Heat can flow from cold to hot
Microcanonical Thermodynamics of finite systems
and the microscopic origin of phase transitions

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Microcanonical Thermodynamics [1] allows the application of Statistical Mechanics to finite and even small systems. As surface effects cannot be scaled away, one has to be careful with the standard arguments of splitting a system into two or bringing two systems into thermal contact with energy or particle exchange: Not only the volume part of the entropy must be considered. The addition of any other macroscopic constraint like a dividing surface, or the enforcement of gradients of the energy/particle reduce the entropy. As will be shown here, when removing such constraint in regions of a negative heat capacity, the system may even relax under a flow of heat against the temperature slope. Thus Clausius formulation of the Second Law: "Heat always flows from hot to cold" can be violated. However, the Second Law is still satisfied and the total Boltzmann-entropy is rising. In the final chapter the general microscopic mechanism leading to the convexity of the microcanonical entropy at phase separation is discussed. This is explained for the liquid–gas and the solid–liquid transition.

I. INTRODUCTION

In conventional (extensive) thermodynamics the thermal equilibrium of two systems is established by bringing them into thermal contact which allows free energy exchange [12]. Equilibrium is established when the total entropy

\[ S_{\text{total}} = S_1 + S_2 \]  

is maximal:

\[ dS_{\text{total}} = dS_1 + dS_2 = 0. \]  

Under an energy flux \( \Delta E_{2\to1} \) from 2 \( \to \) 1 the total entropy changes by

\[ \Delta S_{\text{total}} = (\beta_1 - \beta_2)\Delta E_{2\to1} \]  

\[ \beta = dS/dE = \frac{1}{T} \]

Consequently, a maximum of \( S_{\text{total}}(E = E_1 + E_2) \) will be approached when

\[ \text{sign}(\Delta S_{\text{total}}) = \text{sign}(T_2 - T_1)\text{sign}(\Delta E_{2\to1}) > 0 \]  

From here Clausius' first formulation of the Second Law follows: "Heat always flows from hot to cold". Essential for this conclusion is the additivity of \( S \) under the split (eq[4]). Temperature is an appropriate control parameter for extensive systems.

II. STABILITY AGAINST SPONTANEOUS ENERGY-GRADIENTS

For a small or a very large self-gravitating system, c.f. [1], additivity and extensivity of \( S \), and also of \( E \), is not given. In fact this is the main reason to develop this new and extended version of thermodynamics. At phase separation the microcanonical caloric curve \( T(E) \) is backbending. Here the heat capacity \( C = -(\partial^2 E/\partial T^2) \) becomes negative, the curvature \( \partial^2 S/\partial T^2 \) is positive, and \( S(E) \) is convex. This is the generic signal of a phase transition of first order [1]. The Potts-model illuminates in a most simple example the occurrence of a backbending caloric curve [2] [13]. A typical plot of \( s(e) = S(E = N\epsilon)/N \) in the region of phase separation is shown in fig[1]. Section [14] discusses the general microscopic reasons for the convexity.

Let us split the system into two pieces \( a + b \) by a dividing surface, with half the number of particles each. The dividing surface is purely geometrical. It exists only as long as the two pieces can be distinguished by their different energy/particle \( \epsilon_a \) and \( \epsilon_b \). If the constraint on the difference \( \epsilon_b - \epsilon_a \) is fully relaxed and \( \epsilon_b - \epsilon_a \) can fluctuate freely at fixed \( \epsilon_2 = (\epsilon_a + \epsilon_b)/2 \), the dividing surface is assumed to have no further physical effect on the system. Constraining the energy-difference \( \epsilon_b - \epsilon_a = \Delta \epsilon \) between the two, reduces the number of free, unconstrained degrees of freedom and reduces the entropy by \(-\Delta \Sigma\).

In the convex region (upwards concave like \( y = x^2 \)) of \( s(e) \) this becomes especially evident: at \( e = \epsilon_2 \sim \epsilon_{\text{min}} \), \( \epsilon_a = \epsilon_2 - \Delta \epsilon/e/2 \) and \( \epsilon_b = \epsilon_2 + \Delta \epsilon/e/2 \), the simple algebraic sum of the individual entropies \( s_{\text{sum}} = (s_a + s_b)/2 \) leads to \( s_{\text{sum}} \geq s_2 \). However, \( e^{S_2} \) is already the sum over
From this little exercise we learn that the microcanonical entropy per particle \( s(e, N, \sigma) \) of a finite system depends not only on the energy per particle \( e = E/N \) and possibly still on the particle number \( N \) (for a non-extensive system) but also on the boundary (the container), or any other non-extensive external constraint, via \( \Sigma = N\sigma \). If one splits a given configuration like in eq. (1) one must not forget the change \( -\Delta \Sigma \) in the surface entropy. The correct entropy balance, before and after establishing the energetic split \( e_b > e_a \) of the system, is

\[
s_{\text{after}} - s_{\text{before}} = \frac{s_a + s_b}{2} - s_2 - \Delta \sigma \leq 0 \quad (6)
\]
even though the sum of the first two terms is positive.

In the inverse direction: Only by relaxing the constraint and by allowing, on average, for an energy-flux (\( \Delta e_{b\to a} > 0 \)) opposite to \( T_a - T_b > 0 \), against the temperature-gradient (slope), but in the direction of the energy-slope, an increase of \( s_{\text{total}} \to s_2 \) is obtained. Then, on average both energies \( e_a \) and \( e_b \) become equal \( e_2 \) and \( \Delta \sigma = 0 \). Or in other words, starting with an energy difference \( \Delta e = e_b - e_a \geq 0 \) the allowance of unconstrained energy fluctuations around \( \Delta e = 0 \) between the two subsystems implies the disappearance of \( \Delta \sigma \) and in general leads to an increase of the total entropy. This is consistent with the naive picture of an energy equilibrium. Thus Clausius’ ”Energy flows always from hot to cold” is violated. Of course this shows again that unlike to extensive thermodynamics the temperature is not an appropriate control parameter in non-extensive systems.

In the thermodynamic limit \( N \to \infty \) of a system with short-range coupling \( \Delta \Sigma \sim N^{-2/3} \), \( \Delta \Sigma/N = \Delta \sigma \sim N^{-1/3} \) must go to 0 due to van Hove’s theorem.

III. THE ORIGIN OF THE CONVEXITY OF \( S(E) \) AT PHASE SEPARATION

Here I discuss the general microscopic mechanism leading to the appearance of a convex intruder in \( S(E, V, \cdots) \). This is the signal of phase transitions of first order and of phase-separation within the microcanonical ensemble.

I assume the system is classical and obeys the Hamiltonian:

\[
H = \sum_{i,j=1,N} \left\{ \frac{p_i^2}{2m} \delta_{i,j} + V^{\text{int}}(\vec{r}_i - \vec{r}_j) \right\} \quad (7)
\]

In this case the system is controlled by energy and volume.

A. Liquid–gas transition

The microcanonical sum of states or partition sum is:
\[ W(E, N, \mathcal{V}) = \frac{1}{N!(2\pi\hbar)^{3N}} \int_{\mathcal{V}^N} d^{3N} \mathbf{r}_i \int d^{3N} \mathbf{p}_i \delta[E - \sum_i \frac{p_i^2}{2m_i} - V^{\text{int}}(\mathbf{r}_i)] \]
\[ = \frac{\mathcal{V}^N (E - E_0)^{(3N-2)/2}}{N!(3N/2) (2\pi\hbar^2)^{3N/2}} \int_{\mathcal{V}^N} d^{3N} \mathbf{r}_i \left( \frac{E - V^{\text{int}}(\mathbf{r}_i)}{E - E_0} \right)^{(3N-2)/2} \]
\[ = W^{\text{id-gas}}(E - E_0, N, \mathcal{V}) \times W^{\text{int}}(E - E_0, N, \mathcal{V}) \]
\[ = e^{[S^{\text{id-gas}} + S^{\text{int}}]} \]
\[ \int_{\mathcal{V}^N} d^{3N} \mathbf{r}_i \left( 1 - \frac{V^{\text{int}}(\mathbf{r}_i) - E_0}{E - E_0} \right)^{(3N-2)/2} \]

\[ \mathcal{V} \] is the spatial volume. \( E_0 = \min V^{\text{int}}(\mathbf{r}) \) is the energy of the ground-state of the system.

The separation of \( W(E, N, \mathcal{V}) \) into \( W^{\text{id-gas}} \) and \( W^{\text{int}} \) is the microcanonical analogue of the split of the canonical partition sum into a kinetic part and a configuration part:

\[ Z(T) = \frac{\mathcal{V}^N}{N!} \left( \frac{mT}{2\pi\hbar^2} \right)^{3N/2} \int_{\mathcal{V}^N} d^{3N} \mathbf{r}_i e^{-\frac{V^{\text{int}}(\mathbf{r}_i)}{\mathcal{V}}} \]

In the thermodynamic limit the order parameter of the (homogeneous) liquid-gas transition is the density. The transition is linked to a condensation of the system towards a larger density controlled by pressure. For a finite system we expect the analogue. However, here controlled by pressure. For a finite system we expect the analogue. However, here controlled by pressure.

In eqs. (11,12) the integration is only over regions in 3N-dim coordinate space where \( V^{\text{int}}(\mathbf{r}_i) \) is smaller than \( E \), where the big brackets are positive. The volume \( \mathcal{V}^N(E) \leq \mathcal{V}^N \) is the accessible part of the spatial volume outside of the forbidden 3N-dim regions with \( V^{\text{int}}(\mathbf{r}_i) > E \). I.e. the eigen-volume of the condensate (droplets) at the given energy. \( \mathcal{V}^N(E) \) has the limiting values:

\[ \mathcal{V}^N(E) \] for \( E \) in the gas phase
\[ \mathcal{V}^N_0 \] for \( E = E_0 \)

So that \( W^{\text{int}}(E - E_0, N, \mathcal{V}) \) and \( S^{\text{int}}(E - E_0, N, \mathcal{V}) \) have the property:

\[ W^{\text{int}}(E - E_0) \leq 1, \Rightarrow S^{\text{int}}(E - E_0, N) \leq 0 \]
\[ \Rightarrow \begin{cases} 1 & E \gg V^{\text{int}} \\ \left[ \frac{\mathcal{V}}{V_0} \right]^{N-1} & E \to E_0 \end{cases} \]

\[ S^{\text{int}}(E - E_0) \to \begin{cases} 0 & E \gg V^{\text{int}} \\ \ln \left[ \frac{\mathcal{V}}{V_0} \right]^{N-1} & E \to E_0 \end{cases} \]

All physical details are encrypted in \( W^{\text{int}}(E - E_0, N, \mathcal{V}) \) or \( S^{\text{int}}(E - E_0, N, \mathcal{V}) \) alias \( N \ln |\mathcal{V}(E)| \), c.f. eqs. (13,17): If the energy is high the detailed structure of \( V^{\text{int}}(\mathbf{r}_i) \) is unimportant \( W^{\text{int}} \approx 1 \), \( S^{\text{int}} \approx 0 \). The system behaves like an ideal gas and fills the volume \( \mathcal{V} \). At sufficiently low energies only the minimum of \( V^{\text{int}}(\mathbf{r}_i) \) is explored by \( W^{\text{int}}(E - E_0, N, \mathcal{V}) \). The system is in a condensed, liquid drop (perhaps several) moving freely inside the empty larger volume \( \mathcal{V} \).

One can guess the general form of \( N \ln |\mathcal{V}(E)| \): Near the groundstate \( E \geq E_0 \) it must be flat \( \approx (N - 1) \ln[V_0] + \ln[\mathcal{V}] \) because the liquid drop has some eigen-volume \( V_0 \) in which each particle can move. With rising energy \( \ln |\mathcal{V}(E)| \) rises up to the point \( E_{\text{trans}} \) where it is possible that the drop fissions into two and \( N \ln |\mathcal{V}(E)| \approx \)
and the phenomenon of phase-separation to gas phase transition shows the advantage of the microcanonical thermodynamics and the phenomenon of multi-fragmentation in nuclear systems. This, in contrast to the mathematical Y-L theorem, physical microscopic explanation of the liquid to gas phase transition shows the advantage of the microcanonical statistics on the 3N-coordinate space as presented here.

B. Solid–liquid transition

In contrast to the liquid phase, in the crystal phase a molecule can only move locally within its lattice cell of the size \(d^3\) instead of the whole volume \(V_0\) of the condensate. I.e. in eq. (17) instead we have \(S^{int} \to \ln\left\{\frac{V}{V_0}\right\}^{N-1}\).

C. Summary of section III

The gas–liquid transition is linked to the transition from uniform filling of the container volume \(V\) by the gas to the smaller eigen-volume of the system \(V_0\) in its condensed phase where the system is non-homogeneous (some liquid drops inside the larger empty volume \(V\)). First \(N-1\), later at higher energies less and less degrees of freedom condensate into the drop. First one, then more and more dofs. explore the larger container volume \(V\) leading to upwards jumps (convexities) of \(S^{int}(E)\). The volume of the container controls how close one is to the critical end-point of the transition, where phase-separation disappears. Towards the critical end-point, i.e. with smaller \(V\) the jumps \(\ln[V] - \ln[V_0]\) become smaller and smaller. In the case of the solid–liquid transition the external volume \(V\) of the container has no influence on \(S^{int}(E)\). The entropy jumps are by \(\Delta S^{int} \propto \ln V_0 - \ln d^3\).

At the surface of the drops \(V^{int} > E_0 = \min V^{int}\), i.e. the surface gives a negative contribution to \(S^{int}\) in eq. (17) and to \(S\) at energies \(E \geq E_0\), as was similarly assumed in section III and explicitly in eq. (9).

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[12] The first two sections discuss mainly systems that have no other macroscopic (extensive) control parameter besides the energy. E.g. the particle density is not changed and there are no chemical reactions.
[13] This backbending of \(T(c)\) has nothing to do with the periodic boundary condition used here, as claimed erroneously by Moretto et.al [4]. Many realistic microcanonical calculations for nuclear fragmentation as also for atomic-cluster fragmentation, c.f. [1].
bending *without using periodic boundaries*. These are verified by numerous experimental data in nuclear physics c.f. [3, 7] and cluster physics [3, 8]. The errors of the above paper by Moretto et. al. are commented in more detail also in [10, 11].