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Systems with negative specific heat in thermal contact: Violation of the zeroth law

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Using both numerical simulations and exact expressions for the free energy and microcanonical entropy for a modified Hamiltonian mean-field (HMF) model, we show that when two similar systems with the same intensive parameters but with negative specific heat are weakly coupled, they undergo a process in which the total entropy increases irreversibly. We find that the final equilibrium is such that two phases appear at a temperature (equal in both systems) that is generally different from the initial temperature. We corroborate our results using two different kinds of couplings between the HMF systems. We confirm that our results hold also for the Ising model with long- and short-range interactions, which also has a parameter region with negative specific heat in the microcanonical ensemble. Further, we show that we can couple each system having negative specific heat to a third system that can be used as a thermometer, as long as this thermometer is small enough not to drive the system out of the microcanonical ensemble. Therefore, we show an instance of violation of the zeroth law of thermodynamics.

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I. INTRODUCTION

In recent years, *small* systems [1] (finite systems in which the size is comparable to the range of the interactions between their constituents), such as atomic clusters, and systems with long-range interactions, such as gravitational systems, have been studied extensively [2–8]. In particular, it has been shown that these kinds of systems can show inequivalence between canonical and microcanonical ensembles [9–11]. Perhaps one of the most spectacular instances of this inequivalence is that some of these systems can have negative specific heat in the microcanonical ensemble, at least in some energy interval. In spite of this, the behavior of systems with negative specific heat *per se* has not been as extensively studied [10,12–15]. From a general point of view, such systems are expected to be unstable when they are thermally coupled with the surrounding medium [16]. However, in the microcanonical ensemble, the energy changes that would accompany the instability are suppressed and systems with negative specific heat are allowed. Nevertheless, strange phenomena can be expected to occur when such systems interact with one another. For instance, in general, if any two systems at different temperatures are placed in thermal contact, then, according to Fourier's law, energy flows from the high-temperature system to the low-temperature system. If this were the case, and if these systems have negative specific heat, then, as energy flows, the initial temperature difference will *increase* instead of decreasing, inducing yet more energy to flow between the systems. Further, if the initial temperature difference is zero between the systems, any random fluctuation inducing an energy flow will cause a difference in the temperatures that initiates the above process (this is, in essence, what is behind the thermodynamical instability of such systems). On the other hand, if the two systems are identical and they have the same values of all their intensive parameters, the zeroth law of thermodynamics states that the systems will be in thermodynamic equilibrium, which appears to be at odds with the above discussion. Further, in a recent related work [15], Posch and Thirring studied a particle in a two-dimensional billiard subjected to a gravitational field, which shows negative specific heat. When they coupled N such particles, two *phases* emerged: some particles were condensed in the bottom of the billiard and the others formed a gas far from the bottom.

In this paper, we extend the results we presented in [17]; we show by simulations and by using exact expressions for the free energy and microcanonical entropy that when we couple two systems with negative specific heat, a process through which there is an irreversible increase in the total entropy occurs and two phases appear in the combined system. This irreversible process occurs even when all the intensive quantities of the systems are the same (actually, it occurs even when both systems are identical). This indicates that the equality of the intensive variables is not enough to ensure that both systems are in *stable* equilibrium with one another, in violation of the zeroth law. Moreover, we find that the final temperature reached by the combined system can be different from the initial temperature of the subsystems. We verify these results in two different models: the generalized Hamiltonian mean-field model [18] and the Ising model with long- and short-range interactions. Moreover, we confirm the violation of the zeroth law for these systems under various physical setups; namely, we study two kinds of intersystems coupling, and we also consider the interaction with a third system (with positive specific heat, but small enough to prevent large energy fluctuations that would drive the systems out of the microcanonical scenario), which should act as a "thermometer." Our results demonstrate that the fundamental conclusions reported in [17] do not depend on the kind of coupling between systems, and they suggest that violations of the zeroth law can be expected for any systems with negative specific heat. Futhermore, we demonstrate that this occurs even though we can equilibrate each system with a suitable (small) thermometer, to insure that the temperature of the systems is the same, before putting them in thermal contact.

It is also worth mentioning that negative specific heat has been measured experimentally in atomic clusters [19]. Hence, in addition to the possible implications of our results to the foundations of thermodynamics, the correct description of such systems is of practical interest.

II. THE HMF MODEL

As mentioned above, one model we consider is a generalization of the Hamiltonian mean-field (HMF) model [17,18]. This is a system of N classical XY rotors with phases θ_i and p_i its conjugate momentum, defined by the Hamiltonian

$$H=\sum_{i=1}^{N}\frac{p_i^2}{2}+\frac{J}{2N}\sum_{i,j=1}^{N}[1-\cos(\theta_i-\theta_j)]-K\sum_{i=1}^{N}\cos(\theta_{i+1}-\theta_i), \tag{1}$$

where $J>0$ is a long-distance ferromagnetic coupling, and K is the nearest-neighbor coupling, which can be either negative or positive. The rotors are placed on a one-dimensional lattice with periodic boundary conditions. When $K=0$, Eq. (1) is the classic HMF model, which is known to have a second-order phase transition at the critical temperature $T_c=J/2$ [20] in the canonical ensemble (though when $K=0$, the canonical and microcanonical ensembles are actually equivalent). This phase transition is characterized by the behavior of the order parameter given by the magnetization m,

$$m=\frac{1}{N}\sqrt{\left(\sum_{i=1}^{N}\cos\theta_i\right)^2+\left(\sum_{i=1}^{N}\sin\theta_i\right)^2}. \tag{2}$$

For $K<0$, it has been shown [18] that this system shows inequivalence of ensembles for an interval of values of K. Specifically, there exists a region in which this system shows negative specific heat in the microcanonical ensemble (which, of course, cannot happen in the canonical ensemble).

The canonical equilibrium properties of this system are determined by the free energy per particle $f(\beta)$ [18], which is given by

$$-\beta f(\beta)=\max_{m}\left[\frac{1}{2}\ln\frac{2\pi}{\beta}+\ln\lambda(\beta m,\beta K)-\frac{\beta(1+m^2)}{2}\right], \tag{3}$$

where we have set $J=1$, and $\lambda(z,\alpha)$ is the largest eigenvalue of the operator,

$$(\hat{T}\varphi)(\theta)=\int d\theta'\exp\left[\frac{1}{2}z(\cos\theta+\cos\theta')+\alpha\cos(\theta-\theta')\right]\varphi(\theta'). \tag{4}$$

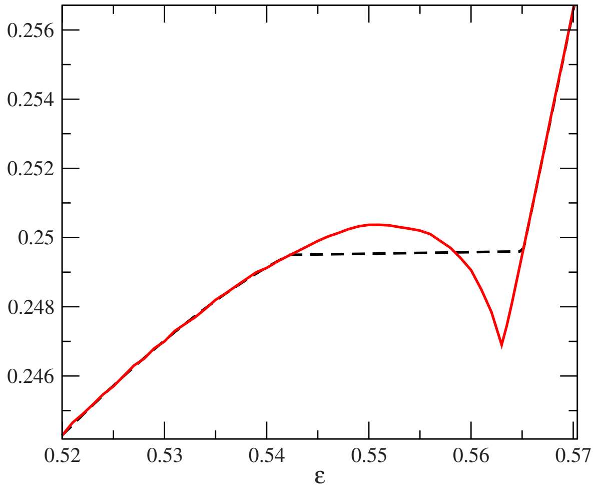

FIG. 1. (Color online) Caloric curves (T vs ε) in the canonical (black dashed line) and microcanonical (solid red curve) ensemble for the model (1) obtained from the exact expressions (3) and (5), $K=-0.178$ (from [17]).

On the other hand, in the microcanonical ensemble the thermodynamic properties are given by the entropy per particle s_μ, which is obtained from Eq. (3) by using the mean-field formalism introduced in Ref. [11],

$$s_\mu(\varepsilon)=\max_{m}\min_{\beta}\left[\beta\varepsilon+\frac{1}{2}\ln\frac{2\pi}{\beta}+\ln\lambda(\beta m,\beta K)-\frac{\beta(1+m^2)}{2}\right], \tag{5}$$

where ε is the energy per particle. We can obtain the canonical entropy s_c from Eq. (3) by a Legendre transformation with respect to β: $s_c(\varepsilon)=\beta^*\varepsilon-\beta^* f(\beta^*)$, where β^* is an extremum of $\beta\varepsilon-\beta f(\beta)$. Since $f(\beta)$ is a concave function, then β^* is a minimum of the last expression. The resulting canonical entropy is obtained by interchanging maxmin conditions in Eq. (5). With this result, it is possible to show that $s_\mu\leqslant s_c$ [11]. In Fig. 1, we show the caloric curves (canonical and microcanonical) within the region of negative specific heat using Eqs. (3) and (5) respectively.

Now, in order to test whether the zeroth law applies, we need to couple two systems with negative specific heat. To do this, we choose for the combined system the Hamiltonian $H=H_1+H_2+H_{\text{int}}$, where $H_\gamma(\gamma=1,2)$ are the Hamiltonians of each system, given by Eq. (1) with parameters $(J_\gamma=1, K_\gamma, N_\gamma)$; and for H_{int} we consider two different kinds of coupling: The first one is defined by

$$H_{\text{int}}^{\theta}=\eta\sum_{i,j=1}^{N_{\text{int}}}[1-\cos(\theta_i^1-\theta_j^2)], \tag{6}$$

and the second is defined by

$$H_{\text{int}}^{p}=\eta\sum_{i=1}^{N_{\text{int}}}p_i^1p_i^2, \tag{7}$$

where $(\theta_i^\gamma, p_i^\gamma)$ are the phase and the momentum of rotor i of system γ, $\eta>0$ is the inter-system coupling constant, and $N_{\text{int}}\leqslant N_\gamma$ is the number of rotors that interact in both systems. The interaction (6), which we will refer to as "phase coupling," is similar to that introduced in [21]. The interaction (7) will be referred to as "momentum coupling" and was studied in [17].

III. NUMERICAL SIMULATIONS

We performed numerical simulations of the HMF system using a fourth-order symplectic algorithm with a time step 0.1 [22]. With this step size the energy is preserved with a precision of order of 10^{-7}. We ran the simulations for an initial time interval τ_{eq} to let each system reach equilibrium without interaction (i.e., $\eta=0$). Once both systems had equilibrated, we increased the coupling linearly during a time interval τ_a, after which it was maintained constant, at a value $\eta>0$.

We choose the parameters of the systems in the region in which they exhibit negative specific heat, and first considered the case in which both systems have both the same size, $N_1=N_2$, and the same energy, $E_1=E_2$. Thus, their intensive parameters initially, before coupling, are of course also the same: the energy per particle (ε), magnetization (m), temperature (T), and specific heat (c). Note that in the microcanonical case, the control parameter is the energy of the system ($E=N\varepsilon$), and it defines the value of the other thermodynamic variables through the microcanonical entropy $[S_\mu(E)=Ns_\mu(\varepsilon)]$: $T(\varepsilon)=[ds_\mu(\varepsilon)/d\varepsilon]^{-1}$ and $c(\varepsilon)=-[d^2s_\mu(\varepsilon)/d\varepsilon^2]^{-1}[ds_\mu(\varepsilon)/d\varepsilon]^2$. The magnetization m is determined by ε too, because the value of m is such that the entropy, for every given value of ε, is a maximum; therefore, we can also write $m=m(\varepsilon)$. Thus, by fixing ε to identical values for both systems, we have effectively fixed m, T, and c to identical values in both systems as well.

In the simulations, we measured the instantaneous kinetic temperature defined by: $T_K(t)=2E_K(t)/N$, where E_K is the total kinetic energy of the system. We verified that the time average of the kinetic temperature, $\overline{T_K(t)}$, corresponds to the thermodynamic temperature T. This was done by measuring the momentum distribution, for which we found a Maxwellian distribution with variance $\sigma=\overline{T_K}$. The instantaneous magnetization $m(t)$ was measured by using the definition above, Eq. (2), using the configuration $\{\theta_i(t)\}$ of the system at times t.

First we studied the behavior of the combined system under the effect of phase coupling (6). In Fig. 2, we show the temporal evolution of the kinetic temperature of each system. There we can see that the systems reach the same final temperature, but that this temperature has a slightly higher value than the initial one. From Fig. 3, it is clear that in each realization, the magnetization and the energy per particle of each system do not stay at a well-defined stationary value. Instead, these variables show large fluctuations that persist over long periods of time. In the next section, we will argue that the equilibrium state should be such that one system is in a magnetized state and the other is in a state with zero magnetization, and the large fluctuations are due to large finite-size effects.

Since the systems begin with the same intensive parameters, from thermodynamics we could have expected that coupling the systems would not produce any noticeable effect; however, the simulations show that the systems actually evolve to a state with different values of the intensive parameters.

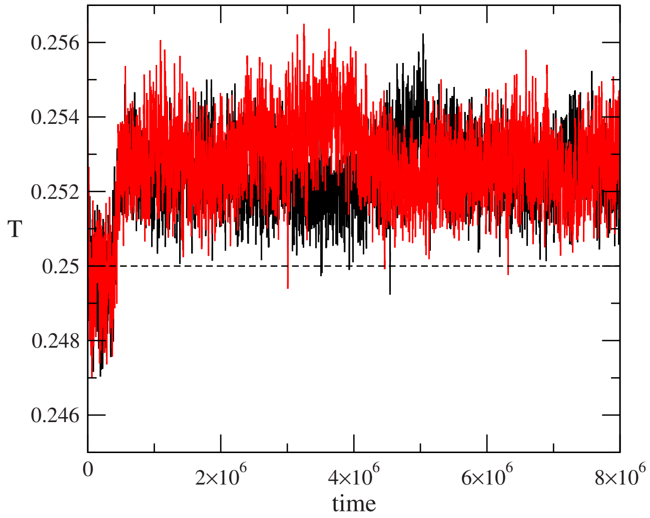

FIG. 2. (Color online) Temporal evolution of the kinetic temperature of system 1 (black curve) and system 2 [gray (red) curve] using the phase coupling (6). The curves were obtained by averaging over a sliding time window spanning 200 points, each of which was collected at 200 time-step intervals. The dashed line is the microcanonical temperature obtained by using Eq. (5) for uncoupled systems. The values of parameters are $K_1=K_2=-0.178$, $N_1=N_2=5000$, $\eta=0.1$, $N_{\text{int}}=10$, $\varepsilon_1^o=\varepsilon_2^o=0.555\,97$.

We also studied the systems under momentum coupling H_{int}^p, because the phase coupling H_{int}^θ, in addition to permitting an exchange of energy, may also induce an effect in which one system, being magnetized, acts as an external field over the other. For the H_{int}^p coupling, such effects do not

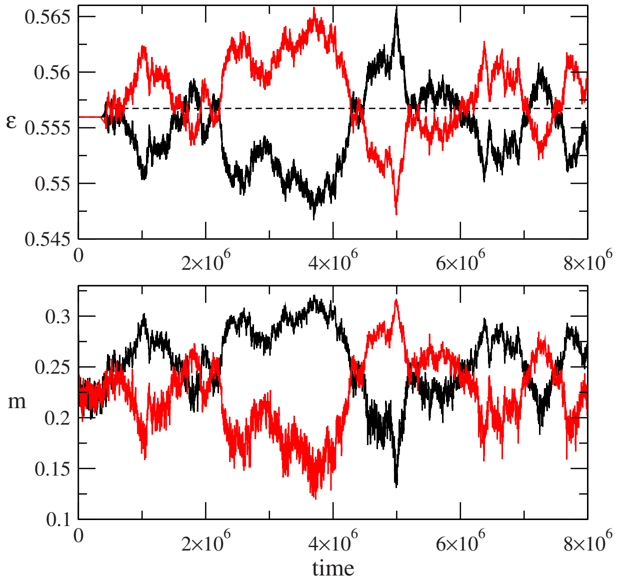

FIG. 3. (Color online) Temporal evolution of energy density (top) and magnetization (bottom) of system 1 (black curves) and system 2 [gray (red) curves]. The curves were obtained by averaging over a sliding time window. The values of parameters are the same as those of Fig. 2.

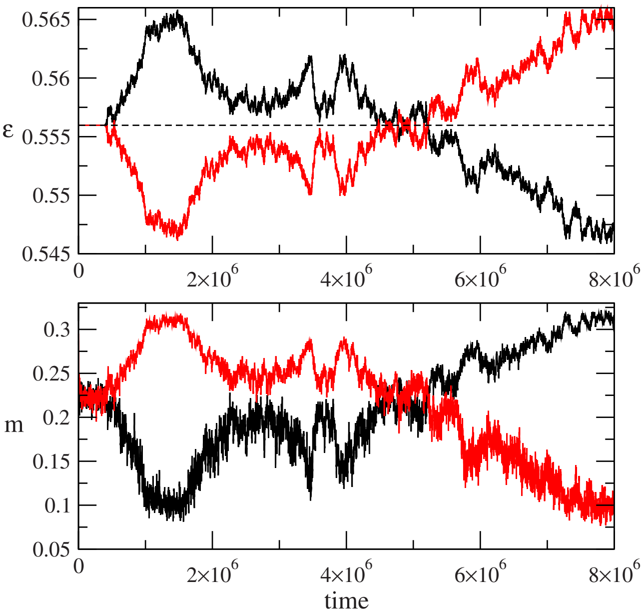

FIG. 4. (Color online) Temporal evolution of energy density (top) and magnetization (bottom) of system 1 (black curves) and system 2 [gray (red) curves], using the momentum coupling H_{int}^{p} (from [17]). The curves were obtained by averaging over a sliding time window. The values of parameters are the same as those of Fig. 2.

appear [17]. As we can see in Fig. 4, the behavior of the magnetization and the energy density is similar to that of Fig. 3. However, the kinetic temperature shows a difference with respect to the case with the phase coupling (6). Whereas in the phase coupled case there exists a small difference between the final and the initial temperature, in the case with H_{int}^{p} we do not observe any temperature difference after the systems are coupled. This can be understood because we can associate a potential energy to the phase coupling (6) and, after we switch on the interaction, the total potential energy will decrease. Since the total energy is nearly constant (the increment for the total energy density due to coupling was ≈0.17%), the total kinetic energy must increase. For the momentum coupling (7) we cannot associate a potential energy, so that in this case we do not observe this temperature increase.

It is important to mention that *in the canonical ensemble*, for this value of K, the isolated systems show a first-order phase transition, between a phase with zero magnetization and a phase with magnetization $m\neq 0$, and for these temperatures the magnetization should be zero. This means that the systems do not relax to the canonical equilibrium state although the energy conservation constraint was removed for each individual system (though not for the combined system). This is, of course, not entirely surprising, since the standard derivation of the canonical ensemble only applies to the case of a very small subsystem coupled weakly to a large thermal bath. Only then, if the total system is in the microcanonical ensemble, is the subsystem in the canonical ensemble. This clearly is not the case here. We show in the following section what is to be expected on theoretical grounds.

IV. MICROCANONICAL APPROACH

Even when we couple both systems, the combined system is still isolated, and the total energy $E=E_1+E_2+E_{\text{int}}$ is constant. As we consider the coupling between the systems to be weak, the interaction energy E_{int} can be neglected, and the total energy can be approximated as the sum of the energies of each individual system. Under these conditions, the total entropy per particle can be written as

$$s(\varepsilon_1,\varepsilon_2)=\frac{1}{2}[s_\mu(\varepsilon_1)+s_\mu(\varepsilon_2)], \qquad (8)$$

with s_μ given by Eq. (5) and the restriction $\varepsilon=(\varepsilon_1+\varepsilon_2)/2=\text{const}$ (total energy conservation). $\varepsilon_{1,2}$ are the energy densities of each system and ε is the energy density of the combined system. We assume that the correct description is given by the microcanonical entropy, although the energy conservation constraint was removed for each individual system. However, we also compute the total entropy using the canonical entropy for comparison. According to the second law of thermodynamics, the parameters $(\varepsilon_1^*,\varepsilon_2^*,m_1^*,m_2^*)$ characterizing the equilibrium state, will be such that the total entropy will be maximum. Now, the total entropy per particle is given explicitly by

$$s(\varepsilon)=\max_{\varepsilon_1}\frac{1}{2}[s_\mu(\varepsilon_1)+s_\mu(2\varepsilon-\varepsilon_1)]=\max_{\varepsilon_1}s(\varepsilon,\varepsilon_1), \qquad (9)$$

thus from this maximization problem we obtain the condition $T_\mu^1(\varepsilon_1^*)=T_\mu^2(2\varepsilon-\varepsilon_1^*)$, where ε_1^* is the energy that maximizes the total entropy and $T_\mu^\gamma(\varepsilon_\gamma)$ is the temperature of the system γ.

Using Eqs. (5) and (9), we can determine the equilibrium values of magnetization, energy density, and temperature of each system. If we use the parameters of the simulations and solve the optimization problem numerically, we find that equilibrium will occur with the following values for the thermodynamic variables: $T_\mu^1=T_\mu^2=0.25$, $\varepsilon_1^*=0.565\,94$, $\varepsilon_2^*=0.546$, $m_1^*=0, m_2^*=0.32$. For comparison, in the microcanonical case, the values of these parameters before the coupling are $\varepsilon=0.555\,97$, $T_\mu^*=0.25$, and $m^*=0.23$. We need to mention that the identical values (within the precision used) of temperatures before and after the coupling are only a coincidence: in general, as we will see later, we expect that there exists a small difference between the temperatures of the uncoupled systems and the temperature reached after coupling them.

In Fig. 5 we show $s(\varepsilon,\varepsilon_1)$ vs ε_1, microcanonical and canonical. For the microcanonical case there are two maxima. Since both systems are identical, both systems can evolve to either state with equal probability. Note that the total entropy when both systems have the same energy is a minimum (it is an unstable state); this is a general result that can be proven by using Eq. (8) and the restriction over the total energy, as long as the specific heat of the systems is negative. The maximum entropy is obtained if the systems have different values of magnetization and energy density, i.e., two *phases* appear. Thus, the total entropy is increased irreversibly when these two systems, with the same intensive parameters and

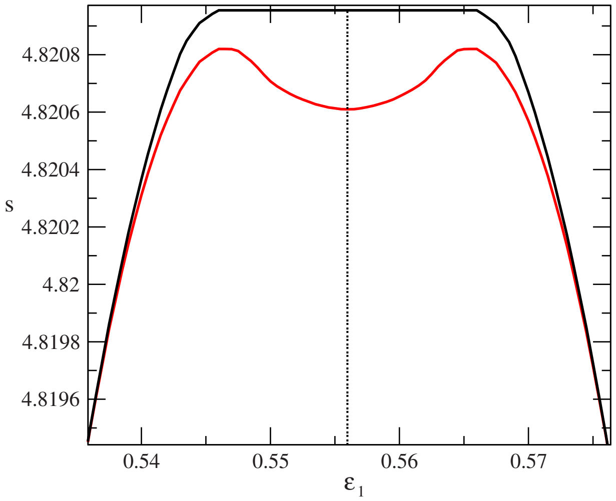

FIG. 5. (Color online) Total entropy per particle (from [17]), $s(\varepsilon,\varepsilon_1)$, for the coupled systems canonical (black curve) and microcanonical [gray (red) curve], the dotted line indicates the value of energy density before coupling, for identical systems with negative specific heat. The values of the parameters are $K_1=K_2=-0.178$, $\varepsilon=0.555\,97$.

with negative specific heat, are thermally coupled (that this could occur was suggested in [12,13]). Note that *weak coupling* is essential for this to occur: were we to couple all particles of subsystem 1 with all particles of subsystem 2 with equal strength, we would, of course, have a single system in the microcanonical ensemble, which would not break up in two phases.

From these results we found that the temperature obtained from the exact expression is close to the numerical value measured from the simulations. It is important to mention that the exact expressions were obtained in the limit $N\to\infty$, and small differences from those results can be expected. Also, as we mentioned in the last section, the increment in the temperature observed in the case when we used the phase coupling H_{int}^{θ} is not observed in the case of momentum coupling since this is a mechanical effect induced by H_{int}^{θ}, and it will disappear in the limit $N\to\infty$.

Let us now try to explain the observed behavior of the magnetization and the internal energy per particle in terms of the equilibrium model described above. As can be seen, these quantities do not settle down to their equilibrium values, but rather, they oscillate slowly as a function of time, whereas the above calculations lead us to assume that each subsystem will take one set of values for these parameters. What appears to be happening is that, over sufficiently long time scales, spontaneous fluctuations in the subsystems, together with the coupling, induce transitions in which each subsystem passes from one of the phases to the other, i.e., the full system jumps between the two degenerate equilibrium states. We will see below that this behavior is compatible with that expected in a process jumping over an appropriate entropy barrier, thus the time intervals between successive jumps diverge as $N\to\infty$. Further, the subsystems do come close to a state in which the value of the magnetization is $m=0.32$, as predicted by our calculations. In this situation, however, the magnetization of the other subsystem never actually reaches $m=0$ (though with the momentum coupling, one of the systems approaches a value closer to zero than with the phase coupling). This can be understood as the manifestation of a very strong finite-size effect, due to the proximity of a second-order phase transition at $\varepsilon_c\approx0.5633$ in the microcanonical ensemble. The systems thus have a large susceptibility for values of ε close to ε_c. The corresponding spontaneous fluctuations of the magnetization are, as a consequence, quite large as well, which results in the observed effect. For the case of phase coupling, an effective magnetic field is created by the coupling, the effect of which is enhanced by the large susceptibility. For the isolated systems, we found by simulations with different values of N that the magnetization behaves as $m\sim N^{-\alpha}$ with $\alpha\approx\frac{1}{4}$ for $\varepsilon=0.566$ and $N\leqslant10^4$ [23]. This is in good agreement with the well-known fact that, *at* the critical point, the fluctuations of the magnetization in the mean-field Ising model satisfy $\langle m^2\rangle=O(N^{-1/2})$. For the case with H_{int}^{θ}, we switched off the interaction between systems when they are near their equilibrium energies, after which the magnetization of one system reached $m\approx0.309$, while the other relaxed to $m\approx0.095$, a value similar to those obtained with H_{int}^{p}. Thus, two phases appear in the combined system and the large fluctuations appear to be due to finite-size effects.

We expect that the behavior of the systems studied above depends only on the presence of a convex "dip" in the microcanonical entropy, and it could be observed in others systems with negative specific heat. To show that it is indeed a general behavior, we apply this microcanonical approach to the Ising model with long- and short-range interactions, defined on a one-dimensional lattice with periodic boundary conditions; the Hamiltonian is given by

$$H=-\frac{K}{2}\sum_{i=1}^{N}(S_iS_{i+1}-1)-\frac{J}{2N}\left(\sum_{i=1}^{N}S_i\right)^2, \qquad (10)$$

where the S_i are spin variables taking the values ±1. This model also shows inequivalence of ensembles for an interval of values of K [24]. We compute the total entropy for two coupled identical systems in the region with negative specific heat, which show the same characteristics as the systems studied above.

In Fig. 6, we show $s(\varepsilon,\varepsilon_1)$, $T_\mu^1(\varepsilon_1)$, $T_\mu^2(2\varepsilon-\varepsilon_1)$ vs ε_1; there we can see that there exists three different energies at which $T_\mu^1=T_\mu^2$ corresponding to the extrema of $s(\varepsilon,\varepsilon_1)$. Again, the minimum corresponds to the state before the coupling (which, as before, is now an unstable state), and we see that $T_\mu^{\text{initial}}<T_\mu^{\text{final}}$. Thus, the final and initial temperatures can again be different (note that this difference is a thermodynamic effect that will still be observed in the limit $N\to\infty$, in contrast to the mechanical effect due to the phase coupling mentioned before). However, the actual temperature change is very small and, as mentioned above, the effects due to finite N are relatively large, making it difficult to observe in the simulations [25].

We now consider the dynamics of this generalized Ising model. For this, we apply the microcanonical Monte Carlo dynamics introduced by Creutz [26]. We choose for the full system the Hamiltonian $H=H_1+H_2+H_{\text{int}}$, where

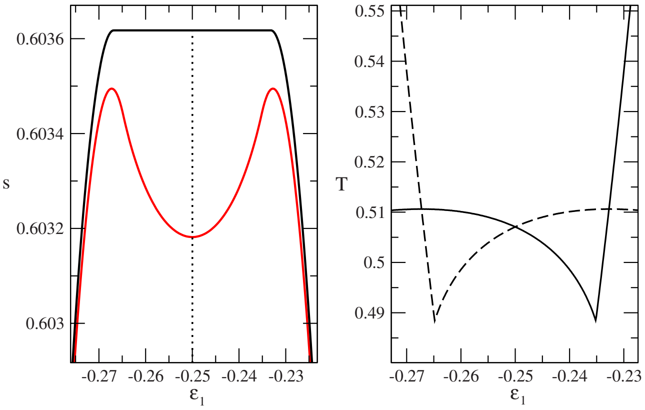

FIG. 6. (Color online) (Left) Total microcanonical [gray (red) curve] and canonical (black curve) entropy $s(\varepsilon,\varepsilon_1)$ for the coupled identical systems with negative specific heat for the Ising model with long- and short-range interactions, obtained using Eq. (10). The dotted line indicates the value of energy density before coupling. (Right) T^1_μ (full line) and T^2_μ (dashed line) vs ε_1. The values of the parameters are $J_1=J_2=1, K_1=K_2=-0.35, \varepsilon=-0.25$.

$H_\gamma(\gamma=1,2)$ is given by Eq. (10) each with parameters $(J_\gamma=1, K_\gamma, N_\gamma)$, and for H_{int} we choose the coupling defined by

$$H_{\text{int}} = -\eta \sum_{i,j=1}^{N_{\text{int}}} S_i^1 S_j^2, \tag{11}$$

where S_i^γ is the spin i of the system γ. The temporal evolution of the energies per particle and the magnetizations after having turned on the interaction and letting the compound system equilibrate are shown in Fig. 7. Note the similarity with the results obtained for the HMF model above: again the two systems settle at two different values of the magnetization, and again the systems change from one phase to the other as time proceeds. We can see that the values of the variables are close to those predicted by the theory, which are $\varepsilon_1^*=-0.267$, $\varepsilon_2^*=-0.233$, $m_1^*=0.425$, and $m_2^*=0$ (though finite-size effects are still expected to exist).

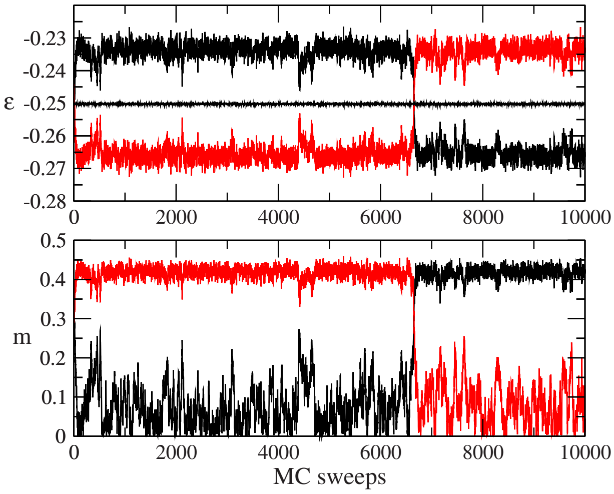

FIG. 7. (Color online) Temporal evolution of energy per particle (top) and magnetization (bottom) of system 1 (black curves) and system 2 [gray (red) curves] for the Ising model with long- and short-range interactions. The values of parameters are $K_1=K_2=-0.35$, $N_1=N_2=10\,000$, $\eta=0.1$, $N_{\text{int}}=10$, $\varepsilon_1^o=\varepsilon_2^o=-0.25$.

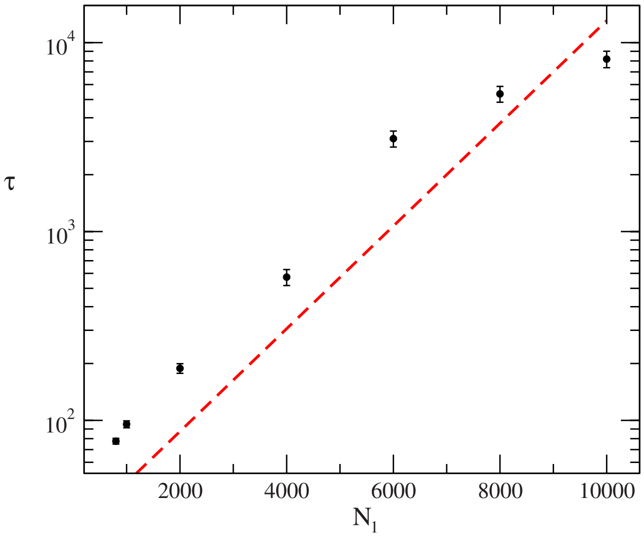

FIG. 8. (Color online) (Linear-Log) Mean switching time τ, obtained by numerical simulations (black dots) for the Ising model with long- and short-range interactions using the microcanonical Monte Carlo method. The dashed gray (red) line corresponds to an exponential with the theoretical slope. The parameters are the same as in Fig. 7.

Further, we have verified that the switching behavior between the two phases is consistent with a process overcoming the entropic barrier that separates the symmetric equilibrium states. More specifically, if we assume that the process is activated, the mean switching time $\tau(N)$ can be expected to increase exponentially with N, according to an expression of the form

$$\tau(N) = \text{const}\exp(N\Delta s), \tag{12}$$

where Δs is the height of the entropy barrier separating the two maxima and the prefactor depends in a complex manner on the details of the dynamics. Note that the entropies at the beginning and at the end of the switching process are equal. However, in the process of going from one state to the other, the system must necessarily go through the unstable symmetric state. We may therefore set $\Delta s = s(\varepsilon,\varepsilon_1^*) - s(\varepsilon,\varepsilon)$. From the last two equations it follows that $\ln \tau(N)$ grows linearly with N with a slope Δs. The measured values of $\tau(N)$ are presented in Fig. 8, where we show $\tau(N)$ vs N_1, (note that $N=2N_1$) in a linear-log plot obtained from numerical simulations. A fit to the first five data points yields a slope $\sigma \approx 0.000\,611$, which is consistent with twice the size of the entropy barrier that appears in the curve of the entropy per particle shown in Fig. 6, which has the value $\approx 0.000\,626$. It is worth mentioning that the last points, corresponding to the largest values of N, appear to be too low. We have no explanation for this fact except that it may be due to poor statistics since switching events in such large systems are few and far apart.

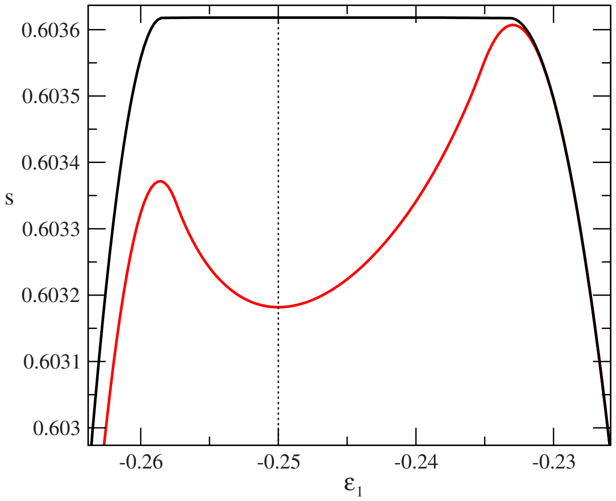

FIG. 9. (Color online) Total microcanonical [gray (red) curve] and canonical (black curve) entropy per particle $s(\varepsilon,\varepsilon_1)$ for the coupled systems with negative specific heat for the Ising model with long- and short-range interactions in the asymmetric setup. The dotted line indicates the value of energy density before coupling. Both systems have the same values of their intensive parameters before the coupling. The values of the parameters are $J_1=J_2=1$, $K_1=K_2=-0.35$, $\varepsilon=-0.25$, $N_2/N_1=0.5$.

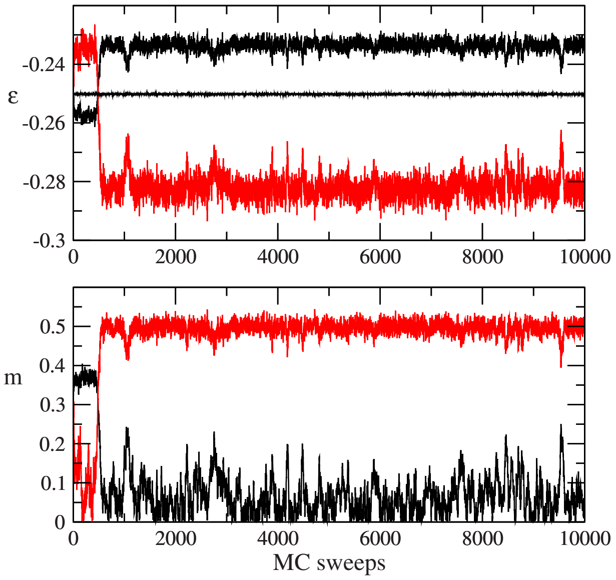

FIG. 10. (Color online) Temporal evolution of energy per particle (top) and magnetization (bottom) of system 1 (black curves) and system 2 [gray (red) curves] for the Ising model with long- and short-range interactions in the asymmetric setup. The values of parameters are $K_1=K_2=-0.35$, $N_1=15\,000$, $N_2=7500$, $\eta=0.1$, $N_{\rm int}=10$, $\varepsilon_1^o=\varepsilon_2^o=-0.25$.

Until now we have only considered a symmetric setup in which the two systems are identical, but the zeroth law applies to any systems with the same intensive parameters, thus it is interesting to study the asymmetric case. For this we considered two generalized Ising systems, both with the same intensive parameters, but one larger than the other. The function $s(\varepsilon,\varepsilon_1)$ is shown in Fig. 9, and now it is not a symmetric function as is clearly seen in the figure. The figure exhibits two maxima: a local one and the other, which is a global maximum. The largest system always evolves to the larger energy and its magnetization decays to zero; the other system decreases its energy and its magnetization increases. This can be understood because the major contribution to the total entropy comes from the larger system, and if its energy increases its entropy increases too. This change of entropy will be larger than that obtained if the small system would increase its energy. For the dynamics we apply Creutz's algorithm for this setup; the results are shown in Fig. 10. After a short transient, the systems evolve to the configuration corresponding to the total entropy maximum, theoretically characterized by $\varepsilon_1^*\approx-0.233$, $\varepsilon_2^*\approx-0.284$, $m_1^*=0$, and $m_2^*\approx0.505$. We can see that the values obtained by the numerical simulations are indeed near to these values predicted by the theory. These results reinforce our expectations about the generality of the behavior of the systems with negative specific heat in contact with other similar systems.

V. USING THERMOMETERS

We now show that it is possible to use a third small system as a "thermometer" to measure the temperature of our negative specific-heat systems before we put them in contact. The point is that we can actually check that our systems are initially in equilibrium with the thermometer, and yet they will not be in proper equilibrium between them. Of course there is a proviso: the thermometer must be *small* in a way that will soon be clear, otherwise the thermometer can act as a *heat bath* driving our systems out of the microcanonical ensemble.

We use the approach of the previous section. Clearly, if we have two different systems with energies and number of particles (E_1,N_1) and (E_2,N_2), and we put them in thermal contact while keeping the full system isolated, then the total energy will be $E_{\rm total}=E_1+E_2$ (where we have neglected the interaction energy). For definiteness, in what follows, system 2 will be our "thermometer," which we will assume to be a one-dimensional ideal gas, and system 1 will be either of the negative specific-heat systems discussed previously. We can also define the parameter $x=\frac{N_2}{N_1+N_2}$, the relative size of system 2, in terms of which the total entropy per particle can be expressed as

$$s(\varepsilon_1,\varepsilon_2)=(1-x)s_\mu^1(\varepsilon_1)+xs_\mu^2(\varepsilon_2), \qquad (13)$$

where s_μ^γ and ε_γ are the entropy and energy per particle of each system $(\gamma=1,2)$. However, we have the restriction $(1-x)\varepsilon_1+x\varepsilon_2=\varepsilon=E_{\rm total}/(N_1+N_2)$; i.e., ε is the total energy per particle of the combined system. Then, the equilibrium state will be such that the total entropy will be maximum, i.e.,

$$s(\varepsilon)=\max_{\varepsilon_1}\left[(1-x)s_\mu^1(\varepsilon_1)+xs_\mu^2\left(\frac{\varepsilon-(1-x)\varepsilon_1}{x}\right)\right]. \qquad (14)$$

From this, of course, we obtain the equilibrium condition

$$T_1(\varepsilon_1) = T_2\left(\frac{\varepsilon - (1-x)\varepsilon_1}{x}\right), \tag{15}$$

where $T_{1,2}$ are the respective temperatures of each system. Since we are using an ideal gas as a thermometer, its entropy per particle is given by

$$s_\mu^2(\varepsilon) = \frac{3}{2} + \frac{1}{2}\ln(4\pi\varepsilon), \tag{16}$$

so

$$T_2(\varepsilon_2) = 2\varepsilon_2 \tag{17}$$

and Eq. (15) becomes

$$T_1(\varepsilon_1) = 2\frac{\varepsilon - (1-x)\varepsilon_1}{x}. \tag{18}$$

This equation can be analyzed graphically by looking at the points where the caloric curve $T_1(\varepsilon_1)$ (see Figs. 1 and 6) intersects with the straight line defined on the RHS of Eq. (18). If x is small, i.e., the thermometer is small, the slope $m=(1-x)/x$ of the straight line is large and it intersects $T_1(\varepsilon_1)$ at only one point, which can be anywhere; in particular, it can be in the region of negative specific-heat. However, as x grows, the line becomes horizontal and it can intersect $T_1(\varepsilon_1)$ at three points, corresponding to three extrema of the total entropy. In such cases, the central point will be in the negative specific-heat region, but the other two solutions will be in the regions of positive specific heat, which are "stable." Thus, the ideal gas thermometer must be small enough to ensure that there is only one intersection point, and if this is the case, the thermometer can indeed be in equilibrium (at the same temperature) with the systems with negative specific heat, even when these are not in stable equilibrium with each other. We therefore obtain an actual contradiction to the commonly given statement of the zeroth law, namely that if system 1 is in thermal equilibrium with system 2 and further system 2 is in thermal equilibrium with system 3, then system 1 is in thermal equilibrium with system 3.

VI. CONCLUSIONS

We have shown that for systems with negative specific heat, having the same intensive parameters does not guarantee that the systems are in equilibrium with each other, which violates the zeroth law of thermodynamics. What we observe is that when two similar systems with negative specific heat are weakly coupled to each other, the final equilibrium is such that the temperature is, of course, the same in both systems, but that it can be different from the initial temperature. Moreover, in agreement with other studies, two phases appear in the combined system. This behavior was found in two different models that show negative specific heat, and it is expected to be a general behavior for these kinds of systems.

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