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2009 J. Phys. A: Math. Theor. 42 095006

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A thermodynamic fluctuation relation for temperature and energy

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Received 15 May 2008, in final form 22 December 2008

Published 4 February 2009

Online at stacks.iop.org/JPhysA/42/095006

Abstract

The present work extends the well-known thermodynamic relation $C = \beta^2 \langle \delta E^2 \rangle$ for the canonical ensemble. We start from the general situation of the thermodynamic equilibrium between a large but finite system of interest and a generalized thermostat, which we define in the course of the paper. The resulting identity $\langle \delta \beta \delta E \rangle = 1 + \langle \delta E^2 \rangle \partial^2 S(E) / \partial E^2$ can account for thermodynamic states with a negative heat capacity $C < 0$; at the same time, it represents a thermodynamic fluctuation relation that imposes some restrictions on the determination of the microcanonical caloric curve $\beta(E) = \partial S(E) / \partial E$. Finally, we comment briefly on the implications of the present result for the development of new Monte Carlo methods and an apparent analogy with quantum mechanics.

PACS numbers: 05.20.Gg, 05.40.-a, 75.40.-s

1. Introduction

From the standard perspective of statistical mechanics, it is customary to start with the Gibbs canonical ensemble given by

$$\hat{\omega}_c(\beta, N) = \frac{1}{Z(\beta, N)} \exp\{-\beta \hat{H}_N\}, \quad (1)$$

providing a macroscopic description of a Hamiltonian system \hat{H}_N in thermodynamic equilibrium with a heat bath (a very large heat reservoir) at constant temperature T , where $\beta = 1/k_B T$. Hereafter, the Boltzmann constant k_B is set to 1. In this context, other thermodynamic parameters of the system, such as the volume V or an external magnetic field H , are also admissible, but we assume in this paper that every parameter remains constant. A straightforward consequence of using this kind of statistical ensemble is that the relation

between the heat capacity $C = \partial E / \partial T$ and the canonical average of the energy fluctuation $\langle \delta E^2 \rangle$ is

$$C = \beta^2 \langle \delta E^2 \rangle. \quad (2)$$

Therefore, the heat capacity within the canonical description is *non-negative*, e.g., $C_V > 0$ for a fluid with volume V , or $C_H > 0$ for a magnetic system in the external magnetic field H . This same result can also be derived from a stability analysis in the framework of standard thermodynamics; therefore, it is usually claimed in several classical textbooks that those macrostates for which this condition is not satisfied are thermodynamically unstable and *cannot exist in nature* (see, for instance, in section 21 of the Landau & Lifshitz book [1]).

Surprisingly, macrostates with negative heat capacities have actually been observed in several systems belonging to different physical scenarios. For example, such heat capacities have been observed in mesoscopic short-range interacting systems such as nuclear, atomic and molecular clusters [2–5], as well as the long-range interacting systems such as astrophysical ones [6–8], often referred to as *nonextensive systems*⁴. This observation illustrates the limited validity of certain standard results of classical thermodynamics and statistical mechanics in such contexts [9]. We provide two illuminating examples below, but first let us explain how negative heat capacities arise in the thermodynamic description.

The usual way to access macrostates with negative heat capacities is via means of the microcanonical description. The fundamental key is to rephrase the heat capacity $C = \partial E / \partial T$ in terms of the Boltzmann entropy $S = \ln W$. Starting from the definition of the microcanonical inverse temperature of the system,

$$\frac{\partial S}{\partial E} = \frac{1}{T}, \quad (3)$$

we obtain then the second derivative of the entropy:

$$\frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2} \frac{\partial T}{\partial E} \Rightarrow C = -\left(\frac{\partial S}{\partial E}\right)^2 \left(\frac{\partial^2 S}{\partial E^2}\right)^{-1}. \quad (4)$$

Since the Boltzmann entropy is a geometrical measure of the microcanonical ensemble, it demands neither the extensive and concave properties usually attributed to its probabilistic interpretation:

$$S_e[p] = -\sum_k p_k \ln p_k, \quad (5)$$

nor a consideration of the thermodynamic limit. Thus, expression (4) states that negative heat capacities are directly related to the presence of macrostates with a *convex* microcanonical entropy, $\partial^2 S / \partial E^2 > 0$.

To our knowledge, the existence of negative heat capacities was first pointed out by Lynden-Bell in an astrophysical context in seminal papers [6, 7]. Interestingly, the presence of this anomaly plays a fundamental role in understanding the evolution of these remarkable physical systems [10]. A simple astrophysical model that shows an energetic region with $C_V < 0$ is the Antonov isothermal model [11]; a system of self-gravitating identical point particles with a total mass M enclosed in a rigid spherical container of radius R , whose microcanonical caloric curve is depicted in figure 1.

The existence of macrostates with negative heat capacities can also be related to the occurrence of phase coexistence phenomena or first-order transitions in finite short-range

⁴ Roughly speaking, a system is nonextensive when it cannot be trivially divided into independent subsystems, which is explained by the existence of underlying interactions or correlation effects whose characteristic length is comparable or larger than the system's linear size. Thus, the total energy in such systems is nonadditive, and frequently, they are spatially nonhomogeneous.

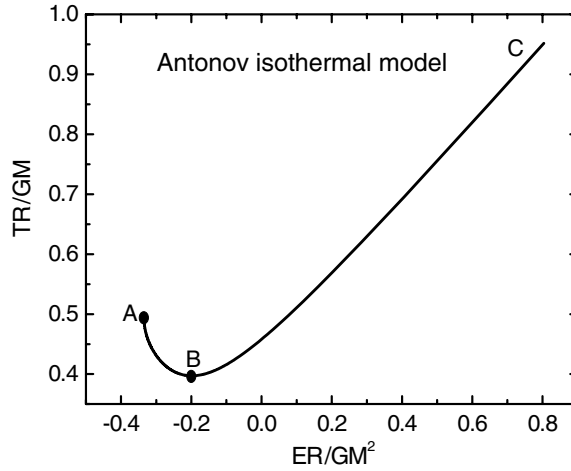


Figure 1. Microcanonical caloric curve of the Antonov isothermal model (after [11]). The branch **AB** represents macrostates where the heat capacity $C_V < 0$. Note also the nonexistence of equilibrium macrostates when $T < T_B \simeq 0.4GM/R$ or $E < E_A \simeq -0.335GM^2/R$, which is related to the occurrence of a gravitational collapse at low temperatures (canonical ensemble) or at low energies (microcanonical ensemble).

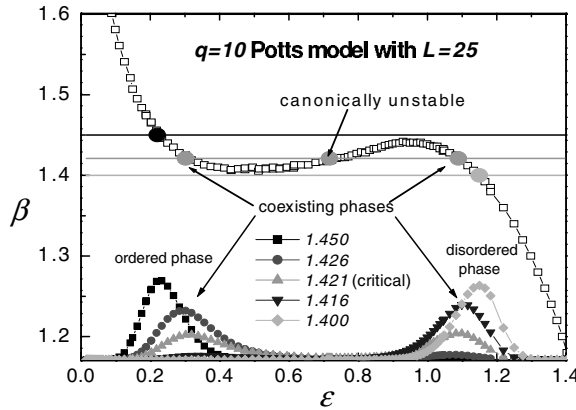


Figure 2. Monte Carlo calculations using equation (7) (see section 3.1) of phase coexistence phenomenon in the $q = 10$ states Potts model on the square lattice $N = L \times L$ with periodic boundary conditions ($\epsilon = E/N$). Note that microcanonical states with negative heat capacities are practically inaccessible by using a thermostat with constant temperature, since these macrostates are canonically unstable.

interacting systems prior to any thermodynamic limit [12–15]. Such a relationship is clearly illustrated in figure 2 for the $q = 10$ states Potts model on a square lattice $N = L \times L$:

$$H_N = \sum_{(i,j)} (1 - \delta_{\sigma_i, \sigma_j}), \tag{6}$$

with periodic boundary conditions and where the sum considers only the nearest-neighbour interactions [16]. Here, the microcanonical caloric curve $\partial S/\partial E$ in terms of the energy per particle $\epsilon = E/N$ shows a backbending indicating the presence of an anomalous region where

$C_H < 0$ at $H = |\mathbf{H}| = 0$.⁵ In the neighbourhood of the critical point $\beta_c \simeq 1.42$, the bimodal character of the energy distribution function within the canonical ensemble,

$$\rho_c(E) dE = \frac{1}{Z(\beta)} \exp(-\beta E) \Omega(E) dE, \quad (7)$$

(where $\Omega(E)$ is the state density of the system) reveals *two coexisting phases* with different energies at the same temperature (ferromagnetic and paramagnetic phases). The localization of the peaks is determined from those intersection points of the microcanonical caloric curve $\partial S/\partial E$ where $\partial^2 S/\partial E^2 < 0$ with the horizontal lines representing here the inverse temperature β of the thermostat (the ordinary equilibrium condition between the thermostat and the system temperature). Since no one peak accesses the region where $\partial^2 S/\partial E^2 > 0$ at any thermostat temperature, macrostates with $C_H < 0$ are *practically inaccessible* (unstable) within the canonical ensemble when the system of interest is large enough. Such a ‘forbidden’ region is the origin of a sudden jump of the canonical average energy $\langle E \rangle$ at the neighbourhood of the critical point β_c , which tells us about the existence of a latent heat q_L for the conversion of one phase into another.

The close relation between macrostates with negative heat capacities and first-order phase transitions in finite short-range interacting systems clarifies that such an ‘anomalous’ behaviour is far from an unusual feature within the thermostatical description, including also all those systems that have been traditionally considered within the standard thermodynamics⁶. The anomalous character of such macrostates reflects that they are physically admissible within the microcanonical description although they are thermodynamically unstable within the canonical description, indicating thus the *inequivalence* of these statistical ensembles for finite systems.

As already discussed, macrostates with $C < 0$ are not treated correctly by the fluctuation relations derived from the usual equilibrium situations of the standard statistical mechanics and thermodynamics; in fact, the condition $C < 0$ in equation (2) cannot be realized in a canonical description, where $\beta = \text{constant}$, or within a microcanonical framework, where $E = \text{constant}$ and δE vanishes. The fundamental aim of this work is to obtain a suitable generalization of the thermodynamic relation (2) that accounts for appropriately the existence of macrostates with $C < 0$.

To derive a generalized fluctuation relation resulting from the present analysis points out the role of macrostates with $C < 0$ in the experimental determination of the microcanonical caloric curve (which implies a simultaneous measurement of the temperature and energy of a given system), contributing in this way to a re-examination of an old question of the thermostatics theory: *could it be possible the existence of certain kind of complementarity between the energy and the temperature?* Such an idea was suggested by Bohr and Heisenberg in the early days of quantum mechanics [17], and so far, it has not received a general consensus in the scientific literature [18].

This paper is organized into sections, as follows: first, in section 2, we introduce concepts such as the generalized thermostat, effective inverse temperature and fluctuation in the Gaussian approximation to derive our fundamental result, equation (33). Second, in section 3, we discuss some implications on thermodynamic control and measurements. Furthermore, we perform a generalization of this result, equation (52), which constitutes an

⁵ The case with $|\mathbf{H}| \neq 0$ is described by the Hamiltonian $\mathcal{H}_N = \hat{H}_N - \mathbf{H} \cdot \mathbf{M}$, where the total magnetization $\mathbf{M} = \sum_i \mathbf{s}_i$ and $\mathbf{s}_i = [\cos(\kappa\sigma_i), \sin(\kappa\sigma_i)]$ with $\kappa = 2\pi/q$.

⁶ The consideration of the thermodynamic limit $N \rightarrow \infty$ with N/V fixed in the thermostatical description of short-range interacting systems is a useful and convenient idealization which dismisses the occurrence of boundary effects. In practice, any physical system is conformed by a very large but finite number of constituents. In fact, the existence of backbending of the microcanonical caloric curve as in figure 2 is just a finite *size effect* associated with the presence of interphases during the occurrence of the first-order phase transitions (see [15]).

‘uncertainty relation’ in thermodynamics. Finally, in section 4, we make some concluding remarks about several theoretical and practical implications of the present formalism.

2. An extending fluctuation relation

2.1. Generalized thermostat

To derive a generalized fluctuation relation (2) to deal with macrostates with $C < 0$ necessitates facing the problem of the ensemble inequivalence. Therefore, we need to start from a more general equilibrium situation of the kind described as ‘system–surrounding’, in which macrostates with negative heat capacities can be thermodynamically stable under the external influence imposed by the system–surrounding.

In thermodynamic equilibrium, the underlying physical conditions of the natural environment lead to a situation in which a given short-range interacting system obeys the Gibbs canonical ensemble (1). The natural environment is a good example of a Gibbs thermostat, since its heat capacity is so large that it can be considered to be infinite in every practical situation. According to Lynden-Bell in [14], a system with a negative heat capacity $C_1 < 0$ can reach thermodynamic equilibrium with a second system with $C_2 > 0$ when $0 < C_2 < |C_1|$. Obviously, such a condition does not hold when the first system is under the influence of the natural environment, since $C_2 \rightarrow \infty$, and therefore, it is not possible to access the macrostates with negative heat capacities. As a corollary to this reasoning, the direct observation of macrostates with negative heat capacities in a given system demands that the external influence of the natural environment be suppressed. Thus, the system of interest can be isolated (microcanonical ensemble) or it can be under the influence of a second system that remains of finite size. The latter possibility allows one to express the energy distribution function of the first subsystem as follows:

$$\rho(E_1) dE_1 = \frac{1}{\Omega_c(E_T)} \Omega_2(E_T - E_1) \Omega_1(E_1) dE_1, \quad (8)$$

where $\Omega_c(E_T) = \int_0^{E_T} \Omega_2(E_T - E_1) \Omega_1(E_1) dE_1$ and as before, $\Omega_2(E_2)$ is the state density of the second system acting as a ‘finite thermostat’, as before, and E_T is the total energy of the closed system $E_T = E_1 + E_2$.

After reading the analysis presented in the subsequent subsections, it can be realized that the consideration of the ansatz (8) is sufficient to arrive at a generalized expression of the fluctuation relation (2): a closed system composed of two independent *finite* subsystems with an *additive* total energy. However, such a physical picture is only admissible when these subsystems are coupled by the incidence of short-range interacting forces or when long-range forces are confined to each subsystem which, however, is in general nonphysical. Even in this case, the assumption presupposes the dismissal of the energy contribution involved in their mutual interactions V_{int} . Although this is a legitimate and useful approximation in standard applications of statistical mechanics and thermodynamics, it may be unrealistic in the case of mesoscopic systems with short-range interactions, and worse, this approach is not applicable in the case of long-range interacting systems. The latter case constitutes a typical scenario where macrostates with negative heat capacities naturally appear. Obviously, the additivity of the total energy is no longer applicable since the interaction energy V_{int} cannot be considered as a ‘boundary effect’ as in the case of large systems with short-range interactions. In addition, separability of a closed system into several parts is a hypothesis that should be carefully applied [19].

Nevertheless, we can find some systems in nature where it is still possible to separate a closed system into subsystems despite the presence of long-range interactions. Good examples

are galaxies and their clusters. Of course, we are unable to dismiss the interaction energy V_{int} in this scenario, but it is reasonable to assume as a consequence of the separability that this energy contribution could be approximated by a certain functional dependence on the internal energies of each subsystems, $V_{\text{int}} \simeq V_{\text{int}}(E_1, E_2)$. Thus, the usual additivity of the total energy E_T could be replaced by the following ansatz:

$$E_T = \Phi(E_1, E_2) \simeq E_1 + E_2 + V_{\text{int}}(E_1, E_2). \quad (9)$$

The number of macrostates of the whole system $\Omega_c(E_T)$ is given by

$$\Omega_c(E_T) = \int \delta[E_T - \Phi(E_1, E_2)] \Omega_1(E_1) \Omega_2(E_2) dE_1 dE_2, \quad (10)$$

which allows us to express the energy distribution of the first subsystem as follows:

$$\rho(E_1; E_T) dE_1 = \omega(E_1; E_T) \Omega_1(E_1) dE_1, \quad (11)$$

and the probabilistic weight $\omega(E_1; E_T)$ by

$$\omega(E_1; E_T) = \frac{1}{\Omega_c(E_T)} \int \delta[E_T - \Phi(E_1, E_2)] \Omega_2(E_2) dE_2. \quad (12)$$

Equation (11) constitutes a more general expression than equation (8), providing a better treatment for a *nonlinear energy interchange* between the subsystems as a consequence of the nonadditivity of the total energy ($\Delta E_1 \neq -\Delta E_2$). This kind of consideration could be applicable to both the case of large systems with long-range interactions and mesoscopic systems with short-range interactions.

Previous discussions have suggested that a general way to account for the energy distribution function $\rho(E) dE$ associated with a general ‘system–surrounding’ equilibrium situation is provided by the ansatz

$$\rho(E) dE = \omega(E) \Omega(E) dE, \quad (13)$$

where $\Omega(E)$ represents the state density of the system with internal energy E , and $\omega(E)$ is a generic probabilistic weight characterizing the energetic interchange of this system with its surrounding. The above hypothesis is very economical since it demands merely the following: (1) the existence of some kind of separability between the system and its surrounding and (2) that all external influences on the system are *fully described* by the probabilistic weight $\omega(E)$. In this work, we are accepting the validity of equation (13) regardless of the internal structure of the surrounding and the *features of their internal equilibrium conditions*. This last idea is very important and deserves to be clarified.

It is almost a rule that a large system with long-range interactions initially far from the equilibrium rapidly reaches a *metastable equilibrium* and spends a long time there [9]. If this is the case, the energy interchange of this large system acting as the ‘surrounding’ of another system cannot be treated by expressions (8) and (11). However, this metastability *does not forbid* the applicability of the ansatz (13) in many physical situations. For example, it is well known that the collisionless dynamics of astrophysical systems leads to a metastable state where the one-particle distribution function $f(q, p)$ depends only on the particle energy $\varepsilon(q, p) = \frac{1}{2m} p^2 + m\varphi(q)$, where $f(q, p) = f[\varepsilon(q, p)]$, whose mathematical form is not Boltzmannian and it is determined from the initial conditions of dynamics [20]. Since the macroscopic behaviour of the system in this metastable state is also ruled by its energy, we can expect that this physical quantity also rules its interaction with other systems. The admittance of the validity of the ansatz (13) for systems in metastable conditions accounts for the claims of some recent authors about the existence of non-Boltzmannian energy distribution functions outside the equilibrium, overall, in systems with a complex microscopic dynamics, e.g., astrophysical systems [20] and turbulent fluids [21]. A unifying framework for many

of these distribution functions is provided by the so-called superstatistics, a theory recently proposed by Beck and Cohen [22], where the presence of a non-Boltzmannian weight $\omega(E)$ seems to be originated from an effective incidence of a fluctuating inverse temperature β at the microscopic level (e.g. on a Brownian particle) obeying the distribution function $f(\beta)$ as follows:

$$\omega(E) = \int \exp(-\beta E) f(\beta) d\beta. \quad (14)$$

Since the microscopic origin and the specific mathematical form of the probabilistic weight $\omega(E)$ are arbitrary, it is expected that the conclusions, which are derived from the ansatz (13), may be applicable to a wide range of equilibrium or meta-equilibrium situations. In this formula, $\omega(E)$ constitutes a generic extension of the usual canonical weight:

$$\omega_c(E; \beta) = C \exp(-\beta E), \quad (15)$$

which rules the energy interchange of the Gibbs thermostat (a very large short-range interacting system). In an analogous way, we shall hereafter refer to the system surrounding associated with the weight $\omega(E)$ as a *generalized thermostat*. Let us now show that this generalized thermostat can also be characterized by certain *effective inverse temperature* β_ω , which controls, as usual, the energetic interchange of this thermostat with the system under study.

2.2. Effective inverse temperature β_ω

A straightforward way to arrive at this important thermodynamic quantity is by using the probabilistic weight $\omega(E)$ in the Metropolis Monte Carlo simulation of the system dynamics in this equilibrium condition. The acceptance probability for a Metropolis move $p(E|E + \Delta E)$ is given by

$$p(E|E + \Delta E) = \min \left\{ \frac{\omega(E + \Delta E)}{\omega(E)}, 1 \right\}. \quad (16)$$

By assuming that the system size is large enough, consequently, the amount of energy $|\Delta E| \ll |E|$, we are able to introduce the approximation,

$$\ln \frac{\omega(E + \Delta E)}{\omega(E)} \simeq \frac{\partial \ln \omega(E)}{\partial E} \Delta E, \quad (17)$$

and rephrase the acceptance probability (16) as follows:

$$p(E|E + \Delta E) \simeq \min\{\exp[-\beta_\omega(E)\Delta E], 1\}. \quad (18)$$

The evident analogy of this last results with the canonical case allows us to define the quantity $\beta_\omega(E)$,

$$\beta_\omega(E) = -\frac{\partial \ln \omega(E)}{\partial E}, \quad (19)$$

as the effective inverse temperature of the generalized thermostat.

It is possible to verify that this definition is not arbitrary. Besides the obvious case of the canonical weight (15) where $\beta_\omega(E)$ is the inverse temperature of the Gibbs thermostat, $\beta_\omega(E) \equiv \beta$, the present definition reduces to the usual microcanonical inverse temperature of the system acting as a ‘finite thermostat’ in equation (8), where $\omega(E) = \Omega_2(E_2)/\Omega(E_T)$ and $\beta_\omega(E) \equiv \beta_2(E_2) = \partial S_2(E_2)/\partial E_2$, being $S_2(E_2) = \ln [\Omega_2(E_2)\delta E_0]$ and $E_2 = E_T - E$.

This inverse temperature is ‘effective’ because it is not always equivalent to the ordinary interpretation of this concept in the standard statistical mechanics. In order to verify this fact, let us consider the equilibrium situation accounted for by equation (11). The internal energy of the second subsystem E_2 can be expressed as follows:

$$E_2 = E_T - E_1 - V_{\text{int}}(E_1, E_2), \quad (20)$$

where the recursive substitution of this last equation in $V_{\text{int}}(E_1, E_2)$ leads to the certain nonlinear dependence of E_2 on the internal energy of the first subsystem E_1 :

$$E_2 = E_2(E_1) \equiv E_T - \Theta(E_1; E_T). \quad (21)$$

Thus, the probabilistic weight of equation (12) is similar to the case of the ‘finite thermostat’:

$$\omega(E_1; E_T) = \frac{\Omega_2[E_2(E_1)]}{\Omega(E)}, \quad (22)$$

but the effective inverse temperature β_ω is given by

$$\beta_\omega(E_1) = \frac{\partial S_2(E_2)}{\partial E_2} \nu(E_1). \quad (23)$$

Here, the factor $\nu(E_1) = -\partial E_2/\partial E_1 = \partial \Theta(E_1; E_T)/\partial E_1 \neq 1$ accounts for the existence of a nonlinear energy interchange as a consequence of the nonadditivity of the total energy. It is remarkable that the ‘effective inverse temperature’ of a very large system surrounding depends on the internal energy E_1 despite the fact that its ‘microcanonical inverse temperature’ $\beta_2 = \partial S_2/\partial E_2$ remains practically unaltered by the underlying energy interchange, as in the case of the Gibbs thermostat.

The physical meaning of the effective inverse temperature β_ω is even more unclear in the case where the probabilistic weight $\omega(E)$ is associated with a system surrounding in a metastable equilibrium. Obviously, this kind of inverse temperature has nothing to do with the inverse temperature β of the integral representation (14) of the superstatistics formalism: while a whole set of values of β for each energy E exists, there is only one value of β_ω for each value of E . The importance of this new concept relies on the possibility of considering a wide class of equilibrium or meta-equilibrium situations in a unifying framework, where it could be possible to extend the validity of some known thermostatical results.

A fundamental identity is the condition of *thermal equilibrium*. This condition commonly follows from the analysis of the most probable macrostate \bar{E} :

$$\max_{\bar{E}} \{\omega(E)\Omega(E)\}, \quad (24)$$

which leads directly to the stationary equation:

$$\beta_\omega(\bar{E}) = \beta_s(\bar{E}), \quad (25)$$

where $\beta_s(E)$ is just the microcanonical inverse temperature of the system:

$$\beta_s(E) = \frac{\partial S(E)}{\partial E}, \quad (26)$$

where, as in the introductory section, we take $S(E) = \ln W(E)$. We have demonstrated that the quantity β_ω also obeys the ordinary form of the *zeroth principle of thermodynamics*. By analysing the expression of β_ω shown in equation (23) associated with the equilibrium between two separable subsystems with a nonadditive total energy, equation (9), we note that it is precisely β_ω , and not β_2 , which becomes equal to microcanonical inverse temperature of the first subsystem β_1 during the thermal equilibrium, $\beta_\omega = \beta_1 \Rightarrow \beta_2 \neq \beta_1$. This result is essentially the same as that presented by Johal in [23].

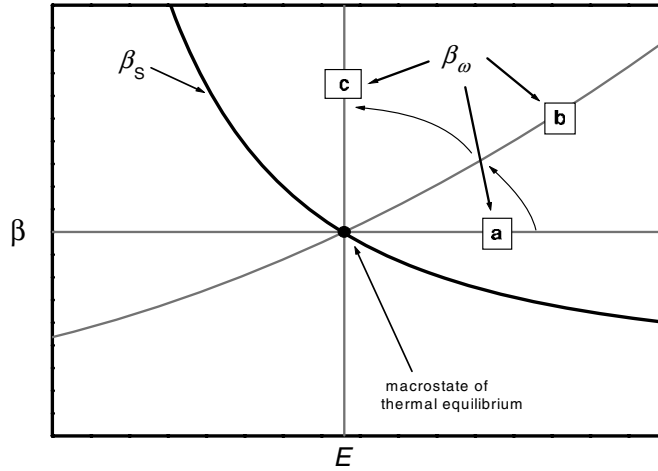


Figure 3. Typical behaviour of the effective inverse temperature β_ω is depicted for: (a) β_ω fixed for all values of E (canonical ensemble), (b) an arbitrary dependence $\beta_\omega(E)$ (generalized thermostat) and (c) E fixed for all values of β_ω (microcanonical ensemble). The black thick point represents the macrostate of thermal equilibrium where $\beta_\omega = \beta_s$ and $\beta_s(E) = \partial S(E)/\partial E$, the microcanonical inverse temperature of the system.

Let us now summarize the fundamental properties of the effective inverse temperature β_ω :

- (A) It characterizes the energy interchange ‘system–surrounding’ at the equilibrium in accordance with equation (18).
- (B) This concept permits the extension of the thermal equilibrium condition, equation (25), to a wide class of physical situations.
- (C) In general, this thermodynamical quantity depends on the internal energy of the system E , $\beta_\omega(E)$.

Properties A and B correspond to the ordinary physical notion of temperature. A new remarkable property is the general dependence of β_ω on the internal energy E of the system (property C). This fact indicates clearly that the underlying energy interchange not only imposes fluctuations on the internal energy E but also provokes the existence of *correlated fluctuations* between the internal energy E and the effective inverse temperature of the thermostat β_ω , $\langle \delta\beta_\omega \delta E \rangle \neq 0$. This simple property has been systematically disregarded in the use of the Gibbs canonical ensemble in standard statistical mechanics. We shall show in the following subsection that property C is precisely the fundamental key for arriving at a suitable generalization of the fluctuation relation (2).

Before the end of this subsection, it is important to remark that the probabilistic weight,

$$\omega_m(E; E_0) = C\delta(E - E_0), \tag{27}$$

associated with the energetic isolation or the microcanonical ensemble can also be considered as a limiting case of a generalized thermostat. The application of the definition (19) leads to an indeterminate value of β_ω :

$$\beta_\omega(E) = -\frac{\partial}{\partial E} \ln \delta(E - E_0) = \text{indeterminate}, \tag{28}$$

meaning that the thermostat inverse temperature β_ω takes any value when the energy of the system is fixed at E_0 . This idea is schematically illustrated in figure 3.

2.3. Fluctuations in the Gaussian approximation

We shall suppose in the present analysis that the system and bath are large enough to support a Gaussian approximation of the energy fluctuations around the most probable macrostate \bar{E} . In addition, we also assume that the energy dependence of the effective inverse temperature $\beta_\omega(E)$ allows for the existence of only one intersection point \bar{E} with the microcanonical caloric curve of the system $\beta_s(E)$ in the thermal equilibrium condition (25). This latter requirement is just the condition of ensemble equivalence. The average square dispersion of the internal energy $\langle \delta E^2 \rangle$,

$$\langle \delta E^2 \rangle = \int (E - \bar{E})^2 \omega(E) \Omega(E) dE, \quad (29)$$

can be estimated as follows:

$$\langle \delta E^2 \rangle^{-1} = -\frac{\partial^2}{\partial E^2} \{\ln \omega(\bar{E}) + S(\bar{E})\}. \quad (30)$$

The fluctuation $\delta\beta_\omega = \beta_\omega(E) - \beta_\omega(\bar{E})$ of the effective inverse temperature can be related to the fluctuation δE of the internal energy of the system:

$$\delta\beta_\omega = -\frac{\partial^2 \ln \omega(\bar{E})}{\partial E^2} \delta E. \quad (31)$$

If we rewrite equation (30) in the following manner,

$$-\frac{\partial^2 \ln \omega(\bar{E})}{\partial E^2} = \langle \delta E^2 \rangle^{-1} + \frac{\partial^2 S(\bar{E})}{\partial E^2}, \quad (32)$$

and combine equations (31) and (32), we arrive at the correlation between the effective inverse temperatures of the generalized thermostat and the internal energy of the system as follows:

$$\langle \delta\beta_\omega \delta E \rangle = 1 + \frac{\partial^2 S(\bar{E})}{\partial E^2} \langle \delta E^2 \rangle. \quad (33)$$

This latter identity is a generalized expression of the fluctuation relation (2). This fact can be noted by rephrasing (33) as follows:

$$C = \beta^2 \langle \delta E^2 \rangle + C \langle \delta\beta_\omega \delta E \rangle, \quad (34)$$

by using the microcanonical definition of the heat capacity, equation (4), being $\beta = \beta_s(\bar{E})$.

3. Discussions

We remark that the fluctuation relation (33) accounts for the specific mathematical form of the probabilistic weight $\omega(E)$ in an implicit way throughout the effective inverse temperature β_ω . Once more, this result supports the notion that the system-surrounding energy interchange is effectively controlled by β_ω . The imposition of the restriction $\delta\beta_\omega = 0$ associated with the Gibbs canonical ensemble (1) into equation (34) leads to the usual identity $C = \beta^2 \langle \delta E^2 \rangle$. However, the restriction $\delta\beta_\omega = 0$ is not compatible with the existence of energetic regions with negative heat capacities $C < 0$. Since the microcanonical entropy is locally convex $\partial^2 S(\bar{E})/\partial E^2 > 0$ in such anomalous regions, the identity (33) leads here to the inequality:

$$\langle \delta\beta_\omega \delta E \rangle > 1. \quad (35)$$

This means that any attempt to impose the canonical condition $\delta\beta_\omega \rightarrow 0$ in regions where $C < 0$ leads to the occurrence of very large energy fluctuations $\delta E \rightarrow \infty$, and conversely, any attempt to impose the microcanonical condition $\delta E \rightarrow 0$ is accompanied by very large fluctuations of the effective inverse temperature of the system surrounding $\delta\beta_\omega \rightarrow \infty$.

Remarkably, this behaviour suggests the existence of some kind of *complementarity* between the internal energy E and the effective inverse temperature β_ω of the surrounding, which is quite analogous to the complementarity between a coordinate q and its conjugated momentum p in quantum mechanics! Also, the divergence $\delta\beta_\omega \rightarrow \infty$, when $\delta E \rightarrow 0$ is not only applicable to regions where $C < 0$; any attempt to reduce the energy fluctuations to zero, $\delta E \rightarrow 0$, in equation (33) for any fixed \bar{E} leads to the result that

$$\lim_{\delta E \rightarrow 0} \langle \delta\beta_\omega \delta E \rangle = 1, \quad (36)$$

indicating the divergence of the effective inverse temperature fluctuations $\delta\beta_\omega \rightarrow \infty$ at this limit. The present results allow us to conclude:

- (i) While macrostates with $C > 0$ are accessible within the canonical ensemble in which the restriction $\delta\beta_\omega = 0$, the anomalous macrostates where $C < 0$ can only be accessed when $\delta\beta_\omega \neq 0$, in other words, using a generalized thermostat whose effective inverse temperature depends on energy as $\beta_\omega(E)$ ensures the validity of the inequality (35).
- (ii) The total energy E of the system and the effective inverse temperature of the generalized thermostat β_ω behave as *complementary thermodynamic quantities* within the regions where $C < 0$.
- (iii) The imposition of the microcanonical restriction $\delta E \rightarrow 0$ leads at any internal energy E to an indetermination of the effective inverse temperature of the system surrounding $\delta\beta_\omega \rightarrow \infty$, as a consequence of the suppression of the underlying energetic interchange.

A deeper understanding of the physical meaning of the previous conclusions is reached by discussing their implications for the two standard ways in which the external influence of the surrounding on the thermodynamic state of a system is used within the thermodynamics:

- as a *control apparatus* (thermostat) or
- as a *measure apparatus* (thermometer).

3.1. Implications on the thermodynamic control

It is well known that the (inverse) temperature is, *in general*, a good control parameter for the internal energy of a system; the contact of a thermostat with a given constant value β leads to the existence of small fluctuations of the internal energy $\delta E \propto \sqrt{N}$, where N is the system size. A remarkable exception is that during the first-order phase transitions. Here, a small variation in β is able to provoke a sudden change in the expectation value of the internal energy $\langle E \rangle$ of the system due to the multimodal character of the energy distribution function in the neighbourhood of the critical inverse temperature β_c inducing very large energy fluctuations $\delta E \propto N$. This physical situation was already illustrated in figure 2 of the introductory section in the case of the thermodynamical description of the $q = 10$ states Potts model on the square lattice (6). In that case, the origin of this anomaly lies in the existence of inaccessible or unstable energetic regions with $C < 0$.

From the perspective of thermodynamic control, *the fluctuation relation* of equation (33) describes the necessary conditions for which the external influence imposed by the surrounding ensures the thermodynamic stability of the system, allowing thus an effective control of the internal energy E of the controlled system. The term ‘effective control’ means that the internal energy of the system is preserved up to the precision of small fluctuations around the average value \bar{E} . This kind of fluctuating behaviour is ensured by ensemble equivalence or the existence of only one sharp peak in the energy distribution function $\rho(E) dE$, mathematically expressed by the existence of only one intersection point \bar{E} in the condition of thermal equilibrium, (25).

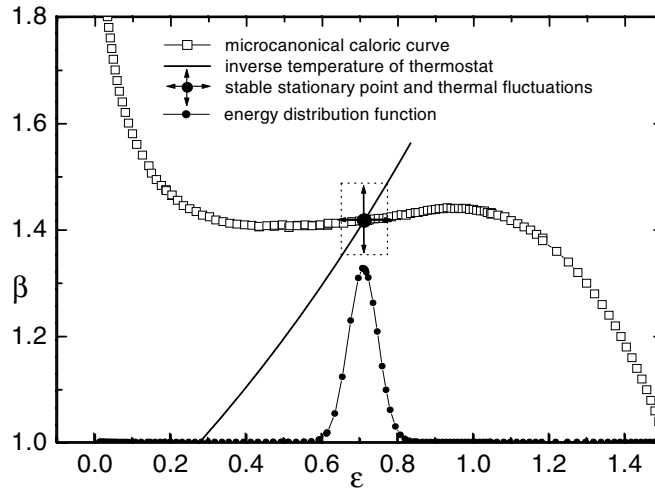


Figure 4. Metropolis Monte Carlo calculations for the 10 states Potts model as in figure 2 using equation (18). Consideration of a thermostat with a variable inverse temperature $\beta_\omega(E)$ can ensure the existence of a unique stable stationary point of the microcanonical caloric curve $\beta_s(E)$ where $\beta_\omega = \beta_s$; in this way the system can be forced to access its anomalous macrostates with $C < 0$, and at the same time, to eliminate the bimodal character of the energy distribution function in the neighbourhood of the critical inverse temperature β_c .

Conclusion (i) claims basically that macrostates with $C < 0$ can be forced to be thermodynamically stable or accessible by a generalized thermostat with an appropriate energy dependence in its effective inverse temperature $\beta_\omega(E)$. This situation is clearly illustrated in figure 4, where this particular external influence has automatically eliminated the bimodal character of the energy distribution function of the $q = 10$ states Potts model in the neighbourhood of the critical temperature as shown in figure 2.

The divergence $\delta E \rightarrow \infty$ when $\delta\beta_\omega \rightarrow 0$ within the region where $C < 0$ indicated in conclusion (ii) accounts for the well-known fact that such macrostates become unstable or inaccessible within the canonical description. This divergence is just a consequence of the Gaussian approximation employed to obtain the fluctuation relation (33), since the energy fluctuations are actually in the order of the system size and diverge only in the thermodynamic limit $N \rightarrow \infty$. Conclusion (iii) is just the mathematical result previously obtained in equation (28) and illustrated in figure 3. The practical implications of this result will be discussed in the following subsection.

As already shown, consideration of a generalized thermostat with an appropriate energy dependence of its effective inverse temperature $\beta_\omega(E)$ is a simple but an effective way to overcome the difficulties associated with the existence of macrostates with $C < 0$. In principle, the practical implementation of the present ideas should lead to the development of some experimental techniques that could be particularly useful in dealing with thermodynamical descriptions of mesoscopic systems of interest in nanosciences, where the presence of macrostates with $C < 0$ is not unusual.

Another important framework for applications is to develop more efficient Monte Carlo methods to deal with the difficulties associated with the presence of first-order phase transitions [24]. A simple and general way to account for the presence of a generalized thermostat with a given effective inverse temperature $\beta_\omega(E)$ is by using the Metropolis method based on the acceptance probability of equation (18). In fact, the microcanonical caloric curve $\beta_s(\varepsilon)$ of the

$q = 10$ states Potts model shown in figures 2 and 4 was obtained using this methodology. We calculated the averages $\langle \varepsilon \rangle$ and $\langle \beta_\omega \rangle$, where the validity of the Gaussian approximation for large N and the condition of thermal equilibrium (25) ensure the applicability of the relations

$$\bar{\varepsilon} = \langle \varepsilon \rangle \quad \text{and} \quad \beta_s(\bar{\varepsilon}) = \langle \beta_\omega \rangle. \quad (37)$$

Numerical results derived from this algorithm agree very well with those obtained using other Monte Carlo methods [25].

The idea of using the generalized thermostat with an appropriate effective inverse temperature $\beta_\omega(E)$ can be easily extended to other Monte Carlo methods based on the Gibbs canonical ensemble. A specific example is the enhancement of the well-known Swendsen–Wang (SW) cluster algorithm [16], which suffers from a *supercritical slowing down*⁷ when applied to the $q = 10$ states Potts model on the square lattice and is unable to capture the $C < 0$ regime of the microcanonical caloric curve. The thermostat inverse temperature β enters into this method via the probability for the cluster formation $p(\beta) = 1 - \exp(-\beta)$, which is used to generate a new system configuration X . While the parameter β remains constant in the original SW algorithm, our modification consists of the substitution of this parameter with the effective inverse temperature of the generalized thermostat β_ω , which is redefined in each Monte Carlo step, $\beta_\omega^i \rightarrow \beta_\omega^{i+1}$. The parameter β_ω^{i+1} used to generate the configuration X^{i+1} takes the value of the effective inverse temperature corresponding to the total energy $E_i = H_N(X^i)$ of the previous system configuration X^i , $\beta_\omega^i = \beta_\omega(E_i)$. Here, H_N is the Hamiltonian of equation (6) and $X = \{\sigma_k\}$ is the spin variables. The microcanonical caloric curve is determined by using the same relations (37) of the Metropolis method as explained before. A comparative study of the ordinary SW method (CE), and the Metropolis and SW methods with an appropriate effective inverse temperature (GCE) is depicted in figure 5. The agreement between these last Monte Carlo algorithms and their advantages over the first method are remarkable. As clearly shown, the present ideas support the development of an alternative framework of the well-known multicanonical Monte Carlo methods [24]. As in figure 3, the Monte Carlo calculations shown in figures 4 and 5 assumed the following effective inverse temperature:

$$\beta_\omega(E) = \eta \exp[\lambda(E - E_0)/N], \quad (38)$$

where η and λ are two real positive parameters controlling the horizontal position and inclination of this dependence, respectively. The value, $\lambda = 0$, corresponds to the canonical ensemble (1), while $\lambda \rightarrow +\infty$ corresponds to the microcanonical ensemble (27). More details of these calculations can be found in [26].

3.2. Implications on the thermodynamic measurements: an uncertainty relation?

Bohr and Heisenberg suggested that the thermodynamic quantities of temperature and energy are complementary in the same way as position and momentum in quantum mechanics [17]. Roughly speaking, their idea was that a *definite temperature* can be attributed to a system only if it is submerged in a heat bath (Gibbs thermostat). Energy fluctuations are unavoidable. In contrast, a definite energy can only be assigned to a system in thermal isolation, thus excluding the simultaneous determination of its temperature. Dimensional considerations suggest the existence of the following relation:

$$\delta\beta\delta E \geq 1. \quad (39)$$

However, these ideas have not reached a general consensus in the literature [18]. One objection is that the mathematical structure of quantum theories is radically different from that

⁷ An exponential divergence of the correlation time τ_N in the thermodynamic limit $N \rightarrow \infty$, $\tau_N \propto \exp(N)$.

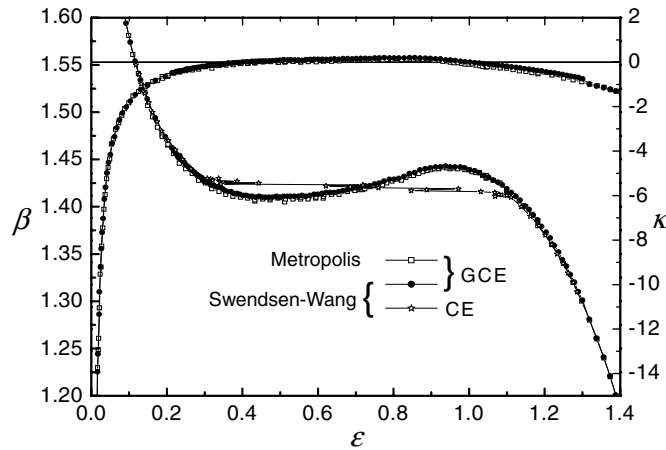


Figure 5. The ordinary Swendsen–Wang cluster algorithm (CE) is unable to account for the $C < 0$ regime of the microcanonical caloric curve $\beta_s(\epsilon) = \partial s(\epsilon)/\partial \epsilon$ of the $q = 10$ states Potts model on the square lattice as shown here by our Monte Carlo calculations. This difficulty is overcome by the Metropolis algorithm and the Swendsen–Wang cluster algorithm based on the use of an effective inverse temperature β_ω (GCE), where one can note a remarkable agreement between these algorithms. In addition, we also show here the energy per particle ϵ dependence of the second derivative of the entropy per particle, $\kappa(\epsilon) = \partial^2 s(\epsilon)/\partial \epsilon^2$, which has been obtained from the fluctuation relation (33) by calculating the fluctuations quantities $\langle \delta \epsilon^2 \rangle$ and $\langle \delta \beta_\omega \delta \epsilon \rangle$. This dependence clearly evidences the existence of an anomalous region where $\kappa(\epsilon) > 0 \Leftrightarrow C < 0$.

of classical physical theories, so there are no noncommuting observables in thermodynamics. Interestingly, the result expressed in equation (35) is quite analogous to the uncertainty relation (39).

Before analysing the implications of the fluctuation relation (33) in thermodynamic measurements, it is important to revise the concept of the temperature of a system. In the Bohr and Heisenberg arguments explained above, as well as in the works of some other authors such as the Landau (see the last paragraph of p 343 in [1]) and Mandelbrot [27], a system has a definite temperature when it is put into contact with a Gibbs thermostat. In this viewpoint, the concept of the temperature of an isolated system is unclear. We think this is a misunderstanding, since the inverse temperature β that enters in the Gibbs canonical ensemble (1) is just the microcanonical inverse temperature of the Gibbs thermostat (th), $\beta = \partial S_{th}/\partial E_{th}$. This quantity does not properly characterize the thermodynamic state of the system, but instead characterizes the thermodynamic state of the thermostat and its thermal influence on the system. Hereafter, we refer to the inverse temperature of a system defined as its microcanonical inverse temperature $\beta_s = \partial S(E)/\partial E$. From this perspective, the temperature of an isolated system is a well-defined quantity and does not undergo fluctuations, $\delta E = 0 \Rightarrow \delta \beta_s = 0$.

Although it is possible to obtain the system temperature at a given energy by calculating the Boltzmann entropy $S(E)$, the practical determination of the temperature is always imprecise. The energy is a quantity with a *mechanical significance*, and it can be determined by performing only one instantaneous measurement on an isolated system. The temperature is a quantity with a *thermostatistical significance*, whose determination demands an appeal to the concept of statistical ensembles. For example, it is derived from the statistics of measurements or temporal averages of certain physical observables with a mechanical significance usually referred to as thermometric quantities (e.g., the length of a mercury column, an electric signal, the pressure

of an ideal gas and the average form of a particles distribution function). In practice, the temperature β_s of a given system is *indirectly measured* from its interaction with another system (usually smaller than the system under study and referred to as a thermometer (th)), whose inverse internal temperature β_{th} depends on a thermometric quantity in a previously known fashion. The fundamental key supporting this procedure is precisely the condition of thermal equilibrium,

$$\beta_s = \beta_{th}. \quad (40)$$

In our approach, the surrounding can also be used as a measurement apparatus (thermometer), so the quantity β_{th} is just the effective inverse temperature β_ω . It is possible to realize that the generalized thermostat used in the previous Monte Carlo calculations has a dual role as both a control and a measure apparatus at the same time. In fact, the energy dependence of the microcanonical inverse temperature β_s of the Potts model is *a priori* unknown, and we estimate it through the effective inverse temperature of the generalized thermostat β_ω via the condition of thermal equilibrium in equation (37). This kind of computational procedure exhibits the essential features of a real determination of the energy–temperature dependence (caloric curve).

Despite the apparent simplicity, the determination of the energy–temperature dependence of a system using this procedure is rather complex, as shown by the two factors affecting its precision:

- (A) This measurement process necessarily involves a *perturbation on the thermodynamic state of the system*.
- (B) The interaction also affects the thermodynamic state of the thermometer in an uncontrollable stochastic way, leading to the existence of *errors in the determination of the effective inverse temperature β_ω* used to estimate β_s via the condition of thermal equilibrium.

It is possible to see in conclusions (ii) and (iii) that the precision factors **A** and **B** are rather *complementary*. The error type **A** can be characterized in terms of the system energy fluctuations δE , since the inverse temperature fluctuation $\delta\beta_s$ is directly correlated with δE . The error type **B** is characterized in terms of the effective inverse temperature fluctuations $\delta\beta_\omega$, which may also depend on δE , but in an indirect way. According to conclusion (iii), any attempt to reduce the perturbation of the system to zero, $\delta E \rightarrow 0$ (error type **A**) leads to a progressive increasing of the error type **B**, $\delta\beta_\omega \rightarrow \infty$ affecting the estimation of β_s using β_ω . The error type **B** can reduce to zero, $\delta\beta_\omega \rightarrow 0$, by imposing the conditions of the Gibbs canonical ensemble (1), which always involves certain perturbations of the system energy $\delta E \neq 0$ (error type **A**). This perturbation is relatively small when the system size is large enough and the heat capacity of the system is positive $C > 0$. However, this situation changes radically when the macrostate of the system is characterized by a negative heat capacity $C < 0$. According to conclusion (ii), the reduction of error type **B** to zero, $\delta\beta_\omega \rightarrow 0$, induces the thermodynamic instability of the macrostates with $C < 0$ and leads to the existence of very large energy fluctuations $\delta E \rightarrow \infty$. In practice, we should admit the simultaneous existence of error types **A** and **B**, which can reasonably be small and unimportant, when the sizes of the system under study and the thermometer are large enough. However, such errors are much significant when the system size N is small (in a system of few bodies or constituents) that the concept of system temperature becomes experimentally unobservable, and therefore, physically meaningless.

As already shown, the fluctuation relation of equation (33) accounts in some way for the limit of precision in the determination of the energy–temperature dependence of a given

system by using a measurement procedure based on thermal equilibrium with another system (thermometer). Although this qualitative behaviour is quite close to the Bohr and Heisenberg intuitive idea of energy–temperature complementarity, the fluctuation relation (33) does not always support a complementary relationship between the system energy E and the effective inverse temperature β_ω or the system energy E and inverse temperature β_s . The reason is that the mathematical structure of equation (33) does not have the form of a complementarity relation. Fortunately, this limitation is not difficult to overcome.

3.3. Generalization: the quantum-statistical mechanics analogy

The derivation of the restricted fundamental result (33) relies on the Gaussian approximation. However, there is a simple way to overcome this difficulty. The inverse temperature fluctuation $\delta\beta_s$ can be expressed for small δE in the following way:

$$\delta\beta_s = \frac{\partial^2 S}{\partial E^2} \delta E, \tag{41}$$

therefore, the fluctuation relation (33) can be rephrased as follows:

$$\langle \delta\eta \delta E \rangle = 1, \tag{42}$$

where η is the difference between the effective inverse temperature of the generalized thermostat and the microcanonical inverse temperature of the system:

$$\eta = \beta_\omega - \beta_s. \tag{43}$$

The validity of the result (42) does not depend on the Gaussian approximation. In order to show this, let us denote by $\rho(E) = \omega(E)\Omega(E)$ the energy distribution function of the ansatz (13). The distribution function $\rho(E)$ is not arbitrary. It obeys the following general mathematical conditions:

- (C1) *Existence*: the distribution function $\rho(E)$ is a non-negative, bounded and differentiable function on the set $\pi \subset R$ of all physically admissible energies E .
- (C2) *Normalization*: this function obeys the normalization condition:

$$\int_\pi \rho(E) dE = 1. \tag{44}$$

- (C3) *Boundary conditions*: this function vanishes together with its first derivative on the boundary $\partial\pi$ of the set π :

$$\forall E \in \partial\pi : \rho(E) = \frac{\partial}{\partial E} \rho(E) = 0. \tag{45}$$

The key of the demonstration is the consideration of the following identity:

$$\left\{ -\frac{\partial}{\partial E} \right\} \rho(E) = \eta\rho(E), \tag{46}$$

which allows us to associate the quantity η with an ‘operator’ $\hat{\eta}$:

$$\hat{\eta} = -\frac{\partial}{\partial E}. \tag{47}$$

By using the identity (46) as well as the properties (C2) and (C3) of the distribution function $\rho(E)$, it is easy to obtain the following results:

$$\langle \eta \rangle = \int_\pi \eta\rho(E) dE = \int_\pi \hat{\eta}\rho(E) dE = 0, \tag{48}$$

$$\langle E\eta \rangle = \int_{\pi} E\eta\rho(E) dE = \int_{\pi} E\hat{\eta}\rho(E) dE = 1. \quad (49)$$

The result (48) is just the condition of thermal equilibrium, equation (25). The fundamental result (42) is immediately obtained from equation (49) by operating as follows:

$$\langle \eta \rangle = 0 \Rightarrow \langle E\eta \rangle - \langle E \rangle \langle \eta \rangle \equiv \langle \delta E \delta \eta \rangle = 1. \quad (50)$$

The result (42) can be rephrased one more time by using the well-known *Schwarz inequality*,

$$\langle \delta A^2 \rangle \langle \delta B^2 \rangle \geq \langle \delta A \delta B \rangle^2, \quad (51)$$

arriving finally at a definitive result:

$$\Delta\eta\Delta E \geq 1, \quad (52)$$

where $\Delta\eta = \sqrt{\langle \delta\eta^2 \rangle}$ and $\Delta E = \sqrt{\langle \delta E^2 \rangle}$.

Undoubtedly, expression (52) has the form of ‘an uncertainty relation’ that exhibits now a very general validity. It clarifies that the complementary relation actually exists for the system energy E and the inverse temperature difference η between the system and its surrounding (acting as a thermostat or a thermometer). Any attempt to perform an exact determination of the system temperature β_s throughout the thermal equilibrium, $\Delta\eta \rightarrow 0$, involves a strong perturbation on the system energy $\Delta E \rightarrow \infty$, thus, E becomes indeterminable; any attempt to reduce this perturbation to zero, $\Delta E \rightarrow 0$, makes impossible to determine the system inverse temperature β_s by using the condition of thermal equilibrium since $\Delta\eta \rightarrow \infty$.

Remarkably, the above thermodynamic complementarity between E and η is quite analogous to the complementarity in quantum theories. In contrast to what was preliminarily objected, this complementarity could be also supported in terms of the noncommutativity of mathematical operators $\hat{E} \equiv E$ and $\hat{\eta} \equiv -\partial_E$:

$$[\hat{E}, \hat{\eta}] = 1 \Leftrightarrow \Delta\eta\Delta E \geq 1. \quad (53)$$

Thus, the relations of equation (53) can be considered as the statistical mechanics counterpart of the familiar quantum relations:

$$[\hat{q}, \hat{p}] = i \Leftrightarrow \Delta q \Delta p \geq 1, \quad (54)$$

where $\hbar \equiv 1$. The formal correspondence is $q \sim E$ and $p \sim \eta$. This quantum-statistical mechanics analogy can also be extended to the properties of the distribution functions: $\rho(q) = |\psi(q)|^2$ and $\rho(E) = \omega(E)\Omega(E)$, since the quantum distribution function $\rho(q)$ also obeys the properties (C1), (C2) and (C3). Demanding a little of imagination, the behaviour of the energy distribution function in the neighbourhood of the critical point illustrated in figure 2 possesses a certain analogy with the tunneling of the distribution function $\rho(q)$ (a wave packet) throughout a classical barrier; that is, the phase coexistence phenomenon can be interpreted as a ‘tunneling’ of the energy distribution function $\rho(E)$ throughout the canonically inaccessible region.

Obviously, such a quantum-statistical mechanics analogy should not be overestimated, although it is licit to recognize that it is very interesting: (1) both are physical theories with a statistical mathematical apparatus; (2) while quantum mechanics is a theory hallmarked by the ondulatory-corpuseular dualism, statistical mechanics is also hallmarked by another kind of dualism since it works simultaneously with physical quantities with a purely *mechanical significance* (e.g., energy) and physical quantities with a purely *thermostatistical significance* (e.g., inverse temperature); (3) thermodynamics is the counterpart theory of classical mechanics: while classical mechanics assumes the simultaneous determination of the position q and momentum p when $\hbar \rightarrow 0$, Thermodynamics assumes the simultaneous

determination of the system energy E and its temperature β_s in the thermodynamic limit $1/N \rightarrow 0$.

Our approach to uncertainty relations in thermodynamics constitutes an improvement in the works of Rosenfeld and Schögl [28, 29] and other efforts related to a kind of generalized canonical distributions (for instance, see [30]), which have also been based on *fluctuation theory* [1]. These authors derived their respective formulations from the consideration of a surrounding in the thermodynamics limit, and hence, this physical situation actually corresponds to the Gibbs canonical ensemble or in general the Boltzmann–Gibbs distribution [18]. Since this work hypothesis presupposes a concrete thermodynamic influence, an experimentalist has no free will to change the fluctuational behaviour of the system in a given thermodynamic state.

This important limitation is overcome in our work: the fluctuational behaviour of the system–surrounding equilibrium is modified by considering a different energy dependence of the effective inverse temperature $\beta_\omega(E)$, which presupposes to use a different experimental arrangement. In addition, it is not necessary to appeal to *statistical inference theory* to arrive at an uncertainty relation, as in the Mandelbrot development [31], which undergoes the same ‘free will limitation’ of the Rosenfeld and Schögl works explained above since it is applicable only to the framework of the Gibbs canonical ensemble. Interestingly, none of the above approaches tells anything about the relevance of anomalous macrostates with $C < 0$ on the practical determination of the system energy–temperature dependence.

4. Conclusions

In an attempt to establish an appropriate framework in order to deal with the existence of macrostates with negative heat capacities in terms of the fluctuation theory, we have introduced the concept of effective inverse temperature β_ω . This concept characterizes the thermodynamic influence of the surrounding on the system under study, and specifically allows the extension of the condition of thermal equilibrium to a wide class of equilibrium or meta-equilibrium situations. Precisely, in terms of this quantity we arrive at a suitable generalization of the well-known canonical relation between the heat capacity and the energy fluctuation, $C = \beta^2 \langle \delta E^2 \rangle$. The new identity, equation (33), defines a criterion capable of detecting macrostates of the system under study with negative heat capacities through the correlated fluctuations of the effective inverse temperature β_ω of the surrounding (generalized thermostat) and the energy E of the system itself. This constitutes a novel kind of mechanics to provide a more effective thermodynamic control on those anomalous macrostates hidden behind the phenomenon of ensemble inequivalence, inspiring the developments of new experimental control techniques to deal with the thermodynamic description for mesoscopic systems, such as those that are now of interest in nanosciences. In addition, this treatment leads to the introduction of new Monte Carlo methods to overcome the difficulties associated with the presence of first-order phase transitions.

We feel a significant aspect of this paper is to provide new physical arguments supporting the existence of a complementarity relation between the system energy and temperature, as postulated by Bohr and Heisenberg in the early days of quantum mechanics. Both the fluctuation relation (33) and its generalization (52), which can be regarded as an uncertainty relation, impose limitations on the precise determination of the energy–temperature dependence (caloric curve) of the system under study using a measurement procedure based on thermal equilibrium with another system (thermometer). While this limitation is unimportant in large enough systems, it invalidates the practical utility of some concepts of thermodynamics in the context of systems with a small number of constituents. Surprisingly, these results

suggest the existence of a remarkable analogy between statistical mechanics and quantum mechanics.

Acknowledgments

It is a pleasure to acknowledge partial financial support by FONDECYT 3080003 and 1051075. LV also thanks the partial financial support by the project PNCB-16/2004 of the Cuban National Programme of Basic Sciences.

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