

# Elasticity modulus of multicomponent thin liquid films

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The expression for the film elasticity modulus is deduced including both the Gibbs elasticity and disjoining pressure contributions and explaining a peak of foam stability near the critical micelle concentration discovered earlier in experiments.

The film elasticity, *i.e.*, the capability of increasing film tension at stretching, is a property that secures the stability of liquid films and foams. Gibbs<sup>1</sup> was first to introduce the film elasticity modulus

$$E = \frac{d\gamma}{d \ln A}, \quad (1)$$

(where  $\gamma$  is the film tension and  $A$  is the film area) and to explain the elasticity of thick soap films, which is now termed as the Gibbs elasticity. Another kind of elasticity appears in thin films due to overlapping the film surface layers and the resulting disjoining pressure introduced first by Deryagin.<sup>2</sup> For a long time, the theories of elasticity developed independently for thick and thin films, and the Gibbs elasticity was mostly attributed to thick films. The mechanism of the Gibbs elasticity is related to the interchange of matter between the film interior and its surface layers in the course of stretching and is inherent only in multicomponent films. This mechanism is irrespective of the film thickness, and it should also function in multicomponent thin films. The goal of this work is to formulate a general theory of the elasticity of multicomponent thin films with account for the Gibbs elasticity.

Similarly to the Gibbs adsorption isotherm, the fundamental thermodynamic equation for the film tension can be written as

$$d\gamma = -\sum_i G_i d\mu_i, \quad (2)$$

where  $G_i$  is the amount of the  $i$ th species per unit film area and  $\mu_i$  is the chemical potential of the  $i$ th species. During a fast elasticity test, a film practically has no exchange with the surroundings. This means that the total amount of each species  $G_i A$  is maintained. Then the condition follows

$$d \ln A = -d \ln G_i. \quad (3)$$

Putting (2) and (3) in the definition of the elasticity modulus (1), we arrive at the expression

$$E = \sum_i G_i^2 \frac{d\mu_i}{dG_i}, \quad (4)$$

which confirms the existence of elasticity since the derivative  $d\mu_i/dG_i$  is positive according to the requirement of thermodynamic stability. Equation (4) also well exhibits how the elasticity modulus diminishes when passing from a close to a partly open film when the constancy of some species amounts is replaced by the constancy of their chemical potentials, and the corresponding terms on the right-hand side of equation (4) disappear.

To relate the elasticity modulus to disjoining pressure, we turn to the isothermal Gibbs–Duhem equation for the bulk phase from which a thin film originates:

$$dp = \sum_i c_i d\mu_i, \quad (5)$$

where  $p$  is the pressure and  $c_i$  is the concentration of the  $i$ th species. The disjoining pressure  $\Pi$  is defined as

$$\Pi \equiv p' - p, \quad (6)$$

where  $p'$  is the outer pressure. If  $p'$  is fixed during the elasticity test, equation (6) yields

$$dp = -d\Pi. \quad (7)$$

Putting now (7) into (5), the equation follows

$$d\Pi = -\sum_i c_i d\mu_i, \quad (8)$$

which, together with equation (4), supplies a complete description for a multicomponent thin film.

If there is, in a film, a dominant species that can be regarded as a solvent, it is convenient to exclude its chemical potential (let it be  $\mu_j$ ) from equations (2) and (8) to give

$$d\gamma = -\sum_i (G_i - G_j c_i / c_j) d\mu_i + (G_j / c_j) d\Pi. \quad (9)$$

The coefficients of equation (9) have a simple geometrical interpretation. If we imagine, on both the sides of a film, two equimolecular dividing surfaces whose separation  $h$  has been chosen as to satisfy the condition  $h = G_j / c_j$ , the coefficient of  $d\mu_i$  has the meaning of the double relative adsorption of the  $i$ th species  $2\Gamma_{i(j)}$ . Equation (9) then becomes

$$d\gamma = -2\sum_i \Gamma_{i(j)} d\mu_i + h d\Pi. \quad (10)$$

Equation (10) is a central relationship of the thermodynamics of thin films based on the method of two dividing surfaces.<sup>3–6</sup>

The concentrations are related to each other by the relationship

$$\sum_i v_i c_i = 1, \quad (11)$$

where  $v_i$  is the partial molar volume of the  $i$ th species. Considering a film as an incompressible condensed system, volumes  $v_i$  are assumed to be constant. In this approximation, concentration  $c_j$  can be excluded from independent variables, and, accounting for (7), the known thermodynamic expression for the chemical potential differential can be written as

$$d\mu_i = -v_i d\Pi + \sum_{k \neq j} (\partial \mu_i / \partial c_k) dc_k. \quad (12)$$

Putting (12) in (10) leads to the expression

$$d\gamma = -2\sum_{i,k \neq j} \Gamma_{i(j)} (\partial \mu_i / \partial c_k) dc_k + h_1 d\Pi, \quad (13)$$

where

$$h_1 \equiv h + 2\sum_i v_i \Gamma_{i(j)} \quad (14)$$

is evident to be the total film thickness (including adsorbed layers at the two equimolecular surfaces). In the above approximation, the total film volume  $A h_1$  is constant, which yields the additional [to equation (3)] relationship

$$d \ln A = -d \ln h_1. \quad (15)$$

Using equations (1), (3), (13) and (15), we obtain the detailed expression for the elasticity modulus of a multicomponent thin film

$$E = 2\sum_{i,k \neq j} \Gamma_{i(j)} \frac{\partial \mu_i / \partial c_k}{d \ln G_i / d c_k} + h_1 E_\perp, \quad (16)$$

where

$$E_{\perp} \equiv -d\Pi/d\ln h_t \quad (17)$$

is the transversal elasticity modulus of a thin film. There are two terms on the right-hand side of equation (16). The first is responsible for the Gibbs elasticity and disappears if a film is composed of a pure liquid ( $\Gamma_{ij} = 0$ ). The second term represents a specific kind of elasticity inherent in thin films and disappears if a film becomes thick.

To illustrate the utility of equation (16), let us consider a binary free (foam) film containing a single surfactant (component 1) and a solvent (component 2). Equation (16) takes the form

$$E = 2\Gamma_{1(2)} \frac{\partial \mu_1 / \partial c_1}{d\ln G_1 / dc_1} + h_t E_{\perp}. \quad (18)$$

The total derivative in (18) is taken at the constancy of the surfactant amount  $AG_1 = A(hc_1 + 2\Gamma_{1(2)})$  and of the film volume  $V_t = A(h + 2\nu_1\Gamma_{1(2)})$ . As a consequence, the ratio  $G_1/(h + 2\nu_1\Gamma_{1(2)})$  is also constant, which yields

$$\frac{d\ln G_1}{dc_1} = \frac{d\ln \Gamma_{1(2)}}{dc_1} + \frac{h}{2\Gamma_{1(2)}(1 - \varphi_1)}, \quad (19)$$

where  $\varphi_1 = \nu_1 c_1$  is the volume fraction of the surfactant in the bulk phase (typically negligible as compared with unity). After putting (19) in (18), the resultant equation is

$$E = \frac{2\Gamma_{1(2)}^2}{d\Gamma_{1(2)}/dc_1 + h/2(1 - \varphi_1)} \frac{\partial \mu_1}{\partial c_1} + h_t E_{\perp}. \quad (20)$$

Let us apply equation (20) to the analysis of the concentration dependence of the elasticity modulus at a given film thickness. Since the critical micelle concentration is typically small, we can set  $\partial \mu_1 / \partial c_1 \approx RT \partial \ln c_{11} / \partial c_1$  where  $c_{11}$  is a monomeric concentration of the surfactant. Equation (20) can be written in the form

$$E = \frac{2RT\Gamma_{1(2)}^2/c_{11}}{d\Gamma_{1(2)}/dc_1 + h/2(1 - \varphi_1)} \frac{\partial c_{11}}{\partial c_1} + h_t E_{\perp}. \quad (21)$$

We have  $c_1 \approx c_{11}$  at concentrations smaller than the critical micelle concentration. Using an appropriate equation of the adsorption isotherm (for example, the Langmuir equation), it is easy to determine the first term on the right-hand side of (21) as an increasing function of concentration at least at a sufficiently small film thickness. The derivative  $\partial c_{11} / \partial c_1$  is unity below the critical micelle concentration, but it decreases dramatically (to almost zero) when passing the critical micelle concentration. This causes a maximum of the elasticity modulus at approaching the critical micelle concentration. As the film elasticity modulus is responsible for the foam stability, one can expect a maximum of foaminess and the foam stability near the critical micelle concentration. Observations of this kind were reported previously,<sup>7–11</sup> but no explanation of this phenomenon was given until now. We can see that the above theory satisfactorily explains the existence of maxima for foaminess and foam stability. Since we operated only with the first term on the right-hand side of equation (21), the conclusion made is equally valid for both thin and thick films.

When explaining the foam stability by the Gibbs mechanism, the question arises that the Gibbs mechanism is of an equilibrium character whereas the foam stability depends on dynamic variations. Indeed, the Gibbs mechanism implies equilibrium between the adsorbed layers and the interior of a film. However, the time  $\tau$  of attainment of equilibrium is strongly dependent on the film thickness  $h$ , and it can be estimated as

$$\tau = \frac{(h/2)^2}{D}, \quad (22)$$

where  $D$  is the surfactant diffusion coefficient. Putting  $D \approx 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and taking the upper limit for the thin film thickness as 100 nm, we come to the conclusion that the relaxation time of a thin film is smaller than  $10^{-6} \text{ s}$  by an order of magnitude. This is enough to include the Gibbs mechanism of elasticity among the foam stability factors. Probably, other mechanisms can also contribute to the generation of extremes of foam stability, but this is to be found in the future.

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