Fundamental Aspects of the Glass Transition

Maximally Random Jammed States: Prototypical Glasses

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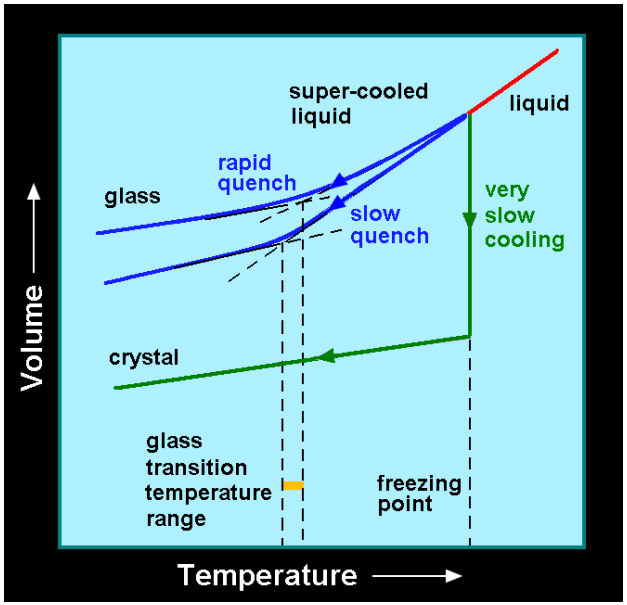
Supercooled Liquids and Glass Transition

- A quantitative understanding of nature of the physics of the glass transition is one of the most fascinating and challenging problems in materials science and condensed-matter physics.
- A sufficiently rapid quench of a liquid into a supercooled regime can avoid crystal nucleation to produce a glass with a relaxation time that is much larger than experimental time scales, resulting in an amorphous characteristic state (without long-range order) that is simultaneously mechanically rigid, i.e., it does not flow like a liquid.



- One phenomenological definition of T_g is the temperature at which the shear viscosity reaches 10^{13} poise.

Supercooled Liquids and Glass Transition

- **Kob (1997) summarizes the following commonly held view:**
  "If a glass former is cooled from its melting temperature to its glass transition temperature T_g, it shows an increase of its relaxation time by some 14 decades without a significant change in its structural properties..."
  I will call this the "frozen-liquid" picture.
  Roughly speaking, glasses are structurally liquids that cannot flow.
- **However, any ergodic amorphous state cannot resist shear. Thus, the rigidity of an amorphous state is a highly nontrivial phenomenon.**
  As P. W. Anderson (1999) puts it: "*We are so accustomed to this rigidity property that we don't accept its almost miraculous nature, that is an 'emergent property' not contained in the simple laws of physics, although it is a consequence of them.***"**
- **Over the course of time many different theories have been put forward to explain the dramatic slowing down on approach to T_g.**
  - **Thermodynamically-based: Entropy theory of Adams, Gibbs and Di Marzio (1958,1965); Random First-Order Transition Theory (Lubchenko and Wolynes, 2006)**
  - **Dynamically-based: Mode-coupling theory of Götze and Sjögren (1992)**

Supercooled Liquids and Glass Transition

- A powerful computational and modeling approach relating the phenomonelogy of vitrification and supercooling to molecular-scale events is the quantification of the liquid's energy landscape, i.e., the multidimensional potential energy surface. Stillinger and Weber, 1985
- A question that has received considerable attention in recent years is whether the growing relaxation times under supercooling have accompanying growing structural length scales.

  Two distinct schools of thought have emerged to address this question:
  - One camp asserts that static structure of a glass, as measured by pair correlations, is indistinguishable from that of the corresponding liquid. There is no signature of increasing static correlation length scales accompanying the glass transition, it identifies growing dynamical length scales. Berthier, Biroli, Bouchaud, Kob, Reichman, Sastry, Chandler
  - The other camp contends that there is a static growing length scale of thermodynamic origin, and therefore one need not look for growing length scales associated with the dynamics. Lubchenko, Wolynes, Hocky, Markland, Reichman

Idealized Jammed Hard-Sphere Models

- Consider packings of frictionless identical spheres in the absence of gravity, which represents an idealization of the laboratory situation for investigations of jammed packings.

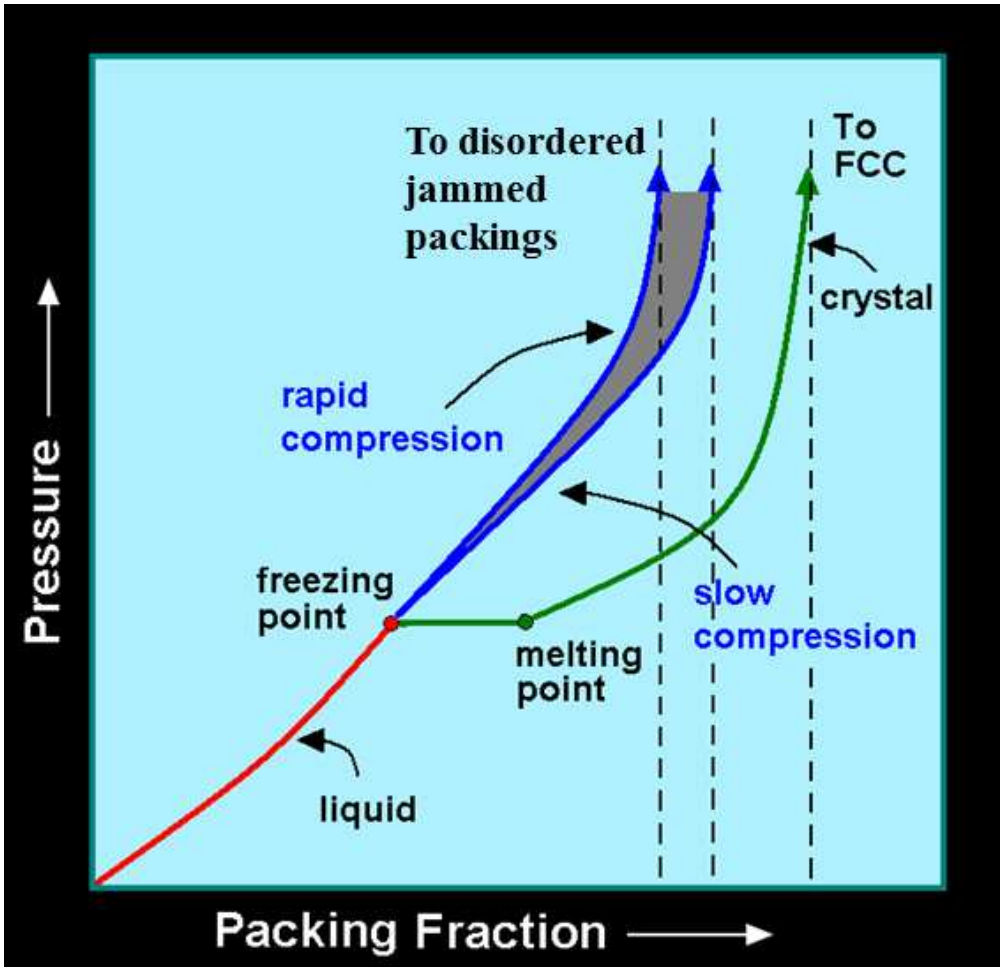
- This simplification follows that tradition in condensed-matter science to exploit idealized models, such as the Ising model, which is regarded as one of the pillars of statistical mechanics.

- In that tradition, this idealization offers the opportunity to obtain fundamental as well as practical insights and to uncover unifying concepts that describe a broad range of phenomena. The stripped-down hard-sphere "Ising model" for jammed packings embodies the primary attributes of real packings and some molecular systems, while simultaneously generating mathematical solutions and challenges.

- A packing of hard spheres has a packing fraction ϕ (fraction of space covered by the spheres).

3D Hard-Sphere Phase Diagram

Torquato & Stillinger, Rev. Mod. Phys. (2010)



- **Rapid compression (increase of ϕ) is like rapid cooling (decrease of T) of molecular liquid.**
- **Maximally random jammed (MRJ) state presumably is the mechanically rigid packing associated with the fastest compression rate .**

MRJ State: Prototypical Glass

- **Maximally random jammed (MRJ) state is a prototypical glass:**
  - **maximally disordered;**
  - **infinite bulk and shear moduli;**
  - **perfectly nonergodic - forever trapped in configuration space**

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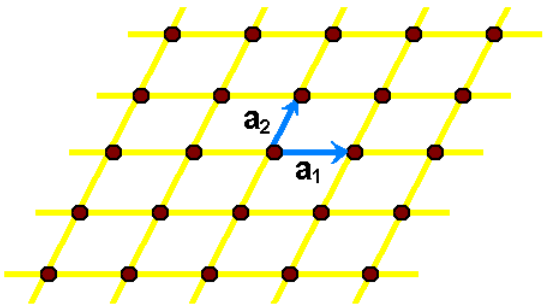
- **MRJ state is definitively not a "frozen liquid" as reflected by the fact that it possesses the exotic hyperuniformity property with quasi-long-range pair correlations.**
- **MRJ state requires us to think more deeply about the nature of randomness in many-particle or many-spin systems.**

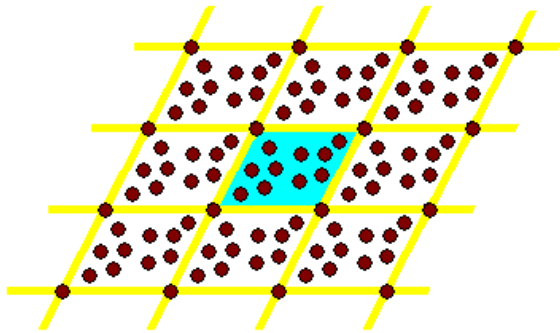
Definitions

- A **point process** in d-dimensional Euclidean space $\mathbb{R}^d$ is a distribution of an infinite number of points in $\mathbb{R}^d$ with configuration $\mathbf{r}_1, \mathbf{r}_2, \ldots$ with a well-defined number density ρ (number of points per unit volume). This is statistically described by the n-particle correlation function $g_n(\mathbf{r}_1, , \ldots, \mathbf{r}_n)$.
- A **lattice** Λ in d-dimensional Euclidean space $\mathbb{R}^d$ is the set of points that are integer linear combinations of d basis (linearly independent) vectors $\mathbf{a}_i$, i.e.,

$$\{n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + \cdots + n_d\mathbf{a}_d \mid n_1, \ldots, n_d \in Z\}$$

  The space $\mathbb{R}^d$ can be geometrically divided into identical regions F called **fundamental cells**, each of which contains just one point. For example, in $\mathbb{R}^2$:





- Every lattice has a **dual (or reciprocal)** lattice Λ^*.
- A **periodic** point distribution in $\mathbb{R}^d$ is a fixed but arbitrary configuration of N points ($N \geq 1$) in each fundamental cell of a lattice.

Definitions

- For statistically homogeneous and isotropic point processes in $\mathbb{R}^d$ at number density ρ , $g_2(r)$ is a nonnegative radial function that is proportional to the probability density of pair distances r.

- We call

$$h(r) \equiv g_2(r) - 1$$

the total correlation function.

- When there is no long-range order in the system, $h(r) \to 0$ [or $g_2(r) \to 1$] in the large-r limit. We call a point process disordered if $h(r)$ tends to zero sufficiently rapidly such that it is integrable over all space.

- The nonnegative structure factor $S(k)$ is defined in terms of the Fourier transform of $h(r)$, which we denote by $\tilde{h}(k)$:

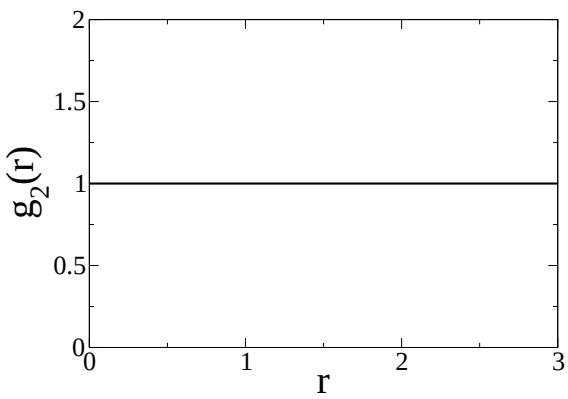
$$S(k) \equiv 1 + \rho\tilde{h}(k),$$

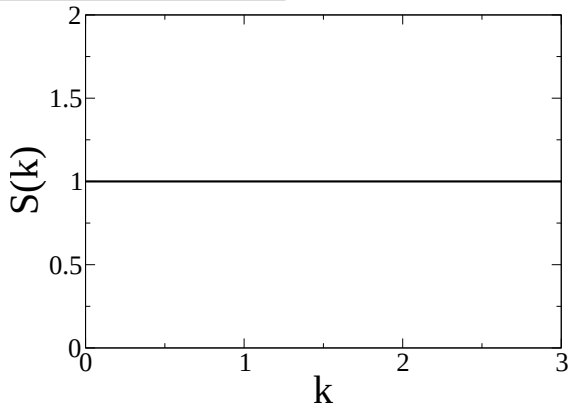
where k denotes wavenumber.

- When there is no long-range order in the system, $S(k) \to 1$ in the large-k limit, the dual-space analog of the aforementioned direct space condition.

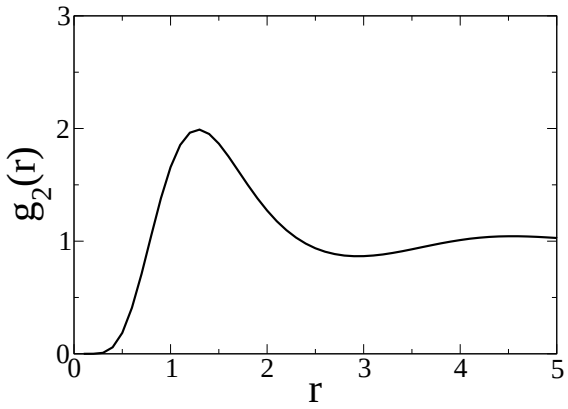
Pair Statistics for Spatially Uncorrelated and Ordered Point Processes

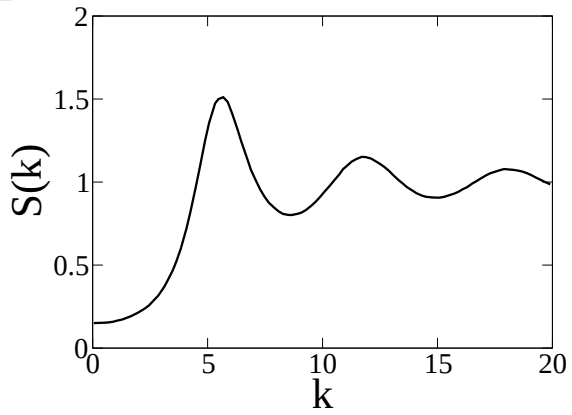
Poisson Distribution (Ideal Gas)



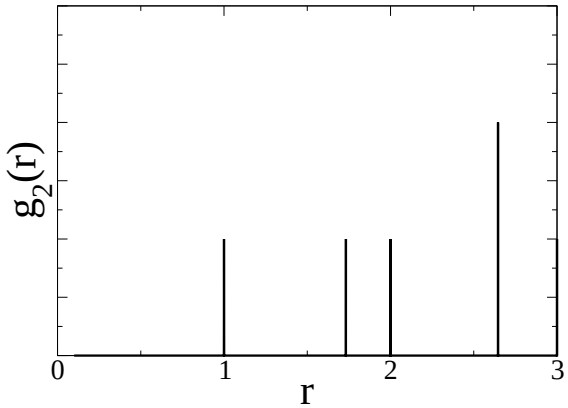


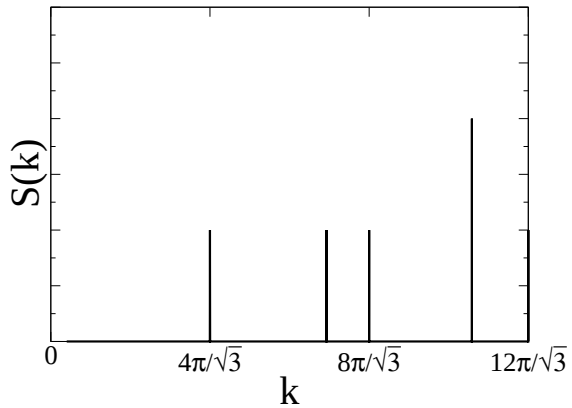
Liquid



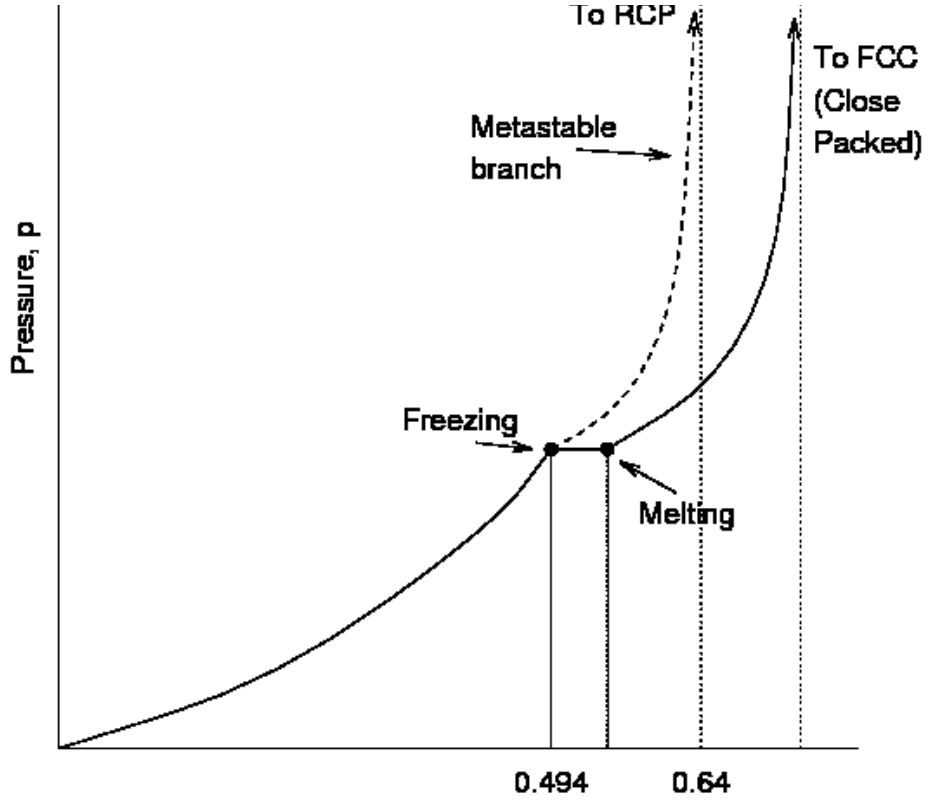


Lattice





Metastable and Glassy States in Hard-Sphere Systems



- **Is there a glass transition at packing fraction $\phi = \phi_g$ such that $\phi_f < \phi_g < \phi_{rcp}$?**
- **How does one identify a metastable extension of stable disordered branch? Previous investigators assumed metastability if $g_2(r)$ exhibited no peak around $r = \sqrt{2}D$.**

Rintoul and Torquato, PRL (1996)

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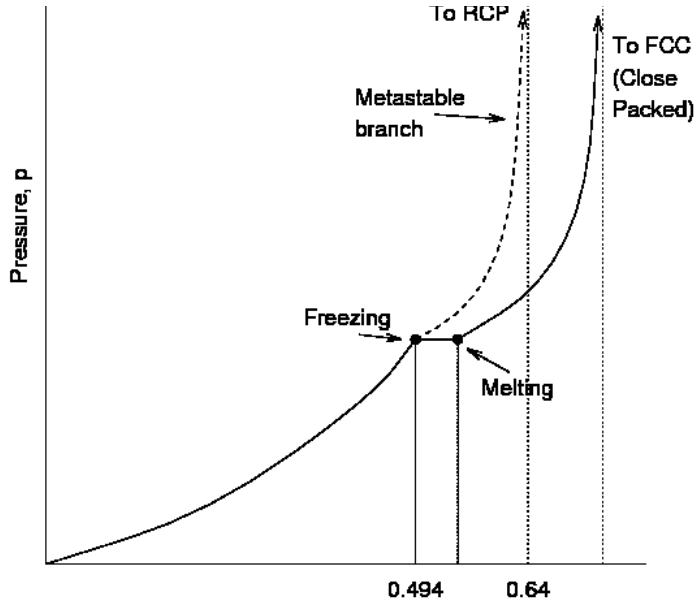

- Previous metastability criterion is deficient. We instead used the bond-orientational parameter Q_6 introduced by Steinhardt, Nelson and Ronchetti (1983) to measure incipient crystallization.

Structure	Q_6
Icosahedral	0.66332
Face-centered Cubic	0.57452
Hexagonal Close Packed	0.48476
Body-centered Cubic	0.51059
Simple Cubic	0.35355

- All systems crystallized on relatively very small time scales and hence found no evidence of a glass transition for $\phi_f < \phi < \phi_{rcp}$.

Random Close Packing (RCP)

- **Bernal (circa 1950's): 'In closing we must not forget the commentary on random packing which Saint Luke attributes to Jesus, "Give and it will be given unto you; good measure, pressed down, and shaken together, and running over. For by your standard of measure it will be measured to you in return."'**

- **An anonymous author summarizes this traditional view as follows: "ball bearings and similar objects have been shaken, settled in oil, stuck with paint, kneaded inside rubber balloons – and all with no better result than (a packing fraction of) ...** 0.636**."**

- **Prevailing notion is that the random close packed (RCP) state corresponds to the maximum density that a large, random collection of spheres can attain and is a universal quantity.**

Is Random Close Packing Well Defined?

Torquato, Truskett and Debenedetti, PRL (2000)

NO!

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Problems with RCP

- **Dynamical parameters: pouring rate, and amplitude and frequency of vibration.**

Interactions: interparticle forces, friction (inhibiting densification), and gravity.

- ϕ_c **value is protocol-dependent!**
- **Randomness was never defined!**

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- ϕ_c **value is protocol-dependent!**
- **Randomness was never defined!**
- **Terms "random" and "close packed" are at odds with one another.**

Resolution

- **By quantifying order (disorder) in compressed hard-sphere systems (generated via molecular dynamics), we showed that the RCP state is ill-defined.**
- **To replace the RCP state, we introduced the concept of the maximally random jammed (MRJ) state, which can be made precise.**

Jamming Categories

Torquato and Stillinger, J. Phys. Chem. B (2001)

- **Locally jammed: Each particle in the system is individually trapped by its neighbors, i.e., each sphere has at least $d+1$ contacting spheres not all in the same hemisphere.**
- **Collectively jammed: A locally jammed configuration is one in which no subset of the particles can be continuously displaced, so that its members move out of contact with the remainder set.**
- **Strictly jammed: A collectively jammed configuration that disallows all uniform volume-nonincreasing deformations.**
  - **Boundary conditions matter!**
  - **Can show strict jamming implies infinite bulk and shear moduli!**
  - **Jamming can be tested rigorously! using linear programming.**

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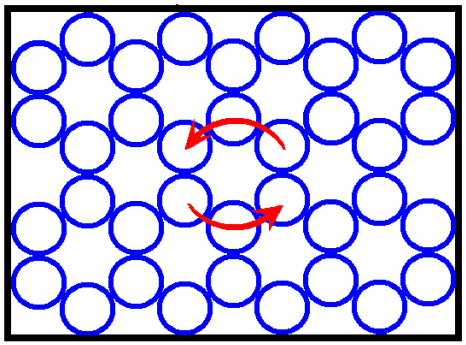
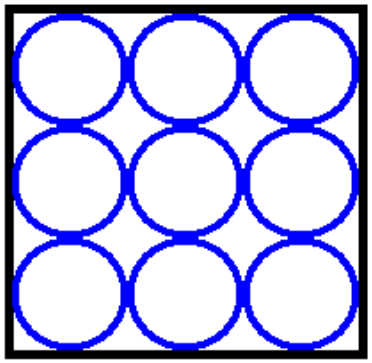
Isostaticity

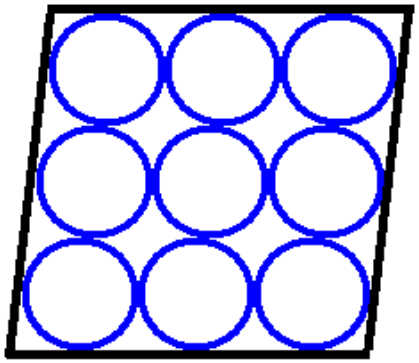
Isostatic packings are those that possess the minimal number of contacts for a jamming category. Determined by the number of degrees of freedom and number of constraints. For frictionless spheres,

- Local jamming requires that each sphere has at least $d+1$ contacts.
- Strict jamming requires that the mean contact number $Z = 2d$.

Jamming Categories

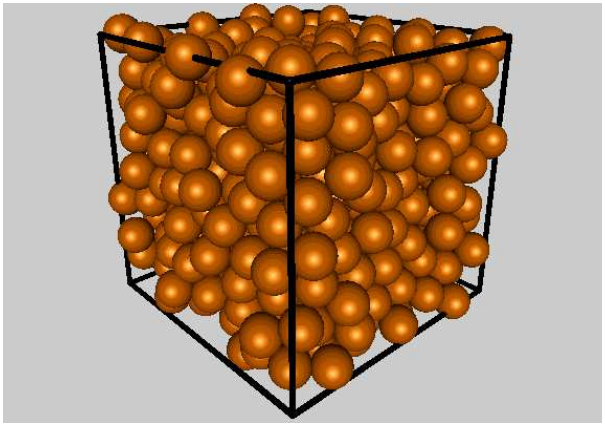


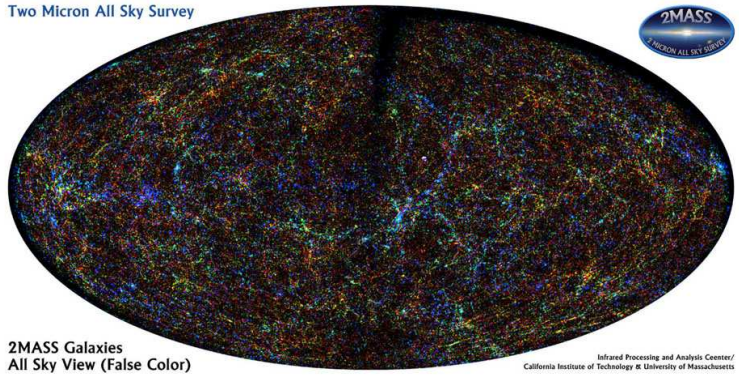




Jamming Animations

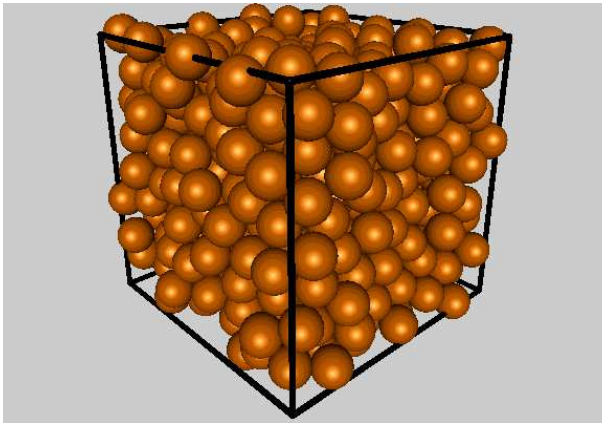
Quantifying Disorder/Order in Condensed Phase Systems

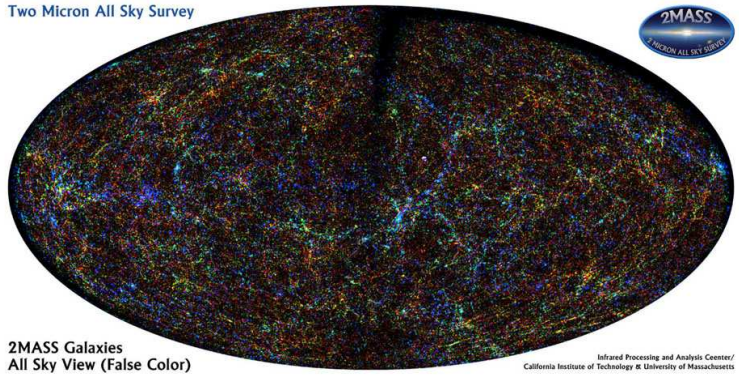




Interesting Spin Configurations

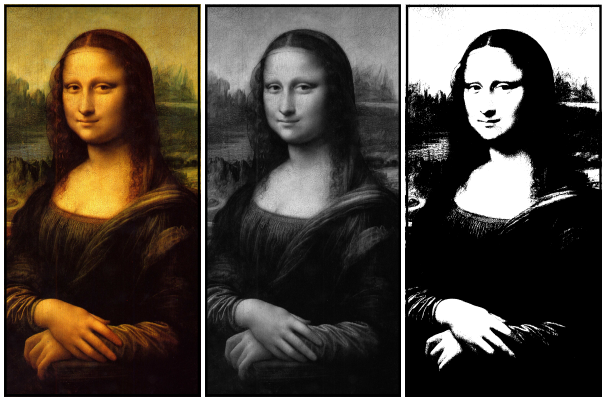
Quantifying Disorder/Order in Condensed Phase Systems





Interesting Spin Configurations

RGB GRAYSCALE BLACK & WHITE



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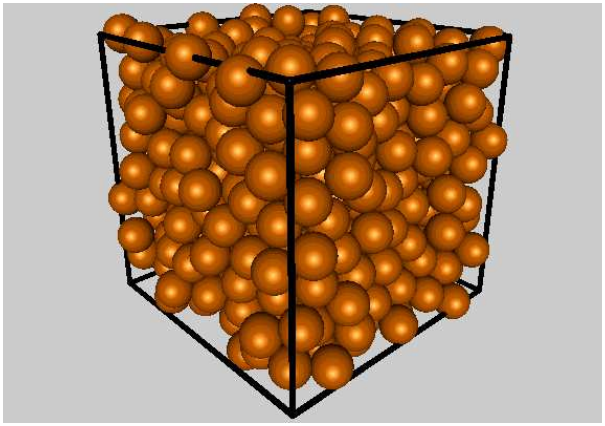

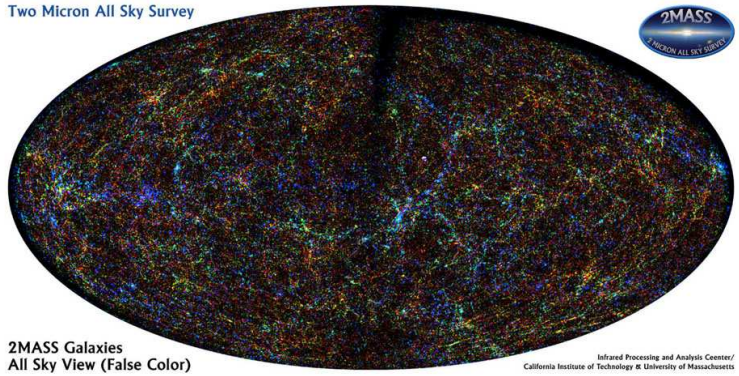

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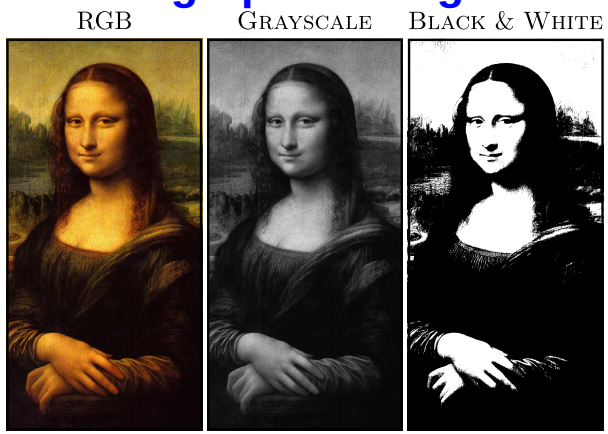
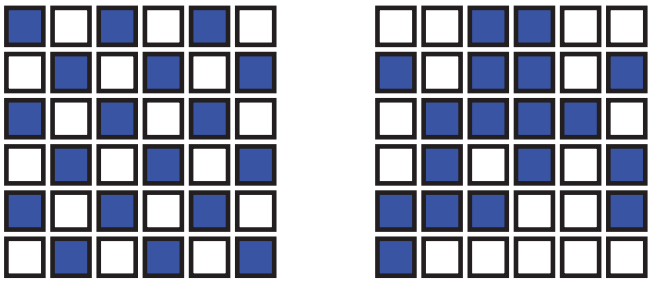




By a certain measure, the binarized Mona Lisa is 10^5 times more ordered than the Poisson case.

Quantifying Disorder/Order in Condensed Phase Systems

- Ideally, one would like to use order metrics to structurally characterize condensed matter. For concreteness, consider a many-body system with configuration $\mathbf{r}^N \equiv \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$.
- Must settle for reduced information. For example, scalar order metrics $\psi_1(\mathbf{r}^N), \psi_2(\mathbf{r}^N), \psi_3(\mathbf{r}^N), \ldots$ that are positively correlated such that $0 \leq \psi_i(\mathbf{r}^N) \leq 1$.
- It is desirable to devise order metrics that rank orders structures in accordance with our intuition:
  - Perfect crystals
  - Perturbed crystals
  - Quasicrystals
  - Highly defective crystals
  - Correlated random systems (e.g., glasses such as the "maximally random jammed" state)
  - Uncorrelated random systems (ideal gases)
- Often, ψ is a distance metric with respect to some reference state.
- More generally, one can devise tensor order metrics.

Scalar Translational and Bond-Orientational Order Metrics

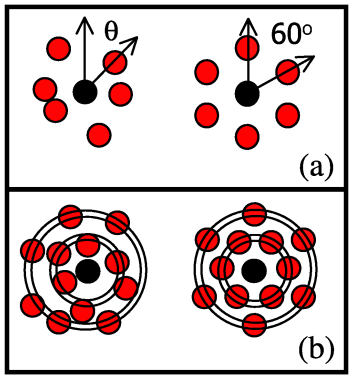
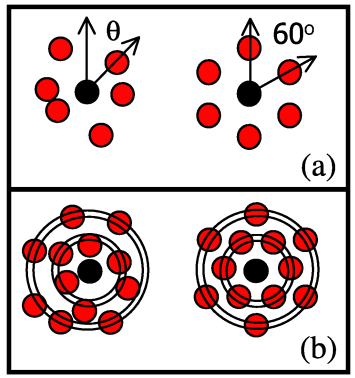


Figure 1: **(a) Bond-orientational order metric Q for the packing of interest (left) contains information about the degree to which near-neighbor bonds have regular six-fold coordination ($e^{i6\theta}$). Triangular lattice (right) has perfect orientational order $Q = 1$. (b) Translational order metric T contains information about relative spacing of particles (left) relative to that of the densest packing at the same density (right).**

Scalar Translational and Bond-Orientational Order Metrics



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Another Translational Order Metric

$$T = \frac{1}{R_c} \int_0^{R_c} |g_2(r) - 1| dr$$

Truskett, Torquato & Debenedetti 2000

Local Order Metric for Tetrahedral Liquid

Orientational order in the vicinity of oxygen atom i of a given molecule:

$$q_i = 1 - \frac{3}{8} \sum_{j>k} [\cos \theta_{ijk} + 1/3]^2$$

where θ_{ijk} is the angle formed by the lines joining the oxygen atom and those of its nearest neighbor j and k (≤ 4).

Chau and Hardwick (1998)

Approaches to Study Jammed Particle Packings

Within the domains of analytical theory and computer simulations, two conceptual approaches for their study have emerged:

- **Ensemble approach - For a given packing protocol, aims to understand typical configurations and their frequency of occurrence.**
  Bernal (1960); Edwards (1994); Liu and Nagel, 1998; OHern et al. (2003); Parisi and Zamponi (2010)

- **Geometric-structure approach - Emphasizes quantitative characterization of single-packing configurations, without regard to their occurrence frequency in the algorithmic method used to produce them.**
  Torquato and Stillinger (2010)

Geometric-structure approach encompasses ensemble approach.

Geometric Structure Approach to Jammed Particle Packings

Torquato & Stillinger, Rev. Mod. Phys. (2010)

Geometric Structure Approach to Jammed Particle Packings

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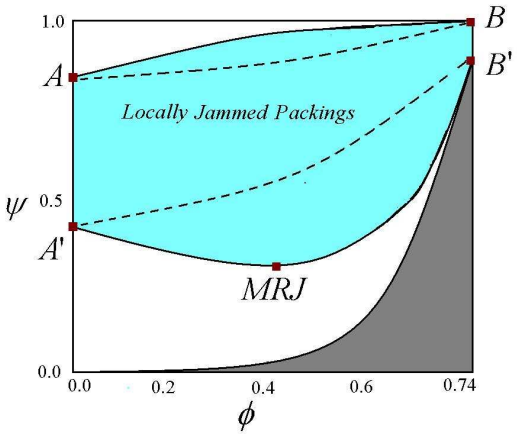
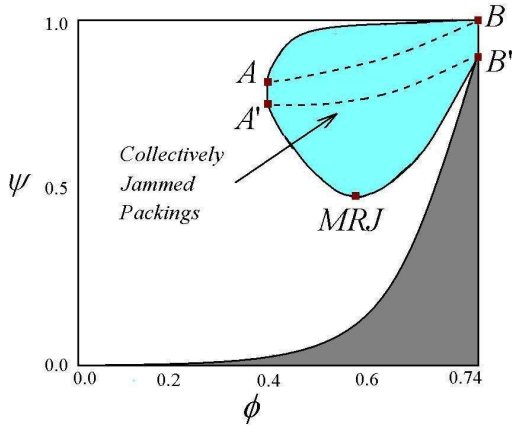
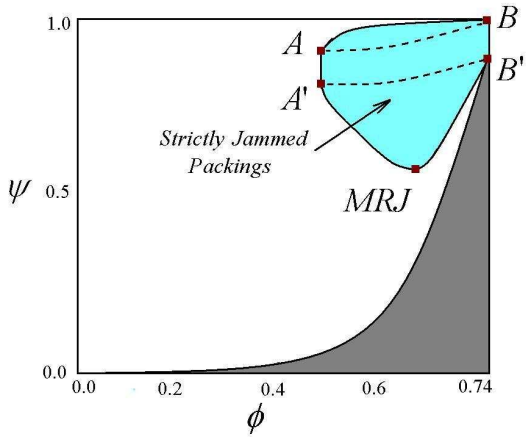
Order Maps for Jammed Frictionless Sphere Packings



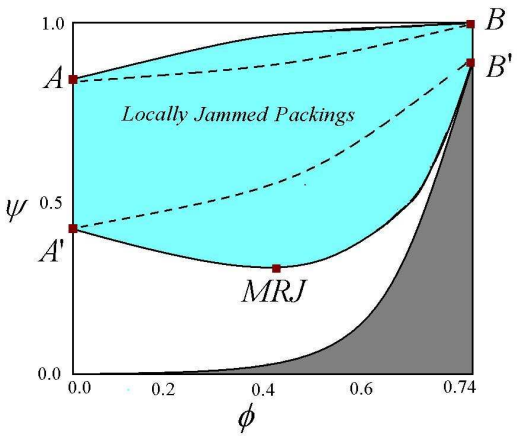


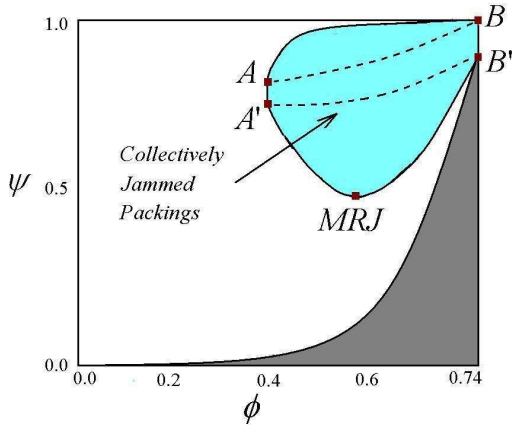


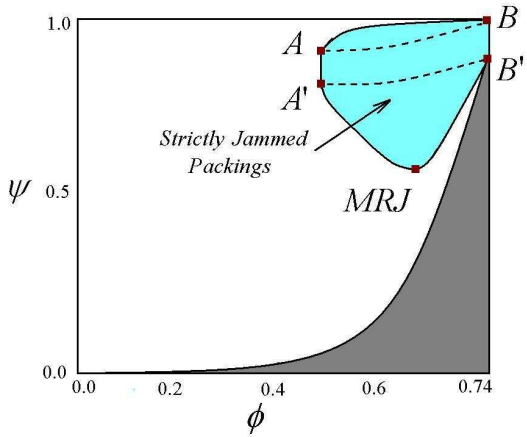
Geometric Structure Approach to Jammed Particle Packings

Torquato & Stillinger, Rev. Mod. Phys. (2010)

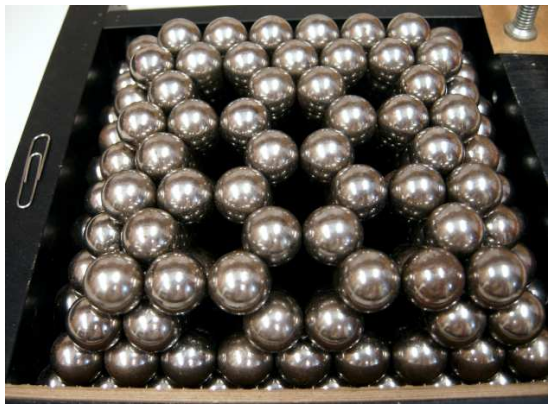
Order Maps for Jammed Frictionless Sphere Packings

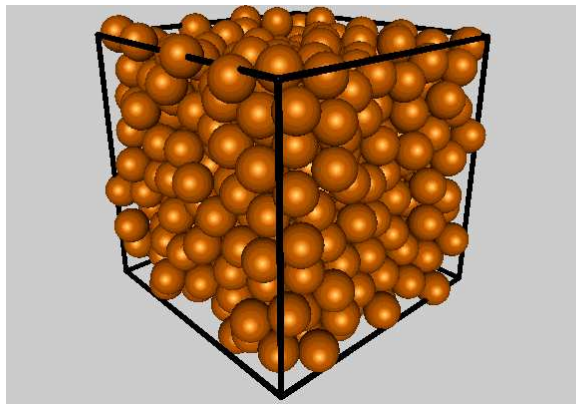


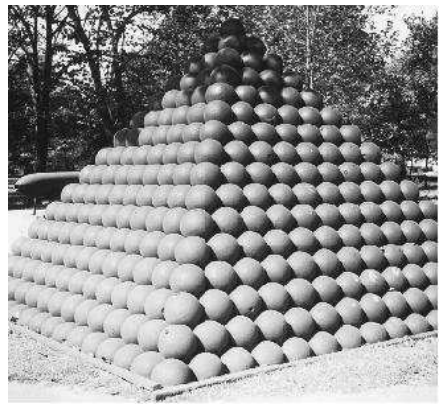




Optimal Strictly Jammed Packings







A: $Z = 7$ **MRJ:** $Z = 6$ **(isostatic)** **B:** $Z = 12$

MRJ state is a prototypical glass in that it is maximally disordered with infinite elastic moduli.

RCP Dramatically Breaks Down in Two Dimensions

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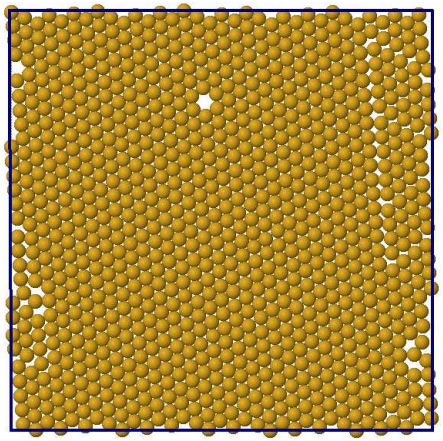

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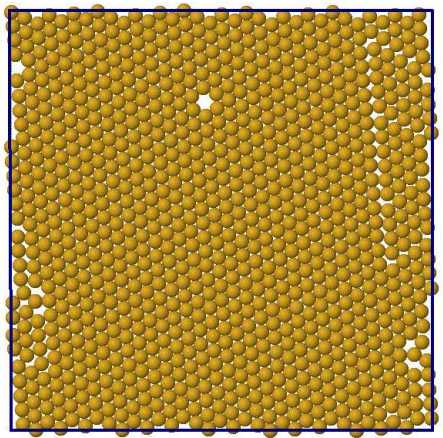
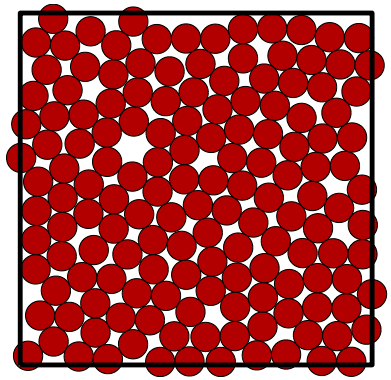
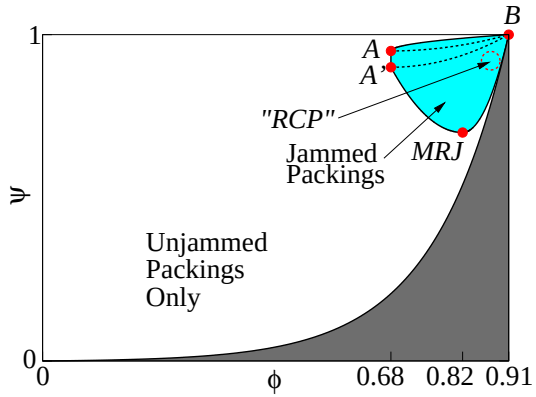


- Using a new packing algorithm, we have recently shown that MRJ isostatic jammed states exist.

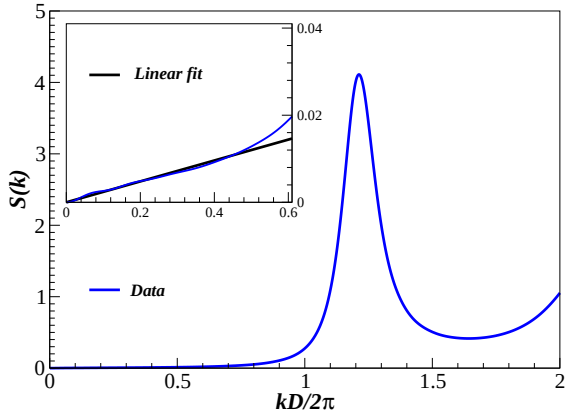




Atkinson, Stillinger & Torquato, PNAS (2014)

MRJ Particle Packings Possess Quasi-Long-Range Correlations

- **Such packings of identical spheres have been shown to be hyperuniform with quasi-long-range (QLR) pair correlations in which $h(r)$ decays as $-1/r^4$ (Donev, Stillinger & Torquato, PRL, 2005).**



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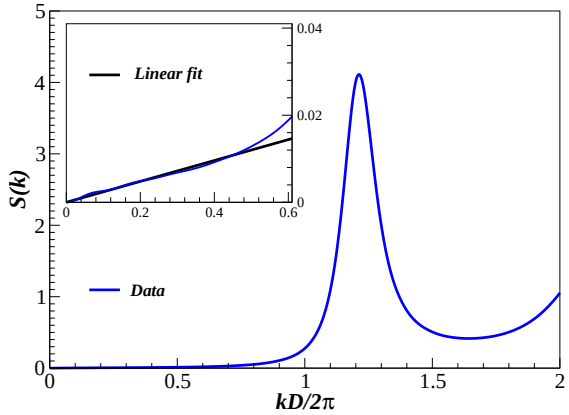


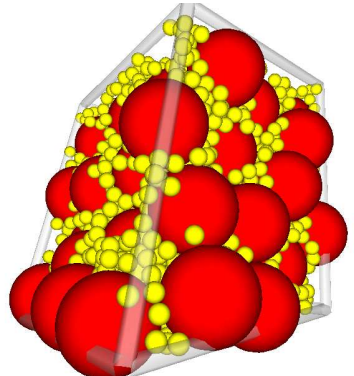
This is to be contrasted with the hard-sphere equilibrium fluid with correlations that decay exponentially fast.

- **Apparently, hyperuniform QLR correlations with decay $-1/r^{d+1}$ are a universal feature of general MRJ packings in $\mathbb{R}^d$.**

Zachary, Jiao and Torquato, PRL (2011): ellipsoids, superballs, sphere mixtures

Berthier et al., PRL (2011); Kurita and Weeks, PRE (2011); Hopkins et al. 2013 : sphere mixtures

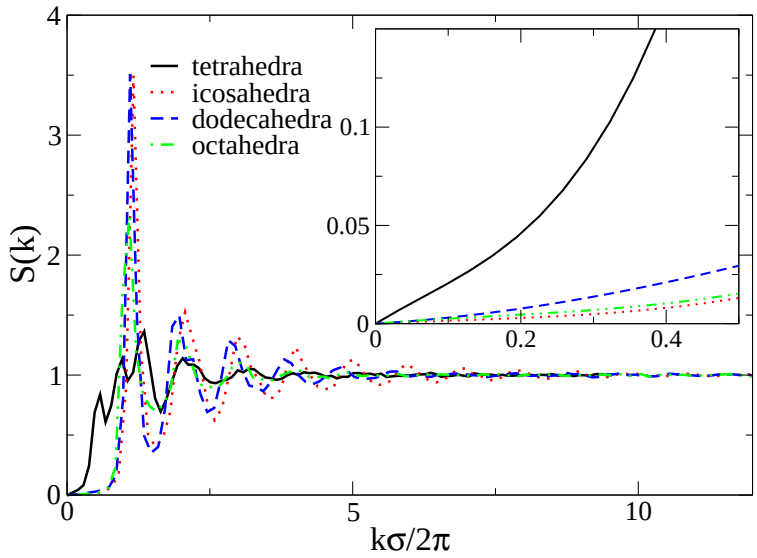
Jiao and Torquato, PRE (2011): polyhedra



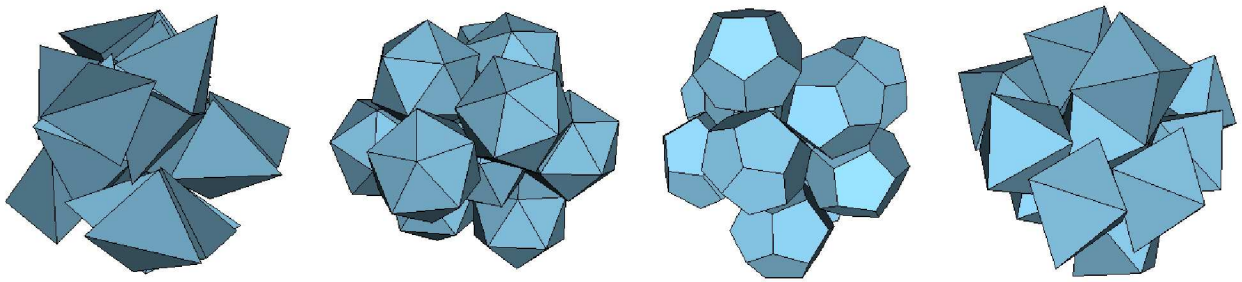
MRJ Packings of Nontiling Platonic Solids

Jiao & Torquato, PRE (2011)

Hyperuniform with quasi-long-rang (QLR) pair correlations ($1/r^4$) and isostatic.



(a)

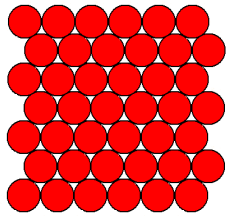


(b)

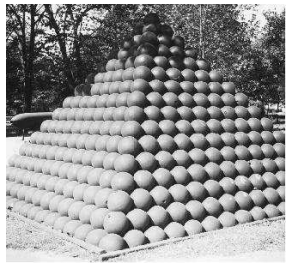
Figure 2: **(a) Structure factor $S(k)$ of the MRJ packings of the nontiling Platonic solids. The inset shows that $S(k)$ is linear in k for small k values. (b) Local contacting configurations: from left to right, tetrahedra, icosahedra, dodecahedra, and octahedra.**

Sphere Packing Problem

- For $d = 2$, triangular lattice: $\phi_{\max} = \pi/\sqrt{12} \approx 0.91$ (Fejes Tóth, 1940).



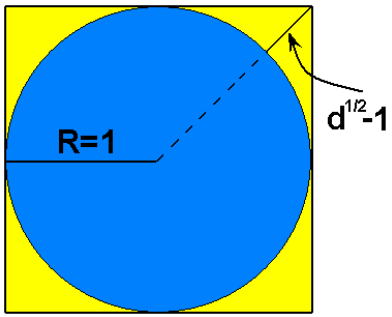
- For $d = 3$, Kepler (1606) conjectured that optimal packing is FCC lattice: $\phi_{\max} = \pi/\sqrt{18} \approx 0.74$ (Hales 1998, 2005).

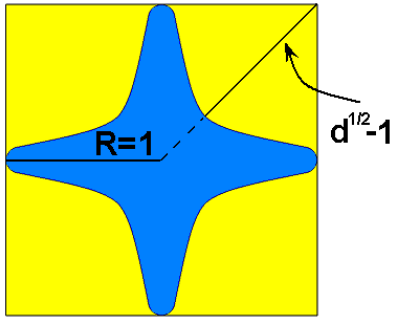


- Each dimension has its own distinct properties.
- In certain sufficiently low dimensions, optimal packings are believed to be lattice packings. Certain dimensions are remarkably symmetric and dense: E_8 lattice (Viazovska, 2016) and Leech lattice (Cohn et al., 2016) are optimal.
- Finding shortest lattice vector for a lattice grows superexponentially with d.
- In $\mathbb{R}^{10}$, the best known arrangement is a non-lattice packing found by Best (1980)!

Holes in d-Dimensional Lattice Packings

- **Hypercubic lattice packing becomes unsaturated at $d = 4$!**





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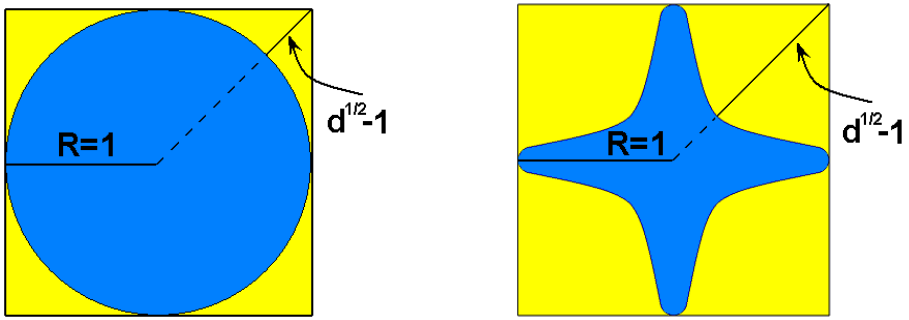

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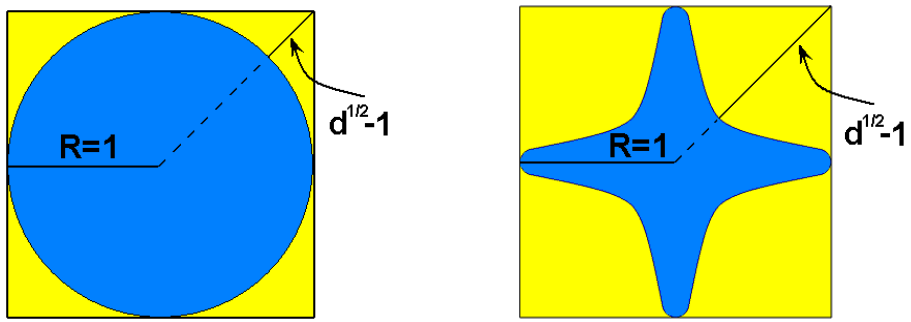

- **In sufficiently high dimensions, all lattice packings are almost surely unsaturated.**

- **GENERAL PRINCIPLE: Almost all volume in a high-dimensional particle is concentrated near the particle surface.**

  Example: The fraction of the volume of a sphere up to 90% of its radius is given by $(9/10)^d$, which tends rapidly to zero as $d \to \infty$.

Minkowski Lower Bound on $\phi_{\max}$ for Lattice Sphere Packings

Minkowski (1905): **The maximal packing density $\phi_{\max}$ of a lattice packing of congruent spheres in $\mathbb{R}^d$ for $d \geq 2$ satisfies**

$$\phi_{\max} \geq \frac{\zeta(d)}{2^{d-1}},$$

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3. For large d, best lower and upper bounds, respectively, are of the form:

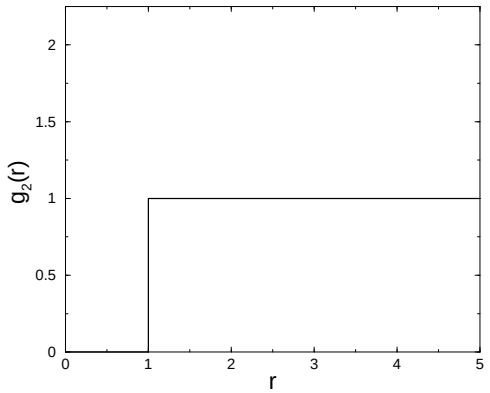
$$\phi \geq \frac{2d}{2^d} \qquad \text{(Ball, 1992)}$$

$$\phi \leq \frac{1}{2^{0.5990d}} \qquad \text{(Kabatiansky and Levenshtein, 1978)}$$

Random Packings Beat Checkerboard Lattice in Relatively Low d.

Torquato and Stillinger, Phys. Rev. E (2006)

- **Disordered sphere packings exist with** $g_2(r) = \Theta(r-1)$ **and** $\phi = 1/2^d$



and the cumulative coordination number is given by

$$Z(r) = \rho s_1(1) \int_1^r x^{d-1} g_2(x) dx = \frac{r^d}{d} - 1 \qquad \text{for} \quad r \geq 1.$$

This disordered packing beats the checkerboard lattice D_d **for** $d > 27$**!**

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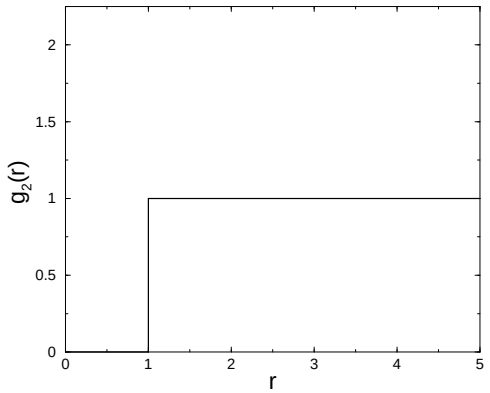

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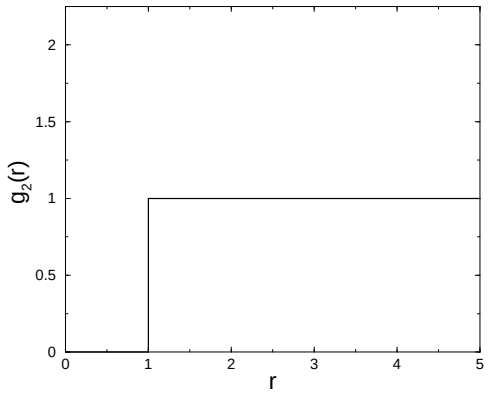

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- **At** $r = \sqrt{3}$ **and** $d > 6$

$$\frac{Z(\sqrt{3})}{Z_3} \sim \frac{3^{d/2}}{4d^6/45} \qquad (Z(\sqrt{3})/Z_3 = 10^{13} \quad \text{for} \quad d = 100)$$

Disordered Packings Might Win in High Dimensions

Using test disordered pair correlation functions and a conjecture concerning the existence of disordered packings, we derived the following conjectural lower bound on $\phi_{\max}$ for sphere packings in $\mathbb{R}^d$:

$$\phi_{\max} \geq \frac{c(d)}{2^{(0.7786\ldots)d}}.$$

This provides the putative exponential improvement over Minkowski's 100-year-old bound ($\phi_{\max} \geq 1/2^d$) for lattices.

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- Also implies that the ground states of systems interacting with LJ-like potentials are highly degenerate and disordered in sufficiently high d.

THANKS TO MY COLLABORATORS!

Pablo Debenedetti (Princeton)

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Bob Connelly (Cornell)

Yang Jiao (Princeton/Arizona State)

Antonello Scardicchio (ICTP, Trieste)

Chase Zachary (Princeton)

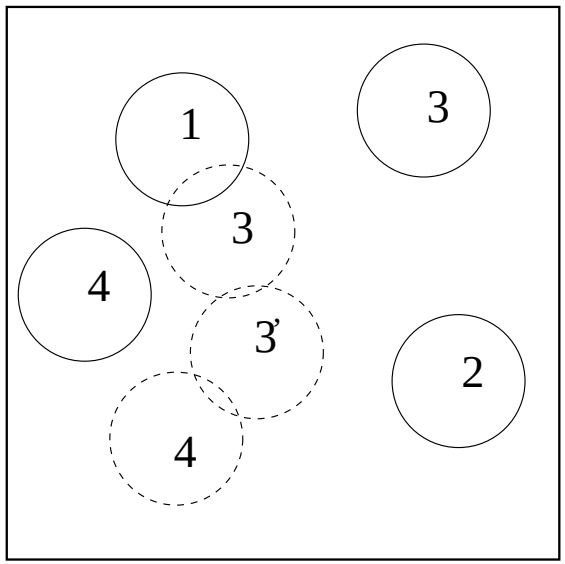
Adam Hopkins (Princeton)

Steve Atkinson (Princeton)

Ghost RSA Packing: An Exactly Solvable Model

Torquato and Stillinger, Phys. Rev. E (2006)

- **The "ghost" random sequential addition (RSA) packing is an exactly solvable model, i.e., all of the n-particle correlation functions (g_2, g_3, etc.) can be expressed exactly for all allowable densities and in any dimension d.**



- **The density at any time t is given by $\phi(t) = [1 - \exp(-2^d t)]/2^d$, and the maximum density is**

$$\phi(\infty) = \frac{1}{2^d},$$

proving that there is a disordered packing that achieves the Minkowski bound!

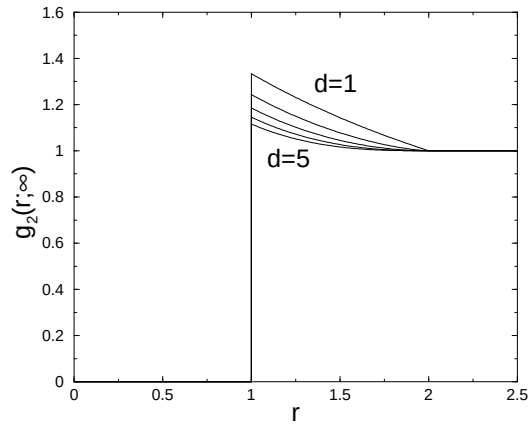
Ghost RSA Packing: An Exactly Solvable Model

- **At small times or, equivalently, low densities, can show**

$$g_2(r;\phi) = \Theta(r-1) + \mathcal{O}(\phi^3).$$

- **At the maximum density $\phi(\infty) = 1/2^d$,**

$$g_2(r;\infty) \equiv \lim_{t\to\infty} g_2(r;t) = \frac{\Theta(r-1)}{1-\alpha_2(r;1)/2}.$$

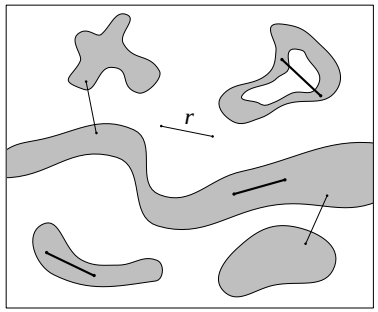


- **In the limit $d \to \infty$ and for $\phi = 1/2^d$,**

$$g_n(\mathbf{r}_{12},\ldots,\mathbf{r}_{1n};\infty) \sim \prod_{i<j} g_2(r_{ij};\infty), \quad \text{and} \quad g_2(r;\infty) \sim \Theta(r-1).$$

A “Nonlinear" Path to Crucial Information: C_2

- Desire finite set of lower-order functions with high sensitivity
- Two-point cluster function: $C_2(r)$



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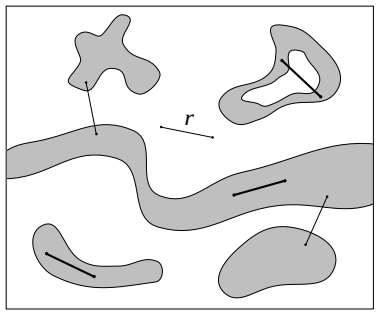

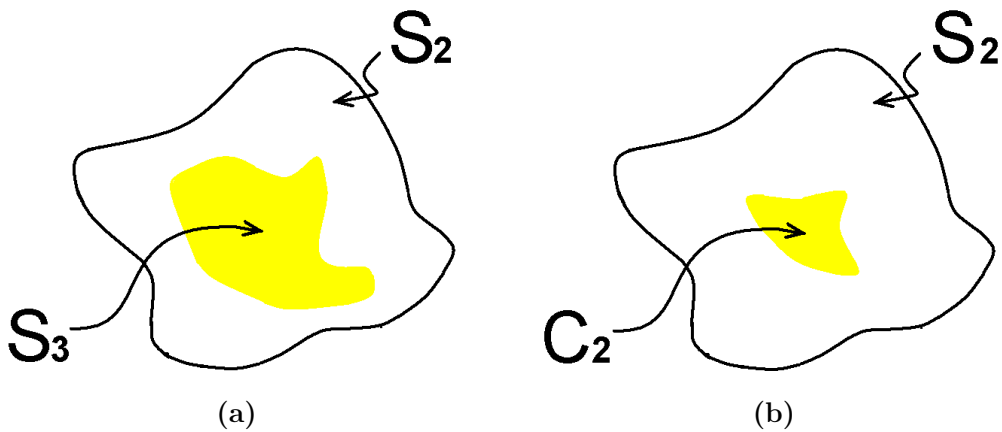

Figure 3: Schematic of set of all microstructures with particular S_2 shown as the region enclosed by the solid contour in both panels. (a) Yellow region shows set of all microstructures associated with the same S_2 and S_3. (b) Smaller yellow region shows set of all microstructures associated with the same S_2 and C_2.

Jiao, Stillinger & Torquato, Proc. Nat. Acad. Sci. (2009)

Existence of Disordered Packings in High Dimensions

Definition: **Disordered packing is one in which $g_2(\mathbf{r})$ decays to 1 faster than $1/|\mathbf{r}|^d$.**

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Definition: **Disordered packing is one in which $g_2(\mathbf{r})$ decays to 1 faster than $1/|\mathbf{r}|^d$.**

- **Existence Theorem for Point Processes:** **A necessary condition for the existence of a nonnegative pair correlation function $g_2(\mathbf{r})$ (nonnegative tempered distribution) of a translationally invariant point process at some number (center) density ρ is that $S(\mathbf{k}) \equiv 1 + \rho\tilde{h}(\mathbf{k}) \geq 0$, where $h(\mathbf{r}) \equiv g_2(\mathbf{r}) - 1$ and $\tilde{h}(\mathbf{k})$ is the Fourier transform of $h(\mathbf{r})$.**

- **Conjecture:** **A hard-core nonnegative tempered distribution $g_2(\mathbf{r})$ is a pair correlation function of a disordered sphere packing in $\mathbb{R}^d$ at number density ρ for sufficiently large d if and only if $S(\mathbf{k}) \geq 0$. The maximum achievable density is the terminal density ϕ_*.**

Existence of Disordered Packings in High Dimensions

Definition: Disordered packing is one in which $g_2(\mathbf{r})$ decays to 1 faster than $1/|\mathbf{r}|^d$.

- **Existence Theorem for Point Processes:** A necessary condition for the existence of a nonnegative pair correlation function $g_2(\mathbf{r})$ (nonnegative tempered distribution) of a translationally invariant point process at some number (center) density ρ is that $S(\mathbf{k}) \equiv 1 + \rho\tilde{h}(\mathbf{k}) \geq 0$, where $h(\mathbf{r}) \equiv g_2(\mathbf{r}) - 1$ and $\tilde{h}(\mathbf{k})$ is the Fourier transform of $h(\mathbf{r})$.

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- **Decorrelation Principle:** Unconstrained spatial correlations in disordered sphere packings that may be present in low dimensions vanish asymptotically in high dimensions; and g_n for any $n \geq 3$ can be inferred entirely (up to some small error) from a knowledge of the number density ρ and the pair correlation function $g_2(\mathbf{r})$.

  - **Why?** ϕ vanishes exponentially fast as $d \to \infty$: $\phi_{\max} \leq 2^{-0.5990d}$.

  Also, other known necessary conditions only have relevance in very low dimensions.

Obtaining Lower Bounds Using Disordered Test Functions

- **Torquato and Stillinger (2002):** **Consider a family of test radial tempered distributions $g_2(r;a)$ at density ϕ, where a denotes a set of parameters. Now consider the optimization problem**

$$\max_a \phi$$

subject to the constraints

$$\begin{aligned} g_2(r;a) &= 0 \quad \text{on} \quad [0,1], \\ g_2(r;a) &\geq 0 \quad \forall r, \\ S(k;a) &\geq 0 \quad \forall k. \end{aligned}$$

We call $\phi_* \equiv \max_a \phi$ the terminal density and note that if such a g_2 at ϕ_* is realizable by a packing, then $\phi_{\max} \geq \phi_*$.

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- **Using this optimization scheme, we can recover the Minkowski and Ball asymptotic lower-bound forms on $\phi_{\max}$ for lattices using disordered test g_2's.**

- **Our optimization problem is the dual of the linear program devised by Cohn and Elkies (2003) for an upper bound on $\phi_{\max}$. The latter involves test pair potentials.**