Freezing on a sphere

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The best understood crystal ordering transition is that of two-dimensional freezing, which proceeds by the rapid eradication of lattice defects as the temperature is lowered below a critical threshold. But crystals that assemble on closed surfaces are required to have a minimum number of lattice defects, called disclinations, that act as conserved topological charges—consider the 12 pentagons on a football or the 12 pentamers on a viral capsid. Moreover, crystals assembled on curved surfaces can spontaneously develop additional lattice defects to alleviate the stress imposed by the curvature. It is therefore unclear how crystallization can proceed on a sphere, the simplest curved surface on which it is impossible to eliminate such defects. Here we show that freezing on the surface of a sphere proceeds by the formation of a single, encompassing crystalline ‘continent’, which forces defects into 12 isolated ‘seas’ with the same icosahedral symmetry as footballs and viruses. We use this broken symmetry—aligning the vertices of an icosahedron with the defect seas and unfolding the faces onto a plane—to construct a new order parameter that reveals the underlying long-range orientational order of the lattice. The effects of geometry on crystallization could be taken into account in the design of nanometre- and micrometre-scale structures in which mobile defects are sequestered into self-ordered arrays. Our results may also be relevant in understanding the properties and occurrence of natural icosahedral structures such as viruses.

1 The remarkable predictions of the Kosterlitz–Thouless–Halperin–Nelson–Young (KTHNY) theory of melting on a plane have been verified both by experiment and simulation in systems as diverse as free electrons on liquid He surfaces, magnetic flux vortices in superconductors, and monolayers of paramagnetic colloidal particles interacting through induced magnetic dipoles. This last system is particularly well characterized—its entire phase behaviour can be reduced to a one-dimensional phase diagram parameterized by a single, dimensionless interaction parameter, \( \Gamma \), defined as the ratio of neighbour magnetic dipole and thermal energies:

\[
\Gamma = \left( \frac{\pi \rho}{k_b T} \right)^{1/2} A
\]

where \( A \) quantifies the magnitude of the dipolar pair potential, \( U(r) = A/r^6 \) (where \( r \) is the separation between particles), \( \rho \) is the number density of particles, \( k_b \) is Boltzmann’s constant, and \( T \) is the absolute temperature. Consistent with this definition, the liquid–crystalline hexatic phase that separates the isotropic fluid from the crystalline solid occupies a narrow window of \( \Gamma \) values, 67 ≤ \( \Gamma \) ≤ 70.

Our system of charged, hydrophobic microspheres adsorbed at oil–aqueous interfaces is accurately described by the same interaction potential. Yet, unlike any system controlled by magnetic fields, these particles are bound to the surface by electrostatic image charge forces (Fig. 1b), and can uniformly decorate the surfaces of spheres, or other curved surfaces, without affecting the form of their interparticle forces (see Supplementary Information section 2). However, the topology of the sphere fundamentally changes the KTHNY picture of ordering by elimination of defects, since at least twelve 5-coordinated disclinations (particles with pentagonal Voronoi cells and positive topological charge) are required. Furthermore, it has been shown that as the size of the system increases (at constant density) it becomes energetically favourable to decorate these 12 disclinations with dislocations (topologically neutral, 5–7 disclination pairs) organized into linear structures called ‘scars’. The total number of dislocations in the system—proportional to the length of the scars—grows as \( R/a \), where \( R \) is the radius of the sphere and \( a \) is the interparticle distance. This is unlike other systems, such as superfluid \( ^3\text{He} \) (ref. 20) and the two-component plasma, that exhibit a related Kosterlitz–Thouless transition on a sphere, but where all topological defects may be eliminated. Consequently, since dislocations are mobile defects that destroy both crystallinity and rigidity, it is natural to ask whether crystallization of particles confined to the surface of a sphere is possible at all, or whether the proliferation of defects leads to liquid or glassy phases even for the strongest interactions (highest \( \Gamma \)).

Confocal micrographs (top panel of Fig. 1a) show clear differences between droplets with high and low \( \Gamma \) values (for methods see Supplementary Information section 1). First, Voronoi tessellations of these surfaces show that disclinations (particles with topological charge equal to 6 less their coordination number) densely and uniformly cover the liquid-like sample, but are much rarer in the more ordered sample and are clustered in scars (middle panel of Fig. 1a). A similar pattern is shown by the two-dimensional bond-orientational order parameter that measures the orientation and degree of hexagonal order around each particle:

\[
\psi_b(r, t) = \frac{1}{N_i} \sum_{j=1}^{N_i} e^{i\theta_{ij}(t)}
\]

where \( N_i \) is the coordination number of the \( i \)th particle, and \( \theta_{ij}(t) \) is the angle between the line connecting particle \( i \) to its \( j \)th neighbour and an arbitrary reference axis. Like the distribution of topological defects (middle panel of Fig. 1a), the time-averaged \( \langle |\psi_b(r, t)| \rangle \) field, \( \langle |\psi_b| \rangle \), is homogeneous over the entire sphere, as shown in the bottom panel of Fig. 1a. For the denser samples, \( \langle |\psi_b| \rangle \) is spatially heterogeneous—the environment around most particles is locally hexagonal for the entire duration of observation, while a small number of particles, in or near the scars, have very low \( \langle |\psi_b| \rangle \) values.

KTHNY theory postulates that the magnitude of this orientational order—as quantified, for example, by the \( \langle |\psi_b(r, t)| \rangle \) field averaged over space and time, \( \langle |\psi_b| \rangle \) —is intimately related to the distribution of topological defects. Indeed, in flat space the number of topological defects drops precipitously over a narrow range of \( \Gamma \) values centred around \( \Gamma \approx 70 \), while \( \langle |\psi_b| \rangle \) increases rapidly. By contrast, while the reduction of defects on spheres with \( N \approx 1,500 \) particles is accompanied by increasing values of \( \langle |\psi_b| \rangle \), the crossover to high-\( \Gamma \) behaviour is broader (especially in the simulations) than what we observe in the flat layers; moreover, the number of topological defects reaches a plateau value much larger than the 12 required by topology (Fig. 1c). In the \( \Gamma, N \to \infty \) limit, the number and clustering of defects has been predicted using continuum elasticity.
Yet, although these globally averaged quantities reflect the increasing order of particles with increasing \( \Gamma \), they do not reflect the clustering of defects that is evident in the micrographs. To understand this clustering better, we compute \( g_{55}(r) \), the pair correlation between 5-coordinated defects (Supplementary Information section 4), for experimental and simulated23–25 particle configurations over a wide range of \( \Gamma \). We find that \( g_{55}(r) \) is flat for \( \Gamma < 70 \)—consistent with a random distribution of defects. However, for \( \Gamma > 70 \), we find a peak in \( g_{55}(r) \) at short distances that grows and widens with increasing \( \Gamma \)—indicating the condensation of defects into clusters. More interestingly, additional peaks in \( g_{55}(r) \) appear for values of \( r \) that correspond to the geodesic distances between the vertices of an icosahedron (Fig. 2a), making it possible to draw a football on the sphere such that most of the defects lie inside its pentagons (Fig. 2b). Nevertheless, this icosahedral ordering of defects develops gradually, and it is difficult to unambiguously identify isolated defect clusters until \( \Gamma \gtrsim 120 \).

The strong coupling between lattice defects and particle mobility in crystalline solids19,22 suggests that the proliferation and spatial segregation of dislocations will also affect the dynamics of our system. To study this we adopt a tool used to describe glasses, labelling particles that move more than a distance \( \lambda' \) over a time \( \tau' \) as ‘mobile’, \( Q = 1 \), and those that do not as ‘caged’, \( Q = 0 \) (Supplementary Information section 6). For large values of \( \Gamma \), we observe clustering of mobile particles reminiscent of the clustering of topological defects (Fig. 2c). To investigate the connection between defects and mobility we compute \( g_{QD}(r) \), the pair correlation function between mobile particles (\( Q = 1 \)) and disclinations (\( D \), defined as particles with any coordination number other than six). We find that \( g_{QD}(r) \) is almost identical to \( g_{55}(r) \), confirming that particle mobility is strongly heterogeneous and becomes confined to the same icosahedrally coordinated ‘seas’ that contain the excess lattice defects.

In two dimensions, long-range correlations of orientational order, captured by \( g_{ij}(r) = \langle \psi_i(x)\psi_j(y) \rangle_{x-y=r} \), are a clear sign of crystallinity; however, vector transport on the sphere changes angles and complicates the definition of a global reference coordinate system. Nevertheless, the icosahedral ordering of defects suggests that it may be possible to detect crystalline order by explicitly referencing this broken symmetry. We thus define an icosahedral ‘net’ by rotating an icosahedron so that its vertices are aligned with the positions of the defects (Supplementary Information section 8). Projecting the particles onto the faces of the icosahedron and unfolding the structure onto a plane reveals the remarkable global orientational coherence of particle configurations with high \( \Gamma \) (Fig. 3a). We quantify this order using the icosahedrally referenced orientational correlation function:

\[
g_{ij}^{(\psi)}(r) = \langle \psi_i(r)\psi_j^{(\psi)}(r) \rangle_{\cos^{-1}(r_i.r_j/r_i^2)=r}
\]

where \( \psi_i^{(\psi)}(r) \) is the icosahedrally referenced value of the bond-orientational order parameter (Fig. 3b, Supplementary Information section 8.2). We note that randomly oriented icosahedral nets, or nets based on polyhedra with different symmetries, will not produce such coherence (Supplementary Information section 8.5).
The emergence of this new broken symmetry now raises the question of whether the extreme retardation in the growth of $\psi_6$ is a finite-size effect, or arises because the spherical geometry fundamentally changes the form of the freezing transition, perhaps requiring an additional order parameter to describe it. Consequently, to explore the $N \to \infty$ limit, we supplement our simulations of spheres decorated with $N = 1,500$ particles, with simulations with $N = 3,000$, $6,000$ and $12,000$ particles, and evaluate two order parameters: the icosahedrally coordinated defect density $g_{\text{icos}}$.

Figure 2 | Emergence of icosahedrally coordinated defect seas. a, Pair correlation of 5-coordinated disclinations, $g_{55}$, for experimental (top) and simulated (bottom) spheres decorated with $N \approx 1,500$ particles. Disordered spheres are uniformly randomly covered with lattice defects, leading to a flat and featureless $g_{55}$. As order increases so does a coherent defect-density modulation with peaks at $0$, $\theta_1$, $\theta_2$ and $\pi$, consistent with their segregation into icosahedrally coordinated seas. b, Rendering of experimentally determined 5- and 7-fold coordinated lattice defect positions over the surface of a suitably oriented football makes the icosahedral ordering apparent. c, Distribution of ‘mobile’ particles (red, see text) over the surface of spheres with $\Gamma = 42$ and $\Gamma = 145$. After a lag time $t$, mobile particles appear randomly over the surface of the disordered sphere (left panels) and quickly cover its surface. Particles on the more ordered sphere (right panels) have far lower absolute mobilities (‘caged’ particles are white), and the mobile particles that appear are segregated into isolated seas. d, Pair cross-correlations of all defects and mobile particles for the same spheres shown in a show similar ordering to $g_{55}$, demonstrating the spatial coincidence of defects and mobility.

Figure 3 | Icosahedral map projections and long-range order. a, The left panel shows a reference icosahedron, oriented by fitting its vertices to the positions of the defect particles. The right panel shows that unfolding this icosahedron reveals long-range order hidden by the extra disclinations. b, Orientational correlation functions, $g'_6(r)$, computed using the reference icosahedra (see text and Supplementary Information section 8). For the samples at low $\Gamma$, orientational correlations decay rapidly, whereas at high $\Gamma$, hexagonal order extends across the entire sphere. At intermediate values of $\Gamma$, the absence of well defined defect clusters means that the correlation of the best-fit icosahedron to the orientational order is low, so many independent configurations must be sampled to produce accurate $g'_6(r)$ curves. Since our experiments sample only a small number of independent configurations, the correlation functions in the top panel of b in the range $85 \leq r \leq 110$ sometimes reach negative values at large $r$, whereas simulation results in the bottom panel are consistent with thorough sampling.
The elucidation of order by the unravelling and flattening of an appropriate polyhedral net may be useful in other contexts, such as liquid crystalline orientations on curved surfaces (for example, the tetrahedrally symmetric, baseball-like texture of a nematic confined to a thin shell, Supplementary Information section 8.6(29)). As in our study, the need for both crystalline and polyhedral order parameters has been invoked in recent models of assembly of icosahedral viral motifs(10). Moreover, the segregation of defects to symmetric sites, and the concomitant mobility near these sites, should prove useful in designing structures where both rigidity and fluidity are desired in specific areas.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

Data Availability Source Data for Figs 1–4 are provided with the online version of the paper. Coordinates and trajectories of particles identified from confocal micrographs for every experimental sample referred to in the paper are available from the Open Science Framework repository ‘Freezing on a Sphere’(31). The same repository contains a snapshot of every simulated dataset referred to in the paper (each stored as an XML file) and corresponding Python scripts, which, together with the HOOMD-blue plugins included in Supplementary Information, can be used to reconstitute all of the simulation data presented here. Raw confocal image data and complete simulation results are available upon request.

Code Availability Numerical simulations were performed using HOOMD-blue v1.3.3 (refs 23, 24) with double-precision arithmetic and custom plug-ins for pairwise interaction potentials and Langevin dynamics integrators. Experimental and simulated datasets were analysed using software written in MATLAB, CUDA, and C. These analysis routines and the HOOMD plug-ins are available in Supplementary Information.

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Figure 4 | Icosahedral order and finite size scaling. a, Scaling of the normalized, three-body, three-dimensional bond-orientation of the defects, \( W_b \), with \( \Gamma \) and system size for simulated particle configurations. Icosahedral order grows approximately linearly beyond a critical value of \( \Gamma \), where the slope of linear fits to the data (dotted lines) appears to diverge as \( N \to \infty \). b, Scaling of the average icosahedrally referenced bond order parameter, \( \langle | \Psi_{6i} |^2 \rangle \), with \( \Gamma \) and system size. The rate at which this order parameter grows increases with system size, and its \( N \to \infty \) extrapolated values remain positive for all \( \Gamma \) that correspond to the flat-space solid.

\[
\tilde{W}_b = -\frac{\sqrt{24}}{11} \sum_{m_1 m_2 m_3} \rho_{6m_1} \rho_{6m_2} \rho_{6m_3} (6 \hat{m}_1 \cdot 6 \hat{m}_2 \cdot 6 \hat{m}_3) \rho_{6m_1 m_2 m_3} (\sum_m |\rho_{6m}|^2)^{3/2}
\]

where the first quantity in the summand is the Wigner 3-j symbol and \( \rho_{6m} = \sqrt{4\pi} \sum_{\{\theta, \phi\}} Y_{6m}(\theta, \phi) \) \( (Y_{6m} \) are the sixth-order spherical harmonics, and \( (\theta, \phi) \) are the polar coordinates of the ith defect). This order parameter is particularly sensitive to the presence of icosahedral symmetry, and is normalized so that \( \tilde{W}_b = 1 \) for a perfect icosahedron.

Plots of these quantities show that increasing the system size increases the rate at which orientational and icosahedral order increase with increasing \( \Gamma \) (Fig. 4a, b). A polynomial extrapolation of \( \langle | \Psi_{6i} |^2 \rangle \) in powers of \( 1/R \propto 1/\sqrt{N} \) shows that, in the thermodynamic (\( N \to \infty \)) limit, \( \langle | \Psi_{6i} |^2 \rangle \) vanishes for \( \Gamma < 67 \), but remains finite for \( \Gamma > 70 \), coinciding with the two-dimensional liquid and crystal phase boundaries. Similarly, \( \tilde{W}_b \) is zero for lower \( \Gamma \), and begins to increase roughly linearly—with a slope approximately proportional to \( N \)—above a critical threshold. We note that both of these order parameters \( \langle | \Psi_{6i} |^2 \rangle \) and \( \tilde{W}_b \) exhibit transitions close to the \( \Gamma \) values of the liquid–hexatic and hexatic–solid transitions in flat space as \( R \to \infty \).
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Supplementary Information is available in the online version of the paper.

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