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Anharmonic magnetic deformation of spherical vesicle: Field-induced tension and swelling effects

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ABSTRACT

We have derived an equation, based on Helfrich's curvature elasticity, describing the equilibrium shape of membrane vesicles in the presence of magnetic fields. We have solved this equation with and without the constraint of constant vesicle area. For vesicles with constant area, an exact calculation using our model confirms Helfrich's estimate (Helfrich, 1973) [20] and predicts a magnetic field induced surface tension. Without the constant area constraint, our model predicts that vesicles with positive diamagnetic susceptibility anisotropy will swell in magnetic fields. It also predicts the anharmonic magnetic deformation of self-assembled nanocapsules of bola-amphiphilic molecules and the linear birefringence observed by Manyuhina et al. (2007) [22] .

Helfrich's spontaneous curvature model [1] has been used for four decades to study the equilibrium shapes and deformations of lipid bilayer vesicles. The model has been used to predict the biconcave discoid shape of red blood cells [2,3] and is well accepted in biophysics [4]. His curvature elasticity model has been extended to investigate shapes in soft matter, such as the helical structures in carbon nanotubes [5] and in bile ribbons [6], cylindrical structures in the smectic-A phase [7] and in peptide nanotubes [8], the circle-domain instability in lipid monolayers [9] and icosahedral structures in virus capsids [10].

Among the many fruitful applications of the Helfrich model, vesicle deformation by external forces (such as by pressure [11–13], capillary forces [14,15] and electric fields [16–19]) has perhaps attracted the most interest. Vesicle deformation by magnetic fields was predicted more than three decades ago by Helfrich [20], however the experimental study has only been recently initiated [21,22]. Helfrich considered infinitesimal deformations of a spherical vesicle of radius $r = r_0$ by a spatially uniform magnetic field $\mathcal{H}$ by minimizing the sum of bending energy [1] (curvature elastic energy) and the free energy of interaction between the magnetic field and the constituent molecules [23];

$$F = F_b + F_{\mathcal{H}} = \frac{1}{2}\kappa \oint (c_1 + c_2 - c_0)^2 dA - \frac{1}{2}\Delta\chi t \oint (\mathcal{H}\cdot\mathbf{n})^2 dA, \quad (1)$$

here κ is the bend modulus, c_1 and c_2 are the principal curvatures, c_0 is the spontaneous curvature, and $\mathbf{n}$ is the outward unit normal. The principal values of the diamagnetic susceptibility are $\chi_{//}$ and $\chi_\perp$ parallel and perpendicular to $\mathbf{n}$, and the susceptibility anisotropy is $\Delta\chi = \chi_{//} - \chi_\perp$ and t is the membrane thickness. From Eq. (1), we deduce that a spherical vesicle with $\Delta\chi > 0$ deforms into an oblate vesicle with rotational symmetry about $\mathcal{H}$. By using a spherical coordinate system centered on the vesicle with $\mathbf{z}$ along $\mathcal{H}$ and keeping the vesicle surface area constant, Helfrich found that the vesicle shape was given by $r = r_0 + a_{20}Y_{20}(\theta,\phi)$, where Y_{lm} is a spherical harmonic and

$$a_{20} = -\alpha r_0^3 \Delta\chi t \mathcal{H}^2/\kappa \quad (2)$$

where $\alpha = \sqrt{\frac{4\pi}{5}}/18$ for $c_0 = 0$ and $\alpha = \sqrt{\frac{4\pi}{5}}/12$ for $c_0 r_0 = 2$ [20,24]. Helfrich also suggested that the predicted deformation could be experimentally accessed through the field-induced birefringence of a suspension of identical vesicles, since the normalised birefringence (last Eq. in [20] and Eq. (4) in [22]) is $\Delta n/\Delta n_{max} \simeq (r(\theta = \frac{\pi}{2}) - r(\theta = 0))/R = (-\frac{3}{2})\sqrt{\frac{5}{4\pi}}(a_{20}/r_0) \propto \mathcal{H}^2/\kappa$, where $R = \sqrt{A/4\pi}$, and A is the surface area of the vesicle. By measuring the birefringence of a system of self-assembled vesicles of bola-amphiphilic sexithiophene molecules, Manyuhina et al. [22], found that the predicted quadratic dependence of the normalized birefringence on $\mathcal{H}$ is well obeyed at low fields, but at higher fields, the bending rigidity κ is enhanced, and hence the observed birefringence has a weaker $\mathcal{H}$ dependence (Fig. 2 in [22]).

To explain this, Manyuhina et al. modified the Helfrich bending energy and included a fourth-order curvature term [22,25]. By fitting the data, using three additional parameters in their model (Eq. (7) in [22]), good agreement with experiment was found. We suggest, however, that agreement with experiment may be found without modifying Helfrich's bending energy.

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In this Letter, we derive a geometric equation for the equilibrium shape of membrane vesicles in a magnetic fields using Helfrich's curvature elasticity model. The general solution describes infinitesimal deformations of a spherical vesicle in a magnetic field. The solution for vesicles with constant area confirms Helfrich's result [20] that the change of radius is quadratic in field strength and also predicts a field-dependent surface tension. The solution for variable vesicle area predicts field-induced swelling of vesicles with positive diamagnetic anisotropy and satisfactorily explains the anharmonic magnetic deformation of self-assembled nanocapsules evidenced by the linear birefringence meaured by Manyuhina et al. [22]. As in Ref. [22], we use the term anharmonic to describe deformations whose result on the birefringence is subquadratic in $\mathcal{H}$.

For the complete theory, the free energy (1) has to be extended by two additional terms [12];

$$F = F_b + F_{\mathcal{H}} + \Delta p \int dV + \lambda \oint dA, \tag{3}$$

where Δp and λ are Lagrange multipliers to ensure constant volume and area, or, alternately, the pressure jump across the membrane (i.e. $\Delta p = p_0 - p_i$) and the membrane tension, respectively. Although this free energy was minimised in Ref. [20] with the constraint of constant area, the effects of Δp and λ were not analysed thoroughly. Here we derive a more complete formula for Eq. (2); the details are given below. To obtain a description of the deformation, we solve the variational equation $\delta F = 0$. For $\mathcal{H} = 0, \delta F_{\mathcal{H}=0} = 0$ takes the form [12]

$$\Delta p - 2\lambda H + \kappa(2H + c_0)(2H^2 - 2K - c_0H) + 2\kappa\nabla^2 H = 0, \tag{4}$$

where $H = -\frac{1}{2}(c_1 + c_2)$ and $K = c_1c_2$ are the mean curvature and Gaussian curvature, respectively, the equilibrium vesicle surface is specified by the position vector $\mathbf{Y}(u, v)$ where u and v are surface parameters, and ∇^2 is the Laplace–Beltrami operator defined as $\nabla^2 = (1/\sqrt{g})\partial_i(g^{ij}\sqrt{g}\partial_j)$. Here $\partial_1 = \partial_u, \partial_2 = \partial_v$, and $g^{ij} = (g_{ij})^{-1}, g = \det(g_{ij})$, and $g_{ij} = \partial_i\mathbf{Y}\cdot\partial_j\mathbf{Y}$ are the coefficients of the first fundamental form of the surface.

As in Ref. [20], we consider the case where the vesicles are spherical in the absence of a magnetic field. In this case, the radius of these spherical vesicles is given by

$$\Delta p r_0^3 + 2\lambda r_0^2 - \kappa c_0 r_0(2 - c_0 r_0) = 0. \tag{5}$$

For $\mathcal{H} \neq 0$, our main interest is the calculation of $\delta F_{\mathcal{H}}$. Assuming the surface $\mathbf{Y}$ to be slightly distorted according to

$$\mathbf{Y}' = \mathbf{Y} + \psi(u, v)\mathbf{n} \tag{6}$$

with $\psi(u, v)$ being a smooth infinitesimal function, we have

$$\delta F_{\mathcal{H}} = -\frac{1}{2}\Delta\chi t\left[\oint (\mathbf{n}\cdot\mathcal{H})^2\delta dA + 2\oint(\mathbf{n}\cdot\mathcal{H})\mathcal{H}\cdot\delta\mathbf{n}dA\right]. \tag{7}$$

In prior letter, we showed that $\delta dA = -2H\psi dA$ (Eq. (18) in [12b]) and $\delta\mathbf{n} = -\nabla\psi$ (Eq. 3.26) in [26]) with

$$\nabla\psi = g^{ij}\mathbf{Y}_i\partial_j\psi \tag{8}$$

where $\mathbf{Y}_i = \partial_i\mathbf{Y}$. Inserting these into Eq. (7) gives

$$\delta F_{\mathcal{H}} = \Delta\chi t\oint\left[(\mathcal{H}\cdot\mathbf{n})^2 H\psi + (\mathcal{H}\cdot\mathbf{n})\mathcal{H}\cdot\nabla\psi\right]dA. \tag{9}$$

We next integrate $\nabla\psi$ by parts. Using results from Ref.[27] (Eq. (17) on p. 232 and setting $\mathbf{U} = (\mathcal{H}\cdot\mathbf{n})\mathcal{H})$, we have

$$\oint(\mathcal{H}\cdot\mathbf{n})\mathcal{H}\cdot\nabla\psi dA = \oint[\nabla\cdot(\psi(\mathcal{H}\cdot\mathbf{n})\mathcal{H}) - \psi\nabla\cdot(\mathcal{H}(\mathcal{H}\cdot\mathbf{n}))]dA. \tag{10}$$

By using the divergence theorem for surfaces ([27], pp. 238,239), we have

$$\oint\nabla\cdot(\psi(\mathcal{H}\cdot\mathbf{n})\mathcal{H})dA = \oint\left[-2(\mathcal{H}\cdot\mathbf{n})^2 H\psi\right]dA. \tag{11}$$

Substituting Eqs. (10) and (11) into Eq. (9) gives

$$\delta F_{\mathcal{H}} = -\Delta\chi t\oint\left[H(\mathcal{H}\cdot\mathbf{n})^2 + \nabla\cdot(\mathcal{H}(\mathcal{H}\cdot\mathbf{n}))\right]\psi dA. \tag{12}$$

Setting $\delta F = \delta(F_{\mathcal{H}=0} + F_{\mathcal{H}}) = 0$ for any infinitesimal function ψ and using Eq. (4) and (12) gives a new form of the shape equation

$$\begin{aligned}&\Delta p - 2\lambda H + \kappa(2H + c_0)(2H^2 - 2K - c_0H) + 2\kappa\nabla^2 H\\ &\quad = \Delta\chi t\left[(\mathcal{H}\cdot\mathbf{n})^2 H + \nabla\cdot(\mathcal{H}(\mathcal{H}\cdot\mathbf{n}))\right].\end{aligned} \tag{13}$$

In the above derivation, we did not assume $\mathcal{H}$ to be spatially uniform, hence the shape equation in Eq. (13) is valid for any magnetic field, $\mathcal{H} = \mathcal{H}(u, v)$. It should be noted that Eq. (13) may also be useful for studying vesicle deformation by an electric field, even an AC electric field at sufficiently high frequencies. According to Helfrich's theory [28], above a threshold frequency (in the so-called dielectric regime) the orientation dependent electric contribution to the free energy in an AC electric field $\mathbf{E}(\omega)$ has the form $-\frac{1}{2}\Delta\epsilon t\oint(\mathbf{E}\cdot\mathbf{n})^2 dA$ where the principal values of the dielectric permittivity are $\epsilon_{//}$ and $\epsilon_{\perp}$ parallel and perpendicular to $\mathbf{n}$, and the dielectric anisotropy is $\Delta\epsilon = (\epsilon_{//} - \epsilon_{\perp})$. The vesicle shape equation for AC electric fields at sufficiently high frequencies thus has the same form as Eq. (13).

We now discuss the derivation of the result of Eq. (2) in light of Eq. (13). As assumed in [20], at $\mathcal{H} = 0$ the vesicle is a sphere, and we use $u = \theta, v = \phi, \mathbf{Y} = r_0(\cos\phi\sin\theta, \sin\phi\cos\theta, \cos\theta)$ and $\mathbf{n} = r_0^{-1}\mathbf{Y}$. For $\mathcal{H} \neq 0$, we consider the solution of Eq. (13) of the form $\mathbf{Y}' = \mathbf{Y} + \psi(u, v)\mathbf{n}$, as in Eq. (6). $\psi(\theta, \phi)$ again describes weak deformations of the radius at (θ, ϕ), i.e. $r = r_0 + \psi(\theta, \phi)$ with

$$\psi = \sum_{l,m} a_{lm}Y_{lm}(\theta, \phi). \tag{14}$$

Here we do not set $a_{20} \neq 0$ *a priori*, but obtain it from the shape equation Eq. (13). We note that the Lagrange multiplier λ in Eq. (5), changes to $\lambda + \delta\lambda(\mathcal{H})$for $\mathcal{H} \neq 0$ to ensure constant area. The general relations

$$\delta H = (2H^2 - K)\psi + \frac{1}{2}\nabla^2\psi, \tag{15}$$

$$\delta K = 2HK\psi + \overline{\nabla}^2\psi, \tag{16}$$

are given in Ref. [12b] (Eq. (16)) and in Ref. [29] (Eq. (6)); here $\overline{\nabla}^2 = (1/\sqrt{g})\partial_i(KL^{ij}\sqrt{g}\partial_j)$, $L^{ij} = (L_{ij})^{-1}$, and L_{ij} are coefficients of the second fundamental form of the surface, defined as $L_{ij} = \mathbf{n}\cdot\partial_i\partial_j\mathbf{Y}$. For a sphere of radius r_0, we have $H = -r_0^{-1}, K = r_0^{-2}$, and

$$(-1/r_0)\overline{\nabla}^2 = \nabla^2 = \left[\frac{1}{r_0^2\sin\theta}\right]\partial_\theta(\sin\theta\partial_\theta) + \left(\frac{1}{r_0\sin\theta}\right)^2\partial_\phi^2, \tag{17}$$

so ∇^2 is the usual Laplace operator on the sphere with $\nabla^2 Y_{lm} = -l(l+1)Y_{lm}/r_0^2$. Using the first-order approximation and substituting Eqs. (5), (14)–(17) and $\mathcal{H} = \mathcal{H}_0(0, 0, 1)$ into Eq. (13) leads to

$$\begin{aligned}&2r_0^{-1}\delta\lambda + \kappa r_0^{-4}\sum_{l,m}\left[\left(\frac{-2\lambda r_0^2}{\kappa} + 4y - y^2\right) + \frac{1}{2}(y^2 - 4y - 4)l(l+1)\right.\\ &\quad\left. + l^2(l+1)^2\right]a_{lm}Y_{lm} = \Delta\chi t\mathcal{H}_0^2 r_0^{-1}\frac{1}{3}\left(1 - 4\sqrt{\frac{4\pi}{5}}Y_{20}\right)\end{aligned} \tag{18}$$