Topological instabilities of spherical vesicles

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Within the framework of the Helfrich elastic theory of membranes and of differential geometry, we study the relative stability of spherical vesicles and double bubbles. We find that not only temperature but also magnetic fields can induce topological transformations between spherical vesicles and double bubbles and provide a phase diagram for the equilibrium shapes.

Self-assembled vesicles were experimentally observed to form a variety of shapes [1]. However most equilibrium vesicles are spherical. This is not surprising because spheres are known to minimize not only the surface energy but also the elastic energy of vesicles [2]. In mathematics it has been proven that spheres have the least area to enclose and separate a given volume. The analogous problem of identifying the surface with least area enclosing and separating more than one volume was first considered by the Belgian physicist Plateau [3] in the 19th century. Surprisingly, only recently it has been proven that a double bubble, a figure composed of two spherical caps separated by a flat disk [Fig. 1(a)], is the solution to the two equal volume isoperimetric problem in the Euclidean space [4]. A general proof for double bubble enclosing two different volumes separated by a nonflat membrane was given later [5].

The connected spherical bubbles often observed in soap are certainly a realization of this "minimum property" of double bubbles since surface tension is the dominant driving force. In this Rapid Communication we explore theoretically whether double bubbles can represent the equilibrium shape of vesicles when not only the surface tension but also other energy terms such as elastic and magnetic energies are relevant. To the best of our knowledge, a double bubble was never considered as a candidate to describe the shape of vesicles. The presence of the membrane S_2 [see Fig. 1(a)] distinguishes double bubbles from dumbbells or pear-shaped vesicles that were extensively studied in phase-separated systems [6]. Two adhering vesicles may look similar to a double bubble, but they have different topology because the membrane S_2 is composed of two interacting membranes [7]. Hence, when vesicles adhere there is no change in topology and the Euler characteristic [8] remains unchanged as for two single vesicles ($\chi=4$), whereas a double bubble has $\chi=3$ [9] that is neither the topology of two single vesicles nor the one of a larger sphere ($\chi=2$). One may therefore refer to a double bubble as an intermediate shape in the topological transformations between one and two spheres. Such transformations might also be relevant to describe the first stage of cell division.

To study the instabilities of spherical vesicles toward double bubbles we start from the well-known model of elastic free energy proposed by Helfrich [10]. This model was successful in explaining the shapes of red blood cells and in predicting some new nontrivial shapes of vesicles [1,2]. However, one cannot apply without restrictions a continuum elastic theory to the shapes with discontinuities since it would yield infinite energy. The discontinuities can be taken into account by introducing a line tension with an effective angular dependence as was proposed in [11]. Similar arguments can be applied to a double bubble, which has a circular rim with a singularity, where three smooth surfaces meet [see Fig. 1(a)]. Therefore, to take into account the rim singularity in the shape of a double bubble, we propose a phenomenological term derived from the Gauss-Bonnet theorem and added to the Helfrich elastic free energy. Although other forms of the rim energy might be plausible, here we investigate the consequences of our ansatz. Assuming that intrinsic parameters of the system entering the phenomenological Helfrich free energy, such as elastic moduli and spontaneous curvature, are temperature and pressure dependent [12], we propose a phase diagram for the studied shapes. It is intuitively clear that shapes similar to a double bubble may occur whenever flat membranes become favorable, for instance, in presence of high magnetic fields that tend to orient diamagnetic molecules. For this case, experimental evidence of deformation of self-assembled spherical vesicles to oblate spheroid was reported in [13,14]. Here, we find that a magnetic field can also influence the relative stability of shapes and can make two spheroidal vesicles less stable than a deformed double bubble or one larger spheroid. The latter transformation was experimentally observed for liposomes [15] in high magnetic fields.

In Fig. 1(a) we show the double bubble as defined mathematically. The double bubble is composed of two spherical
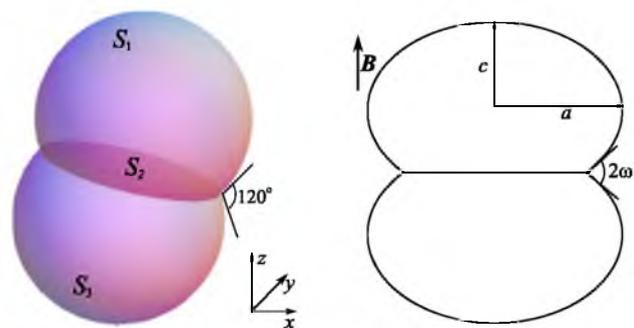

FIG. 1. (Color online) (a) The double bubble is the unique surface of least area that encloses two equal volumes; it is composed of two identical spherical caps S_1 and S_3 separated by a single membrane S_2 that is flat for equal volumes; the three pieces meet along a circle at 120° angle [4]. (b) Cross section of a magnetically deformed double bubble with semiaxes $a > c$; 2ω is the angle between two tangent planes at the meeting circle.

caps S_1 and S_3 separated by a disk S_2, meeting along a common circle (rim) at an angle of 120° [4]. To consider magnetic deformations, we study the modified geometry shown in Fig. 1(b). First, we assume that, during the deformation, the spherical caps S_1 and S_3 (with $S_1 = S_3$) change to oblate spheroids with semiaxes c and a parallel and perpendicular to the magnetic field B, respectively. Second, we allow the angle between the three surfaces to differ from 120° by introducing the parameter ω [see Fig. 1(b)] related to the radius of the membrane as

$$R_m = \frac{a^2 \sin \omega}{\sqrt{a^2 \sin^2 \omega + c^2 \cos^2 \omega}}. \qquad (1)$$

In this Rapid Communication we extend the concept of double bubble from the unique area minimizing surface with $c = a$ and $\omega = \pi/3$ to the set of shapes with $c \in (0, a]$, $\omega \in (0, \pi/2)$.

The equilibrium shapes of fluid membranes are usually studied in terms of the Helfrich model of bending energy [10,16]:

$$\mathcal{F}_{el} = \int dS \{2k(H - H_0)^2 + \bar{k}K\}, \qquad (2)$$

where H and K are the mean and Gaussian curvatures, respectively, and H_0 is the spontaneous mean curvature. The first term, proportional to the bending rigidity k, describes the local deviation from equilibrium curvature H_0, while the second term with Gaussian rigidity $\bar{k}$ influences only the topology and thus is often neglected. For the same reason, $\bar{k}$ is also not measurable if no topological transformations occur. Here we cannot omit this term because we examine different topologies. It was shown theoretically and confirmed experimentally that $-1 < \bar{k}/k < 0$ for monolayer vesicles, while for bilayer vesicles $\bar{k}$ can be positive [12,17]. The values of H_0, k, and $\bar{k}$ depend on pressure and temperature and therefore may be considered as parameters and not as intrinsic properties of the system. We will consider the case with $0.7 < H_0 R_0 < 1.3$, $-1 \le \bar{k}/k \le 1$, where R_0 is the radius of the spherical vesicle and $k = 4 \times 10^{-20}$ J $\approx 10 k_B T$, the latter being a typical value for molecular vesicles. Moreover, we assume that self-assembled molecules keep a constant density, implying the condition of constant surface of the vesicles $S = 8 \pi R_0^2$.

The form of the phenomenological free energy, given by Eq. (2), is valid only for smooth surfaces such as spheroids or the individual surfaces S_1, S_2, and S_3. In order to introduce the energy of the rim phenomenologically, we make use of the Gauss-Bonnet theorem $\int dSK = 2\pi\chi$ [8], where $\chi = 3$ for the double bubble [9]. By integrating explicitly the Gaussian curvature K over the three smooth pieces of the double bubble, namely, the spheroidal caps $\{S_1, S_3\}$ and the flat membrane S_2 ($K = 0$), we find the following expression:

$$\sum_{i=1}^{3} \int_{S_i} dSK = 4\pi(1 + \cos \omega), \qquad (3)$$

which depends only on the angle ω [see Fig. 1(b)]. Since $\int dSK = 6\pi$, the difference with respect to Eq. (3) represents the contribution of the curvature integral over the rim. This integral accounts for the discontinuity of the shape and yields the angle deficit of the rim as $2\pi\chi - \Sigma_{i=1}^{3}\int_{S_i} dSK = 2\pi(1 - 2 \cos \omega)$. We then assume that the phenomenological free energy of a circular rim is proportional to the square of the angle deficit $(1 - 2 \cos \omega)$ multiplied by the rim length $2\pi R_m$

$$\mathcal{F}_{rim} = \gamma(1 - 2 \cos \omega)^2 2\pi R_m, \qquad (4)$$

where the coefficient of proportionality γ represents the line tension. The value of γ can be estimated by considering the formation of vesicles due to edge effects and comparing the free energy of the two limiting cases, namely, a disk with $F_{disc} = 2\pi\gamma R_d = 4\pi\gamma R_0$ and a sphere with $F_{sphere} = 4\pi 2k$, yielding $\gamma = 2k/R_0$ [18]. Our conjecture for the form of the rim free energy $\mathcal{F}_{rim}$ is similar to the line tension with an effective angular dependence proposed in [11] to justify the occurrence of slope discontinuities between different membrane domains. Also for crystals, it has been demonstrated mathematically in [19] that the cusps that are often present at crystal surfaces can be intrinsic property of equilibrium shapes and not necessarily due to defects.

We begin by considering the symmetric case, namely, a double bubble composed of two spherical caps with $c = a = R = R_0\sqrt{8/[4(1 + \cos \omega) + \sin^2 \omega]}$, which yields $R|_{\omega=0} = R_0$. The result for the elastic energy and the rim energy is $\mathcal{F}_{el} = 4\pi k(1 + \cos \omega)[(1 - RH_0)^2 + \bar{k}/(2k)] + 2\pi k \sin^2 \omega (RH_0)^2$ and $\mathcal{F}_{rim} = 4\pi k \sin \omega(1 - 2 \cos \omega)^2 R/R_0$. The ω dependence of these terms is shown in Fig. 2(a). The rim energy vanishes at $\omega = 0$ when two vesicles just touch and at $\omega = \pi/3$ when the angle between three surfaces is $2\omega = 2\pi/3$ (see Fig. 1) that coincides with the Plateau's rule for soap films. However, contrary to soap bubbles, the elastic energy grows with ω so that the total free energy $\mathcal{F}_{tot} = \mathcal{F}_{el} + \mathcal{F}_{rim}$ does not necessarily have a minimum in the vicinity of $\omega = \pi/3$, depending on the relative contribution from $\mathcal{F}_{el}$. These results show that with this approach we can obtain the correct limiting cases. Figure 2(b) presents the phase diagram for the relative stability of spherical vesicles and double bubbles in the plane of the parameters $(\bar{k}/k) - (H_0 R_0)$. Thermal fluctuations can be taken into account via the renormalization of the bending and Gaussian rigidity given by [20] $k_{eff} = k - (3k_B T/8\pi)\log(q_{max}^2/q_{min}^2)$ and $\bar{k}_{eff} = \bar{k} + (5k_B T/12\pi)\log(q_{max}^2/q_{min}^2)$. Therefore, an increase in temperature might be enough to induce shape transformation. In Fig. 3 we show a scanning electron microscopy (SEM) image of a structure formed by self-assembled bolaamphiphilic sexithiophene (6T) molecules that usually form hollow spherical vesicles [13]. The angle between two spherical parts in this image suggests the possibility that this structure is a double bubble and not two adhering vesicles. It would be interesting to apply other experimental techniques, such as transmission electron microscopy (TEM), to investigate this issue.
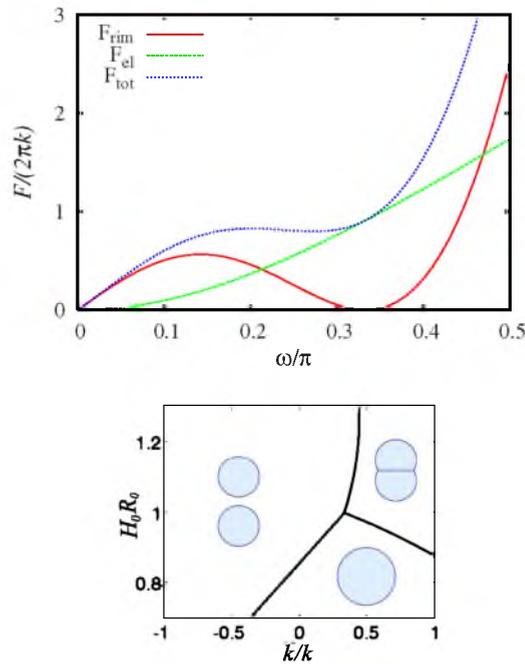
FIG. 2. (Color online) (a) The free-energy terms $\mathcal{F}_{\text{rim}}$, $\mathcal{F}_{\text{el}}$, and $\mathcal{F}_{\text{tot}}$ of double bubble with $c=a$ plotted versus the angle ω. We choose $\bar{k}=0$ and $H_0 R_0=1$ for the elastic part for illustration. (b) Phase diagram showing regions where two spheres with radius R_0, a standard double bubble with $c=a$ and $\omega=\pi/3$, and one single vesicle with radius $\sqrt{2}R_0$ have the lowest free energy. The parameters H_0, k, and $\bar{k}$ depend on temperature and pressure [12].

Now consider the effect of magnetic field, which tends to align diamagnetic molecules and usually leads to deformation of spherical vesicles toward superspheroid such as the one measured and explained in [13,14]. Here, we consider the possibility that magnetic fields could affect the topology as well. We minimize the total free energy

$$\mathcal{F}_{\text{tot}} = \mathcal{F}_{\text{el}} + \mathcal{F}_{\text{rim}} + \mathcal{F}_{\text{mag}}, \tag{5}$$

with respect to the deformation c/a for a given value of ω. The elastic energy $\mathcal{F}_{\text{el}}$ and the rim energy $\mathcal{F}_{\text{rim}}$ are given by
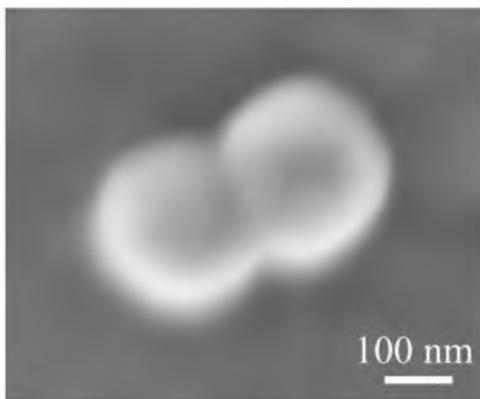

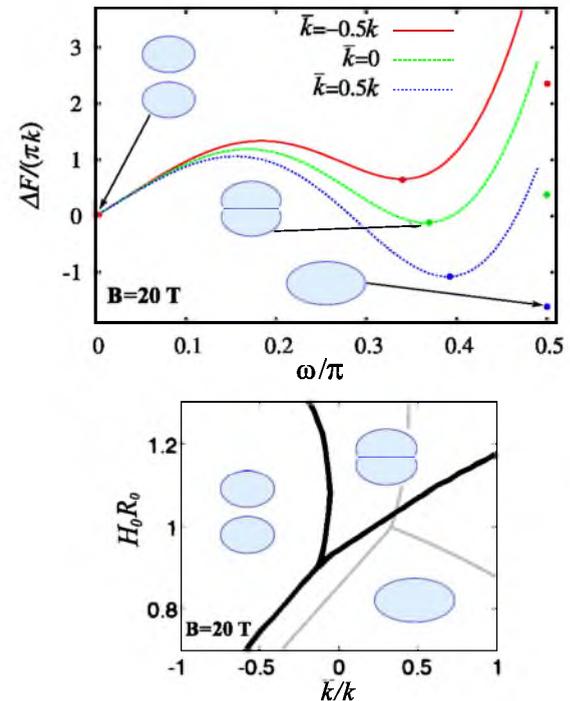FIG. 3. SEM image of 6T vesicles on a metallic surface found after evaporation of a solvent.

FIG. 4. (Color online) (a) Variation in the minimum of the total free energy $\Delta\mathcal{F}=\min_{\omega=\text{const}}\mathcal{F}_{\text{tot}}(c/a)-\min_{\omega=0}\mathcal{F}_{\text{tot}}(c/a)$ for magnetic field $B=20$ T. The thick dots on each curve indicate the local minima separated by barriers. For some cases we show the corresponding equilibrium shapes. For this plot the parameters are $H_0 R_0=1$, $R_0=100$ nm, $D=5$ nm, and $\Delta\chi=10^{-5}$. (b). Phase diagrams enclosing three regions with topologically different shapes: thick black lines ($B=20$ T) and gray thin lines [$B=0$ T same as Fig. 2(b)]. Shapes with different topologies illustrate schematically the regions of the lowest free energy.

Eqs. (2) and (4), respectively, and the magnetic energy, assuming that the membrane S_2 is perpendicular to the direction of the magnetic field, is

$$\mathcal{F}_{\text{mag}} = -\frac{\Delta\chi D B^2}{2\mu_0}\left(\int dS n_z^2 + \pi R_{\text{m}}^2\right), \tag{6}$$

where $\Delta\chi=\chi_{\parallel}-\chi_{\perp}$ is the difference of magnetic susceptibility along the long and short axes of the molecule and D is the length of the molecule and the last term is the contribution of the flat disk with radius R_{m} [Eq. (1)]. Whenever the reduction in magnetic energy $\mathcal{F}_{\text{mag}}$ due to the presence of the membrane compensates the elastic energy $\mathcal{F}_{\text{el}}$ and the energy of the rim $\mathcal{F}_{\text{rim}}$, the formation of a double bubble is favored.

We show first the free energy, minimized over the deformation c/a, for all possible values of ω in a magnetic field chosen as $B=20$ T [see Fig. 4(a)]. We distinguish three deep minima separated by high barriers, corresponding to the three equilibrium shapes. By varying the value of Gaussian rigidity we find as the ground state: two spheroids for $\bar{k}=-0.5k$, a deformed double bubble with $\omega\simeq 0.37\pi$ for $\bar{k}=0$, and a single spheroid for $\bar{k}=0.5k$ with comparable values of deformation c/a. Nevertheless, the presence of three separated minima means that the experimentally observed

shapes would depend on the kinetics of the system and that under certain conditions all three shapes could exist simultaneously. In Fig. 4(b) we illustrate the phase behavior of the studied shapes at $B=20$ T compared to the one at $B=0$ T in Fig. 2(b). As we expected, in presence of a magnetic field, the area in the phase diagram of deformed double bubbles and single spheroids increases significantly, which leads to a larger probability of finding these shapes for the fluctuating spherical vesicles. These results also show that the change in topology from sphere to double bubble can be induced not only by temperature but also by magnetic fields.

In conclusion, we found that the double bubble, the surface of smallest area enclosing two equal volumes, also minimizes under certain conditions the free energy of self-assembled elastic vesicles. We have explicitly shown that magnetic fields can be used to alter not only the shape and the size but also the topology of two diamagnetic vesicles. Considering the possibility of other topologies is useful when analyzing experimental results and establishing whether self-assemblies are in equilibrium or not. The calculations presented in this Rapid Communication may be thought as a first step to consider the formation of foam during self-assembly, such as the one observed in [21]. We hope that our work will provide a motivation for new experiments.

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