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We define a first order phase transition as a bimodality of the event distribution in the space of observations and we show that this is equivalent to a curvature anomaly of the thermodynamical potential and that it implies the Yang Lee behavior of the zeroes of the partition sum. We propose partial energy fluctuations as a directly measurable observable of such a phenomenon in Gibbs as well as Tsallis equilibria.

§1. Introduction

Phase transitions are universal properties of matter in interaction. In macroscopic physics, they are anomalies in the system equation of state (EoS) and hence classified according to the degree of non-analyticity of the EoS at the transition point. On the other side for finite systems, it is generally believed that Phase transition cannot be defined since thermodynamical potentials of a finite system in a finite volume are analytical functions. A classification scheme valid for finite systems has been proposed by Grossmann [1] using the distribution of zeroes of the canonical partition sum in the complex temperature plane [2]. Alternatively it has been claimed that phase transitions in finite systems can be related to a negative microcanonical heat capacity [3),4] or more generally to an inverted curvature of the thermodynamical potential as a function of an observable (i.e. of an equation of state (EOS)) which can then be seen as an order parameter [5]. Recently we have shown that this implies a bimodality of the probability distribution function (PDF) in a statistical ensemble in which this observable is only known in average, and we have shown the link between these different definitions [6]. This provide a consistent framework which allows to define phase transition in finite system knowing that if we can take the thermodynaimical limit the phase transitions we have identify in finite systems converges to the usual macroscopic definition.

§2. Back-bendings of the EOS and bimodalities of PDF of order parameter

Let us first consider the possible definition of a first order phase transition as a curvature anomaly of the thermodynamical potential as a function of one order parameter. This means that we should study a statistical ensemble for which the order parameter is either a conserved quantity or simply a sorting variable. For the liquid gas phase transition, the density can be taken as an order parameter. Since the density is related to the number of particles and the volume, one should consider

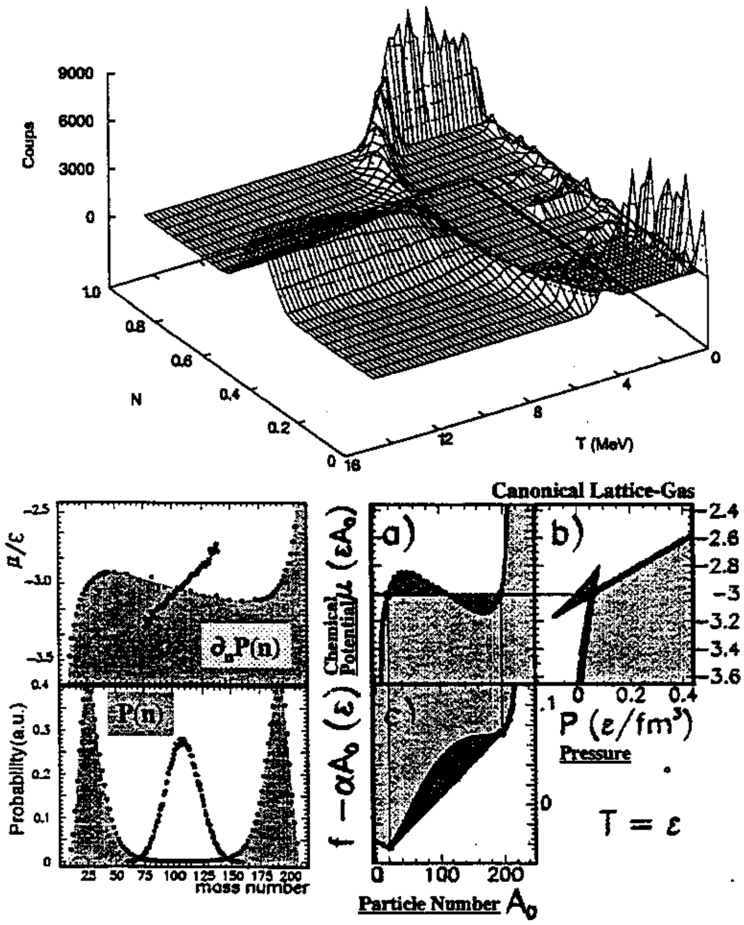

Fig. 1. Lattice gas results. Top Mass distribution as a function of the system temperature Bottom left: Canonical equation of states (top) from the logarithmic derivative of the grancanonical PDF (Bottom) calculated for $\mu = -3\epsilon$ and $T < T_c$ (grey area), $T > T_c$ (symbols). Bottom right: Canonical calculation of the free energy (bottom) and of its derivatives: the chemical potential (above) and the pressure (right).

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$$F = -T \log Z.$$

Therefore, a concavity anomaly of F as a function of N or V should be the signal of the phase transition. This is the result reported in the right part of figure 1 [5]. Using

$$\mu = -\partial_N F,$$

this induces a back bending of the chemical potential as a function of the number of particle. This means that the "susceptibility"

$$\chi^{-1} = \partial_N \mu$$

diverges before becoming negative. This anomaly in the chemical (μ, N) or in the mechanical (P,V) [5] equations of state are analogous to the back bending of the caloric curve (T,E) leading to negative heat capacity.

Let us now study what happens when we do not control the order parameter but the conjugated variable. We can thus consider the grand canonical PDF of particles associated with a chemical potential $\bar{\mu}$. Above the critical temperature the PDF of particle number, $P_{\beta\bar{\mu}}(N)$ is almost gaussian. At the critical temperature the flatness of $P_{\beta\bar{\mu}}$ signals the second order transition point. Below the critical temperature $P_{\beta\bar{\mu}}$ becomes bimodal and defines the coexistence zone (see Fig. 1). Indeed

$$\log P_{\beta\bar{\mu}}(N) = \beta F_{\beta}(N) + \beta\bar{\mu}N - Z_{\beta\bar{\mu}}$$

where $Z_{\beta\bar{\mu}}$ is the grand canonical partition sum. Therefore the curvature anomaly of free energy directly appear as a curvature anomaly of $\log P_{\beta\bar{\mu}}(N)$. The canonical chemical potential is given by

$$\mu_{\beta}(N) = -\beta^{-1}\partial_N \log P_{\beta\mu}(N) + \bar{\mu}$$

and is shown in the upper part of Fig. 1 (left). It should be noticed that a unique grand canonical chemical potential $\bar{\mu}$ gives access to the whole distribution of canonical chemical potentials $\mu_{\beta}(N)$. In the phase transition region μ_{β} presents a back bending which reflects the bimodal structure of the PDF related to the curvature anomaly of the free energy. The canonical chemical potential and the information extracted from the grand canonical calculation through the sorting of events are in perfect agreement.

§3. Bimodality of PDF and Zeros of the partition sum

An important issue is to show how the presented definition can be related to the usual one at the thermodynamical limit. A way to address this problem is to look at the zeros of the partition sum Z_{α} in the complex α Lagrange parameter plane and to use the Lee-Yang theory. Let us consider one couple of conjugated thermodynamical variables (α, b). The partition sum for a complex parameter $\gamma = \alpha + i\eta$ is nothing but the Laplace transform of the PDF

$$P_{\alpha_0}(b) = \int db\, \bar{W}_{\alpha_0}(b)\, e^{-i\alpha_0 b}$$

for a parameter α_0 [7]

$$Z_{\gamma} = \int db Z_{\alpha_0}\, P_{\alpha_0}(b)\, e^{-(\gamma-\alpha_0)b} \equiv \int db\, p_{\alpha}(b)\, e^{-i\eta b}$$

If $p_{\alpha}(b)$ is monomodal while the size is increased toward the thermodynamical limit, we can use a saddle point approximation around the maximum $\bar{b}_{\alpha}$ giving

$$Z_{\gamma} = e^{\phi_{\gamma}(\bar{b}_{\alpha})},$$

with

$$\phi_\gamma(b) = \log p_\alpha(b) - i\eta b + \eta^2 C(b)/2 + \log\left(\frac{2\pi C(b)}{2}\right)$$

where

$$C^{-1} = \partial_b^2 \log p_{\alpha_0}(b).$$

However, if the density of states $\bar{W}_{\alpha_0}(b)$ has a curvature anomaly, then it exists a range of α for which the equation

$$\partial_b \log(\bar{W}_{\alpha_0}(b)) - (\alpha - \alpha_0) = 0$$

has three solutions b_1, b_2 and b_3. Two of these extrema are maxima so that we can use a double saddle point approximation which will be valid close to thermodynamical limit [7]

$$Z_\gamma = e^{\phi_\gamma(b_1)} + e^{\phi_\gamma(b_3)} = 2e^{\phi_\gamma^+}\cosh\left(\phi_\gamma^-\right)$$

where

$$2\phi_\gamma^+ = \phi_\gamma(b_1) + \phi_\gamma(b_3)$$

and

$$2\phi_\gamma^- = \phi_\gamma(b_1) - \phi_\gamma(b_3).$$

The zeros of Z_γ then correspond to

$$\phi_\gamma^- = i(2n+1)\pi/2.$$

The imaginary part is given by

$$\eta = (2n+1)\pi/(b_3 - b_1)$$

while for the real part we should solve the equation

$$\mathrm{Re}\,\phi_\gamma^- = 0.$$

In particular, close to the real axis this equation defines an α which can be taken as α_0. If the bimodal structure persists when the number of particles goes to infinity, the loci of zeros corresponds to a line perpendicular to the real axis with a uniform distribution as expected for a first order phase transition.

§4. Phase transitions out of Gibbs equilibria: the example of Tsallis statistics

The definition of a phase transition based on the PDF can be extended to other ensembles of events which do not correspond to a Gibbs statistics such as non equilibrium, fully dynamical preparations or non ergodic or non mixing systems. One may even apply it to non Hamiltonian systems such as mathematical mapping, traffic jam, cyclothymia, ... any kind of problems characterized by an ensemble of situations (events (n)) for which we may know something (observable $b^{(n)}$) so that we can draw the PDF's $P(b)$. However, these extensions certainly deserve more work.

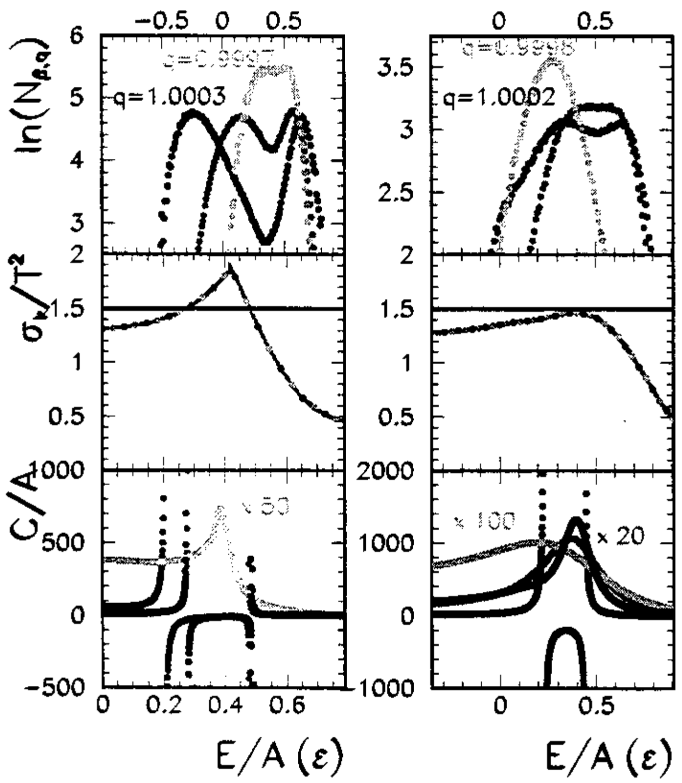

Fig. 2. Upper part: energy PDF for the canonical (medium grey) and the Tsallis (light grey: $q < 1$, dark grey: $q > 1$) ensemble. Medium part: normalized kinetic energy fluctuations. Lower part: heat capacity in the microcanonical ensemble (medium grey), in the Tsallis ensemble (light and dark grey) and estimation from fluctuations (black). The external pressure is $p < p_c$ (left side) and $p \geq p_c$ (right side).

As an example, we analyze the consequence of going from Gibbs to Tsallis [8] ensemble, for a system controlled by an external parameter λ (e.g. a pressure). The canonical PDF of the isobar lattice gas model [12] is displayed in the upper part of figure 2 : at subcritical pressure the convex intruder of the microcanonical entropy can be deduced from the bimodality of the PDF. As in section 2, the bimodality can be interpreted as an evidence of the phase transition in the canonical ensemble: the two peaks can be viewed as precursors of phases, the distance between them gives the latent heat, and the transition temperature is defined as the one for which the two peaks have equal height. At the same time the bimodality of $N_\beta(E)$ demonstrates that negative heat capacity exists in the microcanonical ensemble, because of the exact relation

$$C^{-1} = -T^{-2} d_E^2 \ln N_\beta.$$

This quantity is shown in the lower part of figure 2.

The Tsallis PDF reads ($q_1 = q - 1$) [8]

$$P_\lambda^q(E) = \tilde{W}_\lambda(E)\,(1 + q_1 \beta E)^{-q/q_1} / Z_\lambda^q.$$

Computing first and second derivatives of $\log P_\lambda^q$ one can see that the maximum of

$\log P_\lambda^q$ occurs for the energy which fulfills the relation

$$\bar{T}_\lambda = (\beta^{-1} + q_1 E)/q$$

where $\bar{T}$ is the microcanonical temperature while this point has a null curvature if $\bar{C}_\lambda = q/q_1$ where $\bar{C}_\lambda$ is the microcanonical heat capacity. Then, if $q > 1$ the Tsallis critical point occurs above the microcanonical critical point and one expects a broader coexistence zone in the Tsallis ensemble while for $q < 1$ it is the opposite. This can be seen in figure 2: in the $q < 1$ case the PDF shows no inversion of concavity in a region where the density of states still has an anomaly. Conversely in the case $q > 1$ the PDF stays bimodal even at supercritical pressures[13]. This bimodality can be interpreted as an actual phase transition in the non extensive ensemble. However it is important to remark that in the $q \neq 1$ case the PDF does not allow to extract any information about the density of states.

§5. Abnormal uctuations and phase transition

Microcanonical information can be extracted from the study of partial energy fluctuations, as we shall now show. The important property of the microcanonical ensemble is that it can be accessed from any equilibrium by sorting events in energy bins. Independent of the degree of non-extensivity of the system, a set of microcanonical ensembles can be obtained by analyzing the statistical properties of events within the same energy bin. In particular the microcanonical heat capacity of a classical system is to a good approximation[14] a simple function of the kinetic energy variance σ_k^2 within a given total energy bin

$$C \simeq C_k^2 / \left(C_k - \sigma_k^2/T^2 \right) \tag{5·1}$$

where the kinetic heat capacity C_k as well as the microcanonical temperature T can be estimated from the kinetic equation of state

$$T^{-1} = \partial_E \ln W_k|_{\overline{E_k}};$$

leading to

$$C_k^{-1} = -T^{-2} \partial_E^2 \ln W_k|_{\overline{E_k}}.$$

In the case of a classical system with δ degrees of freedom per particle, these expressions simply reduce to the usual definition of the kinetic thermometer $T = 2\overline{E}_k/A\delta$, $C_k = A\delta/2$, where A is the number of particles and $\overline{E}_k$ is the most probable kinetic energy in the bin. Equation 5·1 comes from the fact that for a given total energy E the kinetic energy E_k serves as a finite size heat reservoir to the potential part E_p. The microcanonical constraint $E = E_k + E_p$ in general narrows the kinetic energy distribution respect to the standard canonical expectation

$$\sigma_k^2/T^2 = C_k$$

leading to a smaller energy fluctuation for the microcanonical ensemble. On the other side in the coexistence region of a first order phase transition the strong jumps of the system between the two phases lead to a wider distribution (abnormal fluctuations) than in Gibbs canonical ensemble and to a negative branch for the microcanonical heat capacity.

The kinetic energy variance of the lattice gas model is compared to the canonical expectation in the medium panels of figure 2. The same abnormal fluctuations are observed in the coexistence zone independent of q. The corresponding heat capacity evaluated from eq.5·1 is displayed in the lower part of figure 2. The agreement with the exact heat capacity of the model is almost perfect for both pressures and for all the q values.

§6. Conclusions

In this paper we have discussed a definition of phase transitions in finite systems based on topology anomalies of the event PDF in the space of observations. We have shown that for statistical equilibria of Gibbs type this generalizes the definitions based on the curvature anomalies of entropies or other potentials. It gives an understanding of coexistence as a bimodality of the event PDF, each component being a phase. It provides a definition of order parameters as the best variable to separate the two maxima of the PDF. Some first applications based on the properties of PDF have already been reported[9)-11)]. The nature of the order parameter provides a bridge toward a possible thermodynamical limit. If it is sufficiently collective it may survive until the infinite volume and infinite particle number limit and the transition becomes the one known in the bulk. Finally phase transitions as a bimodality of the PDF can be identified also in situations out of Gibbs equilibria as in the Tsallis ensemble but the associated properties such as the position of the critical point change. However, abnormal kinetic energy fluctuations give a measure of the microcanonical heat capacity independent of the value of q and can be viewed as a robust method to identify phase transitions even out of Gibbs equilibrium.

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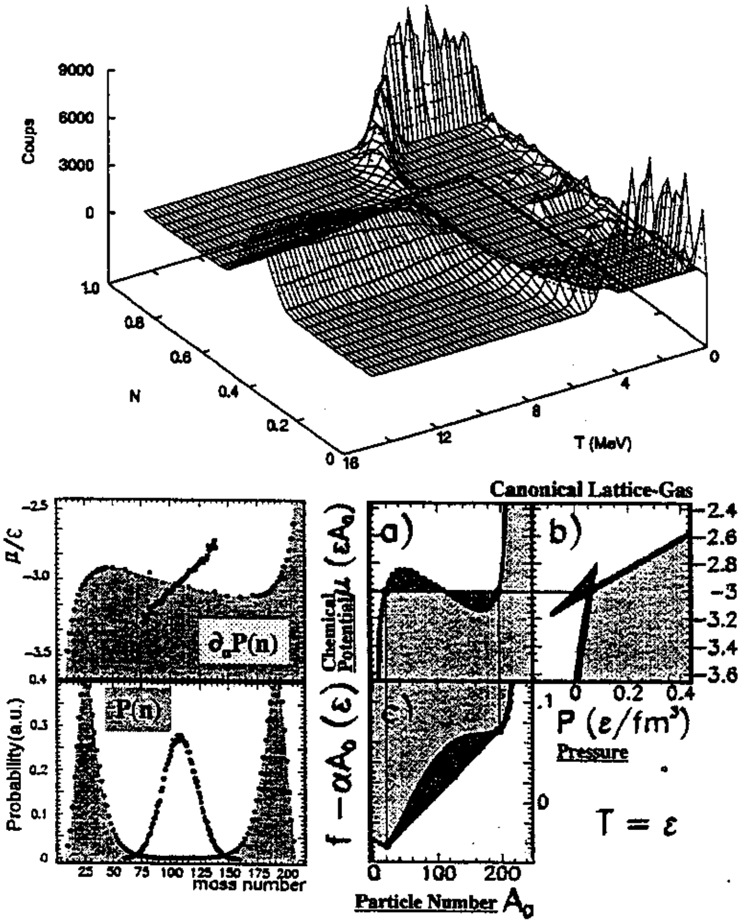

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