

What do emulsification failure and Bose-Einstein condensation have in common?

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(received 18 December 2000; accepted in final form 30 May 2001)

PACS. 03.75.Fi – Phase coherent atomic ensembles; quantum condensation phenomena.

PACS. 82.70.Kj – Emulsions and suspensions.

PACS. 05.70.Fh – Phase transitions: general studies.

Abstract. – Ideal bosons and classical ring polymers formed via self-assembly, are known to have the same partition function, and so analogous phase transitions. In ring polymers, the analogue of Bose-Einstein condensation occurs when a ring polymer of macroscopic size appears. We show that a transition of the same general form occurs within a whole class of systems with self-assembly, and illustrate it with the emulsification failure of a microemulsion phase of water, oil and surfactant. As with Bose-Einstein condensation, the transition occurs even in the absence of interactions.

Bose-Einstein condensation (BEC) is a textbook [1], 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 [2] 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 [3]. Here, we generalise this result to show that there is a class of self-assembling systems which 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 which is a macroscopic number of bosons in a single state. In the analogous transition in self-assembling systems, an aggregate of macroscopic size appears. For the example considered here, a microemulsion, the macroscopic aggregate is a bulk oil phase.

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Self-assembling systems are systems in which the particles are not immutable objects but are formed reversibly [4–6]. Typically we have water, surfactant and sometimes oil. The surfactant molecules then spontaneously assemble into micelles, or coat and stabilise 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 in water as 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. A BEC-like transition occurs when, at equilibrium, some of the oil exists as a macroscopic droplet, *i.e.*, a bulk phase. This transition is called *emulsification failure* [7, 8].

Let us begin by outlining BEC in Feynman’s language [2]. The partition function of N bosons is given in terms of their density matrix $\hat{\rho}$ by

$$Z_N(\beta, V) = \text{tr}_V \hat{\rho}, \quad \hat{\rho} \equiv e^{-\beta H_N}, \quad (1)$$

with H_N the Hamiltonian operator, $\beta = 1/kT$. The density matrix of noninteracting identical bosons can be written in terms of 1-particle density matrices, $\hat{\rho}_1(\mathbf{x}_i; \mathbf{x}'_i)$,

$$\hat{\rho}(\{\mathbf{x}_i\}; \{\mathbf{x}'_i\}) = \frac{1}{N!} \sum_{P \in \Pi_N} \prod_{i=1}^N \hat{\rho}_1(\mathbf{x}_i; P\mathbf{x}'_{P(i)}), \quad (2)$$

where $\{\mathbf{x}_i\} \equiv \{\mathbf{x}_1, \dots, \mathbf{x}_N\}$ and Π_N is the set of permutations of N elements [$P : i \mapsto P(i)$].

Taking the trace over eq. (2) and moving over to the grand canonical ensemble, we obtain for the grand partition function, $\Xi(\beta, z, V)$, and average density of bosons, ϕ ,

$$\ln \Xi = \sum_{n=1}^{\infty} \frac{h_n z^n}{n}, \quad \phi = \frac{1}{V} \sum_{n=1}^{\infty} h_n z^n, \quad (3)$$

with z the activity of the bosons and $h_n = \text{tr}_V \hat{\rho}_1^n = Z_1(n\beta, V)$. It is straightforward to determine that for a d -dimensional cubic box with periodic boundary condition $Z_1(\beta, V) = [\vartheta(\pi/\ell^2)]^d$, where $\ell \equiv V^{1/d}/\Lambda$ is the length of the box in units of the thermal wavelength $\Lambda \equiv h\sqrt{\beta/2\pi m}$, and $\vartheta(y) \equiv 1 + 2 \sum_{k=1}^{\infty} \exp[-yk^2]$. Thus,

$$\phi = \frac{1}{V} \sum_{n=1}^{\infty} z^n [\vartheta(\pi n/\ell^2)]^d. \quad (4)$$

Remarkably, eq. (3) also applies to self-assembling ring polymers, provided z and Λ are properly redefined. To see this, note that by definition [2], the one-particle density matrix, $\hat{\rho}_1 = \exp[-\beta H_1]$, is a solution of the equation $\partial_\beta \hat{\rho}_1 = -H_1 \hat{\rho}_1 = (\hbar^2/2m)\nabla^2 \hat{\rho}_1$. This is just a Fokker-Planck equation for a random walk in “time” β , and with diffusion coefficient $\hbar^2/2m$. Accordingly, $V^{-1} \text{tr}_V \hat{\rho}_1^n (= h_n/nV)$ has an alternative interpretation as the probability of a random walk forming a cyclic path after n “time”-steps of length β . The simplest model of a ring polymer of length n is a cyclic random walk of n steps; hence h_n/nV can also be regarded as the ratio of the partition function of a ring of n monomers, Z_n^{ring} , to that of a chain of $n+1$ monomers, $V\Lambda^{nd}$. With this interpretation Λ has the meaning of the average monomer length. We conclude that $Z_n^{\text{ring}} = \Lambda^{nd} h_n/n$. For an ideal mixture of rings made up of monomers at an activity z , the number density of rings of length n , $\rho(n) = z^n Z_n^{\text{ring}}/V$, and the number density of monomers in rings of length n is just n times this, $(z\Lambda^d)^n h_n/V$. If we absorb a

factor of Λ^d into z then clearly the total number density of monomers in ring polymers is given exactly by the expression for the density of bosons in eq. (3). This well-known mapping of ring polymers onto bosons is called the “classical isomorphism” [9]. It tells us that both systems have *completely equivalent* equilibrium behaviour, and so i) the ring polymer system must undergo the analogue of BEC, and ii) ideal bosons are equivalent to a classical system with self-assembling aggregates.

To locate the phase transition for bosons/ring polymers, let us consider an integer $n_1(V)$ such that $n_1(V) \ll \ell^2(V) \propto V^{2/d}$, as $V \rightarrow \infty$. Then $\vartheta(\pi n/\ell^2) = \ell n^{-1/2} + O(e^{-\pi\ell^2})$ for all $n \leq n_1(V)$, and so we can split the sum of eq. (4), yielding

$$\phi = \frac{1}{\Lambda^d} \sum_{n=1}^{n_1} \frac{z^n}{n^{d/2}} + \frac{1}{V} \sum_{n=n_1}^{\infty} z^n [\vartheta(\pi n/\ell^2)]^d + \epsilon(V), \quad (5)$$

where $\epsilon(V) \rightarrow 0$ as $V \rightarrow \infty$. If we fix $z < 1$ and take the thermodynamic limit then the first sum is less than its value at $z = 1$, $\phi_c = \Lambda^{-d} \sum_{n=1}^{\infty} n^{-d/2}$, and the second sum is zero. When $z > 1$ the first sum is clearly divergent. This implies that all $\phi > \phi_c$ correspond to $z = 1$. Careful analysis of eq. (5) shows [10] that for $\phi > \phi_c$, the density in excess of ϕ_c , *i.e.*, $\phi - \phi_c$, comes from the second sum of eq. (5). This second sum is the contribution of either a macroscopic number of bosons in a single state (the ground state) or a ring polymer of macroscopic size.

We now generalise the preceding theory to describe a whole class of systems with self-assembly. Let us consider monomers which can self-assemble into aggregates, where these aggregates are noninteracting but are otherwise arbitrary. The *internal* partition function of the corresponding aggregates in the new model will differ from that of ring polymers, but density of matter, ϕ , will again be given in terms of the activity, z , through some function $\phi = G(z)$. We will then have a BEC-like transition provided that as z runs over a range $0 \leq z \leq z_c$, the new function takes only values in the limited range $0 \leq G(z) \leq G(z_c)$, and is divergent for $z > z_c$. Furthermore, this phase transition will again occur due to the appearance of macroscopic aggregates.

Let us denote by s the (dimensionless) “size” (volume, surface, length ...) of aggregates, and assume $s_0 \leq s < \infty$. If $\rho(s)$ denotes the number density of aggregates of size s , then the free energy of an ideal mixture of these aggregates is

$$\beta F/V = \sum_{s \geq s_0} \rho(s) [\ln \rho(s) - 1 + f(s) + as] + \rho_0 [\ln \rho_0 - 1 + f_0], \quad (6)$$

where $f(s)$ is the internal free energy of aggregates of size s , with the linear part, as , subtracted off. The second term must be included if aggregates for which $s = 0$ are present (for example, in microemulsions micelles are present which are pure surfactant and do not contribute to ϕ ; see below). In this term ρ_0 and f_0 are the number density and internal free energy of these aggregates. The sum in eq. (6) may be replaced by an integral with only very minor quantitative changes to the behaviour. We will do so when we come to do explicit calculations for microemulsions, for which s may be treated as a continuous variable. Note that ring polymers conform to eq. (6) if s denotes the number of monomers (*i.e.* the dimensionless length), $s_0 = 1$ and $f(s) + as = -\ln[Z^{\text{ring}}(s)/V]$ (the $s = 0$ term is obviously absent).

A microemulsion is an isotropic equilibrium phase composed of water, oil and a surfactant [5, 11]. If there is, say, 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 stabilises the oil droplets dispersed in the water. For microemulsions the sum of eq. (6) is over droplets of different sizes; here s is the reduced volume of a droplet and s_0 is the size of the smallest possible droplet. Micelles, aggregates of pure surfactant, are also present in microemulsions, and as they are pure surfactant they do not contribute to the oil density ϕ . In eq. (6) applied to microemulsions, the second term on the right-hand side accounts for micelles; ρ_0 is the density of micelles. The surfactant is assumed to be restricted to the surface of the droplets and to micelles.

At equilibrium the droplet distribution $\rho(s)$ is given by the minimum of the free energy, subject to the constraints that the total fraction of oil,

$$\phi = \sum_{s \geq s_0} s \rho(s), \quad (7)$$

is fixed, and also that the total amount of surfactant is fixed. Fixing the (reduced) surfactant density ξ requires constraining the sum of the micelle density, ρ_0 , and the $s^{2/3}$ moment of $\rho(s)$. The latter is proportional to the surface area of the droplets per unit volume. This constraint is a single specific example of constrained densities ξ_i of the form

$$\xi_i = c_i \rho_0 + \sum_{s \geq s_0} w_i(s) \rho(s), \quad i = 1, \dots, \nu, \quad (8)$$

where c_i are constants, ρ_0 is a density of a species which contributes to ξ_i but not to ϕ , and $w_i(s)$ are weight functions. Equations (6), (7) and (8) define our model of a system with self-assembly.

Minimising the general free energy, eq. (6), at constant ϕ , eq. (7), under the constraints (8), we obtain the equilibrium densities

$$\rho(s) = e^{-f(s) - \sum_i \lambda_i w_i(s) - \lambda s}, \quad \rho_0 = e^{-f_0 - \sum_i \lambda_i c_i}, \quad (9)$$

where $\lambda = a - \beta\mu$, μ being the chemical potential corresponding to the reduced density ϕ , and λ_i are the Lagrange multipliers corresponding to the constraints (8) (and which are analogous to chemical potentials associated with the fixed densities ξ_i).

Now, if either $f(s)$ or any of the $w_i(s)$ grows faster than s as $s \rightarrow \infty$, then the sum in eq. (7) will converge for *any* value of λ . Furthermore, for *any* set of densities $\{\phi, \xi_i\}$ there will always be a set $\{\lambda, \lambda_i\}$, which will solve eqs. (8) and (7). This means that the free energy will be a smooth function of the densities and no phase transition will occur. Therefore, for a phase transition to occur, it is necessary that a) $f(s), w_i(s) = o(s)$ as $s \rightarrow \infty$. If this condition holds, then the sum in eq. (7) is convergent for $\lambda > 0$ and divergent for $\lambda < 0$. The second condition concerns the limit $\lambda \rightarrow 0^+$. If the sum in eq. (7) diverges in this limit, then again any set of densities will be reachable and no phase transition will occur. Thus, for the transition to appear it is necessary that b) the sum in eq. (7) is convergent for $\lambda = 0$.

If our model fulfills conditions a) and b) in the thermodynamic limit we have that the density ϕ increases to a finite value as λ increases and then suddenly diverges, just as for bosons. Just as with bosons, to study the transition we need to consider explicitly the system size dependence. For this we need to consider a free energy of aggregates which depends on V , *i.e.*, $\ln \rho(s) - 1 + f(s; V) + as$. Now, $f(s; V)$ has to be such that $f(s; V) \rightarrow f(s)$ as $V \rightarrow \infty$, but the convergence cannot be uniform: intuitively, if s is “small” compared to V , then $f(s; V) \approx f(s)$, but if s is “large”, then $f(s; V)$ will differ markedly from $f(s)$. Thus we can always choose a size $s_1(V)$ such that $f(s < s_1; V) \approx f(s)$ and that $s_1(V) \rightarrow \infty$ when $V \rightarrow \infty$. Now, for a finite system no phase transition can occur, so replacing $f(s)$ by

$f(s; V)$ must violate one of the two conditions, a) or b). Condition a) is violated, for instance, when compact aggregates form and the box limits the maximum size of an aggregate. This translates into a sharp increase of $f(s; V)$ at a certain macroscopic size which makes the sum eq. (7) convergent for any value of λ (positive or negative). Case b) is what we have met for ring polymers, for which the finite-size free energy $f(s; V) \sim \ln(Vs)$ as $s \rightarrow \infty$. With this weak s dependence, the sum equation (7) diverges as $\lambda \rightarrow 0^+$. Although there are small differences between the two cases as concerns the finite-size analysis [10], they do not affect the thermodynamic limit itself.

We will report the details of the analysis elsewhere [10], and limit ourselves to describing the resulting phase behaviour. If $\phi < \phi_c$, eqs. (7) and (8) can be solved for λ and λ_i . This yields the densities, eq. (9), as well as the free energy

$$\beta F/V = -\rho - \sum_{i=1}^{\nu} \lambda_i \xi_i + a\phi, \quad (10)$$

with $\rho = \rho_0 + \sum_s \rho(s)$. The phase transition occurs at a density ϕ_c , which is given by setting $\lambda = 0$ in eq. (9) for ρ and inserting the result in eq. (7). When $\phi \geq \phi_c$, the matter in excess of ϕ_c , $\phi - \phi_c$ forms macroscopically big aggregates (the *condensate*), and $\lambda = 0$. The density of non-macroscopic aggregates is then given by eq. (9) with $\lambda = 0$ and $\lambda_i = \lambda_{i,c}$, where $\lambda_{i,c}$ are the solution to eqs. (8) for $\lambda = 0$. In particular, as $f(s)$ increases sublinearly then whenever macroscopic aggregates are present, $\lambda = 0$ and the size distribution of aggregates always decays *slower* than exponentially. Finally, in this regime the free energy has the same form as in eq. (10), but with ρ and λ_i replaced by ρ_c and $\lambda_{i,c}$, the corresponding values for $\lambda = 0$.

Returning to our example of microemulsions, we will explicitly calculate a phase diagram. As mentioned before, s is proportional to the volume. The internal free energy of a droplet has a linear term, as , plus $f(s)$, which comes from the droplet's surface. The surface of the drop can be modeled using a surface tension term plus an elastic free energy of the form introduced by Helfrich [11, 12], which accounts for a preferred curvature of the surfactant layer at the surface of the droplet. The details are given in ref. [10], but, as we might expect, there are three contributions arising from the surface tension (proportional to $s^{2/3}$), the mean curvature (proportional to $s^{1/3}$) and the Gaussian curvature (a constant)⁽¹⁾. Thus we take for $f(s)$

$$f(s) = a_0 - a_1 s^{1/3} + a_2 s^{2/3}, \quad (11)$$

consistent with requirement a) above; $a_1 > 0$, the signs of a_0 and a_2 are not fixed. This expression for $f(s)$ may be inserted in the expression for the free energy, eq. (6), and the sum replaced by an integral; s may be any volume in the range $s_0 \leq s < \infty$. There is a single constraint, that on the surfactant density

$$\xi = c_0 \rho_0 + c_1 \int_{s_0}^{\infty} ds s^{2/3} \rho(s) \quad (12)$$

(c_0 and c_1 are simply geometric factors). Minimising the free energy subject to fixed ϕ and ξ yields the droplet size distribution $\rho(s) = \exp[-a_0 + a_1 s^{1/3} - (a_2 + \lambda_2 c_1) s^{2/3} - \lambda s]$, and

⁽¹⁾ Reiss and coworkers [13] have looked carefully at the function $f(s)$ for microemulsions and found in addition to the terms in eq. (11) a term logarithmic in s . This term essentially accounts for fluctuations of the center of mass of the droplet. Adding such a term to eq. (11) results in a $f(s)$ which still satisfies condition a) for a transition, and thus does not alter the nature of the phase behaviour. It will however shift the phase boundary.

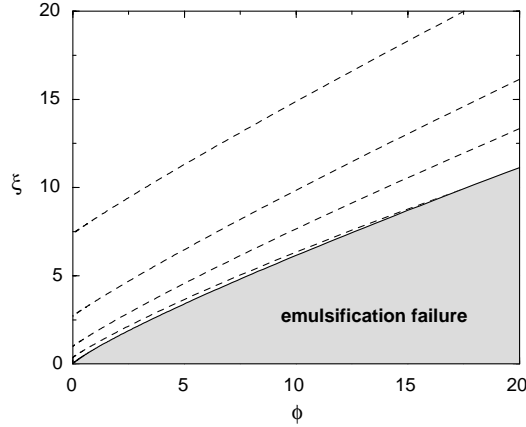


Fig. 1 – Amount of oil in droplets, ϕ , *vs.* amount of surfactant, ξ . In the shaded region a bulk oil phase coexists with the microemulsion (emulsification failure). The solid curve ($\lambda = 0$) signals the phase transition. The dashed curves are at constant micelle density $\rho_0 = e^{-\lambda_2}$. From bottom to top $\lambda_2 = -1, 0, 1, 2$.

density of micelles $\rho_0 = e^{-f_0 - c_0 \lambda_2}$. If $a_2 + \lambda_2 c_1 > 0$ the requirement b) on $f(s)$ also holds and we will have a finite ϕ_c at which a transition occurs. At ϕ_c a macroscopic droplet forms, which is nothing other than a bulk oil phase. So, a bulk phase of excess oil coexisting with the microemulsion phase has formed. This is the so-called *emulsification failure* [7, 8].

To illustrate emulsification failure we take some simple and rather arbitrary values for the parameters of the free energy, namely $a = a_0 = a_2 = f_0 = 0$, $a_1 = c_0 = c_1 = s_0 = 1$, and calculate the phase diagram, fig. 1. At fixed surfactant density ξ there is a maximum oil density ϕ_c beyond which the microemulsion phase coexists with a bulk oil phase. This maximum density increases as the surfactant density increases.

Finally we briefly comment on interaggregate interactions. Their presence will of course affect any transition which is driven by the mechanism outlined in this letter. But in addition, they may induce the transition in systems which in the absence of interactions do not undergo the transition. Zhang *et al.* [14] report evidence of this for a system for which the ideal internal free energy is $f(s) = \text{const}$. There, the *interactions* between the aggregates lead to a size distribution of the form of eq. (9) but with $f(s)$ depending on the density as a result of the interactions, not just arising from an internal free energy [14–16]. If this $f(s)$ satisfies conditions a) and b), there will be a transition induced by the interactions. In other words, interaction may induce a transition analogous to that of *ideal* bosons by inducing an appropriate state-dependent “internal” free energy. A detailed account of this transition in the model of Zhang *et al.* [14] has recently been reported [17].

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 Bose-Einstein condensation 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 [2, 3, 9]. We have shown that the analogy applies to a whole class of self-assembling systems with partition functions which are qualitatively similar, although of a different functional form, to that of ideal bosons/ring polymers. This class is

defined by the requirement that the internal free energy of an aggregate contains a linear term, as , plus others which are sublinear and ensure that the density is finite when the chemical potential $\beta\mu \rightarrow a^-$. We outlined the behaviour of one example here, that of microemulsions. Another example is that of the formation of the lamellar phase, a stack of effectively infinite bilayers of surfactant, which can coexist with small discs of bilayer [18]. This transition, as well as emulsification failure, both occurring in ideal systems, will of course be affected in their details by the presence of interactions between the aggregates. Their influence will, in general, depend on the details of the interactions; nevertheless, we suggest that the effect of interaggregate interactions will be analogous to that of interatomic interactions on the λ transition of liquid ^4He [1], thought to be Bose-Einstein condensation modified by the presence of interactions between the He atoms.

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This work is funded by projects HB1998-0008 (Ministerio de Educación y Cultura and The British Council) and BFM2000-0004 (Dirección General de Investigación, Ministerio de Ciencia y Tecnología, Spain).

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