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Comment

Comment on "Critical analysis of negative heat capacities in nanoclusters" by Michaelian K. and Santamaría-Holek I.

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Contrary to the claims in a recent letter by Michaelian and Santamaría-Holek (MSH) [1], heat capacities can be negative in atomic clusters. This effect has been carefully examined many times in the past [2–7]. Negative heat capacities can be found in noncanonical ensembles, and have been extensively investigated in microcanonical ensembles, whereas they are always positive in the canonical ensemble. The finite size of the system is a sufficient condition for statistical ensembles to be inequivalent. This inequivalence has also been proved for systems in the thermodynamic limit [8], providing various examples with an "S-bend" in the caloric curve. The Gibbs equation invoked by MSH does not hold in the microcanonical ensemble.

On the other hand, both true non-ergodicity and the failure to achieve ergodicity due to a finite observation time may also cause S-bends in caloric curves. Intermediate states with the solid and liquid phases in contact can be thermodynamically unfavourable because of the free-energy cost of introducing the interface [5]. The related energy barriers between the phases increase with system size. In macroscopic systems they may become too high to overcome on the experimental time scale, leading to phase separation, superheating, and supercooling. Various models have been constructed to show that analogous behaviour can occur in small systems [1,5,9]. The tendency for trapping and ergodicity breaking increases at low temperatures and strongly depends on the energy landscape [6]. Signatures for such metastability are hysteresis effects and associated time dependence.

We have performed Monte Carlo (MC) simulations for the Na_{147} cluster modeled with the same empirical potential as in ref. [10]. In order to circumvent trapping, the parallel tempering strategy was used in both the microcanonical and canonical ensembles along with a multiple histogram analysis [3]. The microcanonical caloric curve (fig. 1) exhibits a clear S-bend in the energy range between 7.62 eV and 8.16 eV, confirming the previous molecular dynamics (MD) results [10]; the canonical curve, as expected, does not. The distribution of potential energies in the canonical ensemble is bimodal near $T_{melt} \simeq 180$ K, which is strictly equivalent to the S-bend in the caloric curve and a convex region in the microcanonical entropy [3,4,6,11]. Contrary to the claims of MSH, bimodality of the energy distribution is expected for a finite system in thermal equilibrium near a first-order phase transition [4]. The S-bend found here for Na_{147} can also be reproduced for other clusters for which MSH suggest that previous simulations were not converged, including Lennard-Jones clusters [3] and Al_{147} [12] (results not shown).
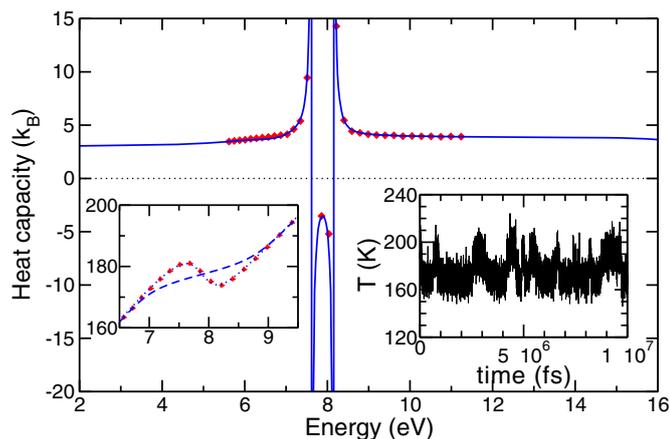

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Fig. 1: (Colour on-line) Microcanonical heat capacity of Na_{147}. The red dots and blue line correspond to values obtained from microcanonical total energy densities of states calculated using microcanonical and canonical parallel tempering MC, respectively. The microcanonical temperature is shown in the lower left inset, along with the canonical curve as a dashed line. The lower right inset shows the variation of the kinetic temperature along an MD trajectory in the coexistence energy range.

The right inset in fig. 1 illustrates dynamical coexistence in Na_{147}. Over 10 ns the cluster exhibits multiple transitions between the solid- and the liquid-like states, at a rate of about one per ns. This result confirms the validity of the experiments [11] that were challenged by MSH. The MD data indicate that the clusters switch several million times between solid-like and liquid-like during the thermalization time. No significant trapping occurs in either state. Furthermore, ergodicity has here been tested experimentally by varying the thermalization time by a factor of ten. No influence on the detected melting points or energy distributions was found. Hence the observed negative heat capacities were not artificially caused by trapping in metastable states as MSH suggest.

The model designed to illustrate nonergodicity by MSH is unsatisfactory in several respects. They assume that the solid-liquid transition involves a gradual change at the molecular level, each atom moving from the solid state to the liquid state individually. This assumption immediately removes any claim to generality, and is also unphysical. Even though many clusters exhibit multi-step melting [13], the solid-liquid transition generally involves two-state behaviour, especially as the system size increases, and melting is a highly cooperative phenomenon.

The MSH model assigns additional degrees of freedom to the "liquid" atoms to represent a higher "rotational energy". In fact the larger heat capacity of the liquid state is due to its higher configurational entropy, which arises from an exponentially larger number of local minima with lower and more anharmonic vibrational frequencies [5]. The MSH model also implies that the physics of the liquid

state can only be described dynamically, and not using statistical mechanics. When applied to two extreme cases, it exhibits either no phase change at all, or a very sharp S-bend. In the latter case, it is rather similar to the system considered by Bixon and Jortner [14], which, contrary to the claims of MSH, neither consists of "discrete energy states" (the level density of *classical* harmonic oscillators is continuous) nor "violates fundamental continuity requirements" (the Heaviside function acts at values where the density of states is continuously differentiable).

We agree with MSH that nonergodicity can cause artificial S-bends in caloric curves, as is well known for macroscopic systems. However, in small atomic clusters such effects are much less likely than MSH have estimated, and can be ruled out for Na_{147} and other systems. The S-bends found here correspond to the negative heat capacities that have a firm foundation in theoretical thermodynamics.

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