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Fluctuations of spherical microemulsions

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A statistical model for microemulsions is used to study the stability of a single phase of spherical droplets to thermal fluctuations. The amplitude of size ($l = 0$ spherical harmonics) and shape ($l = 2$) fluctuations are calculated as a function of the concentration and temperature. The divergences in these fluctuations are shown to define a range of stability for the spherical droplet phase.

I. INTRODUCTION

Microemulsions are multicomponent fluids which are characterized by equilibrium globular, domain, or networklike arrangements of the components on length scales of ~ 100 Å.¹ Although several recent studies²⁻⁷ have focused on the phase separation behavior of these systems, the equilibrium structures in the one-phase regimes have not yet been completely determined. In particular, most treatments of idealized, three-component microemulsions consisting of oil (volume fraction v_o), water (volume fraction v_w), and surfactant (volume fraction v_s) assume a monodispersed solution of spherical droplets, coated with a surfactant layer (for $v_s \ll v_{o,w}$).²⁻⁵ However, recent neutron scattering studies^{6,8} have indicated departures from this picture of monodispersed spheres. It is precisely these size and shape degrees of freedom which are the focus of this work, since they differentiate microemulsions from systems whose behavior is solely determined by the interactions between rigid units.

In this paper, a continuum, statistical model is presented for microemulsions in the one-phase region. The model is used to calculate the thermally induced size and shape fluctuations of spherical microemulsions as a function of concentration and temperature. The present work assumes that the microemulsion structure is globular and questions of percolation or bicontinuous⁹ structures are not addressed. In addition, fluctuations due to phase separation instabilities will be treated in a future publication. Here, it is shown that in the limit of vanishing natural curvature, shape fluctuations of the spheres with d -wave ($l = 2$ spherical harmonic) symmetry are dominant. In this limit, polydispersity effects due to simple size fluctuations ($l = 0$) as well as more complex shape fluctuations ($l > 2$) are small. Results are also presented for finite values of the natural curvature, and it is shown that there exists a range of stability for the nearly spherical phase, which is calculated as a function of the concentrations and temperature.

A general treatment of even an idealized, three-component microemulsion would have to consider nine possible interactions between the oil, water, and surfactant molecules. In order to study the statistical mechanics without introducing so large a number of parameters, the following energy scale (relative to kT) is assumed for the interactions:

- (i) Oil/water, water/surfactant-aliphatic-tail, and

oil/surfactant-polar-head interaction energies are large and repulsive;

(ii) Water/water, oil/oil, water/surfactant-polar-head, oil/surfactant-aliphatic-tail interaction energies are large and attractive;

(iii) Elastic interaction energies between the surfactant molecules are large and are replaced by a constraint of fixed volume per surfactant, which may be weakly temperature dependent;

(iv) Orientational interactions between surfactants are the smallest energies in the problem.

This scale is also assumed by Talmon and Prager⁹ in their theory. The present work differs from their treatment in that here, a detailed calculation of the bending energy for general shapes is presented. The approach of Ref. 9 is more appropriate to the region of equal oil and water concentrations where well-defined globules may not exist. The present work is most applicable to the dilute regime, and focuses on the size and shapes of the globules which are well defined in this regime.

If the energies (i)–(iii) are taken to be infinite, the surfactant molecules are constrained to lie at the interface between pure oil and pure water regions. Hence, the possibilities of micellar arrangements of surfactants are not treated within this model. With these simplifications, the statistical mechanical problem is reduced to the order and fluctuations of these interfacial regions, as treated in the following section.

II. CALCULATION OF FLUCTUATION AMPLITUDE

In this section, the free energy for microemulsions is calculated in terms of the bending energy of the interface H and the configurational entropy S ($F = H - TS$). From F , the amplitude of the size and shape fluctuations of nearly spherical microemulsions is derived. The orientational or bending energy can be written for a set of N general interfaces as

$$H = 4K \sum_{i=1}^N \int dS_i \left(\frac{1}{\rho_i(r)} - \frac{1}{\rho_i} \right)^2, \quad (1)$$

where S_i is the area of the i th interface. The normal (\hat{n}) to the interface is equivalent to the local orientation of the surfactant molecule and the local radius of curvature is $\rho(r) = 2[\nabla \cdot \hat{n}(r)]^{-1}$ (see note added in proof). The tendency for the interface to locally bend to either the oil or water region is accounted for by the parameter

ρ_1 which is the "natural" bending radius of the interface. The sign of ρ_1 determines the predisposition to forming oil-in-water or water-in-oil globules. The convention taken here is for positive radii of curvature to respect oil-in-water globules.

Here it is noted that for $\rho_1^{-1} = 0$, Eq. (1) is identical to the splay energy for a single layer of a smectic liquid crystal where K is typically 0.1 eV,¹⁰ although the addition of cosurfactants or the variation of the salinity of the water can reduce this value for K .¹¹ Previous thermodynamic treatments have also considered the bending energy described by Eq. (1).^{2-4,10} However, those studies have assumed a particular structure, in contrast with the statistical approach presented here which uses Eq. (1) to test the stability of an arbitrary structure to fluctuations [see Ref. 11 for a treatment of the lamellar phase].

The bending energy [Eq. (1)] must be supplemented by constraints on the total number or volume fractions of two of the three microemulsion components ($v_o + v_w + v_s = 1$). In particular, if Eq. (1) is used to investigate the stability of oil droplets in a water rich phase ($v_s < v_o < v_w$), the total surface area of and volume enclosed by the droplets is fixed. Furthermore, Eq. (1) must be supplemented by terms which represent the direct (e.g., van der Waals) and entropic interactions between the droplets as discussed below.

For nearly spherical droplets, the equation which defines the surface of the i th droplet with its center at the origin, is

$$R_i(\mathbf{r}) = r - \bar{\rho}[1 + g_i(\theta, \phi)] = 0, \quad (2)$$

where $\bar{\rho}$ is the average droplet radius which is independent of angle and the index i . To second order in the deviation from monodispersed spheres $\{g_i\}$, the bending energy [Eq. (1)] can be written [see the Appendix for details of Eqs. (3)-(6)]

$$H = 4K \sum_{i=1}^N \int d\Omega \left[\left(1 - \frac{\bar{\rho}}{\rho_i}\right)^2 (1 + g_i \bar{g}_i) + \bar{g}_i (\bar{g}_i - 2g_i) + \left(\frac{\bar{\rho}}{\rho_i}\right)^2 g_i^2 \right], \quad (3a)$$

where

$$\bar{g}_i = \frac{1}{2} L^2 g_i. \quad (3b)$$

In Eq. (3), $d\Omega$ is the differential solid angle, and the operator L^2 is the negative of the angular part of the Laplacian in spherical coordinates. Linear terms in the $\{g_i(\theta, \phi)\}$ sum to zero in H , by definition of $\bar{\rho}$ as the average value.

Since it is expected that the entropy of dispersion and interactions between the globules should be relatively insensitive to their shapes, the entropy is computed in a mean-field model for hard spheres whose volume is the average globular volume. Thus, for volume fraction of globules x , (e.g., for oil droplets in water $x = v_o + \frac{1}{2}v_s$),¹² the configurational entropy $S = Nh(x)$ where

$$h(x) = -\ln x + [1 - (1/x)] \ln(1 - x). \quad (4)$$

Direct interactions between the spheres can also be considered in a similar manner. However, the main

conclusions are much more sensitive to the bending energy than to the detailed form of the entropy or the interactions.

The dimensionless fluctuation amplitudes $\{g_i\}$ are expanded in spherical harmonics as¹³

$$g_i(\theta, \phi) = \sum_{l \neq 1} a_{lm}^i Y_{lm}(\theta, \phi). \quad (5)$$

In the single phase region, the constraint of the constant area and volume enclosed by the globules implies,

$$n \approx n_0 \left[1 - \frac{3}{4\pi} \sum_{lm} \langle |a_{lm}^i|^2 \rangle (b_l - 1) \right] \quad (6a)$$

$$\bar{\rho} \approx \rho_0 \left[1 + \frac{1}{4\pi} \sum_{lm} \langle |a_{lm}^i|^2 \rangle (b_l - 2) \right], \quad (6b)$$

where

$$\langle |a_{lm}^i|^2 \rangle = \frac{1}{N_0} \sum_{i=1}^{N_0} \langle |a_{lm}^i|^2 \rangle, \quad b_l = \frac{1}{2}l(l+1), \quad \text{and } N_0 = n_0 V,$$

with V being the total volume of the system. In Eq. (6), n_0 and ρ_0 depend on the concentrations through $n_0 = x/36\pi \times (v_s/\delta x)^3$ and $\rho_0 = 3\delta x/v_s$, where δ is the characteristic length of the surfactant molecule. It is to be noted that the entire model is meaningful only in the limit of oil/water globules with surfactants at the interface, i.e., $\delta < \rho_0$.

These constraints are used in Eq. (3) to change the sum over $N = nV$ globules (where n is a function of the fluctuation amplitudes) to a sum over $N_0 = n_0 V$ globules, where n_0 depends only on the concentrations. Defining $\tau = 3T/4\pi K$, the free energy $F = H - TS$ is given by

$$F = F_0 + K \sum_{lm} \langle |a_{lm}^i|^2 \rangle \Delta F_l, \quad (7a)$$

with

$$\Delta F_l = -\tau h(x)(1 - b_l) + 4(3 - 4b_l + b_l^2) + 8\left(\frac{\rho_0}{\rho_1}\right)(b_l - 1). \quad (7b)$$

F_0 is the free energy of a monodispersed set of spheres with radius ρ_0 and density (number of spheres per unit volume) n_0 , so

$$F_0 = N_0 \left[16\pi K \left(1 - \frac{\rho_0}{\rho_1}\right)^2 - T h(x) \right]. \quad (7c)$$

Equipartition and Eq. (7a) imply that the average value of the fluctuation, $\langle |a_{lm}^i|^2 \rangle$ is given by

$$\langle |a_{lm}^i|^2 \rangle = \frac{2\pi}{3} \tau / \Delta F_l.$$

III. DISCUSSION

In the limit $\rho_1 \rightarrow \infty$, Eq. (7) indicates that fluctuations with $l=2$ have large, temperature independent amplitudes, while fluctuations with $l=0$ (polydispersity) or $l > 2$ have small amplitudes for values of $K \sim 0.1$ eV and T near room temperature. This is shown as Fig. 1 where the mean square amplitude of the $l=2$ fluctuations, is plotted as a function of the concentration of globules. For $l=0$ and $l > 2$, the fluctuation amplitudes are much smaller except for the $l=0$ fluctuations at temperatures or K values such that $\tau = 0.5$, which have

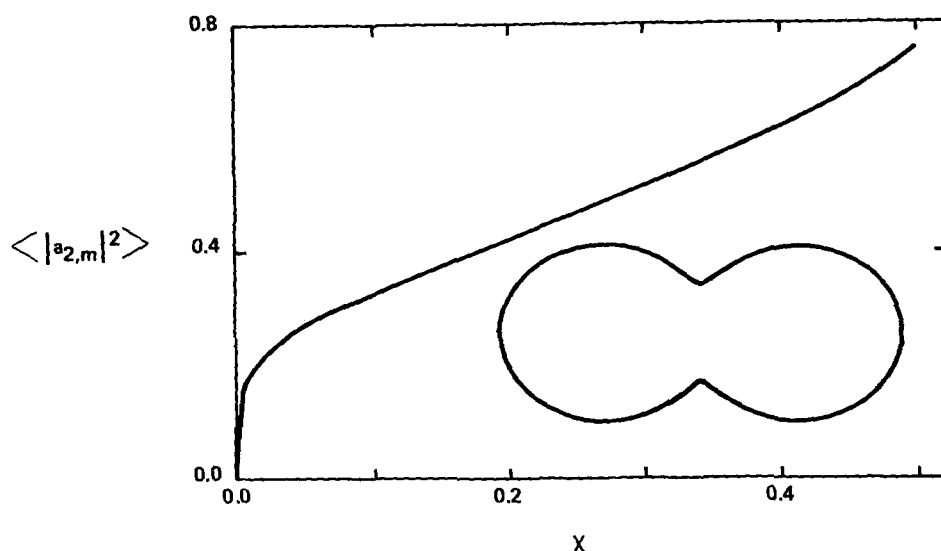


FIG. 1. The dimensionless amplitude of the $l=2$ fluctuations as a function of the concentration of globules x . A sketch of a sphere with a perturbation of $l=2$, $m=0$ symmetry is shown for $a_{20}=1$. The value of ρ_1^{-1} is zero.

normalized amplitudes $\sim 10\%$ for $x > 0.1$. Although results are shown for concentrations of droplets up to 0.5, the present model is only expected to be applicable at relatively small values of the concentration where bicontinuous effects are not important. Furthermore, for some values of x , the system may be unstable to phase separation, whose consequences will be treated in future studies.

The origin of the large amplitude of the $l=2$ shape fluctuations, in the limit $\rho_1 \rightarrow \infty$, is the vanishing of the energy cost of those modes. Although the bending energy is increased by the deviations from spherical symmetry, this increase is cancelled by the decrease in the total bending energy due to the change in the number of globules (relative to the purely spherical case), which is dictated by the constraints. Thus, the $l=2$ modes only increase the entropy of the system, resulting in a relatively large, temperature independent fluctuation amplitude. For the other modes, the scaled temperature τ is small for typical values of T and K , so the finite increase in bending energy of those modes results in a small fluctuation amplitude.

The effects of finite values for ρ_1 are shown in Fig. 2 where the normalized fluctuation amplitude is plotted as a function of ρ_0/ρ_1 for various values of x and T . The $l=0$ fluctuations diverge in amplitude at $\rho_0/\rho_1 \approx 1.5$, almost independent of T and x . As above, the $l=2$ fluctuation amplitudes are large for small values of ρ_0/ρ_1 , and diverge at small negative values of ρ_0/ρ_1 .¹⁴ All other modes with $l > 2$ have small fluctuation amplitudes. The divergences of the $l=0$ and $l=2$ modes at values of $\rho_0/\rho_1 \approx 0$ and 1.5, respectively, determine the range of stability of the picture of nearly spherical globules. It is interesting that this stability is approximately determined by the single parameter ρ_0/ρ_1 , which can be varied by changing the concentrations ($\rho_0 \sim x/v_s$), or by changing materials parameters (e.g., salinity, type of surfactant molecule), thus varying ρ_1 .

In conclusion, the size and shape fluctuations of microemulsion globules have been studied as functions of concentration, temperature, and the natural radius of curvature. For small values of the natural curvature of the interfaces, $l=2$ shape fluctuations are large due to their small energy cost. For $\rho_0/\rho_1 \approx 1.5$, the polydispersity

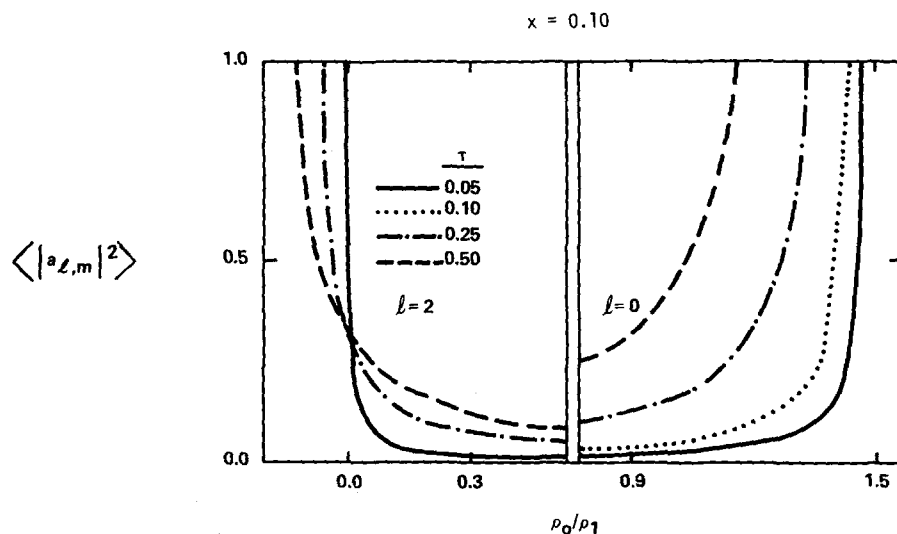


FIG. 2. The dimensionless amplitude of the $l=2$ and $l=0$ fluctuations as a function of the ratio ρ_0/ρ_1 for $x=0.1$ and for various reduced temperatures $\tau=3T/4\pi K$ (Ref. 14).

($l=0$ fluctuations) diverges. These values limit the range of stability of the nearly spherical picture. Although there is some experimental evidence for non-spherical globules,⁸ more detailed experiments as functions of concentration and temperature are desirable. Finally, it is noted that variation of materials parameters, such as salinity, could have different effects on K and ρ_1 . Thus, comparison of theory with experimental studies which vary these parameters (instead of temperature and concentration) can be complicated.

Note added in proof: The orientational splay in Eq. (1) depends on the (local) mean curvature of the surface. In principle, The Gaussian curvature of the surface can enter through "saddle-splay" terms.^{15,16} While these latter are unimportant for liquid crystals and lipid bilayers,¹⁶ they may have interesting effects for microemulsions.¹⁷

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APPENDIX

In this Appendix, the details leading to Eqs. (3)–(6) are given. The bending energy [Eq. (1)] for a single globule is

$$H = K \int dS \left[\nabla \cdot \hat{n} - \frac{2}{\rho_1} \right]^2, \quad (\text{A1})$$

where \hat{n} is the normal to the surface S and the constants ρ_1 and K are defined in the main body of the paper. For a globule with its center at the origin, and its surface defined by

$$R(r) = r - \bar{\rho}[1 + g(\theta, \phi)] = 0 \quad (\text{A2})$$

with (r, θ, ϕ) the usual spherical coordinates. The normal is

$$\hat{n} = \frac{\nabla R(\mathbf{r})}{|\nabla R(\mathbf{r})|} = \frac{\hat{r} - \xi g_\theta \hat{\theta} - \frac{\xi}{\sin \theta} g_\phi \hat{\phi}}{\left[1 + (\xi g_\theta)^2 + \left(\frac{\xi}{\sin \theta} g_\phi \right)^2 \right]^{1/2}}, \quad (\text{A3})$$

where $\xi = \bar{\rho}/r$ and $g_\theta = (\partial g / \partial \theta)$.

To second order in g (the deviation from a sphere with radius $\bar{\rho}$),

$$\nabla \cdot \hat{n} \approx \frac{2}{r} \left[1 - \frac{\xi}{2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} g_\theta \sin \theta + \frac{1}{\sin^2 \theta} g_\phi \right) \right], \quad (\text{A4})$$

where r is evaluated at $r = \bar{\rho}(1 + g)$.

To second order in g , the area element dS is given by

$$dS = d\Omega \left[1 + \frac{\xi^2}{2} \left(g_\theta^2 + \frac{g_\phi^2}{\sin^2 \theta} \right) \right] r^2, \quad (\text{A5})$$

where $d\Omega = d[\cos(\theta)] d\phi$. Writing

$$L^2 = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) - \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (\text{A6})$$

one obtains the result

$$H = 4K \int d\Omega \left[1 + \frac{1}{2} \left(g_\theta^2 + \frac{g_\phi^2}{\sin^2 \theta} \right) \right] \left[\left(1 - \frac{\bar{\rho}}{\rho_1} \right) + \frac{\xi L^2 g}{2} - \frac{g \bar{\rho}}{\rho_1} \right]^2. \quad (\text{A7})$$

The energy H is expanded to second order in g and the relation

$$\int \left(g_\theta^2 + \frac{g_\phi^2}{\sin^2 \theta} \right) d\Omega = \int g L^2 g d\Omega \quad (\text{A8})$$

is used. Summing over the N globules, Eq. (3) is obtained.

Equations (6a) and (6b) are derived from the constraints on the volume of globules ($x = v_s/2 + v_o$) and surfactant (v_s), with

$$v_s = \frac{\delta}{V} \sum_{i=1}^N \int dS_i \quad (\text{A9})$$

$$x = \frac{1}{V} \sum_{i=1}^N \int dV_i \quad (\text{A10})$$

where dS_i and dV_i are the surface and volume elements of the i th globule, and δ is the length of the surfactant molecule. It is assumed $v_o > v_s$. The volume element is related to dS by the divergence theorem so that for a droplet with its center at the origin,

$$dV = \frac{1}{3} (\mathbf{r} \cdot \hat{n}) dS. \quad (\text{A11})$$

Using the previous expression for the normal \hat{n} , it is found that to second order in $\{g_i\}$,

$$x = n \frac{4\pi \bar{\rho}^3}{3} \left[1 + \frac{3}{4\pi N_0} \sum_{i=1}^{N_0} \int g_i^2 d\Omega \right], \quad (\text{A12})$$

$$v_s = n 4\pi \delta \bar{\rho}^2 \left[1 + \frac{1}{4\pi N_0} \sum_{i=1}^{N_0} \int (1 + \frac{1}{2} L^2) g_i^2 d\Omega \right]. \quad (\text{A13})$$

These equations for x and v are solved for n and $\bar{\rho}$ to yield Eqs. (6a) and (6b).

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¹²The volume of the surfactant is split between the interior (e.g., oil) and continuous (e.g., water) phases.

¹³ $l=1$ fluctuations represent translations of the centers of mass of the droplets and hence are excluded.

¹⁴Negative values of ρ_1 indicate that the natural curvature favors droplets of the opposite phase, e.g., water in oil droplets, even though $v_w \gg v_o$.

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