Topological Signature of First Order Phase Transitions

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We show that the presence and the location of first order phase transitions in a thermodynamic system can be deduced by the study of the topology of the potential energy function, \( V(q) \), without introducing any thermodynamic measure. In particular, we present the thermodynamics of an analytically solvable mean-field model with a \( k \)-body interaction which, depending on the value of \( k \), displays no transition (\( k=1 \)), second order (\( k=2 \)) or first order (\( k>2 \)) phase transition. This rich behavior is quantitatively retrieved by the investigation of a topological invariant, the Euler characteristic \( \chi(v) \), of some submanifolds of the configuration space. Finally, we conjecture a direct link between \( \chi(v) \) and the thermodynamic entropy.

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Despite their major physical relevance, first-order phase transitions are still lacking a satisfactory theoretical understanding of their origin. More specifically, nothing comparable to the renormalization group analysis for critical phenomena exists in the case of first order transitions, and, on a more mathematically rigorous background, neither in the Yang-Lee theory for the grand-canonical ensemble nor in the Ruelle, Sinai, Pirogov theory in the canonical ensemble. In particular, in the specific cases of the mean-field topological approach to the study of Phase Transitions (PT) \cite{3,4,5}. Within this approach, that at present has dealt only with second order PTs, the existence of a PT is signaled by a singular point in the energy dependence of some topological invariant. In particular the knowledge of the energy distribution of the critical points (saddle-points) of the potential energy function \( V(q) \) allows one to predict the existence and location of second order PTs.

The present work aims at contributing a step forward on this topic. By simply knowing the microscopic interaction potential, thus even prior to the choice of a statistical measure, we seek a characterization of the occurrence of a phase transition and of its order. As we shall see in what follows, this can be actually achieved within the recently proposed topological approach to the study of Phase Transitions (PT) \cite{3,4,5}. Within this approach, that at present has dealt only with second order PTs, the existence of a PT is signaled by a singular point in the energy dependence of some topological invariant. In particular, in the specific cases of the mean-field XY \cite{3} and of the \( \varphi^4 \) models \cite{6}, it has been shown that it exists a discontinuity in the first energy derivative of the Euler characteristic, \( \chi(v) \), of some submanifolds of the configuration space, located at that energy, \( v_c \equiv v(E_c) \), where the system undergoes a second order PT. The quoted works demonstrated, therefore, that important thermodynamic features -the second order PTs are strictly related to the topology of the potential energy hyper-surfaces. In particular the knowledge of the energy distribution of the critical points (saddle-points) of the potential energy function \( V(q) \) allows one to predict the existence and location of second order PTs.

The -still lacking- extension of the topological approach to first order PTs is obviously of great interest. It would allow to get new insight into the challenging problem of the origin of first order PTs, providing a new method of tackling them, and it would validate the topological approach as a possible theoretical method of unifying the treatment of different kinds of PTs. The latter point is particularly interesting in view of encompassing also more “exotic” transitions, among which it is worth to mention the glass transitions. In this respect, we notice that indication on the existence of a relation between the glass transition and the underlying topology of the potential energy surface already exist. Indeed, it has been shown \cite{6} that, in simulated realistic glasses, the order of the saddles visited at a given temperature \( T \) vanishes when \( T \) approaches the (dynamical) transition temperature.

In this work, we show the existence of a relationship between the topology and the thermodynamics of a dynamical system. In particular, we introduce and discuss here the ”\( k \)-trigonometric model”, an analytically solvable mean-field model with a \( k \)-body interaction. According to the value of the parameter \( k \), the system has no PT (\( k=1 \)), undergoes a second order PT (\( k=2 \)) or a first order one (\( k>2 \)). Remarkably, for this model an exact analytical computation is possible of both the thermodynamics and of a fundamental topological invariant, the Euler characteristic \( \chi(v) \) of the submanifolds \( M_v \) of the configurational space defined by \( V(q) \leq Nv \). In the topological properties, the existence of the PT is signaled, for \( k>1 \), in the usual way \cite{3,4}: a discontinuity of the first derivative of \( \chi(v) \) is observed at \( v_c \equiv v(E_c) \), i.e. at the potential energy level where the PT actually takes place. Remarkably, \textit{this happens also in the case of the first order PT}. But for \( k=2 \) the second derivative \( d^2 \chi(v)/dv^2 \) is negative around the singular point, while for \( k>2 \) it is positive. Therefore: \( i \) A singularity in the first derivative of \( \chi(v) \) is a signature of the PT, both in the first or second order case. \( ii \) The sign of the second derivative of \( \chi(v) \) around the singularity allows to predict the order of the transition. The latter conclusion leads to a further, important implication: it is well known \cite{6} that regions with \( d^2S(E)/dE^2 > 0 \) are not thermodynamically stable (they would correspond to negative specific heat)
and their presence corresponds to the existence of a first order PT; therefore, we conjecture a relation between the thermodynamic entropy and the topological Euler characteristic.

We study the properties of a specific model, the mean field $k$-Trigonometric Model ($k$TM), defined by the Hamiltonian

$$H_k(p, q) = K(p) + V_k(q) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V_k(q) \tag{1}$$

where the potential energy is given by

$$V_k(q) = \frac{\Delta}{N^{k-1}} \sum_{i_1, \ldots, i_k} [1 - \cos \frac{2\pi}{L} (q_{i_1} + \ldots + q_{i_k})] \tag{2}$$

$\Delta$ and $L$ are the energy and length scales. If $k=1$ the $k$TM reduces to the Trigonometric Model (TM) introduced by Madan and Keyes as a model for the Potential Energy Surface (PES) of simple glass-forming liquids that reproduces many properties of the “true” PES of these systems. For a given $k$, the model is a mean-field model with $k$-body interaction. It is convenient to introduce the angular variables $\varphi_i = (2\pi/L)q_i$. The model has then a symmetry group $C_{k\nu}$ obtained by the transformations $\varphi_i \rightarrow \varphi_i + 2\pi l/k$ and $\varphi_i \rightarrow -\varphi_i$. If we think at $\varphi_i$ as the angle between a unitary vector in a plane and the horizontal axis of this plane, these transformations are rotations in this plane of an angle $2\pi l/k$ and the reflection with respect to the horizontal axis respectively. Using the relation $\cos(\varphi_i + \ldots + \varphi_{ik}) = \Re(e^{i\varphi_{i1} \ldots e^{i\varphi_{ik}}})$, the potential can also be written as:

$$V_k(\varphi) = N\Delta [1 - \Re(c(\varphi) + is(\varphi))^k] \tag{3}$$

where $c(\varphi) = \frac{1}{N} \sum \cos \varphi_i$ and $s(\varphi) = \frac{1}{N} \sum \sin \varphi_i$. As usual in simple mean field models it is easy to calculate the microcanonical partition function, given by

$$\Omega_{N,k}(E) = \int \frac{dN p \ dN q}{N!} \delta(H_k - E) \tag{4}$$

Using the integral representation of the delta function, we get

$$\Omega_{N,k}(E) = \int \frac{d\beta}{2\pi} \int \frac{dN p \ dN q}{N!} e^{-i\beta(H_k - E)} \tag{5}$$

Now, as we are looking for a saddle-point evaluation of the integral over $\beta$, we can rotate the integration path on the imaginary axis in the complex-$\beta$ plane. This is justified because, as we will check at the end, the saddle-point is located on this axis. We can now perform the integration over the momenta and use the fact that $V_k(\varphi) = V_k(c(\varphi), s(\varphi))$, see Eq. (3), to obtain

$$\Omega_{N,k}(E) = C_N \rho^N \int d\beta \ d\xi \ d\eta \ \beta^{-\frac{N}{2}} e^{\beta(E - V_k(\xi, \eta))} \cdot \int dN \varphi \ \delta(N - c(\varphi)) \ \delta(N - s(\varphi)) \tag{6}$$

where $\rho = N/L$ and the constant $C_N$ gives only a constant contribution to the entropy per particle, i.e. it is at most of order $e^N$. The last integral can be evaluated using again the integral representation of the delta function, and rotating then the integration path as previously discussed; it turns out to be:

$$\int \frac{d\mu \ d\nu}{(2\pi)^2} e^{-N(\mu \xi + \nu \eta)} \int dN \varphi \ e^{\sum_i (\mu \cos \varphi_i + \nu \sin \varphi_i)} = \int \frac{d\mu \ d\nu}{(2\pi)^2} e^{-N(\mu \xi + \nu \eta)(2\pi I_0(\Lambda))^N} \tag{7}$$

having defined $\Lambda = \sqrt{\mu^2 + \nu^2}$ and the Bessel function

$$I_0(\Lambda) = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \ e^{\Lambda \cos \varphi} \tag{8}$$

We can then write the partition function as

$$\Omega_{N,k}(e) = C_N \rho^N \int dm \ e^{Nf_k(m, e)} \tag{9}$$
where \( m \equiv (\beta, \xi, \eta, \nu) \), \( e = E/N \) and

\[
f_k(m, e) = \beta e - \beta \Delta [1 - \text{Re}(\xi + i\eta)^k] - \frac{1}{2} \log \beta - \mu \xi - \nu \eta + \log I_0(\Lambda) .
\]

Then, using the saddle-point theorem, the entropy per particle, \( s = S/N \), is given by \( (k_B = 1) \):

\[
s_k(e) = \lim_{N \to \infty} \frac{1}{N} \log \Omega_{N,k}(e) = \max_m f_k(m, e) .
\]

To find the maximum of \( f_k(m, e) \) one can calculate analytically some derivatives of \( f \) to obtain a one-dimensional problem that can be easily solved numerically. In Fig. 1 we report the caloric curve, i.e. the temperature vs energy relation \( T(e) = [\partial s/\partial e]^{-1} \) for three values of \( k = 1, 2 \) and \( 3 \). As expected, the temperature is an analytic function of \( e \) for \( k = 1 \), because in this case there is no interaction between the degrees of freedom. For \( k = 2 \) the system undergoes a second order phase transition at a certain energy value \( e_c \), that changes to first order for \( k > 2 \). At the transition point the \( C_{k_c} \) symmetry is broken, the order parameter being the “magnetization” \( m = \langle |c + i\xi| \rangle \); for \( e < e_c \) there are \( k \) pure states related by the symmetry group. It is interesting to note that for the present model, this happens also in the case of the first order transition.

Having an exact solution of the thermodynamics of the system, we can look for some topological signature of the phase transition. In \([3, 4]\) it was stated that the Euler characteristic \( \chi(v) \) of the submanifolds \( M_v \equiv \{ q \mid V(q) \leq Nv \} \) of the configurational space shows a singularity in correspondence of the potential energy value \( v_c = v(e_c) \) at which the transition takes place. The result of \([3, 4]\) was obtained in the case of a second order PT; our aim is to extend this result to the case of a first order PT. Remarkably, the Euler characteristic of \( M_v \) can be calculated analytically in our model. The general definition is \([10]\):

\[
\chi(v) \equiv \chi(M_v) = \sum_{n=0}^{N} (-1)^n \mu_n(M_v) ,
\]

where the Morse indexes \( \mu_n(M_v) \) correspond to the number of critical points of order \( n \) of the function \( V(q) \) that belongs to the manifold \( M_v \). The critical points (saddles) \( \tilde{s} \) are defined by the condition \( dV_k(\tilde{s}) = 0 \), and their order \( n \) is defined as the number of negative eigenvalues of the Hessian matrix \( H_{ij}^k(\tilde{s}) = (\partial^2 V_k/\partial \varphi_i \partial \varphi_j) |_{\tilde{s}} \). To determine the location of the saddles we have to solve the system

\[
\frac{\partial V_k}{\partial \varphi_j} = -\Delta k \text{Re}[c + i\xi]^{k-1} e^{i\psi} = \Delta k \xi^{k-1} \sin[(k-1)\psi + \varphi_j] = 0 , \forall j ,
\]

where we defined \( c + i\xi = \zeta e^{i\psi} \). From Eq. \([3]\) we have \( V_k(\tilde{s}) = N\Delta[1 - \zeta^k \cos(k\psi)] \); then the saddles with \( \zeta = 0 \) have energy \( v = V(\tilde{s})/N = \Delta \). We can neglect them because, as we will see at the end, \( v = \Delta \) is a singular point of \( \chi(v) \). Then Eq. \([3]\) becomes

\[
\sin[(k-1)\psi + \varphi_j] = 0 , \forall j ,
\]

and its solutions are

\[
\varphi_j = [n_j \pi - (k-1)\psi] \mod 2\pi ,
\]

where \( n_j \in \{0, 1\} \). The saddle point \( \tilde{s}^{\infty} \) is then characterized by the set \( \bar{n} \equiv \{n_j\} \). To determine the unknown constant \( \psi \) we have to substitute Eq. \([13]\) in the self-consistency equation

\[
\zeta e^{i\psi} = c + i\xi = N^{-1} \sum_j e^{i\varphi_j} = N^{-1} e^{-i\psi(k-1)} \sum_j (-1)^{n_j} .
\]

If we introduce the quantity \( x(\tilde{s}) \) defined by

\[
x = N^{-1} \sum_j n_j \implies 1 - 2x = N^{-1} \sum_j (-1)^{n_j} ,
\]

then

\[
\zeta e^{i\psi} = N^{-1} \sum_j \bar{n}_j e^{i\varphi_j} = N^{-1} e^{-i\psi(k-1)} \sum_j (-1)^{n_j} .
\]
we have from Eq. (16)

\[ \zeta = |1 - 2x| , \tag{18} \]

\[ \psi_l = \begin{cases} 2l\pi/k & \text{for } x < 1/2 , \\ (2l + 1)\pi/k & \text{for } x > 1/2 , \end{cases} \tag{19} \]

where \( l \in \mathbb{Z} \). Then the choice of the set \( \{n_j\} \) is not sufficient to specify the set \( \{\varphi_j\} \) because the constant \( \psi \) can assume some different values. This fact is connected with the symmetry structure of the potential energy surface (the different values of \( \psi \) generate the multiplets of saddles). We have then obtained that all the saddles of energy \( v \neq \Delta \) have the form

\[ \tilde{\varphi}^n_l = [n_j\pi - (k - 1)\psi_l]_{\text{mod } 2\pi} . \tag{20} \]

The Hessian matrix is given by

\[ H_{ij}^k = \Delta k \Re \left[ N^{-1}(k - 1)(c + is)^{k-2}e^{i\varphi_i + \varphi_j} + \delta_{ij}(c + is)^{k-1}e^{i\varphi_i} \right] . \tag{21} \]

In the thermodynamic limit it becomes diagonal

\[ H_{ij}^k = \delta_{ij} \Delta k \zeta^{k-1} \cos (\psi(k - 1) + \varphi_i) . \tag{22} \]

One can not \textit{a priori} neglect the contribution of the off-diagonal terms to the eigenvalues of \( \mathcal{H} \), but we have numerically checked that their contribution change at most the sign of only one eigenvalue over \( N \). Neglecting the off-diagonal contributions, the eigenvalues of the Hessian calculated in the saddle-point \( \tilde{\varphi} \) are obtained substituting Eq. (20) in Eq. (22):

\[ \lambda_j = (-1)^{n_j} \Delta k \zeta^{k-1} , \tag{23} \]

so the saddle order is simply the number of \( n_j = 1 \) in the set \( \{n_j\} \). We can identify the quantity \( x(\tilde{\varphi}) \) given by Eq. (17) with the fractional order \( n/N \) of \( \tilde{\varphi} \). Then, from Eq. (3), (18) and (19) we get a relation between the fractional order \( x(\tilde{\varphi}) \) and the potential energy \( v(\tilde{\varphi}) = V(\tilde{\varphi})/N \) at each saddle point \( \tilde{\varphi} \):

\[ x(v) = \frac{1}{2} \left[ 1 - \text{sgn} \left( 1 - \frac{v}{\Delta} \right) \left| 1 - \frac{v}{\Delta} \right|^{1/k} \right] , \tag{24} \]
Moreover, the number of saddles of given order \( n \) is simply the number of way in which one can choose \( n \) times 1 among the \( \{n_j\} \), see Eq. (20), multiplied for a constant \( A_k \) that takes into account the degeneracy introduced by Eq. (19). Therefore: \( i \) the fractional order \( x=n/N \) of the saddles is a well defined monotonic function of their potential energy \( v \), given by Eq. (24), and \( ii \) the number of saddles of a given order \( n \) is \( A_k(N)_n \). Then the Morse indexes \( \mu_n(M_v) \) of the manifold \( M_v \) are given by \( A_k(N)_n \) if \( n/N \leq x(v) \) and 0 otherwise, and the Euler characteristic is

\[
\chi(v) = A_k \sum_{n=0}^{N x(v)} (-1)^n \binom{N}{n} = A_k (-1)^{N x(v)} \binom{N - 1}{N x(v)},
\]

using the relation \( \sum_{n=0}^{m} (-1)^N \binom{N}{n} = (-1)^m \binom{N - 1}{m} \).

In Fig. 2 we report \( \sigma(v) = \lim_{N \to \infty} \frac{1}{N} \log |\chi(v)| \), that, from Eq. (25), is given by:

\[
\sigma(v) = -x(v) \log x(v) - (1 - x(v)) \log(1 - x(v)).
\]

It has to be stressed that \( \sigma(v) \) is a purely topological quantity, being related only to the properties of the potential energy surface defined by \( V_{k}(\varphi) \), and, in particular, to the energy distribution of its saddle points. From Fig. 2 we see that there is a signature of the PT that is evident in the analytic properties of \( \sigma(v) \). First, we observe that the region \( v > \Delta \) is never reached by the system, as showed in the inset of Fig. 1; this region is characterized by \( \sigma'(v) < 0 \). We see that: \( i \) for \( k=1 \), where there is no phase transition, the function \( \sigma(v) \) is analytic; \( ii \) for \( k=2 \), when we observe a second order PT, the first derivative of \( \sigma(v) \) is discontinuous at \( v=v_{c} = \Delta \), and its second derivative is negative around the singular point. \( iii \) for \( k \geq 3 \) the first derivative of \( \sigma(v) \) is also discontinuous at the transition point \( v_{c} = \Delta \), but its second derivative is positive around \( v_{c} \). In this case a first order transition takes place. Therefore the investigation of the potential energy topology, via \( \sigma(v) \), allows us to establish the location and the order of the PTs, without introducing any statistical measure.

The previous results allows us to conjecture that there is a relation between the thermodynamic entropy of the system and \( \sigma(v) \). In fact, the presence of the first order transition with a discontinuity in the energy is generally related to a region of negative specific heat, i.e. of positive second derivative of the entropy. Thus, it seems that at least around the transition point the thermodynamic entropy and \( \sigma(v) \) are closely related, in the sense that the jump in the second derivative of \( s(e) \) is determined by the jump in the second derivative of \( \sigma(v(e)) \). Then it should be possible to write

\[
s(e) \sim \sigma(v(e)) + R(e)
\]
where $R(e)$ is analytic (or, at least, $C^2$) around the transition point. We hope that future work will address this point in a more quantitative way.

In conclusion, we have shown that the presence of a phase transition and its order are signaled in a very clear way in the topology changes of the potential energy hyper-surfaces. In our model, the Euler characteristic of the region of phase space in which $V(q) \leq Nv$ shows a discontinuity in its first derivative with respect to $v$ if and only if a phase transition takes place at the same energy value. From the concavity of the Euler characteristic as a function of $v$ around the singular point we can deduce the order of the transition, that is first order if $d^2\chi(v)/dv^2 > 0$ and second order if $d^2\chi/dv^2 < 0$. From the last observation we conjecture a deep relation between the thermodynamic entropy and some topological property of the potential energy landscape, at least around the transition point.

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