Energy Variation of Soft Matter Interfaces

Prerna Gera and David Salac

Department of Mechanical and Aerospace Engineering, University at Buffalo, Buffalo, New York 14260-4400.
E-mail: davidsal@buffalo.edu

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Abstract: The variation of energies associated with soft matter interfaces where surface inhomogeneities are present. These energies include the total bending and splay energy, the variable surface tension energy, a coupling energy between the total curvature and an underlying surface concentration field, the energy due to an external field, and a phase segregation energy. When considering these energies the variation of material properties such a bending rigidity are taken into account, which results in more general variation expressions. These variations can be used to determine the equilibrium interface and concentration configuration or to determine the driving forces for non-equilibrium situations. While the focus of this work are energies associated with multicomponent vesicles, it can easily be extended to any soft matter interface.

1. Introduction

Soft matter interfaces play a critical role in a large number of material systems. For example, additives used in enhanced oil recovery techniques induce low interfacial tension between water and oil which helps in oil displacement and final recovery [1,2]. By controlling the types of surfactants on the interface the emulsions
can be inverted [3]. The interplay between the interface and the surrounding fluids can be used to make skin care products, where nano-emulsions or polymer thickening agents are heavily used [3].

Soft matter interfaces also play a crucial role in the behavior of biological systems such as red blood cells. These interfaces play a vital role since they not only acts as a protective barrier to the cell interior, but they also act as the medium of communication with the environment outside. The composition of the biological membrane also has a direct impact on the fundamental biological processes such as signal transduction, trafficking and sorting processes [4,5,6].

These biological membranes are constituted of various kinds of lipids and cholesterol. As these molecules move freely in the plane of the membrane they often combine to form domains that are energetically more stable than the rest of the membrane. Mechanical properties, such as bending rigidity and membrane spontaneous curvature, can vary depending on the local membrane composition and molecular arrangement. This variation of properties influences not only the the segregation and coarsening processes of the membrane domains, but also the surrounding fluid. The coupling between the composition of the membrane and changes in it’s morphology is therefore interesting and significant.

Pioneering work on biological soft matter interfaces have been done by Canham [7], Helfrich, [8], and Evans [9]. They individually studied the mechanics of the membrane and presented the free energy functional which depends purely on geometric quantities. The variation of this functional was taken to determine the Euler-Lagrange, or “Shape” equation [10,11]. This gave rise to numerous theoretical investigations [12,13, 14,15,16], however, most of these focused on a homogeneous membranes.

In this work the variation with respect to changes of the interface location and changes of a surface concentration field is considered. These variations can be used to determine the equilibrium interface and concentration configuration or to determine the driving forces for non-equilibrium situations. While the focus of this work are energies associated with multicomponent vesicles, it can easily be extended to any soft matter interface including droplets [17], bubbles [18,19], fiber-laden membranes [20], and biopolymers [2].
The energies considered here include the membrane total and splay bending energies, surface tension, the coupling between the total curvature and concentration field, a generic external field, such as an electric or magnetic field, and a phase energy consisting of gradient and mixing terms. The methodology used here is based on the work of Napoli and Vergori [21]. Unlike the prior work, it is assumed that all material parameters, such as total bending rigidity and spontaneous curvature, depend on the underlying concentration field. This results in more general expressions which are valid for a larger number of systems.

The outline of the paper is as follows. The mathematical framework is outlined in Section 2. Here the general expression for variation of the interface free energy with respect to changes of the interface location and surface concentration field will be presented. Specific energy cases are shown in Section 3, where each free energy is considered separately. A brief discussion follows in Section 4. To provide additional clarity, Appendices A and B provide information about various surface calculus and variational identities used in Sections 2 and 3.

2. Mathematical Framework

The mathematical framework used here is based on the work of Napoli and Vergori [21]. In this prior work a systematic method is developed to obtain the equilibrium equations for nematic crystal vesicles. In this section the prior results relevant to the current work are briefly outlined. The addition of an additional energy contribution not considered by Napoli and Vergori is also shown.

Consider a closed interface \( \Gamma \) with an outward facing unit normal of \( n \) which separates two fluids. There could possibly be two components to this interface, with the concentration given by \( q \). This interface is characterized by the second fundamental form, also called the shape tensor, given by \( L = \nabla_s n \), where \( \nabla_s \) represents the surface gradient. This is a symmetric second-order tensor field which only has components tangent to the interface. It also only has two non-zero eigenvalues, \( c_1 \) and \( c_2 \), which are called the principle
curvatures. Using this definition the total and Gaussian curvature can be defined as
\begin{align}
H &= c_1 + c_2 = \text{tr}L = \nabla_s \cdot n, \\
K &= c_1 c_2 = \frac{1}{2} \left[ (\text{tr}L)^2 - \text{tr} \left( L^2 \right) \right],
\end{align}
respectively.

The free energy functional for the interface is defined on the closed surface \( \Gamma \) as
\[ W[\Gamma] = \int_{\Gamma} w(r, n, L, q, \nabla_s q) \, dA, \]
where \( w(r, n, L, q, \nabla_s q) \) is the free energy density which may depend on surface quantities \( n, L, q, \) and \( \nabla_s q \) and the position of the interface, \( r \).

To calculate the first variation of the free energy, assume that the interface \( \Gamma \) undergoes an infinitesimal virtual displacement,
\[ r' = r + \epsilon u, \]
where \( \epsilon \) is a small positive parameter and \( u \) is a virtual displacement field. The prime denotes the quantities and operators relative to the virtually deformed configuration. The variation of a quantity is defined as
\[ \delta (\cdot) = \lim_{\epsilon \to 0} \frac{(\cdot)' - (\cdot)}{\epsilon}, \]
where \( (\cdot) \) denotes any quantity defined on \( \Gamma \). Using the transport theorem, the variation of the free energy can be written as
\[ \delta W[\Gamma] = \int_{\Gamma} \left( \delta w + w \nabla_s \cdot u \right) \, dA, \]
where
\[ \delta w = \frac{\partial w}{\partial \Gamma} \delta \Gamma + \frac{\partial w}{\partial n} \cdot \delta n + \frac{\partial w}{\partial L} \cdot \delta L + \frac{\partial w}{\partial q} \delta q + \frac{\partial w}{\partial \nabla_s q} \cdot \delta \nabla_s q. \]
The component \( (\partial w/\partial \Gamma) \delta \Gamma \) provides the change of the free energy when the interface undergoes bulk shape changes while the others capture changes for interface-only quantities.
The individual components are

\[
\delta \Gamma = \delta r \cdot n = u \cdot n, \\
\delta n = - (\nabla_s u)^T n, \\
\delta L = L (\nabla_s u)^T n \otimes n - \nabla_s (|(\nabla_s u)^T n|) - L (\nabla_s u), \\
\delta (\nabla_s q) = \nabla_s \delta q + [(\nabla_s u)^T n \cdot (\nabla_s q)] n - (\nabla_s u)^T \nabla_s q.
\]

Forms for \(\delta n\), \(\delta (\nabla_s q)\), and \(\delta L\) have been shown previously [21]. As the definition of \(L\) presented here differs from Napoli and Vergori, the derivation of \(\delta L\) has been included in Appendix B.

Introduce the conjugate variables \(\beta\), \(A\), \(a\), \(b\), and \(f\),

\[
\beta = \frac{\partial w}{\partial n}, \quad A = \frac{\partial w}{\partial L}, \quad a = \frac{\partial w}{\partial q}, \quad b = \frac{\partial w}{\partial (\nabla_s q)}, \quad f = \frac{\partial w}{\partial \Gamma} = \nabla w \cdot n,
\]

where \(\nabla w\) only applies to those terms of \(w\) with explicit dependence on spatial location \(r\). It is then possible to write Eq. (7) as

\[
\delta w = [(\nabla w \cdot n)n] \cdot u + \nabla_s \cdot \{[(\nabla_s u)A_s]^T n + b_s \delta q\} + \sigma_E \cdot \nabla_s u + (a - \nabla_s \cdot b_s) \delta q
\]

where \(\sigma_E\) is

\[
\sigma_E = - L A_s - \nabla_s q \otimes b_s - n \otimes \{P(\beta - \nabla_s \cdot A) - L A n - (b \cdot n) \nabla_s q\}
\]

with \(A_s = AP\) and \(b_s = Pb\). Using these expressions the variation of the free energy can then be written as

\[
\delta W = \int_{\Gamma} [(\nabla w \cdot n)n - \nabla_s \cdot \sigma] \cdot u \ dA + \int_{\Gamma} [a - \nabla_s \cdot b_s] \delta q \ dA
\]

where

\[
\sigma = wP + \sigma_E.
\]

From this the variation of the energy due to changes in the interface is given by

\[
\mathcal{F}_\Gamma = f n - \nabla_s \cdot \sigma
\]
while the variation of the energy due to changes in the concentration field is given by

$$F_q = a - \nabla_s \cdot b_s. \quad (18)$$

At equilibrium $\delta W = 0$ for arbitrary $u$ and $\delta q$ and thus both Eqs. (17) and (18) must equal zero. When not in equilibrium the variations are related to the forces which drive the system to equilibrium. For example, consider an interface surrounded by fluid where the surface concentration is modeled using the Cahn-Hilliard equation. The variation associated with the interface, $F_I$, would be related to the force exerted by the interface on the surrounding fluid while the variation with respect to the surface concentration, $F_q$, would define the chemical potential.

3. Specific Cases

Using the framework shown in Section 2 the resulting variations are derived for the case of an interface with total and Gaussian curvature energy, variable surface tension, coupling energy between the surface concentration and the interface curvature, an external field, and where the surface concentration is described using a phase-field energy form. A typical system which contains all of these energies would be a vesicle membrane with multiple lipid species. By ignoring the curvatures energy, it is possible to describe a fluid-fluid or fluid-air interface with a surfactant.
The six energies considered here are:

\[ W_b[\Gamma] = \int_R \frac{k_c(q)(H - c_0(q))^2}{2} \, dA, \]  
\[ W_s[\Gamma] = \int_R k_g(q) K \, dA, \]  
\[ W_\gamma[\Gamma] = \int_R \gamma(q) \, dA, \]  
\[ W_c[\Gamma] = \int_R \eta Hq \, dA, \]  
\[ W_{ext}[\Gamma] = \int_R \frac{m(q)}{2} \mathbf{F}(r) \cdot \mathbf{F}(r) \, dA, \]  
\[ W_q[\Gamma] = \int_R \left[ \frac{k_f}{2} \| \nabla q \|^2 + g(q) \right] \, dA. \]  

The first energy functional, \( W_b \), is the total bending energy of the interface where \( k_c(q) \) and \( c_0(q) \) are the bending rigidity and spontaneous curvature, respectively. The second energy functional, \( W_s \), is the energy component due to splay distortion in the membrane where \( k_g(q) \) is the Gaussian bending rigidity. The energy due to surface tension is given by \( W_\gamma \), where \( \gamma \) is a non-uniform surface tension. The coupling energy between total curvature and surface lipid phase is \( W_c \), where \( \eta \) is the coupling constant. \( W_{ext} \) is the energy due to external force field, where \( \mathbf{F} \) is a generic spatially varying field and \( m(q) \) is a material parameter. For example, if \( \mathbf{F} \) is the magnetic field force then \( m(q) \) would be the magnetic susceptibility while if \( \mathbf{F} \) is the electric field force then \( m(q) \) would be the permittivity [22]. The final energy, \( W_q \), is the phase-field energy which has two contributions. The first is an interface energy where \( k_f \) is a constant and the second is a mixing energy function \( g(q) \).

Unlike prior works, material parameters such as bending rigidities and spontaneous curvatures are taken to vary with the underlying concentration field \( q \). In the remainder of this section each energy is considered separately and for each the expressions for \( \mathcal{F}_f \) and \( \mathcal{F}_q \) are determined.
3.1. Total Bending Energy. The bending free energy in Eq. (19) leads to the following free energy density $w$,

$$w = \frac{k_c(q)(H - c_0(q))^2}{2}. \tag{25}$$

From this energy density the conjugate variables become

$$\beta = 0, \tag{26}$$

$$\Lambda = [k_c(q)(H - c_0(q))] P, \tag{27}$$

$$a = \frac{k_c'(q)}{2} (H - c_0(q))^2 - k_c(q)(H - c_0(q))c_0'(q), \tag{28}$$

$$b = 0, \tag{29}$$

$$f = 0, \tag{30}$$

where $c_0'(q)$ is the derivative of spontaneous curvature and $k_c'(q)$ is derivative of bending rigidity with respect to $q$. Note that this free energy density does not have an explicit dependence on the position of the interface and thus $f = 0$. For this section and all after, the functional dependencies of various quantities on the concentration $q$ will be suppressed from the notation after defining the conjugate variables.

Introduce the modified total curvature as $\tilde{H} = H - c_0$. The tensor $\sigma$ due to the bending energy can be computed using Eq. (16) as follows,

$$\sigma = \frac{\tilde{H}^2 k_c}{2} P - k_c \tilde{H} L + n \otimes \left[ P \nabla_s \cdot (k_c \tilde{H} P) \right]. \tag{31}$$

The surface divergence of the first term can be expanded to

$$\nabla_s \cdot \left( \frac{\tilde{H}^2 k_c}{2} P \right) = \frac{1}{2} \nabla_s \left( \tilde{H}^2 k_c \right) - \frac{1}{2} \tilde{H}^2 k_c H n \tag{32}$$

while the second is

$$\nabla_s \cdot (k_c \tilde{H} L) = L \nabla_s (k_c \tilde{H}) + k_c \tilde{H} \nabla_s \cdot L. \tag{33}$$
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In the last term the quantity $P \nabla_s \cdot (k_c \tilde{H} P)$ can be written as

$$P \nabla_s \cdot (k_c \tilde{H} P) = P \left[ \nabla_s \left( k_c \nabla_s - k_c \tilde{H} H n \right) - k_c \tilde{H} H P n = \nabla_s \left( k_c \tilde{H} \right), \right. \quad (34)$$

which leads to

$$\nabla_s \cdot \left\{ n \otimes \left[ P \nabla_s \cdot (k_c \tilde{H} P) \right] \right\} = \nabla_s \cdot \left[ n \otimes \nabla_s \left( k_c \tilde{H} \right) \right] = L \nabla_s \left( k_c \tilde{H} \right) + n \Delta_s \left( k_c \tilde{H} \right). \quad (35)$$

Using these expressions the surface divergence of Eq. (31) can be written as

$$\nabla_s \cdot \sigma = \frac{1}{2} \nabla_s \left( \tilde{H}^2 k_c \right) - \frac{1}{2} \tilde{H}^2 k_c H n - L \nabla_s \left( k_c \tilde{H} \right) - k_c \tilde{H} \nabla_s \cdot L + L \nabla_s \left( k_c \tilde{H} \right) + n \Delta_s \left( k_c \tilde{H} \right)$$

$$= \frac{1}{2} \nabla_s \left( \tilde{H}^2 k_c \right) - \frac{1}{2} \tilde{H}^2 k_c H n - k_c \tilde{H} \nabla_s \cdot L + n \Delta_s \left( k_c \tilde{H} \right). \quad (36)$$

Using the expressions for $\tilde{H}$ and $\nabla \cdot L$ the variation of the energy with respect to the interface is

$$\mathcal{F}_s = - \nabla_s \cdot \sigma = - \frac{1}{2} \nabla_s \left[ k_c (H - c_0)^2 \right] + \frac{1}{2} k_c H (H - c_0)^2 n$$

$$+ k_c (H - c_0) \left( \nabla_s H - \tilde{H}^2 n + 2 K n \right) - n \Delta_s \left[ k_c (H - c_0) \right]. \quad (37)$$

The standard Euler-Lagrange equation associated with the normal shape variation can be obtained by setting $\mathcal{F}_s \cdot n = 0$ and assuming that $k_c$ and $c_0$ are constant values on the interface [21]:

$$\frac{k_c}{2} (H - c_0) \left( H^2 + c_0 H - 4K \right) + k_c \Delta_s H = 0. \quad (38)$$

Next, consider the variation associated with the concentration field $q$. As $b = 0$ this is simply

$$\mathcal{F}_q = \frac{k_c'}{2} (H - c_0)^2 - k_c (H - c_0) c'_0. \quad (39)$$

In the situation that material properties do not depend on the concentration field the total bending energy has no influence on the concentration field.
3.2. Splay Bending Energy. The splay bending energy in Eq. (20) leads to the following free energy density

\[ w = k_g(q)K. \]  

(40)

From this the conjugate variables are

\[ \beta = 0, \]  

(41)
\[ \Lambda = \frac{k_g(q)}{2} \left[ \frac{\partial (\text{tr} L)^2}{\partial L} - \frac{\partial \text{tr}(L^2)}{\partial L} \right] = \frac{k_g(q)}{2} [2(\text{tr} L)P - 2L] = -k_g(q)(L - HP), \]  

(42)
\[ a = k_g'(q)K, \]  

(43)
\[ b = 0, \]  

(44)
\[ f = 0, \]  

(45)

where \( k_g'(q) \) is derivative of bending rigidity with respect to \( q \).

The \( \sigma \) tensor due to splay energy can be computed as

\[ \sigma = k_g K P + L k_g (L - HP) - n \otimes \{ P \nabla_s \cdot [ k_g (L - HP) ] \} \]
\[ = k_g \left( K P + L^2 - HL \right) - n \otimes \{ P \nabla_s \cdot [ k_g (L - HP) ] \}. \]  

(46)

Using the Cayley-Hamilton Theorem, \( L^2 = HL + KP = 0 \), this simplifies to

\[ \sigma = -n \otimes \{ P \nabla_s \cdot [ k_g (L - HP) ] \}. \]  

(47)

The inner expression can be evaluated as

\[ \nabla_s \cdot [ k_g (L - HP) ] = \nabla_s \cdot (k_g L) - \nabla_s \cdot (k_g LP) \]
\[ = L \nabla_s k_g + k_g \nabla_s \cdot L - \nabla_s (k_g H) + k_g H^2 n \]
\[ = L \nabla_s k_g + k_g \left( \nabla_s H - H^2 n + 2Kn \right) - \nabla_s (k_g H) + k_g H^2 n. \]  

(48)
When including the projection operator and noting that $\nabla_s (k_g H) = k_g \nabla_s H + H \nabla_s k_g$ this becomes
\[ P \nabla_s \cdot [k_g (L - H P)] = L \nabla_s k_g - H \nabla_s k_g. \] (49)
Thus the tensor simplifies to
\[ \sigma = -n \otimes (L \nabla_s k_g) + n \otimes (H \nabla_s k_g). \] (50)

The surface divergence of the first term results in
\[ \nabla_s \cdot [n \otimes (L \nabla_s k_g)] = (\nabla_s n) (L \nabla_s k_g) + n \nabla_s \cdot (L \nabla_s k_g) \]
\[ = L^2 \nabla_s k_g + n [(\nabla_s k_g) \cdot (\nabla_s L) + L : \nabla_s \nabla_s k_g] \]
\[ = L^2 \nabla_s k_g + n (\nabla_s k_g) \cdot (\nabla_s H) + n (L : \nabla_s \nabla_s k_g). \] (51)

The surface divergence of the second term is
\[ \nabla_s \cdot [n \otimes (H \nabla_s k_g)] = (\nabla_s n) H \nabla_s k_g + n \nabla_s \cdot (H \nabla_s k_g) \]
\[ = H L \nabla_s k_g + n [(\nabla_s k_g) \cdot (\nabla_s H) + H \Delta_s k_g]. \] (52)

Combining these two results with the Cayley-Hamilton Theorem the variation of with respect to the interface is
\[ F_r = -\nabla_s \cdot \sigma = -K \nabla k_g + n (L : \nabla_s \nabla_s k_g - H \Delta_s k_g). \] (53)

Due to the simple nature of the conjugate variables, the variation of the energy with respect to the concentration field is simply
\[ F_q = k'_g K. \] (54)

In the case that material properties are de-coupled from the concentration field both $F_r$ and $F_q$ are zero. The fact that $F_r = 0$ in this case should be expected as the Gauss-Bonnet theorem states that $\int_r K \, dA$ is a constant for an interface with a fixed Euler characteristic. So long as the interface has a fixed topology, the splay bending energy should not have any influence when $k_g$ is a constant.
3.3. **Tension Energy.** The tension energy leads to the following free energy density \( w \),

\[
w = \gamma(q). \tag{55}
\]

The conjugate variables are given by

\[
\beta = 0, \tag{56}
\]

\[
\Lambda = 0, \tag{57}
\]

\[
a = \gamma'(q), \tag{58}
\]

\[
b = 0, \tag{59}
\]

\[
f = 0, \tag{60}
\]

where \( \gamma'(q) \) is derivative of tension with respect to \( q \).

The \( \sigma \) tensor due to tension can be computed using Eq. (16),

\[
\sigma = \gamma P. \tag{61}
\]

The variation of the tension energy with respect to interface changes is given by

\[
\mathcal{F}_\Gamma = -\nabla_s \cdot \sigma = -\nabla_s \gamma + \gamma Hn. \tag{62}
\]

The variation of the energy with respect to the concentration field is simply

\[
\mathcal{F}_q = a = \gamma'. \tag{63}
\]

3.4. **Coupling Energy.** The free energy density of the coupling term is

\[
w = \eta Hq. \tag{64}
\]
This leads to the following conjugate variables,

\[ \beta = 0, \quad (65) \]
\[ \Lambda = \eta q P, \quad (66) \]
\[ a = \eta H, \quad (67) \]
\[ b = 0, \quad (68) \]
\[ f = 0. \quad (69) \]

The \( \sigma \) tensor due to the coupling energy is thus

\[ \sigma = \eta q H P - \eta q L + n \otimes \{ P \nabla_s \cdot (\eta q P) \} \]
\[ = \eta q H P - \eta q L + n \otimes \{ P (\nabla_s (\eta q) - \eta q H n) \} \]
\[ = \eta q H P - \eta q L + n \otimes \nabla_s (\eta q). \quad (70) \]

The surface divergence of each term is given by

\[ \nabla_s \cdot (\eta q H P) = \eta \nabla_s (q H) - \eta q H^2 n, \quad (71) \]
\[ \nabla_s \cdot (\eta q L) = \eta L \nabla_s q + \eta q \nabla_s \cdot L, \quad (72) \]
\[ \nabla_s \cdot [n \otimes \nabla_s (\eta q)] = \eta L \nabla_s q + \eta m \Delta_s q. \quad (73) \]

Using these expressions the variation of the coupling energy with respect to the interface is

\[ \mathcal{F}_\Gamma = - \nabla_s \cdot \sigma = - \eta \nabla_s (q H) + \eta q H^2 n + \eta L \nabla_s q + \eta q \nabla_s \cdot L - \eta L \nabla_s q - \eta m \Delta_s q \]
\[ = - \eta q \nabla_s H - \eta H \nabla_s q + \eta q H^2 n + \eta q (\nabla_s H - H^2 n + 2Kn) - \eta m \Delta_s q \]
\[ = \eta (2q Kn - H \nabla_s q - n \Delta_s q). \quad (74) \]

As \( b = 0 \) the variation of the energy with respect to the concentration field is simply

\[ \mathcal{F}_q = \eta H. \quad (75) \]
3.5. **External Field Energy.** The free energy density due to a generic external field is given by

\[ w = \frac{m(q)}{2} \mathbf{F}(r) \cdot \mathbf{F}(r), \quad (76) \]

where \( m(q) \) is a spatially dependent material property associated with the external, spatially-varying field \( \mathbf{F}(r) \).

The conjugate variables in this case are

\[ \beta = 0, \quad (77) \]
\[ A = 0, \quad (78) \]
\[ a = \frac{m'(q)}{2} \mathbf{F}^2(r), \quad (79) \]
\[ b = 0, \quad (80) \]
\[ f = m(q) \mathbf{F}(r) \cdot \nabla \mathbf{F}(r) \cdot \mathbf{n} = m(q) \mathbf{F}(r) \cdot \frac{\partial \mathbf{F}(r)}{\partial n}, \quad (81) \]

where \( m'(q) \) is derivative of the material parameter with respect to \( q \), \( F^2 = \mathbf{F} \cdot \mathbf{F} \), and \( \partial \mathbf{F} / \partial n \) is the variation of the \( \mathbf{F} \) field in the direction normal to the interface.

The \( \mathbf{\sigma} \) tensor due to the external field is

\[ \mathbf{\sigma} = \frac{m}{2} \mathbf{F}^2 \mathbf{P}. \quad (82) \]

The surface divergence of this tensor is

\[ \nabla_s \cdot \mathbf{\sigma} = \frac{1}{2} \left[ \nabla_s (mF^2) - mF^2 H \mathbf{n} \right]. \quad (83) \]

From this expression the variation of the free energy with respect to changes of the interface is

\[ \mathcal{F}_F = f \mathbf{n} - \nabla_s \cdot \mathbf{\sigma} = mF \cdot \frac{\partial \mathbf{F}}{\partial n} \mathbf{n} - \frac{1}{2} \nabla_s (mF^2) + \frac{1}{2} mF^2 H \mathbf{n}. \quad (84) \]

When comparing this expression to the variation for the tension energy, Eq. (62), it becomes apparent that an external field induces a tension-like variation where \( mF^2 / 2 \) is an effective tension, in addition to a contribution in the direction normal to the interface.
For an external field the variation of energy with respect to the concentration field is simply

$$\mathcal{F}_q = \frac{m'}{2} F^2.$$  \hfill (85)

### 3.6. Phase Energy.

The phase free energy density is

$$w = \frac{k_f}{2} (\|\nabla_s q\|^2) + g(q).$$  \hfill (86)

From this energy density the conjugate variables become

$$\beta = 0,$$ \hfill (87)
$$\Lambda = 0,$$ \hfill (88)
$$a = g'(q),$$ \hfill (89)
$$b = k_f \nabla_s q,$$ \hfill (90)
$$f = 0,$$ \hfill (91)

which defines the $\sigma$ tensor as

$$\sigma = \frac{k_f}{2} \|\nabla_s q\|^2 P + gP - k_f \nabla_s q \otimes \nabla_s q.$$ \hfill (92)

The surface divergence of the first term is

$$\nabla_s \cdot \left( \frac{k_f}{2} \|\nabla_s q\|^2 P \right) = \frac{k_f}{2} \nabla_s (\|\nabla_s q\|^2) - \frac{k_f}{2} \|\nabla_s q\|^2 H \mathbf{n}$$
$$= k_f \nabla_s q \cdot \nabla_s q - \frac{k_f}{2} \|\nabla_s q\|^2 H \mathbf{n},$$ \hfill (93)

while the surface divergence of the second term is

$$\nabla_s \cdot (gP) = \nabla_s g - g \mathbf{n}.$$ \hfill (94)

The final term results in

$$\nabla_s \cdot (k_f (\nabla_s q \otimes \nabla_s q)) = k_f \nabla_s \cdot (\nabla_s q \otimes \nabla_s q) = k_f \left[ (\nabla_s \nabla_s q) \nabla_s q + (\nabla_s q) \Delta_s q \right].$$ \hfill (95)
From these expressions the variation of the free energy with respect to the interface is

\[ \mathcal{F}_\Gamma = -\nabla_s \cdot \sigma \]

\[ = -k_f \nabla_s q \cdot \nabla_s \nabla_s q + \frac{k_f}{2} \| \nabla_s q \|^2 H n + k_f (\nabla_s q) \nabla_s q + k_f (\nabla_s q) \Delta_s q - \nabla_s g + g H n \]

\[ = -k_f (\nabla_s q \cdot L \nabla_s q) n + \frac{k_f}{2} \| \nabla_s q \|^2 H n + k_f (\nabla_s q) \Delta_s q - \nabla_s g + g H n, \]

(96)

where the relation \( \nabla_s q \cdot \nabla_s q - (\nabla_s q) \nabla_s q = (\nabla_s q \cdot L \nabla_s q) n \), as shown in Appendix A.3, has been used.

The variation of the energy with respect to changes of the concentration field is

\[ \mathcal{F}_q = a - \nabla_s \cdot b_s = g' - k_f \Delta_s q, \]

(97)

which matches prior results for the chemical potential in the Cahn-Hilliard formulation.

4. Discussion

Based on elegant framework of Napoli and Vergori, the variation of free energies associated with soft matter interfaces have been presented. These variations take into account not only the dependence of the energy on the interface configuration and the distribution of a surface concentration on that interface, but also take into account concentration-dependent material properties.

These variations can be used to determine the equilibrium shape equations for a wide number of material systems, including but not limited to multicomponent vesicles and surfactant-covered droplets. Due to the complex coupling between material properties, surface concentration, and interface shape, closed-form solutions to these equilibrium equations would be difficult to obtain.

If the system is not at equilibrium the derived variational expressions can be used to form the forces which drive the system. For example, consider a multi-component vesicle which includes all of the energies considered here, Eqs. (19)-(24), surrounded by a fluid. The force that the membrane exerts on the surrounding fluid, \( F_{\text{mem}} \), can calculated by summing the contribution from each individual energy. These forces must be balanced by changes in the fluid stress tensor, \( T \), across the interface, \( (T_{\text{out}} - T_{\text{in}}) \cdot n = F_{\text{mem}} \). This
condition can be used in conjunction with a wide number of fluid momentum solvers to obtain the influence of the interface on the surrounding fluid. Note that due to the generalized nature of the expressions derived here components which are normally not used in this force balance can be included. For example, it is common to ignore the tangential contributions from the total bending variation when modeling the dynamics of single-component lipid vesicles [23,24,25]. This may cause errors when considering multicomponent vesicles as tangential flow will influence the surface concentration field.

The variation of the energies with respect to the surface concentration can be similarly used to describe the dynamics of the \( q \) field. Using a Cahn-Hilliard model for surface phase evolution, the summation of each individual energy contribution would be called the chemical potential \( \mu \). Using this chemical potential the evolution of the surface concentration field could be described by \( \partial q / \partial t = \nabla_s (\nu(q) \nabla_s \mu) \), where \( \nu(q) \) is a concentration-dependent mobility. The results here indicate that when additional contributions are included in the interface free energy, it is not sufficient to simply use standard Cahn-Hilliard models. The influence of, for example the total bending energy, must be taken into account when modeling complex systems such as multicomponent vesicles.

### Appendix A  Surface Calculus

When considering derivatives of quantities defined on a curved surface, the variation of the underlying surface must be taken into account. In this section various surface vector calculus identities used to derive the energy variations are derived. Here \( a \) and \( b \) be are generic scalar fields while \( u \) and \( v \) are generic vectors, all defined on the interface.

#### A.1 Basics

Let the interface be orientable with an outward unit normal \( n \). Without loss of generality, it is assumed that the interface is described as the zero contour of a function \( \Psi \) such that \( \Psi \) is the solution to the Eikonal equation, \(|\nabla \Psi| = 1\) within a distance of \( r \) to the interface, where \( r \) depends on the curvature of the interface. With this assumption the normal is simply \( n = \nabla \Psi \). As the normal is now defined in a small
region surrounding the interface, quantities such as the gradient of the unit normal, $\nabla n$, are well-defined near the interface.

The projection operator is given by $P = I - n \otimes n$, or in component form $P_{ij} = \delta_{ij} - n_i n_j$, where $\delta_{ij}$ is the Kronecker delta function. In this work, indices $i$ and $j$ are free indices and other indices are dummy indices. The projection operator is symmetric, $P = P^T$, and idempotent,

$$[PP]_{ij} = P_{ip} P_{pj} = (\delta_{ip} - n_i n_p) (\delta_{pj} - n_p n_j) = \delta_{ij} \delta_{pj} - n_i n_p \delta_p j - n_p n_j \delta_{ip} + n_i n_p n_p n_j = \delta_{ij} - n_i n_j - n_i n_j + n_i n_j = [P]_{ij},$$

(98)

where $[v]_i$ is the $i$-component of a vector $v$, $[A]_{ij}$ is the $i,j$-component of a tensor $A$, and repeated indices indicate summation. There are also no components of $P$ in the normal direction,

$$[P n]_i = P_{ip} n_p = (\delta_{ip} - n_i n_p) n_p = \delta_{ip} n_p - n_i n_p n_p = n_i - n_i = 0.$$  

(99)

The generalized surface gradient function can be written as $\nabla_s A = (\nabla A) \cdot P$, where $A$ can be either a scalar, vector, or tensor field [26,27,28]. For example, the surface gradient of a scalar field $a$ in component form would be written as

$$[\nabla_s a]_i = [((\nabla a) \cdot P)]_i = \frac{\partial a}{\partial x_p} P_{pi},$$

(100)

while the surface gradient for a vector field $v$ would be

$$[\nabla_s v]_{ij} = [((\nabla v) \cdot P)]_{ij} = \frac{\partial v_i}{\partial x_p} P_{pj}.$$  

(101)

The surface divergence of any vector $v$ can be written as $\nabla_s \cdot v = \text{tr} \nabla_s v = P : \nabla v$ [26]. In component form this is written as

$$[\nabla_s \cdot v] = [P : \nabla v] = \frac{\partial v_p}{\partial x_q} P_{pq}.$$  

(102)

The surface divergence of a tensor field $A$ is defined as [26]

$$[\nabla_s \cdot A]_i = [((\nabla A) : P)]_i = \frac{\partial A_{ip}}{\partial x_q} P_{pq}.$$  

(103)
A.2 Derivatives of Interface Quantities. The second fundamental form of the deformable interface \( \Gamma \) is \( L = \nabla_s n \), which is a second order symmetric tensor tangential to the interface and describes the interface curvatures via the first and second invariants:

\[
H = \nabla_s \cdot n = \text{tr}L \quad \text{and} \quad K = \frac{1}{2} \left[ (\text{tr}L)^2 - \text{tr}(L^2) \right].
\]  

(104)

The tensor \( L \) has no components in the normal direction,

\[
[L \cdot n]_i = [\nabla_s n \cdot n]_i = \frac{\partial n_i}{\partial x_q} P_{qp} n_p = 0,
\]

(105)

and does not change under application of \( P \):

\[
[LP]_{ij} = [\nabla_s n P]_{ij} = \frac{\partial n_i}{\partial x_p} P_{pq} P_{qj} = \frac{\partial n_i}{\partial x_p} P_{pj} = [\nabla_s n]_{ij} = [L]_{ij},
\]

(106)

and

\[
L = L^T = (LP)^T = P^T L^T = PL.
\]

(107)

The full contraction of the projection operator and \( L \) results in

\[
[P : L] = P_{pq} L_{pq} = (\delta_{pq} - n_p n_q) \left( \frac{\partial n_q}{\partial x_r} P_{rq} \right) = \delta_{pq} \left( \frac{\partial n_q}{\partial x_r} P_{rq} \right) - n_p \frac{\partial n_p}{\partial x_r} P_{rq} n_q
\]

\[
= \frac{\partial n_p}{\partial x_r} P_{rq} = [\nabla_s \cdot n] = [H]
\]

(108)

The surface divergence of the projection operator and of the second fundamental form have been provided previously [21]. After taking into account the definition of the curvature used here they are,

\[
\nabla_s \cdot P = -H n
\]

(109)

\[
\nabla_s \cdot L = \nabla_s H - H^2 n + 2Kn.
\]

(110)
A.9 Derived Expressions. The surface gradient of the multiple of two scalar fields is

\[
\nabla_s (ab)_i = (\nabla ab)_i = \left( \frac{\partial}{\partial x_p} \frac{\partial b}{\partial x_p} \right) P_{pi} = [a\nabla_s b + b\nabla_s a]_i
\]

while the surface gradient of a vector dot product is

\[
\nabla_s (u \cdot v)_i = \nabla (u \cdot v)_i = \left( \frac{\partial}{\partial x_q} \frac{\partial v_p}{\partial x_q} \right) P_{qi} = [v \cdot \nabla_s u + u \cdot \nabla_s v]_i.
\]

The surface divergence of a scalar field times a vector \( \mathbf{u} \) is

\[
\nabla_s \cdot (a \mathbf{u}) = \frac{\partial}{\partial x_q} \frac{\partial a}{\partial x_q} P_{pq} + \frac{\partial u_p}{\partial x_q} a P_{pq} = [\mathbf{u} \cdot \nabla_s a + a \nabla_s \cdot \mathbf{u}].
\]

The surface divergence of a scalar field times a surface tensor is

\[
\nabla_s \cdot (a \mathbf{A}) = \nabla (a \mathbf{A}) = \frac{\partial}{\partial x_q} \frac{\partial a}{\partial x_q} \mathbf{A}_{qp} + a \nabla_s \cdot \mathbf{A} = [A \nabla_s a + a \nabla_s \cdot \mathbf{A}]_i.
\]

When the surface tensor is the projection operator this results in

\[
\nabla_s \cdot (a\mathbf{P}) = \mathbf{P} \nabla_s a + a \nabla_s \cdot \mathbf{P} = \nabla_s a - aH\mathbf{n}_s,
\]

while when the surface tensor is \( \mathbf{L} \) then

\[
\nabla_s \cdot (a\mathbf{L}) = \mathbf{L} \nabla_s a + a \nabla_s \cdot \mathbf{L} = \mathbf{L} \nabla_s a + a \left( \nabla_s H - H^2 \mathbf{n} + 2K \mathbf{n} \right).
\]

The surface divergence of the tensor (outer) product between two vectors is given by

\[
\nabla_s \cdot (\mathbf{u} \otimes \mathbf{v})_i = [(\nabla (\mathbf{u} \otimes \mathbf{v})]_i = \frac{\partial}{\partial x_q} \frac{\partial (u_i v_p)}{\partial x_q} P_{qp} = \frac{\partial u_i}{\partial x_q} P_{qp} v_p + \frac{\partial v_p}{\partial x_q} P_{pq} u_i = [(\nabla_s \mathbf{u}) \cdot \mathbf{v} + \mathbf{u} \cdot \nabla_s \mathbf{v}]_i.
\]
The surface divergence of a symmetric tensor $\mathbf{A}$ times a vector $\mathbf{u}$ is

$$
[\nabla_s \cdot (\mathbf{A}\mathbf{u})] = P_{pq} \frac{\partial}{\partial x_q} (A_{pr}u_r) = P_{pq} \frac{\partial A_{pr}}{\partial x_q} u_r + P_{pq} A_{pr} \frac{\partial u_r}{\partial x_q}
$$

$$
= u_r \frac{\partial A_{rp}}{\partial x_q} P_{pq} + A_{rp} \frac{\partial u_r}{\partial x_q} P_{pq} = [\mathbf{u} \cdot (\nabla_s \cdot \mathbf{A}) + \mathbf{A} : \nabla_s \mathbf{u}].
$$

Finally, consider the simplification of $\nabla_s a \cdot \nabla_s \nabla_s a - (\nabla_s \nabla_s a) \nabla_s a$. First, the surface Hessian of a scalar field $a$ is

$$
[\nabla_s \nabla_s a]_{ij} = \frac{\partial}{\partial x_p} \left( \frac{\partial a}{\partial x_q} P_{qi} \right) P_{pj} = \frac{\partial^2 a}{\partial x_p \partial x_q} P_{qi} P_{pj} + \frac{\partial a}{\partial x_q} \frac{\partial P_{qi}}{\partial x_p} P_{pj}
$$

Thus,

$$
[\nabla_s a \cdot \nabla_s \nabla_s a - (\nabla_s \nabla_s a) \nabla_s a]_i = \frac{\partial a}{\partial x_r} P_{rs} \left( \frac{\partial^2 a}{\partial x_p \partial x_q} P_{qs} P_{pi} + \frac{\partial a}{\partial x_q} \frac{\partial P_{qs}}{\partial x_p} P_{pi} \right)
$$

$$
- \left( \frac{\partial^2 a}{\partial x_p \partial x_q} P_{qi} P_{ps} + \frac{\partial a}{\partial x_q} \frac{\partial P_{qi}}{\partial x_p} P_{ps} \right) \frac{\partial a}{\partial x_r} P_{rs}
$$

$$
= \frac{\partial a}{\partial x_q} \left( \frac{\partial P_{qs}}{\partial x_p} P_{pi} - \frac{\partial P_{qi}}{\partial x_p} P_{ps} \right) \frac{\partial a}{\partial x_r} P_{rs} = \frac{\partial a}{\partial x_q} \left( -n_q \frac{\partial n_i}{\partial x_p} P_{pi} - n_s \frac{\partial n_i}{\partial x_p} P_{ps} + n_q \frac{\partial n_i}{\partial x_p} P_{pi} + n_s \frac{\partial n_i}{\partial x_p} P_{ps} \right) \frac{\partial a}{\partial x_r} P_{rs}.
$$

Recalling that $[\mathbf{P} \cdot \mathbf{n}]_i = P_{rs} n_s = 0$, $[\mathbf{L}]_{is} = (\partial n_i / \partial x_p) P_{ps} = (\partial n_s / \partial x_p) P_{pi} = [\mathbf{L}]_{si}$ due to the symmetry of $\mathbf{L}$, and $\mathbf{L} = \mathbf{P L}$ this expression simplifies to

$$
[\nabla_s a \cdot \nabla_s \nabla_s a - (\nabla_s \nabla_s a) \nabla_s a]_i = \frac{\partial a}{\partial x_q} L_{qs} \frac{\partial a}{\partial x_r} P_{rs n_i} = \frac{\partial a}{\partial x_q} P_{qp} L_{ps} \frac{\partial a}{\partial x_r} P_{rs n_i}
$$

$$
= [(\nabla_s a \cdot \mathbf{L} \nabla_s a) \mathbf{n}]_i
$$

### Appendix B  First Variation of $\mathbf{L}$

The first variation of $\mathbf{L}$ can be obtain by using $\mathbf{L} = \nabla \mathbf{n} \mathbf{P}$ and the product rule [21],

$$
\delta \mathbf{L} = \delta (\nabla \mathbf{n} \mathbf{P}) = \delta (\nabla \mathbf{n}) \mathbf{P} + (\nabla \mathbf{n}) \delta \mathbf{P}.
$$
Variation of the gradient of normal and the projection operator are given as [21],

\[
\delta(\nabla n) = -\nabla[(\nabla_s u)^T n] - (\nabla n)(\nabla u),
\]

\[
\delta P = (\nabla_s u)^T n \otimes n + n \otimes (\nabla_s u)^T n,
\]

where \( u \) is a virtual displacement field. Therefore,

\[
\delta(\nabla n P) = -\nabla[(\nabla_s u)^T n] P - (\nabla n)(\nabla u) P + (\nabla n) [(\nabla_s u)^T n \otimes n] + (\nabla n) [n \otimes (\nabla_s u)^T n].
\]

This expression can be simplified by noting that

\[
[\nabla n(\nabla_s u)^T n \otimes n]_{ij} = \frac{\partial n_i}{\partial x_s} \frac{\partial u_{rs}}{\partial x_t} P_{ts} n_r n_j = \frac{\partial n_i}{\partial x_s} \frac{\partial u_{ps}}{\partial x_t} P_{ts} n_r n_j
\]

\[
= \frac{\partial n_i}{\partial x_s} P_{ps} \frac{\partial u_{rs}}{\partial x_t} n_j = [\nabla_s n](\nabla_s u)^T(n \otimes n)]_{ij}.
\]

Additionally,

\[
[-(\nabla n)(\nabla u) P + (\nabla n)(n \otimes (\nabla_s u)^T n)]_{ij} = - \frac{\partial n_i}{\partial x_p} \frac{\partial u_{pq}}{\partial x_q} P_{pq} n_j + \frac{\partial n_i}{\partial x_p} \frac{\partial u_{pt}}{\partial x_s} P_{ts} n_j n_t
\]

\[
= - \frac{\partial n_i}{\partial x_p} \frac{\partial u_{pq}}{\partial x_q} \delta_{qj} + \frac{\partial n_i}{\partial x_p} \frac{\partial u_{pt}}{\partial x_s} \delta_{nj}
\]

\[
+ \frac{\partial n_i}{\partial x_p} \frac{\partial u_{pt}}{\partial x_s} n_p n_t \delta_{sj} - \frac{\partial n_i}{\partial x_p} \frac{\partial u_{pt}}{\partial x_s} n_p n_j n_t.
\]

These terms can be rewritten as

\[
\frac{\partial n_i}{\partial x_p} \frac{\partial u_{pq}}{\partial x_q} \delta_{qj} = \frac{\partial n_i}{\partial x_r} \frac{\partial u_{pq}}{\partial x_q} \delta_{pq} \delta_{qj},
\]

\[
\frac{\partial n_i}{\partial x_p} \frac{\partial u_{pq}}{\partial x_q} n_j = \frac{\partial n_i}{\partial x_r} \frac{\partial u_{pq}}{\partial x_q} \delta_{pq} n_j,
\]

\[
\frac{\partial n_i}{\partial x_p} \frac{\partial u_{pq}}{\partial x_q} n_j n_t = \frac{\partial n_i}{\partial x_r} \frac{\partial u_{pq}}{\partial x_q} n_j n_t,
\]

\[
\frac{\partial n_i}{\partial x_p} \frac{\partial u_{pq}}{\partial x_q} n_j n_t n_j = \frac{\partial n_i}{\partial x_r} \frac{\partial u_{pq}}{\partial x_q} n_j n_t n_j n_j.
\]
Using these expression Eq. (127) is now

\[
[-(\nabla n)(\nabla u)P + (\nabla n)((\nabla_s u)^T n)]_{ij} = - \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} \delta_{rp} \delta_{sj} + \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} \delta_{rp} n_p n_j \\
+ \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} n_r n_p n_i n_j - \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} n_r n_i n_j n_p \\
= - \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} (\delta_{rp} \delta_{sj} - \delta_{rp} n_p n_j - n_r n_p \delta_{sj} + n_r n_s n_j n_p) \\
= - \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} (\delta_{rp} (\delta_{sj} - n_r n_j) - n_r n_p (\delta_{sj} - n_s n_j)) \\
= - \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} (\delta_{rp} - n_r n_p) (\delta_{sj} - n_s n_j) \\
= - \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} P_{rp} P_{sj} \\
= - \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} P_{rp} \delta_{sj} \\
= - \frac{\partial n_i}{\partial x_r} \frac{\partial u_p}{\partial x_s} P_{rp} \delta_{sj} \\
= - \left[(\nabla_s n \nabla_s u)_{ij} \right].
\]

Using Eq. (126) and Eq. (132) the first variation of \(L\) is obtained as

\[
\delta L = \delta(\nabla n P) = (\nabla_s n)(\nabla_s u)^T n \otimes n - \nabla_s[(\nabla_s u)^T n] - (\nabla_s n)(\nabla_s u) \\
= L(\nabla_s u)^T n \otimes n - \nabla_s[(\nabla_s u)^T n] - L(\nabla_s u).
\]

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**References**

1. J.-L. Salager, A. M. Forgiarini, Emulsion Stabilization, Breaking, And Inversion Depends Upon Formulation: Advantage Or Inconvenience In Flow Assurance, Energy & Fuels 26 (7) (2012) 4027–4033.
2. L. M. Sagis, Dynamic Properties Of Interfaces In Soft Matter: Experiments And Theory, Reviews of Modern Physics 83 (4) (2011) 1367.
3. A. Perazzo, V. Preziosi, S. Guido, Phase Inversion Emulsification: Current Understanding And Applications, Advances in Colloid and Interface Science 222 (2015) 581–599.
4. K. Simons, D. Toomre, Lipid Rafts And Signal Transduction, Nature Reviews Molecular Cell Biology 1 (1) (2000) 31–39.
5. K. Simons, W. L. Vaz, Model Systems, Lipid Rafts, And Cell Membranes, Annual Review of Biophysics and Biomolecular Structure 33 (2004) 269–295.

6. S. Mukherjee, F. R. Maxfield, Membrane Domains, Annual Review of Cell and Developmental Biology 20 (2004) 839–866.

7. P. B. Canham, The Minimum Energy of Bending as a Possible Explanation of the Biconcave Shape of the Human Red Blood Cell, Journal of Theoretical Biology 26 (1) (1970) 61–81.

8. W. Helfrich, Elastic Properties Of Lipid Bilayers: Theory And Possible Experiments, Zeitschrift für Naturforschung C 28 (11-12) (1973) 693–703.

9. E. A. Evans, Bending Resistance And Chemically Induced Moments In Membrane Bilayers, Biophysical Journal 14 (12) (1974) 923.

10. O.-Y. Zhong-Can, W. Helfrich, Instability And Deformation Of A Spherical Vesicle By Pressure, Physical Review Letters 59 (21) (1987) 2486.

11. O.-Y. Zhong-Can, W. Helfrich, Bending Energy Of Vesicle Membranes: General Expressions For The First, Second, And Third Variation Of The Shape Energy And Applications To Spheres And Cylinders, Physical Review A 39 (10) (1989) 5280.

12. T. Biben, K. Kassner, C. Misbah, Phase-field Approach to Three-dimensional Vesicle Dynamics, Physical Review E 72 (4) (2005) 041921.

13. T. Biben, C. Misbah, Tumbling of Vesicles Under Shear Flow within an Advected-field Approach, Physical Review E 67 (3) (2003) 031908.

14. Q. Du, M. Li, C. Liu, Analysis Of A Phase Field Navier-stokes Vesicle-fluid Interaction Model, Discrete and Continuous Dynamical Systems Series B 8 (3) (2007) 539.

15. Q. Du, C. Liu, X. Wang, Simulating The Deformation Of Vesicle Membranes Under Elastic Bending Energy In Three Dimensions, Journal of Computational Physics 212 (2) (2006) 757–777.

16. D. Jamet, C. Misbah, Towards A Thermodynamically Consistent Picture Of The Phase-field Model Of Vesicles: Local Membrane Incompressibility, Physical Review E 76 (5) (2007) 051907.

17. D. Chatterjee, B. Hetayothin, A. R. Wheeler, D. J. King, R. L. Garrell, Droplet-based microfluidics with nonaqueous solvents and solutions, Lab on a Chip 6 (2) (2006) 199–206.

18. R. L. Stefan, A. J. Szeri, Surfactant Scavenging And Surface Deposition By Rising Bubbles, Journal of Colloid and Interface Science 212 (1) (1999) 1–13.

19. R. Davis, A. Acrivos, The Influence Of Surfactants On The Creeping Motion Of Bubbles, Chemical Engineering Science 21 (8) (1966) 681–685.

20. A. C. Neville, Biology of Fibrous Composites: Development Beyond the Cell Membrane, Cambridge University Press, 1993.
21. G. Napoli, L. Vergori, Equilibrium Of Nematic Vesicles, Journal of Physics A: Mathematical and Theoretical 43 (44) (2010) 445207.

22. E. M. Kolahdouz, D. Salac, Electrohydrodynamics Of Three-dimensional Vesicles: A Numerical Approach, SIAM Journal on Scientific Computing 37 (3) (2015) B473–B494.

23. D. Salac, M. J. Miksis, Reynolds Number Effects On Lipid Vesicles, Journal of Fluid Mechanics 711 (2012) 122–146.

24. J. T. Schwalbe, P. M. Vlahovska, M. J. Miksis, Vesicle electrohydrodynamics, Physical Review E 83 (2011) 046309.

25. P. M. Vlahovska, R. S. Gracia, Dynamics Of A Viscous Vesicle In Linear Flows, Physical Review E 75 (2007) 016313.

26. E. Fried, M. E. Gurtin, A Continuum Mechanical Theory For Turbulence: A Generalized Navier–Stokes-α Equation With Boundary Conditions, Theoretical and Computational Fluid Dynamics 22 (6) (2008) 433–470.

27. M. E. Gurtin, A. Ian Murdoch, A Continuum Theory Of Elastic Material Surfaces, Archive for Rational Mechanics and Analysis 57 (4) (1975) 291–323.

28. G. Napoli, L. Vergori, Surface Free Energies For Nematic Shells, Physical Review E 85 (2012) 061701.