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TOPOLOGY OF EVENT DISTRIBUTIONS AS A GENERALIZED DEFINITION OF PHASE TRANSITIONS IN FINITE SYSTEMS

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We propose a definition of phase transitions in finite systems based on topology anomalies of the event distribution in the space of observations. This generalizes all the definitions based on the curvature anomalies of thermodynamical potentials and provides a natural definition of order parameters. It is directly operational from the experimental point of view. It allows to study phase transitions in Gibbs equilibria as well as in other ensembles such as the Tsallis ensemble.

Phase transitions are amazing examples of self organization of nature. Their universal character is patent. They are observed at all scales. Elementary particles deconfine in particle accelerators. Water boils in kettles. Self gravitating systems collapse in the cosmos.

From the theoretical point of view phase transitions are defined on very robust foundations in the thermodynamical limit. However, many (and maybe most) physical situations fall out of this theoretical framework because the thermodynamical limit conditions cannot be fulfilled. The forces might not be saturating such as the gravitational or the Coulomb forces. The system might be too small such as any mesoscopic system. The statistical ensemble might not be of Boltzmann-Gibbs type such as in Tsallis ensembles, or in non ergodic (or non mixing) systems or even in collections of events prepared in a dynamical way. In all these cases, a proper definition and study of phase transitions far from the thermodynamical limit should be achieved.

The astrophysics community discussed the existence of a microcanonical negative specific heat for collapsing self-gravitating systems [1]. This idea was then extended to the melting and the boiling of clusters [2]. In the nuclear multifragmentation context [3,4] the phase transition has first been related to anomalies in the caloric curve. The first experimental evidences for such a negative heat capacity have been reported in the last months [5–7]. This idea has been generalized to any statistical ensemble with at least one extensive variable allowing to sample the coexistence region [8].

In this paper, we propose a general definition of phase transitions based on anomalies of the probability distribution of observable quantities. From the theory side, this allows to extend the already given definition [8] to any situations even out of Boltzmann-Gibbs equilibria. It clarifies the respective role of order and control parameters. From the experimental point of view, this new definition gives a way to identify the order parameter and to extract the meaningful thermodynamical potential and equation of states.

The order parameter is a quantity which can be known for every single event (n) of the considered statistical ensemble, $\xi = \{n\}$. It is an observable which clearly separates the two phases. It is not necessarily unique. Let us consider a set of K independent observables, $\hat{B}_k$, which form a space containing one possible order parameter. We can sort events according to the results of the measurement $\mathbf{b}^{(n)} \equiv \left(b_k^{(n)}\right)$ and thus define a probability distribution of the observables $P_\xi(\mathbf{b})$.

Within the quantum mechanics framework, the statistical ensemble ξ is described by the density matrix $\hat{D}_\xi \equiv \sum_n \left|\Psi_\xi^{(n)}\right\rangle\ p_\xi^{(n)}\ \left\langle\Psi_\xi^{(n)}\right|$. The states $\left|\Psi_\xi^{(n)}\right\rangle$ are elements of the Fock subspace, $\mathcal{F}$, of the system. The observables $\hat{B}_k$ are operators defined on $\mathcal{F}$. For simplicity we will assume that all the observed operators commute. The result of a measurement on the $n-th$ event is $b_k^{(n)} = \left\langle\Psi^{(n)}\right|\hat{B}_k\left|\Psi^{(n)}\right\rangle$, and so the probability distribution of the results of the observation $\mathbf{b}$ reads

$$p_\xi(\mathbf{b}) = \mathrm{Tr}\hat{D}_\xi\delta\left(\mathbf{b}-\hat{\mathbf{B}}\right) \equiv <\delta\left(\mathbf{b}-\hat{\mathbf{B}}\right)>. \qquad (1)$$

Typical examples of order parameters are one body operators such as the density (or the mean radius) for the liquid gas phase transition or the magnetization in the ferromagnetic transition. One may also use the dynamical response of the system to an external excitation $\hat{F}\exp(-i\omega t) + h.c.$ which corresponds to the observable $\hat{B}(\omega) = \hat{F}\delta\left(\hat{H}-\omega\right)\hat{F}$. The response of the system can also be characterized by its moments associated with the average value of $\hat{B}_k = \left[\hat{F}\left[\hat{H}^k, \hat{F}\right]\right]$.

We propose to define phase transitions through the topology of the probability distribution $P_\xi(\mathbf{b})$. In the absence of a phase transition $P_\xi(\mathbf{b})$ is expected to be normal and $\log P_\xi(\mathbf{b})$ concave. Any abnormal (e.g. bimodal) behavior of $P_\xi(\mathbf{b})$ or any convexity anomaly of $\log P_\xi(\mathbf{b})$ signals a phase transition. More specifically, the larger eigenvalue of the tensor

$$T_\xi^{k,k'} \equiv \frac{\partial^2 \log P_\xi(\mathbf{b})}{\partial b_k \partial b_{k'}} \qquad (2)$$

becomes positive in presence of a first order phase transition. The associated eigenvector defines the local order parameter since it allows the best separation of the probability $P_\xi(\mathbf{b})$ into two components which can be recognized as the precursors of phases which will appear in the thermodynamical limit. If the largest eigenvalue is zero, the number of higher derivatives which are also zero defines the order of the phase transition.

For a unique observable $\hat{B}$, the above definition tells us that when the probability is bimodal we are in presence of a phase coexistence. The observable $\hat{B}$ is then the order parameter. In a multidimensional space if the ensemble of events splits into two components then we are also in presence of a (first order) phase coexistence. The axis allowing to make a best separation of the event cloud into two components is an order parameter. Many tools such as the principal component analysis already exist to perform this topological analysis of the event distribution [9].

The definition of phase transition from the topology of $p_\xi(\mathbf{b})$ contains and generalizes all the definitions based on convexity anomalies of thermodynamical potentials. Any Boltzmann-Gibbs equilibrium is obtained by maximizing the Shannon information entropy $S \equiv \mathrm{Tr}\hat{D}\log\hat{D}$ in the given Fock space $\mathcal{F}$ under the constraints of the various observables $\hat{B}_k$ known in average. A Lagrange multiplier α_k is associated with every constraint. We assume that the observables are either known in average $<\hat{B}_k>= b_k$ or not constrained ($\alpha_k = 0$). Other constraints can be applied to the system through conservation laws on the accessible space $\mathcal{F}$ or through additional Lagrange multipliers λ_ℓ if some other observable $\hat{A}_\ell$ (not related to the order parameter) has an expectation value known in average or imposed by a reservoir. The statistical ensemble is thus defined as $\xi \equiv (\mathcal{F}, \lambda, \alpha)$ and its density matrix reads

$$\hat{D}_{\mathcal{F}\lambda\alpha} = \frac{1}{Z_{\mathcal{F}\lambda\alpha}} \exp\left(-\sum_{\ell=1}^{L}\lambda_\ell\hat{A}_\ell - \sum_{k=1}^{K}\alpha_k\hat{B}_k\right). \quad (3)$$

This ensemble is consistent with the fact that the order parameter is in general not controlled on an event by event basis but measured. It spontaneously takes a non zero average value in one (or both) of the two phases.

It is easy to demonstrate that $P_\xi(\mathbf{b})$ can be written as

$$\log P_{\mathcal{F}\lambda\alpha}(\mathbf{b}) = \log\bar{W}_{\mathcal{F}\lambda}(\mathbf{b}) - \sum_{k=1}^{K}\alpha_k b_k - \log Z_{\mathcal{F}\lambda\alpha} \quad (4)$$

where $\bar{W}_{\mathcal{F}\lambda}(\mathbf{b}) = Z_{\mathcal{F}\lambda\mathbf{0}}P_{\mathcal{F}\lambda\mathbf{0}}(\mathbf{b})$ is nothing but the partition sum of the statistical ensemble associated with fixed values, $\mathbf{b}$, of all the observables. Indeed, the two partition sums are related through the usual Laplace transform

$$Z_{\mathcal{F}\lambda\alpha} = \int d\mathbf{b}\,\bar{W}_{\mathcal{F}\lambda}(\mathbf{b})\exp(-\alpha\mathbf{b}). \quad (5)$$

Eq. (4) clearly demonstrates that the study of convexity anomalies of $\log P_{\mathcal{F}\lambda\alpha}(\mathbf{b})$ for any value of the variables α is equivalent to the study of the curvature anomalies of the thermodynamical potential $\log\bar{W}_{\mathcal{F}\lambda}(\mathbf{b})$ for which the $\mathbf{b}$ are the control parameters. The equations of state related to the partition sum $\bar{W}_{\mathcal{F}\lambda}$ can be obtained from the probability distribution using Eq. (4) through

$$\bar{\alpha}_k(\mathbf{b}) \equiv \frac{\partial\log\bar{W}_{\mathcal{F}\lambda}(\mathbf{b})}{\partial b_k} = \frac{\partial\log P_{\mathcal{F}\lambda\alpha}(\mathbf{b})}{\partial b_k} + \alpha_k. \quad (6)$$

It presents a back-bending in the abnormal curvature region. There, one $\bar{\alpha}_k$ is associated to three values of b_k. This is not the case for the equation of state of the ensemble (3) $< b_k >_{\mathcal{F}\lambda\alpha} = -\partial Z_{\mathcal{F}\lambda\alpha}/\partial\alpha_k$ for which only one $< b_k >$ can be associated to one α_k. Conversely, in the regions where the probability distribution is normal the average $< \mathbf{b} >$ is expected to be close to the most probable $\mathbf{b}_{max}$ characterized by $\bar{\alpha}_k(\mathbf{b}_{max}) = \alpha_k$.

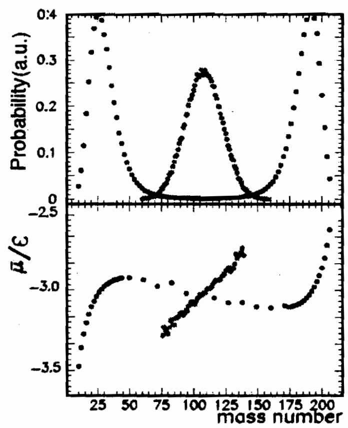

FIG. 1. Grancanonical lattice gas results at $\mu = -3\epsilon$ and $T < T_c$ (blue), $T > T_c$ (pink). Top: total mass distribution. Bottom: canonical equation of states (see text).

Let us take first the example of the energy as a possible order parameter with no other constraints, $\hat{B}_1 = \hat{H}$ and $b_1 = e$. Then the considered ensemble is nothing but the canonical one with $\alpha_1 = \beta$, the inverse of the temperature. The canonical probability reads

$$P_\beta(e) = \exp\left(S(e) - \beta e - \log Z(\beta)\right) \quad (7)$$

where the entropy, $S(e)$, is related to the level density by $S(e) = \log\bar{W}(e)$. A convex intruder in $S(e)$ directly induces a convexity anomaly in $\log P_\beta(e)$ which becomes bimodal in the phase transition region. Therefore the definition of phase transition through the curvature anomalies or a bimodality in the canonical probability distribution contains the former definitions based on the occurrence of negative heat capacities [2,4,7,10], the only condition being that the canonical ensemble exists.

As a second example we consider the grand canonical distribution of particles. We introduce $\hat{A}_1 = \hat{H}$ and

$\hat{B}_1 = \hat{N}$. Taking $\lambda_1 = \beta$ and $\alpha_1 = -\beta\mu$ we recover the usual definitions of the temperature and chemical potential. We present results from the grand canonical lattice-gas model with fixed volume and periodic boundary conditions [11] (see ref. [8] for details) with a closest neighbour interaction $-\varepsilon$. In the following the chemical potential will be kept fixed at its critical value $\mu_c = -3\varepsilon$. Above the critical temperature the distribution of particle number, $P_{\beta\mu}(n)$ is normal. Below the critical temperature the probability distribution becomes bimodal and signals the phase transition (see Fig. 1). Indeed

$$\log P_{\beta\mu}(n) = \log \bar{Z}_\beta(n) + \beta\mu n - Z_{\beta\mu} \tag{8}$$

where $\bar{Z}_\beta(n)$ is the canonical partition sum for n particles while $Z_{\beta\mu}$ is the grand canonical one. The canonical chemical potential is given by

$$\bar{\mu}_\beta(n) \equiv -\beta^{-1}\frac{\partial \log \bar{Z}_\beta(n)}{\partial n} = -\beta^{-1}\frac{\partial \log P_{\beta\mu}(n)}{\partial n} + \mu \tag{9}$$

and is shown in the lower part of Fig. 1. It should be noticed that a unique grand canonical chemical potential μ gives access to the whole distribution of canonical chemical potentials $\bar{\mu}_\beta(n)$. In the phase transition region $\bar{\mu}_\beta$ presents a strong back bending (see fig 1) which comes from the bimodal structure of the probability distribution and which signals the phase transition.

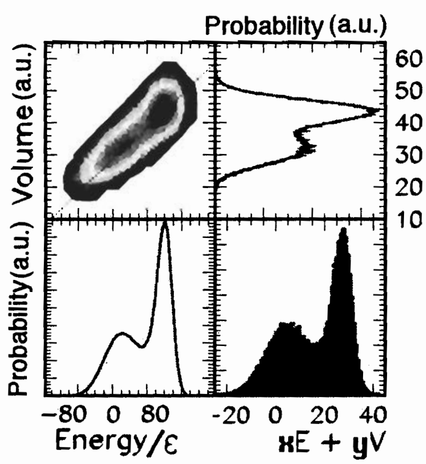

FIG. 2. Volume and energy distribution of a confined canonical lattice-gas model in the first order phase transition region with three associated projections.

In the previous examples both the energy and the particle number are conserved quantities. However there is no reason that the order parameter is associated with any conservation rule. Let us take the example of the liquid-gas phase transition in an open system of N particles for which only the average volume is known. In such a case we can define an observable $\hat{B}_1$ as a measure of the size of the system; for example the cubic radius $\hat{B}_1 = \frac{4\pi}{3N}\sum_i \hat{r}_i^3 \equiv \hat{V}$ where the sum runs over all the particles . Then a Lagrange multiplier λ_V has to be introduced which has the dimension of a pressure divided by a temperature. In a canonical ensemble with an inverse temperature β 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. In principle one could use the tensor (2) to define the topology so that the order parameter axis corresponds to the ridge passing through the saddle point between the liquid and the gas peaks. In the spirit of the principal component analysis 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 $P_{\beta\lambda_v}(e) = \bar{W}_{\lambda_v}(e)\, Z_{\beta\lambda_v}^{-1} \exp(-\beta e)$ giving access to the energy partition sum, $\bar{W}_{\lambda_v}(e)$, at constant λ_v or with the probability $P_{\beta\lambda_v}(v) = \bar{Z}_\beta(v)\, Z_{\beta\lambda_v}^{-1} \exp(-\lambda_v v)$ 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. Both energy in the constant λ_v ensemble or volume in the canonical ensemble can be used as succedanea of the order parameter.

Let us now take another example from the Ising model. In the absence of a magnetic field the Ising system presents a second order phase transition. We can now study the canonical distribution of energy $\hat{B}_1 = \hat{H}$ and magnetization $\hat{B}_2 = \hat{M}$. The pertinent statistical ensemble has two Lagrange multipliers, the canonical temperature $\alpha_1 = \beta$ and a magnetization constraint $\alpha_2 = \beta h$ which has the dimension of a magnetic field divided by a temperature. The canonical distribution of energy and magnetization $P_\beta(e,m)$ is shown in Fig. 3 for three temperatures. Above T_c the distribution is normal, only the paramagnetic phase is present. At T_c the distribution presents a curvature anomaly on the low energy side. Below T_c we observe a first order phase transition, the order parameter being the magnetization. The bimodal structure in the m direction corresponds to a negative suceptibility in a constant magnetization ensemble. It should be noticed that the projection on the energy axis does not show anomalies. The heat capacity remains positive and the energy cannot not be a substitute of the order parameter.

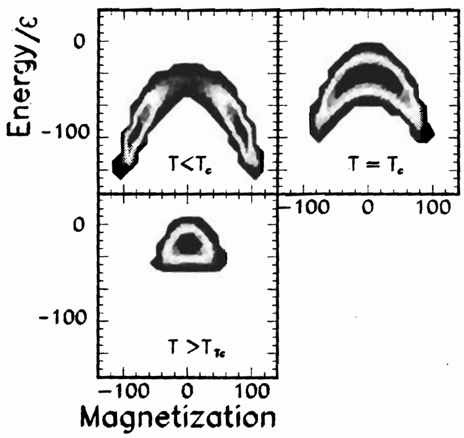

FIG. 3. Magnetization and energy distribution of an Ising model above, at and below the critical temperature.

Finally we stress that the presented definition of phase transition based on the probability distribution can be extended to other ensembles of events which do not correspond to a Gibbs statistics. As an example, we analyze the consequence of going from Gibbs to Tsallis [12] 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 ($q_1 = q - 1$) [12]

$$P^q_\lambda(e) = \frac{\bar{W}_\lambda(e)}{Z^q_\lambda}(1 + q_1\beta e)^{-q/q_1} \tag{10}$$

Computing first and second derivatives of $\log P^q_\lambda(e)$ one can see that the maximum of $\log P^q_\lambda(e)$ occurs for the energy which fulfills the relation $\bar{T}_\lambda(e) = (\beta^{-1} + q_1 e)/q$ where $\bar{T}$ is the microcanonical temperature while this point has a null curvature if $\bar{C}_\lambda(e) = q/q_1$ where $\bar{C}_\lambda$ is the microcanonical heat capacity. Then the Tsallis critical point occurs when $\bar{C}_\lambda(e)$ reaches q/q_1, i.e. above the microcanonical critical point. Therefore, one expects a broader coexistence zone in the Tsallis ensemble extending toward higher pressures. Far from the critical point, the curvature at the maximum of $P^q_\lambda(e)$ is $\bar{T}^2(e)\partial^2 \log P^q_\lambda(e)/\partial e^2 = -1/\bar{C}_\lambda(e) + q_1/q$ Far from the C divergence line, this curvature is not very different from the microcanonical heat capacity since q_1/q is small.

In conclusion, we have proposed 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 all the definitions based on the curvature anomalies of entropies or other potentials. It gives an understanding of coexistence as a simple bimodality of the event distribution, each component being a phase. It provides an intuitive definition of order parameters as the best variable to separate the two maxima of the distribution or as the ridge passing through the saddle point between the peaks associated with the two phases. This provides an experimental tool to define the order parameter and the existence of two phases. The nature of the order parameter provides also a bridge toward a possible thermodynamical limit. If it is sufficiently collective (such as one (or few) body operator) it may survive until the infinite volume and infinite number limit. If the anomaly also survives then the finite size phase transition may become 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 but that the associated properties such as the position of the critical point do change with the ensemble.

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