Topological vacancies in spherical crystal clusters

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Understanding geometric frustration of ordered phases in two-dimensional condensed matters on curved surfaces is closely related to a host of scientific problems in condensed matter physics and materials science. Here we show how two-dimensional Lennard-Jones crystal clusters confined on a sphere resolve the geometric frustration and lead to pentagonal vacancy structures. These vacancies, originated from the combination of curvature and physical interaction, are found to be topological defects and they can be further classified into dislocational and disclinational types. We analyze the dual role of these crystallographic defects as both vacancies and topological defects, illustrate their formation mechanism, and present the phase diagram. The revealed dual role of the topological vacancies may find applications in the fabrication of robust nanopores. This work also suggests the promising potential of exploiting the richness in both physical interactions and substrate geometries to create new types of crystallographic defects, which have strong connections with the design of crystalline materials.

I. INTRODUCTION

Geometric frustration of ordered phases in two-dimensional condensed matters like crystals and liquid crystals confined on curved surfaces can create a myriad of emergent static [1-4] and dynamic [5-8] defect structures. Through the Thomson problem of finding the ground state of electrically charged particles confined on a sphere [9, 13] and the generalized versions on typical curved surfaces [14, 17], several defect motifs in crystalline order like isolated disclinations, dislocations, scars and pleats have been identified in the past decades [15, 19]. As a fundamental topological defect in crystalline order, a disclination refers to a vertex whose coordination number n is deviated from six in two-dimensional triangular lattice, and a topological charge of $q = 6 - n$ can be assigned to an n-fold disclination [11]. A dislocation is a topological dipole composed of a pair of oppositely charged fivefold and sevenfold disclinations. Scars and pleats are strings of fivefold and sevenfold disclinations [2, 15, 20]. These frustration-induced defects are highly involved in many important physical processes like 2D crystal melting [21, 24], crystalline packings of twisted filament bundles [25, 29], self-healing of crystalline order [17, 30], non-equilibrium behaviors in active matters [16, 27, 31, 32], and materials design [33, 38]. In a recent study, by creating depletion-induced attraction between colloidal particles confined in the interior surfaces of spherical water-in-oil droplets, vacancies are observed to proliferate in the resulting spherical crystals [39]. While the disclination structure in spherical crystals has been extensively studied theoretically and experimentally [11, 14, 34-40], 5-7 vacancies are generally unstable in spherical crystals where particles interact by the long-range Coulomb potential [12, 13]. The discovery of the stable vacancies as a new defect motif in the curved crystals composed of attractive colloidal particles raises a number of important questions, such as their topological nature, the mechanism behind their formation, and their connection with the fundamental topological defects of disclinations and dislocations.

A model system suitable to address all these questions is to consider a collection of point particles confined on a sphere interacting via the Lennard-Jones (L-J) potential. The combination of depletion-induced short-range attraction and hard-core repulsion between colloidal particles seems responsible for the experimentally observed vacancies in the rigid, two-dimensional colloidal crystals on spherical droplets. L-J potential possesses both attractive and repulsive components and is a suitable form of interaction potential to study the physics of vacancies. The formally simple L-J potential has also been extensively used to model various chemical and physical bonds. [43] To lower the energy, the L-J particles on a sphere are expected to spontaneously form geometrically frustrated crystal clusters. We resort to numerical simulations in combination with analytical theory to track the frustration of these spherical crystals and analyze the resulting defect structures therein. To highlight the geometric effect and avoid mixing the curvature driven stress and the stress due to the area constraint, we focus on particle clusters not fully occupying the sphere and under free stress boundary condition [44]. Note that the model of L-J spherical crystal has been previously employed to study underlying physics in several aspects of shell assembly like line tension, hole implosion and closure catastrophe, where vacancy structure has been reported but its topological property is still to be clarified [15].

In this work, we reveal the proliferation of pentagonal vacancies in spherical crystal with the accumulation of curvature effect which are absent in planar crystals. According to their topological nature, the pentagonal vacancies can be classified into two categories: the type I dislocational and type II disclinational vacancies. These two types of vacancies are topologically equivalent to 5-7 disclination pairs and 5-7-5 disclination strings, respectively. Remarkably, both vacancies exhibit the identical pentagonal morphology despite their distinct topological properties. Simulations show that their emergence is controlled by the coverage ratio of the crystal cluster...
over the spherical substrate. Geometric and elastic analysis shows the compatibility of the pentagonal vacancies with spherical geometry. The revealed dual role of these crystallographic defects as both vacancies and topological defects may be exploited in the fabrication of nanopore structures in crystalline membranes. \[40, 47\] This work also suggests the promising possibility of using the combination of physical interaction and geometry to create rich types of defects that may find applications in the design of crystalline materials.

II. MODEL

In our model the particles confined on the sphere of radius \(R_0\) interact via the L-J potential \(V(r) = 4\epsilon_0[(\sigma_0/r)^{12} - (\sigma_0/r)^6]\). The balance distance \(r_m = 2^{1/6}\sigma_0\). The initial configuration of the spherical crystal cluster is prepared in the following way. We first place a line of evenly distributed \(M\) particles on the equator of the sphere, and then pile particles layer by layer along the lines of latitude separated by a distance of \(\sqrt{3}\sigma_m/2\) to fabricate a hexagonal crystal cluster. The total number of particles in the constructed spherical cluster is \(N = \frac{1}{2}(3M^2+1)\). The initial configuration is free of stress in the limit of \(R_0 \rightarrow \infty\). We employ the force method in simulations to track the evolution of the prepared crystal cluster towards the lowest-energy state. \[48, 50\] We first calculate the force on each particle by all the other particles, and then simultaneously move all the particles by a small distance of \(s\) in each step until the energy of the system does not reduce any more. Typically, \(s = 10^{-4}r_m\). The system evolves towards the lowest-energy state by repeating this procedure. The underlying topological defect structures in the spherical crystals are analyzed by performing Delaunay triangulation with the software Qhull. \[51\] All the lengths are measured in the unit of \(r_m\). The controlling parameters are the radius of the sphere \(R_0\) and the coverage ratio \(A/A_0\) of the crystal cluster. \(A\) and \(A_0\) are the areas of the crystal cluster and the sphere, respectively. Note that in general a condensed matter system composed of many interacting particles can be easily trapped in a metastable state. \[29, 52\] Furthermore, due to the constraint imposed by the initial configuration of the fixed hexagonal lattice, there is high probability that the resulting lowest-energy particle configurations found in our simulations are not the true ground states. However, it is observed that the defect structures identified in the evolution of the crystal clusters can facilitate the reduction of energy. It is therefore expected that the revealed topological vacancies can characterize the basic defect state in the true ground state.

III. RESULTS AND DISCUSSION

Figure 1 shows the configurations of particles mapped to the \(\{\theta, \phi\}\) plane, where \(\theta\) and \(\phi\) are the polar and azimuthal angles in spherical coordinates. \(\theta \in [0, \pi]\), \(\phi \in [0, 2\pi]\). The stretching and compression of the bonds are indicated by the red and blue lines, and more transparent bonds assume less stress. A planar crystal can wrap a developable surface of zero Gaussian curvature via pure bending without introducing any in-plane stress. \[53\] However, the geometric incompatibility between a planar crystal and a spherical substrate leads to the coupling of bending and in-plane strain. \[54, 55\] In other words, the originally planar crystal must modify its metric by adjusting the bond length when it bends to fit the spherical geometry. The distribution of the in-plane stress in the defect free configuration at \(A/A_0 = 0.08\) is shown in Fig. 1(a). The basic feature of the stress field is that the interior part of the crystal is azimuthally stretched (the hoop stress \(\sigma_{\theta\theta} > 0\) for \(r < r_c\)), the exterior part is azimuthally compressed (\(\sigma_{\theta\theta} < 0\) for \(r > r_c\)), and the crystal is radially stretched everywhere (the radial stress \(\sigma_{rr} > 0\)).

To understand the numerically observed stress pattern on the defect free spherical crystal as shown in Fig. 1(a), we consider the elastic deformation of the originally planar crystal. The two-dimensional crystal cluster can be modelled as an isotropic elastic sheet whose elastic prop-

FIG. 1: Proliferation of pentagonal vacancies (in green) in crystal cluster on a sphere with accumulation of the curvature effect. The stress pattern indicated by colored bonds (red for stretching and blue for compression) is consistent with analytical elasticity theory (see text for more information). The plots are in the plane of the spherical coordinates \(\{\theta, \phi\}\). In each case, the coverage ratio of the crystal cluster \(A/A_0\) is fixed. The inset in (b) is to illustrate the dislocational nature of the vacancy. \(R_0 = 20\).
properties are characterized by the Young’s modulus $Y$ and the bending rigidity $B$. The ratio $t = \sqrt{B/Y}$ is the effective thickness of the sheet. For simplicity, we consider a circular elastic sheet of radius $r_0$. $r_0 << R_0$, and $r_0 >> t$, so the stretching energy of the sheet dominates over the bending energy in the deformation. Therefore, it suffices to analyze the stress state over a planar elastic sheet. The effect of the spherical substrate is to impose a normal force per area $P$ over the elastic sheet and to pull the sheet on its edge by the force $F_T$ per unit length to deform the sheet. The distribution of the in-plane stress is governed by the force balance equations. With the boundary conditions of $\sigma_{rr}(r = 0) = \sigma_{\theta\theta}(r = 0) = 0$, and $\sigma_{rr}(r = r_0) = F_T$, one can derive the analytical expressions for the in-plane stress field: 

$$\sigma_{rr}(r) = \frac{\beta (1 - (r/r_0)^2)}{16 + 1}$$

and

$$\sigma_{\theta\theta}(r) = \frac{\beta (1 - (r/r_0)^2)}{16 + 1}.$$ 

The sheet is under pure tension for $\beta < 8$. For $\beta > 8$, the hoop stress $\sigma_{\theta\theta}$ becomes compressive at the annulus $r \in (r_0 \sqrt{1 + \beta^2}, R_0)$. The coexistence of positive and negative $\sigma_{\theta\theta}$ regions in the spherical crystal in Fig. 1(a) indicates that it falls in the regime of $\beta > 8$.

For larger spherical crystal clusters, we observe the proliferation of vacancies as shown in Fig. 1(b)-1(e). A vacancy in the triangular lattice can be identified where the local particle density is significantly lower than the surrounding lattice. Remarkably, we notice that these vacancies are pentagonal, which are different from the hexagonal vacancies in two-dimensional planar L-J crystals. Geometric analysis reveals the dislocational nature of these pentagonal vacancies. The inset of Fig. 1(b) illustrates the extra (red) line of particles terminated at the vacancy. The integration of the resulting displacement field along any contour enclosing the vacancy returns the constant Burgers vector $\vec{b}$ that characterizes the dislocational nature of the pentagonal vacancy. Delaunay triangulations show the dislocational nature of the vacancies in Fig. 1(b); they can be represented by a pair of fivefold [the red dot on the circled green pentagon in Fig. 1(b)] and sevenfold [the blue dot] disclinations. Here, we note that in the spherical crystals formed by long-range repulsive particles, vacancies and interstitials are attracted and repelled by five-fold disclinations, respectively. Consequently, both vacancies and interstitials typically break up when subjected to interactions with multiple disclinations. These defects are therefore generally unstable, and have never been found in equilibrium spherical crystals where particles interact by the long-range Coulomb potential.

Comparison of the configurations in Fig. 1(a) and Fig. 1(b) shows that the pentagonal vacancies initially appear at the interface of the compression and stretching zones. To account for these preferred sites for the emergent defects, we examine the stress field of an isolated dislocation in a two-dimensional isotropic elastic medium. In polar coordinates, we have the stress field around an isolated dislocation:

$$\sigma_{rr} = \sigma_{\theta\theta} = -\frac{bB \sin \theta}{r}$$

(1)

and

$$\sigma_{r\theta} = \frac{bB \cos \theta}{r},$$

(2)

where $B = \mu/2\pi(1-\nu)$, $\mu$ is the shear modulus, $\nu$ is the Poisson’s ratio, and $b$ is the magnitude of the Burgers vector. $\theta$ is measured with respect to the direction of the Burgers vector. From eqn (1), we see that both radial and hoop bonds are stretched for $\theta \in (0, \pi)$ and compressed for $\theta \in (\pi, 2\pi)$. Our simulations reveal stretched red bonds and compressed blue bonds around the vacancy in the inset of Fig. 1(b). Such a stress pattern is consistent with the above elastic analysis based on the assumption of continuum elastic medium. The superposition of this stress field on the stress pattern in Fig. 1(a) can release both the compression in the exterior region $[\theta \in (0, \pi)]$ and the stretching in the interior region $[\theta \in (\pi, 2\pi)]$. Therefore, the pentagonal vacancies prefer to emerge at the interface of the compression and stretching zones to release the elastic energy.

With the increase of the coverage ratio $A/A_0$, Fig. 1(c)-1(e) show that the spherical crystal is plagued with more dislocational pentagonal vacancies. The arrangement of these defects seems to follow some pattern. The distribution of the defects qualitatively conforms to $p$-fold rotational symmetry. The value for $p$ increases from 2 (at $A/A_0 = 0.09$) to 5 (at $A/A_0 = 0.18$). Note that similar symmetric patterns of boundary defect strings as well as their broken-symmetry states in the form of forked-scar morphologies have been found in crystalline spherical caps under external tension by the combination of...
“free dislocation” simulations and continuum elasticity theory. \[11\] The internal dislocational defects in Fig. 1 also leave their signature in the exterior morphology of the crystal cluster; we will show later that the steps on the contour of the crystal cluster originate from the internal dislocations. In Fig. 1(e), we notice the unevenly distributed vacancies at the same defect string. The equally placed dislocations constitute a grain boundary to separate crystallites of distinct crystalline orientations. \[52\] Here, the spatial gradient in the density of dislocational vacancies will lead to net topological charges according to the elasticity theory of topological defects. \[11\] Furthermore, the observed inhomogeneity in the arrangement of defects in Fig 1(e) implies the appearance of disclinalional defects at even higher coverage ratios.

Further increasing the coverage ratio leads to more pentagonal vacancies as shown in Fig. 2 for $A/A_0 = 0.50$. These vacancies can be classified by their associated topological charge. Through Delaunay triangulation, we identify a new type of pentagonal vacancy carrying positive topological charge. Such a vacancy is of disclinalional nature, and is fundamentally different from the previously discussed dislocational vacancy. In Fig. 2, the two types of vacancies are indicated with different colors: dislocational vacancies by green pentagons, and disclinalional ones by purple pentagons. The distinct nature of the pentagonal vacancies can also be characterized by the deformation of the lattice lines. In the inset of Fig 2, we illustrate that the lines 1 and 2 are still in parallel after passing a type I dislocational vacancy; their separation is increased by a Burgers vector’s length. In contrast, the originally parallel lattice lines 3 and 4 are observed to bend and converge when passing a type II disclinalional vacancy, which resembles the convergence of light rays through a convex mirror. \[15\] \[58\]

We propose a geometric argument based on Gauss-Bonnet theorem to show that the bending of the lattice lines around a type II vacancy is compatible with the underlying spherical geometry. \[54\] For a compact two-dimensional Riemannian manifold $M$ with boundary $\partial M$, Gauss-Bonnet theorem states that $\int_M K_G dA + \int_{\partial M} k_g ds = 2\pi \chi(M)$, where $K_G$ is the Gaussian curvature, $k_g$ is the geodesic curvature, and $\chi(M)$ is the Euler characteristic of the manifold $M$. Applying Gauss-Bonnet theorem on a geodesic triangle $\Delta_{g,t}$, formed by three geodesics on the sphere, we obtain an elegant expression that connects the total curvature with the three angles: \[54\]

$$\int_{\Delta_{g,t}} K_G dA = \frac{3}{2} \sum \theta_i - \pi,$$

where the integration is over the geodesic triangle. It is straightforward to check that the total curvature of a planar triangle is zero.

Now let us consider a region enclosed by two converging geodesics over the sphere. Bidirectional extension of two originally parallel geodesics on the sphere will finally converge to form an eye-like shape. This region can be divided into two geodesic triangles. From eqn (3), we obtain the total curvature

$$\int K_G dA = \alpha_1 + \alpha_2,$$

where $\alpha_1$ and $\alpha_2$ are the angles at the two tips of the eye-like region. The total curvature is smaller when the eye-like shape becomes sharper. The limiting case is two parallel straight lines in a plane where the total curvature vanishes. The convergence of the approximately geodesic lines 3 and 4 in the inset of Fig. 2 is therefore compatible with the positive Gaussian curvature. Note that the convergence of lattice lines through a type II vacancy is also seen in Volterra construction for disclinations. \[52\] Specifically, a positive (or negative) disclinalional defect in two-dimensional triangular lattice can be constructed by removing (or inserting) a wedge of angle $\pi/3$; this operation leads to the convergence (or divergence) of originally parallel lines over a planar disk. \[15\]

In Fig. 3, we present the phase diagram in the parameter space of the coverage ratio $A/A_0$ and the radius $R_0$ of the sphere. It clearly shows that the defect state of the spherical crystal is largely controlled by the coverage ratio, and almost unaffected by the radius of the sphere. Type I dislocational vacancies first emerge when $A/A_0$ exceeds about 0.1. With the increase of the coverage ratio, we observe the nucleation of isolated dislocational vacancies into regularly arranged strings as shown in Fig. 1. In addition, branched defect strings as well as cracks are also numerically observed in some cases. Crack along these vacancy strings occurs in the limit of vanishingly small separation between vacancies. Fig. 3 shows that further increase of the coverage ratio above about 0.2 leads to the proliferation of the type II pentagonal vacancies or isolated fivefold disclinations within the crystal cluster. Here, it is of interest to note that, in the crystalline packings of twisted filament bundles,
the emergence of dislocations and disclinations in cross-sectional crystalline order of the bundles follows a similar phase diagram in the regime of large bundles, where the appearance of these defects is critically controlled by the accumulation of curvature effect.  

We proceed to discuss the microscopic process in the formation of the pentagonal vacancies. In Fig. 4, we present the typical snapshots at different time frames labelled by \( f_n \) in the evolution of the crystal cluster with fixed coverage ratio towards the lowest-energy state. Here, a snapshot at "time frame" \( f_n \) refers to the particle configuration obtained after \( n \) simulation steps in the evolution of our system by the rule prescribed in the Model section. In the upper snapshots in Fig. 4, we show that the formation of type I vacancies is associated with the collective movement of particles in the yellow shadow. This process can also be characterized in terms of the glide of the dislocations. The lower snapshots in Fig. 4 demonstrate the formation of type II vacancies. At \( f_n = 80 \), a pair of neutral linear defect strings appear with the bending of the colored lattice lines. With the extension of the red lattice line and further bending of the blue lattice line, the sevenfold disclination originally sitting at the blue line vanishes at the boundary and a pair of disclinations appear below the lower green box.

We finally briefly discuss about which feature in the L-J potential is responsible for the formation of the vacancies. Is it the local minimum structure or the steepness of the physical potential? While the former feature is obviously responsible for the condensation of particles to form a crystal, it is unknown if it also promotes the emergent vacancies. To answer this question, we change the 12-6 potential to the 4-2 potential \( V_{4-2}(r) = 4\epsilon_0 [(\sigma_0/r)^4 - (\sigma_0/r)^2] \). The \( V_{4-2}(r) \) potential also possesses a local minimum structure, but with a much softer "ductility" than the 12-6 potential. Specifically, the curvature of the 12-6 potential curve at its equilibrium position is about 14 times than that of the 4-2 potential curve. By repeating the simulations leading to the configurations in Fig. 4, we find that the vacancy structures vanish. Instead, dislocations and disclinations appear to resolve the geometric frustrations. Therefore, it is the steepness of the physical potential that is responsible for the formation of the vacancy structures.

In the formation of the pentagonal vacancies in the spherical crystals, the featured sufficiently steep energy minimum in the L-J potential curve can establish a bond structure between neighboring particles, and therefore support vacancies in both planar and curved crystals.  

In simulations, we extend the substrate geometry to hyperbolic paraboloid whose Gaussian curvature is negative. By confining L-J crystal clusters on such negatively curved surfaces, we numerically observe pentagonal vacancies as well as seven-fold disclinations as shown in Fig. 5. We also notice the negative-curvature driven coalescence of vacancies as shown in the region below the lower green box in Fig. 5. This phenomenon suggests that the model system of negatively curved two-dimensional L-J crystal may be used to explore the mechanism of crack formation. In contrast, under pure repulsive potentials, vacancies created by removing particles have been observed to be filled by neighboring particles to form dislocations. Note that in our study we focus on behaviors of vacancies at zero temperature and under the free stress boundary condition, where the particle density is largely determined by the balance distance in the L-J potential. Robustness of vacancies with the variation of both particle density (via imposing stress on the boundary of a crystal cluster) and temperature has been
shown in our previous study of planar L-J crystals, although the mobility of vacancies can be quantitatively affected by particle density and temperature. While it is of interest to investigate the influence of temperature and particle density on the behaviors of topological vacancies, this is beyond the scope of this study.

IV. CONCLUSION

In summary, we study the geometric frustration of Lennard-Jones spherical crystals, and identify the pentagonal vacancies of dislocational or disclinational nature. The transition from the dislocational to the disclinational vacancies of dislocational or disclinational nature is largely controlled by the coverage ratio of the crystal cluster. Clarification of the topological nature of the pentagonal vacancies in this work enhances our understanding about the basic defect structures in crystalline order on curved surfaces. This work also suggests the promising potential of exploiting the richness in both physical interactions and substrate geometries to create new types of crystallographic defects. These defects may find applications in the design of crystalline materials, notably in the fabrication of robust polygonal nanopores on vesicles of spherical topology.

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