

# Length Scale for Configurational Entropy in Microemulsions

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In this paper we study the length scale that must be used in evaluating the mixing entropy in a microemulsion. The central idea involves the choice of a length scale in configuration space that is consistent with the physical definition of entropy in phase space. We show that this scale may be sensitive to the model employed in the description of a microemulsion, but that in most cases it is of the order of the cube root of the average molecular volume in the system. We also show that other much larger length scales used by workers in the field can be partially reconciled with the fundamental scale through a consideration of the constraints to which the microemulsion is subject. We have attempted to perform the analysis in as rigorous a manner as possible. Many interesting features appear and the importance of using the correct length scale as well as methods (some of which are extensions of current theory) for incorporating it into theories of microemulsions are discussed.

## 1. General Introduction

### Physical Entropy

The purpose of this paper is to explore the general problem of configurational entropy, focusing on microemulsions as a relevant and important example. In the present section we define configurational entropy as a *part* of the total entropy of the system that (for whatever reason, but usually as a result of working within a model) must be evaluated in *configuration* space alone. To evaluate this entropy it is necessary to introduce a length scale that distinguishes between different physical states in configuration space. This length scale must be chosen in a manner consistent with the fundamental *physical* definition of entropy in *phase* space.

The evaluation of "configurational entropy" presents a special problem in statistical mechanics since it must always be *defined* . . . usually within the context of a model. The problem is often exacerbated because the model requires the evaluation to be performed in configuration space whereas the fundamental *physical* definition of entropy makes use of the full phase space of the system. Moreover, the models are usually not only mesoscopic, but involve considerable renormalization in the process of which the order of averaging may be inverted.

The so-called mixing entropy in microemulsions forms an example of configurational entropy and the models employed in the prediction of the thermodynamic properties of microemulsions are more often than not mesoscopic.

In statistical mechanics, in the microcanonical ensemble, the *total* entropy (physical entropy) of a system is defined in terms of the number of quantum states of the system consistent with its macroscopic state (of fixed energy). In the phase space representation (in the classical or semiclassical limit) this number of states is associated with a particular volume of phase space. Since, in the semiclassical limit, the dynamical state of the system is described by a set of con-

tinuous coordinates of position and momentum, it is necessary to introduce a "length" scale capable of resolving distinct physical states. For the total entropy, using the phase space representation, there is a natural length (of action) scale that serves this purpose. This is of course Planck's constant that measures the extent (in one degree of freedom) of a particular state.

As indicated above, the phenomenological models within which configurational entropy (forming only a *part* of the total entropy) is defined require it to be evaluated within configuration space alone and not within the full phase space of the system! As a result one cannot appeal directly to Planck's constant as a length scale, and some less direct means must be employed to insure physical consistency.

Often this length scale is ignored, on the basis that one is concerned only with entropy *difference* between two thermodynamic states, a difference that involves the logarithm of the ratio of numbers of configurations. Then the length scale may cancel out of the ratio if it is independent of state, and one is content to work with a ratio of continuous integrals, e.g. configuration integrals of the type that appear in semiclassical partition functions, and which are assumed to be proportional to the numbers of configurations. Unfortunately, the length scale may *not* be independent of the state of the system. Furthermore, the counting of "patterns" alone may, depending on the scale used to resolve them, provide only an *information theoretic* entropy.

An obvious method to avoid this dilemma (at least in principle) involves the choice of a length scale for the resolution of patterns, such that when the configurational entropy based on it is added to the remaining entropy, the sum yields the true *total* physical entropy. This leaves the possibility that the length scales for different models of the *same* system will be different. The length scale is therefore not absolute.

A concrete example of these ideas involves a droplet type microemulsion, and is due to Overbeek and coworkers [1]. Fig. 1.1 is helpful in describing it. On the left we show a droplet type microemulsion in which the drops are water, and the continuous phase is oil. However the drops are all hanging from syringes so they are fixed in space. The drops are assumed large enough to have the intensive properties of

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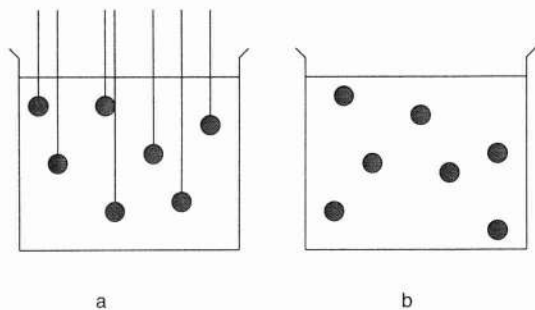


Fig. 1.1  
Droplets hanging on ‘tips of microsyringes’ (a) and droplets that are free to move through the whole system (b)

bulk water and the same is true for the continuous phase. The surfactant monolayer that covers the drops is considered to be an incompressible, elastic surface, having the same chemical potential as it has in a reservoir of pure bulk surfactant. Then the Gibbs free energy of the system on the left is prescribed by

$$G' = N_1\mu_1 + N_2\mu_2 + N_s\mu_s + \sigma A, \quad (1.1)$$

where  $\mu_1$ ,  $\mu_2$  and  $\mu_s$  are the chemical potentials of pure bulk oil, water, and surfactant respectively and  $N_1$ ,  $N_2$  and  $N_s$  are the corresponding total numbers of oil, water, and surfactant molecules in the microemulsion phase.  $\sigma A$  is the interfacial free energy with  $\sigma$  the interfacial tension and  $A$  the area of the total oil-water interface. All interactions between oil, water, and surfactant are accounted for by the interfacial free energy.

If the drops are released from the syringes that immobilize them, so that the picture on the right of Fig. 1.1 applies, they can adopt a continuum of configurations with which mixing entropy will be associated. The full free energy of the unconstrained microemulsion can then be expressed as

$$G = N_1\mu_1 + N_2\mu_2 + N_s\mu_s + \sigma A - TS_{\text{mix}}. \quad (1.2)$$

We neglect, for simplicity, the pressure differences associated with the movements of the drops, since this only leads to slightly different values of the chemical potentials. What is important is that  $S_{\text{mix}}$  is *defined* and makes its appearance because of the nature of the model.

It should be noted that, if the drops in Fig. 1.1 are of different sizes (polydisperse), only those of *one* size could (according to the Gibbs-Thomson relation [2]) be in equilibrium with the surrounding phase. However entropy of mixing when it is large enough, offers the possibility of stabilizing the *total* system by reducing the system free energy. This collective phenomenon can be employed as one means of defining the mesoscopic regime for drops or other small systems.

In the simple case in which there were  $n_d$  drops all of the same size one might first think of evaluating  $S_{\text{mix}}$  by calculating a configuration integral  $Z_D$  corresponding to

the continuum of drop configurations, but as indicated earlier, it is then necessary to convert  $Z_D$  to a pure number  $\Gamma$  through division by the volume  $l^{3n_d}$ , where  $l$  is some length scale. Then

$$\Gamma = Z_D/n_d!l^{3n_d}. \quad (1.3)$$

Division by  $n_d!$  removes configurations obtained by merely permuting identical drops. The ‘entropy of mixing’ is then

$$S_{\text{mix}} = k \ln \Gamma. \quad (1.4)$$

Even if  $l$  can be determined, the problem is not completely solved. In  $G'$ , corresponding to the left of Fig. 1.1, all of the degrees of freedom of the  $N_1 + N_2 + N_s$  molecules in the system have already been utilized, at least in part. In proceeding to the system on the right, the same degrees of freedom must be further utilized and care must be taken to insure that, in the evaluation of  $Z_D$ , they are not used redundantly.

At this point, it is convenient to mention some features of  $S_{\text{mix}}$  that we shall address in further detail later. The first concerns the issue of *polydispersity* and its effect on the mixing entropy. In the example to which Eqs. (1.3) and 1.4) refer, the drops were monodisperse. However if they were polydisperse the different sized drops could be permuted among the syringes to yield *distinct* configurations and therefore some mixing entropy. This would be achieved without allowing the drops to occupy a continuum of positions. Allowing the continuum would lead to an even larger mixing entropy. Later, in Sect. 4, we shall demonstrate the interesting result that the entropy associated with the permutation of drops among syringes *determines* the polydispersity, i.e. the *shape* of the size distribution while that associated with the continuum of positions determines the *height* of the distribution, i.e. the drop population.

Another feature that we mention, at this time, is the fact that the mixing free energy  $-TS_{\text{mix}}$  may not always be easily separated from the surface free energy. The possibility of such nonseparability may be clarified by the following consideration. The mixing entropy can be regarded as originating in the multitude of configurations available to the extended (total) interface in the system. However, this interface can ‘wander’ on a truly microscopic (molecular) level. Such microscopic wanderings are included in the interface entropy that forms a part of the interface free energy or surface tension. The *mixing entropy* is associated with the more coarse grained mesoscopic wanderings of the interface. In many systems the separation of these two scales of surface deformation is relatively easy, but in others it may not be.

What strategies are available for the determination of a length scale consistent with the phase space definition of entropy? The most direct and reliable approach would involve a method that refers the problem back to phase space where the definition of entropy is unambiguous. Although this method cannot always be applied with precision, it offers a starting point where things are well defined. In order to ex-

plore this approach, assume that we are somehow in possession of the *exact* partition function, or what is the same thing, in possession of the *exact* free energy of the system. Denote this free energy by  $G_{\text{exact}}$ . Then substituting  $G_{\text{exact}}$  for  $G$  in Eq. (1.2), and solving for  $S_{\text{mix}}$ , we find

$$S_{\text{mix}}(l) = \frac{1}{T} \{N_1 \mu_1 + N_2 \mu_2 + N_s \mu_s + \sigma A - G_{\text{exact}}\} \quad (1.5)$$

in which we have indicated that  $S_{\text{mix}}$  depends on the length scale  $l$ . In order to make further progress we need a more detailed expression for  $S_{\text{mix}}$ . If, for example, we are dealing with drops, as in Fig. 1.1, we would represent the *continuum* of configurations by the configuration integral  $Z_d$ , the number of configurations  $\Gamma(l)$  would be given by Eq. (1.3), and  $S_{\text{mix}}$  by Eq. (1.4).

Eq. (1.3) can be substituted into Eq. (1.4), and the result into Eq. (1.5), to yield an equation whose solution gives the value of  $l$ . Lest it be overlooked, it should be mentioned that, in the method just described, referral back to phase space is implicit in the use of the exact system partition function or, equivalently, the use of the exact free energy. Of course there are very few examples in which these quantities are known exactly, but it turns out that there are significant situations in which they can be estimated with good precision, and we return to this subject later.

An alternative strategy has been used [3], namely a method in which the referral to phase space is not direct, and indeed has not been regarded as a major step. Nevertheless some success has been achieved. Employing the phenomenological model that forms the basis of Eq. (1.2) the problem of the mixing entropy can be viewed as the enumeration of all the distinct configurations of the extended interface within the system. The interface can then be represented as a continuous phenomenological “renormalized” object describable by a continuum of normal modes that become the central statistical features of the system. The random configurations of the interface can then be represented by a superposition of “random waves” whose amplitudes can be determined, in a mean field sense, by a variation principle on the free energy. There must be a small wavelength cutoff since the system actually consists of discrete molecules, and this cutoff can be interpreted as the length scale. In the most recent work along these lines [3], the cutoff is determined by the theory itself. Although good qualitative and even semiquantitative descriptions of microemulsion behavior can often be obtained within this framework, it remains difficult to refer back to the fundamental phase space definition of physical entropy.

### Sensitivity of Length Scale to Model

It may be demonstrated, by carrying through the referral to phase space, that the length scale for configurational or mixing entropy can depend very sensitively on the *model* under consideration. This demonstration can be performed using systems for which the reference to phase space can be

accomplished exactly. Three such systems involve drops that are modeled as *closed* thermodynamic systems, unable to exchange molecules with a surrounding medium. Since the drops in microemulsions or related systems are not *closed* these models do not have great practical value, but they are useful in demonstrating the sensitivity of the length scale, and we now offer a brief discussion of the models and their associated scales.

First, we consider a model in which the material of the drop is confined to an impermeable spherical container of volume  $v$  whose center always coincides with the center of mass of that material, but where that center of mass is free to move through the total volume  $V$  of the system. The position of the model drop is determined by the position of the center of the container. This representation is not identical with a stationary drop (call it a reference drop) whose center of mass fluctuates about its geometric center. Indeed, the model for the reference drop consists of a spherical volume of the same radius, filled with the same material, but where the center of mass is not constrained to remain at the center of the sphere. In this feature the reference drop is similar to a real (macroscopic) drop. One proceeds to relate the partition function  $q_n$  of the microemulsion drop to the partition function  $\lambda_n$  of the reference drop, where  $n$  indicates the number of molecules in the drop. The relation between  $q_n$  and  $\lambda_n$  is easily established [4].

We express  $\lambda_n$ , in center of mass coordinates, as

$$\lambda_n = \gamma n^{3/2} \int_v d\mathbf{R} \{ (\gamma^{n-1} n^{3/2} / n!) \int_{v'(\mathbf{R})} \dots \int \exp(-\beta \mathcal{U}(\mathbf{r}'_1 \dots \mathbf{r}'_{n-1})) d\mathbf{r}'_1 \dots d\mathbf{r}'_{n-1} \}, \quad (1.6)$$

where  $\mathbf{R}$  is the coordinate of the center of mass and the primed quantities are the coordinates of molecules in the center of mass system while  $v$  is the volume of the sphere.  $\beta = 1/kT$ ,  $\mathcal{U}(\mathbf{r}'_1 \dots \mathbf{r}'_{n-1})$  is the intermolecular potential, while  $\gamma$  is the reciprocal of the cube of the deBroglie wavelength, and we do not concern ourselves with the internal degrees of freedom of the molecules. Finally  $v'(\mathbf{R})$  indicates that the limits of integration (over  $v$ ) in the center of mass system depend on  $\mathbf{R}$ . The quantity  $n^{3/2} n^{3/2} = n^3$  in Eq. (1.6) represents the Jacobian of the transformation from laboratory to center of mass coordinates, and the factor in curly brackets is the internal partition function of the drop under the constraint that the center of mass is held at  $\mathbf{R}$ . We denote this partition function by  $z(\mathbf{R})$  and write

$$\lambda_n = \gamma n^{3/2} \int_v z(\mathbf{R}) d\mathbf{R}. \quad (1.7)$$

Clearly, the definition of  $q_n$  allows us to write

$$q_n = \gamma n^{3/2} \int_V z(0) d\mathbf{R}, \quad (1.8)$$

where the integration now proceeds over the whole volume  $V$ .

Since the center of mass of the model drop is always located at the center of the sphere,  $z$ , for this case, has a

constant value, independent of the position of the center of mass in the laboratory frame. It is convenient to set this constant equal to  $z(0)$  which corresponds to the case where the drop is at the origin. Since  $z(0)$  is constant, the integral in Eq. (1.8) becomes  $z(0) V$  and

$$q_n = \gamma n^{3/2} z(0) V \quad (1.9)$$

comparison of Eqs. (1.7) and (1.9) yields the relation

$$q_n = \lambda_n V \left\{ \int_V \frac{z(0)}{z(\mathbf{R})} d\mathbf{R} \right\} = \lambda_n V P(0) , \quad (1.10)$$

where  $P(0)$  represents the factor in curly brackets whose structure shows that  $P(0)$  must be the probability *density* that the fluctuating center of mass in the reference drop will be found at the origin.

If the system consisted of only a single drop confined to the volume  $V$ , then since  $V P(0)$  is dimensionless (the same is of course true of both  $q_n$  and  $\lambda_n$ ), the length scale in the partition function  $q_n$  is clearly.

$$l = [P(0)]^{-1/3} . \quad (1.11)$$

Indeed, even if the system consisted of a collection of interacting drops, the scale for the system partition function can be shown [4] to be given by Eq. (1.11). Now the length scale in the partition function serves the purpose of converting the configuration integral to a pure number so that the partition function can be dimensionless. But the length scale for the configuration integral is the same as that for the translational or mixing entropy so that Eq. (1.11) also serves as the entropic length scale. [This can be demonstrated more directly by calculating  $G_{\text{exact}}$ , using  $q_n$  and setting

$$\lambda_n = \exp \left( \frac{-1}{kT} [n\mu_2 + \sigma a_n - p v] \right) \text{ where } a_n \text{ is the surface}$$

area of the drop, and then following the prescription embodied in Eq. (1.5)].  $l$  in Eq. (1.10), defined by Eq. (1.11), is a measure of the distance over which the center of mass of the drop fluctuates. If the fluctuation is gaussian,  $P(0)$  can be shown to be the variance of the position of the center of mass. The length scale provided by Eq. (1.11) is of the order of Ångströms for drops having diameters of the order of 10 nm.

Next we consider a slightly different *closed* model. The location of the model drop will still be determined by the position of the center of the impermeable spherical container, but that center will no longer be required to coincide with the center of the center of mass of the material within it. The partition function of the model drop in some *fixed* position is just  $\lambda_n$ , i.e. that of the reference drop of the previous example since at a fixed position the model is identical with the reference drop. However we are interested in the partition function  $q_n^*$  of the model drop able to move throughout the volume  $V$ . Thus we have to augment  $\lambda_n$  as the drop is moved throughout  $V$ . We start by moving its

center through the distance  $dx$ . Then a picture of the drop in its original position, with its image in the displaced position superposed, would show two intersecting spheres with their centers separated by  $dx$ . The augmented partition function would not simply be the sum of two  $\lambda_n$  because the region determined by the overlap of the two spheres could be the seat of redundant counting of molecular configurations. This situation is rooted in the fact that in the initial *undisplaced* sphere there are “fluctuated” configurations that are confined entirely to the region of overlap defined above, while in the case of the displaced sphere the same is true. These confined configurations are physically identical and must not be counted twice. A few simple statistical mechanical steps [5] suffices to eliminate this redundancy as well as the similar additional redundancy that occurs as the drop is displaced further. After it has been moved (integrated) through the entire volume  $V$  the model partition function is found to be

$$q_n^* = \frac{pV}{kT} \lambda_n , \quad (1.12)$$

where  $p$  is the pressure to which the drop is subjected. Comparison with Eq. (1.10) now shows that the entropic length scale for this model is

$$l = \left( \frac{kT}{p} \right)^{1/3} . \quad (1.13)$$

For  $p$  of the order of an atmosphere this scale is of the order of 100 nm, dramatically different from that of the previous model, even through the two models are themselves rather similar. It is worth remarking that the large length scale prescribed by Eq. (1.13) is a result of the considerable *overlap* configurational redundancy that must be compensated in the evaluation of the mixing entropy. Eq. (1.3) shows that a large length scale leads to a smaller  $\Gamma$  and therefore to a smaller entropy, thereby canceling the large spurious entropy associated with the redundant configurations.

Still another model is one in which the drop within the impermeable container is *absolutely* rigid and *absolutely* incompressible while its position is determined by the center of the container which, in this instance, will also be the center of mass. In this case the entropic length scale proves to be the thermal deBroglie wavelength of the center of mass. The requirement of absolute rigidity and incompressibility is necessary in order to eliminate internal degrees of freedom whose excitation would otherwise occur in order to satisfy the equipartition principle [6]. In any event the length scale is once again different from the derived for the previous two models.

These three examples indicate the possible sensitivity of the entropic length scale to the model.

Finally, we note that, in each of the above models, the length scale depends on the thermodynamic state of the system, e.g. on drop size, drop number (composition), pres-

sure, etc. Theories (usually based on a considerable degree of renormalization) can be found in the literature in which the length scale is assumed to be independent of thermodynamic state. In such cases the free energy of formation of, say a microemulsion, from component phases can be evaluated in a manner such that the scale cancels out of the problem, since the separated component phases simply represent another thermodynamic state of the system, and only the *ratio* of the mixing entropies in the microemulsion and the separated states is involved. However, the above discussion indicates the danger inherent in this approach.

As we have indicated, models based on closed systems are not suitable representations of microemulsions. In the next section, therefore, we derive an entropic length scale for an *open* representation of a microemulsion. Since, in this case, the exact system partition function cannot be obtained our result is only an estimate, but one that we think is quite good under a wide range of circumstances that satisfy certain preconditions that we enumerate. We also show how length scales, much larger than the one that we estimate, and which are sometimes used, can be reconciled with the more fundamental scale provided by that estimate. In a sense our method of estimation is a *fluid model* extension of methods based on lattice models [7], and, like those methods, is applicable to bicontinuous as well as globular microemulsions.

In later sections we examine very specific cases involving open systems in which model partition functions *can* be derived exactly and show that the associated length scales agree with our estimate.

## 2. Estimate of the Length Scale

The focus thus far has been largely on globular or drop-like microemulsions, but of course the problem extends to other systems, e.g. vesicles or bicontinuous microemulsions.

As promised, in the present section we develop an *estimate* for the entropic length scale that is generally applicable, e.g. to bicontinuous as well as globular systems. As a first step, we return to Eq. (1.2) and remark that  $\sigma A$  in that equation, which accounts for the interfacial free energy, includes the effect of bending energy. However, this does not imply that bending energy effects are merely included in a multiplicative factor  $\sigma$  that is itself independent of  $A$ . Indeed, it is assumed that the interfacial free energy  $\sigma A$  is partly determined by Helfrich's curvature free energy [8]

$$\sigma A = \sigma' A + \int_A \left[ \frac{K}{2} (c_1 + c_2 - 2c_0)^2 + K_g c_1 c_2 \right] dA, \quad (2.1)$$

where the first term on the right is a curvature independent part of the interfacial free energy, and the second is Helfrich's curvature free energy.  $K$  is the bending elastic modulus,  $c_1$  and  $c_2$  are the principal curvatures,  $c_0$  is the preferred curvature, and  $K_g$  is the modulus for Gaussian curvature.

Next we focus attention on Fig. 2.1. Although, as already indicated, our argument is general enough to include bicontinuous systems, the figure corresponds to a globular phase. It represents a "snapshot" of the microemulsion that illustrates one of the possible configurations of droplike (phase 2) and continuous (phase 1) domains. The figure shows globules of phase 2 whose molecules are represented by filled circles, surrounded by phase 1 (empty circles). The interface between the two domains is delineated by dashed lines. Without loss of generality, since we are only interested in an "estimate" we will assume the molecules of species 1 and 2 to be of the same size and the phases to have the same density.

We can refine this picture of the interface by referring to Fig. 2.2, which is a highly magnified view of a small piece of interface. Here, we have sketched "boundaries" about the molecules such that a closepacked array of irregular cells is produced, each cell containing one, and only one molecule. This array of imaginary cells is drawn purely for visualization, and is not physical . . . we are dealing with a fluid. Indeed, there is no unique way to construct the array!

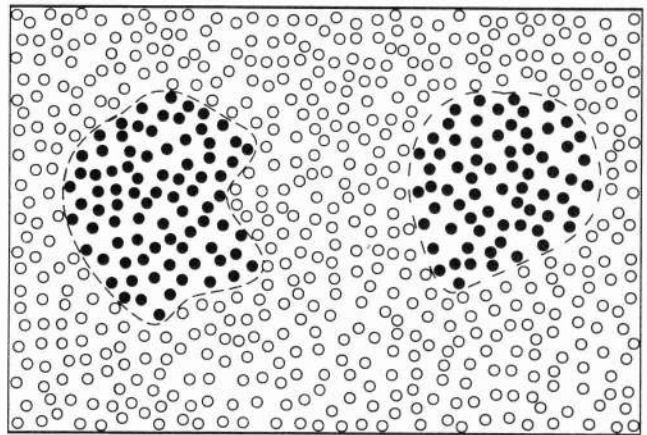


Fig. 2.1

A microscopic view of a region within a microemulsion. Two globules of species 2, whose molecules are represented by filled circles, lie in the domain of species 1, whose molecules are represented by open circles. The oil-water interface is represented by shaded lines

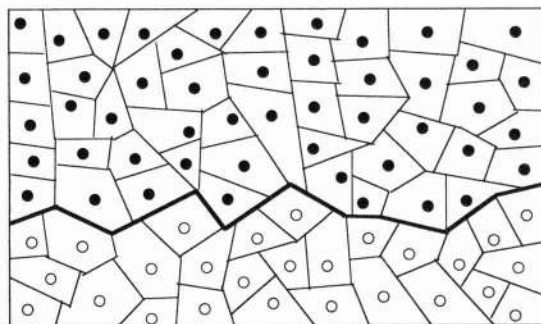


Fig. 2.2

A highly magnified microscopic view of a small piece of the oil-water interface in Fig. 3.1. The array of irregular cells, each containing a single molecule, is an abstraction useful for defining the interface between domains of species 1 and 2. The array is not unique

The interface itself, shown as the dark line in Fig. 2.2, might be defined as the set of cell faces that separate imaginary cells of one phase from cells of the other. Because the construction of the array is itself nonunique, this interface will also not be unique. On the other hand, it is clear that in the thermodynamic limit the possible variations of the area of this interface, allowed by the nonuniqueness, will be small. Thus, we can talk meaningfully, in this picture, about a constant interface area  $A$ , defined by adjacent phase 1 – phase 2 imaginary cell faces. The actual interface between phases in a physical system is of course not a mathematical surface but a transition zone that may be several molecular diameters in thickness, and which, in the case of the microemulsion, will be the locus of surfactant molecules. Therefore it may include more than one cell on either side of the mathematical interface shown in Fig. 2.2. This will have little effect on the general argument presented below, and any energetic and entropic contributions due to this finite thickness will, by definition, appear in the  $\sigma A$  term on the right side of Eq. (1.2).

Now, suppose we fix the area  $A$  and the average bending energy of the interface between the oil and water domains shown in Fig. 2.1, and allow the molecules of types 1 and 2 to move freely within their respective domains. It is clear from Fig. 2.1 that, except at the interface, type 1 molecules are surrounded by type 1 and type 2 molecules by type 2. Thus, if we ignore the interaction between molecules at the interface, the type 1 molecules are completely decoupled from the type 2 molecules. (Actually, using the familiar idea of a dividing surface, the interactions across the interface, relative to those between like molecules, can be treated as an “excess” quantity to be included in the interfacial free energy.) The partition function  $Q^*$  for this *decoupled* two-component, system is then given by the product,

$$Q^* = Q_1(N_1, V_1, T) Q_2(N_2, V_2, T) , \quad (2.2)$$

of the partition function  $Q_2$  for the type 2 molecules in their multiply connected domain, with the partition function  $Q_1$  for the type 1 molecules in their domain, where  $V_2$  and  $V_1$  are the corresponding total volumes of phases 2 and 1. It is important to understand that the configuration integrals corresponding to  $Q_1$  and  $Q_2$  “count” configurations of the molecules within their respective domains, but do not “count” the possible configurations of those domains, since the domain boundaries are fixed. It is also important to emphasize that in spite of the above appeal to imaginary cells as an expository tool, the problem of the absence of communal entropy [9] does not arise, since the molecules are not confined to individual cells, but are free to move through their respective domains, simply or multiply connected.

It should also be remarked that the approximation implicit in the “decoupling” of system 1 from system 2 in Eq. (2.3) must involve serious error when the globules are very small, since then they are all “surface” and the condition that the molecules of each type are surrounded by like molecules fails. It should further be noted that the require-

ment that the domains be of sufficient size is the essence of the mesoscopic model.

Some additional qualifying comments are in order. The globules shown in Fig. 2.1 are determined from a “snapshot” in which the individual molecules are in fixed positions within their respective cells. But in the evaluation of  $Q_1(N_1, V_1, T)$  and  $Q_2(N_2, V_2, T)$  they are moved as the integration proceeds. Once the network of cells is constructed and the interface defined, this movement could be a translation of all of the molecules within a given globule through the same vector displacement without (if the displacement were small enough) moving any molecule out of its original cell. In this sense the globule would be translated rigidly, and it would appear as though the displacement was therefore contributing to the mixing entropy. Indeed the original snapshot might have been taken with the molecules in the displacement positions and a set of cells constructed around molecules in these positions. Thus  $V_2$  is not precisely defined.

However, we note that if the displacement is as large as the typical or average cell dimension the resulting array of cells might just as easily have been constructed as a ‘permutation’ of the two species of molecules among the original set of cells. This is a process that we treat separately below and it does lead to mixing entropy. Displacements smaller than the cell dimension are still possible and are not accounted for by such permutations. However they produce entropy associated with a set of configurations that are mutually shifted by less than a cell dimension and therefore by less than the nominal thickness of the interface. These configurations are therefore comparable to others that are responsible for surface entropy and these effects can easily be included in the surface free energy. Thus within the model as *it is defined*, they do not contribute to the mixing entropy, but rather to the  $\sigma A$  term in  $G$ . In this respect we are reminded that the consistent length scale will depend upon the model, and that the model in question is that to which Eq. (1.2) applies.

As it stands,  $Q^*$  of Eq. (2.2) is also the partition function for one particular configuration of a microemulsion with given interfacial area and given average bending energy (again, ignoring interfacial effects).  $Q^*$  will have the same value for all possible configurations of the domains provided  $N_1, N_2, V_1, V_2$  are fixed. We can however classify configurations such that in a given class each and every such configuration has the same constant value of the interfacial area  $A$  and average bending energy. Since both  $A$  and the average bending energy are constant in a given class, the energetic correction due to those molecules at the interface will be constant in all allowable configurations of that class, and all such allowed configurations will have the same energy.

The total partition function  $Q$  of the microemulsion must include all possible configurations  $\mathcal{P}$  of the two types of domain, constrained by a constant interfacial area  $A$  and a constant average bending energy. Thus, not only  $\sigma$ , but  $\mathcal{P}$  is affected by bending effects. Although for simplicity of notation we will write  $\mathcal{P}$  as a function of  $N_1, N_2$ , and  $A$ ,

when additional constraints such as those due to bending are involved,  $\mathcal{P}$  must also be a function of the thermodynamic variable (variables) corresponding to the new constraint (constraints).

The number of possible configurations  $\mathcal{P}$  of the two types of domain is just the number of permutations of the two species of molecule, among the frozen arrangement of the molecules within the snapshot (Fig. 2.2) subject to the above constraints, that lead to new patterns, or, in other words, new interfacial boundaries as represented by the heavy lines of Fig. (2.2). It is to be emphasized that we are permuting molecules and not imaginary cells, so that we are indeed generating and counting quantum states to complete the specification of the true physical partition function.

The molecules are permuted among the chosen fixed array of single occupancy cells, and the nonuniqueness of the chosen array will clearly have little effect on the ‘bulk’ free energy of the system since all molecules are free to move through their respective bulk domains. The primary effect of the nonuniqueness will appear at the interface where it simply contributes to the interfacial entropy whose evaluation is not at issue here.

The next step in the construction of the full partition function of the microemulsion is the gathering together of all equivalent  $Q^*$  in one class corresponding to a fixed interfacial area and average bending energy to obtain the contribution

$$Q^{**}(N_1, N_2, A, V, T) = \mathcal{P}(N_1, N_2, A) Q_1(N_1, V_1, T) Q_2(N_2, V_2, T), \quad (2.3)$$

where  $V = V_1 + V_2$ , and where it is understood that  $\mathcal{P}(N_1, N_2, A)$  is the number of permutations allowed under the constraints discussed above.

The full partition function  $Q$  of the microemulsion consists of a weighted sum of  $Q^{**}(N_1, N_2, A, V, T)$  and, within the bounds of the model, the weight factor is simply  $\exp(-\sigma A/kT)$ . Thus we find

$$Q = \sum_{\sigma A} \mathcal{P}(N_1, N_2, A) Q_1(N_1, V_1, T) Q_2(N_2, V_2, T) e^{-\sigma A/kT}. \quad (2.4)$$

For the Gibbs free energy of the system we then have

$$G = -kT \ln Q + pV, \quad (2.5)$$

where  $p$  is the external pressure, and by substitution of Eq. (3.4) into Eq. (3.5) we obtain, using the conventional maximum term assumption for the logarithm,

$$G = -kT \ln \mathcal{P} + (-kT \ln Q_1 + pV_1) + (-kT \ln Q_2 + pV_2) + \sigma A \quad (2.6)$$

in which  $\sigma A$  corresponds to its value in the maximum term of Eq. (2.6). The bracketed terms in Eq. (2.6) are clearly

$G_1 = N_1 \mu_1$  and  $G_2 = N_2 \mu_2$  so that Eq. (3.6) may be written in the form

$$G = N_1 \mu_1 + N_2 \mu_2 + \sigma A - kT \ln \mathcal{P}. \quad (2.7)$$

This equation is identical with Eq. (1.2) except for the absence of the term  $N_s \mu_s$ . Since this term scales as  $A$  under the assumption that the surfactant constitutes a saturated monolayer, in the interest of simplicity we have not treated it explicitly in the present analysis, since it could be considered part of  $\sigma A$ . Thus  $-kT \ln \mathcal{P}$  is identified with  $-TS_{\text{mix}}$  and

$$S_{\text{mix}} = k \ln \mathcal{P}. \quad (2.8)$$

Now since the cells of Fig. 2.2 are singly occupied, it is obvious that their number is  $N = N_1 + N_2$ , and that the average volume per cell is

$$\langle v \rangle = V/N = \mathcal{P}^{-1}, \quad (2.9)$$

where we continue to ignore the volume of the extended interface, and where  $\mathcal{P}$  is the density. Thus the permutations are conducted over an irregular lattice of ‘average’ lattice parameter

$$l = \langle v \rangle^{1/3} = \mathcal{P}^{-1/3}. \quad (2.10)$$

This lattice parameter is clearly the length scale that determines the number of configurational states and therefore the length scale for the mixing entropy.

It is important to emphasize that, in arriving at this conclusion, it has *not* been necessary to perform the very difficult explicit evaluation of  $\mathcal{P}(N_1, N_2, A)$  and that  $\mathcal{P}$  itself represents the number of permutations allowed under specific (e.g. constant  $A$  and constant average bending energy) constraints. It should also be noted that the mesophase domains are in effect ‘open’ systems, just as they are in the real microemulsion, and that the analysis applies to bicontinuous, lamellar, etc. phases as well as globular ones.

It should also be emphasized that the length scale that forms the subject of this paper is specifically the scale for the *configurational entropy*, and is not that which measures either the curvature of the interface, the ‘granularity’ of the microemulsion, or the persistence length. However, an interesting partial reconciliation of the more fundamental molecular length scale and the larger more phenomenological scales is possible. A combinatorial problem in which configurations must be counted under possibly severe constraints (e.g. maintenance of constant oil-water interfacial area or constant average bending energy) is involved in the estimate. Constraints reduce the number of allowable configurations and therefore the corresponding entropy. Similarly, the choice of a larger length scale reduces the number of resolved configurations and the corresponding entropy. Therefore it may be possible to perform the combinations, *approximately*, without bothering about the constraints by

using a larger length scale, i.e. the larger length scale represents a kind of renormalized length (usually guessed) that attempts to match the effects of the constraints. Although this approximation may be useful, it is easy to show that such a renormalization can miss many configurations that would have been admitted under the constraint itself, and it remains true that the molecular scale is the most fundamental [10].

Constraints *can*, however, compromise the length scale specified by Eq. (2.10). To understand this we return to Eq. (1.2) from which it is clear that the entire effort of this paper is really concentrated on the sum  $\sigma A - TS_{\text{mix}}$ , because, as indicated earlier,  $\sigma A$  and  $TS_{\text{mix}}$  cannot be separated absolutely. We avoided the problems associated with the nonunique *microscopic* aspects of the interface contour by assigning the effects to *surface entropy*, a quantity that we do not evaluate. This is acceptable as long as the number of permutations responsible for  $S_{\text{mix}}$  is large in comparison to the number of *microscopically* distinct configurations of the interface that give rise to surface entropy. If the constraints are too severe, they may so reduce the number of configurations so that this criterion is no longer met. In that case the estimate prescribed by Eq. (2.10) may be in error.

There are treatments in the literature in which attempts are made to evaluate only the whole quantity  $\sigma A - TS_{\text{mix}}$  without concern for separation. Although there may be situations where this approach has merit,  $\sigma A$  and  $TS_{\text{mix}}$  have such distinct physical bases that it is often best to attempt the separation (e.g. in the case of dispersions of nanocrystals [11]).

Finally, when the two species constituting the mesophases have bulk pure phases of very different molar volumes, some adjustment of the theory is necessary. Part of the problem can be resolved by considering the length scale to be related to the *average* molar volume of the microemulsion, but when the ratio of molar volumes becomes very large, the estimate of this section should probably be modified. However, for most microemulsions this problem will not arise, since the two species usually have comparable volumes.

The conclusion remains that, in most cases, the length scale for the mixing entropy is of the order of the size of the cube root of the average volume per molecule in the microemulsion, and this holds true even in the presence of large persistence lengths or large globules mandated by low concentrations of surfactant. However as we have already indicated, this conclusion is qualified by the following conditions:

1. All components of the system must have comparable molar volumes.
2. The "volume" (transition zone) of the extended interface must be small compared to the bulk volume.
3. The interface entropy must be easily separable from the mixing entropy.
4. Constraints must not so reduce the mixing entropy that it becomes comparable to the interface entropy.

In the remainder of this paper we examine the practical significance of this result. Along the way we will examine special models subject to constraint, but for which  $G_{\text{exact}}$  can be derived exactly, in order to see whether Eq. (2.10) holds even under conditions such that mesodomain sizes and the *equivalent* of the persistence length are large.

### 3. Exact one Dimensional Model

In accordance with the final remark of the previous section, we now examine a model that can be subjected to fairly severe constraint, but for which it is possible to derive the exact partition function and, consequently,  $G_{\text{exact}}$ . This model (a one dimensional system of hard rods) will allow the application of constraints that, in many ways are equivalent to the constraints implicit in the so called random mixing model (RMM) [7] where the lattice parameter (the length scale) has been variously chosen either as the surface persistence length [12] or in such a manner that enough interface to accommodate a close packed film of surfactant would be available [7]. Both of these choices result in scales many times larger than that prescribed by Eq. (2.10).

The argument for choosing the persistence length as the lattice parameter proceeds essentially as follows. A globule having a linear dimension less than the persistence length would have a surface whose radius of curvature was smaller than that length. The surface would then be so "bent" that it would incur a penalty of excessive positive bending energy. Thus globules of linear dimension less than the persistence length would on the average not appear. Then, by choosing the lattice parameter in the RMM equal to the persistence length, we are assured that no globule will be smaller than this desired lower limit.

However, it does not immediately follow that preventing the size of a mesoscopic domain from being less than some minimum size much larger than that of a molecule, requires the length scale for the entropy to exceed this lower limit. We demonstrate this using the above mentioned hard rod system that can be solved exactly, to recover the scale prescribed by Eq. (2.10), thus supporting the semiquantitative argument of section 2. The result of that analysis is also relevant to the RMM in which the domain size, and thus the lattice parameter, is determined by composition [7]. Unfortunately, in one dimension there cannot be a bicontinuous phase, but, as the previous section indicates, the issue of phase type has minimal effect on the entropic length scale as long as the thicknesses of the mesodomains are large compared to that of the interface. On the other hand, the effects of constraints on the possibility of separating surface free energy and mixing free energy *can* depend on phase type. Since, in a one dimensional system this problem never arises, the conclusion of the present section provides no advice on this issue.

In the system to be solved exactly, molecules of both species are hard rods and the respective pure species are one dimensional fluids of hard rods, each of length  $\sigma$  (not to be confused with the surface tension  $\sigma$  used above). The only difference between the two fluids are the labels on the rods,



black for species 2 and white for species 1. Both fluids have the same density

$$\rho = N/L \quad (3.1)$$

i.e.  $N$  rods confined to the length (volume)  $L$ . Fig. 3.1 provides a schematic view of these “pure” systems. The well known formulas for the chemical potentials  $\mu$  and pressures  $p$  of these hard rod systems are [13]

$$\begin{aligned} \mu_1 = \mu_2 &= kT \ln \frac{\Lambda \rho}{1 - \rho \sigma} - kT \frac{\rho \sigma}{1 - \rho \sigma}, \\ p_1 = p_2 &= \frac{\rho k T}{1 - \rho \sigma}, \end{aligned} \quad (3.2)$$

where  $\Lambda$  is the thermal deBroglie wavelength of a rod. From these pure fluids we form the one dimensional microemulsion illustrated schematically in Fig. 3.2. This microemulsion contains  $N_1$  molecules of species 1 and  $N_2$  of species 2 such that

$$(N_1 + N_2)/L = N/L = \rho \quad (3.3)$$

so that the system has the same density  $\rho$  as each of the pure components. It therefore has the same pressure  $p$  as the pure components. In Fig. 3.2 the globules of species 2 are represented as sequences of black rods. Notice that the interfaces between the mesophases are unrestrained so that the globules can “breathe”. This motion is the one dimensional equivalent of both density and shape fluctuations in a three dimensional system. In addition, since there is a dynamic equilibrium between globules of all sizes; the globules are, in effect, “open” systems.

Also, in one dimension, a constraint of constant surfactant content, i.e. constant interfacial area, is translated into a fixed number,  $2B$ , of globule ends. This automatically requires that there be a fixed number  $B$  of globules of species 2 (and ... because of the one dimensionality ... a fixed

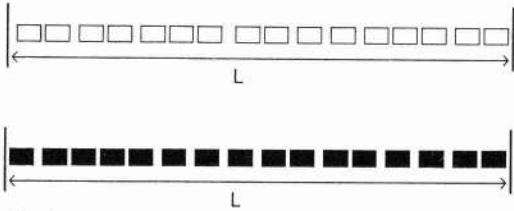


Fig. 3.1  
One dimensional system of pure rods of species 1 (top) and 2 (bottom), i.e.  $N$  rods confined to a length  $L$ , density  $\rho = N/L$



Fig. 3.2  
One dimensional microemulsion formed from the pure fluids depicted in Fig. 4.1

number,  $B$ , of species 1 globules). The constraint imposed by the bending energy (or composition) is now translated, as discussed earlier, into the imposition of a minimum size for a species 2 globule. We denote this minimum size by  $n_{\min} = m$ , and recognize that  $m$  may be quite large.

In the hard rod system there is no surface tension, but this is peripheral to our main argument.

We begin the analysis by evaluating the exact partition function,  $Q_{\text{exact}}$ , and consequently the exact Gibbs free energy,  $G_{\text{exact}}$ . To accomplish this we note that if all the rods in Fig. 3.2 were identical (if all were of the same color), the partition function would have the well known form

$$Q^*(N, L) = \frac{(L - N\sigma)^N}{N! \Lambda^N}. \quad (3.4)$$

Coloring the rods has no effect on the mechanics of the system but does effect the entropy because of the many configurations (sequences) of black and white rods that then become possible. Subject to a fixed number  $B$  of 2-globules and minimum size  $m$  for a species 2 sequence, this number of configurations is

$$\mathcal{P}(N_1, N_2, B, m) = \frac{\binom{B-1+N_2-mB}{(B-1)!(N_2-mB)!}}{\binom{B-1+N_1-B}{(B-1)!(N_1-B)!}}. \quad (3.5)$$

This expression is easily understood when it is realized that, for every species 2 globule,  $m$  black rods must be reserved, since  $m$  is the lower limit of size for such a globule. Thus, since there must also be exactly  $B$  globules,  $mB$  rods of species 2 are not available for permutation among them, i.e. only  $N_2 - mB$  rods are available. For the species 1 globules, only one rod must be reserved per globule so that  $N_1 - B$  rods of species 1 are available for permutation. With these quantities we find

$$Q_{\text{exact}} = \mathcal{P}(N_1, N_2, B, m) Q^*(N, L). \quad (3.6)$$

Then  $G_{\text{exact}}$  is given by

$$\begin{aligned} G_{\text{exact}} &= -kT \ln Q_{\text{exact}} + pL \\ &= -kT \ln \mathcal{P} - kT \ln Q^* + pL \\ &= -kT \ln \mathcal{P} + G^* = -kT \ln \mathcal{P} + N\mu, \end{aligned} \quad (3.7)$$

where  $G^*$  is the Gibbs free energy of a system containing  $N$  rods, all of the same kind, in the length  $L$ , while  $\mu$  is the corresponding chemical potential. But since  $N = N_1 + N_2$  and, according to Eq. (3.2),  $\mu = \mu_1 = \mu_2$  we can write

$$N\mu = N_1\mu_1 + N_2\mu_2 \quad (3.8)$$

so that Eq. (4.7) can be expressed as

$$G_{\text{exact}} = N_1\mu_1 + N_2\mu_2 - kT \ln \mathcal{P}(N_1, N_2, B, \mu). \quad (3.9)$$

If we elect to make use of the mesoscopic model upon which Eq. (1.2) (without the surfactant or surface terms) is based, comparison of that equation with Eq. (3.9) shows that  $S_{\text{mix}}$  must be given by

$$S_{\text{mix}} = k \ln \mathcal{P}(N_1, N_2, B, m) \quad (3.10)$$

if the model is adjusted to give the exact free energy. *This identification forges the connection of  $S_{\text{mix}}$  to phase space, discussed in section 1.* Eq. (3.10) is actually identical to Eq. (2.8), except that it is an *exact* relation whereas Eq. (2.8) is only an *estimate*.

The next step is to evaluate  $S_{\text{mix}}(l)$  within the confines of the mesoscopic model and to equate the result to  $S_{\text{mix}}$  specified by Eq. (3.10). The resulting equation can then be solved for the length scale  $l$ .

Before we can analyze the model it is necessary to define the length  $\lambda_n$  of a globule containing  $n$  rods. This is necessary so that  $Z_D$  in Eq. (1.3) can be evaluated. Since we are dealing with a “model” there is more than one way to define  $\lambda_n$ . However, to be consistent with the use of the mesoscopic model in the past, it is appropriate to define  $\lambda_n$  so that the density of the mesophase is the same as that of the corresponding bulk phase. Thus we write

$$\lambda_n = n/\rho \quad (3.11)$$

Since the globules “breathe” their actual lengths are not constant so that  $\lambda_n$  is really an average length. Choosing  $\lambda_n$  is equivalent to the selection of a Gibbs dividing surface in the thermodynamic analysis of a drop. Among the breathing modes of the globule is one that can be interpreted as a translation, so that a small amount of translational entropy is included in the internal entropy of the globule. However such translations are limited to distances comparable to the thickness of an interfacial zone between the mesophases. As a result this translational entropy could be reinterpreted as part of an interfacial free energy. We could therefore define  $\lambda_n$  in another way such that this interfacial free energy would appear as a separate term. However, this approach will not cause any significant change in the result we obtain below.

In evaluating  $S_{\text{mix}}$  for the model we need to use Eqs. (1.3) and (1.4), modified to account for the fact that now the droplets or globules are not all of the same size. This is accomplished by replacing  $\Gamma$  in Eq. (1.3) by

$$\Gamma = \frac{Z}{l^B \prod_{i=m}^{\infty} n_i!} \quad (3.12)$$

where  $n_i$  represents the number of globules containing  $i$  molecules and  $Z$  is given by

$$Z = (L - \langle \lambda \rangle B)^B \quad (3.13)$$

where  $\langle \lambda \rangle$  is the average globule length

$$\langle \lambda \rangle = N_2/B\rho \quad (3.14)$$

where  $\rho$  appears because we are using Eq. (3.11) for  $\lambda_n$  (or  $\lambda_i$ ). Substitution of Eq. (3.14) into Eq. (3.13), the latter into Eq. (3.12), and the result into Eq. (1.4) gives

$$S_{\text{mix}} = k \ln \left[ \frac{\left( L - \frac{N_2}{\rho} \right)^B}{l^B \prod_{i=m}^{\infty} n_i!} \right] \quad (3.15)$$

We are now faced with the evaluation of  $n_i$  to be used in Eq. (3.15). Since no potential energy is involved in the hard rod system  $n_i$  can be computed as a random quantity constrained only by the requirements

$$\sum_{i=m}^{\infty} n_i = B \quad (3.16)$$

$$\sum_{i=m}^{\infty} i n_i = N_2 \quad (3.17)$$

Furthermore, since  $S_{\text{mix}}$  is based on the logarithm we can use the most probable distribution of  $n_i$ . Thus we choose the distribution that maximizes the quantity

$$H = N_2! / \prod n_i! \quad (3.18)$$

subject to the conditions, Eqs. (3.16) and (3.17). This maximization is easily performed with the result that

$$n_i = B^2 \left[ \frac{(N_2 - mB)^{i-m}}{(N_2 - (m-1)B)^{i-m+1}} \right] \quad (3.19)$$

Now, as promised above, we equate  $S_{\text{mix}}$  in Eq. (3.15) to  $S_{\text{mix}}$  in Eq. (3.10). At the same time we use Eq. (3.5) for  $\mathcal{P}(N_1, N_2, B, m)$  and Eq. (3.19) for  $n_i$ . After some careful algebra we are able to solve for  $l$  and find (taking  $(B-1) \rightarrow B$ ),

$$l = \frac{L(N_1/N) \left( 1 - \frac{B}{N_1} \right)^{N_1/B} e}{N_1 - B} \quad (3.20)$$

where, significantly,  $m$  does not appear. Since  $N_1$  is usually much larger than  $B$ , the factor preceding  $e$  in the numerator of the right side of Eq. (3.20) is essentially  $e^{-1}$ . Making this substitution in Eq. (3.20) yields

$$l = \frac{L(N_1/N)}{N_1 - B} = \frac{\langle v \rangle N_2}{N_1 - B} \cong \langle v \rangle \quad (3.21)$$

where  $\langle v \rangle = L/N$ , and so we recover the result Eq. (2.10). No cube root appears since we are dealing with a one dimensional system. Thus, the exact treatment of the present section recovers the estimate of the previous section. Furthermore, the imposition of a lower limit on the size of a globule does not result in a length scale larger than one of the order of the length per molecule. A more detailed examination of Eq. (3.20) shows that  $l$  increases monotonically from  $l = \langle v \rangle$  for  $B/N_1 \rightarrow 0$  to  $l = e\langle v \rangle$  for  $B/N_1 = 1.0$ .

At least for this system, we must conclude that, even in the face of a constraint incorporating a length scale much larger than that prescribed by Eq. (2.10), the fundamental scale continues to be the one of molecular size appearing in that equation. Coupled with the analysis of section 2, this suggests that the fundamental scale is always of that size. Whether or not the use of a much larger erroneous length scale results in significant error in any particular theory is a separate question that we address later.

#### 4. Role of the Length Scale in the Law of Mass Action

It was emphasized, in connection with Fig. 1.1, that because of the Gibbs-Thomson relation, only a drop of *one particular size* could remain in equilibrium with the surrounding medium. It is also true that this equilibrium could be *unstable* or *stable* depending upon whether the interfacial tension was *positive* or *negative* [14]. It was also noted that, if the drops were numerous enough, the entire assembly could be brought into *collective* equilibrium through the agency of the mixing entropy that acts to reduce the free energy. This collective phenomenon might be regarded as one of the hallmarks of the mesoscopic regime. The collective equilibrium is clearly dynamic in nature and subject to the familiar law of mass action. This, by itself, it is not something fundamentally new. What *is* new is that, in the present context, we are applying it to “reactants” and “products” which are ill defined fragments of bulk phases whose detailed structures are so incompletely specified that they are usually modeled as parametrized, renormalized, phenomenological entities.

For the proper application of the law of mass action, it is necessary to have an expression for the chemical potential of a drop. Usually we are concerned with a dilute “solution” of drops and the time honored expression for the chemical potential of a component of a dilute solution is

$$\mu = \mu^\circ(T, p) + kT \ln X, \quad (4.1)$$

where  $X$  is the mole fraction of the component in question and  $\mu^\circ$ , dependent only on temperature and pressure, is the chemical potential in the standard state. For the case of a drop, the task before us is the specification of  $\mu^\circ$ . In this endeavor it is instructive to first examine a simpler and less rigorous example than that of a drop in a microemulsion. This example is found in the so called classical theory of homogeneous vapor phase nucleation [15, 16, 17] where the nucleus for condensation as well as smaller clusters are modeled as liquid drops in a supersaturated vapor. This

model, to which workers in the field have assigned the name “capillary approximation”, is identical to the “phenomenological model” embodied in Eq. (1.1), except for the absence of the term referring to the surfactant.

There is one difference however. The continuous phase now consists of supersaturated vapor and possesses a molar volume on the order of  $10^4$  times larger than that of the disperse (liquid) phase contained in the drops. Thus one of the criteria for the applicability of Eq. (2.10), namely that both “phases” have comparable molar volumes is violated, and it would seem as though that expression cannot now be used. However, one can advance a plausibility argument that when the molar volumes are *vastly* different, Eq. (2.10) can still be used, provided that  $\langle v \rangle$  is taken to be the molecular volume of the *condensed* phase. This argument is based on a lattice gas treatment of the system, vapor plus liquid drops. At this point it should be reemphasized that Eq. (2.10), which is to be used in situations where the molecular volumes of all components are comparable is by contrast based on more rigorous theory, and not on a plausibility argument.

In classical nucleation theory one is interested in evaluating the so called equilibrium size distribution of clusters for the purpose of applying the principle of detailed balance to the determination of cluster molecular evaporation coefficients, and in evaluating the equilibrium distribution, the law of mass action is used. As indicated above, it is then necessary to have an expression for the chemical potential  $\mu_n$  of a drop (cluster) consisting of  $n$  molecules. There is considerable controversy among workers in the nucleation field over the nature of this expression, and the method that we now use to derive it is not exactly any of those currently in vogue among these workers. Nevertheless, besides providing an introduction to the related size distribution in globular microemulsions, we believe that it is essentially correct.

We begin by rewriting Eq. (1.2) for the nucleation case. We find

$$\begin{aligned} G &= N_{\text{vap}}\mu_{\text{vap}} + N_{\text{liq}}\mu_{\text{liq}} + \sigma A - TS_{\text{mix}} \\ &= N_{\text{vap}}\mu_{\text{vap}} + \sum_n N_n(n\mu_{\text{liq}} + \sigma a_n) - TS_{\text{mix}} \end{aligned} \quad (4.2)$$

in which  $N_{\text{vap}}$  and  $N_{\text{liq}}$  are the total numbers of molecules of vapor and liquid in the system and  $\mu_{\text{vap}}$ ,  $\mu_{\text{liq}}$  are the corresponding chemical potentials of single molecules.  $N_n$  and  $a_n$  are, respectively, the number of drops (clusters) of  $n$  molecules and the surface area of a drop of  $n$  molecules.

The next problem is the specification of  $S_{\text{mix}}$ . We note that, since the assembly of drops is dilute, the configuration integral  $Z_d$  is simply  $\prod_n (V)^{N_n}$  where  $V$  is the total volume of the system. Then for  $\Gamma$  in Eq. (1.3) we can write

$$\Gamma = \prod_n \left\{ \frac{(V/v)^{N_n}}{N_n!} \right\}, \quad (4.3)$$

where, for simplicity, we have written  $v$  for  $\langle v \rangle = l^3$  and  $N_n!$  compensates for the indistinguishability of drops of the same size. Substitution of this relation into Eq. (1.4), and the result into Eq. (4.2), gives

$$G = N_{\text{vap}}\mu_{\text{vap}} + \sum_n N_n(n\mu_{\text{liq}} + \sigma a_n) - kT \ln \prod_n \left\{ \frac{(V/v)^{N_n}}{N_n!} \right\}. \quad (4.4)$$

$\mu_n$  is now computed as follows,

$$\begin{aligned} \mu_n &= \left( \frac{\partial G}{\partial N_n} \right)_{N_{\text{vap}}, N'_n, T, p} = n\mu_{\text{liq}} + \sigma a_n + kT \ln \frac{N_n v}{V} \\ &= n\mu_{\text{liq}} + \sigma a_n + kT \ln \frac{N_n \rho_{\text{vap}}}{N_{\text{vap}} \rho_{\text{liq}}}, \end{aligned} \quad (4.5)$$

where  $\rho_{\text{vap}}$  and  $\rho_{\text{liq}}$  are the densities of vapor and liquid, respectively, and where we have assumed (as is actually the case) that  $N_{\text{vap}} \approx \rho_{\text{vap}} V$ . Since the total number of molecules in the system (counting drops as molecules) is almost indistinguishable from  $N_{\text{vap}}$  we could write  $X_n = N_n / N_{\text{vap}}$  and Eq. (4.5) could be expressed as

$$\mu_n = \left[ n\mu_{\text{liq}} + \sigma a_n + kT \ln \frac{\rho_{\text{vap}}}{\rho_{\text{liq}}} \right] + kT \ln X_n \quad (4.6)$$

from which it is clear, by comparison with Eq. (4.1) that

$$\mu_n^o = n\mu_{\text{liq}} + \sigma a_n + kT \ln \frac{\rho_{\text{vap}}}{\rho_{\text{liq}}}. \quad (4.7)$$

This differs from the standard result in classical nucleation theory by the logarithmic term involving the ratio of the densities. That logarithmic term is a direct result of the inclusion of the full mixing entropy, a quantity that is partially omitted from the classical theory.

In order to obtain the cluster size distribution we now employ the law of mass action in the form

$$\mu_n = n\mu_{\text{vap}} \quad (4.8)$$

and substitute Eq. (4.6) into this relation. The result for the size distribution  $N_n$  is

$$N_n = \left( \frac{\rho_{\text{liq}}}{\rho_{\text{vap}}} \right) N_{\text{vap}} \exp \left\{ -\frac{1}{kT} [n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \sigma a_n] \right\}. \quad (4.9)$$

Except for the factor involving the ratio of densities, this expression is the same as the classical result. That factor which clearly has its origin in the mixing entropy is of the order of  $10^4$  for typical fluids. Although its size is considerable it is worth noting that it has been variously estimated by other means [18] to be as large as  $10^{18}$ . This fac-

tor has been at the center of the so called ‘‘replacement free energy’’ controversy that has visited the field of nucleation for almost thirty years [18, 4]. It can now be seen to represent the same problem as the mixing entropy problem in microemulsion theory.

Since the *rate* of nucleation is essentially proportional to the factor, it is clear that mixing entropy is of great importance in this problem. This provides a partial response to the question concerning the quantitative significance of the entropic length scale. Here we have an example in which it is very important. We should however note that its importance derives from the fact that the mixing entropy, as part of the free energy of formation of the cluster, appears in an exponent so that the logarithm in  $\ln \Gamma$  is effectively canceled and both the size distribution and the associated rate now depend directly upon the very large number  $\Gamma$ . We shall see that the size distribution in a microemulsion similarly depends on the exponential of the mixing entropy so that, in this case too, the length scale acquires a similar importance. It should also be mentioned that in the nucleation case, the surface tension is so large that the mixing entropy cannot, by itself, stabilize the dynamic equilibrium. Yet the mixing entropy still has a pronounced effect on the equilibrium size distribution, in effect, as mentioned earlier, determining its height through the factor involving the density ratio.

We turn now to an example involving a microemulsion or, more accurately, to a system closely resembling a microemulsion. This system is a dispersion of gold nanocrystals in toluene, and we choose to focus on it because rather careful measurements have been made by Leff et al. [11] on certain features of the particle size distribution in the dispersion. The system forms a close analog of a microemulsion since the interface between the gold crystals and the continuous phase of toluene is the locus of a close-packed layer of surfactant. Furthermore Leff et al. obtained evidence [11] that the dispersion was in dynamic equilibrium, much like a microemulsion, since they were able (within limits) to reversibly change the stable crystal size distribution through a change of system composition. The procedure of these authors (omitting details) involved the use of a quaternary ammonium ion to transport  $\text{AuCl}_4^-$  ions into a solution of thiol in toluene. There,  $\text{AuCl}_4^-$  ions were reduced by  $\text{NaBH}_4$  so that Au atoms were released to form gold nanocrystals capped by a closepacked (self assembled) monolayer of 1-dodecanethiol that acted as a surfactant and gave rise to a *negative*, curvature dependent (i.e. exhibiting a bending energy) interfacial tension (between gold and toluene) for which the authors provided a theoretical estimate. Stabilization of the dispersion was primarily due to the negative surface tension, but in accordance with our earlier discussion both population and polydispersity were affected by mixing entropy.

The authors used the law of mass action to evaluate the crystal size distribution in a manner almost identical to that employed for the determination of the cluster size distribution in the nucleation example presented above. In the present case the law of mass action takes the form

$$\mu_{n,t} = n\mu_{\text{Au}}(\text{soln}) + t\mu_{\text{thiol}}(\text{soln}) . \quad (4.10)$$

In this equation  $\mu_{n,t}$  is the chemical potential of a nanocrystal containing  $n$  gold atoms and  $t$  thiol molecules while  $\mu_{\text{Au}}(\text{soln})$  is the chemical potential of a gold atom in the toluene and  $\mu_{\text{thiol}}(\text{soln})$  is the chemical potential of a thiol molecule in the same solution.  $\mu_{n,t}$  can be evaluated in a manner similar to that used in the evaluation of  $\mu_n$  in the previous example involving nucleation (again assuming that the “solution” is dilute with respect to crystals). The result is

$$\mu_{n,t} = n\mu_{\text{Au}} + t\mu_{\text{thiol}} + \sigma A + kT \ln \frac{N_{n,t}}{V/l^3} . \quad (4.11)$$

In this equation  $\mu_{\text{Au}}$  is the chemical potential of a gold atom in bulk crystalline gold,  $\mu_{\text{thiol}}$  is the chemical potential of a thiol molecule (must be estimated) in a self assembled monolayer at the gold-toluene interface,  $\sigma$  is the surface tension,  $a_{n,t}$  is the surface area of a nanocrystal of type  $n,t$ ,  $N_{n,t}$  is the number of crystals of type  $n,t$ , and  $l$  is the length scale.

In complete analogy to the procedure employed in the derivation of the equilibrium size distribution of the clusters of nucleation theory, Eq. (4.11) can now be substituted into Eq. (4.10) and the result can be solved for  $N_{n,t}$ , the nanocrystal size distribution. In essence, in deriving the size distribution, Leff et al. followed the procedure just described. However, for the argument of the logarithm in Eq. (4.11), instead of the quantity  $N_{n,t}/(V/l^3)$ , they used  $X_{n,t}$  the mole fraction of nanocrystals (regarded as molecules) of type  $n,t$ . This form seemed perfectly reasonable in view of the conventional expression, Eq. (4.1), for the chemical potential of a solute in a dilute solution. Furthermore the authors did not write the first three terms on the right hand side of Eq. (4.11) in exactly the form shown, because various of the quantities had to be estimated by means of theory. However what they wrote was equivalent to those first three terms.

Now the mole fraction, used as the argument of the logarithm by the authors, becomes identical to the argument appearing in Eq. (4.11) if the length scale is chosen in accordance with Eq. (2.10), i.e. if the correct scale, referred to phase space, is used! This follows from

$$\frac{N_{n,t}}{V/l^3} = \frac{N_{n,t}}{V/v} = \frac{N_{n,t}}{N} = X_{n,t} \quad (4.12)$$

in which  $N$  is the total number of molecules in the solution and the second step follows from the fact that  $v$  is the average volume per molecule in the system (unlike the nucleation example . . . in this case the molar volumes of *all* components are comparable and the estimate Eq. (2.10) is valid without dependence on a plausibility argument). Thus Leff et al. used the correct length scale implicitly. If they had (somehow) employed another scale the “height” of their derived size distribution would have been different, i.e. they would have predicted a different crystal population

although the “shape” of their size distribution would have been the same. Since only the “shape” is involved in the estimate of the mean crystal size, the length scale has no effect on this mean size. The authors measured the mean (equilibrium) size as a function of system composition. Measurements of the ratio of gold to thiol molar ratios versus the equilibrium mean crystal radius (including the thiol monolayer) established by the particular composition ratio showed a very good agreement with a theory based on Eqs. (4.10) and (4.11) [11].

The implication of this analysis is that, for the case where all molar volumes are comparable, Eq. (4.1) is valid with  $\mu^o$  given by

$$\mu_{n,t}^o = n\mu_{\text{Au}} + t\mu_{\text{thiol}} + \sigma A \quad (4.13)$$

only when the length scale is chosen in accordance with Eq. (2.10).

We close this section with the promised proof (referring to Fig. 1.1) that polydispersity is controlled by the mixing entropy associated with the permutation of drops among the fixed “syringes” while the height of the size distribution (drop population) is determined by the mixing entropy associated with the continuum of positions available to drops not immobilized on syringes. We work with the simpler case of the supersaturated vapor involved in the nucleation example, but it will be obvious that the proof is more general. Thus, we consider single component polydisperse drops such that there are  $N_n$  of them consisting of  $n$  molecules. We rewrite  $\Gamma$ , prescribed by Eq. (4.3), in the form

$$\Gamma = \Gamma_1 \Gamma_2 = \left( \frac{N_d!}{\prod_n N_n!} \right) \left( \frac{V^{N_d}}{N_d! v^{N_d}} \right) , \quad (4.14)$$

where  $N_d$  is the total number of drops. It is clear that  $\Gamma_1$ , the first factor in parentheses, is the part of the mixing entropy obtained by merely permuting the drops among the syringes while  $\Gamma_2$ , the second factor in parentheses, is the remaining part of the mixing entropy associated with the continuum of positions to which the configurational integral  $V^{N_d}$  corresponds.

The mixing entropy is  $k \ln \Gamma_1 + k \ln \Gamma_2$  so that the free energy of the system is

$$G = \sum_n n N_n \mu_{\text{liq}} + N_{\text{vap}} \mu_{\text{vap}} + \sigma \sum_n N_n a_n - kT \ln \Gamma_1 - kT \ln \Gamma_2 . \quad (4.15)$$

In view of Eq. (4.14), this equation is really the same as Eq. (4.4), but we can now truncate it by retaining only one of the logarithmic terms. If we retain the term in  $\Gamma_1$ , only that portion of the mixing entropy involving the permutation of drops among the syringes will be involved. Then, using the truncated expression, we can repeat the steps contained in Eqs. (4.5), (4.8), and (4.9), recalling that

$$N_d = \sum_n N_n , \quad (4.16)$$

to obtain

$$\frac{N_n}{N_d} = \exp \left\{ -\frac{1}{kT} [n(\mu_{\text{vap}} - \mu_{\text{liq}}) + \sigma a_n] \right\}. \quad (4.17)$$

Since  $N_n/N_d$  is the fraction of drops of size  $n$ , Eq. (4.17) characterizes the *polydispersity*. Thus we have shown that the part of the mixing entropy corresponding to permutation of the drops among syringes determines the polydispersity. Since retention of *both* logarithmic terms in Eq. (4.14) leads to Eq. (4.9), it is evident that the inclusion of the second term merely introduces the factor  $\rho_{\text{liq}} N_{\text{vap}} / \rho_{\text{vap}} N_d$  in front of the exponential in Eq. (4.17). Thus, as indicated earlier, we see that the mixing entropy associated with the continuum of drop positions controls the *height* (population) of the drops.

### 5. Effects Associated with the Use of a Length Scale Larger than the Physically Consistent Scale: the (asymmetric) Random Mixing Model

In this section we apply the length scale estimate of Eq. (2.10) to a highly idealized model of a globular microemulsion and compare some of the results with those of the random mixing model.

As mentioned earlier, in the random mixing model (RMM) [7] the length scale for the mixing entropy is chosen to be that of the lattice parameter which, in turn, is determined by the composition of the system and is usually orders of magnitude larger than a length of molecular size. In this section we consider the asymmetric limit of the random mixing model, where the concentration of one of the bulk species is very large, and that of the other very low. In this limit, the model reduces to a highly dilute droplet type microemulsion, the free energy of which can be compared to the results of previous sections.

In the random mixing model [7], the system volume is divided into cubes of side  $\xi$ . This lattice parameter is determined by the composition of the system through the relation

$$\xi = 6\phi(1-\phi)/c_s\sigma_s, \quad (5.1)$$

where  $\phi$  and  $(1-\phi)$  are the volume fractions of species 2 and 1, respectively,  $c_s$  is the surfactant concentration (molecules/volume) and  $\sigma_s$  is the interfacial area occupied by the surfactant. The free energy is expressed [7] in terms of the phenomenological model and is therefore still given by Eq. (1.2). It is assumed that the interfacial free energy  $\sigma A$  is *completely* determined by Helfrich's curvature free energy [8] (see Eq. (2.1))

$$\sigma A = \int_A \left[ \frac{K}{2} (c_1 + c_2 - 2c_0)^2 + K_g c_1 c_2 \right] dA. \quad (5.2)$$

In the model, "bends" are sections of a sphere of diameter  $\xi$  and  $K_g$  is set equal to zero. In order to make our point as

clear as possible, we set  $c_0 = 0$ , and choose species 2 to have the small volume fraction. For a system in which  $n_d$  lattice cells are filled with species 2 (the subscript  $d$  emphasizes that we are dealing with drops) this leads to the scale invariant result [7]

$$\sigma A = 8\pi n_d K \quad (5.3)$$

Note that in the model as described in [7], all contributions to the free energy are defined as densities, i.e. (free energy)/( $n_d + n_1$ ) $\xi^3$ , with  $n_1$  the number of lattice sites filled with species 1, the component that comprises the continuous phase. Then it is easy to see that Eq. (5.3) corresponds to Eq. (2.4) in [7] for  $c_0$  and  $\phi \rightarrow 0$ .

An essential ingredient of the model, without which the most important result (i.e. three phase coexistence between a bicontinuous and two excess phases) is not observed, is the size dependence of  $K$ . This is due thermal undulations and it follows from perturbation theory [19, 20] that

$$K(\xi) = K_0 - \frac{\alpha kT}{4\pi} \ln(\xi/a), \quad (5.4)$$

where  $K_0$  is the *bare* bending elastic modulus (on a molecular scale  $a$ ), and  $\alpha$  is a constant for which values of 1 [20], 2 [21], and 3 [19] have been variously predicted. Eq. (5.3) now becomes

$$\sigma A = 8\pi n_d \left( K_0 - \frac{\alpha kT}{4\pi} \ln(\xi/a) \right). \quad (5.5)$$

The entropy of mixing is defined in the model as [7]

$$S_{\text{mix}} = -k [n_d \ln \phi + n_1 \ln (1-\phi)]. \quad (5.6)$$

At very small  $\phi$  we then have

$$S_{\text{mix}}(\phi \rightarrow 0) = -n_d k (\ln \phi - 1). \quad (5.7)$$

Combining Eqs. (1.2), (5.4), (5.5), and (5.7) yields the free energy

$$G_{\text{RM}} = N_2 \mu_2 + N_1 \mu_1 + N_s \mu_s + 8\pi n_d K_0 + n_d k T (\ln \phi - 1 - 2\alpha \ln(\xi/a)). \quad (5.8)$$

It should be emphasized that the last term in the parentheses on the right of Eq. (5.8) comes from the interfacial free energy of the system and not from the entropy of mixing.

We now compare  $G_{\text{RM}}$ , Eq. (5.8), with the fundamental estimate, Eq. (2.10), for the entropic length scale. Assume a dilute, monodisperse assembly of  $n_d$  model drops containing  $n$  molecules of dispersed phase. The partition function of the microemulsion may be expressed as

$$Q_n = Q_c Q_d = Q_c \frac{(q_n)^{n_d}}{n_d!} \quad (5.9)$$

where  $Q_c$  is the partition function of the continuous phase and

$$Q_d = \frac{(q_n)^{n_d}}{n_d!} \quad (5.10)$$

is the corresponding quantity for the disperse phase. The “decoupling” implicit in the product  $Q_c Q_d$  implies that the surface free energy is considered to be part of the Helmholtz free energy  $f_n$  of the drop (see Eq. (5.12)). The partition function of a single immobilized drop (as held by a “syringe”) is given by

$$q_n = \frac{V}{l^3} \exp(-f_n/kT) \quad (5.11)$$

with  $l$  the length scale, and  $f_n$  the free energy of a single immobilized drop.  $f_n$  is given by

$$f_n = n_2 \mu_2 + n_s \mu_s - p v_d + \sigma a_d \quad (5.12)$$

where  $a_d$  is the surface area of the drop and  $v_d$  its volume. Also, it is clear that

$$\begin{aligned} n_d a_d &= A \\ V_1 + V_2 &= V \\ n_d v_d &= V_2 \\ n_d n &= N_2, \end{aligned} \quad (5.13)$$

where  $V_1$  is the volume of the continuous phase and  $V$  is the total volume of the system.  $Q_c$  in Eq. (5.9) is given by  $kT \ln Q_c = N_1 \mu_1 - p V_1$ , and  $Q_d$  is obtained from Eq. (5.10) and Eq. (5.11) with Eq. (5.12) substituted. Then  $Q_n$  is obtained from Eq. (5.9), and

$$G = -kT \ln Q_n + pV \quad (5.14)$$

Substitution of  $Q_n$  into this equation gives

$$G = \mu_2 N_2 + \mu_1 N_1 + \mu_s N_s + 8\pi n_d K_0 + kT n_d (\ln(\phi) - 1 - 2\alpha \ln(\xi/a) - \ln(v_d/l^3)) , \quad (5.15)$$

where, in Eq. (5.12), we have used Eq. (5.5) and where the volume fraction  $\phi$  of the drops is defined via  $n_d/V = \phi/v_d$ , where we neglect the small amount of dissolved species 2 in the continuous phase. Now taking the length scale for the mixing entropy equal to the cube root of the drop volume, i.e.  $l^3 = v_d$  (orders of magnitude larger than the cube root of the molecular volume), the last term on the right of Eq. (5.15) vanishes and we recover exactly  $G_{RM}$  of Eq. (6.8). It is somewhat remarkable that we recover  $G_{RM}$  exactly since Eq. (5.15), is based on  $Q_n$  evaluated in the continuum while the random mixing model is based on a lattice. However this exact correspondence would not have appeared if  $Q_n$  had not been evaluated in a *dilute* system of

noninteracting drops. We discuss this point somewhat further in section 6. In any event the exact correspondence, in the dilute drop regime, provides a convenient means of comparing the effects of the RMM length scale with those of the more fundamental estimate, Eq. (2.10).

If instead of the large RMM length scale the more fundamental estimate, is substituted into Eq. (5.15), we find

$$G = \mu_2 N_2 + \mu_1 N_1 + \mu_s N_s + 8\pi n_d K_0 + kT n_d (\ln(\phi) - 1 - 2\alpha \ln(\xi/a) - \ln(v_d/a^3)) \quad (5.16)$$

Using  $\ln(v_d/a^3) \cong \ln(\xi^3/a^3)$ , we get

$$G \cong \mu_2 N_2 + \mu_1 N_1 + \mu_s N_s + 8\pi n_d K_0 + kT n_d (\ln(\phi) - 1 - (2\alpha + 3) \ln(\xi/a)) . \quad (5.17)$$

Comparing Eq. (5.17) with Eq. (5.8), it follows that, although the phenomenological model does not explicitly take into account configurations at scales smaller than the lattice parameter  $\xi$ , the functional form of its free energy is still the same as the one following from the more fundamental analysis, the only difference being a larger “effective”  $\alpha$ . The reason is that any length scale  $l$  not proportional to the droplet size (or lattice parameter, in the case considered here), appears in the free energy as a term logarithmic in the drop size. The length scale dependence of the bending elastic modulus also appears as a term, logarithmic in the drop size, in the free energy. It is worth noting that an interfacial free energy, more realistic than Eq. (5.3), i.e. one which  $K_g \neq 0$  and  $c_0 \neq 0$ , also leads to a different “effective”  $\alpha$  [22]. Nevertheless, the analysis presented here shows a significant additional contribution to the coefficient of the term in the free energy, logarithmic in drop size, that has its origin in an effect, completely different from that due to the thermal undulations of the oil-water interface that have been considered until now. Thus, if one attempted to measure the coefficient of the logarithm due to the renormalization of the bending moduli, the influence of the mixing entropy (i.e. the number 3 in the last term in the parentheses on the right of Eq. (5.17)) is essential and should be taken into account. It should also be mentioned that in recent work [23], curvature elastic quantities of the surfactant loaded oil water interface of a droplet type microemulsion were obtained, using an expression for the entropy of mixing equivalent to Eq. (5.7). This expression involves a length scale equal to the drop size. The error caused by the use of this too large length scale is then reflected in incorrect values of the bending elastic quantities.

The analysis of this section provides an answer to the question as to why the “conventional” Random Mixing Model produces results in good qualitative agreement with experiments, in spite of the fact an informational theoretic rather than a physical entropy is used. The RMM of [7] was the first phenomenological model capable of predicting a 3 phase equilibrium (a microemulsion coexisting with almost pure oil and water) as well as the phase transition between a microemulsion and a lamellar liquid crystal phase found

in experiments. This success was due to the use of the bending elastic modulus, renormalized according to Eq. (5.4), which led to an additional contribution to the system's free energy, logarithmic in the size of the oil/water domains (the lattice parameter). The analysis of this section shows that the inclusion of a physically consistent entropy also results in a contribution to the free energy logarithmic in drop size. Because of the simplicity of the model, the phase diagram is, at best, predicted only qualitatively, and therefore the influence of this additional logarithmic contribution may be fully absorbed into the uncertain coefficient  $\alpha$  in Eq. (5.8). The additional term is however of the same order of magnitude as the renormalization coefficients of the bending elastic moduli and its quantitative influence is a significant increase in the entropy of the system.

## 6. Formulation and Significance of Theories Based on the Physically Consistent Length Scale

Although the analysis of section 2 provides an estimate for the physically consistent length scale, the question of how to incorporate it into useful theories still remains. There is a problem rooted in the fact (as emphasized in section 2) that when the fundamental length scale is used it is necessary to perform a combinatorial analysis under the strict constraints to which the system is subject. In simple cases such as those addressed in sections 3 and 4, the constraints are implicit in the configuration integral  $Z$ , i.e. they are enforced during the evaluation of the integral. In the examples of section 4, the assemblies of drops were dilute and the restraint to spherical form achieved expression only in the surface free energy. However, if a nondilute system had been used, additional constraints would have been activated in the restriction of nonoverlap of the spheres (assuming noncoalescence) and the integral would have been quite complex even for a monodisperse system [24]. (This is the basis for the remark that Eq. (5.15) would not have been obtained in a nondilute system.)

Nevertheless, in theories of droplike systems the mode of incorporation of the fundamental scale is clear; the constraints are to be satisfied by the configuration integral.

How are they to be incorporated into more complicated systems? The answer has already been partially supplied by workers in the field who have either used scales much larger than the correct one or various renormalization procedures such as the random wave approach. As indicated in section 2 the use of a large length scale can partially account for constraints without requiring their explicit enforcement. Renormalization procedures offer the possibility of having the length scale cancel out of the problem under the implicit assumption that it is independent of thermodynamic state (an assumption that is not always warranted). Thus, although these methods have merit, they have still avoided a direct referral to the phase space definition of physical entropy. What is therefore needed is a scheme for augmenting them so as to include a proper referral to phase space. Although this may be difficult, it may not be impossible.

For example it may be feasible to formulate the random wave approach in a manner that allows it to evaluate configuration integrals that describe the systems to which it is applied.

How important is it to use the length consistent with the physical definition of entropy as opposed to those which may not be consistent? To explore this question we begin with the theory of deGennes and coworkers [12] that makes use of the so called random mixing model in which the lattice parameter (the length scale for the mixing entropy) is chosen as the persistence length. Since one is primarily concerned with *changes* in entropy, the choice of length scale would cancel out of the problem if the scale did not itself change with thermodynamic state, and therefore its precise specification would not be important. Unfortunately, the persistence length *does* depend on the thermodynamic state, e.g. on composition, so this happy circumstance is not realized in this model. Furthermore, in dilute microemulsions, the random mixing model, by itself, predicts that the mixing entropy per globule at fixed surfactant fraction, diverges whereas it should tend to vanish. The situation is saved by the introduction of bending energy which destabilizes the microemulsion before this entropic catastrophe can occur. The use of the consistent length scale would also destabilize a dilute system because of a reduction in entropy, but this effect could go unnoticed in the presence of a large bending energy [10]. However, one should still be aware of the *qualitative* difference in the phenomenon.

In general, when the focus is on the phase diagram of the microemulsion, predicted results are not too sensitive to an uncritical choice of length scale, because the emphasis is then on the free energy in which the scale makes its appearance in one of the logarithmic terms, insensitive to that scale. There may be exceptional situations, however, in which the scale exerts considerable influence. Such a situation may occur in the case in which a globular microemulsion is in equilibrium with a separate *bulk* phase of the dispersed species. Then there is no limit to the supply of that species, and the constraint of a fixed supply of surfactant that requires a fixed interfacial area, is no longer determinative of the mean size of the drops and, concomitantly, of both the number and the distribution of drops. In this case the mixing entropy could be sensitive to the choice of length scale, because the correction will also occur in  $n_d$  in Eq. (5.17) and will then involve more than the simple addition of a logarithmic term [25].

However, situations in which the length scale has a large effect are those in which the measured variable depends *directly* on the *argument* of the logarithmic term in which the length scale appears. Such situations appear in section 4 and arise because "equilibrium distributions" of clusters are involved, and the relevant equilibrium constants contain the mixing entropy as part of the standard free energy in an exponent. Thus the *argument* of the logarithm becomes involved, and an improper evaluation of the mixing entropy gave rise to predictions that can be seriously in error. For example, in the case of nucleation, rates that differ by as much as a factor of  $10^{18}$  have been predicted [18].



The work of Leff et al. [11] presents the possibility of studying another interesting phenomenon that might be referred to as *modified Ostwald ripening*. In the case of ordinary Ostwald ripening, small crystals are cannibalized by large crystals so that a precipitate coarsens indefinitely. In two famous papers, Lifshitz and Slyozov [26] and Wagner [27] showed that, barring intercrystal interaction, the mean size of the crystals increased as the  $1/3$  power of time. Now Leff et al. have supplied us with a realizable case in which the crystals do not grow indefinitely, but achieve a stationary size distribution governed by a dynamic equilibrium in which mixing entropy plays a role. This means that the relaxation time to equilibrium depends on mixing entropy. Initial formulations of this rate process, that include mixing entropy, in an extension of the Lifshitz-Slyozov theory, indicate that it is once more the exponential of the entropy that enters the theory, so that the use of the correct length scale becomes important [28].

These last examples show that there are already phenomena in which the length scale for mixing entropy must be dealt with critically. Additional important examples will undoubtedly surface in the future.

In closing this section, it is important to emphasize that there may be situations in which the stability of a microemulsion may not depend primarily on mixing entropy, but rather on bending energy. Borcovec, in the paper referred to above, provides an example of such a situation. Nevertheless mixing entropy still plays a role, and in general we cannot dispense with it.

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