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Generalized definitions of phase transitions

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Abstract

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. Moreover, it allows to study phase transitions out of equilibrium.

1 Introduction

From the theoretical point of view phase transitions are defined at the thermodynamical limit through a non-analyticity of the thermodynamical potential. However, in finite systems, since the partition sum is analytical, this definition cannot be applied. Then, it has been proposed[1] to define and classify phase transitions according to the zeroes of the canonical partition sum in the complex temperature plane[2]. Alternatively it has been claimed that phase transitions can be related to a negative microcanonical heat capacity [3–5]. Then, we have generalized this idea to any inverted curvature of any thermodynamical potential as a function of an observable which can then be seen as an order parameter[5]. We have shown that this implies a bimodality of the probability distribution of this observable in a statistical ensemble in which this observable is only known in average. Finally we have shown the link between all these different definitions[6].

2 Back-bending of the chemical potential

Let us first consider the possible general definition of a first order phase transition as the occurrence of a curvature anomaly of the thermodynamical potential as a function of one order parameter. This means that we

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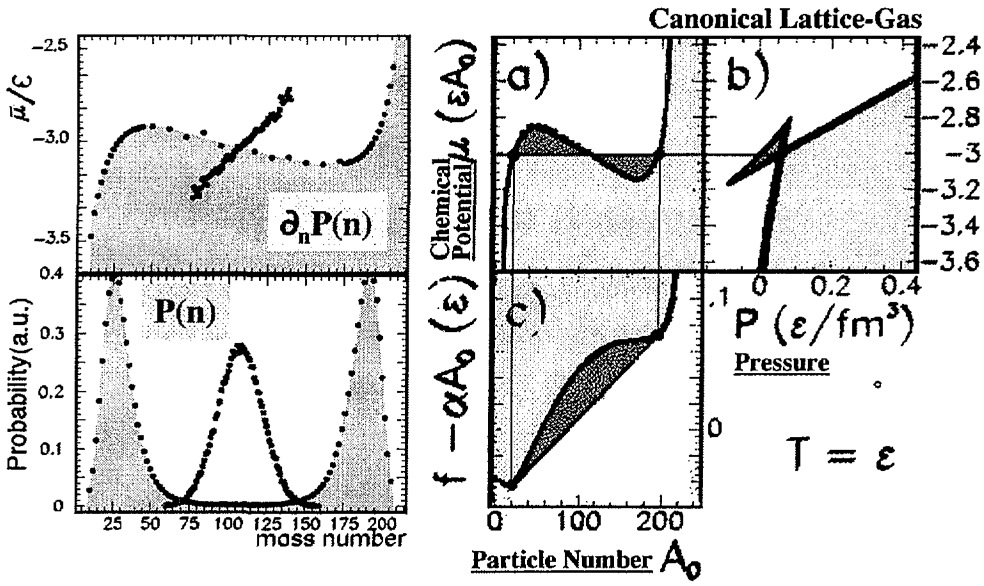

Fig. 1. Lattice gas results. Left: Canonical equation of states (top) from the logarithmic derivative of the grancanonical probability distribution (Bottom) calculated for $\mu = -3\epsilon$ and $T < T_c$ (grey area), $T > T_c$ (symbols). Right: Canonical calculation of the free energy (bottom) and of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

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 both the number of particles and the volume, one should consider an ensemble in which these two extensive variables are state variables. This is the case for the canonical lattice gas calculations in a constant volume container. Then the partition sum $Z\left(\beta = T^{-1}, V, N\right)$ give access to the free energy $F = -T \log Z = E - TS$. Therefore, a concavity anomaly of F as a function of N or V should be the signal of the phase transition. This is exactly the results 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 back bending means that the "susceptibility" $\chi^{-1} = \partial_N \mu$ diverges before becoming negative. In the same article [5], it is shown that the pressure $(P = \partial_V F)$ is presenting the same back-bending behavior as a function of the density (right part of figure1) leading to a negative compressibility. These anomalies in the chemical (μ, N) or in the mechanical (P, V) equations of state are analogous to the back bending of the caloric curve (T, E) leading to the negative heat capacities.

Let us now study what happens when we do not control the order parameter but the conjugated variable. For the lattice gas model we can thus consider the grand canonical distribution of particles associated with a chemical potential $\bar{\mu}$. Above the critical temperature the distribution of particle number,

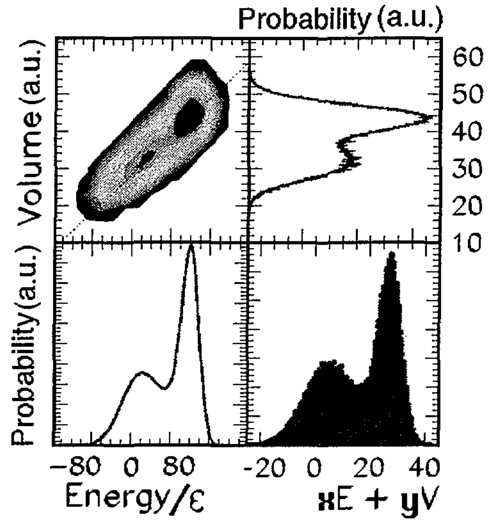

Fig. 2. Volume and energy distribution of a confined canonical lattice-gas model in the first order phase transition region with three associated projections.

$P_{\beta\bar{\mu}}(N)$ 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 strong back bending which reflects the bimodal structure of the probability distribution 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 parfait agreement.

3 Bimodal size distribution and negative compressibility

Let us now take the example of the liquid-gas phase transition in a system of N particles for which only the average volume is known. In such a case we can define a volume observable $\hat{V}$ as a measure of the size of the system; for example $\hat{V} = \frac{4\pi}{3N}\sum_i \hat{r}_i^3$ where the sum runs over all the particles. Then a Lagrange multiplier λ_V has to be introduced in the definition of the statistical ensemble. In a canonical ensemble we can define different distributions which are illustrated in Fig. 2. A complete information is contained in the distribution $P_{\beta\lambda_v}(E,V) = \bar{W}(E,V)\, Z_{\beta\lambda_v}^{-1} \exp -(\beta E + \lambda_v V)$ since events are sorted according to the two thermodynamical variables, E and V. This leads to the density of states $\bar{W}(E,V)$ with a volume V and an energy E. One can see that in the first order phase transition region the probability distribution is bimodal. We can look for an order parameter $\hat{Q} = x\hat{H} + y\hat{V}$ which provides the best separation of the two phases. A projection of the event on this order parameter axis is also shown in Fig. 2. One can see a clear separation of the two phases. On the other hand if we cannot measure both the volume V and the energy E we are left either with i) $P_{\beta\lambda_v}(E) = \bar{W}_{\lambda_v}(E)\, Z_{\beta\lambda_v}^{-1} \exp(-\beta E)$ giving access to the microcanonical partition sum $\bar{W}_{\lambda_v}(E)$ at constant λ_v ii) or $P_{\beta\lambda_v}(V) = \bar{Z}_\beta(V)\, Z_{\beta\lambda_v}^{-1} \exp(-\lambda_v V)$ leading to the isochore canonical partition sum $\bar{Z}_\beta(V)$. Since both probability distribution $P_{\beta\lambda_v}(E)$ and $P_{\beta\lambda_v}(V)$ are bimodal the associated partition sum do have anomalous concavity intruders ,*i.e.* negative heat capacity as well as negative compressibility.

4 Link with the 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 in the complex Lagrange parameter plane and to use the Lee-Yang theory. For sake of simplicity let us consider only one couple of thermodynamical variables (α, b). The partition sum for a complex parameter $\gamma = \alpha + i\eta$ is nothing but the Laplace transform of the probability distribution $P_{\alpha_0}(b) = \int db\, \bar{W}_{\alpha_0}(b)\, e^{-i\alpha_0 b}$ for a parameter α_0 [7,8]

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

If $p_\alpha(b)$ is monomodal while the size is increased toward the thermodynamical limit (when it exists), we can use a saddle point approximation around the maximum $\bar{b}_\alpha$ giving $Z \;= e^{\phi\;(\bar{b}_\alpha)}$, with

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

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] $Z \;= e^{\phi\;(b_1)} + e^{\phi\;(b_3)} = 2e^{\phi^+} \cosh\left(\phi^-\right)$ where $2\phi^+ \;=\; \phi\;\;(b_1) + \phi\;\;(b_3)$ and $2\phi^- \;=\; \phi\;\;(b_1) - \phi\;\;(b_3)$. The zeros of Z then correspond to $\phi^- \;=\; i(2n+1)\pi/2$.

The imaginary part is given by $\eta = (2n+1)\,\pi/\,(b_3 - b_1)$ while for the real part we should solve the equation $\mathrm{Re}\,\phi^- = 0$. 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.

5 Phase transitions out of Gibbs equilibria

The presented definition of a phase transition based on the probability distribution 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. As an example, we analyze the consequence of going from Gibbs to Tsallis[9] ensemble on the existence of a phase transition, for a system controlled by an external parameter λ (e.g. a pressure). For a given λ the system is characterized by a density of states $\bar{W}_\lambda(E)$. For a critical value of $\lambda = \lambda_c$ the associated entropy $S_\lambda(E) = \log \bar{W}_\lambda(E)$ presents a zero curvature and below a convex intruder. The Tsallis probability distribution reads ($q_1 = q - 1$) [9] $P_\lambda^q(E) = \bar{W}_\lambda(E)\,(1 + q_1\beta E)^{-q/q_1}/Z_\lambda^q$. 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. The curvature at the maximum of P_λ^q is $\bar{T}^2\partial_e^2 \log P_\lambda^q = -1/\bar{C}_\lambda + q_1/q$. Far from the C divergence line, this curvature is not very different from the microcanonical heat capacity if q_1/q is small.

6 Conclusions

In conclusion, we have discussed a definition of phase transitions in finite systems based on topology anomalies of the event distribution 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 distribution, each component being a phase. It provides a definition of order parameters as the best variable to separate the two maxima of the distribution. Some first applications based on the properties of probability distributions have already been reported [10–13]. The nature of the order parameter provides also a bridge toward a possible thermodynamical limit. If it is sufficiently collective it may survive until the infinite volume and infinite particle number limit. If the bimodality also survives, then using the zeroes of the partition sum we have shown that the finite size phase transition becomes the one known in the bulk. Finally the proposed definition can be extended to different statistical ensembles such as Tsallis ensemble. We have shown that phase transitions can be identified also in situations out of Gibbs equilibria as a bimodality of the probability distribution but that the associated properties such as the position of the critical point do change with the ensemble. However, it should be noticed that if one applies an energy sorting to a Tsallis ensemble one recovers the usual microcanonical ensemble so that the identification of phase transitions through abnormal kinetic energy fluctuations can be seen as a very robust method (see the contribution by Gulminelli et al.)

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