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# Phase separation in solution of worm-like micelles: a dilute $n \rightarrow 0$ spin-vector model

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**Abstract.** We show how the dilute  $n \rightarrow 0$  spin vector model introduced originally by Wheeler and co-workers for describing the polymerization phenomenon in solutions of liquid sulphur and of living polymers may be conveniently adapted for studying phase separation in systems containing long flexible micelles. We draw an isomorphism between the coupling constant appearing in the exchange Hamiltonian and the surfactant energies in the micellar problem. We solve this problem within the mean-field approximation and compare the main results we have obtained with respect to polymer theory and previous theories of phase separation in micellar solutions. We show that the attractive interaction term  $\chi$  between monomers renormalizes the aggregation energy and subsequently the corresponding size distribution. Under these conditions, we observe that the general aspect of the phase diagram in the  $(\Phi, \chi)$  plane (where  $\Phi$  is the surfactant concentration) is different from previous results. The spinodal line shows a re-entrant behaviour and, at low concentrations, we point out the possibility of specific nucleation phenomena related to the existence of a metastable transition line between a region composed of spherical micelles and another one corresponding to a dilute solution of long flexible micelles.

## 1. Introduction

The study of surfactant molecules in aqueous solutions has drawn considerable effort over the past decades [1]. Above the critical micellar concentration (cmc), surfactant molecules are known to assemble into aggregates or micelles. At low surfactant concentration, these micelles are usually minimum globular aggregates consisting of tens of molecules. However, when the concentration is raised or salt added, these globular aggregates grow into cylindrical ones. This is referred to in the literature as the sphere to rod transition [2]. In most of the systems these aggregates are rod-like (i.e., their total length is much smaller than their persistence length). However, under specific conditions, experimental evidence has been recently reported of the existence of cylindrical micelles long enough to be flexible in dilute solution [3]. These micelle solutions, which may become entangled for concentrations above a few weight per cent, exhibit long relaxation times and strongly viscoelastic behaviour. A wide range of experimental studies such as linear viscoelasticity, temperature jump and light scattering in the semi-dilute region supports a model in which the micelles are large flexible worm-like aggregates entangled but with no cross-links [4]. The dynamic properties of these systems are well understood in terms of classical theory of linear polymers [5]. However, in contrast to polymer solutions, the micelle construction results from a thermodynamic self-assembly process in which several spherical micelles

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assemble to form a long worm-like aggregate. Therefore these systems present a large size distribution which may vary by means of controllable parameters such as surfactant or salt concentration and temperature. The elongation of micelles of ionic surfactant in aqueous solutions is now well understood in the special case where these micelles may be considered as non-interacting ones (i.e., at low concentrations). In such 'ideal solutions', the prevailing treatments of amphiphile self-assembly and micellar growth which combine basic classical thermodynamics and simple phenomenological models for the various contributions help us to understand micellar growth in terms of reversible polymerization [6, 7]. However, when the concentration increases, micelles start overlapping and interacting so that they may eventually show phase separations.

Experimental evidence of lower consolute critical temperature in high salt aqueous solutions of cetylpyridium and cetylmethylammonium bromide, nitrate and chlorate has been recently drawn [8] and are undoubtedly connected with the existence of giant flexible micelles in solution [9]. The exact nature of the physical mechanism leading to a phase separation phenomenon in these systems still provides a large debate because of two possible interpretations. First, at high salt concentrations, the electrostatic repulsions between charged micelles may be screened so much that the Van der Waals interactions become dominant. It then turns out that brine could become a bad solvent for the micelles beyond some experimental conditions. Another mechanism has been considered recently [10, 11]: at high salinity the worm-like micelles could branch and lead to the formation of a connected network through the sample, thus leading to phase separation. Many nonionic surfactant water systems, such as poly(ethylene glycol) alkyl ethers, alkylsulphenyl-ethanol and dimethyl-alkylphosphine oxides, also exhibit lower consolute temperature [12]. The phase boundary of these systems can be qualitatively well reproduced if the micelles are supposed to be rod shaped and flexible at high temperature [13]. The theory of phase separation occurring in these systems is challenging. Micellar solutions are qualitatively distinct from simple liquid solutions in that they involve a multiplicity of aggregate species which continually exchange molecules and do not maintain their identity. Therefore a theory of phase separation in these solutions must include thermodynamic multiple chemical equilibrium between micelles, attractive interactions leading to phase separation and excluded volume. Thus, most of the theories of phase separation in micellar systems [14–17] start from the Flory–Huggins lattice description of polydispersed polymeric chains and follow the works respectively published by Scott as well as Tobolsky *et al* initially devoted to the description of phase equilibria in liquid sulphur solutions [18, 19]. A few years ago, Wang *et al* proposed another approach in which they show that an  $n \rightarrow 0$  *spin vector model* is particularly suited for describing solutions of long flexible micelles with attraction exclusively involving excluded volume effects [20]. Their approach which is parallel to that of Wheeler and Pfeuty [21] for addressing a similar problem characterized by a unidimensional aggregation process describes the phenomenon of micellar growth at any concentration. A so called *dilute  $n \rightarrow 0$  vector model* was later introduced by Wheeler and co-workers to treat equilibrium polymerization of sulphur in solution [22] and polymerization in living polymer systems [23].

The aim of this paper is to present an adapted version of the *dilute  $n \rightarrow 0$  vector model* in order to treat the phase separation in solution of long flexible micelles. The advantage of such an approach is to provide a unified theoretical description of micellar solutions at any concentration. Before proceeding with the definition and analysis of the model presented here, it is worth recalling several significant differences between the intrinsic physics of micellization and that of polymerization in living polymer systems. The controlling variables are different in both sets of problems. In living polymer systems,

polymerization results from the presence of an initiator and its description requires at least two equilibrium constants, one for initiation ( $K_i$ ) and one for growth reaction ( $K_p$ ). When the initiation reaction goes to completion (i.e.  $K_i \gg 1$ ), the initiator concentration fixes the total number of polymers. Wheeler and co-workers have notably focused on the polymerization transition which exhibits a non-classical critical behaviour in the limit of small initiator concentration. Besides, in contrast to the micellar systems, the monomer plays the role of solvent for the polymeric chains. Thus, by comparing with the formalism used in magnetism, the concentration of this initiator is an adjustable parameter that fixes the magnitude of the corresponding magnetic field in the equivalent magnetostatic Hamiltonian. However, for micellization, as we shall see in section 2, the magnitude of this field is fixed by energy parameters. Due to the fact that sets of controlling variables are different in the two problems, here we present new results which are of interest in the field of surfactant micellization because they are experimentally accessible and tunable. These results concern the growth of aggregates with concentration and temperature as well as the osmotic pressure; they allow us to build up a phase diagram including spinodal and binodal lines but also a transition line such as the sphere to rod transition and the dilute–semi-dilute transition. The present paper is organized as follows: In section 2, we discuss the isomorphism that exists between an interacting solution of long flexible micelles and the dilute  $n \rightarrow 0$  spin vector model. Section 3 is devoted to the mean-field solution of this model and to the discussion of the main results obtained with respect to the corresponding ones derived from polymer theory and to previous theories of phase separation in micelles.

## 2. Flexible micelles and statistical treatment

The elongation of micelles results from a thermodynamic self-assembly process which can be modelled as multiple chemical equilibrium between aggregates of different sizes. The size and the distribution of these aggregates vary with surfactant concentration. A natural way to model this self-assembly process consists in using a grand-canonical partition function. We recall in appendix A that the grand-canonical partition function of a system composed of interacting self-avoiding micelles may be mapped onto a dilute  $n \rightarrow 0$  spin vector model. Under these conditions, we consider that elongated micelles result from the condensation of minimum spherical micelles and we neglect surfactant molecules which are not associated into an aggregate. Far above the critical micellar concentration (cmc), the proportion of unassociated surfactant molecules is negligible, essentially constant, and has no influence on the size distribution [24]. We consider an equilibrium between isolated monomers (minimum spherical micelles) and chains of different size. In this respect, we introduce a lattice by sharing the volume into unit cells. Thus, each cell may be respectively occupied by an isolated monomer, a monomer unit which belongs to a chain or by solvent molecules. The cell volume is fixed by the monomer size. Following previous phenomenological treatments [1], we consider that the internal energy  $\mathcal{E}$  of an elongated linear open aggregate consisting of  $n$  monomers is given by:

$$\mathcal{E} = (n - 2)\varepsilon_{int} + 2\varepsilon_{cap} = n\varepsilon_{int} + \delta \quad (1)$$

where  $\varepsilon_{int}$  and  $\varepsilon_{cap}$  are the respective energies of an internal monomer and a monomer belonging to the extremity of a chain. The growth of spherical micelles into elongated ones is exclusively governed by the free energy difference  $\delta$  between an internal and an edge monomer in a chain. The attractive interaction  $\chi$  is treated in the Flory approximation [25] (i.e., only nearest neighbour monomers interact). This approximation previously used by Menes and co-workers for the description of attractive interactions in tubular microemulsions

[26] as well as by Sear and Mulder in solutions of long flexible micelles [17] is correct if the range of interaction is small with respect to the size of the large micelles. This is indeed true for Van der Waals attraction and hydration effects and also reasonable for electrostatic repulsion as long as the ionic strength of the solution is large (whereas the Debye screening length is short). However, we make a further restrictive assumption that turns out to be very important: the attractive interaction only occurs between adjacent monomers (i.e., occupied nearest neighbour sites) not linked directly to each other when they belong to a same chain. At this step one must remember that the link energy of two adjacent monomers corresponds to  $\varepsilon_{int}$  and not  $\chi$ . This restriction does not alter the possibility of intra-micellar interactions since two adjacent monomers may belong to the same chain and may not be connected directly to each other. As a consequence, we will see that this leads to a renormalization of the aggregation constant. Following these considerations, the grand partition function of the system is:

$$Z = \sum_{\{\sigma_k\}} \sum_l \sum_p \sum_m \Gamma(m, l, p, \{\sigma_k\}, M) \exp[\beta\mu(m+1+p)] \exp[-\beta E(m, l, p)] \times \exp(\beta\chi N_{m,m}) \quad (2)$$

where the set  $\{\sigma_k\}$  specifies the particular assignment of solvent ( $\sigma_k = 0$ ) or monomer unit ( $\sigma_k = 1$ ) to each cell;  $\Gamma(m, l, p, \{\sigma_k\}, M)$  is the number of ways of arranging  $p$  linear polymer chains characterized by a total number of  $l$  bonds and  $m$  isolated monomers (single site chain) on a lattice composed of  $M$  sites, for a particular given set  $\{\sigma_k\}$ ;  $\mu$  is the chemical potential of a monomer unit and  $E(l, m, p)$  the internal energy of the configuration described by the set  $\{\sigma_k\}$  in the absence of attractive interaction.  $N_{m,m}$  is the number of nearest neighbour monomers which are not directly connected to each other into the same aggregate. Note that  $E(l, m, p)$  may be defined as:

$$E(l, m, p) = 2p\varepsilon_{cap} + (l-p)\varepsilon_{int} + m\eta \quad (3)$$

where  $\eta$  is the internal energy of an isolated monomer.

Presently, one must introduce the corresponding dilute  $n \rightarrow 0$  spin-vector model where the variable  $\sigma_i$  still determines the presence ( $\sigma_i = 1$ ) or the absence ( $\sigma_i = 0$ ) of a monomer on a site  $i$  (isolated or incorporated into a chain). The basic Hamiltonian may be defined as:

$$-\beta H = K \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \sigma_i \sigma_j + h \sum_{i=1}^M S_{i,1} \sigma_i + \tilde{\mu} \beta \sum_{i=1}^M \sigma_i + \chi \beta \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \left( Q - \frac{h^2}{2} \right) \sum_{i=1}^M S_{i,1}^2 \sigma_i^2 \quad (4)$$

where the generic notation  $\langle i, j \rangle$  refers to the interaction between nearest neighbour sites, independently of the lattice dimensionality. Note that for  $Q = h^2/2$  this Hamiltonian is similar to that one previously introduced by Wheeler and Pfeuty for describing polymerization in solutions of liquid sulphur and living polymers, respectively [22, 23]. In order to make a correspondence between the model of polymerization in solution and the dilute  $n \rightarrow 0$  Hamiltonian model proposed above, the particular choice  $Q = h^2/2$  requires that the value of the constant equilibrium describing the first polymerization step is twice those characterizing the other steps [22, 23]. This factor 2 is motivated for the liquid sulphur solutions by the topology of the monomers which are involved in  $S_8$  rings. Indeed, in the first propagation step, the newly opened active  $S_8$  ring may be connected to either end of the already opened ring in the adjacent cell whereas in the propagation step the newly opened ring has only one active end of a monomer to which it can connect [22]. However, the

same factor 2 has no serious justification for the living polymer solutions and has been fixed there only to bring a correspondence with the  $n \rightarrow 0$  dilute spin-vector Hamiltonian first introduced for describing the polymerization process in liquid sulphur solutions [23]. In appendix A, we also show that fixing  $Q = 0$  is necessary to ensure a correct correspondence between a solution of mutually and self-avoiding micelles with attractive interaction and the dilute  $n \rightarrow 0$  spin-vector model. The partition function  $Z$  associated with this Hamiltonian can be straightforwardly evaluated in the vanishing  $n$  limit by expanding  $\exp(-\beta H)$  in powers of  $S_j$  and by averaging this expression with no weight over all the components of all spins  $S_{i,\alpha}$  ( $i = 1, 2, \dots, M$  and  $\alpha = 1, \dots, n$ ). Such calculations which have been already widely treated in the literature [21–23, 27] do not need to be presented in detail here and are briefly reported in appendix A. Following this procedure and for  $Q = 0$ , it is possible to derive in the  $n \rightarrow 0$  limit that:

$$Z = \sum_{\{\sigma_i\}} \sum_l \sum_p \sum_m \Gamma(m, l, p, \{\sigma_i\}, M) h^{2p} K^l \exp(\beta \chi N_{+1,+1}) \exp[\beta \tilde{\mu}(m + l + p)] \quad (5)$$

where we recall that  $\Gamma(m, l, p, \{\sigma_i\}, M)$  represents the number of ways of arranging on an  $M$  site lattice  $m$  single sites and  $p$  mutually and self-avoiding walks characterized by  $l$  bonds, with the restriction that walks form rings or visit sites without monomers ( $\sigma_i = 0$ ).  $N_{1,1}$  is the number of nearest neighbour pairs of sites  $\langle i, j \rangle$  such that  $\sigma_i = +1$  and  $\sigma_j = +1$ . As a consequence, one can assume the following correspondences between coupling constants in the spin Hamiltonian and microscopic energies in the micellar treatment knowing that  $N_{m,m} = N_{1,1} - l$ :

$$\tilde{\mu} = \mu - \eta \quad Q = 0 \quad K = \exp[-\beta(\tilde{\varepsilon}_{int} + \chi)] \quad (6)$$

$$h = \exp[-\beta(\tilde{\varepsilon}_{cap} - \tilde{\varepsilon}_{int}/2)] \quad (7)$$

with

$$\tilde{\varepsilon}_{cap} = \varepsilon_{cap} - \eta \quad \tilde{\varepsilon}_{int} = \varepsilon_{int} - \eta \quad (8)$$

and where  $\mu$  is the chemical potential of a monomer unit. At this point, it is worth noting that an important approximation inherent to the nature of the involved Hamiltonian (and also made by other authors [21–24, 26, 27] in addressing similar problems) is that we exclude the formation of closed rings. Indeed it is reasonable to assume that the population of closed rings is always small for concentrations higher than the cmc and therefore can be neglected. This is due to the fact that the energetic gain associated with the ring formation is over-compensated by the entropically unfavourable reduction of configurations for a closed ring compare to that of an open chain [28].

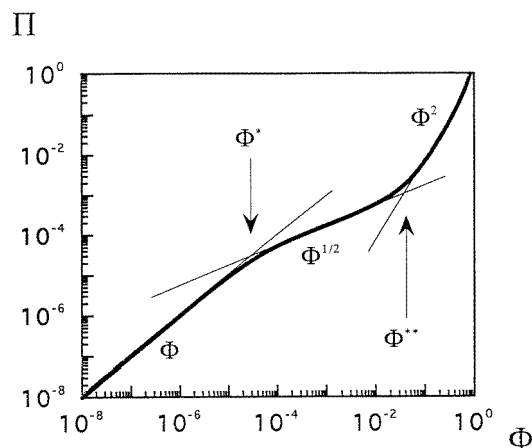
### 3. Mean-field results and discussion

This model solved within the mean-field approximation (see appendix B for a detailed derivation) gives the following expressions for  $\pi$  the osmotic pressure and  $\beta \mathcal{F}/M$ , the free energy per site:

$$-\beta \pi v_0 = -\frac{\ln Z(h, K, \mu, \chi)}{M} = \ln(1 - \Phi) + \frac{qK}{2} \langle S\sigma \rangle^2 + \frac{q\beta\chi}{2} \Phi^2 \quad (9)$$

and

$$\begin{aligned} \frac{\beta \mathcal{F}}{M} = \beta \mu \Phi - \beta \pi v_0 = \Phi \ln \left[ \frac{\langle S\sigma \rangle}{(1 - \Phi)(h + qK \langle S\sigma \rangle)} \right] + \beta \eta \Phi + \ln(1 - \Phi) - \frac{q\beta\chi}{2} \Phi^2 \\ + \frac{qK}{2} \langle S\sigma \rangle^2 \end{aligned} \quad (10)$$



**Figure 1.** Log–log plot of the osmotic pressure versus monomer concentration for  $\varepsilon_{int} = -8 k_B T$ ,  $\varepsilon_{cap} = 4 k_B T$  (i.e., an end energy  $\delta_{end} = 0$ ),  $\eta = 0$  and no attractive inter-intramolecular interactions.  $\Phi^*$  and  $\Phi^{**}$  respectively correspond to the monomer concentration at which sphere/rod transitions and dilute/semi-dilute transitions occur. The values of the osmotic pressure are numerical.

where  $\langle S\sigma \rangle$  is given by:

$$\langle S\sigma \rangle = \frac{\Phi(h + qK\langle S\sigma \rangle)}{(1 + qKh\langle S\sigma \rangle + ((qK)^2/2)\langle S\sigma \rangle^2)}. \quad (11)$$

The osmotic pressure of the solution  $\pi$ , solved numerically within the mean-field approximation, leads to three distinct regimes (figure 1) i.e., to three different power laws  $\Phi^k$ . At low surfactant concentration the regime  $k = 1$  corresponds to spherical micelles with no elongation. Since their number simply increases with  $\Phi$ , it follows from Van't Hoff's law that  $\pi$  is proportional to  $\Phi$  (i.e., the number of colloidal particles). For intermediate concentration range, one has  $k = 1/2$ . The Van't Hoff law is still fulfilled in this regime. However, the number of aggregates in solution is proportional to  $\Phi/N$ ; therefore, as  $N$  varies with  $\Phi^{1/2}$  (figure 2(a)), the average aggregation number finally varies as  $\Phi^{1/2}$ . Indeed, by thoroughly examining equation (11), it is straightforwardly shown that, in the dilute regime which corresponds to condition  $qK\langle S\sigma \rangle \gg h > 1$  (i.e.,  $\Phi > 1/2qK$ ), the average aggregation number  $N$  behaves more precisely as (cf appendix C)

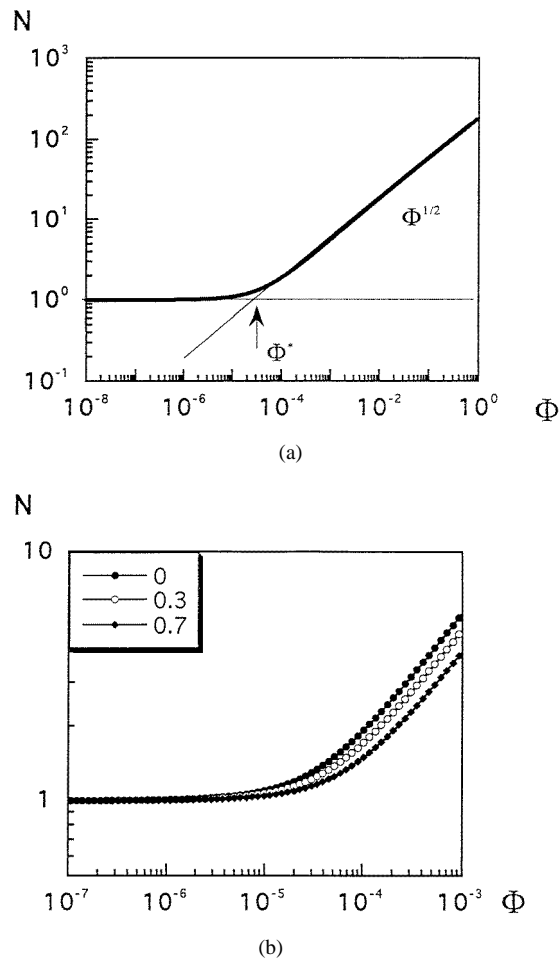
$$N \approx \frac{2\sqrt{2qK\Phi}}{h} \quad (12)$$

in agreement with results found for ideal micelle solutions [1] without taking into account excluded volume and interactions between chains. In the previous section, we have shown that the effect of attractive interactions between monomers described by the parameter  $\chi$  is to renormalize the aggregation constant  $K$  according to:

$$K(\chi) = K(0) \exp(-\beta\chi) \quad (13)$$

and therefore also  $N$ , the average aggregation number (cf equation (12)). Indeed, they oppose the elongation process according to the following expression:

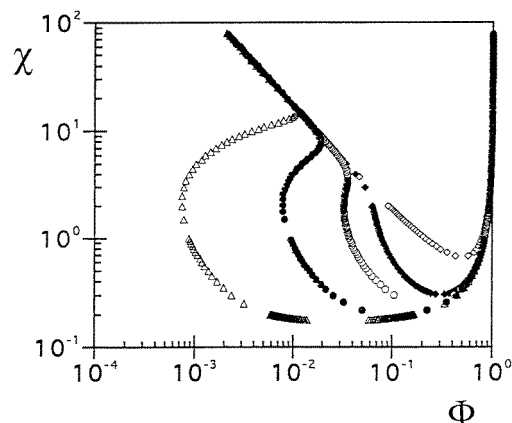
$$N(\chi) \approx N(0) \exp(-\beta\chi/2) \quad (14)$$



**Figure 2.** (a) Log-log plot of the average aggregation  $N$  (numerically determined), versus monomer concentration  $\Phi$ , for an energy  $\varepsilon_{int} = -8 k_B T$  with no attractive interaction. The parameters  $\varepsilon_{cap}$  and  $\eta$  are identical to those of figure 1. (b) Log-log plot of the average aggregation number  $N$  (numerically determined), versus monomer concentration  $\Phi$ , for an energy  $\varepsilon_{int} = -8 k_B T$  and for different values of the energy of attractive interaction. Open circles, closed circles and diamonds correspond respectively to  $\chi = 0.0, 0.3$  and  $0.7 k_B T$ . The parameters  $\varepsilon_{cap}$  and  $\eta$  are identical to those of figure 1.

where  $N(0)$  is the value of  $N(\chi)$  for  $\chi = 0$ . This result differs significantly from the model of Blanckenstein *et al* [16] which predicts that attractive interactions leave the micellar distribution and the average aggregation size unchanged. When the temperature approaches the lower critical point (i.e.,  $\chi$  increases), the average size of the micelles decrease and may have some effects on the scaling of dynamic properties of the solution close to the critical point. At higher concentrations,  $k = 2$  corresponds to the semi-dilute regime for which the micelles start overlapping close to the critical point. Finally and more surprisingly, the effects of attractive interactions are important even at low concentrations. The existence of attractive interaction increases the value of the concentration  $\Phi^*$  at which the sphere to rod transition occurs (figure 2(b)). The value of  $\Phi^*$  can be estimated more precisely by





**Figure 3.** Spinodal curves determined numerically for different energies of aggregation. Open diamonds, closed diamonds, open circles, closed circles and open triangles respectively correspond to binary mixture of monomers in solution ( $\varepsilon_{int} = +\infty$ ), aggregation energies  $\varepsilon_{int} = -2, -4, -8$  and  $-15 k_B T$ ,  $\varepsilon_{cap} = \varepsilon_{int}/2$  and  $\eta = 0$ .

extrapolating equation (12) to  $N = 1$ :

$$\Phi^*(\chi) \approx \frac{h^2}{8qK} \approx \Phi^*(0) \exp(\beta\chi) \quad (15)$$

where  $\Phi^*(0)$  is the value of  $\Phi^*(\chi)$  for  $\chi = 0$ . Figure 3 shows the evolution of the spinodal line in the plane  $(\Phi, \chi)$ , determined numerically for different aggregation energies  $\tilde{\varepsilon}_{int}$  and  $h = 1$ . When the energy of aggregation increases, the spinodal line becomes more asymmetrical and the critical point shifts towards the low concentrations. The critical concentration  $\Phi_c$  varies as a function of  $N(\Phi_c)$ , the average chain length at the critical monomer concentration  $\Phi_c$ , in agreement with the well known results predicted from the Flory–Huggins theory for polymer solutions (figure 4(a)) [25]:

$$\Phi_c = \frac{1}{1 + \sqrt{N(\Phi_c)}}. \quad (16)$$

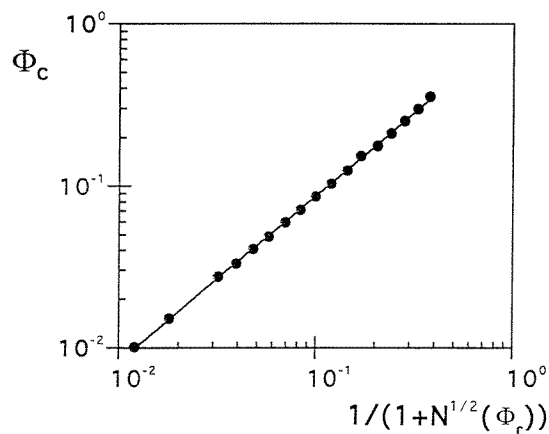
The critical attractive energy  $\chi_c$  decreases when the average aggregation number increases (figure 4(b)). When  $N(\Phi_c)$  becomes infinite, the critical energy of interaction  $\chi_c$  tends to a finite value which is one-quarter of the critical energy of a binary mixture characterized by spherical micelles (i.e.,  $N = 1$ ):

$$\chi_c(N) = \frac{\chi_c(1)}{4} \quad \text{as } N \rightarrow +\infty \quad (17)$$

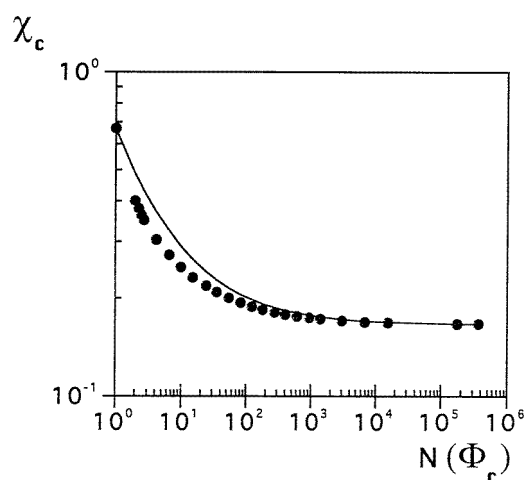
where  $\chi_c(1)$  is the value of  $\chi_c(N)$  with  $N = 1$ . This result is in agreement with the relation predicted from polymer theory [27]:

$$q\beta\chi_c = \frac{(1 + \sqrt{N(\Phi_c)})^2}{2N(\Phi_c)}. \quad (18)$$

However, for intermediate values of  $N$ , there exists a discrepancy between  $\chi_c$  derived from equation (18) and the corresponding value given by the mean-field theory of Flory and Huggins. Once again this is due to the fact that, in that case, attractive interactions renormalize the aggregation number  $K$  and subsequently  $N$ , the average size number. In the infinite- $N$  limit, this discrepancy vanishes because, in this limit, the chain entropic



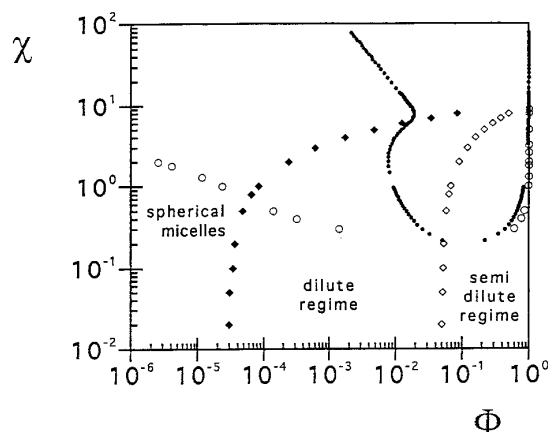
(a)



(b)

**Figure 4.** (a) Critical monomer concentration  $\Phi_c$  versus the average number of aggregation  $N(\Phi_c)$  at  $\Phi_c$ ;  $\Phi_c$  varies as  $1/(1 + \sqrt{N(\Phi_c)})$ . (b) Critical energy of interaction  $\chi_c$  in  $k_B T$ , as a function of the average number of aggregation  $N$  taken at  $\Phi_c$ . The continuous line gives the evolution of  $\chi_c$  versus  $N(\Phi_c)$  predicted from polymer theory:  $(q/2)\beta\chi_c = (1 + \sqrt{N(\Phi_c)})^2 / 2N(\Phi_c)$ .

contributions become negligible with respect to the others (solvent entropy and attractive interaction energy), near the critical point, as for polymers in solution. Using equations (16) and (14) it is possible to determine the aggregation constant  $K$ , from the value of the critical concentration  $\Phi_c$ . However, the knowledge of  $\tilde{\varepsilon}_{int}$  is not direct and also requires the experimental determination of the interaction energy at the critical point (cf equation (13)):  $\chi_c$ . When the elongation process is important ( $\tilde{\varepsilon}_{int} = 10\text{--}20 k_B T$ ), this correction is negligible since  $\chi_c \ll \tilde{\varepsilon}_{int}$ . However it may become important for smaller values of  $\varepsilon_{int}$  (typically for a few  $k_B T$ ) i.e., when the elongation process is not too important. In that case an evaluation of  $\chi_c$  is easily obtained from the value of  $N(\Phi_c)$  and from figure 4(b). The dilute/semi-dilute threshold surfactant concentration  $\Phi^{**}(\chi)$  can be evaluated numerically



**Figure 5.** Phase diagram for an energy of aggregation of  $\varepsilon_{int} = -8 k_B T$ . Black and white circles correspond to the spinodal and binodal curves, respectively; black and white lozenges correspond to the sphere/rod and dilute/semi-dilute transitions, respectively.

from the crossover of the osmotic regime versus monomer concentration between regimes  $k = 1/2$  and  $k = 2$  (figure 2(a)), and for different values of  $\chi$ . This transition line meets the binodal line close to the critical point (figure 5). At this step note that the binodal line has been derived from numerical calculations. Indeed it is qualitatively well known that the critical concentration characterizing a dispersion of random coils corresponds to the situation where the coils just come into close contact [29]. Because of the renormalization of  $K$ , the general aspects of the phase diagram in the plane  $(\Phi, \chi)$  (i.e. for  $\tilde{\varepsilon}_{int}$  and  $\tilde{\varepsilon}_{cap}$  fixed) are very different from the corresponding ones obtained with the classical mean-field Flory–Huggins theory. The aspect of the spinodal line is altered and presents a re-entrant character (see figure 5) when the  $\chi$  values increase. This re-entrant behaviour occurs always in the dilute regime and results directly from the renormalization of  $K$  due to attractive interactions. A qualitative insight of this behaviour can be drawn in the following way: Let us neglect the polydispersity of the micelle solution and assume that it only consists of chains of length  $N$  given by equation (12). When  $N$  is fixed (i.e.,  $N$  does not depend on monomer concentration and attractive interactions), as it is for polymer solutions, the lower concentration of the spinodal line for a fixed value of  $\chi$  increases with decreasing values of  $N$  [5]. In our simplified picture of micellar solutions, the value of  $N$  decreases when  $\chi$  increases, and therefore leads to higher values for the lower concentration of the spinodal line and eventually to a re-entrant behaviour. Of course, a more correct picture requires us to take also into account the concentration dependence of  $N$  as well as the polydispersity of the size distribution. Indeed, a closer look at our model, solved within the mean-field approximation, allows one to give an analytical expression of the spinodal equation in the dilute regime (see equation (B11)):

$$\frac{\partial^2(\beta F/M)}{\partial \Phi^2} = 0 \approx \frac{h}{2\sqrt{2qK}} \frac{1}{\Phi_{spino}^{3/2}} + (1 - q\beta\chi_{spino}). \quad (19)$$

This expression, which is identical to that derived by Cates and Candau [14], leads to a re-entrant behaviour, when the renormalization of  $K$  is taken into account (cf equation (13)). At this step it is worth mentioning that, in contrast to the spinodal line, the binodal line does not show a similar re-entrant character (see figure 5). Thus it is difficult to give strong

physical arguments for justifying such a kind of behaviour; in addition a mathematical derivation would imply heavy calculations which do not carry further information with respect to numerical ones. At low surfactant concentration, the sphere to rod transition line given by equation (15) crosses the spinodal line (equation (19)) and therefore the binodal too. As a consequence, in this low concentration range, one may expect specific nucleation phenomena related to the existence of the sphere to rod transition line in the two phase region. To our knowledge, there do not yet exist any systematic experimental studies on the dynamics of phase separation in micellar systems where a unidimensional aggregation process takes place. We hope that this work will motivate such experimental studies. In the model described here, we have not taken into account the existence of isolated surfactant molecules in solution. Including an isolated surfactant molecule into an aggregate involves a free energy cost  $\mathcal{D}$  of order  $10\text{--}25 k_B T$  which fixes the value of the critical monomer concentration (cmc) according to  $\ln(\text{cmc}) \approx -\mathcal{D}$ . Above the cmc, most of the molecules are included into aggregates and the size distribution is only determined by the end energy  $\delta$  (i.e., the free energy cost for transferring a surfactant molecule from the cylindrical body of the aggregate to its end cap). Our approach is then valid only for concentration higher than the cmc. Note that in a similar way, Wheeler and Pfeuty have not included the existence of the inactive  $S_8$  monomers in their treatment of liquid sulphur solutions. It is worth mentioning again that we have not accounted in this model for the possible formation of rings. We have mentioned in the introduction section that two mechanisms are referred to in the literature to explain the observed phase separations in solution of worm-like micelles: Van der Waals interaction between monomers and the formation of a connected micellar network. It is important to note that while the first possibility is well treated here, the topological mechanism (i.e., formation of crosslinks) is beyond the scope of the current spin formalism. Experimentally it is difficult to conclude between the two mechanisms. Scattering techniques involving neutron or light cannot differentiate a network consisting of crosslinked cylindrical micelles that are multiconnected (topological mechanism) from an entangled network with no crosslinks. However, the dynamical properties such as rheological ones are expected to differ quite considerably. Many experimental observations on worm-like micelles are in agreement with a model developed by Cates [14, 33] which describes the dynamic behaviour of entangled linear micelles (i.e. with no crosslinks) that can break and recombine. In particular, huge increases in the zero shear viscosity and elastic modulus with micellar length have been clearly observed in systems such as CTAB/KBr and are in good agreement with the scaling predictions of this model. However, there exist many discrepancies with this model as well, in other systems. In several systems such as lecithin/trace water/isooctane [34] and CPyClO<sub>3</sub>/NaClO<sub>3</sub>/water [35] a huge increase in micellar length is observed under small variations of a suitable control parameter (water content or ionic strength). This increase is followed by an enormous enhancement of the zero shear viscosity. However as the control parameter is moved further in the same direction, the viscosity falls dramatically again. An explanation of this decrease of viscosity is that the micelles are fusing to form a connected network. This would reduce the viscosity because the branch points are not chemical connections and can slide along the branches or act as a release of entanglements via the existence of branch points. Note that a similar behaviour arises in the case of the sponge phase and bicontinuous microemulsions despite the presence of a continuous two-dimensional sheet [36, 37]. Another possibility is that the micelles are becoming shorter and/or that the kinetic rate for micellar scission increases as the control parameter is moved further. This scenario which is consistent with the increasingly exponential relaxation behaviour that has been reported on one side of the viscosity peak [14, 35] cannot be

ruled out. Indeed, recent cryotransmission electron microscopy experiments seem rather to confirm the existence of branched micelles in aqueous systems [38, 39]. Our model predicts that attractive interactions oppose the elongation process. Many experimental data show that the micellar length (i.e.,  $K$ ) decreases upon raising the temperature [14]. However, it is hard to conclude that this effect is only due to attraction energy between beads since another energy,  $\varepsilon_{cyl}$ , is also involved in the elongating process. An interesting system where our prediction may apply is  $C_{16}E_6$  in 0.5 M NaSCN solutions [40, 41]. Cummins *et al* has studied in this system, which forms long micelles and phase separates as the temperature is raised, the micellar length as a function of the reduced temperature  $(T - T_c)$  where  $T_c$  is the critical temperature and has shown that this effective length presents a maximum as a function of this parameter and decreases on approaching the critical point [42]. This decrease of micellar length on approaching the cloud point is in agreement with the prediction derived from our model. However, it can be also interpreted as the existence of ruler micelles near the cloud point, resulting from a two dimensional growth [43, 44]. Finally, the possibility of specific nucleation phenomena in micellar systems may also exist in solutions where the micelles are branching (provided that the sphere to rod transition line extends to the two phase regions of the phase diagram). We hope that this will motivate experimental studies on the dynamics of phase separation in such systems in a near future.

#### 4. Conclusion

In this article, we have shown that the employed Hamiltonian offers a unified theoretical approach capable of treating phase separation in worm-like micellar solutions at any concentration. In contrast to previous treatments [1–9, 16, 17], it avoids the use of separate models for different concentration ranges and may benefit from general methods used in theories of magnetism (such as renormalization calculations). Solved within the mean-field approximation, this model allows one to retrieve well known results of polymer solutions. Nevertheless, we recall that, in contrast to polymers, the average micelle length is not fixed but does increase as the square root of the concentration and depends on the interaction energy between monomers (cf equations (28), (29)). The presence of attractive interactions between monomer renormalizes the aggregation constant  $K$  and subsequently the average micelle size  $N$  which may alter the critical behaviour of dynamic properties such as viscosity. In a mean-field approximation, the renormalization of the aggregation constant also leads to a different aspect of the phase diagram in the plane  $(\Phi, \chi)$  with respect to the corresponding one given by Flory and Huggins. The spinodal line shows a re-entrant behaviour and, at low concentration, one may expect specific nucleation phenomena related to the existence of the topological (sphere to rod) transition line in the metastable region of the phase diagram. We hope that this will motivate experimental studies on the dynamics of phase separation in systems where a unidimensional aggregation process takes place.

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## Appendix A

Let us consider a lattice composed of  $M$  sites. With each site  $k$  is associated an  $n \rightarrow 0$  spin-vector  $\mathbf{S}_k$  and an occupation number  $\sigma_k$  characterized by the possible values  $+1$  or  $0$  ( $\sigma_k$  tell us whether or not the site is occupied by a monomer unit). Under these conditions one may write the basic Hamiltonian  $H$ :

$$-\beta H = K \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \sigma_i \sigma_j + h \sum_{i=1}^M S_{i,1} \sigma_i + \tilde{\mu} \beta \sum_{i=1}^M \sigma_i + \chi \beta \sum_{\langle i,j \rangle} \sigma_i \sigma_j + \left( Q - \frac{h^2}{2} \right) \sum_{i=1}^M S_{i,1}^2 \sigma_i^2. \quad (\text{A1})$$

When  $n$  tends to zero (which must be only considered as a mathematical trick), the partition function  $Z$  can be related to the problem of polydispersed and mutually and self-avoiding chains on a Flory–Huggins lattice. This surprising analogy between magnetism and polymers was first derived by de Gennes [5, 30] and des Cloizeaux [31] and has been correlatively applied in a large variety of problems including polymerization in liquid sulphur, liquid sulphur solutions, living polymers and solutions of flexible micelles with no phase separation [20–23, 27, 28]. Using a  $2n$ -component model (with  $n \rightarrow 0$ ), Freed [32] has managed to remove the polydispersity inherent to the structure of the original spin-vector model. Let  $\langle F \rangle_0$  be the average of a variable  $F$  over all the equally weighted orientations of each spin. In contrast, the thermal average of the same variable  $F$  (where the states are weighted by the factor  $\exp(-\beta H)$ ) is written as  $\langle F \rangle$ . The relation between the two types of average for any function  $F(\mathbf{S}_1, \mathbf{S}_2, \dots, \mathbf{S}_M)$  is:

$$\langle F \rangle = \frac{\langle F \exp(-\beta H) \rangle_0}{\langle \exp(-\beta H) \rangle_0}. \quad (\text{A2})$$

The partition function  $Z$  is then given by  $\langle \exp(-\beta H) \rangle_0$ . Another possible expression of  $Z$  is given by expanding  $\exp(-\beta H)$  in terms of powers of  $H$ :

$$\frac{Z}{M} = \langle 1 \rangle_0 - \beta \langle H \rangle_0 + \frac{\beta^2}{2} \langle H^2 \rangle_0 + \dots + \frac{(-\beta)^n}{n!} \langle H^n \rangle_0 + \dots \quad (\text{A3})$$

where  $M$  is the total number of lattice sites. This expression cannot be computed because of its very complicated structure. However, in the particular case  $n = 0$ , it turns out that it becomes plainly simpler because of the moment theorem which states:

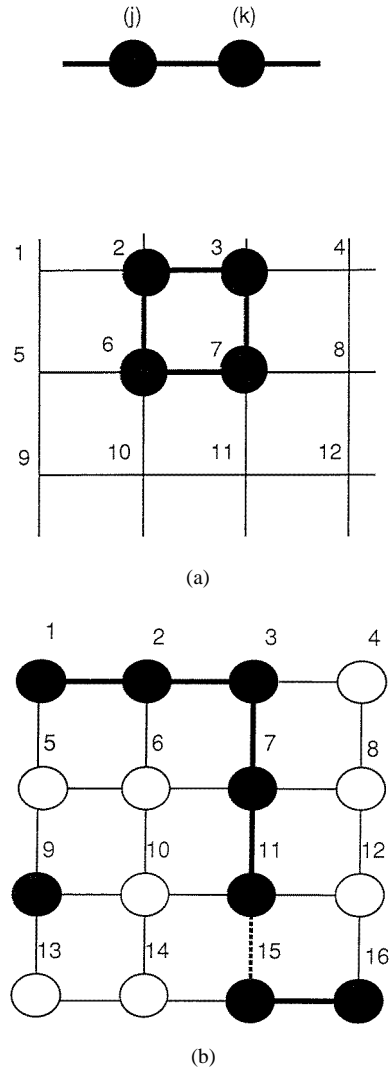
$$\langle S_{i,\alpha} S_{j,\beta} \rangle_0 = \delta_{\alpha,\beta} \delta_{i,j} \quad (\text{A4})$$

and

$$\langle S_{i,\alpha}^m \rangle_0 = \delta_{2,m} + \delta_{0,m}. \quad (\text{A5})$$

Using an expansion similar to that one previously described, the partition function  $Z$  can be expressed as:

$$Z(h, K, \tilde{\mu}, \chi, M) = \left\langle \sum_{\{\sigma_i\}} \prod_{\langle i,j \rangle} \left[ 1 + K \mathbf{S}_i \cdot \mathbf{S}_j \sigma_i \sigma_j + \frac{K^2}{2} (\mathbf{S}_i \cdot \mathbf{S}_j \sigma_i \sigma_j)^2 \right] \times \prod_{i=1}^M \left( 1 + h S_{i,1} \sigma_i + \frac{h^2}{2} (S_{i,1} \sigma_i)^2 \right) \prod_{i=1}^M \left( 1 + \left( Q - \frac{h^2}{2} \right) S_{i,1}^2 \sigma_i^2 \right) \times \exp \left( -\beta \tilde{\mu} \sum_{i=1}^M \sigma_i \right) \exp \left( -\beta \chi \sum_{\langle i,j \rangle} \sigma_i \sigma_j \right) \right\rangle_0 \quad (\text{A6})$$



**Figure A1.** Schematic representation of a link between two nearest neighbour sites. Such a link is related to a prefactor term  $KS_{k,\alpha}S_{j,\alpha}$  in the polynomial expansion of the partition function  $Z$ . In the case of the loop involving four sites, the corresponding contribution is  $(KS_{2,\alpha}S_{3,\alpha})(KS_{3,\alpha}S_{7,\alpha})(KS_{7,\alpha}S_{6,\alpha})(KS_{6,\alpha}S_{2,\alpha})$ . In the limit  $n \rightarrow 0$ , the summation over  $\alpha$  leads to a vanishing contribution. (b) Lattice representation of a configuration consisting of one isolated monomer (site 9), a two-monomer chain (sites 15 and 16) and a five-monomer chain (sites 1, 2, 3, 7 and 11). The corresponding configuration has a prefactor  $K^5h^4$  and its total energy is  $\chi + \eta + 4\varepsilon_{end} + 3\varepsilon_{int}$ .

where  $\{\sigma_i\}$  represents the total number of configurations over the variable  $\sigma_i$  for the whole lattice. Then, expanding  $Z$  as power series of  $S$  leads to a sum of polynomial expressions containing a factor  $S_{k,l}^{m(k)}$  for each site  $k$ . Because of the  $n \rightarrow 0$  limit (cf equations (A4) and (A5)), the non-vanishing contributions to the grand-partition function only correspond to polynomials for which  $m(k) = 0$  or  $2$ . As de Gennes first noticed [5, 30], in that case, all successive terms of  $Z$  may be represented as a graph on a lattice. To each nearest

neighbour link  $K S_i \cdot S_j$  one associates a continuous line (see figure A1(a)). The graphs can never intersect themselves because otherwise the existence of an intersecting site would imply the presence of a term  $\langle S_{i,\alpha}^m \rangle_0$  with  $m > 2$  or a term  $\langle S_{i,\alpha}^p S_{i,\beta}^q \rangle_0$  with  $\alpha \neq \beta$  ( $p$  and  $q$  being larger than or equal to 2) in the sum given by equation (A6). Consequently, the only allowed graphs are those corresponding to linear, mutually and self-avoiding open chains. Remember that configurations containing rings correspond to a vanishing term in the expansion of  $Z(h, K)$  (figure A1(a)). In the expression of the partition function  $Z$ , each non-vanishing loop shows a single value of the component index  $\alpha$  for the whole sites involved in this loop. Therefore, for each closed loop characterized by  $p$  bonds, when the summation over the component index  $\alpha$  is achieved, one gets the contribution  $(\beta K)^p$  in the expansion of  $Z$ . But, since  $n = 0$ , the contribution of closed loops vanish. Linear open chains are characterized by two ends  $h S_{i,\alpha} K S_{i,\alpha} S_{j,\alpha}$  with  $\alpha = 1$ . Chains visiting a site for which  $\sigma_k = 0$  do not contribute to the grand-partition function and are therefore not allowed by the model. At this step one must remember that linear open chains only arise from products such as  $h S_{i,1} \sigma_i$  or  $K S_{i,1} \sigma_i S_{j,1} \sigma_j$ . Therefore, if one site  $k$  of a chain is occupied by solvent, ( $\sigma_k = 0$ ), the corresponding factor cancels so that the correlative contribution drops out in the partition function. Situations for which  $m(k) = 0$  correspond to configurations where the site  $k$  is occupied either by an isolated monomer ( $\sigma_k = +1$ ) or solvent molecules ( $\sigma_k = 0$ ). In addition situations for which  $m(k) = 2$  correspond to configurations where the site  $k$  is occupied by a monomer ( $\sigma_k = +1$ ) belonging to a graph consisting of two monomers or more. Note that the particular choice  $Q = 0$  ensures that the presence of an isolated monomer on site  $k$  does not correspond to a situation where  $m(k) = 2$ . In the polynomial expansion of  $\exp(-\beta H)$ ,  $m(k) = 2$  requires the presence of a term  $(h^2/2) S_{k,1}^2$ . Such a term may arise either from the expansion of  $\exp(h S_{k,1} \sigma_k)$  up to the second order or from the first order of  $\exp[(Q - h^2/2) S_{k,1}^2 \sigma_k]$ . When  $Q = 0$ , the sum of these two contributions vanishes. Consequently, provided that  $Q = 0$ , the number of configurations for which an isolated monomer lies on a site ( $k$ ), i.e.  $\sigma_k = 1$ , is not counted twice, since such configurations only correspond to situation where  $m(k) = 0$ . Thus configurations with  $p$  linear open chains and  $l$  bonds lead to polynomials characterized by the prefactor  $h^{2p} K^l$  (figure A1(b)). The total number of monomers (isolated or incorporated into linear chains) in the configuration is given by the sum over  $k$  (with  $k$  varying from unity to  $M$ ), the current term of which is  $\sigma_k$ . It follows that the partition function  $Z$  may be written as:

$$Z = \sum_{\{\sigma_i\}} \sum_l \sum_p \sum_m \Gamma(m, l, p, \{\sigma_i\}, M) h^{2p} K^l \exp(\beta \chi N_{+1,+1}) \exp[\beta \tilde{\mu}(m + l + p)] \quad (\text{A7})$$

where  $\Gamma(m, l, p, \{\sigma_i\}, M)$  represents the total number of ways of depositing  $(m + p + l)$  monomers on the lattice by imposing the presence of  $m$  isolated monomers,  $p$  linear open chains and  $(l + p)$  monomers incorporated into linear mutually and self-avoiding chains;  $N_{+1,+1}$  is the number of nearest neighbour sites  $\langle i, j \rangle$  such that  $\sigma_i = +1$  and  $\sigma_j = +1$ .

## Appendix B

Let us denote by  $f(S, \sigma)$  the mean-field probability function describing the distribution of a single-site occupation number  $\sigma$  and spin component  $S$ . In the mean-field approximation, the Helmholtz free energy per site  $F/M$  of the Hamiltonian can be written as follows:

$$\frac{\beta F}{M} = \frac{\beta \langle H \rangle}{M} + \sum_{\sigma=0}^1 \int f(S, \sigma) \ln f(S, \sigma) dS. \quad (\text{B1})$$



From now the brackets refer to a mean-field average. The energy per site becomes:

$$\frac{\beta \langle H \rangle}{M} = - \left[ h \langle S \sigma \rangle + \frac{Kq}{2} \langle S \sigma \rangle^2 + \tilde{\mu} \beta \langle \sigma \rangle + \frac{q\chi\beta}{2} \langle \sigma \rangle^2 - \frac{h^2}{2} \langle (S \sigma)^2 \rangle \right] \quad (\text{B2})$$

where  $q$  is the coordination number of any site. Furthermore, the probability function  $f$  must satisfy the normalization condition:

$$\sum_{\sigma=0}^1 \int f(S, \sigma) dS = +1. \quad (\text{B3})$$

Owing to equations (B2) and (B3) one can minimize equation (B1) with respect to  $f$  and it leads to the following expression:

$$f(S, \sigma) = \frac{1}{C} \exp \left[ qK \langle S \sigma \rangle S \sigma + hS \sigma + \beta \tilde{\mu} \sigma + \beta q \chi \langle \sigma \rangle \sigma - \frac{h^2}{2} S^2 \sigma^2 \right] \quad (\text{B4})$$

with

$$C = 1 + \left( 1 + qhK \langle S \sigma \rangle + \frac{(qK)^2}{2} \langle S \sigma \rangle^2 \right) \exp[\beta(\tilde{\mu} + q\chi \langle \sigma \rangle)]. \quad (\text{B5})$$

Then, using the moment theorem associated with the special statistics in the vanishing  $n$  limit (cf equation (A5) in appendix A), it follows:

$$\langle S \sigma \rangle = \sum_{\sigma=0}^1 \int S \sigma f(S, \sigma) dS = \frac{1}{C} \exp[\beta(\tilde{\mu} + q\chi \langle \sigma \rangle)] (h + qK \langle S \sigma \rangle) \quad (\text{B6})$$

and

$$\langle \sigma \rangle = \sum_{\sigma=0}^1 \int \sigma f(S, \sigma) dS = \frac{(C-1)}{C}. \quad (\text{B7})$$

The definition of the occupation number implies that  $\langle \sigma \rangle = \Phi$  where  $\Phi$  is the total monomer concentration. It results from equations (B5)–(B7) that:

$$\langle S \sigma \rangle = \frac{\Phi(h + qK \langle S \sigma \rangle)}{(1 + qKh \langle S \sigma \rangle + ((qK)^2/2) \langle S \sigma \rangle^2)}. \quad (\text{B8})$$

Using the previous equalities, the free energy per site (i.e., the osmotic pressure of the solution  $\pi$ ) is:

$$-\beta\pi v_0 = - \frac{\ln Z(h, K, \mu, \chi)}{M} = \ln(1 - \Phi) + \frac{qK}{2} \langle S \sigma \rangle^2 + \frac{q\beta\chi}{2} \Phi^2 \quad (\text{B9})$$

where  $v_0$  is the elementary volume of a cell. Consequently, the free energy per site of the micelle solution,  $\beta\mathcal{F}/M$ , is given by:

$$\frac{\beta\mathcal{F}}{M} = \beta\mu\Phi - \beta\pi v_0 = \Phi \ln \left[ \frac{\langle S \sigma \rangle}{(1 - \Phi)(h + qK \langle S \sigma \rangle)} \right] + \beta\eta\Phi + \ln(1 - \Phi) - \frac{q\beta\chi}{2} \Phi^2 + \frac{qK}{2} \langle S \sigma \rangle^2. \quad (\text{B10})$$

From the expression of free energy, it is possible to evaluate several properties of the solution such as phase separation and average aggregation number.

For the phase separation, one must take into account the definition of the spinodal line i.e.:

$$\left( \frac{\partial^2 \mathcal{F}}{\partial \Phi^2} \right) = 0. \quad (\text{B11})$$

At this step, one must recall that critical points which lie on the spinodal line verify:

$$\left(\frac{\partial^3 \mathcal{F}}{\partial \Phi^3}\right) = 0. \quad (\text{B12})$$

The average aggregation number  $N$  is given by the ratio of the total number of monomers in solution (i.e.,  $M\Phi$  where  $\Phi$  is the monomer concentration) over the total number of chains (single sites and others)  $\langle p + m \rangle$ . From the expression of the osmotic pressure  $\pi$ , it is possible to estimate  $\langle p \rangle$ :

$$\langle p \rangle = \frac{h}{2} \frac{\partial}{\partial h} \ln Z = \frac{-\beta h M}{2} \frac{\partial \pi}{\partial h}. \quad (\text{B13})$$

In addition one has:

$$\langle l \rangle = -\beta K M \frac{\partial \pi}{\partial K} \quad \langle m \rangle = M\Phi - \langle p \rangle - \langle l \rangle. \quad (\text{B14})$$

Note that, in the grand-canonical ensemble  $Z(h, K, \mu, \chi, \eta)$ ,  $\Phi$  the total monomer concentration is not constant and then must be derived with respect to  $h$  and  $K$  in the previous expressions. This is the reason for which, for evaluating the average aggregation number, it is more convenient to use the canonical ensemble  $\Psi(h, K, \Phi, \chi, \eta)$ . The free energy of the solution of micelles can be then expressed as a function of  $\Psi(h, K, \Phi, \chi, \eta)$ :

$$\beta \mathcal{F} = -\ln \Psi(h, K, \Phi, \chi, \eta) \quad (\text{B15})$$

i.e.:

$$\begin{aligned} \frac{\beta \mathcal{F}}{M} = \beta \mu \Phi - \beta \pi v_0 = \Phi \ln \left[ \frac{\langle S\sigma \rangle}{(1 - \Phi)(h + qK \langle S\sigma \rangle)} \right] + \beta \eta \phi + \ln(1 - \Phi) - \frac{q\beta \chi}{2} \Phi^2 \\ + \frac{qK}{2} \langle S\sigma \rangle^2 \end{aligned} \quad (\text{B16})$$

where  $\langle S\sigma \rangle$  is the solution of equation (B8). In the canonical ensemble, the average number of open chains  $\langle p \rangle$  and intermolecular links  $\langle l \rangle$  are respectively given by:

$$\langle p \rangle = \frac{h}{2} \frac{\partial \ln \Psi(h, K, \Phi, \chi, \eta)}{\partial h} = -\frac{\beta h}{2} \frac{\partial \mathcal{F}}{\partial h} \quad (\text{B17})$$

and

$$\langle l \rangle = K \frac{\partial \ln \Psi(h, K, \Phi, \chi, \eta)}{\partial K} = -K \frac{\partial \mathcal{F}}{\partial K} \quad (\text{B18})$$

$\langle m \rangle$ , the average number of isolated monomers, is simply derived from the conservation of the number of surfactant molecules in solution:

$$\langle m \rangle = \sum_i \sigma_i - \langle p \rangle - \langle l \rangle = M\Phi - \langle p \rangle - \langle l \rangle. \quad (\text{B19})$$

### Appendix C

In the mean-field approximation, the evolution with surfactant concentration of the thermodynamic properties of a worm-like micelle solution requires us to determine  $X(\Phi) = \langle S\sigma \rangle(\Phi)$  which is the solution of the following equation (cf appendix B):

$$X = \frac{\Phi(h + \lambda X)}{(1 + h\lambda X + (\lambda^2/2)X^2)} \quad (\text{C1})$$

where  $\lambda = qK$ .

Indeed, by thoroughly examining this equation, one can distinguish, depending on the surfactant concentration, two regimes where  $X(\Phi)$  can be easily estimated. These two concentration regimes correspond respectively to  $\Phi \ll \Phi^*$  and  $\Phi \gg \Phi^*$  (where  $\Phi^*$  is the surfactant concentration corresponding to the sphere to rod transition).

Let us consider first the case where  $\Phi \ll \Phi^*$ . This case corresponds to the following mathematical assumption in equation (C1):  $\lambda X \ll h$  and  $\lambda \gg h \gg 1$  (i.e., strong aggregation). Within this assumption, the dominant terms in the denominator and numerator of the right term of equation (C1) are respectively 1 and  $\Phi h$  and therefore an estimate for  $X$  in this regime is given by:

$$X \approx \Phi h. \quad (\text{C2})$$

Reporting this expression in equations (B9), (B10) and (B17) leads to:

$$\beta\pi v_0 \approx \Phi \quad (\text{C3})$$

$$\frac{\beta F}{M} \approx \Phi \ln(\Phi) + (1 - \Phi) \ln(1 - \Phi) + \beta\eta\Phi - \Phi^2 \left[ \frac{q\beta\chi}{2} + qK \left( 1 - \frac{h^2}{2} \right) \right] \quad (\text{C4})$$

and

$$N \approx 1 + \frac{qKh^2}{2}\Phi \approx 1; \quad (\text{C5})$$

this region corresponds to surfactant concentrations well below the sphere to rod transition concentration.

Let us now consider the other extreme case corresponding to  $\Phi \gg \Phi^*$ . This case corresponds to the mathematical assumption  $\lambda X \gg h > 1$ . Within this assumption, the dominant terms in the denominator and numerator of the right term of equation (C1) are respectively  $\Phi\lambda X$  and  $(\lambda X)^2/2$ . Therefore a first order estimate of  $X(\Phi)$  in this regime is given by:

$$X \approx \sqrt{\frac{2\Phi}{\lambda}}. \quad (\text{C6})$$

In order to push further the estimate of  $X(\Phi)$ , which is necessary to find for  $\pi$  a  $\Phi^{1/2}$  dependence, we take:

$$X = X_0(1 + u) = \sqrt{\frac{2\Phi}{\lambda}}(1 + u) \quad (\text{C7})$$

where  $u$  is the solution of the following equation:

$$(2\Phi h + X_0) + uX_0(1 + 2\lambda X_0) + u^2 X_0 \left( \frac{3}{2}\lambda^2 X_0^2 + h\lambda X_0 \right) + \frac{\lambda^2}{2} X_0^3 u^3 = 0. \quad (\text{C8})$$

Comparing the magnitude of the different terms (remember that  $\lambda X_0 \gg h$ ) in this equation leads to the following rough estimates of  $u$  and therefore of  $X$ :

$$u \approx -\frac{h}{2\lambda X_0} \quad (\text{C9})$$

$$X \approx \sqrt{\frac{2\Phi}{\lambda}} - \frac{h}{2\lambda}. \quad (\text{C10})$$

Replacing this expression in equations (B9)–(B16) and performing an expansion in  $u$ , gives the following estimates for the osmotic pressure and free energy per site:

$$-\beta\pi v_0 \approx -\ln(1 - \Phi) + \Phi + \frac{q\beta\chi}{2}\Phi^2 - h\sqrt{\frac{\Phi}{2qK}} \quad (\text{C11})$$

$$\frac{\beta \mathcal{F}}{M} \approx (1 - \Phi) \ln(1 - \Phi) + \Phi(1 - \ln(qK)) - \frac{q\beta\chi}{2} \Phi^2 - h \sqrt{\frac{\Phi}{2qK}}. \quad (\text{C12})$$

When the elongation process is important, the dilute regime occurs at low surfactant concentration and the osmotic pressure is roughly given by:

$$\beta\pi v_0 \approx h \sqrt{\frac{\Phi}{2qK}}. \quad (\text{C13})$$

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