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NONEQUIVALENT ENSEMBLES AND METASTABILITY

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This paper reviews a number of fundamental connections that exist between nonequivalent microcanonical and canonical ensembles, the appearance of first-order phase transitions in the canonical ensemble, and thermodynamic metastable behavior.

1. Introduction

The goal of this short paper is to trace a line of relationships that goes from the phenomenon of nonequivalent microcanonical and canonical ensembles to that of thermodynamic metastability. Our approach will aim for the most part at stressing the physics of these relationships, but care will also be taken to formulate them in a precise mathematical language. However, due to the limitation in available space, many mathematical details will have to be left aside, including the proofs of all the results stated here. References containing these proofs, when they exist, will be mentioned to assist the reader. Another more complete paper that treats these relationships with full mathematical details is also in preparation,¹² based on the recent doctoral dissertation of one of us.²¹

Far from being exhaustive, we hope that this short review can serve as a starting point in the literature for the reader interested in knowing about nonequivalent ensembles, as well as those interested in phase transitions and metastable behavior in many-body systems. These proceedings are a testament to the fact that there remain at present many unsolved problems related to metastability, and it is our belief that what has been learned in studies of nonequivalent ensembles could yield useful clues for solving these problems. Perhaps the most obvious of these clues is the fact that many of the systems described in these pages (see, e.g., the contributions on the HMF model) exhibit negative values of the heat capacity at fixed energies at the same time that they exhibit metastable states. The negativity of the heat capacity at fixed energy is well known to be related to the nonequivalence of the microcanonical and canonical ensembles. It is also, as we will see here, a direct indication of metastable behavior.

2. Nonequivalent ensembles

The equivalence of the microcanonical and canonical ensembles is most usually explained by saying that although the canonical ensemble is not a fixed-mean-energy ensemble like the microcanonical ensemble, it must ‘converge’ to a fixed-mean-energy ensemble in the thermodynamic limit, and so must become or must realize a microcanonical ensemble in that limit.^{11,22} This explanation is not far from being entirely valid, but there is a problem with it: the canonical ensemble may not in fact realize at equilibrium all the mean energies that can be realized in the microcanonical ensemble.²² In other words, the range of the equilibrium mean energy u_β realized in the canonical ensemble by fixing the inverse temperature β may be only a subset of the range of definition of the mean energy u itself. If this is the case, then the microcanonical ensemble must be richer than the canonical ensemble because there are values of the mean energy that can be assessed within the microcanonical ensemble, but not within the canonical ensemble. The two ensembles must therefore be nonequivalent.

To see how this possibility can arise, and how it is related in fact to the nonconcavity of the microcanonical entropy function, let us introduce some notation. We consider, as is usual in statistical mechanics, an n -body system with Hamiltonian U and mean entropy $s(u) = S(U)/n$, where $u = U/n$ is the mean energy. To state our first result, we need to define an important concept in convex analysis known as a *supporting line*.^{19,9} This is done as follows: we say that s admits a supporting line at u if there exists $\beta \in \mathbb{R}$ such that $s(v) \leq s(u) + \beta(v - u)$ for all admissible v . From a geometric point of view, the requirement of a supporting line should be clear: it means that we can draw a line above the graph of $s(u)$ that passes only through the point $(u, s(u))$; see Fig. 1. The slope of this line is β .

Theorem 2.1. *Let u_β be the value of the mean Hamiltonian realized at equilibrium in the canonical ensemble with inverse temperature β . (There can be more than one equilibrium value.) Then, for any admissible mean energy value u , there exists β such that $u_\beta = u$ if and only if s admits a supporting line at u with slope β .*

This simple result seems to have floated in the minds of physicists for a long time. It is implicit, for example, when considering the physical meaning of first-order phase transitions in the canonical ensemble and their connection with nonconcave entropies.^{20,17,13,18,14,15,6,16} However, to the best of our knowledge, there has never been a clear formulation of this result until recently.^{21,22} This can be explained in part by the fact that the concept of a supporting line is not well known in physics.

The full application of our first theorem is presented in Fig. 1 which shows the plot of a generic entropy function having a nonconcave part. This figure depicts three possible cases:

(a) Mean energy value u for which s admits a supporting line. In this case, the value u can be realized at equilibrium in the canonical ensemble by setting β equal to the slope of the supporting line passing through $(u, s(u))$. We naturally expect

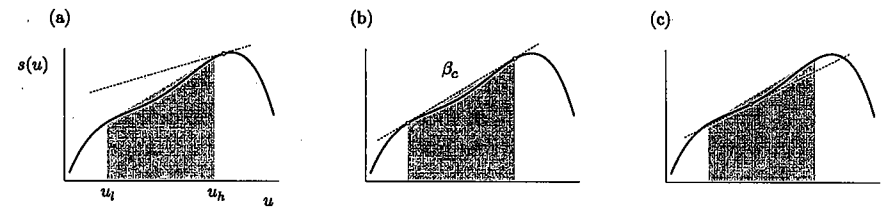


Figure 1. (a) Concave point of the microcanonical entropy function $s(u)$ which admits a supporting line. (b) Two concave points of $s(u)$ which admit the same supporting line. (c) Nonconcave point of $s(u)$ which does not admit a supporting line.

in this case to see the microcanonical ensemble at u give the same equilibrium predictions as the canonical ensemble at β since the latter ensemble reduces to a single-mean-energy ensemble with $u_\beta = u$. Note that β must be such that $s'(u) = \beta$ if s is differentiable.

(b) There exists a single supporting line that touches two points of the graph of the microcanonical entropy. In this case, not one but *two* values of the mean energy—e.g., u_l and u_h in Fig. 1—are realized at equilibrium in the canonical ensemble for β corresponding to the slope of the supporting line. This situation, as will be clear in the next section, corresponds to a state of coexisting phases which universally signals the onset of a first-order phase transition in the canonical ensemble.

(c) Mean energy u for which s admits no supporting line. This also applies for all $u \in (u_l, u_h)$. Theorem 2.1 states for this case that the canonical ensemble must be blind to the properties of the microcanonical ensemble since it cannot realize at equilibrium any of the mean energies $u \in (u_l, u_h)$ for any values of β . This means in particular that the standard thermodynamic relation $\beta = s'(u)$ ceases to be valid in this region.^{11,22} The next theorem relates this case of nonequivalent ensembles with the occurrence of negative values of the heat capacity in the microcanonical ensemble.^{14,15}

Theorem 2.2. *Define the microcanonical heat capacity at the mean energy value u by $c(u) = -s'(u)^2 s''(u)^{-1}$. If $c(u) < 0$, then s does not have a supporting line at u .*

This result is a new formulation—again because the use of supporting lines—of an old result that relates the negativity of c with the nonequivalence of the microcanonical and canonical ensembles. Usually what is concluded is that these two ensembles must be nonequivalent when $c < 0$ because the heat capacity can never be negative in the canonical ensemble.^{20,17,18,14,15} Our formulation has the advantage of stressing the physical root of negative heat capacities, namely that the mean energies u which are such that $c(u) < 0$ are not *equilibrium* mean energies in the canonical ensemble. This point will be discussed further in Section 4. For now, let us note in closing this section that the negativity of c is only a sufficient

condition for ensemble nonequivalence, not a necessary one.^{11,22} Thus it is not true that the canonical ensemble is blind to the microcanonical ensemble only for those mean energy values u such that $c(u) < 0$, as is often claimed.^{20,17,18,14,15} As we have seen, the canonical ensemble is in fact blind to the microcanonical ensemble for all u at which s admits no supporting lines, and that, in general, comprises more values u than only those having $c(u) < 0$; see, e.g., Fig. 1.

3. Nonequivalent ensembles and first-order phase transitions

The previous section makes it clear that what is responsible for the nonequivalence of the microcanonical and canonical ensembles is the occurrence of a first-order phase transition in the canonical ensemble. To be sure, just replace the word ‘blind’ with the word ‘skip’ to obtain a sentence such as: the microcanonical and canonical ensembles are nonequivalent because the canonical ensemble *skips* over an interval of mean energies which can be accessed microcanonically.^{20,18,14,15} The inverse temperature at which the canonical ensemble skips over the microcanonical ensemble corresponds, not surprisingly, to the inverse temperature at which a first-order phase transition appears. This is the subject of the next theorem which relates the nonconcavity property of $s(u)$ with the differentiability property of the free energy function $\varphi(\beta)$, the central thermodynamic quantity of the canonical ensemble which is taken here to be defined by the limit

$$\varphi(\beta) = \lim_{n \rightarrow \infty} -\frac{1}{n} \ln Z_n(\beta), \quad (1)$$

where $Z_n(\beta)$ is the standard n -body partition function.^{9,11}

Theorem 3.1. *Assume that s admits no supporting lines for all $u \in (u_l, u_h)$. Then φ is non-differentiable at a critical value β_c equal to the slope of the supporting line that bridges u_l and u_h . The left- and right-derivatives of φ at β_c equal u_h and u_l , respectively.*

This theorem is a direct result of the fact that $\varphi(\beta)$ is the Legendre-Fenchel transform of $s(u)$, whether $s(u)$ is concave or not, and some basic properties of these transforms.^{13,9,11} It can be found in many works^{20,17,18,14,15} which do not define, however, the concavity of $s(u)$ in terms of supporting lines. This is a minor omission because most of these works use an equivalent method for defining the range of nonconcavity of $s(u)$ based on the so-called Maxwell’s construction.^{14,15} In any case, it is clear in all the works just cited that the nonequivalence of the microcanonical and canonical ensembles arises as a consequence of first-order phase transitions in the canonical ensemble. The nonconcavity of $s(u)$, which translates into a ‘back-bending’ shape of $s'(u)$, is in fact sometimes taken as a definition or a probe of canonical first-order phase transitions.^{14,15,6,16} The opposite is also possible; that is, it is possible to relate the absence of a first-order phase transition in the canonical ensemble with the equivalence of the microcanonical and canonical ensembles.¹¹ This is done in the next theorem.

Theorem 3.2. *If φ is differentiable at β , then s admits a strict supporting line that touches the graph of s only at $u = \varphi'(\beta)$.*

This result implies the following standard result: if φ is differentiable at β , then $u = \varphi'(\beta)$ is the unique mean energy value realized at equilibrium in the canonical ensemble with inverse temperature β .

4. Nonequivalent ensembles and metastability

The last set of results that we will discuss directly pertains to the mean energies which can be assessed microcanonically but not canonically. What we want to show is that these *nonequivalent* mean energies correspond to *nonequilibrium* critical mean energies of the canonical ensemble. This is somewhat obvious given that they cannot be equilibrium mean energies; however, what we want to discuss more specifically is the physical nature of these nonequilibrium critical points. To do so, we have to note that the values u_β of the mean energy that are realized at equilibrium in the canonical ensemble at β are, by definition, the global minimum of the function $F_\beta(u) = \beta u - s(u)$,^{6,16} which we call the nonequilibrium free energy function.^{21,22} This implies in particular that u_β must satisfy $\partial_u F_\beta(u_\beta) = 0$, or equivalently $\beta = s'(u_\beta)$, assuming that s is differentiable. Note however—and this is the crucial point here—that not all the points u satisfying $\beta = s'(u)$ may globally minimize $F_\beta(u)$; some of these critical points may actually correspond to local minimum of $F_\beta(u)$ or even local maximum of $F_\beta(u)$. To determine the precise nature of these *nonequilibrium canonical critical points*, we can look at the sign of the second u -derivative of $F_\beta(u)$ to obtain the following result.

Theorem 4.1. *Suppose that s does not admit a supporting line at u .*

(a) *If $c(u) > 0$, then u is a metastable mean energy of the canonical ensemble, in the sense that it is a local but not global minimum of $F_\beta(u)$ for $\beta = s'(u)$.*

(b) *If $c(u) < 0$, then u is an unstable mean energy of the canonical ensemble, in the sense that it is a local maximum of $F_\beta(u)$ for $\beta = s'(u)$.*

While this result applies to the mean energy, it is interesting to see if anything can be said about general macrostates: e.g., the magnetization or the distribution of states. We all know, for instance, that phase transitions in spin systems can be revealed at the level of the mean energy (thermodynamic level) or at the level of the magnetization (macrostate level) since both levels are related in a one-to-one fashion. Is the same true for metastability? That is, can the metastable behavior of a system be revealed at the macrostate level? If so, can this macrostate level of metastability be related to the thermodynamic level of metastability defined with respect to the mean energy?

The answer to these questions is yes, so long as we are concerned with mean-field systems, which are basically systems for which the Hamiltonian U can be expressed as a function of some macrostate m of interest.^{21,5} In this case, we can formulate the

following result about the macrostate values m^u which are realized at equilibrium in the microcanonical ensemble with mean energy u , but not in the canonical ensemble for any β . The result is formulated in terms of the nonequilibrium free energy $F_\beta(m)$ which is the macrostate generalization of $F_\beta(u)$.²¹

Theorem 4.2. *Suppose that s does not admit a supporting line at u .*

(a) *If $c(u) > 0$, then m^u is a metastable macrostate of the canonical ensemble, in the sense that it is a local but not global minimum of $F_\beta(m)$ for $\beta = s'(u)$.*

(b) *If $c(u) < 0$, then m^u is an unstable macrostate of the canonical ensemble, in the sense that it is a saddle-point of $F_\beta(m)$ for $\beta = s'(u)$.*

What this result says physically is that a macrostate value m^u which is stable in the microcanonical ensemble can become unstable and thus decay in time if we release the energy constraint and fix the inverse temperature instead, as in the canonical ensemble. The precise way in which m^u decays in the canonical ensemble to a different equilibrium value m_β is determined by the local geometry of $F_\beta(m)$ around m^u which is determined, in turn, by the sign of $c(u)$. For more details on this result, the reader is referred to two papers^{1,11} which contain the result of Theorem 4.2 in a more or less conjectured form. A proof of this theorem can be found in a recent proceedings paper of Campa and Giansanti.⁵ Another proof will be presented elsewhere.¹²

5. Concluding remarks

The present paper hardly exhausts the subject of nonequivalent ensembles and metastability. In going further, we could have reviewed recent works on the dynamics of nonequivalent states in the canonical ensemble,^{2,18,4} as well as the dynamical stability of these states¹⁰ which is discussed, for example, in Anteneodo's contribution to these proceedings using an approach based on Vlasov's equation. We could have alluded also to the fact that nonconcave entropies are seen in fields as disconnected as string theory⁷ and multifractal analysis.³ Finally, we could have mentioned our recent work on a generalization of the canonical ensemble which aims at converting unstable and metastable states of the canonical ensemble into stable, equilibrium states of a modified canonical ensemble so as to recover equivalence with the microcanonical ensemble.⁸ Research is ongoing on this topic.

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