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## Theory for polymer coils with necklaces of micelles

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**Abstract.** If many micelles adsorb onto the same polymer molecule then they are said to form a necklace. A minimal model of such a necklace is proposed and shown to be almost equivalent to a one-dimensional fluid with nearest-neighbour interactions. The thermodynamic functions of this fluid are obtained and then used to predict the change in the critical micellar concentration of the surfactant in the presence of the polymer. If the amount of polymer is not too large there are two critical micellar concentrations, one for micelles in necklaces and one for free micelles.

### 1. Introduction

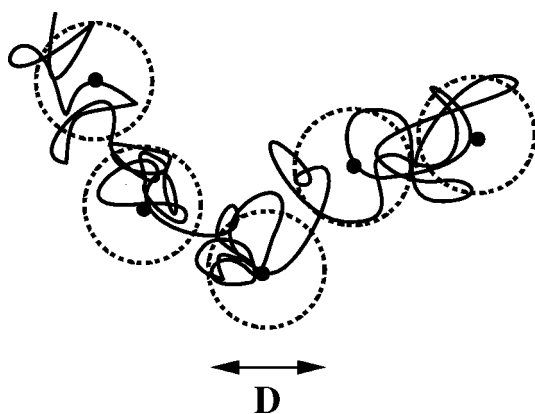
Experiment has shown that some micelles adsorb strongly onto polymer chains. If the polymer molecule is large enough many micelles can adsorb onto one molecule, forming a necklace of micelles along the polymer chain. The most widely studied example is the adsorption of micelles of sodium dodecyl sulphate (SDS) onto poly(ethylene oxide) (PEO); see references [1, 2] and references therein. See reference [3] for work on other systems. The interaction energy of a micelle with a polymer chain can be strong, many times  $kT$  (the thermal energy), and has a large effect on both the polymer and the micelle. The favourable interaction of a micelle with the polymer reduces the surfactant density at which the micelles form; the critical micellar concentration (cmc) is reduced, whilst if many micelles adsorb onto a single polymer the repulsive micelle–micelle interactions cause the polymer chain to swell; the radius of gyration may increase by a factor of two. Below, we propose a simple minimal model for necklaces of micelles adsorbed on a polymer chain. We then go on to calculate the free energy of such a necklace and use this to determine when they form and to look at the competition between free micelles and micelles bound to polymer.

A polymer chain is a linear object; its topological dimension is 1 [4]. So, two micelles adsorbed onto a chain cannot pass each other without one of them detaching from the polymer chain. Therefore the necklace of micelles along a polymer chain behaves as a one-dimensional system. In the limit in which the polymer molecule is very long the necklace is a 1-d bulk fluid. We assume that the micelle–micelle interactions are repulsive and so no two micelles can approach each other closely. This restriction on the relative positions of the micelles of the necklace restricts the configurations that the polymer can adopt and so reduces its entropy. At high density of micelles the micelles are closely spaced along the polymer—that is, the pieces of polymer between the micelles are quite short—and so these short pieces of polymer have to stretch in order to bridge the gaps between the micelles.

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This loss of entropy eventually limits the number of micelles which adsorb on a polymer and when the polymer chains are saturated with micelles, free micelles are formed.

In the next section we derive from first principles a theory of objects with excluded-volume interactions, which are adsorbed onto a linear polymer. This is our main result. Our results are not qualitatively new; they are, however, semiquantitative, unlike previous work whose accuracy was only qualitative [5]. Our mapping onto a one-dimensional problem should also allow the semiquantitative treatment of more complex systems than those studied here, such as micelles adsorbed onto semidilute polymers. First, the polymer-mediated interaction between two micelles is derived, yielding a potential of mean force for the intermicellar interaction. Then this is combined with a theory of one-dimensional fluids to provide the equation of state of particles adsorbed onto a polymer. This is then used in section 3 to calculate the equation of state of a necklace. Combining the equation of state with a standard theory of micelle formation [6, 7] then allows us to calculate how many micelles will form, both adsorbed on polymer and free, as a function of the surfactant density. Finally, we discuss possible extensions of the theory and model.



**Figure 1.** A schematic picture of a polymer coil with a necklace of micelles. The polymer chain is the black curve and the micelles adsorbed onto the chain are represented by dotted circles of diameter  $D$ .

## 2. Theory for necklaces of micelles

The system is a mixture of surfactant and polymer in a common solvent; the mixture is dilute, i.e. the fraction of the volume taken up by the surfactant and polymer is small. The polymer is composed of coils of size  $S$ , where  $S$  is proportional to the number of monomers of a polymer molecule [8, 9]. The coils are ideal, Gaussian, coils and if unperturbed the mean square distance between the two ends of a coil equals  $S$ . Thus  $S$  has dimensions of length squared, and  $S^{1/2}$  is the single relevant length scale for the polymer [8, 9]. We are assuming that the polymer's Kuhn length is much smaller than any length that we consider explicitly. Our theory is entirely mesoscopic: the micelle is treated simply as a sphere and the polymer-micelle interaction is not considered explicitly but is treated phenomenologically via an association constant. A schematic diagram of the model is presented in figure 1. The constant  $\Delta\mu$  is the difference in excess chemical potential between a micelle bound to a piece of a polymer chain and a free micelle. Here, excess means the chemical potential minus its ideal-gas part:  $\ln \rho$ , where  $\rho$  is the (1- or 3-d) density.

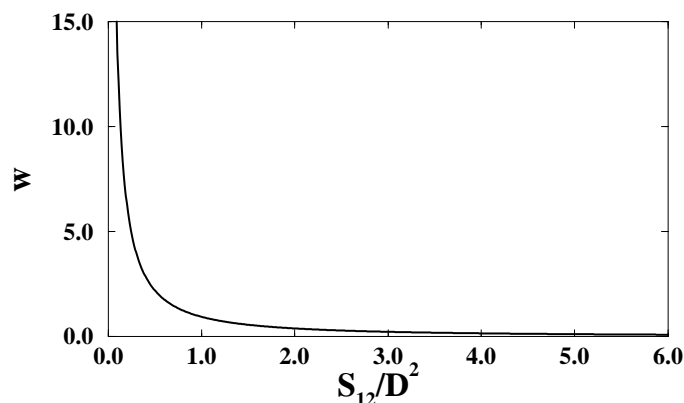
If  $\Delta\mu$  is negative the micelles will tend to adsorb on the chain [10]. This adsorption is due to part of the polymer chain lying near the surface of the micelle and interacting via an attractive interaction with it [2]. However, for simplicity we treat the polymer–micelle interaction as that between the micelle and a point on the polymer; we ignore the amount of polymer taken up in adsorbing to the micelle. With this simplification a micelle adsorbed onto a polymer coil is free to move along the entire contour length of the polymer  $S$ . Because the fractal dimension of the polymer is two not one, its contour length in many ways resembles an area, e.g. the end-to-end distance increases as the square root of the size  $S^{1/2}$ . This is why the contour length has units of length *squared*. As the polymer is a 1-d chain of monomers the micelle acts as a particle on a wire. Even though the polymer is tracing out an extremely convoluted path through 3-d space the configurational space available to a micelle adsorbed onto the polymer is only 1-d.

If there is more than one micelle adsorbed on the same polymer coil then the micelles will interact with each other. We model the micelle–micelle interaction via a simple hard-sphere interaction: no two micelles' centres may be within a distance  $D$  of each other. The size of the micelles,  $D$ , is much less than that of a coil,  $S^{1/2}$ , allowing many micelles to adsorb onto one coil. Above, we assumed that the polymer–micelle adsorption was pointlike, i.e. a negligible amount of the polymer is adsorbed onto a micelle and we have just assumed that two micelles interact with each other out to a distance  $D$ . For these two assumptions to be consistent the physical size of the micelles must be much smaller than the range at which two micelles interact. Essentially, we must have a micelle of diameter  $\ll D$  which is quite highly charged so that no other micelle can approach within  $D$  [7, 11]. As micelles are typically 3–4 nm in diameter,  $D \gg 4$  nm.

The limit of few micelles adsorbed onto a polymer chain, when micelle–micelle interactions are unimportant, is trivial (at our phenomenological level of description). It is just the free energy of a polymer coil plus the excess free energy of a free micelle plus  $\Delta\mu$  plus the log of the 1-d density of micelles on the chain. The first of these is a reference free energy, which we need not specify, and the free energy of a free micelle and  $\Delta\mu$  are parameters of our model. However, at higher densities micelles on the same coil interact. They do so when the micelles are close together, i.e. when the pieces of polymer which connect adjacent micelles are short. The partition function of a piece of polymer chain with a micelle at each end is different from the partition function of the same length of chain without the micelles. In evaluating the partition function when the micelles are present, we must exclude those configurations in which the two micelles' hard spheres overlap. This is done in the following section, and in section 2.1 we use that result to calculate the thermodynamic functions for a necklace of micelles in the limit in which the coil is infinitely long. In section 2.2 this result is used to determine the free energy of a necklace at any density.

### 2.1. The interaction between two micelles adsorbed onto the same polymer coil

We consider two micelles adsorbed onto a coil and separated by a contour length of polymer  $S_{12}$ . The probability of this separation of the micelles is proportional to the partition function of the chain at this separation. The two micelles have split the coil into three pieces, the one between them of length  $S_{12}$  and the two end pieces. The three parts are independent as the coil is ideal. Only the partition function of the centre piece is affected by the micelles; the end pieces are free to adopt any configuration but the ends of the centre piece are each attached to a micelle and so, because of the micelle–micelle interaction, they must be at least  $D$  apart. The partition function of a chain of length  $S_{12}$  whose ends are constrained to be at



**Figure 2.** The polymer-mediated, effective interaction  $w$  between two micelles adsorbed onto a polymer coil, as a function of their separation  $S_{12}$ .

least  $D$  apart is easy to calculate. The partition function for a chain with ends separated by  $r$ , divided by its partition function when free, is just the probability distribution function  $\phi$  for the ends of an unconstrained chain, times  $dr$ . Now,  $\phi$  is [8]

$$\phi(S_{12}, r) = \left(\frac{3}{2\pi S_{12}}\right)^{3/2} \exp\left(\frac{-3r^2}{2S_{12}}\right). \quad (1)$$

Thus, the partition function with the ends at least  $D$  apart, divided by the partition function for an unconstrained chain, is simply

$$4\pi \int_D^\infty \phi(S_{12}, r) r^2 dr = 1 - \frac{4}{\pi^{1/2}} \int_0^{(3/2)^{1/2} D/S_{12}^{1/2}} x^2 \exp(-x^2) dx = \exp[-w(S_{12}/D^2)]. \quad (2)$$

The second equality defines  $w$ , the effective interaction potential between two neighbouring micelles. The probability of the micelles being  $S_{12}$  apart,  $P(S_{12}/D^2)$ , is directly related to the partition function of the chain when the micelles are  $S_{12}$  apart:

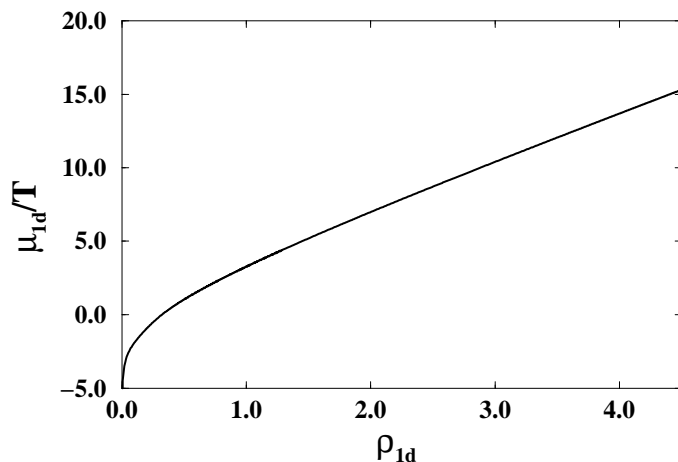
$$P(S_{12}/D^2) = \exp[-w(S_{12}/D^2)] / \left( \int \exp[-w(S_{12}/D^2)] dS_{12} \right) \quad (3)$$

for an infinitely long polymer. We see that  $\exp[-w(S_{12}/D^2)]$  is acting as a Boltzmann weight and so  $w$  is an effective interaction; it is plotted in figure 2. The interaction  $w$  is an athermal but soft repulsion. When two micelles are bound to the polymer less than  $S_{12}^{1/2} \sim D$  apart along a polymer chain then the chain has to stretch to cross the distance between the micelles, which must be  $\geq D$ . Conventionally, the Boltzmann weight is the exponential of minus an energy of interaction but here it is the exponential of minus the free energy of the piece of polymer coil. However, despite its unusual origin  $w$  behaves just as an interaction energy. The pair of micelles behave as a pair of particles on a wire which interact via a potential  $w$ . In the following section we use  $w$  to obtain the thermodynamic functions of a fluid of many micelles on one polymer coil.

## 2.2. A one-dimensional fluid of micelles on a polymer coil

When many micelles are adsorbed onto the same coil they behave as a 1-d fluid. Formally we will take the  $S/D^2 \rightarrow \infty$  limit, producing an infinite fluid. We do not consider effects

due to the finite size of the polymer coils. Each micelle's movement is restricted by the micelle in front and the micelle behind. As the system is effectively 1-d, the micelles form a fluid at all densities; they never solidify or undergo a liquid–vapour transition [12, 13]. Due to the convoluted path taken by the chain, non-adjacent micelles can interact; indeed this interaction will cause the coil to swell and change from being Gaussian to being swollen [8, 14]. However, these interactions are weak in comparison to the interactions between nearest-neighbour micelles and so will be neglected for the purpose of determining the free energy of the necklace of micelles. Each micelle always interacts with the micelles in front and behind it but collisions between different parts of the chain are relatively infrequent [14].



**Figure 3.** The chemical potential of a 1-d fluid of micelles on a polymer coil, interacting via the potential  $w$ .

Therefore we have a simple 1-d fluid. As the interaction between micelles is mediated via the polymer chain the interaction is strictly nearest neighbour. The free energy of the coil is simply a sum of the free energies of the pieces between the micelles and so is just a function of all of the  $S_{12}$ s between neighbouring micelles. The statistical mechanics of 1-d fluids with nearest-neighbour interactions is both well studied and simple [13]. We start from the canonical partition function  $Z_N(S)$  of  $N$  micelles on a coil of length  $S$ . As usual for 1-d systems, molecules fixed at each end of the system define its limits. So, with a micelle fixed at coordinate  $x_0$  and one at  $x_N$ ,  $Z_N$  is

$$Z_N(S) = \int_{x_i < x_{i+1}} \prod_{i=1}^N dx_i \exp \left[ - \sum_{i=1}^{N+1} w(x_i - x_{i-1}) \right] \quad (4)$$

where the factor of  $1/N!$  is absent because we have put the micelles into a sequence: the  $i$ th micelle is always the left-hand neighbour of the  $(i + 1)$ th micelle [13]. The units are defined so that the thermal energy  $kT$  is unity. Progress can be made if we move to the isothermal–isobaric ensemble [13, 15], introducing the pressure  $p$  which is the conjugate variable to the length  $S$ . The isothermal–isobaric partition function  $Z_N(p)$  is

$$Z_N(p) = \int Z_N(S) \exp(-pS) dS. \quad (5)$$

Following the method of Takahashi [13] we note that as the  $(N + 1)$ th particle defines the

limit of our system,  $x_{N+1} = S$ . Then if we define the new coordinates  $r_i = x_i - x_{i-1}$ ,

$$Z_N(p) = \int_{r_i > 0} \prod_{i=1}^{N+1} dr_i \exp \left[ - \sum_{i=1}^{N+1} \{w(r_i) + pr_i\} \right] = \left( \int_0^\infty dr \exp[-w(r) - pr] \right)^{N+1} \quad (6)$$

the partition function has reduced to a simple 1-d integration. The chemical potential  $\mu_{1d}$  is, substituting  $N$  for  $N + 1$  in equation (6),

$$\mu_{1d} = -\frac{1}{N} \ln Z_N(p) = -\ln \int_0^\infty dr \exp[-w(r) - pr] \quad (7)$$

which gives  $\mu_{1d}$  as a function of the pressure  $p$ . We would like it as a function of the reduced 1-d density  $\rho_{1d} = ND^2/S$ . The density  $\rho_{1d}$  is obtained from

$$\rho_{1d} = \left( \frac{\partial \mu_{1d}}{\partial p D^2} \right)^{-1}. \quad (8)$$

Using equation (2) in equation (7) and then equation (8) yields  $\mu_{1d}$  as a function of density  $\rho_{1d}$ ; it is plotted in figure 3. Notice that the chemical potential is almost a linear function of density at high density. For future use we define an excess chemical potential  $\mu_{ex} = \mu_{1d} - \ln \rho_{1d}$ . We now possess the chemical potential of a necklace of micelles as a function of the density of micelles along the polymer chain. In order to determine the density of micelles along a polymer as a function of the surfactant density we require a model for the formation of micelles.

### 3. Micelle formation

Our model for micelle formation is quite standard [6, 7]. We start by assuming that the surfactant monomers, the free micelles and the micelles bound to polymer coils form an ideal ternary mixture. The only interactions considered are those between micelles bound to the same polymer; interactions involving free micelles or monomers are neglected as the surfactant + polymer solution is dilute. The ternary mixture's density and composition are specified by three densities: the density of surfactant monomers  $\rho_0 = N_0 D^3/V$ , of free micelles  $\rho_{fm} = N_{fm} D^3/V$  and of bound micelles  $\rho_{bm} = N_{bm} D^3/V$ .  $N_0$ ,  $N_{fm}$  and  $N_{bm}$  are the numbers of surfactant monomers, free micelles and micelles bound to polymer, respectively, and  $V$  is the volume. The 1-d density of micelles along the polymer chains  $\rho_{1d}$  is related to the density of bound micelles in the mixture  $\rho_{bm}$  by

$$\rho_{bm} = \rho_p \rho_{1d} \quad (9)$$

where  $\rho_p = N_p S D/V$  is a 'segment' density of the polymer. It is the number density of segments of polymer of size  $D^2$ , times  $D^3$ .  $N_p$  is the number of polymer coils. Below, we treat (i) the monomers and free micelles and (ii) the micelles bound to polymer as constituting two different bulk phases. The polymer density  $\rho_p$  just defines the relative volumes of these two parts of our system.

At equilibrium the chemical potential of a surfactant is the same if it is a monomer or is part of either type of micelle. Then the chemical potential of a micelle composed of  $m$  surfactant molecules is  $m$  times that of a monomer. For the chemical potential of a monomer to be equal to that in a free micelle [6, 7]

$$m(\ln \rho_0 + \mu_0) = \ln \rho_{fm} + \mu_{mic} \quad (10)$$

and for it to equal that in a bound micelle

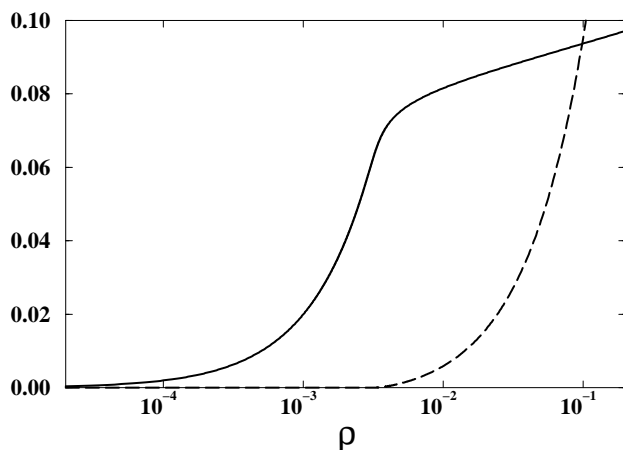
$$m(\ln \rho_0 + \mu_0) = \mu_{1d}(\rho_{1d}) + \mu_{mic} + \Delta\mu = \mu_{1d}(\rho_{bm}/\rho_p) + \mu_{mic} + \Delta\mu \quad (11)$$

where we used equation (9) to go from the middle to the right-hand-side expression. We have assumed that the number of surfactant molecules in a micelle is  $m$  for both free and bound micelles. Micelles are of course not monodisperse and so this is an approximation, although the numbers of micelles much larger or smaller than the most probable size are small [6, 7]. The constants  $\mu_0$  and  $\mu_{mic}$  are the contributions to the chemical potentials of the monomers and micelles, respectively, of the interactions. They are the change in free energy, in excess of the  $\ln \rho$  term, of the system when a monomer or a micelle is inserted [7]. We have neglected the contribution from the momentum degrees of freedom. Thus,  $\mu_{mic} - m\mu_0$  is the difference between the chemical potential (minus the  $\ln \rho$  terms) of  $m$  surfactant molecules in a micelle and  $m$  surfactant monomers.

The first equation for equilibrium between monomers and micelles, equation (10), is easily rewritten in the familiar form

$$\rho_{fm} = \rho_0^m \exp(m\mu_0 - \mu_{mic}). \quad (12)$$

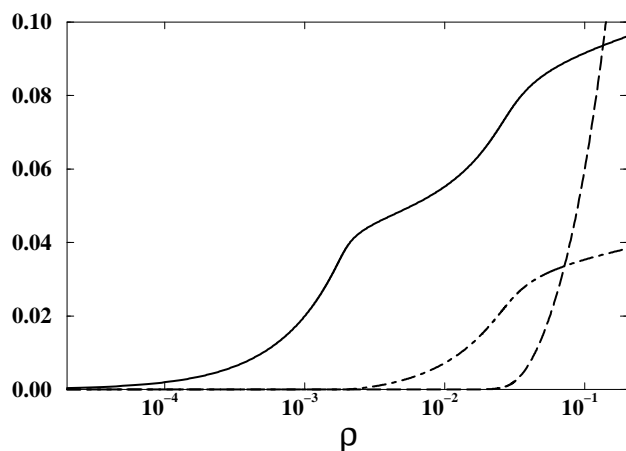
The most convenient thermodynamic variable to work in is  $\rho_0$  which corresponds to controlling the chemical potential of the surfactant:  $\ln \rho_0 + \mu_0$ . The second equation for equilibrium, equation (11), cannot be rewritten in the form ' $\rho_{bm}$  equals a function of  $\rho_0$ ' because the right-hand side includes  $\mu_{1d}$  which is not a simple logarithmic or linear function of  $\rho_{bm}$ . If  $\rho_p$ ,  $\mu_{mic}$  and  $\Delta\mu$  are specified, then equation (11) can be solved as a non-linear equation for  $\rho_{bm}$ , at any value of  $\rho_0$ .



**Figure 4.** The density of surfactant monomers  $\rho_0$  (solid curve), and of free micelles  $\rho_{fm}$  (dashed curve) as a function of total surfactant density  $\rho$ .  $m\mu_0 - \mu_{mic} = 45$  and  $m = 20$ . There is no polymer present.

The total number density of surfactant is proportional to  $\rho = \rho_0/m + \rho_{fm} + \rho_{bm}$ . As all three of the densities ( $\rho_0$ ,  $\rho_{fm}$  and  $\rho_{bm}$ ) are made dimensionless by multiplying by  $D^3$ , the volume fraction of the surfactant is approximately equal to  $\rho$  times the physical volume of a micelle divided by  $D^3$ . The physical volume of a micelle is the volume actually occupied by the surfactant molecules. As the physical volume is much less than  $D^3$ , the surfactant's volume fraction is much less than  $\rho$ . In figures 4 and 5 we plot the densities of monomers and micelles as functions of this total surfactant density. In figure 4 we have





**Figure 5.** The density of surfactant monomers  $\rho_0$  (solid curve), of free micelles  $\rho_{fm}$  (dashed curve), and of bound micelles  $\rho_{bm}$  (chain curve) as a function of total surfactant density  $\rho$ .  $m\mu_0 - \mu_{mic} = 45$ ,  $m = 20$ ,  $\Delta\mu = -15$  and  $\rho_p = 0.01$ .

no polymer and there are only free micelles. The critical micellar concentration (cmc) [7] is clearly around  $10^{-2}$ , although it is not that well defined as our aggregation number  $m$  is not that large,  $m = 20$ . In figure 5, the value of  $\mu_{mic}$  is unchanged from figure 4 but there is polymer present. As  $\Delta\mu$  is negative, the polymer stabilizes the micelles. This has two effects: micelles form at lower densities, the polymer encourages micelle formation and micelles ‘prefer’ to be adsorbed onto a polymer than to be free. So, at low densities where there are few micelles they are nearly all adsorbed onto polymer chains; the density of free micelles is very low, below  $\rho \simeq 3 \times 10^{-2}$ . As the density of micelles increases the density of micelles on the polymer chains becomes quite high and the interaction free energy of these micelles,  $\mu_{ex}$ , is large. The polymer chains are stretching to accommodate the micelles and this stretching is reducing the configurational entropy of the polymer. This reduces the free-energy reduction on adsorption and so we see that free micelles start to form. From equations (10) and (11), it is easy to see that when  $\mu_{ex} = \ln \rho_p - \Delta\mu$  the numbers of free and bound micelles are the same.

Notice that the density of surfactant at which free micelles appear is much higher in figure 5 than in figure 4 because the monomer density is depleted by the formation of bound micelles. Free micelles appear at a  $\rho_0$  determined solely by  $\mu_{mic}$ —see equation (12)—but this corresponds to a higher  $\rho$  if there is competition for monomers. The  $\rho_0$ -curve of figure 5 looks as if there are two cmcs; it has two steps while that in figure 4 has only one. The first is where bound micelles form and the rate of increase of  $\rho_0$  decreases sharply. Then as the density of bound micelles increases the polymer chains become crowded, micelle formation becomes less favourable and the rate of increase of  $\rho_0$  increases. At yet higher density, free micelles form and the rate of increase of  $\rho_0$  decreases again. Of course, if the polymer density  $\rho_p$  increases, then the polymer chains saturate at higher surfactant densities and the second ‘cmc’ is pushed to higher values of  $\rho$ .

The formation of a necklace of micelles causes the ideal polymer coil to expand for two reasons: it stretches the pieces of the polymer chain between the micelles and the micelle–micelle interaction results in the chain being swollen, like a polymer coil in a good solvent [8, 14]. Without micelles, the radius of gyration of the polymer  $R_G = S^{1/2}/\sqrt{6}$ . At low densities of micelles,  $\rho_{1d} \lesssim 1$ , the radius of gyration is difficult to estimate as the

micelles cover only a fraction of the chain. Therefore some parts, with micelles, repel each other but other, bare, parts do not. However, for  $\rho_{1d} > 1$  almost all of the chain is covered with micelles. In order to minimize the stretching of the polymer the spacing between the micelles will be quite regular and near  $D$ . So, we can consider the chain as being composed of  $\rho_{1d}S/D^2$  segments of length  $\sim D$ . Then, as the chain is swollen,  $R_G \sim (\rho_{1d}S/D^2)^{3/5}D$ . As  $S \gg D^2$ , this is much larger than  $S^{1/2}$ .

#### 4. Conclusion

Perhaps the simplest possible model of polymer coils with necklaces of micelles has been proposed and studied. The simplicity of the model has allowed a detailed examination of its behaviour to be carried out with only very minor approximations. This differs from previous theoretical work [5] which involved a highly approximate treatment of a much more detailed, and so complex, model. We have shown that the 1-d topology [4] of a polymer chain implies that the necklace behaves as a 1-d fluid. This allowed us to determine the behaviour of the necklace using the highly developed theory for 1-d systems [13]. In combination with a standard theory for micelle formation it was then straightforward to calculate the densities of micelles formed; see figure 5.

The model was kept simple for the sake of simplicity and clarity. For the purposes of comparison with experiment a more complex and accurate model is required. The theory presented here can be extended to deal with the most unrealistic features of the model. For example, the theory neglects the finite size of the polymer coils. Micelles are quite large,  $\sim 4$  nm across, and so if the polymer coil is small there may be room for only a few micelles to adsorb without stretching the polymer so much that it is not favourable for adsorbing another micelle. Then the fluid of micelles is not a bulk fluid. The finite size of the coil corresponds to a 1-d fluid between two walls,  $S$  apart. Confined 1-d fluids have been considered extensively; see reference [16]. The coils studied in experiment [2] are in a good solvent and so are swollen. Therefore it would be worthwhile to extend our theory for ideal coils to self-avoiding coils. Although self-avoiding coils are more complex and difficult to deal with than ideal coils [8, 14], enough is known about their free energy when they are stretched [14] to perform at least a scaling theory of a polymer with a micellar necklace. Experimental results [11] on a semidilute solution of polymer clearly show the competition between polymer entropy and the free energy of adsorption which we have observed here. We hope that the theory developed here can be applied even to this system.

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