Hexatic Order and Surface Ripples in Spherical Geometries

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In flat geometries, two dimensional hexatic order has only a minor effect on capillary waves on a liquid substrate and on undulation modes in lipid bilayers. However, extended bond orientational order alters the long wavelength spectrum of these ripples in spherical geometries. We calculate this frequency shift and suggest that it might be detectable in lipid bilayer vesicles, at the surface of liquid metals and in multielectron bubbles in liquid helium at low temperatures. Hexatic order also leads to a shift in the threshold for the fission instability induced in the later two systems by an excess of electric charge.

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One of the main predictions of theories of dislocation and disclination mediated melting in two dimensions is that the transition from solid to liquid can be a two-stage process. First, at a temperature $T = T_m$, dissociation of dislocation pairs drives the transition from a crystal to an intervening hexatic phase. This liquid-crystalline phase has no translational order but still exhibits extended orientational correlations. Then, its quasi-long-ranged orientational order is destroyed in a second transition which takes place at a higher temperature $T = T_i$. Here, an unbinding of disclination pairs finally produces an isotropic liquid.

The hexatic phase predicted by theory has now been observed in free standing liquid crystal films, in various types of two dimensional colloidal crystals, in magnetic bubble arrays and in Langmuir-Blodgett surfactant monolayers. Despite the modest time scales available even on the fastest computers, there is now evidence via computer simulations for continuous melting and a narrow sliver of hexatic phase for hard disks and a more substantial hexatic phase for particles interacting with a repulsive $1/r^{12}$ potential.

In the above experiments, two dimensional order was typically probed via diffraction or by direct measurement of correlation functions in real space. It is difficult to use these methods when hexatic order is present in a curved, spherical geometry. Examples where hexatic order might be present include "liposomes", i.e., closed vesicles composed of lipid bilayers, the surface of liquid metal droplets confined in Paul traps, and multielectron bubbles submerged in liquid helium. Two dimensional planar multilayers of the phospholipid DMPC have many similarities to free standing liquid crystal films, which are known to have hexatic phases. Celestini et al. have found evidence from computer simulations for extended orientational correlations at the surface of supercooled liquid metals. Electrons trapped on the surface of liquid helium by a submerged, positively charged capacitor plate have long been used to investigate two dimensional melting. Although these experiments are consistent with dislocation mediated melting, evidence for a hexatic phase and disclination unbinding remains elusive. Multielectron bubbles result when large numbers of electrons ($10^5 - 10^7$) at the helium interface subduct in response to an increase in the anode potential and coat the inside wall of a large sphere (10-100 micron radius) of helium vapor.

One might hope that bond orientational order in a membrane or interface could be detected by its effects on the dynamics of undulation modes or capillary waves. Unfortunately, hexatic order couples only to the Gaussian curvature, which vanishes for a simple sine wave deformation of a flat membrane or an interface (cf. Eq. (1) below). The situation is different, however, when these excitations are superimposed on a non-trivial background geometry such as that of a sphere. Here, we determine the effect of hexatic order on, e.g., the quadrupole and octopole undulation modes and capillary wave excitations for the spherical systems described above. The frequency shift is large for liposomes with hexatic order and might also be observable in liquid metal droplets and in multielectron bubbles in helium.

We first consider liquid droplets with surface hexatic order, either due to surface ordering or to coating with surface active molecules. The equilibrium shape minimizes a free energy $F_d$ given by

$$F_d = \sigma \int dA + \frac{1}{2} K_A \int dA \, D_i n^j D^i n_j, \quad (1)$$

where $\sigma$ denotes the surface tension of the interface connecting a droplet with density $\rho_l$ surrounded by vapor with density $\rho_v$. For a general manifold with internal coordinates $x = (x_1, x_2)$, the surface element is given by $dA = \sqrt{g} dx$, where $g(x)$ is the determinant of the metric tensor $g_{ij}(x)$. For an undeformed sphere with radius $R_0$, $x = (\theta, \varphi)$ with polar coordinates $\theta$ and $\varphi$ and $dA = R_0^2 \sin \theta d\theta d\varphi$. Finally, $\bar{n}$ is a unit vector in the tangent plane with $n_i n^i = 1$ which identifies (modulo $2\pi/6$) the long-range correlations in the hexatic bond directions. Here, $D_i n^j \equiv g^{ik} D_k n_j$, where $g^{ij}$ is the inverse of $g_{ij}$ and $D_i$ denotes a covariant derivative with respect

$$K_A = \int dA \, \left( \frac{1}{2} \sqrt{g} \right)^{1/2} \left( \frac{1}{2} \nabla \bar{n} \cdot \nabla \bar{n} - \Delta_{\bar{n}} \right),$$

where $\Delta_{\bar{n}}$ is the Laplacian of the unit vector $\bar{n}$ defined

$$\frac{\partial}{\partial n} \equiv \frac{1}{\sqrt{g}} \frac{\partial}{\partial x^i} \left( \sqrt{g} g^{ij} \frac{\partial}{\partial x^j} \right).$$
to the metric $g_{ij}$. Thus, $D_i n^j \equiv \partial_i n^j + \Gamma^j_{ki} n^k$, where the $\Gamma^j_{ki}$ are Christoffel symbols of second kind, see e.g. [7]. The hexatic stiffness $K_A \sim E_c (\xi_T/a_0)^2$, where $\xi_T$ is the translational correlation length, $a_0$ is the particle spacing and $E_c$ is the dislocation core energy. The ratio $K_A/k_BT$ jumps from an universal value $72/\pi$ to zero when the hexatic melts into an isotropic liquid at $T = T_i$ [2].

The fundamental assumption which underlies the hexatic free energy discussed above is that the configuration of minimal elastic energy corresponds to a vector field $\vec{n}_0$ where $\vec{n}_0(x+dx)$ can be obtained from $\vec{n}_0(x)$ by parallel transport of $\vec{n}_0$. On a sphere however, curvature introduces “frustration” since parallel transport of $\vec{n}$ along closed loops on the surface leads to a rotation of $\vec{n}$. For geometries frustrated by a nonzero integrated Gaussian curvature $\mathcal{G}$, the state of minimum energy always has topological defects [13].

These defects reduce the elastic energy by screening the Gaussian curvature. This point can be made more precise by introducing a local bond-angle field $\theta$, the angle between $\vec{n}$ and some local reference frame. The singular part of $\theta$ is then connected with the disclination density [18], and the hexatic stiffness $K_A$ becomes [19]

$$K_A = 1/\Delta$$

Here, $1/\Delta$ is the inverse Laplacian, $G(x)$ the Gaussian curvature and $s(x)$ the disclination density [18],

$$s(x) \equiv 1/\sqrt{g(x)} \sum q_i \delta(x-x_i),$$

with $N_d$ disclinations of charge $q_i = \pm 2\pi/6$ at positions $x_i$. The defects minimize $F_h$, by arranging themselves to approximately match the Gaussian curvature. For low temperatures, large core energy $E_c$ and spherical geometries we expect $N_d = 12$, corresponding to 12 5-fold disclinations at the vertices of an icosahedron.

To investigate the influence of hexatic order on droplets, we study deformations about the equilibrium configuration. We expand the free energy $F$ in a small time-dependent displacement field $\delta \vec{R}(x,t)$, where $\vec{R} = \vec{R}_0 + \delta \vec{R}$ is the deformed surface and $\vec{R}_0$ is the radius vector of a sphere. Here, the displacement field can be chosen to be purely normal, $\delta \vec{R}(x,t) = R_0 \zeta(x,t) \vec{N}$, where $\vec{N} = \vec{R}_0/R_0$ is the normal vector of the sphere and $\zeta$ can be expanded in terms of spherical harmonics

$$\zeta(x,t) = \sum_{l=0}^{\infty} \sum_{m=-l}^l r_{lm}(t) Y_{lm}(x).$$

In the absence of defects, the expansion of $F$ in $\zeta$ would be straightforward. On the sphere however, one has to deal with a distribution of discrete disclination charges which produces a small static icosahedral surface deformation. We initially neglect this discreteness and show afterwards that the corrections arising from the discrete nature of $s(x)$ are irrelevant for the oscillation frequencies $\omega(l)$ with $l \leq 6$. These considerations can be made more precise by expanding $s(x)$ in terms of spherical harmonics

$$s(x) = G_0 + \frac{1}{R_0^2} \sum_{l=1}^{\infty} \sum_{m=-l}^l s_{lm} Y_{lm}(x),$$

where $G_0 = 1/R_0^2$ and $s_{lm}$ can be expanded in terms of spherical harmonics [20].

$$\rho \frac{\partial \Phi(r)}{\partial t} \bigg|_{r=(R_0+\zeta R_0)-} - \rho_v \frac{\partial \Phi(r)}{\partial t} \bigg|_{r=(R_0+\zeta R_0)+} = \Delta p(x),$$

where $\Phi(r,x,t)$ is the velocity potential. Eq. [1] thus relates the pressure difference between the inside and outside of the droplet with the generalized pressure discontinuity $\Delta p$ which is caused by the shape displacement. $\Phi(r,x,t)$ is here given by [20]

$$\Phi(r,x,t) = \sum_{l,m} A_{lm}^0 Y_{lm}(x) \left( \frac{r}{R_0} \right)^{l+1}$$

for $r > R_0(1 + \zeta)$ and $\Phi(r,x,t) = \sum_{l,m} A_{lm}^0 Y_{lm}(x) \left( \frac{r}{R_0} \right)^l$ for $r < R_0(1 + \zeta)$. The displacement field $\zeta$ and the velocity potential $\Phi$ are related by the associated boundary condition $R_0 \zeta \equiv 0$ at $r = R_0(1 + \zeta)$, which yields $A_{lm}^0(t) = -R_0^2 r_{lm}(t)/(l + 1)$ and $A_{lm}^0(t) = R_0^2 r_{lm}(t)/l$. Upon setting $\Delta p(x) = \sum_{l,m} (\Delta p_{lm}(t)) Y_{lm}(x)$, one then finds

$$\Delta p_{lm}(t) = \left( \frac{\rho_l}{l+1} + \frac{\rho_v}{l+1} \right) R_0^2 r_{lm}(t),$$

where the generalized surface pressure of the displaced surface is given by $\Delta p_{lm} = -F(r_{lm})/R_0^3 r_{lm}^*$. Since the interfacial energy contribution to Eq. [1] is (cf. e.g. [21])

$$F_l = \frac{1}{2} \pi R_0^3 \sum_{l,m} |r_{lm}|^2 (l-1)(l+2)$$

and the hexatic free energy reads [21]
Next, we discuss the influence of hexatic order on the fluctuations of a vesicle. Here, the free energy is given by

\[ F_v = \frac{1}{2} \kappa \int dA (2H)^2 + \kappa_G \int dA G + \frac{1}{2} K_A \int dA D_i n^i D^i \eta_j, \] (12)

where \( \kappa \) and \( \kappa_G \) are the mean and Gaussian rigidity, respectively. In the following analysis, the second term of Eq. (12) can be neglected since we only consider surface shapes which are topologically equivalent to a sphere.

Since \( \kappa \) plays a similar role for vesicles as \( \sigma \) plays for droplets, hexatic order should lead here to similar effects on the spectrum \( \omega(l) \). However, for vesicles the fluctuations are overdamped and one has to analyze the Stokes equation. This can be done by generalizing the approach of [22] to hexatic membranes. One then obtains [24] (neglecting for simplicity the volume constraint)

\[ \omega(l) = -\frac{i}{\eta R_0} \left( l(l-1)/l(1+1) \right) \left[ \kappa l(1) + K_A \frac{(l-1)(l+2)}{l(l+1)} \right], \] (13)

where \( \eta \) is the liquid viscosity and \( \Gamma(l) \equiv l(l+1)/(2l+1)(2l^2+2l-1) \). In the flat space limit one has

\[ \omega \simeq -\frac{1}{4\eta} \left[ \kappa k^3 + \frac{K_A}{R_0^2} \right], \] (14)

in agreement with [23] for \( R_0 \to \infty \).

The frequency shift (13) now depends on the ratio \( K_A/\kappa \). However, as \( R_0 \to \infty \), we expect that \( K_A \simeq 4\kappa \) (a universal result for flat hexatic membranes at long wavelength [24]) leading to a frequency enhancement by a factor \( \simeq 13/9 \simeq 1.44 \) for \( l = 2 \) quadrupole mode. Thus, bond orientation order has a strong effect on the fluctuations of a membrane and should have experimentally observable consequences in dynamical light scattering [22].

For vesicles, the presence of a finite number of defects also leads to an equilibrium configuration with a deformed surface. The mean curvature \( H(x) \) of the stationary vesicle now satisfies

\[ 2H = 2H_0 + \frac{K_A}{\kappa R_0^2} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \frac{(l-1)(l+2)}{l(l+1)^2} s_{lm} Y_{lm}, \]

leading to nonzero coefficients \( r_0^{lm} = s_{lm} K_A/\kappa R_0^2(l+1)^2 \) in the ground state. However, icosahedral symmetry insures that \( s_{lm} = 0 \) unless \( l = 6, 10, 12, \ldots \). Thus, corrections of order \( s_{lm} \) have no influence on the frequencies \( \omega(l) \) for small \( l \). Provided the positions of the disclinations

\[ F_k = \frac{1}{2} K_A \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \frac{|r_{lm}|^2 (l-1)^2(l+2)^2}{l(l+1)} \] (9)

we set \( r_{lm} = r_0^{lm}(t) e^{-i\omega(l)t} \) and find (for \( l > 0 \) and \( \rho_v < \rho_l \))

\[ \omega^2 = \frac{\sigma}{\rho_l R_0^2} (l(l-1)(l+2)) \left[ 1 + \frac{K_A}{\sigma R_0^2} \frac{(l-1)(l+2)}{l(l+1)} \right]. \] (10)

Note that \( \omega(l) \) vanishes for \( l = 1 \), corresponding to translations of the droplet as a whole. Eq. (10) also shows that hexatic order only affects capillary waves in a curved geometry: In the flat space limit of large \( R_0 \) and \( l \gg 1 \) with \( k \equiv l/R_0 \) fixed, one has

\[ \omega^2 \simeq \frac{k^3}{\rho_l} \left[ \sigma + \frac{K_A}{R_0^2} \right]. \] (11)

The hexatic contribution drops out as \( R_0 \to \infty \) and we recover the result for capillary waves of a flat fluid surface [20]. Thus, it is essential to study deformation of a curved geometry to reveal the presence of hexatic order. In general, the undulation frequency Eq. (10) depends on the ratio \( K_A/\sigma R_0^2 \) which for hexatic order at the surface of supercooled liquid metal droplets is \( K_A/\sigma R_0^2 \simeq (\xi_T/R_0)^2(\epsilon_c/\sigma a_0^3) \). This ratio becomes of order unity when \( \xi_T \approx R_0 \).

Nonzero coefficients \( s_{lm} \) with \( l > 0 \) affect the mean curvature \( H(x) \) of the stationary droplet via the extremal equation [21]

\[ 2H = 2H_0 + \frac{K_A}{\sigma R_0^2} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \frac{(l-1)(l+2)}{l(l+1)} s_{lm} Y_{lm}, \]

with \( H_0 = 1/R_0 \), leading to static surface deformation coefficients \( r_0^{lm} = s_{lm} K_A/\sigma R_0^2(l+1) \) which vanish in the limit \( R_0 \to \infty \). Thus, for \( K_A \neq 0 \) the defects effectively repel each other and deform the droplet, cf. Fig. [1]. However, as we show below, nonzero \( s_{lm} \) have no influence on the frequencies \( \omega(l) \) for \( 0 < l < 6 \).
remain fixed in the lipid matrix on the time scale of an undulation ($\omega(l = 2) \approx 40$ Hz for a $1 \mu$ vesicle) the dispersion relation (13) remains valid for $0 < l < 6$. Because disclination motion is catalyzed by absorption and emission of dislocations with spacing $\xi_T$, the disclination diffusion constant is $D_{\sigma} \approx (a_0/\xi_T)^2 D_{\text{lipid}}$, where $D_{\text{lipid}} \approx 10^{-8}$ cm$^2$/sec. The estimate $(a_0/\xi_T)^2 \approx 10^{-2}$ suggests only minor disclination motion during an undulation period. Similar estimates show that disclination motion is negligible during a capillary wave period for hexatic droplets.

Finally, we will discuss multielectron bubbles in liquid $^4$He. These bubbles can undergo both a freezing transition and a shape instability. Thus, here hexatic order affects not only the fluctuation spectrum but also the instability-threshold for fission. The free energy of a multielectron bubble $F_b = F_d + F_c$ is that of a droplet (cf. Eq. (1)) with an additional Coulomb contribution

$$F_c = \frac{1}{2\varepsilon} \int dA \int dA' \frac{\rho(x)\rho(x')}{|x - x'|}, \quad (15)$$

where $\rho(x)$ denotes the charge distribution on the surface and $\varepsilon$ is the $^4$He dielectric constant. In an equilibrium fluid, $\rho = eN/4\pi R_0^2$ for a sphere with $N$ electrons.

Within the approximations described above, one now finds (with $l > 0$ and neglecting the density inside the bubble)[21]

$$\omega^2 = \frac{\sigma}{\rho_0 R_0^3} (l - 1)(l + 1)$$

$$\times \left[ (l + 2) - 4 \frac{R_{cr}^3}{R_0^3} + \frac{K_A}{\sigma R_0^2} \frac{(l - 1)(l + 2)^2}{l(l + 1)} \right], \quad (16)$$

where $R_{cr}^3 = (eN)^2/16\pi\sigma\varepsilon$ is the critical radius for multielectron bubbles without hexatic order [23]. Thus, for $K_A = 0$ spherical bubbles become unstable to fission if $R < R_{cr}$, i.e. $\omega^2(l = l_c) < 0$ for $R < R_{cr}$ and $l_c = 2$. For $K_A \neq 0$ the stability of charged bubbles is enhanced by the hexatic order of the electrons on the sphere. Thus, for $T_m < T < T_1$ one still has $l_c = 2$ but $\omega^2(l_c = 2) < 0$ for $R_0 < R_c$ with $R_c < R_e$. The icosahedral symmetry of the deformed shape with $s_{lm} \neq 0$ is too high to have an influence on the fission instability which occurs at $l = 2$.

Because the electrons (which determine $K_A$) are far apart relative to the helium atoms (which determine $\sigma$) $K_A/\sigma R_0^2$ will be smaller than for droplets of supercooled liquid metals with $R_0 \approx R_e$. For helium-bubbles with $N \approx 10^6$ one has $R_c \approx 10 \mu$m and we expect that $K_A/\sigma R_0^2 \approx 10^{-3}$. Charged metal droplets undergo the same fission instability. Thus, it might be possible to detect hexatic order by investigating the stability of charged liquid droplets in Paul traps.

The effects discussed here are even larger if the hexatic phase is bypassed and one freezes directly into a curved two-dimensional solid with shear modulus $\mu$ (22).

The resulting frequency shifts can be estimated by setting $K_A = \mu R_0^2$ in the formulas above (although the $l$-dependence will be different). There are also interesting consequences of hexatic order for dynamics of liquids and membranes in a cylindrical geometry [21].

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