



An introduction to the thermodynamic and macrostate levels of nonequivalent ensembles

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Abstract

This short paper presents a nontechnical introduction to the problem of nonequivalent microcanonical and canonical ensembles. Both the thermodynamic and the macrostate levels of definition of nonequivalent ensembles are introduced. The many relationships that exist between these two levels are also explained in simple physical terms.

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1. Introduction

Most textbooks of statistical mechanics (see, e.g., Refs. [1–5]) have sections devoted to demonstrating that the microcanonical and canonical ensembles—the two sets of equations used to calculate the equilibrium properties of many-body systems—always give the same predictions. The arguments given are most often not actual proofs, but variations of an argument originally put forward by Gibbs in his seminal treatise [6] claiming that the canonical ensemble should be equivalent to the microcanonical ensemble in the thermodynamic limit. Gibbs’s reasoning basically is that although a system having a fixed temperature does not have, theoretically speaking, only one definite value of energy (the canonical distribution is spread over many energy values), the fluctuations of the system’s energy should become negligible in comparison with its

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total energy in the limit where the volume of the system tends to infinity. In this limit, the thermodynamic limit, the system should thus appear to observation as having a definite value of energy—the very hypothesis which the microcanonical ensemble is based on.¹ The conclusion then apparently follows, namely: both the microcanonical and the canonical ensembles should predict the same equilibrium properties of many-body systems in the thermodynamic limit of these systems independently of their nature.

Gibbs's treatise is a milestone in the development of equilibrium statistical mechanics. Hence, it is not surprising that it has had a great influence on advancing the idea that it does not matter whether the equilibrium properties of a system are calculated from the point of view of the microcanonical or the canonical ensemble; i.e., whether they are calculated as a function of the energy or the temperature of the system, respectively. Gibbs himself found an explicit formula expressing the temperature of the perfect gas as an invertible function of its internal energy per particle, thus showing that the perfect gas has the same microcanonical and canonical equilibrium properties. Later on, many other many-body systems were shown to behave similarly. Faced with such evidence, it seems then logical to argue, as most physicists now do, that the equilibrium, energy-dependent properties of any large enough system can always be related in a one-to-one fashion with its temperature-dependent properties. But the problem, unfortunately, is that this is not always the case.

Since the 1960s, many researchers, starting with Lynden-Bell and Wood [7], have found examples of statistical mechanical models characterized at equilibrium by microcanonical properties which have no equivalent within the framework of the canonical ensemble. The nonequivalence of the two ensembles has been observed for these models both at the thermodynamic and the macrostate levels of description of statistical mechanics, and, recently, a complete mathematical theory of nonequivalence of ensembles due to Ellis et al. [8] has appeared in an effort to better understand this phenomenon. Our goal in this short paper is to offer a simplified and nontechnical presentation of this theory and to emphasize its physical interpretation so as to give an accessible explanation of the phenomenon of nonequivalent ensembles.

We shall start in the next section by explaining first how the microcanonical and canonical ensembles can be nonequivalent at the thermodynamic level, which is the level that has been studied the most so far. In Section 3, we then discuss a more fundamental definition of nonequivalent ensembles introduced in Ref. [8] by Ellis et al.—the *macrostate* level of nonequivalence of ensembles—and explain intuitively how this level is related to the thermodynamic level of nonequivalent ensembles. We conclude by providing in Section 4 a list of references which illustrate many of the results mentioned here, and offer some thoughts about the possibility of experimentally observing nonequivalent ensembles.

¹ For the average square of the anomalies of the energy, we find an expression which vanishes in comparison to the square of the average energy, when the number of degrees of freedom is indefinitely increased. An ensemble of systems in which the number of degrees of freedom is of the same order of magnitude as the number of molecules in the bodies with which we experiment, if distributed canonically, would therefore appear to human observation as an ensemble of systems in which all have the same energy. [6, p. xi]

2. Thermodynamic nonequivalence of ensembles

In the physics literature, there exist two basic ways by which the microcanonical and canonical ensembles have come to be defined as being nonequivalent at the level of the thermodynamic quantities of a system.² The first way is global in essence. It consists in making a statement about the overall shape of the microcanonical entropy function, which for a system consisting of n particles, is commonly defined by the limit

$$s(u) = \lim_{n \rightarrow \infty} \frac{1}{n} \ln \Omega(u), \quad (1)$$

where $\Omega(u)$ denotes the density of microstates of the system having a mean energy u [1]. From the global point of view, then, we have thermodynamic nonequivalence of ensembles whenever the graph of s contains one or more nonconcave dips that make the first derivative of s a nonmonotonic function of u .

Such a definition is likely to appear odd for physicists because most of them were taught to think that the microcanonical entropy s is an always concave function of u .³ But the truth is that this function *can* be nonconcave, as many researchers have pointed out in recent years, and the dramatic consequence of this insight is the following. If the function $s(u)$ is not concave on its entire domain of definition, then this function cannot be expressed as the Legendre transform, or the Legendre–Fenchel transform⁴, of the free energy function, the basic thermodynamic function of the canonical ensemble defined as

$$\varphi(\beta) = \lim_{n \rightarrow \infty} -\frac{1}{n} \ln Z(\beta), \quad (2)$$

where $Z(\beta)$ denotes the partition function at inverse temperature β [1]. In fact, only in the case where s' exists for all u and s' is known to be monotonic in u does s equal the Legendre transform of $\varphi(\beta)$; in symbols,

$$s(u) = \beta(u)u - \varphi(\beta(u)), \quad (3)$$

where $\beta(u) = s'(u)$.⁵

At this point, we turn to the second thermodynamic way of defining equivalent and nonequivalent ensembles. What we would like to have now is a local criterion—as opposed to the global criterion just presented—for deciding when the microcanonical and the canonical ensembles are equivalent or nonequivalent. To define such a criterion,

² See the concluding section for references.

³ A misconception propagated, once again, by most textbooks on statistical mechanics; see Refs. [9,10] for notable exceptions.

⁴ The Legendre–Fenchel transform is a generalization of the common Legendre transform which can be applied to nondifferentiable functions, and which reduces to the Legendre transform when applied to differentiable functions; see Refs. [11,12].

⁵ One can superficially understand from (3) why a nonconcave $s(u)$ cannot be expressed as the Legendre transform of $\varphi(\beta)$. If $s'(u)$ is nonmonotonic in u , then the differential equation $\beta = s'(u)$, which is the basis of the Legendre transform, will have multiple root solutions in u for some values of β . In such a case, the Legendre transform cannot induce an invertible mapping of the values of u to the values of s' as usually done when s' is a monotonic function of u .

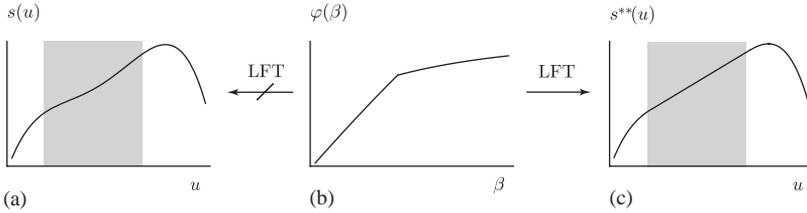


Fig. 1. (a) Nonconcave microcanonical entropy function $s(u)$ and (c) its concave envelope $s^{**}(u)$. The latter function is derived as the Legendre–Fenchel transform (LFT) of the free energy function $\varphi(\beta)$. The concave points of $s(u)$ are defined as the mean energy values u for which we have $s(u) = s^{**}(u)$. The nonconcave points of $s(u)$, on the other hand, correspond to the values of u for which $s(u) \neq s^{**}(u)$ (see shaded region).

we reverse in a way the logic of the global definition by directly defining the double dual of $s(u)$ by the Legendre–Fenchel transform of the free energy $\varphi(\beta)$ as follows:

$$s^{**}(u) = \inf_{\beta} \{ \beta u - \varphi(\beta) \}. \tag{4}$$

Such a function can be shown to be concave on its domain of definition, in addition to be equal to the minimal concave function majorizing $s(u)$ for all u [11]. Given this property of $s^{**}(u)$, it is thus to be expected that if the graph of s possesses any nonconcave dips, then there will be points of s where $s^{**}(u) \neq s(u)$. This observation is, in effect, what enables us to give a local definition of equivalent and nonequivalent ensembles. Namely, if $s^{**}(u) = s(u)$, then the microcanonical and the canonical ensembles are said to be *thermodynamically equivalent* at the mean energy value u . In such a case, the two ensembles are equivalent precisely in the sense that the value of s at u can be calculated from the point of view of the canonical ensemble by taking the Legendre–Fenchel transform of $\varphi(\beta)$, as in (4). Conversely, we say that the two ensembles are *thermodynamically nonequivalent* at the mean energy value u whenever $s^{**}(u) \neq s(u)$, i.e., whenever

$$s(u) \neq \inf_{\beta} \{ \beta u - \varphi(\beta) \}. \tag{5}$$

An illustration of these definitions is given in Fig. 1.

3. Macrostate nonequivalence of ensembles

The macrostate-level definition of nonequivalent ensembles has the same relationship to the thermodynamic level definition of nonequivalent ensembles as statistical mechanics has to thermodynamics: it is a deeper and hence more refined level of conceptualization from which the other level can be derived. A virtue of the macrostate point of view is also that nonequivalent ensembles are defined in a more natural way mathematically than their thermodynamic counterparts. Choosing a macrostate, say m , related to the statistical mechanical model of interest, one needs indeed only to proceed

as follows:

1. Calculate the set \mathcal{E}^u of equilibrium values for m in the microcanonical ensemble with mean energy u .
2. Calculate the set \mathcal{E}_β of equilibrium values for m in the canonical ensemble with inverse temperature β .
3. Compare \mathcal{E}^u and \mathcal{E}_β for the different values of u and β .

If all the members of the microcanonical set \mathcal{E}^u can be put in a one-to-one correspondence with all the members of a canonical set \mathcal{E}_β , i.e., if there exists β such that $\mathcal{E}^u = \mathcal{E}_\beta$, then macrostate equivalence of ensembles is said to hold. On the other hand, if there exists a set \mathcal{E}^u (resp., \mathcal{E}_β) having at least one member which cannot be found in any set \mathcal{E}_β for all β (resp., any set \mathcal{E}^u for all u), then macrostate nonequivalence of ensembles is said to hold. Hence, we have macrostate nonequivalence of the microcanonical and canonical ensembles if one of two ensembles is richer than the other.

These definitions of macrostate equivalence and nonequivalence of ensembles are natural and require us only to check the possible relationships that may exist between the sets \mathcal{E}^u and \mathcal{E}_β . But as definitions they are also useless because they only classify. They predict nothing. What we would like to have, of course, is a list of simple criteria—based, for example, on the knowledge of thermodynamic quantities like $s(u)$ or $\varphi(\beta)$ —to decide whether or not the microcanonical and the canonical ensembles are equivalent at the level of macrostates. Could there be, for instance, any connections between the thermodynamic level of equivalence or nonequivalence of ensembles and the macrostate level of equivalence or nonequivalence of ensembles which could enable us to say anything about the latter level?

In answer to this question, Ellis, Haven and Turkington have provided in Ref. [8] a number of rigorous mathematical results which classify all possible relationships that can exist between \mathcal{E}^u and \mathcal{E}_β for all u and β based on knowledge of the microcanonical entropy function $s(u)$. Their most important results about these relationships are summarized in the following items 1, 2 and 3.⁶

1. (Full equivalence of ensembles.) If $s(u) = s^{**}(u)$ at u , and $s(u)$ is not locally flat around u , then $\mathcal{E}^u = \mathcal{E}_\beta$ for $\beta = s'(u)$.
2. (Nonequivalence of ensembles.) If $s(u) \neq s^{**}(u)$ at u , then $\mathcal{E}^u \cap \mathcal{E}_\beta = \emptyset$ for all β . Thus, thermodynamic nonequivalence of ensembles at u implies nonequivalence of ensembles at the macrostate level. This also shows that the microcanonical ensemble can be richer than the canonical ensemble.
3. (Partial equivalence of ensembles.) If $s(u) = s^{**}(u)$ at u , but $s(u)$ is locally flat around u , then $\mathcal{E}^u \subsetneq \mathcal{E}_\beta$ for $\beta = s'(u)$; i.e., \mathcal{E}^u is a proper subset of \mathcal{E}_β in this case. From this item and the first one, we conclude that thermodynamic equivalence of ensembles at u implies either full equivalence or partial equivalence of ensembles at the level of macrostates.

⁶ For simplicity, the differentiability of $s(u)$ is assumed throughout.

It is not our intention in this paper to prove these mathematical results; full proofs can be found in Ref. [8]. What we would like to do, however, is to attach a physical meaning to these results so as to give the reader an intuitive feeling for their validity. To that end, we shall simply make use of Gibbs’s argument that was stated at the beginning of this paper, although we shall take care now of specifying which values of the mean energy are realized at equilibrium in the canonical ensemble, and—this is the crucial point—how many of them are realized.

First, let us note that the values of the mean energy which are realized at equilibrium in the canonical ensemble must correspond to the global minimizers of the function $I_\beta(u) = \beta u - s(u)$. This is a well-known fact of equilibrium statistical mechanics; see Ref. [1]. From this result it is then not difficult to verify that if $s(v) = s^{**}(v)$ and if s is not locally flat around v , then $I_\beta(u)$ has a unique global minima located at v for $\beta = s'(v)$ [13]. In such a case, Gibbs’s reasoning is thus true; namely, in the limit where $n \rightarrow \infty$, the canonical ensemble with inverse temperature $\beta = s'(v)$ does indeed reduce to the microcanonical ensemble with mean energy v because, in this very limit, the canonical ensemble assumes the unique equilibrium mean-energy value v . This intuitively leads us to the result stated in item 1.

In the case of a point v where $s^{**}(v) \neq s(v)$, we can work out a similar argument; however, the result that we have to use now is the following. If $s^{**}(v) \neq s(v)$ at v , then the mean energy value v can never be realized at equilibrium in the canonical ensemble for all β [13]. In other words, the canonical ensemble must jump over all values of the mean energy for which we have thermodynamic nonequivalence of ensembles. In this case, we intuitively expect to have $\mathcal{E}^u \cap \mathcal{E}_\beta = \emptyset$ for all β , as stated in item 2. Note, as an aside, that this argument leads us to an interesting result: any region of thermodynamic or macrostate nonequivalence of ensembles must give rise to a first-order canonical phase transition.⁷

The final result that we must discuss to complete our interpretation of the macrostate level of nonequivalent ensembles is the result in item 3 about partial equivalence. For this result, one can verify that if $s(v) = s^{**}(v)$ at v , but s is locally flat around v , then the canonical ensemble at inverse temperature $\beta = s'(v)$ gives rise to multiple equilibrium values of the mean energy; specifically all v such that $\beta = s'(v)$. In this situation, we accordingly expect to see the canonical ensemble reduce not to a single microcanonical ensemble, but to many coexisting microcanonical ensembles, each one corresponding to a mean-energy value realized at equilibrium in the canonical ensemble. This represents, of course, nothing but the emergence of a state of coexisting phases which normally takes place at first-order phase transitions. In more symbolic notations, we thus expect to have

$$\mathcal{E}_\beta = \mathcal{E}^{v_1} \cup \mathcal{E}^{v_2} \cup \dots, \tag{6}$$

where v_1, v_2, \dots , denote all canonical equilibrium values of the mean energy satisfying $s'(v_i) = \beta$. Under the assumption that $\mathcal{E}^{v_i} \neq \emptyset$ for all $i = 1, 2, \dots$, we then recover the statement of item 3, namely $\mathcal{E}^v \subsetneq \mathcal{E}_\beta$ with $\beta = s'(v)$.

⁷ See [8,14,15] for a proof of this result based on the properties of the Legendre–Fenchel transform.

4. Concluding remarks

The global approach to the problem of thermodynamic nonequivalence of ensembles based on the observation of nonconcave dips in the graph of $s(u)$ has been suggested by a number of people. We already mentioned the work of Lynden-Bell and Wood [7], who seem to have been the first to observe such dips in the entropy function of certain gravitational many-body systems (see [16] for a historical account). Similar observations have also been reported in the same context by Thirring and Hertel [17,18], and by Gross [19,20] more recently. For a recent survey of the subject, the reader is invited to consult the comprehensive collection of papers edited by Dauxois et al. [21]; it covers a wide range of physical models for which nonconcave anomalies of the microcanonical entropy function have been observed, and contains much information about the physics of these models. Other examples of applications related to lattice-spin systems can be found in Refs. [22–28].

The second approach to the thermodynamic nonequivalence of ensembles presented here, which explicitly focuses on the properties of Legendre–Fenchel transforms and on the local properties of $s(u)$, is due for the most part to Ellis et al. [8], and Eyink and Spohn [29] (see also Ref. [10]). The works of these authors represent also the primary sources of information for the theory of macrostate nonequivalence of ensembles. Various illustrations of this theory, dealing with statistical models of turbulence, can be found in [30,31]. We mention finally our recent work [14] on the mean-field Blume–Emery–Griffiths spin model which can be consulted as an easily accessible introduction to the material surveyed in this paper.

To conclude, we would like to call attention to the fact that no physical experiment has been designed to explicitly measure a discrepancy between the microcanonical and canonical equilibrium macrostate properties of a system. In an attempt to enter this *terra incognita*, there is perhaps no better way to start than to explore the deep connection that exists between nonequivalent ensembles and first-order canonical phase transitions [14,19,20]. Thus, one can look for a system which displays such a type of phase transitions, and then try to imagine a way to block the transition so as to be able to vary the system's energy at will within the range of energy values skipped by the canonical ensemble. The energy of the system, as such, need not be frozen indefinitely in time in order for that system to be microcanonical. In practice, what is required is to be able to select any value of the energy, and to make sure that the relaxation time of the energy fluctuations of the system is greater than the observation time (high Deborah-number-system [32]). If one is to verify the theory of macrostate nonequivalence of ensembles, then it is within the range of canonically forbidden energy values—i.e., within the range of the latent heat—that microcanonical nonequivalent values of macrostates are to be found and nowhere else.

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References

- [1] F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill, New York, 1965.
- [2] K. Huang, *Statistical Mechanics*, Wiley, New York, 1987.
- [3] R. Balian, *From Microphysics to Macrophysics: Methods and Applications of Statistical Physics*, Vol. I, Springer, Berlin, 1991.
- [4] L.D. Landau, E.M. Lifshitz, *Statistical Physics*, Landau and Lifshitz Course of Theoretical Physics, Vol. 5, 3rd Edition, Butterworth Heinemann, Oxford, 1991.
- [5] S.R.A. Salinas, *Introduction to Statistical Physics*, Springer, New York, 2001.
- [6] J.W. Gibbs, *Elementary Principles in Statistical Mechanics with Especial Reference to the Rational Foundation of Thermodynamics*, Yale University Press, Yale, C.T., 1902, reprinted by Dover, New York, 1960.
- [7] D. Lynden-Bell, R. Wood, The gravo-thermal catastrophe in isothermal spheres and the onset of red-giant structure for stellar systems, *Mon. Notic. Roy. Astron. Soc.* 138 (1968) 495.
- [8] R.S. Ellis, K. Haven, B. Turkington, Large deviation principles and complete equivalence and nonequivalence results for pure and mixed ensembles, *J. Stat. Phys.* 101 (2000) 999–1064.
- [9] G.H. Wannier, *Statistical Physics*, Wiley, New York, 1966.
- [10] W. Thirring, *Quantum Mathematical Physics: Atoms, Molecules and Large Systems*, 2nd Edition, Springer, New York, 2002.
- [11] R.T. Rockafellar, *Convex Analysis*, Princeton University Press, Princeton, 1970.
- [12] R.S. Ellis, *Entropy, Large Deviations, and Statistical Mechanics*, Springer, New York, 1985.
- [13] H. Touchette, *Equivalence and Nonequivalence of the Microcanonical and Canonical Ensembles: A Large Deviations Study*, Ph.D. Thesis, McGill University, 2003.
- [14] R.S. Ellis, H. Touchette, B. Turkington, Thermodynamic versus statistical nonequivalence of ensembles for the mean-field Blume–Emery–Griffiths model, *Physica A* 335 (2004) 518–538.
- [15] R.S. Ellis, H. Touchette, Nonequivalent ensembles, metastability, and first-order phase transitions, 2004, in preparation.
- [16] D. Lynden-Bell, Negative specific heat in astronomy, physics and chemistry, *Physica A* 263 (1999) 293–304.
- [17] W. Thirring, Systems with negative specific heat, *Z. Physik.* 235 (1970) 339–352.
- [18] P. Hertel, W. Thirring, A soluble model for a system with negative specific heat, *Ann. Phys. (NY)* 63 (1971) 520.
- [19] D.H.E. Gross, Microcanonical thermodynamics and statistical fragmentation of dissipative systems: the topological structure of the N -body phase space, *Phys. Rep.* 279 (1997) 119–202.
- [20] D.H.E. Gross, *Microcanonical Thermodynamics: Phase Transitions in “Small” Systems*, Lecture Notes in Physics, Vol. 66, World Scientific, Singapore, 2001.
- [21] T. Dauxois, S. Ruffo, E. Arimondo, M. Wilkens (Eds.), *Dynamics and Thermodynamics of Systems with Long Range Interactions*, Lecture Notes in Physics, Vol. 602, Springer, New York, 2002.
- [22] M.K.-H. Kiessling, J. Lebowitz, The micro-canonical point vortex ensemble: beyond equivalence, *Lett. Math. Phys.* 42 (1997) 43–56.
- [23] T. Dauxois, P. Holdsworth, S. Ruffo, Violation of ensemble equivalence in the antiferromagnetic mean-field XY model, *Eur. Phys. J. B* 16 (2000) 659.
- [24] I. Ispolatov, E.G.D. Cohen, On first-order phase transitions in microcanonical and canonical non-extensive systems, *Physica A* 295 (2000) 475.

- [25] M. Antoni, S. Ruffo, A. Torcini, First and second order clustering transitions for a system with infinite-range attractive interaction, *Phys. Rev. E* 66 (2002) 025103.
- [26] E.P. Borges, C. Tsallis, Negative specific heat in a Lennard–Jones-like gas with long-range interactions, *Physica A* 305 (2002) 148–151.
- [27] J. Barré, D. Mukamel, S. Ruffo, Inequivalence of ensembles in a system with long-range interactions, *Phys. Rev. Lett.* 87 (2001) 030601.
- [28] J. Barré, Microcanonical solution of lattice models with long range interactions, *Physica A* 305 (2002) 172–177.
- [29] G.L. Eyink, H. Spohn, Negative-temperature states and large-scale, long-lived vortices in two-dimensional turbulence, *J. Stat. Phys.* 70 (1993) 833–886.
- [30] R.S. Ellis, K. Haven, B. Turkington, Nonequivalent statistical equilibrium ensembles and refined stability theorems for most probable flows, *Nonlinearity* 15 (2002) 239–255.
- [31] R.S. Ellis, K. Haven, B. Turkington, Analysis of statistical equilibrium models of geostrophic turbulence, *J. Appl. Math. Stoc. Anal.* 15 (2002) 341–361.
- [32] M. Reiner, The Deborah number, *Physics Today*, January (1964) 62.