Negative Heat Capacity of Small Systems in the Microcanonical Ensemble

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Abstract. We propose a new mechanism to explain the origin of negative heat capacity in small systems. We show how a particular structure of the potential energy surface combined with a microcanonical treatment results in negative heat capacity. Moreover, this effect occurs under true equilibrium conditions. An energy landscape with a sudden and spatially large opening leads to a negative heat capacity. The magnitude of this effect is related to the extent of the opening and the number of particles in the system.
The positive sign of the heat capacity reflects the fact that adding energy to a system results in an increment of its temperature. However, under special conditions certain specific systems behave in the opposite way. Some examples are clusters of 147 sodium atoms[1], astronomical systems like stars or star clusters[2, 3], magnetically self-contained plasma[4] or fragmenting nuclei[5]. The theoretical explanation of this apparent violation of the laws of thermodynamics is based on the differences between the microcanonical and canonical ensembles when the size of the system is small. In this context, a system is considered small when its size is not large as compared to the range of the forces acting between its constituents[6]. This is the case when the system is composed by a few particles, like in atomic clusters, or when the range of the interactions is very large, like in stars. These systems have in common that the thermodynamic limit is not applicable. Moreover, the extensive character of the energy and the entropy is questionable[7]. Considering that all the experimental systems that display a negative heat capacity are totally or almost totally isolated, and considering that the microcanonical description is always valid independently of the number of particles in the system[6], the microcanonical ensemble appears as the proper theoretical framework for a statistical description of this class of systems. With this in mind, several simple model systems have been identified to have negative heat capacity, like clusters of Lennard-Jones particles[8, 9], an ideal gas constrained by an elastic membrane inside a hollow sphere[10], a self-gravitating, spherically confined N-body system[11] or a confined model glass[12].

Even though the astronomers community has known about this phenomenon for a long time as pointed out by D. Lynden-Bell[2], the nature and the origin of the negative heat capacity is still a matter of intense debate[13, 10, 14, 15, 16, 17, 18, 19, 20]. Here we present a new and simple argument that shows how a negative heat capacity may be originated from a particular feature of the energy landscape of the system. The basic idea can be explained qualitatively using Figure 1. In this cartoon, \( r \) is a generic coordinate that represents the configuration of the system. The potential energy contains a well \( W \) and a relatively open region \( O \). For a given configuration in \( W \), i.e. a given value of \( r \), the kinetic energy \( K \) is the distance from the bottom of the well to the total energy line \( E_1 \). If the total energy is smaller than \( U_0 \), then the \( r \) coordinate is restricted to the relatively small space \( W \). If the total energy is larger than \( U_0 \), the system finds the large space of region \( O \) energetically accessible. Considering the principle of equal a priori probability[21], all these space \( (W + O) \) is explored by the system with the same probability density. Therefore, in the calculation of the average kinetic energy, region \( O \) (of low kinetic energy) has a much larger contribution than region \( W \) (of high kinetic energy). Consequently, as the total energy increases beyond \( U_0 \) the average kinetic energy of the system, and therefore the temperature, decreases. This reduction in temperature occurs only for a small range of total energy slightly above the threshold \( U_0 \), and for a small number of particles. Increasing the energy even further results in a monotonic increase of temperature. For a large enough number of particles, the temperature reduction is overcome by mixing effect of the particles.
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Figure 1. Potential energy leading to a negative heat capacity. For a total energy is \( E_1 \), the system is confined to region \( W \). For a total energy \( E_2 \) the system can explore regions \( W \) and \( O \). The kinetic energy for each case is represented by the vertical arrows. The size of each region is proportional to the weight of each contribution to the average kinetic energy (temperature).

It has been argued that the origin of a negative heat capacity is the lack of ergodicity due to the coexistence of metastable states or no true thermodynamic equilibrium in the system[13, 14, 16, 19]. In particular, some small systems are characterized by high energy barriers which may trap the system in a metastable state preventing the thermodynamic equilibrium. With the mechanism presented in this letter, there is no need for the system to have energy barriers between different regions of the configurational space in order to display a negative heat capacity. Also, we will present an example that can be solved with simple numerical methods leaving no doubts about the thermodynamic equilibrium of the solution. The canonical and microcanonical ensembles are equivalent if and only if the thermodynamic limit can be invoked, which is not correct for small isolated systems. The negative heat capacity appears naturally from a microcanonical formulation of the problem. The canonical formulation, instead, results always in a positive heat capacity[15]. In other words, a negative heat capacity is not only possible but is rather a natural result for isolated small systems with a particular energy landscape.

To exemplify the concept presented above, let us consider an ideal system consisting of \( N \) non-interacting particles trapped in a central potential given by:

\[
U(r) = \begin{cases} 
0, & \text{for } r \in [0, L] \\
U_0 + U_1(x - L)^2, & \text{for } r \in ]L, +\infty[
\end{cases}
\]  

(1)

This funnel like potential, resembling the scheme presented in Figure 1, is a square well of width \( L \), surrounded by a parabolic surface characterized by a quadratic coefficient \( U_1 \). This coefficient controls the extent of the accessible space (region \( O \)) once the energy is large enough so that the particles can exit the square well (region \( W \)).

The microcanonical formalism is based on the foundational equation of statistical mechanics, i.e. the Boltzmann entropy:

\[
S = k_B \ln \omega(N, V, E)
\]  

(2)
Figure 2. Caloric curves for the $N = 1$ system in the microcanonical formalism for different cases of Eq. (1). The black line is for the no-well case, $U_0 = 0$ and $U_1 = 0.1$. Red line corresponds to $U_0 = 0.25$ and $U_1 = 0.1$; green line corresponds to $U_0 = 0.5$ and $U_1 = 0.1$ and the blue line corresponds to $U_0 = 0.5$ and $U_1 = 1$.

Here, $k_B$ is the Boltzmann’s constant, $N$ represents the number of particles, $V$ is the total volume, $E$ the total energy of the system and $\omega(N, V, E)$ is the number of states of the system with total energy $E$:

$$\omega(N, V, E) = \frac{1}{C} \int dxdp \delta(E - H(x, p))$$

(3)

where $C$ is a constant. Following Pearson’s Laplace transform technique[22], the integral in the momenta can be carried out leading to the expression

$$\omega(N, V, E) = \frac{1}{C_1} \int dx (E - U(x))^{(F/2 - 1)} \Theta(E - U(x))$$

(4)

where $F$ is the total number of degrees of freedom and $U(x)$ is the potential energy of the system. The Heaviside step function $\Theta(E - U(x))$ allows only those configurations with total potential energy smaller than or equal to $E$. The microcanonical average of any function of the system coordinates can be expressed as[22]

$$< A >= \frac{\int dx A(x) (E - U(x))^{(F/2 - 1)} \Theta(E - U(x))}{\int dx (E - U(x))^{(F/2 - 1)} \Theta(E - U(x))}$$

(5)

Within this formalism, an expression for the temperature can be obtained using $1/T = (\partial S/\partial E)_V$, which is an equation derived from the conservation of energy and the thermodynamic relation $dS = dQ/T$. The microcanonical temperature results

$$k_B T = \frac{1}{< K^{-1} > \left( \frac{F}{2} - 1 \right)}$$

(6)

where $K$ is the total kinetic energy of the system, and $< K^{-1} >$ is the average of the inverse of the kinetic energy, calculated using Eq. (5).

The relation between $K$ and $T$ of Eq. (6) is a direct consequence of the definition of entropy, Eq. (2). Indeed, if instead of using $\omega(N, V, E)$ as a measure of the number of states we use

$$\Omega(N, V, E) = \frac{1}{D} \int dxdp \Theta(E - H(x, p))$$

(7)
the resulting relation is the more familiar
\[ k_B T = 2/F <K> . \]  

Both relations, Eqs. (6) and (8), are equivalent in the thermodynamic limit, and they show same differences for small \( N \). In all our calculations we have used Eq. (2) as the entropy definition, so the temperature is calculated according to Eq. (6).

The calculation of \( T \) in the microcanonical ensemble for a particular example imply the calculation of the average of the inverse of the kinetic energy, \( < K^{-1} > \). This can be done using Eq. (5) with \( A(x) = 1/(E - U(x)) \). In principle, since we are considering a system of non-interacting particles the calculation could be performed analytically. The solution involves a complicated combination of inverse trigonometric functions that should be evaluated numerically. Alternative and equivalent approaches are: (i) brute force Monte Carlo integration and (ii) importance sampling calculation following a simulation methodology[23]. Both methods are equivalent, although the simulation requires far less computational efforts. The solution of the corresponding canonical equations can be obtained analytically with no major difficulties.

To exemplify the predictions of the microcanonical formalism we show in Figure 2 the caloric curves corresponding to the simple case of \( N = 1 \), and a variety of representative potential energy surfaces. Even though this is a completely deterministic case, it captures the relevant features of larger systems that exhibit negative heat capacity. If the energy surface has no well, and therefore not sudden opening step allowing for a majority of low kinetic energy states, there is a monotonic relation between temperature and total energy, as shown by the black line of Figure 2. For finite values of \( U_0 \), the system experiences a decrease in temperature when the total energy exceed this threshold value. The magnitude of this ‘cooling’ effect depends on the extent of the opening in the potential energy: for a fixed total energy \( E \) (slightly larger than \( U_0 \)) a smaller value of \( U_1 \) results in a larger available region to explore at low kinetic energy,
and consequently a steeper decrease in temperature.

The probability distribution for states of different total energy, $P_T(E)$, is displayed in Figure 3 for one representative potential at three different temperatures. This is a complementary view often used to analyze the results for cluster systems. According to Schmidt et al.[1] a bimodal energy distribution is a necessary and sufficient condition for the system to display a negative heat capacity. For low temperature, the system remains completely in the well and explore configurations of total energy smaller than the threshold value $U_0$. For intermediate temperatures, $P_T(E)$ has a bimodal character, reminiscent of a cluster undergoing the transition from the solid to liquid state as calculated by microcanonical simulations[9]. The bi-modal distribution for the potential energy of Eq. (1) has its first peak at $E = k_B T/2$, and this is only possible if $k_B T/2 < U_0$. Then, in the limit of vanishing well, i.e. $U_0 \rightarrow 0$, the energy distribution cannot be bi-modal at any temperature. For higher temperatures, the distribution changes to a single modal curve, with a small perturbation in the low energy region due to the well.

The effect of the number of particles in the system is shown in Figure 4. For $N = 2$ there is a sharp decrease in the temperature as the total energy increases beyond $U_0$. Moreover, a second (although very weak) minimum is observed for $E > 2U_0$. The first minimum corresponds to one particle having the possibility to leave the potential well, and the second minimum appears once there is enough energy for both particles to explore regions beyond the potential well. Increasing the number of particles results in a weakening of the temperature drop effect due to the mixing entropy of the system. For $N = 5$ the caloric curve shows only a slight change in curvature that reflect the irregularities of the potential energy curve, but no minimum is present for this particular choice of parameters. Moreover, the caloric curve calculated using standard canonical statistics is very close to the one calculated with the microcanonical formalism. All the results presented in Figure 4 were obtained by Monte Carlo simulations, as explained in
ref. [23]. For the case of $N = 3$ we include the result obtained by simple Monte Carlo integration. Clearly, both methods produce the same output. However, the simulation method is far more efficient as displayed by the relative noise of the two results.

We have to emphasize the fact that the negative heat capacity is a true equilibrium phenomena occurring in small isolated systems. The microcanonical formalism is the appropriate theory for the treatment of isolated systems, and the negative heat capacity is a manifestation of the constancy of the system's total energy. The canonical ensemble, since it impose thermal equilibrium with an infinite bath, is inadequate to describe an isolated system. The two ensembles are equivalent in the limit of large number of particles, where no negative heat capacity is possible as it is well known from classical thermodynamics.

The question that arises is how to connect the simple arguments presented in this letter using a simple central field with the complexity of the energy landscape of a true atomic or molecular cluster. We cannot provide a formal connection, however there is some evidence that suggest that our argument is correct. Clusters of Lennard-Jones particles have been studied by several groups for a variety of sizes. Among them, the clusters of $N = 55$ and $N = 147$ particles are the ones that show the stronger negative heat capacity effect. Also, $N = 147$ is the number of atoms in the sodium clusters on which a negative heat capacity was experimentally determined. The optimal configuration of these clusters correspond to closed shell icosahedral structures with a compact inner core that result in a very low total potential energy. There are 42 and 92 particles on the surface of the cluster of $N = 55$ and $N = 147$, respectively. If the total energy of the system is just enough for the surface particles to explore the open space while keeping the core approximated unperturbed, the cluster can do that in many different ways since the majority of the particles are on the surface. Therefore, it is reasonable to think that a relatively large region of the configurational space is available to the surface particles with a small increment of the total energy.

In conclusion, we have presented a simple argument that explains how a negative heat capacity in small systems appears from a particular feature of the potential energy surface. We do not claim that this is the only mechanism that lead to a negative heat capacity. However, our work clearly shows that it is not necessary to have metastable states, large energy barriers or even ergodicity breaking for the system to have a negative heat capacity. A sudden opening in the potential energy landscape is enough to induce a negative heat capacity in small systems when the microcanonical ensemble is used to describe its statistical behavior.

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