Theory of copolymer micellization

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We consider the micellization of block copolymers in solution, employing self consistent field theory with an additional constraint that permits the examination of intermediate structures. From the information for an isolated micelle (structure, binding energy, free energy) we describe how the global thermodynamics of these systems can be obtained, which can be used to build a realistic phase diagram; the role of translational entropy must be addressed in this regard.

I. INTRODUCTION

Amphiphilic molecules, presenting simultaneous solvophobic and solvophilic interactions, form many interesting structures in solution in which the solvophobic residues are screened from the solvent, such as bilayer structures and micelles. The later aggregate is remarkable, since, as they begin to proliferate around what is known as the critical micelle concentration (CMC), its size does not become macroscopic, but is limited by the particular molecular features. It is the main goal of this paper to provide a unifying view of micelle formation for the case of copolymers in solution, in the regime where the micelle concentration is low, so that each micelle can be regarded as isolated; the translational entropy of the aggregates can play an important role in this regime, as we will discuss. (A dense fluid will of course be more complicated, since the interactions between micelles must be taken into account.)

We will use a simple version of self consistent field theory (SCFT). The use of self-consistent theories for copolymer micelles has a long history, beginning with the work of Yuan et al. in 1992. Our approach differs from previous ones in that we are not primarily interested in the calculation of properties of isolated micelles, but rather in how to include this information in a thermodynamic description of the micellar fluid. Even though the importance of the excess free energy of the micelles in defining a proper CMC and distinguishing between competing structures has been recognized since the first works, we feel the connection between it and the concentration of micelles, which can lead to differences between possible definitions of the CMC, has not been explored in detail. Additionally, we also employ the method of Refs. in order to explore intermediate structures, that lie between equilibrium ones.

This method can be classified with previous approaches to obtain the general thermodynamics from the properties of a single aggregate. There are several studies that focus on planar and curved bilayers or monolayers membranes, obtaining quantities like surface tensions and bending rigidities; micelles can be considered as limiting cases of these structures, as is discussed in some cases. There are studies focused mainly on micellar structure and thermodynamics, but few consider a global treatment. (Refs. come quite close, but are mainly concerned with periodic dense phases.)

In section II, we calculate properties of individual micelles; we discuss how to build the global thermodynamics of the system in section III.

II. ISOLATED MICELLES

We have decided to focus on a copolymer–homopolymer mixture, using the standard Gaussian model for polymers treated within SCFT, perhaps the simplest molecular theory that produces realistic results for micellization (just as it is, arguably, the simplest one that produces realistic complex mesophases). This way, we can avoid the complications associated with similar models that are more refined and specific, while keeping a molecular theory that is closer to experimental systems than other models based on hard sphere fluids.

We consider an incompressible mixture of copolymers and homopolymer with volume $V$. The copolymers have $N$ statistical units of volume $\rho_0^{-1}$ and statistical length $a$; these are of type A from one end to monomer $fN$ and type B from there on. The homopolymer is made of monomer $A$ and has $\alpha N$ units of the same volume and length. In a system of volume $V$ there will be an overall homopolymer volume fraction $\phi$, which will be the spatial average of a homopolymer distribution $\phi(r)$. By incompressibility, the corresponding copolymer volume fraction will be $1 - \phi$, and its distribution, $1 - \phi(r)$. Notice the overall copolymer concentration is $\rho_c = \rho_0(1 - \phi)/N$, and the homopolymer one, $\rho_h = \rho_0\phi/(\alpha N)$.

We will consider a grand free energy

$$
\frac{N\Omega}{kT\rho_0 V} = -(zq_h + q_c) + \chi N \int dr \phi_A(r) \phi_B(r) + \int dr [\phi_A(r) w_A(r) + \phi_B(r) w_B(r)]
$$

(1)
FIG. 1: Excess grand free energy as a function of $r_0^2$ for values of $\phi^b = 0.61, 0.65, 0.70, 0.75$. The dotted lines span the range for which no solutions are found. The points correspond to the selected values that are used in Figure 2.

\[ + \int dr \left[ \xi(r)(\phi_A(r) + \phi_B(r) - 1) + \psi(\phi_A(r) - \phi_B(r))\delta(r - r_0) \right]. \] (2)

The first term in the right side is the configurational entropy, $q_0$ and $q_h$ being the partition functions of a homopolymer and copolymer in the corresponding fields and $z$ the fugacity of the homopolymer (by incompressibility, that of the copolymers can be taken to be 1, shifting the scale of chemical potentials). The second term is the interaction energy; the third contains the coupling with the fields $w_A$ and $w_B$; the fourth, a Lagrange multiplier, $\xi(r)$, to enforce incompressibility. The last term introduces an additional variable $\psi$ which lets us sweep a range of metastable structures by “pinning” the profiles to a certain value at some point in space $r = r_0$. (This goes beyond standard SCFT, as was used for this model in Ref. 15 even though this technique was used by the same author in Ref. 8 for a similar system; see also Ref. 9 for an application to related structures, spherical nucleation bubbles, and Ref. 18, in which such a field is helpful to study bilayer fusion; in Ref. 15 hards wall are used in order to explore different micellar sizes.)

The extremization of the grand free energy with respect to all the volume fraction profiles and fields leads to the self-consistent equations that have to be solved, with the copolymer and homopolymer profiles related to the fields through Green functions, $q_c(r, s)$, $q_h(r, s)$, which satisfy the standard diffusion equations and also provide the partition functions $V_q_c = \int dr q_c(1)$, $V_q_h = \int dr q_h(\alpha)$. This kind of theory is well know to produce rich phase diagrams, with many periodic structures. But it is also possible to obtain certain structures that are localized. In these, the volume fraction profiles of the different components tend to their bulk values away from the spatial point where the structure is located. The bulk values are those of the corresponding disordered phase: $\phi(r) \rightarrow \phi^b$, $\phi_A(r) \rightarrow \phi^b + f(1 - \phi^b)$, and $\phi_B(r) \rightarrow (1 - f)(1 - \phi^b)$. These localized structures correspond to isolated bilayers and micelles.

The theory is simple to implement in planar, cylindrical and spherical geometry, but we will focus on the later in this article. The diffusion equations have been solved in real space using Cranck-Nicholson’s method, which is much simpler conceptually (even if not so efficient computationally) than Fourier methods. (This procedure is also useful for problems in which the geometry is not known or which are not very symmetric.) With the help of the additional $\psi$ field, we study spherical micelles, as well as larger, metastable structures, corresponding to spherical bilayer vesicles. Notice this choice of $r_0$ as a “reaction coordinate” has some problems. Bilayer structures have two points at which $\phi_A(r) = \phi_B(r)$; for spherical and cylindrical geometries, it is preferable to assign $r_0$ to the outer one (the one for which $r$ is larger), since the inner one will be seen to disappear as the profiles become micellar. More importantly, for some values of $r_0$, typically one regions of transition between different morphologies, no solution to the SCFT is found, a fact we will discuss below.

We employ the iterative method described in Ref. 20, modified to include the $\psi$ field, to solve the self-consistent equations. It is found that 200 space points per $a\sqrt{N}$ and 4000 points along the chain are enough to provide results that cannot be distinguished from previously published results. A system size of $5a\sqrt{N}$ is sufficient to make finite size effects negligible.

We will choose this set of parameters: $\chi N = 12$, $f = 0.6$, $\alpha = 1$; in Ref. 15 we see this system shows, at high homopolymer concentrations, an “unbinding” of a micellar bcc crystal into isolated spherical micelles. In Fig. 1 we
plot $\Delta \Omega$, the excess grand free energy, as a function of the $r_0^2$ for several values of $\phi^b$, for spherical symmetry. We can see that for larger values of $\phi^b$ (i.e., low values of bulk copolymer), there are no nontrivial stable or metastable solutions. Above a certain value, there appears a minimum, which corresponds to a spherical micelle (this is the value associated with the CMC in some works). The $\Delta \Omega$ is still positive, but becomes negative at lower $\phi^b$, a value that would be close to the CMC. Then, at even lower values, the asymptotic straight lines change slope. This linear behavior, for large aggregates, is characteristic of spherical vesicles, and, as described below, the corresponding profiles are indeed vesicular. The free energy as a function of the area $A$ will tend to a line: $\Delta \Omega \rightarrow \gamma A + 8\pi(\kappa + \kappa_G)$, with slope $\gamma$; the surface tension; $\kappa$ is the bending rigidity and $\kappa_G$ is the Gaussian bending rigidity. That is, the change in slope corresponds to a change in the surface tension of the membrane; indeed, the condition for the stability of a membrane is $\gamma = 0$. There usually is some leeway regarding the definition of the area $A$ (i.e., we could propose $A = 4\pi r_0^2$, hence our choice of $x$ axis), but when $\gamma = 0$ there is none. This method can be used to obtain the rigidities, since the cylindrical geometry can separately provide $\Delta \Omega$. In this particular case, though, the lamellar transition is preempted, since at this point the $\Delta \Omega$ of the micelles is quite negative, as is clearly seen in the curve for $\phi^b = 0.65$ in Fig. 1. This is just what would be expected, since our CMC is just the “cubic phase unbinding” of Ref. 8, i.e., the stable periodic phase corresponding to our choice of parameters is a cubic phase, not a lamellar one.

In Fig. 2 we present some typical profiles for the case $\phi^b = 0.65$, at the points in Fig. 1. Fig. 2(a) corresponds to the stable micellar structure, with a core composed of B copolymer and a corona of A copolymer. As $r_0$ is increased the micelle grows, Fig. 2(b) shows the most “swollen” micelle we are able to obtain, still with the same architecture. After a region of $r_0$ for which no stable profiles are found, the next stable structures show a core composed of the A region of the copolymer and a little solvent, Fig. 2(c). This sort of “proto-vesicle” is a micelle with A-B-A structure, instead of the previous B-A one. For larger values of $r_0$ homopolymer progressively fills the core (which is now of an A nature, and thus compatible with it), while the copolymer profiles tend to the planar A-B-A bilayer structure as in Fig. 2(d), which corresponds to a local maximum in the excess free energy.

We would like to point out it is possible to connect this results with an approximation proposed in Ref. 12, to obtain the whole set of curves for unstable structures from information about critical ones (i.e., at local minima or maxima). Our results show that this approximation works quite well for large radii, but breaks down at small ones. In fact, an examination of the structures shows that the collapse of micellar structures at lower values of $\phi^b$ does not take place because they become unstable with respect to planar membranes (as is the case in Ref. 12), but because the whole system begins to develop long range oscillations — that is, because we reach the spinodal.
III. GLOBAL THERMODYNAMICS

We have seen one of the most important micellar quantities is its excess (grand) free energy, \( \Delta \Omega \); another one is the excess solvent, \( \Delta \phi \), a negative quantity (the excess of copolymer is \( -\Delta \phi \), positive). At low micelle concentrations, the components are either in the bulk or in micelles, so the total concentration of copolymer \( \rho_a = \rho_a^b + \rho_m \Delta N_c \), where \( \rho^b_a \) is the bulk concentration, \( \rho^b_a = \rho_0 (1 - \phi^b) / N \). \( \Delta N_c \) is the excess of copolymer molecules in the micelle (proportional to \( |\Delta \phi| \), as we discuss below) and \( \rho_m \) is the concentration of micelles. This quantity is expected to satisfy \cite{13}:

\[
\rho_m = \frac{1}{v_m} \exp(-\Delta \Omega/kT), \tag{3}
\]

which is dominated by the condition \( \Delta \Omega = 0 \), but the value of the volume \( v_m \), which is related to the translational entropy of the micelles, can make a difference, leading to different choices for the CMC. (Another important discrepancy is that many authors choose to relate the CMC with the point at which the micelles become stable (in general, metastable) \cite{13,14,16,21,22}.) We propose, based on our previous work \cite{13}:

\[
v_m = (\rho_0 / N) \exp[(\Delta E - \Delta F) / (kT \Delta N)],
\]

where \( \Delta E \) is the excess interaction energy, (second term in Eq. 3 minus the bulk energy), \( \Delta F \) is the excess Helmholtz free energy \( (\Delta F = \Delta \Omega + \mu (\Delta \phi)/\alpha) \), and \( \Delta N \) is the total number of molecules in a micelle.

We briefly discuss two problems that can be encountered when calculating \( \rho_m \). First, all the densities are given in units of \( \rho_0 / N \), and all free energy densities in units of \( kT \rho_0 / N \); on the other hand, a well know feature of the Gaussian model is that the spatial variation of the profiles is set by the combination \( a \sqrt{N} \). This means that, in order to obtain \( \Delta \Omega/kT \), we need the ratio between the two measures of volume, \( \lambda \equiv (a \sqrt{N})^3 / (N / \rho_0) = \rho_0 a^3 \sqrt{N} \); i.e., how many polymers would there be in a volume \((a \sqrt{N})^3\). This is basically the parameter that describes the degree of concentration of a polymer solution, and by definition, \( \lambda \gg 1 \) for a melt, but this value must be provided for each particular system. (Remarkably, our expression for \( v_m \) does not depend on \( \lambda \).)

Second, the calculation of \( \Delta N \) is not obvious. There is always some arbitrariness in defining this magnitude; for copolymers, it is natural to propose \( \Delta N_c = \lambda |\Delta \phi| \). But the micelles also include a certain number of solvent molecules (specially in the corona region). Looking at the profiles in Fig. 2, this would be the integral of the homopolymer profiles, dashed lines (together, of course, with a factor of 4 \( \pi r^2 \)). The appropriate choice of our parameters to mimic the lattice model is: \( f = 1/2, \alpha = 1/100, \chi N = 124 \), and \( \lambda = 10 \). Our results deviate markedly from this Reference: the location of the CMC is quite close, but in our case the volume fraction of micelles is high as soon as they become stable, so the assumption of isolated micelles breaks down, and one should consider instead the dense, periodic phase (very likely, a cubic phase) as the proper equilibrium structure. This difference is likely due to the lattice description of chain conformations in Ref. \cite{13}, which can lead to an underestimation of the corresponding entropy and hence to a prediction of a much smaller micellar concentration. In addition, we have checked that spherical micelles are indeed the stable structure, by comparing with cylindrical ones and planar bilayers.

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