Shaping micro-clusters via inverse jamming and topographic close-packing of microbombs

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Designing topographic clusters is of significant interest, yet it remains challenging as they often lack mobility or deformability. Here we exploit the huge volumetric expansion (up to 3000%) of a new type of building block, thermally expandable microbombs. They consist of a viscoelastic polymeric shell and a volatile gas core, which, within structural confinement, create micro-clusters via inverse jamming and topographical close-packing. Upon heating, microbombs anchored in rigid confinement underwent balloon-like blowing up, allowing for dense clusters via soft interplay between viscoelastic shells. Importantly, the confinement is unyielding against the internal pressure of the microbombs, thereby enabling self-assembled clusters, which can be coupled with topographic inscription to introduce structural hierarchy on the clusters. Our strategy provides densely packed yet ultralight clusters with a variety of complex shapes, cleavages, curvatures, and hierarchy. In turn, these clusters will enrich our ability to explore the assemblies of the ever-increasing range of microparticle systems.
Packing and micro-building blocks, including spheres, rods, liquid crystals, and biomaterials from proteins, viruses, and DNA, paves the way to program their collective assemblies in the forms of periodic lattices, aperiodic quasicrystals, “colloidal molecules,” and supramolecules. One of the prerequisites when guiding the formation of densely packed clusters is that the building blocks should be rigid, incompressible, and impenetrable. The face-centered cubic (FCC) and hexagonal close-packed (HCP) lattices assembled from hard spheres have been exploited for their unique optical, electrical, and mechanical properties. As such, there has been increasing interest in synthesizing non-spherical particles or clusters for the most efficient space filling but with the least surface area in three-dimensional (3D) Euclidean space, the so-called Kelvin’s problem, via soft boundaries. The interplay of facets and corresponding face-selectivity, geometry, and topology together with long-range soft interactions could provide the basis for, for example, lock-and-key recognition and the formation of more complex phases such as Frank–Kasper phases (or topologically close-packed phases). Unlike FCC and HCP lattices made of hard spheres, the Frank–Kasper A15 phase, that is, A$_3$B composition consisting of Kasper polyhedral and icosahedra with larger coordination number, can be assembled from soft building blocks, including dendrimers, block copolymers, and giant tetrahedral polyhedral oligomeric silsesquioxane (POSS) cages with favorable boundary conditions, as a counter example to Kelvin’s conjecture.

Meanwhile, jamming, a physical process delineated by crowding and kinetic locking of the constituent particles, including granular materials, glasses, and foams, has led to phase transitions where the aggregates behave like a solid. The jamming transition can be controlled by increasing the particle volume fraction $\phi$ within physical confinement by using changes in density $\rho$, temperature $T$, or stress $\sigma$, facilitated by rapid impact and the application of vacuum or shear stress. Aiming to bridge the two phenomena, i.e., packing and jamming, actively and kinetically, we herein introduce thermally expandable microbombs consisting of a polymeric shell and a volatile gas core. The core undergoes a large volumetric change, up to $\rho$ $\approx$ 3000% above the glass transition temperature ($T_g$) of the polymeric shell, in topographical confinement, providing progress toward programming a library of micro-clusters in a 3D space. To exploit the geometric effect of the physical confinement, we design and prepare microwells via soft lithography with a rigid material that cannot be deformed by the expansion of the microbombs. In the experiments, our system meets all requirements for jamming: an increase in internal stress ($\sigma$↑), a decrease in inter-particle distance ($d$↓), and an increase in interaction energy ($U$↑) between components upon heating the microbombs above $T_g$. In the meantime, the softened viscoelastic shell could freely expand until contacting their neighboring microbombs or the walls of the given confinement. As a result, we created a new type of topographic clusters that have the seemingly contradictory characteristics of dense packing ($\phi$ approaching 1) yet an ultralight weight ($\rho$ ≈ 0, nearly empty, similar to a balloon). For this reason, we refer to the assembly of the microbombs in our system as inverse jamming and topographical close-packing. This strategy leads to a new paradigm of micro-clusters with a wide variety of shapes (e.g., circles, triangles, squares, pentagons, and hexagons in cross-section), partitions (from single to multiple unit cells), edge profiles (from round to sharp corners), and hierarchy.

Results

Introduction of microbombs and their expansion behavior. Unlike conventional hard spheres, the microbomb-building block used in our system has a thin shell of poly(vinylidene chloride-co-acrylonitrile-co-methyl methacrylate) (PVCAMM) encapsulating isobutane gas that has a low boiling point (b.p. $\approx$ −11.7 °C) as illustrated in Fig. 1a. Upon heating above $T_g$ of the polymeric shell, the microbomb can undergo a huge volumetric expansion (> 3000%,...
Thermomechanical properties of the microbombs. Understanding the thermomechanical properties of the microbombs is critical to controlling their expansion, jamming, and packing. A differential scanning calorimetry (DSC) curve showed that the microbomb had a $T_g \approx 97.2$ °C (Fig. 2a). Thermogravimetric analysis (TGA) curves (Fig. 2b) showed that the microbombs lost weight in approximately three stages. At stage one, up to $\approx 100$ °C, there was little loss of weight, probably only dehydration of the microbombs. At stage two, up to $\approx 220$ °C, a steep loss of $\sim 15$ wt% was observed regardless of the heating rates (1, 5, 10, and 20 °C min$^{-1}$). The onset temperature of stage two is consistent with the $T_g$ of the polymeric shell. In contrast, the PVCAMM resin (as a control) showed no weight loss up to 220 °C (see the black curve in Fig. 2b). This result indicates that weight loss at stage two is mainly caused by the isobutane gas escaping through the softened viscoelastic shell. Further heating would lead to gradual thermal decomposition of PVCAMM shell (stage three, $>220$ °C; Supplementary Fig. 2). Below $T_p$, the shell remained glassy, which could restrict high vapor pressure generated by the thermal expansion of isobutane ($\approx 1700$ kPa; Supplementary Table 1). Therefore, no weight loss (Fig. 2c) or volume change (Fig. 2d) was observed at 90 °C. Above $T_p$, however, the shell softened and became viscoelastic such that it could no longer hold its initial form against the accumulated high internal pressures (2000–2700 kPa), leading to volumetric expansion by 600–3000% (Fig. 2d and Supplementary Fig. 3) in $<5$ min. At the highest isothermal temperature ($T = 120$ °C) in the tests, the size of the microbombs decreased after reaching the greatest expansion due to the leakage of
isobutane through the viscoelastic shell (>4 wt%), which in turn would have adverse effects on the jamming and packing; burst clusters were observed (Supplementary Fig. 3d). Therefore, we set the optimal temperature for our studies between 100 and 110 °C, at which the microbombs showed negligible loss of the gas core even after isothermal heating for 2 h.

Overall procedure for fabricating topographic clusters. Figure 3 depicts how microbombs could take advantage of both jamming and packing to shape topographic clusters. First, receding meniscus-induced docking was performed to anchor microbombs to the predefined microwell array. Since the pristine samples showed a broad size distribution, we carried out microfluidic sorting to select the seeds with diameter ranging from 4 to 8 μm (Supplementary Fig. 1). Then, the aq. microbomb solution was dispensed onto PUA patterns with various shapes prepared by soft lithography (Supplementary Figs. 4 and 5). Upon water evaporation, the meniscus receded, and the seeds filled the microwells driven by capillary action (Fig. 3b). After waiting for a few tens of minutes for the microbombs to settle (Fig. 3c), a flat polydimethylsiloxane (PDMS) film was placed with conformal contact on top of PUA microwells to seal the wells. Upon heating, the microbombs expanded to fill the rigid wells, which did not change in size or shape during the process (Fig. 3d). In principle, two aspects were presumed to guide the topographic clustering. First, the initial space or vacancy should be less than the total volume of the microbombs in free expansion. Thus, the microbombs could limit one another’s expansion, converting the internal vapor pressure into the stress need to shape the microbomb clusters within the topographic confinement. Second, the expansion should be sufficiently slow to allow the expanded microbombs to detect the neighboring vacancy, via, for example, rolling and lateral movement. For clarification, we refer to the microbombs before expansion as seeds. On the basis of the high mobility of the microbombs during heating, inverse jamming could occur, leading to monolithic integration of the microbombs via viscoelastic shell-to-shell adhesion. As the end of the procedure, the assembled clusters were detached by using adhesive tape and were released by dissolving the tape in water (Supplementary Movie 2). As seen in Fig. 3e, the partitions within the micro-clusters are reminiscent of the expanded seeds.

Real-time tracking of the deformation of microbombs. To track the packing and jamming processes, we used SEM to examine the clusters after expansion at different temperatures (90, 100, 110, and 120 °C) within square microwells as shown in Fig. 4a. We observed the seeds but no change in the size or shape of individual seeds at 90 °C, topographic clusters with round and sharp edges at 100 and 110 °C, respectively, and burst seeds at 120 °C. These results are in good agreement with the thermomechanical characteristics of the microbombs presented earlier, while the clusters formed at 100 and 110 °C offer a clue for programming the shape of the assembled clusters topographically. The real-time tracking as shown in Fig. 4b–e revealed the high mobility of the microbombs and the trajectory of their jamming and packing processes. For monitoring, pairs of microbombs were seeded into...
Within each well, while the total volume fraction increased with the expansion of the individual seeds (i.e., inverse jamming), the low surface energy of PUA (~20 mJ m$^{-2}$) facilitated the microbombs sliding and rolling to make inter-seed contact. It should be noted that once in contact, the viscoelastic shells formed pressure-sensitive shell-to-shell adhesion; the contact area maintained while the internal stress kept the boundary moving toward any neighboring vacancy. Hence, the paired seeds could show limited mobility yet still be active to the direction that has more free space. Soon, severe stress is applied to the surface in contact as the packing of deformable seeds is much dominant than jamming once they recognize the unyielding walls, topographically deforming the shapes of seeds to yield dense packing similar to the foams in expansion. In the square wells, two distinctive final clusters were observed depending on the initial conditions of the seeds. When they were non-contacted (separated) and positioned at opposite vertices (Fig. 4b), discotic expansion occurred until they met each other ($t < 31$ s; Fig. 4b). At $t \sim 77$ s, a diagonal partition between two triangular unit cells (i.e., the expanded microbombs) was generated. When the two seeds were in contact initially (paired), they expanded isotopically in two dimensions (discotic) as they are free even the contact maintained ($t \sim 10$ s, Fig. 4c). The cluster then asymmetrically expanded side by side by deforming the shells to fulfill the dense-pacing in the well, forming two rectangular cells ($t \sim 92$ s). The evidence of jamming is much clear in addressing initial interaction between the two separated seeds as seen in Fig. 4d (see the black and red circles, <5 s, and Supplementary Fig. 6). We attribute such distinctive differentiation in clustering to the pinning of the seeds at the vertices. In contrast, half-and-half partition of the microbombs within a cluster was always observed in the circular well regardless of the initial positions of the seeds (Fig. 4d, e). Theoretically, in square confinement, the center-to-center distance between two triangular cells is 11.7 µm (defined as $\sqrt{2}L$, where $L$ is the length of the side of the square, 20 µm). In the case of two rectangular cells, the distance is 10 µm. As seen in Fig. 4f, the experimental results are in good agreement with the theoretical prediction. Interestingly, the two curves obtained from the cells in circular confinement converged at the early stage of the process, <0.4 (a time normalized to the on-set time when the center-to-center distance starts to converge) vs. 0.6 in square confinement, implying that the microbombs were much more mobile in the circular well, where only one degree of freedom is programmed in the topographic clustering process. We elucidate further design rules to define degrees of freedom of clusters in the next section.

**Fig. 4** Real-time tracking of the micro-cluster formation. a) SEM images and the corresponding illustrations of the clusters formed at different temperatures. b, c) Optical images and corresponding illustrations of the trajectories of a pair of microbombs that are separated (b) and paired (c) upon explosion in square confinement. d, e) Optical images and the corresponding illustrations of circular confinement of two separated (d) and paired (e) microbombs. f, g) Plots of center-to-center distances between two constituent cells as a function of time normalized by the time required to reach the convergent center-to-center distance within square (f) and circular (g) confinement.

**Programming the degrees of freedom in topographic clusters.** Empirically, the final clusters can be programmed by the number of seeds ($N = 1, 2, 3, …$) and the number of vertices of the well ($V = 0, 3, 4, 5, 6$ for circles, triangles, squares, pentagons, and hexagons, respectively) providing topographic confinement. As shown in Fig. 5a, we analyzed over 2000 clusters. In the confinement of $N = 1$, single-cell particles could be created by...
Fig. 5 A library of topographic clusters. a SEM images of the clusters and the corresponding illustrations. The number of cleavages of each cell corresponds to the number of the initial seeds. b, c Close-up SEM images of the triangular prisms (b) and four-cell cubes (c). The last image of each group shows the cavity within the clusters, for which they were cut by the FIB.

Fig. 6 Hierarchical leveling on the topographic clusters. a SEM image of a single-cell microbump with nanoscallops on the sidewall. b Nanoimprinting on the surface of the cluster particle to achieve further hierarchy. c, d SEM images of the nanoline mold (600 nm line width, c) and the clusters imprinted with nanolines on top (d). e, f SEM images of the mold of hole patterns (e) and the complementary hierarchical clusters with nano-pillars (600 nm in diameter and 600 nm in height) after the explosion (f).
The SEM images in Fig. 5b, c reveal the hollow nature of the clusters from a triangular prism (Fig. 5b) and a cube with walls after the explosion as shown in Fig. 6a (red arrows), where image of the triangular prism reveals nanostructures on the side. Topographical imprinting of microbombs permanently. (FIB) milling. At room temperature, the shell became glassy cleavage connecting four cells (Fig. 5c) after focused ion beam ion-etching process. During the explosion, the internal pressure exceeded 2500 kPa, high enough to push the viscoelastic shells cleavages, the edge profiles, and the hierarchy. We could adopt a library of molds fabricated by soft lithography for physical guidance during the microbomb explosions, which would be useful for exploring the diversity of forms in the final clusters with predesigned vertices V. Clusters with circular, triangular, square, pentagonal, and hexagonal cross-sections have been presented via the in situ, one-step explosion process in this paper. Furthermore, the complexity could be differentiated between clusters with the same vertices by modulating the number of initial seeds (that is, creating cleavages). Depending on the shape of the confinement well, symmetric or asymmetric partitioning of the clusters occurred, and the adjacent microbombs were integrated side by side with no interstitial voids as a result of the inverse jamming and topographically close-packing. Moreover, the edge profile could be modulated by the trigger temperature; sharp edges were obtained at higher temperatures (Supplementary Figs. 7 and 8). Finally, additional complexity and hierarchy could be introduced by imprinting the surfaces of the clusters. Although not a focus here, 3D shaping of the clusters should be possible. As seen in Fig. 7b–d, we prepared pyramidal clusters with various morphologies by precisely controlling the degree of expansion. Further, the hollow and ultralight weight nature of the clusters enables facile collection of them with batch-to-batch processability as shown in Supplementary Figs. 9 and 10, where ~6.25 × 10^6 particles were obtained by the one-step process using the well size of 20 μm × 20 μm × 20 μm with 1:1 spacing ratio from the 10 × 10 cm^2 patterned area. The adhesive interactions between the viscoelastic shells could be further modulated by imprinting against nanoholes (600 nm in diameter; Fig. 6e, f). Since the surface of the pristine microbomb is rough, imprinting on the clusters offers an alternative way to create smooth facets together with introducing hierarchical cleavages. Previously, we demonstrated the creation of structural hierarchy within flexible, free-standing membranes together with multilevel structures. Here topographic assemblies with a hierarchy are obtained by nanoimprinting the microbombs during their expansion and topographic clustering.

**Discussion**

To highlight the capability toward topographic clustering by inverse jamming and packing of microbombs, we illustrated a set of design rules on complexity in Fig. 7a, including the mold shapes (V) for confinement, the number of seeds (N) and partitioning in the cluster to design cleavages, the sharpness of edges around the cluster, and the hierarchy. We could adopt a library of molds fabricated by soft lithography for physical guidance during the microbomb explosions, which would be useful for exploring the diversity of forms in the final clusters with predesigned vertices V. Clusters with circular, triangular, square, pentagonal, and hexagonal cross-sections have been presented via the in situ, one-step explosion process in this paper. Furthermore, the complexity could be differentiated between clusters with the same vertices by modulating the number of initial seeds (that is, creating cleavages). Depending on the shape of the confinement well, symmetric or asymmetric partitioning of the clusters occurred, and the adjacent microbombs were integrated side by side with no interstitial voids as a result of the inverse jamming and topographically close-packing. Moreover, the edge profile could be modulated by the trigger temperature; sharp edges were obtained at higher temperatures (Supplementary Figs. 7 and 8). Finally, additional complexity and hierarchy could be introduced by imprinting the surfaces of the clusters. Although not a focus here, 3D shaping of the clusters should be possible. As seen in Fig. 7b–d, we prepared pyramidal clusters with various morphologies by precisely controlling the degree of expansion. Further, the hollow and ultralight weight nature of the clusters enables facile collection of them with batch-to-batch processability as shown in Supplementary Figs. 9 and 10, where ~6.25 × 10^6 particles were obtained by the one-step process using the well size of 20 μm × 20 μm × 20 μm with 1:1 spacing ratio from the 10 × 10 cm^2 patterned area. The adhesive interactions between the viscoelastic shells could be further modulated by...
applying a low friction coating, allowing for disassembling the unit seeds from the assembled clusters (Supplementary Fig. 1). We believe that the microbombs offer a model system of adaptive building blocks to design more complex yet functional and ultra-lightweight particles by clustering via jamming and packing.

Methods

Microfluidic sorting of microbombs. The microfluidic platform was fabricated by following the designs in literature for sorting microbombs, which have broad size distributions. A PDMS microchannel was replicated from the Si master and connected to a glass slide after oxygen plasma treatment for 1 min ( Femto Science Inc., Cote 90033C). After connecting tubes to both the inlet and the outlets, we introduced the microbombs solution at a flow rate of 1 ml min⁻¹ using a syringe pump (Pump 11 Elite, Harvard Apparatus, Holliston).

Anchoring microbombs for topographic confinement. A mixture of PDMS (Sylgard 184, Dow Corning, MI, USA) and curing agent (10:1 wt/wt) was poured on the water due to the adhesion of the tape with water, the individual clusters dissolving the tape with water, the individual clusters were collected for SEM imaging. To release the clusters, water-soluble adhesive tape (5414, 3M, MN, USA) was used to remove the clusters from the micro-con...
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Author contributions
S.Y. and H.C. contributed equally to this work. C.M.K. and S.Y. led this work. S.Y., H.C., J.P.H., H.P., J.C.J., H.S.K., J.K., and S.H.L. performed experiments. S.Y., H.C., A.S.L., S.Y., and C.M.K. wrote the manuscript. S.M.H., J.H.L., and C.P. analyzed data.

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