Equilibrium fluctuation theorems compatible with anomalous response

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Abstract. Previously, we have derived a generalization of the canonical fluctuation relation between heat capacity and energy fluctuations $C = \beta^2 \langle \delta U^2 \rangle$, which is able to describe the existence of macrostates with negative heat capacities $C < 0$. In this work, we extend our previous results for an equilibrium situation with several control parameters to account for the existence of states with anomalous values in other response functions. Our analysis leads to the derivation of three different equilibrium fluctuation theorems: the fundamental and the complementary fluctuation theorems, which represent the generalization of two fluctuation identities already obtained in previous works, and the associated fluctuation theorem, a result that has no counterpart in the framework of Boltzmann–Gibbs distributions. These results are applied to study the anomalous susceptibility of a ferromagnetic system, in particular, the case of the 2D Ising model.

Keywords: rigorous results in statistical mechanics, classical Monte Carlo simulations
1. Introduction

According to the well-known fluctuation relation

\[ C = k_B \beta^2 \langle \delta U^2 \rangle \]  \hspace{1cm} (1)

between the heat capacity \( C \) and the energy fluctuations \( \langle \delta U^2 \rangle \), the heat capacity should be nonnegative. However, such a conclusion is only an illusion. Since the first theoretical demonstration of the existence of macrostates with negative heat capacities \( C < 0 \) by Lynden-Bell in the astrophysical context [1], this anomaly has been observed in diverse systems [2]–[9]. The fluctuation relation (1) directly follows from the consideration of the Gibbs' canonical ensemble

\[ dp_c (U | \beta) = \frac{1}{Z(\beta)} \exp (-\beta U) \Omega(U) \, dU, \]  \hspace{1cm} (2)

which accounts for the equilibrium thermodynamic properties of a system in thermal contact with a heat bath at constant temperature \( T \) when other thermodynamical variables like the system volume \( V \) or a magnetic field \( H \) are kept fixed, where \( \beta = 1/k_B T \). As already commented, macrostates with \( C < 0 \) can be observed within the thermodynamic description of a given system, but they are unstable under the external influence imposed on the system within the canonical ensemble (2).

The fluctuation relation (1) admits the following generalization [10, 11]:

\[ C = k_B \beta^2 \langle \delta U^2 \rangle + C \langle \delta \beta^2 \delta U \rangle, \]  \hspace{1cm} (3)

which considers an equilibrium situation where the environmental inverse temperature \( \beta^e \) exhibits correlated fluctuations with the total energy \( U \) of the system under study as a consequence of the underlying thermodynamic interaction. The feedback effect \( \langle \delta \beta^e \delta U \rangle \) consideration allows us to detect the presence of a regime with negative heat capacities...
Equilibrium fluctuation theorems compatible with anomalous response

$C < 0$ in the microcanonical caloric curve $1/T(U) = \partial S(U)/\partial U$. In fact, it asserts that macrostates with $C < 0$ are thermodynamically stable provided that the environmental influence obeys the inequality $\langle \delta \beta^2 \delta U \rangle > 1$.

The energy–temperature fluctuation relation (3) has interesting connections with diverse questions within statistical mechanics, such as the justification of a complementary relation between energy and temperature [10]–[12], the extension of canonical Monte Carlo methods to allow the study of macrostates with negative heat capacities and to avoid the super-critical slowing down of first-order phase transitions [13,14], as well as the development of a geometric formulation for fluctuation theory based on the existence of reparameterization dualities [15]. However, equation (3) is applicable to those equilibrium situations where there only the conjugated pair energy–temperature is involved. Consequently, this result merely constitutes a special case of certain equilibrium fluctuation theorems compatible with the existence of anomalous response functions [16]–[21], whose derivation will be the main goal of the present work.

2. Equilibrium fluctuation theorems

2.1. Notations and conventions

From the standard perspective of statistical mechanics, a system–environment equilibrium situation with several control parameters is customarily described using the Boltzmann–Gibbs distributions [22,23]

$$d_{\text{BG}}(U, X| \beta, Y) = \frac{1}{Z(\beta, Y)} \exp\left[-\beta(U + YX)\right] \Omega(U, X) \, dU \, dX. \quad (4)$$

The quantities $X = (V, M, P, N_i, \ldots)$ represent other macroscopic observables acting in a given application (generalized displacements) such as the volume $V$, the magnetization $M$ and polarization $P$, the number of chemical species $N_i$, etc, with $Y = (p, -H, -E, -\mu_i, \ldots)$ being the corresponding conjugated thermodynamic parameters (generalized forces) such as the external pressure $p$, magnetic and electric fields, $H$ and $E$, the chemical potentials $\mu_i$, etc.

The notation employed in thermodynamics always distinguishes energy and temperature from the other thermodynamic quantities. Such a distinction is clearly evident in thermodynamic relations such as $dQ = T \, dS = dU + Y \, dX$. In this work, we shall also adopt the following convention for the generalized displacements: $(U, X) \to I = (I^1, I^2, \ldots)$ and $(\beta, Y) \to \beta = (\beta_1, \beta_2, \ldots)$ for the generalized forces, which allows us to deal with a symmetric and compact notation in the thermodynamic expressions. Thus, the previous example is equivalently expressed as follows: $dS = \beta(dU + Y \, dX) \to dS = \beta_1 dI^1 + \beta_2 dI^2 + \cdots \equiv \beta_i dI^i$. Besides, we shall assume Einstein’s summation convention, which allows us to rewrite the probabilistic weight of the Boltzmann–Gibbs distribution (4) as

$$\omega_{\text{BG}}(I| \beta) = \frac{1}{Z(\beta)} \exp(-\beta_i I^i). \quad (5)$$

For convenience, Boltzmann’s constant $k_B$ is hereafter assumed as unity.
2.2. General fluctuation theorems of a classical distribution function

Let us start from a generic classical distribution function

$$dp(I|\theta) = \rho(I|\theta) dI,$$

where $I$ are the system macroscopic observables that behave as stochastic variables in an equilibrium situation driven by a set $\theta$ of control parameters. Let us denote by $\mathcal{M}_\theta$ the compact space constituted by all admissible values of the macroscopic observables $I$ that are accessible for a given value $\theta$ of control parameters. Let us also admit that the probability density $\rho(I|\theta)$ is everywhere finite and differentiable, and obeys the following boundary conditions for every $I_b \in \partial \mathcal{M}_\theta$:

$$\lim_{I \to I_b} \rho(I|\theta) = \lim_{I \to I_b} \frac{\partial}{\partial I} \rho(I|\theta) = 0.$$

Let us introduce the differential generalized forces $\eta(I|\theta)$ as follows:

$$\eta(I|\theta) = -\frac{\partial}{\partial I} \log \rho(I|\theta).$$

By definition, the differential generalized forces $\eta(I|\theta)$ vanish in those stationary points $\bar{I}$ where the probability density $\rho(I|\theta)$ exhibits its local maxima or its local minima. The global (local) maximum of the probability density is commonly regarded as a stable (metastable) equilibrium configuration in the framework of large thermodynamic systems. In general, the differential generalized forces $\eta(I|\theta)$ characterize the deviation of a given point $I \in \mathcal{M}_\theta$ from these local equilibrium configurations. As stochastic variables, the expectation values of the differential generalized forces $\eta = \eta(I|\theta)$ identically vanish:

$$\langle \eta \rangle = 0,$$

and these quantities also obey the fundamental and the associated fluctuation theorems:

$$\langle \eta_i I_j \rangle = \delta_{ij}, \quad \langle -\partial_i \eta_j + \eta_i \eta_j \rangle = 0,$$

where $\partial_i A = \partial A/\partial I^i$. As already shown in [12], the previous fluctuation relations are directly derived from the following mathematical identity:

$$\langle \partial_i A(I|\theta) \rangle = \langle \eta_i(I|\theta) A(I|\theta) \rangle$$

substituting the cases $A(I|\theta) = 1$, $I^i$ and $\eta_i$ respectively. Here, $A(I)$ is a differentiable function of the macroscopic observables $I$ with definite expectation values $\langle \partial A(I|\theta)/\partial I^i \rangle$ that obeys the following boundary condition:

$$\lim_{I \to I_b} A(I) \rho(I|\theta) = 0.$$

Fluctuation theorems (9) and (10) can be regarded as the counterparts of some known results of inference theory [24, 25]. To clarify this idea, let us admit that the probability density $\rho(I|\theta)$ is everywhere differentiable and finite on the compact space $\mathcal{P}$ constituted by all admissible values of control parameters $\theta$. Introducing the score vectors $\upsilon_{\alpha}(I|\theta)$:

$$\upsilon_{\alpha}(I|\theta) = -\frac{\partial}{\partial \theta_{\alpha}} \log \rho(I|\theta),$$

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it is possible to obtain the following identities:

\[ \langle v_\alpha \rangle = 0, \quad \langle v_\alpha \hat{\theta}^\beta \rangle = -\delta_\alpha^\beta, \quad \langle -\partial_\alpha v_\beta + v_\alpha v_\beta \rangle = 0, \]  

(14)

where \( \hat{\theta}^\alpha = \hat{\theta}^\alpha(I) \) denotes any unbiased estimator of the \( \alpha \)th control parameter \( \theta^\alpha \):

\[ \langle \hat{\theta}^\alpha \rangle = \int_{\mathcal{M}_\theta} \hat{\theta}^\alpha(I) \rho(I|\theta) \, dI = \theta^\alpha, \]  

(15)

and \( \partial_\alpha A = \partial A/\partial \theta^\alpha \). The previous relations are obtained from the identity

\[ \partial_\alpha \langle A(I|\theta) \rangle = \langle \partial_\alpha A(I|\theta) \rangle - \langle A(I|\theta) v_\alpha(I|\theta) \rangle, \]  

(16)

where \( A(I|\theta) \) is any differentiable function of control parameters \( \theta \) with a definite statistical expectation value:

\[ \langle A(I|\theta) \rangle = \int_{\mathcal{M}_\theta} A(I|\theta) \rho(I|\theta) \, dI. \]  

(17)

Introducing the inverse matrix \( g^{\alpha\beta}(\theta) \) of the self-correlation matrix \( g_{ij}(\theta) \):

\[ g_{ij}(\theta) = \langle v_\alpha(I|\theta) v_\beta(I|\theta) \rangle = \int_{\mathcal{M}_\theta} [-\partial_\alpha \log \rho(I|\theta)] [-\partial_\beta \log \rho(I|\theta)] \rho(I|\theta) \, dI \]  

(18)

and the auxiliary quantity \( X^\alpha = \delta \hat{\theta}^\alpha - g^{\alpha\beta} v_\beta \), one can compose the positive definite form:

\[ \langle (\lambda_\alpha X^\alpha)^2 \rangle = \langle X^\alpha X^\beta \rangle \lambda_\alpha \lambda_\beta \geq 0, \]  

(19)

which leads to the positive definition of the matrix:

\[ \langle \delta \hat{\theta}^\alpha \delta \hat{\theta}^\beta \rangle - g^{\alpha\beta}(\theta) \succeq 0. \]  

(20)

Equation (20) is the known Cramer–Rao theorem of inference theory [24, 25] that imposes an inferior bound on the efficiency of unbiased estimators \( \hat{\theta}^\alpha \), where the matrix (20) is referred to as Fisher’s information matrix. Considering the inverse \( M^{ij}(\theta) \) of the self-correlation matrix of the differential generalized forces:

\[ M_{ij}(\theta) = \langle \eta_i(I|\theta) \eta_j(I|\theta) \rangle, \]  

(21)

it is possible to obtain the following matrical inequalities:

\[ \langle \delta I^i \delta I^j \rangle - M^{ij}(\theta) \succeq 0. \]  

(22)

Clearly, this last result is a counterpart of the Cramer–Rao theorem (20) in the framework of fluctuation theory. Introducing the gradient operators \( \partial_i \rightarrow \nabla_I \) and \( \partial_\alpha \rightarrow \nabla_\theta \), the dyadic products \( A \cdot B = A_i B_j \epsilon^i \cdot \epsilon^j \) and \( \xi \cdot \psi = \xi_\alpha \psi_\beta \epsilon^\alpha \cdot \epsilon^\beta \) and the Kronecker deltas \( \delta^1_1 \rightarrow 1_I \) and \( \delta^\theta_\theta \rightarrow 1_\theta \), the underlying analogy between fluctuation theory and inference theory is summarized in table 1.
Equilibrium fluctuation theorems compatible with anomalous response

| Table 1. Analogy between inference theory and fluctuation theory. |
|---------------------------------|---------------------------------|
| Inference theory               | Fluctuation theory              |
| $\nu(I|\theta) = -\nabla_{\theta} \log \rho(I|\theta)$ | $\eta(I|\theta) = -\nabla_{I} \log \rho(I|\theta)$ |
| $\langle \nu(I|\theta) \rangle = 0$ | $\langle \eta(I|\theta) \rangle = 0$ |
| $\langle \nu(I|\theta) \cdot \delta \theta \rangle = -1_{\theta}$ | $\langle \eta(I|\theta) \cdot \delta I \rangle = 1_{I}$ |
| $\langle \nabla_{\theta} \cdot \nu(I|\theta) \rangle = \langle \nu(I|\theta) \cdot \nu(I|\theta) \rangle$ | $\langle \nabla_{I} \cdot \eta(I|\theta) \rangle = \langle \eta(I|\theta) \cdot \eta(I|\theta) \rangle$ |

2.3. Fluctuation theorems for systems in contact with an environment

Let us apply the fluctuation relations (9) and (10) to equilibrium distribution functions of classical statistical mechanics. As discussed elsewhere, classical fluctuation theory starts from the Einstein postulate [22,23]:

$$dp(I|\theta) = A \exp [S(I|\theta)] dI,$$

(23)

which allows us to relate the differential generalized forces with the entropy $S(I|\theta)$:

$$\eta(I|\theta) = -\nabla_{I} S(I|\theta).$$

(24)

Let us assume that the entropy $S(I|\theta)$ can be decomposed into two additive terms:

$$S(I|\theta) = S(I) + S^{\omega}(I|\theta),$$

(25)

where $S(I)$ is the entropy of an isolated system, while $S^{\omega}(I|\theta)$ is the contribution of the total entropy $S(I|\theta)$ when this system is put in thermodynamic equilibrium with a certain environment. Such a decomposition leads to the following distribution function:

$$dp(I|\theta) = \omega(I|\theta)\Omega(I) dI,$$

(26)

where the probabilistic weight $\omega(I|\theta) \sim \exp[S(I|\theta)]$ arises here as a formal extension of the Boltzmann–Gibbs distribution (4). The differential generalized forces can be rephrased as follows:

$$\eta_{i}(I|\theta) = \beta_{\omega}^{i}(I|\theta) - \beta_{i}(I|\theta),$$

(27)

where $\beta_{\omega}^{i}(I|\theta)$ denotes the environmental generalized forces:

$$\beta_{\omega}^{i}(I|\theta) = -\frac{\partial S^{\omega}(I|\theta)}{\partial I^{i}},$$

(28)

and $\beta_{i}(I)$ is the system generalized forces:

$$\beta_{i}(I) = \frac{\partial S(I)}{\partial I^{i}}.$$

(29)

Equation (9) drops to the equilibrium thermodynamic conditions in the form of statistical expectation values:

$$\langle \beta_{i}(I) \rangle = \langle \beta_{\omega}^{i}(I) \rangle.$$

(30)

The relevance of the fundamental fluctuation theorem in equation (14) with the existence of complementary relations of statistical mechanics has been previously discussed in an extensive way [12]. The complementary fluctuation theorem is the generalization of the
Equilibrium fluctuation theorems compatible with anomalous response

identity (30) obtained in [15], which identifies the expectation value of the response matrix of the differential generalized forces \( \zeta_{ij} \):

\[
\zeta_{ij} = \frac{\partial \eta_j}{\partial \eta_i}
\]

and its self-correlation matrix \( \langle \delta \eta_i \delta \eta_j \rangle \). This general fluctuation theorem is a particular expression of the Le Chatelier–Braun principle [23]: the response of a stable system to the action from outside must be a weakened resistance to this action. This behavior is manifested as the positive definite character of the response matrix \( \zeta_{ij} \) in the differential generalized forces \( \eta_i \), which can be inferred from the positive definite character of the self-correlation matrix \( \langle \delta \eta_i \delta \eta_j \rangle \). Fluctuation theorems (10) constitute the most general extension of some known results of classical fluctuation theory. For example, the component of the fundamental fluctuation theorem involving the differential inverse temperature and the volume \( V \) of a fluid system:

\[
\langle \delta V \left( \frac{1}{T^\omega} - \frac{1}{T} \right) \rangle = 0
\]

as well as the term of the complementary fluctuation theorem involving the system internal energy \( U \) and its temperature \( T \):

\[
\left\langle \frac{\partial}{\partial U} \left( \frac{1}{T^\omega} - \frac{1}{T} \right) \right\rangle = \left\langle \left( \frac{1}{T^\omega} - \frac{1}{T} \right)^2 \right\rangle
\]

drop to the familiar expressions [22]:

\[
\langle \delta V \delta T \rangle = 0, \quad T^2/C_V = \langle \delta T^2 \rangle
\]

after considering the first-order approximation discussed below and the constant character of the environmental temperature \( T^\omega \) (canonical ensemble), where \( C_V \) is the system heat capacity at constant volume.

Let us employ the exact theorems (10) to arrive at a suitable extension of the energy–temperature fluctuation relation (3). Hereafter, we shall admit a first-order approximation where the expectation value and the fluctuations of a differentiable function \( A(I) \) can be expressed as follows:

\[
\langle A(I) \rangle \simeq A(\bar{I}), \quad \delta A(I) \simeq \frac{\partial A(\bar{I})}{\partial I^i} \delta I^i
\]

where \( \bar{I} \) represents the most likely state. Additionally, we shall omit the dependence of the thermodynamic functions on the macroscopic observables \( I \) to adopt a simpler notation in the mathematical expressions. Using the approximation rules (35), the fluctuation of the generalized forces \( \beta_i \) can be expressed in terms of the entropy Hessian \( H_{ij} \):

\[
H_{ij} = \frac{\partial \beta_j}{\partial I^i} = \frac{\partial^2 S}{\partial I^i \partial I^j}
\]

as follows:

\[
\delta \beta_i^* = H_{ik} \delta I^k
\]
Using these approximations, one can rephrase the fundamental and the associated fluctuation theorems (10) as follows:

$$\chi_{ij} = \langle \delta I_i \delta I_j \rangle + \chi_{ik} \langle \delta \beta^e_k \delta I_j \rangle,$$

(38)

$$\zeta_{ij} = \langle \delta \eta_i \delta \eta_j \rangle,$$

(39)

where the response matrix $\chi_{ij} = -H_{ij}$ is given by the inverse $H_{ij}$ of the entropy Hessian (36). The previous reasonings support the existence of a third equilibrium fluctuation theorem that has no counterpart in the framework of the Boltzmann–Gibbs distributions (4). This is the associated fluctuation theorem:

$$\langle \delta \beta^e_i \delta \beta^e_j \rangle \langle \delta I^k \delta I^l \rangle = \langle \delta \beta^e_i \delta I^k \rangle \langle \delta \beta^e_j \delta I^l \rangle,$$

(40)

which trivially vanishes for the statistical ensemble (4) since it involves the self-correlation matrix of the environmental control variables $\langle \delta \beta^e_i \delta \beta^e_j \rangle$. Generally speaking, to obtain the correlation matrix $\langle \delta \beta^e_i \delta I^j \rangle$, simultaneous measurements of the macroscopic observables $\{I^j\}$ and the environmental control variables $\{\beta^e_i\}$ must be performed, which are very difficult to carry out in practice. Such a difficulty can be overcome using the associated fluctuation theorem (40), which allows an indirect determination of the correlation matrix $\langle \delta \beta^e_i \delta I^j \rangle$ performing independent measurements of the self-correlation matrices $\langle \delta \beta^e_i \delta \beta^e_j \rangle$ and $\langle \delta I^i \delta I^j \rangle$. The proof of this theorem starts from introducing the Hessian $F_{ij}$:

$$F_{ij} = \frac{\partial \beta^e_i}{\partial I^j} = -\frac{\partial^2 S^e(I|\theta)}{\partial I^i \partial I^j}.$$

(41)

Using the first-order approximation

$$\delta \beta^e_i = F_{ij} \delta I^j,$$

(42)

one can show the following relations:

$$\langle \delta \beta^e_i \delta \beta^e_j \rangle = F_{jk} \langle \delta \beta^e_i \delta I^k \rangle, \quad \langle \delta \beta^e_i \delta I^j \rangle = F_{ik} \langle \delta I^k \delta I^j \rangle,$$

(43)

which can be easily combined to obtain the desired result (40).

Let us rewrite the equilibrium fluctuation theorems (38)–(40) in terms of the ordinary variables considered in thermodynamics, $(U, \beta)$ and $(X,Y)$. The counterpart of the fluctuation theorem (38) within the Boltzmann–Gibbs distribution (4) can be rewritten in compact matrix form as follows:

$$R = C,$$

(44)

where the response and the self-correlation matrices $R$ and $C$ are given by

$$R = -\begin{pmatrix} \partial_\beta \langle H \rangle & \partial_\beta \langle \beta \langle X \rangle \rangle \\ \partial_Y \langle H \rangle & \beta \partial_Y \langle X \rangle \end{pmatrix}, \quad C = \begin{pmatrix} \langle \delta Q^2 \rangle & \beta \langle \delta Q \delta X \rangle \\ \beta \langle \delta X^T \delta Q \rangle & \beta^2 \langle \delta X^T \delta X \rangle \end{pmatrix}.$$

(45)

Here, we have adopted the following matrix conventions:

$$X = (X^1 \ X^2 \ \cdots \ X^n), \quad \partial_X = (\partial_{X^1} \ \partial_{X^2} \ \cdots \ \partial_{X^n}),$$

(46)

$$Y^T = (Y_1 \ Y_2 \ \cdots \ Y_n), \quad \partial_Y = (\partial_{Y_1} \ \partial_{Y_2} \ \cdots \ \partial_{Y_n}),$$

(47)

where $A^T$ denotes the transpose operation. Note that the generalized forces $Y$ and their differential operators $\partial_Y$ represent column vectors while $\langle \delta X^T \delta X \rangle$ and $\partial_Y \langle X \rangle$
Equilibrium fluctuation theorems compatible with anomalous response

are \( n \times n \) square matrices. Besides, \( \mathcal{H} = U + XY \) is the enthalpy (we employ this notation to avoid any ambiguity with the magnetic field \( H \)), and \( \delta Q = \delta U + \delta XY \) the amount of heat absorbed or transferred by the system from its environment at the equilibrium, where \( \langle \delta Q \rangle \equiv 0 \). It is important to bear in mind that the enthalpy fluctuation \( \delta H = \delta Q \) within the Boltzmann–Gibbs distribution (4). Such a relationship does not hold when the fluctuations of the generalized forces \( Y \) are taken into consideration, where \( \delta H = \delta Q + X \delta Y \). The matrix form of the fluctuation theorem (44) in the symmetric representation using the conjugated thermodynamic variables \((U, \beta)\) and \((X, \xi)\) with \( \xi = \beta Y \) reads as follows:

\[
\chi = C, \tag{48}
\]

where the response and the self-correlation matrices \( \chi \) and \( C \) are given by

\[
\chi = -\begin{pmatrix} \partial_\beta \langle U \rangle & \partial_\beta \langle X \rangle \\ \partial_\xi \langle U \rangle & \partial_\xi \langle X \rangle \end{pmatrix}, \quad C = \begin{pmatrix} \langle \delta U^2 \rangle & \langle \delta U \delta X \rangle \\ \langle \delta X^T \delta U \rangle & \langle \delta X^T \delta X \rangle \end{pmatrix}. \tag{49}
\]

Representations (44) and (48) are related by the following transformation rules:

\[
C = TCT^T, \quad R = T\chi T^T, \tag{50}
\]

where the transformation matrix \( T \) is given by

\[
T = \begin{pmatrix} \mathbb{1} & Y \\ 0 & \beta \end{pmatrix}, \tag{51}
\]

with \( \mathbb{1} \) being the \( n \times n \) unitary matrix. Thus, the fundamental fluctuation theorem (38) is rewritten as follows:

\[
\chi = C + \chi D \rightarrow R = C + RD, \tag{52}
\]

where the correlation matrices \( D \) and \( D \) characterizing the environmental feedback effects

\[
D = \begin{pmatrix} \langle \delta \beta^\omega \delta U \rangle & \beta \langle \delta \beta^\omega \delta X \rangle \\ \langle \delta \xi^\omega \delta U \rangle & \beta \langle \delta \xi^\omega \delta X \rangle \end{pmatrix}. \tag{53}
\]

and

\[
D = \begin{pmatrix} \langle \delta \beta^\omega \delta Q \rangle & \beta \langle \delta \beta^\omega \delta X \rangle \\ \langle \delta Y^\omega \delta Q \rangle & \beta \langle \delta Y^\omega \delta X \rangle \end{pmatrix}. \tag{54}
\]

are related by the transformation rule

\[
D = (T^T)^{-1} DT^T. \tag{55}
\]

Here, the quantities \( (\beta^\omega, Y^\omega) \) denote the environmental control variables in the usual representation of thermodynamics.

The complementary fluctuation theorem (39) is written in compact matrix form as follows:

\[
N = F, \tag{56}
\]

where \( N \) and \( F \) are the response and self-correlation matrices of differential generalized forces \( \eta = \beta^\omega - \beta \) and \( \eta_X = \xi^\omega - \xi \) in the symmetric representation

\[
N = \begin{pmatrix} \partial_\eta \eta & \partial_\eta \eta_X^T \\ \partial_\xi \eta & \partial_\xi \eta_X^T \end{pmatrix}, \quad F = \begin{pmatrix} \langle \delta \eta^2 \rangle & \langle \delta \eta \delta \eta_X \rangle \\ \langle \delta \eta_X \delta \eta \rangle & \langle \delta \eta_X \delta \eta_X \rangle \end{pmatrix}. \tag{57}
\]
Using the transformation rules

\[ \mathcal{N} = (T^T)^{-1} N T^{-1}, \quad \mathcal{F} = (T^T)^{-1} F T^{-1}, \]

(58)

this fluctuation theorem can be rewritten as follows:

\[ \mathcal{N} = \mathcal{F} \rightarrow \mathcal{N} = \mathcal{F}, \]

(59)

where \( \mathcal{N} \) and \( \mathcal{F} \) are their respective expressions in the representation of thermodynamics:

\[ \mathcal{N} = \left( T \left( \frac{\partial U}{\partial \eta} - Y \frac{\partial U}{\partial \eta} \right) T \left( \frac{\partial Y}{\partial T} - Y \frac{\partial Y}{\partial T} \right) \right), \]

(60)

\[ \mathcal{F} = \left( \frac{\langle \delta \eta^2 \rangle}{\langle \delta Y \delta \eta \rangle} \frac{\langle \delta \eta \delta Y \rangle}{\langle \delta Y^2 \rangle} \right), \]

(61)

with \( Y = Y^\omega - Y \) being the differential generalized force conjugated with the observable \( X \). Using the same procedure, the associated fluctuation theorem (40) can be written as follows:

\[ BC = D^2, \]

(62)

where \( B \) is the self-correlation matrix of the environmental control variables in the symmetric representation:

\[ B = \left( \begin{array}{cc} \langle (\delta \beta^\omega)^2 \rangle & \langle \delta \beta^\omega (\delta \xi^\omega)^T \rangle \\ \langle \delta \xi^\omega \delta \beta^\omega \rangle & \langle \delta \xi^\omega (\delta \xi^\omega)^T \rangle \end{array} \right). \]

(63)

Considering the transformation rule

\[ B = (T^T)^{-1} B T^{-1}, \]

(64)

this fluctuation theorem can be rewritten as follows:

\[ BC = D^2, \]

(65)

where the self-correlation matrix of the environmental control variables \( B \) in the new representation is given by

\[ B = \left( \begin{array}{cc} \langle (\delta \beta^\omega)^2 \rangle & \langle \delta \beta^\omega (\delta Y^\omega)^T \rangle \\ \langle \delta Y^\omega \delta \beta^\omega \rangle & \langle \delta Y^\omega (\delta Y^\omega)^T \rangle \end{array} \right). \]

(66)

The mathematical expressions of equilibrium fluctuation theorems (38)–(40) manifest the non-preference of the thermodynamic description on a given macroscopic observable. This feature differs from the character of their respective expressions (52), (59) and (65), which explicitly attributes a preference on the energy and its conjugated quantity, the temperature. This second representation allows the matching of the current approach to the thermodynamic quantities obtained from the experiment. However, it is always easier to perform calculations using the symmetric representation, and after, to use the respective transformation rules to express the response and correlation matrices in the second representation.

Fluctuation theorem (10) has been employed to obtain the extension of conventional fluctuation theorems relating the correlation functions of macroscopic fluctuations with response functions. However, one can also rewrite this last fluctuation theorem to
emphasize the complementary character of conjugated thermodynamic quantities, which is precisely its main physical content. Using the transformation rule

$$S = (T^T)^{-1} ST^T,$$

(67)

one can rewrite the original form of the fundamental fluctuation theorem (10) as follows:

$$S = \hat{1} \rightarrow S = \hat{1},$$

(68)

where $\hat{1}$ is the unitary matrix, while $S$ and $\tilde{S}$ represent the correlation matrix between differential generalized forces and the macroscopic observables in these two representations:

$$S = \begin{pmatrix} \langle \delta \eta \delta U \rangle & \langle \delta \beta \delta X \rangle \\ \langle \delta \eta \delta X \rangle & \langle \delta \beta \delta X \rangle \end{pmatrix}, \quad \tilde{S} = \begin{pmatrix} \langle \delta \eta \delta Q \rangle & \beta \langle \delta \eta \delta X \rangle \\ \langle \delta \eta \delta Q \rangle & \beta \langle \delta \beta \delta X \rangle \end{pmatrix}.$$

(69)

3. Application of the present approach

3.1. Relationship among anomalous response and phase transitions

Anomalous response (or states where the response matrix $R$ is non-positive definite) are intimately related to the occurrence of phase transitions. Indeed, a phase transition is the manifestation of a thermodynamic instability and, precisely, macrostates with anomalous response are always unstable within the Boltzmann–Gibbs statistics (4). The best known example is the relation between negative heat capacities and the occurrence of a temperature driven discontinuous phase transition [7,8]. The same kind of relationship also appears in other anomalous response functions, as is evidenced in the thermodynamic description of the ferromagnetic Weiss model [26] shown in figure 1. The magnetization per particle $m = m(H)$ dependence on the external magnetic field $H$ can be rewritten as follows:

$$m(H) = \mu \tanh [\beta \mu (H + \alpha m)] \rightarrow H = \frac{T}{\mu} \tanh^{-1} \left( \frac{m}{\mu} \right) - \alpha m$$

(70)

to reveal the existence of states with negative isothermal susceptibilities $\chi_T < 0$:

$$N \chi_T^{-1} = \frac{T}{\mu^2 - m^2} - \alpha$$

(71)

for temperatures below the critical temperature $T_c = \alpha \mu^2$ of the ferromagnetic transition (panels (a) and (b)). Here, $\mu$ is the magnetic moment and $\alpha$ the molecular field parameter. The unstable character of these diamagnetic states within the Boltzmann–Gibbs distributions can be inferred from the fluctuation relation $\chi_T = \beta \langle \delta M^2 \rangle$, which is only compatible with nonnegative susceptibilities. Both the appearance of a non-vanishing spontaneous magnetization (panel (c)) and the sudden jump of magnetization with a small variation of the external magnetic field $H$ at the value $H = 0$ (panel (d)) are direct consequences of the existence of these anomalous states. This relation can be observed in the calculation of the Helmholtz potential $H(T, H) = \min_M f(M; T, H)$, where $f(M; T, H)$ is given by

$$f(M; T, H) = -\frac{1}{2N} \alpha M^2 + T \int \tanh^{-1} \left( \frac{M}{N \mu} \right) \frac{dM}{\mu} - HM.$$

(72)
Figure 1. Incidence of anomalous diamagnetic states in the thermodynamic description of the ferromagnetic Weiss model. Panel (a): isotherms in the $H-M$ plane. Panel (b): inverse of the isothermal magnetic susceptibility curve $\chi_T$. Panels (c) and (d): behavior of minima and maxima of the function $f(M; T, H)$. Panel (e): phase diagram and magnetization curves at constant magnetic field (dotted lines).

Here, the two minima of $f(M; T, H)$ for $T < T_c$ correspond to the stable and metastable states with $\chi_T > 0$, and its local maximum to an unstable state with $\chi_T < 0$. The distinction among stable (white region), metastable (light gray region) and unstable (dark gray region) states leads to the phase diagram shown in panel (e). Since the critical point (C) is a state of marginal stability located at the boundary of the unstable region, the occurrence of a continuous phase transition is also associated with a region of anomalous response.

3.2. A special condition of thermodynamic stability

The diamagnetic states observed below the critical temperature of the ferromagnetic transition are unstable for the particular equilibrium situation considered in the previous
example: a magnetic system under the influence of constant environmental temperature and constant external magnetic field. The same states, however, could be stable in other equilibrium situations. To illustrate this last possibility, one should obtain the particular expression of the fundamental fluctuation theorem (38) for a magnetic system with internal energy \( U \), total magnetization \( M \) and enthalpy \( H = U - \beta \chi_T \):

\[
R = \left( \frac{T^2 C_H}{\langle \delta M/\delta T \rangle_H} \right) T \left( \frac{\langle \partial M/\partial T \rangle_H}{\beta \chi_T} - \frac{1}{M} \right),
\]

\[
C = \left( \frac{\langle \delta Q^2 \rangle}{\langle \delta M \delta Q \rangle} \beta \langle \delta M \delta Q \rangle \right) \beta \langle \delta M^2 \rangle,
\]

\[
D = \left( \begin{array}{cc}
\langle \delta H^2 \delta Q \rangle & \beta \langle \delta H^2 \delta M \rangle \\
-\langle \delta Q \delta M \rangle & -\beta \langle \delta M \delta H \rangle
\end{array} \right).
\]

Here, \( C_H = (\partial H/\partial T)_H \) is the heat capacity at constant magnetic field and \( \chi_T = (\partial M/\partial T)_T \) the isothermal magnetic susceptibility, where the symmetry of the response matrix \( R \) leads to the thermodynamical identity

\[
\frac{\partial H}{\partial H}_T - T \left( \frac{\partial M}{\partial T}_H \right)_H = M.
\]

Admitting that \( \chi_T \) is the only anomalous response function, one can restrict the analysis to an equilibrium situation where the environmental inverse temperature \( \beta \omega \) takes a constant value \( \beta \), but the external magnetic field \( H^\omega \) undergoes a non-vanishing magnetic feedback effect \( \langle \delta H^\omega \delta M \rangle \). This effect naturally arises when the source of the external magnetic field \( H^\omega \) is disturbed by the magnetic influence of the system. The simplest way to account for this type of situation is when \( H^\omega \) undergoes small fluctuations around its mean value \( H \) coupled to the total system magnetization:

\[
H^\omega = H - \lambda \delta M/N,
\]

where \( N \) is the system size, and \( \lambda \) a coupling constant characterizing the system–environment magnetic interaction. For this particular equilibrium situation, the fluctuation relation involving the isothermal magnetic susceptibility \( \chi_T \)

\[
\beta \chi_T = \beta^2 \langle \delta M^2 \rangle + [T (\partial M/\partial T)_H - M] \beta \langle \delta \beta^\omega \delta M \rangle - \beta^2 \chi_T \langle \delta H^\omega \delta M \rangle
\]

drops to

\[
\chi_T = \beta \langle \delta M^2 \rangle - \beta \chi_T \langle \delta H^\omega \delta M \rangle.
\]

Clearly, this expression is very similar to the energy–temperature fluctuation relation (3), which only involves the system magnetization \( M \) and the external magnetic field \( H^\omega \) as conjugated thermodynamic quantities. This relation can be rewritten as

\[
\beta \langle \delta M^2 \rangle = \frac{\chi_T}{1 + \lambda \chi_T/N},
\]

after using the ansatz (75). Equation (78) can be employed to obtain the self-correlation function of the external magnetic field \( H^\omega \):

\[
\langle (\delta H^\omega)^2 \rangle = 1 - \left( \frac{\chi_T}{N^2 \chi_T^2} \right) \lambda^2 \langle \delta M^2 \rangle = \frac{1}{N^2 \beta} \lambda^2 \chi_T/N = \frac{\chi_T/N}{1 + \lambda \chi_T/N}.
\]

For extensive systems, the isothermal susceptibility \( \chi_T \) usually grows with \( N \) as \( \chi_T \propto N \). Consequently, the self-correlation functions of the system magnetization and the external

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magnetic field behave as \( \langle \delta M^2 \rangle \propto N \) and \( \langle (\delta H^\omega)^2 \rangle \propto 1/N \). Since the fluctuations of the external magnetic field \( H^\omega \) vanish in the thermodynamic limit \( N \to \infty \), the present equilibrium seems to be very similar to the conventional situation where the external magnetic field is constant. However, both the fluctuating behavior described by the expressions (78) and (79), as well as stability condition (80) depend on the coupling constant \( \lambda \). Indeed, the coupling constant \( \lambda \) can be appropriately chosen to force the thermodynamic stability of anomalous diamagnetic states \( \chi_T < 0 \). Since the self-correlation function of the system magnetization \( \langle \delta M^2 \rangle \) is nonnegative, anomalous diamagnetic states \( \chi_T < 0 \) are thermodynamically stable when the condition

\[
\lambda + N/\chi_T > 0 \tag{80}
\]

holds. This last result constitutes the magnetic counterpart of Thirring’s constraint [28]:

\[
C_B < |C| \tag{81}
\]

reobtained in [11] from the energy–temperature fluctuation relation (3) to force the thermal stability of states with negative heat capacities \( C < 0 \), with \( C_B \) being the heat capacity of a finite thermostat.

### 3.3. Monte Carlo study of the 2D Ising model

The consequences derived from the previous analysis are easily tested with the help of Monte Carlo simulations. For example, let us now consider the 2D Ising model on the square lattice \( L \times L \) with periodic boundary condition:

\[
U = -\sum_{\langle ij \rangle} s_is_j, \quad M = \sum_i s_i, \tag{82}
\]

where the spin variables \( s_i = \pm 1 \) and the sum \( \langle ij \rangle \) considers nearest-neighbor interactions only. The existence of a magnetic feedback effect \( \langle \delta H^\omega \delta M \rangle \) can be implemented using a Metropolis algorithm [27] with the acceptance probability

\[
p(U, M | U + \Delta U, M + \Delta M) = \min \{1, \exp \left[ -\beta \Delta U + \beta H^\omega \Delta M \right] \}. \tag{83}
\]

Denoting by \( m = M/N \) the magnetization per particle, the external magnetic field in this study is given by \( H^\omega = \bar{H} + \lambda (m - \bar{m}) \), where \( \bar{m} \) and \( \bar{H} \) are some rough estimations of the expectation values \( \langle m \rangle \) and \( \langle H^\omega \rangle \). Our goal is to obtain the isotherms of the 2D Ising model within anomalous regions with \( \chi_T < 0 \). The isothermal magnetic susceptibility per particle \( \bar{\chi}_T = \chi_T/N \) can be obtained from the fluctuation relation (78) as follows:

\[
\bar{\chi}_T^{-1} = \frac{1 + \beta \langle \delta H^\omega \delta M \rangle}{\beta \langle \delta M^2 \rangle} N = \frac{1 - \lambda \beta \sigma_m^2}{\beta \sigma_m^2}, \tag{84}
\]

where \( \sigma_m^2 = \langle \delta M^2 \rangle/N \) represents the thermal dispersion of magnetization. The values of the parameters \( (\bar{H}, \bar{m}) \) can be provided using the susceptibility per particle \( \bar{\chi}_T \) obtained from a previous Monte Carlo calculation through the expression

\[
\bar{H}_{i+1} = \bar{H}_i + (\bar{\chi}_T)_i^{-1}(\bar{m}_{i+1} - \bar{m}_i), \tag{85}
\]
where the step $\Delta m = \bar{m}_{i+1} - \bar{m}_i$ should be small. Here, the initial value $\bar{m}_0$ is estimated as the average of magnetization calculated from an ordinary Metropolis algorithm with constant magnetic field $H^\omega = H_0$ far enough from the unstable region with $\chi_T < 0$. Although any real value of coupling constant $\lambda$ that satisfies the stability condition (80) is admissible, one can impose a constraint to reduce the thermal fluctuations of the system magnetization (78) and the external magnetic field (79) to as low as possible. According to these expressions, the growth of the coupling constant $\lambda$ provokes a reduction of the magnetization fluctuations and the growth of the external magnetic field $H^\omega$ fluctuations.

Due to this observation, the optimal value of the coupling constant $\lambda$ is chosen to minimize the total dispersion $\sigma^2 = \sigma^2_H + \sigma^2_m$, where

$$\sigma^2_H = N s \langle (\delta H^\omega)^2 \rangle$$

is the thermal dispersion of the external magnetic field. Such an analysis yields

$$\lambda_{\text{opt}}(a) = \sqrt{a^2 + 1} - a,$$

where $a$ is the inverse of the isothermal magnetic susceptibility per particle, $a = \tilde{\chi}_T^{-1}$. Thus, the value of the coupling constant employed in the $i+1$-calculation is estimated from the previous Monte Carlo calculation as

$$\lambda_{i+1} = \lambda_{\text{opt}} \left[ (\tilde{\chi}_T)_i^{-1} \right].$$

Results of Monte Carlo simulations using the procedure previously explained are shown in figure 2. Here, we have restricted the simulations to a lattice with $L = 25$ and considered $n = 10^8$ iterations for each calculated point of these isotherms. Besides, states with positive magnetization $\langle m \rangle > 0$ are only shown due to the existence of the symmetry $M \rightarrow -M$ and $H \rightarrow -H$. These results revealed the presence of anomalous diamagnetic states $\tilde{\chi}_T < 0$ for inverse temperatures $\beta$ above the critical point $\beta_c \simeq 0.41$, that is, for temperatures $T < T_c \simeq 2.44$. Notice that these dependences are very similar to the ones shown in panels (a) and (b) of figure 1 corresponding to the ferromagnetic Weiss model. As illustrated in figure 3, while the existence of a magnetic feedback effect $\langle \delta H^\omega \delta M \rangle$ allows the backbending of isotherms in the $H-M$ diagram to be revealed, these dependences undergo a sudden jump in magnetization around the point $H = 0$ in the presence of a constant external magnetic field. Conventionally, such a sudden jump is interpreted as the occurrence of a discontinuous phase transition. Our simulation, however, demonstrates that this behavior follows as a consequence of the inability of the environmental influence characterized by constant temperature and external magnetic field to control a region with anomalous response. The nonsymmetric appearance of MC simulations at constant external magnetic field is a consequence of a poor relaxation of expectation value of magnetization, which evidences the occurrence of super-critical slowing down associated with discontinuous phase transitions [29]. The incidence of a magnetic feedback effect $\langle \delta H^\omega \delta M \rangle$ can suppress the thermodynamic instability associated with the discontinuous phase transition of the 2D Ising model. Since the sudden jump does not occur, one could claim that the discontinuous phase transition observed within the framework of Boltzmann–Gibbs distributions (4) has been suppressed in the present environmental influence. However, it is worth remarking that one observes the coexistence of magnetic domains with different orientations during the inversion of the system magnetization $M \rightarrow -M$. Along this process, the transition from $\uparrow$-rich towards $\downarrow$-rich domain configurations is gradual and without metastability, which suggests that phase separation actually persists at a macroscopic level. Essentially, this type of behavior is analogous to
4. Concluding remarks

The usual equilibrium fluctuation theorems of statistical mechanics disregard the existence of states with anomalous response. Starting from general fluctuation theorems of any classical distribution function (9) and (10), we have been able to obtain three equilibrium fluctuation theorems compatible with anomalous response, equations (38)–(40). As evidenced in the study of the 2D Ising model, these theorems can be successfully employed
for the analysis of the thermodynamic stability beyond the conventional equilibrium situations. A novel feature is the consideration of environmental feedback effects, described by the correlation matrix $D$, which act as control mechanisms for the states with anomalous response.

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