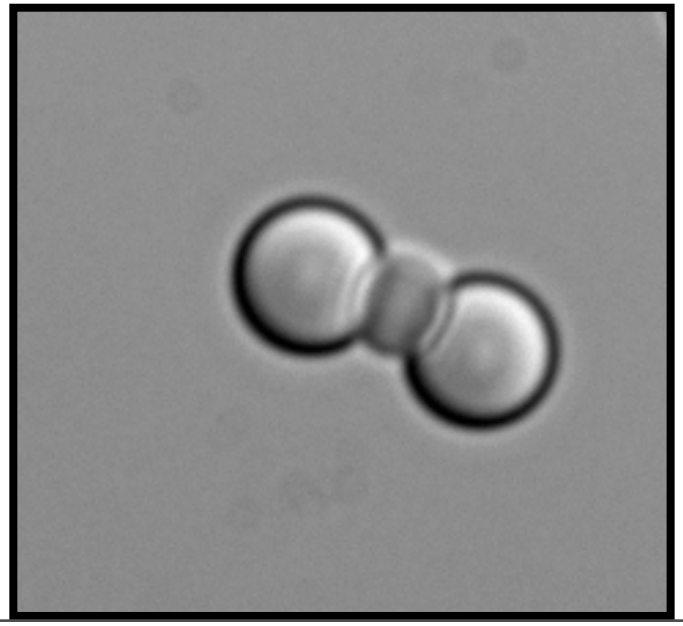
Sexy Colloids

particles with shape and specific attractions

Paul Chaikin, Andy Hollingsworth, David Pine,
Stefano Sacanna, Ned Seeman
Center for Soft Matter Research NYU

- Fundamental studies of Order, Frustration:
  the role of shape on structure
- Technologies for complex processes:
  self-assembly, motility, toward self-replication



Lock and Key

Sexy Colloids

particles with shape and specific attractions

Center for Soft Matter Research NYU

ACE-1 Science Concept Review
NASA GRCs 14 June 2011

Our Team:

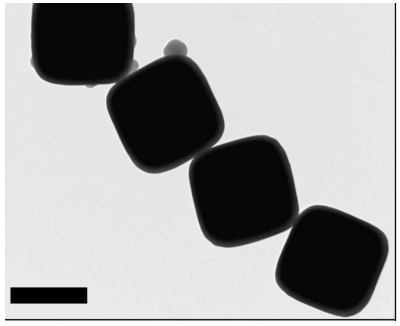
Ned Seeman

Andy Hollingsworth

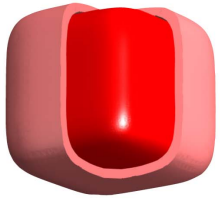
Paul Chaikin

Stefano Sacanna

Dave Pine



SILICA @ HEMATITE



Cubes

Sexy Colloids

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NASA GRCs 14 June 2011

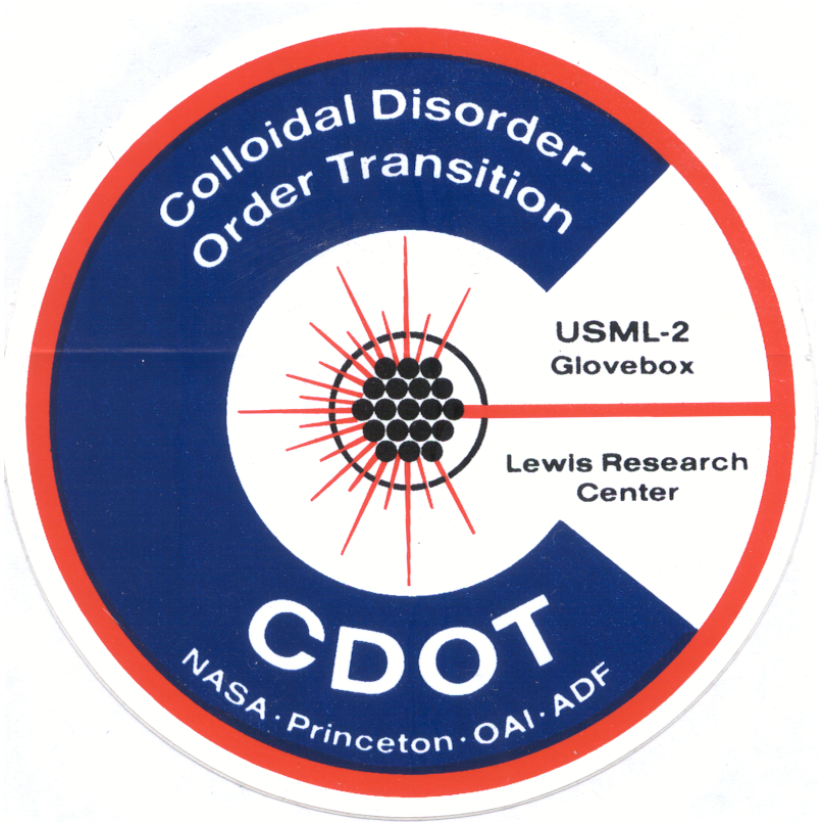
Executive Summary:

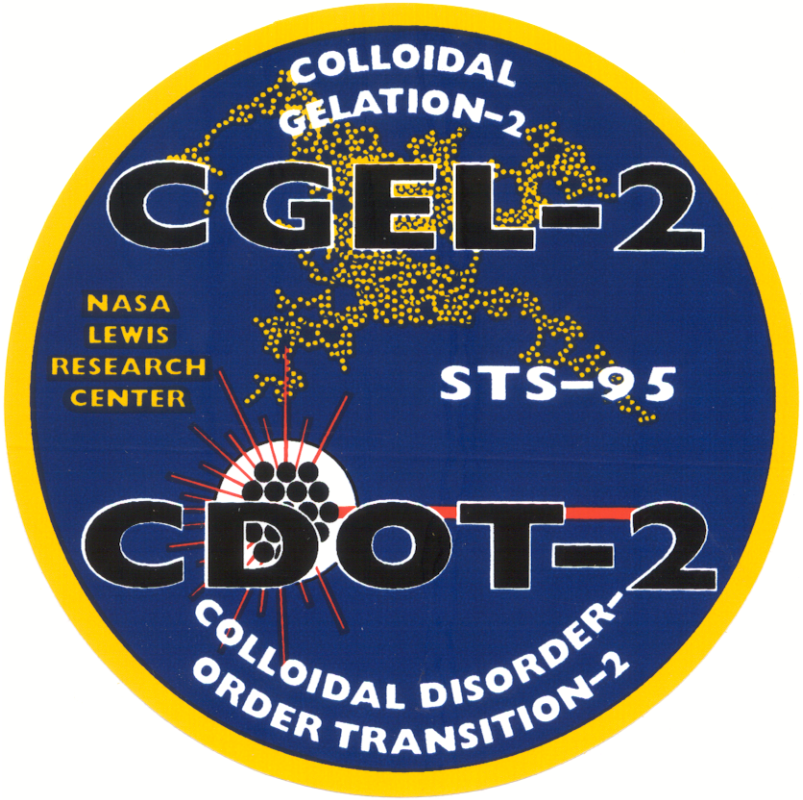
- Ellipsoids, Cubes, DNA functionalized particles, Lock and Key particles, 2-3-4 particle clusters
- Order-disorder phase diagrams
- Exotic Phases - Cubatic, Rotator, Quasicrystal, Soft rotation mode glass, Colloidal polymer w&w/o branching
- Self-assembly - Crystals designed from specific DNA mediated interactions, Assembly of dissimilar particles with Lock & Key, Swimmers as active mixers and superdepletants, Self-replication of sequenced colloidal seeds

Self-thermophoretic swimmers from Lock and Key particles

Light activated

Early Experiments - Hard Spheres


Colloidal Disorder-
Order Transition
USML-2
Glovebox
Lewis Research
Center
CDOT
NASA · Princeton · OAI · ADF


COLLOIDAL
GELATION-2
CGEL-2
NASA
LEWIS
RESEARCH
CENTER
STS-95
CDOT-2
COLLOIDAL DISORDER-
ORDER TRANSITION-2

Phase Diagram by 1g Experiment

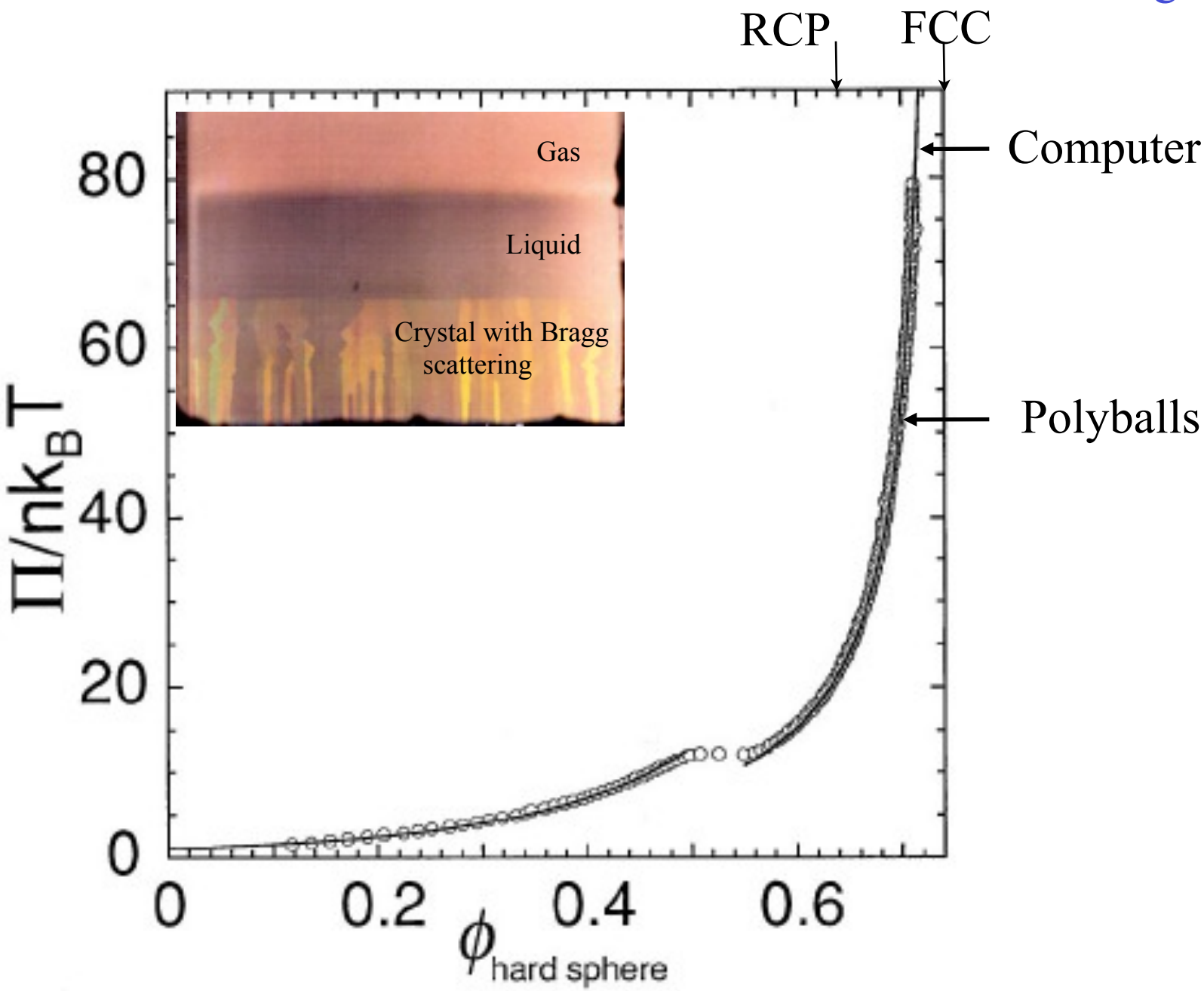
325 *nm* PMMA/decalin/CS2

0.637 0.621 0.595 0.578 0.553 0.528 0.512 0.502 0.478

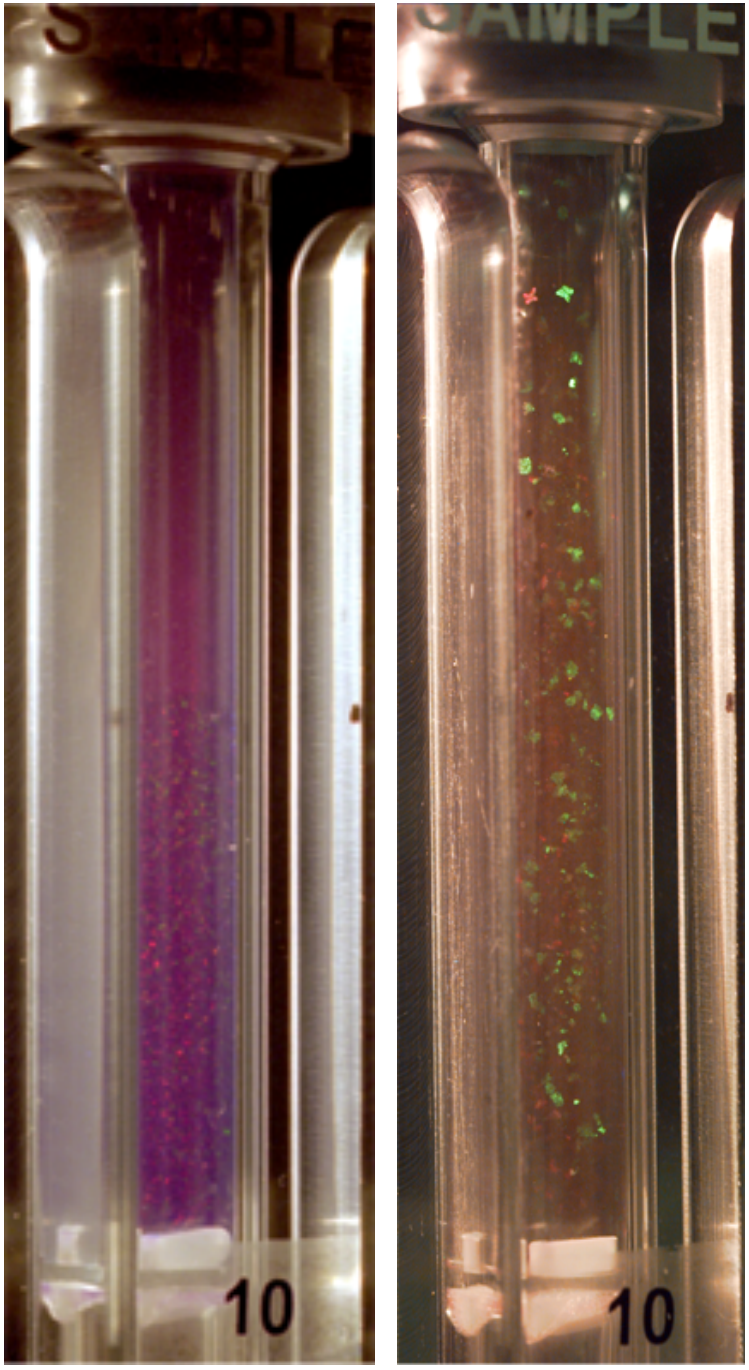
Glass Mainly | Crystal Heterogeneous | Fully crystallized | Coexistence | Liquid

Pusey & van Megen, *Nature, 320 (1986) 340*

M. Rutgers


RCP
FCC
Computer
Polyballs
Gas
Liquid
Crystal with Bragg scattering
80
60
40
20
0
Π/nk_BT
0
0.2
0.4
0.6
$\phi_{\text{hard sphere}}$

Gravity:
Sediment
Profile



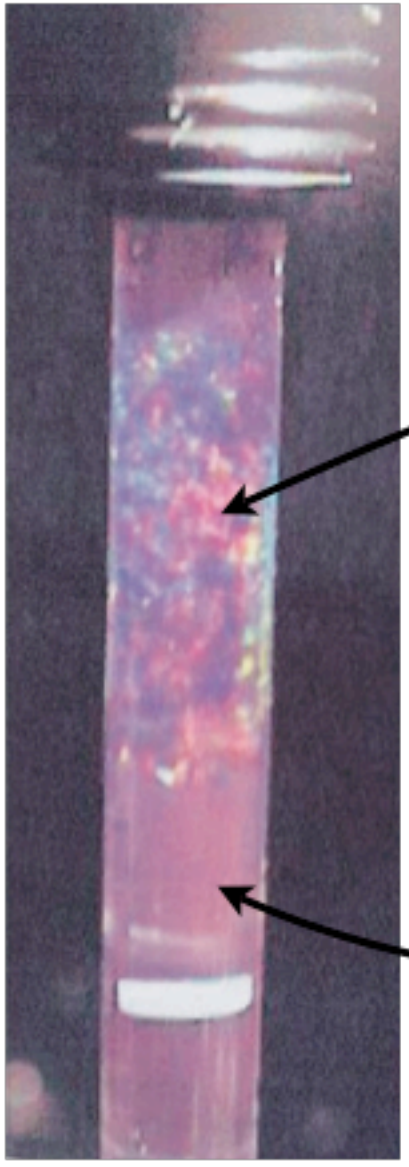
μGravity: no sediment
Dendritic growth

$\phi = 0.504$
508 nm PMMA

J. Zhu, Nature
387, 883-885 (1997)

“Hard Sphere” Colloidal Sample

60% volume fraction

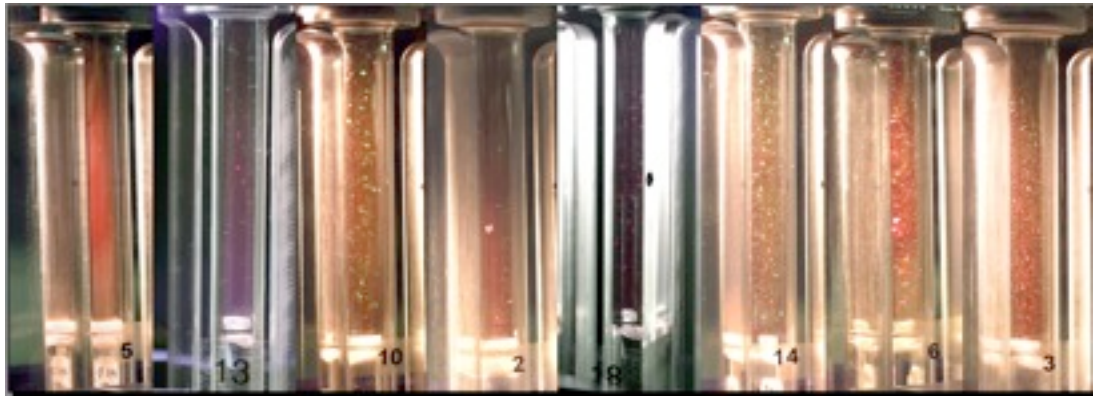


Crystallized in microgravity in space

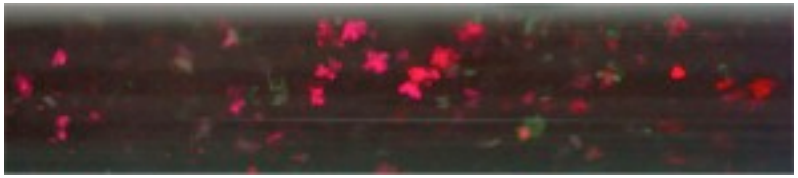
Remelted in gravity forms “glass phase”

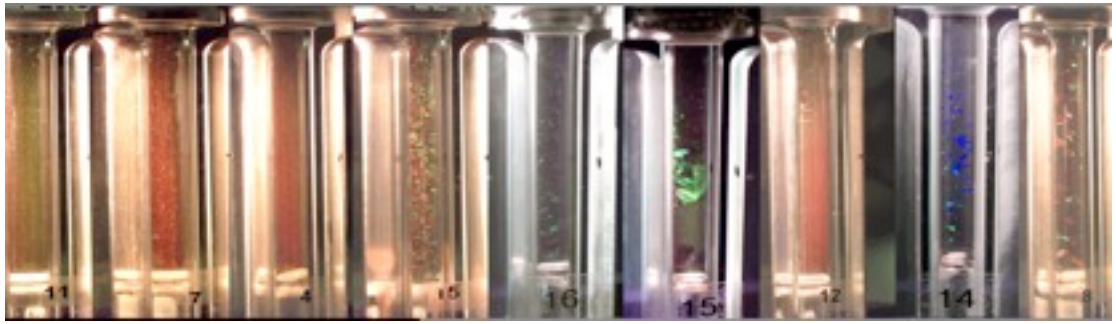
remains glass after ~ 1 year

CDOT 1998



0.50 0.502 0.504 0.512 0.516 0.518 0.524 0.537

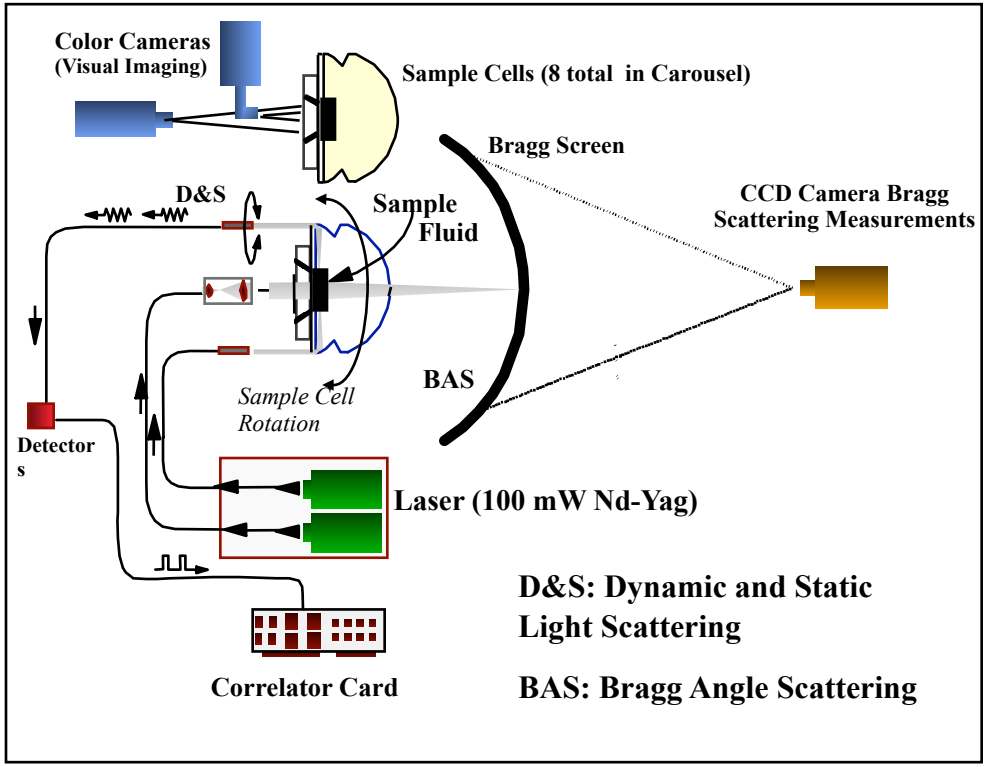


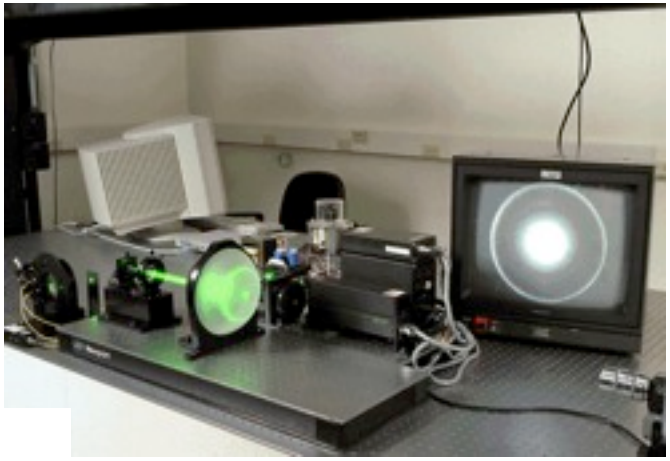


0.547 0.549 0.561 0.591 0.605 0.618 0.619 0.633 0.634

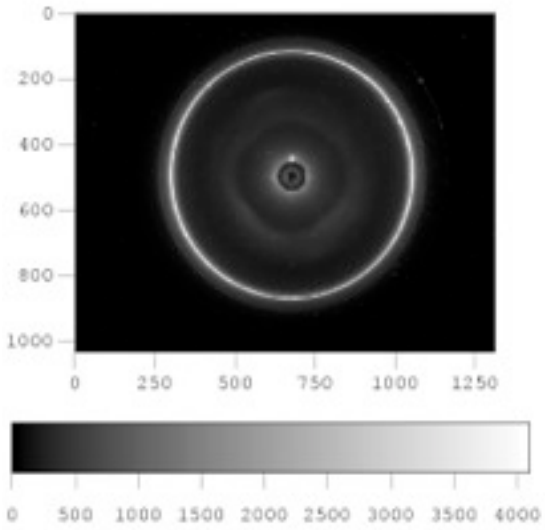
PHaSE
The Physics
of Hard Spheres
Experiment
PHYSICS OF HARD SPHERES EXPERIMENT
PHASE
NASA LaRC - NYMA - ADF - PRINCETON
NASA
nyma
ADF
PrincetonUniversity

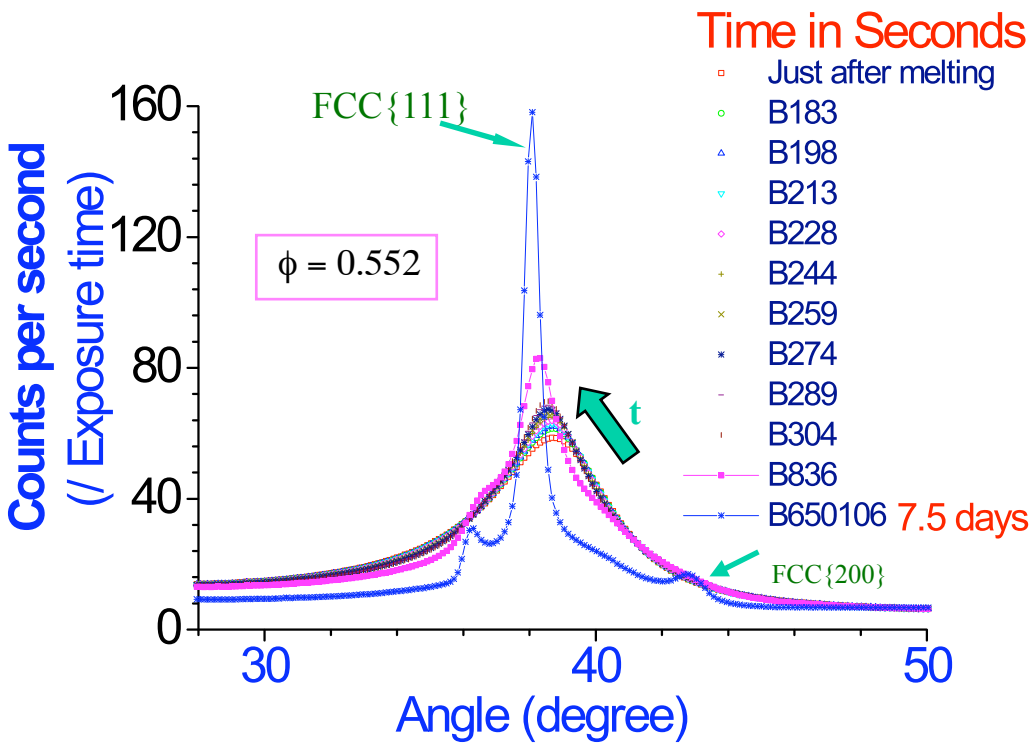
PHASE hardware



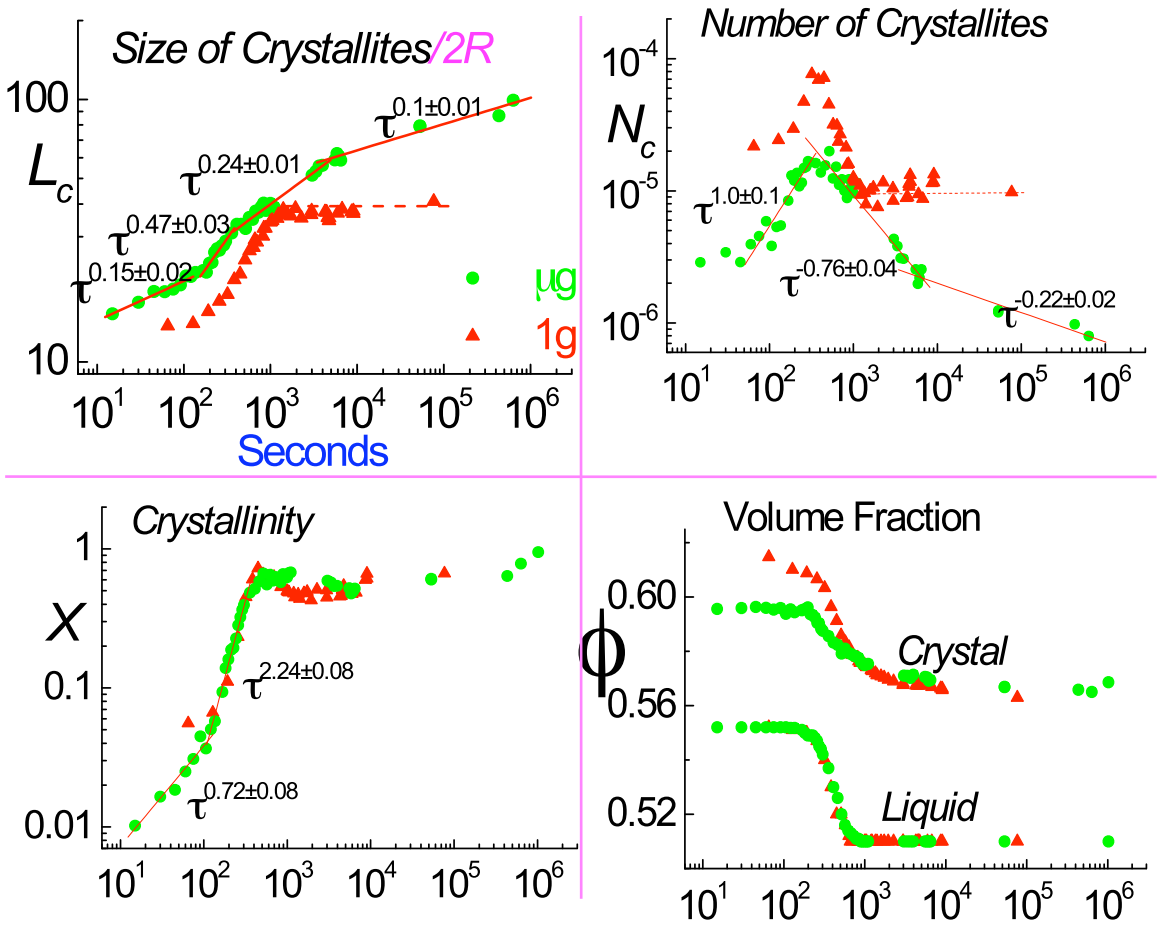


Bragg Scattering





Fully crystallized Sample $\phi = 0.552$



- Compressed and Expanding lattice : Gibbs-Thompson effect
- Nucleation at constant rate
- Growth : (1) diffusion limited < 300s
  (2) intermediate stage
  (3) coarsening non-classically
- Effect of gravity : (1) more small crystal,
  (2) suppress coarsening

Ground based experiments
- Packing anisotropic particles

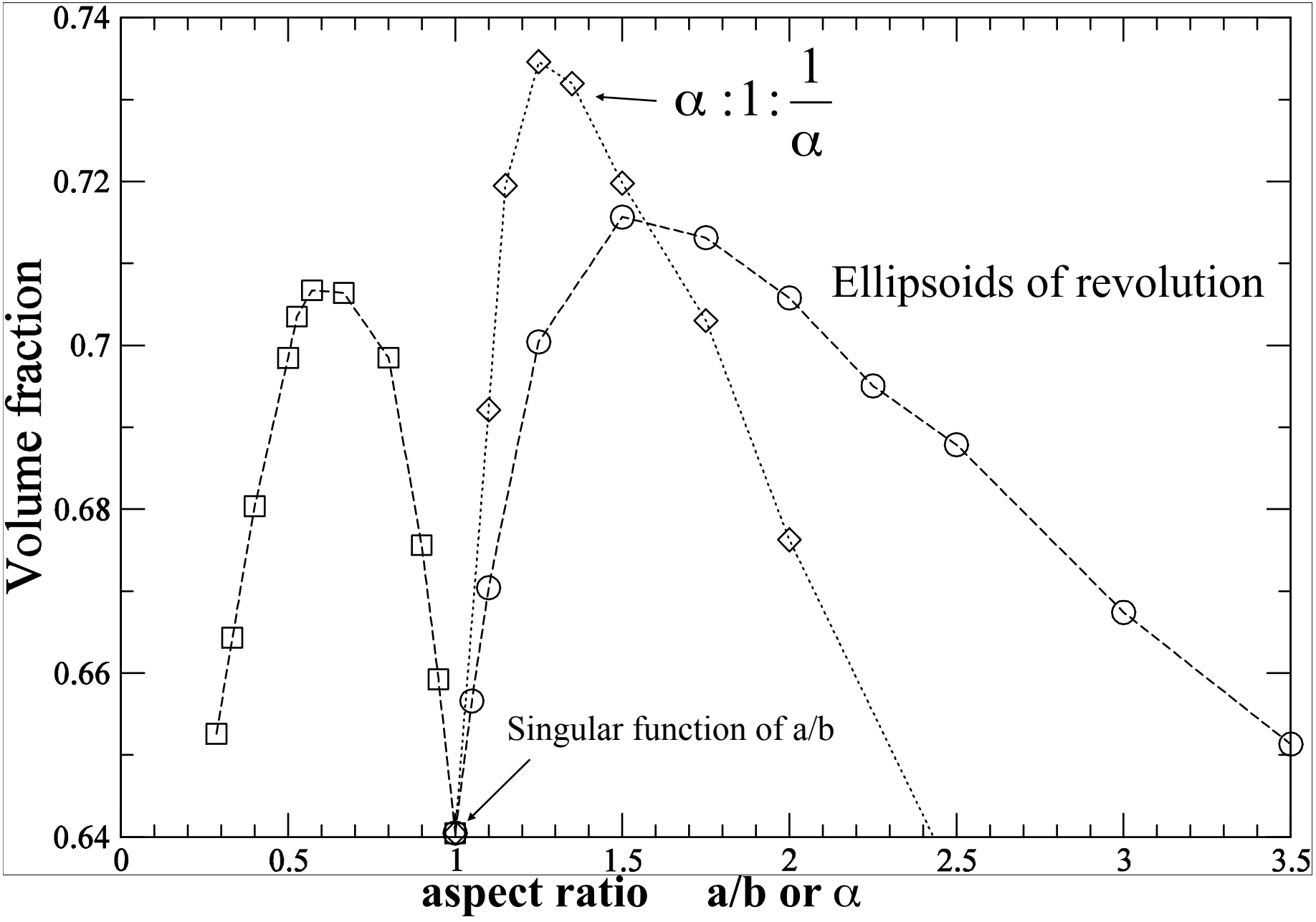
Evan Variano

Which Packs Denser?

$\phi = 0.64$

$\phi = 0.69$

~28,000 m&m's® minis


0.74
0.72
0.7
0.68
0.66
0.64
Volume fraction
0
0.5
1
1.5
2
2.5
3
3.5
aspect ratio a/b or α
α : 1 : 1/α
Ellipsoids of revolution
Singular function of a/b

Stereolithography for 1.25:1:0.8 ellipsoids

Does anything pack better random than crystal?

Ellipsoids

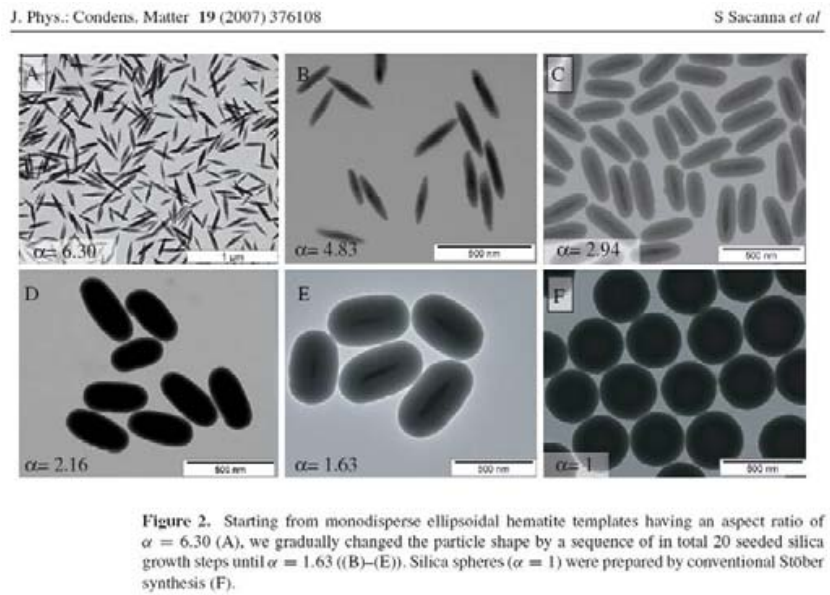


Fig. 8. Hematite-coated silica particles prepared by Dr. Stefano Sacanna (Utrecht University, now at NYU).

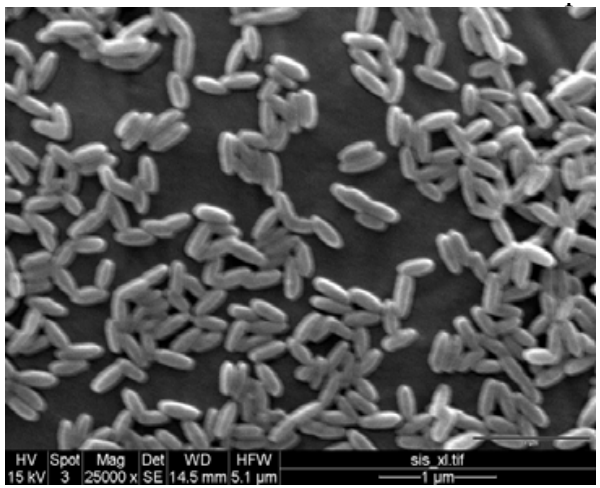


Fig. 9. Hollow silica particles prepared by A.D.Hollingsworth (NYU). The ave. long axis dimension is 380 nm.

Packing, tiling, and covering with tetrahedra

71.7% ?

J. H. Conway* and S. Torquato†‡

*Department of Mathematics and †Department of Chemistry, Program in Applied and Computational Mathematics, Princeton Institute for the Science and Technology of Materials (PRISM), and Princeton Center for Theoretical Physics, Princeton University, Princeton, NJ 08544

Edited by Robion C. Kirby, University of California, Berkeley, CA, and approved May 24, 2006 (received for review March 2, 2006)

It is well known that three-dimensional Euclidean space cannot be tiled by regular tetrahedra. But how well can we do? In this work, we give several constructions that may answer the various senses of this question. In so doing, we provide some solutions to packing, tiling, and covering problems of tetrahedra. Our results suggest that the regular tetrahedron may not be able to pack as densely as the sphere, which would contradict a conjecture of Ulam. The regular tetrahedron might even be the convex body having the smallest possible packing density.

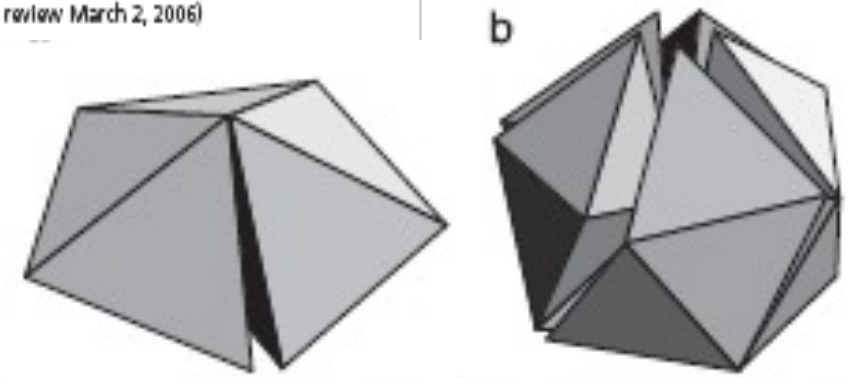


Fig. 1. Certain arrangements of tetrahedra. (a) Five regular tetrahedra about a shared edge. The angle of the gap is 7.36°. (b) Twenty regular tetrahedra about a shared vertex. The gaps amount to 1.54 steradians.

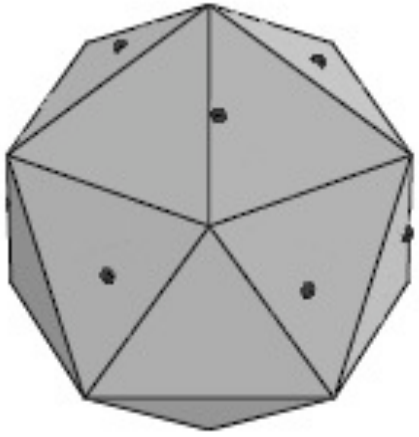


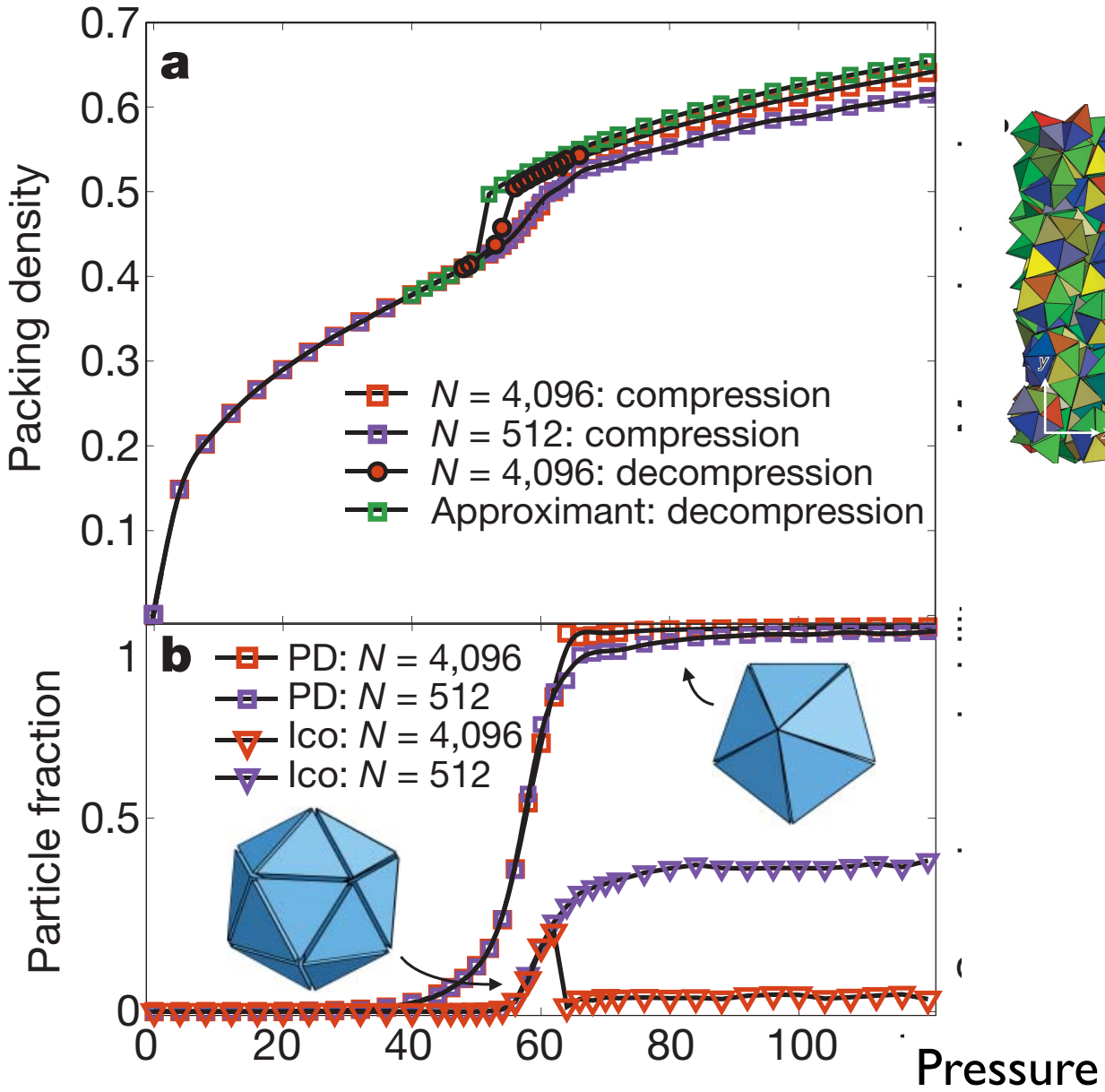
Fig. 7. For Betke and Henk's displaced Scottish packing of icosahedra, the number of contact spots increases to 12. It has density $\Delta = 83.63574\ldots$ % and leads to the displaced Scottish regulars that have density $\Delta = 71.65598\ldots$ %.

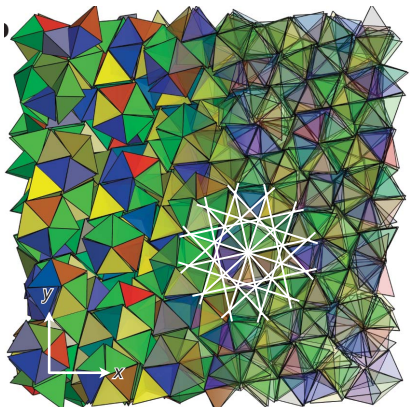
Welsh regulars also fail to be optimal, because these tetrahedra fall into "clumps" of 17, and each clump touches others only at four points. If we replace these points by universal joints, the resulting structure is not rigid, and suitable displacements increase density. One such displaced Welsh packing has density $\Delta = 71.7455\%$, the highest we have yet explicitly achieved. It is obtained by rotating the clumps alternately through ± 0.1131 radians about their vertical (dyad) axes. Before this rotation, each low tetrahedron is hinged as far as possible about the edge it shares with a high one, either "centrifugally" outwards if that edge is horizontal and otherwise in the "lagging" direction (thus, each low tetrahedron goes to the place it would if the displacement of the other tetrahedra were impulsive). Again, still denser reformed Welsh packings might be obtainable by allowing individual tetrahedra to move more freely.

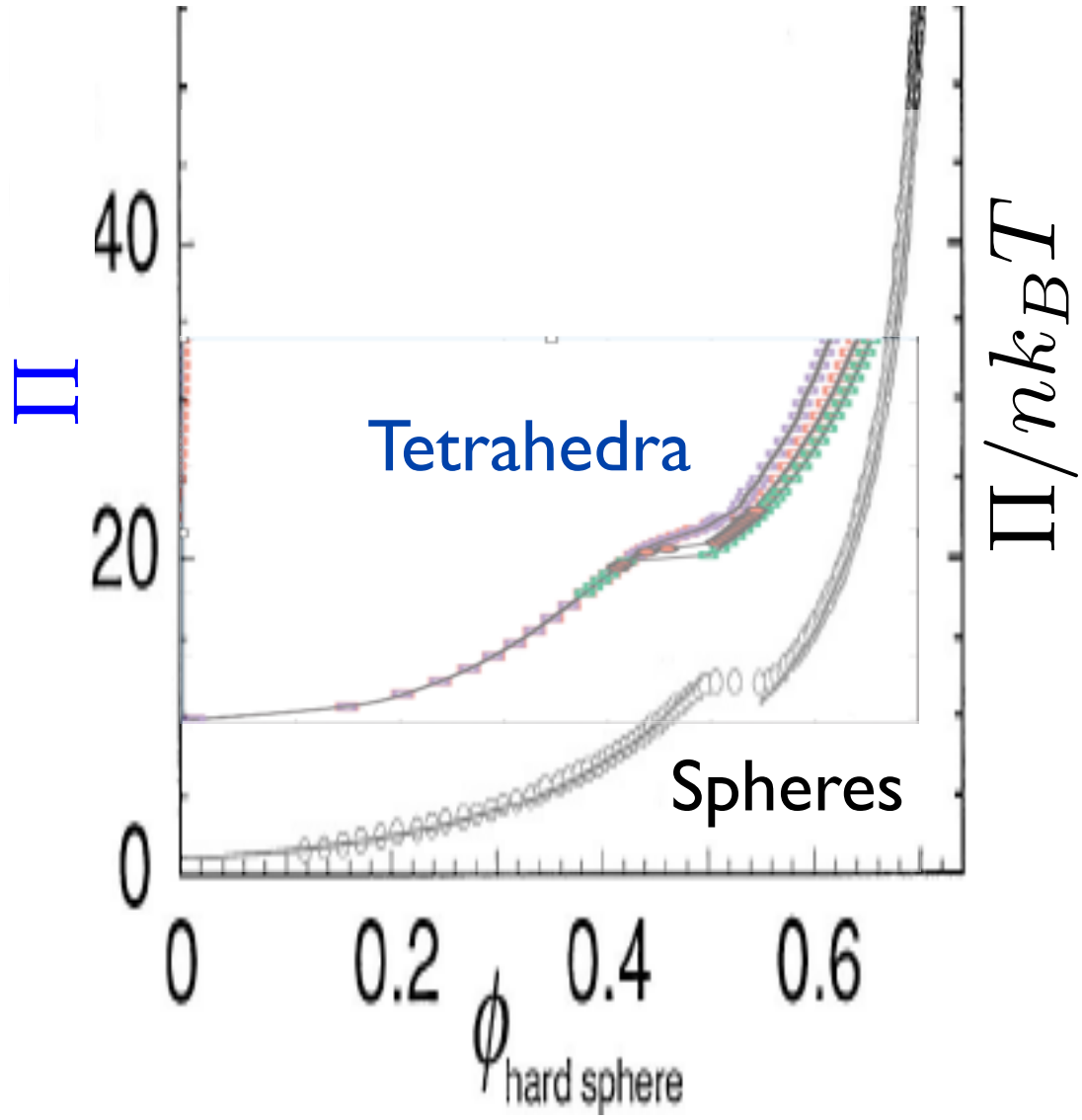
Densest packing of Tetrahedra (Lattice packing 37%)

2006 -71.7%	**ordered**	**Conway andTorquato**
2007 - 74-76%	**random**	**Jaoshvili and Chaikin**
2007 - 75%	**random**	**Torquato**
2008 - 78.2%	**ordered**	**Chen**
2009 - 78.2+	**not ordered**	**Torquato**
2009 - 85	**quasicrystal**	**Glotzer**
2010 - 85.6	**crystal**	**Kallus, Eltzer, Torquato, Chen, Glotzer**

Sharon Glotzer
found that tetrahedra crystallize into a quasicrystal

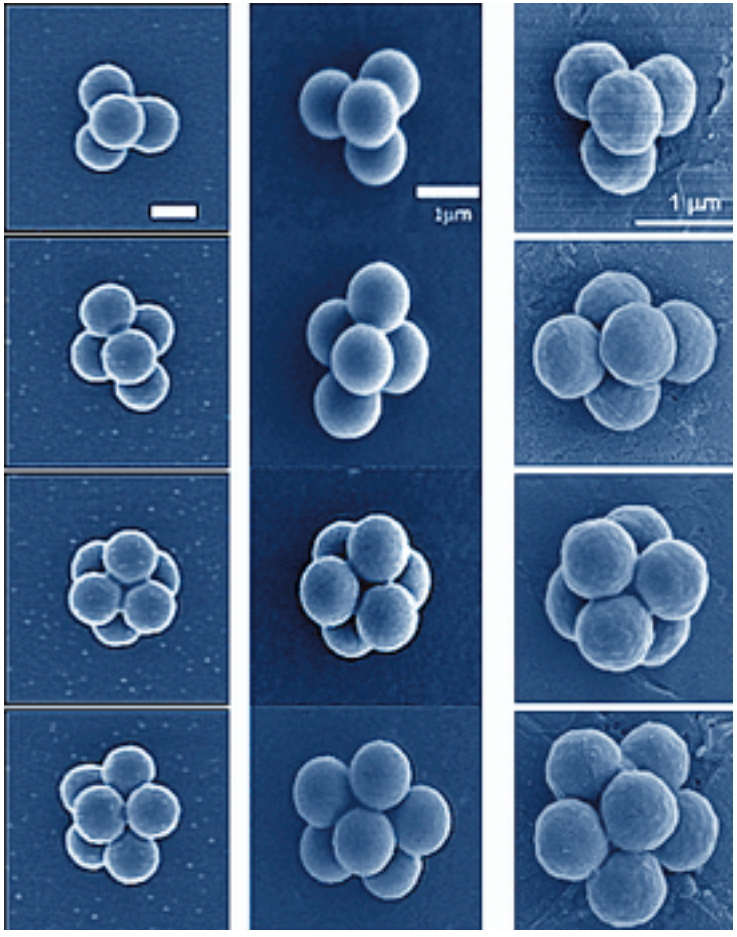





Π
40
20
0
Tetrahedra
Spheres
0
0.2
0.4
0.6
$\phi_{\text{hard sphere}}$
Π/nk_BT

Pine's colloidal clusters

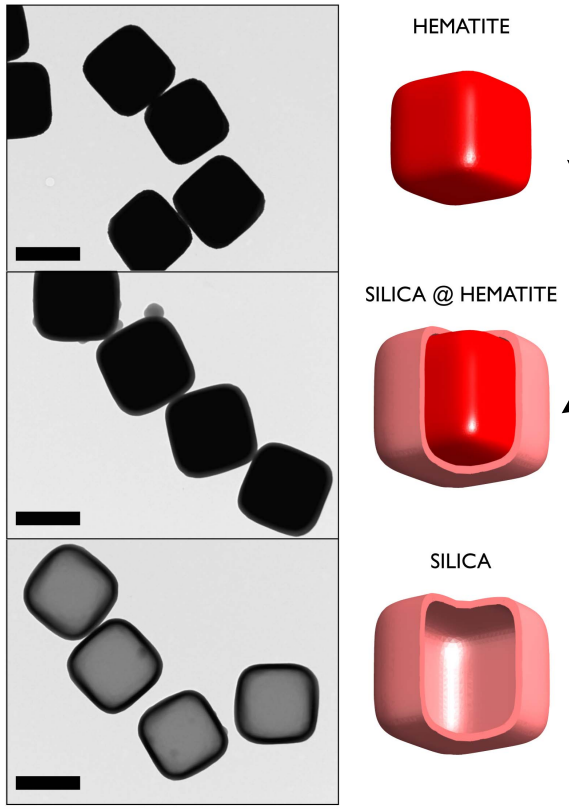
PMMA Silica PS



Cubes !

$$a \sim 1.4\mu$$

Laura Rossi, Stefano Sacanna,
William T. M. Irvine
Paul M. Chaikin, David J. Pine,
Albert P. Philipse



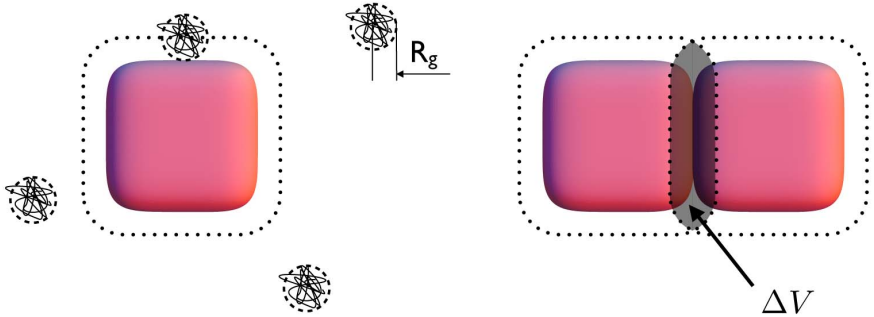
magnetic but

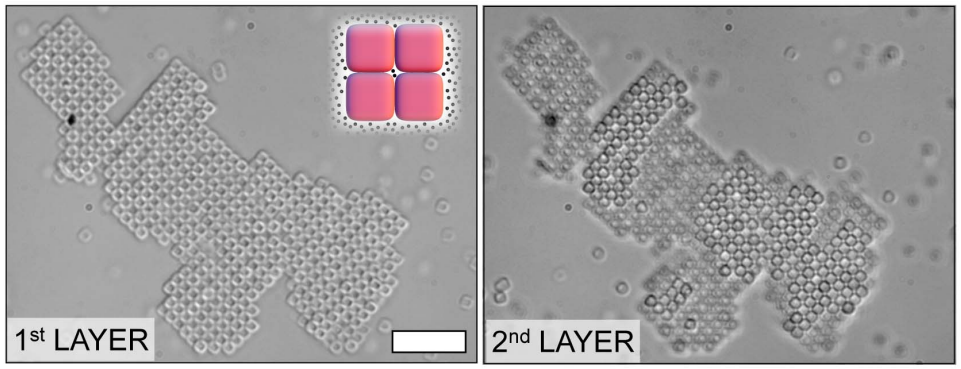
$$h_{grav} \sim 0.1\mu$$

$$h_{grav} \sim 1\mu$$

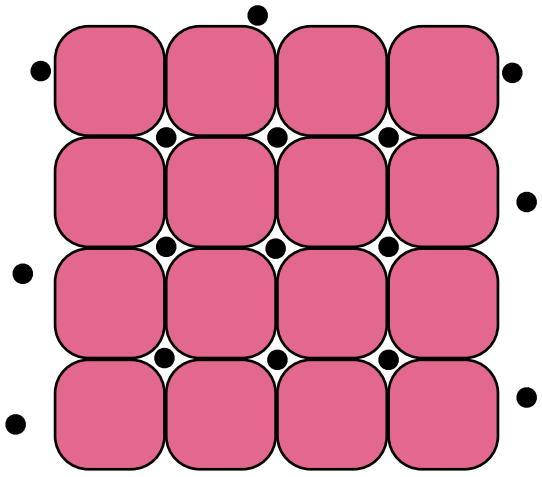
Figure 1: **Silica cubes synthesis.** Left: transmission electron micrograph (TEM) images of bare hematite (α-Fe_2O_3) cubes (**a**), covered with a amorphous silica (**b**) and dissolved by acid yielding hollow silica cubes (**c**), with a total cube length of 1338 nm and a silica shell thickness of 100 nm. Scale bars are 1μm. Cubes are very uniform in shape and size, with a typical size polydispersity of 3%. Right: cubes have rounded edges and can be modelled as super-ellipsoids with semi-major axis lengths a = b = c and shape parameter m = (for William to add) See Ref. [15] and Supplementary Image X.

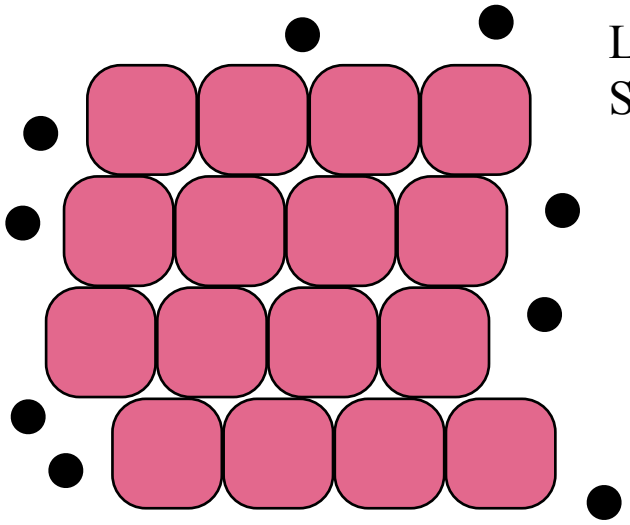
Crystallize by depletion



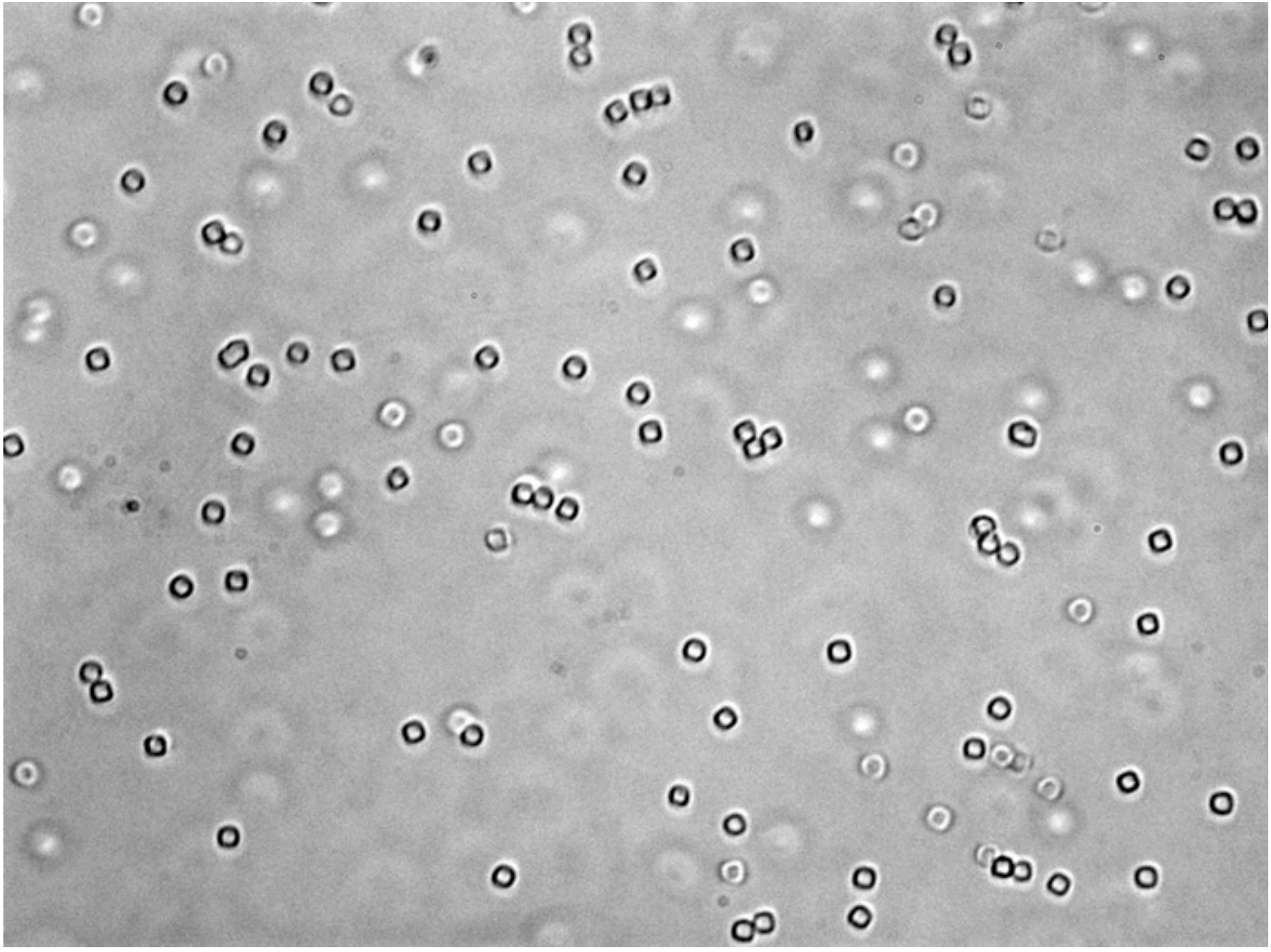


Small depletants lock
Cubic Phase

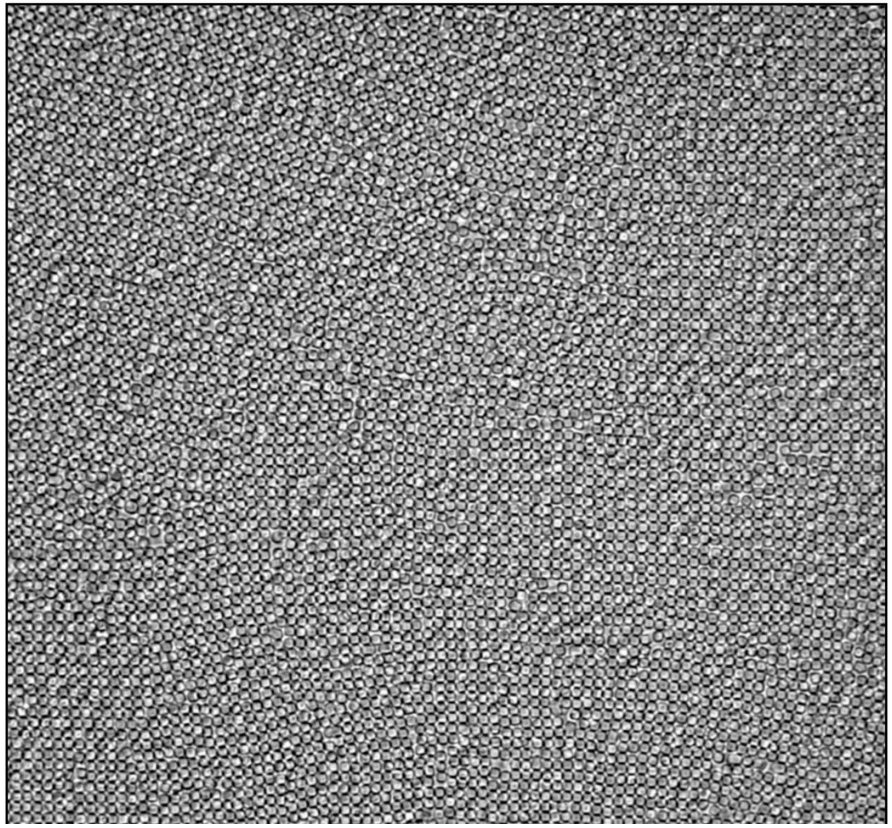


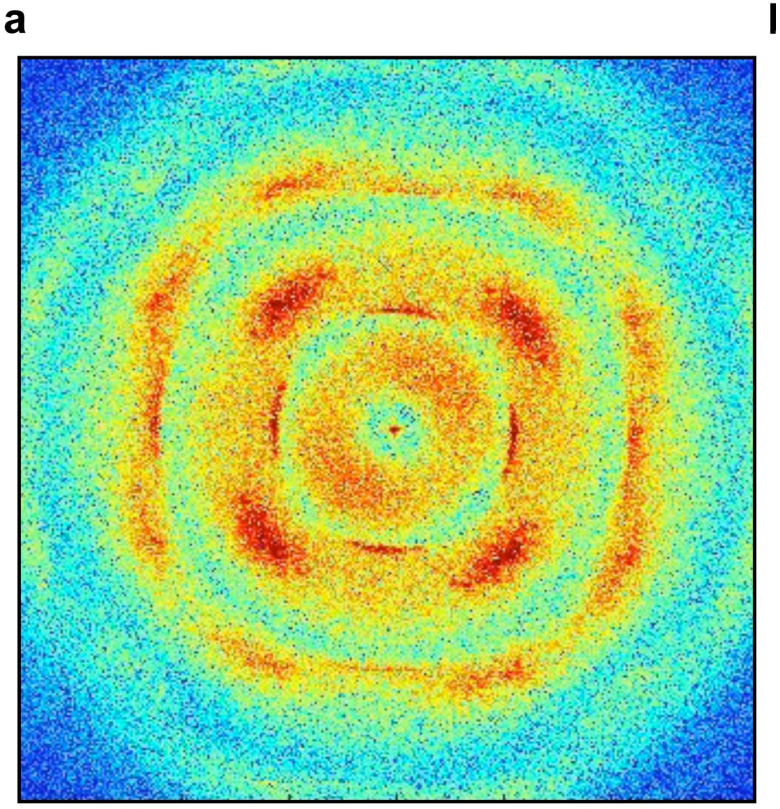


Large depletants
Sliding Phase



Cubatic ??



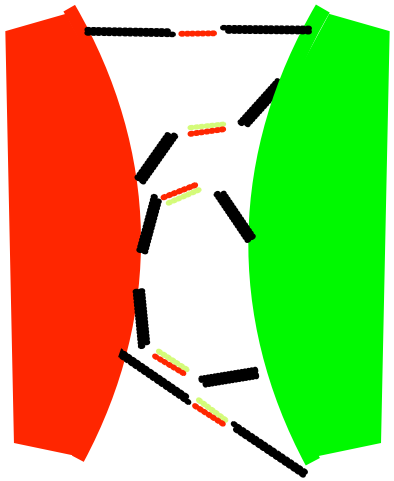


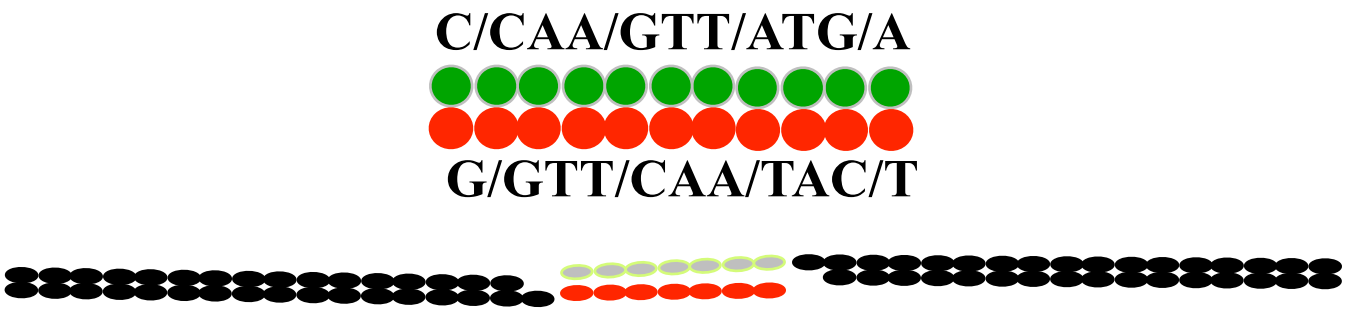
Only two levels because
gravitational height ~ particle height

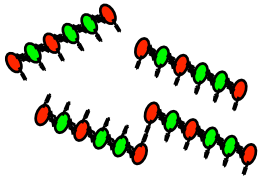
Ground Based
- Specific Reversable interactions

We want specificity, control and reversibility in interactions

Specific Interactions with DNA





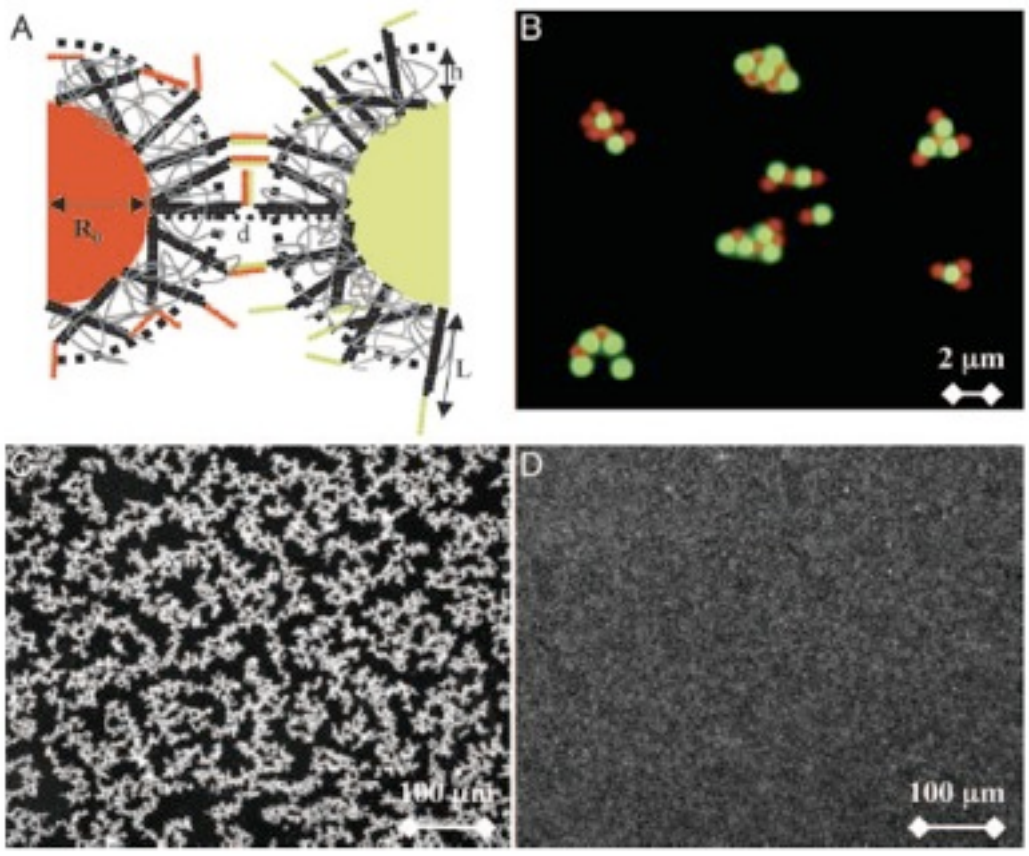


PNAS | March 22, 2005 | vol. 102 | no. 12 | 4225–4229

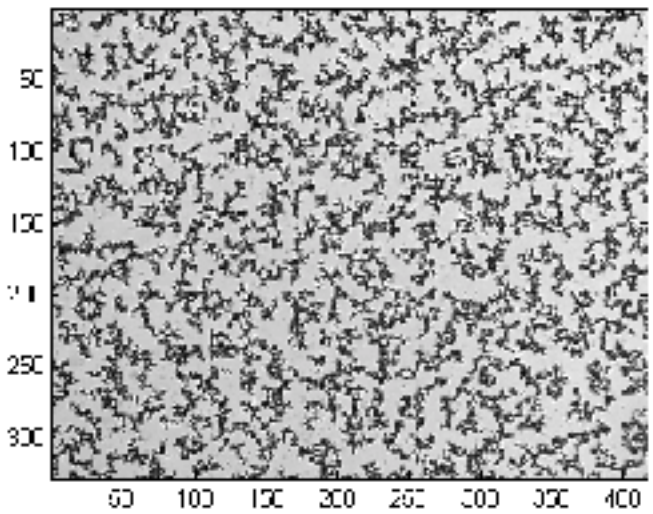
Reversible self-assembly and directed assembly of DNA-linked micrometer-sized colloids

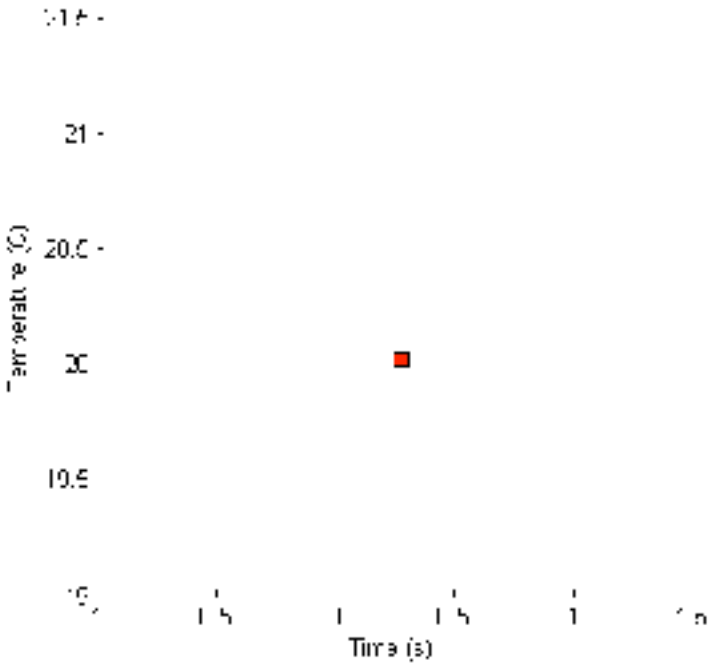
Marie-Pierre Valignat*, Olivier Theodoly†, John C. Crocker‡, William B. Russel§, and Paul M. Chaikin*¶

Departments of *Physics and §Chemical Engineering, Princeton University, Princeton, NJ 08544; †Complex Fluids Laboratory, Unité Mixte de Recherche 166 Centre National de la Recherche Scientifique/Rhodia, CN 7500, Cranbury, NJ 08512; and ‡Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104



Aggregation, reversibility and kinetics

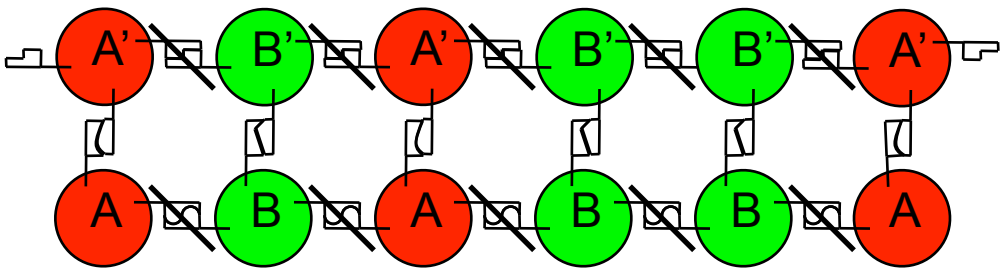




Basic Replication Scheme

assembly
of complementary
daughter

Seed



exposure to UV

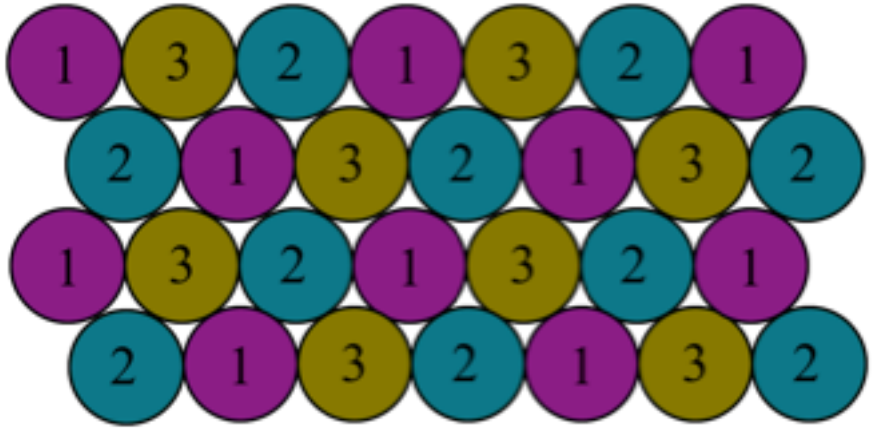
raise T
above Tmelt

With multiple specific interactions can force structures

Arkus and Brenner - say any structure

Duplex particles bind in triangles

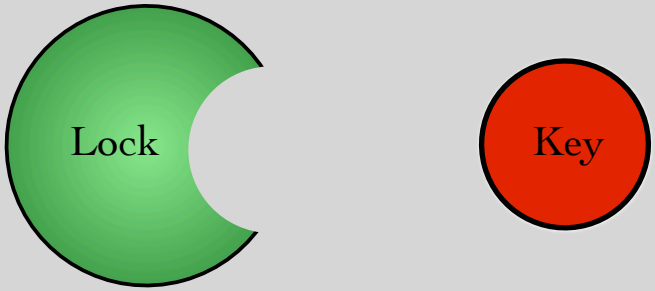
Other pairings don't bind



If you're going to assemble stuff with different density need micro-g

Suppose we want specific reversible interactions without using DNA:

Lock & Key Colloids

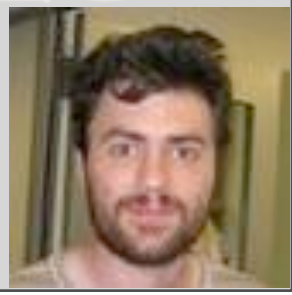


Pac-Man Particles

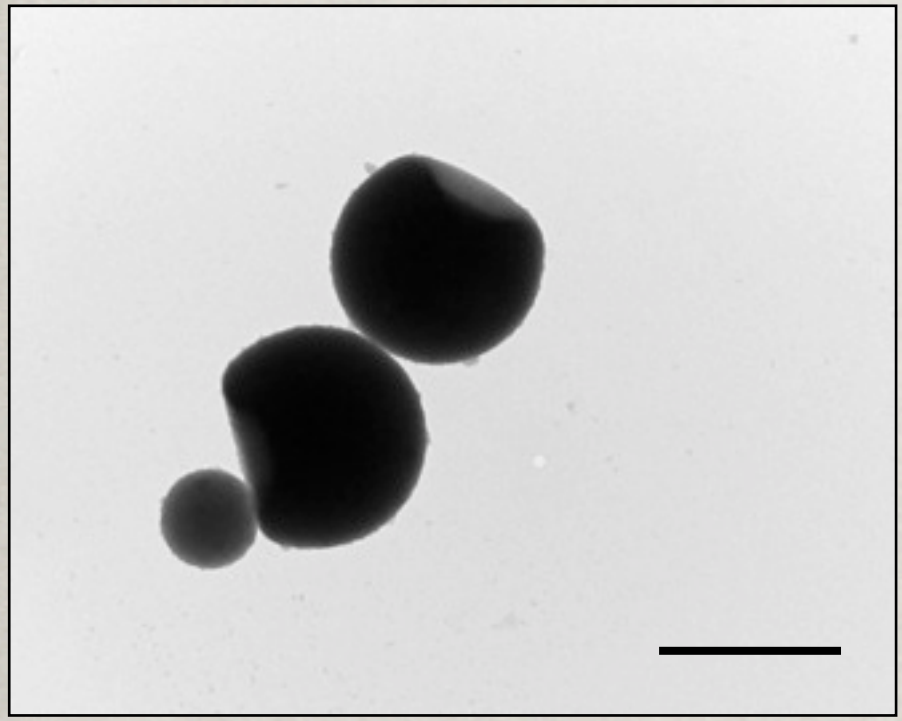
Dave Pine

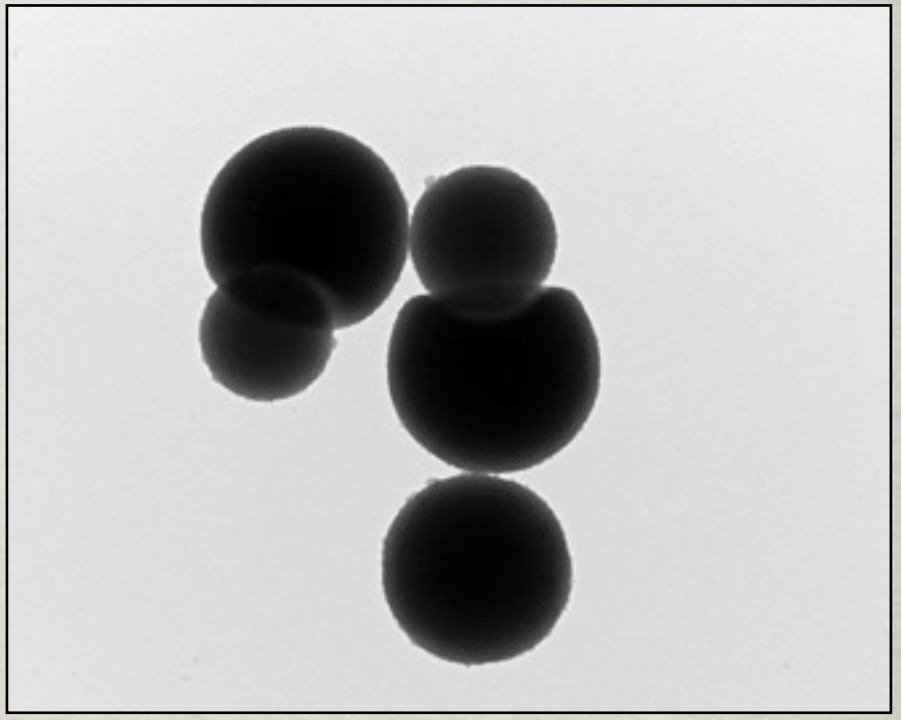
Stefano Sacanna

William Irvine

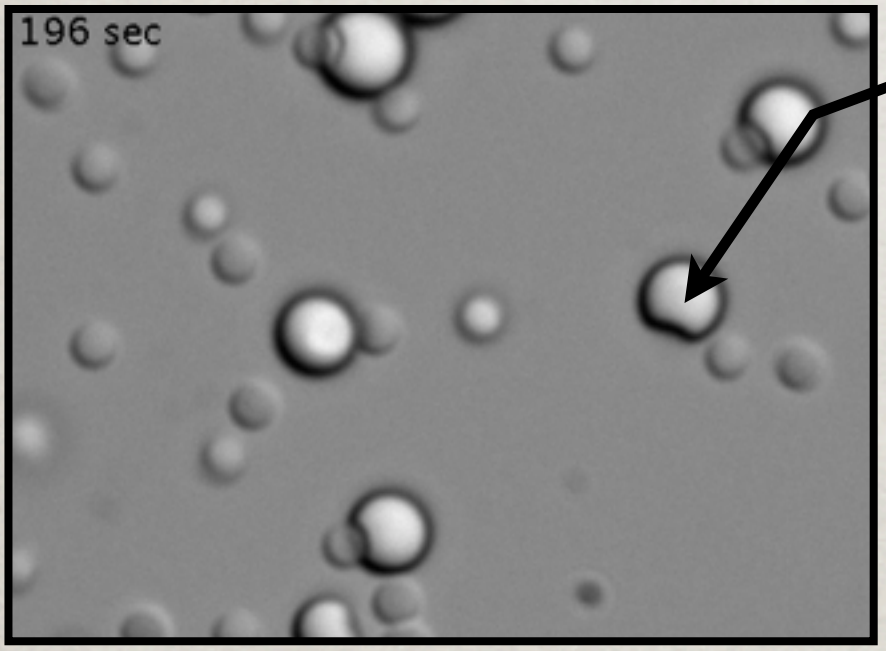


TEM

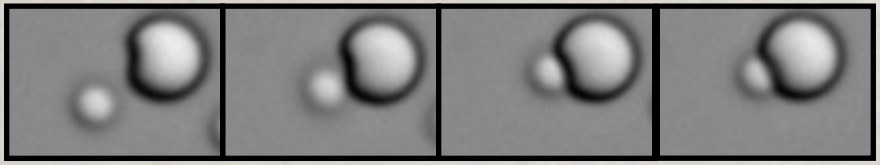


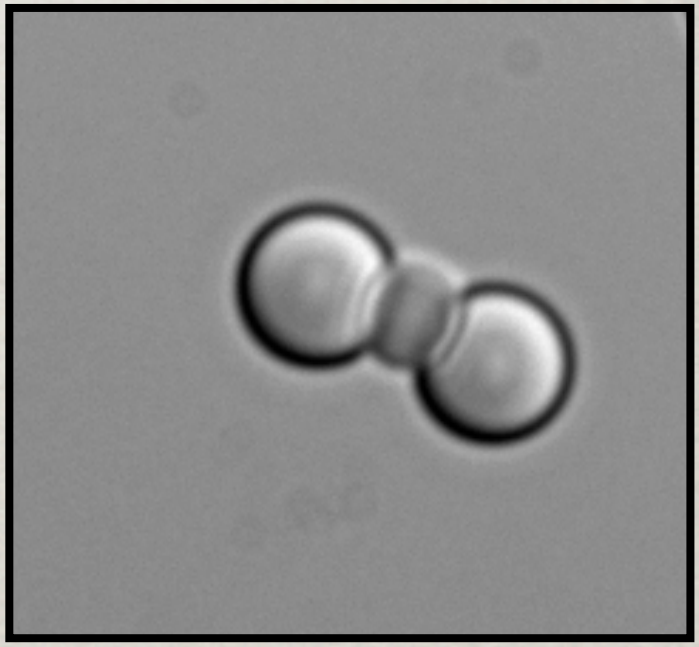


PacMan Depletion Movies



Watch this pac-man

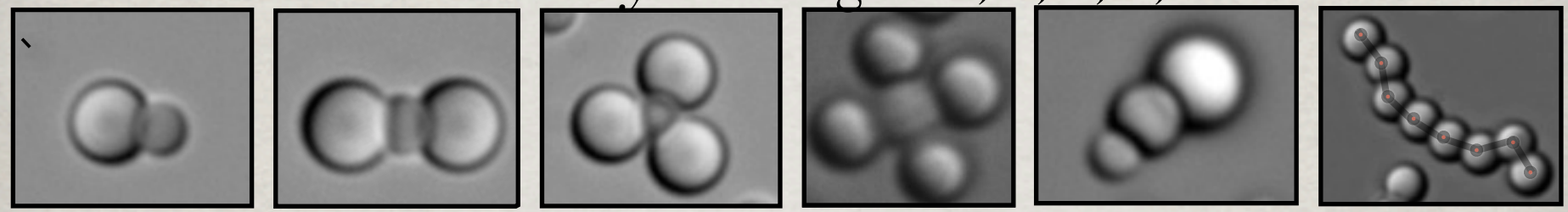


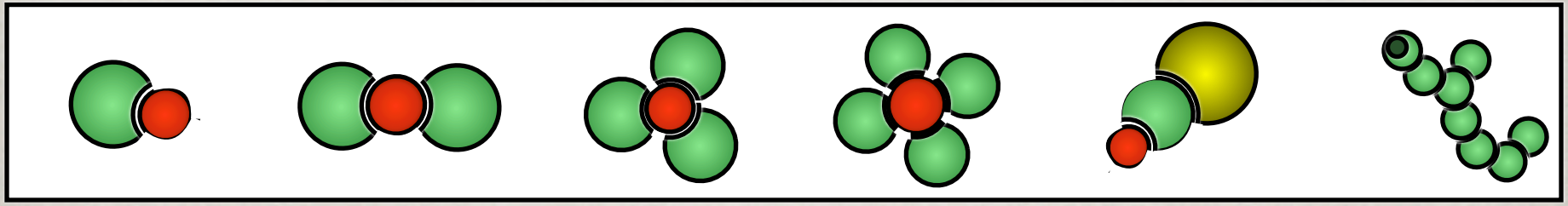


Nature 464, 575 (2010)

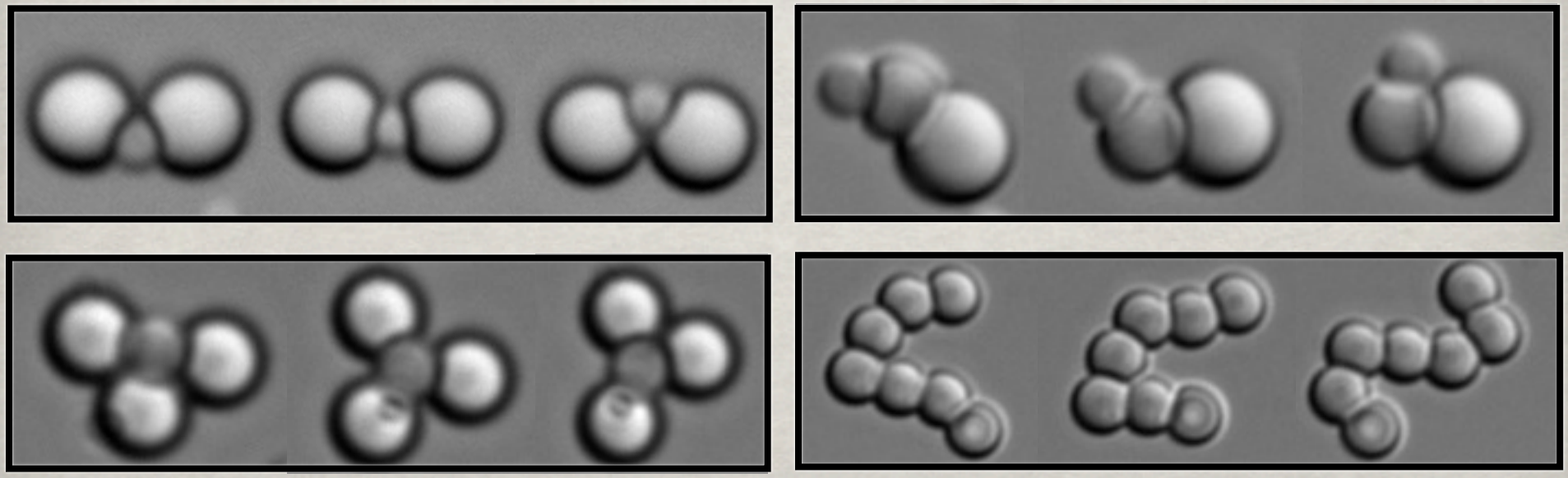
An orgy of colloidal couplings

Locks & keys: ménage à 1, 2, 3, 4, ...





Polymers with flexible bonds

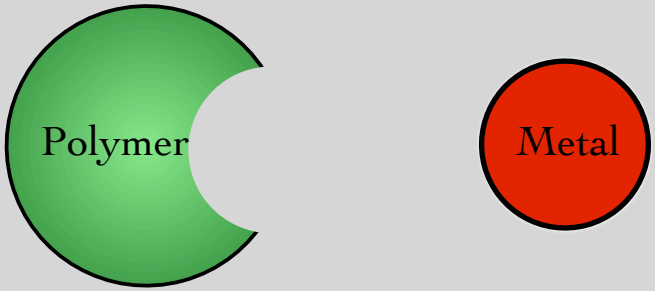


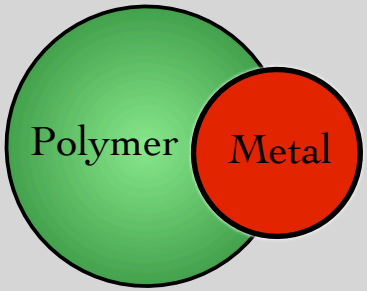
So far, only recreational sex ... babies next year?

Lock & Key Colloids

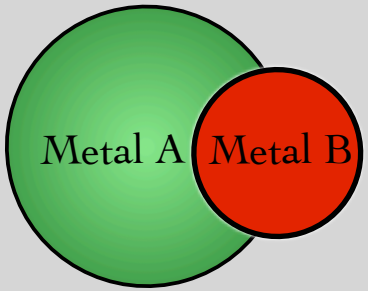
Why μg?

Two or more different materials

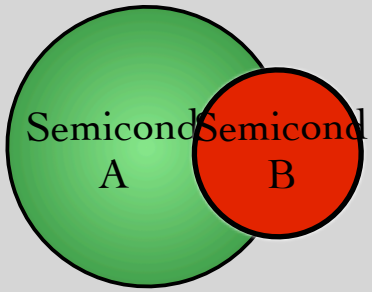




Microswimmer

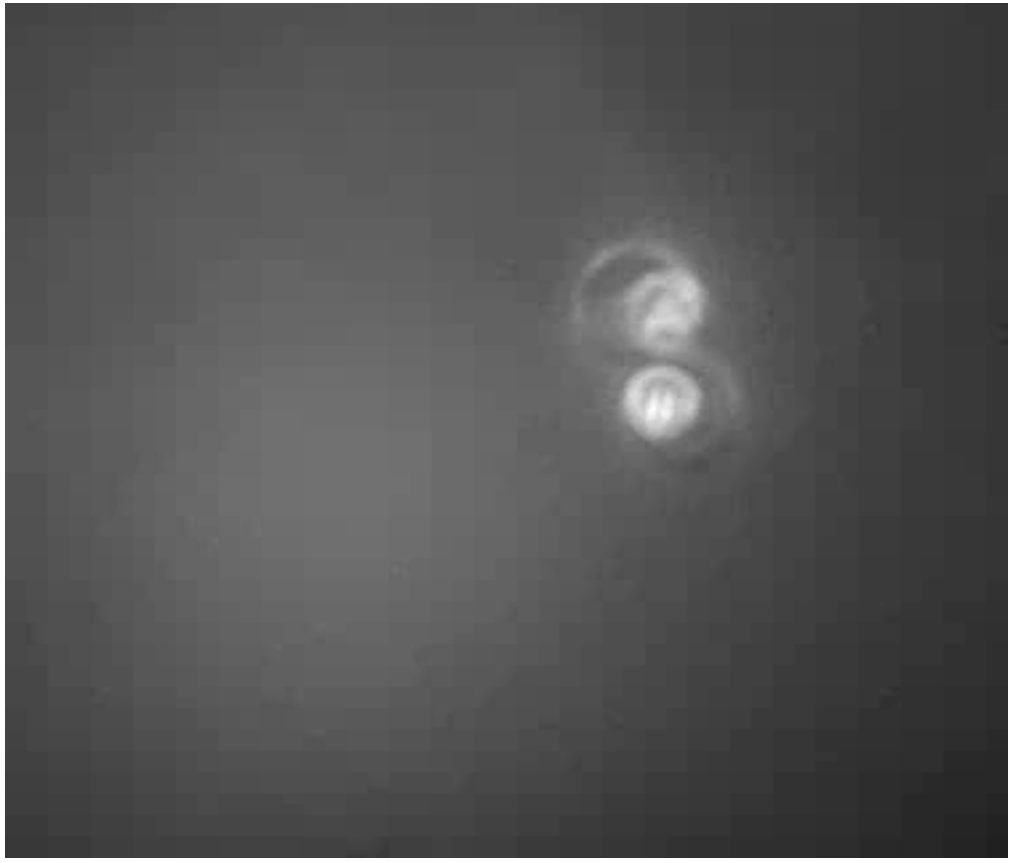


Microbattery



Microphotocell

Phoretic Swimmers
Pacmen with dark inserts



Self - Thermophoresis -- put in Light they swim

Proposed Experiments

Hardware

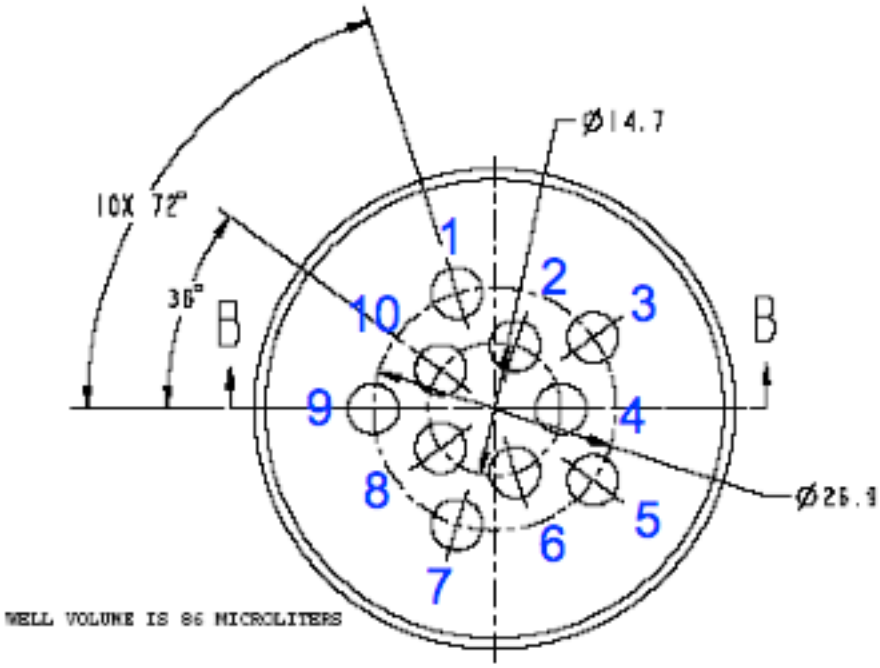


Fig.1: ACE sample cell base: microwell designation

Note: wells no. 11 and no. 12 are not shown in Figure 1 as they may not be realized for ACE1a or ACE1b.

Require/suggest sample cell loaded or loading supervised by PI's

5.9 Science Requirements Summary Table

Note: A schematic is shown in the next section. Any "descoping" must be done by creative solutions to problems rather than simply not meeting the requirements.

Parameter
Section
Requirement

Sample description

5.1, 4.1

- Samples (compositions)

- Hollow silica ellipsoids and cubes in ethanol or an index matching fluid mixture, *e.g.*, dimethylsulfoxide (DMSO), majority, and tetrahydrofurfuryl alcohol (THFA), minority. Some of these colloids may contain their 'template cores' of hematite (α-Fe_2O_3). Poly(*N*-isopropylacrylamide) microgel particles, also known as pNIPAM, silica (*e.g.*, Ludox colloidal silica), and iron oxides (*e.g.*, magnetite, hematite) may be used as a depletant. Lithium nitrate ($LiNO_3$) will be added to the suspending medium to screen electrostatic charges.
- Self recognition particle systems with complementary geometries, *e.g.*, "Pac-man particles" and spheres in aqueous media; "lock" = organosilica polymer*, "key" = silica, polystyrene, poly(methyl methacrylate), or hematite ellipsoids (silica-coated or uncoated); depletant = pNIPAM, Ludox, or iron oxides.
- Self replication particle systems, *e.g.*, PS-DNA spheres in phosphate buffer solutions (aqueous). 2 micron diameter polystyrene particles suspended in 10 mM phosphate buffered saline solution (50 mM NaCl) plus 0.1% surfactant (Pluronic F-127).
- Poly(methyl methacrylate)–*g*–poly(hydroxystearic acid) (PMMA-PHS) spheres and clusters (dimers, trimers, tetramers, *etc.*) in an index matching mixture of 45% decahydronaphthalene (decalin) and 55% tetrahydronaphthalene (tetralin).

*monomer = *3*-methacryloxypropyl trimethoxysilane

- Particle size

- Diameters between 0.1 μm and 15 μm.
- Index of refraction

- Varies between 1.33 and 1.6.
- Some samples will be absorbing, having an imaginary component to the index of refraction.
- Some samples will be metallic, having a negative real part of the dielectric function.
- Some fluorescent samples will not be index matched.

- Volume fractions

- Between 0.001 and 0.63.

- ☒ Mixing

- ☒ Each sample should have a small magnetic stir bar or deburred wire for mixing. For **ACE-1a** experiments, the stirrer will include a permanent magnet that can be used to manually manipulate the stir bar contained within the microwell. The magnet is mounted in a drill chuck that will be manipulated by an astronaut and this action will homogenize the sample in each microwell. The stir bar will be "parked" out of view, *e.g.*, within the fill port when not being used. We strongly desire no mixing "cross-talk" between adjacent cells.
- ☒ For **ACE-1b**, *in-situ* sample mixing (for samples that are not extremely viscous) will be done with a flight-hardened version of small coils placed below the sample cells (out of the optical path). When a current is applied to the coils, the mix magnet in the near-by sample wells will rotate and move about, homogenizing the sample.

Homogenization

5.2.1
- ☒ Be able to homogenize samples one at a time as discussed above.
- ☒ Simultaneous homogenization and video microscopy (via b/w imaging in epi-illumination at up to 100x or back-lighting with a warm-white LED) to view the sample.

Optical imaging

5.2.2

- Visual camera images

5.2.2
4.2.2

- High magnification, high-resolution b/w visual images of both highly index matched (to 0.001) and fluorescent colloidal particles (nominally 0.5–2.0 µm-sized).
- Field of view ranging from 100 µm x 100 µm up to 6 x 6 mm for standard sample cells.
- For a 0.5 µm-sized particle, particle images that enable calculation of resolution of +/– 20 nm in the *x*-and *y*-directions. All positioning is fully motorized and automated.

- *z*-axis resolution of 100 nm. Positioning is fully motorized and automated.
- Resolution depth up to 100 µm into a single scattering sample.
- Q-Imaging Retiga 1300C camera or comparable, 12-bit monochrome with 15 fps at 1024 x 1280.

B&W live data at lower resolution or color video camera, 8-bit with video rates at least 30 Hz; 500 GB memory storage. Dynamic range of 4096 (Desired: color camera 3 x 8-bits, VGA resolution).

- Capability for some near real time downlink of video images to assist with alignment.

Note that the capabilities that would be needed for imaging the above sample types are: bright field imaging using white light illumination, dark field imaging to view crystal morphology from Bragg scattering (future ACE), DIC and phase contrast to view index matched samples (future ACE).

- Bright field

- Automated bright field imaging. Epi-illumination (metal halide lamp with six fluorescence cubes) and warm-white LED back illumination to view isolated particles of at least 0.5 µm diameter.
- Must provide uniform, broadband lighting.
- Provide investigators with LED light source for pre-launch testing purposes at NYU.

- Dark field

- (future ACE)Required to view crystallite and morphology from Bragg scattering to view isolated particles of at least 0.5 µm diameter.

- DIC and phase contrast

5.2.2.1

- (future ACE)Required to view index matched samples; to view isolated particles of at least 0.5 µm diameter

- Need capability to periodically downlink data.
- Prefer color (a B&W camera can become a color camera with R-G-B liquid crystal color filter).

12-bit dynamic range strongly preferred; 8-bit dynamic range is minimum requirement.
As large a field of view as possible.
Highest resolution possible, 1000 x 1000 min. (signal to noise goes as the square root of the number of pixels).

- White light source for imaging

4.0.1
4.0.2

- (future ACE): Imaging of colloidal particles using Köhler illumination for highest resolution.

- Laser diode

- Requested: Exchange one of the two available white-light LEDs for a low power collimated laser diode with a coherence length of about 3 mm. This, when combined with the existing camera will give real time low-angle static and dynamic light scattering capabilities (without any assumption on the statistical properties of the sample). It may also yield absolute, calibration free estimates of the optical thickness of scattering particles. References: F. Ferri *et al.*, "Heterodyne near-field scattering: A technique for complex fluids," *Phys.Rev.E* **70**, 041405 (2004); Magatti *et al.* "Dynamic heterodyne near field scattering," *Applied Phys. Lett.* **92**, 241101 (2008). Potenza *et al.*, "How to measure the optical thickness of scattering particles from the phase delay of scattered waves: application to turbid samples," *Phys. Rev. Lett.* **105**, 193901 (2010).

- Microscope

- Objective turret, fluorescence turret and condenser turret, field diaphragm and aperture diaphragm motorized and automated.
- Oil coupling with 63x, 100x microscope objective.
- Objective lenses

- Chosen to allow range of field of views, from about 100 m to 2 mm.
- Recommended choice: 10x, 20x, 40x, 50x, 63 x (oil on top), 100x (oil on top). ACE-2 is set to provide a trans-illumination condenser with oil immersion optics capabilities.
- One lens should be 100x with an NA of 1.4.
- Must have appropriate DIC prisms (future ACE).

  NOTE: Choice of lenses should be done to optimize all requirements, and will depend highly on manufacturer of the microscope.

- Tube lenses

- Automatically selectable between 0.5x (Bertrand lens), 1.0x 1.25x, and 1.6x.

- Translation stage

- *x*-y stage positioning to 2.5 m and *z* positioning to 100 nm. All positioning is fully motorized and automated.

All components hardened for spaceflight and radiation certified.

Sample Cell Requirements

Cell
5.3

- Ten-well sample disk, approximately 50 mm diameter, containing 2.5 mm diameter wells at ~2 μL per well. Cover slip is 175 microns thick. Material of construction: fused silica or fused quartz with Teflon plug and solvent resistant perfluoroelastomer (Kalrez) plug. NYU samples will consist of both aqueous and nonaqueous particle suspensions. Some of the proposed solvents, *e.g.*, THFA, are not compatible with Viton fluoroelastomer (swelling, degradation). Each well will contain a metal wire for sample homogenization that can be parked in one of the fill ports, out of the field of view.

Volume

5.3
- About 2 μL per sample well.

Sample holder

- ACE sample holder to accommodate sample disk with multiple ~2 μL wells.
- One sample disk (10 – with the possibility of 12 – NYU wells) for June 2012 launch; second sample disk (10 – with the possibility of 12 – NYU wells) for late 2013.

Sample filling

- Due to the limited amount of samples and high volume fractions required, we would prefer to fill the sample cells and ship them to NASA Glenn (Zin Technologies). If this is not possible, we would like to supervise the sample filling operation.

Atmosphere Requirements

5.4

☒ Normal cabin pressures and temperatures environment is sufficient.

Vibration Control and Measurement

5.5

☒ Averaged over an hour, needs no better than 10^{-3} g of dc g-level. See formula in section 5.5 to answer questions of g-jitter.

Imaging requirements (Image viewability requirements)

5.6

☒ Downlinked color CCD images of the samples are needed just before and after mix/melting, and at various stages during crystallization.

Astronaut Involvement

5.7

☒ minimal– depends on the extent of hardware automation.

Data (Storage) Requirements

5.8

☒ Images should be stored with a record of when the time measurement was made, length of measurement, camera position, temperature for each measurement.
☒ Temperature is to be recorded whenever the rack power is on, and with each image data; any change in temperature by more than 0.5°C should be recorded.
☒ Accelerations in excess of 10^{-3} g should be recorded and time-tagged for comparison with data from the experiment.
☒ Collected data should be time-tagged to MET with an accuracy of +/–2 minutes.
☒ Still color digital images of samples are desired just before and after mix melt and periodically.
☒ Need capability to periodically downlink any of the above data.

Temperature control

5.9

- Requested: simple temperature control for some of the samples. The present CVB hardware on the microscope may allow a range of 15 to 35C +/– 0.5C. This may require that we have microbubble in the sample to expand/compress slightly with temperature changes. We might introduce the bubble in the fill channel by first inserting a bit of Teflon (before the elastomeric plug) for samples that don't wet Teflon. This action may tend to draw the bubble into the fill channel and hold it there.

Magnetic interference

☒ Because we are proposing to use hematite ellipsoids as "lock" particles in some experiments, we require minimal magnetic fields in the vicinity of the LMM. We would therefore like to know whether external magnetic fields are going to be a problem and if they can be measured.

5.11.1 Complete Success Criteria

Complete Success is the achievement of all (the remaining) science priorities, *i.e.*, the test matrix elements and their associated the science requirements. This means that there will be sufficient information to provide a crosscheck of all data and calculated factors. This level of success also includes the realization of an additional two sample wells per sample disk, all 12 of which are filled successfully. [Any italicized portions of the Science Requirement Document (SRD) denote "desired, but not required" and need not be met to officially achieve complete mission success; the additional attainment of any of objectives listed in the italicized portions of the SRD would indicate that the complete mission success criteria has been surpassed.]

5.11.2 Significant Success Criteria

The loss of priority number 1 would be a significant disaster to the mission. Assuming that number 1 will always be possible, the loss of any of the other priorities causes a certain lack of verification of the subsequent data in some cases. Losses of capabilities may only be partial and combinations of lost capabilities account for other than Complete Success. Very generally speaking, Significant Partial Success would be realized if priorities 1 and 2 were accomplished and 70% of all the test matrix elements and 70% of all the science requirements for experiments in 3 through 7 were accomplished. This level of success assumes all ten sample wells are filled successfully.

5.11.3 Minimal Success Criteria

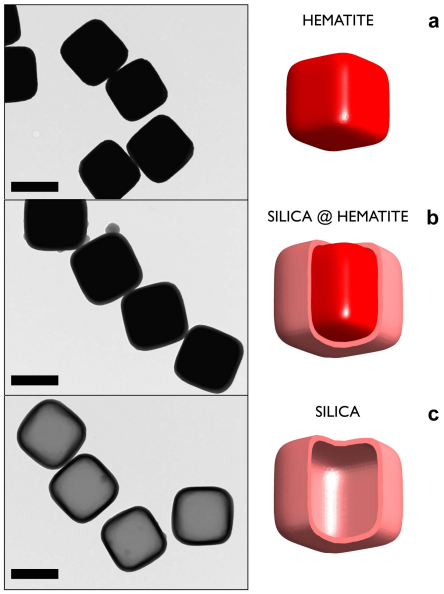
The loss of priority number 1 would be a significant disaster to the mission. Assuming that number 1 will always be possible, losses of capabilities may only be partial and combinations of lost capabilities account for other than Complete Success. Very generally speaking, Significant Partial Success would be realized if priorities 1 and 2 were accomplished and 50% of all the test matrix elements and 50% of all the science requirements for experiments in 3 through 7 were accomplished. This level of success assumes a minimum of eight sample wells are filled successfully.

Success Criteria:

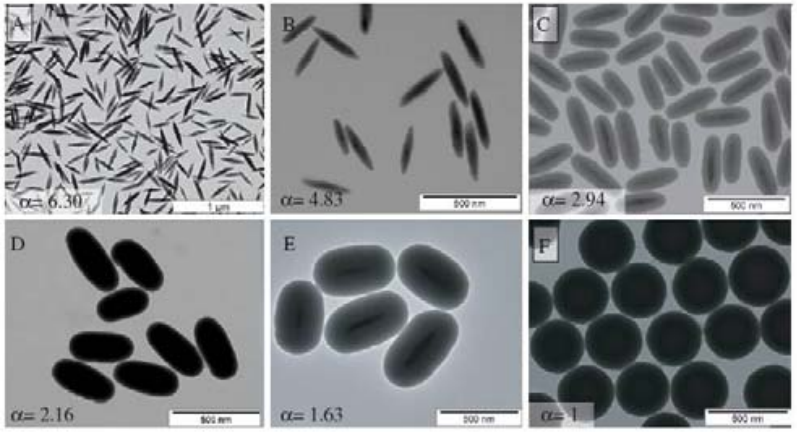
- Successful loading and homogenization of samples
- Real space imaging of samples at 10x, 63x and 100x for all samples
- Reciprocal space imaging with laser diode and Bertram lens for “ordered” samples

Sexy Colloids

particles with shape and specific attractions

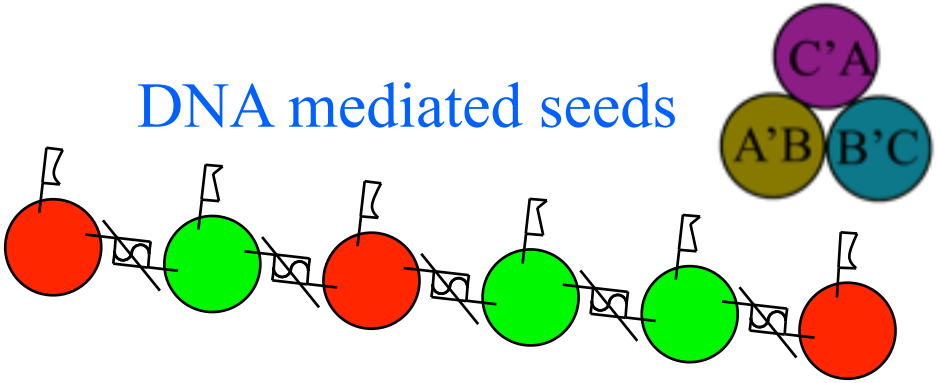


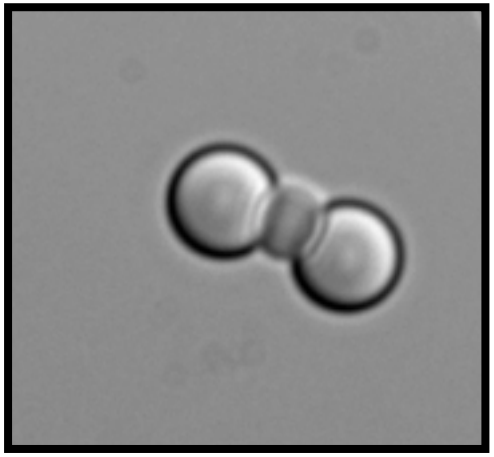
Cubes



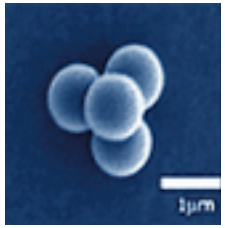
Ellipsoids

DNA mediated seeds





Pacmen



Tetra clusters