Negative heat-capacity at phase-separations in microcanonical thermostatistics of macroscopic systems with either short or long-range interactions

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Abstract

Conventional thermo-statistics address infinite homogeneous systems within the canonical ensemble. However, some 170 years ago the original motivation of thermodynamics was the description of steam engines, i.e. boiling water. Its essential physics is the separation of the gas phase from the liquid. Of course, boiling water is inhomogeneous and as such cannot be treated by conventional thermo-statistics. Then it is not astonishing, that a phase transition of first order is signaled canonically by a Yang-Lee singularity. Thus it is only treated correctly by microcanonical Boltzmann-Planck statistics. This was elaborated in the talk presented at this conference. It turns out that the Boltzmann-Planck statistics is much richer and gives fundamental insight into statistical mechanics and especially into entropy. This can be done to a far extend rigorously and analytically. The deep and essential difference between “extensive” and “intensive” control parameters, i.e. microcanonical and canonical statistics, was exemplified by rotating, self-gravitating systems. In the present paper the necessary appearance of a convex entropy $S(E)$ and the negative heat capacity at phase separation in small as well macroscopic systems independently of the range of the force is pointed out.

Key words: Foundation of classical Thermodynamics, negative heat capacity, macroscopic systems
1 Introduction

Since the beginning of thermodynamics in the first half of the 19th century its original motivation was the description of steam engines and the liquid to gas transition of water. Here water becomes inhomogeneous and develops a separation of the gas phase from the liquid, i.e. water boils.

A little later statistical mechanics was developed by Boltzmann (1) to explain the microscopic mechanical basis of thermodynamics. Up to now it is generally believed that this is given by the Boltzmann-Gibbs canonical statistics. As traditional canonical statistics works only for homogeneous, infinite systems, phase separations remain outside of standard Boltzmann-Gibbs thermostatistics, which, consequently, signal phase-transitions of first order by Yang-Lee singularities.

It is amusing that this fact that is essential for the original purpose of thermodynamics to describe steam engines was never treated completely in the past 150 years. The system must be somewhat artificially split into (still macroscopic and homogeneous) pieces of each individual phase (2). The most interesting configurations of two coexisting phases cannot be described by a single canonical ensemble. Important inter-phase fluctuations remain outside, etc. This is all hidden due to the restriction to homogeneous systems in the thermodynamic limit.

Also the second law can rigorously be formulated only microcanonically: Already Clausius (3) distinguished between external and internal entropy generating mechanisms. The second law is only related to the latter mechanism (4), the internal entropy generation. Again, canonical Boltzmann-Gibbs statistics is insensitive to this important difference.

For this purpose, and also to describe small systems like fragmenting nuclei or non-extensive ones like macroscopic systems at phase-separation, or even very large, self-gravitating, systems, we need a new and deeper definition of statistical mechanics and as the heart of it: of entropy. For this purpose it is crucial to avoid the thermodynamic limit.

As the main aspects of this new thermodynamics were published in (5, 6, 7, 8, 9) I skip here to repeat all the arguments. Instead I will stress here only the fact that negative heat capacity and convex entropy can be seen at proper phase transitions of 1. order, i.e. at phase separation, in small as well in macroscopic systems independently whether they have long or short range interactions. As there was a hot discussion at this conference about this point, it seems necessary to repeat the arguments here.
Negative heat capacity at phase-separation can also be seen in macroscopic systems independently of the range of the interaction.

The argument is simple c.f. (9). At phase separation the weight $e^{S(E)-E/T}$ of the configurations with energy $E$ in the canonical partition sum

$$Z(T) = \int_0^\infty e^{S(E)-E/T} dE$$

becomes bimodal, at the transition temperature it has two peaks, the “liquid” and the “gas” configurations which are separated in energy by the latent heat. Consequently $S(E)$ must be convex ($\partial^2 S/\partial E^2 > 0$, like $y = x^2$) and the weight in (1) has a minimum at $E_{\text{min}}$ between the two pure phases. Of course, the minimum can only be seen in the microcanonical ensemble where the energy is controlled and its fluctuations forbidden. Otherwise, the system would fluctuate between the two pure phases by an, for macroscopic systems even macroscopic, energy $\Delta E \sim E_{\text{lat}} \propto N$ of the order of the latent heat in clear contrast to the usual assumption of the fluctuations in the canonical ensemble $\delta E \propto \sqrt{N}$. The heat capacity is

$$C_V(E_{\text{min}}) = \partial E/\partial T = - \left(\frac{\partial S/\partial E}{\partial^2 S/\partial E^2}\right)_{E_{\text{min}}} < 0.$$

I.e. the convexity of $S(E)$ and the negative microcanonical heat capacity are the generic and necessary signals of any phase-separation (10).

This “convex intruder” in $S(E)$ with the depth $\Delta S_{\text{surf}}(E_{\text{min}})$ has a direct physical significance: Its depth is the surface entropy due to constraints by the existence of the inter-phase boundary between the droplets of the condensed phase and the gas phase and the corresponding correlation. $\Delta S_{\text{surf}}(E_{\text{min}})$ is directly related to the surface tension per surface atom (with number $N_{\text{surf}}$) of the droplets.

$$\frac{\sigma_{\text{surf}}}{T_{\text{tr}}} = \frac{\Delta S_{\text{surf}}(E_{\text{min}})}{N_{\text{surf}}}$$

In my paper together with M. Madjet (11) we have compared the values of $\Delta S_{\text{surf}}(E_{\text{min}})$ calculated by Monte-Carlo using a realistic short range interaction with the values of the surface tension of the corresponding macroscopic system. In these calculations we used the empirical liquid drop parameters for the ground-states energies of the different clusters as given by (12). Table (1) shows the scaling behavior of $\Delta S_{\text{surf}}(E_{\text{min}})$ with the size $N$ of the system.
Fig. 1. Microcanonical Monte-Carlo (MMMC) simulation of the entropy $s(e)$ per atom ($e$ in eV per atom) of a system of $N = 1000$ sodium atoms at an external pressure of 1 atm. At the energy $e \leq e_1$ the system is in the pure liquid phase and at $e \geq e_3$ in the pure gas phase, of course with fluctuations. The latent heat per atom is $q_{lat} = e_3 - e_1$. Attention: the curve $s(e)$ is artificially sheared by subtracting a linear function $25 + e \cdot 11.5$ in order to make the convex intruder visible. $s(e)$ is always a steep monotonic rising function. We clearly see the global concave (downwards bending) nature of $s(e)$ and its convex intruder. Its depth is the entropy loss due to additional correlations by the interfaces. It scales $\propto N^{-1/3}$. From this one can calculate the surface tension per surface atom $\sigma_{surf}/T_{tr} = \Delta s_{surf} \cdot N/N_{surf}$. The double tangent (Gibbs construction) is the concave hull of $s(e)$. Its derivative gives the Maxwell line in the caloric curve $e(T)$ at $T_{tr}$. In the thermodynamic limit the intruder in $s(e)$ would disappear and $s(e)$ would approach the double tangent from below, not of course in $S(E)$, which remains deeply convex: The probability of configurations with phase-separations is suppressed by the (infinitesimal small) factor $e^{-N^{2/3}}$ relative to the pure phases and the distribution remains strictly bimodal in the canonical ensemble in which the region $e_1 < e < e_3$ of phase separation gets lost.

Roughly $\Delta S_{surf}(E) \propto N^{2/3}$ and one may argue that this will vanish compared to the ordinary leading volume term $S_{vol}(E) \propto N$. However, this is not so as $S_{vol}(E)$ at energies inside the phase-separation region (the convex intruder) is the concave hull of $S(E)$ (its slope gives the Maxwell construction of the caloric curve $T(E)$). It is a straight line and its curvature $\partial^2 S_{vol}/\partial E^2 \equiv 0$. Consequently for large $N$

$$\partial^2 S/\partial E^2 \sim \partial^2 S_{vol}/\partial E^2 + \partial^2 \Delta S_{surf}/\partial E^2 + \cdots \approx \partial^2 \Delta S_{surf}/\partial E^2$$

and the depth of the intruder $\Delta S_{surf}(E_{min}) = \sigma/T_{tr} \cdot N_{surf} \sim N^{2/3}$ goes to infinity in the thermodynamic limit. Of course, the ubiquitous phenomena of phase separation exist only by this reason. It determines the (negative) heat capacity as in eq.(2). The physical (quite surprising) consequences are discussed in [8; 8].
Table 1
Parameters of the liquid–gas transition of small sodium clusters (MMMC-
calculation [11, 10]) in comparison with the bulk for a rising number $N$ of atoms,
$N_{\text{surf}}$ is the average number of surface atoms (estimated here as $\sum N_{\text{cluster}}^{2/3}$) of all
clusters with $N_i \geq 2$ together. $\sigma/T_{\text{tr}} = \Delta s_{\text{surf}} * N/N_{\text{surf}}$ corresponds to the surface
tension. Its bulk value is adjusted to agree with the experimental values of the $a_s$
parameter which we used in the liquid-drop formula for the binding energies of small
clusters, c.f. Brechinac et al. [12], and which are used in this calculation [10] for
the individual clusters.

| $N$   | 200   | 1000  | 3000  | bulk |
|-------|-------|-------|-------|------|
| $T_{\text{tr}}$ [K] | 940   | 990   | 1095  | 1156 |
| $q_{\text{lat}}$ [eV] | 0.82  | 0.91  | 0.94  | 0.923 |
| $s_{\text{boil}}$ | 10.1  | 10.7  | 9.9   | 9.267 |
| $\Delta s_{\text{surf}}$ | 0.55  | 0.56  | 0.44  |
| $N_{\text{surf}}$ | 39.94 | 98.53 | 186.6 | $\infty$ |
| $\sigma/T_{\text{tr}}$ | 2.75  | 5.68  | 7.07  | 7.41 |

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