

# Topological defects in spherical crystals

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**Abstract:** Spherical crystals present properties that are quite different from two-dimensional flat crystals. Due to curvature, they demand the presence of topological defects. In this paper, we study the interplay of these defects on spherical shells, as well as their ground-state configurations, and their out-of-equilibrium dynamics under mechanical deformation. To develop these studies, we have performed computer simulations in which particles stay on the surface of a curved template and interact between themselves with a pair-wise potential, either repulsive or attractive. We finally study the mechanical response of these curved crystals when they are subject to cyclic load. We have seen irreversible plastic deformation and the evolution of defects after some cycles of deformation. This plastic behaviour is related to the motion of defects and their spatial distribution and accumulation in the crystal.

## I. INTRODUCTION

Crystals are structures with long-range order where particles interact between themselves in such a way that the potential energy of the lattice is minimised. Particles in a flat two-dimensional space almost always pack in hexagonal lattices (or also called equilateral triangular lattices). In this case, in the lowest energy state, particles are six-fold coordinated; this means that every particle has six closest neighbours. In a non-planar space, this does not happen: not all particles can be six-fold coordinated because they experiment geometrical frustration, which is the impossibility of establishing a preferred local order everywhere in the lattice [1]. These particles, which are not six-fold coordinated in a hexagonal lattice, are called topological defects, and provide mechanical stability. In other words, a topological defect is a place in the lattice where the ordered structure changes from the usual organization. This means that there is a defect where a particle has a different number of closest neighbours from the number that it should have. In practice, curved crystals are important because they are found in nature, e.g., in the icosahedral protein shells of virus [2], named capsids, or in synthetic structures, such as colloidosomes, which work as delivery vehicles of some type of cargo, like drugs or cosmetics.

The aim of this paper is to study defects in spherical crystals both in equilibrium and non-equilibrium conditions. In section II, we describe the kinds of topological defects on spherical shells. In section III, we find the ground-state configuration of these spherical crystals. In section IV, we study the out-of-equilibrium dynamics of these crystals under mechanical deformation. Finally, we conclude summarizing the most relevant properties of these structures and we propose further studies about non-equilibrium dynamics.

## II. TOPOLOGICAL DEFECTS IN A SPHERE

We demonstrate that a spherical crystal must have topological defects in its ordered structure. In order to develop this demonstration, we need to use the Euler formula of topology. This formula says that the number of vertices ( $V$ ), minus the number of edges ( $E$ ), plus the number of faces ( $F$ ) of any given graph is a topological invariant and it only depends on the topology of the space. This invariant is called Euler characteristic (or Euler-Poincaré characteristic), and its value is 2 for a sphere [3]. This formula is the following:

$$V - E + F = 2. \quad (1)$$

We consider a sphere with a hexagonal lattice, where the particles are situated on the vertices. We also divide the lattice into triangles. Each face has three edges, so the number of faces multiplied by three and then divided by two is equal to the number of edges, since each edge is shared by two faces and we are overcounting the number of edges when we multiply by three the number of faces. Hence,  $E = \frac{3}{2}F$ , and introducing this in the Eq. (1), we obtain:  $V - E/3 = 2$ . We define the coordination number  $C_i$  for each vertex or, equivalently, for each particle, as the number of closest neighbours of the particle  $i$ , that is to say, the number of edges that converge in the vertex  $i$ . In this case, for a hexagonal lattice, six edges converge in each vertex and, therefore, the coordination number is  $C_i = 6$ , and it is said that each point has six-fold coordination. Now, using the previous equation, we sum over all vertices in the sphere and, considering that each edge is shared by two vertices, we can write the next expression:  $\sum_{i=1}^N (1 - C_i/6) = 2$ . We multiply by six this equation and, for a vertex  $i$ , we define  $6 - C_i$  as its topological charge. The following expression demonstrates

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that a sphere has necessarily topological defects:

$$\sum_{i=1}^N (6 - C_i) = 12. \quad (2)$$

Therefore, according to Eq. (2), the total topological charge of a spherical shell must be 12. Particles with six closest neighbours (six-fold coordination) have zero topological charge; particles with seven closest neighbours have charge  $-1$  (seven-fold coordination), and those with five have charge  $+1$  (five-fold coordination). Although initially there is no restriction on the type of coordination of each particle, stable spherical crystals have usually six, five- and seven-fold coordination, and rarely four- and eight-fold coordination. Isolated particles with a coordination number different from 6 are called disclinations and they are the most important kind of topological defect demanded in the presence of non-zero Gaussian curvature. Summarizing this, a spherical crystal must have at least 12 disclinations with topological charge  $+1$ ; in other words, it must have 12 five-fold coordinated particles. Nevertheless, spherical shells can also have more disclinations, only if the total topological charge is equal to 12. Other common kind of defect is a dislocation, which is a five-fold coordinated particle next to a seven-fold coordinated one. This pair has zero “disclination” charge. Dislocations are also characterized by a topological charge that is a vector, the so-called Burgers vector [4]. The more dislocations, the more imperfect and disordered the crystal is, but at the same time they are more ductile.

### III. THE GROUND STATE OF A SPHERICAL CRYSTAL

In this section, we want to find the ground state of a spherical crystal. It is observed that the most crystalline and with the lowest energy configuration is that with the minimum number of topological defects. This configuration corresponds to a hexagonal lattice with 12 five-fold disclinations, which are arranged with icosadeltahedral symmetry, like the 12 pentagons on a soccer ball (Fig. 1, on the left). However, the total number of particles in the crystal that fits in this symmetry is restricted. According to the theory developed by Caspar and Klug [5], there are “magic numbers” that allow the icosadeltahedral symmetry and place the system in a local minimum of the free energy. These “magic numbers” are  $N = 10(k^2 + kh + h^2) + 2$ , where  $k$  and  $h$  are positive integers. In our study, for all the simulations, we fix the number of particles to  $N = 272$  ( $k = h = 3$ ).

To find the ground state corresponding to  $N = 272$  particles on the surface of a sphere, we use a Metropolis Monte Carlo algorithm [6]. This method is used to find the equilibrium configuration of a system at a certain temperature. To help the system to crystallise and minimise its potential energy, we use a temperature annealing algorithm, which consists in repeating the following

proces: we lower the temperature and then let the system reach equilibrium. Before starting the algorithm, we create an initial random arrangement on the surface of a sphere. This configuration is not a crystal, since there is no order in the lattice. Then, we start the Metropolis algorithm: in every Monte Carlo step, we propose a small change (a 10% of the main particle spacing) in the position of one of the particles and we repeat this  $N$  times, choosing randomly the particle every time. We calculate the energy increase ( $\Delta E = E_{new} - E_{old}$ ) between the new and the old configuration. This change will be accepted if it minimises the system energy ( $\Delta E < 0$ ); if not, it will only be accepted if  $q < e^{-\frac{\Delta E}{k_B T}}$ , where  $q$  is a random number of the uniform distribution  $U(0, 1)$ . Nevertheless, using this method is not the most efficient way to find the ground state of a spherical shell because of the dependency on the temperature, which provide the system an excess of energy. Therefore, to achieve the lowest energy state it is necessary to do many Monte Carlo steps.

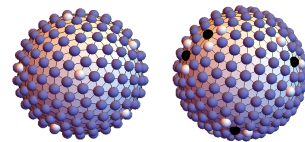


FIG. 1: On the left, the spherical crystal in the ground state. On the right, the results for a spherical crystal with  $N=272$  particles and  $R/a \approx 4.31$ . Black particles are seven-fold disclinations, and white ones are five-fold disclinations.

We use a repulsive interaction potential to ensure that the particles will arrange uniformly on the spherical surface. The interaction potential energy is  $U(\vec{r}_{ij}) = 1/|\vec{r}_{ij}|$ . The exact power of the potential is not very important due to the shape of the crystal depends very little on the form of the interaction potential energy [7].

After lowering sufficiently the temperature and doing as many steps as the system energy keeps constant, we obtain a configuration with the needed 12 five-fold disclinations and 4 dislocations, 3 of them belonging to grain boundary scars (Fig. 1, on the right). These scars are made up of a chain of five-, seven- and five-fold coordinated particles, with a total topological charge  $+1$ . Although this configuration is not the perfect spherical crystal that we wanted to find, it is very clean of topological defects: it only has 4 extra seven-fold coordinated particles, accompanied by 4 extra five-fold coordinated particles to conserve the total topological charge. Despite the fact that we repeat this process improving the algorithm to reach the ground state, we always obtain a crystal with some extra defects. This happens because there are metastables states with similar energy to the ground state.

It is known that isolated disclinations become much more energetically costly if the radius of the spherical shell increases. Thus, the 12 five-fold disclinations induce too much strain, which can be reduced by introducing

dislocations or grain boundaries scars, which is what we have observed in our system. These scars only appear for spherical crystals with

$$R/a \gtrsim 5, \quad (3)$$

where  $a$  is the main interparticle distance, being calculated in the following way:  $a = \sqrt{(8\pi R^2)/(\sqrt{3}(N-2))}$  [7]. Moreover, the number of dislocations grows linearly with the system size (Fig. 2). In our simulations, the radius is  $R = 5l_0$ , where  $l_0$  is the scaling length, and  $R/a \approx 4.31$ , which is in the limit according to Eq. (3). To verify the condition that Eq. (3) imposes, we also find the ground state of spherical shell with  $N = 72$  (also a Caspar and Klug number) and  $R = 2.4l_0$ , which implies  $R/a \approx 2.20$ . The result is indeed a spherical shell with only 12 five-fold disclinations and this agrees with what we expected. Therefore, our simulations are in agreement with the theoretical prediction, in Ref. [7], that the threshold value for the formation of scars is  $(R/a)_c \approx 5$ .

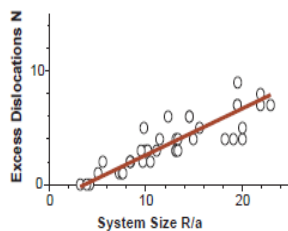


FIG. 2: Excess dislocations as a function of size system. The linear predictions given by theory is shown as a solid red line. Image from Ref. [7].

## IV. DEFORMATION CYCLES OF A SPHERICAL CRYSTAL

### A. Model

In this part, our aim is to study the out-of-equilibrium evolution of topological defects when we deform mechanically a spherical shell in a cyclical manner, always beyond the elastic limit of the crystal. This deformation consists in changing gradually the surface of the shell into an ellipsoid and then returning it to the initial spherical shape. It is important to deform slowly so that the system can relax (quasi-static conditions). We repeat this process cyclically and observe how defects are created and annihilated. For this situation, we use a pair-wise Lennard-Jones potential, which is a short-range potential that combines an attractive part with another repulsive part for very close distances. The attractive part allows the crystal to eventually fracture if the stress exceeds the plastic regime. We consider the model presented in Ref. [8] for doing the computer simulations. We solve

the equations of motion for every particle using molecular dynamics, which is appropriate for non-equilibrium situations. In this model,  $N = 272$  particles are confined on a spherical surface and they interact with the Lennard-Jones potential:  $V_{LJ} = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]$ , where  $\epsilon$  and  $\sigma = 2^{-\frac{1}{6}} \sqrt{(8\pi R^2)/(\sqrt{3}(N-2))}$  are characteristic energy and length scales, respectively [9]. We impose a constraining force field, with the form  $\vec{F} = -K(d(t) - R)(\vec{r}/d(t))$ , where  $K$  is the spring constant, to bind the particles to the shell, with radius  $R$ ,  $d = \sqrt{(x^2 + y^2)/a^2 + z^2/c^2}$ , and  $t$  is the number of steps, which plays the role of time.  $a(t)$  and  $c(t)$  are the principals semiaxes of the ellipsoid, both normalized to the radius  $R$ .  $c(t)$  decreases in time with a deformation velocity  $v$  and  $a(t)$  varies, so that the volume of the spheroid is conserved.

To perform the simulations, we start with the ground state of a spherical crystal, considering the interparticle equilibrium distance:  $r_{min} = 2^{\frac{1}{6}}\sigma$ , which is the minimum of the interaction potential. Once we have started the deformation process, we calculate the deformation rate, in part per unit, with the formula  $\gamma = \Delta c/c_0 = vt/R$ , where  $\Delta c$  is the variation of the semiaxis length,  $v$  is the deformation velocity and  $t$  is the number of steps. As we said previously, the deformation velocity must be slow to allow the system to relax. For all the simulations, we use  $v = 0.01$ .

### B. Results

Macroscopic, bulk materials, when they are subject to cyclic load, suffer a phenomenon called fatigue, whereby materials become weaker and more fragile until they break because of the accumulation of defects in the lattice. Although these defects allow the plastic deformation, the more defects in the lattice, the more fragile the material is. In this section, we are interested in studying the fatigue of curved crystals. The deformation that we introduce to the system is always in a slow manner, so that crystal can relax. However, we have not observed fatigue in our simulations. As shown in Fig. 3, the number of topological defects fluctuates around a fixed value, but eventually, in the last cycles, the system reaches a metastable configuration, in which the number of defects is periodic with the deformation in every cycle. In other words, the shell is not experimenting fatigue because it is not accumulating more defects. This behaviour is different from what happens in bulk materials, where the number of defects grows as the number of loading cycles increases. A plausible argument to explain these results is that the number, together with the spatial arrangement, of the defects accumulated after the very first few cycles could be enough to accommodate the extra bending stress induced by the redistribution of Gaussian curvature in the shell. This curvature increases towards the edge of the ellipsoid. To confirm this hypothesis, we should study

these crystals increasing the system size (keeping the particle surface density constant) in order to observe if the shell is able to stabilize the number of defects.

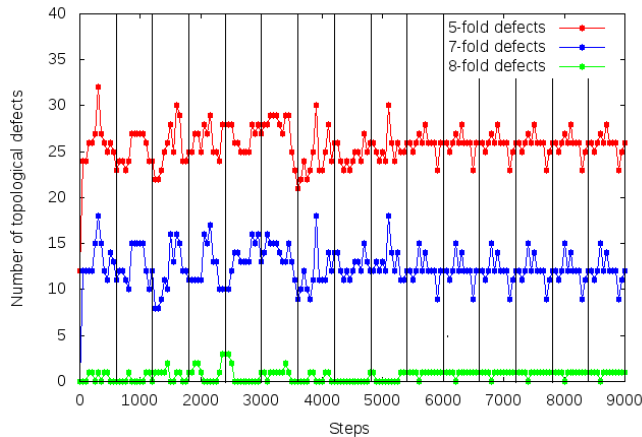


FIG. 3: Evolution of the number of topological defects as a function of the number of steps. Vertical lines separate every cycle from each other. The maximum deformation is  $\Delta c/c_0 = 0.3$ .

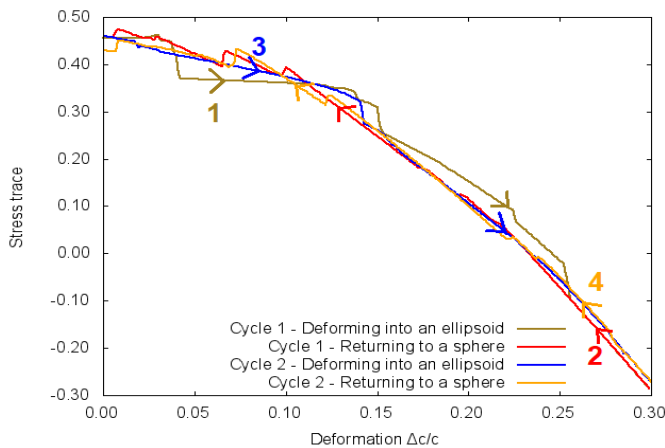


FIG. 4: Stress trace, in simulation units, as a function of the deformation rate for the two first loading cycles.

It is also important to emphasise the irreversibility of these plastic deformations. Although in every cycle the shell recovers the spherical shape, not all the new topological defects created in the compressing process can be annihilated. This fact can be seen in Fig. 3, where, once we have deformed the shell, the number of defects never returns to the ground-state configuration. Furthermore, the system presents hysteresis. As shown in Fig. 4, where the stress trace is plotted as a function of the deformation, the curves by which the shell is deformed into an ellipsoid (curves 1 and 3 in Fig. 4) differ from the curves by which the shell recovers the spherical shape (curves 2 and 4 in Fig. 4) because of the variation of the number of defects is different in every cycle. In spite of that, the

hysteresis is quite small, since the curves are close to each other. In addition, in the last cycle, when the number of defects is periodic in every cycle, the stress trace is also periodic.

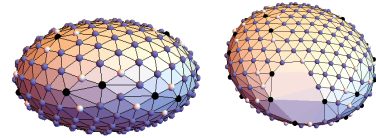


FIG. 5: On the left, the curved crystal  $\Delta c/c_0 = 0.3$ . On the right, the fractured shell with  $\Delta c/c_0 = 0.4$ . The fracture is nucleated where the curvature is greater.

Despite the fact that we have not observed the fatigue of the crystal, for a deformation of 40% the shell fractures. Due to the short-range attractive interaction potential, if any particle moves too far away from its neighbours during the deformation process, it will not feel the interaction and a crack line will be nucleated. Thus, the crystal ends the plastic regime and fails (Fig. 5).

### C. Defect motion

In this subsection, it is interesting to emphasise how defects move in the small crystals. Microscopically, plastic deformation induces the creation and annihilation of topological defects and their migration to the more curved places on the spherical shell. The motion of these defects is not continuous during the deformation process, it is intermittent, as shown in Fig. 6. Creating isolated disclinations is energetically costly and they cannot move without the assistance of dislocations, whose creation in pairs of opposite Burgers vectors (dislocation dipole) requires less energy. Dislocations can glide easily in the direction of the Burgers vector, which is perpendicular to the axis that connects the five- and seven-fold defects of the dislocation. When dislocations glide, they can find an isolated five-fold disclination and then the seven-fold defect of the dislocation and this disclination can annihilate mutually. After this annihilation, the five-fold defect of the dislocation stays isolated and the global result is that the disclination has moved one position in the lattice. This motion is not effective because it requires the nucleation of dislocations. Thus, the motion is intermittent, since these nucleations are repeated throughout the crystal over time. As a result, this motion produces the intermittent signal in Fig. 6. Summarizing, the principal microscopic mechanism through which disclinations move is by the assistance of dislocations, which glide easily over the lattice, as shown in Fig. 7.

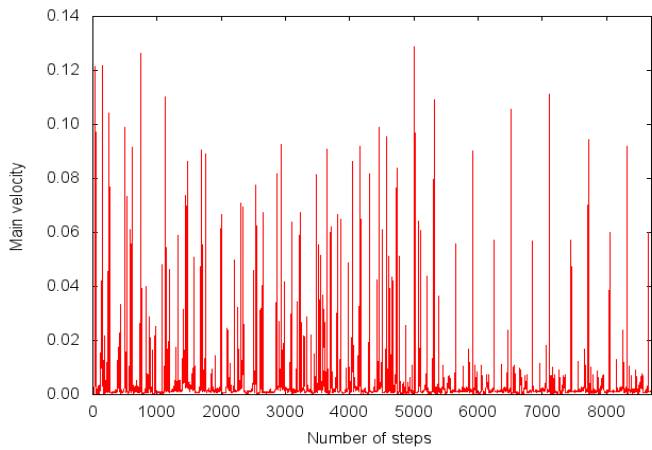


FIG. 6: Main velocity of the particles as a function of the number of steps. This illustrates the intermittent motion of topological defects.

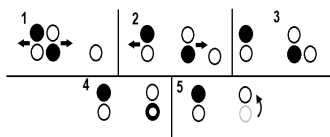


FIG. 7: Schematical process in which an isolated disclination moves one position in the lattice by the assistance of a dislocation. Black balls represent seven-fold defects, and white ones represent five-fold defects.

## V. CONCLUSIONS

The physics of spherical crystals is dominated by topological defects. These defects, required by geometry, determine the energy level of the crystals and allow them to deform plastically. In these crystalline structures, we can find two main types of topological defects: disclinations and dislocations. Disclinations are isolated and energetically costly defects. Curved crystals must have 12 five-fold disclinations. On the other hand, dislocations are pairs of a five- and seven-fold defects, and they require less energy to be created than disclinations.

In equilibrium, the ground state of a spherical shell is

characterized by 12 five-fold disclinations arranged with an icosadeltahedral symmetry. However, as the system size increases, grain boundary scars can appear to reduce the strain caused by the isolated disclinations.

We have also studied the out-of-equilibrium dynamics of spherical shells under controlled mechanical deformation. We wanted to investigate whether these small curved crystals show any sign of fatigue, as in more conventional macroscopic crystals. Nevertheless, in our simulations, after some cycles, the number of defects attains a steady periodic value with deformation. This means that, with this number and spatial disposition, the shell can adapt to the bending stress produced by the redistribution of curvature. It will be convenient to further study the role of the system size in this process. Indeed, we believe system size could be quite relevant. We have also observed that the loading cycles give rise to an irreversible process that exhibits mild hysteresis. Furthermore, the creation and annihilation of topological defects allows the material to deform plastically. Microscopically, plasticity is due to the movement of the dislocations, which can glide easily over the lattice in order to help disclinations to migrate to regions where curvature is greater. However, plasticity has a limit: for a deformation rate of 40%, the shell does not support the stress and eventually fractures.

In summary, since these structures are present in biological research and also in the development of new technology, it would be important to provide further insight by extending these studies. In applications, most of these structures are subject to external forces or deformations; thus it is crucial to characterize its mechanical response in out-of-equilibrium conditions.

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