In recent years, the study of small systems and systems with long range interactions has suggested that these kind of systems can show inequivalence between the canonical and microcanonical ensembles. In particular, it is possible that the specific heat can be negative in the microcanonical ensemble, which is always positive in the canonical ensemble. In spite of this, the behaviour of systems with negative specific heat in thermal contact has not been extensively studied.

We show that systems with negative specific heat in thermal contact can violate the zeroth law of thermodynamics, which is among the most fundamental assumptions concerning macroscopic systems in equilibrium. Since systems with negative specific heat are thermodynamically unstable when they are thermally coupled to the surrounding medium, anomalous behaviour is surely to be expected when such systems interact. However, it is not obvious that this will cause violations of the zeroth law. The reason is that when we test the zeroth law, heat exchange is always allowed, thus the restriction on fixed energy which characterizes the microcanonical ensemble is lifted and we might think that this leads to a canonical-like case, in which the specific heat is always positive.

By numerical simulations and by using exact expressions for free energy and microcanonical entropy for a modified Hamiltonian Mean Field (HMF) model, we show that when two identical systems with the same intensive parameters but with negative specific heat are thermally coupled, they undergo a process that leads to an irreversible change in the intensive parameters of the subsystems. 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. 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 no change is induced via coupling to a sufficiently small system (that will work as a thermometer). Therefore, we show an instance of violation of the zeroth law of thermodynamics.