Colloids in Curved Space

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Self-assembly of nanoscale objects is of essential importance in materials science, condensed matter physics, and biophysics. Curvature modifies the principles and sequence of self-assembly in Euclidean space, resulting in unique and more complex structures. Understanding self-assembly behavior in curved space is not only instrumental for designing structural building blocks and assembly processes from a bottom-up perspective but is also critically important for delineating various biological systems.

Keywords: curved space ; self-assembly ; colloids

1. Introduction

Self-assembly refers to the process by which disordered systems, without external intervention, organize into an ordered structure through interactions among their constituents [1][2][3]. This process is driven by thermodynamic equilibrium, with the organized structure possessing the lowest free energy within the system. Colloids refer to fluid mixtures in which dispersed particles have sizes ranging from 1 nm to 1 µm, which are commonly found in the natural world and biological systems. When colloidal particles aggregate, many fascinating phenomena, including self-assembly, can emerge. In contrast to atomic and molecular systems, the self-assembly of colloidal particles predominantly relies on forces such as DNA-mediated interactions ^[4], van der Waals forces ^[5], electrostatic interactions ^[6], and hydrophobic effects ^[7]. These forces are considerably weaker than chemical bonds [8] and, thereby, cannot entirely dictate the formation of the most stable structure. Thus, entropy plays an indispensable role in the self-assembly of colloidal particles. Self-assembly phenomena are abundant in biological systems, such as viruses [9], bacteria [10], and living cells [11], and a comprehensive understanding of these processes is essential for unraveling the complexity of life. These instances of self-assembly can serve as a source of inspiration for the design of biomimetic systems or play a role in medical applications like targeted drug delivery. However, biological systems often feature numerous curved interfaces, and the presence of interfaces frequently exerts a profoundly influential and determinative impact on the overall system's properties. The introduction of curvature significantly enriches the processes and outcomes of self-assembly. Due to the mismatch between locally favorable structures and curved space or the hindrance of evolution paths by curvature, ordered structures [12][13], phase transitions [14][15], and dynamic processes [16] in curved space differ significantly from normal space. Additionally, the inherent defects brought about by topology create new order structures and generate new physics, making topology an equally important controlling factor alongside free energy. In recent years, the field of interface self-assembly at the nanoscale has gradually emerged [17][18], where curved interfaces often serve as scaffolds for nanodevices, functioning as constraints and templates [19][20][21][22]. At the same time, with the development of nanoscale synthesis methods [23], the variety of particles involved in self-assembly has greatly expanded, including grafted particles [24], Janus particles [25], various shapes of hard particles [26][27][28], mesoporous particles [29], and more. This enables more precise, complex, and widespread self-assembly. Therefore, understanding the physical processes of particle self-assembly in curved space is of great significance, aiding in the design of new heterogeneous materials or offering new perspectives on some biological processes.

2. Colloids in Curved Space

A brief overview of cases of colloidal particle self-assembly in two-dimensional (2D) and three-dimensional (3D) curved spaces is provided. The fundamental physical rules of self-assembly in curved space and the influence of curvature is summarized. This helps illustrate how curvature can be used to control the outcomes and processes of self-assembly.

Consider identical hard disks packing on a 2D plane. In the densest packing arrangement, these particles naturally form a hexagonal lattice structure, with each particle having six nearest neighbors, and the hexagons can densely cover the entire 2D space. When the plane becomes curved, the introduction of curvature changes the distance distribution among the particles because the sum of the interior angles of curved triangles is not equal to π . This alteration in distance

distribution results in a change in the number of nearest neighbors for the particles. By using the Voronoi partition, researchers can determine the number of nearest neighbors for each particle, denoted as *c*, which corresponds to the number of edges of the Voronoi polygons surrounding the particle. The basic idea is to create polygons around each seed point in such a way that every point within a given polygon is closer to the associated seed point than to any other seed point. Particles with a number of nearest neighbors different from 6 are referred to as defects, and the charge of a defect is defined as q=6-c. On a plane, the appearance of defects is only related to the density and polydispersity of particles. Regular and dense crystals are formed at high density. Determining the type and quantity of defect particles on a curved surface requires applying Euler's formula, which relates the number of vertices (*V*), edges (*E*), and faces (*F*) of Voronoi polygons in a network:

$$V - E + F = \chi \tag{1}$$

 χ is the Euler characteristic, determined by the shape of the curved surface. If researchers replace *V*, *E*, and *F* in the Euler formula with the number of edges per Voronoi polygon *c* and the number of Voronoi polygons *N_c*, researchers can obtain the total defect charge determined by topology:

$$\sum (6-c)N_c \ge 6\chi \tag{2}$$

Indeed, you can relate curvature and the Euler characteristic using the Gauss-Bonnet theorem. The theorem states that for a closed surface M with Gaussian curvature K, the Euler characteristic is related to the total Gaussian curvature over the entire surface:

$$\int_{M} K dA + \int_{\partial M} k_{g} ds = 2\pi \chi(M)$$
(3)

where *dA* represents the area element of the surface and *ds* is the line element of the boundary of *M*. This equation provides a valuable relationship between geometry and topology. For a sphere, χ =2, and 12 pentagon defects can form a regular icosahedron structure. For a cylinder and a plane, the Gaussian curvature is zero everywhere, which allows particles to form a defect-free perfect structure. For surfaces with negative curvature, χ <0, and heptagon defects may dominate. In crystallography, isolated defects that alter the rotational symmetry are referred to as disclinations ^[30], while defects formed by the connection of a pentagonal and heptagonal defect, disrupting translational symmetry, are known as dislocations. Dislocations, having positive and negative charges that cancel each other out, do not have a necessary topological existence. They appear to accommodate variations in curvature, driven by local geometric requirements and are consequently referred to as excess defects.

Irvine et al. ^{[13][31]} further investigated the relationship between the total defect charge and interface shape by confining fluorescent PMMA particles to interfaces of various shapes, including spherical, arched, waist-shaped, barrel-shaped, and planar. The topological shape of the interface dictates the total defect charge. For interfaces of different shapes, whether with charged or neutral particles, the total defect charge is approximately equal to the integral of the interface Gaussian curvature. The presence of defects is analogously likened to pleats, and they adapt to the rapid changes in surface curvature by forming continuous dislocations. Subsequent simulations have confirmed and expanded upon these experimental findings ^[32]. The type, location, and orientation of defects are closely related to the curvature. Under weak curvature, excess defects like pleats appear, with their orientation following the direction of the fastest Gaussian curvature change, while under strong curvature, disclinations arise near regions of maximum (minimum) curvature.

Although the aforementioned studies provide a clear topological relationship between the total defect charge and interface shape, in specific systems, the number and spatial arrangement of each type of defect still depend on the potential energy interactions between particles and local geometric requirements. This is exemplified by the scar-like structures on a spherical surface. Bausch et al. ^{[12][33]} explored the self-assembly of colloidal particles with arbitrary repulsive interactions on a constrained spherical surface, where 1 μ m diameter cross-linked polystyrene microspheres adhered to the surface of water droplets with a radius *R*. When the number of particles is low, the spherical surface exhibits only 12 + 1 charge defects. However, when the number of particles, it was discovered that the excess dislocation count is linearly related to *R*/a. In other words, on a larger constrained spherical surface, there are more defects. Observing the distribution of defects further reveals that they exist in the form of scars. On each scar, the coordination number of

particles varies as ... 5-7-5-7-5 ... The total defect charge on each chain of defects is +1. The locations of the twelve scars correspond to a regular icosahedral structure.

On the one hand, these scars act as grain boundaries between different crystal regions, causing a change in crystal axis orientation whenever the crystal axis extends to the scar's position to adapt to the curvature of the sphere. On the other hand, the presence of these scars serves to reduce the elastic energy loss caused by individual pentagonal defects. Using elastic theory ^[34], it can be calculated that the length of each scar in the ground state should be 33.56° . Therefore, the number of excess defects on the sphere follows a linear relationship with *R*/*a*.

From these studies, it can be concluded that the self-assembly in curved space results from the interplay between locally favorable structures, topology, and geometry. This principle applies to 3D space as well. Taking the example of hard sphere packing, as the packing density increases, the system enters an ordered structure at a packing density of approximately 0.64 ^[35] and eventually forms a face-centered cubic (FCC) or hexagonal close-packed (HCP) structure at a packing density of 0.74 ^{[36][37][38]}. Although FCC and HCP structures are energetically favorable, they cannot perfectly fill the entire spherical space, especially under strong confinement. To maximize each particle's free volume or entropy, the structure that aligns better with spherical symmetry is the icosahedron. However, as the degree of confinement decreases with a larger sphere, the system transitions from the icosahedron structure through a rhombicosidodecahedron structure to an FCC structure ^[39]. The observation of such structures changing with the degree of confinement has also been observed in simulations of cylindrical confinement ^[40]. This phenomenon is not limited to spherical confinement but is a general characteristic of self-assembly in 3D confined spaces. The dynamics of this crystallization process, as revealed through event-driven molecular dynamics (EDMD) simulations, suggest that the crystallization initiates at the spherical constrained surface, forming multiple layered structures inward.

In addition to the changes in self-assembled structures, another characteristic of 3D confined self-assembly is the presence of numerous local optimal structures. The number of particles at specific values forms self-assembled structures with better compatibility with spherical symmetry, known as the magic number [41][42]. Whether under attractive potentials or hard interactions, these structures often have enhanced stability, higher packing densities, and average particle-free energy at a local minimum due to maximizing the number of neighboring particles [43]. Not only within a sphere but also within a cylindrical confinement, an optimal cylinder radius exists that maximizes the packing density to achieve a local maximum [44][45][46][47].

In addition to structural, the influence of curvature on self-assembly is also reflected in deeper aspects, such as phase transitions and crystallization dynamics. Phase transitions in 2D systems differ from those in 3D space, and there are various microscopic theories for 2D phase transitions, with the KTNHY theory being the most famous [48][49][50]. This theory predicts that phase transitions in 2D space are mediated by defects and involve two continuous processes: the unbinding of dislocation pairs disrupts translational symmetry while preserving orientational symmetry, leading the system from a solid phase to a hexatic phase. The separation of dislocations forms disclinations, breaking orientational symmetry and transitioning the system into a liquid phase. On a spherical surface, particles with dipole potentials undergo phase transitions as the dimensionless interaction parameter Γ changes, and both crystallization and melting processes follow the KTNHY theory [14][15]. However, due to the presence of inherent defects, the potential strength required for phase transitions differs from the results on a flat plane [51], and the curvature, to some extent, hinders crystallization. During the crystallization process, defects that occur in normal positions are eventually absorbed by grain boundaries, leading to the formation of the twelve scars. This has been confirmed in interstitial experiments on curved surfaces [52][53], where dislocations are more likely to move in the direction parallel to Burger's vector [16] and are subsequently absorbed when they reach a grain boundary. However, what is surprising is that during the melting process, the positions where free dislocations are generated are unrelated to grain boundaries. Instead, they randomly occur within the regular hexagonal lattice.

In Euclidean spatial crystallization, nucleation theory is often used to explain the process. In confined spaces, however, crystallization frequently initiates at the outer layers near the confining interface and progresses inward, resulting in the formation of complex multi-layered structures ^{[26][39][54][55]}. The curved interface acts as a template, influencing the final crystalline structure. When hard spheres crystallize within a sphere or a cylinder ^{[39][40]}, they first form distinct crystal domains on the surface, and then the growth occurs inward. The competition and matching between the external and internal structures determine the final structure. In the case of systems with potentials, the situation is even more complex ^[54], and this competition exists in both thermodynamic and kinetic aspects. Crystallization initially occurs on the surface in the form of defects with icosahedral symmetry. It then grows inward through body-centered cubic (BCC) solid metastable states. Over an extended period, the structures formed by shorter-range (harder) interaction are predominantly FCC but

are separated into icosahedral symmetry regions by the HCP domain. The structures formed by longer-range (softer) interactions are closer to BCC single-crystal.

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