Eur. Phys. J. B **8**, 233–243 (1999)

THE EUROPEAN PHYSICAL JOURNAL B
EDP Sciences

Phase transitions in simple models of rod-like and disc-like micelles

J.A. Cuesta[a] and R.P. Sear[b]

FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

Received: 3 December 1997

Abstract. The interplay of interactions between micelles, and the aggregation of these micelles into large, highly anisotropic micelles, is studied. Simple, hard-body, models of rod-like and disc-like micelles are used, which allows us to apply fundamental measure theory to determine the free energy. Then we study the phase transition from the fluid phase to a liquid crystalline phase. We find that aggregation induces a strongly first order transition from a fluid phase of small micelles to a close packed liquid crystalline phase of infinitely large micelles.

PACS. 64.70.Md Transitions in liquid crystals – 61.30.Cz Theory and models of liquid crystal structure – 61.20.-p Structure of liquids – 61.20.Gy Theory and models of liquid structure – 61.20.Qg Structure of associated liquids: electrolytes, molten salts, etc.

1 Introduction

Many surfactants form approximately spherical micelles at low density but when the surfactant's volume fraction reaches ~ 0.5, intermicellar interactions force the micelles to aggregate into large anisotropic micelles in liquid crystalline phases [1–7]. The interactions provide a driving force for the formation of large micelles because the intermicellar interactions, and hence the interaction part of the free energy, are less for liquid crystalline phases of anisotropic micelles than they are for spherical micelles. The size of the micelles is then very sensitive to density as the interactions are only strong at volume fractions ~ 0.5 or higher. In this work, we study, theoretically, phase transitions which are driven by, or at least strongly affected by, aggregation. For this purpose we have defined two highly simplified models. We have chosen to model aggregates by perfectly aligned, rod-like or disc-like, hard parallelepipeds. We find a fluid–columnar transition for the rod-like micelles and a fluid–lamellar transition for the disc-like micelles. This pattern of transitions is what is found in experiments [3,8,9], although the experimental phase diagrams contain additional phases.

We chose such simplified models both because the simpler the model which shows the behaviour we are interested in, the clearer is the understanding gained, and because the theoretical treatment is simpler. For our models we can then take advantage of the recent studies [10–12] of density functionals for mixtures of parallel hard parallelepipeds within the so-called *fundamental measure theory* (see Refs. [12–14] and references therein). In brief this theory provides a description of certain types of mixtures of hard particles in terms of characteristic geometrical "measures" of the particles, such as volume, surface, or mean radius of curvature. It turns out that the fundamental measure free energy for the uniform phases reduces to a $y3$-expansion [15,16] which has already been used to study similar models [17–19]. The use of the fundamental measure formalism has, nevertheless, two advantages: (i) it is directly extensible to inhomogeneous phases (which cannot be included consistently in the standard $y3$-expansion [17]), and (ii) it avoids the computation of the second and third virial coefficients (although the final expression does contain their exact values), thus yielding a simpler formalism.

By modeling micelles by parallel hard, rigid convex bodies we are deliberately ignoring three features of real aggregates: round shape (spherical for small aggregates or cylindrical for long ones), coupling between orientational order and the growth of micelles, and flexibility. In addition our micelles interact *via* a simple hard-core potential. The phase behaviour of micelle forming surfactants has been extensively studied, see references [2,5,20]. Models of micelles which are both flexible and nonspherical, *e.g.*, [21] and interact *via* a soft repulsion as well as a hard core [2,18,19] have been studied. So, it is a little surprising that no results have been reported for the simpler models considered here. Taylor and Herzfeld [2,18]

---

[a] *Permanent address*: Grupo Interdisciplinar de Sistemas Aplicados, Departamento de Matemáticas, Universidad Carlos III, Avda. de la Universidad 30, 28911 Leganés, Madrid, Spain. e-mail: `cuesta@math.uc3m.es`

[b] *Present address*: Department of Physics, University of Surrey, Guildford, Surrey GU2 5XH, U.K. e-mail: `R.Sear@surrey.ac.uk`

mention phase behaviour for this model similar to that which we have found. They apparently considered it as a pathological feature of the model and so added a soft repulsion to the interaction between the micelles. This additional repulsion qualitatively changes the phase behaviour. We will compare results in Section 6.

A natural question to ask is: what effect do the many simplifications of our model have? Choosing a cuboidal shape changes little apart from the symmetry of the ordered phases, *e.g.*, cubes form a simple cubic lattice while spheres form a face centered cubic lattice. Real micelles can, of course, rotate, whereas our model micelles cannot. The phase diagram of rotating micelles differs from the phase diagrams we obtain, see references [2,20,22], for example there is an isotropic–nematic transition for not too weak aggregation. However, the new degrees of freedom do not change the fact that interactions couple to micellar growth. By choosing perfectly aligned particles we simply focus on the simplest possible scenario, *i.e.*, that of a nematic undergoing interaction-driven aggregation. Finally, both flexibility and an added soft repulsion add an additional extensive contribution to the excess free energy [20–22]. We will find that the ordered phase is close-packed; this is a due to a combination of the rigidity of and hard-core interactions between the micelles. It disappears in the presence of soft repulsions, see references [2,18,19]. However the collapse of the system to close packing was considered a pathology of the hard-core interaction. [2,18,19] We will show in this work that the collapse can be dealt with as a phase transition in which a nematic and a close-packed phase coexist.

By restricting our micelles to aggregate into rods *or* into discs we are considering two rather extreme models. Most surfactants can form both, although some form only rods [8] or discs [9]. The competition between rod- and disc-like micelles in high density surfactant solutions is left for future work. There are also surfactants that form very long, wormlike, micelles even at low densities. This work is not very relevant to these surfactants because the formation of the long micelles is driven not by intermicellar interactions but by the surfactants preference for cylindrical over spherical micelles. Wormlike micelles have been extensively studied theoretically; see references [21,23] and references therein. These long micelles form nematic and columnar phases but as they are long even in the isotropic phase, the coupling between the phase and micellar growth is relatively weak [21,22].

The paper is divided into seven sections. Section 2 reviews the theory of aggregation into rod-like and disc-like micelles in the absence of interactions. Section 3 derives, from fundamental measure theory, the excess free energy of mixtures of aligned rods of different lengths, and of mixtures of aligned square discs with sides of different lengths. Sections 4 and 5 are devoted to the fluid and solid phases, respectively, of micelles. Section 4 uses the excess free energy of a fluid mixture derived in Section 3, and Section 5 uses a cell theory to estimate the excess free energy of the solid phase. We present the phase behaviour in Section 6 and we discuss it in the last section, Section 7.

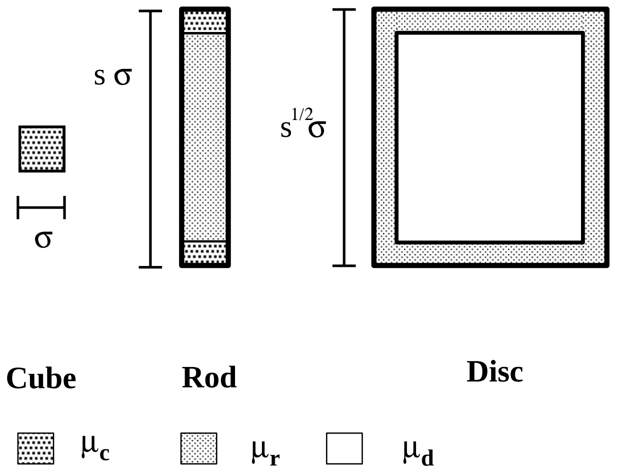

Fig. 1. A schematic of our cuboid model micelles; the rod and disc are shown in side and top views, respectively. On the left is the minimum size of micelle allowed: a cube with sides of length σ. In the center is a rod-like micelle which has a square cross-section of area σ^2 and a length $s\sigma$. On the right is a square disc-like micelle with thickness σ and two sides of length $s^{1/2}\sigma$. We have shaded the different regions of the micelles differently. The three different regions are end, edge and surface regions, with free energies per unit volume of $\mu_c k_B T/\sigma^3$, $\mu_r k_B T/\sigma^3$ and $\mu_d k_B T/\sigma^3$, respectively.

2 Ideal micelles

We will always assume that we are well above the critical micellar concentration and so all the surfactant molecules are part of micelles. Note that we use the term micelle not just for spherical micelles but also for rod-like and disc-like micelles. At low density the high translational entropy means that small cubic micelles are formed, but at high density interactions push the micelles together as the interaction part of the free energy is smaller for a small number of large aggregates than a large number of small aggregates. But even the smallest, cubic, micelles are composed of many surfactant molecules and so we will describe the size of a micelle by a continuous variable s, which is proportional to the volume, and hence the number of surfactant molecules, of the micelle [23,24]. Here, we consider two different types of growth of the micelles: growth into rod-like micelles and growth into disc-like micelles. Cubic, rod-like and disc-like micelles are shown in Figure 1. For simplicity we do not allow the simultaneous formation of rod-like and disc-like micelles.

2.1 Rod-like micelles

First, we consider a surfactant that forms rod-like micelles. The rods have a a constant cross-section of σ^2 and so the number of surfactant molecules and the volume of a micelle is proportional to its length. The length of a micelle is specified by an index s, where s is proportional to the length of a micelle and equal to 1 for a micelle which has a length equal to σ. The number density of micelles of length s is $\rho(s)/\sigma^3$. Thus, $\rho(s)$ is a reduced, dimensionless, number density. The number of surfactant molecules in a micelle is equal to s times the number in the smallest possible, cubic, micelles. Therefore, at fixed total concentration of surfactant

$$\int_1^\infty \rho(s) s ds = \eta, \tag{1}$$

where η is the volume fraction of surfactant. Setting the lower limit of the integration in equation (1) to 1 corresponds to imposing a minimum volume that a micelle can have; this minimum volume is that of the cube of Figure 1.

We start from an assumed form of the free energy of an isolated micelle. We assume that this free energy has three parts: the translational free energy of a molecule of an ideal gas, a part which is extensive, *i.e.*, proportional to s, and a part due to the ends of the micelle, which is independent of s. This is illustrated by Figure 1. The motivation for this form of the free energy is the idea that the environment of a surfactant molecule and hence the excess part of its chemical potential is different in the end of a micelle, where the surface of the micelle forms a hemisphere, and in the main body of the micelle, where the surface of the micelle is cylindrical [1,24]. The two ends of a micelle have a total volume of σ^3, see Figure 1. Note that our cuboid micelles do not have spherical or cylindrical parts. We merely refer to them as such in order to compare with theories for the driving force for the formation of micelles of different shapes. See references [1,24] for a discussion of the reasons why surfactants prefer to lie in a specific geometry such as planar, spherical, *etc.* Treating micelles of different lengths as different components in an ideal mixture [23,25] we have, for the Helmholtz free energy A,

$$\frac{\beta A \sigma^3}{V} = \int_1^\infty \rho(s) \left[\ln \rho(s) - 1 + \mu_c + (s-1)\mu_r \right] ds, \tag{2}$$

where V is the volume, $\beta = 1/k_BT$, k_B is Boltzmann's constant and T is the temperature. Equation (2) omits the contribution to the free energy of the integrals over the momenta of the surfactant molecules. As this contribution is a function only of temperature it has no effect on the phase behaviour. $\mu_c k_BT/\sigma^3$ and $\mu_r k_BT/\sigma^3$ are the internal free energies per unit volume of a rod-like micelle, in the end and middle regions, respectively. By internal free energy we mean the free energy minus that part due to the translational degrees of freedom of a micelle's centre of mass. The first two terms of equation (2) are the translational part.

The surfactant is free to form any distribution of sizes of micelles and so it forms the distribution which minimises the Helmholtz free energy at constant surfactant density η. So, we take a variation of equation (2), impose the constraint of equation (1), and equate to zero [22,23]

$$\ln \rho(s) + \mu_c - \mu_r + s\mu_r + s\lambda' = 0, \tag{3}$$

where λ' is a Lagrange multiplier. The last two terms on the left hand side of equation (3) may be combined, yielding λs, where λ is a new Lagrange multiplier. Physically, this means that the absolute value of μ_r does not affect the behaviour, only the difference $\mu_c - \mu_r = E_r$ does. The difference E_r is often referred to as the end-cap energy [22,23] and is the change in internal free energy when a rod-like micelle is broken into two. Rearranging equation (3)

$$\rho(s) = \exp\left(-E_r - \lambda s\right), \tag{4}$$

the number of micelles with size s deceases exponentially with s.

The free energy of the micelles may now be found by substituting equation (4) into equation (2). If we define an intensive Helmholtz free energy a which is proportional to the free energy per surfactant molecule, we have

$$a = \frac{\beta A \sigma^3}{\eta V} = -\lambda - \frac{\rho}{\eta} + \mu_r, \tag{5}$$

where ρ is the total number density of micelles, *i.e.*, the zeroth moment of $\rho(s)$. The last term is a constant and thus irrelevant. We will neglect it from now on. The number of aggregates, ρ, can be readily obtained to be $\rho = \eta\lambda/(1+\lambda)$. Then equation (5) may be written in terms of just λ as

$$a = -\lambda \left(\frac{2+\lambda}{1+\lambda} \right). \tag{6}$$

The average length $S = \eta/\rho$, and so in terms of λ it is

$$S = \frac{1+\lambda}{\lambda}. \tag{7}$$

The micelles are ideal and so the pressure p is just proportional to the number density of micelles. Then the reduced pressure $\beta p \sigma^3 = \rho$. We can also define a reduced intensive Gibbs free energy $g = \beta G/(\eta V)$ where G is the Gibbs free energy; g is proportional to the surfactant's chemical potential. Using equation (5) and $\beta p \sigma^3 = \rho$, g is given by

$$g = -\lambda. \tag{8}$$

We can determine the Lagrange multiplier λ by substituting equation (4) into equation (1)

$$\eta = e^{-E_r - \lambda} \left(\frac{1}{\lambda} + \frac{1}{\lambda^2} \right). \tag{9}$$

If λ is small, which corresponds to the average length of the micelles being large, the λ dependence of the right hand side of equation (9) simplifies to λ^{-2}. Then,

$$\lambda \simeq e^{-E_r/2} \eta^{-1/2}, \qquad \lambda \ll 1. \tag{10}$$

Also, in this limit $\rho \simeq \lambda\eta$ and so equation (6) for the free energy simplifies to

$$a \simeq -2\lambda, \qquad \lambda \ll 1. \tag{11}$$

From equation (10) we see that when λ is small it varies with density as $\eta^{-1/2}$ and therefore g, equation (8), is a monotonic function of density: there is no phase transition. It is also worth noting that as the micelles grow, g tends to zero.

2.2 Disc-like micelles

Now, we consider a surfactant that forms square disc-like micelles. We force them to be square for simplicity, although if the formation of a rim is unfavourable, *i.e.*, the surfactant molecules prefer to lie in a plane rather than in a cylinder, the discs will tend to be square rather than rectangular, as the ratio of volume to rim length is largest for squares. The discs have a constant thickness of σ and so the number of surfactant molecules in a micelle is proportional to its surface area. The area of a micelle is equal to $s\sigma^2$, and so the length of a side is $s^{1/2}\sigma$. With this definition of s and with the same restriction on the minimum size of a micelle as before, equation (1) still holds.

We now require the form of the free energy of an isolated micelle. A disc is considered to have two parts, see Figure 1, with different internal free energies [4]. There is the middle part, with a free energy per unit volume of $\mu_d k_B T/\sigma^3$, and a rim of width $\sigma/2$, with a free energy per unit volume of $\mu_r k_B T/\sigma^3$. This is motivated by the fact that along the sides of a real disc-like micelle its surface is cylindrical and away from the rim it is planar [1,24]. The volume of the rim within $\sigma/2$ of the edge is $(2s^{1/2}-1)\sigma^3$ and so increases with s as $s^{1/2}$.

Treating micelles of different lengths as different components in an ideal mixture we have [1,24,25],

$$\frac{\beta A\sigma^3}{V} = \int_1^\infty \rho(s)\left[\ln\rho(s) - 1 \right. \\ \left. +(2s^{1/2}-1)\mu_r + (s^{1/2}-1)^2\mu_d\right] ds, \qquad (12)$$

where $\mu_d k_B T/\sigma^3$ and $\mu_r k_B T/\sigma^3$ are the internal free energies per unit volume of micelle, in the rim and middle regions, respectively. Equation (2) omits the contribution to the free energy of the integrals over the momenta of the surfactant molecules.

Again we minimise the Helmholtz free energy at constant η. Taking the variation of equation (12) with respect to $\rho(s)$, imposing the constraint of equation (1), and equating to zero yields

$$\ln\rho(s) + (2s^{1/2}-1)(\mu_r-\mu_d) + s\lambda = 0, \qquad (13)$$

where we have included a factor of μ_d in the Lagrange multiplier λ. Only the difference $\mu_r - \mu_d = E_d/2$ affects the behaviour of the micelles. The free energy change on splitting a disc of size s into two discs of half the size is $2(\sqrt{2}-1)s^{1/2}-1$ and so increases with s. This is different from rod-like micelles, the free energy change of splitting a rod is independent of the rod's length. As before we have only one relevant parameter. Rearranging equation (13)

$$\rho(s) = \exp\left[-E_d(s^{1/2}-1/2) - \lambda s\right], \qquad (14)$$

which is the equivalent for disc-like micelles to equation (4) for rod-like micelles. For discs the exponential contains a term in $s^{1/2}$ as well as a linear term [1,24]. The free energy of the micelles may now be found by substituting equation (14) into equation (12). This results in an equation identical to equation (5) except for the replacement of μ_r with μ_d. We neglect the μ_d term from now on. As our system is ideal the pressure is again equal to ρ, and so the Gibbs free energy is again given by equation (8). The average size S is again given by $S = \eta/\rho$.

Substituting equation (14) into equation (1) yields an equation for λ

$$\eta = e^{E_d/2}\int_1^\infty \exp\left[-E_d s^{1/2} - \lambda s\right] s ds, \qquad (15)$$

which can be solved numerically for λ. However, equation (15) does not possess solutions for all values of η and E_d. For the integral to be finite we require $\lambda \geq 0$, only then does the integrand tend to zero as s tends to infinity. But if $E_d > 0$ the integrand decays with s even if $\lambda = 0$ and this imposes a limit on the value of the right hand side of equation (15). Thus, for $E_d > 0$ there is a maximum density η_{lim}, beyond which a phase of finite disc-like micelles is unstable. For any positive E_d as we increase η, λ decreases until at η_{lim} it becomes zero.

The behaviour of the surfactant above η_{lim} is difficult to determine. However, if we consider a finite system then a negative λ is allowed. Then, for a finite but large system with a negative λ we have $\rho(s)$ which is strongly peaked at values of s near the maximum possible on the finite system. If we then allow the finite system to become larger then the size of the micelles will grow with the system. This is consistent with the suggestion of Israelachvili *et al.* [24] that the surfactant forms infinitely large discs (in the thermodynamic limit). If we assume that the aggregates are infinitely large then the free energy per unit volume, equation (12), tends to $\eta\mu_d$. As we let the size of the micelles go to infinity, the density $\rho \to 0$ and so the ideal mixing part of the free energy (12) becomes zero. Of the internal parts of the free energy only the part proportional to s survives. The Gibbs free energy g tends to μ_d and the pressure to zero. As all three are independent of density it seems that the density of a phase of infinitely large discs is undetermined. We will see later that the presence of interactions between the discs removes this problem.

3 Interaction free energy of mixtures

One of the nice properties of this simplified model is that the contribution to the free energy of the hard core interactions between aggregates can be included using the recently proposed *fundamental measure* free energy functional for an arbitrary mixture of parallel hard parallelepipeds. In brief, fundamental measure theory [13] is a scaled-particle-like theory for inhomogeneous mixtures of hard convex fluids. To date it has only been developed for hard spheres [13,14] and parallel hard parallelepipeds [11,12]. The theory is rather involved and so we cannot give a full account of the details. For this purpose the reader is referred to references [11,12]. Nevertheless the final result of the theory can be summarized in an extraordinarily simple principle, namely that the excess Helmholtz free energy per unit volume of a mixture of hard parallelepipeds, $\Phi^{ex} \equiv \beta A^{ex}/V$, can be readily derived from that of a 0-dimensional equivalent system (a cavity which can hold one particle at most), which can be written as

$$\Phi_0^{ex} \equiv \beta A^{ex,0D} = n_3 + (1 - n_3)\ln(1 - n_3), \tag{16}$$

where n_3 is defined as

$$n_3 = \sum_i \rho_i \sigma_i^x \sigma_i^y \sigma_i^z. \tag{17}$$

In this definition, ρ_i stands for the density of the ith component of the mixture, and σ_i^α, $\alpha = x, y, z$, labels the α-axis edge length for that particular component. Then the excess free energy per unit volume is given by

$$\Phi^{ex} \equiv \beta A^{ex}/V = D_x D_y D_z \Phi_0^{ex}, \tag{18}$$

where D_α denotes the differential operator

$$D_\alpha \equiv \sum_i \frac{\partial}{\partial \sigma_i^\alpha}\cdot \tag{19}$$

Obtaining the final expression is straightforward by using the simple operational rules

$$\begin{aligned} D_\alpha n_3 &= n_2^\alpha, \\ D_\alpha n_2^\beta &= \tau_{\alpha\beta\gamma} n_1^\gamma, \\ D_\alpha n_1^\beta &= \delta_{\alpha\beta} n_0, \end{aligned}$$

where $n_0 \equiv \sum_i \rho_i$ and n_k^α ($k = 1, 2,\ \alpha = x, y, z$) denotes the components of the vectors

$$\mathbf{n}_2 \equiv \sum_i \rho_i(\sigma_i^y\sigma_i^z, \sigma_i^x\sigma_i^z, \sigma_i^x\sigma_i^y), \tag{20}$$

$$\mathbf{n}_1 \equiv \sum_i \rho_i(\sigma_i^x, \sigma_i^y, \sigma_i^z), \tag{21}$$

$\tau_{\alpha\beta\gamma}$ is a 3-rank tensor which equals 1 if all the three indices are different and 0 otherwise, and finally $\delta_{\alpha\beta}$ is the Kronecker symbol.

In terms of the above definitions Φ^{ex} can be expressed as

$$\Phi^{ex} = -n_0\ln(1 - n_3) + \frac{\mathbf{n}_1\cdot\mathbf{n}_2}{1 - n_3} + \frac{n_2^x n_2^y n_2^z}{(1 - n_3)^2}\cdot \tag{22}$$

The pressure is also easily derived from this expression [12] by taking the derivative with respect to n_3. It is then given by

$$\beta p = \frac{n_0}{1 - n_3} + \frac{\mathbf{n}_1\cdot\mathbf{n}_2}{(1 - n_3)^2} + \frac{2n_2^x n_2^y n_2^z}{(1 - n_3)^3}\cdot \tag{23}$$

If we are to deal with a mixture with a continuous distribution $\rho(s)$ of components, as in the present case, ρ_i must be replaced by $\rho(s)$ and the corresponding sum over components by an integral over s.

Equation (22) has already been used to describe this system [17]. It was derived using the $y3$ expansion [15,16]. Simply, this involves expressing the equation of state as a cubic polynomial in the variable $y = n_3/(1-n_3)$. The coefficients of the polynomial are then found by requiring that that the virial expansion of the equation of state is exact up to third order in n_3. Scaled particle theory also yields a $y3$-expansion [15,18,26], but the exactness up to third order in n_3 is not guaranteed. The $y3$-expansion has already been used to study orientational order in a mixture of parallelepipeds aligned along the three coordinate axes [17]. In the scaled particle version it has also been employed to study models of aggregating cubes and parallelepipeds interacting *via* a hard core plus a soft repulsive potential [2,18,26]. In both cases obtaining Φ^{ex} requires cumbersome calculations of virial coefficients [16,26]. The fundamental measure formalism is far simpler because it avoids the direct evaluation of those coefficients. It has another advantage: it can be easily generalised to include inhomogeneous phases at the same level of accuracy [11,12]. The study of inhomogeneous phases, however, is left for future research.

Let us now apply this general form to the two systems we want to describe.

3.1 Rods

In the case of rods the edge lengths are $\sigma_s^x = \sigma$, $\sigma_s^y = \sigma$, $\sigma_s^z = \sigma s$; therefore, according to the definitions introduced in Section 2,

$$\begin{aligned} n_3 &= \sigma^3\eta, \\ \mathbf{n}_2 &= \sigma^2(\eta, \eta, \rho), \\ \mathbf{n}_1 &= \sigma(\rho, \rho, \eta), \\ n_0 &= \rho. \end{aligned} \tag{24}$$

Then

$$\sigma^3\Phi^{ex} = \rho\psi(\eta), \tag{25}$$

where

$$\psi(\eta) \equiv -\ln(1 - \eta) + 3\frac{\eta}{1 - \eta} + \left(\frac{\eta}{1 - \eta}\right)^2, \tag{26}$$

and

$$\beta p\sigma^3 = \rho\frac{1 + \eta}{(1 - \eta)^3}\cdot \tag{27}$$

3.2 Discs

In this case the edge lengths are $\sigma_s^x = \sigma s^{1/2}$, $\sigma_s^y = \sigma s^{1/2}$, $\sigma_s^z = \sigma$, which leads to

$$\begin{aligned} n_3 &= \sigma^3\eta, \\ \mathbf{n}_2 &= \sigma^2(\xi, \xi, \eta), \\ \mathbf{n}_1 &= \sigma(\xi, \xi, \rho), \\ n_0 &= \rho, \end{aligned} \tag{28}$$

where we have introduced the average edge length of the discs, defined by

$$\xi \equiv \int_1^\infty \rho(s) s^{1/2} ds. \tag{29}$$

Now the excess free energy per unit volume is

$$\sigma^3 \Phi^{ex} = \rho\psi(\eta) + \xi^2 \zeta(\eta), \tag{30}$$

where

$$\psi(\eta) \equiv -\ln(1-\eta) + \frac{\eta}{1-\eta}, \quad \zeta(\eta) \equiv \frac{2-\eta}{(1-\eta)^2}, \tag{31}$$

and the pressure

$$\beta p \sigma^3 = \frac{\rho}{(1-\eta)^2} + \frac{2\xi^2}{(1-\eta)^3} \cdot \tag{32}$$

4 Micelles in the fluid phase

As in Section 2, to obtain the equilibrium density distribution $\rho(s)$ we have to minimise the full free energy per unit volume with respect to the function $\rho(s)$, with the constraint of equation (1). As usual, let us consider the two cases separately.

4.1 Rods

The equation for $\rho(s)$ in this case turns out to be

$$\ln \rho(s) + E_r + \psi(\eta) + s\lambda = 0. \tag{33}$$

Thus

$$\rho(s) = \exp(-E_r - \psi(\eta) - \lambda s). \tag{34}$$

The parameter λ is determined by imposing (1), which in this case amounts to solving the equation

$$e^{-\lambda}\left(\frac{1}{\lambda} + \frac{1}{\lambda^2}\right) = \eta\, e^{E_r + \psi(\eta)}. \tag{35}$$

Equations (34, 35) are similar to (4, 9) if we replace E_r by $E_r + \psi(\eta)$; the excess free energy per rod ψ acts as an additional end-cap energy. As we can see from (26), $\psi(\eta)$ is always positive and grows quickly to infinity as η approaches unity. The effect of the interactions manifests itself very clearly, breaking a rod into pieces increases the number of rods and from equation (25) the excess free energy Φ^{ex} is proportional to the number of rods. So, at high concentrations of surfactant where the excess free energy per rod is large the excess free energy cost of breaking a rod is large. This mechanism enhances the aggregation process dramatically, and as we will show in the next section, it eventually yields a phase transition which is missing in the ideal system. Notice in passing that at sufficiently high density, the interactions always dominate, regardless of the value of E_r. So, even if the dilute surfactant forms only compact aggregates, as the concentration rises the interaction forces the formation of large micelles.

Once we have determined λ, and therefore $\rho(s)$, we can determine the full free energy. In terms of λ it is given by the same equation as for ideal micelles, equation (6) and in the $\lambda \ll 1$ limit equation (11).

4.2 Discs

For discs the minimisation of the full free energy leads to

$$\ln \rho(s) + [E_d + 2\xi\zeta(\eta)]s^{1/2} + \psi(\eta) - \frac{E_d}{2} + s\lambda = 0. \tag{36}$$

We can introduce the shorthands $\overline{\psi} \equiv \psi(\eta) - E_d/2$ and $F \equiv E_d + 2\xi\zeta(\eta)$ and then write down the density distribution as

$$\rho(s) = \exp\left(-\overline{\psi} - F s^{1/2} - \lambda s\right). \tag{37}$$

The equations which now determine λ are

$$e^{\overline{\psi}}\eta = e^{-F-\lambda}\left\{\frac{1}{\lambda} - \frac{F}{2\lambda^2} + [F^2 + 4\lambda - F(F^2+6\lambda)\Delta]\frac{1}{4\lambda^3}\right\}, \tag{38}$$

$$e^{\overline{\psi}}\xi = e^{-F-\lambda}\left\{\frac{1}{\lambda} - [F - (F^2+2\lambda)\Delta]\frac{1}{2\lambda^2}\right\}, \tag{39}$$

where

$$\Delta \equiv \sqrt{\frac{\pi}{4\lambda}} e^{\gamma^2} \operatorname{erfc}\gamma, \quad \gamma \equiv \frac{F+2\lambda}{2\sqrt{\lambda}} \cdot \tag{40}$$

The equation for ρ is now

$$e^{\overline{\psi}}\rho = e^{-F-\lambda}\frac{1}{\lambda}(1 - F\Delta). \tag{41}$$

Equations (38, 39) can be used simultaneously to determine the value of λ for every value of η and E_d (notice that ξ can be eliminated in terms of F to leave only two unknowns). Once we have λ the full free energy per unit volume is given by

$$\Phi = -\rho - \lambda\eta - \xi^2\zeta(\eta). \tag{42}$$

5 Micelles at high density

We examine the free energy of rod-like micelles at high density and find that it is a nonconvex function of $v = \eta^{-1}$ and so the micelles cannot form a stable high density phase at a density less than close packing. Strong coupling between micellar growth and the excess part of the free energy causes the micelles to collapse to a phase of infinitely long rodlike micelles at close packing. This is shown in detail for rod-like micelles, as it is possible to derive the density dependence of a analytically. For disc-like micelles the situation is not as clear. For E_d not too small the solid phase cannot be stable purely due to the ideal part of the interactions, as we saw in Section 2. It seems highly likely that intermicellar interactions act to destabilise dense phases of small discs but a negative enough E_d will overwhelm this tendency and stabilise such a dense phase. We are unable to estimate how negative E_d must be in order for an ordered phase of small discs to be stable.

5.1 Rod-like micelles

At high density the micelles presumably form a columnar phase. Polydispersity in the length of the micelles hinders the formation of long range order along the z-axis [27–30]. The micelles form columns parallel to the z-axis, which pack into a square lattice. Due to their polydispersity, there is only long range order perpendicular to the columns. Along a column the successive micelles will be of different lengths and different columns will have micelles of different lengths, and so the z coordinate of the centres of mass of the micelles will not be correlated along the columns. We restrict ourselves to deriving just the density dependence of ψ of the columnar phase as the free energy for the micelles we will find is concave not convex and so does not correspond to a stable phase [31]. Thus, the result of this section is that the micelles are unstable near close packing. Away from close packing a columnar or solid phase is possible if the coupling between growth and the excess free energy is suppressed by a large negative E_r. We estimate that the columnar phase is unstable at densities below close packing for $E_r \gtrsim -4$.

In order to examine dense rod-like micelles we require the excess free energy of a mixture of parallel hard rods in the columnar phase. We are considering a 2-dimensional solid packing (in the xy-plane) of 1-dimensional fluids (the columnar phase is liquid-like along the z-axis), so the excess free energy per particle has two contributions, one which will be estimated by 2D cell theory, and a second one which is the free energy of a 1D fluid. A cell theory is a simple theory of a solid phase, which is particularly accurate near close packing. Cell theories work on the assumption that each micelle is in a cage (here a 2-dimensional cage) formed by the surrounding micelles and the only motion available to it is "rattling" in the cage formed by these neighbours [32,33]. They have been shown to be rather accurate for hard spheres [34].

The area in the xy-plane available to the centre of mass of a micelle is its 2-dimensional free "volume" v_f. Within cell theory, the contribution to the excess free energy ψ from motion in the xy-plane is $\psi = -\ln(v_f/v_{2D})$, where $\eta_{\rm 2D} \equiv v_{\rm 2D}^{-1}$ is the area fraction occupied by the micelles (in any xy-plane), which is equal to the free volume in the absence of interactions. In its simplest form [32,33] the free volume is just

$$v_f \sim (v_{\rm 2D}^{1/2} - v_{cp,\rm 2D}^{1/2})^2\sigma^2, \qquad (43)$$

where $v_{cp,\rm 2D} = \eta_{cp,\rm 2D}^{-1} = 1$. This form may be derived for a solid of hard squares by considering a (square) solid with lattice constant $l = \sigma v_{\rm 2D}^{1/2}$. The distance a cube can move in any direction is then $\sim l - \sigma = (v_{\rm 2D}^{1/2} - 1)\sigma$ and so the cube may move in the area v_f of equation (43).

As to the 1-dimensional fluid contribution to the excess free energy ψ, it is simply given by [35] $-\ln(1-\eta_{\rm 1D})$, where $\eta_{\rm 1D}$ is the length fraction occupied by the micelles within one column. Notice that $\eta_{\rm 2D}\eta_{\rm 1D} = \eta$, the volume fraction or reduced amount of surfactant per unit volume (the unit volume is that of a cubic micelle).

The excess free energy per micelle $\psi \sim -2\ln(1-\eta_{\rm 2D}^{1/2}) - \ln(1-\eta_{\rm 1D})$, so we can obtain the equilibrium densities $\eta_{\rm 2D}$ and $\eta_{\rm 1D}$ by minimising ψ with respect to both while keeping $\eta_{\rm 2D}\eta_{\rm 1D} = \eta$ constant (notice that the ideal free energy only depends on η). The result is simply $\eta_{\rm 2D}^{1/2} = \eta_{\rm 1D} = \eta^{1/3}$, and therefore

$$\psi \sim -3\ln(1-\eta^{1/3}) = -3\ln(1-v^{-1/3}), \qquad (44)$$

where v is the reduced volume per unit amount of surfactant. We can now consider a columnar phase of rod-like micelles with the ψ of equation (44). As ψ will always be large we expect λ to be very small and so, from equation (11),

$$a \simeq -2\lambda \sim -2\frac{\left(1-v^{-1/3}\right)^{3/2}}{e^{E_r/2}}, \quad \lambda \ll 1. \qquad (45)$$

(This same derivation has already been used to account for the columnar phase of a similar aggregation model [18].) Remarkably, the free energy of equation (45) is a concave not a convex function of volume. The free energy of hard particles diverges as the volume fraction approaches close packing. Here the excess free energy per micelle, equation (44), diverges but the number density of micelles tends to 0 more rapidly and so the free energy tends to 0 not infinity. As the Helmholtz free energy is not a convex function of volume the columnar phase is not stable at densities below close packing [31].

The above all holds provided that aggregation is not too strongly suppressed. ψ is quite large in the solid phase, even at a volume fraction of 0.5, $\psi = 4.73$, equation (44). As ψ tends to encourage aggregation there will be significant aggregation in the columnar phase even if $E_r = 0$. However, in the $E_r \to -\infty$ limit our micelles cannot aggregate and we are left with a fluid of hard cubes. A fluid of parallel hard cubes is known to freeze at relatively low packing fractions. Fundamental measure theory predicts a second order freezing at [11,12] $\eta \approx 0.3$, and simulations [36,37] are compatible with a second order freezing at $\eta \approx 0.5$. Polydispersity will shift this transition up in density a little; anyway if E_r is negative enough the coexisting phase will not be close-packed. When we calculate the phase diagram of our micelles we will assume that the solid is close packed which is incorrect for E_r negative and large. We have estimated how negative an E_r is required to see a columnar or solid phase with a density less than 1 by performing calculations without the assumption that $\lambda \ll 1$. The curve of a as a function of v develops a convex part as E_r is made less than approximately -4. Thus, we expect a non-close packed dense phase to appear near this value of E_r.

5.2 Disc-like micelles

Estimating the stability of a solid or liquid crystalline phase for disc-like micelles is more difficult than for rod-like micelles. The equations for λ, equations (38, 39), are more complicated and it is difficult to estimate the contribution of the excess free energy to the free energy cost of splitting a disc into smaller ones. Within fundamental measure theory, this cost contains a part independent of the size of the disc and a part dependent on the length of the rim of the disc. We are unable to say whether this is also true in a solid or smectic phase. However, it seems highly likely that the change in the excess free energy on splitting a disc into smaller ones will be positive and will increase as the density increases. Therefore, if E_d is also positive then there is a density at which $\lambda = 0$ and then beyond this density a phase of small discs is not possible. Then there will be little or no region of stability for the solid phase. For negative E_d the situation is more delicate, if the E_d is sufficiently negative and the density sufficiently low, the contribution of the excess part of the free energy to the free energy change on splitting a disc may be outweighed by the negative free energy change from E_d. Then a solid or other ordered phase of small discs may be the equilibrium phase for a range of densities. We will only present results for $E_d \geq 0$, as we are not confident of the transition not being preempted for $E_d < 0$.

6 Phase behaviour

In a single component system the densities of a pair of coexisting phases are usually found by equating the pressures and chemical potentials in each phase. However, here one of the coexisting phases is at close packing, *i.e.*, at the maximum possible density. As this phase is at the limit of the accessible phase space, the derivative of the free energy with respect to the volume, which is the negative of the pressure, is not well defined. So, in order to determine the density of the fluid phase which coexists with the close packed phase we have to explicitly consider the thermodynamic requirement that the Helmholtz free energy of a fixed number of molecules be a convex function of volume [31]. In Figure 2 the Helmholtz free energy per unit amount of surfactant (over k_BT) a is plotted as a function of v, for rodlike micelles with $E_r = 0$. The situation for rods and discs at all values of E_r and E_d, respectively, is qualitatively the same; rodlike micelles with $E_r = 0$ merely provides a convenient example. The free energy as a function of volume must be convex and so it follows the solid curve for $v > v'$, see Figure 2, but follows the dashed line for $v_{cp} < v < v'$. For volumes between v_{cp} and v', two phases with densities v_{cp}^{-1} and v'^{-1} coexist. From Figure 2 we see that the following equation must be satisfied

$$a(v_{cp}) = a(v') + (v_{cp} - v')\left(\frac{\partial a}{\partial v}\right)_{v=v'}, \qquad (46)$$

where we have indicated the v but not the E_r dependence of a. Using $a(v_{cp}) = 0$, the reduced pressure $p = -\partial a/\partial v$, the Gibbs free energy per unit amount of surfactant $g = a + pv$, and $v_{cp} = 1$, equation (46) becomes

$$0 = g(v') - p(v') \qquad (47)$$

which is the equation for coexistence with the phase at close packing. At the density of the fluid phase which coexists with the close-packed phase the p and g curves cross. Now that we have an equation which can be solved to find coexistence, we can go on to determine the phase behaviour of our rodlike and disc-like micelles.

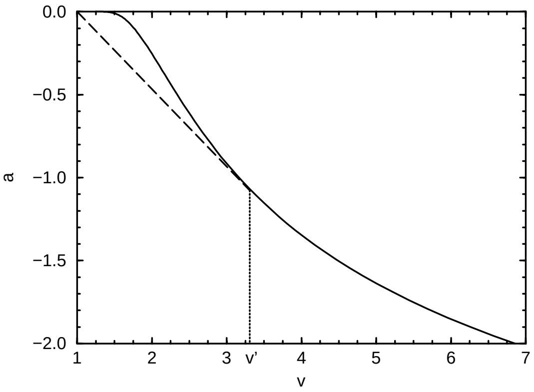

Fig. 2. The Helmholtz free energy per particle over k_BT, a, as a function of reduced volume per particle $v = \eta^{-1}$. The solid curve is obtained using the FMT expression for the excess free energy of a fluid phase mixture. The dashed line connects the two coexisting volumes. The free energy at equilibrium follows the dashed line from $v_{cp} = 1$ to v' and thereafter follows the solid curve. At v' the curve and the dashed line have the same tangent.

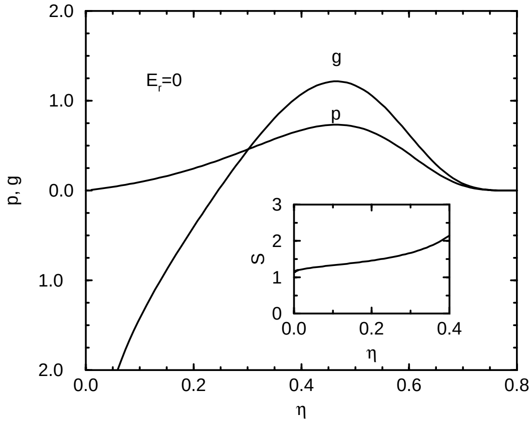

Fig. 3. The pressure p, and Gibbs free energy g, as a function of the density η, for rod-like micelles with an excess free energy derived from fundamental measure theory; $E_r = 0$. The density of the phase which coexists with the close packed phase is given by the crossing of the p and g curves. Higher densities lie within the coexistence region. The inset shows the average length of the micelles S as a function of density.

6.1 Rod-like micelles

The fluid phase of rod-like micelles is unstable at high densities: as shown in Figure 3 the pressure becomes a decreasing function of density which corresponds to a negative compressibility. In the previous section we saw that the columnar phase of the micelles appears to be unstable. This only leaves a transition to the maximum possible density, close packing. The pressure and fluid density at

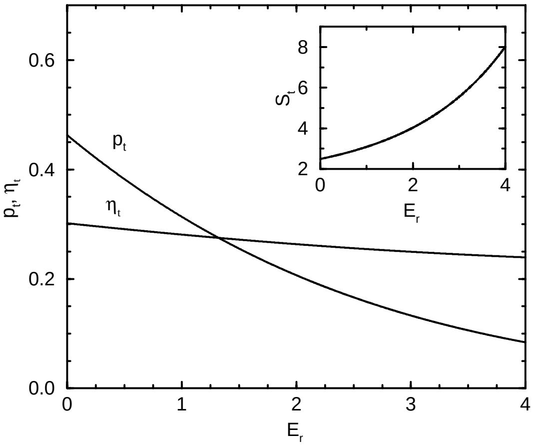

Fig. 4. The pressure p_t and density η_t at the transition from the fluid to the close packed phase, in rod-like micelles, as a function of E_r. The inset shows the length of the micelles at the transition S_t.

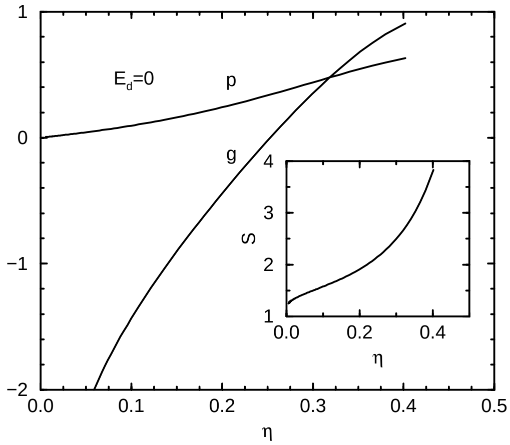

Fig. 5. The pressure p, and Gibbs free energy g, as a function of the density η, for disc-like micelles with an excess free energy derived from fundamental measure theory; $E_d = 0$. The density of the phase which coexists with the close packed phase is given by the crossing of the p and g curves. Higher densities lie within the coexistence region. The inset shows the average size of the micelles S as a function of density.

the transition from the fluid to the close-packed phase are plotted as a function of E_r in Figure 4. As expected, increasing E_r decreases both the pressure and density at the transition. The pressure decreases much faster than the density as the size of the micelles at the transition increases with increasing E_r. For large E_r the transition is from a low density fluid phase of long micelles.

The fluid–close-packed phase transition is only possible due to the aggregation, in nonaggregating systems the free energy diverges as close packing is approached and so a divergent pressure is required to achieve these densities. In contrast, at close packing the free energy of equation (45), $a \to 0$; as close packing is approached the excess free energy per micelle ψ diverges which drives the number density of micelles to zero sufficiently rapidly that the free energy per unit volume and hence a tend to zero.

As E_r is reduced both columnar and solid phases will appear: in the $E_r \to -\infty$ limit we recover hard cubes which form a solid phase and in Section 5 we found that for $E_r \lesssim -4$ the columnar phase was stable for a range of densities. Having determined in Section 5 that neither of these phases is stable when the aggregation is strong we do not consider them further. The addition of a soft repulsive core [2,18,19] suppresses the collapse to close packing, and there is then a region of densities for which the columnar phase is stable.

6.2 Disc-like micelles

The interactions between the disc-like micelles contribute to the free energy cost of splitting a micelle and so encourages growth of the micelles. This is seen for $E_d = 0$ in Figure 5. Also, if this cost becomes too great there are no solutions to equations (38, 39) for λ and the fluid phase cannot be stable. This is very similar to the case of ideal disc-like micelles but the free energy cost of splitting a micelle into smaller ones comes not from an internal rearrangement of the surfactant within the micelles but from intermicellar interactions. In Figure 5 the pressure and Gibbs free energy are plotted up to the point where $\lambda = 0$.

In Section 2 we were unable to determine the phase behaviour of noninteracting disc-like micelles for densities at which equation (15) did not possess a solution. Interactions resolve this problem: at the density which satisfies equation (47), which is always at a density at which equations (38, 39) can be solved, the fluid phase of small discs transforms to a close packed phase of infinitely large discs. It will do so unless an intermediate, ordered, phase is stable and of lower free energy. If E_d is large and positive this is not possible. However, if E_d is negative such a phase may well be present for reasons similar to those of the hard-rod case; thus we only show results for $E_d \geq 0$. In Figure 6 we show the pressure and density at the transition as a function of E_d. Increasing E_d decreases both the pressure and density at the transition, this is similar to the behaviour of rod-like micelles in Figure 4. However, the size of the disc-like micelles at the transition decreases as E_d increases. This is in contrast to the behaviour of rod-like micelles, where increasing E_r increases the size of the micelles at the transition. For large E_d the disc-like micelles are almost cubic at the low transition density. The disc-like micelles hardly grow at all before collapsing to form infinite discs.

The instability of finite discs has been known for some time [24] but to our knowledge this is the first themodynamically consistent description of the behaviour when the phase of finite discs becomes unstable. This transition from small micelles to infinite lamellae is common, see references [4,20]. Taylor and Herzfeld [2,18,19] studied disclike aggregates which in addition to their hard core had a soft repulsion. These formed a smectic phase of finite discs. The qualitative difference in behaviour is remarkable; it is not clear to us why there is this difference.

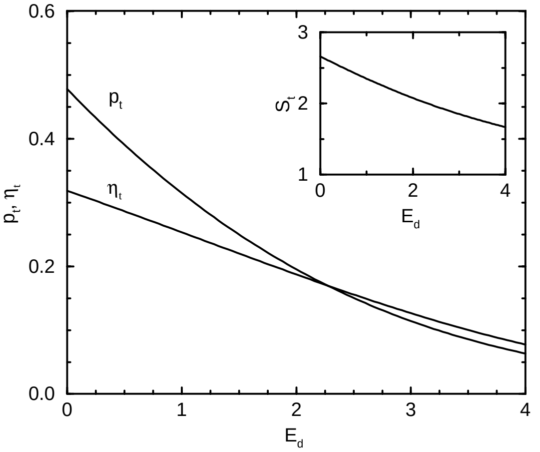

Fig. 6. The pressure p_t and density η_t at the transition from the fluid to the close packed phase, in disc-like micelles, as a function of E_d. The inset shows the size of the micelles at the transition S_t.

7 Discussion

We have studied a very simple model of aggregating hard particles. Hard particles which cannot aggregate have the general phase behaviour: a fluid phase for volume fractions less than 0.4–0.5 and for higher volume fractions a solid phase and/or translationally ordered liquid crystalline phases. If the phase transition from the fluid phase to an ordered phase is first order then the density jump is at most $\sim 10\%$. In the ordered phase the pressure rises steeply as the density is increased. In contrast our aggregating hard particles undergo a strongly first order transition from a relatively dilute fluid phase to a close-packed, ordered phase. This is true so long as aggregation is not suppressed by too negative an E_r or E_d. As the density of hard particles is increased their excess free energy increases, and indeed diverges as close packing is approached. Aggregation reduces the number of free particles and hence reduces the total excess free energy. Indeed at close packing the size of the particles diverges and this reduces the total excess free energy from infinity to zero.

Our two models were made as simple as possible in order to allow the clearest possible demonstration of an aggregation driven transition. Both types of micelles were modelled by rigid, perfectly aligned particles. This is clearly unrealistic, the models are nematic at all densities; there is no isotropic–nematic transition. If the micelles are allowed to rotate then there are two different scenarios. For large positive values of E_r and for E_d near 0, the micelles in the fluid phase are quite large before the transition to the close-packed phase. Then the fluid phase which coexists with the close-packed phase will be nematic. At lower densities there is an isotropic–nematic transition, which our model misses. The second scenario is for small E_r or large positive E_d, then the micelles are small and so the transition will be directly from the isotropic phase to the close packed phase.

The ordered phase is only close packed because our micelles are completely rigid. Flexibility introduces an additional term which is extensive in their length, for large micelles [38,39]. Therefore, aggregation does not reduce its contribution to the excess free energy. The contribution of flexibility to the free energy, diverges as close packing is approached and so flexible micelles form dense but not close packed ordered phases. As a consequence of the density being less than close packing, the length S of flexible rod-like micelles will never be infinite, although it may be very large [21]. The addition of a soft repulsive potential has a very similar effect [2,18]. In contrast, above their transition, disc-like micelles are always infinitely large, as the cost of breaking a disc into smaller ones scales with the size as $s^{1/2}$.

Even without interactions there is an upper limit, for $E_d > 0$, on the density of a phase of disc-like micelles. Above this density, equation (15) cannot be solved. However, without interactions it is not possible to determine what happens to the discs at densities for which equation (15) has no solutions. By incorporating interactions we have been able to show, for the first time for simple model micelles, the transition from finite micelles to a lamellar phase. This transition is typical for surfactants which form disclike aggregates. The effect of interactions is twofold: they impose an upper limit on the volume fraction, and without interactions the equation for coexistence, equation (47), can never be satisfied. The second role of interactions is unexpected, however low the density of the fluid phase at coexistence a contribution from the interactions is required to satisfy equation (47). In contrast, ideal rod-like micelles show no sign of a phase transition, equation (9) can be solved for any values of η and E_r. As the density increases, the micelles grow continuously. A transition is only found if the micelles interact, it is driven by a coupling between the average size of the micelles and the total excess free energy.

The phase diagrams of many surfactant solutions are known, see references [2,5,6,23]. At high volume fractions, $\sim$50%, surfactants typically form both columnar and lamellar phases and may also form other more complicated phases. However, by engineering of the surfactant either the lamellar [8] or the columnar phase [9] may be eliminated. References [8,9] are the experimental systems which are most like our rod- and disc-like micelles, respectively. Thus our simple model micelles reproduce some of the phenomenology of the phase behaviour of real micelles. In both our model micelles and in many real surfactant solutions the formation of large anisotropic micelles is driven by intermicellar interactions.

A closely related model is that of aggregating hard spheres, and the most common theory for them is the thermodynamic perturbation theory (TPT1) of Wertheim [40–44]. However, TPT1 does not predict a phase transition driven by coupling between interactions and aggregation. This is because it is a perturbation theory and implicitly assumes that a pair of aggregates of sizes n and m particles, interact *via* $n \times m$ particle–particle interactions [45]. TPT1 is rather accurate for flexible chains of hard spheres, as has been shown by extensive comparison with computer simulation [43,46]. However, the interaction between a pair of aligned rods is very different from a sum of the interactions between cubes, which couples the interactions with the aggregation and makes TPT1 a poor approximation.

It is a pleasure to acknowledge a careful reading of the manuscript by R. Blaak. JAC acknowledges the Dirección General de Enseñanza Superior (D.G.E.S.) for financial support by the travelling grant no. PR95–558 and the research project no. PB96–0119. RPS acknowledges The Royal Society for the award of a fellowship. We would like to thank the FOM institute AMOLF for its hospitality. The work of the FOM Institute is part of the research program of FOM and is made possible by financial support from the Netherlands Organisation for Scientific Research (NWO).

References

1. J.N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1992).
2. M.P. Taylor, J. Herzfeld, J. Phys.-Cond. **5**, 2651 (1993).
3. N. Boden, *et al.*, J. Chem. Phys. **103**, 5712 (1995).
4. Y. Bohbot, A. Ben-Shaul, R. Granek, W.M. Gelbart, J. Chem. Phys. **103**, 8764 (1995).
5. T. Odijk, Curr. Opinion Colloid Interface Sci. **1**, 337 (1996).
6. L. Cantù, M. Corti, E. Del Favero, A. Raudino, J. Phys.-Cond. **9**, 5033 (1997).
7. L. Sallen, P. Sotta, P. Oswald, J. Phys. Chem. B **101**, 4875 (1997).
8. N. Boden, R.J. Bushby, C. Hardy, F. Sixl, Chem. Phys. Lett. **123**, 359 (1986).
9. N. Boden, S.A. Corne, K.W. Jolley, J. Phys. Chem. **91** 4092 (1987).
10. J.A. Cuesta, Phys. Rev. Lett. **76**, 3742 (1996).
11. J.A. Cuesta, Y. Martínez-Ratón, Phys. Rev. Lett. **78**, 3681 (1997).
12. J.A. Cuesta, Y. Martínez-Ratón, J. Chem. Phys. in press.
13. Y. Rosenfeld, M. Schmidt, H. Löwen, P. Tarazona, J. Phys.-Cond. **8**, L577 (1996); Phys. Rev. E **55**, 4245 (1997).
14. P. Tarazona, Y. Rosenfeld, Phys. Rev. E **55**, R4873 (1997).
15. B. Barboy, W.M. Gelbart, J. Chem. Phys. **71**, 3053 (1979).
16. B. Barboy, W.M. Gelbart, J. Stat. Phys. **22**, 685 (1980); *ibid.*, **22**, 709 (1980).
17. B.G. Moore, W.E. McMullen, J. Phys. Chem. **96**, 3374 (1992); J. Chem. Phys. **97**, 9267 (1992).
18. M.P. Taylor, J. Herzfeld, Langmuir **6**, 911 (1990).
19. M.P. Taylor, J. Herzfeld, Phys. Rev. A **44**, 3742 (1991).
20. *Micelles, Membranes, Microemulsions and Monolayers*, edited by W.M. Gelbart, A. Ben-Shaul, D. Roux (Springer-Verlag, New York, 1994).
21. P. van der Schoot, J. Chem. Phys. **104**, 1130 (1995).
22. P. van der Schoot, M.E. Cates, Langmuir **10**, 670 (1994).
23. M.E. Cates, S.J. Candau, J. Phys.-Cond. **2**, 6869 (1990).
24. J.N. Israelachvili, D.J. Mitchel, B.W. Ninham, J. Chem. Soc. Faraday Trans II **72**, 1525 (1976).
25. K. Olaussen, G. Stell, J. Stat. Phys. **62**, 221 (1991).
26. R. Hentschke, J. Herzfeld, Phys. Rev. A **43**, 7019 (1991).
27. T.J. Sluckin, Liquid Crystals **6**, 111 (1989).
28. T. Koda, H. Kimura, J. Phys. Soc. Jpn **63**, 984 (1994).
29. S.-M. Cui, Z.Y. Chen, Phys. Rev. E **50**, 3747 (1994).
30. R.P. Sear, G. Jackson, J. Chem. Phys. **102**, 2622 (1995).
31. H.B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd ed. (John Wiley, New York, 1985).
32. T.L. Hill, *Introduction to Statistical Thermodynamics* (Addison-Wesley, Reading, Massachusetts, 1960).
33. R.J. Buehler, R.H. Wentorf, J.O. Hirschfelder, C. Curtiss, J. Chem. Phys. **19**, 61 (1951).
34. A.R. Denton, N.W. Ashcroft, W.A. Curtin, Phys. Rev. E **51**, 65 (1995).
35. J.K. Percus, J. Stat. Phys. **15**, 505 (1976).
36. F. van Swol, L.V. Woodcock, Mol. Sim. **1**, 95 (1987).
37. E.A. Jagla, Phys. Rev. E **58**, 4701 (1998).
38. W. Helfrich, Z. Naturforsch. **33a**, 305 (1978).
39. T. Odijk, Macromol. **19**, 2313 (1986).
40. E.A. Müller, K.E. Gubbins, *Equations of State for Fluids and Mixtures* edited by J.V. Sengers *et al.*, (Blackwell Scientific, 1996).
41. M.S. Wertheim, J. Stat. Phys. **42**, 459 (1986); *ibid.* **42**, 477 (1986).
42. Y. Zhou, G. Stell, J. Chem. Phys. **96**, 1504 (1992); *ibid.* **96**, 1507 (1992).
43. G. Jackson, W.G. Chapman, K.E. Gubbins, Mol. Phys. **65**, 1 (1988).
44. R.P. Sear, G. Jackson, *Proceedings of the International School of Physics "Enrico Fermi" Course CXXIX*, edited by M. Baus *et al.* (Kluwer, Dordrecht, 1995).
45. E. Kierlik, M.L. Rosinberg, J. Chem. Phys. **99**, 3950 (1993).
46. D. Ghonasgi, W.G. Chapman, Mol. Phys. **183**, 145 (1994).