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Aggregation models at high packing fraction

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Dense phases of micellar aggregates have strong molecular correlation at two different levels: that of the molecules forming a micelle and that between micelles, leading to a possible phase transition from a micellar fluid to a micellar crystal. The global phase diagram may also include lamellar and other dense phases, which do not have a micellar structure. We present here a generic approach to deal with these systems through a two-level density-functional description, to first describe an isolated micellar aggregate and then the dense micellar system, obtaining the free energy in a self-consistent way from the molecular interactions. Nonmicellar dense phases are included with the same density-functional approach applied at the first level. The results are shown to be very accurate for a one-dimensional model with exact solution, and the method is then applied to a three-dimensional amphiphile model that had been successfully used to describe the properties of diluted amphiphile solutions.

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I. INTRODUCTION

Amphiphilic molecules in water solution organize themselves in micellar structures: dropletlike clusters made of $N_m \sim 10^3$ molecules, with their polar heads in the surface and their hydrophobic tails in the interior. The ‘‘critical micellar concentration’’ (CMC) is a quasiphase transition, when the system goes from a diluted solution of single molecules to a diluted solution of micelles, as the loss of entropy and the decrease of the energy to form the micelles are balanced [1,2]. The description of the CMC and the properties of the micellar dilution have been studied with many different models, phenomenological and microscopic [3], to estimate the ‘‘internal’’ Helmholtz free-energy excess F_m, and grand-potential excess, $\Omega_m(T,\mu)=F_m-\mu N_m$, of a single micelle in a bath of amphiphile at a chemical potential μ and temperature T. The concentration of micelles is then predicted to be

$$\rho_m=\frac{1}{v_m}\exp(-\beta\Omega_m), \tag{1}$$

with the usual $\beta=(k_BT)^{-1}$. This expression implies the treatment of the diluted solution of micelles as an ideal gas of particles, with Helmholtz free energy per volume,

$$\beta f_{\mathrm{id}}(\rho_m)=\rho_m[\log(\rho_m v_m)-1+\beta F_m], \tag{2}$$

where F_{in} plays the role of the ‘‘internal energy’’ per particle and the prefactor v_m in Eq. (1) is the ‘‘unit cell’’ volume in the configurational space of position for the micelles. The ‘‘chemical balance’’ between micelles and their component molecules, $\mu_m \equiv \partial f_{\mathrm{id}}(\rho_m)/\partial\rho_m = N_m\mu$, leads directly from Eq. (2) to Eq. (1).

There has been some confusion about the value of v_m and its dependence on the micellar size, but the dependence of ρ_m on T and μ is given mainly by the exponential factor in Eq. (1), so that the CMC is associated to the vicinity of the line $\Omega_m(T,\mu)=0$ in the thermodynamic space. In a previous paper [4] we analyzed a simple model in one dimension (1D), which presented some qualitative features in common with amphiphilic systems: the existence of molecular aggregates with a well-defined preferential size and structure, as the result of pair molecular interactions and internal degrees of freedom. The model has an exact solution for the equilibrium properties, and the results were compared with those given by approximations that are feasible to use with more realistic models. The main result was a prescription for the prefactor v_m, consistent with the approximation used to calculate F_m,

$$v_m=\Gamma\exp\left(-\beta\frac{F_m-E_m}{N_m}\right), \tag{3}$$

where E_m is the cohesion energy of a micelle, i.e., its internal energy excess, and Γ is the unit cell volume used to measure the configurational phase space in F_m. Although the prefactor Γ in Eq. (3) is a convenient way to give v_m its units of volume, it was shown [4] that v_m, and ρ_m in Eq. (1), are independent of the value of Γ; as it should be for any structural property in classical statistical mechanics [5]. The excess free energy F_m has always a dependence on Γ, with the form $kTN_m\log(\Gamma)$, which cancels out that prefactor. In the following results for βF_m, βf_m, and $\beta\mu$ we have taken $\Gamma=\sigma$ for the 1D model and $\Gamma=\sigma^3$ for the 3D model.

In this paper we address the question of the ‘‘dense phases,’’ in which the density of aggregates ρ_m, becomes too large to neglect their interactions. The treatment of the system in terms of the micellar density may still be appropriate, but with a Helmholtz free energy

$$f(\rho_m)=f_{\mathrm{id}}(\rho_m)+\Delta f(\rho_m), \tag{4}$$

including the excess Δf over the ideal-gas contribution (2). The main contribution of the interaction to the free energy comes from the excluded volume, which may be included by treating the micelles as hard bodies. With such free energy we should be able to describe dense micellar fluids and their phase transition to micellar crystals. The thermodynamic stability of these dense micellar phases has to be compared with other condensed structures, in which the molecules do not keep the micellar organization: lamellar and hexagonal phases may be regarded as packed structures of two- and one-dimensional aggregates, respectively, while bicontinuous or inverse-micelle structures cannot be decomposed in independent elements.

As a first step we analyze here the results of a simple 1D model, which share some qualitative features with these complex systems. Our aim is to test the accuracy of this statistical mechanics description at two separated levels of structure: the molecular level, with the molecules building up the micellar aggregates, and the level of the micellar correlation structure. We then use the same procedure to study a 3D continuous model for a system of amphiphilic molecules in water [6]. This minimal model considers only the distribution of the amphiphile, without internal degrees of freedom other than the orientation of the head-tail direction. The model contains the essential features to represent different types of molecular aggregates [6] (planar bilayer membranes, bilayer vesicles and micelles); it gives a good description of the elastic constants [7] and also of the properties of mixed surfactant systems [8]. The density-functional treatment checked in 1D allows us to obtain the global phase diagrams, in terms of the parameters used to model the molecular interactions.

II. THE 1D MODEL

Our 1D model is an extension of that used to explore the CMC at low density [4], and based on previous models for associating 1D fluids [9,10]. The molecules move along the X axis, with coordinates $x_{i+1} > x_i$ kept in order by hard-core repulsions, and they have an internal variable ξ_i, taking integer values from 0 to m. The molecular hard core has length σ_0 when the internal variable is $\xi = 0$ and larger length σ otherwise. There is a soft interaction potential between neighbor molecules, with relative position $x \equiv x_i - x_{i+1}$ and with internal variables ξ_i, ξ_{i+1} with the form:

$$\phi(x) = \frac{4C}{\Delta^2}(x-\sigma)(x-\sigma-\Delta), \tag{5}$$

if $\sigma \leqslant x \leqslant \sigma + \Delta$ and $1 \leqslant \xi_i = \xi_{i+1} - 1 \leqslant m-1$, and null otherwise. This potential energy acts only between molecules with consecutive values of the internal variable and it has a minimum value $-C$, when the molecules are separated by a distance $x = \sigma + \Delta/2$ (with $\Delta \leqslant \sigma$). This produces an optimal cluster formed by m rods, with internal variables $\xi_k = 1$, $\xi_{k+1} = 2, \ldots, \xi_{k+m-1} = m$. The noncyclic character of the internal variable prevents the growth of clusters beyond this size (see Fig. 1). The internal variable value $\xi = 0$, which has the best packing efficiency, is excluded from these clusters.

A. The exact solution

We explore the low-temperature behavior of the model, with $\beta C \gg 1$. At low density the packing constrains are irrelevant and the model reproduces the behavior obtained in our previous paper [4], with a CMC-like smooth transition from a very diluted 1D gas of uncorrelated rods (with random values of the internal variable ξ), to an ideal gas of aggregates made by m rods with ordered values of ξ. This CMC, defined as the concentration where there are as many isolated molecules as molecules forming parts of micelles, is located around the chemical potential $\mu = -C - kT \log[\pi\Delta^2/(4\beta C)]$ and is independent of the hard-core size. At intermediate densities the packing constrains between the aggregates become important, but their internal structure is maintained: the system becomes a dense 1D fluid made of m-rod aggregates. Their optimal structure needs a separation of about $m\sigma + (m-1)\Delta/2$ between two aggregates, the effective interaction between aggregates being a soft repulsion since the aggregates may be compressed beyond their optimal structure, at the price of reducing their cohesive energy. Moreover, there is a qualitatively different state, formed by molecules with internal variable $\xi = 0$, which has to become relevant at high density, because it reduces the hard-core length to $\sigma_0 < \sigma$.

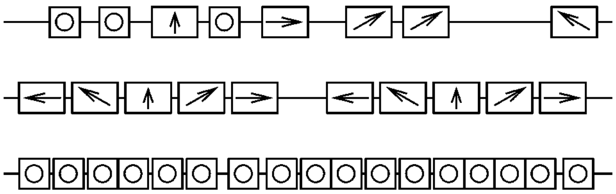

FIG. 1. Sketch of particular configurations of our 1D system for $m=5$. The circle indicates that the molecule has an internal variable $\xi = 0$ and the arrows indicate the other five possibles values of ξ. On upper: a diluted gas. On middle: fluid of micelles (formed by rods with ordered internal variables, going from 1 to m). On lower: the dense phase.

We may compare the system with a solution of amphiphilic molecules in water. At low concentration there is a CMC, where the system changes from an ideal solution of molecules (with random positions and orientations) to an ideal solution of micelles (formed by molecules with strongly correlated positions and orientations). Increasing the concentration, the system behaves as a dense fluid of micelles, and at still higher concentration the packing of the spherical micelles becomes too inefficient and the system changes to a qualitatively different molecular organization, like a lamellar phase. This is represented in our model by the tendency to ''align'' the molecules along the $\xi = 0$ ''direction,'' breaking the micellar structure and creating a dense phase with a qualitatively different structure, as sketched in Fig. 1.

In the isothermal-isobaric ensemble the chemical potential of the model is exactly given by $\beta\mu(T,p) = \log(\lambda_{\max})$, where $\lambda_{\max}(T,p)$ is the largest eigenvalue of transfer matrix $\mathcal{M}$, with elements given by the Laplace transform

$$\mathcal{M}_{\xi,\xi'} = \int_{\sigma(\xi,\xi')}^{\infty} dx \exp\{-\beta[px + \phi(x)\delta_{\xi'\xi+1}]\}, \tag{6}$$

where $\sigma(\xi,\xi')$ is the minimum distance between neighbor rods with internal variables ξ and ξ' (i.e., the half-sum of the ξ-dependent hard-core lengths).

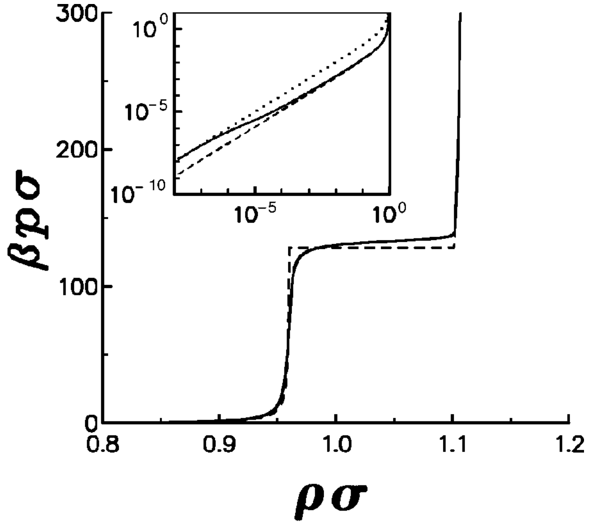

FIG. 2. Equation of state of our 1D model, for $\beta C=20$, $\Delta=0.1$, and $\sigma_0/\sigma=0.9$. The pressure p and the density ρ are presented in dimensionless form with the appropriate factors of $\beta=(k_BT)^{-1}$ and σ. The solid line is the exact result, the dashed line is a mean-field approximation. The inset shows the CMC region, at which the system goes from an ideal gas of rods (dotted lines) to an ideal gas of micelles (dashed lines) on increasing the density.

The exact equation of state, for $\beta C=20$, $\Delta=0.1$, and $\sigma_0/\sigma=0.9$, is presented in Fig. 2. As expected, our 1D system has no phase transition, the changes between the different molecular arrangements are gradual. The CMC is located around a density $\rho_{\mathrm{CMC}}\approx 10^{-5}\sigma^{-1}$, and it has the same characteristics as described in our previous paper [4], because the changes in the hard-core size are irrelevant at low density. The exact correlation structure in the system may also be obtained and shows that for $10^{-4}<\rho\sigma<0.95$ most molecules form micelles and the structure of these micelles is very close to the optimal aggregate: consecutive values of ξ_i, from 1 to m, and a neighbor distance close to $\sigma+\Delta/2$. At intermediate densities there is an increasing tendency, due to the packing effects, to compress the micelles (giving shorter intermolecular distances) and to have neighbor molecules with the same value of the internal variable, so that they cannot form part of a perfect micelle. With the parameters given above, these effects produce the shoulder shown in Fig. 2, with a rather flat region for $\beta p\sigma\approx 130$. We may interpret this plateau as the 1D signature of what in higher dimension could be a first-order phase transition between a dense micelle fluid and a crystalline phase with a long-range-order very different from the molecular order in the micelles. At the lower border of the plateau, $\rho\sigma\approx 0.95$, the correlation structure shows that most molecules form part of a micelle, while at the high-density end, $\rho\sigma\approx 1.1$, most of the molecules form part of ''lamellar'' clusters, large groups of molecules with the same value of the internal variable, $\xi=0$. Along the plateau we find the two kinds of correlation structures combined in different amounts.

Changing the values of the parameters βC, Δ, and σ_0/σ changes the location and the size of the plateau but with the same interpretation as a quasiphase transition between two phases with very different structures. For more realistic models in three dimensions we could expect a true phase transition, or even series of phase transitions, between the micellar fluid and some kind of hexagonal or lamellar phases. On the other hand, no exact result would be available for the models, so that we should rely on approximate treatments.

B. The mean-field treatment

We try now the description of the same one-dimensional model within a mean-field density functional (MF-DF) approach [6] that may be used for more realistic models of amphiphilic molecules, for which no exact solution is available. The idea is to describe the molecular aggregates by the local minima of the grand-potential energy, $\Omega=F[\rho]-\mu N$, where $F[\rho]$ is a density-functional approximation that includes the short-range molecular correlation structure but not the many-body long-ranged correlations required to describe the ''micellar'' aggregates in an exact analysis of the system. There is always a local minimum of Ω given by a homogeneous background density, $\rho_0(\mu)$, which represents the diluted solution of uncorrelated molecules, with $\rho(x,\xi)=\rho_0/(m+1)$. For values of the chemical potential near the CMC and higher, we may find other local minima representing self-maintained local inhomogeneities, with a density distribution $\rho(r)$ going asymptotically to ρ_0 but with an excess number of particles, N_m, and free energy, F_m, which corresponds to the MF-DF description of the molecular aggregates. The system is then analyzed with a ''second level'' of statistical mechanics, including the entropy associated to the location of the micelles, which was not included in the MF-DF description.

Our 1D model is treated with the Helmholtz free-energy functional of the local density of particles with each possible value of the internal variable,

$$F[\rho(x,\xi)]=F_{\mathrm{hr}}[\rho]=\sum_{\xi=1}^{m-1}\int_{-\infty}^{\infty}dx\int_{x+\sigma}^{x+\sigma+\Delta}dx'\times\phi(x'-x)\rho(x,\xi)\rho(x',\xi+1), \tag{7}$$

where $F_{\mathrm{hr}}[\rho]$ is the exact DF of the hard-rod mixture fluid and the second term is the mean-field approximation for the attractive interactions.

At low temperature and background density, $\rho_0(\mu)\ll 1$, the local minima of this free-energy density functional are well represented within the variational family:

$$\rho(x,\xi)=\frac{1}{m+1}\rho_0(\mu)+\sum_{i=1}^{m}\delta_{\xi,i}\left(\frac{\alpha_i}{\pi}\right)^{1/2}\exp[-\alpha_i(x-x_i)^2] \tag{8}$$

with $N_m=m$ and where the Kronecker delta ensures that each Gaussian peak is made of molecules with the correct value of ξ to build a ''micelle.'' Within this variational approach the results for F_m and v_m are analytic and independent of the chemical potential:

$$\beta F_{mn}=-(m-1)\beta C+\frac{m}{2}\log\left[\frac{8\beta C}{\pi\Delta^2}\right]-\log(2) \tag{9}$$

and

$$v_m=2^{1/n}\sqrt{\frac{\pi e\Delta^2}{8\beta C}} \tag{10}$$

leading to a prediction of the CMC close to the exact result, as in our previous paper [4]. To extend the MF-DF treatment to the dense ‘‘micelle fluid,’’ we may represent the micelle-micelle interaction by an effective hard core with the same second virial coefficient as the interaction potential between two micelles, which gives

$$\sigma_m = m\sigma + \frac{m-1}{2}\Delta\left[1-\sqrt{\frac{\pi}{4\beta C m}}\right], \tag{11}$$

where the term in brackets takes into account that the compression of the ‘‘micelles’’ may reduce their effective size to a length slightly shorter than the optimal size.

This representation of the micellar interactions as hard cores leads to a simple form for the free energy of a micellar fluid:

$$\beta f_m(\rho_m) = \rho_m[\log(\rho_m v_m) - 1 + \beta F_m - \log(1-\rho_m\sigma_m)], \tag{12}$$

which recovers Eq. (2) in the diluted regime (when $\rho_m\sigma_m \ll 1$) but also includes the main effects of the repulsion between micelles. The equation of state for the micellar fluid, above the CMC, is then given by

$$\beta p_m = \frac{\rho_m}{1-\rho_m\sigma_m} \tag{13}$$

and the comparison with the exact equation of state (Fig. 2) gives a very good agreement up to densities around 0.96σ, including the sharp rise of the pressure when the total density approaches the nominal maximum within the approximation, $\rho = m\rho_m \to m/\sigma_m$, at which the micelles would be fully packed. In the exact result we may reach higher densities by compressing the micelles beyond their optimal size or having molecules with internal variable $\xi = 0$, which cannot form part of micelles but have a shorter hard-core length σ_0. The later type of configurations may also be found within the MF-DF free energy (7) as a homogeneous dense phase in which all the molecules have $\xi = 0$ so that it behaves as a hard-rod fluid, which has lost the entropy associated to changes of the internal variable ξ and also the binding energy associated to the formation of micelles but has gained entropic stability by the reduction of the hard cores. The free energy for this ‘‘lamellar’’ phase in our model is obtained from the same free-energy density functional (7) with the density distribution $\rho(x,\xi) = \delta_{\xi,0}\rho$:

$$\beta f_1(\rho) = \rho[\log(\rho\sigma) - 1 - \log(1-\rho\sigma_0)] \tag{14}$$

and the equation of state is

$$\beta p_1(\rho) = \frac{\rho}{1-\rho\sigma_0}. \tag{15}$$

Within the MF-DF description the ‘‘micellar fluid’’ and the ‘‘lamellar’’ phase are separated thermodynamic phases (as they would indeed be in a real 3D amphiphilic system), and the phase transition between them is found by the usual double tangent construction between the free energies $f_m(m\rho)$ and $f_l(\rho)$, as given in Eq. (12) and Eq. (14). Figure 3 compares the exact free energy per unit length with the approximations $f_m(m\rho)$ and $f_l(\rho)$ in the intermedium and high-density regimes, respectively. The result shows that $f_m(m\rho)$ is an excellent approximation to the exact $f(\rho)$ up to $\rho\sigma \approx 0.96$ while $f_l(\rho)$ is indistinguishable from the exact results for $\rho\sigma \lesssim 1.1$. In the region between these two values both $f_m(m\rho)$ and $f_l(\rho)$ separate from the exact $f(\rho)$ but the double tangent straight line between the two approximations remains very close to the exact result. The results of the approximation for the equation of state are also presented in Fig. 2; the nearly flat plateau presented by the exact pressure is approximated by the phase coexistence between the dense ‘‘micellar’’ fluid and the denser ‘‘lamellar’’ phase.

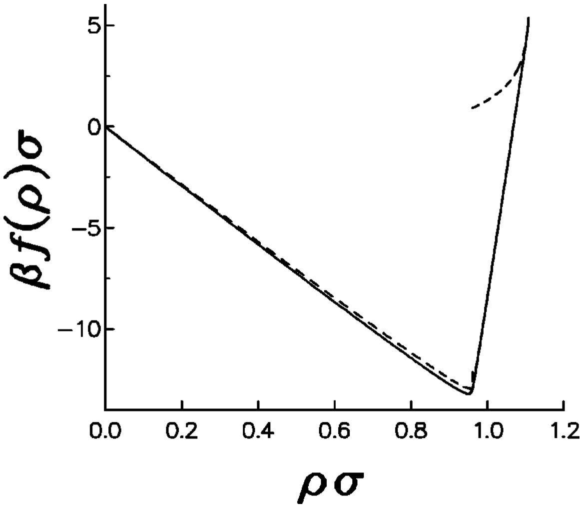

FIG. 3. Dimensionless free-energy density of our 1D model. Solid line: exact result. Dashed lines: mean-field approximation for the ‘‘micellar’’ phase (at low densities) and the ‘‘dense phase,’’ both joined by a double-tangent construction (indistinguishable from the exact result at this magnification).

There is clearly a good agreement between the general trend shown by the exact result and the combined results of the MF-DF approach. The later includes two different descriptions for the ‘‘micellar’’ fluid and the ‘‘lamellar’’ phase. The ‘‘micelles’’ are studied through a ‘‘two-levels’’ statistics; at the first level an isolated molecular aggregated is represented by the local minima of the mean-field density functional $F[\rho]$, to give its microscopic structure, excess free energy, number of molecules, and size. At the second level of the statistics we include the entropy associated to the location of the aggregates (including their packing constraints). On the other hand, the ‘‘lamellar’’ phase is studied directly at a ‘‘one-level’’ statistics, as a macroscopic phase described with the same free-energy functional $F[\rho]$. The mixture of the two description levels, to get the overall behavior of these systems, is the underlying idea in the description of amphiphilic systems with most phenomenological theories [3], however, in any practical implementation of those approaches there are always uncertainties related to the separation of degrees of freedom for the two levels of statistics. The MF-DF gives a self-consistent approach to the problem, with a clearly cut level of approximation at the first level and a consistent recipe for the link between the two levels, through the parameters F_m, v_m, and σ_m. The simple 1D model used here presents qualitative features similar to those of real amphiphilic systems, and its exact solution allows the direct test of these recipes. In the next section we use the approach for a more realistic 3D model of amphiphilic systems.

III. THE 3D MODEL

As in the 1D mean-field treatment, our 3D approach [6] describes the microscopic or mesoscopic molecular aggregates in water as inhomogeneous density distributions, treated within the density-functional formalism and using an approximation for the Helmholtz free-energy density functional, $F[\rho]$, based on an effective molecular interaction model. The model effective interaction should include both effects: the solvatation forces induced by the water and the changes in the entropy associated to the configurations of the flexible tails. We proposed a uniaxial effective pairwise potential, with the head-tail asymmetry described by a unit vector $\hat{\mathbf{u}}_1$ along the molecular axis, which is written as

$$\Phi(\mathbf{r}_2-\mathbf{r}_1,\hat{\mathbf{u}}_2,\hat{\mathbf{u}}_2)=\Phi_{\mathrm{hs}}(r_{21})+\Phi_a(\mathbf{r}_2,\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2). \tag{16}$$

As the simplest choice of a repulsive isotropic interaction, which only depends on the distance between the molecular centers, $r_{21}=|\mathbf{r}_{21}|=|\mathbf{r}_2-\mathbf{r}_1|$, we take it to be the hard-sphere potential, $\Phi_{\mathrm{hs}}(r)$, with a sphere diameter, σ (which we take as the unit length). The anisotropic part may be written as a general expansion in spherical harmonics. In our case we include only the two first terms which do not couple the orientation of the two molecules,

$$\Phi_a(\mathbf{r}_{21},\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2)=\sum_{i=1,2}\Phi_i(r_{21})\times[P_i(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{r}}_{21})+P_i(-\hat{\mathbf{u}}_2\cdot\hat{\mathbf{r}}_{21})], \tag{17}$$

where $\hat{\mathbf{r}}_{21}=\mathbf{r}_{21}/r_{21}$ and $P_i(x)$ are the Legendre polynomials. The first coefficient function of the anisotropic part was taken as an empty core Yukawa potential,

$$\Phi_1(r)=\frac{C}{r}\exp[-\lambda(r-\sigma)]$$

for $r\geqslant\sigma$ and null inside the hard core, $r<\sigma$. The second coefficient function in Eq. (17) is taken to be proportional to the first, $\Phi_2(r)=q\Phi_1(r)$. Thus, the model has three free parameters, C, λ, and q to represent the molecular interactions. As we have shown in our previous paper these parameters may be tuned to represent different properties: the dimensionless parameter βC may be regarded as the inverse temperature or as the representation of a series of different amphiphiles studied at fixed room temperature; the parameter λ controls the number of molecules in the micelles; finally, the main effect of the parameter q is that $q>0$ favors the bilayer structures with respect to the micellar structures, which are more stable for $q=0$. All the results presented here are for $\lambda\sigma=2$, $q=0.3$, and the $\beta C=6.3885$ isotherm.

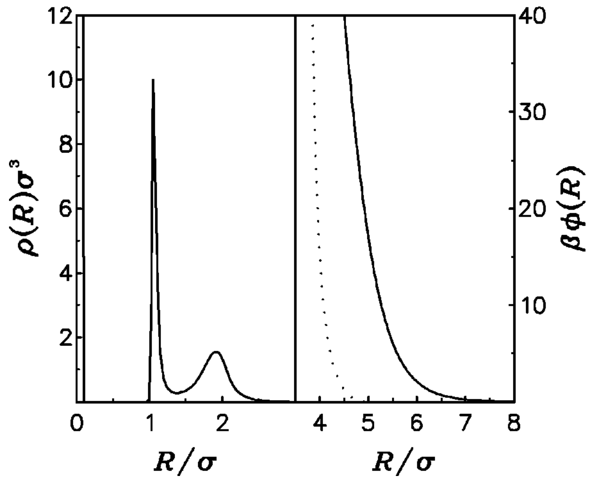

FIG. 4. On the left-hand side the typical micellar density profile obtained for $\beta\mu=-6.2$ in the neighborhood of the CMC. On the right-hand side the effective interaction potential between micelles. Dotted line: free-energy excess coming from the hard molecules core. Full line: full potential including the solvatation force from the soft anisotropic interactions.

The Helmholtz free-energy density functional is approximated by

$$F[\rho(\mathbf{r},\hat{\mathbf{u}})]=F_{\mathrm{hs}}[\rho(\mathbf{r})]+k_BT\int d\mathbf{r}_1 d\hat{\mathbf{u}}_1\rho(\mathbf{r}_1)\alpha(\mathbf{r}_1,\hat{\mathbf{u}}_1)\times\log[4\pi\alpha(\mathbf{r}_1,\hat{\mathbf{u}}_1)]+\frac{1}{2}\int d\mathbf{r}_1 d\hat{\mathbf{u}}_1 d\mathbf{r}_2 d\hat{\mathbf{u}}_2\rho(\mathbf{r}_1,\hat{\mathbf{u}}_1)\times\rho(\mathbf{r}_2,\hat{\mathbf{u}}_2)\Phi_a(\mathbf{r}_{21},\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2). \tag{18}$$

The first term is the density functional for the hard-sphere fluid; it depends on the density distribution, $\rho(\mathbf{r})$, and it is approximated by a well-tested nonlocal density functional [11]. The second term is the rotational entropy and the third one is the mean-field contribution of the anisotropic interactions; they depend on the position and molecular orientation distribution, $\rho(\mathbf{r},\hat{\mathbf{u}})$, with $\alpha(\mathbf{r},\hat{\mathbf{u}})\equiv\rho(\mathbf{r},\hat{\mathbf{u}})/\rho(\mathbf{r})$.

The grand free energy $\Omega[\rho(\mathbf{r},\hat{\mathbf{u}})]$ always has a local minimum for a homogeneous density distribution, in which our model follows the thermodynamics of a hard-sphere system. At low temperature and density there appear other local minima: self-maintained local inhomogeneities, with sharp oscillatory density distribution, $\rho(r)$, and orientational distributions that are qualitatively comparable with the layering and orientations of the real membranes and micelles.

We first study the diluted regime, without interactions between the aggregates, as done in previous papers [4,6]. With the model parameters given above, the minimization of $\Omega=F-\mu N$ gives a local minimum with spherical symmetry, whose radial density distribution is given in Fig. 4(a). As discussed in previous papers, this inhomogeneous density distribution represents a micelle with the molecular hydrophobic tails pointing towards the origin. The excess number of molecules over the diluted bulk density is $N_m\approx 47$, and it has excess internal energy $\beta E_m\approx -536$ and Helmholtz free energy $\beta F_m\approx -291$, with little variations with the chemical potential around $\beta\mu\approx -6$. The configurational unit volume is estimated by Eq. (3) to be $v_m=\exp(-5.2)\sigma^3=0.0055\sigma^3$ and the CMC is predicted for chemical potential $\beta\mu=$

-6.5. At the same isotherm there is a local minimum of $\Omega = F-\mu N$ with planar symmetry that represents a bilayer membrane [6], which would become stable (i.e., with zero excess grand potential) at chemical potential $\beta\mu\approx -5.3$. However, the presence of the CMC at lower $\beta\mu$ pre-empts the formation of free bilayer membranes in the diluted regime, because before reaching this value $\beta\mu$, the system would become a dense micellar fluid and the steric effects between the aggregates have to be included.

The micelle-micelle interaction has two different contributions, coming from the two terms in the molecular interactions (16). The first one describes the direct steric repulsion between amphiphile molecules while the second one represents the solvation forces in the water bath. The later produces an effective soft-repulsive potential between two micelles, which may be calculated (always in the mean-field approximation) from the the density distributions of the aggregates as

$$\begin{aligned}\Phi_{AB}(r) &= \tfrac{1}{2}\int d\mathbf{r}_1 d\hat{\mathbf{u}}_1 d\mathbf{r}_2 d\hat{\mathbf{u}}_2 \\ &\quad\times \rho(\mathbf{r}_1,\hat{\mathbf{u}}_1)\rho(\mathbf{r}_2,\hat{\mathbf{u}}_2)\Phi_a(r',\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2) \\ &= \sum_{k=1,2,}\int d\mathbf{r}_1 d\hat{\mathbf{u}}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1,\hat{\mathbf{u}}_1)\rho(\mathbf{r}_2)\phi_k(r') \\ &\quad\times P_k(r')P_k(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{r}}'),\end{aligned}$$

where $\mathbf{r}'=\mathbf{r}_2+\mathbf{r}-\mathbf{r}_1$. This potential is shown in Fig. 4(b), together with the free-energy excess coming from the hard molecular cores, as a function of the distance between the centers of the two micelles. Clearly, the effective micelle-micelle interaction is dominated by the solvation forces, which create a soft repulsion between micelles at distances beyond direct hard-core molecular contact between the two aggregates.

The excess free energy $\Delta f(\rho_m)$ in Eq. (4) produced by this soft-repulsive potential may be approximated by an effective hard core with diameter σ_m, as usually is done in the theory of simple liquids [12]. We have employed the Barker-Henderson choice to determine a hard-sphere diameter independent of the density, which in the explored isotherm is $\sigma_m=6.6\sigma$. The excess free energy Δf is then given by the Carnahan-Starling approximation [12], with a packing fraction $n_m=\rho_m\pi\sigma_m^3/6$.

With the data for F_m and v_m in Eq. (2), and the choice of σ_m for Δf, the free energy of the micellar fluid (4) is completely determined and we get the total amphiphile density $\rho_t=N_m\rho_m+\rho_b$ and the pressure, p, as functions of the chemical potential, shown in Figs. 5 and 6. The sharp increase of both ρ_t and p at $\beta\mu\approx -6.5$ shows the CMC as a quasiphase transition, with a large increase of the total concentration for very small changes in the chemical potential. When the micelle packing fraction reaches the value $n_m=0.49$ the hard-sphere fluid, representing the micelles, would crystallize in the fcc structure. The equation of state has to be changed from the the Carnahan-Starling approximation, valid for the fluid, to one of the available approximations for the hard-sphere crystal [13]. The transition from the dense micellar fluid to the micellar fcc crystal is a first-order phase transition represented by the small jump in the total density at $\beta\mu=-6.1$ in Fig. 5. The pressure calculated for the solid phase in Fig. 6 becomes larger than that of the fluid at the same chemical potential, indicating that the solid phase is stable with respect to the micellar fluid.

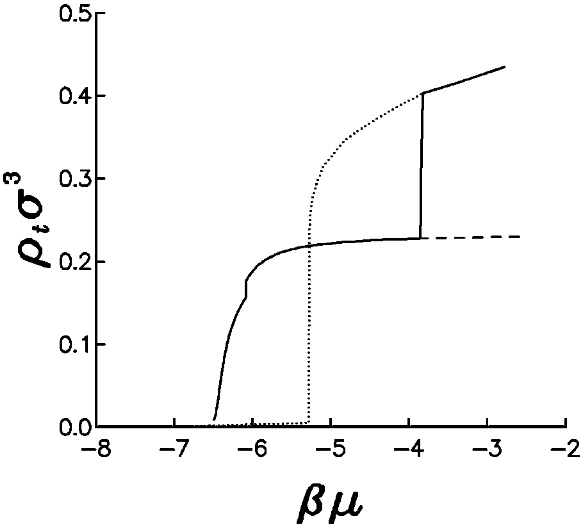

FIG. 5. Equation of state of our 3D model: total density versus chemical potential. The solid line follows the density of the equilibrium phase: micellar fluid, micellar solid, and lamellar phase, with vertical jump at the first-order phase transitions. Dotted line: metastable lamellar phase. Dashed line: metastable micellar crystal.

We now turn to study a dense phase that does not have micellar structure. This is the lamellar structure made by stacking planar bilayer membranes in a periodic structure along one direction. As commented above, the critical aggregation concentration CAC for the formation of free bilayer membranes was, for our present choice of the temperature and the molecular interactions, at higher concentrations than the CMC. We extend the search for inhomogeneous structures minimizing $\Omega=F-\mu N$ with the density-functional

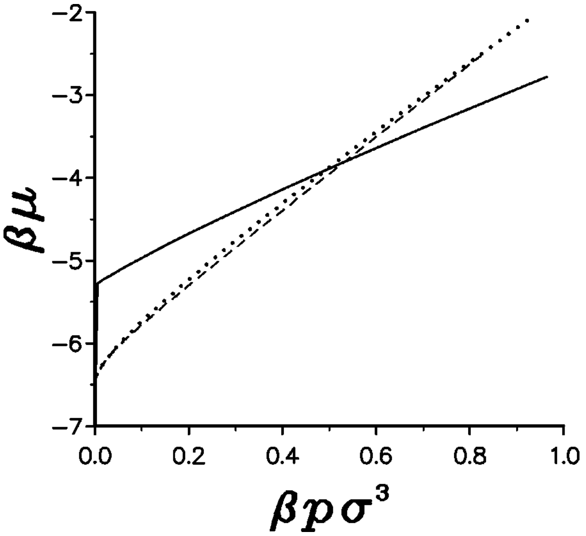

FIG. 6. Chemical potential vs pressure phase equation of state. Solid line: lamellar phase. Dotted line: micellar fluid. Dashed line: micellar crystal. The equilibrium phase is always the lowest line. Note that on the scale of the figure the range of the stability of the fluid is very narrow, around $p=0$.

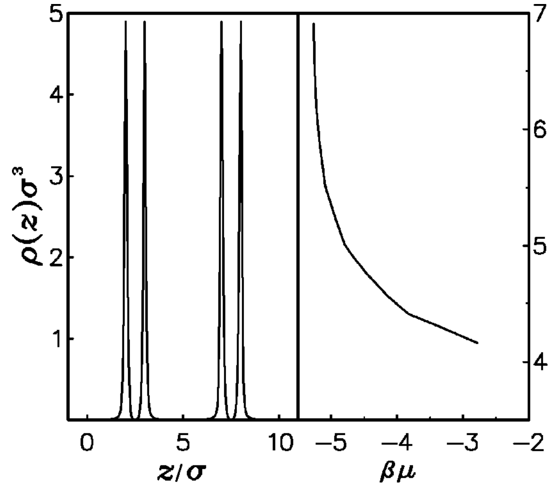

FIG. 7. On the left-hand side the typical lamellar density profile obtained for $\beta\mu = -4.8$ with lamellar period $P_L = 5\sigma$. On the right-hand side the variation of the lamellar period P_L, with the chemical potential.

free energy (18) beyond the diluted limit of isolated bilayers, to find periodic structures, like that shown in Fig. 7(a), with a period which decreases as $\beta\mu$ increases. The CAC in the diluted regime, at $\beta\mu \approx -5.3$ corresponds to the divergence of the period in Fig. 7(b), and as $\beta\mu$ increases, the compressibility of the lamellar phase decreases giving a flatter curve, in qualitative agreement with experimental results for neutral (uncharged) and isoelectric lipids [14]. The equation of state of this lamellar phase is obtained directly from the free-energy functional (18), without need of the second step of statistics done for the micelles, and shown in Figs. 5 and 6 to compare with the later. Figure 5 shows than the density of the lamellar phase increases very sharply at the CAC, $\beta\mu \approx -5.4$, and it immediately reaches a density higher than the micellar phases at the same chemical potential. However, the pressure of the lamellar phase, Fig. 6, remains below that of the micellar crystal up to $\beta\mu \approx -3.8$; at this crossing point in the figure there is a first-order phase transition from the micellar crystal to the lamellar phase, with a large increase in the density, as indicated in Fig. 5. This transition is driven by the balance between the optimal aggregation of the amphiphile in micelles (rather than in bilayer membranes) indicated by having the CMC lower than the CAC, and the packing efficiency of the planar bilayers, which is much higher than that of the spherical micelles. The representation of the lamellar phase directly from the density functional (18), instead of the two consecutive levels used for the micellar fluid, is equivalent to what has been done and tested in the simple 1D model of Sec. II for the dense ordered phase, and we may expect that the approach should be even more accurate in this 3D case, as the global role of the correlations should become less important in higher dimension.

The sequence from low to high densities in our model is then: isolated molecules ($\mu < -6.5$)—micellar liquid ($\mu < -6.1$)—micellar crystal ($\mu < -3.8$)—lamellar ($\mu > -3.8$) phase. The last two transitions are true, first-order, thermodynamic transitions, unlike the first one (the CMC), which is a quasitransition. This sequence maps qualitatively very well with experimental results, Nevertheless, there are several points that would require future attention: the effective micelle-micelle interaction potential in Fig. 4(b) is much softer that the repulsive part of the usual model potentials for simple liquids, so that the description in terms of an equivalent hard-sphere fluid may be less accurate. Using other approaches (like the method of Weeks, Chandler, and Andersen [12]) to fix the effective hard-sphere diameter, does not produce important changes in the predictions in the micellar fluid, but its crystallization may be more affected, including the possible existence of a bcc lattice. Moreover, there are other possible dense phases that should be considered to get the global phase diagram, in particular the hexagonal phase made by two-dimensional packing of cylindrical micelles is very likely to appear between the micellar and the lamellar phases. In the diluted regime our model has local minima of Ω with cylindrical symmetry and with the main characteristics of the cylindrical micelles, although they are usually found to be stable at higher concentrations, intermediate between the CMC for spherical micelles and the CAC for the bilayer membranes. Their packing efficiency should also be intermediate between spheres and planes, so that the hexagonal structure may well be a stable phase for our simple model, as it is in real amphiphiles. The free energy of this and other possible dense phases may in principle be obtained from Eq. (18), exactly in the same way as done for the lamellar phase, i.e., direct minimization of the grand-potential energy with the relevant symmetry. The only difficulty is purely technical; the density distribution of the lamellar phase depends only on one coordinate, while that of the hexagonal phase would depend on two variables, and other possible phases like bicontinuous structures would have three-dimensional unit cells. The minimization of Ω for these phases would require a higher computational effort than for the lamellar phase but it would be similar from the fundamental point of view.

IV. CONCLUSIONS

We have described a microscopic approach that can be used to determine the global phase diagram of amphiphilic systems. It combines two levels of description for the micellar phases and one level for the dense amphiphilic structures. We have first compared the results of this approach to the exact results of a 1D CMC model. We have then considered a minimal 3D model that had been used before to study the diluted amphiphile solutions. The conclusions of the present paper are twofold; first to show that the simple molecular interaction model [Eqs. (16)–(18)] captures the main features of real amphiphilic systems, with the formation of micelles at a low CMC, and the transition to other dense phases as the poor packing efficiency of these spherical structures makes them unfavorable. This is a typical problem in soft-condensed matter, with two levels of molecular organization playing relevant roles at the same temperature, and it is interesting to find simple models with the same behavior. The molecular interaction parameters in our model may be qualitatively associated to the main features of real amphiphiles, thus the parameter C corresponds roughly to the lengths of the hydrophobic tails, so that at fixed temperature the CMC decreases exponentially with increasing C, and the parameter q gives a measure of the size ratio between those tails and polar heads: low values of q produce stable micelles and higher values produce stable bilayer membranes in the diluted regime. The study of dense phases within the model should show whether the global phase diagrams of the model are similar to those observed experimentally and how they depend on the molecular interactions.

The second conclusion of this paper is to validate the proposed approach to study the dense micellar phases with a consistent two-levels approximation from a mean-field density functional. The comparison with the exact results in the simple 1D model and the application to the 3D model show that the approach is both accurate and computationally feasible. Clearly the approach may be extended to more realistic models of amphiphilic molecules and copolymers, taking into account flexible tails or nonspherical hard cores. The estimation of the configurational unit volume for the micelles (3), and the mean-field effective interaction between them [Eq. (19)] are employed consistently with the free-energy functional used to obtain the structure of a single aggregate and the thermodynamics of other dense phases, without reference to any empirical parameter beyond those in the molecular interaction model. In this respect, one could also use a theory different from the MF-DF one, like the self-consistent field theory for polymers, which has been recently applied to dense amphiphilic systems [15] and apply the same two-level approach to the micellar phases and the one-level description for the hexagonal, lamellar, or bicontinuous phases.

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