

Curvature Elasticity Models of Microemulsions

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Key Words: Interfaces / Membranes / Microemulsions / Statistical Mechanics / Surfaces

We review the theory of curvature elasticity of thin, fluid films starting with a phenomenological formalism motivated by microscopic, physical examples. The effects of finite compressibility of the layer, exchange of molecules between the film and the solution, and the intrinsic bending stiffness of the film are taken into account; these degrees of freedom account for all the important molecular modes of the system. The effects of fluctuations of the number of molecules in the film (which is in equilibrium with surfactant molecules or micelles in solution) and in the area per molecule about its equilibrium value is shown to soften the curvature elastic moduli. The relationship of the bending moduli to the pressure distribution in the film is discussed and it is demonstrated that isotropic liquid films have no bending modulus, in the continuum limit. The bending moduli for charged membranes and for block copolymers are estimated. Finally, some recent experimental measure of curvature elasticity are discussed and compared with the theory.

1. Introduction

The fascinating and useful variety of shapes, sizes, and forms found in microemulsions (three-component solutions of water, oil, and surfactant) is related to the flexibility of the amphiphilic interface to change its geometry. Although the term microemulsion has been used to denote systems best described as water-oil-surfactant mixtures, with perhaps only short-range correlations between the components, we focus here on microemulsions with domain sizes much larger than molecular scales where one can speak of a surfactant interfacial monolayer, separating large oil and water domains. It is precisely these systems that give rise to the most striking macroscopic behavior and the many of their properties can be rationalized and predicted in terms of the elastic behavior of the surfactant interface. In this review, we show that as opposed to usual, bulk fluids whose response to perturbations such as thermal fluctuations is determined by compressional/extensional elasticity, it is the *curvature elasticity* of these interfaces that is responsible for their form. We begin with an outline of the theory of curvature elasticity in fluid [2] films from both phenomenological and microscopic points of view. We then review the implications of the curvature elasticity on experimentally measurable quantities and show how the various parameters which enter into the theory can be obtained from (and checked by) experiment.

The focus of this article is to define the conditions under which a membrane (we chose to deal mostly with monolayer membranes for simplicity) can be described as tensionless (that is, with an area that is self-adjusting) but responding to perturbations (such as thermal fluctuations, conservation constraints, or external forces) with a restoring force that arises from the tendency of the membrane to resist certain changes in its curvature. This force comes from an energy for the film which is independent of the area of the film and depends only on the film curvature as emphasized early on by Helfrich [1]. The energy per unit area of membrane is written:

$$f_b = \frac{1}{2} k (H - H_0)^2 + \bar{k} K \quad (1.1)$$

where k and \bar{k} are the bending and saddle-splay moduli, respectively, H is the mean curvature (average of the two curvatures) and K is the Gaussian curvature [3] (product of the two curvatures) of the film. The first term represents the change in energy if the average curvature of the membrane deviates from the spontaneous curvature which is a property of a given membrane in a particular environment. The second term represents the part of the energy which depends on the Gaussian curvature, and hence on the topology of the membrane. While one can regard this energy as a phenomenological expansion of the energy in terms of the two invariants of the surface [3] (the mean and Gaussian curvatures), a deeper understanding of this expression requires an explanation of (i) the thermodynamics of surfactant solutions to see to what extent one can focus only on the interface, as well as (ii) an understanding of both the thermodynamics and microscopics of the energy required to deform a surfactant monolayer or bilayer. This is precisely the focus of the present paper.

The organization of this review is as follows: We begin in Sec. II with phenomenological models of membranes and outline the thermodynamics of the films which are in equilibrium with surfactant (or micelles) in solution. Some new results on the softening of the bending modulus due to fluctuations in the number and area per surfactant are derived. We then show how the bending moduli which characterize Eq. (1.1) are related to the internal pressure of the film. Section III reviews several microscopic models for curvature elasticity including charged and polymeric surfactants. Finally, in Section IV we conclude with a discussion of how the theoretical elastic parameters are related to experimental measurements.

II. Phenomenological Theory of Curvature Elasticity

Although fluid membranes can be composed of many different types of chemical and molecular species, their behavior (shapes, fluctuations, thermodynamics) can be understood from a unified point of view that considers the free energy of deformation of the membrane. If the membrane were constrained to lie in a plane, the only relevant

energy would be the compression of the molecules — i.e. change of the average area per molecule. This is analogous to sound waves in a three-dimensional fluid; there is no low-frequency response of the system to shear. However, since the membrane can also deform in the normal direction (out of the plane), there is an additional set of “modes” describing the conformations of the film. These out-of-plane deformations are known as bending or curvature modes and the free energy associated with such modes is known as the curvature free energy. For a membrane with finite thickness, we denote as pure curvature deformations those perturbations of the membrane that do not change the overall membrane volume, but where there may be local stretching and compression of different parts of the film. While a general deformation of the membrane involves both a change of volume and curvature, we shall see that the lowest energy deformations usually involve only the curvature with no change in volume of the film.

A. Thermodynamics of Interfaces

We consider a fluid, monolayer membrane at a water-oil interface in equilibrium with a dilute solution of amphiphiles in the water and oil. In general, there is an equilibrium between those amphiphiles adsorbed at the interface and those in the bulk solution. For extremely small volume fraction of amphiphile, the surfactants will preferentially remain in solution due to their higher entropy of mixing with the solvent; the interface will have a relatively small number of amphiphiles adsorbed per unit area. However, this is not the case when the amphiphilic molecules are strongly insoluble in either solvent due to the unfavorable interactions of the polar groups with hydrocarbon solvents and of the hydrocarbon groups with polar solvents. The large energy cost of keeping these molecules in solution overcomes their entropy of mixing and at even moderately small volume fractions (which in practice can be very low $\sim 10^{-4}$ or less for surfactants which strongly prefer the interface), the free energy cost for being in solution is too high and the amphiphiles will tend to accumulate at the interface.

As one increases the volume fraction of amphiphiles in the solution, more and more would go to the interface and the area per molecule, Σ , on the interface would decrease. However, the molecules cannot pack at infinite density at the interface. In the case where there exists a minimum in the packing energy of the flat interface at a value of $\Sigma = \Sigma_0$, the system will keep adding amphiphiles to the flat interface until Σ is reduced to a value close to Σ_0 . If even more molecules are added to the system, instead of decreasing Σ further and thus *increasing* the free energy (since $\Sigma = \Sigma_0$ is a minimum), the amphiphiles will maintain their packing at $\Sigma \approx \Sigma_0$ and accommodate the extra molecules by creating *more* interface (e.g. by rippling the flat interface or by incorporating oil into the water with the additional molecules located at the extra interface that is thus generated). When this happens, one says that the interface is saturated; instead of changing the packing area, the

system accommodates more amphiphiles by making more interface under the condition of minimizing the free energy with respect to Σ . Of course, the interface may then have some curvature and the actual value Σ may depend on the curvature.

In general, one must consider the chemical potential of a molecule at the interface and in the solution. The equality of these two chemical potentials is the criterion for equilibrium and hence determines the area per molecule on the interface. When the amount of interface is fixed, as in the case of a single water-oil interface, this equality fixes Σ . However, when the amount of interface can vary to minimize the free energy, Σ is determined by minimizing the interfacial free energy per molecule; the chemical potential then determines the *number* of interfaces that exist in the system as well as the (small) volume fraction of surfactant that is not incorporated in these interfaces; the properties of *each* interface are determined to a first approximation by the minimization of the local free energy of the film.

The thermodynamics of these processes are discussed in detail in the following section and in Ref. [4], where it is shown that there is a critical volume fraction of surfactant, ϕ_s^c above which there are many interfaces in the system, and the amount of surfactant not incorporated into these interfaces is small and remains approximately constant as the overall amount of surfactant, ϕ_s , is increased (ϕ_s^c is analogous to a critical micelle concentration). One usually considers the simple case of surfactants that are strongly surface active (strongly insoluble in the bulk) so that at even very small volume fractions of amphiphile ($\phi_s^c \ll \phi_s \ll 1$), there are *many* interfaces (e.g., vesicles, microemulsions) in the system in equilibrium. In this approximation, the fraction of surfactants in solution is very small and their volume fraction is approximately constant. However, in the following section we show how the equilibrium between the surfactant in the film and that in solution can be taken into account; the net effect is to soften the bending constants (i.e. the renormalized moduli are functions of ϕ_s); this is a major effect for the case where $\phi_s \sim \phi_s^c$.

Once the bending free energy has been found, the properties of the system are obtained by focusing on the properties of the interfaces. When, in addition, the interactions between these interfaces and their translational entropy can be neglected compared with the local deformation energies of the films, one can first minimize these local deformation energies to find the size and shape of the interfaces and then take into account the entropic and interaction effects as higher order corrections to the shape as determined by the curvature energy defined previously.

In addition to being characterized by the area per amphiphile, the interfacial membrane is also characterized by its thickness, λ , which can also change under deformations of the film. For simplicity, we assume that the equation of state of the flat membrane determines the thickness as a function of the area per molecule. (A simple example is the case of an incompressible film where the product of $\lambda\Sigma$ is constrained to equal the molecular volume so that $\lambda \sim 1/\Sigma$.) We thus take the flat membrane to be characterized only by

the area per molecule, Σ ; the curved membrane is characterized by both its curvature and area per molecule.

First consider a locally flat, isolated interface. Saturation occurs when the interfacial free energy achieves a minimum:

$$\frac{\partial f_0}{\partial \Sigma} = 0 \quad (2.1)$$

where f_0 is the free energy per molecule for a flat layer and Σ is the area per molecule. The free energy per molecule is minimized when $\Sigma = \Sigma_0$. The optimal value of the area per molecule arises from a balance of terms such as the entropy, and the interfacial-tension terms or attractions. The entropy favors a large area per molecule – because of the larger number of center of mass positions and chain conformations – while the interfacial-tension terms (e.g. contact of the hydrocarbon chains with the water) and molecular (e.g. van der Waals) attractions favor a small value of Σ . Of course, there can be deviations in the area per molecule from this minimum and the energy cost of such a compression or expansion is

$$\Delta f_0 = \frac{1}{2} f_0'' (\Sigma - \Sigma_0)^2 \quad (2.2)$$

where the primes signify a derivative with respect to Σ . However, these deformations are typically of higher energy than the curvature deformations; a membrane can change its shape or size with a much lower free energy cost than that required to compress or expand it. Below, we show how these fluctuations soften the bending moduli of the system; however, the basic picture of a set of films with curvature elasticity is maintained even if one allows area fluctuations. It is important to remember therefore, that for insoluble amphiphiles, it is the saturation of the interface and the minimization of the area per molecule that permits the usual surface-tension term to be neglected; the derivative $\partial f / \partial \Sigma = 0$. The surface tension is no longer relevant since the molecules adjust their area to optimize the free energy and it is therefore the curvature energy that mainly determines the properties of the film.

B. Interfaces in Equilibrium with Monomers

The standard treatment of curvature elasticity focuses on the compressibility and bending elasticity of isolated interfaces. The free energy of an interfacial film with fixed curvature and a fixed number of surfactants is minimized with respect to the area per molecule, and the bending energy is then derived. In reality, the number of molecules which comprise these interfaces is not fixed since they coexist and exchange with the surfactant monomers in the solution. In what follows we show that even in this case one can still derive an effective bending free energy for the surfactant film. The curvature energy is obtained by minimization of the total free energy of both the surfactant molecules in the

film as well as the molecules in the solution with which they exchange. The effect of monomers in the solution was discussed in the context of block copolymer self-assembly [4]. Here we use a similar formalism to specifically calculate the effective curvature energy and examine its dependence on the surfactant volume fraction. It is found that the presence of surfactant molecules in the solution induces a softening of the film, i.e. the effective curvature moduli decrease from their nominal values. Additionally, we show how the adjustment of the area per surfactant upon bending, can further soften the elastic parameters of the film.

To be specific, we consider a system of surfactant monolayers in a water-oil-surfactant microemulsion (the same conclusion also apply to bilayers in one-component solution). The volume fractions of water and oil, which are assumed to be insoluble, are ϕ_w and ϕ_o , respectively and the total volume fraction of amphiphile in the system is ϕ_s . The surfactant molecules are partitioned among the water, the oil, and the monolayer films with volume fractions ϕ_s^w , ϕ_s^o and ϕ_s^f respectively. The local concentrations of surfactant in water and oil are ψ_w and ψ_o respectively (it is assumed that the water and oil do not penetrate into the film so that the local concentration of surfactant in the film is $\psi_s = 1$). The local surfactant volume fractions, ψ_o and ψ_w are related to the concentrations relative to the whole system, ϕ_s^o and ϕ_s^w by

$$\phi_s^o = \phi_o \psi_o / (1 - \psi_o) ; \quad \phi_s^w = \phi_w \psi_w / (1 - \psi_w) ; \quad (2.3)$$

Since we focus on the case where the surfactant is highly insoluble in the water and oil regions, we assume that the amphiphile in these regions can be described as an ideal gas of molecules. However, the main conclusions remain valid even for interacting monomers in the solution. The free energy per unit volume of the surfactant molecules in the water and oil regions, f_w and f_o , respectively, can be written as

$$f_w = \psi_w (\log \psi_w - 1 + \chi_w) ; \quad f_o = \psi_o (\log \psi_o - 1 + \chi_o) , \quad (2.4)$$

where χ_w and χ_o are the energy of one molecule solubilized in water and oil, respectively, relative to the same molecule in a flat, lamellar configuration (taken to be the zero of energy). In Eq. (2.4), f_w , f_o , χ_w and χ_o are taken in units of $k_B T / v_0$, where v_0 is the volume per molecule and T is the temperature.

The surfactant film is characterized by a free energy, $f_f(\Sigma, H, K)$, which depends on the area per molecule, Σ , and the mean and Gaussian curvatures, H and K , respectively. In what follows we shall use an expansion to quadratic order in the curvature,

$$f_f(\Sigma, H, K) = f_0(\Sigma) + f_1(\Sigma)H + f_2(\Sigma)H^2 + \bar{f}_2(\Sigma)K . \quad (2.5)$$

appropriate for small curvature [3]. This free energy also includes the contributions from the short-range interactions of the film with the water and oil molecules. The total free

energy per unit volume, f_T , includes the energy of the surfactant in the water region, $(\phi_w + \phi_s^w)f_w$, and that of the molecules in the oil region, $(\phi_o + \phi_s^o)f_o$. (Note that the water phase is composed of water and the dissolved surfactant, and occupies a fraction of $\phi_w + \phi_s^w$ of the total volume. A similar expression applies for the oil phase). The contribution of the film energy to the total energy is $\phi_s^f f_f$. Thus, the total energy is

$$f_T = (\phi_o + \phi_s^o)f_o + (\phi_w + \phi_s^w)f_w + \phi_s^f f_f. \quad (2.6)$$

We are interested in the limit of low solubility of the surfactant molecules in both water and oil, when $\phi_s^{o,w} \ll \phi_{o,w}$, and the total energy per unit volume, f_T , is thus approximated by $f_T = \phi_o f_o + \phi_w f_w + \phi_s^f f_f$. This form of free energy assumes extensivity of the system, i.e. the energies are calculated for isolated films and the entropy of mixing as well as the interaction among the films is neglected. This assumption is valid since the entropy (per unit volume) of the self-assembled films is smaller by a factor of R^{-3} than the entropy of the same amount of separate surfactant molecules, where R is a characteristic size of a microemulsion droplet. The interaction energy can be neglected as long as the solution is dilute. Here we neglect both the entropy and the interactions in the calculation of the local packing area and the curvature energy and keep the curvatures and size of the microemulsion regions fixed. Of course, to determine these latter properties of the films one *must* include entropy and interactions in the minimization of the free energy with respect to H and K .

In what follows, the total free energy, f_T , is minimized with respect to all the other degrees of freedom: the surfactant concentrations in each region, ψ_o , ψ_w and ϕ_s^f , and the area per molecule in the film, Σ . The system is defined by its composition (ϕ_w , ϕ_o and ϕ_s) and by the fixed curvatures H and K . This procedure enables us to derive an effective curvature energy which does take into account the effect of the monomers in the solution. The free energy, f_T , is minimized subject to the constraint of conservation of the total amount of the surfactant:

$$\phi_s^w + \phi_s^o + \phi_s^f = \phi_s. \quad (2.7)$$

For low solubility of the surfactant it follows from Eq. (2.3) that the constraint of Eq. (2.7) can be approximated by $\phi_w \psi_w + \phi_o \psi_o + \phi_s^f = \phi_s$. The constrained minimization with respect to ψ_o , ψ_w and ϕ_s^f is calculated using the method of Lagrange multipliers. The physical equivalent of this procedure is that all three regions consist of surfactants with the same chemical potential which turns out to be proportional to $f_f(\Sigma, H, K)$, the energy per surfactant in the film. One finds that the values at the minimum are

$$\begin{aligned} \psi_o &= \exp(f_f - \chi_o); \quad \psi_w = \exp(f_f - \chi_w); \\ \phi_s^f &= \phi_s - \phi_o \psi_o - \phi_w \psi_w. \end{aligned} \quad (2.8)$$

The physical situation is completely analogous to micellization. There is a critical volume fraction of surfactant, ϕ_s^c ,

under which all the surfactant monomers are in the solution [4]. It is determined from Eq. (2.8) with $\phi_s^f = 0$ to be

$$\phi_s^c = \phi_o \psi_o + \psi_w \phi_w. \quad (2.9)$$

Only for larger values of volume fraction, $\phi_s > \phi_s^c$, do the film layers begin to appear. With the ratio of water to oil, ϕ_w/ϕ_o kept constant, one can relate the volume fractions by

$$\phi_s^f = \frac{\phi_s - \phi_s^c}{1 - \phi_s^c}.$$

The total energy per unit volume obtained after minimization is

$$\begin{aligned} f_T &= \phi_w (f_f - 1) \exp(f_f - \chi_w) \\ &+ \phi_o (f_f - 1) \exp(f_f - \chi_o) + \phi_s^f f_f. \end{aligned} \quad (2.10)$$

One can define an effective curvature energy per surfactant molecule by $f^* \equiv f_T/\phi_s$ (f^* is in units of $k_B T$). In previous treatments, the surfactant was treated as totally insoluble, $\psi_o = \psi_w = 0$, and the effective energy is equal to the bare curvature energy, $f^* = f_f$; here we determine the correction to f_f from the finite solubility of the surfactant. In the remaining discussion it is assumed, as a matter of convenience [5], that the solubilities in the water and the oil are equal, $\chi_w = \chi_o = \chi$. The effective free energy now takes a simplified form:

$$f^* = f_f - \frac{1 - \phi_s}{\phi_s} \exp(f_f - \chi). \quad (2.11)$$

Of course, the system also responds to changes in the curvature by adjusting the area per molecule to minimize the total energy. We find that this tends to further reduce the bare bending modulus, f_2 by an amount related to the spontaneous curvature. Expansion of the generic form of the film energy to the second order in the change of the area per molecule, Σ , (2.5) yields [6]

$$\begin{aligned} f_f(\Sigma, H, K) &= f_0(\Sigma_0) + \frac{1}{2} f''(\Sigma_0) (\Sigma - \Sigma_0)^2 + f_1(\Sigma_0) H \\ &+ f'_1(\Sigma_0) (\Sigma - \Sigma_0) H + f_2(\Sigma_0) H^2 + \bar{f}_2(\Sigma_0) K, \end{aligned} \quad (2.12)$$

where Σ_0 is the area per molecule at the minimum of the flat film energy f_0 . Substitution of Eq. (2.12) into Eq. (2.11) and minimization with respect to Σ , yields $\partial f_f / \partial \Sigma = 0$, i.e. the area per molecule at the minimum of the effective energy, f^* , has the same value of the area per molecule at the minimum of f_f

$$\Sigma^* = \Sigma_0 - \frac{f'_1}{f''_0} H. \quad (2.13)$$

Substitution of Σ^* back into Eq. (2.11) and expansion of the curvature part of the free energy, $f_f - f_0 \ll f_f$ yields

$$f^* = f_0^* + f_1^* H + f_2^* H^2 + \bar{f}_2^* K, \quad (2.14)$$

with the coefficients $f_0^* = f_0 + r - 1$; $f_1^* = f_1 r$

$$f_2^* = \left(f_2 - \frac{1}{2} \frac{f_1'^2}{f_0''} \right) r \quad (2.15)$$

and $\bar{f}_2^* = \bar{f}_2 r$, where

$$r = 1 - \frac{1 - \phi_s}{\phi_s} \exp(f_0 - \chi). \quad (2.16)$$

The area fluctuations thus serve to reduce the bare bending modulus, f_2 , by an amount proportional to the square of the spontaneous curvature, f_1' , divided by the compressibility; for very incompressible systems (large values of f_0'') these changes are small, while for anomalously compressible systems, this softening effect can be more significant. In any case, the expression for the change in f_2 is always negative; the extra degree of freedom of the area allows the system to lower its free energy.

We now return to the effect of the fluctuations in the surfactant between the film and the solution. Comparison of the coefficients of f^* with Eqs. (2.12–2.16) shows that r is also the ratio of the effective and the nominal curvature moduli $r = \kappa^*/\kappa = \bar{\kappa}^*/\bar{\kappa}$. The spontaneous curvature remains the same: $c_0^* = c_0$. Using the definition of ϕ_s^c and Eq. (2.8), Eq. (2.16) can be rewritten in the form

$$r = \frac{1 - \bar{\phi}_s^c/\phi_s}{1 - \bar{\phi}_s^c} \quad (2.17)$$

where $\bar{\phi}_s^c = \phi_s^c(H=K=0)$ is the critical volume fraction for creation of flat interfaces (we note that ϕ_s^c depends upon the curvature energy). In Fig. 1 we show a plot of r vs. $\bar{\phi}_s^c/\phi_s$. It is evident that even for high surfactant concentrations there is a correction that behaves like $\kappa - \kappa^* = \kappa \bar{\phi}_s^c/\phi_s$. As ϕ_s decreases, the effective curvature moduli decrease until they vanish at the critical volume fraction, $\bar{\phi}_s^c$

$$\kappa(\phi_s = \bar{\phi}_s^c) = \bar{\kappa}(\phi_s = \bar{\phi}_s^c) = 0.$$

The mechanism underlying the softening of the curvature moduli arises from the ability of the surfactant molecules in the film to exchange with monomers in the solution. If the system composition is near critical, $\phi_s \sim \phi_s^c$ there is a small amount of surfactant in the films, $\phi_s^f \ll \phi_s^c$. Now, if one increases slightly the curvature energy of the film, f_f , the solubilities, $\psi_w = \exp(f_f - \chi_w)$ and $\psi_o = \exp(f_f - \chi_o)$, will increase and surfactant molecules from the films will be transferred to the solution. Hence, the average free energy per molecule, f^* , will not increase according to the nominal curvature moduli but according to their decreased values, which takes into account the free energy of the molecules in

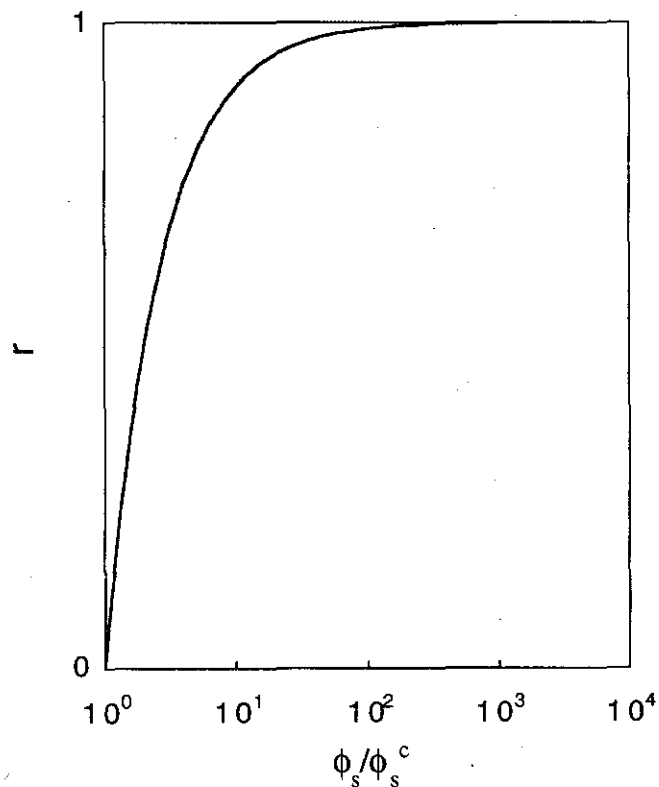


Fig. 1 Renormalization factor r which quantifies the softening of the bending moduli as a function of the ratio of the surfactant volume fraction, ϕ_s , to its critical value, ϕ_s^c , where the film layers first occur. The factor r is approximately given by $r \sim 1 - \bar{\phi}_s^c/\phi_s$, where $\bar{\phi}_s^c$ is the critical surfactant volume fraction for the occurrence of flat sheets, as discussed in the text

the solution. This is a major effect for relatively small surfactant volume fractions, when there is a small amount of amphiphile in the films. In this case, when the curvature energy is increased, large portions of the films can be reabsorbed in the solution. However, when there are many interfaces in the system, only a negligible fraction of the surfactant can be reabsorbed in the solution, and thus the corrections to the nominal values of curvature moduli are small. In this case, where $\phi_s \gg \bar{\phi}_s^c$, the microemulsion can be approximated by a system in which the surfactant molecules are totally insoluble and are (nearly) all contained at the interfaces. This is the situation usually treated and discussed in the remainder of this review, where one considers only the film energy and then optimizes the packing area at fixed curvature in order to derive the curvature free energy.

In summary, we have shown that when the exchange of the molecules in the film with those in the solution is taken into account the curvature moduli are decreased. The nominal moduli are renormalized by a factor which depends on the volume fraction of the surfactant. The curvature moduli vanish at the critical concentration. For amphiphile volume fractions much larger than the critical value, the correction is small and the films are thus well approximated by a system in which all the surfactant is the film. The softening phenomena – which also occurs for compressible films as the area per molecule adjust to the curvature, resulting in a reduction of the bending moduli – is an example of a general physical principle, which suggests

that the energy of a system decreases when one removes constraints. Here the constraint which was removed is the requirement of either fixed area or that all the surfactant is contained in the films.

C. Pressure and Bending

For small curvatures, Eq. (1.1) shows that the curvature energy of a thin film is characterized by the three parameters k , \bar{k} , and c_0 . The qualitative behavior of any system, including such properties such as the equilibrium shape, magnitude of thermal fluctuations, and any phase transitions, can of course be calculated as a function of these constants. However, the physics of the system can be radically different depending on the physical parameters; e.g. a change in c_0 can induce shape changes in the system. It is thus of interest to relate the bending elastic moduli and the spontaneous curvature to the physics of the particular system. This section first shows how these parameters are related to the pressure distribution in the membrane which is a general property of surfactant films. Applications of these ideas occur in calculations of the bending elastic constants of charged membranes where the pressure distribution arises from the spatially dependent counterion concentration [7–10] and in the bending of block copolymer films where the pressure distribution is related to the monomer density [4, 11–13]. Both these cases are briefly reviewed in the subsequent discussion of microscopic models.

The bending elastic moduli are determined by the curvature dependence of the free energy of the system i.e. there is a resistance of the system to curvature. This curvature dependence is associated with a local area change; curvature changes the local area element. For an isotropic and homogeneous fluid, the work done in changing the volume is calculated using the relationship

$$\Delta F = - \int_{V_0}^V \Pi(V') dV' , \quad (2.18)$$

where ΔF is the change in free energy due to an incremental, volume change from V_0 to V and $\Pi(V)$ is the local pressure (for a compressible system) or osmotic pressure (for a system of solvent and solute) against which this work is done. In general, Π can be a function of V and Eq. (2.18) accounts for the total work that is done in expanding the system from V_0 to V ; this requires a knowledge of Π at all pressures between V and V_0 and not just $\Pi(V_0)$. However, thin, liquid films that show a resistance to bending are anisotropic and one must consider separately the longitudinal pressure, Π_l , which resists changes in the film thickness and the transverse pressure, Π_t , which resists changes in the film area. In general, these quantities may vary within the film.

For solid films (i.e. films with a shear modulus), there is an additional resistance to bending arising from the resistance to shear deformations [14]. This results in a nonzero curvature modulus even for a system which is

elastically isotropic in the bulk. As shown below, this is not the case for systems with zero shear modulus; isotropic fluids show no resistance to bending deformations.

The curvature energy is essentially the work done in changing the *local* volume of the membrane related to the change in the area element due to the curvature; this work is done even if there is no *global* change in the volume of the membrane. We will therefore use a local version of Eq. (2.18) to calculate the curvature energy and consider the volume change due to curvature. This method for calculating the bending energy was introduced in Refs. [12, 15] where the area change was considered.

We consider an infinitely large membrane of thickness λ and area per molecule Σ (defined on the “bottom” ($\zeta = 0$) plane of the membrane) and calculate of curvature free energy as a function of these parameters that characterize the global properties of the membrane. In practice, both Σ and λ are functions of curvature. However, it is simplest to first keep these parameters fixed and derive the curvature energy expansion; this requires that we know Π for any given Σ and λ . Afterward, one can minimize the free energy with respect to these parameters (equivalent to determining an equation of state) and/or use constraints of constant volume to constrain either or both of them. (See the previous section for an example of how the equilibrium of the area per molecule can affect the bending modulus.) For example, the thickness of the membrane can be found by requiring that the curvature energy include only pure curvature deformations – i.e. that there be no overall compression or expansion of the membrane. Here, we make this choice and determine the film thickness of the curved film, λ , by requiring that the total volume of the system is kept constant (enforcing global incompressibility).

The details of this calculation are summarized in Ref. [3]. Here we quote only the results for the curvature moduli in terms of the pressure distribution through the thin film. The local transverse pressure (which responds to an area change in the film) is written $\Pi_t(\zeta, \lambda_0)$, where ζ is the local height within the film (measured, for example, from the lower surface) and λ_0 is an effective thickness of the bent film defined by:

$$\lambda_0 \Sigma = \lambda_f \Sigma_f \quad (2.19)$$

where λ_f and Σ_f are the thickness and area per molecule in the flat film and Σ is the area per molecule in the bent film, whose value is to be determined by a separate minimization and is here regarded as a constant (for given curvatures). The transverse pressure (which responds to thickness changes of the film) is denoted by $\Pi_t(\zeta, \lambda_0)$. We define the longitudinal and transverse pressures in the flat film as $\Pi_{l0}(\zeta, \lambda_0)$ and $\Pi_{t0}(\zeta, \lambda_0)$; the subscript 0 on Π and λ indicates that these are the flat film values.

The work done to bend the film can be calculated in terms of the pressure distributions with the film [3] and the result is the curvature elastic energy of Eq. (1.1). The elastic constants are given by:

$$k c_0 = \frac{1}{2} \int_0^{\lambda_0} \tilde{\Pi}_0(\zeta, \lambda_0) \zeta d\zeta \quad (2.20)$$

$$\bar{k} = - \int_0^{\lambda_0} \tilde{\Pi}_0(\zeta, \lambda_0) \zeta^2 d\zeta \quad (2.21)$$

$$k = - \int_0^{\lambda_0} \left(\left[\frac{\partial \tilde{\Pi}}{\partial H} \right]_0 + \frac{1}{2} \left(\left[\frac{\partial \Pi_1(\lambda_0, \lambda_0)}{\partial H} \right]_0 - \left[\frac{\partial \Pi_1(\lambda, \lambda)}{\partial (1/\lambda)} \right]_{\lambda=\lambda_0} \right) \right) \zeta d\zeta \quad (2.22)$$

where

$$\tilde{\Pi}_0(\zeta, \lambda_0) = \Pi_{10}(\zeta, \lambda_0) - \Pi_{10}(\lambda_0, \lambda_0) \quad (2.23)$$

If the pressure field is continuous in space, then the thickness, λ_0 can be set to infinity and $\Pi_{10}(\lambda_0, \lambda_0) = 0$, corresponding to a zero pressure boundary condition for away from the membrane. If the pressure is nonzero in only a finite region (e.g. a fluid or a gas contained between two walls with a finite thickness), the dependence on the difference in pressures in Eq. (2.20–2.23) guarantees that there is no curvature energy for an isotropic, fluid system with $\Pi_t = \Pi_1$ constant. (In this case, our expressions differ somewhat from those of Refs. [12, 15].) For a solid, however, the shear response of the system results in a nonzero bending modulus, even for an isotropic elastic medium [14]. We note that the combination $k c_0$ and the saddle-splay modulus \bar{k} are simply related to the moments of the pressure distribution of the flat membrane, while the bending modulus itself requires that the change in pressure due to curvature be calculated to linear order in H . For a given microscopic model (e.g. charged membranes, polymers at an interface), this requires a solution of the density profile and the resulting free energy and pressure in the curved geometry. However, k and \bar{k} often scale in an identical manner with the microscopic parameters (e.g. charge density, membrane thickness); one can therefore find \bar{k} quite simply and infer that k scales similarly. Finally, we observe that for membranes with stress-free boundaries at $\zeta = \lambda$, $(\Pi_1(\lambda, \lambda)) = 0$ for all values of λ , and the expression for k simplifies.

Note that the elastic constants still depend on the area per molecule via their dependence on λ_0 (see Eq. 2.19). In the previous section, we showed how one can include the fluctuations of the area per molecule, Σ , and obtain the effective bending energy along with a prediction of how the minimal value of Σ varies with the curvature of the film.

III. Microscopic Models

In this section, we supplement the phenomenological discussion of curvature elasticity by more microscopic models. The discussion of these models is not meant to be exhaustive, but rather illustrative of the fact that many dif-

ferent microscopic scenarios all result in the curvature elastic energy (per unit area) of a surfactant monolayer. We begin with a very simple review of a ball and spring model of surfactant molecules and then proceed to relate the bending elastic constants to the inhomogeneous pressure distributions in charged films and monolayers composed of block copolymers.

A. Ball and Spring Models

The simplest models of surfactant molecules that give rise to the curvature elastic energy [16] treat the molecules as (asymmetric) dumbbells with the polar head groups and the chains each idealized as a point particle, attached by a rigid rod. The heads of different molecules are attached to each other by springs as are the chains. While this model yields expressions for the elastic constants in terms of the spring constants and equilibrium spring lengths which are physically reasonable, we use a slightly different formulation in which the surfactant chains are treated not as point-like entities, but as spring-like molecules themselves. This provides a simple example for the treatment of block copolymer surfactants.

As a simple microscopic model that will allow some more physical insight into the meaning of the curvature elastic moduli, we consider a monolayer of chains that we model as springs with a spring constant, k_s , and with an equilibrium spring length, l_s . We denote the actual (stretched or compressed) length of the spring by l . We assume that the chains form an incompressible "melt" with no penetration of solvent into the chains. Their free energy is proportional only to the stretch of the springs; such a picture is applicable to polymeric molecules that pack incompressibly, but are stretched near an interface, so that the free energy cost for deformations arises from stretching. The area per chain at the interface is assumed to be fixed at a value Σ_0 ; in reality, this value is determined by the interactions that act on the polar head groups and our simple model assumes that these interactions are much stronger than the chain stretching energies, so that the optimal head area, Σ_0 , determined by the interactions in the polar layer, is not affected by the chains. The energy per chain is thus

$$f = \frac{1}{2} k_s (l - l_s)^2 \quad (3.1)$$

and the incompressibility of the chains implies that the volume occupied by the layer is constant. For a flat layer, this would be written: $\Sigma_0 l = v_0$ where v_0 is the molecular volume. For a curved layer, the volume occupied by the chains depends on the curvature. The volume per molecule is

$$v_0 = \Sigma_0 l \left(1 + lH + \frac{1}{3} l^2 K \right), \quad (3.2)$$

where H and K are the mean and Gaussian curvatures. (This formula is based on the integral of the expression for the

area of a parallel surface, discussed in Ref. [3]; it can also be derived by considering the cases of a sphere and a cylinder.)

Thus, the incompressibility condition relates the layer thickness, l , and the area per molecule, Σ_0 . For fixed Σ_0 , this determines the free energy as a function of curvature obtained by solving Eq. (3.2) for l and using this value for l in Eq. (3.1). The result is

$$l = l_0 + l_1 H + l_2 H^2 + l_3 K, \quad (3.3)$$

where $l_0 = v_0/\Sigma_0$, $l_1 = -l_0^2$, $l_2 = 2l_0^3$, $l_3 = -l_0^3/3$. Note that for a flat layer, the incompressibility constraint determines the layer thickness to be equal to v_0/Σ_0 ; in general, this will not be equal to the thickness l_s which minimizes the chain stretching energy. The flat layer is not, in general, the minimal energy state, implying that this monolayer has a spontaneous curvature related to the difference between the imposed thickness $\approx l_0$, and the preferred thickness, l_s . Only when these two lengths are equal is the flat monolayer relieved of the frustration induced by the mismatch of these two lengths.

Using the incompressibility relation, we find that when $c_0 l_0 \ll 1$, the elastic energy per chain is given to lowest order by

$$f = \frac{k_s l_0^4}{2} \left[(H - c_0)^2 - \frac{2c_0 l_0}{3} K \right], \quad (3.4)$$

where a higher order term in $c_0 l_0 H^2$ has been neglected. The spontaneous curvature, c_0 , is related to the difference between the chain length dictated by the molecular volume conservation and the head packing, l_0 , and that preferred by the chain stretching energy, l_s :

$$c_0 = \frac{(l_0 - l_s)}{l_0^2} \quad (3.5)$$

Eq. (3.4) is equivalent to the "Helfrich" form of the curvature free energy by a simple transformation to convert from energy per molecule to energy per unit area. The bending modulus (coefficient of H^2) and the saddle-splay modulus (coefficient of K) both increase as a power of the chain length. Of course, the spring constant, k_s , also depends on the equilibrium spring length, l_s ; a simple polymeric analogy yields in the limit of small curvatures, $k_s \sim 1/l_s \approx 1/l_0$. In that case, the bending modulus $k \sim l_s^3$. This variation of the bending modulus with the cube of the thickness is also characteristic of a bent, solid elastic plate as discussed in [14]. There it is also shown that for an isotropic solid, the origin of the bending modulus is the shear modulus of the material.

Recent estimates of the curvature elastic constants from analysis of neutron scattering on fluctuating microemulsion droplets and from surface tension measurements [17] have shown that increasing the chain length of the surfactants from C_8 to C_{10} results in an increase in the elastic constant

in a factor of 2, while increasing from C_8 to C_{12} results in an increase of 3.6 in the elastic constant. These very nonlinear dependencies of the bending moduli on the chain length are consistent with the predictions mentioned above.

The quantity c_0 is the spontaneous curvature of the membrane, which this model endows with a simple physical meaning: When the imposed head area, Σ_0 is larger than the optimal area, v_0/l_s , dictated by the chain packing, the preferred curvature is negative; the system prefers to pack with the heads on the "outside". Note that the free energy of the curved interface is lower than that of the flat interface; the system accommodates part of the strain induced by the mismatch between the heads and chains by bending.

B. Polar Head Groups: Electrostatic Contributions

The previous section indicated how in a very simple model, one can account for the contribution of the hydrocarbon chains in the bending modulus of a surfactant monolayer. The heads were modeled as an incompressible two-dimensional fluid which enforced a specific packing area. In this section, we consider the contribution to the bending modulus from the polar heads; in general, this requires a detailed molecular calculation which takes into account their packing and interactions. However, we focus here on the more universal aspects of these interactions and consider the case where the surface of polar groups can be idealized by a charged sheet of fixed charge with counterions distributed in the water. We then ask what is the energy to bend such a sheet (allowing the counterions to respond) and use the relationship between the pressure distribution and the bending moduli to study the scaling of k , \bar{k} as a function of the charge density and the distance between layers.

Detailed theories of these effects have been presented in Refs. [7–10]. Here we use dimensional considerations to relate the bending constants to the electrostatic properties of the charged polar head groups, the counterions, and any electrolyte that may be present in the water. We begin by recalling Eqs. (2.20–2.23) which relate the bending moduli to the pressure distribution. In the case of charged layers with counterions distributed inhomogeneously in the water, the relevant pressure distribution is that of the counterion "gas". We note that the bending constants scale as the product of the transverse pressure difference and the cube of a characteristic length which characterizes the thickness over which the transverse pressure difference is significant.

From quite general considerations, the transverse pressure, Π_t , of the gas of counterions in a system of charge monolayers is equal to [3] to the product of the temperature (we use units where the Boltzmann constant is set to unity) and twice the difference between the charge density at a given point, $n(z)$, and the midplane between layers which is taken at $z = 0$:

$$\Pi_t = T(2n(z) - n(0)) \quad (3.6)$$

Although this resembles the ideal gas result, one must remember that the charge distribution of the counterions in solution is inhomogeneous. For an infinite surface of fixed charge (with a charge per unit area σ_0) with no added electrolyte, the charge density varies with distance z from the surface of fixed charge as [3, 7]:

$$n(z) = \frac{1}{2\pi l} \frac{1}{(z + \lambda)^2}, \quad (3.7)$$

where $l = e^2/(\epsilon T)$ is the Bjerrum length, characterizing the ratio between the electrostatic attraction of the counterions (with unit charge e) to the surface of fixed charge and the translational entropy of the counterions in the water (whose dielectric constant is ϵ). The parameter λ accounts for the fixed charge with

$$\lambda = 1/(\pi l \sigma_0). \quad (3.8)$$

Thus, the charge density at the surface of fixed charge, where the bending occurs and where the pressure difference is largest, scales as $n(0) \sim 1/(\lambda^2 l)$. The pressure at that surface is the product of $Tn(0) \sim T/(\lambda^2 l)$. On the other hand, the pressure difference at a distance d from the surface of fixed charge (the polar head groups) scales as $Tn(d)$ and if $d \gg \lambda$ this is proportional to $T/(d^2 l)$. To determine the characteristic length scale over which this pressure is effective we consider three different cases: (i) the case of no added electrolyte, but where there is an array of charged sheets, as in a lamellar phase and the spacing between sheets $d \ll \lambda$; this is relevant in the limit of very small surface charge densities (see Eq. 3.8) which is sometimes termed the ideal gas limit (ii) as in (i) but where the charge density is relatively high so that $d \gg \lambda$ (iii) the case of added electrolyte of concentration n_s where the relevant length scale is the screening length $\lambda_s \sim 1/\sqrt{n_s l}$.

(i) For an array of sheets in the case of no electrolyte and weak surface charge ($d \ll \lambda$), the length scale over which the pressure difference is significant is the entire distance between the sheets d while the pressure difference is proportional to $T/(\lambda^2 l)$. We thus estimate that the bending modulus scales as:

$$k \sim T \frac{d^3}{\lambda^2 l} \quad (3.9)$$

Using the expressions for l and λ , we see that the bending modulus is proportional to the strength of the Coulomb interaction energy; if, in this nearly-ideal gas limit of weak surface charge, the counterions were distributed completely uniformly (with absolutely no effect of the electrostatic interactions), the bending modulus would vanish, as discussed previously.

(ii) For an array of sheets in the case of no electrolyte and strong surface charge ($d \gg \lambda$), the length scale over which the pressure difference is significant is still d , but the

pressure over most of that region is better estimated by $T/(d^2 l)$. The bending modulus thus scales as:

$$k \sim T \frac{d}{l} \quad (3.10)$$

Here we see that bending modulus is indeed proportional to temperature with an additional factor of T/e^2 which accounts for the electrostatics. This proportionality indicates the role of the entropy in determining the spatial distribution of the counterions; if the entropy were ignored, in this strong surface charge limit, all the counterions would collapse onto the fixed charge and there would be no resulting contribution to the bending energy.

(iii) For the case of added electrolyte, the relevant length scale where the pressure difference is effective is the screening length, λ_s and this screening length plays the role of d in cases (i) and (ii). Thus, for example, in the weak surface charge limit

$$k \sim T \frac{\lambda_s^3}{\lambda^2 l} \quad (3.11)$$

Here the screening length plays the role of the interlayer spacing d in case (i).

Typical values of λ (for unit charge per polar group) and l are on the order of 10 \AA . We thus see that the electrostatic contributions to the bending energies can be significant compared with $k_B T$ when either the interlayer spacing (for systems with no added electrolyte) or the screening length (for systems with added salt) are large compared to λ or l . When the screening is strong, the screening length is small, and the contributions to the bending energy can be negligible. On the other hand, when there is no added electrolyte and a large interlayer spacing, the electrostatic contribution to the bending modulus can be quite significant. The exact values of k depends, of course, on numerical factors not given by our scaling arguments. These factors are discussed in Refs. [7–10] for the various cases and sometimes give rather small numerical prefactors on the order of $1/10$ or smaller. Furthermore, the sign of the saddle-play modulus \bar{k} is negative; this tends to favor spherical topologies over saddle-like or flat structures. The spherical shape for the surface of polar heads allows for more volume and thus relatively greater entropy of the counterions [18, 19]. In addition, as noted in the previous section and as we emphasize in the following section, the chain contributions to the bending energy scale with powers of the chain length. Thus, crudely speaking, one must compare the interlayer spacing or the screening length for the charged head-group electrostatic contributions with the chain length for the tail contributions to determine whether the bending modulus is dominated by the heads or chains.

Finally, we note that these results depend parametrically on the packing density of the fixed charge and hence of the polar head groups; here we have taken this quantity to be constant. In practice, the free energy should be further minimized with respect to fluctuations in the area per

molecule; this results in a downwards renormalization of the bending modulus as we have previously shown.

C. Polymeric Amphiphiles: Chain Contributions

While the previous discussion of the electrostatic contribution to the bending energy is applicable to strongly charged systems, one expects that for non-ionic surfactants (or even zwitterionic surfactants where there is a permanent dipole moment of the polar head group, but no large spatial separation between the charges), the contributions of the hydrocarbon chains will dominate the bending modulus; the polar head groups will enter in providing packing constraints on the area per molecule, Σ , but the bending response of the thin film, will be mostly that of the tail region.

Detailed treatments of the response of both grafted polymer chains [11] and block copolymers [4, 20] to bending have been presented. Here, for simplicity, we use scaling arguments to relate the transverse pressure distribution in the polymeric layer to the bending moduli. As in the previous section, the bending modulus scales as the product of the transverse pressure difference and the cube of the relevant length scale. The transverse pressure itself scales as the free energy per unit volume.

We begin by considering a grafted polymer layer in a good solvent with area per molecule, Σ which at this point we regard as being fixed. The free energy consists of two contributions: (i) the excluded volume interactions of the polymeric segments with each other which scales (in a good solvent) like $vc(z)^2$, where $c(z)$ is the local concentration of monomers and v is the excluded volume per monomer (ii) the stretching energy of the chains which increases quadratically with the extent (distance from the grafting surface to the chain end) of each chain. The balance of these two terms yields [3, 21] a parabolic density profile [11, 21] with

$$c(z) = \frac{1}{v} \left(d_0 - \frac{1}{2} \left(\frac{z}{Na} \right)^2 \right), \quad (3.12)$$

where N is the number of monomers in the chain and a is the monomer size. The constant d_0 scales like $1/\Sigma^{2/3}$. The grafted chains are thus seen to deviate sharply from those of free chains in good solvents where the extent of the chains scales as $N^{1/2}$ and the chains are stretched with an extent that scales linearly with N . Thus the relevant length scale over which there is a significant transverse pressure difference scales linearly with N and we therefore expect the bending moduli to scale like N^3 (since the pressure itself is a function of z/N).

As mentioned above, however, the area per molecule does relax to minimize the total free energy and this reduces the effective bending modulus compared with the case where the area is fixed (irreversibly grafted chains). In the case where the polar groups by their own packing strongly dictate a particular value of Σ which is unrelated to the chain length, we still expect the chain contribution to the

bending modulus to indeed scales as N^3 . If the head groups provide only a dividing surface between the water and oil at which one must account for the interfacial tension, one can minimize the sum of the chain free energy (which depends on both Σ and N and the interfacial energy (which scales linearly with Σ) to find the optimal value of Σ which will now depend on the chain length.

This calculation can be performed for various cases, using the more quantitative theory for the polymer concentration profile described in Ref. [11, 20]. The results, are given for the case of a block copolymer with a total of N segments with identical persistence lengths and excluded volume parameters but where the A (B) block has N_A (N_B) segments so that $N = N_A + N_B$. One can think of the A block as being the "head" and the B block as the tail of this amphiphilic surfactant. We characterize the asymmetry of the "head-tail" packing by $\varepsilon = (N_B - N_A)/N$ and define the interfacial tension relative to $k_B T$ between the water and oil as γ . We take all the microscopic parameters – persistence length, excluded volume – to scale with the same microscopic length, a . The moduli and spontaneous curvature are then given for two different cases to lowest and order in ε , for small asymmetry (for more details see [20]):

(1) For the case of a block copolymer in a good solvent:

$$k = 0.0881 T \gamma^{9/11} N^{24/11} \quad (3.13)$$

$$\bar{k} = -0.0499 T \gamma^{9/11} N^{24/11} \quad (3.14)$$

$$c_0 = 3.853 \varepsilon \gamma^{-2/11} N^{-9/11} / a \quad (3.15)$$

(2) For the case of a block copolymer melt (no penetration of the solvent into the block copolymer layers) the results are similar but with somewhat different scaling exponents:

$$k = 0.067 T \gamma^{4/3} N^{5/3} \quad (3.16)$$

$$\bar{k} = -0.053 T \gamma^{4/3} N^{5/3} \quad (3.17)$$

$$c_0 = 2.134 \varepsilon \gamma^{-1/3} N^{-2/3} / a \quad (3.18)$$

These results provide us with a "microscopic" model for a system of interacting chains which can be used to estimate the bending moduli from the first principles of the polymer statistics. The theory can be extended to treat the case of mixed chains and provide insight into how the interactions between long and short chains can dramatically modify the bending moduli; these ideas have been used to suggest a mechanism for spontaneous vesicle formation in mixed chain systems [13].

IV. Experimental Tests

In this section, we briefly review several experimental tests on the influence of the curvature energy on the properties of microemulsions. While microemulsions exhibit a wide variety of interesting morphologies and phases, the

simplest case is where the domains are spherical and the system can be pictured as consisting of a nearly monodisperse set of spherical droplets. This picture is applicable to systems with relatively large spontaneous curvatures of the monolayer and large bending moduli. Since the structure is simple in these cases, one can study these systems more quantitatively to see if the properties reflect in an unambiguous way the determining influence of the curvature energy. Here we present two examples whereby the scaling of experimentally measurable quantities with drop size provide strong evidence for the relevance of the bending energy (and not the stretching energy) to large-scale microemulsions. More recent work [22] has shown that the unusual closed-loop phase diagrams [23] observed in non-ionic systems can be explained by a model which incorporates both the bending energy and interactions between droplets, but this is outside the scope of the present paper.

A. Emulsification Failure:

Drop Size and Interfacial Tension

While the presence of a spherical phase of droplets cannot by itself either prove or disprove the dominance of the bending energy in determining the properties of microemulsion, the transitions from a single phase to multiphase coexistence can be an important indicator. Neglecting fluctuations in the droplet size and shape (fluctuations of the nearly spherical droplets are discussed in the next subsection), conservation of the internal phase (to be specific we shall assume it is water) and the surfactant with volume fractions ϕ_w and ϕ_s respectively, imply that the radius of the spherical droplets is given by $R = 3\delta\phi_w/\phi_s$, where δ is a typical surfactant size. This conservation law neglects changes in the area per molecule with curvature which gives higher order corrections to this law (or order δ/R) and the observation of a nearly linear increase of the drop size with increasing ratio of ϕ_w/ϕ_s is one indication of the fact area per molecule is nearly equal to its value in the flat film. Naturally, this approximation breaks down when R/δ becomes of order unity, but as mentioned at the outset, we focus on the properties of microemulsions with large domain sizes compared to molecular scales.

For a phase of spherical droplets, the conservation laws determine the drop size; the bending energy enters in setting an optimal droplet size. Minimization of Eq. (1.1) with respect to the curvature indicates that the optimal drop size, R^* is proportional to c_0^{-1} ; the spontaneous curvature sets the drop size which minimizes the bending free energy. Thus if $R < R^*$, the system has no choice but to keep a uniform phase of spherical droplets (when R differs significantly from R^* other shapes are possible [3]); but when $R > R^*$, the droplets cease to grow and expel the excess inner phase (e.g. water) into a coexisting phase. This has been termed an emulsification failure instability [24]. The simple picture described here is somewhat modified by contributions coming from the fluctuations of the droplet shape, the entropy of mixing, and possible (weak) interactions between the

droplets, but in the limit of large bending moduli ($k \gg k_B T$) our approximations do apply.

Thus, the bending energy predicts a maximum drop size with a two-phase equilibrium with the excess internal phase. On the triangular phase diagram, this phase boundary which occurs when $R \sim \phi_w/\phi_s \sim c_0^{-1}$ should be a straight line. The droplet size at emulsification failure is a measure of the spontaneous curvature. Measurements of the drop size along the phase boundary for the coexistence of nearly spherical microemulsion drops with excess internal phase (oil) in non-ionic systems [25] indicates that the spontaneous curvature varies linearly with temperature in this regime. For these systems, it appears that corrections to the linear phase boundary due to entropy of mixing effects are small.

The observation of such a straight line phase boundary is therefore an indication of the validity of this picture. A consistency check consists of measurements of the interfacial tension between the microemulsion (in our example, water-in-oil) of optimal droplets with the excess phase (water, in our example). This interface would have a monolayer of surfactant and the tension is just the energy to make more flat interface from the preferred droplets — i.e. the bending energy cost of a flat interface in a system with a strong spontaneous curvature. This energy cost per unit area is just proportional to $(k - 2\bar{k})/R^2$. Thus measurements of the tension as a function of droplet size are predicted to have an inverse square relationship due to the bending energy.

Recent experiments [17, 26] using both scattering techniques and interfacial tension measurements have shown that a variety of microemulsion forming non-ionic surfactants obey the scaling relationship $\gamma \sim 1/R^2$. In addition, the bending moduli extracted [17] from the dependence of this relationship on k and \bar{k} is consistent with the moduli deduced from analysis of the neutron scattering spectra for fluctuating microemulsion droplets.

B. Dynamical Fluctuations of Droplet Microemulsions

Another manifestation of the curvature energy of microemulsions occurs in the response of droplets to thermal fluctuations. Even though the equilibrium droplet shape may indeed be spherical, thermal fluctuations cause deviations from this configuration. The restoring force which resists the fluctuations (which of course increase the entropy of the film and hence of the system as a whole) will determine the ultimate amplitude and dynamics of these corrugations. The theoretical details are outlined in Refs. [27, 28]. The bending energy model predicts a particular response of the droplets to fluctuations and this manifests itself in characteristic neutron scattering spectra which measure the density fluctuations of the system.

In general, the comparison of theory and experiment is complex; however, there is an interesting scaling relationship that is predicted by the curvature energy model that can be compared in a simple way with some dynamical experiments. The dynamical response of the droplets to ther-

mal undulations can be shown to result in a characteristic frequency (ω , that is the inverse of a characteristic time scale for a corrugation of the droplet shape to decay), that obeys:

$$\omega_{lm} = \frac{k}{\eta R^3} g_b(l, m) \quad (4.1)$$

Here the fluctuation mode is characterized by the indices (l, m) which correspond to the spherical harmonic decomposition of the droplet shape, and $g_b(l, m)$ is a function of these indices [28] and is characteristic of the fact that the droplet is responding by bending without stretching. In Eq. (4.1), k is the bending modulus, η the viscosity of the water and oil, and R is the droplet radius. The relationship between the characteristic frequency and the droplet radius can be obtained from dimensional analysis, provided, one accepts the bending energy model. For example, if the drops were to deform and stretch (a mode which causes a change in the area per molecule)

$$\omega_{lm} = \frac{\gamma}{\eta R} g_s(l, m), \quad (4.2)$$

where now ω is predicted to vary inversely with the droplet size and linearly with the surface tension ($g_s(l, m)$ is a function of the indices (l, m) that is again characteristic of a stretching response of the droplet).

Thus, a study of the dependence of the characteristic frequency on the drop size can determine whether the primary restoring force at that time scale is bending without stretching or simple stretching deformations. Experimental results [29] for AOT/water/decane microemulsions with drop sizes $27.5 \text{ \AA} < R < 70 \text{ \AA}$ indicate that the characteristic frequency observed in dynamical neutron scattering varies with the inverse of the cube of the radius, consistent with a model of a nearly incompressible surfactant monolayer with bending modes.

This work was supported by the Minerva Foundation, the Israel Academy of Arts and Sciences, and the Israel-French collaborative program supported by the Israel Ministry of Science.

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Presented at the Discussion Meeting of the Deutsche Bunsen-Gesellschaft für Physikalische Chemie "Microemulsions - Experiment and Theory" in Göttingen, September 4th to September 6th, 1995 E 9093