Comment on “First-order phase transitions: equivalence between bimodalities and the Yang-Lee theorem”

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I discuss the validity of a result put forward recently by Chomaz and Gulminelli [Physica A 330 (2003) 451] concerning the equivalence of two definitions of first-order phase transitions. I show that distributions of zeros of the partition function fulfilling the conditions of the Yang-Lee Theorem are not necessarily associated with nonconcave microcanonical entropy functions or, equivalently, with canonical distributions of the mean energy having a bimodal shape, as claimed by Chomaz and Gulminelli. In fact, such distributions of zeros can also be associated with concave entropy functions and unimodal canonical distributions having affine parts. A simple example is worked out in detail to illustrate this subtlety.

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Chomaz and Gulminelli \cite{CG2003} have studied recently the equivalence of two different definitions of first-order phase transitions—one based on the nonconcavity of the microcanonical entropy function and another based on the distribution of the zeros of the partition function. My goal here is to question and correct one of their results with the help of a counterexample which I will then explain using some basic results of convex analysis. To start, let me summarize the main results found in Ref. \cite{CG2003}. The notation I will be using throughout is less general than the one used in \cite{CG2003}; it is simpler, but captures nevertheless the essence of the problem.

Consider an $n$-body system with energy $U$ and mean energy $u = U/n$. The partition function of the system is defined as

$$Z_n(\beta) = \int \Omega_n(u) e^{-\beta nu} du,$$  \hspace{1cm} (1)

where $\Omega_n(u)$ represents the density of microstates with mean energy $u$. It is well-known from the work of Yang and Lee \cite{YangLee52} that one way to make sense of nonanalytic points of the canonical free energy function

$$\varphi(\beta) = \lim_{n \to \infty} -\frac{1}{n} \ln Z_n(\beta),$$  \hspace{1cm} (2)

which signal the onset of phase transitions, is to study the distribution of complex zeros of $Z_n(\beta)$ in the limit $n \to \infty$. In the case of first-order phase transitions, in particular, it is known that, as $n \to \infty$, there is an accumulation of zeros of $Z_n(\beta)$ around some positive real value $\beta_c$ of the inverse temperature corresponding to the value at which $\varphi(\beta)$ is nondifferentiable, and that the loci of zeros in the vicinity of $\beta_c$ is parallel to the imaginary axis. This phenomenon is what Chomaz and Gulminelli refer to as the Yang-Lee Theorem. I shall refer to it myself as the Yang-Lee Condition (YLC). Thus we say that a first-order phase transition appears in the thermodynamic limit of the canonical ensemble when the zeros of $Z_n(\beta)$ satisfy YLC.

Now, what Chomaz and Gulminelli purported to show in \cite{CG2003} is that YLC is equivalent to another definition of first-order phase transitions based on the bimodal shape of the density function $\Omega_n(u)$ (see \cite{CG2003} and references therein). They showed first that if $\Omega_n(u)$ has a bimodal shape which persists as $n \to \infty$, a condition which I shall refer to as the Bimodal Condition (BC), then YLC is satisfied. Actually, the quantity which they focused on was not $\Omega_n(u)$ but the canonical distribution $p_{n,\beta}(u)$, given by

$$p_{n,\beta}(u) = \frac{\Omega_n(u)e^{-\beta nu}}{Z_n(\beta)} \approx e^{-n[\beta u - s(u)]}. \hspace{1cm} (3)$$

Yet since a bimodality of $\Omega_n(u)$ translates into a bimodality of $p_{n,\beta}(u)$, and vice versa, it does not matter which quantity we refer to, and, for the purpose of the presentation, I shall stick to $\Omega_n(u)$.

It should be noted in passing that the result “BC implies YLC” had already been proved by Lee \cite{Lee72}. The real novelty of \cite{CG2003} is to attempt to prove the converse result, namely that YLC implies BC. It is this second result that Chomaz and Gulminelli claim to have proven, but which cannot be true in fact, as exemplified by the following counterexample.

Consider a density of microstates of the form

$$\Omega_n(u) = \begin{cases} e^{n\Delta} & u \in [0, \Delta] \\ 0 & \text{elsewhere,} \end{cases} \hspace{1cm} (4)$$

with $\Delta > 0$. The partition function for this form of $\Omega_n(u)$ is trivially evaluated and has for expression

$$Z_n(\beta) = e^{n\Delta} \frac{(1 - e^{-\beta n\Delta})}{\beta}. \hspace{1cm} (5)$$

Setting $Z_n(\beta) = 0$ and solving for $\beta \in \mathbb{C}$, we find that the zeros of the partition function must solve the equation $e^{-\beta n\Delta} = 1$ with the exclusion of $\beta = 0$. This is equivalent to $e^{-\beta n\Delta} = e^{\pm 2\pi ik}$, $k = 1, 2, \ldots$, and so we find the zeros of $Z_n(\beta)$ to be given by $\beta_k = \pm 2\pi ik/(n\Delta), \ k =$
1, 2, . . . . In terms of the fugacity $z = e^{-\beta}$, these can be re-expressed as

$$z_k = \exp \left( \pm \frac{2\pi i k}{n\Delta} \right), \quad k = 1, 2, \ldots \quad (6)$$

Now comes the contradiction: $\Omega_n(u)$ does not satisfy BC, but the zeros of the partition do satisfy YLC. In fact, the zeros of $Z_n(\beta)$ are all aligned on the imaginary axis and pinch the real axis at the critical value $\beta_c = 0$ as $n \to \infty$. Following the Yang-Lee theory, we then know that $Z_n(\beta)$ must develop a nonanalytic point at $\beta_c$ as $n \to \infty$, which translates into a nondifferentiable point of $\varphi(\beta)$. This can be verified by a direct calculation of the free energy:

$$\varphi(\beta) = \lim_{n \to \infty} \frac{-1}{n} \ln \left[ \frac{e^{n\Delta}}{n} \left( 1 - e^{-\beta n\Delta} \right) \right]$$

$$= \begin{cases} -\Delta & \beta > 0 \\ -\Delta + \beta \Delta & \beta \leq 0. \end{cases} \quad (7)$$

The left- and right-derivatives of the free energy at $\beta_c = 0$ being equal to $\varphi'(\beta = 0^-) = \Delta$, $\varphi'(\beta = 0^+) = 0$, respectively, we also find that the latent heat for this example is equal to $\Delta$.

The important conclusion that we reach from this simple counterexample is clear: YLC does not imply BC in general, as claimed in [1]. To determine what the correct implication should be, I shall recall at this point three important results of equilibrium statistical mechanics and convex analysis (see [2, 3]):

(i) If $\Omega_n(u)$ has a bimodal shape that persists when $n \to \infty$, then $s(u)$ must be nonconcave over some range of mean energy. The converse statement is also true.

(ii) The free energy function $\varphi(\beta)$ is always the Legendre-Fenchel transform of the microcanonical entropy function $s(u)$; in symbols,

$$\varphi(\beta) = \inf_u \{ \beta u - s(u) \}. \quad (8)$$

This holds no matter what the shape of $s(u)$ is, be it concave or not.

(iii) Regions of mean energies over which $s(u)$ is nonconcave or is affine (i.e., is a line) are indicated at the level of the canonical free energy $\varphi(\beta)$ by the existence of points of $\varphi(\beta)$ where this function is nondifferentiable. The fact that affine parts of $s(u)$ also translate into non-differentiable points of $\varphi(\beta)$ can be understood by noting that $s(u)$ and its concave envelope $s^{**}(u)$, defined by

$$s^{**}(u) = \inf_{\beta} \{ \beta u - \varphi(\beta) \}, \quad (9)$$

have the same Legendre-Fenchel transform, namely,

$$\varphi(\beta) = \inf_u \{ \beta u - s(u) \} = \inf_u \{ \beta u - s^{**}(u) \}; \quad (10)$$

see Fig. 1.

These results indicate altogether that a first-order phase transition in the canonical ensemble emerges from the point of view of the microcanonical ensemble in basically two ways: either $s(u)$ is nonconcave somewhere or else $s(u)$ is affine somewhere. The first possibility is what was considered in [1], whereas the second possibility is what I have considered in the counterexample, and what is precisely absent from [1]. Hence at this point we have all the ingredients to conjecture what the correct relationship between YLC and BC is, namely: if the zeros of $Z_n(\beta)$ satisfy YLC, then either $\Omega_n(u)$ is bimodal or else it has an affine part. Let me refer to the second possibility as the Affine Part Condition (APC). Then, the result is simply: YLC implies BC or APC. Combining this result with what we already had, namely that BC implies YLC, we arrive finally at the following: YLC is satisfied if and only if BC or APC is satisfied. (This result should be understood as a conjecture rather than a rigorously proved result because, at this point, it remains to rigorously prove that YLC is a necessary and sufficient condition for $\varphi(\beta)$ to have a nondifferentiable point.)

In the end, one may wonder whether entropies having affine parts are anything to worry about. There seems indeed to be a lack of structural stability inherent with such entropies, and so it is questionable whether they can show up in realistic models. This concern, however, is out of the scope of the present comment. Affine entropies present one with a theoretical possibility that one has to take into account when deriving general theoretical results.

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