

Gravitational and Space Research

Colloidal molecules in microgravity assembled by critical Casimir forces

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Abstract

Space-based research can provide fundamental insight into assembly processes that are of central importance in physics, material science and biology. Colloidal particles have served as a model system to study the assembly at convenient time and length scales, and microgravity research has played an important role in studying these assembly processes in their purest form without disturbance by sedimentation. Recently, anisotropic particles have emerged, opening the door to the study of complex structures; specifically, patchy particles enabling directed bonding promise the assembly of structures that could mimic those of molecular compounds.

Based on previous space research on tunable attractive particles, here we explore the use of patchy colloidal particles for studying the assembly of complex structures in space. The particles interact along their patches via temperature-tunable critical Casimir interactions with bond energies of several (ten) $k_B T$, the thermal energy. The tunability and reversibility of these critical Casimir forces allows convenient remote control of the colloidal interactions from the ground, enabling the repeated formation and break-up of the structures without much intervention by the astronaut. Together with the confocal microscope extension of the Light Microscopy Module on board the International Space Station, this offers unique opportunities for investigating complex structure formation in real space without disturbance by gravity.

Keywords

Colloidal assembly • Patchy particles • Self-assembly in microgravity • critical Casimir force

Introduction

The assembly of micro and nanometer-scale colloidal particles is both of scientific interest to address fundamental questions such as crystallization and the glass transition, and for applications in photonics and optoelectronics. The ability to tailor the building blocks and their interactions make these colloidal systems particularly useful for the assembly of new materials from the bottom up. Recently, anisotropic interactions have moved into the focus as they enable higher structural complexity, allowing in principle the assembly of structures as complex as those of molecules.

While many theoretical and simulation studies exist, achieving directional bonding in experiments on colloidal systems is challenging, and reliable systems allowing interaction control on the scale of $k_B T$, the thermal energy, are scarce [1-3]. Recently developed “patchy” particles, i.e., particles with patches of specific surface chemistry arranged in well-defined symmetries, are good candidates, allowing to reproduce the geometry of valence bonds [4-8]. Fine control of these interactions opens up assembly degrees of freedom similar to those of organic molecules, opening the door to “colloidal

molecular chemistry”: Molecules that consist of colloidal particles instead of atoms, reacting at the nano and micrometer scale, directly observable by microscopy. This, in turn, could unlock design paths for micro- and nanostructured materials. On the ground, however, any study of particle assembly is perturbed by gravity, as the growing structures sediment, subjecting them to shear forces and altering their growth. Microgravity research has been instrumental in studying the assembly processes in their purest form, without disturbance by gravity [9-12].

However, typically the particle interactions are fixed, and the assembly process irreversible, making repeated measurements with varying particle interactions difficult, especially in a restricted space-based environment. To reversibly control the interactions between the particles on the $k_B T$ scale, solvent-mediated interactions have been employed in recent years [13-18]. These interactions use two-component solvents close to their critical point to achieve surface affinity-specific binding. The confinement of fluctuations of the solvent close to its critical point gives rise to attractive and repulsive critical Casimir forces [14-17] depending on the boundary conditions, in analogy to the

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confinement of vacuum fluctuations in the quantum mechanical Casimir effect. Because in the thermodynamic analogue, the correlation length of the fluctuations is set by temperature T , this offers direct *in-situ* control of the colloidal interactions to guide colloidal assembly [18]. Specifically, the critical Casimir interaction strength is controlled by the temperature offset $DT = T_c - T$ from the solvent critical temperature T_c , where typical temperature offsets are on the order of a few tenth of a Kelvin. This offers remote control of the particle interactions via the suspension's temperature. For microgravity research, such remote control of colloidal interactions has unique advantages: Experiments can be performed with ground control, without much intervention by the astronaut, and repeated many times by simply adjusting the temperature. This allows studies under well-defined particle interaction conditions, increasing statistical significance and scanning of diverse regions of structural phase space. Furthermore, because of its direct and reversible control of particle interactions, the critical Casimir effect offers exciting opportunities for studying the assembly in and out-of-equilibrium: The direct interaction control allows temperature quenches or ramps to be employed to attain kinetically arrested structures or anneal to perfect equilibrium structures.

Here, we explore the application of critical Casimir forces to study complex colloidal assembly in microgravity. Based on successful microgravity research on isotropically interacting particles and ground-based experiments on patchy particles, we describe assembly experiments in microgravity, in which particles interact via temperature-tunable, directed interactions. These experiments open the door to studying complex structure formation in real space in microgravity, using remote control.

Critical Casimir interactions in microgravity

The first experiments of this kind used simple spherical particles; by varying the attractive strength through small changes in temperature, phase transitions from colloidal gas to colloidal liquid and to crystal were observed [19,20]. Particle-scale images of these transitions are shown in Fig. 1a-c. The microscope images show particles which are dispersed far below the solvent critical temperature T_c but form condensates of mobile particles, characteristic of the liquid phase, at $DT = 0.3^\circ\text{C}$ below T_c , as shown in Fig. 1a and b. Even closer to the critical temperature, at $DT = 0.2^\circ\text{C}$, the particles inside the growing condensates order to form a face-centered cubic (fcc) crystal (Fig. 1c). Furthermore, quenching the system from far below T_c to $DT = 0.12^\circ\text{C}$, leads to particles arrest in a fractal structure (Fig. 1d). In this out-of-equilibrium process, the fractal dimension can be adjusted from ~ 1.8 to 2.5 by varying the quench depth [21].

Direct measurement of the effective pair potentials allowed confirmation of the observed phase behavior by Monte Carlo simulations [22]. The pair potentials were determined from particle pair correlation functions measured in dilute suspensions [20] and subsequently compared with predictions based on critical Casimir scaling theory and the Derjaguin approximation [23]. The corresponding phase diagram is shown in Fig. 1e, where gas (G), liquid (L) and crystal (C) phases are indicated as a function of colloidal volume fraction ϕ and experimental temperature offset DT from T_c . Gas-liquid and liquid-crystal transitions are predicted to occur sufficiently close to T_c , in an experimentally accessible temperature window, in good agreement with the experimental observations (black data points and error bars). Temperature thus offers a unique control parameter to tune the colloidal interactions to study equilibrium phase behavior in attractive colloidal systems. Furthermore, the interaction is reversible; using temperature cycling, the structures can be broken up and reformed repeatedly.

These results motivate a deeper study of out-of-equilibrium assembly processes. On ground, however, gravity precludes observation of the genuine assembly process: the assembling structures sediment, altering the growth process, and ultimately hindering the observation of large, fully grown structures. To observe the assembly process under ideal conditions, a series of microgravity experiments was performed on board the International Space Station (ISS), which provided insight into how these out-of-equilibrium structures grow [12], what their genuine gravity-free structure is [24], and how they initially nucleate in their incipient stage [25]. Systematic studies of the attraction-dependent assembly were conducted by monitoring the structure factor after temperature jumps to various temperature offsets DT . The measurements employed a near-field scattering technique [26] to observe the aggregation process in space and time; the monitoring of both the static and dynamic structure factor provided full information about the growing aggregates, allowing determination of the fractal dimension from the evolution of the radius of gyration, R_g , and the compactness of the aggregate, from the ratio of the hydrodynamic to the gyration radius, $b = R_h/R_g$. Remarkably, while measurements on ground found only one type of aggregate with fractal dimension 1.65, in microgravity, the fractal dimension varied systematically between 1.8 and 2.55, decreasing with increasing attractive strength. Furthermore, distinct differences in the growth process were observed: while on ground, the aggregates formed in a rapid reaction-limited process, in microgravity, a slow diffusion-limited process took place: particle transport to the growing aggregates was limited by diffusion, while on ground it was provided by sedimentation, and the growth process was only limited by particle attachment to the surface. Furthermore, in microgravity, observation of the fully grown aggregates allowed reliable measurement of the

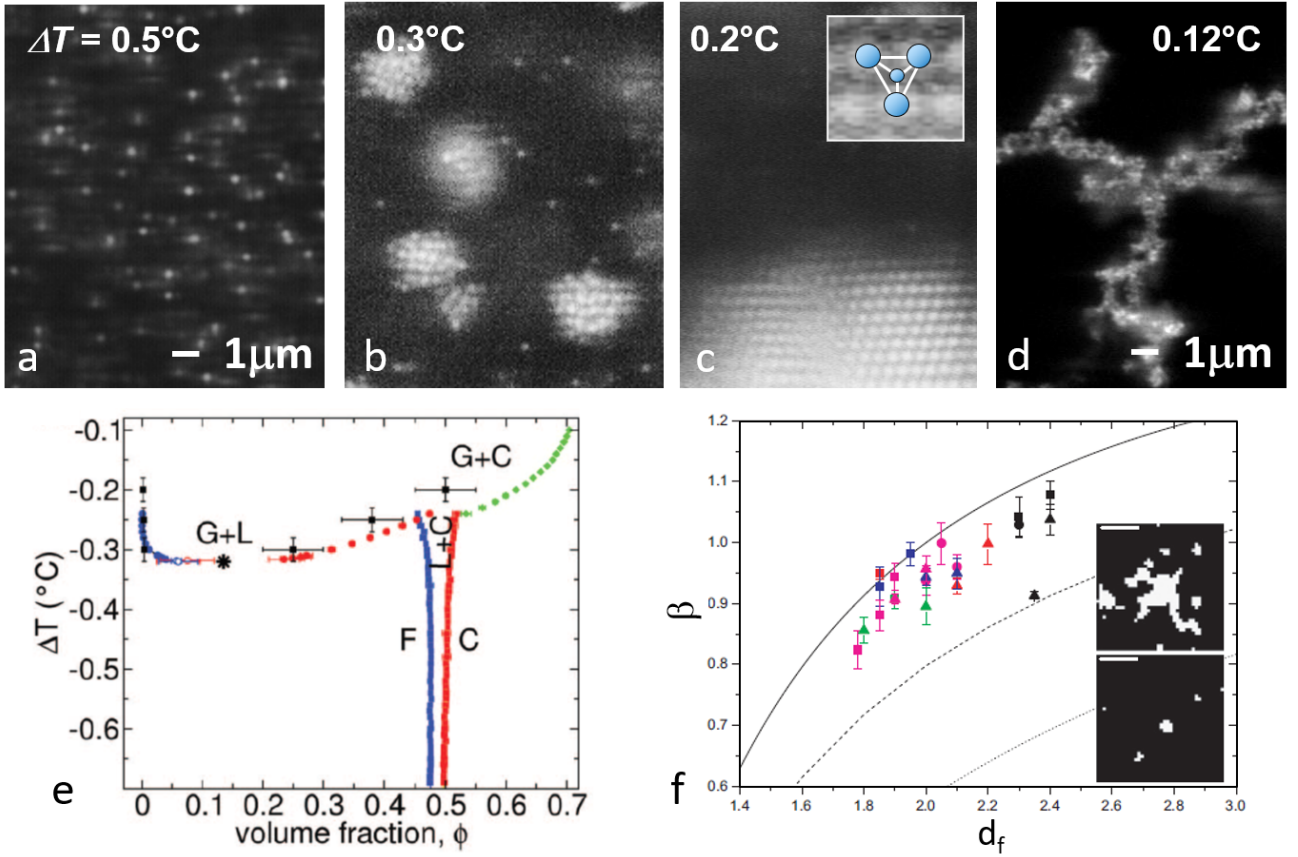


Figure 1. Assembly of equilibrium and out-of-equilibrium structures by critical Casimir forces. (a-d) Confocal microscopy images of particles in equilibrium gas (a), liquid (b) and crystal (c) phases, and out-of-equilibrium, fractal aggregate (d). Temperature offsets $\Delta T = T_c - T$ are indicated. (e) Corresponding equilibrium phase diagram computed using Monte Carlo simulations with effective critical Casimir interactions as input. Experimental data: black dots and error bars; gas-liquid critical point is indicated by a star. Reprinted from [22] with the permission of AiP Publishing. (f) Space measurements of fully grown aggregates in microgravity. The compactness $b = R_H/R_g$ is plotted as a function of the fractal dimension d_f . Lines indicate relation for unit-step (solid), Gaussian (dashed) exponential (dotted) density-density correlation function of the aggregates. Insets show holographic reconstructions of aggregates grown at highest (top) and lowest (bottom) attraction. Reprinted with permission from [24].

aggregate structure. The data in Fig. 1f show that as the fractal dimension increases upon quenching to lower attraction, the aggregate structure becomes more compact, as reflected in a higher ratio b . This is confirmed by real-space holographic reconstructions of aggregates grown at the highest and lowest attraction, as shown in the insets. Comparison with b values obtained for a unit-step density distribution (solid curve), for a softer Gaussian density profile (dashed curve), and for an exponential profile (dotted curve), shows that the aggregates have a fairly compact internal structure, regardless of the fractal dimension and the attractive strength.

Density-matched samples employing hydrogel (PNIPAM) particles on the ground allowed further studies of the aggregation. These studies focused on the gelation, i.e., the percolation of clusters of aggregated particles. Real-space imaging by confocal microscopy revealed an intriguing nonequilibrium percolation process behind the colloidal

gelation of these short-range attractive particles [27]. Upon approaching the gelation point, the cluster size and correlation length diverged with exponents ~ 1.6 and 0.8 , respectively, consistent with percolation theory, while detailed balance in the particle attachment and detachment processes was broken. The results are consistent with an analytic model based on a kinetic master equation for partially reversible aggregation, solved in the limit of single-particle break up [28].

Patchy particles for complex structure formation

These measurements highlight the versatility of the tunable model system, allowing insight into equilibrium and out-of-equilibrium assembly. Beyond the structures made from simple spherical particles, more complex structures can be assembled using patchy particles with anisotropic interactions,

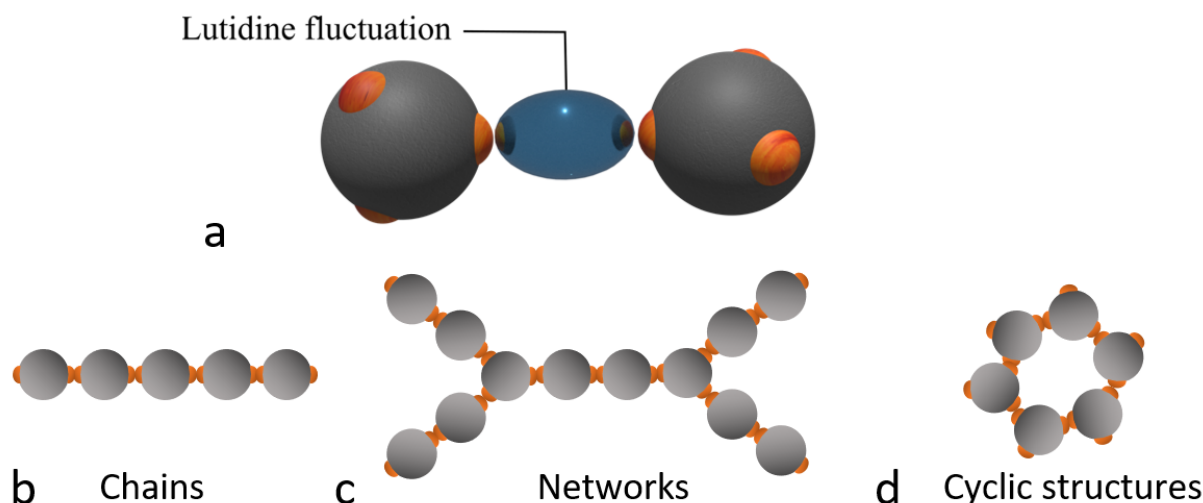


Figure 2. Directional bonding by critical Casimir forces. (a) Illustration of patchy colloids binding via their patches. The attraction is mediated by solvent fluctuations, localized between the patches by their hydrophobic affinity. (b-d) Possible structures formed by di-patch (b), mixtures of di- and tetra-patch (c) and pure tetra-patch particles (right).

providing specific valency [4]. The idea is illustrated in Fig. 2: The patchy particles, exhibiting hydrophobic or hydrophilic surface patches, localize solvent fluctuations between their patches when suspended in binary solvents close to their critical point. The resulting attractive critical Casimir force between the patches leads to patch-to-patch assembly. This directional bonding mimics the covalent bonding of molecules, allowing assembly of specific molecular structures, see Fig. 2b-d. The hydrophobic or hydrophilic patches set the adsorption preference for one of the components of the liquid mixture; for example, hydrophobic patches exhibit affinity for the less polar component of the binary solvent, i.e., lutidine in a lutidine-water mixture, thereby localizing lutidine-rich solvent fluctuations between patches and inducing attractive critical Casimir interactions between them (Fig. 2a). Using divalent or tetravalent particles, these patch-oriented interactions should lead to chains, networks or other open or cyclic molecular structures (Fig. 2b-d). Indeed, experiments on the ground confirmed the formation of these structures. Examples of chains assembled from dipatch particles are shown in Fig. 3a-d. The patch-patch bonding is clearly observed in the fluorescent image in Fig. 3a highlighting the dyed patches as white dots. The microscope images in Fig. 3b-d show that the chain length is controlled by the attractive strength: The smaller the temperature offset DT , i.e., the stronger the attraction, the longer the resulting chains [29]. In equilibrium, the chain length x is set by the balance of particle association and dissociation according to Flory theory [30], resulting in exponential length distributions $P(x) \propto e^{-(x/\langle x \rangle)}$ where $\langle x \rangle$ is the average chain length, which depends on the patch attraction. Indeed, these ground-based measurements showed

distributions that follow closely exponential distributions with characteristic lengths growing with increasing attraction or decreasing DT (Fig. 3e). Detailed Monte Carlo simulations [31] confirm that these results are consistent with equilibrium predictions. Interesting deviations from equilibrium arise when the surface coverage is increased and the growth becomes kinetically hindered. In this case, the limited space can lead to alignment of the chains, and concomitant slowdown of the polymerization process in two dimensions and shorter chains [29].

Adding a small number of 4-patch particles, the chains cross-link and eventually form networks (Fig. 3f). The higher-valency particles introduce branching points that link the chains into a polymer network. The cluster size distributions then show a transition from exponential to power-law (Fig. 3g), indicating the emerging percolation of the network. The remarkable feature of this network is that its topology is set by the valency and bonding angles of the particles, independent of the quench history. These networks are known as equilibrium gels [32] and their properties can be derived from equilibrium statistical mechanics alone [33,34], unlike common colloidal gels that form by arrest in an out-of-equilibrium process. While the existence of equilibrium networks of limited-valency particles has been shown in simulations [35-37], their direct experimental observation has been challenging. The networks grown on a cover slip show indeed some agreement with equilibrium predictions [38], yet full three-dimensional measurements are needed to accurately test equilibrium predictions. In principle, the two-dimensional network in Fig. 3f can be extended into the third dimension by using smaller particles (Fig. 3h) or density

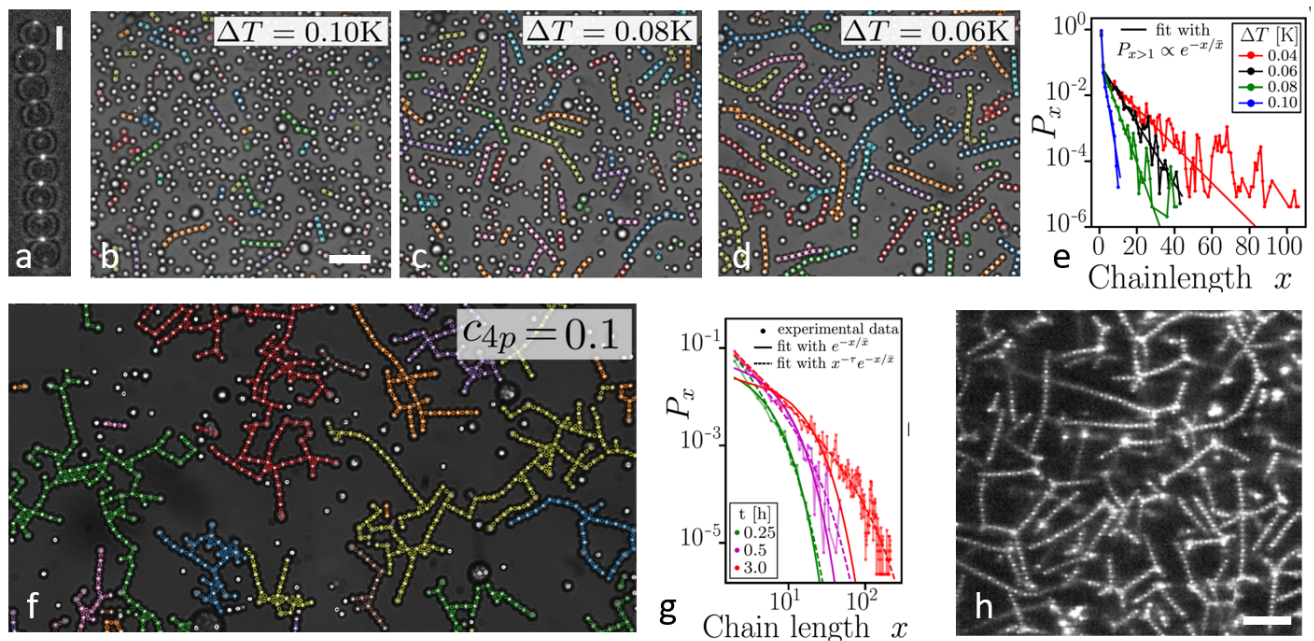


Figure 3. Equilibrium polymerization of di-patch particles. (a) Fluorescence image showing a chain of particles bonded by critical Casimir forces via their patches (bright dots). Scale bar is $3\mu\text{m}$ (b-d) Microscope images of di-patch particle chains at increasing attractive strength (decreasing ΔT) at a surface coverage of $f \approx 0.28$. Colors mark connected chains. Scale bar is $20\mu\text{m}$. (e) Corresponding chain length distributions for the different ΔT (see legend). Lines are exponential fits. (f) Chain network obtained with addition of a small fraction (10%) of tetra-patch particles. (g) Cluster size distributions after different growth times (see legend). Dotted lines indicate power-law fits with exponent $\tau \sim -1.5$ and exponential cutoff $\bar{x} = 4, 11, 68$ (dotted). (h) Confocal microscope image of three-dimensional network of di- and tetra-patch particles achieved with smaller ($1\mu\text{m}$) particles having larger gravitational height. Scale bar is $10\mu\text{m}$. Panels (d)-(g) reprinted with permission from [29]. Copyright (2021) by the American Physical Society.

matching, but microgravity experiments are needed to grow large three-dimensional network structures to thoroughly test equilibrium predictions.

Further molecule-like structures arise when using tetra-patch particles alone: the bond angles of these particles mimic sp^3 -coordinated carbon, promising a rich variety of structures that are known from organic chemistry. Such structures are indeed observed when the critical Casimir interaction becomes sufficiently strong close to T_c , as illustrated in Fig. 4a-e [39]. The particles are observed to assemble into analogues of alkane backbones, including butane, 2-butyne and cyclic compounds such as cyclobutane, cyclopentane and cyclohexane. The colloidal model then allows visualizing the individual particles in real-time, offering insight into molecular transition states and reactions in the classical limit. An interesting case is cyclopentane, whose 5-fold symmetry is not entirely compatible with the 109.5° bond angle of the tetra-patch particle: In planar cyclopentane, the bond angles are slightly lower, 108° , leading to bond strain in this planar configuration. To relieve the bond bending strain, the particles of the ring can pop out of plane. Indeed, direct observation of colloidal cyclopentane has shown that the molecule exhibits puckered conformations such as twist and envelope (Fig. 5a) that interconvert continuously [39]. For atomic

molecules, this interconversion is known as pseudo-rotation [40] but has been observed only indirectly by spectroscopic techniques [41-43]. Using the colloidal analogue, pseudo-rotation can be directly observed in real-space and real-time (Fig. 5b and c).

The formation of larger structures could give insight into equilibrium reactions of larger molecules, but on earth their observation is limited to small gravitational heights and disturbed by gravity. Any larger structure settles while it forms, thus disturbing the growth process as well as the equilibrium dynamics and reactions. This precludes insight into the genuine assembly processes, especially for large, complex structures.

Patchy particles in microgravity

To overcome this limitation, experiments exploring patchy particle assembly in microgravity have been performed during the ACE-T2 mission on board the International Space Station (ISS). The samples contained suspensions of dipatch particles in a binary solvent, tetra-patch particles in a binary solvent and mixtures of di- and tetra-patch particles in this solvent. The suspensions are composed of 0.2% vol patchy

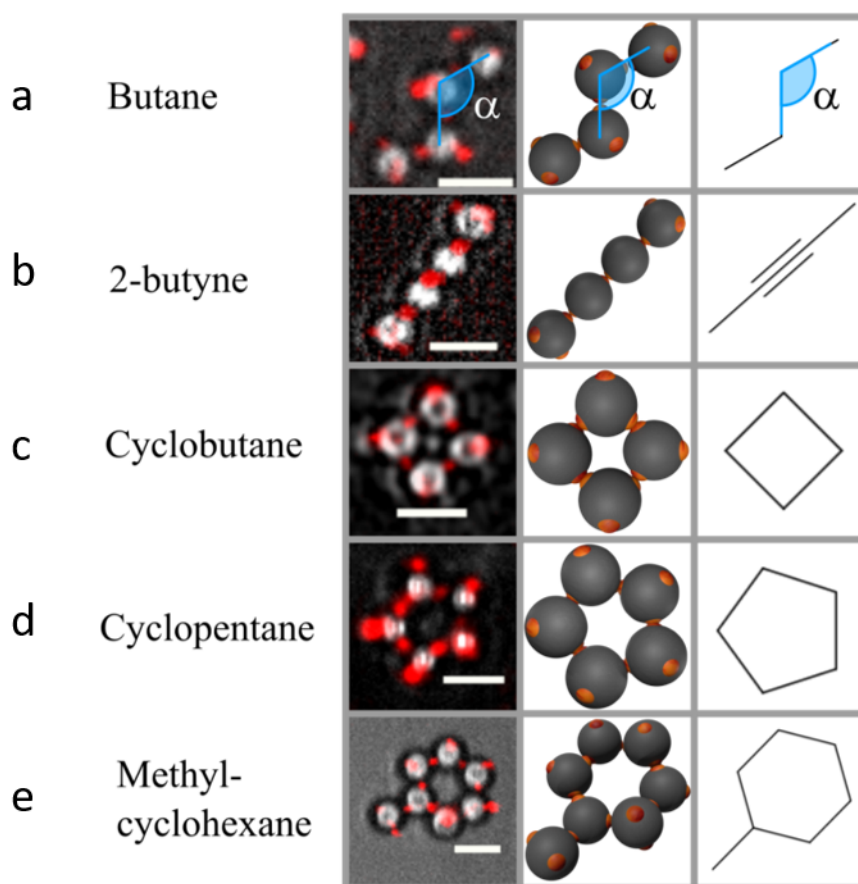


Figure 4. Assembly of colloidal organic molecules. Backbones of colloidal organic-molecule analogues ("colloidal alkanes"), assembled from tetra-patch particles: Colloidal butane (a), 2-butyne (b), cyclobutane (c), cyclopentane (d) and methylcyclohexane (e), microscopy image (left) reconstruction (center) and chemical symbol (right). Reproduced with adaptation from [39].

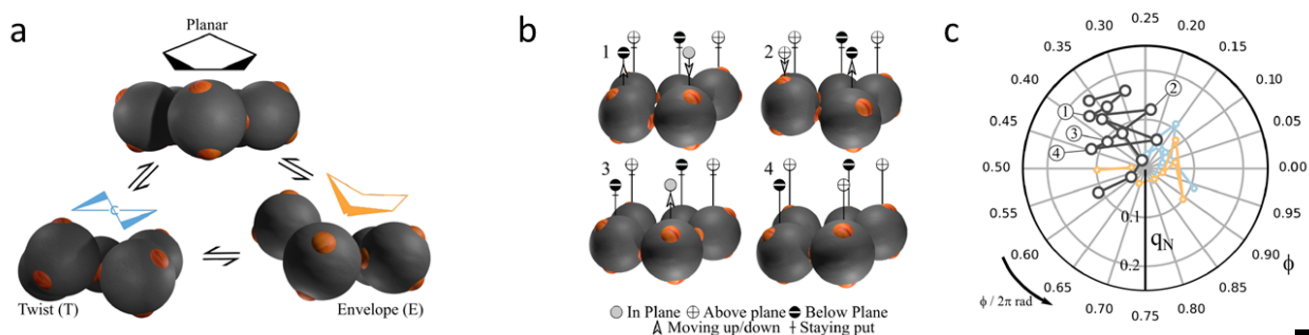


Figure 5. Conformations and pseudorotation of colloidal cyclopentane. (a) Three-dimensional reconstructions of typical conformations of colloidal cyclopentane: Planar conformation (top), twist (or 'half-chair') conformation (bottom left), and envelope (or 'bend') conformation (bottom right). (b) Time series of three-dimensional configurations showing pseudo-rotation of colloidal cyclopentane. Snapshots are $t = 12\text{s}$ apart. The typical relaxation time of a conformation is 24s , allowing for convenient observation. Symbols + and - indicate particles above and below the average plane, respectively, and arrows indicate particle movement towards the next time step. (c) Transition states in polar space during pseudorotation of three colloidal cyclopentane rings. Black trajectory: numbers correspond to snapshots in (b). Reproduced with adaptation from [39].

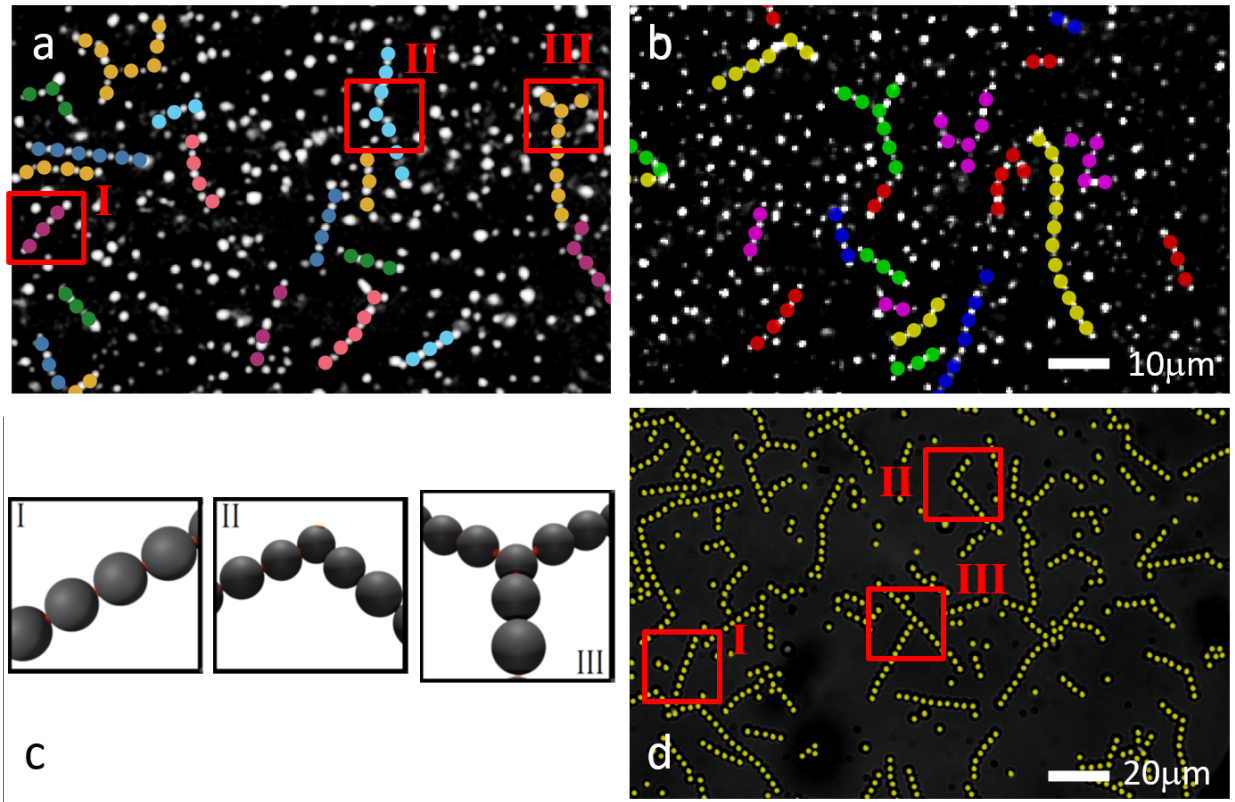


Figure 6. Assembly of patchy particles in microgravity. (a,b) Preliminary results of assembled di- and tetra-patch particles, obtained during the ACE-T2 experiments. The pictures show confocal microscope images of the assembled particles with overlays indicating a few of the assembled structures. (c) Characteristic motifs: chains formed from di-patch particles (I), kinks (II) and branching points (III) due to tetra-patch particles. (d) Bright-field image of a ground experiment performed under similar conditions ($DT \sim 0.05^\circ\text{C}$) showing the same basic motifs.

particles (composite spherical particles with polystyrene body and TPM patches [29]) in a binary aqueous solvent of 25% vol Lutidine and 75% vol H_2O with 1mM MgSO_4 salt. The divalent salt increases the attraction contrast between the hydrophobic patches and the hydrophilic bulk, leading to clearly distinct patch–patch attraction between particles for this solvent composition. Phase separation of the binary mixture is expected near $T_c = 33.82^\circ\text{C}$ [29]. The suspensions are filled in glass capillaries, and the experiments are performed on the Light Microscopy Module (LMM) in space, an automated microscope that has been built up in stages. The current stage allowed flexible imaging (bright field and confocal microscopy) with temperature control for physical experiments, controlled remotely from the ground. The experiment (ACE-T2) included confocal microscopy using a 532-nm laser, a confocal scanner, and an 8- to 12-bit digital CCD camera. To avoid heat sinks or gradients in the sample that would greatly affect the temperature-sensitive assembly, we used air objectives that have a lower numerical aperture (NA), and thus lower optical resolution, but avoid direct thermal contact with the sample.

The operations included two stages: First, a temperature ramp with a low-magnification lens was used to determine the particle aggregation temperature, T_A , and solvent phase transition temperature T_c . This was done by ramping around the expected critical temperature, T_c , from $T_c - 3^\circ\text{C}$ to $T_c + 1^\circ\text{C}$ during 4h, at a ramp rate of $1^\circ\text{C}/\text{hour}$, and allowed setting an internal temperature reference. As the absolute temperature was not sufficiently reliable, the measurement of both T_A and T_c allowed internal calibration and determination of the temperature difference $DT = T_c - T$, which sets the strength of the critical Casimir attraction. Using a higher magnification (63x) air objective, the aggregation temperature was then determined more closely by ramping the temperature from $T_A - 0.3^\circ\text{C}$ to $T_A + 0.3^\circ\text{C}$ at a low ramp rate of $0.1^\circ\text{C}/\text{hour}$. To study particle assembly, the samples were finally heated to temperatures $T > T_A$ below the critical temperature T_c and observed by confocal microscopy. To ascertain similar initial conditions, the temperature jump to the desired temperature always started from a fixed reference temperature $T_A - 2^\circ\text{C}$, sufficiently below the aggregation temperature, where

the particles did not exhibit any attractive critical Casimir interaction, and the samples were mixed for at least 30 min. Unfortunately, only sample 3, i.e., the mixture of dipatch and tetra-patch particles, survived the launch into space. This sample indeed showed aggregation, as depicted by two representative images 300 min after heating to $DT=0.07^{\circ}\text{C}$ in Fig. 6a and b. Bright white spots indicate the particle patches, which are fluorescently dyed for imaging. The overlaid colored dots indicate a few of the assembled structures. The particles form characteristic motifs as illustrated in Fig. 6c: the dipatch particles assemble into chains (I), while the tetra-patch particles, due to the different angular arrangement of patches and higher valency, form kinks (II) and branching points (III). These structures resemble the early stages of aggregation on the ground, where similar motifs are observed; see Fig. 6d. At later stages, these structures are expected to connect into networks that form equilibrium gels [38]. As the structure of these equilibrium gels is determined uniquely by the bonding geometry of the particles, dictated by equilibrium statistical mechanics, this allows prediction and reverse-engineering of these gels, unlike regular colloidal gels that form by dynamic arrest [32-37]. Unfortunately, the space experiments did not allow observation of the later stages of aggregation due to time limitations. On the ground, the equilibrium networks could be observed, yet in quasi two dimensions only, after the particles had sedimented to the bottom of the sample cell. Therefore, the equilibrium predictions of cluster-size distributions and free energies could only indirectly be confirmed [38]. The current space experiments show the feasibility of performing these temperature-sensitive particle-scale experiments in space using the LMM. Future investigations should focus on the later assembly stages to provide insight into the three-dimensional structure of these networks, their assembly dynamics and reactions of patchy particles and patchy particle clusters. The microgravity environment offers a unique opportunity to observe the assembly of these more complex structures in three dimensions, and under ideal diffusion-limited conditions. The provided temperature control in combination with air objectives, avoiding any heat sink or temperature gradients, then allows for sufficiently accurate remote control of the assembly process, and systematic scanning of the assembly phase space.

Acknowledgement

P.S. and P.S acknowledge support by the VICI personal grant scheme from the Netherlands Organization for Scientific Research (NWO). W.V.M. acknowledges support from the Universities Space Research Association (USRA) with the Glenn Engineering and Research Support (GEARS) contract 80GRC020D0003.

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