Microscopic statistical basis of classical thermodynamics of finite systems.

D.H.E. Gross

Hahn-Meitner Institute and Freie Universität Berlin,
Fachbereich Physik. Glienickerstr. 100; 14109 Berlin, Germany

Heat can flow from cold to hot at any phase separation. Therefore Lynden-Bell’s gravo-thermal catastrophe must be reconsidered. The original objects of Thermodynamics, the separation of phases at first order phase transitions, like boiling water in steam engines, are not described by a single canonical ensemble. Inter-phase fluctuations are not covered. The basic principles of statistical mechanics, especially of phase transitions have to be reconsidered without the use of the thermodynamic limit. Then thermo-statistics applies also to nuclei and large astronomical systems. A lot of similarity exists between the accessible phase space of fragmenting nuclei and inhomogeneous multi stellar systems.

Since the beginning of Thermodynamics in the first half of the 19. 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 gaseous phase from the liquid, i.e. water boils. This will be analyzed from the new perspective of microcanonical statistics in section III.

A little later statistical mechanics was developed by Boltzmann 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 thermo-statistics, 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. 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 distinguished between external and internal entropy generating mechanisms. The second law is only related to the latter mechanism, 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.

I. WHAT IS ENTROPY?

Entropy, S, is the characteristic entity of thermodynamics. Its use distinguishes thermodynamics from all other physics; therefore, its proper understanding is essential. The understanding of entropy is sometimes obscured by frequent use of the Boltzmann-Gibbs canonical ensemble, and the thermodynamic limit. Also its relationship to the second law is beset with confusion between external transfers of entropy \(d_s S\) and its internal production \(d_i S\).

The main source of the confusion is of course the lack of a clear microscopic and mechanical understanding of the fundamental quantities of thermodynamics like heat, external vs. internal work, temperature, and last not least entropy, at the times of Clausius and possibly even today.

Clausius defined a quantity which he first called the “value of metamorphosis”, in German “Verwandlungswert” in \(\text{[1]}\). Eleven years later he gave it the name “entropy” \(S\):

\[
S_b - S_a = \int_a^b \frac{dE}{T}. \tag{1}
\]

where \(T\) is the absolute temperature of the body when the momentary change is done, and \(dE\) is the increment (positive resp. negative) of all different forms of energy (heat and potential) put into resp. taken out of the system.

From the observation that heat does not flow from cold to hot (see section III formula \(\text{[5]}\) however section III) he went on to enunciate the second law as:

\[
\Delta S = \oint \frac{dE}{T} \geq 0, \tag{2}
\]

which Clausius called the uncompensated metamorphosis. As will be worked out in section III the second law as presented by eq. \(\text{[2]}\) remains valid even in cases where heat flows from low to higher temperatures.
Prigogine\[2, c.f. [3]\], quite clearly stated that the variation of $S$ with time is determined by two, crucially different, mechanisms of its changes: the flow of entropy $d_s S$ to or from the system under consideration; and its internal production $d_i S$. While the first type of entropy change $d_s S$ (that effected by exchange of heat $d_s Q$ with its surroundings) can be positive, negative or zero, the second type of entropy change $d_i S$ is fundamentally related to its spontaneous internal evolution ("Verwandlungen", "metamorphosis"\[4\]) of the system, and states the universal irreversibility of spontaneous transitions. It can be only positive in any spontaneous transformation.

Claussius gives an illuminating example in\[2\]: When an ideal gas suddenly streams under isolating conditions from a small vessel with volume $V_1$ into a larger one ($V_2 > V_1$), neither its internal energy $U$, nor its temperature changes, nor external work done, but its internal (Boltzmann)-entropy $S_i$ eq.(3) rises, by $\Delta S = N \ln (V_2/V_1)$. Only by compressing the gas (e.g. isentropically) and creating heat $\Delta E = E_i [(V_2/V_1)^2/3 - 1]$ (which must be finally drained) it can be brought back into its initial state. Then, however, the entropy change in the cycle, as expressed by integral \(\int\), is positive ($= N \ln (V_2/V_1)$). This is also a clear example for a microcanonical situation where the entropy change by an irreversible metamorphosis of the system is absolutely internal. It occurs during the first part of the cycle, the expansion, where there is no heat exchange with the environment, and consequently no contribution to the integral \(\int\). The construction by eq.(2) is correct though artificial. After completing the cycle the Boltzmann-entropy of the gas is of course the same as initially. All this will become much more clear by Boltzmann’s microscopic definition of entropy, which will moreover clarify its real statistical nature:

Boltzmann\[2\] later defined the entropy of an isolated system (for which the energy exchange with the environment $d_s Q \equiv 0$) in terms of the sum of possible configurations, $W$, which the system can assume consistent with its constraints of given energy and volume:

$$S = k_B \ln W$$

(3)
as written on Boltzmann’s tomb-stone, with

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

(4)
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:

$$W(E, N, V) = \sum \text{all eigenstates } n \text{ of } H \text{ with given } N, V,$n \text{ and } E < E_n \leq E + \epsilon_0$$

(5)
and $\epsilon_0 \approx$ the macroscopic energy resolution. This is still up to day 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.(4), $W(E, N, V, \cdots)$ 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. It is further important to notice that $S(E, N, V)$ is everywhere analytical in $E$\[7\]. In the microcanonical ensemble are no “jumps” or multi-valuedness in $S(E)$, independently of whether there are phase transitions or not, in clear contrast to the canonical $S(T, N, V)$. A fact which underlines the fundamental role of microcanonical statistics.

The Boltzmann-Planck formula has a simple but deep physical interpretation: $W$ or $S$ measure 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\[5\]. To have complete knowledge of the system we would need to know (within its semiclassical approximation\[4\]) the initial positions and velocities of all $N$ particles in the system, which means we would need to know a total of $6N$ values. Then $W$ would be equal to one and the entropy, $S$, would be zero. However, we usually only know the value of a few parameters that change slowly with time, such as the energy, number of particles, volume and so on. We generally know very little about the positions and velocities of the particles. The manifold of all these points in the $6N$-dim. phase space, consistent with the given macroscopic constraints of $E, N, V, \cdots$, is the microcanonical ensemble, which has a well-defined geometrical size $W$ and, by equation (3), a non-vanishing entropy, $S(E, N, V, \cdots)$. The dependence of $S(E, N, V, \cdots)$ on its arguments determines completely thermostatics and equilibrium thermodynamics.

Clearly, Hamiltonian (Liouvillean) dynamics of the system cannot create the missing information about the initial values - i.e. the entropy $S(E, N, V, \cdots)$ cannot decrease. As has been further worked out in\[8\] the inherent finite resolution of the macroscopic description implies an increase of $W$ or $S$ with time when an external constraint is relaxed. Such is a statement of the second law of thermodynamics, which requires that the internal production of entropy be positive for every spontaneous process. Analysis of the consequences of the second law by the microcanonical ensemble is appropriate because, in an isolated system (which is the one relevant for the microcanonical ensemble), the changes in total entropy must represent the internal production of entropy, see above, and there are no additional uncontrolled fluctuating energy exchanges with the environment.
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. Equilibrium is established when the total entropy

\[ S_{1+2}(E, E_1) = S_1(E_1) + S_2(E - E_1) \]  

(6)
is maximal. Under an energy flux \( \Delta E_{2\rightarrow1} \) from 2 \( \rightarrow \) 1 the total entropy changes to lowest order in \( \Delta E \) by

\[ \Delta S_{1+2}|_E = (T_2 - T_1)\Delta E_{2\rightarrow1}. \]

(7)

Consequently, a maximum of \( S_{\text{total}}(E, E_1) \mid_E \geq S_{1+2} \) will be approached when

\[ \text{sign}(\Delta S_{\text{total}}) = \text{sign}(T_2 - T_1)\text{sign}(\Delta E_{2\rightarrow1}) > 0. \]

(8)

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

It is further easy to see that the heat capacity of an extensive system with \( S(E, N) = 2S(E/2, N/2) \) is necessarily positive

\[ C_V(E) = \partial E / \partial T = - \frac{(\partial S / \partial E)^2}{\partial^2 S / \partial E^2} > 0: \]

(9)
The combination two pieces of \( N/2 \) particles each, but with different energy per particle, 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, \( \partial^2 S / \partial E^2 < 0 \) and eq. 9 follows. In the next section we will see that therefore extensive systems cannot have phase separation, the characteristic signal of transition of first order.

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

At phase separation the weight \( e^{S(E) - E/T} \) of the configurations with energy \( E \) in the definition of the canonical partition sum

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

(10)
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 \( (\partial^2 S / \partial E^2 > 0, \text{like } y = x^2 \) and the weight in eq. 10 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 \( \Delta E \sim E_{\text{lat}} \) of the order of the latent heat. The heat capacity is

\[ C_V(E_{\text{min}}) = \partial E / \partial T = - \frac{(\partial S / \partial E)^2}{\partial^2 S / \partial E^2} < 0. \]

(11)

i.e. the convexity of \( S(E) \) and the negative heat capacity are the generic and necessary signals of phase separation \[14\]. It is amusing that this fact, which is essential for the original purpose of Thermodynamics to describe steam engines, seems never been really recognized in the past 150 years. However, such macroscopic energy fluctuations and the resulting negative specific heat are already early discussed in high-energy physics by Carlitz \[12\].

The existence of the negative heat capacity at phase separation has a surprising but fundamental consequence: Combining two equal systems with negative heat capacity and different energy per particle, they will relax with a flow of energy from the lower to the higher temperature! 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 as emphasized by Hertz \[13\] is violated. Of course this shows quite clearly that unlike to extensive thermodynamics the temperature is not the appropriate control parameter in non-extensive situations like e.g. at phase separations, nuclear fragmentation, or stellar systems \[17\].

By the same reason the well known paradox of Antonov in astro-physics due to the occurrence of negative heat capacities must be reconsidered: By using standard arguments from extensive thermodynamics Lynden-Bell \[11\] claims that a system a with negative heat capacity \( C_n < 0 \) in gravitational contact with another b with positive heat capacity \( C_b > 0 \) will be unstable: If initially \( T_a > T_b \) the hotter system a transfers energy to the colder \( b \) and by this both become even hotter! If \( C_b > -C_a \), \( T_a \) rises faster than \( T_b \) and if the heat capacities don’t change, this will go for ever. This is Lynden-Bells gravitational catastrophe. This is wrong because just the opposite happens, the hotter \( a \) may even absorb energy from the colder \( b \) and both systems come to equilibrium at the same intermediate temperature c.f. \[14\] \[15\]. Negative heat can only occur in the microcanonical ensemble.

As phase separation exists also in the thermodynamic limit, by the same arguments as above the curvature of \( S(E) \) remains convex, \( \partial^2 S / (\partial E)^2 > 0 \). Consequently, the negative heat capacity should also be seen in ordinary macroscopic systems studied in chemistry!

Searching for example in Guggenheims book \[3\] one
finds some cryptic notes in §3 that the heat capacity of steam at saturation is negative. No notice that this is the generic effect at any phase separation! Therefore let me recapitulate in the next section how chemists treat phase separation of macroscopic systems and then point out why this does not work in non-extensive systems like fragmenting nuclei, at phase separation in normal macroscopic systems, or large astronomical systems.

IV. MACROSCOPIC SYSTEMS IN CHEMISTRY

Systems studied in chemical thermodynamics consist of several homogeneous macroscopic phases \(\alpha_1, \alpha_2, \ldots\) cf.[3]. Their mutual equilibrium must be explicitly constructed from outside.

Each of these phases are assumed to be homogeneous and macroscopic (in the “thermodynamic limit” \(N_\alpha \to \infty, \rho_\alpha = \text{const}\)). There is no common canonical ensemble for the entire system of the coexisting phases. Only the canonical ensemble of each phase separately becomes equivalent in the limit to its microcanonical counterpart.

The canonical partition sum of each phase \(\alpha\) is defined as the Laplace transform of the underlying microcanonical sum of states \(W(E)_\alpha = e^{S_\alpha(E)}\) [16, 17]

\[
Z_\alpha(T_\alpha) = \int_0^\infty e^{S_\alpha(E)/T_\alpha} dE.
\] (12)

The mean canonical energy is

\[
< E_\alpha(T_\alpha) > = T_\alpha^2 \partial \ln Z_\alpha(T_\alpha)/\partial T_\alpha.
\] (13)

In chemical situations proper the assumption of homogeneous macroscopic individual phases is of course acceptable. In the thermodynamic limit \(N_\alpha \to \infty, \rho_\alpha = \text{const}\) of a homogeneous phase \(\alpha\), the canonical energy \(< E_\alpha(T_\alpha) >\) becomes identical to the microcanonical energy \(E_\alpha\) when the temperature is determined by

\[
T_\alpha^2 = \partial S_\alpha(E, \rho_\alpha)/\partial E_\alpha.
\]

The relative width of the canonical energy

\[
\Delta E(T)_\alpha = \sqrt{< E_\alpha^2 >_T - < E_\alpha >_T^2} \propto 1/\sqrt{N_\alpha}.
\] (14)

The heat capacity at constant volume is

\[
C_\alpha|V_\alpha = \frac{< E_\alpha^2 >_T - < E_\alpha >_T^2}{T_\alpha^2} \geq 0.
\] (15)

Only in the thermodynamic limit \(N_\alpha \to \infty, \rho_\alpha = \text{const}\) does the relative energy uncertainty \(\Delta E_\alpha \to 0\), and the canonical and the microcanonical ensembles for each homogeneous phase \(\alpha\) become equivalent. This equivalence is the only justification of the canonical ensemble controlled by intensive temperature \(T\), or chemical potential \(\mu\), or pressure \(P\). I do not know of any microscopic foundation of the canonical ensemble and intensive control parameters apart from the limit.

The positiveness of any canonical \(C_V(T)\) or \(C_P(T)\) is of course the reason why the inhomogeneous system of several coexisting phases \((\alpha_1, \ldots, \alpha_\ell)\) with an overall negative heat capacity cannot be described by a single common canonical distribution [11, 18].

This new but fundamental interpretation of thermodynamics was introduced to the chemistry community in [14, 15].

V. NEW KIND OF PHASES WELL SEEN IN HOT NUCLEI OR MULTI-STAR SYSTEMS.

The new lesson to be learned is that if one defines the phases by individual peaks [20] in \(e^{S(E)/T}\) or \(e^{S(E)/V}\) in [19], then there exist also inhomogeneous phases like in fragmented nuclei or stellar systems. The general concept of thermodynamics becomes enormously widened.

Now, certainly neither the phase of the whole multifragmented nucleus nor the individual fragments themselves can be considered as macroscopic homogeneous phases in the sense of chemical thermodynamics (ChTh). Consequently, (ChTh) cannot and should not be applied to fragmenting nuclei and the microcanonical description is ultimately demanded. This becomes explicitly clear by the fact that the configurations of a multi-fragmented nucleus have a negative heat capacity at constant volume \(C_V\) and also at constant pressure \(C_P\) (if at all a pressure can be associated to nuclear fragmentation [11]). Meanwhile a huge amount of experimental evidences of negative heat capacities has accumulated; Nuclear fragmentation e.g. [20], atomic clusters e.g. [21], astrophysics e.g. [22], conventional macroscopic systems at phase separation e.g. [23].

The existence of well defined peaks (i.e. phases as defined above) in the event distribution of nuclear fragmentation data is demonstrated very nicely in [23] from various points of view. A lot more physics about the mechanism of phase transitions can be learned from such studies.

VI. OUTLOOK

It is a deep and fascinating aspect of nuclear fragmentation: First, in nuclear fragmentation we can measure the whole statistical distribution of the ensemble event by event including eventual inter-phase fluctuations. Not only their mean values are of physical interest. Statistical mechanics can be explored from its first microscopic principles in any detail well away from the thermodynamic limit. Initiated by our theoretical studies of nuclear fragmentation we found the very general appearance of a backbending caloric curve \(T(E)\) corresponding to a negative heat capacity, e.g. [24]. [24] (an early review in [27]) similar effects were proposed in the melting of atomic clusters [24]. Years later its existence in nuclear fragmentation was verified experimentally [24]. However,
the necessary convexity of the entropy $S(E)$ at any phase separation seems to be little known in thermodynamics. Clausius’ version of the second law “heat always flows from hot to cold” is in general violated at any phase separation even in macroscopic systems. Nowadays, the non-equivalence of the micro- and the canonical ensemble at phase-separations is discussed by many authors, see e.g. several relevant papers in [27].

In nuclear fragmentation there may be other conserved control parameters besides the energy: E.g. in the recent paper by Lopez et al. [28] the importance of the total angular momentum of the excited nucleus was emphasized. In this paper a bimodality, i.e. phase separation, in the mass-asymmetry of the fragments is demonstrated controlled by the transferred spin and not by excitation energy. This is an interesting, though still theoretical, example of the rich facets of the fragmentation phase transition in finite systems which goes beyond the liquid-gas transition and does not exist in macroscopic chemistry.

Angular momentum is also a very crucial control parameter in stellar systems, see below.

Second, and this may be more important: For the first time phase transitions to non-homogeneous phases can be studied where these phases are within themselves composed of several nuclei. This situation is very much analogous to multistar systems like rotating double stars during intermediate times, when nuclear burning prevents their final implosion. The occurrence of negative heat capacities is an old well known peculiarity of the thermodynamics of self-gravitating systems [11, 22]. Also these cannot be described by a canonical ensemble. It was shown in [10, 11] how the microcanonical phase space of these self-gravitating systems has the realistic configurations which are observed. Of course, the question whether these systems really fill uniformly this phase space, i.e. whether they are interim equilibrized or not is not proven by this observation though it is rather likely.

[1] D. Lynden-Bell and R. Wood. The gravo-thermal catastrophe in isothermal spheres and the onset of red-giant structure for stellar systems. Mon. Not. R. astr. Soc., 138:495, 1968.
[2] E. A. Guggenheim. Thermodynamics, An Advanced Treatment for Chemists and Physicists. North-Holland Personal Library, Amsterdam, 1967.
[3] L. Boltzmann. Weitere Studien über das Wärmegleichgewicht unter Gas-Molekülen. Sitzungsbericht der Akademie der Wissenschaften, Wien, 66:275–370, 1872.
[4] R. Clausius. Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie. Annalen der Physik und Chemie, 93:481–506, 1854.
[5] P. Glaisher and I. Prigogine. Thermodynamic Theory of Structure, Stability and Fluctuations. John Wiley & Sons, London, 1971.
[6] R. Clausius. Uber verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie. Annalen der Physik und Chemie, 125:353–400, 1865.
[7] D.H.E. Gross. The microcanonical entropy is multiply differentiable no dinosaurs in microcanonical gravitation: No special "microcanonical phase transitions". cond-mat/0403582:3.
[8] J.E. Kilpatrick. Classical thermostatistics. In H. Eyring, editor, Statistical Mechanics, number II, chapter 1, pages 1–52. Academic Press, New York, 1967.
[9] D.H.E. Gross. Ensemble probabilistic equilibrium and non-equilibrium thermodynamics without the thermodynamic limit. In Andrei Khrennikov, editor, Foundations of Probability and Physics, number XIII in PQ-QP: Quantum Probability, White Noise Analysis, pages 131–146, Boston, October 2001. ACM, World Scientific.
[10] D.H.E. Gross. A new thermodynamics from nuclei to stars. Entropy, 6:158–179, cond-mat/0505190 (2004).
[11] D.H.E. Gross. Microcanonical thermodynamics: Phase transitions in “Small” systems, volume 66 of Lecture Notes in Physics. World Scientific, Singapore, 2001.
[12] R.D. Carlitz. Hadronic matter at high density. Phys.Rev.D, 5:3231–3242, 1972.
[13] P. Hertz. Über die mechanische Begründung der Thermodynamik II. Ann. Phys. (Leipzig), 33:537, 1910.
[14] D.H.E. Gross and J.F. Kenney. The microcanonical thermodynamics of finite systems: The microscopic origin of condensation and phase separations; and the conditions for heat flow from lower to higher temperatures. Journal of Chemical Physics, cond-mat/0503604 (2005).
[15] D.H.E. Gross. Classical equilibrium thermostatistics, "sancta sanctorum of statistical mechanics", from nuclei to stars. Physica A340/1-3:76, (2004).
[16] O. Schapiro, D.H.E. Gross, and A. Ecker. Microcanonical monte carlo. First International Conference on Monte Carlo and Quasi-Monte Carlo Methods in Scientific Computing, volume 106, pages 346–353, Las Vegas, Nevada, 1995.
[17] D.H.E. Gross and M.E. Madjet. Microcanonical vs. canonical thermodynamics. cond-mat/0611192.
[18] D.H.E. Gross and M.E. Madjet. Cluster fragmentation, a laboratory for thermodynamics and phase-transitions in particular. Proceedings of "Similarities and Differences between Atomic Nuclei and Clusters", pages 203–214. Tsukuba, Japan 1997. AIP.
[19] D.H.E. Gross. Geometric foundation of thermo-statistics, phase transitions, second law of thermodynamics, but without thermodynamic limit. PCCP, 4:863(2002), cond-mat/0201235.
[20] M. D’Agostino et al. Negative heat capacity in the critical region of nuclear fragmentation: an experimental evidence of the liquid-gas phase transition. Phys.Lett.B, 473:219–225, 2000.
[21] M. Schmidt, R. Kusche, T. Hippler, J. Donges, W. Krammiller, B. von Issendorff, and H. Haberland. Negative heat capacity for a cluster of 147 sodium atoms. Phys.Rev.Lett., 86:1191–1194, 2001.
[22] W. Thirring. Systems with negative specific heat. Z. f. Phys., 235:339–352, 1970.
[23] M.Pichon and the INDRA and ALADIN collaboration. Bimodality in binary Au + Au collisions from 60 to 100 MeV/u. Proceedings XLI Winter Meeting, Bormio, 2003, p.149.

[24] D.H.E. Gross, Y.M. Zheng, and H. Massmann. New kind of phase transition in hot nuclei. Phys. Lett., B 200:397–400, 1987.

[25] D.H.E. Gross. Statistical decay of very hot nuclei, the production of large clusters. Rep.Progr.Phys., 53:605–658, 1990.

[26] D.J. Wales and S. Berry. Freezing, melting, spinodals, and clusters. J. Chem. Phys., 92:4473–4482, 1990.

[27] In T. Dauxois, S. Ruffo, E. Arimondo, and M. Wilkens, editors, Dynamics and Thermodynamics of Systems with Long Range Interactions, Lecture Notes in Physics, 602, Heidelberg, 2002. Springer.

[28] O. Lopez, D. Lacroix, and E. Vient. Bimodality as signal of liquid-gas phase transition in nuclei? nucl-th/0504027

[29] Here I do not mean irregularities of the order of $N^{-1/3}$ due to the discreteness of the quantum level distributions