Topology of event distributions as a generalized definition of phase transitions in finite systems

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We propose a definition of first order phase transitions in finite systems based on topology anomalies of the event distribution in the space of observations. This generalizes the definitions based on the curvature anomalies of thermodynamical potentials, provides a natural definition of order parameters, and can be related to the Yang-Lee theorem in the thermodynamical limit. 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.

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Phase transitions are universal examples of self-organization. From the theoretical point of view they are defined on very robust foundations in the thermodynamical limit through nonanalyticities of the thermodynamical potential. However, many physical situations fall out of this theoretical framework because the thermodynamical limit is not reached. The forces might not be saturating such as the gravitational [1] or the Coulomb forces. The system might be too small such as any mesoscopic system [2–4,6,7]. Since the partition sum of a finite system is analytical, the standard definition of phase transitions cannot be applied. Then a proper definition independent of the thermodynamical limit should be achieved.

This issue is debated since 1960s. It has been proposed [8] to define and classify phase transitions according to the distribution of zeroes of the canonical partition sum in the complex temperature plane [9]. Alternatively it has been claimed that phase transitions in finite systems can be univocally signed through a curvature anomaly of the entropy [7,10]. The existence of a link between these two definitions based on two different statistical ensembles is still to be proven. In particular it is not clear if phase transitions exist independently of the ensemble or if they can be studied only through the topological properties of the microcanonical entropy.

In this paper, we propose the possible bimodality of the probability distribution of observable quantities as a connection between these ideas, and we establish a bridge to the thermodynamical limit. This definition is already under application in experiments [6,3–5].

The order parameter is a quantity that can be known for every single event (i) of the considered statistical ensemble, $\xi=\{i\}$. It is an observable that clearly separates the two phases. It is not necessarily unique. Typical examples of order parameters are one body operators such as the density for the liquid gas phase transition or the magnetization in the ferromagnetic transition.

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 $\mathbf{b}^{(i)}\equiv(b_k^{(i)})$ 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 $\hat{D}_\xi \equiv \Sigma_n |\Psi_\xi^{(i)}\rangle \; P_\xi^{(i)} \; \langle\Psi_\xi^{(i)}|$. The states$|\Psi_\xi^{(i)}\rangle$ are elements of the Fock subspace $\mathcal{F}$ of the system. The observables $\hat{B}_k$ are operators defined on $\mathcal{F}$. The probability distribution of the results of the observation $\mathbf{b}$ reads

$$P_\xi(\mathbf{b}) = \mathrm{Tr}\,\hat{D}_\xi \delta(\mathbf{b}-\hat{\mathbf{B}}) \equiv \langle \delta(\mathbf{b}-\hat{\mathbf{B}})\rangle.$$

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

$$T_\xi^{k,k'} \equiv \frac{\partial^2 \ln P_\xi(\mathbf{b})}{\partial b_k \partial b_{k'}} \tag{1}$$

becomes positive in presence of a first order phase transition [10]. The associated eigenvector defines the local order parameter since it allows the best separation of the probability $P_\xi(\mathbf{b})$ into two components that can be recognized as the precursors of phases. If the largest eigenvalue is zero, the number of higher derivatives that are also zero defines the order of the phase transition. In this paper we shall concentrate on first order.

The definition of phase transition from the topology of $P_\xi(\mathbf{b})$ contains and generalizes the definitions based on convexity anomalies of thermodynamical potentials. Any Boltzmann-Gibbs equilibrium is obtained by maximizing the Shannon information entropy $S\equiv -\mathrm{Tr}\,\hat{D}\ln\hat{D}$ 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. 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 $\hat{A}_\ell$ has an expectation value known in average or imposed by a reservoir. The statistical ensemble is defined as $\xi\equiv(\mathcal{F},\lambda,\alpha)$ and its density matrix reads

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$$\hat{D}_{\mathcal{F}\lambda\alpha}=\frac{1}{Z_{\mathcal{F}\lambda\alpha}}\exp\left(-\sum_{\ell=1}^{L}\lambda_\ell\hat{A}_\ell-\sum_{k=1}^{K}\alpha_k\hat{B}_k\right). \qquad (2)$$

This ensemble is consistent with the fact that the order parameter is in general not controlled on an event by event basis but measured. $P_\xi(\mathbf{b})$ can be written as

$$\ln P_{\mathcal{F}\lambda\alpha}(\mathbf{b})=\ln\overline{W}_{\mathcal{F}\lambda}(\mathbf{b})-\sum_{k=1}^{K}\alpha_k b_k-\ln Z_{\mathcal{F}\lambda\alpha}, \qquad (3)$$

where $\overline{W}_{\mathcal{F}\lambda}(\mathbf{b})=Z_{\mathcal{F}\lambda 0}P_{\mathcal{F}\lambda 0}(\mathbf{b})$ 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

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

Equation (3) clearly demonstrates that the convexity anomalies of the thermodynamical potential $\ln\overline{W}_{\mathcal{F}\lambda}(\mathbf{b})$ can be traced back from $\ln P_{\mathcal{F}\lambda\alpha}(\mathbf{b})$. The equations of state related to $\ln\overline{W}_{\mathcal{F}\lambda}$ then read

$$\overline{\alpha}_k(\mathbf{b})\equiv\frac{\partial\ln\overline{W}_{\mathcal{F}\lambda}(\mathbf{b})}{\partial b_k}=\frac{\partial\ln P_{\mathcal{F}\lambda\alpha}(\mathbf{b})}{\partial b_k}+\alpha_k. \qquad (4)$$

If $\overline{W}_{\mathcal{F}\lambda}$ has an abnormal curvature, then α_k presents a back bending. For this statistical ensemble where the b_k are the control parameters, the coexistence can be defined as the region where one $\overline{\alpha}_k$ is associated with three values of b_k because of the anomalous curvature. For α_k in this region the associated probability distribution presents two maxima and a minimum. In the statistical ensemble (3) where the α_k are controlled, the coexistence is then signalled by the bimodality of the probability distribution and the value of α_k where the two maxima have equal height is the first order transition point.

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

$$P_\beta(e)=\exp[S(e)-\beta e-\ln Z(\beta)],$$

where the entropy $S(e)$ is related to the level density by $S(e)=\ln\overline{W}(e)$. A convex intruder in $S(e)$ directly induces a convexity anomaly in $\ln P_\beta(e)$ that 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 [2,7,10,6,12], 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 three-dimensional grand canonical lattice-gas model with fixed volume and periodic boundary conditions [9]. The sites of a cubic three-dimensional lattice are characterized by an occupation number $n_i=0,1$, with the total number of particles $n=\Sigma n_i$. The Hamiltonian consists of a kinetic term and a closest neighbor interaction $-\varepsilon$ (see Refs. [11,12] for details). 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 almost Gaussian. At the critical temperature the flatness of $P_{\beta\mu}$ signals the second order transition point. Below the critical temperature $P_{\beta\mu}$ becomes bimodal and defines the coexistence zone (see Fig. 1). Indeed

$$\ln P_{\beta\mu}(n)=\ln\overline{Z}_\beta(n)+\beta\mu n-Z_{\beta\mu},$$

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

$$\overline{\mu}_\beta(n)\equiv-\beta^{-1}\frac{\partial\ln\overline{Z}_\beta(n)}{\partial n}=-\beta^{-1}\frac{\partial\ln P_{\beta\mu}(n)}{\partial n}+\mu \qquad (5)$$

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 $\overline{\mu}_\beta(n)$. In the phase transition region $\overline{\mu}_\beta$ presents a strong back bending that reflects the bimodal structure of the probability distribution.

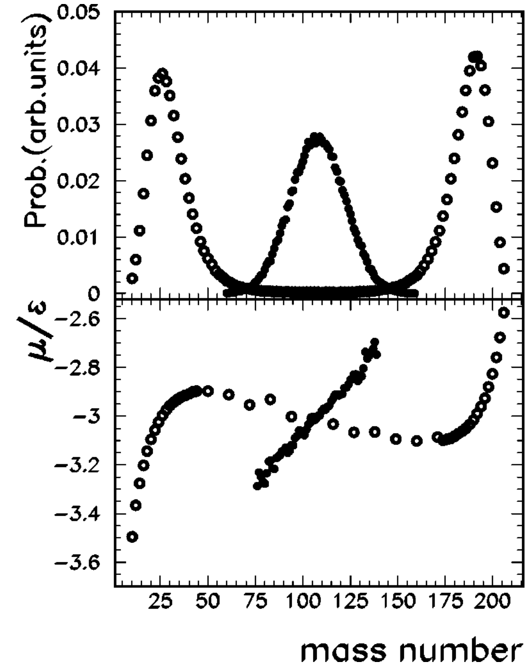

FIG. 1. Grand canonical lattice-gas results at $\mu=-3\epsilon$ and $T<T_c$ (open symbols), $T>T_c$ (filled symbols). Top: particle mass number probability distribution n. Bottom: canonical equation of states from Eq. (5).

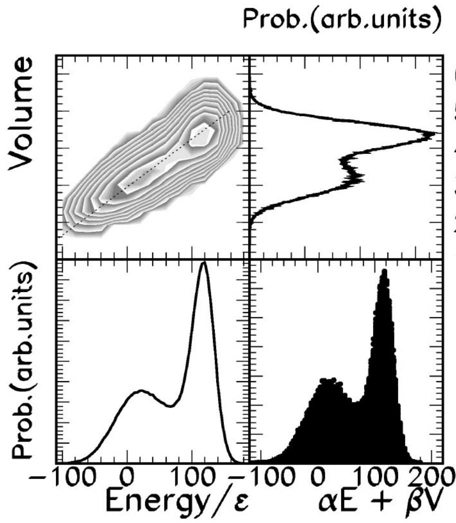

FIG. 2. Volume and energy distribution of a confined canonical lattice-gas model in the first order phase transition region with three associated projections.

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 an observable $\hat{B}_1$ as a measure of the size of the system; for example the cubic radius $\hat{B}_1 = 4\pi/3n\Sigma_i \hat{r}_i^3 \equiv \hat{V}$ where the sum runs over all the particles . Then a Lagrange multiplier λ_V has to be introduced that has the dimension of a pressure divided by a temperature. In a canonical ensemble with an inverse temperature β we can define different distributions that are illustrated in Fig. 2. A complete information is contained in the distribution $P_{\beta\lambda_v}(e,v) = \overline{W}(e,v) Z_{\beta\lambda_v}^{-1} \exp-(\beta e + \lambda_v v)$ since events are sorted according to the two thermodynamical variables, e and v. This leads to the density of states $\overline{W}(e,v)$ 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 the spirit of the principal component analysis we can look for an order parameter $\hat{Q} = x\hat{H} + y\hat{V}$ that 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 $P_{\beta\lambda_v}(e) = \overline{W}_{\lambda_v}(e) Z_{\beta\lambda_v}^{-1} \exp(-\beta e)$ giving access to the microcanonical partition sum $\overline{W}_{\lambda_v}(e)$ at constant λ_v or with the probability $P_{\beta\lambda_v}(v) = \overline{Z}_\beta(v) Z_{\beta\lambda_v}^{-1} \exp(-\lambda_v v)$ leading to the isochore canonical partition sum $\overline{Z}_\beta(v)$. Since both probability distribution $P_{\beta\lambda_v}(e)$ and $P_{\beta\lambda_v}(v)$ are bimodal the associated partition sum does have anomalous concavity intruders, i.e., negative heat capacity as well as negative compressibility.

Let us now study the canonical distribution of energy $\hat{B}_1 = \hat{H}$ and magnetization $\hat{B}_2 = \hat{M}$ the Ising model. The pertinent statistical ensemble has two Lagrange multipliers, the canonical temperature $\alpha_1 = \beta$ and a magnetization constraint $\alpha_2 = \beta h$ that has the dimension of a magnetic field divided by a temperature. Some distributions $P_\beta(e,m)$ are shown in Fig. 3. Above T_c only the paramagnetic phase is present. Below T_c we observe a first order phase transition. 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: at variance with recent claims [13], the energy cannot not be an order parameter. At T_c the distribution presents a curvature anomaly only on the low energy side respect to the maximum. Therefore at this point the curvature passes through zero signalling a second order phase transition. Since in finite systems the canonical distribution for any β,μ allows a complete exploration of the microcanonical entropy surface (in the limit of the total number of events analyzed), the whole microcanonical phase diagram can in principle be drawn from any single canonical temperature. As an example the croissant shape of the distribution at T_c not only defines the critical energy e_c and magnetization m_c of the second order phase transition but also allows to infer the coexistence line where the first order phase transition takes place. Indeed a constant energy cut of the distribution below e_c directly represents the entropy as a function of magnetization and has a bimodal shape.

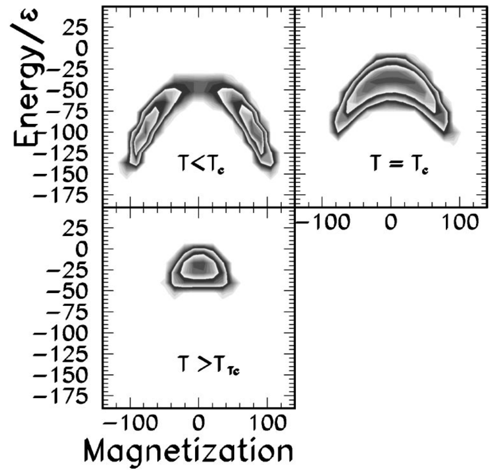

FIG. 3. Magnetization and energy distribution of a canonical Ising model in an external field above, at and below the critical temperature.

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 $Z_{\mathcal{F}\lambda\alpha}$ in the complex α plane and to use the Lee-Yang theory. For sake of simplicity let us consider only one couple of thermodynamical wariables (α,b) Using Eq. (3) we see that the partition sum for a complex parameter $\gamma = \alpha + i\eta$ is nothing but the Laplace transform of the probability distribution $P_{\alpha_0}(b)$ for a parameter α_0 [14,15]

$$Z_\gamma = \int dbZ_{\alpha_0}\;\; P_{\alpha_0}(b) e^{-(\gamma-\alpha_0)b}. \equiv \int dbp_\alpha(b) e^{-i\eta b}.$$

In order to study the thermodynamical limit (when it exists), if $p_\alpha(b)$ is monomodal we can use a saddle point approximation around the maximum $\overline{b}_\alpha$ giving $Z_\gamma . = e^{\phi_\gamma(\overline{b}_\alpha)}$, with

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

where $C^{-1} = \partial_b^2 \ln p_{\alpha_0}(b)$. However, if $\overline{W}_{\alpha_0}(b)$ [see Eq. (4)] has a curvature anomaly it exists a range of α for which the equation $\partial_b \ln[\overline{W}_{\alpha_0}(b)] - (\alpha - \alpha_0) = 0$ 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 that will be valid close to thermodynamical limit [14] $z_\gamma = e^{\phi_\gamma(b_1)} + e^{\phi_\gamma(b_3)} = 2e^{\phi_\gamma^+}\cosh(\phi_\gamma^-)$, 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 $\phi_\gamma^- = i(2n+1)\pi$. The imaginary part is given by $\eta = 2(2n+1)\pi/(b_3 - b_1)$ while for the real part we should solve the equation Re $\phi_\gamma^- = 0$. In particular, close to the real axis this equation defines an α that 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.

Finally we stress that the presented definition of phase transition based on the probability distribution can be extended to other ensembles of events that do not correspond to a Gibbs statistics. As an example, we analyze the consequence of going from Gibbs to Tsallis [16] ensemble on the existence of a phase transition, for a system controlled by an external parameter λ (e.g. pressure). For a given λ the system is characterized by a density of states $\overline{W}_\lambda(e)$. For a critical value of $\lambda = \lambda_c$ the associated entropy $S_\lambda(e) = \ln \overline{W}_\lambda(e)$ presents a zero curvature and below a convex intruder. The Tsallis probability distribution reads ($q_1 = q - 1$) [16]

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

Computing first and second derivatives of $\ln P_\lambda^q$ one can see that the maximum of $\ln P_\lambda^q$ occurs for the energy that fulfills the relation $\overline{T}_\lambda = (\beta^{-1} + q_1 e)/q$ where $\overline{T}$ is the microcanonical temperature while this point has a null curvature if $\overline{C}_\lambda = q/q_1$ where $\overline{C}_\lambda$ is the microcanonical heat capacity. Then the Tsallis critical point occurs above the microcanonical critical point and one expects a broader coexistence zone in the Tsallis ensemble. The curvature at the maximum of P_λ^q is $\overline{T}^2 \partial_e^2 \ln P_\lambda^q = -1/\overline{C}_\lambda + q_1/q$. 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 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 [6,3–5]. From the experimental point of view, one may worry about the statistical significancy of the curvature analysis in a finite sample of events. For any sorting variable b, if K_i events belong to the bin b_i, the uncertainty on the extracted entropy curvature estimated through a three point derivative is $6\Delta b^2/K_i$. For instance for a reliability of 99.99% in a negative heat capacity measurement, one needs $K_i > 18c^2T^4/(\Delta e^4 n^2)$, where n is the number of particles, T is the temperature, and e,c are the energy and heat capacity per particle. These statistical uncertainties are generally well under control in actual experiments [3].

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 number limit. If the anomaly also survives the saddle point approximation will be correct and 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.

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[1] W. Thirring, Z. Phys. **235**, 339 (1970); D. Lynden-Bell, e-print cond-mat/9812172.
[2] P. Labastie and R.L. Whetten, Phys. Rev. Lett. **65**, 1567 (1990); F. Calvo, Ann. Phys. (Paris) **24**(4), (1999).
[3] M. D'Agostino *et al.*, Phys. Lett. B **473**, 219 (2000).
[4] R. Bougault *et al.*, in *Proceedings of the XXXVIII Winter Meeting on Nuclear Physics, Bormio (Italy), 2000*, edited by I. Iori (Universita di Milano, Milano, 2000), p. 404.
[5] O. Lopez *et al.*, in *Proceedings of the XXXIX Winter Meeting on Nuclear Physics, Bormio (Italy), 2000*, edited by I. Iori (Universita di Milano, Milano, 2000).
[6] M. Schmidt *et al.*, Phys. Rev. Lett. **79**, 99 (1997); Nature (London) **393**, 238 (1998).
[7] M.S.S. Challa and J.H. Hetherington, Phys. Rev. Lett. **60**, 77 (1988); Phys. Rev. A **38**, 6324 (1988).
[8] S. Grossmann and W. Rosenhauer, Z. Phys. **207**, 138 (1967); P. Borrmann *et al.*, Phys. Rev. Lett. **84**, 3511 (2000).
[9] C.N. Yang and T.D. Lee, Phys. Rev. **87**, 410 (1952).
[10] D. Gross, e-print cond-mat/0004268; cond-mat/0006087.
[11] F. Gulminelli and P. Chomaz, in *Proceedings of the XXXVI Winter Meeting on Nuclear Physics, Bormio (Italy), 1998*, edited by I. Iori (Universita di Milano, Milano, 2000), p. 404; Phys. Rev. Lett. **82**, 1402 (1999).
[12] F. Gulminelli *et al.*, Europhys. Lett. **50**, 434 (2000).
[13] M. Pleimling and A. Hueller, e-print cond-mat/0011116.
[14] K.C. Lee, Phys. Rev. E **53**, 6558 (1996).
[15] M.S.S. Challa *et al.*, Phys. Rev. B **34**, 1841 (1986).
[16] C. Tsallis *et al.*, Physica A **261**, 534 (1998).