TOPOLOGY AND PHASE TRANSITIONS: TOWARDS A PROPER MATHEMATICAL DEFINITION OF FINITE N TRANSITIONS

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Abstract

A new point of view about the deep origin of thermodynamic phase transitions is sketched. The main idea is to link the appearance of phase transitions to some major topology change of suitable submanifolds of phase space instead of linking them to non-analyticity, as is usual in the Yang-Lee and in the Dobrushin-Ruelle-Sinai theories. In the new framework a new possibility appears to properly define a mathematical counterpart of phase transitions also at finite number of degrees of freedom. This is of prospective interest to the study of those systems that challenge the conventional approaches, as is the case of phase transitions in nuclear clusters.

1 Introduction

The current mathematical definitions of thermodynamical phase transitions are based on the loss of analyticity of thermodynamical observables. This is to some extent suggested, though not implied, by the experimental relations among macroscopic observables. This conflicts with the analytic character of the statistical weights that are attributed by any ensemble in statistical mechanics to the microscopic configurations. Thus, as it has been proved by the Onsager solution of the 2D Ising model and by the Yang-Lee theorem, the only way to eliminate this conflict is to consider the limit \( N \rightarrow \infty \) (thermodynamic limit)\[a\].

Obviously phase transitions in Nature occur at finite \( N \), but it is commonly argued that – for macroscopic objects – \( N \) is so large that it can be considered “infinite” from a physical point of view. However, by looking at a small and embroidery-like snowflake that melts into a drop of water one can wonder why such a phenomenon should ever be explained only in terms of the infinite \( N \) limit.

Moreover, there is a growing experimental evidence that phase transitions can occur also at \textit{finite and small} \( N \), i.e. with \( N \ll \text{Avogadro} \).

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number. Some examples of small $N$ systems undergoing phase transitions are: 

- nuclear clusters as well as atomic and molecular clusters;
- nano and mesoscopic systems;
- polymers and proteins;
- small drops of quantum fluids (BEC, superfluids and superconductors).

Whence the prospective interest of a new mathematical characterization of thermodynamical phase transitions which, instead of resorting to the loss of analyticity of macroscopic observables, might naturally encompass also finite $N$ systems. The search for a broader mathematical definition of phase transitions is also of potential interest to the treatment of other important topics in statistical physics, as is the case of amorphous and disordered systems (like glasses and spin-glasses), or for a better understanding of phase transitions in the microcanonical ensemble, for first-order phase transitions, and so on.

1.1 Heuristic arguments

Everything here refers to classical Hamiltonian systems with continuous variables and described by a standard Hamiltonian

$$H[p = (p_1, \ldots, p_N), q = (q_1, \ldots, q_N)] = \sum_i \frac{1}{2} p_i^2 + V(q) . \quad (1)$$

As a consequence of a systematic study of the dynamical counterpart of thermodynamical phase transitions, performed by numerically solving the Hamilton equations of motion of (1), it has been found that Lyapunov exponents display “singular” energy and temperature patterns at the transition point. Thus, since in a differential-geometric description of Hamiltonian chaos Lyapunov exponents are seen as probes of the geometry of certain submanifolds of configuration space, it has been conjectured that a phase transition could be due to some major geometrical, and possibly topological, change in the support of the statistical measures. This is to say that it is on the basis of the just mentioned work that we have been led to formulate the following argument.

Let us consider the canonical configurational partition function

$$Z_c(\beta, N) = \int_{\mathcal{R}^N} d^N q \ e^{-\beta V(q)} = \int_0^{+\infty} dv \ e^{-\beta v} \int_{\Sigma_v^{N-1}} \frac{d\sigma}{\|\nabla V\|} \quad (2)$$

where a co-area formula has been used to unfold the structure integrals

$$\Omega_N(v) \equiv \int_{\Sigma_v^{N-1}} \frac{d\sigma}{\|\nabla V\|} \quad (3)$$

i.e an infinite collection of purely geometric integrals on $\Sigma_v^{N-1}$ the *equipotential hypersurfaces* of configuration space defined by $\Sigma_v^{N-1} \equiv \{q \in \mathcal{R}^N | V(q) = v\} \subset \mathcal{R}^N$. 
If we consider the microcanonical ensemble, the basic mathematical object is the phase space volume

\[ \Omega(E) = \int_0^E d\eta \Omega^(-)(E - \eta) \int d^N p \delta\left(\sum_i \frac{1}{2}p_i^2 - \eta\right) \]

where

\[ \Omega^(-)(E - \eta) = \int d^N q \Theta[V(q) - (E - \eta)] = \int_0^{E-\eta} dv \int_{\Sigma_v} \frac{d\sigma}{\|\nabla V\|} \tag{4} \]

whence

\[ \Omega(E) = \int_0^E d\eta \left(\frac{2\pi\eta}{\eta^2}\right)^{N/2} \int_0^{E-\eta} dv \int_{\Sigma_v} \frac{d\sigma}{\|\nabla V\|} \tag{5} \]

also here, as in the above decomposition of \(Z_c(\beta, N)\), the only non-trivial objects are the structure integrals \(\int \).  

Once the microscopic interaction potential \(V(q)\) is given, the configuration space of the system is automatically foliated into the family \(\{\Sigma_v\}_{v \in \mathbb{R}}\) of equipotential hypersurfaces independently of any statistical measure we may wish to use. Now, from standard statistical mechanical arguments we know that the larger is the number \(N\) of particles the closer to some \(\Sigma_v\) are the microstates that significantly contribute to the statistical averages of thermodynamic observables. At large \(N\), and at any given value of the inverse temperature \(\beta\), the effective support of the canonical measure is narrowed very close to a single \(\Sigma_v = \Sigma_{v(\beta)}\); similarly, in the microcanonical ensemble, the fluctuations of potential and kinetic energies tend to vanish at increasing \(N\) so that the effective contributions to \(\Omega(E)\) come from a close neighborhood of a \(\Sigma_v = \Sigma_{v(E)}\).

Now, the “topological conjecture” consists in assuming that some suitable change of the topology of the \(\{\Sigma_v\}\), occurring at some \(v_c = v_c(\beta_c)\) (or \(v_c = v_c(E_c)\)), is the deep origin of the singular behavior of thermodynamic observables at a phase transition; (by change of topology we mean that \(\{\Sigma_v\}_{v<v_c}\) are not diffeomorphic to the \(\{\Sigma_v\}_{v>v_c}\)). In other words, the claim is that the canonical and microcanonical measures must “feel” a big and sudden change – if any – of the topology of the equipotential hypersurfaces of their underlying supports, the consequence being the appearance of the typical signals of a phase transition, i.e. almost singular energy or temperature dependences of the averages of appropriate observables. The larger is \(N\) the narrower is the effective support of the measure and hence the sharper can be the mentioned signals. Eventually, in the \(N \to \infty\) limit this sharpening will lead to non-analyticity.
2 A theorem about topology and phase transitions

We have recently proved a theorem stating that topological changes of the hypersurfaces $\Sigma_v$ are necessarily at the origin of phase transitions. It applies to physical systems described by short-range potentials $V$, bounded below, of the general form:

$$V(\{q\}) = \sum_{(\alpha,\gamma)} V_0(||q_\alpha - q_\gamma||) + \sum_{\alpha} \Phi(||q_\alpha||) .$$

The theorem is proved in the reversed formulation: if the surfaces $\Sigma_v$ with $v = V/N \in I = [v_m, v_M]$ are diffeomorphic, then no phase transition will occur in the corresponding temperature interval $[\beta(v_m), \beta(v_M)]$. The proof is lengthy and rather complicated but it proceeds along a logically simple path. Diffeomorphicity of the $\Sigma_v$, after the “non-critical neck theorem” in Morse theory, implies the absence of critical points of $V$, i.e. $\nabla V \neq 0$. In the absence of Morse critical points:

$$\frac{d^k}{dv^k} \left( \int_{\Sigma_v} \frac{d\sigma}{\|\nabla V\|} \right) = \int_{\Sigma_v} D^k \left( \frac{1}{\|\nabla V\|} \right) d\sigma$$

where

$$D^1(||\nabla V||^{-1}) = 2||\nabla V||^{-2} M_1 - ||\nabla V||^{-3} \Delta V$$

and where $M_1$ is the trace of the shape operator of the hypersurface $\Sigma_v$. There is an operator algebra to generate the powers $D^k$ so that, being $S_N(v) = \frac{1}{N} \ln \Omega_N (v)$ the microcanonical configurational entropy, it is possible to show that

$$\sup_{N,v \in I} S_N(v) < \infty ; \sup_{N,v \in I} \frac{\partial^k S_N}{\partial v^k}(v) < \infty , k = 1, \ldots, 4$$

that is: if the $\Sigma_v$ are diffeomorphic then $S_N(v)$ is uniformly convergent in $C^3(I)$ as $N \to \infty$, and, by using the Legendre transform relationship $S_N(v) = f_N(\beta) + \beta \cdot v + o(N)$ between microcanonical configurational entropy and the canonical free energy $f_N(\beta) = \frac{1}{N} \ln Z_v(\beta, N)$, this implies that – in the $N \to \infty$ limit – the canonical configurational free energy is $f_\infty(\beta) \in C^2(I)$, i.e. at least twice differentiable, thus there are neither first nor second order phase transitions according to their standard definition. There is not a one-to-one correspondence between phase transitions and topology changes of the $\Sigma_v$, the latters are necessary but not sufficient. Sufficiency conditions, to point out the special class of topology changes that give rise to phase transitions, are based on relations like

$$\frac{d\Omega_N(v)}{dv} \simeq \int_{\Sigma_v} \frac{M_1}{\|\nabla V\| \|\nabla V\|} d\sigma \sim c(v)[Vol(S_1^{(N-1)})]^{1/N} \left[ \sum_{i=0}^N b_i(\Sigma_v) \right]^{1/4}$$
that bridge thermodynamics and topology; here $b_i(\Sigma_v)$ are the Betti numbers (cohomological invariants) of $\Sigma_v$. It turns out that a “second order” topology change, i.e. a sudden change in the way of changing of topology as a function of $v$, is sufficient to entail a first or a second order phase transition. Such topological discontinuities can exist and can be detected at any finite $N$, though they yield non-analyticity of thermodynamic observables only when the support of the statistical measure indefinitely shrinks with $N \to \infty$. In other words, we have here the possibility of properly defining phase transitions also at finite $N$, whose detection, direct or indirect, can be performed through quantities that probe the topology of the $\Sigma_v$. It is an interesting and open question how to make the link with other approaches tackling the finite $N$ transitions in a macroscopic phase space of thermodynamic variables.

3 A direct numerical confirmation

The family of $\{\Sigma_v\}_{v \in \mathbb{R}}$ associated with the $\varphi^4$ model on a $d$-dimensional lattices $\mathbb{Z}^d$ with $d = 1, 2$ has been used for a numerical check of the scenario sketched in the previous section. The model is described by

$$V = \sum_{i \in \mathbb{Z}^d} \left( -\frac{\mu^2}{2} q_i^2 + \frac{\lambda}{4} q_i^4 \right) + \sum_{\langle ik \rangle \in \mathbb{Z}^d} \frac{1}{2} J(q_i - q_k)^2$$

$\langle ik \rangle$ stands for nearest-neighbor sites, and in $d = 2$ it undergoes a second order phase transition. In order to directly probe if and how the topology change – in the sense of a breaking of diffeomorphicity of the surfaces $\Sigma_v$ – is actually the counterpart of a phase transition, a diffeomorphism invariant has to be computed. This is a very challenging task because of the high dimensionality of the manifolds involved. One possibility is afforded by the Gauss-Bonnet-Hopf theorem that relates the Euler characteristic $\chi(\Sigma_v)$ with the total Gauss-Kronecker curvature $K_G$ of the manifold

$$\chi(\Sigma_v) = \gamma \int_{\Sigma_v} K_G d\sigma$$

which is valid in general for even dimensional hypersurfaces of euclidean spaces $\mathbb{R}^N$, and where $\gamma = 2/V ol(S^1)$ is twice the inverse of the volume of an $n$-dimensional sphere of unit radius, and $d\sigma$ is the invariant volume measure induced from $\mathbb{R}^N$. In Fig., $\chi(\Sigma_v)$ is reported vs $v$: the 1d case gives a “smooth” pattern of $\chi(v)$, whereas the 2d case yields a cusp-like shaped $\chi(v)$ at the phase transition point. There is here a direct evidence of a major and very sharp “second order” topological transition that underlies the phase transition, it is also remarkable that with a very small lattice of $N = 7 \times 7$ sites such a sharp signal would never be obtained through standard thermodynamic observables.
Figure 1: Euler characteristic $\chi(\Sigma_v)$ for 1-d and 2-d $\varphi^4$ lattice models. Open circles: 1-d case, $N = 49$; full circles: 2-d case, $N = 7 \times 7$. The vertical dotted line, computed separately for larger $N$, accurately locates the phase transition. Data are from Ref. [8].

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