

# Phase transition analogous to Bose-Einstein condensation in systems of noninteracting surfactant aggregates

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(Received 15 August 2001; published 27 February 2002)

Ideal bosons and a classical system of monomers that aggregate forming noninteracting ring polymers are known to have the same partition function. So, the ring polymers have a phase transition, the analogue of Bose-Einstein condensation of bosons. At this phase transition macroscopic polymers are formed. The link between these systems is made via Feynman's path integrals: these integrals are the same for the trajectories of the bosons in imaginary time and for the configurations of the polymers. We show that a transition of this general form occurs within a whole class of aggregating systems. Examples are the lamellae formation in suspensions of disclike micelles or the emulsification failure observed in water-oil-surfactant emulsions. As with bosons, the transition occurs even when aggregates do not interact. The  $\lambda$ -transition in  $^4\text{He}$  is believed to be Bose-Einstein condensation modified by interatomic interactions. We suggest that interaggregate interactions too only modify the transition we have found.

DOI: 10.1103/PhysRevE.65.031406

PACS number(s): 03.75.Fi, 82.70.Kj, 05.70.Fh

## I. INTRODUCTION

Bose-Einstein condensation (BEC) is a textbook [1,2], but rather unusual, phase transition. It occurs for noninteracting bosons, in contrast to more conventional transitions such as that of the Ising model, which are driven by interactions. Feynman [3] showed that the statistical mechanics of bosons can be performed via what he called path integrals. These integrals are, in turn, equivalent to integrals over the configurations of ring polymers. Thus, the path integral formalism of Feynman implies that noninteracting bosons and self-assembling, noninteracting ring polymers have partition functions of exactly the same form. Necessarily then, ring polymers must undergo a phase transition precisely analogous to BEC [4]. Here, we generalize this result to show that there is a class of self-assembling systems that undergo a phase transition analogous to BEC. This phase transition occurs in the absence of interactions between the aggregates formed by self-assembly. At BEC a condensate appears that is a macroscopic number of bosons in a single state. In the analogous transition in self-assembling systems, an aggregate of macroscopic size appears. This may be, for example, an infinite bilayer of surfactant or a bulk phase. The aggregates that coexist with the macroscopic aggregate have both a constant number density and a size distribution which decays more slowly than exponentially with their size. For example, within our simple model for a microemulsion, at coexistence with a bulk oil phase, the number density of droplets of size  $s$  decays as  $\exp(-s^{2/3})$ .

Self-assembling systems are systems in which the par-

ticles are not immutable objects but are formed reversibly [5,6]. Typically, we have a solution of surfactant with possibly a cosurfactant or oil. The surfactant molecules then spontaneously assemble into micelles, or coat and stabilize droplets of oil. Both the micelles and the droplets are what we term aggregates. For example, in a microemulsion, equilibrium is obtained when the oil is dispersed as a polydisperse distribution of oil droplets whose surfaces are coated with surfactant. These droplets are more stable than just a single bulk oil phase because with a single bulk phase there is no extensive oil-water interface, and the amphiphilic surfactant molecules have the lowest energy at this interface. The distribution of droplets changes with density and temperature, as varying either one changes the balance of the equilibrium between droplets of different sizes. A BEC-like transition occurs when the balance is shifted such that at equilibrium, some of the oil exists as an infinite droplet, a bulk phase. This transition is called emulsification failure [7].

Our predictions are for very simple models of what are quite complex experimental systems: they contain water, one or more surfactants (which are rather complex molecules), oil, possibly even a cosurfactant as well. However, if the aggregates formed have free energies that *scale* in certain ways (see Sec. III) then our prediction of a phase transition will be correct. In Sec. IV, we study three examples: disclike micelles, microemulsions, and wormlike micelles. It should be borne in mind that wormlike micelles only undergo a BEC-like phase transition in the limit that their end cap energy is infinite. Of course in experiment the energy will not be infinite and so the transition will be rounded off by the presence of chains. The other two systems do have phase transitions.

In this contribution we consider models of surfactant solutions, which have a BEC-like transition. Remarkably, a bewildering range of physical systems also have partition func-

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tions that are closely related to that of ideal bosons or ring polymers. The ordered phase of systems which are in the universality class of the  $XY$  model [8] in three dimensions, supports defect loops. This universality class is a class of systems that, when they order, break a  $U(1)$  symmetry [8]; examples are superfluid  $^4\text{He}$  [9,10], and a phase transition in the early universe [9–11]. The defect loops (called vortex loops in  $^4\text{He}$ ) are defects in the ordering that are rings in the sense that the defect is one dimensional and it is closed—no ends. If interactions between these defect loops are neglected, we have simply our system of noninteracting ring polymers. Within this picture the transition from the ordered phase to the disordered phase occurs when an infinite defect loop (in BEC language a condensate) forms. Defect loops have also been studied in a nematic phase [12], and their behavior is similar even though the symmetry of the nematic phase is different to that of an ordered  $XY$  model. So, the  $XY$  model in three dimensions and the nematic phase both have defects that can be described (within an approximation) as ideal ring polymers and therefore within this approximation, have a partition function of the same form as ideal bosons in three dimensions.

Percolation can be regarded as an aggregation phenomenon in which clusters of links or nodes (called “animals”) are formed. When looked at from this point of view, the percolation transition is of the BEC type [13], with the percolating cluster playing the role of the condensate (as a matter of fact, the percolation transition on the Bethe lattice is the same as that of ideal bosons in three dimensions [14]).

A surprising connection appears in some kinds of random networks [15,16]. These are systems out of equilibrium, but the analogy with BEC appears when studying the asymptotic distribution of links among nodes as time goes to infinity (long time plays the role of the thermodynamic limit in these systems). Under certain conditions one node takes a finite fraction of all the links, thus forming the analog to the condensate [15].

A final example is of models of the statistics of so-called baby universes [17,18], which arise in the study of quantum gravity.

As well as their use in modeling a diverse range of phenomena, free energies of the type we study in Sec. III are some of the simplest free energies to exhibit a phase transition. As such they have been employed as simple models in the study of the dynamics of phase transitions [19,20]. They are what Godrèche and Luck [20] call the monkey class of urn models, as it corresponds to the image of a monkey playing at exchanging balls between boxes.

This paper is organized as follows. We start, in the following section Sec. II, by studying BEC and ring polymers. First in Sec. II A, we present the basics of BEC in order to establish both the nature of the transition and some of the functions and notation that we will require later on. Then in Secs. II B and II C, we describe Feynman’s path integral approach and show that the partition function is identical in form to that of a model of ring polymers. In Sec. III, we will consider the free energy function for noninteracting aggregates. It has two parts: an internal free energy of an aggregate as a function of its size and a translational entropy term

that favors the formation of many aggregates to maximize this translational entropy; see Refs. [5,21–24] for examples of the use of free energies of this type. We will define what is required of the internal part of the free energy in order to observe a BEC-like phase transition, and show, in Sec. IV, a few examples of aggregating systems exhibiting this kind of transition. The last section is a conclusion.

Our results for our general model (Sec. III) and for microemulsions (Sec. IV B) have been published previously in a shorter form [25].

## II. BOSE-EINSTEIN CONDENSATION

### A. The standard approach

Let us summarize briefly the way BEC is derived in textbooks, for example [1,2]. This will enable us to establish both the required notation and to describe the essentials of the transition that lies at the heart of this paper, in order to stress the main points involved. Let us suppose we have a system of ideal (spinless) bosons distributed among an infinite, discrete set of energy levels. The grand canonical ensemble partition function  $\Xi$ , of bosons at a chemical potential  $\mu$ , and a temperature  $T$ , is

$$\ln \Xi = - \sum_{\epsilon} \ln(1 - z e^{-\beta\epsilon}), \quad (1)$$

where  $z = e^{\beta\mu}$  is the activity, with  $\beta = 1/kT$  ( $k$  is Boltzmann’s constant). From Eq. (1) it follows that  $0 < z < e^{\beta\epsilon_0}$ , where  $\epsilon_0$  is the ground-state energy, and that  $\ln \Xi$  diverges as  $z$  approaches the upper bound.

Our system is now assumed to be a  $d$ -dimensional cubic box of (hyper)volume  $V = L^d$ , with no external potential. By introducing periodic boundary conditions, the set of possible energy levels is given by

$$\beta\epsilon = \pi \frac{\Lambda^2}{L^2} |\mathbf{n}|^2, \quad \mathbf{n} \in \mathbb{Z}^d, \quad (2)$$

with  $\Lambda = h/\sqrt{2\pi mkT}$  the thermal wavelength, and so the ground-state energy  $\epsilon_0 = 0$ . When  $L \gg \Lambda$  we can transform the sum (1) into an integral and this yields

$$\ln \Xi = - \frac{1}{\Gamma(d/2)} \frac{V}{\Lambda^d} \int_0^\infty dx x^{d/2-1} \ln(1 - z e^{-x}). \quad (3)$$

Expanding in powers of  $z$  it follows

$$\ln \Xi = \frac{V}{\Lambda^d} G_{d/2+1}(z), \quad G_\mu(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^\mu}. \quad (4)$$

The average density is then given by

$$n = \frac{1}{\Lambda^d} G_{d/2}(z). \quad (5)$$

If  $d > 2$ , then both Eqs. (4) and (5) are convergent for  $z = 1$  ( $= e^{\beta\epsilon_0}$ ), while the original expression for  $\ln \Xi$ , Eq. (1)

diverged at this point. The reason for this is that the counting of levels for a given energy yielding the  $x^{d/2-1}$  factor in the integral (3), gives zero weight to the ground state, which is the cause of the divergence. We can get rid of this problem by separating out its contribution to  $\ln \Xi$ , i.e., by adding  $-\ln(1-z)$  to the expression for  $\ln \Xi$ , Eq. (4). Correspondingly, this adds the contribution  $V^{-1}z/(1-z)$  to the expression for  $n$ , Eq. (5), and we can realize that, given  $V$  large but finite, by choosing  $z$  sufficiently close to 1, the new contribution to  $n$  can be made arbitrarily large. The number of bosons in the ground state is then macroscopic, forming the so-called *condensate*. In the  $V \rightarrow \infty$  limit there is a phase transition, BEC. If  $n < n_c = \Lambda^{-d} G_{d/2}(1)$ , then  $\ln \Xi$  is given by Eq. (4) with the solution for  $z$  of Eq. (5) (the density in the ground state is 0), whereas if  $n > n_c$ , then  $\ln \Xi$  is a constant,  $\ln \Xi = V \Lambda^{-d} G_{d/2+1}(1)$ , and  $n - n_c$  is the density of bosons in the ground state.

We stress three points: first, the transition occurs when, on increasing  $z$ , the density of bosons in excited states Eq. (5) saturates; second, that at the transition a condensate appears that is a macroscopic population of bosons in a single state, and third, that in order to calculate the behavior at and beyond the transition, we needed to consider explicitly finite system sizes.

### B. Feynman's path integral approach

Feynman introduced an alternative approach to this problem [3] using the density matrix in the space representation. This involves mapping bosons onto ring polymers, and provides the link between low-temperature bosons and the classical systems we are interested in. We therefore sketch his derivation; for more details see Ref. [3]. For a set of  $N$  particles, the partition function is given by

$$Z_N = \text{tr } \hat{\rho}, \quad \hat{\rho} \equiv e^{-\beta H_N}, \quad (6)$$

with  $H_N$  the Hamiltonian operator. For noninteracting distinguishable particles  $\hat{\rho}_D(\{\mathbf{x}_i\}; \{\mathbf{x}'_i\}) = \hat{\rho}_1(\mathbf{x}_1; \mathbf{x}'_1) \cdots \hat{\rho}_1(\mathbf{x}_N; \mathbf{x}'_N)$  ( $\{\mathbf{x}_i\}$  denotes the set of coordinates  $\{\mathbf{x}_1, \dots, \mathbf{x}_N\}$ ). In the  $V \rightarrow \infty$  limit  $\hat{\rho}_1$  is a Gaussian

$$\hat{\rho}_1(\mathbf{x}; \mathbf{x}') = \frac{1}{\Lambda^d} \exp\left\{-\frac{\pi}{\Lambda^2}(\mathbf{x} - \mathbf{x}')^2\right\}. \quad (7)$$

Quantum particles are indistinguishable, so in the case of bosons, the trace in Eq. (6) has to be taken *only* over symmetric states. A symmetric density matrix  $\hat{\rho}$  can be obtained from that of distinguishable particles  $\hat{\rho}_D$  as

$$\hat{\rho}(\{\mathbf{x}_i\}; \{\mathbf{x}'_i\}) = \frac{1}{N!} \sum_{P \in \Pi_N} \hat{\rho}_D(\{\mathbf{x}_i\}; \{P\mathbf{x}'_i\}), \quad (8)$$

$\Pi_N$  being the set of permutations of  $N$  elements, and  $\{P\mathbf{x}'_i\}$  denoting the result of performing the permutation  $P$  on the set  $\{\mathbf{x}'_1, \dots, \mathbf{x}'_N\}$ .

Thus, the partition function for a system of  $N$  noninteracting bosons takes the form

$$\begin{aligned} Z_N &= \int_{V^N} d^N \mathbf{x} \hat{\rho}(\{\mathbf{x}_i\}; \{\mathbf{x}_i\}) \\ &= \frac{1}{N!} \sum_{P \in \Pi_N} \int_{V^N} d^N \mathbf{x} \prod_{i=1}^N \hat{\rho}_1(\mathbf{x}_i; P\mathbf{x}_i). \end{aligned} \quad (9)$$

Permutations can be split into cycles [26]; therefore, the integral above factorizes into terms of the form

$$h_n = \int_{V^n} d^n \mathbf{x} \hat{\rho}_1(\mathbf{x}_1; \mathbf{x}_2) \hat{\rho}_1(\mathbf{x}_2; \mathbf{x}_3) \cdots \hat{\rho}_1(\mathbf{x}_n; \mathbf{x}_1). \quad (10)$$

If there are  $C_n$  cycles of length  $n$  in a given permutation

$$\int_{V^N} d^N \mathbf{x} \prod_{i=1}^N \hat{\rho}_1(\mathbf{x}_i; P\mathbf{x}_i) = \prod_{n \geq 1} h_n^{C_n}.$$

There are  $N! / (\prod_{n \geq 1} C_n! n^{C_n})$  permutations in  $\Pi_N$  that split into  $C_n$  cycles of length  $n$  [3], hence

$$Z_N = \sum_{\sum_n n C_n = N} \prod_{n \geq 1} \frac{h_n^{C_n}}{C_n! n^{C_n}}. \quad (11)$$

As usual, we can get rid of the combinatoric constraints by using the grand partition function

$$\Xi = \sum_{N=0}^{\infty} z^N Z_N = \prod_{n \geq 1} \sum_{C_n=0}^{\infty} \frac{(h_n z^n / n)^{C_n}}{C_n!}, \quad (12)$$

from which we obtain

$$\ln \Xi = \sum_{n=1}^{\infty} \frac{h_n z^n}{n}. \quad (13)$$

There only remains the calculation of  $h_n$ . For that it is helpful to rewrite Eq. (10) as  $h_n = \text{tr } \hat{\rho}_1^n$ , which according to the definition (6), is nothing but  $Z_1$  computed at a temperature given by  $\beta' = n\beta$  (equivalently,  $\Lambda'^2 = n\Lambda^2$ ). If we—as Feynman [3]—use Eq. (7) for  $\hat{\rho}_1$ , we obtain  $h_n = (V/\Lambda^d) n^{-d/2}$ . Inserting this into Eq. (13), we recover Eq. (4); again we have not taken the condensate into account. The neglect lies in that Eq. (7) for  $\hat{\rho}_1$  is obtained *after* taking the thermodynamic limit. In order to overcome this deficiency, we are going to determine  $\hat{\rho}_1$  for a  $d$ -dimensional cubic box of side length  $L$  with periodic boundary conditions. In this box, the eigenfunctions of the Laplace operator are  $V^{-1/2} \exp\{-2\pi i \mathbf{n} \cdot \mathbf{x}/L\}$ , with  $\mathbf{n} \in \mathbb{Z}^d$ . Then

$$\hat{\rho}_1(\mathbf{x}; \mathbf{x}') = \frac{1}{V} \prod_{i=1}^d \vartheta_3\left[e^{-\pi \Lambda^2 / L^2}, \frac{\pi}{L}(x_i - x'_i)\right], \quad (14)$$

where  $\vartheta_3(q, \varphi)$  is one of Jacobi's theta functions, defined as [27]

$$\vartheta_3(q, \varphi) = 1 + 2 \sum_{k=1}^{\infty} q^{k^2} \cos 2k\varphi.$$

Equation (14) coincides with Eq. (7) in the  $L \rightarrow \infty$  limit. With this expression for  $\hat{\rho}_1$ , we obtain

$$h_n = [\vartheta_3(b^n, 0)]^d, \quad b = e^{-\pi\Lambda^2/L^2}; \quad (15)$$

therefore,

$$\ln \Xi = \sum_{n=1}^{\infty} \frac{z^n}{n} [\vartheta_3(b^n, 0)]^d. \quad (16)$$

The expansion (16) distinguishes two regimes: the ‘‘large’’  $n$  and the ‘‘small’’  $n$  terms. Suppose  $n \gg L^2/\Lambda^2$ , then  $b^n \ll 1$  and  $\vartheta_3(b^n, 0) \sim 1$ ; these terms approach those of the expansion of  $-\ln(1-z)$ . Suppose now that  $n \ll L^2/\Lambda^2$ , then  $b^n \sim 1$ . If we make use of the property (consequence of the Poisson summation formula [28])

$$\vartheta_3(e^{-\pi\lambda}, 0) = \lambda^{-1/2} \vartheta_3(e^{-\pi/\lambda}, 0),$$

then  $\vartheta_3(b^n, 0) \sim (L/\Lambda)n^{-1/2}$ . Hence these terms approach those of Eq. (4). If  $z$  is sufficiently smaller than 1, then the former are negligible and  $\ln \Xi$  is again given by Eq. (4). However, as  $z$  gets close enough to 1, the large  $n$  terms grow so as to add a macroscopic contribution approximately given by  $-\ln(1-z)$ . We thus reproduce BEC exactly as discussed in the preceding section, all in the single formula (16).

### C. The classical isomorphism

The appearance of cyclic paths in the partition function of bosons, as a consequence of their being indistinguishable, establishes a connection between this system and a model of ring polymers, usually referred to in the literature as the ‘‘classical isomorphism’’ [29,30]. In the so-called Gaussian model of polymers [2] the probability density for two neighboring monomers in a  $d$ -dimensional polymer chain to be separated by a distance  $r$  is given by

$$P(r) = \left( \frac{3}{2\pi a^2} \right)^{d/2} \exp\left\{ -\frac{3r^2}{2a^2} \right\}, \quad (17)$$

where  $a$  is a length scale usually known as the persistence length. For a chain of  $n+1$  monomers the probability that they are at positions  $\mathbf{x}_0, \mathbf{x}_1, \dots, \mathbf{x}_n$ , is

$$P(\{\mathbf{x}_i\}) = \frac{1}{Z_n} \exp\left\{ -\frac{3}{2a^2} \sum_{i=1}^n (\mathbf{x}_{i-1} - \mathbf{x}_i)^2 \right\}, \quad (18)$$

the normalizing constant  $Z_n = V(2\pi a^2/3)^{nd/2}$  being the partition function of the chain. The factor  $V$  arises because the first monomer can be placed anywhere in the volume  $V$ .

From this expression we can obtain the partition function of a ring polymer (a chain whose ends are joined together) of  $n$  monomers, as

$$Z_n^{\text{ring}} = \frac{1}{n} Z_n \langle \delta(\mathbf{x}_0 - \mathbf{x}_n) \rangle, \quad (19)$$

where the factor  $1/n$  comes in because there are  $n$  ways in which a ring can be split to form a chain, and the angled brackets indicate an average over  $P(\{\mathbf{x}_i\})$ . Now,

$$V \langle \delta(\mathbf{x}_0 - \mathbf{x}_n) \rangle = \left( \frac{3}{2\pi a^2} \right)^{nd/2} \int_{V^n} d\mathbf{x}_1 \cdots d\mathbf{x}_n \exp\left\{ -\frac{3}{2a^2} \times \sum_{i=2}^n (\mathbf{x}_{i-1} - \mathbf{x}_i)^2 - \frac{3}{2a^2} (\mathbf{x}_1 - \mathbf{x}_n)^2 \right\}, \quad (20)$$

an equation that reproduces Eq. (10) upon identifying  $\Lambda^2 \equiv 2\pi a^2/3$ . Hence

$$Z_n^{\text{ring}} = (\Lambda^d)^n \frac{V}{\Lambda^d} \frac{1}{n^{d/2+1}}. \quad (21)$$

For a system of  $N$  monomers that can self-assemble to form noninteracting ring polymers of arbitrary length, the contribution to the grand potential of rings of length  $n$  is  $z^n Z_n^{\text{ring}}$ . The activity of a ring of length  $n$  is  $z^n$  at equilibrium because its chemical potential must be  $n$  times that of a monomer [22,21,5]. Therefore, the grand canonical partition function,  $\Xi$ , of self-assembling ring polymers, is just Eq. (13) with  $h_n/n$  replaced by  $Z_n^{\text{ring}}$ , i.e.,

$$\ln \Xi = \sum_{n=1}^{\infty} z^n Z_n^{\text{ring}} = \frac{V}{\Lambda^d} G_{d/2+1}(z\Lambda^d), \quad (22)$$

and the density of monomers will be

$$n_{\text{mon}} = \sum_{n=1}^{\infty} n z^n \frac{Z_n^{\text{ring}}}{V} = \frac{1}{\Lambda^d} G_{d/2}(z\Lambda^d). \quad (23)$$

As  $n_{\text{mon}} = \sum_n n \rho(n)$ , with  $\rho(n)$  the density of ring polymers of length  $n$ , then

$$\rho(n) = z^n \frac{Z_n^{\text{ring}}}{V}. \quad (24)$$

Equations (22) and (23) reproduce Eqs. (4) and (5) with the ‘‘renormalized’’ fugacity  $\tilde{z} = z\Lambda^d$ . This is the isomorphism.

Once again, we have derived an equation that is only valid up to the transition. The corresponding equation for the density of monomers Eq. (23) saturates. But the mapping of ring polymers onto bosons is exact so for noninteracting self-assembling ring polymers with periodic boundary conditions on the monomer density, we obtain Eq. (14) for the probability that the two ends are at positions  $\mathbf{x}$  and  $\mathbf{x}'$ . Using this we obtain Eq. (16), but with  $\tilde{z}$  replacing  $z$ , and the  $\Lambda$  appropriate to ring polymers not bosons.

Due to this exact isomorphism between ideal bosons and self-assembling ring polymers, they have partition functions with identical forms and therefore the two, at first sight very different systems, behave completely analogously. The first consequence of this is that the behavior of bosons can be interpreted in terms of a classical system of ring polymers (interactions can also be accounted for by introducing path

integrals [3,30]). This has been widely exploited in studies of bosons; see the review of Ceperley [30]. The second consequence is the complete analogy between the equilibrium behavior of self-assembling ring polymers and that of bosons. Ring polymers undergo a “Bose-Einstein condensation” transition. From the analysis of BEC carried out in Sec. II B, we can conclude that the Bose condensate is equivalent to the formation of macroscopically long ring polymers [4]. So, if the concentration of monomers is larger than a critical value [given by Eq. (5) with  $z=1$ ], there appear macroscopically long rings. Note that a transition is enforced by the fact that the series  $G_{d/2}(z)$  with  $d>2$  takes only values in some limited range ( $[0,2.612]$  for  $d=3$ ) for  $z\leq 1$  and is divergent for  $z>1$ .

### III. GENERAL MODEL

We have considered monomers that self-assemble into ring polymers. Let us generalize this and consider monomers that can self-assemble into aggregates, where these aggregates are noninteracting but are otherwise arbitrary. This is motivated by the following observation. What happens if we replace the free energy of a ring-polymer or boson density matrix by some other free energy that has the property that in Eq. (23) for the monomer density,  $G_{d/2}(z)$  is replaced by a different sum  $G(z)$ ? If, as  $z$  runs over a range  $0\leq z\leq z_c$ , this new sum takes only values in the limited range  $0\leq G(z)\leq G(z_c)$  and is divergent for  $z>z_c$ , then there must be a phase transition, and this phase transition must occur due to the appearance of a macroscopic aggregate.

To be as general as possible we will denote the size of each aggregate by a (dimensionless) size  $s$ , which we allow to have any value  $s_0\leq s<\infty$ . If the number density of aggregates of size  $s$  is denoted by  $\rho(s)$ , then the free energy of our system will be given by the expression

$$\beta F/V = \int_{s_0}^{\infty} ds \rho(s) [\ln \rho(s) - 1 + f(s) + as], \quad (25)$$

where  $f(s) + as$  is the internal free energy (in units of  $kT$ ) of an aggregate of size  $s$ . The rest of the contribution of aggregates of size  $s$  to the free energy,  $\ln \rho(s) - 1$ , is simply the ideal mixing free energy. We use an integral not a sum in Eq. (25), partly for simplicity and partly as integrals are most commonly used to study self-assembling systems. If the specific model requires aggregates to be distinguished by an integer index (as in the preceding section), all the integrals of this section should be replaced by sums. As we will discuss later, the conclusions are unaffected by this distinction. Ring polymers are a specific case of the general free energy, (25). The free energy of a gas of ring polymers where the density of polymers of length  $s$  is  $\rho(s)$  is given by Eq. (25) with  $f(s) + as = -\ln[Z_s^{\text{ring}}/V]$ .

For generality, let us also allow the system to have imposed constraints

$$\xi_i = \int_{s_0}^{\infty} ds w_i(s) \rho(s), \quad i = 1, \dots, \nu, \quad (26)$$

where the  $\xi_i$  play the role of “generalized densities.” An example of a constraint would be a fixed total surface area of the aggregates. This would apply to a situation where the surface of the aggregates are coated with a layer of, say, a surfactant: for all the surfactant to lie at the surface of the aggregates the total area of the aggregates must equal the number of surfactant molecules times the surface area of a single molecule.

Depending on the actual shape of  $f(s)$  and the “weights”  $w_i(s)$ , this model may have very different phase behaviors. The one we are interested in (related to BEC) requires that all these functions behave as  $o(s)$  as  $s\rightarrow\infty$  (the reason will be made clear below).

The equilibrium distribution of aggregate sizes for this model can be found as the minimum of Eq. (25) at constant amount of “matter”

$$\phi = \int_{s_0}^{\infty} ds s \rho(s), \quad (27)$$

under the constraints (26), i.e.,

$$\frac{\delta}{\delta \rho(s)} \left[ \frac{\beta F}{V} + \sum_{i=1}^{\nu} \lambda_i \xi_i - \mu \phi \right] = 0;$$

this produces

$$\ln \rho(s) + f(s) + \sum_{i=1}^{\nu} \lambda_i w_i(s) + (a - \mu)s = 0. \quad (28)$$

Here  $\mu$  is the chemical potential (in  $kT$  units) corresponding to the reduced density  $\phi$ , and  $\lambda_i$  are the Lagrange multipliers corresponding to the constraints (26) (and which are analogous to chemical potentials associated to the “densities”  $\xi_i$ ). For notational simplicity, let us introduce  $\lambda = a - \mu$ . Then Eq. (28) gives an expression for the density distribution of aggregates

$$\rho(s) = \exp \left\{ -f(s) - \sum_{i=1}^{\nu} \lambda_i w_i(s) - \lambda s \right\}, \quad (29)$$

cf. Eq. (24), the equation for the density of ring polymers derived from the isomorphism with bosons. Hence the equilibrium free energy (25) becomes

$$\beta F/V = -\rho - \sum_{i=1}^{\nu} \lambda_i \xi_i + (a - \lambda)\phi, \quad (30)$$

with  $\rho$  defined as

$$\rho = \int_{s_0}^{\infty} ds \rho(s). \quad (31)$$

To illustrate all this consider again the case of ring polymers. For this model there are no constraints imposed, and as we have already mentioned,  $f(s) + as = -\ln[Z_s^{\text{ring}}(s)/V]$ ; hence the equilibrium size distribution (29) is  $\rho(s) = z^s Z_s^{\text{ring}}(s)/V$ , as in Eq. (24). Therefore,  $\phi$

$=\Lambda^{-d}G_{d/2}(z\Lambda^d)$ , thus recovering the expression for the density of monomers obtained before (23).

Because of the behavior of  $f(s)$  and  $w_i(s)$  as  $s\rightarrow\infty$  it follows that the convergence of the integrals of  $\rho(s)$  is dominated by the chemical potential, i.e.,

$$\rho(s)\sim e^{-\lambda s} \quad \text{as } s\rightarrow\infty. \quad (32)$$

Therefore, as long as  $\lambda>0$ , Eq. (26) permit us to eliminate the  $\lambda_i$  as functions of the constraints  $\xi_i$  and of  $\lambda$ . Equation (27) then yields  $\phi$  as a function of  $\lambda$ , and given that  $\phi$  is a monotonically decreasing function of  $\lambda$  (see Appendix A), it can be inverted to yield  $\lambda$  as a function of  $\phi$ .

Obviously  $\phi\rightarrow 0$  as  $\lambda\rightarrow\infty$ , and  $\lambda>0$  is required to guarantee convergence of the integrals in Eqs. (26) and (27). Thus,  $\lambda$  is restricted to the range  $(0,\infty)$ . Two different possibilities arise in the limit  $\lambda\rightarrow 0^+$ : either  $\phi$  remains finite or  $\phi\rightarrow\infty$ . We define  $\phi_c$  as the limit value of  $\phi$ , i.e.,

$$\phi_c = \int_{s_0}^{\infty} ds s \exp\left\{-f(s) - \sum_{i=1}^{\nu} \lambda_i w_i(s)\right\}. \quad (33)$$

If  $\phi_c=\infty$  then the equation  $\phi=\phi(\lambda)$  can be inverted for any finite value of  $\phi$ , and there is a well-defined aggregate distribution (29) and therefore a well-defined free energy (25), for all values of  $\phi$ . However, if  $\phi_c<\infty$  then we can invert the equation only in the finite range  $\phi\leq\phi_c$ . Now,  $\phi_c<\infty$  so long as

$$\lim_{s\rightarrow\infty} s^2 \exp\left\{-f(s) - \sum_{i=1}^{\nu} \lambda_i w_i(s)\right\} = 0, \quad (34)$$

as then the integral for  $\phi_c$ , Eq. (33) converges.

The convergence of the integral for  $\phi_c$  leads to a transition analogous to BEC. Note that the condition for convergence of the integral (34) is also the condition for a sum over the integrand of Eq. (33) to converge. So, the change from the sums in the preceding section to the integrals here does not affect the phase behavior.

As mentioned in the Introduction there has been a great deal of work on models that have free energies which can be written in the form of Eq. (25) [12,13,15–20]. However, in all this work, the equivalent to the function we call  $f(s)$  has always been a logarithmic function of  $s$ , i.e.,  $f(s)=\tau\ln(s)$ , where  $\tau$  is some constant. As we will see in Sec. IV, surfactant systems have  $f(s)$  functions that do not vary as  $\ln(s)$ , and so our results will be a little different from those in previous work. Ideal bosons in  $d$  dimensions are described by a logarithmic  $f(s)$  with  $\tau=d/2+1$ . We can see this from Eq. (4) where the weight of states occupied by  $n$  bosons varies as  $n^{-(d/2+1)}$ . This weight is essentially the exponential of minus our  $f(s)$  function.

### A. Finite-size analysis

Analogously to the case of bosons, we have to do a finite-size analysis in order to study the macroscopic aggregate, the condensed phase. See Ref. [31] for a detailed finite-size analysis of a system with an  $f(s)$  that varies logarithmically

with  $s$ . This analysis amounts to considering a free energy of an aggregate of size  $s$ ,  $\ln\rho(s)-1+f(s;V)$ , which depends on  $V$ . Obviously  $f(s;V)\rightarrow f(s)$  as  $V\rightarrow\infty$ , but the convergence is not uniform. Intuitively, if  $s$  is “small” compared to  $V$ , then  $f(s;V)\approx f(s)$ , but if  $s$  is “large,” then  $f(s;V)$  strongly differs from  $f(s)$ . Thus, there is a typical size  $s_1(V)$  such that it is the largest for which  $f(s<s_1;V)\approx f(s)$ . The convergence of  $f(s;V)$  to  $f(s)$  when  $V\rightarrow\infty$  occurs essentially because  $s_1(V)\rightarrow\infty$  in this limit. We expect that in a finite volume aggregates that span this volume will have their free energy increased by their confinement in it.

Now, for a finite system, the equation

$$\phi = \int_{s_0}^{\infty} ds s \exp\{-f(s;V) - W(s) - \lambda s\} \quad (35)$$

must necessarily be solvable for  $\lambda$  for any value of  $\phi$ . (For notational simplicity we have introduced  $W(s)\equiv\sum_i\lambda_i w_i$ .) This can only happen in two ways, given the assumptions we made for  $f(s)$ : either (a) the above integral diverges when  $\lambda\rightarrow 0^+$ , or (b)  $f(s;V)$  increases superlinearly with  $s$ , i.e.,  $s^{-1}f(s;V)\rightarrow\infty$  as  $s\rightarrow\infty$ . In case (a) we have the same situation as we met before for ring polymers [for which  $f(s;V)\sim\ln(Vs)$  as  $s\rightarrow\infty$ ], and  $\lambda$  is now constrained to remain strictly positive. In case (b) the integral (35) converges for *any*  $\lambda\in\mathbb{R}$  because  $f(s;V)$  dominates the large  $s$  decay. Also, the value of the integral increases arbitrarily as  $\lambda\rightarrow-\infty$ . This case is met, for instance, in a system of compact aggregates, for which there is an upper bound to the size an aggregate can have in order to fit in the box [in this example  $f(s;V)$  would diverge when  $s$  approached the maximum possible size an aggregate can reach  $S_M$ ].

It is important to notice that, for any given  $\phi$  and any finite  $V$ , Eq. (35) with the corresponding constraints [Eqs. (26) with  $f(s;V)$  instead of  $f(s)$ ] can only have a single solution  $\lambda(\phi;V)$ . This is obvious because the integral is a monotonically decreasing function of  $\lambda$ . What we need to determine now is the limit of  $\lambda(\phi;V)$  when  $V\rightarrow\infty$ , which we will denote  $\lambda^*(\phi)$ . With this aim we can make use of the nonuniform convergence of  $f(s;V)$  to  $f(s)$  and split the integral (35) as

$$\begin{aligned} \phi \approx & \int_{s_0}^{s_1(V)} ds s \exp\{-f(s) - W(s) - \lambda s\} \\ & + \int_{s_1(V)}^{\infty} ds s \exp\{-f(s;V) - W(s) - \lambda s\}. \end{aligned} \quad (36)$$

Let us also denote  $\lambda(\phi)$ , for any  $\phi\leq\phi_c$ , the solution for  $\lambda$  to Eqs. (26) and (27) with  $\rho(s)$  given by Eq. (29).

Assume  $\phi<\phi_c$  and take  $V$  sufficiently large [such that  $\lambda(\phi)s_1(V)\gg 1$ ]. Then, for  $\lambda\approx\lambda(\phi)$ , the first integral of Eq. (36) is approximately  $\phi$  whereas the second one is approximately 0. This means that  $\lambda(\phi;V)\rightarrow\lambda(\phi)$  as  $V\rightarrow\infty$ , so  $\lambda^*(\phi)=\lambda(\phi)$ .

Assume now  $\phi>\phi_c$ . In this case  $\lambda^*(\phi)$  cannot be positive, because the  $V\rightarrow\infty$  limits of the first and second integrals of Eq. (36) are  $<\phi_c$  and 0, respectively, for  $\lambda>0$ ; so the right-hand side of Eq. (36) would be  $<\phi_c$ . Therefore,

$\lambda^*(\phi) \leq 0$ . We have to discuss both cases, (a) and (b), separately. In case (a),  $\lambda^*(\phi)$  cannot be negative either, because then the first integral of Eq. (36) (and maybe the second one as well) would diverge; hence  $\lambda^*(\phi) = 0$ . In case (b) the monotonicity of the integral (35) forces  $\lambda(\phi, V) < 0$ , if  $\phi > \phi_c$ ; as we have shown that the limit  $\lambda^*(\phi) \geq 0$ , for these two things to hold simultaneously the only possibility is that  $\lambda^*(\phi) = 0$ .

We have thus proven that for  $V \rightarrow \infty$ , if  $\phi < \phi_c$ ,  $\lambda$  ( $> 0$ ) is given by the solution of Eq. (27), whereas if  $\phi > \phi_c$ ,  $\lambda = 0$ . There is then a phase transition at  $\phi = \phi_c$ . In order to understand what the nature of this transition is let us take a closer look at Eq. (36). If  $\phi > \phi_c$  then  $\lambda = 0$ ; but for  $\lambda = 0$ , the first integral of this equation approaches  $\phi_c$ , therefore, the limit of the second one when  $V \rightarrow \infty$  must be  $\phi - \phi_c$ . But this latter integral only contains contributions of macroscopic aggregates [with size  $s > s_1(V)$ ], so above the transition, the excess of mass (with respect to  $\phi_c$ ) goes into macroscopic aggregates (as we have seen in the preceding section for the particular case of ring polymers).

In Appendix B, we have worked out in more detail the finite-size analysis of the simple case in which there is a hard cutoff to the distribution [ $f(s; V) = f(s)$  all the way up to a macroscopic size  $S_M$ , above which aggregates cannot form, so that  $f(s > S_M; V) = 0$ ].

There only remains to determine the values of  $\lambda_i$  for  $\phi > \phi_c$ . For that we perform on Eqs. (26) the same splitting as we did for  $\phi$ ,

$$\xi_i \approx \int_{s_0}^{s_1(V)} ds w_i(s) \exp\{-f(s) - W(s) - \lambda s\} + \int_{s_1(V)}^{\infty} ds w_i(s) \exp\{-f(s; V) - W(s) - \lambda s\}, \quad (37)$$

with  $\lambda = \lambda(\phi; V)$ . If  $V$  is sufficiently large, the second integral is bounded above by

$$\frac{w_i(s_1)}{s_1} \int_{s_1(V)}^{\infty} ds s \exp\{-f(s; V) - W(s) - \lambda s\}.$$

If  $\phi > \phi_c$ , as we have seen, this integral tends to  $\phi - \phi_c$  when  $V \rightarrow \infty$ , but  $w_i(s_1)/s_1 \rightarrow 0$  in the same limit, so the contribution of the second integral of Eq. (37) above  $\phi_c$  vanishes in the thermodynamic limit. Thus, Eqs. (37) tend to Eqs. (26) with  $\lambda = 0$ ; there is no additional contribution to the densities  $\xi_i$  above  $\phi_c$ .

### B. Behavior in the thermodynamic limit

The previous analysis can be summarized in a very simple recipe: in the thermodynamic limit, all equations for the relevant thermodynamic quantities derived at the beginning of this section, and which were valid for  $\phi < \phi_c$ , are also valid for  $\phi > \phi_c$  by just setting  $\lambda = 0$ . In particular, the free energy (30) is given by

$$\beta F/V = -\rho_c - \sum_{i=1}^{\nu} \lambda_{i,c} \xi_i + a\phi, \quad \phi \geq \phi_c, \quad (38)$$

where  $\lambda_{i,c}$  are given by Eq. (26) with  $\lambda = 0$ , and  $\rho_c$  is given by Eq. (31) with  $\lambda = 0$  and  $\lambda_i = \lambda_{i,c}$ .

As for the size distribution, we have shown that above  $\phi_c$  macroscopic aggregates coexist with a distribution of microscopic aggregates. This distribution is given by Eq. (29) with  $\lambda = 0$  and  $\lambda_i = \lambda_{i,c}$ . It therefore decays slower than exponentially, and this is an important prediction of our theory.

A final remark is appropriate, concerning the finite-size analysis we have performed. For a system such as a porous medium it is possible that when the thermodynamic limit is taken  $s_1(V)$  instead of diverging plateaus at some finite value. For a porous medium, aggregates larger than the pore size might be unable to form. Then there would be no phase transition in the thermodynamic limit, although if the pore size is large, abrupt changes of thermodynamic behavior will still be found around  $\phi_c$ .

## IV. EXAMPLES

In this section, we will apply the general theory to specific models. These examples will make contact with experiment and illustrate the behavior of models of the type considered here. Within the theory of the preceding section a model is specified by specifying  $f(s)$ , which is the sublinear part of the internal free energy of an aggregate of size  $s$ , and if there are constraints, by specifying both the form of the  $w_i$  and the values of  $\xi_i$ . This determines the free energy and hence the phase behavior and the aggregate size distribution  $\rho(s)$ .

### A. Dislike micelles

As our first example we choose dislike aggregates, i.e., two-dimensional aggregates. This is a simple example, there are no constraints ( $\nu = 0$ ). The size distribution of micelles in a finite box exhibits a sharp cutoff: aggregation in micelles larger than a certain macroscopic size  $S_M(V)$  are strongly inhibited. So it is reasonable to model  $f(s; V)$  in the simplest possible way, i.e.,  $f(s \leq S_M; V) = f(s)$ ,  $f(s > S_M; V) = \infty$  (the hard cutoff treated in Appendix B). The discussion of this approximation is postponed to the end of this section. We will take advantage of the simplicity of this model to perform numerical calculations at a number of finite system sizes. Thus, we will see the scaling of  $\lambda$  at and around  $\phi_c$  for large and increasing  $S_M$ . The experimental system we have in mind is a solution of surfactant molecules that self-assemble to form dislike micelles (by dislike we mean that their thickness is that of a back-to-back layer of surfactant molecules but their size in the other two directions is limited only by the system size), for example the system of Ref. [32]. Here, the size  $s$  of an aggregate is proportional to its surface area.

The free energy of a disc of surfactant molecules with a size  $s$  contains a linear term in  $s$ ,  $as$ , proportional to the number of surfactant molecules in the disc, plus a term from the edges. The edges have a different free energy density from that at the center of a disc, well away from any edge. This different free energy density leads to a term proportional to the length of the edges, which is proportional to the square root of the area  $s^{1/2}$ . As  $f(s)$  does not include the

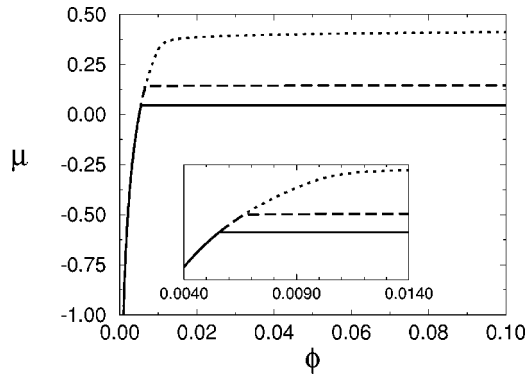


FIG. 1. Chemical potential  $\mu$  as a function of the density  $\phi$ , for the model of Eq. (39). The dotted, dashed, and solid curves are for maximum aggregate sizes  $S_M = 10^2$ ,  $10^3$ , and  $10^4$ , respectively. The inset shows the region near the (rounded off) transition on a larger scale.

extensive part it consists solely of this  $s^{1/2}$  term  $f(s) = e_d s^{1/2}$ . A free energy of this form is widely used to study self-assembly into two-dimensional aggregates, see Refs. [21,5,23,33,24].  $e_d$  is a dimensionless proportionality constant that simply controls the value of  $\phi_c$  without affecting the nature of the transition, providing that  $e_d > 0$ —otherwise there is no transition because  $\phi_c$  diverges; we set  $e_d = 5$ . Less positive values of  $e_d$  increase the transition density. A positive  $e_d$  corresponds to the free energy density being higher at the edges of a dislike micelle, i.e., edges are disfavored.

So, for simplicity we set  $s_0 = 1$  and  $a = 0$ , and then we have a model described by the free energy

$$\beta F/V = \int_1^{S_M} ds \rho(s) [\ln \rho(s) - 1 + e_d s^{1/2}], \quad (39)$$

just a specific example of the general expression for the free energy (25), but with a finite cutoff. By taking the variation of this free energy with respect to  $\rho(s)$  and setting it equal to the chemical potential  $\mu$  we obtain an expression for  $\rho(s)$ ,

$$\rho(s) = \exp(-e_d s^{1/2} + \mu s), \quad (40)$$

just a specific example of the general expression for  $\rho(s)$  (29). Inserting this in Eq. (27) for  $\phi$ , with its upper limit of integration set to  $S_M$ , we solve the resulting nonlinear equation for  $\mu$ . Then we have the chemical potential, the free energy, and the function  $\rho(s)$  at that value of  $\phi$ .

We perform calculations for large but finite values of the maximum allowed aggregate size  $S_M$ . Figure 1 shows the chemical potential as a function of density  $\phi$  for  $S_M = 10^2$ ,  $10^3$ , and  $10^4$ . As  $S_M$  is finite there is no phase transition of course;  $\mu$  is a differentiable function of  $\phi$  at all points. However, a sharp change in slope is obvious. This sharp change is just the discontinuity found in thermodynamic limit rounded off due to finite-size effects. In the thermodynamic limit there is a phase transition at  $\phi_c = 0.0051$ . Also note that as the size of the largest aggregates is increased  $\mu$  at and above the transition tends towards 0. If we compare Eqs. (B2) and

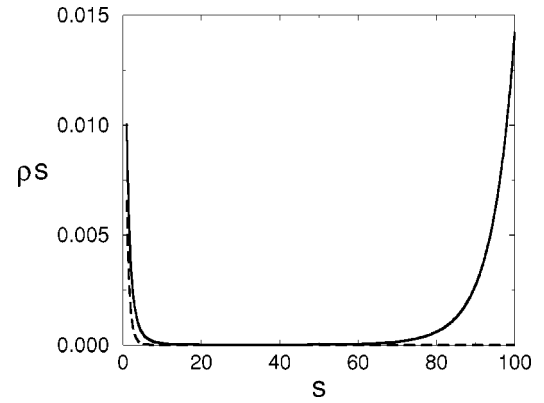


FIG. 2. Amount of matter in aggregates of size  $s$ ,  $\rho(s)s$ , as a function of  $s$ , for the model of Eq. (39). The maximum aggregate size is  $s_m = 10^2$ . The dashed and solid curves are for  $\phi = 0.005$  and  $0.1$ , respectively.

(40) we see that  $\varphi(s) \sim s^{1/2}$ . From Eq. (B6) of the Appendix B, we find that beyond  $\phi_c$  and at large  $S_M$ ,  $\mu \sim S_M^{-1/2}$ . We observe this inverse square root dependence of the chemical potential in Fig. 1.

In Fig. 2 we have plotted the (unnormalized) density of matter  $\rho(s)s$  as a function of the aggregate size  $s$  above (solid curve) and below (dashed curve) the transition density of the infinite system. Clearly, above the transition a significant fraction of the material is a part of aggregates with sizes near the maximum allowed,  $S_M$ . There is a range of sizes  $1 \ll s \ll S_M$  in which the amount of matter is very small. This justifies the analysis performed in Appendix B. We also observe (not shown) that  $\rho(s)$  for  $s$  of order unity (i.e., the distribution of small aggregates), changes by barely perceptible amounts beyond the transition, for  $S_M = 1000$  and greater.

We have imposed a hard cutoff on the distribution of aggregates: the free energy of an aggregate is  $\ln \rho(s) - 1 + f(s)$ , right up to a maximum value  $S_M$ , and beyond that it is  $\infty$ . This cutoff is not realistic: we assume that aggregates of size just less than  $S_M$  exist in large numbers and that their center of mass can explore the whole volume; both are requirements for the translational entropy of an aggregate to be  $1 - \ln \rho(s)$ . If the value of  $S_M$  is set by the size of the system there may be few aggregates of size  $s \leq S_M$  and as their size is a significant fraction of the system size their center of mass may be restricted to a volume significantly less than the volume of the system (think of a disc of side less than but of the same order as the length of cubic box that encloses the system). However, if we replace the hard cutoff at  $S_M$  by a softer cutoff, which would be some rapidly increasing free energy cost for aggregates with sizes greater than around  $S_M$ , then for large  $S_M$  the soft and hard cutoffs lead to essentially indistinguishable results. In Fig. 1, we see that the results for  $S_M = 10^3$  and  $10^4$  are close. A soft cutoff, which started to reduce the density of aggregates at around  $10^3$  and made  $\rho(s)$  effectively 0 by  $10^4$  would yield a  $\mu$  as a function of  $\phi$  that lay between the  $S_M = 10^3$  and  $10^4$  curves in Fig. 1. As  $S_M \rightarrow \infty$  the free energy for any reasonable cutoff affecting aggregates with  $s \geq S_M$  tends towards the same thermodynamic limit.



Returning to Fig. 1, we note that the slope of  $\mu$  as a function of  $\phi$  is nonzero at the transition. We can obtain this slope in our general model as (see Appendix A)

$$\frac{d\mu}{d\phi} = - \left( \frac{d\phi}{d\lambda} \right)^{-1} = \left[ \int_{s_0}^{\infty} ds \left( s + \frac{d\lambda_i}{d\lambda} w_i(s) \right)^2 \rho(s) \right]^{-1}, \quad (41)$$

taking the limit  $\lambda \rightarrow 0^+$ . If any of the functions  $f(s)$ ,  $w_i(s)$ ,  $i=1, \dots, \nu$ , diverges superlogarithmically with  $s$ , then this integral will remain finite at the transition, and so  $d\mu/d\phi > 0$ . This is the case for disklike micelles, for which  $f(s) \sim s^{1/2}$ . However, if all those functions diverge logarithmically, then the integral above may diverge, then  $d\mu/d\phi = 0$  at the transition. In the simplest case (no constraints)  $f(s) = \tau \ln s$ , where  $\tau > 2$  is required for there to be a transition. Inserting this  $f(s)$  in Eq. (41) it is easily seen that if  $\tau \leq 3$  the integral will diverge, and otherwise it will be finite. This result has been obtained in a number of earlier works, e.g., Refs. [18]. As for ideal bosons  $\tau = d/2 + 1$ ,  $d\mu/d\phi = 0$  at the transition for  $d=3,4$ , and  $d\mu/d\phi > 0$  at the transition for  $d > 4$ . So, qualitatively, disklike micelles behave as ideal bosons in more than four dimensions.

### B. Microemulsions

A second example will illustrate the effect of constraints in the model. A microemulsion is an isotropic equilibrium phase composed of water, oil, and a surfactant [34,6]. If we have that, say, there is much less oil than water then the microemulsion consists of droplets of oil, nanometers across, coated with the surfactant and dispersed in the water. Without the surfactant, at equilibrium we would have bulk oil and water phases but as surfactant prefers to lie in the water-oil interface it stabilizes the oil droplets dispersed in the water. So, the system consists of droplets of one bulk phase dispersed in another with a third component at the surface of the droplets. References [7,35] are recent experimental work on the transition we study here.

The volume fraction of oil, proportional to the total volume of the droplets, will be our concentration  $\phi$ . Our size variable  $s$  is then proportional to the volume of a droplet. The surfactant can either lie on the surface of a droplet (the amount on the surface scales as the surface area  $s^{2/3}$ ) or in micelles. Micelles are small aggregates composed entirely of surfactant; as they contain no oil they do not contribute to  $\phi$ . They do, however, contribute to the total amount of surfactant, which we will constrain. For a droplet, there is a contribution to its free energy that is proportional to its volume or equivalently to the amount of oil; as before we denote this by  $as$ . The surface of the droplet will determine  $f(s)$ , it gives the sublinear contributions to the free energy of a droplet (=aggregate). We need an explicit expression for the free energy contribution of the surfactant coated surface of a droplet. We do so by modeling the surface as an elastic sheet, whose free energy is given by Helfrich's expression [36]

$$f_{el} = \sigma A + \frac{K_b}{2} \int dA (\kappa_1 + \kappa_2 - 2\kappa_0)^2 + K_s \int dA \kappa_1 \kappa_2, \quad (42)$$

where  $A$  is the total surface area of the sheet and the integrations are over this area.  $\sigma$  is the surface free energy of a sheet with the spontaneous curvature  $\kappa_0$ ;  $\kappa_1$  and  $\kappa_2$  are the local curvatures of the membrane;  $K_b$  and  $K_s$  are, respectively, the bending and the saddle-splay moduli; and  $\kappa_0$  is the spontaneous curvature. These elastic moduli and the spontaneous curvature depend on variables such as the temperature.

Depending on the values of the curvature moduli  $K_b$  and  $K_s$  the system can be found in different phases [34]. The two most typical are the microemulsions considered here, and bicontinuous (spongelike) phases. For a boundaryless, orientable surface  $\Sigma$ , the integral of the Gaussian curvature  $\kappa_1 \kappa_2$ , is

$$\int_{\Sigma} dA \kappa_1 \kappa_2 = 4\pi(1-g), \quad (43)$$

where  $g$  is the genus of the surface (in short, the number of "holes"). If  $K_s > 0$  the last term in Eq. (42) lowers the free energy by increasing  $g$ , thus giving rise to bicontinuous phases. However, if  $K_s < 0$  the free energy is minimized for  $g=0$ . Negative values of  $K_s$  then favor the formation of microemulsion phases. In addition, large negative values of  $K_s$  inhibit shape fluctuations and increase size fluctuations [37]. It is in this regime that modeling microemulsion droplets as spheres makes sense.

For a spherical droplet of size (volume)  $s$ , the Gaussian curvature term of Eq. (42) is trivially obtained from Eq. (43) with  $g=0$ . On the surface of the sphere the local curvatures  $\kappa_1 = \kappa_2 = 1/R$ , where  $R$  is the radius of the sphere, related to  $s$  by  $s = (4/3)\pi R^3$ . Thus, Eq. (42) becomes

$$f_{el}(s) = (36\pi)^{1/3} \sigma s^{2/3} + 8\pi K_b [1 - (s/\sigma_0)^{1/3}]^2 + 4\pi K_s, \quad (44)$$

where  $\sigma_0 = 4\pi/(3\kappa_0^3)$ . So, we have zeroth,  $s^{1/3}$  and  $s^{2/3}$  terms, hence we write  $f(s)$  as [38]

$$f(s) = a_0 - a_1 s^{1/3} + a_2 s^{2/3}, \quad (45)$$

where only  $a_1 > 0$  has a well-defined sign.

The free energy of Eq. (25) is an integral over the contributions of aggregates, here droplets, with all values of  $s$ , from the minimum value  $s_0$  upwards. We also have micelles that contribute to the free energy but have  $s=0$ . So we must add a term to the free energy from the micelles. Treating these micelles as an ideal gas then, if their density is  $\rho_0$ , the required term is  $\rho_0[\ln \rho_0 - 1 + f_0]$ , where  $f_0$  is the internal free energy of a micelle. Thus, Eq. (25) becomes

$$\beta F/V = \rho_0[\ln \rho_0 - 1 + f_0] + \int_{s_0}^{\infty} ds \rho(s) \times [\ln \rho(s) - 1 + f(s) + as], \quad (46)$$

with  $f(s)$  given by Eq. (45). Equation (27) for  $\phi$  is unchanged. We constrain the total amount of surfactant to be  $\xi$ , so

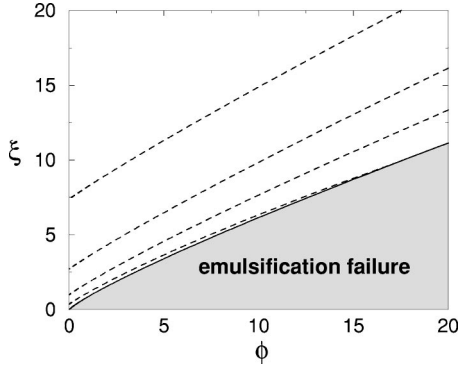


FIG. 3. Phase diagram of the microemulsion model:  $\phi$  is the amount of oil enclosed in droplets of surfactant, and  $\xi$  the total amount of surfactant. In the shaded region there appears a macroscopic phase of oil (emulsification failure), due to the lack of surfactant. It occurs through a phase transition, signaled by the solid line (corresponding to  $\lambda=0$ ). The dashed lines represent the curves  $\xi(\phi)$  at constant  $\lambda_2$  ( $=-1,0,1,2$  from bottom to top), or equivalently, at constant  $\rho_0=e^{-\lambda_2}$ , the excess of surfactant.

$$\xi = c_0 \rho_0 + c_1 \int_{s_0}^{\infty} ds s^{2/3} \rho(s), \quad (47)$$

with  $c_0$  and  $c_1$  appropriate geometric factors. Equation (47) is slightly modified with respect to Eq. (26), by the addition of the contribution to the total amount of surfactant from the micelles. This gives rise to the size distribution

$$\rho(s) = \exp\{-a_0 + a_1 s^{1/3} - (a_2 + \lambda_2 c_1) s^{2/3} - \lambda s\}, \quad (48)$$

where as before  $a$  has been absorbed into the Lagrange multiplier  $\lambda$ . Also we obtain the equilibrium  $\rho_0$

$$\rho_0 = e^{-f_0 - c_0 \lambda_2}. \quad (49)$$

When  $a_2 + \lambda_2 c_1 > 0$ , then we have a finite  $\phi_c$  at which a transition occurs. This is just as discussed in the preceding section. At  $\phi_c$  a macroscopic droplet form, and a macroscopic droplet is nothing other than a bulk oil phase. A bulk phase coexisting with the microemulsion has formed. This phenomenon is known as *emulsification failure* [7]. To illustrate emulsification failure we take some simple and rather arbitrary values for the parameters of the free energy. We make the simple choice  $a = a_0 = a_2 = f_0 = 0$ ,  $a_1 = c_0 = c_1 = 1$  and fix the smallest droplet size  $s_0 = 1$ . With this choice,  $\phi$  and  $\xi$  are related to  $\lambda$  and  $\lambda_2$  by

$$\phi = \int_1^{\infty} ds s \exp\{s^{1/3} - \lambda_2 s^{2/3} - \lambda s\}, \quad (50)$$

$$\xi = e^{-\lambda_2} + \int_1^{\infty} ds s^{2/3} \exp\{s^{1/3} - \lambda_2 s^{2/3} - \lambda s\}. \quad (51)$$

The transition line is determined by setting  $\lambda=0$ . In that case, both  $\phi(\lambda_2)$  and  $\xi(\lambda_2)$  can be explicitly found in terms of error functions. The solution is plotted in Fig. 3. Also shown in the same figure are a few lines of constant  $\lambda_2$  (equivalently, constant  $\rho_0$ ), easily obtained by numerical in-

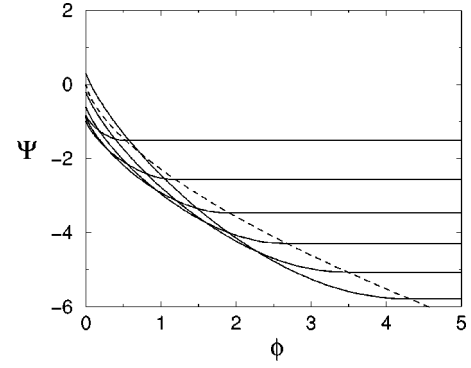


FIG. 4. Reduced free energy per unit volume  $\Psi \equiv \beta F/V$  as a function of the amount of oil in the microemulsion  $\phi$  for different values of the amount of surfactant  $\xi$  ( $=0.5, 1.0, 1.5, 2.0, 2.5,$  and  $3.0$ , from top to bottom). The dashed line marks the transition. Beyond that point, the free energy remains a constant.

tegration of Eqs. (50) and (51) at different values of  $\lambda$ . Notice that  $\rho_0$  increases when we move upward or leftward in the phase diagram. This means that either increasing  $\xi$  (the amount of surfactant) or decreasing  $\phi$  (the amount of fluid in the droplets) yields an excess of surfactant that does not form droplets. On the other hand, moving in the opposite direction we find the  $\lambda=0$  line in which there is not enough surfactant to accommodate the droplet distribution and that produces a transition in which a bulk oil phase forms.

According to Eq. (46) and the expressions for the intervening functions and variables, the free energy per unit volume for this model is given by

$$\beta F/V = \begin{cases} -e^{-\lambda_2} - \rho - \lambda_2 \xi - \lambda \phi & \text{if } \phi < \phi_c, \\ -e^{-\lambda_{2,c}} - \rho_c - \lambda_{2,c} \xi & \text{if } \phi \geq \phi_c, \end{cases} \quad (52)$$

where  $\rho$  is the integral of  $\rho(s)$  and the subscript  $c$  denotes the corresponding quantities at  $\lambda=0$ . This free energy is plotted in Fig. 4 as a function of  $\phi$  for several values of  $\xi$ . As discussed in Sec. III, for  $\phi \geq \phi_c$  we have  $\lambda=0$  when an infinite aggregate forms (in this case, when there is a bulk phase of the emulsion); therefore,  $\lambda_2$  is just a function of  $\xi$ , and so is  $\rho_c$ . Thus, for fixed  $\xi$  the free energy is simply a constant.

Returning to our general free energy of a microemulsion, we consider the case where micelles do not form. If the surfactant were unable to form micelles, then  $\phi$  and  $\xi$  would be given by

$$\phi = \int_{s_0}^{\infty} ds s \rho(s) = s_0^2 \int_1^{\infty} dt t \rho(s_0 t),$$

$$\xi = \int_{s_0}^{\infty} ds s^{2/3} \rho(s) = s_0^{5/3} \int_1^{\infty} dt t^{2/3} \rho(s_0 t).$$

But  $t^{2/3} \leq t$  for any  $t \geq 1$ , so  $\xi \leq s_0^{-1/3} \phi$ , which means that for a given  $\phi$  there is a maximum amount of surfactant the system can accommodate. Smaller droplets at the same volume fraction have a larger surface area than larger droplets but if

there is a minimum droplet size then there is a maximum total area of the droplets and hence a maximum amount of surfactant that can be accommodated. This means that the large  $\xi$ , small  $\phi$  part of the phase diagram of Fig. 3 is inaccessible. A single microemulsion phase is not possible beyond a certain maximum concentration of surfactant.

### C. Ring polymers revisited

Ring polymers are the bridge between BEC and the macroscopic aggregation of self-assembling models. On one side ring polymers are “paths in imaginary time” of the bosons, and on the other side they are aggregates of monomers. For this reason they have served us as the first instance of the general model introduced in Sec. III and so we have already determined that they undergo a transition completely analogous to BEC. This is not a novel observation, it is of course implicit in the exact mapping between the two systems and was already studied, in the context of polymer aggregation in a lattice model, by Petschek *et al.* [4]. So, there only remains to relate the transition to experiment and previous theory.

There are solutions of surfactant molecules in which the molecules aggregate into wormlike micelles: micelles that are roughly cylindrical with a radius limited to the length of one surfactant molecule, but whose lengths can be arbitrarily large [22,40]. These wormlike micelles form chains as well as rings, the competition between the two being determined by the free energy cost of forming ends and that of bending a micelle around to form a ring; see Refs. [22,41]. The presence of chains destroys the phase transition, although if there are many rings present then there are traces of the transition in the behavior [42,43].

## V. CONCLUSIONS

There is a class of systems in which aggregates of all sizes can reversibly self-assemble, and in which, without interaggregate interactions, there is a phase transition. This phase transition occurs when an infinite aggregate or aggregates form. It is analogous to the BEC of ideal bosons: in neither case are there interactions, and the macroscopic aggregates we find play the same role as the condensate of a macroscopic number of bosons. This analogy for the specific case when the aggregates are ring polymers is implied by Feynman’s path integral approach for bosons [3,30,4]. We have shown that the analogy applies to a whole class of self-assembling systems with partition functions that are qualitatively similar, although of a different functional form, to that of ideal bosons or ring polymers. This class is defined by the requirement that the internal free energy of an aggregate contains a linear term  $as$  plus others that are sublinear and ensure that the density is finite when the chemical potential  $\mu \rightarrow a^-$ . This requirement is also satisfied by an extremely diverse set of objects that are not surfactant aggregates, such as defects in superfluid helium [9,10], baby universes [17,18], and percolating clusters [13,14]. It is remarkable that our analogy implies an analogy between the statistics of some surfactant phases and the statistics of so-called baby universes studied in work on quantum gravity. We gave three examples: ideal disclike micelles, microemul-

sions, and ring polymers. We suggest that the formation of the lamellar phase [32] and emulsification failure [7] found in experiments on systems with surfactant are related to the transition we have described, although modified by the presence of interactions between the aggregates.

Finally, we consider interaggregate interactions. In general, we expect the contribution of interactions to the free energy to be some functional  $F_{\text{ex}}$  of the size distribution function of aggregates. Then the free energy of Eq. (25) becomes

$$\beta F/V = \int_{s_0}^{\infty} ds \rho(s) [\ln \rho(s) - 1 + f(s) + as] + F_{\text{ex}}[\rho(s)]. \quad (53)$$

Minimizing and imposing the constraints Eq. (26), we obtain

$$\rho(s) = \exp \left\{ -f(s) - \sum_{i=1}^{\nu} \lambda_i w_i(s) + (\mu - a)s - \frac{\delta F_{\text{ex}}}{\delta \rho(s)} \right\}. \quad (54)$$

If  $\delta F_{\text{ex}}/\delta \rho(s) \sim bs$  for  $s \rightarrow \infty$ , and if when  $\mu = a + b$  the integral for  $\phi$ , Eq. (27) converges to a finite value  $\phi_c$ , then we expect the conclusions of Sec. III to follow. The analysis in the presence of interaction is complicated by the fact that  $\rho(s)$  depends on a functional of itself. In the ideal case the presence of the transition relies on either  $f(s)$  or a constraint ensuring that  $\phi_c$  is finite. With interactions a transition is present even if  $f(s) = 0$  and there are no constraints, provided that the functional derivative in Eq. (54) makes  $\rho(s)$  decay sufficiently fast as to render  $\phi_c$  finite.

This effect was seen in Ref. [24] for surfactant aggregation into rodlike micelles. There is no transition if the system is ideal, because  $f(s) = \text{const}$ , but a simple excluded-volume interaction suffices to induce the transition by this mechanism. Also, Zhang *et al.* [44] report simulation results and theoretical calculations for a model of interacting aggregates. The simulations show the appearance of two aggregates not much smaller than the size of the system simulated. The calculations using an approximate excess free energy  $F_{\text{ex}}$  also determined  $\phi_c$ . The simulations were inconclusive due to finite-size effects, and the calculations did not extend beyond  $\phi_c$ . Very recently, Blaak and Cuesta [45] have performed an analysis of this system following the scheme suggested by Eq. (54) to account for the excluded volume interactions. They have also carried out new simulations taking into account the existence of a macroscopically large aggregate. The agreement between theory and simulations is impressive.

We also note that a variation of the model of Zhang *et al.* has been studied by Blaak [46]. In his model,  $s$  is proportional to the surface rather than the volume. Therefore, the free energy contains a superlinear  $s^{3/2}$  term. Within the analysis of Sec. III, this does not result in a phase transition. Again, this is consistent with Blaak’s results that show no sign of the appearance of large aggregates.

**ACKNOWLEDGMENTS**

We would like to thank D. Johnston for bringing the related work on quantum gravity [17,18] and in other fields to our attention. We acknowledge partial support through project HB1998-0008 funded by Acciones Integradas con el Reino Unido (Ministerio de Educación y Cultura) and The British Council. J.A.C.'s work is part of the Project BFM2000-0004 of the Dirección General de Investigación (Ministerio de Ciencia y Tecnología, Spain).

**APPENDIX A: MONOTONICITY OF  $\phi(\lambda)$** 

$\phi$  is a function of  $\lambda$  not only explicitly, but also through the  $\lambda_i$  because of the constraints, Eq. (26). When there are no constraints,

$$\phi'(\lambda) = - \int_{s_0}^{\infty} ds s^2 \rho(s) < 0, \quad (\text{A1})$$

and then  $\phi$  is obviously monotonically decreasing with  $\lambda$ . However, if there are constraints the proof is not so simple. Let us introduce the notation

$$\langle X(s) \rangle = \int_{s_0}^{\infty} ds X(s) \rho(s). \quad (\text{A2})$$

Then we can express  $\phi = \langle s \rangle$ , and  $\xi_i = \langle w_i(s) \rangle$ . If we now differentiate  $\phi$  with respect to  $\lambda$ ,

$$\phi'(\lambda) = - \langle s^2 \rangle - \sum_{i=1}^{\nu} \langle s w_i(s) \rangle \lambda'_i(\lambda), \quad (\text{A3})$$

and we determine the derivatives  $\lambda'_i$  by differentiating the constraints,

$$0 = \langle s w_i(s) \rangle + \sum_{j=1}^{\nu} \langle w_i(s) w_j(s) \rangle \lambda'_j. \quad (\text{A4})$$

If we multiply this equation by  $\lambda'_i$  and sum in  $i$  we obtain

$$0 = \sum_{i=1}^{\nu} \langle s w_i(s) \rangle \lambda'_i + \sum_{i,j=1}^{\nu} \langle w_i(s) w_j(s) \rangle \lambda'_i \lambda'_j. \quad (\text{A5})$$

Subtracting Eq. (A3) from Eq. (A5) we get

$$- \phi'(\lambda) = \left\langle \left( s + \sum_{i=1}^{\nu} \lambda'_i w_i(s) \right)^2 \right\rangle > 0, \quad (\text{A6})$$

and so  $\phi'(\lambda) < 0$ , which completes the proof.

**APPENDIX B: FINITE-SIZE DEPENDENCE OF  $\lambda$** 

Here, we consider the case in which  $f(s < S_M; V) = f(s)$  and  $f(s > S_M; V) = \infty$ ,  $S_M(V) (\rightarrow \infty \text{ as } V \rightarrow \infty)$  being the size of the largest aggregate a box of volume  $V$  can accommodate. Our aim is to determine the scaling of  $\lambda$  with  $S_M$ . The second integral of Eq. (36) can be written as

$$\phi_l = \int_{s_1}^{S_M} ds s e^{-\lambda s - \varphi(s)}, \quad (\text{B1})$$

where  $\varphi(s)$  denotes the sum of the sublinear terms,

$$\varphi(s) = f(s) + \sum_{i=1}^{\nu} \lambda_i w_i(s). \quad (\text{B2})$$

Let us change the variable to  $t = (-\lambda)(S_M - s)$ , and define  $T_M = (-\lambda)(S_M - s_1)$ ; then

$$\phi_l = \frac{e^{-\lambda S_M}}{(-\lambda)} \int_0^{T_M} dt (S_M + \lambda^{-1} t) e^{-t - \psi(t)}, \quad (\text{B3})$$

with  $\psi(t) = \varphi(S_M + \lambda^{-1} t)$ . From this expression it follows that  $\lambda S_M \rightarrow \infty$  as  $S_M \rightarrow \infty$ , for if  $\lambda S_M = O(1)$ , then  $\phi_l \sim S_M^2 \exp\{-\varphi(S_M)\} \rightarrow 0$  as  $S_M \rightarrow \infty$  [recall condition (34) for the convergence of Eq. (27) for  $\lambda = 0$ ]. Therefore, for  $S_M$  sufficiently large we can harmlessly replace  $T_M$  by infinity. To carry on the calculations a little farther, notice that the relevant contribution of  $\psi(t)$  to the integral comes from the small values of  $t$ , so we can just Taylor expand about  $t = 0$ ,

$$\psi(t) = \varphi(S_M) + \lambda^{-1} \varphi'(S_M) t + \dots, \quad (\text{B4})$$

to find

$$\begin{aligned} \phi_l &\sim \exp[-\lambda S_M - \varphi(S_M)] / (-\lambda) \int_0^{\infty} dt (S_M + \lambda^{-1} t) \\ &\quad \times \exp\{-t[1 + \lambda^{-1} \varphi'(S_M)]\} \\ &= \exp[-\lambda S_M - \varphi(S_M)] \frac{S_M}{[-\lambda - \varphi'(S_M)]^2} \\ &\quad \times [1 - \lambda - \varphi'(S_M)]. \end{aligned} \quad (\text{B5})$$

From this we finally obtain the asymptotic behavior

$$\lambda \sim -S_M^{-1} \{ \varphi(S_M) + \ln[\phi_l(-\varphi(S_M)/S_M)'] + \dots \} \quad (\text{B6})$$

as  $S_M \rightarrow \infty$ .

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