Dynamic Equations of Surfactants and Surfaces

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We present a general theory of dynamics of two-component surfactants on surfaces separating two fluids. The surface free energy consists of two contributions: one is determined by the surface curvature and the surfactant densities and the other is the gradient part arising from areal inhomogeneities of the surfactant densities. Our dynamic equations together with generalized boundary conditions at the surface can be used to describe highly nonlinear phenomena in which phase separation and surface deformations are coupled. Our theory can also be reformulated for cases with a nonconserved order parameter.

\[
\frac{\partial}{\partial t} u = -v_n n \cdot \nabla u = -v_n \dot{\zeta}.
\] (2)

Recently much attention has been paid to phase transition phenomena of amphiphilic systems localized on two-dimensional deformable surfaces.\(^{1-3}\) Examples are the phase separation on air-water interfaces (Langmuir films)\(^4\) and that of surfactant binary mixtures composing bilayer membranes.\(^{1-3}\) In some cases the order parameter arises from complex internal structures and is not a conserved variable.\(^{5,6}\) Here the coupling of phase transition and surface deformations is one of the most interesting features of the phenomena. Most of these studies have treated static aspects; hence, the aim of this letter is to present basic dynamic equations describing surfactant motion. A similar hydrodynamic theory is given in ref. 7.

(A) Basic Relationships. We represent a surface by the equation \(u(r, t) = 0\) in terms of a smooth subsidiary field \(u(r, t)\). Then the normal unit vector \(n\) is written as \(n = \zeta^{-1} \nabla u\) with \(\zeta = |\nabla u|\) and the surface integral \(\int da(\cdots)\) may be expressed as \(\int d\delta(r)(\cdots)\) with

\[
\dot{\delta}(r) = \zeta \delta(u), \tag{1}
\]

which is the \(\delta\)-function along the normal. In our problem the surface is highly deformable and its velocity in the normal direction will be denoted by \(v_n\). The \(u\)-field also depends on \(t\) and obeys

\[
v_{\alpha, n} = v_n \quad \text{for} \quad \alpha = 1, 2. \tag{3}
\]

The lateral part \(v_{\alpha, \perp} = (I - nn) \cdot v_{\alpha} = v_{\alpha} - v_n n\) is the velocity on the surface, with \(I\) as the unit tensor. Hereafter the subscript \(\perp\) of vectors denotes taking the transverse part.

To derive hydrodynamic equations on the surface we introduce "bulk density" \(\dot{\rho}_a\) and "bulk current" \(\dot{J}_a\) as

\[
\dot{\rho}_a = \rho_a \dot{\delta}, \tag{4}
\]

\[
\dot{J}_a = \rho_a v_a \dot{\delta}. \tag{5}
\]

They should satisfy the continuity equation

\[
\frac{\partial}{\partial t} \dot{\rho}_a = -\nabla \cdot \dot{J}_a. \tag{6}
\]

Using eqs. (1) and (2), we obtain \(\partial \dot{\delta}/\partial t = -(n \cdot \nabla)(\dot{\delta}v_n)\) and find the conservation law on the surface

\[
\frac{\partial}{\partial t} \rho_a + v_{\alpha} \cdot \nabla \rho_a + \rho_a D_a = 0, \tag{7}
\]
where \( D_a \) is the areal expansion rate

\[
D_a = \nabla \cdot v_a - nn \cdot \nabla v_a = v_n H + (\nabla \cdot v_a) - nn \cdot \nabla v_a. \tag{8}
\]

Hereafter \( A : B = \sum_{ij} A_{ij} B_{ji} \) for any tensors \( A \) and \( B \) and \( H = \nabla \cdot n \) is the sum of the two principal curvatures. The first two terms of eq. (7) may also be expressed as \( Dp/DT + v_{a \perp} \cdot \nabla \rho_a \) where \( Dp/DT = \partial p/\partial t + v_{a \perp} \cdot \nabla \rho_a \) is the time derivative in the local reference frame moving with the interface. The \( \nabla \perp \) is the gradient operator on the surface

\[
\nabla \perp = (I - nn \cdot n) \cdot \nabla = \nabla - n(n \cdot \nabla). \tag{9}
\]

The first contribution \( v_n H \) in eq. (8) is the increasing rate of the local surface area due to the surface motion, while the second contribution arises from the surfactant motion on the plane perpendicular to \( n \). On the other hand, the equation of motion in the bulk form reads

\[
\frac{\partial}{\partial t} \hat{J}_a + v_a \cdot (v_a \cdot \nabla) = F_a \hat{\delta}, \tag{10}
\]

where \( F_a \) is the areal force density on the \( \alpha \)-th component. Using eq. (6) we may remove \( \hat{\delta} \) from eq. (10) to obtain

\[
\rho_a \left[ \frac{\partial}{\partial t} v_a + (v_a \cdot \nabla) v_a \right] = F_a. \tag{11}
\]

In this letter, for simplicity, temperature inhomogeneities on the surface will be neglected and then the reversible part of \( F_a \) should be equal to \( -\rho_a \nabla \perp \mu_a \), where \( \mu_a \) is a chemical potential of the \( \alpha \)-th component. Its explicit expression will be given below. We also neglect thermocapillary effects arising from the temperature dependence of the surface tension. Hence

\[
F_a = -\rho_a \nabla \perp \mu_a + F'_a, \tag{12}
\]

where \( F'_a \) is the dissipative part of the areal force density.

(B) Surface Free Energy and Boundary Conditions. We assume a surface free energy functional of the form

\[
F = \int da \left[ f(H, \rho_1, \rho_2) + \frac{1}{2} C_{\alpha \beta} (\nabla \perp \rho_\alpha) \cdot (\nabla \perp \rho_\beta) \right], \tag{13}
\]

where \( da \) is the surface element \( H = \nabla \cdot n = 1/\sqrt{1 + 1/R_a} \) is the mean curvature \( (1/R_1 + 1/R_2) / 2 \) multiplied by 2, and the repeated indices, \( \alpha \) and \( \beta \) in eq. (13), mean the summation over them. The areal density \( f \) depends on \( H, \rho_1, \) and \( \rho_2 \) and its functional form is not specified here. The second contribution in (13) arises from the lateral gradient \( \nabla \perp \rho_\alpha \), which is indispensable in describing phase separation on the surface. We allow that the coefficients \( C_{\alpha \beta} \) may depend on \( \rho_1 \) and \( \rho_2 \). To avoid complicated notation we hereafter set

\[
a_\alpha = \nabla \perp \rho_\alpha. \tag{14}
\]

The gradient free energy density is then

\[
f_{inh} = C_{\alpha \beta} a_\alpha a_\beta / 2.
\]

Although neglected here for simplicity, a term of the form \( \kappa(r_1, r_2) / R_1 R_2 \) can in principle be present in the integrand of eq. (13). This term can be neglected only when \( \kappa \) is independent of \( \rho_1 \) and \( \rho_2 \) and topology-changing deformations of the surface are not considered. Therefore we should examine its role in future work. We also neglect the dipolar interaction among the surfactant molecules.

Next we examine how \( F \) is changed by an infinitesimal surface displacement, \( r \to r' = r + \xi \), to calculate the force of the surface acting on the surrounding fluids. The displaced subsidiary field \( u' \) satisfies \( u'(r) = u(r) \) or \( u'(r) - u(r) \equiv -\xi \cdot \nabla u \). The displaced derivatives are given by \( \partial / \partial x_i \equiv \partial / \partial x_i - (\partial \xi / \partial x_i) \partial / \partial x_i \). The surfactants are assumed to move with the surface, so that \( \rho'_a(r) \equiv \rho_a(r)(1 - D) \), where \( D = \nabla \cdot \xi - nn \cdot \nabla \xi \) is the increment of the areal expansion ratio. After some calculation, we express the increment \( \delta F \equiv F' - F \) in the form

\[
\delta F = \int da (n \cdot \xi) W_\beta + \int da \xi_a \cdot \rho_a \nabla \perp \mu_a, \tag{15}
\]

where

\[
W_\beta = (\Delta_T + 2K) \frac{\partial f}{\partial H} - (f + f_{inh} - \rho_\alpha \mu_\alpha) H + C_{\alpha \beta} a_\alpha a_\beta \cdot \nabla n.
\]

Here \( \Delta_T \) is the Laplace-Beltrami operator on the surface and may be expressed as \( \Delta_T = \xi^{-1} \nabla \cdot (I - nn) \cdot \nabla \xi \) with \( \xi = \nabla \cdot u \). The \( K = 1/R_1 R_2 \) is the Gaussian curvature and \( f_{inh} \) is the gradient
free energy density in eq. (13). The chemical potential \( \mu_n \) is defined by
\[
\mu_n = \frac{\partial}{\partial \rho_n} f + \frac{1}{2} \left( \frac{\partial}{\partial \rho_n} C_{\beta \gamma} \right) a_\beta \cdot a_\gamma - C_{\alpha \beta} \Delta T \rho_\beta
\]
\[-(\partial C_{\alpha \beta} / \partial \rho_\beta) a_\alpha \cdot a_\beta. \tag{17}\]
The \( W_\beta \) is the areal force density on the fluids and should balance with the discontinuity of the normal stress
\[
W_\beta = p_1 - p_2 - \sigma_*^{(1)} + \sigma_*^{(2)}. \tag{18}\]
Here \( p \) is the fluid pressure and \( \sigma_n = n \cdot \sigma \cdot n \), where \( \sigma \) is the viscous stress tensor. The "1" denotes quantities in the fluid region immediately "outside" the surface, while "2" denotes those immediately "inside" the surface. The normal vector \( n \) is taken to point from "2" to "1". The boundary condition (18) is a generalized Laplace law and is more general than a previous one in ref. 8.

We also notice that the fluids exert the following tangential force density on the surface
\[
F_{\text{ext}} = (\sigma_*^{(1)} \cdot n - \sigma_*^{(2)} \cdot n) \cdot n, \tag{19}\]
where \((\cdots) \cdot n\) denotes the transverse part. It originates from drag forces exerted by the fluid molecules on the surfactant molecules. In many cases we may assume
\[
F_{\text{ext}} = F_{\text{ext}}' = \rho_n \nabla \cdot \mu_n + \rho_n \left[ \frac{\partial}{\partial t} + v_n \cdot \nabla \right] v_n, \tag{20}\]
where \( F_{\text{ext}}' \) is the dissipative force density defined by eqs. (11) and (12). Here we neglect the surface viscosity, which gives rise to a term of the form \( \eta_n \alpha \Delta T v_n \) in \( F_{\text{ext}}' \). Such a viscous term would arise if surface were floating in vacuum.

In stationary cases all the velocities vanish and we obtain the equilibrium conditions, \( W_\beta = p_1 - p_2 \) and \( \nabla \cdot \mu_n = \nabla \cdot \mu_2 = 0 \). We notice that the former of these relations, the generalized Laplace law, contradicts those in ref. 3. We also note that the generalized Laplace law does not follow from mere minimization of the surface free energy density, the integrand of eq. (13), with respect to \( H \). This is because the surface shape should also be varied in eq. (15). However, \( F \) may be easily calculated for spheres and its minimization with respect to the radius leads to eq. (16).

Near the demixing phase transition in mixtures, the concentration \( \phi = \rho_1 / (\rho_1 + \rho_2) \) is the order parameter with enhanced fluctuations. In this case we may set \( f_{\text{inh}} = C |\nabla \phi|^2 / 2 \), neglecting inhomogeneous fluctuations of \( \rho = \rho_1 + \rho_2 \). This is still a special case of eq. (13). It follows a natural expression for the chemical potential difference,
\[
\mu_1 - \mu_2 = \frac{1}{\rho} \left( \frac{\partial}{\partial \rho} f - C \Delta \phi \right), \tag{21}\]
where \( f = f(H, \phi, \rho) \) is regarded as a function of \( H, \phi, \) and \( \rho \). The average chemical potential is simply given by \( \bar{\mu} = \mu_1 + (1 - \phi) \mu_2 = \partial f / \partial \rho \) and the generalized Laplace law is \( W_\beta = (\Delta \phi + H^2 - 2K) \partial f / \partial H - (f + f_{\text{inh}} - \rho \partial f / \partial \rho) \)
\[H + C \nabla \phi \cdot \nabla \phi \cdot \nabla \phi \cdot \nabla n \text{ together with } (18).\]

We also consider the simple case in which \( f \) is independent of \( H \) and \( f_{\text{inh}} = 0 \). Then eq. (16) reduces to the usual form \( W_\beta = -\gamma \phi \), where \( \gamma \) is the effective surface tension** equal to \( -\rho_0 \partial f / \partial \rho_\alpha \), and eq. (20) becomes \( F_{\text{ext}} = -\nabla \cdot \gamma + \rho_n [\partial / \partial t + v_n \cdot \nabla] v_n \). On the other hand, the literature\(^{(9-12)}\) has traditionally assumed \( F_{\text{ext}} = -\nabla \cdot \gamma \), which follows in our scheme if the acceleration terms and the inertia terms of the surfactants are neglected.

(C) **Energy Dissipation.** We now examine the energy dissipation in our system. In addition to \( F \), given by eq. (13), we consider the surface kinetic energy \( F_{\kappa} = \frac{1}{2} da (1/2) \rho_n v_n^2 \) and the bulk kinetic energy \( F_{\delta} \) of the surrounding fluids. Using the dynamic equations and boundary conditions obtained so far, we obtain
\[
\frac{d}{dt} (F + F_{\kappa} + F_{\delta}) = \int da [v_n \cdot F_n - v_{f_n} \cdot \sigma^{(1)} \cdot n]
\[+ v_{f_n} \cdot \sigma^{(2)} \cdot n] - \int d\sigma \cdot \nabla v_{\gamma}, \tag{22}\]

** For homogeneous surfactant densities the surface energy is \( AF \), with \( A \) as the total area. By fixing the surfactant numbers, \( N = A \rho_\alpha \), we differentiate it with respect to \( A \) to obtain the effective surface tension given here.
where \( v_f \) is the fluid velocity, \( v_f^{(1)} \) and \( v_f^{(2)} \) are those immediately outside and inside the surface, and \( \sigma \) is the fluid viscous stress tensor. Terms proportional to the normal velocity \( v_n \) cancel to vanish in eq. (22) due to eq. (18). The first term is the dissipation on the interface, while the second term is the bulk dissipation and is negative-definite. We note that the surface part vanishes if all the tangential velocities coincide and eqs. (19) and (20) hold.

Particularly in the case of Langmuir films the viscous stress in the gas region may be set equal to zero in eq. (21). Then the first term of eq. (22) simply becomes \( \int da (v_n \perp - v_f \perp) \cdot F_x \) with the aid of eq. (20), where \( v_f \) is the velocity in the water region near the surface. Because this quantity must be negative-definite, we may propose phenomenological relationships for the air-water case

\[
F_x = -\zeta_m (v_1 - v_2) - \zeta_1 (v_1 - v_f), \\
F_x = -\zeta_m (v_2 - v_1) - \zeta_2 (v_2 - v_f). \tag{23}
\]

The coefficient \( \zeta_m \) arises from the mutual friction between the two components, while \( \zeta_1 \) and \( \zeta_2 \) arise from that between the surfactants and the fluid. In these equations only the transverse parts of the velocities appear because the normal parts are the same. On the other hand, the same results also follow in the symmetric bilayer case if the fluid velocity is assumed to be continuous at the surface (namely, \( v_f^{(1)} = v_f^{(2)} \)).

(D) Lucassen Mode. The classic theories\(^5\)\textsuperscript{2-12} treated air-water interfaces with a single component surfactant, neglecting the curvature dependence of the surface free energy and the gradient part. In this simplified situation, let us consider relaxation of small deviations \( \approx e^{i \omega t} \) on a planar interface to compare our scheme with previous ones. From (11) and (23) we obtain the equation for the surfactant velocity \( v_1 \)

\[
\rho_1 \frac{\partial}{\partial t} v_1 \equiv -\rho_1 \nabla \perp \mu_1 - \zeta_1 (v_1 - v_f), \tag{24}
\]

where the second component is absent and "1" denotes the surfactant. The fluid velocity \( v_f \) obeys the linearized Navier-Stokes equation in the water region. The longitudinal surface mode with \( \nabla \perp \cdot v_1 \perp \neq 0 \) turns out to have the following dispersion relation

\[
\omega \left( \frac{S \zeta_1}{S + \zeta_1} + i \omega \rho_1 \right) = -K_s k^2, \tag{25}
\]

where \( K_s = \rho \frac{\partial}{\partial t} \mu_1 / \rho_1 = \rho \frac{\partial}{\partial t} \mu_1 / \rho_1 \) is the in-plane compression modulus and \( k \) is the wave number on the plane. The \( S \) is a complicated function of \( \omega \); it tends to \( 2 \eta_0 k \) as \( \omega \to 0 \) and to \( (\rho_0 \eta_0)^{1/2} (i \omega)^{1/2} \) for \( |\omega| \gg \eta_0 k^2 / \rho_0 \), where \( \eta_0 \) is the fluid viscosity and \( \rho_0 \) is the fluid mass density. Note that the last term of eq. (24) is now \( -\zeta_1 (v_1 - v_f) = -\alpha v_1 \perp \) with \( 1/\alpha = 1 / (S + 1/\zeta_1) \) after elimination of \( v_f \). The quantity \( \eta_0 / S \) represents the characteristic length of a backflow in the fluid region induced by the surface tension gradient on the surface.

By estimating \( \zeta_1 \approx \eta_0 a^{-1} \), and \( \rho_1 \approx \rho_0 a \), a being a microscopic length, we notice that we can take the limit \( \zeta_1 \to \infty \) and set \( \rho_1 = 0 \) for \( ka \ll 1 \) on the left hand side of eq. (25). Then we obtain \( \omega S = -K_s k^2 \), which indeed follows from the previous theories based on the assumptions, \( F_{\text{ext}} = \rho_1 \nabla \perp \mu_1 \) and \( v_1 = v_f \). When \( K_s \) is much smaller than the surface tension \( \gamma \), there are two characteristic wave numbers, \( k_0 \) and \( k_c \), defined as \( k_0 = \rho_0 \gamma / \eta_0^2 \) and \( k_c = \rho_0 K_s / \eta_0^2 \). As has been discussed in the literature,\(5\textsuperscript{2,11-14} \) the longitudinal mode behaves in a very singular manner as \( i \omega \approx -(K_s / 2 \eta_0) k \) for \( k_c \ll k < k_0 \) and as \( i \omega \approx -(1/2)(1 \pm i \sqrt{3}) \) \((\rho_0 \eta_0)^{-1/3} k^{2/3} k^{4/3} \) for \( k < k_c \). It slows down as the instability point \((K_s = 0)\) is approached. In the one component case the surfactant density is not governed by the usual diffusion law due to the backflow effect. On the other hand, in the two-component case the relative composition relaxes diffusively,\(5\)\textsuperscript{8} as will be justified in a forthcoming paper.

(E) Nonconserved Order Parameter. We additionally comment on the case with a scalar, nonconserved order parameter \( \phi \) such as the thickness of a bilayer\(5\) or the difference of the surfactant densities in inner and outer layers\(5\) (which should not be confused with the composition in mixtures). We set \( f = f(H, \phi) \) and \( F_{\text{inh}} = C (\nabla \phi)^2 / 2 \) neglecting the fluctuations of the surfactant density. When the relaxation of \( \phi \) is fast, we may assume that \( \phi \) is determined by the local equilibrium condition,
\[
\frac{\partial f}{\partial \phi} - CA_T \phi = 0, \quad (26)
\]

in slow relaxation processes. Under this condition the surface does not support the shear stress and \( F_{\epsilon c} = 0 \) in eq. (19). The generalized Laplace law becomes
\[
\frac{\partial f}{\partial H} = -\left[ f + C(\nabla_\perp \phi)^2 / 2 \right] + C(\nabla_\perp \phi)(\nabla_\perp \phi) \cdot \nabla n
\]
together with (18) as in the conserved case. We will investigate surface patterns and dynamics using these relations.

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References


Note added in proof—The free energy \( F_G = \int d\xi (\rho_\alpha, \rho_\beta)K \)
arising from the Gaussian curvature \( K \) gives rise to the following contributions to \( W_G \) and \( \mu_G \),
\[
W_{G} = K H \left( \rho_\alpha \frac{\partial}{\partial \rho_\alpha} \kappa \right),
\]
\[
\mu_{G} = K \frac{\partial}{\partial \rho_\beta} \kappa,
\]
which should be added on the right hand sides of eqs. (16) and (17). Here topology-changing deformations are neglected.

Honda and Kimura proposed a theory of the ripple phase in membranes to explain the reentrant phase changes.15 Unfortunately, they assumed an unrealistic gradient free energy for the internal variable. Their idea, which is respectable and similar to that in ref. 6, should be incorporated into our mathematical scheme to explain the ripple patterns.