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Comment on "Spin-1 aggregation model in one dimension"

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Girardi and Figueiredo have proposed a simple model of aggregation in one dimension to mimic the self assembly of amphiphiles in aqueous solution [Phys. Rev. E **62**, 8344 (2000)]. We point out that interesting results can be obtained if a different set of interactions is considered, instead of their choice (the $s=1$ Ising model).

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Girardi and Figueiredo [1] (GF) have considered the $s=1$ Ising model in one dimension as a system that could possibly show some of the features of micellar systems, especially the existence of a critical micelle concentration (CMC). Several definitions of the CMC may be provided, since this phenomenon is actually a crossover, not a well-defined phase transition. Following the classic work of Wennerström and Lindman [2], they focus on the distribution of aggregates with n molecules, $\rho(n)$. In real systems, the curve $n\rho(n)$ is expected to show a sharp maximum at $n=1$, an intermediate minimum and another maximum at some $\bar{n}$ corresponding to the micelles, typically of the order $\bar{n}\approx 10^2$.

This is indeed the case, at least in some regimes, in the two- and three-dimensional models previously studied by the same group [3,4], of which GF is a logical extension. In those works, the difference between the minimum and the maximum at $\bar{n}$ was used as a sort of "order parameter," whose vanishing could be associated with the CMC. In the case studied in GF, it was found that this function is never bimodal and so a CMC cannot be properly defined.

While their methods are not to be questioned, since they have carried out Monte Carlo simulations and, most importantly, it is possible to obtain an exact solution to the model, we feel that the model considered is not the best one if one wants to compare with real amphiphilic systems, and that the failure to find a clear CMC seems natural in retrospect. As discussed in [5], the mean feature of a micellar aggregate is the existence of a preferred aggregate size, which in real systems is a consequence of the effective geometry of the molecules (as exemplified by the well-known picture of Israelachvili's [6]). A model, even a highly simplified one, should include some kind of preferred aggregate size in order to present a CMC.

In a nutshell, the interaction considered in GF may be described by the following choice of spin interactions:

	↑	↓	○
↑	$-J$	J	0
↓	J	$-J$	0
○	0	0	0,

where the arrows represent the $+1$ and -1 spins and the circle the 0 one. Consider, instead, the following choice, in which we choose a left-right picture of the spins, instead of the usual updown:

	←	→	○
←	0	$-J$	0
→	0	0	$-J$
○	$-J$	0	0.

We can expect this choice (which is basically an application of the potential used in [5] to a lattice) to provide "micelles" consisting of spin pairs with orientation ←→ on a "solvent" of ○ spins, since this is the configuration energetically favored. This is indeed the case: e.g., we have checked that the slope of the chemical potential as a function of the logarithm of the amphiphilic density changes from 1 to a value of 1/2, and this crossover corresponds to the CMC [5]; this change in slope is not found with the GF model.

However, this model is too simple to address the behavior of $n\rho(n)$, since there is no possible aggregate between $n=1$ and $n=2$ where the distribution would have a minimum. Our model may then be trivially extended to another one with m spins ($m-1$ orientations for the amphiphiles and one for the solvent) [7]

	←	↖	···	→	○
←	0	$-J$	···	0	0
⋮	⋮	⋮	⋱	⋮	⋮
→	0	0	···	0	$-J$
○	$-J$	0	···	0	0.

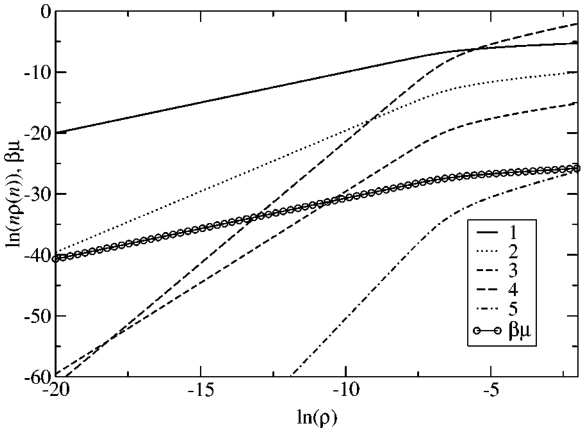

FIG. 1. Concentration of sites belonging to aggregates with different n (given in the legend) as a function of amphiphilic density, given as $\ln[n\rho(n)]$ vs $\ln(\rho)$, we also plot the chemical potential, $\beta\mu$; $m=5$ and $\beta J=20$.

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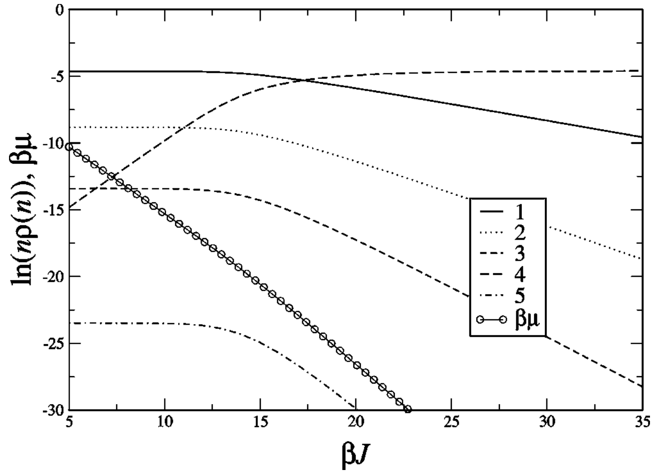

FIG. 2. Same as Fig. 1, but now for a fixed amphiphilic density $\rho = 0.01$ and varying βJ.

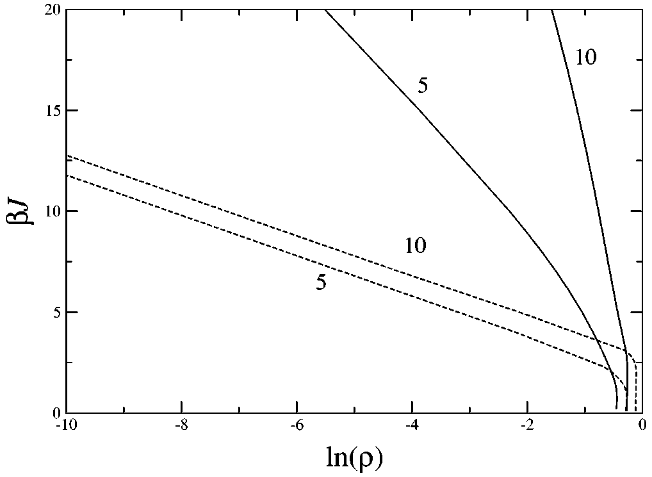

FIG. 3. Location of the CMC in the ln(ρ)–βJ plane, defined as $\rho(1) = \overline{n}\rho(\overline{n})$ (solid lines) and as $\overline{n}\rho(\overline{n}) = (\overline{n}-1)\rho(\overline{n}-1)$ (dashed lines), both for $m=5$ and $m=10$.

In Fig. 1, we show the chemical potential versus the logarithm of the amphiphile density for the particular choice $m=5$ to show the expected change in slope for 1 to 1/4. We also plot the corresponding values of $n\rho(n)$. It is clearly seen how the feature sought in GF is indeed obtained at ln(ρ)≈ -18: at this point a unimodal distribution with a maximum at $n=1$ turns into a bimodal with a second maximum at $\overline{n}=4$ (in general, one finds $\overline{n}=m-1$); the order parameter defined in GF is seen to vanish linearly.

However, this point is quite far from the CMC one would define from the chemical potential, ln(ρ)≈ -6; on the other hand, the crossing between the $n=1$ and the $\overline{n}=4$ lines does lie in this range. We suggest that this kind of criterion for the CMC (in general, $\overline{n}\rho(\overline{n}) = \rho(1)$, so that an order parameter could be defined as the difference between the $n=1$ and the $\overline{n}$ maxima) should perhaps be a better choice that the one in GF and previous works (Refs. [3,4]).

We can also fix the concentration at some value and vary the interaction parameter βJ. In Fig. 2, we show results for $\rho = 0.01$. The results are quite similar to the ones in Fig. 1, except that the chemical potential is now determined by our choice of density and does not show any particular feature. These two choices of crossing the CMC line yield the same results, which we have combined in Fig. 3. There, we present results for $m=5$ and also for $m=10$. We can see the CMC lines with the $\overline{n}\rho(\overline{n}) = \rho(1)$ criterion showing the expected dependence on m, with the slopes approaching a slope $m-2$ at high interactions and low densities (since each aggregate contains $m-2$ favorable bonds). The other criterion, based on the bimodality of the distribution [i.e., $\overline{n}\rho(\overline{n}) = (\overline{n}-1)\rho(\overline{n}-1)$] is seen to provide very different results, with a limiting slope of one, independent on m. Nevertheless, the discrepancies between these two criteria can be expected to be smaller in real amphiphilic systems, since the energy will quickly grow for aggregates either smaller or larger than $\overline{n}$, not linearly (for $n<\overline{n}$) as in our case.

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[7] We have also checked that extensions of the model in GF to higher spin Ising and Potts models fail to produce CMC features.