

Some results concerning the potential energy of interfaces with nonuniformly distributed surfactant

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A functional is presented for the stored energy content, or potential energy, of a nonuniform distribution of surfactant on a liquid interface. This is the energy available to drive fluid motion using surface-tension-gradient forces. The functional is shown to be non-negative. An energy evolution equation is derived for the motion of a thin liquid film, whose shape evolves under the combined influence of surface tension, viscous, and surfactant effects. Numerical calculations show the time history of these global energy components. Results are relevant to the flow behavior of wetting agents, soap films, foams, and emulsions with possible applications in the industrial and biological worlds. © 2001 American Institute of Physics. [DOI: 10.1063/1.1398535]

As will be shown below, an intuitive representation of the energy of an interface, when surfactant is present, is quite inadequate to describe the potential of the system to drive fluid flow. It is our primary purpose in this Brief Communication to present an appropriate potential energy functional. The results are relevant to a variety of situations where surfactant plays an important role. These include flows in soap films, foams, and emulsions as well as liquid coatings and certain problems in cell biology. We obtain the functional by calculating the work required to generate a given surfactant distribution, starting with the same amount of uniformly distributed surfactant. A general formulation of the global energy balance for a thin-layer fluid system with interfaces is given. The surfactant energy functional is shown to be consistent with this energy equation. Several properties of the functional will be established. Computations of the time history of the energy components, for a particular thin-layer fluid motion, are also given.

A portion of the energy content of an interface between two fluid phases is

$$E_0 = \int \int \sigma dA, \quad (1)$$

where A is the area of the interface and σ is the interfacial tension or interfacial energy density. The interfacial tension is reduced by the presence of surfactant, of surface concentration c . If this reduction is small, a simple linear law can be used, i.e.,

$$\sigma = \sigma_0 - Kc, \quad (2)$$

where K is a positive constant. For a given total quantity of surfactant,

$$c_0 A = \int \int c dA, \quad (3)$$

the energy, according to (1), is simply $E_0 = (\sigma_0 - Kc_0)A$, which is seen to be independent of the manner in which the surfactant is distributed on the interface.

Clearly, however, there is stored energy for a surface upon which the surfactant is distributed nonuniformly. If the surface tension is not uniform, a force balance on a surface element yields $\boldsymbol{\tau} = \nabla \sigma$, where $\boldsymbol{\tau}$ is the tangential stress applied to the surface by the surrounding or underlying fluid.¹ Consider a general curved surface upon which there is initially a uniform concentration of surfactant c_0 . The surfactant is considered to be insoluble. Let an element of the surface of initial area dA_0 be moved to a new position on the surface along a path whose arclength is s . As the element moves, both the area dA and concentration c will change, but the total amount of surfactant, e.g., the number of molecules,

$$cdA = c_0 dA_0, \quad (4)$$

remains constant. The total work done in moving the element to its final position on the surface is

$$dW = - \int \mathbf{dF} \cdot \mathbf{ds}. \quad (5)$$

Using (2),

$$\mathbf{dF} = \boldsymbol{\tau} dA = -K \nabla c dA, \quad (6)$$

but $\nabla c \cdot \mathbf{ds} = (dc/ds) ds = dc$ along the path. From (4) we have

$$dW = Kc_0 dA_0 \int_{c_0}^c \frac{dc}{c} = Kc_0 dA_0 \ln \frac{c}{c_0}. \quad (7)$$

The total work done over the entire surface is the integral of (7). In order to evaluate the energy of a particular surfactant configuration, this integral must be performed over the “final” area A rather than A_0 . Thus using (4) once more, the total work done, which is equal to the potential energy of surfactant nonuniformity E_c , is

$$E_c = W = K \int \int c \ln \frac{c}{c_0} dA. \quad (8)$$

This remarkably simple expression is seen to be independent of the gradients of c on the interface. E_c is also “path independent,” in that it does not depend on the manner in which

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the surfactant distribution was achieved. We now show, for the simplified case of a thin liquid layer with a free upper surface, that this is a potential energy term in an overall energy evolution equation.

Using the long-wave or lubrication approximation for slow flow of a thin Newtonian liquid film on a flat substrate, the governing equation for the velocity field is

$$\nabla p = \mu \nabla^2 \mathbf{V} \approx \mu (\partial^2 \mathbf{V} / \partial z^2), \tag{9a}$$

where μ is the constant value of viscosity, p is pressure, and where $\nabla = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$. The substrate ($z=0$) and approximate free-surface [$z=h(x,y,t)$] boundary conditions are

$$\mathbf{V}(x,y,0) = \mathbf{0}, \quad \mu \mathbf{V}_z(x,y,h) = \boldsymbol{\tau}(x,y), \tag{9b}$$

where the subscript denotes partial differentiation. Because the liquid layer is thin, the pressure is virtually independent of z , and this system is readily integrated to yield

$$\mu \mathbf{V} = [(z^2/2) - hz] \nabla p + z \boldsymbol{\tau}. \tag{10a}$$

Thus

$$\mathbf{V}(x,y,h) \equiv \mathbf{V}(h) = \frac{h}{\mu} \boldsymbol{\tau} - \frac{h^2}{2\mu} \nabla p \tag{10b}$$

and

$$\mathbf{Q} = \int_0^h \mathbf{V} dz = -\frac{h^3}{3\mu} \nabla p + \frac{h^2}{2\mu} \boldsymbol{\tau} \tag{10c}$$

is the areal flow rate. Each of the vector fields that appear in (10b) and (10c) is two dimensional in the substrate coordinates (x,y) . The overall rate of viscous dissipation, for a liquid above a substrate with area elements $dxdy$, is

$$\begin{aligned} \dot{E}_\mu &\approx \mu \int \int dxdy \int_0^h (\mathbf{V}_z \cdot \mathbf{V}_z) dz \\ &= - \int \int \mathbf{Q} \cdot \nabla p dxdy + \int \int \boldsymbol{\tau} \cdot \mathbf{V}(h) dxdy, \end{aligned} \tag{11}$$

using the relations (10). Equation (11) states the obvious fact that the rate of viscous loss of energy is equal to the power expended in pumping the liquid within the layer plus the rate of working by the surface traction field, as expected for creeping motion. Because integration has been performed across the thin or z dimension, the quantities in the thin-layer theory do not depend on z . Thus the ∇ operator henceforth represents differentiation only with respect to the substrate coordinates x and y . The pressure, in the first term, is due to surface tension and is given by

$$p = -\sigma \nabla^2 h \approx -\sigma_0 \nabla^2 h. \tag{12}$$

Consistent with the long-wave approximation, the error in Eqs. (9)–(12) is of the order of the negligibly small quantity $|\nabla h|^2$ since $|\nabla h|$ is itself assumed to be small. Moreover, the ratio of the area of a substrate element, and the area of the element of the inclined interface lying above it, is $1 + O(|\nabla h|^2)$. Thus, within the long-wave approximation, these area elements are interchangeable: $dA \approx dxdy$. The further approximation in (12) requires the change in surface

tension caused by the presence of surfactant to be relatively small. This is consistent with the linear law (2).

The evolution equation for the free surface, using mass conservation, is

$$h_t = -\nabla \cdot \mathbf{Q} = -\frac{\sigma_0}{3\mu} \nabla \cdot (h^3 \nabla \nabla^2 h) + \frac{K}{2\mu} \nabla \cdot (h^2 \nabla c), \tag{13}$$

and involves the unknown concentration field $c(x,y,t)$.

The energy balance equation (11) can be recast in a particularly transparent form:

$$\dot{E}_\mu = -\frac{dE_\sigma}{dt} - \frac{dE_c}{dt}, \tag{14}$$

which states that the instantaneous rate of viscous dissipation is equal to the rate of decrease of the potential energies due to capillarity and surfactant, respectively. Assume the no-flow and reflection symmetry conditions on the boundary $\partial\mathcal{D}$ of the flow domain \mathcal{D} ,

$$\mathbf{Q} \cdot \mathbf{n} = \nabla h \cdot \mathbf{n} = \nabla c \cdot \mathbf{n} = 0,$$

where \mathbf{n} is a unit normal vector in (x,y) on $\partial\mathcal{D}$. Then the pressure–work integral in (11) may be transformed into the capillary term in (14) by repeated use of the divergence theorem and the mass conservation relation in (13). The result is

$$E_\sigma = \frac{\sigma_0}{2} \int \int \nabla h \cdot \nabla h dxdy. \tag{15}$$

E_σ is essentially the increased area of a deformed surface, relative to a flat one, multiplied by the surface tension. Details of this transformation may be found in Ref. 2.

The equivalence of the traction term in (11) to dE_c/dt in Eq. (14) may be shown using a general transport relation. For a scalar property F on a moving, dilating surface A , we have

$$\begin{aligned} \frac{d}{dt} \int \int F dA &= \int \int \frac{d}{dt} [F dA] \\ &= \int \int \left(\frac{\partial F}{\partial t} + \mathbf{V}(h) \cdot \nabla F + F \nabla \cdot \mathbf{V}(h) \right) dA, \end{aligned} \tag{16}$$

because

$$(d/dt)(dA) = [\nabla \cdot \mathbf{V}(h)] dA.$$

First, let $F_1 = c$ in (16); then, since surfactant is conserved on any moving element of A ,

$$(\partial c / \partial t) + \mathbf{V}(h) \cdot \nabla c + c \nabla \cdot \mathbf{V}(h) = 0. \tag{17}$$

Second, let $F_2 = -Kc \ln c$ in (16) and using (17), we verify that

$$\begin{aligned} -K \frac{d}{dt} \int \int c \ln c dA &= -K \int \int \mathbf{V}(h) \cdot \nabla c dA \\ &= \int \int \mathbf{V}(h) \cdot \boldsymbol{\tau} dA \end{aligned} \tag{18}$$

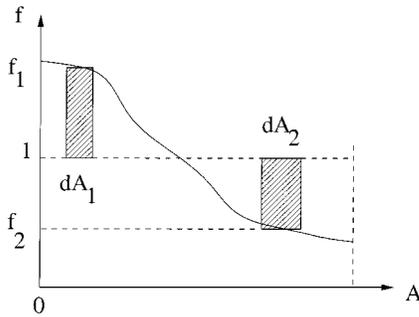


FIG. 1. Partition of the integral in Eq. (19). This construction is used to establish that the surfactant potential energy functional is non-negative. The two shaded areas in the figure are equal.

using the global surfactant conservation condition $\iint c dA = \text{const}$. The expression on the left of (18) is equal to the time rate of change of E_c as given in (8) since $\ln c_0$ is constant.

Several properties of the surfactant potential energy functional (8) can be established. The first of these is non-negativity when the total amount of surfactant on A is held constant. Define $f \equiv c/c_0$ and consider

$$\hat{E} = \iint f \ln f dA \tag{19a}$$

subject to

$$\frac{1}{A} \iint f dA = 1. \tag{19b}$$

Uniform distribution of surfactant with concentration c_0 is the reference state. In that case \tilde{E} in (19a) is zero. Because \tilde{E} depends only on the spectrum of values of f but not the position of elements relative to one another, one may reorder the surface elements so that f is monotonic, as shown schematically in Fig. 1. The integral may be partitioned as shown with $f_1 > 1$ and $f_2 < 1$. Clearly the entire integral can be evaluated using such pairs; thus positivity of a single pair implies positivity of (19a). The element of energy for the pair shown is $d\tilde{E} = f_1 \ln f_1 dA_1 + f_2 \ln f_2 dA_2$; but $(f_1 - 1)dA_1 = (1 - f_2)dA_2$; thus

$$\frac{1}{f_1 - 1} \frac{d\tilde{E}}{dA_1} = \frac{f_1 \ln f_1}{f_1 - 1} - \frac{f_2 \ln f_2}{f_2 - 1} \equiv g(f_1) - g(f_2).$$

The function $g(f) = f \ln f / (f - 1)$ is easily shown to be a monotonically increasing function of f on $(0, \infty)$. Thus $g(f_1) - g(f_2) > 0$, establishing that E_c is greater than zero whenever the c distribution is nonuniform.

It can also be shown that positive work, and a corresponding increase in the surfactant distribution energy, must be done when additional surfactant is added locally in a region where the concentration already exceeds the average value c_0 . The calculation of this energy change is applicable to an important problem in biology. One theory for cell division, or cytokinesis, stipulates that a cell that is about to divide behaves similarly to a liquid droplet immersed in a second immiscible phase. The analogy between cells and inert droplets, including experimental observation of remark-

ably “lifelike” motions when surfactant was added to the droplets, has been pursued for many years.^{3,4} Theoretical and numerical models, employing various mechanisms leading to surface tension gradients, have met with some success in reproducing aspects of the experimental observations.^{5,6} A completely successful model should allow a theoretical estimate of the energy required for cell motility and cleavage. The changes in E_c associated with surfactant addition is one part of the work requirement.

If we add a new amount $\epsilon c_1(x, y)$ to the existing distribution $c(x, y)$, the new energy is

$$E_{c1} = K \left(\iint (c + \epsilon c_1) \ln(c + \epsilon c_1) dA - A(c_0 + \epsilon \bar{c}_1) \ln(c_0 + \epsilon \bar{c}_1) \right),$$

where

$$\bar{c}_1 = \frac{1}{A} \iint c_1 dA.$$

Expanding for ϵ small, the energy change is

$$\Delta E_c = E_{c1} - E_c = \epsilon K \iint c_1 \ln \frac{c}{c_0} dA + O(\epsilon^2).$$

Thus, if one were to add a localized “packet” of extra surfactant to a region on the surface where c is already greater than c_0 , for example, positive work would be required to effect this addition. It may also be shown, by a similar method, that a uniform addition of surfactant over the entire surface will reduce the available energy for driving flow. It is noteworthy that experimental studies report that the addition of surfactant to a culture medium in which cells are multiplying immediately causes cell division to cease.⁷

Calculation of the time history of the energy components in (14) gives a useful overview of the relevant flow processes. A simple example is the leveling of a thin liquid layer with a free surface containing insoluble surfactant that is uniformly distributed initially. This is a problem that was treated by us several years ago.⁸ It was shown, at that time, that it is sometimes possible for a liquid coating layer containing a large amount of surfactant to become level more quickly than a similar layer that contains a smaller, but still finite, amount of surfactant. This is, perhaps, a puzzling result. Leveling flow is driven by differences in capillary pressure in an uneven liquid coating layer. Surfactant generally retards this flow because the flow causes the concentration of surfactant to become nonuniform. The resulting surface tension gradients are surface shear stresses that will oppose the motion. It was shown that when a large amount of surfactant is present, the surface tension gradients will lock up or “harden” the free surface causing it to behave like a “no-slip” interface. Leveling will still occur, but at a rate that is about one-quarter of the rate expected for a perfectly clean interface. Conversely, for smaller amounts of surfactant, larger shear stresses can develop, leading to significant back-flow along the surface that opposes the leveling flow. The surfactant energy functional developed here can be shown to give direct measures of these competing effects.

The evolution equation (13) contains two unknown functions: $h(x,y,t)$ and $c(x,y,t)$. A second coupled equation is required for the simultaneous determination of these quantities. The concentration c of insoluble surfactant can be expected to satisfy the convection–diffusion equation,

$$c_t + \nabla \cdot [c \mathbf{V}(h)] = \nabla \cdot (D \nabla c). \tag{20}$$

We will solve the system (13) and (20) in one space dimension; thus $\nabla \rightarrow \partial/\partial x$. The initial condition is a sinusoidal coating thickness variation with uniformly distributed surfactant, $h(x,0) = h_0 + a \cos(\pi x/L)$, $c(x,0) = c_0 = 1$, while the boundary conditions are $h_x(0,t) = h_x(L,t) = h_{xxx}(0,t) = h_{xxx}(L,t) = c_x(0,t) = c_x(L,t) = 0$. We will not include diffusion in the simulation.

The problem may be simplified by nondimensionalization. Dimensionless variables are introduced using $x = L\tilde{x}$, $h = h_0\tilde{h}$ and $t = T^*\tilde{t}$, where h_0 is the average layer thickness and the characteristic time is $T^* = (3\mu L^4)/(\sigma_0 h_0^3)$. With diffusion neglected, and the initial concentration normalized arbitrarily to one, there is only a two-parameter family of solutions. The parameters are $\tilde{a} = a/h_0$ and $R = 3(K/\sigma_0) \times (L/h_0)^2$. The dimensionless system of equations is

$$\tilde{h}_t = -(\tilde{h}^3 \tilde{h}_{\tilde{x}\tilde{x}\tilde{x}})_{\tilde{x}} + (R/2)(\tilde{h}^2 c_{\tilde{x}})_{\tilde{x}}, \tag{21a}$$

and

$$c_t + (c\tilde{V})_{\tilde{x}} = 0, \tag{21b}$$

where

$$\tilde{V} = -R\tilde{h}c_{\tilde{x}} + \frac{3}{2}\tilde{h}^2\tilde{h}_{\tilde{x}\tilde{x}\tilde{x}}. \tag{21c}$$

The system (21) is integrated using second-order-accurate finite differences in space and implicit time marching to ensure numerical stability.

The dimensionless potential energy components, defined by

$$\tilde{E}_c = \frac{E_c L}{\sigma_0 h_0^2} = \frac{R}{3} \int_0^1 c \ln c d\tilde{x}, \quad \tilde{E}_\sigma = \frac{E_\sigma L}{\sigma_0 h_0^2} = \frac{1}{2} \int_0^1 \tilde{h}_x^2 d\tilde{x},$$

are plotted versus time, for $\tilde{a} = 0.9$ and two different values of the surfactant strength parameter R , in Fig. 2. The figure shows transfer of energy from the surface deformation function \tilde{E}_σ , labeled “s,” to the surfactant energy functional \tilde{E}_c , labeled “c,” for each case. This transfer is much greater for the weaker surfactant $R = 1$. The ability of a relatively weak surfactant to act as a temporary repository for potential energy is another way of explaining the result that the more strongly surface active case $R = 100$ produces more complete leveling when compared to the weaker $R = 1$ case. Good leveling behavior is an important requirement for high value-added coating applications such as automotive painting. Thus surface-active components of these coating mixtures, which are often considered to function primarily as “wetting agents,” may also be instrumental in leveling, as demonstrated here.

Calculations similar to those discussed above could also have started with a flat interface but with a nonuniform sur-

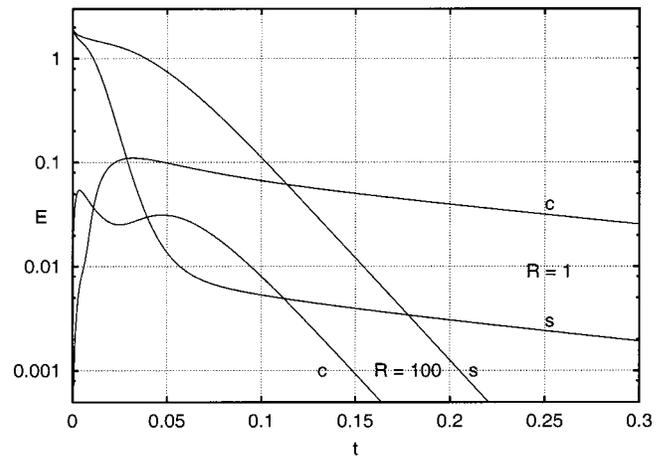


FIG. 2. Calculated variation in the surface (s) and distributed-surfactant (c) potential energy components with time for an initially sinusoidal coating layer of liquid. Two values of the surfactant strength parameter R are compared. The energies and the time are expressed in dimensionless units given in the text. The surface energy (s) is a measure of surface ripple amplitude.

factant distribution. In that case the energy transfer would be from \tilde{E}_c to \tilde{E}_σ . Thus the surfactant will cause a uniform coating to become undulatory. In extreme cases, concentrated surfactant may lead to effective dewetting of the substrate, where a contaminant particle has landed on the wet coating. This is the origin of so-called “crater” defects, millimeter-size perforations in an otherwise continuous dry coating.⁹ Another possible extension is the replacement of the linear equation of state (2) with a more general surface tension–concentration law. Three-dimensional time-dependent simulation, for thin liquid layers, is also possible.

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