Entropy, Macroscopic Information, and Phase Transitions

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Abstract. The relationship between entropy and information is reviewed, taking into account that information is stored in macroscopic degrees of freedom, such as the order parameter in a system exhibiting spontaneous symmetry breaking. It is shown that most problems of the relationship between entropy and information, embodied in a variety of Maxwell demons, are also present in any symmetry breaking transition.

I INTRODUCTION

The relationship between entropy and information has been subject of a long controversy, almost as old as the Second Law of Thermodynamics. The history of this controversy, closely linked to the analysis of the Maxwell demon, has been presented in detail in the excellent book of reprints collected by Leff and Rex [1].

Maxwell devised his demon to show the probabilistic nature of the Second Law of Thermodynamics: a being capable of measuring the position and velocity of the molecules of a gas could in principle violate the Second Law. Operating a door in an adiabatic wall between two gases at different temperatures, the demon could induce a flow of energy from the cold to the hot gas. The conclusion is that information about the microscopic details of a system allows one to beat the Second Law.

One of the most relevant sequels of the Maxwell demon is the Szilard engine [1,2]. It consists of a box with a single-particle gas, i.e., a particle that thermalizes in any collision with the walls. A piston can be introduced (or removed) either at the middle of the box or at two opposite walls (see Figure 1).

The engine operates as follows. We insert the piston in the middle of the box and measure in which side the particle gets trapped. Then we let the gas expand quasistatically and remove the piston. In the expansion the gas performs work:

\[ W = \int_{V}^{V/2} PdV = kT \ln 2. \]  

\[ (1) \]

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This work can be used, for instance, to lift a weight and store $kT \ln 2$ as potential energy. The energy is taken from the thermal bath, since the internal energy of the gas is constant. Therefore, the Szilard engine extracts energy from a single thermal bath and performs work, in contradiction with the Second Law of Thermodynamics.

Notice that, for the engine to work properly, it is absolutely necessary to know in which side the particle gets trapped. In this way, we can exert a pressure on the piston equal and opposite to the pressure of the gas and let it expand quasistatically. On the other hand, if the direction of the pressure were not correct, the gas would expand irreversibly and Eq. (1) would not hold. As in the original Maxwell demon, the Szilard engine can beat the Second Law of Thermodynamics only if some information about the state of the system is available.

The literature on the Szilard engine, as well as on the Maxwell demon, has focused mainly on the heat dissipation accompanying the measurement, i.e., the acquisition of information, and/or accompanying the erasure of this information [1–5]. As an exception, Magnasco presented in Ref. [6] an interesting analysis of the topology of the phase space of the engine.

Nevertheless, none of these papers has analyzed one of the obscure points of the Szilard engine, namely, that it consists of microscopic and macroscopic degrees of freedom interacting with each other. This mixture of micro (the particle) and macro (the piston) makes the Szilard engine a rather difficult and unclear problem for many physicists, even for those working on Statistical Mechanics.

In this paper I address this question, by giving a novel interpretation to one of the steps of the Szilard engine. The insertion of the piston in the middle of the box can be interpreted as a second order phase transition or spontaneous symmetry breaking. The Hamiltonian of the particle is symmetric under the permutation of the two sides of the box. However, the particle gets trapped in only one of the sides. This is equivalent to what happens in an Ising model when it is driven from a paramagnetic to a ferromagnetic phase in the absence of external magnetic field.

We will see below that all the astounding facts of the Szilard engine are revealed in the following steps:

![Figure 1. The Szilard engine.](image-url)
produced in the Ising model and in any system exhibiting second order phase transitions.

The benefit of this new interpretation is twofold. On one side, it helps to understand better the Szilard engine and the relationship between entropy and information, since we will reach the same conclusions without the use of single-particle gases interacting with pistons. On the other side, it reveals that the consequences of this relationship and the intriguing aspects of the Szilard engine are not restricted to academic and artificial constructions, such as the Maxwell demon and the Szilard engine itself, but they are present in any spontaneous symmetry breaking, that is to say, almost everywhere in Nature.

The paper is organized as follows. In Section II, I analyze the energetics of two processes in the Szilard engine. Section III is a brief review of the concept of spontaneous symmetry breaking and the Ising model. In Section IV, I introduce two processes in the Ising model which are equivalent to the processes studied in Section II. Section V discusses the implications of the above results on the definition of entropy and on the general validity of the Second Law. Finally, in Section VI, I present some conclusions and a list of open problems.

II TWO PROCESSES IN THE SZILARD ENGINE

Consider the Szilard gas and the processes $A$ and $C$ described in Fig. 2. In $C$, the piston is inserted in the middle of the box and the particle gets trapped in one of the sides. In $A$, the piston is introduced in the rightmost wall and moved slowly to the middle of the box. Then, $C$ is the first step of the Szilard cycle and $A$ is the inversion of the rest of the cycle (cf. Figs. 1 and 2).

Let us investigate the energetics of these two processes, i.e., the energy transfer between the particle and its surroundings. The particle exchanges energy with two external systems: the thermal bath, and some external agent that handles the

![Figure 2](image.jpg) FIGURE 2. Processes $A$ and $C$ in the Szilard engine.
piston, exerting pressure when it is needed. As in Thermodynamics, I call heat, \( Q \), the energy transferred from the thermal bath to the particle in a given process and, work, \( W \), the energy transferred from the system to the external agent. Finally, if \( U \) is the internal energy of the particle, the First Law of Thermodynamics, \( \Delta U = Q - W \), holds for any process.

In our particular case, process \( C \) does not require any work, or at least the work can be arbitrarily small. On the other hand, process \( A \) involves a compression of the single-particle gas to half of its volume and in this compression, if carried out quasistatically, a work \( kT \ln 2 \) is done by the external agent. Therefore, as defined above, work is given by:

\[ W_A = -kT \ln 2 ; \quad W_C = 0. \]  

The internal energy of the particle remains constant since the two processes are isothermal. Thus, the heat in each process is:

\[ Q_A = -kT \ln 2 ; \quad Q_C = 0 \]  

i.e., along \( A \), energy is transferred from the system to the thermal bath.

The difference in the energetics of \( A \) and \( C \) is the key point of the Szilard engine. The engine is nothing but the cycle \( CA^{-1} \), where \( A^{-1} \) is the inverse of process \( A \). The energetics of \( A^{-1} \) is \( W_{A^{-1}} = -W_A \) and \( Q_{A^{-1}} = -Q_A \), only if \( A^{-1} \) is the true inversion of \( A \), i.e., if the external agent exerts a pressure equal to the pressure of the gas and thus the expansion is done adiabatically. In this case, we have \( W_{CA^{-1}} = kT \ln 2 \).

Notice that so far I have restricted the discussion to energy. The consequences of the above results on the definition of entropy will be explored in Section V.

### III SYMMETRY BREAKING TRANSITIONS

I have split the Szilard cycle into processes \( A \) and \( C \), and showed that the paradoxical nature of the engine lies in the energetics of these two processes.

Moreover, as mentioned in the Introduction, process \( C \) can be seen as a spontaneous symmetry breaking and process \( A \) as a forced or non-spontaneous symmetry breaking. In fact, symmetry breaking is the only necessary ingredient to reproduce all the relevant features of the Szilard engine.

Let us remind first what a spontaneous symmetry breaking is. If \( \mathcal{H}(x) \) is the Hamiltonian of a system, \( x \) being a point in the phase space \( \Gamma \), Statistical Mechanics prescribes that the probability density for the equilibrium state of the system at temperature \( T \) is given by the Gibbs distribution:

\[ \rho_T(x) = \frac{e^{-\beta \mathcal{H}(x)}}{Z} \]  

where \( \beta = 1/kT \) and \( Z = \int_{\Gamma} e^{-\beta \mathcal{H}} \) is the partition function. From Eq. (4) we see that \( \rho_T(x) \) has the same symmetries as \( \mathcal{H}(x) \). Nevertheless, in some cases, a
The macroscopic system is not described by the Gibbs distribution. The phase space splits into $n$ pieces, $\Gamma_1, \Gamma_2, \ldots, \Gamma_n \subset \Gamma$ and the macroscopic system is confined within one of them. The distribution that describes the system is:

$$\rho_i(x) = \frac{e^{-\beta H(x)}}{Z_i} \chi_{\Gamma_i}(x)$$

(5)

where $\chi_A(x)$ is the indicator function of the set $A \subset \Gamma$, i.e., $\chi_A(x) = 1$ if $x \in A$ and $\chi_A(x) = 0$ if $x \notin A$, and $Z_i$ is the partition function restricted to $\Gamma_i$. The distributions $\rho_i(x)$, called macroscopic phases, have less symmetries than the Hamiltonian. The partition of the phase space, called the coexistence of macroscopic phases, occurs for some values of the temperature and the parameters of the Hamiltonian. Finally, which of the macroscopic phases is chosen depends on the past of the system and/or on thermal fluctuations.

The globally coupled Ising model is one of the simplest systems exhibiting coexistence of macroscopic phases [7]. Its Hamiltonian is:

$$H(\{s_i\}; J, B) = -\frac{J}{N} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} s_i s_j - B \sum_{i=1}^{N} s_i$$

(6)

where the spins take values $s_i = \pm 1$, with $i = 1, 2, \ldots, N$. It depends on two parameters: the coupling $J$ between spins and the external field $B$. It is called globally coupled because every spin interacts with all the others.

The system exhibits coexistence of two macroscopic phases when $B = 0$ and $J/kT > 1$. One of the phases is restricted to $\Gamma_+$, the set of configurations $\{s_i\}$ with positive global magnetization $M = \sum_i s_i > 0$, and the other is restricted to $\Gamma_-$, the set of configurations with negative magnetization. Each phase breaks the symmetry $\{s_i\} \rightarrow \{-s_i\}$ that the Hamiltonian possesses for $B = 0$.

When temperature is lowered, keeping $B = 0$, from an initial value above the critical temperature $T_c \equiv J/k$, a second order phase transition occurs at $T = T_c$. Below $T_c$ the system is in one of the two macroscopic phases. None of the phases is favored along the process, since $B = 0$. Therefore, the system chooses the macroscopic phase at random or, more precisely, the choice is induced by thermal fluctuations.

The globally coupled Ising model also exhibits first order phase transitions when the field crosses $B = 0$ below $T_c$. The external field breaks the symmetry $\{s_i\} \rightarrow \{-s_i\}$ of the Hamiltonian and, if the coexistence region is reached decreasing a positive field, the macroscopic phase is the one with positive magnetization. This can be called forced or non-spontaneous symmetry breaking.

To reproduce in the Ising model the two processes, $A$ and $C$, discussed in Section II for the Szilard engine, we need to induce a spontaneous symmetry breaking at constant temperature (remember that processes $A$ and $C$ in the Szilard engine are isothermal). This can be achieved if we tune the coupling $J$ at constant temperature $T$. The spontaneous symmetry breaking occurs then for a critical coupling $J_c \equiv 1/kT$, and for $B = 0$ and $J > J_c$ the system exhibits coexistence of phases.
IV TWO PROCESSES IN THE ISING MODEL

Consider the following two processes on the plane \((J, B)\) (see Figure 3):

- **Process A**: starting at \((0, 0)\), the field is increased up to \(B_f > 0\), then the coupling is increased up to \(J_f > J_c\), then the field is decreased down to zero.

- **Process C**: starting at \((0, 0)\), the coupling is increased up to \(J_f > J_c\), keeping \(B = 0\).

The two processes are quasistatic in the following sense: they are slow enough for the system to relax within each possible macroscopic phase, but fast enough for the system to remain in one of the two phases.

Applying to process A the formalism described in the Appendix, one finds the following energetics, up to order \(kT\) [8]:

\[
W_A = -\mathcal{F}(T, J_f, 0) + \mathcal{F}(T, 0, 0) - kT \ln 2 \tag{7}
\]

where \(\mathcal{F}(T, J, B) = -kT \ln Z(\beta, J, B)\) and \(Z(\beta; J, B) = \sum e^{-\beta H}\) is the partition function of the system. \(Z(\beta; J, B)\) and \(\mathcal{F}(T, J, B)\) must be considered here as mere mathematical definitions and we should refrain from attributing them any physical meaning at this stage of the discussion. For process \(C\) one has:

\[
W_C = -\mathcal{F}(T, J_f, 0) + \mathcal{F}(T, 0, 0). \tag{8}
\]

Therefore, \(W_A - W_C = -kT \ln 2\), i.e., the external agent has to do more work to complete process \(A\) than to complete \(C\), exactly as in the Szilard engine.

The whole discussion on the Szilard engine in Sections I and II can be applied to the Ising model. For instance, one can design a cyclic engine as \(CA^{-1}\).

Let us first analyze the inverse processes \(A^{-1}\) and \(C^{-1}\) in detail. The inversion of \(C\) does not present any difficulty. The energetics of \(C^{-1}\) is simply \(W_{C^{-1}} = -W_C\) and \(Q_{C^{-1}} = -Q_C\).

\[\text{FIGURE 3. Processes A and C in the Ising model. The two black circles are the initial and final states of both processes.}\]
On the other hand, if we try to invert $A$, the sign of the field must be the same as the sign of the initial magnetization of the system. If we start to increase a positive field on a system with negative magnetization, the system becomes metastable, it runs along one of the branches of a hysteresis cycle and eventually relaxes irreversibly to the stable state for some value of the field $B$ (see Fig. 4).

The most general case is when we have an ensemble of systems. If initially a fraction $\alpha$ of them have negative magnetization, the energetics of $A^{-1}$ is given by:

$$W_{A^{-1}} = -W_A - \alpha \frac{A_{hys}}{2}$$

where $A_{hys}$ is the area of the hysteresis cycle at $J = J_f$, as shown in Fig. 4.

The hysteresis phenomenon is not present in the Szilard engine. However, it has similar consequences as exerting the pressure in the wrong direction along the expansion, since in both cases the system evolves irreversibly doing less work.

Consider now the equivalent to the Szilard engine, i.e., the cycle $CA^{-1}$ on an ensemble of Ising models. Its energetics (per system) is immediately obtained from Eqs. (7-9):

$$W_{CA^{-1}} = W_C + W_{A^{-1}} = kT \ln 2 - \alpha \frac{A_{hys}}{2}.$$  

where $\alpha$ is the fraction of systems with magnetization of the same sign as the field in $A^{-1}$. There are two consequences of this expression.

First, if instead of an ensemble we take a single system and measure its magnetization after $C$ to decide the sign of the field, then $\alpha = 0$ and $W_{CA^{-1}} = kT \ln 2 > 0$, i.e., the system is extracting energy from the thermal bath and converting it into work. We recover the same result as in the Szilard engine but now with a genuine macroscopic system. Thus, we have a Maxwell demon with the important novelty that he needs to measure a macroscopic quantity.

Second, for an ensemble, $\alpha = 1/2$, and we still can beat the Second Law unless:

$$A_{hys} \geq 4kT \ln 2.$$  

This inequality is a byproduct of this theory and clarifying its origin is one of the open problems of the present work.

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**FIGURE 4.** Hysteresis cycle in the Ising model.
V ENTROPY AND MACROSCOPIC UNCERTAINTY

The above discussion has focused on energy. I will explore in this Section the consequences of the previous results on the definition of entropy.

The change of entropy in the thermal bath along a process is given by \( \Delta S_{\text{bath}} = -\frac{Q}{T} \), whereas the entropy of the external agent is constant because its interaction with the system is purely mechanical. Then the change of the total entropy is:

\[
\Delta S_{\text{total}} = -\frac{Q}{T} + \Delta S_{\text{syst}}. \tag{12}
\]

Second Law of Thermodynamics tells us that, if a process is reversible, \( \Delta S_{\text{total}} = 0 \), and, if it is irreversible, \( \Delta S_{\text{total}} > 0 \). In particular, for a cyclic process, \( \Delta S_{\text{syst}} = 0 \) hence \( Q \leq 0 \). This is the Kelvin-Planck statement of the Second Law: it is not possible to extract energy from a single thermal bath in a cyclic process.

However, Eq. (12) and the Second Law lead to contradictions when applied to processes \( A \) and \( C \). For instance, \( \Delta S_{\text{total}}^{CC^{-1}} = \Delta S_{\text{total}}^{AA^{-1}} = 0 \). Therefore, \( AA^{-1} \) and \( CC^{-1} \) are reversible and so are their components, \( A, A^{-1}, C, \) and \( C^{-1} \). On the other hand \( \Delta S_{\text{total}}^{AC^{-1}} = k \ln 2 \), hence \( AC^{-1} \) is irreversible. Moreover, if \( A \) and \( C \) are reversible, we obtain \( \Delta S_{\text{syst}}^{C} = \Delta S_{\text{syst}}^{A} + k \ln 2 \).

These contradictions are usually explained with the following definition for the thermodynamic entropy of the system:

\[
S_{\text{syst}}^{(\text{ens})} = -k \langle \ln \rho_{\text{ens}} \rangle, \tag{13}
\]

where \( \rho_{\text{ens}} \) is the probability distribution describing an ensemble of systems. After process \( C \), \( \rho_{\text{ens}} = (\rho_+ + \rho_-)/2 \) where \( \rho_+ \) and \( \rho_- \) are the probability distribution of the two macroscopic phases (see Section III). On the other hand, after \( A \), \( \rho_{\text{ens}} = \rho_+ \). Then, \( S_{\text{syst}}^{(\text{ens})} \) is \( k \ln 2 \) bigger after \( C \) than after \( A \).

This picture is, however, rather unsatisfactory if we deal with single systems instead with ensembles, since \( \rho_{\text{ens}} \) becomes a subjective quantity. For instance, the physical state of an Ising model after process \( A \) is the same as after \( C \) if the final magnetization is positive. The only difference between these two situations is that we ignore the magnetization after \( C \). Then \( S_{\text{syst}}^{(\text{ens})} \), as defined in Eq. (13), is a subjective quantity for single systems. Mathematically, this can be expressed as:

\[
S_{\text{syst}}^{(\text{ens})} = -k \langle \ln \rho_{\text{single}} \rangle + H. \tag{14}
\]

Here, \( \rho_{\text{single}} \) is the invariant measure that gives the temporal average of any magnitude and it is a fully objective distribution for a single system [9]. \( H \) is the ignorance or uncertainty that we have about the macrostate of the system. It is measured using Shannon formula: \( H = -k \sum_i p_i \ln p_i \) where \( p_i \) is the probability of having an instance \( i \) (in the Szilard and Ising case, after \( C \), \( H = 1 \text{bit} = k \ln 2 \)).

Moreover, in this interpretation not only entropy is subjective but also the concept of reversibility. Consider \( C^{-1} \) on a single system: it is reversible if we do not know the initial macroscopic magnetization and it is irreversible if we do know it.
I propose a simpler interpretation of the above results. In this new interpretation, entropy is an objective magnitude for single systems, but we are forced to admit that it decreases along some processes, in contradiction with some formulations of the Second Law. However, the main limitation imposed by the Second Law, namely, the Kelvin-Planck statement, remains valid, since these processes cannot be used to construct cycles. Ishioka and Fuchikami, in these proceedings [10], have reached similar conclusions. The assumptions for this interpretation are the following:

1. The thermodynamic entropy of a system is given by:

\[ S_{\text{syst}} \equiv -k \langle \ln \rho_{\text{single}} \rangle. \] (15)

2. If an external agent induces, in a quasistatic and isothermal way, a spontaneous symmetry breaking with \( n \) phases, the total entropy (the sum of the entropies of the system, thermal bath, and external agent) decreases by \( k \ln n \). I will call these processes anti-irreversible (in [10] the term partitioning processes is used instead) and they correspond to the creation of macroscopic uncertainty.

3. Along the inverse of an anti-irreversible process, the total entropy increases by \( k \ln n \). I will call these processes quasi-irreversible or simply irreversible.

Process \( C \) is anti-irreversible and \( C^{-1} \) is quasi-irreversible. The reason of the names is the following: \( C^{-1} \) cannot be truly reversed because, after \( C^{-1}C \) the initial magnetization could be opposite to the final one. Processes \( A \) and \( A^{-1} \) are reversible in the standard sense, i.e., total entropy does not change. The reader can check that every combination of processes \( A, C \) and their inversions are explained with the above three rules. Moreover, entropy and reversibility become fully objective concepts.

The measurement process can be also explained with this new Thermodynamics. Consider, as a model of a system and a measurement device, the Hamiltonian:

\[ H(\{s_i^{(1)}\}, \{s_i^{(2)}\}; J_1, J_2, J_{12}) = -\frac{J_1}{N} \sum_{j>i}^N s_i^{(1)} s_j^{(1)} - \frac{J_2}{N} \sum_{j>i}^N s_i^{(2)} s_j^{(2)} - \frac{J_{12}}{N} \sum_{i,j=1}^N s_i^{(1)} s_j^{(2)} \]

which corresponds to two coupled Ising models, 1 (system) and 2 (measurement device or ‘pointer’). The following table shows the behavior of the total entropy, as defined by (12) and (15), and the macroscopic uncertainty \( H \), along two isothermal and quasistatic processes:

| Step | \( S_{\text{total}} - S_{\text{total}}^0 \) | \( H \) |
|------|-----------------|-----|
| 1) \( J_1 : 0 \to J_f \) | \(-k \ln 2\) | 1 bit |
| 2) \( J_{12} : 0 \to J_f \) | \(-k \ln 2\) | 1 bit |
| 3) \( J_2 : 0 \to J_f \) | \(-k \ln 2\) | 1 bit |
| 4) \( J_1 : J_f \to 0 \) | \(-k \ln 2\) | 1 bit |
| 5) \( J_{12} : J_f \to 0 \) | \(-k \ln 2\) | 1 bit |
| 6) \( J_2 : J_f \to 0 \) | 0 | 0 |

| Step | \( S_{\text{total}} - S_{\text{total}}^0 \) | \( H \) |
|------|-----------------|-----|
| 1) \( J_1 : 0 \to J_f \) | \(-k \ln 2\) | 1 bit |
| 2) \( J_{12} : 0 \to J_f \) | \(-k \ln 2\) | 1 bit |
| 3) \( J_2 : 0 \to J_f \) | \(-k \ln 2\) | 1 bit |
| 4) \( J_{12} : J_f \to 0 \) | \(-k \ln 2\) | 1 bit |
| 5) \( J_1 : J_f \to 0 \) | 0 | 1 bit |
| 6) \( J_2 : J_f \to 0 \) | \( k \ln 2\) | 0 |
Both processes involve a spontaneous symmetry breaking (step 1), copying the outcome (steps 2-3) and erase of the copy and the original (steps 4-6).

The first process (left column) can be interpreted as a reversible measurement. Measurement can be defined in a rather general way as any procedure which allows one to drive a system from the region of coexistence of phases to a region of non-coexistence along a reversible process, i.e., avoiding the critical point as well as the possibility of hysteresis. This is done in step 4 of the first column, where $J_1$ is decreased down to zero along a reversible process. As a result, the total entropy is lowered by $k \ln 2$ in the first five steps. Notice also that, to drive the whole system $1+2$ to its initial state, we have to reset the measurement device 2, by crossing again a critical point, i.e., along a quasi-irreversible process (step 6). We thus recover Bennet’s interpretation of the Szilard engine [4].

I have included the other process (right column in the table) to show how subtle the measurement and the erasure processes can be. If subsystem 1 is uncoupled before driven to its initial state, then it crosses a critical point and the entropy increases. Step 5 in the right column is quasi-irreversible, because initially the magnetizations of 1 and 2 have the same sign, and, if step 5 were reversed the final magnetizations would be uncorrelated. A similar effect of the correlation between the particle and the measurement device in the Szilard engine was pointed out by Fahn in Ref. [5].

VI CONCLUSIONS AND OPEN PROBLEMS

Two objections can be raised against the Thermodynamics proposed in the last Section. The first is that energy is an extensive property, i.e., of order $NkT$, and terms of order $kT \ln 2$ are negligible and even much smaller than the energy fluctuations. This objection applies to any Maxwell demon but it is not sufficient to exorcize it. The reason is that the demon can repeat the cycle as many times as he wants, converting a macroscopic amount of heat into work.

The second objection is that the increase of entropy can be derived from non-equilibrium theories, such as the Fokker-Planck formalism. If $q$ are the (over-damped) degrees of freedom of a system, the probability distribution obeys the Fokker-Planck equation (FPE):

$$\partial_t \rho(q, t) = -\nabla \cdot J(q, t)$$

where the current is $J(q, t) = [-\nabla \mu(q, t)]\rho(q, t)$ and the chemical potential is defined as $\mu(q, t) \equiv V(q, t) + kT \ln \rho(q, t)$. From these equations one can derive the following identity [6]:

$$-k \partial_t \int dq \: \rho(q, t) \ln \rho(q, t) = \frac{1}{T} \int dq V(q, t) \partial_t \rho(q, t) + \frac{1}{T} \int dq \frac{|J(q, t)|^2}{\rho(q, t)}$$

$$= \frac{\dot{Q}}{T} + \frac{1}{T} \int dq \frac{|J(q, t)|^2}{\rho(q, t)}$$

(17)
If the left-hand side of this equation is interpreted as $\dot{S}_{\text{syst}}$, the change of the entropy of the system per unit of time, then the total change of entropy, $\dot{S}_{\text{total}} = -\dot{Q}/T + \dot{S}_{\text{syst}}$, is always positive. A similar result can be obtained for underdamped degrees of freedom [11]. How then have we obtained $\dot{S}_{\text{total}} < 0$ for some processes involving phase transitions? The answer is that the distribution that appears in the FPE (16) is $\rho_{\text{ens}}$ and not $\rho_{\text{single}}$. Then, the FPE is not appropriate to describe single macroscopic systems.

One of the open problems of the present work is to characterize $\rho_{\text{single}}$ and derive an evolution equation similar to the FPE. Other open problems are: (a) analyze the role of hysteresis and the origin of inequality (11); (b) extend the above discussion to the breaking of a continuous symmetry, where an infinite number of macroscopic phases coexist; (c) include the external agent in the Hamiltonian as a set of macroscopic degrees of freedom and (d) explore the implications of the decrease of entropy along anti-irreversible processes, specially in cosmology.

**APPENDIX**

Consider a system whose Hamiltonian $\mathcal{H}(x; R)$ depends on a set of external parameters collected in a vector $R$. We are interested in the energetics of a process along which the system is in contact with a thermal bath at temperature $T$ and the parameters are changed by an external agent as $R(t)$ with $t \in [0, T]$.

The expressions for work and heat per unit of time along this process are [11,12]:

$$\dot{Q} = \int_{\Gamma} dx \mathcal{H}(x; R(t)) \frac{\partial \rho(x; t)}{\partial t} ; \quad \dot{W} = -\int_{\Gamma} dx \rho(x; t) \frac{\partial \mathcal{H}(x; R(t))}{\partial t}$$

(18)

where $\Gamma$ is the phase space of the system and $\rho(x; t)$ the probability density for the state $x$. Heat and work, as given by Eq. (18), obey the First Law of Thermodynamics: $\dot{U} = \dot{Q} - \dot{W}$.

If the process is quasistatic, $T \to \infty$, the probability density at time $t$ depends only on the value of the external parameters at $t$, i.e., $\rho(x; t) = \rho(x; R(t))$. In this case, the heat and the work in the whole process are given by:

$$Q = \int_A \delta Q(R) ; \quad W = \int_A \delta W(R)$$

(19)

where $A$ is the path that $R(t)$ describes along the process and the infinitesimal work and heat are given by:

$$\delta Q(R) = \int_{\Gamma} dx \mathcal{H}(x; R) \frac{\partial \rho(x; R)}{\partial R} \cdot dR$$

$$\delta W(R) = -\int_{\Gamma} dx \rho(x; R) \frac{\partial \mathcal{H}(x; R)}{\partial R} \cdot dR.$$ 

(20)

The most familiar implementation of the above expressions is obtained when the state of the system is the Gibbs distribution, $\rho_T(x; R) \equiv e^{-\beta \mathcal{H}(x; R)}/Z(\beta, R)$. For this particular case, Eqs. (20) reduce to
\[ \delta Q(R) = T \frac{\partial S(T, R)}{\partial R} \cdot dR ; \quad \delta W(R) = - \frac{\partial F(T, R)}{\partial R} \cdot dR \quad (21) \]

where \( S(T, R) = -k \int \rho_T(x; R) \ln[\rho_T(x; R)] \) and \( F(T, R) = -kT \ln Z(\beta, R) \) are, respectively, the free energy and the entropy of the system.

Although processes \( A \) and \( C \) considered in the text are isothermal and quasistatic, the state \( \rho(x; R) \) is not equal to \( \rho_T(x; R) \) in the region of coexistence of macroscopic phases. Consequently their energetics, up to terms of order \( kT \), differ from the one prescribed by standard equilibrium Thermodynamics.

To get Eqs. (2), I have used Eqs. (19) and (20) with the following prescription for \( \rho(\{s_i\}; J, B) \) along process \( C \): \( \rho(\{s_i\}; J, 0) = \rho_T(\{s_i\}; J, B) \) if \( J < J_c \) and \( \rho(\{s_i\}; J, 0) = \rho_+ (\{s_i\}; J, B) \) if \( J \geq J_c \), where \( \rho_+ \) is \( \rho_T \) restricted to \( \Gamma_+ \), the set of configurations with positive magnetization. The precise location of the replacement of \( \rho_T \) by \( \rho_+ \) does not affect the results. In fact, the energetics is the same as if calculated using \( \rho_T \), for symmetry reasons [8].

Along process \( A \), the state is given by: \( \rho_T(\{s_i\}; J, B) \) if \( J = 0 \) or \( B = B_f \) (first two steps of \( A \)) and by \( \rho_+ (\{s_i\}; J, B) \) if \( J = J_f \) (last step). Again the energetics, up to order \( kT \), does not depend on where precisely the system changes from \( \rho_T \) to \( \rho_+ \). The above prescription has been chosen for simplicity. The replacement of \( \rho_T \) by \( \rho_+ \) is only significant at the end of the last step, i.e., when the system is close to the region of coexistence. \( W_A \) can be calculated by using (21) along the first two steps and using the partition function restricted to \( \Gamma_+ \) along the third step. It can be rigorously proven that the energetics is the one given by (2) plus terms of order \( kTe^{-\gamma N} \), where \( \gamma \) is positive and of order \( o(1) \) if \( B_f \) and \( J_f \) are large enough. Details of the calculations will be given elsewhere [8].

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