Are sticky colloids geometrically frustrated?

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Collaborators

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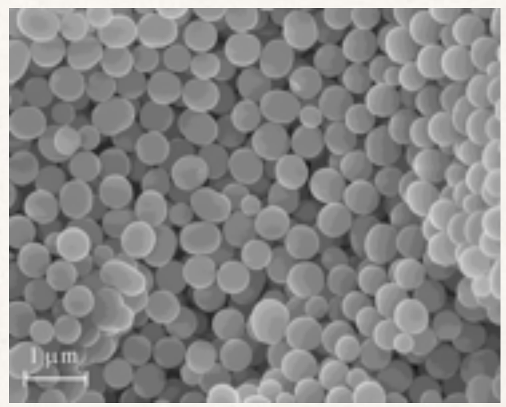
Bob Connelly (Cornell)
Michael Overton (NYU)

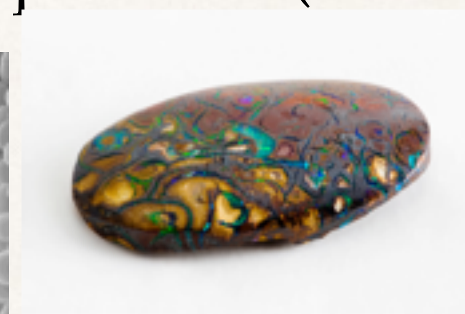
US Dept of Energy, National Science Foundation

Colloidal particles (colloids)

- *Colloidal* particles: diameters ~ 10^{-8}-10^{-6} m. (≫ atoms, ≪ scales of humans)
- Potential to make new materials (∵ size ~ wavelength of light) + memory
- Range of interaction ≪ diameter of particles (unlike atoms)

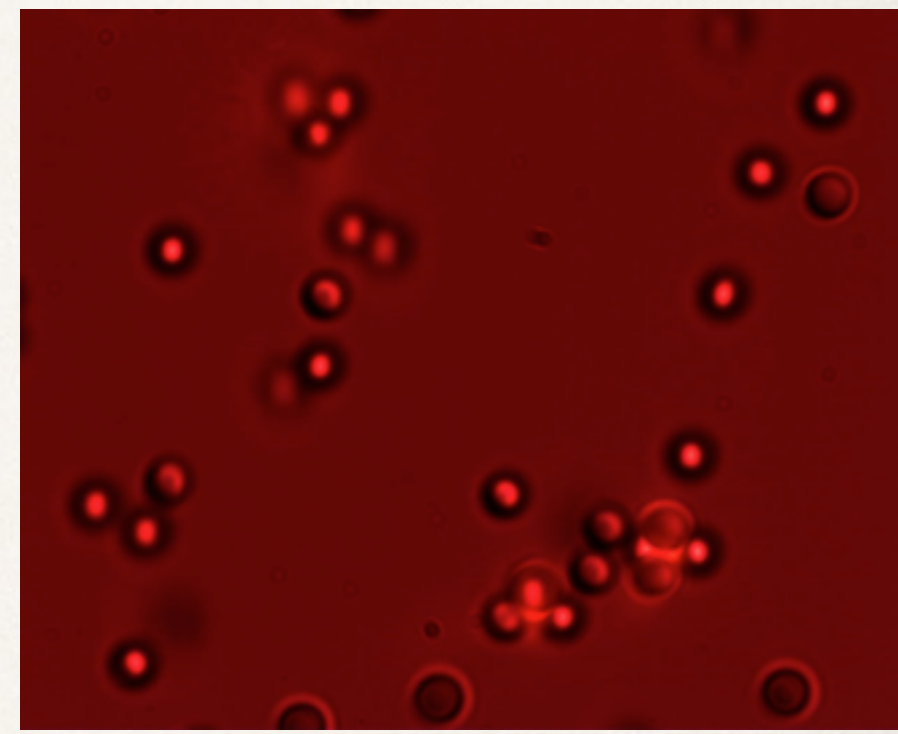
mayonnaise



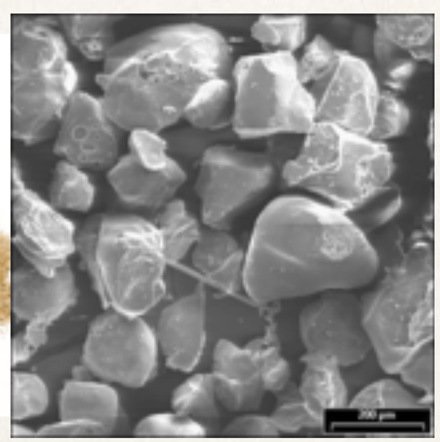


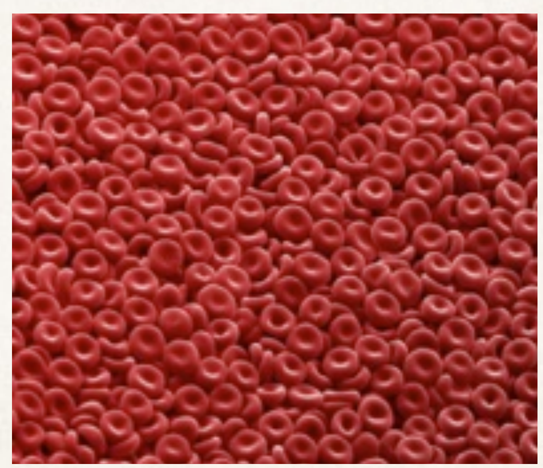
opal

red blood cells

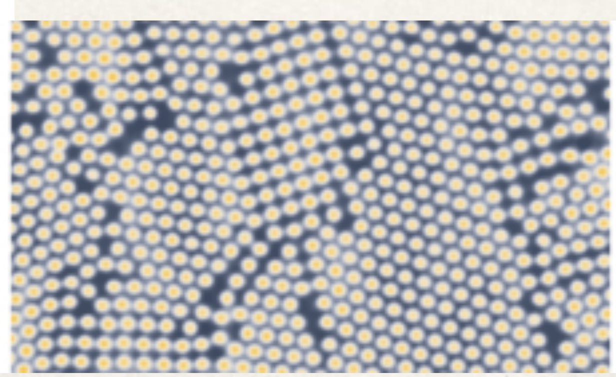


sand





cornstarch



paint

ketchup

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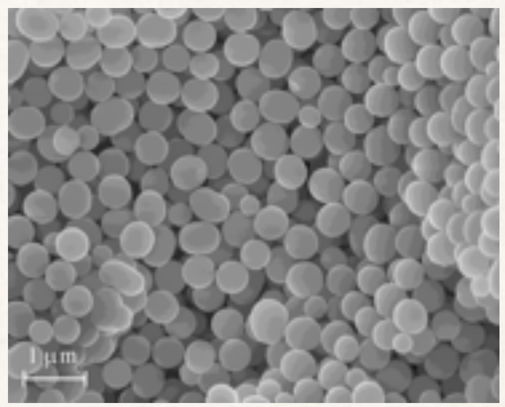
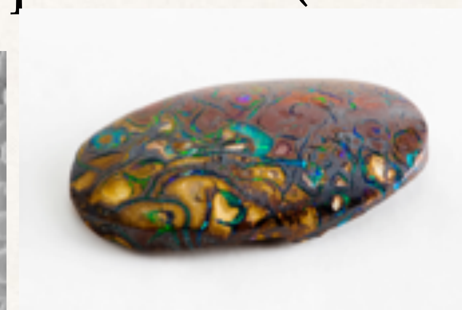
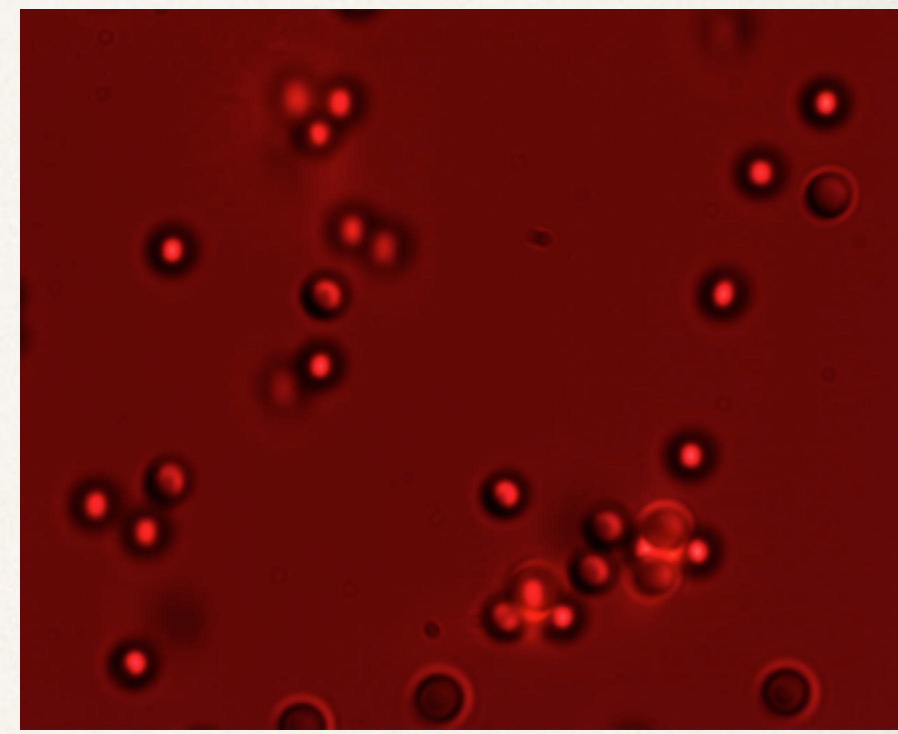




opal



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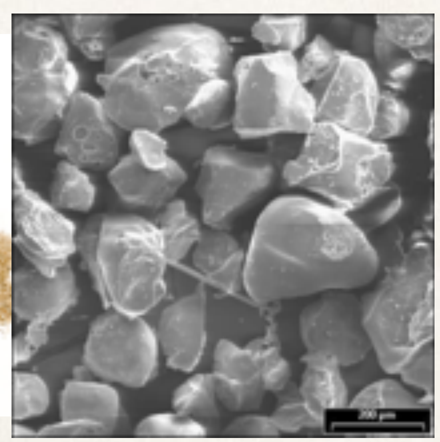

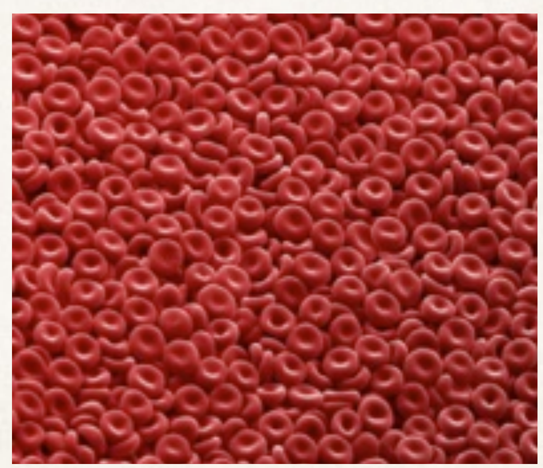

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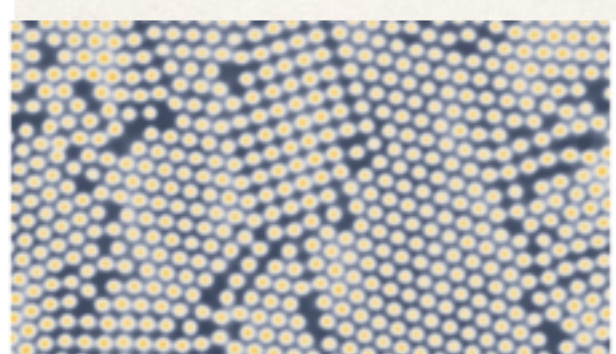

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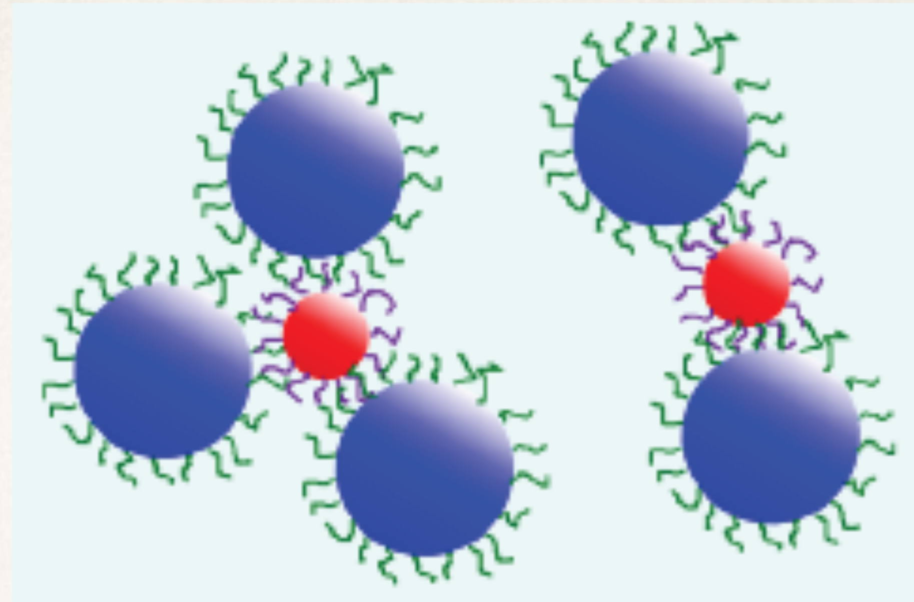
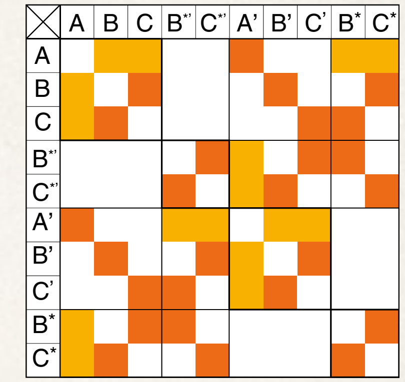
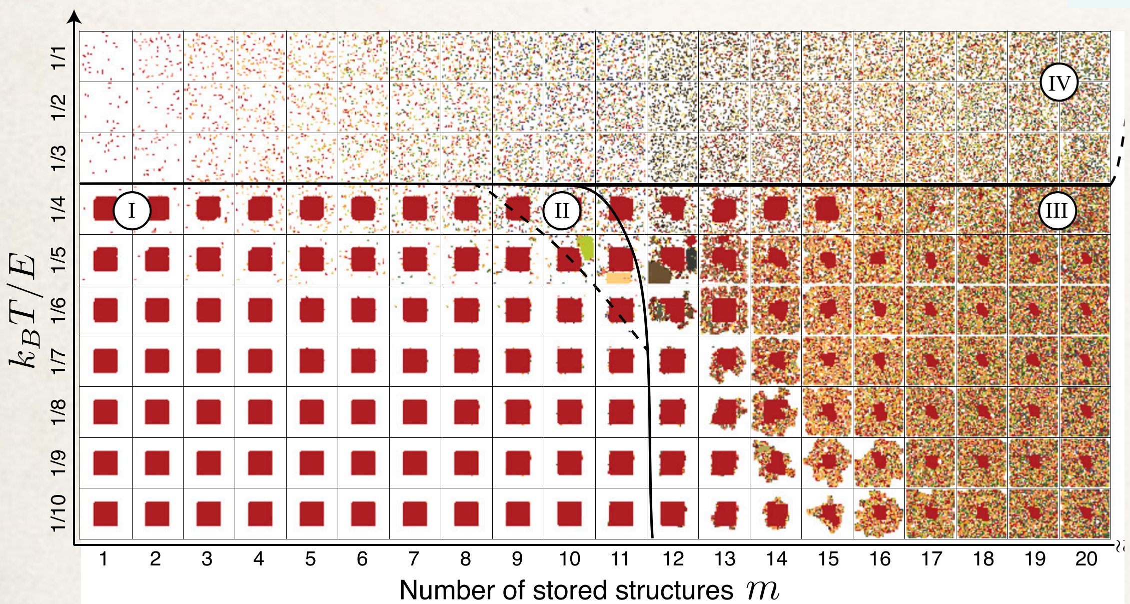
Colloids could be programmed to have memories:

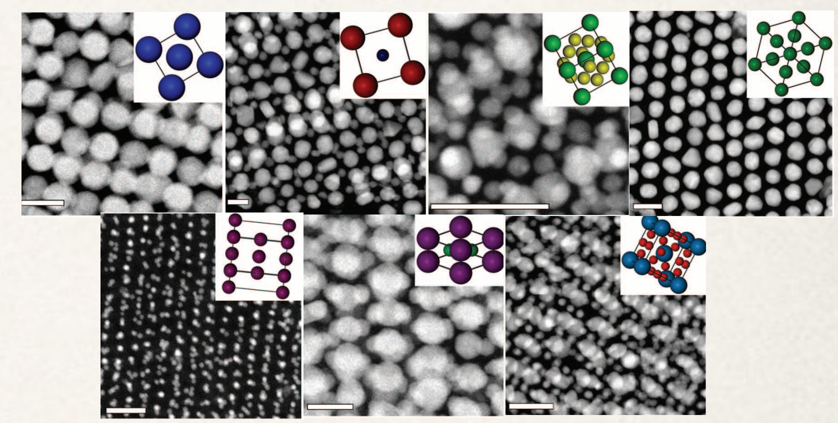
DNA —> highly specific interactions





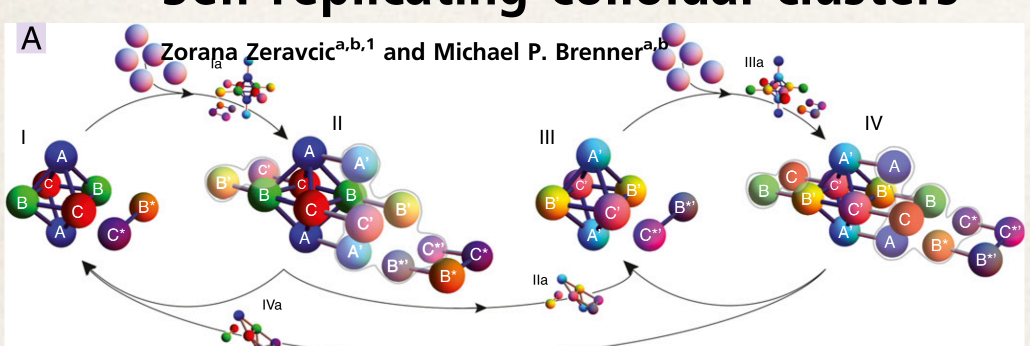


Murugan, Zeravcic, Brenner, Leibler, PNAS (2015)



Macfarlane et al, Science (2011)

Self-replicating colloidal clusters

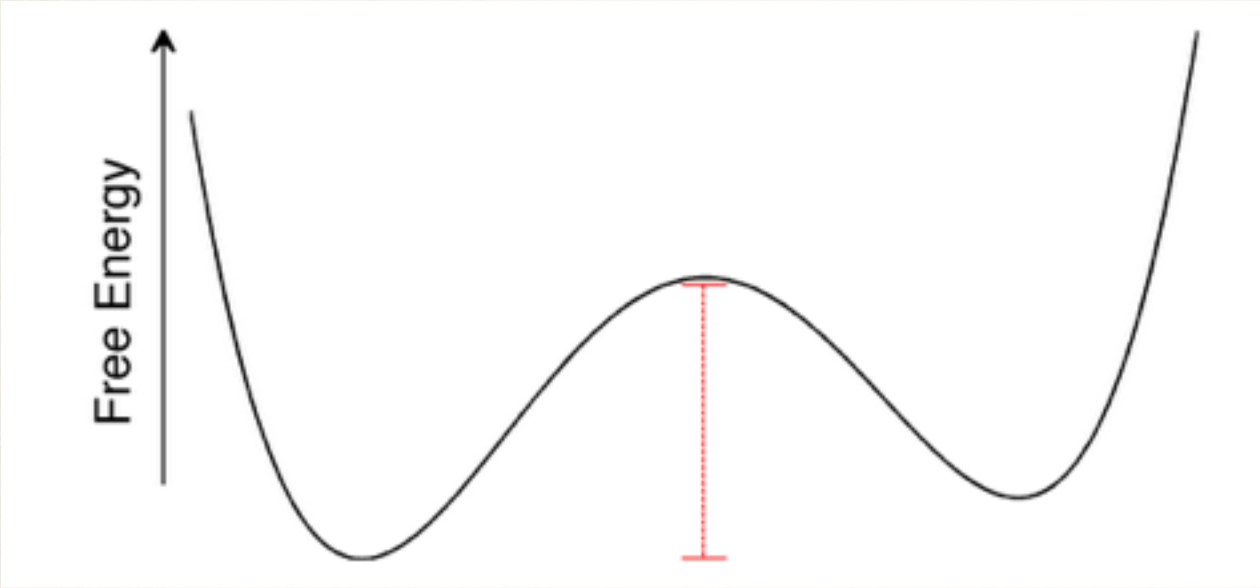


+ what else ????

… to be continued (see end of presentation)….


Memory at Sands Beach

Challenges of very short-ranged interactions



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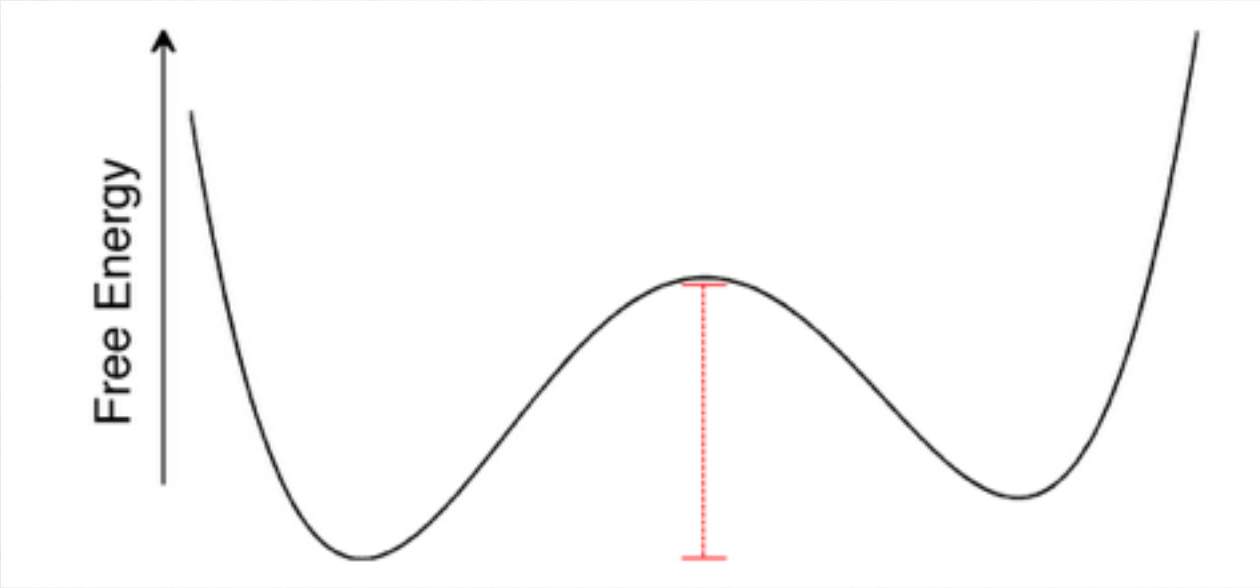

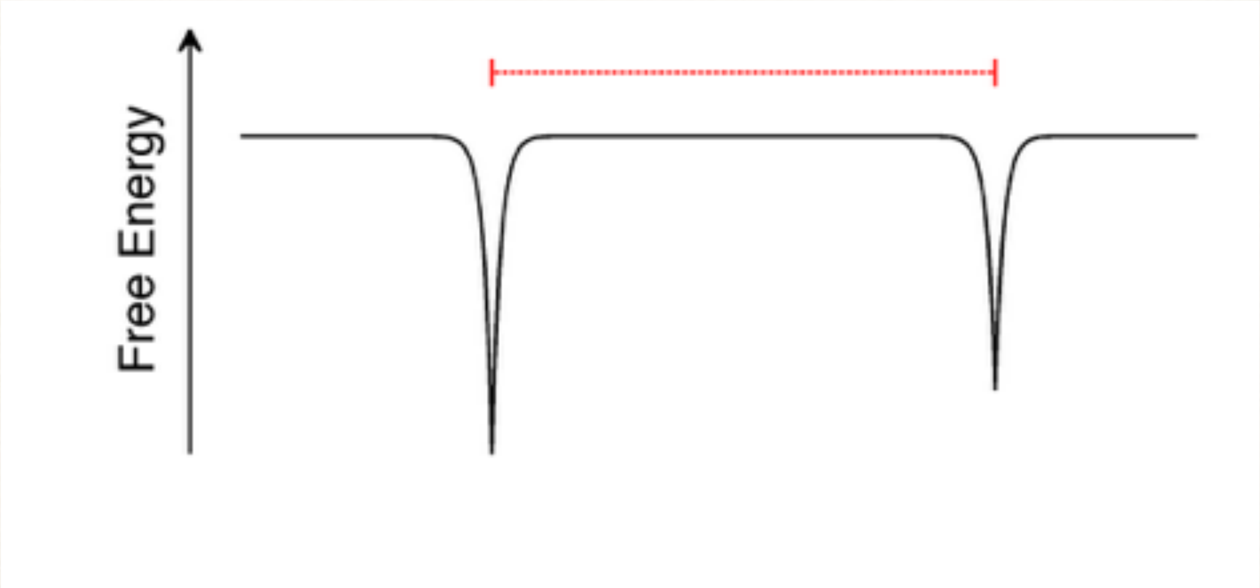

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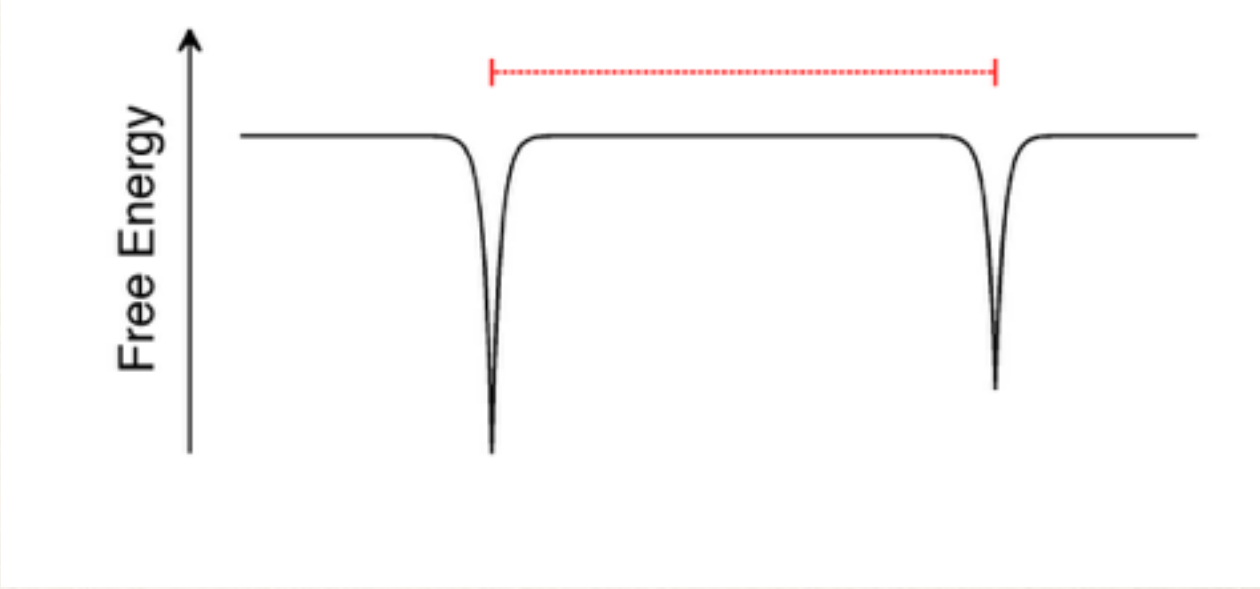

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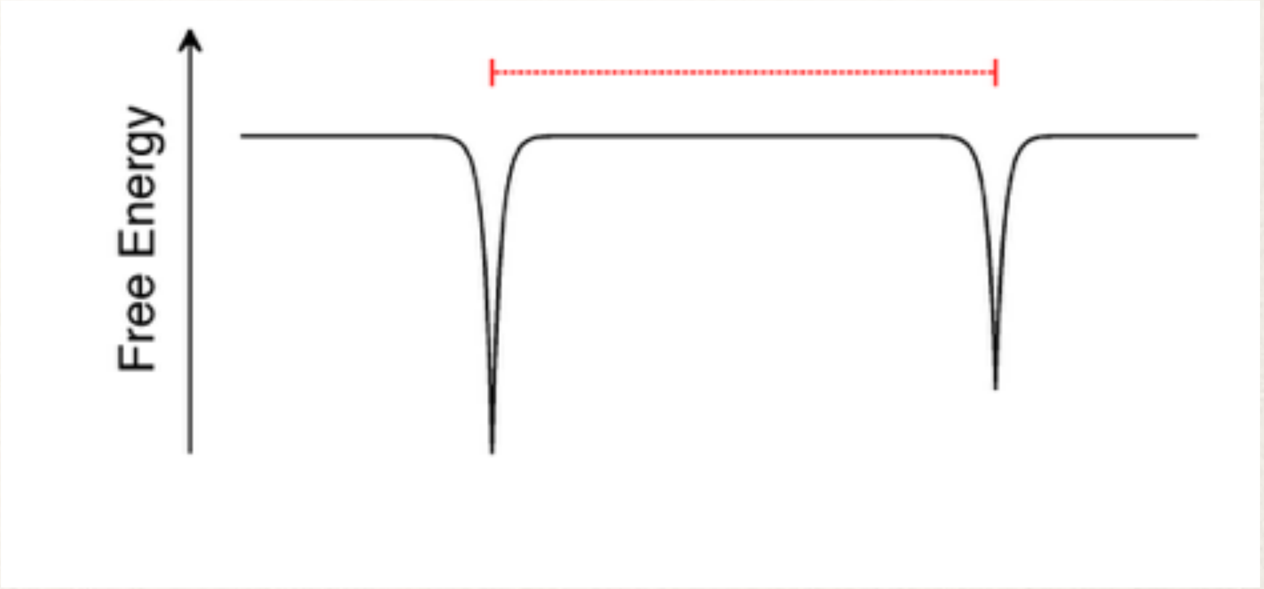
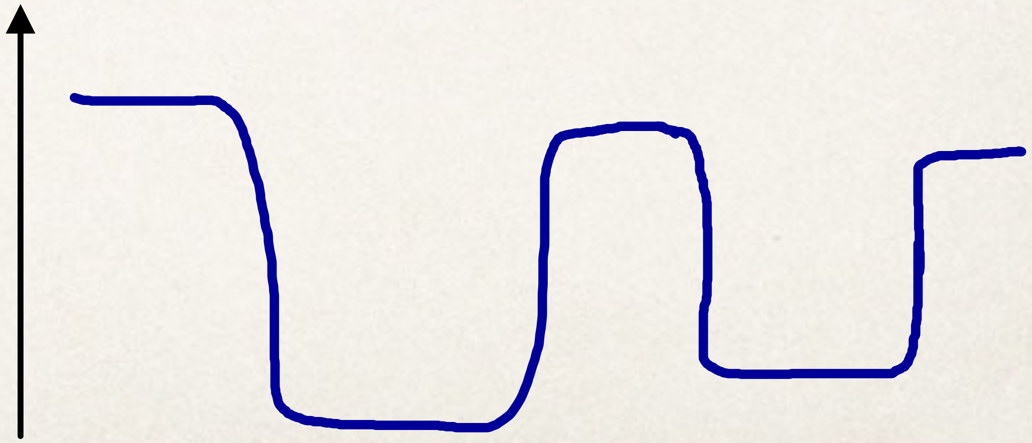
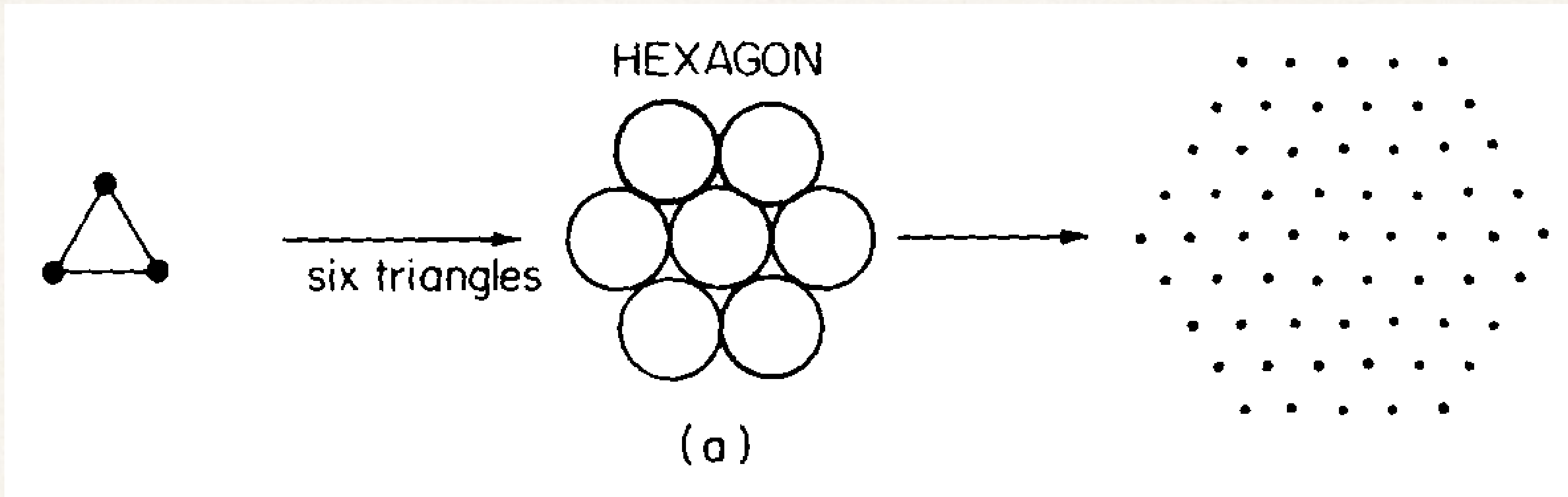
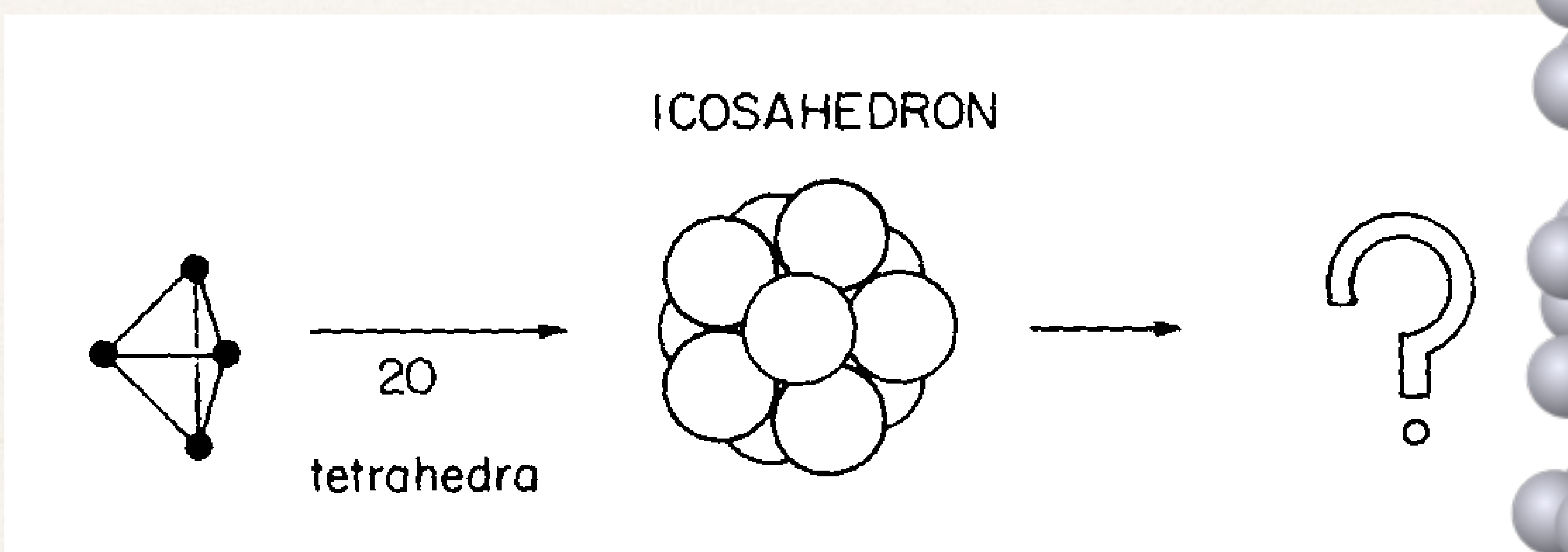


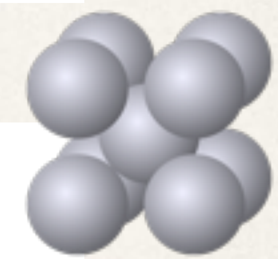


What is Geometrical Frustration?

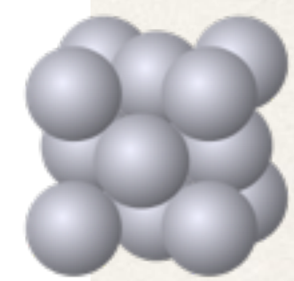
D. Nelson, F. Spaepen, Solid State Phys. 42, 1 (1989)



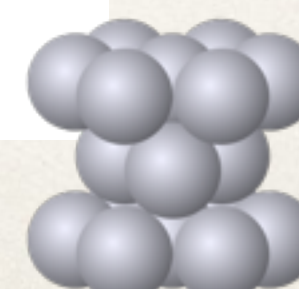




bcc unit cell



fcc unit cell



hcp unit cell

Geometric frustration: locally preferred order ≠ globally preferred order

Behaviour of small groups of particles can help understand thermodynamic or dynamic phenomena

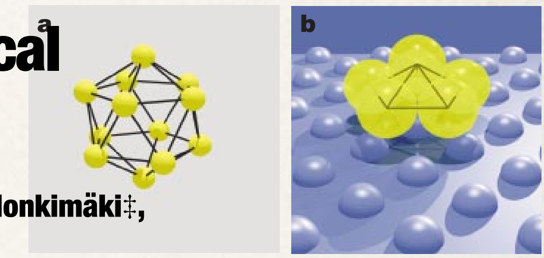
nucleation, phase transitions, glass transition, gel formation, jamming, etc

The theoretical argument is misleading also. Consider the question: 'In how many different ways can one put twelve billiard balls in simultaneous contact with one, counting as different the arrangements which cannot be transformed into each other without breaking contact with the centre ball?' The answer is *three*. Two which come to the mind of any crystallographer occur in the face-centred cubic and hexagonal close-packed lattices. The third comes to the mind of any good schoolboy, and is to put one at the centre of each face of a regular dodecahedron. That body has five-fold axes, which are abhorrent to crystal symmetry: unlike the other two packings, this one cannot be continuously extended in three dimensions. You will find that the outer twelve in this packing do not touch each other. If we have mutually attracting deformable spheres, like atoms, they will be a little closer to the centre in this third type of packing; and if one assumes they are argon atoms (interacting in pairs with attractive and repulsive energy terms proportional to r^{-6} and r^{-12}) one may calculate that the binding energy of the group of thirteen is 8·4 % greater than for the other two packings. This is 40 % of the lattice energy per atom in the crystal. I infer that this will be a very common grouping in liquids, that most of the groups of twelve atoms around one will be in this form, that freezing involves a substantial rearrangement, and not merely an extension of the same kind of order from short distances to long ones; a rearrangement which is quite costly of energy in small localities, and only becomes economical when extended over a considerable volume, because unlike the other packing it can be so extended without discontinuities.

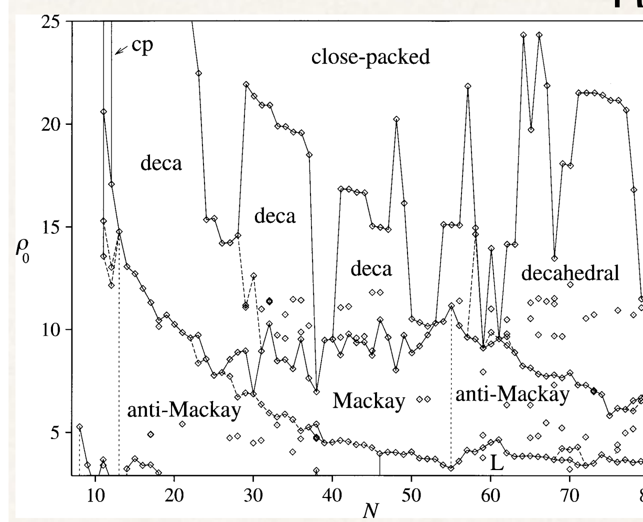
F.C. Frank, Proc. R. Soc. Lond. A Math. Phys. Sci. 215, 43 (1952)

Observation of five-fold local symmetry in liquid lead

H. Reichert*, O. Klein*†, H. Dosch*, M. Denk*, V. Honkimäki‡, T. Lippmann§ & G. Reiter||

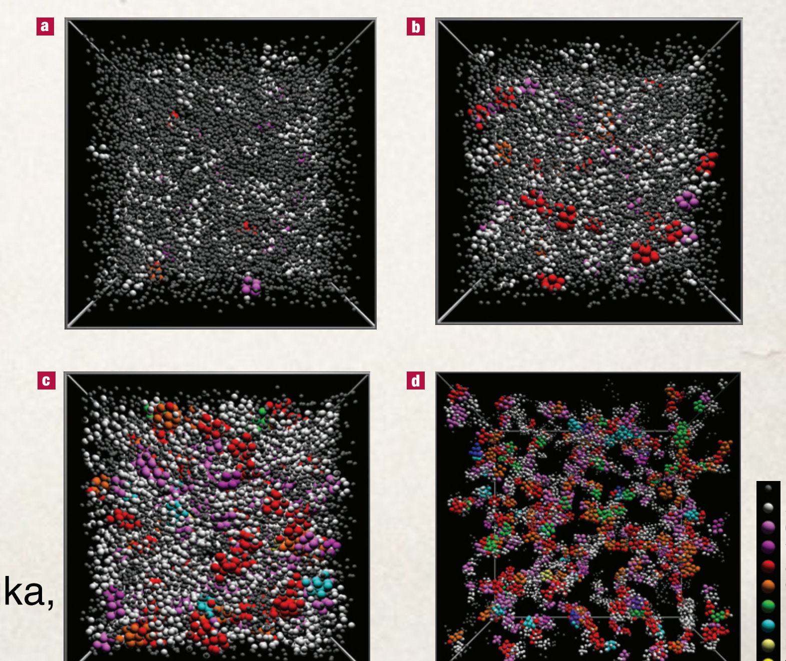


Relchert et al, Nature (2000)



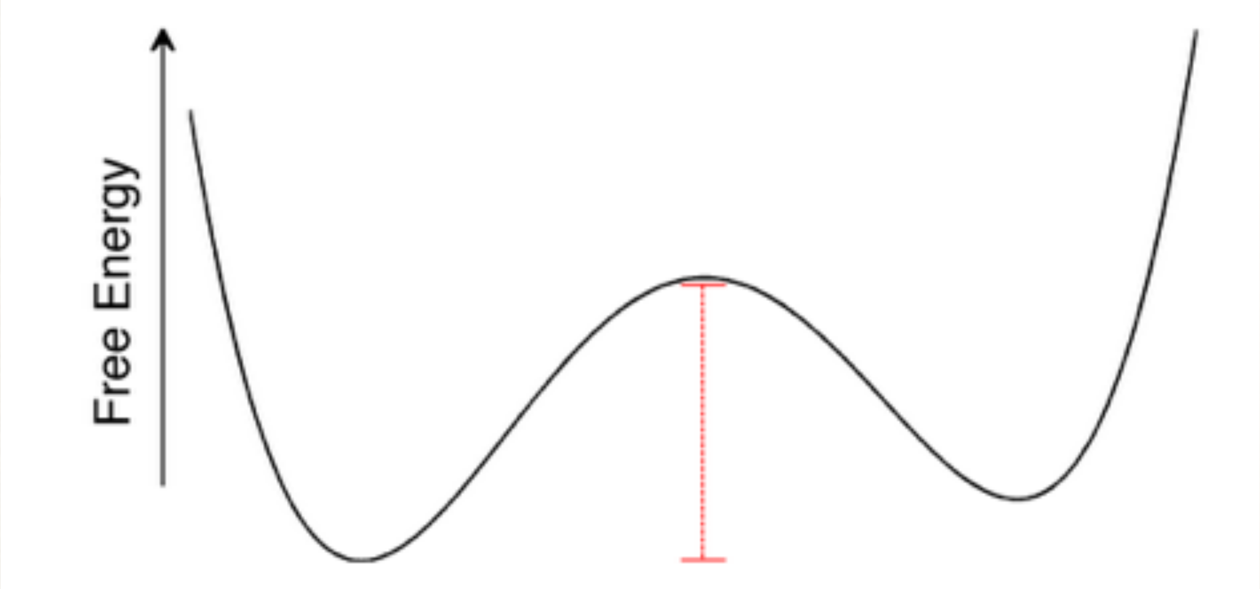
Doye & Wales, Faraday Trans (1997)

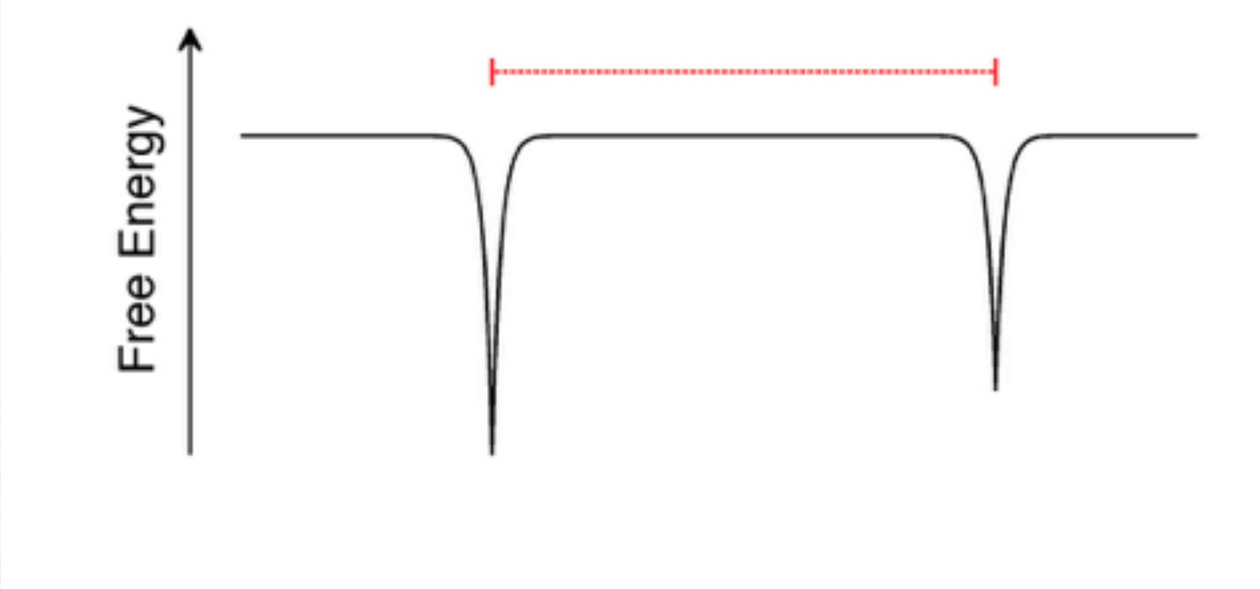
creation of local "global minima" leads to gel formation



C. Patrick Royall, S. R. Williams, T. Ohtsuka, H. Tanaka, Nat. Mater. 7, 556 (2008)

What about frustration in colloids?





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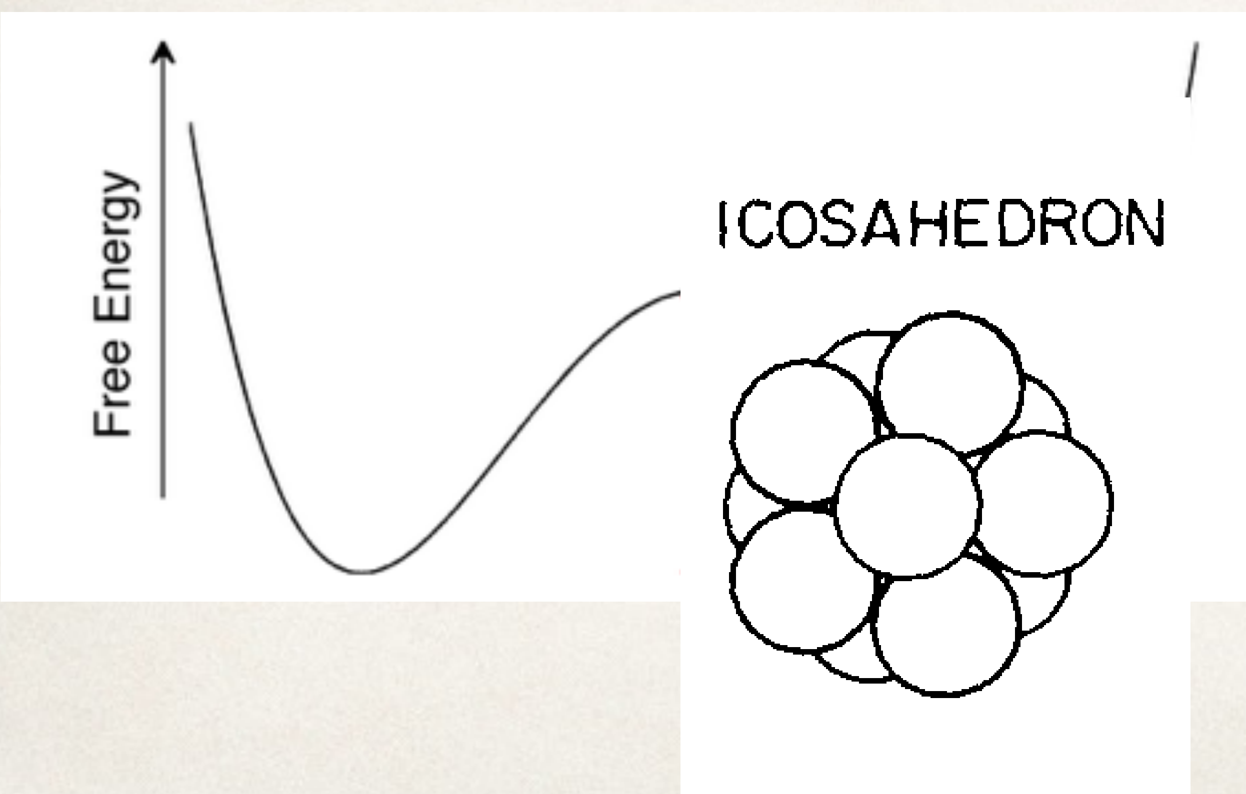

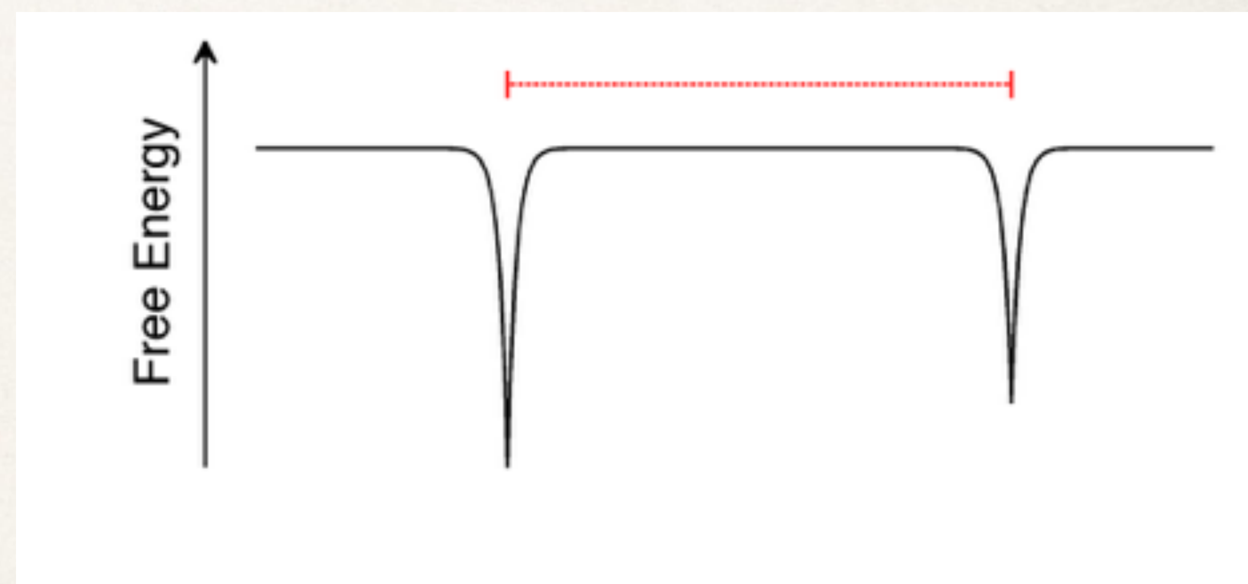

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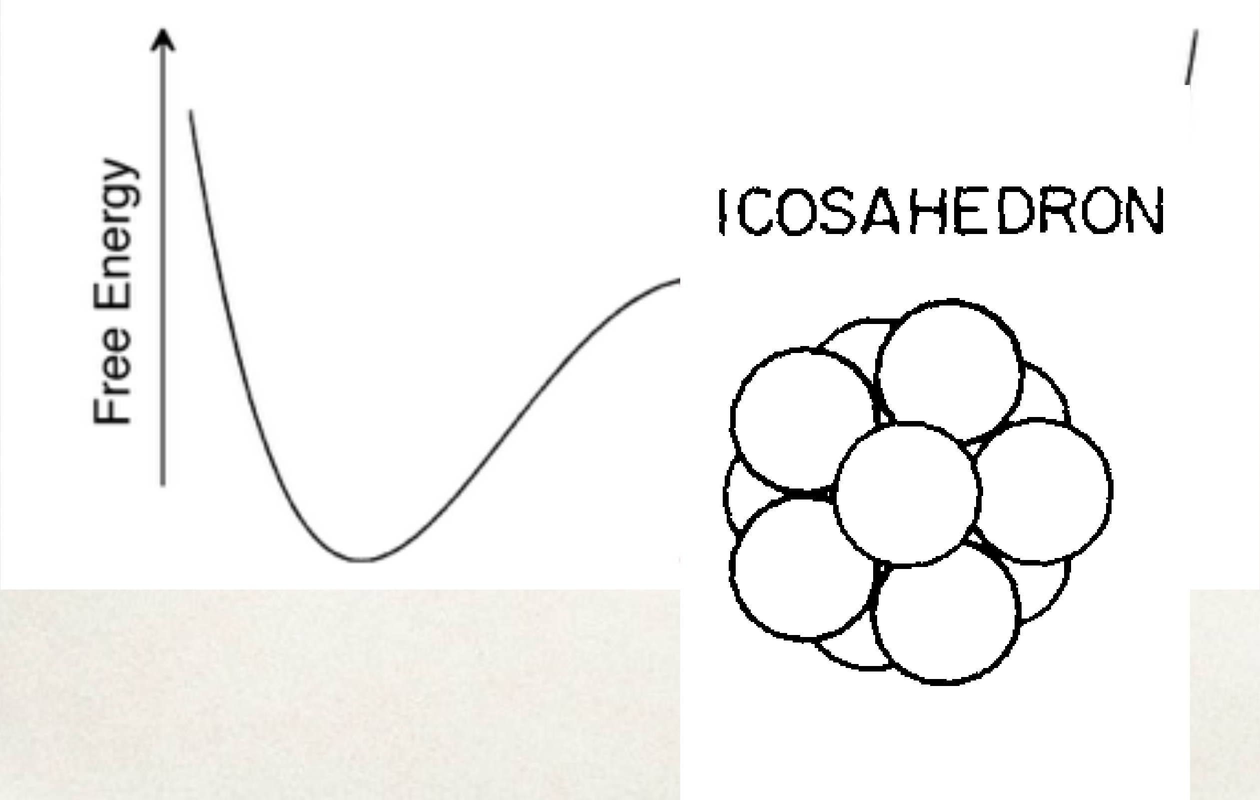

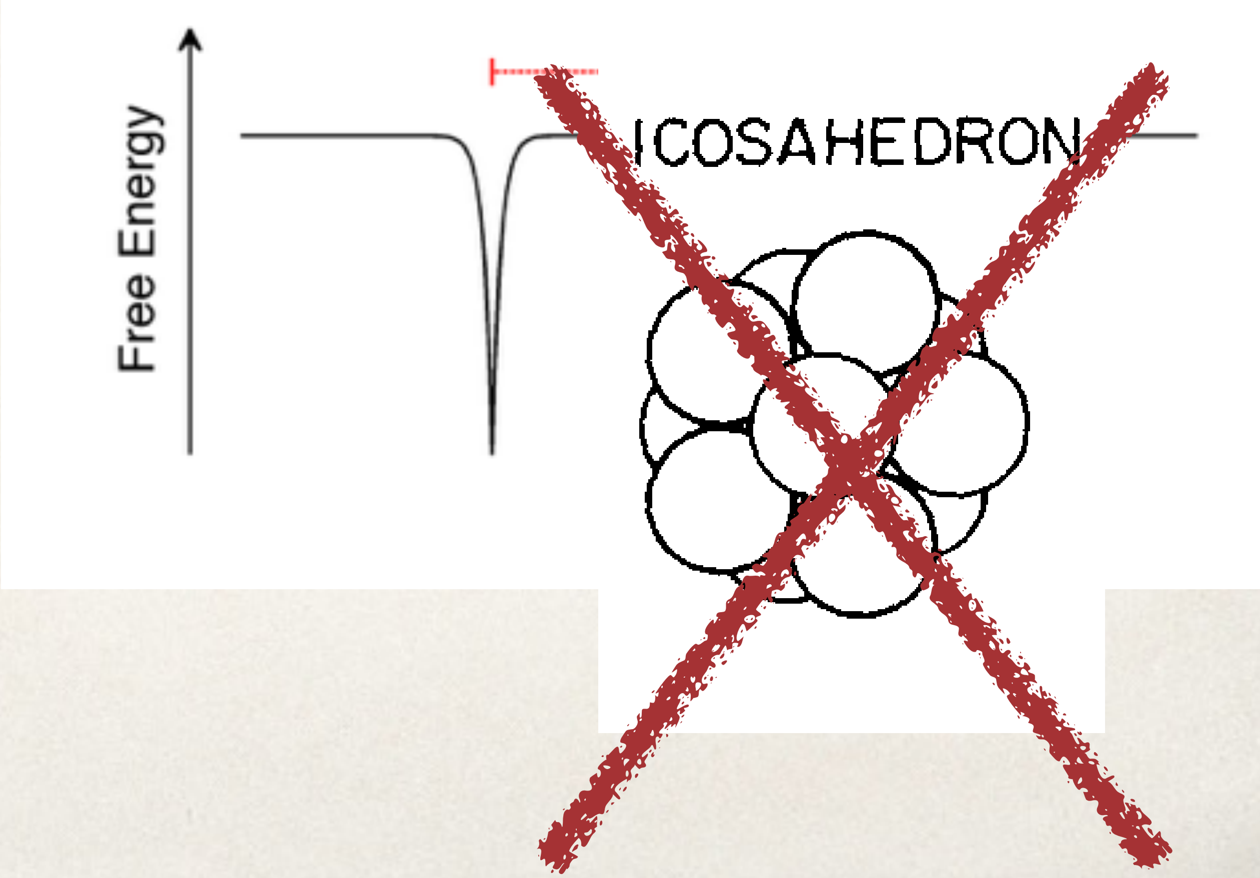

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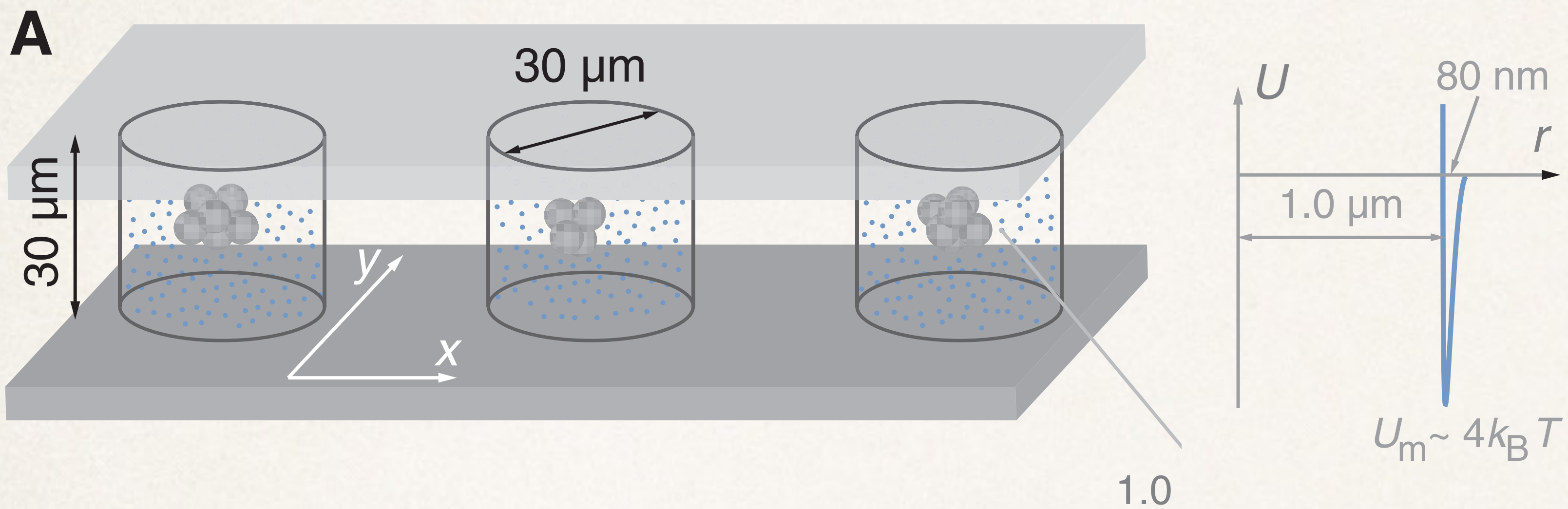

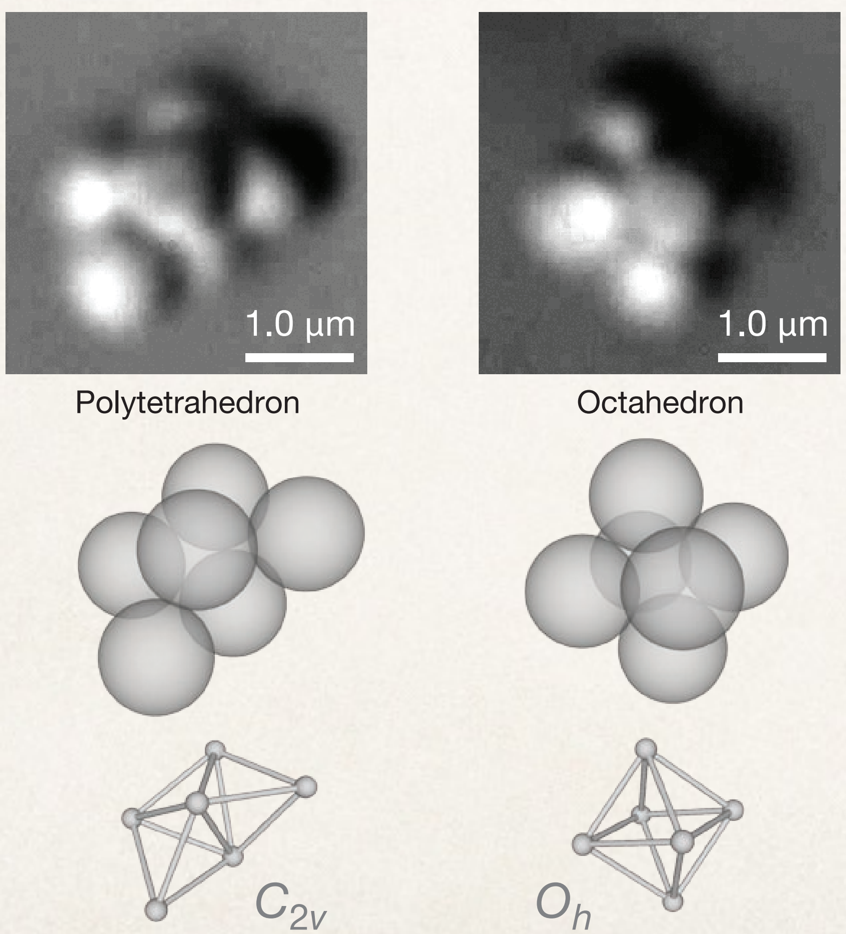

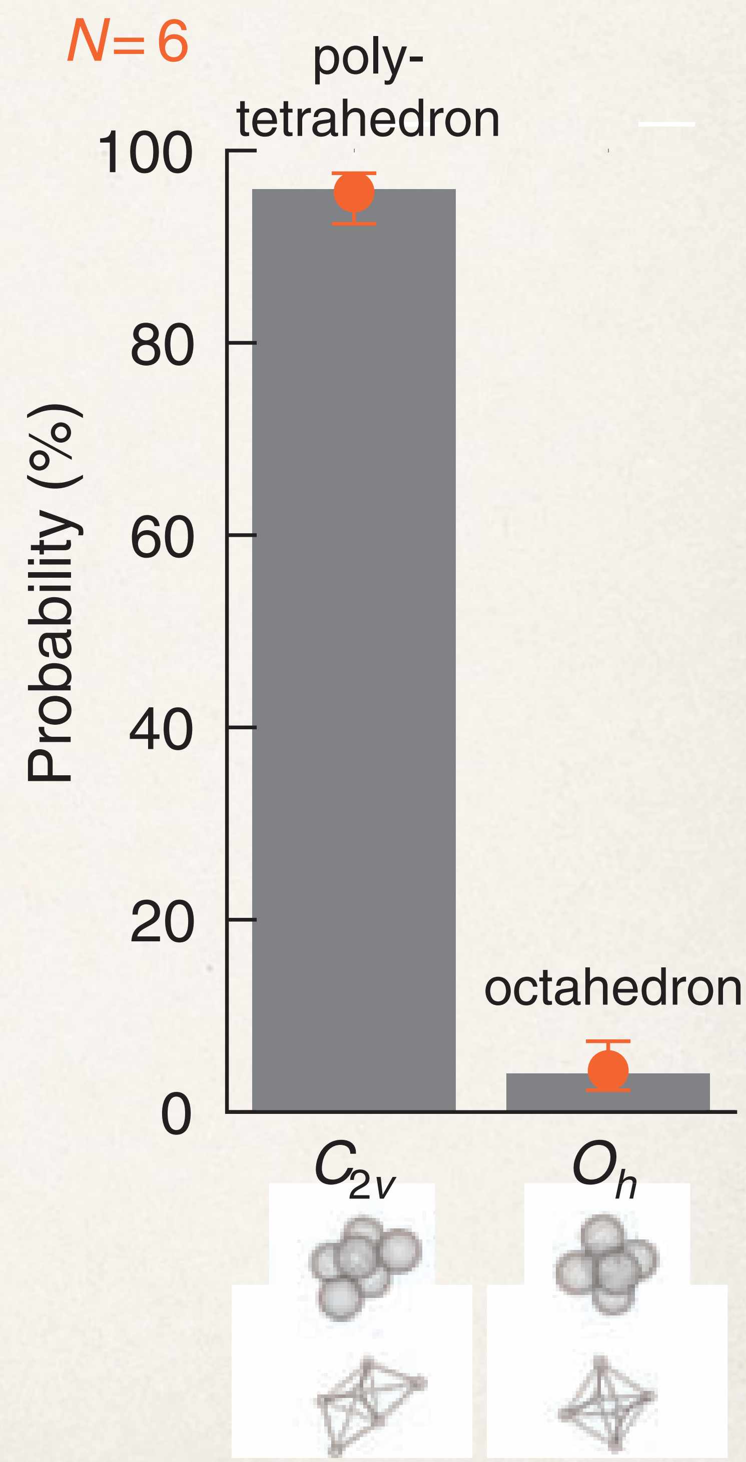

G. Meng, N. Arkus, M. P. Brenner, V. N. Manoharan, Science 327 (2010)

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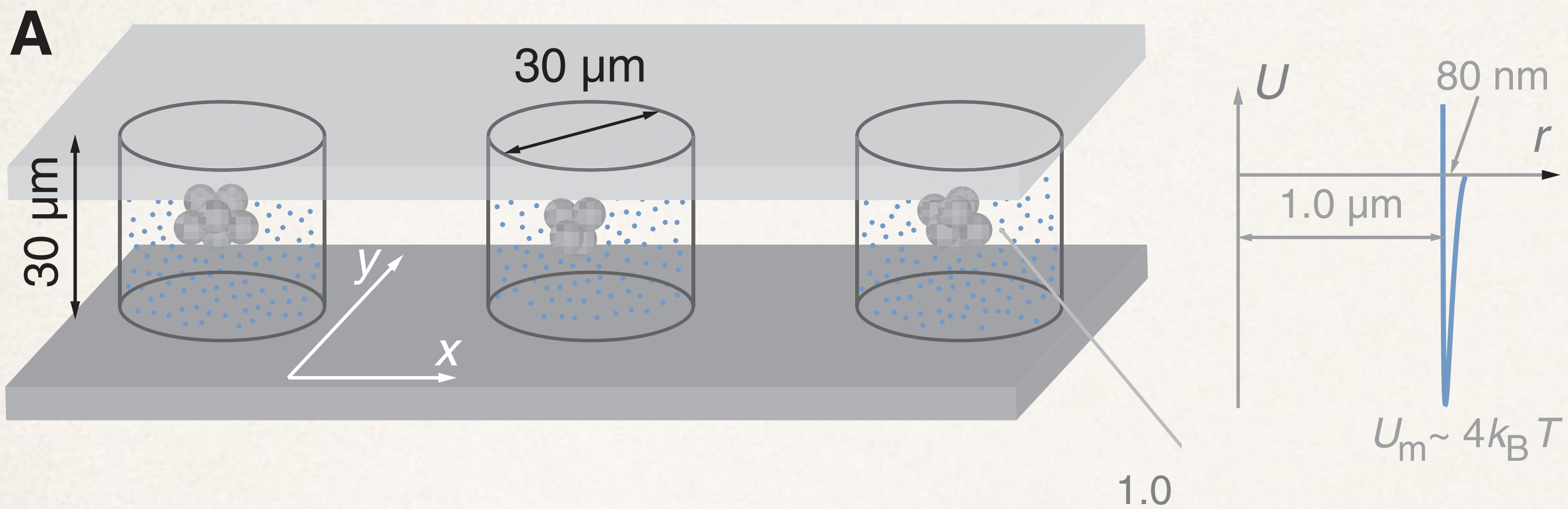
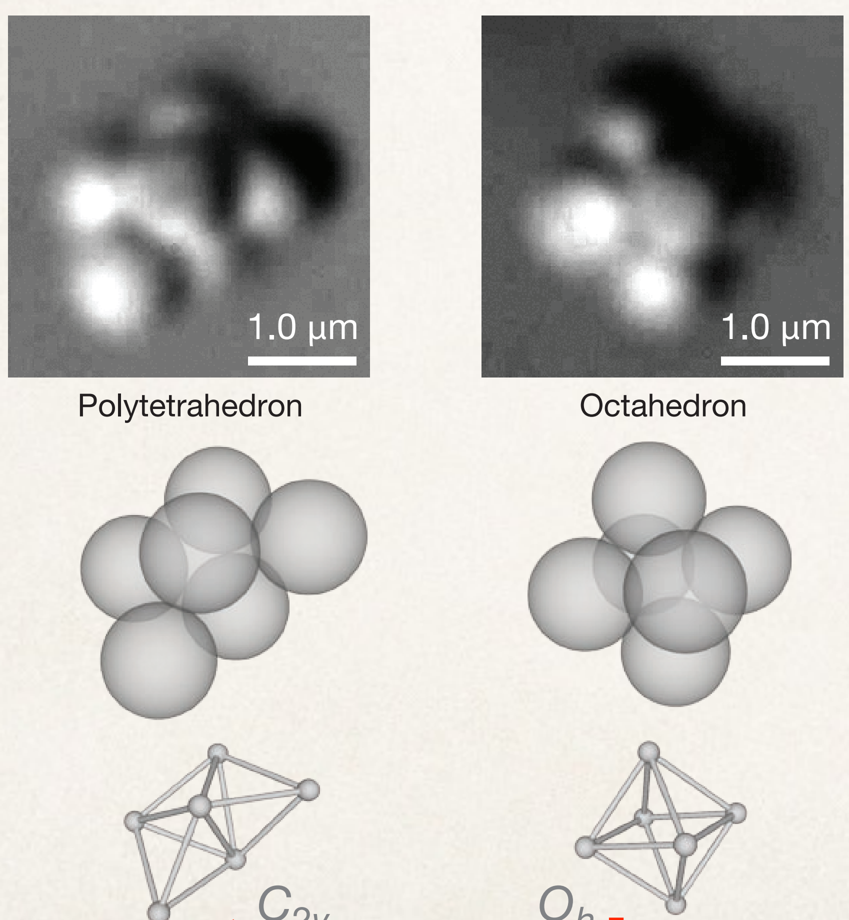
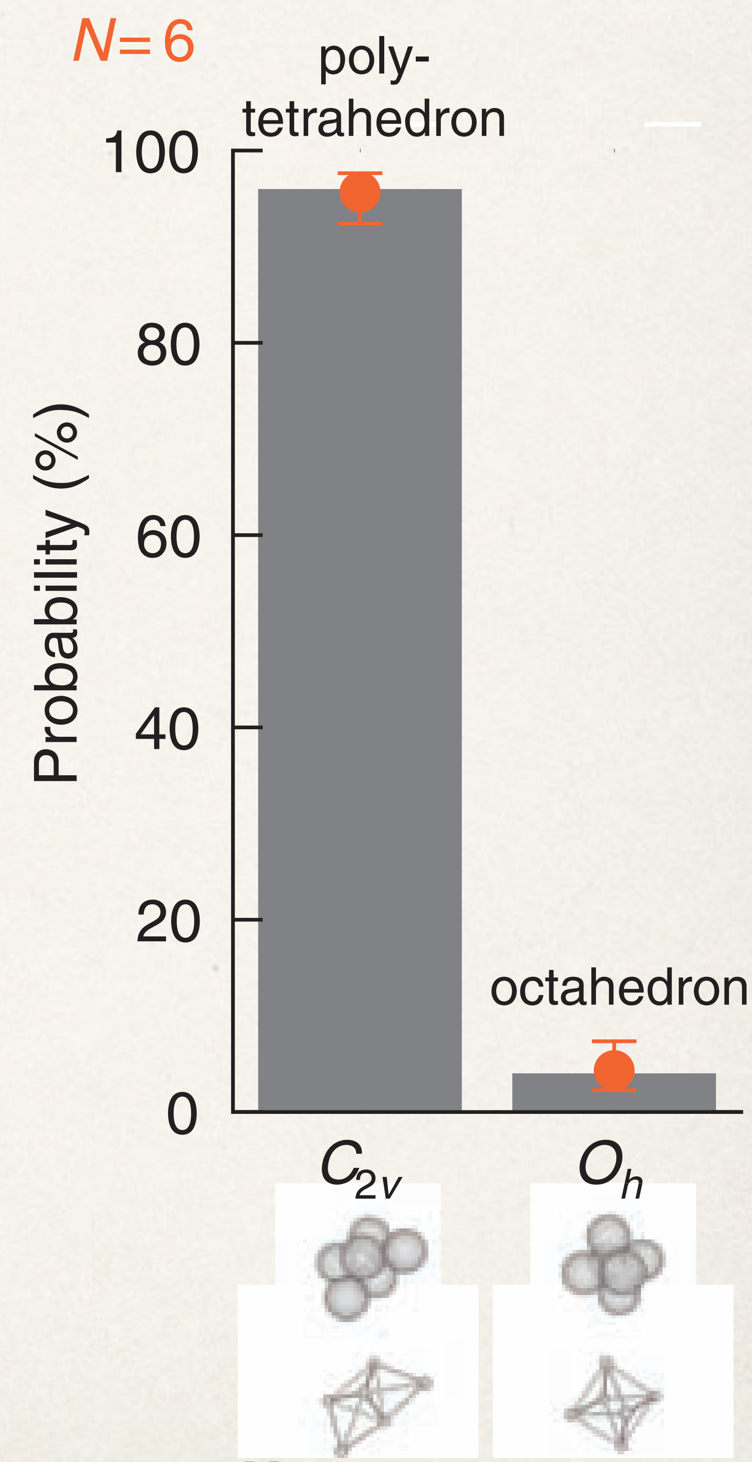






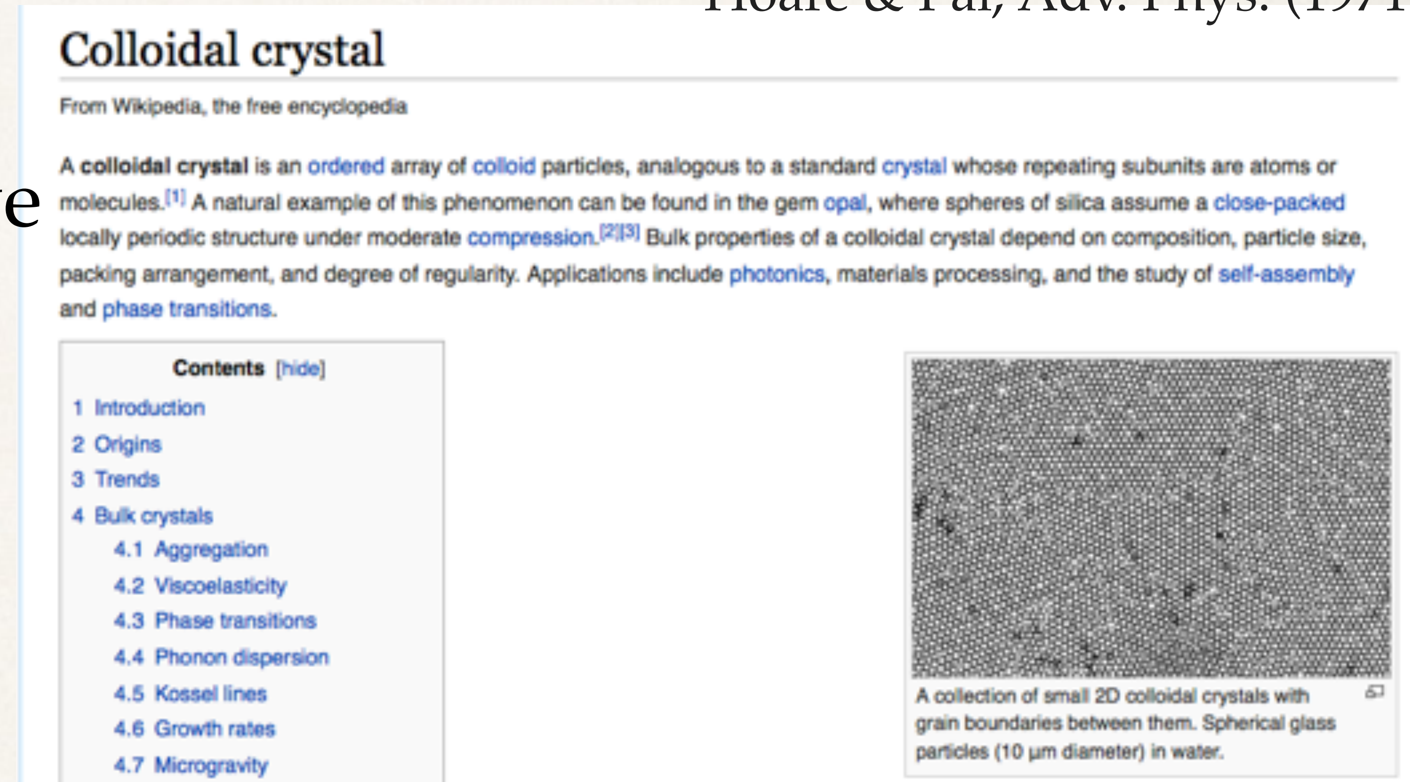
Symmetry number explained the huge discrepancy!

G. Meng, N. Arkus, M. P. Brenner, V. N. Manoharan, Science 327 (2010)

(1) Colloids are different from atoms

Colloids: asymmetric states
Atoms: symmetric states.
Lennard-Jones potential: octahedron is ~8% lower in energy

Hoare & Pal, Adv. Phys. (1971)


Colloidal crystal

From Wikipedia, the free encyclopedia

A **colloidal crystal** is an ordered array of colloid particles, analogous to a standard crystal whose repeating subunits are atoms or molecules.[1] A natural example of this phenomenon can be found in the gem opal, where spheres of silica assume a close-packed locally periodic structure under moderate compression.[2][3] Bulk properties of a colloidal crystal depend on composition, particle size, packing arrangement, and degree of regularity. Applications include photonics, materials processing, and the study of self-assembly and phase transitions.

Contents [hide]

A collection of small 2D colloidal crystals with grain boundaries between them. Spherical glass particles (10 μm diameter) in water.

(2) Small groups of colloids behave differently from large ones

Small: disordered
Large: crystals

Frustration = competition between asymmetric/disordered, and crystalline state.

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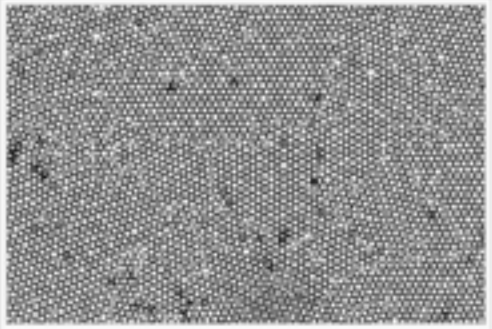


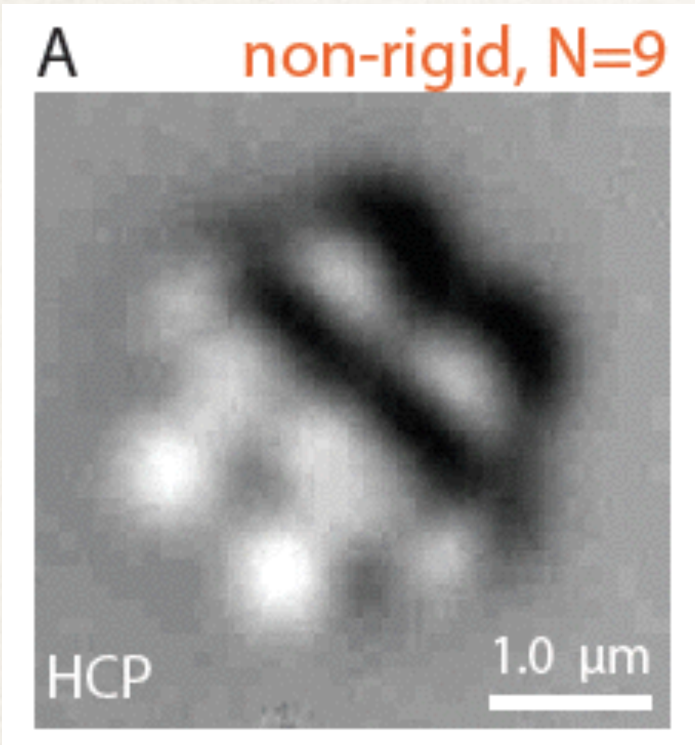
A collection of small 2D colloidal crystals with grain boundaries between them. Spherical glass particles (10 μm diameter) in water.

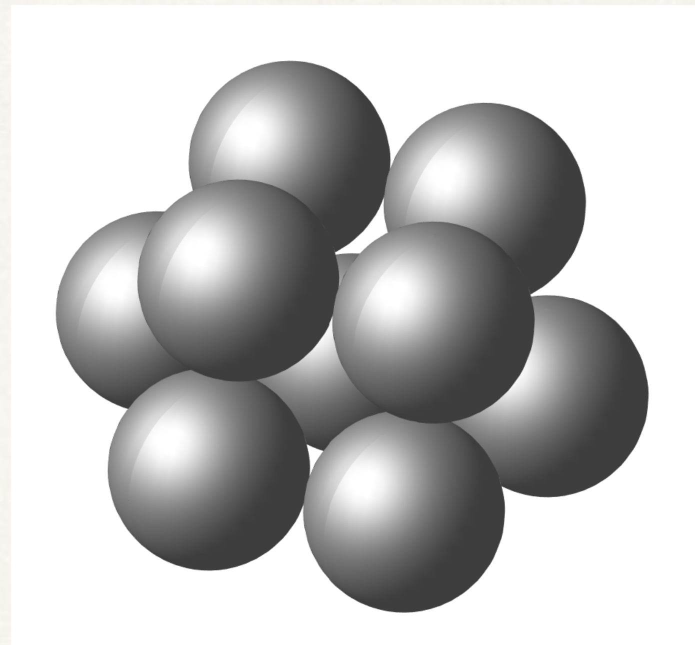
Frustration = competition between asymmetric/disordered, and crystalline state.

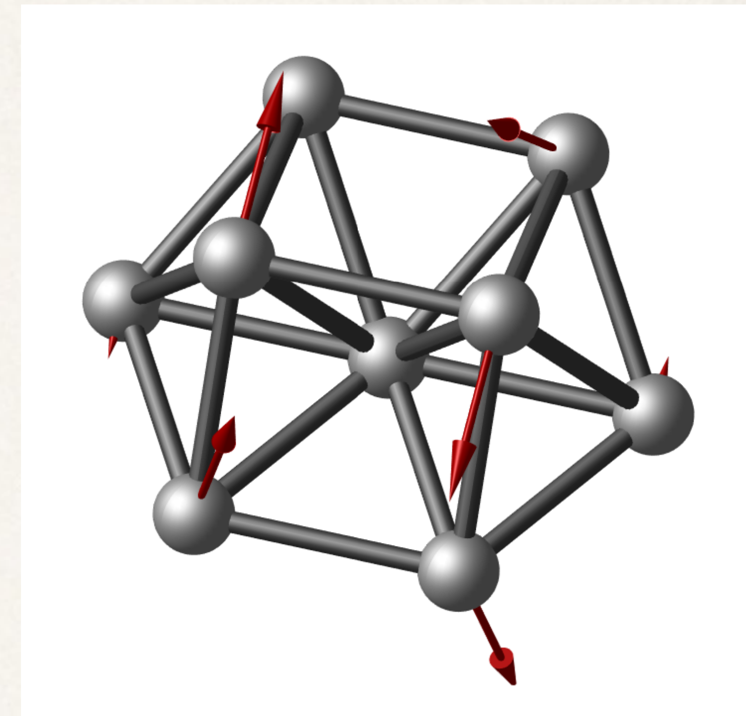
but…. these systems were small.

<u>Goal</u>: show a different kind of competition for higher N (N ≥ 10)
show symmetry is not that important

Data for N=9



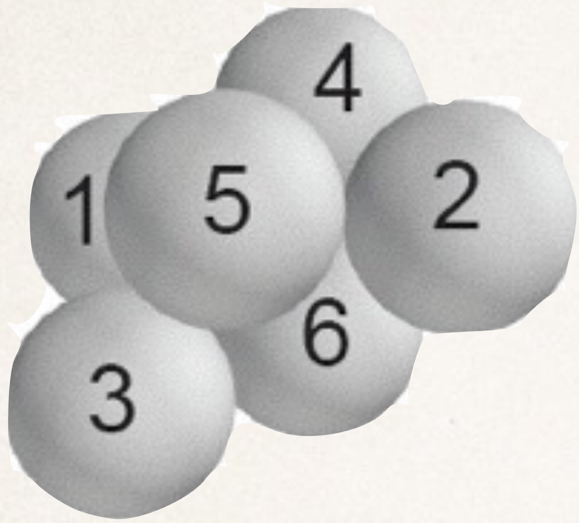


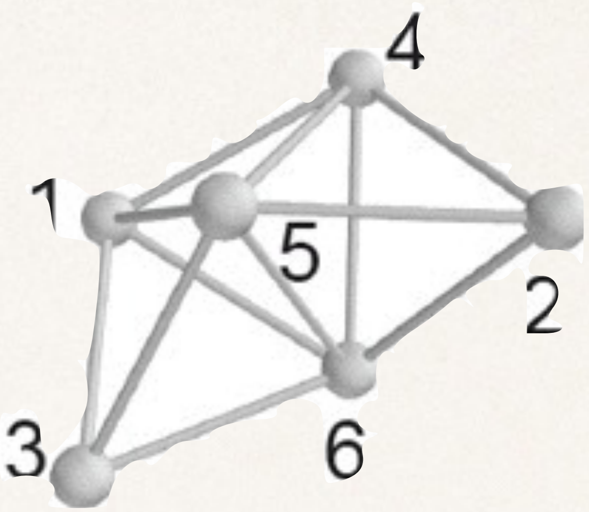


G. Meng, N. Arkus, M. P. Brenner, V. N. Manoharan, Science 327 (2010)

- One cluster dominated — probability = 11%! (out of 52 clusters total)
- It has a fair amount of symmetry —> symmetry cannot be that important…
- Seems to be "floppy" — has an infinitesimal zero mode.
- *Important property* — it's not actually floppy — it's rigid!

What is rigid?





adjacency matrix A

$$\begin{pmatrix} 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 1 \\ 1 & 1 & 1 & 1 & 1 & 0 \end{pmatrix}$$

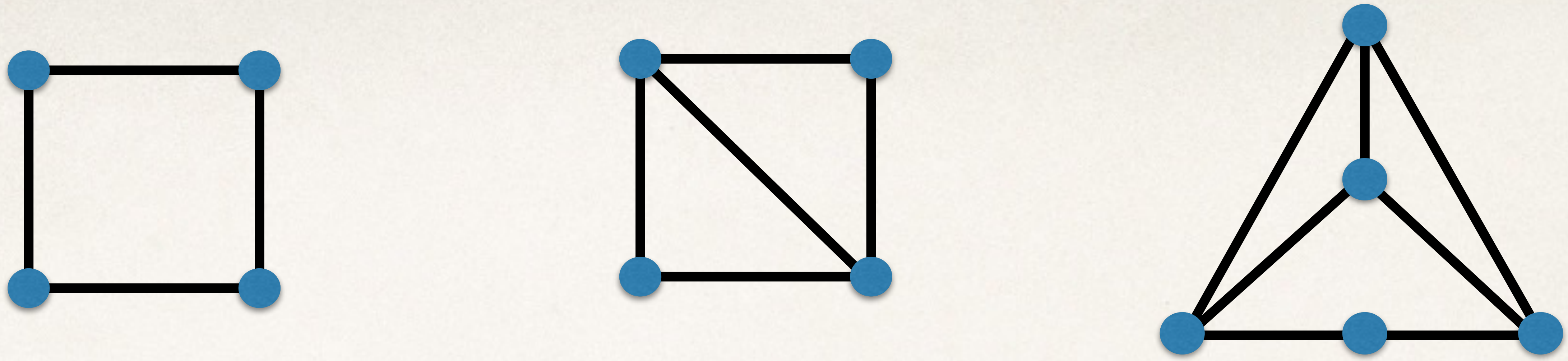
- Each adjacency matrix corresponds to a system of quadratic equations and inequalities ($x_i \in \mathbb{R}^3$):

$$|x_i - x_j|^2 = d^2 \qquad \text{if } A_{ij} = 1$$

$$|x_i - x_j|^2 \geq d^2 \qquad \text{if } A_{ij} = 0$$

- A cluster (x,A) with $x = (x_1, x_2, \ldots, x_N)$ is *rigid* if it is an isolated solution to this system of equations (modulo translations, rotations) (e.g. Asimow&Roth 1978)
$\Leftrightarrow$ There is no finite, continuous deformation of the cluster that preserves all edge lengths.
- It is *first order rigid* if it is rigid and the equations above are linearly independent
$\Leftrightarrow$ rigid and there are no infinitesimal zero-modes in the above equations

Quiz!



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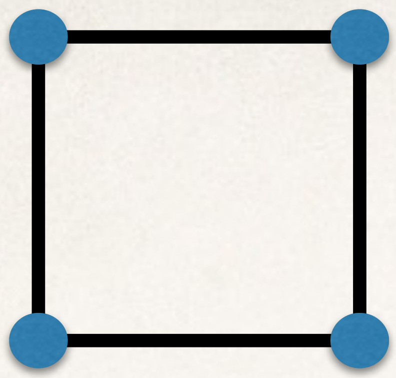
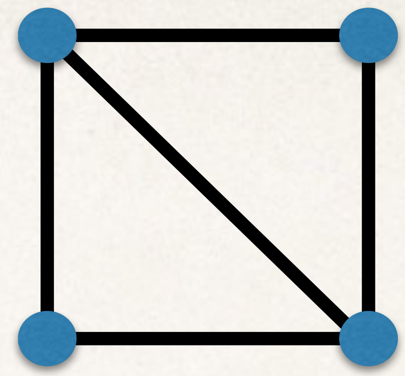
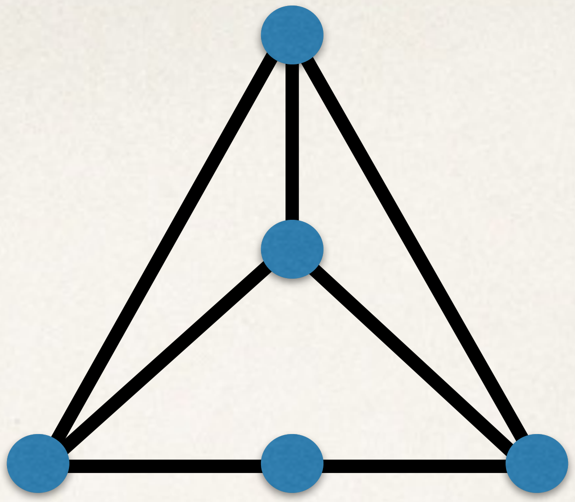


floppy (in R^2,R^3)





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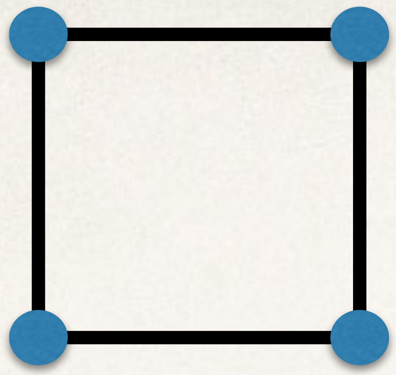

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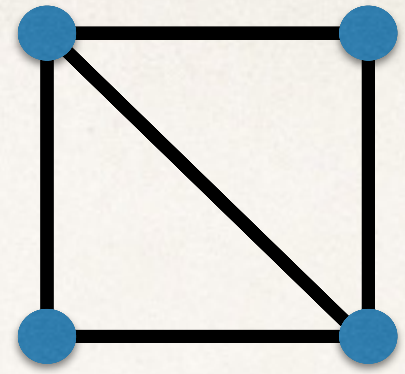
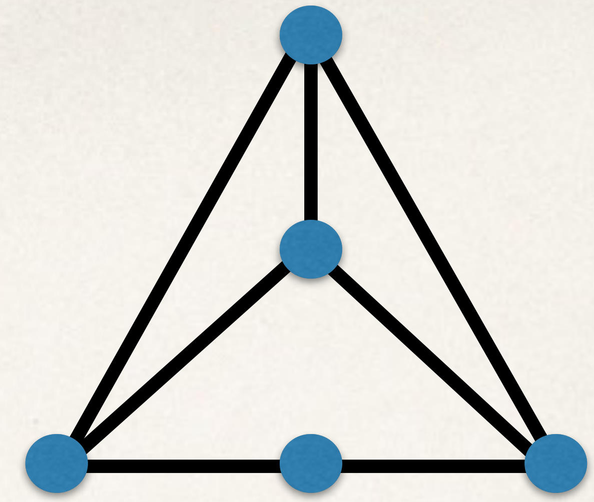
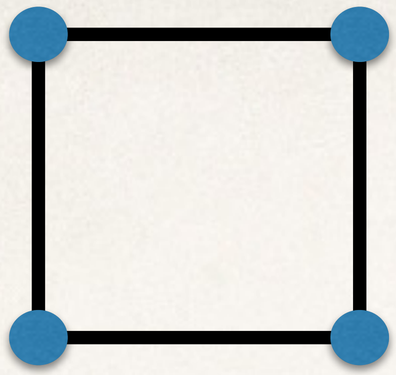


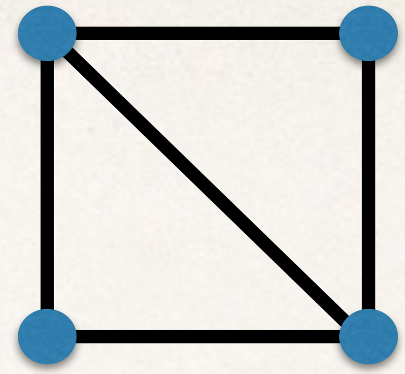
first-order rigid (in R^2)
floppy (in R^3)



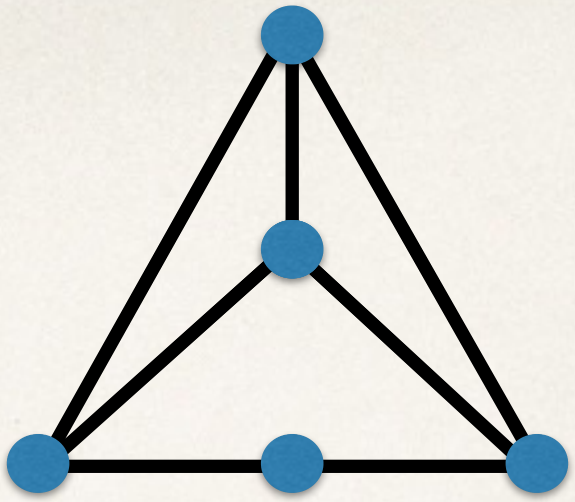
Quiz!



floppy (in R^2,R^3)

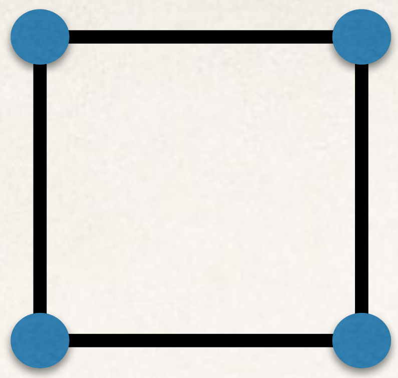


first-order rigid (in R^2)
floppy (in R^3)

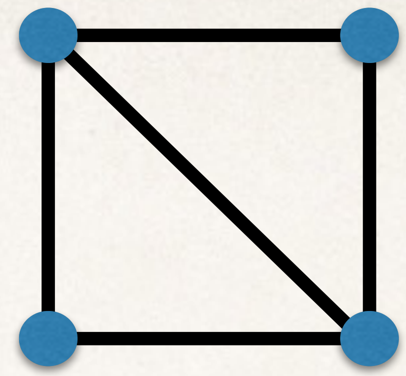


rigid (R^2)
not first-order rigid (R^2)

Quiz!



floppy (in R^2,R^3)



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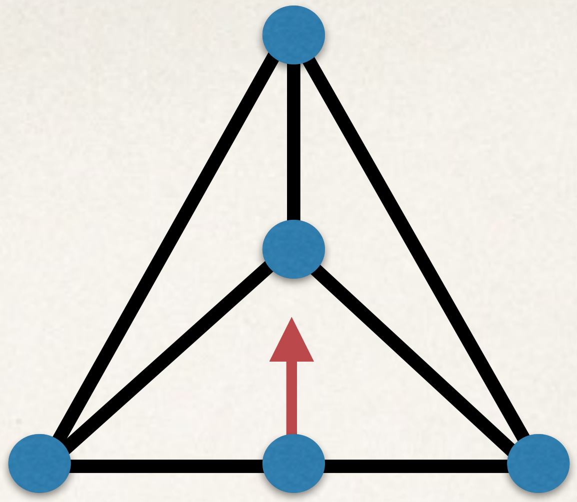

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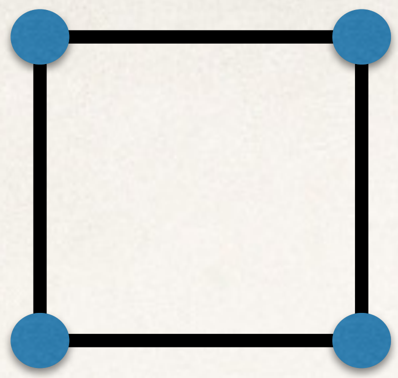

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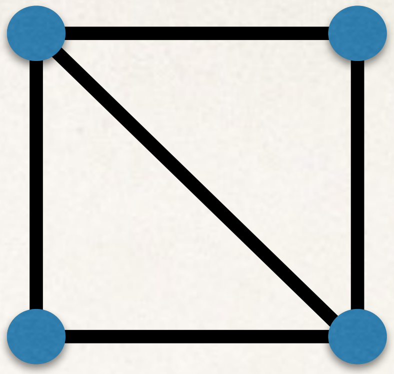

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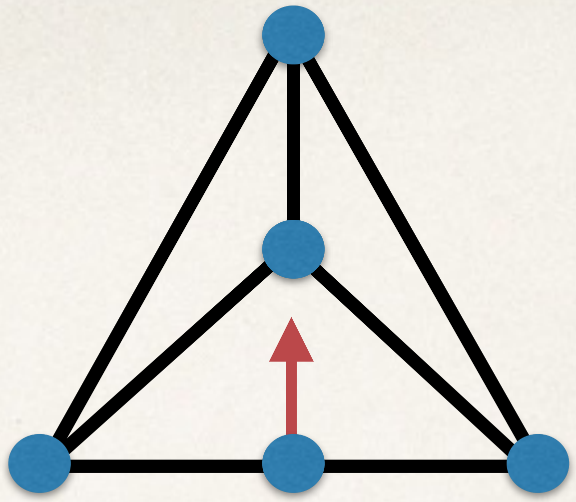
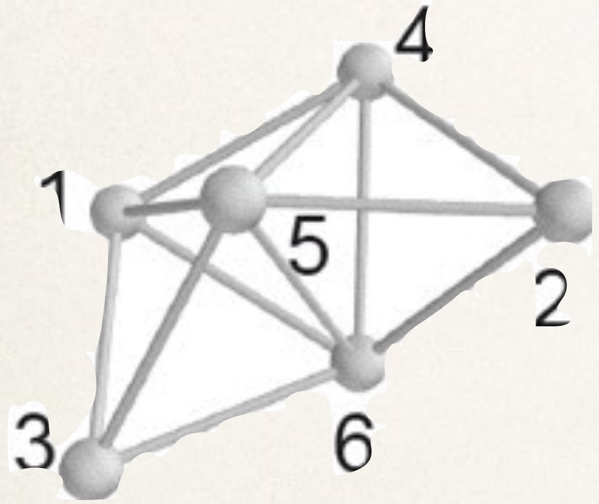
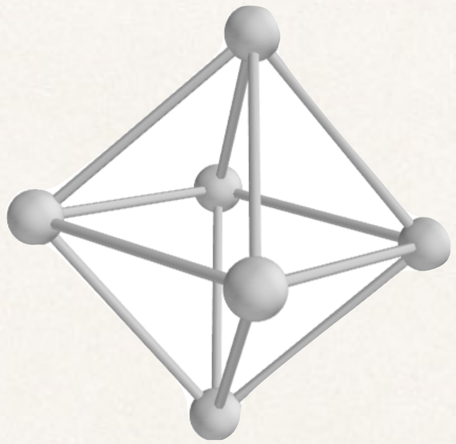
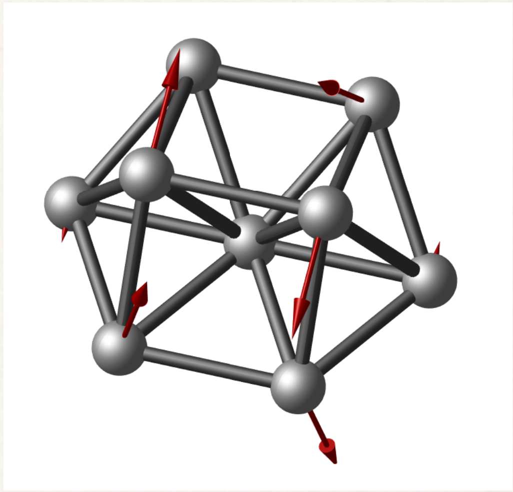
floppy (in R^3)



rigid (R^2)
not first-order rigid (R^2)







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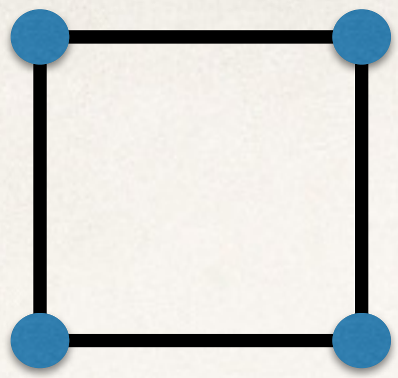
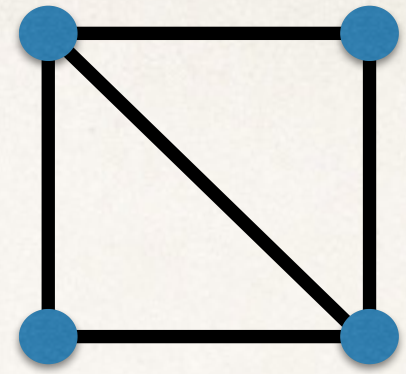
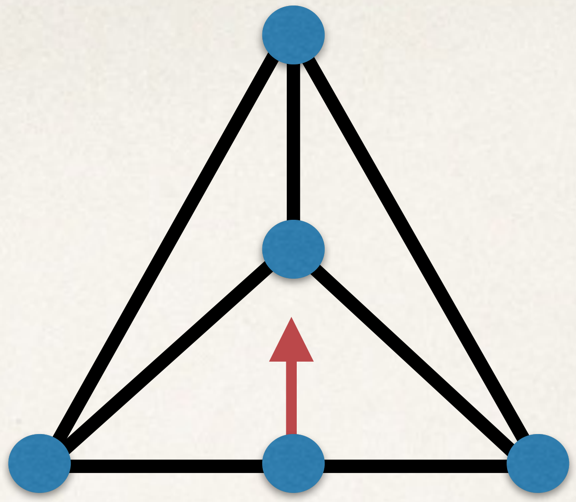


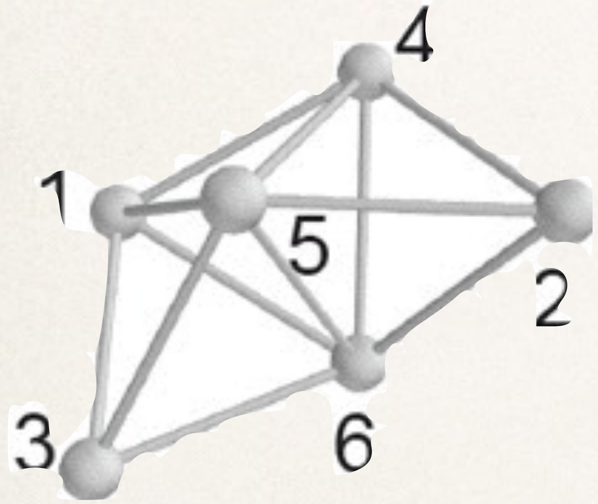
floppy (in R^2,R^3)



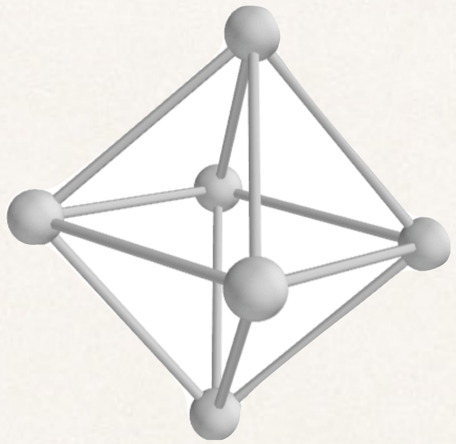
first-order rigid (in R^2)
floppy (in R^3)

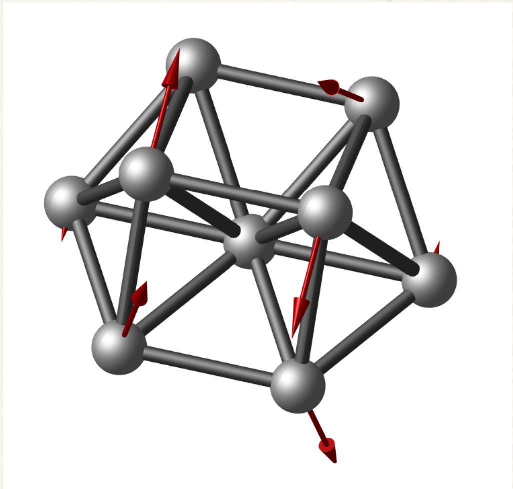


rigid (R^2)
not first-order rigid (R^2)

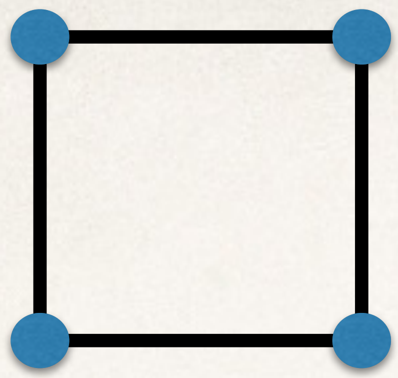


first-order rigid (in R^3)





Quiz!



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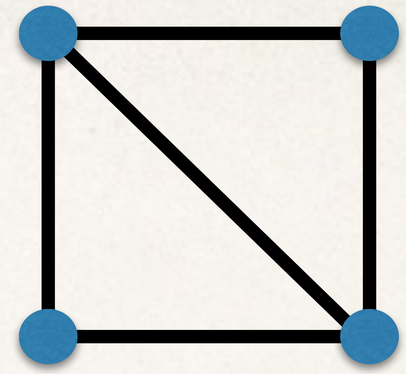
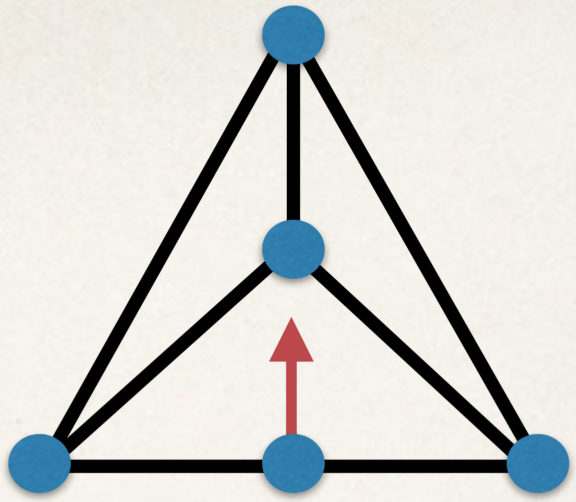
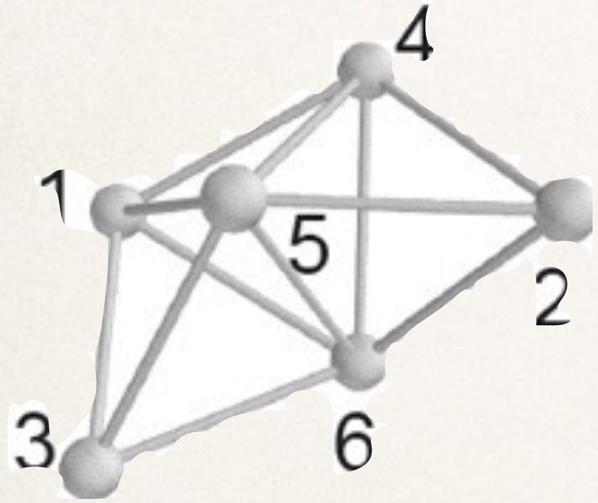


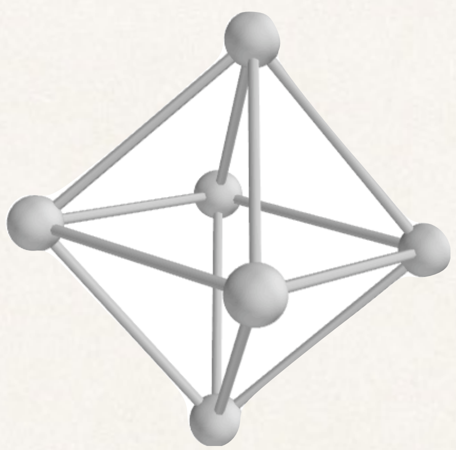
first-order rigid (in R^2)
floppy (in R^3)



rigid (R^2)
not first-order rigid (R^2)



first-order rigid (in R^3)



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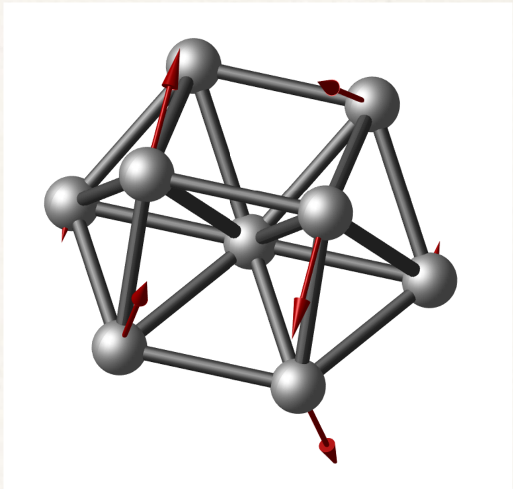
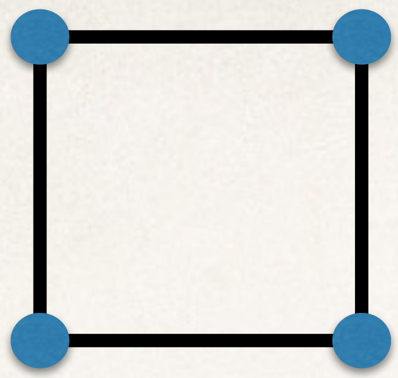
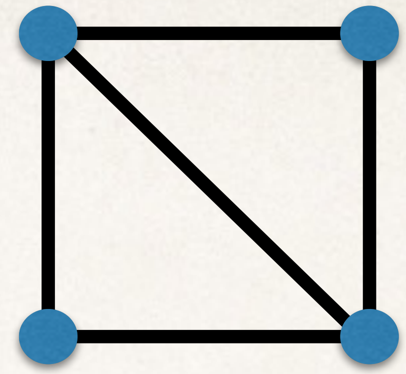


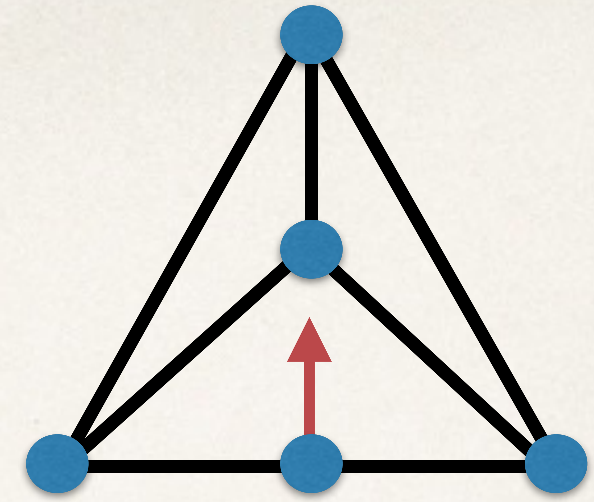
Quiz!



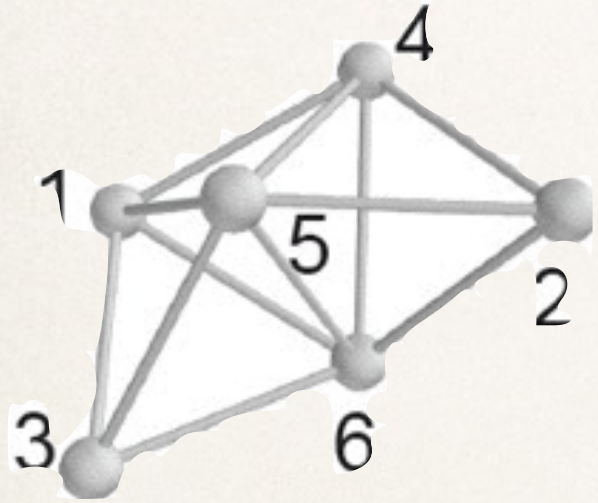
floppy (in R^2,R^3)



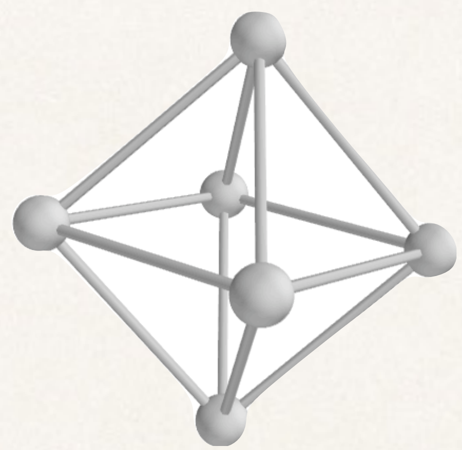
first-order rigid (in R^2)
floppy (in R^3)



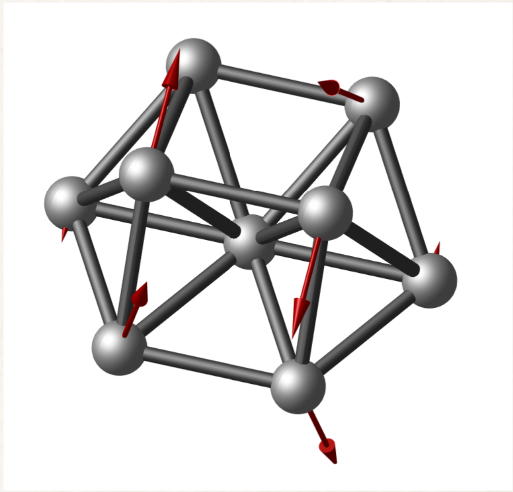
rigid (R^2)
not first-order rigid (R^2)



first-order rigid (in R^3)

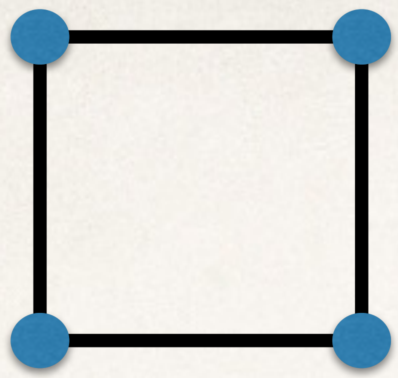


first-order rigid (in R^3)

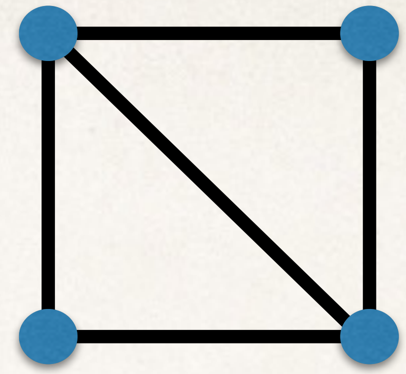


rigid (R^3)
not first-order rigid (R^3)

Quiz!



floppy (in R^2,R^3)



first-order rigid (in R^2)
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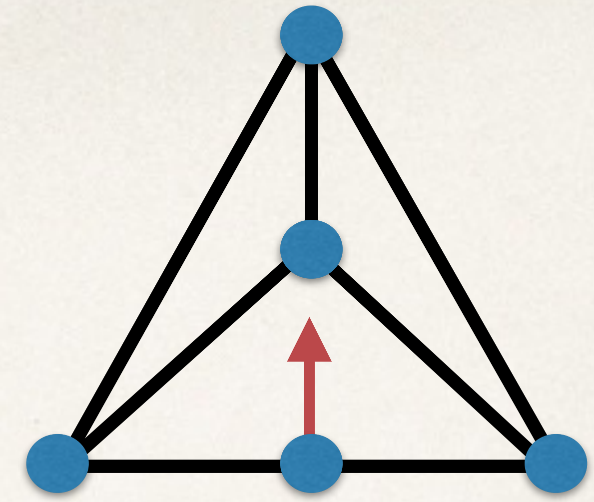

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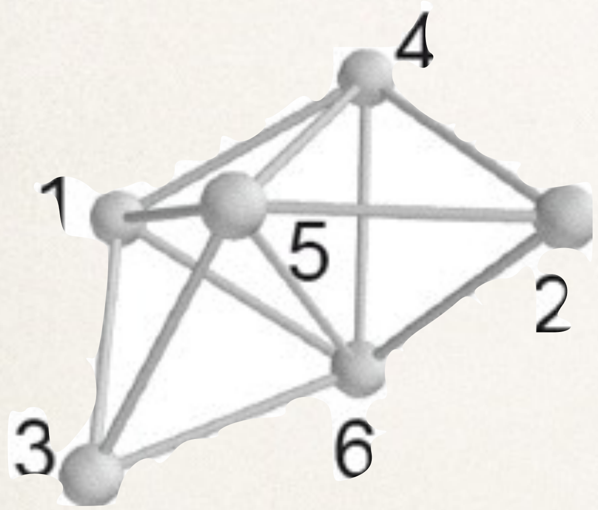

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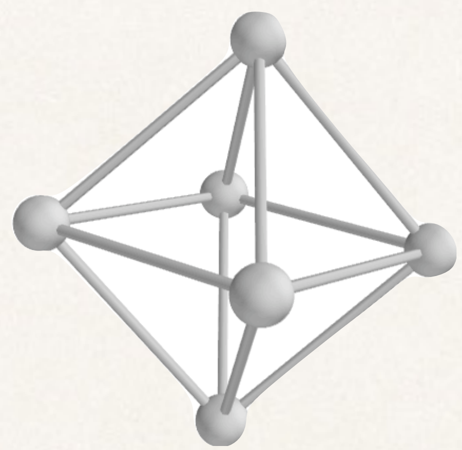

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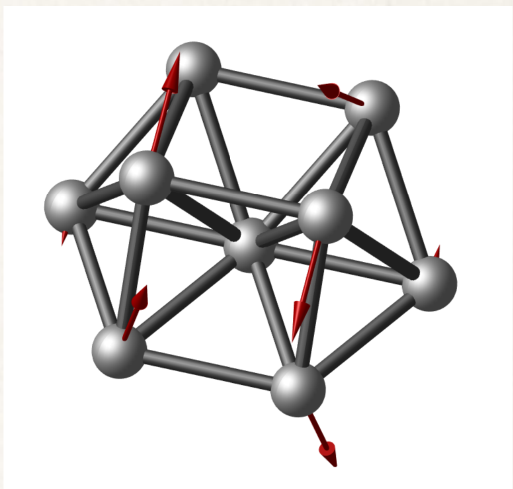
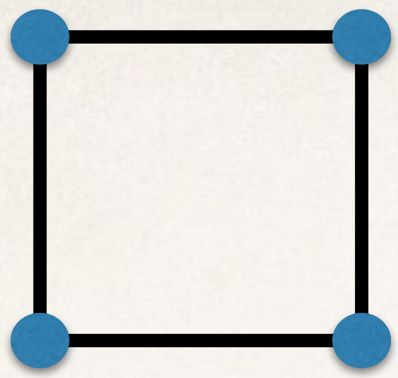


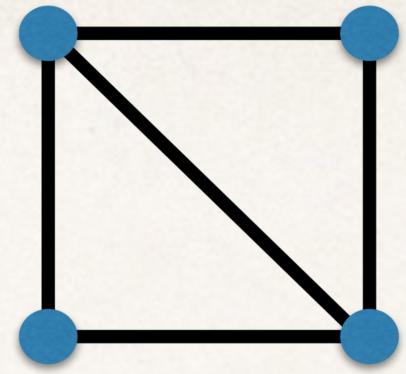
rigid (R^3)
not first-order rigid (R^3)

Singular: rigid but NOT first-order rigid

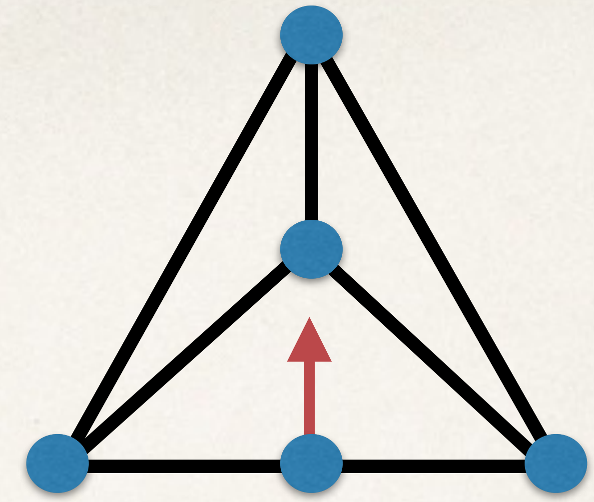
Quiz!



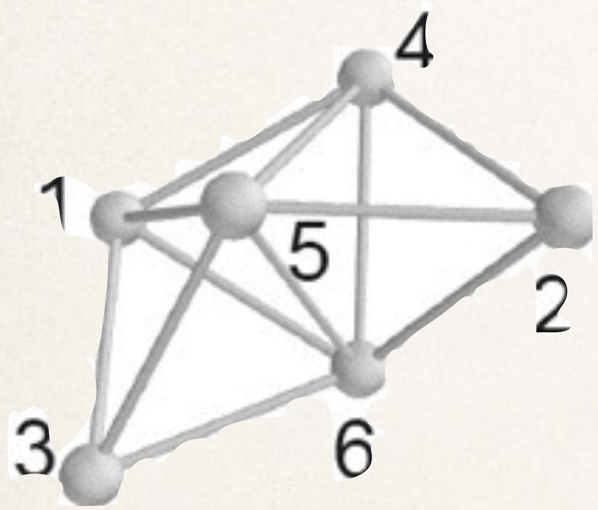
floppy (in R^2,R^3)



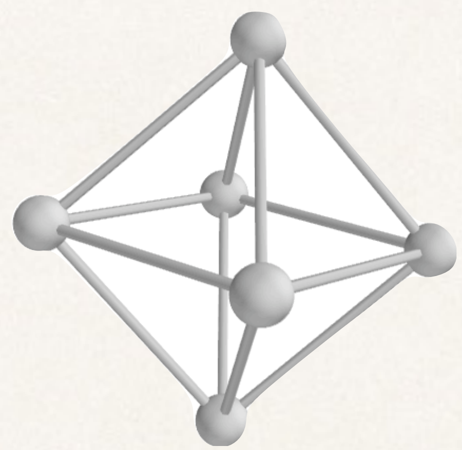
first-order rigid (in R^2)
floppy (in R^3)



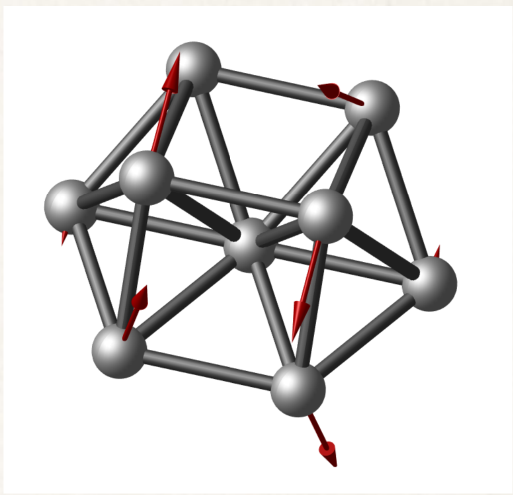
rigid (R^2)
not first-order rigid (R^2)



first-order rigid (in R^3)



first-order rigid (in R^3)



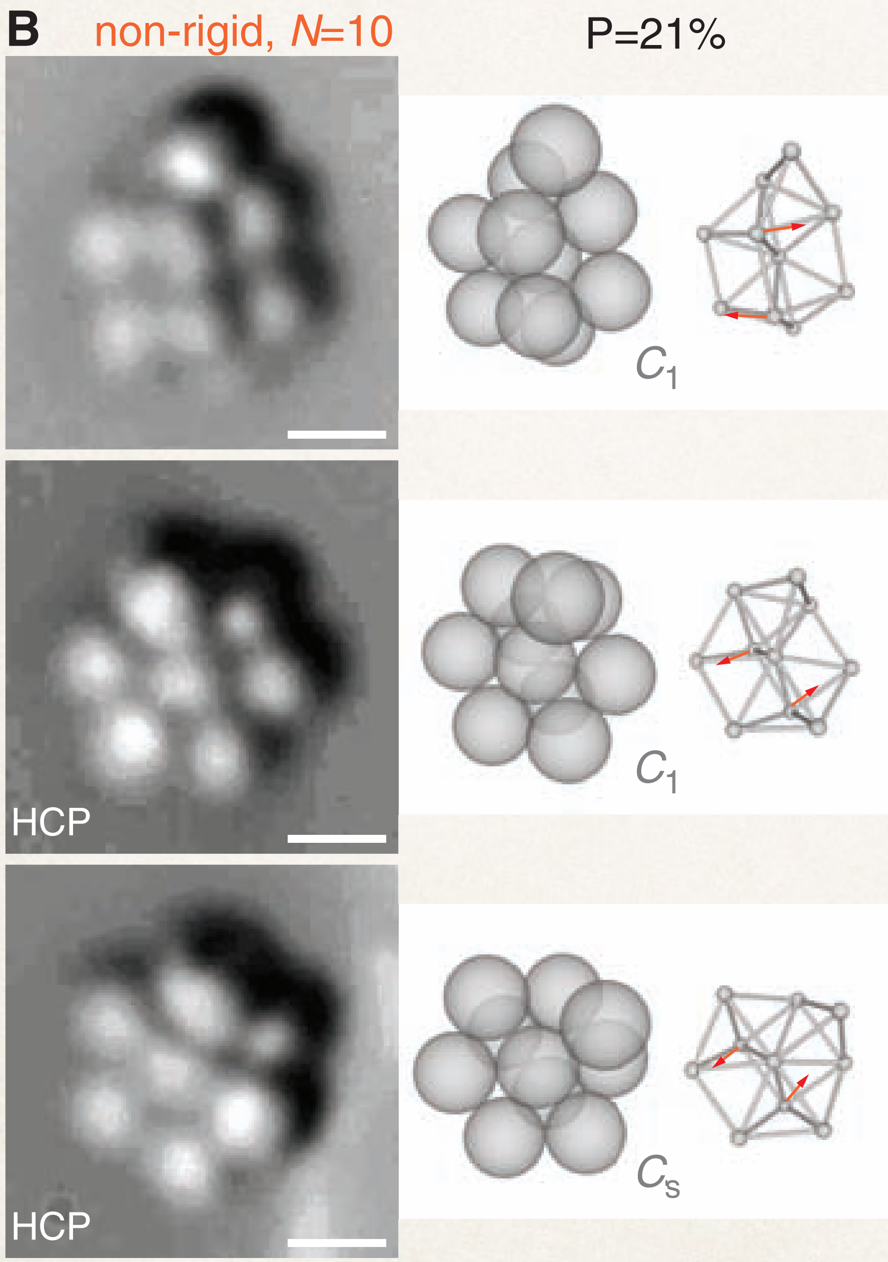
rigid (R^3)
not first-order rigid (R^3)

Singular: rigid but NOT first-order rigid

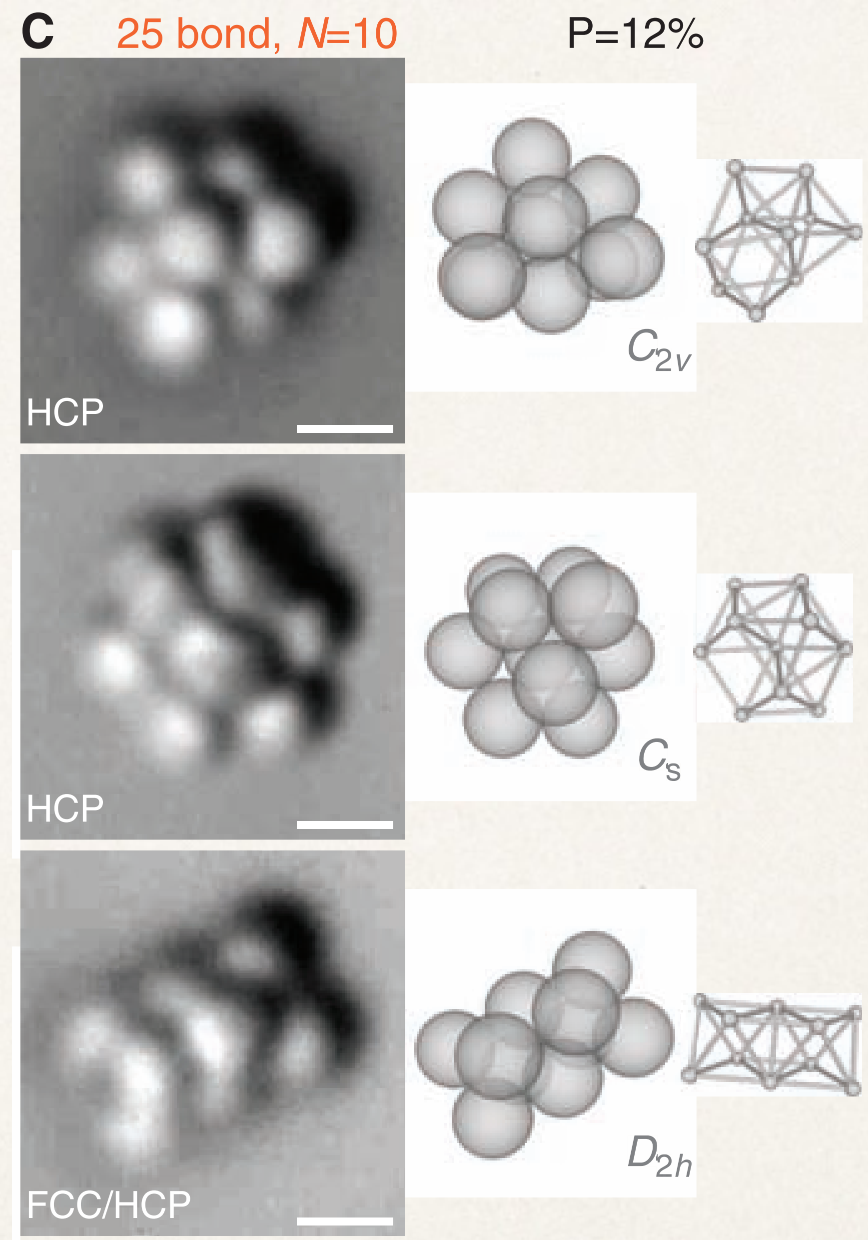
Regular: rigid AND first-order rigid

N=10

Singular clusters:



Hyperstatic clusters:



Singular 21%, Hyperstatic 12%, > 250 total clusters!

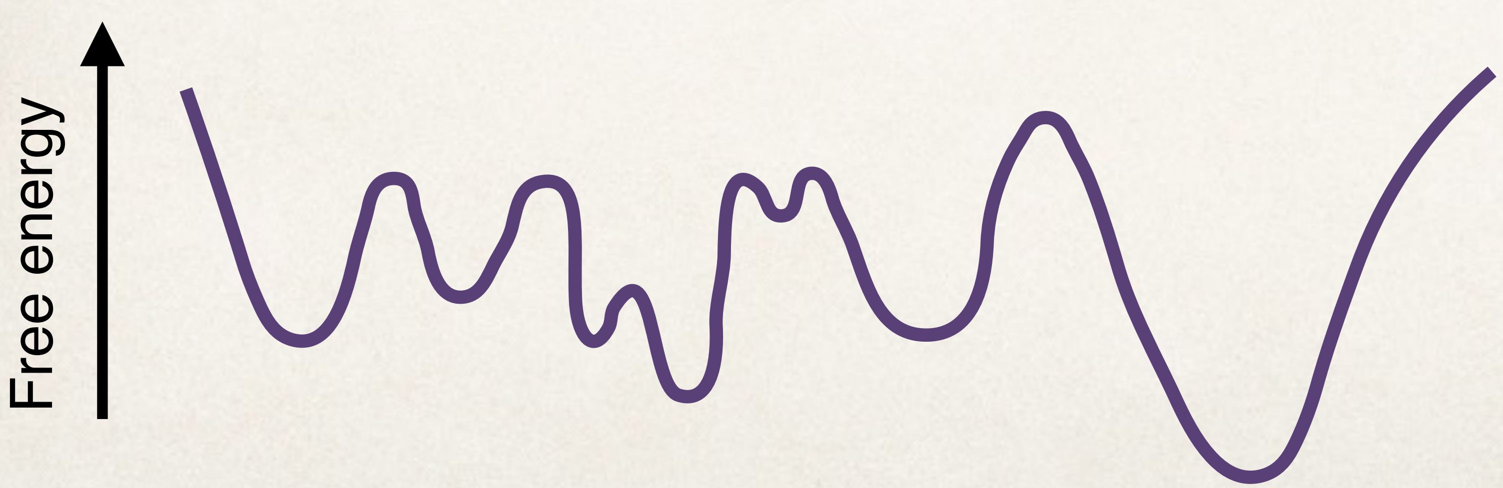
Question:

Is there a competition between singular & hyperstatic clusters as N increases?

What can we say about this competition mathematically?

Strategy:

- Look at all local minima on energy landscape of N sticky spheres
- Evaluate their partition functions
- Compare them

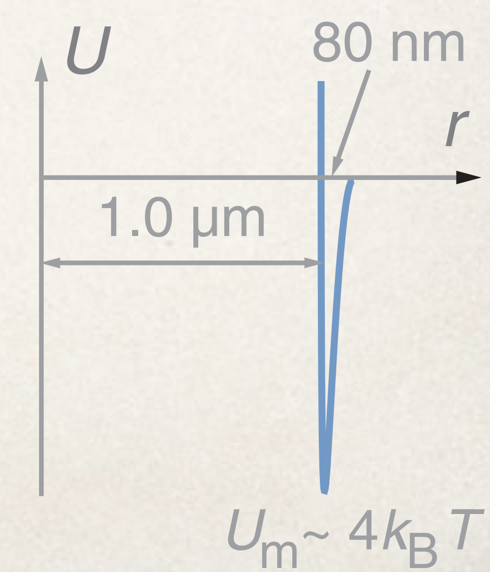


Sticky: interacting with infinitestimally short-ranged (&deep) pair potential

i.e.

range —> 0

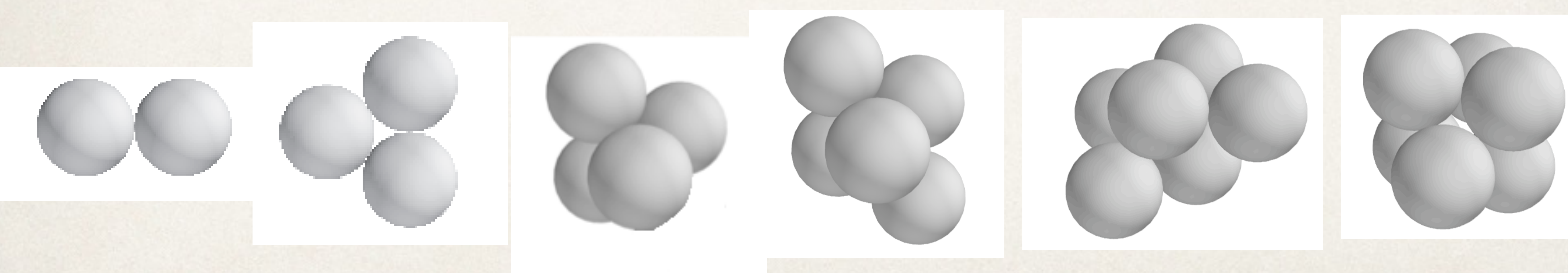
depth—> ∞



What do local minima look like?

Local minima are rigid clusters:

- Spheres are either touching, or not
- Energy of cluster of N spheres ∝ # of contacts
- Lowest-energy clusters = those with maximal number of contacts
- These are (typically) **rigid**: they cannot be continuously deformed without breaking a contact (=crossing an energy barrier.)
- More generally: energetic local minima have a locally maximal number of contacts, so are (typically) rigid.



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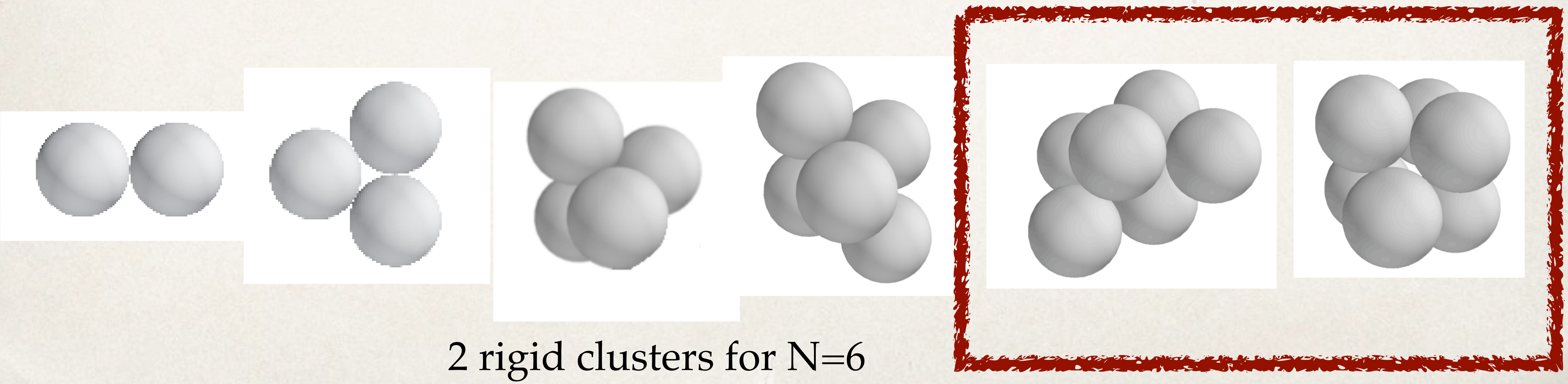

2 rigid clusters for N=6

What are all the rigid clusters of N identical spheres?

H.-C. (2016) *SIAM Review*

Algorithms to find rigid clusters

- List all adjacency matrices with 3N-6 contacts; for each adjacency matrix, solve (analytically or with computer) for the positions of the particles, or argue that no solution exists.
  - N. Arkus, V. N. Manoharan, M. P. Brenner. *Phys. Rev. Lett., 103 (2009)*
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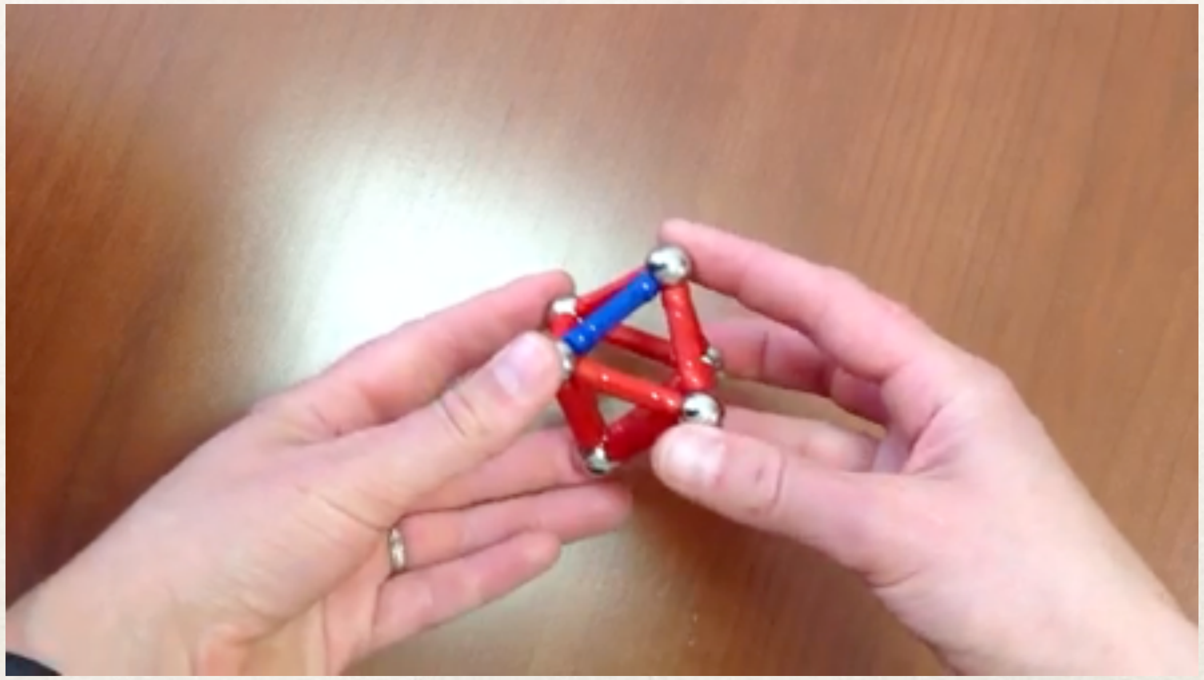
  - R. S. Hoy, J. Harwayne-Gindansky, C. O'Hern, *Phys. Rev. E*, 85 (2012)
  - R. S. Hoy, *Phys. Rev. E*, 91 (2015)

  Analytical: to N=10
  Computer: to N=13 (though many were missed)

- Move from cluster to cluster dynamically, via one-dimensional transition paths
  H.-C., *SIAM Review* (2016)



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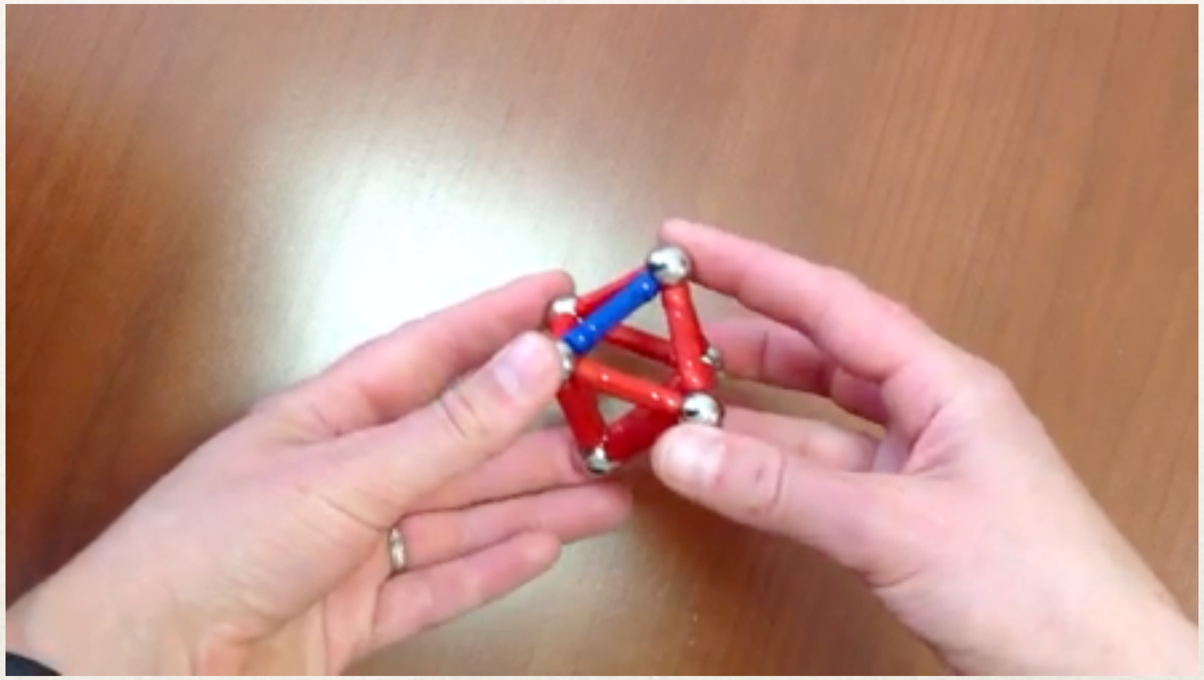
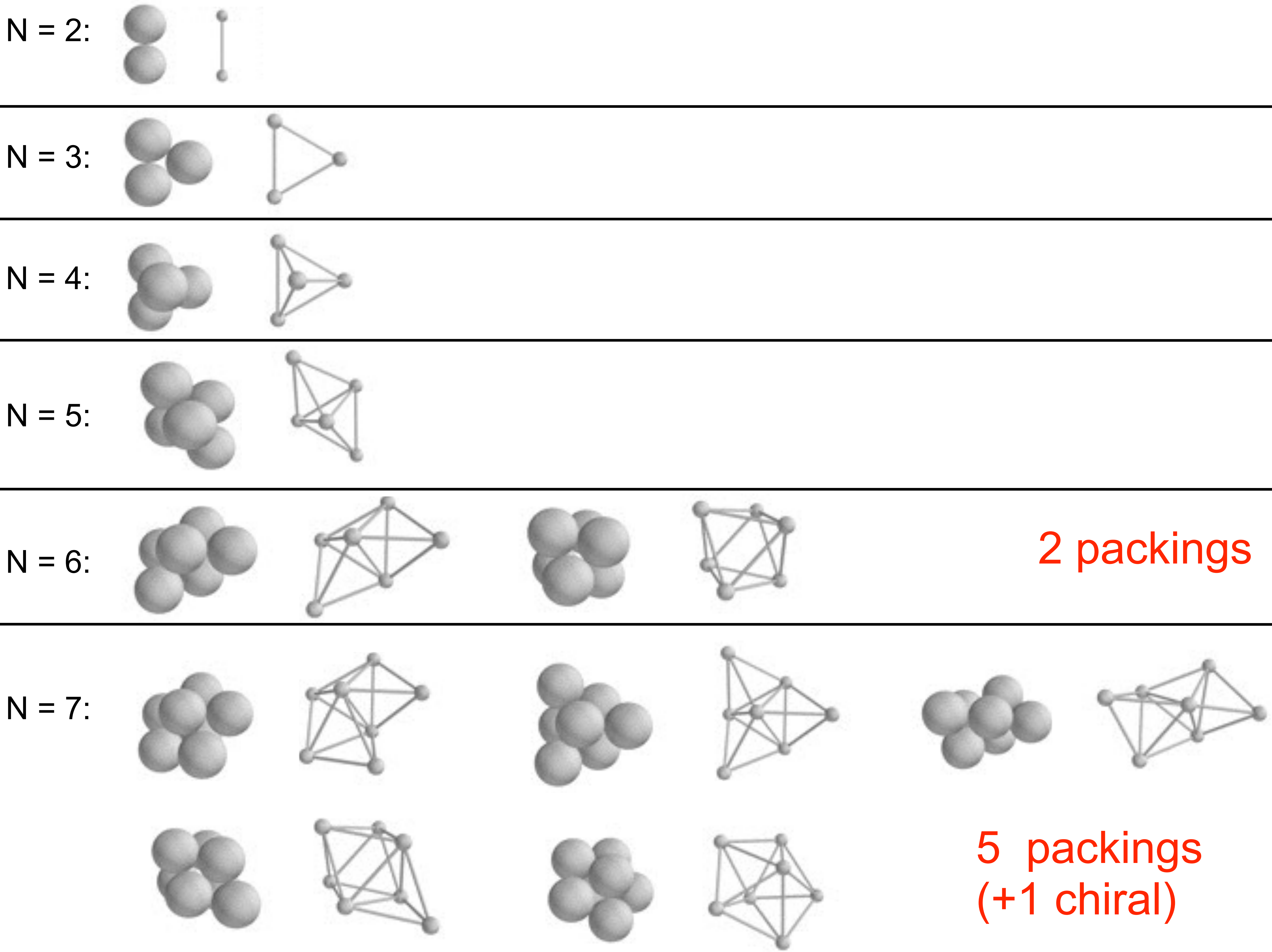
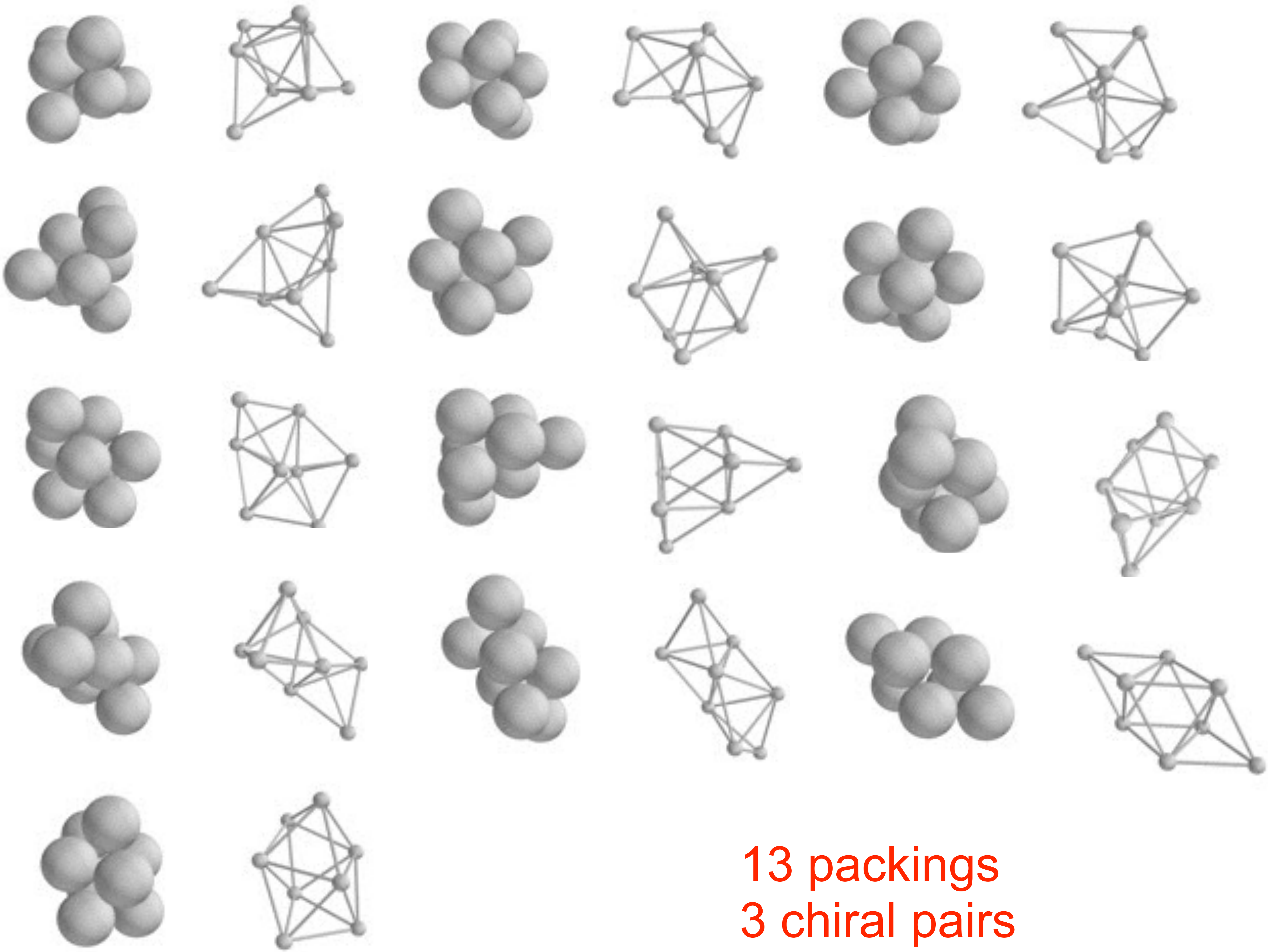


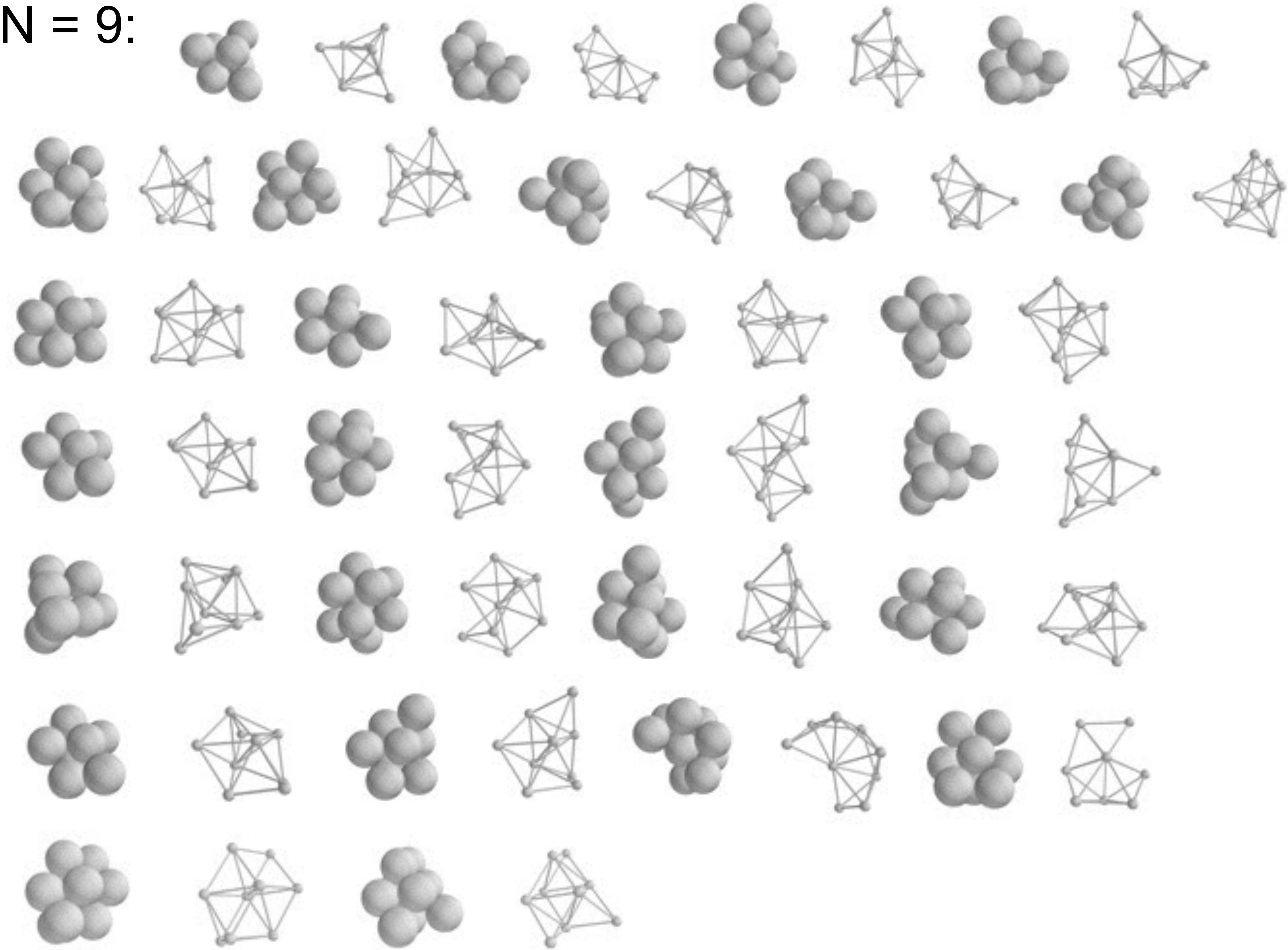

N = 2:
N = 3:
N = 4:
N = 5:
N = 6:
2 packings
N = 7:
5 packings
(+1 chiral)

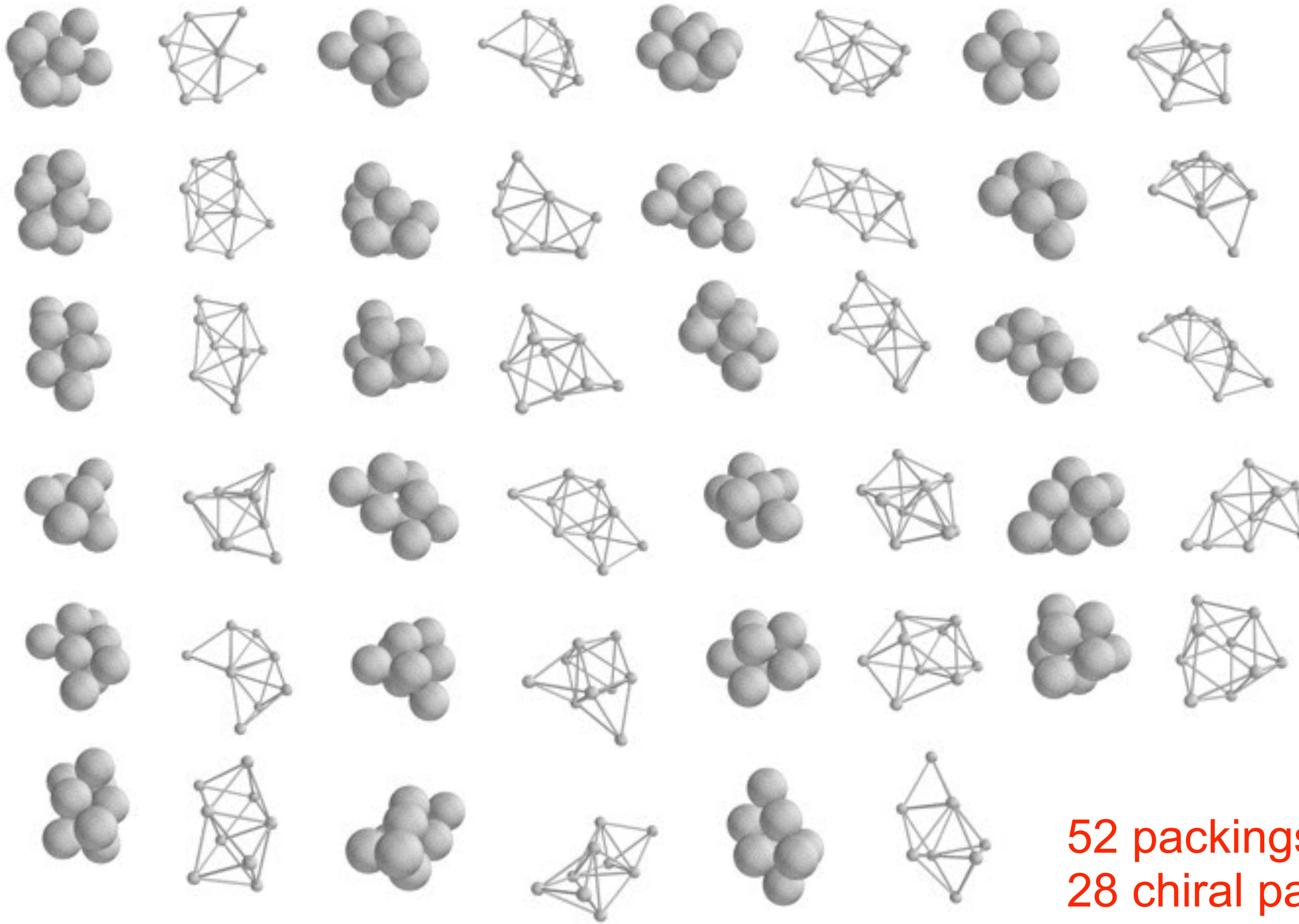
N = 8:



13 packings
3 chiral pairs

N = 9:





52 packings
28 chiral pairs

Total number of clusters computed

n	number of contacts								
	$3n-9$	$3n-8$	$3n-7$	$3n-6$	$3n-5$	$3n-4$	$3n-3$	$3n-2$	Total
5				1					1
6				2					2
7				5					5
8				13					13
9				52					52
10			1	259	3				263
11		2	18	1618	20	1			1659
12		11	148	11,638	174	8	1		11,980
13		87	1221	95,810	1307	96	8		98,529
14	1	707	10,537	872,992	10,280	878	79	4	895,478
	$3n-4$	$3n-3$	$3n-2$	$3n-1$	$3n$	$3n+1$	$3n+2$		
15	7675	782	55	6					(9×10^6 est.)
16		7895	664	62	8				(1×10^8 est.)
17			7796	789	85	6			(1.2×10^9 est.)
18				9629	1085	91	5		(1.6×10^{10} est.)
19					13,472	1458	95	7	(2.2×10^{11} est.)

(N=20,21 also; data not shown)

Total number of clusters computed

n	number of contacts								
	$3n-9$	$3n-8$	$3n-7$	$3n-6$	$3n-5$	$3n-4$	$3n-3$	$3n-2$	Total
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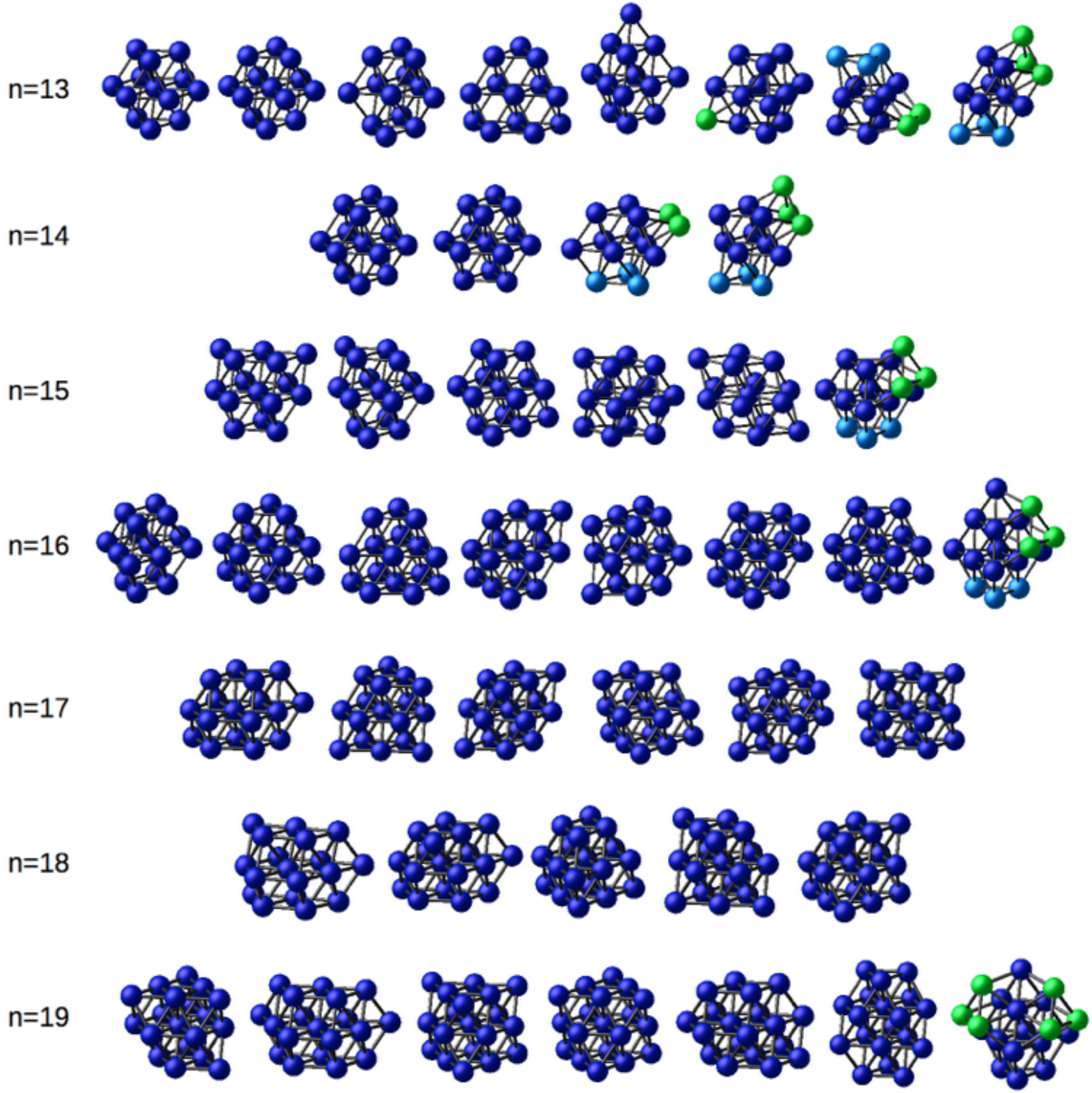
18				9629	1085	91	5		(1.6×10^{10} est.)
19					13,472	1458	95	7	(2.2×10^{11} est.)

(N=20,21 also; data not shown)

hyperstatic


n=13
n=14
n=15
n=16
n=17
n=18
n=19

H.-C. (2016) *SIAM Review*

Total number of clusters computed

n	number of contacts								
	$3n-9$	$3n-8$	$3n-7$	$3n-6$	$3n-5$	$3n-4$	$3n-3$	$3n-2$	Total
5				1					1
6				2					2
7				5					5
8				13					13
9				52					52
10			1	259	3				263
11		2	18	1618	20	1			1659
12		11	148	11,638	174	8	1		11,980
13		87	1221	95,810	1307	96	8		98,529
14	1	707	10,537	872,992	10,280	878	79	4	895,478
	$3n-4$	$3n-3$	$3n-2$	$3n-1$	$3n$	$3n+1$	$3n+2$		
15	7675	782	55	6					(9×10^6 est.)
16		7895	664	62	8				(1×10^8 est.)
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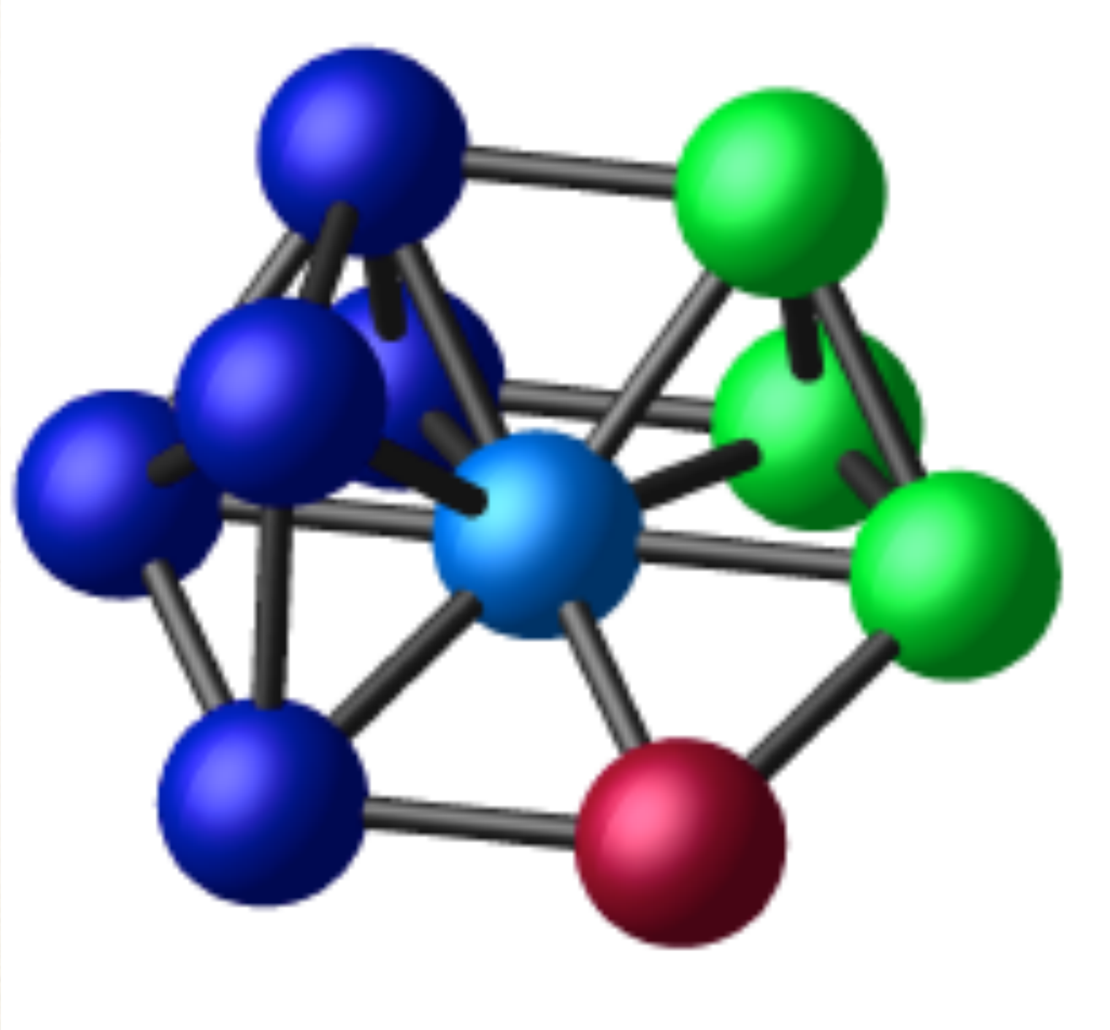
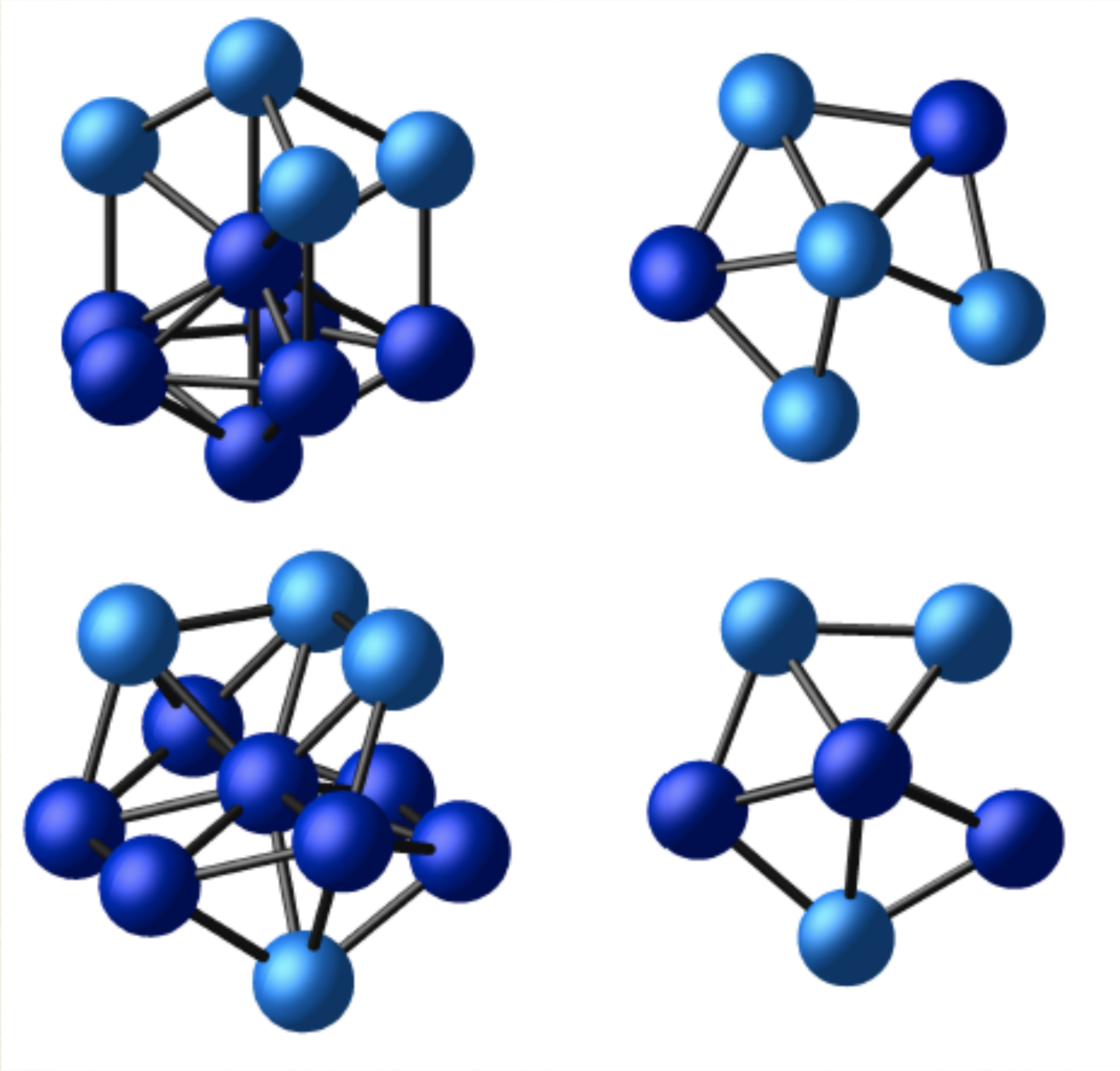
(N=20,21 also; data not shown)

hypostatic

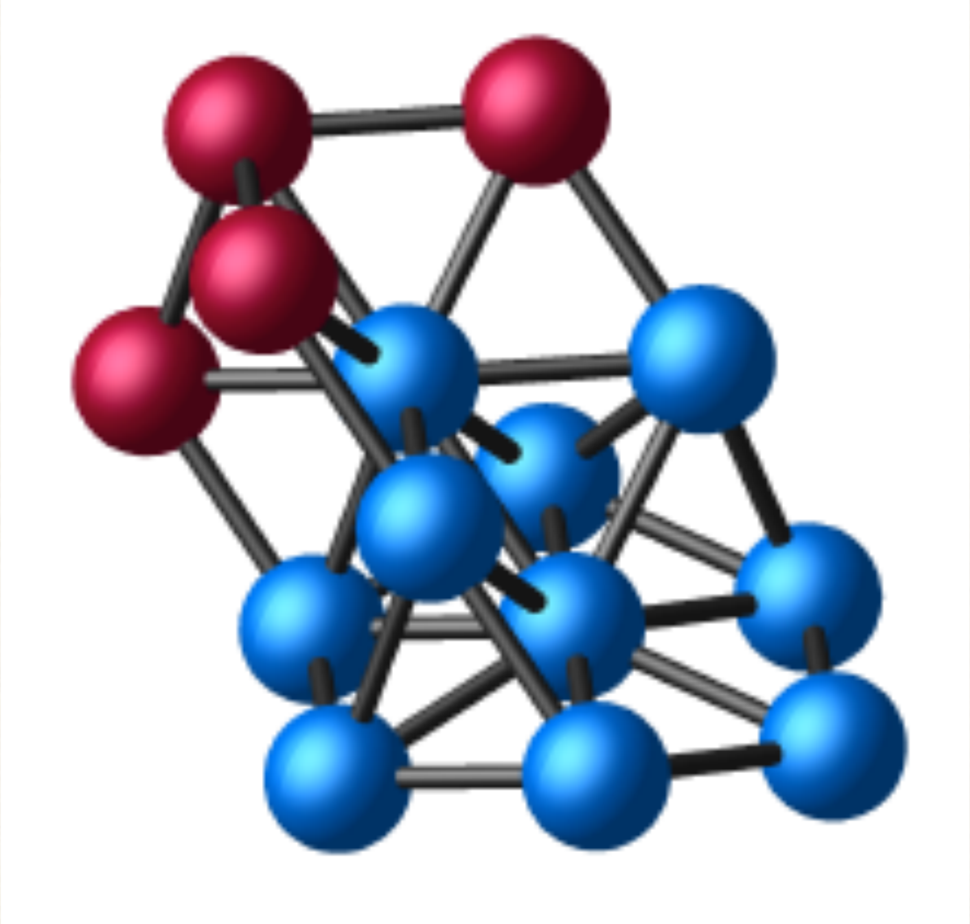
A cluster “missing” one contact, N=10



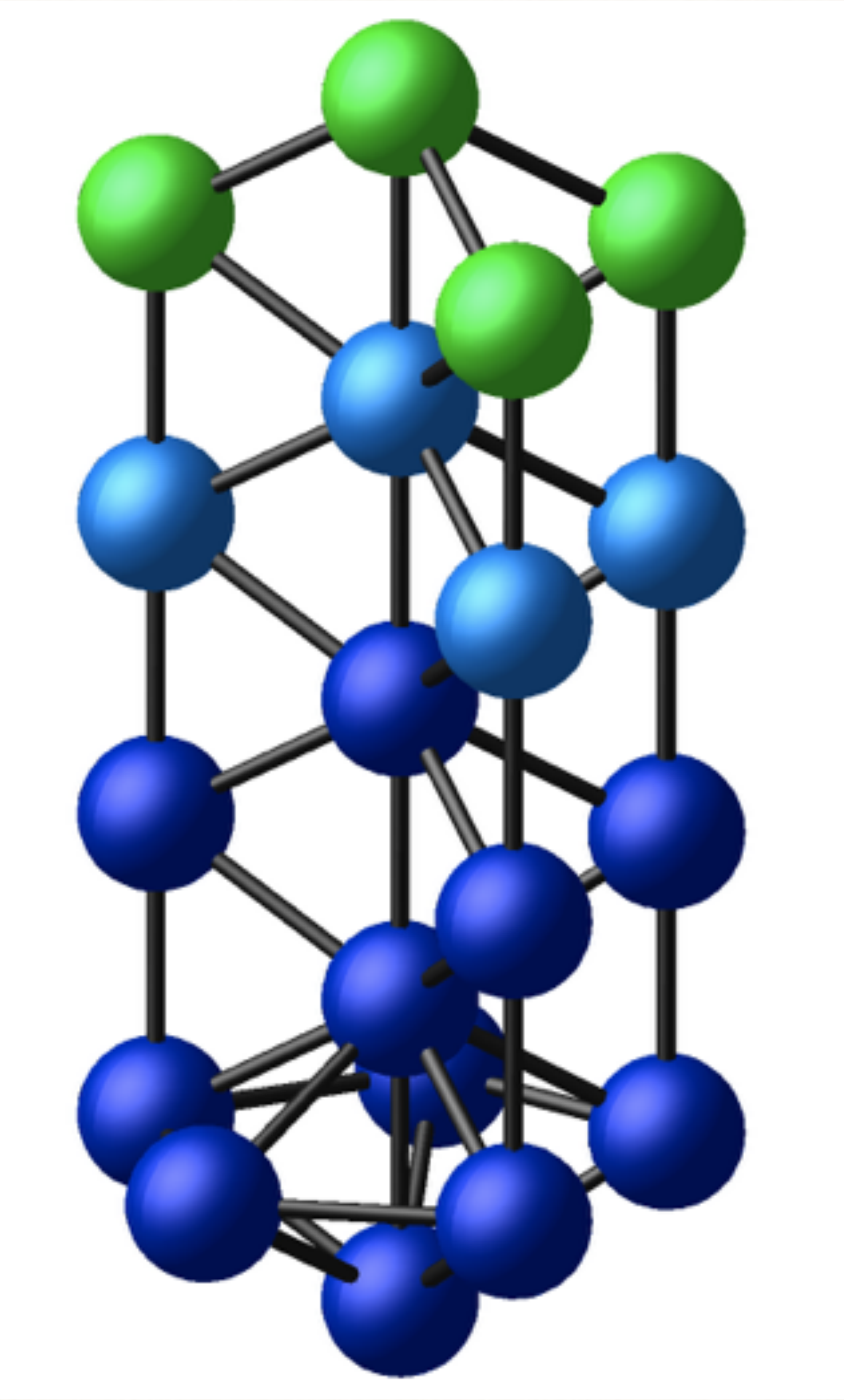
clusters missing two contacts, N=11



cluster missing three contacts, N=14

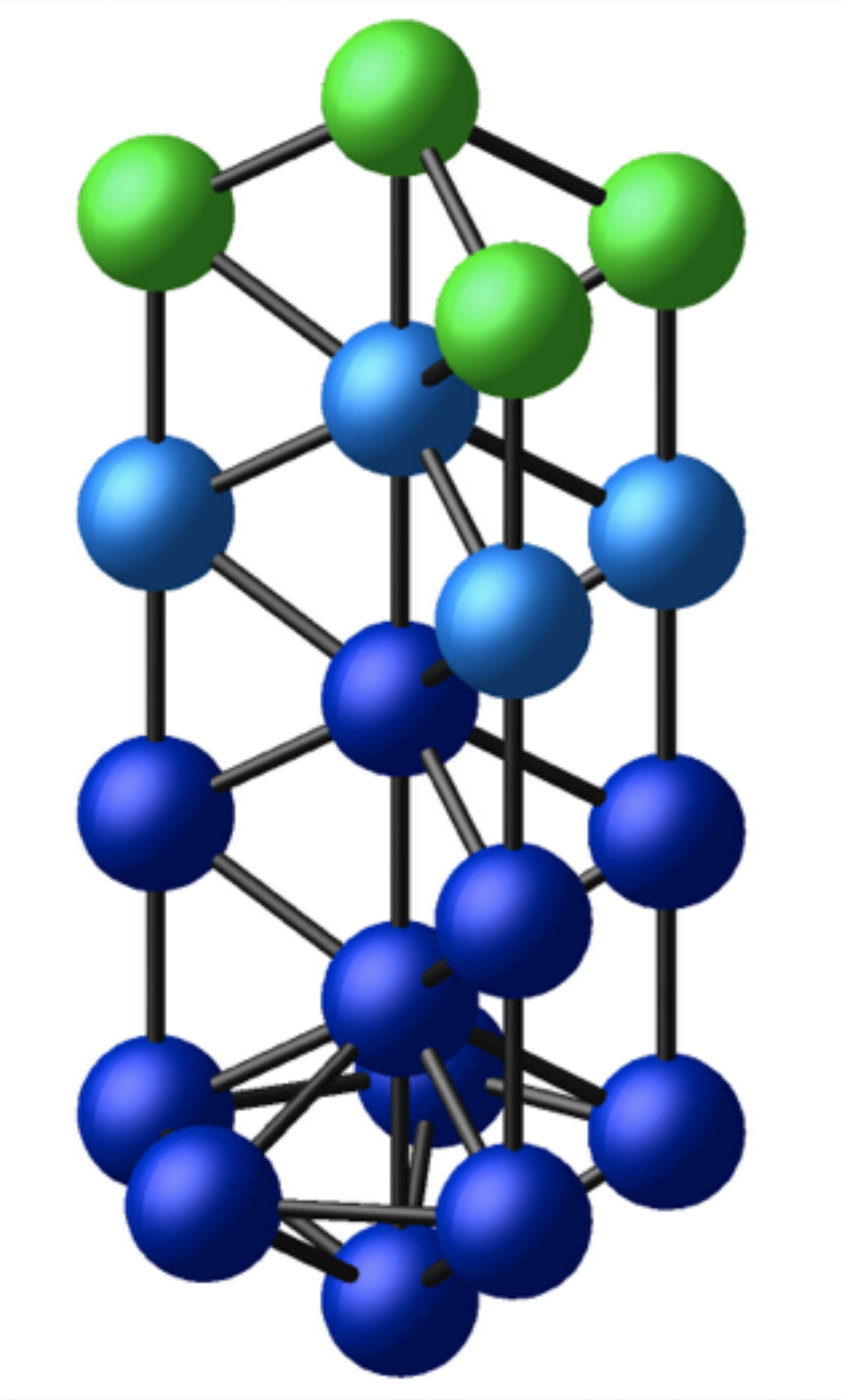


cluster missing arbitrarily many contacts



# of contacts ~ 2N when N large

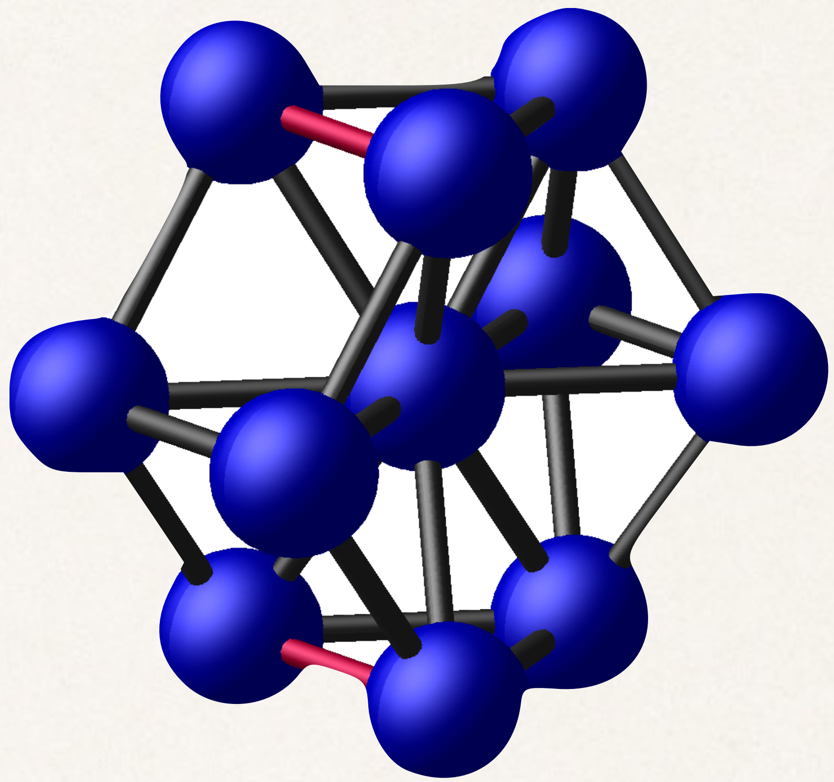
cluster missing arbitrarily many contacts



# of contacts ~ 2N when N large

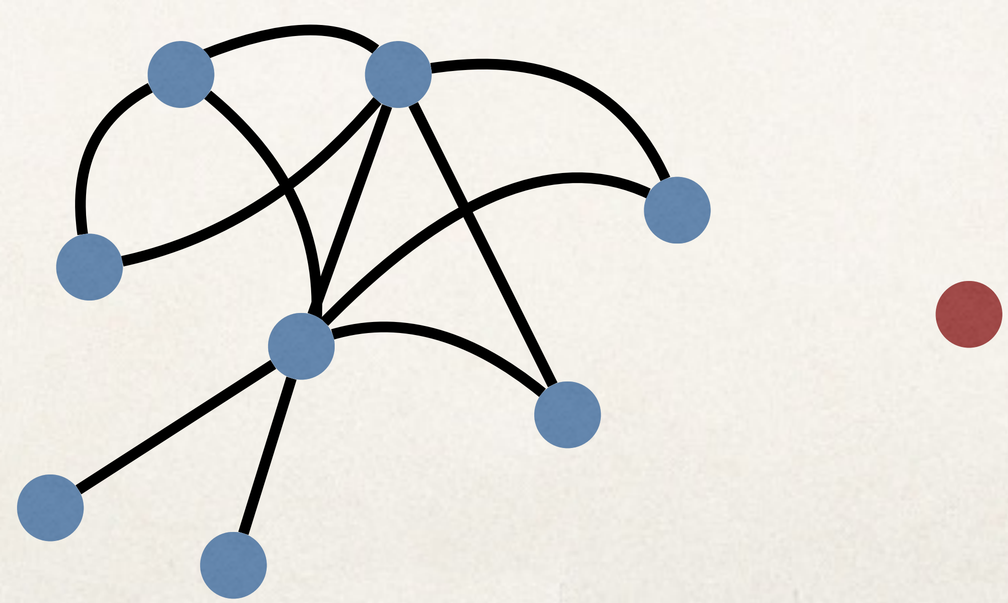
Does the algorithm find everything?

No……… here's an example:



N=11
hypostatic
3N-7 contacts
hcp fragment

Cluster landscape looks like:

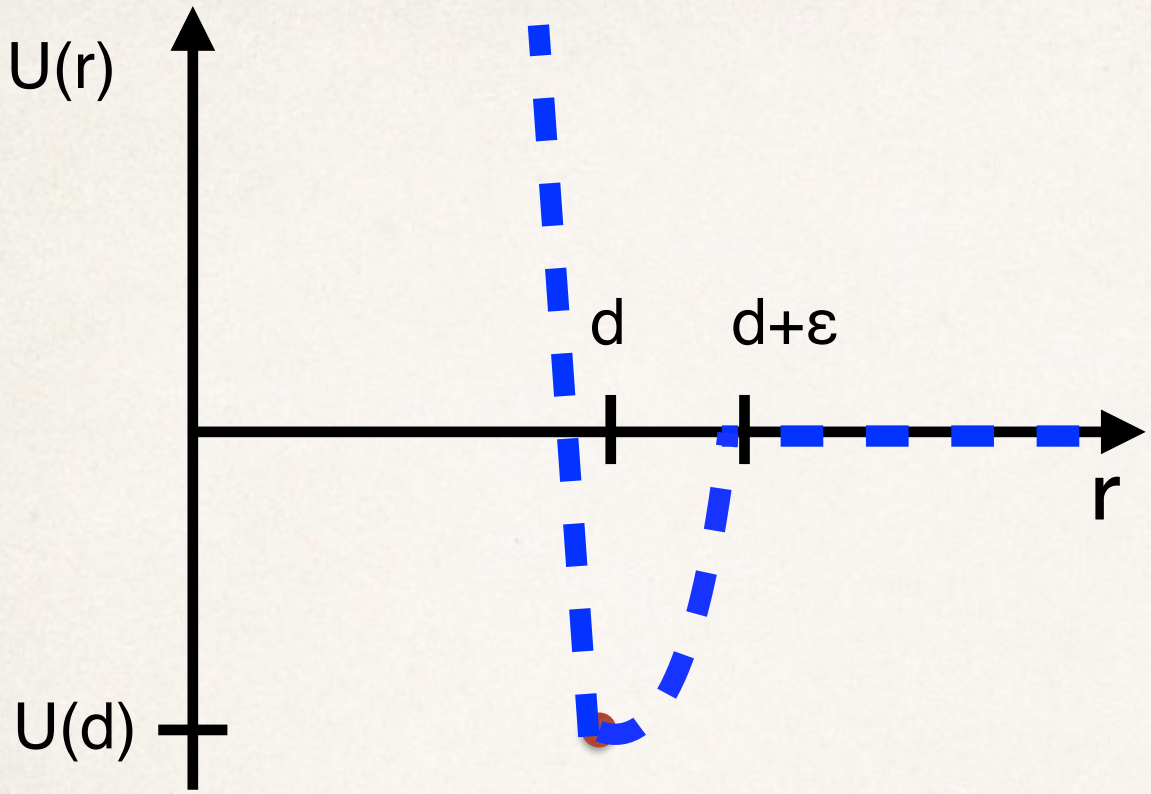


Question:
Is the landscape ever connected (by 1 dof motions), under additional assumptions?
e.g. clusters are regular, isostatic, have random diameters, ….

What is the partition function of a rigid cluster in the sticky-sphere limit?

Y. Kallus and M. H.-C., Phys Rev E (2017).

Interactions short-ranged (compared to diameter of particles) :



Sticky-sphere limit:

- Range ε « d
- Depth U(d) » 1

—> Really stiff springs

energy of a pair = U(| x_i-x_j |), x_i=center of i^{th} sphere, $x = (x_1, x_2, \ldots, x_N)$

energy of a cluster of N spheres = V(x) = $\sum_{i \neq j} U(|x_i - x_j|)$

What is partition function in the sticky-sphere limit?

$$Z_x = \int_{N(x)} e^{-\beta V(x')} dx'$$

$\beta = 1/k_B T$
= inverse temperature

N(x) = neighbourhood of x, including translations, rotations, permutations, and bonds with lengths ∊ (d - ε, d + ε)

“Geometry” of the calculation

Write $y_k(x) = |x_{i_k} - x_{j_k}| - 1$

$\{x : y_k(x) = 0\}$ is hypersurface where sphere i_k touches sphere j_k

exponential function just introduces a pre-factor

$$Z_x \sim e^{-\beta BU(d)} \int_{\{-\epsilon \leq y_k(x) \leq \epsilon\}_{k=1}^{B}} dx$$

evaluate asymptotically as ε —> 0

B = # of bonds

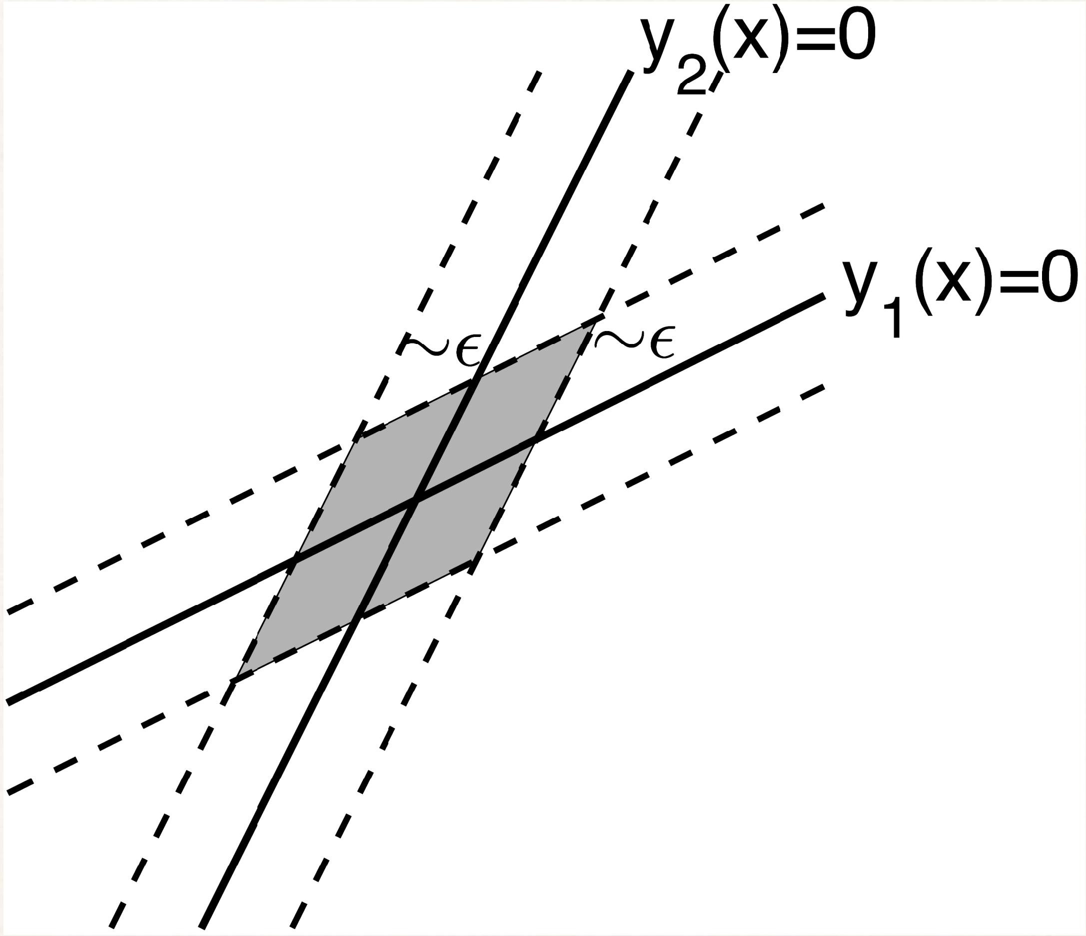
- “Fatten” constraint surfaces by amount ε on either side
- Look at volume of intersection region, as ε —> 0
- Pull out Boltzmann factor

Example (regular)

$x \in R^2$

$y_1(x) = v_1 \cdot x$

$y_2(x) = v_2 \cdot x$



$$\mathrm{Vol} = 4 \,|\, v_1 \times v_2 \,|^{-1} \, \varepsilon^2$$

"Regular" constraints should have volumes that scale as

$\varepsilon^{\text{dimension of intersection set}}$

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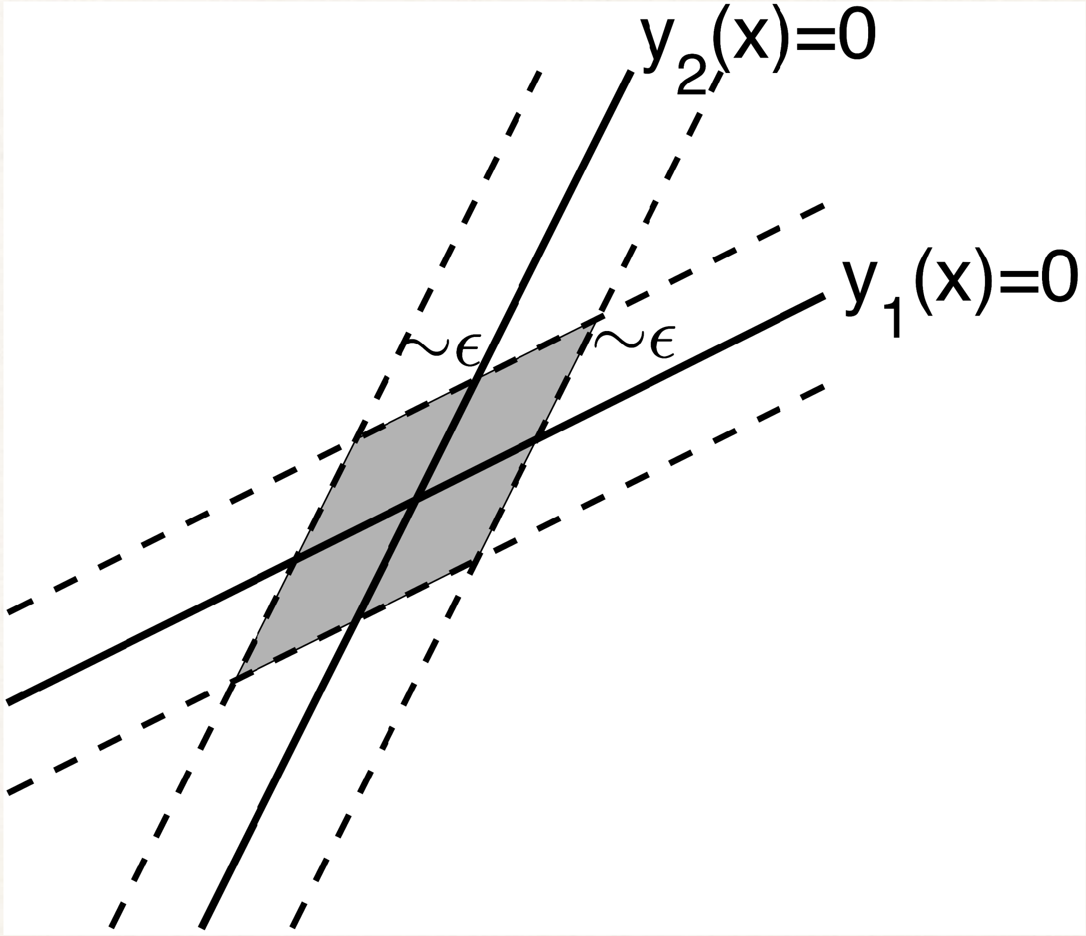

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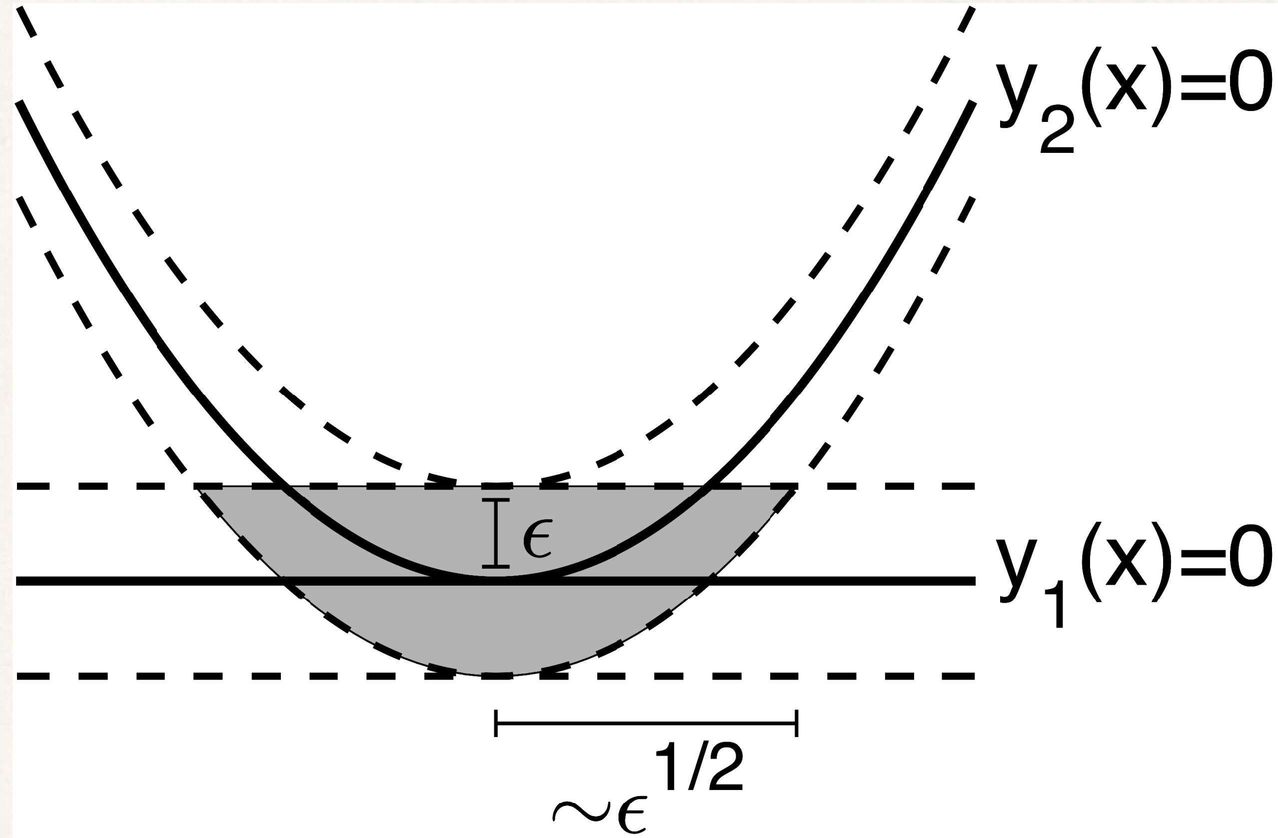

$x \in R^2$

$y_1(x) = x_2$

$y_2(x) = (x_1)^2 - x_2$

$Y_1 = y_1/\varepsilon$

$Y_2 = y_2/\varepsilon^{1/2}$

$$\frac{\partial Y}{\partial x} = 2\epsilon^{-3/2}\sqrt{Y_1 + Y_2}$$

$$\text{Vol} = \epsilon^{3/2} \iint\limits_{\substack{1 \le Y_1 \le 1 \\ 1 \le Y_2 \le 1 \\ Y_1 + Y_2 \ge 0}} \frac{1}{2\sqrt{Y_1 + Y_2}} dY_1 dY_2 = \epsilon^{3/2} \cdot O(1)$$

blows up as $(Y_1,Y_2) \longrightarrow (0,0)$, but in an integrable way

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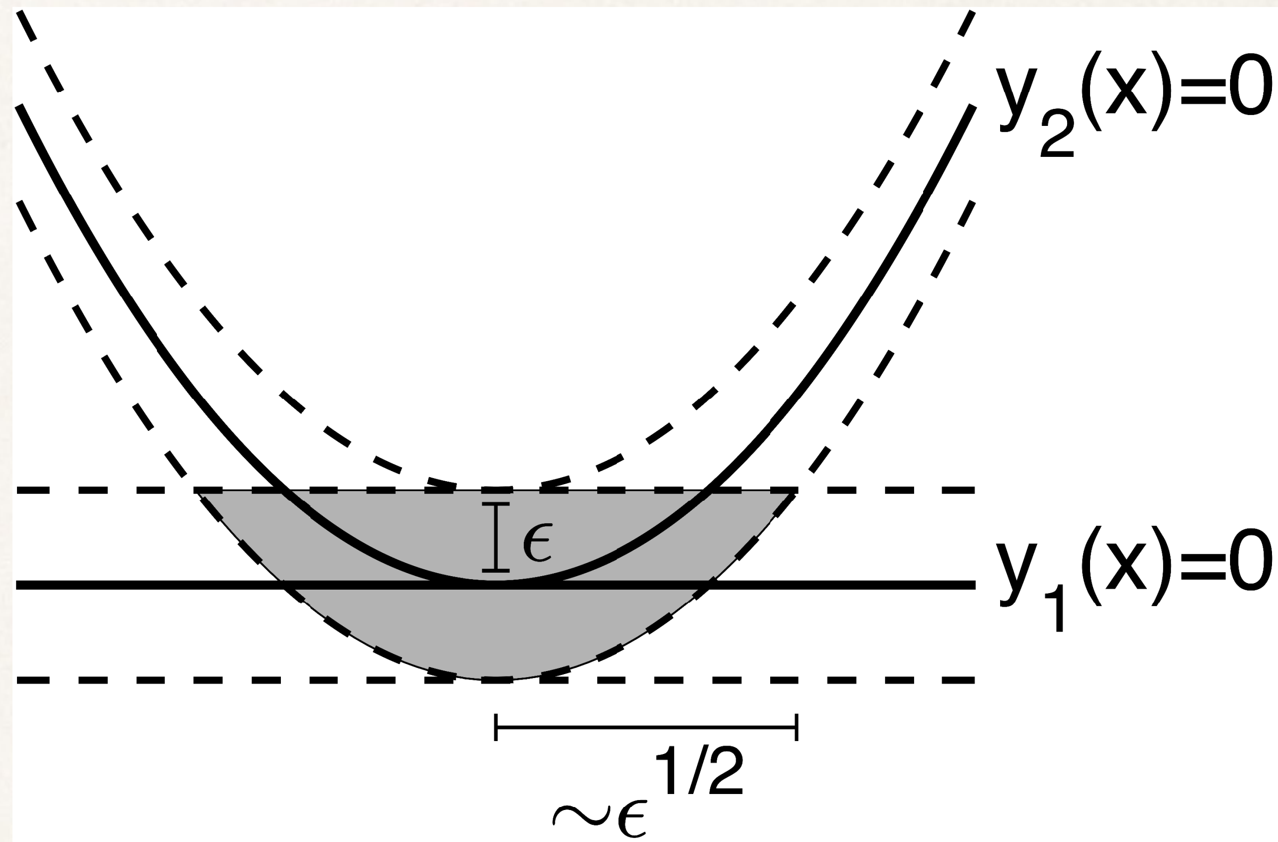

$Y_1 = y_1 / \varepsilon$

$Y_2 = y_2 / \varepsilon^{1/2}$

$$\frac{\partial Y}{\partial x} = 2\epsilon^{-3/2}\sqrt{Y_1 + Y_2}$$

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blows up as (Y_1, Y_2)—>(0,0), but in an integrable way

$$\frac{\text{Vol(Example 2)}}{\text{Vol(Example 1)}} \sim \frac{1}{\epsilon^{1/2}} \qquad \nearrow \infty \quad \text{as } \epsilon \to 0$$

—> Equilibrium probability of singular clusters should dominate that of regular clusters (with the same number of contacts), in the sticky-sphere limit.

Physically, they have more *entropy*.

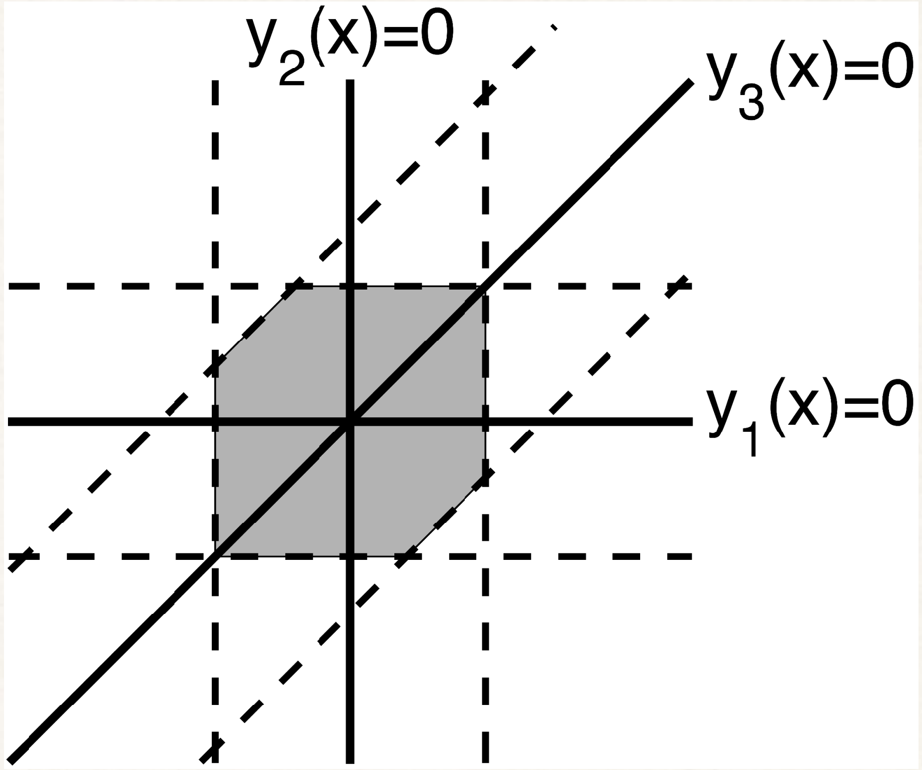
Example (hyperstatic)

$x \in R^2$

$y_1(x) = v_1 \cdot x$

$y_2(x) = v_2 \cdot x$

$y_3(x) = v_3 \cdot x$



$$\text{Vol} \propto \varepsilon^2 \qquad Z_x \propto e^{-3\beta U(d)} \epsilon^2$$

$$\frac{Z_x(\text{hyperstatic example})}{Z_x(\text{regular example})} \propto e^{-\beta U(d)} \to \infty \quad \text{as } U(d) \to -\infty$$

—> Free energy of hyperstatic clusters should dominate that of regular clusters, in the sticky-sphere limit.

Physically, they have lower *energy*.

Example (hyperstatic)

x∊R^2

$y_1(x) = v_1 \cdot x$

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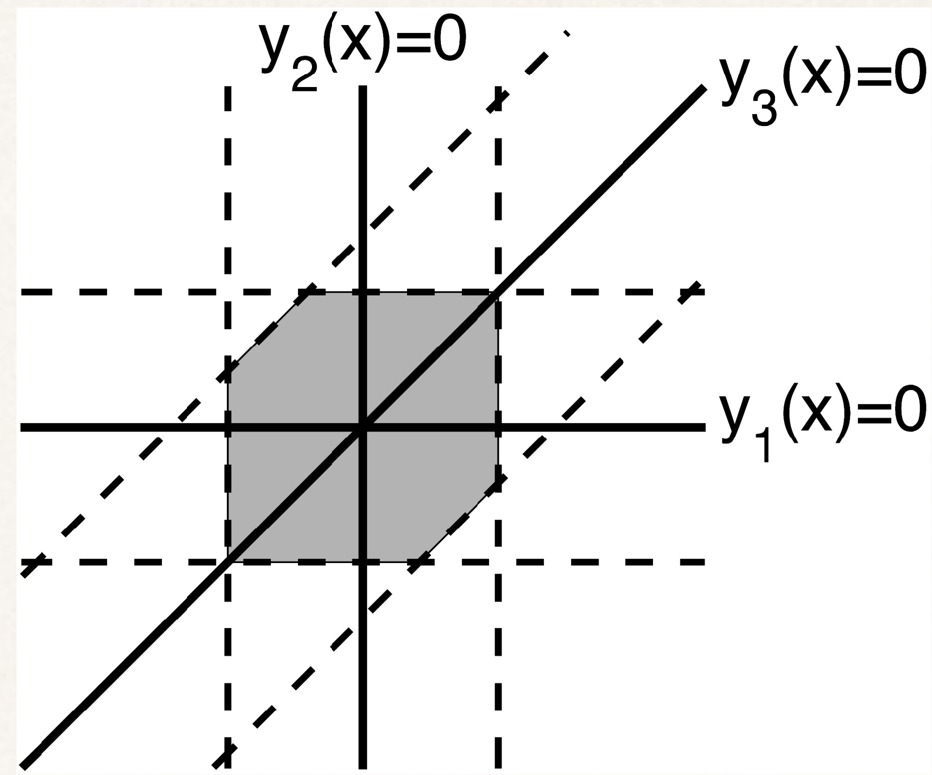

Vol $\propto$ ε^2

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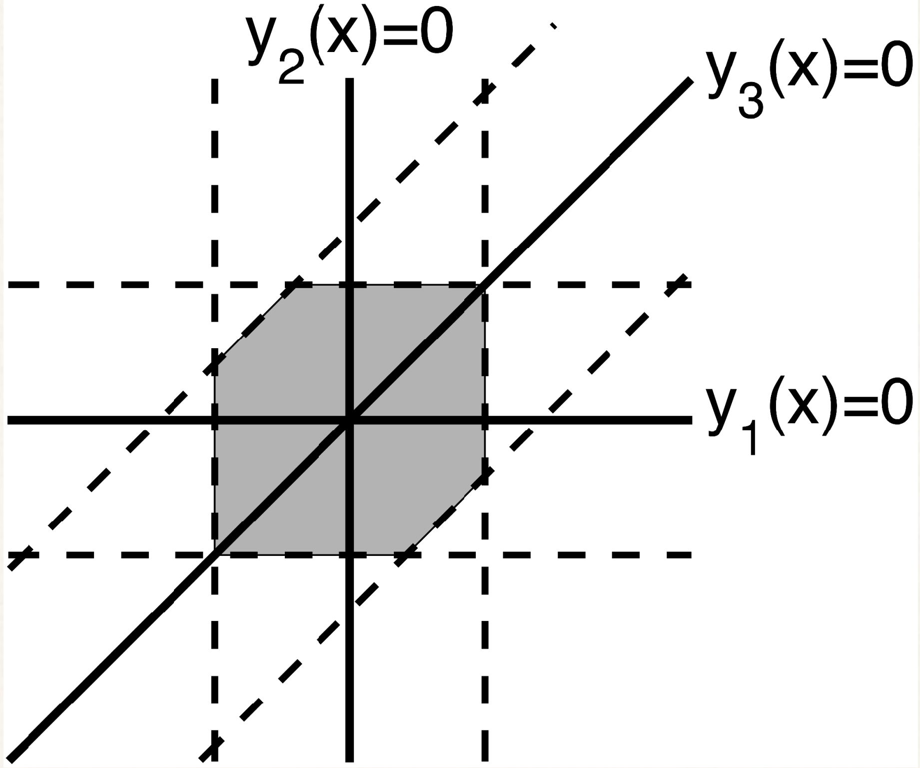

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Physically, they have lower *energy*.

Who wins: singular clusters or hyperstatic clusters?

General case

How does the free energy of singular clusters scale with ε?

Algebraic geometry:

$$\mathrm{Vol} \sim \epsilon^{q} (\log \epsilon)^{k}, \qquad q \in \mathbb{Q}, \quad k \in \mathbb{Z}$$

q,k related to the algebraic nature of the singularity, i.e. what it looks like once it is "resolved"

IGUSA INTEGRALS AND VOLUME ASYMPTOTICS IN ANALYTIC AND ADELIC GEOMETRY

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Received 24 December 2009
Revised 11 October 2010

We establish asymptotic formulas for volumes of height balls in analytic varieties over local fields and in adelic points of algebraic varieties over number fields, relating the Mellin transforms of height functions to Igusa integrals and to global geometric invariants of the underlying variety. In the adelic setting, this involves the construction of general Tamagawa measures.

Keywords: Heights; Poisson formula; Manin's conjecture; Tamagawa measure.

AMS Subject Classification: 11G50 (11G35, 14G05)

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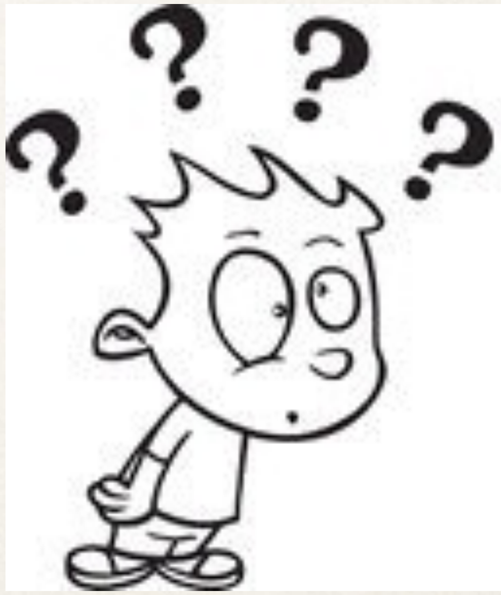

Our approach

$$Z_x = \int_{N(x)} e^{-\beta V(x')} dx'$$

- Taylor-expand the potential V(x) = $\sum_{i \neq j} U(|x_i - x_j|)$

$$\partial_1\partial_2\partial_3 V = \sum_{\langle i,j \rangle} U_0'''(\partial_1 r \partial_2 r \partial_3 r) + U_0''(\partial_{13} r \partial_2 r + \partial_{23} r \partial_1 r + \partial_{12} r \partial_3 r)$$

$$\partial_1\partial_2\partial_3\partial_4 V = \sum_{\langle i,j \rangle} U_0''''(\partial_1 r \partial_2 r \partial_3 r \partial_4 r)$$
$$+ U_0'''(\partial_{14} r \partial_2 r \partial_3 r + \partial_{13} r \partial_2 r \partial_4 r + \partial_{12} r \partial_3 r \partial_4 r + \partial_{24} r \partial_1 r \partial_3 r + \partial_{23} r \partial_1 r \partial_4 r + \partial_{34} r \partial_1 r \partial_1 r)$$
$$+ U_0''(\partial_{123} r \partial_4 r + \partial_{124} r \partial_2 r + \partial_{234} r \partial_1 r + \partial_{12} r \partial_{34} r + \partial_{13} r \partial_{24} r + \partial_{14} r \partial_{24} r)$$

- Evaluate integral using Laplace asymptotics

- Asymptotically the same scaling as square-well potential:
log(Z_{square}) ~ log(Z_x) as ε→0, U(d)→∞ (Kallus & H.-C., Phys Rev E (2017))

Partition function for second-order rigid cluster

$$Z_x = (\text{const}) \cdot \ \gamma^{\Delta B} \alpha^{d_X} \ z_x$$

where the geometrical part is

$$z_x = (\text{const}) \cdot \ \frac{\sqrt{I(x)}}{\sigma} \prod_{\lambda_i \neq 0} \lambda_i^{-1/2}(x) \int_X e^{-Q(\tilde{\mathbf{x}})} d\tilde{\mathbf{x}}$$

parameters are

$$\begin{aligned} \gamma &= e^{-\beta U(d)} \\ &\approx \exp(\text{depth}) \\ \alpha &= (U''(d)\beta d^2)^{1/4} \\ &\approx \text{width}^{-1/2} \end{aligned}$$

geometry-dependent variables are

$$\begin{aligned} \Delta B &= B - (3N - 6) \\ &= \#\text{ of bonds beyond isostatic} \\ d_X &= \#\text{ of singular directions} \\ I(x) &= \text{determinant of moment of inertia tensor} \\ \sigma &= \text{symmetry number} \\ \lambda_i(x) &= \text{eigenvalues of Hessian } \nabla\nabla V = R(x)R^T(x) \\ Q(\mathbf{x}) &= \text{quartic function on subspace of} \\ &\quad \text{singular directions} \end{aligned}$$

Y. Kallus and M. H.-C., Phys. Rev. E (2017).

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Only TWO parameters needed!

geometry-dependent variables are

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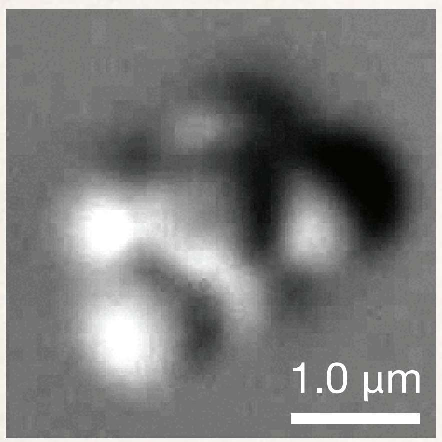
Y. Kallus and M. H.-C., Phys. Rev. E (2017).

Comparing hyperstatic & singular clusters

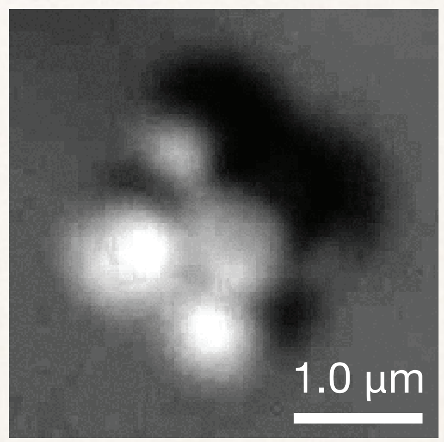
N ≤ 8

- All rigid clusters are first-order rigid
- Symmetry number is most important factor: more asymmetric —> more probable.

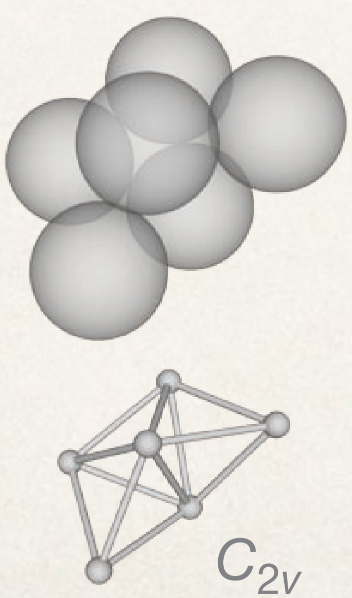
$$Z_x = \kappa^B \frac{\sqrt{I}}{\sigma} \prod_{i=1}^{3N-6} \lambda_i^{-1/2}$$

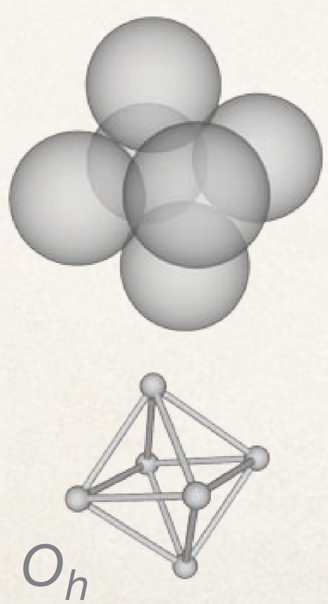


Polytetrahedron



Octahedron

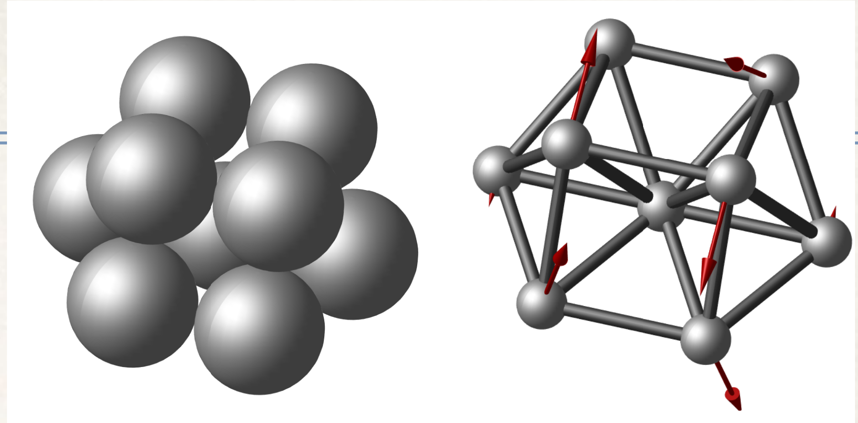




	poly	octa	ratio
κ^B	κ^{12}	κ^{12}	1
$I^{1/2}$	3.2	2.8	1.1
Z_{vibr}	0.061	0.034	1.8
σ^{-1}	2^{-1}	24^{-1}	12
P_{theory}	96.0%	4.0%	24
P_{obs}	95.7%	4.3%	22.3

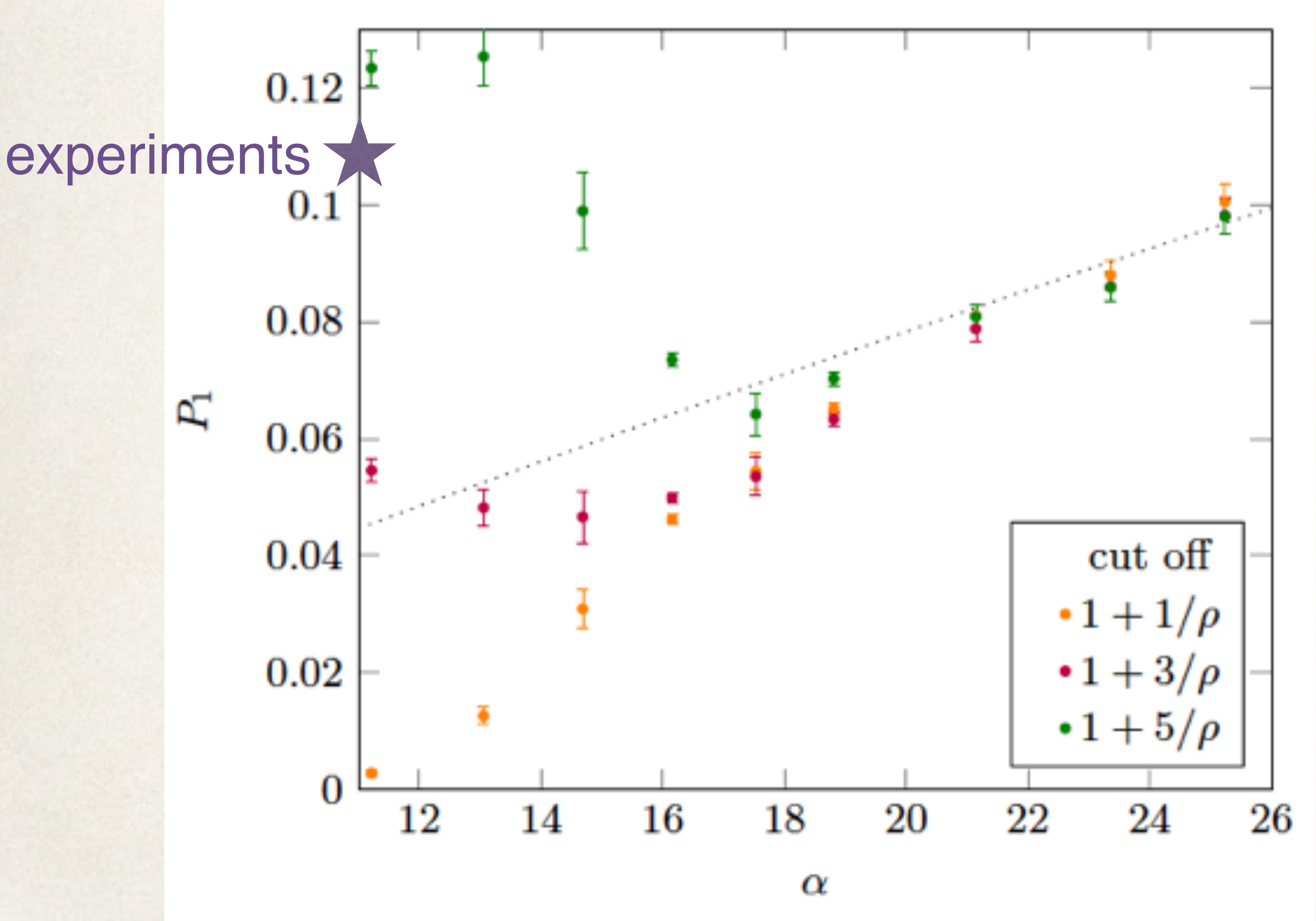
G. Meng, N. Arkus, M. P. Brenner, V. N. Manoharan, Science 327 (2010)

N = 9



- 1 singular cluster, 51 regular clusters

$$P(\text{singular}) = \frac{\alpha}{235 + \alpha} \qquad \alpha = (U''(d)\beta d^2)^{1/4} \sim \text{width}^{-1/2}$$



- Agrees with simulations for large α (small width)
- For small α, no robust way to identify clusters —> likely due to non-nearest neighbour interactions, since gaps are small.
- Experiments: P_1=11% (4%-27%), $\alpha \approx 10$.

N ≥ 10: group by type

Total partition function of all rigid clusters Z

$$Z \propto \sum_{\Delta B, d_X} \alpha^{d_X} \gamma^{\Delta B} z_{\Delta B, d_X}$$

$$z_{\Delta B, d_X} = \text{sum of geometric contributions of all clusters with } \Delta B \text{ extra bonds and } d_X \text{ singular directions}$$

$$\alpha \sim \text{width}^{-1/2}, \quad \log \gamma \sim \text{depth}$$

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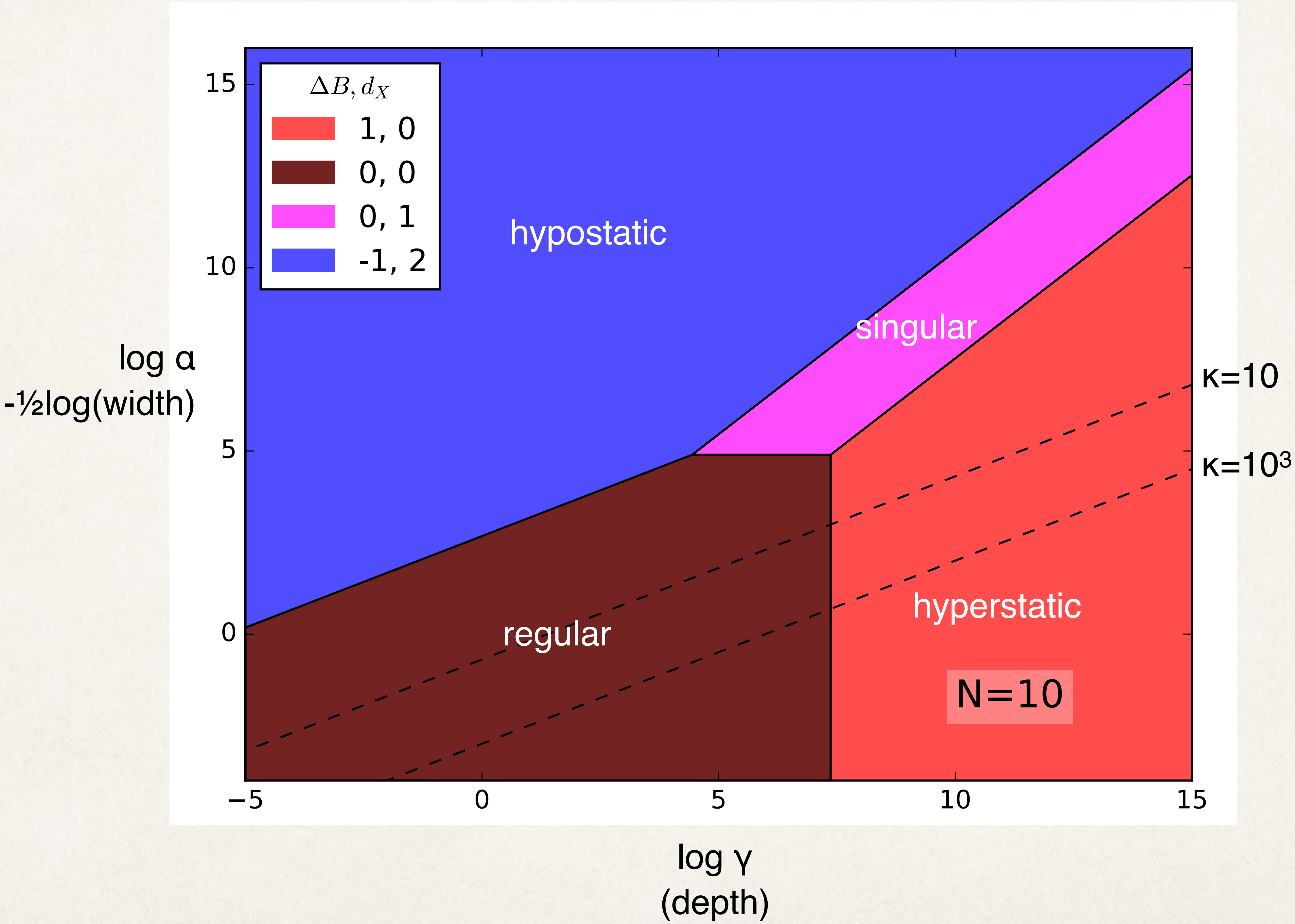
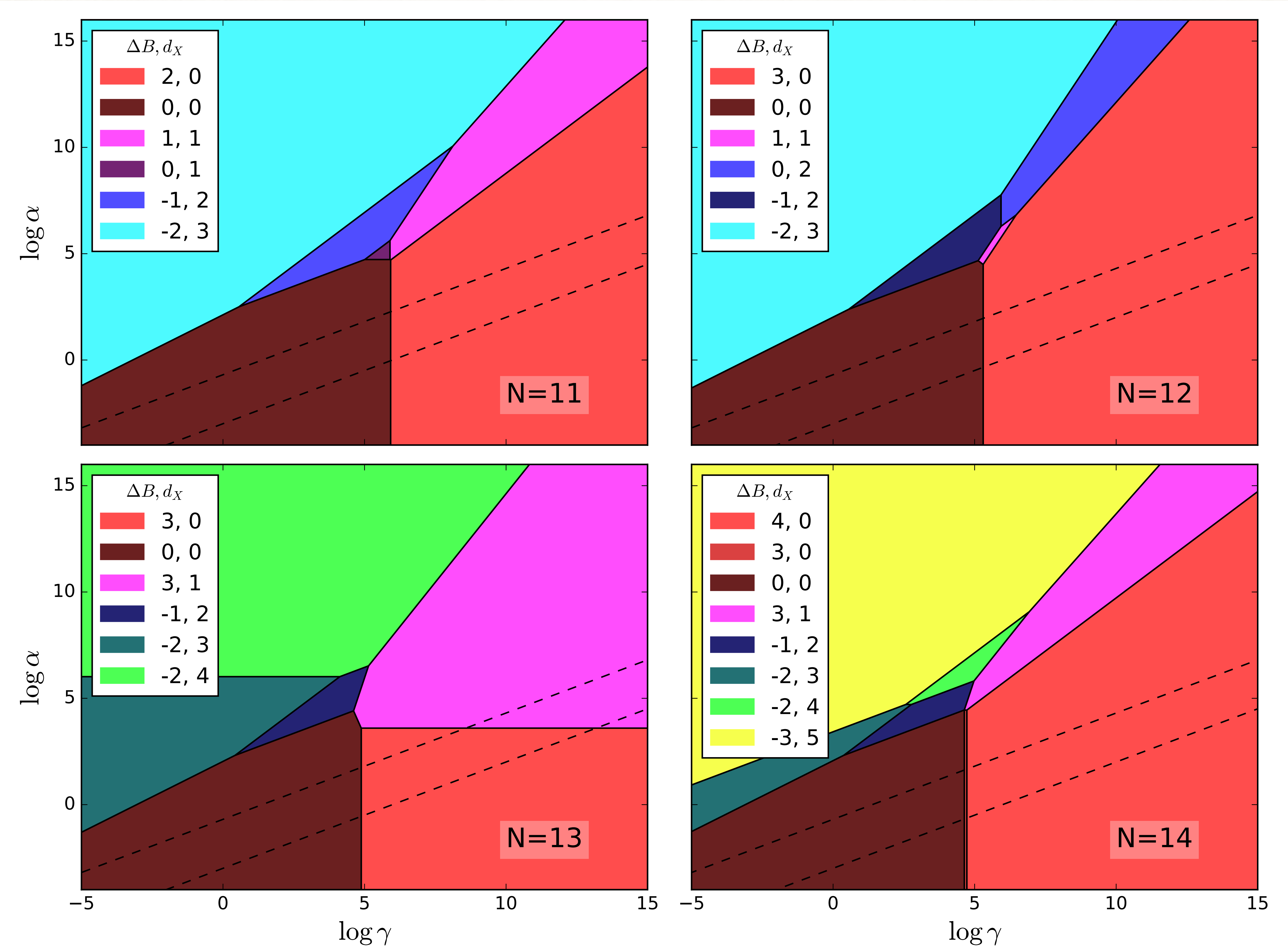
Which term is largest as a function of γ, α ?

N = 10



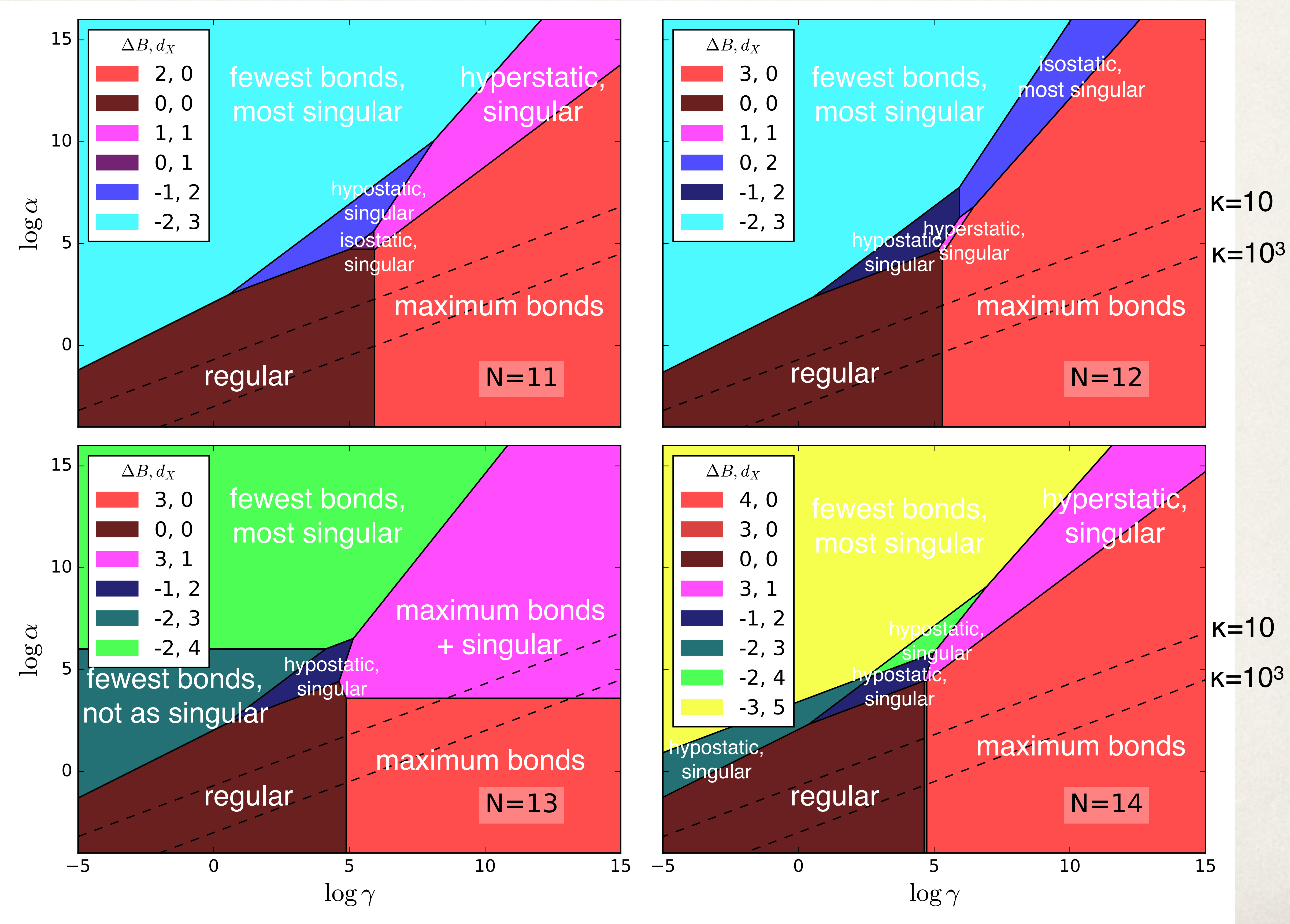
$\Delta B, d_X$
1, 0
0, 0
0, 1
-1, 2
hypostatic
singular
regular
hyperstatic
N=10
κ=10
κ=10³
log α
-½log(width)
log γ
(depth)
15
10
5
0
−5
0
5
10
15

N = 11-14



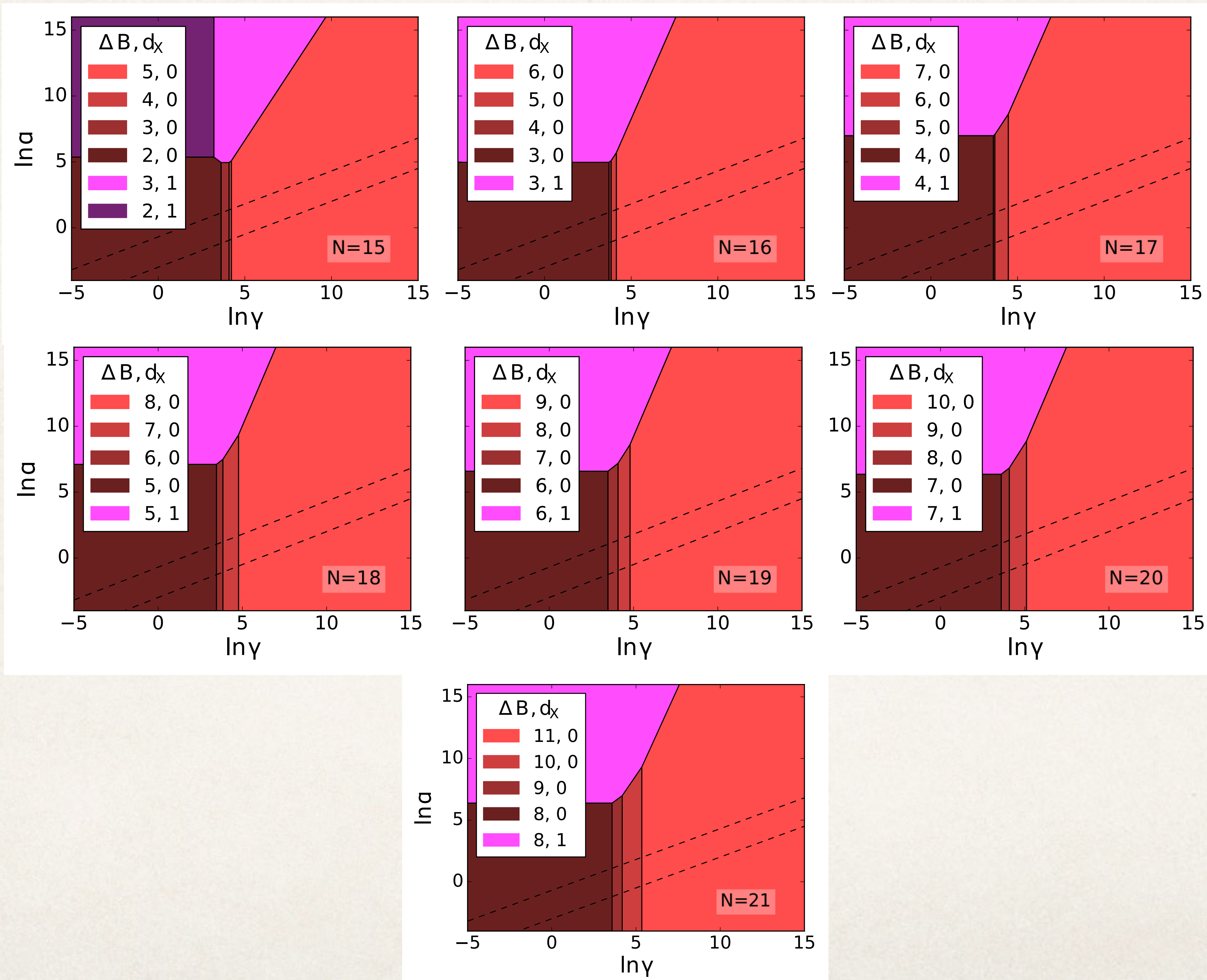
$\Delta B, d_X$
2, 0
0, 0
1, 1
0, 1
-1, 2
-2, 3
N=11
$\Delta B, d_X$
3, 0
0, 0
1, 1
0, 2
-1, 2
-2, 3
N=12
$\Delta B, d_X$
3, 0
0, 0
3, 1
-1, 2
-2, 3
-2, 4
N=13
$\Delta B, d_X$
4, 0
3, 0
0, 0
3, 1
-1, 2
-2, 3
-2, 4
-3, 5
N=14
$\log \alpha$
$\log \gamma$
−5
0
5
10
15

N = 11-14



$\Delta B, d_X$
2, 0
0, 0
1, 1
0, 1
-1, 2
-2, 3
fewest bonds, most singular
hyperstatic, singular
hypostatic, singular
isostatic, singular
maximum bonds
regular
N=11
$\Delta B, d_X$
3, 0
0, 0
1, 1
0, 2
-1, 2
-2, 3
fewest bonds, most singular
isostatic, most singular
hypostatic, singular
hyperstatic, singular
maximum bonds
regular
N=12
κ=10
κ=10³
$\Delta B, d_X$
3, 0
0, 0
3, 1
-1, 2
-2, 3
-2, 4
fewest bonds, most singular
fewest bonds, not as singular
hypostatic, singular
maximum bonds + singular
maximum bonds
regular
N=13
$\Delta B, d_X$
4, 0
3, 0
0, 0
3, 1
-1, 2
-2, 3
-2, 4
-3, 5
fewest bonds, most singular
hyperstatic, singular
hypostatic, singular
hypostatic, singular
hypostatic, singular
maximum bonds
regular
N=14
κ=10
κ=10³
$\log \alpha$
$\log \gamma$

N=15-21


ΔB, d_X
5, 0
4, 0
3, 0
2, 0
3, 1
2, 1
N=15
ΔB, d_X
6, 0
5, 0
4, 0
3, 0
3, 1
N=16
ΔB, d_X
7, 0
6, 0
5, 0
4, 0
4, 1
N=17
ΔB, d_X
8, 0
7, 0
6, 0
5, 0
5, 1
N=18
ΔB, d_X
9, 0
8, 0
7, 0
6, 0
6, 1
N=19
ΔB, d_X
10, 0
9, 0
8, 0
7, 0
7, 1
N=20
ΔB, d_X
11, 0
10, 0
9, 0
8, 0
8, 1
N=21
lnα
lnγ
−5
0
5
10
15

… back to frustration ….

- Symmetry (or lack thereof) doesn't seem to be particularly important
- Competition is between

energy (of extra bonds),   and *"singular" entropy* (of 0-frequency modes):

energy   entropy

$$Z_x = (\text{const}) \cdot \gamma^{\Delta B} \alpha^{d_X} \; z_x$$

and *combinatorial entropy* (total number of states)

(also global entropy term — neglected here)

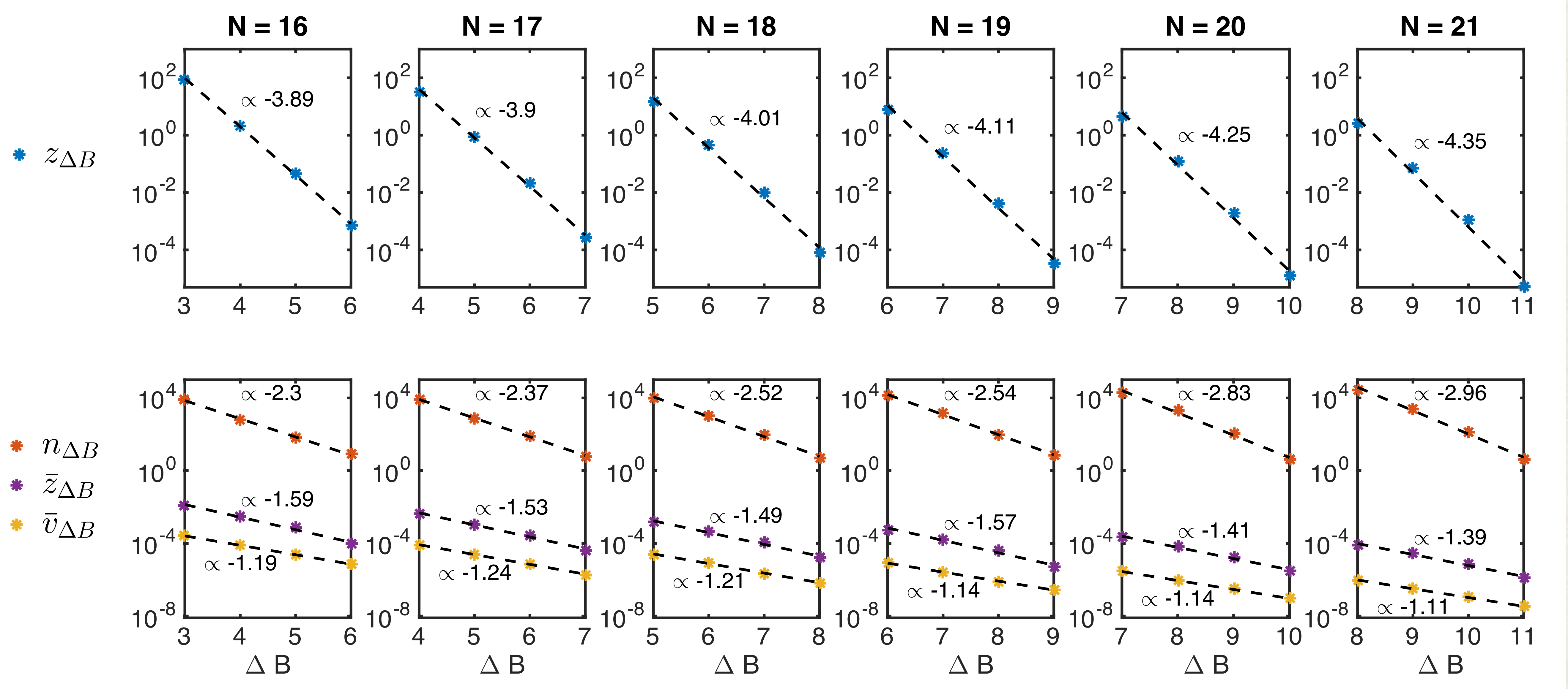
- For *identical spheres,* energy beats "singular entropy":
Max-bond, crystalline states win for N ≥ 10, strong enough bonds

—> Sticky spheres do not appear to be frustrated!

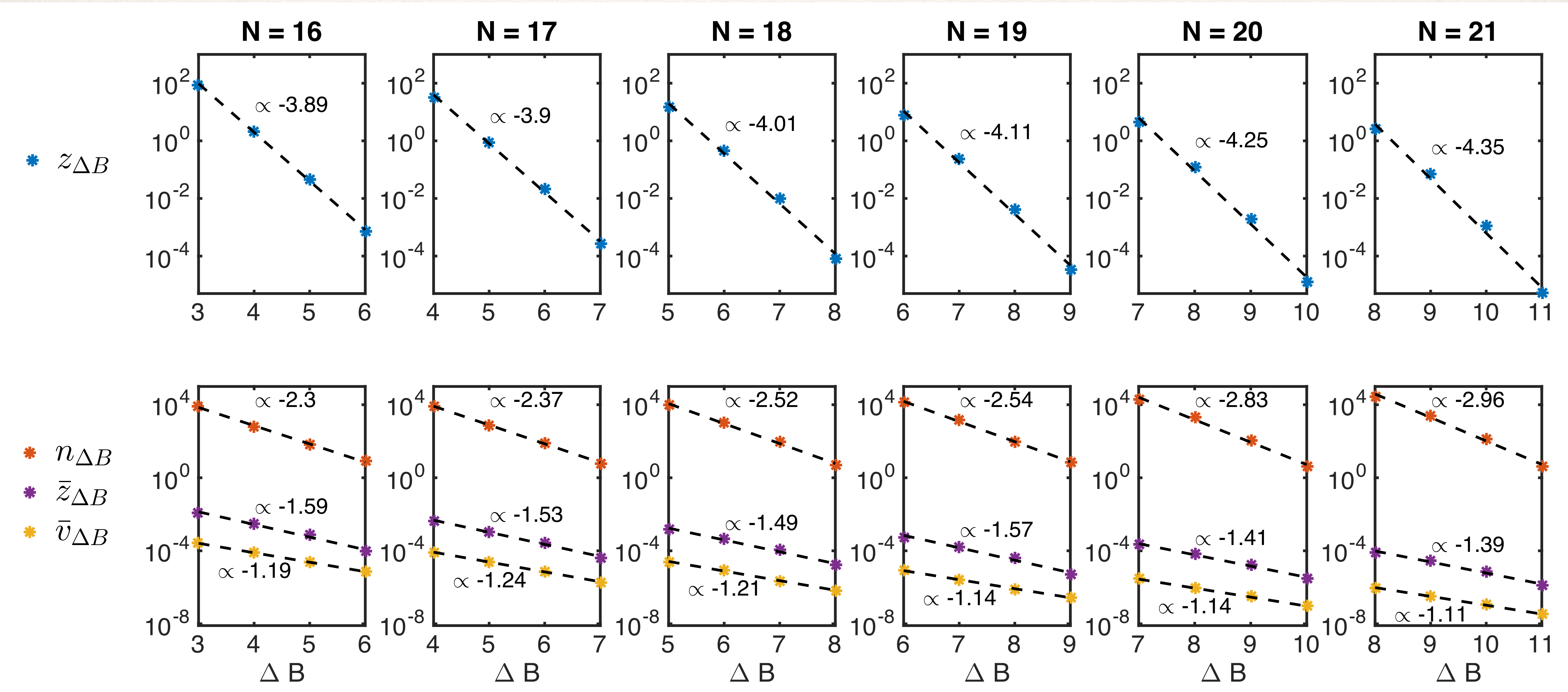
- Question: Are there systems where "singular entropy" dominates?
(non-identical spheres, ellipsoids, …?)

Thanks to: Steven Gortler, Yoav Kallus, John Ryan, Louis Theran, **US DOE, NSF-FRG**

Why do the landscapes look so similar?



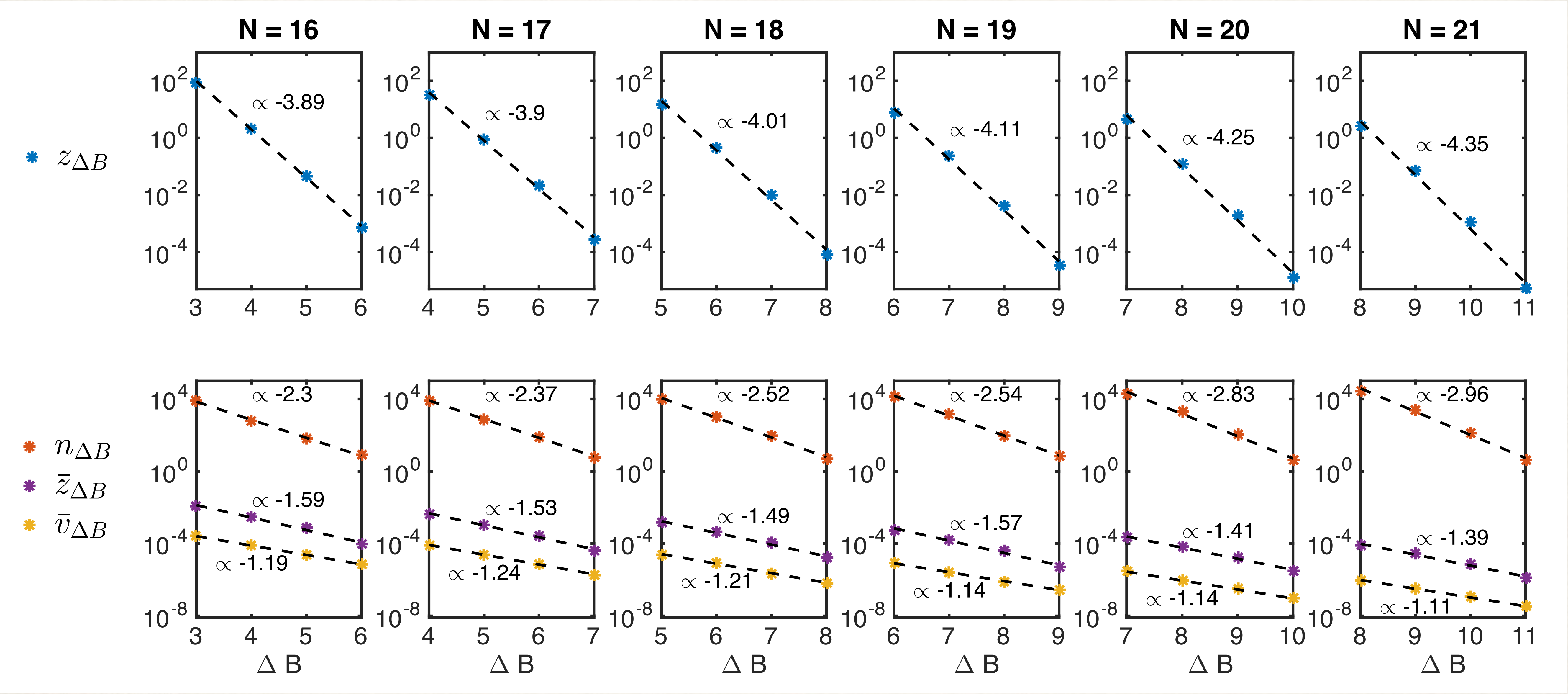
Why do the landscapes look so similar?



Why all these exponential scaling laws?

Do the exponents approach a common value as N→∞ ?

Why do the landscapes look so similar?



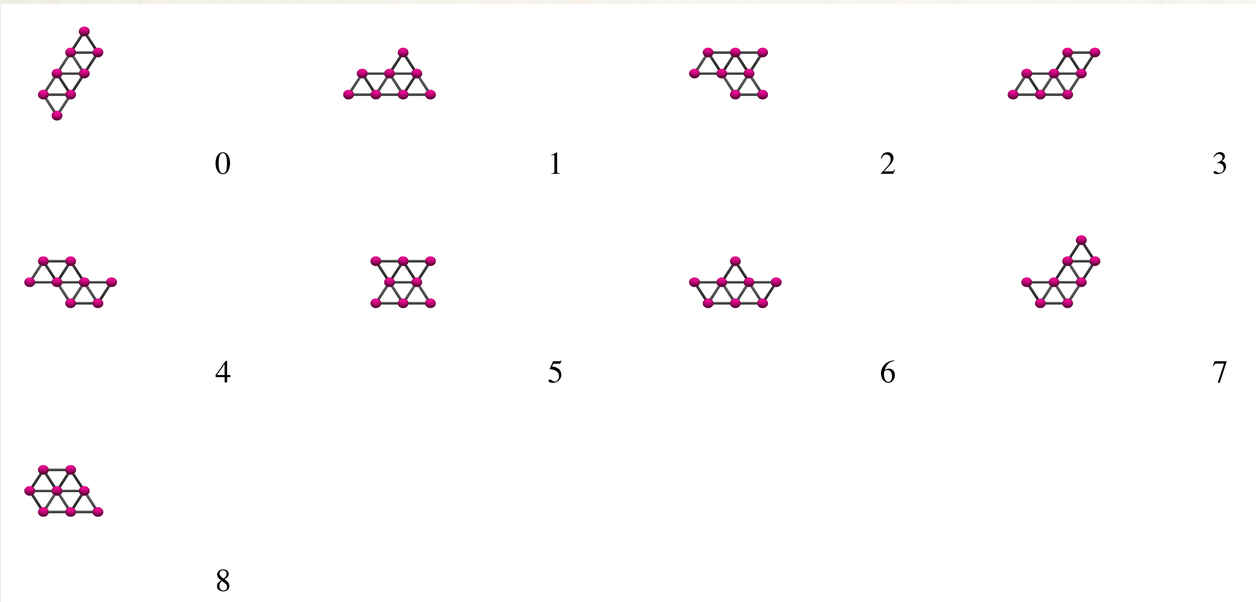
Why all these exponential scaling laws?

Do the exponents approach a common value as N→∞ ?

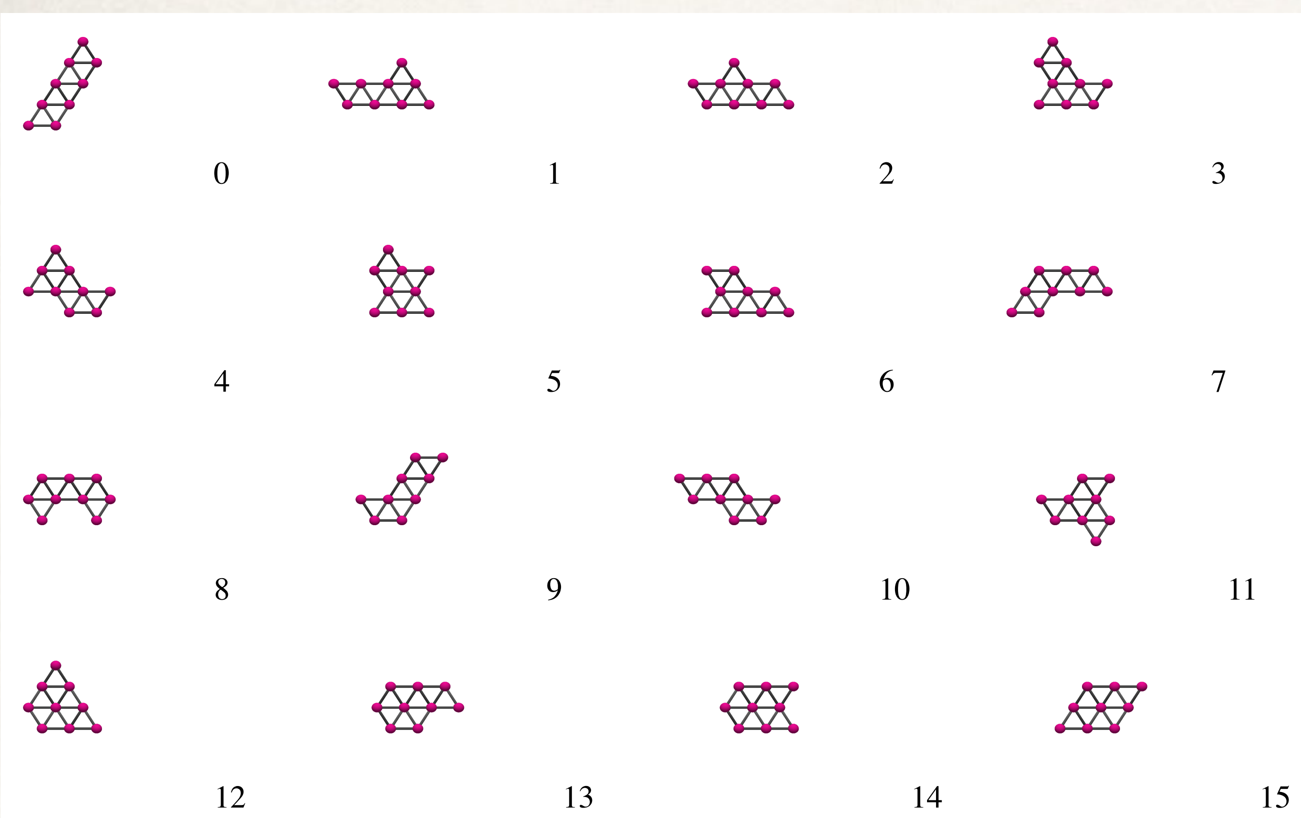
can explain using geometry, combinatorics, random matrix theory, …?

Two-dimensional rigid clusters

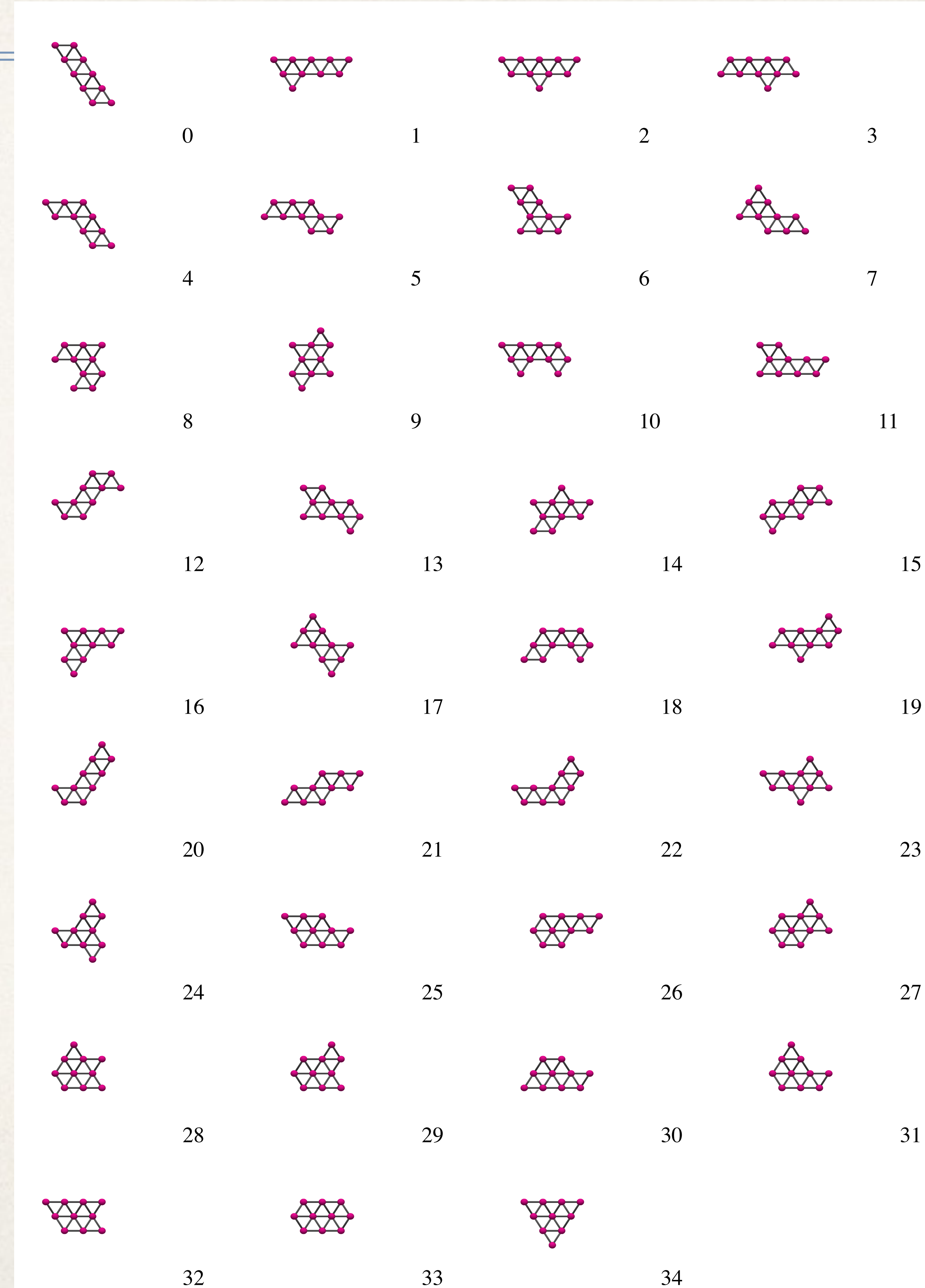
N=8



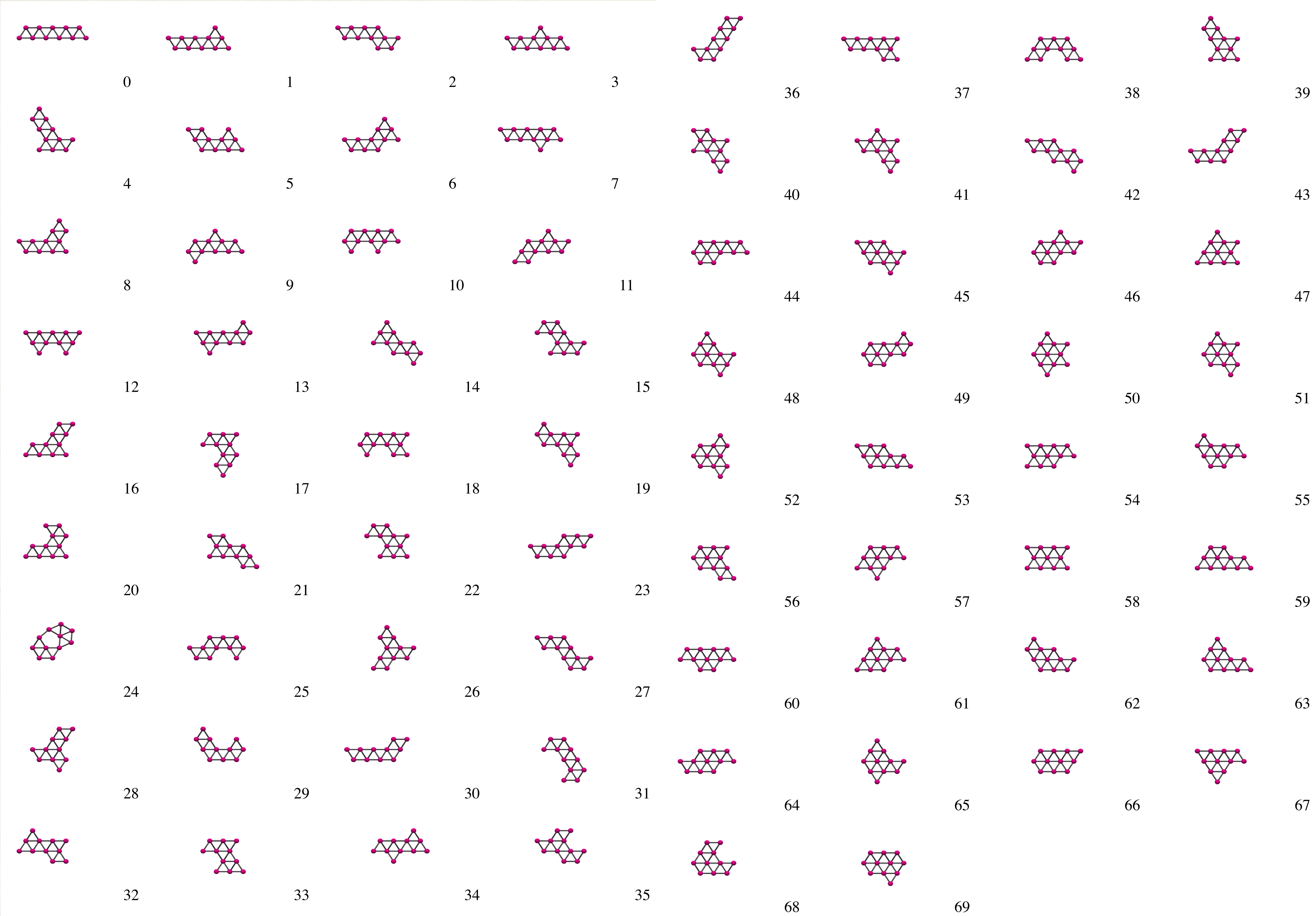
N=9



N=10



N=11



0 1 2 3
4 5 6 7
8 9 10 11
12 13 14 15
16 17 18 19
20 21 22 23
24 25 26 27
28 29 30 31
32 33 34 35
36 37 38 39
40 41 42 43
44 45 46 47
48 49 50 51
52 53 54 55
56 57 58 59
60 61 62 63
64 65 66 67
68 69

Back to memory

1. Colloids could be programmed to contain memories
   - realize memories in physical system
   - make multi-function devices
   - requires quantitative computation & optimization on free energy landscape (tools under development), to account for real & important constraints imposed by geometry

2. Link to continuous attractor
   - Folding experiment….
   - entropy may help stabilize (states & memories), via kinetics — but memory is a kinetic phenomenon

3. Observed colloidal crystals contain memory (J. Crocker, GRC 2017)
   - colloids have "slow" kinetics (c.f. atomic vibrational timescales, for e.g.)
   - how can we predict which structures will form? Given that it is not only the lowest free-energy structure, but also one which favours growth?