Long-lived structural fluctuations and crystallization of a binary mixture

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Glass and Time

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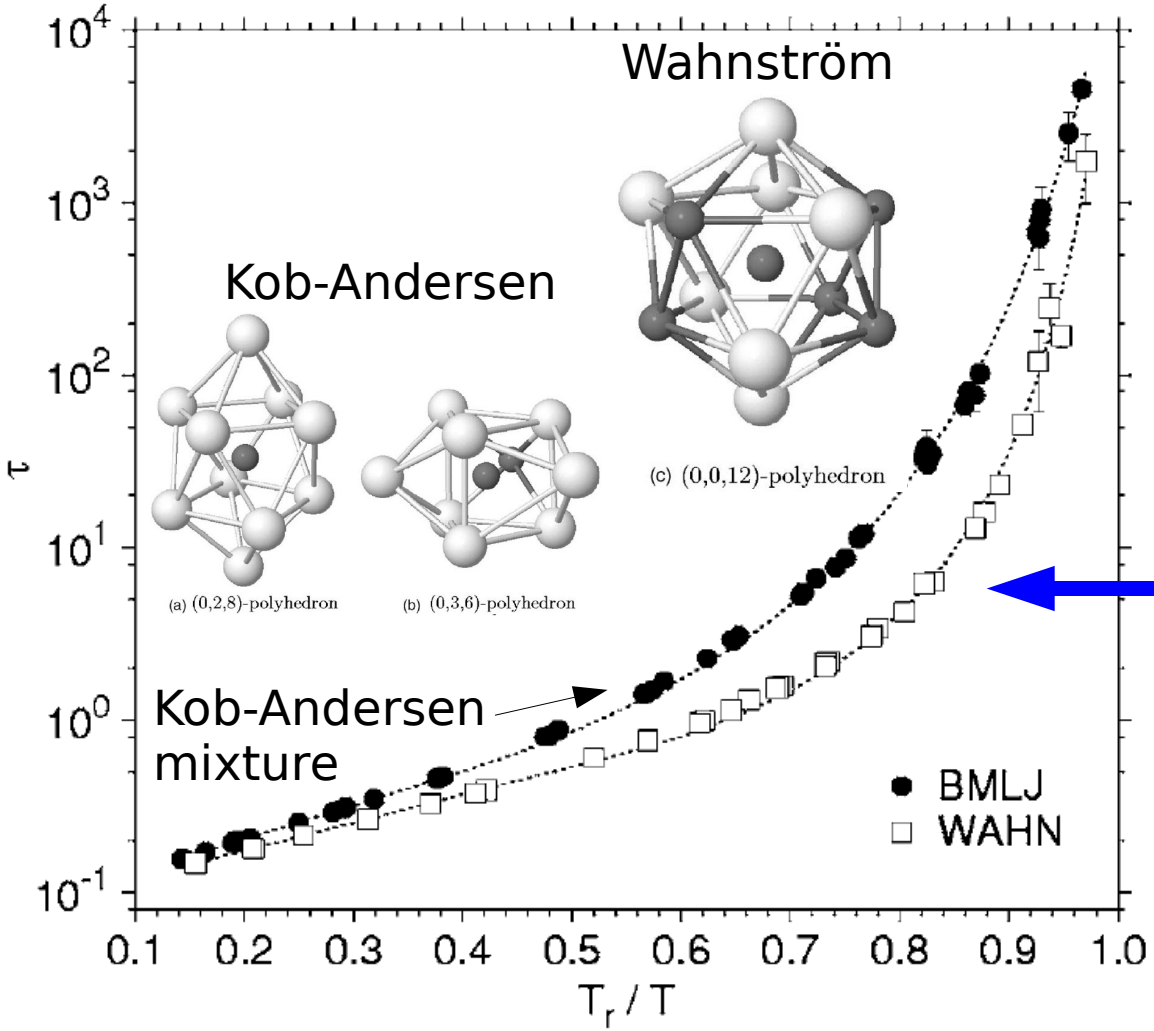
Model; Wahnström mixture

Binary Lennard-Jones mixture with size-ratio of 1.2 [Wahnström 1991]



$$U_{ij} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

$\varepsilon_{AA} = \varepsilon_{AB} = \varepsilon_{BB}$

$\sigma_{BB} = 1.2\sigma_{AA}$

$\sigma_{AB} = 1.1\sigma_{AA}$

$N_a = N_b = 512$

$\rho = 0.75$

MD simulations

A standard liquid

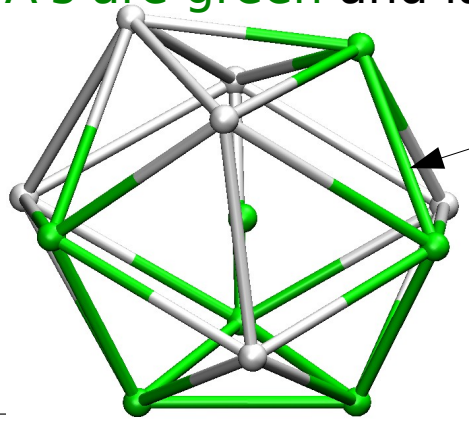
(Kob-Andensen mixture is more studied)

from [Coslovich & Pastore (2007) *J. Chem. Phys.* 127, 124504]

WAHN, Tr=0.623 KA, Tr=0.574

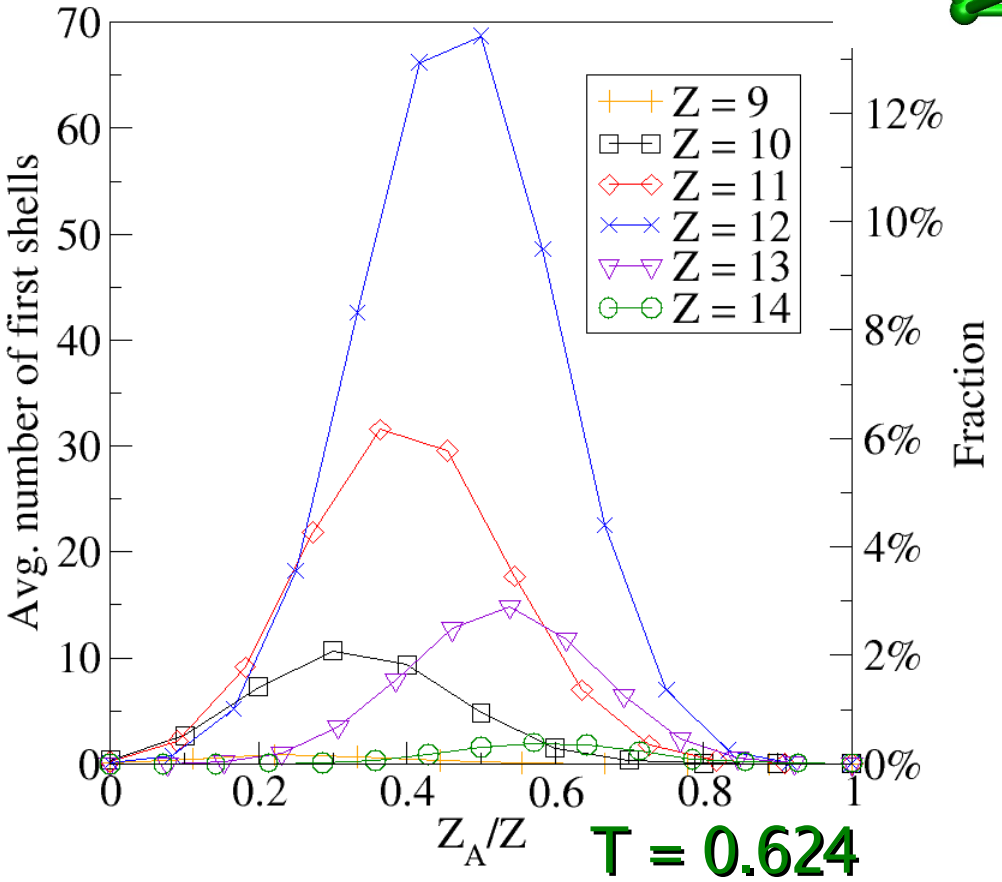
Long-lived first shells

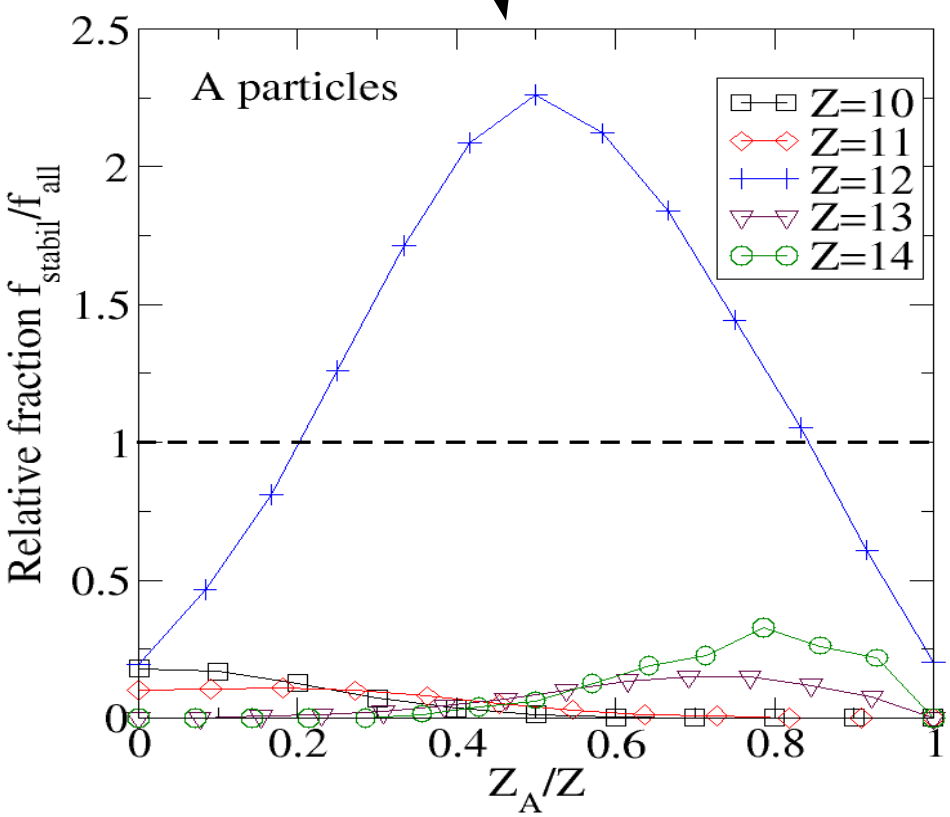
Color code: Smaller A's are green and larger B's are white



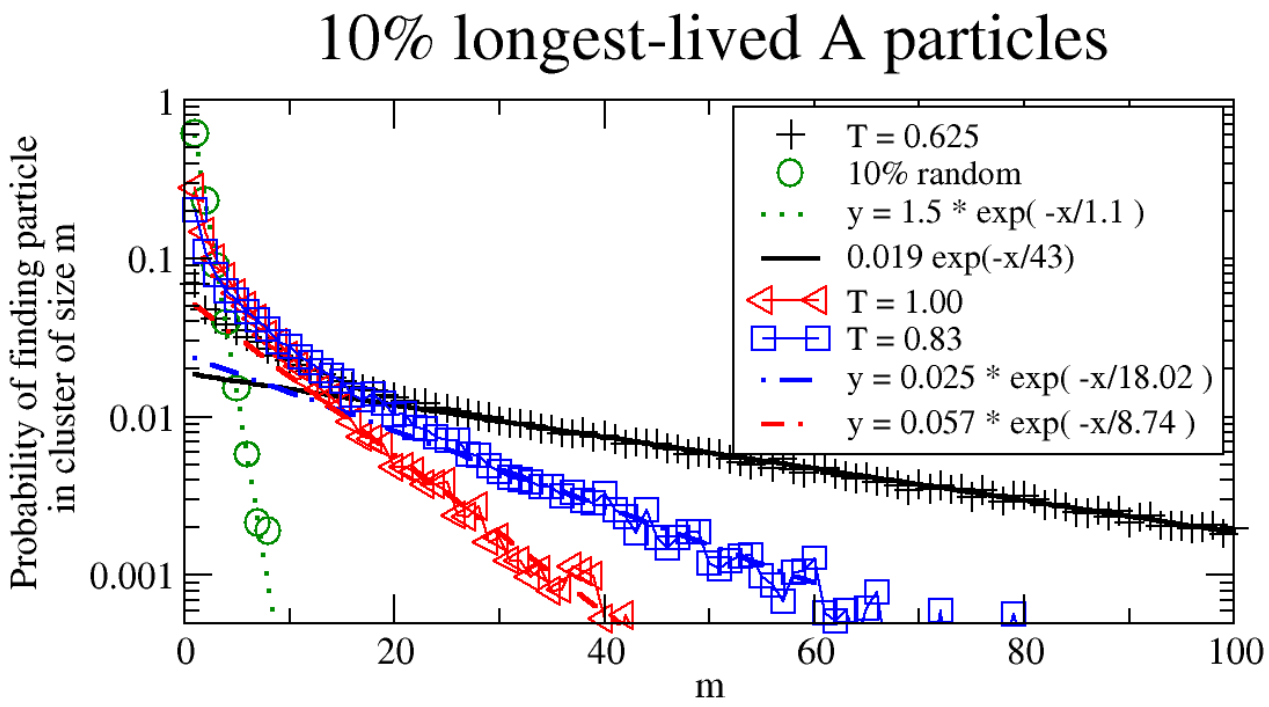
The (disordered) icosahedra

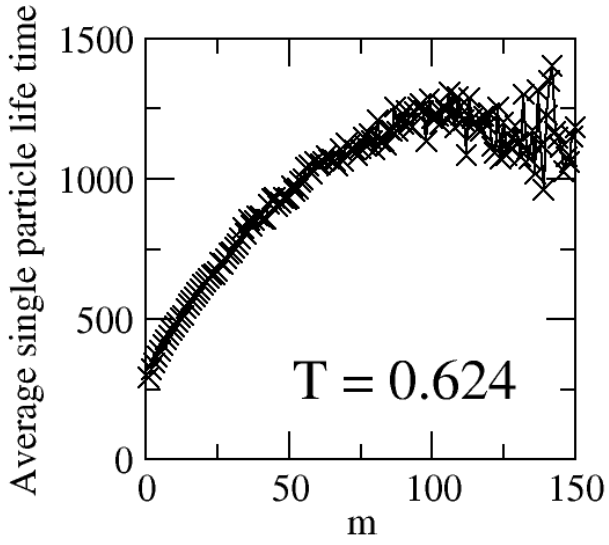
10% longest-lived first shells

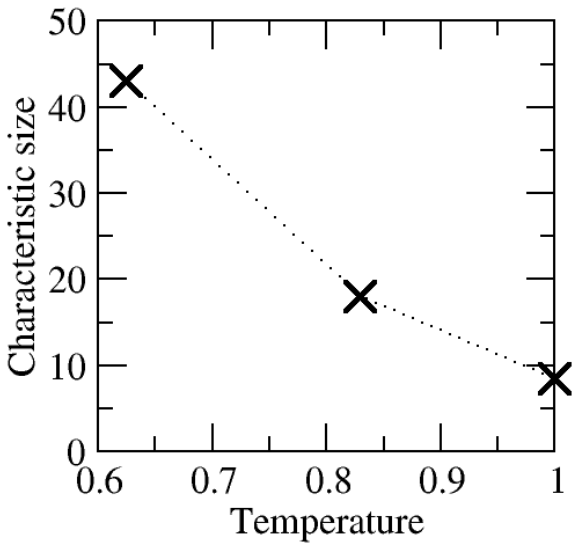




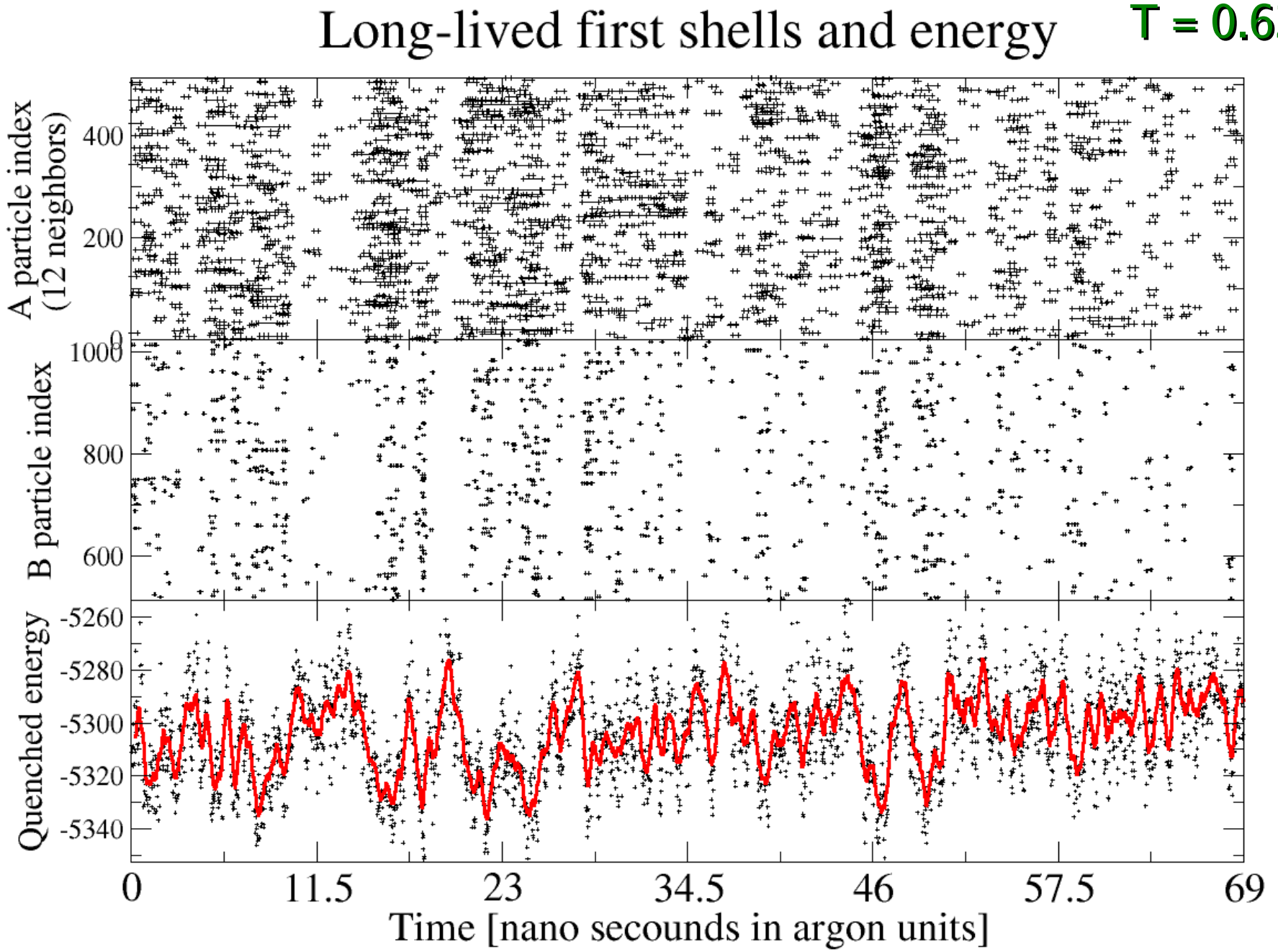
Cluster analysis





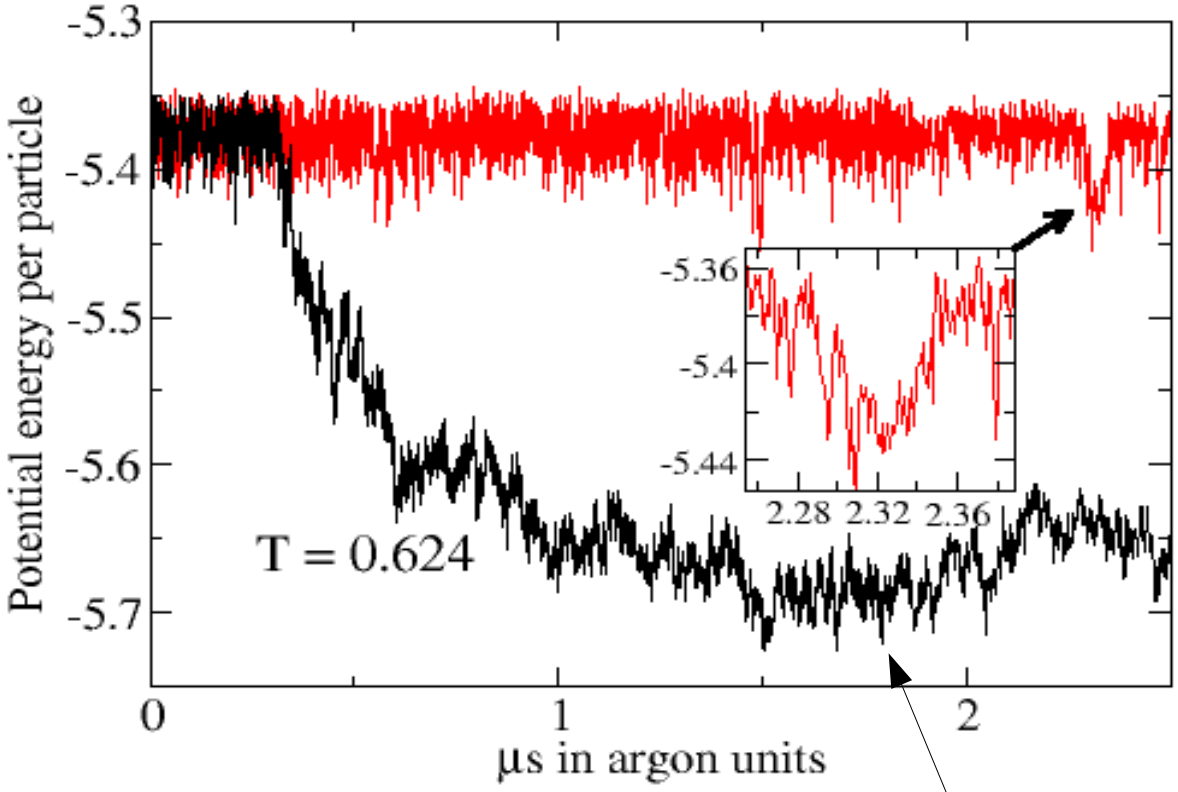


Long-lived structural fluctuations



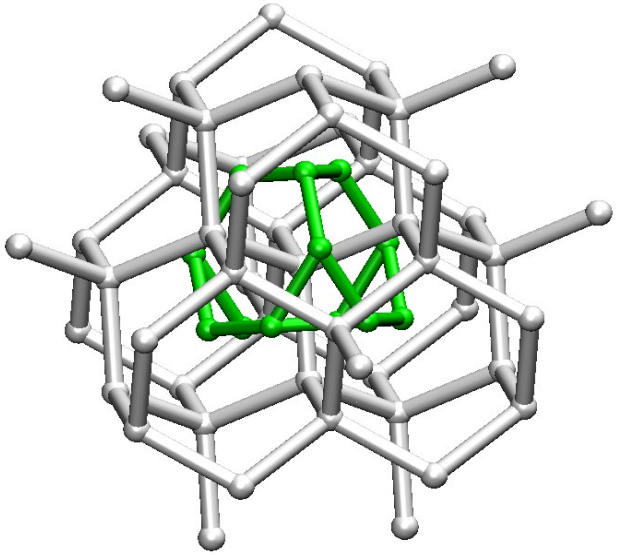
When simulated for really long times

roughly $10^4\tau_\alpha$ or 15μs in Argon units (at T=0.624)



Drop in energy due to freezing

The close-packed $MgZn_2$ Laves structure [Frank & Kasper (1959)]



B's in hexagonal diamond structure.

A's Z=12 with $Z_A=Z_B=6$

complex: 12 atoms/unit-cell

simulation is off-composition

Note: Kob-Andersen mix. can also crystallizes.

See Søren Toxværd's poster or [arXiv:0712.0377]

Crystal nucleation or glass transition

Upon supercooling,
a liquid can have two fates:

- arrest in a glass

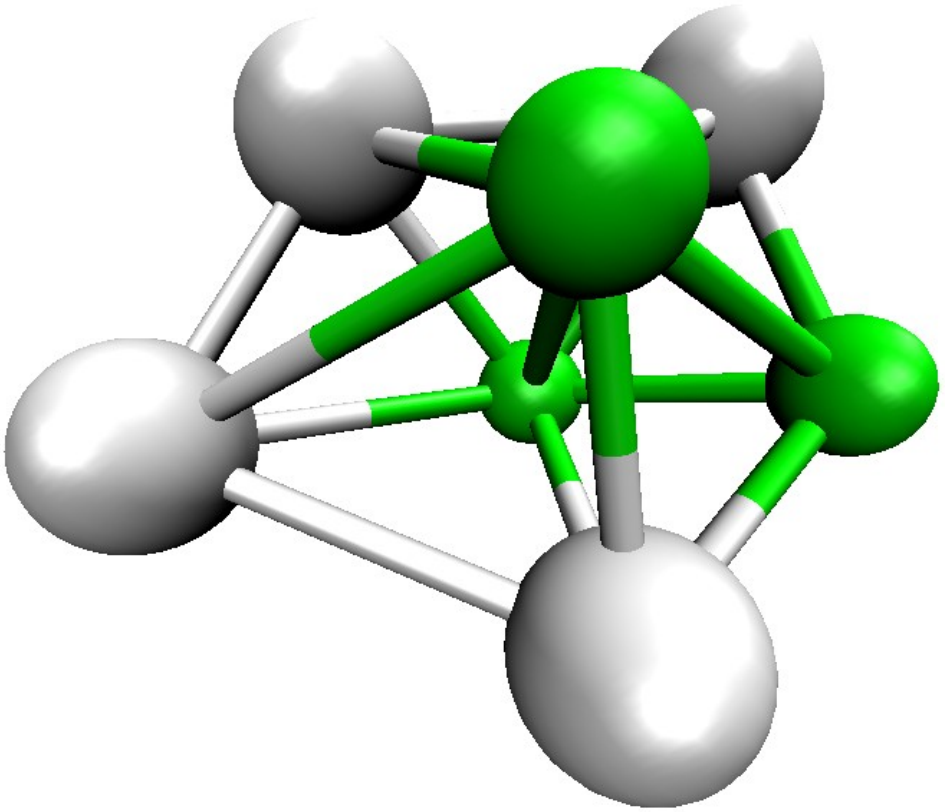
- crystal growth

The glass puzzle is:

how can mechanical stable structures
avoid the ‘trap’ of crystal growth?

Common neighbor bipyramids (CNB)

Characterizing common neighbor arrangements



Six integers

1 AA “bond” with
- 1 for AA,
- 2 for AB
- 3 for BB

1 common A and
4 common B's having,
0 AA “bond”s,
2 AB “bond”s and
3 BB “bond”s.

... gives 114023

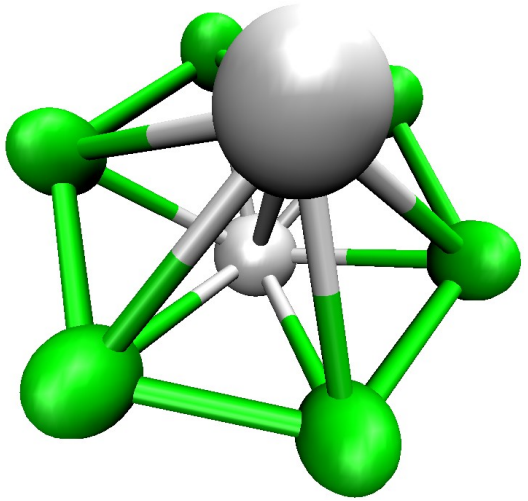
“bond”; within first minimum of g(r)

Color code: Smaller A's are green and larger B's are white

Crystal:

114023 (AA)
123122 (AA)
132221 (AA)
232140 (AB)
360600 (BB)

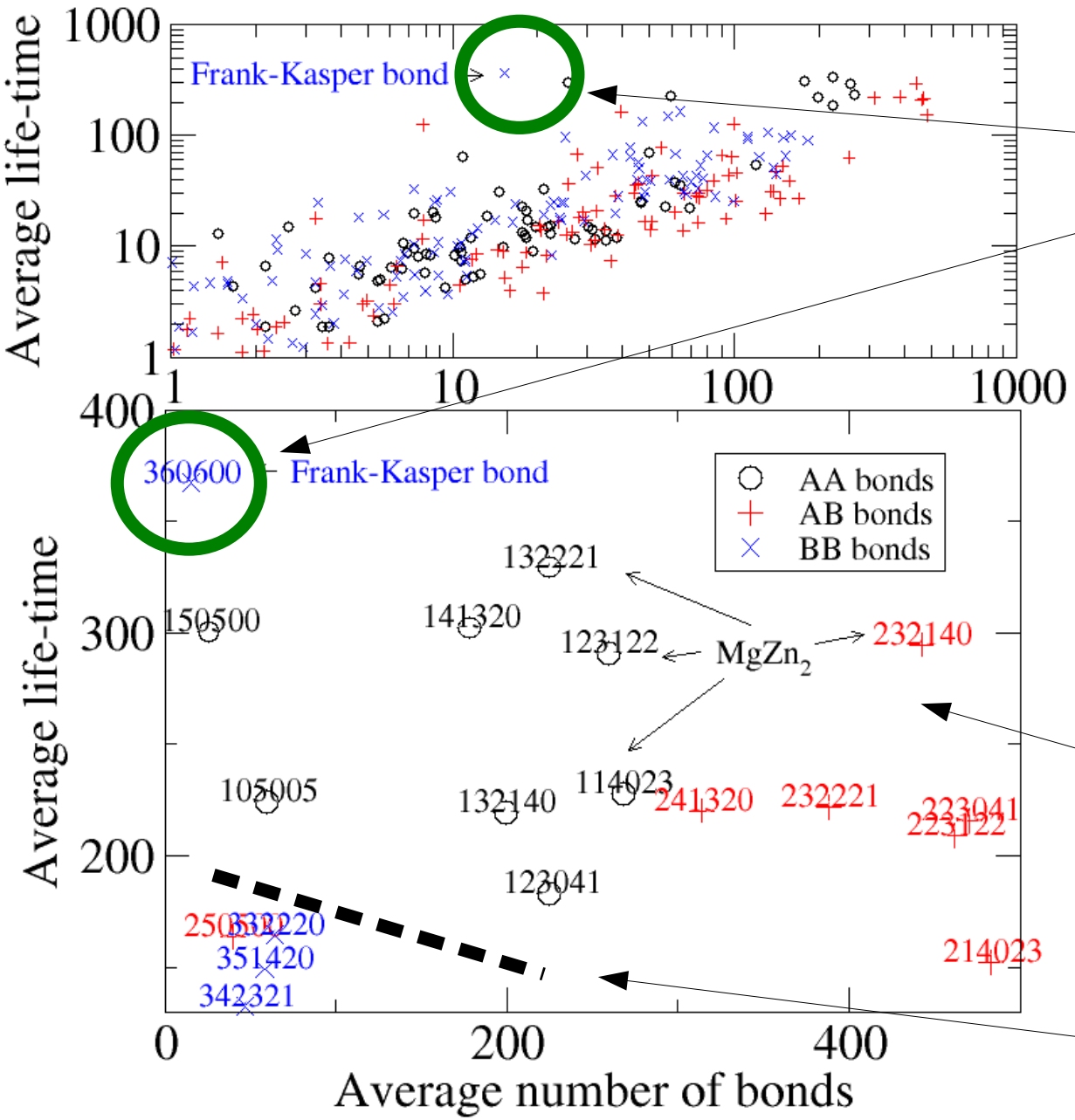
The BB “bond”,



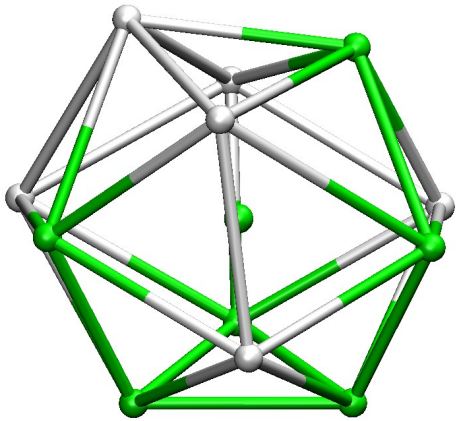
“Frank-Kasper bond”

Variation of Honeycutt & Andersen's common neighbor analysis [J. Phys. Chem. 91, 4950 (1987)]

Abundance and life-time of CNB's



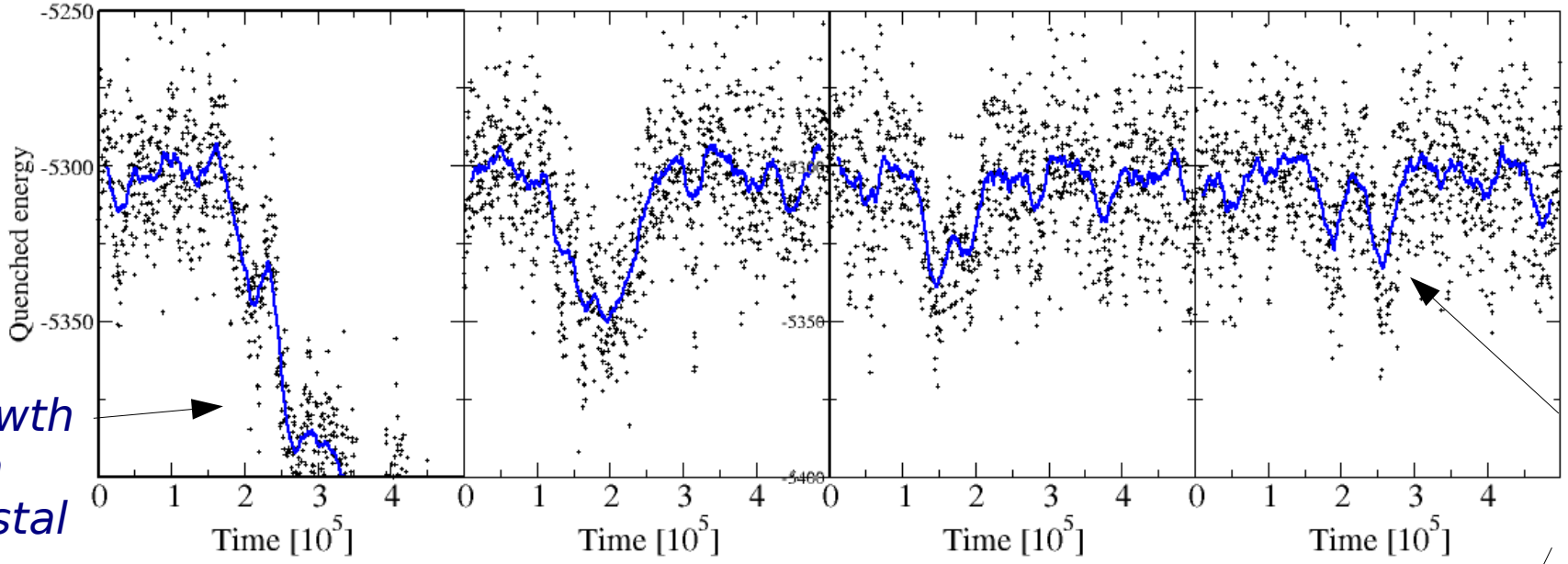
Frank-Kasper bonds are rare and long-lived



Crystal structures "pre-built" in liquid

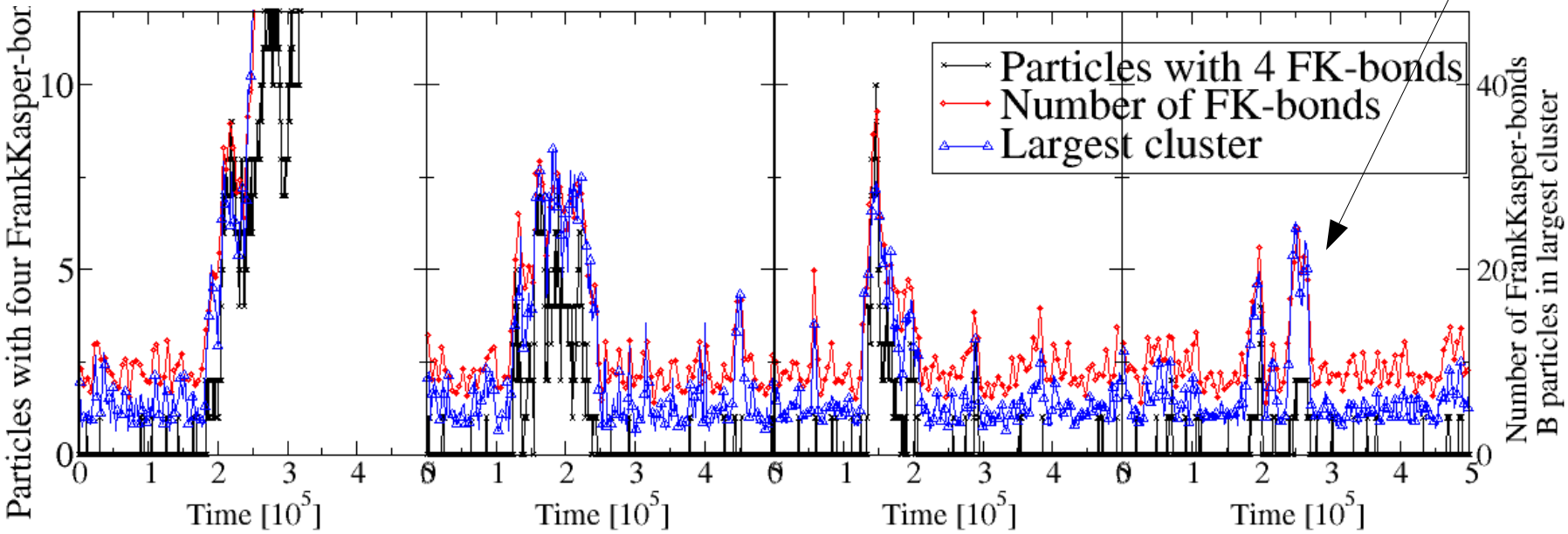
All possible ways of having 5 bonded common neighbors are above

Frank-Kasper clusters, I



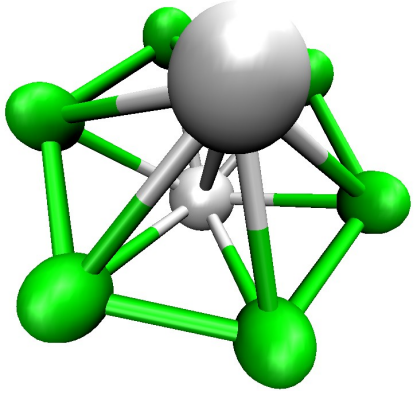
growth of a crystal

Dips in energy: "Frank-Kasper" clusters

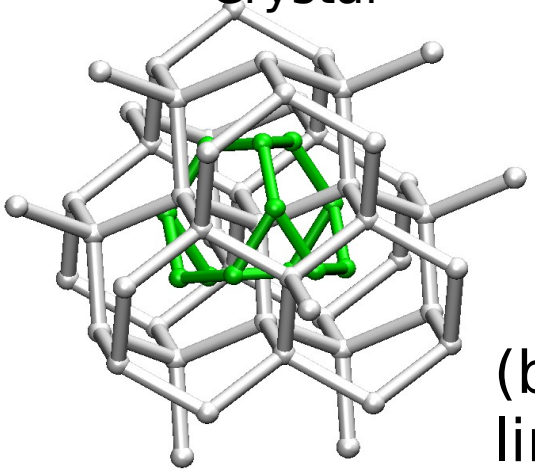


Frank-Kasper clusters, II

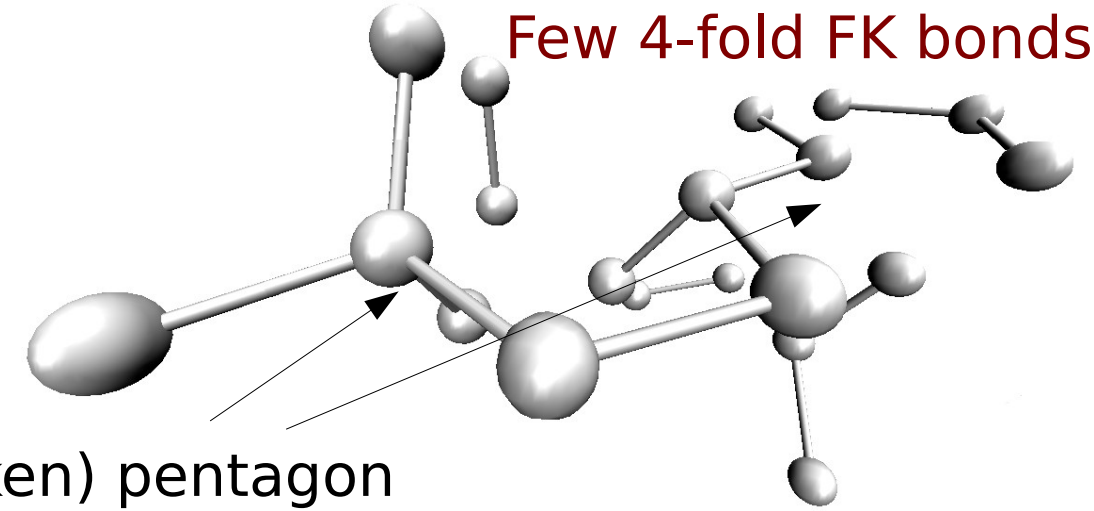
Frank-Kasper bond



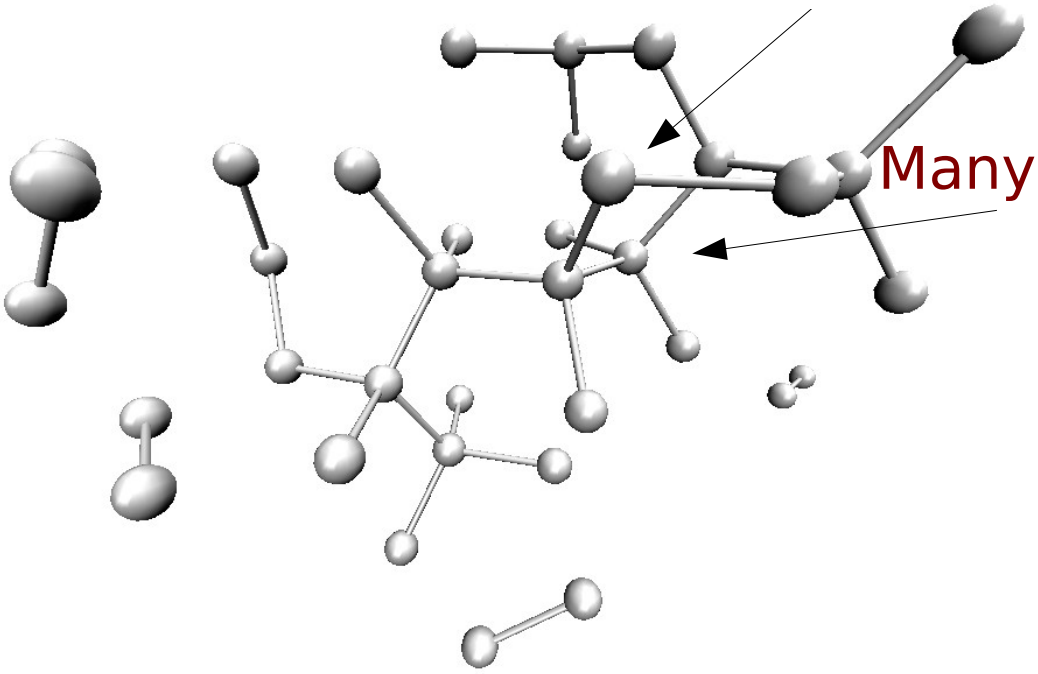
Crystal



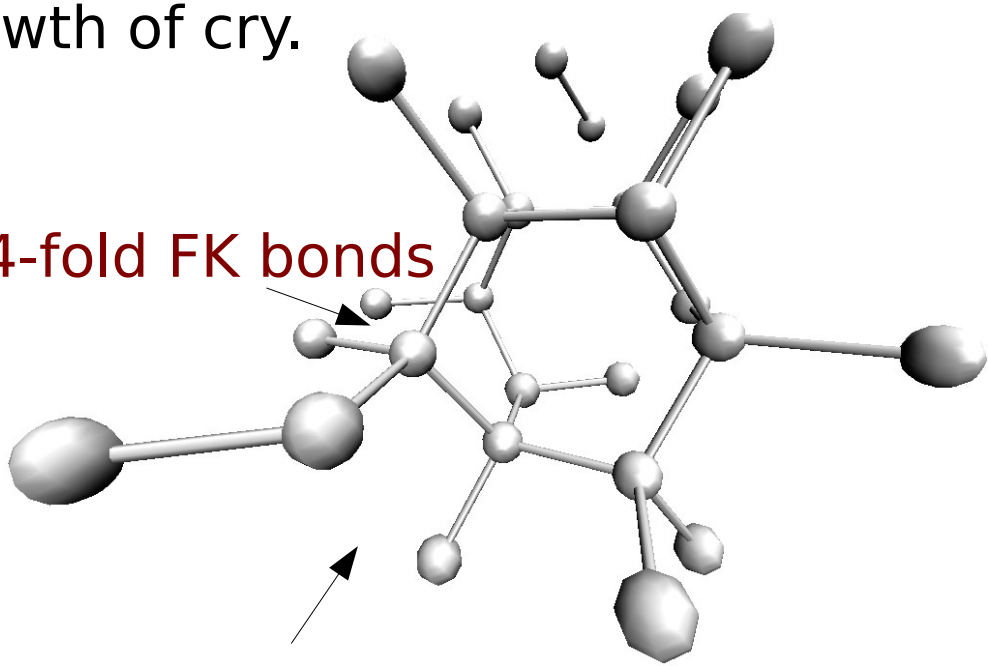
Few 4-fold FK bonds



(broken) pentagon
limits growth of cry.



Many 4-fold FK bonds



Similar to crystal

So why?

The glass puzzle is:

how can mechanical stable structures
avoid the ‘trap’ of crystal growth?

Here, local preferred structure **can** fill space (crystal),
(no geometric frustration)

but can also build disordered structures
(“entropic frustration”)

Recall:
Local preferred structure of spheres
(icosahedra) cannot fill space
[Frank 1952]

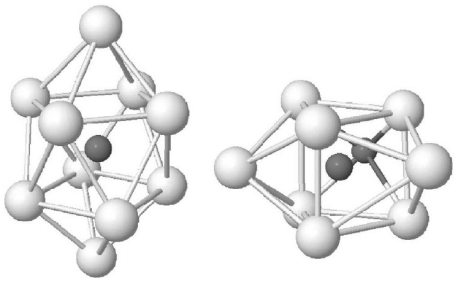
Conclusion

Long-lived clusters
intermediate between
liquid and crystal

Frank-Kasper bond
onset of crystallization

Comment

Kob-Andersen mixture
can also form a crystal
another mechanism



(a) (0,2,8)-polyhedron (b) (0,3,6)-polyhedron

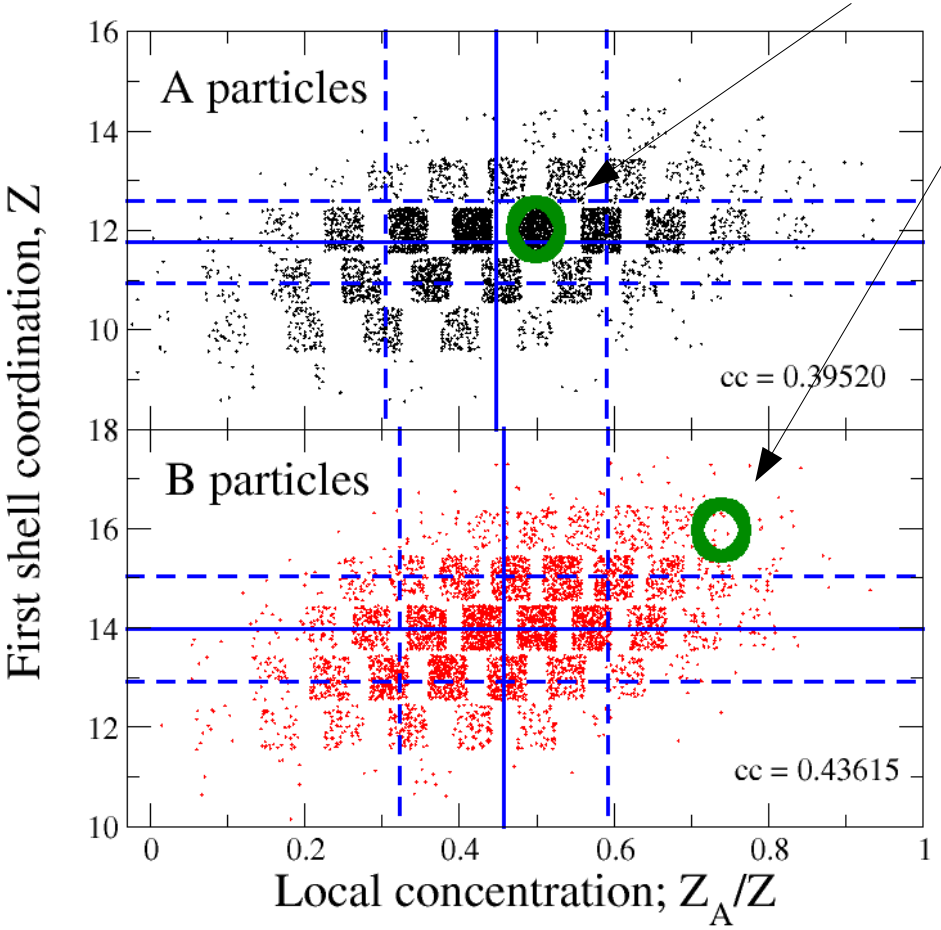
The end

Thanks for your attention

Looking for post.doc position

Coordination in metastable liquid vs crystal

Coordination in crystal



Z_A: Number of A's in the first shell

In the AB liquid, most A's have same coordination number as crystal

The B environments are very different from those in the crystal

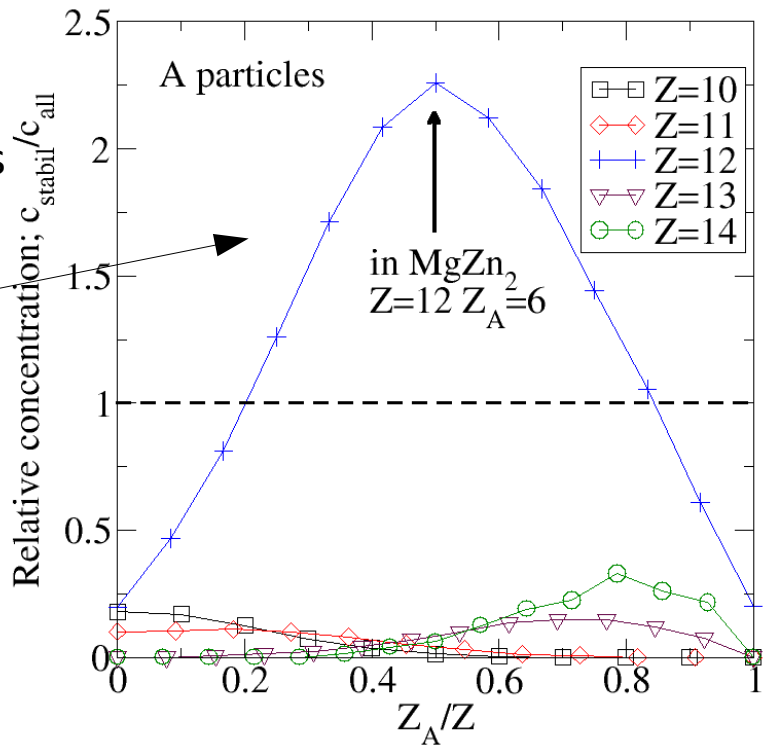
Crystallization must be accompanied by rearrangement around B's

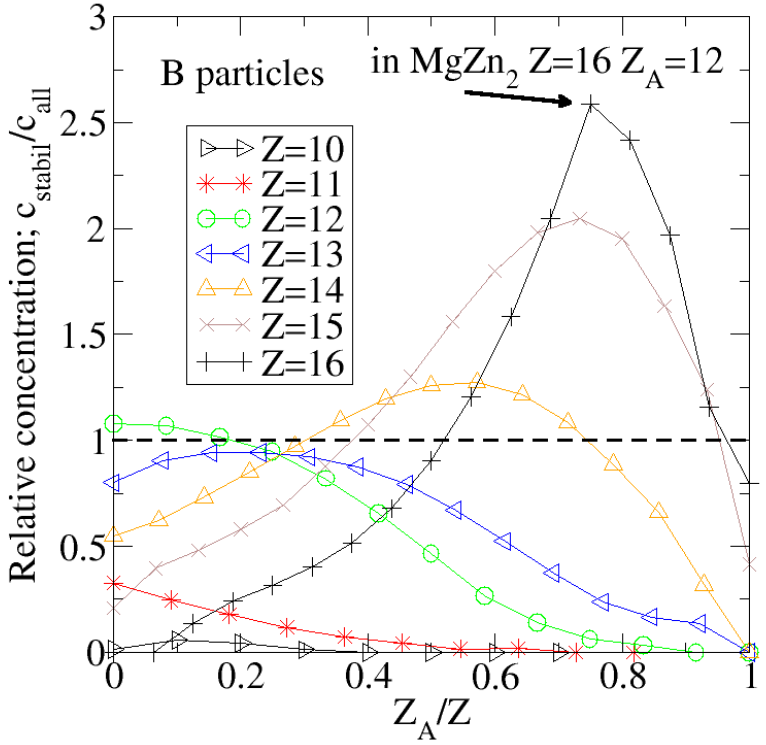
Particles in first peak of g(r) (using first minimum as cut-off) are considered neighbors

Coordination of stable particles in liquid

On y-axis: Concentration of different kinds of first shells of stable particles relative to the over all concentration

Stable structures are completely dominated by 12-fold coordinated A particles



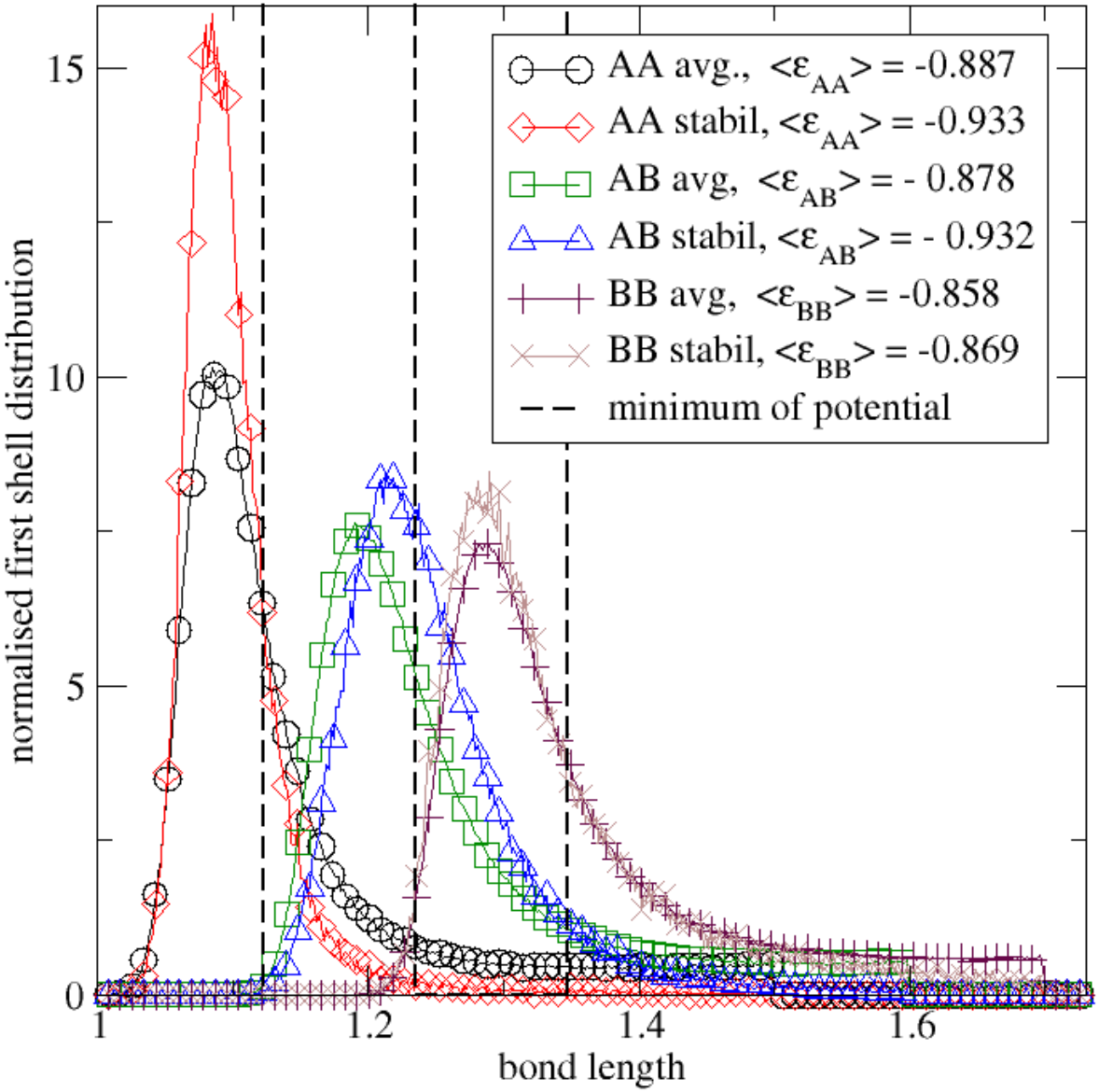


Stable particle: Amongst the 10% with the longest lifetime of first shell

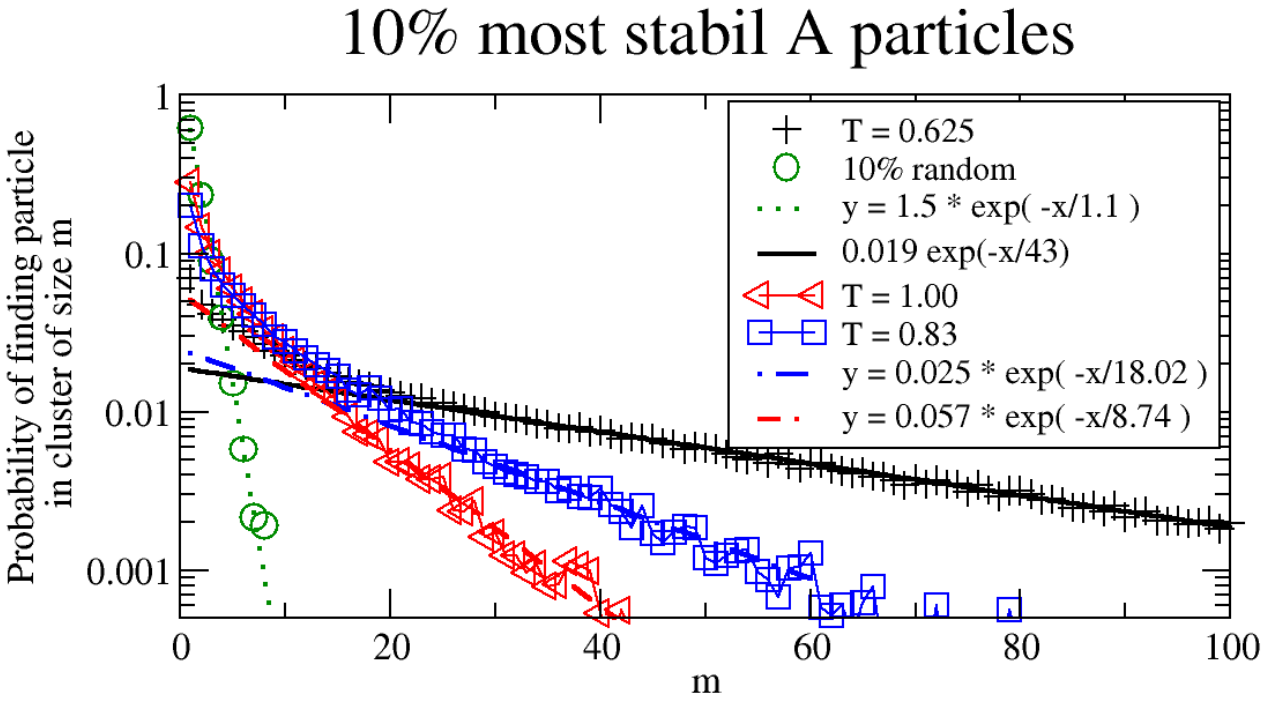
Lifetime: Time between first and last occurrence

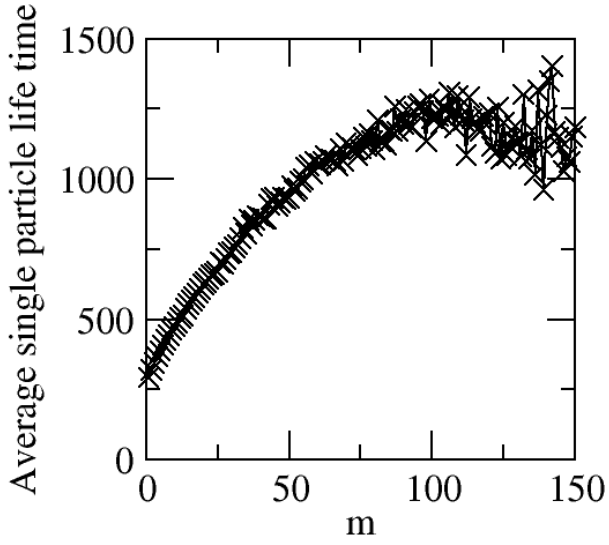
Stable structures in liquid tend to be crystal-like but variations also provide stability.

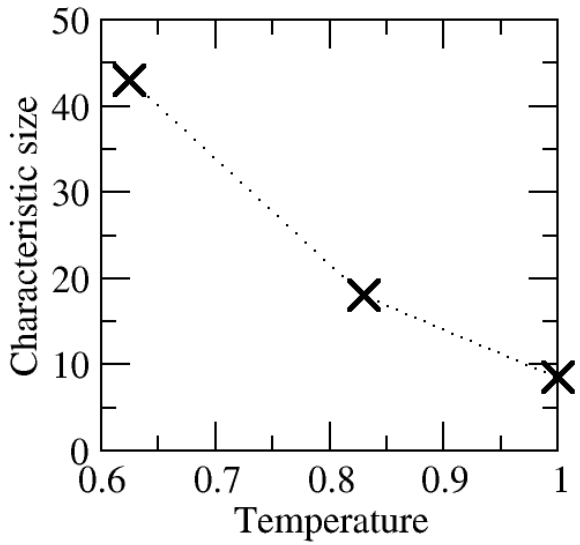
Relating structure and energy



Stable particles cluster



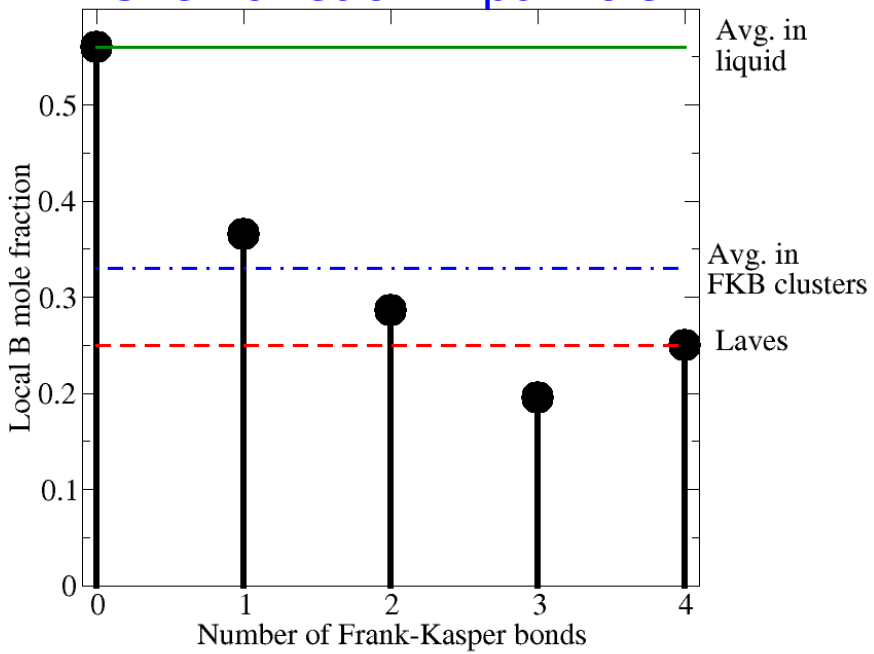




Stability:
Life time of first shell

FK clusters are connected to a local composition fluctuation

‘Local composition’: the mole fraction of B particles in the coordination shell of each B particle

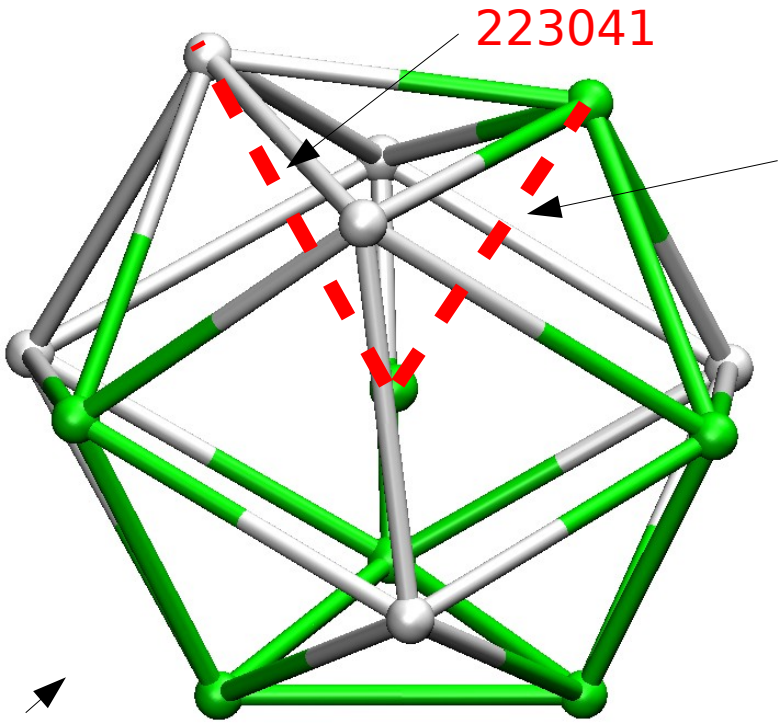


Structure is coupled to local composition

Common neighbor bipyramids (CNB)

Common neighbor 'bonds' correspond to various irregular bipyramids.
These represent a useful class of elementary units for resolving structures
– amorphous or crystalline.

Six integers are used to distinguish between different geometrical arrangements



First shell
of an A particle
(in liquid)

Example of the notation

1 AA contact
(1 for AA, 2 for AB
and 3 for BB) with
1 common A
4 common B's having,
0 AA contacts,
2 AB contacts and
3 BB contacts.
Notation: 114023

The crystal is build up of the following kind of bipyramids

114023 (AA)
123122 (AA)
132221 (AA)
232140 (AB)
360600 (BB)

The latter BB contact with six touching common A neighbors is referred to as a

Frank-Kasper bond

Note: an A particle with Z=12 and Z_A=6 but different from the crystal ones

Color code:
Smaller A's are green
and larger B's are white

Conclusions, I

The AB liquid exhibits
a tendency to local
coordination similar
to those in the crystal

i.e. some crystal structure
is ‘pre-organized’
in the liquid

Structural relaxation is
slowed in the supercooled
mixture by the appearance
of stable clusters
of well packed particles.

How stable these clusters
can be without explicit
crystal organization
determines whether
one gets a metastable liquid
or crystal.

Conclusions, II

Clusters exhibit features intermediate between that of the liquid and the crystal

– i.e. there is no need to invoke completely new non-crystalline structures to explain liquid stability.

Large unit cell crystal structures provide more opportunities for these stable fragments.

A kind of "entropic frustration".

Conclusions, II

Clusters exhibit features intermediate between that of the liquid and the crystal

– i.e. there is no need to invoke completely new non-crystalline structures to explain liquid stability.

Large unit cell crystal structures provide more opportunities for these stable fragments.
A kind of entropic frustration.

The improved packing in the clusters involves significant fluctuations in the local composition.

What happens if we suppress these fluctuations by strengthening the AB attraction?
(last slide)