Nuclear statistics, microcanonical or canonical? 
The physicists vs. the chemists approach.

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Nuclei are small and inhomogeneous. Multi-fragmented nuclei are even more inhomogeneous and the fragments even smaller. System studied in chemical thermodynamics (CTh) consist of several homogeneous macroscopic phases cf. [1]. Evidently, macroscopic statistics as in Chemistry cannot and should not be applied. Taking this serious, fascinating perspectives open for statistical nuclear fragmentation.

I. INTRODUCTION

Boltzmann developed statistical mechanics to explain thermodynamics on a microscopic and mechanical basis. To that purpose, he introduced the microcanonical ensemble of all realizations of a given many-body system under the few macroscopic constraints of particle number \( N \), energy \( E \) and its external volume \( V \). The number of cells, with size \((2\pi\hbar)^3\), in the \(6N\)-dim phase space of such systems is \( W(E,N,V) \). Then he identified the thermodynamic entropy by the famous formula which written on his tombstone:

\[
S = k^*\ln W
\]  

(1)

The physical meaning of this formula is: The entropy measures the amount of our microscopic ignorance of the considered many-body system. If we would have a complete knowledge, if we would know the positions and the momenta of all particles at time \( t \) (within quantum-mechanical uncertainty), \( W \) would be a single cell in the \(6N\)-dim. phase space of size \((2\pi\hbar)^3\) and \( S \) would be zero.

If our system is homogeneous (in a single phase) then the three fundamental ensembles of statistical mechanics, the grand-canonical and the canonical are equivalent to the microcanonical one in the thermodynamic limit \( N \rightarrow \infty \rightarrow \rho = N/V = \text{const} \). Otherwise, however, they are not equivalent. As only the above equivalence of the ensembles guarantees the physical meaning of the (canonical) ensembles, these have no physical justifications whenever the equivalence is not given.

To apply statistical mechanics to such inhomogeneous systems like small systems, or systems, even macroscopic, at phase separation, or very large self-gravitating systems the following considerations must be taken seriously.

II. MACROSCOPIC SYSTEMS IN CHEMISTRY

Microcanonical Boltzmann-Planck statistics is the basis of any statistical mechanics, see e.g. Landau-Lifshitz [2], even Guggenheim defines statistical mechanics starting from the microcanonical ensemble ([1], chapter 2), see also my paper [3, 4] v3.

Systems studied in chemical thermodynamics consist of several homogeneous macroscopic phases \( \alpha \), cf. [1]. Their mutual equilibrium must be explicitly constructed from outside. Each of these phases are assumed to be macroscopic (in the "thermodynamic limit" \( (N_\alpha \rightarrow \infty) | _{\rho_\alpha = \text{const}} \)). 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 \( W(E) = e^{S_\alpha(E)} \)

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

(2)

The mean canonical energy is

\[
< E_\alpha(T_\alpha) > = -\partial \ln Z_\alpha(T_\alpha) / \partial \beta_\alpha.
\]  

(3)

In chemical situations proper the assumption of macroscopic individual phases is of course acceptable. In the thermodynamic limit \( (N_\alpha \rightarrow \infty) | _{\rho_\alpha = \text{const}} \) 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

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

(4)
The relative width of the canonical energy is
\[ \Delta E_\alpha = \frac{\sqrt{E_\alpha^2} - <E_\alpha>^2}{<E_\alpha>} \propto \frac{1}{\sqrt{N_\alpha}} \] (5)
The heat capacity at constant volume is (care must be taken about the constraints (!))
\[ C_\alpha|V_\alpha = \frac{\partial <E_\alpha(T_\alpha,V_\alpha)>}{\partial T_\alpha} = \frac{<E_\alpha^2> - <E_\alpha>^2}{T_\alpha^2} \geq 0. \] (6)

Only in the thermodynamic limit \((N_\alpha \to \infty)|_{\beta_\alpha=\text{const}}\) does the energy uncertainty \(\Delta E_\alpha \to 0\), and the canonical and the microcanonical ensembles become equivalent. I do not know of any microscopic foundation of the canonical ensemble 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 \((\alpha_1 & \alpha_2)\) with an overall negative heat capacity cannot be described by a single common canonical distribution \([3, 6]\).

III. APPLICATION TO NUCLEAR FRAGMENTATION

Now, certainly, neither the phase of the whole multi-fragmented nucleus nor the individual fragments themselves can be considered as macroscopic homogeneous phases in the sense of chemical thermodynamics (CTh). Consequently, (CTh) 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 \([4]\)).

However, there 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. Not only their mean values are of physical interest. Statistical Mechanics can be explored from its first microscopic and mechanical principles in any detail well away from the thermodynamic limit. This gives us an immediate insight how statistical mechanics works. We can measure the entire distribution also if they are not sharply Gaussian. No exotic non-extensive statistics like Tsallis statistics \([5, 8]\) is demanded for equilibrated non-extensive systems. The “Sancta sanctorum of statistical mechanics” i.e. the microcanonical Boltzmann-Planck statistics covers all equilibrium systems \([7]\).

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 out of several nuclei. This situation is very much analogous to multi star systems like rotating double stars during intermediate times, where 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 \([10]\). Also these cannot be described by a canonical ensemble. It was shown in \([8, 11]\) how the microcanonical phase space of these self-gravitating systems has all the realistic configurations which are observed, more details in my WEB-page http://www.hmi.de/people/gross/. Of course, the question whether these systems are interim equilibrized or not is not proven by this observation though it is rather likely.

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