

Remarks on Negative Heat Capacities of Clusters

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Abstract. The concept of negative heat capacities of clusters has been examined and argued. This discussion examines the arguments and concepts with the goal of clarifying the inherent ambiguities in the concept itself. We also show how one must use caution with this and related concepts that extend to nonequilibrium systems properties that are well defined just for equilibrium systems.

INTRODUCTION—PECULIARITIES OF CLUSTERS

Atomic and molecular clusters have many properties that bulk matter cannot show, such as bands of temperature and pressures within which two or more phase-like forms may coexist, e.g., solid and liquid or two solid forms. Thermodynamics of such small systems sometimes looks very unlike the textbook thermodynamics that undergraduates learn, but thermodynamics and thermodynamic properties retain their validity for ensembles of small systems just as much as for ensembles of bulk systems. However, there are some phenomena that clusters exhibit that cannot be found for bulk matter. In particular, the phase changes of clusters are quite different from those of macroscopic systems.¹ The equilibrium for two phases, whether of a bulk or microscopic system, can be described by an equilibrium constant, e.g., $K_{\text{eq}}(T) = [\text{liquid}]/[\text{solid}]$ for a solid–liquid transition. Such a constant is related, of course, to the free energy difference $\Delta F(T)$ of the two forms: $K_{\text{eq}}(T) = \exp(-\Delta F/kT) = \exp(-N\Delta\mu/kT)$, where N is the number of particles in the system and $\Delta\mu$ is the mean difference in the chemical potentials of the two phases. Hence, even if $\Delta\mu/kT$ is very small, e.g., 10^{-10} , but N is of order 10^{20} , then the thermodynamically unfavored phase is so unfavored that it is simply unobservable. However, if N is of order 10 or 1000, then, so long as each phase persists long enough to establish conventional properties by which we recognize it as such, it can be quite easy to find ranges of temperature and pressure, *bands* of T and p , in which two—or even more—phases may coexist *in thermodynamic equilibrium*. In such situations, the distinction is lost between “phase” and

“component”, insofar as isomers can be considered components.

HEAT CAPACITIES, NORMAL AND OTHERWISE

One of the properties that has long been discussed in such contexts is the heat capacity of a cluster.^{2–4} Under most circumstances, such a heat capacity is qualitatively like that of its bulk counterpart. However, in a region of coexistence of two or more phases, things may be more complicated, especially if one looks at ensembles that are not canonical. In particular, the possibility arises that clusters may exhibit negative heat capacities. Such behavior came to attention when simulations of clusters showed caloric curves—energy E vs. temperature T —with “S-bends,” regions in which the temperature was said to decrease when the energy of the cluster increased.

This phenomenon came under closer scrutiny, particularly regarding the conditions under which negative heat capacities appeared as regions of negative slope in curves of T vs. E .⁵ Wales et al. argued that such S-bends and corresponding negative heat capacities could occur in simulations under conditions of constant energy, but not under conditions of constant temperature.^{6–9} This meant that the *mean* energy of a system at specified temperature would be a strictly increasing function of temperature, but that the *mean* or *effective* temperature need not be a strictly increasing function of energy. Many aspects of this subject have been summarized in a very recent book by Wales¹⁰ (especially Chapter 8), so we shall not attempt to give a thorough discussion of all

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aspects of this subject here. Rather, we will focus on a few cogent issues that have not received much attention.

The temperature T is a well-defined, unambiguous variable for describing systems at thermodynamic equilibrium, and can be used almost as well for many kinds of systems very close to equilibrium. Among these are flow systems in which small but macroscopic regions can be considered as having constant local temperatures, yet the temperatures of successive regions along the flow path are not the same. These are described as systems in "local thermal equilibrium." Likewise, lasers have been described in terms of one temperature for all the energy levels and degrees of freedom that are not directly involved in the lasing process, and other temperatures, based just on the population of the lasing levels, for those states. However in systems or ensembles far from equilibrium, the concept of temperature is not so simply established. Extreme cases are, for example, microcanonical ensembles and evaporative ensembles.¹¹ Let us examine microcanonical ensembles and the meaning of "temperature" for them, and then consider the relation of such temperature(s) to the possibility of negative heat capacities.

Two definitions have been used for the *effective* temperature of a microcanonical ensemble. One such definition is $T_1 \equiv (\partial S/\partial E)_{N,V}^{-1}$. This definition, of course, requires that the entropy be the *microcanonical* entropy. The corresponding relation for an isothermal system, based on the canonical entropy, is a physical relation, not simply a definition. The other commonly used definition is $T_2 \equiv 2 \langle E_{\text{kinetic}} \rangle / k_B (3N - 6)$, i.e., the mean kinetic energy per degree of freedom in units of the Boltzmann constant k_B . These two formulas are equivalent for canonical distributions with the canonical entropy. However, they are not, in general, equivalent for microcanonical ensembles or for other nonequilibrium ensembles. In fact, they may differ by an amount proportional to $1/N$.^{12,13}

A very simple, well-known physical argument makes clear why and how the heat capacity, $C = \partial E/\partial T$, (with volume V , pressure p , or other variables held constant, as appropriate) of a canonical ensemble must be positive.¹⁴ The heat capacity is directly related to the fluctuations of energy in the isothermal systems: $C = \langle (E - \langle E \rangle)^2 \rangle / k_B T^2$. This is clearly a positive quantity.

An equally straightforward argument makes clear why and how the effective heat capacity of a microcanonical ensemble, $C'' \equiv \partial E/\partial T_2$, based on temperature T_2 defined in terms of the mean kinetic energy, may be negative. This is an argument from a microscopic viewpoint, requiring us to interpret phase-like forms of clusters in terms of where they reside on their potential energy surface. When a cluster is in a solid

form, it is localized in a relatively deep, narrow potential well, so that the atomic motions have small amplitudes. When the cluster is liquid, it resides on a sort of rolling plain, so that the atoms are mobile and can move rather readily through many conformations, without encountering high barriers. But that rolling plain must have a mean potential energy high relative to the bottom of the well corresponding to the solid. At low energies, the system cannot escape the deep minimum, and is therefore solid. At high enough energies, the system moves between the well of the solid and the high rolling plain essentially as readily as it moves about in that plain, and is therefore simply a liquid. However, many clusters show ranges of energy (or temperature) in which solid and liquid forms exist in recognizable, dynamic equilibrium. To be recognizable, the systems must spend intervals long enough in each region to develop properties characteristic of each phase. Hence there must be enough of a barrier that separates the solid and liquid regions of the potential surface to yield those sufficiently long dwell times. The barrier must at least partly be energetic in origin because of the necessity of forming interior voids to make the liquid.

If the system is indeed at constant energy, then it moves on a plane of that constant energy above the potential energy surface. When the system is in the solid region, it is high above the deep well of the solid and therefore has a high kinetic energy, and is therefore a hot solid! When it is above the high, rolling plain of the liquid, it has a much smaller kinetic energy, and is therefore a cold liquid! At a fixed energy in the interval of solid-liquid coexistence, therefore, the system passes between being a hot solid and a cold liquid.¹⁵

Now we turn to the effective heat capacity. In most situations, perhaps all, the available volume of phase space above the rolling plain of the liquid increases more rapidly with energy than that above the well of the solid. Hence as the total energy of the cluster increases, it spends a larger fraction of time in the liquid region, of high potential energy and low kinetic energy. Especially if increasing the energy allows the system to climb into regions of ever higher potential energy, then the average kinetic energy of the liquid may remain low, even as its total energy increases. This is exactly the situation in which increasing the energy of the system and the ensemble *lowers the mean kinetic energy*, and thereby lowers the kinetic temperature T_2 . This is precisely the basis for a negative heat capacity, based on this definition of temperature.

There is now considerable experimental evidence for negative heat capacities of microcanonical ensembles of clusters.¹⁶⁻¹⁸ It is likely that the effective temperatures inferred for these ensembles are the kinetic tempera-

tures, T_2 . There are now many persuasive results from simulations and analytic theory to give credence to the negative heat capacities of clusters of adequate size.^{6,9,13,19–25} Clusters as small as Ar_{13} , however, do not exhibit negative heat capacities, even though they do show regions of coexisting phases. On the other hand, Ar_{55} does show an S-bend in its microcanonical caloric curve, when the kinetic definition of temperature is used.

Now we come to the final point of this discussion. Suppose we use the definition based on the microcanonical entropy, T_1 , rather than the kinetic definition. In this case, the conditions that would give a negative heat capacity are far less immediately physically plausible than those invoked for a heat capacity based on T_2 . In most physical systems with unbounded spectra of energy levels, we expect the density of states to be a monotonically increasing function of energy—not necessarily a smooth function—but nonetheless monotonic. Hence the microcanonical entropy must also be a monotonically increasing function of energy. Therefore T_1^{-1} or $\partial S/\partial E > 0$, a perfectly natural relation, (apart from situations in which negative temperatures are invoked to describe inverted populations among finite numbers of energy levels). The heat capacity is still $\partial E/\partial T$, for whatever T we choose, in this case T_1 . The independent variable is, however, the energy and not the temperature, so it is more appropriate to consider C^{-1} or $\partial(\partial E/\partial S)/\partial E$ as the quantity whose sign we want to understand. So long as the slope of E , as a function of entropy, increases with energy, this microcanonical heat capacity is positive. Only if $\partial E/\partial S$ had a dependence of the form $E^{-\alpha}$ in some energy range (for positive α), or $\partial S/\partial E$ varied as E^α , would the heat capacity itself be negative in that range. But this S is the logarithm of the density of states, $\Omega(E)$, so this microcanonical heat capacity can be negative if the fractional change of Ω with energy follows a power law, $\Omega^{-1}(\partial\Omega/\partial E) \propto E^\alpha$. Under most conditions, we would normally expect that the fractional change in the density of states with energy would be a flat or slowly decreasing function, although the density itself typically increases rapidly. For example, if $\Omega(E)$ increases as E^γ with γ positive, then the fractional change in $\Omega(E)$ varies as E^{-1} ; if $\Omega(E)$ increases exponentially, the fractional change is of course constant. However, there is probably nothing to rule out the possibility that it could increase at a faster rate in some energy range, and, thereby, lead to a negative heat capacity in that region.

CONCLUSION AND FUTURE DIRECTIONS

We infer that the effective heat capacity of the systems in a microcanonical ensemble may have at least two

nonequivalent definitions, depending on how the effective temperature is defined. Moreover, with either of these definitions the heat capacity may be negative in some range of energy, but the two heat capacities may have different signs. It will be a challenge to find cases in which $C'(E)$, that based on “entropic temperature,” is positive and $C''(E)$, based on the kinetic temperature, is negative, and cases in which both are negative. It will also be a challenge to find the necessary and sufficient conditions for both of these sign relationships. A still more subtle challenge will be to determine whether there are any conditions under which C'' is positive and C' is negative, the opposite of what we would normally expect. Further, we may well ask similar questions about the other related functions for compressibility, magnetization, and electric polarization. All of these reveal some of the striking aspects of the behavior of small systems, a subject that has fascinated Joshua Jortner, and to which he and his colleagues have made monumental contributions.

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