Geometrical Frustration: Hard Spheres vs Cylinders

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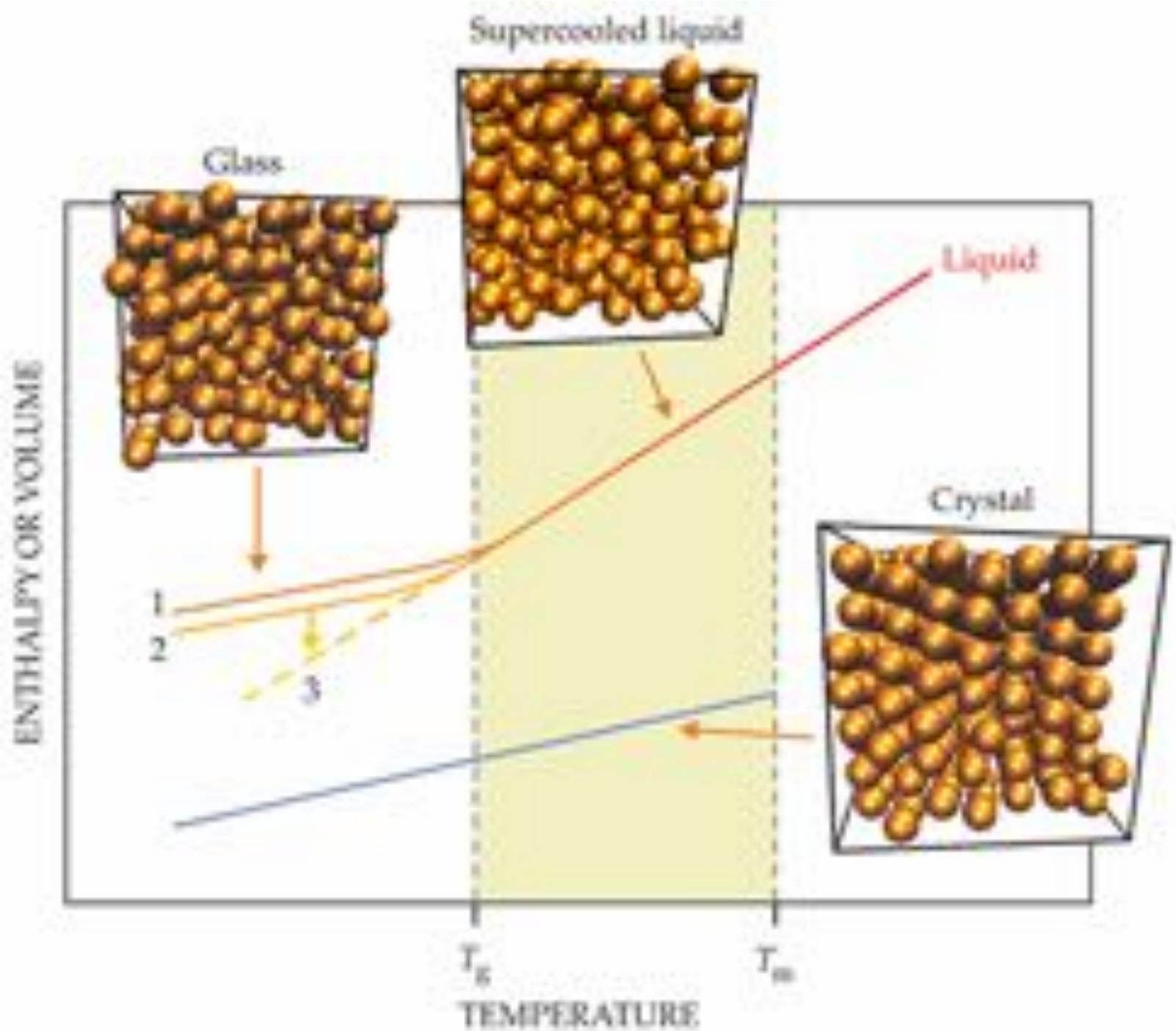
Prologue: (First) Glass Problem

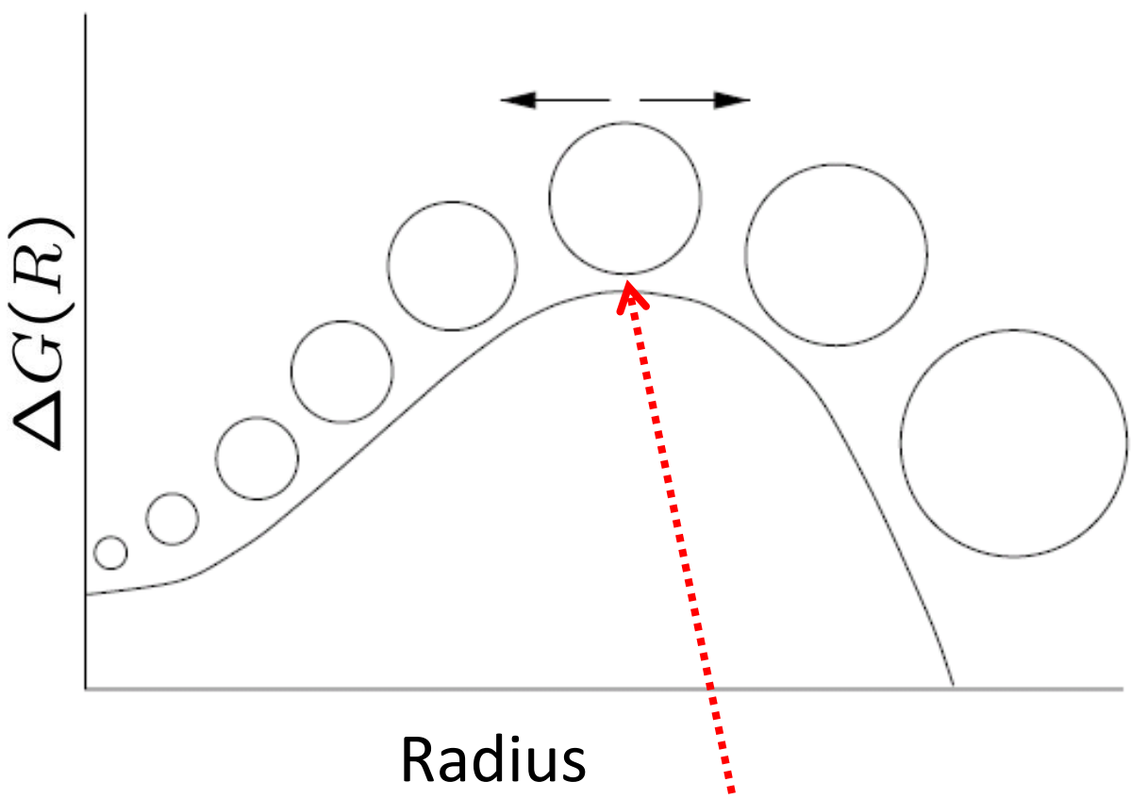



Credit: Patrick Charbonneau, 2012

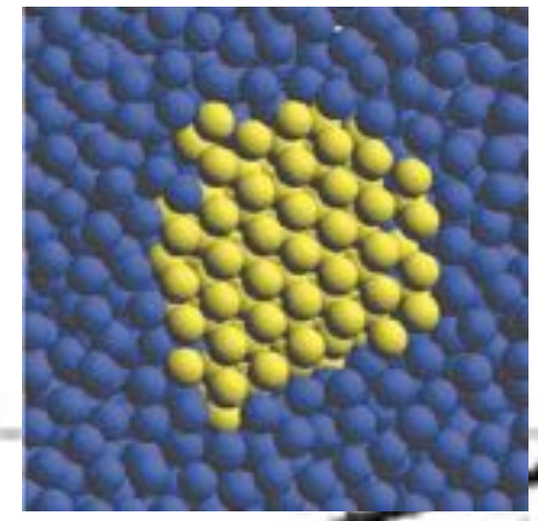
Berthier and Ediger, Physics Today (2016)

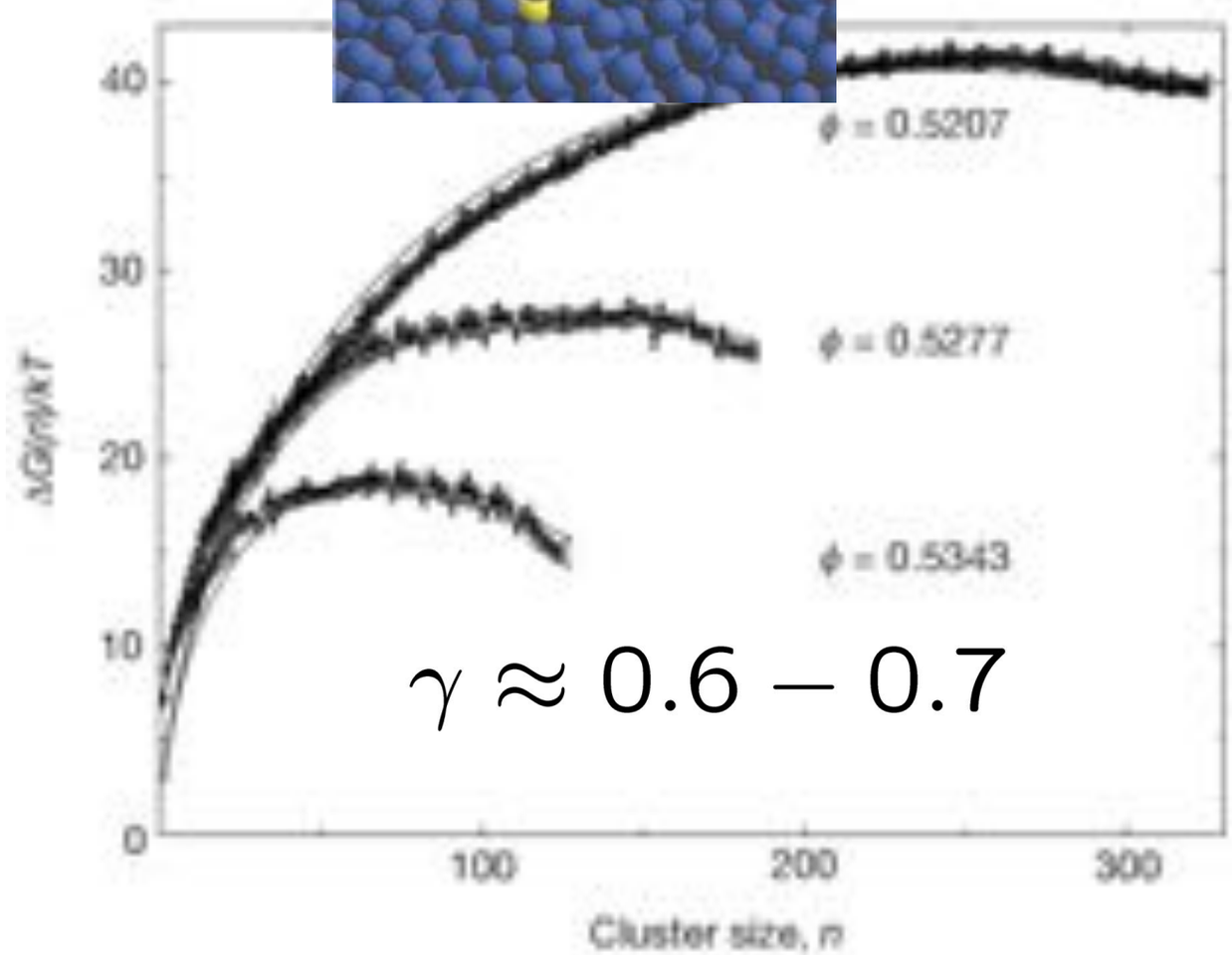
Crystal Nucleation

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



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





$$\gamma \approx 0.6 - 0.7$$

Auer and Frenkel, Nature (2002)

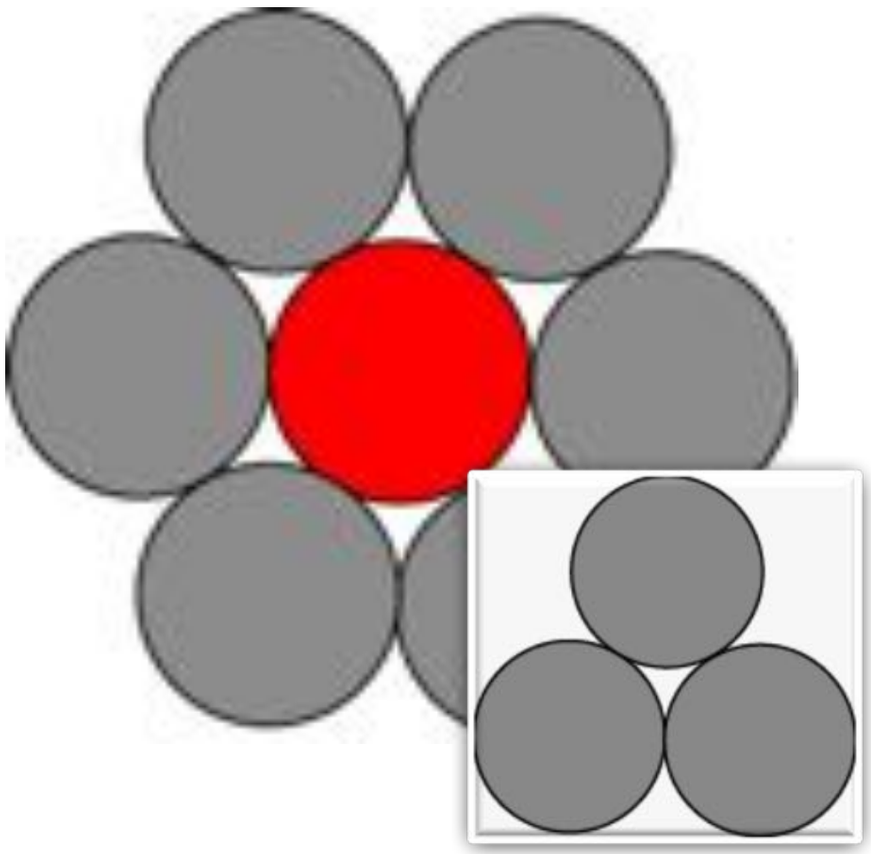
Frank: Grandfather of Geometrical Frustration

The theoretical argument is misleading also. Consider the question: 'In how many different ways can one put twelve billiard balls in simultaneous contact with one, counting as different the arrangements which cannot be transformed into each other without breaking contact with the centre ball?' The answer is *three*. Two which come to the mind of any crystallographer occur in the face-centred cubic and hexagonal close-packed lattices. The third comes to the mind of any good schoolboy, and is to put one at the centre of each face of a regular dodecahedron. That body has five-fold axes, which are abhorrent to crystal symmetry: unlike the other two packings, this one cannot be continuously extended in three dimensions. You will find that the outer twelve in this packing do not touch each

the lattice energy per atom in the crystal. I infer that this will be a very common grouping in liquids, that most of the groups of twelve atoms around one will be in this form, that freezing involves a substantial rearrangement, and not merely an

Frank, Proc. Roy. Soc. A (1952)

Geometrical Frustration

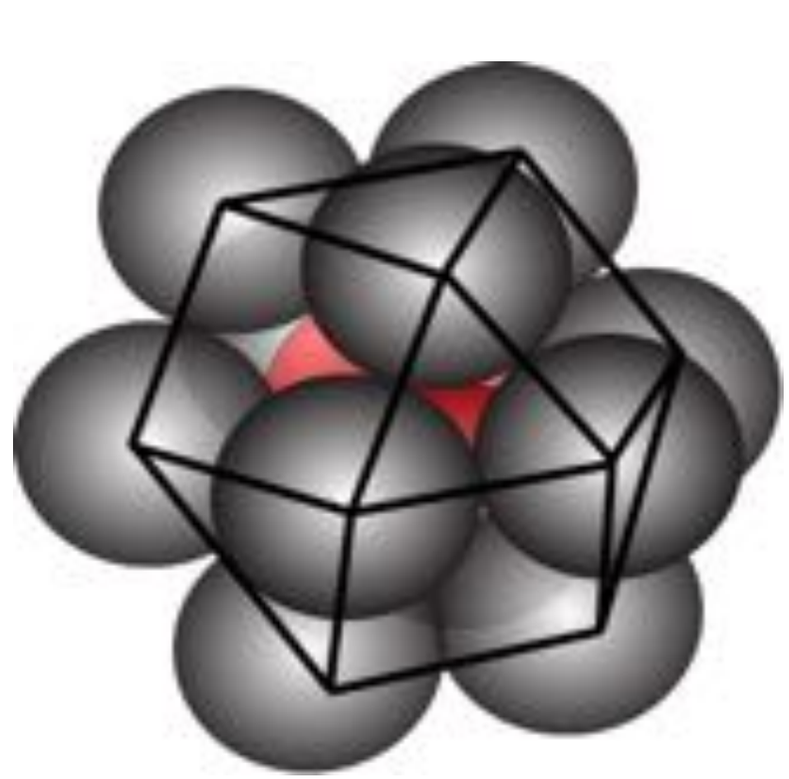


Triangular Lattice

AND

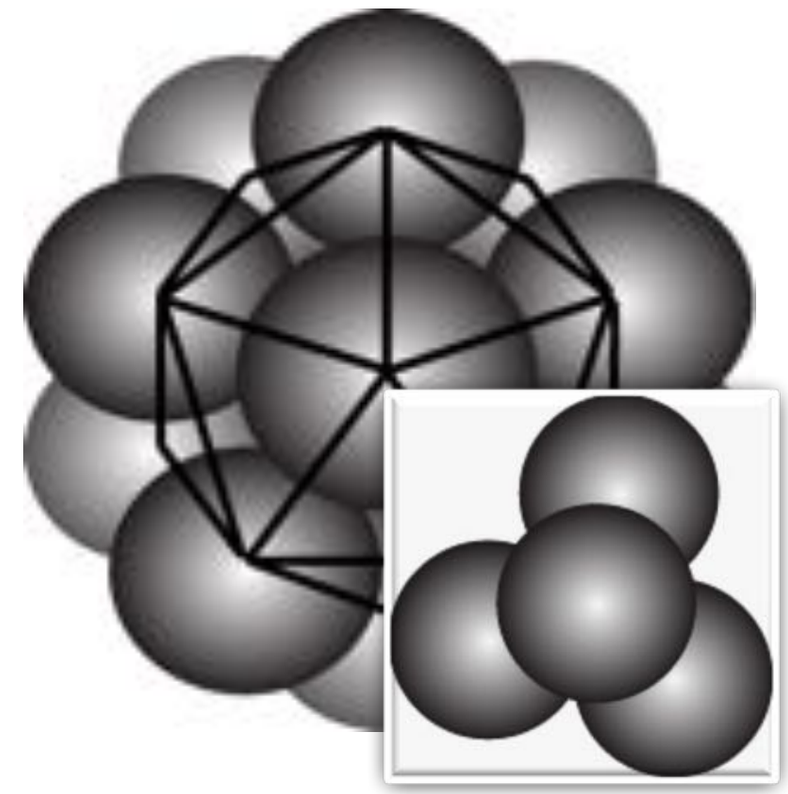
2-Simplex

(triangle)



FCC Lattice

vs.



Icosahedron

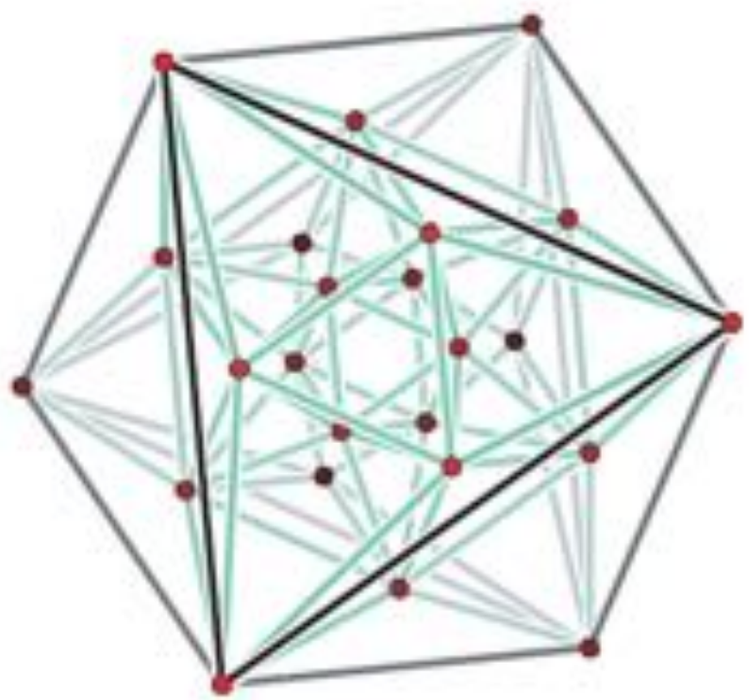
~AND

3-Simplex

(tetrahedron)

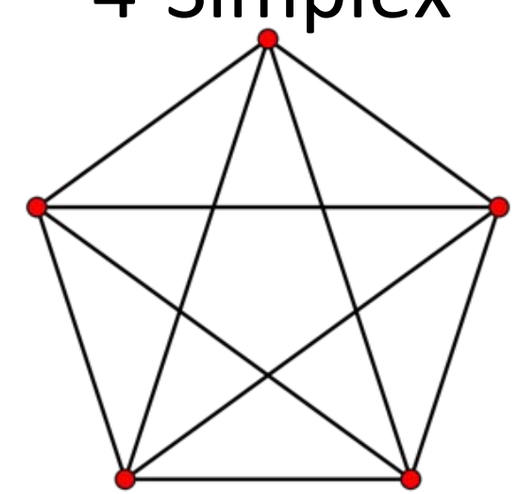
Geometrical Frustration in 4D

The 24-cell (uniquely) comes to the mind
of any good schoolchild!



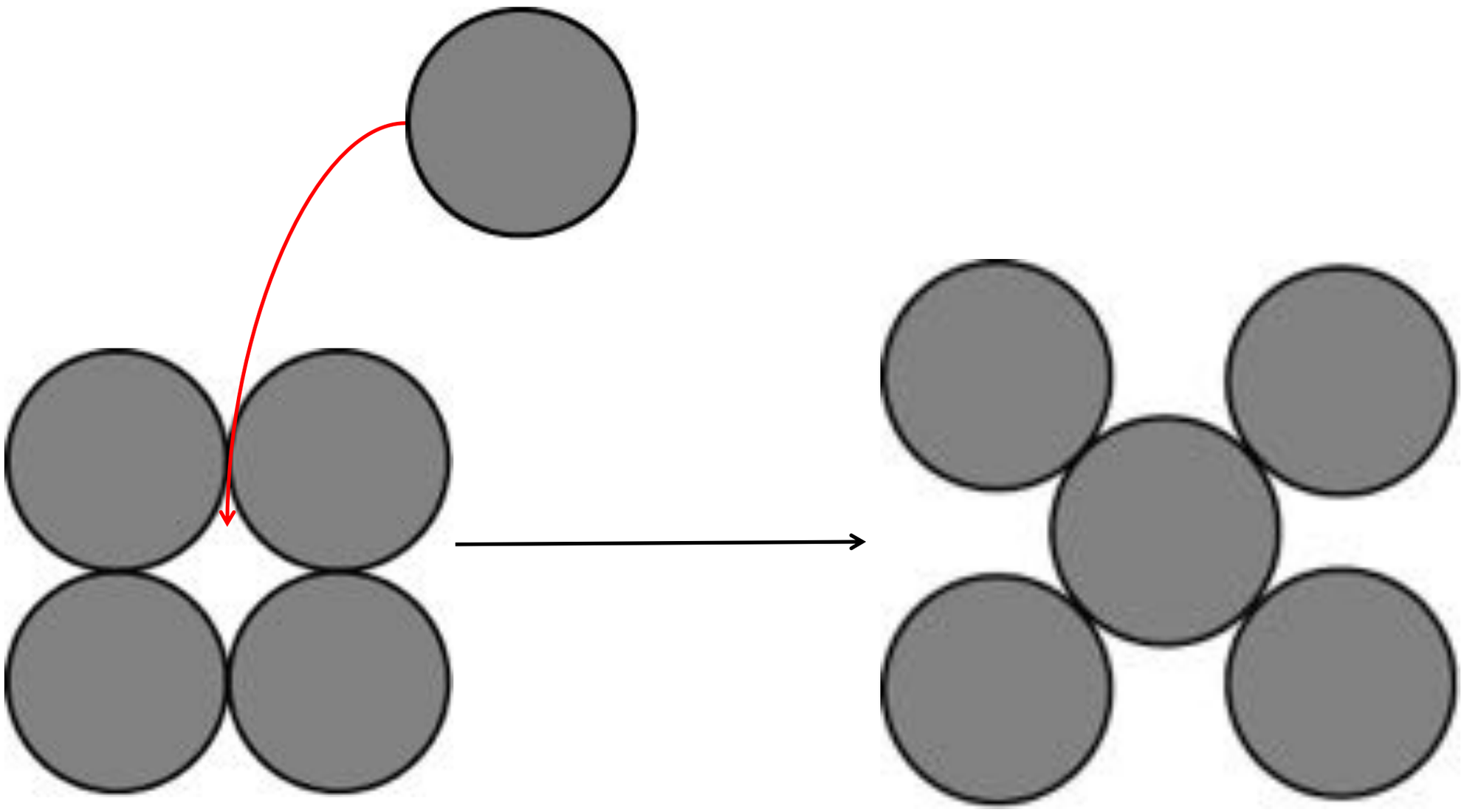
D_4 Lattice
IS NOT
Simplex Based

4-Simplex



Musin (2004); Pfender and Ziegler, Notices AMS (2004)

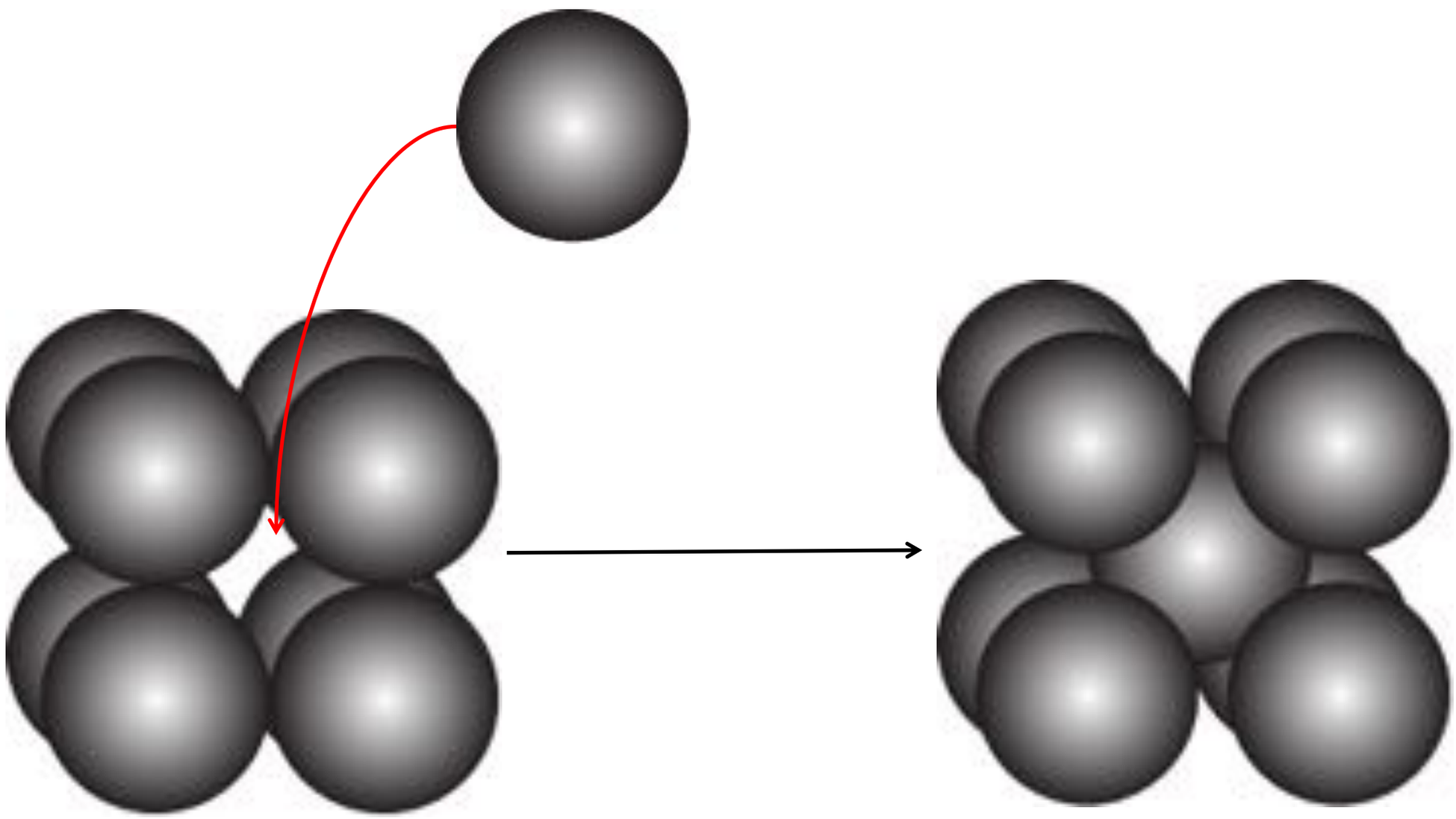
2D Packing



Simple Square

Rotated Simple Square

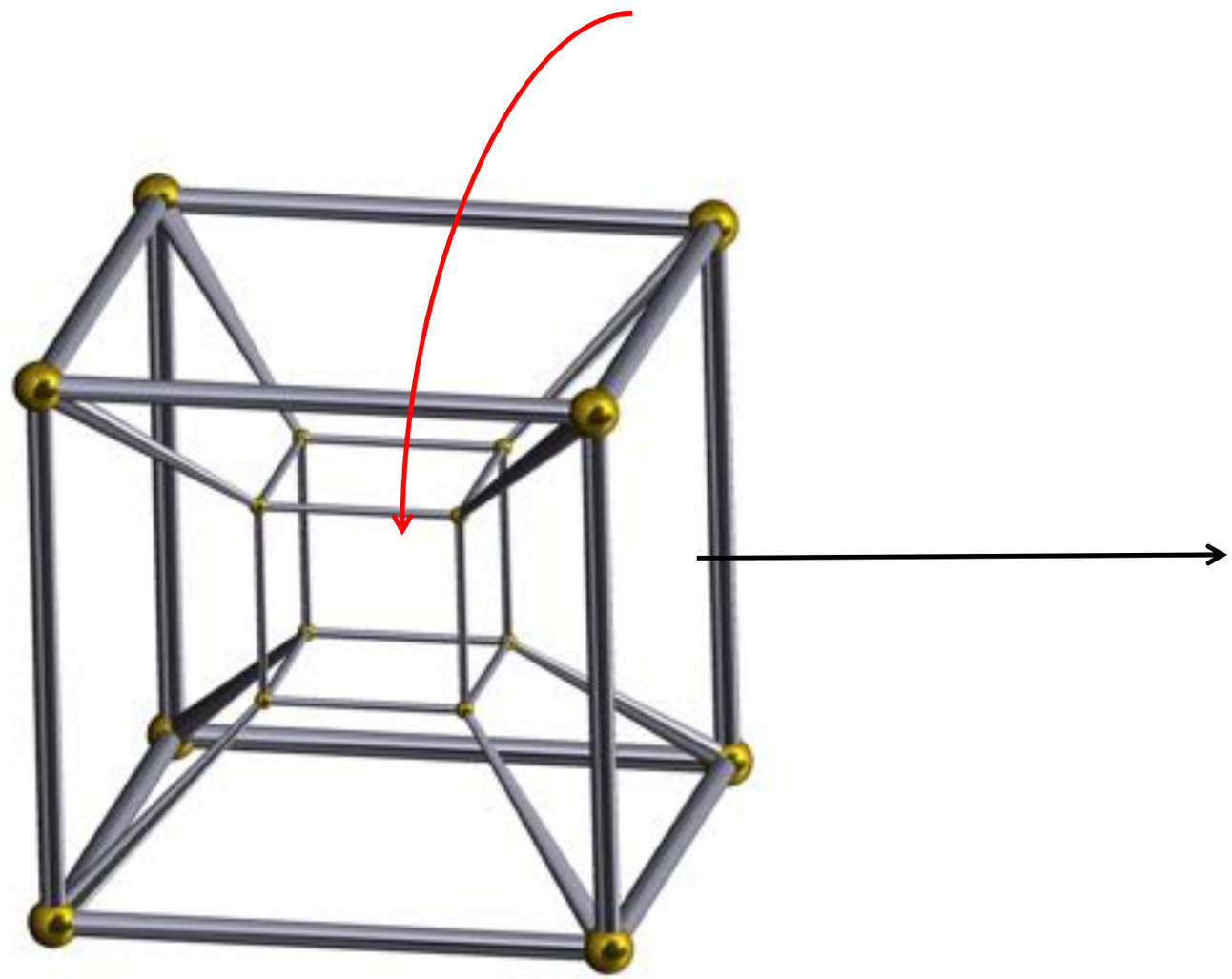
3D Packing



Simple Cubic

Body-Centered Cubic

4D Packing

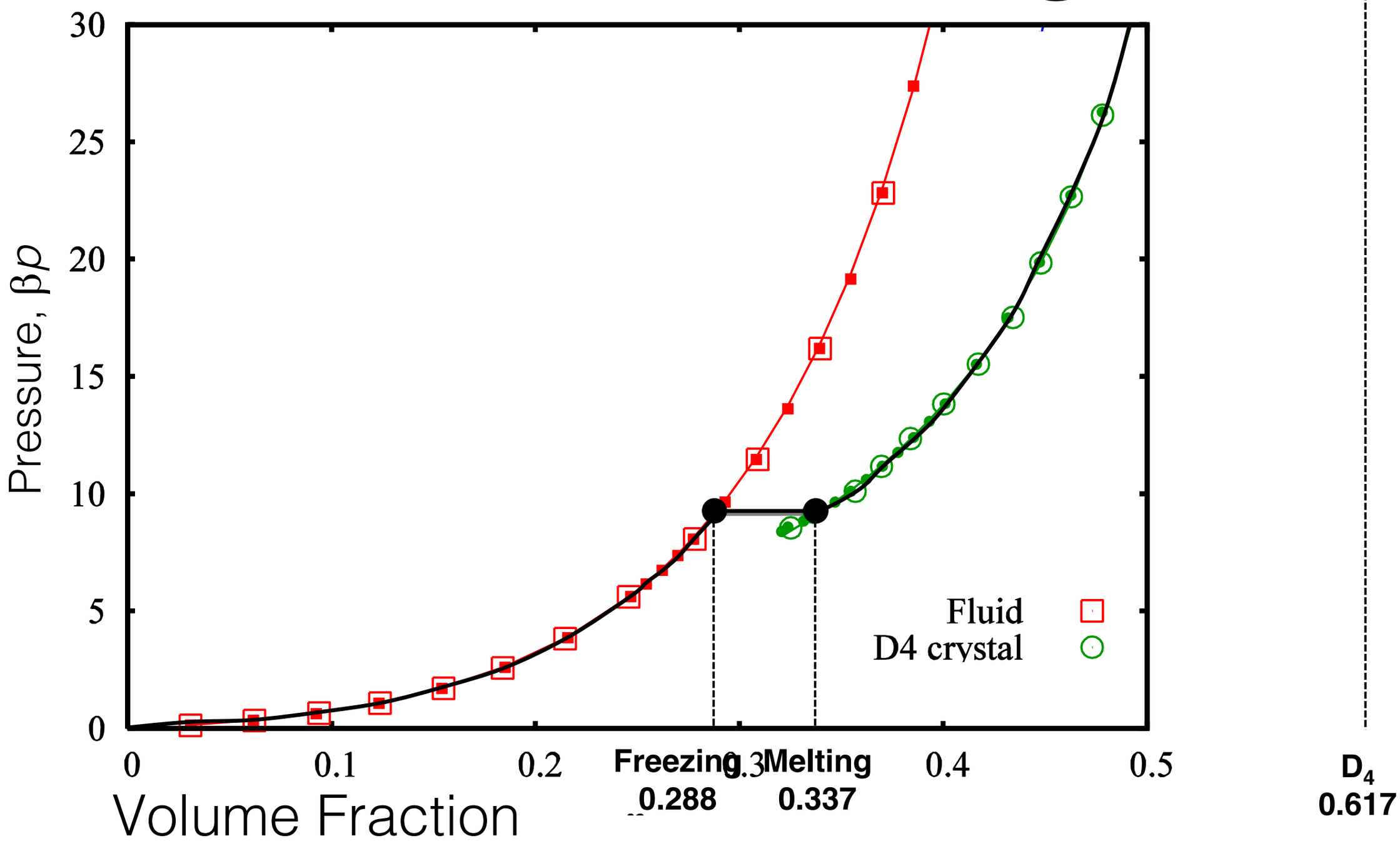


(1/2, 1/2, 1/2, 1/2)

Simple Hypercubic

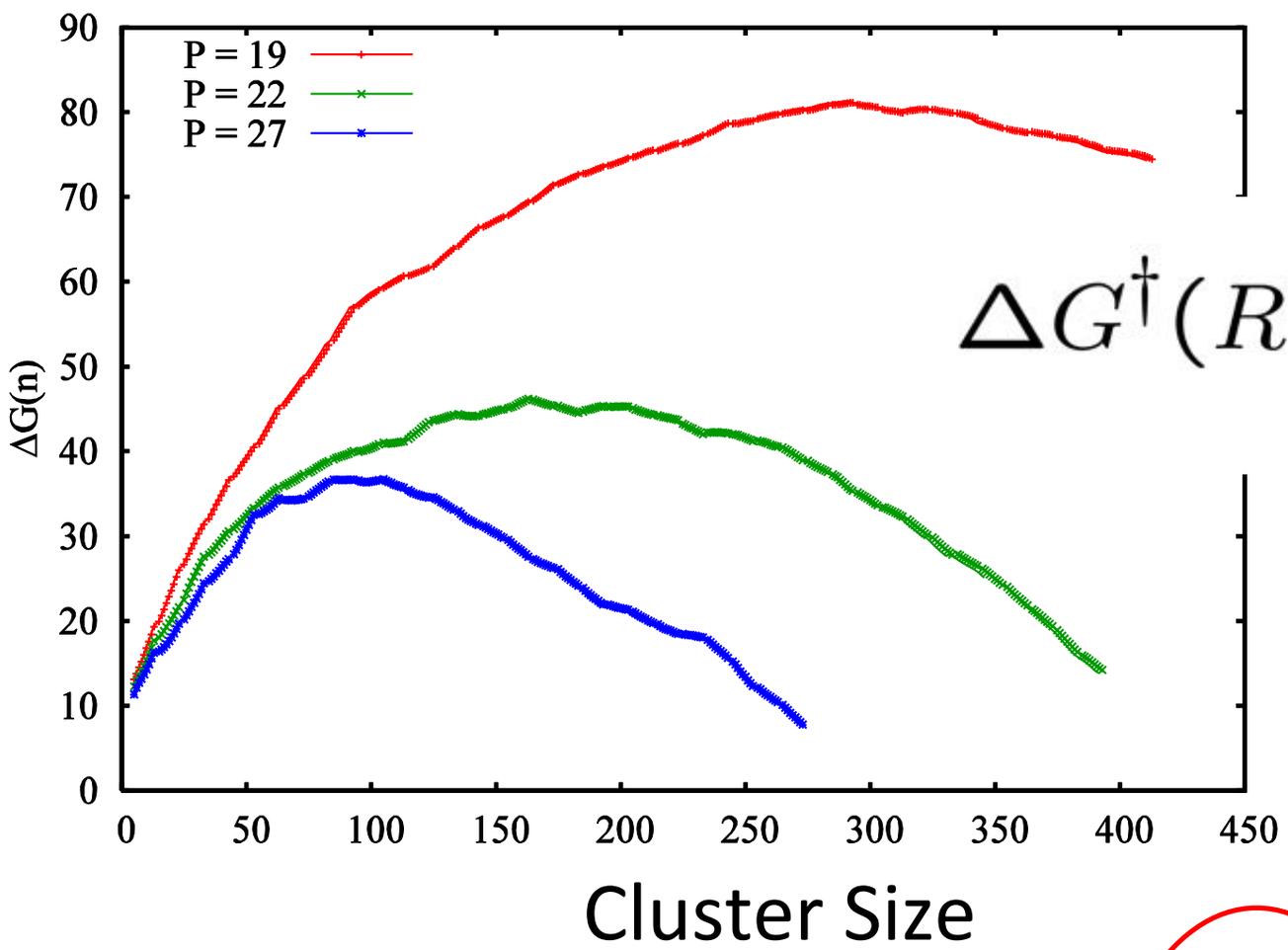
D4

4D HS Phase Diagram



van Meel, Frenkel, Charbonneau, PRE (2009)

Nucleation Barrier



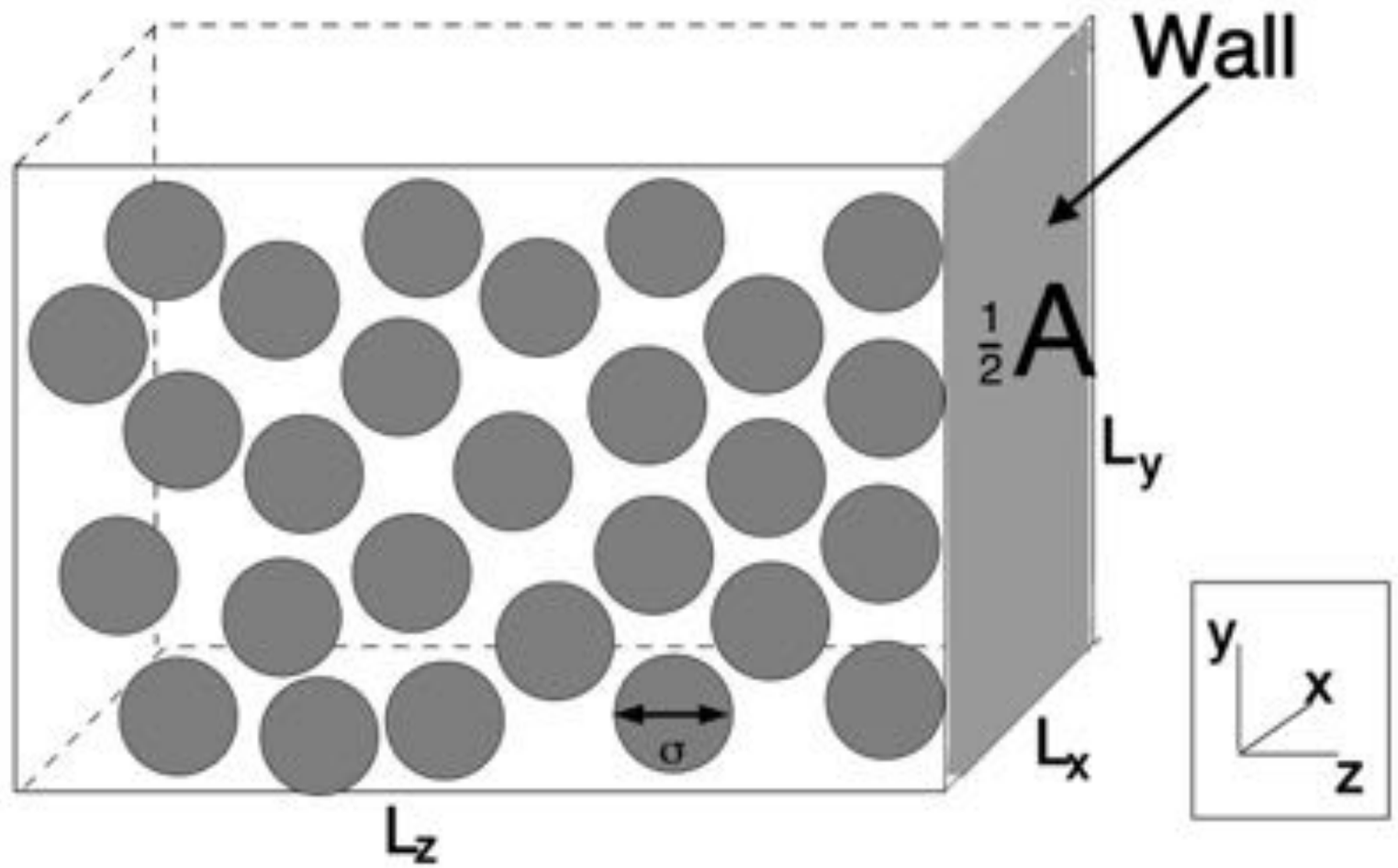
$$\Delta G^{\dagger}(R^*) = \frac{27\pi^2\gamma^4}{2\rho_{D_4}^3\Delta\mu^3}$$

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

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

van Meel, Frenkel, Charbonneau, PRE (2009)

How frustrated is it?



At fluid-crystal coexistence density

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

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

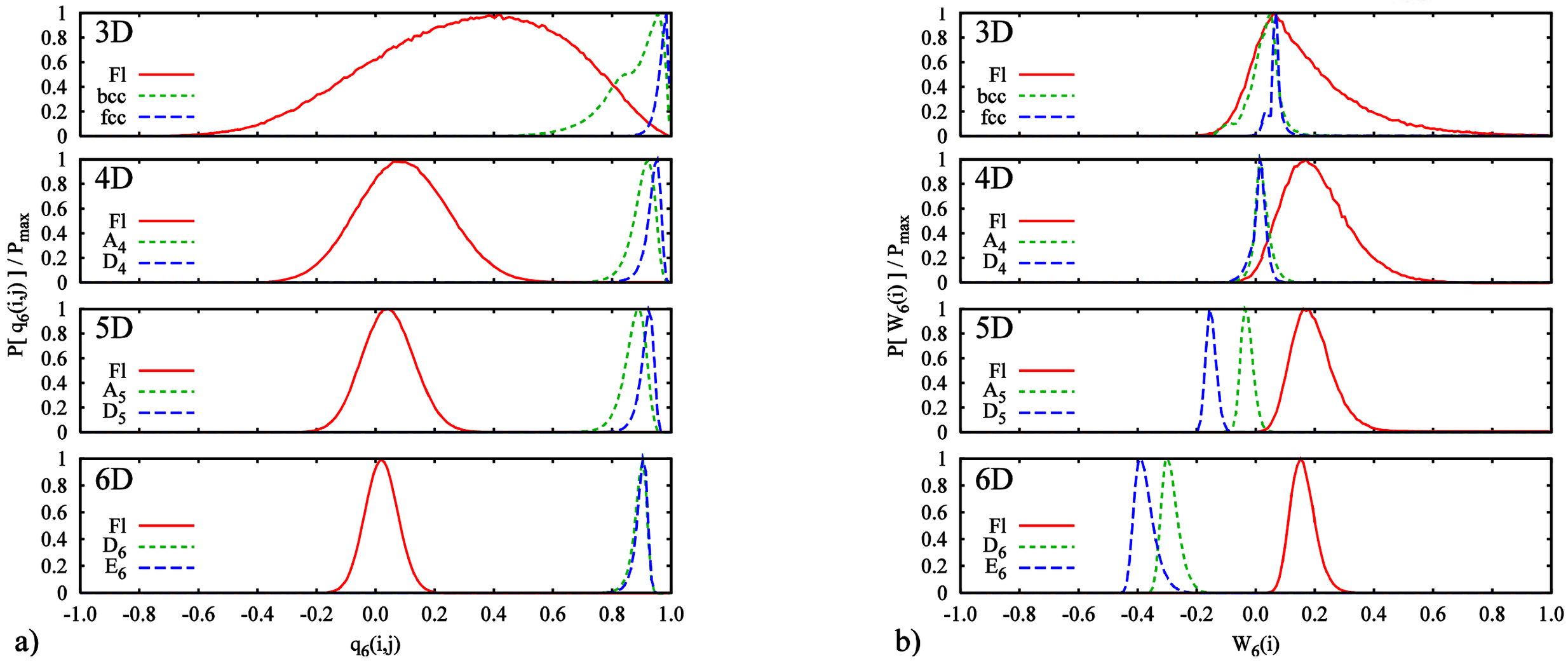
Laird and Davidchack, J. Phys. Chem. C (2007)
van Meel, Charbonneau, Fortini, Charbonneau, PRE (2009)

Geometrical Explanation

Bond-order parameters *à la* Steinhardt-Nelson

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

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



Liquid/crystal resemblance vanishes with dimension.

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

Conclusion of Prologue

2D is not frustrated.

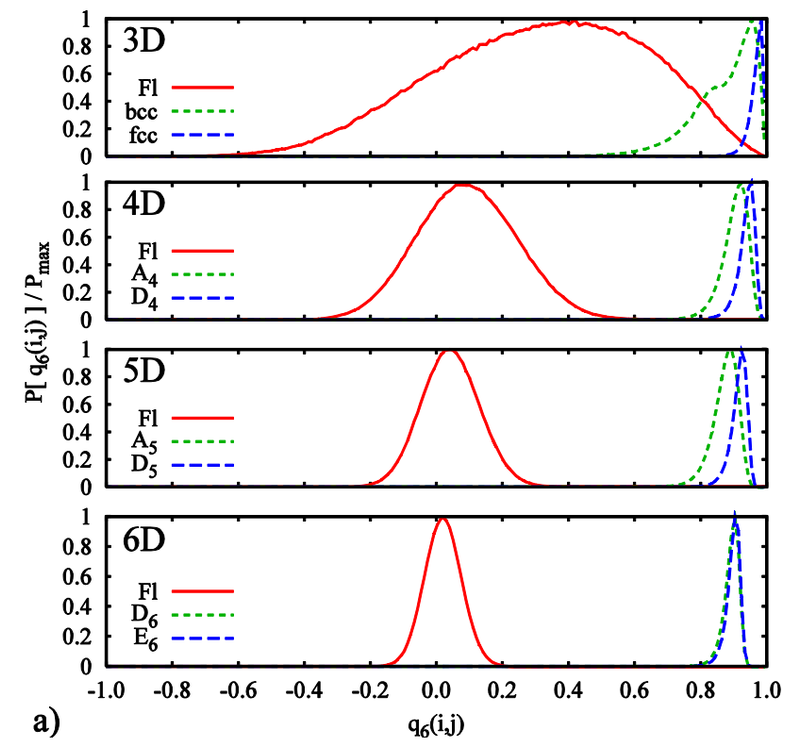
- Gives rise to two-step freezing.

3D is somewhat frustrated.

- Monodisperse HS freeze rather easily.
- But icosahedral order is not singular.

4D is truly frustrated.

- Optimally packed *cluster* matters little.
- “Polytetrahedral” frustration dominates.



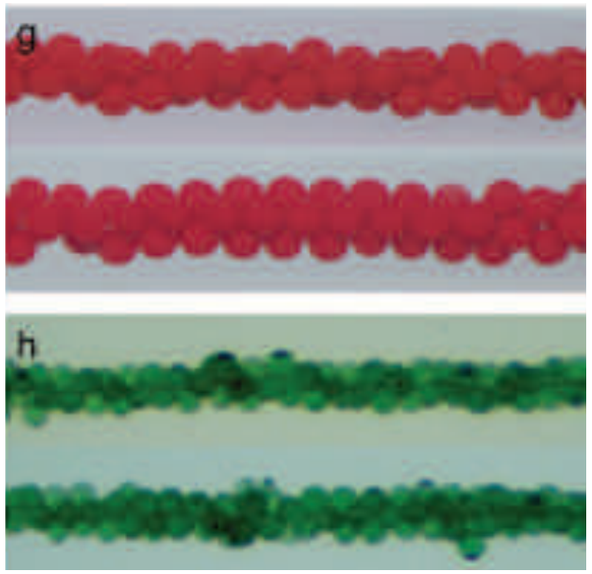
High-dimensional liquids form glasses easily.

- =>“Cracking the Glass Problem”

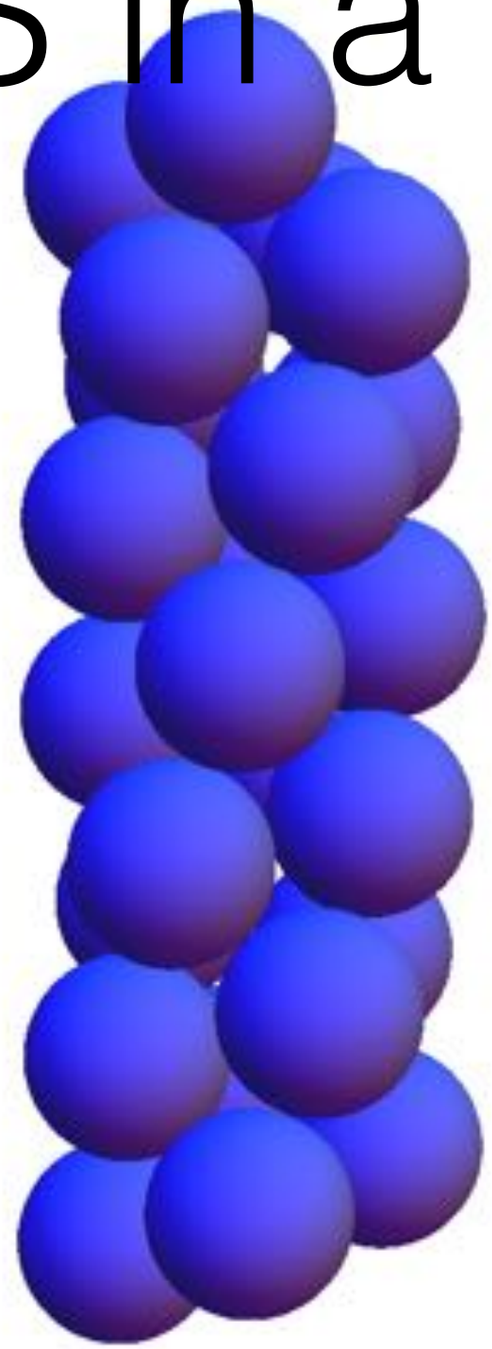
SIMONS FOUNDATION

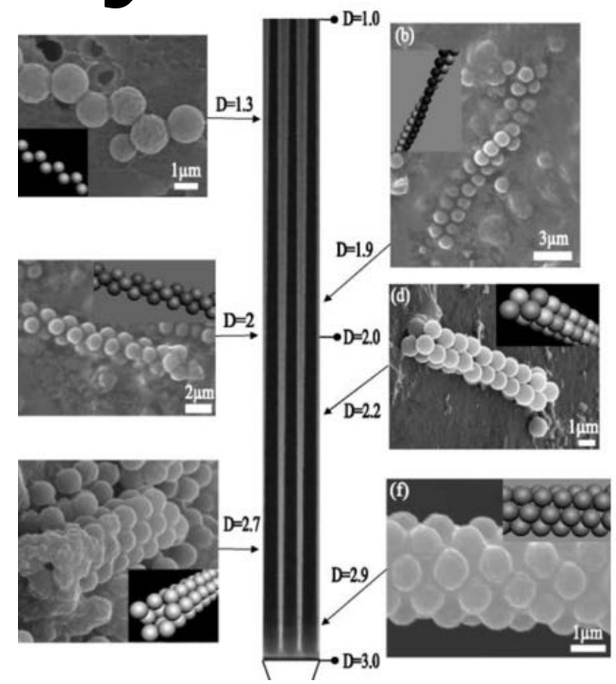
What about simplexes in other contexts?

Intro: HS in a cylinder

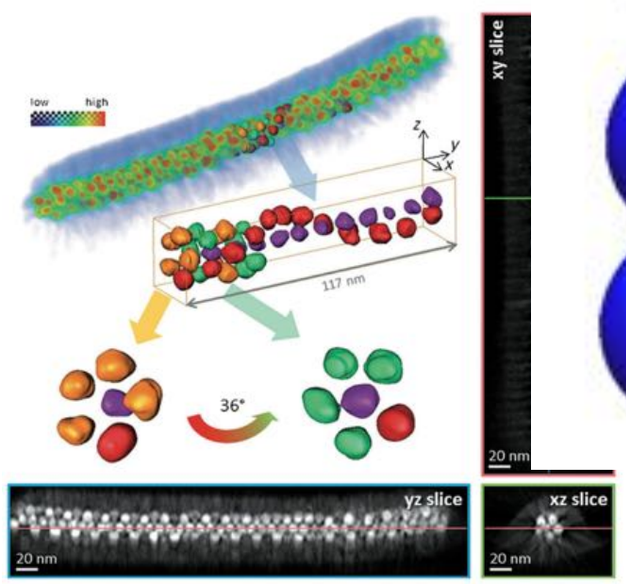


Floating particles in a rotating
Lee *et al.*, Adv. Mater. 20

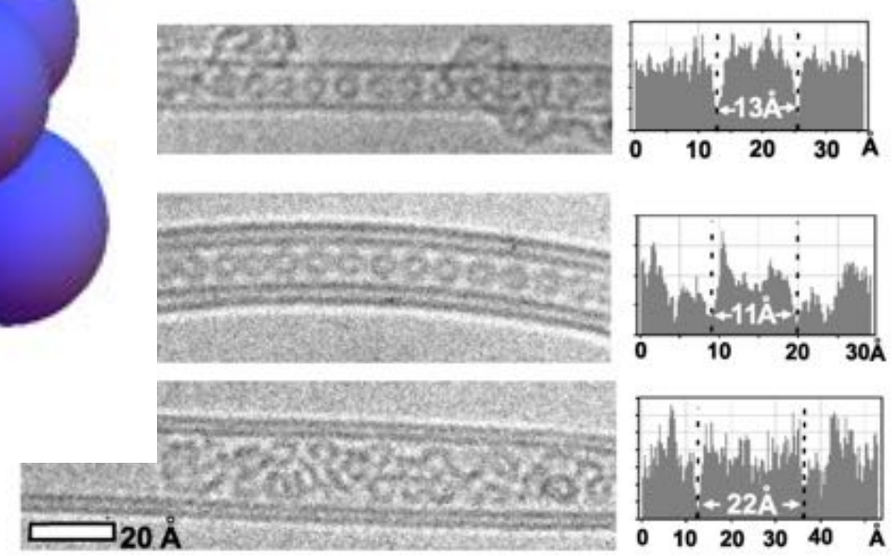




ene spheres in silicon membrane pores
ymczenko *et al.*, Adv. Mater. 2008

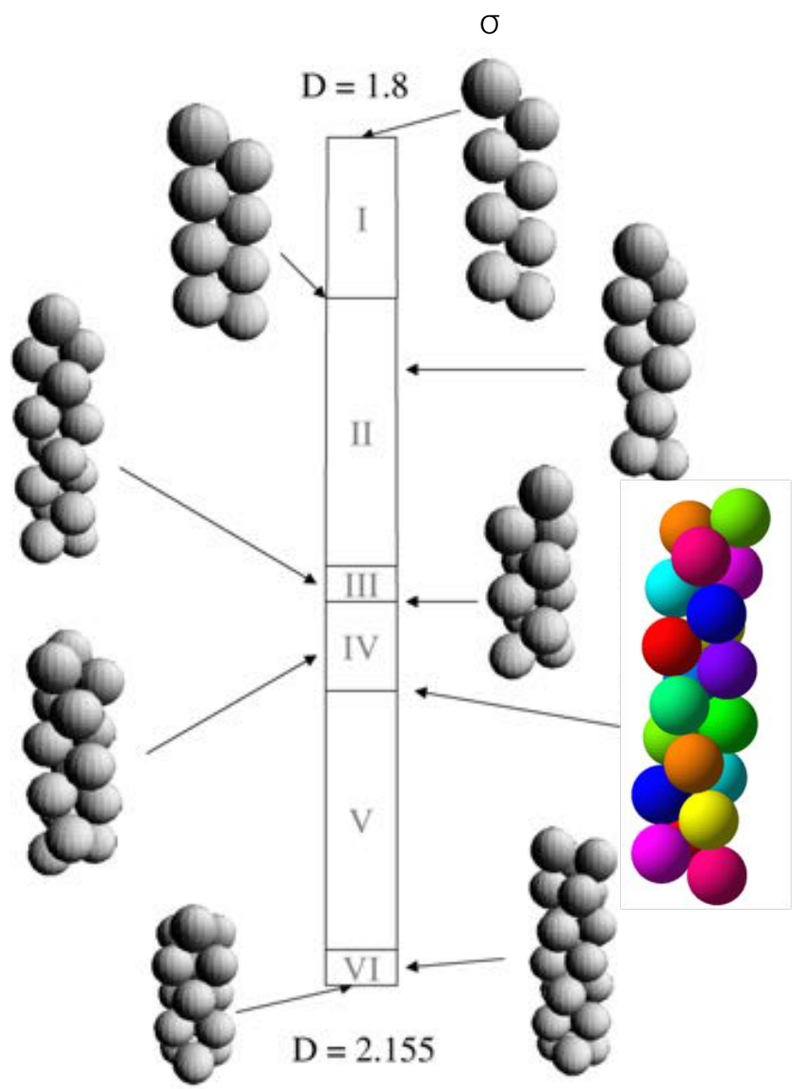


Nanoparticles in diblock copolymer cylinders
Sanwaria *et al.*, Angew. Chem. 2014

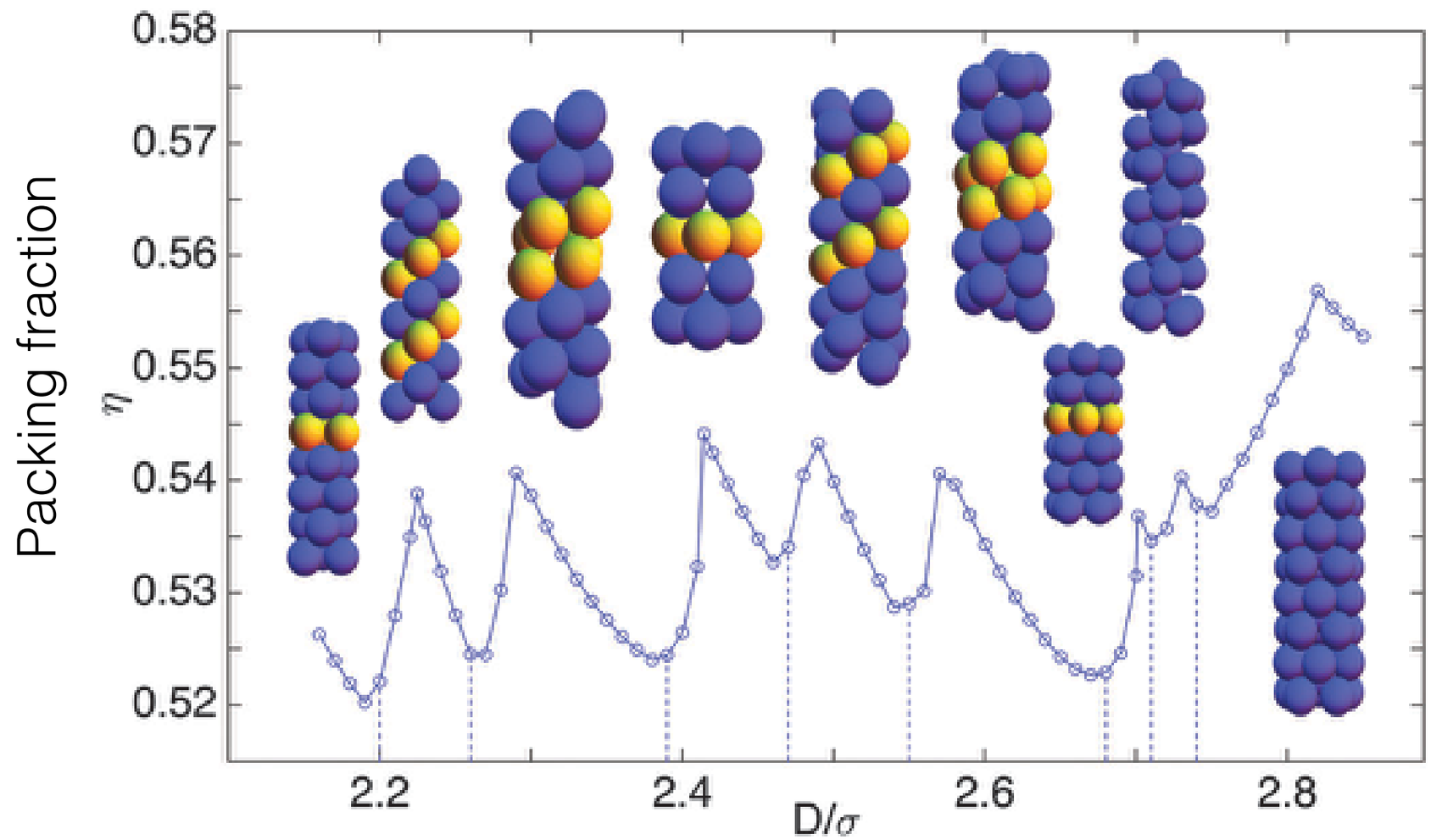


Fullerenes in carbon nanotubes
Briggs *et al.*, PRL, 2004

Earlier Results



Pickett *et al.*, PRL, 2000



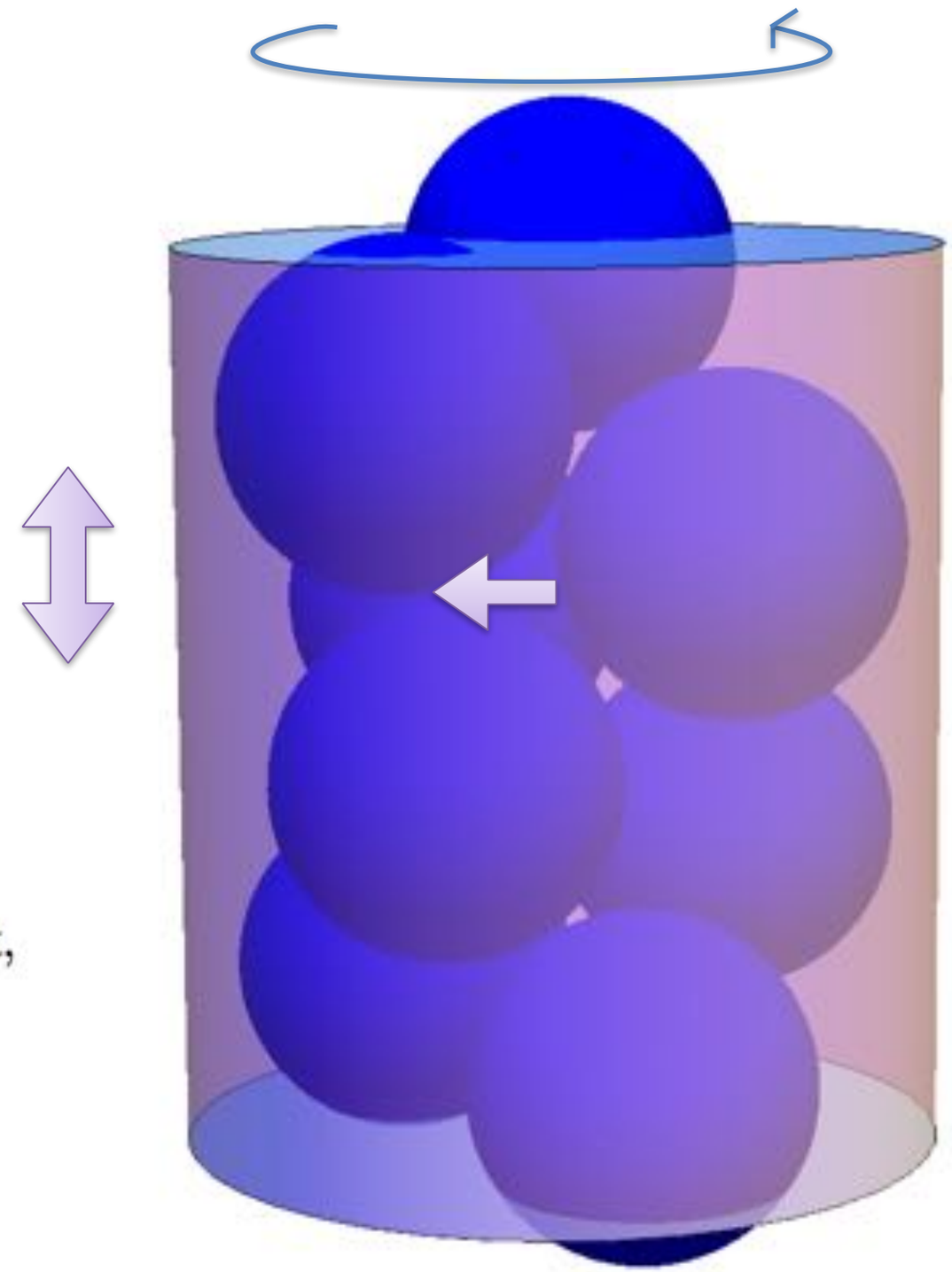
Mughal *et al.*, PRE, 2012

Boerdijk-Coxeter helix is present. Other fibrated ones?

Sequential Linear Programming

- Periodic cylinder with a twist

- Three types of moves:
  A. Displacement particles
  B. Change unit cell height
  C. Change boundary twist



Maximize : η

Subject to :

$$r_{mn}^{\mathrm{n}} \geq \bar{D}_{mn}, \forall \text{ neighbor pairs } (\mathrm{m} \neq \mathrm{n}) \text{ of interest,}$$

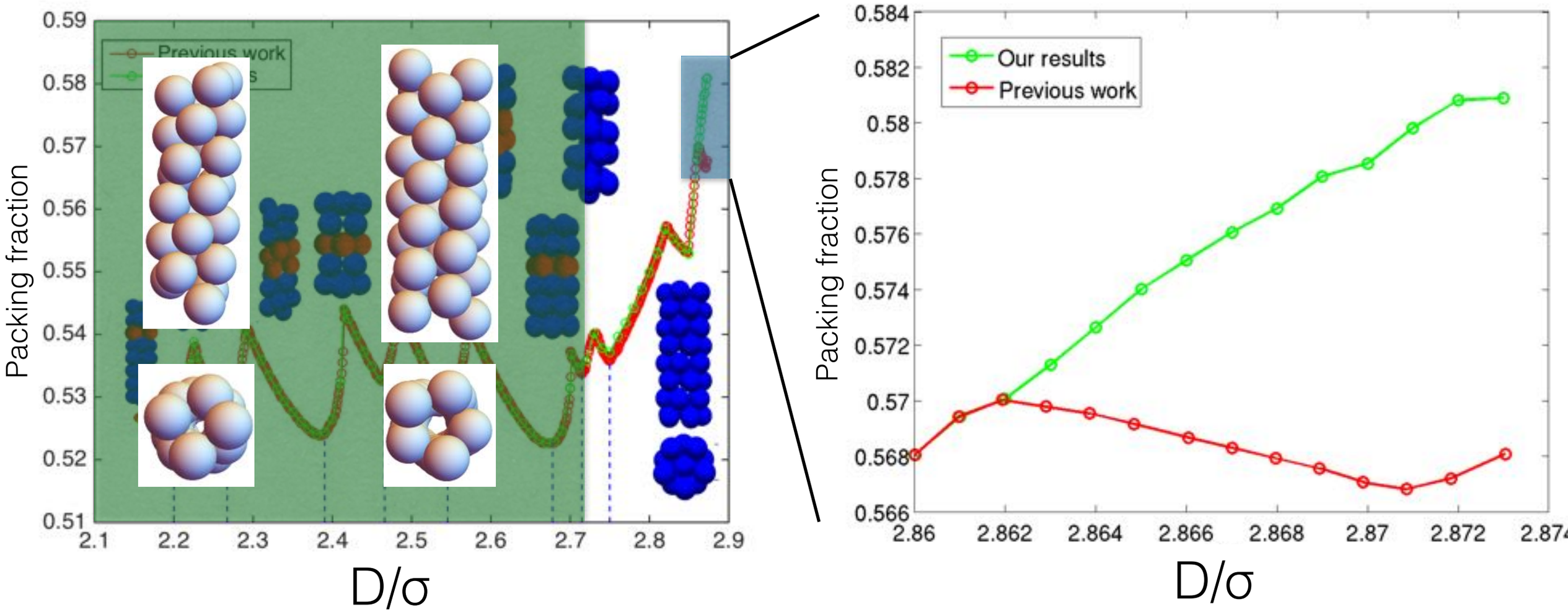
$$r_{i\mathrm{r}} + \Delta r_{\mathrm{r}} + R_i \leq R_{\mathrm{c}}, \ \forall\, i = (1,2,\ldots,N),$$

$$\Delta \boldsymbol{r}^{\mathrm{lower}} \leq \Delta \boldsymbol{r}_i \leq \Delta \boldsymbol{r}^{\mathrm{upper}}, \ \forall\, i = (1,2,\ldots,N)$$

$$\varepsilon^{\mathrm{lower}} \leq \varepsilon \leq \varepsilon^{\mathrm{upper}},$$

Torquato and Jiao, PRE, 2010

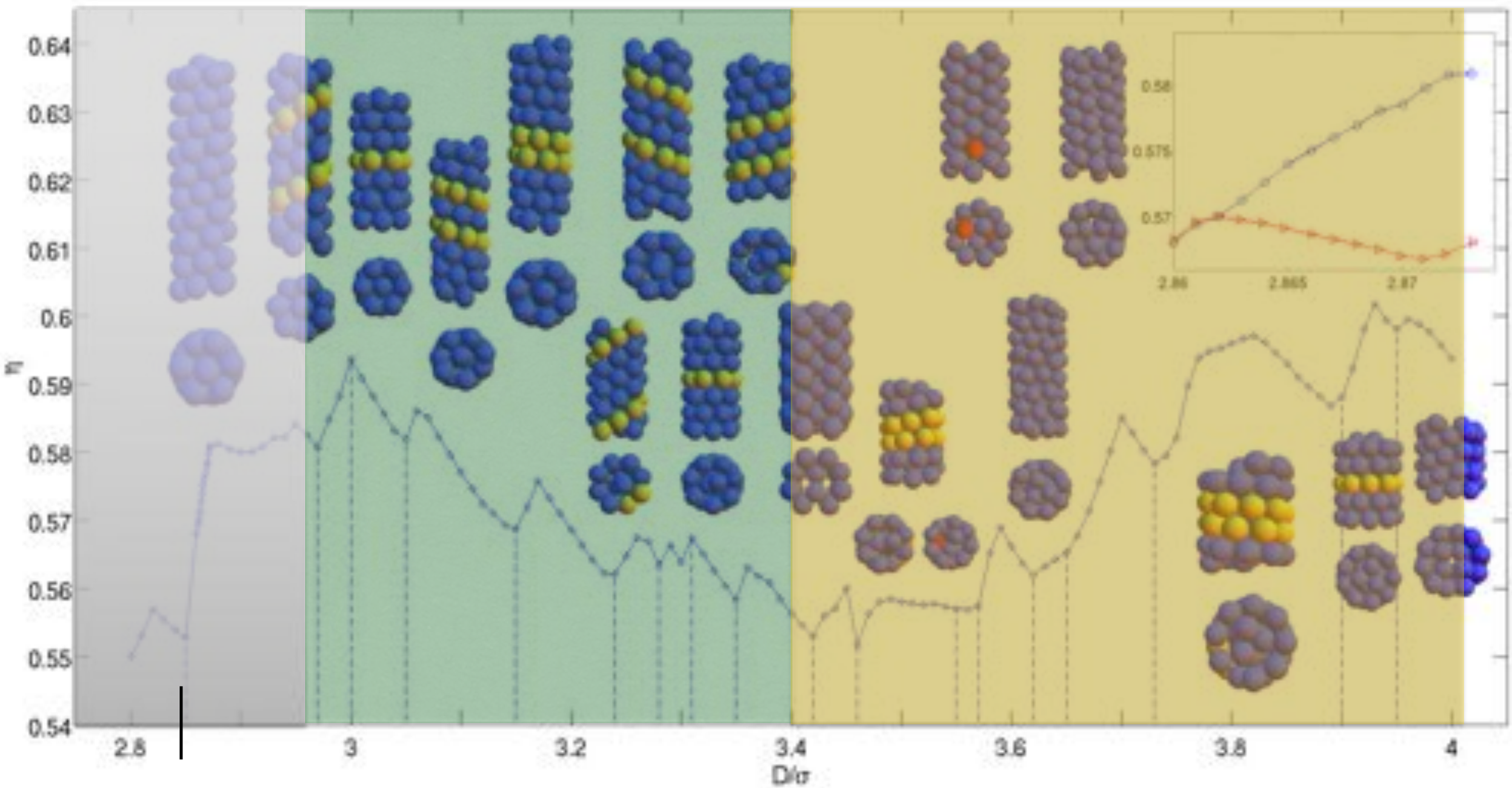
Results: Comparison



Mughal *et al.*, PRE, 2012

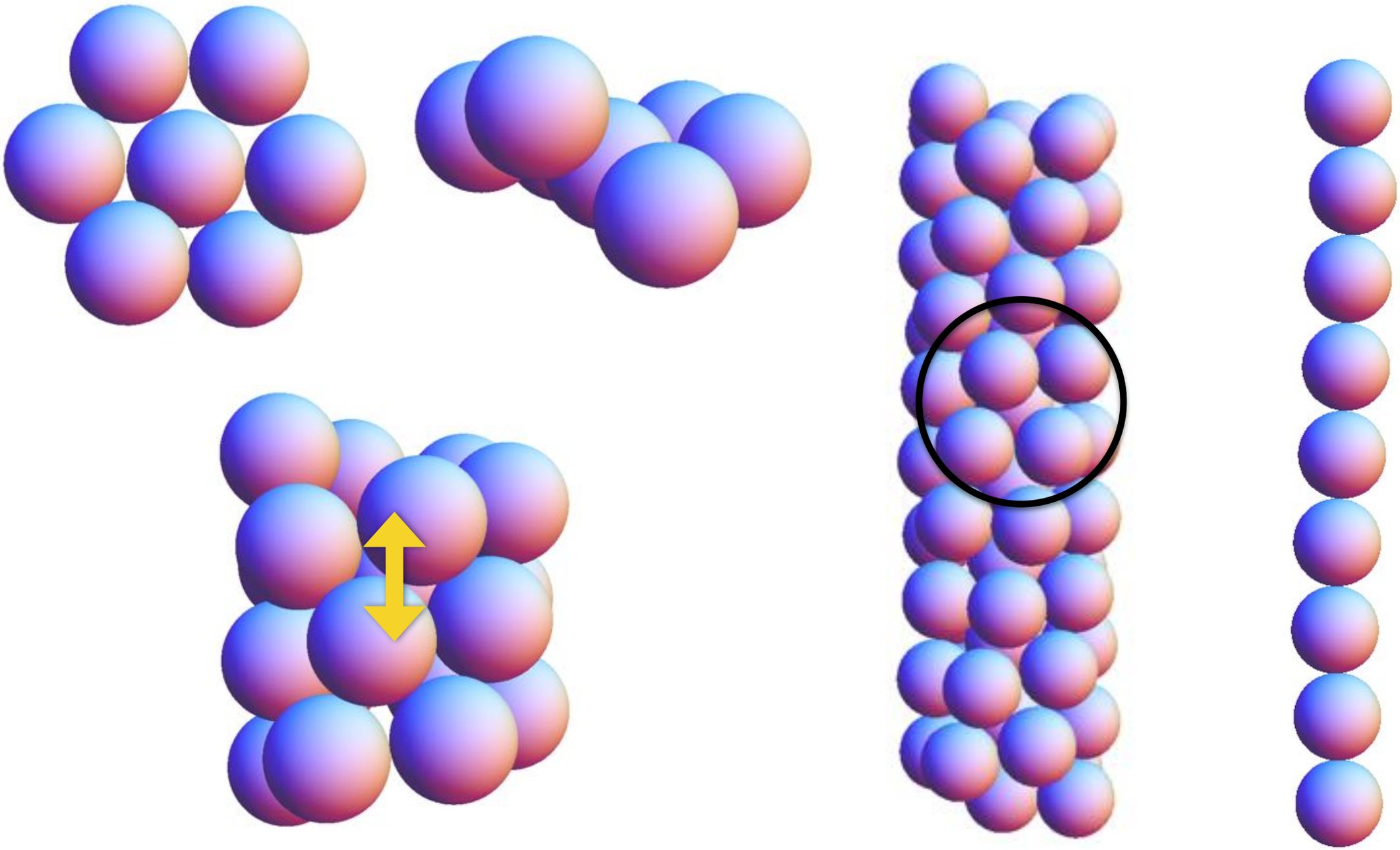
Fu, Steinhardt, Zhao, Socolar, Charbonneau, ***Soft Matter***, 2016

Results: Extension



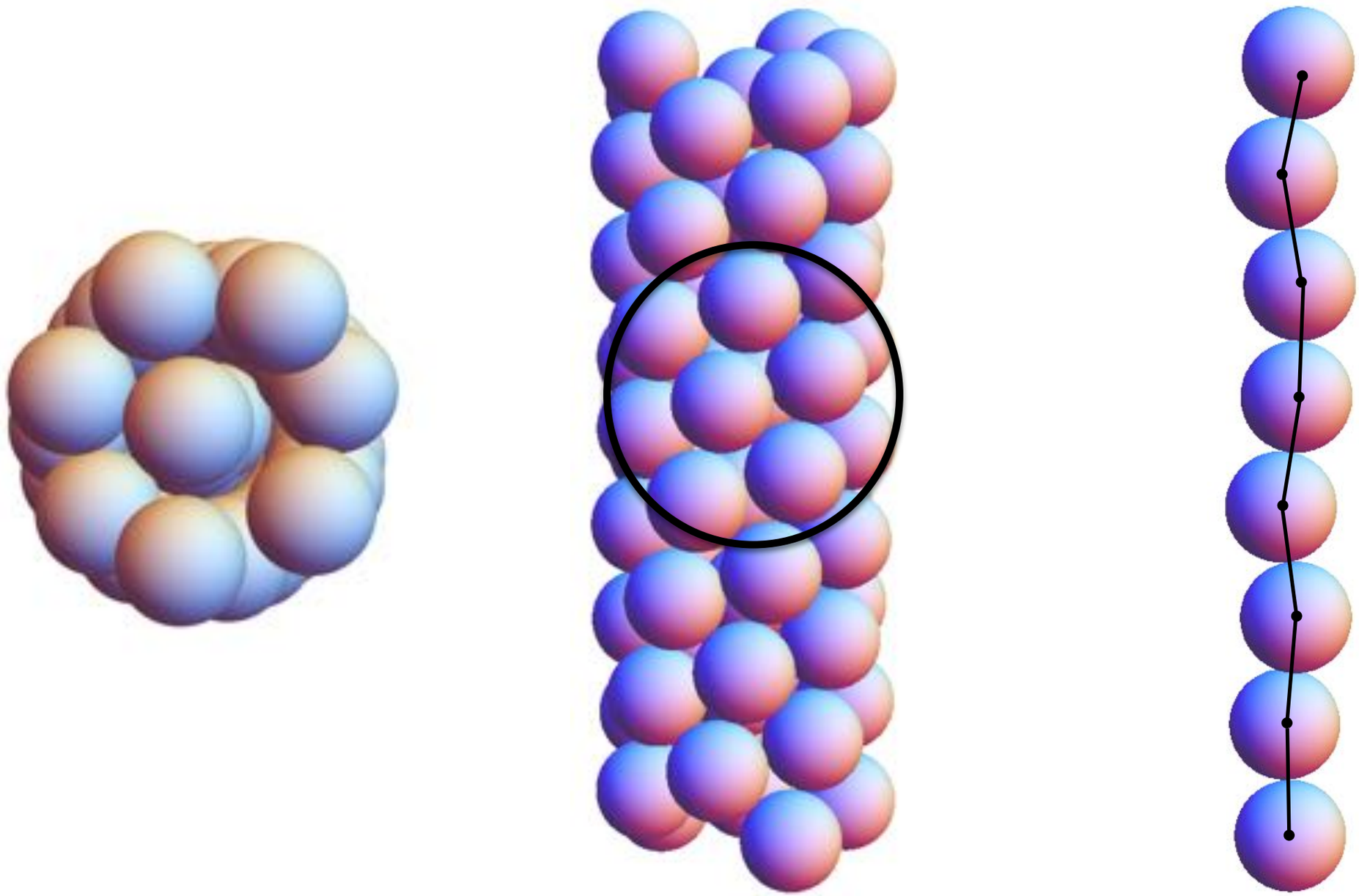
Region I Region II Region III

Region I



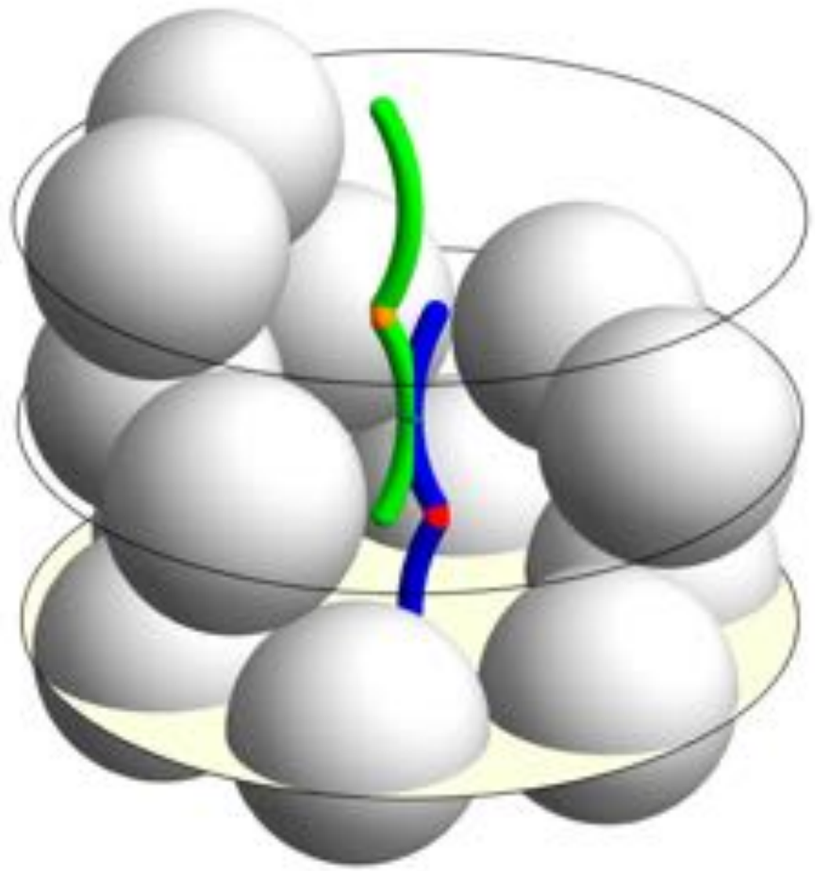
Loose outer shell (gaps between particles), and close-packed core.

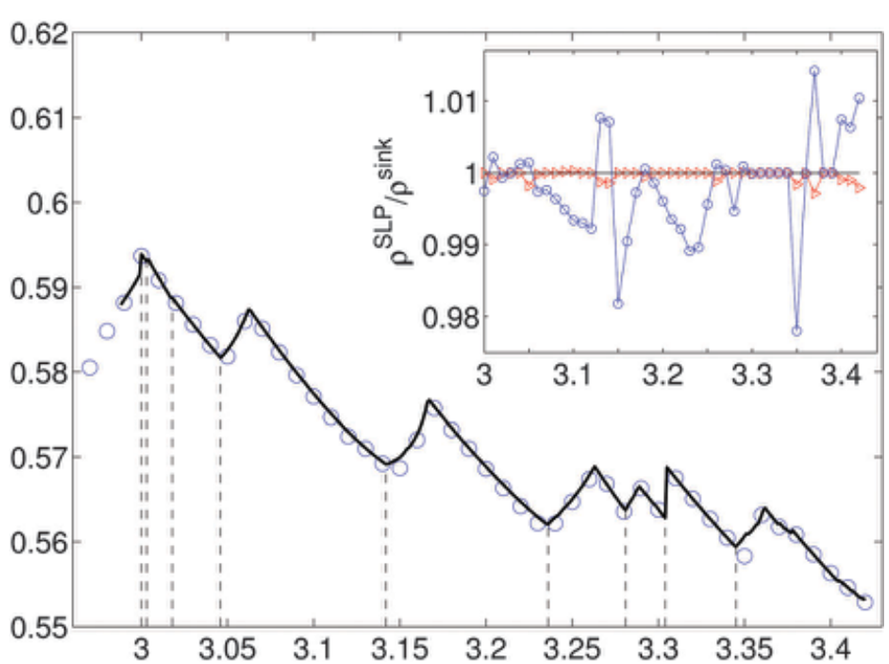
Region II



Close-packed outer shell and core, with rich interplay.

Region II

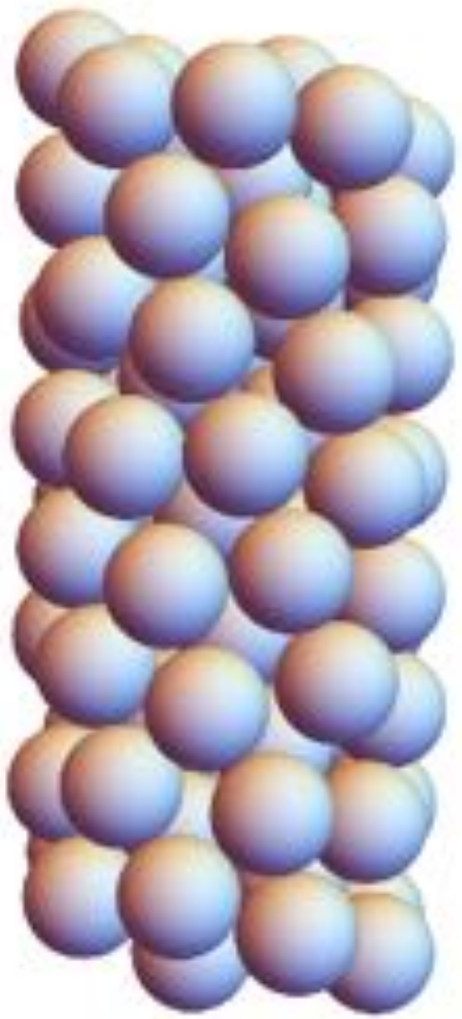


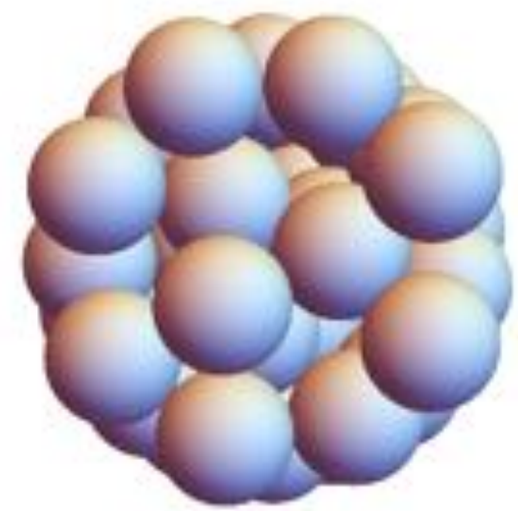


Core appears quasiperiodic.

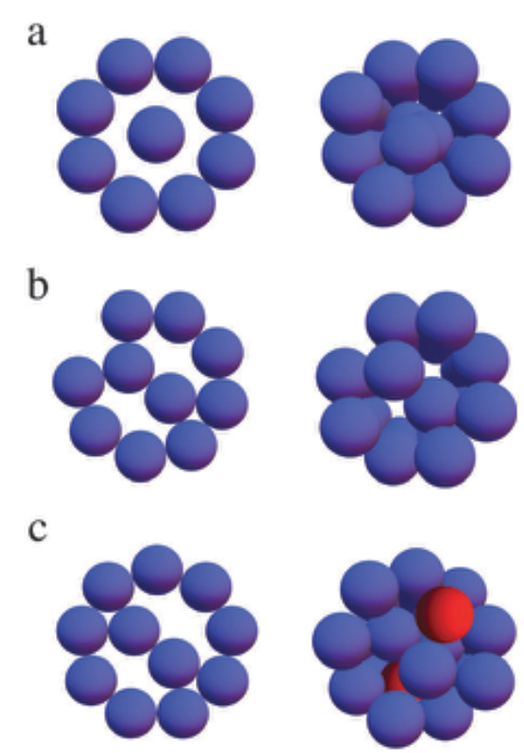
Sinking algorithm gives many quasiperiodic structures denser than LP structures.

Region III





D=3.64σ

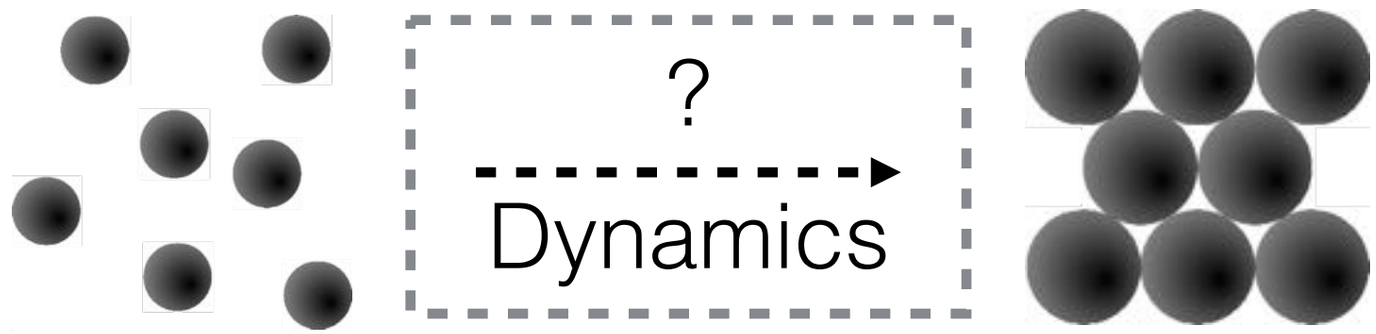


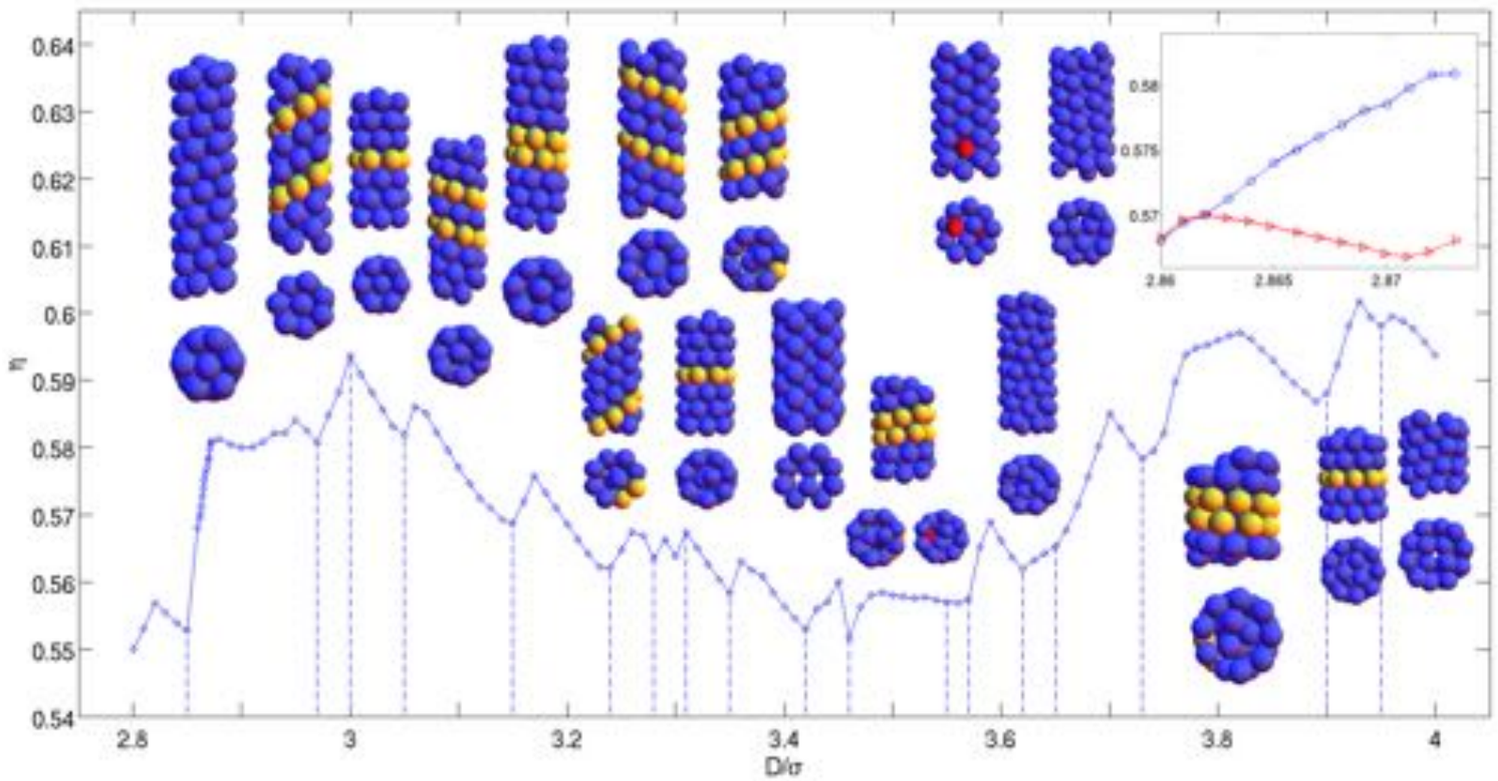
Some cross-sections are akin to packing of disks in a disk.

Summary I

- Densest packings rely on different mechanisms in different D regimes.
- Some packings might be quasiperiodic.
- Structures are likely very rich until D=10~20σ, where the system (likely) reaches the bulk limit (FCC).
- For D=2~4σ, no structure resembles fibrated ones. Frustrated 2D ordering dominates 3D (less) frustrated ordering.

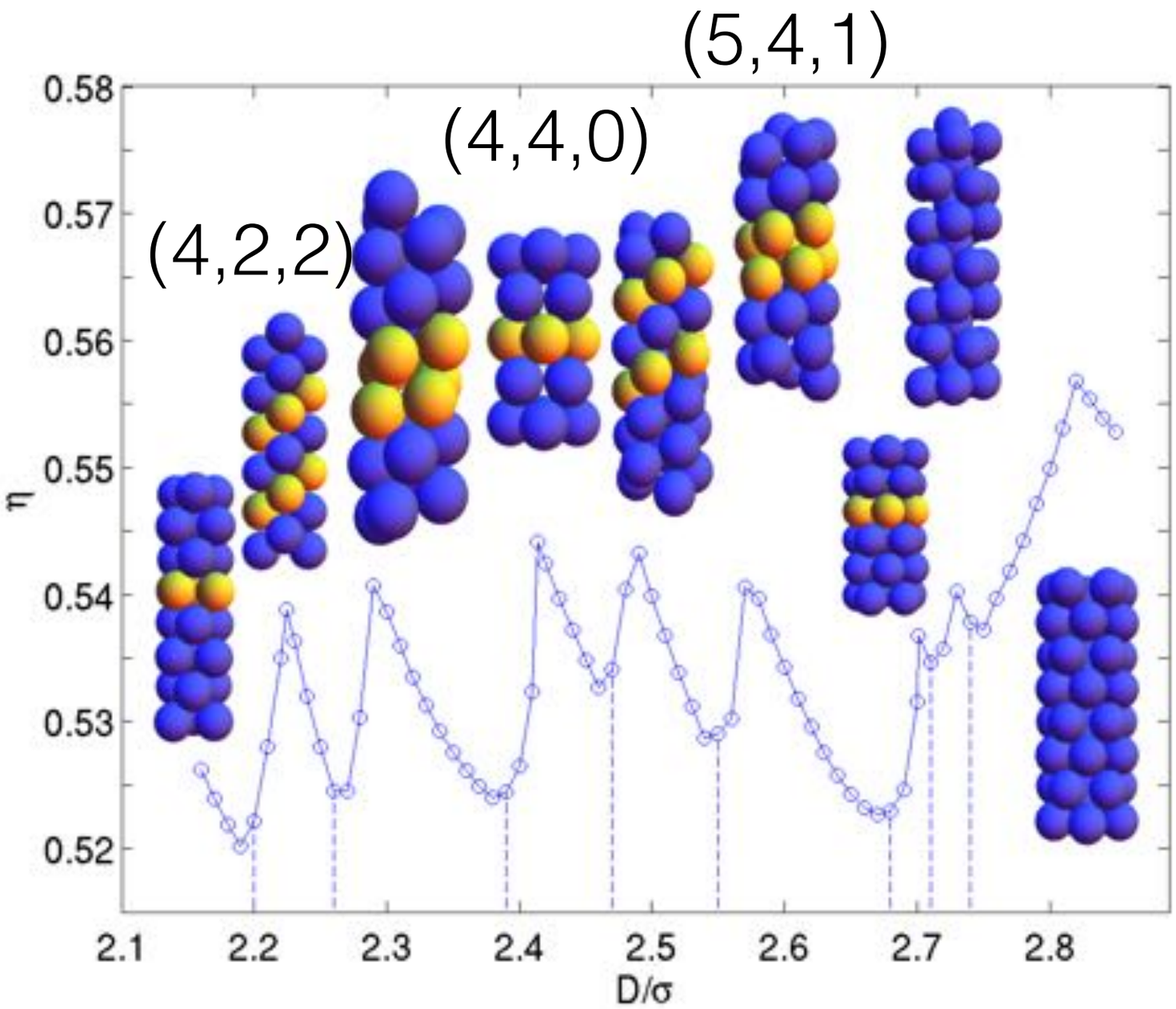
Assembly Dynamics

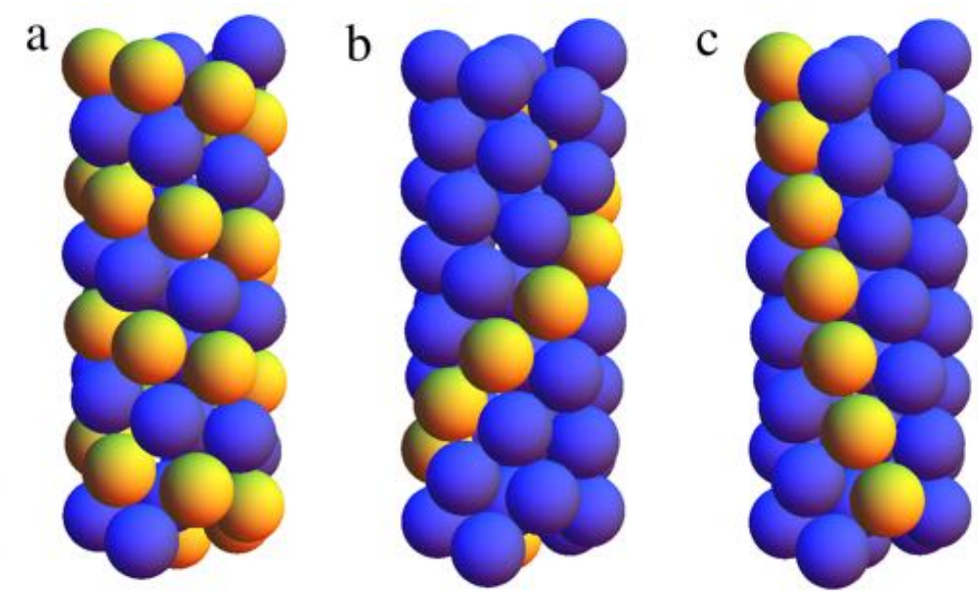




Fu, Bian, Shields, Cruz, López, Charbonneau, ***Soft Matter***, 2017

Structural Notation





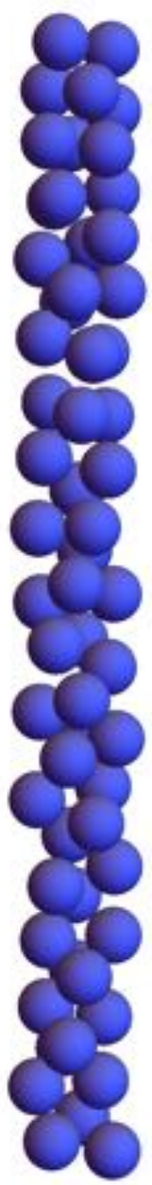
2 5 7

(7,5,2)

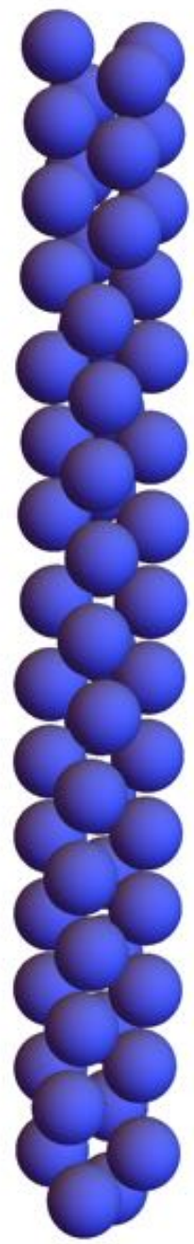
Mughal *et al.*, PRE, 2012, Fu *et al.*, Soft Matter, 2016

Structures Along Compression

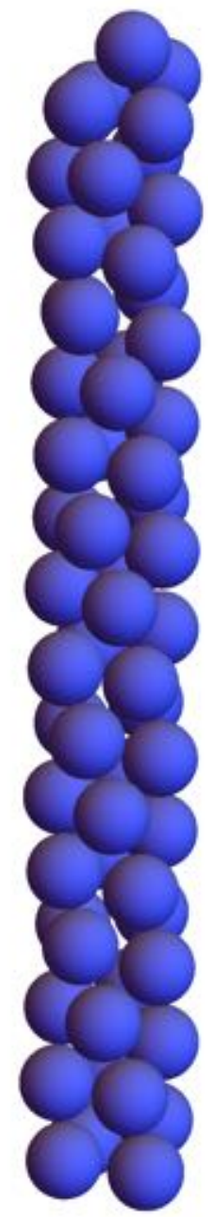
Disordered



(4,2,2)

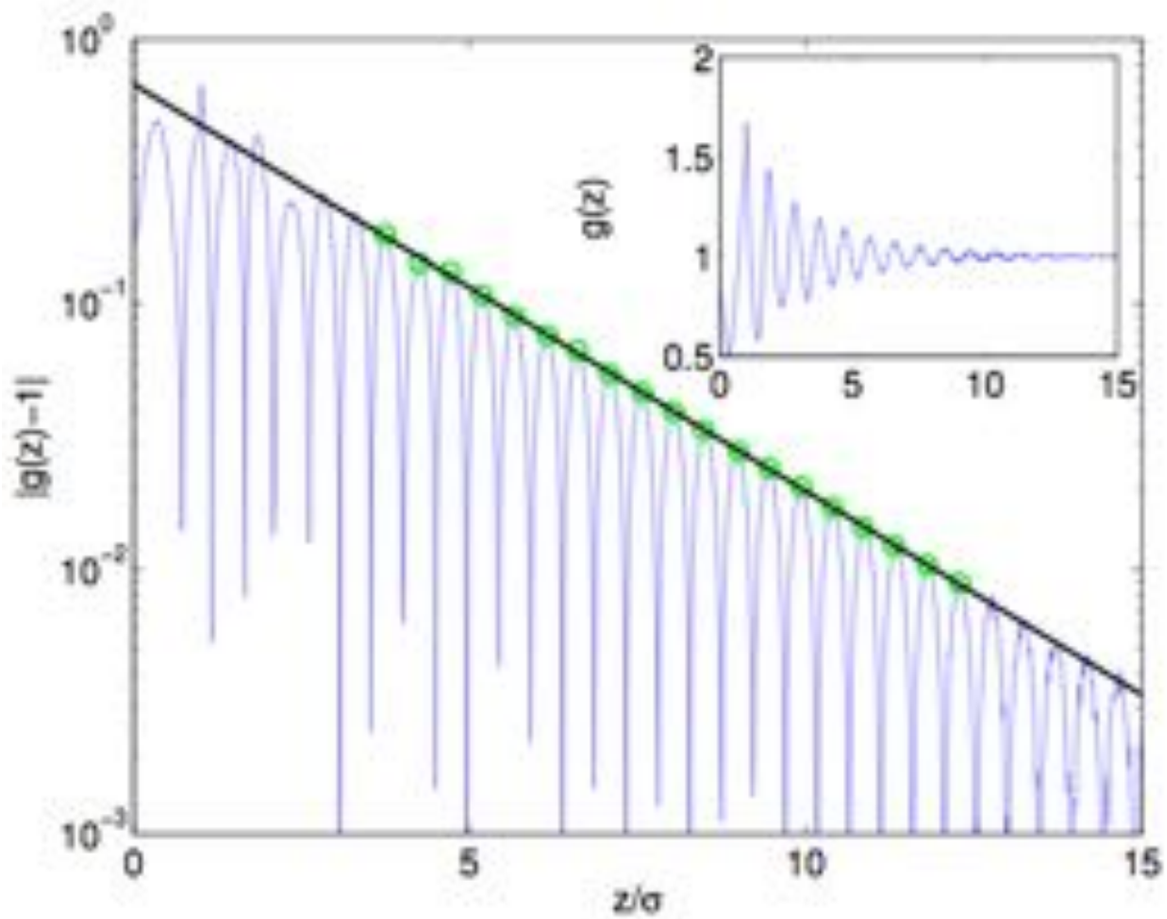


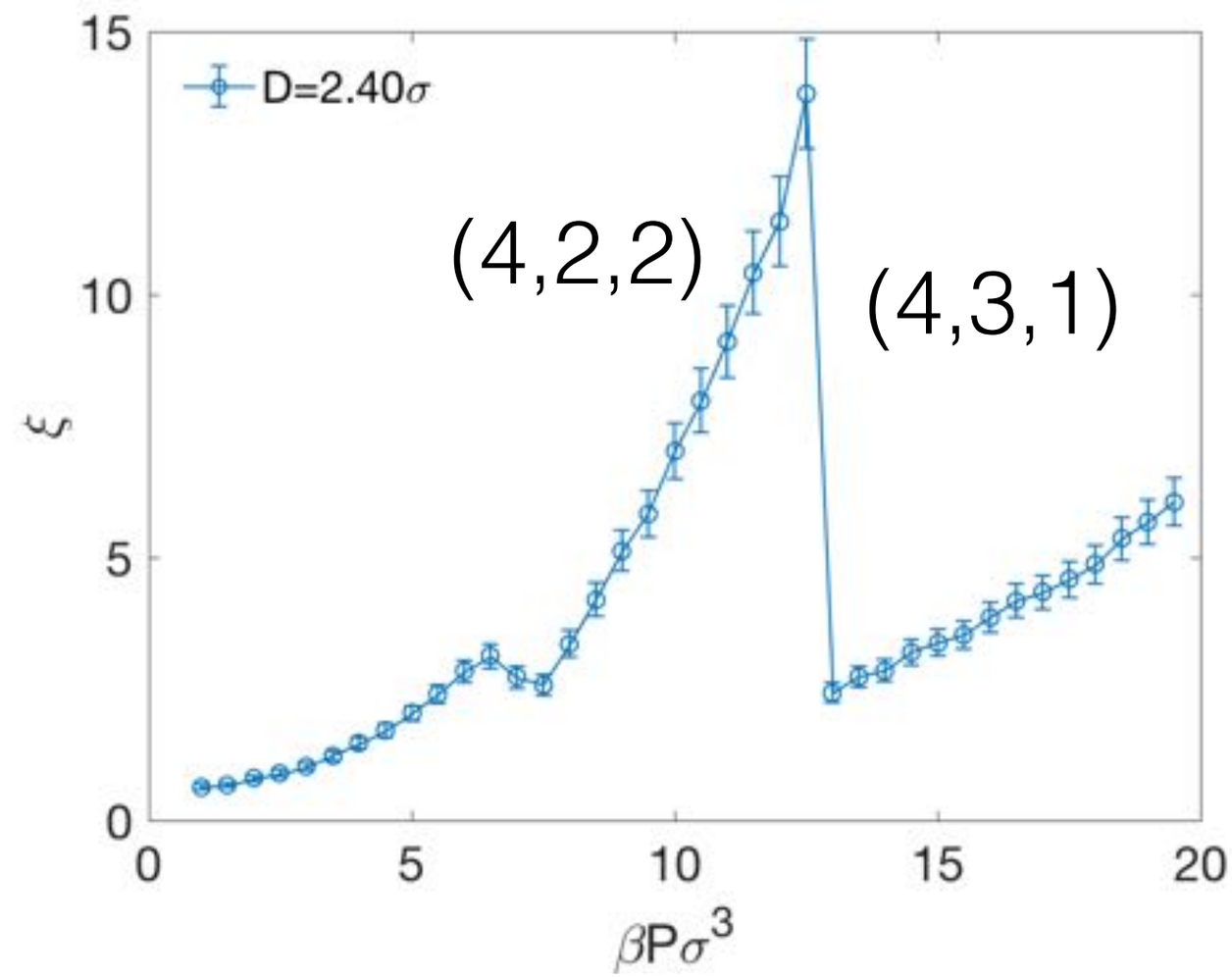
(4,3,1)



D=2.4σ P increases ⟶

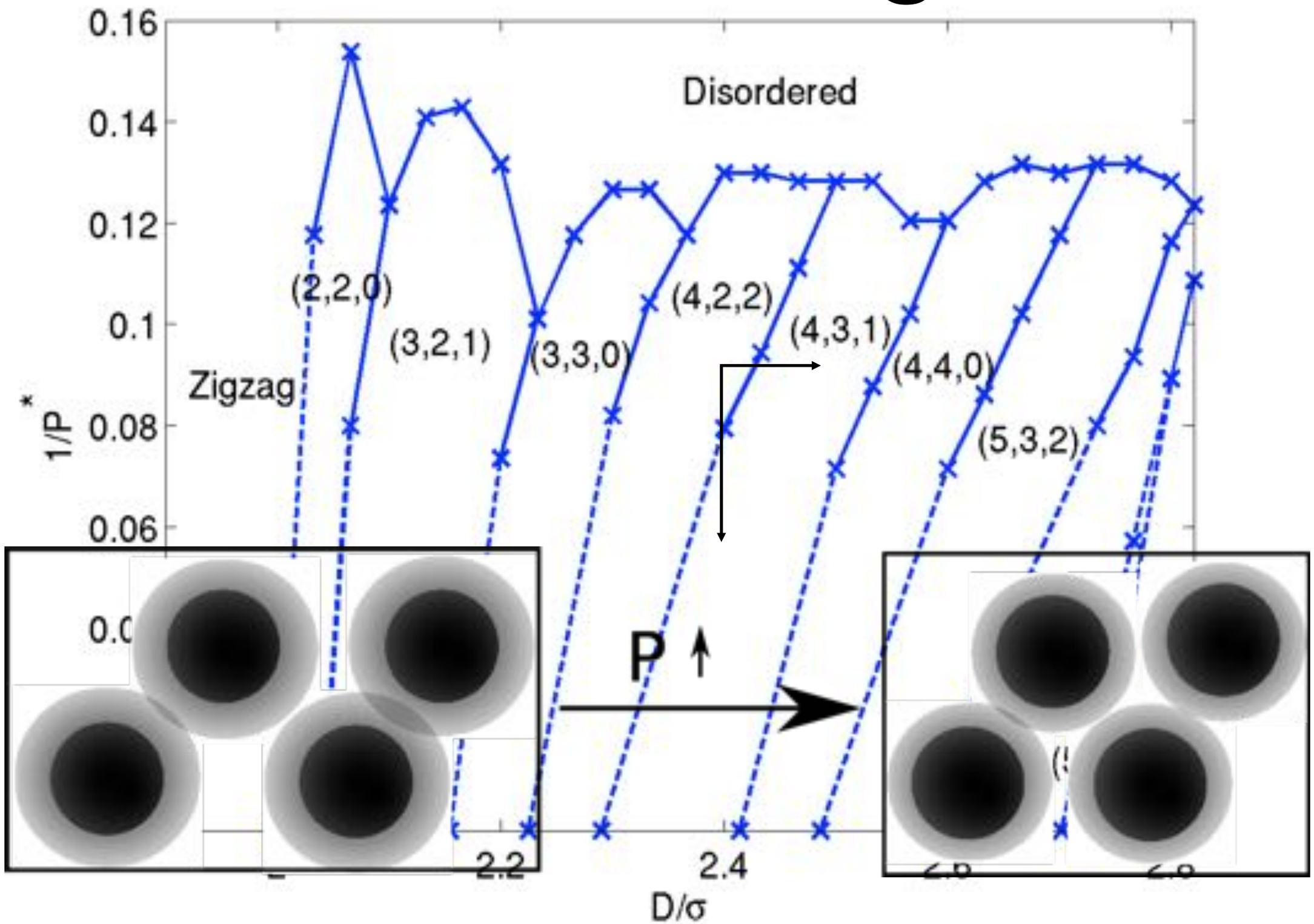
Structure Crossovers



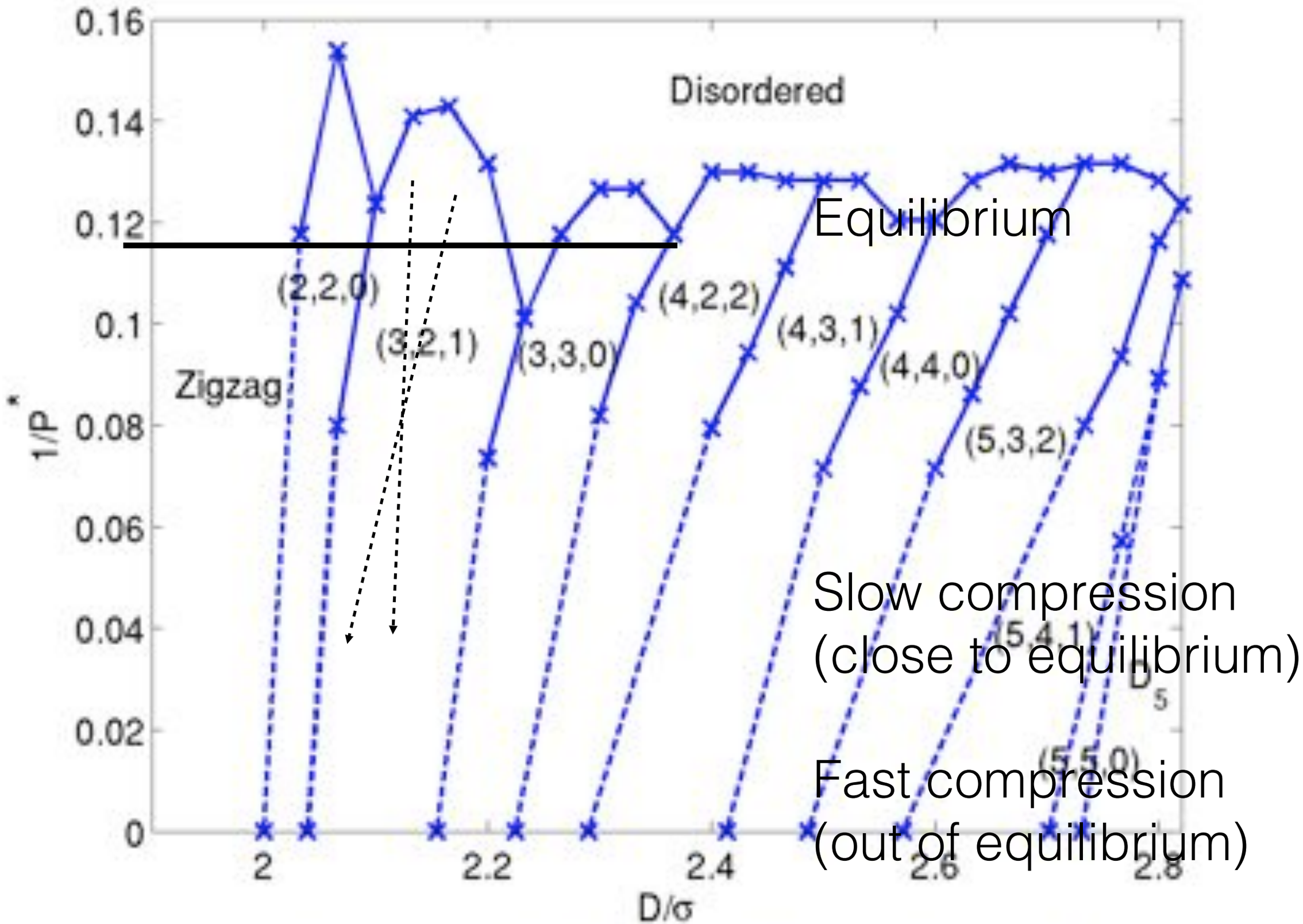


Non-monotonicity of the correlation length around structure crossovers.

Structure Diagram



Helical Self-assembly



Diffusionless assembly: line slips

(l,m,n)

↓

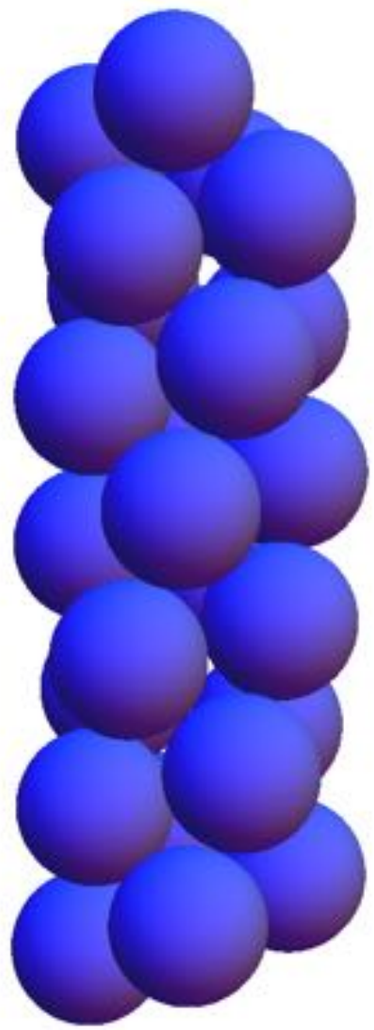
(l,m+1,n-1)

or

(l+1,m+1,n)

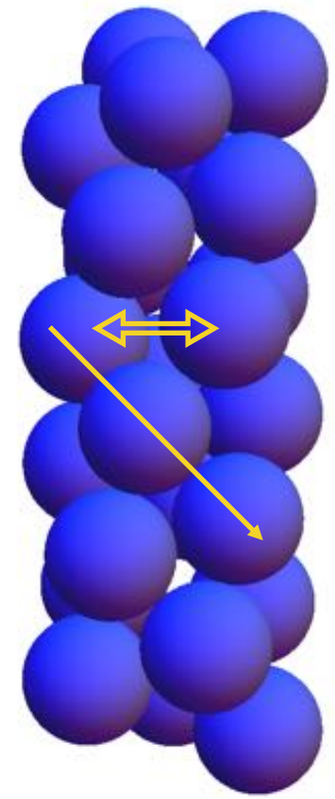
or

(l+1,m,n+1)

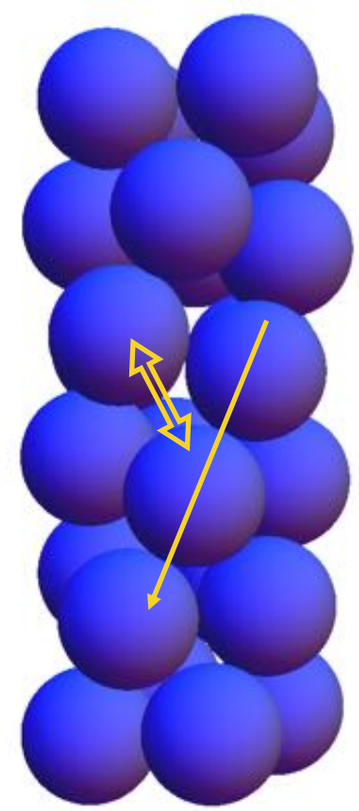


(4,3,1)

(4,**3**,1)

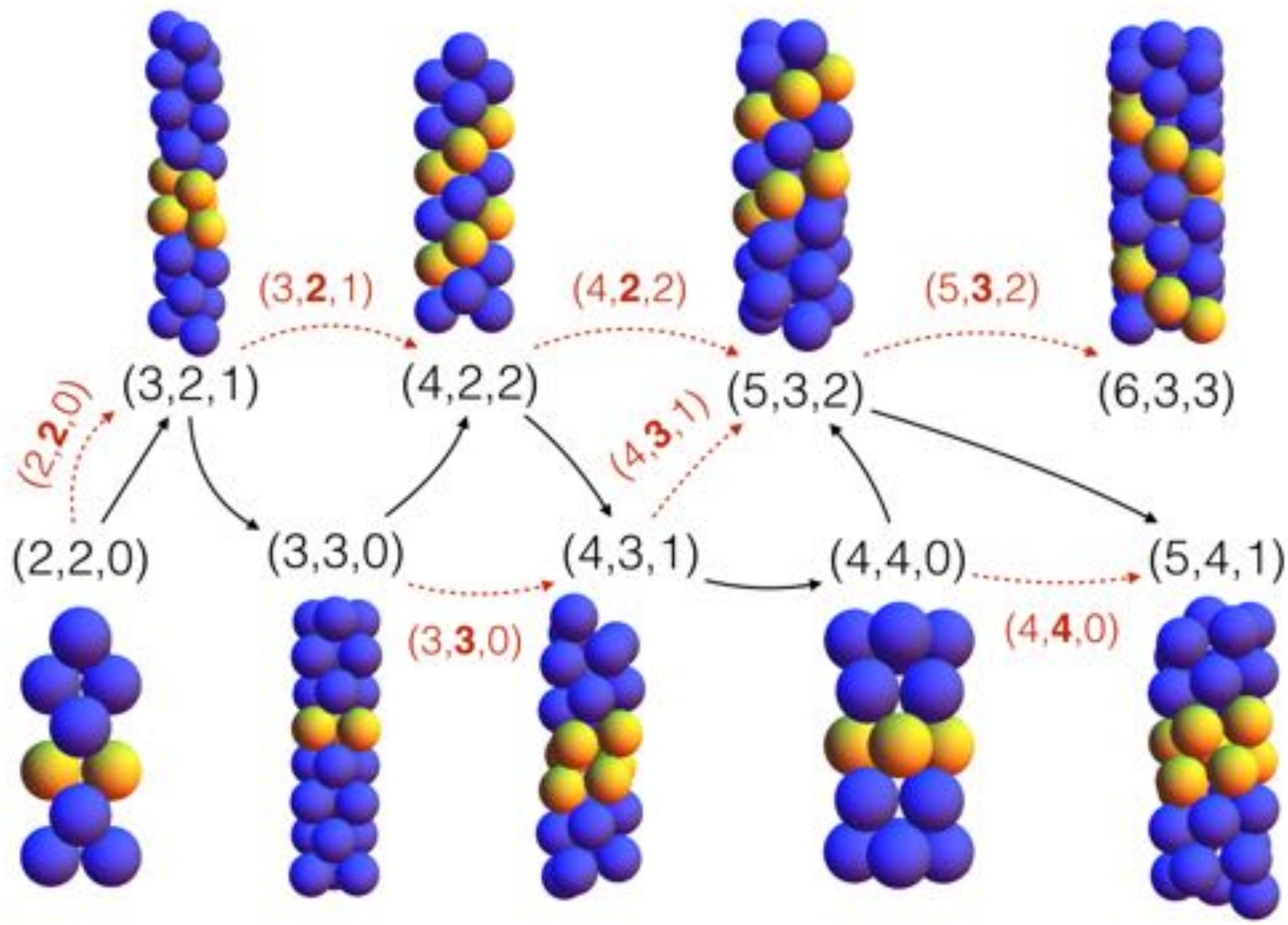


(**4**,3,1)



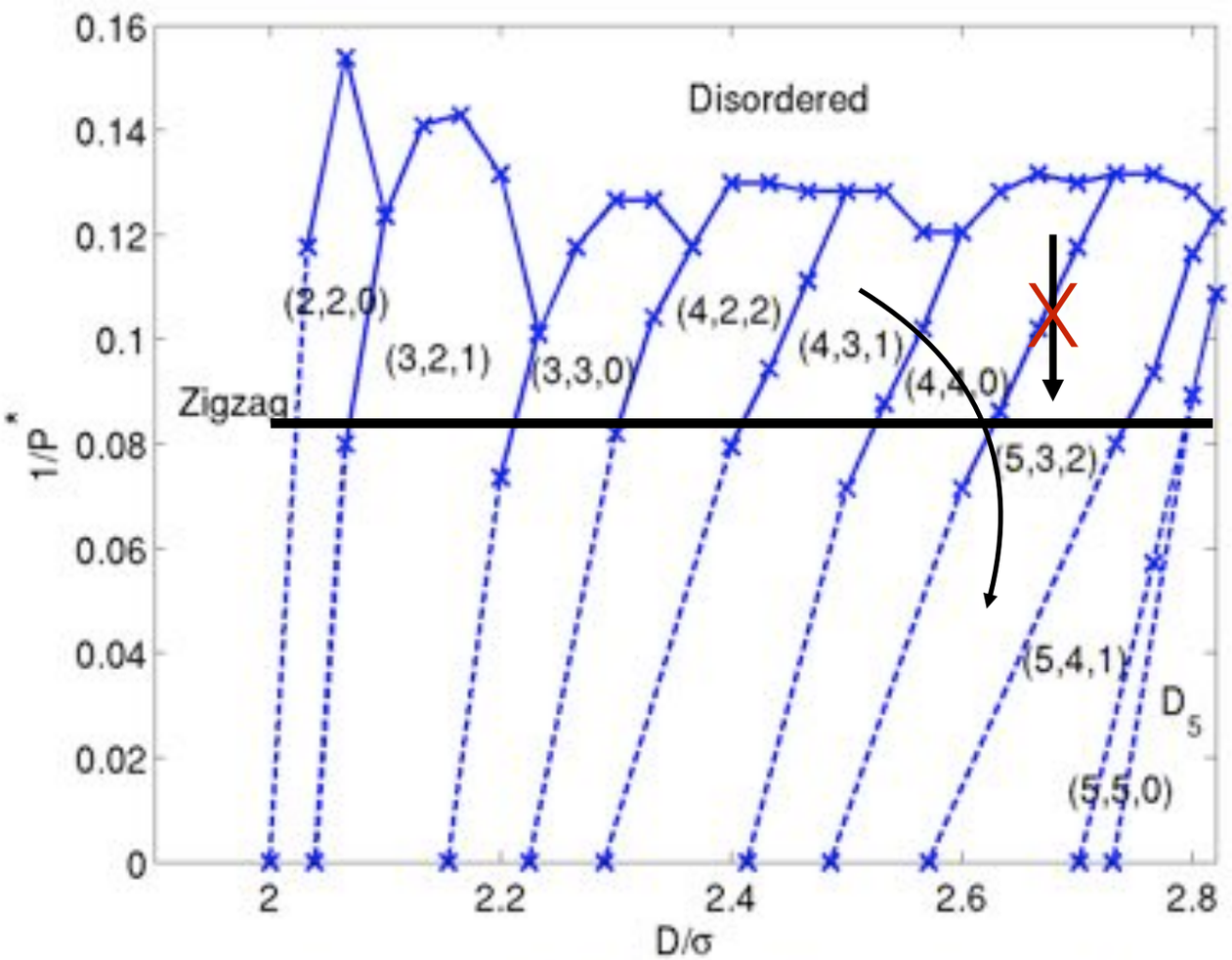
The densest slip wins!

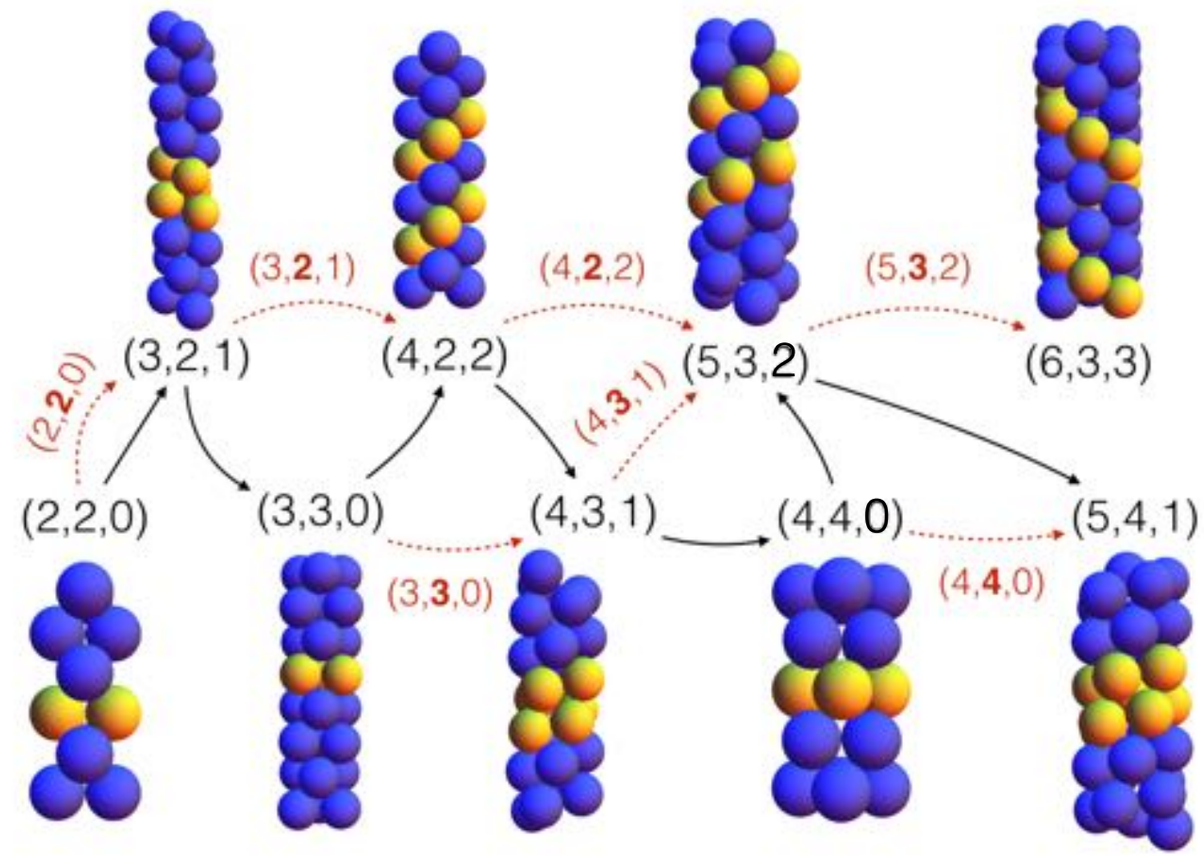
Kinetically favored pathways

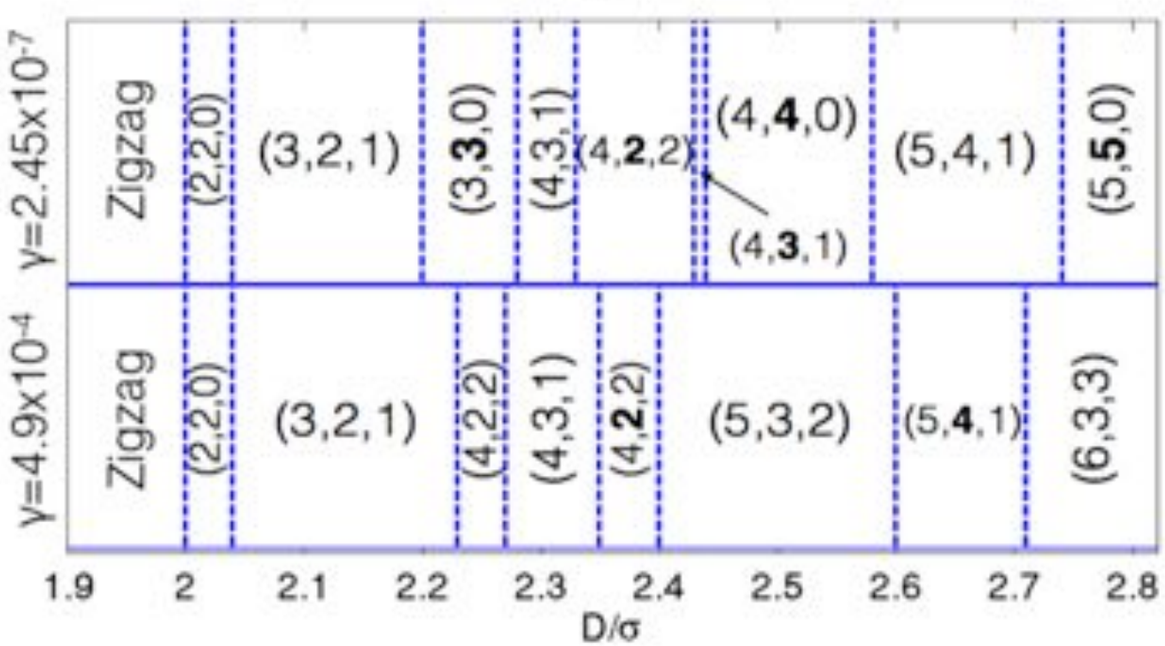


D increases ⟶

Structure diagram revisited







Slow compression

Fast compression

Summary II

- Facile assembly of helices is controlled by line slips. Crossovers without a single line slip are (geometrically) frustrated self-assembly processes.

- Almost all equilibrium crossovers are frustrated, hence intermediate structures can be skipped under fast compressions.

Open Questions

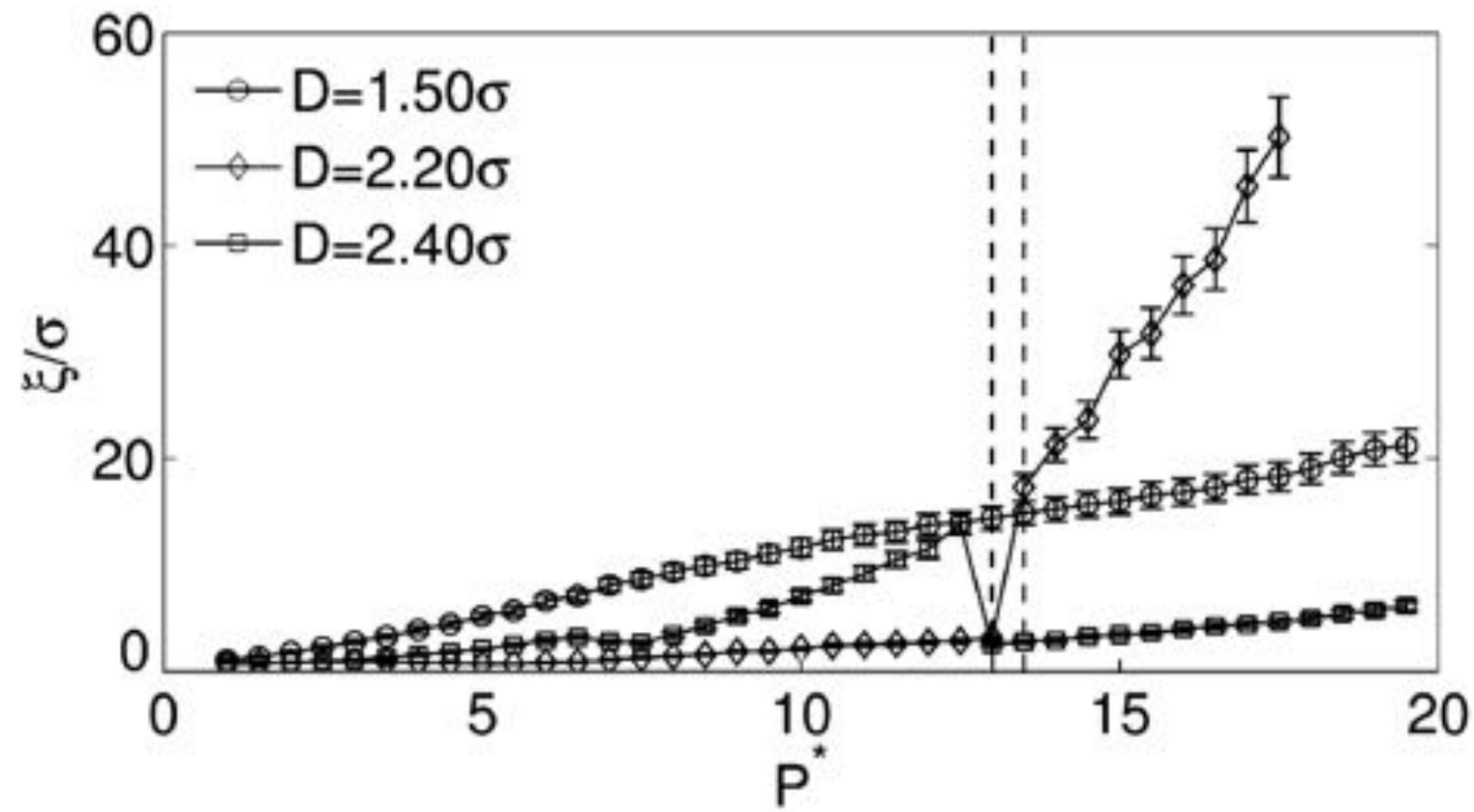
- Can polytetraheral order ever win at larger *D*?
- How frustrated is the assembly of close-packed structures at larger *D*? How long can an amorphous solid be kept (meta)stable in quasi-1D?
- What is the impact of imperfections (e.g., ellipsoidal cross-section) on cylindrical confinement?
- Are (systematic) formal packing proofs possible?

Epilogue: Correlation lengths in q1D models

Simulations show sharp changes of correlation length with pressure, for smooth equations of state.

Possible phase transition? (e.g., Yamchi & Bowles, PRL (2015)

BUT THM: (q)1D system with short-range interactions cannot undergo phase transitions.



What is the proper theoretical explanation?

Correlation lengths in q1D model

Strongly confined q1D models of HS are amenable transfer-matrix treatment.

Generalized the approach to NNN interactions for HS in cylinders (D<2σ).

- Correlation function

$$g_r(i,j) = \langle r_i r_j \rangle - \langle r_i \rangle^2$$

$$\lim_{|i-j|\to\infty} g_r(i,j) \sim e^{-|i-j|/\xi_r}$$

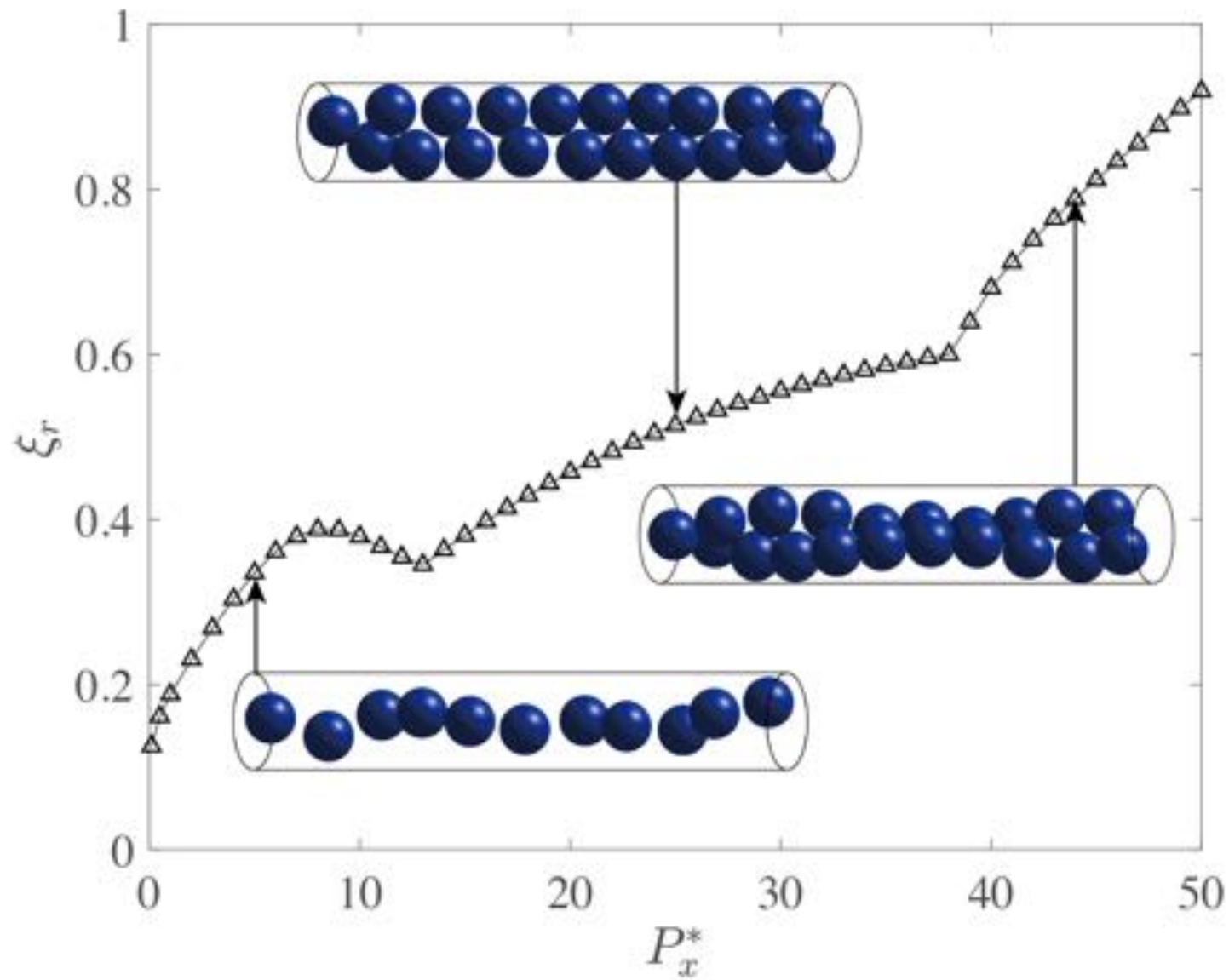
- Correlation length

$$\xi_r^{-1} = \ln(\lambda_0/|\lambda_1|)$$

Y. Hu, L. Fu, and P. Charbonneau, arxiv:1804.00693

Correlation lengths in q1D model

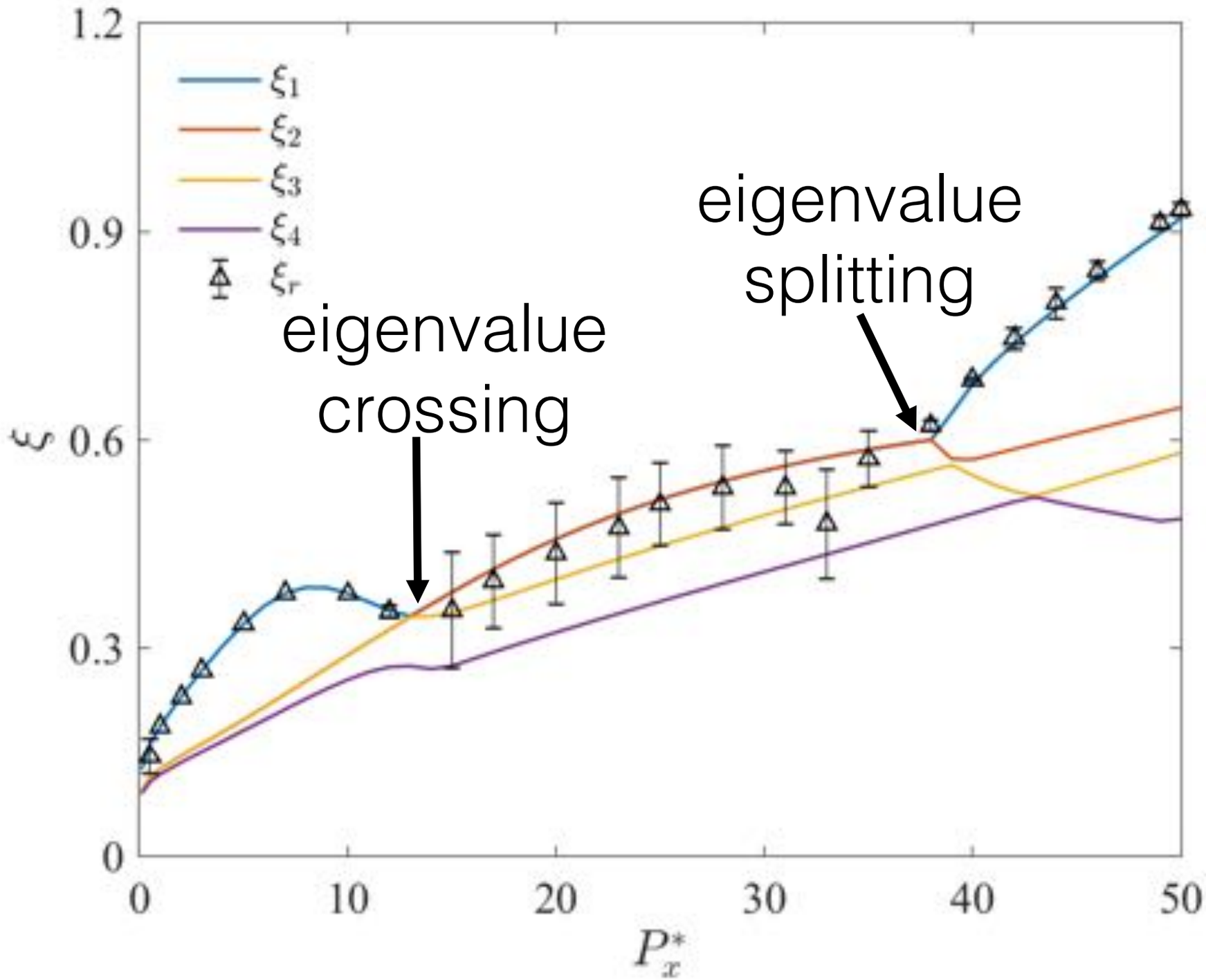
Crossovers and kinks are associated with changes in ordering.



straight chain -> zig-zag -> helix

Y. Hu, L. Fu, and P. Charbonneau, arxiv:1804.00693

Correlation lengths in q1D model



- Kinks result from eigenvalue crossing and splitting.
- Complex decay of correlations is associated with eigenvalue conjugation.

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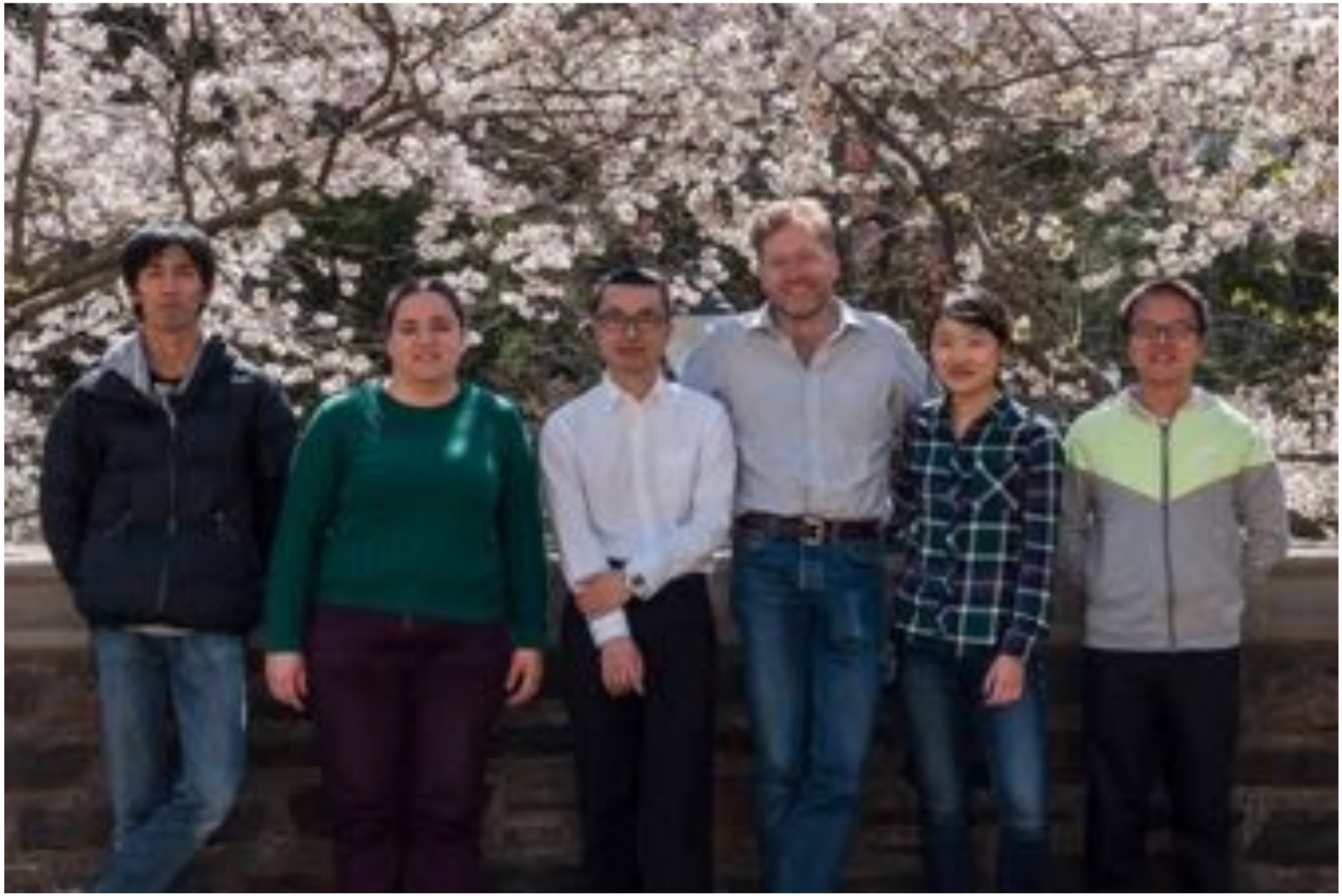

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