A New Thermodynamics, 
From Nuclei to Stars

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Abstract
Equilibrium statistics of Hamiltonian systems is correctly described by the microcanonical ensemble. Classically this is the manifold of all points in the \(N\)-body phase space with the given total energy. Due to Boltzmann’s principle, \(e^S = \text{tr}(\delta(E - H))\), its geometrical size is related to the entropy \(S(E, N, \cdots)\). This definition does not invoke any information theory, no thermodynamic limit, no extensivity, and no homogeneity assumption, as are needed in conventional (canonical) thermo-statistics. Therefore, it describes the equilibrium statistics of extensive as well as non-extensive systems. Due to this fact it is the fundamental definition of any classical equilibrium statistics. It can address nuclei and astrophysical objects as well. All kind of phase transitions can be distinguished sharply and uniquely for even small systems. For transitions in nuclear physics the scaling to an hypothetical uncharged nuclear matter with an \(N/Z\)–ratio like realistic nuclei is not needed.

1 Introduction

Classical Thermodynamics and the theory of phase transitions of homogeneous and large systems are some of the oldest and best established theories in physics. It may look strange to add anything new to it. Let me recapitulate what was told to us since > 100 years:

- Thermodynamics addresses large homogeneous systems at equilibrium (in the thermodynamic limit \(N \to \infty|_{N/V = \rho, \text{homogeneous}}\)).

- Phase transitions are the positive zeros of the grand-canonical partition sum \(Z(T, \mu, V)\) as function of \(e^\beta \mu\) (Yang-Lee-singularities). As the partition sum for a finite number of particles is always positive, zeros can only exist in the thermodynamic limit \(V|_{\beta, \mu} \to \infty\).
• Micro and canonical ensembles are equivalent.  

• Thermodynamics works with intensive variables $T, P, \mu$.

• Unique Legendre mapping $T \rightarrow E$.

• Heat only flows from hot to cold (Clausius).

• Second Law only in infinite systems when the Poincarré recurrence time becomes infinite (much larger than the age of the universe (Boltzmann)).

Under these constraint only a tiny part of the real world of equilibrium systems can be treated. The ubiquitous non-homogeneous systems: nuclei, clusters, polymer, soft matter (biological) systems, but also the largest, astrophysical systems are not covered. Even normal systems with short-range coupling at phase separations are inhomogeneous and can only be treated within conventional homogeneous thermodynamics (e.g. van-der-Waals theory) by bridging the unstable region of negative compressibility by an artificial Maxwell construction. Thus even the original goal, for which Thermodynamics was invented some 150 years ago, the description of steam engines is only artificially solved. There is no (grand-)canonical ensemble of phase separated and, consequently, inhomogeneous, configurations. It has a deep reason as I will discuss below: here the systems have a negative heat capacity (resp. susceptibility). This, however, is impossible in the (grand-)canonical theory where $c \propto (\delta E)^2$.

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1 How does one prove this?: The general link between the microcanonical probability $e^{S(E,N)}$ and the grand-canonical partition function $Z(T,\mu)$ is by the Laplace transform:

$$Z(T,\mu,V) = \int_0^\infty \int_0^\infty \frac{dE}{\epsilon_0} dN e^{-\left[\frac{E-\mu N - TS(E,N)}{T}\right]/T}$$

$$= \frac{V^2}{\epsilon_0} \int_0^\infty \int_0^\infty de dn e^{-V(e-\mu n - T s(e,n))/T}$$

$$\approx e^{\text{const.} + \text{lin.} + \text{quad.}}$$

If $s(e,n)$ is concave then there is a single point $e_s, n_s$ with

$$\frac{1}{T} = \frac{\partial S}{\partial E} \bigg|_{e_s}$$

$$\mu = -\frac{\partial S}{\partial N} \bigg|_{e_s}$$

In the thermodynamic limit $(V \rightarrow \infty)$ the quadratic approximation in equ. 3 becomes exact and there is a one to one mapping of the microscopic mechanical $e = E/V, n = N/V$ to the intensive $T, \mu$. This on the other hand shows explicitly that the intensive variables $T, \mu$ are ill defined in small systems like nuclei. They, as well as free energy $F = E - TS$, or enthalpy $H = E + PV$, etc.., should not be used.
1.1 Example: Why one should not use conventional scaling theory to fix phase transitions in Nuclear Physics

Still many authors addressing phase-transitions in nuclear physics believe they should link these phenomena by finite size scaling to "nuclear matter" in the thermodynamic limit. This is the way how phase transitions can be located in conventional canonical statistics of ordinary extensive systems with short-range interactions.

However, infinite nuclear matter with the same \( N/Z \) ratio as ordinary nuclei does not exist. The Coulomb self-energy of such a system would be infinite. Therefore the Coulomb interaction between the fragments of a hot nucleus must be switched off in such studies. There is no sense in using conventional scaling analysis to relate transition phenomena seen in nuclear collisions to anything that does not exist in real life. The Coulomb field has an important effect on the fragmentation of real nuclei (see e.g. the article by LeFevre at this conference) which one must understand by statistical fragmentation simulations. Thus, in the conventional approach there is the only choice, either one describes realistic but small nuclei without any connection to phase transitions. Or one has a scaling theory to something that does not exist in reality: uncharged nuclear matter with fixed neutron to proton ratio.

If anything like phase-transitions exist in real nuclei then only in the sense of a new generalized thermodynamics. In the rest of this paper I will describe such a generalization which takes Boltzmann’s principle serious and avoids the thermodynamic limit. This opens Thermodynamics to the much larger world of non-extensive systems. The most prominent example are of course self-gravitating astrophysical systems which I will discuss here also.

2 Boltzmann’s principle

The Microcanonical ensemble is the ensemble (manifold) of all possible points in the \( 6N \) dimensional phase space at the prescribed sharp energy \( E \):

\[
W(E, N, V) = \epsilon_0 \mathrm{tr} \delta(E - H_N)
\]

\[
\mathrm{tr} \delta(E - H_N) = \int \frac{d^3N \, d^3Nq}{N!(2\pi\hbar)^{3N}} \delta(E - H_N).
\]

Thermodynamics addresses the whole ensemble. It is ruled by the topology of the geometrical size \( W(E, N, \cdots) \), Boltzmann’s principle:

\[
S = k \ln W
\]

is the most fundamental definition of the entropy \( S \). Entropy and with it microcanonical thermodynamics has therefore a pure mechanical, geometrical foundation. No information theoretical formulation is needed. Moreover, in contrast to the canonical entropy, \( S(E, N, \cdots) \) is everywhere single valued and multiple
differentiable. There is no need for extensivity, no need of concavity, no need of additivity, and no need of the thermodynamic limit. This is a great advantage of the geometric foundation of equilibrium statistics over the conventional definition by the Boltzmann-Gibbs canonical theory. However, addressing entropy to finite eventually small systems we will face a new problem with Zermelo’s objection against the monotonic rise of entropy, the Second Law, when the system approaches its equilibrium. This is discussed elsewhere [1, 2]. A further comment: In contrast to many authors like Schrödinger [3] our ensemble is not an ensemble of non-interacting replicas of the considered system which may exchange energy. I do not consider the different ways to distribute energy over the different replicas. I consider the manifold of the same system at the precisely given energy under all possible different distributions of the momenta and positions of its constituents (particles) in the 6N-dimensional phase space. The result is then the average behaviour when one does not know the precise position and momentum of every particle but only the total energy.

3 Topological properties of $S(E, \cdots)$

The topology of the Hessian of $s(E, \cdots)$, the determinant of curvatures of $s(e, n)$, determines completely all kinds phase transitions. This is evidently so, because $e^{S(E)−E/T}$ is the weight of each energy in the canonical partition sum at given $T$, see footnote 1. Consequently, at phase separation this has at least two maxima, the two phases. And in between two maxima there must be a minimum where the curvature of $S(E)$ is positive. I.e. the positive curvature detects phase separation. This is of course also in the case of several conserved control parameters.

$$d(e, n) = \begin{vmatrix} \frac{\partial^2 s}{\partial e^2} & \frac{\partial^2 s}{\partial e \partial n} \\ \frac{\partial^2 s}{\partial n^2} & \frac{\partial^2 s}{\partial n^2} \end{vmatrix} = \lambda_1 \lambda_2$$

$$\lambda_1 \geq \lambda_2 \rightarrow \text{eigenvectors: } v_1, v_2$$

Of course for a finite system each of these maxima of $S(E, \cdots) − E/T$ have a non-vanishing width. These are intrinsic fluctuations in each phase.

3.1 Unambiguous signal of phase transitions in a ”Small” system

Nevertheless, the whole zoo of phase-transitions can be sharply seen and distinguished. This is here demonstrated for the Potts-gas model on a two dimensional lattice of finite size of 50 × 50 lattice points, c.f. fig. 1. 
Figure 1: Global phase diagram or contour plot of the curvature determinant (Hessian), eqn. (5), of the 2-dim Potts-3 lattice gas with $50 \times 50$ lattice points, $n$ is the number of particles per lattice point, $e$ is the total energy per lattice point. The line (-2,1) to (0,0) is the ground-state energy of the lattice-gas as function of $n$. The most right curve is the locus of configurations with completely random spin-orientations (maximum entropy). The whole physics of the model plays between these two boundaries. At the dark-gray lines the Hessian is $\det = 0$, this is the boundary of the region of phase separation (the triangle $AP_mB$) with a negative Hessian ($\lambda_1 > 0, \lambda_2 < 0$). Here, we have Pseudo-Riemannian geometry. At the light-gray lines is a minimum of $\det(e,n)$ in the direction of the largest curvature ($v_{\lambda_{\text{max}}}, \nabla \det = 0$) and $\det = 0$, these are lines of second order transition. In the triangle $AP_mC$ is the pure ordered (solid) phase ($\det > 0, \lambda_1 < 0$). Above and right of the line $CP_mB$ is the pure disordered (gas) phase ($\det > 0, \lambda_1 < 0$). The crossing $P_m$ of the boundary lines is a multi-critical point. It is also the critical end-point of the region of phase separation ($\det < 0, \lambda_1 > 0, \lambda_2 < 0$). The light-gray region around the multi-critical point $P_m$ corresponds to a flat, horizontal region of $\det(e,n) \sim 0$ and $\nabla \lambda_1 \sim 0$ and consequently to a somewhat extended cylindrical region of $s(e,n)$, details see [4, 5]; $C$ is the analytically known position of the critical point (second order transition) which the ordinary $q = 3$ Potts model (without vacancies) would have in the thermodynamic limit.
3.2 Systematic of phase transitions in the micro-canonical ensemble without invoking the thermodynamic limit

- A single stable phase of course with some intrinsic fluctuations (width) by $\lambda_1 < 0$. Here $s(e, n)$ is concave (downwards bending) in both directions. Then there is a one to one mapping of the canonical ↔ the micro-ensemble.

- A transition of first order with phase separation and surface tension is indicated by $\lambda_1(e, n) > 0$. $s(e, n)$ has a convex intruder (upwards bending) in the direction $v_1$ of the largest curvature $\geq 0$ which can be identified with the order parameter $\nu$. Three solutions of

$$\beta = \frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_s$$
$$\nu = \frac{\mu}{T} = -\left. \frac{\partial S}{\partial N} \right|_s$$

determine the intensive temperature $T = 1/\beta$ and the chemical potential $T\nu$. 

In the thermodynamic limit the whole region \( \{o_1, o_3\} \) is mapped into a single point in the canonical ensemble which is consequently non-local in \( o \). I.e. if the curvature of \( S(E, N) \) is \( \lambda_1 \geq 0 \) both ensembles are not equivalent even in the limit.

- A continuous ("second order") transition with vanishing surface tension, where two neighboring phases become indistinguishable. This is indicated by a line with \( \lambda_1 = 0 \) and extremum of \( \lambda_1 \) in the direction of order parameter \( v_{\lambda=0} \cdot \nabla \lambda_1 = 0 \). These are the catastrophes of the Laplace transform \( E \rightarrow T \).

### 3.3 CURVATURE

We saw that the curvature (Hessian) of \( S(E, N, \cdots) \) controls the phase transitions. What is the physics behind the curvature? For short-range force it is linked to the interphase surface tension.

Table 1: Parameters of the liquid–gas transition of small sodium clusters (MMMC-calculation [5]) in comparison with the bulk for a rising number \( N_0 \) of atoms, \( N_{surf} \) is the average number of surface atoms (estimated here as \( \sum N_{cluster}^{2/3} \)) of all clusters with \( N_i \geq 2 \) together. \( \sigma/T_{tr} = \Delta s_{surf} * N_0/N_{surf} \) 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. Brechignac et al. [6], and which are used in this calculation [5] for the individual clusters.

|   | \( N_0 \) | 200 | 1000 | 3000 | bulk |
|---|----------|-----|------|------|------|
| Na | \( T_{tr} [K] \) | 940 | 990 | 1095 | 1156 |
|   | \( q_{lat} [eV] \) | 0.82 | 0.91 | 0.94 | 0.923 |
|   | \( s_{boil} \) | 10.1 | 10.7 | 9.9 | 9.267 |
|   | \( \Delta s_{surf} \) | 0.55 | 0.56 | 0.44 |     |
|   | \( N_{surf} \) | 39.94 | 98.53 | 186.6 | \( \infty \) |
|   | \( \sigma/T_{tr} \) | 2.75 | 5.68 | 7.07 | 7.41 |
Figure 2: MMMC [5] simulation of the entropy $s(e)$ per atom ($e$ in eV per atom) of a system of $N_0 = 1000$ 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 $q_{\text{lat}} = e_3 - e_1$. Attention: the curve $s(e)$ is artificially sheared by subtracting a linear function $25 + e \times 11.5$ in order to make the convex intruder visible. $s(e)$ is always a steeply 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 $\sigma_{\text{surf}}/T_{\text{tr}} = \Delta s_{\text{surf}} * N_0/N_{\text{surf}}$. The double tangent (Gibbs construction) is the concave hull of $s(e)$. Its derivative gives the Maxwell line in the caloric curve $T(e)$ at $T_{\text{tr}}$. In the thermodynamic limit the intruder would disappear and $s(e)$ would approach the double tangent from below. Nevertheless, even there, the probability $\propto e^{Ns}$ of configurations with phase-separations are 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. The region $e_1 < e < e_3$ of phase separation gets lost.
3.4 Heat can flow from cold to hot

\textbf{Potts-Model, } q=10

![Graph](image-url)

\( e = \frac{E}{N} \)

Figure 3: Potts model, \((q = 10)\) in the region of phase separation. At \(e_1\) the system is in the pure ordered phase, at \(e_3\) in the pure disordered phase. A little above \(e_1\) the temperature \(T = \frac{1}{\beta}\) is higher than a little below \(e_3\). Combining two parts of the system: one at the energy \(e_1 + \delta e\) and at the temperature \(T_1\), the other at the energy \(e_3 - \delta e\) and at the temperature \(T_3 < T_1\) will equilibrate with a rise of its entropy, a drop of \(T_1\) (cooling) and an energy flow (heat) from \(3 \to 1\): i.e.: Heat flows from cold to hot! Clausius formulation of the Second Law is violated. Evidently, this is not any peculiarity of gravitating systems! This is a generic situation within classical thermodynamics even of systems with short-range coupling and \textit{has nothing to do with long range interaction.}
4 Negative heat capacity as signal for a phase transition of first order.

4.1 Nuclear Physics

A very detailed illustration of the appearance of negative heat capacities is given by d.Agostino et al. [29]. Here I want to remember one of the oldest experimental finding of a "back"-bending caloric curve in Nuclear Physics.

Figure 4: Experimental excitation energy per nucleon $e^*$ versus apparent temperature $T_{app}$ for backward $p$, $d$, $t$ and $\alpha$ together with heavy evaporation residues out of incomplete fusion of 701 Mev $^{28}$Si+$^{100}$Mo. The dotted curves give the Fermi-gas caloric curves for the level-density parameter $a = 6$ to 12. (Chbihi et al. Eur.Phys.J. A 1999)
4.2 Atomic clusters

Here I show the simulation of a typical fragmentation transition of a system of 3000 sodium atoms interacting by realistic (many-body) forces. To compare with usual macroscopic conditions, the calculations were done at each energy using a volume $V(E)$ such that the microcanonical pressure $P = \frac{\partial S}{\partial V} = 1 \text{ atm}$.

The inserts above give the mass distribution at the various points. The label "4:1.295" means 1.295 quadrimers on average. This gives a detailed insight into what happens with rising excitation energy over the transition region: At the beginning ($e^* \sim 0.442 \text{ eV}$) the liquid sodium drop evaporates 329 single atoms and 7.876 dimers and 1.295 quadrimers on average. At energies $e > \sim 1 \text{ eV}$ the drop starts to fragment into several small droplets ("intermediate mass fragments") e.g. at point 3: 2726 monomers, 80 dimers, $\sim 5$ trimers, $\sim 15$ quadrimers and a few heavier ones up to 10-mers. The evaporation residue disappears. This multifragmentation finishes at point 4. It induces the strong backward swing of the caloric curve $T(E)$. Above point 4 one has a gas of free monomers and at the beginning a few dimers. This transition scenario has a lot similarity with nuclear multifragmentation. It is also shown how the total interphase surface area, proportional to $N_{\text{eff}}^{2/3} = \sum_i N_i^{2/3}$ with $N_i \geq 2$ ($N_i$ the number of atoms in the $i$th cluster) stays roughly constant up to point 3 even though the number of fragments ($N_{fr} = \sum_i$) is monotonic rising with increasing excitation.
4.3 Stars

Self-gravitation leads to a non-extensive potential energy $\propto N^2$. No thermodynamic limit exists for $E/N$ and no canonical treatment makes sense. At negative total energies these systems have a negative heat capacity. This was for a long time considered as an absurd situation within canonical statistical mechanics with its thermodynamic “limit”.

However, within our geometric theory this is just a simple example of the pseudo-Riemannian topology of the microcanonical entropy $S(E,N)$ provided that high densities with their non-gravitational physics, like nuclear hydrogen burning, are excluded. We treated the various phases of a self-gravitating cloud of particles as function of the total energy and angular momentum, c.f. the quoted paper. Clearly these are the most important constraint in astrophysics.

Figure 6: Phases and Phase-Separation in Rotating, Self-Gravitating Systems, Physical Review Letters–July 15, 2002, cover-page, by (Votyakov, Hidmi, De Martino, Gross)
Figure 7: Microcanonical phase-diagram of a cloud of self-gravitating and rotating system as function of the energy and angular-momentum. Outside the dashed boundaries only some singular points were calculated. In the mixed phase the largest curvature $\lambda_1$ of $S(E,L)$ is positive. Consequently the heat capacity or the correspondent susceptibility is negative. This is of course well known in astrophysics. However, the new and important point of our finding is that within microcanonical thermodynamics this is a generic property of all phase transitions of first order, whether there is a short- or a long-range force that organizes the system.
5 Conclusion

Entropy has a simple and elementary definition by the area $e^{S(E,N,\cdots)}$ of the microcanonical ensemble in the $6N$ dim. phase space. Canonical ensembles are not equivalent to the micro-ensemble in the most interesting situations:

1. at phase-separation (heat engines!), one gets inhomogeneities, and a negative heat capacity or some other negative susceptibility,

2. Heat can flow from cold to hot.

3. phase transitions can be localized sharply and unambiguously in small classical or quantum systems, there is no need for finite size scaling to identify the transition.

4. also really large self-gravitating systems can be addressed.

Entropy rises during the approach to equilibrium, $\Delta S \geq 0$, also for small mixing systems. i.e. the Second Law is valid even for small systems [1, 2]. With this geometric foundation thermo-statistics applies not only to extensive systems but also to non-extensive ones which have no thermodynamic limit. For the application to Nuclear Physics I believe one should not define phase transitions by scaling arguments towards a non-existing "nuclear matter". This may overlook the non-extensivity of realistic nuclear systems. The Coulomb field of a fragmenting nucleus has an important influence on the mass and charge distribution of multifragmentation.

References

[1] 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.

[2] D.H.E. Gross. Second law in classical non-extensive systems. In D. Sheehan, editor, Proceedings of the First International Conference on Quantum Limits to the Second Law, pages cond-mat/0209467. University of San Diego, 2002.

[3] E. Schrödinger. Statistical Thermodynamics, a Course of Seminar Lectures, delivered in January-March 1944 at the School of Theoretical Physics. Cambridge University Press, London, 1946.

[4] D.H.E. Gross and E. Votyakov. Phase transitions in "small" systems. Eur.Phys.J.B, 15:115–126, (2000), http://arXiv.org/abs/cond-mat/?9911257
[5] D.H.E. Gross. Microcanonical thermodynamics: Phase transitions in “Small” systems, volume 66 of Lecture Notes in Physics. World Scientific, Singapore, 2001.

[6] C. Bréchignac, Ph. Cahuzac, F. Carlier, J. Leygnier, and J.Ph. Roux. J.Chem.Phys., 102:1, 1995.

[7] D.H.E. Gross. Thermo-statistics or topology of the microcanonical entropy surface. 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, pages 21–45. cond-mat/0206341, Heidelberg, 2002. Springer.

[8] G. Gallavotti. Statistical Mechanics. Texts and Monographs in Physics. Springer, Berlin, 1999.

Some papers on Negative Heat in chronological order:

[9] W. Thirring. Systems with negative specific heat. Z. f. Phys., 235:339–352, 1970.

[10] D.H.E. Gross. New developments in microcanonical monte carlo sampling of nuclear fragmentation. In Proc. Intern. Workshop on Semiclassical and Phase Space Approaches to the Dynamics of the Nucleus, pages 119–124, Aussois, 1987. Suppl. Journ. de Physique,FASC6,C2.

[11] D.H.E. Gross and H. Massmann. Statistical fragmentation of very hot nuclei, complete microcanonical approach. Nucl. Phys, A 471:339c–350c, 1987.

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

[13] P. Labastie and R.L. Whetten. Statistical thermodynamics of the cluster solid-liquid transition. Phys.Rev.Lett., 65:1567, 1990.

[14] H.R. Jaqaman and D.H.E. Gross. Signal of the liquid-gas phase transition. Nucl. Phys., A 524:321–343, 1991.

[15] D.H.E. Gross. Multifragmentation. In R.Bock, H.Emling, E.Grosse, U.Grundinger, K.D.Hildenbrand, and J. Knoll, editors, Proceedings of the International Nuclear Physics Conference, Wiesbaden, July 26-August 1,1992, Wiesbaden,Germany,invited plenary talk, pages 175c–190c, Amsterdam, 1993. Nuclear Physics A553.

[16] D.H.E. Gross and R. Heck. What is wrong with the bethe formula ? - measurable differences between the grandcanonical and microcanonical ensemble. Phys. Lett.B, 318:405–409, 1993.

[17] R.M. Lynden-Bell. Negative specific heat in clusters of atoms. to be published in Galactic Dynamics, ?, 1995.
[18] D.H.E. Gross and M.E. Madjet. Microcanonical vs. canonical thermodynamics. [http://xxx.lanl.gov/abs/cond-mat/9611192] 1996.

[19] D.H.E. Gross, A. Ecker, and X.Z. Zhang. Microcanonical thermodynamics of first order phase transitions studied in the potts model. *Ann. Physik*, 5:446–452, 1996, and [http://xxx.lanl.gov/abs/cond-mat/9607150]

[20] D.H.E. Gross and M.E. Madjet. Cluster fragmentation, a laboratory for thermodynamics and phase-transitions in particular. In Abe, Arai, Lee, and Yabana, editors, *Proceedings of “Similarities and Differences between Atomic Nuclei and Clusters”*, pages 203–214, Tsukuba, Japan 97, 1997. The American Institute of Physics.

[21] D.H.E. Gross, M.E. Madjet, and O. Schapiro. Fragmentation phase transition in atomic clusters i — microcanonical thermodynamics. *Z.Phys.D*, 39:75–83, 1997 [http://xxx.lanl.gov/abs/cond-mat/9608103]

[22] D.H.E. Gross and M.E. Madjet. Fragmentation phase transition in atomic clusters iv — the relation of the fragmentation phase transition to the bulk liquid-gas transition. *Z.Physik B*, 104:541–551, 1997; and [http://xxx.lanl.gov/abs/cond-mat/9707100]

[23] D. Lynden-Bell. Negative specific heat in astronomy, physics and chemistry. *Physica A*, 263:293 [http://xxx.lanl.gov/avs/cond–mat/9812172], 1999.

[24] A. Torcini and M. Antoni. Equilibrium and dynamical properties of two dimensional self-gravitating systems. *Phys.Rev.* [http://xxx.lanl.gov/abs/cond-mat/9808068] E59:2746–2763, 1999.

[25] M. Antoni, S. Ruffo, and A.Torcini. Dynamics and statistics of simple models with infinite-range attractive interaction. *World Scientific*, page 1, 1999.

[26] L. Casetti, M. Pettini, and E.G.D. Cohen. Geometric approach to hamiltonian dynamics and statistical mechanics. [cond-mat/9912092] 1999.

[27] F. Gulminelli and Ph. Chomaz. Critical behavior in the coexistence region of finite systems. *Phys.Rev.Lett.*, 82:1402–1405, 1999.

[28] M. Schmidt, R. Kusche, T. Hippler, J. Donges, W. Kornmüller, B. von Issendorff, and H. Haberland. Negative heat capacity for a cluster of 147 sodium atoms. *submitted to Nature*, 2000.

[29] M. D’Agostino, F. Gulminelli, Ph. Chomaz, M. Bruno, F. Cannata, R. Bougault, F. Gramegna, I. Iori, N. le Neindre, G.V. Margagliotti, A. Moroni, and G. Vannini. 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.
[30] M. Schmidt, R. Kusche, T. Hippler, J. Donges, W. Kornmüller, B. von Issendorff, and H. Haberland. Negative heat capacity for a cluster of 147 sodium atoms. Phys. Rev. Lett., 86:1191–1194, 2001.

[31] D.H.E. Gross. Phase transitions in "small" systems – a challenge for thermodynamics. Nucl. Phys., A681:366c–373c, 2001; http://arXiv.org/abs/cond-mat/0006087.

[32] C. Tsallis, B.J.C. Cabral, A. Rapisarda, and V. Latora. Comment on "negative specific heat for a cluster of 147 sodium atoms" by schmidt et al., pages cond-mat/0112266, 2001.

[33] F. Leyvraz and S. Ruffo. Ensemble inequivalence in systems with long-range interactions. cond-mat/0112124, 2001.

[34] F. Leyvraz and S. Ruffo. Ensemble inequivalence: A formal approach. cond-mat/0112131, 2001.

[35] I. Ispolatov and E.G.D. Cohen. On first-order phase transition in microcanonical and canonical non-extensive systems. http://xxx.lanl.gov/abs/cond-mat/0101311, 2001.

[36] L.G. Moretto, J.B. Elliot, L. Phair, and G.J. Wozniak. Negative heat capacities and first order phase transitions in nuclei and other mesoscopic systems. pages nucl–theor/0012037, 2001.

[37] D.H.E. Gross. Comment on "negative heat ..." by moretto et al. http://arXiv.org/abs/nucl-th/0012047, page 1, 2000).

[38] I. Hidmi, D.H.E. Gross, and H.R. Jaqaman. On the fragmentation of multiply charged sodium clusters. EPJD, 20:87–92; http://arXiv.org/abs/cond-mat/0205126, 2002.

[39] L.G. Moretto, L. Phair and J.B. Elliot and, and G.J. Wozniak. Negative heat capacities and first order phase transitions in nuclei. Phys. Rev.C, 66:041601(R),nucl–theor/0208024, 2002.

[40] D.H.E. Gross. Comment on "negative heat and first order phase transitions in nuclei" by moretto et al. pages http://arXiv.org/abs/nucl–th/0208034, 2002).

[41] A. Rapisarda and V. Latora. Negative specific heat in out-of-equilibrium nonextensive systems. preprint, pages nucl–th/0202075, 2002.