Microcanonical Thermostatistics as Foundation of Thermodynamics

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Conventional thermo-statistics address infinite homogeneous systems within the canonical ensemble. However, some 150 ears ago the original motivation of thermodynamics was the description of steam engines, i.e. boiling water. Its essential physics is the separation of the gas phase from the liquid. Of course, boiling water is inhomogeneous and as such cannot be treated by conventional thermo-statistics. Then it is not astonishing, that a phase transition of first order is signaled canonically by a Yang-Lee singularity. Thus it is only correctly treated by microcanonical Boltzmann-Planck statistics. It turns out that the Boltzmann-Planck statistics is much richer and gives even analytical insight into the statistical mechanics of condensation or, complementary, fragmentation phenomena and especially into entropy.

In this talk I will give the physical meaning of entropy and present a new statistical interpretation of the second law. Eventually I will explain why there is a critical end-point for the liquid-gas phase-coexistence while there seems to be none for the solid-gas one. Then I will illuminate the deep and essential difference between "extensive" and "intensive" control parameters, i.e. microcanonical and canonical statistics, exemplified by rotating, self-gravitating systems.

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Most Fundamental,
Straight,
Simplest way to Thermo-Statistics :

Macroscopic Information
is redundant microscopically

Microcanonical ensemble $\equiv$ set of points in:

$$W(E,N,V) = \epsilon_0 tr\delta(E-H_N)$$
$$tr\delta(E-H_N) = \int \frac{d^{3N}p\, d^{3N}q}{N!(2\pi\hbar)^{3N}}\delta(E-H_N).$$

Thermodynamics addresses the whole ensemble

Its geometrical size

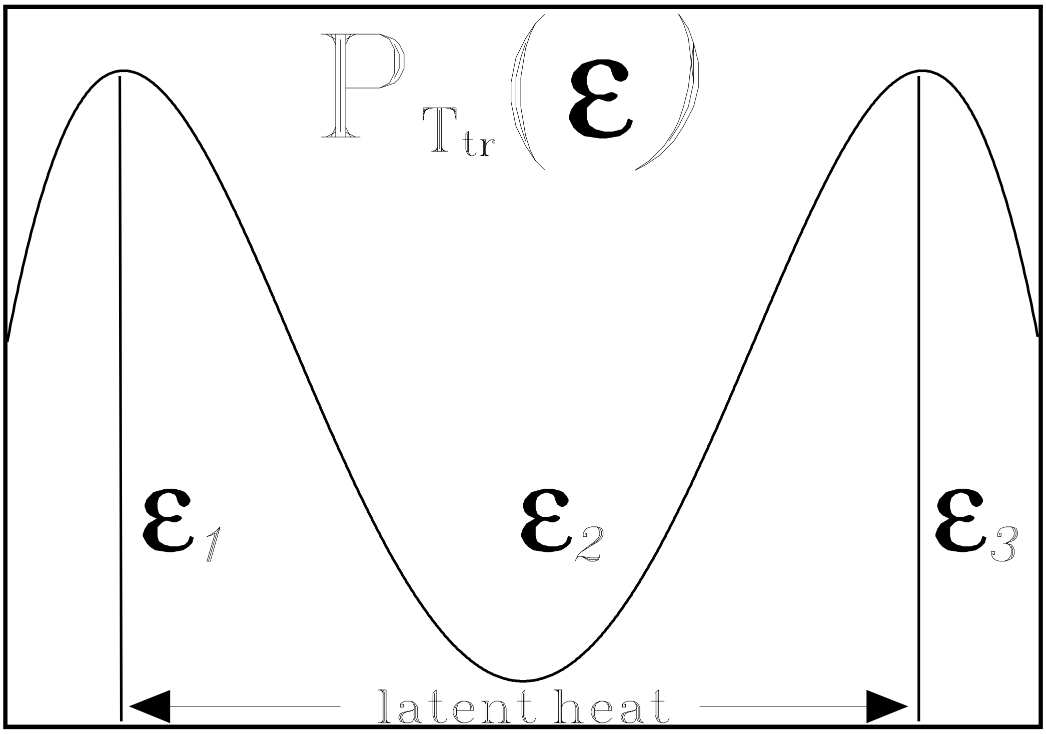
S=k*lnW

measures our ignorance of the complete $6N$ degrees of freedom.

(Boltzmann-Planck)

This is the physical meaning of entropy.

Conventional Boltzmann-Gibbs statistics address homogeneous, infinite systems. It is thus unable to describe phase-separation as e.g. boiling water.



$$P_{tr}(E) = e^{S(E)-E/T_{tr}}$$

Microcanonical Entropy

$$W(E,N,\mathcal{V}) \;=\; e^{S(E)} =$$

$$\frac{1}{N!(2\pi\hbar)^{3N}}\int_{\mathcal{V}^N} d^{3N}\,\vec{r}_i \int d^{3N}\,\vec{p}_i\,\delta[E-\sum_i^N \frac{\vec{p}_i^{\,2}}{2m_i} - V^{int}\{\vec{r}_i\}] =$$

$$\frac{\mathcal{V}^N(E-E_0)^{(3N-2)/2}\prod_1^N m_i^{3/2}}{N!\Gamma(3N/2)(2\pi\hbar^2)^{3N/2}}\int_{\mathcal{V}^N}\frac{d^{3N}r_i}{\mathcal{V}^N}\left(1-\frac{V^{int}\{\vec{r}_i\}-E_0}{E-E_0}\right)^{(3N-2)/2}$$

$$= W^{id-gas}(E-E_0,N,\mathcal{V}) \times W^{conf}(E-E_0,N,\mathcal{V})$$

$$= \; e^{[S^{id-gas}+S^{conf}]}$$

Rigorous split into ideal gas and configuration entropy

$$W^{conf}(E-E_0,N,\mathcal{V}) \;=\; \left[\frac{\mathcal{V}(E)}{\mathcal{V}}\right]^N \leq 1$$

$$[\mathcal{V}(E)]^N \;\stackrel{\text{def}}{=}$$

$$\int_{\mathcal{V}^N} d^{3N}r_i\left(1-\frac{V^{int}\{\vec{r}_i\}-E_0}{E-E_0}\right)^{(3N-2)/2}$$

$$S^{conf}(E-E_0,N,\mathcal{V}) \;=\; N\ln\left[\frac{\mathcal{V}(E)}{\mathcal{V}}\right] \leq 0$$

$$S^{conf}(E-E_0) \;\to\; \begin{cases} 0 & E \gg V^{int} \\ ln\{[\frac{\mathcal{V}_0}{\mathcal{V}}]^{N-1}\} < 0 & E \to E_0 \end{cases}$$

$$S^{id-gas}(E) \sim \frac{3N}{2}\ln\{E\}$$

is concave in E

Upwards jump (convexity) of configuration entropy where the droplet either fissions into two droplets or evaporates one particle.

There one additional cm-dof moves in the larger volume $\mathcal{V} - \mathcal{V}_{0(N-1)}$

$$\delta\Delta S^{conf} \sim \ln\{\frac{\mathcal{V} - \mathcal{V}_{0(N-1)}}{\mathcal{V}_{0(N-1)}}\}$$

Critical end point:

Where the curvature $S''_{total}(E) = 0$ or the up-bend of the configuration entropy $\delta\Delta S_{conf}$ equals the down-bend of the ideal gas entropy due to its concave curvature $\delta\Delta S_{id-gas}$:

$$
\begin{aligned}
S''_{total}(E) &= 0 \\
&= S''_{conf} + S''_{id-gas} \\
&\sim \delta\Delta S_{conf} - \delta\Delta S_{id-gas}
\end{aligned}
$$

Stars and galaxies

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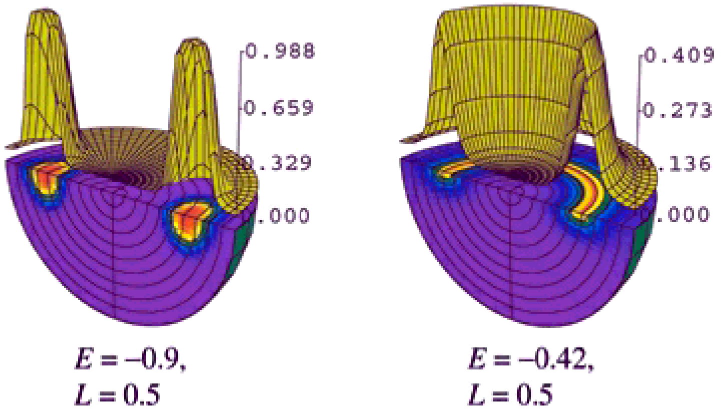

Contour plots and density profiles of a rotating, self-gravitating *N*-body system showing the formation of a stable double cluster (left) and an unstable ring (right) at different energies. The double-cluster structure illustrates the spontaneous breaking of rotational symmetry at intermediate energy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

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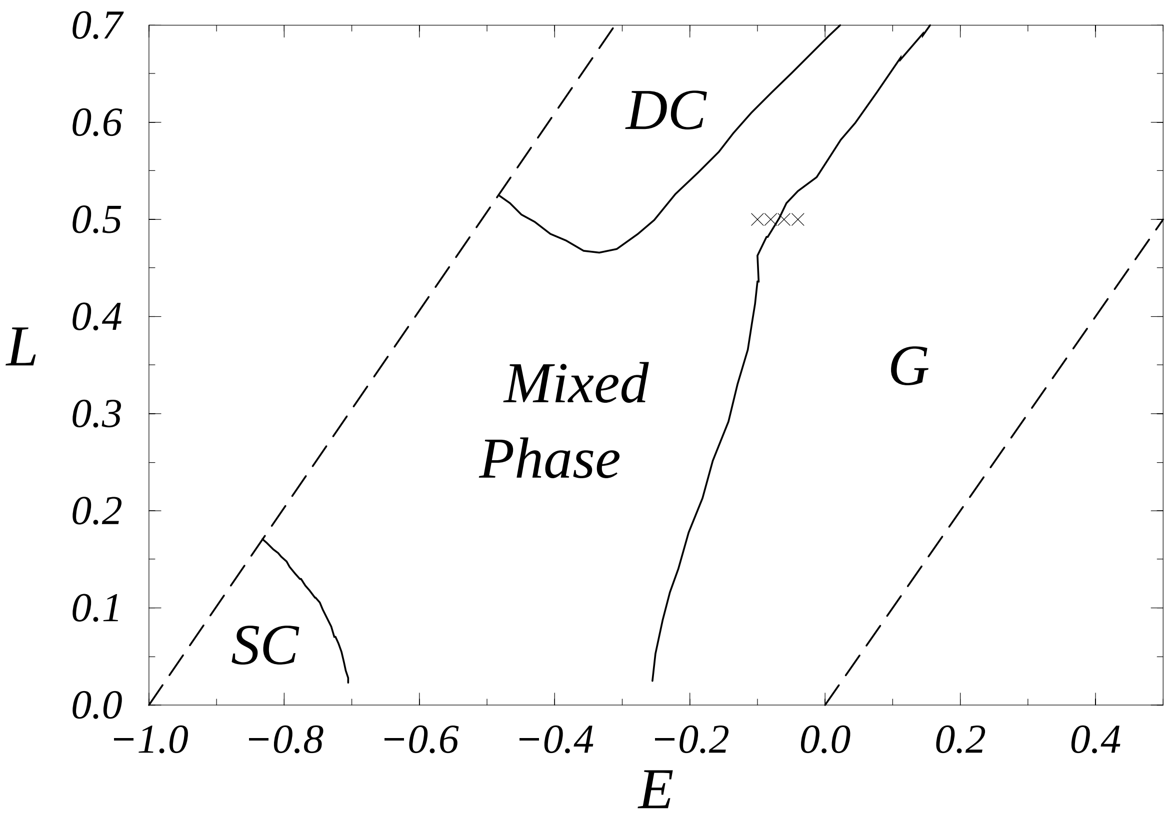
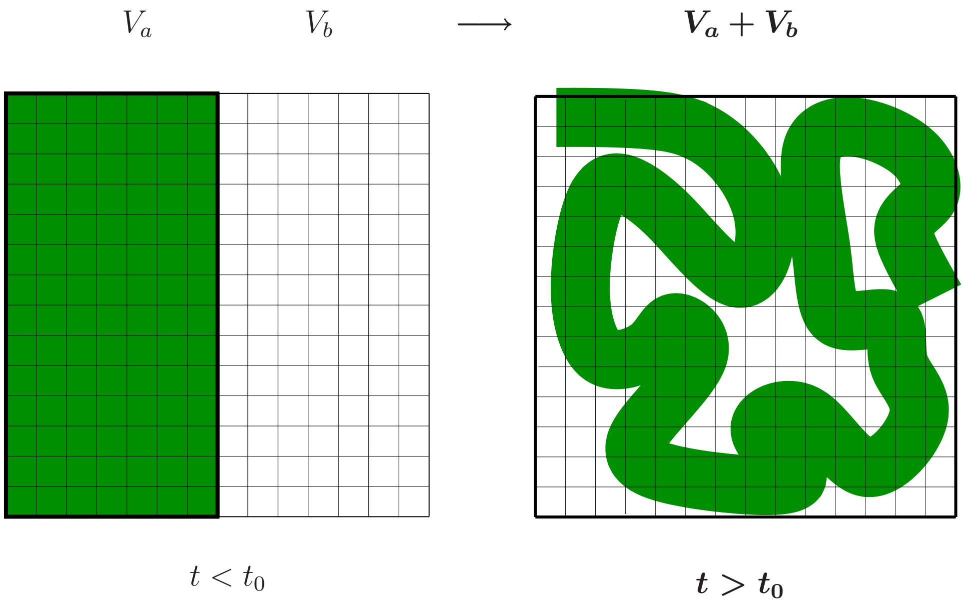
Phase diagram of self-gravitating and rotating system

$$intensive\ \Omega : E_{random} = E - \frac{\Theta\Omega^2}{2} - E_{pot}$$

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





Second Law of Thermodynamics

Problem:
Due to Liouville Hamilton dynamics is area-conserving.
Thus one has to redefine Boltzmann's W.
Main idea:
Calculate $W(E)$ not as Riemann (or better Lebesgue) integral but by "box-counting" which gives the area of the closure of $\overline{W}$: Thus $\overline{W(t \to \infty)} = W_{a+b}$. Thus any subjectivity is avoided.

Conclusion:

All interesting Thermodynamics is encrypted in
$S^{conf}(E)$

Only microcanonical Thermodynamics allows to describe phase transitions of first order thus it fulfills the original task of Thermodynamics

This is possible only by the use of "extensive" order parameters intensive T, P, μ not suited for inhomogeneous systems

Open problems:

- **Second law: more thoughts about spin-echo experiment.**
- **Gravitation: How to avoid closed boundaries $\Leftrightarrow$ evaporation ?**
- **Cosmology: Relation field theory $\Leftrightarrow$ extensive thermodynamics.**
- **Black hole entropy $\propto$ surface.**
- **Nuclear fragmentation:**
  Correlation between freeze-out volume and size distribution.