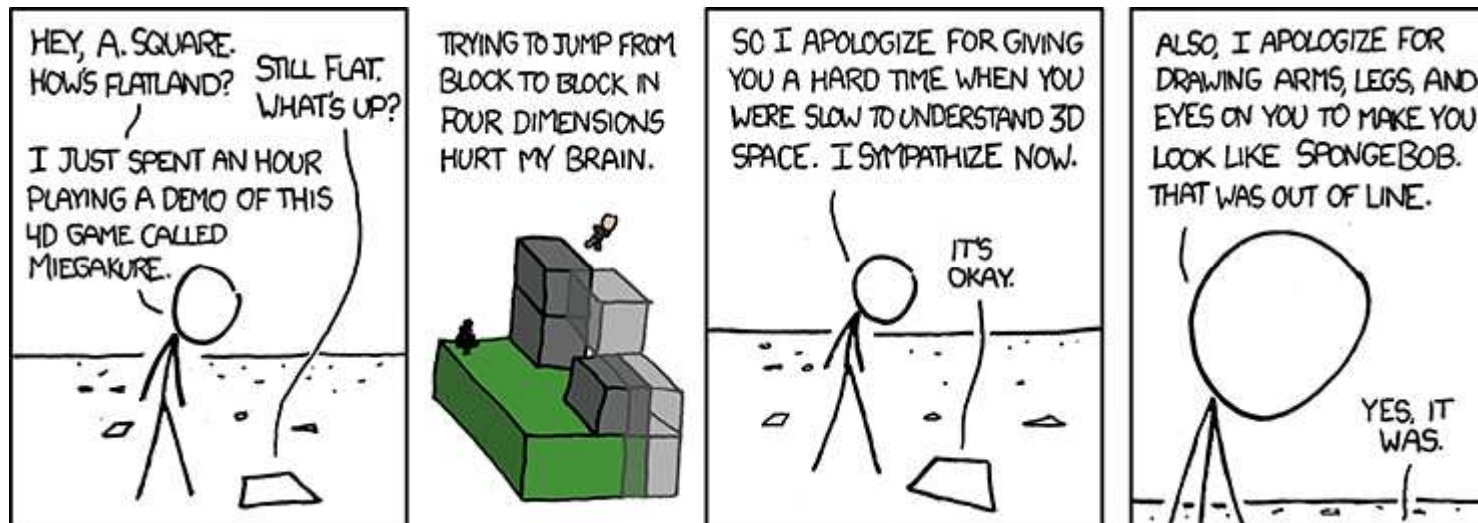# How hard is it to form a glass? Insights from beyond 3D.

The Physics of Glasses 2010 @ KITP

Patrick Charbonneau

Duke University

In 4D we can experience more…

[…] that ye, being rooted and grounded in love, May be able to comprehend with all saints what is the breadth, and length, and depth, and height;
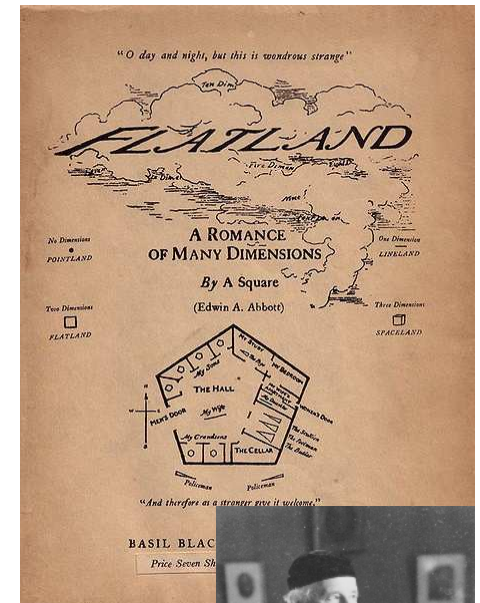
-Ephesians III, 17-18 (KJV)

Spirits have four dimensions

-Henry More (1614-1687)

Cambridge mystical philosopher

Spissitude is used to describe a fourth spatial dimension in which he believed the spiritual realm extended, and refers to a measurement of an object's length in that dimension.

Miegakure is a puzzle platform indie video game that explores the fourth dimension in the same way that a 2D object explores 3D.
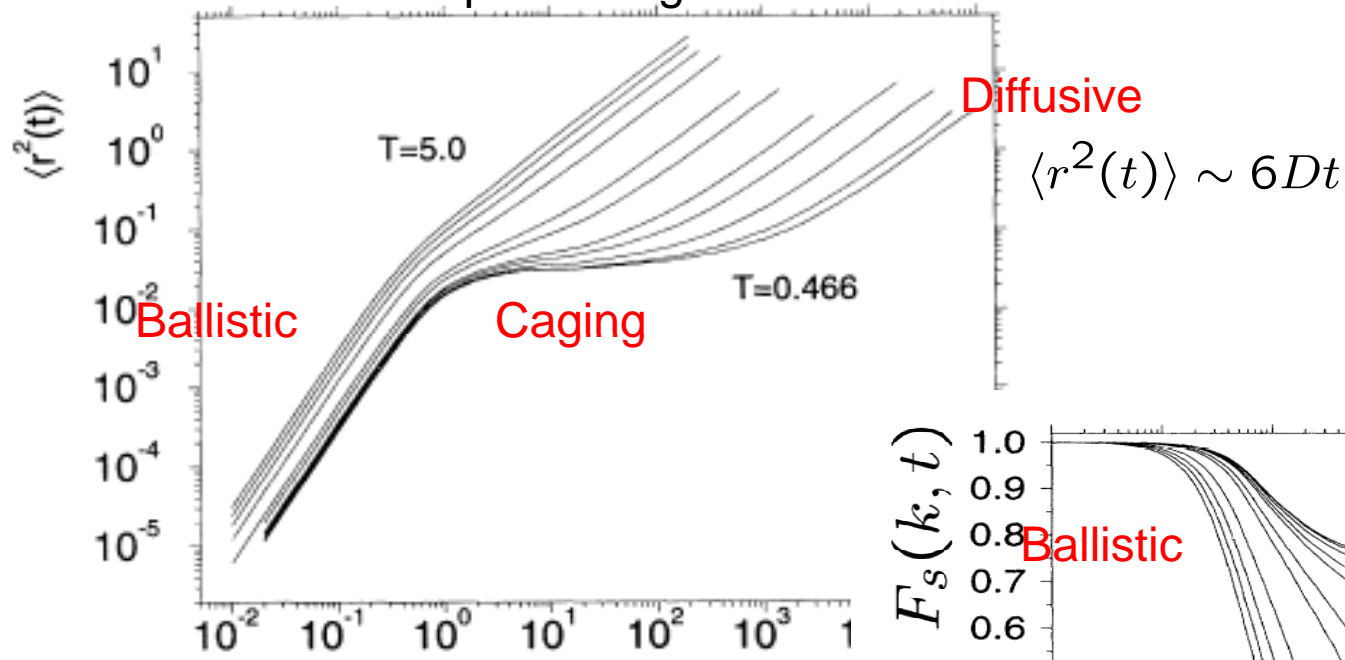
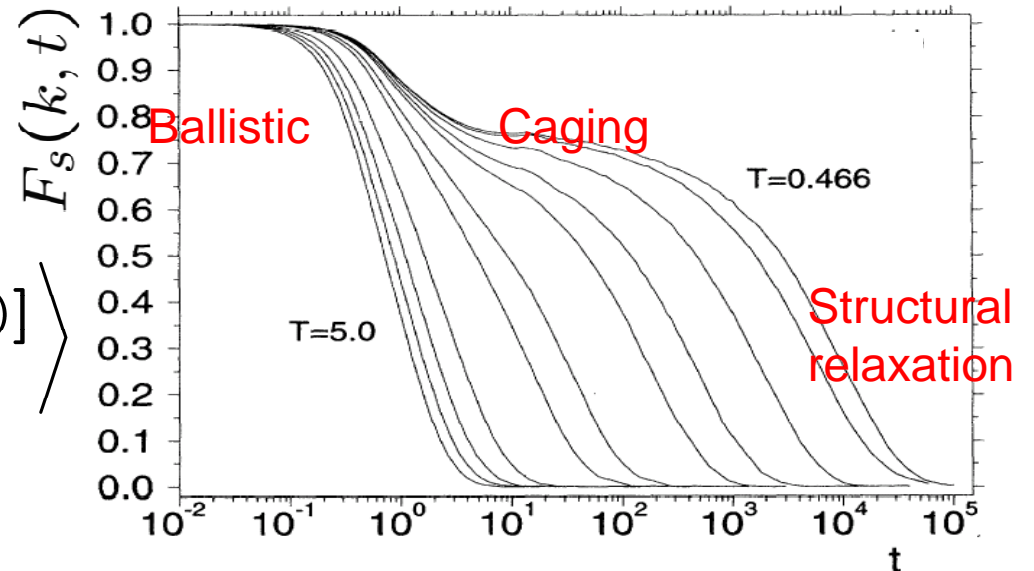Edwin Abbott Abbott was an English schoolmaster and theologian.
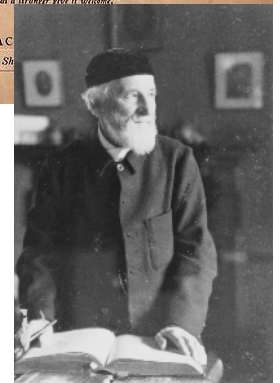
Fragile Caging

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

Diffusive

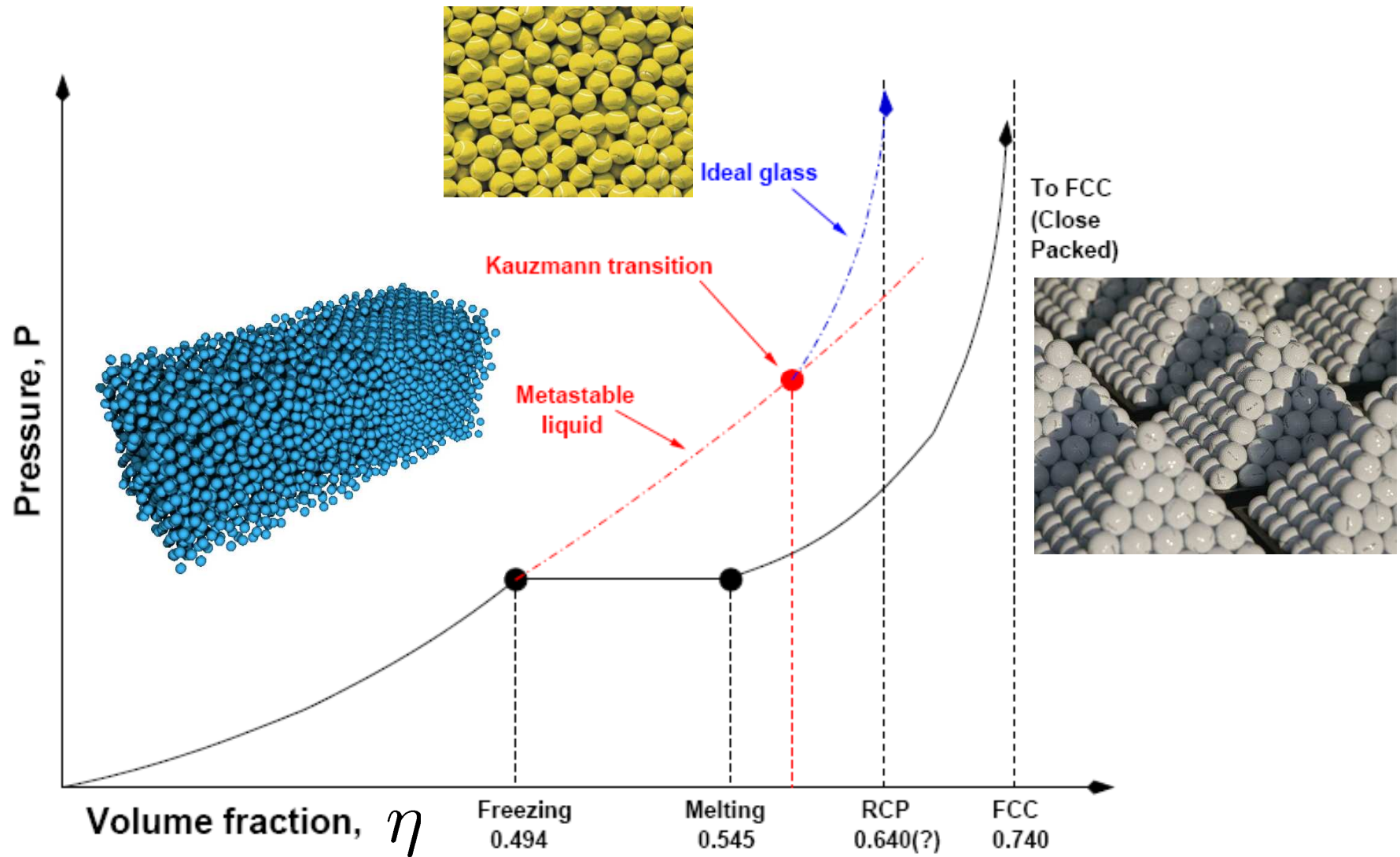$$\langle r^2(t) \rangle \sim 6Dt$$

T=5.0

Ballistic   Caging

T=0.466

$$F_s(k,t) = \left\langle \frac{1}{N} \sum_j e^{i\mathbf{q}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]} \right\rangle$$

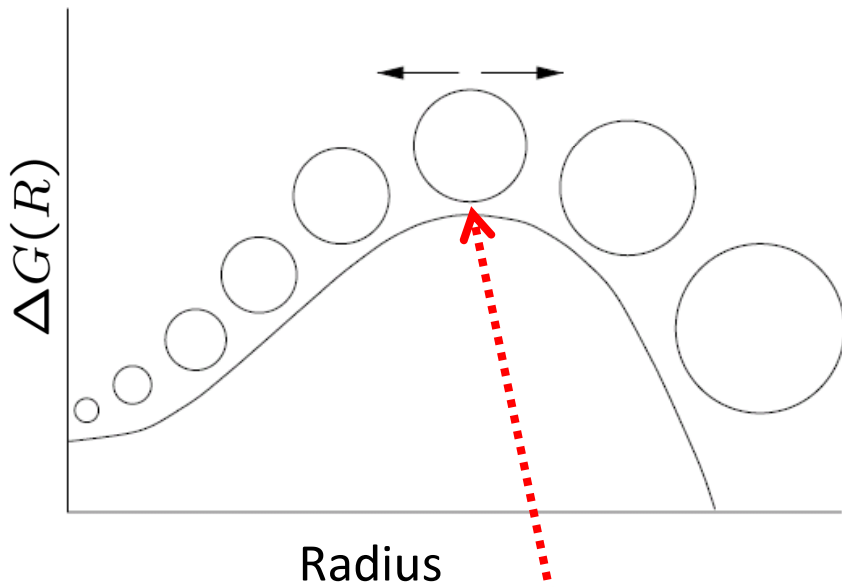$$F_s(k,t) \sim A e^{(-t/\tau_\alpha)^\gamma}, \gamma < 1$$

Ballistic   Caging

T=0.466

T=5.0

Structural relaxation

Kob and Andersen, PRE (1995)

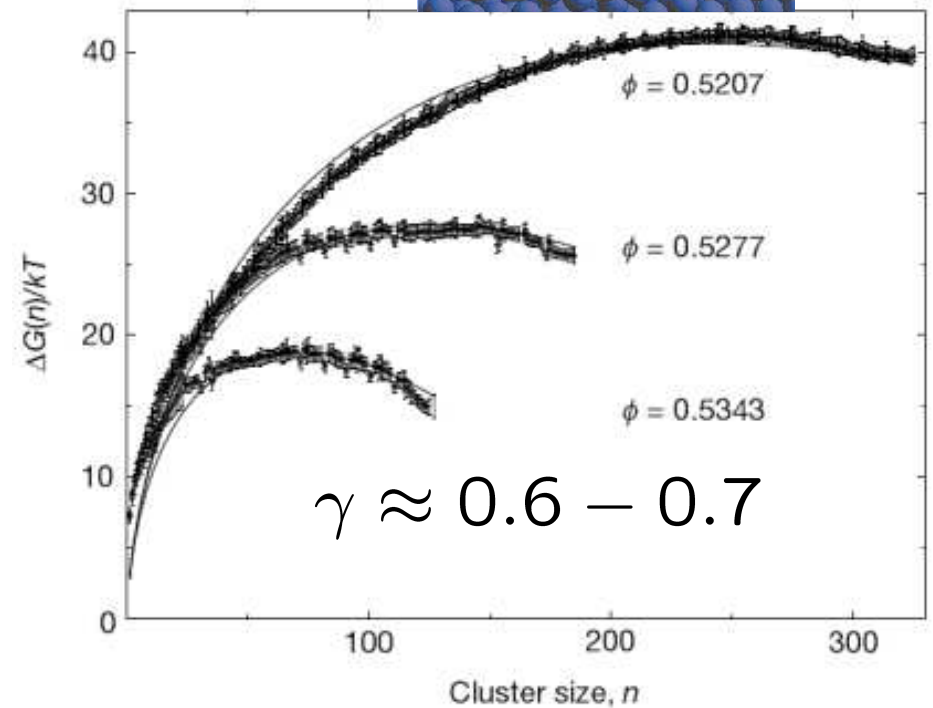# Hard Sphere Glasses

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

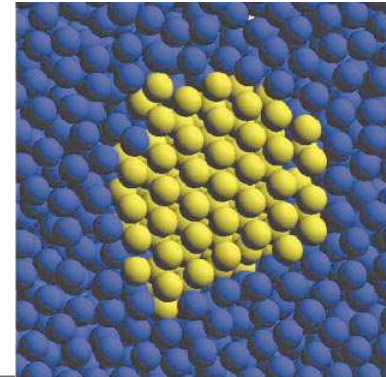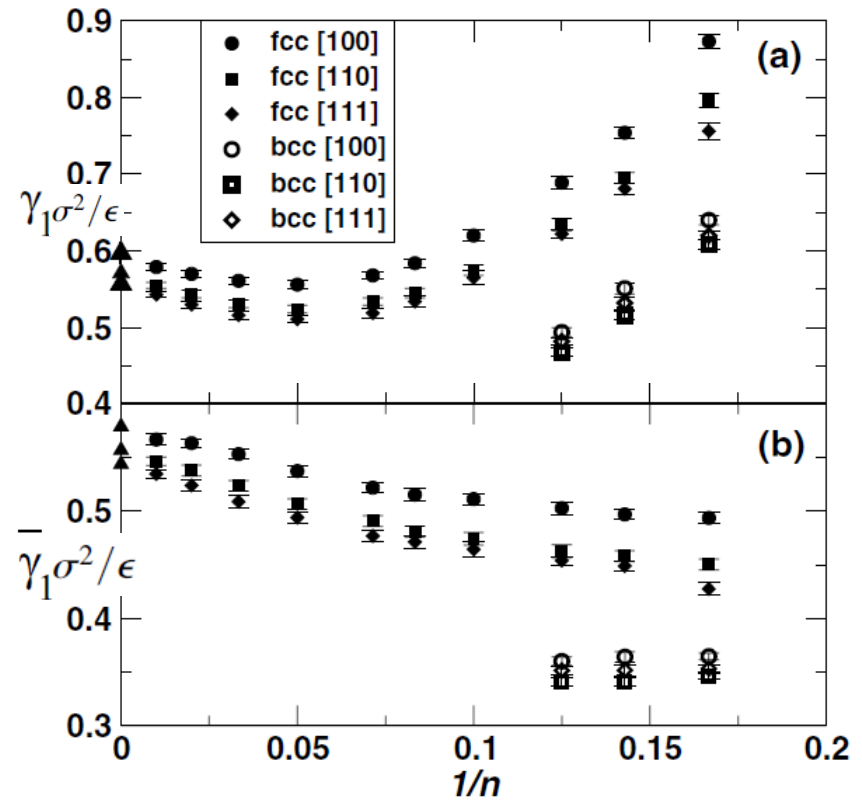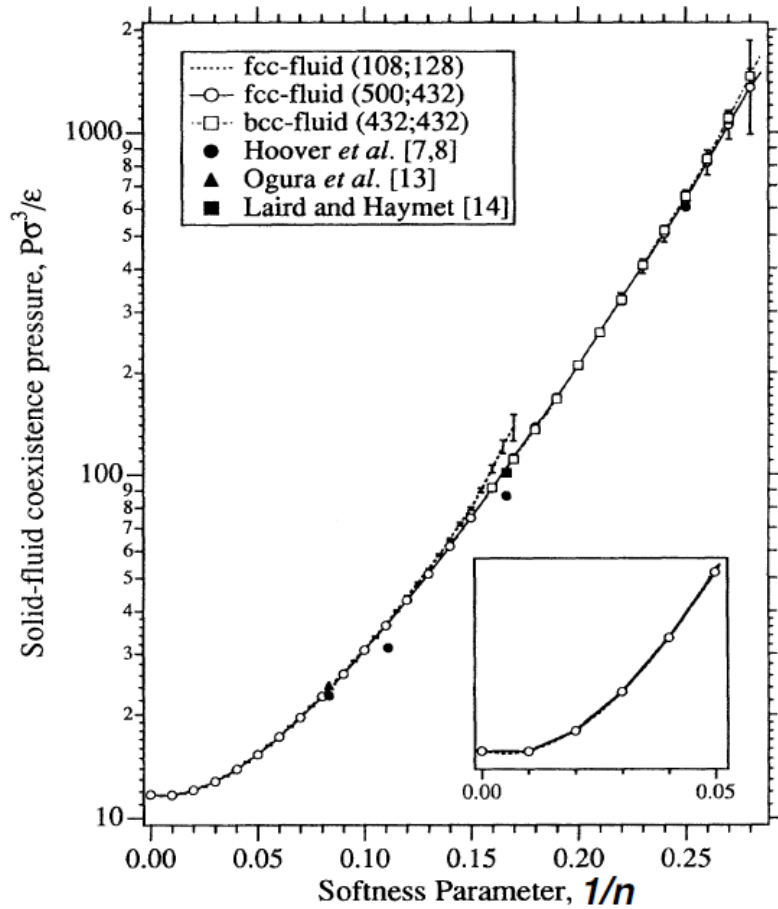# Crystal Nucleation

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

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

$$\gamma \approx 0.6 - 0.7$$

Auer and Frenkel, Nature (2002)

Aside: On the Normality of HS

$$U(r) = \epsilon \left(\frac{\sigma}{r}\right)^n$$

Agrawal and Kofke, PRL (1995)
Davidchack and Laird, PRL (2005)

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 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.

TOPICAL REVIEW

The frustration-based approach of supercooled liquids and the glass transition: a review and critical assessment

G Tarjus[1], S A Kivelson[2], Z Nussinov[3,4] and P Viot[1]

What has often been taken as the paradigm of (geometric) frustration in amorphous systems is the case of icosahedral order in simple one-component liquids in which the atoms interact through spherically symmetric pair potentials. The ground state of four atoms is a perfect tetrahedron, with the atoms sitting at the vertices, and 20 such tetrahedra can be combined to form a regular 13-atom icosahedron (figure 5). Frank [25] was the first to stress the importance of local icosahedral order in simple atomic liquids and liquid metals. He showed that the most stable cluster made of a central atom and a shell of 12 neighbours is indeed an icosahedron, and not an arrangement associated with the actual crystalline phases, bcc, fcc, or hcp. In three-dimensional Euclidean space, however, this locally preferred structure (tetrahedral or icosahedral) cannot propagate freely to tile the whole space: this is what is meant by *geometric frustration.* The global ground state of the system is instead an fcc or hcp crystal.

The concept of frustration is more easily grasped by contrasting the case of spherical particles in three dimensions with other situations [26, 27]. Systems of spherical particles in two-dimensional Euclidean space, i.e. discs on a plane, are not subject to frustration: the locally preferred structure is a regular hexagon, with one atom at the centre and six neighbours at the

Geometrical Frustration
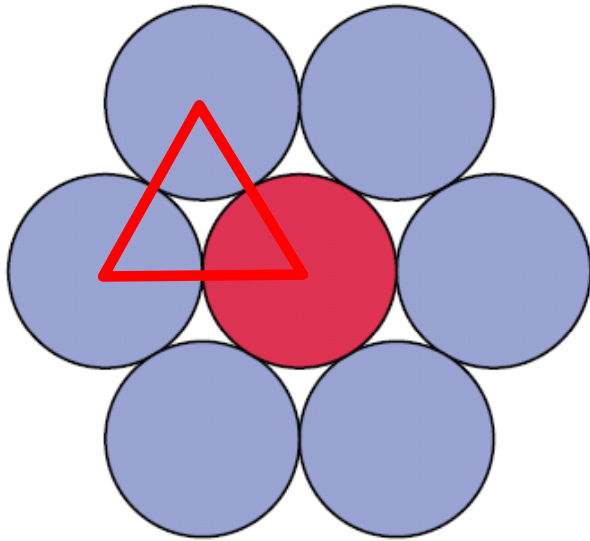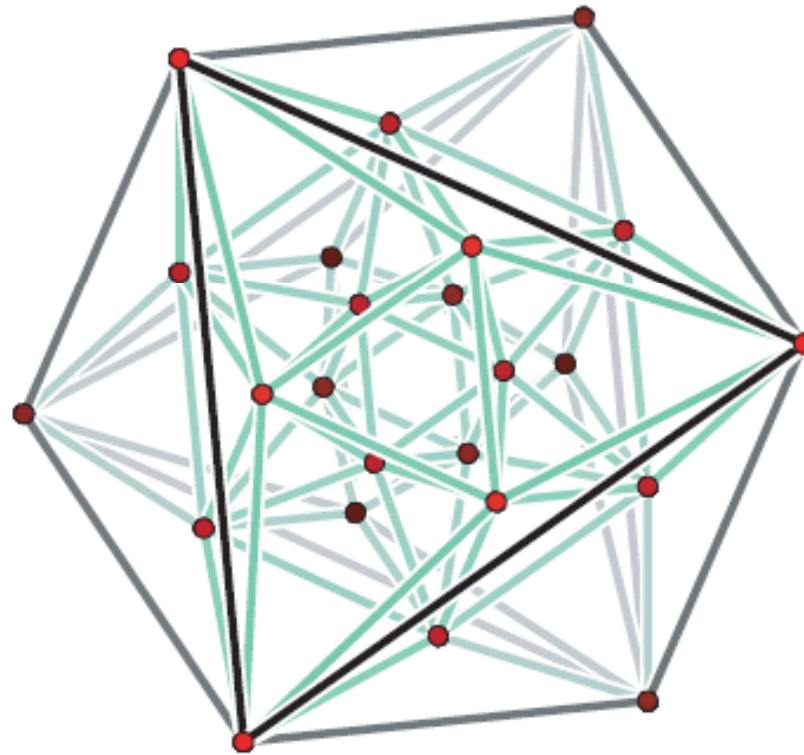

Triangular Lattice
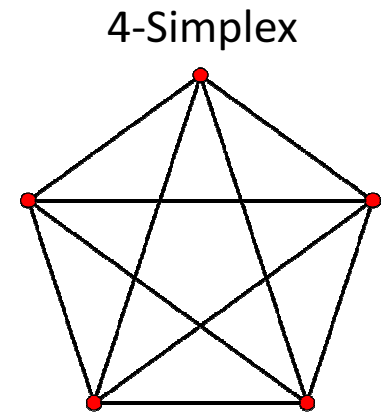AND
2-Simplex
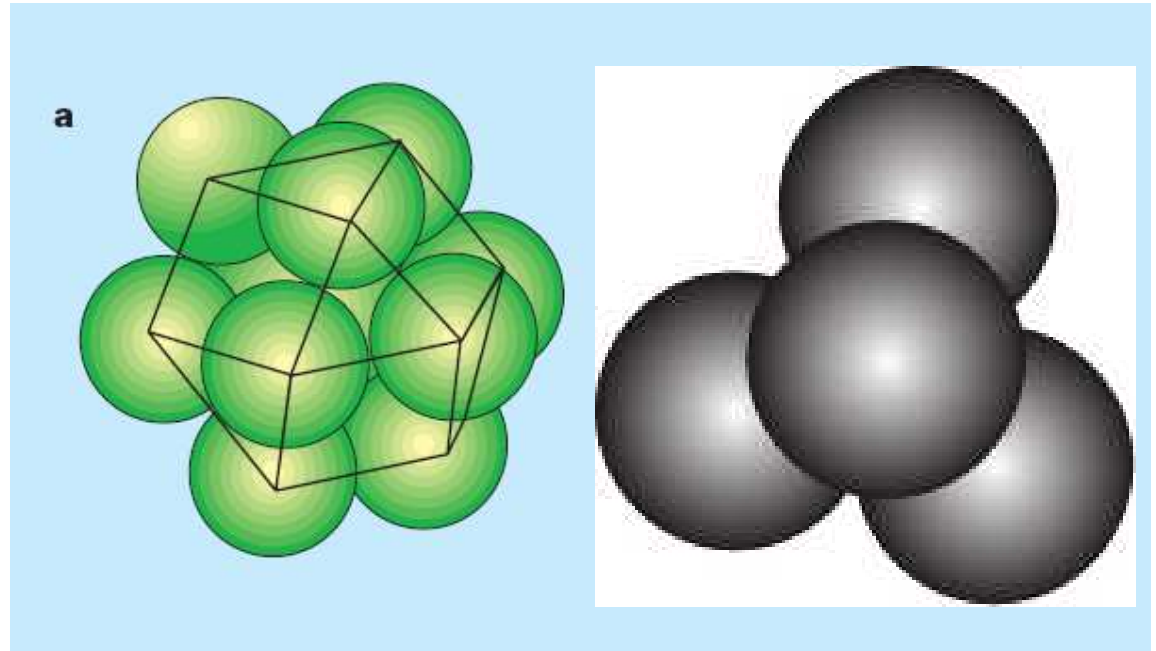
FCC Lattice   vs.   ~~Icosahedron~~
3-Simplex

Spaepen, Science (2000)

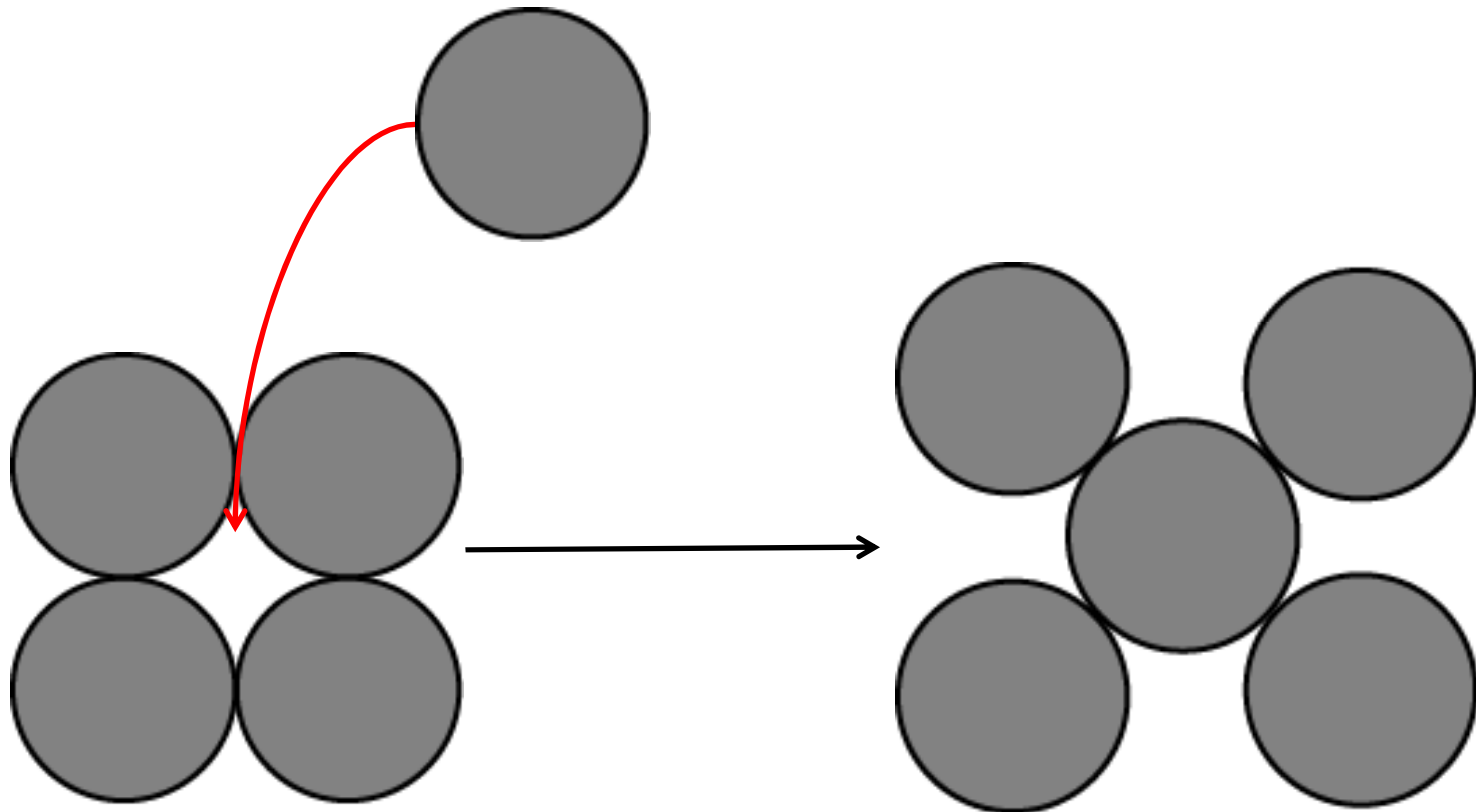# Geometrical Frustration in 4D

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

D_4 Lattice
IS NOT
Simplex Based

4-Simplex

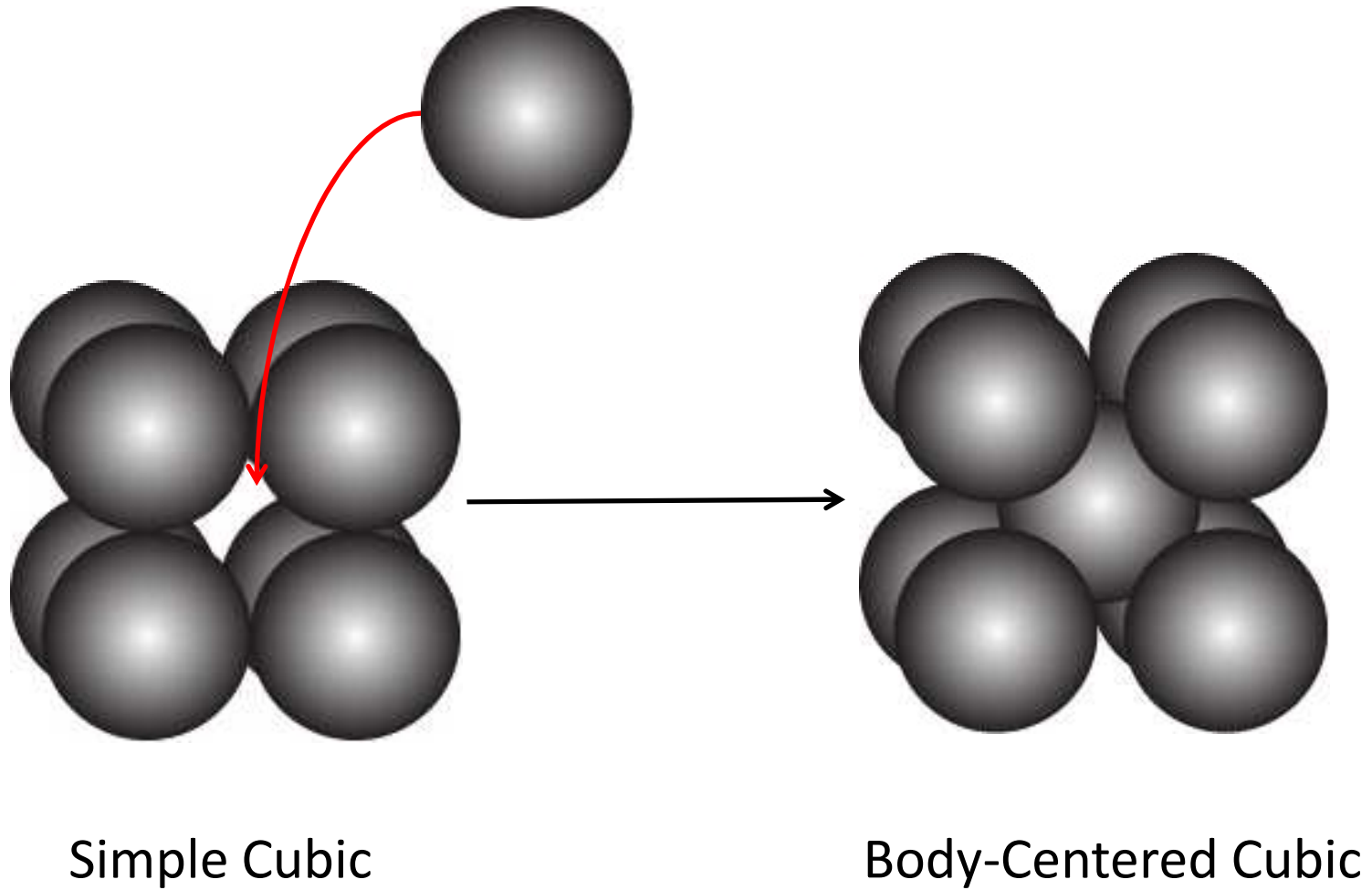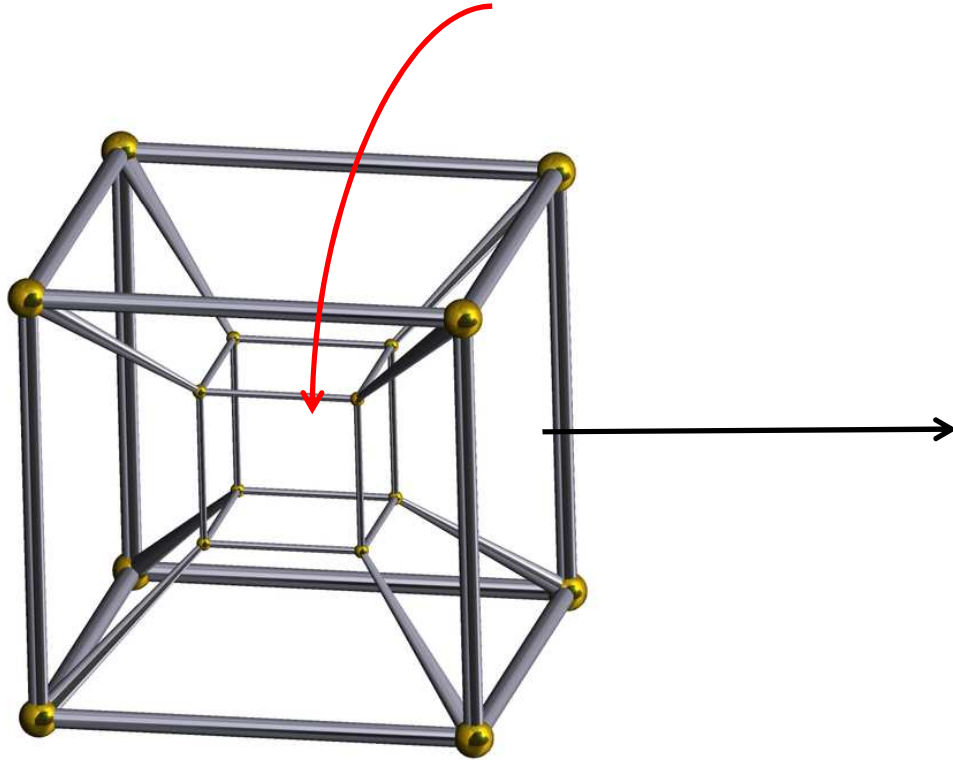# 2D Packing

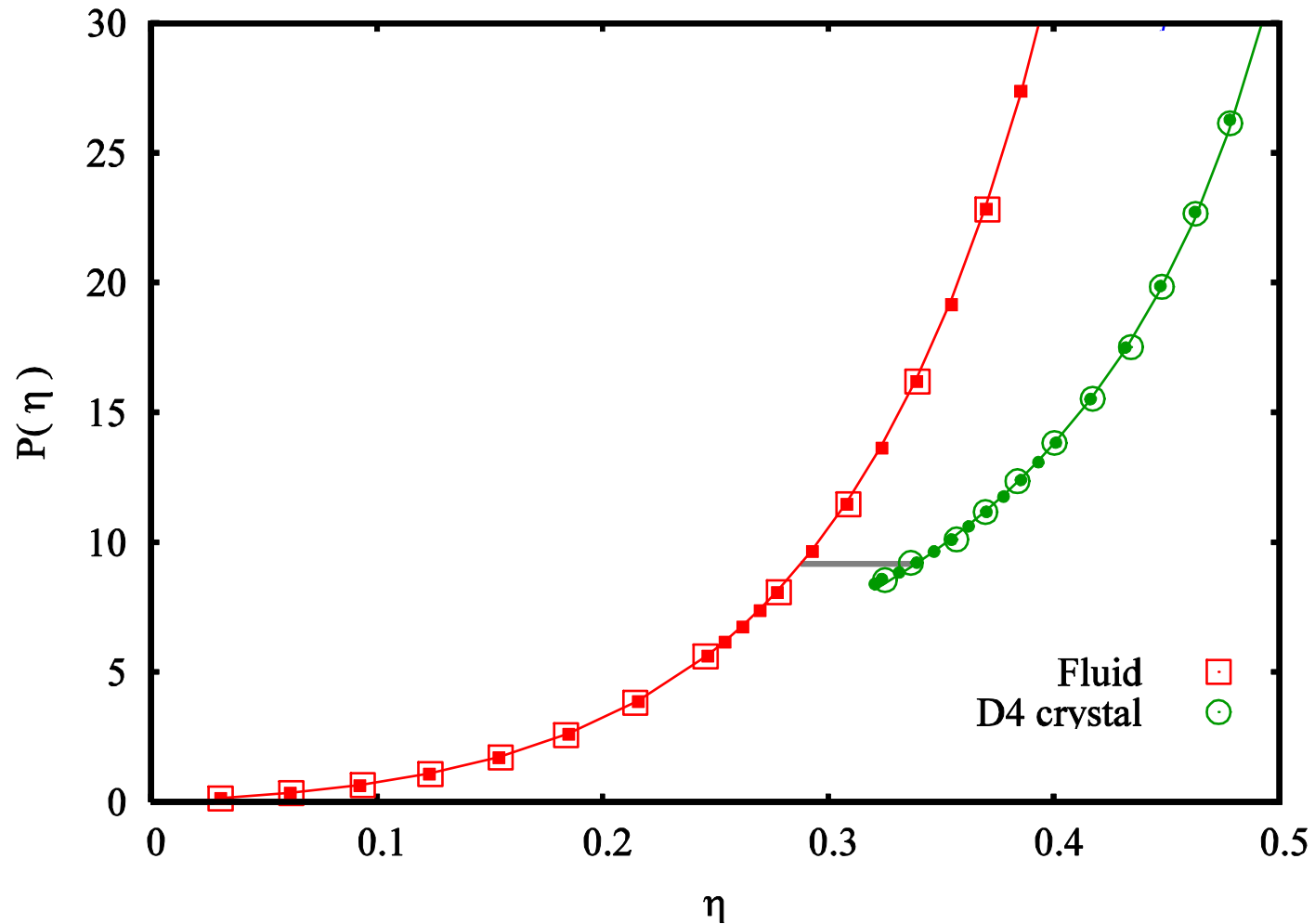Simple Square   Rotated Simple Square

3D Packing

Simple Cubic

Body-Centered Cubic

4D Packing

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

Simple Hypercubic

D4

4D Equation of State

van Meel, Frenkel, Charbonneau, PRE (2009)

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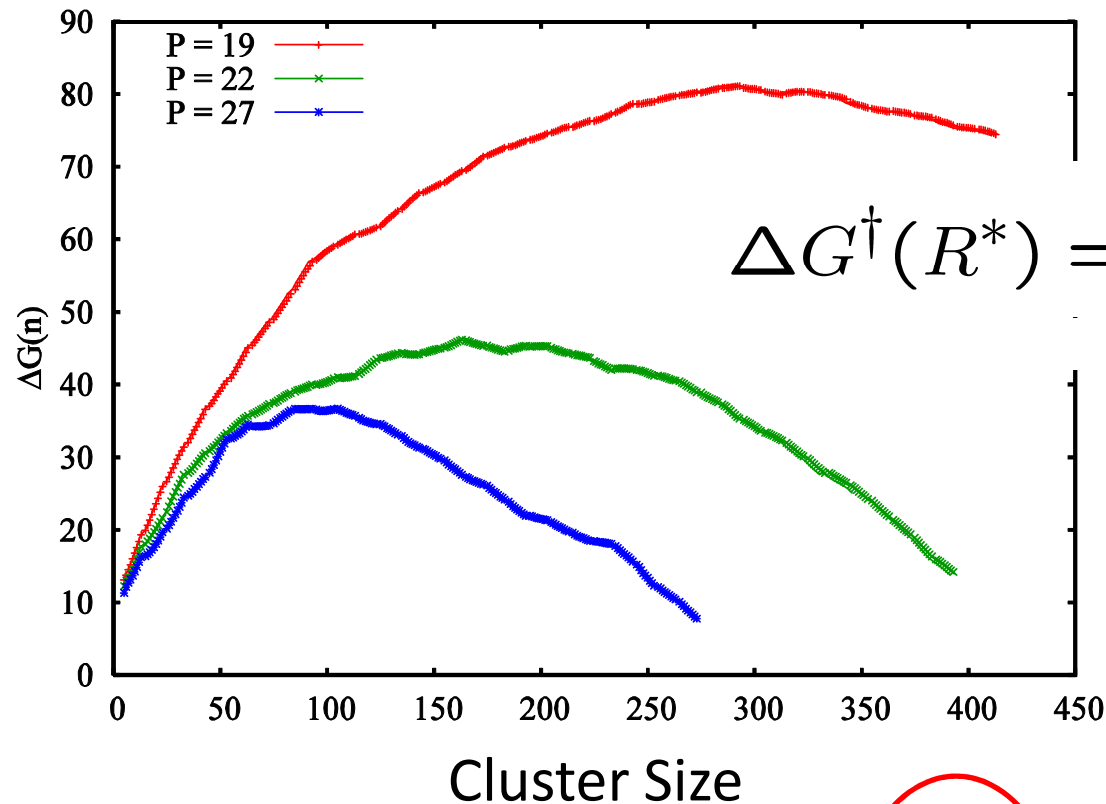
$$\Delta G^\dagger(R^*) = \frac{27\pi^2 \gamma^4}{2\rho_{D_4}^3 \Delta\mu^3}$$

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?
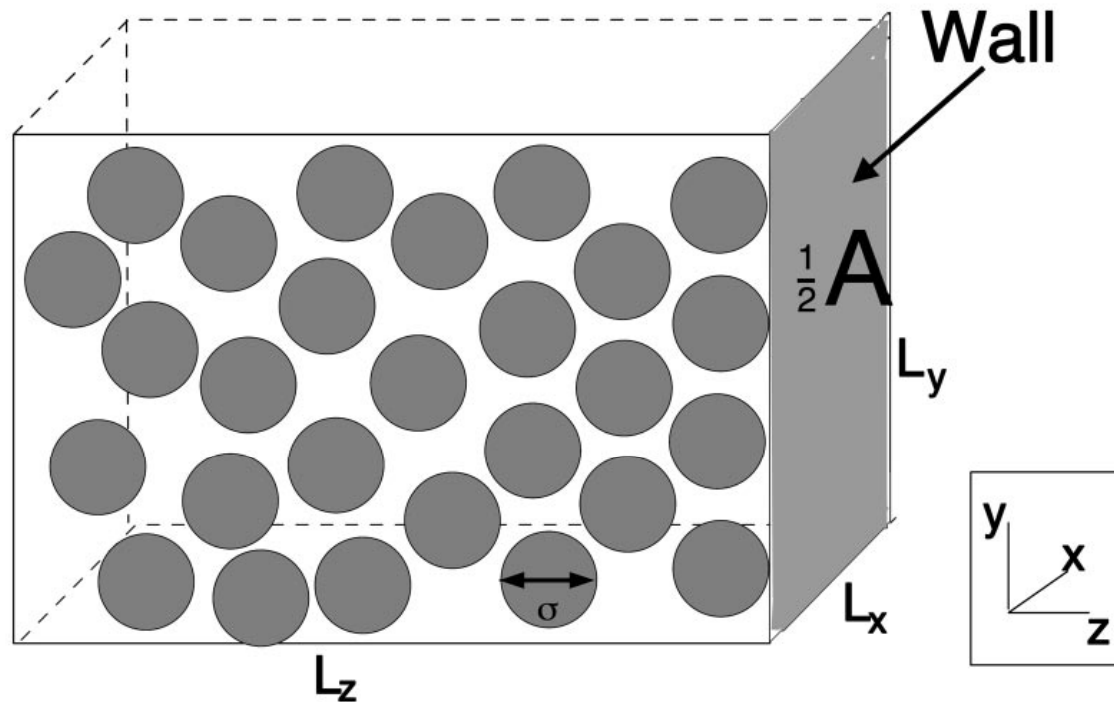
$$\gamma_{\text{crystal}}^{\text{3D}} \approx 0.557 \qquad \gamma_{\text{wall}}^{\text{3D}} \approx 1.98$$

$$\gamma_{\text{crystal}}^{\text{4D}} \approx 1.0 \qquad \gamma_{\text{wall}}^{\text{4D}} \approx 1.96$$

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

Aside: Insights Into Polydispersity

Crystal-melt interfacial free energy of binary hard spheres from capillary fluctuations

Majeed Amini

Department of Physics, University of Kansas, Lawrence, Kansas 66045, USA

Brian B. Laird[*]

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, USA

Using molecular-dynamics simulation coupled with an analysis of equilibrium capillary fluctuations in interfacial position, we compute the magnitude and anisotropy of the interfacial free energy γ for a binary hard-sphere system with a diameter ratio $\alpha=0.9$. This system, in which the fluid mixture coexists with a randomly substituted face-centered-cubic solid solution, is a useful reference model for alloys. Our results
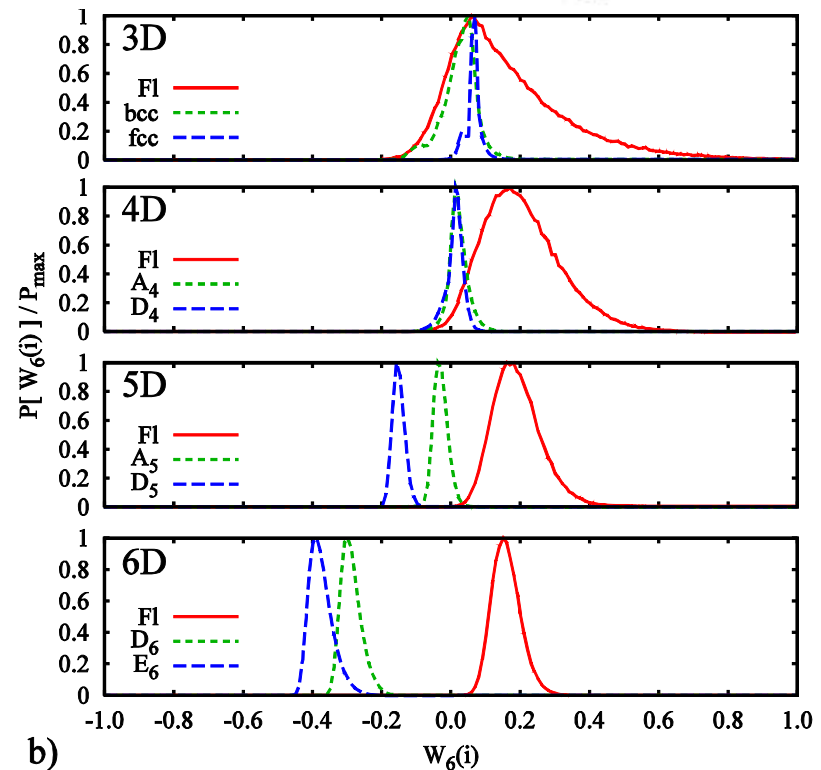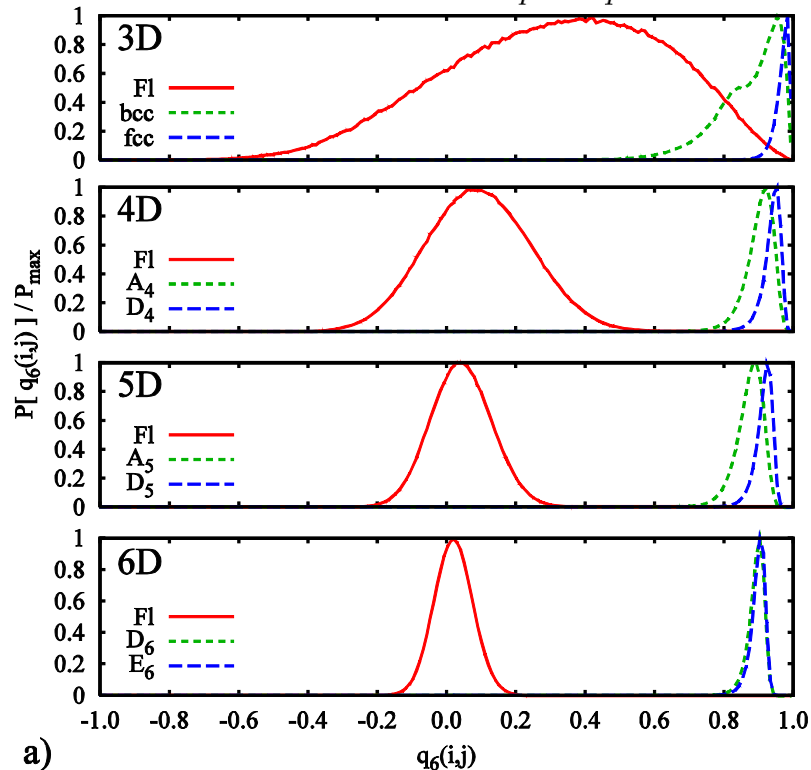
$$\gamma_0 A = \Delta(PV)$$

x_f	x_c	$P(kT/\sigma_2^3)$	$\gamma_0(kT/\sigma_2^2)$	ΔV
1.0	1.0	11.57	0.591(17)	0.0510
0.89	0.947	12.23	0.617(9)	0.0505
0.75	0.865	13.13	0.633(9)	0.0482
0.54	0.71	14.70	0.663(18)	0.0451
0.38	0.47	16.19	0.667(11)	0.0412

A Possible Explanation

Bond-order parameters *à la* Steinhardt and Nelson

Liquid/crystal structural resemblance vanishes with dimension.

van Meel, Charbonneau, Fortini, and Charbonneau, PRE (2009)
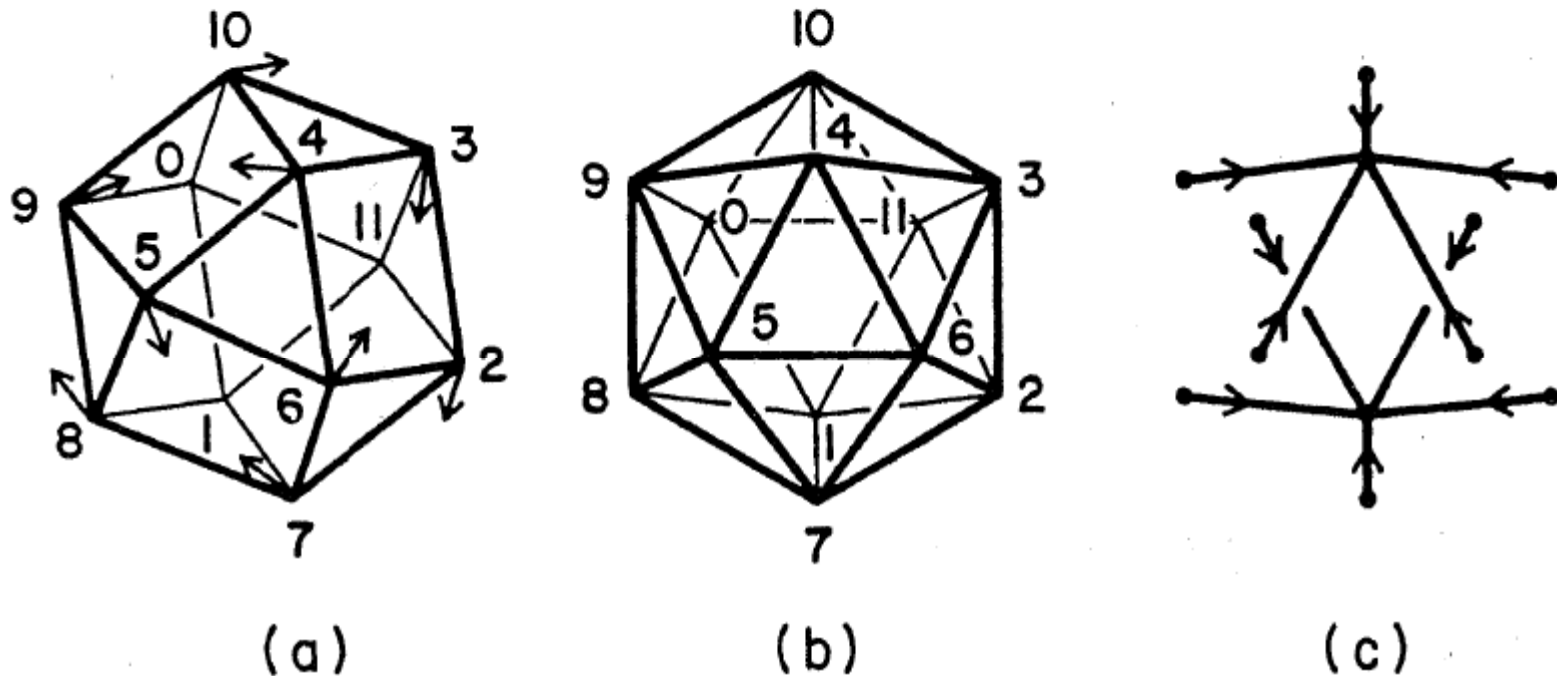
More Explanations

Figure 1.7. How to permute the planets.

Could the icosahedral configuration in fact help crystallization?
Suggests that BCC is entropically unlikely. Is it purely energetic?

Precursor-mediated crystallization process in suspensions of hard spheres

T. Schilling

Theory of Soft Condensed Matter, University of Luxembourg, Luxembourg

H. J. Schöpe, M. Oettel

Institut für Physik, Universität Mainz, Germany

G. Opletal, I. Snook

School of Applied Sciences, RMIT University, Melbourne Australia

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.

Crystallization of Hard-Sphere Glasses

E. Zaccarelli,[1] C. Valeriani,[2] E. Sanz,[2] W. C. K. Poon,[2] M. E. Cates,[2] and P. N. Pusey[2]

[1]*Dipartimento di Fisica and CNR-INFM-SOFT, Universitá di Roma La Sapienza, Piazzale Aldo Moro 2, 00185, Roma, Italy*
[2]*SUPA, School of Physics and Astronomy, The University of Edinburgh, James Clerk Maxwell Building, The King's Buildings, Mayfield Road, Edinburgh, EH9 3JZ, United Kingdom*

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.
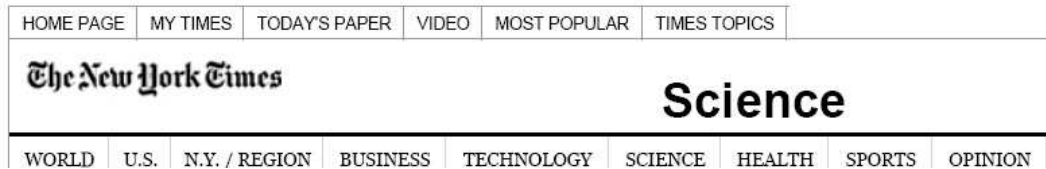
a)

b)
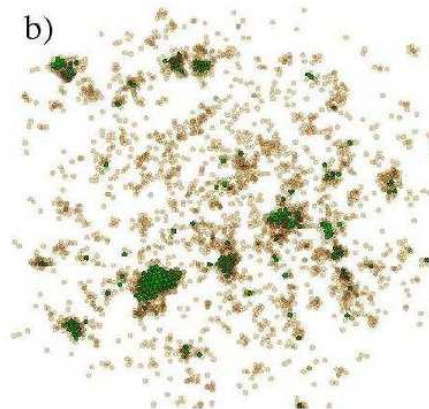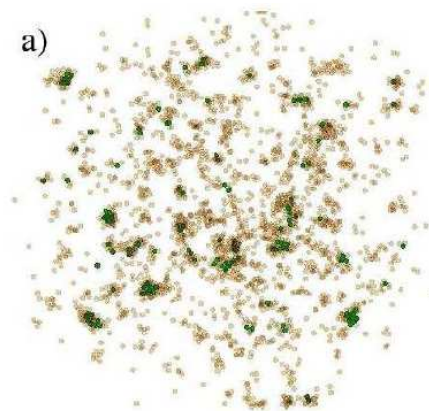
$\eta = 0.54$

What Have We Learned?

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

Testing!

The New York Times

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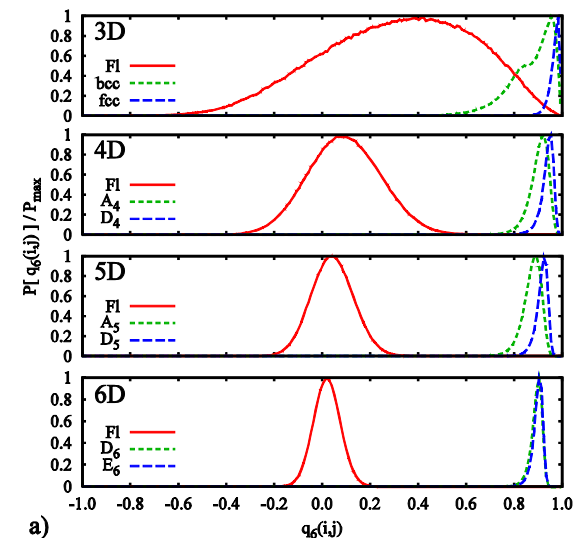
David A. Weitz, a physics professor at Harvard, joked, "There are more theories of the glass transition than there are theorists who propose them." Dr. Weitz performs experiments using tiny particles suspended in liquids to mimic the behavior of glass, and he ducks out of the theoretical battles. "It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

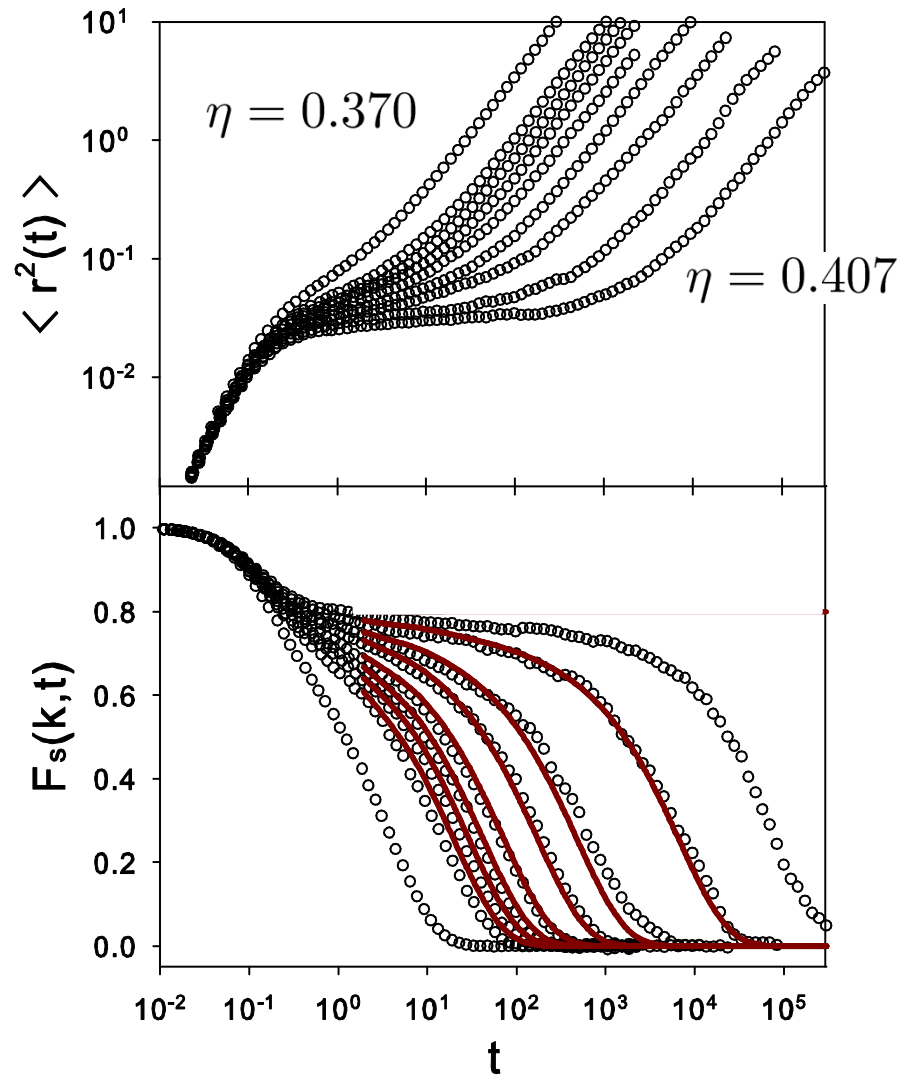The Nature of Glass Remains Anything but Clear

Mark Interrante

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

-Ecclesiastes 12:12

Monodisperse Glass Former

Charbonneau, Ikeda, van Meel, and Miyazaki, PRE (2010)
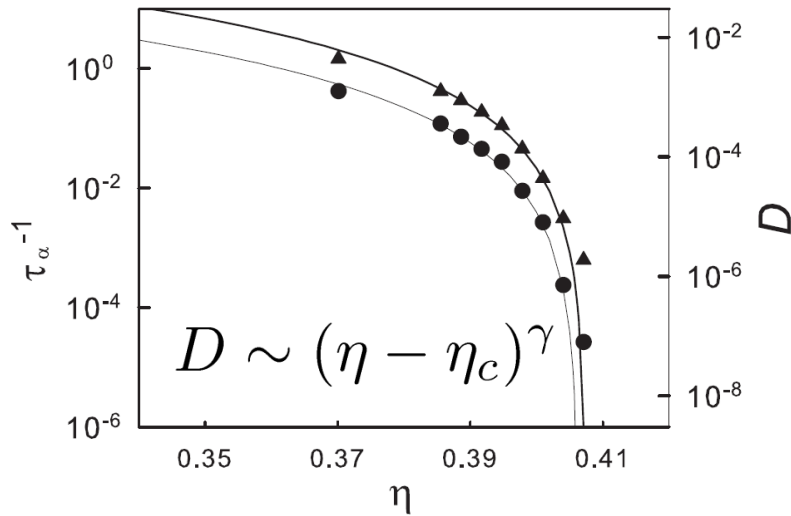
Mode-Coupling Theory (MCT)

$$\ddot{F}(k,t) + \Omega_k^2 F(k,t) + \int_0^t ds \ M(k,t-s)\dot{F}(k,s) = 0$$

$$M_{\mathsf{MCT}}(k,t) = \int_0^\infty dq \int_{|q-k|}^{|q+k|} dp \ V_k(q,p)F(q,t)F(p,t)$$

Dynamical mean-field theory that does not include hopping (improved upon by K. Schweizer et al., and others).

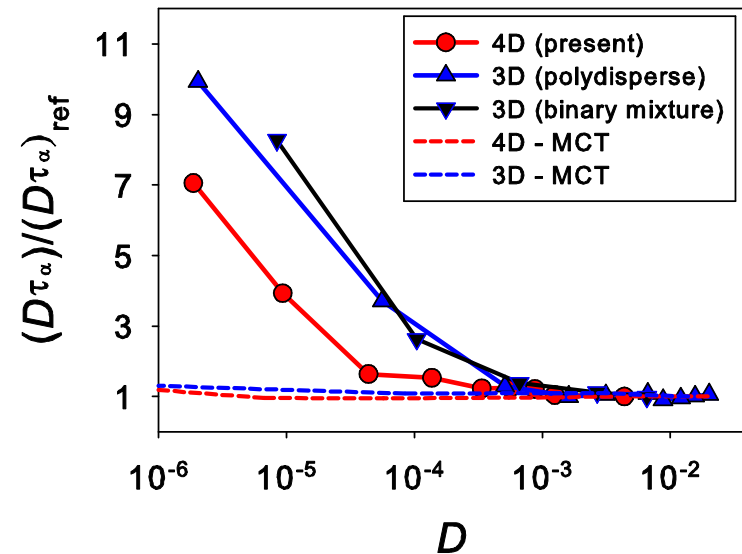Upper critical dimension of MCT is postulated to be 8.

Testing MCT

$$D \sim (\eta - \eta_c)^\gamma$$
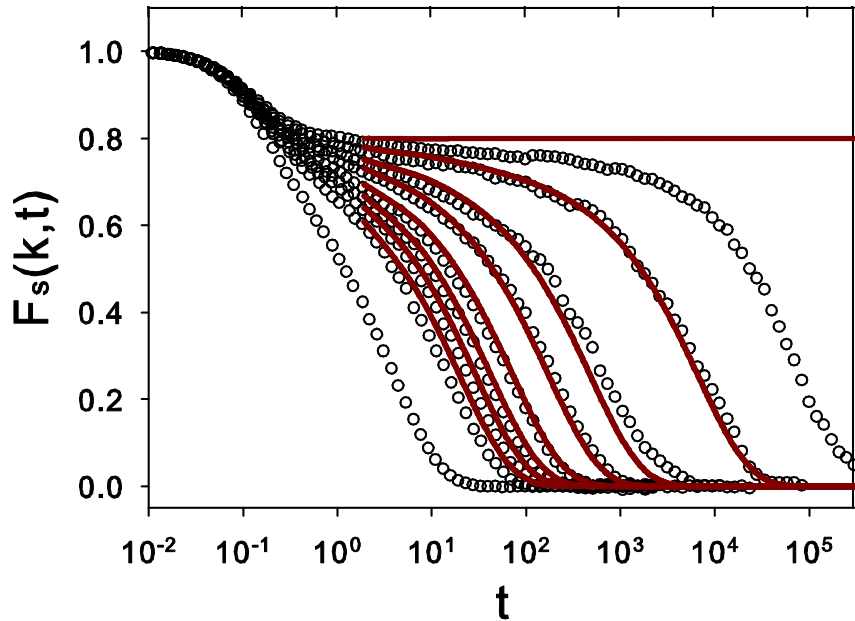
Mode-coupling theory works better in 4D than in 3D!

Dynamical heterogeneity appears reduced.

But MCT is dysfunctional in higher dimension: arXiv:1003.5472

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

Testing Jamming I

Why is Random Close Packing Reproducible?

Randall D. Kamien and Andrea J. Liu

Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania, 19104, USA
(Received 15 January 2007; published 9 October 2007)

We link the thermodynamics of colloidal suspensions to the statistics of regular and random packings. Random close packing has defied a rigorous definition yet, in three dimensions, there is near universal agreement on the volume fraction at which it occurs. We conjecture that the common value of $\phi_{rcp} \approx 0.64$ arises from a divergence in the rate at which accessible states disappear. We relate this rate to the equation of state for a hard-sphere fluid on a metastable, noncrystalline branch.

$$V_{\mathsf{D}}P = \frac{2^{\mathsf{D}}\phi}{1 - (\phi_{\mathsf{max}}/\phi)^{-1/\mathsf{D}}}$$

Squeezed Out of Equilibrium
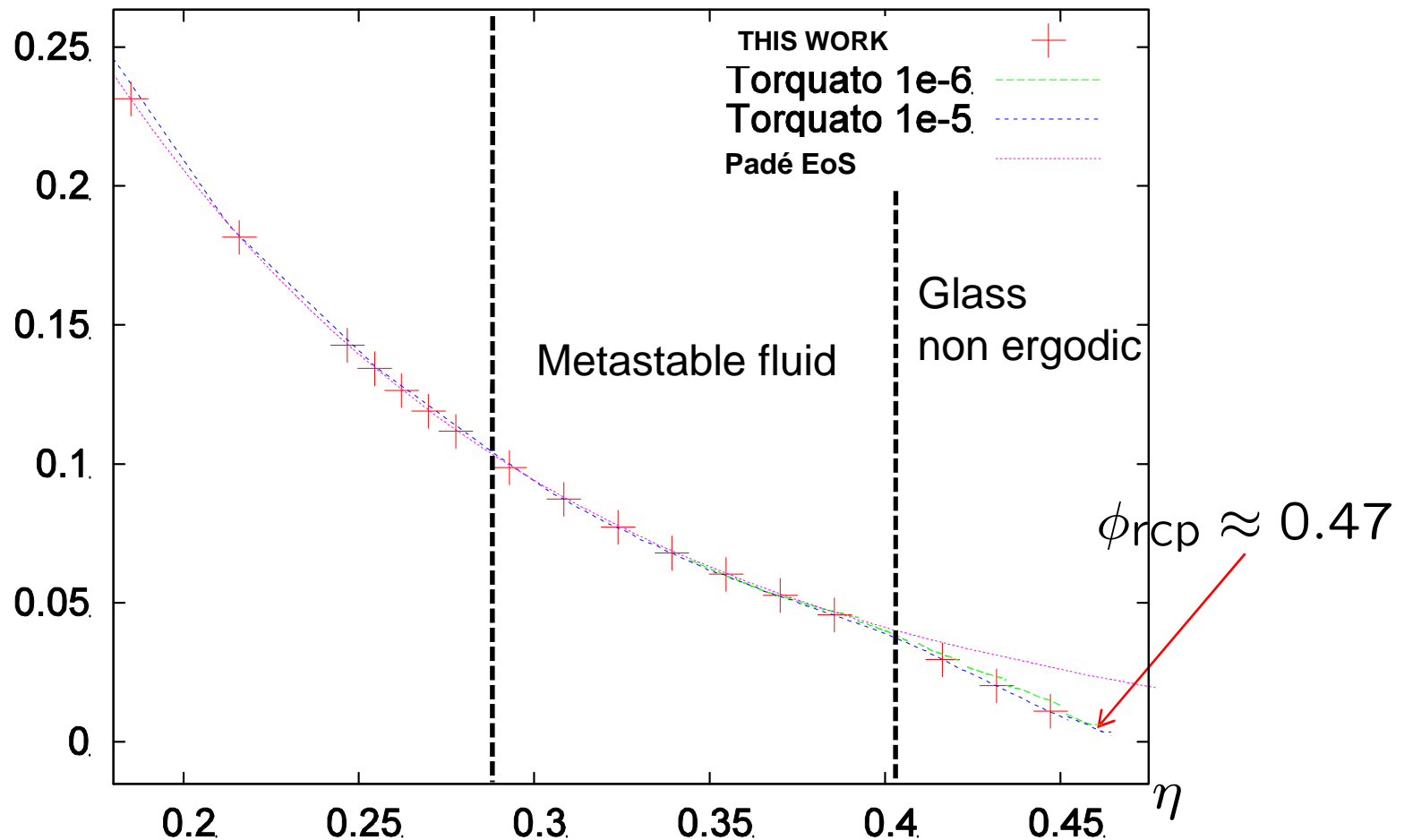
Parisi and Zamponi, Rev. Mod. Phys. (2010)
using van Meel and Charbonneau data

Testing Jamming II

nature

LETTERS

A phase diagram for jammed matter

Chaoming Song[1], Ping Wang[1] & Hernán A. Makse[1,2]

The problem of finding the most efficient way to pack spheres has a long history, dating back to the crystalline arrays conjectured[1] by Kepler and the random geometries explored[2] by Bernal. Apart from its mathematical interest, the problem has practical relevance[3] in a wide range of fields, from granular processing to fruit packing. There are currently numerous experiments showing that the loosest way to pack spheres (random loose packing) gives a density of ~55 per cent[4–6]. On the other hand, the most compact way to pack spheres (random close packing) results in a maximum density of ~64 per cent[2,4,6]. Although these values seem to be robust, there is as yet no physical interpretation for them. Here we present a statistical description of jammed states[7] in which random close packing can be interpreted as the ground state of the ensemble of jammed matter. Our approach demonstrates that random packings of hard spheres in three dimensions cannot exceed a density limit of ~63.4 per cent. We construct a phase diagram that provides a unified view of the hard-sphere packing problem and illuminates various data, including the random-loose-packed state.

Mean field theory of hard sphere glasses and jamming

Giorgio Parisi[1, *] and Francesco Zamponi[2, †]
[1]Dipartimento di Fisica, INFM-CNR SMC, INFN, Università di Roma "La Sapienza", P.le A. Moro 2, 00185 Roma, Italy
[2]Laboratoire de Physique Théorique, École Normale Supérieure, 24 Rue Lhomond, 75231 Paris Cedex 05, France
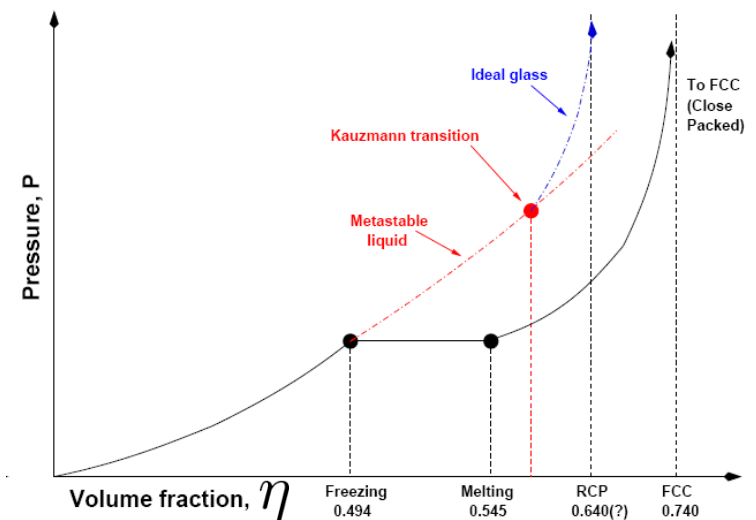
Not all Mean Fields are Equal

D	η_{MRJ}^{fV}	η_{MRJ}^{comp}	η_{MRJ}^{stat}	η_{MRJ}^{rep}
3	0.64	0.64	0.64	0.68
4	0.47	0.46	0.43	0.49
5	0.31	0.31	0.28	0.33
6	0.21	0.20	0.17	0.22

Skoge, Donev, Stillinger, and Torquato, PRE (2006)
Song, Wang, and Makse, Nature (2008)
Parisi and Zamponi, Rev. Mod. Phys. (2010)
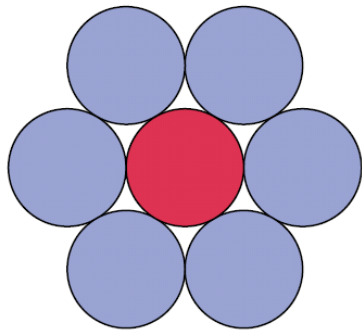van Meel, Charbonneau, Fortini, and Charbonneau, PRE (2009)

Delaunay Tessellation

A **Delaunay tessellation** for a set **P** of points in space is a tessellation DT(**P**) such that no point in **P** is inside the circumsphere of any simplex in DT(**P**).

Dual of a Voronoi tessellation.

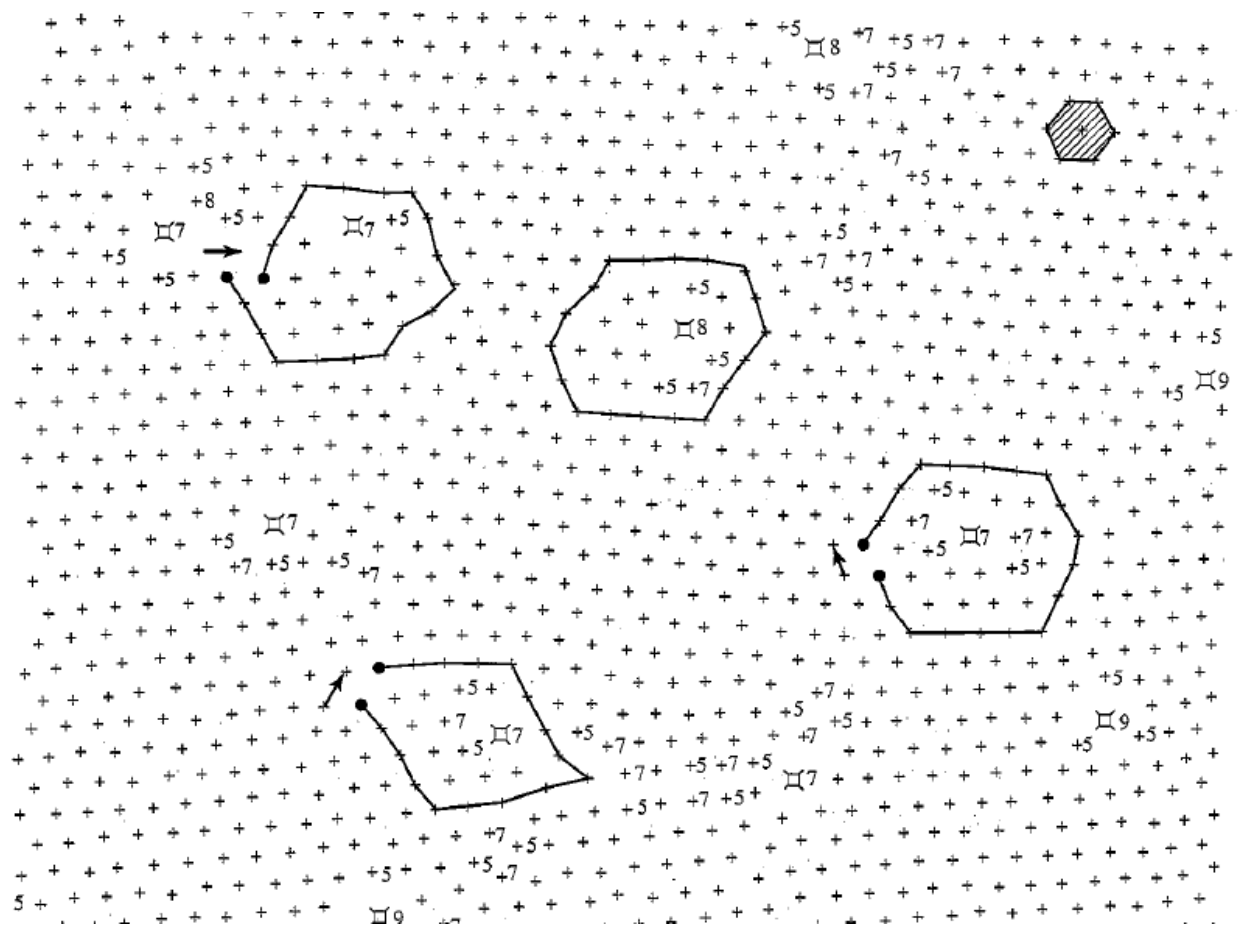http://en.wikipedia.org/wiki/Delaunay_triangulation
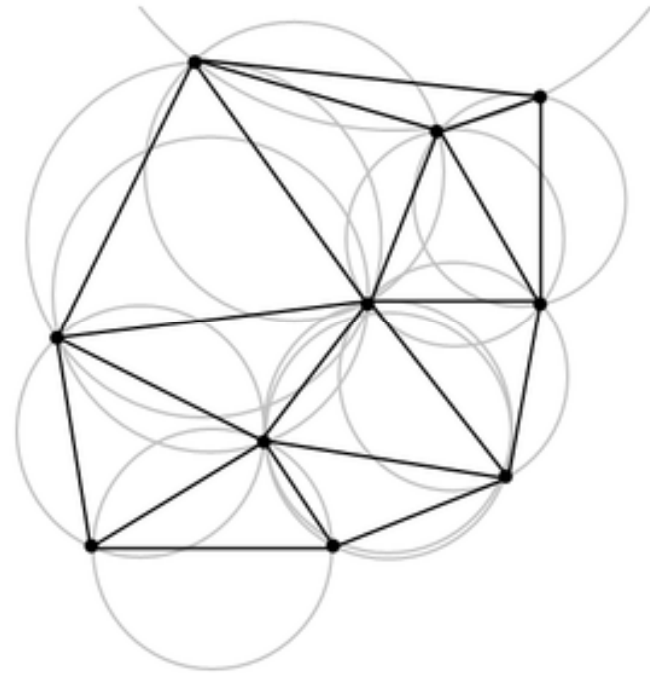
Spindles and Disclinations in 2D

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

At high densities 5-7 defects are paired.

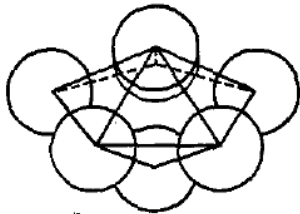Basis for KTNHY 2D melting theory.

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

Spindles and Disclinations in 3D

$$\bar{q}_{\text{spindle}} = \frac{2\pi}{\arccos(1/3)} = 5.104$$
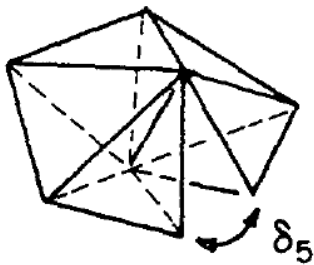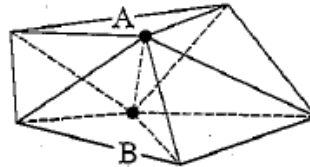
Nelson, *Defects and Geometry in Condensed Matter Physics* (2002)
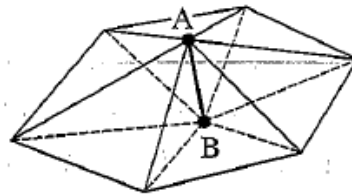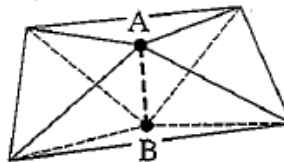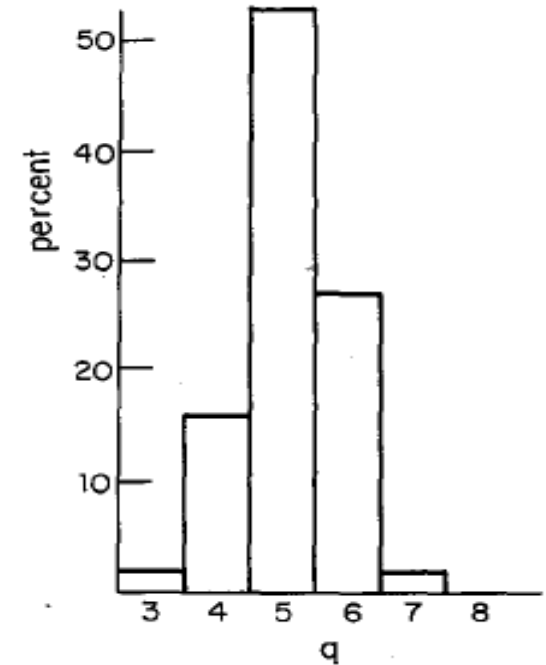
Disclination Lines

Frank-Kasper crystal phases for alloys are polytetrahedral.

TABLE I

| NAME	EXAMPLES	ATOMS PER UNIT CELL	SPACE GROUP	$Z=12$	$Z=14$	$Z=15$	$Z=16$	$\bar{Z}$	$\bar{q}$
$A15$	$\beta-W$, Cr_3Si	8	$Pm\bar{3}n$	2	6	0	0	13.500	5.1111
σ	$Cr_{46}Fe_{54}$, $\beta-U$	30	$P4_2/mnm$	10	16	4	0	13.467	5.1089
H	Complex	30	$Cmmm$	10	16	4	0	13.467	5.1089
K'	Complex	82	$Pmmm$	28	42	12	0	13.463	5.1087
F	Complex	52	$P6/mmm$	18	26	8	0	13.462	5.1086
J	Complex	22	$Pmmm$	8	10	4	0	13.455	5.1081
ν	$Mn_{81.5}Si_{18.5}$	186	$Immm$	74	80	20	12	13.441	5.1072
Z	Zr_4Al_3	7	$P6/mmm$	3	2	2	0	13.428	5.1064
P	$Mo_{42}Cr_{18}Ni_{40}$	56	$Pbnm$	24	20	8	4	13.428	5.1064
δ	$MoNi$	56	$P2_12_12_1$	24	20	8	4	13.428	5.1064
K	$Mn_{77}Fe_4Si_{19}$	220	$C2$	100	76	16	28	13.418	5.1057
R	$Mo_{31}Co_{18}Cr_{51}$	159	$R\bar{3}$	81	36	18	24	13.396	5.1042
μ	Mo_6Co_7	39	$R\bar{3}m$	21	6	6	6	13.385	5.1034
—	K_7Cs_6	26	$P6_3/mmc$	14	4	4	4	13.385	5.1034
$p\sigma$	$W_6(Fe, Si)_7$	26	$Pnam$	14	4	4	4	13.385	5.1034
M	$Nb_{48}Ni_{39}Al_{13}$	52	$Pnam$	28	8	8	8	13.385	5.1034
I	$V_{41}Ni_{36}Si_{23}$	228	Cc	132	24	24	48	13.369	5.1024
C	$V_2(Co, Si)_3$	50	$C2/m$	30	4	4	12	13.360	5.1018
T	$Mg_{32}(Zn, Al)_{49}$	162	$Im\bar{3}$	98	12	12	40	13.358	5.1017
X	$Mn_{45}Co_{40}Si_{15}$	74	$Pnnm$	46	4	4	20	13.351	5.1012
—	Mg_4Zn_7	110	$C2/m$	70	4	4	32	13.345	5.1008
$C14$	$MgZn_2$	12	$P6_3/mmc$	8	0	0	4	13.333	5.1000
$C15$	$MgCu_2$	24	$Fd\bar{3}m$	16	0	0	8	13.333	5.1000

FRANK–KASPER PHASE
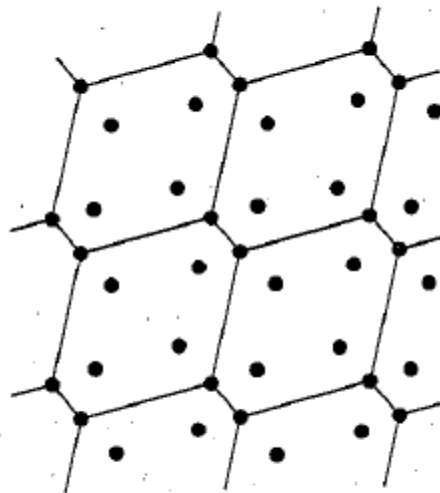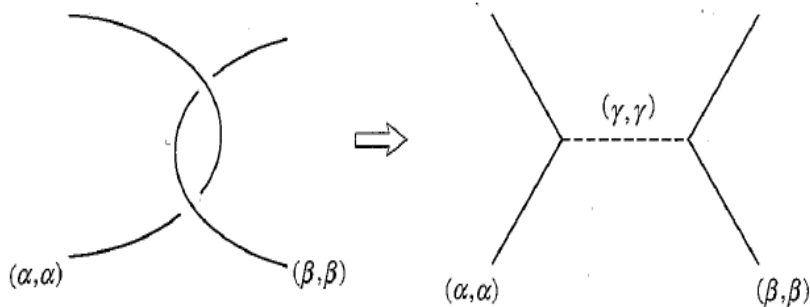
MOLTEN LIQUID
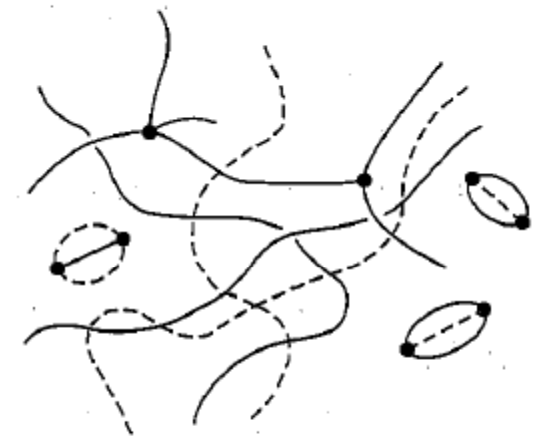
T_c

T

Fig. 4.11. Entanglement of disclination lines.

——— $= -72°$ disclination line

------ $= +72°$ disclination line

(α, α) (β, β) $\Rightarrow$ (γ, γ) (α, α) (β, β)

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

Higher-D liquids

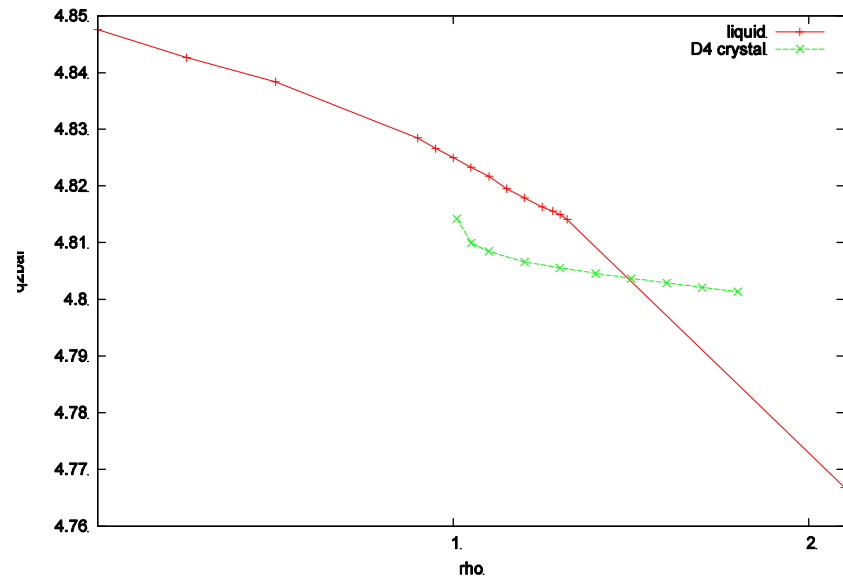## 4D Spindle Dist.
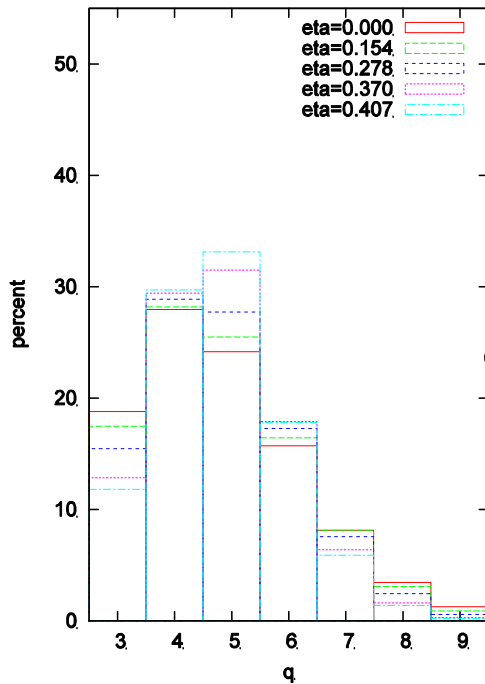
3D Spindle Dist.
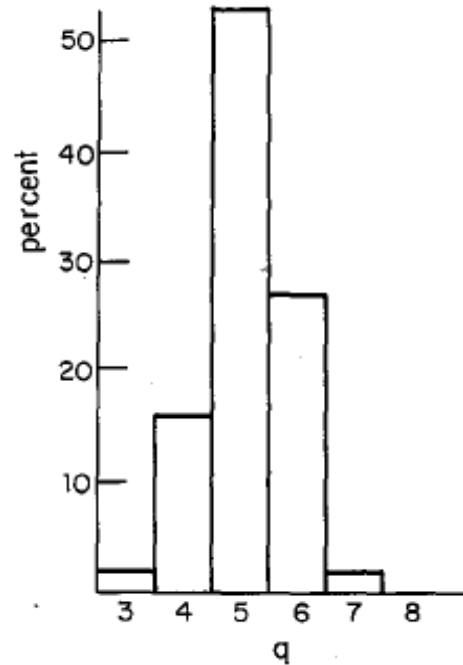
$$\bar{q}_{\text{spindle}}(d) = \frac{2\pi}{\arccos(1/d)}$$

$$\bar{q}_{\text{spindle}}(4) = 4.7668$$

$$\bar{q}_{\text{spindle}}(\infty) = 4$$

Inherent (relaxed or compressed) structure has more defects in 4D.

Charbonneau and Charbonneau, unpublished

Could I get married in 4D?

It might be easier if metallic glasses remain in vogue…

End of Talk

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THANK YOU!