

Replacement Free Energy and the 1/S Factor in Nucleation Theory as a Consequence of Mixing Entropy

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In this paper we emphasize the *mixing entropy* phenomenon, which is common to both microemulsion and nucleation theory, and call upon its commonality to both areas to aid in the understanding of both the *replacement free energy* and *1/S factor* in nucleation theory. In microemulsion theory the mixing entropy must be evaluated by the identification of a physically consistent *length scale*. After a brief summary of previous work in this direction, we use the same method, in nucleation theory, with the result that both the replacement free energy factor and the 1/S factor appear in a natural and physically consistent manner.

1. Introduction: Mixing Entropy in Microemulsions

An important goal of this paper is the use of the identity of the phenomenological models used in both microemulsion and nucleation theory to arrive at a natural solution of the much discussed issues (in nucleation theory) known as the replacement free energy factor¹ R and the $1/S$ factor.^{1–3} Actually, the replacement free energy issue appears in microemulsion theory in connection with the evaluation of the *mixing entropy*,^{4,5} and this evaluation suggests a means for deriving both R and $1/S$ in nucleation theory. The solution depends upon the determination of the fundamental *length scale*⁶ that must be used in the evaluation of a *part* of the total entropy of a system, a part that, because of the model, must be evaluated in *configuration* or *coordinate* space whereas *physical* entropy is defined in *phase* space.

The model of microemulsions that we consider is in fact referred to as the *phenomenological model*, but in nucleation theory, it emerges as the *capillarity approximation*.⁷ Its main feature is the treatment of mesodomains, e.g., large clusters, drops, or mesoscopic entities of arbitrary shape, as fragments of bulk phases having the same intensive properties as those macroscopic phases. It is convenient to begin our discussion with a summary of the mixing entropy problem in microemulsions as reported in a recent paper by the authors.⁶

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 continuous 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.

The phenomenological model within which mixing entropy or configurational entropy (forming only a *part* of the total entropy) is defined requires 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 ensure physical consistency.

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 co-workers.⁸ Figure 1 is helpful in describing it. On the left we show a droplet-type microemulsion consisting of drops of water surrounded by a continuous phase of 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 bulk water, and the same is true for the continuous phase. A 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 μ_1 , μ_2 , and μ_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. σA is the interfacial free energy with σ 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 Figure 1 applies, they can adopt a continuum of configurations with which mixing entropy S_{mix} will be associated. The full free energy of the unconstrained microemulsion can then be expressed as

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

It is important to realize that S_{mix} is *defined* and makes its appearance because of the nature of the model.

It should be noted that, if the drops in Figure 1 are of different sizes (polydisperse), only those of *one* size could (according to the Gibbs–Thomson relation⁹) be in equilibrium with the surrounding phase. However, entropy of mixing, when it is

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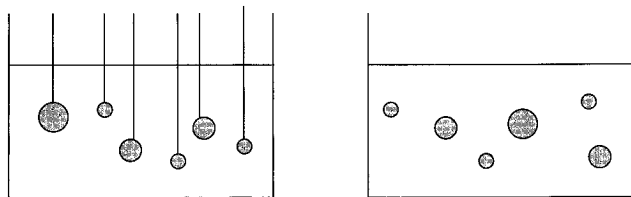


Figure 1. Schematic of a polydisperse globular microemulsion. On the left, the drops are immobilized on “syringes”. On the right, the drops are free to assume a continuum of configurations.

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 are n_d drops, all of the same size, one might first think of evaluating S_{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 Γ 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 Figure 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 ensure that, in the evaluation of Z_d , they are not used redundantly.

At this point it is convenient to mention some features of S_{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, 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!

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. To explore 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_{exact} . Then substituting G_{exact} for G in eq 1.2 and solving for S_{mix} , we find

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

where we have indicated that S_{mix} depends on the length scale l . To make further progress we need a more detailed expression

for S_{mix} . If, for example, we are dealing with drops, as in Figure 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_{mix} , by eq 1.4. Equation 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.

2. Analysis of the Length Scale

The method implicit in eq 1.5 has been used, in ref 6, to study the entropic length scale in several systems and under a variety of conditions. These studies involve simple ideal cases where l can be determined exactly and more realistic cases where it can only be *estimated* in a reasonably accurate manner. The simple cases involve models for thermodynamically *closed* spherical drops and one-dimensional systems of hard rods. An important conclusion derived from these studies with simple systems is that the length scale can depend very sensitively on the model. The closed drop models had been studied earlier¹⁰ within the context of the replacement free energy problem, although not from the perspective of the mixing entropy phenomenon, and a replacement free energy correction to the nucleation rate of the order of 10^4 was derived in place of the more dramatic factor of 10^{18} , originally suggested by Lothe and Pound.¹ Below, we shall also arrive at a factor of 10^4 by invoking the mixing entropy, but this should not be viewed as a confirmation of the method used in ref 10. That method arrived fortuitously at a correction of the proper order of magnitude because of the size of the drop that was considered. Had it been applied to a sufficiently large drop, it would have predicted an even larger correction than the 10^{18} of Lothe and Pound. In reality, the *closed* model upon which it was based could not represent an actual drop in contact with vapor since an actual drop is an *open* system! The same is true of the mesophases found in microemulsions; they are also *open* systems.

In ref 6 open models representing microemulsions were examined. However, for these systems an exact result for the length scale could not be obtained. Instead, a very good estimate could be made. The estimate was based on what might be called a “fluidization” of a lattice or cell model in which the cells were restricted to single occupancy by molecules. Lattice models, based on almost single occupancy, have been successfully applied to the study of microemulsions.^{11,12} However, the model used in ref 6 was not the strict lattice model that ultimately corresponds to a solid but was truly representative of a fluid. Among other things, the system of cells was a nonunique array of singly occupied pseudocells whose usefulness lay chiefly in its ability to provide a visual aid as well as a framework for discussion. In addition, real fluid partition functions were involved in the estimate. The reader is referred to ref 6 for further details.

The length scale estimate derived from this study was

$$l = \langle v \rangle^{1/3} = \rho^{-1/3} \quad (2.1)$$

where $\langle v \rangle$ is the average volume per molecule in the microemulsion and ρ is the average number density. This value for

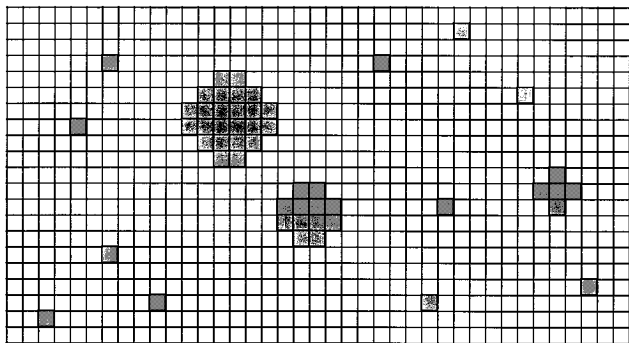


Figure 2. Lattice version of a supersaturated vapor. Isolated shaded cells contain single vapor molecules, each free to move through its cell. Shaded clumps of cells are schematic representations of liquid drops. Each cell in a clump is singly occupied.

the scale was much smaller (orders of magnitude smaller) than many other scales⁵ that had been used previously and had been chosen on a somewhat ad hoc basis. The length scale prescribed by eq 2.1 is the more fundamental, but some of the larger more heuristic scales could be reconciled with it, approximately, by considering constraints imposed on the average curvature of the oil–water interface and on the total area of that interface. Constraints limit the number of allowable permutations of oil and water molecules and therefore reduce the mixing entropy. However, a larger length scale also leads to a reduced entropy and can therefore imitate the effects of constraints. It is interesting to note that the lack of consensus concerning the length scale for the mixing entropy is the microemulsion counterpart of the replacement free energy issue in nucleation theory. For further details the reader is again referred to ref 6.

Reference 6 lists several qualifications underlying the validity of eq 2.1. We will only discuss the one that is fundamental to the transfer of ideas to the nucleation problem, namely, the qualification that eq 2.1 is generally only valid when the molar volumes of all components in the system are of comparable magnitude. In the case of nucleation, say in a supersaturated vapor, the liquid drops (clusters) play the role of the disperse phase (e.g., water droplets) in a microemulsion and the surrounding vapor plays the role of the continuous phase (e.g., oil) in the microemulsion. Clearly the molar or molecular volumes in the drops and the vapor are vastly different so that eq 2.1 would not appear to be applicable. However, it is possible to advance a strong plausibility argument to show that, when the molecular volumes are so vastly different, eq 2.1 is once again valid, provided that the length scale is chosen to be that of the *denser* phase, i.e., the molecular volume of the liquid. We address this issue in the following section.

3. Lattice Gas Argument for the Length Scale

Figure 2 is a lattice-cell model representation (schematic) of a supersaturated vapor containing a fixed distribution of drop sizes. The drops are represented as approximately spherical clumps of molecules (singly occupied shaded cells), while the vapor molecules lie in the singly occupied, isolated shaded cells. This model is very similar to the model employed in arriving at the estimate, eq 2.1, except that it is a strict lattice model whereas in the microemulsion case the array of singly occupied cells did not constitute a periodic lattice and, in fact, was nonunique. As mentioned earlier, it was introduced primarily as a visual aid and for its value as a tool in the organization of the argument.

The reader should not assume, because of our reference to a *strict lattice model*, that we are using this model to develop the “length scale” theory for the nucleation case. In fact, we refer

to this schematic model only as a means of clarifying the essential physical picture that we have in mind and not as a quantitative tool. Our goal is to render the use of the length scale result, obtained with greater rigor for the microemulsion case, both plausible and reasonable. Once that result is accepted it becomes unnecessary to concern ourselves with such standard replacement free energy problems as those associated with continuous translation and rotation of the drops (clusters). These processes are automatically accounted for in the evaluation of the fluid partition functions corresponding to the phenomenological or capillarity approximation model. For the details of this argument the reader is again referred to ref 6.

As indicated above, in the microemulsion case, all species had comparable molar volumes. In that case (see ref 6), the step leading to the mixing entropy involved the permutation (subject to constraints) of the oil and water molecules among the various cells. In this way it was possible to move whole mesodomains and even change their shapes (again within the constraints).

The same thing can be done with the “drops” of Figure 2. For example, the drops can be “moved” by permuting their molecules among the cells. However, these permutations must be limited to those that preserve the size and spherical shape of each drop. Furthermore, the vapor molecules must not be allowed to aggregate to form new drops; otherwise, the requirement that we are dealing with a *particular* distribution of drop sizes will be violated. These are the constraints to which the permutation must conform.

It is obvious that, in order to move whole drops of fixed density by permutation, the cells must have volumes equal to the molecular volume of a molecule in the drop, i.e., to the molecular volume of the liquid. We notice that at the same time this restriction does not prevent the vapor molecules from being permuted.

This simple argument makes it extremely plausible that the length scale for the permutation, and therefore for the mixing entropy, is again given by eq 2.1 with the proviso that $\langle v \rangle$ is the molecular volume of the liquid. It does seem possible to increase the rigor of this claim, but we leave such further analysis to a later paper.

4. Derivation of the Factor due to Replacement Free Energy

The so-called “equilibrium distribution” of clusters^{13,14} in nucleation theory is usually obtained through an application of the “law of mass action”. The most popular procedure for applying mass action refers the problem to the *saturated* vapor.¹⁴ However, in reality, there is nothing wrong with performing the analysis entirely within the *supersaturated* vapor in accordance with the earlier custom. Referral to the saturated vapor is convenient when the vapor is *nonideal*, since in that case activity coefficients must be introduced, and these cannot be easily measured in the supersaturated vapor. Since we shall be concerned with ideal, or nearly ideal, vapors we shall take the simpler route and perform the analysis in the supersaturated vapor.

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 μ° , 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 μ° .

We begin by rewriting, for the nucleation case, eq 1.2. We find

$$G = N_{\text{vap}}\mu_{\text{vap}} + N_{\text{liq}}\mu_{\text{liq}} + \sigma A - TS_{\text{mix}} = N_{\text{vap}}\mu_{\text{vap}} + \sum_{n=2} N_n(n\mu_{\text{liq}} + \sigma a_n) - TS_{\text{mix}} \quad (4.2)$$

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

The next problem is the specification of S_{mix} . We note that, since the assembly of drops is dilute, the configuration integral Z_d is simply $\prod_{n=2} (V)^{N_n}$ where V is the total volume of the system. Then for Γ in eq 1.3 we can write

$$\Gamma = \prod_{n=2} \left[\frac{(V/v)^{N_n}}{N_n!} \right] \quad (4.3)$$

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

$$G = N_{\text{vap}}\mu_{\text{vap}} + \sum_{n=2} N_n(n\mu_{\text{liq}} + \sigma a_n) - kT \ln \prod_{n=2} \left[\frac{(V/v)^{N_n}}{N_n!} \right] \quad (4.4)$$

μ_n is now computed as follows:

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

where ρ_{vap} and ρ_{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_{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

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

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, as we shall see, is partially omitted from the classical theory.

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

$$\begin{aligned} N_n &= \left(\frac{\rho_{\text{liq}}}{\rho_{\text{vap}}} \right) N_{\text{vap}} \exp \left\{ - \frac{1}{kT} [n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \sigma a_n] \right\} \\ &= \frac{\rho_{\text{liq}} \rho_{\text{vap}}^{(e)}}{\rho_{\text{vap}}^{(e)} \rho_{\text{vap}}} N_{\text{vap}} \exp \left\{ - \frac{1}{kT} [n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \sigma a_n] \right\} \\ &= \frac{\rho_{\text{liq}}}{\rho_{\text{vap}}^{(e)}} \frac{1}{S} N_{\text{vap}} \exp \left\{ - \frac{1}{kT} [n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \sigma a_n] \right\} \\ &= R \frac{1}{S} \left[N_{\text{vap}} \exp \left\{ - \frac{1}{kT} [n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \sigma a_n] \right\} \right] \end{aligned} \quad (4.9)$$

where the subscript (e) refers to the saturated vapor and where

$$S = \frac{\rho_{\text{vap}}}{\rho_{\text{vap}}^{(e)}} \quad (4.10)$$

is the supersaturation and

$$R = \frac{\rho_{\text{liq}}}{\rho_{\text{vap}}^{(e)}} \quad (4.11)$$

is the factor due to the replacement free energy, an interpretation that is clear since the factor in square brackets in the last form of eq 4.9 is the classical expression for the equilibrium number of clusters of size n (which, interestingly enough, would have been our full result if for $\langle v \rangle = v$ we had used the molecular volume in the vapor instead of the molecular volume in the liquid). Thus both R and $1/S$ have their origins in the inclusion of the *mixing entropy* in the theory, a fact which shows that the problems in both the nucleation and microemulsion fields are, in essence, identical except that they go by different names.

Even more important is the fact that both the replacement factor and the $1/S$ factor arise naturally when the full mixing entropy is taken into account. The replacement factor prescribed by eq 4.11 is on the order of 10^4 rather than the 10^{18} suggested by Lothe and Pound!¹ The analysis in ref 10 arrived at a value of R having the same order of magnitude but, as explained earlier, this agreeable result was fortuitous.

Now we turn to the question concerning the relation of mixing entropy to both *polydispersity* and *population*, a question raised earlier in connection with Figure 1. We will prove (referring to Figure 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 consider single-component polydisperse drops such that there are N_n of them consisting of n molecules. We rewrite Γ , prescribed by eq 4.3, in the form

$$\Gamma = \Gamma_1 \Gamma_2 = \left(\frac{N_d!}{\prod_{n=2} N_n!} \right) \left(\frac{V^{N_d}}{N_d! v^{N_d}} \right) \quad (4.12)$$

where N_d is the total number of drops. It is clear that Γ_1 , the first factor in parentheses, is the part of the mixing entropy obtained by merely permuting the drops among the syringes while Γ_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

$$G = \sum_{n=2} n N_n \mu_{\text{liq}} + N_{\text{vap}} \mu_{\text{vap}} + \sigma \sum_{n=2} N_n a_n - kT \ln \Gamma_1 - kT \ln \Gamma_2 \quad (4.13)$$

In view of eq 4.12, 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 Γ_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

$$N_d = \sum_{n=2} N_n \quad (4.14)$$

to obtain

$$\frac{N_n}{N_d} = \exp\left\{-\frac{1}{kT}[n(\mu_{\text{liq}} - \mu_{\text{vap}}) + \sigma a_n]\right\} \quad (4.15)$$

Since N_n/N_d is the *fraction* of drops of size n , eq 4.15 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 RN_{vap}/SN_d in front of the exponential in eq 4.15. Thus we see that the mixing entropy associated with the continuum of drop positions controls the *height* (population of drops) of the distribution. The N_n of classical nucleation theory does contain the exponential function of eq 4.15 so that it must include at least that part of mixing entropy associated with the permutation of drops on the fixed syringes.

Finally, we should not conclude this paper without calling attention to a remarkable but little quoted paper of Kikuchi¹⁵ in which the problem of the replacement free energy is addressed, not explicitly in terms of the mixing entropy, but in a manner such that this quantity is involved, at least implicitly. Kikuchi already arrived at the conclusion that the length scale was on the order of the cube root of the volume per molecule in the liquid, although he did not put his conclusion in these terms, but rather in terms of a statement that he called the "molecular volume theorem". Kikuchi also made use of a

lattice. Our plausibility argument is in some ways a restatement of Kikuchi's theorem and the two results are mutually reinforcing.

5. Conclusion

This paper has featured several issues. An important feature is the demonstration that the mixing entropy problem in the field of microemulsions is essentially identical with the replacement free energy problem in the field of nucleation. Another important feature is the demonstration that both the replacement and $1/S$ factors arise naturally when the mixing entropy is included in the theory. Still another feature is the resolution of the mixing entropy into two types, *syringe-fixed* entropy and *continuum* entropy, and the demonstration that the first type determines polydispersity while the second type determines the height of the drop size distribution. Finally, we have shown that the classical theory of nucleation is recovered if the length scale is taken to be the cube root of the molecular volume in the vapor rather than the cube root of the molecular volume in the liquid. The authors hope that these various demonstrations will generate consensus in the discussions concerning both the replacement free energy and $1/S$.

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