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Deformation of membrane vesicles due to chiral surface proteins

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Chiral, rod-like molecules can self-assemble into cylindrical membrane tubules and helical ribbons. They have been successfully modeled using the theory of chiral nematics. Models have also predicted the role of chiral lipids in forming nanometer-sized membrane buds in the cell. However, in most theoretical studies, the membrane shapes are considered fixed (cylinder, sphere, saddle, etc.), and their optimum radii of curvatures are found variationally by minimizing the energy of the composite system consisting of membrane and chiral nematics. Numerical simulations have only recently started to consider membrane deformation and chiral orientation simultaneously. Here we examine how deformable, closed membrane vesicles and chiral nematic rods mutually influence each other's shape and orientation, respectively, using Monte Carlo (MC) simulation on a closed triangulated surface. For this, we adopt a discrete form of chiral interaction between rods, originally proposed by Van der Meer *et al.*, for off-lattice simulations. In our simulation, both conical and short cylindrical tubules emerge, depending on the membrane stiffness and the intrinsic chirality of the molecules. We show that the Helfrich–Prost term, which couples nematic tilt with local membrane curvature in continuum models, can account for most of the observations in the simulation. At higher chirality, our theory also predicts a chiral tweed phase on cones, with varying bandwidths.

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1 Introduction

Chiral molecules can self-assemble into membrane-like structures. A broad class of chiral lipids, both synthetic,^{2,3} as well as biological,^{4,5} are known to self-assemble into membrane bilayers which take the shape of long cylindrical tubules and helical ribbons. The lipid orientations ($\hat{n}_i$) often exhibit constant tilt (θ) with respect to the local membrane normal ($\hat{k}$) as in a smectic-C film. The projection of these tilted molecules ($\sin \theta$) on the cylindrical membrane surface shows helical striped patterns on tubules. These have been the subject of many theoretical studies^{6–10} which have employed the theory of chiral nematics¹¹ to understand nematic textures on curved membrane surfaces. The so-called colloidal membrane is another example where chiral, rod-like virus particles, exhibiting strong depletion interaction among themselves, self-assemble into monolayers,¹² but with a spatially non-uniform tilt. The monolayers can exhibit different shapes and curvatures depending on the experimental conditions.^{12,13}

While all these examples of self-assembled chiral membranes exhibit open structures with free edges, we will focus here on

closed vesicles that are more constrained (by volume and area) in adjusting their shapes such that chiral interaction energy is minimized simultaneously. It has been proposed^{14,15} that such chiral lipid membranes could form spherical buds of very small sizes in the order of 50 nm, although this has not been directly verified in experiments. However, most of the studies on chiral membranes start with a predefined shape of the membrane (cylinder, ribbon, sphere, saddle *etc.*) and look for the nematic texture that minimizes the total energy of the system. Often the optimum curvature of the surface is computed variationally. For narrow long tubes, the studies in ref. 6 and 10 predicted a uniform tubular radius $r = 2\kappa/c_0$, where κ is the membrane bending modulus and c_0 is the coupling strength between molecular chirality and the surface curvature. These initial theories had also predicted a uniform tilt pattern of 45° with respect to the cylinder axis. In contrast, ref. 8 predicted modulated tilt patterns. Recently ref. 16 showed that such modulated patterns on uniform cylinders may not constitute the global minima of the system; instead modulated tilt patterns were shown to be stable on rippled cylinders. In contrast, here we use Monte Carlo (MC) simulation to search for minimum energy configurations by varying both the vesicle shapes and the corresponding nematic texture simultaneously, which opens up much wider possibilities in terms of shapes and patterns. Our analytical theory, in the second half of this paper, however, searches for optimum nematic texture on fixed shapes, which are found in our simulations.

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The scope of this study is even broader: the physics of uniformly tilted lipids is equally applicable to situations where an achiral membrane is decorated with rod-like chiral proteins that lie completely on the tangent surface of the membrane. Given that many membrane binding proteins are chiral in nature (*e.g.*, proteins with BAR domains) their influence on the membrane shape is of interest. For example, dynamin and ESCRT-III are well known filamentous proteins, which form helical spirals and strongly modify membrane shapes. A recent study¹⁷ has explored this angle; the researchers used MD simulations to report shape transitions in cylindrical, open vesicles where chiral proteins bind to an achiral membrane.

Before describing the models let us note that chirality is essentially a three-dimensional feature and therefore chiral order cannot be achieved if the rod-like molecules are lying on a flat surface. But if the surface is curved (deformed) then even if the rods lie on the local tangent plane of the curved surface it is possible to have a chiral order. Chirality implies that successive rods would like to maintain a preferred relative angle. This is however different from splay and bend. One good example is when the nematic rods are tangents to a helical space curve. This can be readily achieved when the nematics decorate the surface of a membrane tube.

1.1 Model

The projection of the nematic rod, on the tangent plane of the membrane forms a 2D vector field $\mathbf{m}(\mathbf{r})$ of fixed magnitude $m = \sin \theta$. We will ignore this fixed magnitude and study the behavior of a unit vector field $\mathbf{m}(\mathbf{r})$. Following ref. 7, 8, 14, 15 and 18 the energy functional for chiral nematics is

$$E_f = \int dA \left\{ K \left[\left(\vec{\nabla} \cdot \vec{m} \right)^2 + \left(\vec{\nabla} \times \vec{m} \right)^2 \right] + K_c \left(\vec{\nabla} \cdot \vec{m} \right) \left(\vec{\nabla} \times \vec{m} \right) + c_0 \gamma_{ij} m^i m^j K_k^i + \beta m_i m^i K_j^i \right\}. \quad (1)$$

Here $\vec{m}$ is a 2D unit vector field in the tangent plane of the membrane. The first and the second terms are the splay and bend terms (with the same modulus K).¹¹ The third term linear in $\vec{\nabla} \times \vec{m}$ promotes chiral order. In 2D, $\text{Curl } \vec{m} = \gamma_{ij} \partial^i m^j$ is a pseudo scalar as $\gamma_{ij} = \sqrt{g} \epsilon_{ij}$, where ϵ_{ij} is the fully antisymmetric 2nd rank Levi-Civita tensor and g is the determinant of the metric tensor for the curved membrane surface. The invariant area differential dA also contains $\sqrt{g}$, see eqn (3) later. In the 3rd term, K_c is the strength of this chiral interaction. This term is not allowed for an open membrane¹⁸ as it violates the $\vec{N} \rightarrow -\vec{N}$ symmetry of the local surface normal. But here since we are dealing with a closed vesicle, whose outside is distinct from the inside, the membrane is not symmetric with respect to its two sides, *i.e.*, the $\vec{N} \rightarrow -\vec{N}$ symmetry is broken. This term has been considered in earlier studies also.^{14,15} Both the 4th and 5th terms couple the nematic field with the local surface curvature. In particular, the 4th term, known as the Helfrich–Prost term⁶ is also chiral in nature. Next, we will describe our discrete model that shares the symmetries of the above

continuum model. Below we will also include the elastic energy terms for the pure membrane.

In the model below $\hat{n}_i$ is the 3-D nematic director located at the i th vertex of the triangulated network and it lies on the local tangent plane. The 3-D cross product $\hat{n}_i \times \hat{n}_j$ below is a pseudo-vector, which contains the crucial chiral effect.

$$E_d = \frac{\kappa_b}{2} \int dA (2H)^2 + \sigma A + \Delta p V - \epsilon_{LL} \sum_{nn} (\hat{n}_i \cdot \hat{n}_j)^2 - 2\epsilon_C q_0 \sum_{nn} \hat{r}_{ij} \cdot (\hat{n}_i \times \hat{n}_j) (\hat{n}_i \cdot \hat{n}_j) \quad (2)$$

The first three terms are due to membrane bending (Helfrich), surface tension, and pressure difference across the membrane ($\Delta p = p_{\text{out}} - p_{\text{in}}$). The next two terms are discrete, involving only nearest neighbour (nn) pairs (i, j) on the triangulated network. $\hat{n}_i$ and $\hat{n}_j$ lie on the tangent planes of the nn i, j -th vertices, and $\hat{r}_{ij}$ is the unit vector along $(\vec{r}_j - \vec{r}_i)$, linking the i, j -th vertices. The ϵ_{LL} term (Lebwohl–Lasser interaction¹⁹) accounts for splay, bend and twist in the nematics and the last term, with modulus ϵ_C , is the twist energy contribution due to intrinsic chirality, proposed by Van der Meer.¹ All the nematic terms have local inversion symmetry $\hat{n}_i \rightarrow -\hat{n}_i$ required by uniaxial nematics.

We use one constant approximation $\epsilon_{LL} = \epsilon_C$ and rescale the energy expression by ϵ_{LL} . The resulting energy functional is used to perform MC simulation and the free-energy minimized shapes are studied as a function of the dimensionless parameters κ_b/ϵ_{LL} and q_0 , at fixed σ and Δp . For convenience we set $\epsilon_{LL} = 1$. Note that the last term is the only chiral term in our model, and is a pseudo scalar due to the presence of a single cross product. Note that the nematic interactions in the continuum eqn (1) had two chiral terms (with coefficients c_0 and K_c) whereas here, in eqn (2), we have only one with coefficient q_0 . The chiral term couples local membrane curvature and the nematic tilt. For a flat membrane $\hat{n}_i \times \hat{n}_j$ would be perpendicular to the plane, while $\hat{r}_{ij}$ would lie on the plane, resulting in zero contribution from the dot product.

The simulation results presented here are for a self-avoiding closed triangulated network of N vertices, $3N - 6$ links, and $2N - 4$ triangles. The simulation scheme is the same as that in ref. 20 except for the additional computation due to the chiral term in eqn (2). Briefly, there are three types of Monte Carlo (MC) moves in our simulations—vertex move, link flip, and nematic move. In the vertex move, a vertex is randomly displaced from its position, which changes the local membrane shape and curvature. In a link-flip move, when the length of a link, connecting two neighboring vertices, increases beyond an upper bound or shrinks below a lower bound, it is erased. Subsequently, a new link is created between two other vertices, which are both the nearest neighbors to the previously connected vertices. The link flip move ensures the fluidity of the membrane.²⁰ A nematic move is carried out by randomly rotating the nematic in the tangent plane of the vertex. The vertex move and the link flip move are subjected the minimisation of eqn (2). The details of the curvature calculation and the parallel transport method can be found in ref. 20. For rigid spherical surfaces we used

$N = 677$ vertices, and for the rigid cylinder and deformed vesicle we used $N = 2030$ vertices. For deformable soft vesicles, we take as the initial condition a spherical vesicle, uniformly covered by nematics (*i.e.*, one nematic director on each vertex), having random orientation in the tangent plane. We have also checked that starting from some other initial configuration, for example configuration 'f' in Fig. 4, we can reach configuration 'd' by running the simulation with $q_0 = 5$. In order to reach equilibrium the simulations were run in the range of 0.5–2.5 million MC steps for different parameter sets. As mentioned earlier, we set $\varepsilon_{LL} = \varepsilon_C = 1$ and present our results in terms of two parameters κ_b and q_0 . We study two ensembles: (a) conserved volume and (b) conserved Δp . Conserved volume is relevant for fluid filled vesicles with an impermeable membrane. Biological cells, for example, have been found to maintain a constant volume during cell division. For both ensembles we fix the surface tension σ and keep the area unconstrained. The unit of energy here is ε_{LL} , which is of the order $K \times$ (molecular dimension), where K is the continuum splay/bend/twist modulus. Using $K \sim 10^{-6}$ dyne and molecular dimension ~ 1 nm, we get $\varepsilon_{LL} \sim 10$ pN nm $\sim 2.5 k_B T$. The unit of length here is the typical link length between two neighboring vertices, $a \sim 4R/\sqrt{N}$. To estimate this, the area of the vesicle is taken as $4\pi R^2$ and N is the total number of vertices in the triangulated network. This is obtained assuming the triangles to be approximately equilateral with area $\sqrt{3}a^2/4$ and there are about $2N$ triangles in the network. For $R \sim 20$ μm , with $N = 2030$, we get $a \sim 1.7$ μm .

Note that in a 3D Euclidean space, before taking the dot or cross product (in eqn (2)), the origins of the vectors $\hat{n}_i$ and $\hat{n}_j$ can be made coincident by transporting one of them along the straight line $\vec{r}_{ij}$, which belongs to the 3D space. But on a discretized curved surface (see Fig. 14 in Appendix A2) $\vec{r}_{ij}$ does not belong to the surface and hence parallel transport along the geodesic is necessary. A scheme for constructing the geodesic and executing the parallel transport is given in detail in ref. 20. We describe this in Appendix A2 using Fig. 14. For dot products, this scheme has been successful.²⁰ Other parallel transport schemes have also been used for studying the XY model on curved surfaces.²¹ But for the chiral cross product term, the parallel transport scheme of ref. 20 faces numerical problems (which we discuss in Fig. 14) and fails to capture the chiral effect. In contrast, when we ran the MC simulations without parallel transport, significant chiral effects could be captured, which we present in the Results section. All vectors were expressed in the 3D lab frame before computing dot or cross products. Note that the calculation of $(\hat{n}_i \cdot \hat{n}_j)$ in the LL-term does not suffer from any problems (explained in Fig. 14) and gives nearly the same result with and without parallel transport. We conclude that the combination of the surface discretization scheme and the parallel transport algorithm, as given in ref. 20, is not error-proof so far as computation of cross products are concerned.

We note that when the discretization is reasonably good the local tangent planes of vertices i and j are close to parallel. This makes the effect of parallel transport minimal, but more importantly the absence of parallel transport reduces the

numerical error involved in the parallel transport operation over nearly parallel planes. To verify the validity of this scheme we first reproduced (see the Results section) all the standard chiral and achiral nematic patterns known for spherical and cylindrical surfaces.

2 Results

Before presenting our main results on the vesicle deformations due to chiral nematics and the patterns of nematic arrangements on them, we first verify various ground state nematic textures, on spherical and cylindrical surfaces, which are well known in the literature.^{10,14,15}

2.1 Chiral nematics on rigid surfaces

Sphere. Equilibrium nematic texture on a rigid vesicle is well known. Four $+1/2$ defects form and they try to maintain equal distance and as a result the defects arrange on a symmetrical tetrahedron. When the nematic rods are chiral, we find that only at low q_0 value are the non-chiral defect arrangements (*i.e.*, four $+1/2$ s') recovered (see Fig. 1). As q_0 is increased, the population of both $+1/2$ and $-1/2$ defects increases. This is due to the fact that an increase in q_0 increases the relative tilts between the neighbouring directors and as a result the directors arrange themselves on nearly closed loops. The radius of these loops decrease with increasing q_0 . Also note that the reflection symmetry of the texture around a $+1/2$ defect is broken when q_0 is non-zero.

In ref. 15 a plausible nematic texture was proposed for the bud structure (see Fig. 2) with two centres of chirality at the top and the bottom. They also performed variational calculation to derive the energy of such a texture. By imposing two $+1$ defects at the north and the south pole, using our MC simulation on the rigid sphere, we could verify this as the lowest energy configuration at small q_0 . The standard "S"-like pattern on the spherical surface is shown in Fig. 2c.

Fig. 1 As intrinsic chirality q_0 increases (left to right) the number of defects increases. At low q_0 (leftmost figure) only four $+1/2$ defects can be seen which is the lowest energy defect structure for a sphere. As defects repel each other elastic energy due to nematic distortion increases with the population of defects, but at higher q_0 this cost could be offset by the energy gain from the chiral term. We have indicated the core of the $\pm 1/2$ defects by red circles. On the leftmost figure we mark a loop of nematics around a $+1/2$ defect. The loop does not have reflection symmetry due to chirality. At higher chirality as more $+1/2$ defects form, $-1/2$ defects also appear in order to bring down the total charge to $+2$ (Poincaré–Hopf index theorem).

Fig. 2 Chiral S-like patterns with two +1 defects imposed at the two poles of a spherical vesicle. (a) shows the low energy nematic texture for a bud, which is connected to the base of a membrane vesicle by a narrow neck as was proposed in ref. 15. (b) and (c) are the results from our simulation. (b) Shows the top view and (c) the side view of the nematic texture. Orientations of the nematics inside the red circle were held fixed to impose the +1 defects (and similarly at the opposite pole). In the side view (c), approximate S-like patterns can be seen (see two successive red lines). A perfect S-like pattern requires that the number of latitude lines originating from the poles have to be same as the ones crossing the equator. This requires that the density of nematics has to be high near the poles. This is not the case in our triangulation scheme. We have a roughly uniform density of vertices on the sphere. As a result, we have a greater number of latitudes crossing the equator than those coming out from the pole.

Cylinder. The nematic arrangements on a cylindrical surface have been studied theoretically by various authors.^{9,15,16} In ref. 15, the authors used symmetry arguments to arrive at the conclusion that the nematic rods must form a uniform tilt pattern on a cylinder, to break the reflection symmetry. They argued, in order to break the reflection symmetry, the nematic rods must form an angle between 0° and 90° with respect to the equator. So, the simplest of this kind of configuration will be a pattern with a uniform angle all over the cylinder. In this section, we discuss the uniform tilt pattern on a rigid cylinder using numerical simulations (see Fig. 3).

For our simulations, we considered a triangulated cylinder with nematic rods distributed uniformly from the base to the top of the cylinder. We performed the simulations with a fixed cylinder for two cases: (i) without any boundary condition and (ii) with fixed boundary conditions imposed at the top and bottom two layers of the nematic arrangements. For the first case, with $q_0 = 0$, we found that the nematics almost aligned parallel to each other making an angle close to 90° with respect to the equator (see Fig. 3a). This configuration does not break the reflection symmetry as it does not have a distinct mirror image, hence it is a non-chiral arrangement. However, as we increased the q_0 value, we observed a uniform tilt phase, where the nematic rods make an uniform angle ($\Phi \approx 45^\circ$) with respect to the local azimuthal direction $\hat{\phi}$ (see Fig. 3(b and c)), which was predicted in ref. 15. We observe that for a finite q_0 value the system prefers a left-handed configuration, which can be seen in Fig. 3b, c, e and f. Note that a change in the sign of q_0 can alter a left-handed configuration to a right-handed configuration and *vice versa*. We observed that a further increase in q_0 value beyond $q_0 = 10$ forms similar configurations of uniform tilt pattern, which are not qualitatively distinct from each other. However, these patterns satisfy a common criteria – they break the reflection symmetry.

Fig. 3 Chiral nematic patterns on a fixed cylinder with increasing intrinsic chirality (q_0). In (a–c), no boundary conditions were imposed on the nematic orientations at the top and bottom. In (d–f), the nematic directors were held fixed along the azimuthal direction at the top and bottom. For both cases, 45° minimal orientation was attained in the bulk when chirality was finite. At zero chirality, nearly uniform axial and azimuthal orientation was obtained.

In the second case, we imposed a fixed boundary condition at the two top and bottom layers of the cylinder. The nematic rods at these layers were kept fixed in simulation; however, the bulk nematic rods were allowed to vary. At these boundary layers, the nematic rods were aligned along the azimuthal direction of the cylinder, *i.e.*, they make an angle 0° with the equator. For low q_0 , we observed that the nematic rods almost lie along the equatorial direction, in accordance with the boundary conditions imposed at the boundaries of the cylinder (Fig. 3d). However, as we increase the q_0 value, we recover the uniform tilt pattern in the bulk part of the cylinder (Fig. 3e and f). Near the two boundary layers at the top and bottom of the cylinder, the nematic rods try to mimic the boundary condition. However, as we move towards the bulk part, the nematic rods slowly deviate from the imposed boundary condition and try to form a uniform tilt pattern ($\Phi \approx 45^\circ$), breaking the reflection symmetry. Similar to the previous case, the tilt patterns for $q_0 > 10$ does not produce qualitatively distinct patterns. So, our simulations show the effects of chirality on the system in a narrow range of q_0 value. We did not observe modulated tilt patterns as proposed in ref. 8.

2.2 Chiral nematics on deformable vesicles

Chiral nematic rods can attain their intrinsic chirality easily on curved surfaces in order to minimize the contribution of the chiral term(s) in the Hamiltonian. As a result, we saw the emergence of chiral rolls of increasingly smaller radii, on rigid spherical surfaces, as q_0 was increased. This occurred even at the cost of proliferation of defects (see Fig. 1). When the vesicle

is soft and deformable it is interesting to ask what type of deformations will emerge, which will minimize the full Hamiltonian (eqn (2)) consisting of the membrane energy (the first three terms) and the nematic energy costs (the rest of the terms). In Fig. 4 we show the result of our simulations for chiral nematics on deformable vesicles for different values of κ_b and q_0 .

The simulation results show conical and tubular protrusions depending on the values of κ_b and q_0 . At low q_0 , we observe conical protrusion of different sizes depending upon the strength of κ_b . As we increase κ_b , the size of cones increases, but the number of cones decreases (Fig. 4g–d–a) because the vesicle would like to minimise its mean curvature resulting in a lesser number of conical protrusions. The area increases as we decrease κ_b (e.g., a $\rightarrow$ d $\rightarrow$ g), because for low bending energy it is less costly to produce protrusions of high local curvature. For the same reason, despite having the same q_0 , the radius of the chiral rolls increases upwards (g $\rightarrow$ d $\rightarrow$ a) as the system is forced to have wider cones due to higher κ_b . At fixed κ_b , as we increase q_0 (along the rows of Fig. 4), the conical protrusions gradually transition into a large number of narrow tubular protrusions and the area of the vesicle also increases. This increases the bending energy as well as the surface energy but is compensated by large negative contribution from the chiral energy.

Fig. 4 Shape deformation of a vesicle due to chiral nematics in the constant volume ensemble. Surface tension is fixed at $\sigma = 0.5$. Shapes are shown as a function of intrinsic chirality q_0 and scaled membrane bending rigidity κ_b . While volume is held constant, the area of the equilibrium shape (a–i) varies by $<15\%$. The area increases with the number of protrusions. Conical and cylindrical protrusions of varying radii and lengths are seen at different parameter values. As q_0 is increased (along the rows) chiral rolls with smaller pitch form on narrow tubes as the inter-nematic inclination angle changes over small length scales. At high κ_b and low q_0 , we observe wider conical protrusions (a and d). While at high q_0 (third column), we observe cylindrical protrusions for both high and low κ_b .

At high q_0 , the inter-nematic angles are higher and as a result the nematics exhibit a smaller helical pitch. This is only possible if the protrusions have smaller radii, as in the second and third columns of Fig. 4. A closer inspection into the chiral rolls on the protrusions show this effect more clearly, see Fig. 6. As shown in Fig. 6, with an increase in q_0 value, the chiral roll spirals in faster, making a smaller radius.

In Fig. 5 we explore the constant pressure and constant surface tension ensemble, with unconstrained volume and surface area. Although the surface area does not change significantly, large volume changes occur. The trends are described in the caption of the figure. Cylindrical protrusions proliferate due to a large negative contribution from chiral energy. This occurs despite the rise in the bending energy and the nematic alignment energy (LL-term) costs.

The decrease in the number of conical protrusions for higher κ_b also raises the obvious question of what will happen at sufficiently high κ_b ? We show one such result for high κ_b , in the constant volume ensemble, and compare it with a low κ_b case, at fixed q_0 , in Fig. 7. As expected, instead of cones, blunt (rounded) protrusions emerge.

So far, we had set the pressure difference Δp to be zero. We explore the effect of nonzero Δp (at fixed κ_b and q_0) in Fig. 8. As expected, we see a reduction in volume as Δp ($=p_{\text{out}} - p_{\text{in}}$) is increased from negative to positive values. The largest reduction occurs for $\Delta p = -0.25 \rightarrow 0$. However, in the same range

Fig. 5 Shape deformations in the constant pressure ensemble, with $\Delta p = 0$ and $\sigma = 0.5$. Shapes are shown as functions of q_0 and κ_b , as in Fig. 4. But now the cylindrical protrusions take up most of the volume and the bulk region shrinks, except at high κ_b and low q_0 , where rounded structures dominate. We observe that (i) the volume decreases with increasing q_0 and decreasing κ_b , (ii) the area varies $<9\%$ across 'a' through 'i' and (iii) the number of tubes increases and their radii decrease with higher chirality q_0 and lower κ_b , driven by the chiral term, despite the increasing bending energy cost.

Fig. 6 A closer look at the chiral rolls around membrane protrusions. These shapes are from the second row of Fig. 4. At low intrinsic chirality ($q_0 = 5$) chiral rolls with larger radii are observed. However, with an increase in q_0 , the chiral rolls appear with smaller radii because of a larger angular variation at each successive layer. The lower panel (taken from the top row of Fig. 4) shows how the shape of the protrusion changes from conical to cylindrical as q_0 is increased.

Fig. 7 Comparison of shapes at low and high κ_b for a fixed $q_0 = 5$. At high κ_b , only broad protrusions can occur since sharp cones cost very high bending energy. Interestingly, both the arm-like protrusions at the top have left-handed nematic arrangement on them, separated by a $-1/2$ defect in the middle. Here, $\sigma = 0.5$ and $\Delta p = 0$.

Fig. 8 Vesicle deformations for different Δp ($= p_{\text{out}} - p_{\text{in}}$) values across the membrane, at fixed $\kappa_b = 10$, $q_0 = 5$ and $\sigma = 0.5$. While volume decreases by a large amount from left to right (as p_{out} increases), the area decreases by 10% only. Conical protrusions change to a branched tubular structure.

$\Delta p = [-0.25, 1]$ the area reduces only by 10%. Conical protrusions become cylindrical and the bulk region vanishes. Again, this is

driven by the chiral energy despite the rise in bending energy, nematic alignment energy, and the $\Delta p V$ term.

Motivated by the formation of distinct conical and cylindrical tubules from closed vesicles, we examine the possible arrangements of the chiral nematics on these shapes, using the continuum theory. These tubules typically exhibit an aster type $+1$ topological defect at the tip and as a result nematic directors splay away from the tip. We will use this feature as a boundary condition.

3 Theory: nematic ordering on cone and cylinder

We now use the continuum Frank free-energy, given in eqn (1) (reproduced below) to study the arrangement of chiral nematics on conical and cylindrical tubules.¹⁵ Here we have omitted the non-chiral curvature coupling term (with coefficient β),

$$E_f = \int \sqrt{g} d^2x \left[\frac{K_1}{2} (\text{Div } \vec{m})^2 + \frac{K_2}{2} (\text{Curl } \vec{m})^2 + K_c (\text{Div } \vec{m})(\text{Curl } \vec{m}) + c_0 \gamma_{ij} m^i m^j K_k^j \right] \quad (3)$$

We define the local tangent plane on a conical surface (of height H and semi-angle α), by unit vectors $(\vec{e}_\theta, \vec{e}_l)$. Here $\vec{e}_\theta$ is the standard azimuthal vector in a cylindrical coordinate system and $\vec{e}_l$ is orthogonal to $\vec{e}_\theta$ and points away from the apex. The surface is represented in the cylindrical coordinate system using the position vector $\vec{R} = (r(l)\cos\theta, r(l)\sin\theta, l\cos\alpha)$. Here l is the distance from the apex of the cone and α is the semi-angle. From Fig. 9, $r(l) = l\sin\alpha$, and $z = l\cos\alpha$. The nematic lies in the tangent plane making an angle Φ with $\vec{e}_l$. Φ depends on only l as we assume azimuthal symmetry.

Here, $\text{Div } \vec{m}$ and $\text{Curl } \vec{m}$ represent the covariant divergence and curl on the conical surface, and g is the determinant of the corresponding metric tensor g_{ij} of the curved surface. All these are computed explicitly in the Appendix, for a conical surface. The first and the second terms here represent the generalized splay and bending, respectively. The third and the last terms are chiral in nature, *i.e.*, they change sign under reflection ($\Phi \rightarrow -\Phi$). The antisymmetric tensor $\gamma_{ij} = \sqrt{g} \epsilon_{ij}$, ensures the chirality of the last term, and its nonzero off-diagonal elements are $\gamma_{12} = -\gamma_{21} = \sqrt{g}$ and $\gamma_{11} = \gamma_{22} = 0$.

The Euler-Lagrange equation for eqn (3), for a cone, is given in the Appendix (see eqn (13)). We solve the non-linear differential equation (eqn (13)) numerically, using Mathematica. To mimic the nematic directors splaying away from the apex we impose the boundary conditions $\Phi(l=0) = 0$, *i.e.*, directors pointing towards the apex. To avoid the singularity at the apex we impose this boundary condition infinitesimally away from the apex, *i.e.*, $\Phi(l=\delta \rightarrow 0)$. For the closed vesicles that we simulated, the base of the conical protrusions is attached to the main body of the vesicle where the nematic orientations are not precisely known. Typically, this is the starting point of a spiral of unknown pitch. We therefore impose torque-free boundary conditions²² at the base of the cone, at $l = H/\cos\alpha$, so that the pitch is not constrained by

Fig. 9 Orthogonal basis vectors $\vec{e}_\theta$ and $\vec{e}_l$ on the tangent plane of a cone, with semi-angle α and height H . The inset shows the nematic director $\vec{m}(\theta, l)$ making an angle Φ with $\vec{e}_l$ in the tangent plane.

this boundary condition. It amounts to $\frac{\partial \mathcal{F}}{\partial \Phi'(l)} = 0$, where Φ' implies the derivative with respect to l and $\mathcal{F}$ is the energy density. We discuss the solutions next.

We first study the effects of the chiral Helfrich–Prost term. We fix the value of $K_c = 0.1$, and vary only c_0 . The results are shown in Fig. 10. At small c_0 , the director angle Φ , increases monotonically from 0° , at the vertex, close to $\pi/2$ at the base of

Fig. 10 Left panel: Variation of $\Phi(l)$ with l for fixed K_c and changing c_0 . Right panel: Corresponding nematic arrangement (red line segments) on a cone (yellow surface). c_0 increases from top to bottom (see legends). Higher c_0 values induce modulated tilt-patterns on the cone's surface.

the cone. However, for larger c_0 values, Φ oscillates with l with increasing wavelength as the radius $r(l)$ increases. This gives rise to band like patterns similar to tweed-texture,^{15,23} but with variable bandwidth. Band-like modulated tilt patterns (with uniform bandwidth) have been predicted theoretically on cylindrical surfaces by Selinger *et al.*¹⁰ The larger variation of Φ at higher c_0 is forced by the stronger chiral interaction requiring a relatively larger angle between the neighboring directors. This is equivalent to shorter pitch in the spirals, obtained in our simulations, at larger q_0 values. As a result, the nematic directors rapidly change their orientation in subsequent layers (away from the apex) before reaching the boundary, producing multi-valued solutions of Φ . However, our simulation does not produce multiple bands on the conical tubules; there only the pitch increases with q_0 , similar to the low c_0 structures produced here in the continuum theory. We also found that at low c_0 values, variation of K_c does not have much effect (data not shown). However at higher c_0 , an increase in K_c can give rise to a banded tweed-like nematic texture of increasing width, see Fig. 11.

Next, we look for chiral nematic patterns on a cylindrical surface of height H and radius r (see Fig. 13). The Euler–Lagrange equation for a cylinder is derived in the Appendix (see eqn (17)). To solve eqn (17), we imposed the same boundary conditions as in the case of a cone, *i.e.*, $\Phi(0) = 0$ and torque-

Fig. 11 Left panel: Variation of $\Phi(l)$ with l for fixed $c_0 = 0.9$ and changing K_c . The right panel shows corresponding nematic arrangements (red line segments) on a cone (yellow surface). K_c increases from top to bottom (see legends). Higher K_c values induce modulated tilt-patterns on the cone's surface.

Fig. 12 Left panel: Variation of $\Phi(z)$ with z , for varying c_0 (from top to bottom). Right panel: The corresponding nematic arrangement (red line segments) on the cylinder's surface (yellow). Parameters: $K_c = 0.1$ and height of the cylinder $H = 10$. Higher c_0 value produces modulated tilt patterns on the cylinder, which are qualitatively similar to the tweed-texture discussed in ref. 15.

Fig. 13 Schematic representation of a cylinder and its basis vectors. The nematic director makes angle $\Phi(z)$ with the basis vector $\vec{e}_z$, while $\vec{e}_\theta$ is the basis vector along the azimuthal direction.

free boundary at H . The results for the cylinder are shown in Fig. 12. Here, we kept K_c fixed and varied only the c_0 value. A monotonic increase of tilt angle Φ is seen at small c_0 values, with higher pitch at a relatively higher c_0 value. Uniform tweed-texture is obtained at a high c_0 value, see Fig. 12. Here $\Phi(z)$ oscillates in the range $[0, \pi/2]$ in a regular fashion.

4 Discussion

We will now discuss what is new that we learnt from this work. It is well known that chiral order is frustrated in the bulk of a flat surface but can be easily satisfied on curved surfaces or at surface boundaries. This is because the nematic rods can access greater angular space to maintain a relative tilt with their neighbors. This effect is manifest in certain chiral lipids that self-assemble into long cylindrical tubules. However, it was not obvious that even closed vesicles can overcome bending energy costs and grow protrusions (conical or cylindrical) due to chirality. The size of the protrusion depends on κ_b and chirality strength q_0 . Using a discrete model of chiral nematics on a triangulated closed surface we demonstrated this effect. We validated our model and the numerical scheme by verifying the standard chiral patterns on rigid spheres and cylinders, predicted in the literature by continuum models. While the standard continuum model that we considered had two chiral terms (the Helfrich–Prost term and the K_c -dependent term which is allowed by the inside–outside asymmetry of a closed vesicle), our discrete model had only one chiral term. In the continuum theory we had ignored the non-chiral curvature coupling term ($\beta \bar{m}_i m^j K_j^i$), anisotropic curvature terms and other terms of higher-order in $\bar{m}$ allowed by symmetry.^{15,24} Our texture calculation showed that between the two chiral terms the Helfrich–Prost term turned out to be more dominant in promoting the modulated tilt patterns on the surfaces of cones and cylinders. However our modulated tilt pattern on the cylinder is probably a metastable structure,¹⁶ which is stabilized due to our boundary condition $\Phi = 0$, at $z = 0$.

Within the resolution of our simulation we did not observe a clear bud-like membrane protrusion as predicted in ref. 15 for chiral nematics. There could be two reasons for this: (a) in ref. 15 the emergence of a spherical bud required positioning of two +1 topological defects (due to Poincaré–Hopf index theorem for a sphere) at the top and the base of the bud. However, this requirement of total +2 charge for a genus zero surface can be satisfied only when the bud detaches from the main body and not necessarily for a partial bud, which is topologically connected to the basal surface. (b) In ref. 15 the bud formation (or narrowing of the neck) also requires a line tension at the neck where one type of lipid, constituting the bud, forms a raft like patch in the background of a second type of lipid. In our simulation the membrane is homogeneous or uniformly covered with one type of surface protein and therefore a case for line tension does not arise.

Conflicts of interest

There are no conflicts to declare.

A Appendix

A.1 Calculations with cone and cylinder

The divergence and curl on a curved surface can be found by using covariant derivatives. In this appendix, we outline the

calculations for the derivation of Euler-Lagrange equations for cone and cylinder.

To write the Euler-Lagrange equation, we need to calculate the expression for the Frank free energy, which involves the calculation of divergence and curl on the 2D curved surface. So, we define the following quantities that we will need for the derivation of curl and divergence¹⁵

$$\vec{N} = \frac{\vec{e}_i \times \vec{e}_j}{|\vec{e}_i \times \vec{e}_j|}; \quad \gamma_{ij} = \begin{pmatrix} 0 & \sqrt{g} \\ -\sqrt{g} & 0 \end{pmatrix} \quad (4)$$

$$K_{ij} = -\vec{N} \cdot \frac{\partial \vec{e}_j}{\partial x^i}; \quad D_i m^k = \frac{\partial m^k}{\partial x^i} + \Gamma_{ij}^k m^j$$

where $\vec{N}$ is the unit normal to the surface, γ_{ij} is the antisymmetric tensor, g is the determinant of the metric tensor matrix, and K_{ij} is the curvature matrix. D_i is the covariant derivative on the curved surface and Γ_{ij}^k is the Christoffel symbol given by,

$$\Gamma_{ij}^k = \vec{e}^k \cdot \frac{\partial \vec{e}_j}{\partial x^i} \quad (5)$$

Now, the divergence and curl on the surface of a cone can be written as¹⁵

$$\text{Div } \vec{m} = D_i m^i; \quad \text{Curl } \vec{m} = \gamma_{ij}^i D_i m_j \quad (6)$$

Euler-Lagrange equation for cone. The points on the surface of the cone can be represented by the three dimensional position vector $\vec{R}$. As we will be working on the surface of the cone, we can replace the cylindrical coordinate variables z and r as a function of l . From Fig. 9, we can write $r(l) = l \sin(\alpha)$, and $z = l \cos(\alpha)$. The position vector (already given in Section 3), in cylindrical coordinates, is $\vec{R} = (r(l) \cos \theta, r(l) \sin \theta, l \cos \alpha)$. From R we can construct a covariant basis from the expression $\vec{e}_i = \frac{\partial \vec{R}}{\partial x^i}$, where $i = 1, 2$. Then the components of the metric tensor can be found from these basis vectors by using the definition $g_{ij} = \vec{e}_i \cdot \vec{e}_j$. So, for a conical surface, the metric tensor and curvature matrix (from eqn (4)) can be written as follows

$$g_{ij} = \begin{pmatrix} r(l)^2 & 0 \\ 0 & 1 \end{pmatrix}; \quad K_j^i = \begin{pmatrix} \frac{\cos \alpha}{r(l)} & 0 \\ 0 & 0 \end{pmatrix} \quad (7)$$

Now, using the curvature matrix we can write the Helfrich-Prost term

$$c_0 \gamma_{ij} m^i m^k K_k^j = -\frac{c_0 \cos \alpha}{r(l)} \sin \Phi(l) \cos \Phi(l) \quad (8)$$

The components of $\vec{m}$ along $\hat{e}_l$ and $\hat{e}_\theta$ are $m_l = \cos \Phi$ and $m_\theta = \sin \Phi$, respectively. Now, using the expressions for

divergence and curl in eqn (6) we can write,

$$\text{Div } \vec{m} = -\Phi'(l) \sin \Phi(l) - \frac{\cos \Phi(l) \sin \alpha}{r(l)} \quad (9)$$

$$\text{Curl } \vec{m} = -\Phi'(l) \cos \Phi(l) + \frac{\sin \Phi(l) \sin \alpha}{r(l)} \quad (10)$$

Prompted by the chiral nematic patterns found in our simulations (see Fig. 3–6) we assume azimuthal symmetry, *i.e.*, Φ is independent of θ . Using eqn (4) and (6) we can now write the Frank free energy,

$$E_f = -\frac{\sin 2\Phi(c_0 l \cot \alpha + K_c)}{2l^2} + \frac{l\Phi'[l\Phi'(K_c \sin 2\Phi + 1) - 2K_c \cos 2\Phi] + 1}{2l^2} \quad (11)$$

The corresponding Euler-Lagrange equation is

$$\frac{d}{dl} \left(\frac{\partial(\sqrt{g} E_f)}{\partial \Phi'} \right) - \frac{\partial(\sqrt{g} E_f)}{\partial \Phi} = 0, \quad (12)$$

which yields,

$$\frac{\cos 2\Phi(K_c \sin \alpha + c_0 l \cos \alpha)}{l} + \sin \alpha [l\Phi''(K_c \sin 2\Phi + 1) + \Phi'(K_c l \Phi' \cos 2\Phi + K_c \sin 2\Phi + 1)] = 0 \quad (13)$$

Numerical solutions of this equation are discussed in the main text (Fig. 10 and 11).

Euler-Lagrange equation for cylinder. Following the procedure described in the previous section, we proceed to compute the Frank free energy, starting with the position vector $\vec{R} = (r \cos \theta, r \sin \theta, z)$,

$$g_{ij} = \begin{pmatrix} r^2 & 0 \\ 0 & 1 \end{pmatrix}; \quad K_j^i = \begin{pmatrix} \frac{1}{r} & 0 \\ 0 & 0 \end{pmatrix} \quad (14)$$

$$\text{Div } \vec{m} = -\Phi'(z) \sin \Phi(z) \\ \text{Curl } \vec{m} = -\Phi'(z) \cos \Phi(z) \quad (15)$$

$$c_0 \gamma_{ij} m^i m^k K_k^j = -\frac{c_0}{r} \sin \Phi \cos \Phi$$

Assuming azimuthal symmetry, as before, Φ is a function of z only. Now using the above expressions, the Frank free energy reads

$$E_f = \frac{-c_0 \sin 2\Phi + r\Phi'^2(K_c \sin 2\Phi + 1)}{2r} \quad (16)$$

Using eqn (12), with Φ as a function of z , we can write the EL equation for a cylinder

$$\cos 2\Phi(K_c r \Phi'^2 + c_0) + r\Phi''(K_c \sin 2\Phi + 1) = 0 \quad (17)$$

Note that each of the above expressions for a cylinder can be derived from the respective expressions for the cone, in the limit $\alpha \rightarrow 0$, $l \rightarrow \infty$, keeping $r(l) = l \sin \alpha$ finite.

A.2 Parallel transport

Fig. 14 The nematic directors $\hat{n}_i$ and $\hat{n}_j$ lie on the tangent planes of the respective vertices i and j . The corresponding surface normals are $\vec{N}_i$ and $\vec{N}_j$. $\hat{n}_{j'}$ is the parallel transported form of $\hat{n}_j$ onto the i th plane. The parallel transport was done along the geodesic, following the scheme in ref. 20. The projections of the connecting vector $\hat{r}_{ij}$ onto the j th and i th tangent planes define the local geodesic directions $\hat{j}$ and $\hat{i}$, respectively. Note that in the 3D absolute frame (lab frame) $\hat{n}_j$ has changed from $\hat{n}_j$ to $\hat{n}_{j'}$, but $\hat{n}_{j'}$ maintains the same angle as $\hat{n}_j$ with the local geodesic, i.e., $\hat{o}i$ and $\hat{j}o$. On a gently curved and finely triangulated surface the changes $\hat{n}_j \rightarrow \hat{n}_{j'}$ are small as the surface normals $\vec{N}_j$ and $\vec{N}_i$ differ by a small angle. Now since the director field varies smoothly $\hat{n}_i$ and $\hat{n}_{j'}$ also differ by a small angle. Therefore $\hat{n}_i \times \hat{n}_{j'}$ is small and is directed along $-\vec{N}_i$ (or $\vec{N}_i$, depending on the relative orientations of $\hat{n}_i$ and $\hat{n}_{j'}$). A dot product between $\hat{n}_i \times \hat{n}_{j'}$ and $\hat{r}_{ij}$ reduces the contribution of this chiral term further, since $\hat{r}_{ij}$ is nearly perpendicular to $\vec{N}_i$. In the Monte Carlo scheme, any trial move that rotates the director $\hat{n}_i$ in its tangent plane changes the chiral contributions coming from all the neighbors (typically 5–6) of the i th vertex. Note that the sign of each of these contributions can be positive or negative depending on whether $\hat{n}_i \times \hat{n}_{j'}$ is directed along $-\vec{N}_i$ or $+\vec{N}_i$, respectively. Since these signs depend on small angles, which can be contaminated by discretization errors coming from the surface triangulation, the chiral term summed over 5–6 neighbors fails to show a systematic dependence on the local curvature. However, the dot product term $(\hat{n}_i \cdot \hat{n}_{j'})^2$ being positive definite is robust with respect to numerical discretization errors.

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