Violation of the Zeroth Law of Thermodynamics in Systems with Negative Specific Heat

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We show that systems with negative specific heat can violate the zeroth law of thermodynamics. By both numerical simulations and by using exact expressions for free energy and microcanonical entropy it is shown that if two systems with the same intensive parameters but with negative specific heat are thermally coupled, they undergo a process in which the total entropy increases irreversibly. The final equilibrium is such that two phases appear, that is, the subsystems have different magnetizations and internal energies at temperatures which are equal in both systems, but that can be different from the initial temperature.

Keywords:

The zeroth law of thermodynamics is among the most fundamental assumptions concerning macroscopic systems in equilibrium. In its textbook form, it concerns three systems $A$, $B$ and $C$ at equilibrium, that is, such that their macroscopic variables are time-independent: if $A$ and $B$ are in thermal equilibrium with each other, that is, if no heat flow arises when they are brought into thermal contact, and if further system $B$ is similarly in thermal equilibrium with system $C$, then the zeroth law states that system $A$ will also be in equilibrium with system $C$. By bringing two systems in thermal contact, one means allowing a weak coupling through which energy can be exchanged between the systems. From the above statement of the zeroth law follows the existence of an intensive variable, the temperature, which serves to predict the behaviour of two initially isolated systems at equilibrium when they are brought into thermal contact. It states that the equality of the temperature parameter is a necessary and sufficient condition that no irreversible heat exchange will occur.

It is of considerable interest to fully understand the possible limitations of such a basic law. In the following, we shall show that systems with negative specific heat can indeed violate the zeroth law. This is more than just an academic concern: systems with negative specific heat do exist in Nature. Although it is readily shown that systems well described by the canonical ensemble, such as those which are weakly coupled to an environment at fixed temperature, cannot have negative specific heat, others may. In particular, if a system is entirely isolated, that is, if it is in the microcanonical ensemble, the specific heat may well become negative. To this end, however, it is obviously necessary that the microcanonical ensemble lead to significantly different predictions from the canonical one. This cannot happen for large systems with short-range interactions. However, if either the interactions are long-range or, perhaps more realistically, if the system is small with respect to the interaction range, then it is not possible to refer to general statements concerning the equivalence of ensembles and negative specific heats can be, and indeed have been, observed. Such systems include among others gravitational systems (long-range interactions) and atomic clusters (small systems), see $[2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]$. Analytically, mean-field models, involving interactions of all particles with all, are well-known to display negative specific heats $[9, 15]$ in the microcanonical ensemble for parameters which, in the canonical ensemble, would correspond to the vicinity of a tricritical point $[10]$.

Since systems with negative specific heat are thermodynamically unstable when they are thermally coupled to the surrounding medium $[17]$, anomalous behaviour is surely to be expected when such systems interact. However, it is not apparent that this will cause violations of the zeroth law. The reason is precisely that the zeroth law always involves coupling between systems. Heat exchange is thus always allowed whenever the zeroth law is tested, and one might hence think that this always leads to a canonical-like case, in which the restriction on fixed energy is lifted and negative specific heats cannot occur. We shall show that this is not the case.

In order to test the zeroth law for small systems in the microcanonical ensemble, one also faces yet another issue: for such systems it is often not straightforward how to define the temperature posited by the zeroth law. Under these circumstances, how, then, shall we know whether two systems really have the same temperature or not?

A simple way around the last question is straightforward: it suffices to take two identical systems, that is, two systems having the same Hamiltonian with the same energy, volume and number of particles, and then to couple them weakly. Under these conditions, whatever the temperature is in each system, it certainly will be the same for both; yet irreversible changes may occur in the composite system even under such circumstances.

To be specific, let us focus on the following Hamilton-
nian describing a system of $N$ classical XY-rotors with phases $\theta_i$, defined by
\[
H = \sum_{i=1}^{N} \frac{\theta_i^2}{2} + \frac{J}{2N} \sum_{i,j=1}^{N} (1 - \cos(\theta_i - \theta_j)) - K \sum_{i=1}^{N} \cos(\theta_{i+1} - \theta_i),
\]
where $J > 0$ is the global ferromagnetic coupling and $K$ is the nearest neighbors coupling; it can be negative or positive. The rotors are placed on a one-dimensional lattice with periodic boundary conditions. When $K = 0$, Eq. (1) is the classic Hamiltonian Mean Field model introduced in [18], which has a second order phase transition at the critical temperature $T_c = J/2$ [18] in the canonical ensemble (though the microcanonical and the canonical ensembles are equivalent when $K = 0$). This phase transition is characterized by the behavior of the magnetization order parameter $m$,
\[
m = \frac{1}{N} \sqrt{\left( \sum_{i=1}^{N} \cos \theta_i \right)^2 + \left( \sum_{i=1}^{N} \sin \theta_i \right)^2}.
\]
For $K < 0$ it was shown [15] 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.

The canonical equilibrium properties are determined by the free energy per particle $f(\beta)$ [15] ($J = 1$),
\[
-\beta f(\beta) = \max_m \left[ \frac{1}{2} \ln \frac{2\pi}{\beta} + \ln \lambda(\beta m, \beta K) \right. \\
- \frac{\beta(1 + m^2)}{2},
\]
where $\lambda(z, \alpha)$ is the largest eigenvalue of the transfer matrix given by the following operator
\[
(\tilde{T}_\varphi)(\theta) = \int d\theta' \exp \left[ \frac{1}{2} z(\cos \theta + \cos \theta') \right. \\
+ \alpha \cos(\theta - \theta') \left. \right] \varphi(\theta').
\]
In the microcanonical ensemble the thermodynamic properties are given by the entropy per particle $s_\mu$ that is obtained from (3) by using the mean-field formalism introduced in Ref. [16],
\[
s_\mu(\varepsilon) = \max_m \min_\beta \left[ \beta \varepsilon + \frac{1}{2} \ln \frac{2\pi}{\beta} + \ln \lambda(\beta m, \beta K) \right. \\
\left. - \frac{\beta(1 + m^2)}{2} \right],
\]
where $\varepsilon$ is the energy per particle. The canonical entropy $s_c$ is found from (3) by a Legendre transformation with respect to $\beta$ and has therefore the usual concavity property. The same does not hold, however, for $s_\mu(\varepsilon)$ as is seen in figure [11].

When we now couple both systems, the full system is still isolated and the total energy $E = E_1 + E_2 + E_{int}$ is constant. As we consider weak couplings, the interaction energy can be neglected, so the total energy is the sum of the individual energies of each subsystem. Under this condition the total entropy per particle can be written as
\[
s(\varepsilon_1, \varepsilon_2) = \frac{1}{2} \left[ s_\mu(\varepsilon_1) + s_\mu(2\varepsilon - \varepsilon_1) \right],
\]
with $s_\mu$ given by (5) and the restriction $\varepsilon_2 = 2\varepsilon - \varepsilon_1$. Here $\varepsilon_\gamma$ is the energy density of subsystem $\gamma$ and $\varepsilon$ is the energy density of the full system, which is constant. The correct description of the full system is thus given by the microcanonical entropy, although the energy conservation constraint was removed for each individual subsystems. By the second law of thermodynamics, the equilibrium state $(\varepsilon_1^*, \varepsilon_2^*, m_1^*, m_2^*)$ will be such that the total entropy will be maximum. So, the total entropy per particle is given by
\[
s(\varepsilon) = \max_{\varepsilon_1} \left[ \frac{1}{2} \left[ s_\mu(\varepsilon_1) + s_\mu(2\varepsilon - \varepsilon_1) \right] \right] = \max_{\varepsilon_1} s(\varepsilon, \varepsilon_1) \equiv \varepsilon_1^*(\varepsilon),
\]
From this optimization problem we obtain the following condition for the maximum entropy: $T^1_\mu(\varepsilon_1^*) = T^2_\mu(2\varepsilon - \varepsilon_1^*)$, where $\varepsilon_1^*$ is the energy that maximizes the total entropy and $T^\gamma_\mu(\varepsilon_\gamma)$ is the temperature of the subsystem $\gamma$ defined as the inverse derivative of the entropy with respect to the energy at constant $N, V$.

By using (5) and (7) we can predict the equilibrium values of magnetization, energy density and temperature of each subsystem. In figure [2] we show $s(\varepsilon, \varepsilon_1)$ vs $\varepsilon_1$, microcanonical and canonical. For the microcanonical case there are two maxima. Because both subsystems

\[FIG. 1: \text{Caloric curves (T vs } \varepsilon) \text{ in the canonical (black) and microcanonical (red) ensemble for the model (1) obtained from the exact expressions (6) and (7).} K = -0.178.\]
are identical, in principle which subsystem evolves to the higher energy is random. The total entropy before the coupling is now a minimum, that is, an unstable state. That this can occur was already noted in \[5\]. Therefore, the state of maximum entropy is now obtained when the subsystems have different values of magnetization and energy density, i.e. when two phases appear (a similar phenomenon was observed in \[13\]). The total entropy is therefore increased irreversibly if two subsystems with the same intensive parameters with negative specific heat are thermally coupled. Note that the final temperatures of both subsystems are identical, but in general differ from the initial temperature \[20\]. This difference is often too small to be detected numerically but its existence is rigorously established by the analytical results.

To confirm our results we have performed numerical simulations of the complete system using a fourth-order symplectic algorithm with a time step 0.1 \[21\]. We run the simulations for a time interval \(\tau_{eq}\) to let both subsystem reach equilibrium without interaction (i.e. \(\eta = 0\)). Once they have equilibrated, we increase the coupling linearly during a time interval \(\tau_c\), after which the coupling is maintained constant, \(\eta > 0\).

We choose parameters in the region in which the uncoupled subsystems exhibit negative specific heat, and both subsystems have the same values of all their parameters initially: energy per particle \((\varepsilon_1 = \varepsilon_2)\), magnetizations \((m_1 = m_2)\) as well as particle numbers \((N_1 = N_2)\). From these equalities it follows that the derived variables, temperatures \((T)\) and specific heats \((c)\) are identical as well. The value of these thermodynamic variables are defined through the microcanonical entropy: \(T(\varepsilon) = (d\mu(\varepsilon)/d\varepsilon)^{-1}\) and \(c(\varepsilon) = -(d^2\mu(\varepsilon)/d\varepsilon^2)^{-1}(d\mu(\varepsilon)/d\varepsilon)^2\). The value of the magnetization is such that the entropy for \(\varepsilon\) fixed is maximum, therefore \(m = m(\varepsilon)\) as well. Note further that for Hamiltonians with a quadratic kinetic energy, as \([1]\), we may without appreciable error evaluate the temperature using the expression for the kinetic temperature, which is given in this case as twice the mean kinetic energy per particle, since the finite \(N\) microcanonical corrections are negligible. This identification was verified by comparing with the momentum distribution, which we found to be Maxwellian. The measurement of the temperature in the simulation is therefore straightforward in this case.

Here we report the effect of the following choice for the coupling Hamiltonian

\[ H_{int}^p = \eta \sum_{i=1}^{N_{int}} p_i^1 p_i^2, \]  

where \(p_i^\gamma\) is the momentum of the \(i\)-th particle of subsystem \(\gamma\). The advantage of this apparently peculiar choice is that this coupling does not exert a direct influence on the magnetizations of the two subsystems.

In Figure 3 we show the behaviour of the internal energy and the magnetization of both subsystems. Clearly, they do not remain at their initial equilibrium values; rather, due to finite size effects, the systems jump between the two degenerate equilibrium states of the coupled system \[22\]: thus either subsystem one is in a magnetized state and subsystem two in an \(m = 0\) state, or vice versa. The oscillation does indeed roughly take place between the two equilibrium values of the magnetization, which for the parameter values used here can be computed, along the lines described above, to be \(T_1^p = T_2^p = 0.25\), \(\varepsilon_1^* = 0.56594\), \(\varepsilon_2^* = 0.546\), \(m_1^* = 0\), \(m_2^* = 0.32\). There is a problem, however, with the fact that neither subsystem ever comes reasonably close to being truly paramagnetic \((m = 0)\)[22]. As it turns out, this is also a finite-size effect. As is readily seen, the mean-field Ising model at

\[ FIG. 2: \] Total entropy per particle, \(s(\varepsilon, \varepsilon_1)\), for the coupled subsystems canonical (black) and microcanonical (red), the dotted line indicates the value of energy density before coupling, for identical subsystems with negative specific heat. The values of the parameters are \(K_1 = K_2 = -0.178\), \(\varepsilon = 0.55597\).

\[ FIG. 3: \] Temporal evolution of energy density (top) and magnetization (bottom) of subsystem 1 (black) and subsystem 2 (red), using the coupling \(H_{int}^p\). The curves were obtained by averaging over a sliding time window. The values of parameters are \(K_1 = K_2 = -0.178\), \(N_1 = N_2 = 5000\), \(\eta = 0.1\), \(N_{int} = 10\), \(\varepsilon_1^* = \varepsilon_2^* = 0.55597\).
criticality satisfies
\[ \langle m^2 \rangle = \text{const.} \cdot N^{-1/2} \] (9)
which states that the typical magnetization fluctuations at, or in the vicinity of, a second order phase transition are of order \( N^{-1/4} \). A study of the \( N \)-dependence of the magnetizations observed in our system is compatible with this scaling behavior [20]. Thus, these large fluctuations due to the vicinity of a second order phase transition, which is known to exist at \( \varepsilon_c \approx 0.5633 \), are the reason why the zero magnetization phase is not clearly observed in our finite systems.

The reason for the appearance of two phases lies, of course, in the thermodynamic instability of systems with negative specific heat, as discussed previously. Such systems can only exist through the existence of constraints, such as the conservation of energy, which keeps them from relaxing to a more probable state. What we have therefore shown is simply that coupling two such systems with each other provides enough freedom for an irreversible relaxation process to take place. It can also be shown [20] that this phenomenon is not limited to the specific case studied here: any system with negative specific heat will show similar behavior. The type of coupling used is also unimportant.

Further, it is possible to use a third system (with positive specific heat) as a thermometer to measure the temperature of the systems with negative specific heat. Thus, we can check that our systems are in a stable equilibrium with the thermometer at the same temperature before we put them in thermal contact. There exists, however, a condition over the third system: it needs to have a small heat capacity, otherwise it may allow large enough energy fluctuations to drive the system with negative specific heat out of the microcanonical ensemble (this condition on the thermometer was already discussed in [3, 4, 5]; explicit simulations of this situation will be presented in [20], where we use an ideal gas as the thermometer).

Summarizing, we have shown how coupling two systems with negative specific heat leads to an irreversible change in the intensive variables of the subsystems. In the simulations, the entire system does not settle down to a well-defined state. Rather, it displays slow oscillations between two degenerate states of thermodynamic equilibrium due to the finite size of the systems. It should further be noted that neither of these states corresponds to the canonical equilibrium state.

Since both subsystems began at equilibrium with the same intensive parameters, the validity of the zeroth law implies that the coupling should not produce any noticeable effect. Since, as we have seen both through an analytical approach and by explicit numerical work, the system in fact relaxes to an inhomogeneous state in which the two weakly coupled subsystems have widely different values of the magnetization and of the internal energy, we have unambiguously observed a instance of a violation of the zeroth law of thermodynamics.

[1] D. H. E. Gross, *Microcanonical Thermodynamics: Phase Transitions in Small Systems* World Scientific, 2001.
[2] D. Lynden-Bell and R. Wood, Mon. Not. R. Astr. Soc. 138 495 (1968).
[3] W. Thirring, Z. Physik 235 339 (1970).
[4] E. B. Aronson and C. J. Hansen, Astrophys. J. 177 145 (1972).
[5] D. Lynden-Bell and R. M. Lynden-Bell, Mon. Not. R. Astr. Soc. 181 405 (1977).
[6] D. Lynden-Bell, Physica A 263 293 (1999).
[7] V. Laliena, Phys. Rev. E 59 4786 (1999).
[8] P. H. Chavanis, Phys. Rev. E 65 056123 (2002).
[9] J. Barré, D. Mukamel, and S. Ruffo, Phys. Rev. Lett. 87 030601 (2001).
[10] I. Ispolatov and E.G.D. Cohen, Physica A 295 475 (2001).
[11] P. Labastie and R. L. Whetten, Phys. Rev. Lett. 65 1567 (1990).
[12] J. A. Reyes-Nava, I. L. Garzón and K. Michaelian, Phys. Rev. B 67 165401 (2003).
[13] M. Schmidt, *et al.* Phys. Rev. Lett. 86 1191 (2001).
[14] H. A. Posch and W. Thirring, Phys. Rev. Lett. 95 251101 (2005).
[15] A. Campa, A. Giasanti, D. Mukamel, and S. Ruffo, Physica A 365 120 (2006).
[16] F. Leyvraz and S. Ruffo. J. Phys. A: Math. Gen. 35 285 (2002).
[17] L. E. Reichl, *A Modern Course in Statistical Physics* Wiley Interscience, 1998.
[18] M. Antoni, and S. Ruffo, Phys. Rev. E 52 2361 (1995).
[19] H. A. Posch and W. Thirring, Phys. Rev. E 74 051103 (2006).
[20] A. Ramírez–Hernández, H. Larralde and F. Leyvraz, to be published
[21] I. McLachlan, and P. Atela, *Nonlinearity* 5 541 (1992).
[22] We have performed simulations with different values of \( N \) for our systems and found that the jumps between the two degenerate equilibrium states indeed become less frequent as \( N \) grows. For a careful study of the \( N \) dependence of fluctuations inducing transitions between different entropy maxima in gravitational systems see J. Katz and I. Okamoto, Mon. Not. R. Astr. Soc. 317 163 (2000)
[23] Negative specific heat may arise in systems that are of mean-field type as defined in [18], near the tricritical point. For this kind of systems we can write a Landau-like free energy density and we can approximate it by \( \phi = a_2 m^2 + a_4 m^4 + a_6 m^6 \). If the system is near the tricritical point (\( a_2 \approx 0, a_4 \approx 0 \)) then \( m \sim N^{-\alpha} \) with \( \alpha = 1/6 \), but if the system is near a critical point, \( a_2 \approx 0 \) and \( a_4 \) is non zero, then \( \alpha = 1/4 \). In either case, for very large \( N \) the normal \( \alpha = 1/2 \) behaviour is recovered.