Linking local structure and mechanics in quiescent and sheared ~~glasses~~

Tanniemola Liverpool
School of Mathematics, Bristol

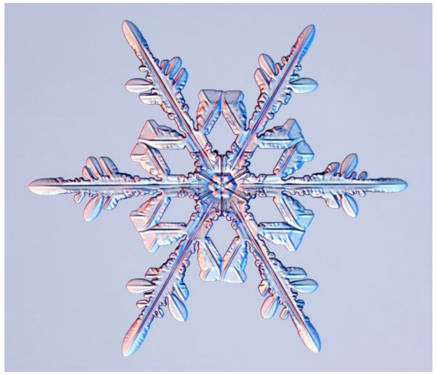
University of BRISTOL

KITP,Santa Barbara, march 2017

Linking local structure and mechanics in quiescent and sheared supercooled liquids

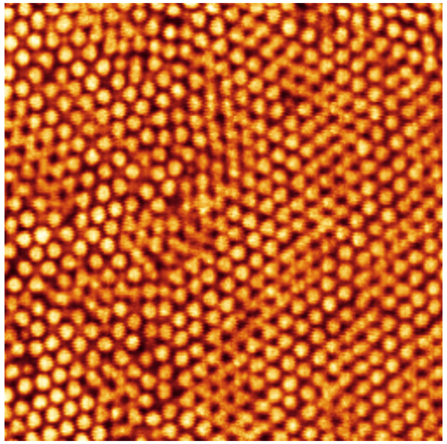
Tanniemola Liverpool

snowcrystals.com

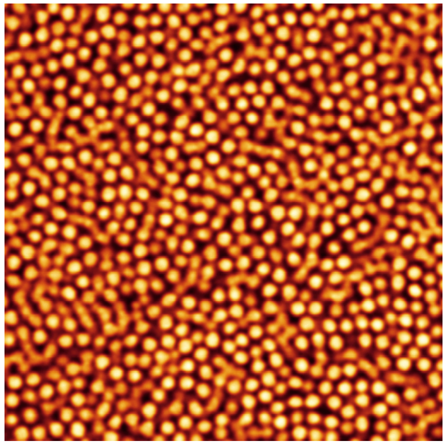


?

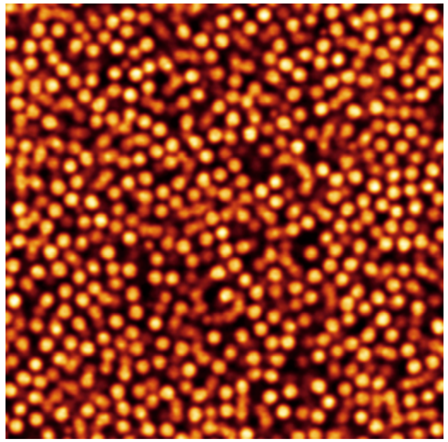
colloid experiment



rigidity



disorder



Crystal

Glass

Liquid

KITP,Santa Barbara, march 2017

Royall and coworkers,

Acknowledgements

Paddy Royall

Rhiannon Pinney

Alex Malins
Francesco Turci

R. Pinney, T.B. Liverpool & C.P Royall, J. Chem. Phys.**143**, 244507 (2015)

R. Pinney, T.B. Liverpool & C.P Royall, J. Chem. Phys.**145,** 234501. (2016)

R. Pinney, T.B. Liverpool & C.P Royall, Phys. Rev. E**, in press** (2018)

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IOP Institute of Physics

Plan

1. Glasses & supercooled liquids
2. Identifying locally favoured structures
3. Local structures & relaxation in quiescent systems
4. Steady state shear behaviour
5. Transients in sheared systems

(atomic) glasses : a primer

τ_α relaxation of density fluctuations

at crystallisation/melting $\tau_\alpha = \sqrt{ma^2/k_B T_m} \sim \text{ ps}$

quench -> supercooling-> =glass when $\tau_\alpha \geq \tau_{glass} \approx 100 \text{ s}$

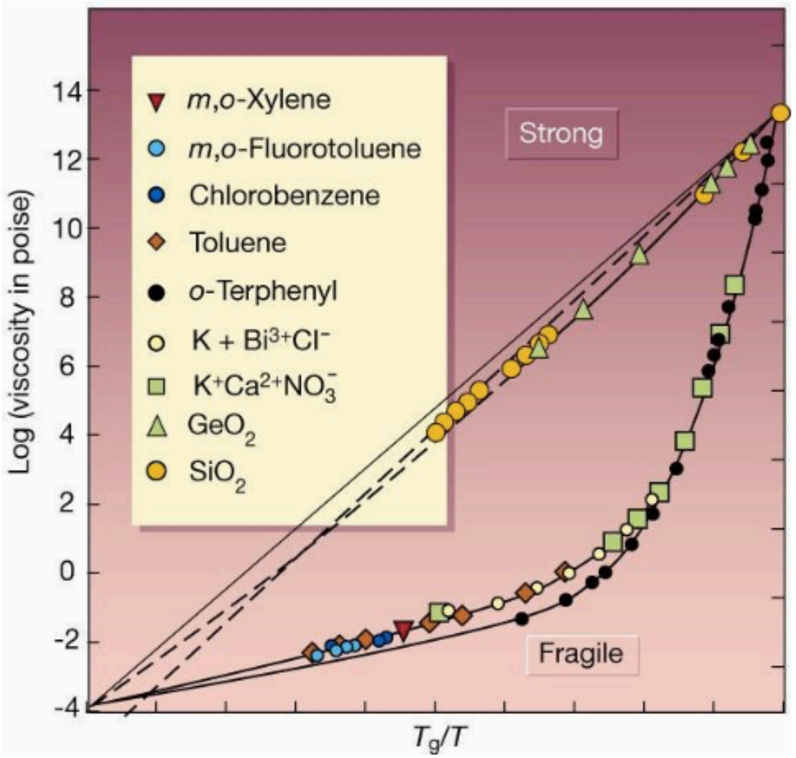
Maxwell model -> viscosity $\eta = G_\infty \tau_\alpha$

at crystallisation/melting $\eta \sim 10^{-1}$ Poise

=glass when viscosity $\eta \geq \eta_{glass} \approx 10^{13}$ Poise

14 orders of magnitude increase

strong v fragile



$$\tau_\alpha = \tau_0 e^{E/k_B T}$$

arrhenius
energy barriers, E

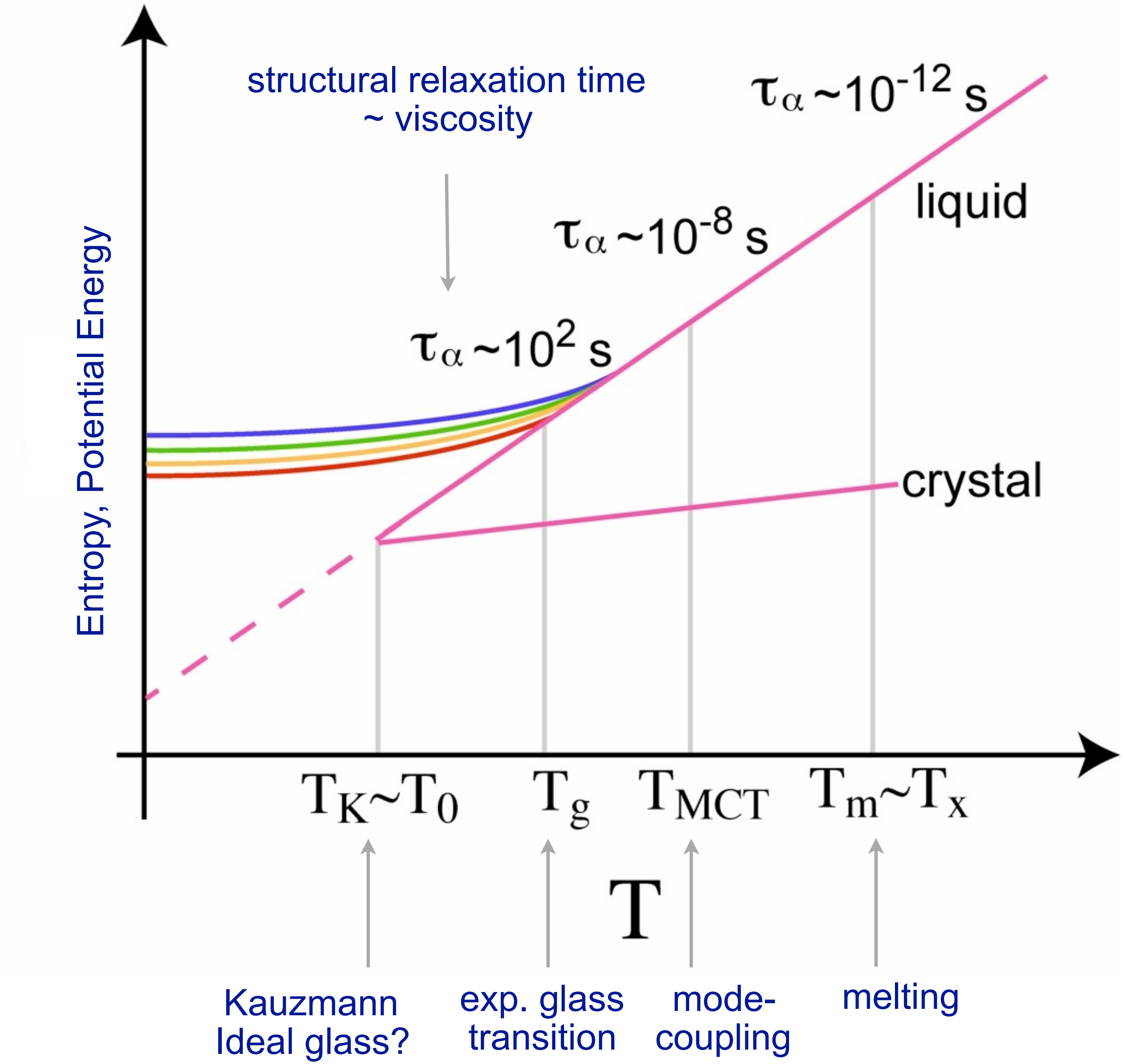
E indep. T

super-arrhenius

E ↗ as T ↘

fragile -> complex activation-> collective behaviour

What do we mean by "ideal glass"?



Royall and Williams *Phys. Rep.* **560** 1-75 (2015)

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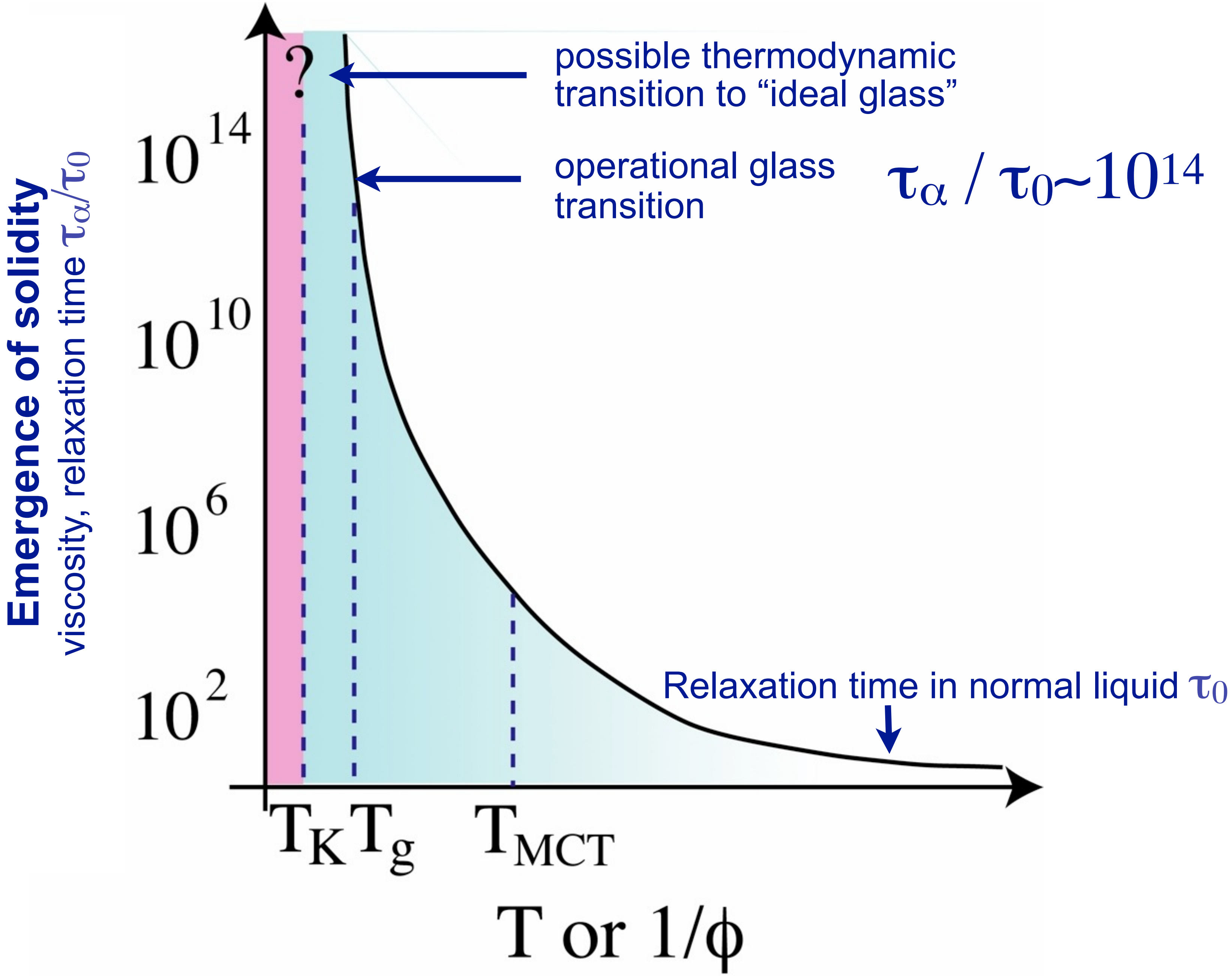
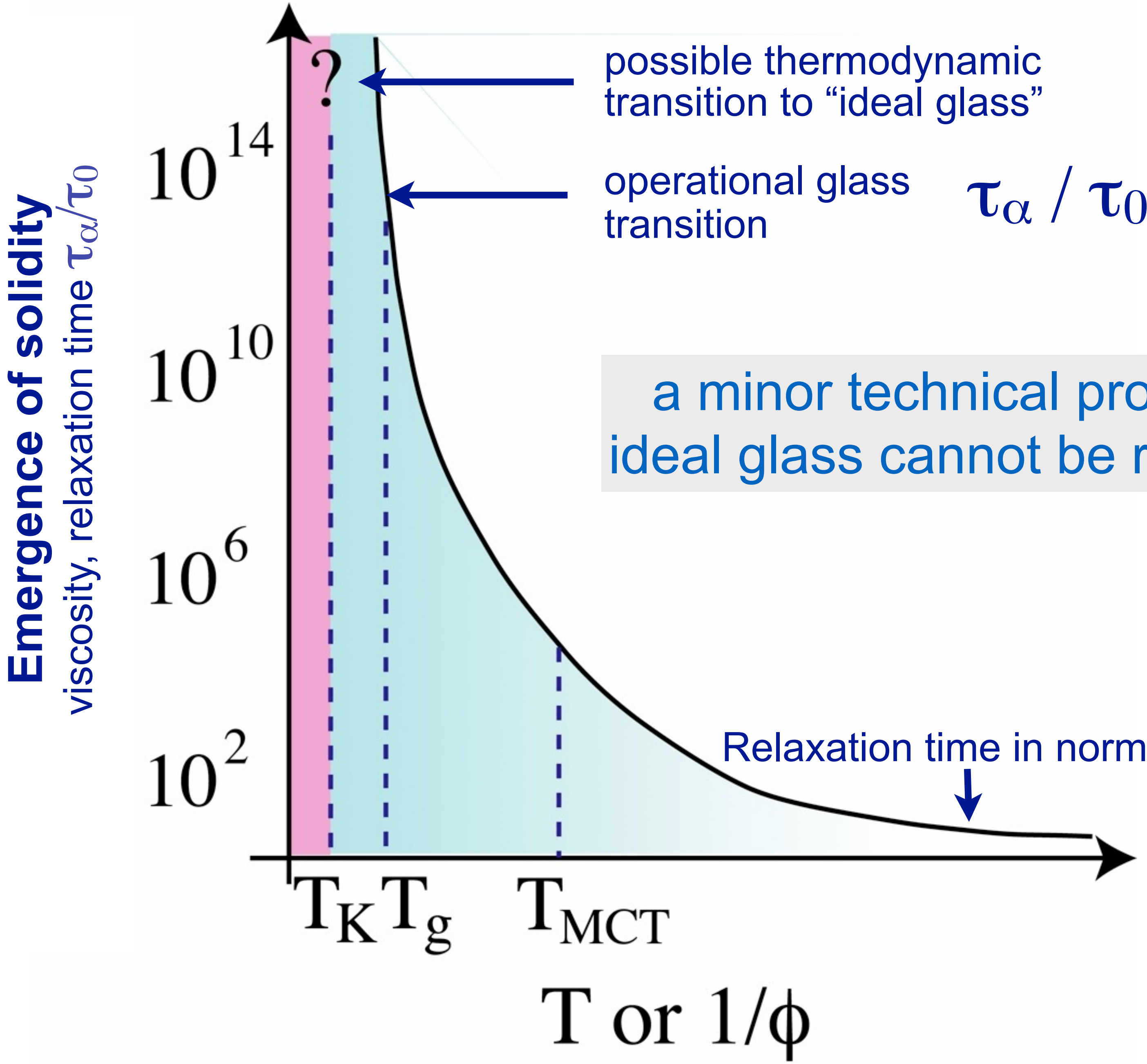


For colloids packing fraction $\phi \sim 1/T$

What do we mean by "ideal glass"?



$\tau_\alpha / \tau_0 \sim 10^{14}$

a minor technical problem:
ideal glass cannot be reached

For colloids packing fraction $\phi \sim 1/T$

molecular dynamics

- NVT/NVE simulations (equilibration/sampling)
- Nosé-Hoover/Nosé-Poincaré thermostat
- Wahnström model

$$\mathcal{H} = \mathcal{T} + \mathcal{V}$$

$$\dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i}$$

$$\alpha, \beta \in A, B$$

$$\mathcal{V} = \sum_{i<j,\alpha,\beta} u_{\alpha\beta}(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\beta|)$$

$$u_{\alpha\beta}(r) = 4\epsilon \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right]$$

$$\mathcal{T} = \sum_{\alpha,i} \frac{|\mathbf{p}_i^\alpha|^2}{2m_\alpha}$$

$$m_A = 2m_B = m$$

$$\frac{12}{11}\sigma_{AB} = \frac{6}{5}\sigma_{BB} = \sigma_{AA}$$

$$N = 10976, 87808$$

non-dimensionalisation

Quantity	Conversion
mass	$m^* = m'/m$
length	$r^* = r/\sigma$
density	$\rho^* = \rho\sigma^3$
energy	$E^* = E/\epsilon$
temperature	$T^* = k_B T/\epsilon$
pressure	$P^* = P\sigma^3/\epsilon$
time	$t^* = (\epsilon/m\sigma^2)^{1/2} t$

$$0.575 \leq T \leq 2.5$$

start FCC at high T - simulate till random - quench to low T
-then equilibrate for 500 alpha relaxation times with NVT
-then generate statistical ensembles from NVE

intermediate scattering function

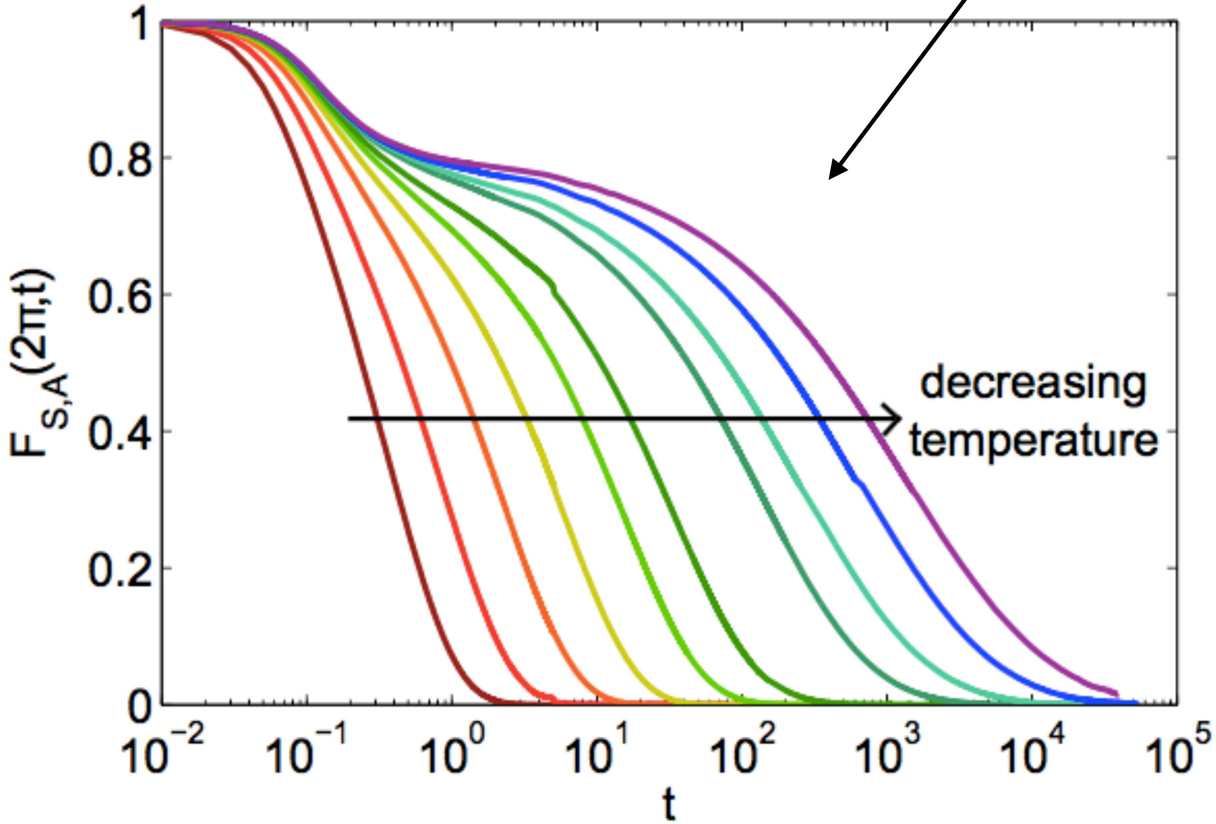
obtaining τ_α

α-relaxation

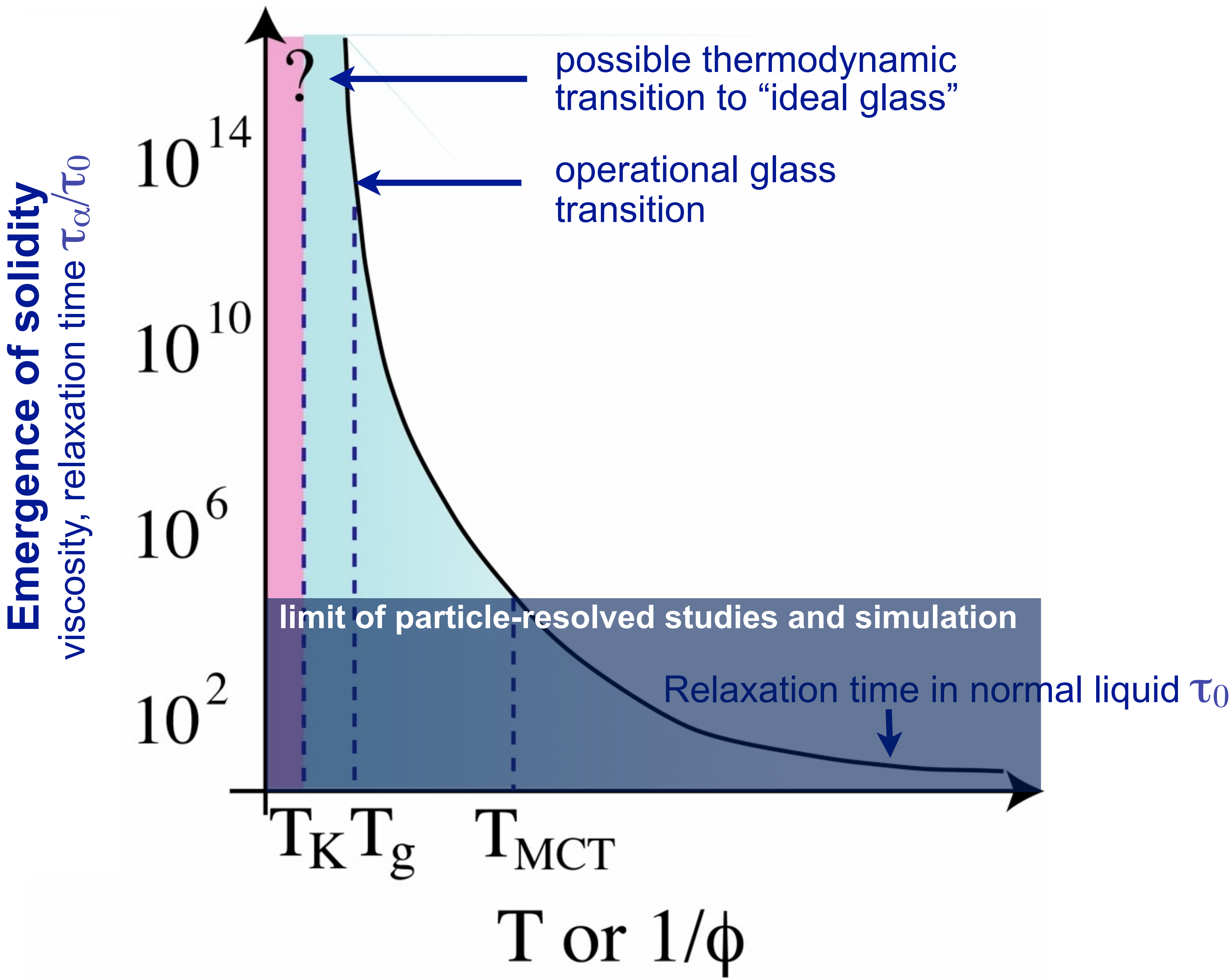
$$F(\mathbf{q},t) = \left\langle \frac{1}{N}\rho_{\mathbf{q}}(t)\rho_{-\mathbf{q}}(0) \right\rangle$$

$$\sim e^{-(t/\tau_\alpha)^\beta}$$

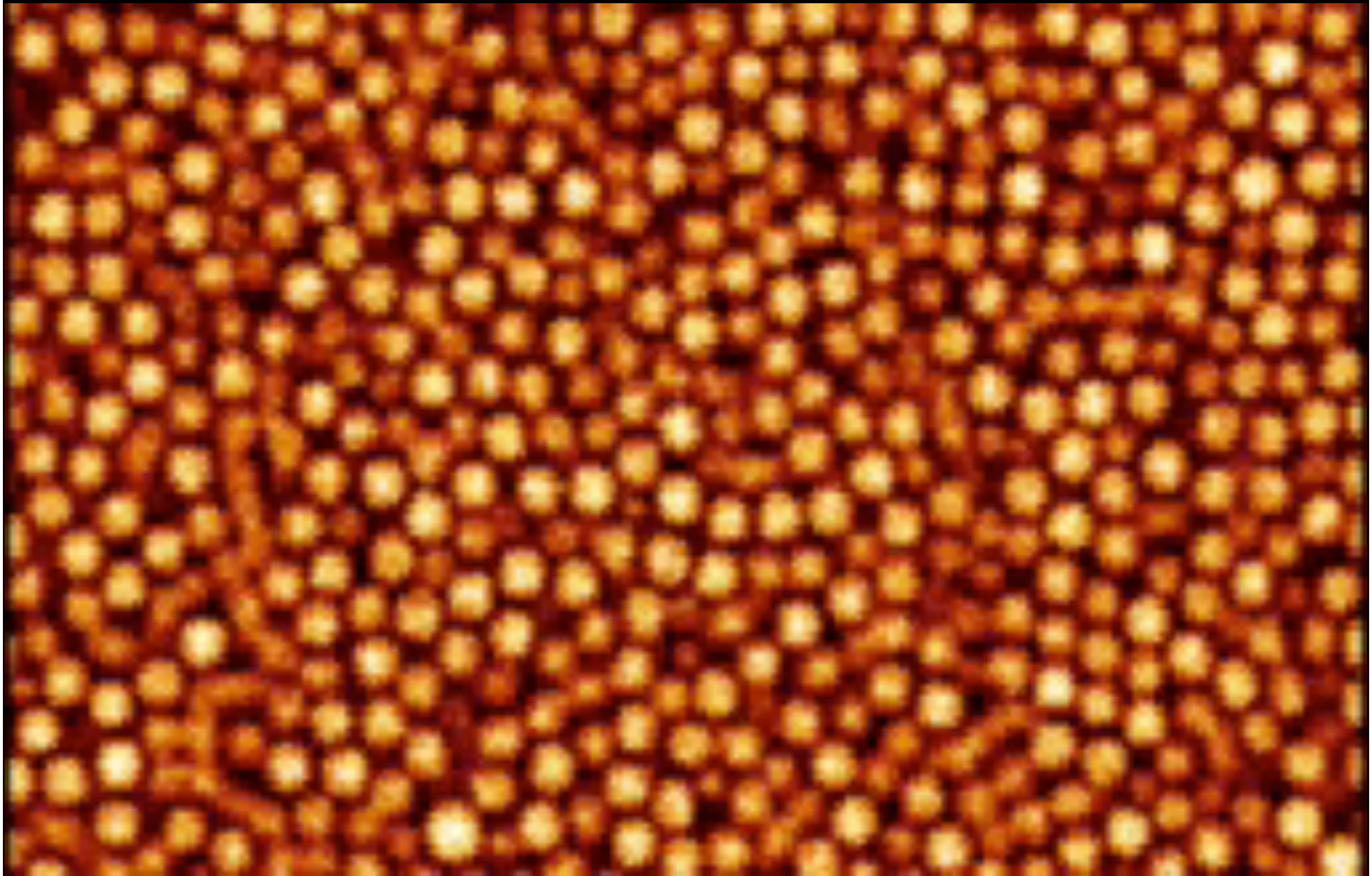
$$\rho_{\mathbf{q}}(t) = \sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_j}$$



How far can we get with Brute force?

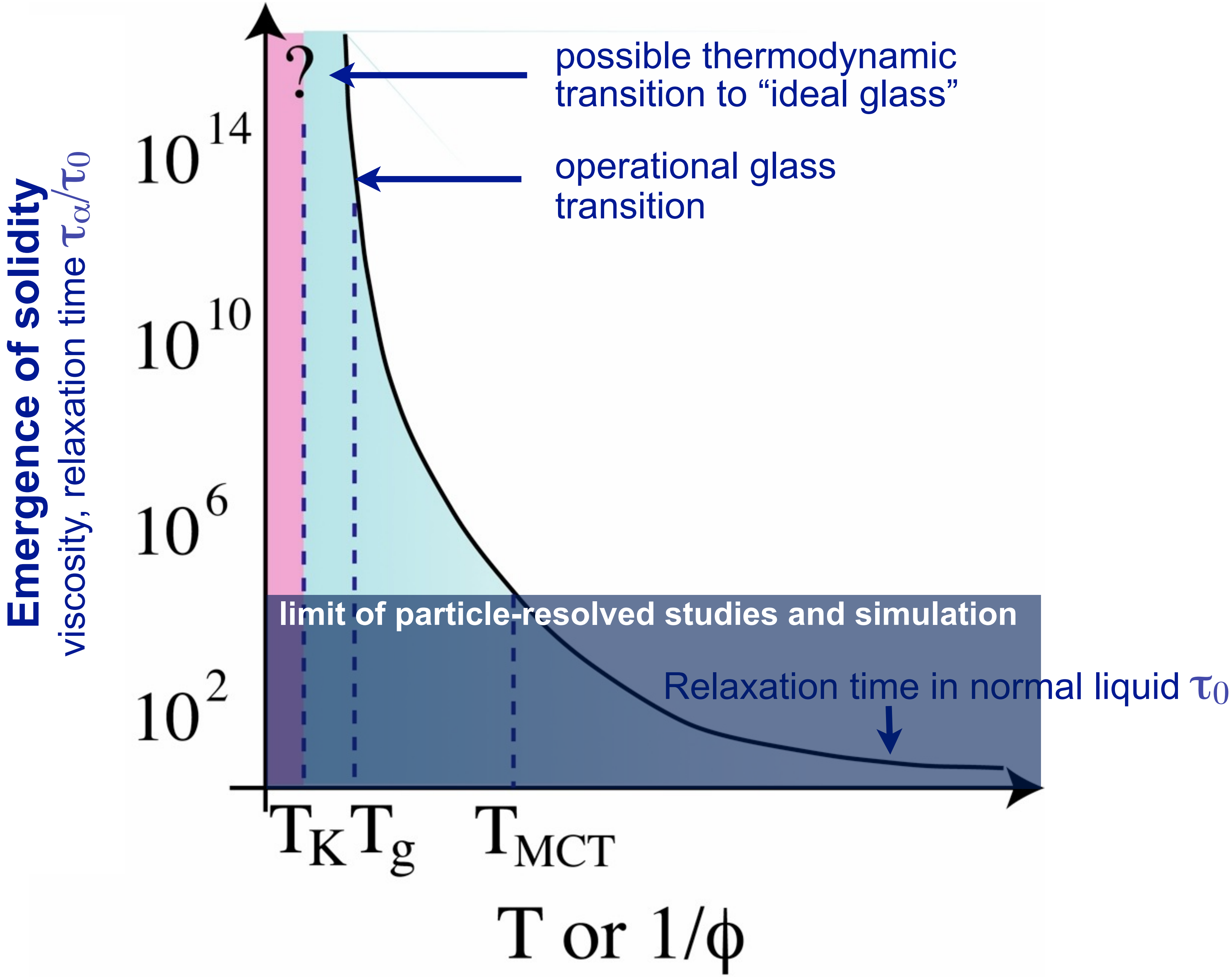


Particle-resolved studies->colloidal particles in microscope



colloidal supercooled liquid near mode coupling transition

How far can we get with Brute force?

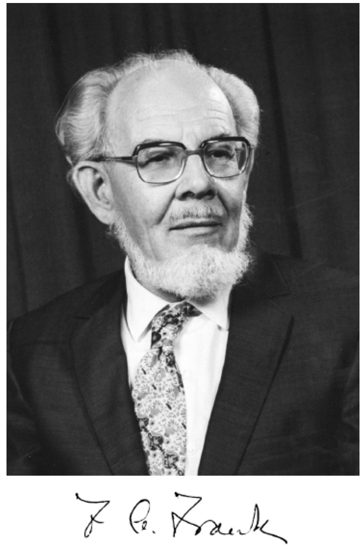


Particle-resolved studies->colloidal particles in microscope

a long time ago …

Sir F. Charles Frank

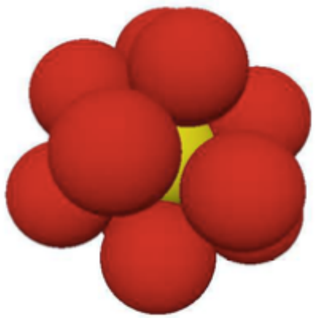
H Wills Professor, Bristol (1954-1998)

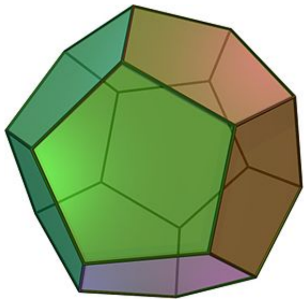


regular icosahedron, five-fold symmetry

Frank, *Proc. R. Soc.* **215** 43 (1952)

lower minimum energy of 13 LJ particles than FCC/HCP





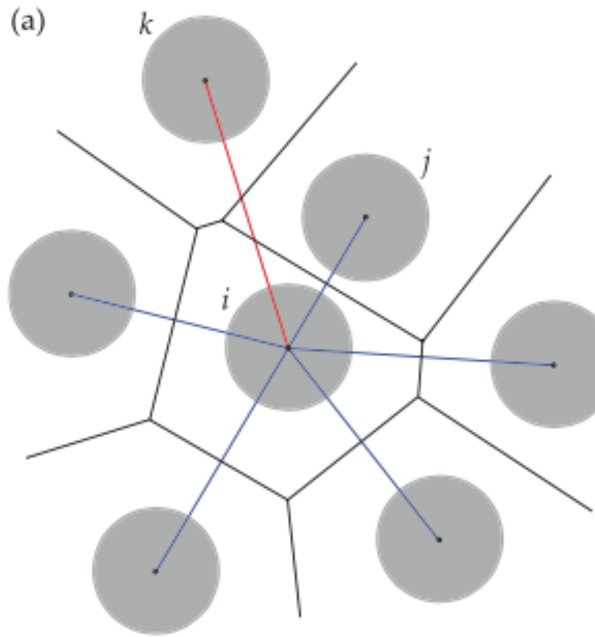
we can look for other minimum energy clusters …..

Topological Cluster Classification

min. energy clusters, voronoi tessellation, neighbours

(1) cell has all points closer to particle than any other -> convex polyhedra

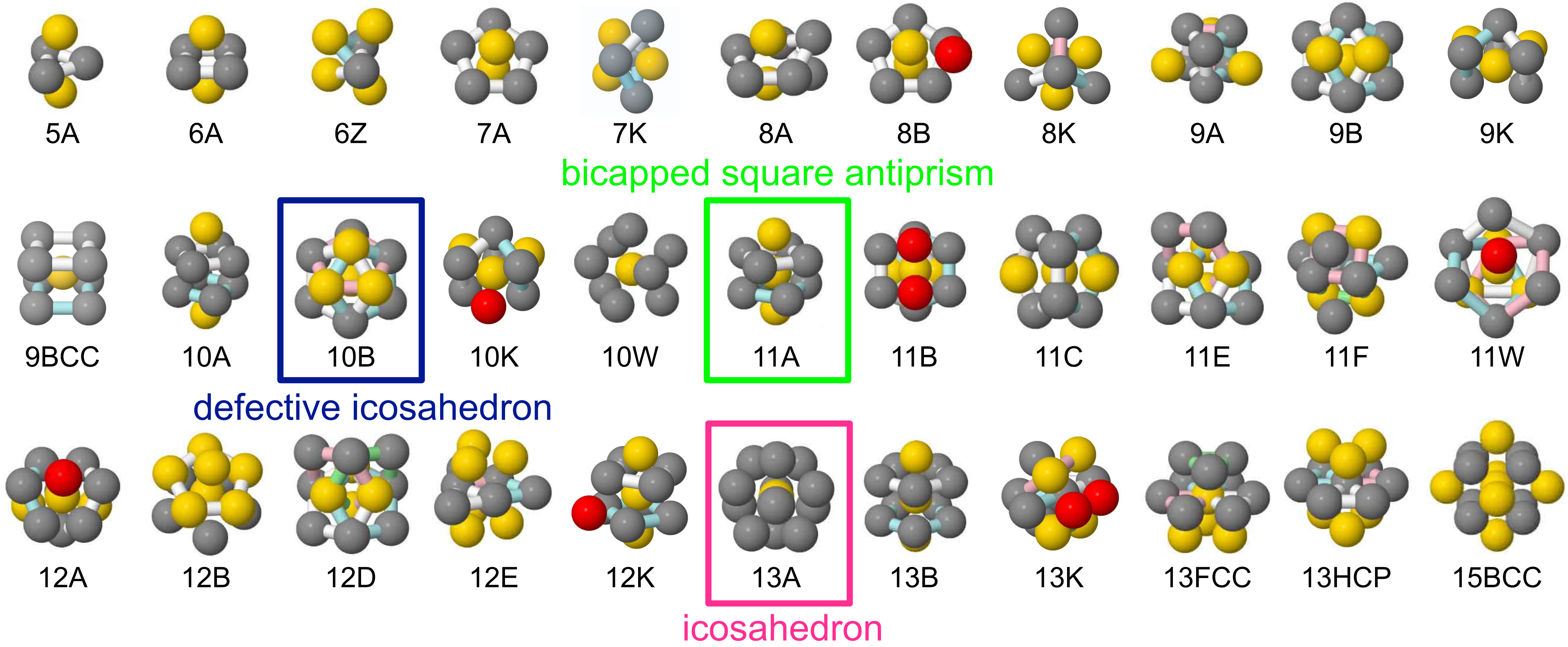
(2) neighbours if cells share face and line joining centres intersects shared face
(3) shortest path rings of 3,4 or 5 particles of neighbours.
(4) build clusters out of shortest rings



Malins et al, *J. Chem. Phys.* **139** 234506 (2013); Royall et.al. *Nature Materials* **7** 556 (2008)

The bottom of the (local) energy landscape

break down into local structures

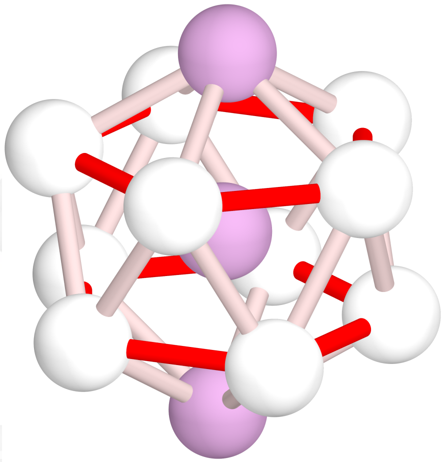


numbers=number of particles
letters=different model systems

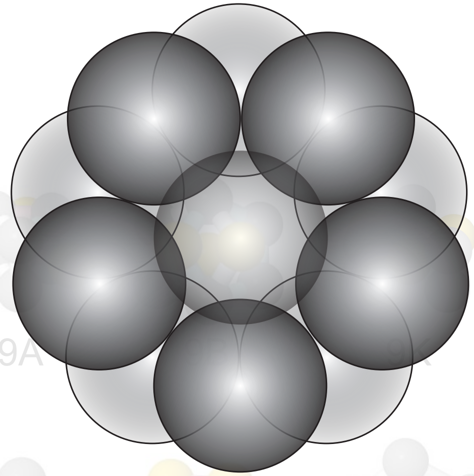
Mossa and Tarjus *J. Chem. Phys.* **119** 8069 (2003); Doye and Wales *J. Chem. Phys.* **103**, 4234-4249 (1995)
Malins et al, *J. Chem. Phys.* **139** 234506 (2013); Royall et.al. *Nature Materials* **7** 556 (2008)

The bottom of the (local) energy landscape

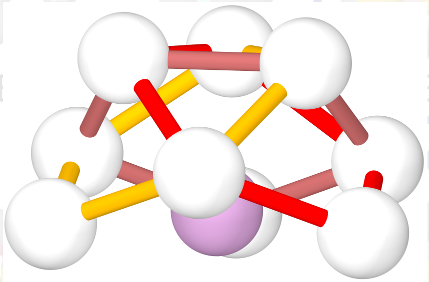
local structures - a Noddy's guide



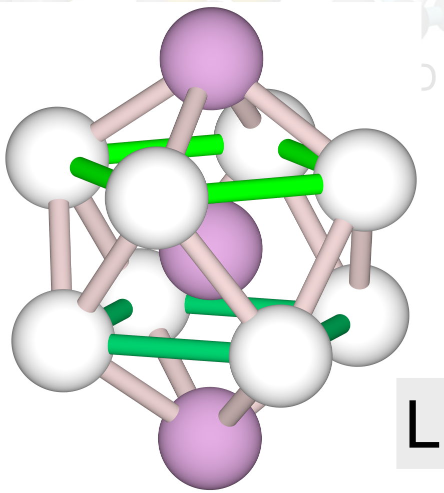
icosahedron
canonical local structure
Frank, *Proc. R. Soc.* **215** 43 (1952)



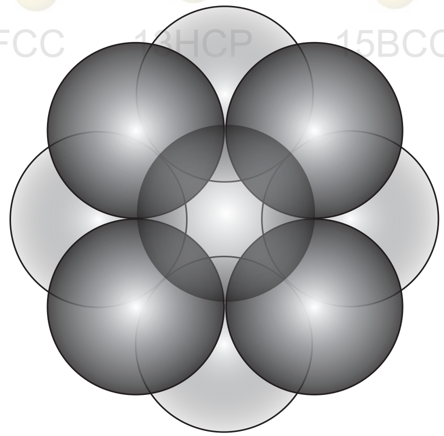
less overlap in icosahedron
bicapped square antiprism:
non-additive mixtures



defective
icosahedron



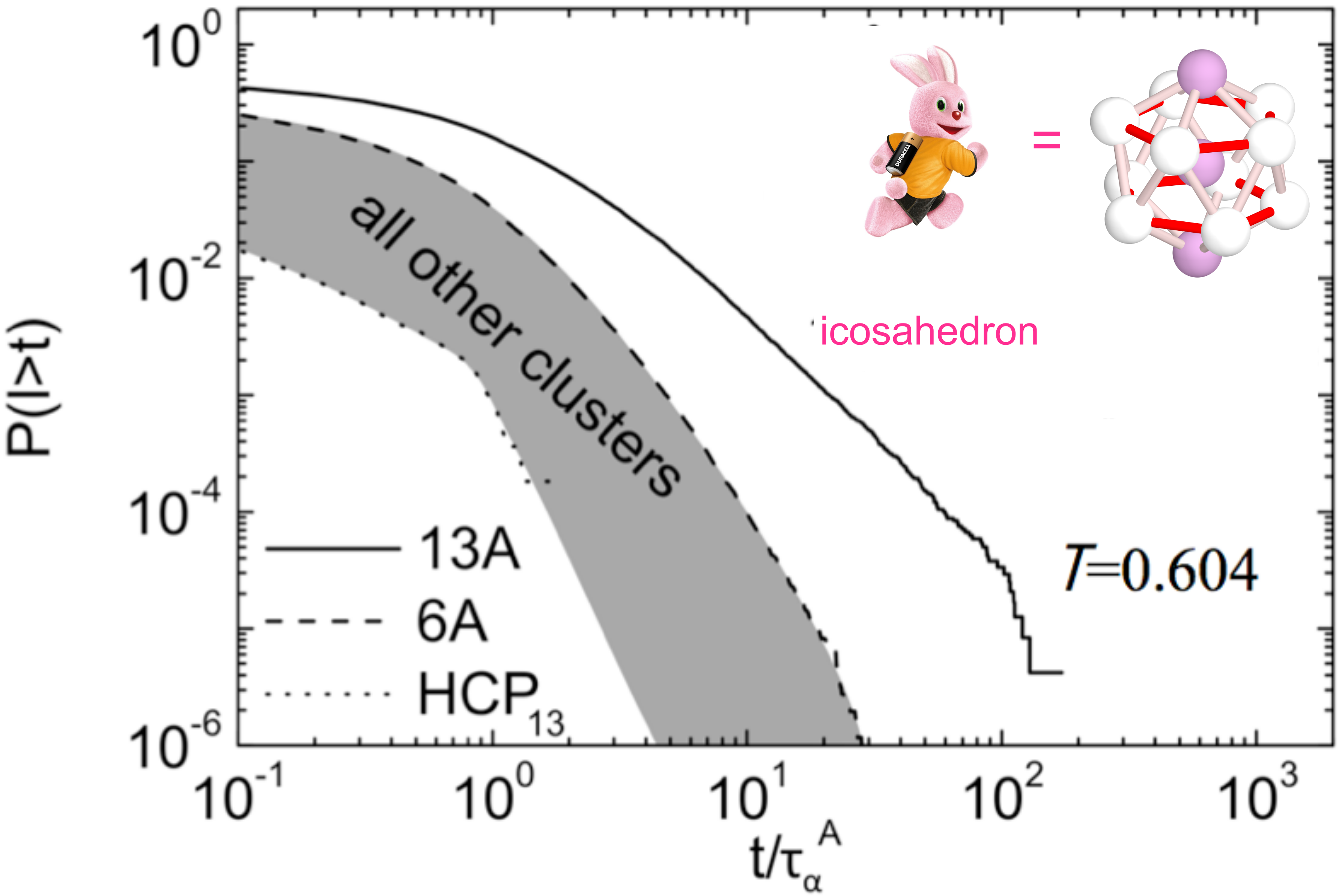
bicapped square
antiprism



top view

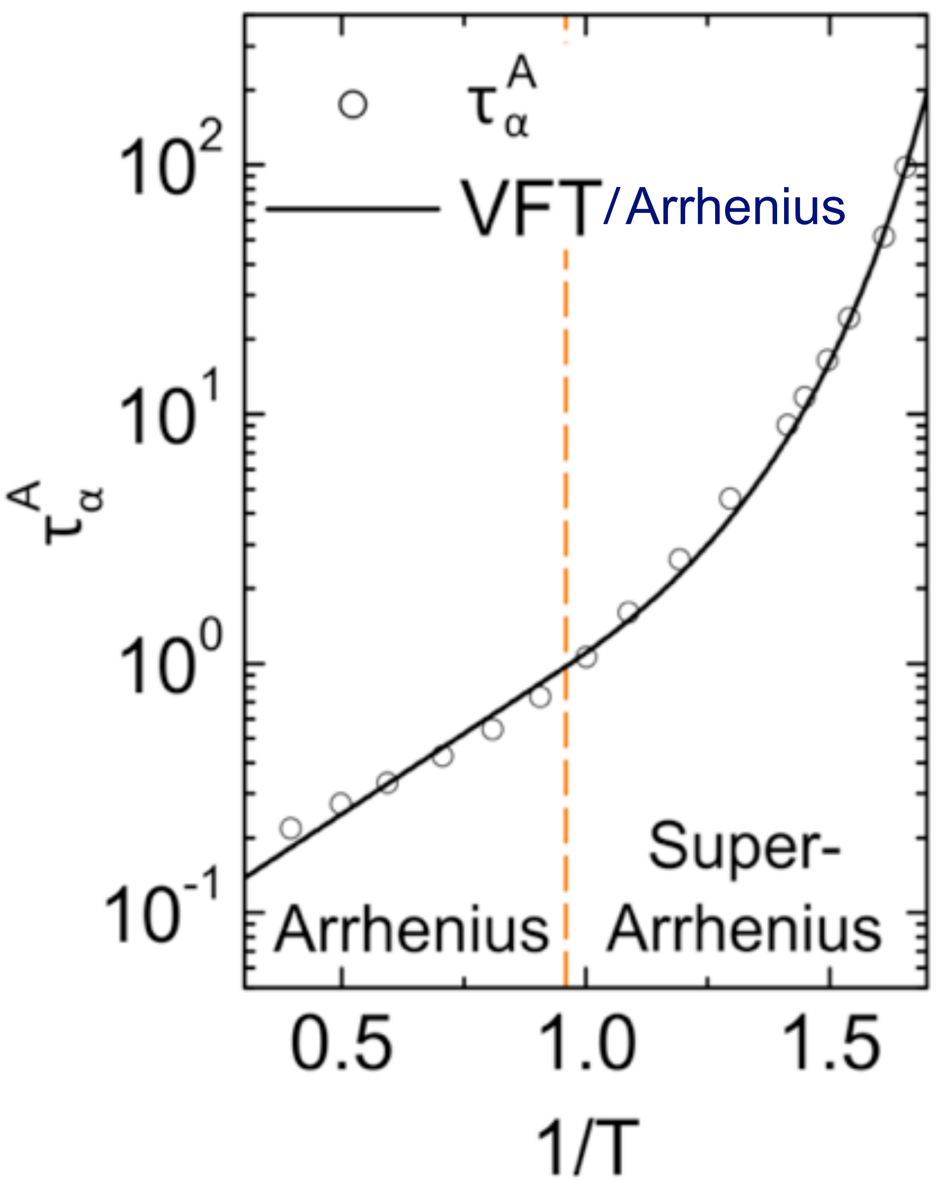
LPS and numbers change with system

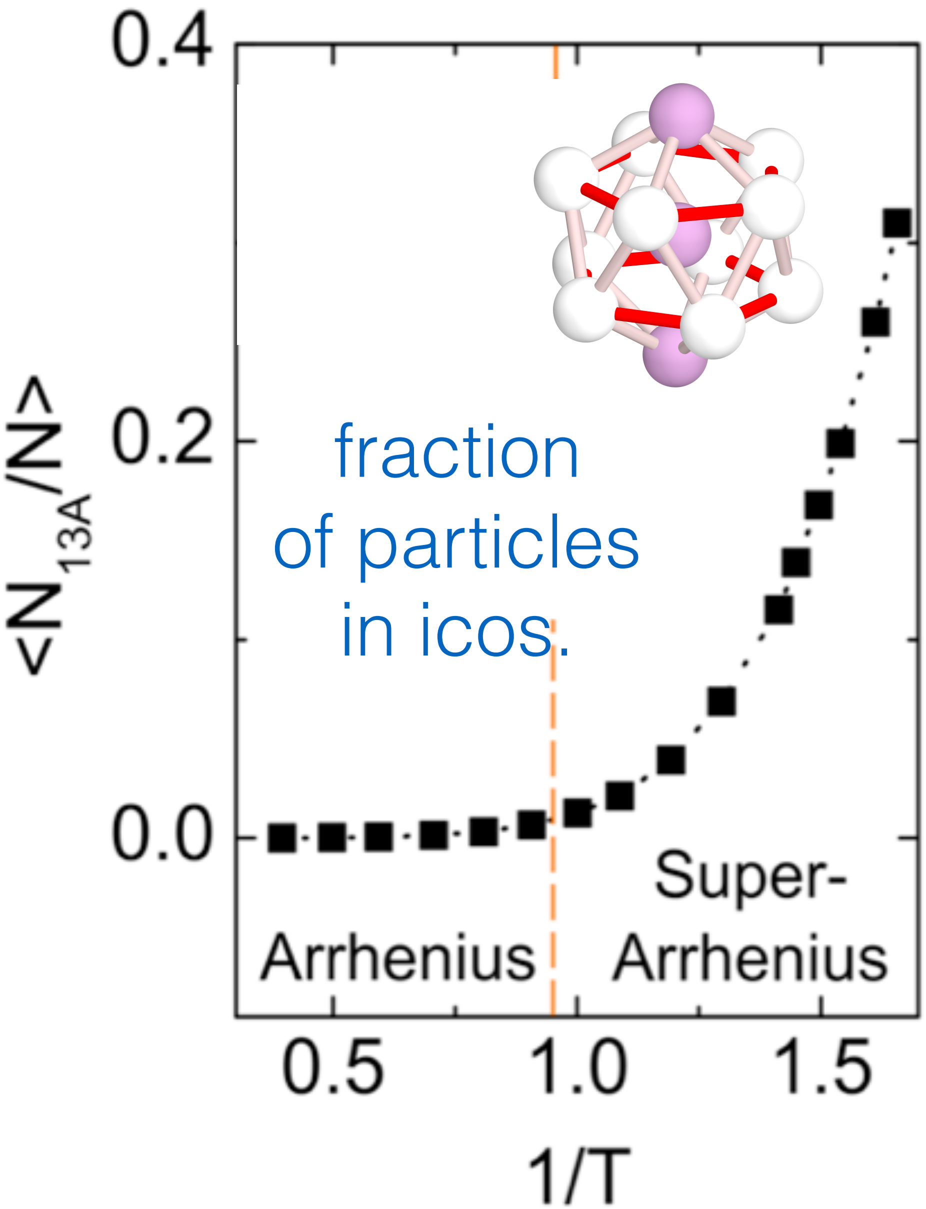
Local structure and emergence of solidity



Wahnstrom Binary Lennard-Jones mixture $\sigma_A=5/6\sigma_B$. Molecular Dynamics simulation
Royall and coworkers *J. Chem. Phys.* **138** 12A535 (2013)

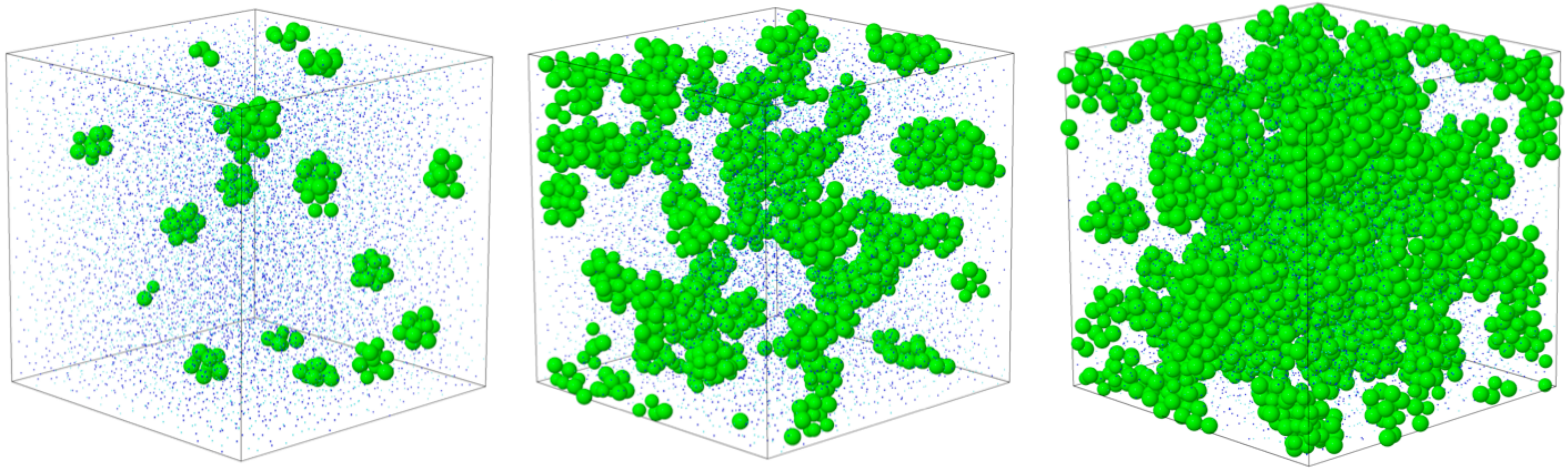
Local structure and emergence of solidity





Malins et al, *J. Chem. Phys.* **138** 12A535 (2013); Coslovich and Pastore *J. Chem. Phys.* **127** 124504 (2007)

Growth of domains of icosahedra upon cooling



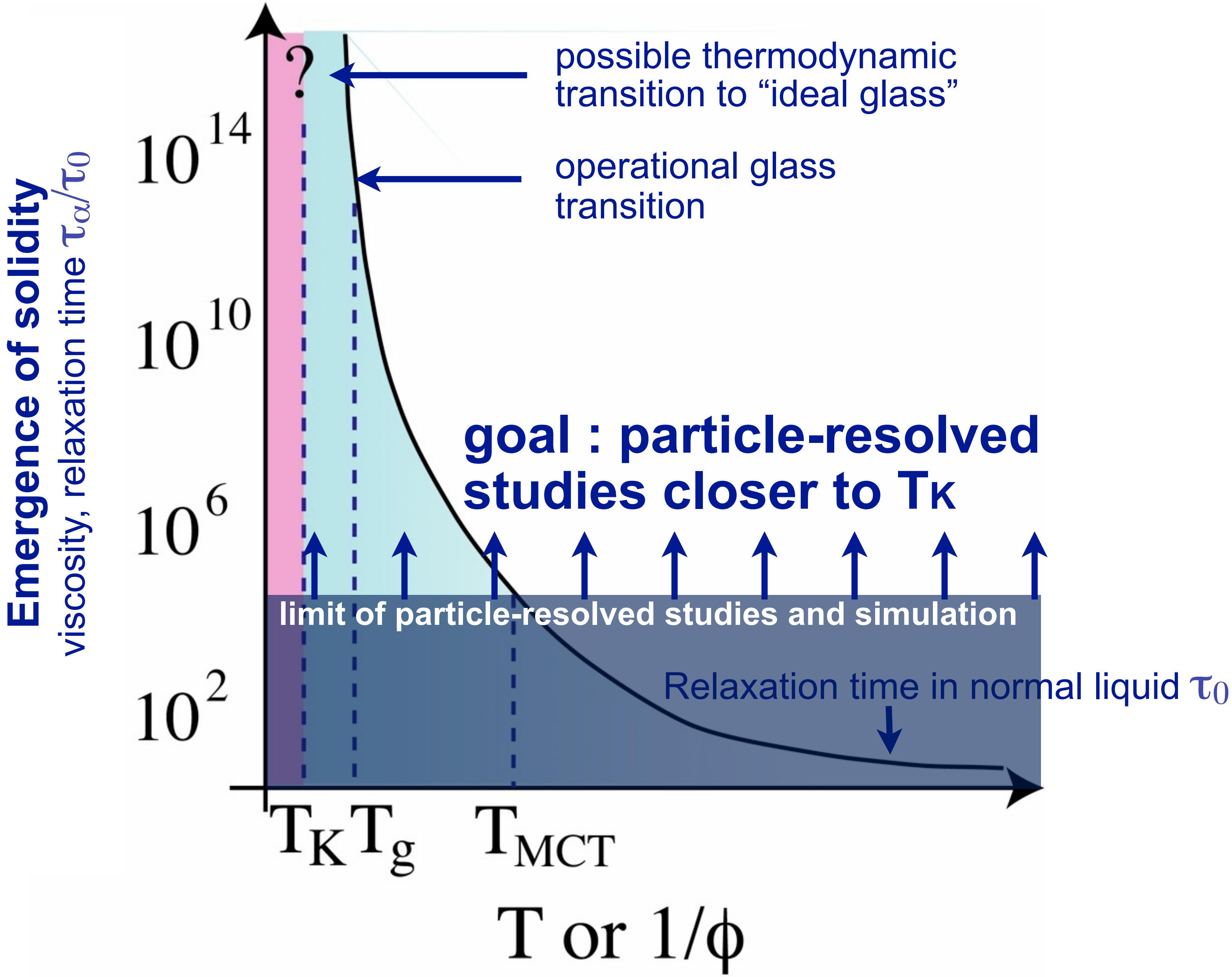
T=1.00 *T*=0.707 *T*=0.620

domains larger at lower T….
icosahedra in clusters live longer ….

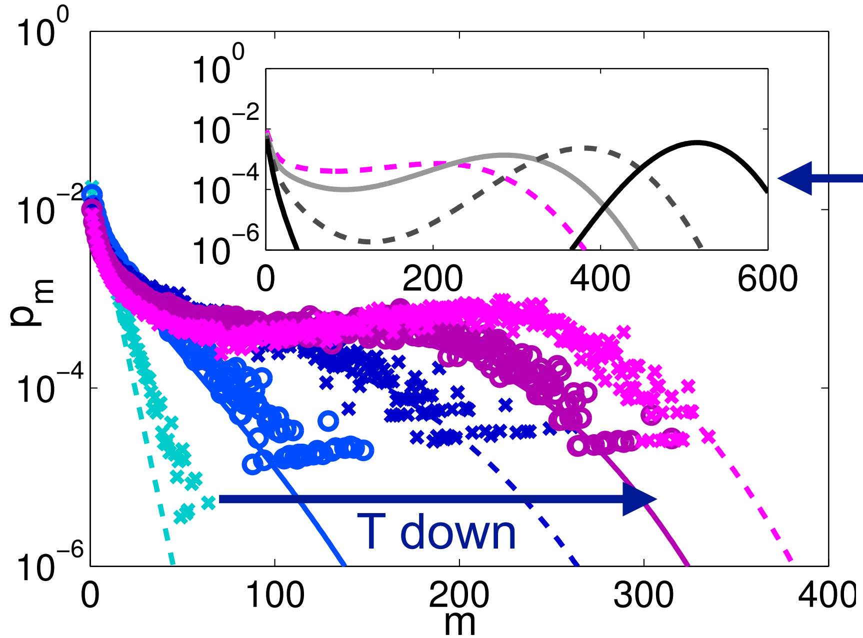
Emergence of network of icosahedral (slow) particles. Fractal dimension=2

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

How far can we get with Brute force?



Recasting with effective system of icosahedra



T in range beyond that accessible to simulation

$$T \gg 1 \quad \Rightarrow \quad \tau_\alpha^{Arr} = \tau_0 \exp(A/T)$$

$$\tau_0 = 0.11$$
$$A = 2.98$$

describe distribution of domains of icosahedra of size *m* with population dynamics model

$$\dot{p}_1 = g_0 p_0 + r_2 p_2 - [g_1 + r_1] p_1$$
$$\dot{p}_m = g_{m-1} p_{m-1} + r_{m+1} p_{n+1} - [g_m + r_m] p_n$$
$$\dot{p}_M = g_{M-1} p_{M-1} - r_M p_M$$

$$\sum_{i=1}^{M} p_i = \phi$$

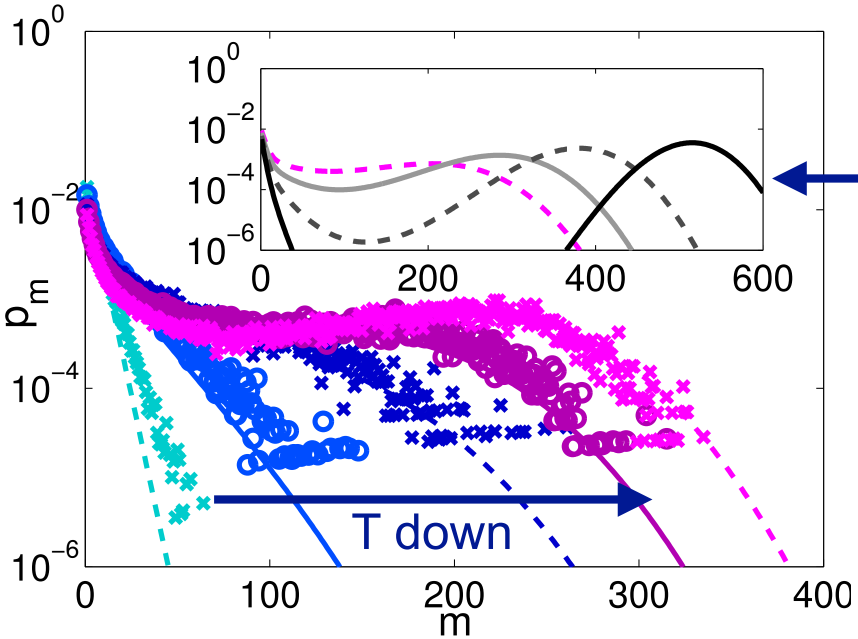
parameterise model from simulation data

p_m population of domain size m

g, r growth and reduction rates

Pinney, Liverpool and Royall *J. Chem. Phys.* (2015)

Recasting with effective system of icosahedra



T in range beyond that accessible to simulation

$T > 0.62 \quad \Rightarrow \text{no percolat.} \quad \Rightarrow p_m = a(T)^{m-1} p_1$

describe distribution of domains of icosahedra of size *m* with population dynamics model

$T < 0.62 \quad \Rightarrow \text{percolation} \quad \Rightarrow p_m = a(T) W_m(T) p_{m-1}$

$$\dot{p}_1 = g_0 p_0 + r_2 p_2 - [g_1 + r_1] p_1$$

$$\dot{p}_m = g_{m-1} p_{m-1} + r_{m+1} p_{n+1} - [g_m + r_m] p_n$$

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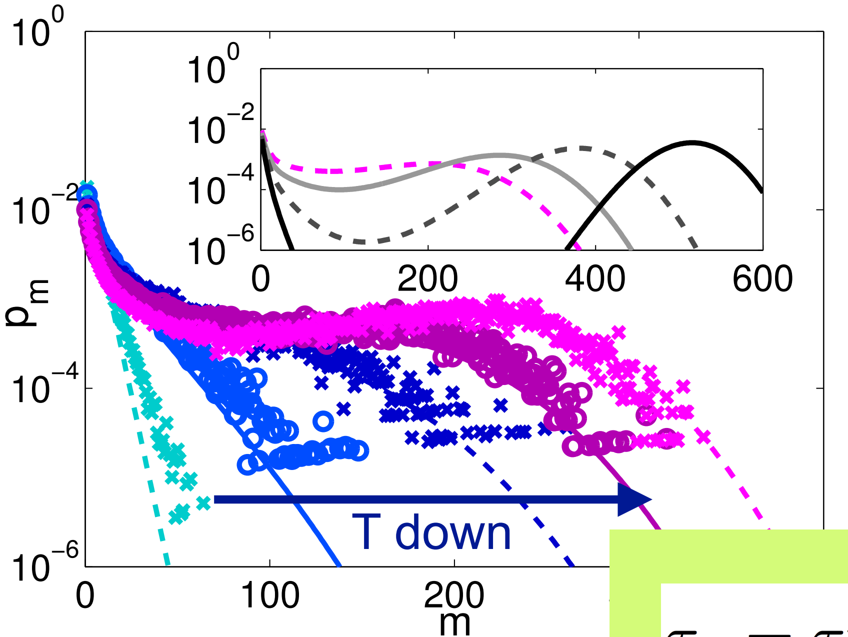

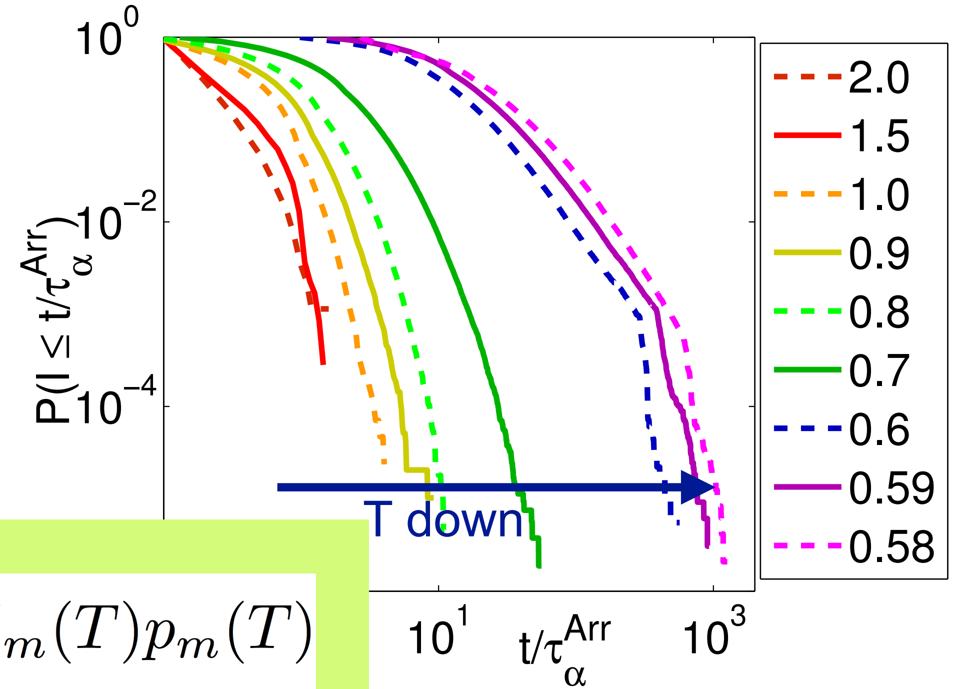

$$\tau_\alpha = \tau_\alpha^{\mathrm{Arr}} \sum_m l_m(T) p_m(T)$$

describe distribution of domai

icosahedra of size *m* with pop

dynamics model

$$\dot{p}_1 = g_0 p_0 + r_2 p_2 - [g_1 + r_1] p_1$$

$$\dot{p}_m = g_{m-1} p_{m-1} + r_{m+1} p_{n+1} - [g_m + r_m] p_n$$

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parameterise model from simulation data

p_m population of mesocluster size m

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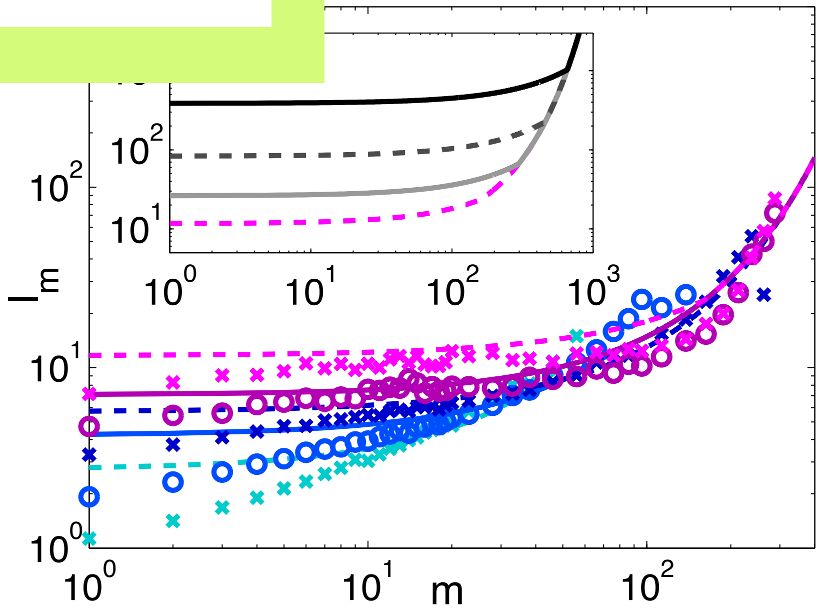
Dynamics : domain lifetimes l_m scaled by Arrhenius dynamics



Pinney, Liverpool and Royall *J. Chem. Phys.* (2015)

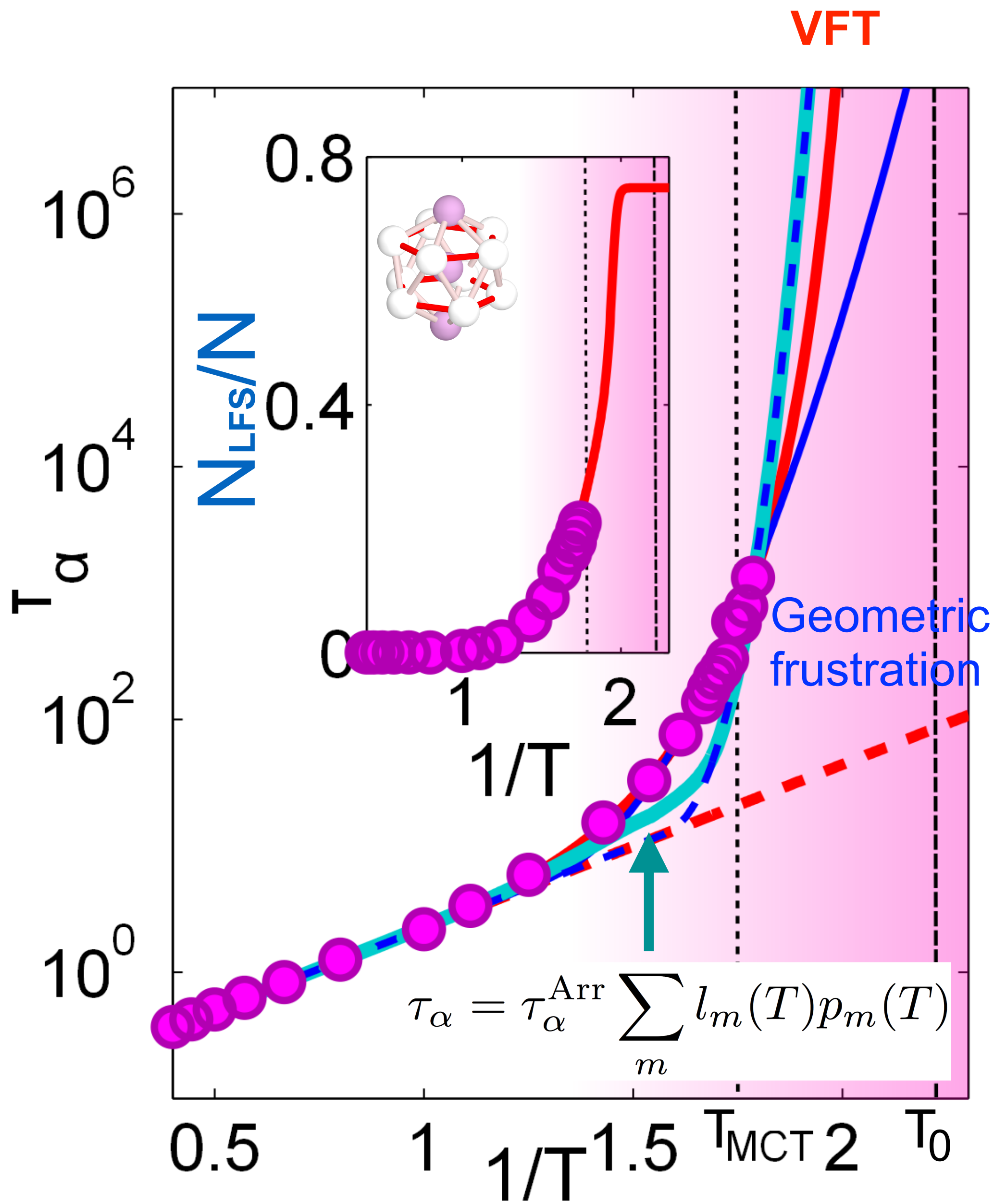
Recasting with effective system of icosahedra

No (thermodynamic) transition

Model well-described by geometric frustration

$$\tau_\alpha(T) = \tau_\infty \exp\left(\Delta E^*(T) + E_\infty / k_B T\right)$$
$$\Delta E(T) = B k_B T_c \left(1 - \frac{T}{T_{\rm on}}\right)^\psi$$

Tarjus *et al. J. Phys: Condens. Matter* **17**, R1143 (2005)



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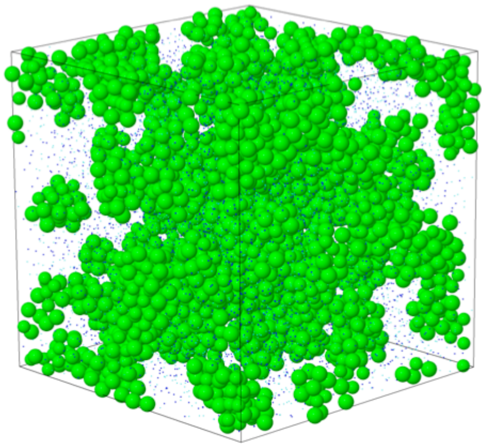
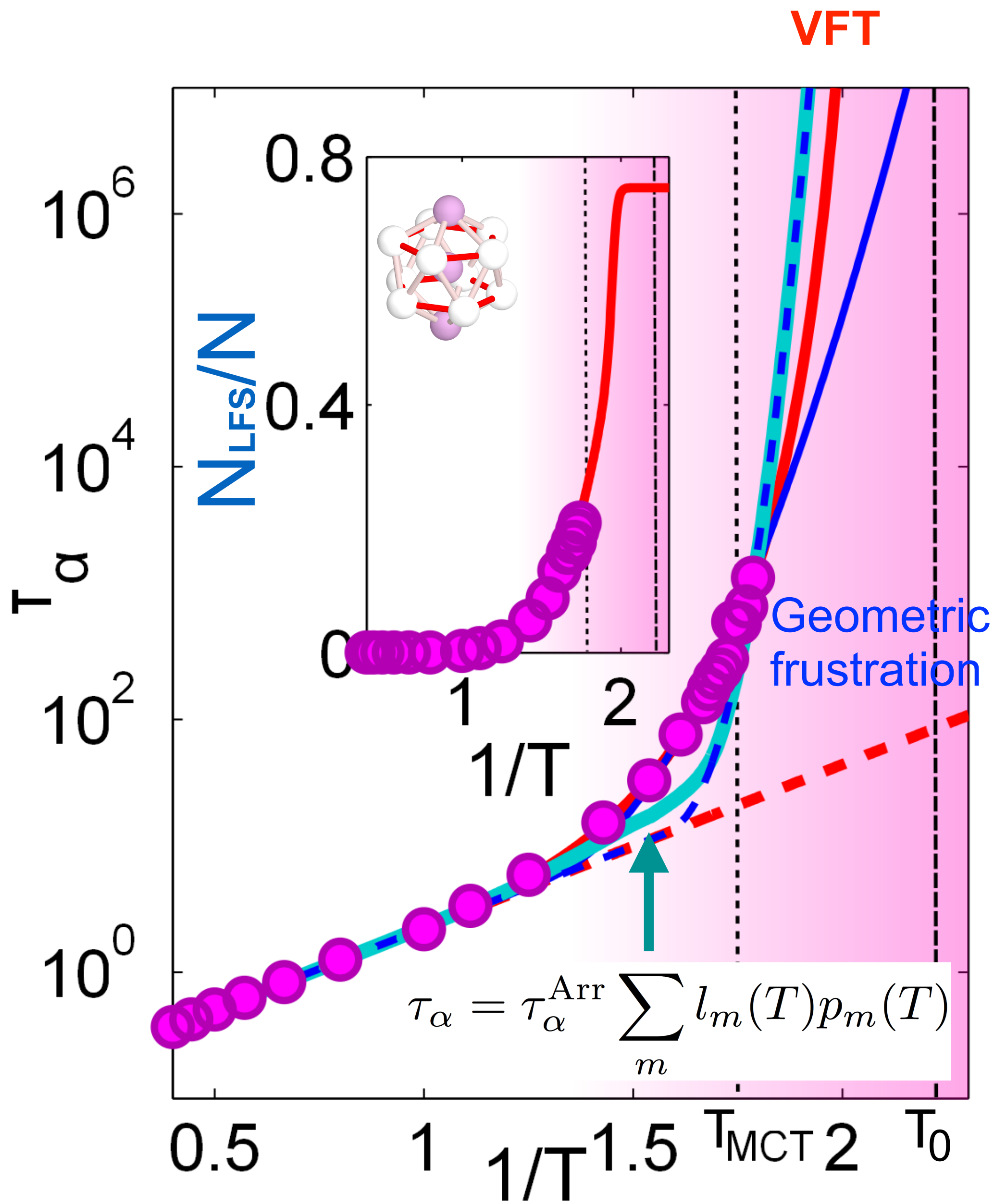
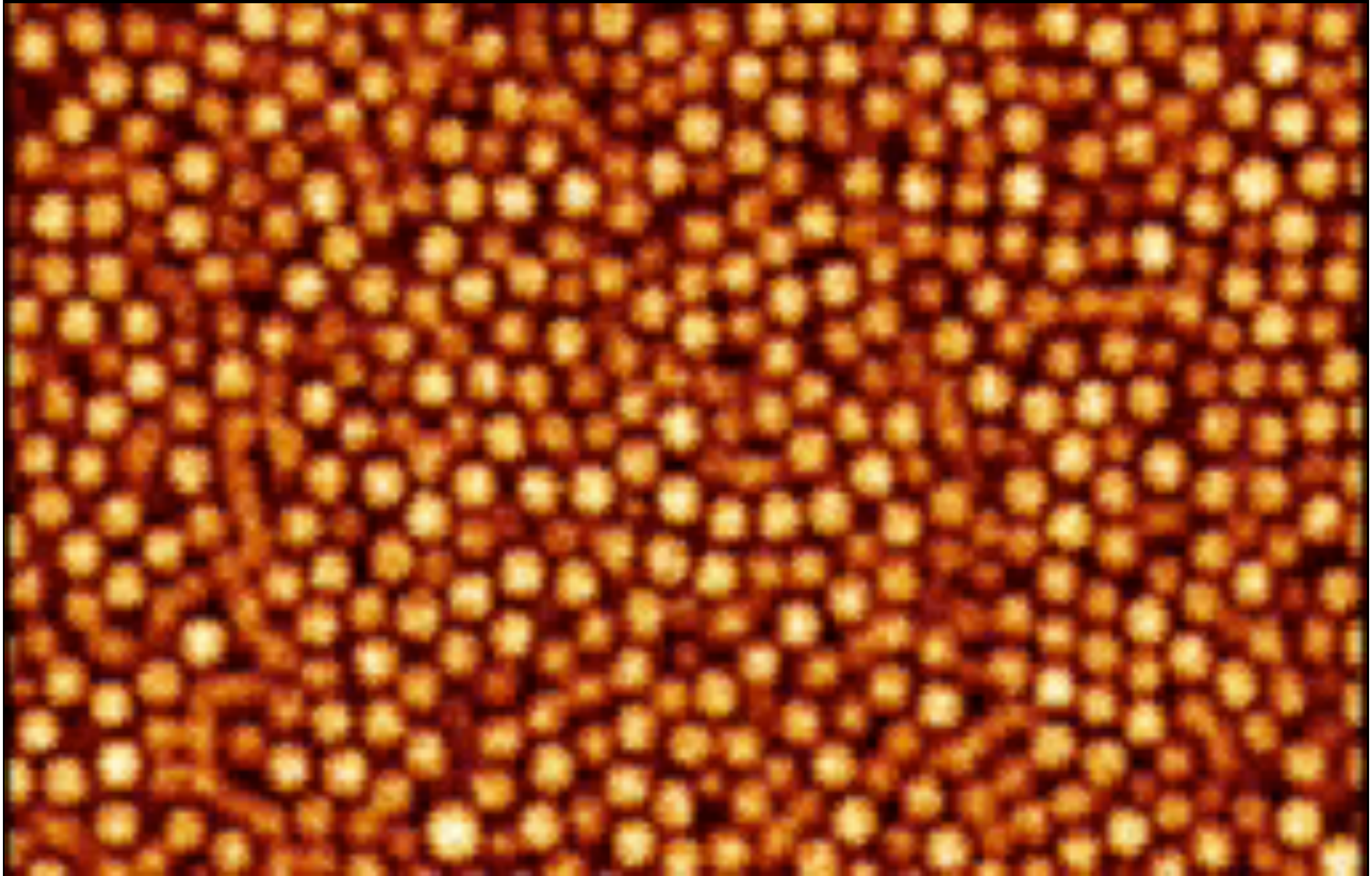




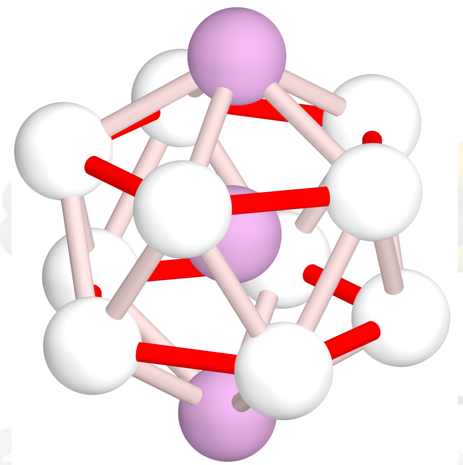
Pinney et al, *J. Chem. Phys.* (2015)



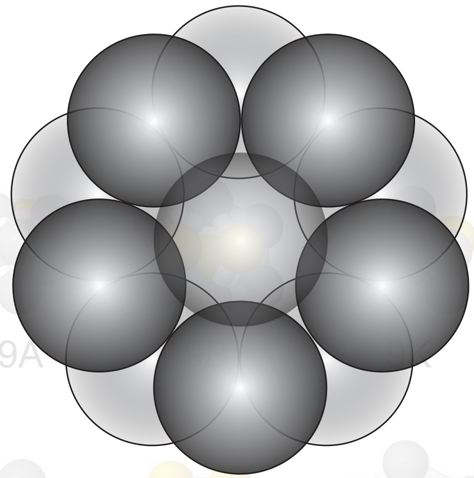
colloidal supercooled liquid near mode coupling transition

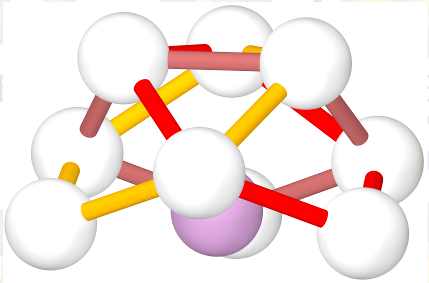
The bottom of the (local) energy landscape

local structures - a Noddy's guide



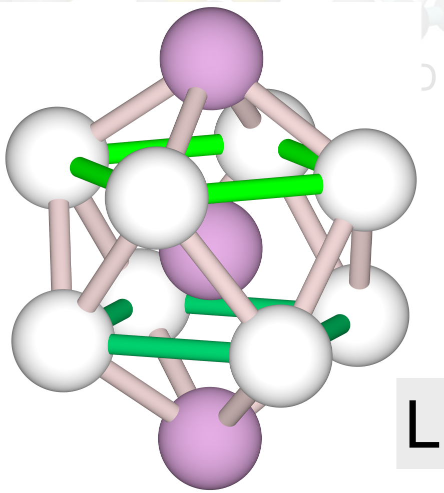
icosahedron
canonical local structure
Frank, *Proc. R. Soc.* **215** 43 (1952)



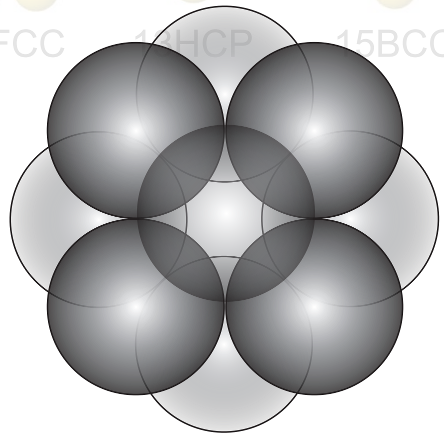


defective
icosahedron

less overlap in icosahedron
bicapped square antiprism:
non-additive mixtures



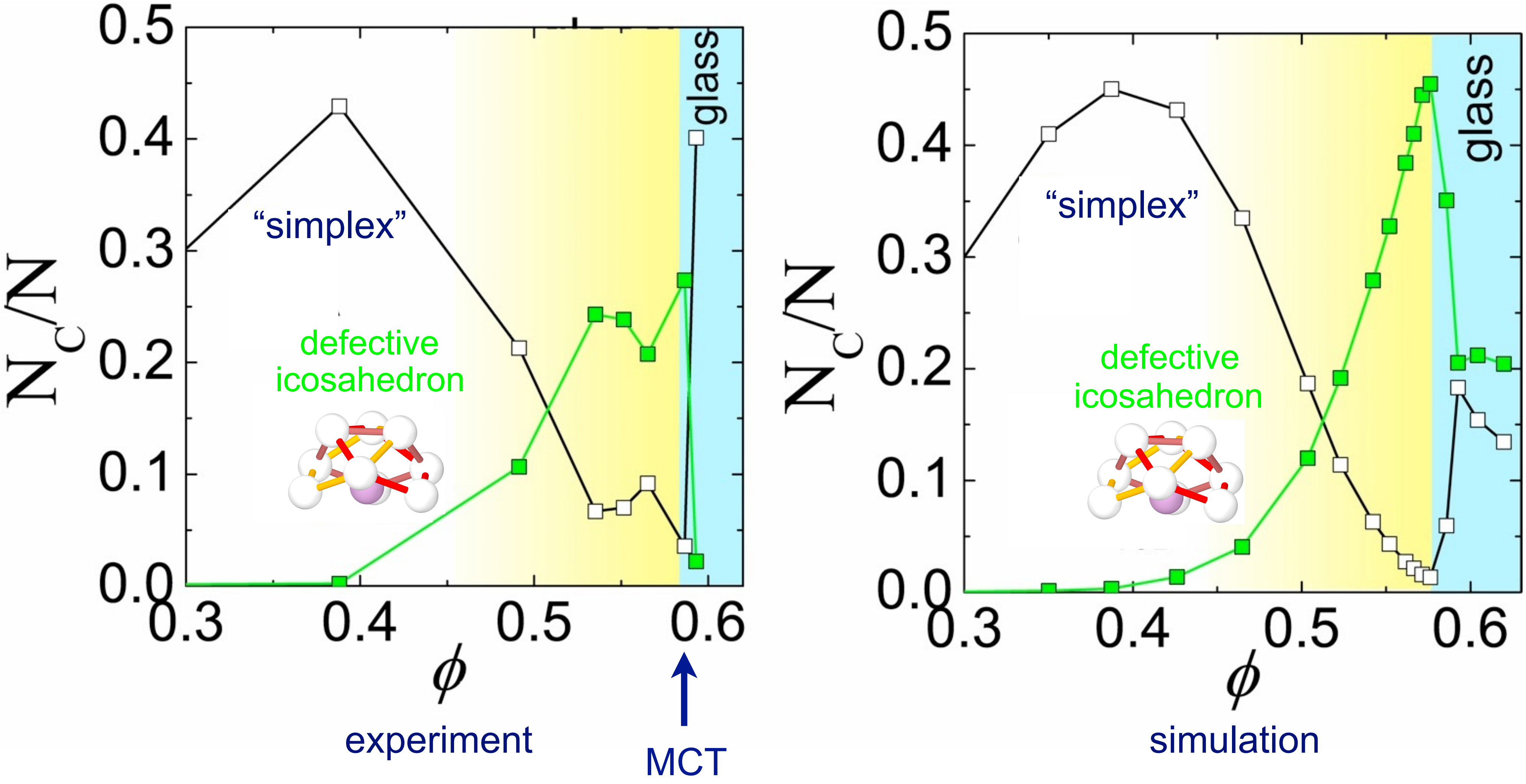
bicapped square
antiprism



top view

LPS and numbers change with system

Particle-resolved studies take us to MCT

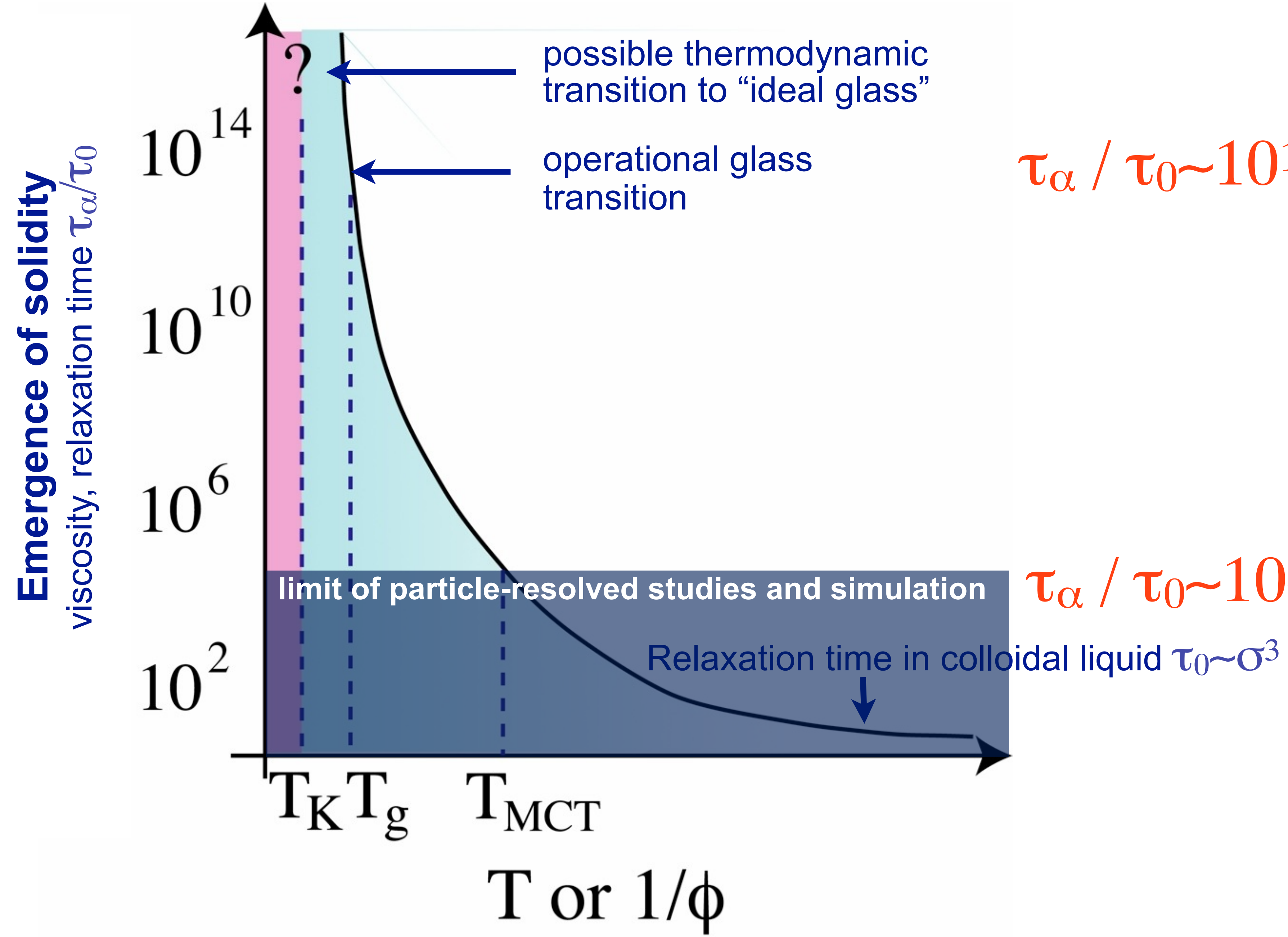


Hard spheres: defective icosahedron is LPS. Falling out of equilibrium (ϕ=0.58): "simplex"

simplex~tetrahedron

Royall et al. *J. Non-Cryst. Solids* 407 34-43 (2014)

Another route to deep supercooling

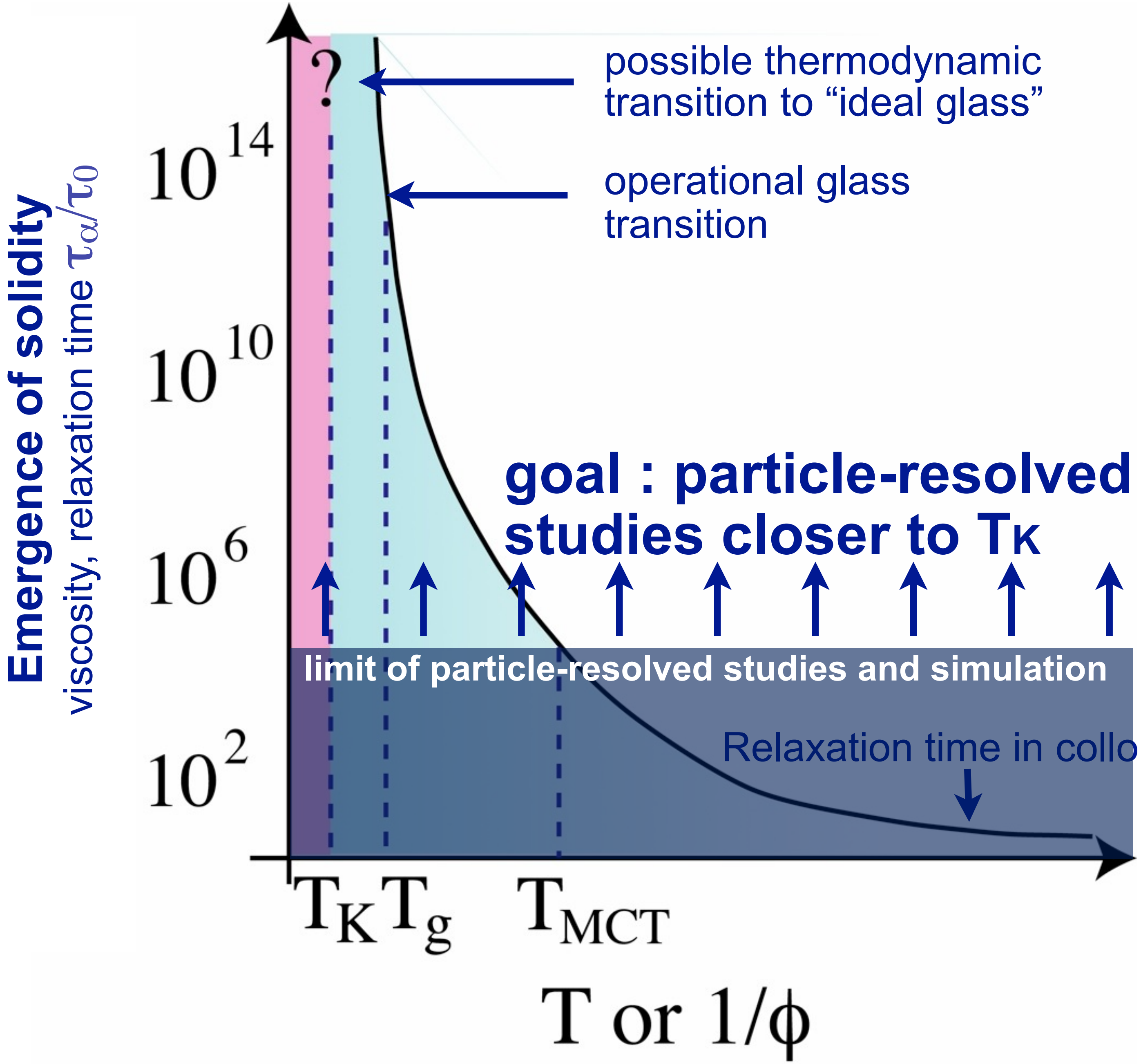


$\tau_\alpha / \tau_0 \sim 10^{14}$

$\tau_\alpha / \tau_0 \sim 10^{5}$

σ diameter of colloidal particle

Another route to deep supercooling

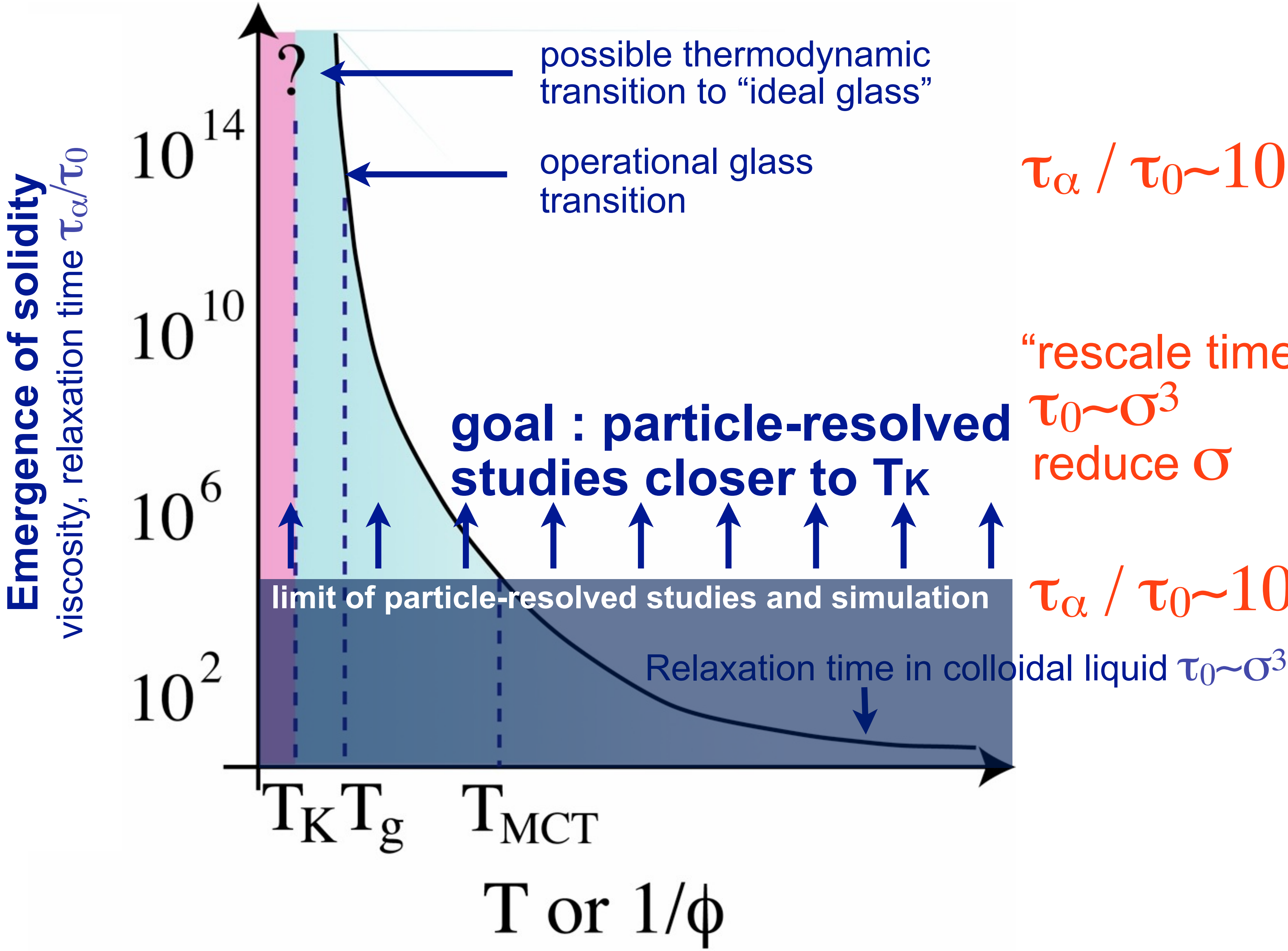


$\tau_\alpha / \tau_0 \sim 10^{14}$

$\tau_\alpha / \tau_0 \sim 10^5$

σ diameter of colloidal particle

Another route to deep supercooling



$\tau_\alpha / \tau_0 \sim 10^{14}$

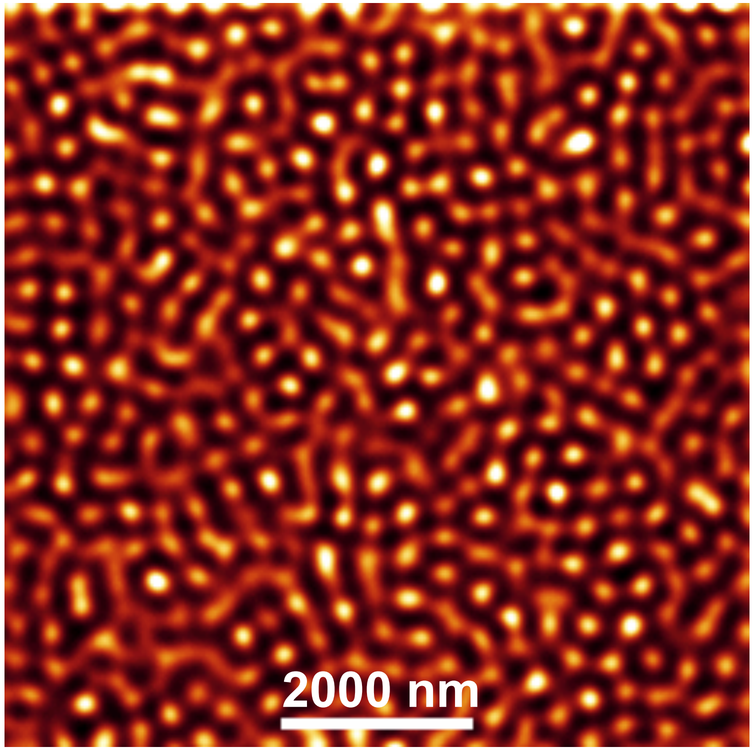
"rescale time"
$\tau_0 \sim \sigma^3$
reduce σ

$\tau_\alpha / \tau_0 \sim 10^{5}$

σ diameter of colloidal particle

Super-resolution STED "nanoscopy"

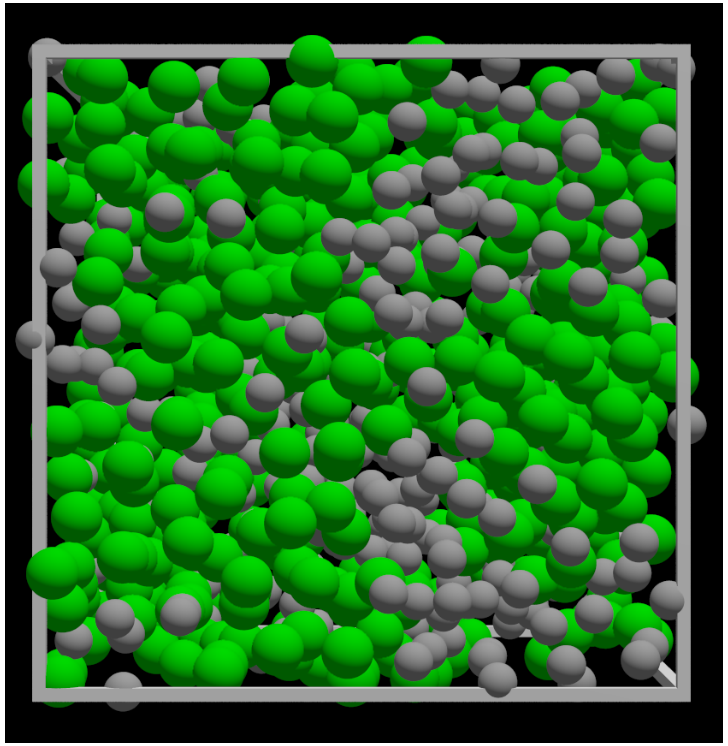
nano-particle resolved studies



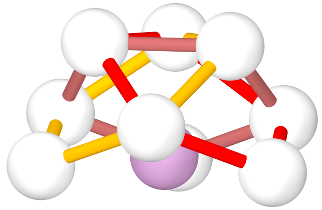
conventional particle-resolved studies
typical size ~ 3000 nm diameter

nano-particle-resolved studies
460 nm diameter (so far)

~3 decades deeper supercooling
for same experimental time



ϕ ~0.59
41% of system LFS



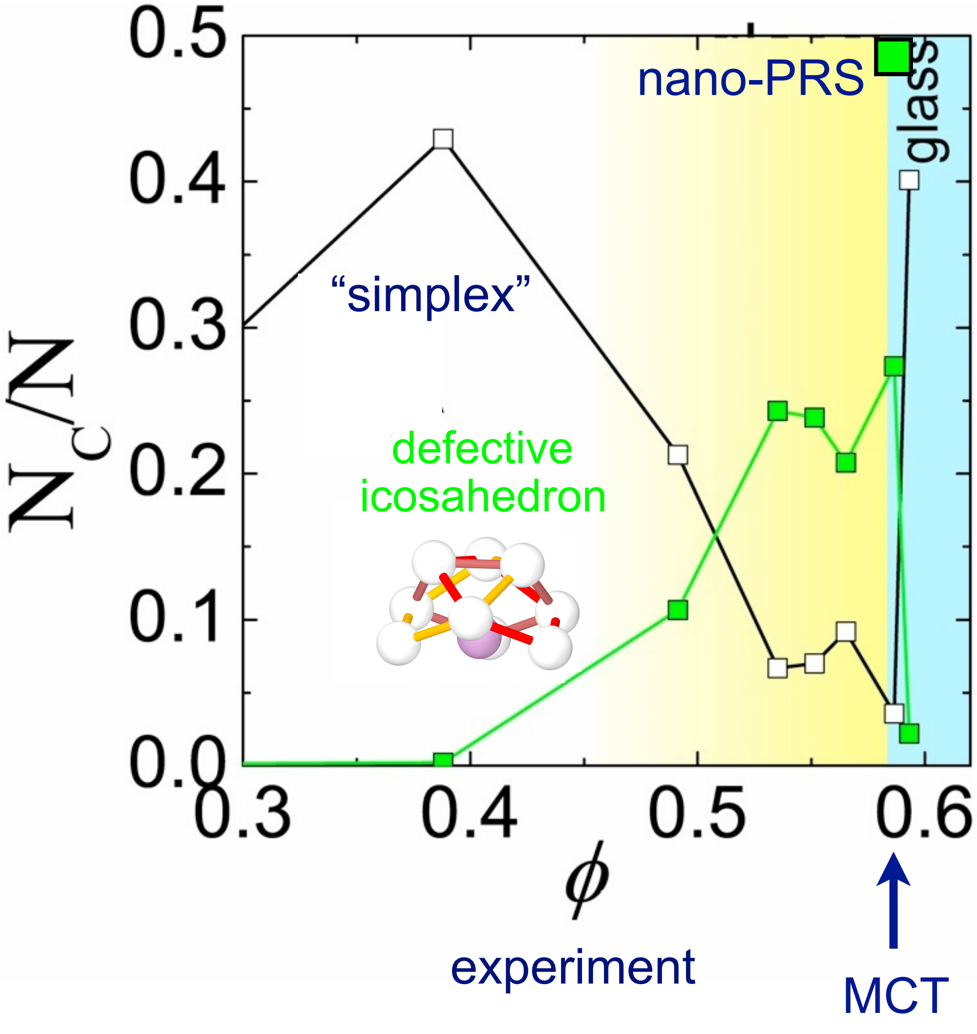
defective
icosahedron

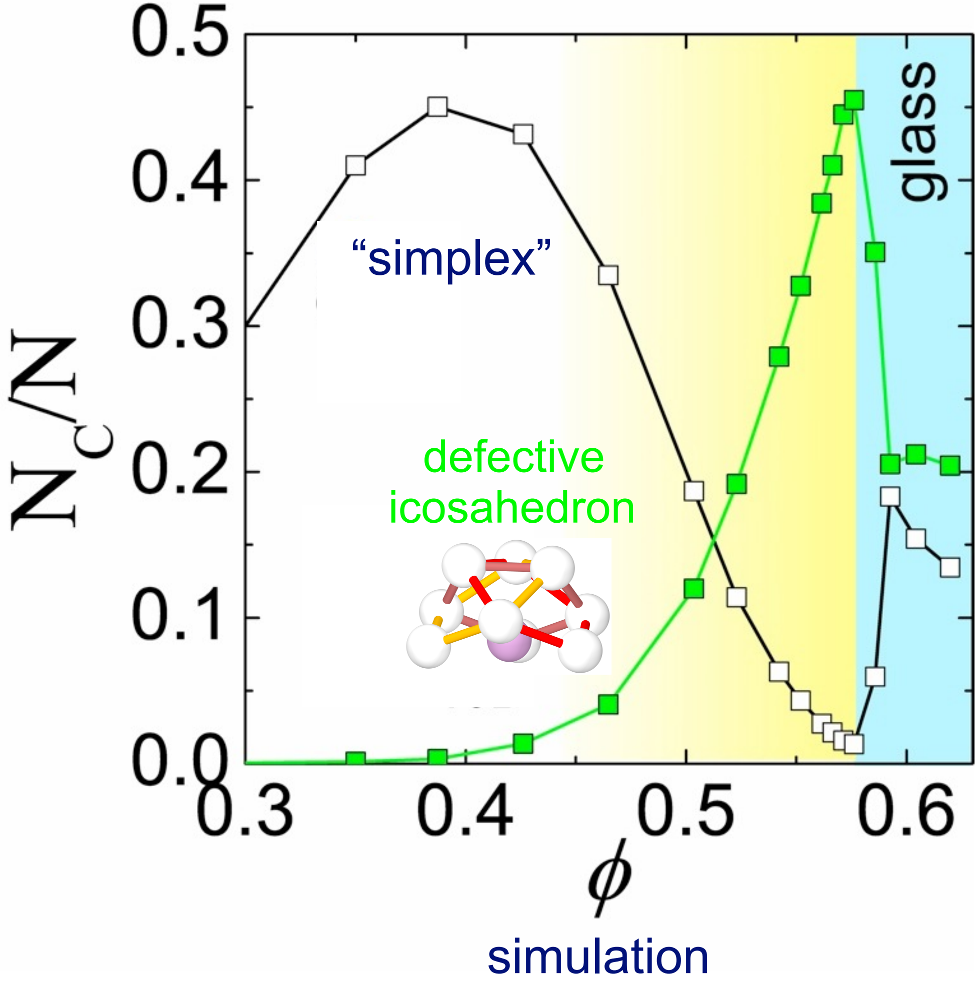
silica, rhodamine labelled, tetrahydrofurfuryl alcohol solvent

STED: "Stimulated Emission via Depletion"

Particle-resolved studies take us to MCT

nano-particle resolved studies take us past MCT





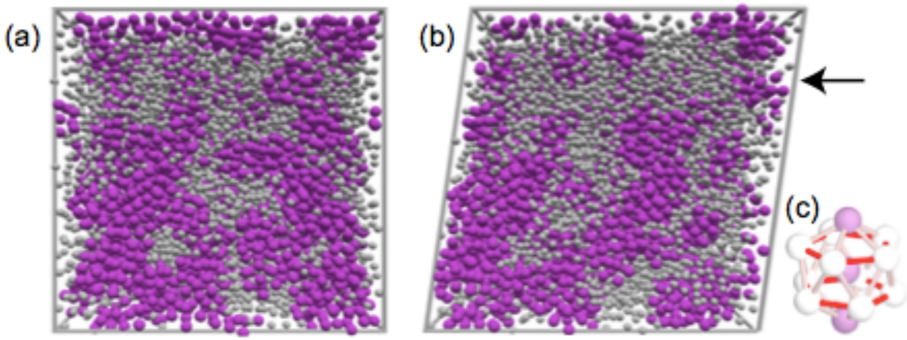
Hard spheres: defective icosahedron is LPS. Falling out of equilibrium (ϕ=0.58): "simplex"

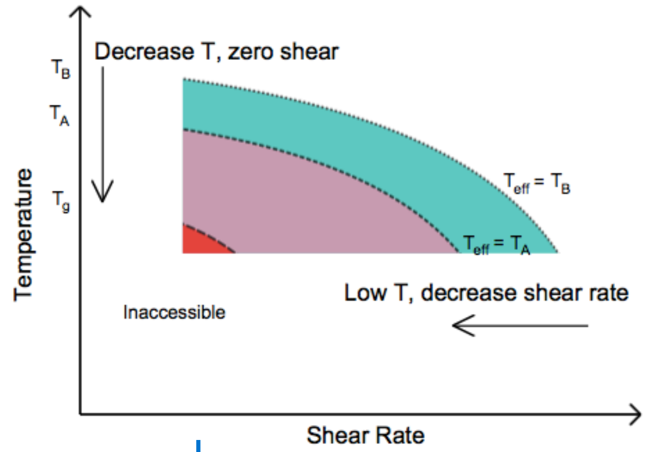
simplex~tetrahedron

Royall et al. *J. Non-Cryst. Solids* 407 34-43 (2014)

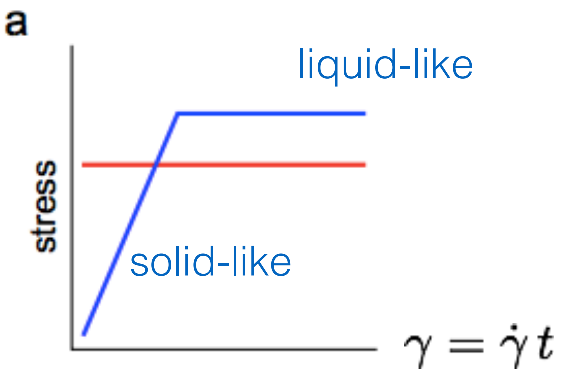
shearing supercooled liquid

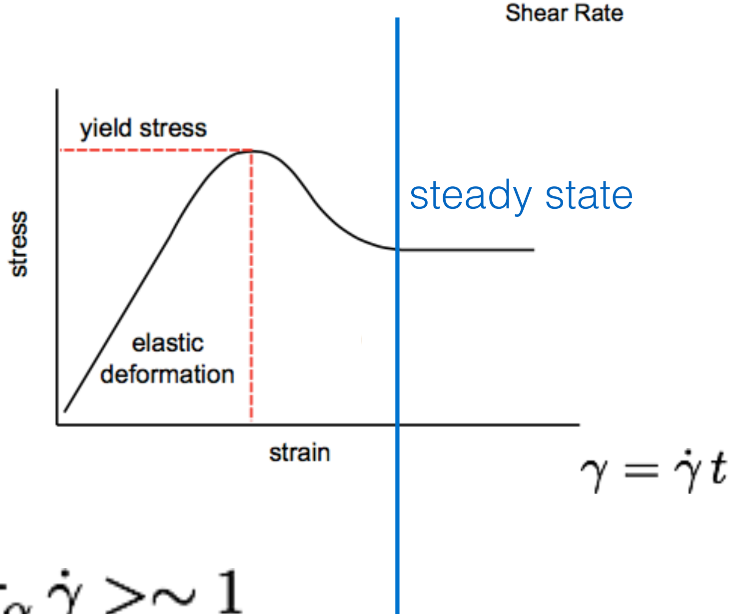
what happens to local structure under shear ?





constant strain rate $\dot{\gamma}$





$\tau_\alpha \dot{\gamma} << 1$

$\tau_\alpha \dot{\gamma} >\sim 1$

Pinney, Liverpool and Royall *J. Chem. Phys.* (2016)

SLLOD dynamics

- NVT simulations (equilibration) then SLLOD
- Lees-Edwards PBC
- Wahnström model

$$\mathcal{H} = \mathcal{T} + \mathcal{V}$$

$$\dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} + \vec{x}\dot{\gamma}y_i$$

$$\dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} - \vec{x}\dot{\gamma}p_{y,i}$$

$$10^{-5} \leq \dot{\gamma} \leq 0.25 \quad \text{for} \quad 0.56 \leq T \leq 0.8$$

$$2.5 \times 10^{-6} \leq \dot{\gamma} \leq 10^{-5} \quad \text{for} \quad 0.3 \leq T \leq 0.5$$

$$N = 10976$$

Pinney, Liverpool and Royall *J. Chem. Phys.* (2016)

steady-state shear

- yield at $\gamma \simeq 0.1$, steady state $\gamma > 1$
- inhomogeneous flow profile
- non affine deformation parameter

$$D(r) \uparrow \ \dot{\gamma}(r) \uparrow$$

M. L. Falk and J. S. Langer, Phys. Rev. E **57**, 7192 (1998)

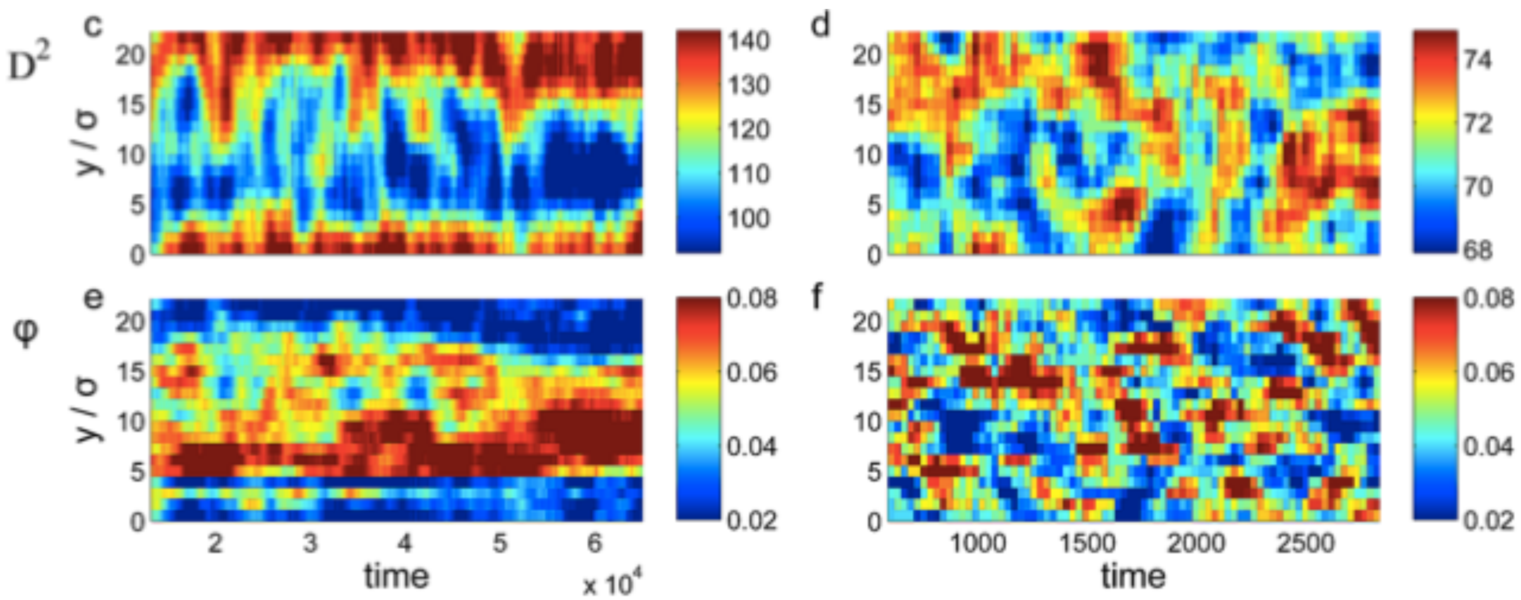
$$D^2(\tau, t) = \sum_{n=1}^{N} \mathbf{R}_n \cdot \mathbf{R}_n^T,$$

$$\mathbf{R}_n = \left(\mathbf{r}_n(t) - \mathbf{r}_0(t)\right) - \left(\mathbf{X}\mathbf{Y}^{-1}\right) \cdot \left(\mathbf{r}_n(\tau) - \mathbf{r}_0(\tau)\right),$$

$$\mathbf{X} = \sum_{n=1}^{N} \left(\mathbf{r}_n(t) - \mathbf{r}_0(t)\right)\left(\mathbf{r}_n(\tau) - \mathbf{r}_0(\tau)\right),$$

$$\mathbf{Y} = \sum_{n=1}^{N} \left(\mathbf{r}_n(\tau) - \mathbf{r}_0(\tau)\right)\left(\mathbf{r}_n(\tau) - \mathbf{r}_0(\tau)\right).$$

$T = 0.56,\ \dot{\gamma} = 0.013$ $\qquad$ $T = 0.8,\ \dot{\gamma} = 5.9 \times 10^{-5}$



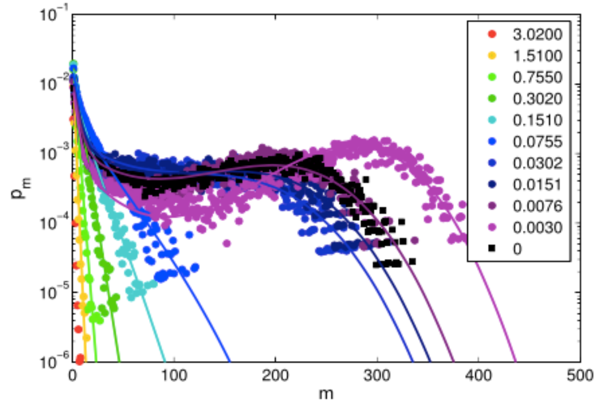
icos. density

Pinney, Liverpool and Royall *J. Chem. Phys.* (2016)

“banding”/“effective T”

$$S_h = D^2_{\rm av} + \frac{D^2_{\rm max} - D^2_{\rm av}}{A},$$

$$S_l = D^2_{\rm av} - \frac{D^2_{\rm av} - D^2_{\rm min}}{A},$$

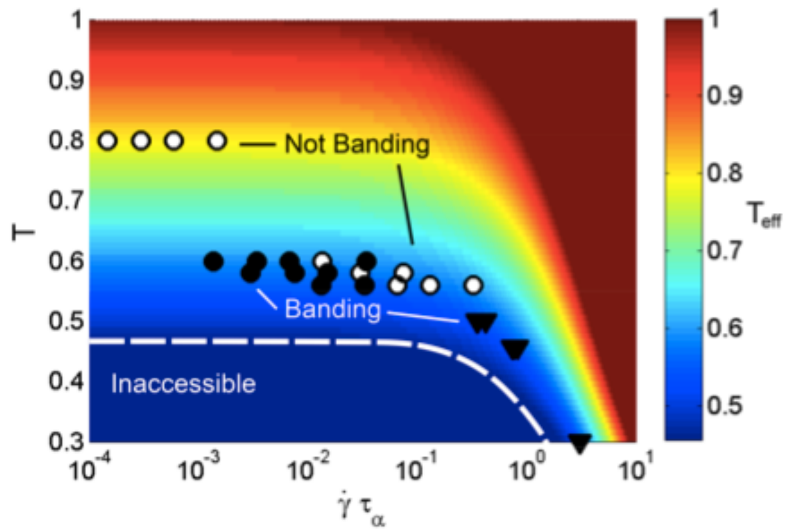


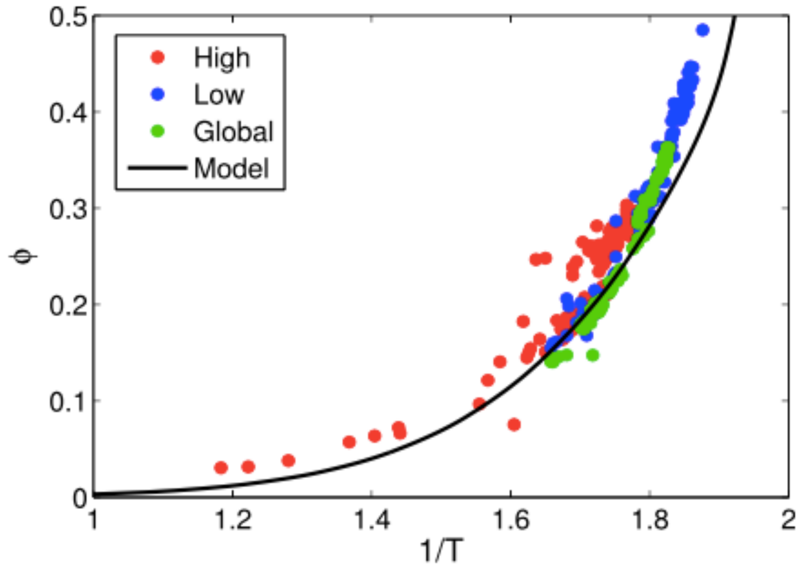
$D^2 > S_h \quad \Rightarrow \quad$ high eff. T band

$D^2 < S_l \quad \Rightarrow \quad$ low eff. T band

property of whole distribution

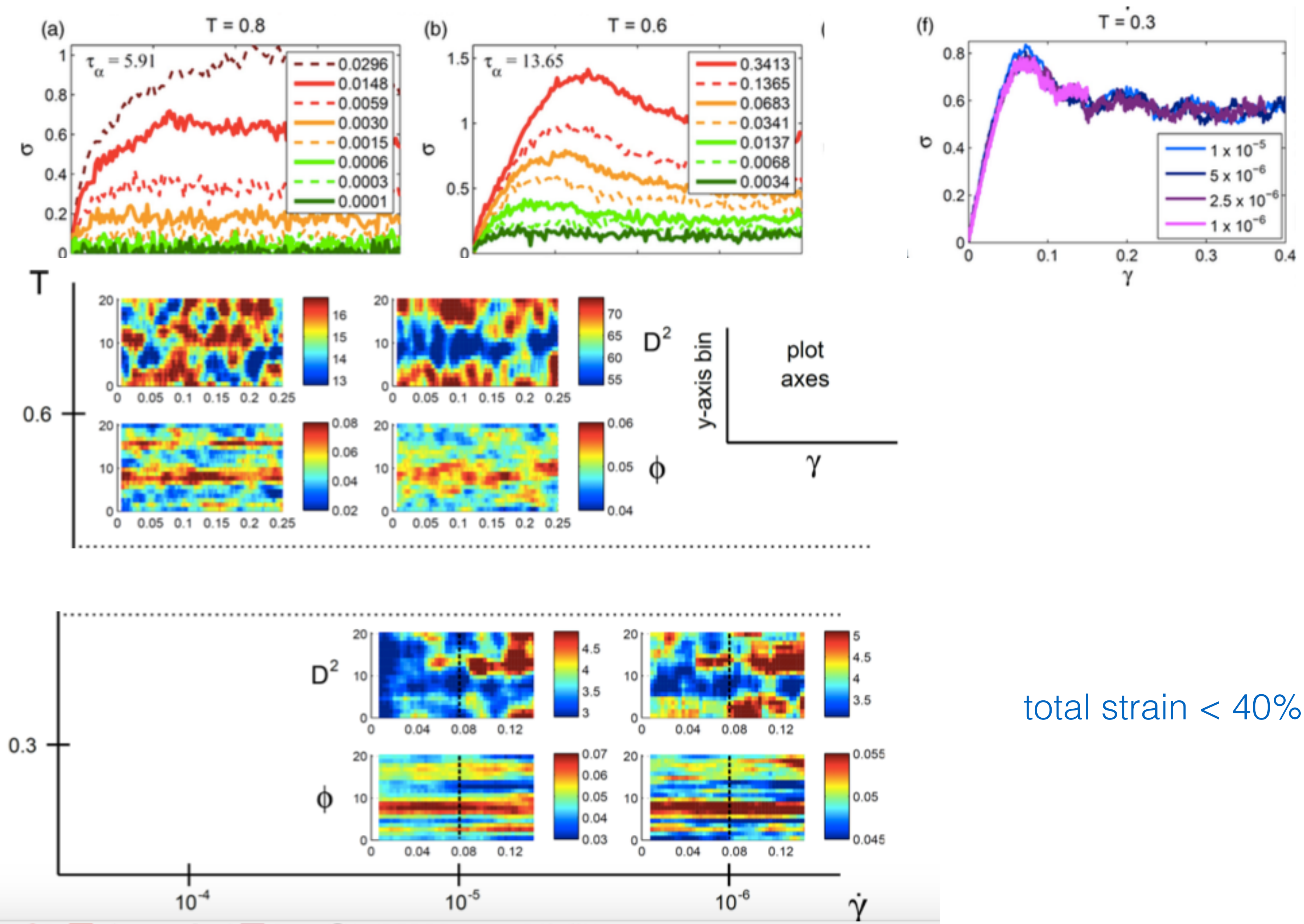
$$T_{\rm eff}/T_{\rm true} \simeq 0.271\dot{\gamma}\tau_\alpha + 1$$





Pinney, Liverpool and Royall *J. Chem. Phys.* (2015)

transient shear



total strain < 40%

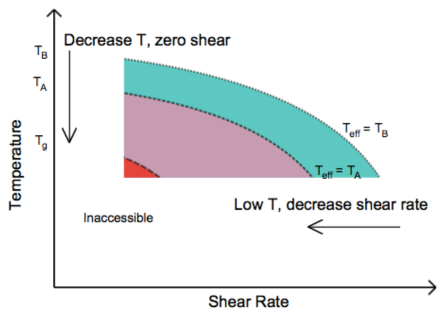
Pinney, Liverpool and Royall *Phys. Rev. E* (2018)

summary/perspectives

- **hierarchy of mechanics** : interparticle potential -> locally favoured structures -> mesoclusters of LFS -> percolation of mesoclusters -> ultra slow dynamics & inhomogeneous deformation

- suggests **both** a diverging length-scale and dynamic heterogeneity

- at the mesocluster level an equivalence of T and shear rate



perspectives

- a gross simplification but surprisingly successful - why ?
- only most favoured structure, what about the others ?
- mean-field mesocluster model
- quantifying how the LFS link together to form mesoclusters
- can athermal systems be described by the limit T -> 0 at finite strain rate ?