ISS Increment 65 Science Symposium

Advanced Colloids Experiment (Temperature controlled) – ACE-T2-3

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Presented by:

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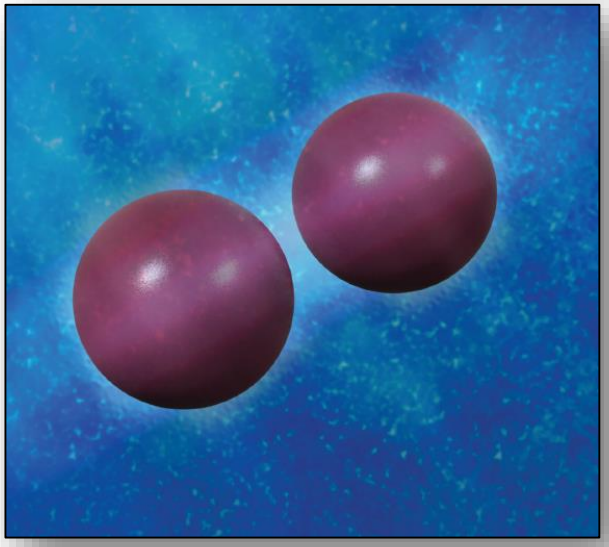
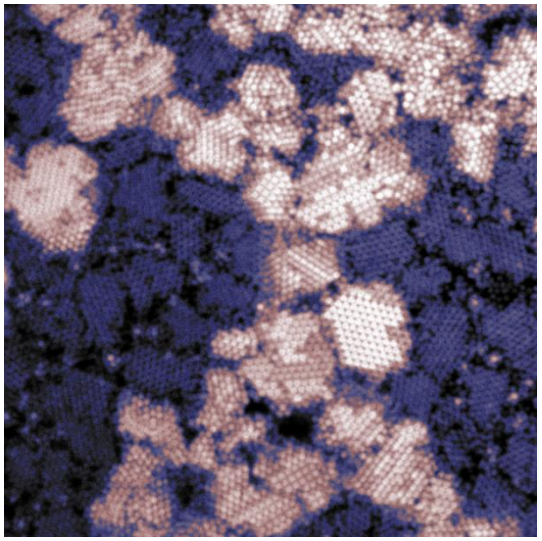
ASSEMBLY OF COLLOIDAL SUPERSTRUCTURES BY CRITICAL CASIMIR FORCES IN MICROGRAVITY

UNIVERSITY OF AMSTERDAM

Piet Swinkels, Gerard Wegdam, Peter Schall

– University of Amsterdam –





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Prof. Peter Schall– University of Amsterdam

- Science Team
- Science Background and Hypothesis
- Investigation goals and objectives
- Measurement approach
- Importance and reason for ISS
- Expected results and how they will advance the field
- Earth benefits/spin-off applications

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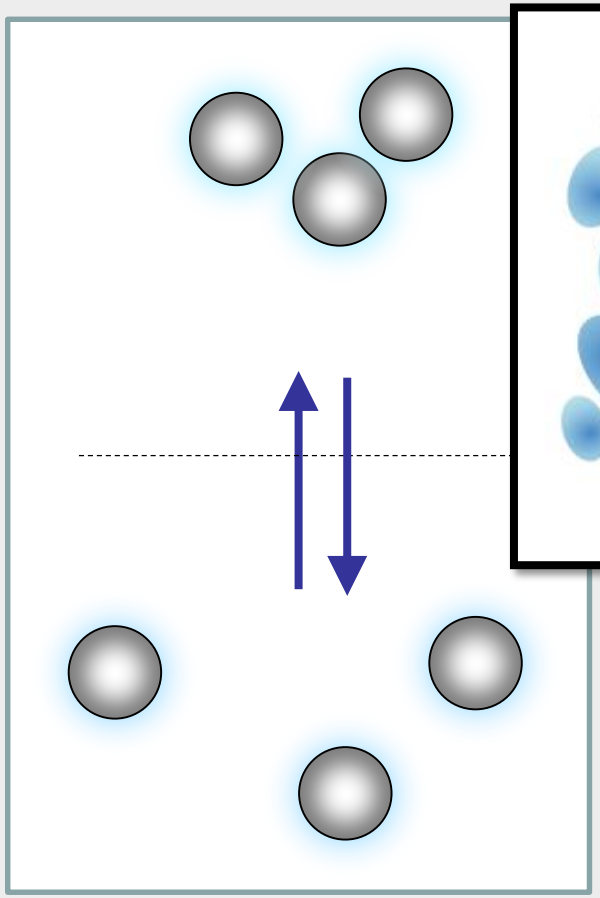
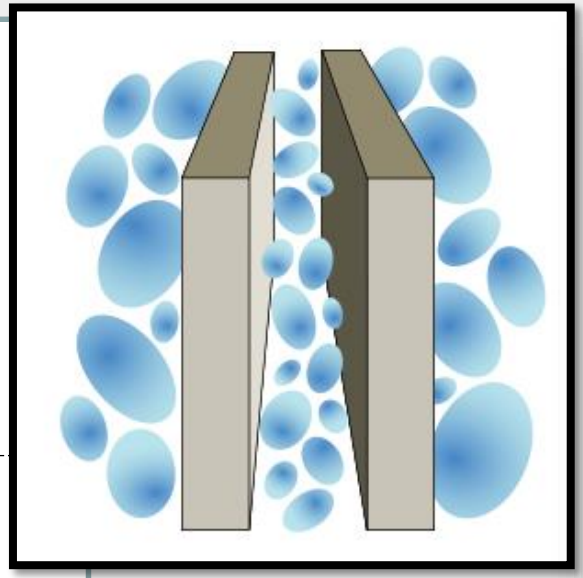
Science Background and Hypothesis – 1/6

The Critical Casimir effect

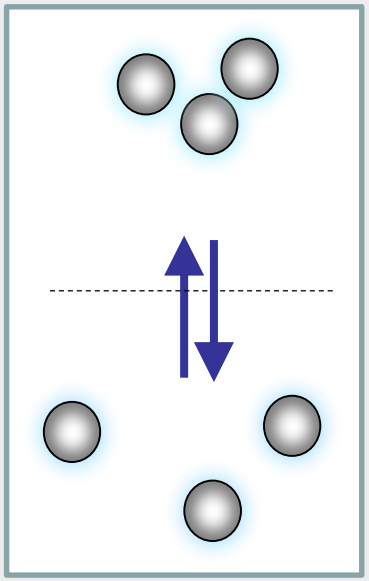


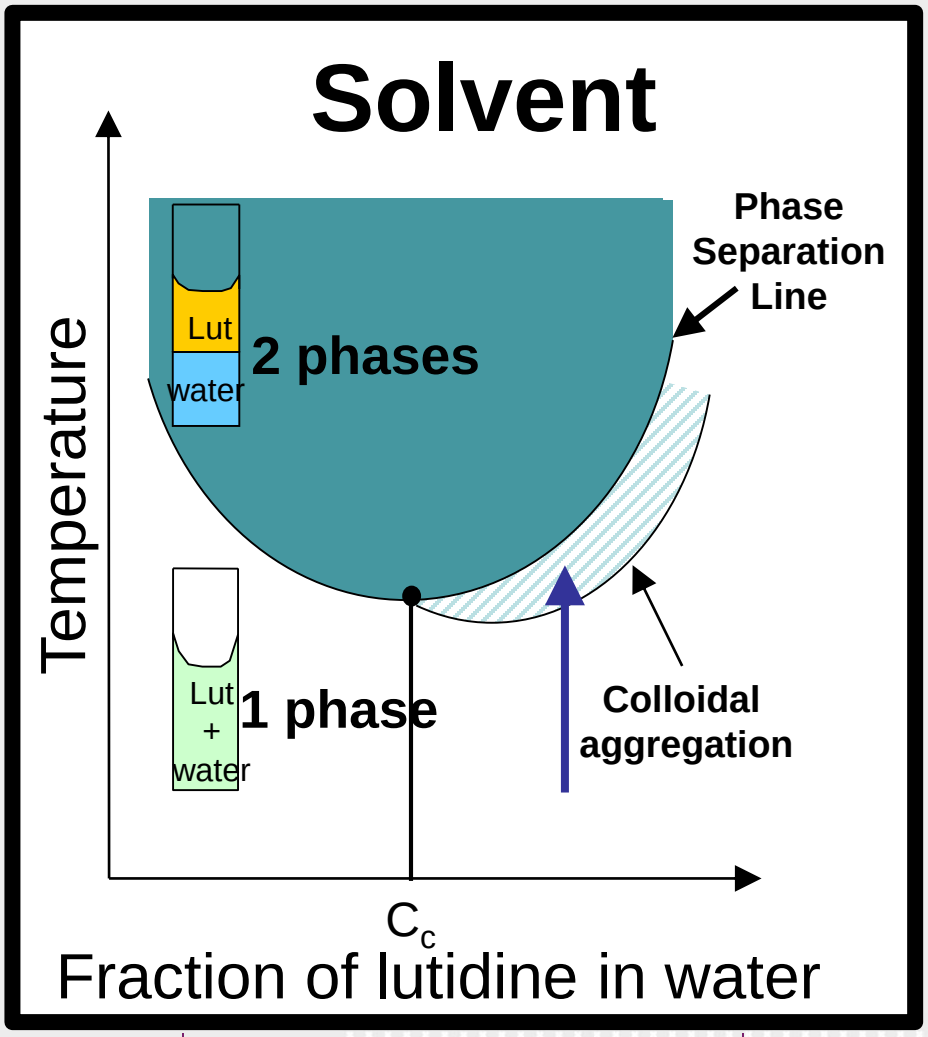


Science Background and Hypothesis – 2/6

The Critical Casimir effect

Concentration fluctuations will become larger as you increase the temperature towards the phase separation line. As the fluctuations grow bigger, the attraction will become stronger and longer ranged and colloids will start to aggregate.





Science Background and Hypothesis – 3/6

Particle interactions

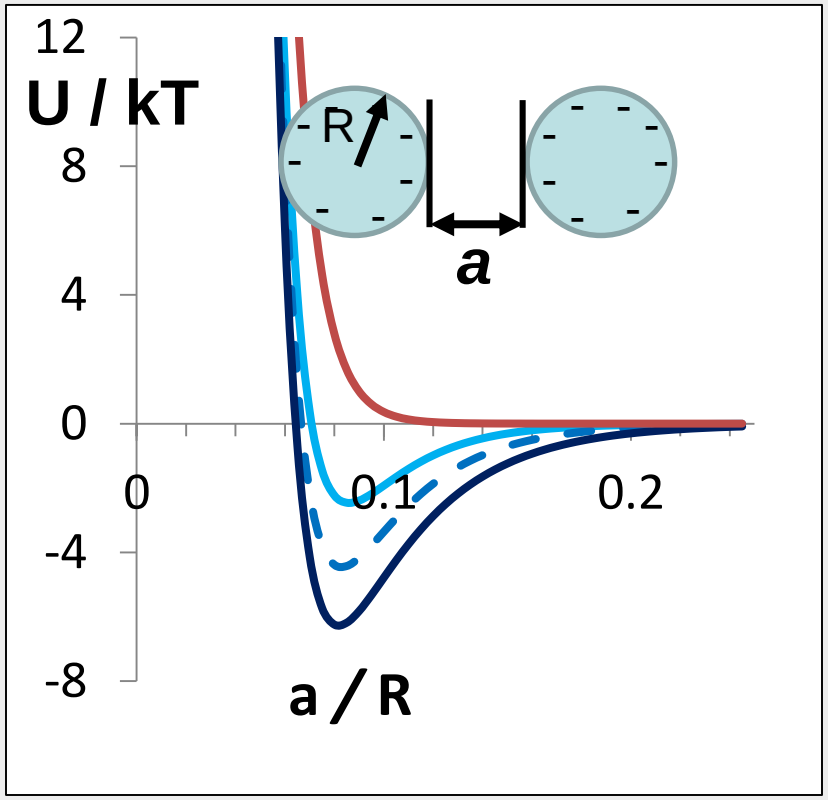
Electrostatic repulsion

$$V_{el}(a) \propto \lambda_d^2 e^{-a/\lambda_d}$$

+

Critical Casimir attraction

$$V_{casimir}(a) \propto -\frac{1}{\xi} e^{-a/\xi}$$



where ξ is the bulk correlation length of the solvent

Schall et al., PRL **103**, 156101 (2009)

Science Background and Hypothesis – 4/6

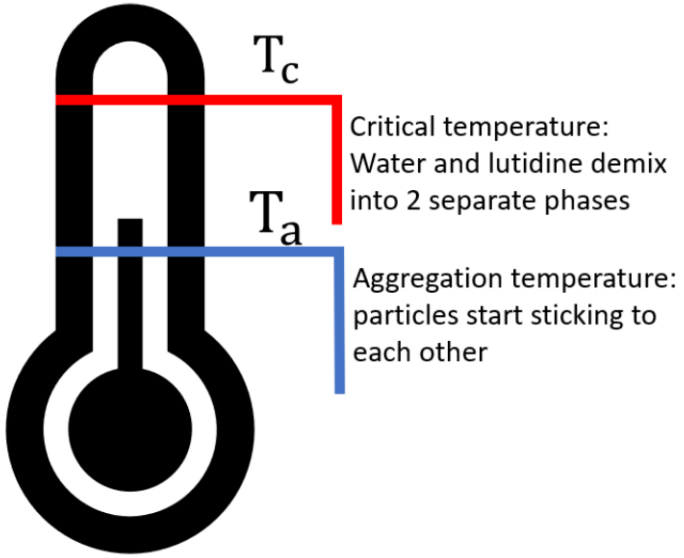


Figure 1: Aggregation temperature vs critical temperature. *The difference between Ta and Tc depends on the particles, the solvent, and other environmental factors. In our case, it is probably between 0.4-0.6 K.*

A very short guide to the ACE-T2-3 samples

Piet Swinkels

Last update: 26 January 2021

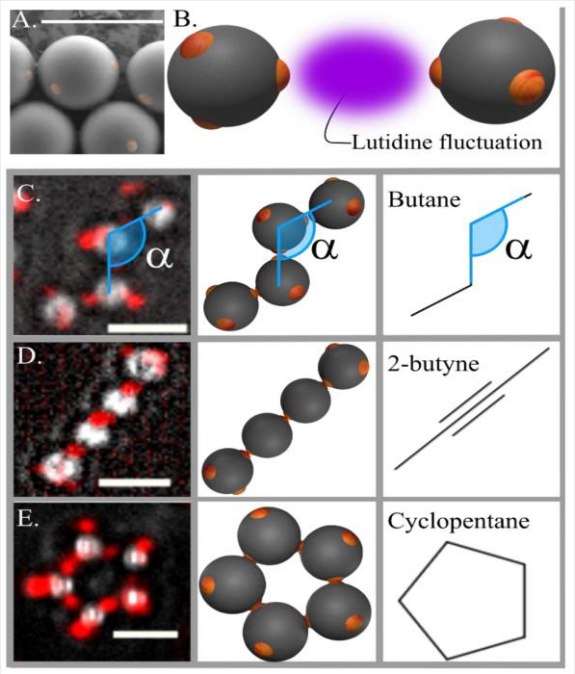
The Solvent

In the ACE-T2 samples, we have colloidal particles suspended in a mixture of lutidine and water. The mix of lutidine and water is an interesting one, because it can cause attractive force between the particles in the sample. At low temperatures, lutidine and water are mixed, but when we increase the temperature, the mixture phase separates into a water phase and a lutidine phase. The temperature at which this occurs is the *critical temperature* (or "Tc") of the system. Upon approaching this critical temperature, fluctuations in the solvent will lead to an attractive force between surfaces (typically the surfaces of colloidal particles, but also the sample wall is a surface, and can thus attract) in the solution: *the Critical Casimir force*. How this works exactly is quite complex, but for now we can just assume there is a magical attractive force between particles if you approach the critical temperature. If you want to know more, I can give you a reading list…

In our experiments, we typically slowly approach Tc, until we reach the *aggregation temperature*(or Ta) of the particles, the temperature at which point particles start attracting each other and form clusters or aggregates. As we get closer to Tc, the attractive strength becomes larger and larger. This means that the attraction can be tuned in strength by varying the temperature, which makes it very convenient for doing all kinds of experiments.

Apart from the water and lutidine, the sample also contains a little bit of salt, to screen the electrostatic repulsion between particles.

Science Background and Hypothesis – 5/6



The Particles

We work with very special colloidal particles: patchy particles. What this means is that the particles are decorated with pieces made of a different material then the bulk of the particle. We have two types of patchy particle: particles with two patches (dipatch particles) which are linearly orientated, and particles with 4 patches (tetrapatch particles) which are tetrahedrally oriented (think of the geometry of a carbon atom) -see Figure 1A & B.

We can tune the particles and the critical Casimir force in a way such that only the patches attract each other, while the bulk does not. This means that when we reach Ta, particles do not randomly aggregate, but form very distinct clusters, see some small examples in Figure 1C, D & E.

Ideally, we would grow larger structures. From computer simulation, there are *a lot* of predictions about interesting properties that large 3D clusters could have. I will not go into detail here about what exactly those are, but there are many, and basically no one has ever managed to test if any of the simulations bear a passing resemblance to reality. So, this is what we want to do: build large colloidal superstructures and see if they do indeed have these interesting properties that are predicted.

The problem is that when we start growing bigger things with our particles: gravity starts getting in the way. Our particles are in the order of 1 micron in radius, which mean they will sink to the bottom of our sample. Small structures will still readily form, but large networks or crystals made of these particles are really out of the question when we have gravity to fight against, thus the need for experiments in space. That is not to say we cannot build nice things out of patchy particles while on earth by the way, we just need to stay in 2D, see Figure 2 (on the next slide) for a recent example.

Figure 1: Patchy particles.

A) Patchy particles under a scanning electron microscope, with patches indicated in orange. B) 3D representation of two tetrapatch particles being attracted by the critical Casimir force. C),D),E) Examples of the type of small structures you can form with the patchy colloids. In the left column the red colour is fluorescence and we can see the patches. In white we see the 'normal', bright field microscopy. In the middle column, some 3D representations are shown. The structures look a lot like molecules, see the right column, because the particles have a shape very similar to carbon atoms.

Science Background and Hypothesis – 6/6

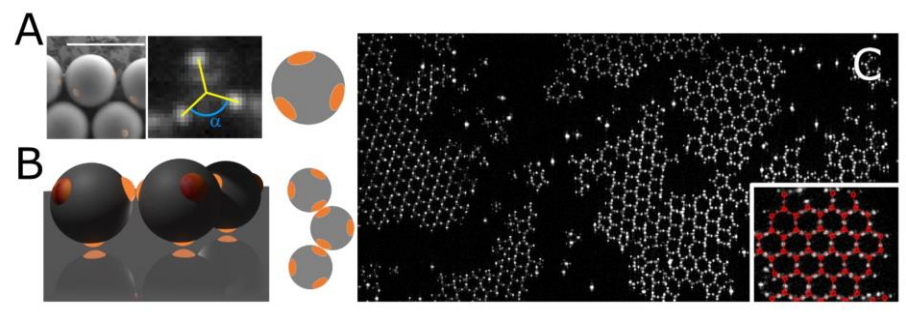


Figure 2: Building a honeycomb lattice on Earth. *Using tetrahedral patchy particles we can build large crystals, as long as they are 2D, like the honeycomb lattice (similar to graphene) shown here.*

Our particles are synthesized such that the patches are fluorescent, which means we can use a confocal microscope to determine the position, orientation, and bonding of each particle. This will give us a lot of information about whatever it is that is formed by our particles.

Our samples

We sent 3 samples to study. The 3 different samples all contain the water-lutidine mixture and patchy particles, but they are all slightly different.

Sample 1 has a mix of dipatch and tetrapatch particles in it. This mix of particles should form a so-called “equilibrium gel”, which has an interesting way of growing and assembling into its final structure. Basically, we expect a network made of long chains of dipatch particles with tetrapatch particle ‘hubs’ that connect these chains together. Sample 1 consist of pretty small particles, so we may not be able to image every particle individually. Rather, we intend to observe the structure as a whole.

Sample 2 also has a mix of dipatch and tetrapatch particles in it, but the particles are quite a lot bigger. This should make no difference for the eventual structure, but it makes particles easier to image individually. However, the assembly process will be (much) slower.

Sample 3 is likely not functional (it has a significant air bubble), it contains purely tetrapatch particles. Theoretically these particles could form a diamond crystal, which has interesting properties (and would have looked very cool!).

Investigation goals and objectives – 1/2

Study Critical Casimir assembly
Use temperature control

→ Tune attractions
→ Follow structure formation
→ "Complex crystallisation kinetics"

Vary Temperature → Vary attraction strength

Vary Rate of change → Eqilibrium vs. out-of-equilibrium

Reverse Temperature → Repeat Experiment

Investigation goals and objectives – 2/2

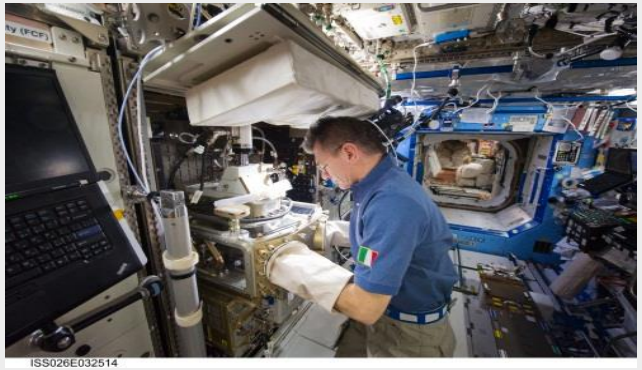
Investigation of assembly of complex structures from micron-scale colloidal particles interacting via tunable attractive interactions.

Regulating temperature enables control of particle interactions.

The goal is to understand how complex interactions lead to complex structures, and to understand the dynamics of growth of these structures.

Measurement approach – 1/4

The assembly of 3D structures and their formation kinetics will be directly followed with the LMM microscope on the ISS.



Using the Light Microscopy Module (microgravity microscope) aboard the International Space Station (ISS).

[Continued]

Measurement approach – 2/4

Operational Requirements:

Overall, one experiment (capillary cell) is conducted every two days, depending on the number of *z*-layers and speed of growth of the structures. The experiment is repeated until all capillaries are tested. Sample modules are switched if air bubbles are too big. Use the rest of the week to analyze data, re-write scripts, and adjust parameters. The number of capillaries per experiment is limited by data bottlenecks on IPSU (internet protocol setup utilities) and IOP (input/output operations per second). We will need to check *XYZ* position repeatability and oil availability. More specifically, we will need to return to the same Region of Interest (ROI), *e.g.*, single particle crystallite – or to maintain *XYZ* coordinates during an experiment. This requirement implies maintaining one capillary position. If this requirement takes an excessive amount of time, we will need to find a solution.

Operational Protocols: Descriptive overview of the investigation on orbit procedures. Experiment Steps:

The general experimental protocol includes imaging the dynamics of colloidal assemblies in each capillary. We will inspect all samples before mixing the colloid using the *in situ* mixer. Next, define *XY* offsets. Locate and image particles, adjusting the camera parameters using the 2.5x objective and Texas red (or FITC) filter (fluorophore = Cy3MM, Harvard Fluorophore, Cy3-like). Survey capillary at 2.5x, scanning in the *X* direction over a range of at least 10 millimeters. Determine bubble locations and possible primary / secondary Regions of Interest (ROI). If the 2.5x objective is difficult to switch in and out with the 63x air objective, then find ROI capillary cells before using 100x oil objective. If both ends of the capillary can be used (no big air bubble), then apply immersion oil to half of the capillary to allow imaging with 100x oil *and* 63x air objective without astronaut intervention. Select primary locations away from stir bar or bubble.

[Continued]

Measurement approach – 3/4

Operational Protocols [Continued]:

A. Determine aggregation and solvent phase separation temperature

Use low magnification lens to determine particle aggregation temperature, T_{AA}, and solvent phase transition temperature T_c. To do so, survey and record best Z-depth at each primary test location. Ramp temperature slowly from ~27°C to ~31°C during 4h (ramp rate 1°C/hour) while recording microscope video. Note aggregation temperature $T_a=T_{AA}$ when particle aggregates start to appear, and phase separation temperature T_c, where the solvent separates into two components.

B. Confocal video, time series

Go back to room temperature, and stir for 30min. After that, switch in 63x air objective. Increase temperature to T_a-0.3°C. Record microscope video (confocal imaging), while slowly ramping temperature to T_a+0.3°C during 6 hours (ramp rate 0.1°C/hour). These direct particle-scale observations should allow determining the colloidal liquid condensation and crystallization temperatures T_{liq} and T_{cryst}. If possible, record confocal z-stacks of the characteristic liquid phase (at $T>T_{liq}$) and crystal phase (at $T>T_{cryst}$). Each z-stack should consist of ~200-300 images, 0.1μm apart, starting from ~10-20μm into the capillary (above the glass wall). The *Z*-scanning rate should be set as fast as possible, potentially 10 frames per second. No pixel binning, 8 bits per pixel (highest supported), full frame images. After z-stack is taken, continue recording microscope video (at same location and depth as before)

[Continued]

Measurement approach – 4/4

Operational Protocols [Continued]:

C. Confocal stacks

Go back to room temperature, and stir for 30min. Use 63x air objective.
After aggregation temperatures have been refined in (B.), go to T_{liq} and keep the temperature constant. Record confocal stack time series (each z-stack consisting of ~200-300 images, 0.1μm apart, starting from ~10-20μm into the capillary, taken with high scan rate). Record 1 z-stack per 2 min, in total 50 z-stacks over 100 minutes. After this time series, when colloidal liquid has formed, go to T_{cryst} and repeat the same z-stack time series, again taking one z-stack every ~2min, 50 –stacks total over 100min.

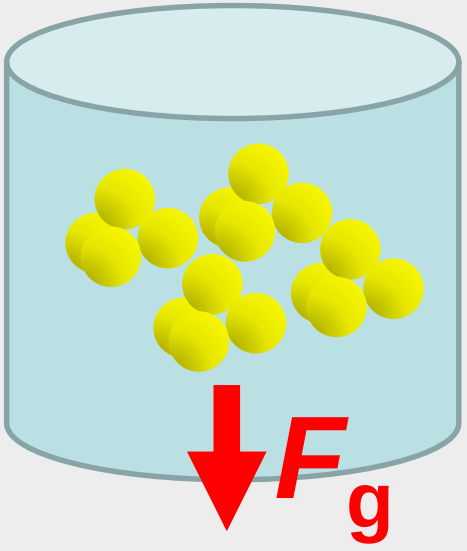
D. Imaging with 100x oil

For better image quality, imaging with 100x oil objective is preferred. However, this will introduce a heat gradient as heat is sucked away from the imaging location into the objective. The heat gradient may also induce particle flows, which are detrimental for the study of particle assembly. To find T_{liq} and T_{cryst} with the 100x air objective, start from T_a and repeat ramping procedure in (A), ramping to ~31°C during 4h (ramp rate 1°C/hour). After aggregation temperatures have been found, refine with a slower ramp rate 0.1°C/hour. Cool down and stir for 30min. Then, go to refined T_{liq} and record confocal z-stack time series as described in (C). After that, go to T_{cryst}, and again record confocal z-stack time series.

Repeat A. – D. for all sample capillaries.

Importance and reason for ISS – 1/2

1. Growth of large structures



$$F_g = \Delta\rho\, g\, V$$

where:

F_g [force of gravity]

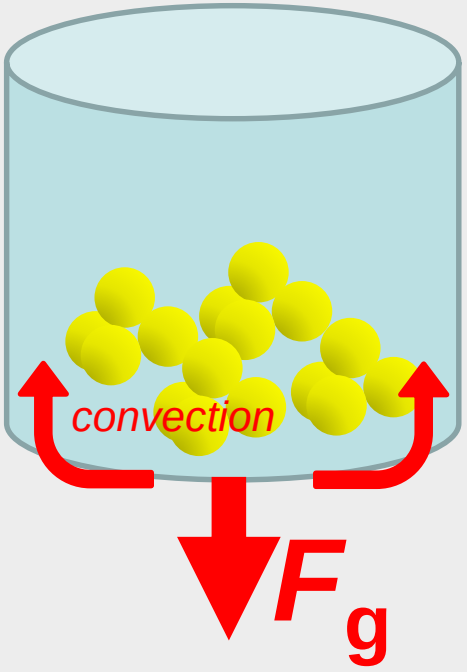
$\Delta\rho = \rho_{Colloid} - \rho_{Solvent}$ [density]

g [gravity]

V [Volume]

Importance and reason for ISS – 2/2

2. Temperature is the control parameter

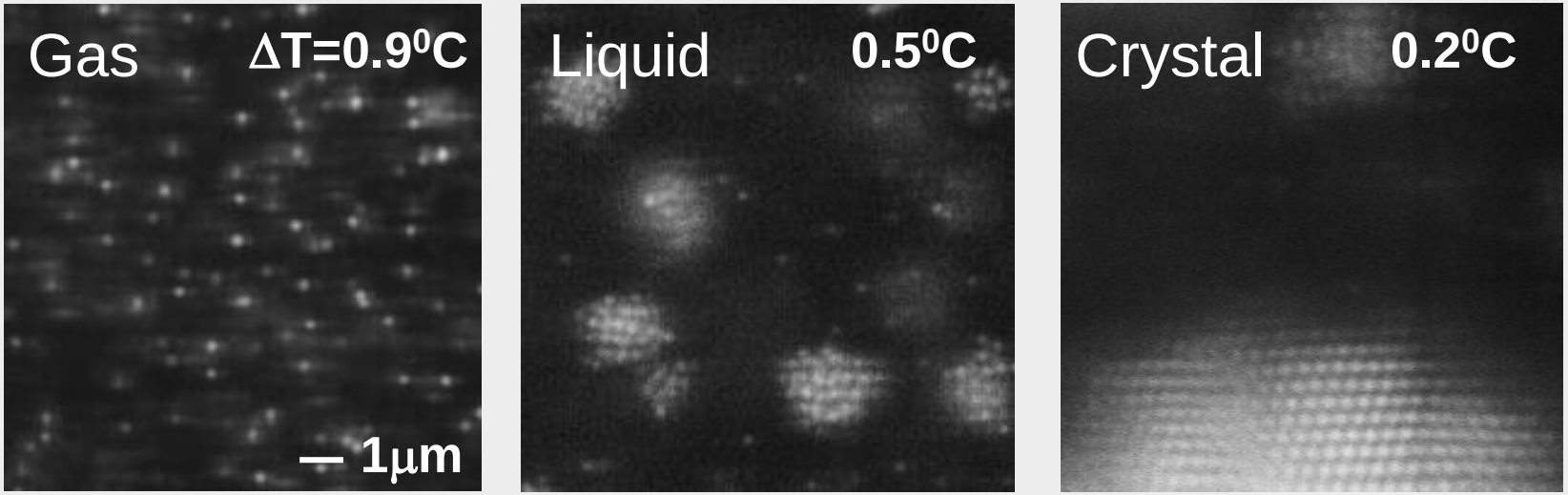


- Change Temperature
  $\Delta\rho$ changes
- Temperature → Convection disrupts growth

These structures and the growth process are strongly affected by sedimentation and convection. The goal of the ACE-T-2 experiment is to study the diffusion-limited growth of these complex structures without the disturbing effects of gravity.

Expected results and how they will advance the field

1-Component system



Microscopy: Ground-based work (2D structures)

Expected results and how they will advance the field

Space-based (microgravity) work – 3D

- What do we expect to see?
  - Observation of *temperature - controlled assembly,*
  - *Which is reversible and repeatable.*
  - *Recent ISS experiment results shown on next slide.*

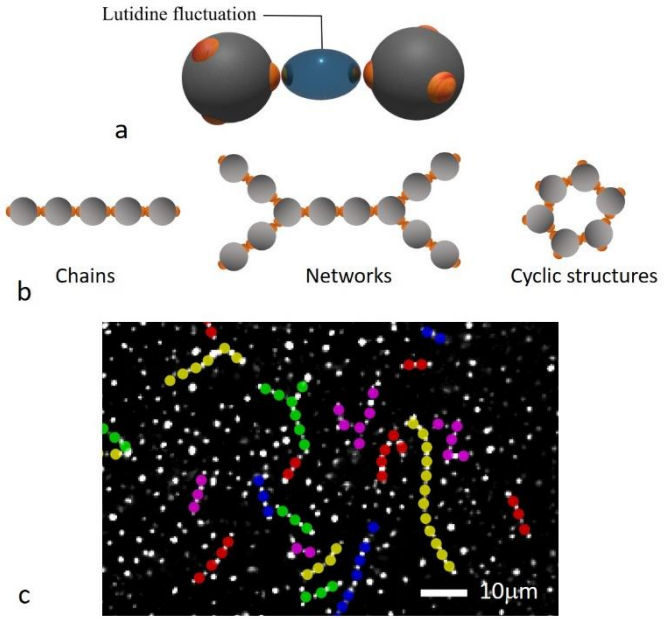


Fig. 1 Patchy particles and resulting structures.
(a) Colloids binding via their patches. The attraction is mediated by the solvent. (b) Possible structures of pure di-patch (left), mixtures of di- and four-patch (center) and four-patch particles (right). (c) Microscope image from our space experiment with superimposed colored dots illustrating the assembled particles clusters.

ACE-T2-3 experiment is using self-assembly to create engineered structures

The ACE-T2-3 experiment provides a new way of controlling the simultaneous self-assembly of many colloidal and nanoparticle structures that have been predesigned. Structures of this kind will be important for smart mechanical materials, that is, materials that reconfigure themselves for different situations, (e.g., for tunable shock-absorbing applications), as well as for optoelectronics (e.g., for enhanced displays, LEDs, and solar cells made from nanoparticles). This parallelization process can be used for commercial applications, where large quantities of 3D structures can be formed by using colloidal engineering.

This microgravity experiment has been investigating the assembly of "patchy" particles (Fig. 1) using critical Casimir forces. These particles attract each other in certain directions only, mirroring very precisely the specific angles between atoms in chemical bonds, which determine the way in which atoms arrange into molecules. On Earth, because of sedimentation, we have only seen 2D structures forming on the glass walls, while in microgravity the full 3D structures become apparent.

Earth benefits / spin-off applications

Understanding self-assembly processes will teach ways to grow complex nanostructured materials. Furthermore, these experiments will provide fundamental insight into the nature of temperature-controlled super structure assembly, the relation between complex interactions and complex equilibrium and non-equilibrium structures, and the dynamics of both equilibrium and non-equilibrium growth processes.

Collaborators

- Tom Kodger (Wageningen)
- Peter Bolhuis (Amsterdam, Simulations)
- S. Dietrich (MPI Stuttgart)
- Ania Maciolek (MPI Stuttgart)

The International Space Station (ISS)
Light Microscopy Module (LMM)

ACE-T2-3 BACKUP SLIDES

ACE-T2-3 Success Criteria

Success Level	Accomplishment
Minimum Success	• Homogenize and observe at least 1 of the 3 capillary samples. This includes observing the time evolution with microscopy (using bright field and fluorescent microscopy as needed) for several days to weeks, depending on rates of change determined in real time as data is downlinked to Earth (these cannot be predicted accurately ahead of time in the 1g environment). Have sufficient data (both in terms of frequency and duration) from microscopy of sufficient quality to observe, characterize, and quantify the rates of growth of structures formed as a result of the physical process of interest in microgravity, including but not limited to self-assembly, the relation between complex interactions and complex equilibrium and non-equilibrium structures, and the dynamics of both equilibrium and non-equilibrium growth processes. We hope that these processes will generate new structures formed in microgravity, that may direct further earthbound studies and inspire new directions for materials synthesis and fundamental physics understanding.
Significant Success	• Accomplish the above for 2 of the 3 different fluid samples launched.
Complete Success	• Accomplish the above for all launched samples, with multiple runs to repeat the experiment and assess reproducibility.

ACE-T2-3 samples

Description: UvA ACE-T2-3 Flight Sample #1

P/N: UvA_T2-3_Flight_Sample1

Total volume: 0.1ml

Composition: Suspension of 0.2%vol composite PS/TPM spheres (dipatch and tetrapatch particles, size 1.2μm) in a binary aqueous solvent of 25% Lutidine and 75% H_20 with 1mM $MgSO_4$ salt.

Description: UvA ACE-T2-3 Flight Sample #2

P/N: UvA_T2-3_Flight_Sample2

Total volume: 0.1ml

Composition: Suspension of 0.2%vol composite PS/TPM spheres (dipatch and tetrapatch particles, size 3.8μm) in a binary aqueous solvent of 25% Lutidine and 75% H_20 with 1mM $MgSO_4$ salt.

Description: UvA ACE-T2-3 Flight Sample #3

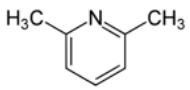
P/N: UvA_T2-3_Flight_Sample3

Total volume: 0.1ml

Composition: Suspension of 0.2%vol composite PS/TPM spheres (tetrapatch particles, size 3.8μm) in a binary aqueous solvent of 25% Lutidine and 75% H_20 with 1mM $MgSO_4$ salt.

All capillaries used were provided by Zin Technologies. The primary seals are composed of Krytox GPL 205 grease, and the secondary seals are composed of NOA 81 UV Curing Adhesive.

Notes:

- Lutidine = 2,6-Lutidine, C_7H_9N  from Sigma-Aldrich
- PS = Polystyrene
- TPM = 3-(trimethoxysilyl)propyl methacrylate