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Nuclear multifragmentation, its relation to general physics

A rich test ground of the fundamentals of statistical mechanics

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Abstract. Heat can flow from cold to hot at any phase separation even in macroscopic systems. Therefore also Lynden-Bell's famous gravo-thermal catastrophe must be reconsidered. In contrast to traditional canonical Boltzmann-Gibbs statistics this is correctly described only by microcanonical statistics. Systems studied in chemical thermodynamics (ChTh) by using canonical statistics consist of several *homogeneous macroscopic* phases. Evidently, macroscopic statistics as in chemistry cannot and should not be applied to non-extensive or inhomogeneous systems like nuclei or galaxies. Nuclei are *small and inhomogeneous.* Multifragmented nuclei are even more inhomogeneous and the fragments even smaller. Phase transitions of first order and especially phase separations therefore cannot be described by a (*homogeneous*) canonical ensemble. Taking this serious, fascinating perspectives open for statistical nuclear fragmentation as test ground for the basic principles of statistical mechanics, especially of phase transitions, *without the use of the thermodynamic limit.* Moreover, there is also a lot of similarity between the accessible phase space of fragmenting nuclei and inhomogeneous multistellar systems. This underlines the fundamental significance for statistical physics in general.

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1 Introduction

In 1981 Randrup and Koonin [1] proposed the statistical (grand-canonical) decay of an excited nucleus into several light fragments. As the grand-canonical ensemble fixes the mean mass by an intensive control parameter, the chemical potential μ, but has no information about the total mass M_t of the decaying nucleus, this works only for fragment masses $M_i \ll M_t$. This touches already the central point of the discussion to follow, the difference between intensive parameters (fields) used in canonical statistics in contrast to the mechanical extensive control parameters used in microcanonical statistics.

The statistical *multifragmentation* of a hot nucleus simultaneously into larger fragments was introduced by [2,3] (details of the historical development of the theory of statistical multifragmentation is discussed in appendix A of [4].) Of course the finiteness of the total mass and charge is then crucial. Meanwhile statistical multifragmentation developed to a powerful and successful description even of sophisticated correlations seen in nuclear multifragmentation, cf. also [5–8]. A presentation of its far-reaching implications for the fundamental understanding of statistical mechanics in general is now demanding.

Here I will give mainly the motivation. In sect. 2 I address the general basis of statistical mechanics without invoking the thermodynamic limit. Then I give the physical definition of entropy S, I show how phase-separation is necessarily linked to convexities of $S(E)$ and negative heat capacities. In [9] I discussed in detail the general topology of the entropy surface $S(E)$ indicating phase transitions in general. In sect. 3 I present shortly the application to three characteristic phenomena: Nuclear multifragmentation, the fragmentation of small atomic clusters and finally the fragmentation of stellar objects under large angular momentum.

In sect. 3.1 I only discuss the implications of the new formalism for statistical nuclear fragmentation. In this topical issue there will be many contributions that compare detailed experimental data to the predictions of the different models for statistical multifragmentation of hot nuclei. Here I will put the new statistics of nuclear multifragmentation into a more general perspective: I show how, similar to nuclear fragmentation, also atomic clus-

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ters fragment with rising excitation into more and more medium-sized fragments. In close similarity to nuclear multifragmentation also the accessible phase space of self-gravitating astro-physical systems splits under rising energy and/or angular momentum into various inhomogeneous phases of single stars, rotating multi-star systems, and sometimes even more exotic configurations as ring systems and others.

2 Fundamentals of thermostatistics without thermodynamic limit

Since the beginning of thermodynamics in the first half of the 19th century its original motivation was the description of steam engines and the liquid-to-gas transition of water. Here water becomes inhomogeneous and develops a separation of the gas phase from the liquid, *i.e.* water boils. Thus, *phase separations* were in the focus some 170 years ago. Every child realizes phase separation by the inter-phase surface. And every child distinguishes a solid crystal from a liquid by the hard surface of the latter. It is an irony of the history of statistical mechanics that phase transitions of first order can only be signaled indirectly by the academic construct of a Yang-Lee singularity [10]. There is no information about the necessary and characteristic inter-phase surface. Of course this is because of the use of the thermodynamic limit and the use of intensive Lagrange parameters as control parameters.

A little later statistical mechanics was proposed by Boltzmann [11,12] 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 standard Boltzmann-Gibbs thermostatistics, which, consequently, signal phase transitions of first order by Yang-Lee singularities.

It is amusing that this fact that is essential for the original purpose of thermodynamics to describe steam engines was never treated completely in the past 150 years. The system must be somewhat artificially split into (still macroscopic and homogeneous) pieces of each individual phase [13]. The most interesting configurations like two coexisting phases cannot be described by a *single* canonical ensemble. Important *inter-phase fluctuations* remain outside the picture, etc. Of course these are essential for the fragmentation process. These *inter-phase fluctuations* are also responsible for the negative heat capacity [14]. This is all hidden due to the restriction to homogeneous systems in the thermodynamic limit and the use of intensive control parameters like temperature, pressure, chemical potentials etc. What may be more surprising is the fact that the curvature of $S(E)$ can stay convex even at the thermodynamic limit. The leading volume term of $S(E)$ follows the Maxwell double tangent (concave hull) and has curvature 0. In the intermediate energy range between the liquid and the gas the surface contribution $\delta^2 S_{surf} \propto N^{2/3} > 0$ is the *dominant curvature.* It leads to a deep intruder in $S(E)$ *also in the thermodynamic limit.*

Also the second law can rigorously be formulated only microcanonically. Already Clausius [15–17] distinguished between external and internal entropy generating mechanisms. The second law is only related to the latter mechanism [18], 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 self-gravitating very large systems, we need a new and deeper definition of statistical mechanics and at the heart of it, of entropy.

2.1 What is entropy?

Entropy, S, is *the* characteristic entity of thermodynamics and statistics. 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 often beset with confusion between external transfers of entropy d_eS and its internal production d_iS.

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 but not least entropy, at the times of Clausius and possibly even today.

Clausius [15,16] defined a quantity which he first called the *"value of metamorphosis"*, in German *"Wert der Verwandlung"* in [16]. Eleven years later he [17] gave it the name "entropy" S:

$$S_b - S_a = \int_a^b \frac{\mathrm{d}E}{T} \,, \tag{1}$$

where T is the absolute temperature of the body when the momentary change is done, and $\mathrm{d}E$ is the increment (positive, respectively, negative) of all different forms of energy (heat and potential) put into, respectively, taken out of the system. (Later, however, we will learn that care must be taken of additional constraints on other control parameters like, *e.g.*, the volume, see below.)

From the observation that heat does not flow from cold to hot (see, however, sect. 2.2) he went on to enunciate the second law as

$$\Delta S = \oint \frac{\mathrm{d}E}{T} \geq 0, \tag{2}$$

which Clausius called the "*uncompensated metamorphosis*". As will be worked out later, the second law as presented by eq. (2) remains valid even in cases where heat (energy) flows during relaxation from low to higher temperatures.

Prigogine [18], cf. [13], 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_eS to or from the system under consideration, and its internal production d_iS. While the first type of entropy change d_eS (that effected by exchange of heat d_eQ with its surroundings) can be positive, negative or zero, the second type of entropy change d_iS is fundamentally related to the spontaneous internal evolution ("Verwandlungen", "metamorphosis" [15]) of the system, and states the universal irreversibility of spontaneous transitions. It can be only positive or zero in any spontaneous transformation.

Clausius gives an illuminating example in [16]: When an ideal gas suddenly streams under insulating 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 $\Delta E = E_1[(V_2/V_1)^{2/3} - 1]$ (which must be finally drained) it can be brought back into its initial state. Then, however, the entropy production in the cycle, as expressed by integral (2), 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 no work done, and consequently no contribution to the integral (2). 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 [11,12] later defined the entropy of an isolated system (for which the energy exchange with the environment $d_eQ \equiv 0$) in terms of the sum of possible configurations, W, which the system can assume consistent with its constraints of given energy and volume:

$$\boxed{\boxed{S = k * \ln W}} \tag{3}$$

as written on Boltzmann's tombstone, with

$$W(E,N,V) = \int \frac{\mathrm{d}^{3N}\vec{p}\,\mathrm{d}^{3N}\vec{q}}{N!(2\pi\hbar)^{3N}}\epsilon_0\ \delta(E - H\{\vec{q},\vec{p}\}) \tag{4}$$

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:

$$W(E,N,V) = \mathrm{Tr}[\mathcal{P}_E] \tag{5}$$
$$= \sum \begin{array}{l}\text{all eigenstates } n \text{ of } H \text{ with given } N,\ V,\\ \text{and } E < E_n \le E + \epsilon_0\end{array}$$

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 sub-manifold of points in the $6N$-dimensional phase space (Γ-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.

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 [19]. To have complete knowledge of the system we would need to know (within its semi-classical 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 $6N$-dimensional 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 eq. (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 [20] and more recently in [21] the inherent finite resolution of the macroscopic description implies an increase of W or S with time when an external constraint is relaxed. This is a statement of the second law of thermodynamics, which requires that the *internal* production of entropy be positive or zero for every spontaneous process. The 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.

2.2 The zeroth law in conventional extensive thermodynamics

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

$$S_{1+2}(E,E_1) = S_1(E_1) + S_2(E - E_1) \tag{6}$$

is maximal:

$$\mathrm{d}S_{1+2}(E,E_1)|_E = \mathrm{d}S_1(E_1) + \mathrm{d}S_2(E - E_1) = 0. \tag{7}$$

Under an energy flux $\varDelta E_{2\to 1}$ from $2 \to 1$ the total entropy changes to lowest order in $\varDelta E$ by

$$\varDelta S_{1+2}|_E = (\beta_1 - \beta_2)\varDelta E_{2\to 1}, \tag{8}$$

$$\beta = \mathrm{d}S/\mathrm{d}E = \frac{1}{T}\,. \tag{9}$$

Consequently, a maximum of $S_{total}(E = E_1+E_2, E_1)|_E \geq S_{1+2}$ will be approached when

$$\mathrm{sign}(\varDelta S_{total}) = \mathrm{sign}(T_2 - T_1)\,\mathrm{sign}(\varDelta E_{2\to 1}) > 0. \tag{10}$$

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. (6)). 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 $S(E,N) = Ns(e = E/N) = 2S(E/2, N/2)$ is necessarily non-negative:

$$C_V(E) = \partial E/\partial T = -\frac{(\partial S/\partial E)^2}{\partial^2 S/\partial E^2} \geq 0. \tag{11}$$

The combination of two pieces of $N/2$ particles each, one at the specific energy $e_a = e_2 - \varDelta e/2$ and a second at $e_b = e_2 + \varDelta e/2$, 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 for extensive systems 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 non-convex,* $\partial^2 S/\partial E^2 \leq 0$ and eq. (11) follows. In the next subsection we will see that therefore *extensive systems cannot have phase transitions of first order.*

2.3 No phase separation, no boiling water, 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

$$Z(T) = \int_0^\infty e^{S(E)-E/T}\mathrm{d}E \tag{12}$$

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 ($\partial^2 S/\partial E^2 > 0$, like $y = x^2$) and the weight in (12) 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 $\varDelta E \sim E_{lat} \propto N$ of the order of the latent heat. Canonically, phase separations are unstable, however, not microcanonically, and of course not in real nature. The heat capacity is

$$C_V(E) = \partial E/\partial T = -\frac{(\partial S/\partial E)^2}{\partial^2 S/\partial E^2} < 0. \tag{13}$$

I.e., the convexity of $S(E)$ *and the negative heat capacity are the generic and necessary signals of phase separation* [4]. It is amusing that this fact that is essential for the original purpose of thermodynamics to describe steam engines and boiling water 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 [22].

2.3.1 Physical origin of positive curvature, the surface tension

For short-range forces the depth of the convex intruder into $S(E)$ is linked to the inter-phase surface tension. This is demonstrated by fig. 1 which shows an MMMC simulation of the entropy per atom of a cluster of 1000 sodium atoms.

At the energy $e \leq e_1$ the system is in the pure liquid phase and at $e \geq e_3$ in the pure gas phase, of course with fluctuations. The latent heat per atom is $q_{lat} = e_3 - e_1$. *Attention:* the curve $s(e)$ is artifically sheared by subtracting a linear function $25 + e * 11.5$ 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 $\sigma_{surf}/T_{tr} = \varDelta s_{surf} * N_0/N_{surf}$. This quantity, as well as other relevant parameters of the transition, is given in table 1. The double tangent (Gibbs construction) is the concave hull of $s(e)$. Its derivative gives the Maxwell line

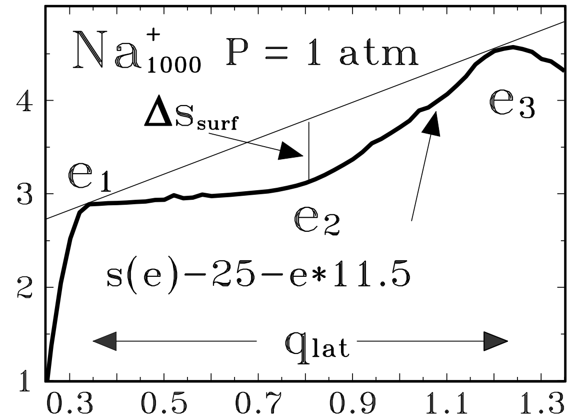


Fig. 1. MMMC [4] simulation of the entropy $s(e)$ per atom (e in eV per atom) of a system of $N_0 = 1000$ sodium atoms at an external pressure of 1 atm.

Table 1. Parameters of the liquid-gas transition of small sodium clusters (MMMC calculation [4]) 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, cf. Brechignac *et al.* [23], and which are used in this calculation [4] 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
	Δs_{surf}	0.55	0.56	0.44	
	N_{surf}	39.94	98.53	186.6	∞
	σ/T_{tr}	2.75	5.68	7.07	7.41

in the caloric curve $T(e)$ at T_{tr}. In the thermodynamic limit the intruder would disappear and $s(e)$ would approach the double tangent from below. Nevertheless, even there, the probability 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. Consequently, the intruder can only be seen when the system is insolated (thermo-flask) and the energy can be controlled. *I.e., in the microcanonical situation.*

The existence of the negative heat capacity at phase separation has a surprising but fundamental consequence: Combining two systems with negative heat capacity 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 thermostatistics, as emphasized by Hertz* [24], *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* [25].

2.3.2 Lynden-Bell's paradox

By the same reason the well-known paradox of Antonov in astro-physics due to the occurrence of negative heat capacities must be reconsidered: Lynden-Bell [26] uses standard arguments from extensive thermodynamics that a system a with negative heat capacity $C_a < 0$ 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 this will go for ever. This is wrong because just the opposite happens, the hotter a even *absorbs* energy from the colder b and both system come to equilibrium at the same intermediate temperature, cf. [25,27]. Negative heat capacity can only occur in the microcanonical ensemble. Temperature is *not* controlling the direction of energy (heat) flow when the heat capacity is negative. This is controlled by *entropy* according to the second law. Isothermal self-gravitating systems appear somehow paradoxical. Moreover, one cannot argue, as for extensive systems, that $S_{1+2} = S_1 + S_2$ and $E_{1+2} = E_1 + E_2$ as discussed above. There are far-reaching correlations between the two systems due to long-ranged gravity.

In the thermodynamic limit $N \to \infty$ of a system with short-range coupling the depth of the convex intruder $\Delta S_{surf} \sim N^{2/3}$, *i.e.* $\Delta S_{surf}/N = \Delta s_{surf} \propto N^{-1/3}$ must go to 0 due to van Hove's theorem. Of course it is only the *specific* surface entropy $\Delta S_{surf}/N$ which disappears. 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 at phase separation should also be seen in ordinary macroscopic systems in chemistry!*

Searching for example in Guggenheims book [13] 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!*

It is interesting to notice that, if ordinary macroscopic thermodynamics is used in describing finite systems, artificial unphysical effects need to be invoked to obtain negative heat capacities at first-order phase transitions [28]. Therefore, let me recapitulate in the next subsection 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.

2.4 Macroscopic systems in chemistry

Systems studied in chemical thermodynamics consist of several *homogeneous macroscopic* phases $\alpha_1, \alpha_2, \cdots$ cf. [13]. Their mutual equilibrium must be explicitly constructed from outside.

Each of these phases are assumed to be homogeneous and macroscopic (in the "thermodynamic limit" ($N_\alpha \to \infty|_{\rho_\alpha=\mathrm{const}}$)). 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 α is defined as the Laplace transform of the underlying microcanonical sum of states $W(E)_\alpha = e^{S_\alpha(E)}$ [29,30]

$$Z_\alpha(T) = \int_0^\infty e^{S_\alpha(E) - E/T_\alpha} \mathrm{d}E. \tag{14}$$

The mean canonical energy is

$$\langle E_\alpha(T_\alpha)\rangle = -\partial \ln Z_\alpha(T_\alpha)/\partial \beta_\alpha,$$
$$\beta_\alpha = \frac{1}{T_\alpha}\,. \tag{15}$$

In chemical situations proper the assumption of homogeneous macroscopic individual phases is of course acceptable. In the thermodynamic limit ($N_\alpha \to \infty|_{\rho_\alpha=\mathrm{const}}$) of a *homogeneous* phase α, the canonical energy $\langle E_\alpha(T_\alpha)\rangle$ becomes identical to the microcanonical energy E_α when the temperature is determined by

$$T_\alpha^{-1} = \beta_\alpha = \left.\frac{\partial S_\alpha(E,V_\alpha)}{\partial E}\right|_{E_\alpha}. \tag{16}$$

The relative width of the canonical energy is

$$\Delta E(T)_\alpha = \frac{\sqrt{\langle E_\alpha^2\rangle_T - \langle E_\alpha\rangle_T^2}}{\langle E_\alpha\rangle_T} \propto \frac{1}{\sqrt{N_\alpha}}. \tag{17}$$

The heat capacity at constant volume is (care must be taken about the constraints (!))

$$C_\alpha|_{V_\alpha} = \frac{\partial\langle E_\alpha(T_\alpha,V_\alpha)\rangle}{\partial T_\alpha} \tag{18}$$

$$= \frac{\langle E_\alpha^2\rangle_{T_\alpha} - \langle E_\alpha\rangle_{T_\alpha}^2}{T_\alpha^2} \geq 0. \tag{19}$$

Only in the thermodynamic limit ($N_\alpha \to \infty|_{\rho_\alpha=\mathrm{const}}$) does the relative energy uncertainty $\Delta E_\alpha \to 0$, and the canonical and the microcanonical ensembles for each homogeneous phase (α) become equivalent. This equivalence is the *only* justification of the canonical ensemble controlled by intensive temperature T, or chemical potential μ, or pressure P. I do not know of any microscopic foundation of the canonical ensemble and intensive control parameters apart from the limit. This is also the reason why, *e.g.*, the Clausius-Clapeyron equation as an equation between intensive variables is *not* applicable away from the thermodynamic limit, *e.g.* in nuclei.

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 (α_1 and α_2) with an overall *negative* heat capacity cannot be described by a *single common* canonical distribution [4,31]. The inter-phase fluctuations are ignored.

This new fundamental interpretation of thermo statistics was introduced to the chemistry community in [32,33].

2.5 A remark on "non-equilibrium" thermodynamics of small sytems

Prigogine quite clearly gives a short introduction into the logical foundations of non-equilibrium thermodynamics in [34]. The system is assumed to be composed by small subsystems internally in thermodynamic equilibrium. Each one is itself macroscopic and homogeneous that the conventional canonical Boltzmann-Gibbs statistics applies. However, the individual subsystems are not assumed to be in mutual thermodynamic equilibrium. There are temperature and/or pressure gradients, there may be a flow of the subsystems etc. Hydrodynamics or heat conductivity are examples. Clearly, this is certainly not possible in small systems like atomic nuclei or atomic clusters. Therefore, attempts to transfer macro-thermo-dynamic concepts like temperature or Gibbs-free energy $G(T,P)$ to nano-objects [35] like single biological molecules and the exploration of Jarzynski's equalitity [36] must be considered with reservation cf. [37,38]. Temperature, and pressure are ill defined in such small objects [39].

3 Statistical fragmentation

3.1 Nuclear fragmentation

The new lesson to be learned is that if one defines the phases by individual peaks in $e^{S(E)-E/T}$ in (12), then there exist also *inhomogeneous phases* like in fragmented nuclei or stellar systems. The general concept of thermo-statistics becomes enormously widened.

However, before applying the microcanonical thermo-statistics to nuclear collisions, a clarification is necessary: Nuclear collisions are *transient* phenomena. Thus, a theory of statistical nuclear fragmentation is an *approximation* to a *dynamical* process. This is well known and applies as well to the old Weisskopf theory of the statistical decay of a compound nucleus. The scenario one has in mind is that the emissions of fragments over the barrier is so slow that all accessible exit channels are tested. This is the open phase space *at or on top of the exit barrier.* In the statistical fragmentation model MMMC [4] this is taken care of by sampling all fragments under non-overlapping conditions inside a "freeze-out" volume corresponding to $\sim 5 \times V_0$ the volume of the nucleus in its ground state. The average distance between neighboring fragments is then about 2 fm. The experimental discovery of nuclear *multifragmentation* by [40] and its theoretical interpretation by [3] was the clear recognition that within a time of $\ll 10^{-21}$ s *several* medium-sized fragments can cross the decay barrier. This is much shorter than the time the fragments need to come out of mutual Coulomb fields, a fact discussed in detail in Chapt. 5.2.1 of my book [4].

At this point a clarifying comment must be made on the paper *Information theory of open fragmenting systems* and its relevance for nuclear fragmentation [41] especially to the established statistical fragmentation models. The authors write on p. 2: "*More important, to specify the density matrix, the projector P_S* (which projects on the given boundary condition (my explanation)) *has to be exactly known and this is in fact impossible. The nature of P_S is intrinsically different from the usual global observables A_l. Not only it is a many-body operator, but P_S requires the exact knowledge of each point of the boundary surface while no or few parameters are sufficient to define the A_l. This infinity of points corresponds to an infinite amount of information to be known to define the density matrix... the same is true for the standard (N,E,V) ensembles when dealing with finite unbound unconfined systems.*" The (N,E,V) ensemble of a bound system is the most fundamental ensemble of statistical mechanics. The treatment of the ideal gas in a box is one of the most elementary exercises in statistical mechanics that can be solved analytically. It is *the* paradigm of statistical mechanics and we should keep close to it as much as we can,

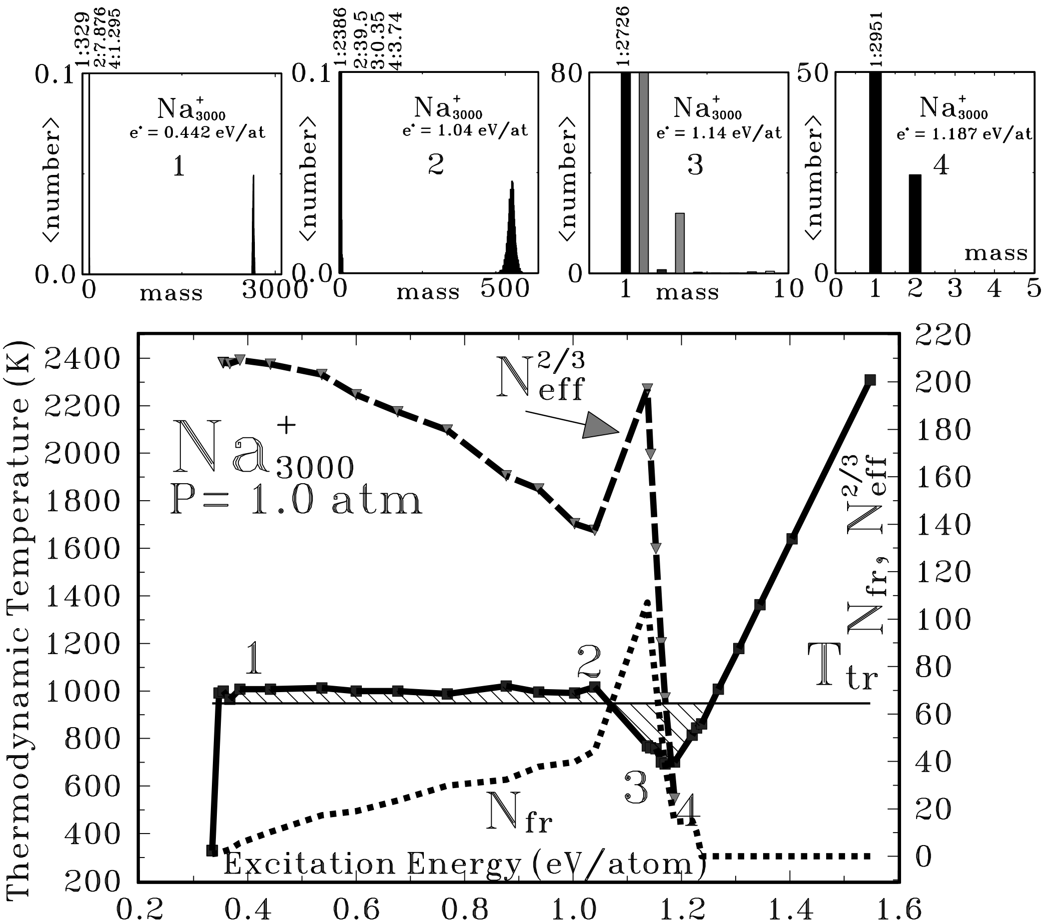


Fig. 2. Atomic cluster fragmentation, see sect. 3.2.

when we are going to extend standard statistical mechanics into the domain of systems far off the thermodynamic limit. There is no infinity of information needed. Of course the box potential must be included in the Hamiltonian which characterizes the system under consideration.

In our MMMC model we have a very specific physical picture in mind. It saves us not to enter dangerous new grounds of "dynamical" statistical mechanics. Moreover it gives us an idea why and how the system may explore statistically the whole accessible phase space. We took care of the fact that the fragments are trapped for $\approx 100\,\mathrm{fm}/c$ behind the Coulomb barrier. This can clearly be seen in BUU dynamical calculations [4]. The Coulomb barrier defines the freeze-out volume. The fragmenting system is assumed to be in statistical equilibrium during this time. So the ensemble imagined is a standard (N, E, V) ensemble and NOT some unbound unconfined system. Of course this is a simplifying approximation to a much more complicated *dynamical* situation. But judged from its great success this is a very reasonable simplification.

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 multifragmented nucleus have a *negative* heat capacity at constant volume C_V [42,43], and further references therein, and also at constant pressure C_P (if at all a pressure can be associated to nuclear fragmentation [4]).

The existence of well-defined and separated peaks (phases, *if distinguished by conserved control parameters*) in the event distribution of nuclear fragmentation data is demonstrated in [44] from various points of view. This signal is in a small system like a nucleus by far more sophisticated and detailed than the simple jumping from liquid to gas in traditional macroscopic systems in chemistry. A lot more physics about the mechanism of phase transitions can be learned from such studies. This will be the topic of the contributions by P. Chomaz, F. Gulminelli and by O. Lopez and M.F. Rivet, as also by B. Tamain, to this topical issue.

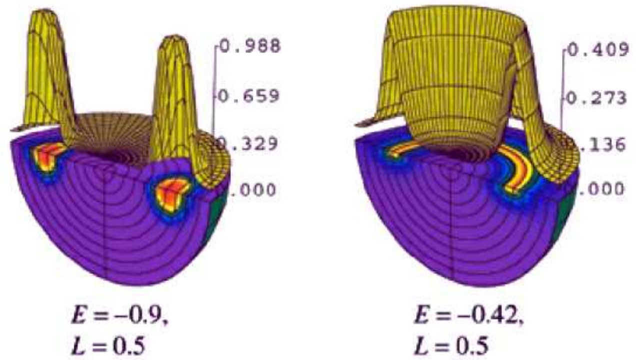
3.2 Atomic clusters

As there are several examples for nuclear multifragmentation in this paper I will show the analogous development of the fragmentation of a single charged cluster of 3000 Na atoms with rising excitation energy from the evaporation of a few Na atoms over multifragmentation into monomers, dimers up to 10-mers towards finally the total vaporisation of the original cluster (see fig. 2). Notice that this occurs all within the range of the backbending (*i.e.* the negative heat capacity) of the caloric curve.

To compare with usual macroscopic conditions, the calculations were done at each energy using a volume $V(E)$ such that the microcanonical pressure $P = \frac{\partial S}{\partial V} / \frac{\partial S}{\partial E} = 1\,\text{atm}$. The inserts on the top of the figure give the mass distribution at the various points. *E.g.*, in insert 1 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 per atom $e \gtrsim 1\,\text{eV}$ the drop starts to fragment into several small droplets ("intermediate mass fragments") *e.g.* at point 3: 2726 monomers, 80 dimers, ~ 5 trimers, ~ 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 of similarity with nuclear multifragmentation. The total inter-phase surface area $\propto N_{eff}^{2/3} = \sum_i N_i^{2/3}$ 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 ($N_{fr} = \sum_i$) rises monotonically. Notice, the caloric curve between point 1 and 2 looks like the "compound nucleus for ever" proposed by [45], though the temperature is higher than T_{tr} and the decay is not evaporation for ever. In contrast to claims in [45] the phase transiton finishes with considerable multifragmentation and a deep back-bend of the caloric curve $T(E)$.

3.3 Fragmentation of astrophysical systems

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 we restrict to densities $\leq$ the density of normal hydrogen burning stars, *i.e.* to ordinary visible stars. We treated the various phases of a self-gravitating cloud of particles as a function of the total energy and angular momentum as shown in fig. 3. Clearly, these are the most important constraints in stellar physics. The necessity of using "extensive" instead of "intensive" control parameter is explicit in astrophysical problems. *E.g.*, for the description of rotating stars one conventionally works at a given temperature and fixed angular velocity Ω, cf. [46]. Of course in reality there is neither a heat bath nor a rotating disk. Moreover, the latter scenario is fundamentally wrong as at the periphery of the disk the rotational velocity may even become larger than velocity of light. Non-extensive systems like astro-physical ones do not allow a "field-theoretical" description controlled by intensive fields!



$E = -0.9$, $L = 0.5$ $E = -0.42$, $L = 0.5$

Fig. 3. Contour plots and density profiles of a rotating, self-gravitating N-body system showing the formation of a stable double cluster (left) and an unstable ring (right) at different energies. The double-cluster structure illustrates the spontaneous breaking of rotational symmetry at intermediate energy and high angular momentum (from [47]).

E.g., configurations with a maximum of random energy

$$E_{random} = E - \frac{\Theta \Omega^2}{2} - E_{pot} \tag{20}$$

and consequently with the largest entropy are the ones with smallest moment of inertia Θ, compact single stars. Just the opposite happens when the angular momentum L and not the angular velocity Ω are fixed:

$$E_{random} = E - \frac{L^2}{2\Theta} - E_{pot}. \tag{21}$$

Then configurations with large moment of inertia are maximizing the phase space and the entropy. *I.e.* eventually double or multistars are produced, as observed in reality.

In fig. 4 one clearly sees the rich and realistic microcanonical phase diagram of a rotating gravitating system controlled by the "extensive" parameters energy and angular momentum [47].

3.4 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. This is interesting as the character of the distribution, deeply bimodal *vs.* energy or more equal, tells about the constraint in the experiment, *e.g.* by temperature (unlikely) or by energy. Not only their mean values are of physical interest. Statistical mechanics can be explored from its first

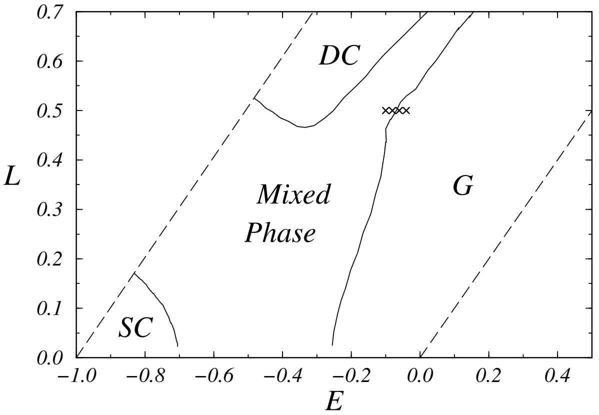


Fig. 4. Phase diagram of rotating self-gravitating systems in the energy angular-momentum (E, L)-plane [47]. DC: region of double stars, G: gas phase, SC: single stars. In the mixed region one finds various exotic configurations like ring systems in coexistence with gas, double stars or single stars. In this region of phase separation the heat capacity is negative and the entropy $S(E, L)$ is convex. The dashed lines $E - L = -1$ (left) and $E = L$ (right) delimit the region where systematic calculations were carried out.

microscopic principles in any detail well away from the thermodynamic limit. By our studies of nuclear fragmentation we found [30,31] the very general appearance of a negative heat capacity and the necessary convexity of the entropy $S(E)$ at any phase separation which 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.*

In nuclear fragmentation there may be other conserved control parameters besides the energy: *e.g.* in the recent paper by Lopez *et al.* [48] a bimodality in the mass asymmetry of the fragments is demonstrated to be 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 chemistry.* Angular momentum is a very crucial control parameter in stellar systems.

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 statistics of self-gravitating systems [26,49]. Also these cannot be described by a canonical ensemble. It was shown in [21,27] how the *microcanonical* phase space of these self-gravitating systems has many of 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 equilibrated or not is not proven by this observation though it is rather likely.

Microcanonical thermostatistics is proven to give a realistic, objective picture of a broad scenario of real physical phenomena, much broader than conventional canonical thermodynamics. Moreover, one of the original objects of thermodynamics, the description of the liquid-gas phase *separation* in steam engines, can now be understood within statistical mechanics.

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