Understanding critical behavior in the framework of the extended equilibrium fluctuation theorem

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Abstract. Recently, we have derived a fluctuation theorem for systems in thermodynamic equilibrium compatible with anomalous response functions, e.g. the existence of states with negative heat capacities $C < 0$. In this work, we show that the present approach of the fluctuation theory introduces new insights in the understanding of critical phenomena. Specifically, the new theorem predicts that the influence of the environment can radically affect the critical behavior of systems, e.g. to provoke a suppression of the divergence of correlation length $\xi$ and some of its associated phenomena such as spontaneous symmetry breaking. Our analysis reveals that while response functions and state equations are intrinsic properties of a given system, critical behaviors are always relative phenomena, that is, their existence crucially depends on the underlying environmental influence.

Keywords: rigorous results in statistical mechanics, classical Monte Carlo simulations, classical phase transitions (theory), correlation functions (theory)
1. Introduction

Critical phenomena is the collective name associated with the physics of critical points [1], which originate as a consequence of the divergence of the correlation length $\xi$. The understanding of critical phenomena has motivated the development of new mathematical tools for the study of phase transitions such as the renormalization group theory, which has had a significant impact in condensed matter and high energy physics [2]. In this work, we present simple theoretical arguments and simulations that reveal new aspects of the understanding of critical phenomena. We show that the influence of the environment can radically affect the critical behavior of systems, for example provoking a suppression of the divergence of correlation length $\xi$ and some of its associated phenomena like spontaneous symmetry breaking.

Our arguments are based on a framework of equilibrium fluctuation theory recently proposed in [3]–[7]. The main contributions of this approach are the derivation of a set of fluctuation theorems compatible with anomalous response functions [3]–[6] as well as uncertainty relations involving thermodynamic quantities [7]. For the sake of self-consistency of this paper, we first present a brief review of the so-called fundamental equilibrium fluctuation theorem and some of its most immediate consequences [6]. Then, this theorem will be considered to analyze the role of environmental influence on critical phenomena. The results of this analysis will be illustrated with a study of critical behavior in the 2D Ising model. Finally, we present some concluding remarks.

2. Extended equilibrium fluctuation theorem

The fundamental equilibrium fluctuation theorem (EFT)

$$\mathcal{R} = C + \mathcal{RD}$$

(1)

describes the relation between the system response functions and its fluctuating behavior [6]. The quantity $\mathcal{R}$ represents the response matrix:

$$\mathcal{R} = - \begin{pmatrix} \frac{\partial \beta \mathcal{H}}{\partial Y} & \frac{\partial \beta (\beta X)}{\partial Y} \\ \frac{\partial Y \mathcal{H}}{\partial \beta} & \beta \frac{\partial Y X}{\partial \beta} \end{pmatrix},$$

(2)

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which characterizes the system’s response to an environmental influence, whereas \( Y = (p, -\vec{E}, -\vec{H}, \ldots) \) denotes a generalized force (pressure, electric field, magnetic field, etc) and \( X = (V, \vec{P}, \vec{M}, \ldots) \) is the corresponding generalized displacement (volume, polarization, magnetization, etc). Besides, \( \mathcal{H} = U + YX \) and \( U \) are the system enthalpy and the internal energy, respectively, while \( \beta = 1/T \) denotes the inverse temperature and \( \partial_x A \) is the partial derivative \( \partial A/\partial x \). The quantity \( C \) is the self-correlation matrix that characterizes the system’s fluctuating behavior:

\[
C = \begin{pmatrix} \langle \delta Q^2 \rangle & \beta \langle \delta Q \delta X \rangle \\ \beta \langle \delta X \delta Q \rangle & \beta^2 \langle \delta X^2 \rangle \end{pmatrix},
\]

while the correlation matrix \( D \):

\[
D = \begin{pmatrix} \langle \delta \beta \delta Q \rangle & \beta \langle \delta \beta \delta X \rangle \\ \beta \langle \delta Y \delta Q \rangle & \beta \langle \delta Y \delta X \rangle \end{pmatrix}
\]

describes the existence of environmental feedback effects among the system’s macroscopic observables \((U, X)\) and the environmental control variables \((\beta, Y)\) due to the underlying thermodynamic interaction. As expected, the amount of heat exchanged between the system and the environment at the equilibrium \( \delta Q = \delta U + Y \delta X = T \delta S \) obeys the condition \( \langle \delta Q \rangle = 0 \).

EFT (1) represents a suitable extension of the usual fluctuation theorem [8]

\[
\mathcal{R} = C
\]

derived from the Boltzmann–Gibbs (BG) distributions

\[
dp_{BG} (U, X | \beta, Y) = \frac{\exp[-\beta(U + YX)]}{Z(\beta,Y)} \Omega(U, X) dU dX.
\]

Here, \( \Omega(U, X) \) is the system density of states, while \( Z(\beta,Y) \) is the partition function. Equation (5), as an example, contains the fluctuation relations

\[
C_p = \beta^2 \langle \delta Q^2 \rangle, \quad V K_T = \beta \langle \delta V^2 \rangle, \quad \chi_T = \beta \langle \delta M^2 \rangle,
\]

where \( C_p = T(\partial S/\partial T)_p \) is the isobaric heat capacity, \( K_T = -V^{-1}(\partial V/\partial p)_T \) is the isothermal compressibility and \( \chi_T = (\partial M/\partial H)_T \) is the isothermal magnetic susceptibility. Despite their wide application in statistical mechanics, BG distributions (6) have a restricted applicability due to the environmental inverse temperature \( \beta \) and its generalized force \( Y \) being regarded as constant parameters. Such a restriction demands the consideration of thermal contact with a bath with infinite heat capacity or a reservoir with an infinite number of particles, as other idealizations assumed in conventional applications (usually attributed to the natural environment). In a general equilibrium situation, the internal state of the system acting as the ‘environment’ is also perturbed by the underlying thermodynamic interaction. This is the origin of environmental feedback effects described by the correlation matrix \( D \) in the extended EFT (1).

Conventional EFT (5) is only compatible with states with a positive definite response matrix \( \mathcal{R} \). Considering its particular fluctuation relations (7), this last requirement implies the positive character of the heat capacity \( C_p \), the isothermal compressibility \( K_T \) and the magnetic susceptibility \( \chi_T \). Remarkably, thermodynamics also supports the existence

\[\text{Boltzmann constant } k_B \text{ has been set as the unity.}\]
of states with negative heat capacities and other anomalous response functions, that is, a non-positive definite response matrix $\mathcal{R}$. Mathematically, the existence of anomalous response is associated with the presence of states where the entropy $S = \log W$ is a non-concave function. Such a relationship comes from the possibility of expressing the response matrix $\mathcal{R}$ as follows:

$$\mathcal{R} = -TH^{-1}T^\top,$$

where $H$ is the entropy Hessian

$$H = \begin{pmatrix} \frac{\partial^2 S}{\partial U \partial U} & \frac{\partial U \partial X}{\partial U} \\ \frac{\partial X \partial U}{\partial U} & \frac{\partial^2 S}{\partial X \partial X} \end{pmatrix},$$

and the transformation matrix $T$ is

$$T = \begin{pmatrix} 1 & Y \\ 0 & \beta \end{pmatrix}.$$

Moreover, the thermodynamic quantities $\beta$ and $Y$ are also obtained from the entropy $S$ via the expressions

$$\beta = \left( \frac{\partial S}{\partial U} \right)_X, \quad \beta Y = \left( \frac{\partial S}{\partial X} \right)_U.$$

The states with anomalous response conform to so-called regions of ensemble inequivalence [3–6]. Physically, the anomalous response is a consequence of the incidence of non-extensive effects [3–6], for example the presence of long-range interactions or the development of spatial non-homogeneities during the occurrence of discontinuous phase transitions [9–11]. The presence of a long-range force like gravitation explains the existence of negative heat capacities in astrophysical systems [9–11]. The development of interphases induces the existence of surface correlations, which are the origin of the negative heat capacities $C < 0$ observed during the phase coexistence phenomenon [9]. Analogously, such surface correlations explain the anomalous states with negative susceptibility $\chi_T < 0$ observed in a magnetic system below the critical temperature, which owe their origin to the formation of magnetic domains [6].

Direct consequences of the conventional EFT (5) are known [8]:

- The system’s fluctuating behavior is determined by its own response to the external conditions.

- The stable states are those ones where the response matrix $\mathcal{R}$ is also positive definite because the self-correlation matrix $C$ is always positive definite.

- The simultaneous divergence of some components of the response matrix and their corresponding correlation functions at the critical points, $\mathcal{R}^{ij} \to \infty \Rightarrow C^{ij} \to \infty$, which is related to the divergence of correlation length, $\xi \to \infty$.

The presence of the correlation matrix $D^{ij}$ in the extended EFT (1) introduces the following radical changes in the previous implications:

- The system’s fluctuating behavior depends both on its response functions and the nature of the environmental influence.

- The stable states are those ones where $\mathcal{R}(I - D)$ is a positive definite matrix, with $I$ being the identity matrix. States with anomalous response functions can be thermodynamically stable under certain environmental conditions.
The divergence of the correlation functions $C^{ij}$ and the correlation length $\xi$ can be suppressed by the environmental influence despite the divergence of some components of the response matrix $R^{ij}$ at the critical point.

The first and the second implications, together, claim that both the system’s fluctuating behavior and its thermodynamic stability depend on the nature of the environmental influence. A trivial example is found in the case of an isolated system, where $\delta Q \equiv 0$. Clearly, there is no direct relation between the heat interchange and the heat capacity $C_p$ for this particular situation, which gives evidence about the restricted applicability of the fluctuation relation $C_p = \beta^2 \langle \delta Q^2 \rangle$. For a better understanding, let us consider a particular system where the unique relevant observable is the internal energy $U$. In this case, the EFT (1) drops to the following energy–temperature fluctuation relation [3]:

$$C = \beta^2 \langle \delta U^2 \rangle + C \langle \delta \beta \delta U \rangle,$$

which constitutes an extension of the fluctuation relation $C = \beta^2 \langle \delta U^2 \rangle$ obtained from the Gibbs’ canonical ensemble (a special case of BG distributions):

$$dp_G(U|\beta) = \frac{\exp(-\beta U)}{Z(\beta)} \Omega(U) dU.$$

Equation (12) is compatible with the existence of states with negative heat capacities $C < 0$ as long as the correlation function $\langle \delta \beta \delta U \rangle$ obeyed the stability condition:

$$\langle \delta \beta \delta U \rangle > 1.$$

The simplest scenario with non-vanishing correlated fluctuations, $\langle \delta \beta \delta U \rangle \neq 0$, is where the system is put in thermal contact with other short-range interacting system with a finite heat capacity $C^e$. In this case, the second system (environment) experiences a temperature fluctuation $\delta T = -\delta U/C^e$ whenever the system absorbs or releases an amount of energy $\delta U$. Substituting this last expression into equation (12), one obtains the self-correlation function of the internal energy $U$:

$$\frac{C^e C}{C^e + C} = \beta^2 \langle \delta U^2 \rangle.$$

Accordingly, the environmental heat capacity $C^e$ drives the system’s fluctuating behavior and imposes the standard microcanonical and canonical conditions in the asymptotic limits $C^e \to 0$ and $C^e \to \infty$, respectively. The stability condition (14) leads to the so-called Thirring constraint $C^e < |C|$ necessary for the stability of negative heat capacities in the framework of short-range interacting systems [10].

3. Implications for critical phenomena

Let us enter into the central discussion of this work: the implication of the extended EFT (1) for critical phenomena. Our interest is to analyze the thermodynamic behavior of a magnetic system when the same one is immersed into an environment with constant inverse temperature $\beta$; at the same time, it is put under the influence of an external magnetic field, $H$, that experiences a non-vanishing magnetic feedback effect $\langle \delta H \delta M \rangle$. This kind of environmental influence naturally appears when the magnetic field $H^*$
associated with the system magnetization $M$ affects the source of the external magnetic field $H$ and induces the existence of non-vanishing correlations $\langle \delta H \delta M \rangle$. For the sake of simplicity, it has been assumed that the external magnetic field $H$ is weakly perturbed by the magnetization fluctuations, so that, this effect can be considered within the linear approximation $H = H_0 - \lambda \delta M/N$, where $N$ is the system size, $H_0 = \langle H \rangle$ is the expectation value of the external magnetic field, and $\lambda$ is an effective coupling constant that characterizes the system–environment magnetic interaction. In the case of $\lambda = 0$, it considers the equilibrium situation described by BG distributions (6). Conversely, a value $\lambda \neq 0$ only ensures the constancy of the external magnetic field $H$ in an average sense. Application of the extended EFT (1) to this equilibrium situation leads to the following relation for the susceptibility $\chi_T$: \[
abla \chi_T = \beta^2 \langle \delta M^2 \rangle - \beta^2 \chi_T \langle \delta H \delta M \rangle, \tag{16}\]
and therefore \[
abla \langle \delta M^2 \rangle = \frac{\chi_T}{1 + \lambda \chi_T/N} \Rightarrow \langle \delta H^2 \rangle = \frac{\lambda}{\beta N} \frac{\lambda \chi_T/N}{1 + \lambda \chi_T/N}. \tag{17}\]
Admitting an extensive growth of the susceptibility $\chi_T$ with $N$ as $\chi_T \propto N$, it is possible to verify that the self-correlation of the external magnetic field behaves as $\langle \delta H^2 \rangle \propto 1/N$. From the thermodynamic viewpoint, $\lambda \neq 0$ does not differ from $\lambda = 0$ when $N \to \infty$. However, the positive character of the self-correlation function $\langle \delta M^2 \rangle$ now leads to the following condition of thermodynamic stability: \[
abla + N/\chi_T > 0. \tag{18}\]
According to equation (17), the self-correlation function of magnetization $\langle \delta M^2 \rangle$ remains finite when $\chi_T \to \infty$ as long as the coupling constant $\lambda$ takes a positive value. Consequently, there is no divergence of the correlation length $\xi$ for this special equilibrium situation. Moreover, the consideration of a coupling constant with $\lambda > 0$ enables access to diamagnetic states $\chi_T < 0$ that exist below the critical temperature, which are schematically represented in figure 1.

Let us suppose that the magnetic system is initially set at a state $O$ in the line with zero magnetization at figure 1(a), where $\beta < \beta_c$ and $H_0 = 0$. Considering that the environmental inverse temperature $\beta$ is increased with and without the magnetic feedback effect $\langle \delta H \delta M \rangle$, a relevant question emerges: what is the system behavior under these two external influences? The states with zero magnetization, $M = 0$, inside the region with $\chi_T < 0$ are unstable within the BG distribution (6). In this case, the self-correlation function $\langle \delta M^2 \rangle$ diverges for $\lambda = 0$ when the system approaches the critical point $C$ (where $\chi_T \to \infty$). For $\beta > \beta_c$, the system is forced to move along the stable symmetric curves $\alpha$ or $\alpha'$ with non-vanishing magnetization, where it undergoes a spontaneous symmetry breaking. Conversely, diamagnetic states $\chi_T < 0$ turn stable, choosing a positive value of the coupling constant $\lambda$. In this latter situation, the self-correlation function $\langle \delta M^2 \rangle$ does not diverge when the system approaches the critical point $C$. For $\beta > \beta_c$, the system remains on the line with zero magnetization $M = 0$ inside the region with $\chi_T < 0$, which implies a suppression of the spontaneous symmetry breaking. Thus, the system critical behavior can be modified by the environmental influence. It is noteworthy that the incidence of a non-vanishing feedback effect $\langle \delta H \delta M \rangle$ can also force the divergence of
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Figure 1. (a) Schematic representation of the regions of thermodynamic stability of a magnetic system within the BG distributions (6) in the \( M-U \) diagram (magnetization–internal energy). White region: stable states with \( \chi_T > 0 \) and \( M \cdot H > 0 \); gray region: metastable states with \( \chi_T > 0 \) and \( M \cdot H < 0 \); light-gray region: unstable states with \( \chi_T < 0 \) and \( M \cdot H < 0 \). The critical point \( C \) with \( \beta = \beta_c \) and \( H = 0 \) is a state of marginal stability for BG distributions. (b) Behavior of some typical isotherms in the \( H-M \) diagram.

the self-correlation function \( \langle \delta M^2 \rangle \) at an arbitrary state \( P \) inside the region with negative magnetic susceptibility. The occurrence of this phenomenon demands a coupling constant \( \lambda \equiv -N/\chi_T(P) > 0 \). Thus, the simultaneous divergence of the correlation length \( \xi \) and the response function \( \chi_T \) is only admissible if \( \lambda = 0 \), that is, in the framework of BG distributions (6).

The previous analysis can be verified through appropriate Monte Carlo (MC) simulations. For this purpose, we consider the Ising model on a square lattice \( L \times L \) with periodic boundary conditions, with internal energy \( U = -\sum_{(ij)} \sigma_i \sigma_j \) and magnetization \( M = \sum_i \sigma_i \), where \( \sigma_i = \pm 1 \) and \( \langle ij \rangle \) denotes the nearest neighbor sites. As in the case of a conventional Metropolis importance sample [13] based on BG distributions (6), the present situation with \( \langle \delta H \delta M \rangle \neq 0 \) can be implemented through the following acceptance probability \( p \) for a MC step from the state \( (U, M) \) to \( (U + \Delta U, M + \Delta M) \):

\[
p = \min \{ \exp \left[ -\beta (\Delta U + H \Delta M) \right], 1 \},
\]

(19)

where the magnetic field \( H \) has an implicit dependence on the magnetization fluctuations. The magnetization dispersion \( \sigma_m^2 = \langle \delta M^2 \rangle / N \) can be employed to obtain the inverse
susceptibility per particle as $\bar{\chi}_T^{-1} = N\chi_T^{-1} = (1-\lambda \beta \sigma_m^2)/\beta \sigma_m^2$. For Monte Carlo simulations with $\langle \delta H \delta M \rangle \neq 0$, the value of the coupling constant $\lambda$ is redefined for each calculated point using the optimal value $\lambda_{opt} = \sqrt{1+(\bar{\chi}_T^{-1})^2-\bar{\chi}_T^{-1}}$, which minimizes the total dispersion $\sigma^2 = \langle \delta M^2 \rangle/N + N\langle \delta H^2 \rangle$ and satisfies the stability condition (18).

A comparative study of Monte Carlo simulations with and without a magnetic feedback effect $\langle \delta H \delta M \rangle$ is shown in figure 2. According to the results that we show in figure 2(c), the magnetization dispersion $\sigma_m^2$ diverges at the critical point $\beta_c(L = 25) \simeq 0.41$ in Monte Carlo simulations with coupling constant $\lambda = 0$. Conversely, the same quantity remains finite when $\lambda > 0$, which indicates a suppression of the long-range order associated with the divergence of correlation length $\xi \to \infty$. Simultaneously, there exists a suppression of the spontaneous symmetric breaking, which is manifested in figures 2(a) and (b) as a persistence of diamagnetic states, $\chi_T < 0$, with $\langle M \rangle = 0$ for $\beta > \beta_c$. Remarkably, the absolute values $|\bar{\chi}_T|$ of these negative susceptibilities are very large. The suppression of the spontaneous symmetry breaking is also manifested as a bifurcation of caloric curves and the inverse isothermal susceptibility $\bar{\chi}_T^{-1}$ at the critical point $C$ shown.
in figures 2(b) and (d), a fact that demonstrates the different thermodynamic behavior of this system inside the region with negative susceptibilities.

4. Concluding remarks

As already evidenced, the extended EFT (1) reveals some new insights in the understanding of statistical physics. This theorem clearly distinguishes two different types of thermodynamic properties for a real system: the intrinsic properties and the relative ones. Examples of intrinsic properties are the response functions (2), the state equations (11), as well as any other information derived from the thermodynamics of the isolated system; in particular, from the knowledge of the entropy $S$. Conversely, the relative thermodynamic properties depend on the environmental influence acting in a concrete equilibrium situation, for example any information concerning the system’s stability and its fluctuating behavior. The divergence of correlation length $\xi$ and its associated critical behaviors (spontaneous symmetry breaking, critical opalescence, etc) takes place at states with a marginal stability (see in figure 1(a)). Since stability conditions, e.g. equation (18), crucially depend on the environmental influence, any critical behavior is always a relative phenomenon. Hence, the divergence of any response function component $R_{ij} \to \infty$ is not an authentic critical behavior but an intrinsic phenomenon that has nothing to do with the divergence of correlation length $\xi$. The above remarks show that the consideration of BG distributions (6) can potentially lead to some incorrect predictions about a system’s thermodynamical behavior overall, when one assumes these equilibrium distribution functions outside the context of its traditional applications. This could be the case for collective phenomena involving systems with long-range interactions like non-screened plasmas and astrophysical systems [11], or small and mesoscopic systems like the case of nuclear multifragmentation [12], where the existence of states with an anomalous response is almost a rule rather than an exception.

Before end this section, we would like comment on three possible application frameworks of our approach, which could merit special attention in future works. Previously, this framework of fluctuation theory have been successfully applied to overcome slow sampling problems in Monte Carlo simulations associated with the incidence of discontinuous phase transitions [14,15]. Analogously, the suppression of divergence of the correlation length $\xi$ at the critical point could be also employed to design new Monte Carlo algorithms to deal with difficulties associated with continuous phase transitions. The second application framework is quantum theories at finite temperature [16], which exploit the analogy between the evolution operator $\hat{T} = e^{-\beta \hat{H}/\hbar}$ and the statistical operator $\hat{\omega} = e^{-\beta \hat{H}/k_B}$. In high energy physics, these formulations have been applied to study processes that took place in the early universe as a whole, for example spontaneous symmetry breaking of electro-weak interactions. Since these processes are special cases of critical phenomena, the application of the present framework of fluctuation theory could reveal new insights into understanding them. Finally, the analogy between electric and magnetic systems strongly suggests the existence of anomalous dia-electric states (the electric counterpart of diamagnetic states) below the critical temperature of a ferro-electric system, which should not be detected using experimental techniques based on Boltzmann–Gibbs distributions (6). We think that the ideas discussed in this work could inspire new experimental techniques to clarify
the existence (or nonexistence) of these anomalous states. As discussed elsewhere [17],
the presence of a hypothetic dia-electric medium favors the formation of Cooper-pairs, a
mechanism that triggers the development of high-temperature superconductivity.

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