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Morphology of fluctuating spherical vesicles with internal bond-orientational order

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Abstract

We investigate the tangent-plane n-atic bond-orientational order on a deformable spherical vesicle to explore continuous shape changes accompanied by the development of quasi-long-range order below the critical temperature. The n-atic order parameter $\psi = \psi_0 e^{in\Theta}$, in which Θ denotes a local bond orientation, describes vector, nematic and hexatic orders for $n = 1, 2$ and 6 respectively. Since the total vorticity of the local order parameter on a surface of genus zero is constrained to 2 by the Gauss–Bonnet theorem, the ordered phase on a spherical surface should have $2n$ topological vortices of minimum strength $1/n$. Using the phenomenological model including a gauge coupling between the n-atic order and the curvature, we find that vortices tend to be separated as far as possible at the cost of local bending, resulting in a non-spherical equilibrium shape, although the tangent-plane n-atic order expels the local curvature deviation from the spherical surface in the ordered phase. Thus the spherical surface above the transition temperature transforms into ellipsoidal, tetrahedral, octahedral, icosahedral and dodecahedral surfaces along with the development of the n-atic order below the transition temperature for $n = 1, 2, 3, 6$ and 10 respectively.

1. Introduction

When surfactant molecules, or amphiphiles, which consist of molecules that combine both polar and non-polar parts, are dissolved in a single solvent such as water, these molecules tend to form bilayer membranes where the hydrophobic hydrocarbon chains of each monolayer are aggregated in the middle of the bilayer to reduce the contact with the water. These membranes are not covalently bonded, but are rather stabilized by weaker hydrophobic interaction. These membranes can have characteristic sizes which may be much larger than those of a single molecule. The sizes and shapes of these membranes can change as a function of temperature, salinity and/or surfactant concentration. Depending on the physical conditions of the system, these membranes can form random extended surfaces, regular periodic structures or closed vesicles separating an interior from an exterior [1]. Furthermore, some bilayer membranes are

prototypes of biological systems, although it should be noted that true biological membranes have several kinds of amphiphilic molecules and greater complexity due to embedded proteins.

In a wide class of membranes, molecules are free in lateral motion within the membrane, forming a two-dimensional fluid offering little resistance to changes in membrane shape. Such membranes are physical examples of random surfaces, which can undergo violent shape changes. Molecules in membranes can also exhibit varying degrees of orientational and positional order including tilt (smectic-C), hexatic and crystalline orderings similar to those found in free-standing liquid crystal films [2–4]. These ordered membranes provide fascinating laboratories for the study of the coupling between order and geometry, analogous in many ways to the coupling between matter and geometry in general relativity. The underlying cause of this coupling is as follows. A field describing orientational order cannot be parallel everywhere if it is forced to lie on a surface, such as that of a sphere, that curves in two directions having non-zero Gaussian curvature. It could lower its energy by flattening the surface. An additional complication arises when order develops on closed surfaces. A closed surface can be classified according to its genus h: the number of handles. Orientational order on a closed surface necessarily has topological defects (vortices) with total strength (vorticity) equal to the Euler characteristic $\chi = 2(1-h)$ of the surface [5]. Tangent-plane order on a sphere (torus) will have vorticity 2(0), since a sphere (torus) has genus 0(1) respectively. The continuous development of vector order on a deformable surface of genus zero will be accompanied by a continuous change from spherical to ellipsoidal shape [6]. Since vortices are energetically costly, it may be favourable for a closed physical membrane to transform into an open cylindrical structure when tangent-plane algebraic order develops in response to changes in temperature or other control variables [7]. Indeed, there are a number of experimental examples of shape changes that may be explained by the development of tangent-plane order.

Orientational orders for smectic-C and hexatic liquid crystals are described by an n-atic order parameter $\psi = \psi_0 e^{in\Theta}$ with $n = 1$ and 6 respectively [8]. The existence of the Kosterlitz–Thouless (KT) transition of the n-atic order on a deformable surface of genus zero is investigated in [9]. In this paper we present the shape changes of a deformable surface of genus zero along with the development of the n-atic order below the KT transition temperature from spherical to non-spherical. An n-atic order parameter can have vortices of strength $1/n$, and, since it is generally favourable to form vortices of minimum strength, we expect $2n$ maximally separated vortices of strength $1/n$ to be present in the ordered phase (low-temperature phase). Thus for $n = 1$ we find two antipodal vortices, and for $n = 2$, 3, 6 and 10 we find vortices to be located at the vertices of a tetrahedron, an octahedron, an icosahedron and a dodecahedron respectively. This is consistent with the calculations on a rigid sphere [10]. Furthermore, we find that the shape of the surface changes from spherical to prolate spheroidal, tetrahedral, octahedral, icosahedral or dodecahedral respectively. The icosahedral surface shape shown in figure 1 looks very similar to the surface of Sindbis virus [11]. The surface of Sindbis virus is made up of 240 copies of two virus-encoded membrane glycoproteins (called E1 and E2). The proteins are organized into trimers of E1–E2 pairs. Eighty of these trimers are linked together to form an icosahedral structure. On the face of an icosahedral surface, E1–E2 pairs show hexatic ordering, while at the vertices disclinations (vortices of hexatic order) of strength $1/6$ are found.

In this paper, we present the explicit calculations, extending the results given in [6], for the continuous shape changes accompanied by the the development of quasi-long-range order below the critical temperature. In addition, we study another case of n-atic order with $n = 10$ which generates 20 vortices at the vertices of the dodecahedron and produces dodecahedral shape changes. Our calculations are based on a phenomenological Hamiltonian for a complex order parameter field whose coupling to shape occurs via a covariant derivative and via change

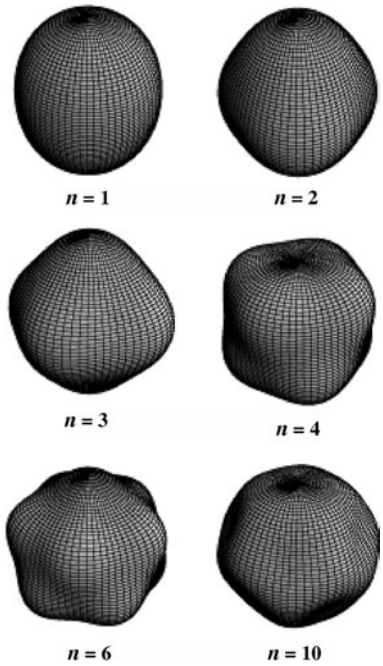

Figure 1. Mean-field shapes of deformable surfaces of genus zero with vector ($n = 1$), nematic ($n = 2$), triatic ($n = 3$), tetratic ($n = 4$), hexatic ($n = 6$) and decatic ($n = 10$) orders. Above the mean-field transition temperature, the equilibrium shape is spherical for all n. Below the transition temperature, the equilibrium shape depends on n and has polyhedral forms with $2n$ topological vortices with strength $1/n$ located at the vertices of prolate sphere, tetrahedron, distorted cube, octahedron, icosahedron, and dodecahedron respectively.

in the metric tensor [12]. The model is almost identical to the Ginzburg–Landau theory of a type II superconductor except that vorticity is fixed by surface topology rather than energetically determined by an external magnetic field. The ordering transition we find is very similar to the transition from a normal metal to the Abrikosov vortex lattice in a superconductor, and indeed our analysis follows very closely that of Abrikosov [13]. We find a highly degenerate set of functions that diagonalize the harmonic Hamiltonian on a rigid sphere. This degenerate set has exactly $2n$ zeros at arbitrary positions on the sphere and is very similar in form to the Laughlin wavefunction of fractional quantum Hall effect [14]. This paper is organized as follows. In section 2, we review fluid membranes briefly and describe their free energy as a function of curvature. We introduce a tangent-plane orientational order parameter and its coupling to shape fluctuations in section 3. In section 4, the Hamiltonian for a deformable spherical membrane with n-atic order is presented and shapes for the cases $n = 1, 2, 3, 4, 6$ and 10 below the transition temperature are given in a free energy minimization scheme. Discussions are given in section 5.

2. Fluid membranes

Although fluid membranes can be composed of many different types of chemical and molecular species, their behaviour (shapes, fluctuations, thermodynamics) can be understood from a unified point of view that considers their free energy of deformation. If the membrane were constrained to lie in a plane, the only relevant energy would be the compression of

the molecules, that is, change of the average area per molecule. This is analogous to sound waves in a three-dimensional fluid; there is no low-frequency response of the system to shear. However, since the membrane can also deform in the normal direction, there is an additional set of modes describing the conformations of the film. These out-of-plane deformations are known as bending or curvature modes and the free energy associated with such modes is known as the curvature free energy.

To construct the effective free energy for fluid membranes, it is convenient to introduce general curvilinear coordinates $\boldsymbol{u} = \{u^1, u^2\}$ and the metric structure. Defining locally a system of coordinates $\boldsymbol{u}$ on the membrane and denoting by $\boldsymbol{R}(\boldsymbol{u})$ the position of the point $\boldsymbol{u}$ in bulk d-dimensional Euclidean space, the metric tensor $g_{\alpha\beta}(\boldsymbol{u})$ induced by the embedding is

$$g_{\alpha\beta}(\boldsymbol{u}) = \boldsymbol{t}_\alpha(\boldsymbol{u}) \cdot \boldsymbol{t}_\beta(\boldsymbol{u}); \qquad \boldsymbol{t}_\alpha = \frac{\partial \boldsymbol{R}(\boldsymbol{u})}{\partial u^\alpha}, \tag{1}$$

where $\boldsymbol{t}_\alpha$ is a tangent vector to the surface, and the element of area is

$$\mathrm{d}A = \mathrm{d}^2u\,\sqrt{g}; \qquad g = \det(g_{\alpha\beta}). \tag{2}$$

The extrinsic curvature tensor $\boldsymbol{K}_{\alpha\beta}$ is defined by

$$\boldsymbol{K}_{\alpha\beta}(\boldsymbol{u}) = D_\alpha D_\beta \boldsymbol{R}(\boldsymbol{u}), \tag{3}$$

where D_α is a covariant derivative with respect to the metric $g_{\alpha\beta}$. In general, $\boldsymbol{K}_{\alpha\beta}$ is normal to the surface [3]. Therefore, in the particular case of a surface in R^3, $\boldsymbol{K}_{\alpha\beta}$ is proportional to the unit normal vector $\boldsymbol{N}$ to the surface and is written as

$$\boldsymbol{K}_{\alpha\beta} = K_{\alpha\beta}\boldsymbol{N}, \tag{4}$$

where $K_{\alpha\beta}$ is a symmetric tensor. We can discuss the curvature energy using symmetry considerations. The free energy must be only a function of the field $\boldsymbol{R}(\boldsymbol{u})$, invariant under displacements, rotations in R^d and reparametrization. Expanding in local terms involving more and more derivatives and keeping only the terms relevant by naive power counting, the most general form of the curvature energy $\mathcal{H}_\kappa$ up to quadratic order in the curvatures has only three terms [1] and can be written in terms of the tension term and the mean and Gaussian curvature terms

$$\mathcal{H}_\kappa = \tau \int \mathrm{d}^2u\,\sqrt{g} + \frac{\kappa}{2}\int \mathrm{d}^2u\,\sqrt{g}(M - M_0)^2 + \frac{\bar{\kappa}}{2}\int \mathrm{d}^2u\,\sqrt{g}G. \tag{5}$$

Here, τ is the tension of membrane, M is twice the mean curvature, K^α_α, and G is the Gaussian curvature given by $\det K^\beta_\alpha$. The tension term can be dropped since we consider the fluid membrane which has vanishing tension and the Hamiltonian with the curvature energies was discussed by Helfrich and Canham [15]. The mean curvature that minimizes the energy has a value M_0, termed the spontaneous curvature of the membrane. The energy cost of deviation from the spontaneous curvature is the bending modulus, κ. The parameter $\bar{\kappa}$, known as the saddle-splay modulus, measures the energy cost of saddle-like deformation. The spontaneous curvature describes the tendency of the bilayer membrane to bend. It is viewed to arise from the fact that the two layers of the bilayer may not have the same number of molecules in the outside part and the inside part of bilayer membrane. The bending moduli, κ and $\bar{\kappa}$, arise from the elastic constants determined by the head–head and tail–tail interactions. It is expected that these moduli are sensitively dependent on the surfactant chain length but only weakly dependent on the head–head interaction strength. The parameters M_0, κ and $\bar{\kappa}$ can be derived from a simple microscopic model that incorporates both the changes in the area per molecule and the curvature. We note that a stable membrane will always have $\kappa > 0$. However, the sign of $\bar{\kappa}$ can be either positive or negative. Membranes that prefer isotropic shapes where the Gaussian curvature $G > 0$, such as spheres or planes, will have $\bar{\kappa} > 0$, while membranes that

Table 1. The nth rank symmetric traceless tensors, $Q^{(n)}$, for $n = 1, 2, 3$, and 4 in d-dimensional space.

$Q_i^{(1)} = m_i$
$Q_{ij}^{(2)} = m_i m_j - \frac{1}{d}\delta_{ij}$
$Q_{ijk}^{(3)} = m_i m_j m_k - \frac{1}{d+2}(\delta_{ij}m_k + \delta_{ik}m_j + \delta_{jk}m_i)$
$Q_{ijkl}^{(4)} = m_i m_j m_k m_l - \frac{1}{d+4}\,(\delta_{ij}m_k m_l +$ the other 5 permutations) $+ \frac{1}{(d+2)(d+4)}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$

prefer saddle shapes where the Gaussian curvature $G < 0$ will have $\bar{\kappa} < 0$. One can show that the requirement of a positive-definite quadratic term implies that membranes are only stable if $\kappa - 2\bar{\kappa} > 0$; otherwise higher-order curvature terms are needed to stabilize the system. Since we consider the spherical membrane whose topology is fixed, the Gaussian curvature energy gives a constant contribution by the Gauss–Bonnet theorem $\int \sqrt{g}G = 2\pi\chi = 4\pi(1-h)$ and can be dropped. Thus the free energy of the fluid membrane with fixed topology contains only the bending curvature energy.

3. Orientational order

In a fluid membrane, molecules can flow freely to adapt themselves to any particular shape of the surface. If correlations among the molecular positions of the molecules forming the membrane exist, the molecules may exhibit in-plane crystalline order and form a kind of two-dimensional solid. On the other hand, the molecules may exhibit a weaker order in which only orientations are correlated at a long distance scale. Orientational order means that to each point on the membrane is associated a preferred direction within the tangent plane of the membrane. For example, the stable phase of the membrane at high temperature is generally the liquid phase with no translational or orientational order for the hexatic order, or the smectic-A phase in which molecular axes are normal to the surface for the vector order. At lower temperature, the membrane can condense into a hexatic phase in which there is quasi-long-range six-fold bond-angle order or into a smectic-C (Sm-C) phase in which molecules tilt relative to the surface normal. To describe Sm-C (vector) and/or hexatic order, we introduce at each point $\boldsymbol{X}(\boldsymbol{u})$ on the membrane a unit vector $\boldsymbol{m}(\boldsymbol{u})$ in the tangent plane of the membrane. For Sm-C order, $\boldsymbol{m}(\boldsymbol{u})$ is a true vector, invariant under rotations of $2p\pi$ (p is an integer) about the unit surface normal $\boldsymbol{N}(\boldsymbol{u})$ erected at $\boldsymbol{X}(\boldsymbol{u})$. For hexatic order, rotations of $\boldsymbol{m}(\boldsymbol{u})$ by $2p\pi/6$ about $\boldsymbol{N}(\boldsymbol{u})$ lead to physically equivalent states. More generally, we consider 'n-atic' order in which rotations of $\boldsymbol{m}(\boldsymbol{u})$ by $2p\pi/n$ produce physically equivalent states. A two-dimensional nematic with an in-plane symmetric traceless tensor order parameter is an example of a 2-atic. Although we know of no physical realizations of other n-atics yet, we find it instructive to consider how the development of such order affects morphological changes in spherical vesicles for $n = 1, 2, 3, 4, 6$ and 10.

To describe the tangent-plane n-atic order, we introduce orthonormal unit vectors $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ at each point on the membrane. $\boldsymbol{e}_1(\boldsymbol{u}) \cdot \boldsymbol{m}(\boldsymbol{u}) = \cos\Theta(\boldsymbol{u})$ defines a local angle $\Theta(\boldsymbol{u})$. n-atic order is then described by the order parameter $\psi(\boldsymbol{u}) = \mathrm{e}^{\mathrm{i}n\Theta(\boldsymbol{u})}$, which can be related to the nth rank symmetric traceless tensor constructed from the unit vector $\boldsymbol{m}$. The nth rank symmetric traceless tensors are the nth rank spherical tensors (table 1).

In general, there are 2^n components in the nth rank spherical tensor $\boldsymbol{Q}^{(n)}_{i_1 i_2 \cdots i_n}$ on the tangent plane since $i_1, i_2, \ldots, i_n$ can be either 1 or 2. By permutational symmetry, there are only $(n+1)$

possible independent components. However, there are $(n-1)$ additional traceless conditions. Hence, there are only two independent components in $\boldsymbol{Q}^{(n)}_{i_1 i_2 \cdots i_n}$. The linear combination of these nth rank spherical tensors

$$\sum_{i_1,i_2,\ldots,i_n}^{1,2} \mathrm{i}^k \boldsymbol{Q}^{(n)}_{i_1 i_2 \cdots i_n}, \tag{6}$$

where k is the number of 2s in $(i_1, i_2, \ldots, i_n)$, becomes $(m_1+\mathrm{i}m_2)^n$ where $m_1 = \boldsymbol{e}_1 \cdot \boldsymbol{m} = \cos\Theta$ and $m_2 = \boldsymbol{e}_2 \cdot \boldsymbol{m} = \sin\Theta$. Thus the n-atic order parameter is described by

$$\psi = \sum_{i_1,i_2,\ldots,i_n}^{1,2} \mathrm{i}^k \boldsymbol{Q}^{(n)}_{i_1 i_2 \cdots i_n} = \mathrm{e}^{\mathrm{i}n\Theta}. \tag{7}$$

Note that since $\Theta(\boldsymbol{u})$ depends on the choice of orthonormal vectors $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$, the order parameter $\psi(\boldsymbol{u})$ does as well. This means that any spatial derivatives in a phenomenological Hamiltonian for ψ must be covariant derivatives.

We now describe the Hamiltonian of the membrane with orientational order in a reparametrization-invariant way. For a flat membrane the vector Hamiltonian corresponds to the usual XY model

$$\mathcal{H} = \tfrac{1}{2} K_n \int \mathrm{d}^2 x \; \partial_\alpha \boldsymbol{m} \cdot \partial_\alpha \boldsymbol{m}. \tag{8}$$

Using the fact that any spatial derivatives must be covariant derivatives and

$$D_\alpha \boldsymbol{m} = (D_\alpha m^\beta) \boldsymbol{t}_\beta \tag{9}$$

is the tangential component of $\partial_\alpha \boldsymbol{m}$, one can show that the only possible free energy term for $\boldsymbol{m}$ which respects this Z_1 symmetry is

$$\mathcal{H} = \tfrac{1}{2} K_1 \int \mathrm{d}^2 u \; \sqrt{g} D_\mu m^\alpha D^\mu m_\alpha. \tag{10}$$

The dimensionless coupling constant K_1 is the vector-order stiffness and measures the strength of the coupling between the orientations of neighbouring vectors. We then generalize this XY-like Hamiltonian for the vector order to the n-atic Hamiltonian using the nth-rank spherical tensors. In general, the n-atic Hamiltonian can be written as

$$\mathcal{H} = \frac{1}{2} K_n \int \mathrm{d}^2 u \; \sqrt{g} \frac{D_\mu \boldsymbol{Q}^{(n)^{\alpha_1 \cdots \alpha_n}} D^\mu \boldsymbol{Q}^{(n)}{}_{\alpha_1 \cdots \alpha_n}}{\boldsymbol{Q}^{(n)^{\alpha_1 \cdots \alpha_n}} \boldsymbol{Q}^{(n)}{}_{\alpha_1 \cdots \alpha_n}}, \tag{11}$$

where K_n is the n-atic rigidity. Using the spherical tensors in table 1, we find

$$\boldsymbol{Q}^{(n)^{\alpha_1 \cdots \alpha_n}} \boldsymbol{Q}^{(n)}{}_{\alpha_1 \cdots \alpha_n} = \frac{1}{2(n-1)}, \tag{12}$$

and

$$D_\mu \boldsymbol{Q}^{(n)^{\alpha_1 \cdots \alpha_n}} D^\mu \boldsymbol{Q}^{(n)}{}_{\alpha_1 \cdots \alpha_n} = \frac{n^2}{2(n-1)} D_\mu m^\alpha D^\mu m_\alpha, \tag{13}$$

for $n > 1$. Hence, the Hamiltonian for the n-atic order becomes

$$\mathcal{H}_n = \tfrac{1}{2} n^2 K_n \int \mathrm{d}^2 u \; \sqrt{g} D_\mu m^\alpha D^\mu m_\alpha. \tag{14}$$

In this form of $\mathcal{H}_n$, we neglected all terms that are irrelevant at large distance by power counting. Other terms such as $m_\alpha K^\alpha_\beta K^{\beta\gamma} m_\gamma$ which couple $\boldsymbol{m}$ to the principal directions of curvature of the membrane are not invariant under the global rotation by $2\pi/n$ of $\boldsymbol{m}$, and are irrelevant at large distance. Thus, this free energy has a full $O(2)$ rotational symmetry. This is similar

to the fact that a two-dimensional crystal with hexagonal or triangular structure has isotropic elastic properties at large distance scale. For n-atics with $n \geqslant 3$, there is only one elastic constant K_n. For $n = 1$ or 2, there are in general two elastic constants. For simplicity, we will consider the single elastic constant approximation for all n-atics.

To describe this Hamiltonian in terms of a local angular order parameter Θ, at each point we introduce two orthonormal vectors $\boldsymbol{e}_a(\boldsymbol{u})(a = 1, 2)$ tangential to the membrane. This is equivalent to introducing a zweibein $e_a^i(\boldsymbol{u})$ compatible with the induced metric $g_{\alpha\beta}(\boldsymbol{u})$. In components,

$$\boldsymbol{e}_a = e_a^\alpha \boldsymbol{t}_\alpha \tag{15}$$

and the orthonormality $\boldsymbol{e}_a \cdot \boldsymbol{e}_b = \delta_{ab}$ implies

$$e_a^\alpha e_b^\beta g_{\alpha\beta} = \delta_{ab}; \qquad e_a^\alpha e_b^\beta \delta^{ab} = g^{\alpha\beta}. \tag{16}$$

The angular order parameter is frustrated by the rotation of tangent vectors that occurs under parallel transport on a curved surface. The amount of frustration is given by the gauge field A_α, i.e. the covariant derivative of $\boldsymbol{e}_a$ in direction α defines the gauge field A_α. Under parallel transport in direction $\mathrm{d}u^\alpha$, each $\boldsymbol{e}_a$ is rotated by an angle $A_\alpha \,\mathrm{d}u^\alpha$. Thus the gauge field A_α is defined by

$$D_\alpha \boldsymbol{e}_a = -A_\alpha \varepsilon_{ab} \boldsymbol{e}_b, \tag{17}$$

where ε_{ab} is the antisymmetric tensor with $\varepsilon_{12} = -\varepsilon_{21} = 1$. $A_\alpha \varepsilon_{ab}$ is called the spin-connection and describes how the basis vector $\boldsymbol{e}_a$ rotates under parallel transport according to the Gaussian curvature G of the surface. In fact, the curl of the gauge field A_α is related to the Gaussian curvature by

$$\eta^{\alpha\beta} D_\alpha A_\beta = G, \tag{18}$$

where $\eta^{\alpha\beta}$ is the antisymmetric tensor density

$$\begin{aligned} \eta_{\alpha\beta} &= \boldsymbol{N} \cdot (\boldsymbol{t}_\alpha \times \boldsymbol{t}_\beta) = \sqrt{g}\varepsilon_{\alpha\beta}, \\ \eta^{\alpha\beta} &= g^{\alpha\alpha'} g^{\beta\beta'} \eta_{\alpha'\beta'}. \end{aligned} \tag{19}$$

The covariant derivative of $\boldsymbol{m} = \cos\Theta \boldsymbol{e}_1 + \sin\Theta \boldsymbol{e}_2$ is written as

$$\begin{aligned} D_\alpha \boldsymbol{m} &= (D_\alpha m_a)\boldsymbol{e}_a + m_a (D_\alpha \boldsymbol{e}_a) \\ &= (D_\alpha m_a)\boldsymbol{e}_a - m_a A_\alpha \varepsilon_{ab} \boldsymbol{e}_b \\ &= (D_\alpha \Theta)(-\sin\Theta \boldsymbol{e}_1 + \cos\Theta \boldsymbol{e}_2) - A_\alpha(\cos\Theta \boldsymbol{e}_2 - \sin\Theta \boldsymbol{e}_1) \\ &= (D_\alpha \Theta - A_\alpha)\boldsymbol{m}_\perp, \end{aligned} \tag{20}$$

where $\boldsymbol{m}_\perp = -\sin\Theta \boldsymbol{e}_1 + \cos\Theta \boldsymbol{e}_2$ satisfying $\boldsymbol{m} \cdot \boldsymbol{m}_\perp = 0$. Then the n-atic Hamiltonian is written as

$$\mathcal{H}_n = \tfrac{1}{2} n^2 K_n \int \mathrm{d}^2 u \, \sqrt{g} g^{\alpha\beta} (\partial_\alpha \Theta - A_\alpha)(\partial_\beta \Theta - A_\beta). \tag{21}$$

This form of the free energy is invariant under local transformations $\Theta(\boldsymbol{u}) \to \Theta(\boldsymbol{u}) + \Lambda(\boldsymbol{u})$, $A_\alpha(\boldsymbol{u}) \to A_\alpha(\boldsymbol{u}) + \partial_\alpha \Lambda(\boldsymbol{u})$. This gauge invariance corresponds to a local rotation of the reference frame $\boldsymbol{e}_a$. In terms of the complex order parameter ψ, the Hamiltonian for n-atic order becomes

$$\mathcal{H}_n = \tfrac{1}{2} K_n \int \mathrm{d}^2 u \, \sqrt{g} g^{\alpha\beta} D_\alpha \psi (D_\beta \psi)^* \tag{22}$$

where $D_\alpha \psi = (\partial_\alpha - \mathrm{i} n A_\alpha)\psi$. In this description, all n-atics have the same long-wavelength elastic energy. Their properties can differ, however, because their topological excitations are characterized by different winding numbers. Since we assume that in the disordered state the

membrane forms a spherical shape and there is no topological deformation of the membrane shape, order in ψ is necessarily accompanied by the topological excitations called vortices. As the total winding vorticity of a vector field on a closed surface with h handles is equal to the Euler characteristic $\chi = 2(1-h)$, vector fields on the surface of a sphere ($h = 0$) have total vorticity 2. The minimum winding number disclination for an n-atic is $1/n$. The energy of an individual disclination on both flat and curved surfaces is proportional to the square of its winding number. It is therefore always favourable to form disclinations with the lowest possible winding number. In addition, disclinations with the same sign repel each other. These considerations imply that the ground state of a sphere with the tangent-plane n-atic order will have $2n$ maximally separated disclinations of winding number $1/n$.

4. Shape changes below the transition temperature

It has been shown that the structure of the KT transition of a vortex-monopole Coulomb gas on a rigid sphere is the same as in the planar case [16]. For a fluctuating spherical surface, there is an effective KT transition in a certain region in the parameter space (κ, K_n). In [9], it has been shown that for $n^2 K_n/\kappa \ll 1/4$ there exists a KT transition at the finite temperature $T_{\mathrm{KT}} = \pi K_n/2$. To describe the phase transition and the corresponding shape changes, we introduce the magnitude of the complex n-atic order parameter as in $\psi = \psi_0 \mathrm{e}^{\mathrm{i}n\Theta}$ and consider the simplest long-wavelength Ginzburg–Landau Hamiltonian for the n-atic order parameter ψ

$$\mathcal{H}_{\mathrm{GL}} = \int \mathrm{d}^2u\,\sqrt{g}\left(r|\psi|^2 + \frac{1}{2}u|\psi|^4\right) + \frac{K_n}{2}\int \mathrm{d}^2u\,\sqrt{g}\,g^{\alpha\beta}(\partial_\alpha^* + \mathrm{i}nA_\alpha)\psi^*(\partial_\beta - \mathrm{i}nA_\beta)\psi. \quad (23)$$

This is similar to the Ginzburg–Landau Hamiltonian for a type II superconductor in an external magnetic field,

$$\mathcal{H}_{\mathrm{GL}}^{\mathrm{sc}} = \int \mathrm{d}^3x\left(r|\psi|^2 + C|(\boldsymbol{\nabla} - \mathrm{i}e^*\boldsymbol{A})\psi|^2 + \frac{1}{2}u|\psi|^4 + \frac{1}{8\pi}(\nabla\times\boldsymbol{A} - \boldsymbol{H})^2\right) \quad (24)$$

where $e^* = 2e/\hbar c$. Both have a complex order parameter ψ with covariant derivatives providing a coupling between ψ and a 'vector potential' $\boldsymbol{A}$ or A_α. In a magnetic field, the superconductor can undergo a second order mean-field transition from a normal metal to the Abrikosov vortex lattice phase with a finite density of vortices determined energetically by temperature and the magnetic field $\boldsymbol{H}$. The magnetic field is conjugate to the vortex number N_{v} since $\int \mathrm{d}^3x\,(\nabla\times\boldsymbol{H}) = LN_{\mathrm{v}}\phi_0$, where L is the length of the sample along $\boldsymbol{H}$ and $\phi_0 = hc/2e$ is the flux quantum. On a closed surface with n-atic order, there is a second-order mean-field transition to a state with vortex number determined by topology rather than conjugate external field. Thus, the mean-field n-atic transition on a closed surface is analogous to the transition to an Abrikosov phase with a fixed number of vortices rather than fixed field conjugate to vortex number. However, a Meissner phase with zero vortices does not exist because we do not have an analogue for magnetic intensity $\boldsymbol{H}$; rather topology fixes vortex number.

The complete Hamiltonian for n-atic order on a deformable surface is $\mathcal{H} = \mathcal{H}_\kappa + \mathcal{H}_{\mathrm{GL}}$. Using the spherical angles $\boldsymbol{\Omega} = \{\theta, \phi\}$ for the local curvilinear coordinates $\boldsymbol{u}$, the field $\rho(\boldsymbol{\Omega})$ in $\boldsymbol{R}(\boldsymbol{\Omega}) = R_0(1 + \rho(\boldsymbol{\Omega}))\boldsymbol{e}_r$ can be expanded in Laplace series with spherical harmonic components. Any isotropic change in $\boldsymbol{R}$ can be described by R_0. In addition, uniform translation which changes neither the shape nor the energy of the vesicle corresponds to distortions in ρ with $l = 1$, and can be discarded by fixing the position of the centre of mass of the vesicle. These considerations imply that ρ will have no $l = 0$ or 1 components in the spherical harmonic expansion:

$$\rho(\boldsymbol{\Omega}) = \sum_{l=2}^{\infty}\sum_{m=-l}^{l}\rho_{lm}Y_l^m(\boldsymbol{\Omega}). \quad (25)$$

The shape and size of the vesicle are determined entirely by the parameters R_0 and ρ_{lm}.

In spherical polar coordinates with origin at the centre of the vesicle, the metric is given by

$$g_{\alpha\beta} = \partial_\alpha \boldsymbol{R} \cdot \partial_\beta \boldsymbol{R} = R_0^2\{(1+\rho)^2 \bar{g}_{\alpha\beta} + \partial_\alpha\rho\partial_\beta\rho\}; \tag{26a}$$

$$\bar{g}_{\alpha\beta} = \begin{pmatrix} 1 & 0 \\ 0 & \sin^2\theta \end{pmatrix}, \tag{26b}$$

and hence

$$\sqrt{g} = \sqrt{\det g_{\alpha\beta}} = R_0^2(1+\rho)^2 \sin\theta \sqrt{1 + \left(\frac{\nabla\rho}{1+\rho}\right)^2} \tag{27}$$

where $(\nabla\rho)^2 = (\partial_\theta\rho)^2 + (\partial_\phi\rho/\sin\theta)^2$. The curvature tensor in the same representation is

$$K_{\alpha\beta} = \boldsymbol{N} \cdot D_\alpha D_\beta \boldsymbol{R} = \frac{-R_0}{\sqrt{1 + \left(\frac{\nabla\rho}{1+\rho}\right)^2}} k_{\alpha\beta} \tag{28a}$$

$$k_{\alpha\beta} = \begin{pmatrix} 1+\rho-\partial_\theta^2\rho + \dfrac{2(\partial_\theta\rho)^2}{1+\rho} & \cot\theta\partial_\phi\rho - \partial_\theta\partial_\phi\rho + \dfrac{2(\partial_\theta\rho)(\partial_\phi\rho)}{1+\rho} \\ (k_{\theta\phi} = k_{\phi\theta}) & (1+\rho)\sin^2\theta - \sin\theta\cos\theta\partial_\theta\rho - \partial_\phi^2\rho + \dfrac{2(\partial_\phi\rho)^2}{1+\rho} \end{pmatrix}. \tag{28b}$$

The reduced tensors $\bar{g}_{\alpha\beta}$ and $k_{\alpha\beta}$ do not depend on R_0. Therefore, R_0 can be expressed as a function of $\mathcal{A}$ and ρ_{lm} via the relation

$$\begin{aligned} \mathcal{A} &= \int \mathrm{d}^2u\,\sqrt{g} = \int R_0^2\,\mathrm{d}\Omega\,\{(1+\rho)^2 + \tfrac{1}{2}(\nabla\rho)^2 + \mathcal{O}(\rho^4)\} \\ &\simeq 4\pi R_0^2\left\{1 + \frac{1}{8\pi}\sum_{l=2}^{\infty}\sum_{m=-l}^{l}(l(l+1)+2)|\rho_{lm}|^2\right\}. \end{aligned} \tag{29}$$

In the disordered phase above T_{KT}, $\rho = 0$ and $R = R_0$. We will use the Hamiltonian $\mathcal{H}$ expressed in terms of reduced parameters and the constant area $\mathcal{A}$ in our calculations of shape changes below the second-order disordered-to-n-atic transition.

The Hamiltonian is a functional of $\psi(\boldsymbol{\Omega})$ and $\rho(\boldsymbol{\Omega})$ at the fixed area $\mathcal{A}$. To find the equilibrium form of $\psi(\boldsymbol{\Omega})$ and $\rho(\boldsymbol{\Omega})$, we need to minimize $\mathcal{H}$ over $\psi(\boldsymbol{\Omega})$ and $\rho(\boldsymbol{\Omega})$. There is a considerable simplification if we restrict our attention to the neighbourhood of the transition temperature T_{KT}. Near the critical temperature, to order ψ^4, the variation of the curvature energy is of order $\kappa\rho^2$. When this is comparable to the Ginzburg–Landau free energy for ψ, we only need to keep couplings of order $\rho\psi^2$. If we set the spin-connection $A_\alpha = \bar{A}_\alpha + a_\alpha$ with the rigid sphere contribution $(\bar{A}_\theta, \bar{A}_\phi) = (0, -\cos\theta)$, the Ginzburg–Landau Hamiltonian for ψ becomes

$$\begin{aligned} \mathcal{H}_{\mathrm{GL}} = &\int \mathrm{d}\Omega\, R_0^2(1+2\rho)(r|\psi|^2 + \tfrac{1}{2}u|\psi|^4) \\ &+ \frac{K_n}{2}\int \mathrm{d}\Omega\,\bar{g}^{\alpha\beta}\{(\bar{D}_\alpha\psi)^*(\bar{D}_\beta\psi) + J_\alpha a_\beta + \mathcal{O}(\rho^2|\psi|^2)\}, \end{aligned} \tag{30}$$

where $\bar{D}_\alpha \equiv \partial_\alpha + \mathrm{i}n\bar{A}_\alpha$, and the current density is given by

$$J_\alpha = \mathrm{i}n(\psi^*\partial_\alpha\psi - \psi\partial_\alpha\psi^* - 2\mathrm{i}n\bar{A}_\alpha|\psi|^2). \tag{31}$$

Keeping the order of approximation consistent with $|\psi|^4$ and $\rho|\psi|^2$, the curvature energy is given by

$$\mathcal{H}_\kappa = \frac{\kappa}{2}\int \mathrm{d}\Omega\,[(\nabla^2+2)\rho]^2 \tag{32}$$

where the spontaneous curvature $1/R_0$ is used, and R_0^2 can be replaced by $\mathcal{A}/4\pi$. Hence the Hamiltonian can be decomposed into $\mathcal{H} = \mathcal{H}^0[\psi] + \mathcal{H}'[\psi, \rho]$:

$$\mathcal{H}^0 = \int \mathrm{d}\boldsymbol{\Omega}\, \frac{\mathcal{A}}{4\pi}\left(r|\psi|^2 + \frac{1}{2}u|\psi|^4\right) + \frac{K_n}{2}\int \mathrm{d}\boldsymbol{\Omega}\, (\bar{D}^\alpha\psi)^*(\bar{D}_\alpha\psi) \tag{33}$$

which does not depend on $\rho(\boldsymbol{\Omega})$, and

$$\mathcal{H}' = \int \mathrm{d}\boldsymbol{\Omega}\, \rho\cdot\frac{\mathcal{A}}{2\pi}\left(r|\psi|^2 + \frac{1}{2}u|\psi|^4\right) - \frac{K_n}{2}\int \mathrm{d}\boldsymbol{\Omega}\, \frac{\rho}{\sin\theta}\partial_\alpha(\eta^{\beta\alpha}J_\beta\sin\theta) + \frac{\kappa}{2}\int \mathrm{d}\boldsymbol{\Omega}\, [(\nabla^2+2)\rho]^2 \tag{34}$$

which contains $\rho(\boldsymbol{\Omega})$ with the metric $\bar{g}_{\alpha\beta}$ taken on the unit sphere. Thus the full terms, up to quadratic in ρ, can be rearranged in ascending powers of ρ:

$$\mathcal{H} = \mathcal{H}^0 + \int \mathrm{d}\boldsymbol{\Omega}\, \rho(\boldsymbol{\Omega})\tilde{\Phi}(\boldsymbol{\Omega}) + \frac{\kappa}{2}\iint \mathrm{d}\boldsymbol{\Omega}\, \mathrm{d}\boldsymbol{\Omega}'\, \rho(\boldsymbol{\Omega})\mathcal{M}(\boldsymbol{\Omega}, \boldsymbol{\Omega}')\rho(\boldsymbol{\Omega}') \tag{35}$$

with

$$\tilde{\Phi}(\boldsymbol{\Omega}) = \frac{\mathcal{A}}{2\pi}\left(r|\psi|^2 + \frac{1}{2}u|\psi|^4\right) - \frac{K_n}{2\sin\theta}\partial_\alpha(\eta^{\beta\alpha}J_\beta\sin\theta) \tag{36}$$

$$\mathcal{M}(\boldsymbol{\Omega}, \boldsymbol{\Omega}') = \sum_{l=2}^{\infty}\sum_{m=-l}^{l} Y_l^{m*}(\boldsymbol{\Omega})(l-1)^2(l+2)^2 Y_l^m(\boldsymbol{\Omega}'). \tag{37}$$

By completing the square with respect to the $\rho(\boldsymbol{\Omega})$ field, the minimum energy configuration,

$$\rho(\boldsymbol{\Omega}) = -\frac{1}{\kappa}\int \mathrm{d}\boldsymbol{\Omega}'\, \mathcal{M}^{-1}(\boldsymbol{\Omega}, \boldsymbol{\Omega}')\tilde{\Phi}(\boldsymbol{\Omega}'), \tag{38}$$

is obtained. The inverse differential operator $\mathcal{M}^{-1}$ satisfies the orthonormality condition

$$\int \mathrm{d}\boldsymbol{\Omega}'\, \mathcal{M}(\boldsymbol{\Omega}_1, \boldsymbol{\Omega}')\mathcal{M}^{-1}(\boldsymbol{\Omega}', \boldsymbol{\Omega}_2) = \delta_{(l\geqslant 2)}(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_2) \tag{39}$$

where $\delta_{(l\geqslant 2)}(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_2)$ is the Dirac delta function in spherical harmonics space with $l \geqslant 2$. Substituting this relation into $\mathcal{H}$, we have the effective Hamiltonian with the ψ field only

$$\mathcal{H}_{\mathrm{eff}} = \int \mathrm{d}\boldsymbol{\Omega}\left\{\frac{\mathcal{A}}{4\pi}\left(r|\psi|^2 + \frac{1}{2}u|\psi|^4\right) + \frac{K_n}{2}(\bar{D}^\alpha\psi)^*(\bar{D}_\alpha\psi)\right\} - \frac{1}{2\kappa}\sum_{l=2}^{\infty}\sum_{m=-l}^{l}\frac{|\tilde{\Phi}_{lm}|^2}{(l-1)^2(l+2)^2}, \tag{40}$$

where

$$\tilde{\Phi}_{lm} = \int \mathrm{d}\boldsymbol{\Omega}\, Y_l^{m*}(\boldsymbol{\Omega})\tilde{\Phi}(\boldsymbol{\Omega}). \tag{41}$$

Before proceeding with our analysis of the n-atic transition on a deformable sphere, it is useful to recall Abrikosov's calculation of the transition to the vortex state. The first step is to calculate the eigenfunctions of the harmonic part of $\mathcal{H}_{\mathrm{GL}}$ when $\boldsymbol{\nabla}\times\boldsymbol{A} = \boldsymbol{H}$. These can be divided into highly degenerate sets separated by an energy gap, $\hbar\omega_c = 2Ce^*H$. In the Landau gauge, say $\boldsymbol{A} = (0, Hx, 0)$, the eigenfunctions in the lowest energy manifold are $\psi_k = \mathrm{e}^{\mathrm{i}ky}\mathrm{e}^{-e^*H(x-x_k)^2}$ where $x_k = k/e^*H$. The order parameter $\psi(\boldsymbol{x})$ of the ordered state is expressed as a linear combination $\psi(\boldsymbol{x}) = \sum\alpha_k\psi_k$, where the complex parameters α_k are determined by minimization of $\mathcal{H}_{\mathrm{GL}}$.

With this analogy in mind, we will follow Abrikosov's treatment of the superconducting transition near H_{c2} to study the development of n-atic order on a sphere. We first diagonalize

$\mathcal{H}$ in the harmonic level, that is, we determine the functions ψ which satisfy $K_n D_\alpha D^\alpha \psi = \varepsilon\psi$ for $\rho = 0$ and $A_\alpha = \bar{A}_\alpha$. Nonlinearities arise from the $|\psi|^4$ term in the Ginzburg–Landau Hamiltonian for ψ and from the fact that A_α and $g_{\alpha\beta}$ depend nonlinearly on the deviation from the ideal spherical shape. To minimize $\mathcal{H}_{\rm eff}$, we first seek the lowest energy configurations of the operators corresponding to the harmonic terms only. Then, we linearly combine these eigenfunctions to get the function which has the lowest energy for $\mathcal{H}_{\rm eff}$. That is, the manifold of the lowest energy eigenstates of the harmonic terms is highly degenerate. Nonlinear terms pick out the lowest energy state that is a linear combination of the degenerate eigenstates of the harmonic terms and lift the degeneracy. We divide $\mathcal{H}_{\rm eff}$ into a harmonic part, $\mathcal{H}_{\rm har}$, and a nonlinear part, $\mathcal{H}_{\rm nl}$ as follows:

$$\mathcal{H}_{\rm har} = \int \mathrm{d}\mathbf{\Omega} \left\{ \frac{\mathcal{A}}{4\pi} r|\psi|^2 + \frac{K_n}{2} (\bar{D}^\alpha \psi)^* (\bar{D}_\alpha \psi) \right\}; \tag{42}$$

$$\mathcal{H}_{\rm nl} = \frac{\mathcal{A}}{4\pi} \int \mathrm{d}\mathbf{\Omega}\, \frac{1}{2} u|\psi|^4 - \frac{1}{2\kappa} \sum_{l=2}^{\infty} \sum_{m=-l}^{l} \frac{|\tilde{\Phi}_{lm}|^2}{(l-1)^2(l+2)^2}, \tag{43}$$

where the covariant Laplacian for $\mathcal{H}_{\rm har}$ is

$$\begin{aligned} \bar{\Delta} = \Delta|_{\bar{g}_{\alpha\beta}} &= \frac{1}{\sqrt{\bar{g}}} (\partial_\alpha - \mathrm{i}n\bar{A}_\alpha) \sqrt{\bar{g}}\, \bar{g}^{\alpha\beta} (\partial_\beta - \mathrm{i}n\bar{A}_\beta) \\ &= \partial_\theta^2 + \cot\theta\, \partial_\theta + \mathrm{cosec}^2\,\theta\, \partial_\phi^2 + 2\mathrm{i}n\, \mathrm{cosec}\,\theta \cot\theta\, \partial_\phi - n^2 \cot^2\theta \end{aligned} \tag{44}$$

in the spherical polar representation.

Now then, for disclinations at $\mathbf{\Omega}_j \equiv (\theta_j, \phi_j)$ specifying the position of the jth zero of ψ, we have

$$|\psi|^2 = \frac{\psi_0^2}{\mathcal{N}(\{\mathbf{\Omega}_j\})} \prod_{j=1}^{2n} \frac{1 - \cos\omega_j}{2} \equiv \frac{\psi_0^2}{\mathcal{N}(\{\mathbf{\Omega}_j\})} W(\mathbf{\Omega}; \{\mathbf{\Omega}_j\}) \tag{45}$$

where $\cos\omega_j = \cos\theta\cos\theta_j + \sin\theta\sin\theta_j\cos(\phi - \phi_j) = \mathbf{\Omega}\cdot\mathbf{\Omega}_j$ is the direction cosine, and $\mathcal{N}$ is the normalization factor such that $\int \mathrm{d}\mathbf{\Omega}\, W(\mathbf{\Omega}; \{\mathbf{\Omega}_j\}) = \mathcal{N}(\{\mathbf{\Omega}_j\})$; ($W(\mathbf{\Omega}; \{\mathbf{\Omega}_j\})$ is derived in appendix A).

Since ψ of equation (A.11) is the most general function in the lowest energy manifold, the order parameter and vesicle shape just below the transition temperature are obtained by minimizing $\mathcal{H}_{\rm eff}$ over ψ_0 and the positions of zeros. Inserting this expression for ψ,

$$\mathcal{H}_{\rm eff}[\psi, \{\mathbf{\Omega}_j\}] = \frac{\mathcal{A}}{4\pi} \int \mathrm{d}\mathbf{\Omega} \left((r - r_c)|\psi|^2 + \frac{1}{2} u|\psi|^4 \right) - \frac{1}{2\kappa} \sum_{l=2}^{\infty} \sum_{m=-l}^{l} \frac{|\tilde{\Phi}_{lm}|^2}{(l-1)^2(l+2)^2} \tag{46}$$

where $r_c = -2\pi n K_n/\mathcal{A}$, and from equation (36)

$$\tilde{\Phi}(\mathbf{\Omega}) = -nK_n \left((1-n)|\psi|^2 + 2\left| \frac{\partial\psi}{\partial\theta} \right|^2 \right) \equiv -\frac{nK_n\psi_0^2}{\mathcal{N}} \Phi(\mathbf{\Omega}) \tag{47}$$

with

$$\Phi(\mathbf{\Omega}; \{\mathbf{\Omega}_j\}) = \left\{ 1 - n + \frac{1}{2} \sum_{j,k}^{2n} \frac{\cos\omega_{jk} - \cos\omega_j\cos\omega_k}{(1-\cos\omega_j)(1-\cos\omega_k)} \right\} W(\mathbf{\Omega}; \{\mathbf{\Omega}_j\}). \tag{48}$$

If we define

$$\tilde{r}(\{\mathbf{\Omega}_j\}) = (r - r_c) \int \mathrm{d}\mathbf{\Omega}\, W(\mathbf{\Omega}; \{\mathbf{\Omega}_j\}); \tag{49a}$$

$$\tilde{u}(\{\mathbf{\Omega}_j\}) = u \int \mathrm{d}\mathbf{\Omega}\, W^2(\mathbf{\Omega}; \{\mathbf{\Omega}_j\}) - \frac{4\pi n^2 K_n^2}{\kappa\mathcal{A}} \sum_{l=2}^{\infty} \sum_{m=-l}^{l} \frac{|\Phi_{lm}|^2}{(l-1)^2(l+2)^2}, \tag{49b}$$

Table 2. The coefficients $c_m^{(n)}$.

m	$c_m^{(2)}$	$c_m^{(3)}$	$c_m^{(4)}$	$c_m^{(6)}$	$c_m^{(10)}$
2	—	—	-2.19×10^{-4}	—	—
3	$\frac{4\sqrt{7\pi}}{945}$	—	—	—	—
4	$\frac{4\sqrt{\pi}}{3645}$	$\frac{\sqrt{\pi}}{297}$	-3.51×10^{-3}	—	—
5	—	—	1.28×10^{-3}	—	—
6	—	$\frac{\sqrt{13\pi}}{60\,060}$	2.31×10^{-4}	$\frac{15\,488\sqrt{13\pi}}{275\,559\,375}$	$-\frac{15\,488\sqrt{13\pi}}{275\,559\,375}$
7	—	—	8.30×10^{-5}	—	—
8	—	—	-1.84×10^{-5}	—	—
10	—	—	—	$\frac{256\sqrt{21\pi}}{692\,803\,125}$	$-\frac{256\sqrt{21\pi}}{692\,803\,125}$
12	—	—	—	$-\frac{512\sqrt{\pi}}{6834\,953\,125}$	$\frac{512\sqrt{\pi}}{6834\,953\,125}$

minimization over the magnitude leads to $\psi_0^2 = -\mathcal{N}\tilde{r}/\tilde{u}$ and the corresponding effective free energy density,

$$\mathcal{F}(\{\mathbf{\Omega}_j\}) = -\frac{1}{8\pi}\frac{\tilde{r}^2(\{\mathbf{\Omega}_j\})}{\tilde{u}(\{\mathbf{\Omega}_j\})} = -\frac{(r-r_c)^2\mathcal{N}^2}{8\pi u}\left[\int \mathrm{d}\mathbf{\Omega}\, W^2 - \frac{4\pi n^2 K_n^2}{u\kappa\mathcal{A}}\sum_{l=2}^{\infty}\sum_{m=-l}^{l}\frac{|\Phi_{lm}|^2}{(l-1)^2(l+2)^2}\right]^{-1}, \tag{50}$$

depends only on the positions $\{\mathbf{\Omega}_j\}$ of the zeros of $\psi(\mathbf{\Omega})$. The final step is to minimize $\mathcal{F}(\{\mathbf{\Omega}_j\})$, or $\tilde{u}(\{\mathbf{\Omega}_j\})$, with respect to the vortex configuration $\{\mathbf{\Omega}_j\}$. Once we get the minimum configuration, shape changes are described by $\rho(\mathbf{\Omega}) = \sum_{l=2}^{\infty}\sum_{m=-l}^{l}\rho_{lm}Y_l^m(\mathbf{\Omega})$ with

$$\rho_{lm} = -\frac{1}{\kappa(l-1)^2(l+2)^2}\int \mathrm{d}\mathbf{\Omega}\, Y_l^{m*}(\mathbf{\Omega})\tilde{\Phi}(\mathbf{\Omega}) = \frac{nK_n\psi_0^2}{\kappa\mathcal{N}(\{\mathbf{\Omega}_j\})}\frac{\Phi_{lm}(\{\mathbf{\Omega}_j\})}{(l-1)^2(l+2)^2}\bigg|_{\psi_0^2=-\tilde{r}\mathcal{N}/\tilde{u}}, \tag{51}$$

which is derived from equation (38).

In the disordered phase $\psi_0 = 0$, and $\rho = 0$, which signifies the vesicle of the spherical shape. In the low-temperature phase of quasi-long-range order, we have been able to evaluate $\mathcal{F}[\{\mathbf{\Omega}_j\}]$ analytically for $n = 1$ and 2. For these two cases, we find that the minimum energy configurations are those with zeros of $\psi(\mathbf{\Omega})$ at opposite poles and at the vertices of a tetrahedron respectively. The shape function $\rho(\mathbf{\Omega}) = (nK_n\psi_0^2/\kappa)\bar{\rho}^{(n)}(\mathbf{\Omega})$ associated with n-atic order is proportional to $\psi_0^2 \sim |r - r_c|$ to the order of our calculations. In general, the Legendre decomposition of $\bar{\rho}^{(n)}$ will contain Legendre polynomials of order $2n$. For $n = 1$ and 2, we find

$$\bar{\rho}^{(1)} = \frac{\sqrt{5\pi}}{20}Y_2^0 \tag{52}$$

with antipodal configuration of vortices, and

$$\bar{\rho}^{(2)} = c_3^{(2)}\left\{Y_3^0 + \sqrt{\tfrac{2}{5}}(Y_3^3 - Y_3^{-3})\right\} + c_4^{(2)}\left\{Y_4^0 - \sqrt{\tfrac{10}{7}}(Y_4^3 - Y_4^{-3})\right\} \tag{53}$$

with each azimuth of the bottom triangle of vertices at $\pm\pi/3$ and π. Table 2 gives coefficients $c_m^{(n)}$ and figure 1 shows the shapes described by these functions. The transformations from

the initial spherical shape to distorted shapes occur continuously. Our calculations for the shape are valid to order $(r - r_c)$. With lowering temperature, higher-order terms in $(r - r_c)$ and higher-order spherical harmonics are needed to describe the equilibrium shape. In [7], a variational function for ψ and spherical harmonics up to order $l = 8$ were used to calculate the shape for $n = 1$ for temperatures well below the transition.

For $n = 3$, 6 and 10 we found the zeros of $\psi(\mathbf{\Omega})$ to lie, respectively, at the vertices of an octahedron, an icosahedron and a dodecahedron. The shape functions are given by

$$\bar{\rho}^{(3)} = c_4^{(3)}\left\{Y_4^0 + \sqrt{\tfrac{5}{14}}(Y_4^4 + Y_4^{-4})\right\} + c_6^{(3)}\left\{Y_6^0 - \sqrt{\tfrac{7}{2}}(Y_6^4 + Y_6^{-4})\right\}, \tag{54}$$

$$\bar{\rho}^{(6)} = c_6^{(6)}\left\{Y_6^0 - \sqrt{\tfrac{7}{11}}(Y_6^5 - Y_6^{-5})\right\} + c_{10}^{(6)}\left\{Y_{10}^0 + \sqrt{\tfrac{33}{13}}(Y_{10}^5 - Y_{10}^{-5}) + \sqrt{\tfrac{187}{247}}(Y_{10}^{10} + Y_{10}^{-10})\right\} + c_{12}^{(6)}\left\{Y_{12}^0 - \sqrt{\tfrac{286}{1071}}(Y_{12}^5 - Y_{12}^{-5}) + \sqrt{\tfrac{247}{357}}(Y_{12}^{10} + Y_{12}^{-10})\right\}, \tag{55}$$

$$\bar{\rho}^{(10)} = c_6^{(10)}\left\{Y_6^0 + \sqrt{\tfrac{7}{11}}(Y_6^5 - Y_6^{-5})\right\} + c_{10}^{(10)}\left\{Y_{10}^0 - \sqrt{\tfrac{33}{13}}(Y_{10}^5 - Y_{10}^{-5}) + \sqrt{\tfrac{187}{247}}(Y_{10}^{10} + Y_{10}^{-10})\right\} + c_{12}^{(10)}\left\{Y_{12}^0 + \sqrt{\tfrac{286}{1071}}(Y_{12}^5 - Y_{12}^{-5}) + \sqrt{\tfrac{247}{357}}(Y_{12}^{10} + Y_{12}^{-10})\right\}. \tag{56}$$

For $n = 4$, we can see that the zeros lie at the vertices of a distorted cube obtained by compressing the top and bottom faces along its fourfold axis and twisting the faces about that axis by $\pi/4$. For this case, we minimized the energy over two parameters describing the separation and relative rotation between the top and bottom faces and obtained

$$\bar{\rho}^{(4)} = c_2^{(4)}Y_2^0 + c_4^{(4)}Y_4^0 + c_6^{(4)}Y_6^0 + c_5^{(4)}(Y_5^4 + Y_5^{-4}) + c_7^{(4)}(Y_7^4 + Y_7^{-4}) + c_8^{(4)}\{Y_8^0 - 0.578\,715(Y_8^8 + Y_8^{-8})\}. \tag{57}$$

5. Discussions

We have presented the general n-atic Hamiltonian in terms of the nth-rank spherical tensors and an analysis of the mean-field transition to n-atic order on a fixed-area surface of genus zero with the corresponding continuous shape changes. We are dealing with two kinds of order: the n-atic and the positional order of vortices. In the mean field theory, these two kinds of order develop simultaneously. Below the transition temperature, we have found not only the n-atic order developing but also the positional ordering of the positions of vortices and the corresponding shape changes. Since our results are based on the mean field theory, all the shapes are the shapes averaged over thermal fluctuations. For $n = 1$, 2, 3, 6, and 10, we have found the shape changes into ellipsoidal, tetrahedral, octahedral, icosahedral and dodecahedral shapes respectively. However, for $n = 4$ we have found a distorted cubic shape instead of the cube which we might expect naively. Our result for $n = 4$ shows that vortices lie at the vertices of a distorted cube obtained by rotating its top face by $\pi/4$ about its four-fold axis and compressing opposite faces. We are certain about the rotation angle $\pi/4$ for the equilibrium shape, but our result for the compressing or stretching of opposite faces is not conclusive since our analysis is to the lowest non-trivial order and it seems that compression or stretching depends on the order of the approximation. Thus, further analysis of the 4-atic-order shape change is necessary.

Our analysis is very similar to that of Abrikosov for the transition from a normal-to-vortex lattice transition of a type II superconductor at H_{c2} with the effects of fluctuations ignored. The Abrikosov phase is to the n-atic phase with bond-orientational order what the vortex lattice is to the positional order of vortices. In the Abrikosov phase, fluctuations of the vortex lattice destroy superconductivity but not long-range periodic order [17]. In two-dimensions,

screening of vortices drives T_{KT} in an infinite superconductor in zero field to zero. Both of the above effects may be important for n-atic order on a sphere. It has been shown that in the parameter region $n^2K_n/\kappa \ll 1/4$, the effect of shape fluctuations is irrelevant [9] and will not lead to qualitative changes in our results. For $n^2K_n/\kappa \gg 1/4$, on the other hand, shape fluctuations are relevant. The interaction between the vortices is screened according to the massive sine-Gordon theory and hence is equivalent to a neutral Yukawa gas on a sphere. Consequently, due to this screening effect the KT transition is suppressed at finite temperature, and vortices are always unbound for a non-zero temperature.

In [18], Evans has discussed the shape changes of the n-atic Hamiltonian in the opposite limit (high-temperature limit) to the mean-field limit described in this paper. Using the lowest Landau level approximation, the effect of thermal fluctuations are discussed. We agree with him in that the amplitudes of deformations have zero thermal average. We are not sure, however, if this approximation is valid in the high-temperature phase where thermally excited vortex–antivortex pairs are always unbound, since the lowest Landau levels include only the ground state vortices. Thus we believe the effects of fluctuations on the shape changes in the disordered state deserve further investigation.

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Appendix A. Lowest energy manifold with topological vortices

One possible form of the eigenfunctions of $\bar{\Delta}$ has the structure of $\sin^n\theta$

$$-\bar{\Delta}\sin^n\theta = n\sin^n\theta. \tag{A.1}$$

The complete spectrum and the eigenfunctions are derived in appendix B. Introducing the projection representation, we can reparametrize the sphere using the stereographic projection defined by

$$z = \tan\frac{\theta}{2}\mathrm{e}^{\mathrm{i}\phi}; \qquad z^* = \tan\frac{\theta}{2}\mathrm{e}^{-\mathrm{i}\phi}, \tag{A.2}$$

the inverse transformation of which gives

$$\theta = 2\tan^{-1}\sqrt{z^*z}; \qquad \phi = \frac{1}{2\mathrm{i}}\ln\frac{z}{z^*}. \tag{A.3}$$

The corresponding metric tensor, spin connection and surface Laplacian $\bar{\Delta}$ can be written as follows.

$$\bar{g}^{ab} = \frac{2}{(1+|z|^2)^2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \tag{A.4a}$$

$$\bar{A}_z = -\frac{1}{2\mathrm{i}z}\frac{1-|z|^2}{1+|z|^2}; \qquad \bar{A}_{z^*} = \frac{1}{2\mathrm{i}z^*}\frac{1-|z|^2}{1+|z|^2}, \tag{A.4b}$$

$$\bar{\Delta} = (1+|z|^2)^2[(\partial_z\partial_{z^*} - \bar{A}_z\bar{A}_{z^*}) - 2\mathrm{i}n(\bar{A}_z\partial_{z^*} + \bar{A}_{z^*}\partial_z)]. \tag{A.4c}$$

The eigenfunction $\sin^n\theta$ can be written as

$$f(|z|^2) = \left(\frac{2|z|}{1+|z|^2}\right)^n. \tag{A.5}$$

This eigenfunction has vortices at $|z| = 0$ and ∞. Now, the vortices can be arbitrarily placed by multiplying $Q(z)$ which is a function of z alone. Since $\bar{\Delta} f(|z|^2) = -nf(|z|^2)$,

$$-\bar{\Delta}[f(|z|^2)Q(z)] = n[f(|z|^2)Q(z)], \tag{A.6}$$

which implies that the full eigenfunctions of $\bar{\Delta}$ are the product of $f(|z|^2)$ and the arbitrary function $Q(z)$. In particular, for $n = 1$, we have

$$f(|z|^2) = \frac{2|z|}{1+|z|^2}. \tag{A.7}$$

By taking $Q(z) = (z - z_1)(z - z_2)/z$,

$$\psi \propto \frac{2|z|}{1+|z|^2}\frac{(z-z_1)(z-z_2)}{z}, \tag{A.8}$$

which means that ψ has the vortices at $z = z_1$ and z_2 and that ψ goes to $z_1 z_2 \mathrm{e}^{-\mathrm{i}\phi}$ as z goes to 0 and ψ goes to $\mathrm{e}^{\mathrm{i}\phi}$ as z goes to ∞. This means there is an enormous degeneracy in the lowest energy manifold of the harmonic terms. In the lowest energy manifold of the harmonic terms, ψ will have exactly $2n$ zeros specifying the vortex positions, each of strength $1/n$.

In view of this vortex strength and distribution, we choose $Q(z)$ as

$$Q(z) = \frac{\alpha}{z^n}\prod_{j=1}^{2n}(z - z_j), \tag{A.9}$$

where α, z_j are arbitrary and $z_j \neq z_k$ if $j \neq k$. By minimizing $\mathcal{H}_{\mathrm{eff}}$ with the degenerate eigenfunctions of $\bar{\Delta}$,

$$\psi = \alpha\left(\frac{2|z|}{1+|z|^2}\right)^n \frac{1}{z^n}\prod_{j=1}^{2n}(z - z_j), \tag{A.10}$$

the nonlinear terms pick out the set $\{z_j \mid 1 \leqslant j \leqslant 2n\}$ that gives the lowest energy for $\mathcal{H}_{\mathrm{eff}}$. This set $\{z_j\}$ also gives $|\psi|$, vortex positions and the shape changes $\rho(\boldsymbol{\Omega})$ of the membrane. In terms of spherical coordinates,

$$\psi \propto \prod_{j=1}^{2n}\left(\sin\frac{\theta}{2}\cos\frac{\theta_j}{2} - \cos\frac{\theta}{2}\sin\frac{\theta_j}{2}\mathrm{e}^{\mathrm{i}(\phi-\phi_j)}\right) = W(\Omega, \{\Omega_j\}). \tag{A.11}$$

Appendix B. Complete spectrum of $\bar{\Delta}$

The covariant surface Laplacian for the harmonic Hamiltonian $\mathcal{H}_{\mathrm{har}}$,

$$\bar{\Delta} = \partial_\theta^2 + \cot\theta\,\partial_\theta + (\mathrm{cosec}\,\theta\,\partial_\phi + \mathrm{i}n\cot\theta)^2, \tag{B.1}$$

would be encountered in the Hamiltonian describing the field of a Dirac magnetic monopole. The Schrödinger equation of an electron on a spherical shell under the influence of a magnetic monopole at the origin plus the Dirac string extended along the negative z-axis can be cast as

$$-\tfrac{1}{2}(\boldsymbol{\nabla} - \mathrm{i}\boldsymbol{A})^2\Psi = \varepsilon\Psi \tag{B.2}$$

with

$$A_\theta = 0; \qquad A_\phi = \frac{g(1-\cos\theta)}{\sin\theta} + \frac{F}{2\pi\sin\theta}, \tag{B.3}$$

where g is the strength of the monopole and F the magnitude of the flux. Setting $g = n$ and $F = -2\pi n$, we find $A_\phi = -n\cot\theta$, and so $(\boldsymbol{\nabla} - \mathrm{i}\boldsymbol{A})^2$ is exactly identical to $\bar{\Delta}$. Hence, the differential operator $-\bar{\Delta}$ is equivalent to the Hamiltonian of a Dirac monopole of strength n at

the origin with an infinitely long and thin solenoid carrying flux $2\pi n$ along the positive z-axis. Following the method in [19], we define the 'angular momentum' operator

$$\boldsymbol{J} \equiv -\mathrm{i}\boldsymbol{r} \times (\boldsymbol{\nabla} - \mathrm{i}\boldsymbol{A}) - n\boldsymbol{r} \tag{B.4}$$

with the associated ladders and z-component

$$\begin{aligned} J_{\pm} &= J_x \pm \mathrm{i}J_y \\ &= \mathrm{e}^{\pm\mathrm{i}\phi}\left[\pm\partial_\theta + \mathrm{i}\cot\theta(\partial_\phi + \mathrm{i}n) - \frac{n\sin\theta}{1+\cos\theta}\right]; \end{aligned} \tag{B.5}$$

$$J_z = -\mathrm{i}(\partial_\phi + \mathrm{i}n) - n \tag{B.6}$$

which obeys the formal commutation relations

$$[\boldsymbol{J}, \bar{\Delta}] = 0; \qquad [J_i, J_j] = \mathrm{i}\varepsilon_{ijk}J_k, \tag{B.7}$$

for $\sin\theta \neq 0$. Then we find

$$-\bar{\Delta} = J^2 - n^2, \tag{B.8}$$

and the eigenvalue problem reduces to that of the 'angular momentum' squared. Let us denote

$$J^2\psi(\boldsymbol{\Omega}) = l(l+1)\psi(\boldsymbol{\Omega}), \tag{B.9}$$

where we set

$$\psi(\boldsymbol{\Omega}) = \mathrm{e}^{\mathrm{i}m\phi}P_m(\cos\theta); \qquad m = 0, \pm1, \pm2, \ldots. \tag{B.10}$$

Then

$$J_z\psi(\boldsymbol{\Omega}) = m\psi(\boldsymbol{\Omega}). \tag{B.11}$$

The eigenvalues of J^2 are found to be given by $l(l+1)$ with

$$\begin{aligned} &l = k + \tfrac{1}{2}(|m+n| + |m-n|) \\ &k = 0, 1, 2, 3, \ldots; \qquad m = 0, \pm1, \pm2, \ldots. \end{aligned} \tag{B.12}$$

The corresponding orthonormal eigenfunctions are

$$\psi^{(k,m)}(\boldsymbol{\Omega}) = \alpha_{km}\left(\frac{1-\cos\theta}{2}\right)^{|m+n|/2}\left(\frac{1+\cos\theta}{2}\right)^{|m-n|/2}P_k^{(|m+n|,|m-n|)}(\cos\theta)\mathrm{e}^{\mathrm{i}m\phi}, \tag{B.13}$$

where $P_k^{(a,b)}$ denote Jacobi polynomials, and

$$\alpha_{km} = \left[\frac{k!\Gamma(|m+n| + |m-n| + k + 1)\Gamma(|m+n| + |m-n| + 2k + 1)}{4\pi\Gamma(|m+n| + k + 1)\Gamma(|m-n| + k + 1)}\right]^{\frac{1}{2}}. \tag{B.14}$$

The complete spectrum of the operator $-\bar{\Delta}$ is

$$\begin{aligned} \varepsilon &= \{k + \tfrac{1}{2}(|m+n| + |m-n|)\}\{k + 1 + \tfrac{1}{2}(|m+n| + |m-n|)\} - n^2 \\ &= [\max(n, |m|) + k][\max(n, |m|) + k + 1] - n^2 \end{aligned} \tag{B.15}$$

where $k = 0, 1, 2, \ldots$ and $m = 0, \pm1, \pm2, \ldots$. Hence the ground states ($k = 0$, $n \geqslant |m|$) are given by

$$\varepsilon = n(n+1) - n^2 = n. \tag{B.16}$$

The corresponding ground state orthonormal eigenfunction has the form

$$\psi^{(0,m)}(\boldsymbol{\Omega}) = \alpha_{0m}\left(\sin\frac{\theta}{2}\right)^{n+m}\left(\cos\frac{\theta}{2}\right)^{n-m}\mathrm{e}^{\mathrm{i}m\phi} \tag{B.17}$$

which is the same as that in equation (A.11).

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