Jammed Packings of Hard Particles

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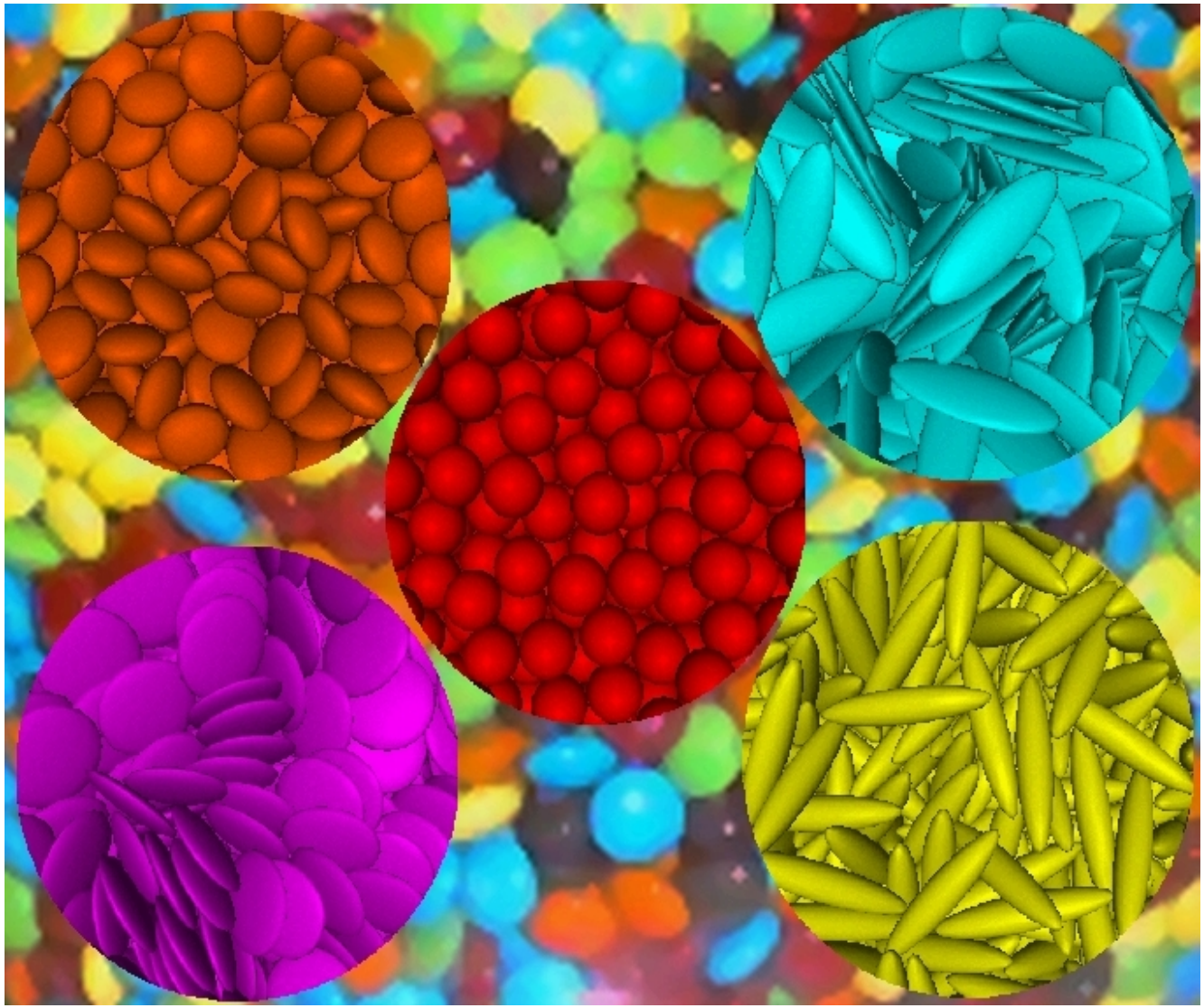
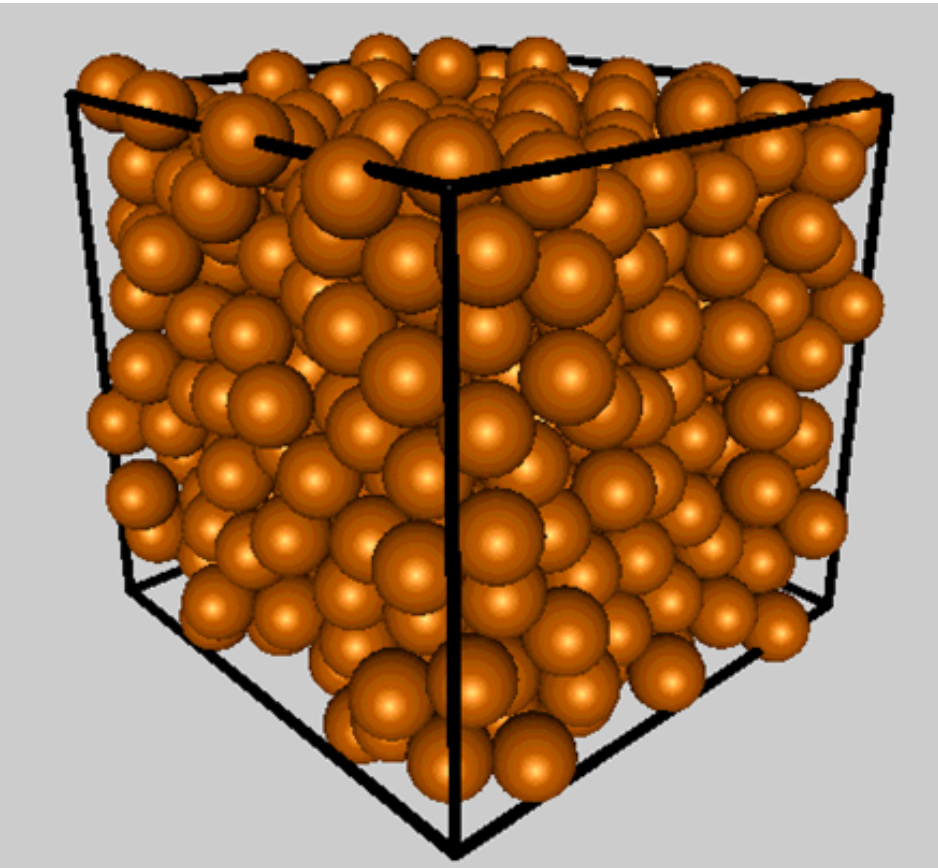
9th June 2006

FPO Presentation

What my dissertation is about?

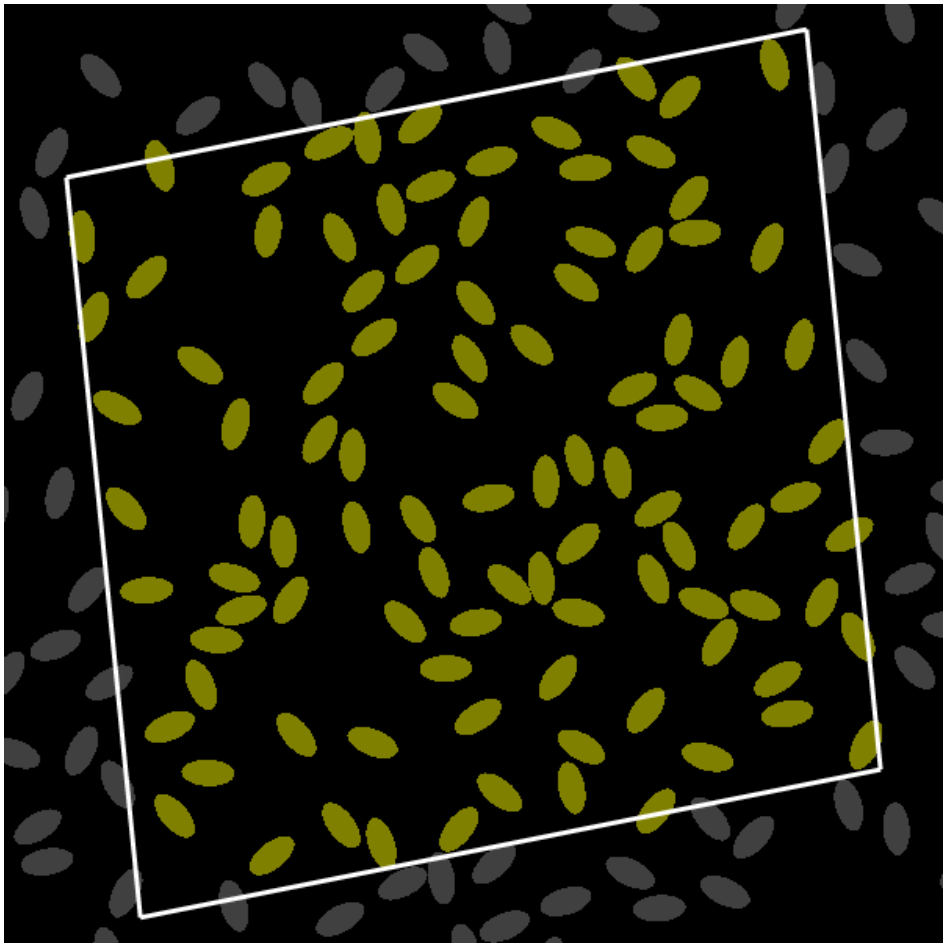


Why Study Packings?



- Good starting **models** for the structure of diverse **materials**: *granular media*, *colloids*, *liquids*, *glasses*, *crystals*...
- Packing problems are **ancient** in mathematics and in real-life: *Densest packing* of a shape in $\mathcal{R}^d$
- Hard-particle problems are **hard**!
- **Multidisciplinary** field: *physical sciences*, *mathematics*, *engineering*, *computer science*, *biology*.

Jamming



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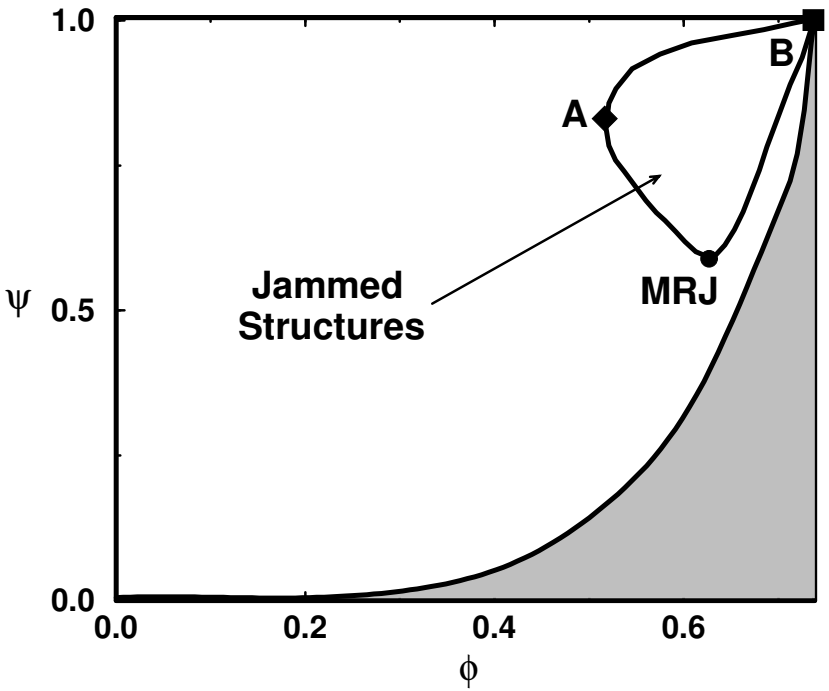
- **Jammed (rigid) packing**: Particles are locked in their positions despite thermal agitation/shaking and/or boundary deformations/loading.
- **Boundary conditions** determine different **jamming categories** (*local*, *collective*, *strict*):
  - frozen particles, hard walls, or periodic
  - fixed or flexible

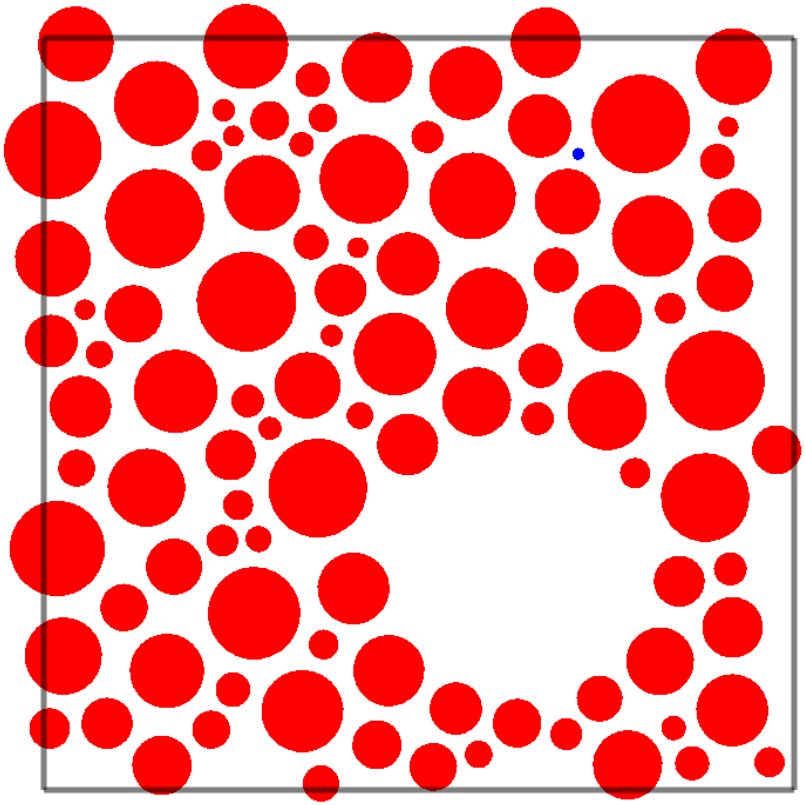
Randomness



Distinguish configurations based on **how disordered** they are

- A **scalar order metric** $0 \leq \psi \leq 1$ (translational, orientational, bond-orientational, etc.)
- Special **dynamics-independent** point: **Maximally Random Jammed** (MRJ) state
- *Is there a "universal" order metric:* **Entropy** *(information-content)?*

Configurational-Space View



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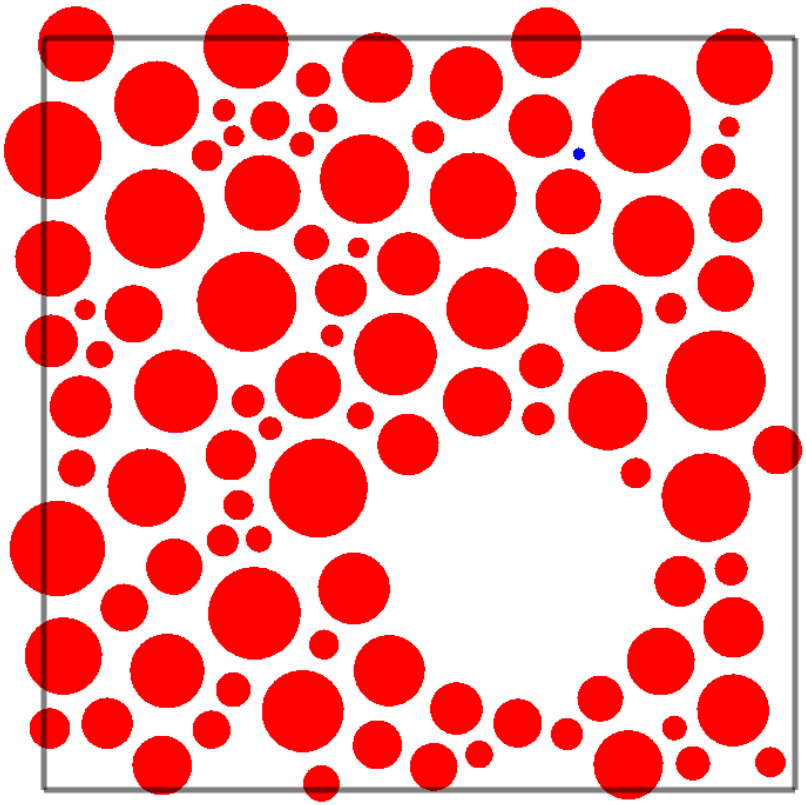


(MNG)

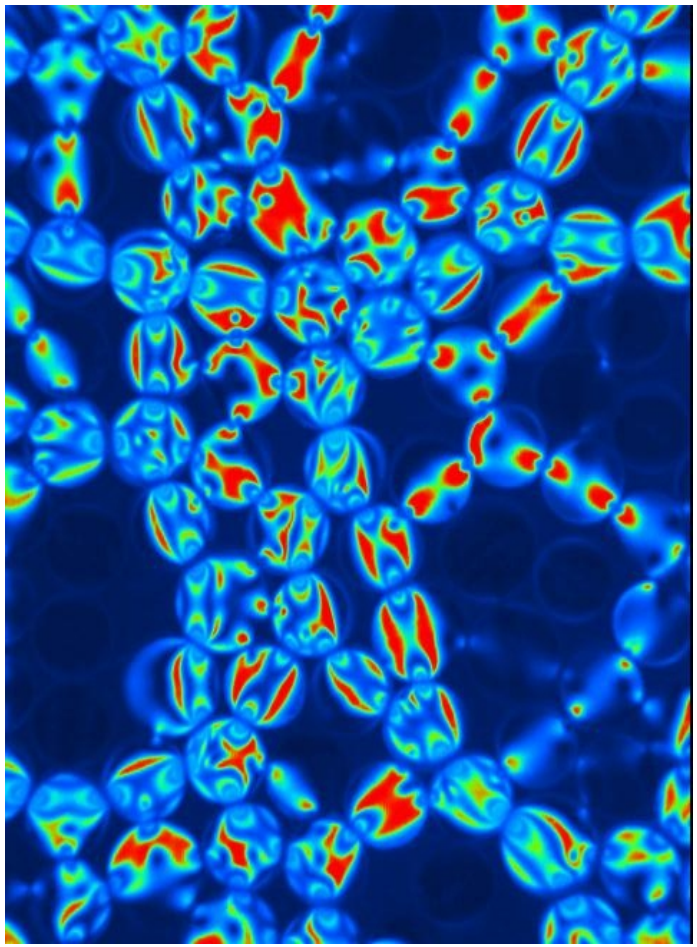
Faster (fastest?) compression leads to MRJ (MNG).

Summary of Main Results

In this dissertation, we *develop* and *discover that*:

- Event-driven MD algorithms for nonspherical particles.
- Algorithms based on rigidity theory and mathematical programming to test for jamming.
- Asphericity dramatically affects the density and contact number.
- Experimentally verify the simulation predictions.
- The densest-known crystal packing of ellipsoids.
- Unexpected short-range and long-range correlations in disordered hard sphere packings for $d \geq 3$.
- Orientationally-disordered tetratic solid phase for hard dominos.
- There is no ideal glass transition for binary hard-disk mixtures.

Molecular Dynamics (MD) Algorithm



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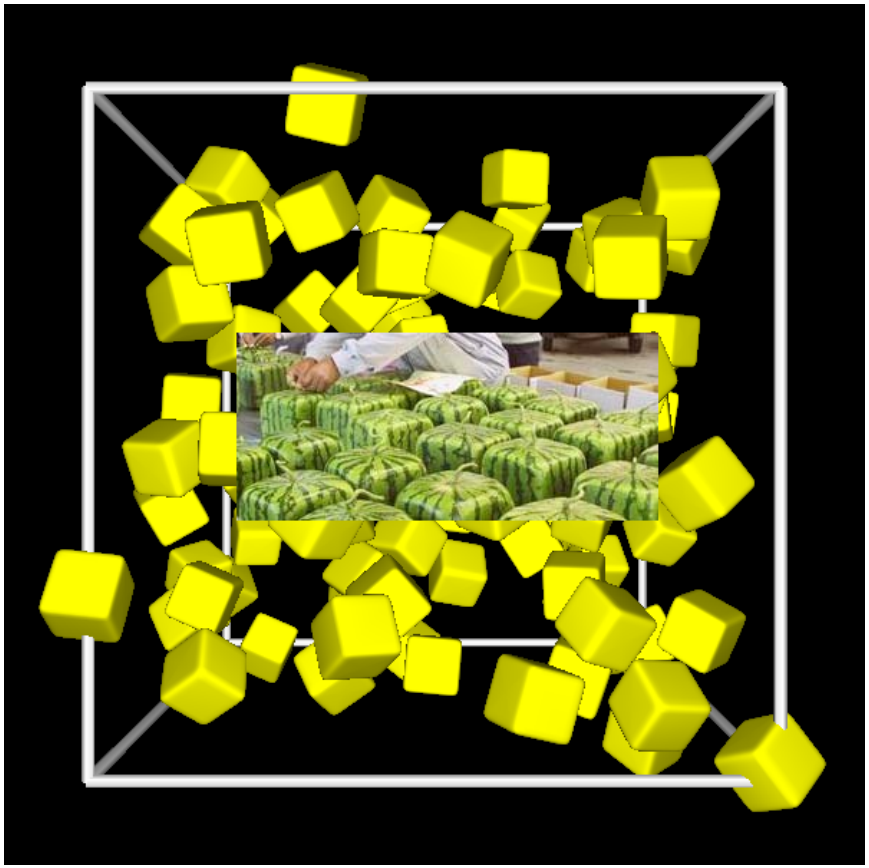
Behringer et al.

- Event-driven MD (**EDMD**) packing algorithm *ala* **Lubachevsky-Stillinger**
- Sophisticated optimized algorithm (**NNL**s, bounding complexes, etc.) tailored for hard particles.
- The workhorse of this research program!
- "*Neighbor List Collision-Driven Molecular Dynamics Simulation for Nonspherical Particles.*"
  A. Donev, F. H. Stillinger, and S. Torquato
  J. Comp. Phys, **2005**

Packing for Different Shapes/Containers



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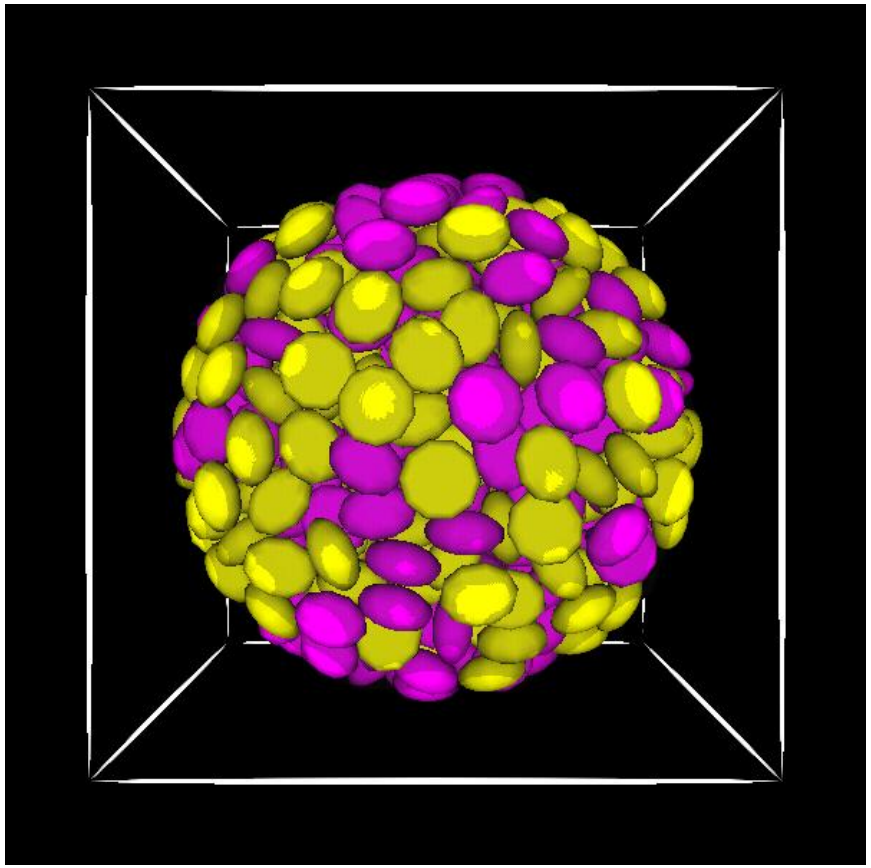

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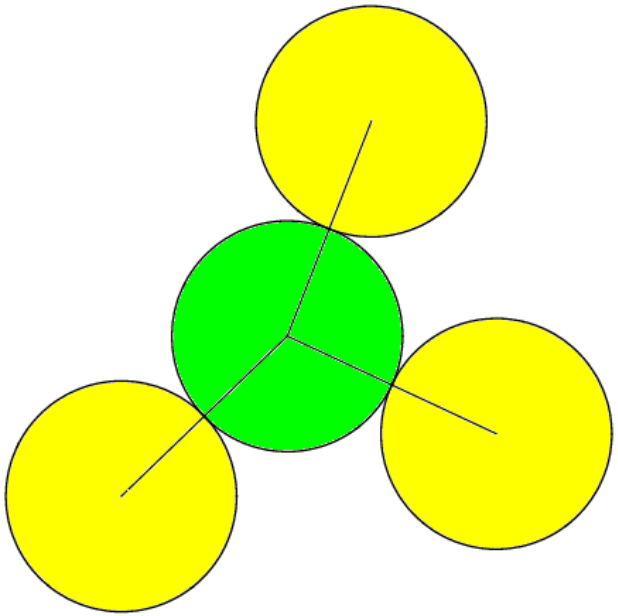
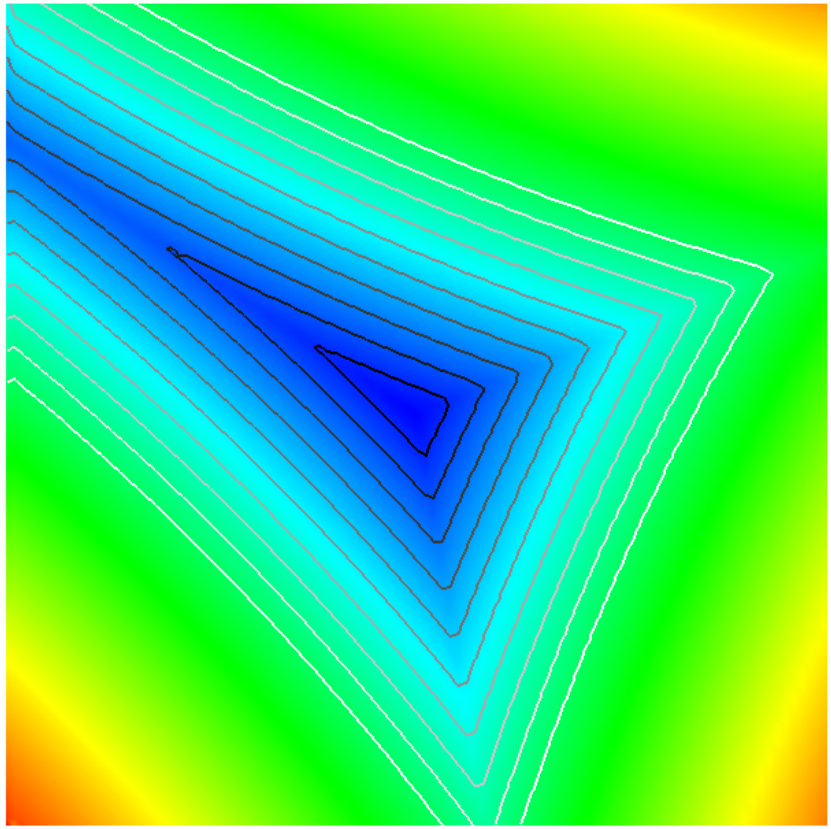
Jamming as Configurational Entrapping





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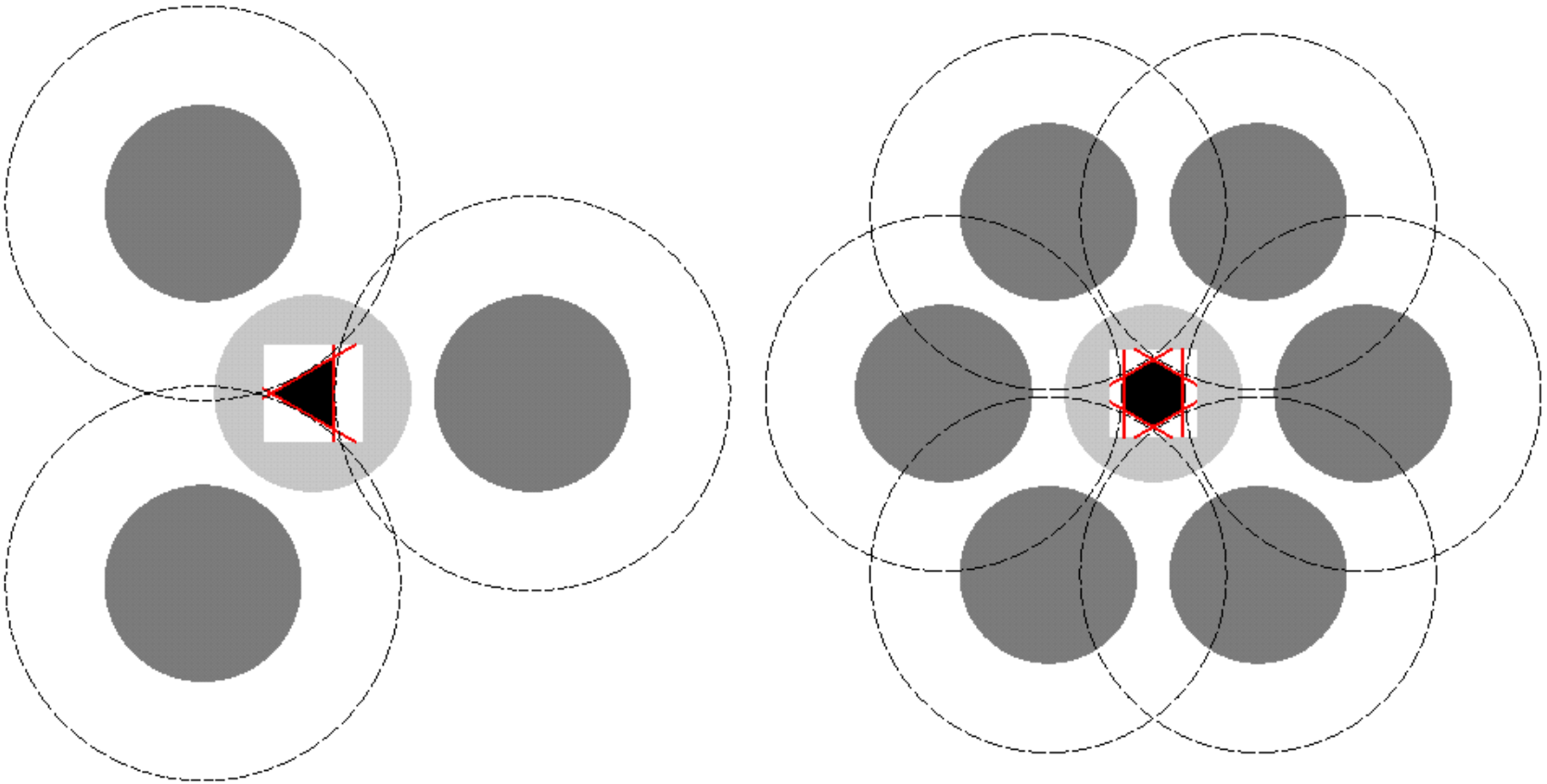
Jamming Polytope $\mathcal{P}_{\Delta \mathbf{R}}$

- We have a **jamming polytope** $\mathcal{P}_{\Delta \mathbf{R}}$: $\mathbf{A}^T \Delta \mathbf{R} \leq \Delta \mathbf{l}$, as given by the **rigidity matrix A**.
- Jamming *implies* existence of **contact forces**:

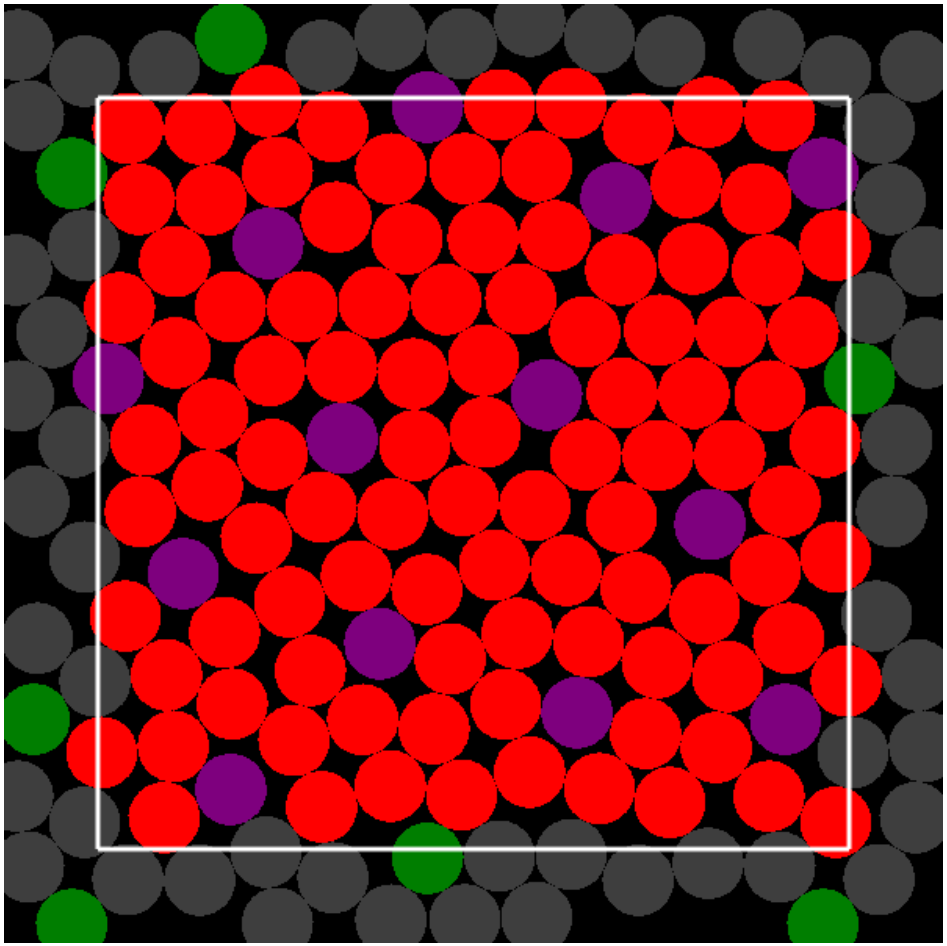
$$\mathbf{Af} = 0 \text{ and } \mathbf{f} \geq 0$$

- Theorem: If the packing is jammed than $\mathcal{P}_{\Delta \mathbf{R}}$ is closed for $\phi > \phi_J \left[1 - \delta_{\max}(N)\right]$.
- If the number of contacts $M = N_f \approx Nd$, i.e., $\bar{Z} = 2d$, the jamming polytope is a **simplex**, corresponding to an **isostatic** packing.

Simplices and Isostatic Packings



Collective Unjamming Motions



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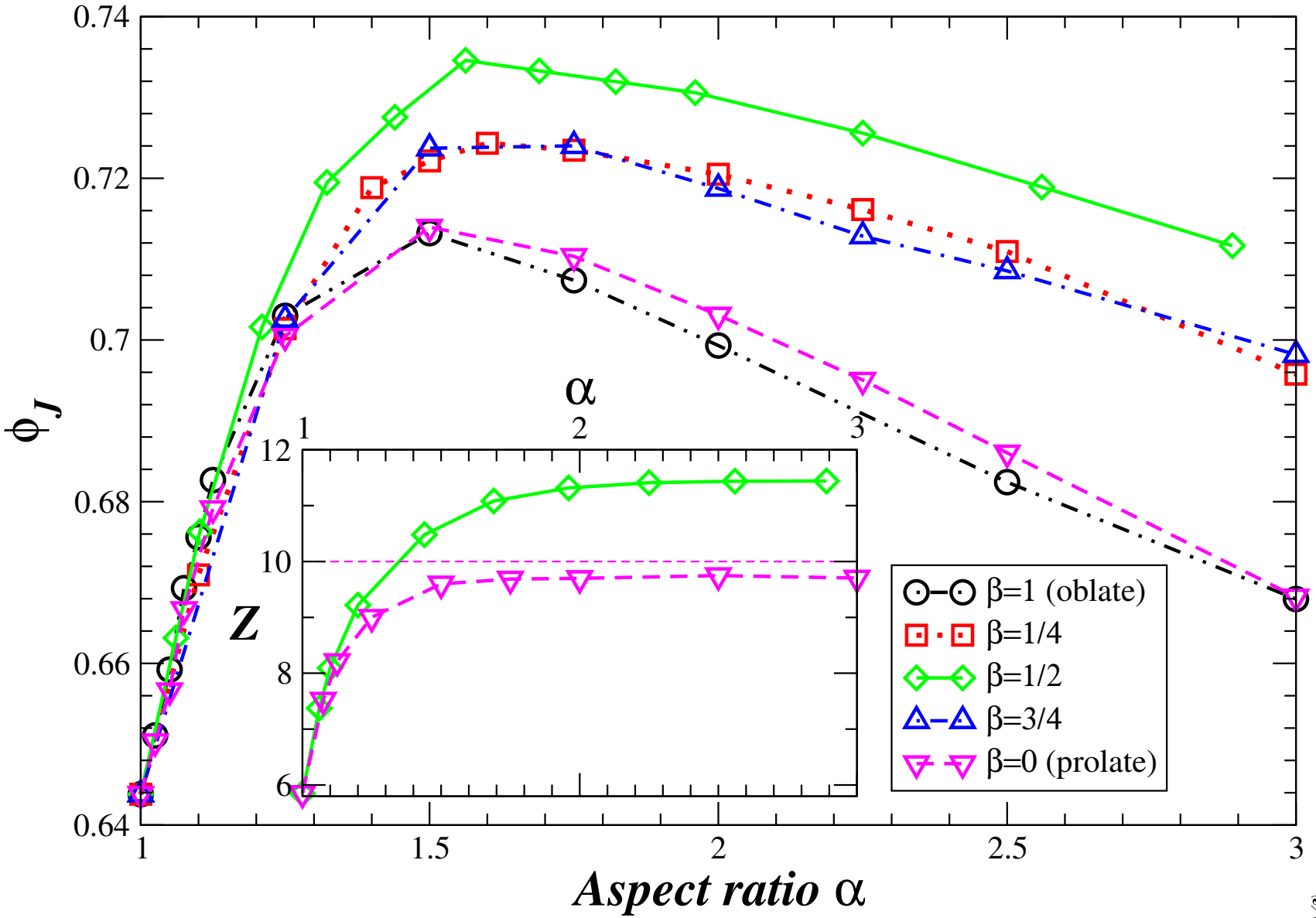
- Using *randomized* sequential **linear programming** to find collective unjamming motions.
- "*A Linear Programming Algorithm to Test for Jamming in Hard-Sphere Packings*" **A. Donev**, S. Torquato, F. H. Stillinger, and R. Connelly, **J. Comp. Phys, 2004**

Random Packing of Ellipsoids

- If the EDMD algorithm is applied to spheres with **random initial conditions** and a growth rate γ that is on the order of $10^{-2} - 10^{-5}$ times smaller than the velocity, the terminal **disordered** (**random**) **packings** have a (**jamming**) density $\phi \approx 0.64 - 0.65$.
- *Extrapolation*: Apply the same procedure to ellipsoids with axes $a : b : c = 1 : \alpha^{\beta} : \alpha$.
- Here $\alpha > 1$ is the **aspect ratio** (ratio of subscribed and circumscribed sphere diameters).
- And $0 \leq \beta \leq 1$ is the "oblateness", or **skewness** ($\beta = 0$ is **prolate**, $\beta = 1$ is **oblate**).

Density ϕ and Contact Number $\bar{Z}$



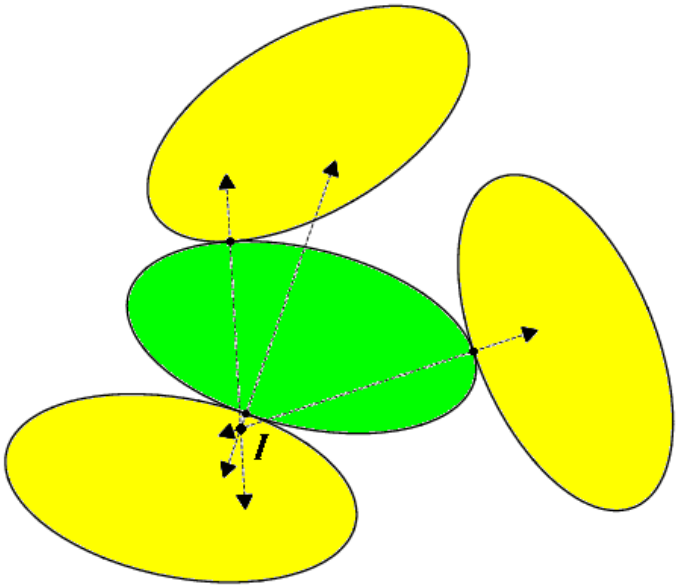
Isostaticity Breaks Down for NonSpheres

- The maximum ϕ (and $\bar{Z}$!) is for axes $0.8:1:1.25$ ($\beta = 0.5$, $\alpha \approx 1.6$) and it approaches that of **crystalized spheres**, $\phi \approx 0.735$. These are **ollipsoids**.
- **Isostatic conjecture:** Large random jammed packings have

$$Z \to 2d_f$$

  where d_f is the number of degrees of freedom *per particle*.
- For spheres, $Z_{\text{isostatic}} = 6$, for spheroids $Z_{\text{isostatic}} = 10$, and for asymmetric shapes $Z_{\text{isostatic}} = 12$
- For ellipsoids with large $\alpha \gtrsim 2$ the isostatic conjecture holds *approximately*, but generally $Z < Z_{\text{isostatic}}$.

When Curvature Matters



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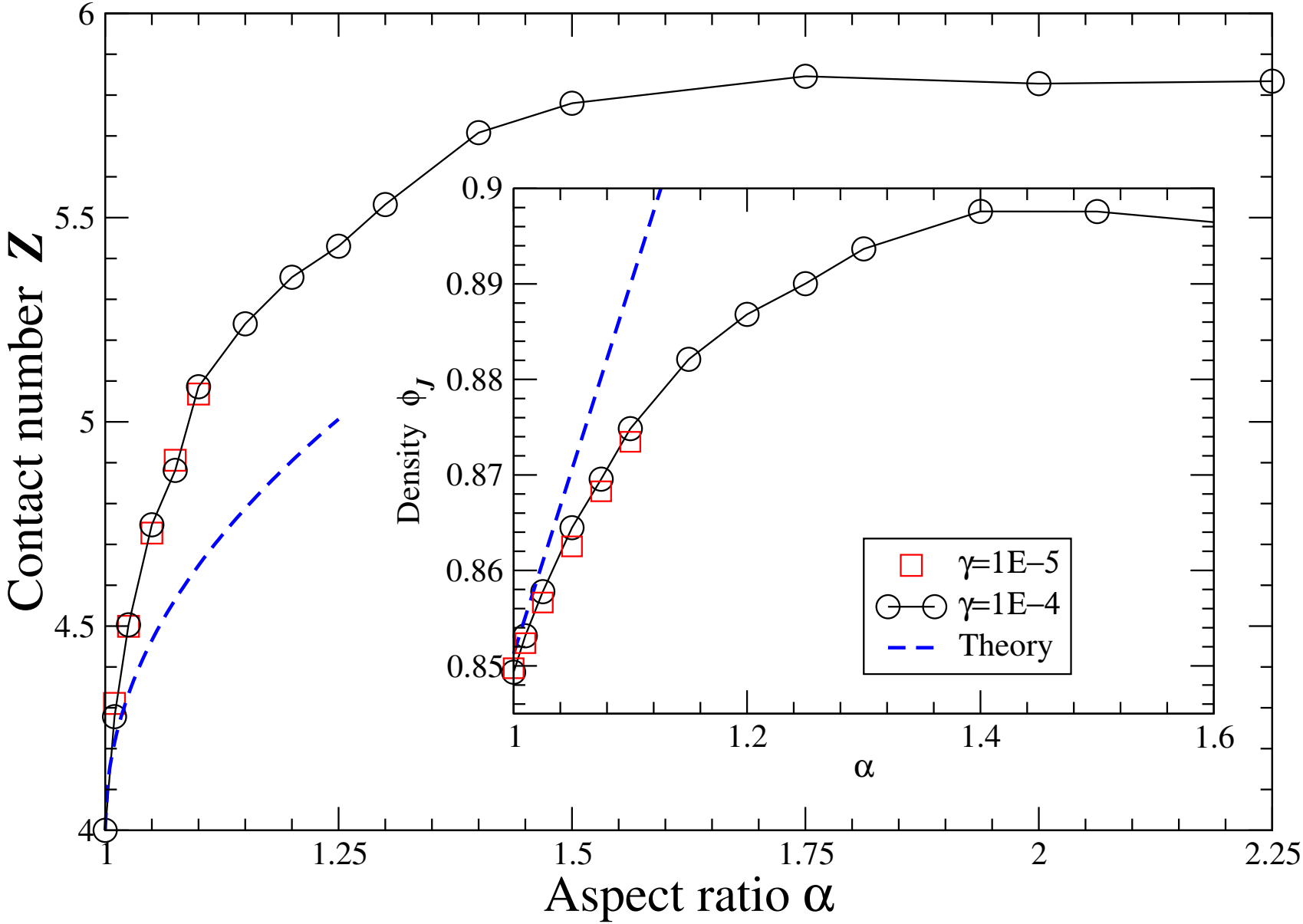
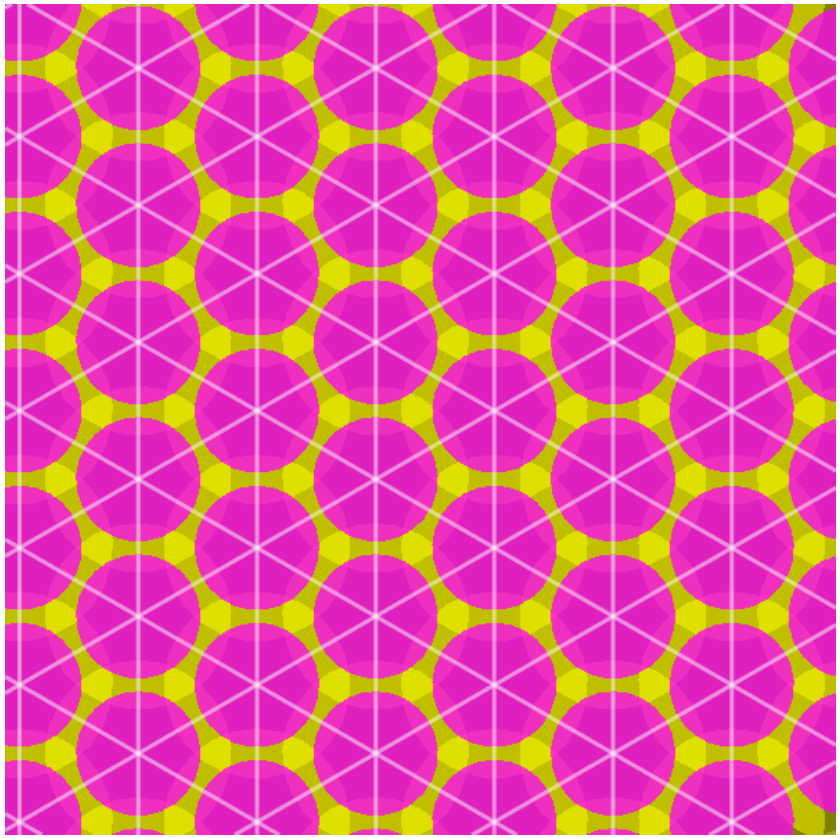
- Forces are balanced, and the torque is identically zero!
- Application of torque will cause a **finite deformation** decreasing with the elastic moduli.
- "*Hypostatic Jammed Packings of Hard Ellipsoids*"
  A. Donev, R. Connelly, F. H. Stillinger and S. Torquato, **Phys. Rev. E**

Near-Sphere Expansion



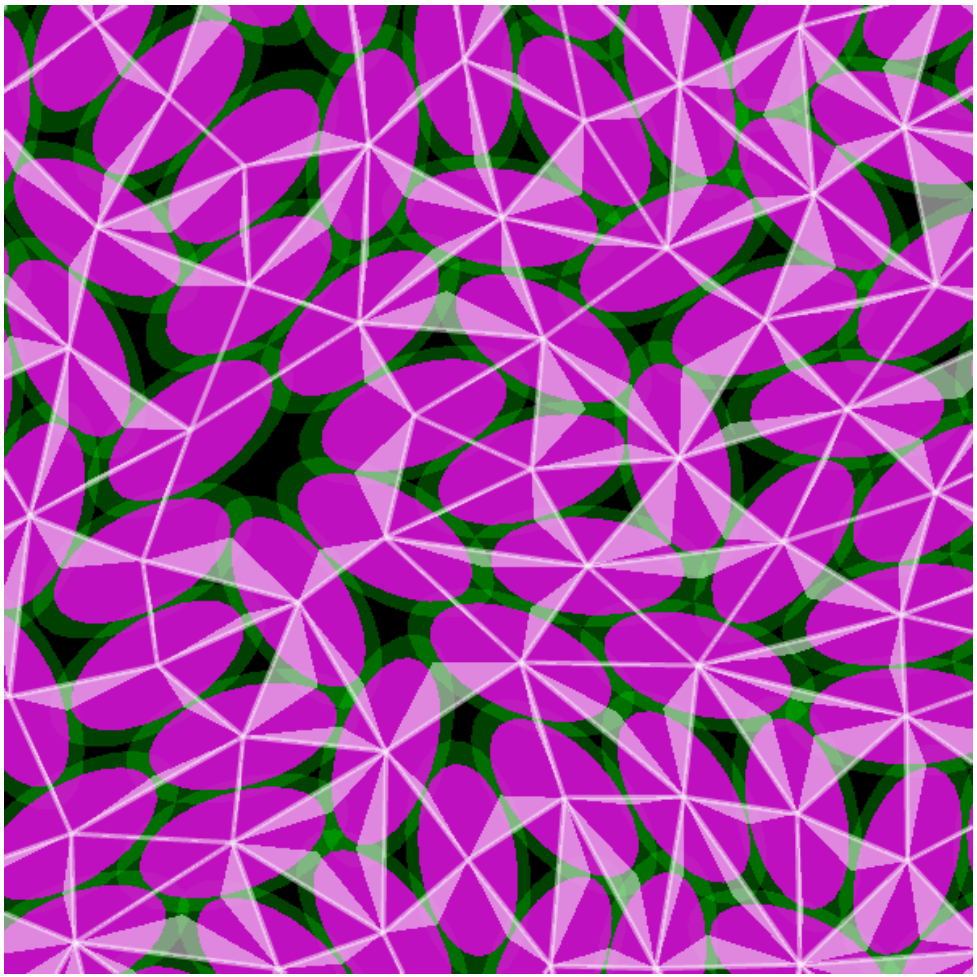
The BCMD Algorithm: Disks



Link: `Graphics/LSD.HS.2D.BCMD.mpg`

"*Calculating the Free Energy of Nearly Jammed Hard-Particle Packings Using Molecular Dynamics*",
A. Donev, F. H. Stillinger and S. Torquato, **J. Comp. Phys.**

The BCMD Algorithm: Ellipses

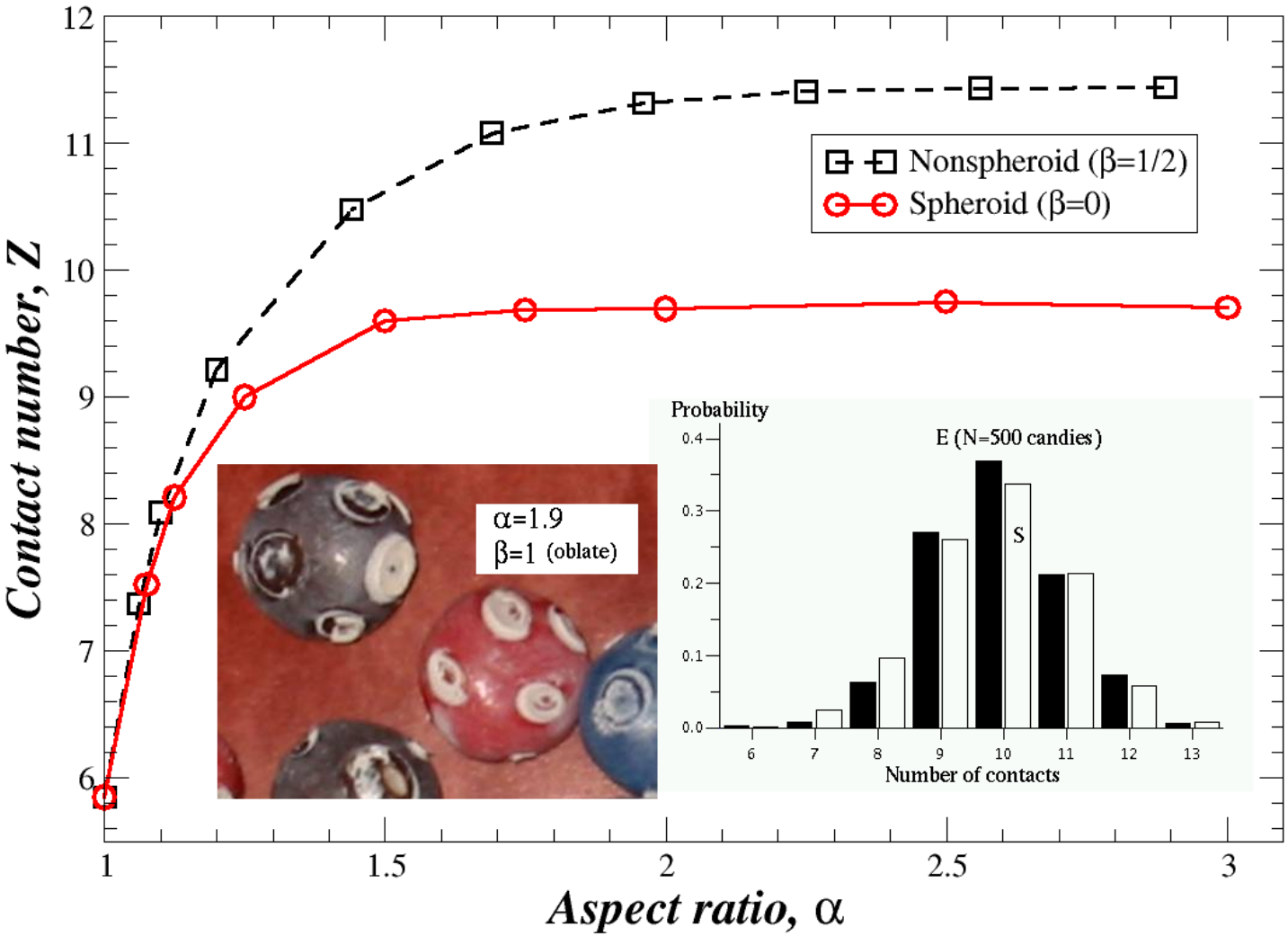


Link: `Graphics/LSD.HE.2D.BCMD.mpg`

Packing MMs

- Compare computer-generated packings to experiments with M&Ms!
- "*Improving the Density of Jammed Disordered Packings using Ellipsoids*"
  A. Donev, I. Cisse, D. Sachs, E. A. Variano, F. H. Stillinger, R. Connelly, S. Torquato and P. M. Chaikin
  Science, 2004

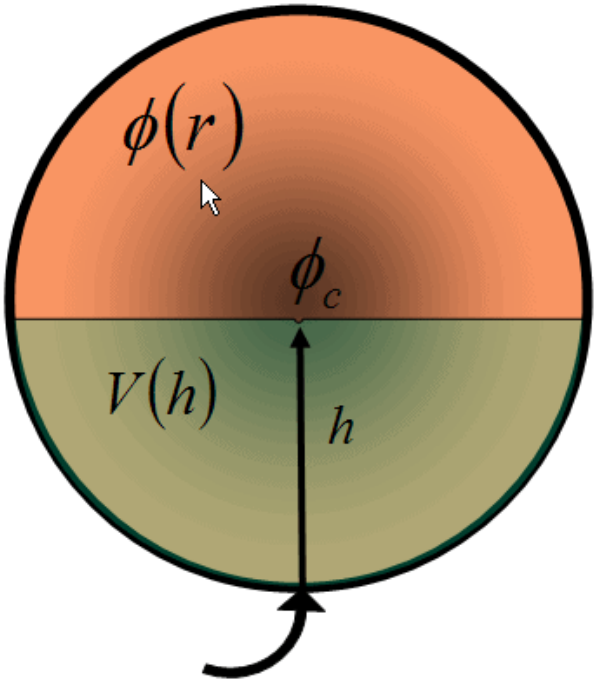
Contact Number Z



Comparing Simulation to Experiment

- Manufacture 1000 ollipsoids using **stereolithography**.
- We need to correct for the strong **finite-size** and **boundary** effects!
- "*Experiments on Random Packings of Ellipsoids*" W. Man, **A. Donev** , F. H. Stillinger, M. T. Sullivan, W. B. Russel, D. Heeger , S. Inati, S. Torquato and P. M. Chaikin **Phys. Rev. Lett., 2005**

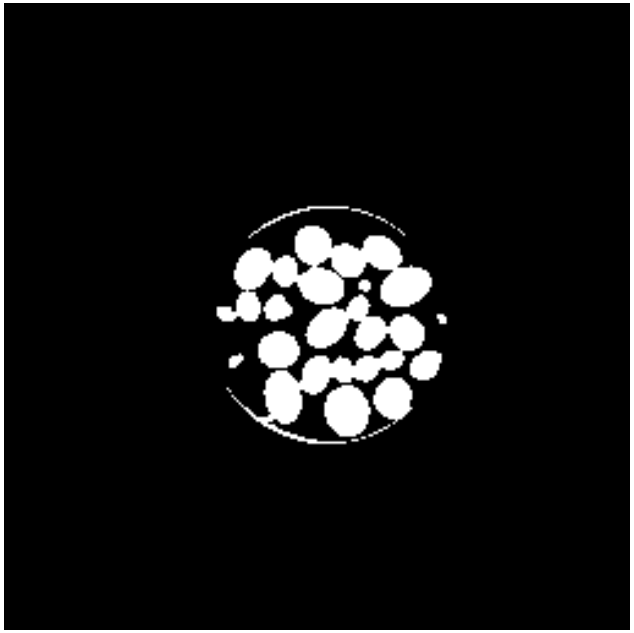
High-School Approach



- Formally $1-\phi(r)=\frac{1}{2\pi r}\frac{\partial^2 V(h=r)}{\partial h^2}$.
- Fitting $V(h)=\frac{\pi}{3}(1-\phi_c)h^3-AR^2+B$ with a **cubic fit** works well!
- It confirmed that $\phi_c\approx 0.74$ but it cannot really determine $\phi(r)$.
- Use MRI to really determine the structure!

$$V(h)=\int_h^R 2\pi r^2(1-\frac{h}{r})\,[1-\phi(r)]\,dr$$

High-Tech Approach



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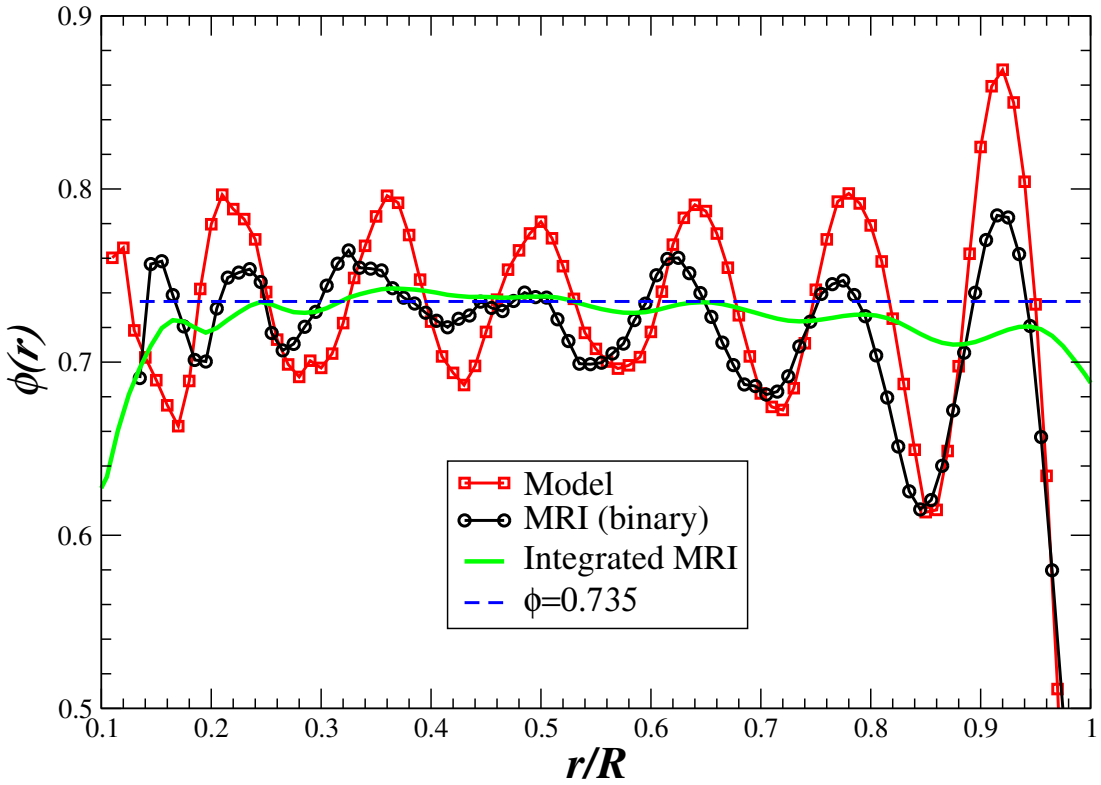
Compare **MRI** with previous techniques

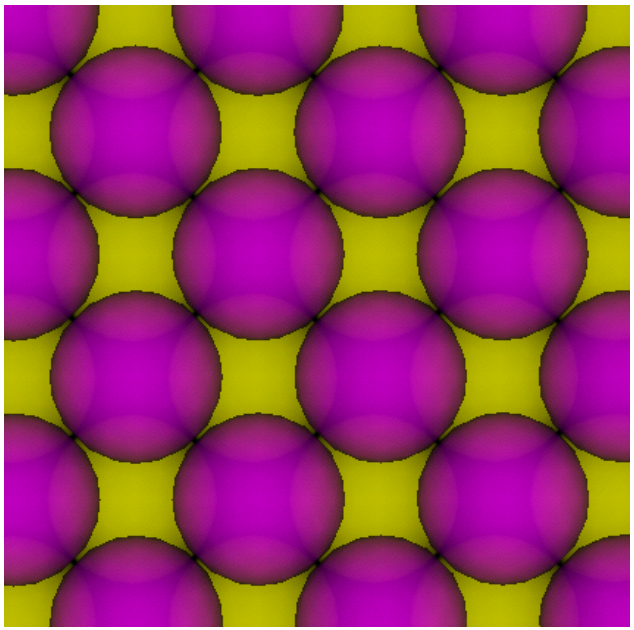
Confocal microscopy (colloids, Makse, 2004)

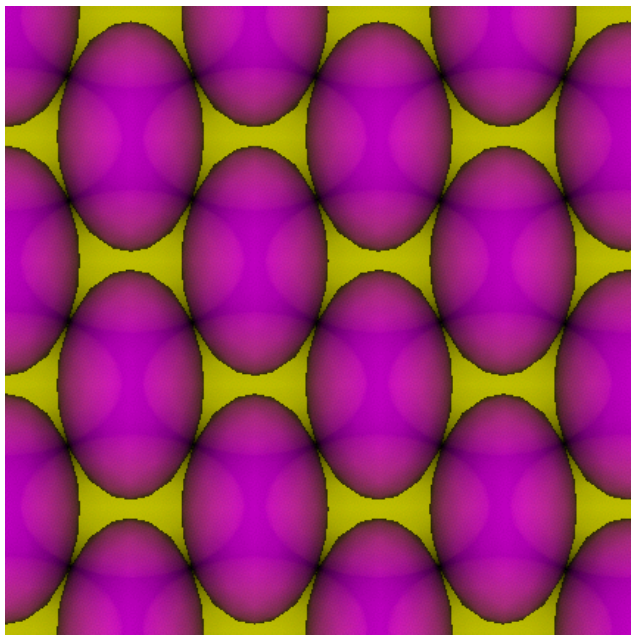
X-ray tomography (ball bearings, Aste, 2004)



Layered Ellipsoid Crystal

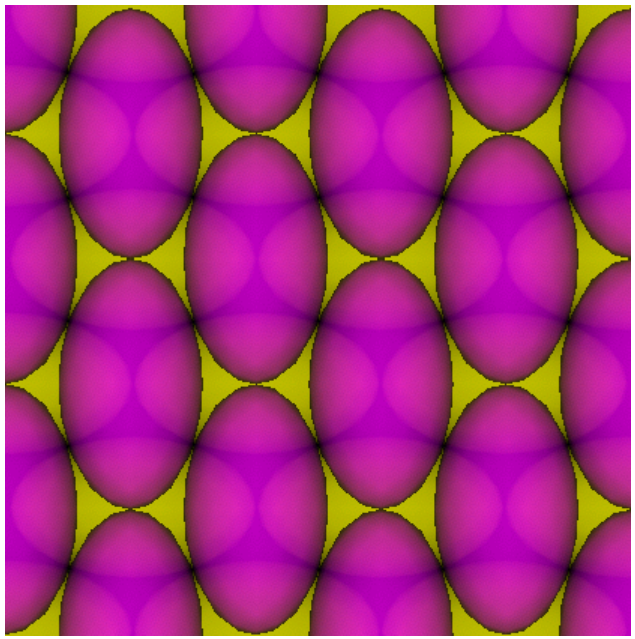
- "*Unusually Dense Crystal Packings of Ellipsoids*"
  A. Donev, F. H. Stillinger, P. M. Chaikin and S. Torquato, **Phys. Rev. Lett., 2004**
- *MD recipe*: **Slow growth, small systems, deforming unit cell**

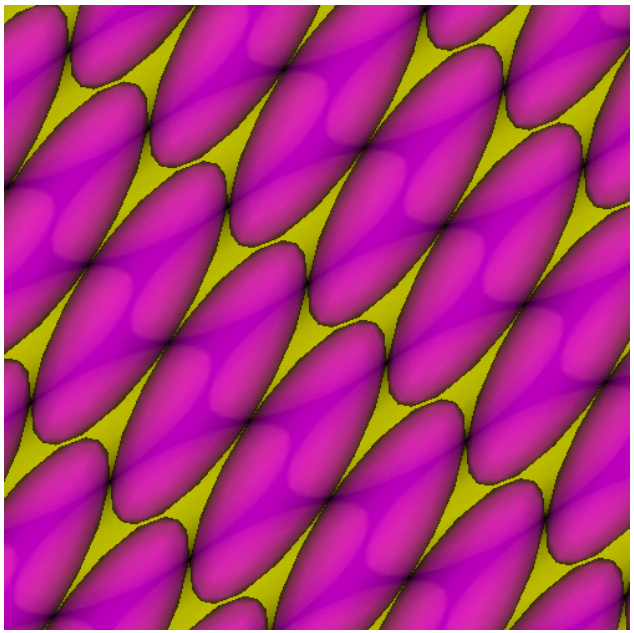




The Densest Ellipsoid Packing

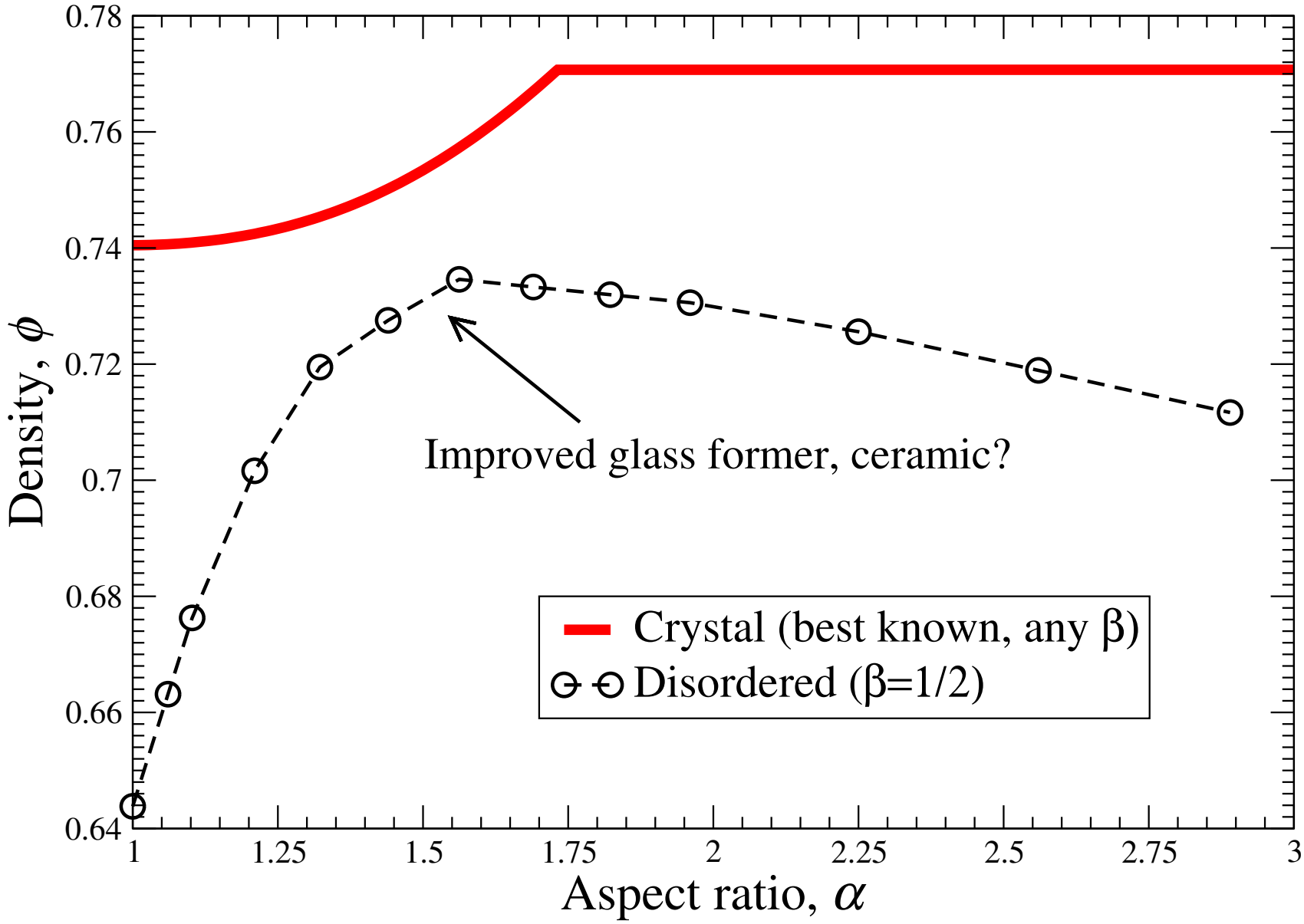
- Higher symmetry leads to higher densities: $\phi \approx 0.77$, $Z = 14$
- Works for $\alpha = 1 + \sqrt{3}$ or higher: Just apply an **affine** stretch!





- We do **not** know if there are denser packings of ellipsoids...some equilibrium thermodynamics indications!

Disordered vs. Ordered Packing Density

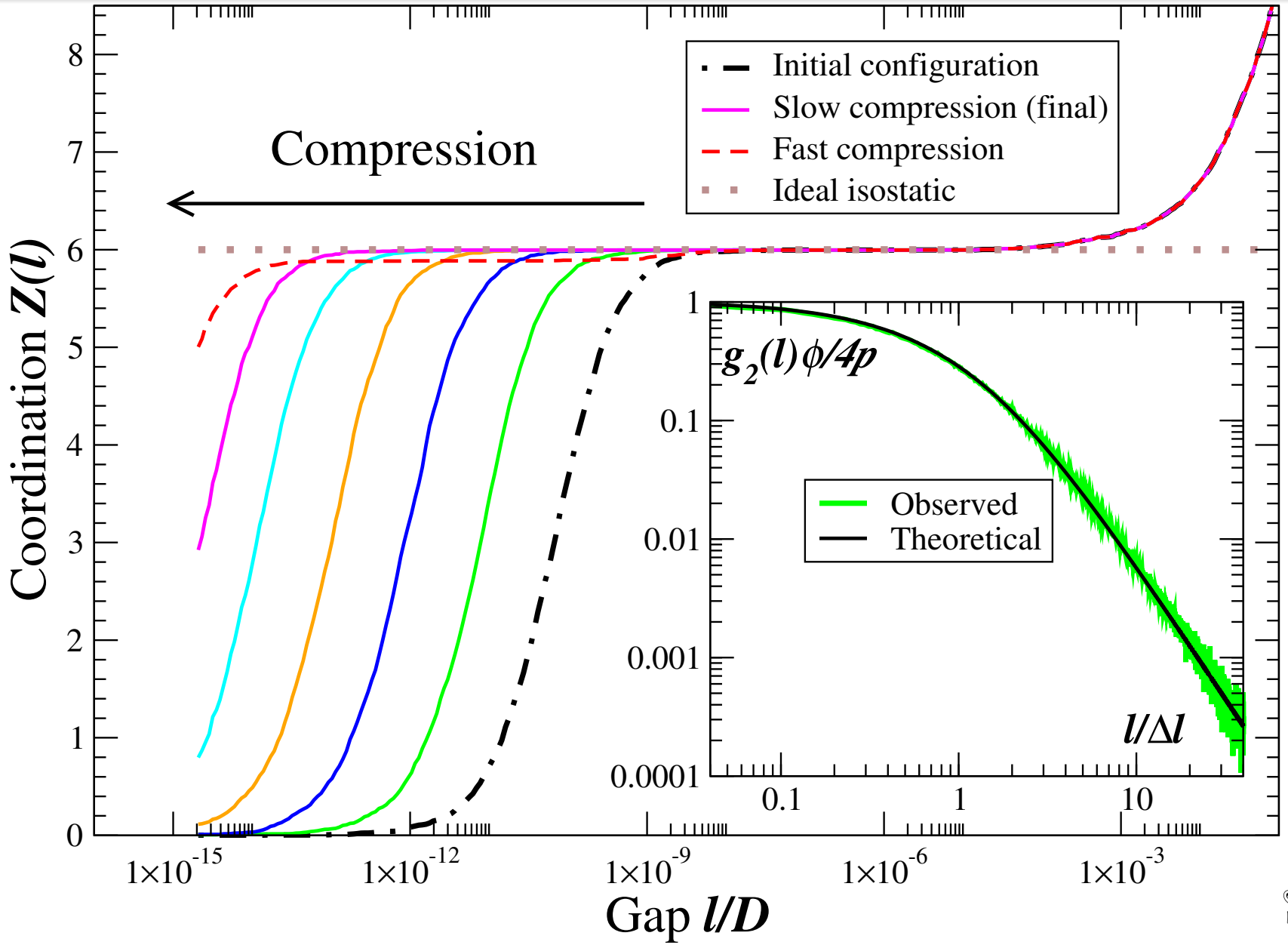


Pair-Correlation Function

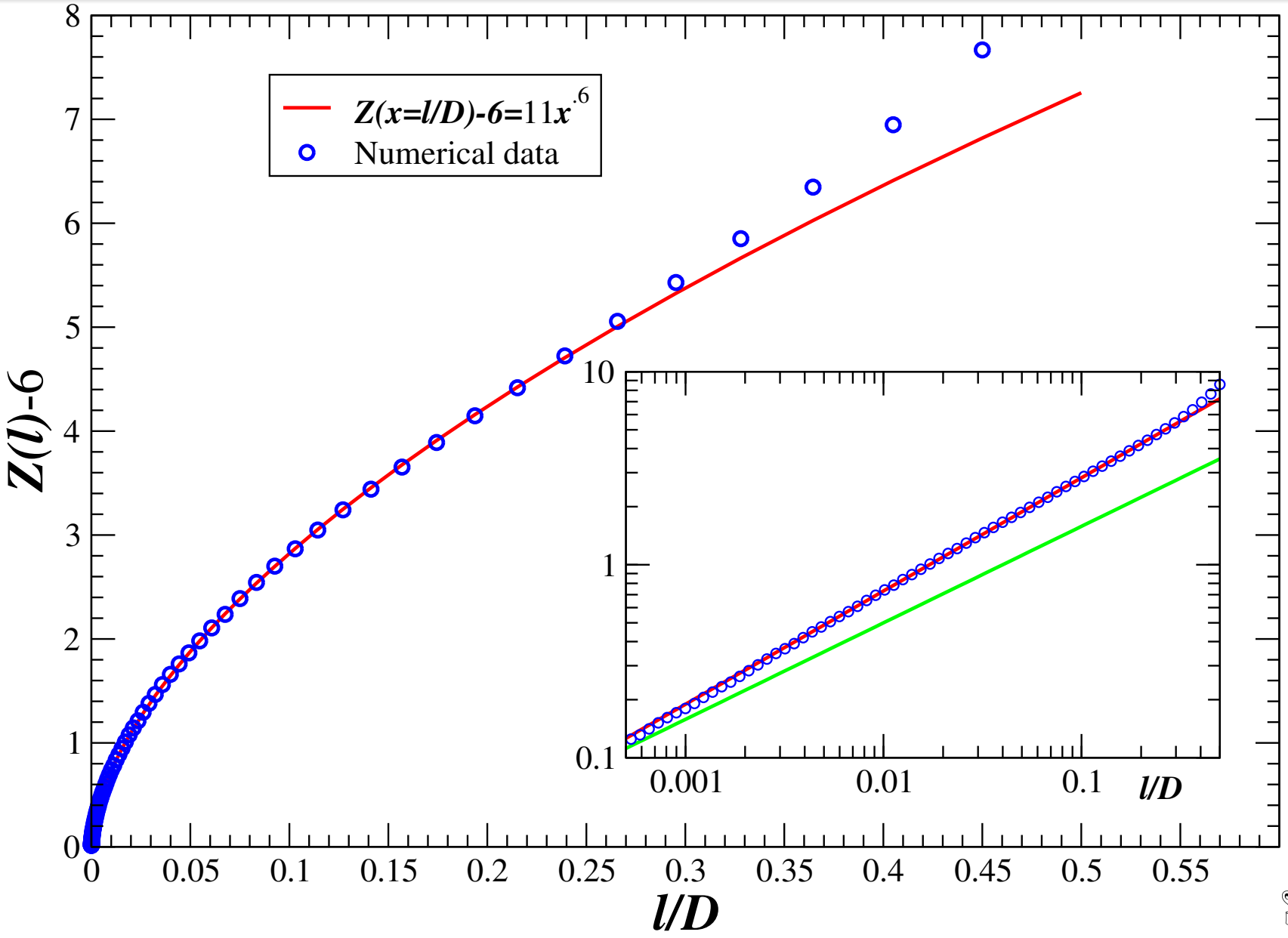
- $g_2(r) = \frac{\langle P(r) \rangle}{\rho s_1(r)} = \frac{\bar{Z}\delta(r-D)}{\rho s_1(D)} + g_2^{(b)}(r) + g_2^{(rest)}(r)$
- Use the *cumulative coordination number* $Z(l) = \frac{N}{V}\int_{r=D}^{D+l} 4\pi r^2 g_2(r) dr$
- **Delta-function region** $g_2^{(\delta)}(x)$, gap $x = (r-D)/D$
- **Near-contact region** (background) $g_2^{(b)}(x)$
- **Split second-peak** and remaining oscillations

"*Pair Correlation Function Characteristics of Nearly Jammed Disordered and Ordered Hard-Sphere Packings*", **A. Donev**, S. Torquato and F. H. Stillinger, **Phys. Rev. E, 2005**

Delta-Function Region



Near-Contact Region



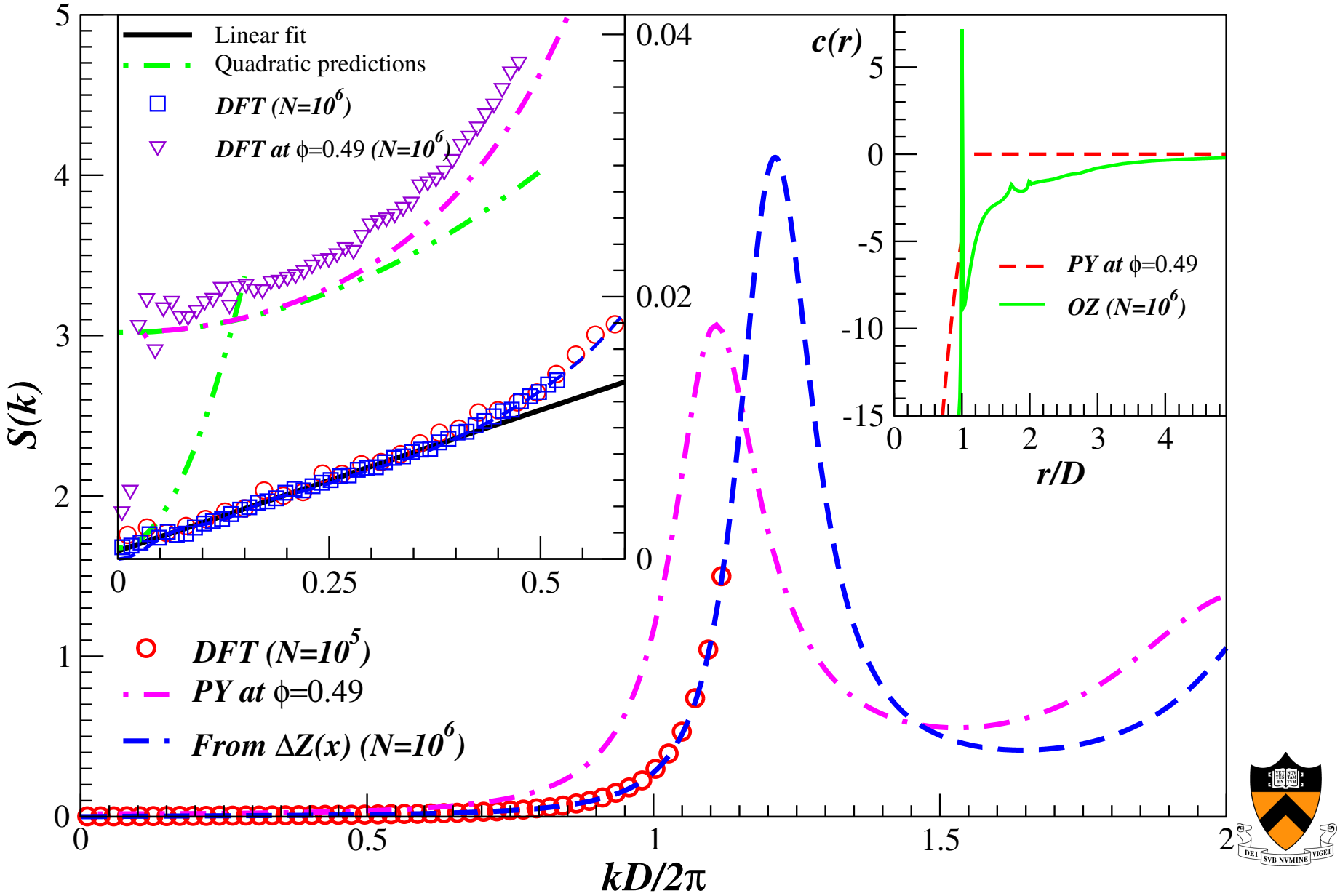
Structure Factor

- Fourier transform of the total correlation function $h(r) = g_2(r) - 1$,

$$S(k) = 1 + \rho \hat{h}(k).$$

- For disordered hard sphere packings $S(k)$ shows a large peak at $kD = 2\pi$ due to short-range ordering.
- The width of the first peak is inverse correlation length.
- **Hyperuniform** systems: Infinite wavelength density fluctuations vanish, $S(k = 0)$.
- "*Unexpected Density Fluctuations in Jammed Disordered Sphere Packings*", **A. Donev**, S. Torquato and F. H. Stillinger, **Phys. Rev. Lett., 2005**

Non-analytic $S(k) \sim |k|$

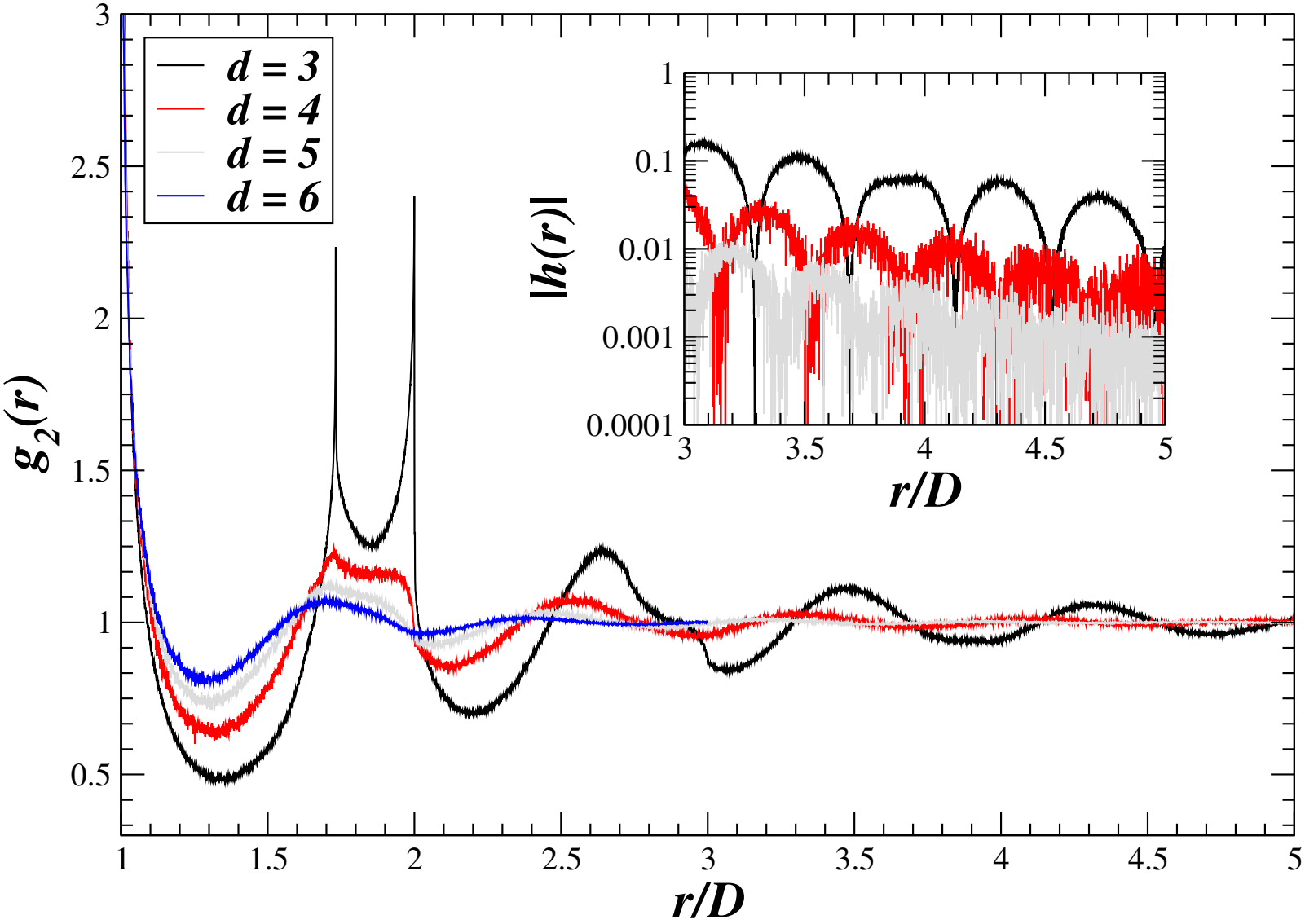


Packing Densities

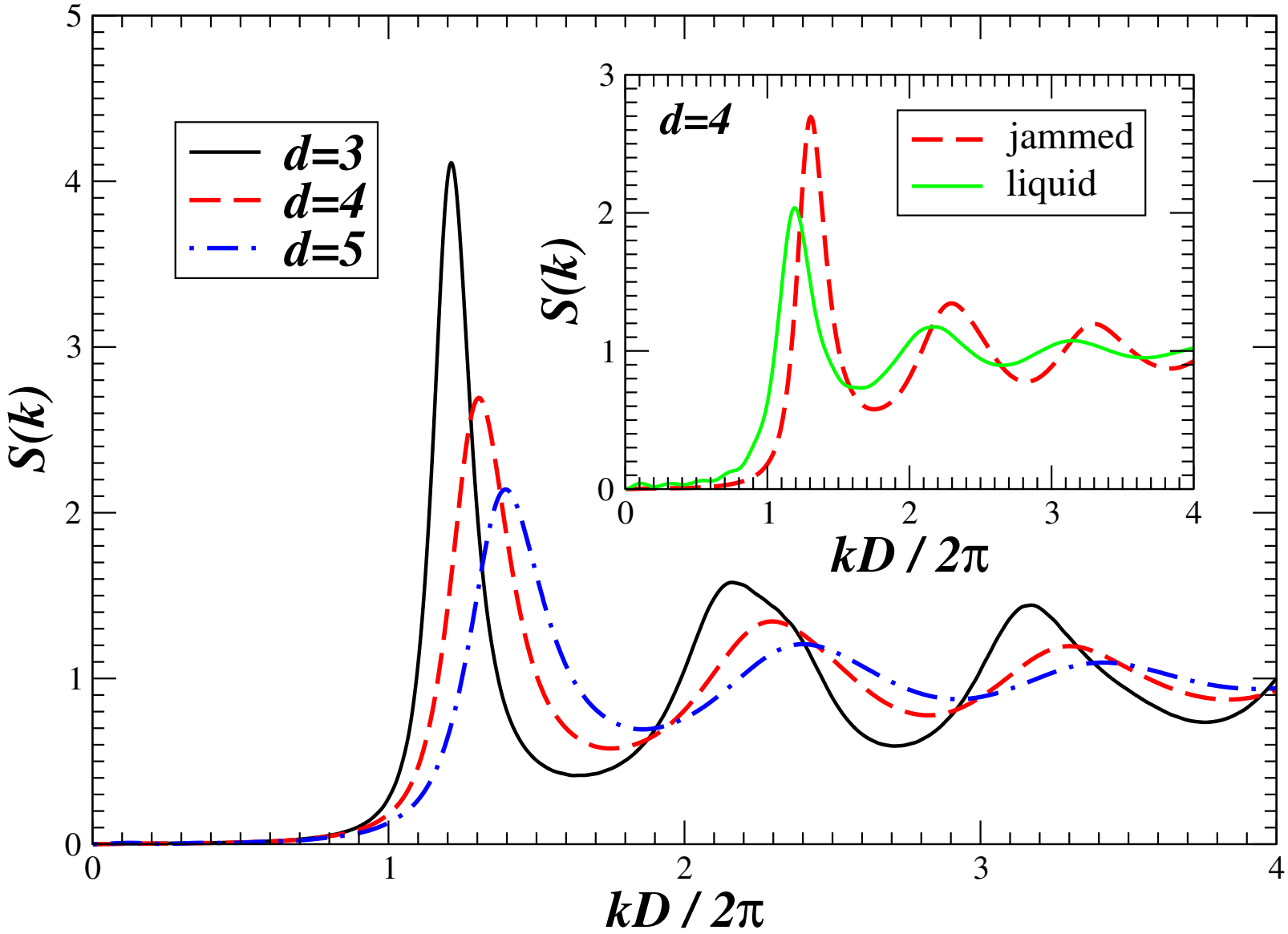
Packing fraction	$d = 3$	$d = 4$	$d = 5$	$d = 6$
ϕ_F	0.494	$0.32 \pm 0.01^*$	$0.19 \pm 0.01^*$	-
ϕ_M	0.545	$0.39 \pm 0.01^*$	$0.24 \pm 0.01^*$	-
ϕ_{MRJ}	0.645 ± 0.005	$0.46 \pm 0.005^*$	$0.31 \pm 0.005^*$	$0.20 \pm 0.01^*$
ϕ_{max}	$0.7405\ldots$	$0.6169\ldots$	$0.4652\ldots$	$0.3729\ldots$
Lattice	FCC/HCP	Checker D_4	D_5	Root E_6
Z_{max}	12	24	**40**-46	**72**-82

"*Packing Hyperspheres in High-Dimensional Euclidean Spaces*", M. Skoge, **A. Donev**, F. H. Stillinger and S. Torquato, **Phys. Rev. E**

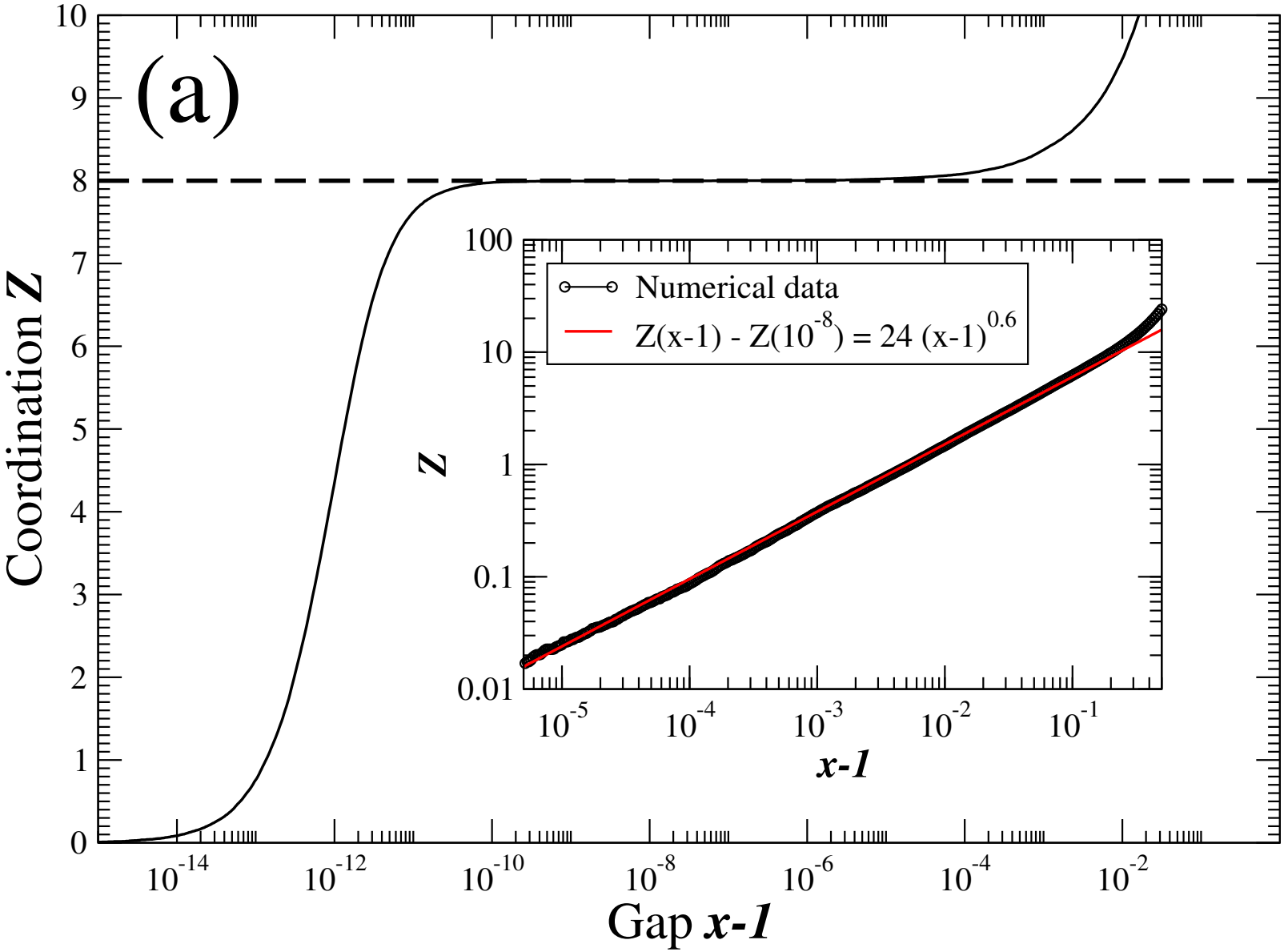
$g_2(r)$ Decorrelation



$S(k)$ Decorrelation



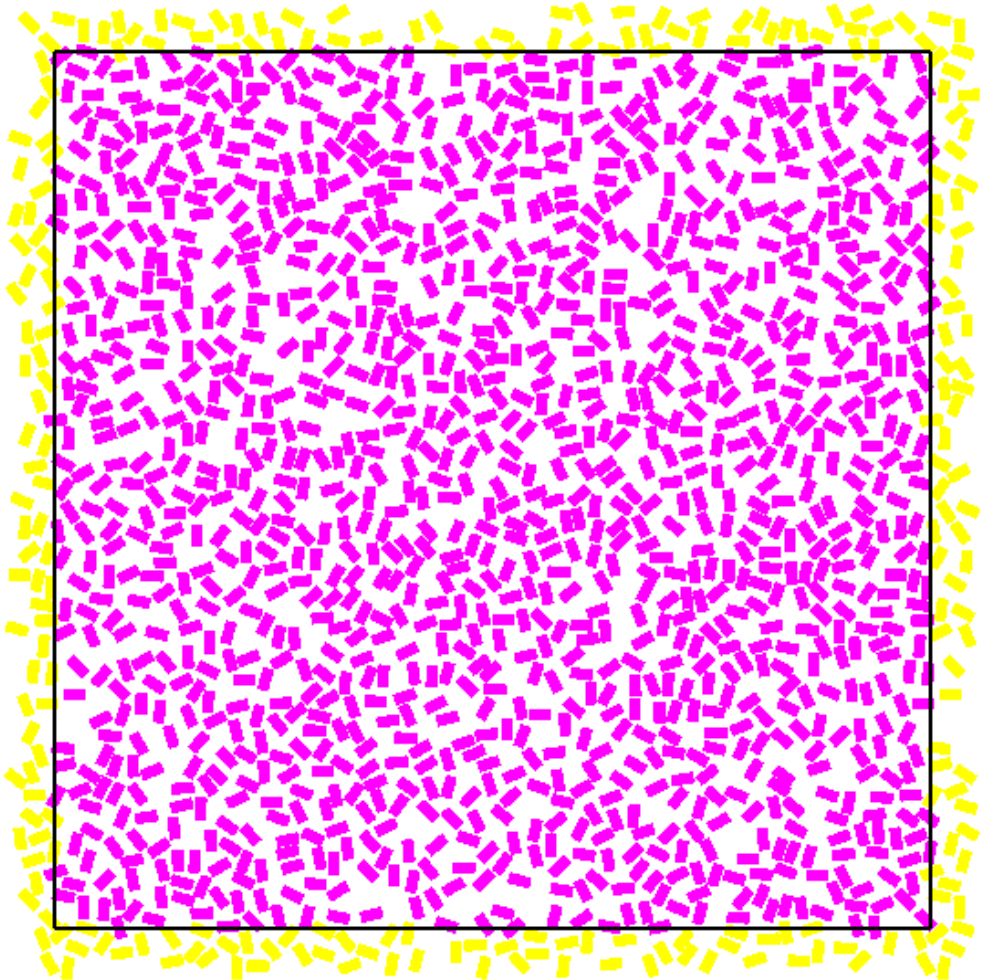
Near-Contact Region



Near-Contact Divergence

- We numerically observe $Z(x) = \bar{Z} + Z_0 x^{0.6}$, where $\bar{Z} = 2d$
- We measure $Z_0^{3D} = 11$, $Z_0^{4D} = 24$, and $Z_0^{5D} = 40$.
- Compare to **kissing numbers** $Z_{max}^{3D} = 12$, $Z_{max}^{4D} = 24$, $Z_{max}^{5D} = 40 - 46$, $Z_{max}^{6D} = 72 - 80$.
- Disordered packings might be **deformed crystal packings**, in which the true contacts are deformed into near contacts, and only the minimal number of contacts necessary for jamming is preserved.

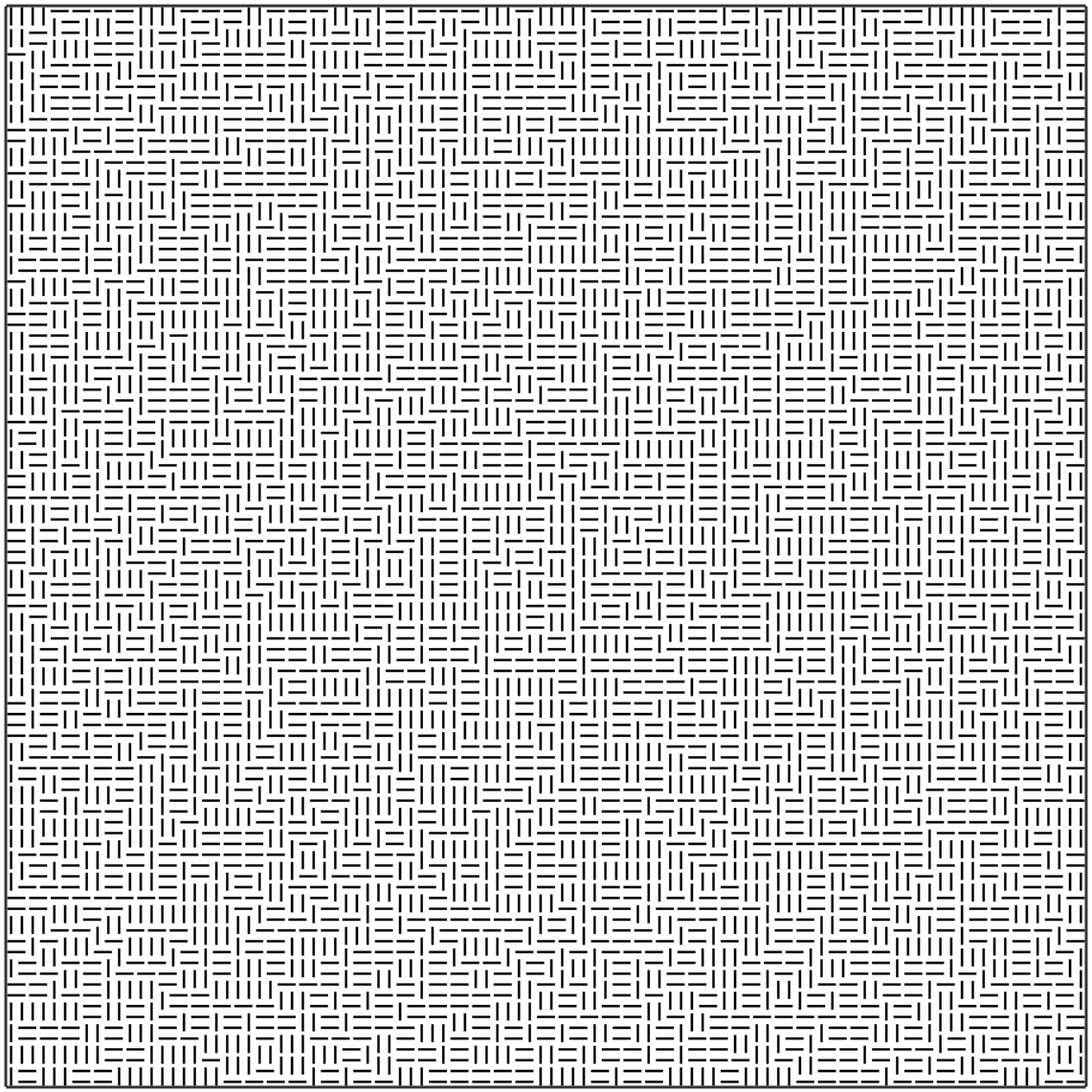
Hard-Domino Systems



(MNG) (GIF)

- **Tetratic** liquid phase is observed (quasi-KTHNY?).
- Can a "disordered" **domino tiling** be the stable solid phase?
- "*Tetratic Order in the Phase Behavior of a Hard-Rectangle System*"
  A. Donev, J. Burton, F. H. Stillinger and S. Torquato, Phys. Rev. B., 2006

Random Domino Tilings



Analogies: Soft versus Hard

Soft	Hard	Notes
$T \downarrow$	$p \uparrow$	State control variable
$T \downarrow$	$\phi \uparrow$	Alternative state
inherent structure	**jammed packing**	Exact in certain limit
U_{IS}	ϕ_J	Basin depth
saddle point	**hypostatic packing**	$x \equiv (M - N_f)/N$
f_{vib}^{IS}	$\ln \lvert \mathcal{P}_{\Delta \mathbf{R}} \rvert / N$	Exact for isostatic
Cooling rate	**Expansion rate**	Quenching
Barrier height	?	No energy, only entropy!

"*Do Binary Hard Disks Exhibit an Ideal Glass Transition?*", **A. Donev**, F. H. Stillinger and S. Torquato, **Phys. Rev. Lett., 2006**

"*Configurational Entropy of Binary Hard-Disk Glasses*", **J. Chem. Phys.**

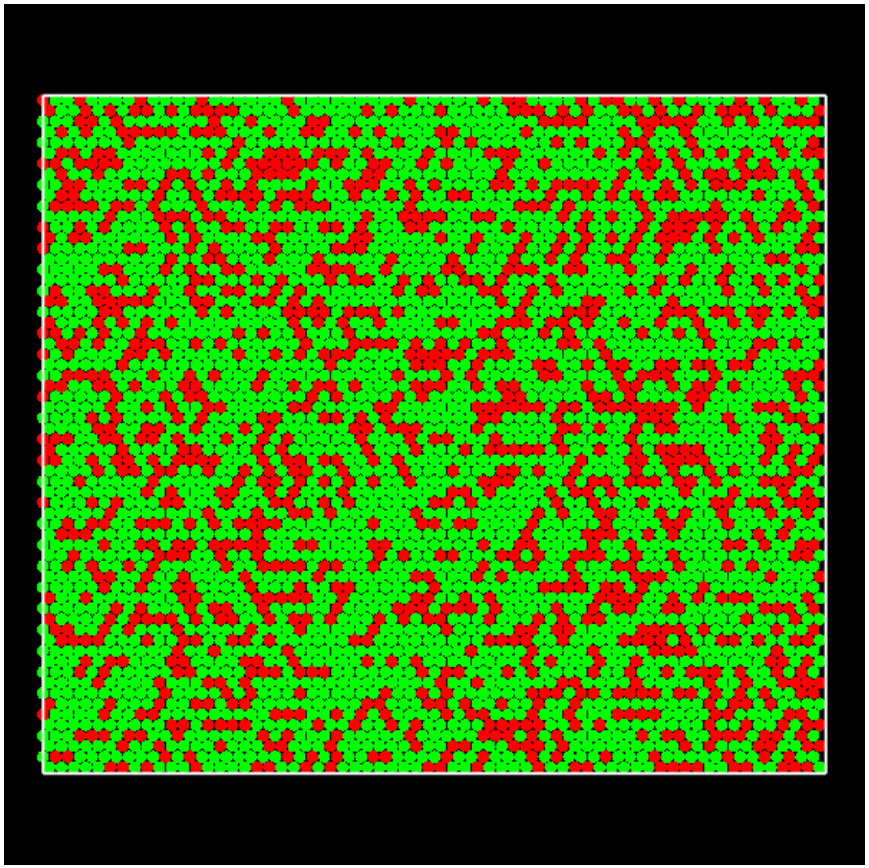
Inherent-Structure Formalism

- Let the number of jammed packings be $N_g(\phi_J) = \exp\left[S_c(\phi_J)\right] = \exp\left[N \cdot s_c(\phi_J)\right]$, where the **configurational entropy** $s_c(\phi_J)$ must vanish at some density $\phi_J^{\max} < \phi_{CP}$.
- Liquid free energy embodies competition between **free-volume** and **degeneracy**:

$$f_L(\phi) = f_{FV}\left[\phi, \hat{\phi}_J(\phi)\right] - s_c\left[\hat{\phi}_J(\phi)\right] = -\left[d \ln\left(1 - \frac{\phi}{\hat{\phi}_J}\right) - f_J\right] - s_c(\hat{\phi}_J)$$

- At an **ideal glass transition density** ϕ_g, $\hat{\phi}_J(\phi_g) = \phi_J^{\max}$, and $s_c = 0$.
- *The configurational entropy is very close to the* **mixing entropy** *near the kinetic glass transition!*

Most Disordered Binary Disk Packings



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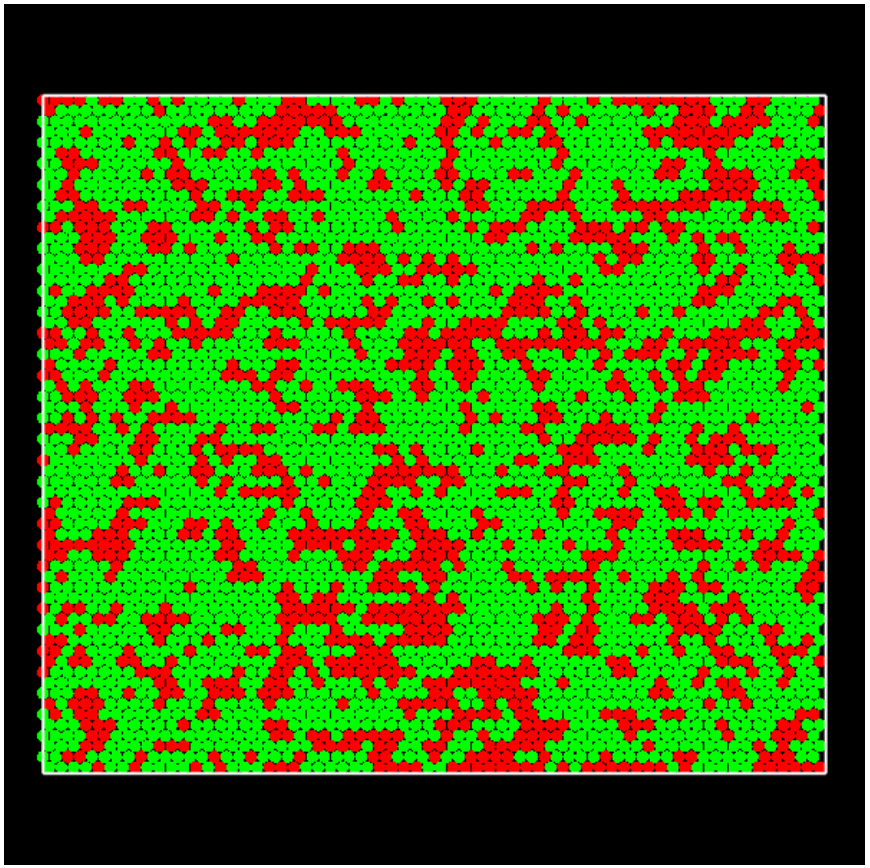

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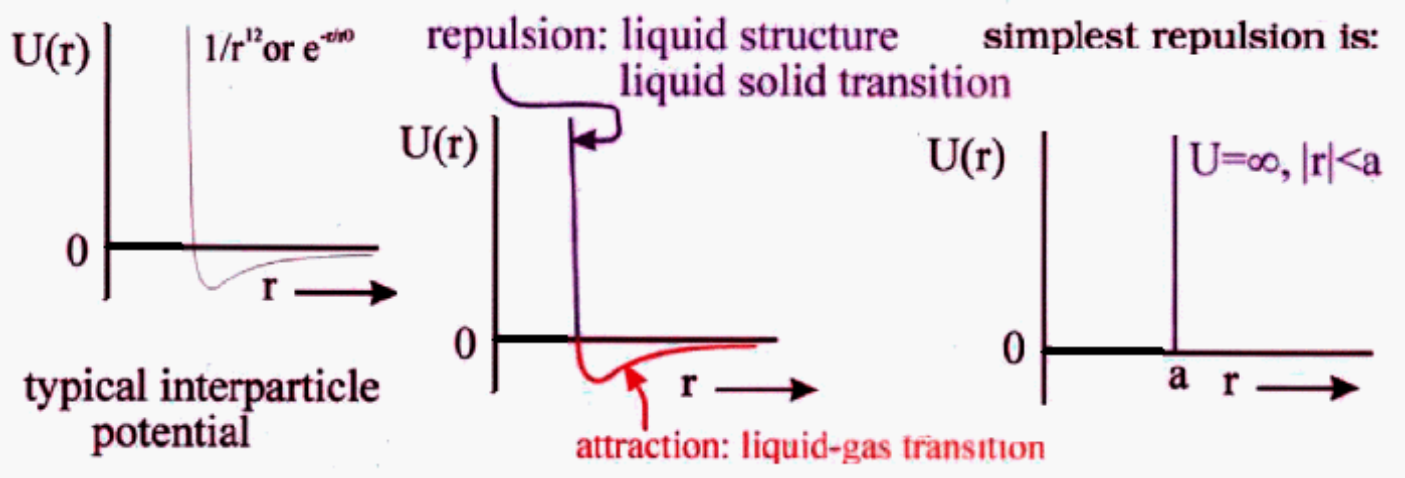
Is There a Most Dense Amorphous Packing?

- Using specific statistical models for micro-clustering (we use **Leveled Random Gaussian Fields**) we can calculate **entropy** (degeneracy) $s = \ln(N_P)/N$.
- Starting with more clustered initial configurations generates denser final packings: tradeoff between **density** and **disorder**!
- Ideal glass transition is **naively extrapolated** to $s_c = 0$, which requires overcoming the entropy of mixing, i.e., **demixing**
- The presumed "ideal glass" is nothing but a fully demixed, i.e., **phase-separated crystal**
- An **exponential majority** of packings are *most disordered* (MRJ)?

Why *Frictionless Hard* Particles?



Hard-particle systems:

- Extract the **essence** of the problem: **Geometry**
- Are **simple**: *No potential energy, temperature, or dissipation*
- Exhibit behavior almost as **rich** as more realistic models
- Can often be **simulated** more efficiently/easily

What is a Packing?

- **A packing $\mathcal{Q}$ is a collection of (static) convex objects (particles) in Euclidean space $\mathcal{R}^d$ such that no two objects overlap** (no compactness). Focus on **congruent** objects (monodisperse systems) with a specified particle **shape**.
- We usually consider **periodic packings** obtained by replicating a **unit cell** containing N particles, giving $N_f \sim N$ **degrees of freedom**.
- A packing $\mathcal{Q} = (\mathbf{Q}, \phi)$ is characterized by
  - The **configuration** $\mathbf{Q} = (\mathbf{q}_1, \ldots, \mathbf{q}_N; \mathbf{\Lambda}) \in \mathcal{R}^{N_f}$, determining the positions and orientations of each particle
  - The **covering fraction** (**density**), ϕ, determining the size of the particles.

Large Random Jammed Packings

- We are particularly interested in the **thermodynamic limit**, $N \to \infty$.
- The collection of all packings at a given density ϕ specifies the **set of allowed configurations** $\mathcal{Q}(\phi) \subset \mathcal{R}^{N_f}$. Understanding the **topology** and **geometry** of this set is the holy grail!
- Focus on **jammed packings** (compactly packed, mechanically stable). *Intuition*: Particles are locked in their positions despite thermal agitation/shaking and/or boundary deformations/loading.
- *Intuition* for **randomness** (**disorder**): Lack of correlations/predictability between different particles and different parts of the packing.

Old-School: Packing of Hard Spheres

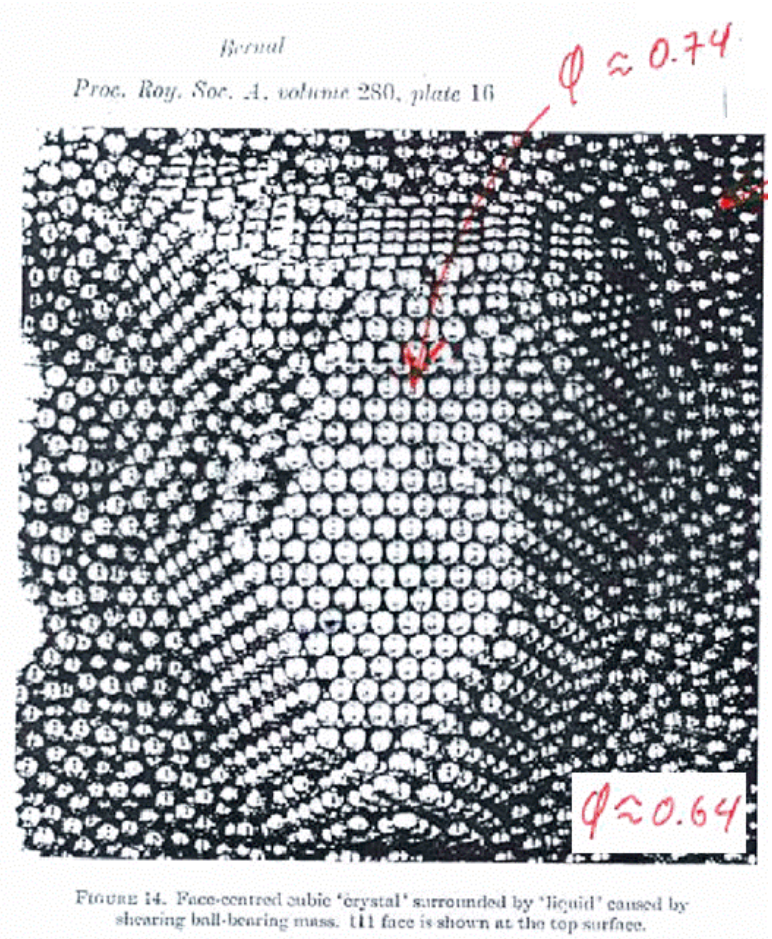
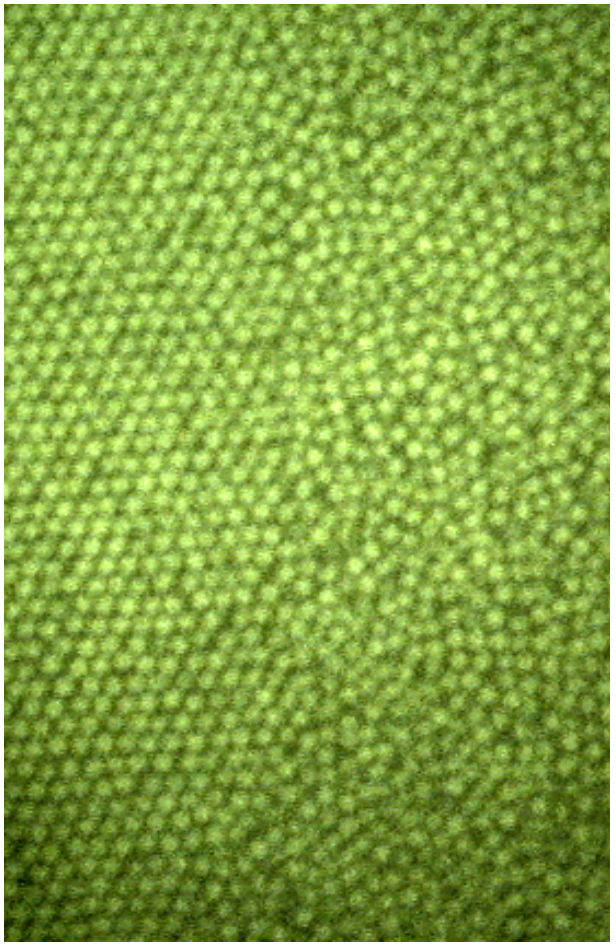


FIGURE 14. Face-centred cubic 'crystal' surrounded by 'liquid' caused by shearing ball-bearing mass. 111 face is shown at the top surface.



MRJ

- We need definitions for:
  - **Jammed packing** (coming up)
  - **Random (disordered, amorphous) packing**
- Prevailing 50-year old view (Bernal): *Random close packing (RCP) is the maximum density that a large random collection of spheres can attain.*
- The problem: **What is random?** (Torquato *et al.*, 2000) Randomness can be measured by using **order metrics**: Something can be **more random** than something else.
- Contradiction: *Higher density implies less random, so there is* **no** *"most dense random packing"!*

Basic Notation

- Thermal system of hard particles with covering fraction (or **density**) ϕ at temperature $kT = 1$.
- Particle displacements $\Delta\mathbf{Q} = (\Delta\mathbf{q}_1, \ldots, \Delta\mathbf{q}_N)$ from an ideal *jammed* configuration $\mathbf{Q}_J$ with jamming density ϕ_J
  - For spheres $\Delta\mathbf{q} \equiv \Delta\mathbf{r}$
  - For nonspherical particles $\Delta\mathbf{q} = (\Delta\mathbf{r}, \Delta\boldsymbol{\varphi})$
  - We mostly focus on spheres for simplicity
- Think about **configuration space** $\Delta\mathbf{Q} \in \mathcal{R}^{N_f}$, where $N_f = Nd_f$, and d_f is number of *degrees of freedom* per particle.
- There can be additional degrees of freedom due to, for example, the boundary.

Jamming: Kinematic View

- Definition **A**, discarded
  (S. Alexander, 1998): "A packing is "**geometrically rigid**" if it cannot be "deformed continuously by rotating and translating the constituent grains without deforming any of them and without *breaking* the contacts between any two grains".
- Definition **B** (**kinematically rigid**)
  (R. Connelly, 1996): There is no non-trivial continuous path (motion) starting at $\mathbf{Q}_J$ (**immobility**).
  (S. Torquato & F. Stillinger, 2001): No global boundary-shape change accompanied by collective particle motions can exist that respects the nonoverlap conditions.

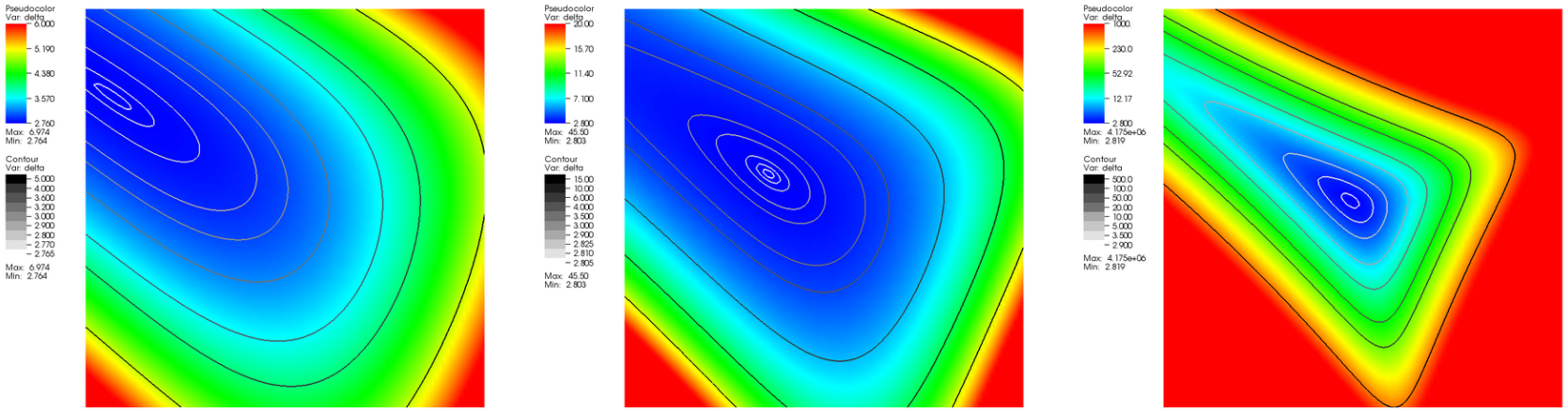
Jamming: Static View

- Definition **C** (**statically rigid**)
  (T. Witten, 1999): "We will consider a packing to be **mechanically stable** if there is a nonzero measure set of external forces which can be balanced by interbead ones." Replace "nonzero measure set" with "all".
- Definition **D** (**jammed**)
  (Z. Salsburg, 1962): "**A configuration is stable if for some range of densities slightly smaller than ϕ_J, the configuration states accessible from $\mathbf{Q}_J$ lie in the neighborhood of $\mathbf{Q}_J$.** More formally, if for any small $\epsilon > 0$ there exists a $\delta(\epsilon, N) > 0$ such that all points $\mathbf{Q}$ accessible from $\mathbf{Q}_J$ satisfy $\|\mathbf{Q} - \mathbf{Q}_J\| < \epsilon$ provided $\phi \geq \phi_J - \delta$."
- Theorem (R. Connelly): **For spheres, definitions B, C and D are equivalent**.

The Accessible Region $\mathcal{J}_{\Delta\mathbf{R}}$

- Shrink the particles from the terminal jamming point $(\mathbf{R}_J, \phi_J)$ by a scaling factor
$$\mu = (1-\delta) = (1+\Delta\mu)^{-1}$$
- $\phi = \phi_J (1-\delta)^d \approx \phi_J (1-d\delta)$, where $\delta \approx \Delta\mu$ is a small **jamming gap**.
- $\mathbf{R} = \mathbf{R}_J + \Delta\mathbf{R}$ remains trapped in a small **jamming neighborhood** $\mathcal{J}_{\Delta\mathbf{R}}(\delta)$ around $\mathbf{R}_J$.
- Jamming assumption: There is a small $\delta_{\max}(N) > 0$ such that $\mathcal{J}_{\Delta\mathbf{R}}(\delta_{\max})$ is "small" and **bounded**.
- Note: Even for $\delta > \delta_{\max}$ the configuration is often **dynamically localized** around $\mathbf{R}_J$ (**glassiness**)!

Soft Potentials: $U \sim x^{-p}$



Energy surface for $p = 12, 25, 100$, hard-limit: $p \to \infty$, $U \sim \delta$

Jamming Polytope $\mathcal{P}_{\Delta\mathbf{R}}$

We have a **jamming polytope** $\mathcal{P}_{\Delta\mathbf{R}} \subset \mathcal{J}_{\Delta\mathbf{R}}$, as given by the **rigidity matrix A**:

$$\mathcal{P}_{\mathbf{x}}: \ \mathbf{A}^T\mathbf{x} \leq \mathbf{e} \text{ with columns} \quad \begin{matrix} \{i,j\} \\ \downarrow \end{matrix} \begin{bmatrix} \vdots \\ i \rightarrow \ \mathbf{u}_{ij} \\ \vdots \\ j \rightarrow -\mathbf{u}_{ij} \\ \vdots \end{bmatrix}$$

- $\mathcal{P}_{\Delta\mathbf{R}}$ is just a **scaled** version of $\mathcal{P}_{\mathbf{x}}$.
- $\mathcal{P}_{\mathbf{x}}$ (**geometry**) **determines everything** at the jamming point!

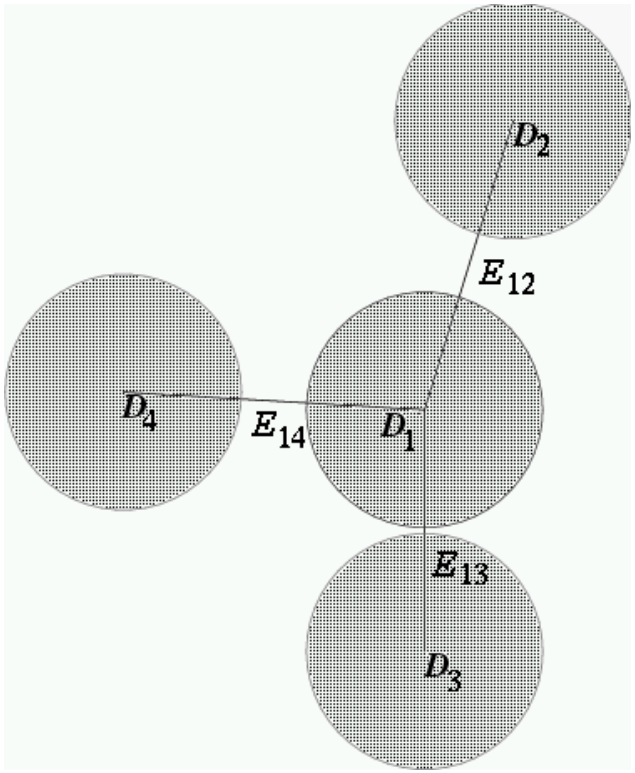
Contact Forces

- Jamming (for spheres) *implies* existence of **contact forces**:

$$\mathbf{Af} = 0 \text{ and } \mathbf{f} \geq 0$$

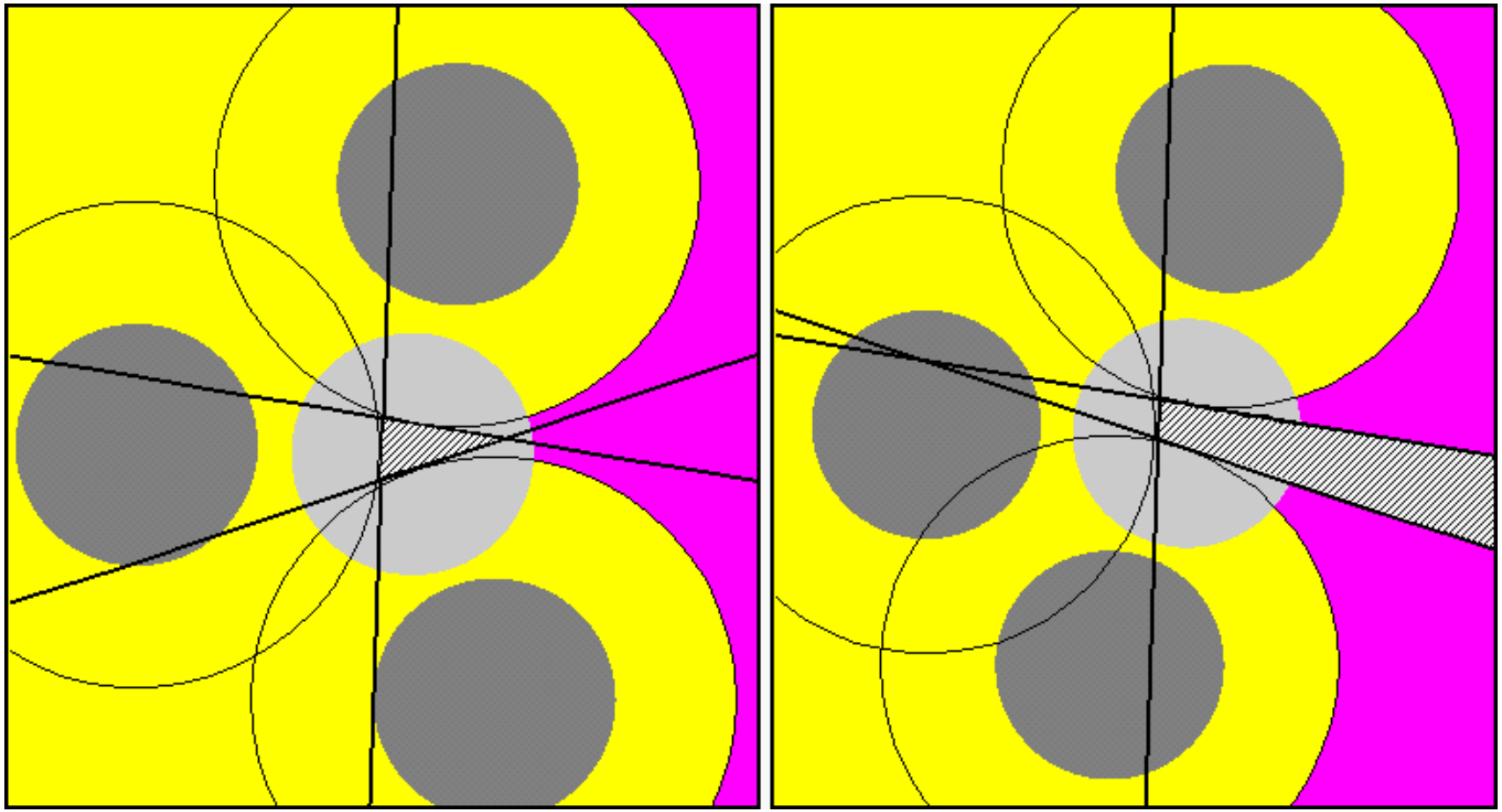
- Each force proportional to the **surface area** of the polytope face, $f_{ij} \sim S_{ij}$.
- Theorem: If $\mathcal{P}_{\mathbf{x}}$ is closed than the packing is jammed for $0 \leq \delta \leq \delta_{\max}(N)$!
- "*A Linear Programming Algorithm to Test for Jamming in Hard-Sphere Packings*"
  A. Donev, S. Torquato, F. H. Stillinger, and R. Connelly, **J. Comp. Phys, 2004**

Example



$$\mathbf{A} = \begin{array}{c} \\ D_1 \\ D_2 \\ D_3 \\ D_4 \end{array} \begin{array}{c} \begin{array}{ccc} E_{12} & E_{13} & E_{14} \end{array} \\ \begin{bmatrix} \mathbf{u}_{12} & \mathbf{u}_{13} & \mathbf{u}_{14} \\ -\mathbf{u}_{12} & & \\ & -\mathbf{u}_{13} & \\ & & -\mathbf{u}_{14} \end{bmatrix} \end{array}$$

How Good is First-Order



Suprisingly High Density!

- The maximum density is for axes $0.8 : 1 : 1.25$ ($\beta = 0.5$, $\alpha \approx 1.6$) and it approaches that of **crystalized spheres**, $\phi \approx 0.735$. These are **ollipsoids**.
- Denser packing is important in different fields:
  - Rocket **fuel powders** (but also polydispersity)
  - Improved sintered materials (**ceramics**)
  - **Fish eggs**
- Is the high density robust to shape and size dispersity?
- Is there an even better particle shape?

Packing Ollipsoids in Flasks

- **Finite-size** effects are strong
- One can try to extrapolate to infinite container, $R \to \infty$,

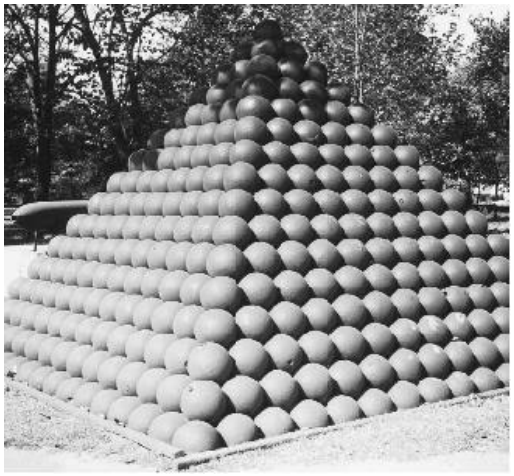
$$\phi(R) = \phi_b - \frac{a}{R}.$$

But we only have 1000 particles!

- Find the **radial density profile** $\phi(r)$ and estimate the **core density** $\phi_c \approx \phi_b$ instead.

Packing Cannon Balls & Oranges

- The answer: FCC/HCP lattice, $\phi_{\max} = \pi/\sqrt{18} = 0.7405$!



- Computer-assisted proof by Hales *et al.* (2000)
- For ellipsoids it was thought the answer is the same: **Affinely stretch** the FCC lattice?
- Our simulations led to **exact** results showing the contrary!

Nonspherical Particles

- For spheres all constraints are **concave**, and one can prove that the jamming polytope picture describes the jamming limit
- For nonspherical particles (ellipsoids) we can still linearize

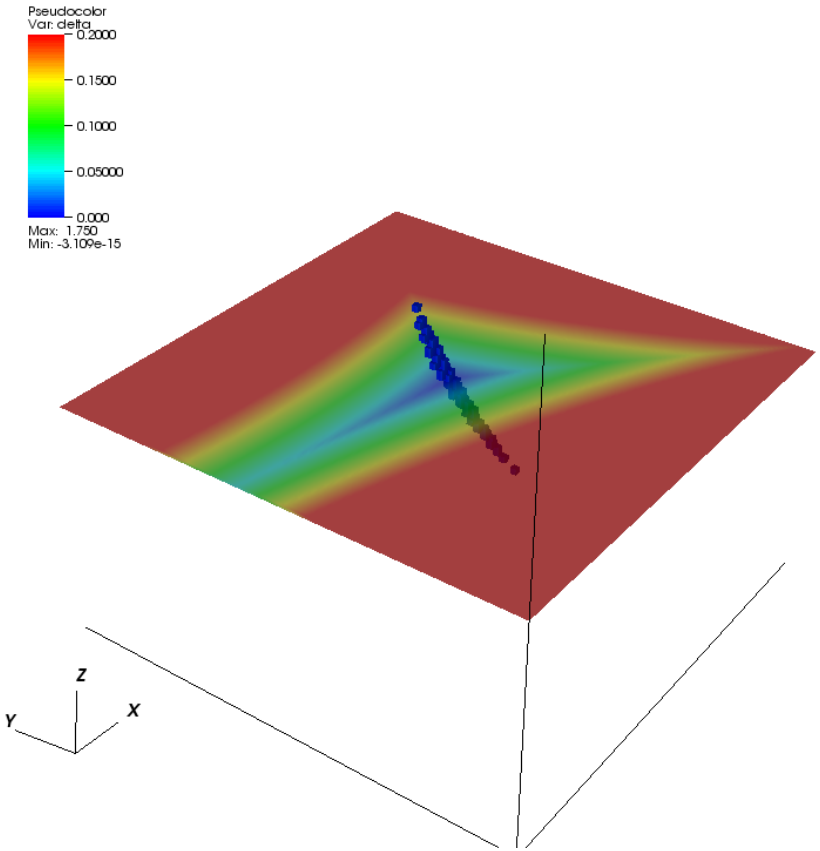
$$\mathbf{A}^T \Delta \mathbf{Q} \leq \Delta \mathbf{l}$$

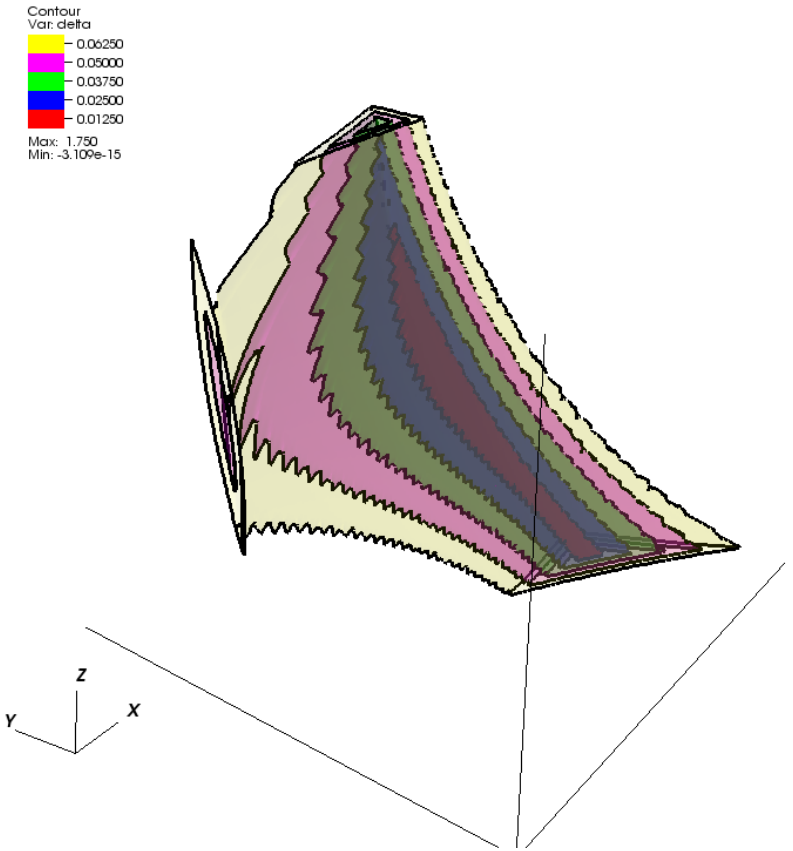
- **A** is a **generalized rigidity matrix**, containing blocks of the form

$$\begin{bmatrix} \mathbf{n} \\ \mathbf{r}_C \times \mathbf{n} \end{bmatrix}$$

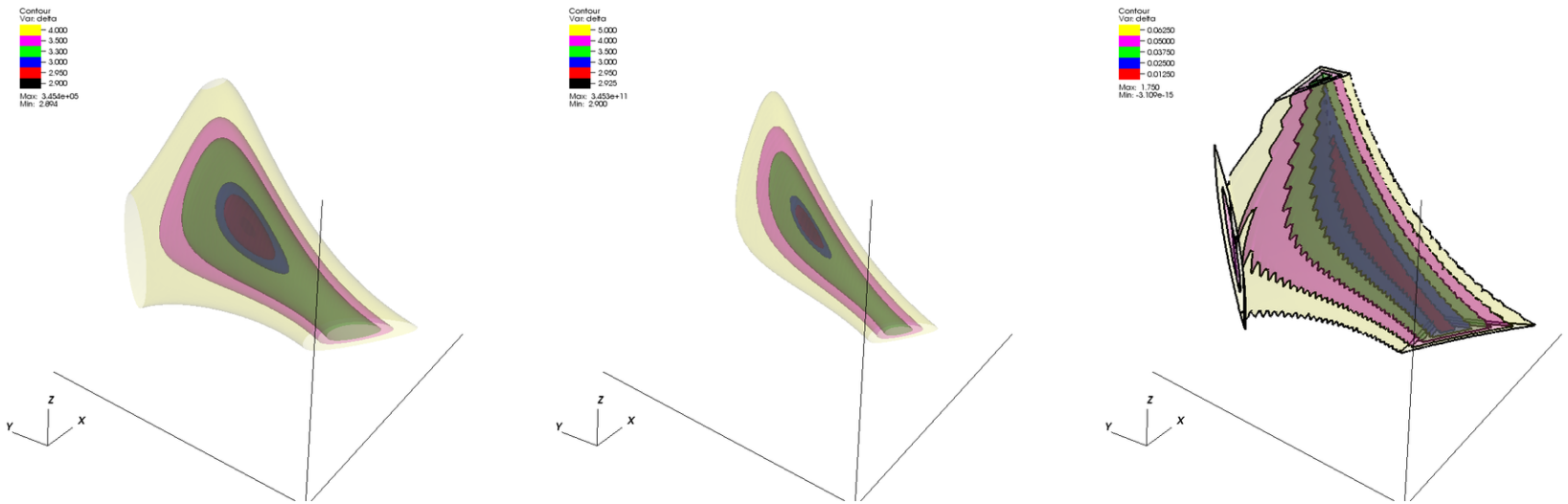
- But some constraints can be **convex** and the linearization can break down!
- There exist some packings for which the polytope picture applies, and we focus on those for now.

When Polytopes are Not Enough



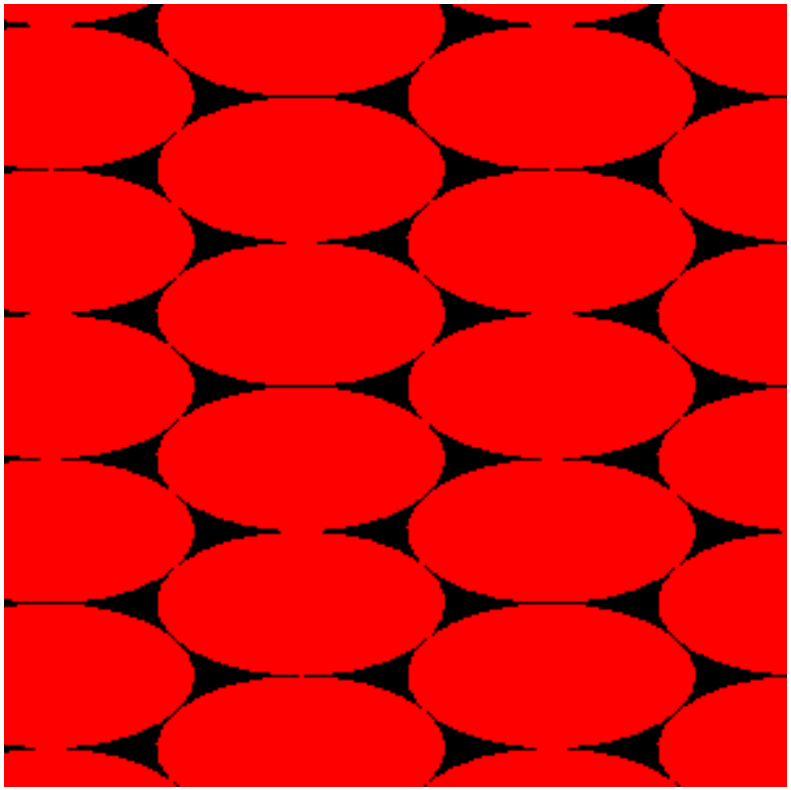


Soft Potentials: $U \sim x^{-p}$



Energy contours for $p = 12, 25, \infty$

Rotation vs. Translation



(MNG) (MPEG)

- Translational jamming can happen without rotational jamming: Spheres are the ultimate (**singular**) example!
- Jammed sphere packing $\Longrightarrow$ translationally-jammed ellipsoid packing with $\alpha = 1 + \delta_{\max}$.
- Achieving the isostatic $Z = 12$ requires **translational ordering**.
- Understanding ellipsoid packings is a challenge for the **future**!

Energy, Hessians, and Jamming

- **Overlap potential**: A smooth continuous pairwise interaction $U(\Delta\mathbf{q_A}, \Delta\mathbf{q_B})$ which strictly increases *iff* touching particles overlap.
- *Theorem* (R. Connelly): If there exists an overlap potential such that the configuration $\mathbf{Q}_J$ is a **stable energy minimum**, then the packing is jammed.
- *First-order condition*: Gradient vanishes $\equiv$ **force/torque balance**

$$\mathbf{Af} = 0 \text{ and } \mathbf{f} \geq 0$$

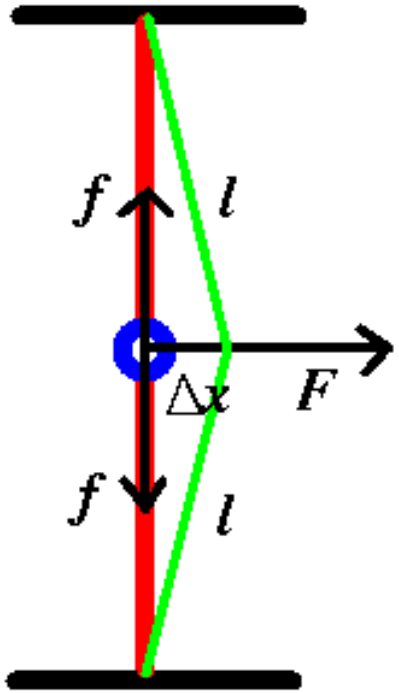
- *Second-order condition*: Hessian is **positive definite**:

$$\mathbf{H} = \mathbf{ACA}^T + \mathbf{f} \otimes (\boldsymbol{\nabla}_\mathbf{q}\mathbf{A}) \succ \mathbf{0}, \text{ and for spheres } \boldsymbol{\nabla}_\mathbf{q}\mathbf{A} \prec \mathbf{0}$$

Eigenvalues, Soft-Modes, and Sphericity

- *Theorem*: $\mathbf{ACA}^T \succ \mathbf{0}$ if $\mathbf{A}$ is full-rank, which requires **iso-** or **hyper-staticity**, $Z \geq 2f$. For small $\mathbf{f}$, $\mathbf{H} \succ \mathbf{0}$, but for large enough $\mathbf{f}$, **buckling** instability modes may appear (M. Wyart *et al*, 2005).
- *Theorem*: $\mathbf{ACA}^T$ has zero eigenvalues (**floppy modes**) if $\mathbf{A}$ is not full-rank, for example, for hypostatic packings, $Z < 2f$. These modes may be rigidified by the stress term $\mathbf{f} \otimes (\boldsymbol{\nabla}_{\mathbf{q}}\mathbf{A})$ for **non-spheres only** (R. Connelly)!
- (S. Alexander, 1998): "*The basic claim...is that one cannot understand the mechanical properties of amorphous materials if one does not explicitly take into account the direct effect of stresses.*"

Prestress Stability



- Let $l = 1$. Then $f\Delta x = F$ and $\Delta l = \Delta x^2$.
- If **not pre-stressed**, $f = 0$, then $\Delta U = \frac{1}{2}k\Delta l^2 = \frac{1}{2}k\Delta x^4$ and $\Delta x = (F/k)^{1/3}$
- If **pre-stressed**, $f > 0$, then $\Delta U = f\Delta l = f\Delta x^2$ and $\Delta x = F/f$
- *Pre-stressing can make otherwise rigid/floppy structures un/stable.* Is this what happens to ellipsoids near the sphere point?

Free Energy

- **Free energy** determines the whole thermodynamics of the system

$$F = -\ln |\mathcal{J}_{\Delta \mathbf{R}}| = Nf$$

- In the jamming limit $|\mathcal{J}_{\Delta \mathbf{R}}| \to |\mathcal{P}_{\Delta \mathbf{R}}| = \delta^{N_f} |\mathcal{P}_{\mathbf{x}}|$, where we recall $\mathcal{P}_{\mathbf{x}}: \ \mathbf{A}^T \mathbf{x} \leq \mathbf{e}$
- Pressure $P = -\partial F / \partial V$ giving

$$p = \frac{PV}{NkT} = \frac{1}{\delta} = \frac{d_f}{(1 - \phi/\phi_J)}$$

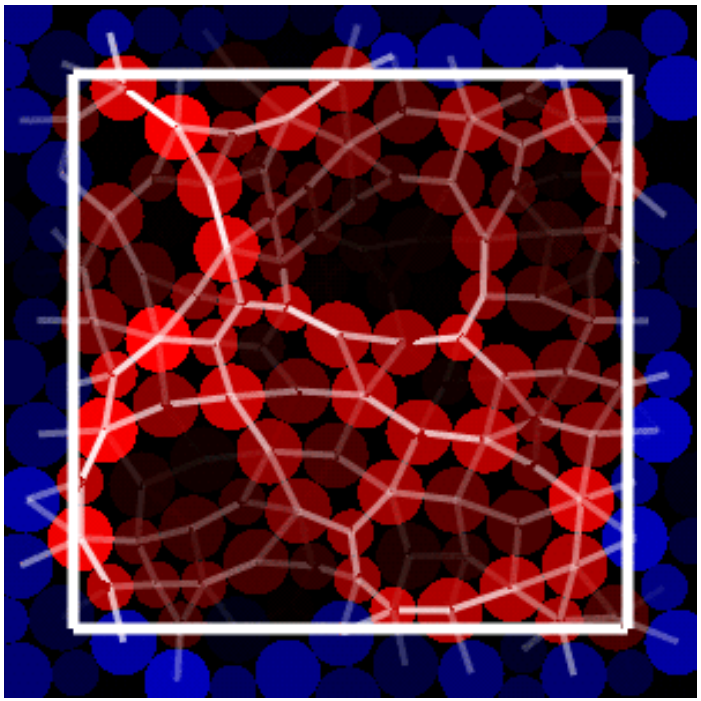
- The crux is in the constant f_J

$$f = -d_f \ln \delta - \frac{\ln |\mathcal{P}_{\mathbf{x}}|}{N} = -d_f \ln \delta - f_J$$

For Any Polytope

- Free energy $F/NkT \;\; - \ln |\mathcal{P}_{\Delta\mathbf{R}}| / N$, and $p = -\partial F/\partial V$
- $|\mathcal{P}_{\Delta\mathbf{R}}| = (\delta D)^{Nd} |\mathcal{P}_{\mathbf{x}}|$, giving:

$$p = \frac{PV}{NkT} = \frac{1}{\delta} = \frac{d}{(1 - \phi/\phi_J)}$$



Link: `Graphics/LSD_stress.mpg`

Isostatic Packings

- **Isostatic** packings, for *collective* jamming

$$M = \begin{cases} 2N - 1 \text{ for } d = 2 \\ 3N - 2 \text{ for } d = 3 \end{cases}$$

where $\bar{Z} = 2M/N \approx 2d = 6$ is the *mean coordination number*

- The forces are *unique* for a simplex:

$$\mathbf{f} = \begin{bmatrix} \mathbf{A} \\ \mathbf{e}^T \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{0} \\ 1 \end{bmatrix}$$

The Volume of a Simplex

- Computing $|\mathcal{P}_{\mathbf{x}}|$ is a well-known #P-hard problem (as a function of N_f)
- Optimal are **randomized** polynomial algorithms [at present $O^*(N_f^4)$]
- But for a **simplex** (hyperplane) $\mathcal{H}$-representation, $\mathbf{Ax} \leq \mathbf{b}$, and $\mathbf{x} \in \mathcal{R}^n$, we can do it easily

$$V^{-1} = n! \left|\tilde{\mathbf{A}}\right| \prod_{i=1}^{n+1} a_i$$

where $\tilde{\mathbf{A}}^T \mathbf{a} = \begin{bmatrix} \mathbf{0} \\ 1 \end{bmatrix}$ and $\tilde{\mathbf{A}} = \begin{bmatrix} \mathbf{A} & \mathbf{b} \end{bmatrix}$

- The calculation can be done fully in sparse matrix mode
- We have a *physical interpretation*, for example, $\mathbf{a} \equiv \mathbf{f}$

Calculating Free Energies

- The free energy is usually computed relative to a **reference state**, for example, for liquids:

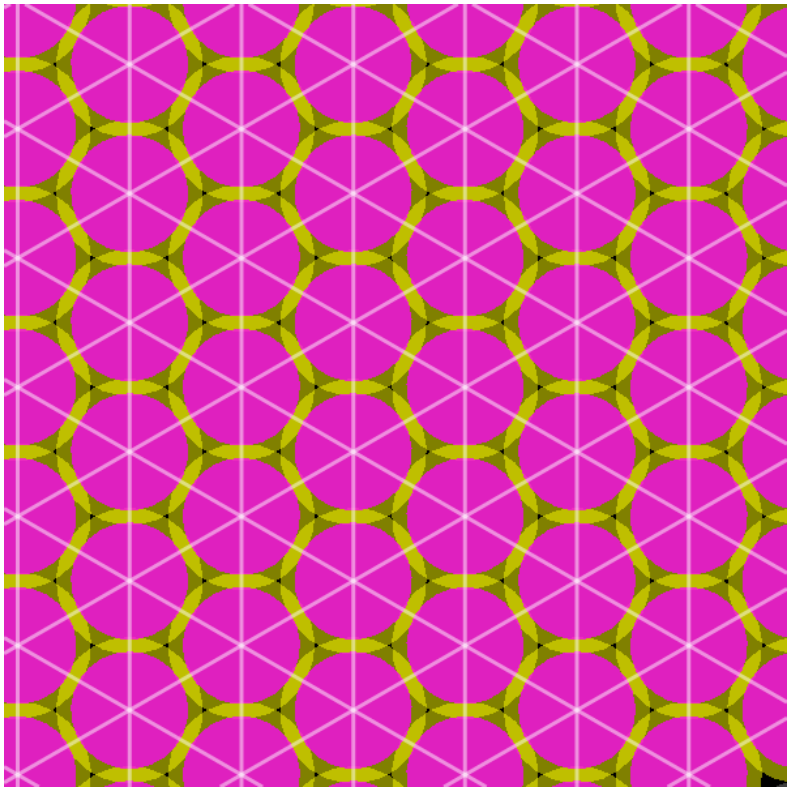
$$f(\phi) = f_{\text{ideal}} + \int_0^{\phi} \frac{p(\phi)}{\phi} d\phi \text{ where } f_{\text{ideal}} = -\frac{1}{N} \ln \frac{V^N}{N!} \approx -\ln \frac{V}{N} - 1$$

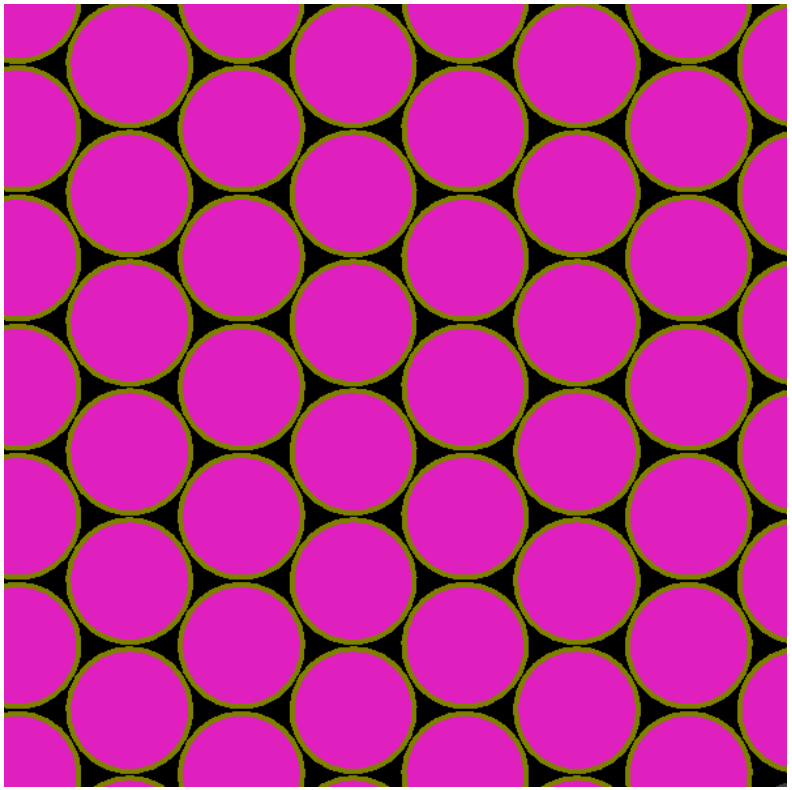
- Problem is posed for solids because of **first-order phase transitions**
- Usual solid reference state used in Monte Carlo: the **Einstein solid** (collection of independent harmonic oscillators)

$$\Delta U = \frac{k}{2} \sum_{i=1}^{N} \left\| \mathbf{r}_i - \mathbf{r}_i^J \right\|^2$$

- We want an event-driven molecular-dynamics algorithm: **Only hard interactions allowed**!

Example





Links: `Graphics/LSD.HS.2D.NNL.mpg` `Graphics/LSD.HS.2D.cells.disjoint.mpg`

BCMD Theory

This Bounding Cell MD algorithm uses a **single-occupancy-cell** (SOC) model with the cell scaling μ as a parameter

- Add time-dependence $\mu = 1 + \Delta\mu = \mu_{\max} - \gamma_\mu t$ with a constant *cell reduction rate* γ_μ.
- The pressure on the walls of a cell $p_c = P_c V_c / kT$ gives

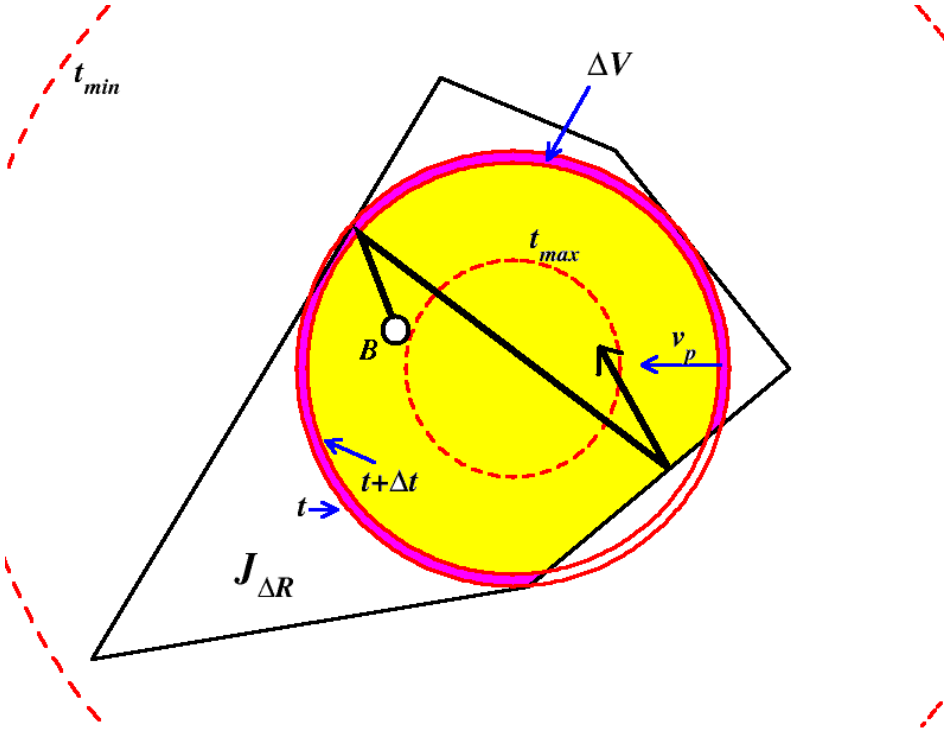
$$f = f_c\left(\Delta\mu_{\min}\right) - \int_{V_c^{\max}}^{V_c^{\max}} p_c \frac{dV_c}{V_c}$$

- For the disjoint-cell model we know $f_c\left(\Delta\mu\right)$ theoretically

$$f_c\left(\Delta\mu\right) = -d_f \ln \Delta\mu - f_c^J \text{ where } f_c^J = \ln(\pi/6) \text{ for spheres}$$

- Use adaptive reduction rate $\gamma_\mu\left(\mu\right) = \gamma_\mu\left(\mu_{\max}\right)\left(\frac{\Delta\mu}{\Delta\mu_{\max}}\right)^{\vartheta}$

In High Dimensions



An **ergodic billiard ball** $\mathcal{B} \in \mathcal{R}^{N_f}$ elastically bounces inside $\mathcal{J}_{\Delta\mathbf{R}}$. Add constraints $\hat{\mathcal{J}} = \tilde{\mathcal{J}}_{\Delta\mathbf{R}} \cap \mathcal{J}_{\Delta\mathbf{R}}$ where $\tilde{\mathcal{J}}_{\Delta\mathbf{R}}(\xi \to 0) = \{\mathbf{R}_J\}$ and $\tilde{\mathcal{J}}_{\Delta\mathbf{R}}(\xi \to \infty) = \mathcal{R}^n$ and the volume $\left|\tilde{\mathcal{J}}_{\Delta\mathbf{R}}(\xi)\right|$ is known. Assume $\tilde{\mathcal{J}}_{\Delta\mathbf{R}}(\xi_{\max}) = \mathcal{J}_{\Delta\mathbf{R}}$ and $\tilde{\mathcal{J}}_{\Delta\mathbf{R}}(\xi_{\min}) = \tilde{\mathcal{J}}_{\Delta\mathbf{R}}(\xi)$

The Mathematics

- Pressure on the walls of $\hat{\mathcal{J}}$ is $P = kT/V$, where $kT = 2K/N_f$
- Collisions with the moving walls of $\tilde{\mathcal{J}}_{\Delta \mathbf{R}}$ are **elastic**

$$v_\perp^{\text{after}} - v_\perp = -\left(v_\perp^{\text{before}} + v_\perp\right)$$

- The billiard heats up due to the shrinking of $\hat{\mathcal{J}}$

$$\Delta K_c = \frac{m}{2}\left(v_\perp^{\text{after}} - v_\perp^{\text{before}}\right)\left(v_\perp^{\text{after}} + v_\perp^{\text{before}}\right) = v_\perp \Delta \pi_c$$

- During a short time interval from t to $t + \Delta t$ the volume $V = \left|\hat{\mathcal{J}}(\xi)\right|$ decreases by $\Delta V = S v_\perp \Delta t$, and

$$\Delta K = v_\perp \Delta \pi = \frac{\Delta \pi}{S \Delta t} \Delta V = P \Delta V = kT \frac{\Delta V}{V(\xi)} = \frac{2K}{N_f} \frac{\Delta V}{V}$$

Contd.

- Continium limit gived ODE $dV/V = (N_f/2)dK/K$ with solution

$$\ln \frac{|\mathcal{J}_{\Delta \mathbf{R}}|}{|\tilde{\mathcal{J}}_{\Delta \mathbf{R}}(\xi_{\min})|} = \frac{N_f}{2} \ln \frac{K}{K_0}$$

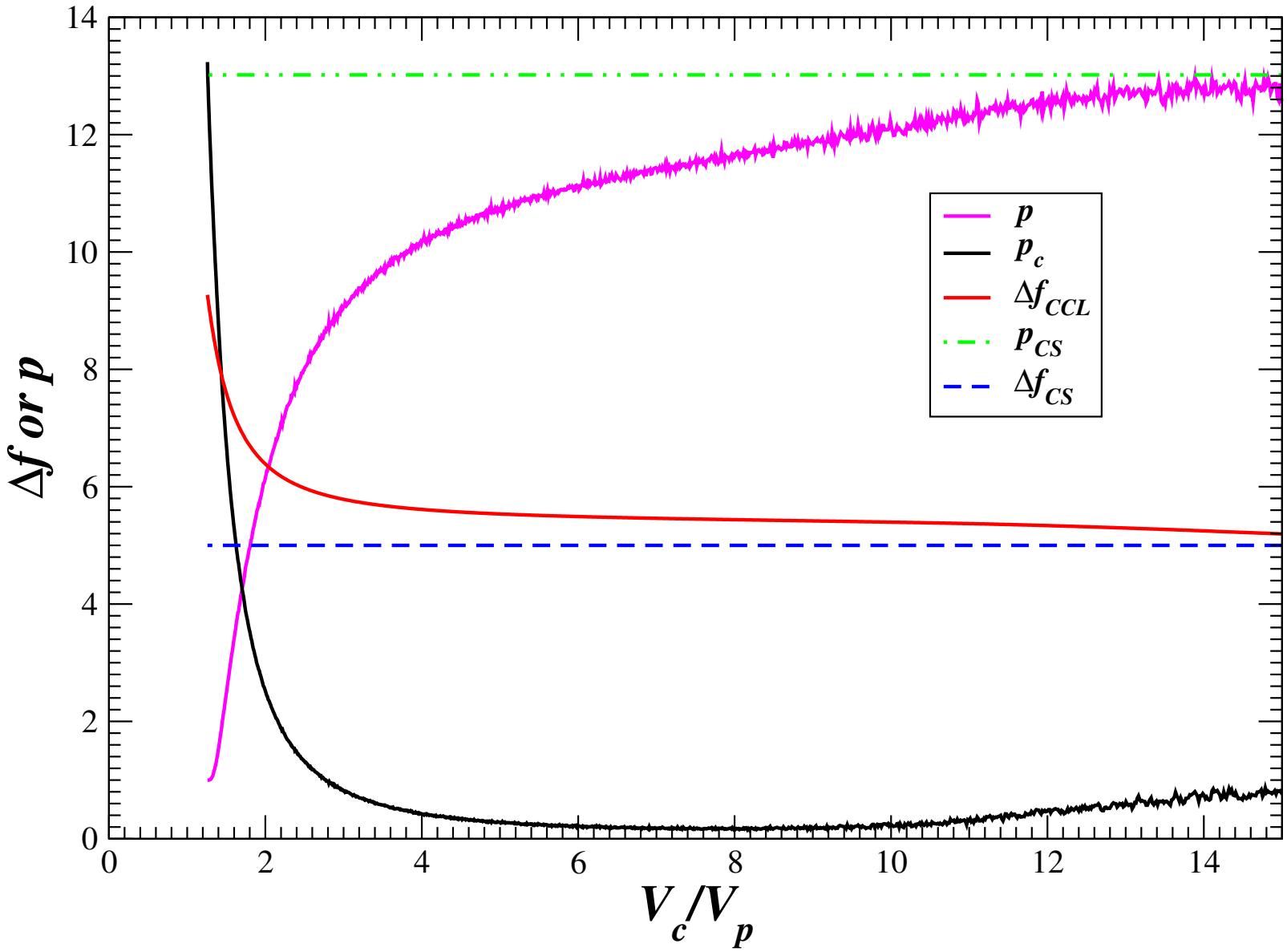
- For the particle system this translates to $\Delta f = \frac{d_f}{2} \ln \frac{K}{K_0}$
- Instead of integrating pressures, simply measure the *relative increase in the kinetic energy*! This can be used in **nonequilibrium** situations as well.

Comparison to MC

Compare to randomized MC algorithms for volume of convex bodies in high dimensions:

- MC algorithms use a **random walk** instead of **billiards motion** (but how about Hit-and-Run random walks?)
- MC algorithms use a **sandwiching** step: What does it correspond to?
- The optimal MC algorithm is $O^*(n^4/\epsilon^2 \ln \frac{1}{\eta})$ oracle calls, and uses simulated annealing (Lovacz and Vempala, 2004)
- Can we use the exisiting mathematical tools to analyze the BCMD algorithm rigorously and find the γ_μ ($\Delta\mu$)to use to get a desired absolute error in f?

Example: Hard Sphere Liquid at $\phi = 0.50$



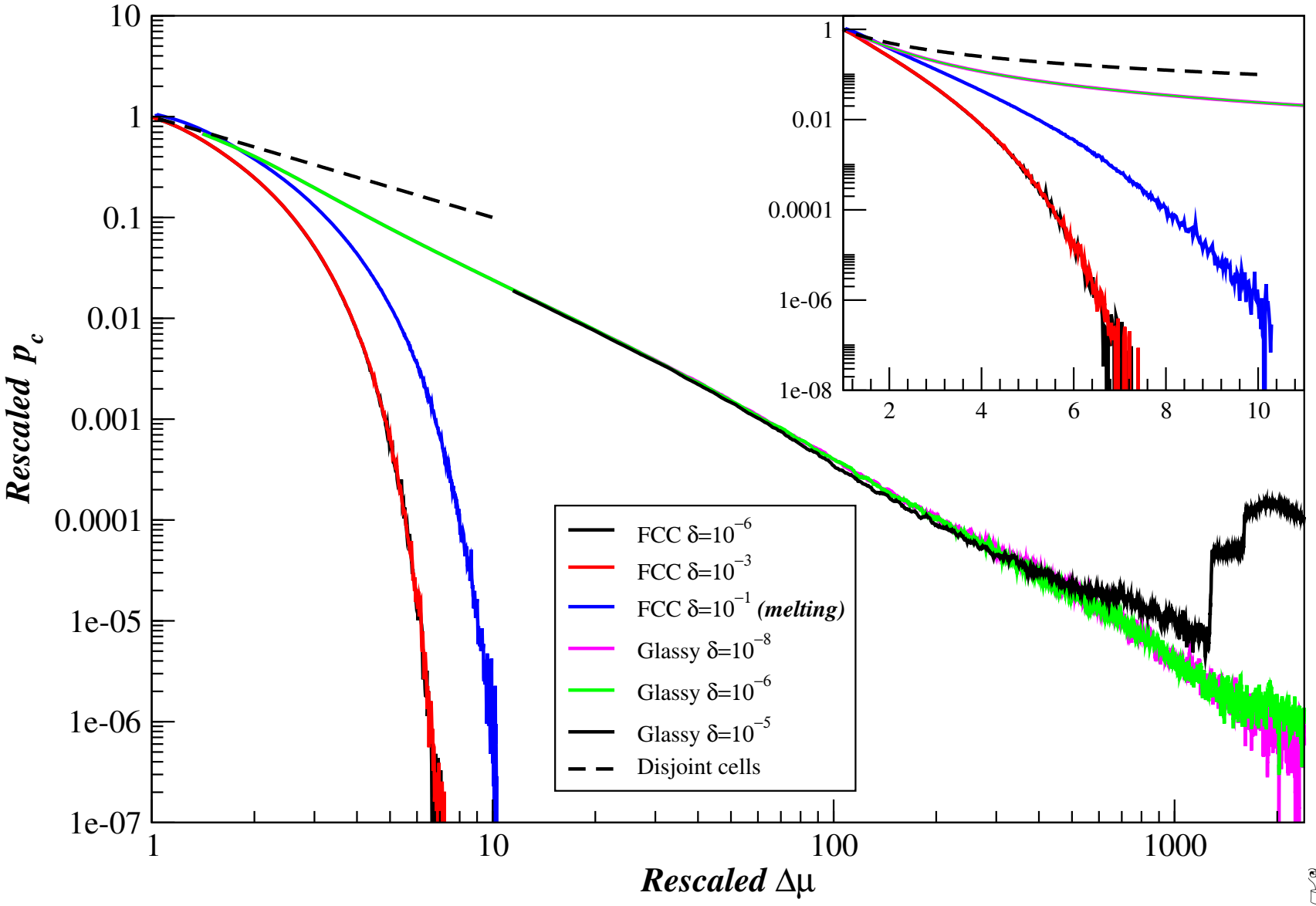
Methodology

- Initial test: **FCC** hard-sphere crystal near melting:
  - Best MC result $\Delta f_{FCC}(\phi = 0.545) = 5.91916(1)$ [is it really that accurate?]
  - BCMD algorithm with $\Delta\mu_{\max} = 1$, $\gamma_\mu(\mu_{\max}) = 0.001$ and $\vartheta = 1$ produces 5.919(0)
- Start at exactly the jammed configuration $\mathbf{R}_J$, the cells will become disjoint when $\Delta\mu_{\min} = \delta$,

$$\Delta f = \frac{d_f}{2} \ln \frac{K}{K_0} = \left(-f_c^J - d_f \ln \delta\right) - \left(-d_f \ln \delta - f_J\right) = f_J - f_c^J$$

- Notice the independence on δ: The scaled $\tilde{p_c}(\Delta\tilde{\mu} = \Delta\mu/\delta) = \delta p_c$ should be a universal function
- We **freeze one particle** to eliminate trivial translations

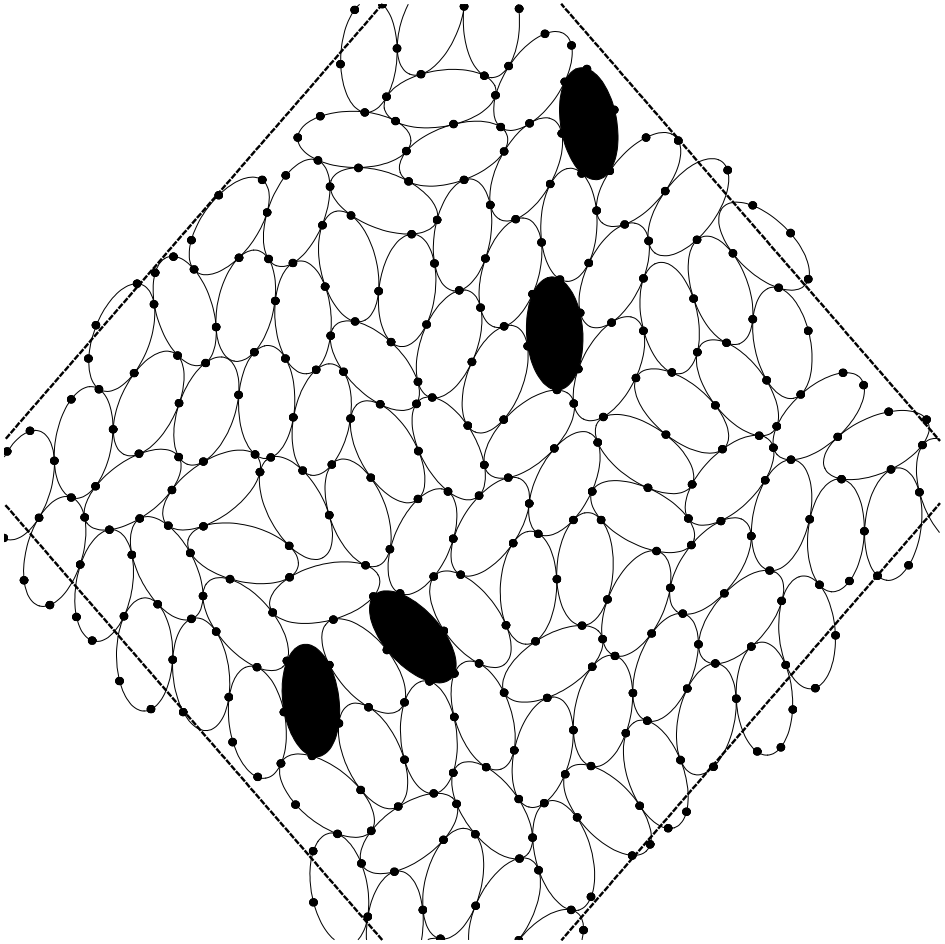
Nearly Jammed Packings



Numbers: Spheres

- FCC crystals:
  - For FCC the literature says $\left[f_J - f_c^J\right]_{FCC} = 2.160 \pm 0.001$
  - BCMD runs with $N = 10,000$, $\delta = 10^{-6}$, $\Delta\mu_{\max} = 10^{-5}$ with $\gamma_\mu\left(\mu_{\max}\right) = 0.001$ and $\vartheta = 0.5$
    Results: $\left[f_J - f_c^J\right]_{FCC} = 2.1599 \pm 0.0005$ and $\left[f_J - f_c^J\right]_{HCP} = 2.1593 \pm 0.0005$
- But we cannot give **rigorous error estimates** until a theory is developed!
- For an isostatic disordered (random) packing of spheres ($N = 1,000$)
  - From the volume of the simplex $f_J = (N-1)^{-1}\left[\ln\left|\mathcal{P}_{\mathbf{x}}\right|\right]$, we get $f_J - f_c^J \approx 4.9479$
  - Sample result $\delta = 10^{-8}$, $\Delta\mu_{\max} = 2.5 \cdot 10^{-5}$, $\gamma_\mu\left(\mu_{\max}\right) = 0.01$ and $\vartheta = 0.5$ gives $f_J - f_c^J = 4.9485 \pm 0.001$

Numbers: Ellipses



Simplex volume gives $f_J - f_c^J = 3.6693$, BCMD algorithm at $\delta = 10^{-4}$ with $\Delta\mu_{\max} = 1.5 \cdot 10^{-2}$ with $\gamma_\mu(\mu_{\max}) = 0.001$ and $\vartheta = 0.5$ gave $f_J - f_c^J = 3.61 \pm 0.01$

There are numerical difficulties with the implementation which need to be resolved...

Isostatic Packings

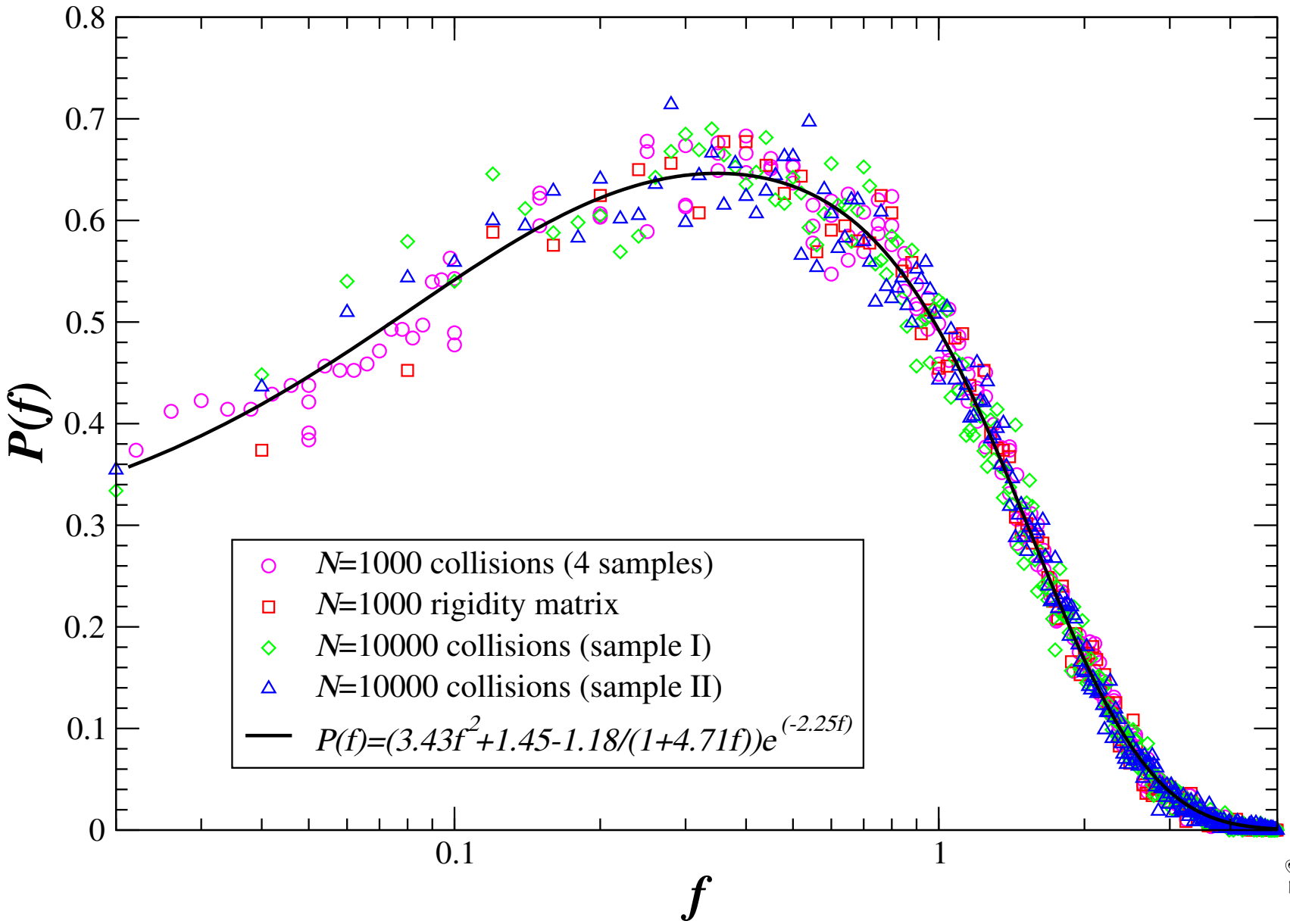
Using the simplex nature of the polytope, we get:

$$g_2^{(\delta)}(l) = \frac{p}{4\phi}\mathcal{L}_{l/\Delta D}\left[fP_f(f)\right]$$

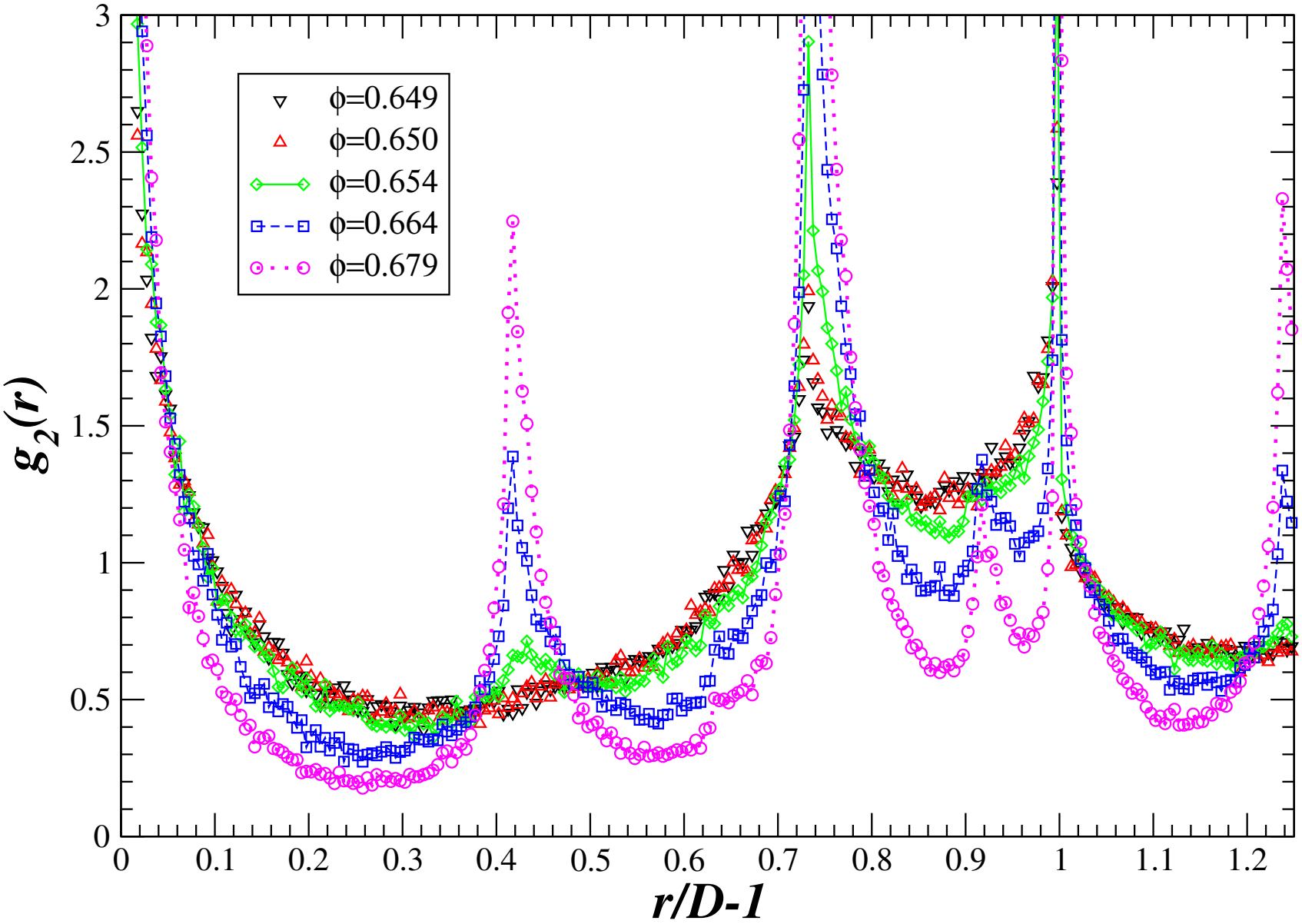
- Using empirical $P_f(f) = (Af^2 + B)e^{-Cf}$ to get

$$\mathcal{L}_x\left[fP_f(f)\right] = \frac{6A}{(x+C)^4} + \frac{B}{(x+C)^2}.$$

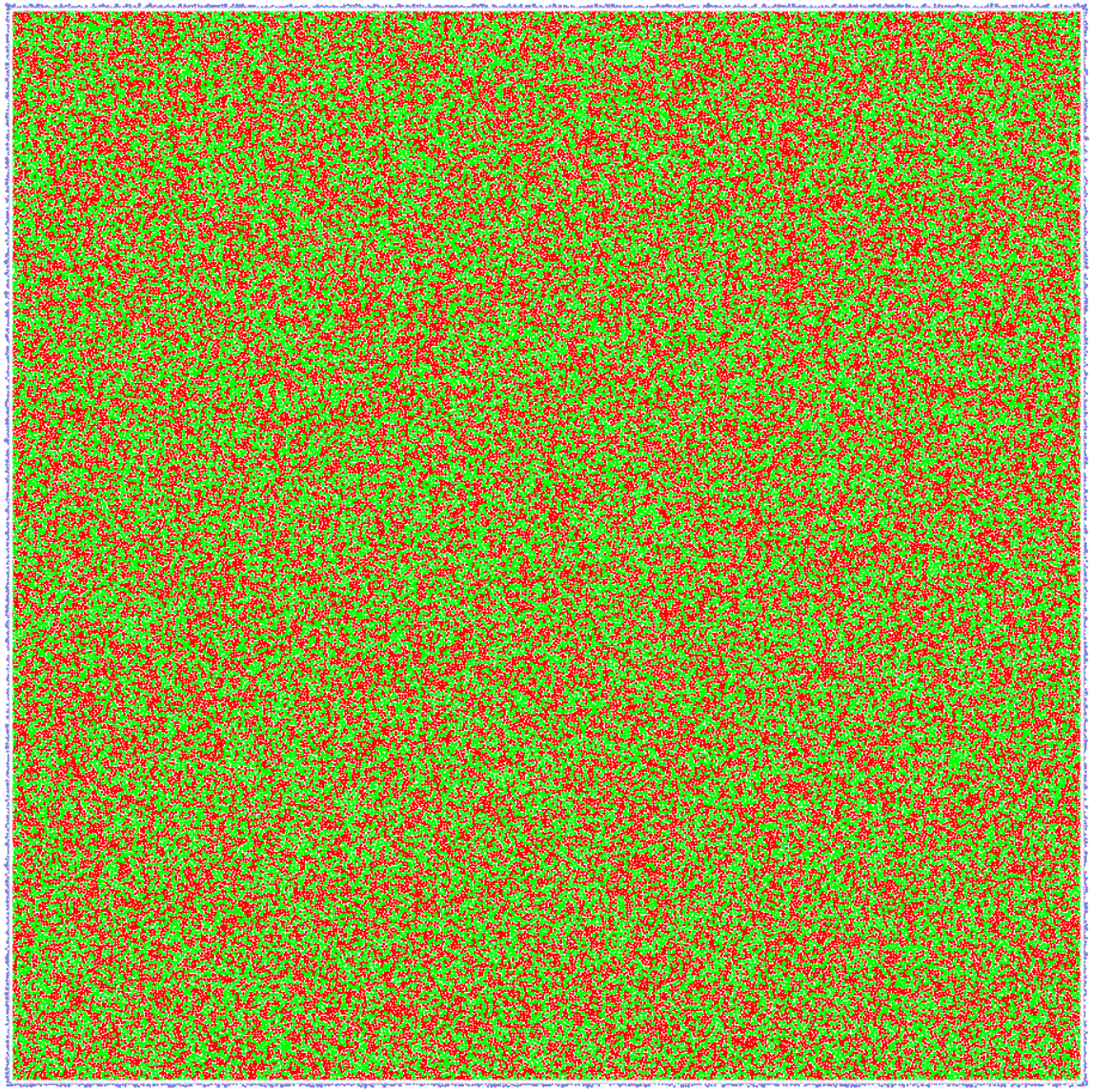
Force Distribution



Ordered Packings



Hyperuniformity in 2D



Near Contacts in High Dimensions

- Gap x at which the cumulative coordination $Z(x)$ equals the kissing number, $x \simeq 0.35$, 0.34, $0.31 - 0.36$ and $0.33 - 0.36$ in $d = 3$, 4, 5 and 6, respectively.
- Gap x at the **first minimum** in g_2, $x \simeq 0.35$, 0.32, 0.30 and 0.28.
- Disordered packings might be **deformed crystal packings**, in which the true contacts are deformed into near contacts, and only the minimal number of contacts necessary for jamming is preserved.
- Contrast with the usual interpretation of disordered packing in $d = 3$ in terms of **tetrahedral** or **icosahedral** packings, without relation to the crystal (FCC) packing.

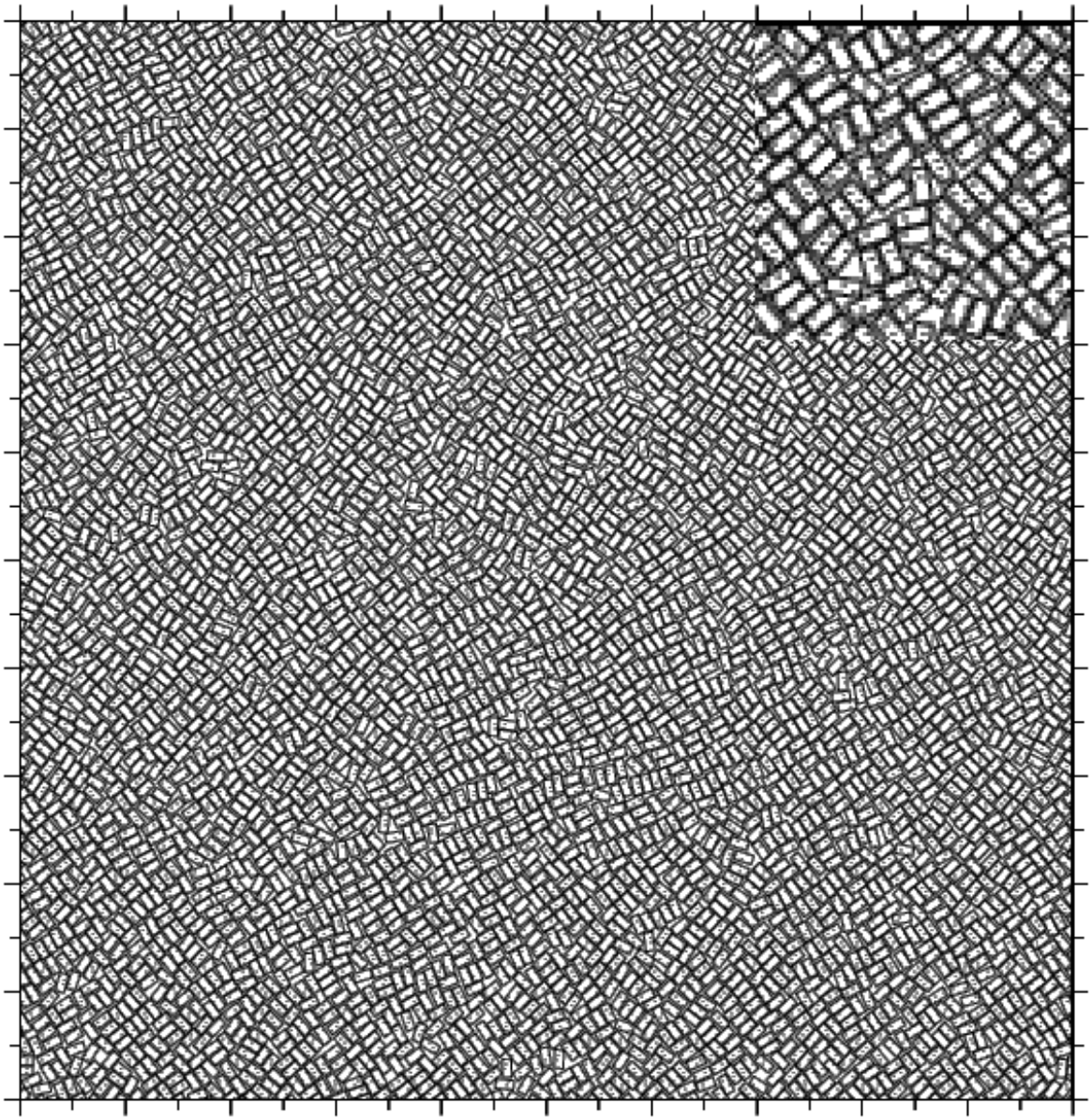
Infinite Dimension

- Suggested scaling is

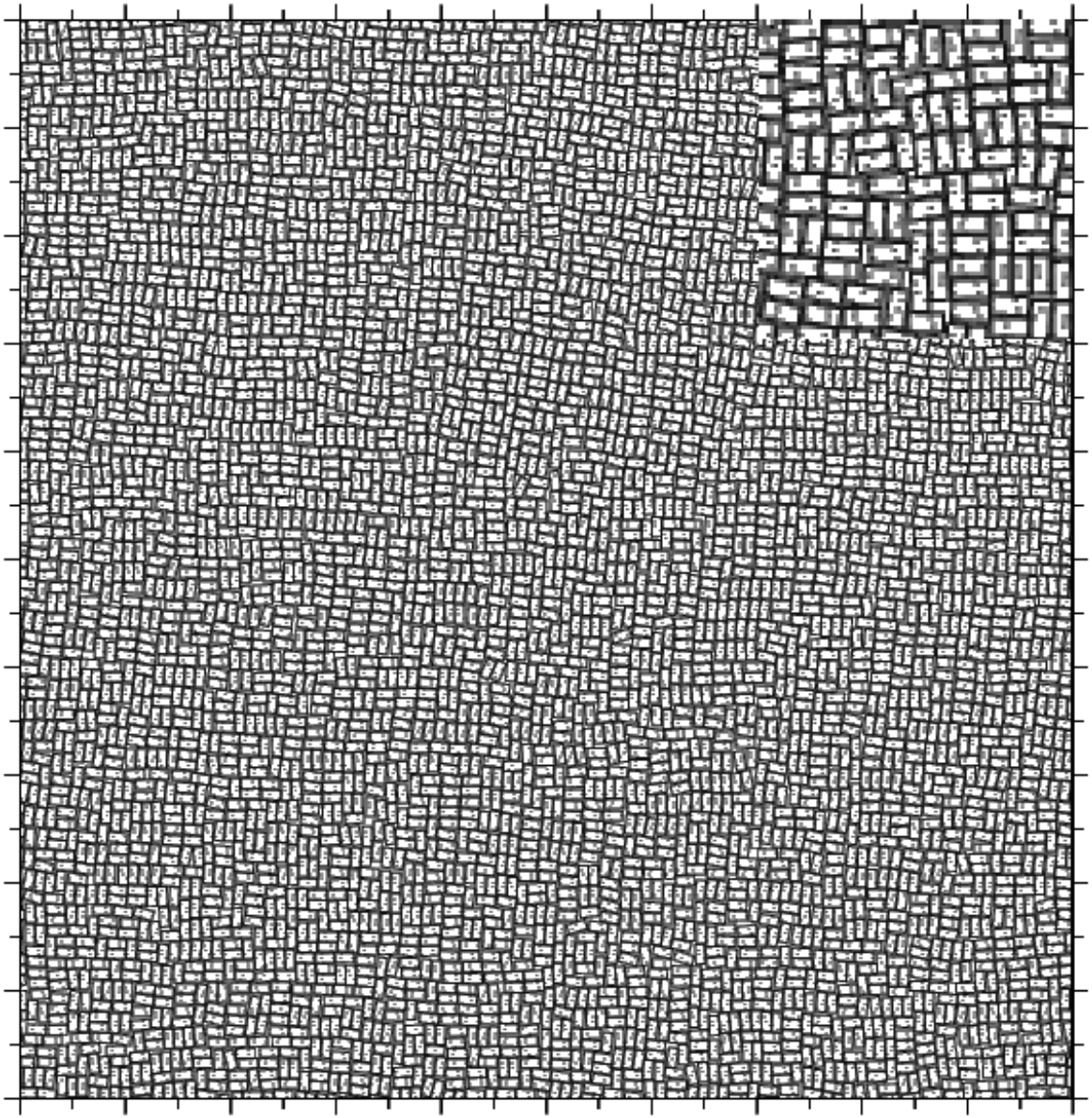
$$\phi_{MRJ} = \frac{(c_1 + c_2 d)}{2^d}$$

- For jammed packings $c_1 = -2.72$ and $c_2 = 2.56$.
- Similar scaling is observed for Random Sequential Addition as well!
- *Will disordered packings be densest as* $d \to \infty$?

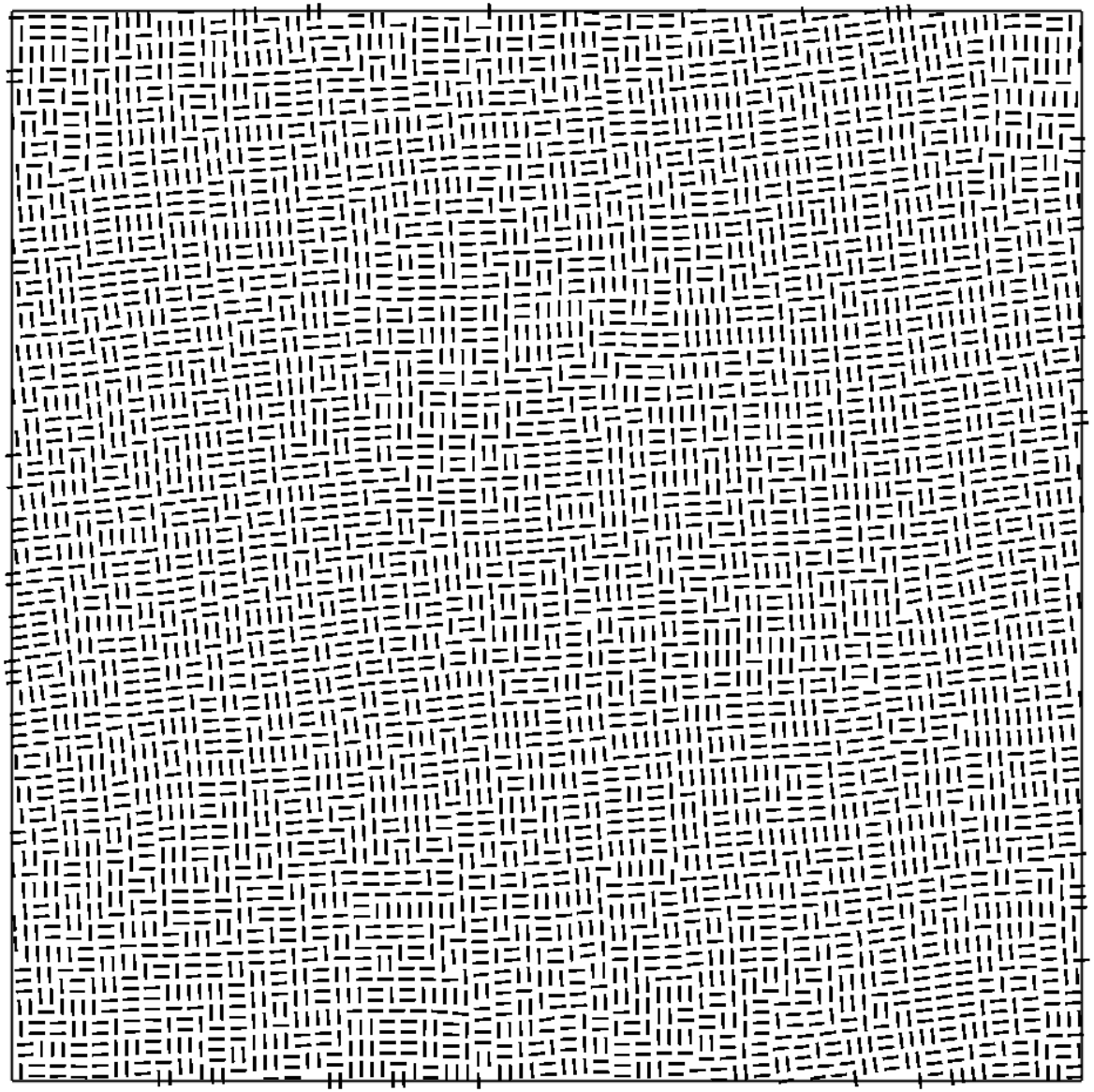
Tetratic Liquid Phase



Tetratic Liquid Phase



MRJ Domino Packings?



Thermodynamics of Hard Spheres

- Hard-particle systems are athermal, so set $T = 1$: Corresponds to fixed density for soft particles
- The only state variable is ϕ: High density corresponds to low temperature for soft particles
- **Free energy** is simply the available volume in configuration space

$$F = -S = -\ln |V_{\text{conf}}| = Nf$$

- True thermodynamic equilibrium state: The majority of the configurational volume is in the state of *minimum free energy*
- For many systems it is firmly established that there is a first-order phase transition from **liquid** (isotropic and homogeneous, diffusive, low-density) to **crystal** (periodic, frozen, high-density)

Hard-Sphere Glasses

- Very dense liquids have negligible diffusivity (on experimental scales) above some **glass-transition density** ϕ_g
- Dense liquids have very slow diffusion, i.e., infrequent particle rearrangements
- The particles in a liquid spend a long time vibrating around glassy configurations. **Glasses correspond to jammed packings**!
- Partition configuration space among all the different jammed packings and assume that most of configurational volume is accounted for

$$V_{\text{conf}} = \sum_{i \in \text{Jammed}} |\mathcal{J}_{\Delta \mathbf{R}_i}| \approx \sum_{i \in \text{Jammed}} |\mathcal{P}_{\Delta \mathbf{R}_i}|$$

- Group the jammed packings into statistically equivalent sets based on ϕ_J

Inherent-Structure Formalism

- Let the number of jammed packings (glasses) with jamming density ϕ_J be $N_g(\phi_J) = \exp[S_c(\phi_J)] = \exp[s_c(\phi_J)N]$, where **configurational entropy** $s_c(\phi_J)$ must vanish at some density $\phi_J^{\max} < \phi_{CP}$
- Decompose

$$V_{\text{conf}}(\phi) = \int N_g(\phi_J) \exp[-N f_{vib}(\phi, \phi_J)]\, d\phi_J = \int \exp[-N f_L]\, d\phi_J$$

- The integral is dominated by the maximum of the exponential

$$f_L(\phi) = f_{vib}(\phi, \phi_J) - s_c(\phi_J) = -d \ln\left(1 - \frac{\phi}{\phi_J}\right) - f_J(\phi_J) - s_c(\phi_J)$$

where $\phi_J(\phi)$ is the jamming density which minimizes $f_L(\phi)$

- Assume that $f_J(\phi_J) = \text{const}$

The Ideal Glass Transition

- The term $-d \ln\left(1 - \frac{\phi}{\phi_J}\right)$ prefers larger ϕ_J (**more free volume**), while the term $-s_c(\phi_J)$ prefers more disordered packings (**more degeneracy**)
- It is reasonable to assume that $s_c(\phi_J)$ is monotonically decreasing at high densities, and goes through zero at $\phi_J^{\max}$
- As ϕ increases the system will sample packings with higher ϕ_J
- At an **ideal glass transition density** ϕ_g, $\phi_J(\phi_g) = \phi_J^{\max} = \phi_{\mathrm{IG}}$, and there is no higher-density glasses left so the densest glass starts dominating the thermodynamics from then on.
- The assumption everyone makes, implicitly or explictly: **The ideal glass corresponds to an amorphous structure** with $\phi_{\mathrm{IG}} < \phi_{\mathrm{crystal}}$

Measuring $s_c(\phi_J)$

- The liquid free energy can be calculated by integrating EOS from liquid state

$$f_L = f_{\text{ideal}} + \int_0^{\phi} \frac{p-1}{\phi} d\phi$$

- The vibrational or glass free energy can be obtained from the BCMD algorithm, i.e., via the **single-occupancy-cell** (SOC) model with cells of the "right" size

$$f_{vib} \approx f_{SOC}(\Delta\mu \approx 1)$$

- Estimate: $s_c = f_{SOC} - f_L$ and calculate ϕ_J by jamming the system. It has been done before in various studies for a variety of glass formers, most notably, Lennard-Jones and hard sphere bidisperse disk or sphere packings.

contd...

- Problems:
  - True equilibrium EOS is very difficult to measure close to glass transition due to **sluggish dynamics**
  - Far from jamming f_{SOC} is not well-defined: It depends on **cell-size**!
  - The underlying model itself is approximate, especially at low densities, where at the very least partially jammed packings (**saddle points**) need to be considered
  - The **crystal** has been ignored: Instead of true thermodynamically stable structure look for **metastable liquid structure**. Is it well-defined?
- But let's try it anyway for a bidisperse hard disk packing with size ratio $\kappa = 1.4$ with $1/3$ large disks and $2/3$ small disks!

Basics

- Use **event-driven molecular dynamics** for maximal efficiency
- Use nonequilibrium MD in which particles grow or shrink in size with **expansion rate** $\gamma = dD/dt$
- In the limit $\gamma \to 0$ we obtain true equilibrium, for small γ we have **quasi-equilibrium** transformation
- **Validation** strategy: If significant reduction in γ does not change the thermodynamic properties, we can be confident the results are in "equilibrium", local (metastable) or global (stable).
- If changes in γ change results we should **not** be talking about equilibrium of any sort nor invoke **thermodynamics**: It is **kinetics**!

EOS

- Instead of $p(\phi)$, assume free-volume EOS holds and estimate the jamming density

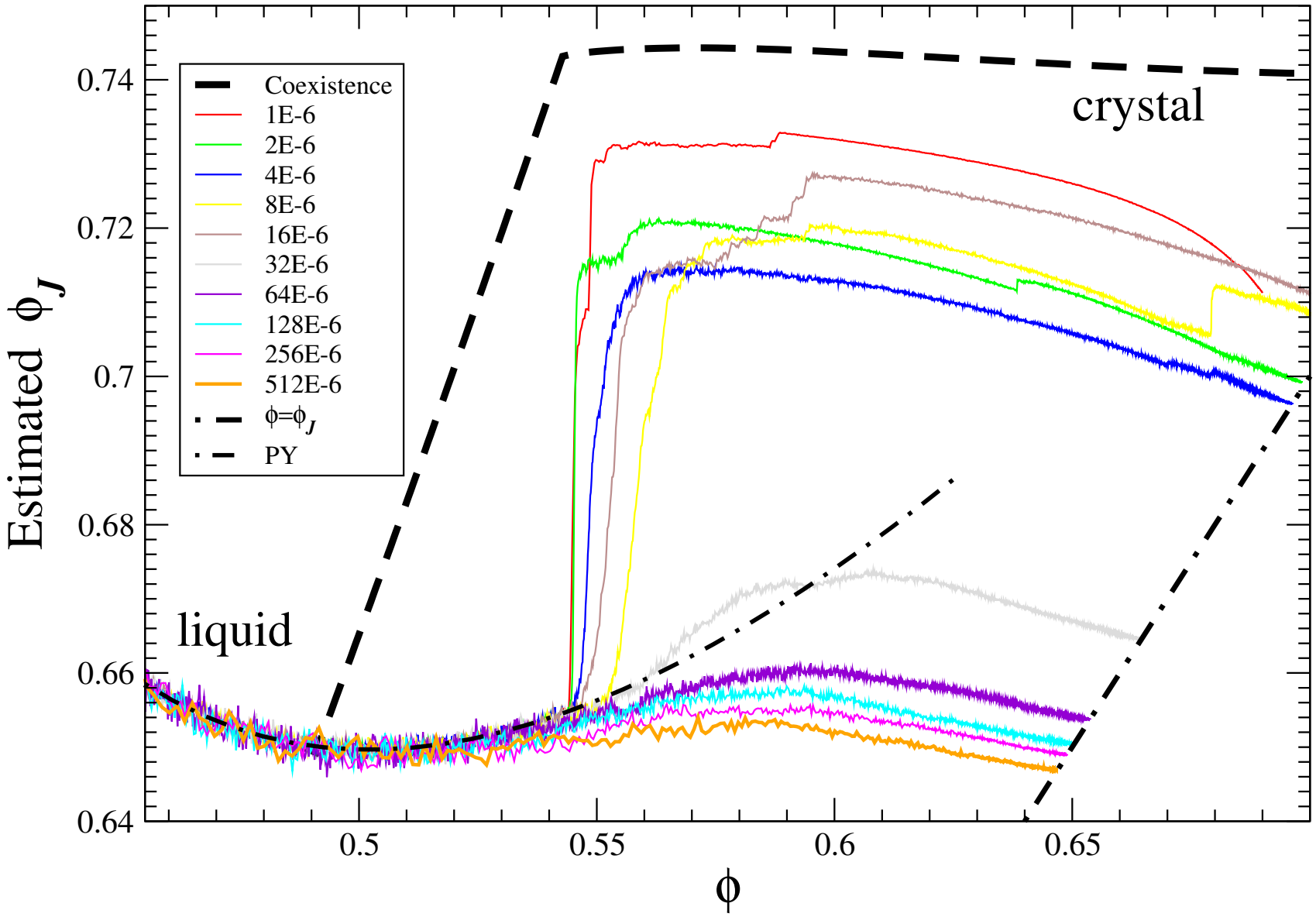
$$\tilde{\phi_J} = \frac{\phi}{1 - d/p(\phi)}$$

- In jamming limit or for crystals we have $\tilde{\phi_J} \approx \phi_J = \text{const}$, which makes plots nicer
- For (isostatic) disordered (MRJ) packings **very** close to jamming $\tilde{\phi_J} \approx \phi_J = \text{const}$ rigorously. However, **empirically**, it seems that over a much wider range of densities of interest nearly jammed packings follow

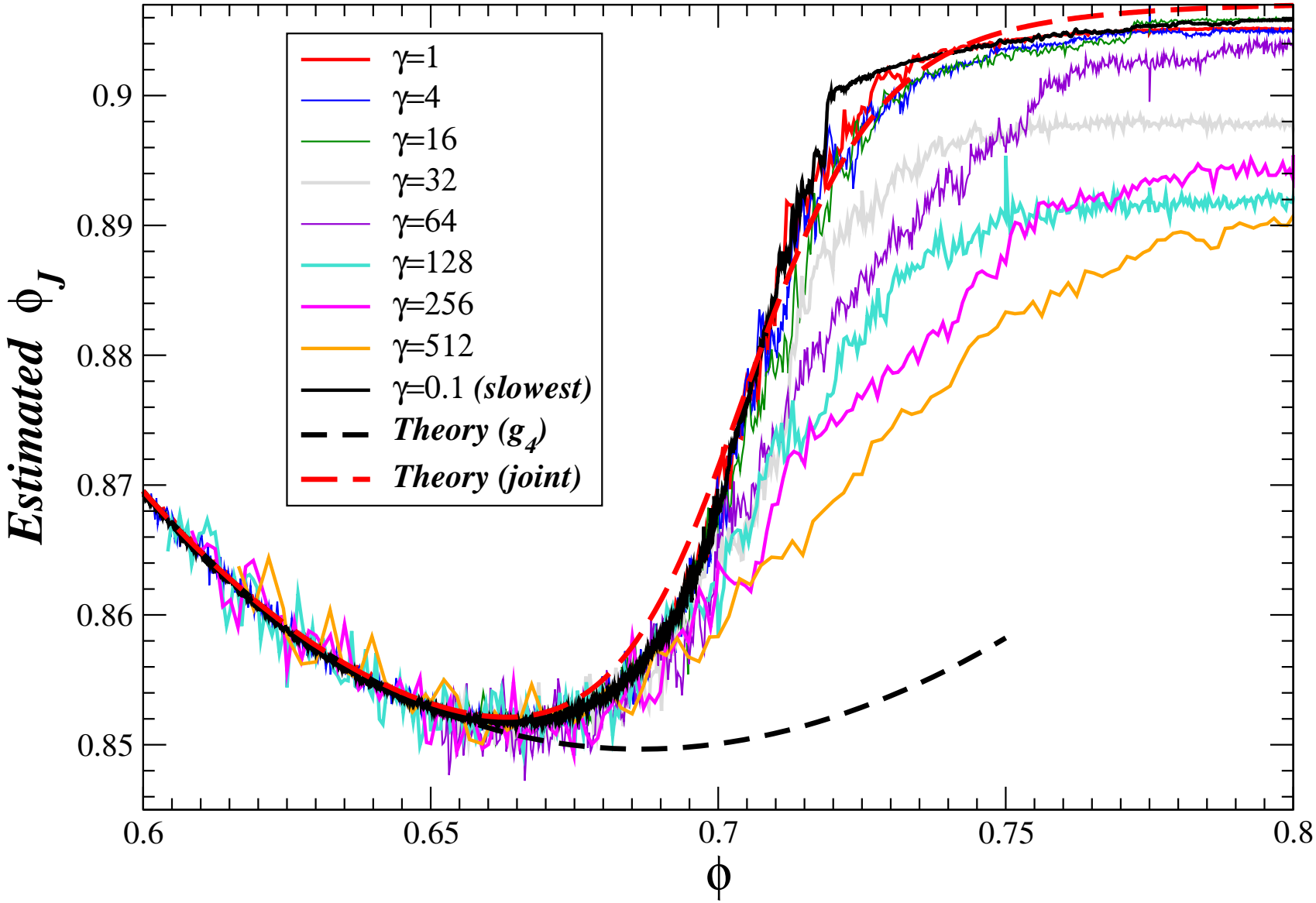
$$\tilde{\phi_J} \approx (1 - \alpha)\phi_J + \alpha\phi \text{ where } \alpha \sim 0.1$$

- We will see that plots of $\tilde{\phi_J}$ highlight the kinetic glass transition very well

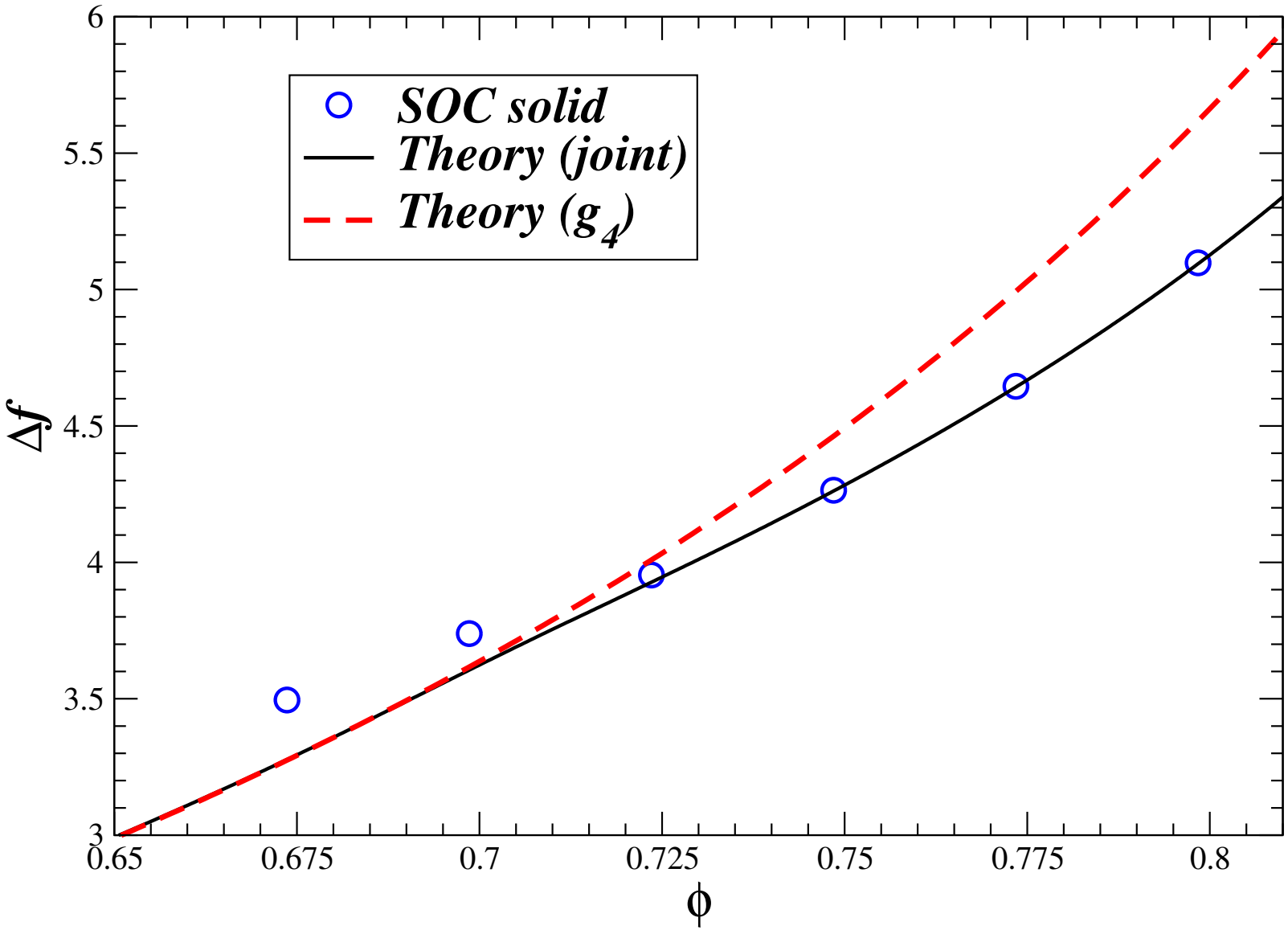
Why Binary and not 3D Mono?



Preliminary: Monodisperse Disks



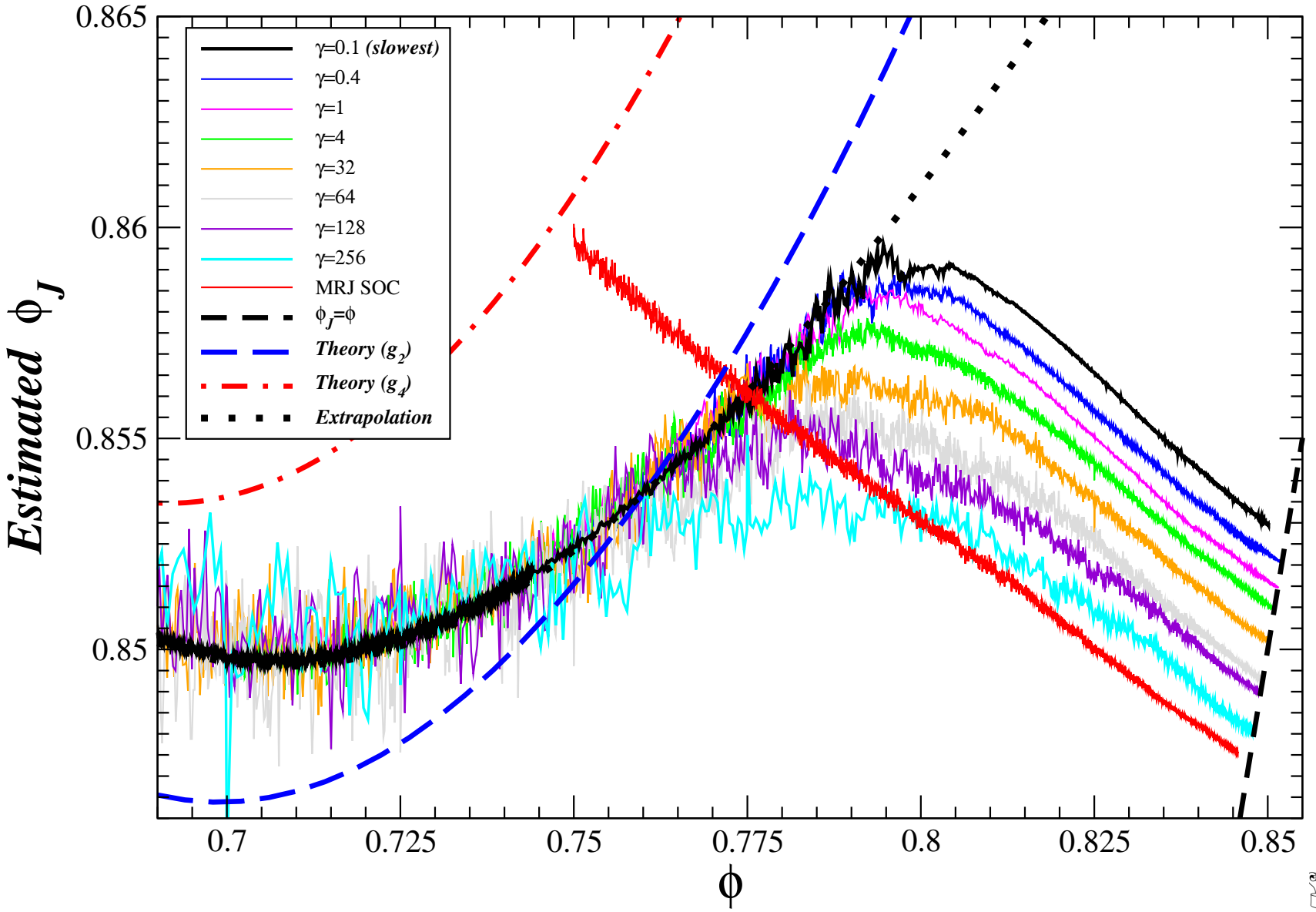
Configurational Entropy



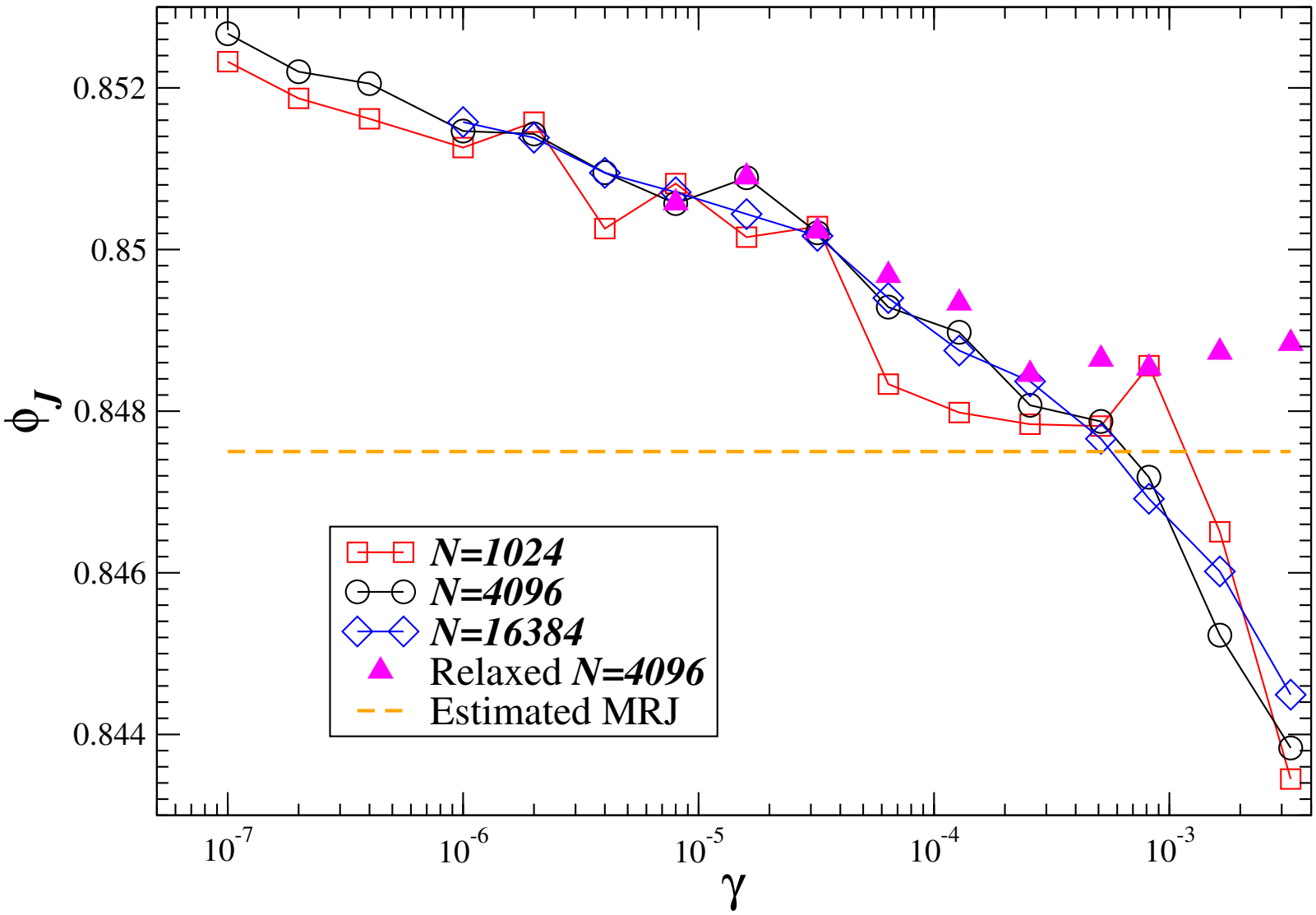
Bidisperse Disks

- $x_A = 2/3$ and $x_B = 1/3$ binary mixture, $\kappa = D_B/D_A = 1.4$
- This system is a well-studied **model glass former**, with strongly suppresed crystallization. We have never observed direct crystallization of a liquid (in large systems), even in very lenghy runs.
- We use $N = 4096 = 64^2$ particles for most runs, which is much larger than typical studies (~ 256 particles in 3D!)
- It is widely believed that the crystal structure here is a **phase-separated** (hexagonal) crystal
- The phase diagram is believed to be of a **eutectic** type, with the liquid first precipitating a **crystal of large disks**

Liquid/Glass EOS



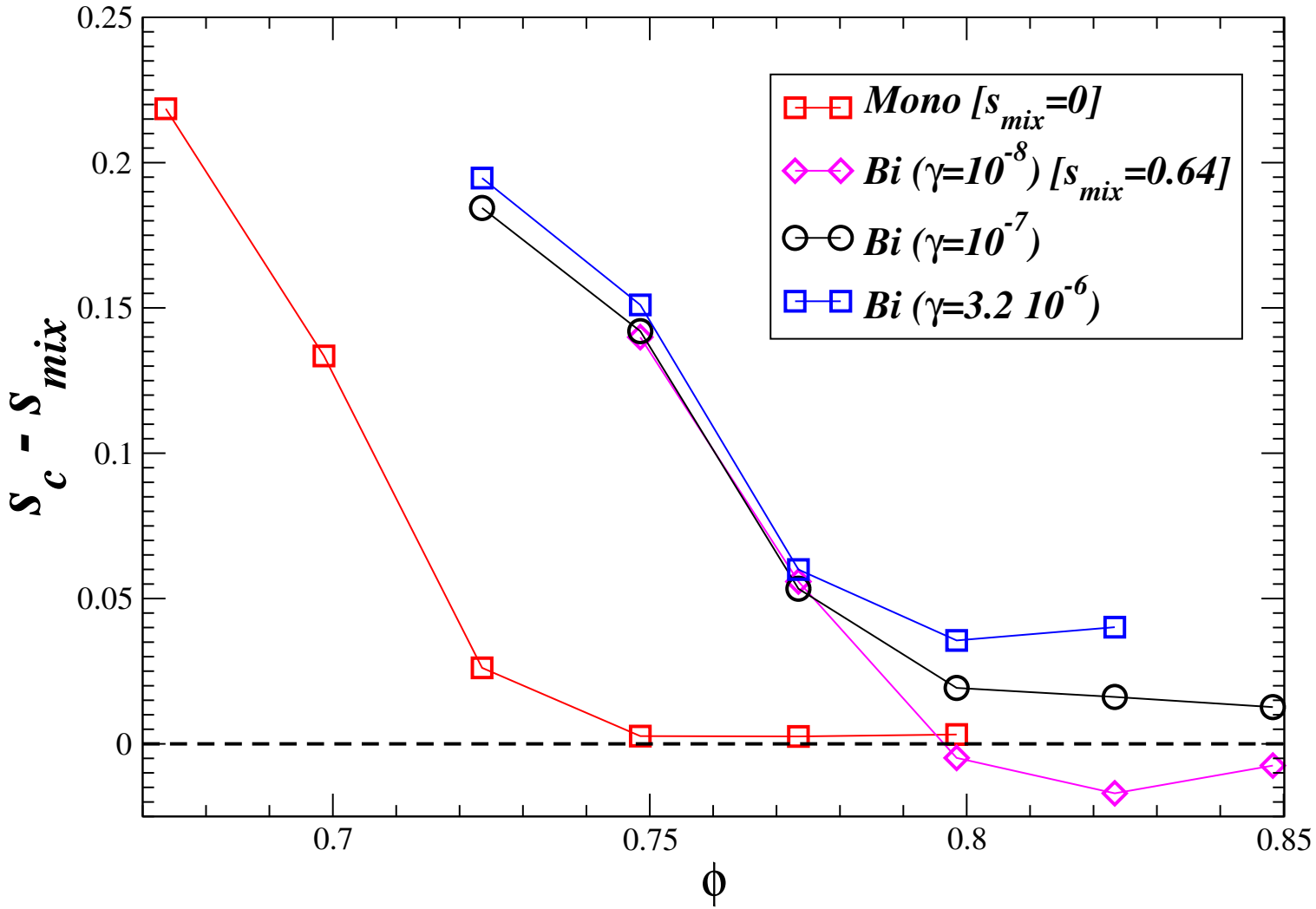
Effect of Expansion (Cooling) Rate



Observations

- We do not really have the liquid EOS beyond the kinetic glass transition density $\phi_g^{\text{kinetic}} \approx 0.8$. The best known theories do not work well!
- A free energy calculation *assuming* a first-order transition, shows that the **freezing density** is $\phi_L^{\max} \approx 0.775$, with mixed isotropic liquid coexisting with a crystal of large particles at $\phi_S^{\min} \approx 0.842$. The full phase diagram is difficult to calculate.
- To estimate of $s_c(\phi)$ we can use the actual EOS for slower compressions:
  - We won't attempt to use the true liquid EOS: use measured EOS instead
  - We use the BCMD algorithm on SOC models of actual snapshots saved during the compression
  - Note that for fast compressions it is not possible to measure/define the EOS exactly!

Numerical s_c



$$s_{\mathrm{mix}} = x_A \ln x_A + x_B \ln x_B = \mathrm{const}$$

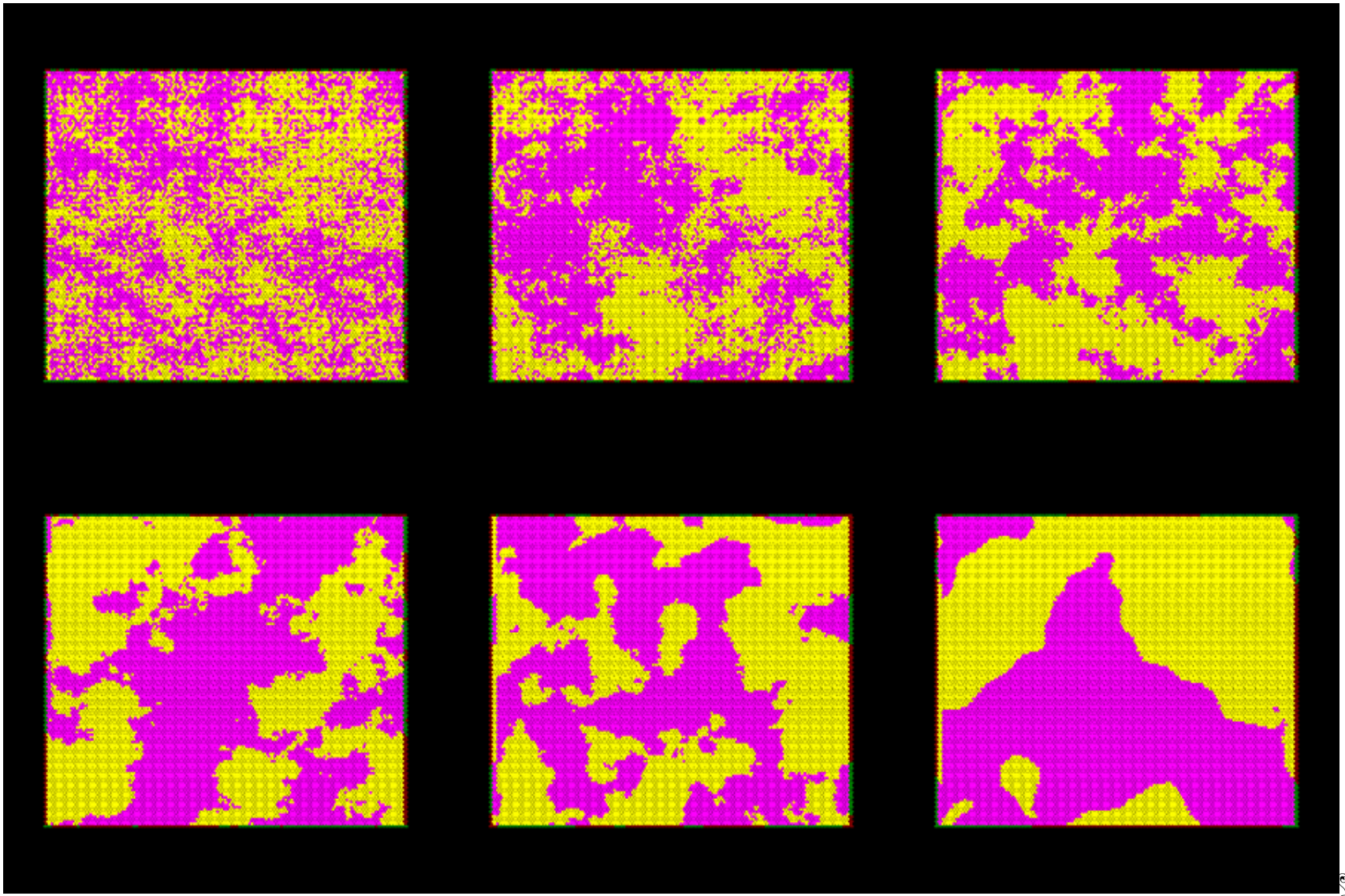
Observations/Conclusions

- **The configurational entropy is very close to the mixing entropy near the glass transition**
- All numerical studies reported in the literature have $s_c \approx s_{\mathrm{mix}}$ for the lowest temperature or highest density reported!
- Ideal glass transition is **naively extrapolated** to $s_c = 0$, which requires overcoming the entropy of mixing, i.e., **demixing**
- *Proposition*: The presumed "ideal glass" is nothing but a fully demixed, i.e., **phase-separated crystal**
- Upon increasing ϕ it seems **partial demixing**, i.e., clustering of large particles, should occur. We see this in the simulation results!

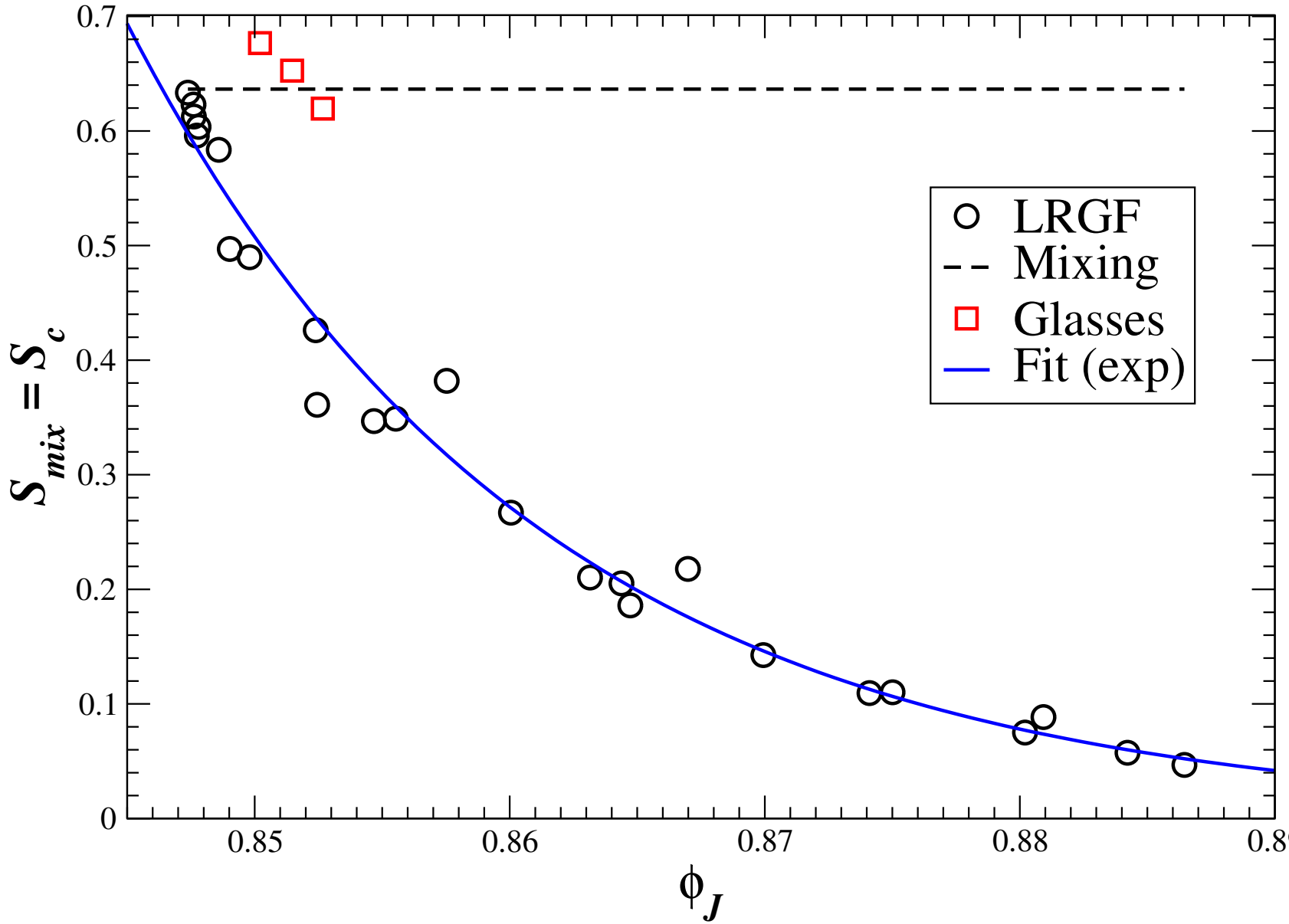
Is There a Most Dense Amorphous Packing?

- The observation $s_c \approx s_{\mathrm{mix}}$ suggests that there is an almost one-to-one correspondence between random partitionings of the triangular lattice and disordered jammed packings
- Idea: Start with a monodisperse disk crystal and choose which particles will be large, and which small—grow the first and shrink the latter till the aspect ratio is 1.4
- Starting with more clustered initial configurations will generate denser final packings!
- Ultimate tradeoff between **free volume** and **degeneracy**!
- Using specific statistical models for clustering we can calculate the degeneracy exactly or numerically (we use **Leveled Random Gaussian Fields)**

Leveled Random Gaussian Fields



Mixing Entropy vs Clustering



Can Entropy Really be Measured?

- Can disorder be measured for **finite sample**s without appealing to **ensambles** of packings?
- *Can we generalize to other systems: monodisperse spheres in 3D, 4D, etc.?*
- Can we **discretize the problem** of enumerating jammed packings? Disks are special because jammed monodisperse configurations are (poly)crystalline!
- Blind attempt at monodisperse spheres: Filling **octahedral holes** ($p = 0.05$, $p = 0.65$, $p = 0.95$)

Conclusions

- There is no reproducible metastable mono sphere liquid above $\phi \approx 0.55$, so talking about a **metastable liquid EOS is not justified**
- Monodisperse disks do not show any glassy behavior and freeze in a nearly continuous manner
- Bidisperse disks show a pronounced dynamical slowdown near $\phi \approx 0.80$, and no known algorithm can equilibriate above that density
- All measurements of s_c to date have been done on bidisperse systems and are close to s_{mix} close to the glass transition

Contd.

- We have constructed by an explicit model an **exponential** number of amorphous jammed packings as dense as the crystal
- Extrapolating $s_c(\phi)$ to zero is unjustified: It crosses zero only for a phase-separated crystal
- There is no (thermodynamic) ideal glass transition (in the sense proposed so far) for binary disk mixtures
- We expect this result to apply to all other models, and in particular bidisperse spheres
- Similarly for monodisperse packings: **The old RCP concept assumed that there is some magical most disordered jammed packing**, but there is none: *You can trade partial ordering (clustering into small crystals) for density, and still have a positive configurational entropy*!