

Large Deviations Workshop

Paddy Royall





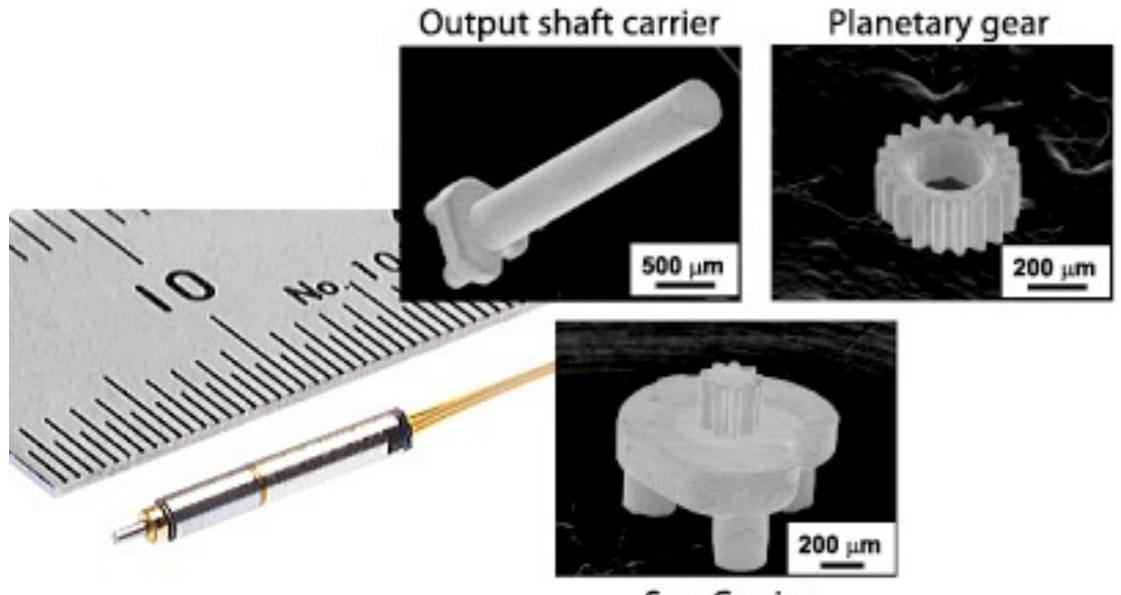
Introduction to glass

The glass transition challenge

Recent developments in large deviation approaches to glass



Metallic glass formers



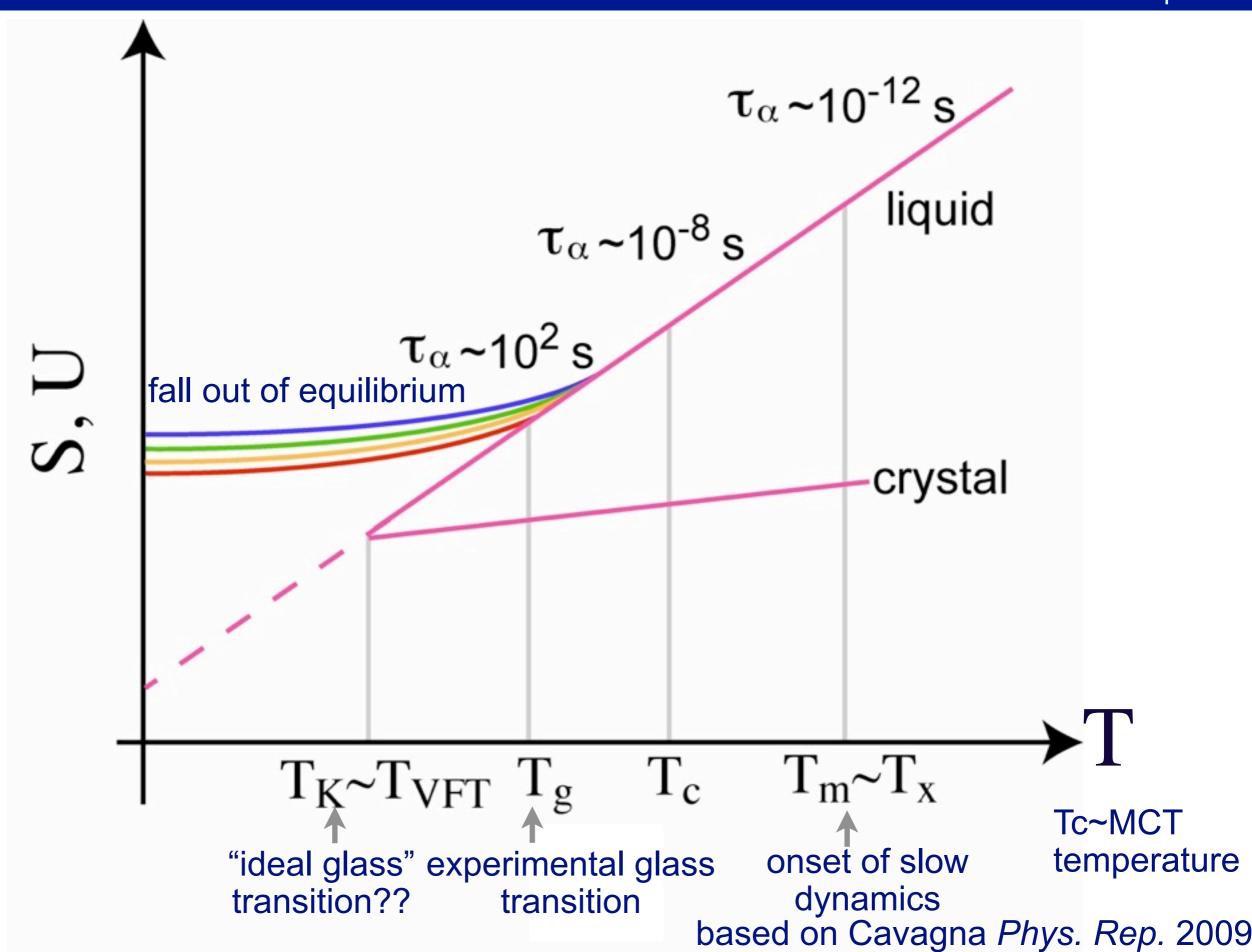
Sun Carrier

Small mechanical parts, Namiki Precision, Singapore

Metallic glassformers exhibit high hardness, toughness and tensile strength in a combination that is not otherwise available

..but formation of metallic glass fraught with difficulty due to crystallisation

Inoue, Rev. Mat. Sci. 2008



How should the relaxation time behave?

There is some energy associated with relaxation

The Boltzmann relation tells us that the relaxation time should follow an Arrhenius law

$$au_{lpha} \propto e^{E_{
m a}/k_{
m B}T}$$

...so if you plot $\log \tau_{\alpha}$ against 1/T, you get a straight line

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$$\tau_{\alpha} = \tau_0 e^{\tilde{E}_{\rm a}/k_{\rm B}(T - T_0)}$$

This is the Vogel-Fulcher-Tamman law. Interestingly, To~Tκ.

The Angell plot

lines are VFT fits

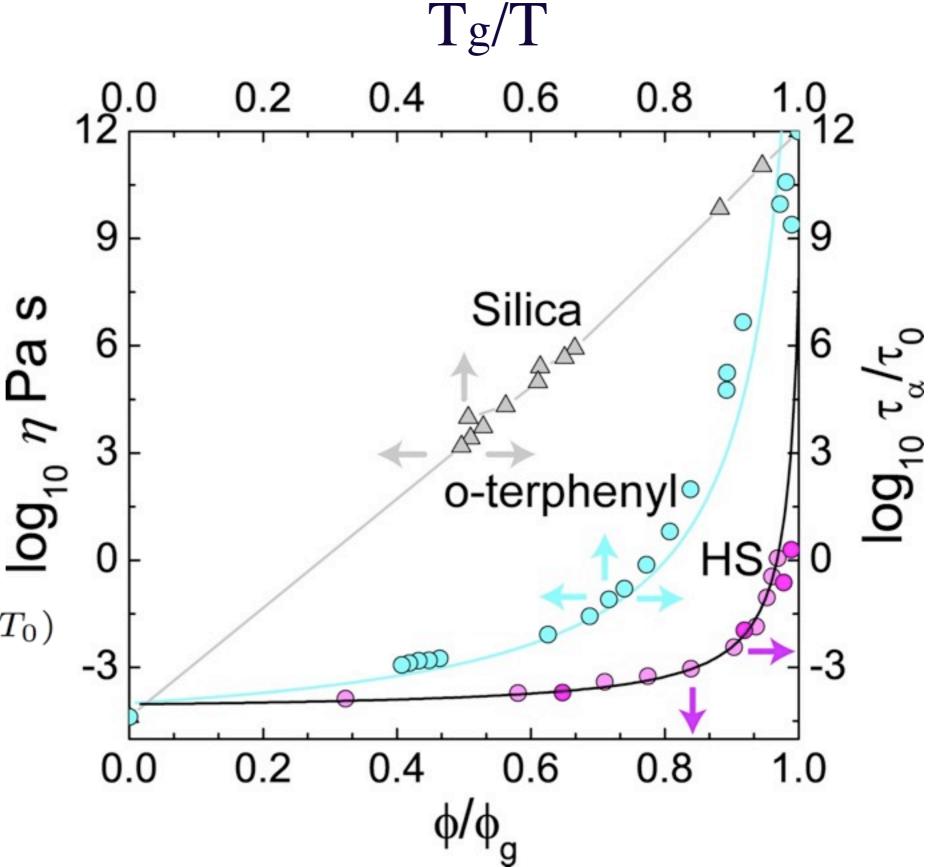
Fragility->more going on than one form of relaxation

Ea~increases with 1/T

Change in mechanism of relaxation

Well described by Vogel-Fulcher-Tamman (VFT)

$$\tau_{\alpha} = \tau_0 e^{\tilde{E}_{\rm a}/k_{\rm B}(T - T_0)}$$

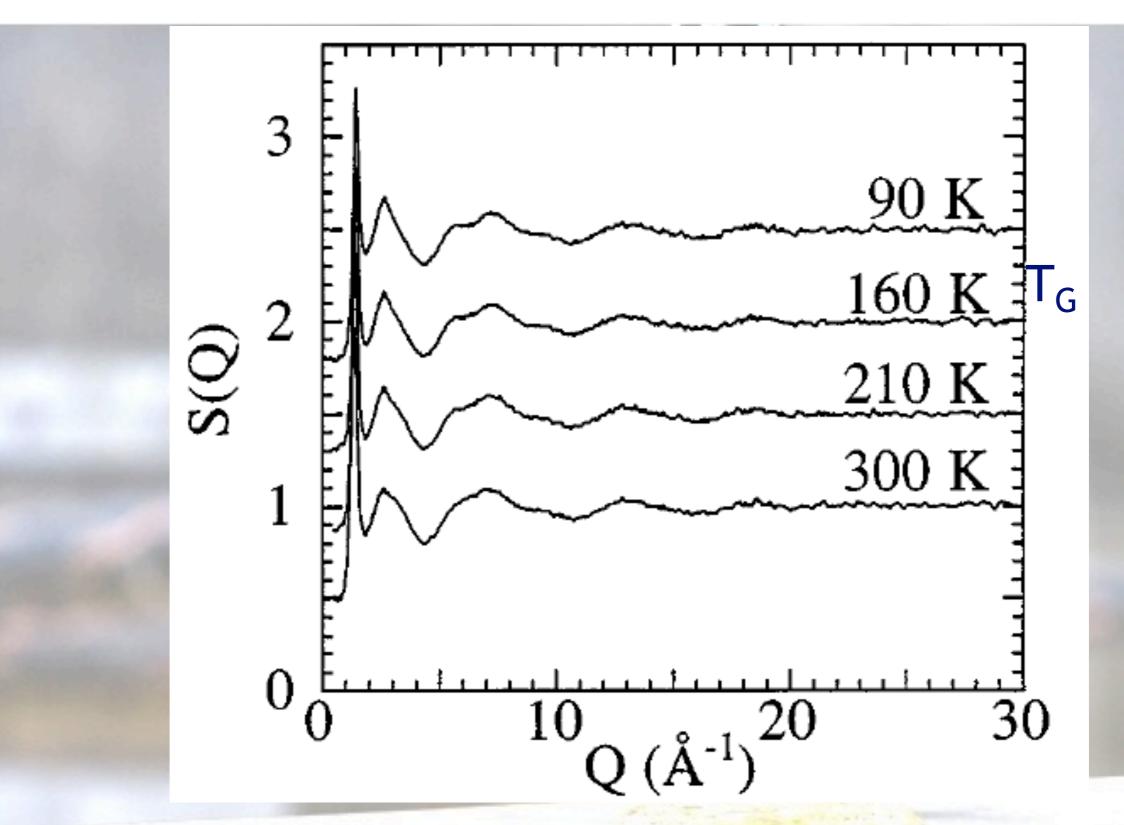


Based on Angell *J. Non-Cryst. Solids* **102**, 205–221 (1988).

Relaxation dynamics in a supercooled liquid

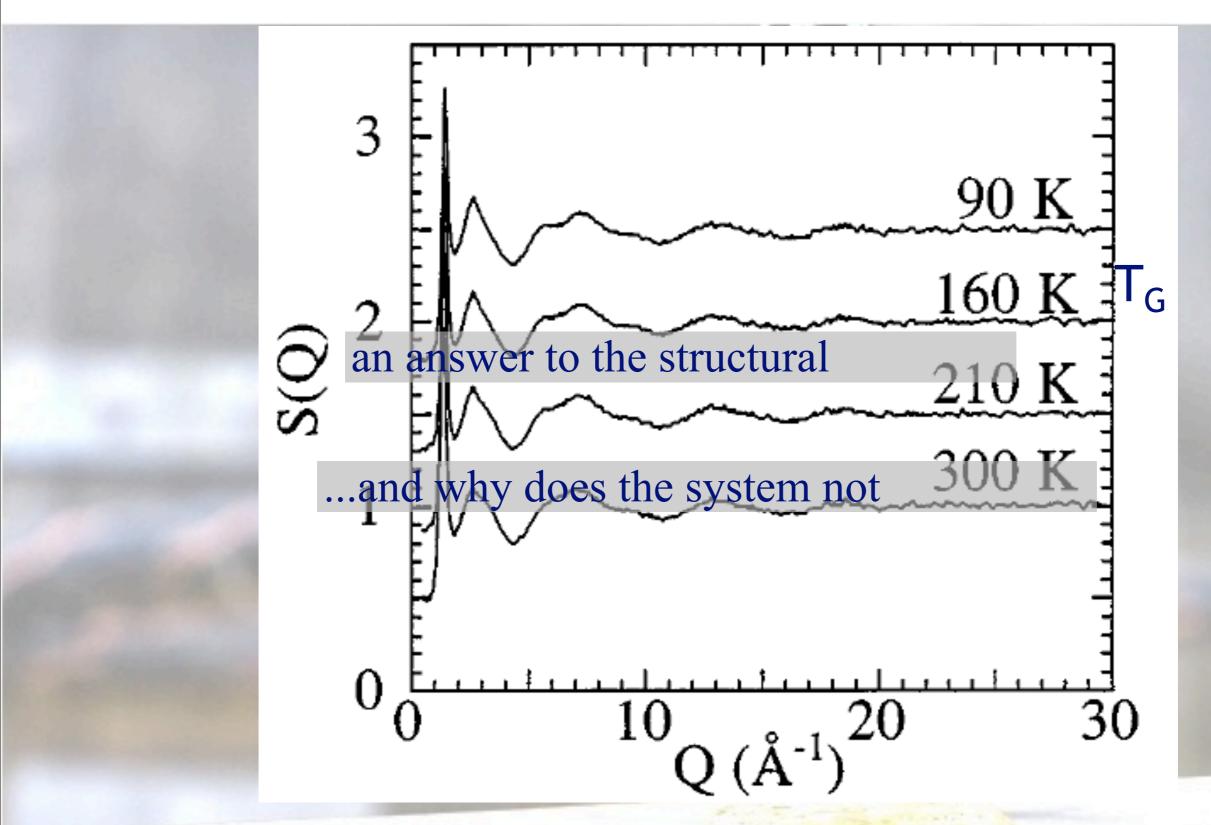
Royall/Glass

"The arrangement of atoms and molecules in glass is indistinguishable from that of a



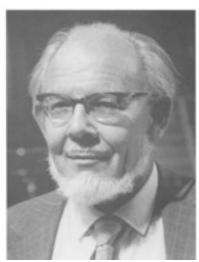
Neutron scattering on propylene glycol ~ Leheny et. al. J. Chem. Phys. 1996

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Why have we not got a crystal?



Sir Charles Frank Physics 1946-1998

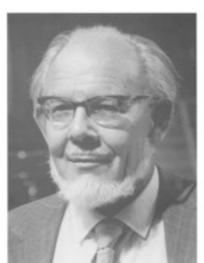
Supercooling of liquids

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.

Why have we not got a crystal?



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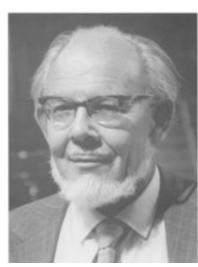
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Icosahedrakinetic frustration to crystallisation

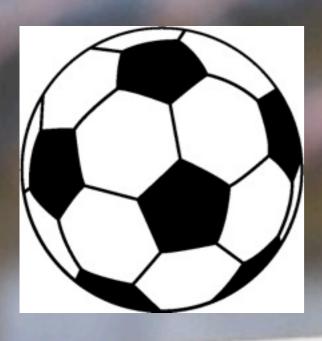
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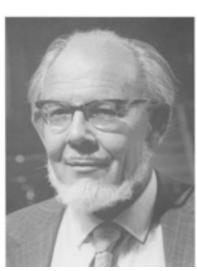


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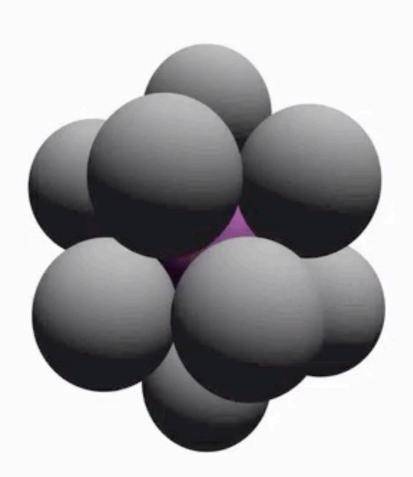
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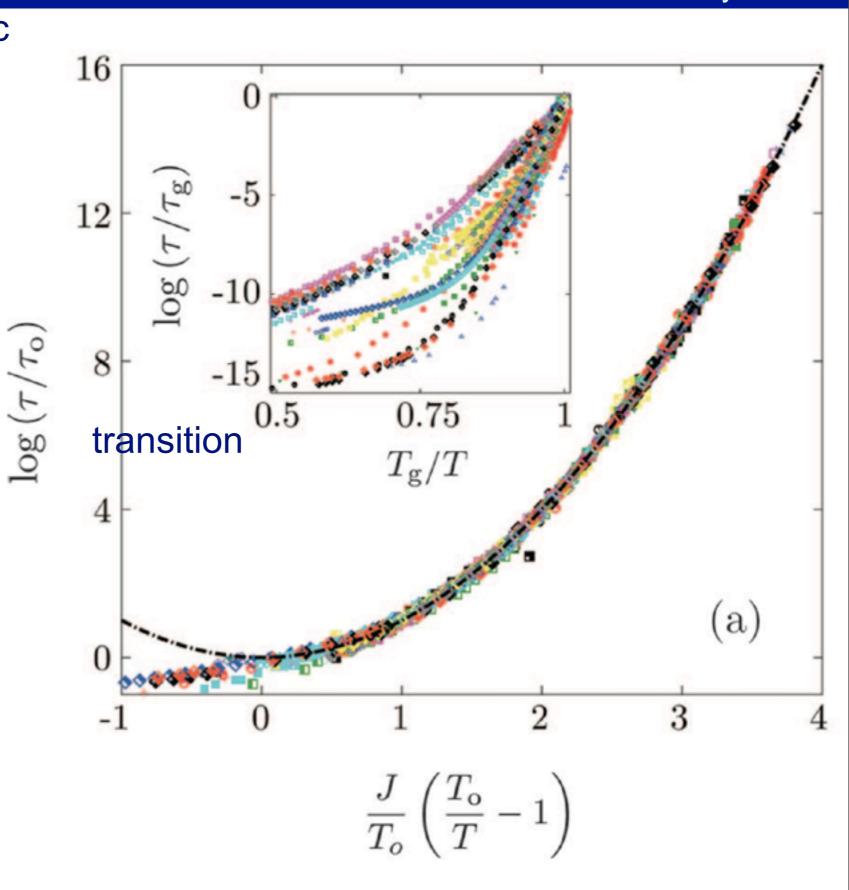
or....

Dynamic facilitation

Glass transition purely dynamic

VFT fit not unique (not even the best fit to the data)

Kinetically Constrained Models (KCMs) reproduce glassy behaviour but are thermodynamically ideal gases



Elmatad and Chandler JCP 2009

Nature of the glass transition

Structural, thermodynamic

Adam-Gibbs theory: vanishing of configurational entropy around T0

Adam and Gibbs JCP 1965

Random First Order Theory: transition to "mosaic state" around Tc + entropy crisis ~ T0

Lubchenko and Wolynes Ann. Rev. Phys. Chem. 2007

Geometric Frustration: icosahedra (and friends) cannot tile space Frank Proc. R. Soc. 1952, Tarjus JPCM 2005

Mode-coupling theory: dynamic transition takes structural data as its input

Goetze 2009

Dynamic

Dynamic facilitation: the glass transition is a purely kinetic phenomenon Chandler and Garrahan Ann. Rev. Phys. Chem. 2010

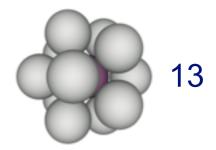


Structure and glass

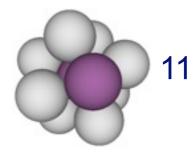
Structure in glassformers

Lennard-Jones models

Wahnstrom (50:50), additive, одд=1 овв=0.833 icosahedron (13A) - Coslovich 2007 ...and Frank-Kasper bonds ("8C") - Pedersen 2010

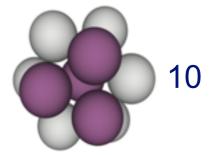


Kob-Andersen (80:20), non-additive, ода=1 овв=0.833 bicapped square anti-prism (11A) - Coslovich 2007



Experiments

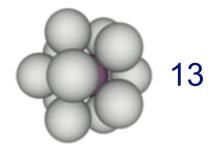
Particle-resolved studies of colloids `Hard' spheres (+ MD simulations) 6-8% polydisperse



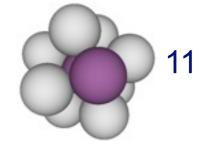
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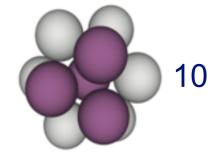


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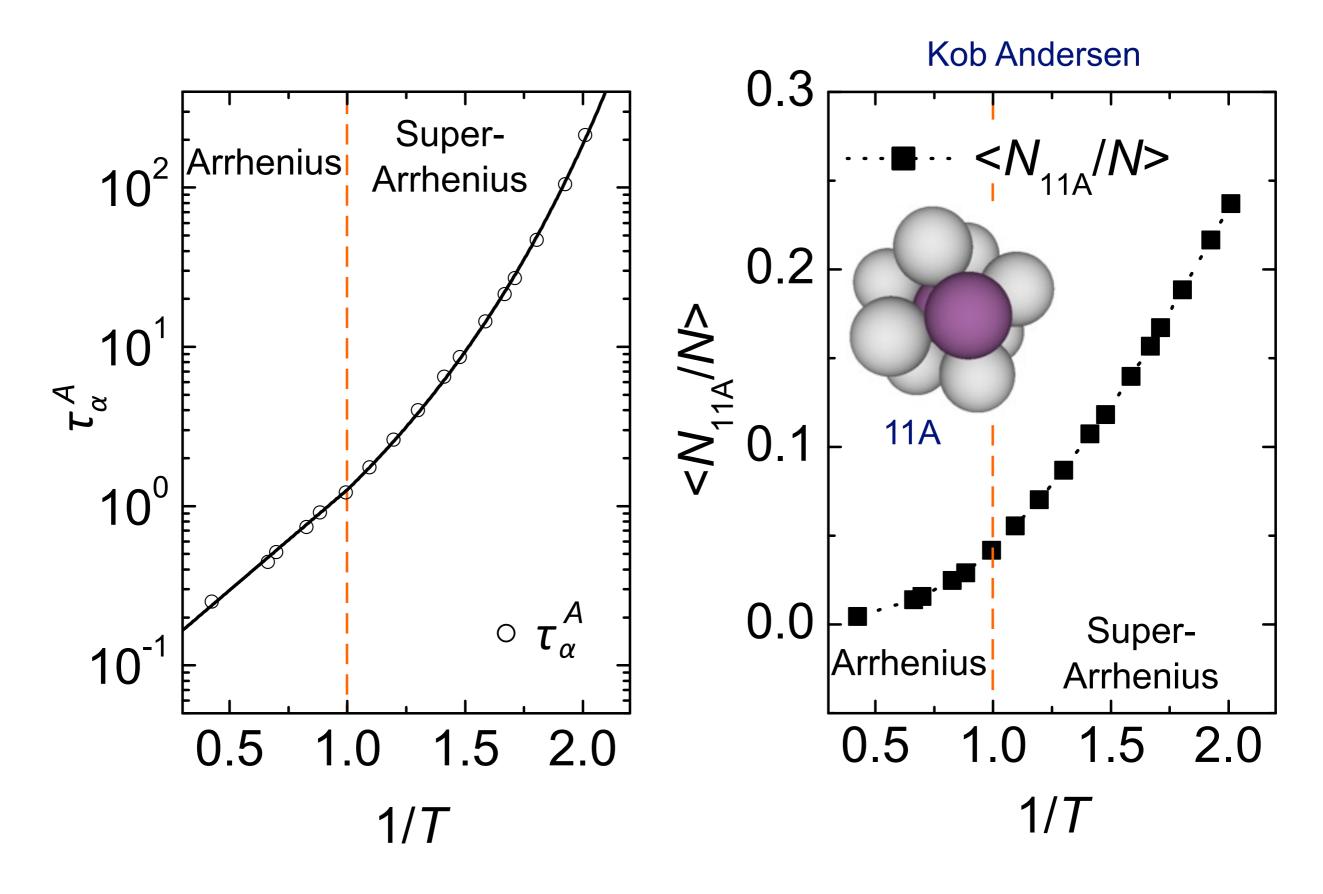
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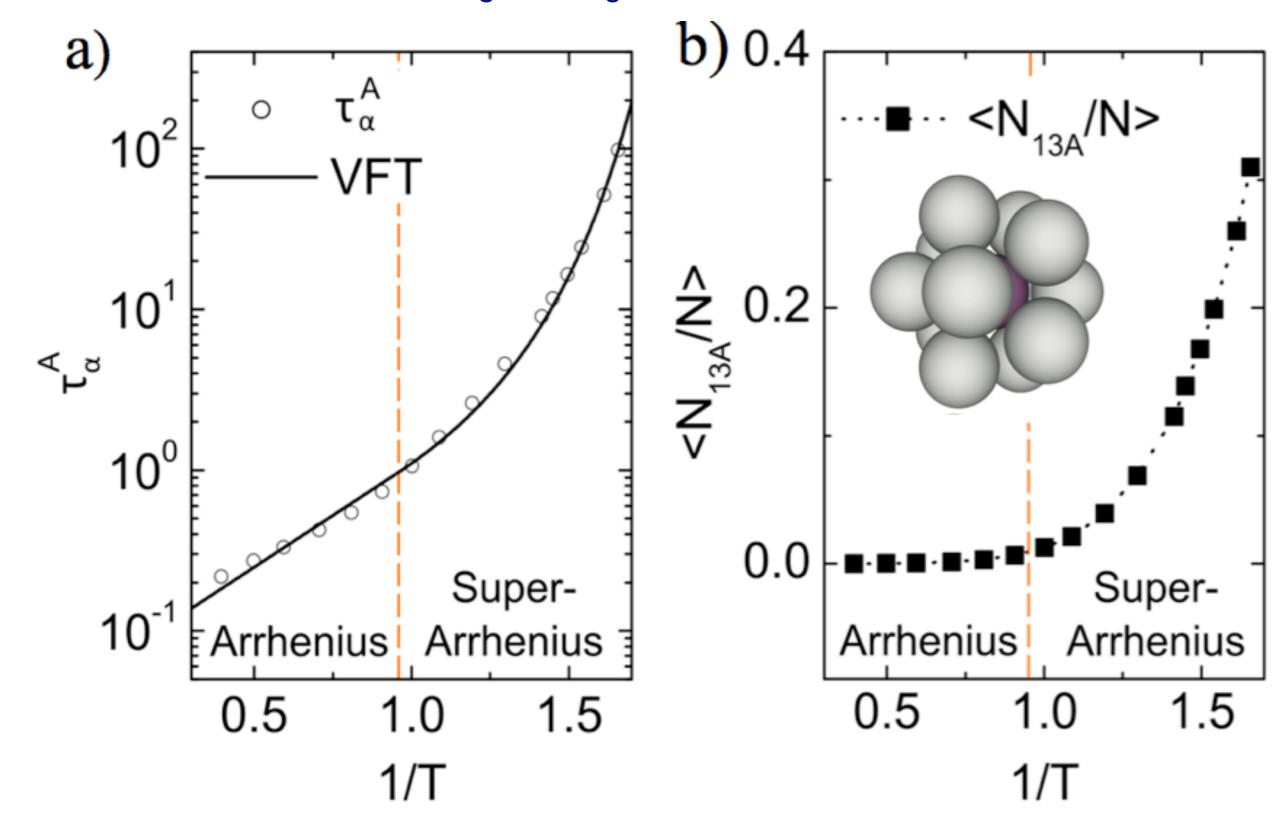
Change in dynamics...and structure

Structural change upon cooling



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

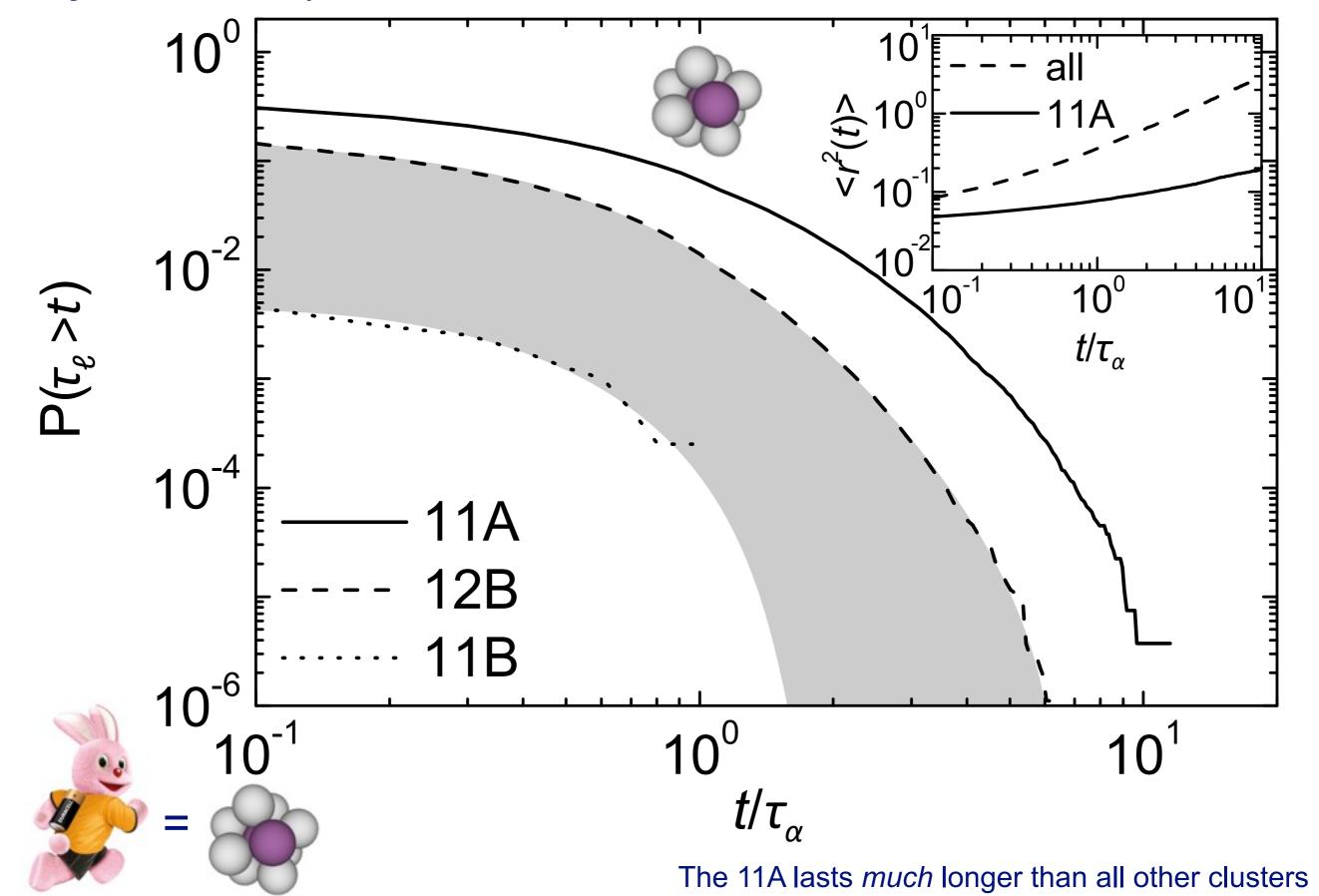
Towards a structural "understanding" of the glass transition



Binary Lennard-Jones mixture (Kob-Andersen) Molecular Dynamics simulation. Royall and coworkers arXiv:1306.2983 (2013); accepted for Faraday discussions

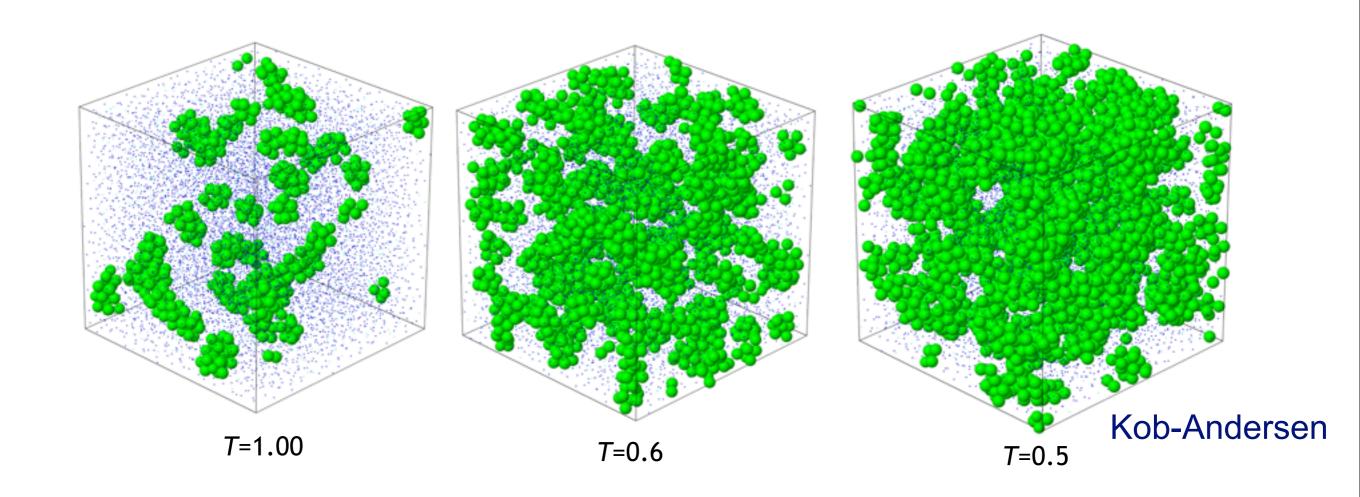
Dynamic Toplogical cluster classification

Linking structure and dynamics



11A domain growth upon cooling

Emergence of network of particles in 11A clusters

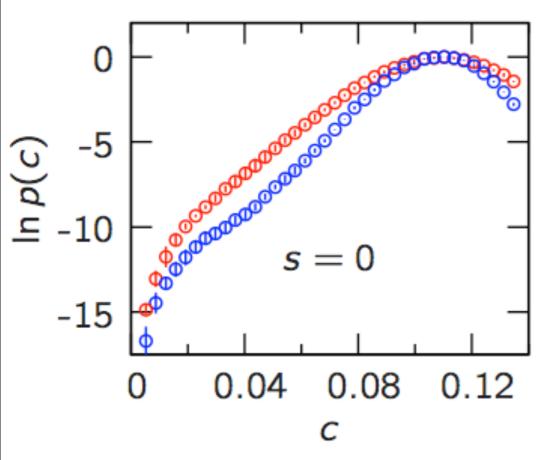




A different *tack* to the glass transition : The *s*-ensemble

we are used to cooling/compressing a system for solidification

A glass transition without cooling



s=0 no biasing (normal

The s-ensemble

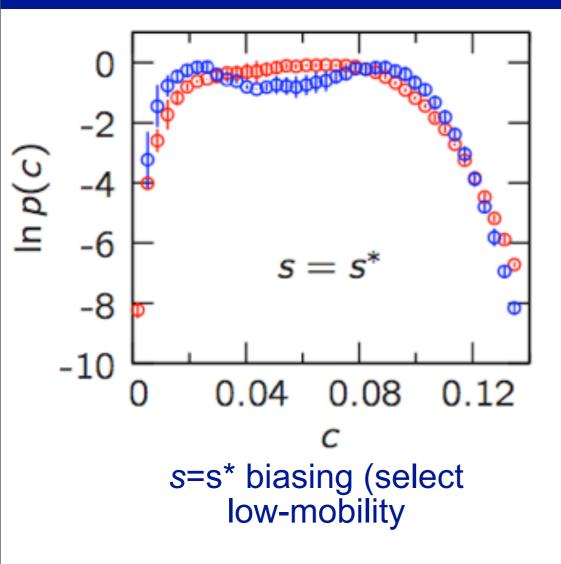
Trajectory space sampling at T>glass transition (T=0.6)

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

1st-order transition

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

A glass transition without



The s-ensemble

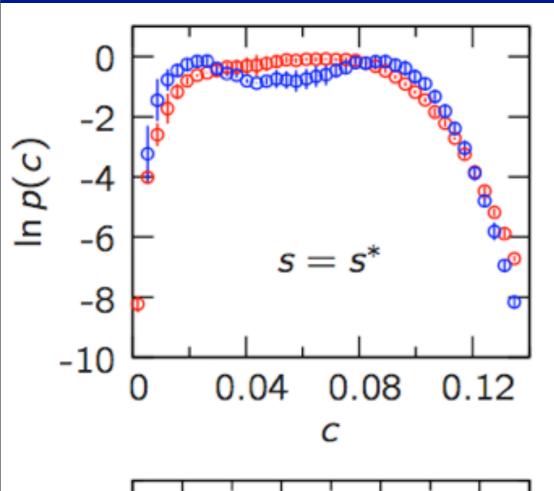
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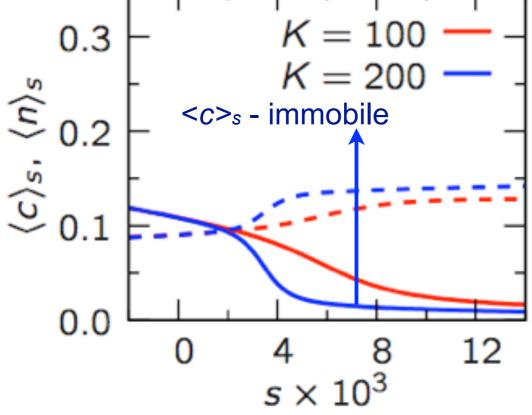
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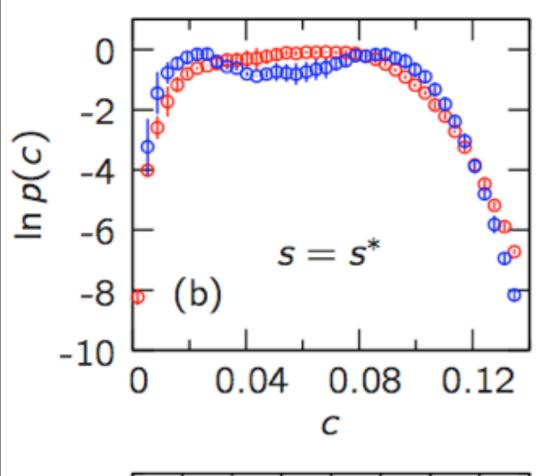
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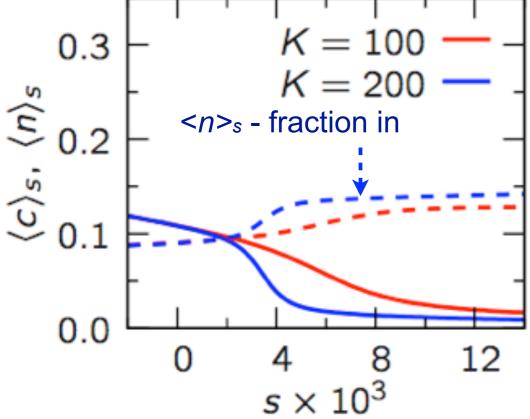
Hedges, Jack, Garrahan and Chandler Science 323 1309 (2009)

Evidence for first-order transition

Speck Malins and Royall PRL 109 195703 (2012)

A glass transition by biasing





The s-ensemble

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What about structure?

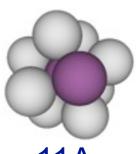
Jack, Hedges, Garrahan and Chandler PRL **107**, 275702 (2011):

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

Kob-Andersen -> increase in 11A?

Structure as the biasing field?

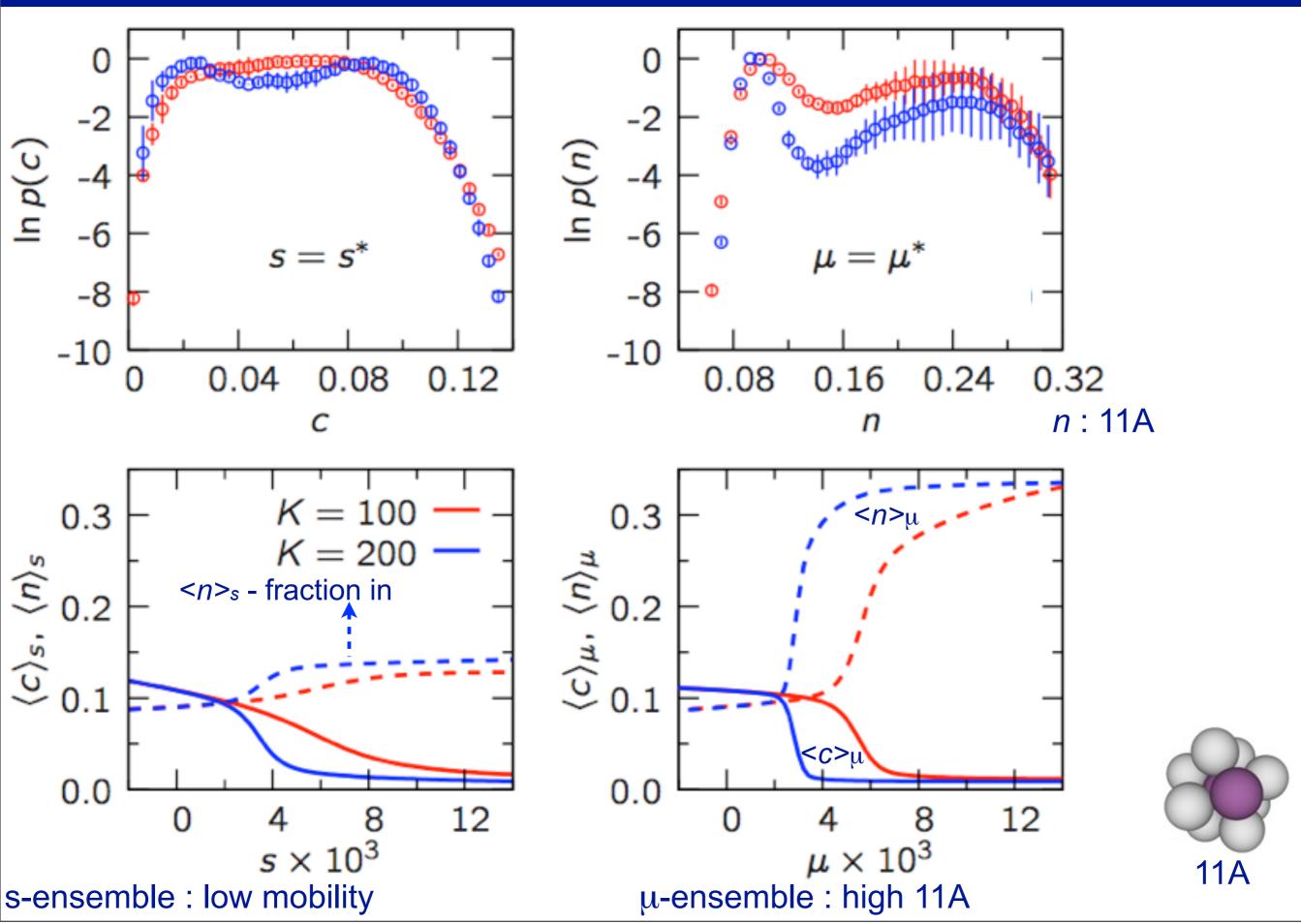
The μ -ensemble



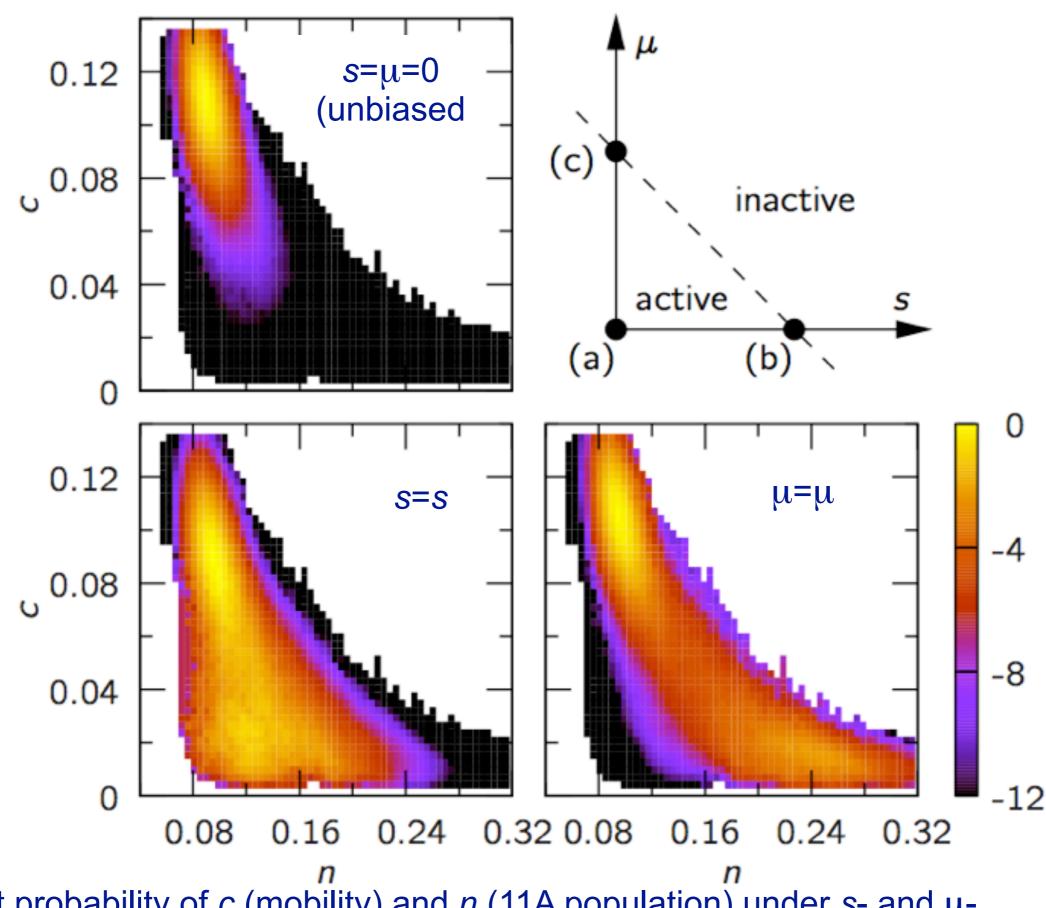
11A

K length of

A glass transition by biasing

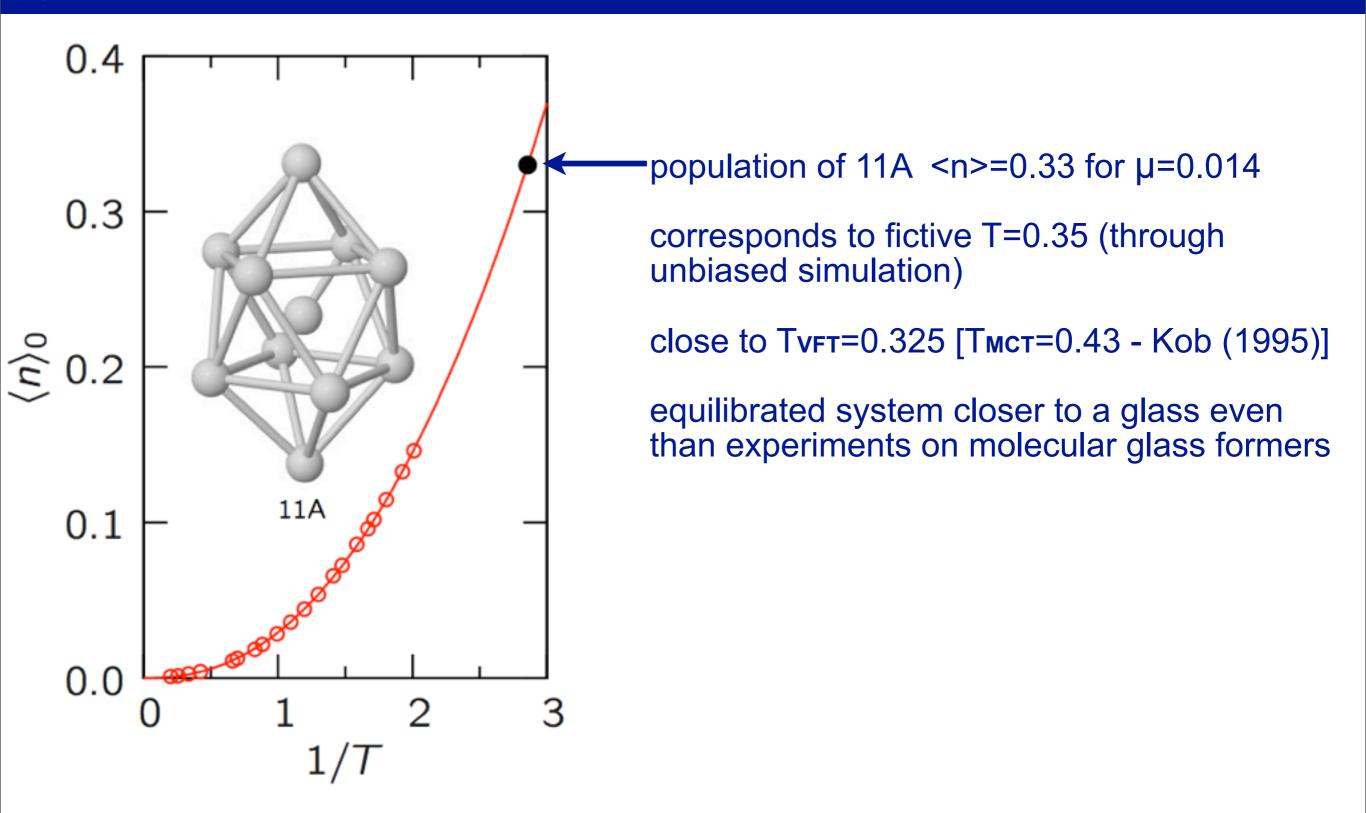


Unified dynamical and structural transition



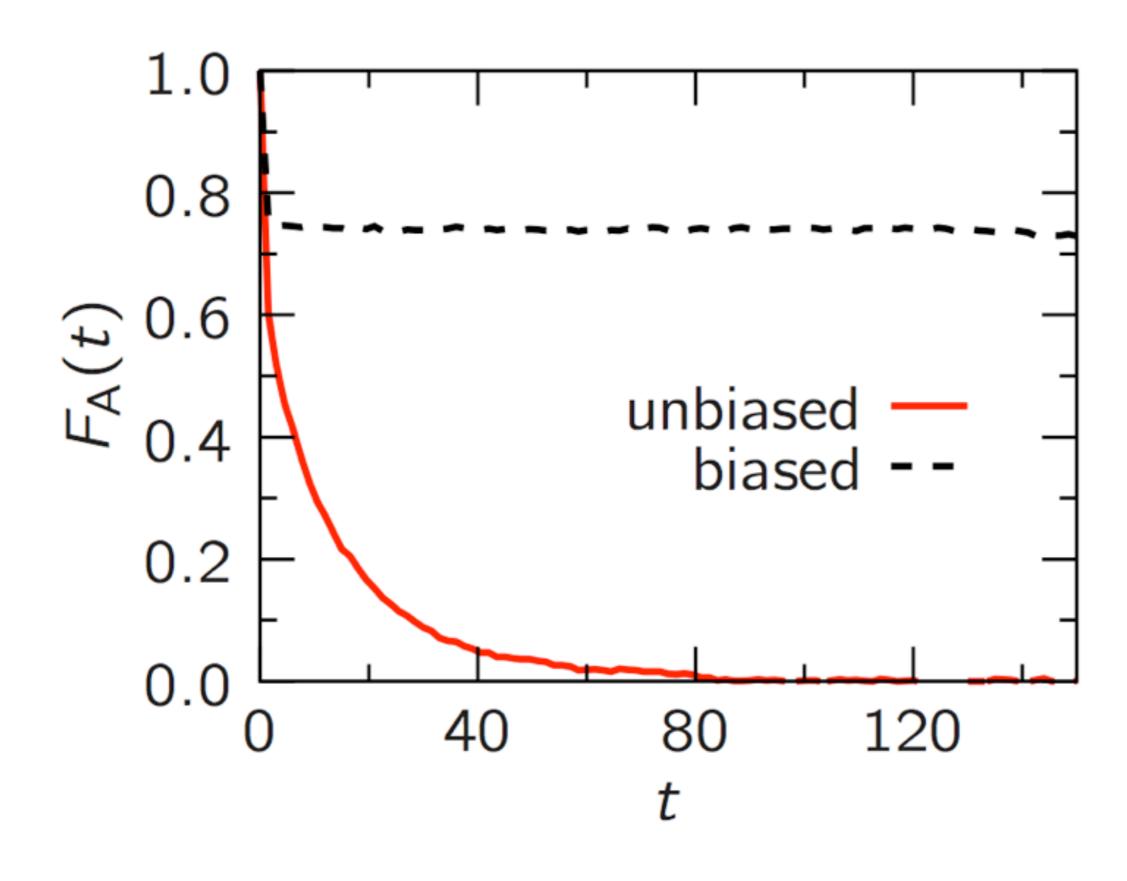
joint probability of c (mobility) and n (11A population) under s- and μ -

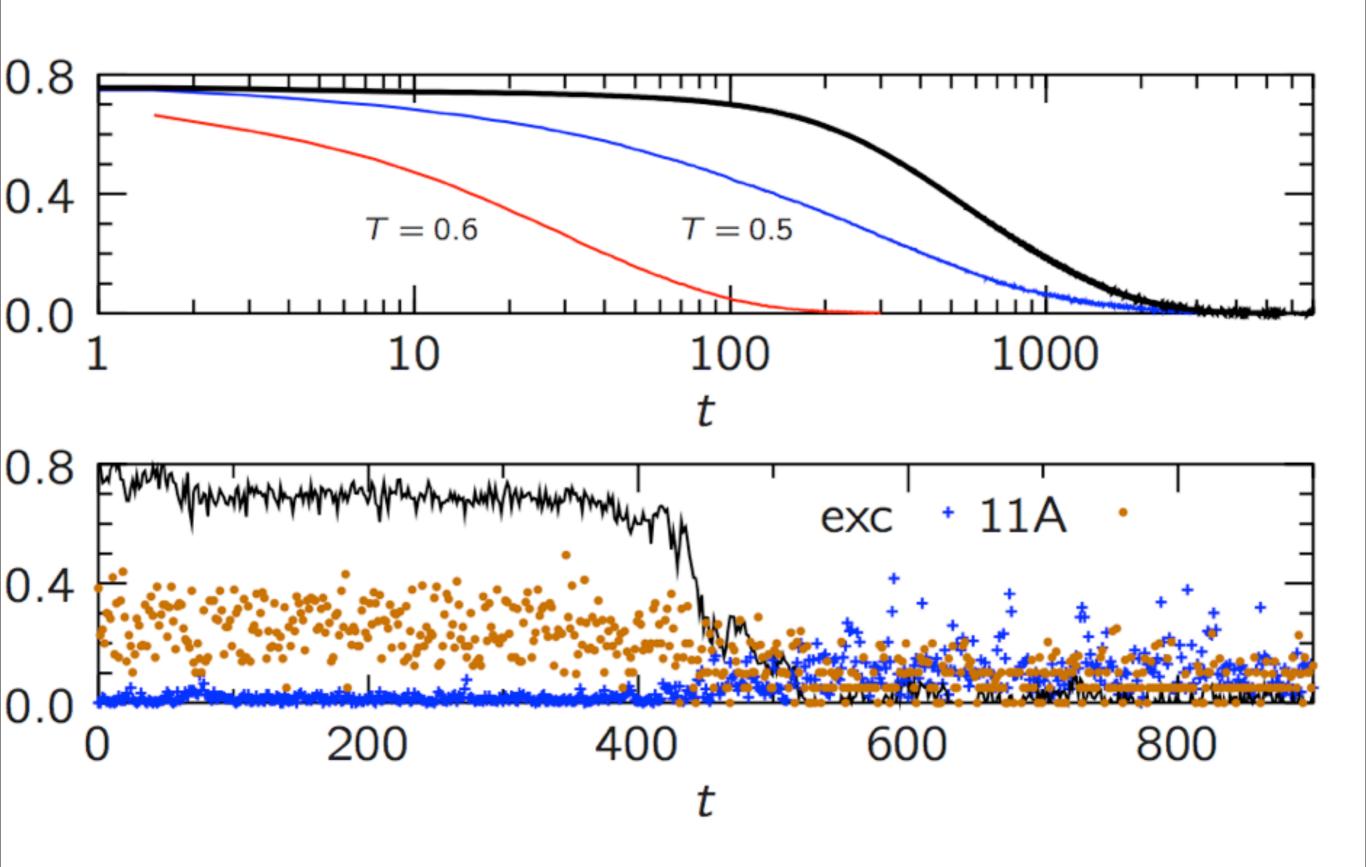
μ-ensemble corresponds to exceptionally deep quench

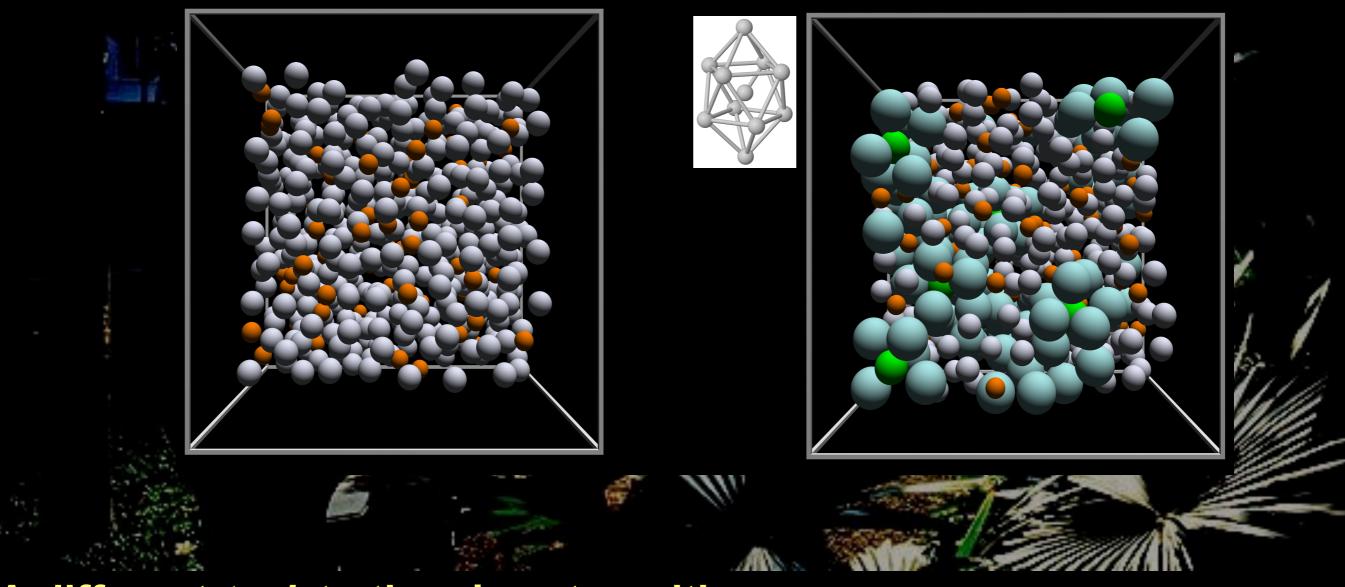


TVFT T at which structural relaxation time diverges according Vogel-Fulcher-Tamman law

Intermediate scattering function μ -ensemble







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

we are used to cooling a system for solidification

Speck Malins and Royall PRL 109 195703 (2012)

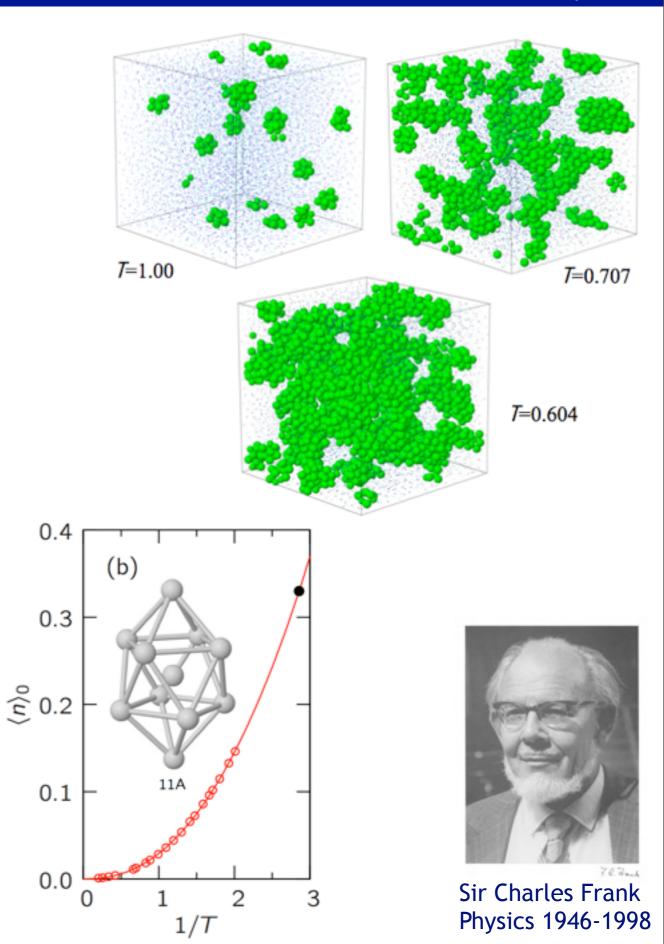
The glass transition presents a challenge due to the difficulty of equilibration in its vicinity

Whether it is purely dynamic or thermodynamic is unclear

It is possible to measure changes in structure approaching the transition

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

In the limit that trajectory length->0, the µ-ensemble transition (fat tail) disappears



Thanks for your attention

Series in Soft Condensed Matter Vol.4 **Complex Plasmas and Colloidal Dispersions:** Particle-resolved Studies of **Classical Liquids and Solids** Alexei Ivlev, Hartmut Löwen, Gregor Morfill and C. Patrick Royall World Scientific



S-

$$h_k^{\rm m}(t) = \Theta(|\hat{\mathbf{r}}_k(t) - \hat{\mathbf{r}}_k(t - \Delta t)| - a)$$

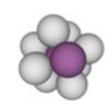
mobile / immobile particle if moves more/less than a (radius) in Δt

$$\mathcal{C} = \sum_{ik} h_k^{\mathrm{m}}(t_i)$$
 total number of mobile

$$c = \mathcal{C}/(NK)$$
 fraction of mobile particles (K trajectory

μ-

$$\mathcal{N} = \sum_{ik} h_k^{11\mathrm{A}}(t_i)$$
 total number of particles in



$$n=\mathcal{N}/[N(K+1)]$$
 fraction of particles in 11A (K trajectory

s and µ-

$$\langle \mathcal{O} \rangle_s = \frac{\langle \mathcal{O} e^{-s\mathcal{C}} \rangle}{\langle e^{-s\mathcal{C}} \rangle}, \qquad \langle \mathcal{O} \rangle_\mu = \frac{\langle \mathcal{O} e^{\mu \mathcal{N}} \rangle}{\langle e^{\mu \mathcal{N}} \rangle}$$

The New York Times

The nature of glass remains anything but clear

"Many people tell me this is very contentious." I disagree violently with them." Peter Wolynes, UCSD "The arrangement of atoms and molecules in glass is indistinguishable from that of a

New York Times July 2008