Exact results and mean field approximation for a model of molecular aggregation

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We present a simple one-dimensional model with molecular interactions favouring the formation of clusters with a defined optimal size. Increasing the density, at low temperature, the system goes from a nearly ideal gas of independent molecules to a system with most of the molecules in optimal clusters, in a way that resembles the formation of micelles in a dilution of amphiphilic molecules, at the critical micellar concentration. Our model is simple enough to have an exact solution, but it contains some basic features of more realistic descriptions of amphiphilic systems: molecular excluded volume and molecular attractions which are saturated at the optimal cluster. The comparison between the exact results and the mean field density functional approximation suggests new approaches to study the more complex and realistic models of micelle formation; in particular it addresses the long-standing controversy surrounding the separation of internal degrees of freedom in the formulation of cluster association phenomena.

\section{I. INTRODUCTION}

The study of systems with strong effects of molecular aggregation sets problems of fundamental and applied interest. One of the most important examples are the dilute solutions of amphiphiles in water. The polar head in the molecule attracts the water, which is repelled by the hydrocarbon tails in the same molecule, and the frustration of these opposite tendencies leads to the formation of micelles, droplets with hundreds or thousands of molecules, which have their polar heads on the surface (in contact with the water) and the interior filled with the hydrocarbon tails. The radius of the micelles is limited by the length of the molecular chains, so that the droplets cannot grow far beyond it as spherical drops. From a theoretical point of view, micellar solutions could be regarded as extreme cases of non-ideal solutions, with strong molecular correlation described as microscopic clusters (micelles). However, the large number of molecules in each micelle makes impracticable the use of the virial expansion as with ordinary dilution. The alternative is to split the description of the systems into two levels: first the description within some approximate scheme, of a single cluster of $k$ molecules to get its internal grand potential energy, $\Omega_k$, and then the whole system is regarded as an ideal mixture, with the density of clusters proportional to the internal Boltzmann factor

$$\rho_k \sim \exp\left[-\beta \Omega_k\right], \quad (1)$$

with $\beta = (k_B T)^{-1}$. There remains controversy about the proportionality factor, which should provide the units of inverse volume to $\rho_k$ in Eq. (1), and how this factor may depend on the cluster size and mass.\textsuperscript{1,2} see also the series of articles by Reiss et al.\textsuperscript{7,8}, and references therein. The indeterminacy in this factor is directly associated to the problem of how to define the \textit{internal} grand-potential energy, when the process of micelle formation is described as a chemical reaction the problem is transferred to the usual indeterminacy in the \textit{standard} chemical potential.\textsuperscript{7,8} The problem may be avoided assuming that the dependence of $\rho_k$ with the temperature and the total concentration of amphiphiles is dominated by the exponential factor. For $\Omega_k > 0$ micelles of size $k$ are scarce, while for $\Omega_k < 0$ they should be abundant; the \textit{critical micellar concentration} (CMC) is then associated with conditions at which the minimum value of $\Omega_k$, for the optimal size, $n$, becomes zero. This semi-quantitative analysis provides useful information from empirical thermodynamic approximations for $\Omega_k$, with surface and volume contributions, which may include the qualitative effects of molecular shape\textsuperscript{9} and the role of the flexible chains\textsuperscript{2}. However, attempts to develop a quantitative link between approximated (mean field) descriptions of an aggregate at microscopic level, and the density $\rho_k$ of these aggregates at equilibrium\textsuperscript{10} requires consistent microscopic approximations for the prefactor in Eq. (1). In this paper we explore the problem with a simple model for molecular aggregation that may be solved both exactly and with a mean field density functional approximation (MFA) comparable to that used in more realistic models\textsuperscript{11}. The comparison allows us to establish a workable approach linking the two levels of statistical description in these systems, to be used in more sophisticated models which do not have exact solution.

\section{II. SIMPLE MODEL FOR MOLECULAR AGGREGATION}

Our model for molecular aggregates is a system of hard rods, with length $\sigma$, moving along the $X$ axis. Consecutive rods have positions $x_{i+1} \geq x_i + \sigma$, and each rod has a discrete internal degree of freedom $\xi = 1, \ldots, n$. Besides the hard-core repulsion there is an interaction energy between nearest neighbour pairs, $\phi(x_{i+1} - x_i, \xi_{i+1} - \xi_i)$ restricted to the range $\sigma \leq x_{i+1} - x_i \leq 2\sigma$. As a simple model with this behaviour we take
\[ \beta \phi(x, \xi) = K \frac{\xi (x - \sigma)(x - 2\sigma)}{\sigma^2} \]  

(2)

if \( \xi \equiv \xi_{i+1} - \xi_i = \pm 1 \) and zero otherwise. The dimensionless parameter \( K \) gives the inverse temperature, in units of the interaction strength. The optimal aggregate, represented in Fig. 1, is made of \( n \) rods with consecutive values of \( \xi_i \) from \( \xi_1 = 1 \) to \( \xi_n = n \), keeping relative distances between neighbours close to \( l_0 = 3\sigma/2 \), to be at the minimum of \( \phi(x, \xi) \). The non-cyclic character of the internal variable \( \xi \) precludes the growth of larger aggregates, playing (in a rather different way) the same role as the chain-packing constrains in real amphiphiles. Small fluctuations around the optimal distance \( \sigma \) still have a cohesive energy and provide some internal entropy for the aggregate. The aggregates compete with fully disordered configurations, which maximize entropy but do not get cohesive energy from Eq. (2).

![Fig. 1](image)

FIG. 1. Sketch of an optimal molecular aggregate in our one dimension model with \( n = 4 \). The hard rods are separated by the optimal distance, \( l_0 \), and the internal variable \( \xi \) takes consecutive values from \( \xi_1 = 1 \) to \( \xi_n = n \) as indicated by the numbers in each rod in (a). In the lower representation (b), the internal variable is represented by an angular variable with half-clock \( n \) possible values, to give a more intuitive idea of how the non-cyclic character of \( \xi \) prevents the grow of aggregates with more than \( n \) rods.

A. Exact results

The exact properties of the model are easily obtained in a statistical ensemble with constant temperature, \( T \), and pressure, \( p \), in terms of a \((n \times n)\) transfer matrix with elements, \( \mathcal{M}_{j,k}(x) = \exp[-\beta(\phi(x, k - j) - px)] \) for \( j, k = 1, \ldots, n \). The integral of \( \mathcal{M}_{j,k}(x) \) from \( x = 1 \) to infinity gives the elements of the transfer matrix for the internal variable, \( Q_{j,k} \), and its largest eigenvalue \( \lambda_{\text{max}} \) provides the thermodynamic properties of the system, through the chemical potential \( \beta\mu(T, p) = -\ln(\lambda_{\text{max}}) \), and the density of rods, \( \rho(T, p) = (\partial p/\partial \mu)_T \). The isotherms \( K = 20 \) for \( n = 2 \) and \( n = 12 \) presented in Fig. 1, give \( \beta\mu \) versus \( \rho \sigma / n \) (with logarithmic scale). Very diluted systems present ideal gas behaviour, with curves of slope 1 in the figure. When the molecular association becomes important the curves change to have slope 1/\( n \), which corresponds to an ideal mixture of \( n \)-molecule clusters, until the packing effects show up and the slopes increase.

![Fig. 2](image)

FIG. 2. Isothermal representation of the chemical potential versus the molecular density in our model for \( K = 20 \). The full lines are the exact results for \( n = 2 \) and \( n = 12 \). Broken lines are the results with the mean field approximation. The dotted line is the ideal gas limit.

Any property measuring the correlation structure can also be obtained from \( \mathcal{M}(x) \) and \( Q \). In particular, the density of aggregates, which is a property of \( n \)-rod correlations, is

\[
\rho_n = \rho \lim_{N \to \infty} \frac{\text{Tr}[Q^{N-n+1}W]}{\text{Tr}[Q^N]},
\]

(3)

where the matrix \( W \) depends on our exact definition for the aggregate. In the following we define the full aggregate (or micelle in a rather loose sense of the word) as any group of \( n \) rods with \( \sigma \leq x_{i+1} - x_i \leq 2\sigma \), and \( \xi_i + 1 - \xi_i = 1 \), starting with \( \xi = 1 \), so that every bond gets some cohesion energy from Eq. (2). With this definition we have

\[
W_{j,k} = \delta_{j,1}\delta_{k,n} \prod_{i=1}^{n-1} \int_{-\sigma}^{2\sigma} dx \mathcal{M}_{i,i+1}(x).
\]

(4)

Slightly different definitions of micelle would lead to other forms for \( W \), but they would change \( \rho_n \) very little, as long as they include the optimal and nearby configurations. In a similar way we may calculate the density, \( \rho_k \), of incomplete aggregates, with \( k < n \) rods, and the density \( \rho_1 \) of isolated rods, which do not get any cohesion from Eq. (2). In Fig. 1A we present \( k \rho_k / \rho \), i.e., the proportion of rods forming part of cohesive clusters of different sizes, as a function of the total density \( \rho \), along an isotherm. In qualitative agreement with real systems of amphiphilic molecules, there is a low concentration regime, with very
few micelles, where \( \rho \approx \rho_1 \), and a higher concentration regime, dominated by clusters of the preferential size \( n \), so that \( \rho \approx n \rho_n \). The density at the transition between the two regimes represents the critical micellar concentration (CMC, again in a loose sense of the term), which may be defined at the point where \( \rho_1 = n \rho_n \), so that there are as many isolated molecules as molecules forming part of complete micelles. In the neighbourhood of the CMC there are significative amounts of incomplete aggregates, with size between 2 and \( n \). The CMC corresponds to the region where the slopes of the curves \( \rho \) change from 1 to \( 1/n \). These changes are smoother in our simple, one-dimensional model than in real amphiphilic systems, but as the CMC is never a true phase transition, the use of a one-dimensional model does not change the quantitative behaviour of the system.

At low temperatures \( (K \gg 1) \) the asymptotic analysis of our exact results gives the CMC at

\[
\beta \mu_c = -\frac{1}{2} \left[ K + \ln \left( \frac{n}{2K} \right) \right],
\]

independent of the optimal cluster size \( n \). In Fig. \ref{fig:1}A we compare Eq. \ref{eq:5} with the exact results obtained from the numerical solution of Eq. \ref{eq:3,4}. The deviations from the asymptotic limit at low \( K \) (i.e., high temperature) represent the effects of the molecular packing, which force the relative distances between neighbour rods below the optimal value \( l_0 \), with a compromise between the tendency to build the optimal aggregates and the packing constrains (which push the rods towards the distance \( \sigma \) given by the hard core). In real systems of amphiphilic molecules, this compromise leads to very complex phase diagrams, with lamellar, hexagonal, cubic phases. In our one-dimensional system with short range interactions, however, the exact result cannot include any phase transitions.

**B. Mean field approximation**

We now consider the same model with a density functional approximation, to describe the aggregates as mesoscopic self-maintained inhomogeneities in a homogeneous bulk phase, corresponding to local minima of the grand-potential energy as a functional of the distribution of rods with each value of the internal parameter, \( \rho(x, \xi) \),

\[
\Omega[\rho(x, \xi)] = \mathcal{F}_{hr}[\rho(x)] - \mu \int dx \rho(x) + \sum_{j,k=1}^{n} \int \int_{x \leq x'} dx dx' \phi(x' - x, k - j) \rho(x, j) \rho(x', k),
\]

were \( \mathcal{F}_{hr} \) is the exact free energy density functional for hard rods \( \xi \), which depends only on \( \rho(x) = \sum_{\xi} \rho(x, \xi) \), and the second line is the mean field (mf) approximation for the interaction Eq. \ref{eq:3}. This treatment of the model...
is equivalent to what can be done for more realistic models in three dimensions. As in those cases, \( \Omega[\rho(x,\xi)] \) in Eq. (3) always has a local minimum, with value \( \Omega_e \), for a homogeneous density distribution \( \rho(x,\xi) = \rho/n \), in which, for our model, the contribution of \( \phi(x,\xi) \) vanishes, and the system follows the thermodynamics of a hard rod system. However, at low temperature other local minima may appear, with value \( \Omega_e + \Omega_k \), in which the density distribution \( \rho(x,\xi) \) is made of a series of \( k \) narrow peaks, over the uniform background density (Fig. 3). The distance between the peaks and the dependence with \( \xi \) at the value \( \xi = 1 \) on the left peak and \( \xi = 2 \) on the right one.

The degeneracy of \( \Omega[\rho(x,\xi)] \) with respect to the position of the micelle also implies the existence of local minima with two or more micelles well separated along the system, and with an excess grand potential which is \( \Omega_k \) times the number of micelles. Some weak effective attraction may appear between micelles, mediated by the monomer density, \( \rho_1 \), and as the chemical potential increases, the absolute minimum of \( \Omega[\rho(x,k)] \) goes to dense periodic structures.

III. IDEAL MIXTURES OF MOLECULAR AGGREGATES

A. General approach

In this section we consider the generic problem of how to obtain the global behaviour of a system from a mean field description of the molecular aggregates in the limit of low total density, \( \rho \). We use the notation appropriate for systems in three dimensions to get general expressions, which we later apply to our simple model in one dimension. We assume that there may be several types of molecular aggregates, and we label them by their number of molecules \( k \). There is always some arbitrariness, at this level of description, in what is called an \( n \)-molecule aggregate, but the existence of micelles with a well defined size and structure makes it easy to find natural choices, like the one used in our simple model leading to (2–3). As discussed above, the use of reasonable variants would have very little effect in the results.

In the limit of low total density the system may be considered as an ideal gas of aggregates. The partition function of an ideal mixture with \( N_k \) aggregates of size \( k \), and a total number of molecules \( N = \sum_k kN_k \), is factorized into the contributions of each aggregate,

\[
Z(T, V, \{N_k\}) = \prod_k \left( \frac{Z_k(T, V)}{N_k!} \right)^{N_k},
\]

where \( Z_k(T, V) \) is the canonical partition function of the \( k \)-molecules aggregate, as a function of the temperature and the total volume of the system, \( V \). This partition function may be factorized into a translational part, proportional to the volume, and the internal part, \( Z_k^{int}(T) \) which is independent of \( V \). We make it explicit as

\[
Z_k(T, V) = e^{-\beta E_k} \frac{V (v_k)^{k-1}}{\Gamma^k} = \frac{V}{\Gamma} Z_k^{int}(T),
\]

where we have separated the Boltzmann factor, with the mean energy of the aggregate \( E_k \), and the phase space volume with a factor \( V \). The \( k - 1 \) factors \( v_k \) (for which Eq. (8) may be considered a definition) include the phase space volume associated with the relative positions of all the molecules in the aggregate and any rotational or internal degree of freedom of the molecules, as well as any combinatorial factor. The total configuration integral over positions has dimensions of volume to the power

![FIG. 5. The mean field representation of an aggregate as an inhomogeneous density distribution which is a local minimum of the grand potential energy in our model with \( n = 2 \), for \( K = 16 \) and bulk density \( \rho_1 = 0.02 \sigma^{-1} \). The full line is the total density with two narrow peaks, and the dashed line is the internal order parameter \( \xi(x) \) which is nearly saturated at the value \( \xi = 1 \) on the left peak and \( \xi = 2 \) on the right one.](image-url)
$k$, which are cancelled by the factor $\Gamma^k$ in the denominator, where $\Gamma$ is the unit cell volume in the configuration phase space. The matching between classical and quantum statistics may be used to fix $\Gamma$, e.g., for a monatomic ideal gas with atomic mass $m$, the integral over the momenta give $\Gamma = \Lambda^3$, in terms of the thermal wavelength, $\Lambda = h/(2\pi m)^{1/2}$. However, within the range of validity for the classical statistical mechanics all the results related to the positions of the molecules, like $\rho_k$ or any molecular correlation structure, will be invariant if $\Gamma$ is multiplied by an arbitrary factor (or if the molecular mass $m$ is changed). Thus, we keep the term $\Gamma^k$ in Eq. (6), to get a dimensionless partition function $Z_k$, but we know that $\Gamma$ and $m$ have to disappear in any final expression for the density of aggregates. By taking $\Gamma$ as an arbitrary constant (independent of $T$) we neglect the molecular kinetic energy, which would add (for each classical degree of freedom) a contribution $(2\beta)^{-1}$ to the internal energy, without changing any relevant result here.

The mean number of $k$-molecule aggregates in the system, $N_k$, is easily obtained from Eq. (6) in the grand-canonical ensemble, $N_k = -\partial(Z_k \exp(k\beta\mu))/\partial \beta E_k$, and the factor $V$ in Eq. (6) provides a well defined density of clusters

$$\rho_k \equiv N_k/V = \frac{1}{v_k} \exp\left[ -\beta(E_k - k\mu) - k \ln(\Gamma/v_k) \right]. \quad (9)$$

The total density is then given by

$$\rho(T, \mu) \equiv \frac{N}{V} = \rho_1 + \sum_{k>1} k \rho_k, \quad (10)$$

where we have separated the density $\rho_1$ of isolated molecules, which are not considered to form part of any aggregate. For a given total density, $\rho$, the chemical potential may be written as

$$\mu = \mu_{id} + \Delta \mu = \beta^{-1} \ln(\rho \Gamma) + \Delta \mu(\rho, T), \quad (11)$$

where we have separated the ideal gas contribution from the contribution of the molecular interactions. The former takes all the dependence on the phase space unit $\Gamma$, through the form $\beta \mu_{id} = \ln(\rho \Gamma)$. Substitution of Eq. (11) into Eq. (6) shows the perfect cancellation of the $\Gamma$ factors in the density of aggregates, $\rho_k(\rho, T)$ when it is written as a function of the total density and the temperature.

Consider now the description of the same system with a generic mean field density functional approximation for the grand potential energy $\Omega[\rho]$. There is always a relative minimum of $\Omega$ for a homogeneous bulk density distribution, which we associate with the density $\rho_1(T, \mu)$ of unaggregated molecules in Eq. (10). There may be other functional local minima, for inhomogeneous distribution functions, and each one is associated with a type of molecular aggregate. Compared with the uniform bulk phase, this aggregate has an excess of $k$ molecules (which again we use to label the type of aggregate) and an excess Helmoltz free energy, $F_m^{mf}$. In the limit of a very dilute bulk we may represent the mean field approximation for the partition function on the $k$ molecules as

$$Z_k^{mf}(T) \equiv \exp[-\beta F_m^{mf}] = e^{-\beta E_k^{mf}} \left( v_k^{mf}/k \right)^{k} \quad (12)$$

where $E_k^{mf}$ is the energy given by the mean field approximation, and $v_k^{mf}$, defined through Eq. (12), gives the volume in the configuration phase space per molecule in the same approximation. The qualitative difference between Eq. (12) and the exact result Eq. (6) is the lack of a volume factor $V$. This factor arises from the overall position of the aggregate, but in our mean field description we are neglecting the collective mode associated to $k$-molecules correlations. The translational invariance is still reflected in the degeneracy of the density functional minimum, but it does not contribute to $F_m^{mf}$, which is independent of the total volume in the system.

We now make explicit the use of the mean field approximation for the statistics of the aggregates by using the exact expression Eq. (6) for $\rho_k$, with the results of the mean field approximation for $E_k$ and $v_k$; the expression in the exponential becomes

$$-\beta(E_k^{mf} - k\mu) - k \ln(\Gamma/v_k) = -\beta \Omega_k^{mf} + k\beta \mu \quad (13)$$

which is precisely $-\beta \Omega_k^{mf}$, as in empirical treatments, but we now get an explicit approximation for the prefactor:

$$\rho_k = \frac{1}{v_k^{mf}} e^{-\beta \Omega_k^{mf}} \quad (14)$$

where $v_k^{mf}$ may be obtained through Eq. (12), from the difference between the internal energy and the Helmoltz free energy in the same mean field approximation,

$$v_k^{mf} = \frac{1}{\rho_1} \exp \left[ \beta \frac{E_k^{mf} - \Omega_k^{mf}}{k} - \beta \Delta \mu(\rho_1) \right] \quad (15)$$

in terms of the bulk density of unaggregated molecules, the internal energy $E_k^{mf}$ and the grand potential excess $\Omega_k^{mf}$.

Within this approach we may obtain the thermodynamics and the structure of a system with a strong degree of molecular aggregation from a mean field description of each separated cluster. For each local minimum of $\Omega[\rho]$ we get a type of cluster, which at a given temperature and chemical potential, may coexist with a bulk of density $\rho_1(T, \mu)$ of uncorrelated molecules. The total density of the system is given by Eq. (10), adding to $\rho_1$ the contribution Eq. (14) of each type of aggregate (i.e., each local minimum of $\Omega$). The proposed expression Eq. (13) for the prefactor in Eq. (14), is based on the formal comparison of the exact and the mean field partition functions. The factor $V$ of the free translational mode,
which is missing in the MFA, is added in substitution of an average mode with contribution $v_k^{mf}$. There are different recipes to get $v_k$, and most of them are based on the phase space unit $\Gamma$ (taken in terms of the thermal wavelength), which depends on the molecular mass, inconsistent with the use of classical statistics. An empirical recipe proposed by us was based on the micelle compressibility as a way to estimate the contribution of the average mode. That approximation was used in the description of micelles, in a three-dimensional model of amphiphilic systems, with sensible results. However, it was too sensitive to the structure of the aggregates, and it was difficult to use for crystal micelles with strong internal structure.

Our present proposal is a consistent thermodynamic evaluation of $v_k^{mf}$ from the entropy of the aggregate, as given in the same MFA as used for the grand potential energy $\Omega_k^{mf}$. This requires getting the grand potential and the internal energy $E_k^{mf}$ from the same approximation. Obviously, this level of description is always based on an approximation; there is not an exact value for the prefactor in Eq. (11) because the exact description of the system (as we have done with the simple one-dimensional model) would not give any local minima of the grand potential energy for inhomogeneous density distributions, and there is not an exact value for the exponent $\Omega_n$. In the next subsection we use our simple model of molecular aggregation to check the precision of this approach by direct comparison with the exact results, which is obviously not possible in more realistic models.

### B. Application to the one-dimensional model

It is straightforward to use Eqs. (10, 14 and 13) for our simple model in one dimension. The mean field approximation Eq. (1) has explicit separation between the internal energy and the entropic contributions to $\Omega[\rho]$. At low temperatures ($K \gg 1$), we may use a Gaussian parametrization of the density distribution:

$$\rho(x, \xi) = \frac{\rho_1}{n} + \sum_{i=1}^{m} C_i(\xi) \exp[-\alpha_i(x-x_i)^2],$$

with $C_i(\xi)$, $\alpha_i$, and $x_i$, as free variational parameters to minimize $\Omega[\rho]$. The homogenous diluted bulk with density $\rho_1$ corresponds to have $C_i(\xi) = 0$ for all $i$ and $\xi$. With the same value of the chemical potential, $\beta\mu(\rho, \rho_1) = \ln(\rho_1 \Gamma/n)$, we may find other local minima with the structure of complete or incomplete aggregates, with $k \leq n$ Gaussian peaks with the correct sequence of the internal variable, $C_i(\xi) \approx (\alpha_i/\pi)^{1/2}$, if $\xi = i$ and $C_i(\xi) \approx 0$ otherwise. The distance between Gaussians is given by the minimum of the interaction potential Eq. (11), $x_{i+1} - x_i = l_0 = 3\sigma/2$, and the Gaussian widths are $\alpha_i \approx 4K/\sigma^2$ for the inner Gaussians and $\alpha_i \approx 2K/\sigma^2$ for those at the ends of the aggregates.

Within this parametrization, with normalized Gaussian peaks, the excess of internal and Helmholtz free energies of an aggregate of size $k$ are obtained analytically as

$$\beta E_k^{mf} = -\frac{k-1}{2}K + \frac{k}{2}$$

and

$$\beta F_k^{mf} = -\frac{(k-1)K}{2} + \frac{k}{2} \ln\left(\frac{4KT^2}{\pi\sigma^2}\right) - \ln(2).$$

We have checked, for the simplest case $n = 2$, that these expressions are very close to the results of the full (numerical) functional minimization of $\Omega[\rho]$, for the relevant region of $K > 20$ and $\rho_1 < 10^{-2}\sigma^{-1}$.

From Eqs. (17 and 18), we get $\Omega_k^{mf}$ and $v_k^{mf}$ in Eq. (19), for each of the local minima

$$\beta\Omega_k^{mf} = -\frac{(k-1)K}{2} - k \ln\left(\frac{\rho_1\sigma\pi^{1/2}}{2nK^{1/2}}\right) - \ln(2)$$

and

$$v_n^{mf} = 2^{1/n} \left[\frac{e\pi}{4K}\right]^{1/2} \sigma.$$  

Both magnitudes become independent of the phase space unit volume $\Gamma$; they depend on the parameters of the interaction potential $n$, $K$ and $\sigma$, the latter providing the only physical length scale in the model.

We now use Eqs. (19 and 20) in Eqs. (10 and 14) to get the MFA result for the total density $\rho$. In Fig. 1A the results of this MFA are compared with the exact results along the isotherm $K = 20$ for $n = 2$ and 12. The qualitative trends are similar: the ideal gas is recovered at very low bulk density, but there is a smooth transition (around the CMC) to a regime in which $\beta\mu$ has a slope of $1/n$, which corresponds to the ideal gas of full aggregates. In this regime the MFA goes nearly parallel to the exact curves, until the packing effects (neglected at this level of the MFA) become relevant. The CMC, still defined from $\rho_1\rho_n = \rho_1$, is shifted from the exact asymptotic result Eq. (1), by

$$\beta(\mu_c^{mf} - \mu_c) = \frac{n-2}{2n} \ln(2) + \frac{1}{2(n-1)}.$$  

In Fig. 1A we compare the the exact and the MFA results for the CMC with $n = 2$ and 12. In the asymptotic regime the difference is independent of $K$. The MFA prediction for the CMC is shifted to larger values of the chemical potential: $\beta(\mu_c^{mf} - \mu_c) = 1/2$, for $n = 2$, and $\ln \sqrt{2} = 0.346$ for large $n$. Within our approach this shift reflects the combination of the error made by the MFA in the estimation of $\beta E_k^{mf}$ (in the asymptotic regime Eq. (17) is 1/2 larger than the exact value), and the error associated with the MFA estimation of the cluster internal entropy required to get $\Omega_k^{mf}$.
system we may compare the latter with the exact $v_n$, as defined in Eq. (8). In the limit $K \gg 1$ we get

$$v_n = \left[ \frac{e \pi}{2K} \right]^{1/2} \sigma$$

(22)

This exact result is independent of the optimal cluster size, $n$, and it is proportional to $T^{1/2}$ (through the parameter $K \sim T^{-1}$). The value given by the mean field approximation Eq. (12) shows the same dependence with the temperature and becomes identical to the exact value for $n = 2$. For larger $n$ the result Eq. (22) goes like $2^{1/n}$ and saturates at large $n$ with a discrepancy of $\sqrt{2}$ with the exact result. As comparison, the identification of $v_n$ with the thermal wavelength of the aggregate would lead to a qualitatively different dependence on $n$ and $T$,

$$v_n = \frac{\Lambda_n}{h(2\pi \beta/(n \mu))^{1/2}} \sim (n T)^{-1/2},$$

and with an unphysical dependence on the molecular mass and $h$. In our simple, one-dimensional, model the aggregates have a strong crystalline structure, described by the narrow Gaussian peaks in the MFA density distribution, which becomes very rigid at $K \gg 1$. This character of the aggregates is responsible for the complete failure of the empirical recipe for $v_n$, which was proposed by one of us in terms of an aggregate compressibility. That empirical recipe was used in a three-dimensional model, with much softer aggregates in which every molecule could move over the whole aggregate, like in a liquid drop. The application to our present model leads to a problematic formulation of $v_n$ (as the square root of a negative number) and should be fully discarded.

IV. CONCLUSIONS

We have approached the study of ideal mixtures of molecular aggregates from a mean field approximation for the structure and internal free energy of the isolated aggregates. The general analysis in Section III A suggests a consistent approximation to get the missing factor in the relation Eq. (1) between the internal grand-potential energy of a cluster and its abundance in the equilibrium solution. The simple one-dimensional model of molecular aggregation presented in Section II, provides a test for our approach. As in more realistic models, it includes hard-core repulsions and saturating attractive interactions, which set an optimal cluster size $n$. The exact solution of the model shows qualitative agreement with the behaviour of a system of amphiphilic molecules around the critical micellar concentration. Along an isotherm the system goes from an ideal gas of independent molecules (at very low chemical potential) to an ideal gas of optimal clusters or micelles, at higher chemical potential. This transformation takes place over a range of $\mu$ which becomes narrower as $n$ increases (although at a very slow rate because of the one-dimensional character of the model). The same model is then solved within a mean field approximation equivalent to what may be done in tridimensional models, and the consistent mean field result for the density of clusters Eqs. (14 and 15) may be compared with the exact result. The comparison serves to validate our proposed approximation Eq. (15) for the prefactor $v_n$ in the density of aggregates. As it should be expected, this prefactor is not related to the thermal wavelength of the aggregate, which would imply an unphysical dependence on the molecular mass and the wrong dependence on the temperature and the size of the aggregate. Our approximation reproduces the exact dependence on the temperature, and for large aggregates $n \gg 1$ it recovers (asymptotically) the exact independence on $n$. The numerical discrepancy between the exact and the MFA values of $v_n$ should be regarded as inherent to the mean field description of the aggregates. The thermodynamic consistency of the approximations for the exponent $\Omega_n$ and the prefactor $v_n$ in the density of aggregates is the new feature of our proposal, and it could be used for any, more realistic, model of mesoscopic aggregates.

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