The Abdus Salam
International Centre for Theoretical Physics

United Nations
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2254-7

Workshop on Sphere Packing and Amorphous Materials

25 - 29 July 2011

How Hard Is It To Form a Glass? Insights from beyond 3D

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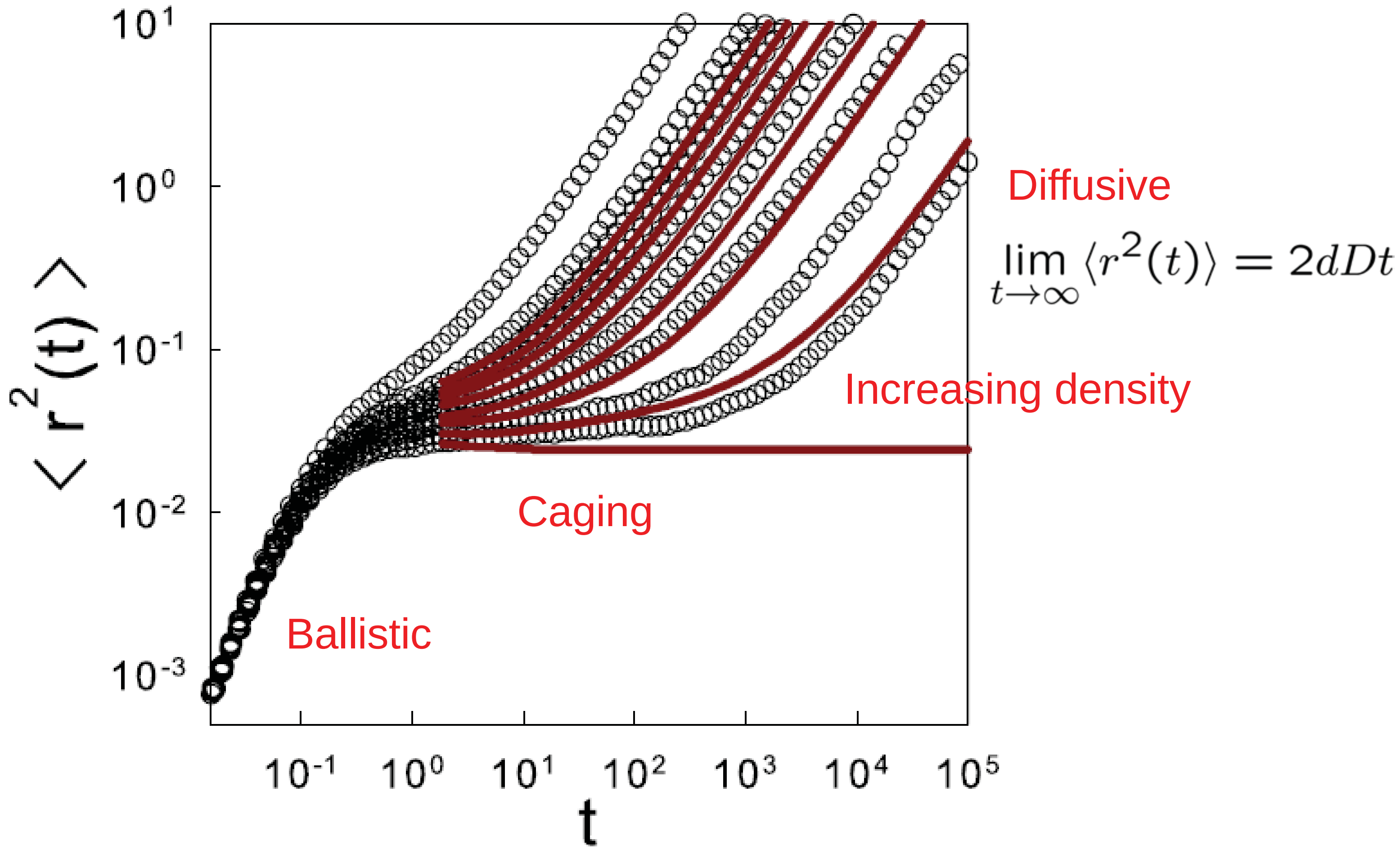
How hard is it to form a glass?

Insights from beyond 3D.

Patrick Charbonneau (Duke U.) @ ICTP

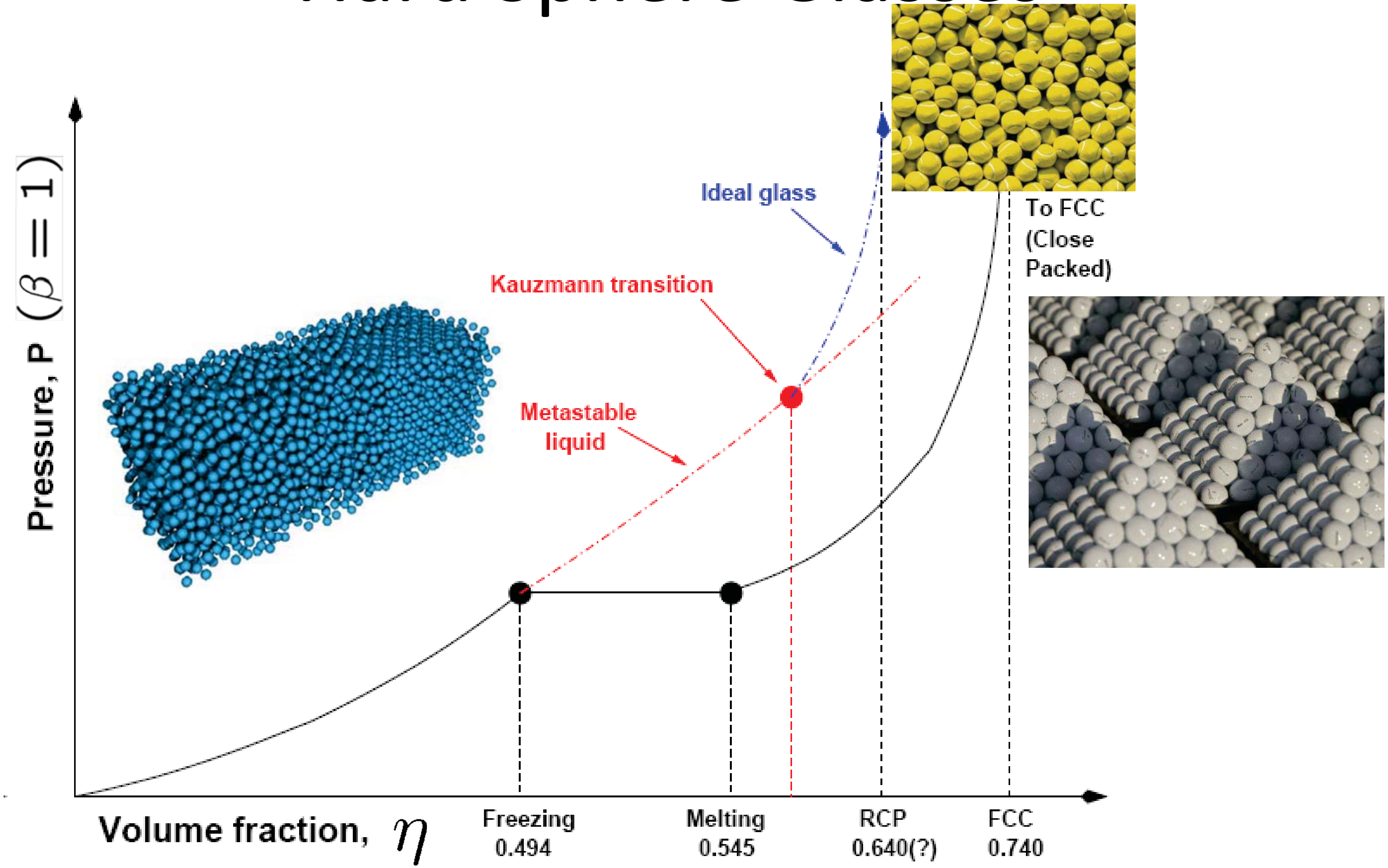
Caging

Between the ballistic and the diffusive regimes, the caging regime extends with supercooling.



Charbonneau, Ikeda, van Meel, Miyazaki, PRE (2010)

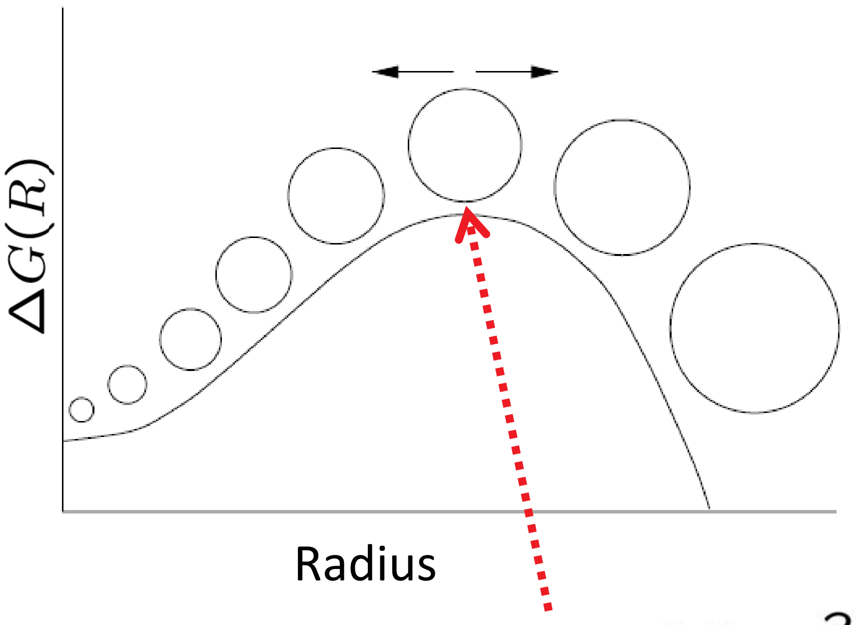
Hard Sphere Glasses



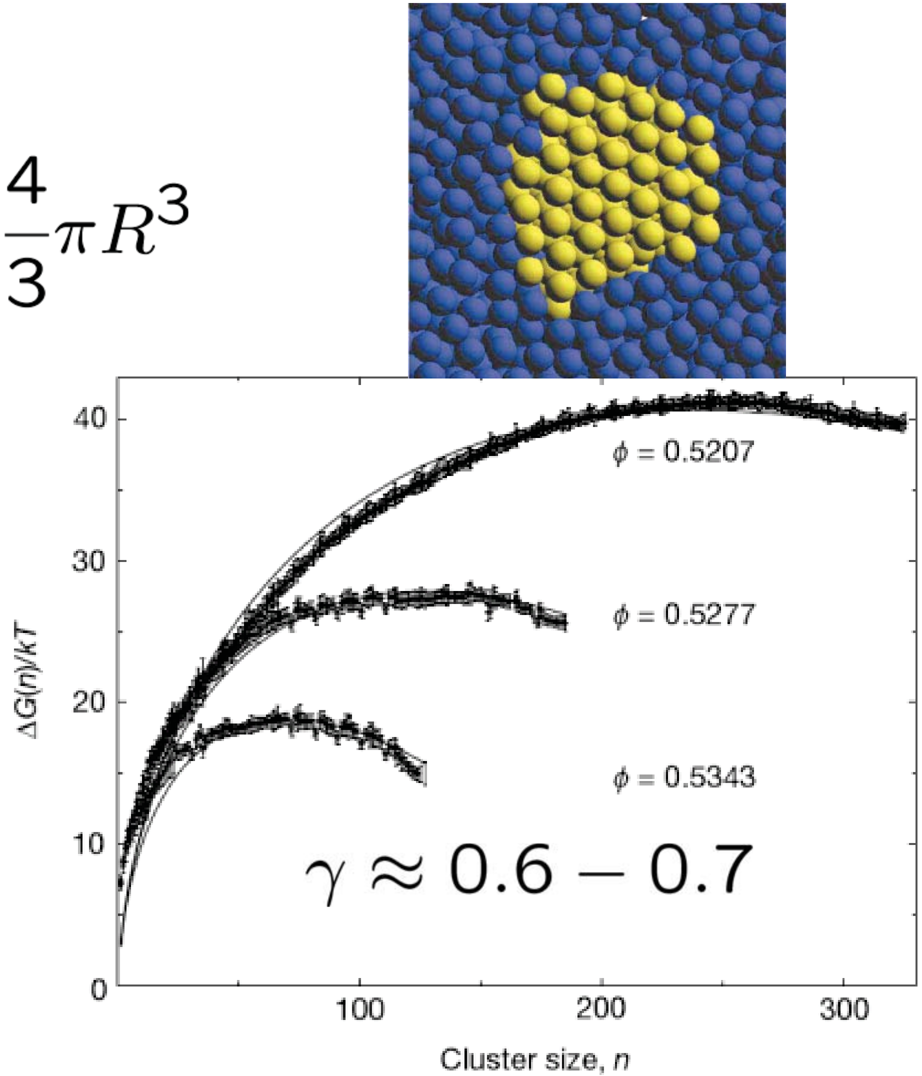
Parisi and Zamponi, Rev. Mod. Phys. (2010)
Zamponi, Nature (2008)

Crystal Nucleation

$$\Delta G(R) = \gamma 4\pi R^2 - \Delta\mu \rho_s \frac{4}{3}\pi R^3$$



$$\Delta G^{\dagger}(R^*) = \frac{16\pi\gamma^3}{3(\Delta\mu)^2}$$



Auer and Frenkel, Nature (2002)

SUPERCOOLING OF LIQUIDS

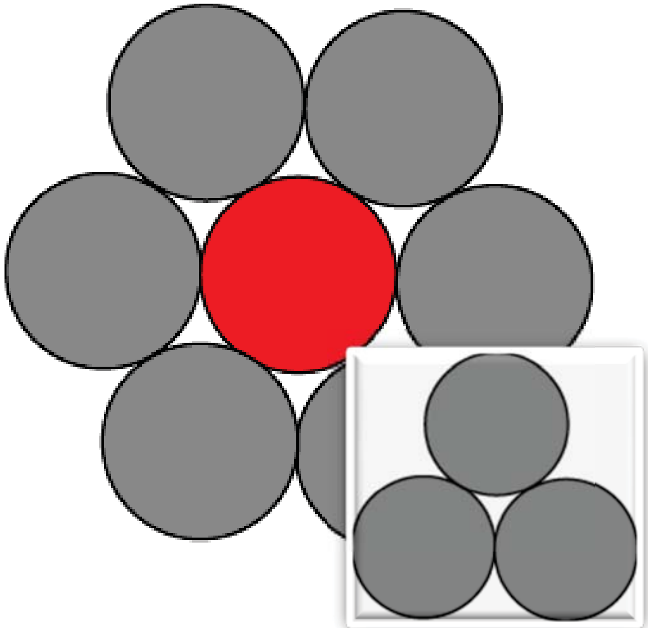
BY F. C. FRANK
H. H. Wills Physics Laboratory, Bristol University

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

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

Proc. Roy. Soc. A (1952)

Geometrical Frustration

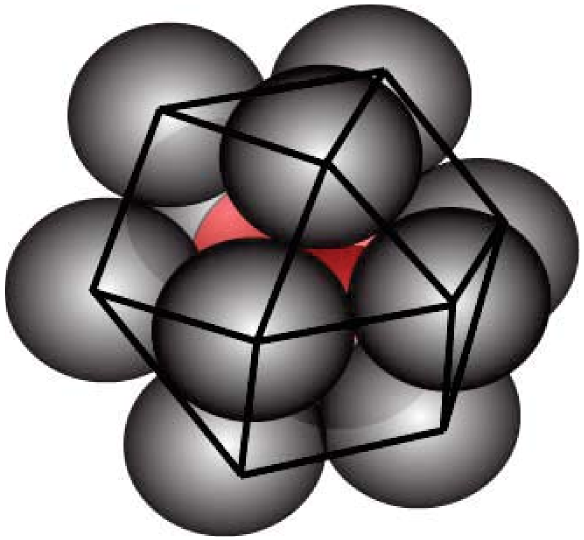


Triangular Lattice

AND

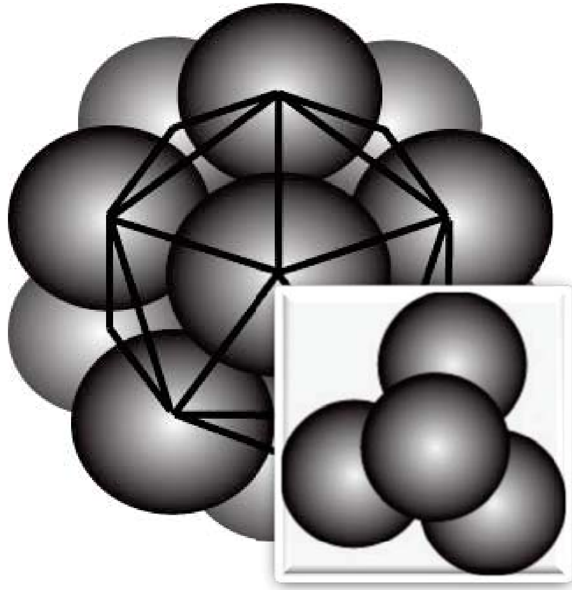
2-Simplex

(triangle)



FCC Lattice

vs.



Icosahedron

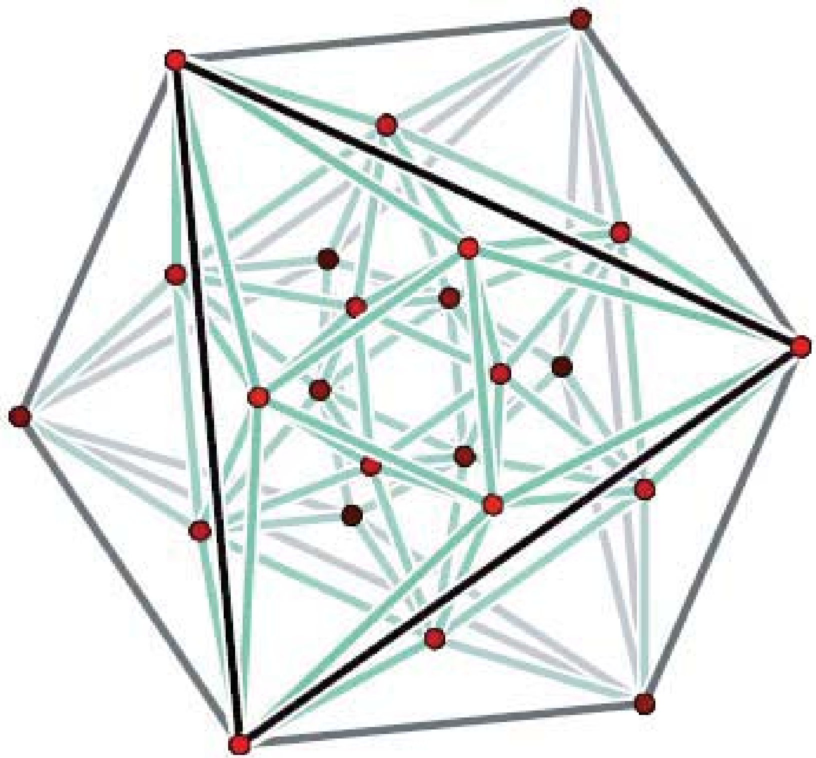
~AND

3-Simplex

(tetrahedron)

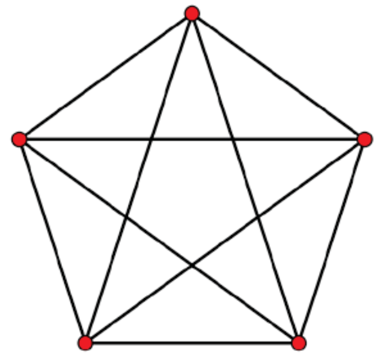
Geometrical Frustration in 4D

The 24-cell comes to the mind of any good schoolboy (and is unique)!



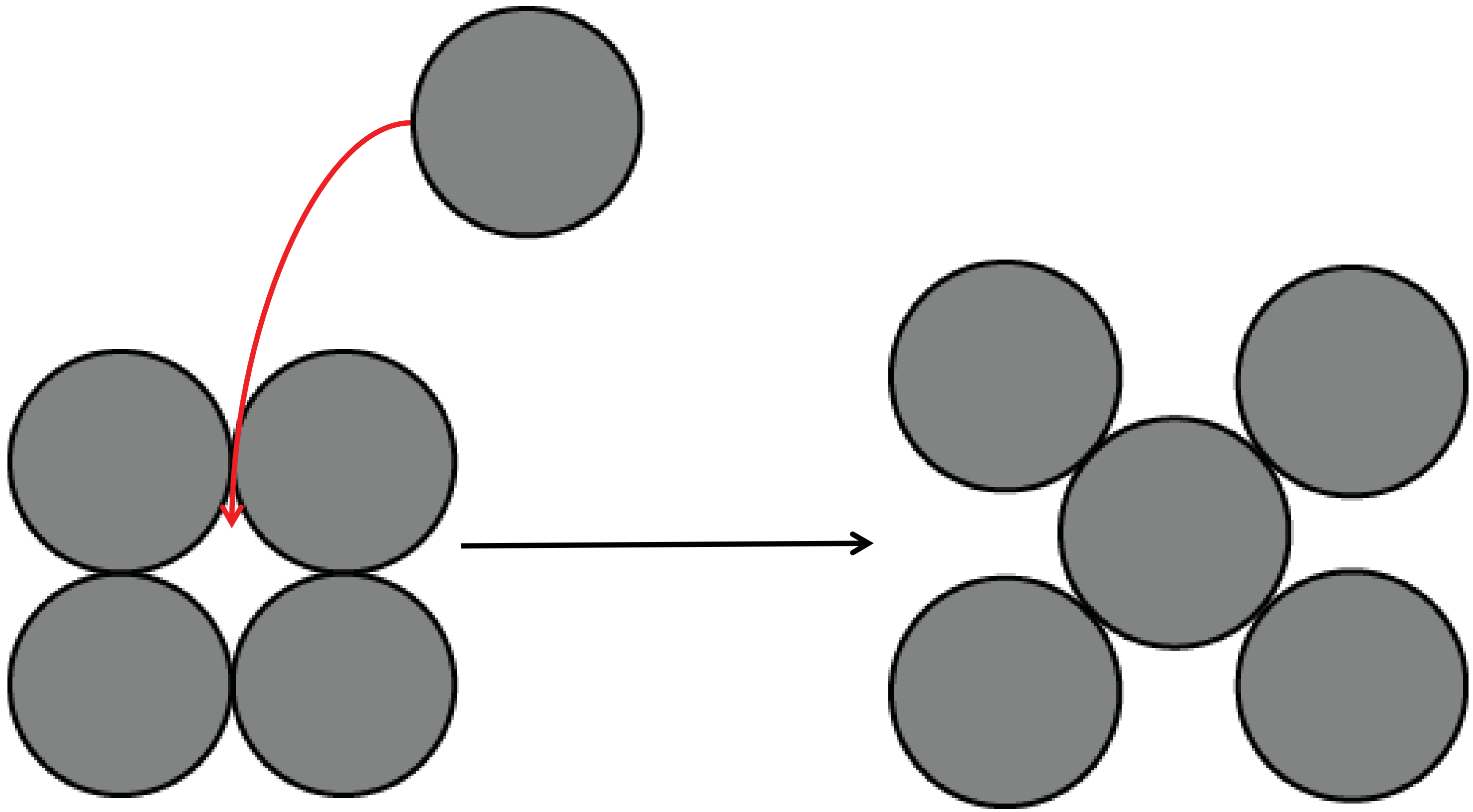
D_4 Lattice
IS NOT
Simplex Based

4-Simplex



Pfender and Ziegler, Notices AMS (2004)

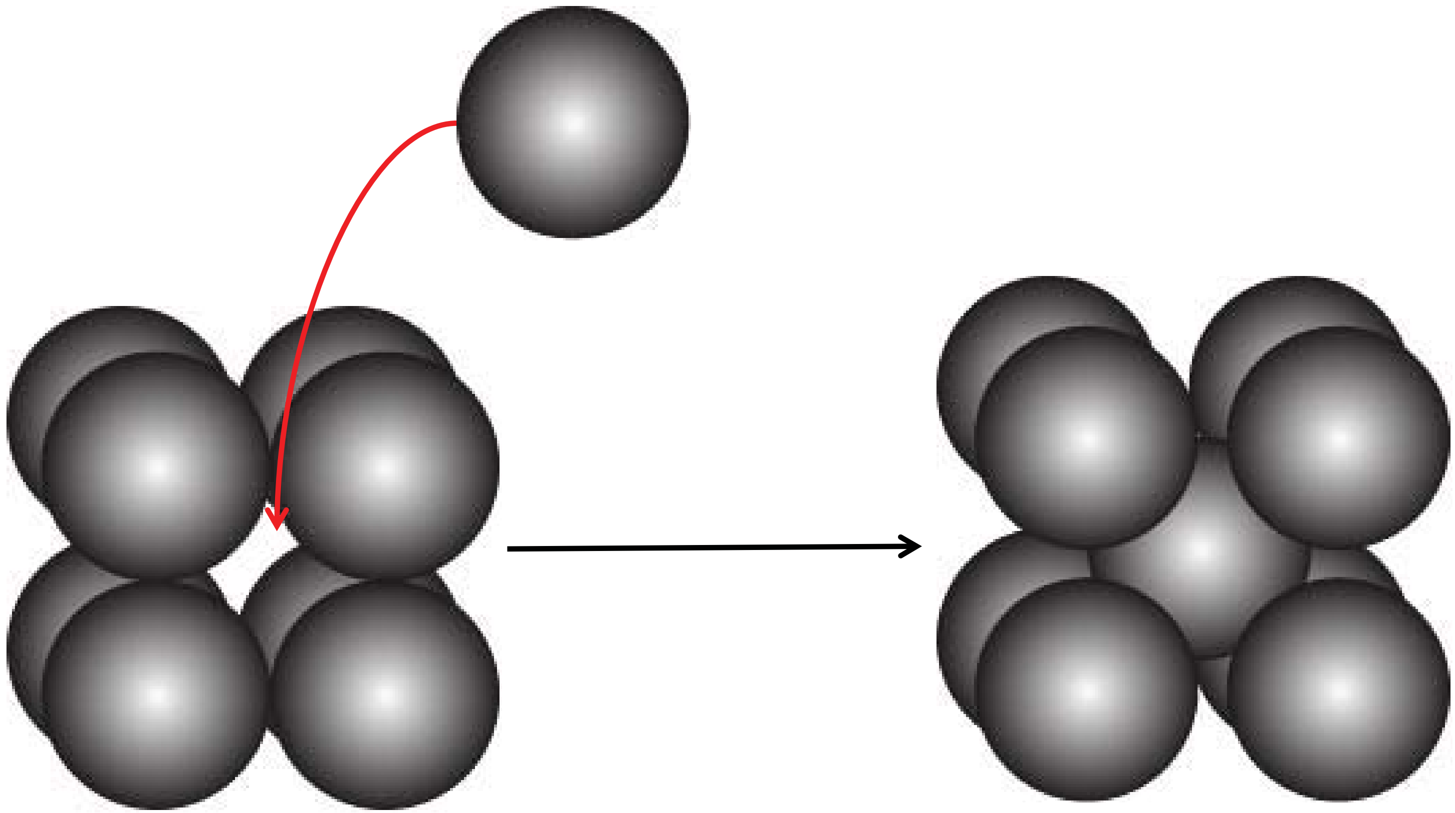
2D Packing



Simple Square

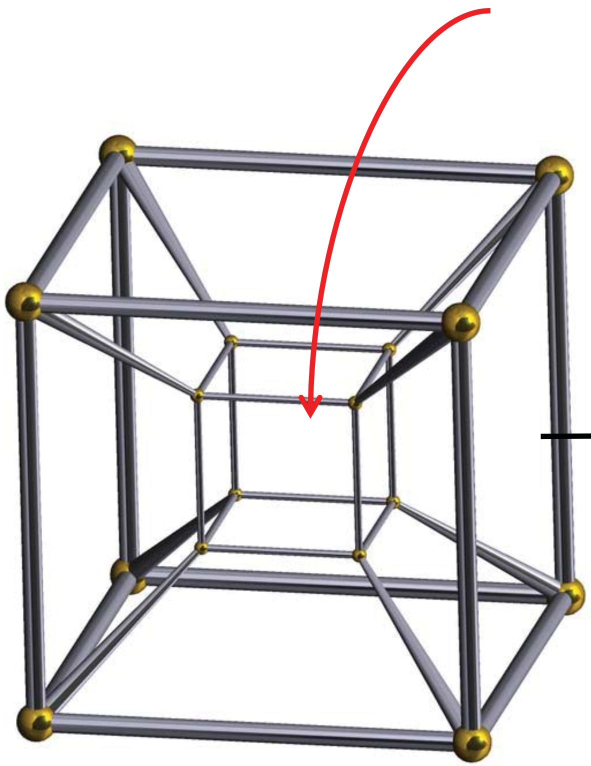
Rotated Simple Square

3D Packing



Simple Cubic Body-Centered Cubic

4D Packing

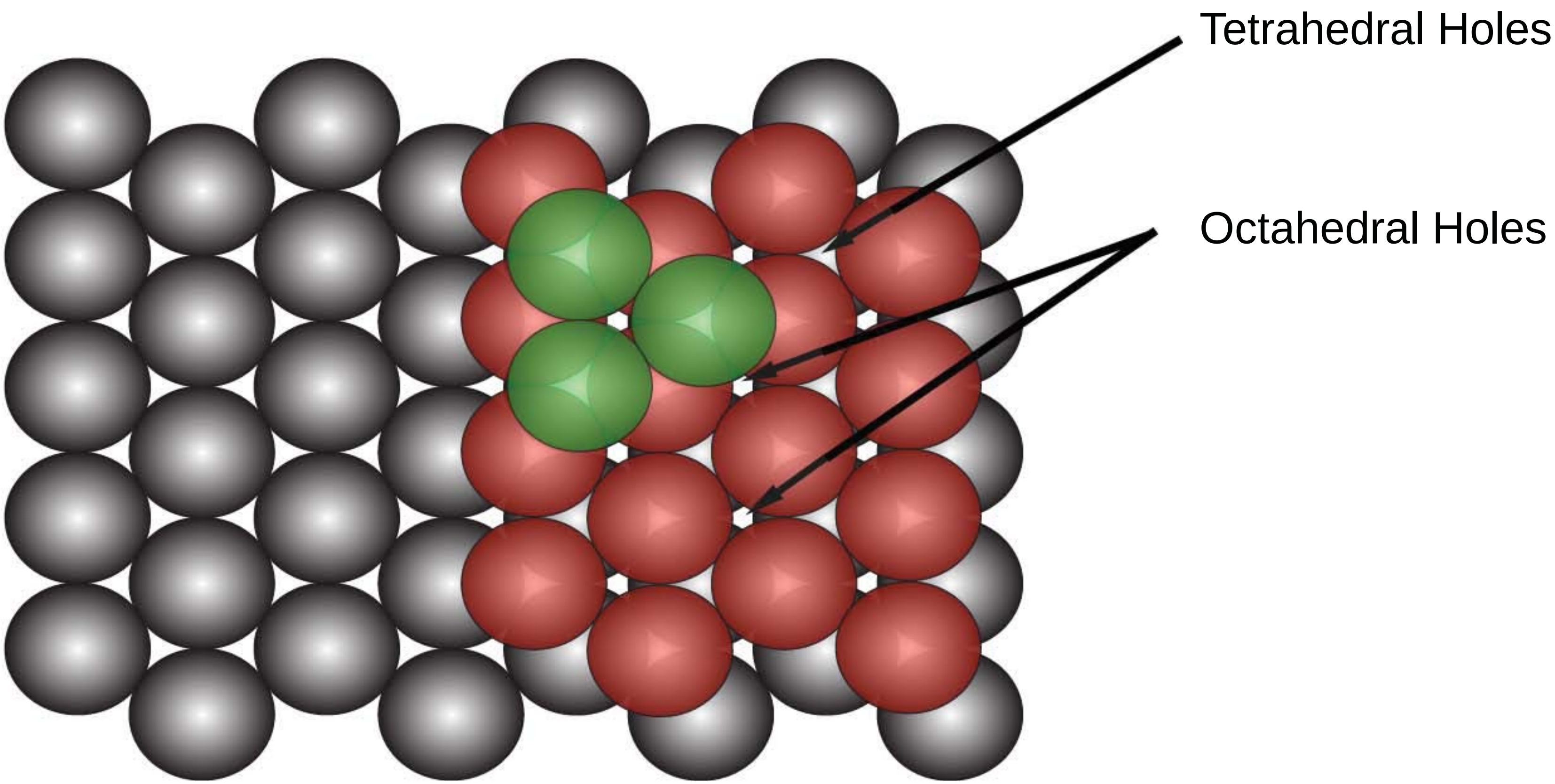


(1/2, 1/2, 1/2, 1/2)

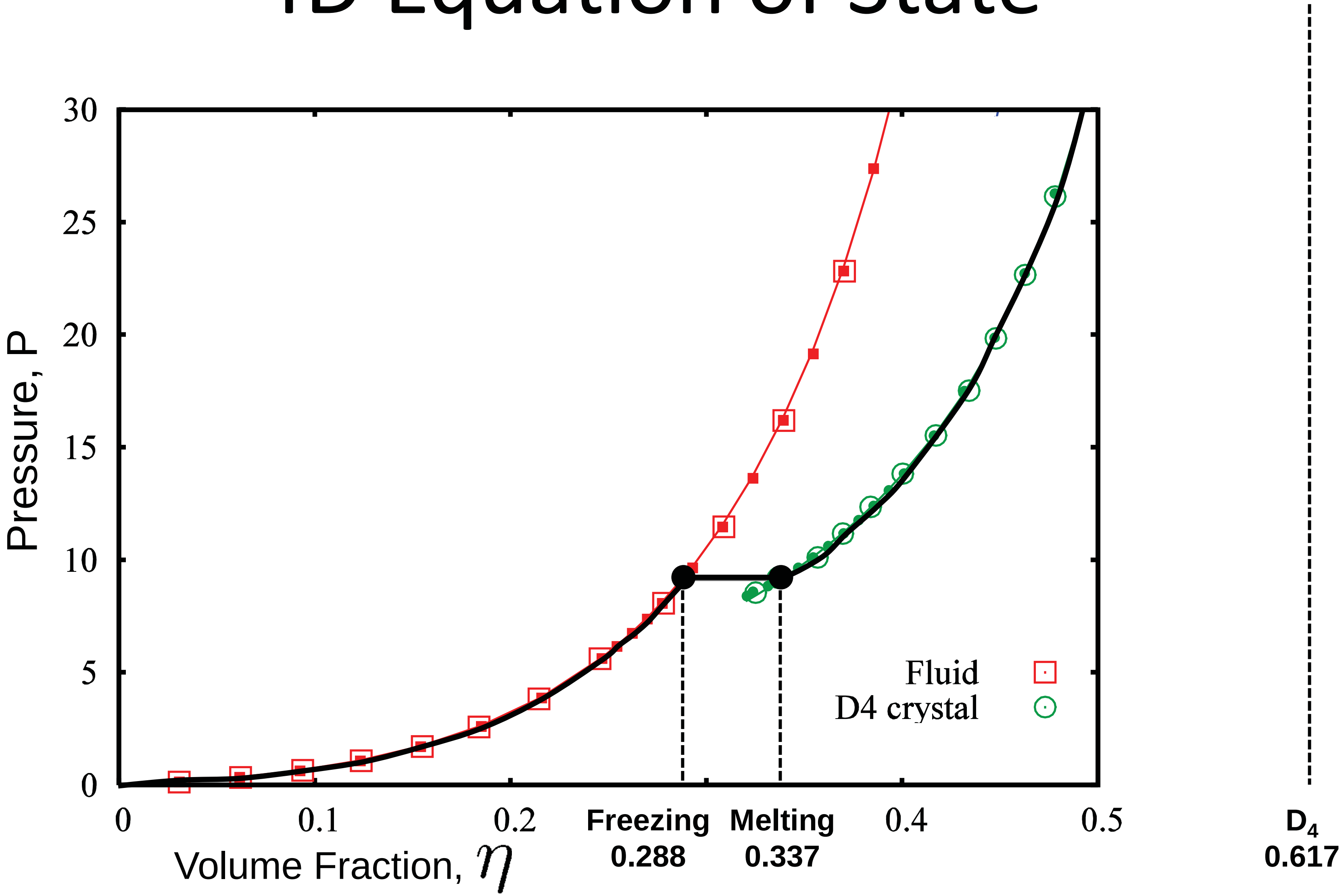
Simple Hypercubic

D4

Alternatively via FCC

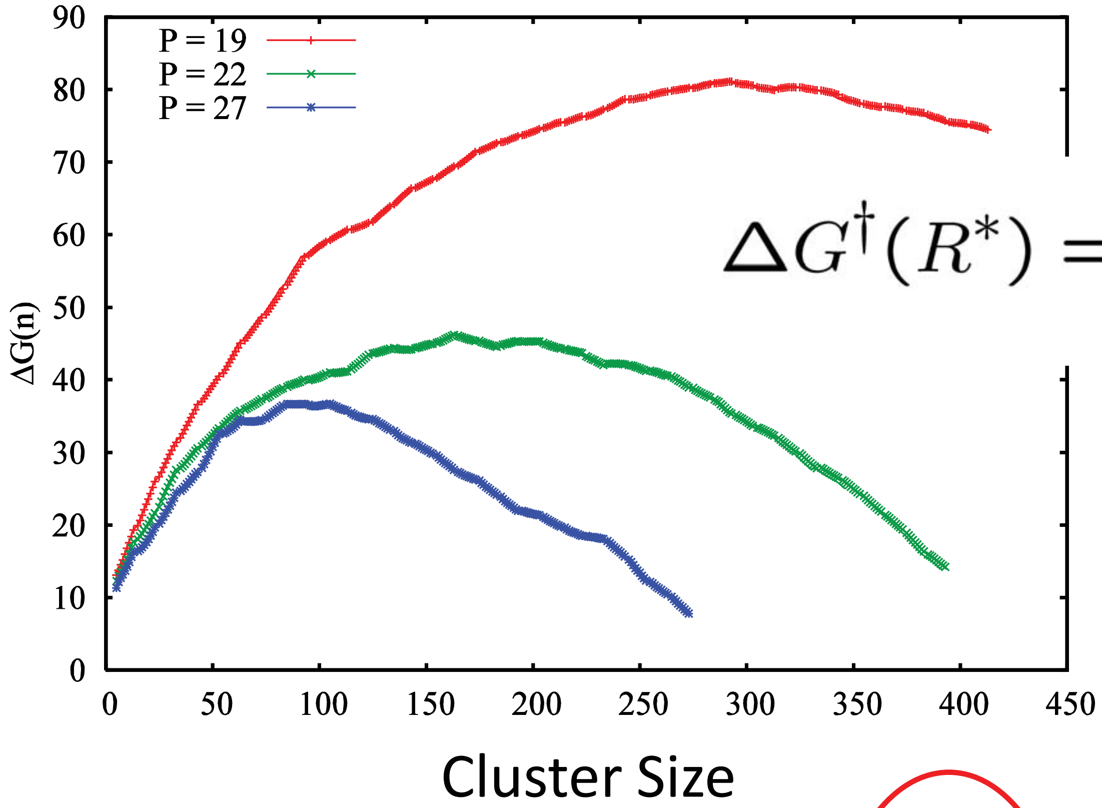


4D Equation of State



van Meel, Frenkel, Charbonneau, PRE (2009)

Nucleation Barrier



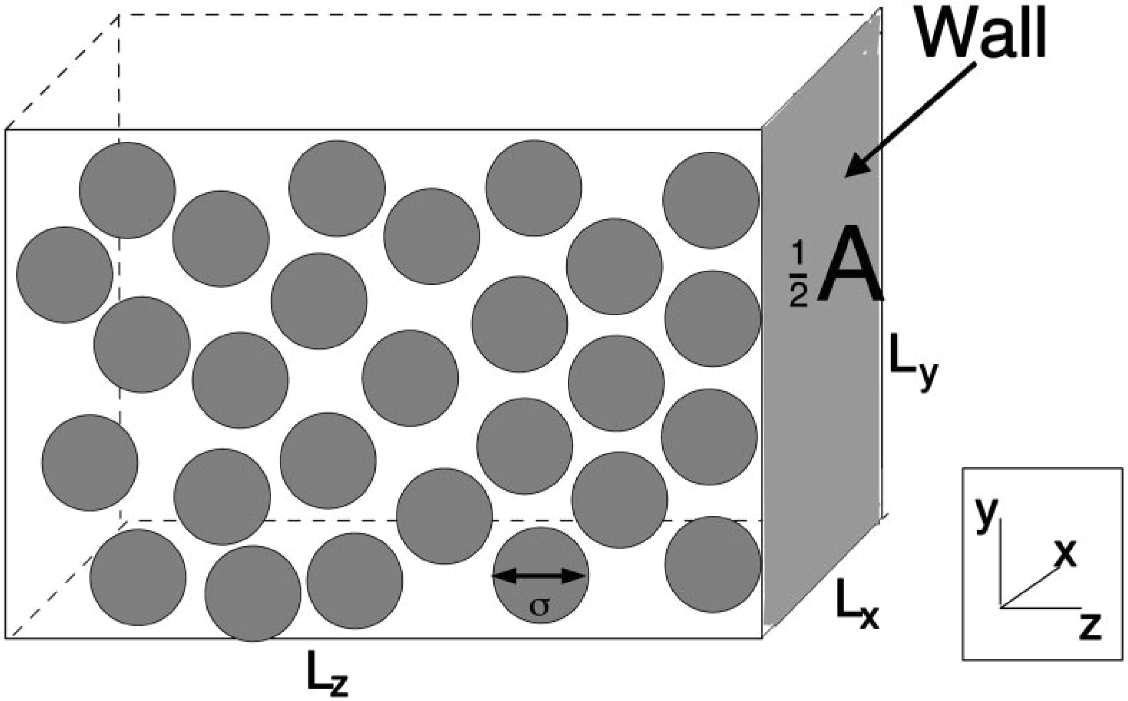
$$\Delta G^{\dagger}(R^*) = \frac{27\pi^2\gamma^4}{2\rho_{D_4}^3\Delta\mu^3}$$

In 3D, the surface tension is 2-3 times smaller for similar supersaturations!

P	$\Delta\mu$	ΔG^*	γ_{CNT}	n^*	n^*_{CNT}
19	-1.8	81	1.80	157	133
22	-2.3	42	1.94	75	60
27	-3.2	37	2.4	40	35

van Meel, Frenkel, Charbonneau, PRE (2009)

How frustrated is it?



At fluid fluid-crystal coexistence density

$$\gamma^{3D}_{\text{crystal}} = 0.557 \qquad \gamma^{3D}_{\text{wall}} = 1.98$$

$$\gamma^{4D}_{\text{crystal}} \approx 1.0 \qquad \gamma^{4D}_{\text{wall}} = 1.96$$

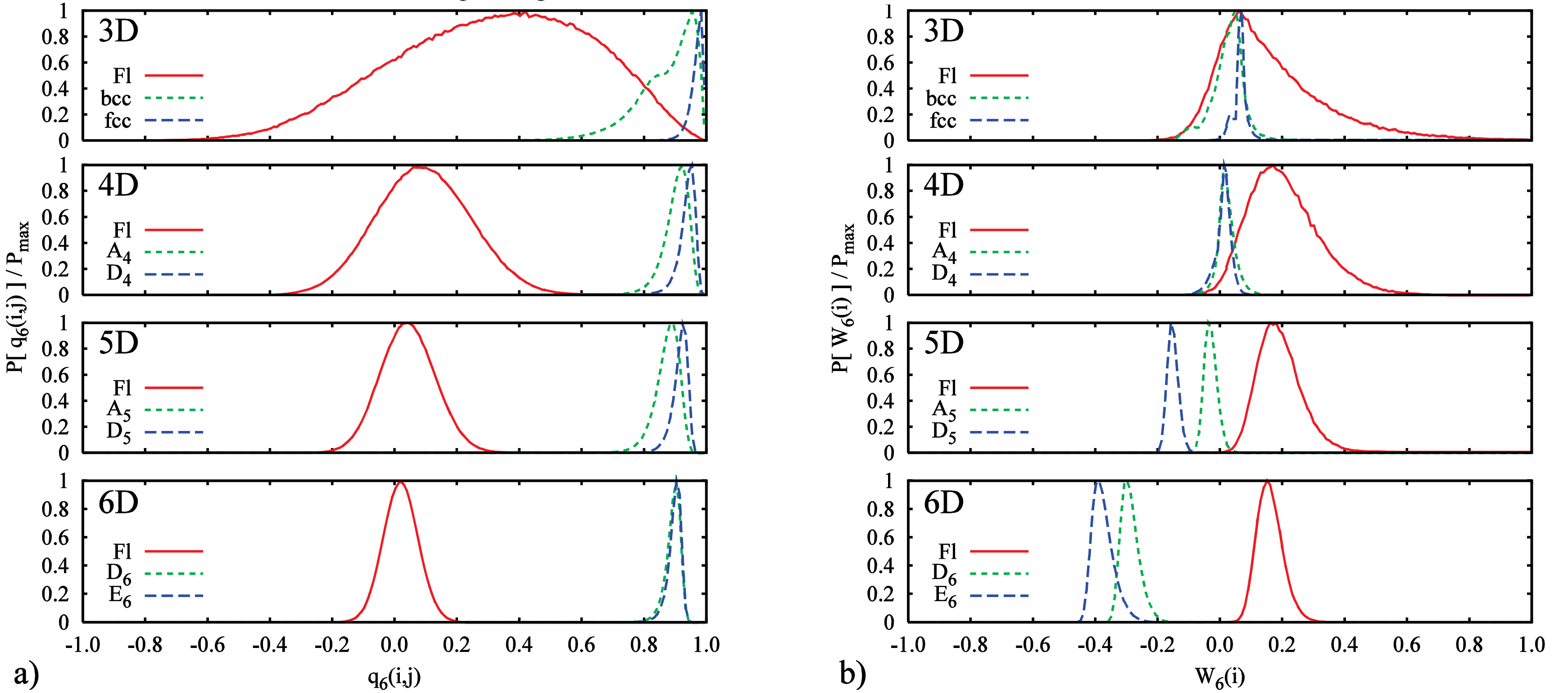
Laird and Davidchack, J. Phys. Chem. C (2007)
van Meel, Charbonneau, Fortini, Charbonneau, PRE (2009)

A Possible Explanation

Bond-order parameters *à la* Steinhardt and Nelson

$$\mathbf{q}_k(i)\cdot\mathbf{q}_k(j) = \frac{1}{N(i)N(j)}\sum_{p=1}^{N(i)}\sum_{q=1}^{N(j)} G_k^1(\hat{\mathbf{r}}_{pi}.\hat{\mathbf{r}}_{qj})$$

$$W_l(i) = c_l^d \frac{\sum_{\alpha,\beta,\delta}^{N(i)} \tilde{w}_l^d(\hat{\mathbf{r}}_{i\alpha}\cdot\hat{\mathbf{r}}_{i\beta}, \hat{\mathbf{r}}_{i\alpha}\cdot\hat{\mathbf{r}}_{i\delta}, \hat{\mathbf{r}}_{i\beta}\cdot\hat{\mathbf{r}}_{i\delta})}{2^{d-2}[N(i)]^3[q_l(i,i)]^{3/2}}$$



Liquid/crystal structural resemblance vanishes with dimension.

van Meel, Charbonneau, Fortini, Charbonneau, PRE (2009)

Some Speculation

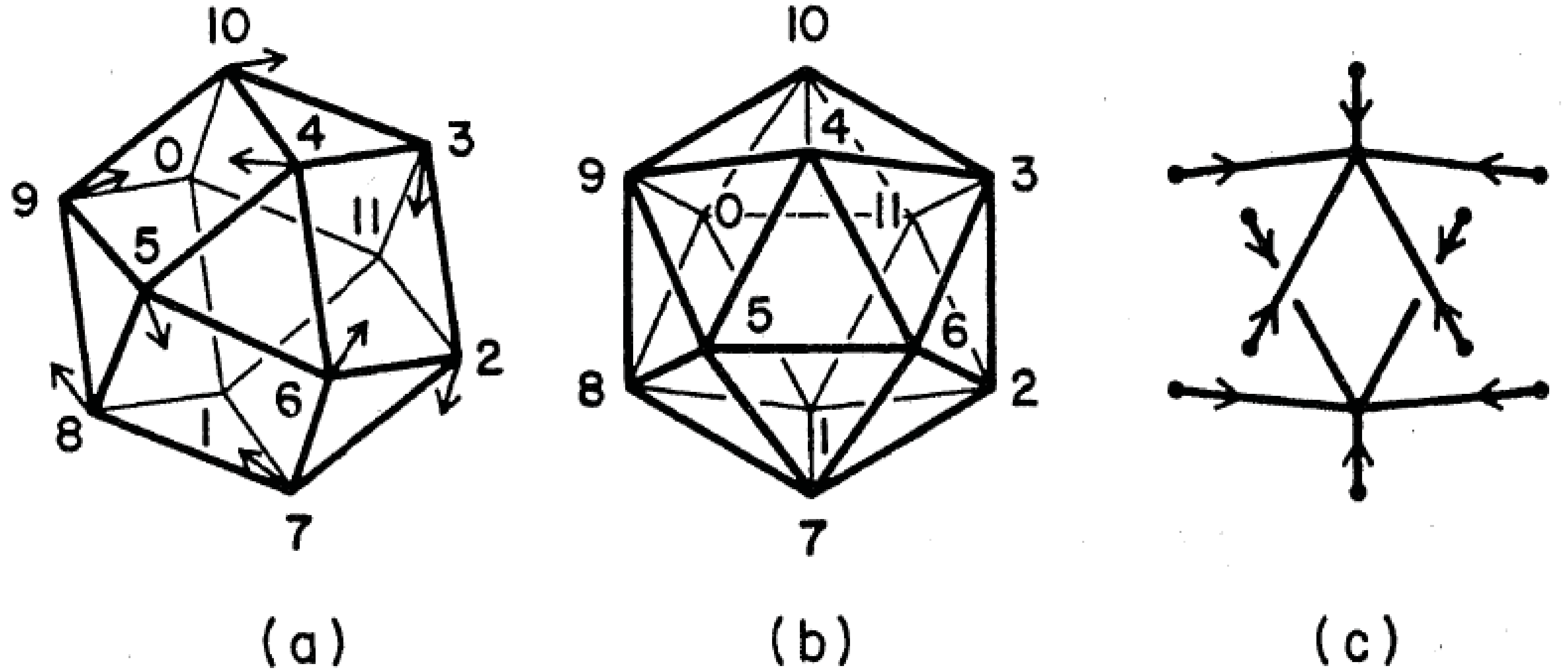


Figure 1.7. How to permute the planets.

Could the icosahedral configuration in fact help crystallization…

Conway and Sloane, a.k.a. the bible of sphere packings (1999)

PRL **103,** 135704 (2009) PHYSICAL REVIEW LETTERS week ending 25 SEPTEMBER 2009

Crystallization of Hard-Sphere Glasses

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(Received 11 May 2009; published 25 September 2009)

We study by molecular dynamics the interplay between arrest and crystallization in hard spheres. For state points in the plane of volume fraction ($0.54 \leq \phi \leq 0.63$) and polydispersity ($0 \leq s \leq 0.085$), we delineate states that spontaneously crystallize from those that do not. For noncrystallizing (or precrystallization) samples we find isodiffusivity lines consistent with an ideal glass transition at $\phi_g \approx 0.585$, independent of s. Despite this, for $s < 0.05$, crystallization occurs at $\phi > \phi_g$. This happens on time scales for which the system is aging, and a diffusive regime in the mean square displacement is not reached; by those criteria, the system is a glass. Hence, contrary to a widespread assumption in the colloid literature, the occurrence of spontaneous crystallization within a bulk amorphous state does not prove that this state was an ergodic fluid rather than a glass.

PRL **105,** 025701 (2010) PHYSICAL REVIEW LETTERS week ending 9 JULY 2010

Precursor-Mediated Crystallization Process in Suspensions of Hard Spheres

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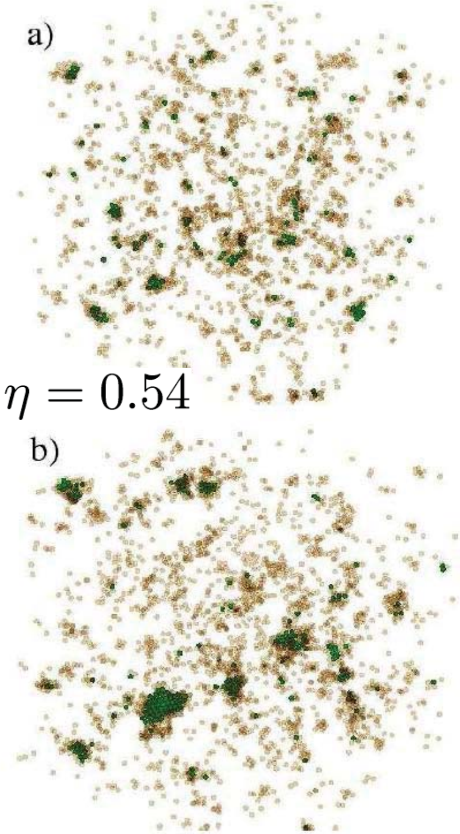
(Received 11 March 2010; revised manuscript received 15 April 2010; published 8 July 2010)

We report on a large scale computer simulation study of crystal nucleation in hard spheres. Through a combined analysis of real- and reciprocal-space data, a picture of a two-step crystallization process is supported: First, dense, amorphous clusters form which then act as precursors for the nucleation of well-ordered crystallites. This kind of crystallization process has been previously observed in systems that interact via potentials that have an attractive as well as a repulsive part, most prominently in protein solutions. In this context the effect has been attributed to the presence of metastable fluid-fluid demixing. Our simulations, however, show that a purely repulsive system (that has no metastable fluid-fluid coexistence) crystallizes via the same mechanism.



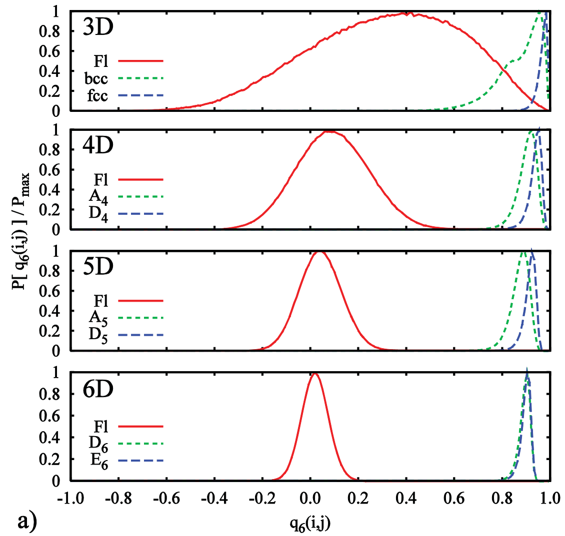
a)

$\eta = 0.54$

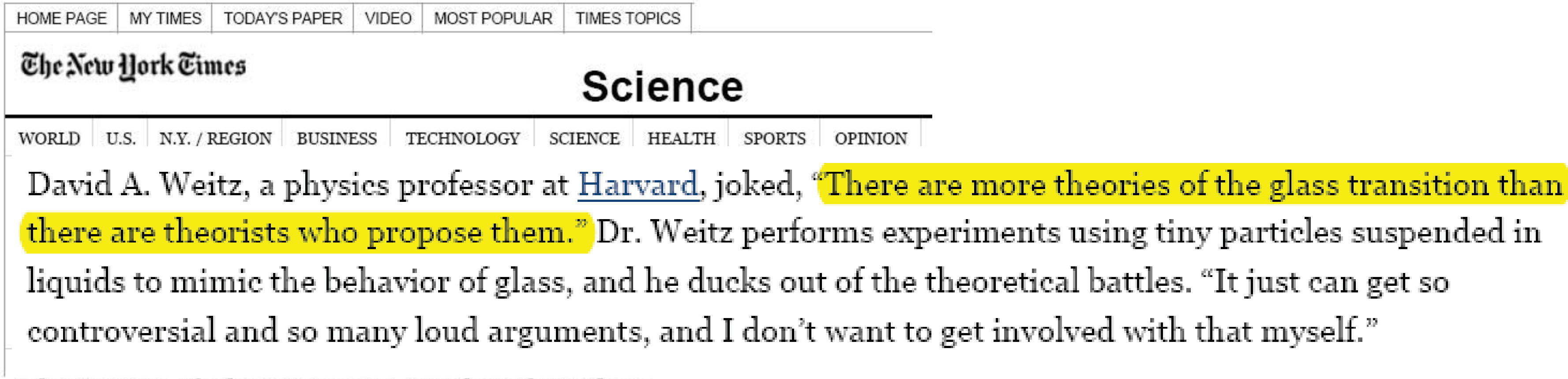
b)

What Have We Learned?

- 4D is truly hard to crystallize!
  - Optimally packed *cluster* matters little.
  - Polytetrahedral frustration dominates.
- 3D is marginally frustrated.
  - Monodisperse hard spheres freeze rather easily.
  - Icosahedral order is not singular.



D-testing!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The New York Times — Science

WORLD | U.S. | N.Y. / REGION | BUSINESS | TECHNOLOGY | SCIENCE | HEALTH | SPORTS | OPINION

David A. Weitz, a physics professor at Harvard, joked, "There are more theories of the glass transition than there are theorists who propose them." Dr. Weitz performs experiments using tiny particles suspended in liquids to mimic the behavior of glass, and he ducks out of the theoretical battles. "It just can get so controversial and so many loud arguments, and I don't want to get involved with that myself."

The Nature of Glass Remains Anything but Clear

Mark Interrante

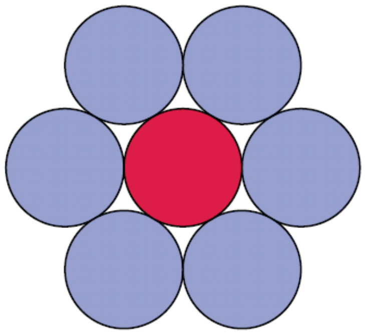
And further, my son, take note of this: of the making of ~~books~~ theories there is no end, and much learning is a weariness to the flesh.

-Ecclesiastes 12:12

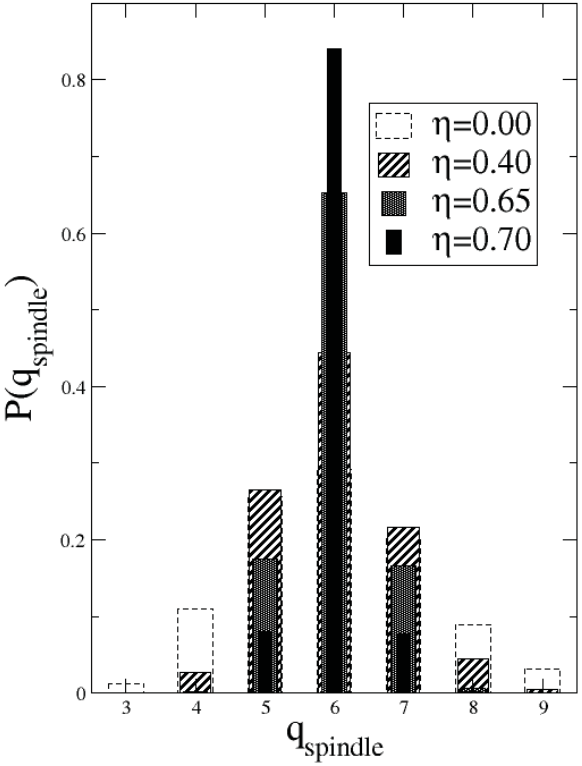
cf. Francesco's talk and arXiv:1107.4666v2

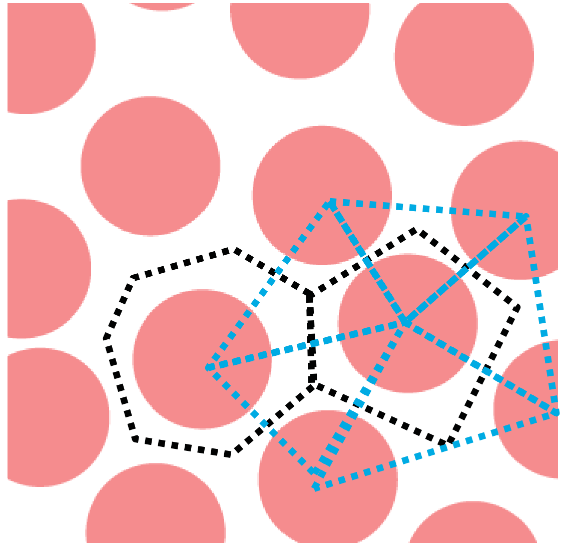
K. Chang, NYT, 29/07/2008

Disclinations in 2D



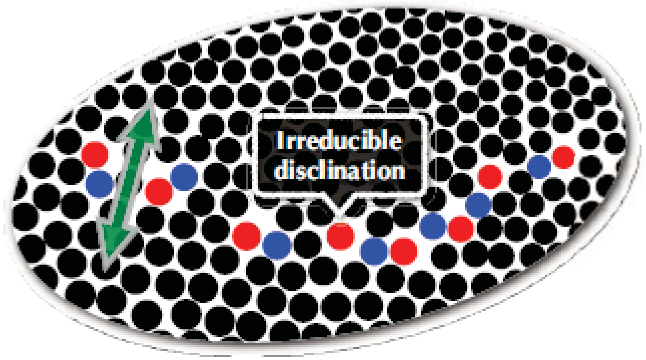
$$\bar{q}_{\text{spindle}} = \frac{2\pi}{\arccos(1/2)} = 6$$

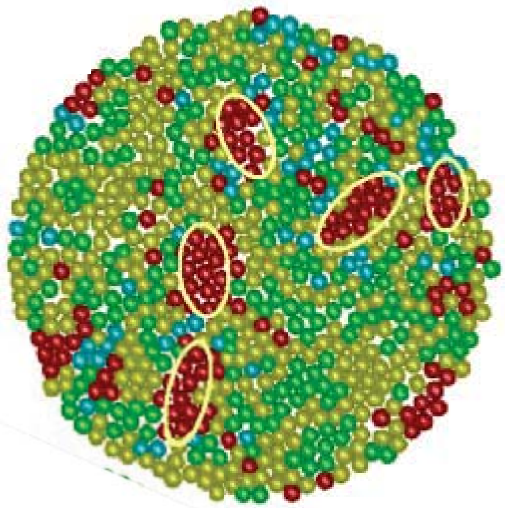




Basis for KTHNY 2D melting theory: at high densities 5-7 defects are paired.

Curvature and size dispersity lead to an imbalance in defects and to an ordering length scale.

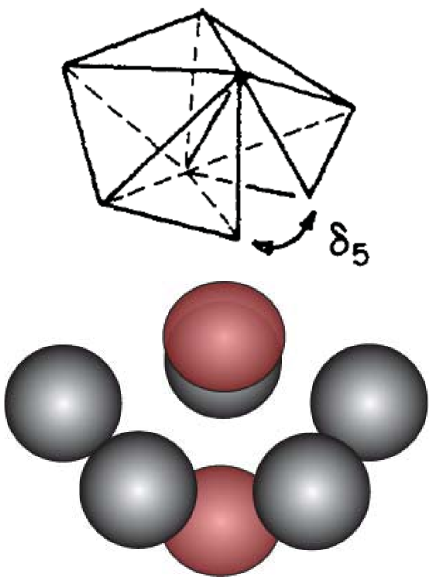


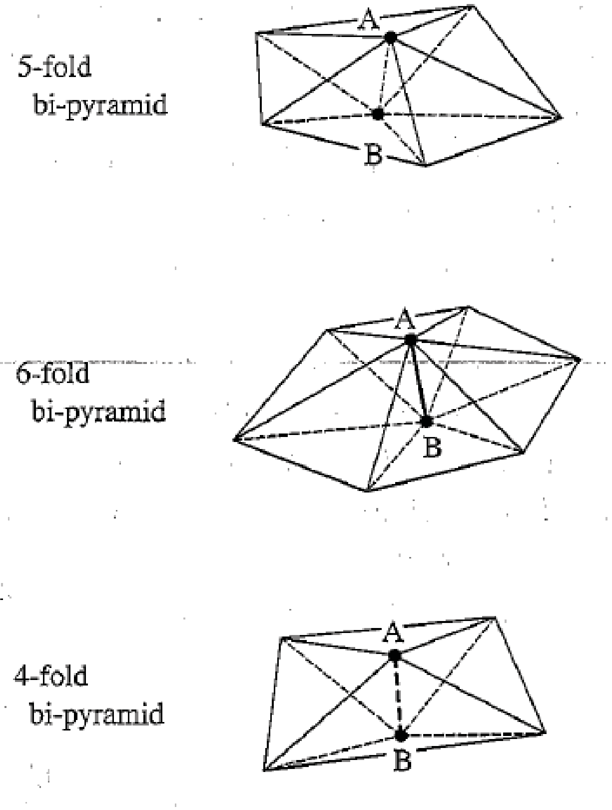


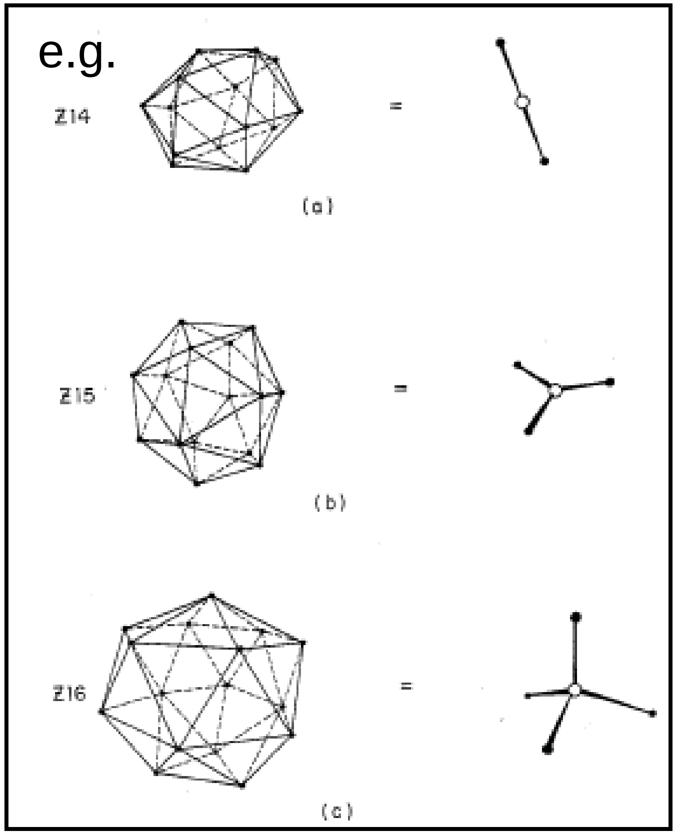
Sausset and Tarjus (2010)
Watanabe and Tanaka (2008)

Bond Spindles (Disclinations) in 3D

In (frustrated) Euclidean space: $$\bar{q}^{\text{ideal}}_{\text{spindle}} = \frac{2\pi}{\arccos(1/3)} = 5.104$$

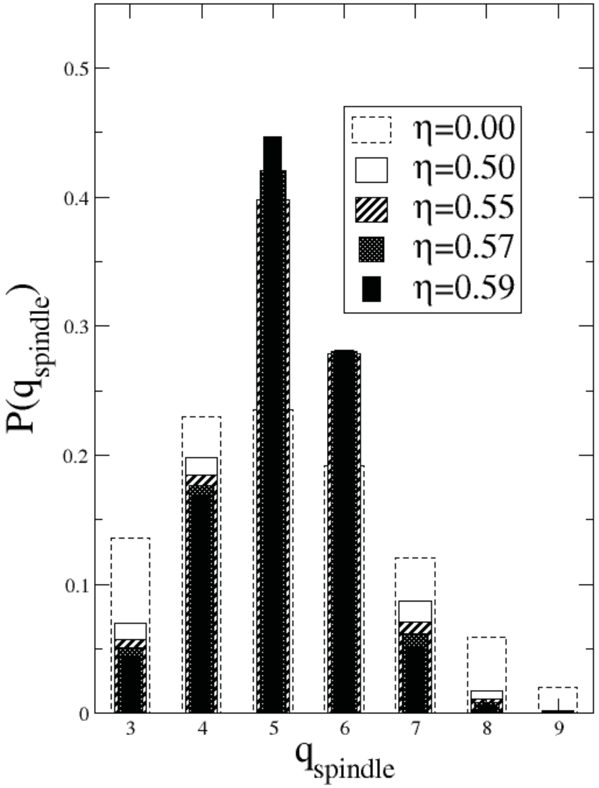






Nelson, *Defects and Geometry in Condensed Matter Physics* (2002)

Bond Spindle Lines



Frank-Kasper phases are polytetrahedral with ordered disclinations.

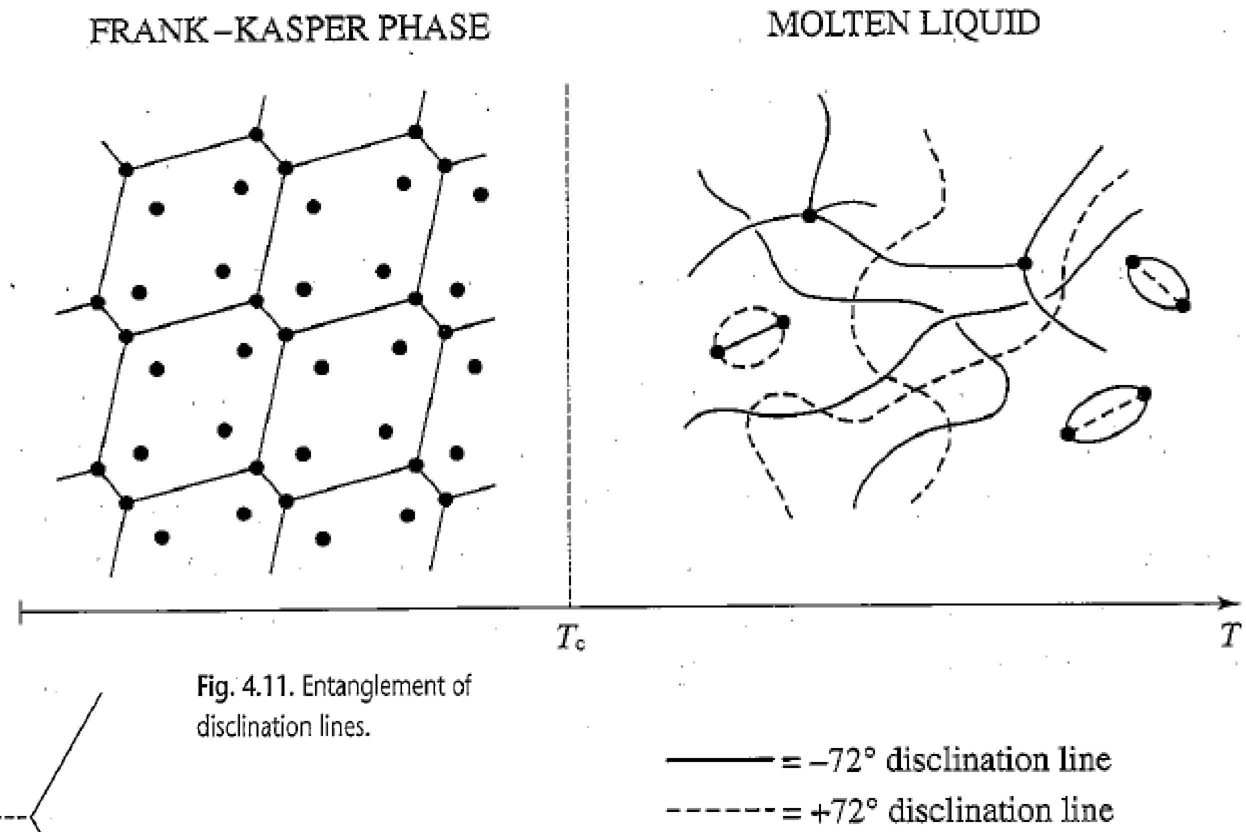
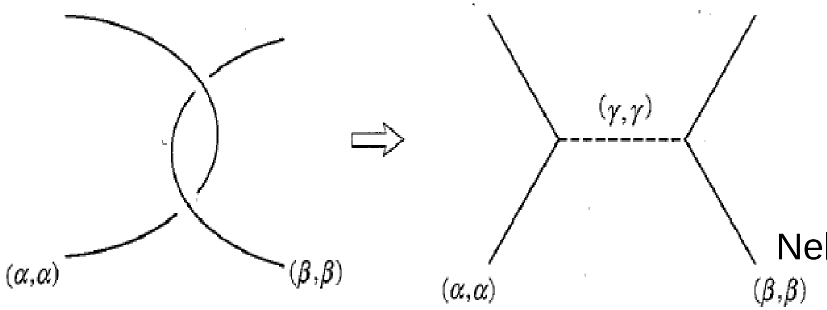
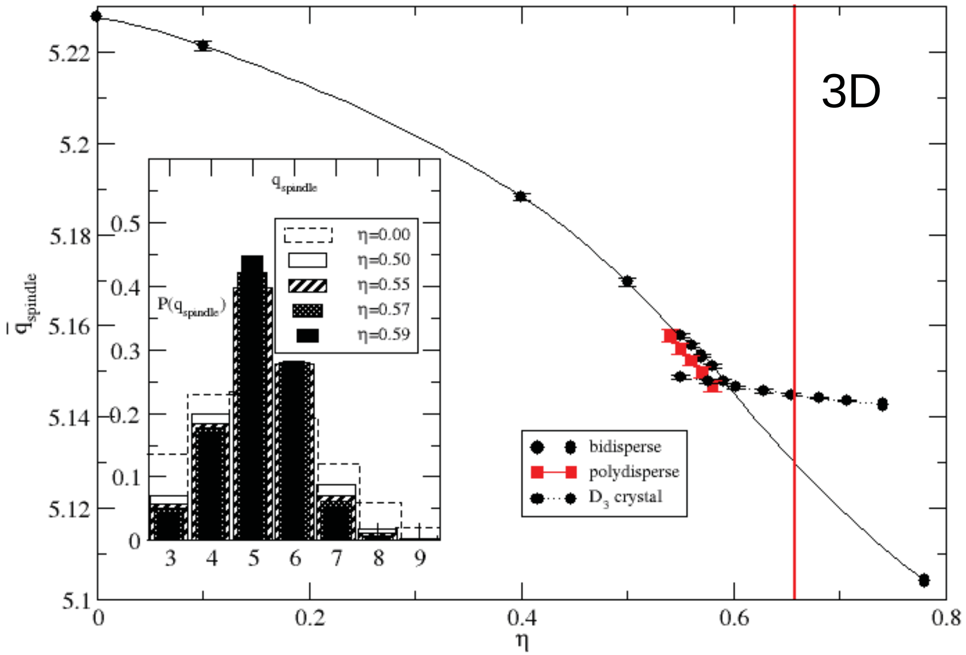


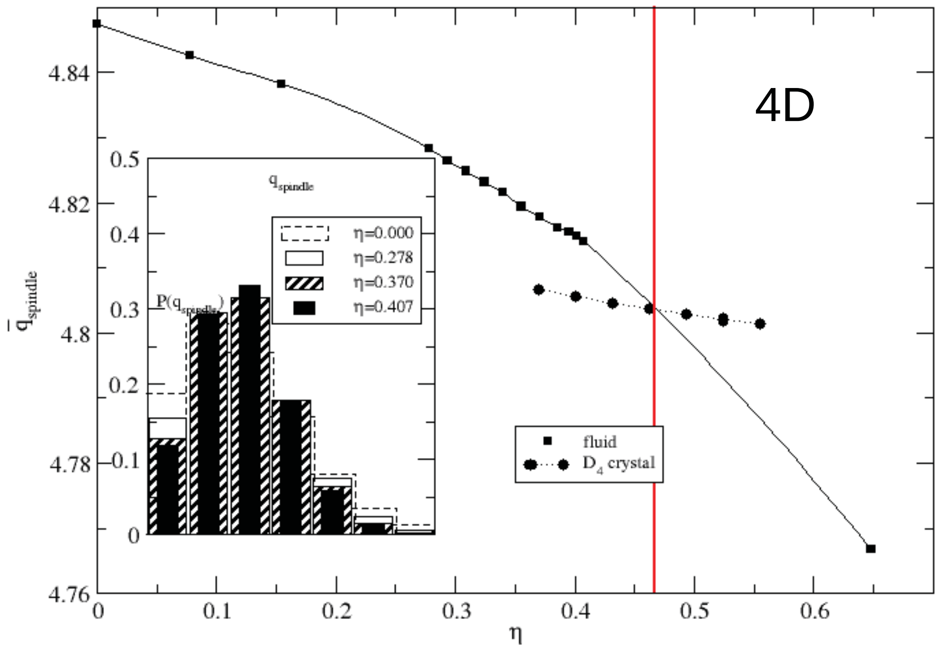
Fig. 4.11. Entanglement of disclination lines.

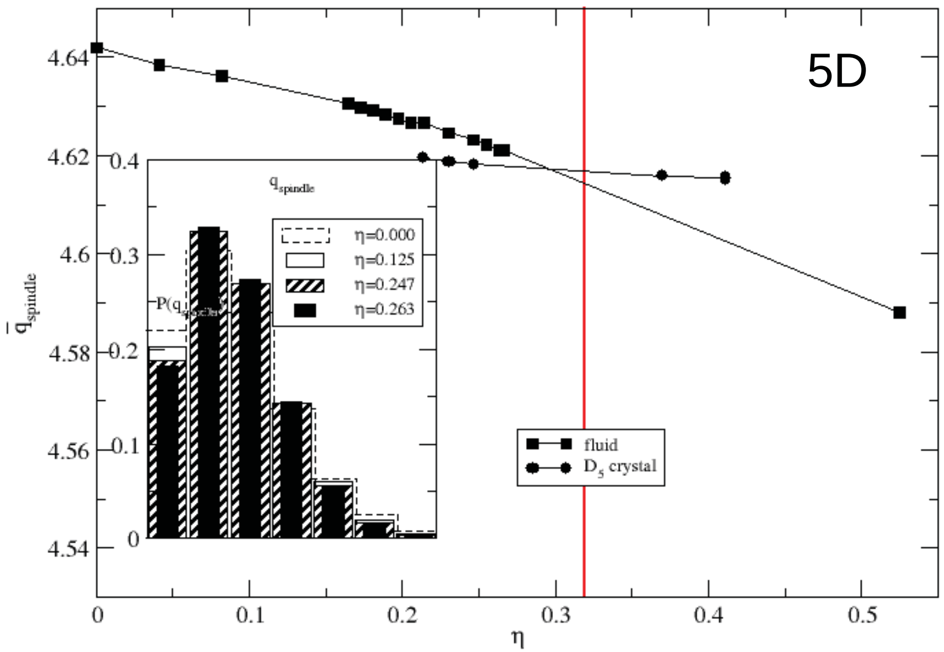


Nelson, *Defects and Geometry in Condensed Matter Physics* (2002)
Charbonneau, Charbonneau, Tarjus (in preparation)



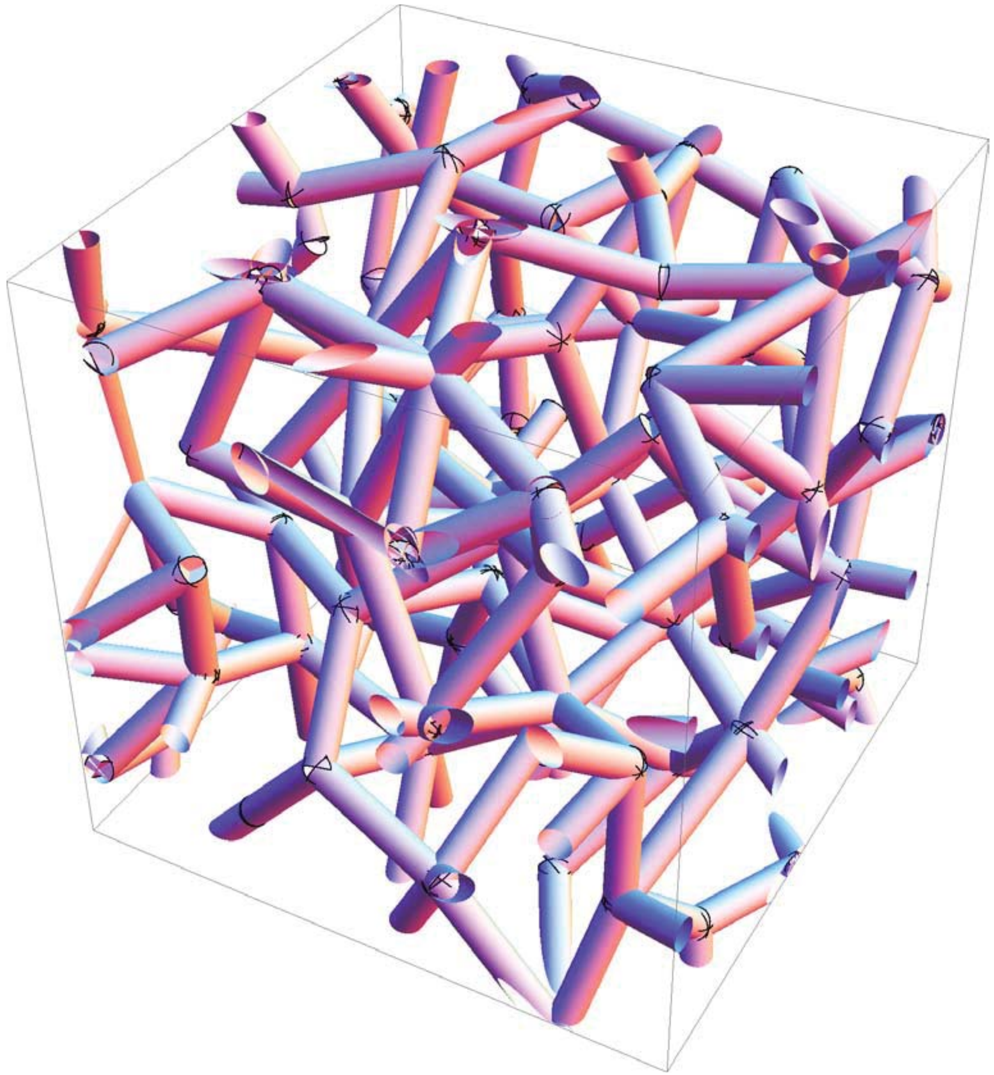
Ordering is appears to vanish with dimension.





Charbonneau and Charbonneau (in preparation)

q=6 bond spindle network



Although the network of 5-fold spindles percolates, it still leaves 6-7 defects per particle...

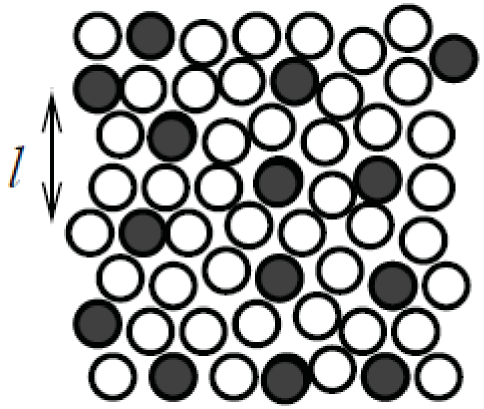
Charbonneau, Charbonneau, Tarjus, arXiv:1108.2494v1

(Agnostic) Static Length

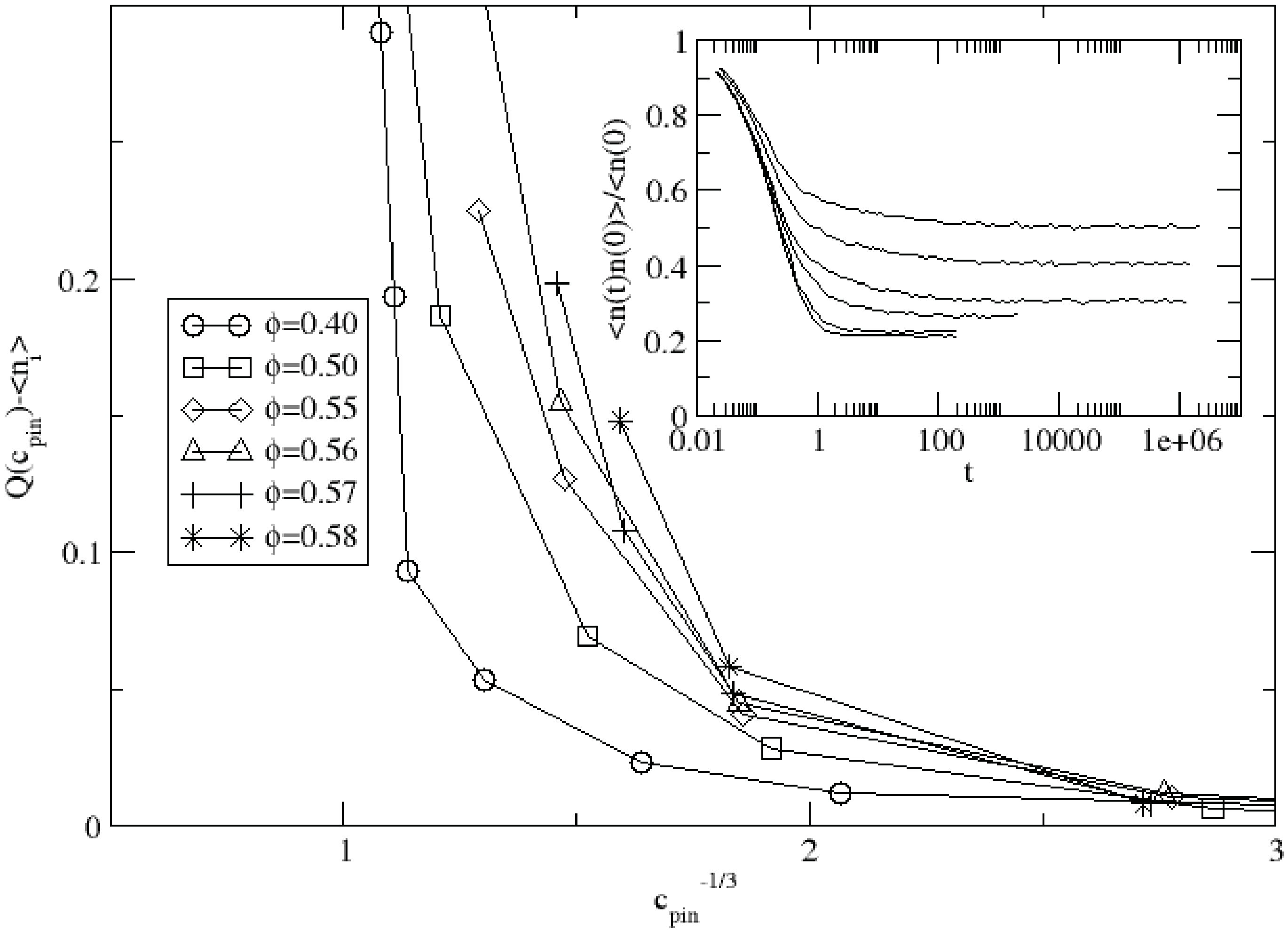
- Rigorous bounds between length and time scales imply the divergence of a point-to-set length when the relaxation time diverges (Montanari and Semerjian, 2006; Cavagna *et al.* 2007).

- Is there a growing static length of spindle order?

Pinning Overlap

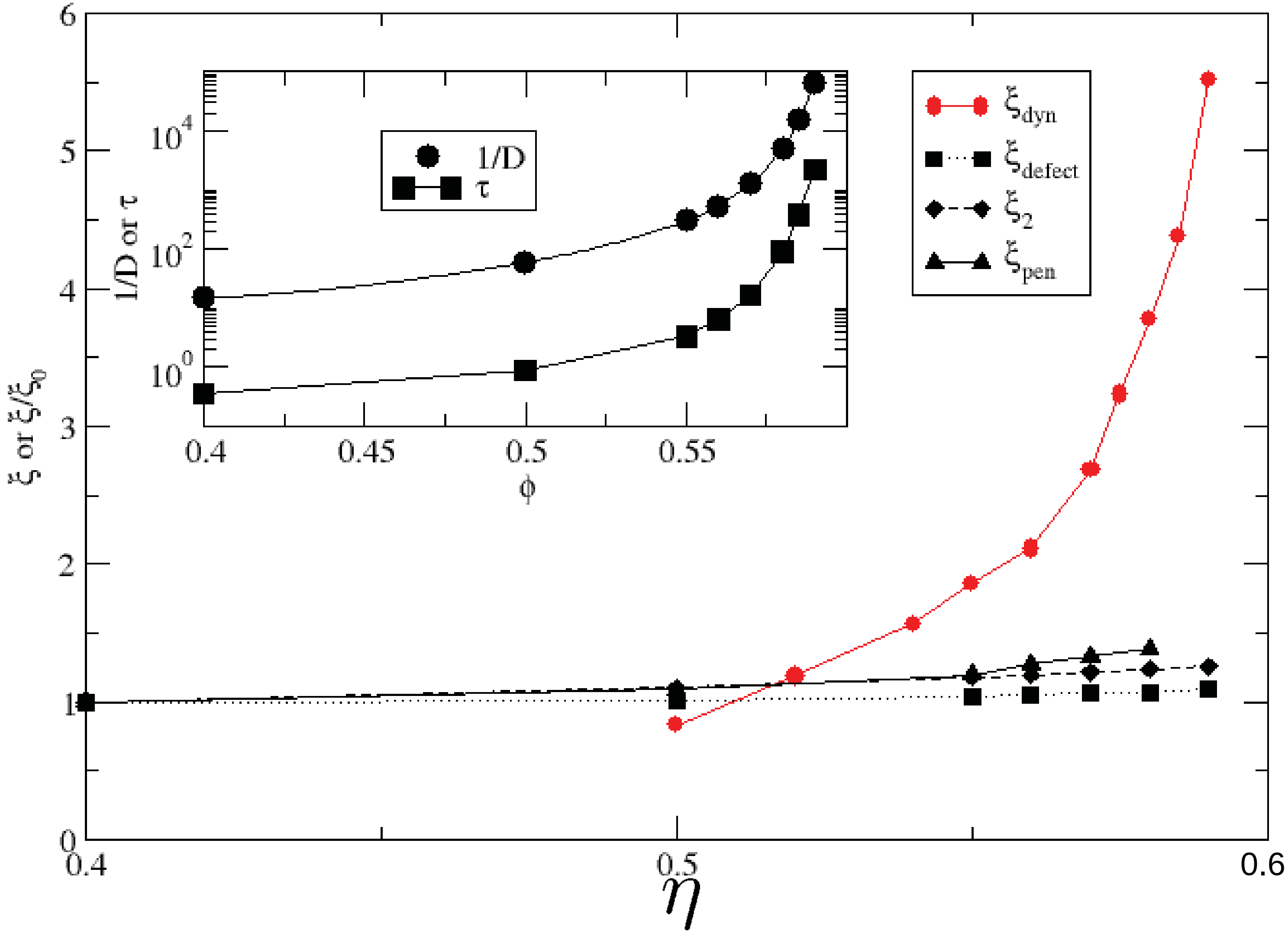


Berthier and Kob,
arXiv:1105.6203v1



Charbonneau, Charbonneau, Tarjus, arXiv:1108.2494v1

Static v Dynamic Lengthscale



Charbonneau, Charbonneau, Tarjus, arXiv:1108.2494v1
Flenner, Zhang, Szamel (2011)

Summary

- The topological defect scenario may only work for $d \leq 3$
- In d=3 Euclidean space, it is (seemingly) not a useful description.
- May work on S^3 with a smaller radius.
- A static lengthscale can be defined, but it does not seem to play a key role at early stages of the dynamical slowdown.

Collaborators:

- Benoit Charbonneau (St. Jerome's U. and Waterloo)
- Andrea Fortini (U. Bayreuth)
- Koos van Meel (FOM Amolf)
- Gilles Tarjus (Paris VI – UPMC)

Special thanks to:

- David Nelson (Harvard)

&

THANK YOU!