

CELEBRATING 350 YEARS





Large Deviations Workshop

Paddy Royall

Acknowledgements

Isla

3743年

Zhang

Marcus Bannerman (help with DynamO)

Stephen Williams (Canberra) Jens Eggers Karoline Wiesner

Andrew Dunleavy

Thomas Speck (Duesseldorf)

Hajime Tanaka

an

Jade Taffs

(Tokyo)

2013年8月7日水曜日

Shelley Taylor



Introduction to glass

The glass transition challenge

Recent developments in large deviation approaches to glass

We know all about 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

Roadmap to the glass transition



There is some energy associated with relaxation

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

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

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

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

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

This is the Vogel-Fulcher-Tamman law. Interestingly, T₀~Tκ.

The Angell plot



Relaxation dynamics in a supercooled liquid

Royall/Glass

Simulation Keys et al. Phys. Rev. X

"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.

Frank, Proc. R. Soc.

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Icosahedrakinetic frustration to crystallisation

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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

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

Royall/Glass

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, $\sigma_{AA}=1 \sigma_{BB}=0.833$ icosahedron (13A) - Coslovich 2007 ...and Frank-Kasper bonds ("8C") - Pedersen 2010

Kob-Andersen (80:20), non-additive, $\sigma_{AA}=1 \sigma_{BB}=0.833$ bicapped square anti-prism (11A) - Coslovich 2007

Experiments

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







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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)

Kob-Andersen binary Lennard

Speck Malins and Royall PRL 109 195703 (2012)

A glass transition without



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1st-order transition

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

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)

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



A glass transition by biasing



11A

Unified dynamical and structural transition



$\mu\text{-ensemble corresponds to exceptionally deep quench$



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

Intermediate scattering function µ-ensemble







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we are used to cooling a system for solidification

Speck Malins and Royall PRL 109 195703 (2012)

Large deviations in the glass transition

Structure and Spheres

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





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SC. THE ROYAL Society

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Shelley Taylor

s and μ -

S-

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

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

$$\mathcal{C} = \sum_{ik} h_k^{
m m}(t_i)$$
 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