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Towards a thermodynamically consistent picture of the phase-field model of vesicles: Local membrane incompressibility

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A phase-field model for vesicles including hydrodynamics was presented in two and three dimensions [T. Biben and C. Misbah, Phys. Rev. E **67**, 031908 (2003); T. Biben, K. Kassner, and C. Misbah, Phys. Rev. E **72**, 041921 (2005)]. A particularly important feature for vesicles is that their membrane is locally incompressible. In these works a tension field defined everywhere in the bulk was introduced in order to fulfill local membrane inextensibility. Here we reconsider the original model by treating the phase field as a thermodynamic variable and develop a picture which is consistent with the second law of thermodynamics. This enables us to write the phase-field evolution equations in terms of a thermodynamical potential. This potential acquires, at global equilibrium, a Lyapunov functional character. The goal of this paper is twofold: (i) The first and primary goal is purely conceptual, in that we can write down a first and second principle for membranes, from which the evolution equations follow, thanks to the evaluation of the entropy production and the use of concepts of irreversible thermodynamics. (ii) Due to the monotonous character of the evolution of the functional (at global equilibrium), we expect this formulation to be more appropriate for numerical studies. The formalism developed to account for the local incompressibility of the membrane is believed to offer a systematic framework in order to include naturally other physical ingredients, as briefly discussed here and demonstrated in future works.

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I. INTRODUCTION

Vesicles are closed membranes suspended in an aqueous solution (Fig. 1). They constitute an attractive model system for the study of mechanical and viscoelastic properties of real cells, such as red blood cells. Their nonequilibrium dynamics have revealed quite rich behaviors. For example, under shear flow vesicles can exhibit tank treading (the membrane, which is fluid, moves as tank tread, while the vesicle keeps a fixed orientation in the flow) [1,2], tumbling [1,3,5,6], and vacillating-breathing (VB) (the vesicle long axis oscillates around the flow direction, while the shape executes a breathinglike motion) [7]. Furthermore, vesicles manifest interesting rheological properties [8] which are triggered by the above dynamics, and are believed to represent a simple model for the blood rheology.

Analytical results on vesicles have been obtained in the small excess area limit (i.e., in the quasispherical limit) [7,9]. In general, however, the problem is fully nonlinear and nonlocal, and one must resort to numerical studies. Originally the numerical methods have been based on the integral representation, by means of the Green's function technique [2,10,11]. This technique could be generalized to a large number of vesicles in principle, but its efficiency is not obvious, notwithstanding the fact that one has to keep track of each vesicle position in the course of time. Other alternatives to Green's function techniques are based on dynamically triangulated models [12] or particle-based mesoscale solvent, multiparticle collision dynamics [13]. The combination of dynamically triangulated models and particle-based mesoscale solvent, multiparticle collision dynamics, has been studied in shear and capillary flows [14].

A promising alternative in order to circumvent front tracking is to make use of a phase-field approach. This was originally proposed for two-dimensional (2D) vesicles in [3] and later extended to three dimensions [4]. Phase-field models have now become popular tools for the study of free boundary problems (like solid-liquid or liquid-vapor interfaces) [15]. Instead of defining, as was traditionally done, an interface in a sharp manner, the idea is to encode the interface

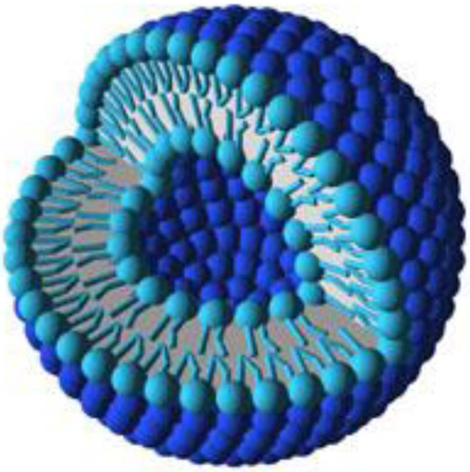

FIG. 1. (Color online) Schematic view of a vesicle made of a bilayer of phospholipid molecules.

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position in a rapid variation of a field φ which is defined in the entire space and is a function of time. This field takes a constant value in each of the coexisting phases, but it varies quite abruptly from one phase to the other. Typically $\varphi \sim \tanh(r/\sqrt{\lambda})$, where r is the coordinate normal to the interface, and $\sqrt{\lambda}$ is a small parameter representing the width of the interfacial region. The advantage of the phase-field approach is that the evolution equations are defined in the whole domain without explicit reference to an interface. The virtue of the phase field is that it enables a straightforward numerical implementation, together with a systematic account for topology changes. A method which is worth of mention, and which bears some similarities with the phase field one, is the so-called the immersed boundary method, which has first been suggested by Peskin [16] and used to model some properties of red blood cells [17].

In [3,4] a phase-field model has been presented for vesicles. In this model, the membrane is considered as a diffuse interfacial zone. In reality, the membrane is made of a bilayer (Fig. 1), very much like cytoplasmic membranes of real cells. The membrane may be in the fluid state (as is the case in physiological conditions), in which we are interested here, or in the gel state (at low enough temperature). In the fluid state each phospholipidic molecule may diffuse like a molecule as a usual fluid state does; the main difference is that the phospholipidic motion is confined to two dimensions. Due to its fluid character, the membrane does not resist to shear forces. Owing to the cohesive forces between the phospholipids, the membrane behaves as a two-dimensional incompressible fluid. The only possible (soft) mode is the bending mode of the membrane. The enclosed fluid, usually water (or water and some additives, such as sugar, or polymers in order to act on the internal viscosity), is also incompressible. The typical vesicle diameter lies in the range $1-100\ \mu$m, while the thickness of the membrane is of the order of few nanometers, so that the membrane may be viewed as a two-dimensional surface.

Unlike other interfacial problems where the area between the phases may increase or decrease, the vesicle problem brings a new feature in that the area is locally preserved. Indeed, there is no exchange between the bilayer and the surrounding fluid solution. This means that the area occupied by a phospholipidic molecule remains constant in the course of time. The membrane is thus incompressible. This constraint is not only global, but must be local, like an incompressibility condition for ordinary fluids. Note that other phase-field models have been presented since the first model [3]. The two groups [18,19] did not include hydrodynamics flow and they disregard the notion of local membrane incompressibility.

In the sharp interface picture [11,20] the local area incompressibility can be handled by introducing a space and time dependent Lagrange multiplier. This amounts to writing the contribution of the membrane energy related to the local membrane incompressibility condition as

$$E_{inc} = \int \zeta(\boldsymbol{r}_m, t)\, dA, \tag{1}$$

where the integration is performed over the vesicle membrane, and $\boldsymbol{r}_m$ is the vector position of the membrane. The Lagrange multiplier ζ is then determined by imposing

$$(\boldsymbol{I} - \boldsymbol{nn}):\nabla \boldsymbol{v} = 0, \tag{2}$$

where $\boldsymbol{v}$ is the fluid velocity, $\boldsymbol{n}$ is the unit normal vector to the vesicle, and $\boldsymbol{I}$ is the identity tensor. The above expression is nothing but the divergence along the membrane. The Lagrange multiplier ζ does not appear in the above equation which is the associated constraint, just like the pressure does not appear in the solenoidal constraint in incompressible hydrodynamics. However, like the pressure, we show in the following that ζ appears in the other equations of the model (it couples to the velocity field). In the phase field spirit [3,4] the idea is to define ζ everywhere (and not only along the membrane) but confine its action to the membrane region. We then write

$$E_{inc} = \int \zeta(\boldsymbol{r}, t) |\nabla \varphi| dV, \tag{3}$$

where dV is the volume element of the total domain. Because $\varphi \sim \tanh(r/\sqrt{\lambda})$, it is clear that $|\nabla\varphi|$ is a Dirac-like function of width $\sqrt{\lambda}$. This implies that the energy acts in the membrane region only, as it should be.

In [3,4] the tension field was postulated to obey the following equation (apart from the Laplacian term which was included in [4] for some numerical regularization):

$$\frac{d\zeta}{dt} = T(\boldsymbol{I} - \boldsymbol{nn}):\nabla \boldsymbol{v}, \tag{4}$$

where d/dt is the material derivative, and $\boldsymbol{n} = \nabla\varphi/|\nabla\varphi|$ is the unit normal vector to the line of iso-φ. T is a tensionlike parameter which is chosen large enough, so that minimal energy condition would enforce $(\boldsymbol{I} - \boldsymbol{nn}):\nabla\boldsymbol{v} \simeq 0$, that is a local quasi-incompressibility. This field was built on the basis of intuition and knowledge of the sharp interface problem [11,20].

The aim of this paper is to analyze theoretically the introduction of a membrane incompressibility in the framework of a phase-field model. In particular, this allows us to justify Eq. (4) from a theoretical point of view. In that perspective, the phase field is treated as a thermodynamic variable and the incompressibility of the membrane is introduced through a relevant thermodynamic energy functional. The thermodynamic model is presented in Sec. II. The equations of motion out of equilibrium are then derived in Sec. III; this derivation is based on the application of the second law of thermodynamics, which ensures the thermodynamic consistency of the model proposed. These equations are then generalized in Sec. V to account for hydrodynamics.

Vesicle membranes are endowed with other physical features than local surface incompressibility, the most important property being the bending energy. Likewise, the phase-field model considered in this paper reduces to its most simple expression, which implies that a surface tension exists, whereas vesicles' membranes do not exhibit such a surface tension. However, in this paper, only the theoretical study of the membrane incompressibility is addressed. Solutions to eliminate surface tension [21] and to account for bending energy [3] have been presented with an empirical spirit. Including both effects in a thermodynamical spirit requires an extended study which we have just performed. However, the discussion is lengthy and conceptually nontrivial at some stages, notwithstanding the various technical points. So it seems to us important to defer these two issues to the near future.

II. THERMODYNAMIC MODEL

The idea now is to treat the tensionlike-field ζ in a way that is inspired by the notion of pressure for fluids, which is a thermodynamic variable and which can also be interpreted as a Lagrange multiplier associated to the bulk incompressibility. We shall thus treat ζ as a thermodynamic variable. The other two variables are φ and $\nabla\varphi$. Then we introduce a potential that is a function of these three variables. We denote the sought after potential as $\Psi(\varphi,\nabla\varphi,\zeta)$, which will be required to represent the relevant thermodynamic function (its link with the free energy F is presented later on). We propose the following expression for this potential:

$$\Psi(\varphi,\nabla\varphi,\zeta)=W(\varphi)+\frac{\lambda}{2}(\nabla\varphi)^2+\zeta|\nabla\varphi|-\frac{\zeta^2}{2\theta}. \tag{5}$$

In the original model [3,4] the last term was not introduced. The first two terms are the usual phase-field terms that ensure a $\tanh(r/\sqrt{\lambda})$ behavior. The third term [which appears in [4], the last term in Eq. (5) in that paper] was introduced to observe local incompressibility [see Eq. (3)]. Note that here we do not account for the membrane bending modes, but will rather focus on the tension field only. The incorporation of bending modes will be the subject of a future work.

It will turn out that the last term in Eq. (5) allows one to build a thermodynamic picture of the model. We shall see that θ plays the same role as the "strength" T introduced in Eq. (4).

Let us define

$$\sigma\hat{=}\left(\frac{\partial\Psi}{\partial\zeta}\right)_{\varphi,\nabla\varphi}. \tag{6}$$

In the particular case where the expression for $\Psi(\varphi,\nabla\varphi,\zeta)$ is given by Eq. (5), one has

$$\sigma(\varphi,\nabla\varphi,\zeta)=-\frac{\zeta}{\theta}+|\nabla\varphi|. \tag{7}$$

The free energy F is supposed to be the Legendre transformation of the potential Ψ with respect to the variable ζ. Thus one has

$$F=\Psi-\sigma\zeta. \tag{8}$$

The free energy is thus a function of $(\varphi,\nabla\varphi,\sigma)$ and its differential yields:

$$dF=\mu d\varphi-\zeta d\sigma+\boldsymbol{\phi}\cdot d\nabla\varphi \tag{9}$$

which defines in particular μ and $\boldsymbol{\phi}$ (which is a vector). Note that we can write in terms of Ψ

$$d\Psi=\mu d\varphi+\sigma d\zeta+\boldsymbol{\phi}\cdot d\nabla\varphi. \tag{10}$$

In the particular case where the expression for $\Psi(\varphi,\nabla\varphi,\zeta)$ is given by Eq. (5), one has

$$F(\varphi,\nabla\varphi,\sigma)=W(\varphi)+\frac{\lambda}{2}(\nabla\varphi)^2+\frac{\theta}{2}(|\nabla\varphi|-\sigma)^2, \tag{11}$$

$$\mu(\varphi,\nabla\varphi,\sigma)=\frac{dW}{d\varphi}, \tag{12}$$

$$\boldsymbol{\phi}(\varphi,\nabla\varphi,\sigma)=(\lambda+\theta)\nabla\varphi-\theta\sigma\frac{\nabla\varphi}{|\nabla\varphi|}. \tag{13}$$

In the spirit of phase transition phenomena (as will be discussed below) it can be recognized that F plays the role of the free energy, while Ψ is the analog of the Gibbs energy.

In the following, the expression for $\boldsymbol{\phi}$ as a function of ζ instead of σ will be useful. Given the expression (7) for σ, Eq. (13) becomes

$$\boldsymbol{\phi}(\varphi,\nabla\varphi,\zeta)=\lambda\nabla\varphi+\zeta\frac{\nabla\varphi}{|\nabla\varphi|}. \tag{14}$$

III. EQUATIONS OF MOTION

We assume that the equations of motion are the following:

$$\frac{\partial\varphi}{\partial t}=A, \tag{15}$$

$$\frac{\partial\sigma}{\partial t}=0, \tag{16}$$

$$\frac{\partial F}{\partial t}=-\nabla\cdot\boldsymbol{q}-\Delta, \tag{17}$$

where the expressions for A, $\boldsymbol{q}$, and Δ must be determined. The second law of thermodynamics imposes that, whatever the motion is, the dissipation of energy Δ must be positive. Equation (16) is quite intuitive since σ will be shown to play a role of lipid density. For the two other equations we are of course at liberty to write them in this manner since for the moment A and Δ could be any combination of the thermodynamic variables. These functions will be fixed by the thermodynamic requirements.

Using Eq. (9), Eq. (17) leads to

$$\mu\frac{\partial\varphi}{\partial t}+\zeta\frac{\partial\sigma}{\partial t}+\boldsymbol{\phi}\cdot\frac{\partial\nabla\varphi}{\partial t}=-\nabla\cdot\boldsymbol{q}-\Delta.$$

Using Eqs. (15) and (16), the previous equation allows one to determine the following expression for the dissipation of energy Δ:

$$\Delta=-\nabla\cdot(\mathbf{q}+\boldsymbol{\phi}A)-A(\mu-\nabla\cdot\boldsymbol{\phi}). \tag{18}$$

To ensure the condition $\Delta\geqslant 0$, we propose the following expression for A:

$$A=-\kappa(\mu-\nabla\cdot\boldsymbol{\phi}), \tag{19}$$

where $\kappa\geqslant 0$. This choice means that we have set $\boldsymbol{q}=-\boldsymbol{\phi}\partial\varphi/\partial t$. This nonclassical heat flux is well known in fluid mechanics in the framework of the van der Waals model of capillarity [22]. It ensures the thermodynamic well-posedness of the model.

The equations of motion (15) and (16) thus take the following form:

$$\frac{\partial \varphi}{\partial t} = - \kappa (\mu - \boldsymbol{\nabla} \cdot \boldsymbol{\phi}), \tag{20}$$

$$\frac{\partial \sigma}{\partial t} = 0. \tag{21}$$

These equations are thermodynamically consistent, in the sense that they ensure a decrease of the free energy F at global equilibrium, as shown below.

In order to compare these evolution equations to those originally presented in [3,4] it is more appropriate to reexpress the above equations in terms of the variables (φ, ζ). By making use of Eqs. (7) and (14) the previous equations take the following form:

$$\frac{\partial \varphi}{\partial t} = - \kappa \left[\frac{dW}{d\varphi} - \boldsymbol{\nabla} \cdot \left(\lambda \boldsymbol{\nabla} \varphi + \zeta \frac{\boldsymbol{\nabla} \varphi}{|\boldsymbol{\nabla} \varphi|} \right) \right], \tag{22}$$

$$- \frac{1}{\theta} \frac{\partial \zeta}{\partial t} + \frac{\partial |\boldsymbol{\nabla} \varphi|}{\partial t} = 0. \tag{23}$$

It can be shown that [23]

$$\frac{d|\boldsymbol{\nabla} \varphi|}{dt} = (\boldsymbol{I} - \boldsymbol{nn}) : \boldsymbol{\nabla v}, \tag{24}$$

where d/dt designates the material derivative. As will be seen in Sec. V the partial derivatives will be substituted by material derivatives. So that we anticipate that we can write from the above relation and Eq. (23)

$$\frac{1}{\theta} \frac{d\zeta}{dt} = (\boldsymbol{I} - \boldsymbol{nn}) : \boldsymbol{\nabla v}. \tag{25}$$

This is nothing but Eq. (4), presented in [3,4] where $T = \theta$. It is worth noting that, in the case where $\theta \to \infty$, the postulated equation of local conservation of σ (16) degenerates to the equation of local conservation of $|\boldsymbol{\nabla} \varphi|$ [cf., Eq. (23)].

Some remarks are in order. In [3,4] the contribution of the tension field, represented by $\zeta \boldsymbol{\nabla} \varphi / |\boldsymbol{\nabla} \varphi|$, that enters Eq. (22), is not included in the evolution equation for φ [Eq. (1) in [4]], but rather in the Stokes equation [Eq. (3) in [4]]. The idea in [4] was to *deliberately* keep the phase-field evolution equation as passive as possible, and to include the physical forces in the Stokes equation only. This philosophy was motivated by the fact that the phase-field function was sought to be a passive function, advected by the flow, and not containing any source of physics. The spirit developed in the present paper is quite different in that it is wished to build the phase-field model by fulfilling a demand of a monotonous evolution of the thermodynamic potential from which the phase-field equations follow. Both spirits lead to the same asymptotic equations in the sharp limit (i.e., when $\lambda \to 0$). We expect, in principle, the present method to reinforce numerical stability of the evolution, since a Lyapunov function exists at global equilibrium, namely the free energy F.

TABLE I. Analogy between the mass balance equation in fluid mechanics and the equation of conservation of σ in the present model.

Mass balance equation	Conservation of σ
ρ	σ
P	ζ
$(\partial P / \partial \rho)$	θ
c	$\lvert\boldsymbol{\nabla} \varphi\rvert$

IV. DISCUSSION

A. Sign of the parameter θ

Hitherto we have made no assumption on the sign of θ. From Eq. (23) together with intuition we expect θ to have a fixed sign in order to guarantee thermodynamic stability. An elementary analysis of thermodynamic stability shows that, for the "phases" to be thermodynamically stable, it is necessary that $\theta > 0$.

B. Conditions of thermodynamic equilibrium

From a thermodynamic point of view, the equilibrium state is characterized by the following condition:

$$\delta \int_V (F + L_1 \sigma) dV = 0,$$

where L_1 is the Lagrange multiplier accounting for the constraint of conservation of σ, which, from its expression (7), becomes a condition of conservation of $|\boldsymbol{\nabla} \varphi|$ in the limit $\theta \to \infty$.

One finds the following equilibrium conditions:

$$\zeta = L_1$$

$$\frac{dW}{d\varphi} - \boldsymbol{\nabla} \cdot \left(\lambda \boldsymbol{\nabla} \varphi + \zeta \frac{\boldsymbol{\nabla} \varphi}{|\boldsymbol{\nabla} \varphi|} \right) = 0.$$

C. Analogy with the mass balance equation

The evolution equation for σ (16) has been *postulated*. This equation corresponds to the conservation of σ and not of $|\boldsymbol{\nabla} \varphi|$. Nevertheless, the form (23) of this equation shows that the "principle" postulated degenerates to an equation of local conservation of $|\boldsymbol{\nabla} \varphi|$ when $\theta \to \infty$.

It is useful to make a parallel with the mass balance equations in fluid mechanics, as shown in Table I.

In Table I, c is a thermodynamic variable (the mass fraction in a binary alloy, for instance) which obeys a certain evolution equation. The evolution equation for σ is thus equivalent to the mass balance equation and its form (23) is the equivalent of the equation of propagation of the pressure P.

The limit $\theta \to \infty$ states incompressibility. It is worth noting that, in this limit, the thermodynamic potential Ψ is the only relevant quantity since the free energy F becomes ill-defined. As shown in [4] the tension field scales formally in the asymptotic limit as $1/\sqrt{\lambda}$. In the numerical treatment this quantity was set to a bit larger value (ten times at most) than $1/\sqrt{\lambda}$. We expect *a priori* typically similar order of magnitude for θ in order to fulfill in a satisfactory manner local area incompressibility.

V. GENERALIZATION TO HYDRODYNAMICS

The generalization to hydrodynamics (including flow) is rather simple. We do not prove the following equations because this is identical to those known for the Cahn-Hilliard model [24]:

$$\nabla \cdot \boldsymbol{v} = 0, \tag{26}$$

$$\frac{d\varphi}{dt} = -\kappa \tilde{\mu}, \tag{27}$$

$$\frac{d\sigma}{dt} = 0, \tag{28}$$

$$\rho_0 \frac{d\boldsymbol{v}}{dt} = -\nabla P - \nabla \cdot (\boldsymbol{\phi} \otimes \nabla \varphi) + \nabla \cdot \boldsymbol{\tau}^d, \tag{29}$$

where

$$\tilde{\mu} \hat{=} \frac{dW}{d\varphi} - \nabla \cdot \boldsymbol{\phi}, \tag{30}$$

$$\boldsymbol{\phi} = \lambda \nabla \varphi + \zeta \frac{\nabla \varphi}{|\nabla \varphi|}, \tag{31}$$

$$\boldsymbol{\tau}^d = \eta(\varphi)[\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^T]. \tag{32}$$

$\boldsymbol{\tau}^d$ is the viscous stress tensor and $\eta(\varphi) \geqslant 0$ is the dynamic viscosity that accounts for a possible viscosity contrast between the interior and the exterior of the vesicle [26].

Let us compare this system with that proposed in the original 3D model [4]. The form (29) of the momentum balance equation is not appropriate to be compared to that proposed in [4]. An equivalent form is derived in Sec. VI that is more suitable for comparison with [4].

The term $\lambda(\nabla\varphi)^2$ in the energy (5) naturally introduces a surface energy contribution. In the present formulation, this contribution is present in both Eqs. (27) and (29), which are the phase-field and the momentum balance equations, through the term $\lambda \nabla \varphi$ in the expression for the vector $\boldsymbol{\phi}$ [Eq. (31)]. In [4] the surface term was not introduced in the momentum balance (since as stated above, no extra force from the phase field was intended to be added there). However, the phase-field equation in [4] [Eq. (1)] contains a term like $\lambda(\nabla\varphi)^2$. Since a vesicle has no surface energy, the "artificial" contribution produced by $\lambda(\nabla\varphi)^2$ has been eliminated in [4] (to leading order) by adding a term like $\hat{c}|\nabla\varphi|$, where $\hat{c}$ is the curvature of the contour line φ=const. However, no energy has been shown to be associated to the corresponding model, since it was not intended in [4] to build a thermodynamically consistent picture. In a forthcoming work, we shall include the bending energy and will also show how the surface energy associated with $\lambda(\nabla\varphi)^2$ can be subtracted by still keeping the thermodynamic consistency of the model.

VI. VARIATIONAL FORMULATION

In the following, we prove that the above set of equations are such that the total energy of the system is a decreasing function of time.

If one dot-products the momentum balance equation (29) with the velocity $\boldsymbol{v}$, one finds the kinetic energy balance equation:

$$\rho_0 \frac{d(\boldsymbol{v}^2/2)}{dt} = -\nabla \cdot [\boldsymbol{v} \cdot (P\boldsymbol{I} + \boldsymbol{\phi} \otimes \nabla \varphi - \boldsymbol{\tau}^d)] + (\boldsymbol{\phi} \otimes \nabla \varphi - \boldsymbol{\tau}^d) : \nabla \boldsymbol{v}.$$

Given the expression (9) for the differential of F, it is easy to show that

$$\frac{dF}{dt} = \tilde{\mu} \frac{d\varphi}{dt} + \nabla \cdot \left(\boldsymbol{\phi} \frac{d\varphi}{dt} \right) - (\boldsymbol{\phi} \otimes \nabla \varphi) : \nabla \boldsymbol{v}.$$

Adding these two relations and accounting for Eq. (27), one finds

$$\frac{d}{dt}\left(F + \rho_0 \frac{\boldsymbol{v}^2}{2} \right) = -\kappa \tilde{\mu}^2 - \boldsymbol{\tau}^d : \nabla \boldsymbol{v} + \nabla \cdot \left[\boldsymbol{\phi} \frac{d\varphi}{dt} - \boldsymbol{v} \cdot (P\boldsymbol{I} + \boldsymbol{\phi} \otimes \nabla \varphi - \boldsymbol{\tau}^d) \right].$$

Since the last term of this equation is written in a conservative form and since the first two terms are always negative, if one integrates this relation over the entire closed fluid domain and accounting for the nonslip condition at the boundaries, one finds that *the total energy of the system is a decreasing function of time*.

For other boundary conditions, such as in the presence of an imposed shear flow, or in a Poiseuille geometry (two particularly important cases), the above analysis still holds. However, as one expects, it is then no longer possible to identify a Lyapunov functional (a monotonically decreasing function of time), as is generic in nonequilibrium situations.

One can also provide a "potential" form for the momentum balance equation (following the denomination introduced in [24]). One only has to use the following relations:

$$\nabla \cdot (\boldsymbol{\phi} \otimes \nabla \varphi) = \nabla \cdot \boldsymbol{\phi} \nabla \varphi + \boldsymbol{\phi} \cdot \nabla\nabla \varphi,$$

$$\nabla \Psi = \mu \nabla \varphi + \boldsymbol{\phi} \cdot \nabla\nabla \varphi + \sigma \nabla \zeta.$$

The momentum balance equation (29) can thus be written in the following form:

$$\rho_0 \frac{d\boldsymbol{v}}{dt} = -\nabla(P+\Psi) + \tilde{\mu}\nabla\varphi + \sigma\nabla\zeta + \nabla\cdot\boldsymbol{\tau}^d, \tag{33}$$

where it is reminded that

$$\sigma = -\frac{\zeta}{\theta} + |\nabla\varphi|.$$

Using Eqs. (30) and (31), Eq. (33) reads

$$\rho_0 \frac{d\boldsymbol{v}}{dt} = -\nabla p + \tilde{\mu}_\varphi \nabla\varphi + \boldsymbol{F}_\zeta + \nabla\cdot\boldsymbol{\tau}^d, \tag{34}$$

where $p = P + \Psi$ and

$$\tilde{\mu}_\varphi = \frac{dW}{d\varphi} - \lambda\nabla^2\varphi, \tag{35}$$

$$\boldsymbol{F}_\zeta = |\nabla\varphi|(\boldsymbol{I} - \boldsymbol{n}\otimes\boldsymbol{n})\cdot\nabla\zeta - \mathcal{C}\zeta\nabla\varphi - \frac{\zeta}{\theta}\nabla\zeta, \tag{36}$$

where $\boldsymbol{n} = \nabla\varphi/|\nabla\varphi|$ and $\mathcal{C} = \nabla\cdot\boldsymbol{n}$ represent respectively the unit normal to the interface and its mean curvature.

The momentum balance equation (34) has to be compared to Eq. (3) in [4]. The pressure and viscous terms are identical. The main difference comes from the force $\tilde{\mu}_\varphi$ that does not exist in [4]. This is because this force is directly related to the surface tension force induced by the introduction of a contribution in $(\nabla\varphi)^2$ in the energy. Physically, a membrane does not exhibit any surface tension and this contribution has therefore not been considered in [4]. However, it turns out that the mathematical description of the system using the classical phase-field model exhibits a surface tension force. For the mathematical model to be coherent with the physical modeling, the surface tension force must be eliminated; this issue will be thoroughly analyzed in a forthcoming work. The force $\boldsymbol{F}_\zeta$ [Eq. (36)], must be compared to the force $\boldsymbol{F}_\xi$ in [4] [Eq. (7)]. The expression for these two forces is identical except that our last term is not present in [4]. This difference comes from the thermodynamic consistency of the present model. Indeed, in [4], the question of a thermodynamic consistency was not a main objective. However, the main interest was in the limit where the relaxation parameter, interpreted as θ in the present model, tends to infinity. In this limit, the last term of Eq. (36) vanishes and the two models coincide. However, the present analysis shows that, in order that the relaxation equation (28) and the momentum balance equation (34) are thermodynamically consistent, it is necessary to account for the last term of Eq. (36) in the expression for the tensionlike force. In this regard, the model proposed in [4] did not focus on a thermodynamically consistent picture: the expression (36) reduces to the force $\boldsymbol{F}_\xi$ only in the limit where $\theta\to\infty$. This is to be contrasted with the evolution equation for the tensionlike force (25) where in [4] one had to keep θ *finite* albeit very large. The present formulation treats, so to speak, the two equations at the same level of description as far as the magnitude of θ is concerned.

VII. CONCLUSION

We have provided a thermodynamically consistent model for vesicles under flow. We have confined ourselves to the situation of a quasi-incompressible membrane and have then focused on a phase field model that incorporates the physics associated to the membrane. We have left open here the fact that the phase field induces an "artificial" surface tension, as well as the bending forces. These two issues will be addressed in future works. Several other issues deserve future considerations. Of particular importance is the treatment of possible dissipation due to the sliding of the monolayers forming the membrane as well as the permeation of the membrane. Further studies should also deal with the possibility that the membrane, in addition to bending forces, may possess elastic forces. This is motivated by the fact that real cells, such as red blood cells, have a cytoskeleton which exhibits (nonlinear) elastic behaviors [25].

Finally it is an important task for future investigations to solve numerically the phase-field equations for vesicles and possibly compare their efficiency with regard to previous studies. This issue is currently under investigation.

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[26] It is worth noting that a possible variation in ζ and $|\nabla\varphi|$ is also possible theoretically but is not accounted for here for the sake of simplicity.