Self-consistent field theory for the nucleation of micelles

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We report the first molecular model for the transition states (critical nuclei) that determine the rate of micelle formation and breakdown. These processes, and homogeneous nucleation of macroscopic phase separation are handled in a unified way. It turns out that with micelle-forming amphiphiles several new features appear that do not occur with ordinary phase separation. We predict that the activation free-energy barrier for micelle formation is maximal but finite at the critical micelle concentration (CMC) and decreases with concentration. The barrier for micelle breakdown vanishes at the CMC and increases with concentration. Furthermore, our results indicate formation of transient large aggregates upon quenches far beyond the CMC. © *1999 American Institute of Physics.* [S0021-9606(99)50610-7]

INTRODUCTION

Self assembly by amphiphilic molecules such as surfactants and biolipids in aqueous media, and block copolymers in selective solvents is scientifically intriguing but also of great practical relevance. The equilibrium properties of selfassembled objects have been extensively studied. In the context of processes such as emulsification, flotation, and detergency, the *rates* of formation and breakdown of micelles are of key importance. So far, these rates could not be derived from molecular properties. This motivates the present study.

In relaxation experiments on micellar systems usually two characteristic times are observed. Following the kinetic analysis of Aniansson and Wall,¹⁻³ the so called "fast process" is usually interpreted in terms of an adjustment of micellar sizes. The "slow process" is assumed to be a change of the total number of proper micelles. Up until now, no theoretical approach has been available to estimate and interpret these rates in molecular terms because no models have been available for the transition states involved. A rare exception is the theory by Halperin and Alexander which focuses on the fast process in polymeric micelles.⁴ The present paper deals with the transition state preceding the formation or breakdown of entire micelles (the slow process). We will introduce a method to model these transition states, and we will demonstrate the most important general features by examining some selected examples. We will pay special attention to the similarities and differences between nucleation behavior of simple phase-separating molecules and of self assembling amphiphiles.

There are close parallels between nucleation of new micelles and of a new phase.⁵ A transition state which dominates the rate of such a process corresponds to a saddle point in the free-energy surface: the lowest "pass" in the free energy "ridge" separating the initial metastable homogeneous state from the new inhomogeneous state. At this saddle point, the free-energy is a maximum with respect to the reaction coordinate, for which we can take the aggregation number N^a . It is a minimum with respect to all other internal variations. In the context of nucleation of phase transformations, the labile aggregate corresponding to such a saddle point is usually called a *critical nucleus*.^{2,3,5–11} We will also use this term for the case of micelle formation. A little more quantitatively: the reversible work to create an aggregate at a fixed position at conditions of constant temperature *T*, chemical potentials μ , and pressure *p* is given by

$$W = U - TS - \boldsymbol{\mu} \cdot \boldsymbol{N} + p \, \boldsymbol{V},\tag{1}$$

where U is the energy, S is the entropy, N is the numbers of molecules, and V is the volume of the system containing an aggregate. Clearly, W vanishes for homogeneous bulk systems. Although it is inevitable in a finite closed system that μ and in some cases also p change eventually as the medium gets depleted of the aggregating species, it is justified to assume that T, μ , and p remain constant during the nucleation stage, even for a closed system, because a nucleus is very small relative to the whole macroscopic system. A maximum of $W(N^a)$ plays the role of an activation barrier in the kinetics of aggregation. It can be derived that the rate of formation of aggregates (micelles or droplets of a new macroscopic phase) can be expressed in the form of an Arrhenius-type equation:^{2,3,5,8,9}

$$J = J_0 \exp(-W^*/kT),$$
 (2)

where W^* is the maximum of $W(N^a)$. The pre-exponential factor J_0 is proportional to the arrival rate of molecules at an aggregate of about the critical size, and inversely proportional to the width of the activation barrier along the reaction coordinate N^a . Obviously, J is much more sensitive to W^* than to J_0 . An approach to obtain J_0 will be deferred to a future publication. In the present paper we will concentrate on W^* and on the characteristic properties of the critical nucleus.

For values *T*, μ , and *p* corresponding to a supersaturated metastable solution, $W(N^a)$ for nonamphiphilic molecules exhibits a maximum only.^{3,5} Beyond that maximum, $W(N^a)$

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decreases without bounds upon increasing N^a . Hence, aggregates will tend to grow without bounds (as long as T, μ , and p remain constant), and there is no corresponding equilibrium aggregate size distribution. Self assembly might be regarded as an arrested phase separation: For amphiphiles at concentrations above the critical micelle concentration (CMC, the concentration above which micelles appear), $W(N^{a})$ exhibits both a maximum and a minimum, corresponding to a minimum and a maximum, respectively, in the equilibrium aggregate-size distribution.^{2,3} The abundancy of free amphiphiles and of proper micelles [typically N^a = O(100)] is relatively high. In micelles, lyophobic parts of the amphiphilic molecules are segregated from lyophilic parts and the solvent. Aggregates of intermediate sizes, near the maximum of $W(N^a)$, are scarce. Because $W(N^a)$ contains a term $-N^a \mu_o$, where the subscript *o* denotes the aggregating compound, it decreases sharply upon increasing μ_{o} . As a consequence, increase of the concentration of amphiphiles beyond the CMC will predominantly lead to an increase of the equilibrium concentration of micelles, whereas the equilibrium concentration of free amphiphiles remains fairly constant.

For phase separation by homogeneous nucleation, several density-functional theories (DFT) have been published in which W^* and other properties of the critical nucleus were calculated.^{6–11} These theories in which the density distribution of a critical nucleus is obtained by a variational calculation are important improvements over the so-called classical nucleation theory in which a nucleus is presumed to be a droplet of the new phase. However, these density-functional theories (DFT) were either phenomenological and did not specify molecular properties,^{6,7} or they were restricted to rather simple spherical molecules.^{8–11} As a consequence, they are completely inadequate to handle self-assembling molecules.

THEORETICAL APPROACH FOR CRITICAL NUCLEI

Our approach is based on a theory in which complex flexible chain molecules, e.g., co-oligomers (chains consisting of different segments) can be handled. This theory is a generalization of the self-consistent field lattice theory (SFT), originally developed by Scheutjens and Fleer for polymer adsorption at planar surfaces.¹² Because we consider spherical nuclei (like in the DFT treatments), a curved pseudo-lattice consisting of concentric spherical layers is used in the same way as in work on equilibrium properties of self assembled spherical aggregates.^{13–16} At the mean-field level, the only relevant properties of the pseudo-lattice are the number of sites L(z) in each layer z, and the a priori transition probabilities, $\lambda_{\Delta z}(z)$, of going from a site at layer z to a site at $z + \Delta z$, Δz is -1, 0, or +1.¹³⁻¹⁶ Molecules are modelled as single segments or flexible chains of segments. Each segment occupies one lattice site. Segments on neighboring sites may interact. These interactions are quantified by the Flory-Huggins (FH) interaction parameter χ_{xy} which represents, in units of kT, the work of transferring an x segment from "pure x" to a "pure y" medium, or the other way around.12,17

In the present theory, the distribution $\{n_i^c\}$ of molecular states is evaluated (n_i^c) is the number of molecules of species *i* in state c). In this context, a molecular state is defined by the layer numbers of each chain segment. Hence, in the present approach different possible conformations of flexible chain molecules are accounted for, in contrast to the DFTs in which just the density distribution of rigid molecules is evaluated. A molecular state, as defined here, is degenerate: the number of possible realizations is given by $l_i^c(s)Z^{r_i-1}$, where Z is the coordination number of the lattice, r_i is the number of segments of an *i* chain, $l_i^c = L_i^c(s) \Lambda_i^c(s)$ where $L_i^c(s)$ is the number of sites of the layer where some segment s, belonging to an *i* chain in state c, is located, and $\Lambda_i^c(s)$ is the multiple product of the a priori transition probabilities of going from the layer where segment s is located to the layer where s+1 is located, etc., until the last segment, and of going from s to s-1, etc., down to the first segment. Consistency of all the $\lambda_{\Delta z}(z)$ ensures that the choice of the segment number s, from which an evaluation of l_i^c starts, is immaterial. The Helmholtz energy of an inhomogeneous mixture characterized by the distribution $\{n_i^c\}$, can be expressed as

$$\frac{\widetilde{F}(\{n_i^c\},T)}{kT} = \sum_{i,c} n_i^c \ln\left(\frac{n_i^c}{l_i^c}\right) + \frac{1}{2} \sum_{z,x,y} n_x(z) \langle \phi_y(z) \rangle \chi_{xy}.$$
 (3)

In this expression, terms linear in $\{n_i\}$ are omitted because they are irrelevant. The first term, in which the sum extends over all molecule species and conformations, represents the configuration entropy. The second term represents the nearest neighbor interactions between segments. Here $n_x(z)$ is the number of segments of type x at layer z, $\langle \phi_{y}(z) \rangle$ $=\lambda_{-1}(z)\phi_{v}(z)+\lambda_{0}(z)\phi_{v}(z)+\lambda_{1}(z)\phi_{v}(z), \text{ with } \phi_{v}(z)$ $=n_{y}(z)/L(z)$, is the average fraction of y segments among nearest neighbors of a segment at layer z. An admissible distribution $\{n_i^c\}$ should satisfy the constraints $\sum_x n_x(z)$ =L(z) for each layer z, and $\sum_{c} n_{i}^{c} = n_{i}$ for each molecular species *i*. The reversible work of creating an inhomogeneity at a fixed position is $W = \tilde{F} - \tilde{\mu} \cdot N$ with μ_i $=(\partial \tilde{F}/\partial n_i)_{T,n_{i\neq i}}$. An expression for the abundance of each molecular state in terms of a molecular field is obtained by evaluating $\partial W / \partial n_i^c = 0$ for each *i*, *c*, subject to the above mentioned constraints. It is possible to obtain the segment density distribution, which determines the molecular field, by means of a chain-conformation propagation scheme.¹² This enables an efficient numerical calculation in which it is not needed to compute all the n_i^c explicitly. The aggregation number of an aggregate is calculated as the excess number of accumulated molecules:

$$N^{a} = \sum_{z} L(z)(\phi(z) - \phi^{b})/r,$$
(4)

where $\phi(z)$, ϕ^b are the volume fractions of the aggregating species at layer *z*, in the bulk. In theories like the present SFT and in DFT, one obtains states of the system for which $(\partial W/\partial N^a)_{\mu,p,T}=0$, the maxima and minima of $W(N^a)$ as discussed in the Introduction. These will be labeled by an asterisk. The computational approach will be fully described elsewhere.

Equation (3) is a generalization towards inhomogeneous systems of the Flory-Huggins (FH) expression for a homogeneous polymer solution.^{12,17} So, FH theory provides the description for homogeneous isotropic systems and for the miscibility phase diagram that is consistent with the present treatment of inhomogeneous systems.

RESULTS AND DISCUSSION

In order to bring out the effects of amphiphilicity, it is instructive to compare results for solutions of an amphiphilic co-oligomer and of a homo-oligomer with the same number of segments, and for which the *average* interaction strength with the solvent is also the same. In terms of FH parameters the latter means that for the homo-oligomer

$$\chi = f_a \chi_{as} + f_b \chi_{bs} - f_a f_b \chi_{ab} , \qquad (5)$$

where subscripts *s*, *a*, and *b* indicate the solvent and the two segment types of the co-oligomer, and f_a and f_b are the fractions of *a* and *b* segments in the oligomer. FH theory for homogeneous bulk systems would give the same results for a co-oligomer as for a homo-oligomer if the interaction parameters are related as in Eq. (5) However, as we will see, allowing for inhomogeneity in a system, there are marked differences between behavior of the homo-oligomer and the co-oligomer.

For the present example $f_a = f_b = \frac{1}{2}$, $\chi_{as} = 2$ and χ_{bs} $=\chi_{ab}=\frac{1}{2}$, so the *a* segments are strongly lyophobic, and the b segments much less so. The average according to Eq. (5) is $\chi = 1\frac{1}{8}$. This exceeds the critical χ value for a chain of 20 segments, and FH theory predicts that the volume fraction at the low-concentration phase boundary (binodal) is 6.03 $\times 10^{-4}$. The boundary between the metastable and the unstable regime, the spinodal, is given by $\phi = 4.14 \times 10^{-2}$. It should be mentioned that a sharp spinodal is, strictly speaking, a mean-field concept. In reality, the boundary between metastable and unstable states and consequently between the conditions at which nucleation and growth and at which spinodal decomposition occurs is somewhat vague. For the present purpose of demonstrating certain principles, we did not attempt to find parameters that would adequately fit specific real-life molecules. Still, the present values do reasonably well in reproducing certain experimental properties of nonionic surfactants in aqueous solutions, e.g., the dependency of the CMC upon the length of the hydrophobic tail.

When we apply SFT to the aggregation of nonamphiphilic molecules in a supersaturated solution, e.g., monomers or simple chain molecules for which all segments are the same, we obtain results such as the dashed curves in Fig. 1. W^* decreases monotonically with the concentration between the binodal and the spinodal; at the spinodal it vanishes, whereas it diverges at the binodal. The aggregation number diverges both at the binodal and at the spinodal. Close to the binodal, the critical nucleus for the homooligomer is described adequately as a droplet of the incipient equilibrium phase [see the radial segment-density profile in-Fig. 2(a)]. The density inside the nucleus is similar to the incipient equilibrium phase (in fact it is slightly higher because of the Laplace-pressure difference across the curved



FIG. 1. (a) Work of formation of critical aggregates as a function of bulk volume fraction (volume fraction of free molecules). (b) Excess number of molecules accumulated in such aggregates. Drawn curves are for a cooligomer $a_{10}b_{10}$, dashed curves are for a homo-oligomer of 20 identical segments for which the *average* interaction with the solvent is the same as for the co-oligomer. The binodal and spinodal for the latter oligomer are indicated on the ordinate. The values of the interaction parameters are given in the text.

interface). The surface of the critical nucleus is similar to the planar macroscopic interface between coexisting phases at equilibrium, which can also be calculated from Eq. (3). Near the spinodal, the density varies smoothly over the entire cross section; no part of the critical nucleus is homogeneous [see Fig. 2(c), dashed curve]. At the spinodal the local excess concentration in the nucleus, $\phi(z) - \phi^b$, vanishes, and so does W^* . Yet, the radius of the critical nucleus and N^a both diverge. These general trends are the same as obtained by DFT treatments. The predicted behavior near the spinodal is an especially important improvement over classical droplet model, which does not exhibit any singularity at the spinodal, and predicts W^* to remain nonzero for all finite concentrations. The results from DFT treatments and from the present approach are consistent with the notion that at the spinodal, where $\partial^2 F / \partial \phi^2$ changes sign from positive to negative, the mixture turns from metastable to unstable, and that beyond the spinodal no activation barrier impedes phase separation.3,5,6,17

We now turn our attention to the central results, namely the behavior of W^* for an amphiphilic molecule also given in Fig. 1 (solid curves). These curves have a surprising structure, especially at low concentrations, which indicates that the behavior is fundamentally different from that of simple nonamphiphilic molecules. Rather than to diverge at a binodal concentration, as in the previous case, W^* exhibits cusps (labeled B at $\phi^B = 5.91 \times 10^{-4}$ and C at $\phi^C = 4.14 \times 10^{-4}$). Branch BC represents proper micelles. The corre-



FIG. 2. Radial volume-fraction profiles of aggregates. (a) Homo-oligomer at $\phi = 7.7 \times 10^{-3}$ (this is just above the binodal). This profile is very similar to that of a planar interface between coexisting phases as calculated for the same parameters. (b) Co-oligomer at the CMC ($\phi = 4.14 \times 10^{-4}$). This aggregate exhibits a pronounced segregation of lyophobic *a* segments and lyophilic *b* segments. (c) Co-oligomer and homo-oligomer at $\phi = 3.8 \times 10^{-2}$ (slightly below the spinodal). Segregation of *a* and *b* segments is almost absent, and the overall profile of the co-oligomer and the homo-oligomer are nearly the same. Small ticks indicate the centers of the lattice layers. To guide the eye, calculated points are connected by straight lines.

sponding aggregates have a segregated structure as is expected for micelles [see Fig. 2(b)]. The lyophobic *a* segments are found in the core of the aggregate whereas the relatively lyophilic *b* segments are located at the periphery. Such structures cannot be handled by the versions of DFT mentioned above. The modeling by SFT of micelles at equilibrium has been discussed elsewhere.^{13–16} In these treatments the work of formation of an aggregate at a fixed position, as plotted in

Fig. 1(a), is supplemented with a translational entropy term. In this way, the equilibrium concentration of micelles is obtained. The concentration of free molecules at which cusp C occurs is identified as the CMC. By comparing this CMC with the binodal concentration given above, we see that micelle formation sets in at a concentration below that at which separation of a macroscopic internally homogeneous phase would occur. As was already mentioned in the Introduction, the work of formation of micelles decreases steeply with increasing chemical potential and thus with the concentration of free amphiphiles, so that upon addition of amphiphiles beyond the CMC, the increase of the concentration of micelles is orders of magnitude larger than for free amphiphiles.

The branch AC in Fig. 1(a) gives the work of formation of critical nuclei. Close to the CMC, the critical nuclei of branch AC have a similar segregated structure as depicted in Fig. 2(b). Owing to this segregation, the work of formation of the critical nuclei is smaller for the amphiphile than for the homo-oligomer, and remains finite. Increasing the concentration from the CMC towards the spinodal point A, the critical nuclei are less and less structured, and finally become structureless, diffuse objects similar as for homo-oligomers. This is illustrated by the radial density profiles in Fig. 2(c). Such behavior is as expected: upon approach of the spinodal the bulk correlation length increases and the density profiles become more and more diffuse, resembling critical point behavior. Near the spinodal the correlation length exceeds the size of the chain molecule and the effects of chain amphiphilicity are washed out. As a consequence, all the properties of the amphiphilic labile aggregates gradually converge with those of the critical nuclei formed by the homo-oligomer. Indeed, also the work of formation of the labile aggregates becomes more and more similar to that for the homooligomer, and the curves for the amphiphile and the homooligomer meet at the spinodal [point A in Fig. 1(a)].

For homogeneous mixtures with $\phi^{C} < \phi < \phi^{B}$, points of branch AC represent the activation barrier in the process of formation of a micelle of branch BC. As shown in Fig. 1(a), this activation barrier decreases upon increasing concentration. For $\phi > \phi^{B}$ micelles cannot exist, and branch AC represents the activation barrier for the formation of aggregates that would grow on without bounds, if *T*, *p*, and μ would remain constant (similarly as discussed above for homogeneous nucleation of phase separation). However, it is inevitable in any finite closed system that the concentration of free molecules decreases as the aggregates grow. Hence, eventually ϕ will drop below ϕ^{B} and the large aggregates that form initially will disappear. The final result will be a micellar solution.

For the sake of clarity we have so far only considered aggregation processes occurring in a homogeneous solution in which no other aggregates are yet present. However, the most common situation in experiments on micelle kinetics is that micelles are already present. A quench will lead to a change of the distribution of micelles; both the total number of proper micelles changes as well as the size distribution of the micelles. Because a low concentration of micelles hardly influences the activity of the amphiphiles, we can without

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much error apply the graphs of Fig. 1 if we read for ϕ the volume fraction of unaggregated molecules. The activation barrier that has to be overcome in order to dissolve a micelle is given by the difference between the work of formation of a micelle [a point on branch BC in Fig. 1(a)], and the work of formation of a corresponding labile critical nucleus [the corresponding point on branch AC in Fig. 1(a)]. As can be seen in Fig. 1(a), this activation barrier vanishes at the CMC, where the work of formation of a proper micelle and of a critical nucleus coincide. Upon increasing the concentration above the CMC the activation barrier for micelle breakdown increases.

For a quench of a micellar system beyond ϕ^{B} , the micelles that are present can evolve into transient large aggregates such as discussed above, but in this case without the need to pass an activation barrier. Again, the resulting large aggregates will disappear as the solution gets depleted of unaggregated amphiphiles, and the final result will be a micellar solution. This may explain the initial angle-dependent increase of scattering intensity observed in recent *T*-jump experiments on "Pluronics"¹⁸ because with these amphiphilic compounds a temperature jump can bring the system quite far beyond the CMC.

There is also a third branch in Fig. 1(a), that originates from point B, and goes up steeply (intersecting AC). Radial density profiles (not included in the present paper) analogous to Fig 2(b) show that the aggregates corresponding to this branch are bilayer vesicles. A region with dilute solution is enclosed by a thin film of amphiphiles with a thickness that is about the same as the diameter of the micelle as shown in Fig. 2(b). This film has a stratified structure with *a* segments in the middle and *b* segments enriching the inner and outer surfaces. For the present system, these vesicles will be scarce at equilibrium because *W* for vesicles exceeds that for micelles.

In this paper we have chosen to present results for only a few characteristic examples of binary mixtures. However, the approach to nucleation that is introduced here is quite versatile and easily applied to other systems. Apart from nucleation of phase separation and of micelle formation and breakdown in binary systems, examples of which are examined above, the approach is applicable to more complex mixtures as well, e.g., to the case where nucleation of phase separation is influenced by a third, surface active component. These more complex cases will be elaborated in future work.

In the present study we have established a unified picture

for activation barriers occurring in nucleation of phase separation and in the kinetics of micelle formation and breakdown. We arrived at some striking predictions that should be experimentally accessible but that have so far not been considered in the interpretation of experiments. For the nucleation of phase transformations it was already well known that the activation barrier is infinite at the binodal, and decreases upon increasing activity (~concentration) of the component that will form the new phase. Our results indicate that with micelle formation there is also a significant dependency upon the depth of a quench. The activation freeenergy barrier for micelle formation is maximal but finite at the CMC and decreases as the activity of the amphiphiles increases. The activation barrier for micelle breakdown vanishes at the CMC and increases with increasing activity of the amphiphiles. Furthermore, our results indicate that for quenches far beyond the CMC, transient large aggregates will be formed. Those aggregates will disappear as the solution gets sufficiently depleted of unaggregated amphiphiles and a micellar solution will eventually form.

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