I. WHAT IS ENTROPY?

Entropy \(S\) is the key quantity of all Thermostatistics and Thermodynamics. Therefore, its proper understanding is essential. In the literature this is sometimes clouded by the frequent use of the thermodynamic limit and/or the use of the Boltzmann-Gibbs canonical statistics. In what follows, I will try to define it with minimum bias.

Boltzmann’s epitaph reads

\[ S = k \ln W \]  

(1)

with

\[ W(E,N,V) = \int \frac{d^3N \, \delta(p)}{N! (2\pi \hbar)^3N} e^{-\beta(E - H(q,p))} \]  

(2)

in semi-classical approximation. \(E\) is the total energy, \(N\) is the number of particles and \(V\) the volume. Or, more appropriate for a finite quantum-mechanical system:

\[ W(E,N,V) = \text{Tr} \left[ \rho(E) \right] \sum \delta(E - E_n) \delta(H(q,p) - E_n) \]  

(3)

and \(\epsilon_0 \approx \) the macroscopic energy resolution. This is still up to the deepest, most fundamental, and most simple definition of entropy. There is no need of the thermodynamic limit, no need of concavity, extensivity and homogeneity. In its semi-classical approximation, eq.(2), \(W(E,N,V,\cdots)\) simply measures the area of the submanifold of points in the \(6N\)-dimensional phase-space \((\Gamma\)-space\) with prescribed energy \(E\), particle number \(N\), volume \(V\), and some other time invariant constraints which are here suppressed for simplicity. Because it was Planck who coined it in this mathematical form, I will call it the Boltzmann-Planck principle.

There are various reviews on the mathematical foundation of Statistical Mechanics e.g. the detailed and instructive article by Alfred Wehrl [2]. He shows how the Boltzmann-Planck formula (1), with (3) can be generalized to the famous definition of entropy in Quantum Mechanics by von Neumann[3]

\[ S = -\text{Tr} \left[ \rho \ln(\rho) \right], \]  

(4)

addressing general (non projector like) densities \(\rho\).
Wehrl discusses the conventional canonical Boltzmann-Gibbs statistics where all constraints are only fixed to their mean, allowing for free fluctuations. He points to the many serious complications of this definition. However, in the case of conserved observables we know more than their mean. We know these quantities sharply. In Microcanonical Thermodynamics we don’t need von Neumann’s definition (4) and can work on the level of Boltzmann-Planck’s original definition of S by eqs.(1 and 3). We thus explore Statistical Mechanics and entropy on its most fundamental level. This has the great advantage that the axiomatic level is extremely simple. Because it does not demand scaling or extensivity, it can further be applied to the much wider group of non-extensive systems from nuclei to galaxies [4] and address the original object of Thermodynamics for which it was invented some 150 years ago: phase separations.

The Boltzmann-Planck formula has a direct and simple but deep physical interpretation: W or S are the measure of our ignorance about the complete set of initial values for all 6N microscopic degrees of freedom which are needed to specify the N-body system unambiguously [5]. Usually we only know the few time-independent control parameters E, N, V, · · · , of the system (conserved or very slowly varying) but have no control of the other fast changing degrees of freedom. If the information would be complete, i.e. all 6N-degrees of freedom sharply known at some time t0, W would be a single cell of size (2πℏ)\(^3\)N in the 6N-dim. phase space, and S would be 0.

However, many initial values are consistent with the same values of E, N, V, · · · , (redundancy of control parameters). All the other degrees of freedom vary with time, usually fast, and are normally not under control. The manifold of all these points in the 6N-dim. phase space is the microcanonical ensemble. It has a well defined geometrical size W and due to eq.(1) a non-vanishing entropy S(E, N, V, · · · ). The dependence of S(E, N, V, · · · ) on its arguments gives the complete thermostatics and equilibrium thermodynamics.

It is further clear that the Hamiltonian (Liouvillean) dynamics of the system cannot create the missing information about the initial values. I.e. the entropy S(E, N, V, · · · ) cannot decrease. As is further worked out in [6] and more recently in [4] the inherent finite resolution of the macroscopic description implies usually an increase of W or S with time when a constraint is removed (Second Law of Thermodynamics).

It should be emphasized that this proper statistical definition of the entropy S(E, N, V, · · · ) characterizes the whole microcanonical ensemble [5]. It measures the total number of the possible states of the system under the information given. Eqs. (2,3) are in clear contrast to the definition suggested by [7-10]:

\[
W_{\text{bulk}}(E) = \int \frac{d^{3N}q}{N!(2\pi\hbar)^{3N}}\Theta(E - H(q, \vec{p}))
\]

\[
= \sum \text{all eigenstates } n \text{ of } H \text{ with } N, V, \text{ and } 0 < E_n \leq E = e^{S_{\text{bulk}}(E,N,V)}
\]

Our statistical definition (2.3) called S_{surf} in [10] has a priori not much to do with the adiabatic invariants of a single trajectory in the 6N-dim. phase space.

As we will see later in section (III) the entropy S(E) for non-extensive systems can be convex in contrast to the assumption made by Hertz [7]. Then the temperature or the mean kinetic energy per particle do not control the energy flow during the equilibration of two systems in thermal contact as was the crucial argument of Hertz [7] to introduce S_{bulk}(5-7). In contrast, the Boltzmann entropy eq.(2) does still control the direction of the energy-flow under equilibration even in these somewhat astonishing and unconventional though ubiquitous situations. This clearly underlines the role of the Boltzmann entropy (2) as the fundamental quantity and not the temperature for statistical mechanics. I am fully aware that this contradicts opposite statements given by [7, 8, 10].

Moreover, the definition of the bulk entropy S_{bulk}(E, N, V) (5-7) contains also, energetically, inaccessible states with less energy, which are clearly excluded by our knowledge of the total energy. Thus, S_{bulk} does not represent the redundancy, or ignorance, of the available information. Therefore it is not acceptable by conceptual reasons. This is a clear warning that one should not follow some formal definitions and forget the original clear meaning of entropy and statistics as is often done in the literature. Of course, for macroscopic systems the difference between the two alternative definitions of the entropy eqs.(2-3) and eqs.(5,7) disappears.

II. THE ZERO’TH LAW IN CONVENTIONAL EXTENSIVE THERMODYNAMICS

In conventional (extensive) thermodynamics thermal equilibrium of two systems (1 & 2) is established by bringing them into thermal contact which allows free energy exchange[27]. Equilibrium is established when the total entropy

\[
S_{\text{total}}(E, E_1) = S_1(E_1) + S_2(E - E_1)
\]

is maximal:

\[
dS_{\text{total}}(E, E_1)|_E = dS_1(E_1) + dS_2(E - E_1) = 0.
\]

Under an energy flux \(\Delta E_{2\rightarrow 1}\) from 2 \(\rightarrow\) 1 the total entropy changes to lowest order in \(\Delta E\) by

\[
\Delta S_{\text{total}}|_E = (\beta_1 - \beta_2)\Delta E_{2\rightarrow 1}
\]

\[
\beta = dS/dE = \frac{1}{T}
\]
Consequently, a maximum of $S_{\text{total}}(E = E_1 + E_2, E_1)$ will be approached when

$$\text{sign}(\Delta S_{\text{total}}) = \text{sign}(T_2 - T_1)\text{sign}(\Delta E_{2-1}) > 0 \quad (12)$$

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.8). There are no correlations, which are destroyed when an extensive system is split. Temperature is an appropriate control parameter for extensive systems.

### III. NO PHASE SEPARATION WITHOUT A CONVEX, NON-EXTENSIVE $S(E)$

Since the beginning of Thermodynamics in the middle of the 19th century its main motivation was the description of steam engines and the liquid to gas transition of water. Here water prefers to become inhomogeneous and develop a separation of the gas phase from the liquid, i.e. water boils. As conventional canonical statistics works only for homogeneous, infinite systems, phase separation remains outside of standard Boltzmann-Gibbs thermo-statistics.

The weight $e^{S(E)-E/T}$ of the configurations with energy $E$ in the definition of the canonical partition sum

$$Z(T) = \int_0^\infty e^{S(E)-E/T} dE \quad (13)$$

becomes here 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 and the weight in (13) has a minimum 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 $\Delta E \sim E_{\text{lat}}$ of the order of the latent heat. I.e. the convexity of $S(E)$ is the generic signal of a phase transition of first order and of phase-separation[1]. It is amusing that this fact that is essential for the original purpose of Thermodynamics to describe steam engines was never treated correctly in the past 150 years.

The ferromagnetic Potts-model illuminates in a most simple example the occurrence of a convex intruder in $S(E)$ which induces a backbending caloric curve $T(E) = (\partial S/\partial E)^{-1}$ with a decrease of the temperature $T(E)$ with rising energy [11][28]. A typical plot of $s(e, N) = S(E = Ne)/N$ in the region of phase separation is shown in fig(1). Section IV discusses the general microscopic reasons for the convexity.

This has far reaching consequences which are crucial for the fundamental understanding of thermo-statistics and Thermodynamics: Let us split the system of figure (1) 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 $e_a$ and $e_b$. Constraining the energy-difference $e_b - e_a = \Delta e$ between the two, reduces the number of free, unconstrained degrees of freedom and reduces the entropy by $-2\Delta S_{\text{surf-corr.}}$. (Moreover, if the

FIG. 1: Ferromagnetic Potts model ($q = 10$) on a 50 * 50-lattice with periodic boundary conditions in the region of phase separation. At the energy $e_1$ per lattice point the system is in the pure ordered phase, at $e_3$ in the pure disordered phase. At $e_a$ little above $e_1$ the temperature $T_a = 1/\beta$ is higher than $T_2$ and even more than $T_b$ at $e_b$ a little below $e_3$. At $e_a$ the system separates into a few bubbles of disordered phase embedded in the ordered phase or at $e_b$ into a few droplets of ordered phase within the disordered one. If we combine two equal systems: one with the energy per lattice site $e_a = e_1 + \Delta e$ and at the temperature $T_a$, the other with the energy $e_b = e_3 - \Delta e$ and at the temperature $T_b < T_a$, and allowing for free energy exchange, then the systems will equilibirize at energy $e_2$ with a rise of its entropy. The temperature $T_a$ drops (cooling) and energy (heat) flows (on average) from $b \to a$. I.e.: Heat flows from cold to hot! Thus, the Clausius formulation of the Second Law is violated. This is well known for self-gravitating systems. However, this is not a peculiarity of only gravitating systems! It is the generic situation at phase separations within classical thermodynamics even for systems with short-range coupling and has nothing to do with long-range interactions.
effect of the new surface would also be to cut some bonds: before the split there were configurations with attractive interactions across the surface which are interrupted by the dividing surface, their energy shifts upwards outside the permitted band-width \( e_0 \), and thrown out of the partition sum (3). I.e. the entropy will be further reduced by the split.

If the constraint on the difference \( e_b - e_a \) is fully relaxed and \( e_b^2 - e_a \) can fluctuate freely at fixed \( e_2 = (e_a + e_b)/2 \), the dividing surface is assumed to have no further physical effect on the system.

For an extensive system \[ S(E,N) = N s(e = E/N) = 2S(E/2,N/2) \]. One would argue as follows: The combination of two pieces of \( N/2 \) particles each, one at \( e_a = e_2 - \Delta e/2 \) and a second at \( e_b = e_2 + \Delta e/2 \), must lead to \( S(E_2,N) \geq S(E_a/2,N/2) + S(E_b/2,N/2) \), the simple algebraic sum of the individual entropies because by combining the two pieces one normally loses information. This, however, is equal to \[ S(E_a,N) + S(E_b,N) \]/2, thus \( S(E_2,N) \geq S(E_a,N) + S(E_b,N) \)/2. I.e. the entropy \( S(E,N) \) of an extensive system is necessarily concave.

For a non-extensive system we have in general \( S(E,N) \geq 2S(E/2,N/2) \) because again two separated, closed pieces have more information than their unification. Now, if \( E_2 \) is the point of maximum positive curvature of \( S(E,N) \) (convexity = upwards concave like \( y = x^2 \)) we have \( S(E_2,N) \leq S(E_a,N) + S(E_b,N) \)/2 like in fig.(1). However, the r.h.s. is larger than \( S(E_a/2,N/2) + S(E_b/2,N/2) \). I.e. even though \( S(E,N) \) is convex at const. \( N \), the unification of the pieces with \( E_a/2,N/2 \) and \( E_b/2,N/2 \) can still lead to a larger entropy \( S(E_2,N) \).

The difference between \[ S(E_a,N) + S(E_b,N) \]/2 and \( S(E_a/2,N/2) + S(E_b/2,N/2) \) we call henceforth \( \Delta S_{surf-corr} \). The correct entropy balance, before and after establishing the energetic split \( e_b > e_a \) of the system, is

\[
S_{after} - S_{before} = \frac{S_a + S_b}{2} - \Delta S_{surf-corr} - S_2 \leq 0 \quad (14)
\]
even though the difference of the first and the last term is positive.

In the inverse direction: By relaxing the constraint and allowing, on average, for an energy-flux \( \Delta E_{b \rightarrow a} > 0 \) opposite to \( T_a - T_b > 0 \), against the temperature-gradient (slope), but in the direction of the energy-slope, the entropy \( S_{total} \rightarrow S_2 \) increases. This is consistent with the naive picture of an energy equilibration. Thus Clausius’ "energy flows always from hot to cold", i.e. the dominant control-role of the temperature in thermo-statistics [7] is violated. Of course this shows again that unlike to extensive thermodynamics the temperature is not the appropriate control parameter in non-extensive systems.

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

IV. THE MICROcanonical MECHANISM LEADING TO CONDENSATION, PHASE SEPARATION AND THE ORIGIN OF THE CONVEXITIES OF \( S(E) \)

Many theoretical applications of microcanonical thermodynamics to realistic examples of hot nuclei, atomic clusters, and rotating astro-physical systems have been been presented during the past 20 years and show convex intruders in the microcanonical entropy and, consequently, negative heat capacities, c.f. e.g. the publication list on my WEB-site http://www.hmi.de/people/gross/, see also refs.[12–15]. Here I will illuminate the general microscopic mechanism leading to the appearance of a convex intruder in \( S(E,N,V,\cdots) \).

I assume the system is classical and obeys the Hamiltonian:

\[
H = \sum_i \frac{p_i^2}{2m} + \Phi^{int}[\{\vec{r}^i\}] \quad (15)
\]

\[
\Phi^{int}[\{\vec{r}^i\}] := \sum_{i<j} \Phi(\vec{r}^i - \vec{r}^j)
\]

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

A. Liquid–gas transition

The microcanonical sum of states or partition sum is:
$W(E,N,V) = \frac{1}{N!(2\pi\hbar)^3N} \int_{V_N} d^3N r \int d^4N p_1 \epsilon_0 \delta(E - \sum_{i} \frac{p_i^2}{2m_i} - \Phi^{int}[\{\vec{r}\}])$

$= \frac{\nu^N \epsilon_0 (E - E_0)^{(3N-2)/2} \prod_{i} m_{i}^{3/2}}{N! \nu(3N/2)(2\pi\hbar^2)^{3N/2}} \int_{V_N} d^3N r \frac{E - \Phi^{int}[\{\vec{r}\}]}{E - E_0}^{(3N-2)/2}$

$W_{id-gas}(E - E_0, N, V) \times W_{int}(E - E_0, N, V)$

$= e^{[S_{id-gas} + S_{int}]}$

$W_{id-gas}(E, N, V) = \frac{\nu^N \epsilon_0 E^{(3N-2)/2} \prod_{i} m_{i}^{3/2}}{N! \nu(3N/2)(2\pi\hbar^2)^{3N/2}}$

$W_{int}(E - E_0, N, V) = \int_{V_N} d^3N r \Theta(E - \Phi^{int}[\{\vec{r}\}]) \left(1 - \frac{\Phi^{int}[\{\vec{r}\}] - E_0}{E - E_0}\right)^{(3N-2)/2}$

$W_{int}(E - E_0, N, V) = \left[\frac{\nu(E, N)}{V}\right]^N \leq 1 \quad (21)$

$\nu(E, N) \equiv \int_{V_N} d^3N r \Theta(E - \Phi^{int}[\{\vec{r}\}])$ (22)

$S_{int}(E - E_0, N, V) = N \ln \left[\frac{\nu(E, N)}{V}\right] \leq 0 \quad (23)$

The separation of $W(E, N, V)$ into $W_{id-gas}$ and $W_{int}$ is the microcanonical analogue of the split of the canonical partition sum into a kinetic part and a configuration part, in the micro, however, without assuming any thermodynamic limit or homogeneity.

$Z(T) = \frac{\nu^N}{N!} \left(\frac{mT}{2\pi\hbar^2}\right)^{3N/2} \int_{V_N} d^3N r e^{-\frac{\Phi^{int}[\{\vec{r}\}]}{\nu}} \quad (20)$

$\nu$ is the spatial volume. $E_0 = \min \Phi^{int}[\{\vec{r}\}]$ is the energy of the ground-state of the system.

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 it is controlled by the constant available system volume $V$. At low energies the $N$ particles condensate into a droplet with much smaller volume $V_{0N}$, the system does not fill the volume $V$. $N-1$ internal coordinates are limited to $V_{0N}$. Only the center of mass of the droplet can move freely in $V$ (remember we did not fix the C.M. in eq.(16)). The system does not fill the $3N$-configuration space $\nu^N$. Only a stripe with width $\nu_{0N}^{1/3}$ in $3(N-1)$ dimensions of the total $3N$-dim space and with the width $\nu^{1/3}$ in the remaining $3$ dimensions of center of mass motion is populated. The system is non-homogeneous even though it is equilibrated and, at low energies, internally in the single liquid phase. It is not characterized by an intensive homogeneous density. In fact, $W_{int}(E - E_0, N, V)$ can be written as:

$W_{int}(E - E_0, N, V) = \left[\frac{\nu(E, N)}{V}\right]^N \leq 1 \quad (21)$

The first factor $\Theta(E - \Phi^{int}[\{\vec{r}\}])$ in eq(22) eliminates the energetically forbidden regions. Only the potential holes (clusters) in the $3N$-dim potential surface $\Phi^{int}[\{\vec{r}\}]$ remain. Their volume $\nu^N(E, N) \leq \nu^N$ is the accessible part of the $3N$-dim spatial volume where $\Phi^{int}[\{\vec{r}\}] \leq E$. I.e. $\nu^N(E, N)$ is the total $3N$-dim. eigen-volume of the condensate (droplets), with $N$ particles at the given energy, summed over all possible partitions, clusterings, in $3N$-configuration space. The relative volume fraction of each partition compared with $\nu^N(E, N)$ gives its relative probability. $\nu^N(E, N)$ has the limiting values:

$\nu^N(E, N) = \begin{cases} 
\frac{\nu^N}{\nu_{0N}^{N-1}V} & \text{for } E = E_0 \\
\nu^N & \text{for } E > E_0
\end{cases}$

The first factor $\Theta(E - \Phi^{int}[\{\vec{r}\}])$ in eq(22) eliminates the energetically forbidden regions. Only the potential holes (clusters) in the $3N$-dim potential surface $\Phi^{int}[\{\vec{r}\}]$ remain. Their volume $\nu^N(E, N) \leq \nu^N$ is the accessible part of the $3N$-dim spatial volume where $\Phi^{int}[\{\vec{r}\}] \leq E$. I.e. $\nu^N(E, N)$ is the total $3N$-dim. eigen-volume of the condensate (droplets), with $N$ particles at the given energy, summed over all possible partitions, clusterings, in $3N$-configuration space. The relative volume fraction of each partition compared with $\nu^N(E, N)$ gives its relative probability. $\nu^N(E, N)$ has the limiting values:

$W_{int}(E - E_0, N, V)$ and $S_{int}(E - E_0, N, V)$ have the limiting values:

$W_{int}(E - E_0) \leq 1 \Rightarrow S_{int}(E - E_0, N) \leq 0$

$\Rightarrow \begin{cases} 
E \gg \Phi^{int} & E \rightarrow \infty \\
\frac{\nu^N}{\nu_{0N}^{N-1}V} & E \rightarrow E_0
\end{cases}$

$S_{int}(E - E_0) \rightarrow \begin{cases} 
0 & E \gg \Phi^{int} \quad (24) \\
\ln \left[\frac{\nu^N}{\nu_{0N}^{N-1}V}\right] < 0 & E \rightarrow E_0
\end{cases}$

(25)
All physical details are encrypted in $W_{\text{int}}(E-E_0, N, V)$ or $S_{\text{int}}(E-E_0, N, V)$ alias $N \ln[V(E, N)]$, c.f. eqs.(21–25): If the energy is high the detailed structure of $\Phi_{\text{int}}[\{ r \}]$ is unimportant $W_{\text{int}} \approx 1$, $S_{\text{int}} \approx 0$. The system behaves like an ideal gas and fills the volume $V$. At sufficiently low energies only the minimum of $\Phi_{\text{int}}[\{ r \}]$ is explored by $W_{\text{int}}(E-E_0, N, V)$. The system is in a condensed phase, a single liquid drop, which moves freely inside the empty larger volume $V$, the $3(N-1)$ internal ds are trapped inside the reduced volume $V_{0N} \ll V$.

One can guess the general form of $N \ln[V(E, N)]$ near the groundstate $E \gtrsim E_0$ it must be flat $\approx (N-1) \ln[V_{0N}] + \ln[V - V_{0N}]$ because the liquid drop has some eigen-volume $V_{0N}$ in which each particle can move (liquid). With rising energy $\ln[V(E, N)]$ rises up to the point ($E_{\text{trans}}$) where it is possible that the drop fissions into two. Here an additional new configuration opens in 3N-dim configuration space: Either one particle evaporates from the cluster and explores the larger external volume $V$, or the droplet fissions into two droplets and the two CM coordinates explore the larger $V$. This gives a sudden jump in $S_{\text{int}}(E)$ by something like $\sim \ln\{ V - V_{0N}(N-1) \}$ and similar in the second case.

Of course, this sudden opening of additional parts of the 3N-dim. configuration space gives also a similar jump upwards in the total entropy

$$S(E) = S_{\text{id-gas}} + S_{\text{int}} \propto \ln \int_{V_{0N}} d^{3N}r \left( E - \Phi_{\text{int}}[\{ r \}] \right)^{(3N-2)/2}$$

by $\sim \ln\{ V - V_{0N}(N-1) \}$. Later further such "jumps" may follow. Each of these "jumps" induce a convex upwards bending of the total entropy $S(E)$ (eq.17). Each is connected to a bifurcation and bimodality of $e^{S(E)} - E/T$ and the phenomenon of phase-separation.

In the conventional canonical picture for a large number of particles this is hidden and hidden behind the familiar Yang-Lee singularity of the liquid to gas phase transition.

In the microcanonical ensemble this is analogue to the phenomenon of multifragmentation in nuclear systems [1, 16]. This, in contrast to the mathematical Yang-Lee theorem, physical microscopic explanation of the liquid to gas phase transition sheds light on the physical origin of the transition, the sudden change in the inhomogeneous population of the 3N-dim. configuration space.

B. Solid–liquid transition

In contrast to the liquid phase, in the crystal phase a molecule can only move locally within its lattice cage of the size $d^3$ instead of the whole volume $V_{0N}$ of the condensate. I.e. in eq.(25) instead we have $S_{\text{int}} \rightarrow \ln\{ d^3/\lambda \}^{N-1}$.

C. Summary of section IV

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 $3(N-1)$, later at higher energies less and less positional degrees of freedom condensate into the drop. First three, then more and more dofs. (C.M.-coordinates of the drops) explore the larger container volume $V$ leading to upwards jumps (convexities) of $S_{\text{int}}(E)$. 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 $\ln[V - V_0] - \ln[V_0]$ become smaller and smaller. In the case of the solid–liquid transition, however, the external volume $V$ of the container confines only the C.M.-position of the crystal resp. the droplet. As long as both $d^3$ and $V_{0N}$ remain small compared to $V$, the latter has no direct influence on $S_{\text{int}}(E)$. The entropy jumps during melting are by $\Delta S_{\text{int}} \propto \ln V_{0N} - \ln d^3$.

At the surface of a drop $\Phi_{\text{int}} > E_0 = \min \Phi_{\text{int}}$, i.e. the surface gives a negative contribution to $S_{\text{int}}$ in eq.(22) and to $S$ at energies $E \gtrsim E_0$ as was similarly assumed in section (III) and explicitly in eq.(14).

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I am grateful to J. Møller for insistent, therefore helpful, discussions. J.F. Kenney made numerous illuminating suggestions, I hope he finally can agree with this version.

VI. APPENDIX, A SIMPLE MODEL FOR CONDENSATION

Let’s assume the various potential-pockets are attractive square-wells with depths $\Phi_\lambda < 0$. With the (somewhat schematic) abbreviation:

$$I(K) := \int_{V^{3N}} d^{3N}r \Theta(E - \Phi_\lambda[\{ r \}]) \left( E - \Phi_{\text{int}}[\{ r \}] \right)^{(3N-K)/2}$$

$$= \sum_{\lambda=1,N} \left( E - \Phi_\lambda \right)^{(3N-K)/2} \left( V - \sum_{k=1}^{N-\lambda} V_{0k} \right) \prod_{k=1}^{N-\lambda} V_{0k}$$

Here $\Phi_\lambda \leq 0$ are different topological regions of $\Phi_{\text{int}}[\{ r \}]$; Single cluster ($\lambda = 1$), two clusters ($\lambda = 2$), several clusters or, finally, if energetically possible, ($\lambda = N$) free particles, $\Phi = 0$. Depending on $\lambda$ there are $3\lambda$ C.M. coordinates which can move over the whole volume $V$ in contrast to the rest $3(N-\lambda)$ internal coordinates which are limited to smaller cluster volumes $V_{0k}$.
All particles condensed into one single cluster (λ = 1) will have the lowest potential Φ₁ and consequently the largest $E - \Phi$. On the other hand the volume factor $\sim V/V_{0(N-1)}$ ≫ 1 appears only once. Then other terms with $\lambda > 1$ may dominate if $(V/V_{0(N-λ)})^{λ} \ast (E - \Phi_{λ})^{(3N-K)/2} > V/V_{0(N-1)} \ast (E - \Phi_{1})^{(3N-K)/2}$.

In terms of $I(\mathbf{K})$ the partition sum $W(E)$ and its derivatives are expressed as:

$$W(E, N, V) \propto I(2)$$

$$\frac{\partial W(E, N, V)}{\partial E} \propto \frac{3N-2}{2} I(4)$$

$$\frac{\partial^2 W(E, N, V)}{\partial E^2} \propto \frac{(3N-2)(3N-4)}{4} I(6)$$

$$\beta(E) = \frac{3N-2}{2} I(2)$$

$$\beta'(E) = \frac{3N-2}{2}$$

$$\times \left( \frac{3N-4}{2} I(6) - \frac{3N-2}{2} \left( \frac{I(4)}{I(2)} \right)^{2} \right)$$

To get a convexity ($\beta' \geq 0$), we must have:

$$\frac{I(6)I(2)}{[I(4)]^2} > 1 + \frac{2}{3N-4} \tag{33}$$

### A. Some examples

#### 1. A single phase

When calculating eq.(31–33) one immediately sees that for a *sharply mono-dispersed* sum (27), $\lambda \sim \lambda_0$ (single phase)

$$I(\mathbf{K} - 2) \sim (E - \Phi_{\lambda_0})I(\mathbf{K}) \tag{34}$$

Then l.h.s. of criterion (33) becomes 1 and there is no convexity.

$$\beta = \frac{3N-2}{2} \frac{1}{E - \Phi_{\lambda_0}}$$

$$\beta' = -\frac{2}{3N-2} \beta^2$$

I.e. the heat capacity is:

$$Nc(E) = \frac{\beta^2}{\beta'} = \frac{3N-2}{2} \tag{37}$$

equal to the ideal gas value, independently of whether the system is condensed or not. (Remember, in eq.(27) we assumed for simplicity that $\Phi_{\lambda}$ has a flat bottom).

### 2. Bimodal distribution, phase-separation

When the massdispersion (27) is bimodal, when e.g. two terms in the sum dominate, i.e. when

$$I(\mathbf{K}) \approx \sum_{\lambda=\lambda_1, \lambda_2} \left( (E - \Phi_{\lambda})^{(3N-K)/2} \right) \left( \sqrt{\lambda} \sum_{k=1}^{N-\lambda} V_{0k} \right)^{\lambda} \prod_{k=1}^{N-\lambda} V_{0k}$$

then the different $I(\mathbf{K})$ are not anymore proportional for different $\mathbf{K}$ as in eq.(34), and the curvature $\beta'$, eq.(32) can very well be positive.

I.e. as anticipated in our previous discussion in section (IV), the volume-factor $V/V_{0} > 1$ controls whether the system can perform a phase-transition and whether the transition has a critical end-point and if, where it is, i.e. where the region of convexity disappears.

### 3. Hard disks, the Alder-Wainwright Transition [17, 18]

For hard disks the potential is:

$$d = | \vec{r} - \vec{r}' | \tag{39}$$

$$\phi(d) = \begin{cases} \infty & d \leq d_{disk} \\ 0 & d > d_{disk} \end{cases}$$

$$\phi^{int}[\{\vec{r}\}] = \sum_{i>k} \phi(\vec{r}_i - \vec{r}_k)$$

$$\lambda_0 = 0 \tag{42}$$

$$I(\mathbf{K}) = E^{(3N-K)/2} \sum_{\lambda} (\sqrt{\lambda} - V_{0\lambda})^{\lambda} \prod_{\lambda=1}^{\lambda} V_{0\lambda}^{N-\lambda} \tag{43}$$

With $V_{0\lambda} = \sqrt{d}/\sqrt{2}$ the closed packing volume.

Due to the criterion (33) there is no bimodality vs. energy and the heat capacity is everywhere the ideal-gas value $Nc(E) = \frac{3N-2}{2}$.

The only interesting change of $W$ is as function of the external volume $V$. To get some feeling for this, we make the following simplified ansatz:

We assume each cluster with $n$ disks has the closed-packing volume $V_{0n} = \frac{\pi}{3\sqrt{3}} V_{0N}$. Moreover, each cluster has a constant surface layer of volume $d$ around to separate it from other clusters. In a configuration of $\lambda$ clusters there are $3\lambda$ positional degrees of freedom that can move free in volume of $V - V_0 - \lambda d$ whereas $3(N-\lambda)$ internal positional degrees of freedom are limited to the condensate volume $V_{0\lambda}^{(N-\lambda)}$. For number of states we have after these simplifying assumptions, cf. eq.(43):

$$W \propto \sum_{\lambda} W_{\lambda}$$

$$W_{\lambda} = (\sqrt{\lambda} - V_{0\lambda})^{\lambda} \times (V_{0N})^{N-\lambda} \tag{44}$$

The form of $W_{\lambda}$ as function of the external volume is shown in fig(2):

Evidently, $W_{\lambda}(V)$ is for every $\lambda$ a sharp mono-dispersed function of number of clusters and shows no
FIG. 2: Simplified Alder-Wainwright transition, Normalized cluster-number (λ) distributions $W_\lambda(V)$ as function of the external volume $V$.

8 bimodality v.s. $\lambda$. Consequently there is no phase-separation also in the $P(V)$ curve. This is not a phase-transition of first order.

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[27] This and the next (III.) section 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.

[28] This backbending of $T(e)$ has nothing to do with the periodic boundary condition used here, as claimed erroneously by Moretto et.al [19]. Many realistic microcanonical calculations for nuclear fragmentation as also for atomic-cluster fragmentation, c.f. [1, 20], show the backbending *without using periodic boundaries*. These are verified by numerous experimental data in nuclear physics c.f. [21, 22] and cluster physics [23, 24]. The errors of the above paper by Moretto et. al. are commented in more detail also in [25, 26]
Potts-Model, $q=10$
$W = \frac{(V-V_0-kd)}{V_0}$

$V_0 = 4.67 \quad d = 0.03$