Title: The physics and geometry of self-assembly

Date: Mar 03, 2010 02:00 PM

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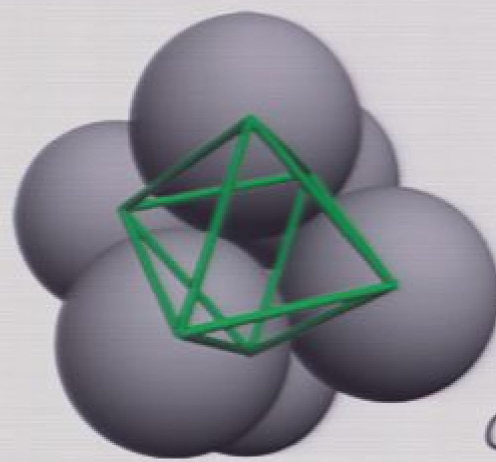
Abstract: Self-assembly refers to any thermodynamic process in which a bunch of particles (molecules, biomolecules, polymers, colloids) come together in solution to form an ordered structure. In living things it is a widely used and robust manufacturing tool: DNA, RNA and proteins spontaneously form three dimensional structures, and supramolecular structures emerge from protein aggregates with staggering degrees of ordering and specificity. By contrast, most synthetic systems in soft condensed matter do not assemble robustly. In this talk I will discuss experiments on simple systems that allow us to probe the physics and thermodynamics of self-assembly. We use systems consisting of small numbers (N ⇐ 12) of confined spherical colloidal particles to understand what physical parameters (interactions) determine how a system will assemble. We find that the probability of self-assembling a particular configuration can be understood in terms of the geometry of sphere packings. The geometrical model gives some insights into how phase transitions emerge as N approaches the bulk limit. At the same time, it yields some general insights into the design principles for robust self-assembly.

The physics and geometry of self-assembly

Guangnan Meng, Natalie Arkus, Jesse Collins, Michael Brenner,
Vinothan N. Manoharan

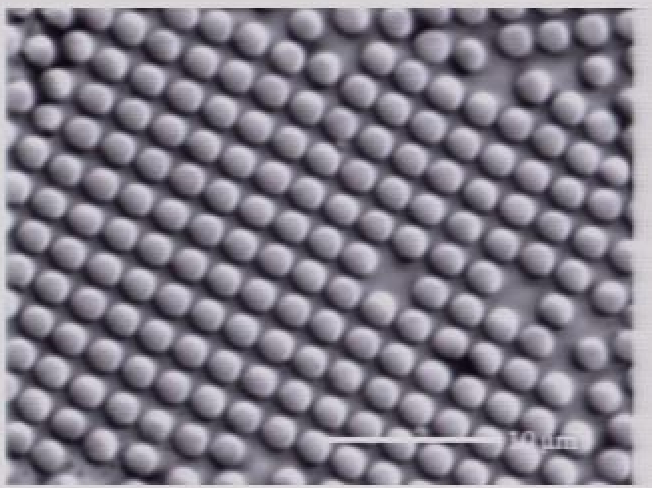
School of Engineering and Applied Sciences
Department of Physics,
Harvard University



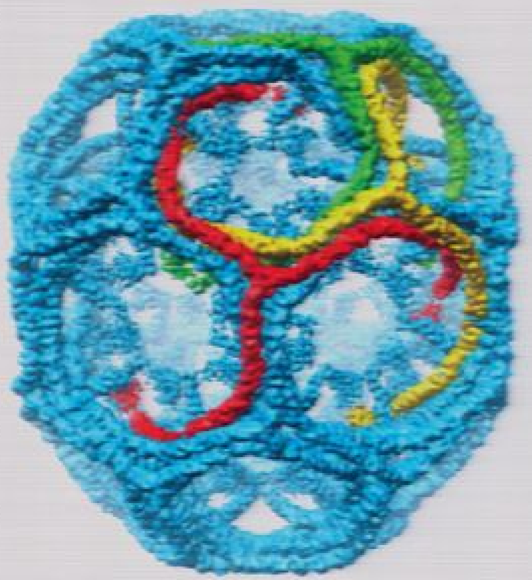
Funding: NSF MRSEC, NSF CAREER, NSF NIRT, Harvard HUSEC Seed Fund

Self-assembly

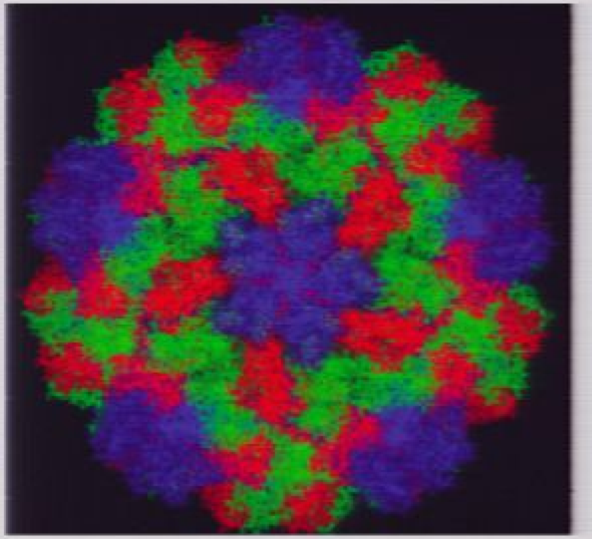
Any process in which a bunch of stuff (molecules, particles, polymers) in solution spontaneously forms an ordered structure



Crystals



Vesicles



Viruses

Self-assembly from the engineer's point of view: a great idea, in principle

(In principle) A way to cheaply and easily build materials with complex, 3-D [nano]structures

General recipe:

- Synthesize building blocks with specific interactions
- Assemble the blocks in solution or melt (by heating, stirring, activating, concentrating, or subjecting to external fields)
- Chemically treat the resulting structure to make a functional material

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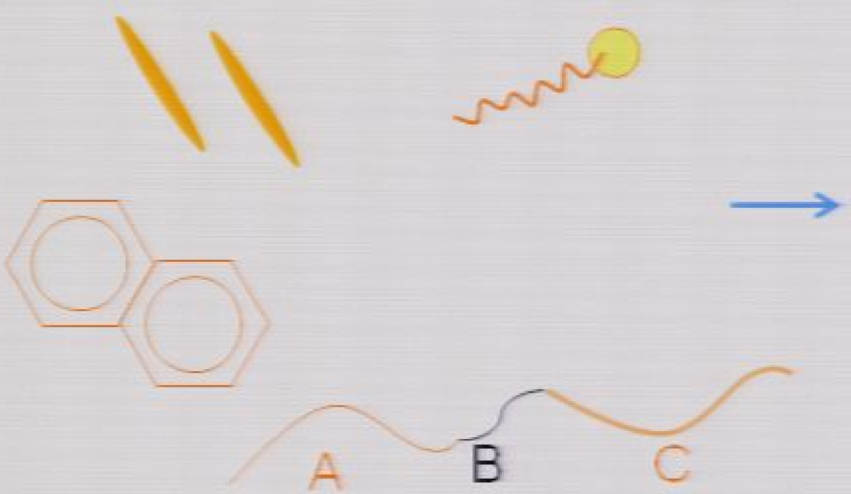
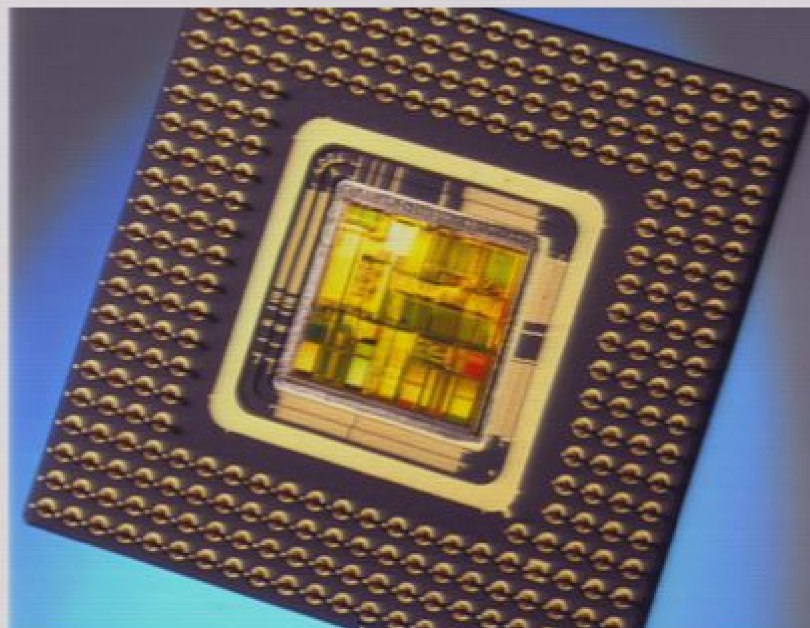
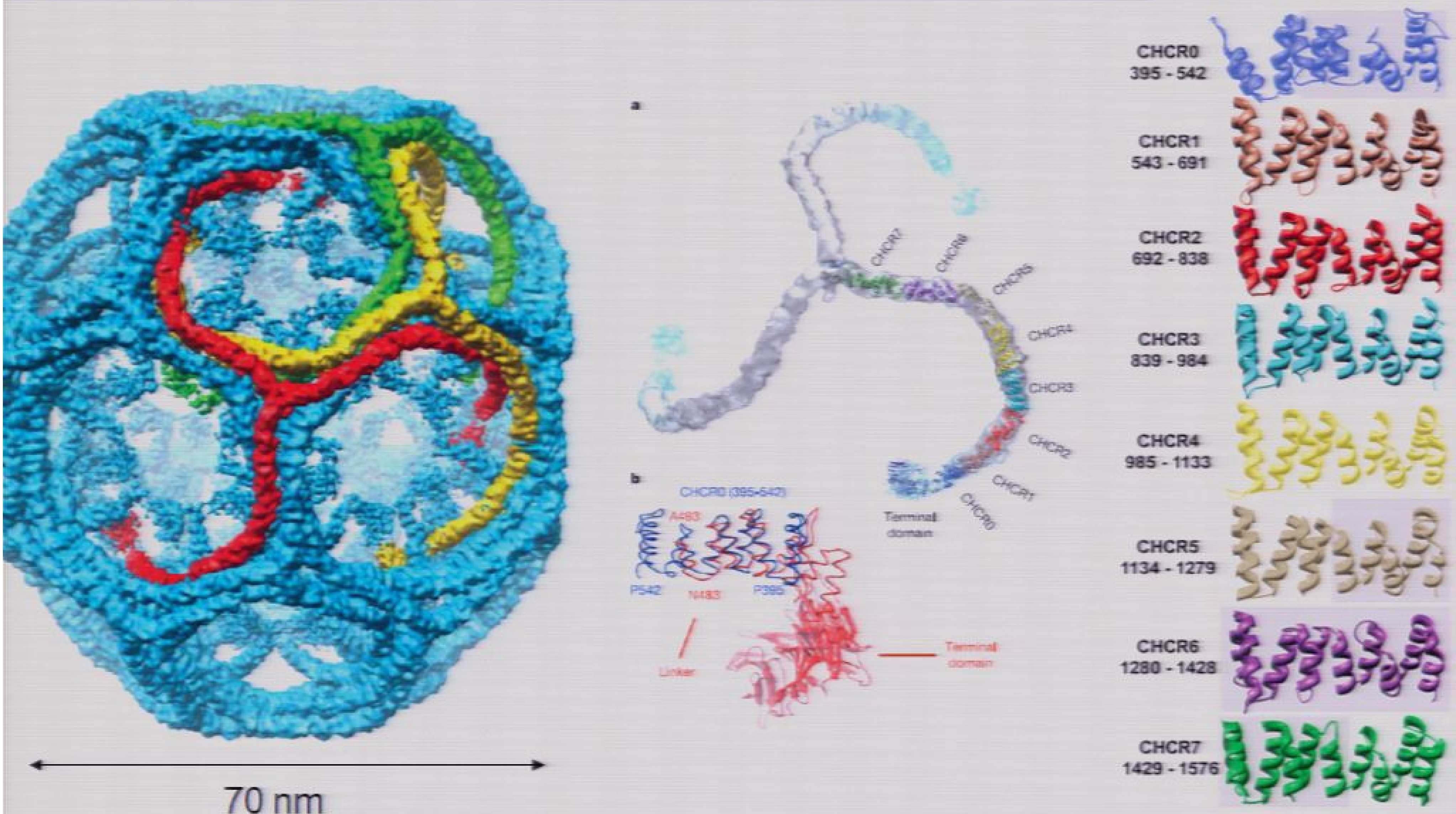




Soup of building blocks

Functional device

Self-assembly from the biologist's point of view: (yawn)



A. Fotin, Y. Cheng, P. Sliz, N. Grigorieff, S.C. Harrison, T. Kirchhausen, T. Walz, *Nature* **432** (2004)

Self-assembly from the physicist's point of view: statistical mechanics

More Is Different

Broken symmetry and the nature of the hierarchical structure of science.

P. W. Anderson

"The behavior of large and complex aggregates of elementary particles…is not to be understood in terms of simple extrapolation of the properties of a few…"

P. W. Anderson, *Science* 177 (1972)

Self-assembly from the physicist's point of view: statistical mechanics

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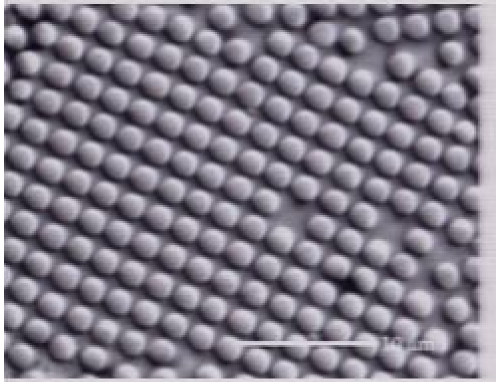
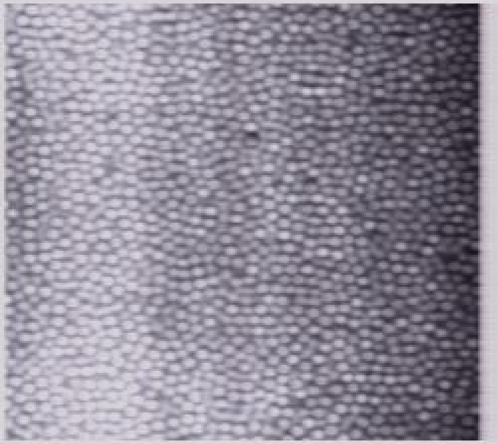
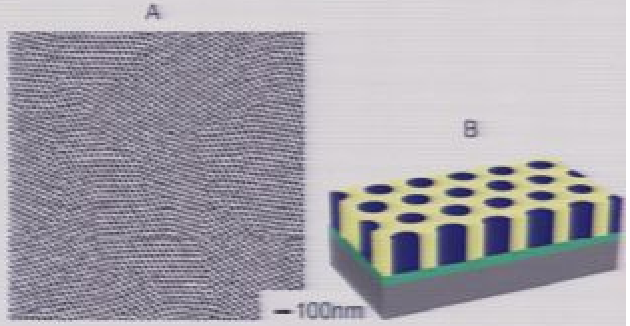


Crystallization and nucleation



Glass transition

Biological self-assembly, protein folding



Nanotechnology

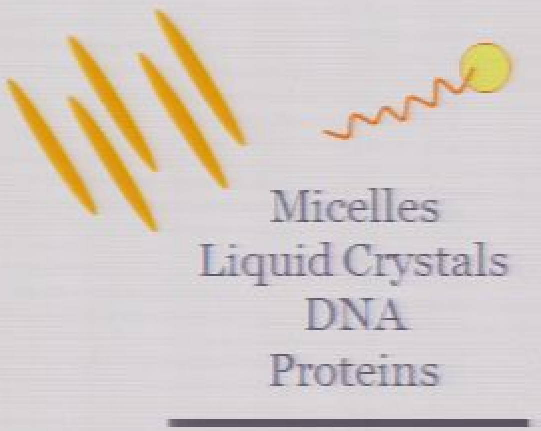
All of these problems must be related to some set of physical principles

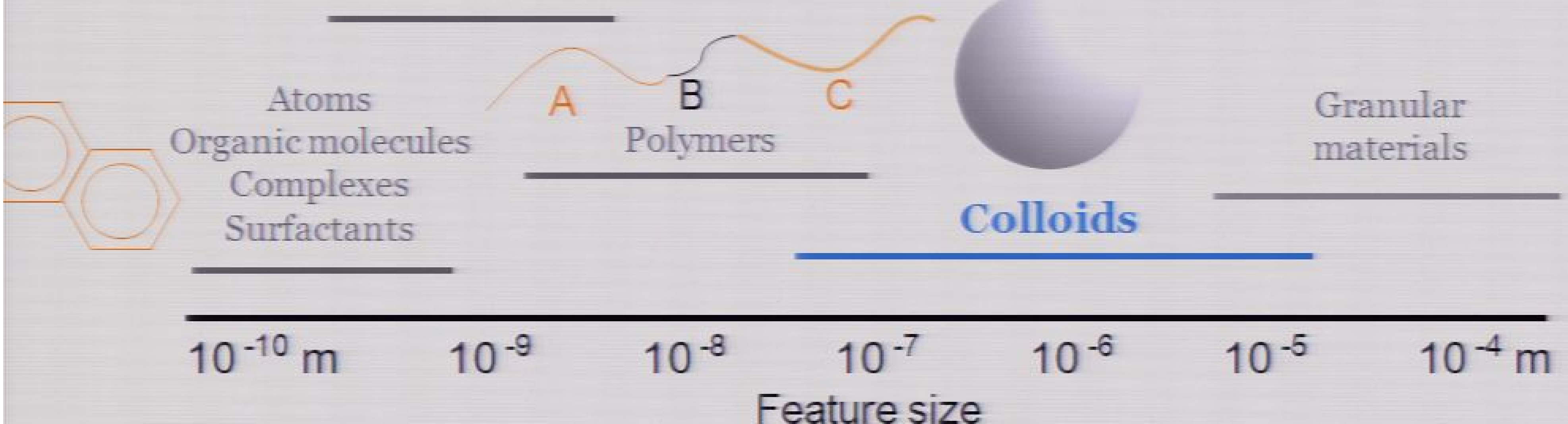
P. W. Anderson, *Science* 177 (1972)

Colloids: a model experimental system for self-assembly

Colloids: much larger than a molecule, but small enough to diffuse and self-assemble

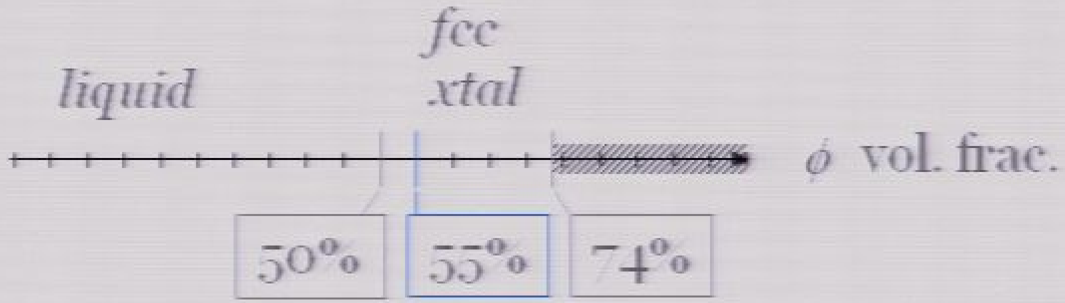
Materials: polymer, silica, liquids (emulsions)

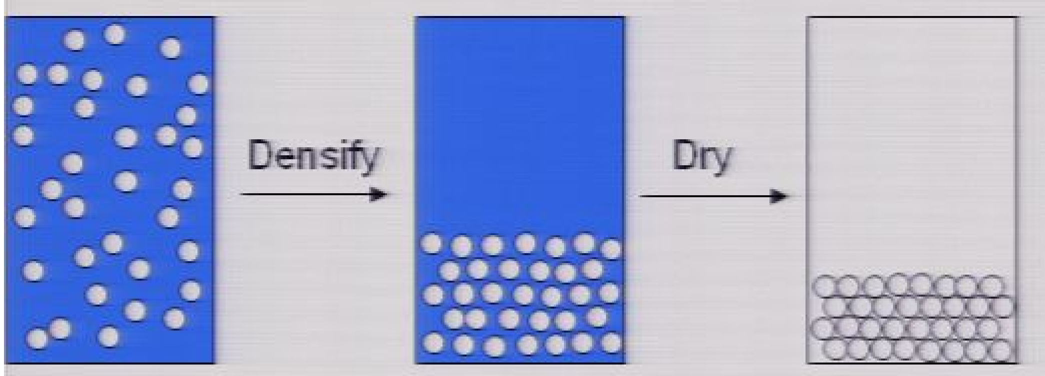




Colloids self-assemble into crystals

Phase diagram: hard sphere colloids





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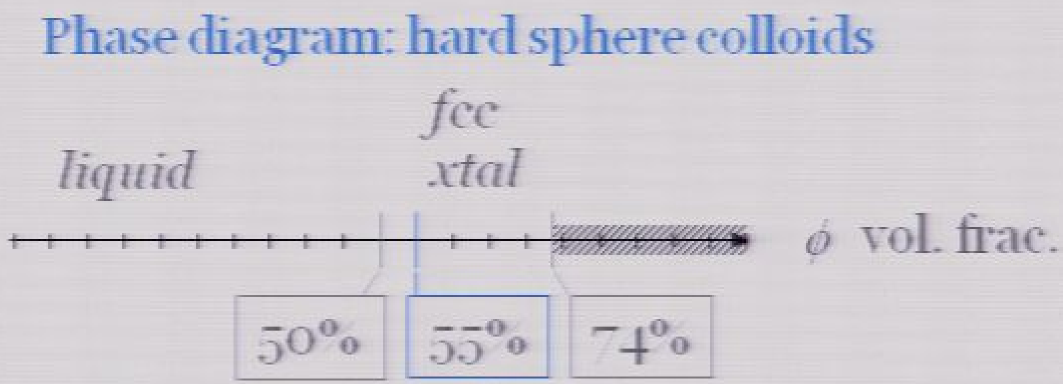
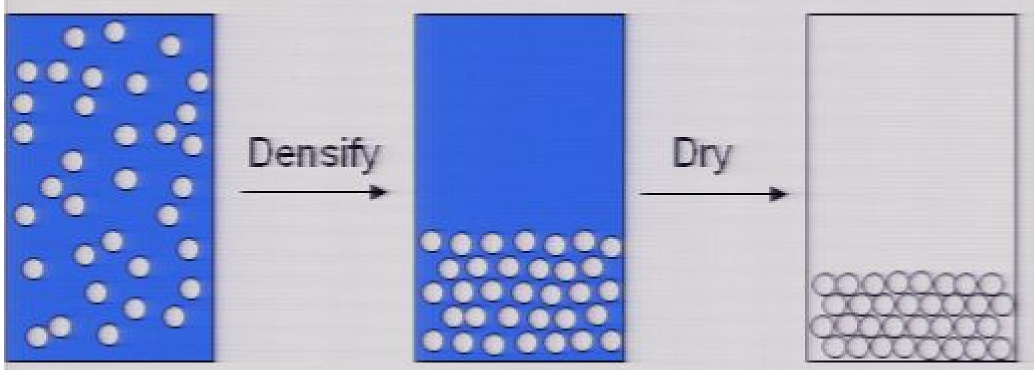


Crystallization driven by entropy

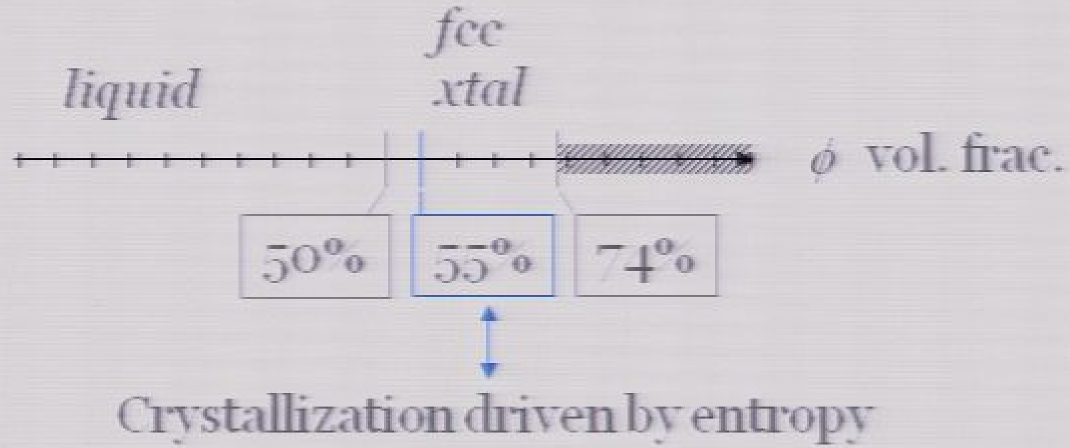


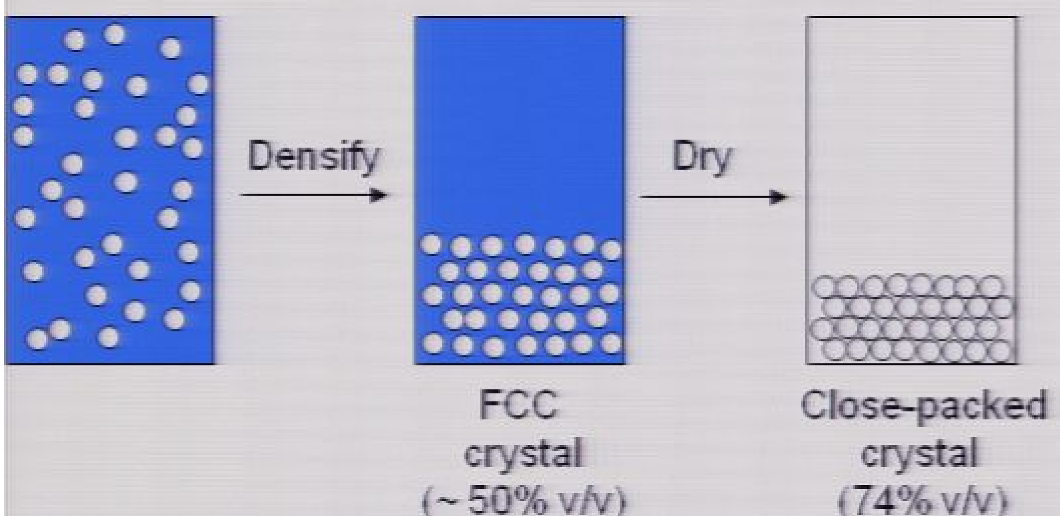
FCC crystal (~50% v/v)

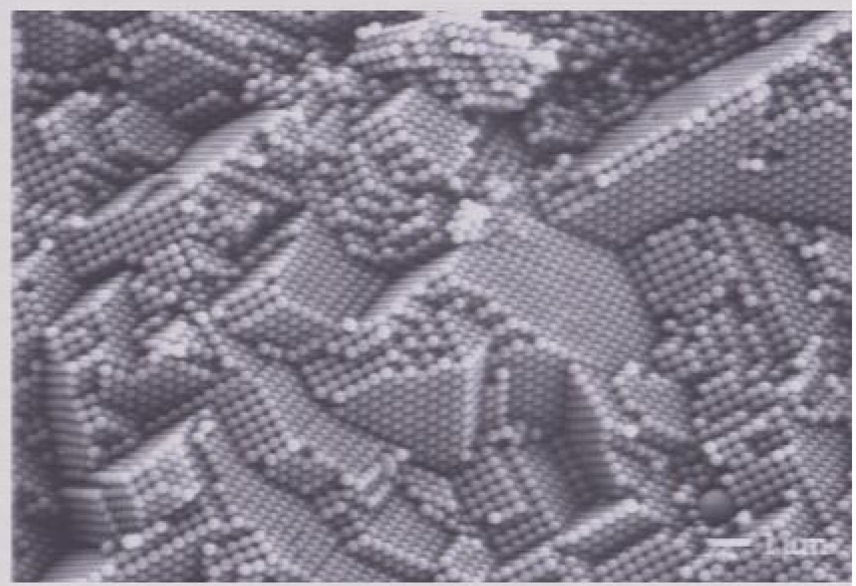
Close-packed crystal (74% v/v)

Colloids self-assemble into crystals

Phase diagram: hard sphere colloids

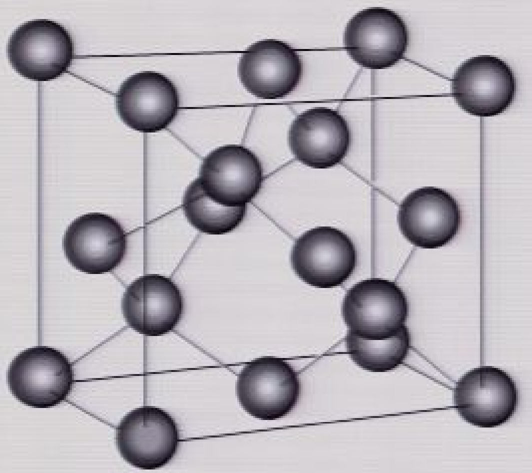




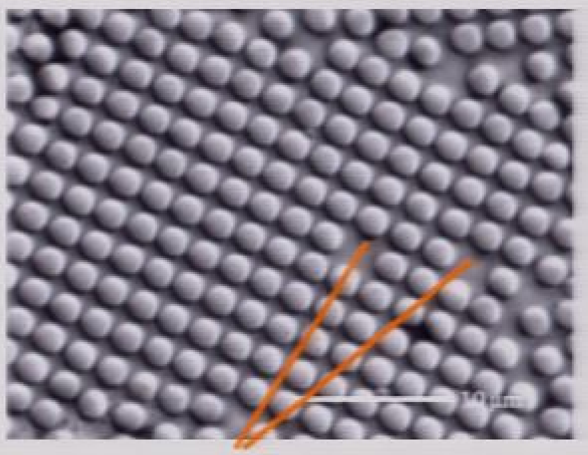


But [colloidal] self-assembly seems pretty limited...

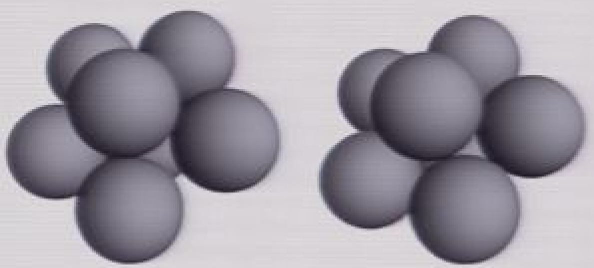
No easy or general way to control:



Crystal structure



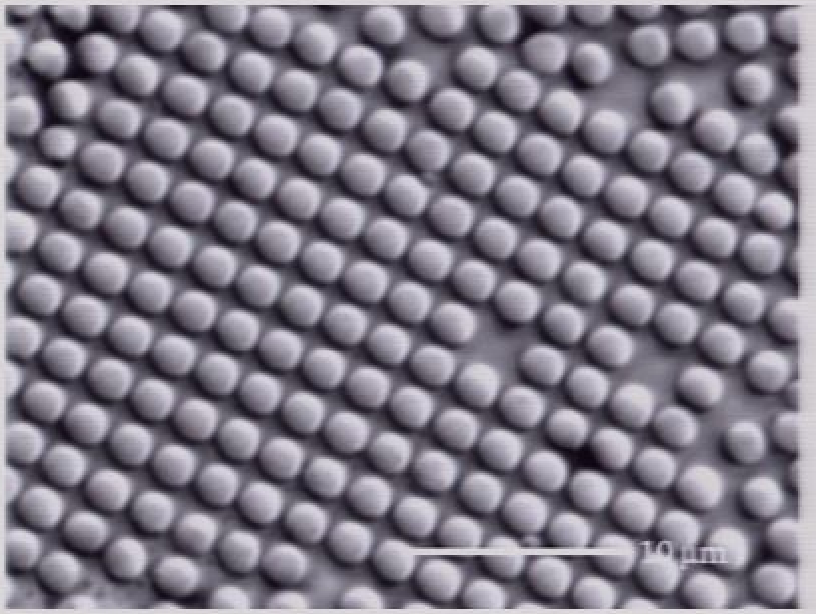
Defect structure



Nonperiodic (point group) structure

The same is true for many different types of synthetic "building blocks" (for example, polymers)

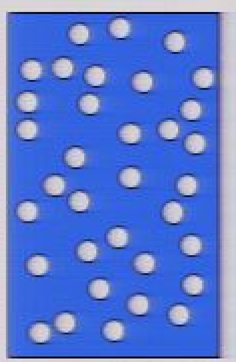
Why can't we self-assemble structures that are as robust and complex as living things?



But really...

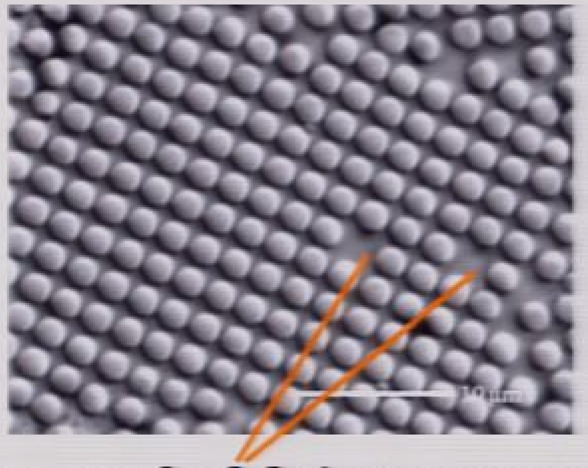
How much do we really know about how even the simplest systems self-assemble?

A self-assembly challenge

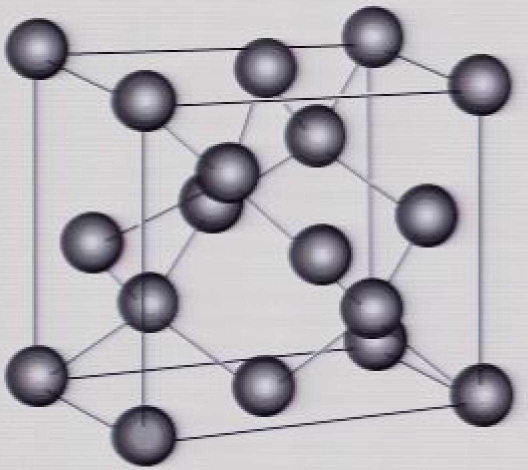


Beaker of spherical
colloidal particles

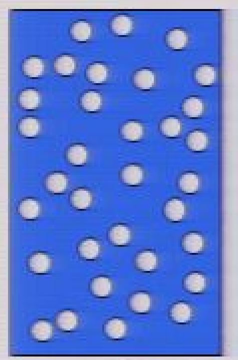
A self-assembly challenge



Prescribed defect structure

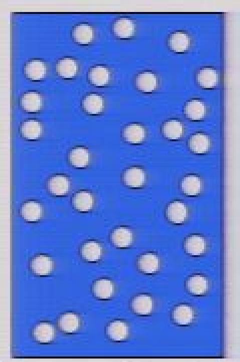


Any crystal structure



Beaker of spherical colloidal particles

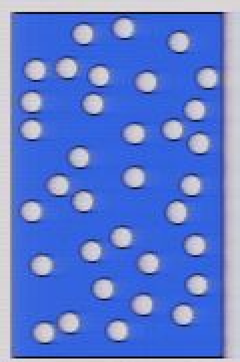
A self-assembly challenge



Beaker of spherical colloidal particles

A self-assembly challenge

Dream: Take a suspension of spherical particles with isotropic interactions, have them self-assemble robustly into an arbitrary 3D structure

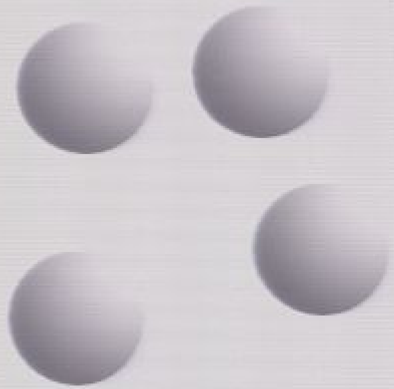


Beaker of spherical colloidal particles

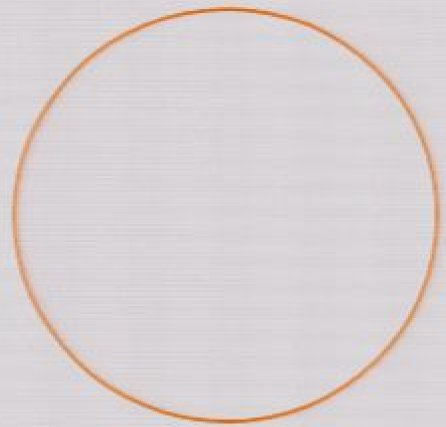
Arbitrary 3D structure

Big Ben Photo: Ian Britton, http://www.freefoto.com,

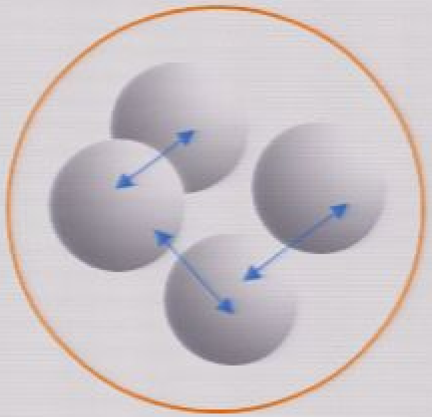
First step: Figure out how small numbers of colloids self-assemble



N hard spheres



A container



Short-range attraction between spheres

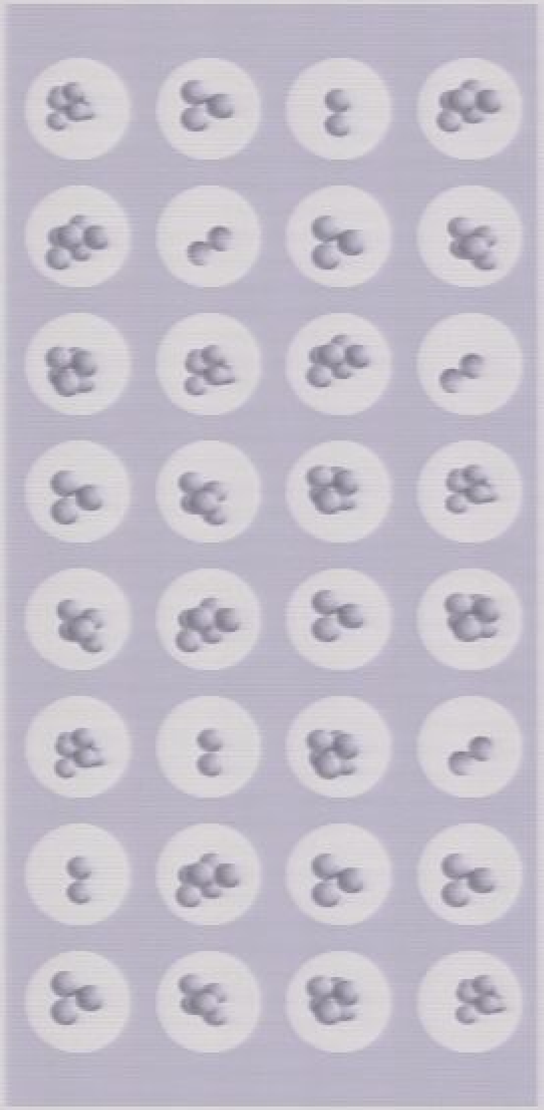
Problem: What are the equilibrium and metastable states of a system of *N* hard spheres with short-ranged attractions?

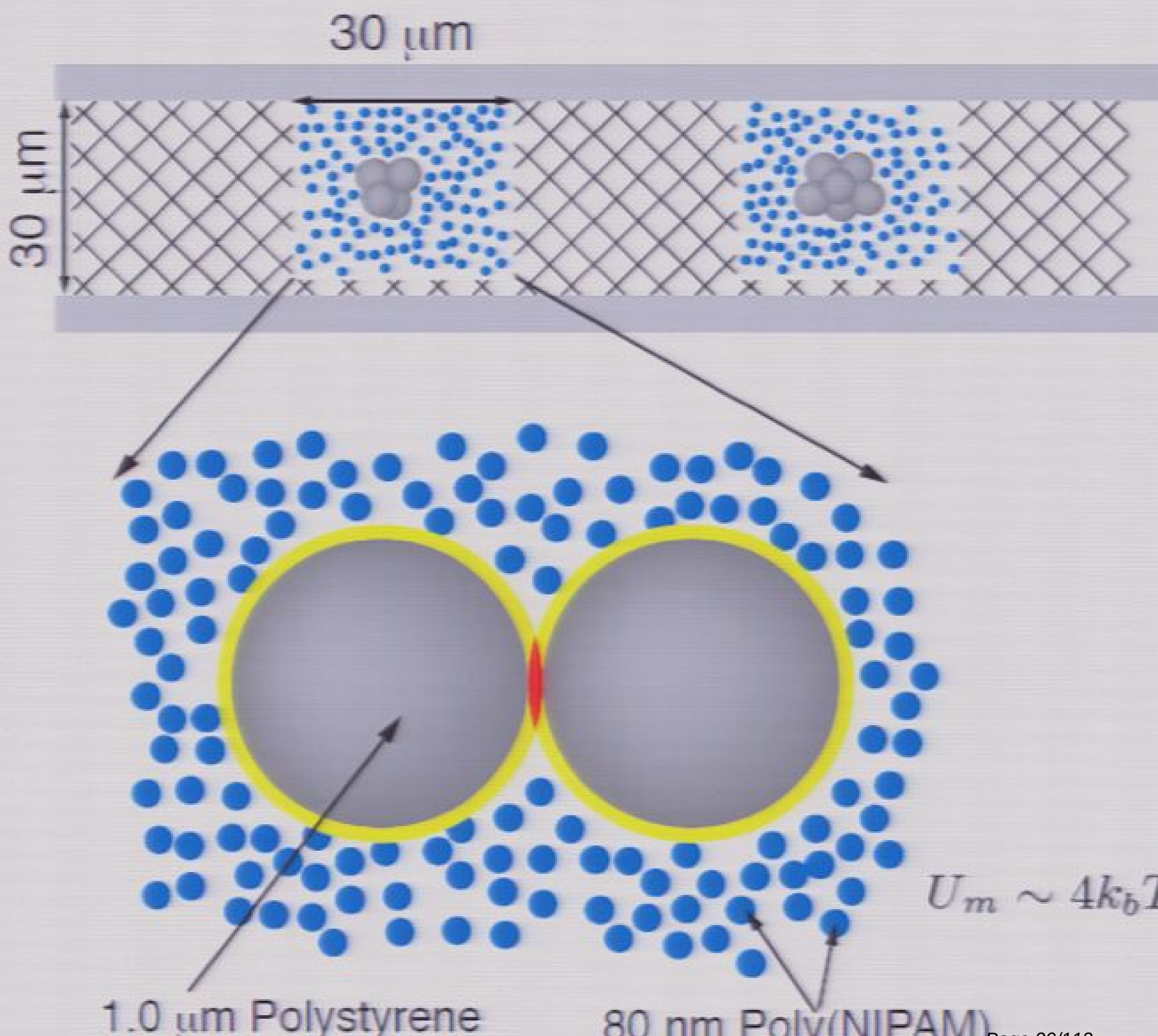
Motivation:

enumerating the possibilities for self-assembly
analogy to atomic clusters (Lennard-Jones, Au clusters)
possible connections to nucleation, bulk behavior

Nelson and Spaepen, "Polytetrahedral order in condensed matter," *Solid State Physics* 42: 1-90 (1989)

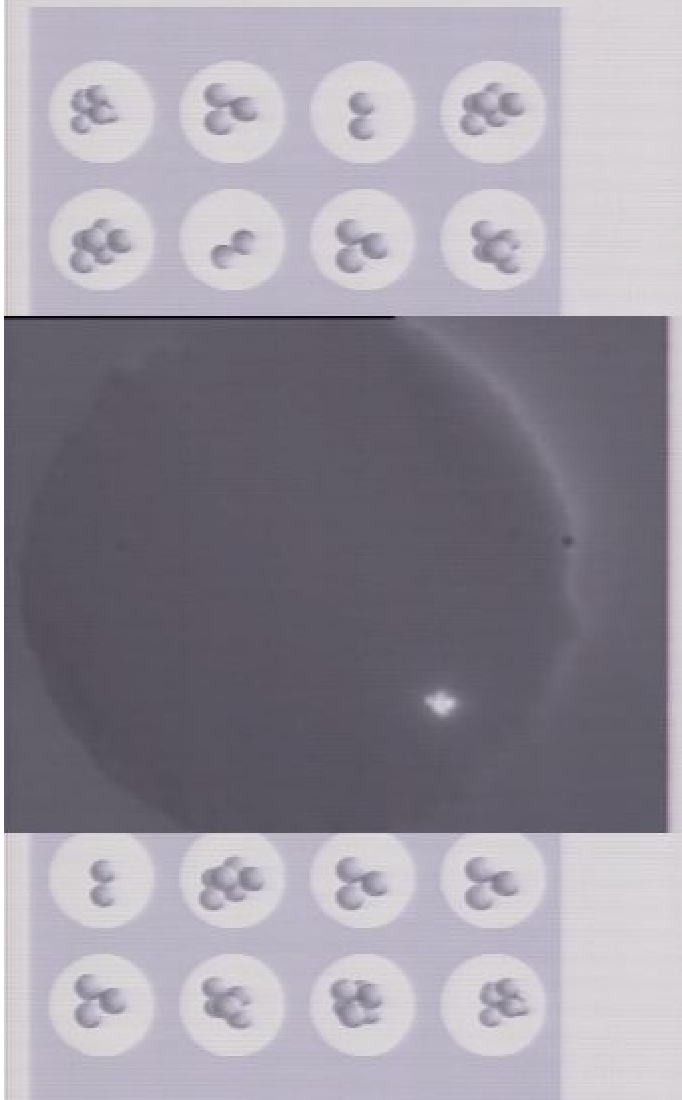
Experimental realization: an ensemble of particles inside microwells

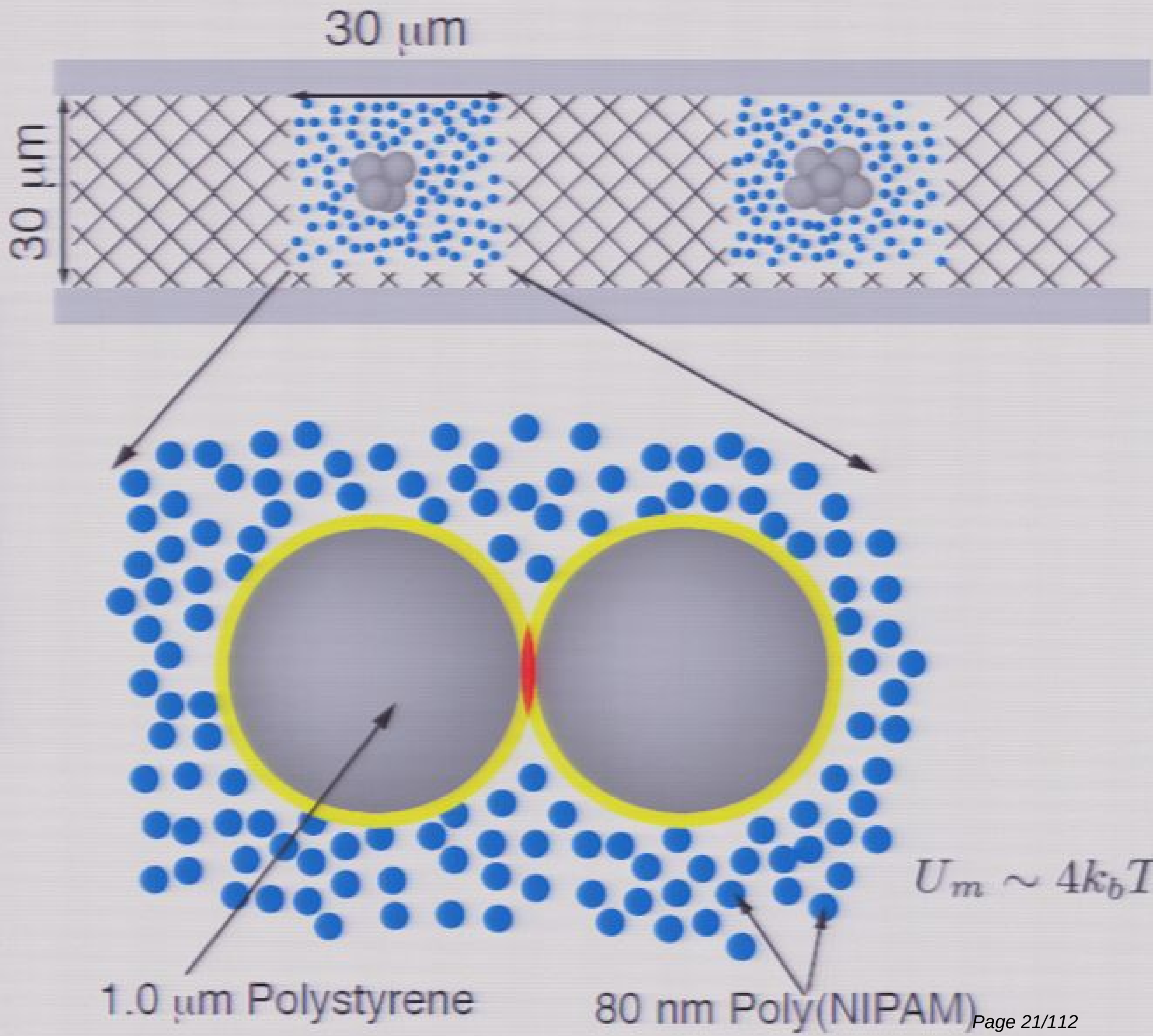

Microwell plate (hydrogel)



$U_m \sim 4k_bT$

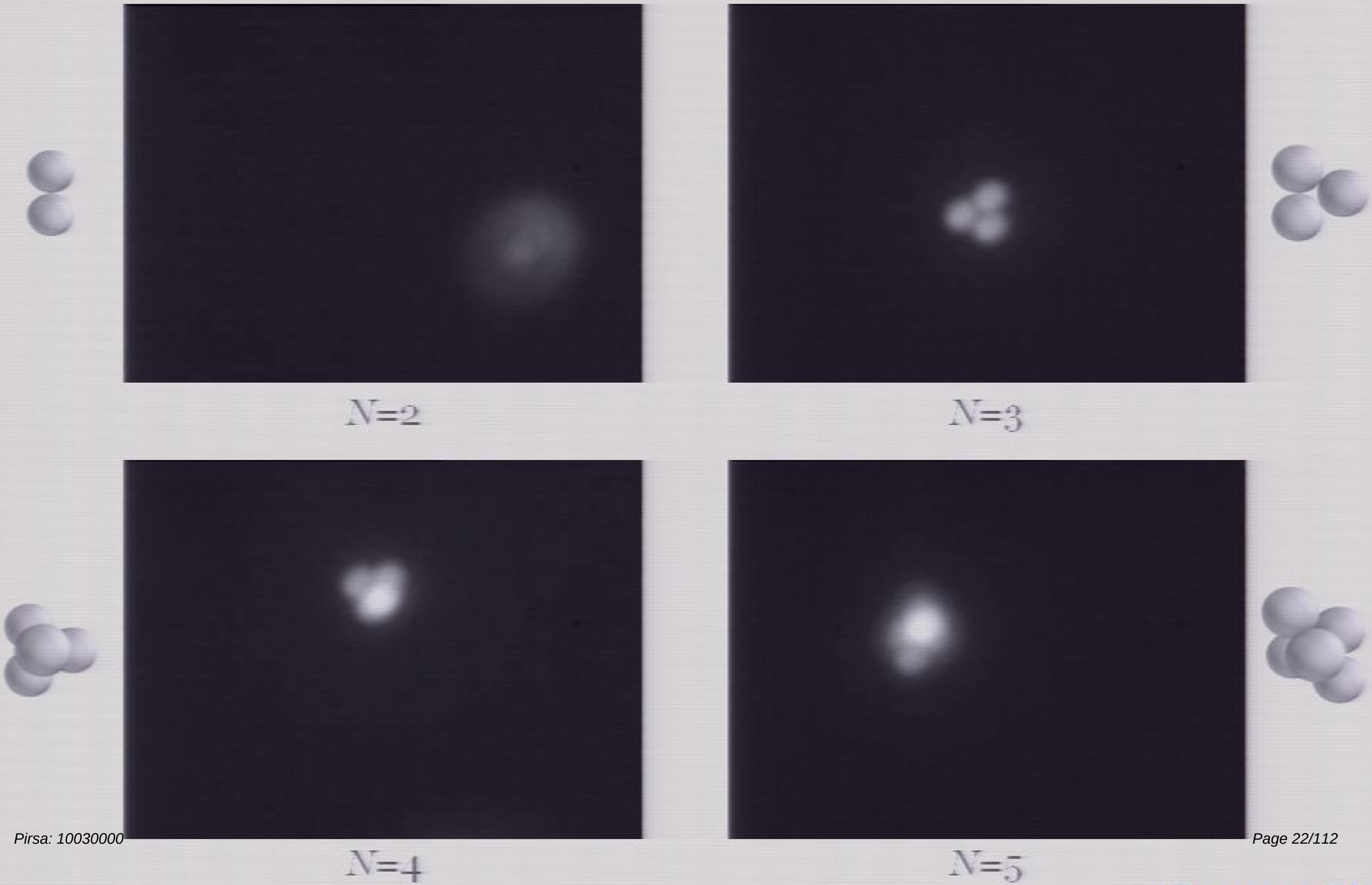
Experimental realization: an ensemble of particles inside microwells



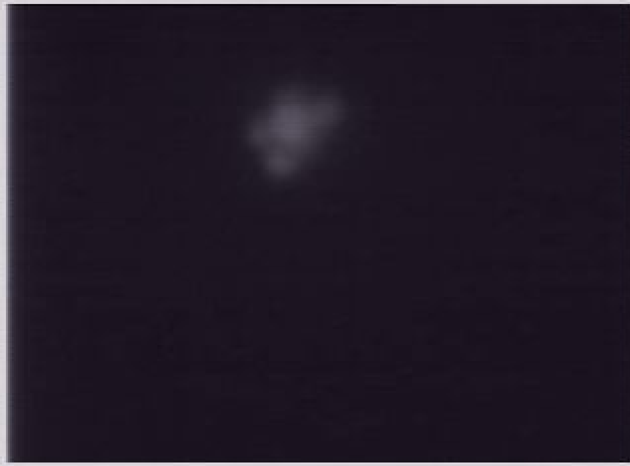


Microwell plate (hydrogel)

Results: N = 2-5

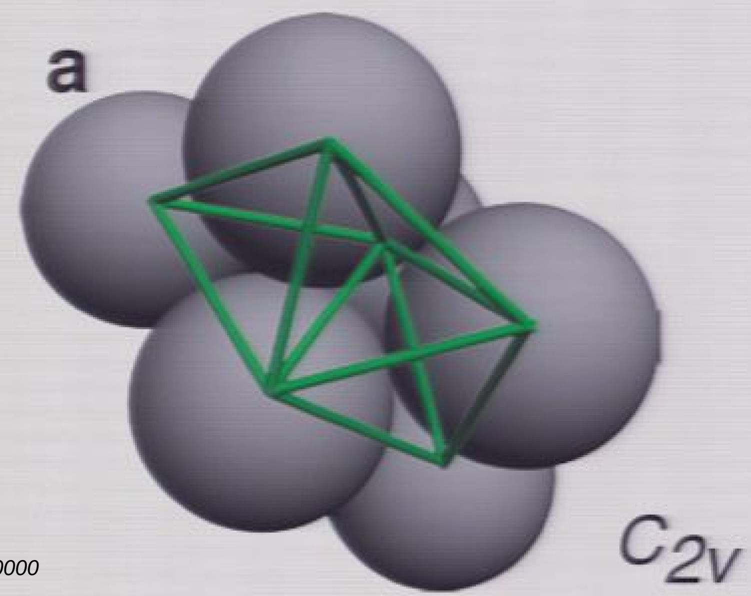


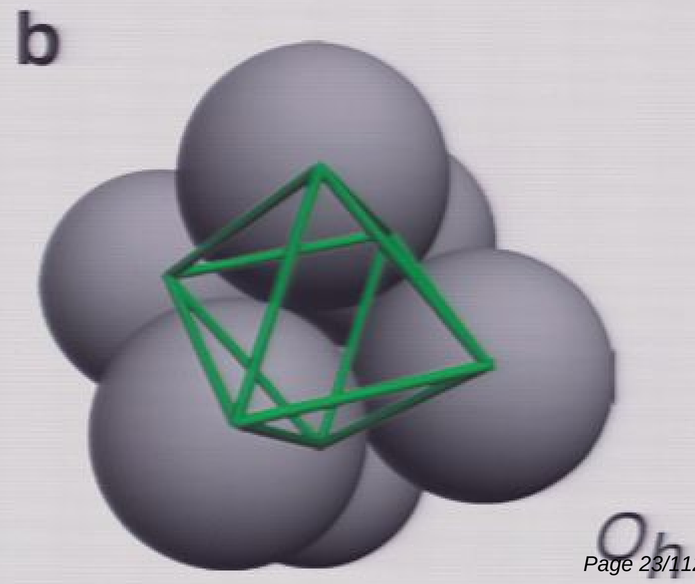
Results: N = 6



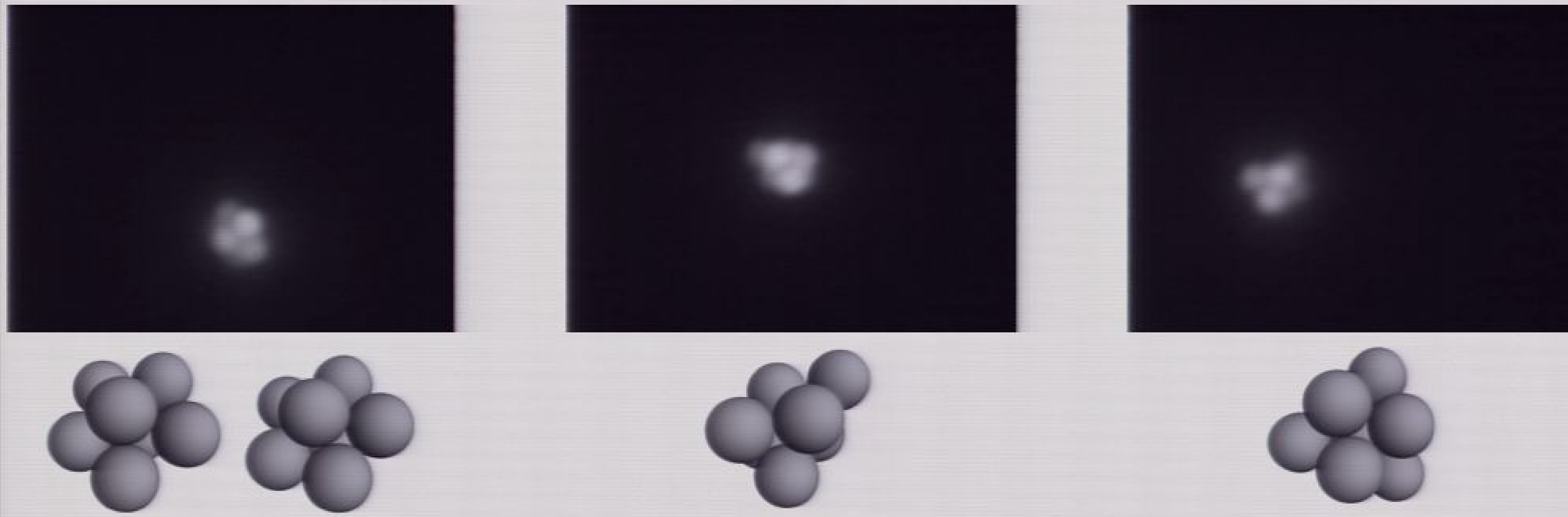
Tri-tetrahedron ("Polytetrahedron")

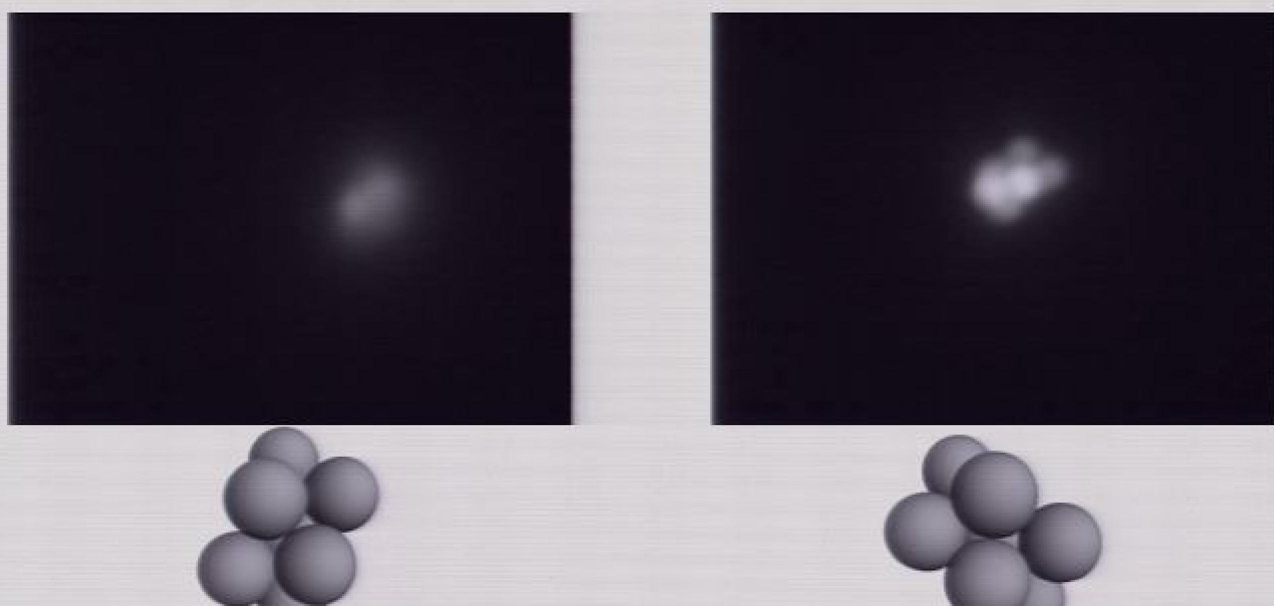
Octahedron





Results: N=7

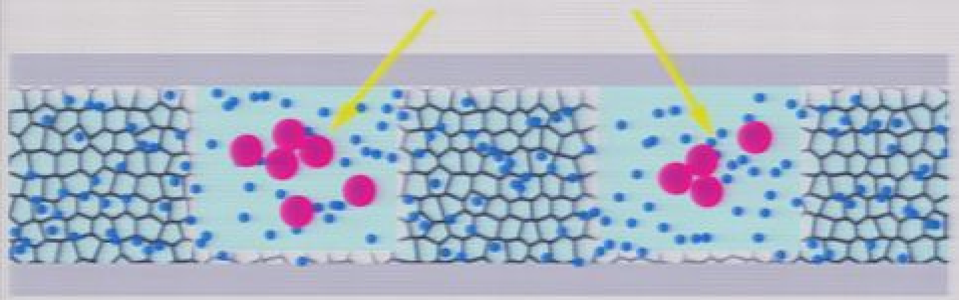


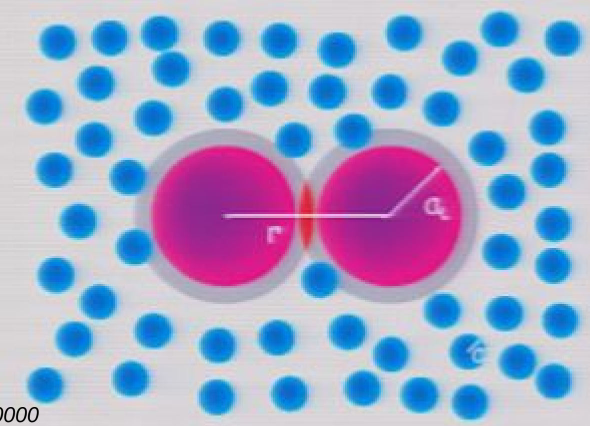


Experiment meets Theory

Experimental system:

- *N* colloidal particles in a microwell interacting through a short-ranged depletion attraction





$U_m \propto \rho_s a_s^2 a_l$

Theoretical problem:

- Statistical mechanics viewpoint:

  Determine the structures and internal energies of all the potential minima of the system for each *N*

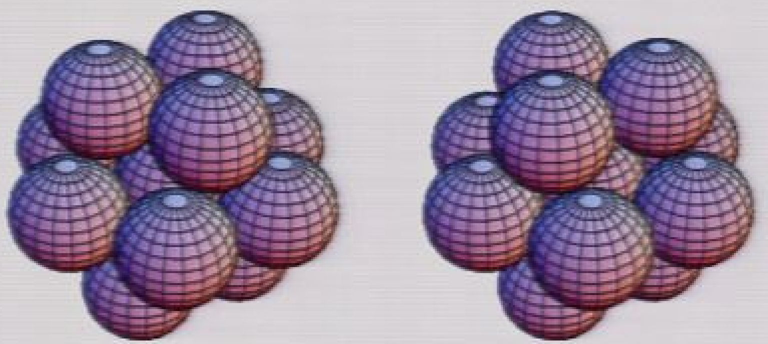
- Mathematical viewpoint:

  Determine all the rigid packings of *N* spheres and the number of contacts in each

Natalie Arkus

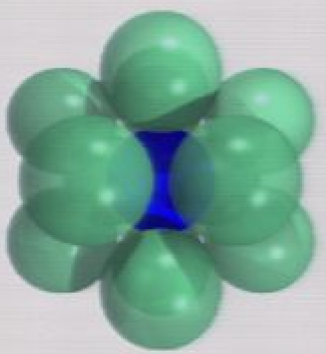
Theoretical approach: Why it so difficult?

Packing problems are hard...



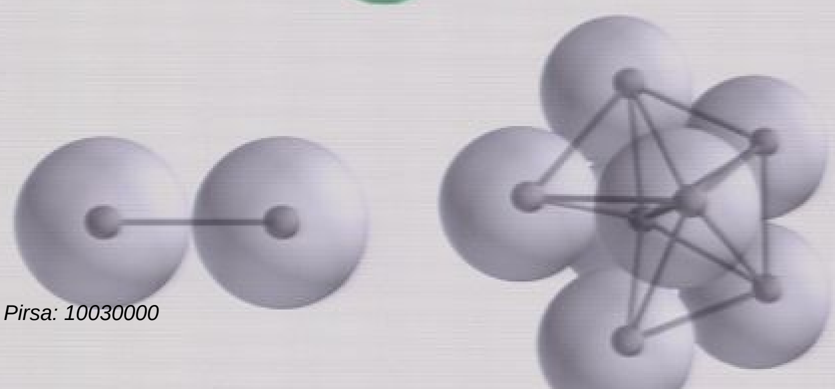
Kepler Conjecture (1611)

Hales – computer aided proof (1998)



Kissing Number Problem (1694)

3 dimensional proof (1874)



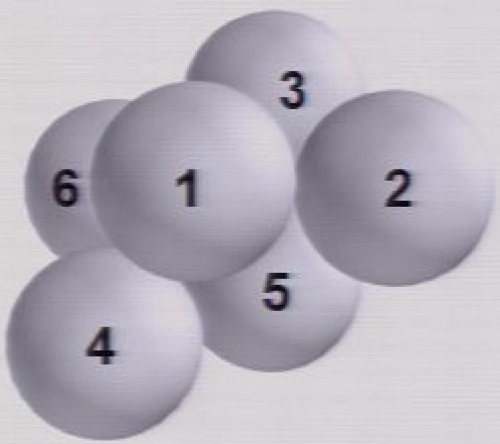
Erdos Unit Distance Problem (1946)

Unsolved

Natalie Arkus

An exact (computational) solution to the packing problem through graph theory

Structures Can be Defined by Adjacency Matrices



$$\begin{array}{c|cccccc} & 1 & 2 & 3 & 4 & 5 & 6 \\ \hline 1 & 0 & 1 & 1 & 1 & 1 & 1 \\ 2 & 1 & 0 & 1 & 0 & 1 & 0 \\ 3 & 1 & 1 & 0 & 0 & 1 & 1 \\ 4 & 1 & 0 & 0 & 0 & 1 & 1 \\ 5 & 1 & 1 & 1 & 1 & 0 & 1 \\ 6 & 1 & 0 & 1 & 1 & 1 & 0 \end{array}$$

1 if particles touch

0 if do not touch

Step 1: Construct all possible adjacency matrices

(Subset of which necessarily includes all rigid packings)

Natalie Arkus

Rigidity constraints limit the number of adjacency matrices: >3N-6 total contacts

$\frac{n(n-1)}{2}$ relative distances $\rightarrow$ $2^{\frac{n(n-1)}{2}}$ possible adjacency matrices

Number of Particles	Number of Adjacency Matrices	Non-Isomorphic Adjacency Matrices
1	1	1
2	2	2
3	8	4
4	64	11
5	1,024	34
6	32,768	156
7	2,097,152	1,044
8	268,435,456	12,346
9	$6.8719 \cdot 10^{10}$	274,668
10	$3.5184 \cdot 10^{13}$	12,005,168

nauty22 by Brendan McKay.

Natalie Arkus

Rigidity constraints limit the number of adjacency matrices: >3*N*-6 total contacts

$\frac{n(n-1)}{2}$ relative distances → $2^{\frac{n(n-1)}{2}}$ possible adjacency matrices

Number of Particles	Number of Adjacency Matrices	Non-Isomorphic Adjacency Matrices	Adjacency Matrices with 3 Contacts per Particle	Adjacency Matrices with $3n-6$ Total Contacts
1	1	1	1	1
2	2	2	1	1
3	8	4	1	1
4	64	11	1	1
5	1,024	34	3	1
6	32,768	156	19	4
7	2,097,152	1,044	150	29
8	268,435,456	12,346	2,590	438
9	$6.8719 \cdot 10^{10}$	274,668	84,245	13,828
10	$3.5184 \cdot 10^{13}$	12,005,168	5,203,135	750,352

nauty22 by Brendan McKay.

Step 2: Determine which subset corresponds to rigid sphere packings...

Natalie Arkus

Solving for Packings

$$\begin{pmatrix} 0 & 1 & 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 0 & 1 & 0 \\ 1 & 1 & 0 & 0 & 1 & 1 \\ 1 & 0 & 0 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 1 \\ 1 & 0 & 1 & 1 & 1 & 0 \end{pmatrix} \longrightarrow \begin{pmatrix} 0 & 1 & 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & r_{24} & 1 & r_{26} \\ 1 & 1 & 0 & r_{34} & 1 & 1 \\ 1 & r_{24} & r_{34} & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 1 \\ 1 & r_{26} & 1 & 1 & 1 & 0 \end{pmatrix}$$

Adjacency Matrix Distance Matrix

Each adjacency matrix encodes a structure

How to solve for structure?

Adjacency matrix corresponds to a system of quadratic equations:

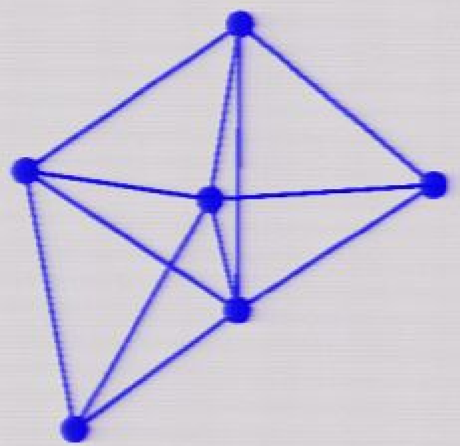
$$\begin{aligned} (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 &= R^2: \text{ if } A_{ij} = 1 \\ (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 &\geq R^2: \text{ if } A_{ij} = 0 \end{aligned}$$

Problem becomes one of solving the system of n(n-1)/2 equations.

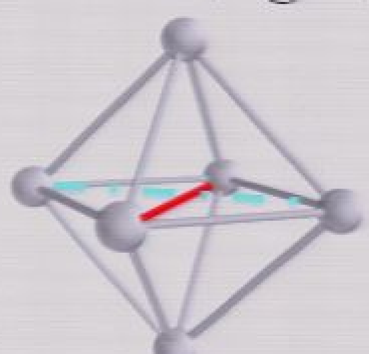
Natalie Arkus

A geometric solution

Iterative Packings: packings built from smaller (rigid) packings



New Seed: packing that can not be built from any combination of smaller (rigid) packings



Natalie Arkus

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4	64	11	1	1
5	1,024	34	3	1
6	32,768	156	19	4
7	2,097,152	1,044	150	29
8	268,435,456	12,346	2,590	438
9	$6.8719 \cdot 10^{10}$	274,668	84,245	13,828
10	$3.5184 \cdot 10^{13}$	12,005,168	5,203,135	750,352

nauty22 by Brendan McKay.

Natalie Arkus
Michael Brenner

Number of Particles	Number of Adjacency Matrices	Non-Isomorphic Adjacency Matrices	Adjacency Matrices with 3 Contacts per Particle	Adjacency Matrices with $3n-6$ Total Contacts
1	1	1	1	1
2	2	2	1	1
3	8	4	1	1
4	64	11	1	1
5	1,024	34	3	1
6	32,768	156	19	4
7	2,097,152	1,044	150	29
8	268,435,456	12,346	2,590	438
9	$6.8719 \cdot 10^{10}$	274,668	84,245	13,828
10	$3.5184 \cdot 10^{13}$	12,005,168	5,203,135	750,352

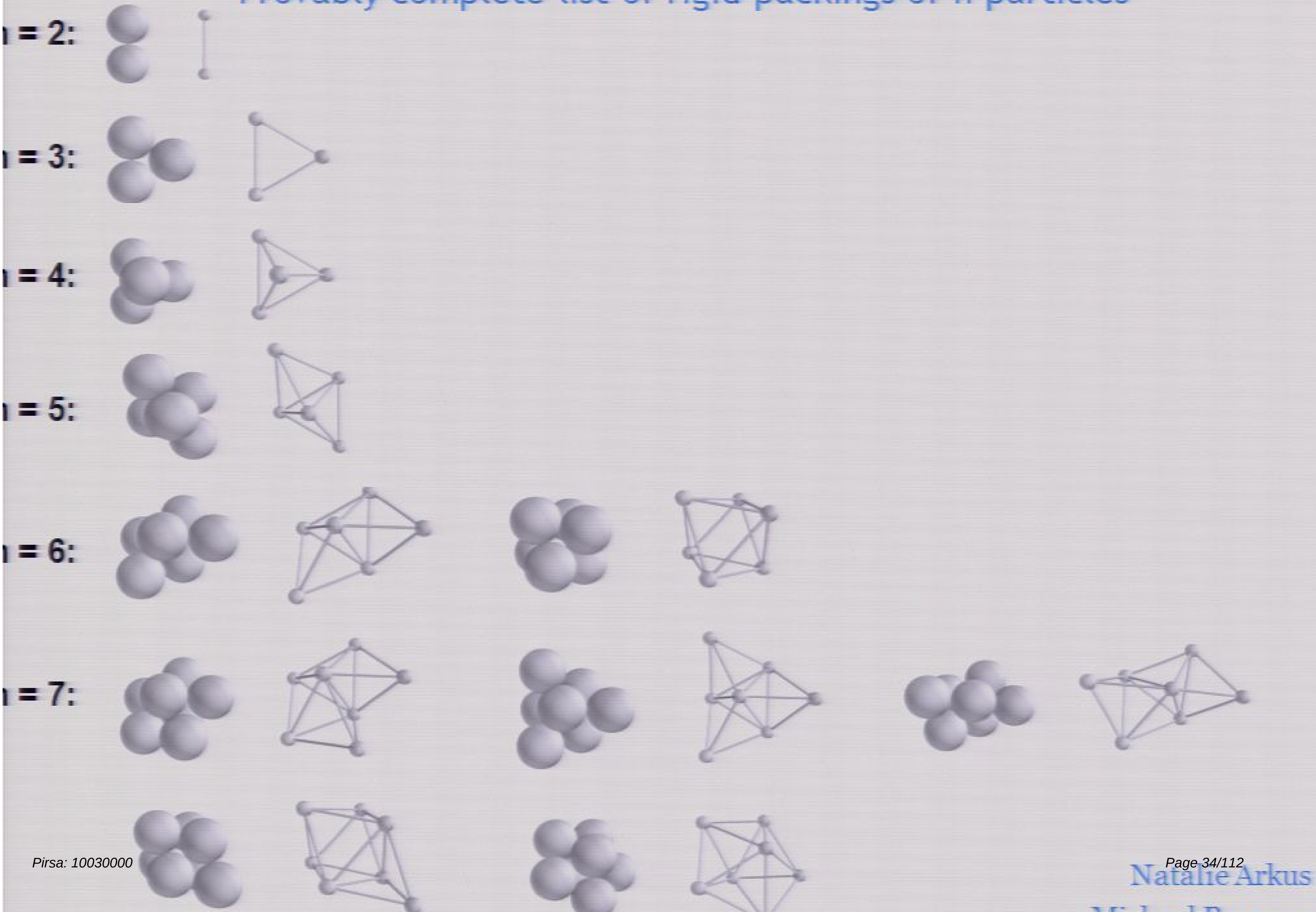
nauty22 by Brendan McKay.

Number of Particles	Number of Adjacency Matrices	Iterative Adjacency Matrices	Non-Iterative Adjacency Matrices
6	4	3	1
7	29	26	3
8	438	437	1
9	13,828	13,823	5
10	750,352	750,226	126

↑ Apply General Rule

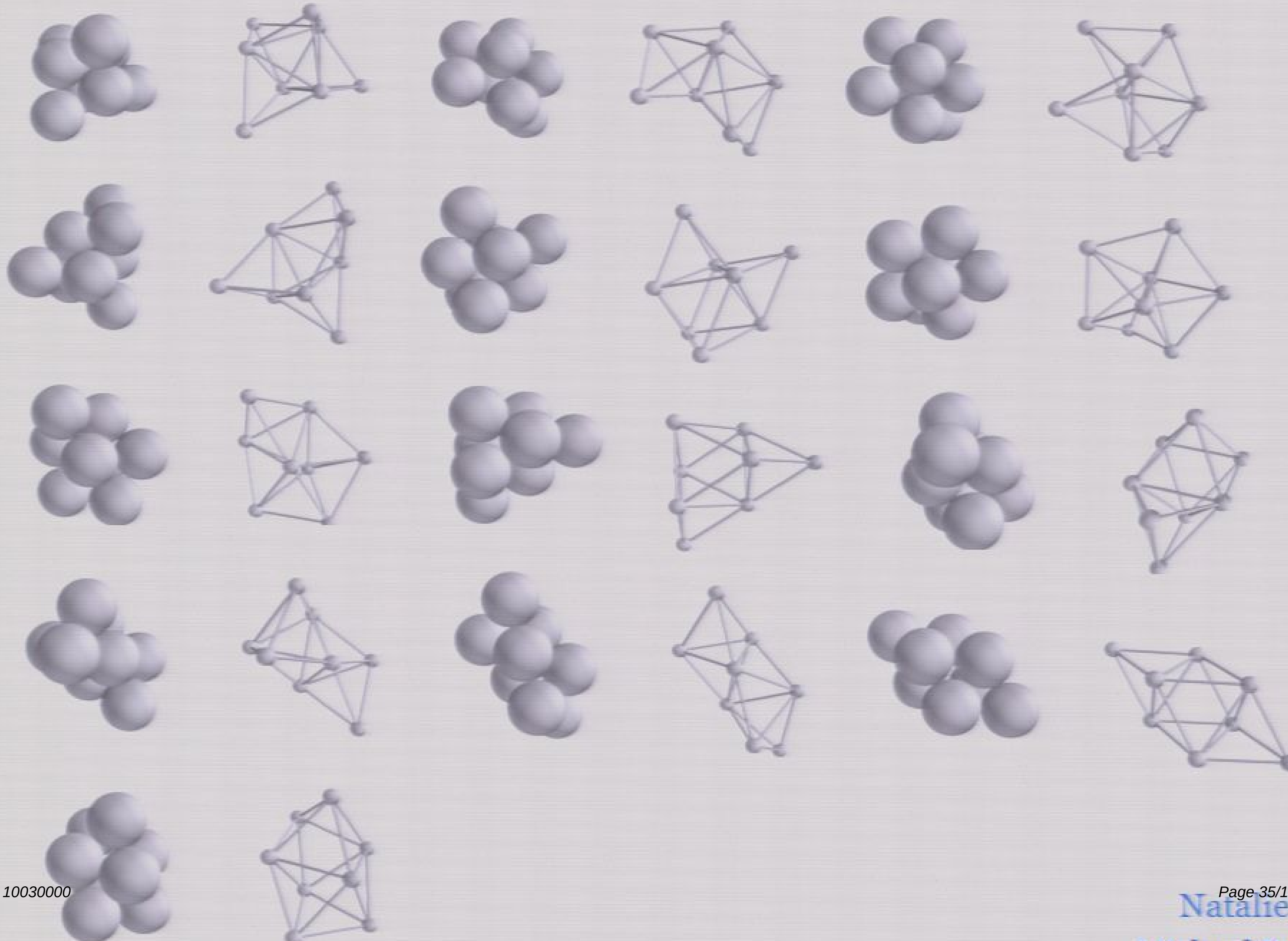
↑ Derive New Geometrical Rules

Provably complete list of rigid packings of n particles



Provably complete list of rigid packings of n particles

n = 8:



Natalie Arkus

Packings summary

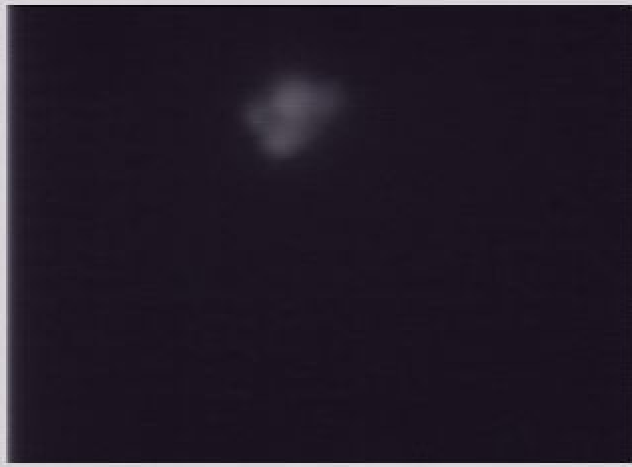
n	Packings from [1]	Total Packings (Current Study)	New Seeds	Non-Rigid Packings	Chiral	Total States
2	1	1	0	0	0	1
3	1	1	0	0	0	1
4	1	1	0	0	0	1
5	1	1	0	0	0	1
6	2	2	1	0	0	2
7	4	5	1	0	1	6
8	10	13	1	0	3	16
9	32	50	4	1	27	77
10	113	223	8	4		

All of these structures are degenerate at each $N < 10$!

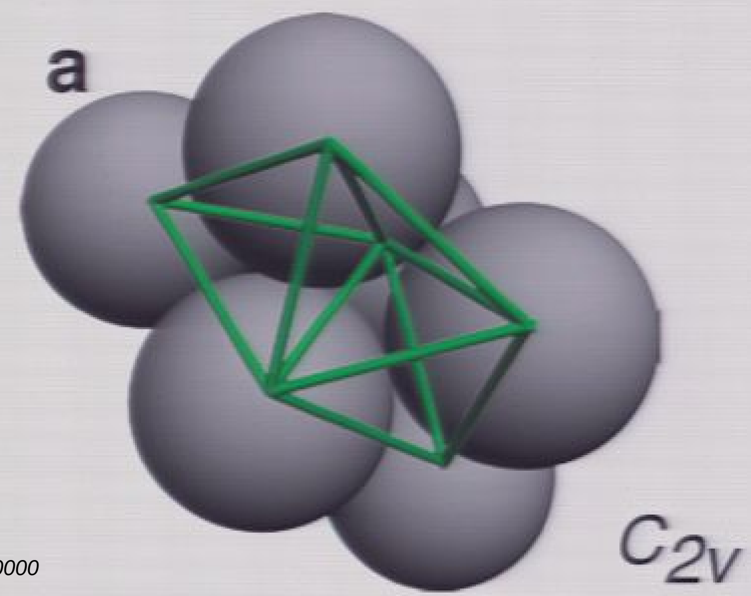
[1] Hoare and McInnis, *Faraday Disc. Chem. Soc.* **61** (12): 1976

Natalie Arkus

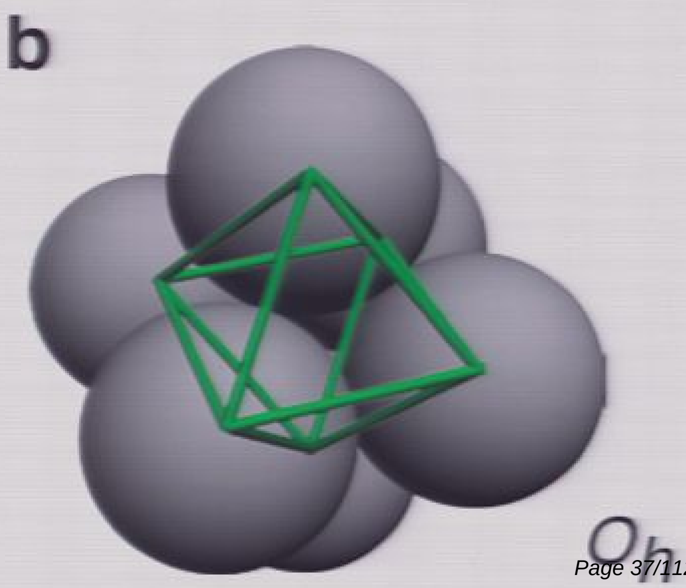
N = 6: Two degenerate structures, two very different experimental probabilities



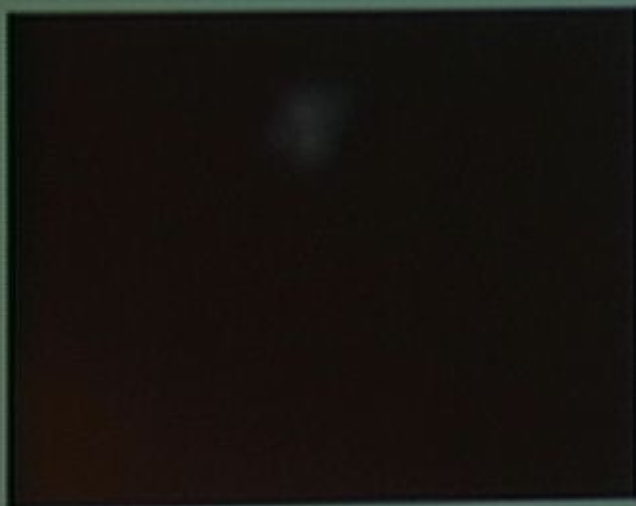
Poly-tetrahedron, 266 (≈95.6%)



Octahedron, 12 (≈4.3%)



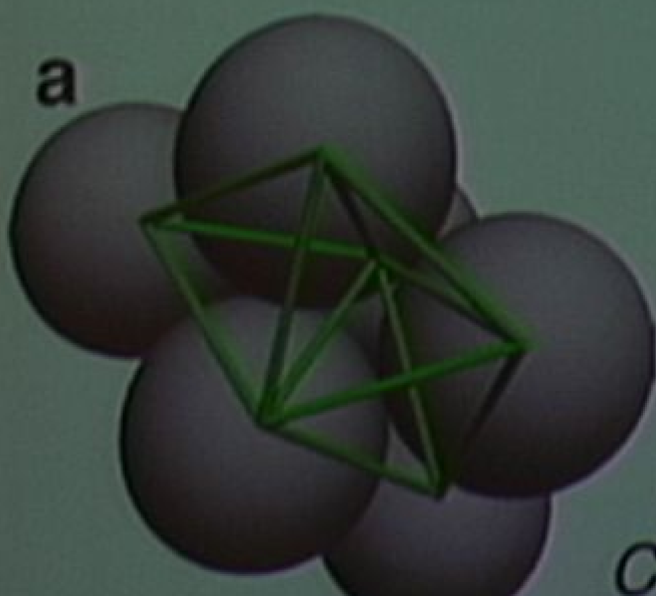
N = 6: Two degenerate structures, two very different experimental probabilities



Poly-tetrahedron, 266 (≈95.6%)

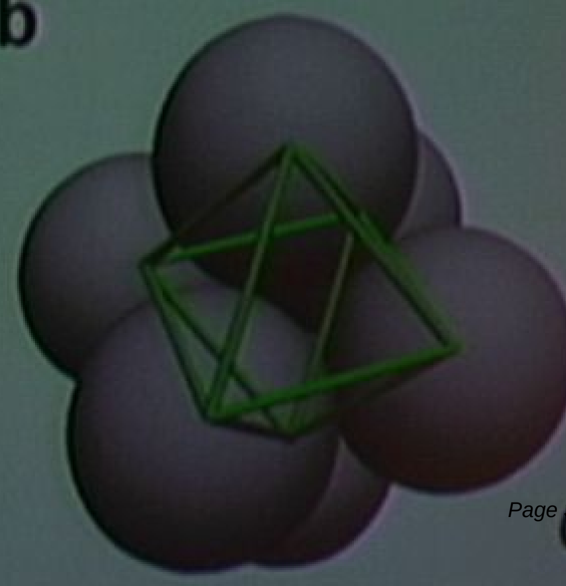
Octahedron, 12 (≈4.3%)

a



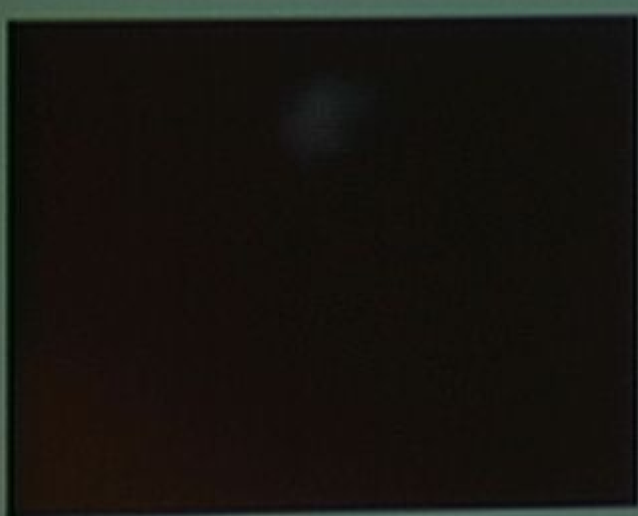
C_{2v}

b



O_h

$N = 6$: Two degenerate structures, two very different experimental probabilities



Poly-tetrahedron, 266 (≈95.6%)

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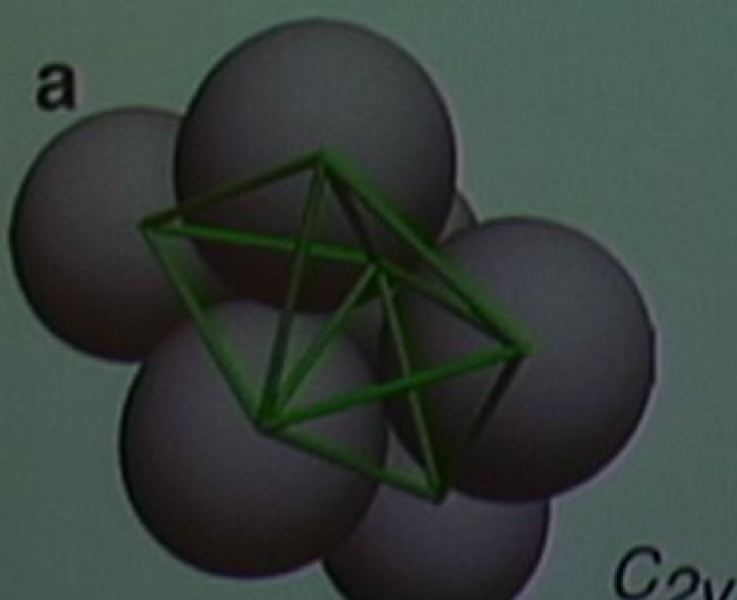
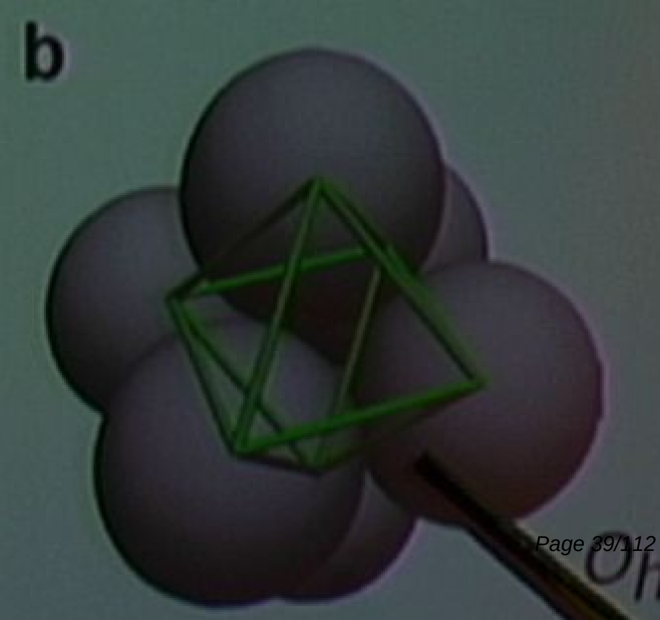
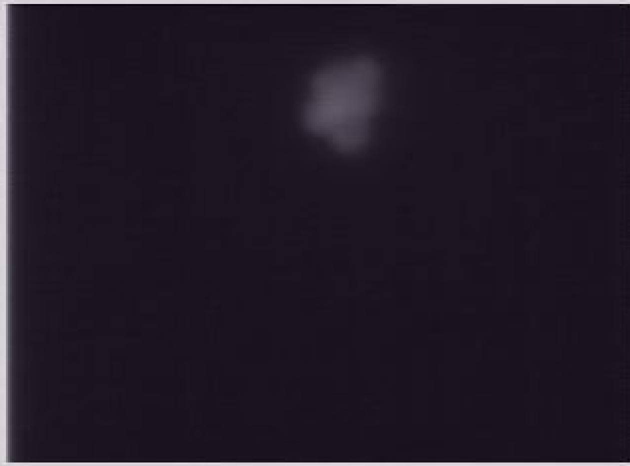




N = 6: Two degenerate structures, two very different experimental probabilities



Poly-tetrahedron, 266 (≈95.6%)

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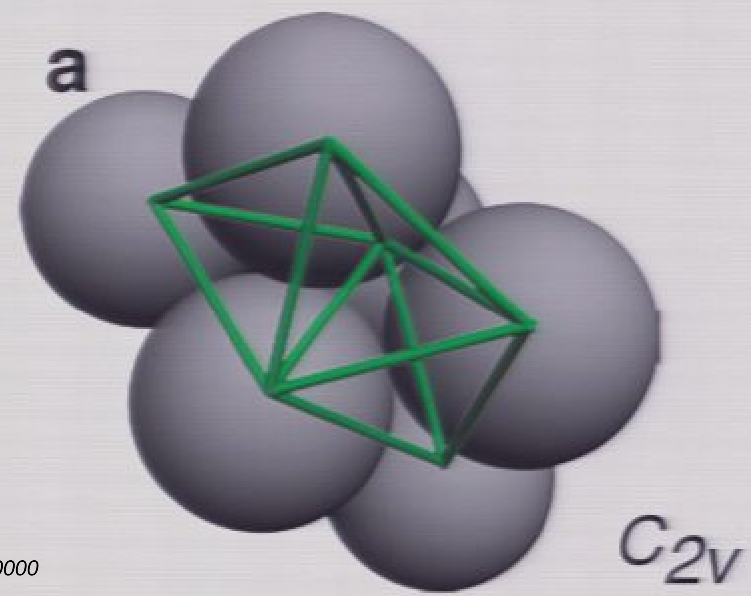
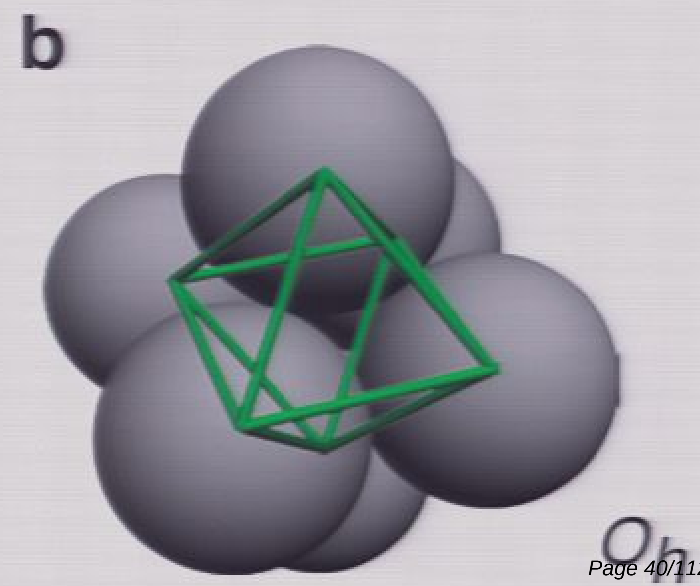
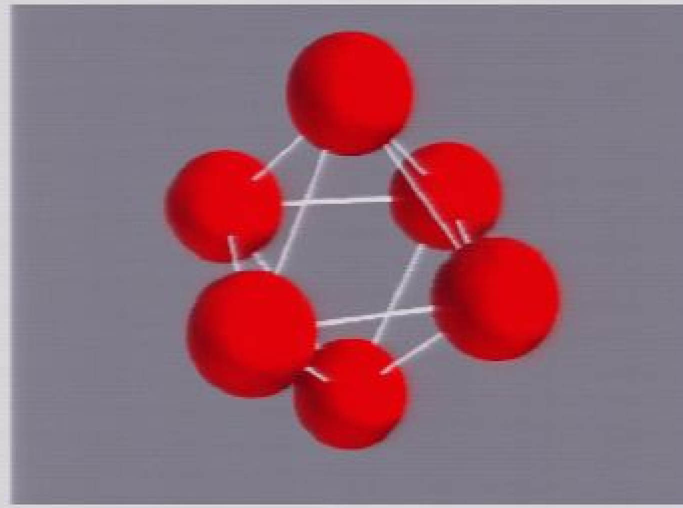




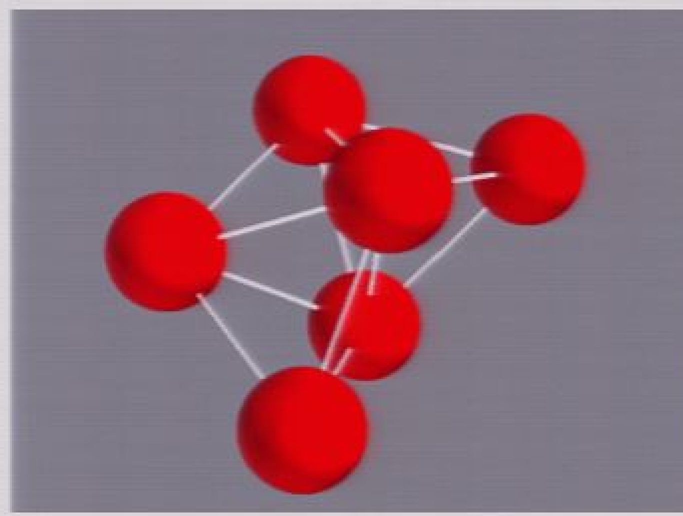
Vibrational entropy doesn't explain the discrepancy

$$\frac{p_{oct}}{p_{poly}} = \frac{Z_r}{Z_r'} \cdot \frac{Z_v}{Z_v'} \cdot \frac{Z_t}{Z_t'} = \quad (4.51\%\ \text{expt})$$

Z_v: normal mode analysis



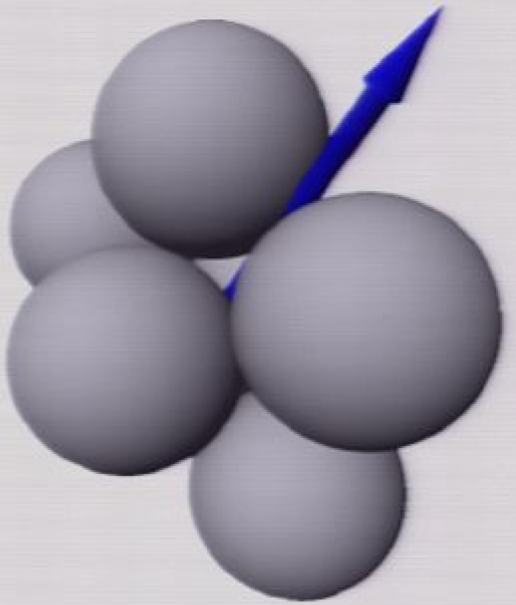
$$Z_v = c_v \prod_{\alpha}^{3N-6} \sqrt{\frac{2\pi}{k_\alpha}}$$



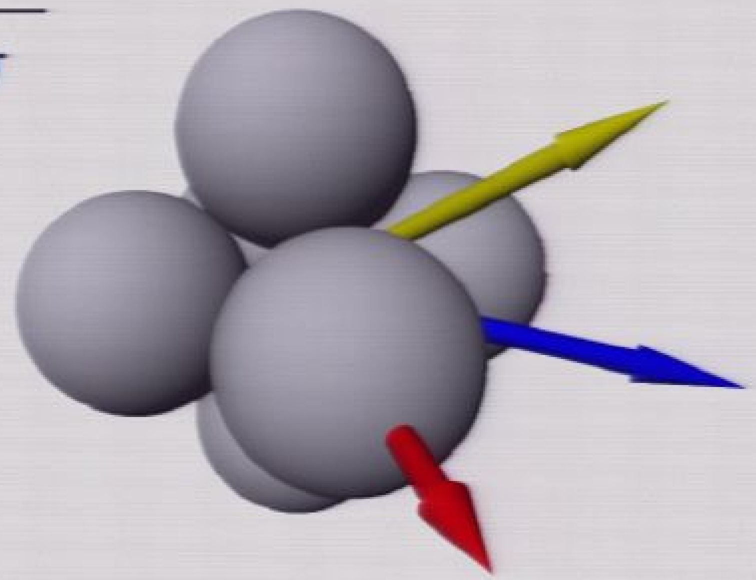
Contributes only a factor of 1.8 (ratio of Zpoly/Zoct)

What about rotational entropy?

$$Z_r \propto \frac{\sqrt{I}}{\sigma}$$



$C_{2v} \quad \sigma = 2$

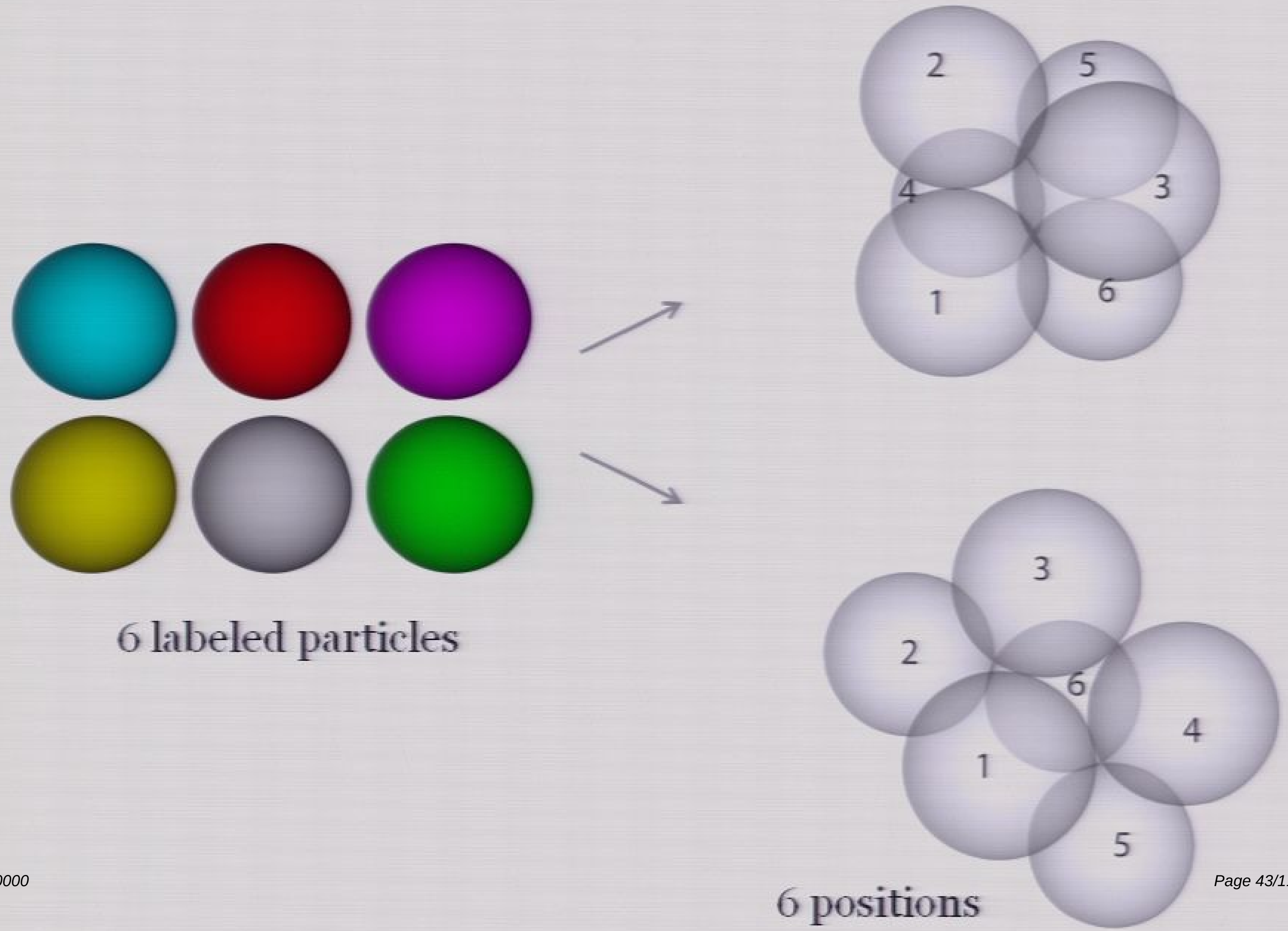


$O_h \quad \sigma = 24$

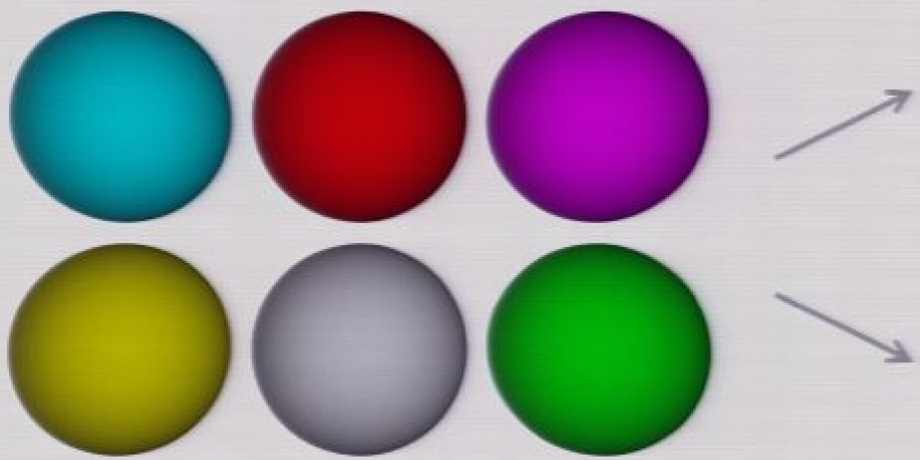
σ: The symmetry number

"...obtained by imagining all identical atoms to be labelled, and then counting the number of different but equivalent arrangements that can be obtained by rotating the molecule..." (IUPAC Gold Book)

Rotational entropy: symmetry and permutations

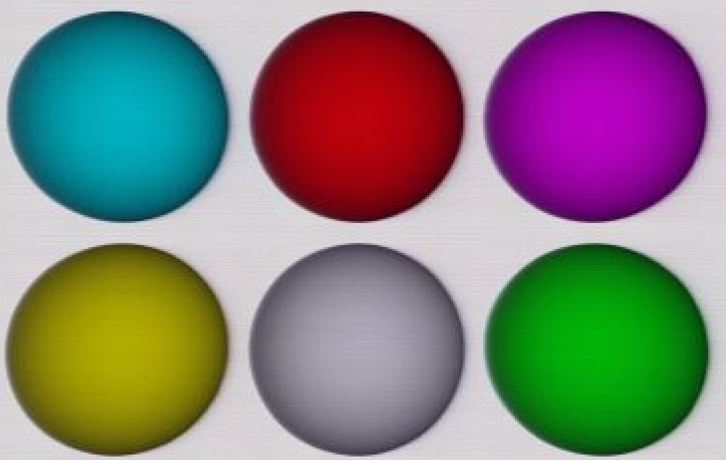


Rotational entropy: symmetry and permutations

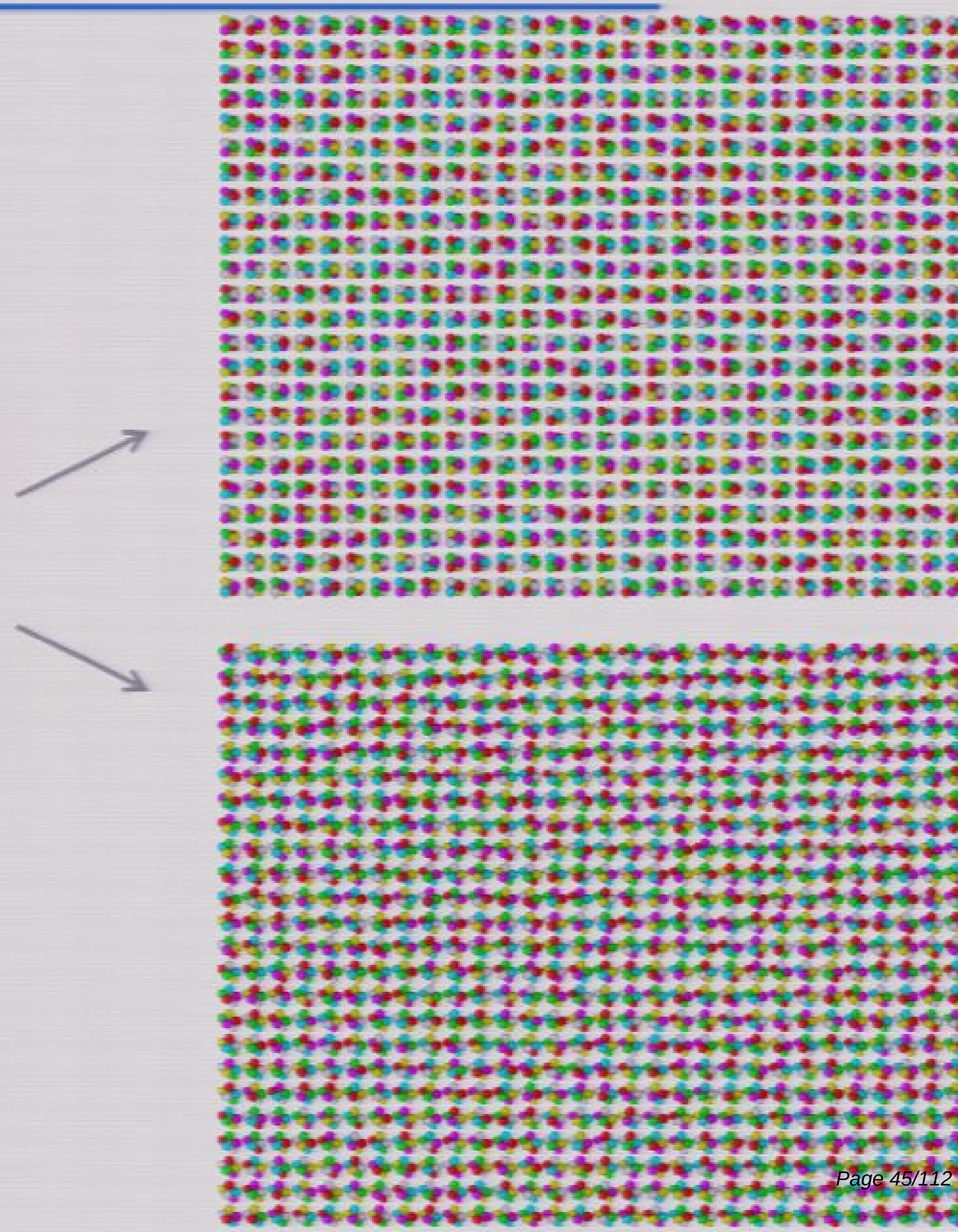


6! = 720 possibilities

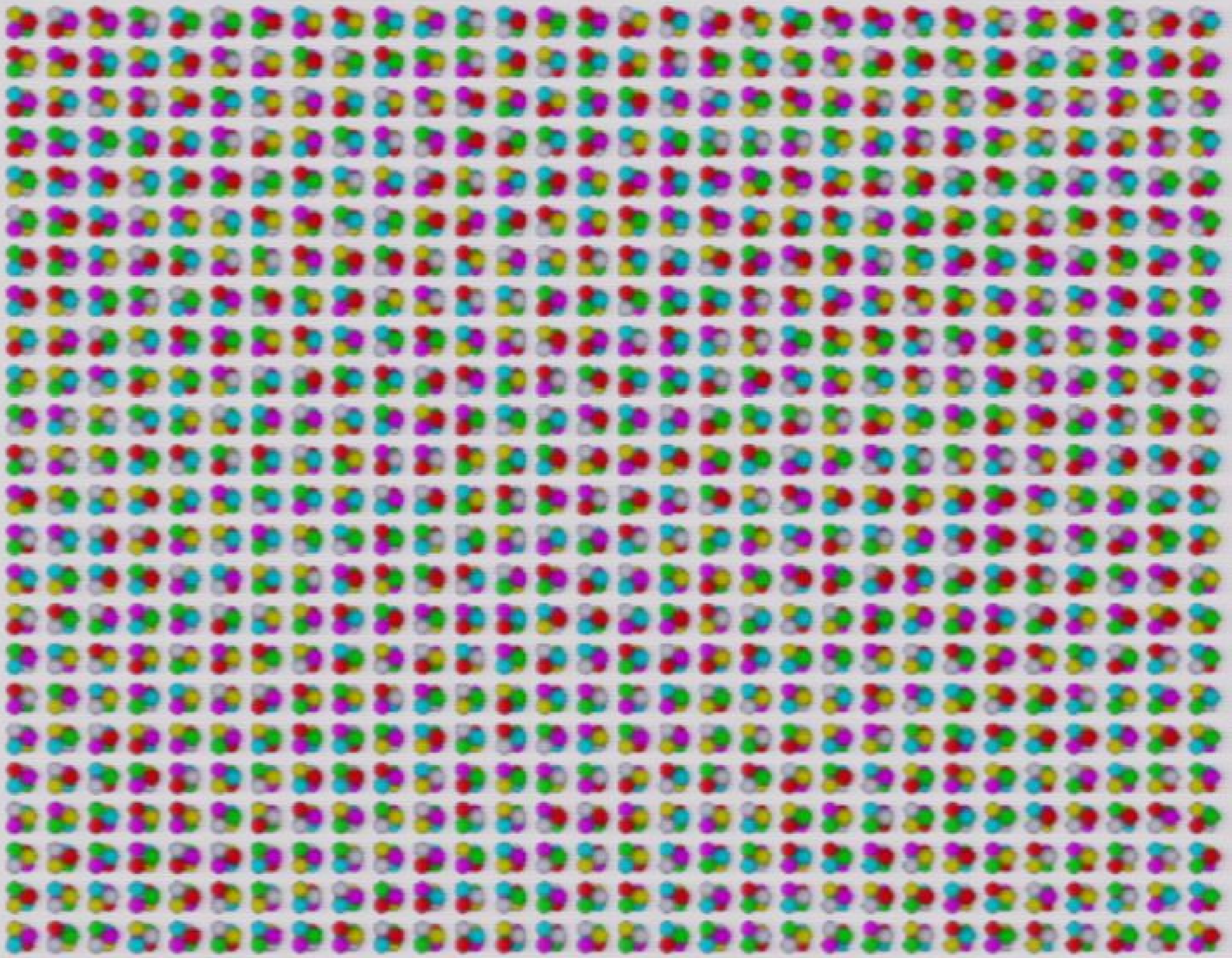
Rotational entropy: symmetry and permutations



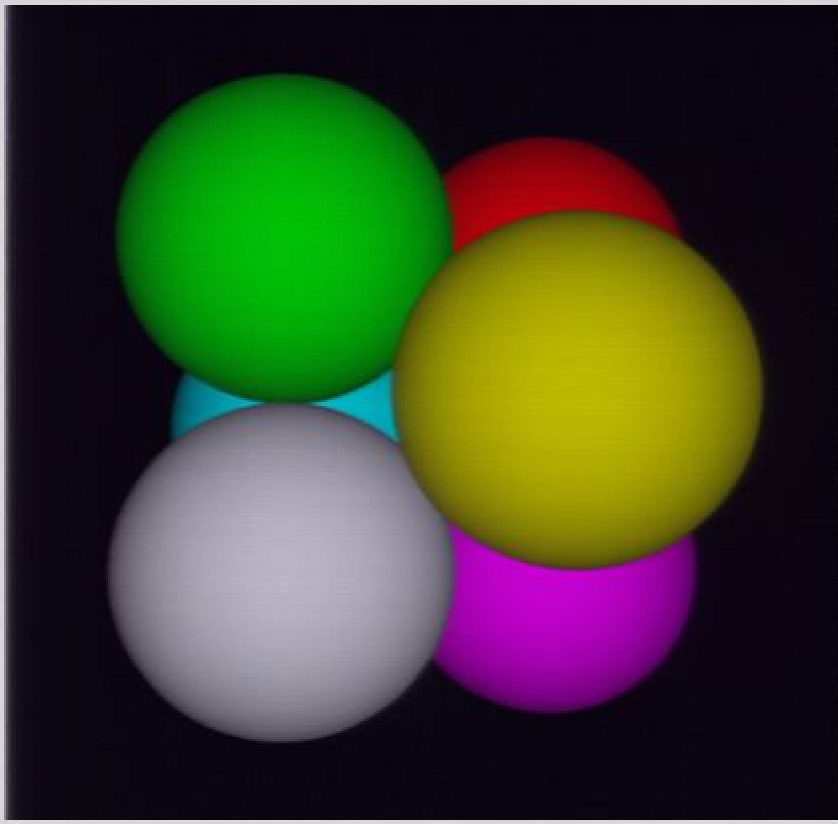
6! = 720 possibilities

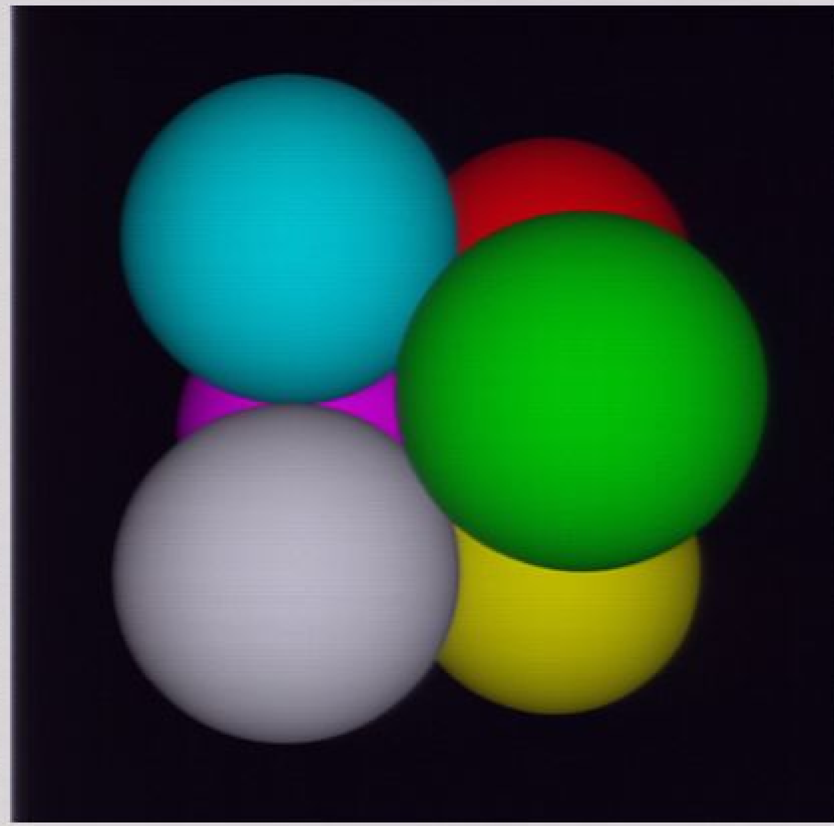


Rotational entropy: symmetry and permutations

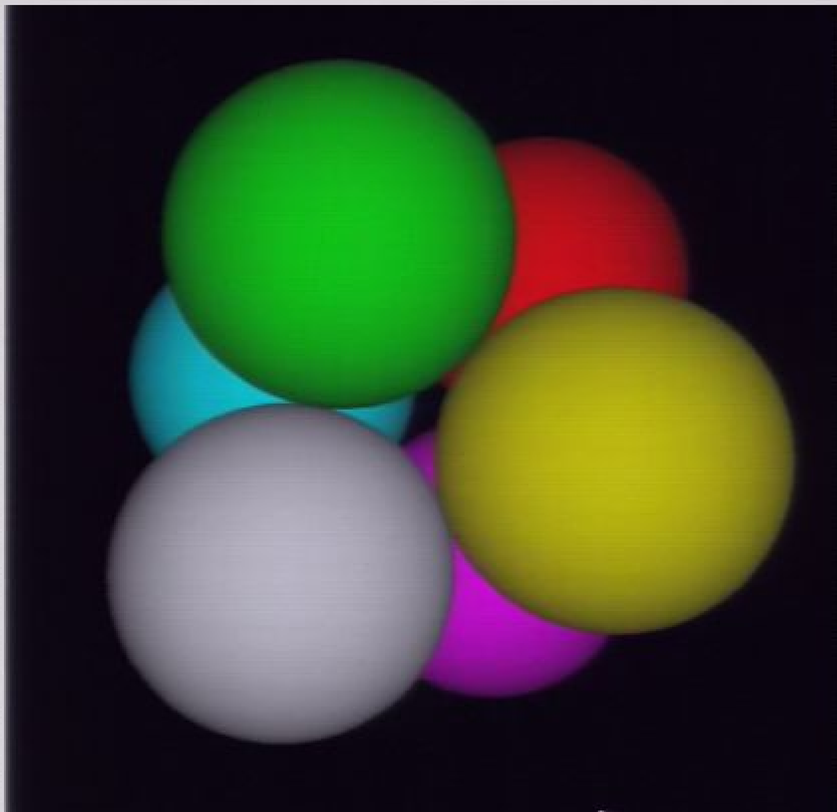


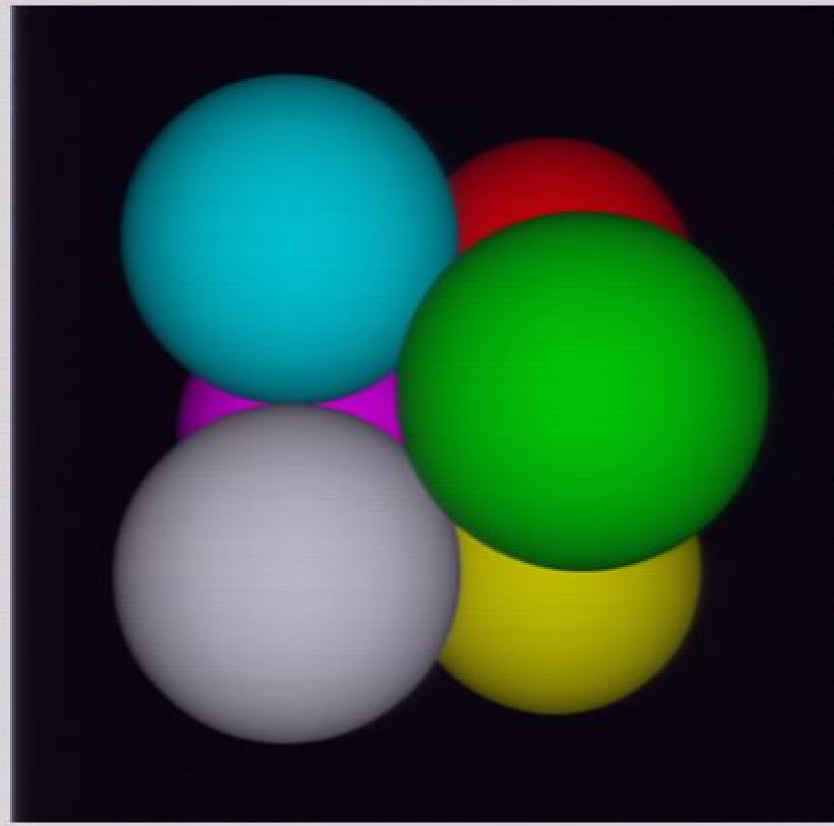
Rotational entropy: symmetry and permutations



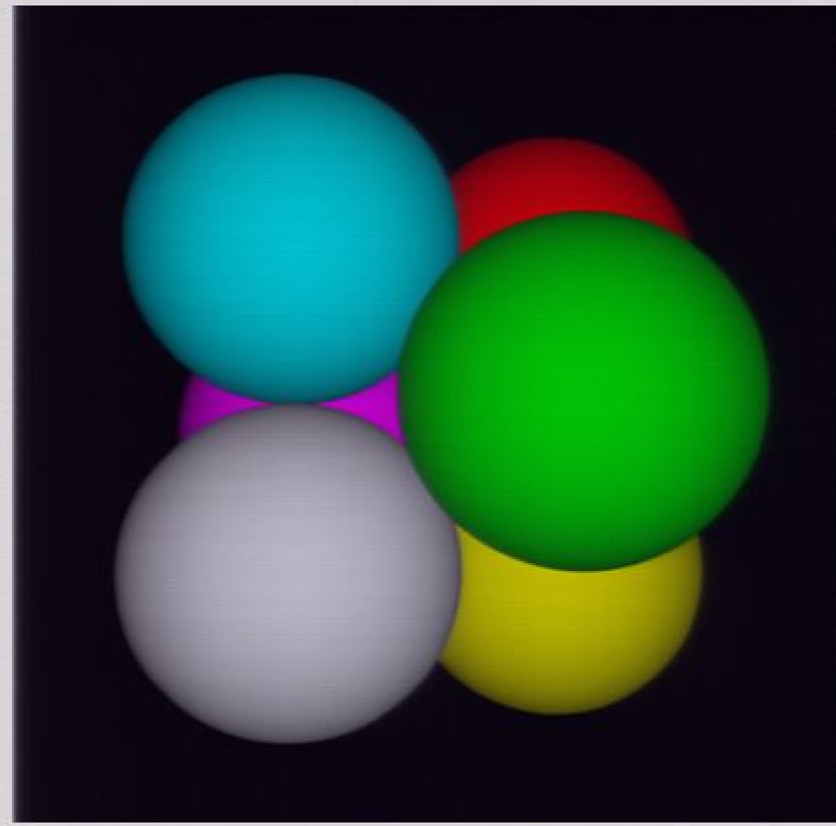


Rotational entropy: symmetry and permutations

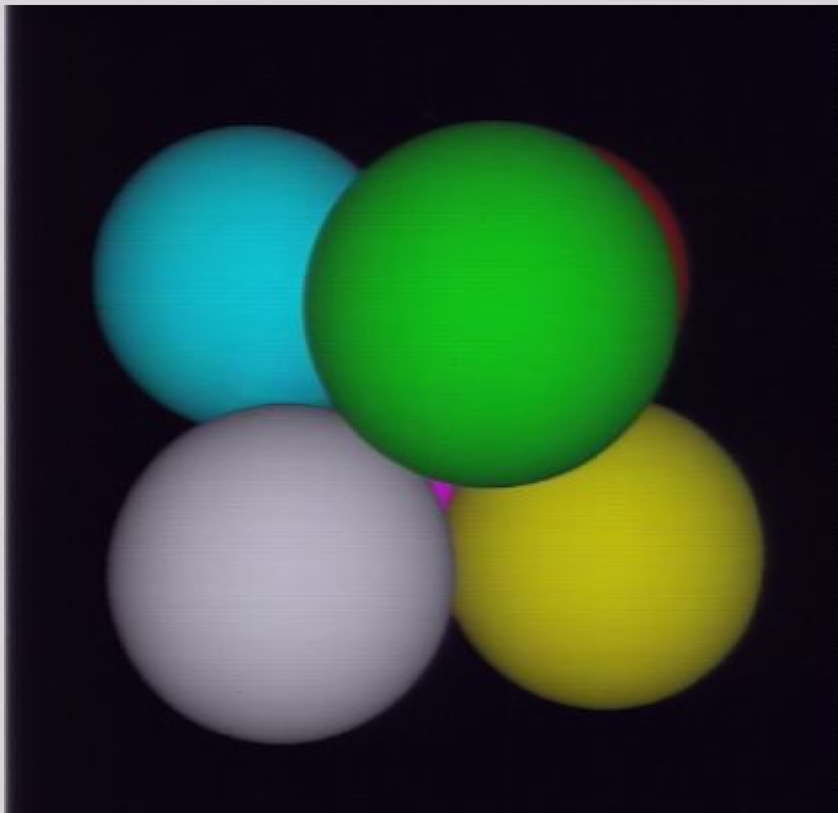


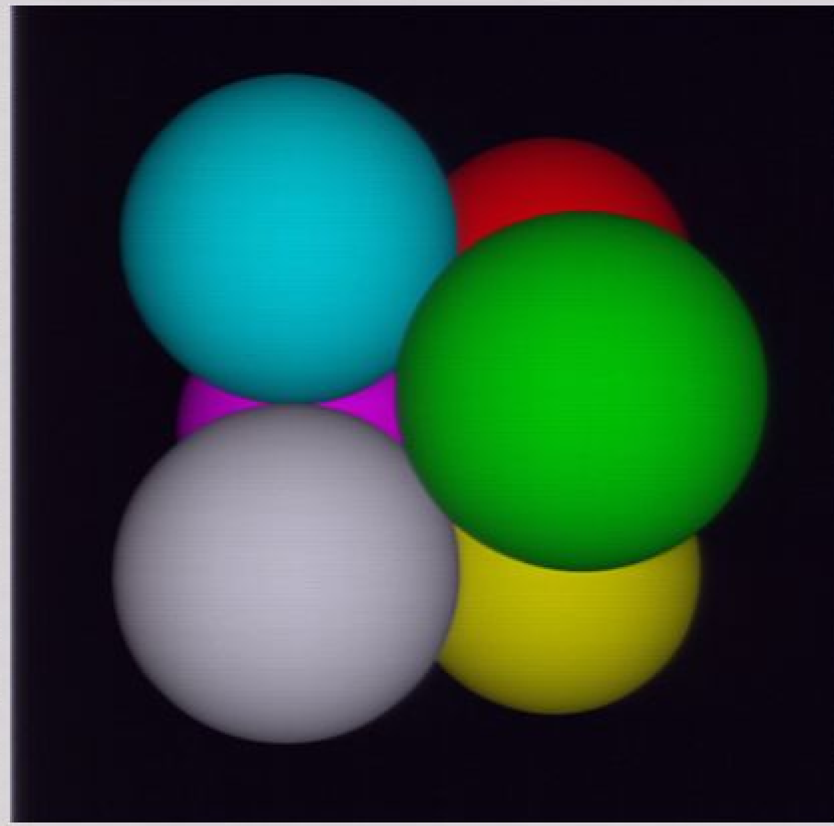


Rotational entropy: symmetry and permutations

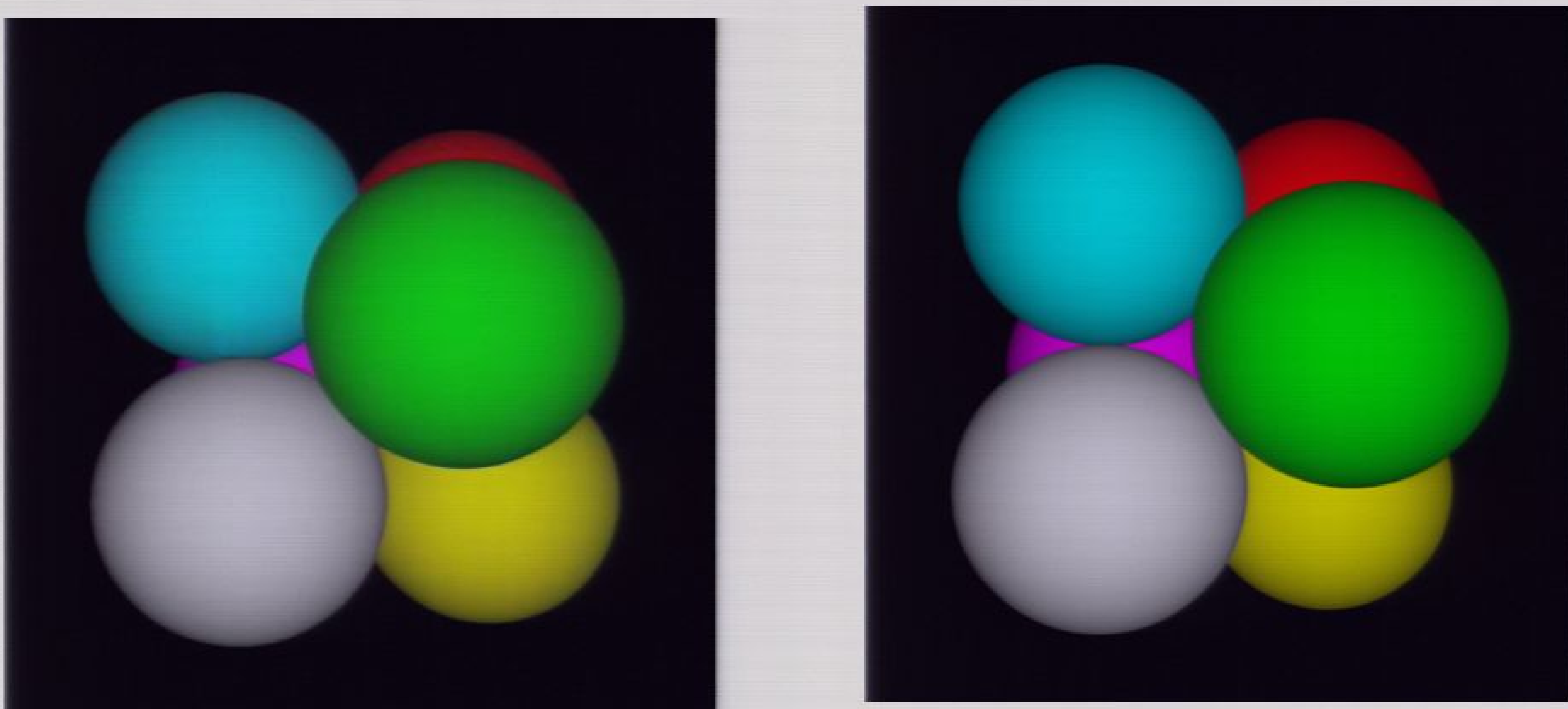


Rotational entropy: symmetry and permutations

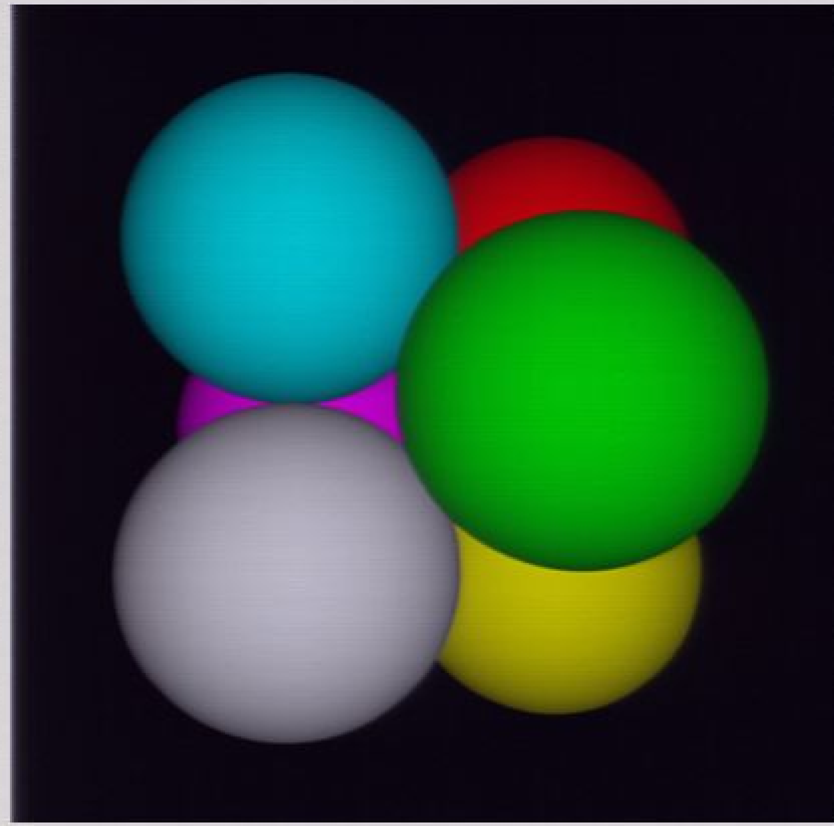




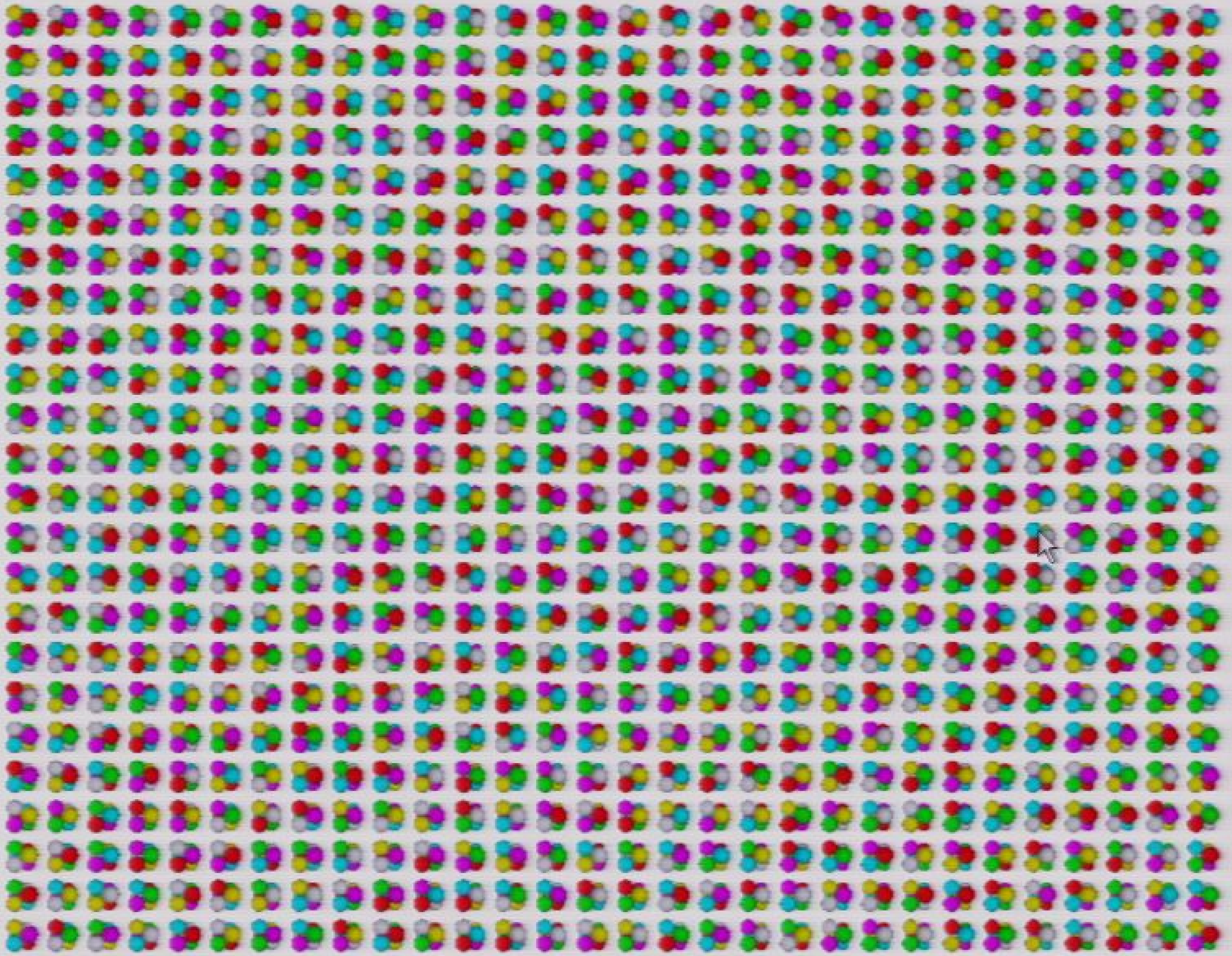
Rotational entropy: symmetry and permutations



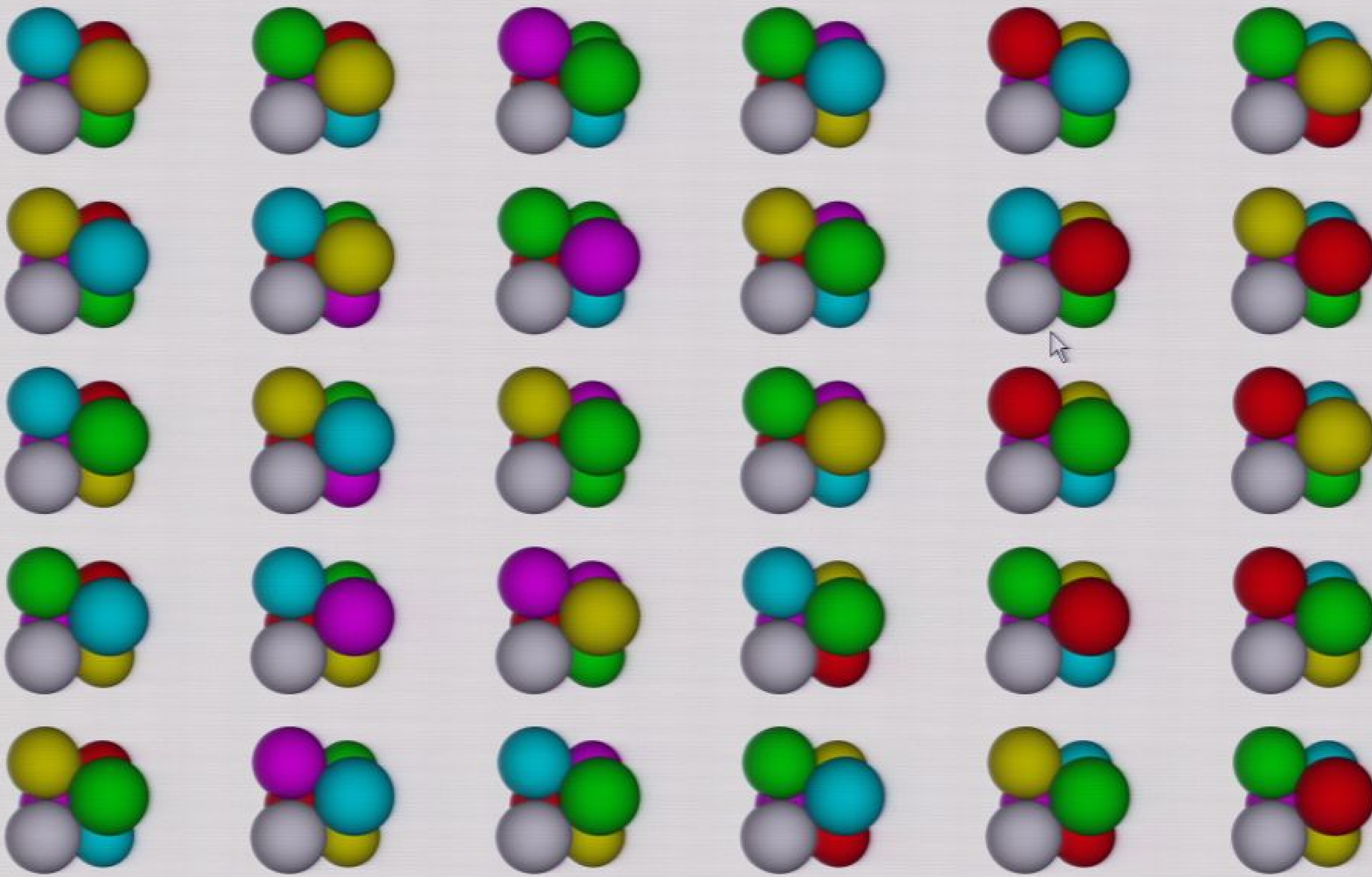
Rotational entropy: symmetry and permutations



Rotational entropy: symmetry and permutations

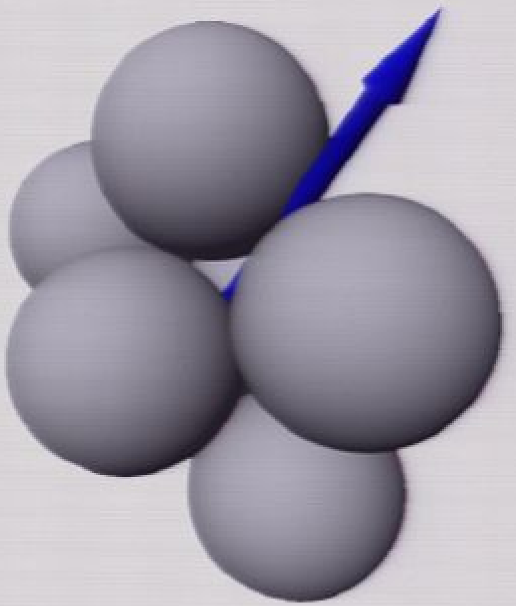


Rotational entropy: symmetry and permutations

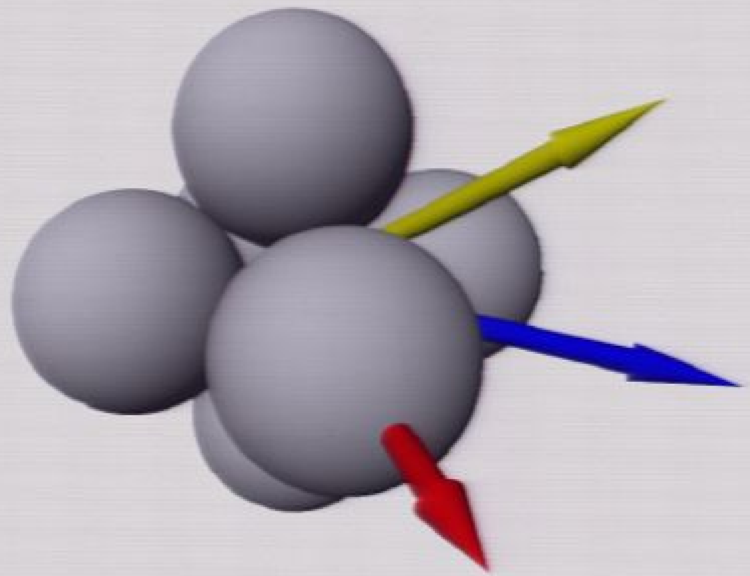


octahedron: 6!/24 = 30 distinct permutations

Rotational entropy: symmetry and permutations

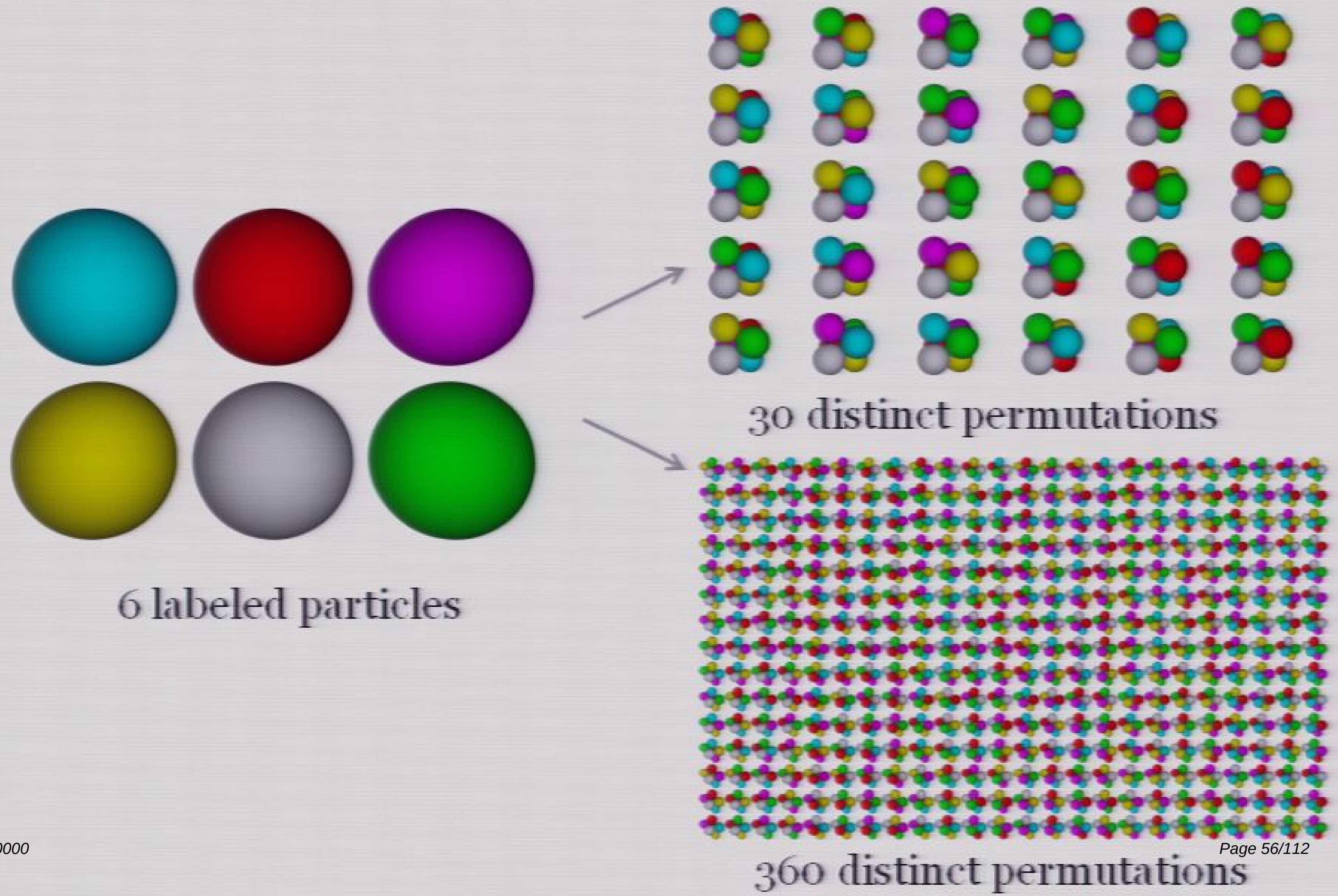


$C_{2v}\quad \sigma = 2$

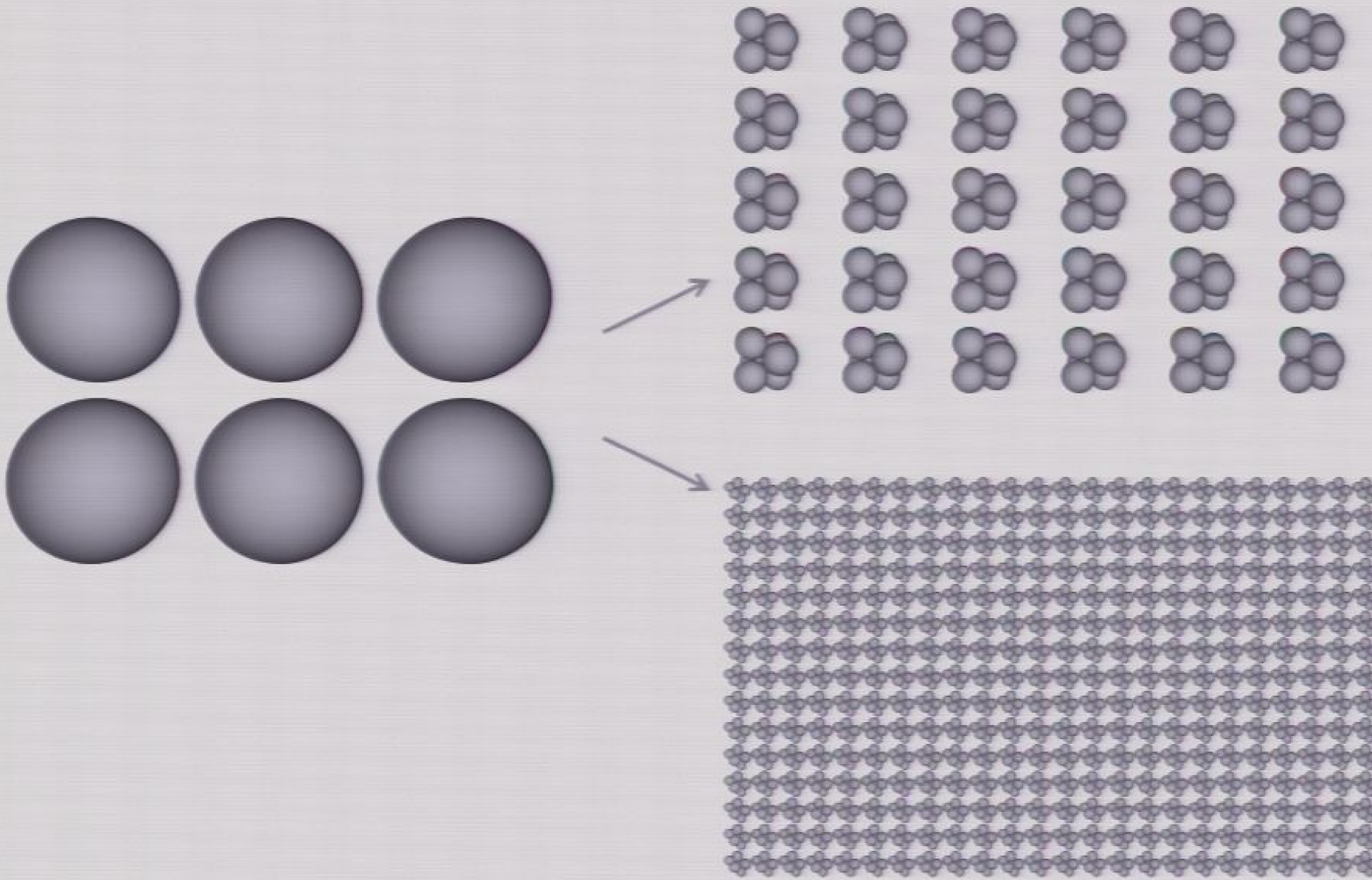


$O_h\quad \sigma = 24$

Rotational entropy: symmetry and permutations



Rotational entropy: symmetry and permutations



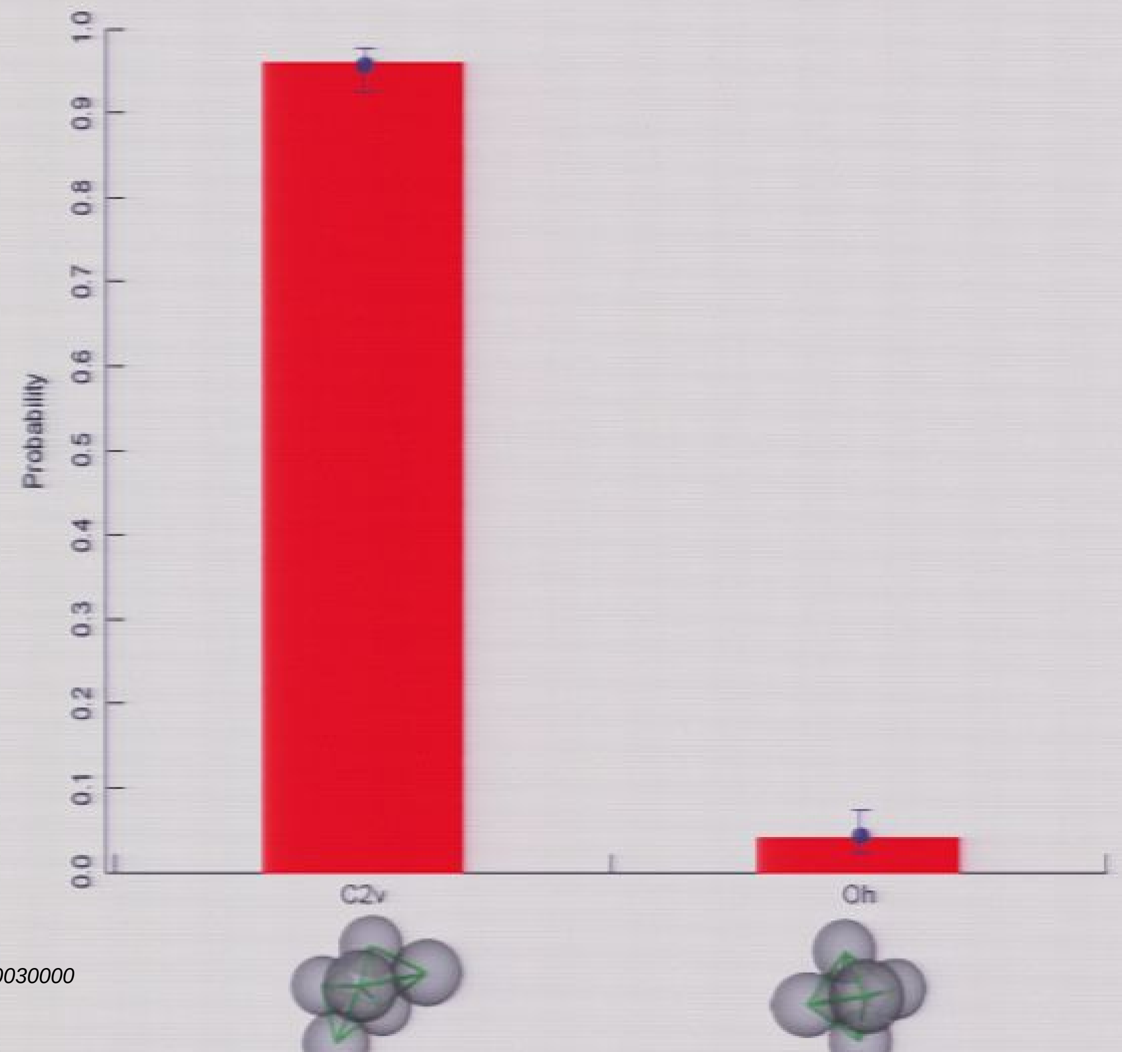
Highly symmetric structures are unfavorable at equilibrium

$$\frac{p_{oct}}{p_{poly}} = \frac{Z_r}{Z_r'} \cdot \frac{Z_v}{Z_v'} \cdot \frac{\not{Z_t}}{\not{Z_t'}} = 5.57\% \quad (4.51\% \text{ expt})$$

Z_r: symmetry analysis

Z_v: normal mode analysis

$$Z_r \propto \frac{\sqrt{I}}{\sigma}$$



12	Contacts	12
2	Symmetry number	24
3.2	Moment of inertia$^{1/2}$	2.8
1.6	Z_r (rotational)	0.12
0.061	Z_v (vibrational)	0.034
96.0%	Predicted P	4.0%
95.7%	Observed P	4.3%

Highly symmetric structures are unfavorable at equilibrium

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normal mode analysis

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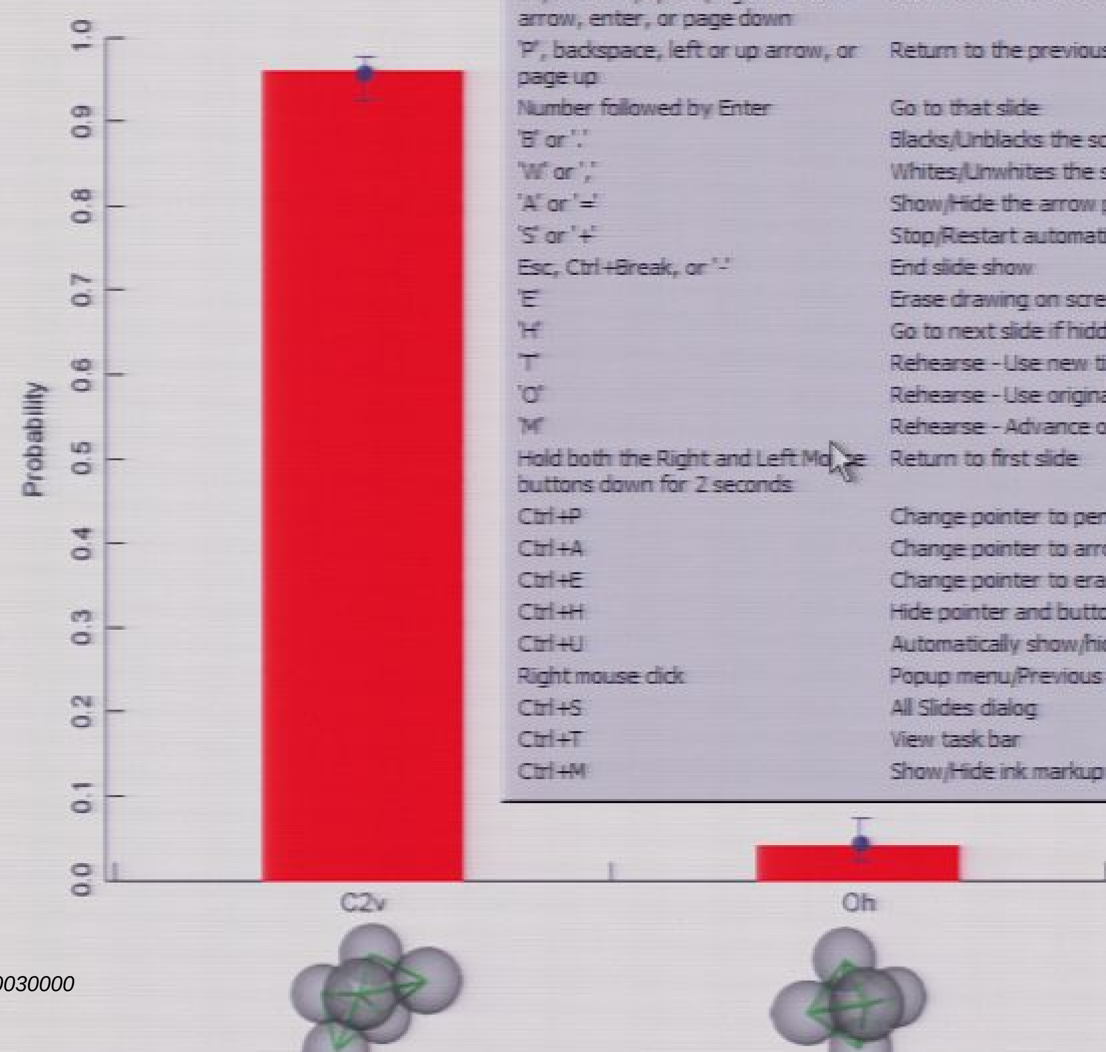

2	Contacts	12
	Symmetry number	24
2	Moment of inertia$^{1/2}$	2.8
6	Z_r (rotational)	0.12
61	Z_v (vibrational)	0.034
0%	Predicted P	4.0%
7%	Observed P	4.3%

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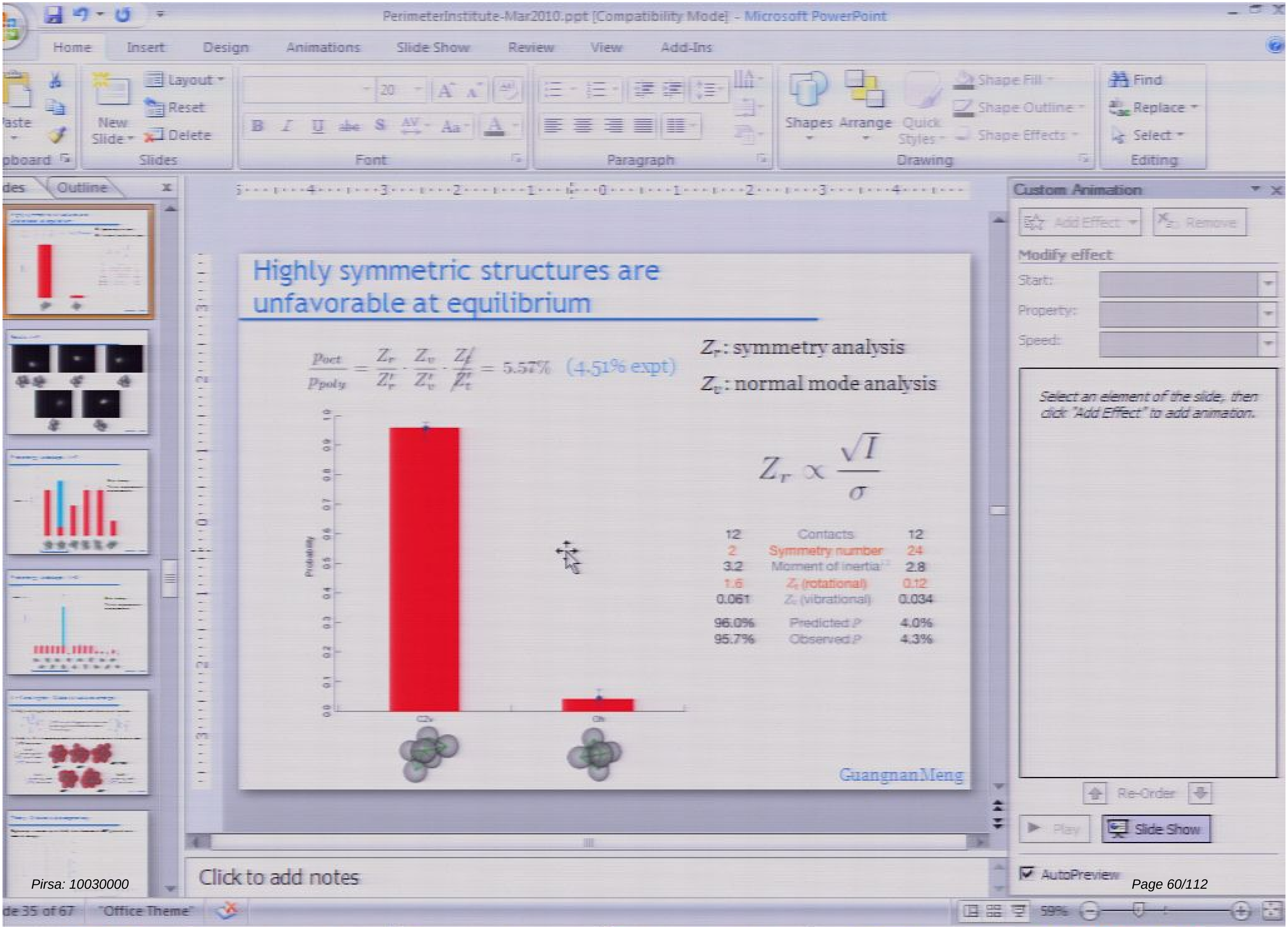
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Highly symmetric structures are unfavorable at equilibrium
$\frac{p_{oct}}{p_{poly}} = \frac{Z_r}{Z_r'} \cdot \frac{Z_v}{Z_v'} \cdot \frac{Z_t}{Z_t'} = 5.57\%$ (4.51% expt)
Z_r: symmetry analysis
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$Z_r \propto \frac{\sqrt{I}}{\sigma}$
12 Contacts 12
2 Symmetry number 24
3.2 Moment of inertia 2.8
1.6 Z_r (rotational) 0.12
0.061 Z_v (vibrational) 0.034
96.0% Predicted P 4.0%
95.7% Observed P 4.3%
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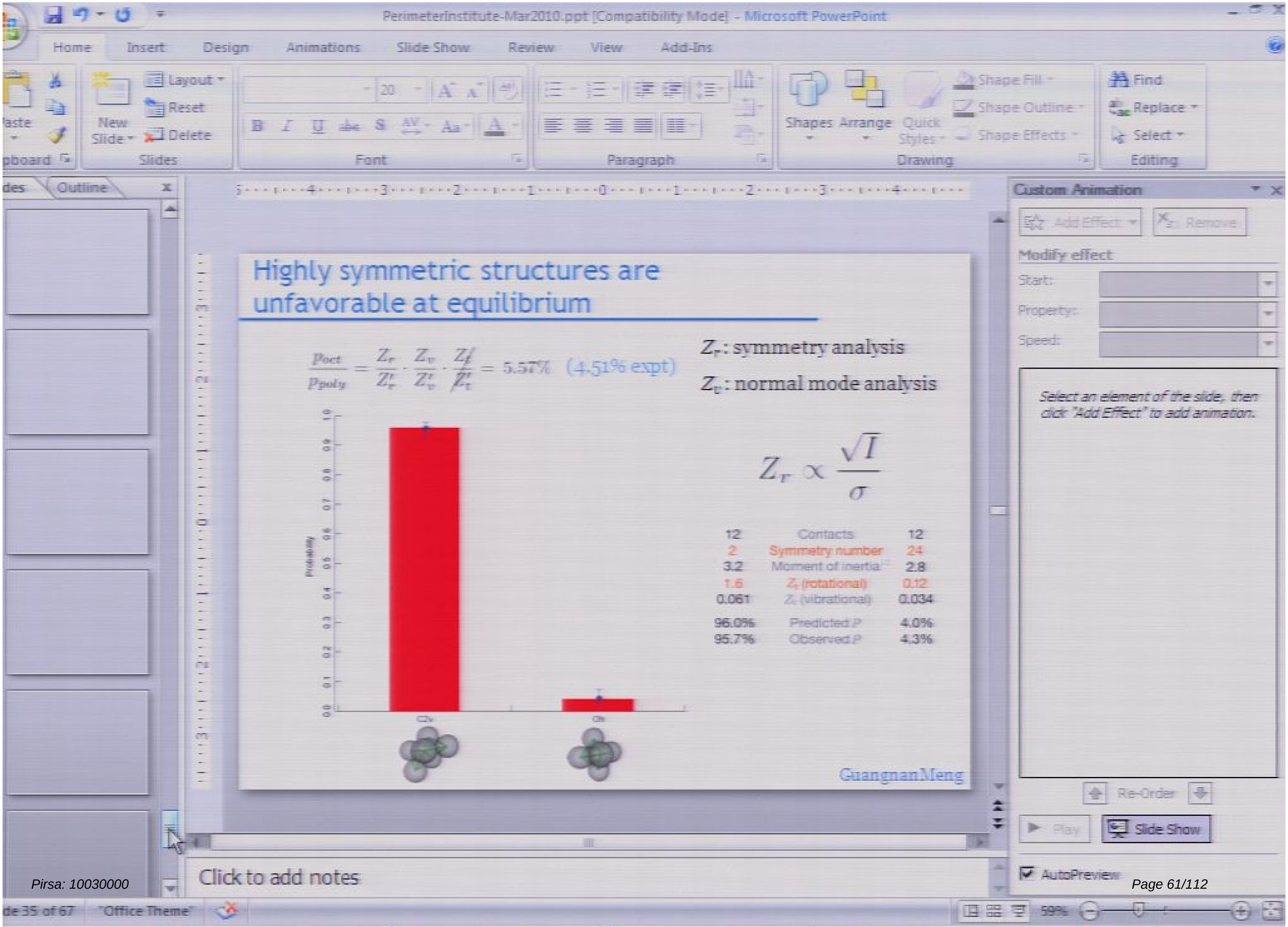
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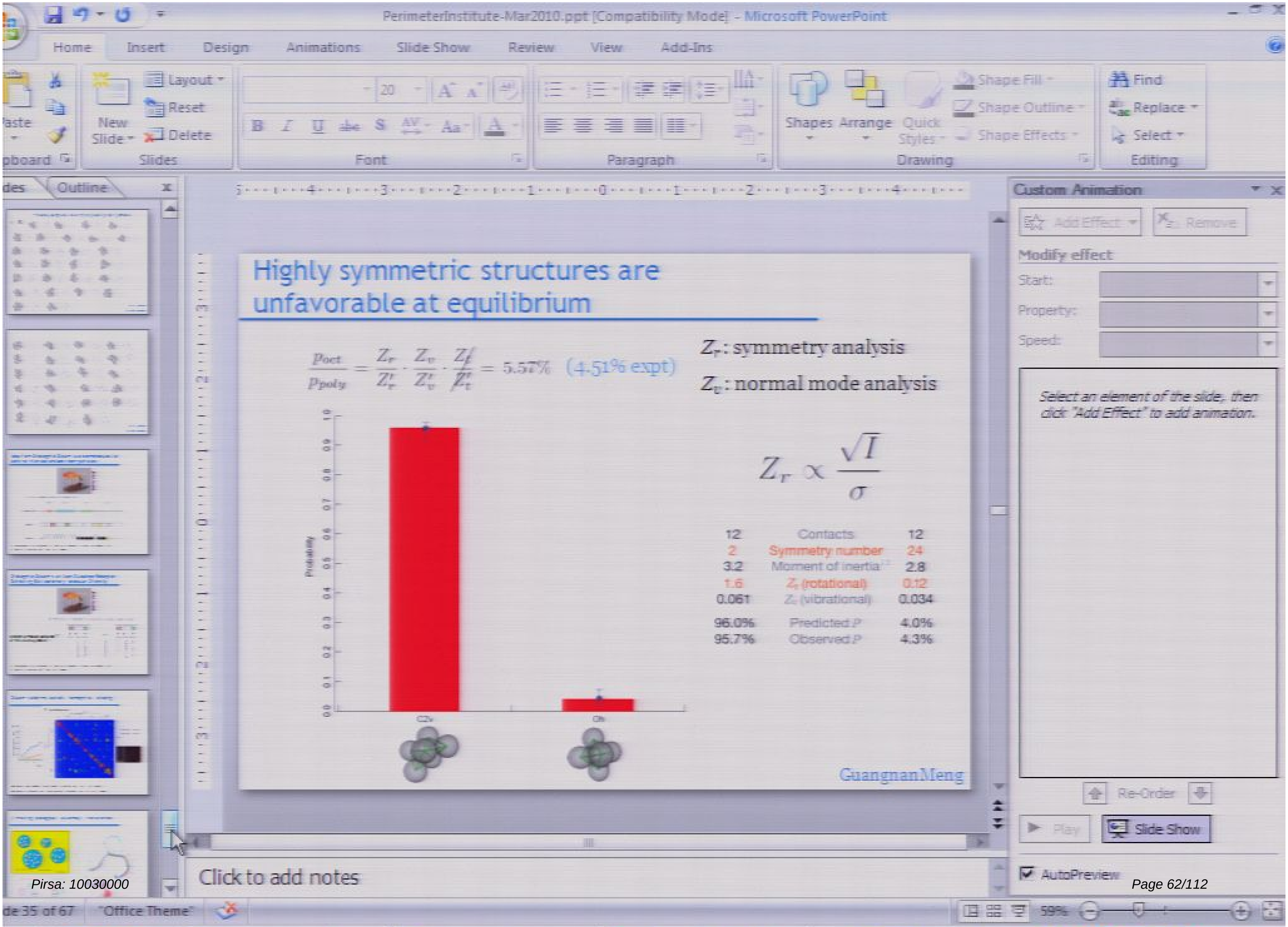
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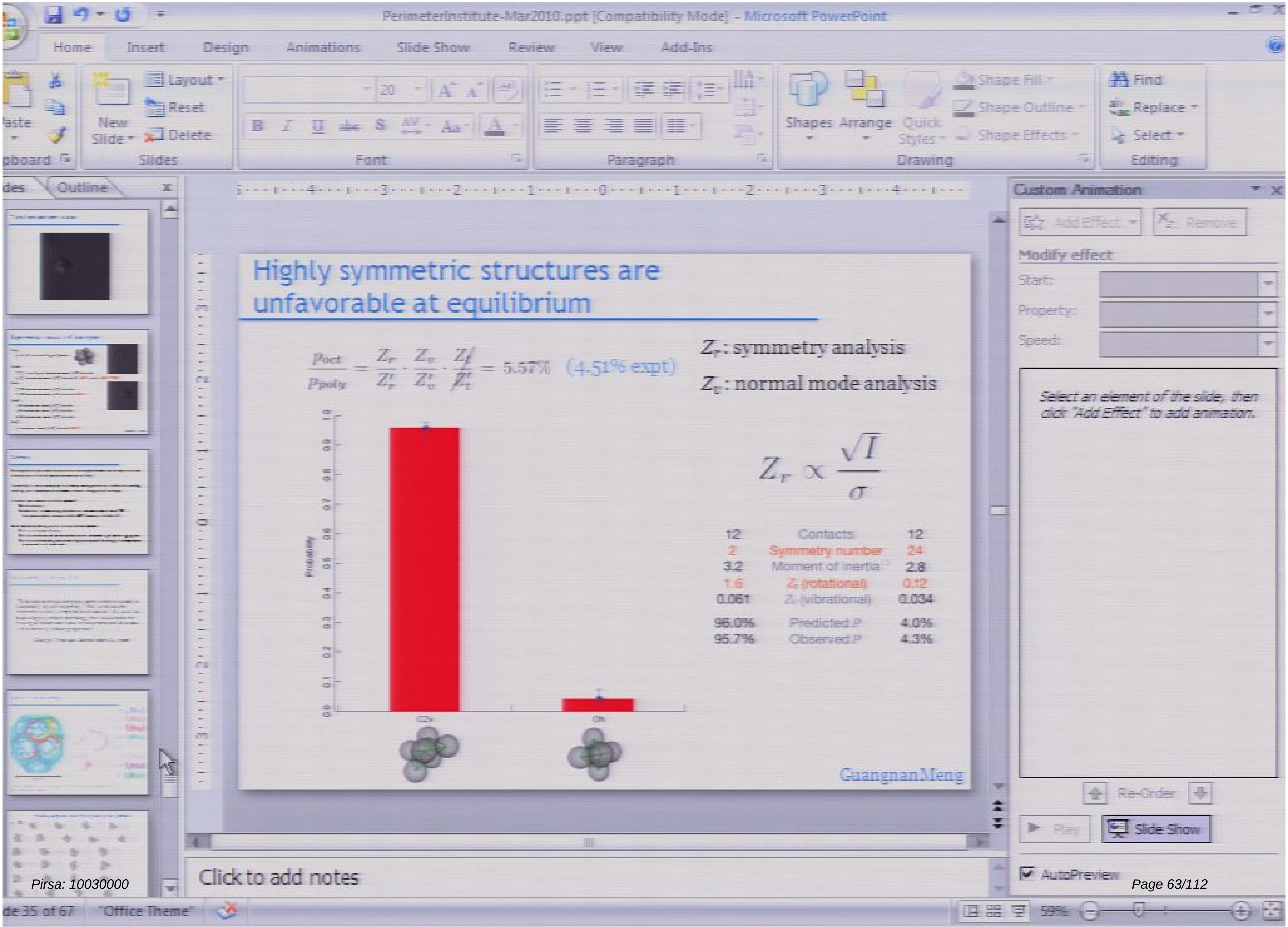
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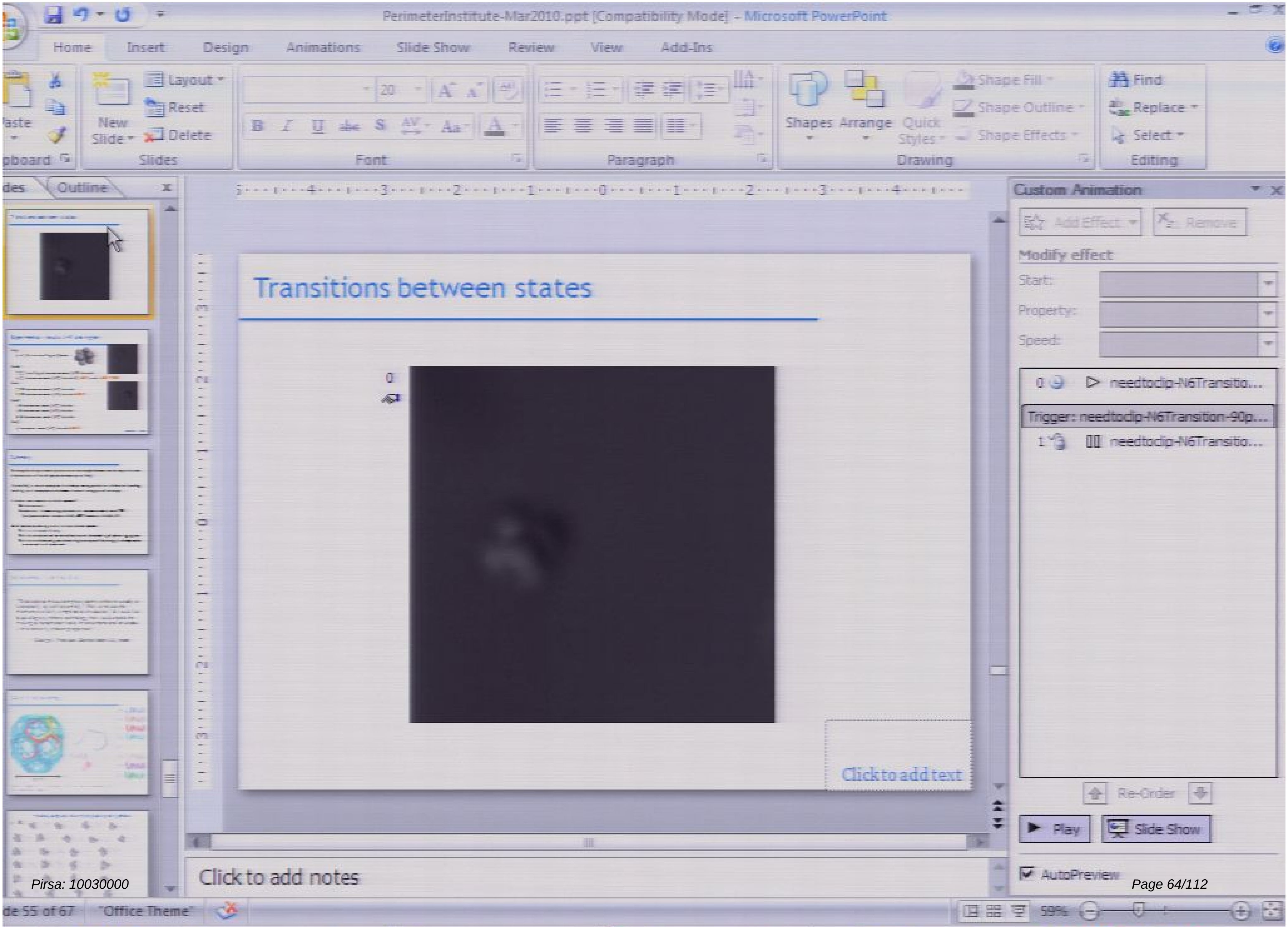
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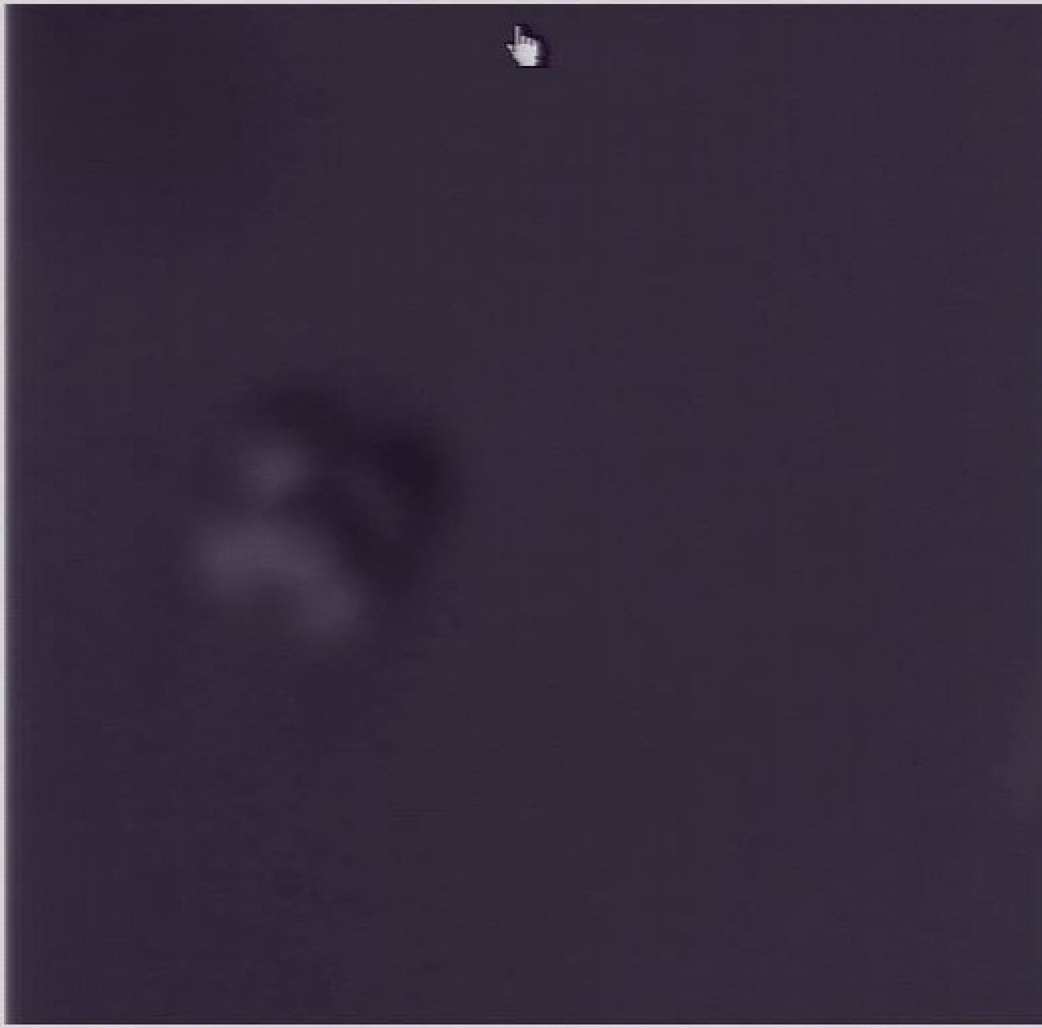

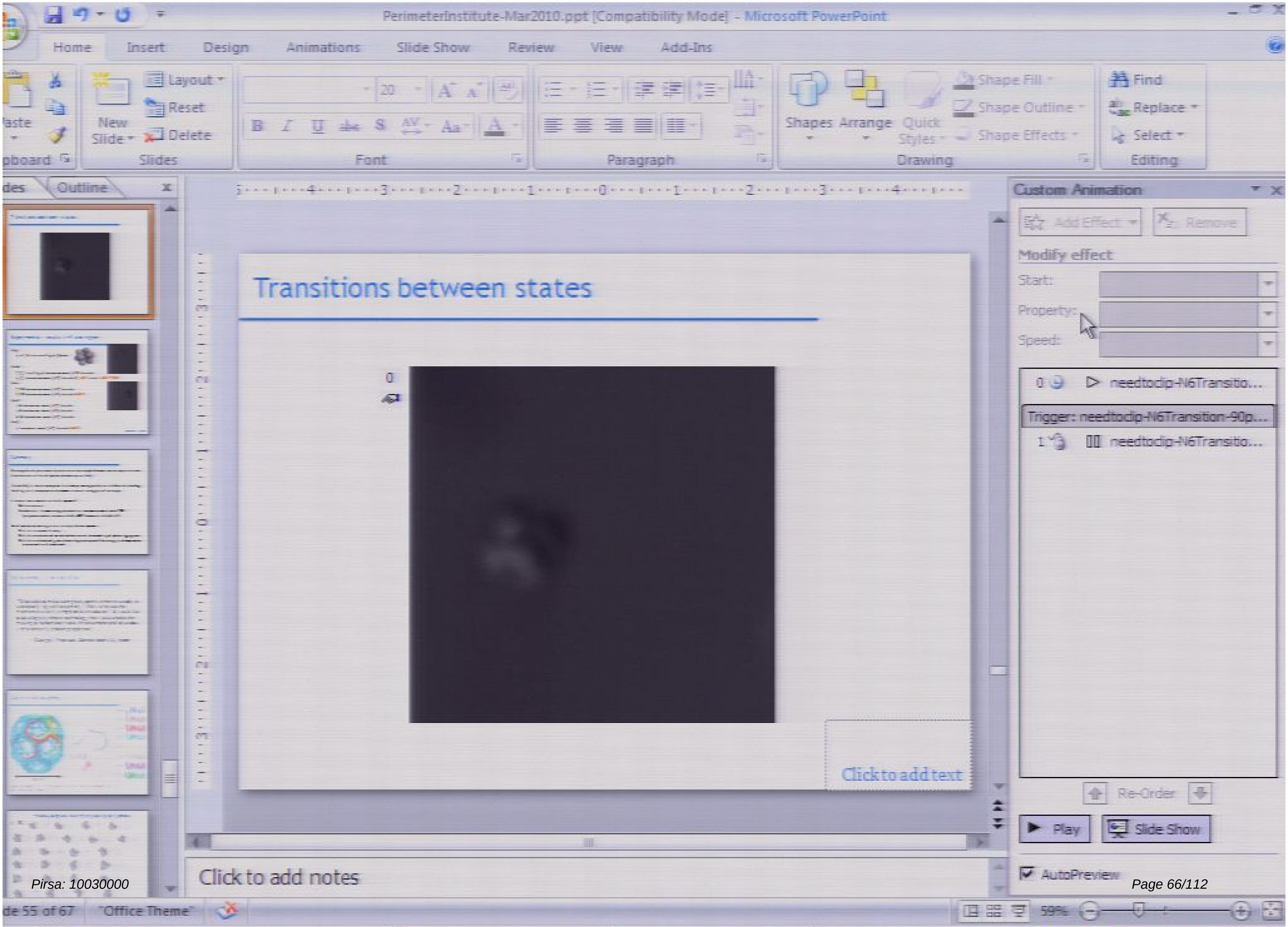
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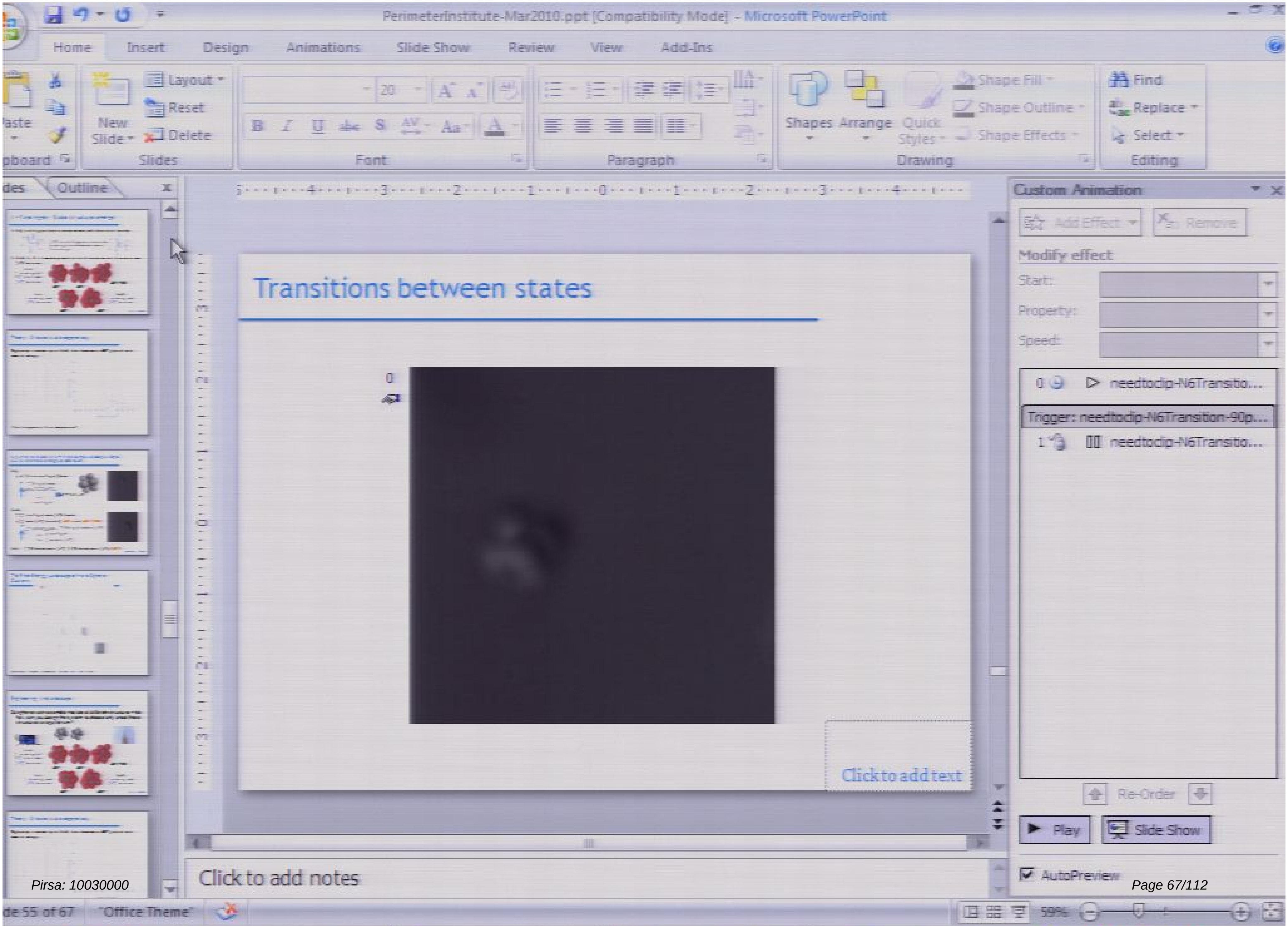
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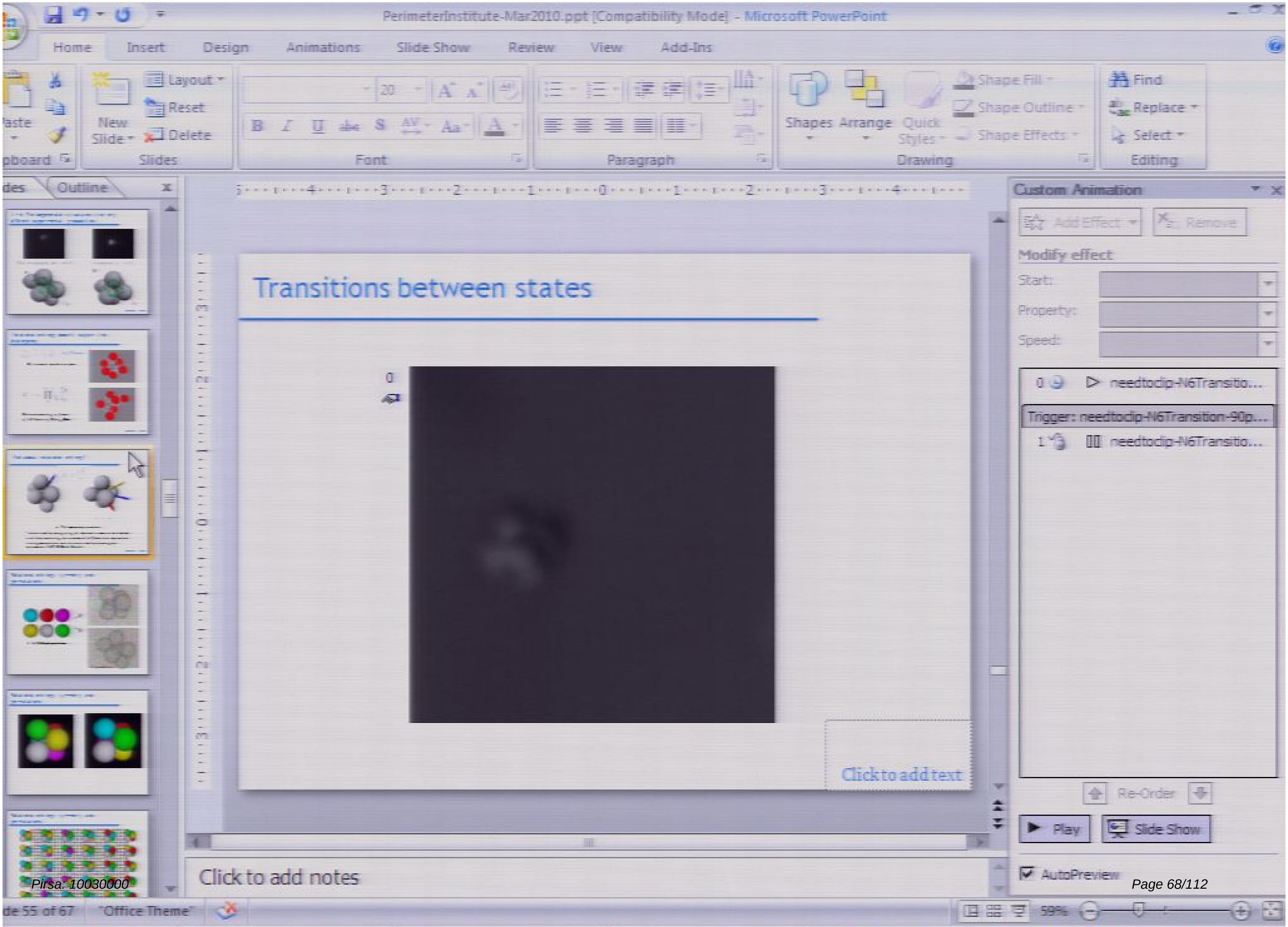
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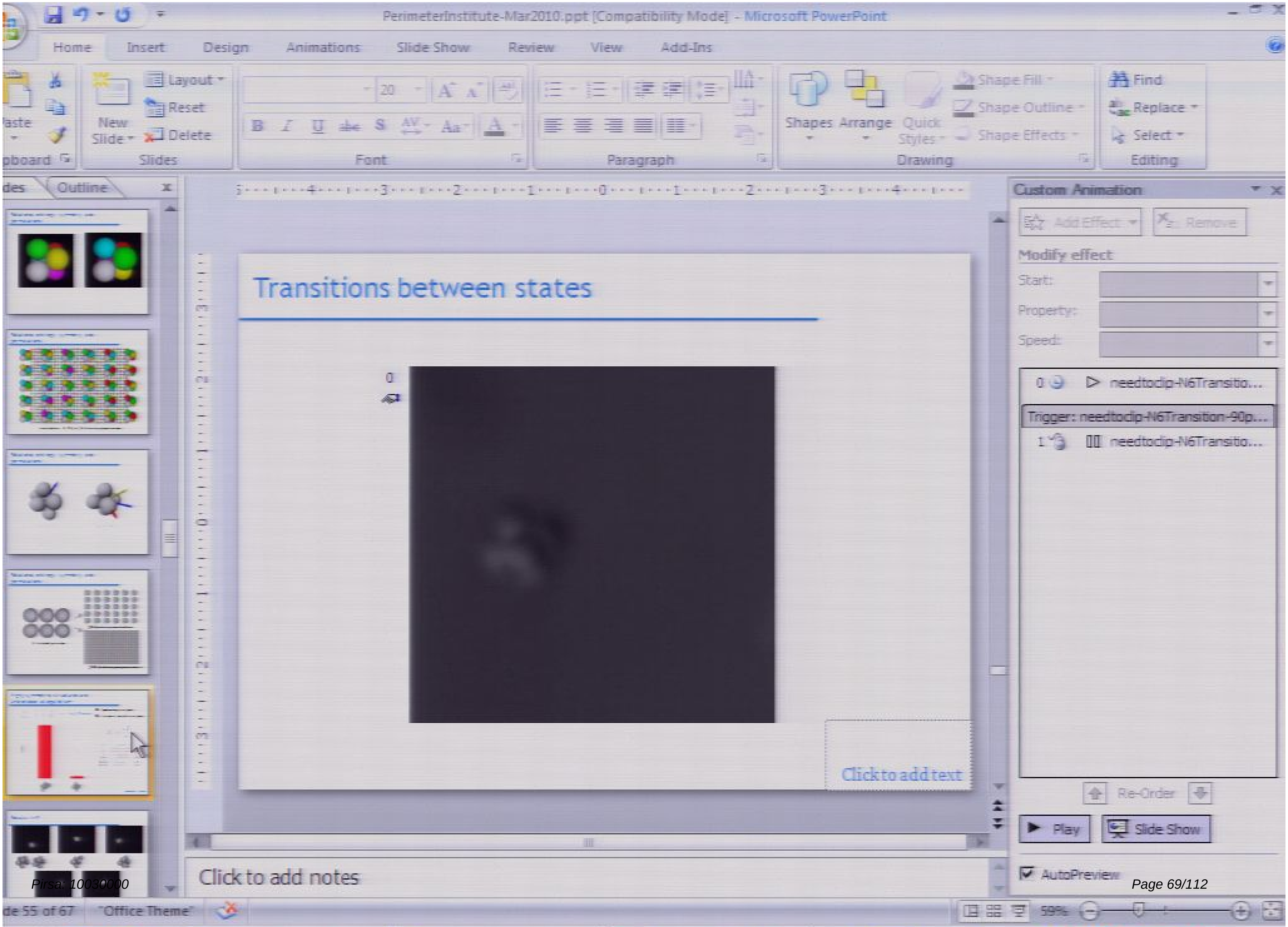
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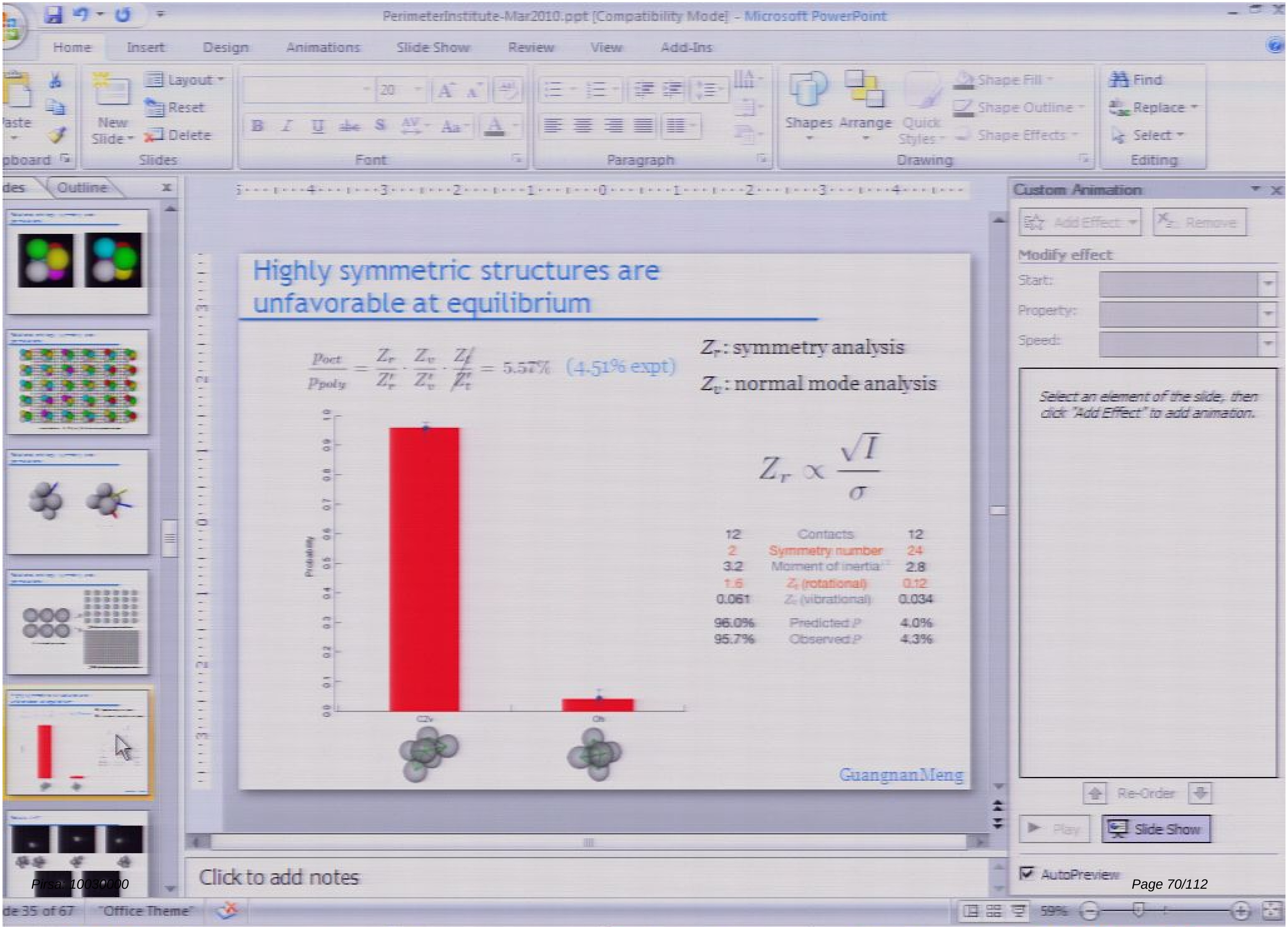
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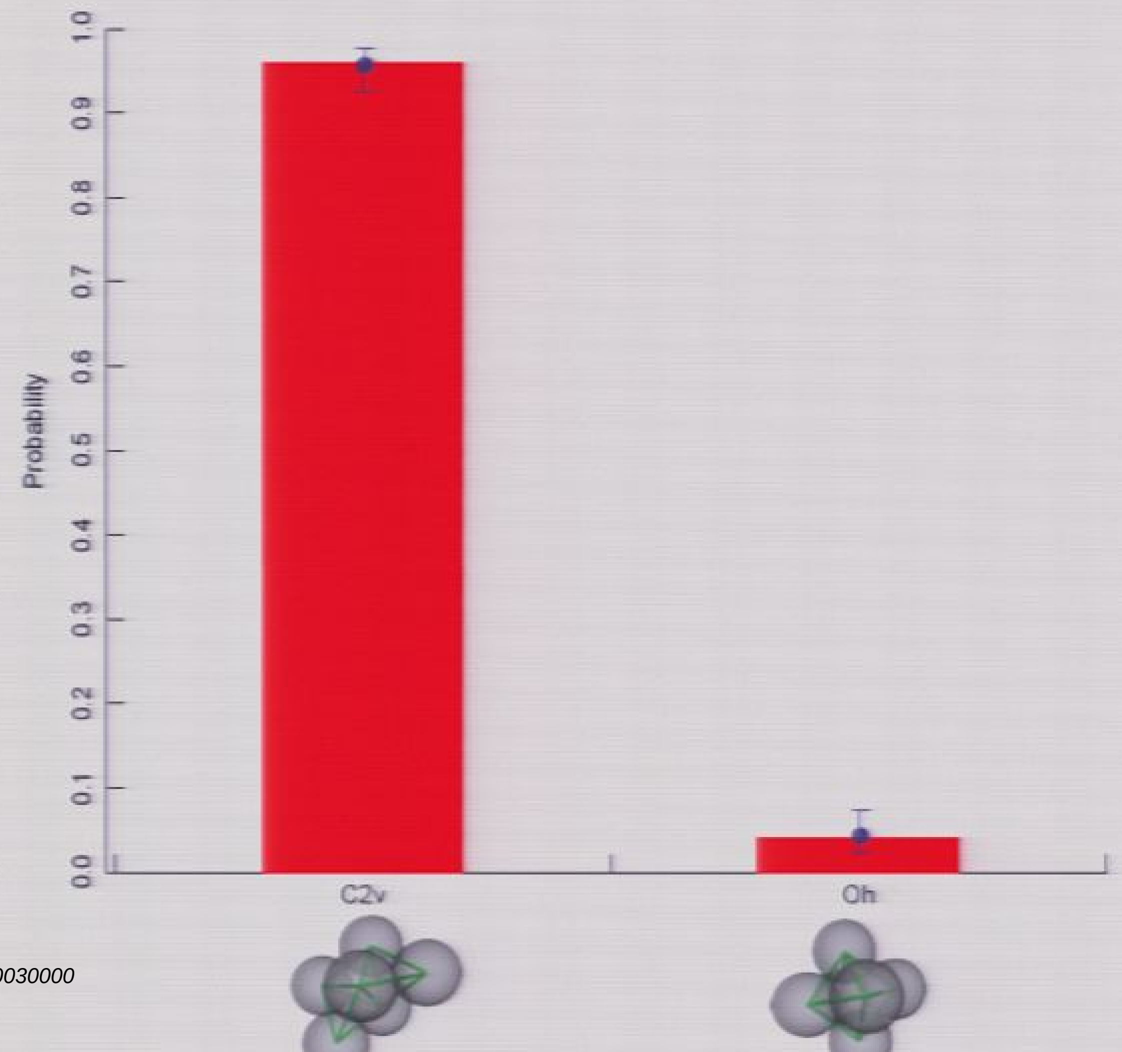
Highly symmetric structures are unfavorable at equilibrium
$\frac{p_{oct}}{p_{poly}} = \frac{Z_r}{Z_r'} \cdot \frac{Z_v}{Z_v'} \cdot \frac{Z_t}{Z_t'} = 5.57\%$ (4.51% expt)
Z_r: symmetry analysis
Z_v: normal mode analysis
$Z_r \propto \frac{\sqrt{I}}{\sigma}$
12 Contacts 12
2 Symmetry number 24
3.2 Moment of inertia 2.8
1.6 Z_r (rotational) 0.12
0.061 Z_v (vibrational) 0.034
96.0% Predicted P 4.0%
95.7% Observed P 4.3%
Guangnan Meng
Custom Animation
Modify effect
Select an element of the slide, then click "Add Effect" to add animation.
Click to add notes
Slide 35 of 67
"Office Theme"

Highly symmetric structures are unfavorable at equilibrium

$$\frac{p_{oct}}{p_{poly}} = \frac{Z_r}{Z_r'} \cdot \frac{Z_v}{Z_v'} \cdot \frac{\cancel{Z_t}}{\cancel{Z_t'}} = 5.57\% \quad (4.51\%\ \text{expt})$$

Z_r: symmetry analysis

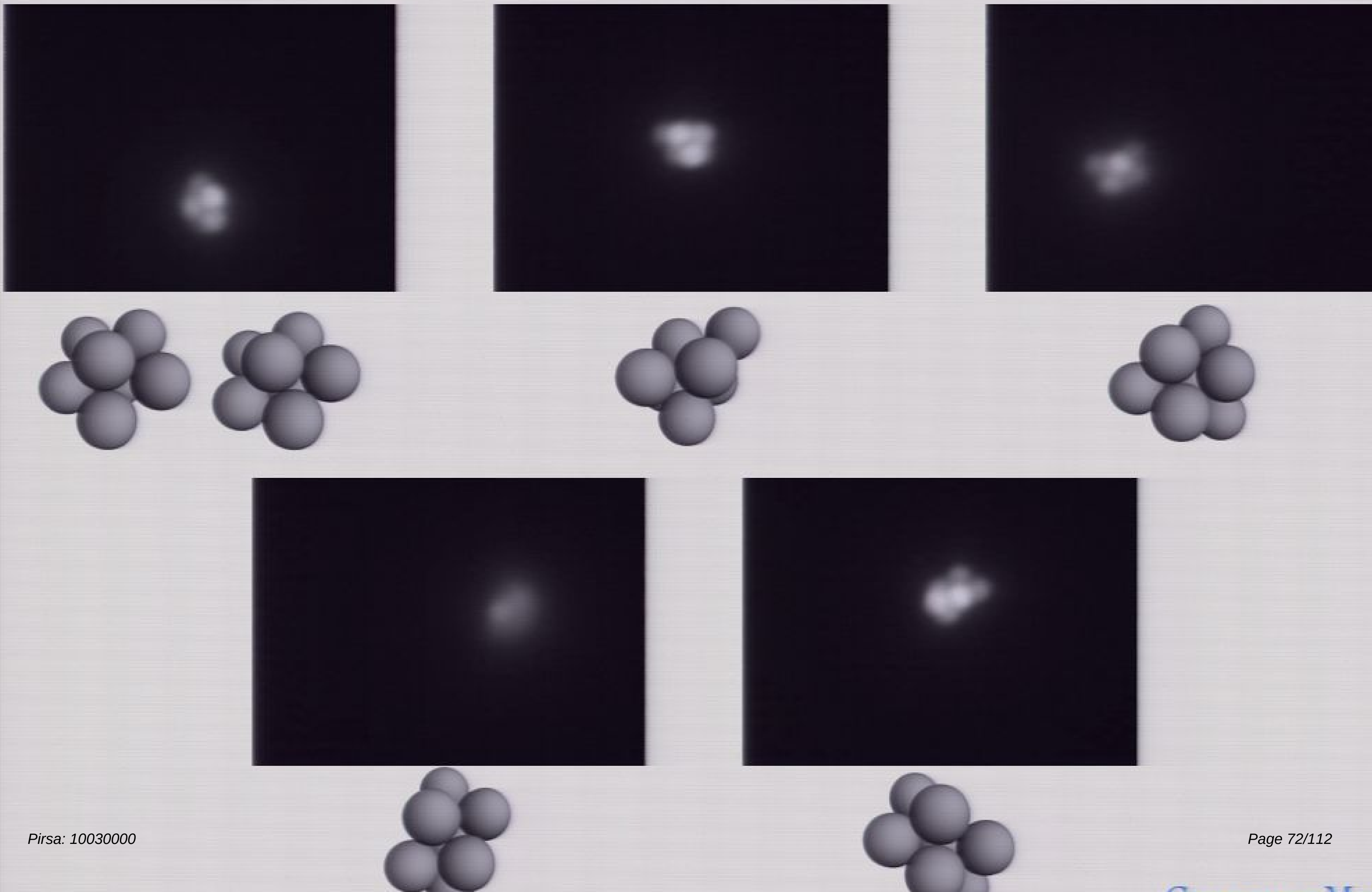
Z_v: normal mode analysis



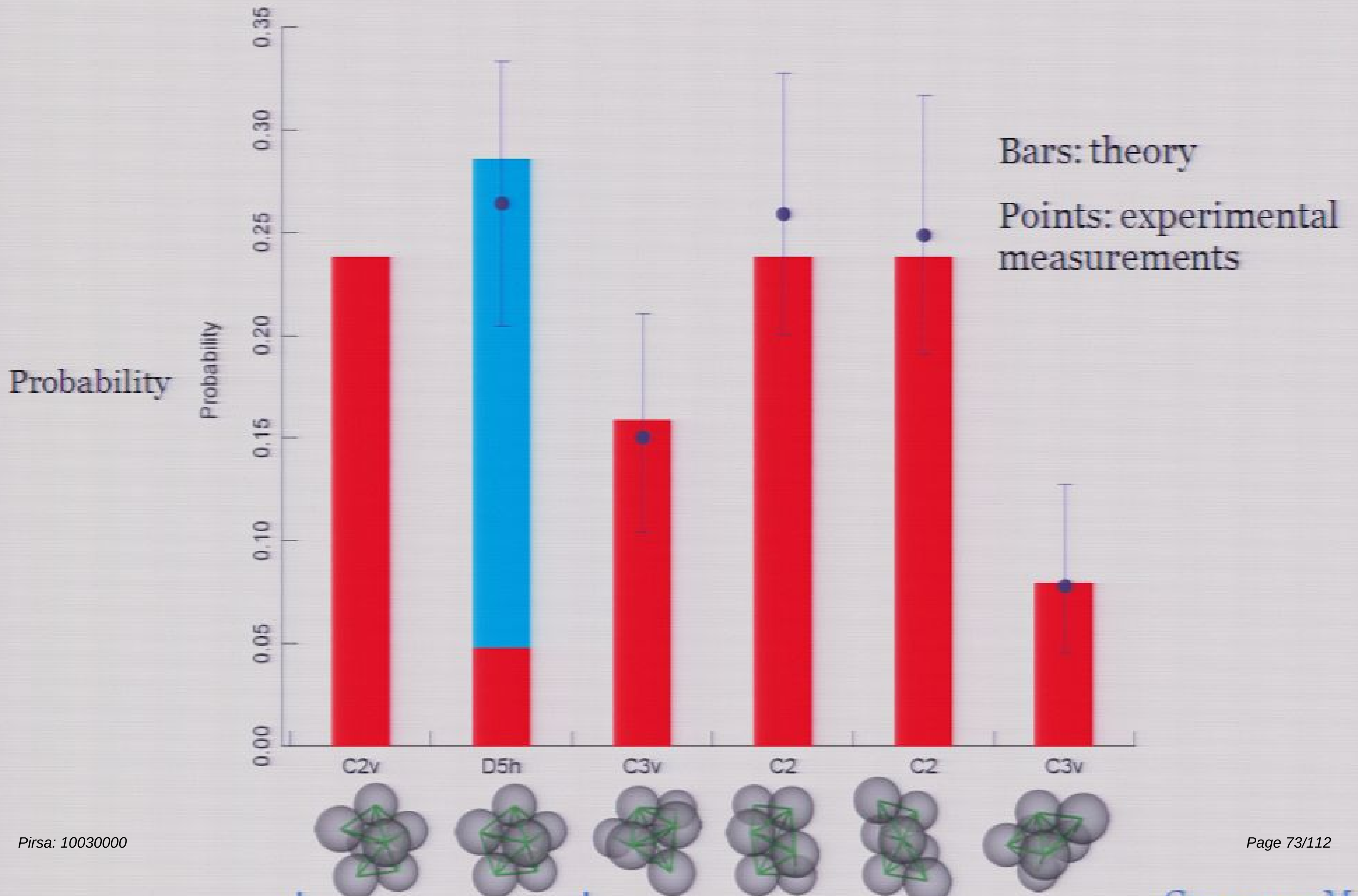
$$Z_r \propto \frac{\sqrt{I}}{\sigma}$$

12	Contacts	12
2	Symmetry number	24
3.2	Moment of inertia$^{1/2}$	2.8
1.6	Z_r (rotational)	0.12
0.061	Z_v (vibrational)	0.034
96.0%	Predicted P	4.0%
95.7%	Observed P	4.3%

Results: N=7

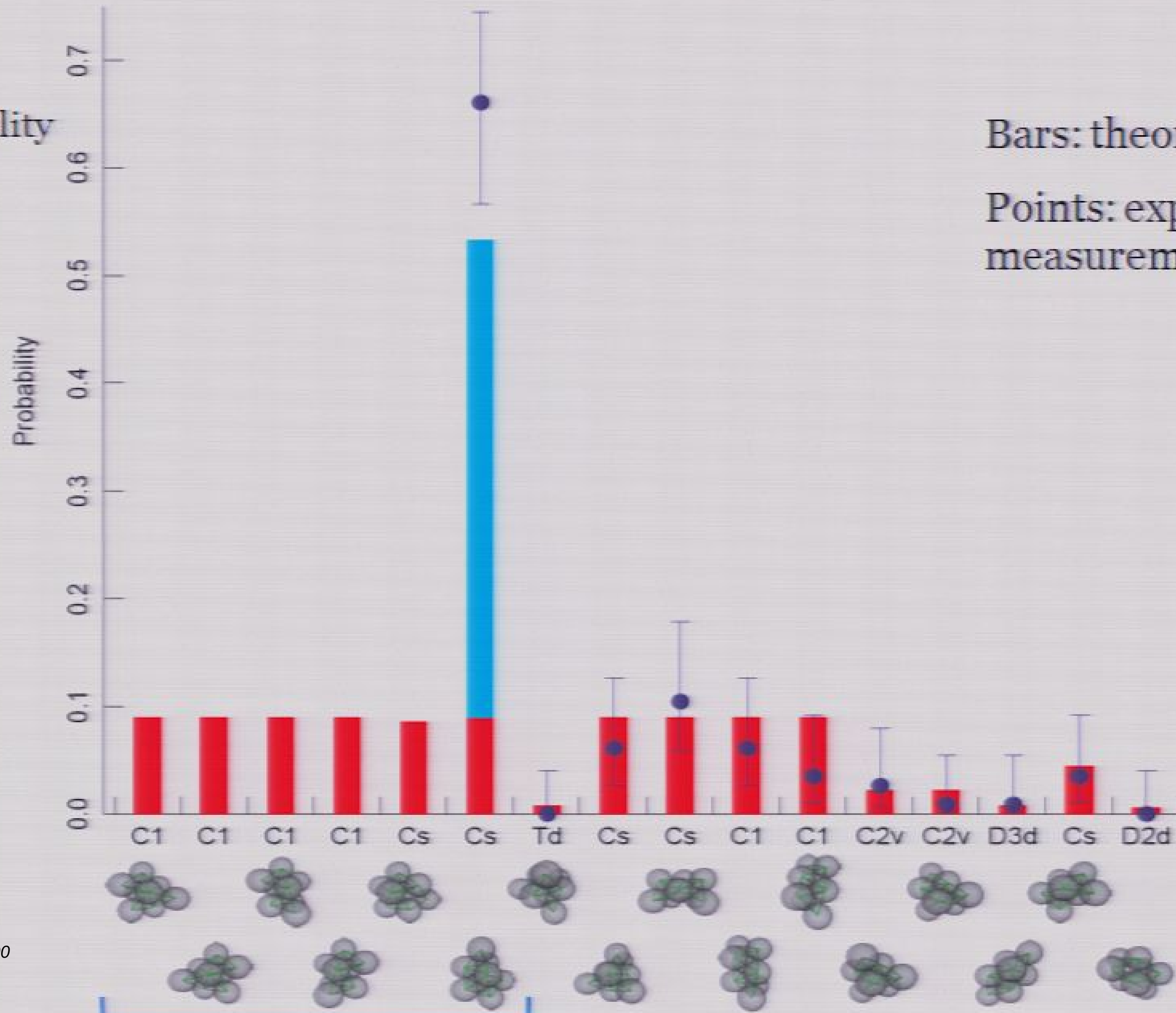


Free energy landscape, N=7



Free energy landscape, *N*=8

Probability

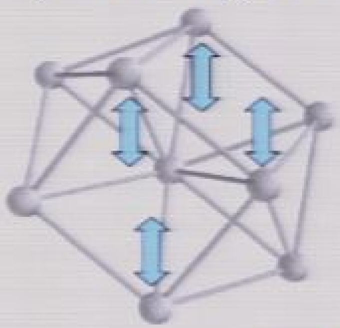


Bars: theory

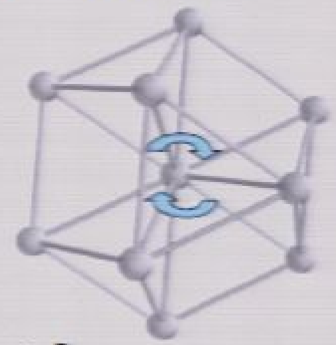
Points: experimental measurements

N = 9 and higher: Stable structures emerge

At N=9 and higher there are structures with soft vibrational modes:



3N-6 bonds (degenerate with other packings) but deformable over a finite range

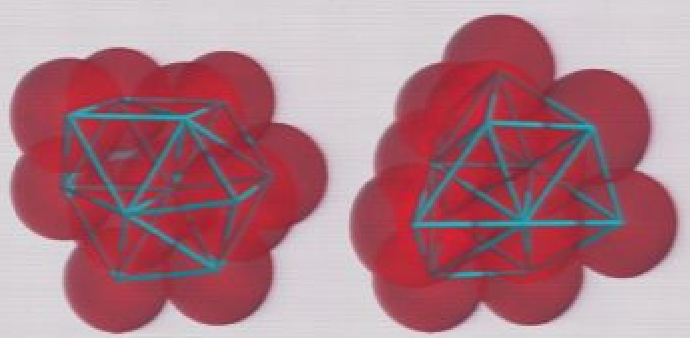


At N=10, 11, 12 it becomes possible to build structures that have more than 3N-6 contacts:

N=10
3 packings (of 223 total) with 3N-5 contacts

(a) $N = 10$

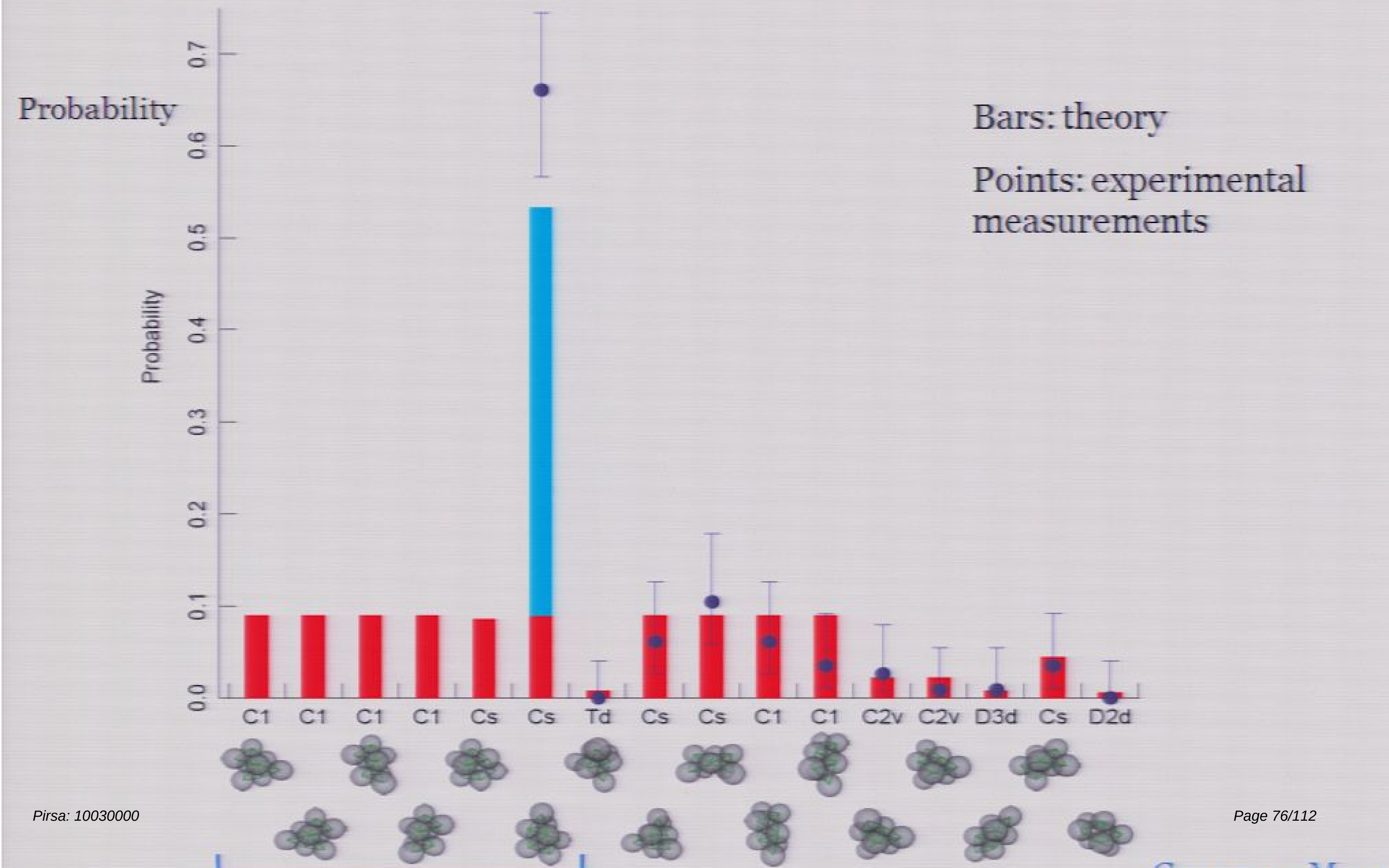
N=11
1 packing with 3N-4 contacts



(b) $N = 11$ (c) $N = 12$

N=12
1 packing with 3N-3 contacts

Free energy landscape, N=8



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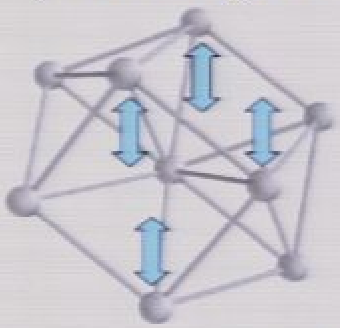
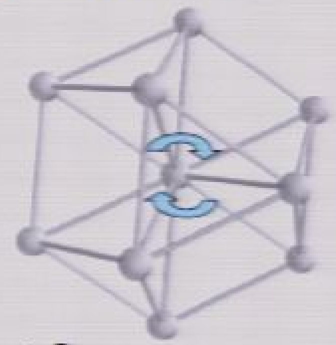


3N-6 bonds (degenerate with other packings) but deformable over a finite range



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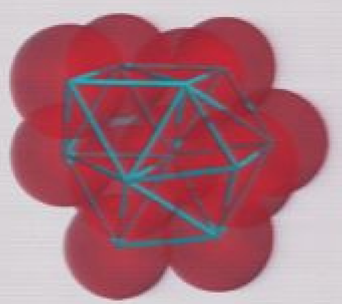


(b) $N = 11$

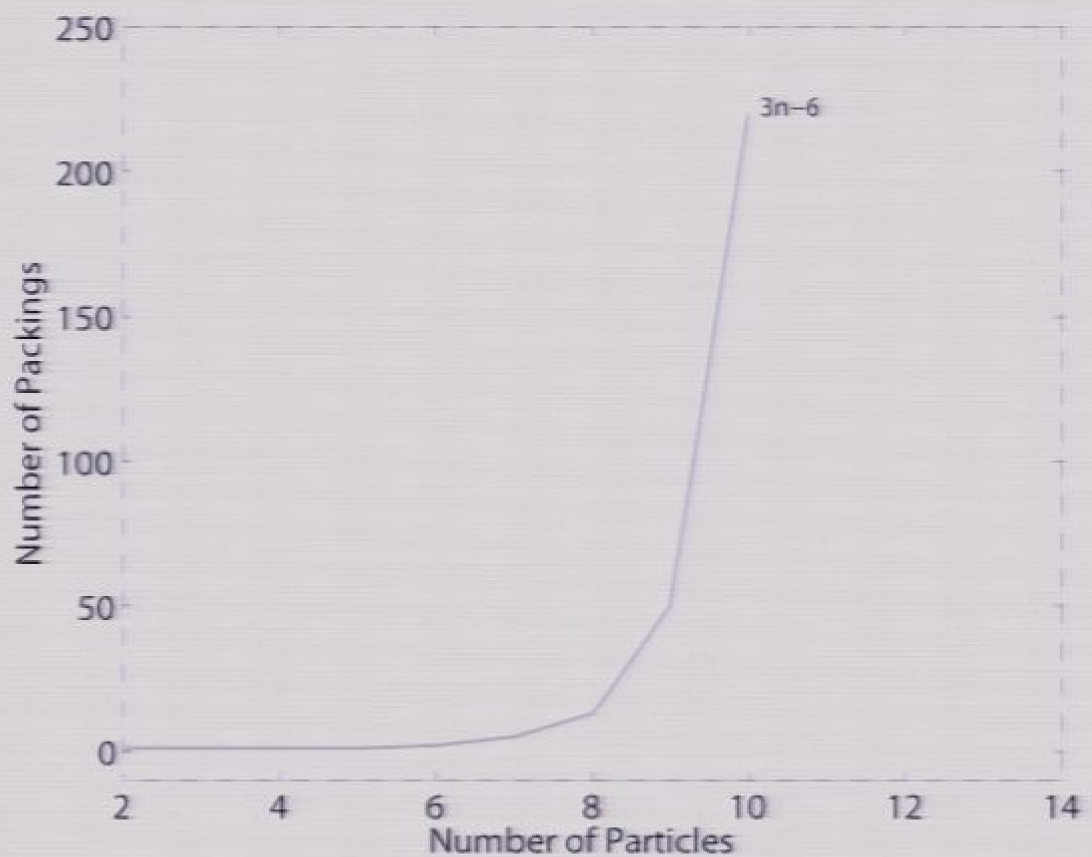
(c) $N = 12$

N=12
1 packing with 3N-3 contacts

Theory: Ground state degeneracy

Degeneracy increases up to N=10, then decreases as HCP ground state seems to emerge

n	$3n-6$	$3n-5$	$3n-4$	$3n-3$
2	1	0	0	0
3	1	0	0	0
4	1	0	0	0
5	1	0	0	0
6	2	0	0	0
7	5	0	0	0
8	13	0	0	0
9	50	0	0	0
10	223	3	0	0
11		9	1	0
12			5	1
13				7



What happens at finite temperature?

Experimental results: at *N*>=9 a more complex landscape emerges due to vibrational entropy and extra bonds

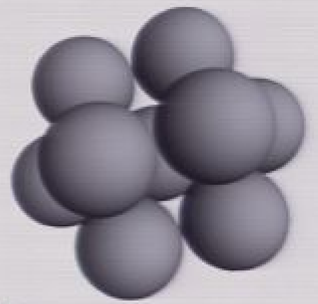
N=9:

4 of 36 are non-rigid 9-mers

F ~50 rigid states

$\Delta F \sim 2.2\, k_B T$

1 non-rigid



N=10:

7/33 non-rigid with 3*N*-6 bonds

4/33 with 3*N*-5 bonds (3 HCP and 1 HCP/FCC)

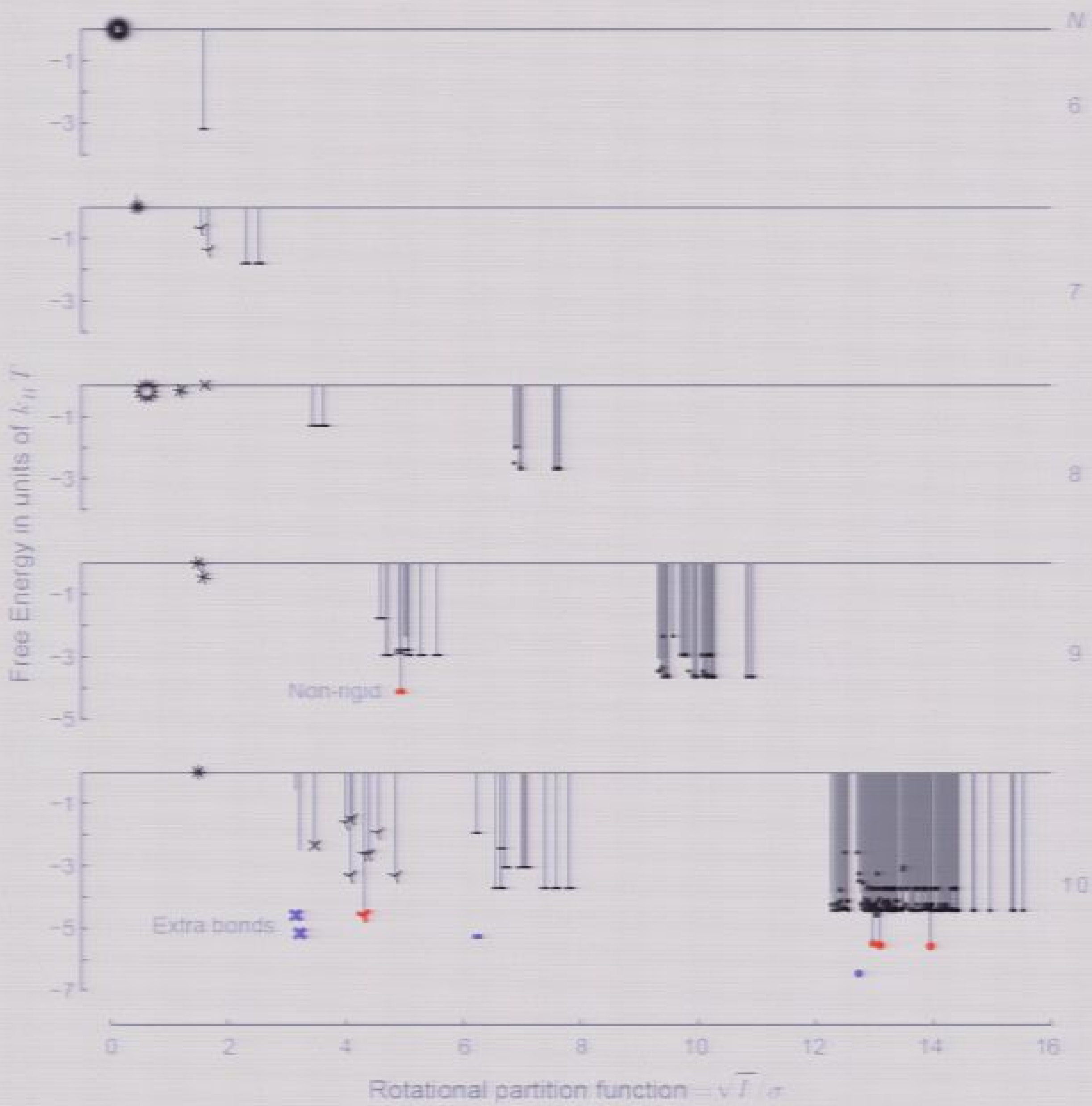
F ~200 rigid states at 3*N*-6

4 non-rigid

3 states at 3*N*-5

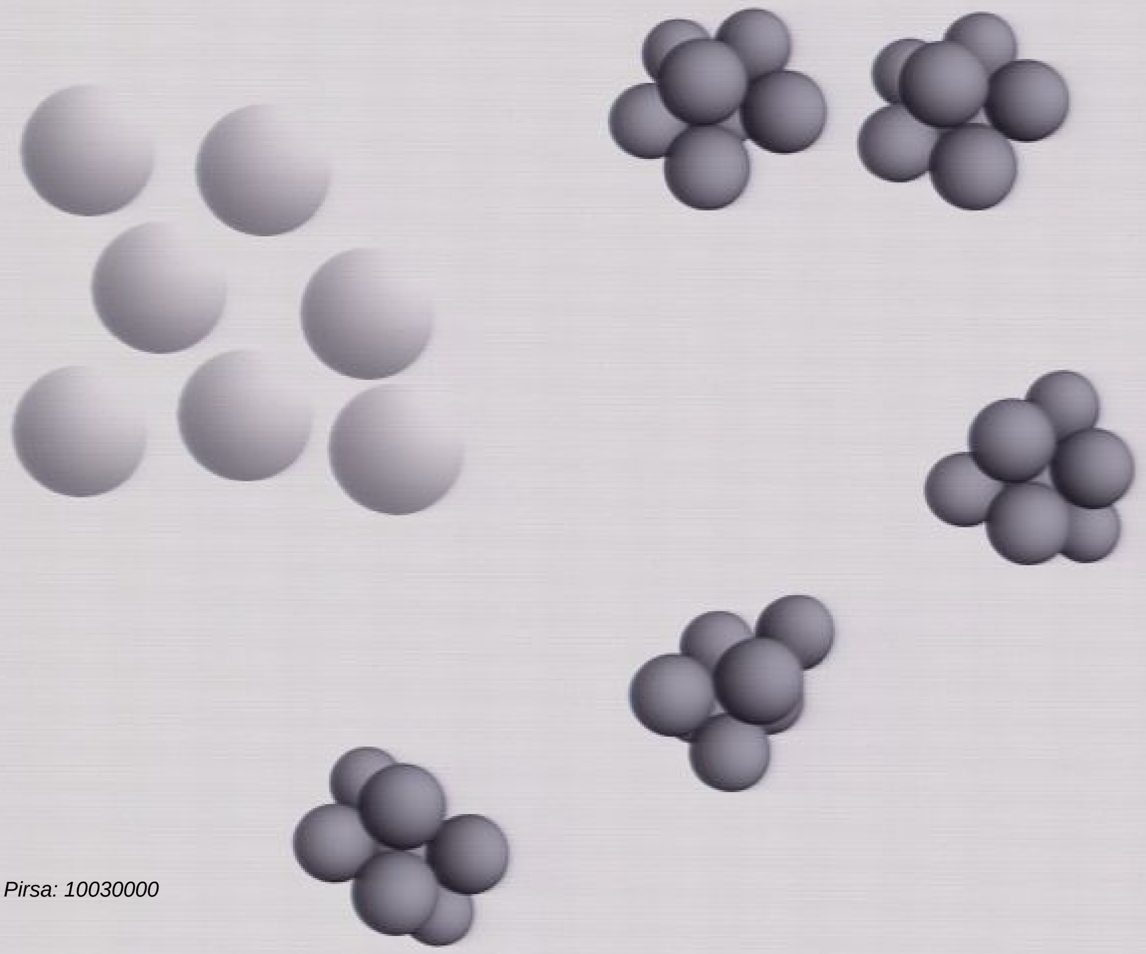
N=11: 7/28 structures at 3*N*-5, 2/28 structures at 3*N*-4 (HCP)

The Free Energy Landscape of Hard Sphere Clusters



Engineering the landscape

So spheres can assemble into lots of different structures – but how can you design the system to choose only one of those structures at equilibrium?



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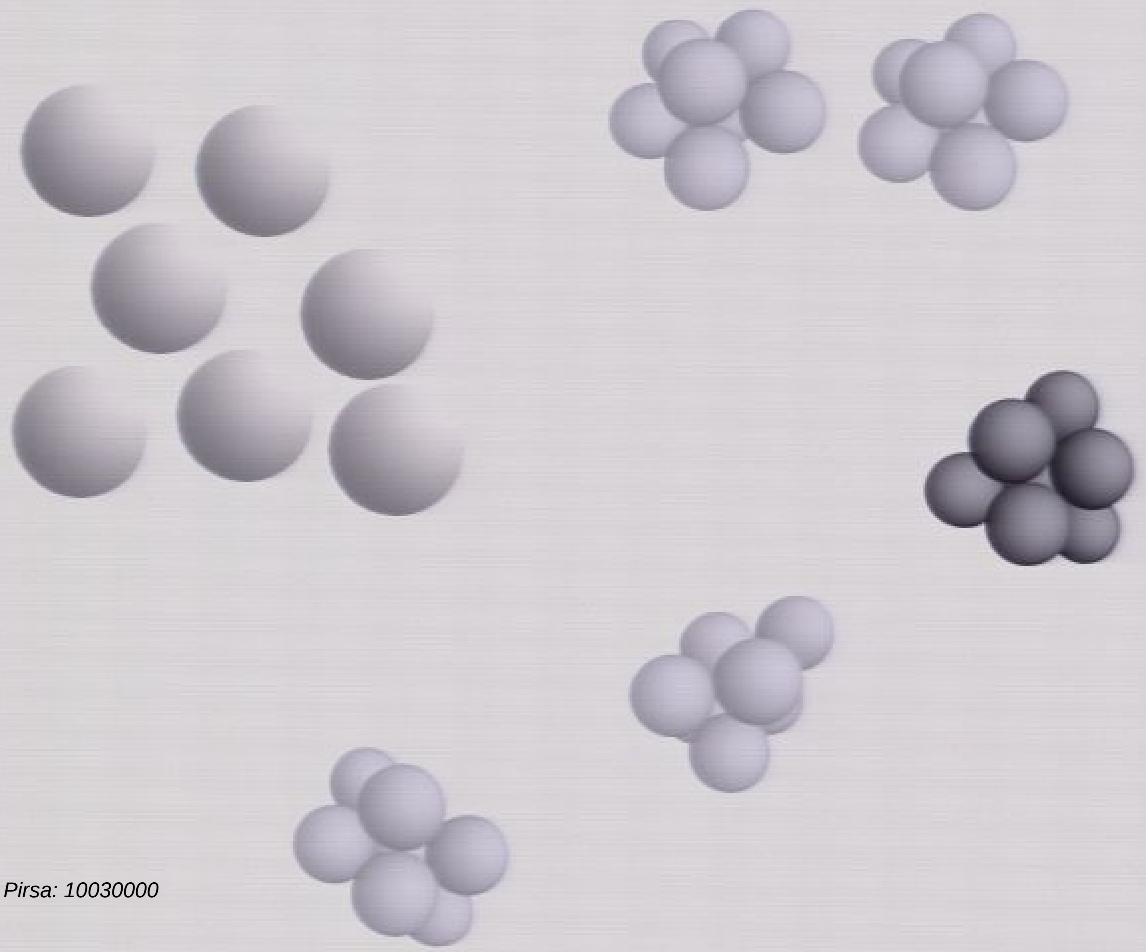

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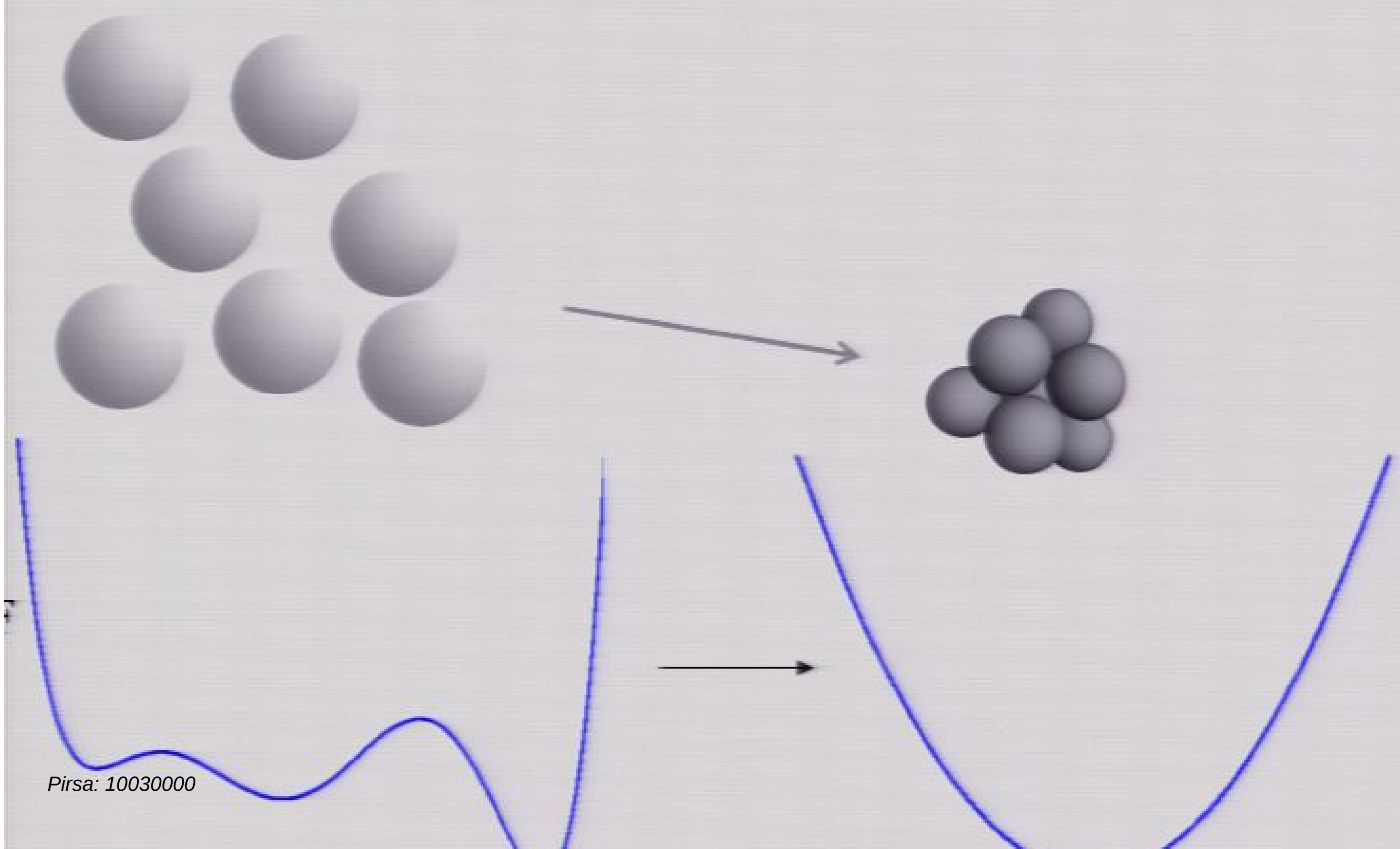

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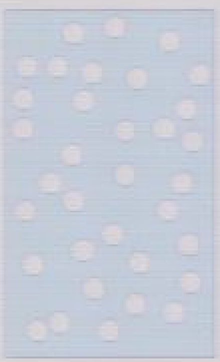

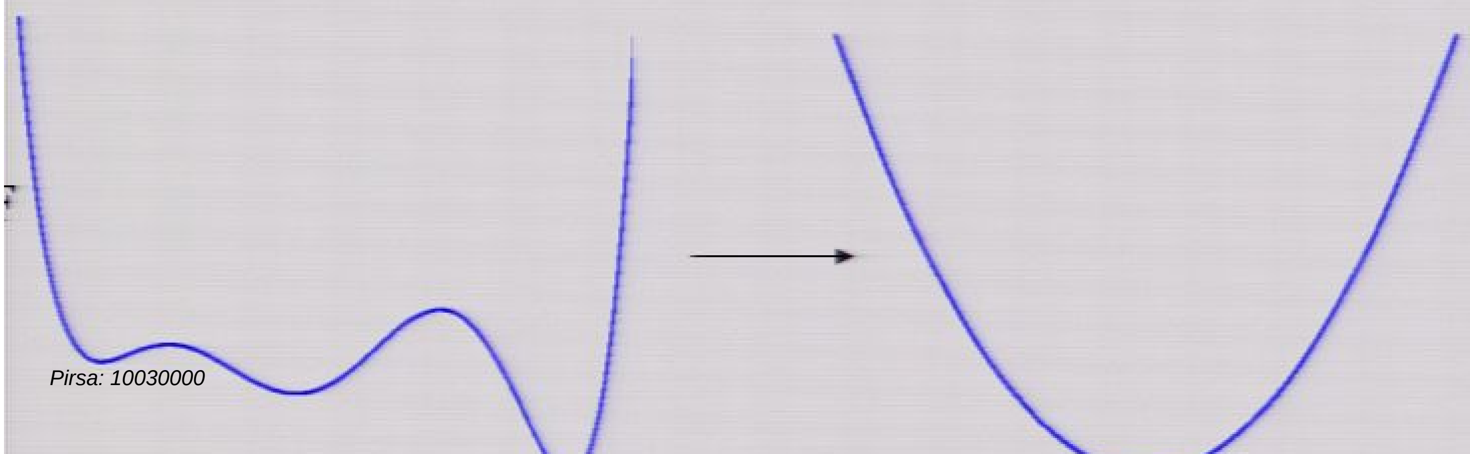

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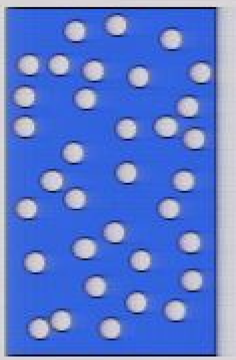
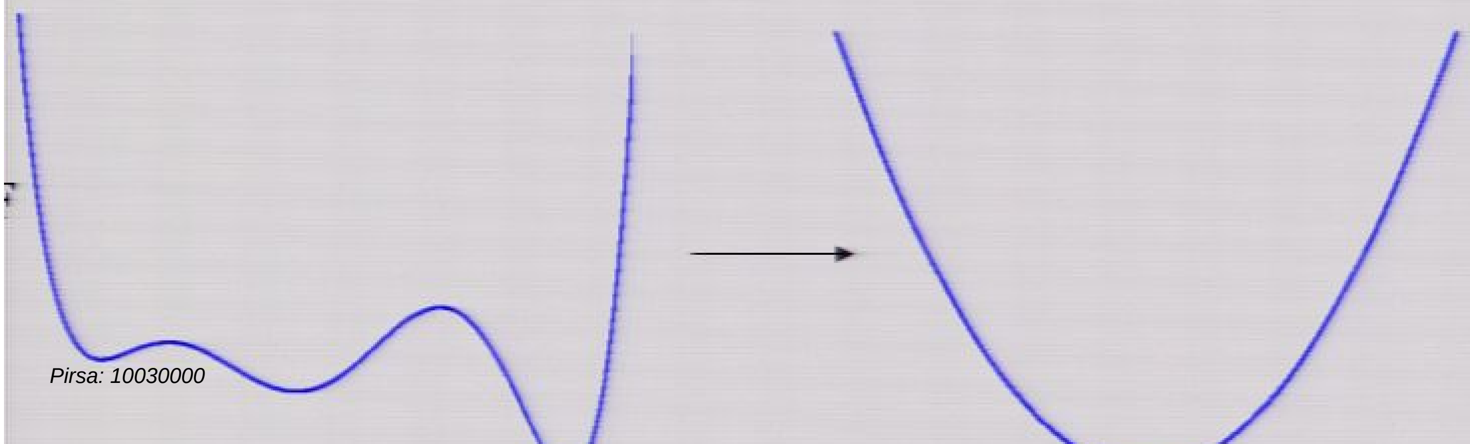
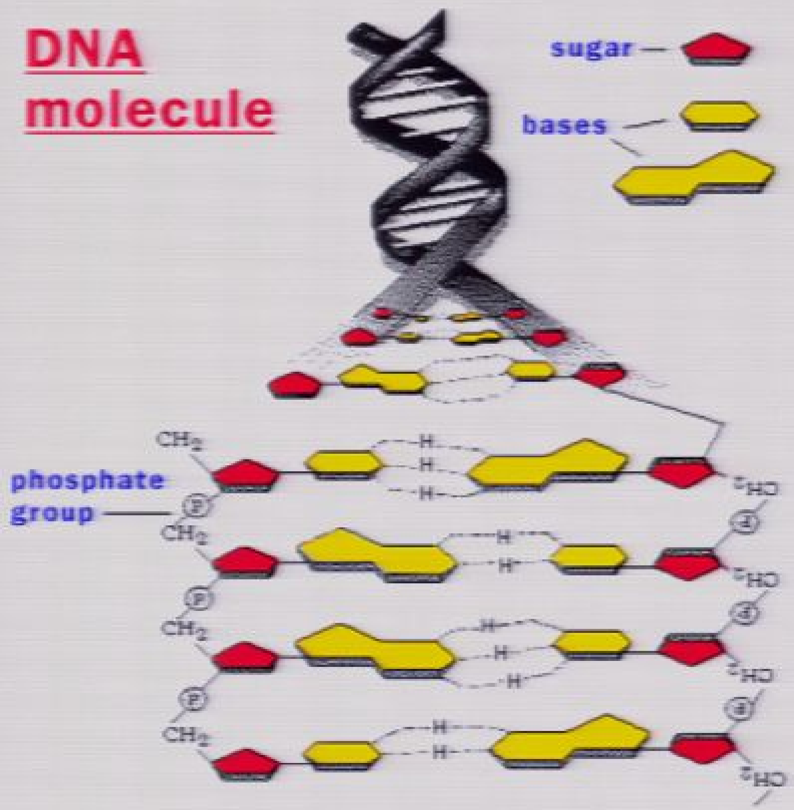
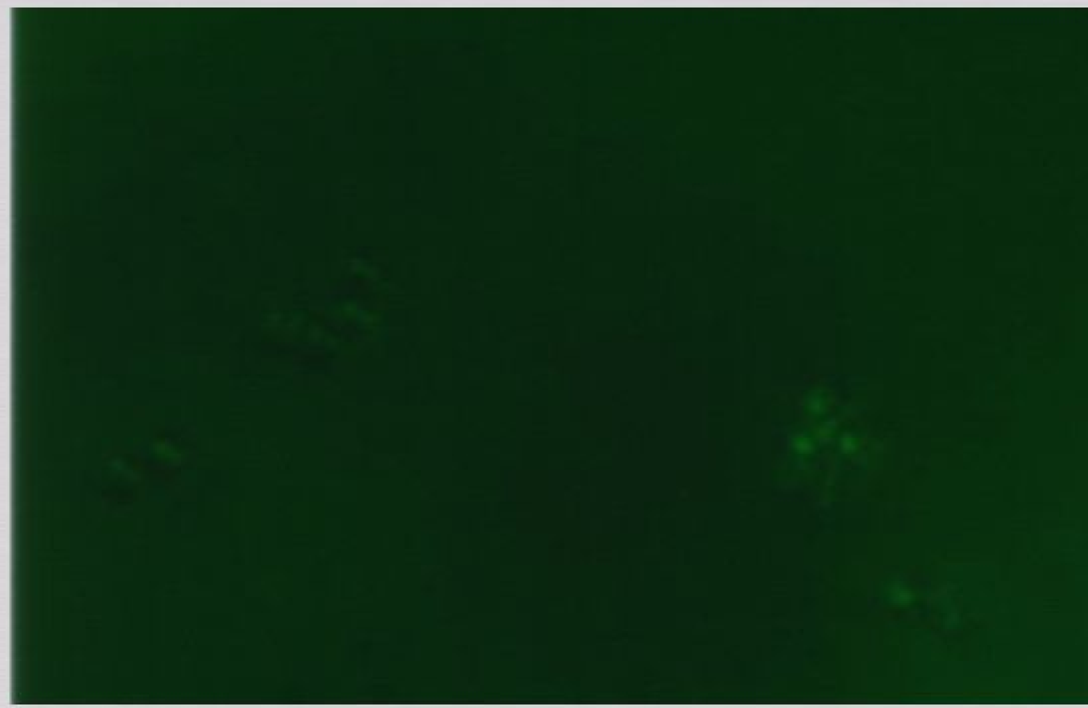
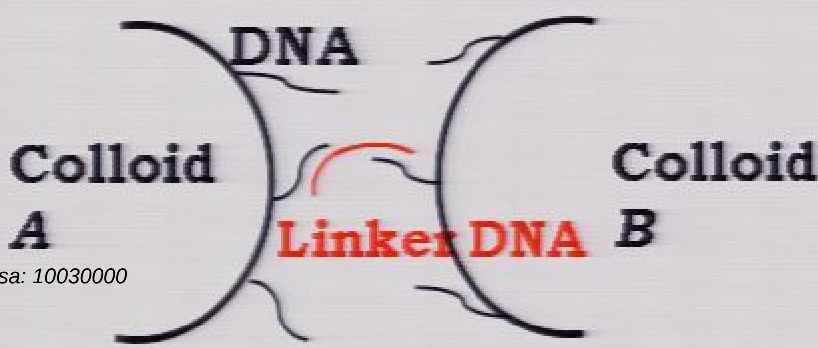




Using specific interactions to guide assembly





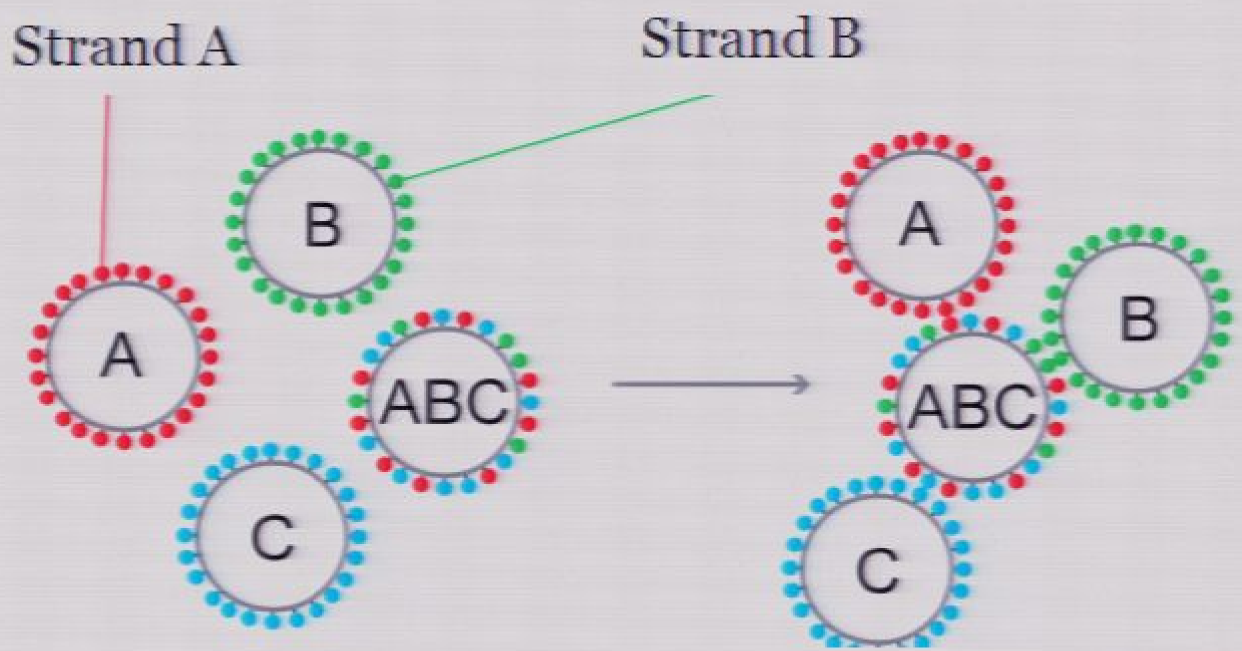


Self-assembly in the presence of multiple specific interactions

Binding logic:

A binds to A,

B binds to B



Introducing Binding Specificity

- Specificity matrix

  Determines which particle pairs can bind (set by labeling)

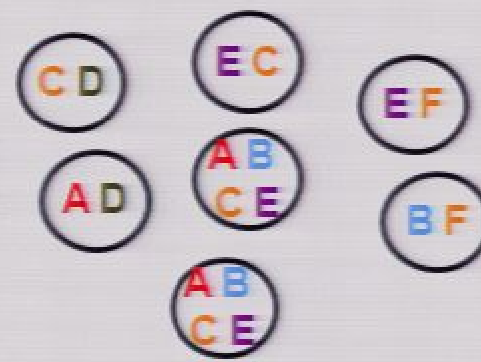
- If specificity matrix = adjacency matrix for a particular packing

  That packing becomes the unique ground state, save for enantiomers ($N < 10$)

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

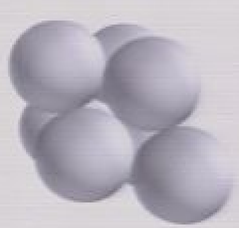
which corresponds to this packing

and to the following labeling of particles:



Is the following conformation possible?

$$\begin{pmatrix} 0 & 1 & 0 & 1 & 1 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 & 1 & 0 \\ 0 & 1 & 0 & 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 0 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & \text{[illegible]} & \text{[illegible]} & 1 & 1 & 0 & 0 \end{pmatrix}$$

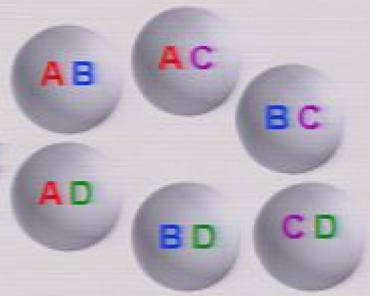


No – only 2 of the 3 particles having 5 contacts are allowed under the above labeling of particles.

Natalie Arkus

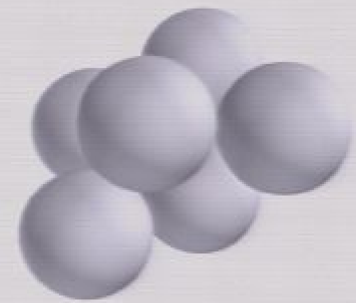
Encoding the equilibrium state in a 6-particle system

This labeling



Stabilizes this packing

Over this packing



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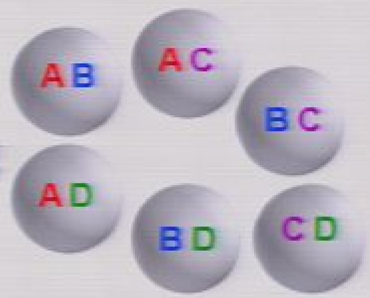

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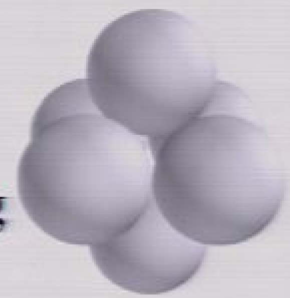

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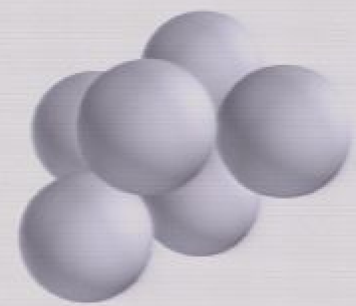

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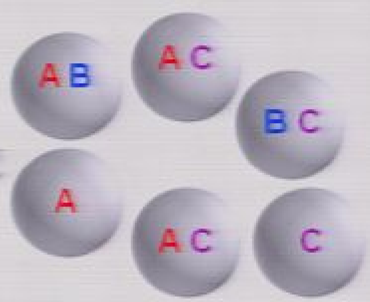

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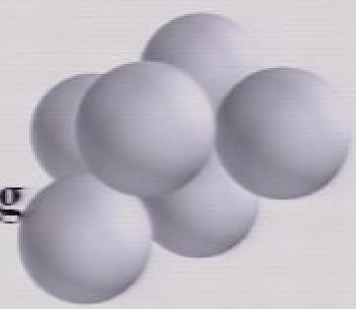

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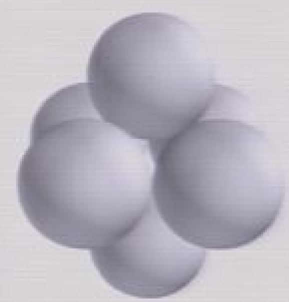
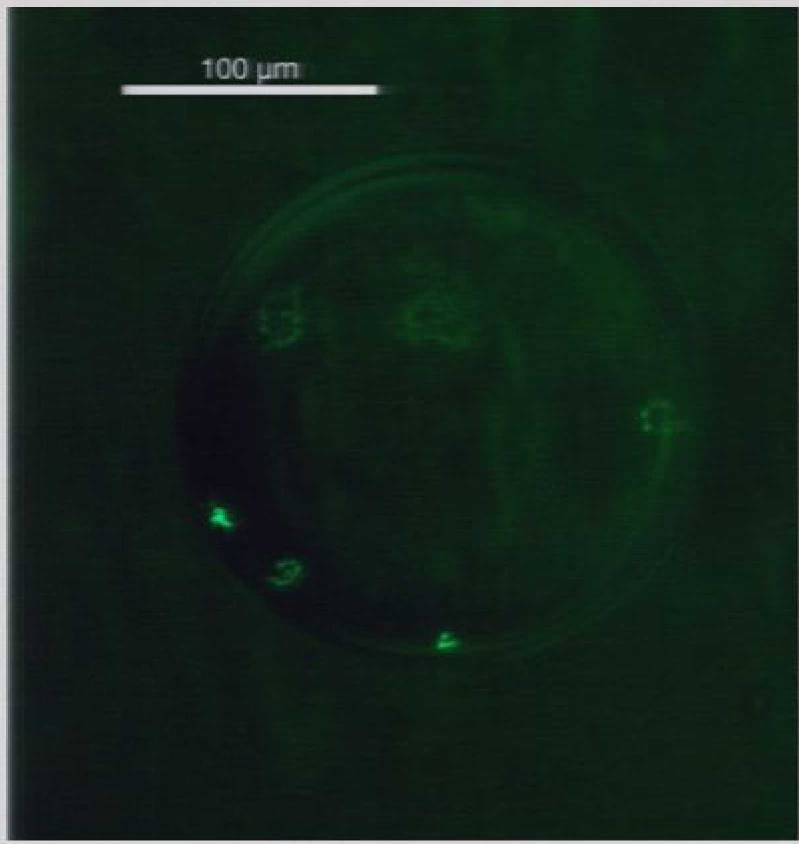
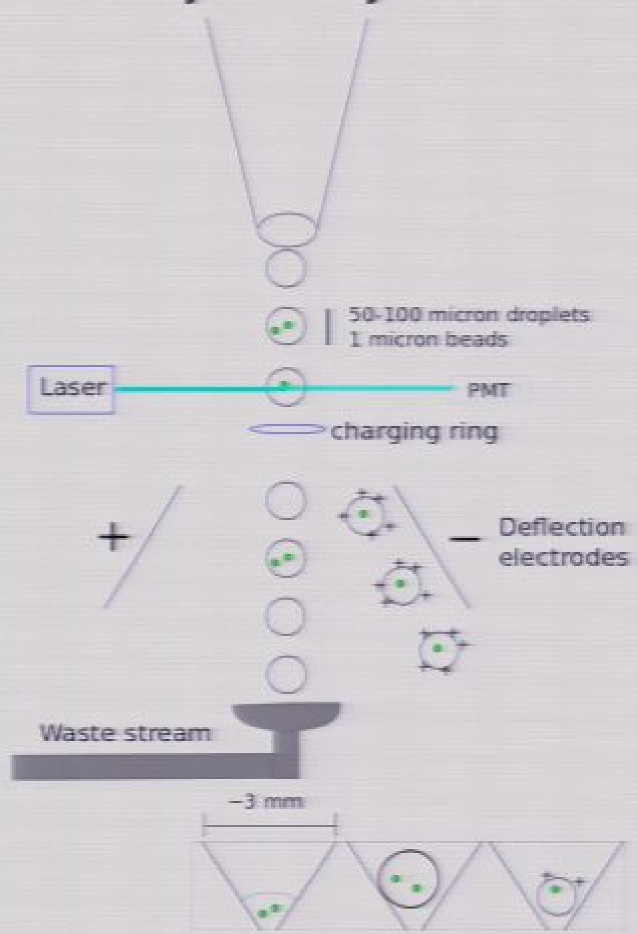


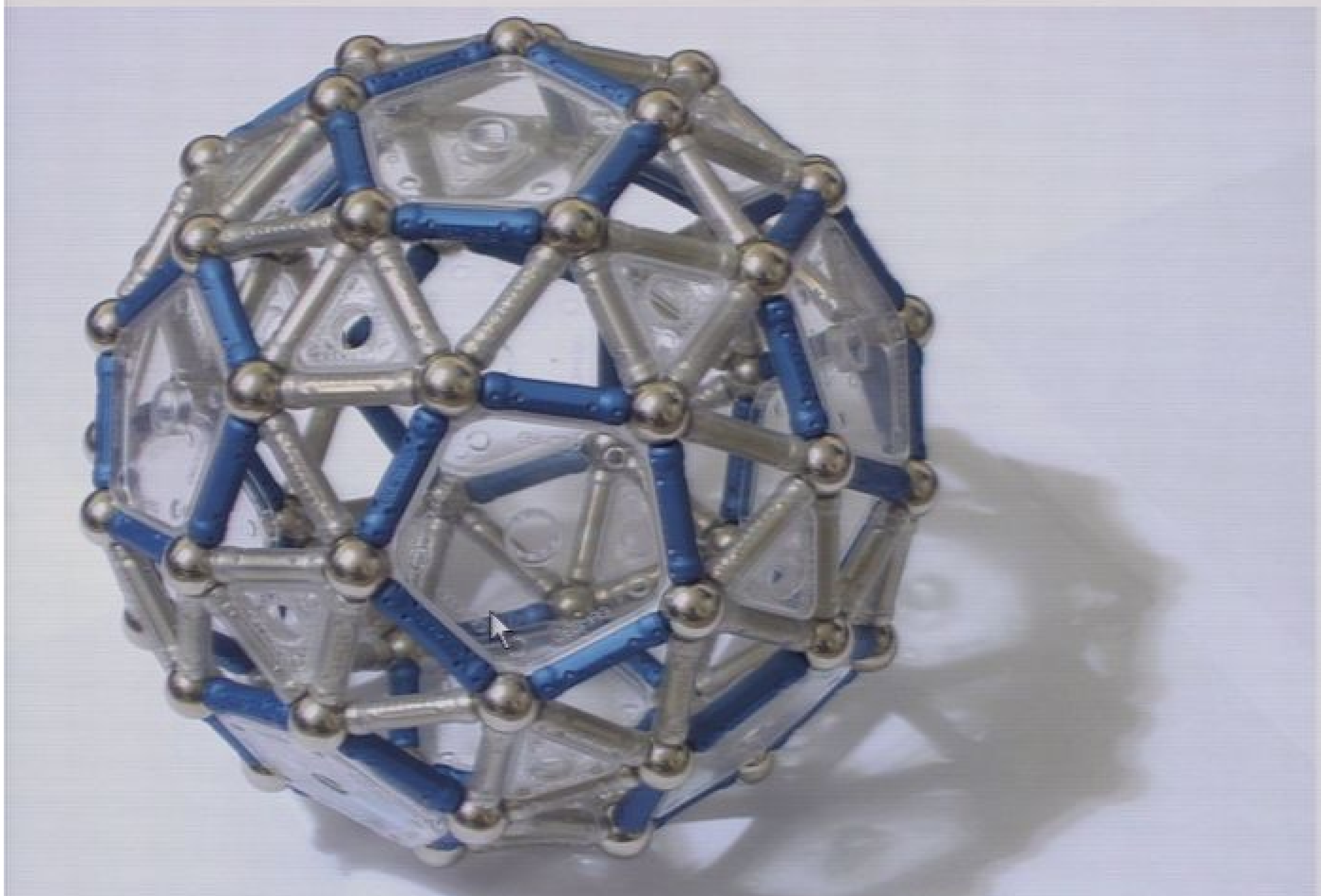
How do you program the system?

Need to mix the particles in the right combinations and numbers:





What interesting structures can be made by packing spheres at higher N?



Geomags (wikipedia)

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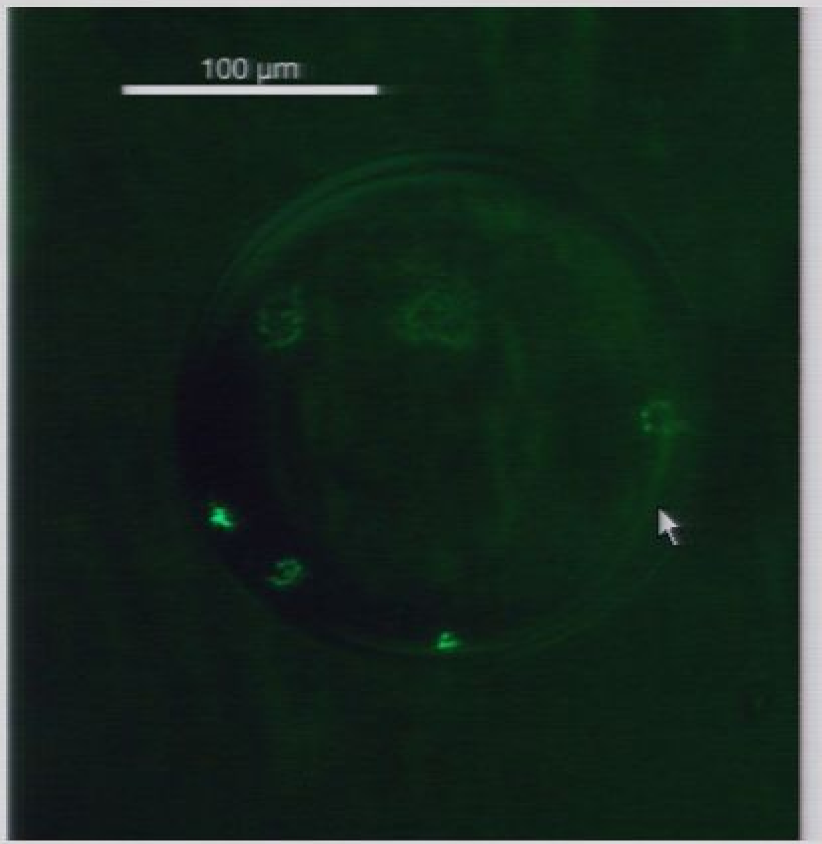

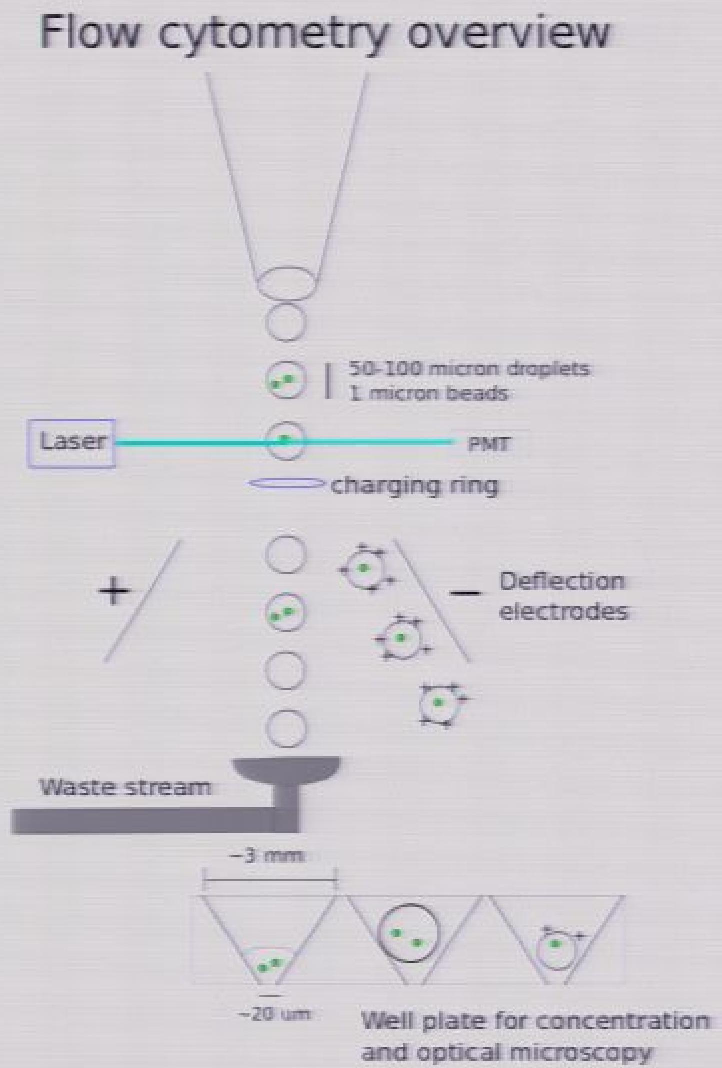

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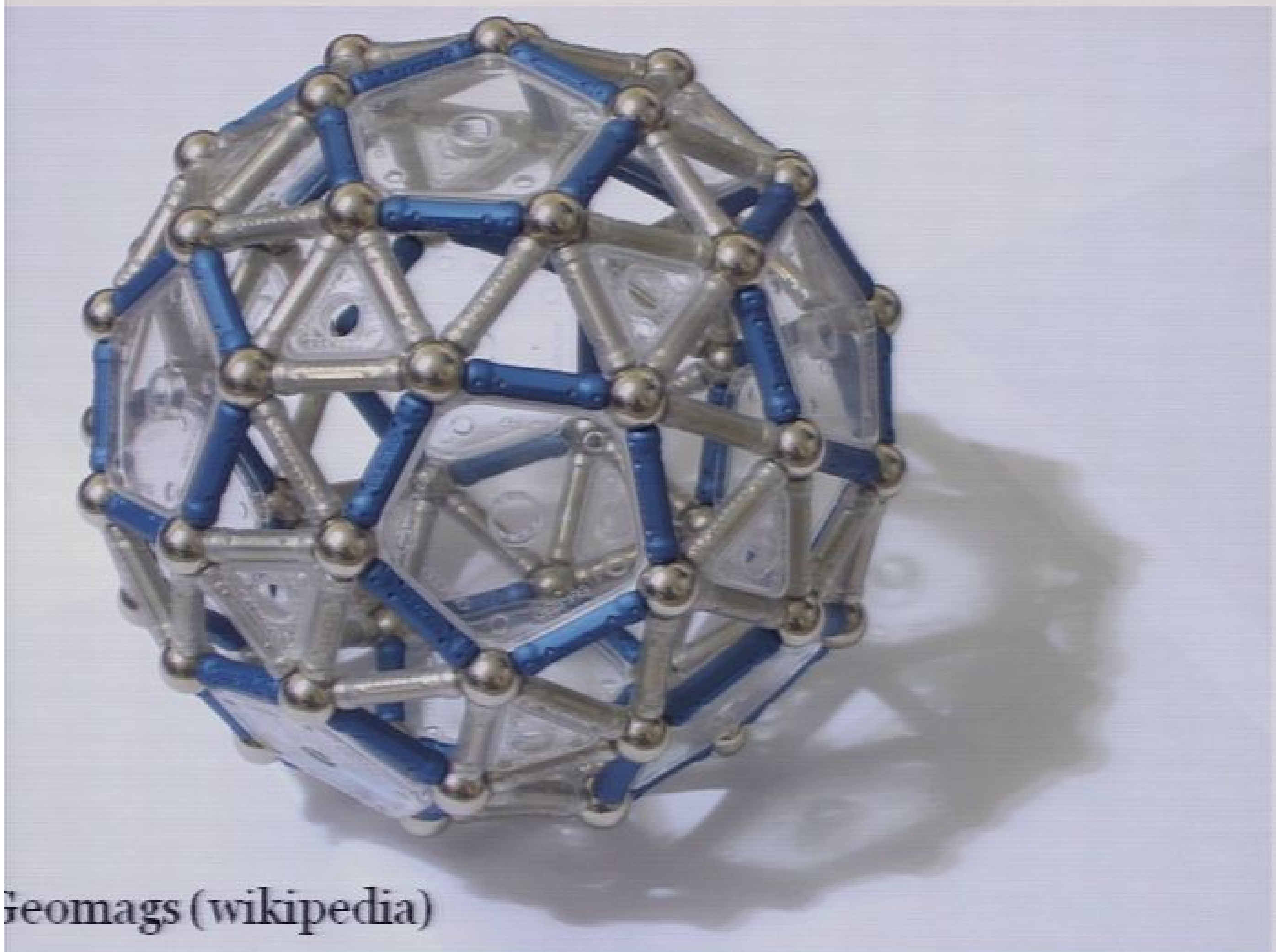

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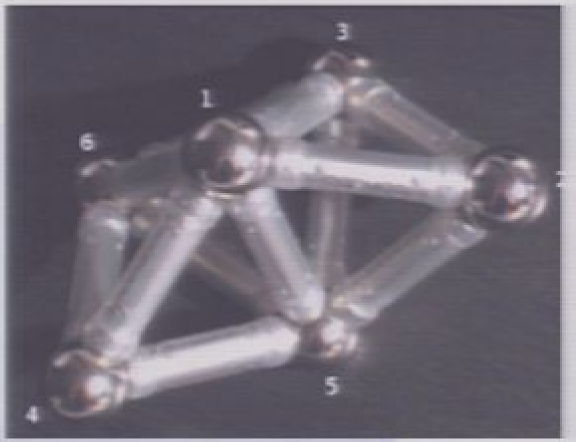

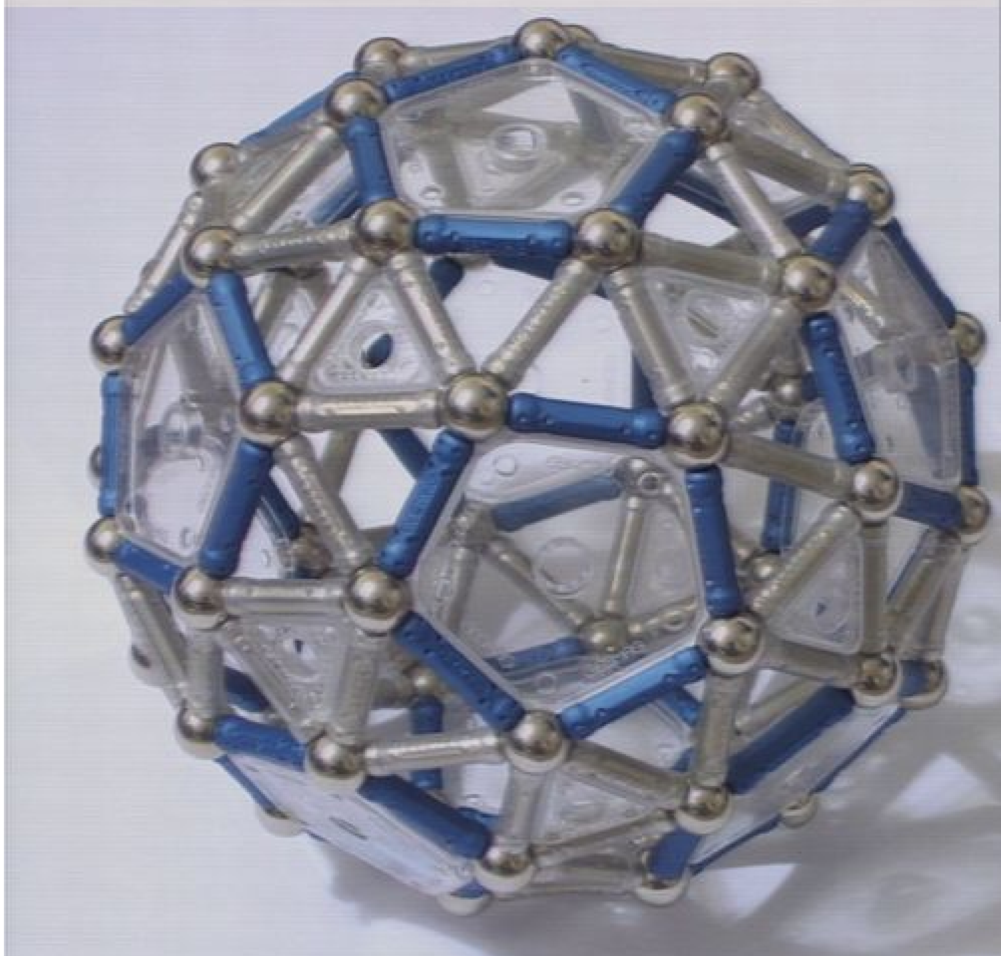

Geomags (wikipedia)

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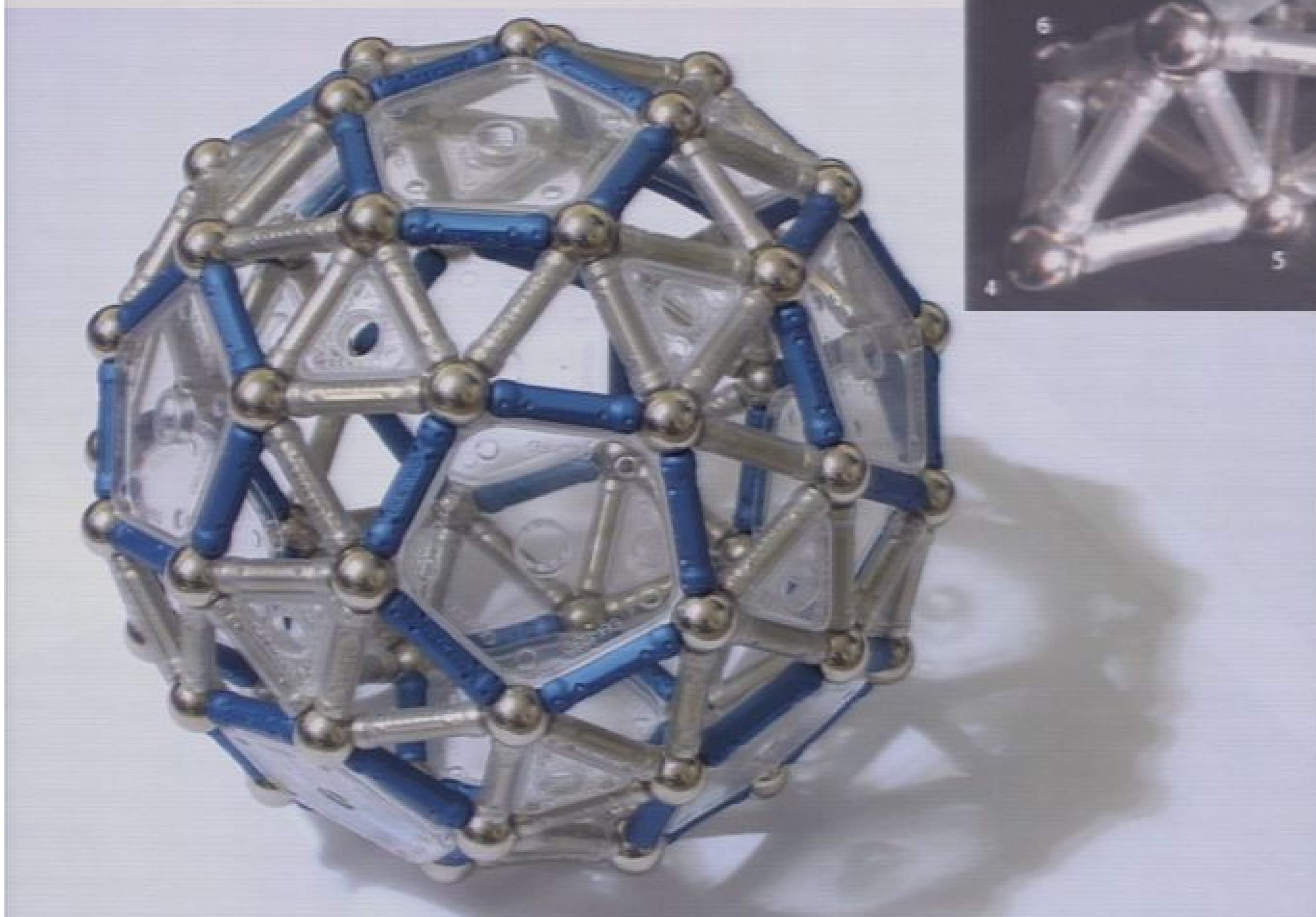
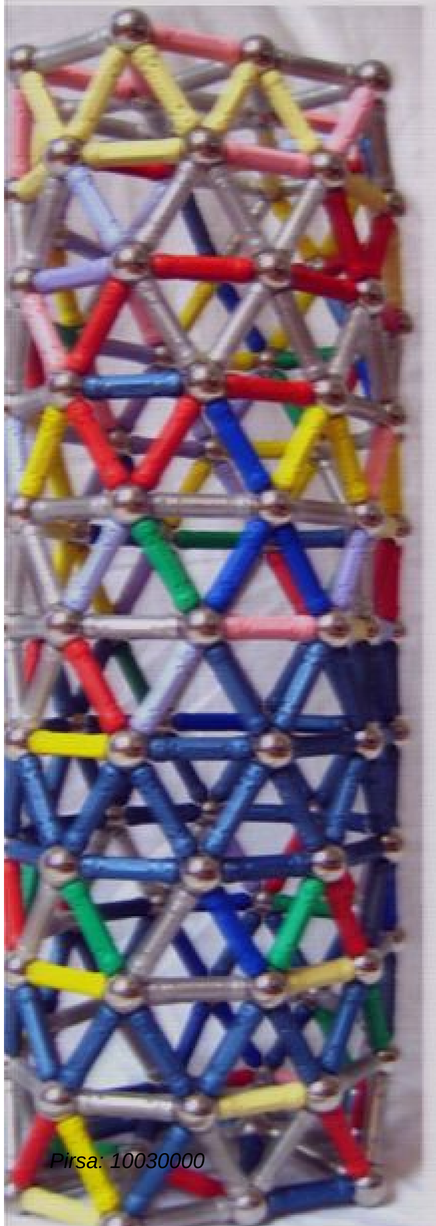


Geomags (wikipedia)

Palais du Chaillot, Paris

Encoding a cylindrical shell as the ground state



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particle 2: 0,1,12,14,15
particle 3: 0,1,5,7,8
particle 4: 1,8,10,11,12
particle 5: 2,153,154,164
particle 6: 2,3,161,163,164
particle 7: 2,3,154,156,157
particle 8: 3,157,159,160,161
particle 9: 4,16,18
particle 10: 4,6,18
particle 11: 5,6,7,20
particle 12: 7,9,20
particle 13: 8,9,10,23
particle 14: 10,11,23,25
particle 15: 11,13,25
particle 16: 12,13,14,28
particle 17: 14,17,28
particle 18: 15,16,17
particle 19: 18,19,31,33
particle 20: 6,19,21,34
particle 21: 20,21,22,36
particle 22: 9,22,24,38
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particle 109: 151,153,165
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particle 111: 143,154,155,156
particle 112: 144,156,158
particle 113: 145,157,158,159
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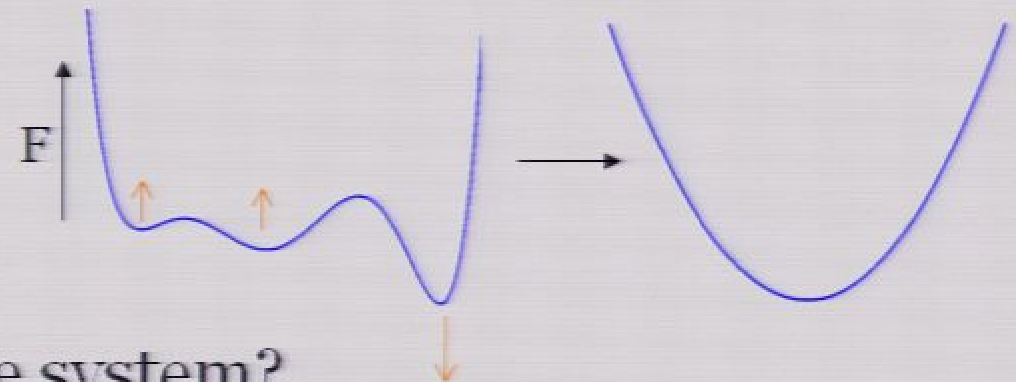
particle 115: 147,160,162
particle 116: 148,161,162,163
particle 117: 149,163,166
particle 118: 152,164,165,166

Total labels = 167
For N = 118.

Natalie Arkus

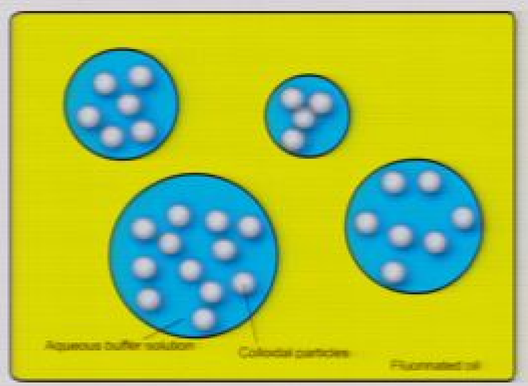
Directions and questions

- Engineering the landscape to destabilize kinetic traps: optimization of labels



- How do we program the system?

  Our approach: droplet-based microfluidics



- Is there a labeling algorithm that yields a self-limiting aggregation state? Can design new kinds of frustration

Summary

The thermodynamics of self-assembly of spherical particles:

- Can be measured directly
- Can be understood quantitatively: potential energy surface and free energy landscape
- Highly symmetric structures are highly unfavorable; nonrigidity confers stability

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People and Acknowledgements

Natalie Arkus

Guangnan Meng

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Michael Brenner

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Jerome Fung, Ryan McGorty

Jon Fan, Dina Aronzon

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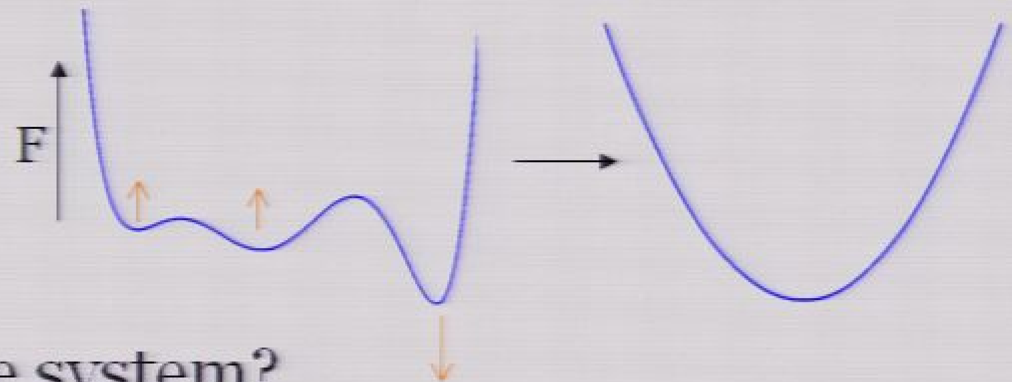

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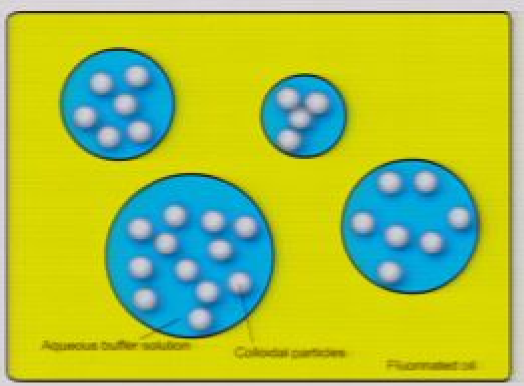

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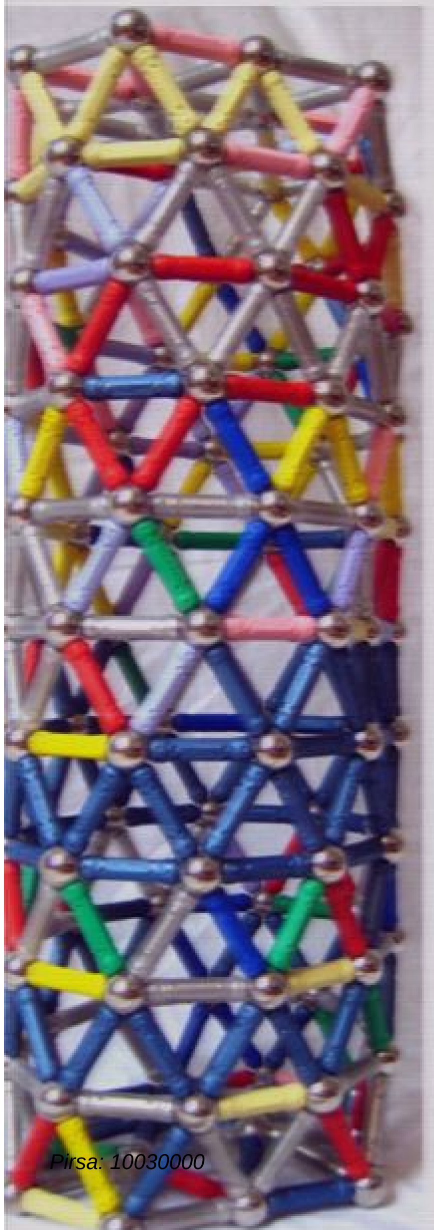
Encoding a cylindrical shell as the ground state



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particle 4: 1,8,10,11,12
particle 5: 2,153,154,164
particle 6: 2,3,161,163,164
particle 7: 2,3,154,156,157
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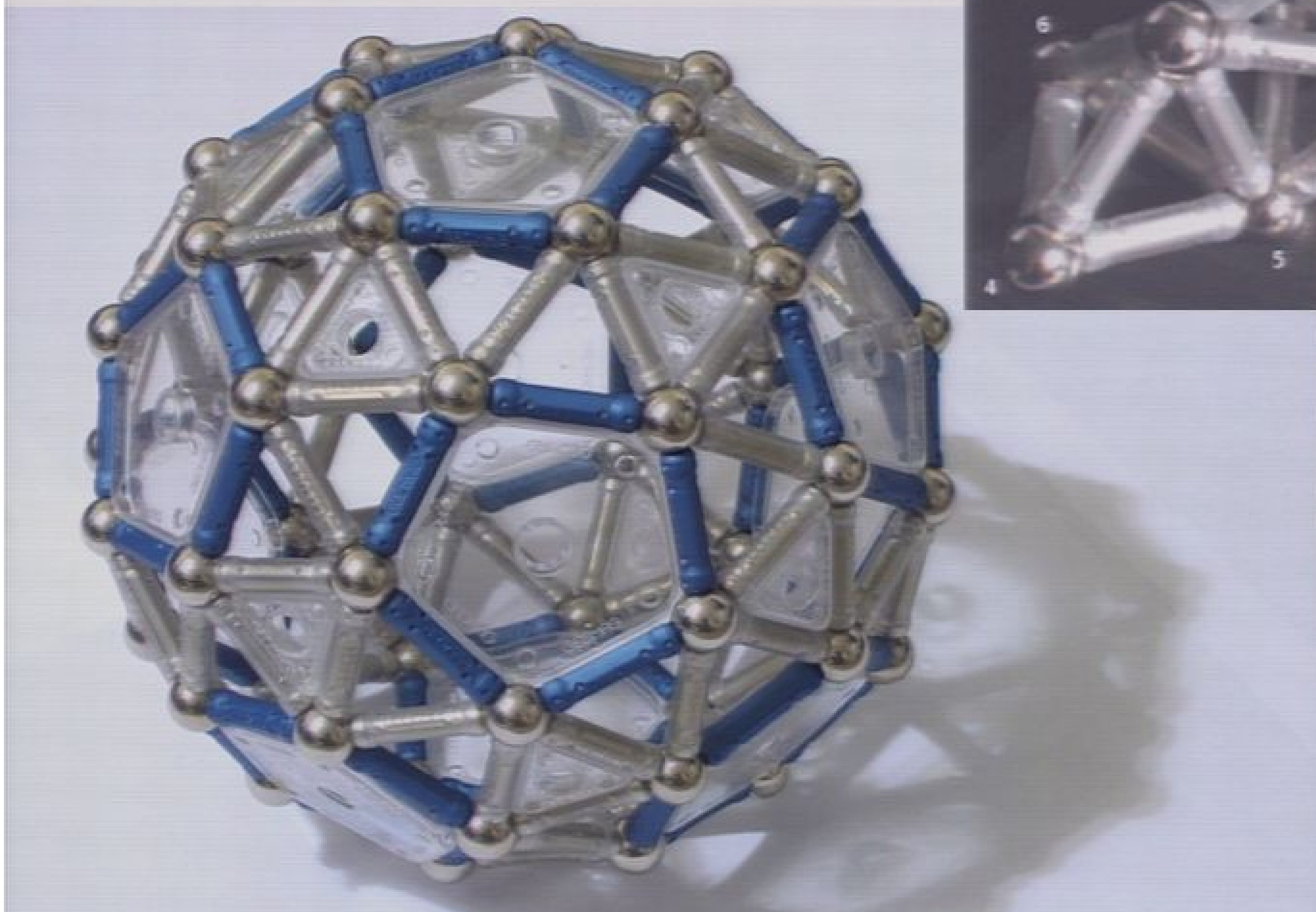
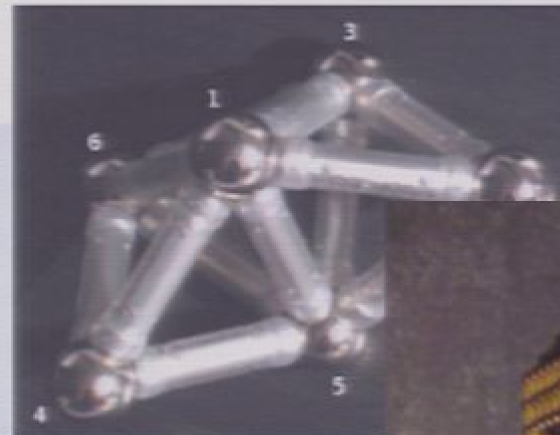
Natalie Arkus

What interesting structures can be made by packing spheres at higher *N*?



Geomags (wikipedia)



Palais du Chaillot, Paris

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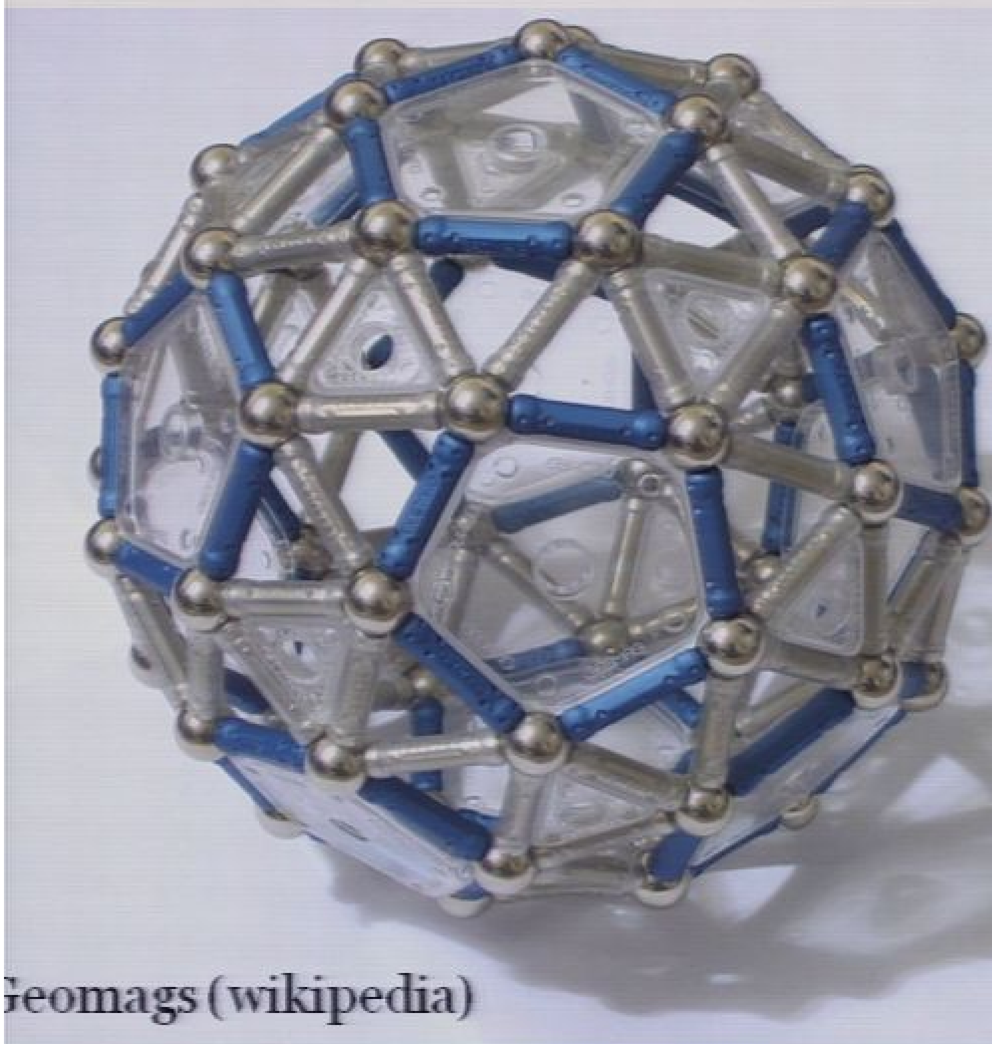

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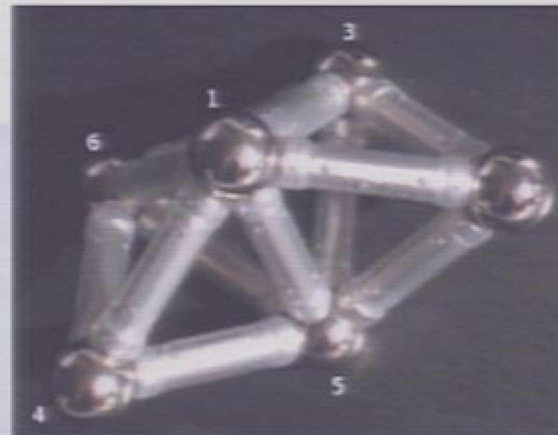

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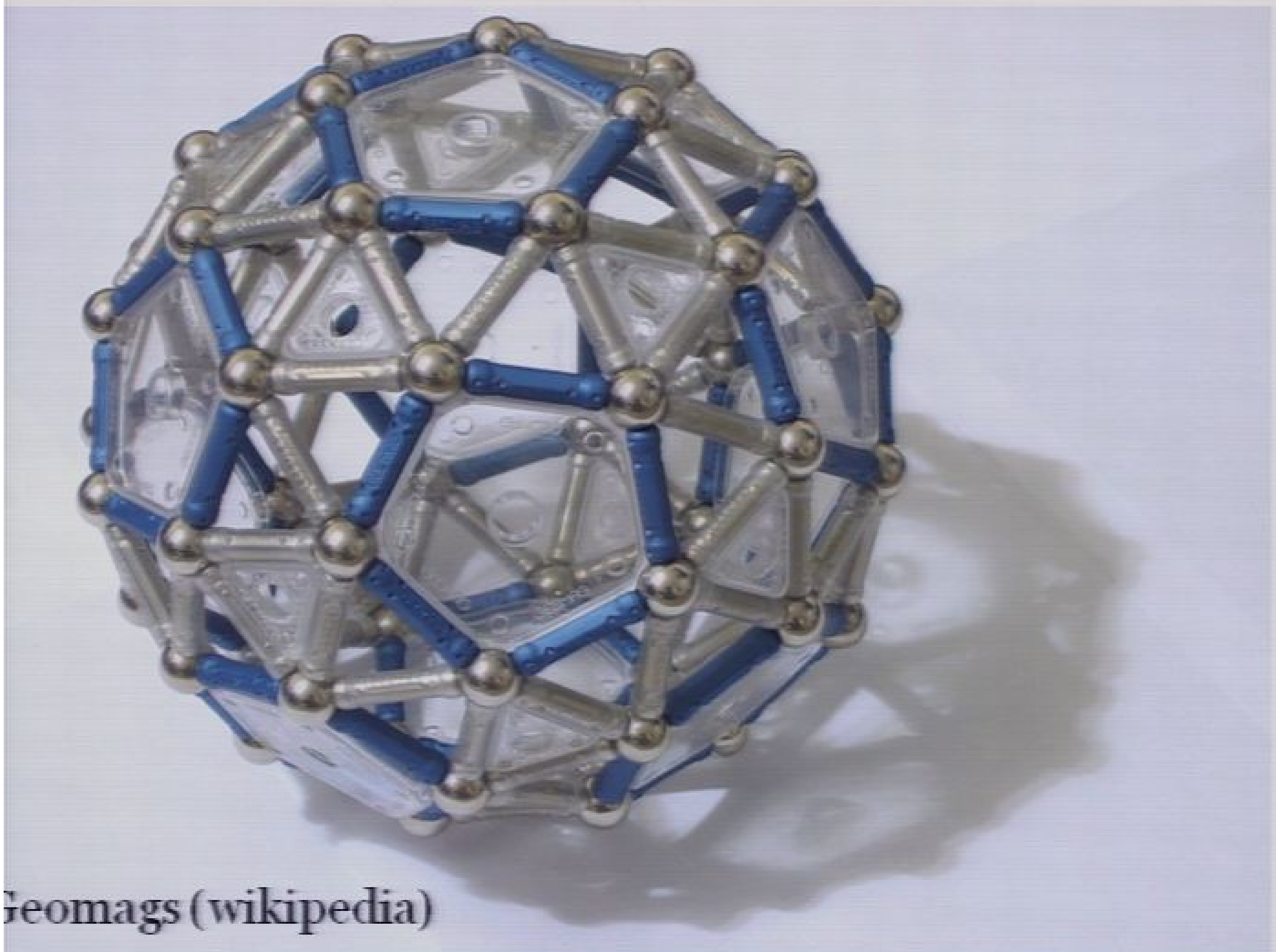
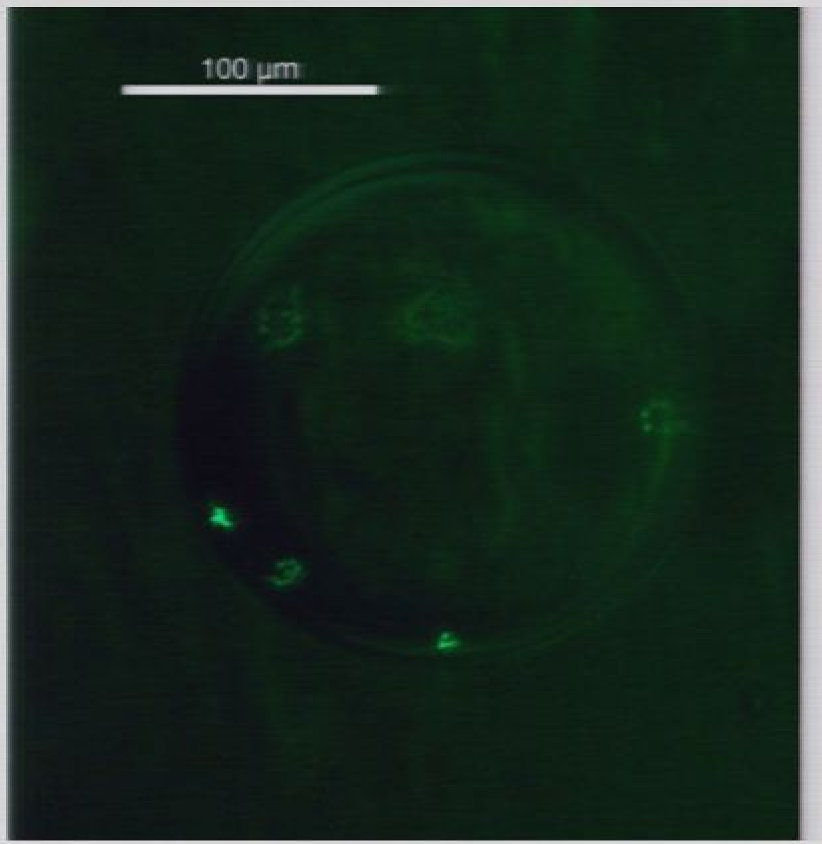


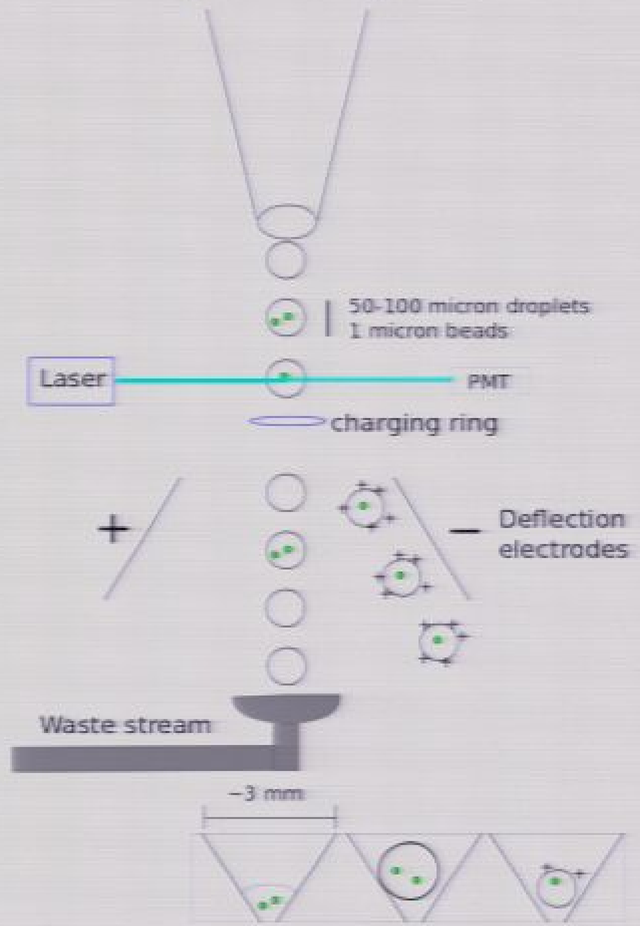
Geomags (wikipedia)

How do you program the system?

Need to mix the particles in the right combinations and numbers:



Flow cytometry overview



Introducing Binding Specificity

- Specificity matrix

  Determines which particle pairs can bind (set by labeling)

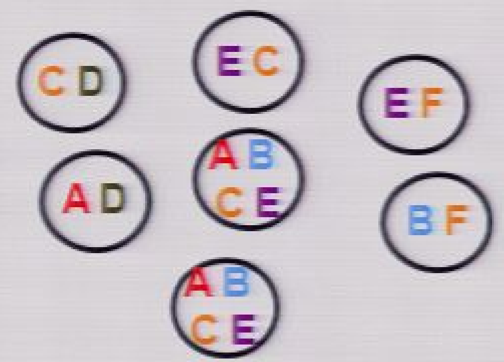
- If specificity matrix = adjacency matrix for a particular packing

  That packing becomes the unique ground state, save for enantiomers ($N < 10$)

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

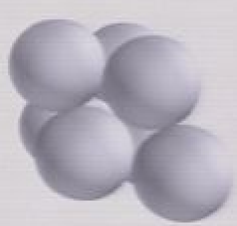
which corresponds to this packing

and to the following labeling of particles:



Is the following conformation possible?

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

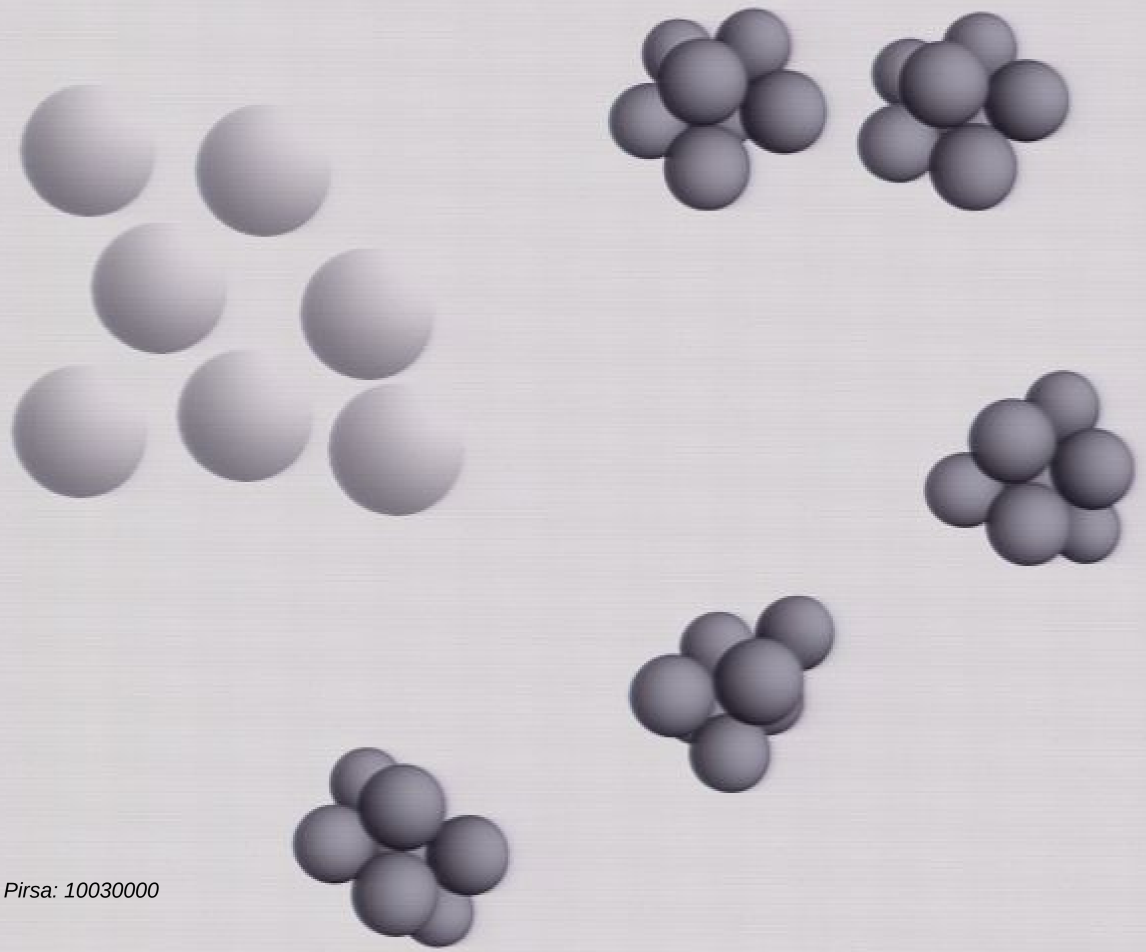


No – only 2 of the 3 particles having 5 contacts are allowed under the above labeling of particles.

Natalie Arkus

Engineering the landscape

So spheres can assemble into lots of different structures – but how can you design the system to choose only one of those structures at equilibrium?



The Free Energy Landscape of Hard Sphere Clusters