

Metastability within the generalized canonical ensemble

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Available online 31 January 2006

Abstract

We discuss a property of our recently introduced generalized canonical ensemble [M. Costeniuc, R.S. Ellis, H. Touchette, B. Turkington, The generalized canonical ensemble and its universal equivalence with the microcanonical ensemble, *J. Stat. Phys.* 119 (2005) 1283]. We show that this ensemble can be used to transform metastable or unstable (nonequilibrium) states of the standard canonical ensemble into stable (equilibrium) states within the generalized canonical ensemble. Equilibrium calculations within the generalized canonical ensemble can thus be used to obtain information about nonequilibrium states in the canonical ensemble.

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Keywords: Nonequivalent ensembles; Nonconcave entropy; Generalized canonical ensemble; Metastability

The calculation of the equilibrium properties or *states* of systems having a nonconcave microcanonical entropy function (entropy as a function of the mean energy) is plagued by a fundamental problem. Because of the nonconcavity of the entropy function, these systems possess energy-dependent equilibrium states in the microcanonical ensemble that have no equivalent whatsoever within the set of temperature-dependent equilibrium states of the canonical ensemble [1–6]. These so-called *nonequivalent microcanonical states* cannot, as a result, be calculated or predicted from the point of view of the canonical ensemble. To assess them, one must either resort to the microcanonical ensemble, with all the analytical or numerical complications that this may imply, or else one must find a method with which one can study the nonequilibrium (i.e., metastable or unstable) states of the canonical ensemble. Indeed, it is known that nonequivalent microcanonical states correspond in general to metastable or unstable critical states of the canonical ensemble [1, 7–10]. Hence, if one is able to calculate all the critical states of the canonical ensemble (equilibrium and nonequilibrium), then one has a complete knowledge of all the microcanonical equilibrium states, including the nonequivalent ones.

Recently, we have followed this last line of thought to propose a generalization of the canonical ensemble which effectively transforms some of the metastable and unstable critical states of the canonical ensemble into equilibrium states of a generalized canonical ensemble [11, 12]. The generalized canonical ensemble is defined

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by the following probability measure

$$P_{g,\alpha}(\omega) = \frac{1}{Z_g(\alpha)} e^{-\alpha H(\omega) - ng(H(\omega)/n)}, \tag{1}$$

where

$$Z_g(\alpha) = \int e^{-\alpha H(\omega) - ng(H(\omega)/n)} d\omega \tag{2}$$

represents a generalized canonical partition function. In these expressions, ω denotes the microstate of an n -body system with Hamiltonian $H(\omega)$, α is an analog of an inverse temperature, and g is some continuous function of the mean energy $H(\omega)/n$ which is as yet unspecified. The canonical ensemble is a special instance of this measure obtained, obviously, by choosing $g = 0$ and $\alpha = \beta$. The case of quadratic functions $g(u) = \gamma u^2$ defines a statistical–mechanical ensemble known as the Gaussian ensemble [13,14].

We have reported many properties of the generalized canonical ensemble in two recent papers [11,12]—one containing rigorous results and their detailed proofs [11], and another one which is more “physical” in its presentation [12]. The main point formulated in these papers is that the generalized canonical ensemble can be used, with suitable choices of the function g , to assess all the microcanonical equilibrium states of a system, including those not found at equilibrium in the canonical ensemble. In other words, for suitable choices of g , the generalized canonical ensemble can be made equivalent with the microcanonical ensemble in the thermodynamic limit. The conditions on g that ensure equivalence are stated in these papers both in terms of the microcanonical entropy function and in terms of a generalized canonical free energy function defined from $Z_g(\alpha)$.

Our aim in this short contribution is to discuss one interesting property of the generalized canonical ensemble that we have alluded to above, namely that the generalized canonical ensemble can be used to transform metastable or unstable (nonequilibrium) states of the canonical ensemble into stable (equilibrium) states. We shall try to explain herein how this is possible and how this works in practice.

The framework of our discussion is the same as in our previous papers [11,12]. We consider an n -body system described by some Hamiltonian function $H(\omega)$, with ω denoting the microstate of the system. In the canonical ensemble, that is, in a situation where the system is in contact with a fixed-temperature heat bath, all the equilibrium properties of the system are calculated using Gibbs’s canonical measure

$$P_\beta(\omega) = \frac{e^{-\beta H(\omega)}}{Z(\beta)}, \quad Z(\beta) = \int e^{-\beta H(\omega)} d\omega. \tag{3}$$

To calculate, for example, the equilibrium or thermodynamic-limit value of the mean Hamiltonian $h(\omega) = H(\omega)/n$ associated with a given value β of the inverse temperature, one first writes the probability measure for h , i.e.,

$$P_\beta(u) = \int_{\{\omega:h(\omega)=u\}} P_\beta(\omega) d\omega = \int \delta(h(\omega) - u) P_\beta(\omega) d\omega, \tag{4}$$

and then finds the global maximum of $P_\beta(u)$ in the limit where $n \rightarrow \infty$. The result of these steps is well-known: the global maximum of $P_\beta(u)$, which corresponds again to the equilibrium value of $h(\omega)$ in the canonical ensemble with inverse temperature β , is given by the global minimum of the function

$$F_\beta(u) = \beta u - s(u) \tag{5}$$

evaluated at fixed β . The function $s(u)$ in this expression is the microcanonical entropy function defined by the usual limit

$$s(u) = \lim_{n \rightarrow \infty} \frac{1}{n} \log \int \delta(h(\omega) - u) d\omega. \tag{6}$$

In the remainder, we shall denote the global minimum of $F_\beta(u)$ at fixed β by u_β .

This calculation of the equilibrium value u_β enables us to understand in a very simple manner how metastable and unstable states can arise in the canonical ensemble. Also, we can understand with it why these

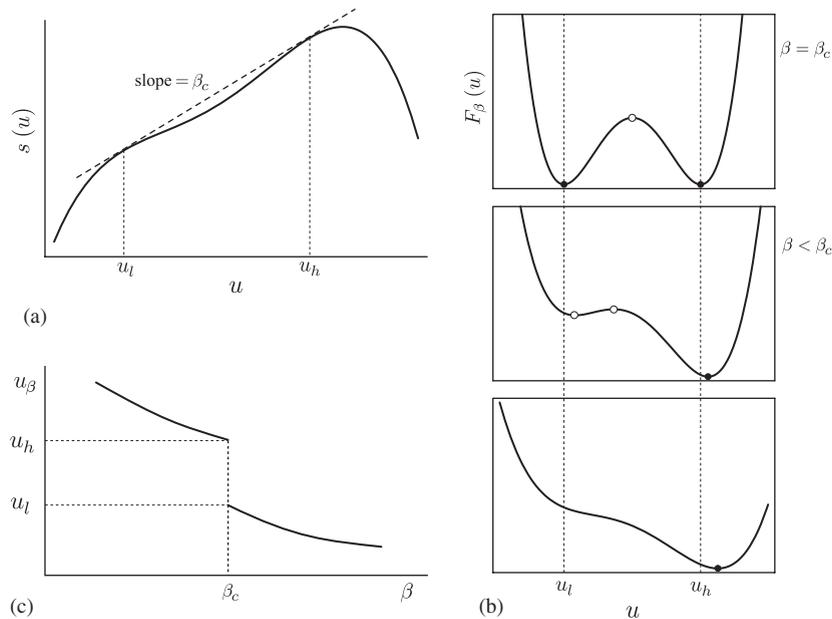


Fig. 1. (a) Generic nonconcave microcanonical entropy function. (b) The function $F_\beta(u)$ constructed from $s(u)$ shows, for some values of β , a local minimum and a local maximum in addition to a global minimum. The global minimum defines the canonical equilibrium mean energy u_β , while the local min and local max correspond to metastable and unstable mean energies of the canonical ensemble, respectively. (c) Behavior of u_β as a function of β . The nonconcavity of $s(u)$ leads to a first-order phase transition in the canonical ensemble. This is reflected in $F_\beta(u)$ by the fact that the global minima of this function never enter the range (u_l, u_h) .

states must arise in connection with nonequivalent ensembles and nonconcave entropies. The key points to observe here are the following (see also Fig. 1):

- There can be mean-energy values u in the domain of $F_\beta(u)$ that do not correspond to global minima of $F_\beta(u)$ for any β . In other words, the set of all possible values of u_β , i.e., its range, can be a proper subset of the domain of $F_\beta(u)$, which is the same as the domain of $s(u)$. This happens when there is a first-order phase transition in the canonical ensemble; see Fig. 1.
- The domain of $s(u)$ indicates which values of the mean energy are accessible to the microcanonical ensemble, while the range of u_β indicates which values of the mean energy are accessible to the canonical ensemble by varying β . The previous point, therefore, implies the nonequivalence of the microcanonical and canonical ensemble—there are energy values accessible to the microcanonical ensemble, but not to the canonical ensemble.
- Those values of u that are not global minima of $F_\beta(u)$ for any β can be local minima or local maxima of $F_\beta(u)$ for certain values of β . The local minima correspond physically to metastable states of the canonical ensemble, while the local maxima correspond to unstable states. Note that the critical points of $F_\beta(u)$ (minima, maxima or saddle-points) are given by $F'_\beta(u) = 0$ or, equivalently, $s'(u) = \beta$ if $s(u)$ is differentiable.
- In order to have local minima and local maxima of $F_\beta(u)$, $F_\beta(u)$ must be nonconvex, which implies that $s(u)$ must be nonconcave. Accordingly, the nonconcavity of $s(u)$ is a necessary condition for having metastable and unstable states in the canonical ensemble (it is also a sufficient one).

These points have all been discussed at various levels of rigor in the literature; see, e.g., Ref. [15] for a list of references on the subject of metastable and unstable states, and Ref. [10] for more recent references on the connection with nonequivalent ensembles. For our purpose, what is important to keep in mind is that, for a given β , $F_\beta(u)$ may have local minima and local maxima in addition to one or more global minima corresponding to equilibrium states, and that all of these critical points of $F_\beta(u)$ satisfy the equation $s'(u) = \beta$ if $s(u)$ is differentiable. Additionally, the stability of these critical points is determined by the sign of $s''(u)$,

provided that $s(u)$ is twice differentiable. Indeed, by basic calculus, we have that if a point \hat{u} satisfying $F'_\beta(\hat{u}) = 0$ is such that $F''_\beta(\hat{u}) = -s''(\hat{u}) > 0$, then that point must be a minimum of $F_\beta(u)$, either local or global. If the same point is such that $F''_\beta(\hat{u}) = -s''(\hat{u}) < 0$, then it is a local maximum of $F_\beta(u)$.

Now, let us consider in more details the situation in which \hat{u} is a microcanonically allowed but canonically unallowed value of $h(\omega)$ at equilibrium; i.e., suppose that \hat{u} is in the domain of $s(u)$ but not in the range of u_β . As we have noted above, \hat{u} can correspond to a metastable or unstable critical point of $F_\beta(u)$, but never to a stable point of $F_\beta(u)$, for the simple reason again that the stable points of $F_\beta(u)$ correspond to the equilibrium mean energies u_β in the canonical ensemble. However, and this is the central point of this paper, \hat{u} can correspond to an equilibrium mean energy of the generalized canonical ensemble defined by Eq. (1). The analog of $F_\beta(u)$ in the generalized canonical ensemble is the function

$$F_{g,\alpha}(u) = \alpha u + g(u) - s(u). \tag{7}$$

Therefore, the previous claim can be rephrased alternatively as following: *there is a choice of function g and value α that make \hat{u} a global minimum of $F_{g,\alpha}(u)$.*

To demonstrate our claim, let us study the critical points of $F_{g,\alpha}(u)$; these are defined by the condition

$$F'_{g,\alpha}(u) = \alpha + g'(u) - s'(u) = 0, \tag{8}$$

assuming that $s(u)$ and $g(u)$ are differentiable functions of u . Assuming further that these functions are twice differentiable, we can take the second derivative of $F_{g,\alpha}(u)$ with respect to u to obtain

$$F''_{g,\alpha}(u) = g''(u) - s''(u). \tag{9}$$

From this equation, we readily see that the stability of the critical points of $F_\beta(u) = F_{g=0,\alpha=\beta}(u)$ can be changed at will by choosing various functions g . Suppose, for example, that \hat{u} is local maximum of $F_\beta(u)$ satisfying $s'(\hat{u}) = \beta$ and $s''(\hat{u}) > 0$. Selecting g such that $g''(\hat{u}) > s''(\hat{u})$, and choosing α in the generalized canonical ensemble to be equal to the difference $s'(\hat{u}) - g'(\hat{u})$, we have now that \hat{u} must be a minimizer of $F_{g,\alpha}(u)$, for then we have $F'_{g,\alpha}(\hat{u}) = 0$, and $F''_{g,\alpha}(\hat{u}) > 0$ instead of $F''_\beta(\hat{u}) < 0$. This shows that a maximizer of $F_\beta(u)$ can be changed to a minimizer of $F_{g,\alpha}(u)$.

Whether or not \hat{u} is a local or a global minimizer of $F_{g,\alpha}(u)$ is undetermined at this point. To distinguish between the two types of minimizers, we need further notions of convex analysis that we shall not discuss here; see Ref. [4]. However, it is possible to see with a specific example that the critical points of $F_\beta(u)$ can be transformed into global minima of $F_{g,\alpha}(u)$ without any problems. Indeed, consider a quadratic function g of the form $g(u) = \gamma(u - \hat{u})^2$, where \hat{u} is a critical point of $F_\beta(u)$. The function $F_{g,\alpha}(u)$ of the generalized canonical ensemble then has the form

$$F_{\gamma,\alpha}(u) = \alpha u + \gamma(u - \hat{u})^2 - s(u). \tag{10}$$

Its first derivative evaluated at \hat{u} is

$$F'_{\gamma,\alpha}(\hat{u}) = \alpha - s'(\hat{u}) = 0, \tag{11}$$

so that the critical point \hat{u} of $F_\beta(u)$ is also a critical point of $F_{\gamma,\alpha}(u)$. Now to be sure that this critical point of $F_{\gamma,\alpha}(u)$ is a global and not just a local minimum of $F_{\gamma,\alpha}(u)$, we only have to choose a large, positive value for γ that will make the term $\gamma(u - \hat{u})^2$ dominate in $F_{\gamma,\alpha}(u)$. Changing γ in this case does not change the fact that \hat{u} is a critical point of $F_{\gamma,\alpha}(u)$, but it changes its “height” with respect to the other critical points of $F_{\gamma,\alpha}(u)$.

This transformation of the critical points of some function to global minima of a different function involving an added quadratic term is well-known in the field of optimization [16], and has been described in the specific context of nonequivalent ensembles by Ellis et al., [17]. Our work on the generalized canonical ensemble can be seen as an extension of this previous work: it generalizes the quadratic-transformation trick to arbitrary penalty functions g in the way sketched above. At the statistical–mechanical level, the added function g leads, as we have seen, to the definition of a generalized canonical ensemble, and the basic property that g must possess in order to ensure that local minima or local maxima of $F_\beta(u)$ are properly transformed into global minima of $F_{g,\alpha}(u)$ can be related physically to the existence of first-order transitions in the generalized canonical ensemble [12].

To understand this last point, recall that the metastable and unstable mean energies of $F_{g,\alpha}(u)$ lie in a forbidden range of mean-energy values for u_β , whose existence defines physically a first-order phase transition in the canonical ensemble. By transforming these metastable and unstable mean energies of the canonical ensemble to stable mean energies of a generalized ensemble, what one does, in effect, is to “shorten” or “inhibit” the range of forbidden mean energies in the generalized ensemble. That is, by choosing g , one seeks to make the jump of u_β seen in the canonical ensemble (Fig. 1c) disappear in the generalized canonical ensemble. With this in mind, one can guess that the ultimate choice of g is one that makes the function $s(u) - g(u)$ concave. In this case, $F_{g,\alpha}(u)$ must be concave for any value α , which implies that $F_{g,\alpha}(u)$ can possess only one global minimizer for every α . Local minimizers or local maximizers are then not allowed, whereby it can be proved that one recovers full equivalence between the microcanonical and generalized canonical ensembles. The complete details as to which choices of g produce this effect can be found in Refs. [11,12]; see, e.g., Theorems 3 and 4 in Ref. [12], as well as Fig. 3 in that reference.

To conclude this paper, we comment on four points:

- Our discussion of metastability was confined to the level of the energy, but it can be generalized to describe metastability at the macrostate level as well. Many spin models are known, for example, to have magnetization states which are seen at equilibrium in the microcanonical ensemble as a function of the energy, but not in the canonical ensemble as function of the temperature; see, e.g., Refs. [7,18,19]. Such nonequivalent magnetization states correspond to metastable or unstable magnetization states in the canonical ensemble, and could, in theory, be transformed to equilibrium, stable states of a properly chosen generalized canonical ensemble. Work on this topic is ongoing [20].
- The generalized canonical ensemble ($g \neq 0$) can be interpreted physically as describing a system in thermal contact with a *finite-size* heat bath, as opposed to the canonical ensemble ($g = 0$) which describes systems in thermal contact with an infinite-size heat bath. For more details on this interpretation, the reader is referred to the original work of Challa and Hetherington which introduced the Gaussian ensemble [13,14], as well as Refs. [21,22].
- The generalized canonical ensemble describes extensive systems. In defining it, it is assumed that the Hamiltonian H scales like $O(n)$ in the thermodynamic limit, that $\ln Z_g(\alpha)$ scales also like $O(n)$, and that the limit defining the microcanonical entropy in Eq. (6) exists.
- Toral recently showed by direct calculation that the equilibrium properties of a mean-field spin model can be obtained by using a modified form of the partition function, which can be thought of to define a generalized canonical ensemble [23]. His generalization of the partition function is related to our own generalization of the canonical ensemble (compare Eq. (4) in Ref. [23] with Eq. (2) of this paper). Unfortunately, Toral does not provide in his work any criteria for determining when the generalized canonical ensemble is actually useful, that is, when it is equivalent to the microcanonical ensemble or even the canonical ensemble. These criteria can be found in Refs. [11,12].

One of us (H.T.) would like to thank the organizing committee of the NEXT- $\Sigma\Phi$ 2005 Conference for the invitation to give a talk. H.T. is supported by NSERC (Canada), the Royal Society of London, and the School of Mathematical Sciences at Queen Mary, University of London. The research of R.S.E. is supported by the National Science Foundation (NSF-DMS-0202309). B.T. is also supported by the National Science Foundation (NSF-DMS-0207064).

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