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2009 J. Phys. A: Math. Theor. 42 335003

(http://iopscience.iop.org/1751-8121/42/33/335003)

IOP PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND THEORETICAL

J. Phys. A: Math. Theor. **42** (2009) 335003 (21pp) doi:10.1088/1751-8113/42/33/335003

Geometrical aspects and connections of the energy–temperature fluctuation relation

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Received 13 April 2009, in final form 25 June 2009
Published 30 July 2009
Online at stacks.iop.org/JPhysA/42/335003

Abstract

Recently, we have derived a generalization of the known canonical fluctuation relation $k_B C = \beta^2 \langle \delta U^2 \rangle$ between heat capacity C and energy fluctuations, which can account for the existence of macrostates with negative heat capacities $C < 0$. In this work, we present a panoramic overview of direct implications and connections of this fluctuation theorem with other developments of statistical mechanics, such as the extension of canonical Monte Carlo methods, the geometric formulations of fluctuation theory and the relevance of a geometric extension of the Gibbs canonical ensemble that has been recently proposed in the literature.

PACS numbers: 05.20.Gg, 05.40.−a, 75.40.−s, 02.70.Tt

1. Introduction

Recently, we have obtained a suitable extension of the canonical fluctuation–dissipation relation involving the heat capacity C and energy fluctuations [1]:

$$k_B C = \beta^2 \langle \delta U^2 \rangle + C \langle \delta \beta_\omega \delta U \rangle, \tag{1}$$

which considers a *system-surroundings* equilibrium situation in which the inverse temperature $\beta_\omega = 1/T_\omega$ of a given thermostat exhibits non-vanishing correlated fluctuations with the total energy U of the system under study as a consequence of the underlying thermodynamic interaction, $\langle \delta \beta_\omega \delta U \rangle \neq 0$. Clearly, equation (1) differs from the canonical equilibrium situation due to the realistic possibility that the internal thermodynamical state of the thermostat can be affected by the presence of the system under study. This allows us to describe the fluctuating behavior of the system under more general equilibrium situations rather than those associated with the known canonical and microcanonical ensembles.

The fluctuation relation (1) possesses interesting connections with some challenging problems related to statistical mechanics, such as (i) compatibility with the existence of macrostates exhibiting *negative heat capacities* $C < 0$ [1, 2], a thermodynamic anomaly that appears in many physical contexts (ranging from small nuclear, atomic and molecular clusters [3–6] to the astrophysical systems [7–10]) associated with the existence of *nonextensive properties* [11–14]; (ii) a direct application for the extension of available Monte Carlo methods based on the consideration of the Gibbs canonical ensemble in order to capture the presence of a regime with $C < 0$ and avoid the incidence of the so-called *super-critical slowing down* [1, 15] (a dynamical anomaly associated with the occurrence of discontinuous (first-order) phase transitions [16], which significantly reduces the efficiency of Monte Carlo methods [17]); (iii) finally, a direct relationship with an *uncertainty relation* supporting the existence of some *complementary character* between thermodynamic quantities of energy and temperature [1, 2], an idea previously postulated by Bohr [18] and Heisenberg [19] with a long history in the literature [20–23].

Our aim in this work is to present a more complete study of the existing connections of the fluctuation–dissipation relation (1). The core of our analysis is focused on certain geometric aspects relating the present approach to other geometric formulations of fluctuation theory [24]. Such ideas straightforwardly lead to a geometric generalization of the Gibbs canonical ensemble describing a special family of equilibrium distributions recently proposed in the literature [25, 26], which can also be obtained from some known formulations of statistical mechanics, such as Jaynes's reinterpretation in terms of information theory [27] as well as Mandelbrot's approach based on inference theory [28].

2. A brief review

2.1. Compatibility with negative heat capacities

Our main motivation behind deriving the fluctuation–dissipation relation (1) was to arrive at a suitable extension of the known fluctuation relation

$$k_B C = \beta^2 \langle \delta U^2 \rangle \tag{2}$$

that is compatible with the existence of macrostates with negative heat capacities [1, 2]. As discussed in many standard textbooks on statistical mechanics [16], the latter relation follows as a direct consequence of the consideration of the Gibbs canonical ensemble:

$$p_c(U|\beta) = \frac{1}{Z(\beta)} \exp\left(-\frac{1}{k_B}\beta U\right) \Omega(U)\, dU, \tag{3}$$

which constitutes a starting point for many applications of equilibrium statistical mechanics. However, such a relation is only compatible with macrostates having non-negative heat capacities, and hence all these macrostates with negative heat capacities $C < 0$ cannot be appropriately described by using this statistical ensemble. In fact, such macrostates are thermodynamically unstable under this kind of equilibrium situation (a system submerged in a certain environment (heat reservoir or bath) with constant inverse temperature β).

One can easily verify from equation (1) that a macrostate with a negative heat capacity $C < 0$ is thermodynamically stable provided that the correlation function $\langle \delta\beta_\omega \delta U \rangle$ considering the existence of correlative effects between the system and its surroundings obeys the following inequality:

$$\langle \delta\beta_\omega \delta U \rangle > k_B. \tag{4}$$

A simple interpretation (but not the only one possible) of the above fluctuating constraint follows from admitting that the thermostat or the surroundings is a finite system with a positive heat capacity C_ω. Clearly, the existing energetic interchange between these systems imposes the occurrence of thermal fluctuations on the thermostat temperature T_ω, $\delta T_\omega = -\delta U / C_\omega$,

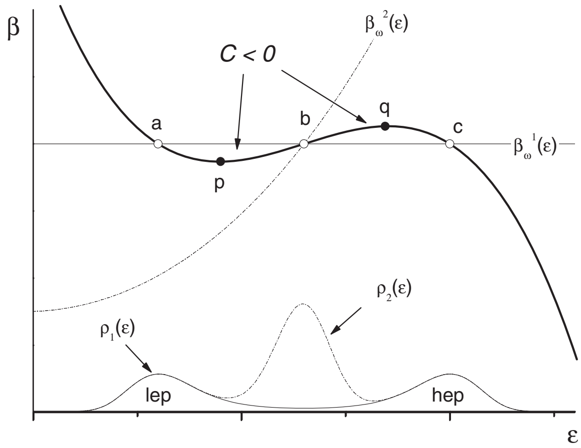

Figure 1. Schematic behavior of the microcanonical caloric $\beta(\varepsilon) = \partial s(\varepsilon)/\partial\varepsilon$ of a finite short-range interacting system undergoing a first-order phase transition. Here, $\rho_1(\varepsilon)$ and $\rho_2(\varepsilon)$ respectively represent the energy distribution functions when this system is placed in thermal contact with a Gibbs thermostat with inverse temperature $\beta^1_\omega(\varepsilon) = \text{const}$ and a heat bath having a finite positive heat capacity and, therefore, a variable (fluctuating) inverse temperature $\beta^2_\omega(\varepsilon)$.

with δU the being amount of energy released or absorbed by the system around its equilibrium value. Such fluctuations can be rephrased as follows:

$$\delta\beta_\omega = \beta^2\delta U/C_\omega, \tag{5}$$

where the condition of thermal equilibrium $\beta = \beta_\omega$ is considered. By substituting equation (5) into the fluctuation–dissipation relation (1), we obtain

$$k_B\frac{CC_\omega}{C + C_\omega} = \beta^2\langle\delta U^2\rangle. \tag{6}$$

Finally, it is possible to arrive at the following inequalities:

$$\frac{C}{C + C_\omega} > 1 \Leftrightarrow 0 < C_\omega < |C| \tag{7}$$

by combining equations (4)–(6). Essentially, this last result is the same constraint derived by Thirring in order to ensure the thermodynamic stability of macrostates with a negative heat capacity [9].

2.2. Extension of canonical Monte Carlo methods

The study of macrostates with negative heat capacities demands that such macrostates be found in a stable equilibrium situation. As already discussed, such a demand could be implemented by considering an equilibrium situation in which the system is found to be in thermal contact with a bath having a *positive and finite heat capacity* C_ω that obeys Thirring's constraint (7). The equilibrium condition associated with the Gibbs canonical ensemble (3) is unsuitable here, since the invariability of the Gibbs thermostat temperature presupposes a system with an infinite heat capacity, $C_\omega \to +\infty$, which is incompatible with inequality (7).

The differences between these equilibrium situations are schematically illustrated in figure 1. In this figure, the thick solid line represents the typical microcanonical caloric curve $\beta(\varepsilon) = \partial s(\varepsilon)/\partial\varepsilon$ of a finite short-range interacting system undergoing a first-order phase transition, which is characterized by the existence of a regime with negative heat capacities (the branch p–q), with $\varepsilon = U/N$ being the energy per particle. The thin solid lines $\beta^1_\omega(\varepsilon)$ and $\beta^2_\omega(\varepsilon)$ are respectively the inverse temperature dependences on the system energy per particle ε of a Gibbs thermostat (with $C_\omega \to +\infty$) and a thermostat having a positive finite heat capacity $0 < C_\omega < +\infty$, with $\rho_1(\varepsilon)$ and $\rho_2(\varepsilon)$ being the corresponding energy distribution functions.

The intersection points derived from the condition of thermal equilibrium $\beta(\varepsilon) = \beta_\omega(\varepsilon)$ determine the positions of the energy distribution function $\rho(\varepsilon)$ maxima and minima. Clearly, the thermal contact with a Gibbs thermostat ensures the existence of only one intersection point or, equivalently, a unique peak of the canonical energy distribution function $\rho_1(\varepsilon)$ for most of the admissible values of the thermostat inverse temperature. The important exception takes place in the inverse temperature interval $[\beta_p, \beta_q]$, where there are *three intersection points* (two maxima ε_a and ε_c with $C > 0$ and one minimum ε_b with $C < 0$), a fact that leads to a *bimodal character* for the distribution function $\rho_1(\varepsilon)$. Since no single peak can be located within the branch with negative heat capacities $C < 0$, such macrostates are poorly accessed within the Gibbs canonical ensemble. In fact, they turn practically inaccessible when the system size is sufficiently large. The existence of such a *hidden* energetic region constitutes the origin of the latent heat q_L necessary for the conversion of one phase into the other during the coexistence of low and high energy phases (lep and hep), which are represented here by the coexisting peaks of the canonical energy distribution function $\rho_1(\varepsilon)$.

The replacement of the Gibbs thermostat by a thermostat having a finite positive heat capacity crucially modifies the fluctuating behavior and the thermal stability conditions of the system. In fact, one can ensure the existence of only one intersection point, regardless of the positive or negative character of its heat capacity C, by choosing the appropriate thermostat and its internal conditions. In particular, it is necessary to ensure the applicability of Thirring's constraint (7) for macrostates with negative heat capacities $C < 0$.

The above ideas have a significant impact on the framework of Monte Carlo simulations. As has been discussed elsewhere [17], large-scale Monte Carlo simulations are often plagued by slow sampling problems, which manifest themselves as a rapid increase in the dynamic relaxation time τ with the system size N, causing large-size simulations to converge extremely slowly. These sampling problems are especially severe in systems near the critical point, where it is possible to distinguish two kinds of dynamical anomalies: (1) the so-called *critical slowing down*, where the relaxation time shows a power-law dependence on $N, \tau \propto N^\alpha$, which can be associated with the occurrence of a continuous (second-order) phase transition, and (2) the so-called *super-critical slowing down*, where the dynamic relaxation time exhibits a worse divergence with the system size: an exponential increasing $\tau \propto \exp(\alpha N)$, whose incidence is associated with discontinuous (first-order) phase transitions.

In Monte Carlo simulations which are based on a consideration of the Gibbs canonical ensemble, the origin of the super-critical slowing down is closely related to the existence of a multimodal character of the energy distribution function. Indeed, this phenomenon manifests itself as an *effective trapping* of the system macrostates in one of the coexisting peaks of the energy distribution function. As the system size increases, the mathematical form of these peaks is almost a Gaussian distribution:

$$\rho(\varepsilon) \simeq \frac{1}{\sqrt{2\pi\sigma^2}} \exp[-(\varepsilon - \bar{\varepsilon})^2/2\sigma^2], \tag{8}$$

whose width behaves as $\sigma \propto 1/\sqrt{N}$. The transition to any other peak demands the occurrence of a large energy fluctuation, whose probability p exponentially decreases as the system size decreases: $p \propto \exp(-\alpha N)$. Consequently, the characteristic timescale for the occurrence of such rare events grows as $\tau \propto 1/p \sim \exp(\alpha N)$, which explains the slow relaxation observed for canonical expectation values in large-scale Monte Carlo simulations. The existence of the above slow relaxation can be avoided if one could eliminate the multimodal character of the energy distribution function by considering a better control of the energy fluctuations. Fortunately, such an aim is easily achieved by considering a thermostat having a finite positive heat capacity C_ω.

Under this latter equilibrium situation, the thermostat inverse temperature β_ω and the system energy (per particle) ε undergo thermal fluctuations around their equilibrium values $\langle\beta_\omega\rangle$ and $\langle\varepsilon\rangle$, which provide a suitable estimation of the intersection point of the system microcanonical caloric curve $\beta(\varepsilon) = \partial s(\varepsilon)/\partial\varepsilon$ derived from the thermal equilibrium condition $\beta(\varepsilon) = \beta_\omega(\varepsilon)$. Moreover, the study of the fluctuating behavior in terms of correlation functions $\langle\delta\beta_\omega\delta\varepsilon\rangle$ and $\langle\delta\varepsilon^2\rangle$ allows us to obtain the heat capacity C via the fluctuation–dissipation relation (1). Once the microcanonical caloric curve $\beta(\varepsilon) = \partial s(\varepsilon)/\partial\varepsilon$ has been obtained, one can easily derive other thermodynamic potentials by using known integration formulae, e.g. the entropy $s(\varepsilon)$

$$\Delta s(\varepsilon) = s(\varepsilon) - s(\varepsilon_0) = \int_{\varepsilon_0}^{\varepsilon} \beta(\varepsilon)\,\mathrm{d}\varepsilon, \tag{9}$$

the Helmholtz free energy $f(\beta) = -T\log Z(\beta)/N$

$$Z(\beta) = N\int \exp\{-N[\beta\varepsilon - s(\varepsilon)]\}\,\mathrm{d}\varepsilon \tag{10}$$

and the canonical averages of a certain observable $O(\varepsilon)$

$$\langle O\rangle = \frac{1}{Z(\beta)} N\int O(\varepsilon)\exp\{-N[\beta\varepsilon - s(\varepsilon)]\}\,\mathrm{d}\varepsilon. \tag{11}$$

The simplest and most general way to implement the use of a thermostat having a finite heat capacity in a classical Monte Carlo calculation is through the known Metropolis importance sample [29]. Its extension is achieved by replacing the use of a constant inverse temperature in the acceptance probability

$$p(U|U + \triangle U) = \min\{\exp(-\beta_B\Delta U), 1\} \tag{12}$$

with a variable inverse temperature, $\beta_B \to \beta_\omega(\varepsilon)$. This kind of procedure can also be used to extend some other classical Monte Carlo methods, such as the known Swendsen–Wang (SW) clusters algorithm [30–32], applicable to the Ising model and its generalization, and the q-state Potts model:

$$H_q = \sum_{ij\in n\cdot n} \left(1 - \delta_{\sigma_i,\sigma_i}\right) \tag{13}$$

(where $n\cdot n$ represents a set of nearest-neighbor lattice sites, $\sigma_i = [1, 2, \ldots, q]$), which exhibits a regime with negative heat capacities when the number of spin states q is greater than a certain critical value depending on the lattice dimensionality D, e.g. $q > 3$ with $D = 2$. A direct demonstration of the applicability of the extended SW method using the present ideas in order to study the anomalous regime with $C < 0$ in the 2D ten-state Potts model is shown in figure 2, whose decorrelation time τ shows a weak power-law dependence $\tau \sim N^\alpha$ with $\alpha \simeq 0.2$ at the critical point of the discontinuous phase transition β_c.

Generally speaking, the consideration of a finite thermostat in order to capture the anomalous regime with negative heat capacities and to avoid the super-critical slowing down should not depend on the classical or quantum nature of the system under analysis. Consequently, one can expect that this idea could be used for enhancing the potentialities of some known quantum Monte Carlo methods.

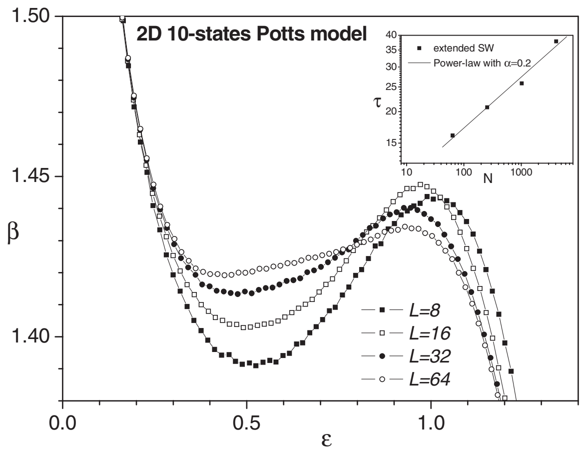

Figure 2. Microcanonical caloric curves of the 2D ten-state Potts model on a square lattice $L \times L$ obtained from Monte Carlo simulations using the extended version of the Swendsen–Wang clusters algorithm (extended SW). Inset: power-law dependence of the decorrelation time τ with the system size $N = L^2$ at the critical point β_c, $\tau \sim N^{\alpha}$, with $\alpha \simeq 0.2$.

2.3. Complementarity character between energy and temperature

The fluctuation–dissipation relation (1) constitutes a particular case of a very general fluctuation relation

$$\langle \delta\eta \delta U \rangle = k_{\mathrm{B}} \tag{14}$$

involving the inverse temperature difference between the surroundings (heat reservoir or bath) and the system $\eta = \beta_{\omega} - \beta$. In fact, equation (1) is obtained after substituting the first-order approximation

$$\delta\beta \simeq -\beta^2 \delta U / C \tag{15}$$

into equation (14).

Alternatively, one can consider the known *Schwartz inequality*

$$\langle \delta A \delta B \rangle^2 \leqslant \langle \delta A^2 \rangle \langle \delta B^2 \rangle \tag{16}$$

in order to rewrite the fluctuation relation (14) as follows:

$$\Delta\eta \Delta U \geqslant k_{\mathrm{B}}, \tag{17}$$

where $\Delta x = \sqrt{\langle \delta x^2 \rangle}$ denotes the thermal uncertainty of a physical observable x. Clearly, equation (17) is a thermo-statistic analogy of the quantum mechanics uncertainty relation

$$\Delta q \Delta p \geqslant \hbar \tag{18}$$

between position q and momentum p, which suggests the existence of a certain complementary character between thermodynamic quantities of energy and (inverse) temperature [18–23].

It is well known that the nature of the temperature is radically different from a direct observable quantity such as energy. In fact, this is a thermodynamic quantity whose physical meaning can only be attributed through the concept of the statistical ensemble. In practice, the system temperature is indirectly measured by using the temperature of a second system through the thermal equilibrium condition, which plays the role of a measuring apparatus (thermometer), whose internal temperature dependence on some direct *thermometric quantity* (e.g. electric signal, force, volume, etc) is previously known. As expected, such a measuring process unavoidably involves a perturbation on the internal state of the system under analysis.

According to the uncertainty relation (17), it is impossible to simultaneously reduce the thermal uncertainties of the inverse temperature difference $\Delta\eta$ and the system energy ΔU to zero; any attempt to reduce the perturbation of the system energy to zero, $\Delta U \to 0$, leads to a divergence of the inverse temperature difference uncertainty $\Delta\eta \to \infty$ and vice versa. Consequently, it is impossible to simultaneously determine the energy and inverse temperature of a given system using the standard experimental procedures based on the thermal equilibrium with a second system.

Clearly, we have to admit non-vanishing thermal uncertainties $\Delta\eta$ and ΔU during any practical determination of the energy–temperature dependence of a given system, that is, its caloric curve. While such thermal uncertainties are unimportant during the study of large thermodynamic systems, they actually impose a fundamental limitation on the practical utility of thermodynamic concepts such as temperature and heat capacity in systems with few constituents. In order to avoid any misunderstanding, it must be clarified that one can obtain the energy dependence of the inverse temperature of a given system *by calculating* its Boltzmann's entropy:

$$S = k_{\mathrm{B}} \log W \to \beta = 1/T = \partial S/\partial U, \tag{19}$$

which it is possible to achieve regardless of the system size. The limitation associated with the uncertainty relation (17) refers to the precision of *experimental measurement* of the microcanonical caloric curve of a thermodynamic system.

3. Geometrical aspects in fluctuation theory

3.1. Starting considerations

As previously discussed in detail in our first paper on this subject [1], the rigorous fluctuation relation (14) is derived from the following ansatz for the energy distribution function:

$$\mathrm{d}p = \rho(U)\,\mathrm{d}U = \omega(U)\Omega(U)\,\mathrm{d}U, \tag{20}$$

where $\Omega(U)$ is the state density of the system and $\omega(U)$ is the probabilistic weight considering the thermodynamic influence of the surroundings (thermostat). Such functions are defined on a certain subset M_u of the Euclidean real space R, $M_u \subset R : U \in [U_{\mathrm{inf}}, U_{\mathrm{sup}}]$.

The next important consideration is the definition of the *effective* inverse temperature of the surroundings:

$$\beta_\omega(U) = -k_{\mathrm{B}} \frac{\partial \log \omega(U)}{\partial U}. \tag{21}$$

The latter assumption is not arbitrary, since it reduces to the conventional interpretation of this concept when one considers a closed system composed of two separable short-range interacting systems in thermal contact and final thermodynamic equilibrium, which allows us to express the probabilistic weight $\omega(U)$ in terms of the state density of the second system $\Omega_B(U_B)$, $\omega(U) \propto \Omega_B(U_T - U)$.

However, the probabilistic weight $\omega(U)$ in equation (20) also admits more general system-surrounding equilibrium situations considering other modifying conditions, such as the existence of nonlinear effects driving the system-surroundings thermodynamic interaction, e.g. the presence of long-range interactions [33, 34], or a system acting as the surroundings that is found in a metastable equilibrium whose relaxation time is so long that its dynamic evolution can practically be disregarded, such as the case of systems with *glassy dynamics* [35]. Such circumstances explain why we refer to the inverse temperature (21) as *effective*.

The number of microstates W used to obtain Boltzmann's entropy (19) is given by the *coarse grained* definition

$$W = \Omega\delta\epsilon, \tag{22}$$

with $\delta\epsilon$ being a certain small constant energy that makes W dimensionless. The work hypothesis (20) and definitions (21) and (22) allow us to express the inverse temperature difference as

$$\eta(U) = \beta_\omega(U) - \beta(U) \equiv -k_B \frac{\partial \log \rho(U)}{\partial U}. \tag{23}$$

With the above relation, one can easily obtain the thermodynamic identities

$$\langle \eta \rangle = \int_{U_{\text{inf}}}^{U_{\text{sup}}} \eta(U)\rho(U)\,\mathrm{d}U = 0, \tag{24}$$

$$\langle U\eta \rangle = \int_{U_{\text{inf}}}^{U_{\text{sup}}} U\eta(U)\rho(U)\,\mathrm{d}U = k_B, \tag{25}$$

which are derived by integrating by parts and considering the following boundary conditions:

$$\rho(U_{\text{inf}}) = \rho(U_{\text{sup}}) = 0, \tag{26}$$

$$\frac{\partial \rho(U_{\text{inf}})}{\partial U} = \frac{\partial \rho(U_{\text{sup}})}{\partial U} = 0. \tag{27}$$

Equation (24) is simply the thermal equilibrium condition expressed in terms of *statistical expectation values*:

$$\langle \beta \rangle = \langle \beta_\omega \rangle. \tag{28}$$

This rigorous result clarifies that the known equalization of (inverse) temperatures during the thermodynamic equilibrium of two systems actually takes place in an average sense. The fluctuation relation of equation (14) is obtained from equations (24) and (25) after using the identity $\langle \delta U \delta\eta \rangle = \langle U\eta \rangle - \langle U \rangle\langle \eta \rangle$.

Let A be a continuous and differentiable function on M_u, which also admits a bound expectation value $\langle A \rangle$, $|\langle A \rangle| < +\infty$. Under these assumptions, one can obtain the following thermodynamic identity:

$$\left\langle k_B \frac{\partial A}{\partial U} \right\rangle = \langle A\eta \rangle \equiv \langle \delta A \delta\eta \rangle. \tag{29}$$

In particular, this identity reduces to equations (24) and (25) for $A = 1$ and $A = U$ respectively. Moreover, it also drops to the remarkable fluctuation relation

$$\left\langle -k_B \frac{\partial \eta}{\partial U} + \delta\eta^2 \right\rangle = 0 \tag{30}$$

for $A = \eta$. This latter identity, hereafter referred to as the *complementary fluctuation relation*, accounts for the same information about the system stability conditions derived from the fluctuation relation of equation (14). For instance, by using the Gaussian approximation (see section 3.4)

$$\left\langle \frac{\partial \eta(U)}{\partial U} \right\rangle \simeq \frac{\partial \eta(\bar{U})}{\partial U} \tag{31}$$

and focusing on the equilibrium situation between two separable short-range interacting systems, we obtain the fluctuation relation

$$\beta^2 \frac{C + C_\omega}{CC_\omega} k_B = \langle \delta\eta^2 \rangle, \tag{32}$$

which leads to the same stability criterion derived from equation (6).

3.2. Reparametrization invariance

Let us consider a bijective application $\Theta(U) : R \to R$, which is a piece-wise continuous and two-time differentiable function of variable U. Such a function allows for the existence of a bijective map $\Theta : M_u \to M_\phi$ of the subset M_u on another subset $M_\phi \subset R : \Theta \in [\Theta_{\text{inf}}, \Theta_{\text{sup}}]$. It could be said that these subsets constitute two equivalent *coordinate representations* of all admissible macrostates of the system, which shall be denoted as R_u and R_ϕ respectively. The coordinate transformation induced by the bijective function $\Theta(U)$ is referred to as a *reparametrization*.

Since the elementary subset $[U, U + \mathrm{d}U]$ represents the same system macrostates considered by the elementary subset $[\Theta, \Theta + \mathrm{d}\Theta]$, the elementary probability $\mathrm{d}p$ that the system is found under such conditions, equation (20), does not depend on the coordinate representation used for its expression:

$$\mathrm{d}p = \rho_u(U)\,\mathrm{d}U = \rho_\phi(\Theta)\,\mathrm{d}\Theta. \tag{33}$$

Here, $\rho_u(U)$ and $\rho_\phi(\Theta)$ denote the system distribution functions in the representations R_u and R_ϕ, respectively, which are mutually related by the transformation rule:

$$\rho_\phi(\Theta) = \rho_u(U)\left[\frac{\partial\Theta}{\partial U}\right]^{-1}. \tag{34}$$

Let $\mathrm{d}W$ be the elementary volume considering the number of microstates belonging to the elementary subset $[U, U + \mathrm{d}U]$. According to the case of the elementary probability $\mathrm{d}p$, $\mathrm{d}W$ does not depend on the coordinate representation and, hence, it obeys the following properties:

$$\mathrm{d}W = \Omega_u(U)\,\mathrm{d}U = \Omega_\phi(\Theta)\,\mathrm{d}\Theta, \tag{35}$$

$$\Omega_\phi(\Theta) = \Omega_u(U)\left[\frac{\partial\Theta}{\partial U}\right]^{-1}. \tag{36}$$

Consequently, the probabilistic weight $\omega_u(U)$ considering the thermodynamic influence of the surroundings behaves as a *scalar function* under reparametrizations:

$$\omega_u(U) = \omega_\phi(\Theta) \equiv \omega_u[U(\Theta)], \tag{37}$$

with $U(\Theta)$ being the inverse function of $\Theta(U)$.

The reparametrization invariance of the probability distribution function also leads to the reparametrization invariance of the expectation value of any physical observable $A = A(U) = A(\Theta)$ (scalar function):

$$\langle A\rangle_\phi = \int_{\Theta_{\text{inf}}}^{\Theta_{\text{sup}}} A(\Theta)\rho_\phi(\Theta)\,\mathrm{d}\Theta \tag{38}$$

$$= \int_{U_{\text{inf}}}^{U_{\text{sup}}} A(U)\rho_\phi(U)\,\mathrm{d}U = \langle A\rangle_u, \tag{39}$$

such that one can denote the expectation values without indicating the coordinate representation used for its expression:

$$\langle A\rangle_u = \langle A\rangle_\phi \equiv \langle A\rangle. \tag{40}$$

A remarkable equilibrium situation of the conventional thermodynamics and statistical mechanics is the system in energetic isolation, whose probabilistic weight

$$\omega_u^{\text{mic}}(U|U_0) = \frac{1}{\Omega_u(U_0)}\delta(U - U_0) \tag{41}$$

defines the known *microcanonical ensemble*. This probabilistic weight possesses the notable feature that its mathematical form does not depend on the representation

$$\omega_u^{\mathrm{mic}}(U|U_0) = \omega_\phi^{\mathrm{mic}}(\Theta|\Theta_0) = \frac{1}{\Omega_\phi(\Theta_0)}\delta(\Theta - \Theta_0), \tag{42}$$

a property that is straightforwardly derived from the identity

$$\delta(\Theta - \Theta_0) = \delta(U - U_0)\left[\frac{\partial\Theta(U_0)}{\partial U}\right]^{-1} \tag{43}$$

and the transformation rule (36).

3.3. Reparametrization duality

Let us define the thermostat inverse temperature in representation R_ϕ as

$$\beta_\omega^\phi = -\frac{\partial \log \omega_\phi(\Theta)}{\partial\Theta}. \tag{44}$$

Therefore, it obeys the transformation rule

$$\beta_\omega^\phi = \beta_\omega^u \left[\frac{\partial\Theta}{\partial U}\right]^{-1} \tag{45}$$

as a consequence of the scalar character of the probabilistic weight ω_ϕ, with β_ω^u being the thermostat (effective) inverse temperature expressed in equation (21).

Boltzmann's entropy of the system in this representation can be defined by

$$S_\phi = k_{\mathrm{B}} \log W_\phi, \tag{46}$$

where $W_\phi = \Omega_\phi \delta\epsilon_\phi$, with $\delta\epsilon_\phi$ being a suitable constant that makes W_ϕ dimensionless. The above coarsed-grained definition of Boltzmann's entropy is not properly a scalar function according to the case of the probabilistic weight (37). In fact, it obeys the transformation rule

$$S_\phi = S_u - k_{\mathrm{B}} \log\left(\frac{\partial\Theta}{\partial U}\frac{\delta\epsilon_u}{\delta\epsilon_\phi}\right). \tag{47}$$

As already pointed out by Ruppeiner (see section II.B of [24]), the density distribution function derived from Einstein's postulate

$$\rho_x(x)\,\mathrm{d}x = C \exp\left[\frac{S(x)}{k_{\mathrm{B}}}\right]\mathrm{d}x \tag{48}$$

obeys different mathematical forms under different coordinate representations, $x \to y(x)$, if one assumes that the entropy is a *state function* whose value does not depend on the representation (scalar function), $S(x) = S(y)$. A simple analysis allows us to verify that the left-hand side of equation (48) behaves as

$$\rho_x(x)\,\mathrm{d}x = \rho(x)\left|\frac{\partial x(y)}{\partial y}\right|\mathrm{d}y = \rho_y(y)\,\mathrm{d}y, \tag{49}$$

while its right-hand side behaves as

$$C \exp\left[\frac{S(x)}{k_{\mathrm{B}}}\right]\mathrm{d}x = C \exp\left[\frac{S(x)}{k_{\mathrm{B}}}\right]\left|\frac{\partial x(y)}{\partial y}\right|\mathrm{d}y \neq C' \exp\left[\frac{S(y)}{k_{\mathrm{B}}}\right]\mathrm{d}y. \tag{50}$$

This fact not only constitutes an important defect in order to develop a *Riemannian formulation* of fluctuation theory, but it also presupposes some inconsistencies with the thermodynamic arguments behind Einstein's postulate for the fluctuation formula of equation (48). In this work, we shall assume the entropy modification (47) associated with reparametrizations and analyze its direct consequences. Clearly, such an alternative definition allows us to preserve the functional dependence of fluctuation formula (48) in any coordinate representation. It requires the fact that the entropy is no longer a state function with a scalar character, as is usually assumed in other geometric formulations of fluctuation theory [24].

Under these above assumptions, the system inverse temperature β^{ϕ} in the representation R_{ϕ} is given by

$$\beta^{\phi}=\frac{\partial S_{\phi}}{\partial\Theta} \tag{51}$$

and obeys the transformation rule

$$\beta^{\phi}=\left[\beta^{u}-k_{\mathrm{B}}\frac{\partial}{\partial U}\log\left(\frac{\partial\Theta}{\partial U}\frac{\delta\epsilon_{u}}{\delta\epsilon_{\phi}}\right)\right]\left[\frac{\partial\Theta}{\partial U}\right]^{-1}. \tag{52}$$

As expected, the inverse temperature difference in the representation R_{ϕ} can be expressed as

$$\eta_{\phi}(\Theta)=\beta_{\omega}^{\phi}(\Theta)-\beta^{\phi}(\Theta)=-k_{\mathrm{B}}\frac{\partial\log\rho_{\phi}(\Theta)}{\partial\Theta}. \tag{53}$$

By only admitting regular reparametrizations obeying the constraints

$$0<\left|\frac{\partial\Theta}{\partial U}\right|<+\infty,\qquad 0<\left|\frac{\partial^{2}\Theta}{\partial U^{2}}\right|<+\infty \tag{54}$$

at every point $U\in M_{u}$, one can easily show the validity of the boundary conditions

$$\rho_{\phi}(\Theta_{\mathrm{inf}})=\rho_{\phi}(\Theta_{\mathrm{sup}})=0, \tag{55}$$

$$\frac{\partial\rho_{\phi}(\Theta_{\mathrm{inf}})}{\partial\Theta}=\frac{\partial\rho_{\phi}(\Theta_{\mathrm{sup}})}{\partial\Theta}=0 \tag{56}$$

by starting from equations (26) and (27).

As already shown in the previous subsection, definition (53) and the boundary conditions (55) and (55) lead to the following extensions of the rigorous identities (24), (25) and (29):

$$\langle\eta_{\phi}\rangle=\int_{\Theta_{\mathrm{inf}}}^{\Theta_{\mathrm{sup}}}\eta_{\phi}(\Theta)\rho_{\phi}(\Theta)\,\mathrm{d}\Theta=0, \tag{57}$$

$$\langle\Theta\eta_{\phi}\rangle=\int_{\Theta_{\mathrm{inf}}}^{\Theta_{\mathrm{sup}}}\Theta\eta_{\phi}(\Theta)\rho_{\phi}(\Theta)\,\mathrm{d}\Theta=k_{\mathrm{B}}, \tag{58}$$

$$\left\langle -k_{\mathrm{B}}\frac{\partial A}{\partial\Theta}+A\eta_{\phi}\right\rangle=0, \tag{59}$$

the generalized fluctuation theorems:

$$\langle\delta\Theta\delta\eta_{\phi}\rangle=k_{\mathrm{B}}, \tag{60}$$

$$\left\langle -k_{\mathrm{B}}\frac{\partial\eta_{\phi}}{\partial\Theta}+\delta\eta_{\phi}^{2}\right\rangle=0, \tag{61}$$

and, finally, the thermodynamic uncertainty relation:

$$\Delta\Theta\Delta\eta_{\phi}\geqslant k_{\mathrm{B}}. \tag{62}$$

Thus, the consideration of coordinate changes makes it possible to extend the results already derived by using the energy representation R_{u}. Although the thermodynamic identities

(24), (25) and (57), (58), and the fluctuation theorems (14), (30) and (60), (61), as well as the uncertainty relations (17) and (62), are closely related, they represent different thermodynamic relations characterizing the same equilibrium situation. It could be said that all of these mutually related identities account for the existence of a special kind of internal symmetry, which shall be hereafter referred to as *reparametrization duality*.

The invariance under reparametrizations (coordinate transformation or *diffeomorphisms*) is the same kind of symmetry considered by Einstein's theory of gravitation. However, there exist radical differences between this latter physical theory and the geometric statistical formalism developed in this work as follows. (i) While the gravitation theory is defined in terms of *local quantities*, the rigorous thermodynamic identities obtained here are expressed in terms of *statistical expectation values* defined over the entire subset M_ϕ representing all admissible system macrostates in the present equilibrium situation, that is, this is a *non-local theory*, similar to quantum mechanics. (ii) Furthermore, Einstein's theory refers to the same physical laws in different representations, while the above thermodynamic identities consider a family of *different fluctuation relations* exhibiting the same mathematical appearance under different coordinate representations of a given equilibrium situation. That is why we refer to it as reparametrization duality instead of reparametrization symmetry.

In the following subsection, we shall arrive at a local formulation of the present approach with a Riemannian-like structure closely related to other geometric approaches of fluctuation theory existing in the literature [24]. We shall see, however, that such a development presupposes the consideration of certain unexpected approximations.

3.4. Riemannian approach

Let us assume that the systems under consideration are large enough to deal with the thermodynamic fluctuations by using a *Gaussian approximation*. An essential assumption considered here is that the system undergoes small thermal fluctuations close to its equilibrium point, which is determined by *the most likely macrostate*.

A problem encountered is that the most likely macrostate actually depends on the coordinate representation used for describing the system behavior, which is a direct consequence of the non-scalar character of the system entropy. In order to show this fact, let us consider the transformation rule of the inverse temperature difference:

$$\eta_\phi = \frac{\partial U}{\partial \Theta}\left[\eta_u + k_B \frac{\partial}{\partial U}\log\left(\frac{\partial \Theta}{\partial U}\frac{\delta\epsilon_u}{\delta\epsilon_\phi}\right)\right]. \tag{63}$$

The stationary condition associated with the most likely macrostate in each representation is given by

$$\eta_u(\bar{U}) = 0 \quad \text{for} \quad R_u \quad \text{and} \quad \eta_\phi(\bar{\Theta}) = 0 \quad \text{for} \quad R_\phi. \tag{64}$$

According to equation (63), the vanishing of η_u does not correspond to a vanishing of η_ϕ and vice versa, a result that shows that the most likely macrostate depends on the coordinate representation.

This last result contrasts with the general validity of the thermal equilibrium condition in terms of statistical expectation values (equation (57)). It clearly indicates that the method generally used for deriving such a condition in terms of the most likely macrostate is just a suitable approximation. Nevertheless, it could be easily noted that the modification involved during the reparametrization change is just a second-order effect. The transformation rule (63) can be combined with equations (24) and (57) in order to obtain

$$\left\langle \delta\eta_\phi \delta\Lambda_u^\phi \right\rangle = \left\langle k_B \frac{\partial}{\partial U}\log\left(\Lambda_u^\phi \frac{\delta\epsilon_u}{\delta\epsilon_\phi}\right)\right\rangle, \tag{65}$$

where the following notation is considered:

$$\Lambda^{\phi}_{u}=\frac{\partial\Theta(U)}{\partial U}. \tag{66}$$

Equation (65) indicates that the second additive term on the right-hand side of the transformation rule (63) is just a small correction, which can be disregarded in most practical applications. Therefore, one can admit the approximate relation

$$\bar{\eta}_{\phi}=\bar{\eta}_{u}\left(\bar{\Lambda}^{\phi}_{u}\right)^{-1}\equiv 0, \tag{67}$$

where $\bar{A}$ denotes the value of the function $A(U)$ at the most likely macrostate, $\bar{A}\equiv A(\bar{U})$.

Basically, the approximation assumed in equation (67) is equivalent to considering Boltzmann's entropy (46) as a scalar function, and hence the approximate transformation rule of the system inverse temperature is given by

$$\bar{\beta}^{\phi}=\bar{\beta}^{u}\left(\bar{\Lambda}^{\phi}_{u}\right)^{-1}. \tag{68}$$

In general, the Gaussian approximation allows us to consider the fluctuations of an arbitrary energy function $A(U)$ as

$$\delta A=\frac{\partial A(\bar{U})}{\partial U}\delta U. \tag{69}$$

In particular, it allows us to introduce the following transformation rule:

$$\delta\Theta=\bar{\Lambda}^{\phi}_{u}\delta U. \tag{70}$$

Moreover, by starting from equation (67), we obtain

$$\delta\eta_{\phi}=\left(\bar{\Lambda}^{\phi}_{u}\right)^{-1}\left[\delta\eta_{u}-\bar{\eta}_{u}\frac{\partial}{\partial U}\log\left(\bar{\Lambda}^{\phi}_{u}\frac{\delta\epsilon_{u}}{\delta\epsilon_{\phi}}\right)\delta U\right], \tag{71}$$

which reduces to

$$\delta\eta_{\phi}=\left(\bar{\Lambda}^{\phi}_{u}\right)^{-1}\delta\eta_{u}, \tag{72}$$

after considering the thermal equilibrium condition $\bar{\eta}^{u}=0$. Using these latter transformation rules, one can obtain the transformation rules of some fluctuation relations:

$$\langle\delta\Theta^{2}\rangle=\left(\bar{\Lambda}^{\phi}_{u}\right)^{2}\langle\delta U^{2}\rangle, \tag{73}$$

$$\left\langle\delta\eta_{\phi}^{2}\right\rangle=\left(\bar{\Lambda}^{\phi}_{u}\right)^{-2}\left\langle\delta\eta_{u}^{2}\right\rangle, \tag{74}$$

$$\langle\delta\Theta\delta\eta_{\phi}\rangle=\langle\delta U\delta\eta_{u}\rangle\equiv k_{\mathrm{B}}. \tag{75}$$

Equations (73)–(75) correspond to transformation rules of contravariant second-rank tensors, covariant second-range tensor and scalar functions in a differential geometric theory, respectively. In order to provide a *Riemannian structure* to the present geometrical approach, we must introduce an appropriate *metric*. Such a role could be carried out by the *global curvature* K_{ϕ},

$$K_{\phi}=\frac{\partial\eta_{\phi}}{\partial\Theta}=-k_{\mathrm{B}}\frac{\partial^{2}\log\rho_{\phi}}{\partial\Theta^{2}} \tag{76}$$

evaluated at the most likely macrostate, which allows for the conversion between the fluctuations of the conjugated thermodynamic quantities (covariant and contravariant vectors) within the Gaussian approximation:

$$\delta\eta_{\phi}=\bar{K}_{\phi}\delta\Theta. \tag{77}$$

The global curvature obeys the transformation rule

$$K_\phi = \left(\Lambda_u^\phi\right)^{-2}\left\{K_u - \eta_u\frac{\partial c_\phi}{\partial U} + k_\mathrm{B}\left[\frac{\partial^2 c_\phi}{\partial U^2} - \left(\frac{\partial c_\phi}{\partial U}\right)^2\right]\right\} \tag{78}$$

with $c_\phi = \log\left(\Lambda_u^\phi \delta\epsilon_u / \delta\epsilon_\phi\right)$, which reduces to

$$\bar{K}_\phi = \left(\bar{T}_u^\phi\right)^{-2}\bar{K}_u \tag{79}$$

after considering the thermal equilibrium condition $\bar{\eta}_u = 0$ and dismissing small contributions associated with the non-scalar character of Boltzmann's entropy (the two terms associated with Boltzmann's constant k_B). Clearly, the global curvature can only be considered as a second-rank covariant tensor under the above approximations, since the general transformation rule (78) does not correspond to this kind of geometric object. Interestingly, such a function appears in the complementary fluctuation relation (61), which establishes the non-negative character of its expectation value in any coordinate representation:

$$k_\mathrm{B}\langle K_\phi\rangle = \left\langle \delta\eta_\phi^2\right\rangle. \tag{80}$$

As already commented, this rigorous fluctuation relation satisfies, as a whole, the reparametrization duality, which is not the case of the global curvature K_ϕ considered as an individual entity.

By using the global curvature $\bar{K}_\phi$, one can easily obtain other fluctuation relations such as

$$\left\langle\delta\eta_\omega^\phi\delta\Theta\right\rangle = \bar{K}_\phi\langle\delta\Theta^2\rangle = \bar{K}_u\langle\delta U^2\rangle = \left\langle\delta\eta_\omega^u\delta U\right\rangle = k_\mathrm{B} \tag{81}$$

and rewrite the distribution function ρ_ϕ in this Gaussian approximation as follows:

$$\rho_\phi(\Theta|\bar{\Theta})\,\mathrm{d}\Theta = \sqrt{\frac{\bar{K}_\phi}{2\pi k_\mathrm{B}}}\exp\left[-\frac{1}{2k_\mathrm{B}}\bar{K}_\phi(\Theta-\bar{\Theta})^2\right]\mathrm{d}\Theta. \tag{82}$$

4. Generalized Gibbs canonical ensemble

Let us denote by T_ϕ the thermostat temperature in the representation R_ϕ, with $\beta_\omega^\phi = 1/T_\phi$. One can formally introduce the heat capacity C_ϕ of this representation as

$$C_\phi = \frac{\partial\Theta}{\partial T_\phi}, \tag{83}$$

which allows us to obtain a geometric extension of the fluctuation–dissipation relation (1):

$$k_\mathrm{B}\bar{C}_\phi = \left(\bar{\beta}_\omega^\phi\right)^2\langle\delta\Theta^2\rangle + \bar{C}_\phi\left\langle\delta\beta_\omega^\phi\delta\Theta\right\rangle \tag{84}$$

after combining the Gaussian approximation

$$\delta\beta_\phi = -\bar{\beta}_\phi^2/\bar{C}_\phi\delta\Theta \tag{85}$$

with definition (53) and the fluctuation relation (60). A relevant case among the admissible equilibrium situations considered by the above fluctuation–dissipation relation is the one that obeys the constraint $\delta\beta_\omega^\phi \equiv 0$, which is associated with the following distribution function:

$$\mathrm{d}p_c\left(\Theta\middle|\beta_c^\phi\right) = \frac{1}{Z\left(\beta_c^\phi\right)}\exp\left(-\frac{1}{k_\mathrm{B}}\beta_c^\phi\Theta\right)\Omega_\phi(\Theta)\,\mathrm{d}\Theta. \tag{86}$$

This is just the analogous version of the Gibbs canonical ensemble in the R_ϕ representation, with β_c^ϕ being a constant parameter. By rewriting this particular distribution function in the energy representation R_u

$$\mathrm{d}p_c\left(U\middle|\beta_c^\phi\right) = \frac{1}{Z\left(\beta_c^\phi\right)} \exp\left[-\frac{1}{k_B}\beta_c^\phi\Theta(U)\right]\Omega_u(U)U, \tag{87}$$

one arrives at the same expression found for the so-called *generalized canonical ensemble* recently proposed in the literature [25, 26]. Let us now analyze its general mathematical properties.

4.1. General mathematical properties

As usual, the partition function $Z\left(\beta_c^\phi\right)$ derived from the normalization condition

$$Z\left(\beta_c^\phi\right) = \int_{U_{\inf}}^{U_{\sup}} \mathrm{e}^{-\frac{1}{k_B}\beta_c^\phi\Theta(U)}\Omega_u(U)\,\mathrm{d}U \tag{88}$$

allows us to obtain the *generalized Planck's thermodynamic potential*:

$$P_\phi\left(\beta_c^\phi\right) = -k_B \log Z\left(\beta_c^\phi\right), \tag{89}$$

which provides two relevant statistical expectation values:

$$\langle\Theta\rangle = \frac{\partial P_\phi\left(\beta_c^\phi\right)}{\partial\beta_c^\phi}, \qquad \langle\delta\Theta^2\rangle = -k_B\frac{\partial^2 P_\phi\left(\beta_c^\phi\right)}{\partial\left(\beta_c^\phi\right)^2}. \tag{90}$$

These last results can be combined in order to obtain the canonical version of the fluctuation–dissipation relation (84):

$$-k_B\frac{\partial\langle\Theta\rangle}{\partial\beta_c^\phi} = \langle\delta\Theta^2\rangle \quad\Rightarrow\quad k_B C_\phi^c = \left(\beta_c^\phi\right)^2\langle\delta\Theta^2\rangle, \tag{91}$$

with C_ϕ^c being the canonical heat capacity:

$$C_\phi^c = \frac{\partial\langle\Theta\rangle}{\partial T_\phi}. \tag{92}$$

Clearly, this theorem states that the stable thermodynamical macrostates are those with a non-negative heat capacity $C_\phi^c > 0$.

Let us now rewrite Planck's thermodynamic potential in the R_ϕ representation:

$$\mathrm{e}^{-P_\phi(\beta_c^\phi)/k_B} = \int_{\Theta_{\inf}}^{\Theta_{\sup}} \mathrm{e}^{-\frac{1}{k_B}\beta_c^\phi\Theta}\Omega_\phi(\Theta)\,\mathrm{d}\Theta \tag{93}$$

$$= \int_{\Theta_{\inf}}^{\Theta_{\sup}} \mathrm{e}^{-\frac{1}{k_B}[\beta_c^\phi\Theta - S_\phi(\Theta)]}\frac{\mathrm{d}\Theta}{\delta\epsilon_\phi} \tag{94}$$

and develop a Gaussian approximation (the second-order power expansion in Θ) around the local maxima:

$$\simeq \mathrm{e}^{-P_\phi^*/k_B}\int_{\Theta_{\inf}}^{\Theta_{\sup}} \mathrm{e}^{-\frac{1}{2k_B}\kappa_\phi^*\Delta\Theta^2}\frac{\mathrm{d}\Theta}{\delta\epsilon_\phi} \tag{95}$$

with $\Delta\Theta = \Theta - \Theta_c$ and P_ϕ^* given by

$$P_\phi^* = \inf_{\Theta_s}\left\{\beta_c^\phi\Theta - S_\phi(\Theta)\right\}. \tag{96}$$

The local maxima Θ_c are derived from the stationary and stability conditions:

$$\beta_c^{\phi} = \frac{\partial S_{\phi}(\Theta_s)}{\partial\Theta} \equiv \beta^{\phi}(\Theta_c), \qquad \kappa_{\phi}^{*} = -\frac{\partial^2 S_{\phi}(\Theta_s)}{\partial\Theta^2} > 0. \tag{97}$$

By admitting the existence of only one maximum, this approximation yields

$$P_{\phi}\left(\beta_c^{\phi}\right) \simeq P_{\phi}^{*} - \frac{1}{2}\log\left(\frac{2\pi k_B}{\kappa_{\phi}^{*}\delta\epsilon_{\phi}^{2}}\right), \tag{98}$$

$$\langle\Delta\Theta^2\rangle = k_B\frac{1}{\kappa_{\phi}^{*}}. \tag{99}$$

Clearly, the additive logarithmic term in the Gaussian estimation of the Planck thermodynamic potential (98) constitutes a small correction in the case of sufficiently large systems. By dismissing such a small contribution, one finds that Planck's thermodynamic potential is approximately given by the known *Legendre transformation*:

$$P_{\phi}^{*}\left(\beta_c^{\phi}\right) = \inf_{\Theta_s}\left\{\beta_c^{\phi}\Theta - S_{\phi}(\Theta)\right\}. \tag{100}$$

The stationary condition is merely the condition of thermal equilibrium associated with this representation, while the stability condition is simply the requirement of non-negativity of the microcanonical heat capacity C_{ϕ}:

$$\frac{\partial^2 S_{\phi}(\Theta_s)}{\partial\Theta^2} = -(\beta^{\phi})^2\frac{1}{C_{\phi}} < 0 \quad\Rightarrow\quad C_{\phi} > 0. \tag{101}$$

Equations (88)–(101) correspond to many well-known dual expressions previously obtained within the Gibbs canonical ensemble (3). Obviously, these two ensembles are intimately related. By considering the scalar character of the probabilistic weight ω_{ϕ}

$$\omega_{\phi}\left(\Theta\middle|\beta_c^{u}\right) = \frac{1}{Z\left(\beta_c^{\phi}\right)}\exp\left(-\frac{1}{k_B}\beta_c^{\phi}\Theta\right), \tag{102}$$

the thermostat inverse temperature β_{ω}^{u} in the energy representation R_u is given by

$$\beta_{\omega}^{u}(U) = \beta_c^{\phi}\frac{\partial\Theta(U)}{\partial U}. \tag{103}$$

This latter result clarifies that the generalized canonical ensemble (87) corresponds to a special kind of equilibrium situation with a variable (fluctuating) inverse temperature of all admissible states accounted for by the fluctuation–dissipation relation (1), that is, a situation with non-vanishing system-surrounding correlative effects $\left\langle\delta\beta_{\omega}^{u}\delta U\right\rangle \neq 0$.

By considering the transformation rule for the microcanonical curvature κ_{ϕ}:

$$\kappa_{\phi} = \left(\Lambda_u^{\phi}\right)^{-2}\left\{\kappa_u + \beta^{u}\frac{\partial c_{\phi}}{\partial U} + k_B\left[\frac{\partial^2 c_{\phi}}{\partial U^2} - \left(\frac{\partial c_{\phi}}{\partial U}\right)^2\right]\right\}, \tag{104}$$

one can find that the requirement $\kappa_{\phi} > 0$ can be combined with the existence of macrostates with $\kappa_u < 0$ in the energy representation with an appropriate selection of the reparametrization $U \to \Theta(U)$.[3] This fact is more evident when working in the energy representation R_u, where the stability condition reads as follows:

$$\bar{\kappa}_u + \beta_c^{u}\frac{\partial^2\Theta(\bar{U})}{\partial U^2} = \bar{\kappa}_u + \frac{\partial\beta_{\omega}^{u}(\bar{U})}{\partial U} > 0. \tag{105}$$

[3] The presence of additive terms with Boltzmann's factor k_B in equation (104) takes into account the modification of the system entropy during a reparametrization and the consequent correction of the most likely macrostate.

By considering the relations $\kappa_u = (\beta^u)^2/C_u$ and $\partial\beta^u_\omega/\partial U = \left(\beta^u_\omega\right)^2/C^u_\omega$, with C_u and C^u_ω being the heat capacities of the system and the thermostat respectively (their usual definitions), as well as by using the thermal equilibrium condition $\bar{\beta}^u = \bar{\beta}^u_\omega = \beta$, one arrives at the expression

$$\frac{C_u C^u_\omega}{C^u_\omega + C_u} > 0, \tag{106}$$

which leads to Thirring's stability condition (7) for macrostates with $C_u < 0$.

As in the case of the Gibbs canonical ensemble (3), the present geometric extension (87) becomes equivalent to the microcanonical ensemble with an increasing system size N, $\Delta\Theta/\Theta \sim 1/\sqrt{N}$; this equivalence that can be ensured even for macrostates with $C_u < 0$ or $\kappa_u < 0$ with an appropriate selection of the reparametrization $\Theta(U)$. This remarkable property makes this ensemble a very attractive thermo-statistical framework, since besides exhibiting many notable properties of the usual Gibbs canonical ensemble, it also provides a better treatment of the phenomenon of ensemble inequivalence associated with the presence of negative heat capacities, as already discussed in [25, 26]. In particular, this statistical ensemble constitutes a suitable framework for extending Monte Carlo methods, as discussed in section 2.2.

4.2. Derivation from information theory

It is possible to realize that the generalized Gibbs canonical ensemble (87) can also be derived from Jaynes's reinterpretation of statistical mechanics in terms of the information theory of Shannon [27], e.g., by considering the maximization of the known statistical (extensive) information entropy:

$$S_e = -\sum_k p_k \log p_k, \tag{107}$$

under the normalization condition

$$\langle 1 \rangle = \sum_k p_k = 1 \tag{108}$$

and the following nonlinear energy-like constraint:

$$\langle \Theta \rangle = \sum_k \Theta(U_k)\, p_k. \tag{109}$$

Such a derivation was developed by Toral in [26]. The interested reader can refer to this work for more details.

Clearly, the bijective character of the reparametrization $U \leftrightarrow \Theta(U)$ should ensure that this generalized ensemble exhibits almost the same stationary properties obtained from the application of the Gibbs canonical ensemble in sufficiently large systems, where one usually assumes the appropriateness of the Gaussian approximation. However, the nonlinear character of the bijective application $\Theta(U)$ produces a deformation in the canonical description, which conveniently modifies the system fluctuating behavior and the accessible regions of the subset of all admissible system macrostates M_u.

4.3. Connections with inference theory: generalization of Mandelbrot's approach

Generally speaking, *statistical inference* can be described as the problem of deciding how well a set of outcomes $(x_1, x_2, \ldots, x_m)$, obtained from independent measurements, fits to a proposed probability distribution:

$$\mathrm{d}p(x|\theta) = \rho(x|\theta)\,\mathrm{d}x. \tag{110}$$

If the probability distribution is characterized by one or more parameters (θ), this problem is equivalent to inferring the value of the parameter(s) from the observed measurement outcomes x. To make inferences about the parameter, one constructs estimators, i.e. functions

$$\hat{\theta}(x_1, x_2, \ldots, x_m) \tag{111}$$

of the outcomes of m independent repeated measurements [36]. The value of this function represents the best guess for θ.

Commonly, there exist several criteria imposed on estimators in order to ensure that their values constitute *good* estimates of the parameter θ, such as

- *unbiasedness*:

$$\langle\hat{\theta}\rangle = \int \hat{\theta}(x_1, x_2, \ldots, x_m) \prod_{k=1}^{m} \mathrm{d}p(x_k|\theta) = \theta, \tag{112}$$

- *efficiency* or minimal statistical dispersion:

$$\langle\delta\hat{\theta}^2\rangle = \int (\hat{\theta} - \langle\hat{\theta}\rangle)^2 \prod_{k=1}^{m} \mathrm{d}p(x_k|\theta) \to \text{minimum}, \tag{113}$$

- *sufficiency*:

$$\mathrm{d}p(x_1, x_2, \ldots, x_m|\theta) = f(x_1, x_2, \ldots, x_m)\, \mathrm{d}p(\hat{\theta}), \tag{114}$$

  where $\mathrm{d}p(\hat{\theta})$ is the marginal distribution of $\hat{\theta}$ and $f(x_1, x_2, \ldots, x_m)$ is an arbitrary function of the measurements, independent of θ.

Since any statistical estimator $\hat{\theta}$ represents a stochastic quantity, it is natural in inference problems that an estimator obeys the unbiasedness (112) and efficiency (113) conditions. However, there exists a remarkable theorem of inference theory, *Cramér–Rao's inequality*, which places an inferior bound on the efficiency of an arbitrary unbiased estimator:

$$\langle\delta\hat{\theta}^2\rangle \geqslant \frac{1}{I_{\mathrm{F}}(\theta)}, \tag{115}$$

where $I_{\mathrm{F}}(\theta)$ is the so-called *Fisher's information entropy*:

$$I_{\mathrm{F}}(\theta) = \int \left[\frac{\partial \log \rho(x|\theta)}{\partial\theta}\right]^2 \rho(x|\theta)\, \mathrm{d}x. \tag{116}$$

On the other hand, efficiency condition (114) ensures that, given the value of $\hat{\theta}(x_1, x_2, \ldots, x_m)$, the values of the data $(x_1, x_2, \ldots, x_m)$ are distributed independent of θ, containing in this way all information about parameter θ that can be obtained from the data. Similar to unbiasedness and efficiency, sufficiency is also a natural desirable condition in inference problems. However, a theorem by Pitman and Koopman [37] states that sufficient estimators only exist for a reduced family of distribution functions, the so-called *exponential family*:

$$\mathrm{d}p(x|\theta) = \exp[A(\theta) + B(x)C(\theta) + D(x)]\, \mathrm{d}x. \tag{117}$$

Mandelbrot was the first investigator to realize the intimate connection between statistical mechanics and inference theory [28]. Clearly, the Gibbs canonical ensemble (3) constitutes a relevant physical example of the probabilistic distribution function belonging to the exponential family (117). According to the well-known Kinchin work in the framework of information theory [38], Mandelbrot proposed a set of axioms in order to justify a direct derivation of the Gibbs canonical ensemble in the framework of inference theory. Moreover, he also focused the inference problem of the inverse temperature β, which appears as a parameter of the Gibbs canonical ensemble (3), through some unbiased estimator $\hat{\beta}$ defined for a set of outcomes of the system energy U. Thus, this author provided an interpretation of the *energy–temperature complementarity* previously postulated by Bohr and Heisenberg [18, 19]:

$$\Delta_c\hat{\beta}\Delta_c U \geqslant k_{\mathrm{B}}, \tag{118}$$

with $\Delta_c x \equiv \sqrt{\langle\delta x^2\rangle_c}$, a result that follows from Cramér–Rao's inequality (115) after noting that Fisher's information entropy (116) for the Gibbs canonical distribution (3) is simply the canonical expectation value $\langle * \rangle_c$ of the energy dispersion, $I_{\mathrm{F}}(\beta) \equiv \langle\delta U^2\rangle_c$.

After reading the present discussion, one can point out some critiques of Mandelbrot's approach. In regard to his interpretation of energy–temperature complementarity, equation (118), it is clear that such an uncertainty relation only applies in the framework of the Gibbs canonical ensemble (3). Moreover, this inequality accounts for the limits of precision of a statistical estimation of the inverse temperature β appearing as a parameter of the canonical ensemble (3). Clearly, this quantity has nothing to do with the system inverse temperature, but rather the inverse temperature of the Gibbs thermostat. This is a common misunderstanding of some contemporary developments of statistical physics, where no distinction is made between these two temperatures, leading in this way to some limitations and inconsistencies. Clearly, such difficulties are overcome by the uncertainty relation (17) associated with the energy–temperature fluctuation–dissipation relation (1).

The differences between the Gibbs temperature of the canonical ensemble (3) and Boltzmann's definition (5) are irrelevant in the case of large short-range thermodynamic systems considered in conventional applications of statistical mechanics and thermodynamics in those physical situations where the necessary conditions for the equivalence between canonical and microcanonical descriptions apply. However, the existing differences become critical when one considers the thermodynamical description of long-range interacting systems such as the astrophysical ones, where the presence of macrostates with *negative heat capacities* constitutes an important thermodynamic feature that rules their macroscopic behavior and dynamical evolution [13, 14]. As already discussed, such an anomaly cannot be described by using the Gibbs canonical description (3). Besides, there does not exist in this context an appropriate Gibbs thermostat that ensures the existence of a thermal contact (a boundary interaction) in the presence of a long-range interacting force such as gravity.

The above limitations also extend to other physical contexts such as small or mesoscopic nuclear, molecular and atomic clusters, where the presence of a negative heat capacity is not an unusual feature [13], while the thermodynamic influence of a Gibbs thermostat constitutes a very strong perturbation of its internal thermodynamic state. In this kind of scenario, there does not always exist a clear justification for the direct application of some theoretical developments based on the consideration of the Gibbs canonical ensemble, e.g. the use of finite-temperature calculations for the study of collisions in high energy physics. Interestingly, a collective phenomenon such as the *nuclear multi-fragmentation* resulting from collisions of heavy nuclei is simply a first-order phase transition revealing the experimental observation of macrostates with negative heat capacities $C < 0$ [3, 5]. Clearly, such a realistic phenomenon cannot be appropriately described by using the canonical ensemble.

Remarkably, it is easy to note that the Gibbs canonical ensemble (3) is not the only probabilistic distribution function justified in terms of inference theory, as originally presupposed by Mandelbrot in his approach. In fact, the whole family of the generalized Gibbs canonical ensembles (87) also belongs to the exponential family (117), and hence such distributions also ensure the existence of sufficient estimators $\hat{\beta}^{\phi}_c$ obeying uncertainty relations *á la Mandelbrot*:

$$\Delta_\phi\hat{\beta}^{\phi}_c\Delta_\phi\Theta \geqslant k_{\mathrm{B}}, \tag{119}$$

as a consequence of the underlying reparametrization duality discussed in this work. As expected, $\Delta_\phi x \equiv \sqrt{\langle \delta x^2 \rangle_\phi}$, with $\langle * \rangle_\phi$ being the generalized canonical expectation values derived from the generalized ensemble (87).

5. Conclusions

We have provided in this work a panoramic overview of direct implications and connections of the energy–temperature fluctuation–dissipation relation (1) with different challenging questions of statistical mechanics.

As briefly discussed, the main motivation and most direct consequence of this generalized fluctuation relation was the compatibility with macrostates having negative heat capacities in the framework of fluctuation theory. Such a feature makes it possible to analyze and apply the necessary conditions for the thermodynamical stability of such anomalous macrostates in order to extend the available Monte Carlo methods based on the consideration of the Gibbs canonical ensemble (3), a procedure that also allows one to avoid the incidence of the so-called *super-critical slowing down* encountered in large-scale simulations. Moreover, the fluctuation–dissipation relation constitutes a particular expression of a fluctuation relation leading to the existence of a complementary relationship between thermodynamic quantities of energy and (inverse) temperature (17).

The consideration of geometric concepts, such as coordinate changes or *reparametrizations*, leads to a direct extension of many old and new rigorous results of statistical mechanics in terms of a special kind of internal symmetry that we refer to here as a *reparametrization duality*. Such a basis inspires the introduction of a geometric generalized version of the Gibbs canonical ensemble (87), which has been recently proposed in the literature [25, 26]. This latter probabilistic distribution allows for a better treatment of the phenomenon of ensemble inequivalence or for the consideration of anomalous macrostates with negative heat capacities. At the same time, this family of distribution functions still preserves many notable properties of the Gibbs canonical ensemble, including its derivation from Jaynes's reinterpretation of statistical mechanics in terms of information theory as well as Mandelbrot's approach based on inference theory.

Acknowledgments

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

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