Landau theory provides a framework for the analysis of phase transitions and spontaneous symmetry breaking. When complex fluids solidify, emergent density modulations typically adopt a variety of contending symmetries and Landau theory has proven to be a powerful tool for the analysis of the phase diagram of such systems [1,2]. In this letter, we discuss Landau theory as applied to the solidification of chiral molecules on a spherical surface in the context of the assembly of viral shells. We encounter two types of solidification transitions. The first type is a conventional first-order phase transition from a uniform to an icosahedral state, described by a single icosahedral spherical harmonic of even \( l \). The chiral pseudo-scalar term in the free energy does not affect the transition. The second type is anomalous: icosahedral spherical harmonics with odd \( l \) are unstable. Stability is recovered when admixture with the neighboring \( l + 1 \) icosahedral spherical harmonic is included. This is in apparent conflict with the principle of Landau theory that symmetry-breaking transitions are characterized by a single irreducible representation of the symmetry group of the uniform phase. The chiral term selects one of two isomeric mixed-\( l \) icosahedral states. A direct transition is possible only over a limited range of parameters. Outside this range, a non-icosahedral state with the symmetry of an isotropy subgroup of the icosahedral group interposes between the uniform and icosahedral states.

Abstract – We present a generalized Landau-Brazovskii free energy for the solidification of chiral molecules on a spherical surface in the context of the assembly of viral shells. We encounter two types of solidification transitions. The first type is a conventional first-order phase transition from a uniform to an icosahedral state, described by a single icosahedral spherical harmonic of even \( l \). The chiral pseudo-scalar term in the free energy does not affect the transition. The second type is anomalous: icosahedral spherical harmonics with odd \( l \) are unstable. Stability is recovered when admixture with the neighboring \( l + 1 \) icosahedral spherical harmonic is included. This is in apparent conflict with the principle of Landau theory that symmetry-breaking transitions are characterized by a single irreducible representation of the symmetry group of the uniform phase. The chiral term selects one of two isomeric mixed-\( l \) icosahedral states. A direct transition is possible only over a limited range of parameters. Outside this range, a non-icosahedral state with the symmetry of an isotropy subgroup of the icosahedral group interposes between the uniform and icosahedral states.

This paper is dedicated to the memory of our friends and colleagues William Klug and Vladimir Lorman.
Thus, in the current Landau theory [10,11], the smallest chiral icosahedral shells should have a density modulation proportional to \( Y_6(l = 15) \) while larger capsids should correspond to odd icosahedral spherical harmonics with larger values of \( l \). A systematic comparison between viral capsids and the odd-\( l \) icosahedral spherical harmonics can be found in refs. [10,11].

This description raises questions. First, though the density profiles of capsids lack inversion symmetry, they also are not odd under inversion. Next, a striking consequence of only allowing odd \( l \) values is that odd order non-linear scalar densities in the free energy integrate to zero. Because of the absence of third-order nonlinear terms, the solidification transition of chiral molecules on a spherical surface would be a continuous transition. However, in the limit that the sphere radius goes to infinity, the solidification of chiral molecules on a spherical surface should reduce to that of the solidification of chiral molecules on an infinite planar surface and solidification transitions of solids composed of chiral molecules are conventional first-order phase transitions [14]. In this letter we generalize the current Landau theory by adding the lowest-order non-zero pseudo-scalar density [14]. In this approach, which follows Landau theories developed for chiral liquid crystals [1,15,16], the irreps of \( SO(3) \) and the symmetry group of the broken symmetry state are not pre-selected but, instead, determined by free-energy minimization.

The free-energy density for the solidification of chiral molecules on a spherical surface that we investigated is

\[
F = \int_{S^2} \left[ \frac{1}{2} \left( (\Delta + k_2^2)\rho \right)^2 + \frac{\rho^2}{3} + \frac{u}{4}\rho^4 + \ldots \right] + \chi \left( \nabla \rho \cdot (\nabla^2 \rho) \cdot (\mathbf{n} \times \nabla \rho) \right) dS. \tag{1}
\]

The function \( \rho \) represents the coarse-grained density distribution of the centers of mass (COM) of molecular groups present in the disordered precursor state that solidify into the ordered capsid. These could be either individual capsid proteins or “capsomers”, such as hexamers or pentamers of capsid proteins. The actual density profile, as measured in microscopy or X-diffraction studies, is constructed by distributing the molecular groups over the surface of the sphere in conformity with \( \rho \). The integral is over a spherical surface \( S^2 \) of radius \( R \). The first term inside the square brackets is a version of the Landau-Brazovskii (LB) free-energy density for solidification\(^2\). While the second term is the lowest-order pseudo-scalar density, with \( \chi \) a measure of the strength of the chiral interactions between the precursor molecular groups. The term \( (\Delta + k_2^2)\rho^2 \) in the LB free-energy density is minimized by density modulations with periodicity \( a = 2\pi/k_0 \). In the present case, \( a \) is identified as the characteristic size of the molecular groups in the precursor state, while \( \Delta \) is the Laplace-Beltrami operator. The next three terms are an expansion of the free-energy density in powers of \( \rho \) with \( r, u, \) and \( v \) expansion coefficients. In the limiting case of a planar surface, the LB free energy describes – for negative \( u \) and positive \( v \) – a first-order solidification transition of a two-dimensional fluid into a hexagonal solid represented as the superposition of three density waves whose wave vectors have magnitude \( k_0 \) [18].

The pseudo-scalar density can be constructed in the limiting case of a planar surface from a general expansion for the density in powers of \( \rho \) and its first and second derivatives. Pseudoscalar densities are identified as terms that are invariant under translation and rotation but odd under inversion. The lowest-order non-zero pseudoscalar density is \( \nabla \rho \cdot (\nabla^2 \rho) \cdot (\mathbf{n} \times \nabla \rho) \), where \( \mathbf{n} \) is a unit vector normal to the surface. This term is closely related to the pseudoscalar density constructed by Helfrich and Prost for deformable chiral surfaces [16] but this density integrates to zero over a spherical surface. The quartic pseudoscalar density of eq. (1) is the lowest-order term that does not integrate to zero over a spherical surface. The generalization from a flat to a curved surface follows from covariance.

Returning to eq. (1) on a spherical surface, the spherical harmonics \( Y_m^l \) are eigenfunctions of the \( \Delta \) with eigenvalues \( -l(l+1)/R^2 \). One can now associate an effective reduced temperature \( t_1 = r + l(l+1)/R^2 - k_0^2 \) with instabilities of the uniform state characterized by spherical harmonics with index \( l \). The index \( l \) that dominates for given \( k_0 R \) is the one that generates the lowest value of \( t_1 \). One can then divide up the \( k_0 R \) axis into segments \( l^2 < k_0 R^2 < (l + 1)^2 \) so that, in a given segment, the quadratic term in the free energy for that particular value of \( l \) becomes unstable before any of the other segments as \( r \) is decreased.

The expansion coefficients of the density \( \rho \) in the dominant subspace formed by the \( 2l+1 \)-dimensional \( Y_m^l \) basis are obtained by minimizing the free energy. Note that we do not impose icosahedral symmetry \( a \) priori. The minimization procedure results in \( 2l+1 \) coupled non-linear equations of the form \( \langle Y_m^l | \Delta F(\rho) | Y_m^l \rangle = 0 \). For a particular solution of these equations to be thermodynamically stable, the eigenvalues of the stability matrix \( \langle Y_m^l | \delta^2 F(\rho) | Y_m^l \rangle \) must be positive, apart from three zero eigenvalues corresponding to global rotation.

We start with the first interval along the \( k_0 R \) axis that supports an icosahedral state, which is for \( 36 < k_0 R^2 < 49 \) corresponding to \( l = 6 \). The 13 coupled equations \( \langle Y_6^m | \delta F(\rho) | Y_6^m \rangle = 0 \) are solved for \( \chi = 0 \) by \( \rho_6 = \xi \partial Y_6(6) \), where

\[
\partial Y_6(6) = Y_6^0 + \sqrt{\frac{7}{11}} (Y_6^5 - Y_6^{-5}). \tag{2}
\]

is the first non-trivial icosahedral spherical harmonic. The order parameter (OP) \( \xi \) the cubic equation

\[
r\xi + u\xi^2 + w\xi^3 = 0, \tag{3}
\]
with \( \tilde{a} = u(50\sqrt{13}/323\sqrt{r}) \) and \( \tilde{w} = 2145w/(1564\pi) \). This equation has the standard form for a first-order phase transition. The non-zero eigenvalues of the 13 \(	imes\) 13 stability matrix are all positive.

The achiral non-linear terms in the free energy couple the icosahedral state \( Y_h(6) \) to the subdominant neighboring segments \( l = 5 \) and \( l = 7 \), neither of which supports an icosahedral state. Because both of these states are odd under inversion, the achiral non-linear terms do not produce terms of the form \( c_m\xi^2 \) or \( c_m\xi^3 \) that are linear in the expansion coefficients \( c_m \) of the \( l = 5 \) or \( l = 7 \) spherical harmonics. As a consequence, the formation of the \( l = 6 \) icosahedral state does not entrain secondary ordering in spherical harmonics. It is thus consistent to set these \( c_m \) to zero.

Turning to the case \( \chi \neq 0 \), it can be shown that for any \( l \), the integral

\[
\int_{S^2} \nabla Y_{m_1}^l \cdot (\nabla \nabla Y_{m_2}^l) \cdot (\nabla \nabla Y_{m_3}^l) \cdot (n \times \nabla Y_{m_4}^l) \, dS = 0 \quad (4)
\]

is zero for any set of \((m_1, m_2, m_3, m_4)\). This also holds if any of the spherical harmonics is replaced by its complex conjugate. It follows that if the minimization of \( F \) is restricted to any given \( l \) sector then the chiral term has no effect at all. However, the chiral term can be non-zero when it combines spherical harmonics with different \( l \) indices. The quartic pseudoscalar could in principle support terms of the form \( c_m\xi^3 \) and \( c_m c_m \xi \). It can be shown that terms of the form \( c_m\xi^3 \) that are linear in \( c_m \) and that could induce entrainment are zero. Terms of the form \( c_m c_m \xi \) are non-zero but they do not induce entrainment. For icosahedral ordering in the \( l = 6 \) sector, the chiral term is practically “invisible”. Similar even-\( l \) icosahedral ordering transitions that are insensitive to chirality are encountered in the \( l = 10 \) and \( l = 12 \) segments.

The next icosahedral intervals are \( l = 15, 16, 18, 20, 21, \) and \( 22 \). While the corresponding icosahedral spherical harmonics remain solutions of the projection equations \((Y_{m_1}^l Y_{m_2}^l)/(\sqrt{m_1!m_2!}) = 0\), the stability matrices of these states have negative eigenvalues, with the exception of \( l = 18 \). We will focus on the case of \( l = 15 \) because of its importance for viral assembly. First note that the \( l = 16 \) neighboring segment does support an icosahedral state. Accordingly, we enlarged the search space for the minimization of the free energy to the union of the \( l = 15 \) and \( l = 16 \) subspaces, henceforth referred to as \( l = 15 + 16 \). We first searched for free-energy extrema with icosahedral symmetry of the general form

\[
\rho(\zeta, \xi) = \zeta Y_h(15) + \xi Y_h(16), \quad (5)
\]

where \((\zeta, \xi)\) are a pair of variational parameters. For \( \chi = 0 \), the free energy has an extremum when \((\zeta, \xi)\) obey the pair of coupled cubic equations:

\[
\begin{align*}
(c_{16} + r)\zeta^2 + u_1\zeta^2 + v_1\xi^3 + u_2\xi^2 = 0, \quad (6a) \\
(c_{15} + r)\xi^3 + u_3\zeta\xi + v_3\zeta^2 + v_4\zeta^2 = 0. \quad (6b)
\end{align*}
\]

The absence of a \( \xi^2 \) term in the second equation reflects the fact that \( Y_h(15) \) is odd. As a consequence, if \((\zeta, \xi)\) is a solution of these equations then so is \((-\zeta, \xi)\). The two solutions are related by inversion symmetry and thus constitute a pair of isomers, to be denoted by D and L. For \( \chi = 0 \), the transition from a uniform to an icosahedral state represents a form of chiral symmetry breaking. If \( \chi \neq 0 \), then the free energy of the D and L branches shifts by unequal amounts \( \Delta F_\zeta = \chi(a_1\xi_0^3 + a_2\zeta_0^3) \) where \((\xi_0, \zeta_0)\) is the \( \chi = 0 \) solution. Since \( \Delta F_\zeta \) is odd in \( \zeta_0 \), the degeneracy between the D and L branches under inversion is lifted so there is no chirality symmetry breaking at the ordering transition. In addition, because there is a term linear in \( \xi \) in \( \Delta F_\zeta \), icosahedral ordering in the \( l = 15 \) sector entrains icosahedral ordering in the \( l = 16 \) sector. Evidently, the chiral term is very “visible” in the mixed \( l = 15 + 16 \) state and does affect the order parameter, i.e., it selects which one of the two isomer branches has the lower free energy and causes entrainment.

The stability matrix of the mixed \( l = 15 + 16 \) icosahedral state has negative eigenvalues over a significant part of the \( k_0R-r \) phase diagram, as shown in fig. 1. A direct transition from the uniform to the icosahedral state as \( r \) is reduced only takes place over a short interval of \( k_0R \) values near the border between the \( l = 15 \) and \( l = 16 \) segments at \( k_0R = 16 \). The transition is discontinuous but the magnitude of the discontinuity goes to zero at \( k_0R \approx 15.96 \). For \( k_0R \) less than 15.96, a modulated state that lacks icosahedral symmetry interposes between the uniform and icosahedral states. The lowest free-energy state we found in this regime is 5-fold symmetry. The icosahedral state is, in this case, a saddle point of the free energy. Similarly, for \( k_0R \) larger than about 16, a non-icosahedral state with 3-fold symmetry intervenes. The lowest
The free-energy state we found in this region has 3-fold symmetry.

Insight into this phase diagram follows from the eigenvalues and eigenvectors of the stability matrix of the icosahedral state (see fig. 2). For \( k_0 R = 15.96 \) – when the transition is continuous – there is a single icosahedral solution branch with positive eigenvalues for any \( r \) (fig. 2(A)). For \( k_0 R = 16 \) – when the transition is weakly first-order – there are two solution branches, one of which is stable (fig. 2(B)). For \( k_0 R = 15.8 \), when a non-icosahedral state interposes between the uniform and icosahedral states, the icosahedral state is stable only for lower values of \( r \). As \( r \) is increased, a group of 3 degenerate eigenvalues become negative at the blue dot in fig. 2(C). The corresponding eigenvectors of the stability matrix have 2-fold, 3-fold, and 5-fold axial symmetry and are shown in fig. 3. Increasing \( r \) further, close to the transition to the uniform state, one encounters a second instability where another group of 4 degenerate eigenvalues changes sign. The corresponding eigenvectors have tetrahedral or \( D_3 \) symmetry (see fig. 3).

The boundary lines in fig. 1 between the icosahedral and non-icosahedral modulated states denote a form of symmetry breaking that differs from the uniform-icosahedral transition. The symmetry group \( G_0 \) here is the chiral icosahedral group \( I \). This group has a single one-dimensional (“1D”) irrep, two 3D irreps, a 4D and a 5D irrep [19]. The three eigenvalues that changes sign along these lines are associated with one of the two 3D irreps, the one usually denoted by “3”. The isotropy subgroups of \( I \) associated with irrep 3 are \( C_3 \), \( C_3 \), and \( C_2 \). A natural orthogonal coordinate system in the 3D space of irrep 3 is one with the \((1,1,1)\) direction along a threecold symmetry direction, the \((0,0,1)\) direction along a twofold direction. In this coordinate system, the OP is a 3D vector to sixth order in \( \eta \). Importantly, this form is a general expression independent of the particular value, or values, of \( l \) that were used to construct the icosahedral state, and independent of the form of the original free-energy equation (1). Here, \( \lambda_3 \) is the 3-fold degenerate eigenvalue that changes sign at the transition while \( V \) and \( W \) are positive constants. A continuous transition takes place at \( \lambda_3 = 0 \). For \( \Delta = 0 \), this Landau energy is isotropic under rotations in \( \eta \) space. For \( \Delta \) negative, the stable minimum of \( \delta F(\eta) \) lies along the \( C_3 \) direction while for \( \Delta \) positive, it lies along the \( C_5 \) direction. For negative \( \lambda_3 \), the system thus has either a threefold or a fivefold axis, in good agreement with our numerical results (see fig. 1). A similar scenario enfolds for \( k_0 R \) close to 22, but now involving the \( l = 21 \) and \( l = 22 \) segments. In general, for any \( Y_l(l) \) with \( l \) odd, there is an adjacent even \( l \) icosahedral spherical harmonic \( Y_l(l+1) \) that mixes with due to the non-linear terms in the free energy.

In summary, we proposed a Landau-Brazovskii theory to describe ordering transitions of chiral molecules on spherical surface in the context of viral assembly. As a function of the dimensionless radius \( k_0 R \), we encountered two types of transitions from a uniform state to an icosahedral state. The first type is associated with the \( l = 6 \), \( 10 \), and \( 12 \) icosahedral harmonics. It has the form of a conventional first-order phase transition. The chiral pseudoscalar term in the free energy has no significant effect. The second type, exemplified by \( l = 15 \), is anomalous in the sense that the icosahedral state is unstable unless one allows the \( l = 16 \) icosahedral spherical harmonic to mix in with the \( l = 15 \) icosahedral spherical harmonic, in seeming contradiction with Landau’s principle that a symmetry-breaking transition is characterized by only a single irrep of the symmetry group of the uniform phase. A direct transition between the uniform and icosahedral

**Fig. 3:** (Colour online) Unstable eigenvectors of the \( 15 \times 16 \) chiral icosahedral states with, respectively, \( C_5 \), \( C_3 \), \( C_2 \), tetrahedral and \( D_3 \) symmetry.
states is possible over only a small range of parameter. More generally, a non-icosahedral state that transforms as an isotropy subgroup of $I$, interposes between the isotropic and icosahedral states.

Numerical simulations of 72 interacting particles confined to a spherical surface allow for tests of the theory. The $l = 16$ icosahedral state has 72 maxima. A stable state with icosahedral order of this system should be described as a $15 + 16$ mixture with $k_0 R$ comparable to or larger than 16. Simulations of 72 interacting particles have been carried out on a rigid surface in refs. [20–24] and the icosahedral state was found to be very fragile. A recent simulation study [23] reports that the icosahedral states is possible over only a small range of parameter. The $l = 10$, and $l = 12$ play a role in viral assembly. We hope to address these questions in a future paper. The most striking prediction of the theory is that of the interposition of non-icosahedral states between the uniform and icosahedral states. Recently, the asymmetric cryo-EM structure determinations of viruses without icosahedral averaging has become a reality [26], which opens the possibility of imaging the proposed non-icosahedral intermediate states. **

We would like to thank VLADIMIR LORMAN and ALEXANDER GROSBERG for helpful discussions. We would like to thank the NSF for support under DMR Grant No. 1006128 and the Aspen Center for Physics for hosting a workshop on the physics of viral assembly.

REFERENCES

[1] KATS E., LEBEDEV V. and MURATOV A., Phys. Rep., 228 (1983) 1.