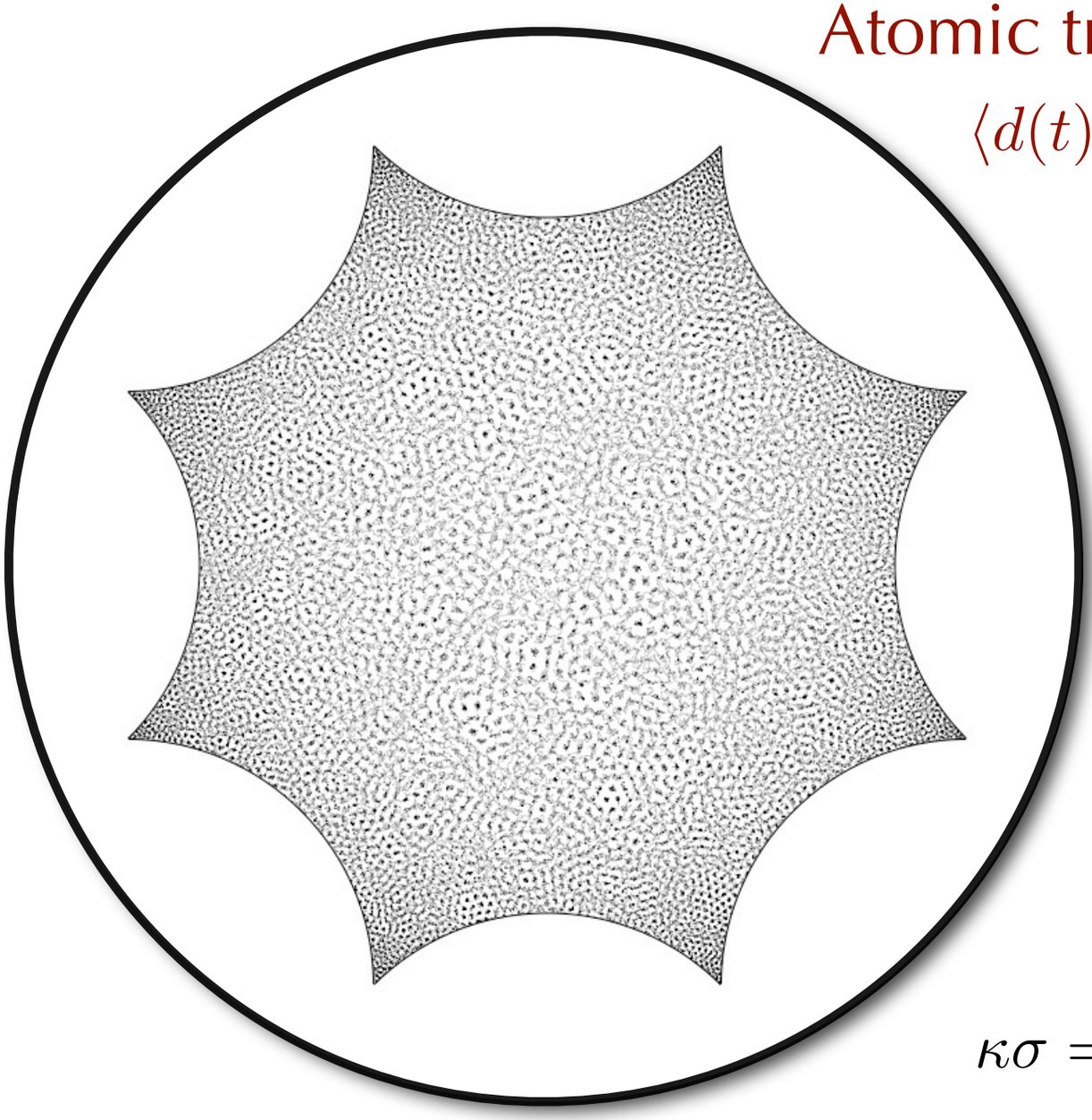
Rescaled relaxation time vs T*/T

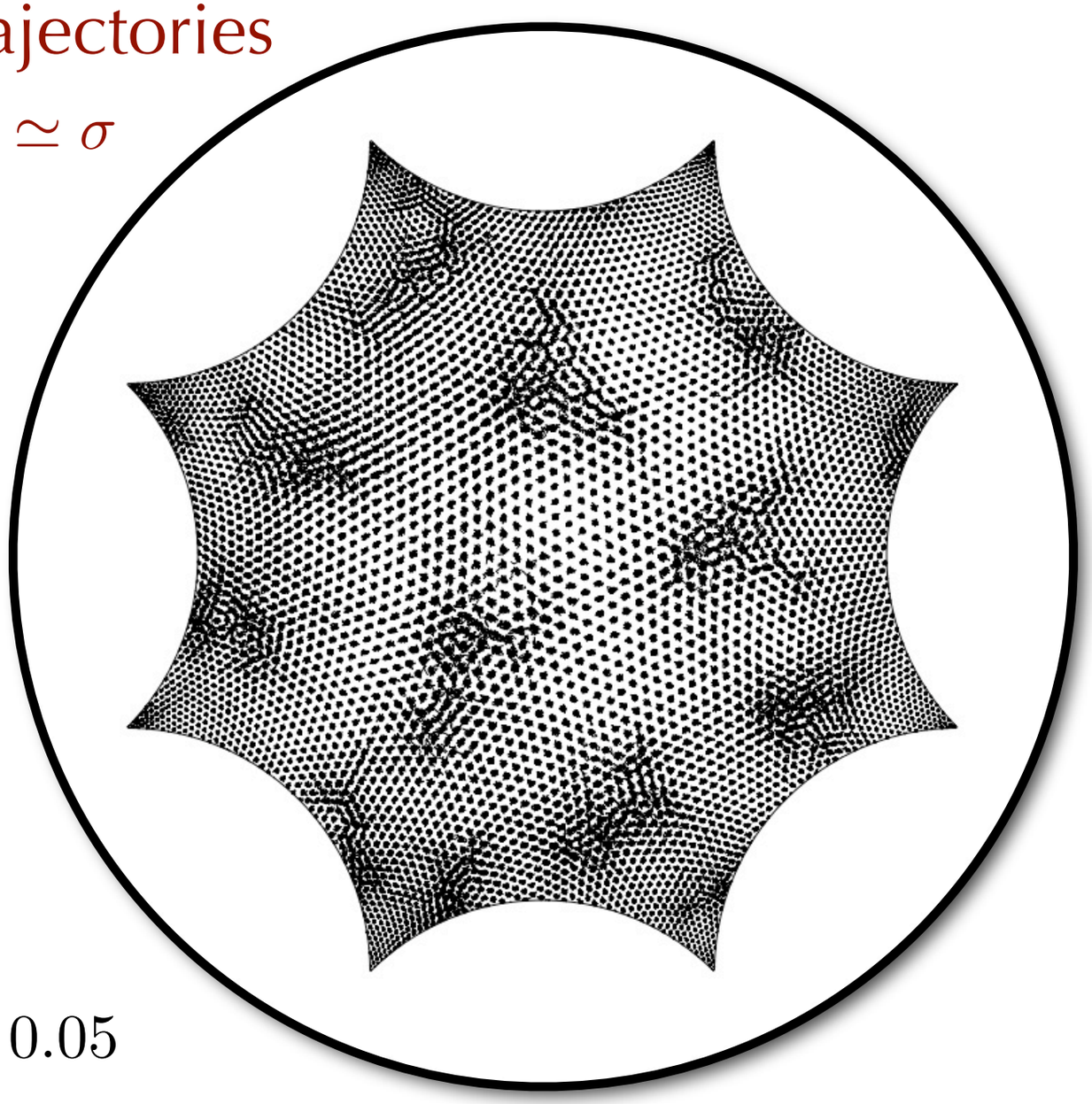


Dynamic heterogeneities

Atomic trajectories

$\langle d(t) \rangle \simeq \sigma$





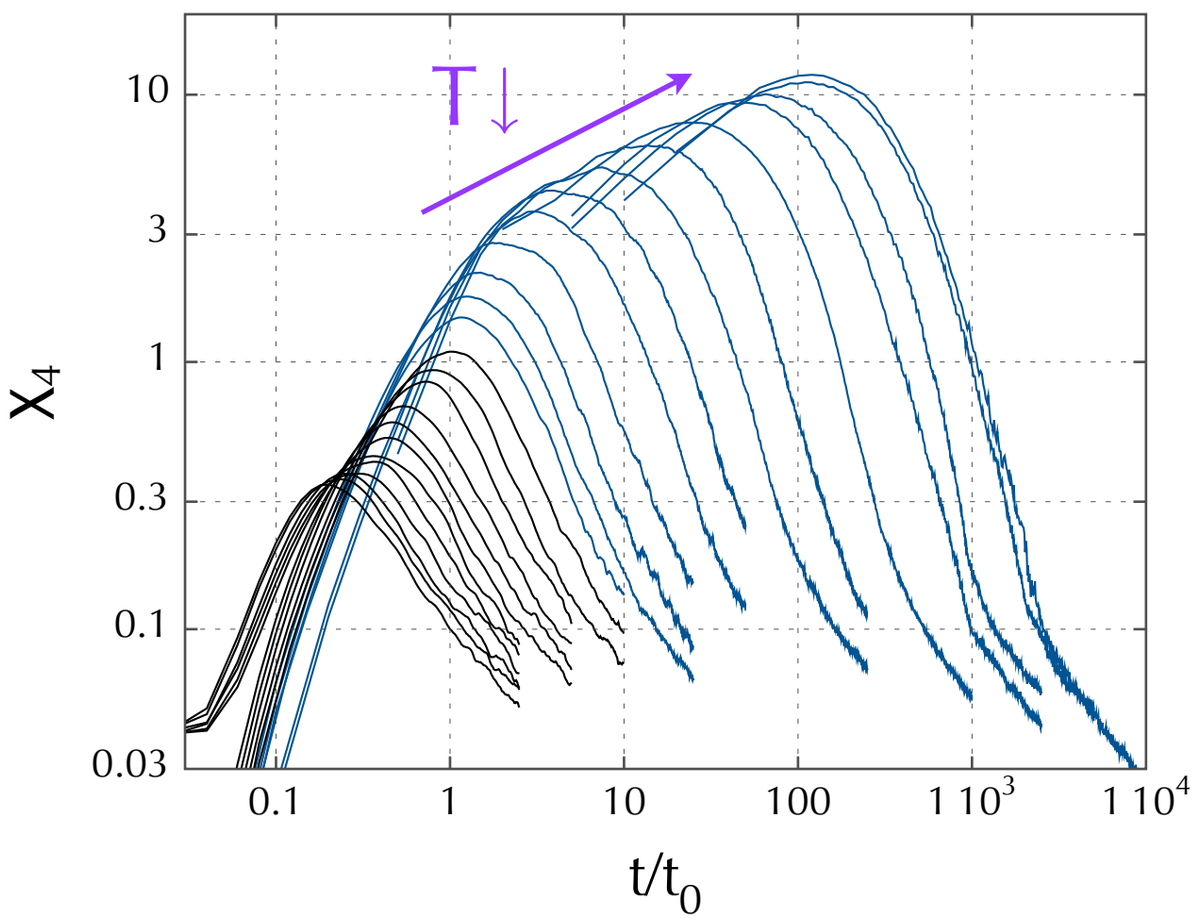
$\kappa\sigma = 0.05$

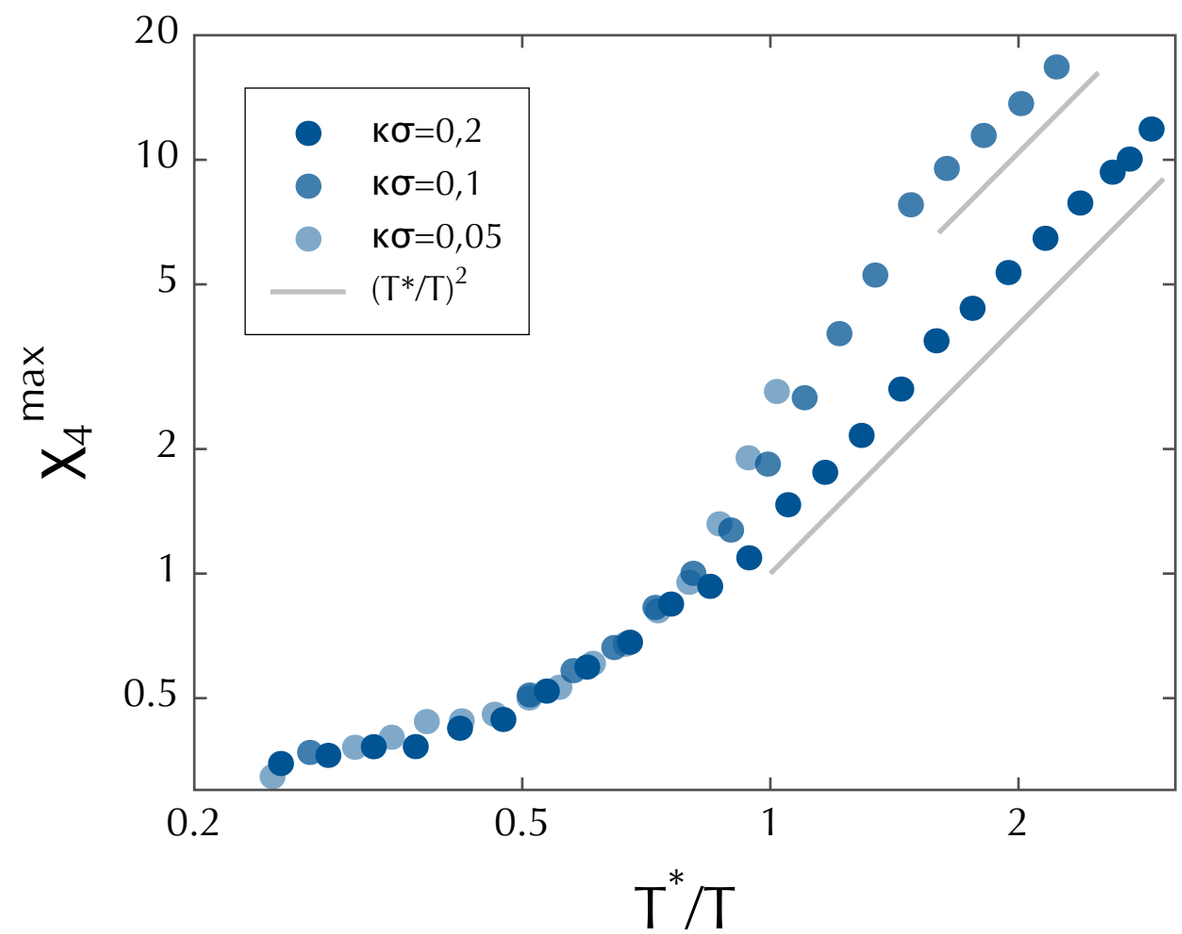
T/T*=1.80

T/T*=0.39

Growing spatial correlations in the dynamics as T↓

4-pt dynamic susceptibility χ_4^{NVE}

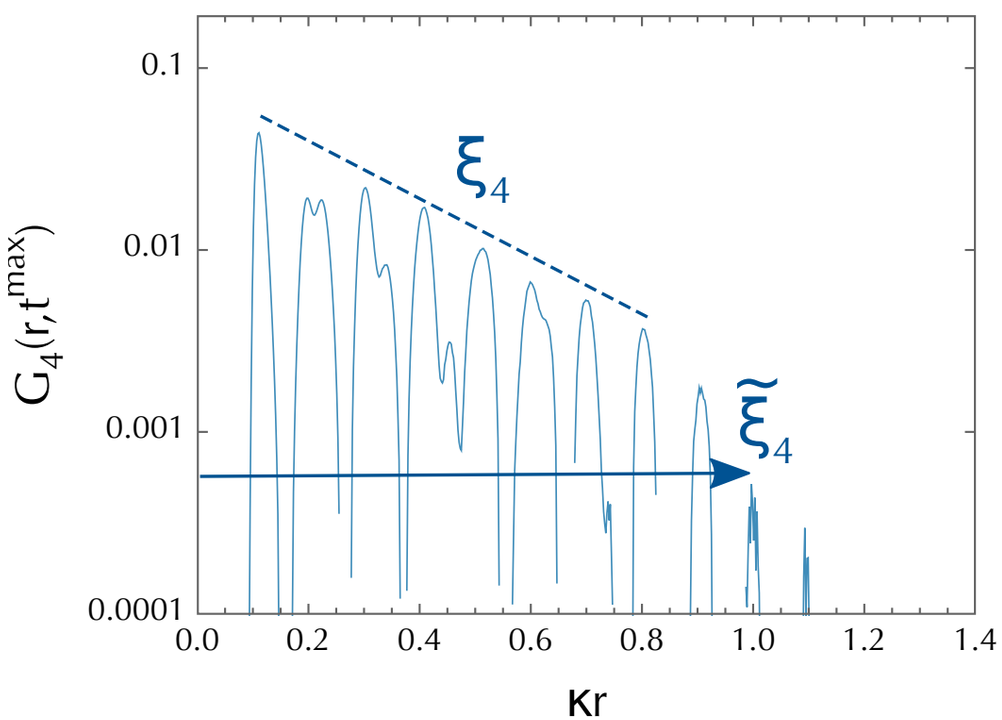


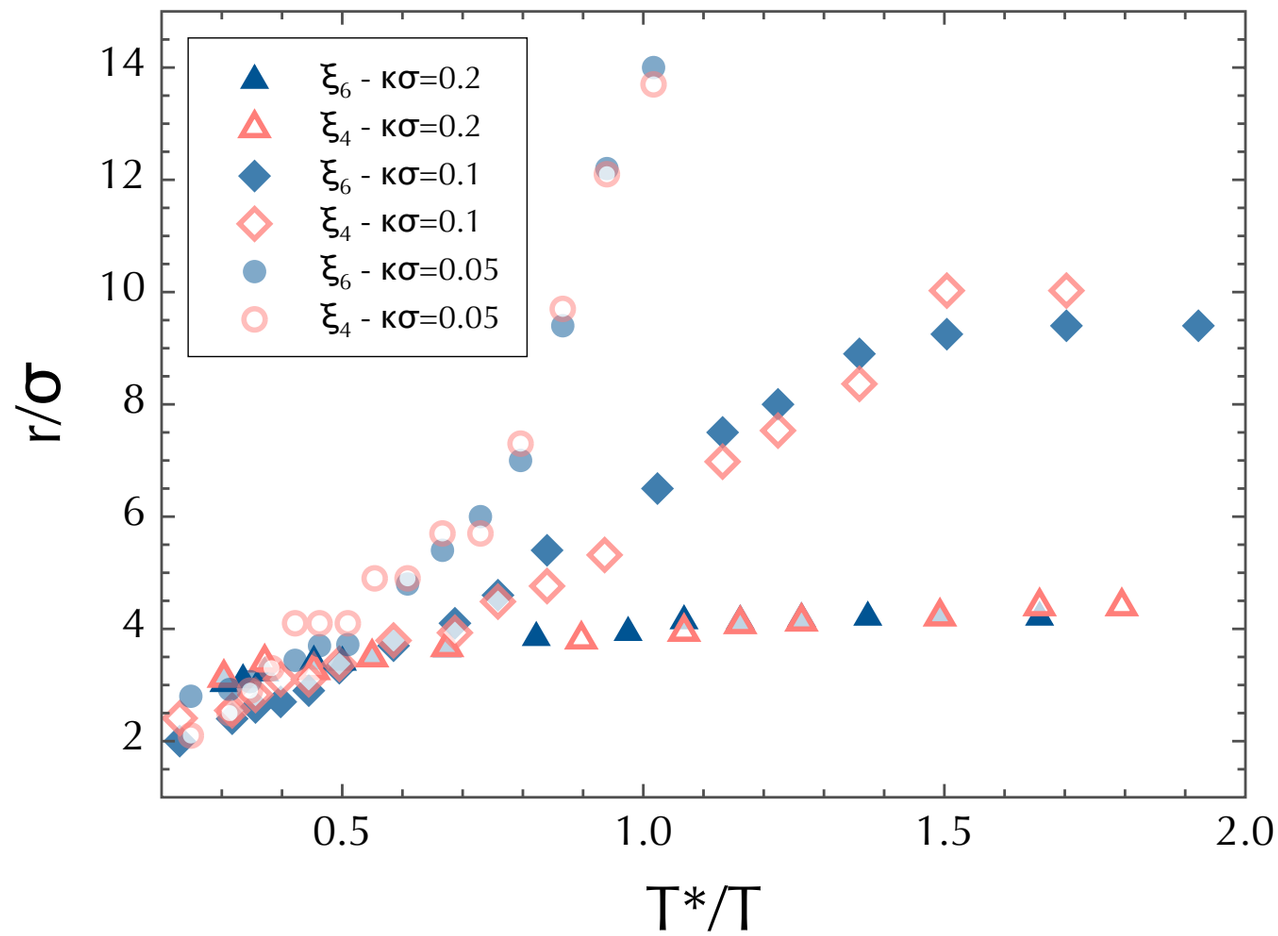


Growing spatial correlations in the dynamics: link with structure

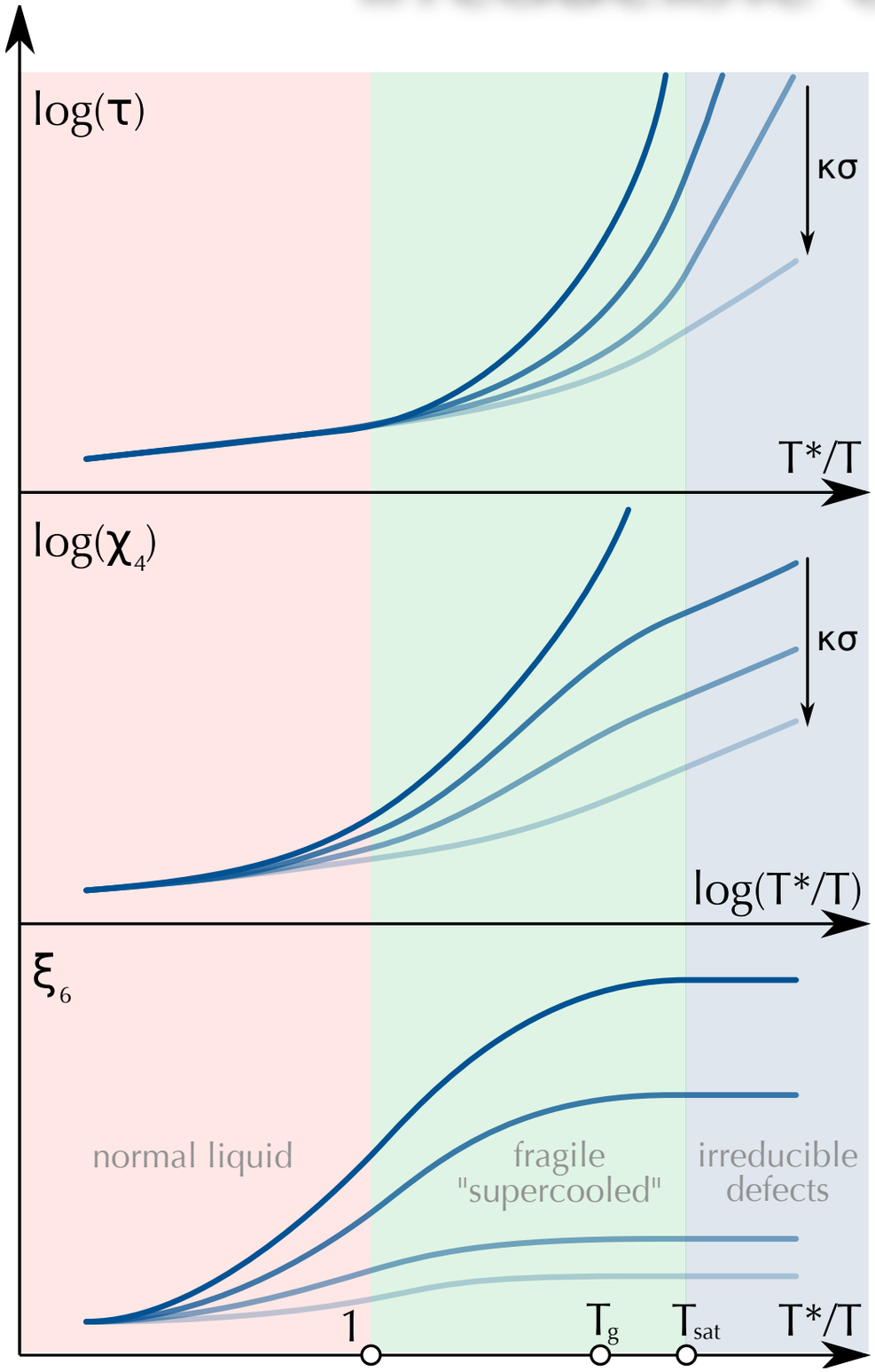
Dynamic (ξ_4) and static (ξ_6) lengths go together in regime dominated by proximity to T*

From the 4-point space-time correlation function $G_4(r,t)$:





Frustration-induced low-T crossover to irreducible-defect regime



At low enough T, growth of local (hexatic) order saturates and crossover from regime controlled by avoided transition to regime dominated by irreducible defects

Conclusion

- Frustration approach provides:
  - ✳ Physical mechanism for slowdown
  - ✳ Avoided singularity for scaling and "universality"
  - ✳ Strategy for exaggerating collective properties.

- Could (some) theories be compatible or even complementary ?

Octagonal p.b.c.: topology of 2-hole torus

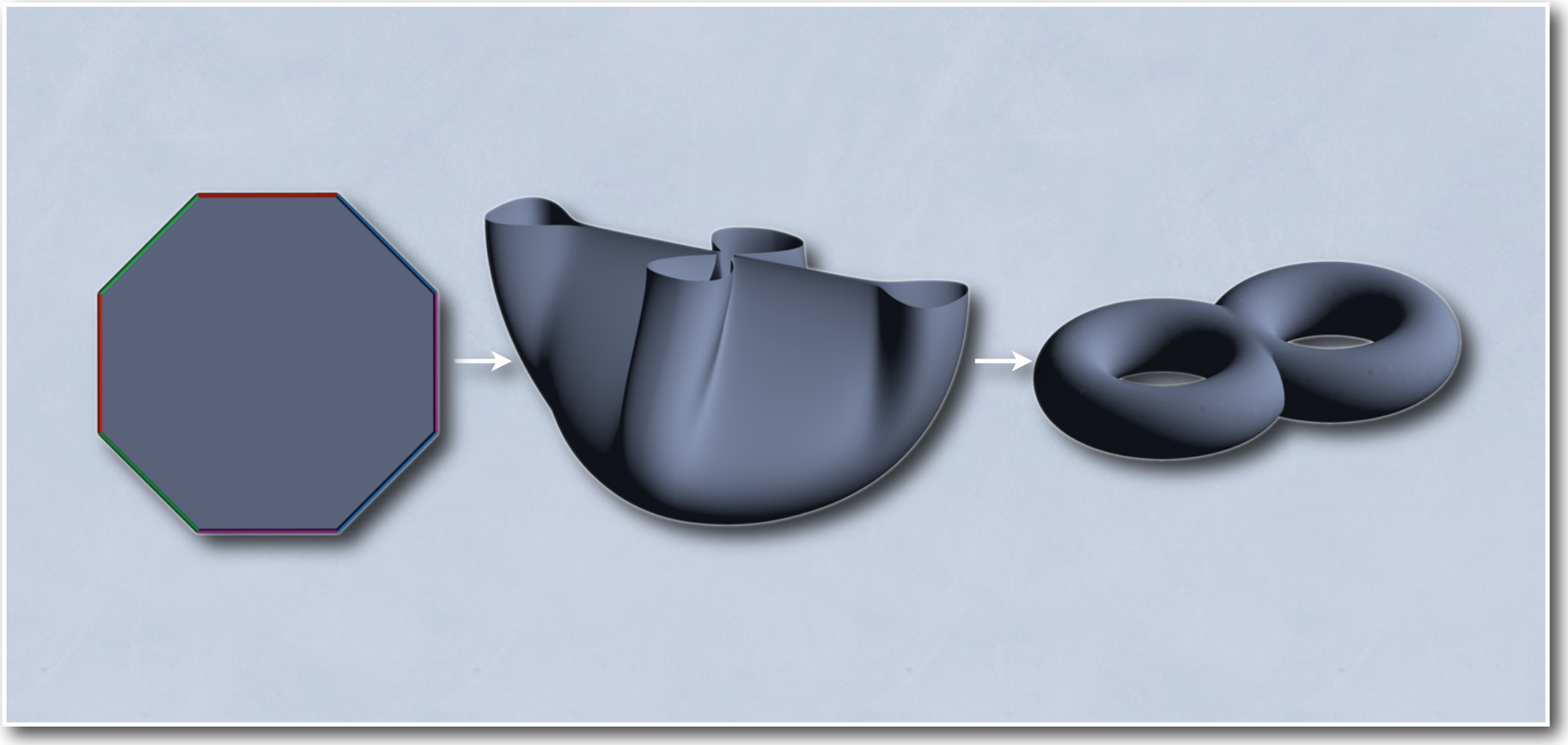


Illustration for one atom: