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

Ramírez-Hernández *et al.* [1] argue that two systems with negative heat capacity put into thermal contact can violate the zeroth law of thermodynamics. However, we submit that systems with negative heat capacity are not representative of physically consistent systems in thermodynamic equilibrium. This criterion is implicit in the enunciation of the zeroth law of thermodynamics.

Equilibrium thermodynamics is derivable from statistical mechanics under the axioms of *a priori* equal probability and independence of the microstates [2]. Under these axioms, it is possible to demonstrate that an extremum maximum in the number of microstates Ω exists, with respect to partition of an unconstrained extensive thermodynamic variable X, only if $\Omega\Omega''/\Omega'^2 < 1$, where $\Omega'' \equiv \partial^2\Omega/\partial X^2$ and $\Omega' \equiv \partial\Omega/\partial X$ [3]. The extremum maximum corresponds to a stable thermodynamic equilibrium state with homogeneous intensive variables [3].

In situations where the condition on Ω is not met (either through unphysical model design or by nonergodic simulation [3]), an extremum in the number of microstates may exist (again giving homogeneous intensive variables), but this extremum is a minimum, and therefore the least likely of all possible macrostates. A maximum in the number of microstates may exist, but this is not an extremum, rather it corresponds to an end point in which all of the unconstrained extensive variables will be found in one part of the system (giving inhomogeneous intensive variables). Such systems cannot attain thermodynamic equilibrium. Application of equilibrium thermodynamic formalism will lead to inconsistencies such as negative heat capacity, violations of fundamental thermodynamic laws, unphysical singularities, and differences between results obtained in different ensembles [3].

Systems not satisfying the condition on Ω can be identified by a convex intruder in their entropy function and negative heat capacity [3]. The model of Ramírez-Hernández *et al.* gives a convex intruder in the entropy function of subsystem 1 for $0.556 \leq \varepsilon_1 \leq 0.563$ (Fig. 2), precisely where its heat capacity is calculated as negative (Fig. 1). Since these states on the convex intruder do not have an extremum maximum, they are *not* representative of thermodynamic equilibrium [2–5]. Their heat capacity also flips, unphysically, from positive to negative infinity (where the slope of their caloric curve goes to zero) at *two* energy values bounding the region of negative heat capacity.

There are many ways to construct unphysical models not satisfying the condition on Ω (e.g., models with competing infinite and short range interactions, the case of Ramírez-Hernández *et al.*). However, the existence of pure quantum states, interaction with the quantum vacuum, and a finite Planck's constant imply that natural quantum systems satisfy *a priori* the fundamental axioms and the condition on Ω and thus are, in principle, able to attain thermodynamic equilibrium [2,3].

Simulations using physically consistent models but with long range forces may also lead to a *determined* Ω which violates the above condition. Small atomic clusters simulated in the microcanonical ensemble may become trapped from visiting some energetically available microstates until the total energy is raised sufficiently to surmount an energy barrier. This skewed *measurement* of Ω leads to failure of the condition for an extremum maximum. This is the origin of the erroneous determination of negative heat capacity and ensemble inequivalence for these systems [4–6].

We have determined [5] that, for certain initial temperatures, a system with negative heat capacity put into thermal contact with a system with positive heat capacity cannot possibly arrive at thermal equilibrium without violating the second law of thermodynamics. Ramírez-Hernández *et al.* have shown that two systems with negative heat capacity put into thermal contact cannot possibly arrive at thermal equilibrium without violating the zeroth law of thermodynamics. These results do not imply violations of established fundamental laws; rather, they indicate models, or trapped systems, not representative of physically consistent systems in thermodynamic equilibrium. Equilibrium thermodynamic formalism simply does not apply.

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