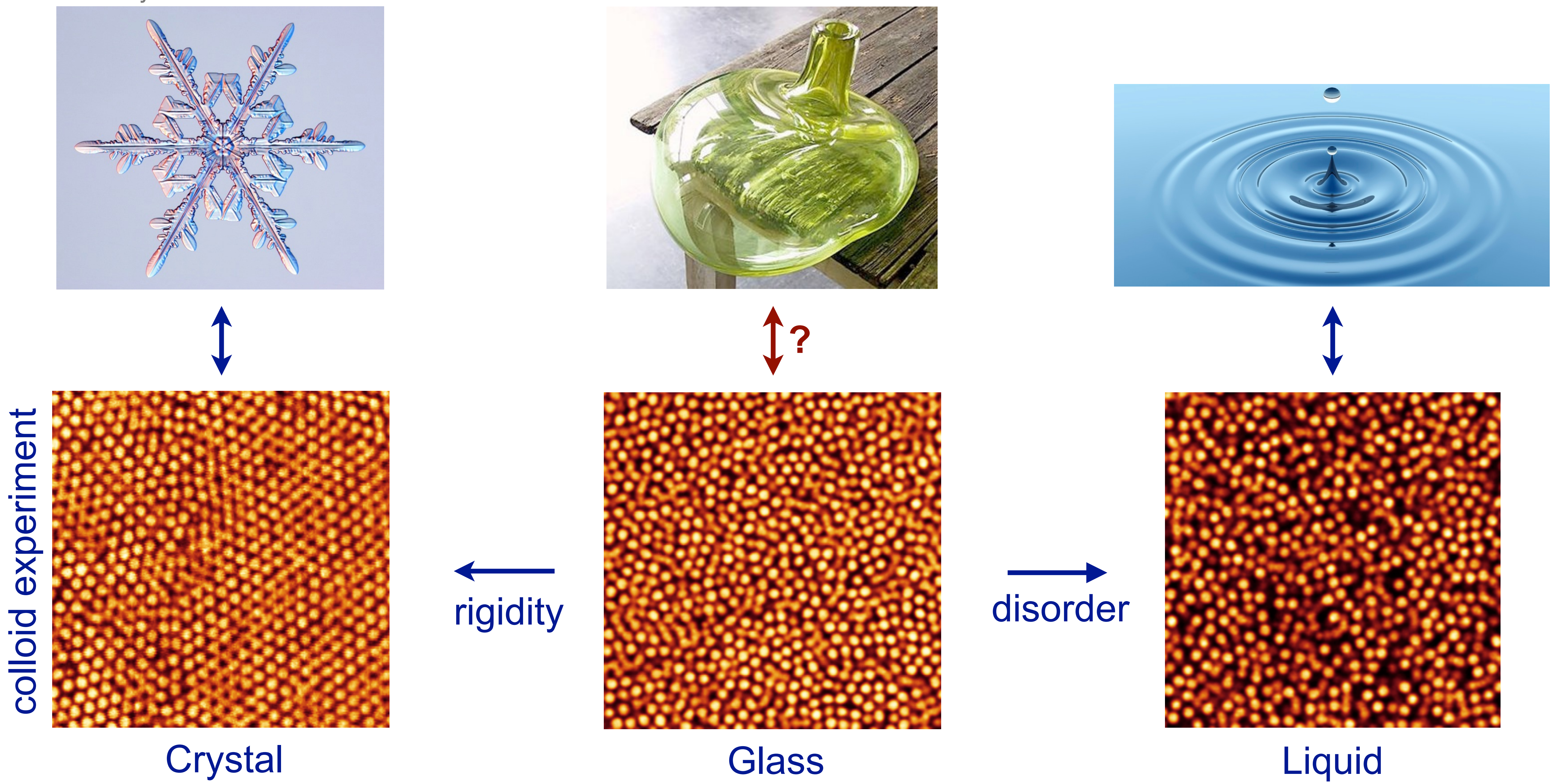
Static and dynamic length scales in glass forming liquids

Paddy Royall

"The perceived wisdom is that structure determines dynamics"
- Peter Harrowell

snowcrystals.com



Royall and coworkers,
"Complex plasmas and colloidal dispersions: particle-resolved studies of classical liquids and solids", World Scientific (2012)"

Acknowledgements

The Plan

Why do we expect structure to play a role in the glass transition?

How do we measure - *and identify* - the relevant structure?

Is structure really a cause for slow dynamics?

- coincidence of structural and dynamic length scales
- structural correlations in the isoconfigurational ensemble
- vitrification by changing structure - the μ-ensemble

The Angell plot

Fragility->more than one form of relaxation

Well described by Vogel-Fulcher-Tamman (VFT)

$$\tau_\alpha = \tau_0 \exp\left(\frac{A}{T - T_0}\right)$$

Hard spheres : equivalent to T is reduced presssure

Berthier and Witten PRE **80** 021502 (2009)

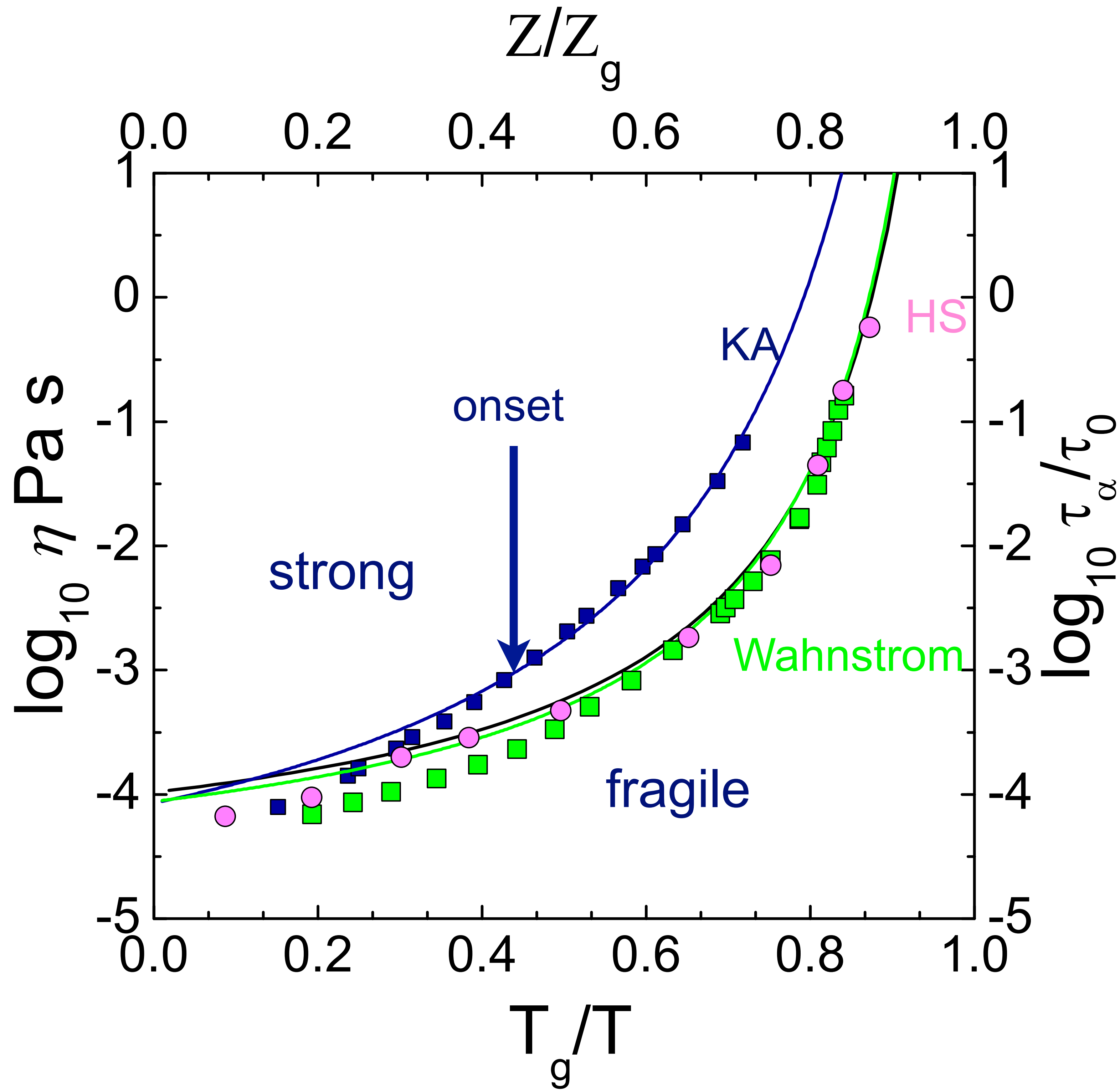
$$\tau_\alpha = \tau_0 \exp\left(\frac{A}{Z_0 - Z}\right)$$

$$Z = \frac{\Pi}{k_B T \rho}$$

Pressure from Carnahan-Starling EoS

$$\Pi = n k_B T \frac{1 + \phi + \phi^2 - \phi^3}{(1-\phi)^3}$$

lines are VFT fits



Richert and Angell *JCP* **108**, 9016 (1998)

inspired by Angell *J. Non-Cryst. Solids* **102**, 205–221 (1988)

HS hard sphere colloids

The Angell plot

Fragility->more than one form of relaxation

Well described by Vogel-Fulcher-Tamman (VFT)

$$\tau_\alpha = \tau_0 \exp\left(\frac{A}{T - T_0}\right)$$

Hard spheres : equivalent to T is reduced presssure

Berthier and Witten PRE **80** 021502 (2009)

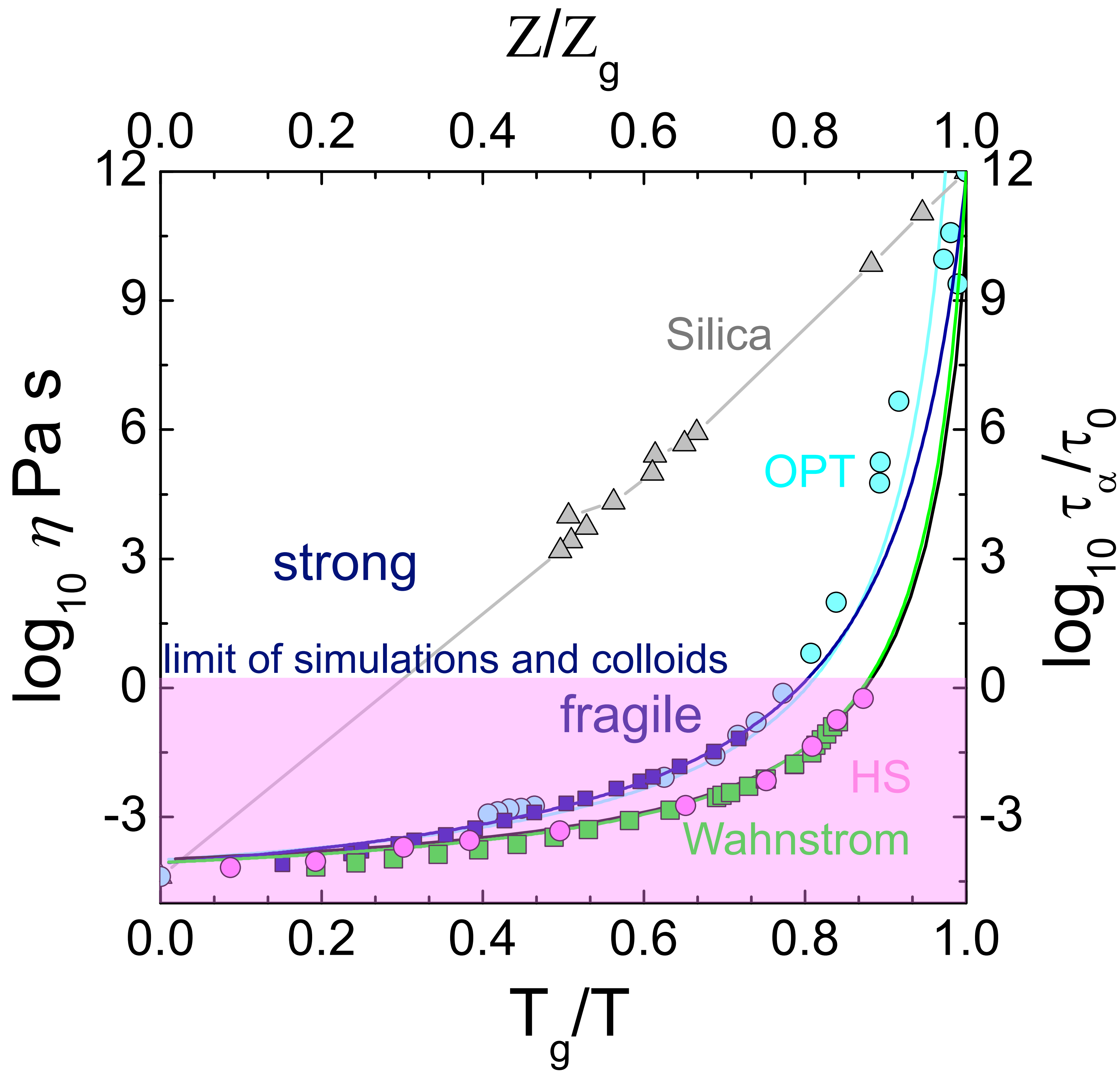
$$Z = \frac{\Pi}{k_B T \rho}$$

$$\tau_\alpha = \tau_0 \exp\left(\frac{A}{Z_0 - Z}\right)$$

Pressure from Carnahan-Starling EoS

$$\Pi = n k_B T \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}$$

lines are VFT fits



HS hard sphere colloids

Richert and Angell *JCP* **108**, 9016 (1998)

inspired by Angell *J. Non-Cryst. Solids* **102**, 205–221 (1988)

Cooperatively rearranging regions Adam-Gibbs and RFOT

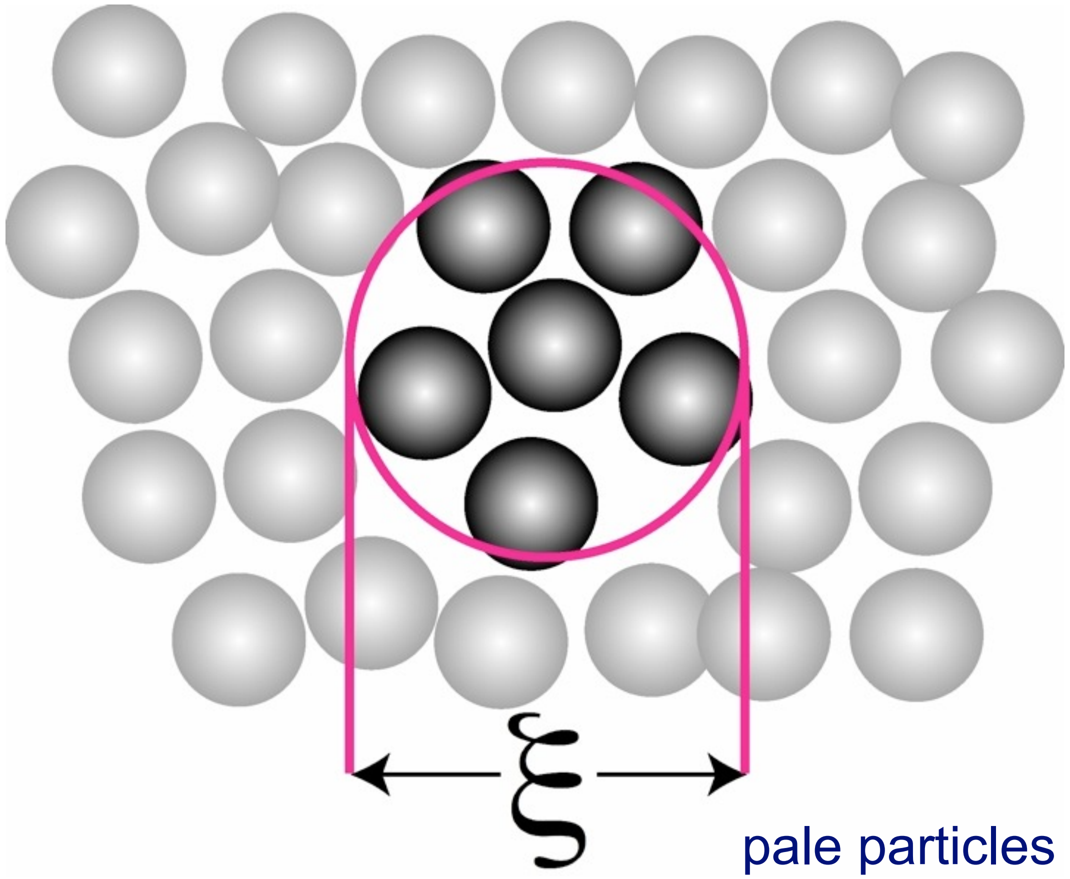
Assume a group of molecules which relax and leave the others fixed

Adam-Gibbs theory assumes a few (M) states accessible to the molecules in the cavity of size ξ^3

$$S_{\mathrm{conf}}(T) \sim k_{\mathrm{B}} \xi^{-3} \ln M$$

Assume energy barrier to re-arrangement ~ ξ^3
The time to rearrange between these M states is ~

$$\tau_\alpha = \tau_0 \exp\left[\frac{C_0 \ln M}{T S_{\mathrm{conf}}(T)}\right] \text{ VFT}$$



pale particles are fixed

Adam and Gibbs *JCP* **43**, 139-146 (1965)

Random First Order Theory
A first-order transition to a random mosiac state

Like crystallisation but the low-T state has very many configurations

Relaxation via entropic nucleation. $T S_{\mathrm{conf}}(T) \xi^3$

Relaxation opposed by surface tension $\Upsilon \xi^\theta$

Equate for mosiac lengthscale $\xi = \left(\frac{\Upsilon}{T s_c(T)}\right)^{1/(3-\theta)} \longrightarrow \log\left(\frac{\tau_\alpha}{\tau_0}\right) = c \frac{\Upsilon}{k_B T}\left(\frac{\Upsilon}{T s_c(T)}\right)^{\psi/(3-\theta)}$

VFT, again

Lubchenko and Wolynes *Ann. Rev. Phys. Chem.* **58**, 235-66 (2007)

Cooperatively rearranging regions Adam-Gibbs and RFOT

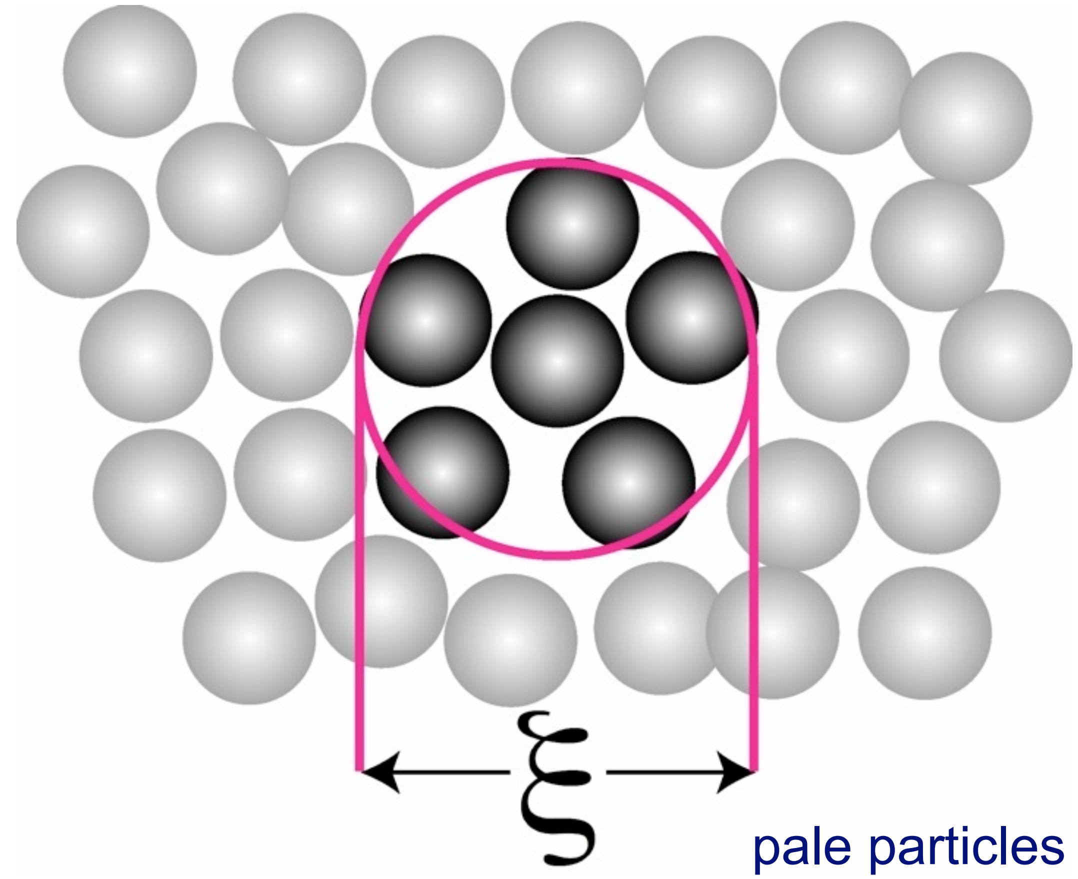
Assume a group of molecules which relax and leave the others fixed

Adam-Gibbs theory assumes a few (M) states accessible to the molecules in the cavity of size ξ^3

$$S_{\rm conf}(T) \sim k_{\rm B}\xi^{-3}\ln M$$

Assume energy barrier to re-arrangement ~ ξ^3
The time to rearrange between these M states is ~

$$\tau_\alpha = \tau_0 \exp\left[\frac{C_0 \ln M}{T S_{\rm conf}(T)}\right] \quad \text{VFT}$$



pale particles are fixed

Adam and Gibbs *JCP* **43**, 139-146 (1965)

Random First Order Theory
A first-order transition to a random mosiac state

Like crystallisation but the low-T state has very many configurations

Relaxation via entropic nucleation. $T S_{\rm conf}(T)\xi^3$

Relaxation opposed by surface tension $\Upsilon \xi^\theta$

Equate for mosiac lengthscale $\xi = \left(\frac{\Upsilon}{T s_c(T)}\right)^{1/(3-\theta)} \longrightarrow \log\left(\frac{\tau_\alpha}{\tau_0}\right) = c\,\frac{\Upsilon}{k_B T}\left(\frac{\Upsilon}{T s_c(T)}\right)^{\psi/(3-\theta)}$

VFT, again

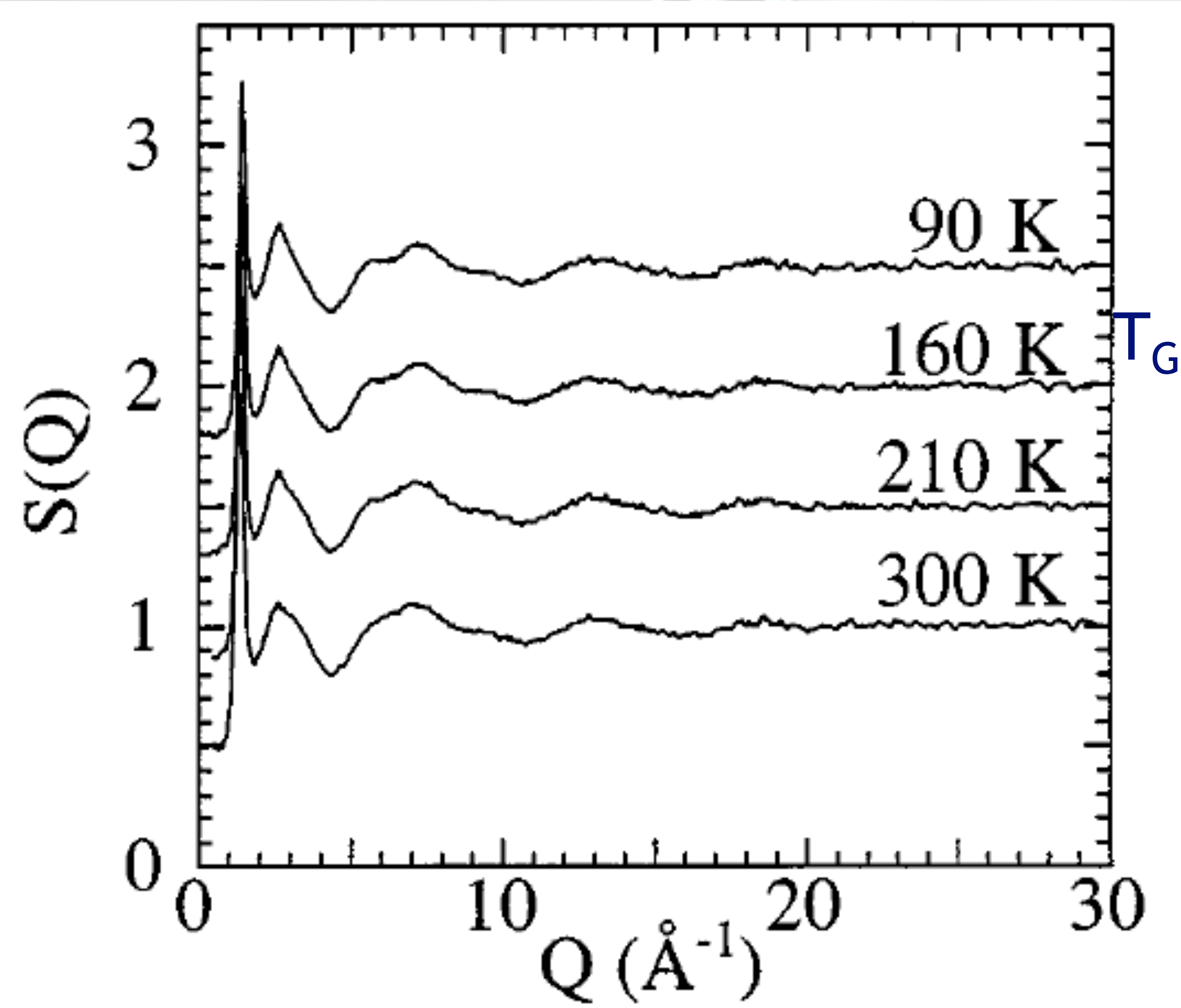
Lubchenko and Wolynes *Ann. Rev. Phys. Chem.* **58**, 235-66 (2007)

Both Adam-Gibbs and RFOT suggest a growing lengthscale upon supercooling

Montanari-Semmerjian : at sufficient cooling, there must be a growing lengthscale for super-Arrhenius dynamics

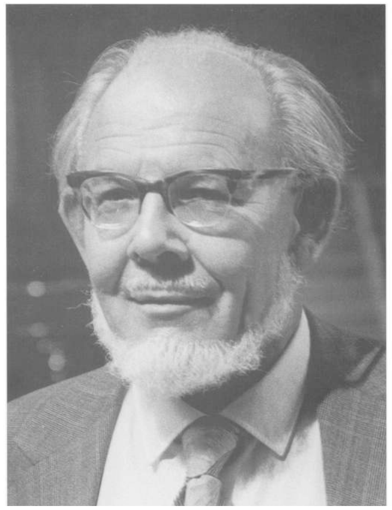
So we would expect a growing structural lengthscale
...but what is the structure?

“The arrangement of atoms and molecules in glass is indistinguishable from that of a liquid.”



Neutron scattering on propylene glycol ~ Leheny et. al. *J.Chem. Phys.* 1996

Why have we not got a crystal?



Sir Charles Frank
Physics 1946-1998

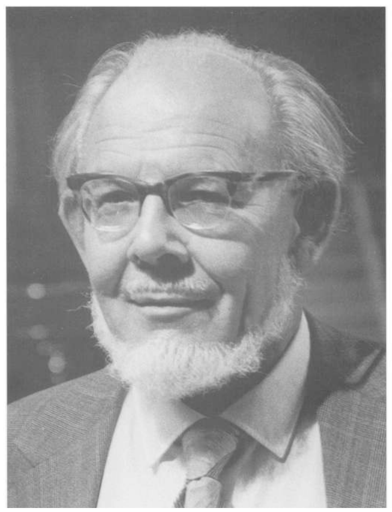
SUPERCOOLING OF LIQUIDS

By F. C. FRANK
H. H. Wills Physics Laboratory, Bristol University

The theoretical argument is misleading also. Consider the question: 'In how many different ways can one put twelve billiard balls in simultaneous contact with one, counting as different the arrangements which cannot be transformed into each other without breaking contact with the centre ball?' The answer is *three*. Two which come to the mind of any crystallographer occur in the face-centred cubic and hexagonal close-packed lattices. The third comes to the mind of any good schoolboy, and is to put one at the centre of each face of a regular dodecahedron. That body has five-fold axes, which are abhorrent to crystal symmetry: unlike the other two packings, this one cannot be continuously extended in three dimensions. You will find that the outer twelve in this packing do not touch each other. If we have mutually attracting deformable spheres, like atoms, they will be a little closer to the centre in this third type of packing; and if one assumes they are argon atoms (interacting in pairs with attractive and repulsive energy terms proportional to r^{-6} and r^{-12}) one may calculate that the binding energy of the group of thirteen is 8·4 % greater than for the other two packings. This is 40 % of the lattice energy per atom in the crystal. I infer that this will be a very common grouping in liquids, that most of the groups of twelve atoms around one will be in this form, that freezing involves a substantial rearrangement, and not merely an extension of the same kind of order from short distances to long ones; a rearrangement which is quite costly of energy in small localities, and only becomes economical when extended over a considerable volume, because unlike the other packing it can be so extended without discontinuities.

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

Why have we not got a crystal?



Sir Charles Frank
Physics 1946-1998

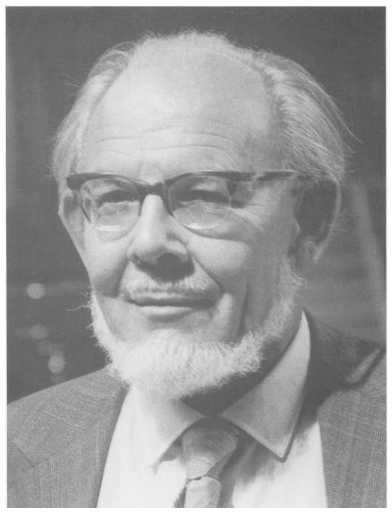
Supercooling of liquids

By F. C. Frank
H. H. Wills Physics Laboratory, Bristol University

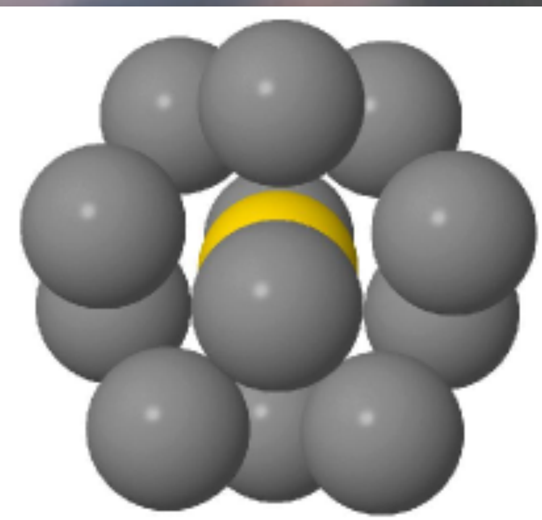
The theoretical argument is misleading also. Consider the question: 'In how many different ways can one put twelve billiard balls in simultaneous contact with one, counting as different the arrangements which cannot be transformed into each other without breaking contact with the centre ball?' The answer is *three*. Two which come to the mind of any crystallographer occur in the face-centred cubic and hexagonal close-packed lattices. The third comes to the mind of any good schoolboy, and is to put one at the centre of each face of a regular dodecahedron. That body has five-fold axes, which are abhorrent to crystal symmetry: unlike the other two packings, this one cannot be continuously extended in three dimensions. You will find that the outer twelve in this packing do not touch each other. If we have mutually attracting deformable spheres, like atoms, they will be a little closer to the centre in this third type of packing; and if one assumes they are argon atoms (interacting in pairs with attractive and repulsive energy terms proportional to r^{-6} and r^{-12}) one may calculate that the binding energy of the group of thirteen is 8·4 % greater than for the other two packings. This is 40 % of the lattice energy per atom in the crystal. I infer that this will be a very common grouping in liquids, that most of the groups of twelve atoms around one will be in this form, that freezing involves a substantial rearrangement, and not merely an extension of the same kind of order from short distances to long ones; a rearrangement which is quite costly of energy in small localities, and only becomes economical when extended over a considerable volume, because unlike the other packing it can be so extended without discontinuities.

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

Why have we not got a crystal?



Sir Charles Frank
Physics 1946-1998



SUPERCOOLING OF LIQUIDS

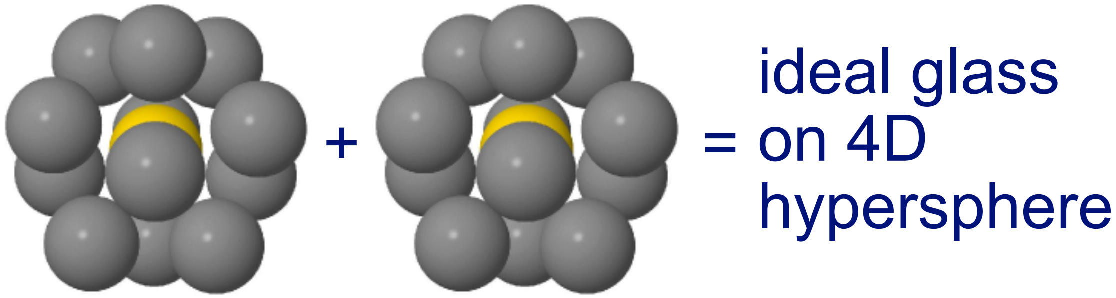
BY F. C. FRANK
H. H. Wills Physics Laboratory, Bristol University

The theoretical argument is misleading also. Consider the question: 'In how many different ways can one put twelve billiard balls in simultaneous contact with one, counting as different the arrangements which cannot be transformed into each other without breaking contact with the centre ball?' The answer is *three*. Two which come to the mind of any crystallographer occur in the face-centred cubic and hexagonal close-packed lattices. The third comes to the mind of any good schoolboy, and is to put one at the centre of each face of a regular dodecahedron. That body has five-fold axes, which are abhorrent to crystal symmetry: unlike the other two packings, this one cannot be continuously extended in three dimensions. You will find that the outer twelve in this packing do not touch each other. If we have mutually attracting deformable spheres, like atoms, they will be a little closer to the centre in this third type of packing; and if one assumes they are argon atoms (interacting in pairs with attractive and repulsive energy terms proportional to r^{-6} and r^{-12}) one may calculate that the binding energy of the group of thirteen is 8·4 % greater than for the other two packings. This is 40 % of the lattice energy per atom in the crystal. I infer that this will be a very common grouping in liquids, that most of the groups of twelve atoms around one will be in this form, that freezing involves a substantial rearrangement, and not merely an extension of the same kind of order from short distances to long ones; a rearrangement which is quite costly of energy in small localities, and only becomes economical when extended over a considerable volume, because unlike the other packing it can be so extended without discontinuities.

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

Geometric frustration

In some non-frustrated scenario, there is a continuous transition to an “ideal glass” of the locally favoured structure (LFS) of the liquid.



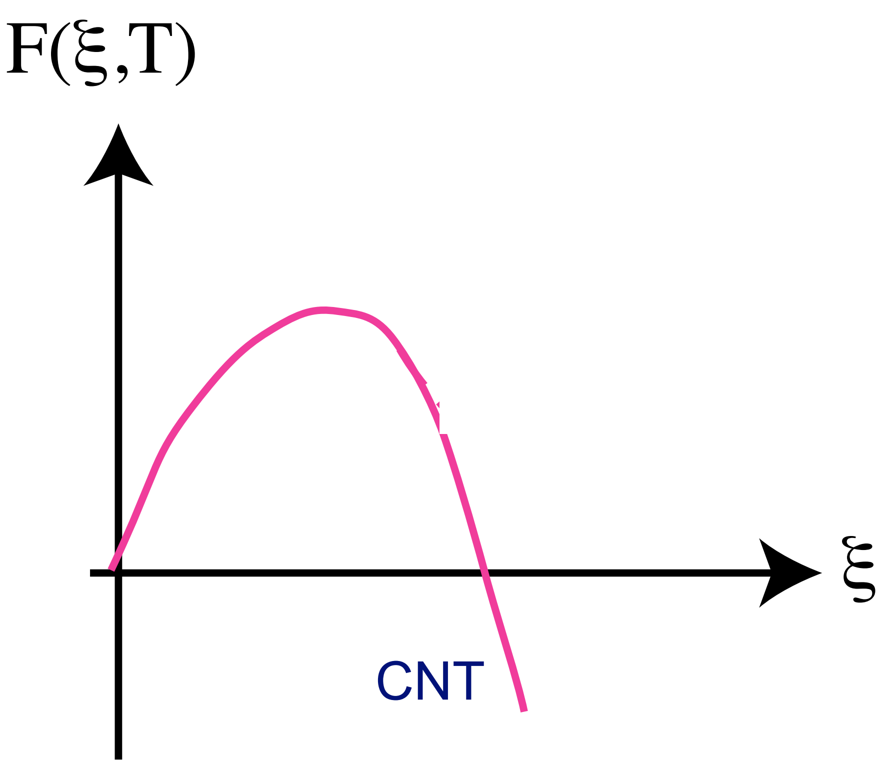
120 spheres tesselate into icosahedra on the surface of a 4D hypersphere

...back in the real world...

The growth of domains of LFS are frustrated. Free energy :

$$F(\xi, T) = \Upsilon(T)\xi^{\theta} + \delta F_{\mathrm{bulk}}(T)\xi^{3}$$

classical nucleation theory



ξ measure of the LFS domain size

Is curved space vs Euclidean space the only frustration scenario?

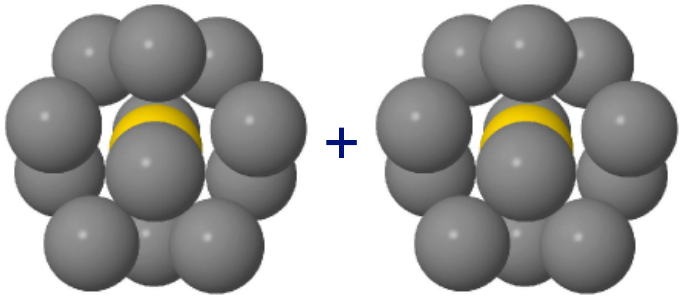
curved 3D space on 4D hypersphere forms an “ideal glass” of 120 identical spheres - but we know identical spheres in 3D are not an ideal glassformer

δF_{BULK} change in bulk free energy between “crystal” and liquid

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

Geometric frustration

In some non-frustrated scenario, there is a continuous transition to an "ideal glass" of the locally favoured structure (LFS) of the liquid.



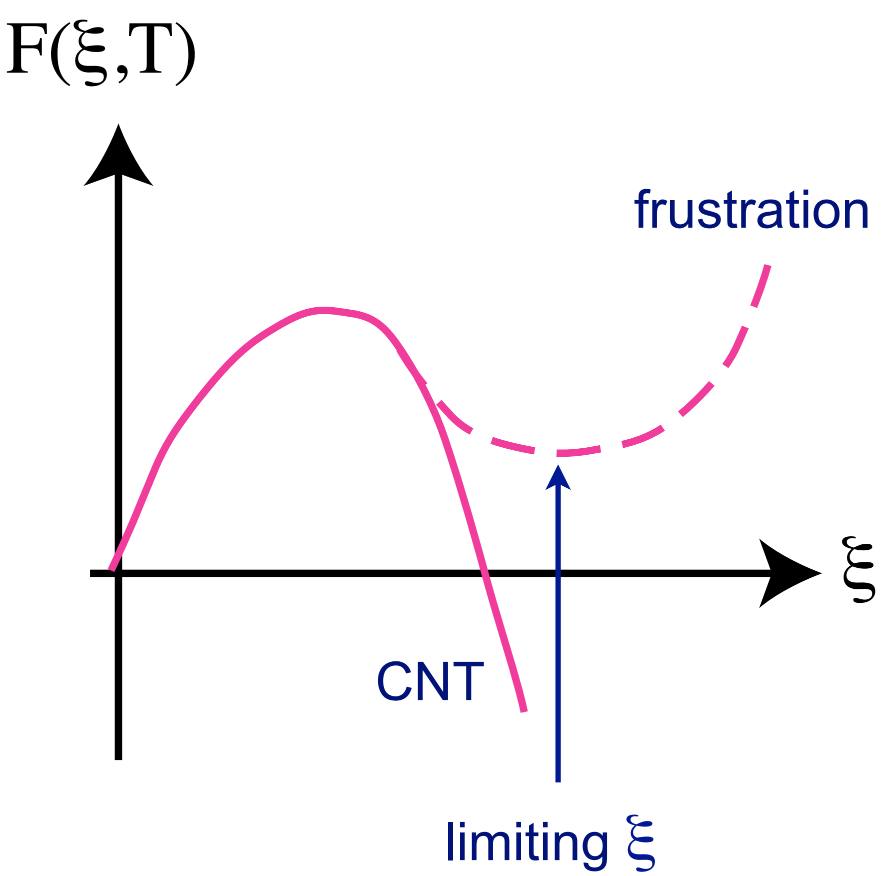
120 spheres tesselate into icosahedra on the surface of a 4D hypersphere

...back in the real world...

The growth of domains of LFS are frustrated. Free energy :

$$F(\xi, T) = \Upsilon(T)\xi^{\theta} + \delta F_{\text{bulk}}(T)\xi^{3} + s(T)\xi^{5}$$

classical nucleation theory — frustration



ξ measure of the LFS domain size

Is curved space vs Euclidean space the only frustration scenario?

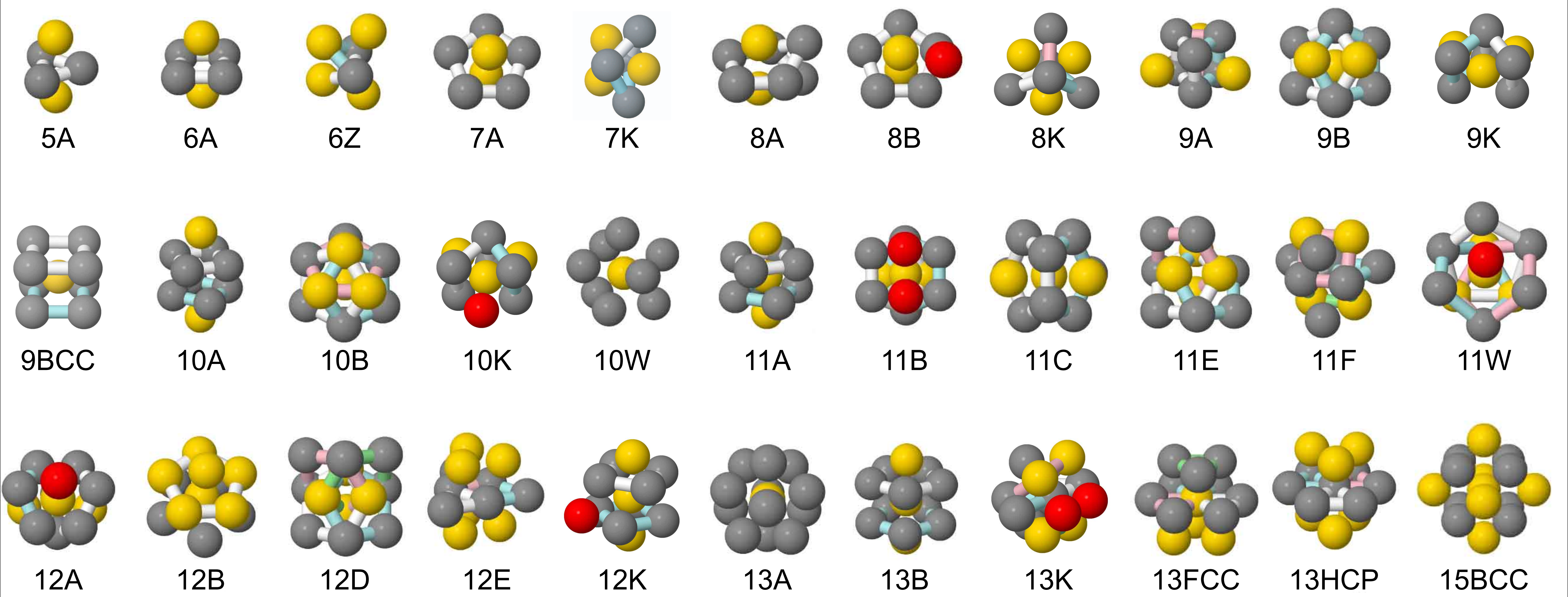
curved 3D space on 4D hypersphere forms an "ideal glass" of 120 identical spheres - but we know identical spheres in 3D are not an ideal glassformer

δF_{BULK} change in bulk free energy between "crystal" and liquid

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

Structure and glass : beyond the icosahedron

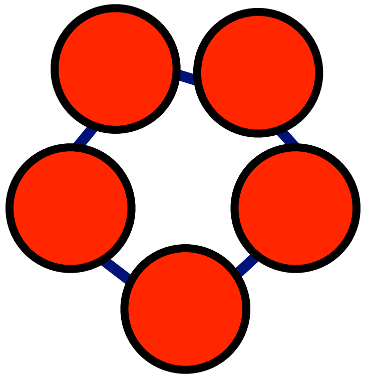
Structures identified by the topological cluster classification



Malins, Williams, Eggers and Royall *JCP* **139** 234506 (2013); Royall et.al. *Nature Materials* **7** 556 (2008))

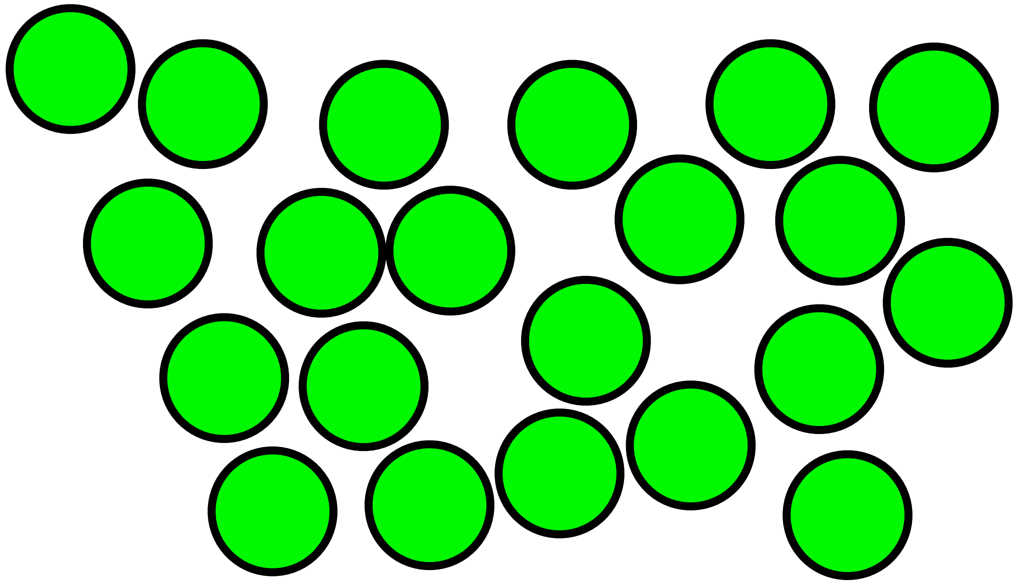
Toplogical cluster classification

how to identify structures in bulk systems



5-membered ring cluster

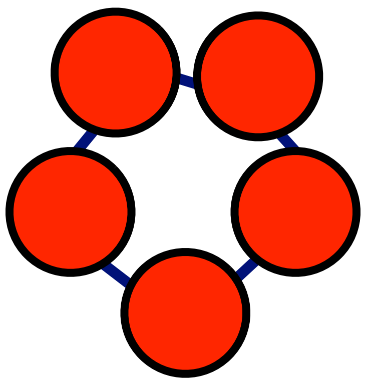
How to identify five-membered rings in bulk?



Malins, Williams, Eggers and Royall *JCP* **139** 234506 (2013); Royall et.al. *Nature Materials* **7** 556 (2008))

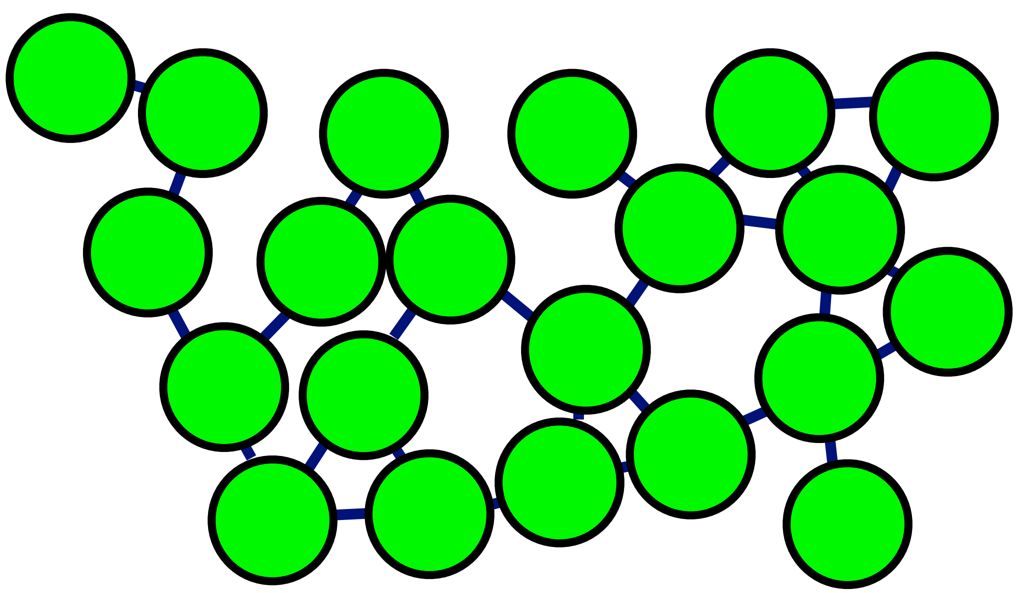
Toplogical cluster classification

how to identify structures in bulk systems



5-membered ring cluster

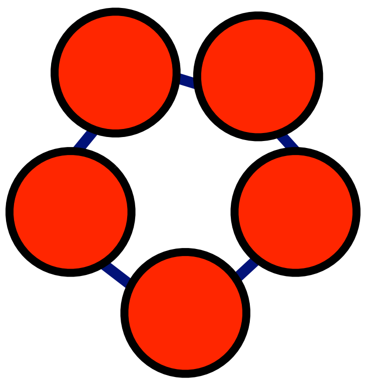
How to identify five-membered rings in bulk?



Malins, Williams, Eggers and Royall *JCP* **139** 234506 (2013); Royall et.al. *Nature Materials* **7** 556 (2008))

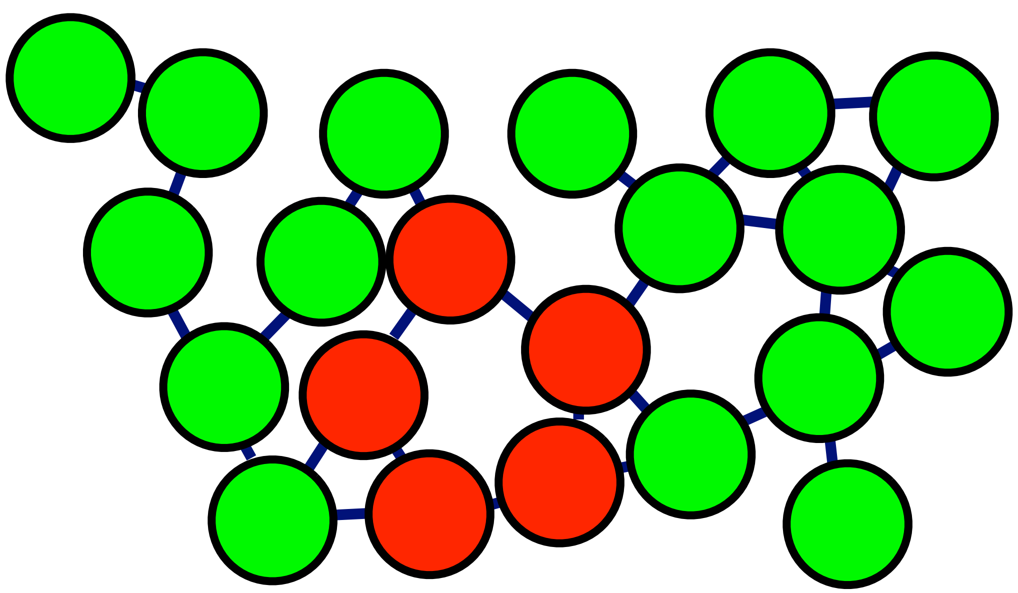
Toplogical cluster classification

how to identify structures in bulk systems



5-membered ring cluster

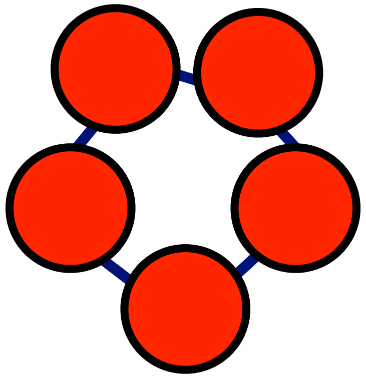
How to identify five-membered rings in bulk?



Malins, Williams, Eggers and Royall *JCP* **139** 234506 (2013); Royall et.al. *Nature Materials* **7** 556 (2008))

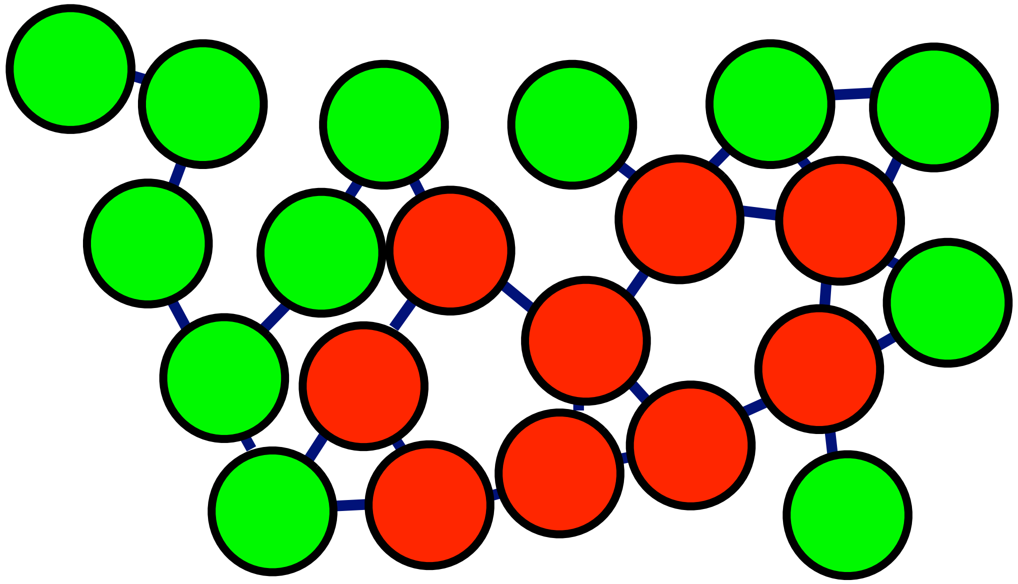
Toplogical cluster classification

how to identify structures in bulk systems



5-membered ring cluster

How to identify five-membered rings in bulk?

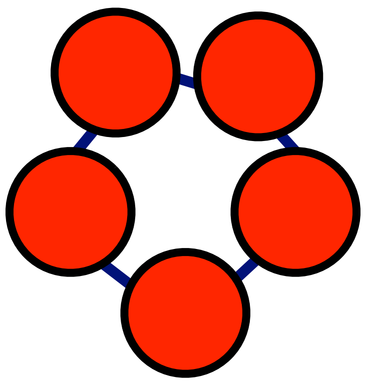


Clusters can overlap

Malins, Williams, Eggers and Royall *JCP* **139** 234506 (2013); Royall et.al. *Nature Materials* **7** 556 (2008))

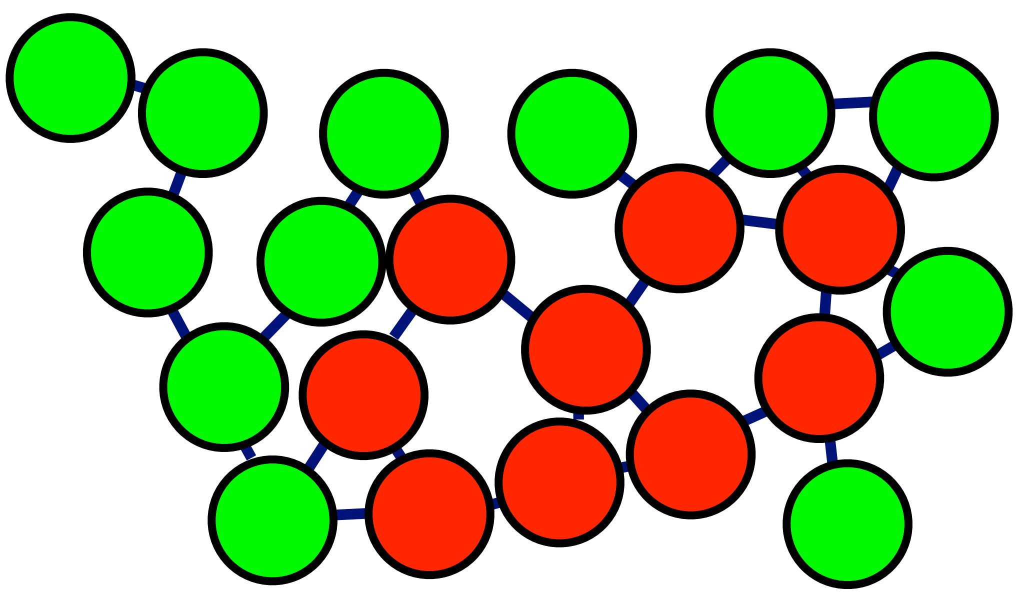
Toplogical cluster classification

how to identify structures in bulk systems



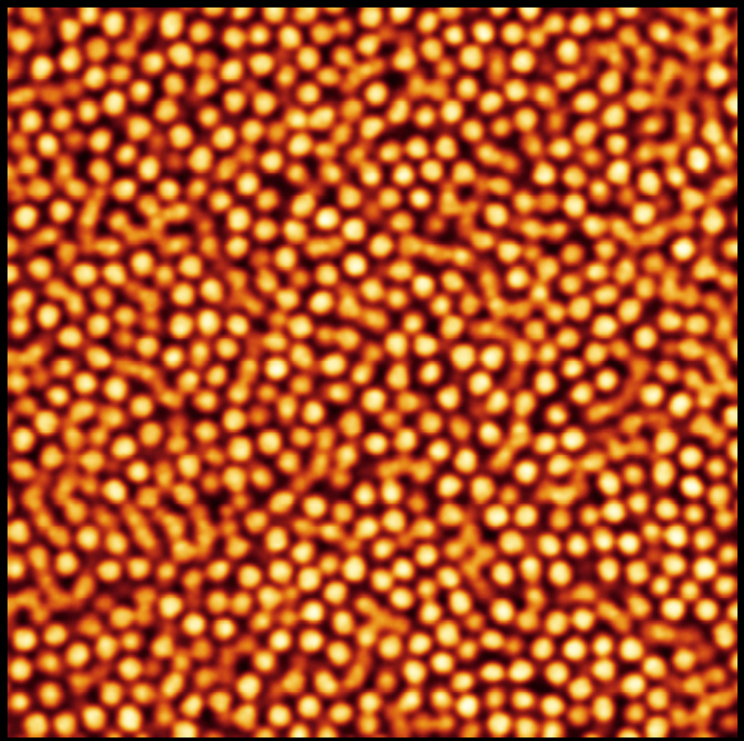
5-membered ring cluster

How to identify five-membered rings in bulk?

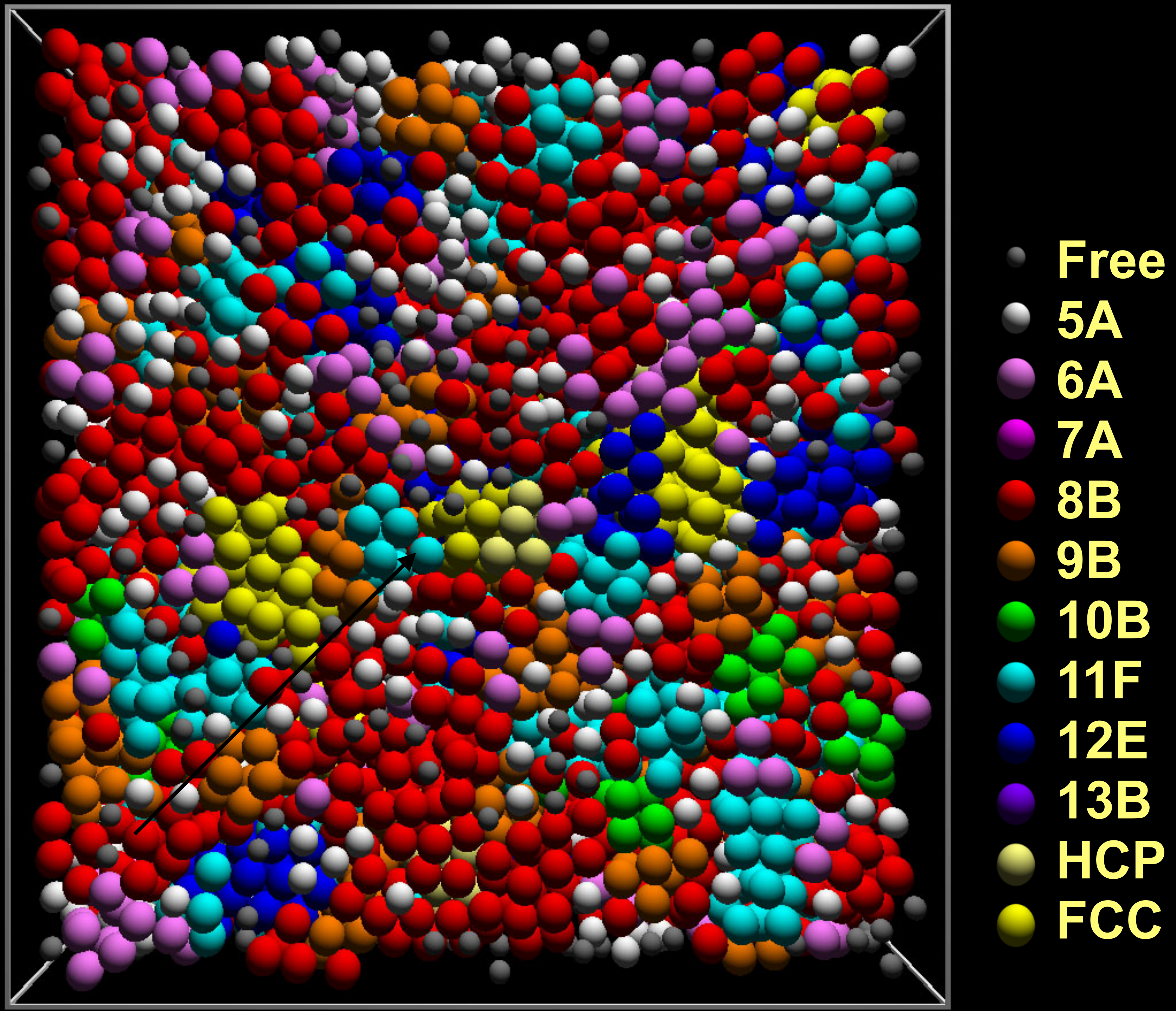


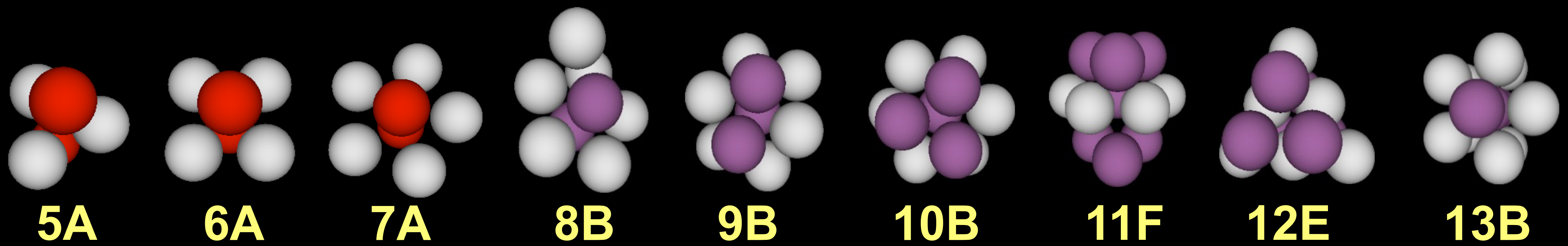
Strategy:
Search for clusters in bulk, for m<14.
If small clusters contained within larger, only consider larger
Also identify BCC, FCC and HCP

Malins, Williams, Eggers and Royall *JCP* **139** 234506 (2013); Royall et.al. *Nature Materials* **7** 556 (2008))



3D coordinate tracking

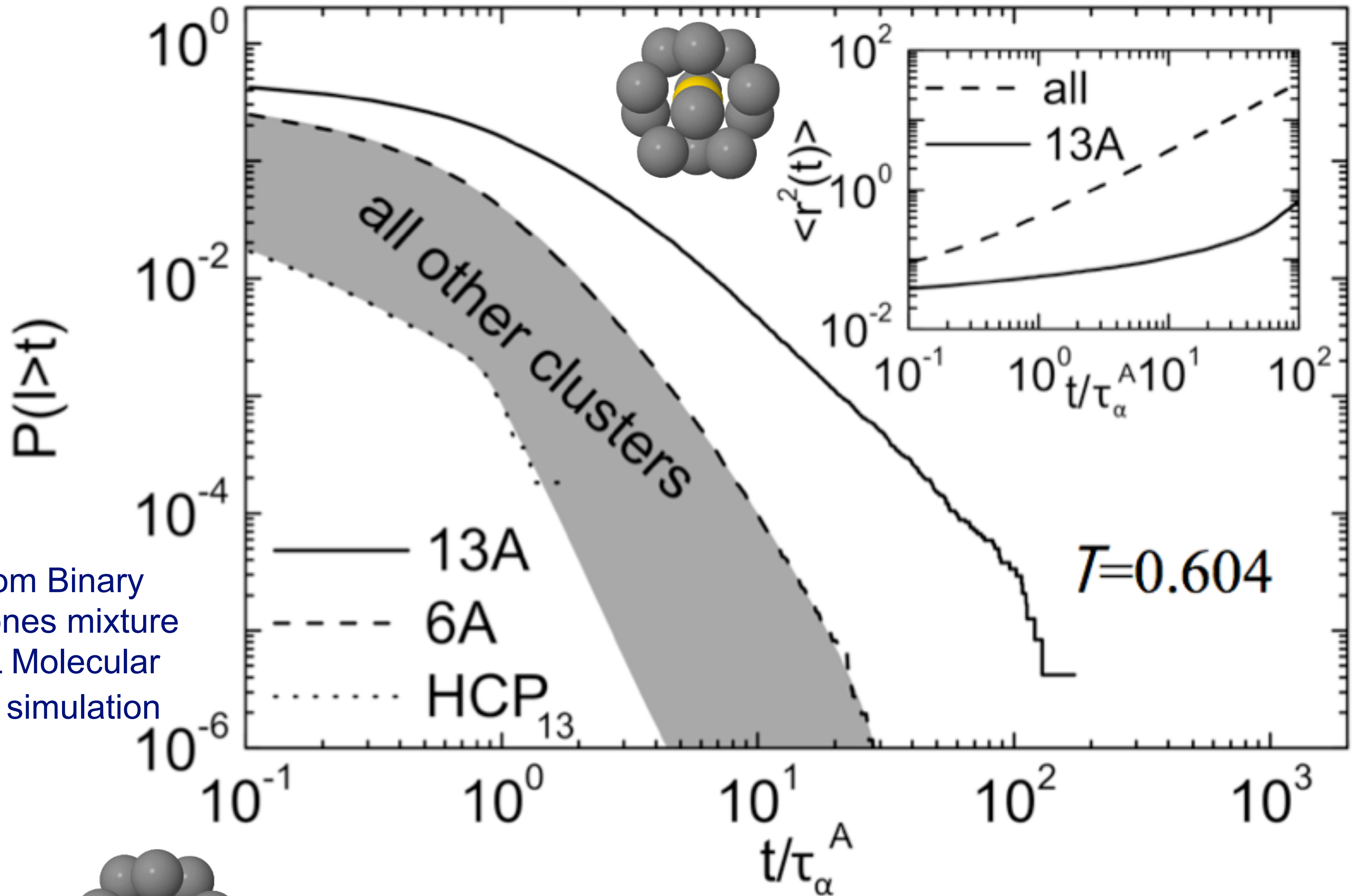




Experimental “hard sphere” data

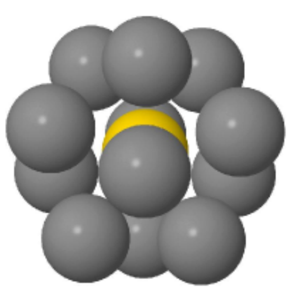
Dynamic Toplogical Cluster Classification

Linking structure and dynamics



Wahnstrom Binary Lennard-Jones mixture $\sigma_A = 5/6\sigma_B$. Molecular Dynamics simulation

=

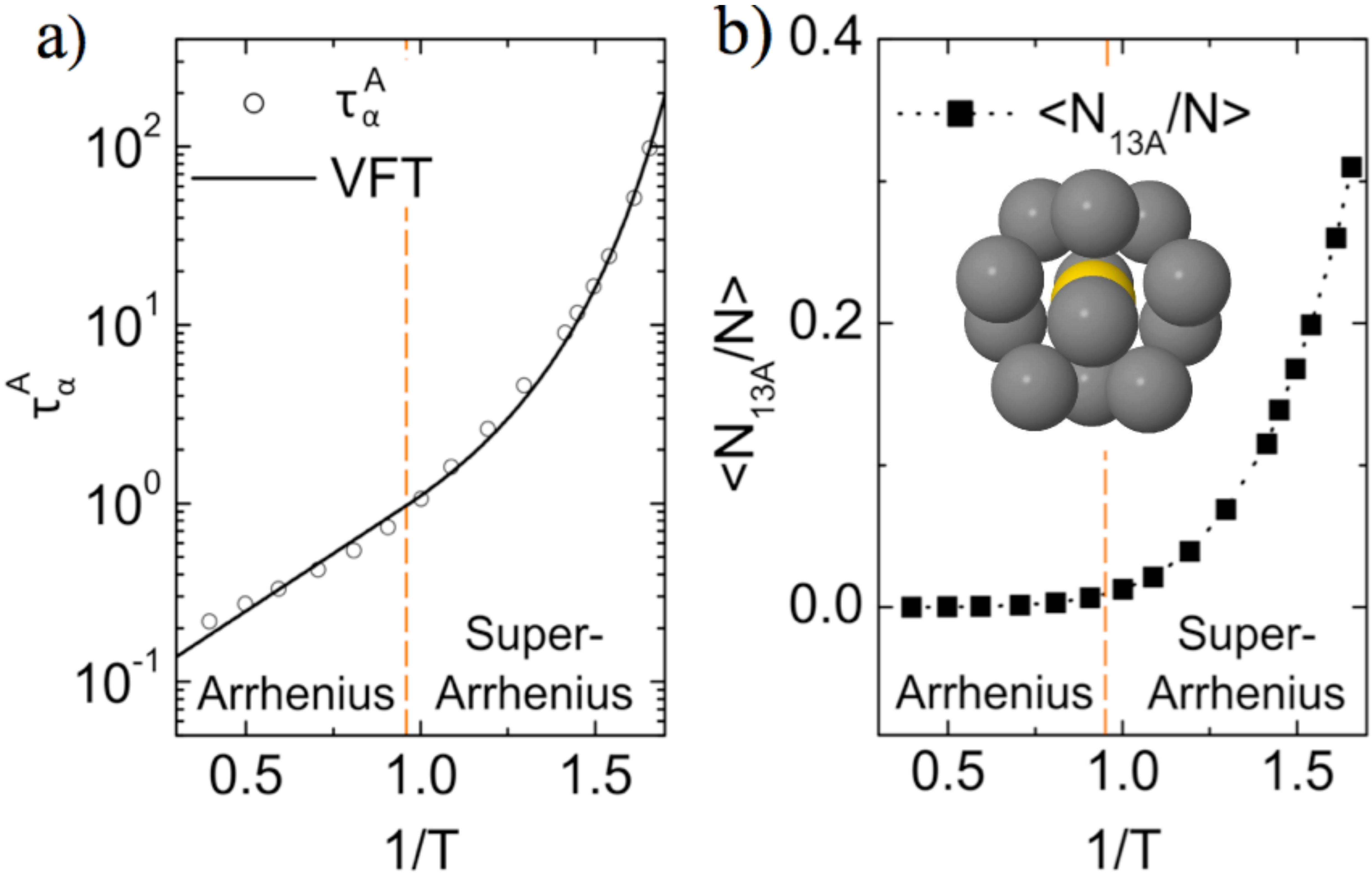


The icosahedron lasts *much* longer than all other clusters

Malins, Eggers, Tanaka and Royall *Faraday Disc.* **167** paper 16 (2013)

But what about Lennard-Jones...and Frank's Icosahedra?

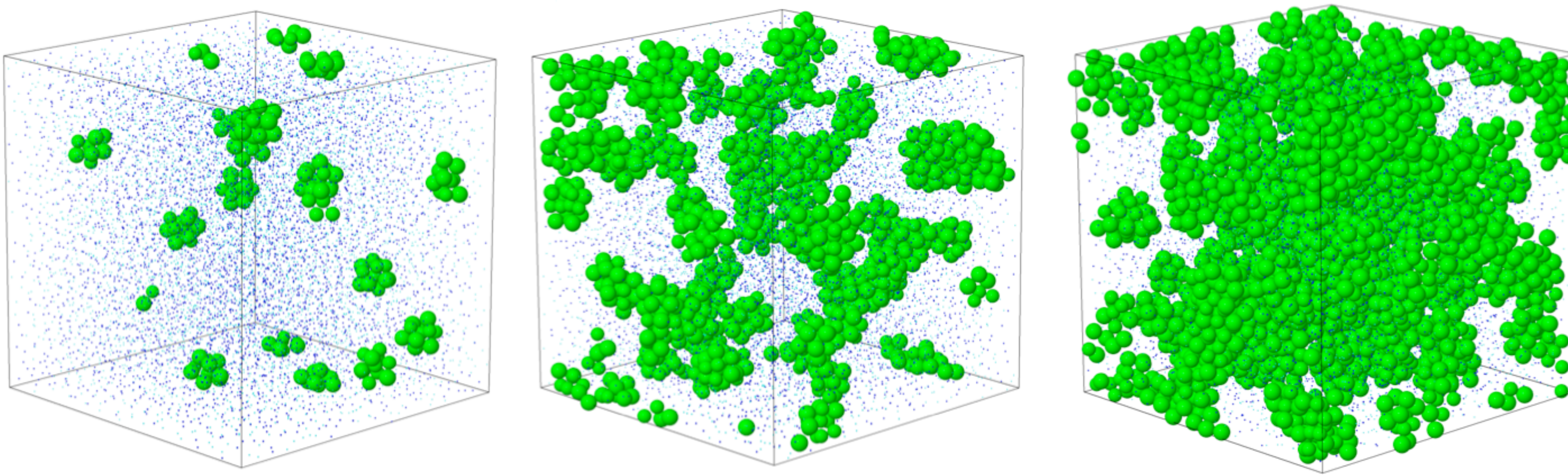
Binary Lennard-Jones mixture (Wahnstrom) additive, $\sigma_A=5/6\sigma_B$. Molecular Dynamics simulation



Malins, Eggers, Tanaka and Royall *Faraday Disc.* **167** paper 16 (2013)

Icosahedra domain growth upon cooling

Binary Lennard-Jones mixture (Wahnstrom) additive, $\sigma_A=5/6\sigma_B$. Molecular Dynamics simulation



T=1.00 T=0.707 T=0.620

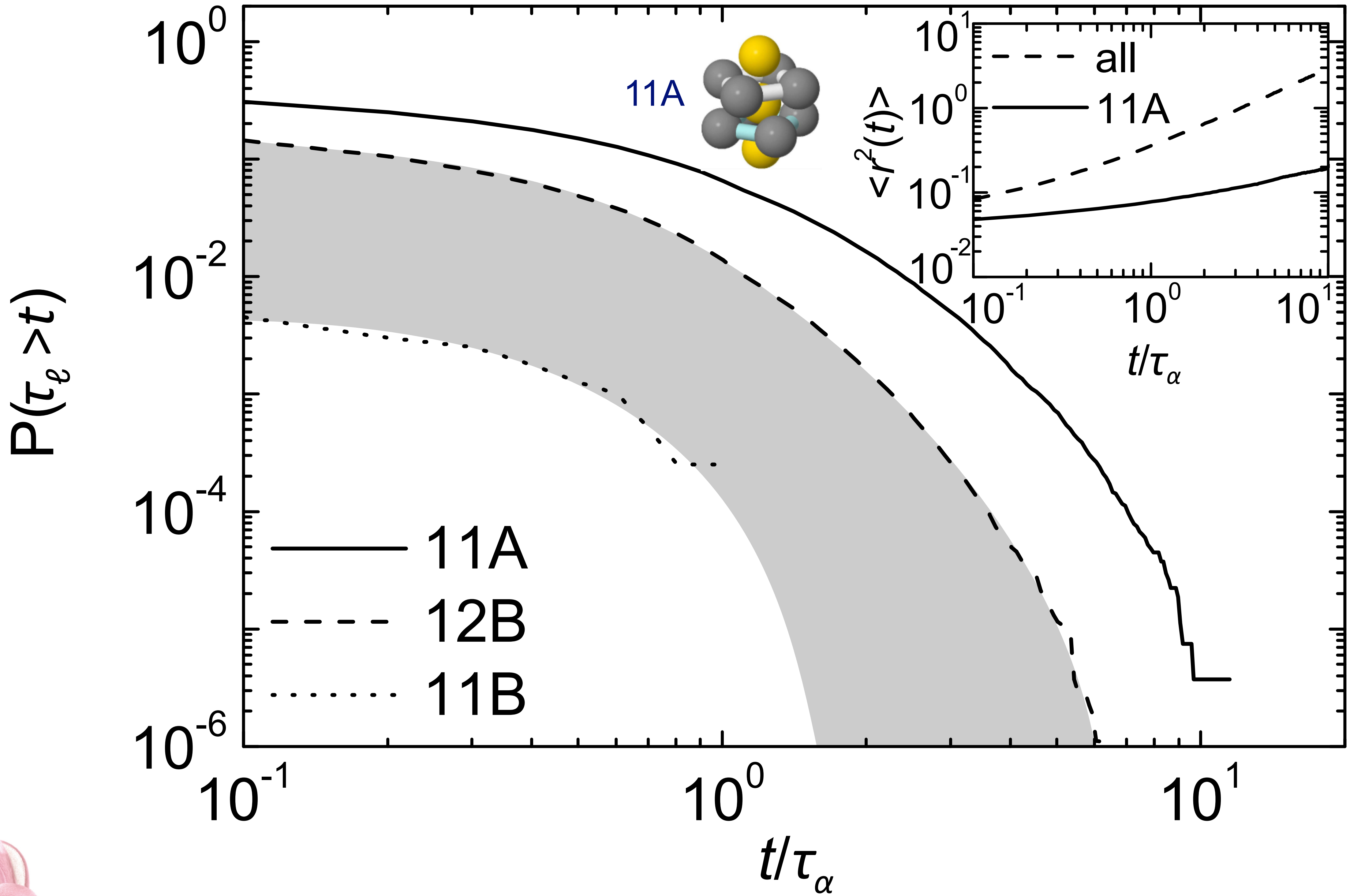
Emergence of network of icosahedral (slow) particles

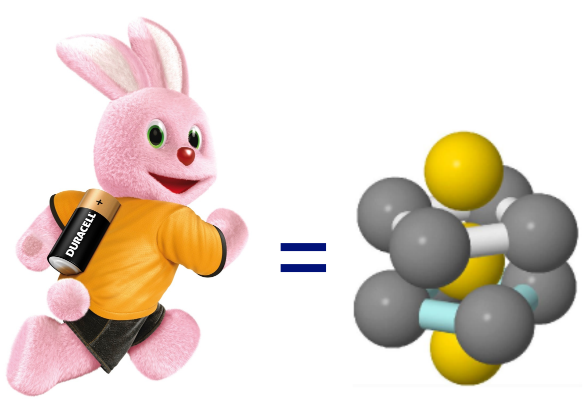
Malins, Eggers, Tanaka and Royall *Faraday Disc.* **167** paper 16 (2013)

Dynamic Toplogical cluster classification

Linking structure and dynamics

Kob-Andersen (80:20), non-additive, $\sigma_{AA}=1$ $\sigma_{BB}=0.88$



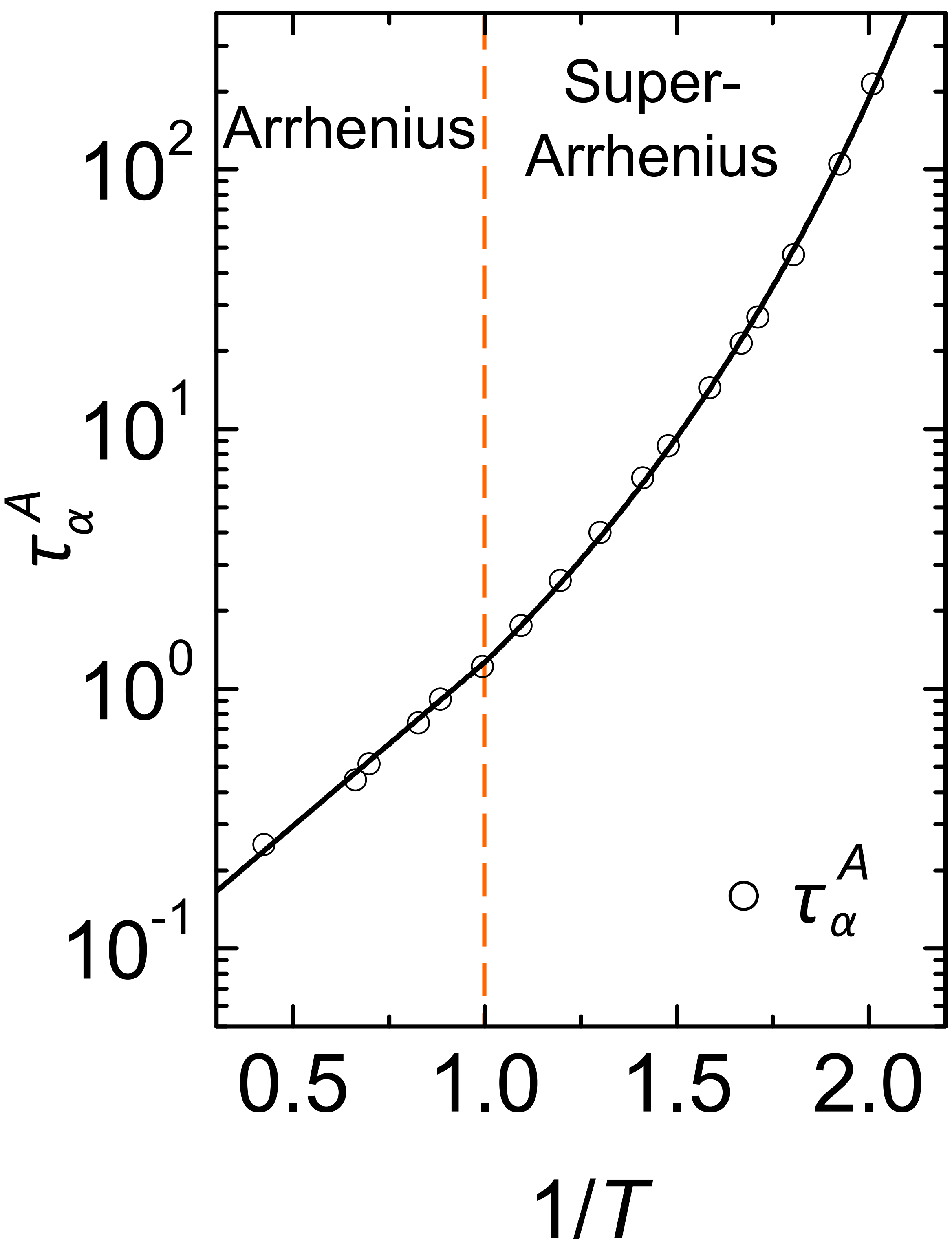


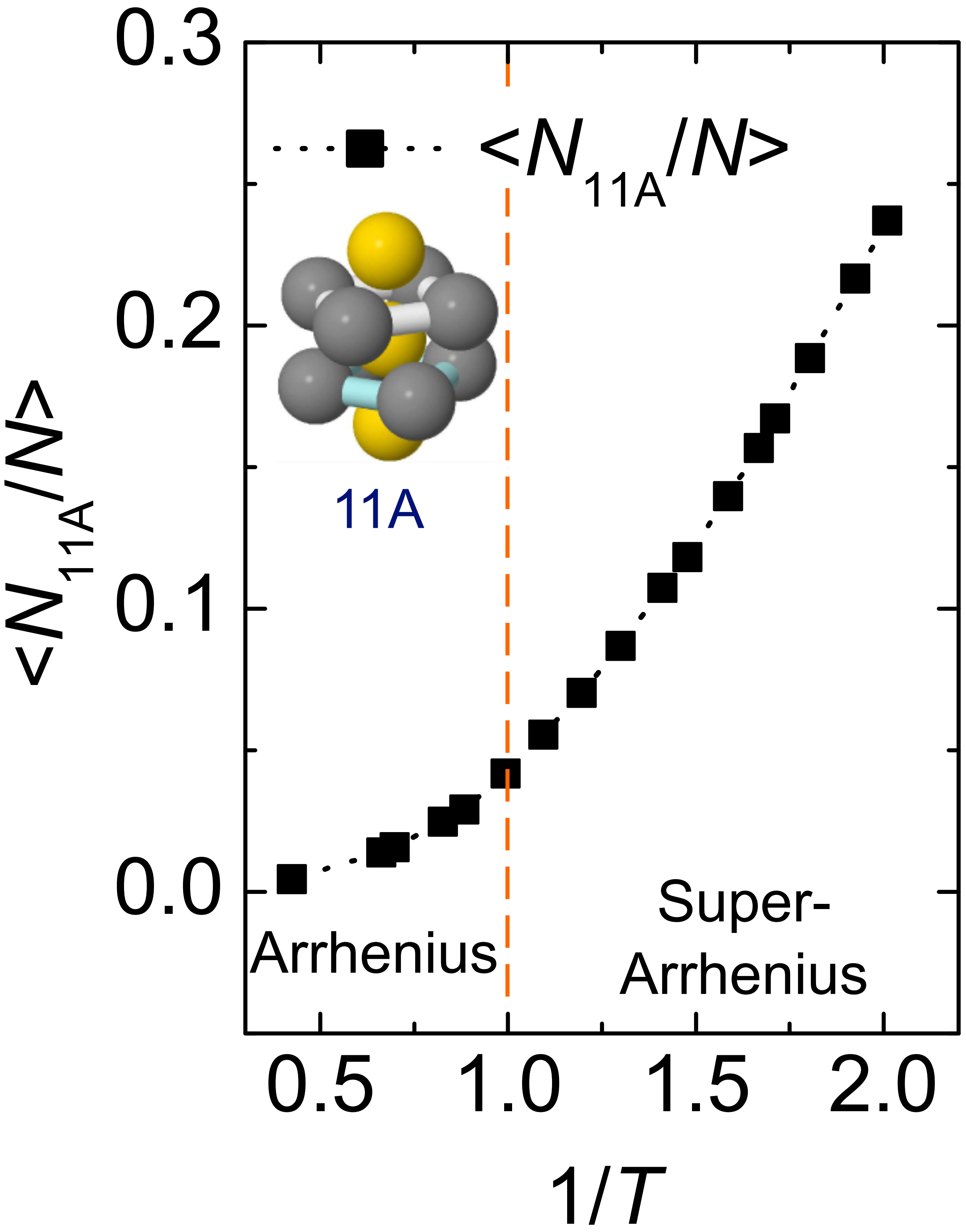
11A lasts *much* longer than all other clusters

Malins, Eggers, Tanaka and Royall *Faraday Disc.* **167** paper 16 (2013)

Change in dynamics...and structure

Kob-Andersen (80:20), non-additive, $\sigma_{AA}=1$ $\sigma_{BB}=0.88$

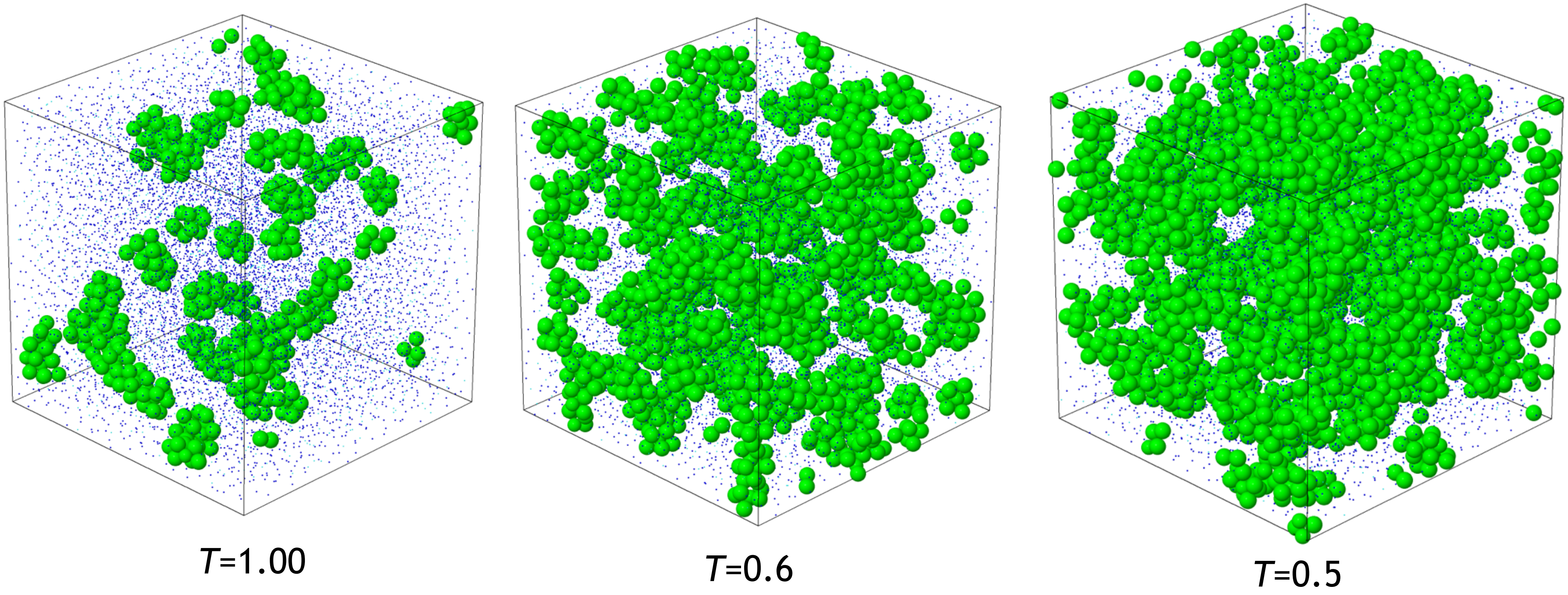




Malins, Eggers, Tanaka and Royall *Faraday Disc.* **167** paper 16 (2013)

11A domain growth upon cooling

Kob-Andersen (80:20), non-additive, σ_{AA}=1 σ_{BB}=0.88

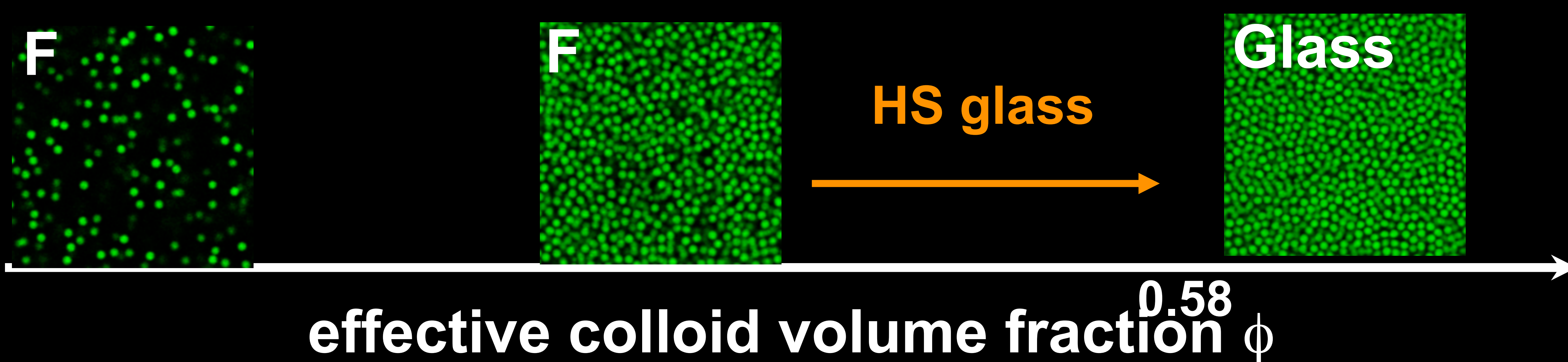


Emergence of network of particles in 11A clusters

Malins, Eggers, Tanaka and Royall *Faraday Disc.* **167** paper 16 (2013)

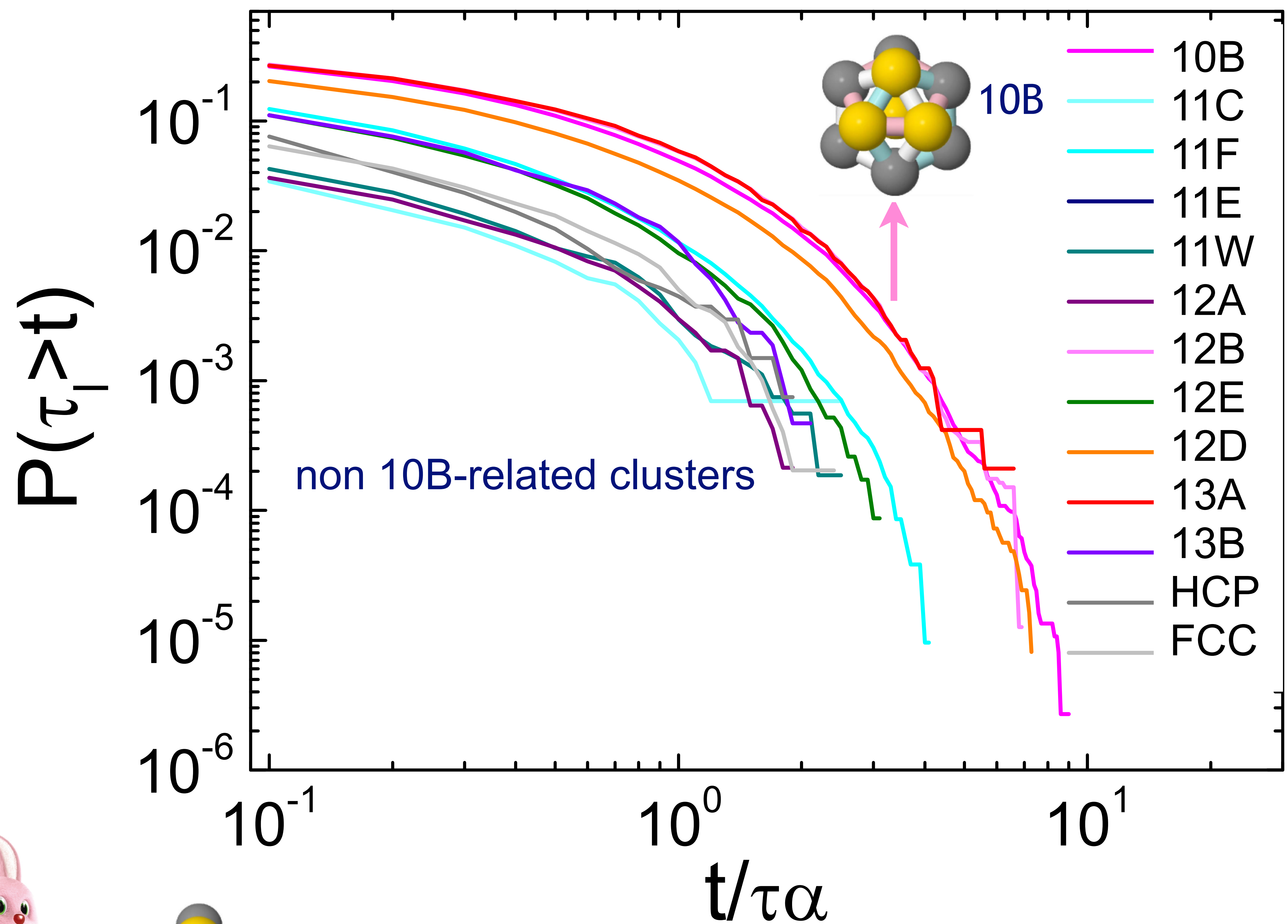
Experiments!

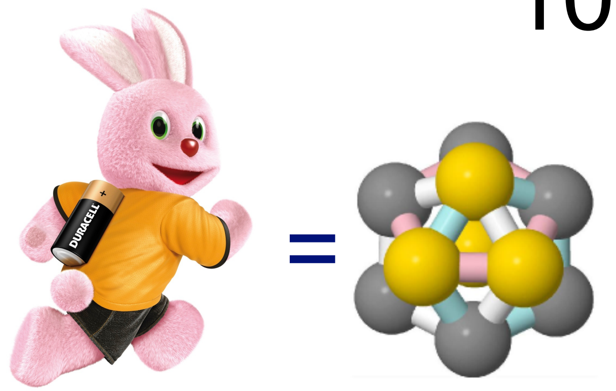
"Hard" spheres - "quench" by increasing density



Dynamic TCC - cluster lifetimes

Hard spheres (MD)

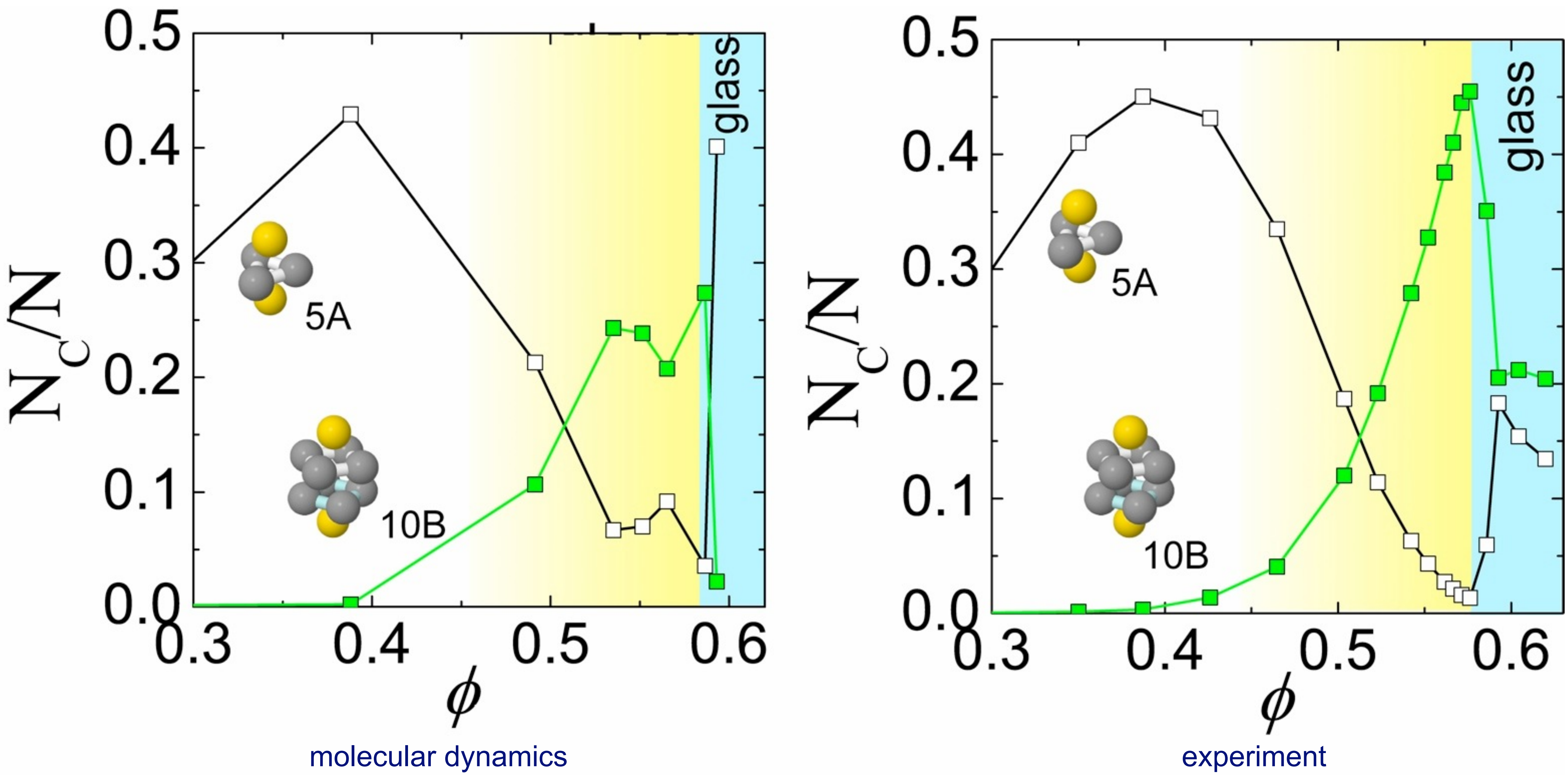




The 10B lasts *much* longer than all other clusters
12D, 13A are 10B with additional particles (and found in trace quantities)

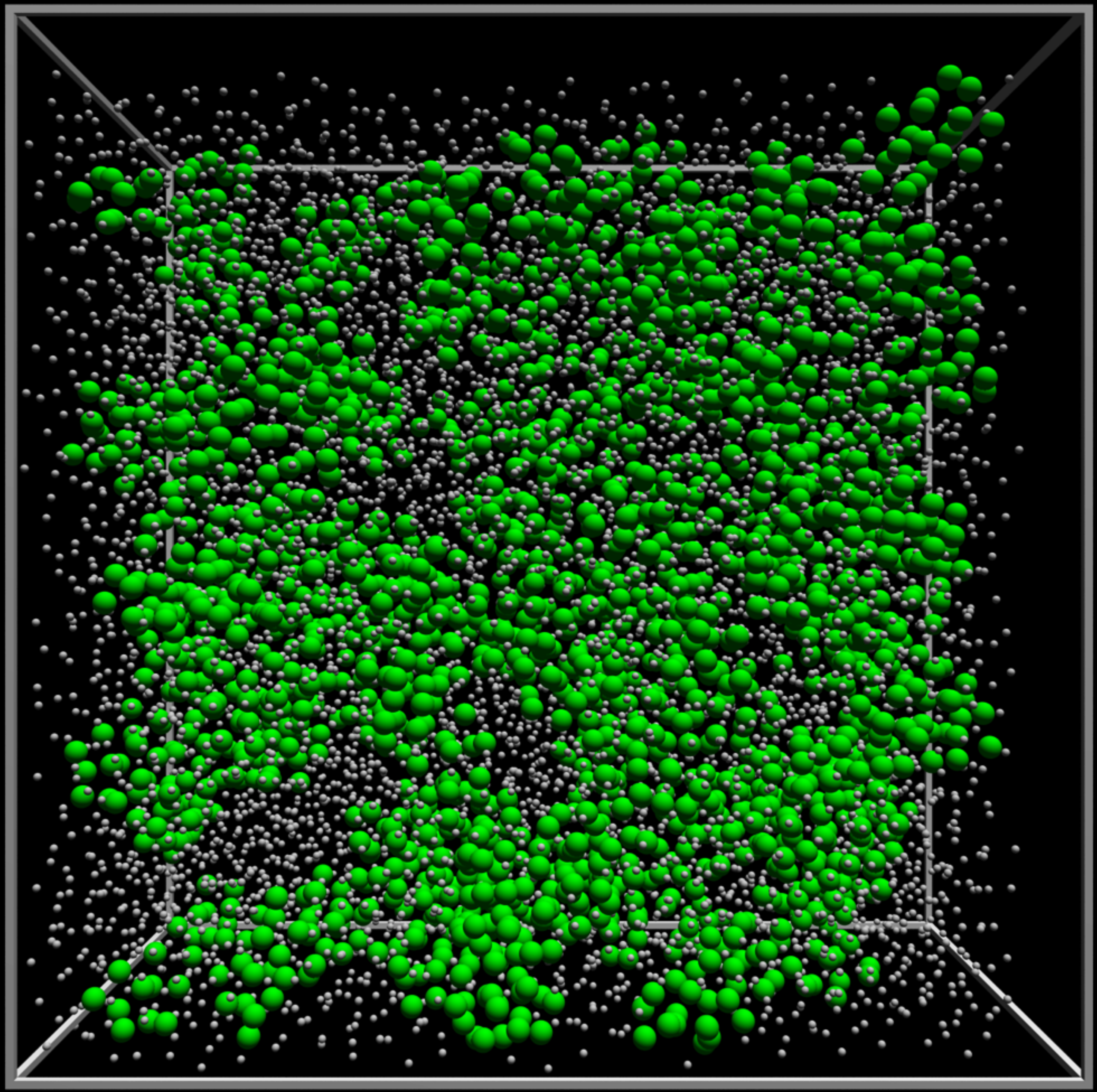
Royall et al. *proceedings of this meeting*

Change in structure in hard spheres



Similar to Lennard-Jones models 10B increases with compression. Falling out of equlibrium (ϕ=0.585) : 5A triangular bipyramid

Royall et al. *proceedings of this meeting*



Experimental data at ϕ=0.585. Network of 10B

Each model has its own locally favoured structure

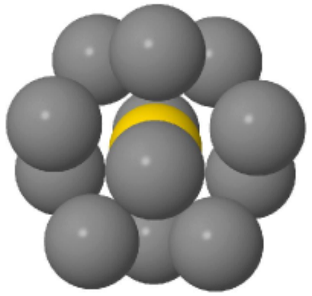
Lennard-Jones models

Wahnstrom (50:50), additive, σ_{AA}=1 σ_{BB}=0.833
icosahedron (13A) - Coslovich 2007
...and Frank-Kasper bonds - Pedersen 2010
Royall and coworkers *JCP* **138** 12A535 (2013)

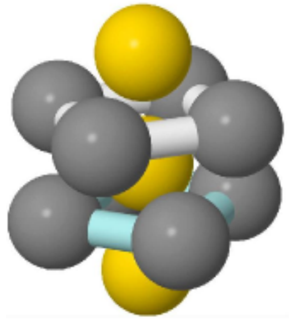
Kob-Andersen (80:20), non-additive, σ_{AA}=1 σ_{BB}=0.88
bicapped square anti-prism (11A) - Coslovich 2007
Malins, Eggers, Tanaka and Royall *Faraday Disc.* **167** paper 16 (2013)

Colloid experiments

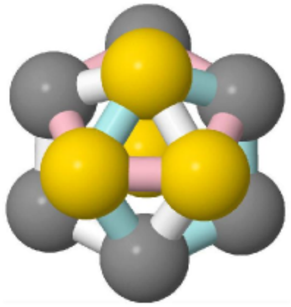
Particle-resolved studies of colloids
`Hard' spheres (+ MD simulations)
6-8% polydisperse
Royall *et al. proceedings of this meeting*



icosahedron



11A



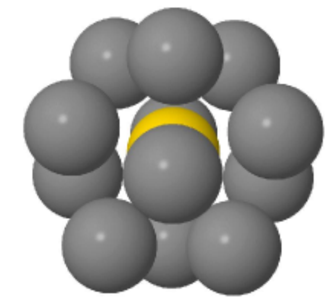
10B

Each model has its own locally favoured structure

Lennard-Jones models

Wahnstrom (50:50), additive, $\sigma_{AA}=1$ $\sigma_{BB}=0.833$
icosahedron (13A) - Coslovich 2007
...and Frank-Kasper bonds - Pedersen 2010

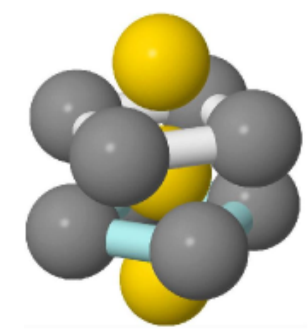
Royall and coworkers *JCP* **138** 12A535 (2013)



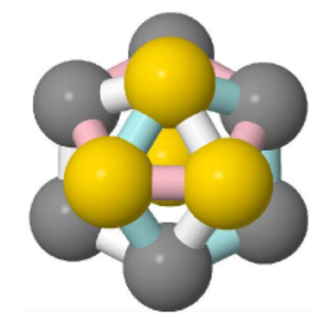
icosahedron

Kob-Andersen (80:20), non-additive, $\sigma_{AA}=1$ $\sigma_{BB}=0.88$
bicapped square anti-prism (11A) - Coslovich 2007

Malins, Eggers, Tanaka and Royall *Faraday Disc.* **167** paper 16 (2013)



11A



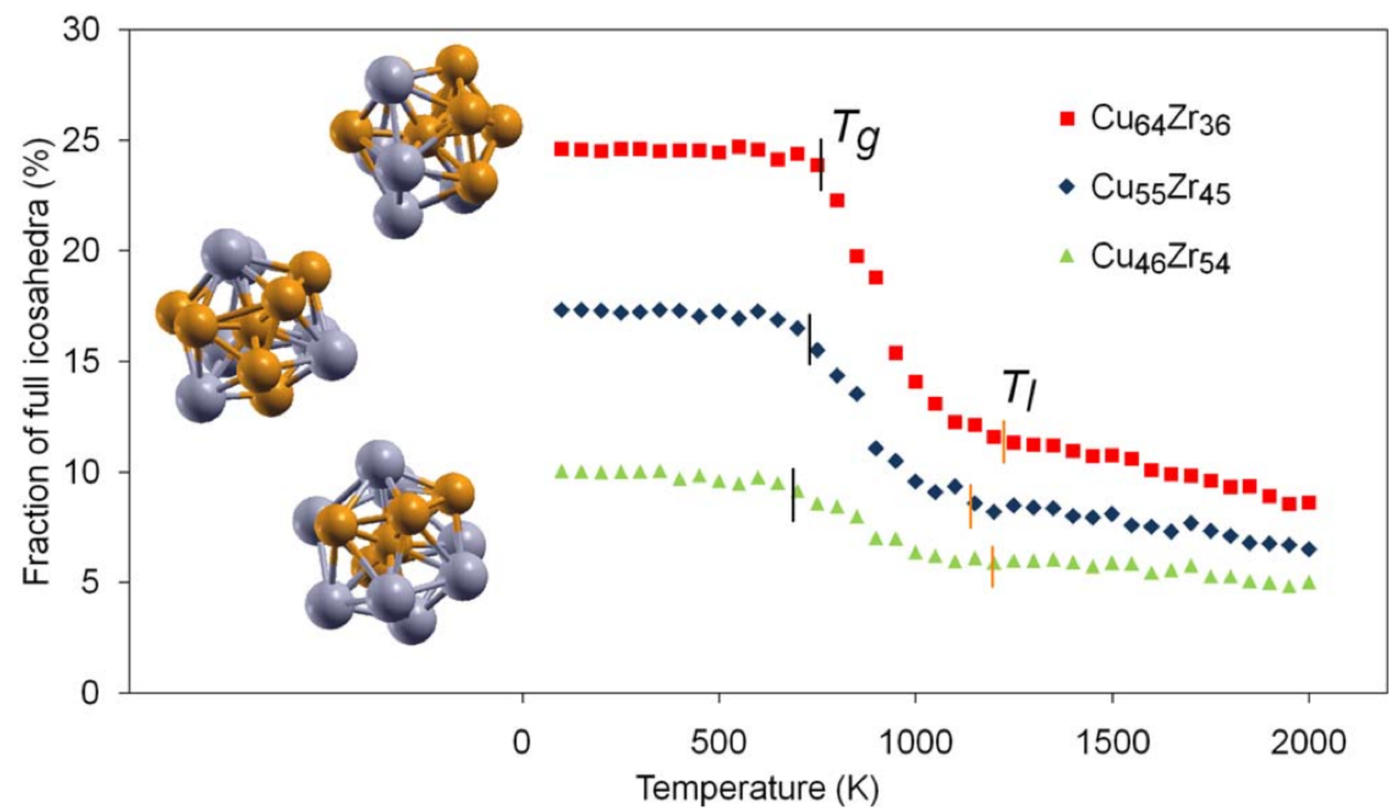
10B

Colloid experiments

Particle-resolved studies of colloids
`Hard' spheres (+ MD simulations)
6-8% polydisperse

Generality???

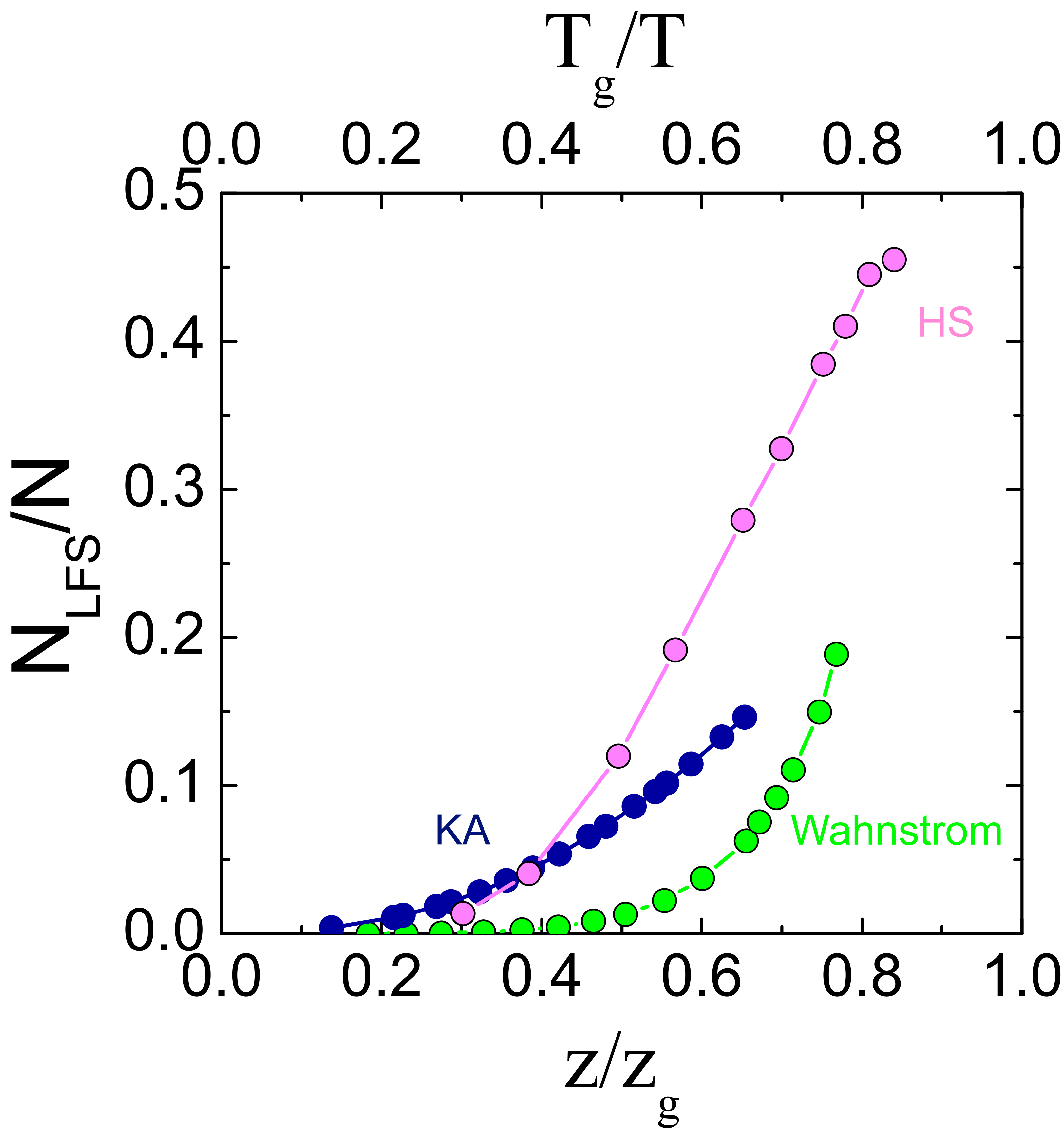
Icosahedra in embedded atom model simulations of CuZr
Cheng, Sheng and Ma PRB **78**, 014207 (2008)



11A bicapped square anti-prisms in Al-based alloys
Evteev et al. Acta. Mater. **51** 2665 (2003)

cf Ken Kelton's talk

Change in structure in different systems



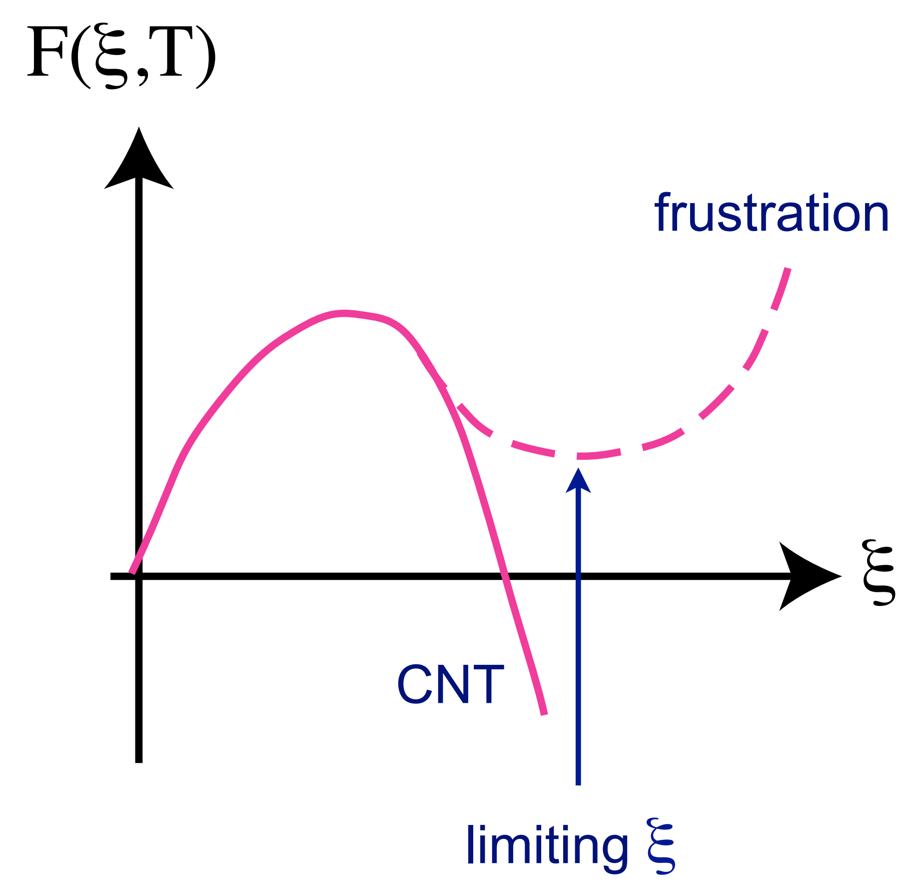
correlation with fragility ??

Royall et al. *proceedings of this meeting*

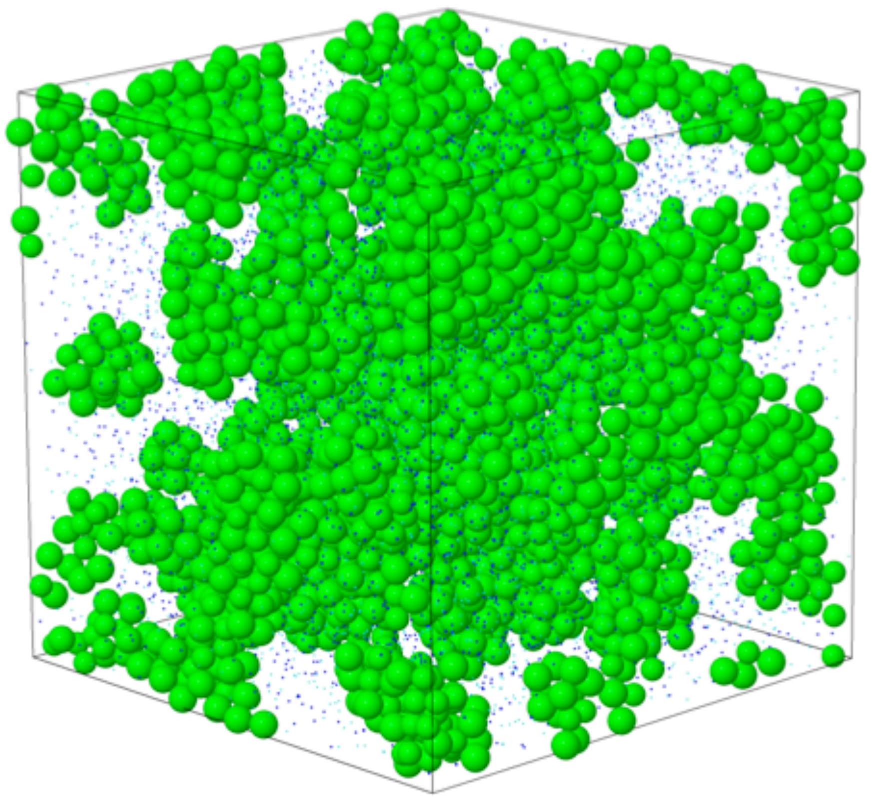
Geometric Frustration

$$F(\xi, T) = \Upsilon(T)\xi^{\theta} + \delta F_{\text{bulk}}(T)\xi^{3} + s(T)\xi^{5}$$

classical nucleation theory frustration



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



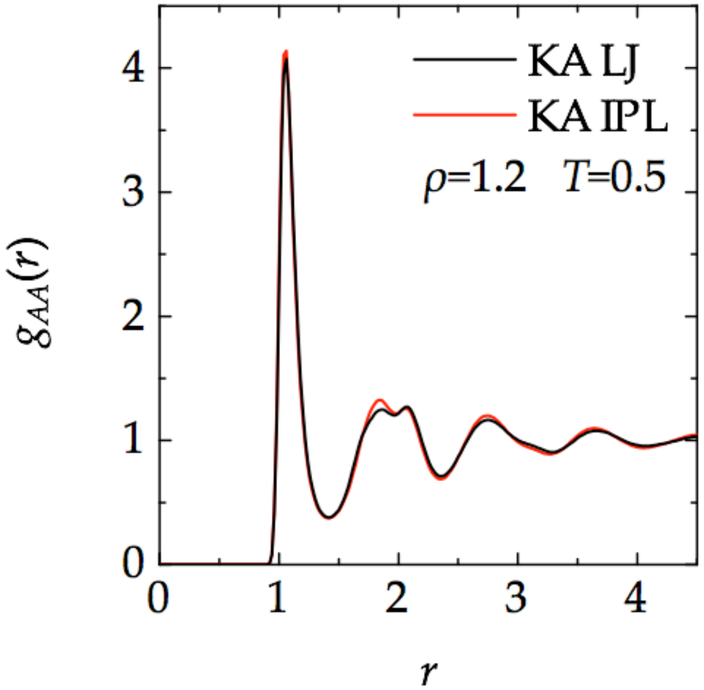
T=0.620

We see a lot of networks of locally favoured structures

1D length compatible with strong frustration

strong frustration : Charbonneau^2, Tarjus *JCP* **138** 12A515 (2013)

Investigating isomorphs with the TCC

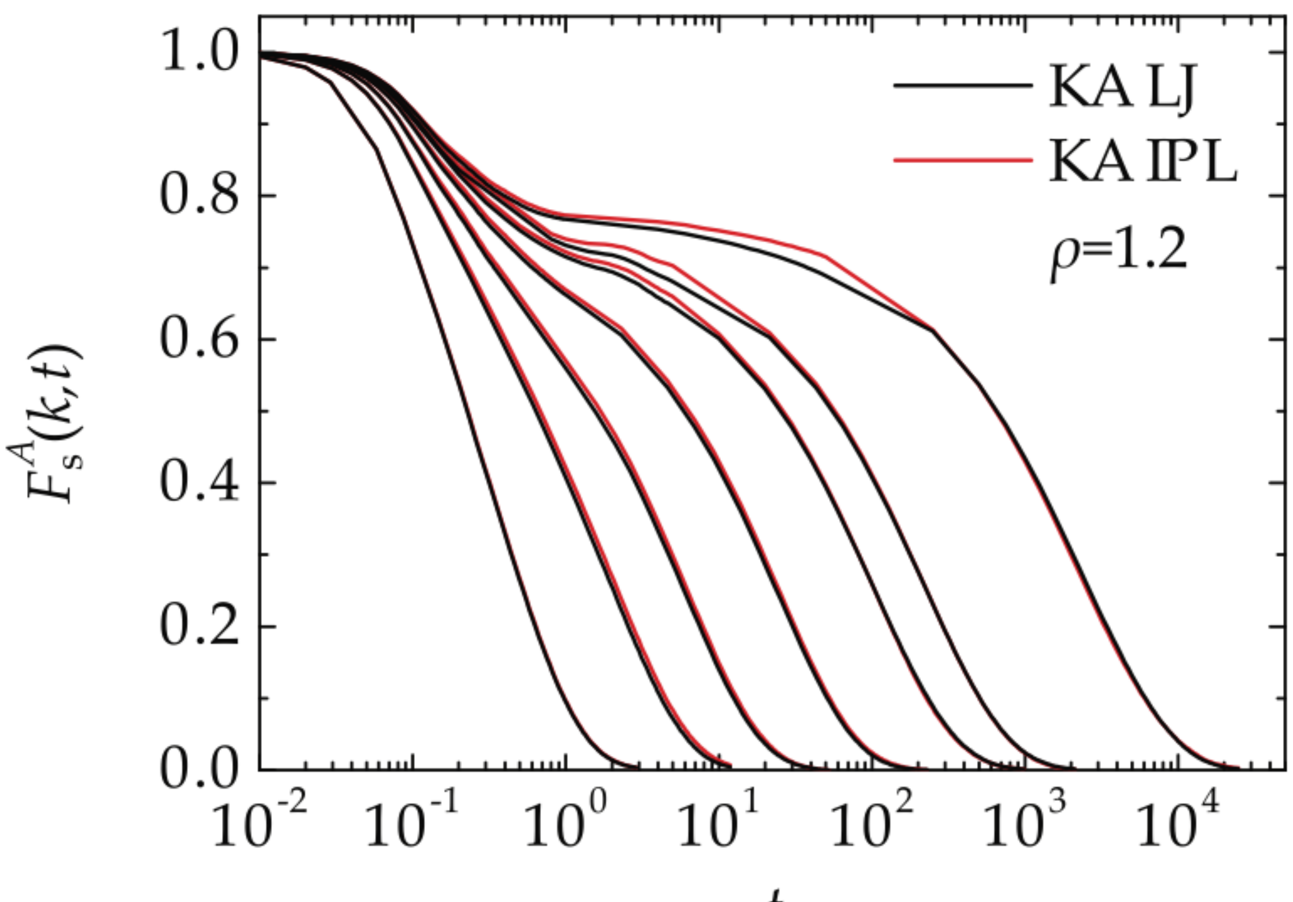


Kob-Andersen (80:20), non-additive, σ_{AA}=1 σ_{BB}=0.88

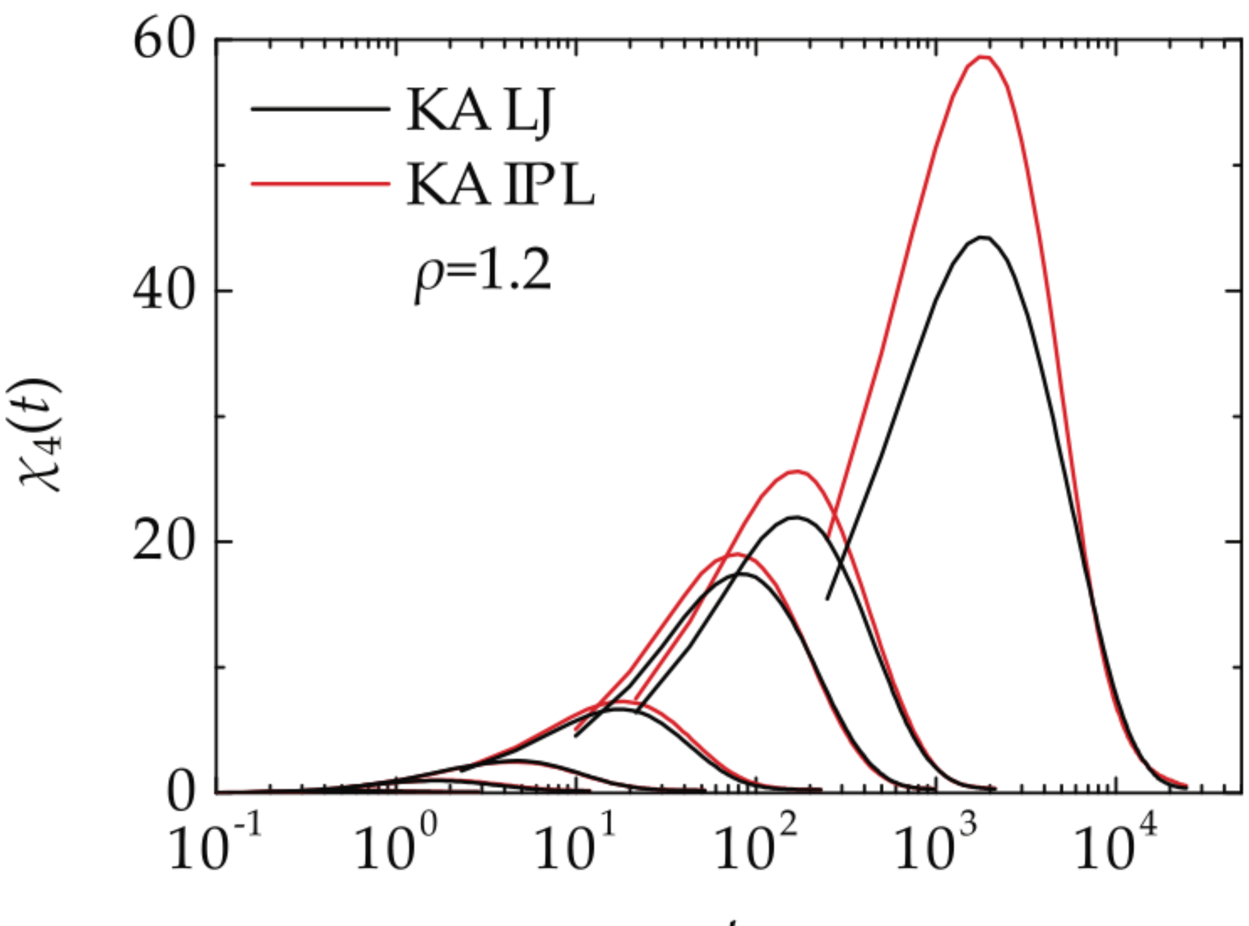
Inverse power law (IPL) mapped to Lennard-Jones following isomorphism

Dyre *PRE* **87** 022106 (2013)

2-point similar to Pedersen *et al. PRL* **105** 157801 (2011), 2-point dynamics agree



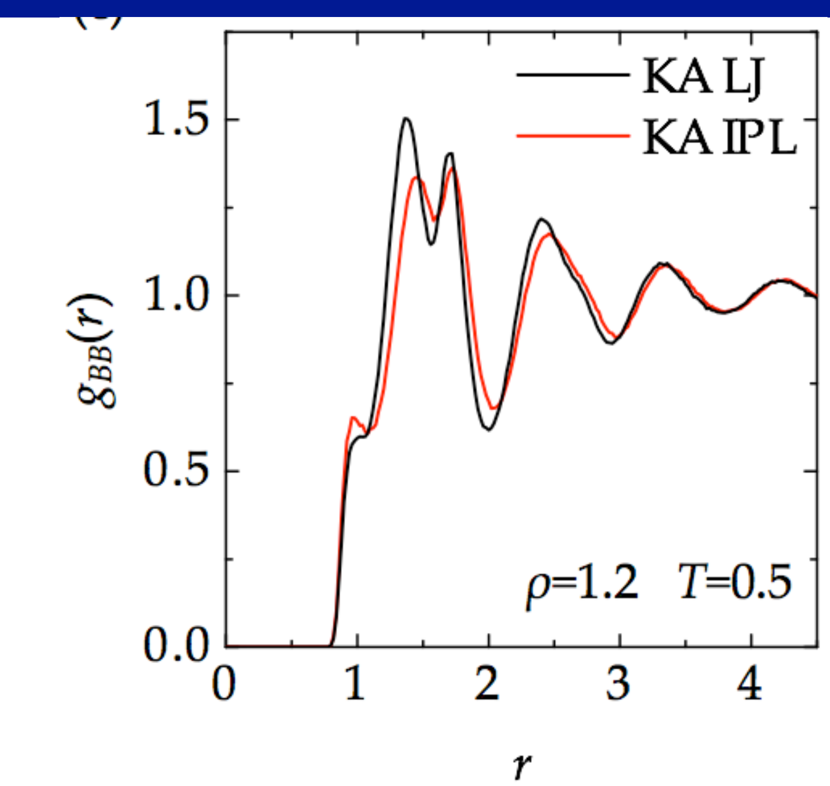
T=2.0...0.45



T=2.0...0.45

Malins, Eggers, Royall *JCP* **139** 234505 2013 (2013)

Investigating isomorphs with the TCC

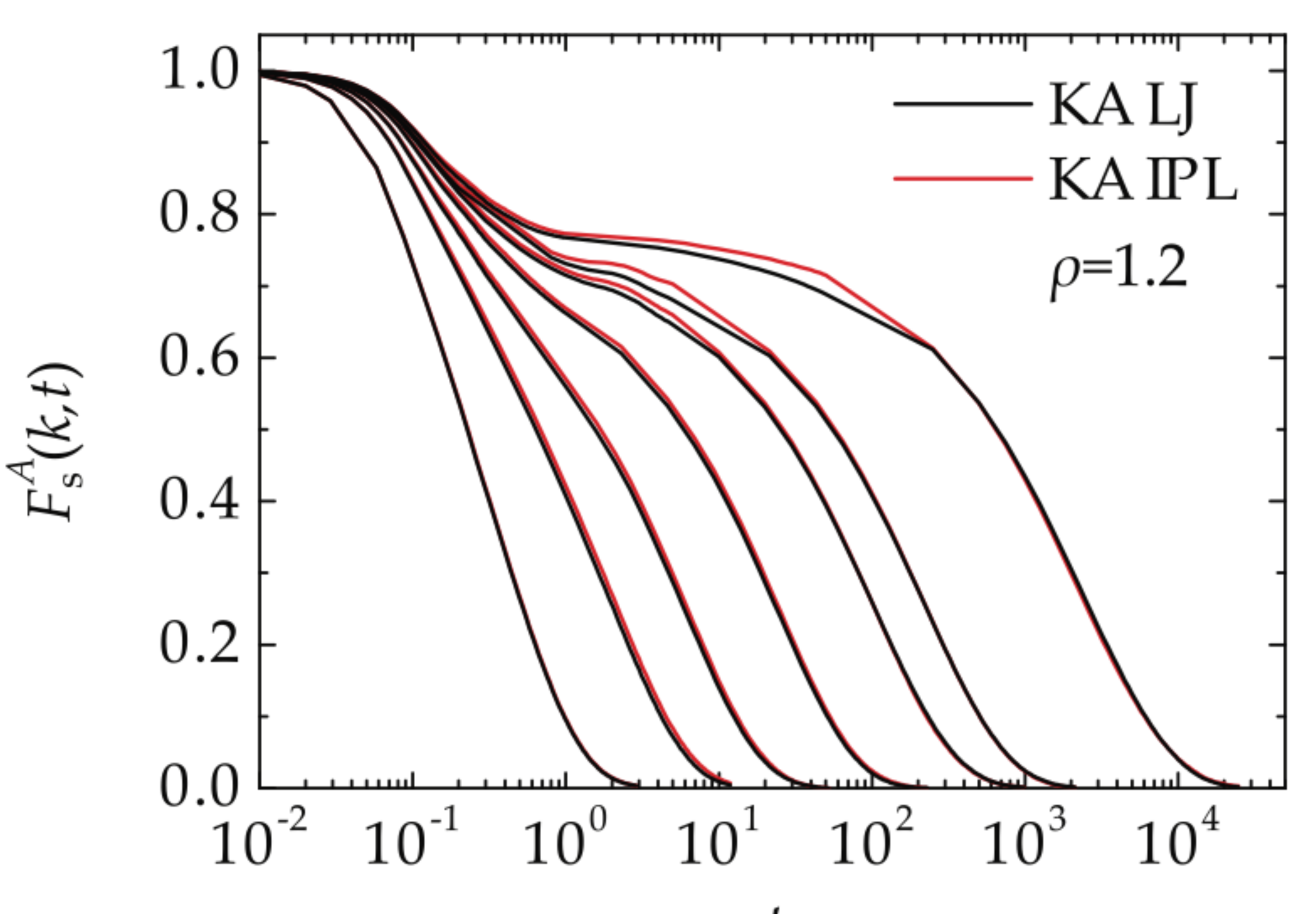


Kob-Andersen (80:20), non-additive, σ_{AA}=1 σ_{BB}=0.88

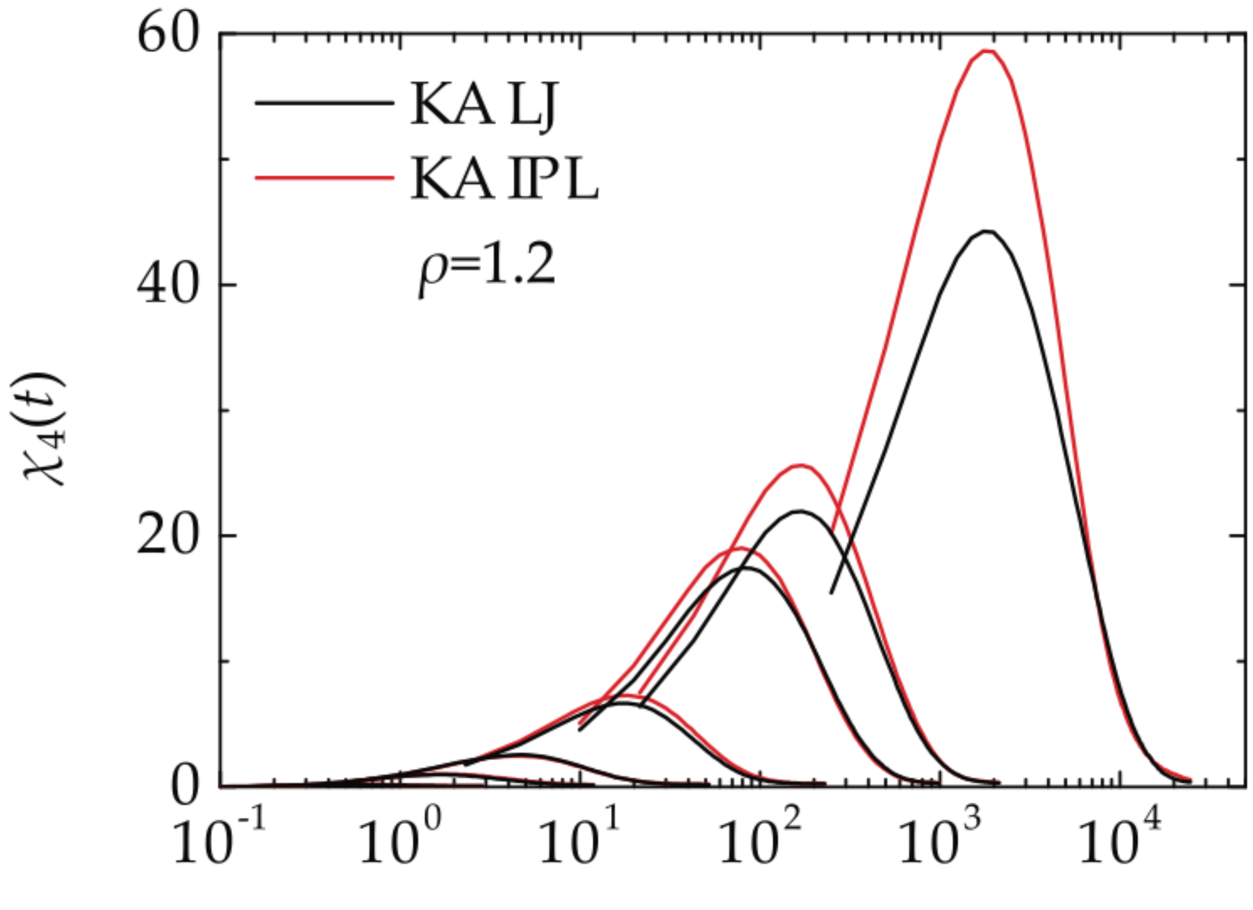
Inverse power law (IPL) mapped to Lennard-Jones following isomorphism

Dyre *PRE* **87** 022106 (2013)

2-point similar to Pedersen *et al. PRL* **105** 157801 (2011), 2-point dynamics agree



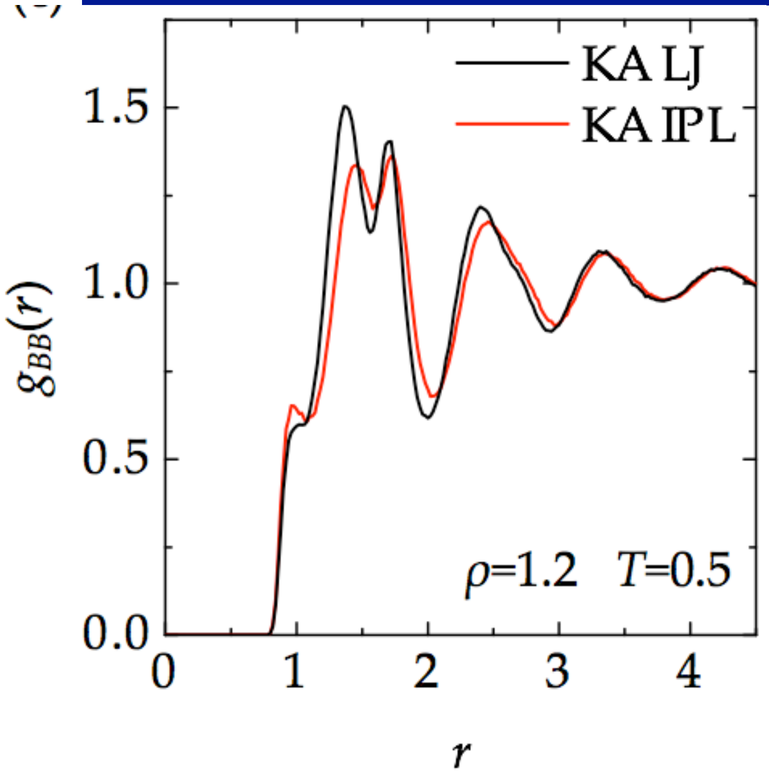
T=2.0...0.45



T=2.0...0.45

Malins, Eggers, Royall *JCP* **139** 234505 2013 (2013)

Investigating isomorphs with the TCC

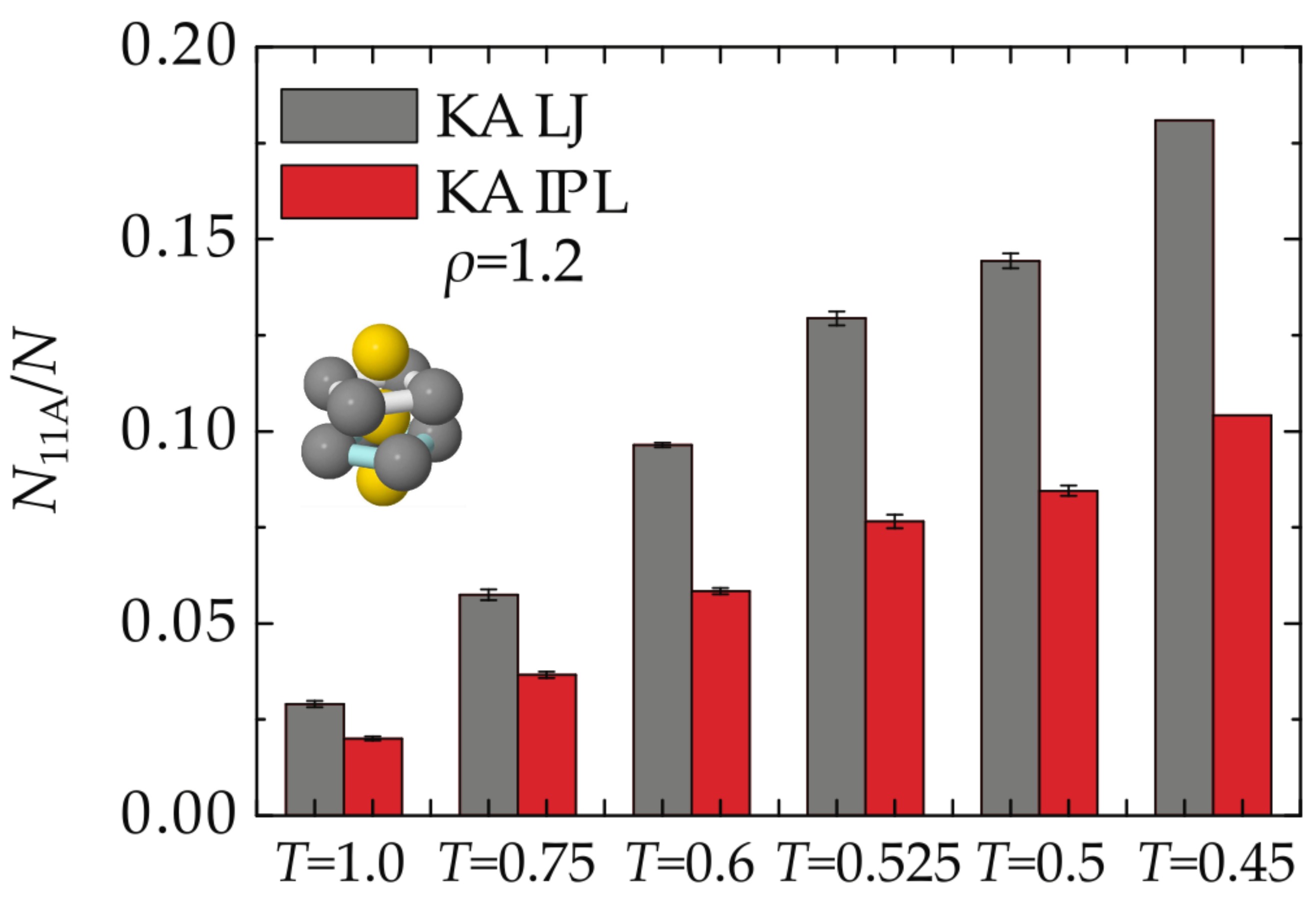


Kob-Andersen (80:20), non-additive, σ_{AA}=1 σ_{BB}=0.88

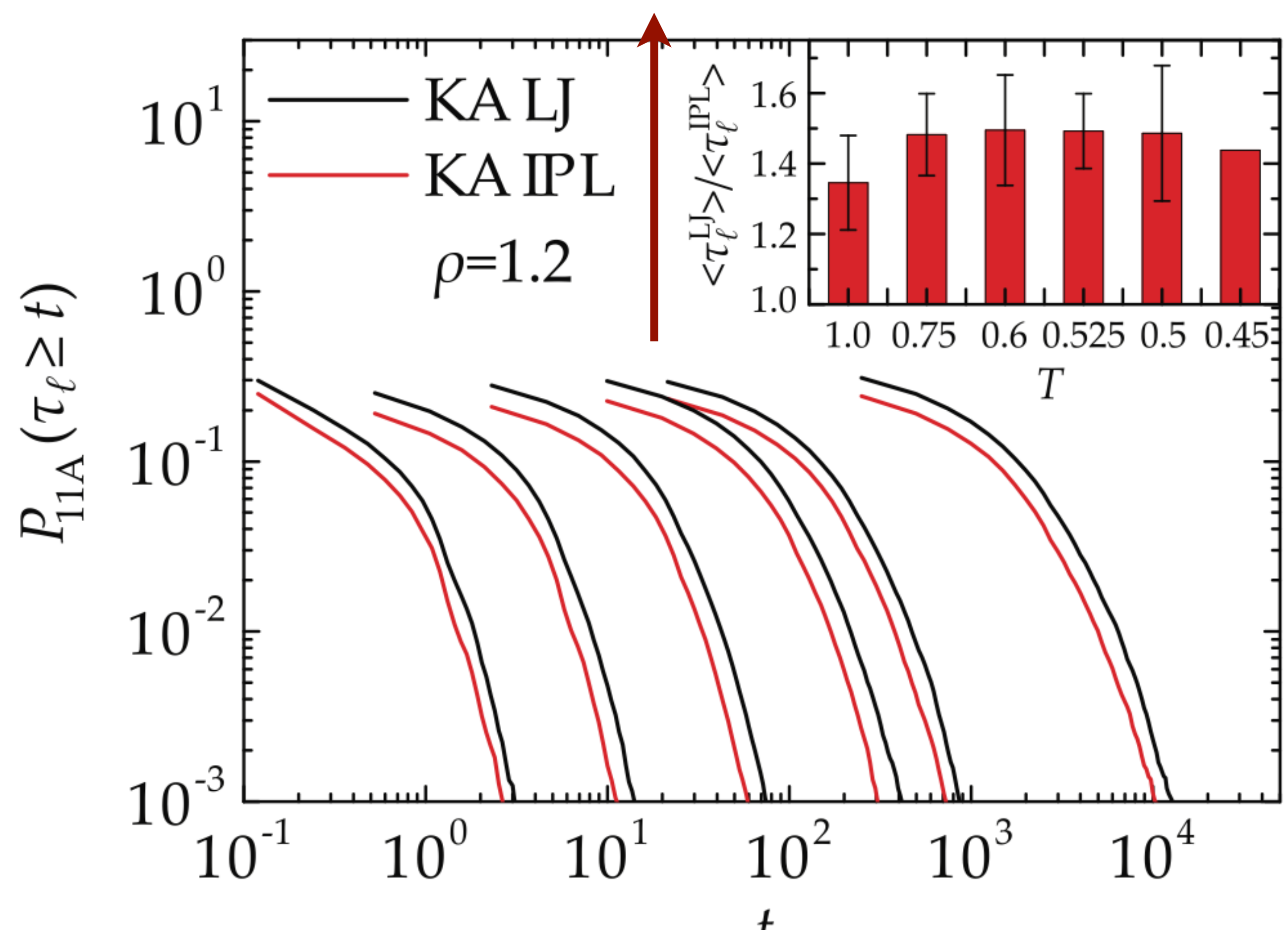
Inverse power law (IPL) mapped to Lennard-Jones following isomorphism

Dyre *PRE* **87** 022106 (2013)

2-point similar to Pedersen *et al. PRL* **105** 157801 (2011), 2-point dynamics agree



increase in 11A lifetime in LJ



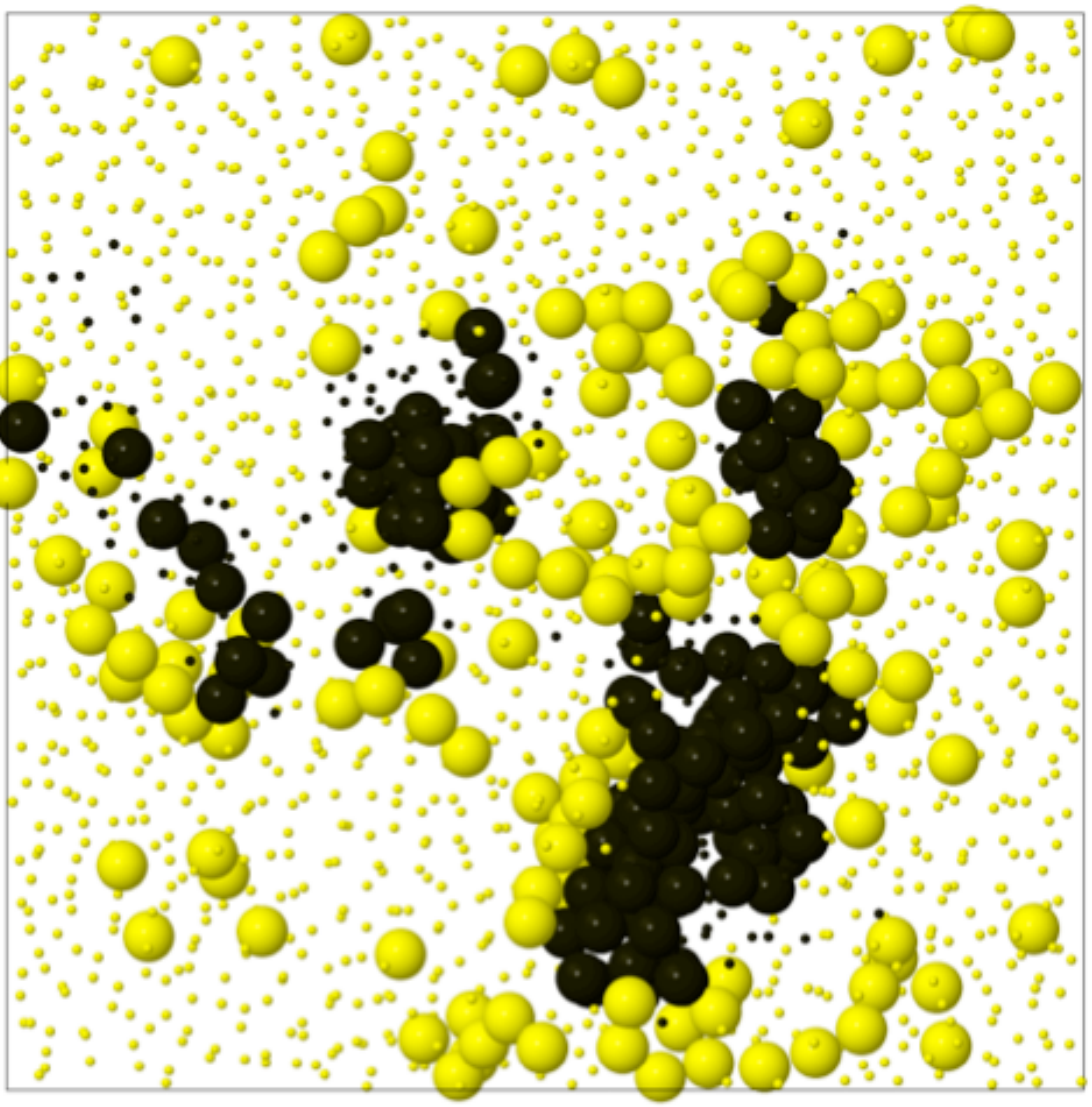
Malins, Eggers, Royall *JCP* **139** 234505 2013 (2013)

if structure were a cause for the glass transition we might expect structural lengthscales to grow with dynamic lengthscales

Do the lengthscales grow together?
Yes! Tanaka Nature Materials (2010), Nature Comms (2012), Mosayebi et al PRL (2010) and more…
Non! Famille Charboneau and Tarjus PRL (2011), Karmakar et al PNAS (2009) Kob et al. Nature Physics (2011), Charbonneau and Tarjus JCP (2013), Hocky et al PRL (2012), Dunleavy et al. PRE (2012) and more…

Dynamic lengthscales

Wahnstrom Binary Lennard-Jones



$<r^2(t_h)>$: <0.043

So far - structure and local influence

What are the dynamics (and how do they couple to the structure)

Spatially heterogeneous dynamics

Cool supercooled liquid - increasing dynamic correlation length ξ_4 - lengthscale of dynamically heterogeneous regions

ξ_4 - "standard definition" - fit low q end of $S_{SlowSlow}(q) = 1/(1-\xi_4^2 q^2)$

Lacevic *et al.* *JCP* **119** 7372 (2003)

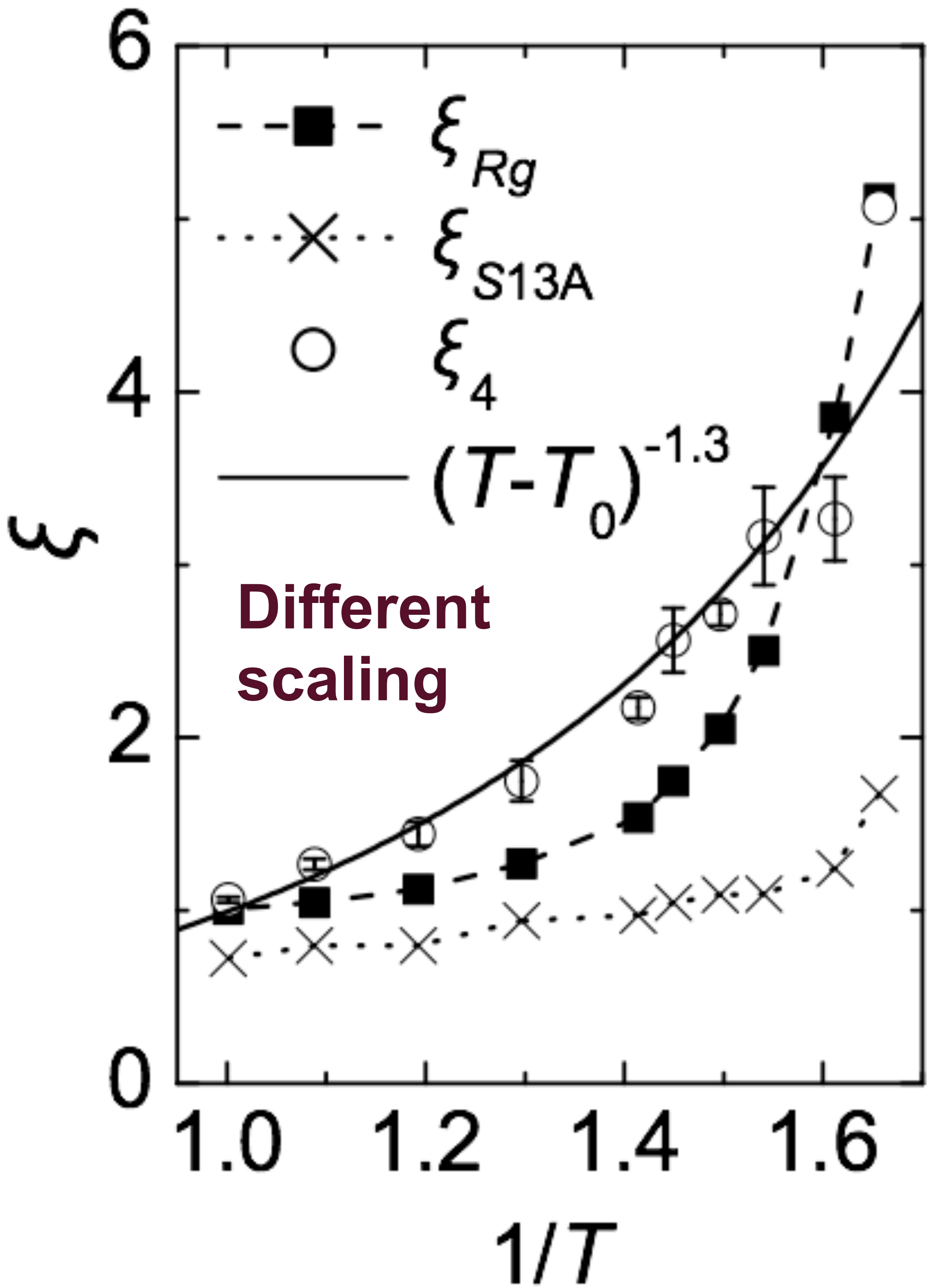
Also have structural correlation lengths.

ξ_{S13A} "standard definition" for icosahedra

ξ_{Rg} radius of gyration of domains of icosahedra

Malins, Eggers, Royall, Williams and Tanaka *JCP* **138** 12A535 (2013)

Dynamic lengthscales



So far - structure and local influence

What are the dynamics (and how do they couple to the structure)

Spatially heterogeneous dynamics

Cool supercooled liquid - increasing dynamic correlation length ξ_4 - lengthscale of dynamically heterogeneous regions

ξ_4 - “standard definition” - fit low q end of $S_{SlowSlow}(q) = 1/(1-\xi_4^2 q^2)$ [Lacevic *et al* JCP 2003]

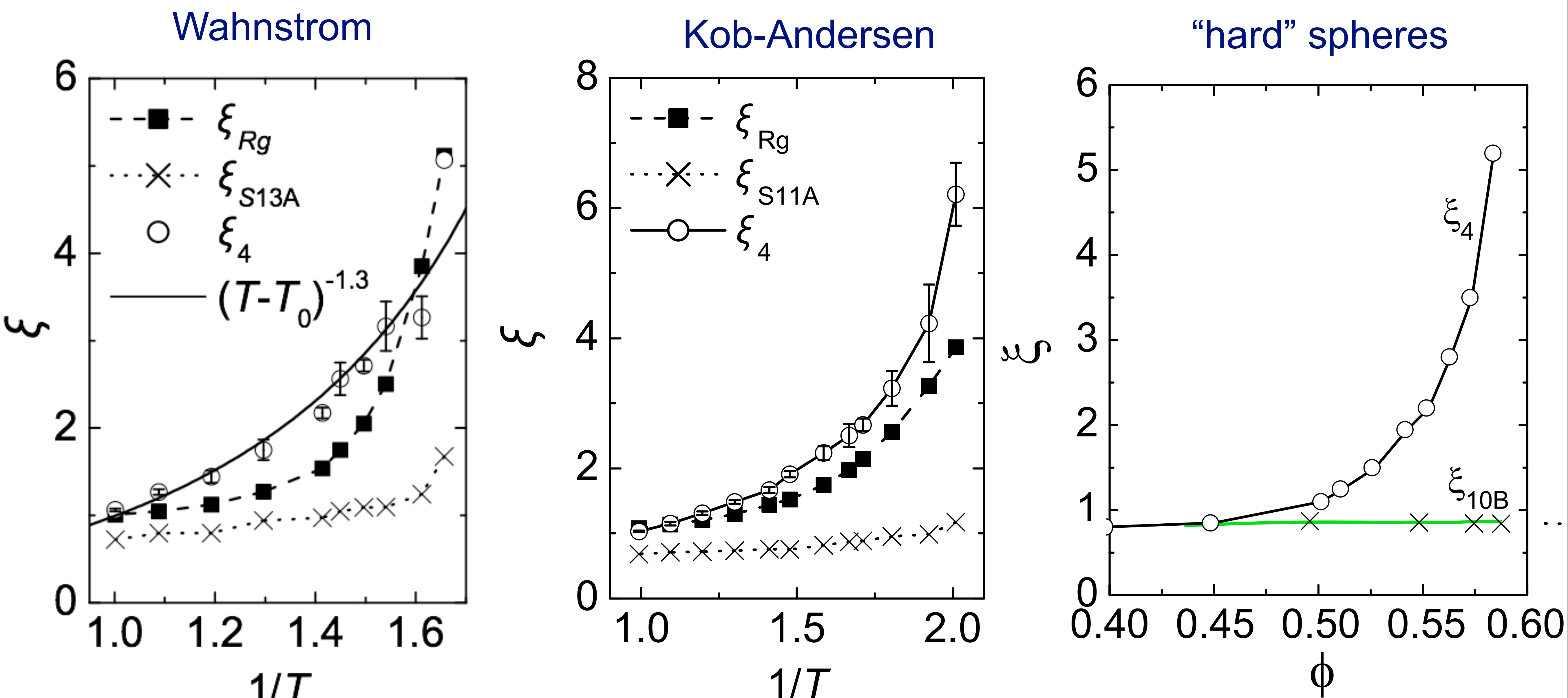
Also have structural correlation lengths.

ξ_{S13A} “standard definition” for icosahedra

ξ_{Rg} radius of gyration of domains of icosahedra

see also Famille Charboneau and Tarjus *PRL* (2011), Tanaka *Nature Mat* (2010), Kob et al. *Nature Physics* (2011)

Dynamic and static lengthscales do not scale together



Dynamic lengthscales and static lengthscales do *not* scale together

Malins, Eggers, Tanaka and Royall *Faraday Disc.* **167** paper 16 (2013)

Malins, Eggers, Royall, Williams and Tanaka *JCP* **138** 12A535 (2013)

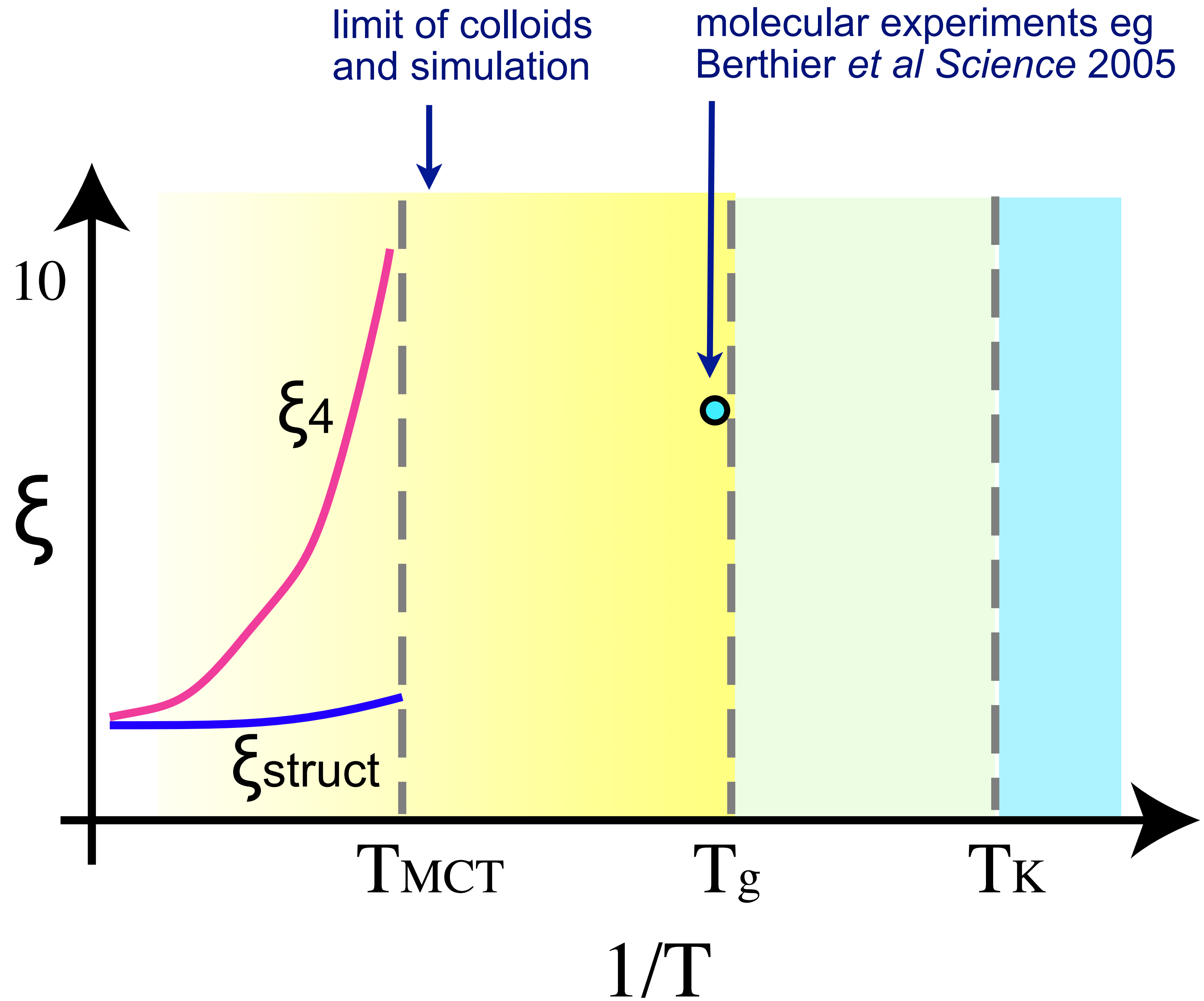
What happens to the dynamic lengthscale ????

Dynamic correlation length cannot continue to increase beyond ~T_{MCT}.

ξ_{dyn} and ξ_{struct} come together at lower T?

Non-monotonic or new scaling behaviour of ξ_{dyn}? Kob et al (2011), Szamel 2011,2012

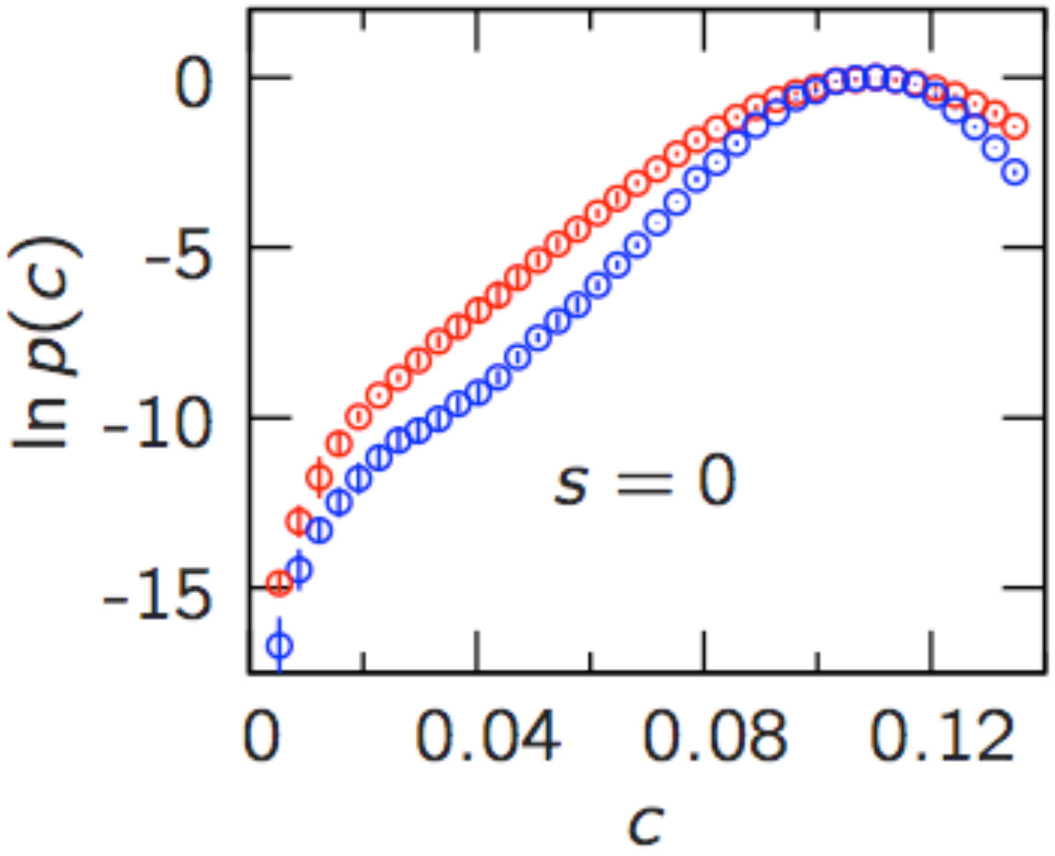
Is ξ_4 the "right" choice?
Harrowell in Dyn, Het. Berthier ed. (2011)



A different *tack* to the glass transition :
The μ-ensemble

we are used to cooling/compressing a system for solidification

A glass transition without cooling



The s-ensemble

Trajectory space sampling at T>glass transition (T=0.6)

Mobility *c* of trajectory of ~216 particles

Apply field *s* such that trajectories with low mobility (*c*) are selected

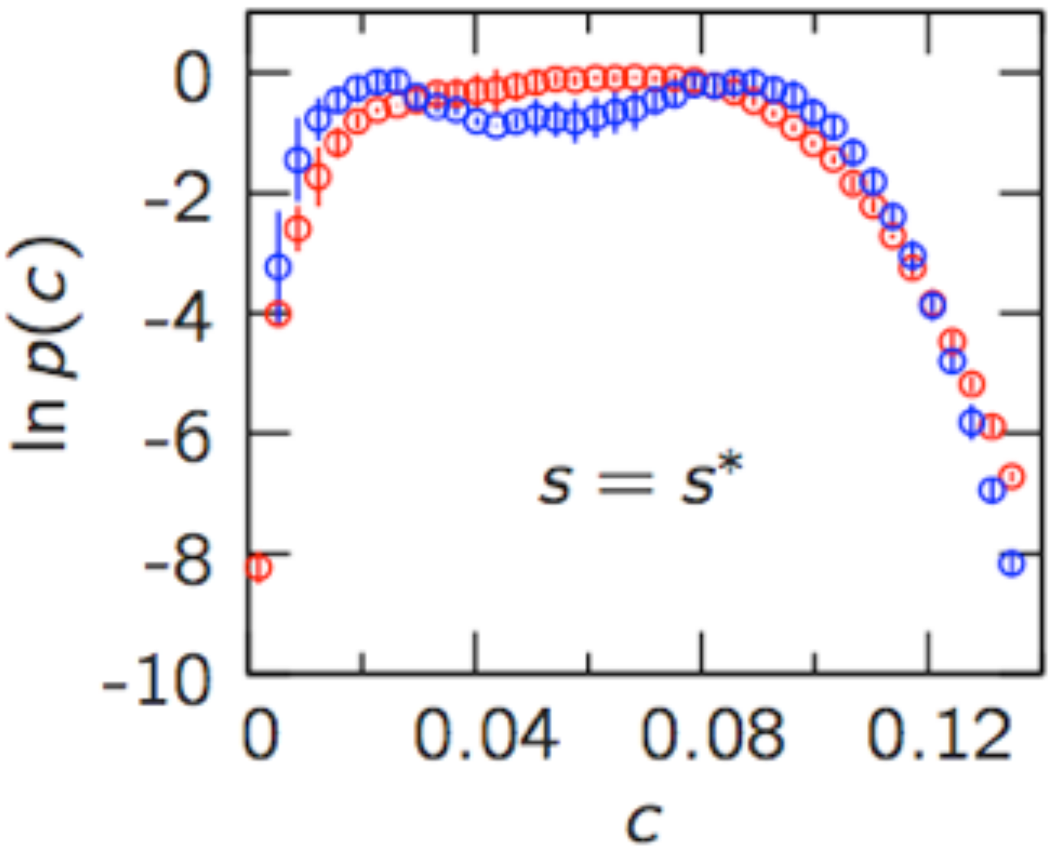
Hedges, Jack, Garrahan and Chandler *Science* **323** 1309 (2009)

s=0 no biasing (normal simulation)

Kob-Andersen binary Lennard Jones

Speck Malins and Royall *PRL* **109** 195703 (2012)

A glass transition without cooling



s=s* biasing (select low-mobility trajectories)

The s-ensemble

Trajectory space sampling at T>glass transition (T=0.6)

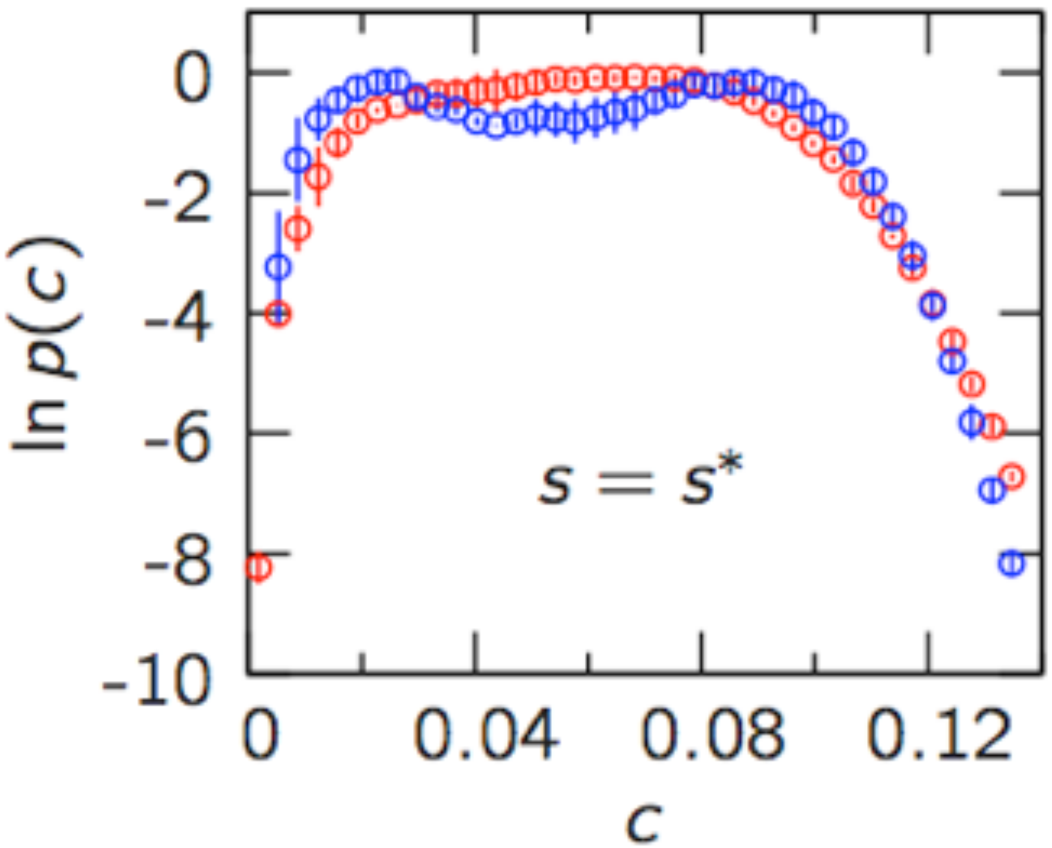
Mobility *c* of trajectory of ~216 particles

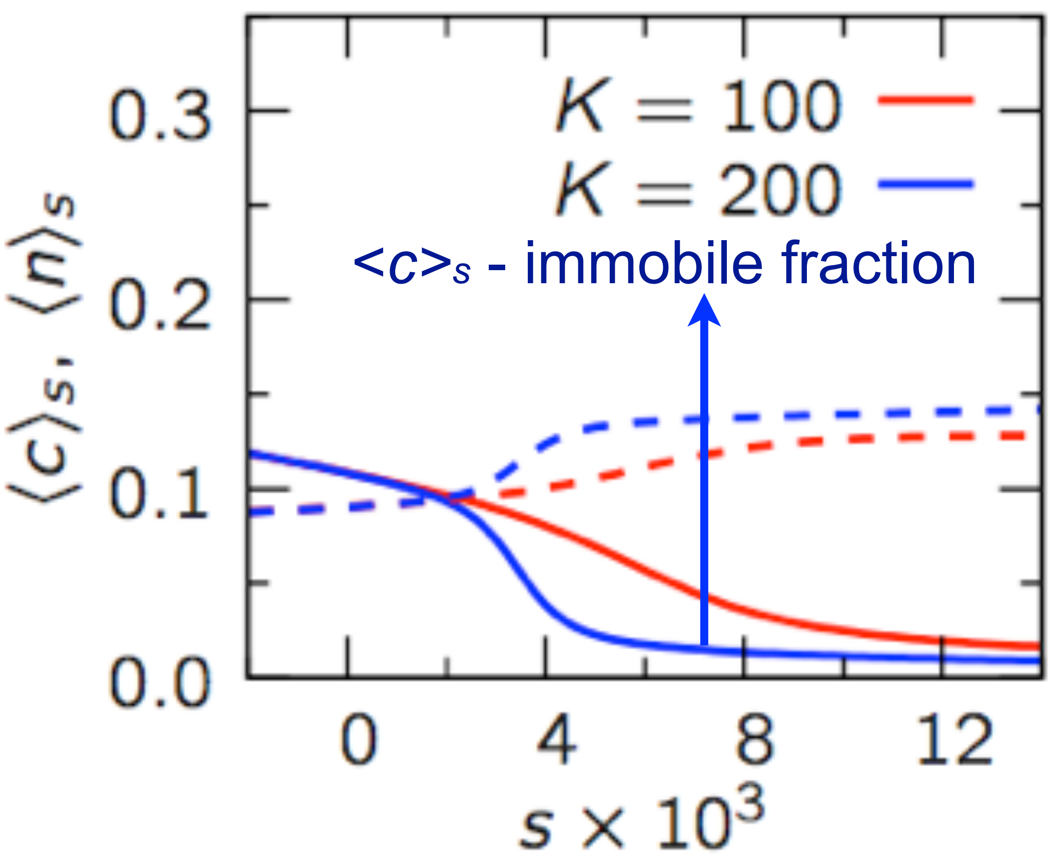
Apply field *s* such that trajectories with low mobility (*c*) are selected

Hedges, Jack, Garrahan and Chandler *Science* **323** 1309 (2009)

Speck Malins and Royall *PRL* **109** 195703 (2012)

A glass transition without cooling





The s-ensemble

Trajectory space sampling at T>glass transition (T=0.6)

Mobility *c* of trajectory of ~216 particles

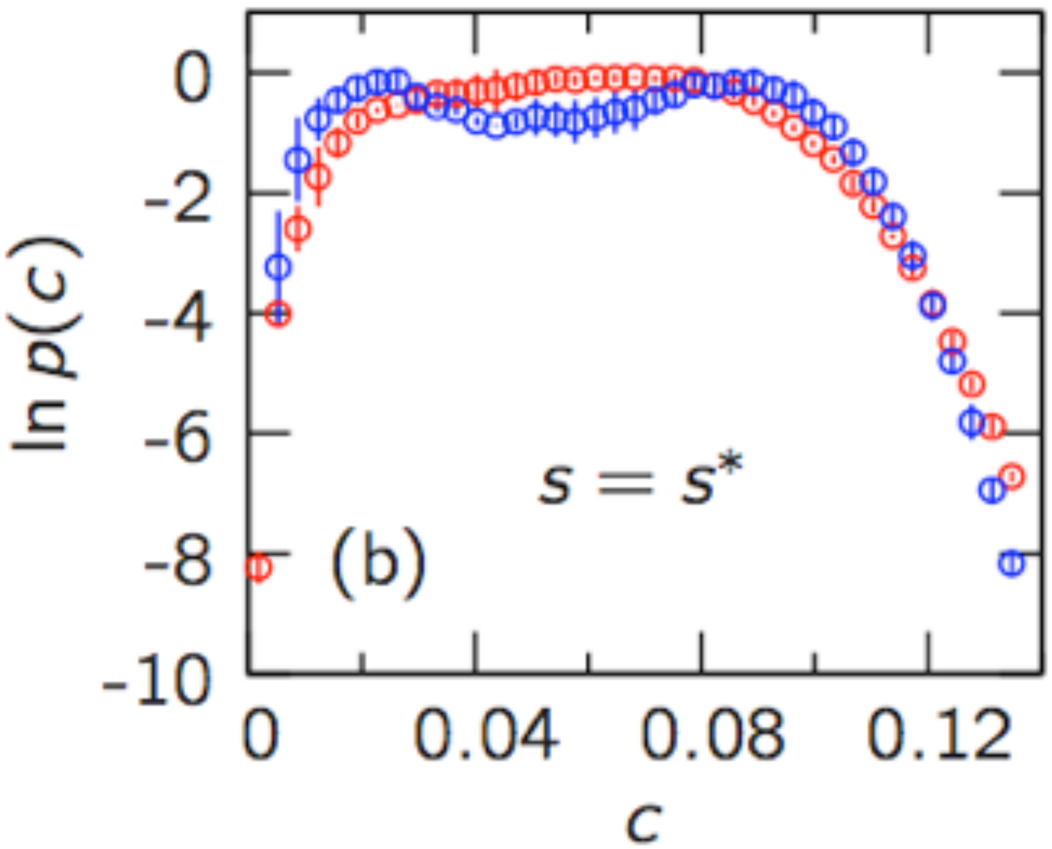
Apply field *s* such that trajectories with low mobility (*c*) are selected

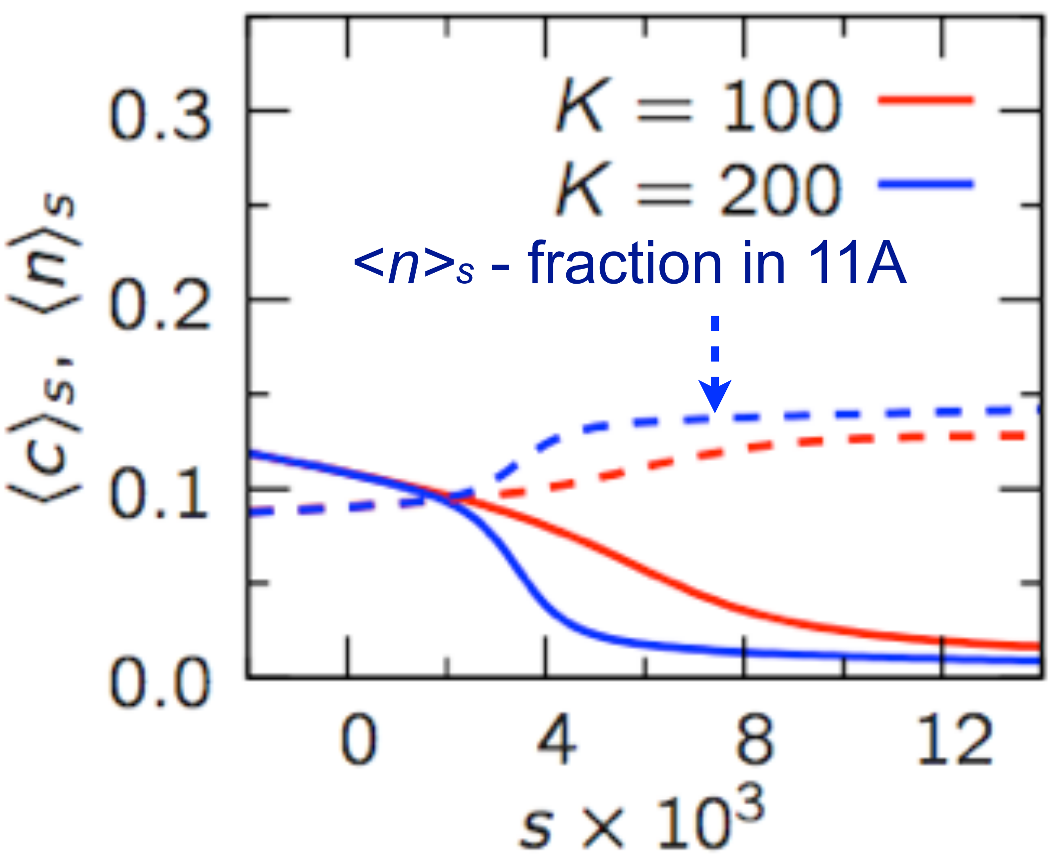
Hedges, Jack, Garrahan and Chandler *Science* **323** 1309 (2009)

Evidence for first-order transition

Speck Malins and Royall *PRL* **109** 195703 (2012)

A glass transition by biasing structure??





K length of trajectory

The s-ensemble

Trajectory space sampling at T>glass transition (T=0.6)

Mobility *c* of trajectory of ~216 particles

Apply field *s* such that trajectories with low mobility (*c*) are selected

Hedges, Jack, Garrahan and Chandler *Science* **323** 1309 (2009)

What about structure?

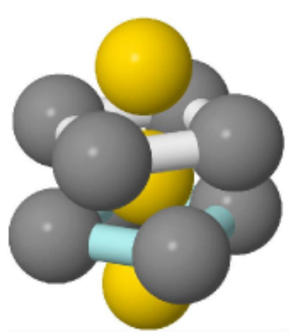
Jack, Hedges, Garrahan and Chandler PRL **107**, 275702 (2011) :

Very stable states from *s*-ensemble
- have these a different structure??

Kob-Andersen -> increase in 11A?

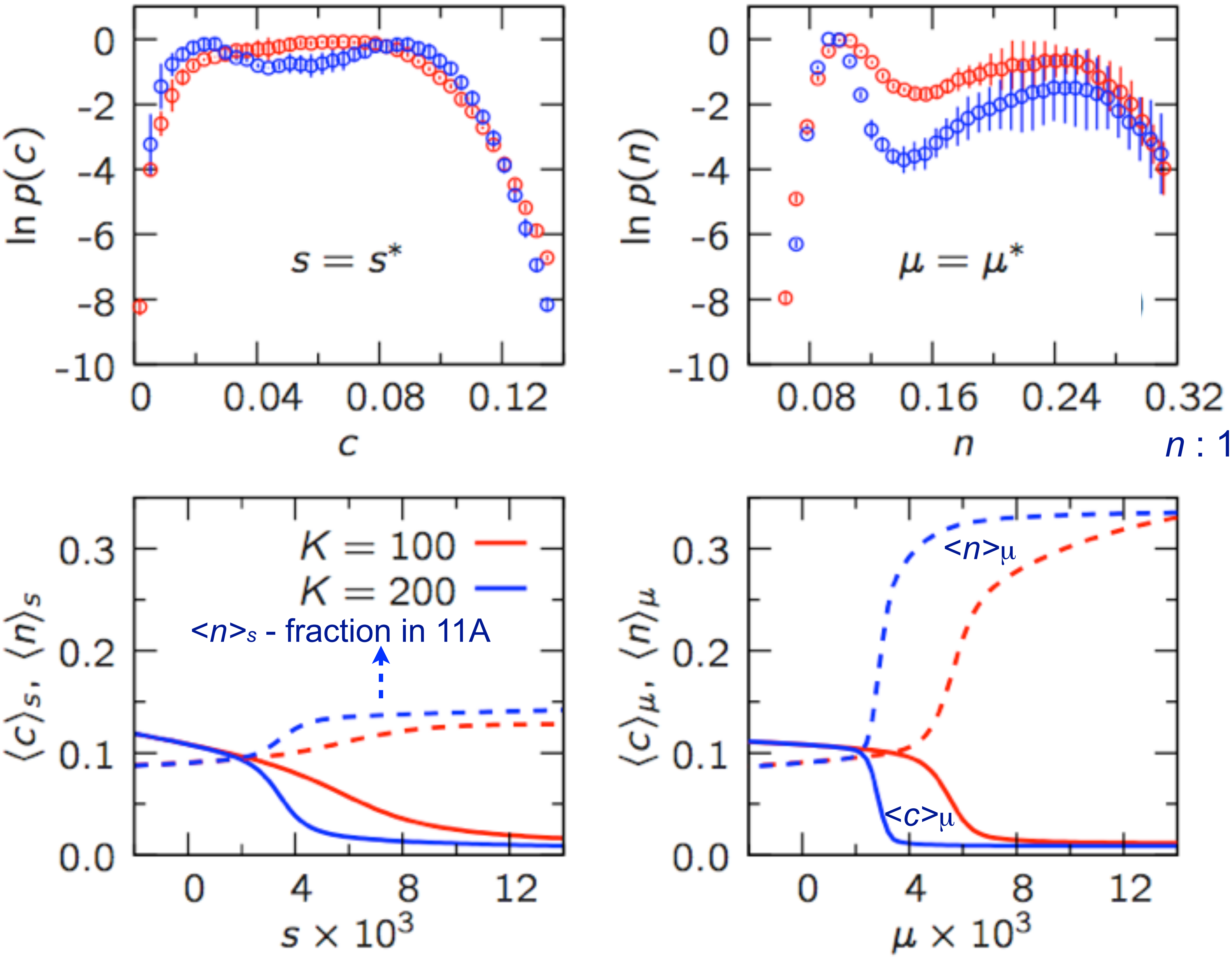
Structure as the biasing field?

The μ-ensemble

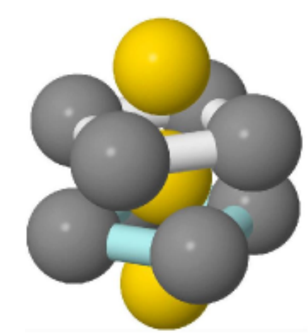


11A

A glass transition by biasing structure??



n : 11A population

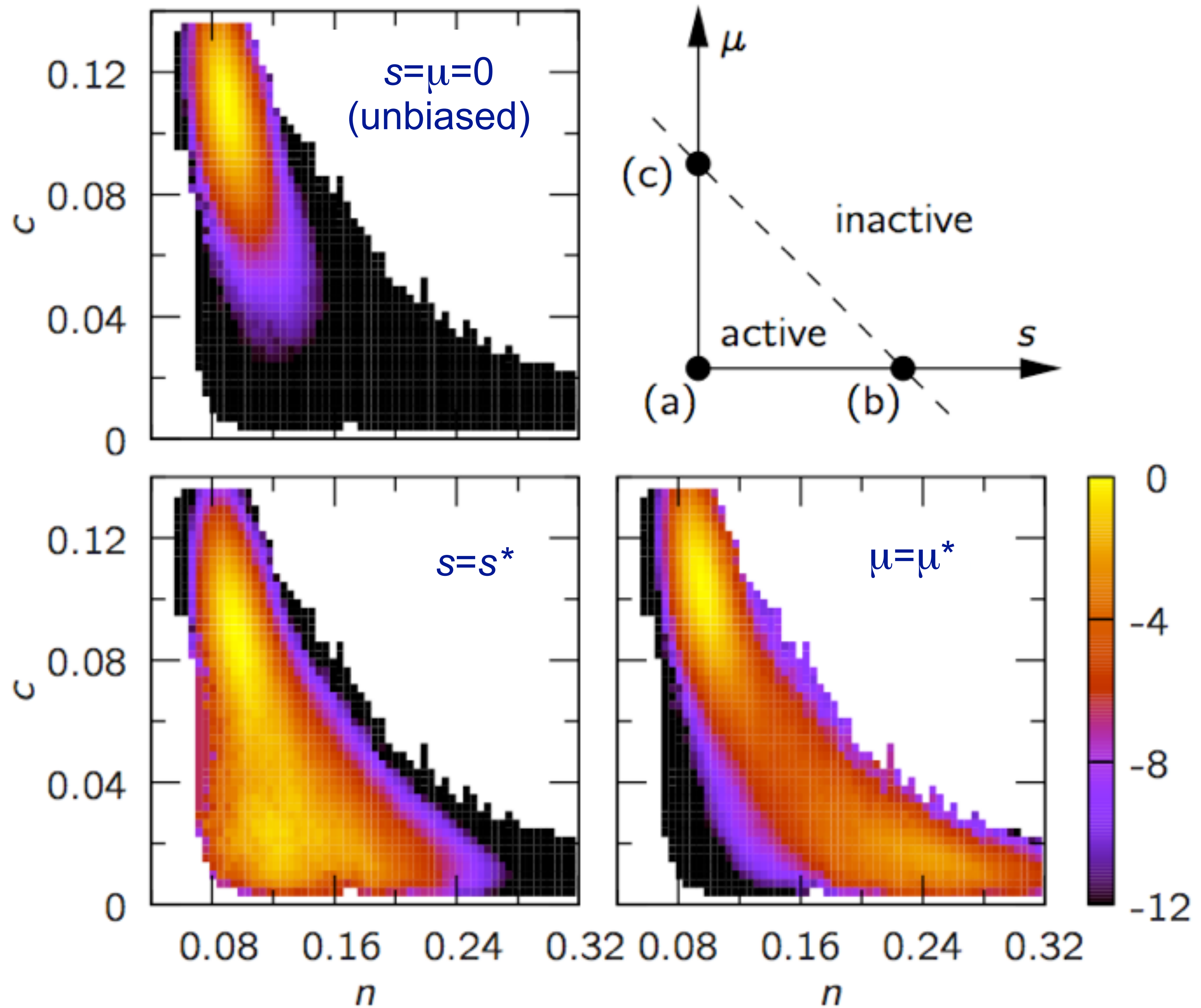


11A

s-ensemble : low mobility trajectories

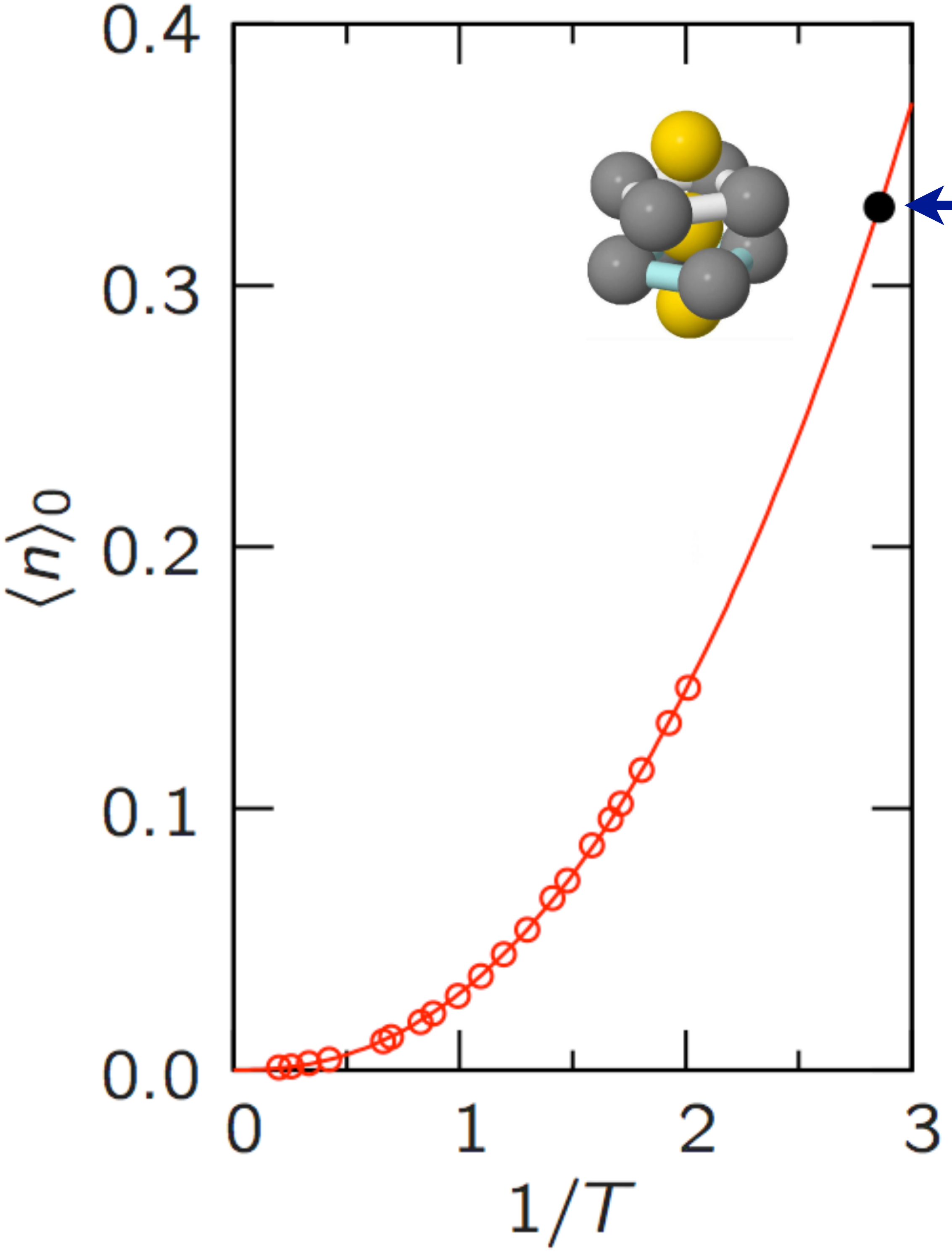
μ-ensemble : high 11A trajectories

Unified dynamical and structural transition



joint probability of c (mobility) and n (11A population) under s- and μ-ensembles

μ-ensemble corresponds to exceptionally deep quench



population of 11A <n>=0.33 for μ=0.014

corresponds to fictive T=0.35 (through unbiased simulation)

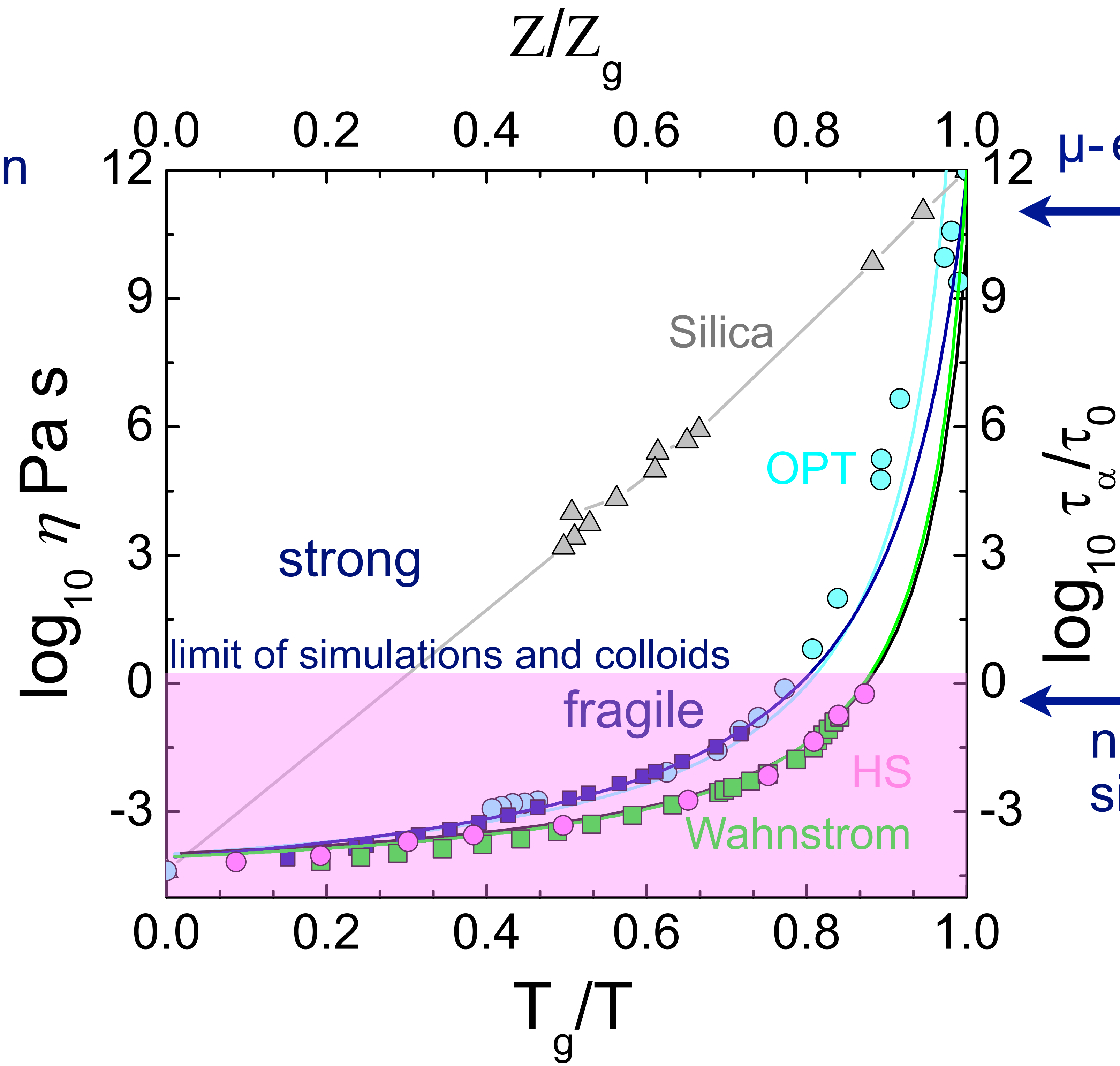
close to T_{VFT}=0.325 [T_{MCT}=0.43 - Kob (1995)]

equilibrated system closer to a glass even than experiments on molecular glass formers

T_{VFT} T at which structural relaxation time diverges according Vogel-Fulcher-Tamman law

The Angell plot

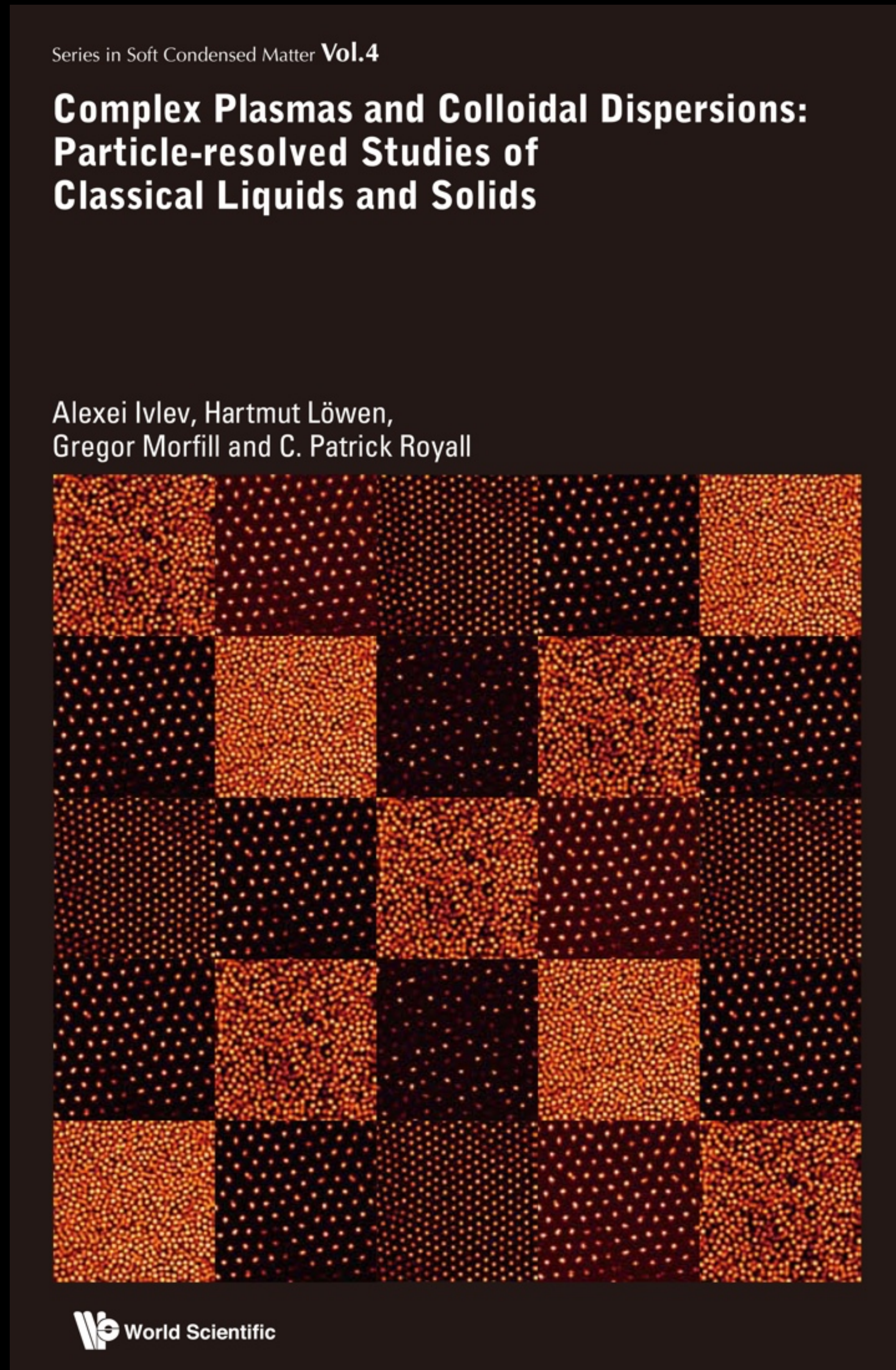
μ-ensemble can prepare very stable glassy states



μ- ensemble

normal simulation

Thanks for your attention

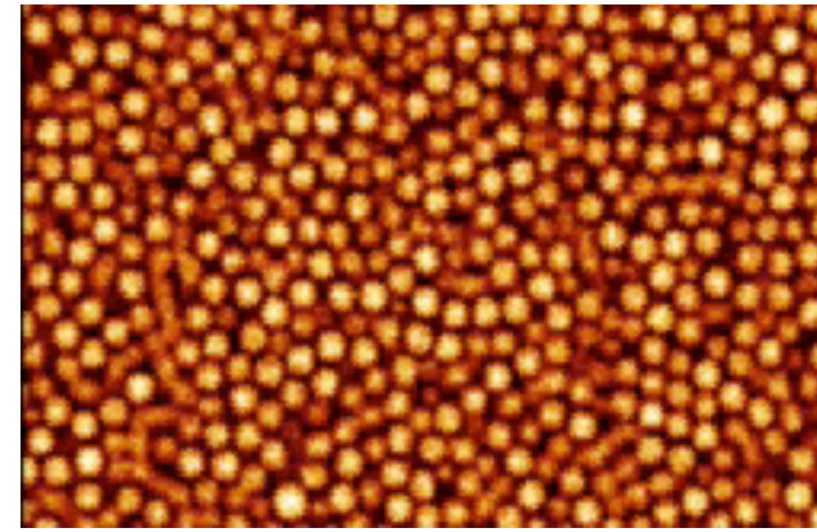


Out now!

Our soft matter workshop

Our soft matter workshop

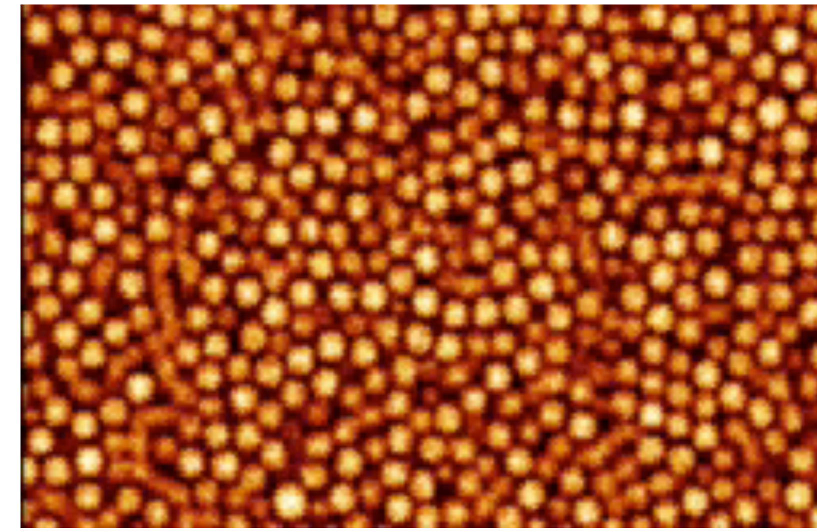
Protocol for our meeting



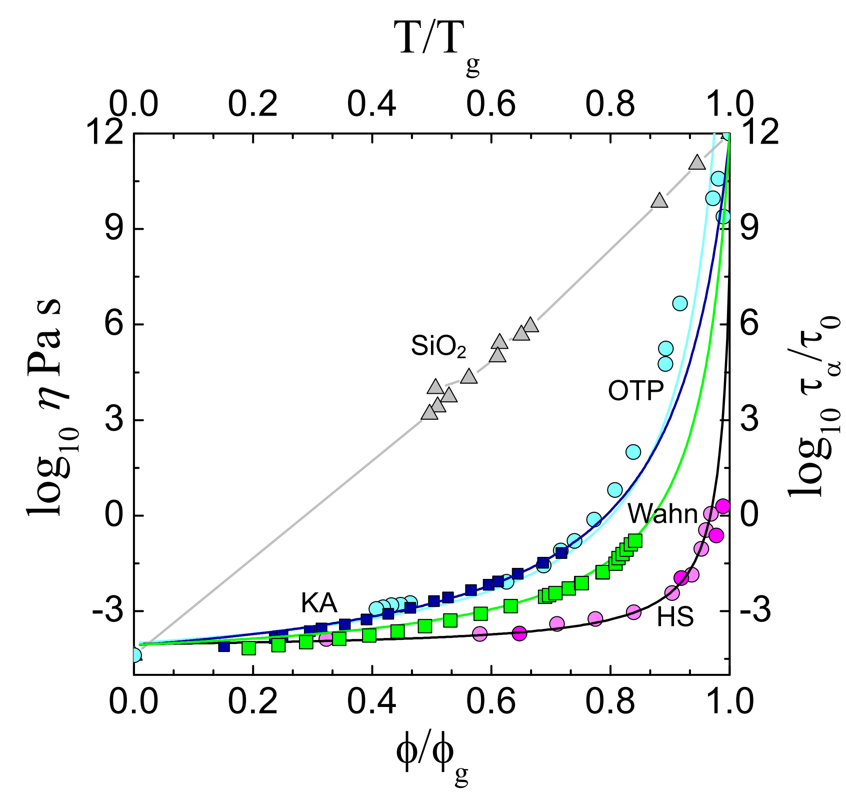
Theorists must know the acronym PMMA

Our soft matter workshop

Protocol for our meeting



Theorists must know the acronym PMMA



Soft matter experimentalists must be able to describe the physical basis of this plot

Static and dynamic length scales in glass forming liquids

Topological cluster classification - a zoo of locally favoured structures

Locally favoured structures - model-specific

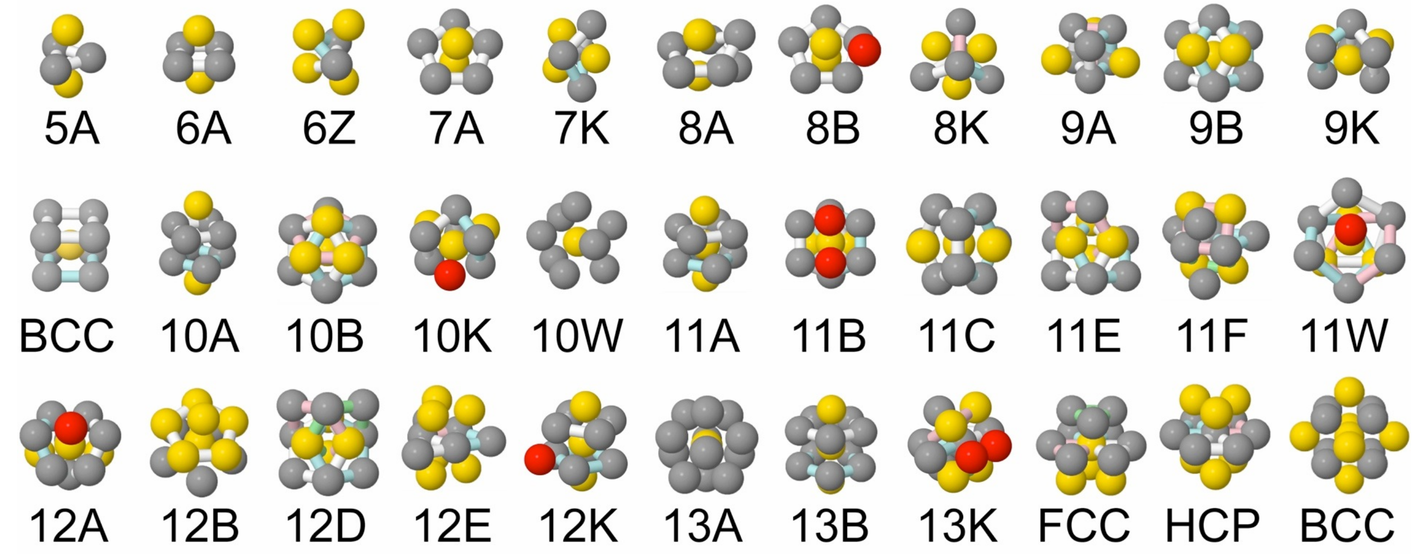
Strong frustration - little linear growth - network of locally favoured structures

Decoupling between ξ_4 and ξ_{struct} in the accessible regime. Deeper quenching???

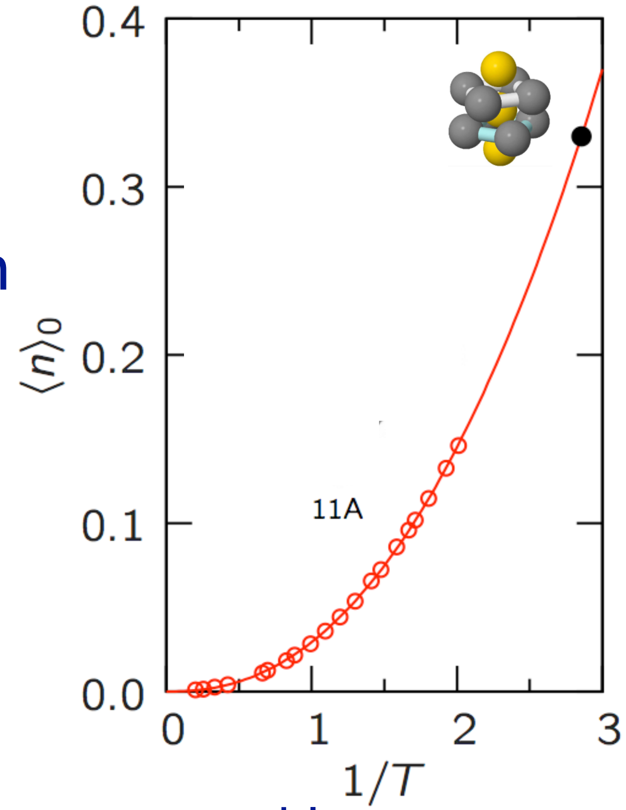
Isoconfigurational ensemble : local structure for high mobility and a solution to the discrepancy in ξ_4 and ξ_{struct} ?

Two large deviation ensembles - s and μ. Both concern the same transition.

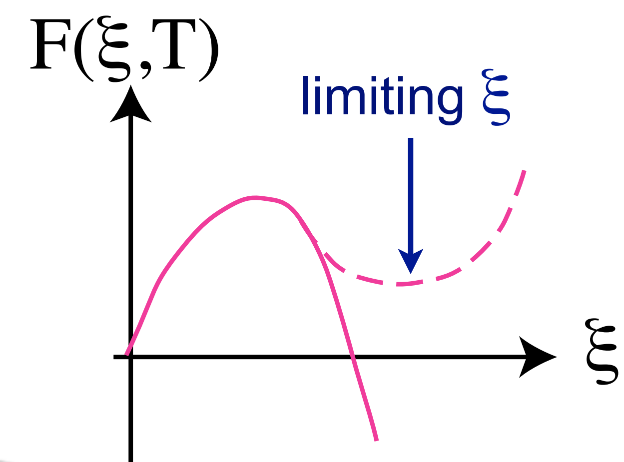
μ-ensemble melting : structure->slow dynamics

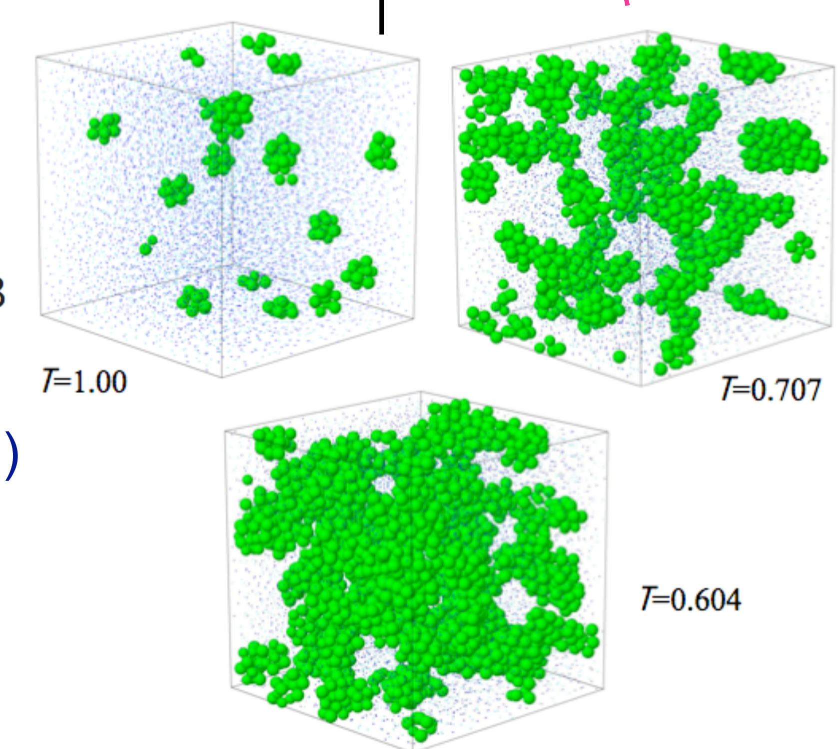


TCC : *JCP* **139** 234506 (2013)



μ-ensemble
PRL **109** 195703 (2012)





Wahnstrom : *JCP* **138** 12A535 (2013)
KA : *Faraday Disc.* **167** paper 16 (2013)
Hard spheres and frustration : proceedings of this meeting