Violation of Fundamental Thermodynamic Law or Invalid Microstate Densities?

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Abstract. It is often incorrectly assumed that the number of microstates $\Omega(E,V,N,...)$ available to an isolated system can have arbitrary dependence on the extensive variables $E,V,N,...$. However, this is not the case for natural systems which can reach thermodynamic equilibrium since restrictions exist arising from the underlying equilibrium axioms of independence and a priori equal probability of microstate, and the fundamental constants of Nature. Here we derive a concise formula specifying the condition on $\Omega$ which must be met for real systems. Models which do not respect this condition will present inconsistencies when treated under equilibrium thermodynamic formalism. This has relevance to a number of recent models in which negative heat capacity and violation of fundamental thermodynamic law have been reported. Natural quantum systems obey the axioms and abide by the fundamental constants, and thus natural systems, in the absence of infinite range forces, can, in principle, attain thermodynamic equilibrium.

1. Introduction

A large number of theoretical models and experiments, purporting to represent real systems in thermodynamic equilibrium, have been published in which exotic thermodynamic behavior is found, such as negative susceptibilities (e.g. negative heat capacity). These results are usually obtained in systems with long-range forces (long with respect to the physical size of the system). Examples are; gravitational systems [1,2], nanoclusters [3,4,5,6,7], heavy ion fragmentation [8,9], spin systems [10], magnetically self-confined plasmas [11], and general models [12]. Other works have gone even further to claim violation of fundamental thermodynamic law for such systems [13]. In light of these persistent and disconcerting claims, it is prudent to review the statistical mechanical foundation of equilibrium thermodynamic formalism in order to examine the validity of applying such a formalism on these systems. It is, of course, well known that if equilibrium thermodynamic formalism is applied to systems which are not in thermodynamic equilibrium, inconsistencies will appear in the formalism [14].

Equilibrium thermodynamic formalism is derivable from statistical mechanics only under the fundamental axioms of statistical independence and a priori equal probability of the microstates. These conditions place restrictions on the dependence of the number of microstates $\Omega$ on the
extensive variables $X: E, V, N, ...$ for the system. In particular, we show here that the increase in the number of microstates with any one of the extensive variables $X$ is limited by the inequality $\Omega''/\Omega^2 < 1$, where $\Omega' \equiv \partial \Omega / \partial X$ and $\Omega'' \equiv \partial^2 \Omega / \partial X^2$, and that model systems not respecting this constraint do not have an extremum-maximum with respect to partition of the extensive variable $X$ and thus can never be assumed to be in thermodynamic equilibrium. Such models lack thermodynamic stability and are not representative of nature. Inconsistencies will then result when such models are treated under equilibrium thermodynamic formalism. These inconsistencies should not be considered as exotic new physics, but simply as inconsistencies arising from unjustified application of the formalism.

There are a number of ways to construct models which do not satisfy the extremum-maximum condition on $\Omega$. Specific examples of these will be discussed in section 6. Nature, however, is constrained by fundamental symmetries and constants in its system building. The existence of pure quantum states, quantum tunneling, and interactions with the quantum vacuum, means that natural systems respect a priori the equilibrium thermodynamic axioms of microstate independence and equal probability. Natural systems also respect the fundamental constants of nature. One such fundamental constant, leading to the quantization of natural systems, is Planck’s constant, $h$. We show here that, in the absence of infinite-range forces, quantization endows natural systems with a number of microstates dependence on the extensive variables, $\Omega(X)$, which is a scale invariant power law. All power law relations for $\Omega(X)$ satisfy the above stability constraint on $\Omega$. Such natural systems can therefore, in the isolated time relaxed regime, always be treated with equilibrium thermodynamic formalism.

In the following section we discuss the statistical mechanical foundation of equilibrium thermodynamic formalism and derive the above mentioned condition of the dependence of the number of microstates $\Omega$ on the extensive variables, required if the systems is to have an extremum-maximum with respect to partition of an extensive variable, and thus the possibility of attaining thermodynamic equilibrium. In section 3 we describe how this condition negates the possibility of negative heat capacity and convex intruders in the entropy function for systems in thermodynamic equilibrium. Section 4 shows how the condition on $\Omega$ may also be violated, even for physically consistent models, if $\Omega$ is determined through non-ergodic simulations. Such a violation, whatever the origin, also leads to in-equivalence of results obtained in the microcanonical and canonical ensembles. Section 5 demonstrates that natural quantum systems, in the absence of infinite-range forces, obey a priori the condition on $\Omega$ and thus can, in principle, reach thermodynamic equilibrium. Section 6 identifies a number of common oversights in model building which lead to violation of the condition on $\Omega$, and thus to inconsistencies in the thermodynamic formalism and claims of exotic physics. Conclusions are given in section 7.

### 2. Equilibrium: An Extremum-Maximum in the Number of Microstates

Consider an isolated system with fixed extensive variables; total energy $E$, volume $V$, particle number $N$, and any other extensive variable (to be specified by “...”). Assume that the system is composed of two subsystems, 1 and 2, and that each subsystem may have a different equation of state (different dependencies of the number of microstates on the extensive variables) as determined by $\Omega_1(E_1, V_1, N_1, ...)$ and $\Omega_2(E_2, V_2, N_2, ...)$, but each individually is spatially homogeneous. Assume that between subsystems there are fixed walls impermeable to the exchange of all extensive variables except one, for example the energy $E$, which is free to be exchanged between the two subsystems. Assuming independence of the microstates, the total number of microstates available to the combined system is,

$$\Omega(E, V, N, ...) = \int_0^E \Omega_1(E_1', V_1, N_1, ...)\Omega_2(E - E_1', V_2, N_2, ...)dE_1'. \quad (1)$$

The further assumption of a priori equal probability of the microstates then implies that the
time evolved, most probable macrostate of the isolated system, named the *equilibrium state*, is that macrostate specified by the particular partition of the energy between subsystems which has the largest number of microstates consistent with the all constraints. To determine the most probable partition of the total fixed energy \( E \), we first consider the contribution to the total number of microstates for a particular energy partition “p” with definite values for \( E_1 \) and \( E_2 = E - E_1 \),

\[
\Omega_p(E_1 : E, V, N, \ldots) = \Omega_1(E_1, V_1, N_1, \ldots)\Omega_2(E - E_1, V_2, N_2, \ldots)
\]

and look for an extremum-maximum of this function with respect to variation of \( E_1 \) or \( E_2 \), with \( E \) fixed. For example, in terms of \( E_1 \), the extremum is determined by,

\[
\frac{\partial \Omega_p(E_1 : E, V, N, \ldots)}{\partial E_1}|_{E,V,N} = \frac{\partial \Omega_1(E_1, V_1, N_1, \ldots)}{\partial E_1}|_{V_1,N_1} \cdot \Omega_2(E_2, V_2, N_2, \ldots) + \frac{\partial \Omega_2(E_2, V_2, N_2, \ldots)}{\partial E_2}|_{V_2,N_2} \frac{\partial E_2}{\partial E_1}\Omega_1(E_1, V_1, N_1, \ldots) = 0.
\]

It is easy to verify that this leads to the condition \[15\]

\[
\frac{\partial}{\partial E_1} [\log \Omega_1(E_1)] = \frac{\partial}{\partial E_2} [\log \Omega_2(E_2)],
\]

where, for brevity, we have suppressed the dependence on the other, assumed constrained, extensive variables. The connection with phenomenological thermodynamic formalism is made by assigning the entropy of both subsystems as \[14\]

\[
S(E) \equiv k_B \log \Omega(E)
\]

and thus the condition defining the extremum, Eq. \[4\], becomes

\[
\frac{\partial S_1(E_1)}{\partial E_1} = \frac{\partial S_2(E_2)}{\partial E_2} \Rightarrow \frac{1}{T_1} = \frac{1}{T_2},
\]

implying equal temperatures. Note that equation \[11\] and definition \[5\] imply that the entropy of the combined system (with the wall impermeable to energy removed) is only approximately additive. For the entropy to be exactly additive, we would require that \( \Omega(E, V, N, \ldots) = \Omega_1(E_1, V_1, N_1, \ldots)\Omega_2(E - E_1, V_2, N_2, \ldots) = \Omega_p(E_1 : E, V, N, \ldots)|_{T_1=T_2} \), which, however, is a good approximation for large systems in equilibrium (thus giving extensivity in the thermodynamic limit) since in this case there are extraordinarily more microstates consistent with the equilibrium partition than with any other partition. The additivity or not of the entropy, however, is not relevant to the issues to be discussed here.

The total energy \( E \) will thus be partitioned among the subsystems such that the resulting equilibrium macrostate, with definite values of \( E_1 \) and \( E_2 \), will be the most probable, that corresponding to the largest number of microstates, and this will be the partition giving equal temperatures. Likewise, the equilibrium partition of the volume, or of the number of particles, with the other extensive variables constrained by impermeable walls, is that which equalizes the pressure over temperature, \( P/T \), or the chemical potential over temperature, \( \mu/T \), respectively \[15\].

Therefore, statistical mechanics, under the assumptions of independence and equal probability of the microstates, explains the equilibrium state as that macrostate, among all possible macrostates, with the maximum number of microstates consistent with all constraints. The question then arises; *Does an extremum-maximum in the number of microstates, with respect*
to partition of an unconstrained extensive variable, always exist for whatever dependency of $\Omega$ on the extensive variable?

We will now show that the general answer to this question is no, and thus not all model systems can attain, even in principle, thermodynamic equilibrium. The criterion, to be obtained below, on the functional form of the dependence of $\Omega$ on the extensive variables, can thus be used to discriminate between models which can attain thermodynamic equilibrium, and models which cannot, even in principle, obtain thermodynamic equilibrium.

2.1. The Extremum-maximum Condition

We have tacitly assumed that the extremum as given by (3) or (4) corresponds to a maximum in the number of microstates. This, however, must be verified for whatever system by determining the curvature of $\Omega_p(X_1 : X)$ evaluated at its extremum, i.e. the sign of the second derivative of the contribution to the total number of microstates of a particular partition, $\Omega_p$, with respect to the unconstrained extensive variable $X_1$. For the extremum to correspond to a maximum it is thus required that,

$$\frac{\partial^2 \Omega_p}{\partial X_1^2} \Omega_1 + \frac{\partial^2 \Omega_2}{\partial X_2^2} \Omega_2 - 2 \frac{\partial \Omega_1}{\partial X_1} \frac{\partial \Omega_2}{\partial X_2} < 0,$$

or in general (dropping the subscripts), giving that

$$\Omega'' \Omega' / \Omega'^2 < 1,$$

where $X$ represents any extensive variable which is unconstrained, and where $\Omega_1$, $\Omega_2$, and their derivatives, are to be evaluated at the extremum.

Consider now the particular case that the two independently homogeneous subsystems are identical. Since at the extremum the intensive variable, corresponding to the unconstrained extensive variable $X_1$ (or $X_2$), is homogeneous (see, for example, Eq. (6)) we must necessarily have that $\Omega_1 = \Omega_2$, $\partial \Omega_1 / \partial X_1 = \partial \Omega_2 / \partial X_2$, $\partial^2 \Omega_1 / \partial X_1^2 = \partial^2 \Omega_2 / \partial X_2^2$, etc., where each is to be evaluated at the extremum. The extremum-maximum condition (7) then becomes

$$\frac{\partial^2 \Omega_p}{\partial X_1^2} = 2 \frac{\partial \Omega_1}{\partial X_1} \Omega_1 - 2 \frac{\partial \Omega_1}{\partial X_1} \frac{\partial \Omega_1}{\partial X_1} < 0,$$

or, in general (dropping the subscripts), giving that

$$\Omega'' \Omega' / \Omega'^2 < 1,$$

where $\Omega'' \equiv \partial^2 \Omega / \partial X^2$ and $\Omega' \equiv \partial \Omega / \partial X$. Equation (8) is thus a very general relation that must be satisfied for the number of microstates dependence on any one of the extensive variables if the model is to be representative of a physically consistent system that has an extremum-maximum and can thus reach thermodynamic equilibrium (see Fig. 1(a)).

For example, while a power law dependence of the form $\Omega(E) \propto (E/E^*)^D$, for some positive constant $E^*$, satisfies condition (8) for the exponent $D > 0$, an exponential dependence, $\Omega(E) \propto \exp((E/E^*)^D)$, only satisfies condition (8) if $D < 1$. If $D = 1$, $\Omega'' \Omega / \Omega'^2 = 1$, and thus no extremum exists. If $D > 1$, then the extremum of (2) is a minimum, not a maximum, i.e. $\Omega'' \Omega / \Omega'^2 > 1$ (see Fig. 1(b)). Functions of sums of two power laws (for example $\Omega(E) \propto [(E/E^*)^D + (E/E^*)^G]$), with the powers greater than zero but different, can also fail to satisfy (8) near the energy $E^*$ . This latter case is directly related to the erroneous determination of negative heat capacity for nanoclusters, which are often trapped in the microcanonical ensemble (see below and [16]).

In summary, models which purport to represent real systems in thermodynamic equilibrium, but which have a number of microstates (or phase space volume) dependence on any one of the extensive variables which does not satisfy condition (8), can never reach thermodynamic equilibrium, simply because there exists no macrostate that corresponds to an extremum which
Figure 1. Contribution of the partition $\Omega_p$ to the total number of microstates as a function of the partition of the extensive variable (in this case the energy). (a) The case of a system satisfying condition (8), a thermodynamic equilibrium exists. (b) The case of a system not satisfying condition (8), no thermodynamic equilibrium exists, only end points at which all of the extensive variable is in one part of the system.

is a maximum in the number of microstates. The extremum, if it exists, is a minimum (see figure 1(b)), and thus homogeneity of the intensive variables, e.g. temperature, pressure, or chemical potential, are the least likely macrostates, and therefore are not synonymous with thermodynamic equilibrium. These models may have a maximum in the number of microstates, but it is not an extremum, it corresponds to the end points where all of the unconstrained extensive variable will be found in one singular part of the system, leading to inhomogeneous intensive variables. For classical systems, this, in fact, would correspond to a singularity in the unconstrained extensive variable at some point in the volume. Such systems are inherently unstable and not representative of natural systems in thermodynamic equilibrium.

Note that for classical isolated small systems with long-range forces (with respect to the size of the system), the factorization of the microstates, Eq. 1, will in general not apply, and the total number of microstates of the combined system cannot be obtained by simple decomposition of the system into subsystems. However, in this case, the very notion of subsystems and constraints becomes unworkable. In fact, it makes little sense to speak of the volume or the energy distribution over the volume of such a system. The system will in general be trapped
in a reduced sub-space of the allowed phase space, the particular region being dependent on the initial conditions. The system cannot be considered to be in equilibrium and therefore equilibrium thermodynamic formalism simply does not apply. If one insists on using the entropy such as the Gibbs entropy \( S_G = -k_B \sum_{i=1}^n p_i \ln p_i \) or the Boltzmann entropy \( S = k_B \ln \Omega \) (obtained from the Gibbs entropy by assigning equal probability to each microstate \( p_i = 1/\Omega \)) then one will frequently arrive at inconsistencies such as negative heat capacity or violations of established fundamental laws since raising the energy may un-trap the system and allow it to reach previously unaccessible phase space (for example, the volume, assumed constant, could suddenly increase).

Small classical systems with long range forces treated in the canonical ensemble, however, can, in principle, be treated with equilibrium thermodynamic formalism since in this case energy can be obtained from the heat bath to avoid permanent trapping and the system will eventually visit all of allowed phase space. However, the crucial point here is the word “eventually” since barriers in energy or angular momentum, etc., may be so high that true thermodynamic averages become impractical for lack of time. This is the case when bimodal energy distributions are found \( [4] \). For a system considered in the canonical ensemble, our equation (8) still applies but now the microstates are of the system plus heat bath.

In reality, true isolated systems do not exist in Nature. All material exists in a world in which the system is immersed in a quantum vacuum, which can be thought of as providing a canonical ensemble. As long as the forces are not of infinite range, any real system therefore can in principle attain thermodynamic equilibrium. The distribution of the measured number of states with any of the extensive variables for real systems (plus quantum vacuum) must satisfy our equation (8).

3. Negative Heat Capacity and Convex Intruders

Using the thermodynamic definitions of the entropy, \( S(E) = k_B \ln \Omega(E) \), the temperature \( T \equiv \left( \frac{\partial E}{\partial S} \right)_{V,N} \), and the heat capacity \( C_{V,N} \equiv \left( \frac{\partial E}{\partial T} \right)_{V,N} \), it is straightforward to show that the heat capacity in terms of the number of microstates is

\[
C_{V,N}(E) = k_B \left[ 1 - \frac{\Omega''}{\Omega'} \frac{\Omega'}{\Omega} \right]^{-1}.
\] (9)

From this relation, it is obvious that if the heat capacity of a model system is to become negative, it is required that \( \Omega''/\Omega'^2 > 1 \), but this contradicts the extremum-maximum condition required for a stable thermodynamic equilibrium, Eq. (8). Therefore, any system displaying negative heat capacity cannot simultaneously be in thermodynamic equilibrium.

Furthermore, it is also evident from (9) that if the heat capacity of a system is to change from being positive to being negative at some energy, then it must first go through positive infinity, then flip to negative infinity, which is obviously physically inconsistent.

Given the Boltzmann relation \( S(E) = k_B \ln \Omega(E) \), the entropy function will show a convex intruder if

\[
\frac{\partial^2 S}{\partial E^2} = k_B \left[ \frac{\Omega''}{\Omega} - \frac{\Omega'^2}{\Omega^2} \right] > 0,
\]
giving that \( \Omega''/\Omega'^2 > 1 \), which, again, is in direct contradiction to the condition required for thermodynamic equilibrium. Therefore, any system showing a convex intruder in the entropy function (or, equivalently, a concave intruder in the energy function) cannot simultaneously be in thermodynamic equilibrium.
4. Ergodicity and Inequivalence of Ensembles

Negative heat capacity and convex intruders may result even when employing physically consistent models but when using simulations to determine Ω which are not ergodic, leading to a determined Ω which does not satisfy (8). Long-range forces in small systems lead to large energy barriers separating different regions of the energetically available phase space. For classical simulations, independence and a priori equal probability of the microstates cannot be assumed if there is not sufficient energy available in the system to surmount the barriers. This occurs frequently below the solid to liquid transition energy in small nanoclusters when treated in the classical microcanonical ensemble [16].

The determined Ω from these simulations may not satisfy the extremum-maximum condition (8), even though the ergodically determined Ω does, since on surmounting an energy barrier, suddenly (in energy) a large portion of previously unaccessible phase space becomes available. The measured energy dependence of Ω may thus increase arbitrarily rapidly with energy, leading to the erroneous determination of negative heat capacity. The problem is not easy to identify beforehand as it is related to the particularly difficult task of proving the ergodicity of a dynamical system.

This, however, is not an “in principle” problem for simulations in the canonical ensemble since any amount of energy can be obtained from the heat bath for surmounting whatever barrier. This assumes, however, that sufficient time is allowed for the trajectory to visit all allowed microstates. If not, bi-modal energy distributions at a fixed temperature may be found [16]. The Laplace transform between the ensembles is not valid for these non-ergodic simulations. This is the origin of the inequivalence of the canonical and microcanonical ensembles for such simulations.

In the case of convex intruders, the thermodynamically stable states correspond to points on the tangent lines lying everywhere above the entropy function [14]. Taking these tangent lines to define the stable states is equivalent to ignoring the barriers and imposing equal probability to all of the microstates, including the mixed solid-liquid states energetically available but not accessible because of high energy barriers [16].

Taking the determined entropy function with a convex intruder, obtained by non-ergodic simulation as the fundamental relation, will result in inconsistencies in the equilibrium thermodynamic formalism (see also [16, 17, 18, 19]).

5. Natural Quantum Systems

We now show that natural quantum systems, in the absence of infinite-range forces, obey the equilibrium thermodynamic axioms of independence and equal probability of the microstates and, as a result of quantization, have a number of microstates dependence that satisfies condition (8) at all energies.

Non-ergodicity, or trapping by barriers, is not an “in principle” problem in quantum systems because of quantum tunneling and interaction of the system with the quantum vacuum. The principle of detailed balance, resulting from the time reversibility of the Schrödinger equation, then ensures that all microstates have a priori equal probability [14].

The existence of a finite Planck’s constant implies that the energy, volume, particle, and any other extensive variable, eigenstates are quantized. Consider, for example, a state space of a simple system of fixed energy $E$, volume $V$, and particle number $N$, containing $D$ degrees of freedom for storing energy. Assume that the energy is quantized in units of $\hbar\omega_0$ (for example, the Einstein model of a solid [14], where $D = 3N$, with $N$ equal to the number of particles). The number of microstates available to this system corresponds to the number of ways to distribute the $E/\hbar\omega_0$ energy packets over $D$ degrees of freedom, which is $\begin{pmatrix} D + E/\hbar\omega_0 - 1 \\ D - 1 \end{pmatrix}$.
\[ \Omega(E) = \frac{(D - 1 + E/\hbar\omega_0)!}{(D - 1)!\left(E/\hbar\omega_0\right)!} \approx \frac{1}{D!} \left( \frac{E}{\hbar\omega_0} \right)^D = \frac{1}{3N!} \left( \frac{E}{\hbar\omega_0} \right)^{3N}, \tag{10} \]

where the result to the right of the \( \approx \) sign is obtained by calculating the number of quantum states with energy less than, or equal to, \( E \), which is a very good approximation for the number of microstates \( \Omega(E) \) with energy between \( E \) and \( E + \delta E \), as long as \( D \gg 1 \) \[14\]. The number of microstates of a quantum system thus increases as a scale invariant power law in energy \( E \), with the exponent of the power law being equal to the number of independent degrees of freedom \( D \). This result does not depend on whether the frequencies of all modes are the same, \( \omega_0 \), or whether there exists a spectrum of values \( \omega_i \).

A similar power law can be obtained for the number of microstates dependence on the other extensive variables, such as the volume \( V \), or the particle number \( N \). For example, the dependence of \( \Omega \) on the number of particles \( N \) can be found by holding constant the total energy and allowing \( N \) to vary. By the inherent symmetry apparent in the term to the left of the \( \approx \) sign in equation (10), and for \( E/\hbar\omega_0 \gg 1 \), it is easy to see that the result is

\[ \Omega(N) \approx \left( \frac{E}{\hbar\omega_0} \right)! \left( \frac{3N}{\hbar\omega_0} \right)^E. \]

It is trivial to show that all power law relations satisfy condition [5], thus \( \Omega \) is satisfied by natural quantum systems at all energies, particle numbers, and volumes. Therefore, all isolated natural systems in the absence of infinite-range forces can, in principle, attain stable thermodynamic equilibrium.

In the limit \( \hbar \to 0 \), the exponent of the power law \( \to \infty \), and it is easy to verify that \( \Omega\Omega'/\Omega'' \to 1 \), and thus, in this limit, there exists no extremum-maximum, no thermodynamic equilibrium. Quantization of the energy, or the existence of a finite Planck’s constant, is therefore a necessary condition to ensure thermodynamic stability of an isolated macroscopic system. The same holds true for quantization of particle number, volume, and spin, etc. This is the macroscopic analogue of the fact that quantization is a necessary condition to ensure the stability of the atom.

6. Non-physical Model Design

Models meant to provide insight on the thermodynamic behavior of natural systems must have incorporated in their construction all the degrees of freedom and their correspondent constraints that the system is subject to in Nature. For example, models representing isolated systems must respect conservation of energy, momentum, angular momentum, volume, charge, particle number, etc. However, there are other constraints that arise because of the fundamental constants of Nature. For example, maximum signal rates (velocity of interaction) cannot exceed the velocity of light, \( c \). Also, the number of microstates within a given volume \( \Gamma \) of state space cannot exceed the value \( \Gamma/\hbar^{D/2} \), \[14\] where \( D \) is the dimensionality of state space, which is limited by the finite value of Planck’s constant \( \hbar \). This requirement is equivalent to the quantization of thermodynamic variables, including those arising from internal degrees of freedom, such as spin. Furthermore, quantum tunneling and interaction with the vacuum, plus the reversibility of the Schrödinger equation, then ensures equal probability of the microstates \[14\]. In counting microstates, it is also important to take into account the indistinguishability of elementary particles and their particular statistics (Fermi-Dirac, or Bose-Einstein). Although at high temperatures or low pressures, the quantum description often coincides with the classical description for some thermodynamic properties, this is not the case for counting microstates, as the Gibb's paradox makes explicitly clear \[14\].
Relevant models must also be physically consistent. For example, internal interaction fields providing an exchange of energy cannot be presumed to exist in isolation, but must necessarily arise from internal material sources. External fields affecting the internal energy or entropy, must be taken into account by, for example, modifying the chemical potential \[20\].

Still another important condition for the thermodynamic analysis to be free of inconsistencies is that the number of extensive variables used in the analysis must be commensurate with the number of degrees of freedom in the models state space, which depends on the particular Hamiltonian of the system \[14\] \[21\]. For example, inconsistencies in the thermodynamic analysis of molecular hydrogen gas lead to the discovery of ortho- and para-hydrogen \[14\].

Models not respecting these restrictions will present inconsistencies when treated under equilibrium thermodynamic formalism constructed on the basis of the existence of these \[14\]. In particular, such models may fail the condition for the existence of a extremum-maximum, \(\Omega''/\Omega^2 < 1\). Neglect of these considerations when constructing models has often lead to the reporting of the inconsistencies as if they were indicative of new physical phenomena, or of violations of fundamental thermodynamic law. Below we identify particular cases exemplifying some of the typical neglect of consideration mentioned above.

In \[3\], a model is presented purporting to demonstrate the possibility of negative heat capacity in nanoclusters. The energies of the microstates in this model are arbitrarily assigned and not derived from a physically consistent Hamiltonian using the Schrödinger equation, or by quantization of a classical phase space volume. The model, in fact, violates the condition of energy quantization and has an arbitrarily large degeneracy in energy of the higher energy states, leading to a violation of the extremum-maximum condition on \(\Omega\). Such models do not respect a finite Planck's constant which implies a power law distribution of the energy states, and furthermore do not respect correct particle statistics, and, therefore, cannot be used for elucidating equilibrium thermodynamic properties of real nanoclusters.

Another model, also purporting to lend support for negative heat capacity in real systems, is given in \[2\]. Here, internal fields not arising from material sources are included, and the volume is arbitrarily defined by a non-interacting sphere. Alternatively, if the authors had intended the field to be external, then it should have been taken into account consistently by defining new intensive variables (e.g. new chemical potentials) that includes the energy exchanged with the system \[17\].

Non-ergodic experiments or simulations, although employing physically consistent models, can lead to a determined energy dependence of \(\Omega\) that does not respect the extremum-maximum condition, thereby giving “apparent” negative heat capacity. Such results on nanoclusters have been frequently presented in the literature \[3, 5, 7, 1, 22, 23\]. The prevailing consensus regarding these results is that negative heat capacity arises from a particular, but inherent, distribution of the energy states of the nanocluster \[3, 5, 4, 23\]. However, these explanations consistently ignore the additional degrees of freedom for carrying energy that arise as the system changes phase. For example, proponents of this explanation derive an identical heat capacity for the liquid as for the solid, which is clearly in contradiction with both experiment and results from simulations \[7\]. It is, in fact, the occulting of these additional degrees of freedom in the microcanonical ensemble due to large energy barriers that leads to the erroneous determination of negative heat capacity \[16\].

The correct \(\Omega\) for nanoclusters contains sums of contributions of the different mixed solid-liquid states, and these contributions increase with energy as different power laws \[16\]. The powers are different because of the different number of degrees of freedom for storing energy for those atoms in the liquid portion compared to those in the solid portion. In the liquid phase, in addition to the vibrational modes, the atoms can carry kinetic energy related to their diffusion about the cluster. This gives rise to the observed different heat capacities of the two phases. Including the mixed solid-liquid states at the relevant energy results in no negative
heat capacity being found [16]. Including only the states in which all atoms are in the solid, and then, on passing a high barrier at energy $E^*$, including only the states in which all atoms are in the liquid, gives a determined number of microstates with an energy dependence of form

$$\Omega(E) \propto \left(\frac{E}{E^*}\right)^D + \left(\frac{E}{E^*}\right)^G$$

where $D$ is proportional to the number of degrees of freedom for storing energy in the solid and $G$ is proportional to the number of similar degrees of freedom in the liquid. As mentioned in section 2.1 this functional form for $\Omega$ can, depending on the difference of $G$ from $D$ (which also depends on the size of the system), violate the extremum-maximum condition [8] and thus lead to apparent negative heat capacity.

Still another example of violating the condition on $\Omega$, concluding negative heat capacity, and further suggesting the violation of a fundamental thermodynamic law, is given in [13]. The model consists of $N$ rotors (spin). A kinetic energy term and an infinite-range spin-spin interaction are modeled by a Hamiltonian of form

$$\sum_{i=1}^{N} p_i^2/2 + J/N \sum_{i,j=1}^{N} (1 - \cos(\theta_i - \theta_j)),$$

where $J$ is the spin-spin coupling constant, and $\theta$ the angle of the rotor with respect to a given axis. This system, in fact, has no spatial dimension so the Hamiltonian does not depend on the volume of the system. When the thermodynamic analysis of this system is carried out using an entropy function dependent on only two extensive variables, the total energy per particle and a total magnetization order parameter $m$, the thermodynamic results are consistent, and the microcanonical and canonical ensemble results are equivalent [13].

However, the authors then add a “nearest neighbor” interaction to the Hamiltonian of form

$$-K \sum_{i=1}^{N} \cos(\theta_{i+1} - \theta_i),$$

with periodic boundary conditions. The introduction of a nearest neighbor interaction implies the introduction of a new coordinate. The most reasonable interpretation of their model leads us to suppose that this coordinate is one-dimensional length. Spin density, and also energy density, then become relevant intensive variables to be distributed over this new coordinate. Because of the symmetry inherent in such a one dimensional chain of rotors, one would normally expect a macroscopically homogeneous distribution of the magnetization and energy for such a system in thermodynamic equilibrium. However, the authors find that the distribution of these variables is non-homogeneous when the entropy is maximum, implying a situation similar to that of figure 1(b). Their system does not have an extremum-maximum, but instead endpoint maxima at which all the magnetization or energy is in one part of the system.

According to our analysis given in the previous sections, this results from a number of microstates, as a function of the partition of the energy or the magnetization, which fails to satisfy the condition for the existence of an extremum-maximum, Eq. [8]. This failure, in turn, is related to the non-physical nature of the model (infinite-range interaction and non-quantization of spin nor of the energy, see section 5). Negative heat capacity and “evidence” for the violation of the zeroth law of thermodynamics are simply inconsistencies obtained on a non-physical model which is not in thermodynamic equilibrium and which, in fact, can never reach thermodynamic equilibrium.

7. Conclusions
Using a model to obtain the thermodynamic properties of a real system requires recognition of all the macroscopic and internal degrees of freedom as well as their constraints. We have identified a general condition [8] on the dependence of the number of microstates on any of the extensive variables which must be satisfied if the model system is to have the possibility of attaining thermodynamic equilibrium. Model systems not satisfying this condition are systems which can never reach thermodynamic equilibrium. Negative heat capacity, convex intruders in the entropy function, non-physical singularities, differences obtained in different ensembles, and violations of fundamental thermodynamic laws are all inconsistencies resulting from the application of equilibrium thermodynamic formalism to these deficient model systems. The quantization inherent in natural systems ensures the compliance with condition [8] giving an
extremum-maximum in the number of microstates with respect to partition of an unconstrained extensive variable, and thus the possibility of natural systems to arrive at thermodynamic equilibrium.

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