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Colloids and Surfaces

A: Physicochemical and Engineering Aspects 183–185 (2001) 347–360

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Entropy and droplet size distributions of Winsor I and II microemulsions

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Abstract

A review is presented of some general notions underlying the current theory of Winsor I and II microemulsions where the exposition is based on a comparison between the droplet kind of approach and the corresponding multiple equilibrium treatment. We show that the droplet size distributions derived earlier, although put in different mathematical forms in the respective treatments, are in effect the same, of the type $S(R) \exp(-4\pi R^2 \sigma/kT)$ where the preexponential factor, $S(R)$, is due to the fluctuations in size and shape of the droplets, and the droplet surface tension, σ is curvature-dependent in accordance with the Helfrich expression. Full consistency is demonstrated among the two approaches, at least insofar as surfactant density fluctuations are not explicitly taken into account. Moreover, on the basis of the multiple equilibrium model, we can actually estimate the length scale parameter l introduced earlier in the droplet kind of treatment to fully account for the entropy of dispersion, to be about 1 nm, in fair agreement with previous estimates. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Curvature free energy of microemulsion droplets; Entropy of dispersion of microemulsions; Fluctuations in size and shape of microemulsions; Multiple equilibrium description of Winsor I and II microemulsions; Size distribution of microemulsion droplets

1. Introduction

During the past half-century, the field of thermodynamically stable microemulsions has been rather thoroughly explored, experimentally as well as theoretically. In due course a common understanding of some salient features has been at-

tained, such as the importance of generating a sufficiently low, curvature-dependent interfacial tension and the role of the spontaneous curvature [1–4]. Nevertheless, within the scientific community we are still far from having reached consensus as to what an introduction to the subject preferably might include. Aiming to contribute in this particular regard, the Utrecht and Stockholm research groups involved in the theoretical description of microemulsions, have recently taken

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some joint measures to try to pinpoint what the differences really are between their approaches which originally were presented in Refs. [5–8], respectively. For simplicity, we first focused on Winsor I and II type of microemulsions coexisting in equilibrium with an excess oil (I) or water (II) phase. Fairly soon it was realized that entropy questions were at the core of the discussion, albeit cloaked in various disguises.

For a full background concerning experimental results and earlier theoretical endeavours as to droplet microemulsions, the reader may consult the above-mentioned Refs. [5–8], a recent review article by Kegel et al. [9], and references therein.

One can describe the Overbeek–Lekkerkerker–Kegel ('Utrecht') treatment as being primarily a droplet approach, whereas the Eriksson–Ljunggren–Bergström ('Stockholm') treatment is founded on a quasi-statistical–mechanical multiple equilibrium model. Regardless of what initial approach that is chosen, however, there will always be a need to take into account the thermal fluctuations, in one way or the other, as they are bound to be of significance because of the small size of a microemulsion droplet, its liquid nature and comparatively low surface tension.

Issues of this nature were first addressed in a comprehensive manner by Terrel L. Hill in his renowned treatise of small systems thermodynamics, published in two volumes in 1964 and 1965 [10,11]. Accordingly, we can set out by considering a microemulsion droplet of average size, shape and composition, and invoke the proper fluctuation entropy terms later on. As an alternative to fully account for the reversible droplet/aggregate formation, we may invoke a whole set of stoichiometrically different 'complexes' and employ a multiple equilibrium scheme. In principle, the Utrecht approach is of the former kind, whereas the Stockholm approach is basically of the latter kind.

Both treatments, however, make use of the well-known Helfrich expression [2]

$$\sigma = \sigma_0 + 2k_c(H - H_0)^2 + \bar{k}_c K \quad (1)$$

in order to reckon with the curvature-dependence of the droplet surface tension σ , where H stands for the mean curvature, $(1/R_1 + 1/R_2)/2$, and $K =$

$(R_1 R_2)^{-1}$ for the Gaussian curvature. H_0 is the spontaneous mean curvature (where, for a cylindrical interface the surface tension σ equals σ_0), and k_c and \bar{k}_c are the bending constants connected with the mean and Gaussian curvatures, respectively, nota bene at fixed chemical potentials in the droplet environment. A special version of the Helfrich expression, to be used repeatedly in the present paper, is the following (truncated) expansion in curvature

$$\sigma = \gamma + k_1/R + k_2/R_2, \quad (2)$$

where spherical geometry is presumed and γ stands for the interfacial tension of the *planar* o/w interface (which is actually present in the two-phase systems under consideration) given by

$$\gamma = \sigma_0 + 2k_c H_0^2. \quad (3)$$

By comparison, we also have

$$k_1 = -4k_c H_0, \quad (4)$$

$$k_2 = 2k_c + \bar{k}_c. \quad (5)$$

Moreover, in both of our treatments non-Gibbsian surface thermodynamics is applied where curvature-related terms are explicitly included in the Laplace equation. When put in a form due to Kralchevsky [12] it is readily seen that the general Laplace equation as derived by Boruvka and Neumann [13] (which holds for an arbitrary dividing surface) can be written

$$\Delta p \equiv p_i - p_e = 2H\sigma - (H^2 + D^2) \left(\frac{\partial \sigma}{\partial H} \right)_{T, \mu, D} - 2HD \left(\frac{\partial \sigma}{\partial D} \right)_{T, \mu, H} \quad (6)$$

for interfaces of uniform curvature. Here D stands for the deviatoric curvature $(1/R_1 - 1/R_2)/2$. Thus, for the special case of a spherical droplet submerged in a solvent we obtain the following Δp expression

$$\Delta p = \frac{2\sigma}{R} + \left(\frac{\partial \sigma}{\partial R} \right)_{T, \mu_i} \quad (7)$$

from which it appears that the interior droplet pressure, p_i may well become equal to the outside solution pressure, p_e , provided σ is curvature-dependent. In fact, for the Winsor I and II cases, Δp

equals zero where the overall droplet free energy $4\pi R^2\sigma$ has a minimum. This circumstance right away implies that unlike an ordinary small droplet having a size-independent interfacial tension, but similarly to a spherical surfactant micelle, a microemulsion droplet can be thermodynamically stable.

A central mathematical function belonging to the theory of droplet microemulsions, is the size distribution. For Winsor I and II systems where an excess phase of oil or water, respectively, is always present, the size distribution function can be written in the form of an exponential times a preexponential factor,

$$\phi_R = S(R) e^{-4\pi R^2\sigma/kT}, \quad (8)$$

where $\phi_R dR$ is the volume fraction of droplets with radii between R and $R + dR$. The exponential is, of course, rather easily comprehended as $4\pi R^2\sigma$ accounts for the (Helmholtz) free energy it takes to form the surfactant-laden oil–water surface of the droplet at the chemical potentials prevailing in the surrounding solution. On this very point, the Utrecht and Stockholm (as well as a few other) treatments do agree. The residual concerns are mainly:

1. the rationale for using volume fraction on the l.h.s. of Eq. (8), i.e. how to properly evaluate the entropy of mixing large droplets with a practically structureless solvent, and how to comprehend the need of introducing a special length scale parameter l in this context,
2. the quantification of the preexponential factor $S(R)$,
3. the accounting of finite size effects in addition to curvature effects, and
4. how to cope with droplet–droplet interactions.

In the following, we illuminate all these points but the last one, and show how issues (i) and (ii) largely can be resolved by referring to the multiple equilibrium approach, resulting in an estimate of the configurational entropy length scale employed in the Utrecht treatment. Additionally, we argue that insofar as the effect of interfacial composition fluctuations is left out of consideration, there is little need to invoke the corresponding mixing-entropy-limiting size effect in the droplet tension function $\sigma(R)$.

2. The entropy of mixing monodisperse colloidal particles with a structureless solvent

Both mole fraction as well as volume fraction have been used in the past as concentration measures of micelles and microemulsion droplets in the dilute regime. A common view is that this choice is little else but a formality, devoid of physical significance. However, as we will bring to bear in the following, the consistency that in the end is required is most readily attained by choosing the volume fraction concentration scale since only for this choice does the associated particle/droplet standard state agree with the state of the bulk phase from which the particles/droplets supposedly have arisen.

Let us consider a dilute dispersion of microemulsion droplets, all of equal size, or, even better, of monodisperse (spherical) particles (component 2) undergoing Brownian motion in a continuous solvent (component 1). As to the state of the solvent as such it is evident that it will be virtually unaffected by the presence of the particles. Nonetheless, despite the lack of ordinary molecular mixing, the chemical potential of the solvent, μ_1 will to some appreciable extent depend on the particle concentration, simply because varying the solvent volume affects the entropy of the encompassed particle system.

In the dilute (Henry's law) range, below volume fractions ϕ_2 of about 0.01, we have the following approximate expression for the chemical potential of the suspended particles

$$\mu_2 - \mu_2^0 = kT \ln \phi_2. \quad (9)$$

As the definition of the standard state we have then adopted

$$\mu_2^0 = \lim_{\phi_2 \rightarrow 0} (\mu_2 - kT \ln \phi_2), \quad (10)$$

which amounts to claiming that the standard state corresponds to non-interacting particles filling up all the available volume to a density that is equal to the single-particle density. In case of a Winsor II microemulsion, for example, this means that, in the standard state, the water cores are made up of water in exactly the same intrinsic state as the water present in the form of an excess bulk phase. To put it otherwise, the only difference between

the standard (bulk phase) state and the dilute microemulsion droplet state of the water cores is that, in the latter state, the droplet cores have access to a larger volume.

On the other hand, for the chemical potential of the solvent, μ_1 standard thermodynamic considerations using Eq. (9) and the Gibbs–Duhem condition, show that the ordinary mole fraction-based expression

$$\mu_1 - \mu_1^0 = kT \ln x_1 \quad (11)$$

holds at low particle concentrations, irrespective of the particle size, where the pure solvent is the standard state.

Let us now combine Eqs. (9) and (11) to derive expressions for the overall free energy of mixing, ΔG_{mix} as well as for the entropy of mixing, ΔS_{mix} (assuming the energy of mixing to be zero), the result being

$$\Delta G_{\text{mix}}/kT = -\Delta S_{\text{mix}}/k = N_1 \ln x_1 + N_2 \ln \phi_2. \quad (12)$$

Another version of Eq. (12), in essence employed by Andelman et al. [14] in their works on microemulsions, is obtained by dividing the overall volume V and using the approximations $\ln x_1 \approx -x_2$ as well as $\ln \phi_1 \approx -\phi_2$

$$-\Delta S_{\text{mix}}/V = (k/v_2)(\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2) \quad (13)$$

showing that the mixing entropy per volume unit tends to zero, as it should, upon increasing the particle volume v_2 while simultaneously keeping the volume fractions constant. Note also that in this last expression, the length scale is determined by the size of the suspended particles. Hence, the solvent is in effect treated as a continuum.

Still, another form of Eq. (12) will be required below, viz.,

$$\Delta S_{\text{mix}}/k = -N_2 \ln(\phi_2/e), \quad (14)$$

which is obtained by inserting $\ln x_1 \approx -x_2 \approx -N_2/N_1$.

Now, in the case of a dilute dispersion of microemulsion droplets, even if they are of the same average size, one has to quantify the fluctuation entropies, which go along with the size and shape polydispersity of the droplets. To this end, we may imagine that owing to the thermal fluctuations, there is an ensemble of droplets present in

the solution, which is made up of subensembles that are statistical–mechanically different in being characterized by different sets of stoichiometric numbers. These notions provide the physical background for making use of a multiple equilibrium scheme to account for the droplet/complex formation.

This very problem can also be handled by introducing a length scale parameter, l , which is a measure of the pertinent length scale associated with the quantification of the configurational state of the dispersed droplet system, i.e. the length over which a droplet contour should be shifted to be counted as a new configuration (Fig. 1). As was first discussed by Reiss [15], and later on by Reiss et al. [16,17] and Kegel and Reiss [18], this leads to a mixing entropy given by

$$\Delta S_{\text{mix}}/k = -N_2 \ln\left(\frac{\phi_2 l^3}{v_2 e}\right), \quad (15)$$

which thus incorporates the entropy effects of the size and shape fluctuations of the (soft) droplets. By comparing with experimental data and carrying out model calculations, it was shown that the factor v_2/l^3 typically is on the order of 10^5 and, hence, there is a vast numerical difference between

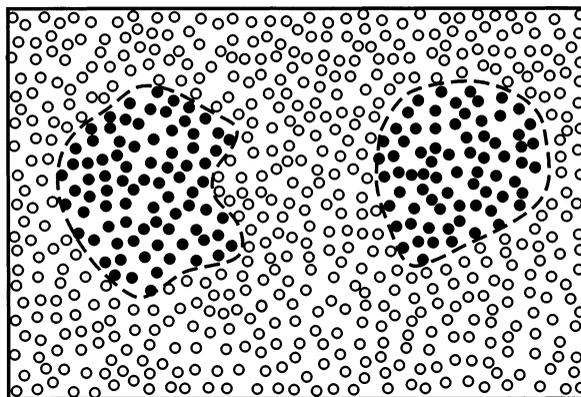


Fig. 1. Sketch of size- and shape-fluctuating microemulsion droplets. The thermal fluctuations will result in a variable number of constituent molecules and hence make the droplets statistical–mechanically different, i.e. they can be treated as loosely coupled molecular complexes of variable stoichiometry dispersed in a solvent. Indirectly, the fluctuations necessitate introducing a molecular length scale l of great significance when accounting for the configurational entropy of a droplet following the Utrecht scheme.

the two ΔS_{mix} expressions (14) and (15). The latter is for the most part over 10 k units more positive per particle than the former.

The chemical potential expression resulting from Eq. (15) is

$$\mu_2 = \mu_2^0 + kT \ln(\phi_2 l^3 / v_2) \quad (16)$$

and predicts, of course, much lower μ_2 -values than Eq. (9), provided the standard chemical potentials are taken to be the same.

In the following, we compare the Utrecht and Stockholm size distributions in a detailed manner, and by doing so, we are able to estimate the length scale parameter l . Moreover, we can actually demonstrate that a factor of the form v_2/l^3 emerges naturally from the multiple equilibrium treatment by invoking *coupled* shape and size fluctuations (Appendix A).

3. Thermodynamic relations

Let us next focus on the Winsor II microemulsion case, taking the excess water phase to be the reference state as discussed above. We assume this excess phase to be composed of almost pure water. To derive the Gibbs free energy of a microemulsion droplet, $G_d(= A_d + p_e v_d, p_e$ denoting the external, atmospheric pressure), we may imagine that a number of equal-sized, yet thermodynamically *open* water packages containing N_w water molecules first are formed out of the reference phase without causing any free energy changes, and then dispersed in the oil phase. Neglecting, for the time being, the interfacial contributions, the free energy per dispersed water core (that is taken to be the same as the *particle* chemical potential denoted by μ_2 in the previous section) is, in accordance with Eq. (9), given by

$$G_{\text{core}}(N_w) = G_{\text{core}}^0(N_w) + kT \ln \phi_{N_w}, \quad (17)$$

where ϕ_{N_w} is the volume fraction of the water cores containing N_w water molecules. In a second deduction step, we take into account that these water cores actually become dressed with a surfactant film, writing

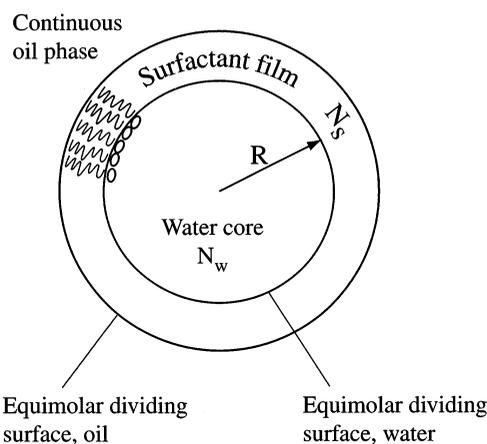


Fig. 2. Surface-thermodynamic idealization of a Winsor II microemulsion droplet showing the water core part extending up to the equipolar dividing surface of the water component, and the (pure) surfactant film which is separated from the surrounding oil phase by an equipolar dividing surface for the oil component.

$$G_d(N_w, N_s) = G_{\text{core}}^0(N_w) + kT \ln \phi_{N_w, N_s} + G_f(N_w, N_s), \quad (18)$$

where subscript d is short for ‘droplet’, f for ‘film’, and ϕ_{N_w, N_s} denotes the water volume fraction of a droplet aggregate composed of N_w water molecules and N_s surfactant molecules. The interfacial free energy $G_f(N_w, N_s)$ refers to the (pure) surfactant film composed of N_s surfactant molecules which is defined by two equipolar dividing surfaces, one for the water component on the inside, and one for the oil component on the outside (Fig. 2).

Note that the droplets need not be perfectly spherical. For a non-spherical droplet, N_s will obviously be larger than $4\pi R^2/a_s$, R denoting the radius of the inner dividing surface and a_s the surface area per surfactant molecule at that same dividing surface. Moreover, it should be realized that G_f depends not just on N_s but, in addition, on the curvature of the interface which is influenced by N_w .

In a third step, we make use of the standard condition for aggregation equilibrium,

$$G_d(N_w, N_s) = N_w \mu_w + N_s \mu_s, \quad (19)$$

where the water chemical potential, μ_w , is primarily determined by the state of the coexisting water phase, and the surfactant chemical potential, μ_s , by the surfactant concentration in the oil phase. Deducting the above equilibrium condition from both sides of Eq. (18), and introducing the droplet excess free energy by the relation

$$\varepsilon_d(N_w, N_s) = G_{\text{core}}^0(N_w) + G_f(N_w, N_s) - N_w\mu_w - N_s\mu_s, \quad (20)$$

where, for a Winsor II microemulsion,

$$G_{\text{core}}^0(N_w) = N_w\mu_w \quad (21)$$

we arrive at the central relationship

$$\varepsilon_f(N_w, N_s) + kT \ln \phi_{N_w, N_s} = 0, \quad (22)$$

$\varepsilon_f(N_w, N_s) \equiv G_f - N_s\mu_s$ denoting the excess free energy (in the Ω -potential sense) of the surfactant film alone.

Firstly, it is worth noting that the droplet free energy ε_d of Eq. (20) is in effect a Helmholtz free energy (A) as the $p_e V$ -parts of the droplet Gibbs free energies cancel against the corresponding $p_e V$ -parts of $N_w\mu_w$ and $N_s\mu_s$. Secondly, Eq. (21) is perhaps somewhat less evident than it might seem at first. It presupposes that an excess water bulk phase is actually present in the system, and that we have chosen this phase as the reference state of the droplets. If, in fact, the excess phase were not present, i.e. if we were dealing with an one-phase microemulsion, we would have had to invoke the difference between $G_{\text{core}}^0(N_w)$ and $N_w\mu_w$ equal to $N_w\Delta\mu_w$, representing the free energy it takes to form the droplet core from molecularly dispersed water at its activity in the microemulsion [7–9].

Furthermore, if we had decided about choosing the mole fraction rather than volume fraction particle concentration scale it would have been necessary to switch to the corresponding reference state, $G_{\text{core}}^\theta = G_{\text{core}}^0 + kT \ln(v_{\text{core}}/v_1)$, implying that the droplet excess free energy formally would have been larger by the amount $kT \ln(v_{\text{core}}/v_1)$, v_1 denoting the molecular volume of the (organic) solvent. In such a case the alternative but, entirely equivalent equilibrium condition

$$\varepsilon_f(N_w, N_s) + kT \ln(v_{\text{core}}/v_1) + kT \ln x_{N_w, N_s} = 0 \quad (23)$$

would have resulted, verifying that the final outcome, as it should, is indeed independent of the choice of standard state as $(v_{\text{core}}/v_1) \times N_w N_s$ equals ϕ_{N_w, N_s} .

For the case of spherical geometry one obtains

$$\varepsilon_f(N_w, N_s) = \varepsilon_f(R) = 4\pi R^2\sigma, \quad (24)$$

whereby the curvature-dependent droplet surface tension $\sigma(R)$ is introduced thermodynamically and likewise the droplet surface area $\mathcal{A} = 4\pi R^2$, both quantities being defined with respect to the equimolar dividing surface of the water component.

Taken together, Eqs. (22) and (24) imply, of course, the attractively simple relationship

$$4\pi R^2\sigma + kT \ln \phi_{N_w, N_s} = 0, \quad (25)$$

which, however, applies just to spherical droplet shapes. For these shapes, the stoichiometric numbers N_w and N_s are both simple functions of the radius R . Counting the number of different spherical states one can then preferably choose to regard N_s as an independent (discrete) variable and N_w as a dependent variable, in line with the earlier Utrecht treatment [9]. This is a point, however, to which we shall return in the next section.

The notion of a balance between the local excess free energy of colloidal particles and the free energy of dispersing particles in a solvent medium, as expressed by Eq. (25), was put forward earlier by Volmer [19], and Reh binder and Shchukin [20,21]. Further, it was the point of departure of Reiss's microemulsion paper [15] from 1975 and a chief ingredient of the celebrated paper from the following year on the theory of surfactant micelles by Israelachvili et al. [22]. Yet, exhaustive derivations of Eqs. (22) and (25) are scarce. Note, in particular, that the multiple equilibrium model implies that a free energy compensation of this kind occurs for each and every one of the various droplet complexes present in a microemulsion characterized by different sets of independent stoichiometric numbers N_w and N_s .

Moreover, returning to spherical droplets, the surface tension σ will generally be a function of the interfacial curvature as well as of the packing density in the surfactant film. Apparently, it is the

radial dependence we focus on by introducing the Helfrich expression in the form of Eq. (2), tacitly assuming that some very minor adjustments of the surfactant area a_s will suffice to satisfy the boundary condition $\mu_s = \text{constant}$. Thus, in effect, when counting the number of stoichiometric states, the interfacial film is supposed to be laterally incompressible.

In addition to the (integral) chemical potential of the droplet as given by Eq. (18) one may introduce a (partial) chemical potential of the water inside the water cores, corresponding to simultaneously increasing the number of water molecules from N_w to $N_w + 1$ in all the droplets of the N_w subensemble while keeping T , p_e (the external pressure) and μ_s constant, i.e.

$$\mu_{N_w} = \partial(G_d - N_s\mu_s)/\partial N_w)_{T,p_e,\mu_s} \quad (26)$$

The water chemical potential defined in this manner will vary, of course, with the pressure variations accompanying the size and shape changes. As noted already in Section 1, for spherical droplets, $\Delta p = p_i - p_e$ becomes zero for the particular droplet radius (R_{eq}) where the overall droplet free energy has a minimum. Hence,

$$\mu_{N_w}(R_{eq}) = \mu_w \quad (27)$$

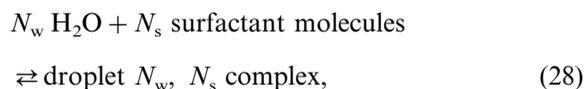
This physico-chemical ('phase') equilibrium condition accordingly signifies the fully equilibrated, spherically shaped droplet of radius $R = R_{eq}$ about which, however, significant fluctuations in shape and size occur that we in the next section are going to treat in detail by means of the multiple equilibrium scheme.

An additional remark of interest in this context might be that the shape fluctuations for the most part are likely to occur while keeping a constant and homogenous pressure p_i inside each droplet as it is well known that a multitude of geometrically closed shapes are compatible with the general Laplace equation [23,24].

4. The droplet size distributions ϕ_R and ϕ_j , and the length scale l

In order to derive the droplet size distribution of Winsor II microemulsions on the basis of the

multiple equilibrium approach, we assume a set of equilibrium reactions of the kind



where N_w and N_s serve as stoichiometric coefficients. For each of the droplet complexes present, Eq. (22) must be fulfilled at aggregation equilibrium. Consequently,

$$\phi_{N_w, N_s} = e^{-\epsilon(N_w, N_s)/kT} \quad (29)$$

In other words, every N_w, N_s complex is associated with a Boltzmann factor where the droplet excess free energy occurs in the exponent. In order to obtain the total volume fraction of droplets, one has to sum over all the various stoichiometric states

$$\phi_{tot} = \sum_{N_w} \sum_{N_s} e^{-\epsilon(N_w, N_s)/kT}. \quad (30)$$

Incidentally, from this expression it is evident that ϕ_{tot} plays the role of a (grand) partition function. Next, we switch to droplet variables: the radius R and the shape factor $\chi = \mathcal{A}/4\pi R^2$, the latter being defined for a *fixed* droplet volume equal to $4\pi R^3/3$. Moreover, by writing

$$\epsilon_t(N_w, N_s) = 4\pi R^2 \chi \sigma / kT, \quad (31)$$

we anticipate that it might be sufficient to assume that the surface tension σ is independent of χ and thus equal to $\sigma(R)$ of the undistorted spherical droplet ($\chi = 1$). Approximating the double sum of Eq. (30) by the corresponding double integral, the total volume fraction of droplets is now given by the expression

$$\phi_{tot} = \int_0^\infty \int_1^\infty e^{-4\pi R^2 \chi \sigma / kT} |J| d\chi dR \quad (32)$$

that includes the Jacobi determinant

$$J = \begin{vmatrix} \frac{\partial N_w}{\partial R} & \frac{\partial N_s}{\partial R} \\ \frac{\partial N_w}{\partial \chi} & \frac{\partial N_s}{\partial \chi} \end{vmatrix}. \quad (33)$$

Additionally, assuming incompressibility we have the obvious relations

$$N_w v_w = 4\pi R^3/3, \quad (34)$$

$$N_s a_s = \mathcal{A} = 4\pi R^2 \chi, \quad (35)$$

resulting in

$$|J| = \frac{16\pi^2 R^4}{v_w a_s}. \quad (36)$$

Supposing the droplet surface tension σ to remain the same everywhere and equal for all droplets of a given volume but of variable shape, we can readily carry out the integration over the shape factor χ , resulting in the ϕ_{tot} integral

$$\phi_{\text{tot}} = \frac{4\pi}{v_w a_s} \int_0^\infty \frac{R^4}{(\sigma R^2/kT)} e^{-4\pi R^2 \sigma/kT} dR, \quad (37)$$

which implies the size distribution

$$\phi_R = \frac{4\pi R^4}{v_w a_s (\sigma R^2/kT)} e^{-4\pi R^2 \sigma/kT}. \quad (38)$$

It turns out, however, that σR^2 is practically constant in the size range where the distribution peaks, with an average value close to the minimum value of the $\sigma R^2/kT$ function (Fig. 3(b)), a minimum value for convenience denoted by M . Typically, M is found to be about 1.0–2.5. Hence,

$$\phi_R = \frac{4\pi R^4}{v_w a_s M} e^{-4\pi R^2 \sigma/kT}. \quad (39)$$

A less approximate form of the ϕ_R size distribution can be derived by considering in some detail how the overall curvature free energy depends upon the shape [25]. Accordingly, we find that the above ϕ_R distribution has to be replaced by a closely related distribution (Fig. 4),

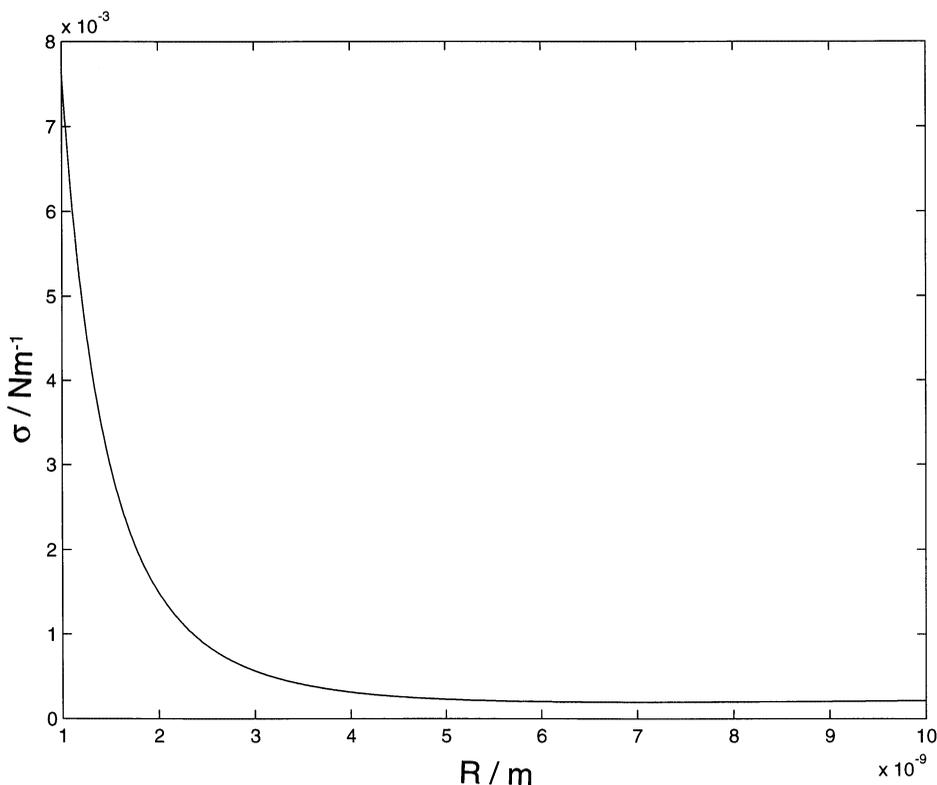


Fig. 3. (a) The surface tension function $\sigma(R)$, and (b) the quadratic σR^2 potential well for a case of small droplets. The former has a minimum for $R = 7.03$ nm, whereas the latter is centred about $R = R_{\text{eq}} = 3.59$ nm. The corresponding Helfrich expression parameters are $\gamma = 4.0 \times 10^{-4}$ N/m, $k_1 = -2.87 \times 10^{-12}$ N, $k_2 = 1.009 \times 10^{-20}$ J.

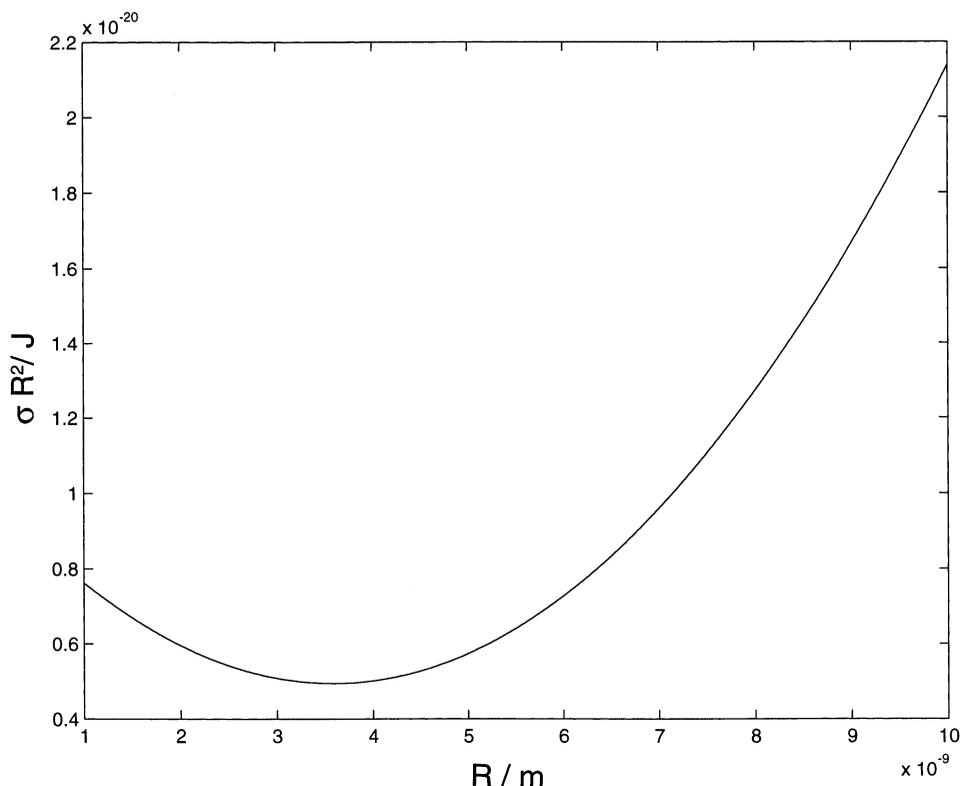


Fig. 3. (Continued)

$$\phi_R = \frac{4\pi R^4}{v_w a_s M (1 + 4k_c/MkT)} e^{-4\pi R^2 \sigma/kT}, \quad (40)$$

where the preexponential factor is about 1/5 of the one in Eq. (39). This more exact result indicates that in reality the resistance towards shape changes is likely to be greater than what we implicitly assume by putting σ independent of χ when deriving Eq. (39).

To demonstrate the validity of the Utrecht size distribution takes even less labour, especially so if we start out from the chemical potential expression (16), and restrict the treatment to spherical shapes (for which N_w and N_s are dependent), resulting in the equilibrium condition

$$4\pi R^2 \sigma + kT \ln(\phi_{N_s} l^3/v_d) = 0 \quad (41)$$

from which the distribution function immediately follows,

$$\phi_{N_s} = \frac{4\pi R^3}{3l^3} e^{-4\pi R^2 \sigma/kT}. \quad (42)$$

In order to stress the use of N_s as a discrete, independent variable, we may make a change of notation from N_s to j and write down the distribution in the same way as in several previous publications by the Utrecht group, i.e.,

$$\phi_j = \frac{4\pi R_j^3}{3l^3} e^{-4\pi R_j^2 \sigma/kT}. \quad (43)$$

Switching to integration over R , the integrand has to be multiplied by the derivative

$$\frac{dj}{dR} = \frac{8\pi R}{a_s} \quad (44)$$

and, hence, the ϕ_R distribution in correspondence with Eq. (43) becomes

$$\phi_R = \frac{32\pi^2 R^4}{3l^3 a_s} e^{-4\pi R^2 \sigma/kT}. \quad (45)$$

With due satisfaction we note, of course, that the preexponential factor of the above distribution is

proportional to R^4 , in full correspondence with the size distributions (39) and (40) above. Furthermore, by comparing the preexponential factors of Eqs. (40) and (45) we get, inserting $M = 1.75$ and $k_c = 1.5 kT$,

$$l^3 \cong 65v_w \cong 2 \text{ nm}^3 \quad (46)$$

implying that the length scale parameter l has to be on the order of 1 nm to yield numerical agreement between the two treatments. It is reassuring that this is about the same order of magnitude as estimated earlier in various ways by the Utrecht group on the basis of experimental data and making model calculations [9].

The close agreement thus established may seem somewhat fortuitous at first sight as the preexponential factors appear to have quite different backgrounds in the two treatments. As to the

Stockholm distribution, this factor stems formally from the Jacobian of Eq. (36) and involves the size (R^2) as well as the shape (R^2) fluctuations. As regards the Utrecht ϕ_j distribution, on the other hand, the droplet volume (R^3) divided by the length scale parameter l raised to the power of 3 is introduced to account for the additional entropic advantage related with the dispersed droplet state in comparison with the state of the excess phase, whereas the dj/dR derivative of Eq. (44) merely yields a factor of R .

To come to grips with the above differences it seems as a reasonable idea to calculate the number of additional droplet/aggregate states that are generated by *coupled* shape/size fluctuations occurring under a constraint of *constant droplet surface area*. These fluctuations will leave N_s unchanged while lowering N_w from its maximum

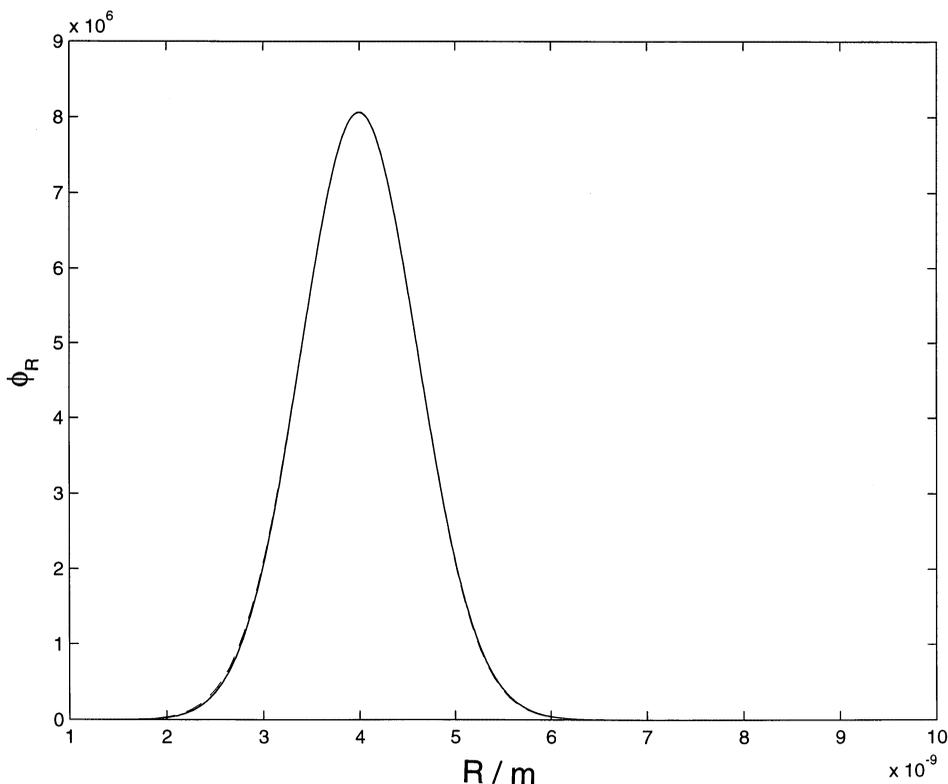


Fig. 4. The size distribution according to Eq. (40) obtained by using the parameter values in Fig. 3, assuming \bar{k}_c to be zero and putting $M = 1.2$. The maximum occurs for $R = R_{\max} = 4.00$ nm. The corresponding Gaussian distribution Eq. (52), which is indicated by the dashed curve is almost indistinguishable from the original distribution. With $G_{\max} = 1.552$ the relative half width, σ_R/R_{\max} equals 0.153. According to Eq. (55), the total (water) volume fraction of microemulsion droplets amounts to 0.0124.

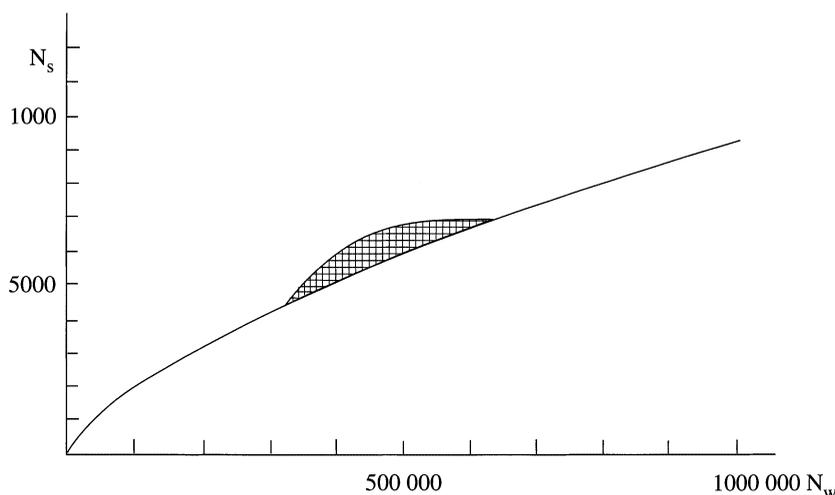


Fig. 5. Graphical representation of the function $N_s(N_w)$ for spherical w/o microemulsion droplets assuming $a_s = 50 \times 10^{-20} \text{ m}^2$ and $v_w = 30 \times 10^{-30} \text{ m}^3$. The chequered area above the drawn line symbolizes the region in the N_s – N_w plane from where we get significant contributions to the ϕ_{tot} integral upon considering N_s and N_w as stochastic variables. According to the Utrecht scheme this region is traversed horizontally towards the left, whereas according to the Stockholm scheme, the same region is traversed upwards in the vertical direction. Evidently, for one and the same set-up of parameter values, the resulting size distributions must be equivalent.

value for the undistorted spherical droplet, and belong, in fact, to the physical scenario of the Utrecht ϕ_j distribution (Fig. 5). As shown in Appendix A, an approximate calculation along these lines yields the size distribution

$$\phi_j = \frac{R_j^3}{2Mv_w} e^{-4\pi R_j \sigma / kT}, \quad (47)$$

which is practically the same as the above Eq. (43) inserting $M = 1.75$ and $l = 0.76 \text{ nm}$. Thus, by referring to the multiple equilibrium model we can actually rationalize the preexponential factor of the Utrecht ϕ_j distribution that primarily relates to the number of surfactant molecules in the surfactant film of spherical droplets. The R^3 dependence can be understood as a consequence of the N_w fluctuations of each droplet occurring under a constraint of constant droplet surface area, i.e. constant $j = N_s$.

The ϕ_R size distribution derived above that is proportional to $R^4 \exp(-4\pi R^2 \sigma / kT)$ is slightly different from the one published earlier by the Stockholm group: $\sim R^5 \exp(-4\pi R^2 \sigma / kT)$ for the Winsor I and II cases. The reason for this after all rather minor change of the preexponen-

tial factor is that, in due course, we have realized that the effect of the fluctuations of the average surfactant packing density in the surfactant film (which would have yielded a factor R more) should not be separately invoked here. These fluctuations certainly contribute to the free energy of a single droplet but, on the basis of a statistical–mechanical analysis using the grand canonical ensemble, we may conclude that this contribution is automatically included by means of the Helfrich expression (2) where γ refers to the *macroscopic* w/o interfacial tension.

5. Approximating the size distribution by a Gaussian function

The preexponential factor $S(R)$ of the ϕ_R distribution, which for Winsor II microemulsions we have established is proportional to R^4 is numerically very large, typically $10^{13} - 10^{18} \text{ m}^{-1}$. Consequently, it contributes greatly to raising the overall volume fraction of droplets for realistic values of the droplet surface tension ($10^{-3} - 10^{-6} \text{ N/m}$). Moreover, the R^4 factor tends to

favour large droplets, shifting the size distribution towards radii above the thermodynamic equilibrium radius R_{eq} . Now, it is well known that for practical purposes, a distribution function of the form $R^n \exp(-\text{const} \times \Delta R^2)$ can often be approximated by an ordinary Gaussian function. Below we present a simple scheme for the R^4 case of this sort, similar in scope to the one already available for the R^5 case [8], with the purpose of facilitating the evaluation of the three Helfrich parameters γ , $k_1 = -4k_c H_0$, and $k_2 = 2k_c + \bar{k}_c$ from experimental data.

We set out by writing σR^2 as a quadratic function of R in the form

$$\sigma R^2/kT = \gamma \text{ i.e. } (R - R_{\text{eq}})^2/kT + M, \quad (48)$$

where, as before, M stands for the minimum value of $\sigma R^2/kT$ at $R = R_{\text{eq}}$. Hence, we can rewrite ϕ_R as given by Eq. (40) in the following way

$$\phi_R = \frac{4\pi R^4 e^{-4\pi M}}{v_w a_s M(1 + 4k_c/MkT)} e^{-4\pi\gamma(R - R_{\text{eq}})^2/kT}. \quad (49)$$

Introducing the radius where the size distribution peaks, R_{max} by writing

$$R = R_{\text{max}} + \Delta R \quad (50)$$

and the relative deviation y from R_{max} as

$$y = \Delta R/R_{\text{max}}, \quad (51)$$

it is easily verified that the above ϕ_R distribution can be approximated by means of the following Gaussian function (Fig. 4)

$$\phi_R = \frac{4\pi R_{\text{max}}^4 e^{-4\pi M} e^{-1/\pi G_{\text{max}}}}{v_w a_s M(1 + 4k_c/MkT)} e^{-2y^2(1 + 2\pi G_{\text{max}})}, \quad (52)$$

where G_{max} equals the value of $\gamma R^2/kT$ for $R = R_{\text{max}}$ at the peak of the size distribution. In addition, we have as a condition for having a maximum at R_{max} :

$$R_{\text{eq}}/R_{\text{max}} = 1 - \frac{1}{2\pi G_{\text{max}}} \quad (53)$$

relating $R_{\text{eq}}/R_{\text{max}}$ and G_{max} . From Eq. (52), it is obvious that relative width (polydispersity) of the distribution is given by the expression

$$\sigma_R/R_{\text{max}} = \frac{0.5}{\sqrt{1 + 2\pi G_{\text{max}}}}. \quad (54)$$

As G_{max} normally falls in the range 1–4, σ_R/R_{max} values within the interval 0.1–0.2 are generally anticipated, in broad agreement with a multitude of experimental data as well as previous estimates [8]. By integrating Eq. (52), we get the total volume fraction of droplets,

$$\phi_{\text{tot}} = \frac{4\pi R_{\text{max}}^5 e^{-4\pi M} e^{-1/\pi G_{\text{max}}}}{v_w a_s M(1 + 4k_c/MkT)} \left(\frac{\pi}{2 + 4\pi G_{\text{max}}} \right)^{1/2}, \quad (55)$$

where the two main competing factors are the dimensionless ($R_{\text{max}}^5/(v_w a_s)$) factor related with the size and shape fluctuations, on the one hand, and the $\exp(-4\pi M)$ factor that includes the minimum value M of the droplet free energy, on the other. The somewhat complex numerical factor $(\exp(-1/\pi G_{\text{max}})(\pi/(2 + 4\pi G_{\text{max}})))^{0.5}$ typically amounts to but about 0.3, whereas the factor in the denominator $(1 + 4k_c/MkT)$ usually is about 5. It follows from Eq. (55) by putting G_{max} equal to 1.50 (which according to Eq. (54) implies $\delta_R/R_{\text{max}} = 0.155$) that $M = 1.2$ would correspond to a volume fraction of about 0.01 of droplets having an average radius of 4 nm, while $M = 2.3$ would correspond roughly the same volume fraction of droplets having an average radius of 70 nm. Here, it should be recalled that by definition we have the relation

$$M = k_2/kT - G_{\text{max}}(R_{\text{eq}}/R_{\text{max}})^2. \quad (56)$$

The primary purpose of the above scheme is to facilitate computing values of the parameters γ , k_1 and k_2 from experimental data on δ_R/R_{max} , R_{max} and ϕ_{tot} . Note, by the way, that additional experimental information is needed in order to obtain k_c and \bar{k}_c separately. However, as discussed in Refs. [8] and [26] there is evidence in support of assuming \bar{k}_c to be much smaller than k_c as we have done, for instance when deriving the size distribution (40).

6. Discussion

In this paper, we have demonstrated that the Utrecht and Stockholm treatments of Winsor I

and II microemulsions can be fully reconciled within a common theoretical framework based on a rather simple multiple equilibrium scheme encompassing size and shape fluctuations (Fig. 5). Accordingly, in the Utrecht treatment the effect of coupled shape–size fluctuations at fixed surface area, \mathcal{A} is in principle covered by the extra term $kT \ln(I^3/v_2)$ in the droplet chemical potential expression (Eq. (16)). This term was originally introduced to account for the influence of the detailed configurational state of the microemulsion. On the other hand, according to the Stockholm approach, for any given number of molecules making up the droplet core, a set of shape states of variable surface area \mathcal{A} is invoked. Yet, the resulting Utrecht and Stockholm size distributions are, in essence, equivalent. The corresponding multiple equilibrium treatment published by Borkovec et al. [27] over a decade ago, though conceptually closely related, is restricted to spherical droplet shapes.

Whether or not some additional finite size effects of entropic nature, besides the size and shape fluctuations, should be brought into the picture, is still a matter of discussion. However, by referring to a rather general statistical–mechanical argument valid for independent, open subsystems, we have concluded that the effect of the fluctuations in mean surfactant density of the surfactant film of a microemulsion droplet can be left aside provided one refrains from making any finite size corrections of the entropy associated with the polar head group–water mixing as well as the hydrocarbon tail–oil mixing. Hence, for the time being and lacking compelling experimental evidence in support of the opposite, it seems justifiable to stick to the notion of a size distribution consisting of a preexponential factor that relates merely to the size and shape fluctuations, times an exponential of a purely thermodynamic origin. The corresponding physical model can be visualized as a small droplet with a curvature-dependent surface tension, which is subject to random variations (due to the thermal fluctuations) of its core volume and surface area. Each kind of droplets present, incorporating a certain number of water and a certain number of surfactant molecules, has to be treated as a distinct complex in a multiple equilibrium scheme.

Finally, it is worth noting that *single phase microemulsions* can be treated in much the same way by introducing a hypothetical excess phase subject to a reduced external pressure p_e , whereas for multicomponent Winsor I and II microemulsions, the present treatment should be applicable essentially without any change, a major difference being, however, that the Helfrich expression parameters would then become composition-dependent.

Acknowledgements

Jan Christer Eriksson gratefully acknowledges financial support while staying as a guest professor at the Department of Physical and Colloid Chemistry of the University of Utrecht where the present paper was outlined. Professor emeritus Agienus Vrij and Dr. Magnus Bergström are warmly thanked for valuable comments on central parts of the present exposition.

Appendix A

Using the ϕ_{tot} integral over N_w and N_s as the starting-point, viz.,

$$\phi_{\text{tot}} = \int_{N_w} \int_{N_s} e^{-4\pi r^2 \chi \sigma / kT} dN_w dN_s \quad (\text{A.1})$$

we shall carry out the integration over N_w while keeping N_s constant. For each N_s we have $r^2 \chi = \text{constant} = R^2$, where r denotes the radius of a sphere with the same volume as the distorted sphere of the surface area $4\pi R^2$. Inserting $dN_w = (4\pi R^2/v_w) dr$ and introducing x by

$$r = R(1 - x) \quad (\text{A.2})$$

we have

$$I_{\text{shape/size}} = \frac{4\pi R^3}{v_w} \int_0^1 e^{-4\pi R^2 \sigma / kT (1-x)^2} dx, \quad (\text{A.3})$$

where σ is assumed to depend on x only (i.e. on r but not of χ) at the integration, similarly to how we went about deriving Eq. (39). Now, $x \ll 1$ in the range of the size distribution peak and, hence, we can put $(1-x)^2 \approx 1$. Furthermore, from the Helfrich expression (2) one obtains

$$\sigma(r) = \gamma + \frac{k_1}{R(1-x)} + \frac{k_2}{R^2(1-x)^2}$$

$$\cong \sigma(R) + 2MkTx/R^2, \quad (\text{A.4})$$

where in the second step k_1 is put equal to $-2\gamma R_{\text{eq}} = -2\gamma R$ and M to $(k_2 - \gamma R^2)/kT$. Thus,

$$I_{\text{shape/size}} \cong \frac{4\pi R^3}{v_w} e^{-4\pi R^2 \sigma(R)/kT} \int_0^1 e^{-8\pi Mx} dx \quad (\text{A.5})$$

resulting in

$$I_{\text{shape/size}} \cong \frac{R^3}{2Mv_w} e^{-4\pi R^2 \sigma(R)/kT} \quad (\text{A.6})$$

and the ϕ_j size distribution

$$\phi_j = \frac{R_j^3}{2Mv_w} e^{-4\pi R_j \sigma/kT}. \quad (\text{A.7})$$

Comparing with the Utrecht distribution, Eq. (43), the length parameter l is estimated to 0.76 nm (for $M=1.75$) which is slightly less than obtained by comparing Eqs. (40) and (45). However, the present calculation is less accurate, closely corresponding to the one resulting in Eq. (39). In fact, by multiplying Eq. (A.7) with $8\pi R$ we obtain Eq. (39), indicating full consistency. On the other hand, when deriving the distribution (40) we took into account that the droplet free energy will increase by more than just $\sigma\Delta A$, even when a spherical droplet is but slightly deformed.

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