

Theorem on the Origin of Phase Transitions

Roberto Franzosi*

*Dipartimento di Fisica, Università di Pisa, I.N.F.N., Sezione di Pisa, and I.N.F.M., Unità di Pisa,
via Buonarroti 2, I-56127 Pisa, Italy*

Marco Pettini†

*Istituto Nazionale di Astrofisica, Largo E. Fermi 5, 50125 Firenze, I.N.F.M., Unità di Firenze, and I.N.F.N., Sezione di Firenze, Italy
(Received 16 July 2003; published 10 February 2004)*

For physical systems described by smooth, finite-range, and confining microscopic interaction potentials V with continuously varying coordinates, we announce and outline the proof of a theorem that establishes that, unless the equipotential hypersurfaces of configuration space $\Sigma_v = \{(q_1, \dots, q_N) \in \mathbb{R}^N | V(q_1, \dots, q_N) = v\}$, $v \in \mathbb{R}$, change topology at some v_c in a given interval $[v_0, v_1]$ of values v of V , the Helmholtz free energy must be at least twice differentiable in the corresponding interval of inverse temperature $(\beta(v_0), \beta(v_1))$ also in the $N \rightarrow \infty$ limit. Thus, the occurrence of a phase transition at some $\beta_c = \beta(v_c)$ is necessarily the consequence of the loss of diffeomorphicity among the $\{\Sigma_v\}_{v < v_c}$ and the $\{\Sigma_v\}_{v > v_c}$, which is the consequence of the existence of critical points of V on $\Sigma_{v=v_c}$, that is, points where $\nabla V = 0$.

DOI: 10.1103/PhysRevLett.92.060601

PACS numbers: 05.70.Fh, 02.40.-k, 64.60.-i

Phase transitions (PTs) are phenomena which bring about *qualitative* physical changes at the macroscopic level in the presence of the same microscopic forces acting among the constituents of a system. Their mathematical description requires one to translate into *quantitative* terms the mentioned qualitative changes. The standard way of doing this is to consider how the values of thermodynamic observables, obtained in laboratory experiments, vary with temperature, volume, or an external field, and then to associate the experimentally observed discontinuities at a PT to the appearance of some kind of singularity entailing a loss of analyticity. Despite the smoothness of the statistical measures, after the Yang-Lee theorem [1], we know that in the $N \rightarrow \infty$ limit nonanalytic behaviors of thermodynamic functions are possible whenever the analyticity radius in the complex fugacity plane shrinks to zero, because this entails the loss of *uniform convergence* in N (number of degrees of freedom) of any sequence of real-valued thermodynamic functions, and all this depends on the distribution of the zeros of the grand canonical partition function. Also, the other developments of the rigorous theory of PTs, such as that due to Dobrushin, Lanford, and Ruelle on Gibbs measures [2,3], identify PTs with the loss of analyticity.

However, we can wonder whether this is the ultimate level of mathematical understanding of PT phenomena, or if some reduction to a more basic level is possible. The present Letter addresses just this point and aims at providing a nontechnical presentation of a new rigorous result, reported in Ref. [4], making its conceptual meaning and prospective physical interest accessible without going through the details of a lengthy mathematical proof. The new theorem says that nonanalyticity is the “shadow” of a more fundamental phenomenon occurring in configuration space: a *topology change* [5]

within the family of equipotential hypersurfaces $\Sigma_v = \{(q_1, \dots, q_N) \in \mathbb{R}^N | V(q_1, \dots, q_N) = v\}$, where V and q_i are the microscopic interaction potential and coordinates, respectively. This topological approach to PTs stems from the numerical study of the Hamiltonian dynamical counterpart of phase transitions, and precisely from the observation of discontinuous or cuspy patterns displayed by the largest Lyapunov exponent at the transition energy [6] (or temperature). Lyapunov exponents measure the strength of dynamical chaos and cannot be measured in laboratory experiments, at variance with thermodynamic observables, thus being genuine dynamical observables they are measurable only in numerical simulations of the microscopic dynamics. To get a hold of the reason why the largest Lyapunov exponent λ_1 should probe configuration space topology, let us first remember that, for standard Hamiltonian systems, described by $H = \sum_{i=1}^N \frac{1}{2} p_i^2 + V(q_1, \dots, q_N)$, λ_1 is computed by solving the tangent dynamics equation:

$$\frac{d^2 \xi_i}{dt^2} + \left(\frac{\partial^2 V}{\partial q^i \partial q^j} \right)_{q(t)} \xi^j = 0, \quad (1)$$

where $q(t) = [q_1(t), \dots, q_N(t)]$, and then $\lambda_1 = \lim_{t \rightarrow \infty} 1/2t \ln \{ \sum_{i=1}^N [\dot{\xi}_i^2(t) + \xi_i^2(t)] / \sum_{i=1}^N [\dot{\xi}_i^2(0) + \xi_i^2(0)] \}$. If there are critical points of V in configuration space, that is points $q_c = [\bar{q}_1, \dots, \bar{q}_N]$ such that $\nabla V(q)|_{q=q_c} = 0$, according to the *Morse lemma* [7], in the neighborhood of any critical point q_c there always exists a coordinate system $\tilde{q}(t) = [\tilde{q}_1(t), \dots, \tilde{q}_N(t)]$ for which

$$V(\tilde{q}) = V(q_c) - \tilde{q}_1^2 - \dots - \tilde{q}_k^2 + \tilde{q}_{k+1}^2 + \dots + \tilde{q}_N^2, \quad (2)$$

where k is the index of the critical point, i.e., the number of negative eigenvalues of the Hessian of V . In the neighborhood of a critical point, Eq. (2) yields $\partial_{ij}^2 V = \pm \delta_{ij}$

which, substituted into Eq. (1), gives k unstable directions which contribute [8] to the exponential growth of the norm of the tangent vector ξ . This means that the strength of dynamical chaos, measured by the largest Lyapunov exponent λ_1 , is affected by the existence of critical points of V . In particular, let us consider the possibility of a sudden variation, with the potential energy v , of the number of critical points (or of their indexes) in configuration space at some value v_c ; it is then reasonable to expect that the pattern of $\lambda_1(v)$ —as well as that of $\lambda_1(E)$ since $v = v(E)$ —will be consequently affected, thus displaying jumps or cusps or other “singular” patterns at v_c [this heuristic argument has been given evidence in the case of the XY -mean-field model (see [6,9]). On the other hand, *Morse theory* [7] teaches us that the existence of critical points of V is associated with topology changes of the hypersurfaces $\{\Sigma_v\}_{v \in \mathbb{R}}$, provided that V is a good Morse function (that is, bounded below, with no vanishing eigenvalues of its Hessian matrix). Thus, the existence of critical points of the potential V makes possible a conceptual link between dynamics and configuration space topology, which, on the basis of both direct and indirect evidence for a few particular models, has been formulated [6] as a *topological hypothesis* about the relevance of topology for PTs phenomena. In what follows, we show that, for a large class of physically meaningful potentials, this conjectural status of the art turns into a qualitatively new one because we can prove the following.

Theorem.—Let $V(q_1, \dots, q_N): \mathbb{R}^N \rightarrow \mathbb{R}$ be a smooth, bounded from below, finite-range, and confining potential [10]. Denote by $\Sigma_v := V^{-1}(v)$, $v \in \mathbb{R}$, its level sets, or equipotential hypersurfaces, in configuration space. Then let $\bar{v} = v/N$ be the potential energy per degree of freedom.

If there exists N_0 , and if for any pair of values \bar{v} and \bar{v}' belonging to a given interval $I_{\bar{v}} = [\bar{v}_0, \bar{v}_1]$ and for any $N > N_0$

$$\Sigma_{N\bar{v}} \text{ is diffeomorphic to } \Sigma_{N\bar{v}'},$$

then the sequence of the Helmholtz free energies $\{F_N(\beta)\}_{N \in \mathbb{N}}$ —where $\beta = 1/T$ (T is the temperature) and $\beta \in I_\beta = (\beta(\bar{v}_0), \beta(\bar{v}_1))$ —is uniformly convergent at least in $C^2(I_\beta)$ (the space of twice differentiable functions in the interval I_β), so that $\lim_{N \rightarrow \infty} F_N \in C^2(I_\beta)$ and neither first nor second order phase transitions can occur in the (inverse) temperature interval $(\beta(\bar{v}_0), \beta(\bar{v}_1))$.

Where the inverse temperature is defined as $\beta(\bar{v}) = \partial S_N^{(-)}(\bar{v}) / \partial \bar{v}$ and $S_N^{(-)}(\bar{v}) = N^{-1} \log \int_{V(q) \leq \bar{v}N} d^N q$ is one of the possible definitions of the microcanonical configurational entropy. The intensive variable \bar{v} has been introduced to ease the comparison between quantities computed at different N values.

This theorem means that a topology change of the $\{\Sigma_{\bar{v}N}\}_{\bar{v} \in \mathbb{R}}$ at some \bar{v}_c is a *necessary* condition for a phase transition to take place at the corresponding energy or temperature value. The topology changes implied here are

those described within the framework of Morse theory through *attachment of handles* [7,11].

Remark 1.—The topological condition of diffeomorphicity among all the hypersurfaces $\Sigma_{N\bar{v}}$ with $\bar{v} \in [\bar{v}_0, \bar{v}_1]$ has an analytical consequence: the absence of critical points of V in the interval $[\bar{v}_0, \bar{v}_1]$. This is proved in Lemma 1 of Ref. [4] by adapting to the Σ_v Bott’s “critical neck theorem” [11] which applies to the manifolds $M_v = \{(q_1, \dots, q_N) \in \mathbb{R}^N | V(q_1, \dots, q_N) \leq v\}$. Apart from this initial link with topology, the proof proceeds in the domain of Analysis.

Remark 2.—In the proof, we resort to the concept of *uniform convergence*—from elementary functional analysis—of a sequence of functions, and to the fact that the limit of a sequence of smooth functions can be nonsmooth. This way of tackling the thermodynamic limit is in the spirit of the celebrated Yang-Lee theorem [1].

Let us now outline the proof by focusing on the main ideas (details can be found in [4]).

Under the *crucial hypothesis of diffeomorphicity* of the hypersurfaces $\Sigma_{N\bar{v}}$ for $\bar{v} \in [\bar{v}_0, \bar{v}_1]$, we want to prove that the thermodynamic limit of the Helmholtz free energy, $F_\infty(\beta) = \lim_{N \rightarrow \infty} F_N(\beta)$, is at least twice differentiable, so that first or second order phase transitions are absent. For standard Hamiltonians, each function $F_N(\beta)$ reads as $F_N(\beta) = -(2\beta)^{-1} \log(\pi/\beta) - f_N(\beta)/\beta$, sum of a part coming from the kinetic energy term, and a configurational part $f_N(\beta) = (1/N) \log \int d^N q \exp[-\beta V(q)]$. Thus, in order to prove that $F_\infty(\beta) \in C^2(I_\beta)$, we have to show that the sequence of smooth functions $\{F_N(\beta)\}_{N \in \mathbb{N}}$ is uniformly convergent at least in $C^2(I_\beta)$ in the limit $N \rightarrow \infty$, or equivalently, since $(2\beta)^{-1} \log(\pi/\beta)$ remains always smooth in the limit $N \rightarrow \infty$, we have to show that the sequence of smooth functions $\{f_N(\beta)\}_{N \in \mathbb{N}}$ is uniformly convergent in $C^2(I_\beta)$ when $N \rightarrow \infty$. Now, at any N , $f_N(\beta)$ is related to the microcanonical configurational entropy $S_N^{(-)}$ through the Legendre transform: $S_N^{(-)}(\bar{v}) = f_N(\beta) + \beta\bar{v}$. Hence, to prove that $f_\infty(\beta)$ is twice differentiable with respect to β , we need to prove that $S_\infty^{(-)}(\bar{v})$ is 3 times differentiable with respect to \bar{v} .

Eventually, we consider the equivalent definition, at large N , of the configurational microcanonical entropy

$$S_N(v) = \frac{1}{N} \log \Omega(v, N) \equiv \frac{1}{N} \log \int_{\Sigma_v} \frac{d\sigma}{\|\nabla V\|}, \quad (3)$$

which also implicitly defines Ω as the surface integral on the right-hand side (rhs), where $d\sigma$ is the $(N-1)$ -dimensional surface element of Σ_v , and where $\|\nabla V\| = [\sum_{i=1}^N (\partial V / \partial q_i)^2]^{1/2}$; since $S_N(\bar{v})$ has the same thermodynamic limit of the entropy $S_N^{(-)}(\bar{v})$, that is, $S_\infty^{(-)}(\bar{v}) = S_\infty(\bar{v})$, we are left with the problem of proving that the sequence of smooth functions $\{S_N(\bar{v})\}_{N \in \mathbb{N}}$ [where $S_N(v) = S_N(\bar{v}N)$] is uniformly convergent in $C^3(I_{\bar{v}})$, the space of 3 times differentiable functions in the interval $I_{\bar{v}}$, in the limit $N \rightarrow \infty$. The reason for using $S_N(\bar{v})$ instead of $S_N^{(-)}(\bar{v})$ will be soon clear. After the Ascoli theorem [12],

in order to prove that $S_\infty(\bar{v})$ is 3 times differentiable, we need to prove that, for $\bar{v} \in I_{\bar{v}} = [\bar{v}_0, \bar{v}_1]$ and for any N , the function $S_N(\bar{v})$ and its first four derivatives are uniformly bounded in N from above; that is, for any $N \in \mathbb{N}$ and $\bar{v} \in [\bar{v}_0, \bar{v}_1]$,

$$\sup |S_N(\bar{v})| < \infty, \quad \sup \left| \frac{\partial^k S_N}{\partial \bar{v}^k} \right| < \infty, \quad k = 1, \dots, 4. \quad (4)$$

We prove the Theorem by proving that these bounds are the consequence of the diffeomorphicity among the $\Sigma_{N\bar{v}}$, for $\bar{v} \in [\bar{v}_0, \bar{v}_1]$.

From Eq. (3), the first four derivatives of $S_N(\bar{v})$ are trivially computed:

$$\frac{\partial S_N}{\partial \bar{v}}(\bar{v}) = \frac{1}{N} \frac{\Omega'(v, N)}{\Omega(v, N)} \frac{dv}{d\bar{v}} = \frac{\Omega'(v, N)}{\Omega(v, N)}, \quad (5)$$

and, using a compact notation, $\partial_{\bar{v}}^2 S_N = N[\Omega''/\Omega - (\Omega'/\Omega)^2]$, $\partial_{\bar{v}}^3 S_N = N^2[\Omega'''/\Omega - 3\Omega''\Omega'/\Omega^2 + 2(\Omega'/\Omega)^3]$, and $\partial_{\bar{v}}^4 S_N = N^3[\Omega^{iv}/\Omega - 4\Omega'''\Omega'/\Omega^2 - 3(\Omega''/\Omega)^2 + 12\Omega''(\Omega')^2/\Omega^3 - 6(\Omega'/\Omega)^4]$, where the prime indices stand for derivations of $\Omega(v, N)$ with respect to $v = \bar{v}N$. In order to verify whether the conditions (4) are fulfilled, we must be able to estimate the N dependence of all the addenda in these expressions for the derivatives of S_N .

Being the assumption of diffeomorphicity of the $\Sigma_{N\bar{v}}$ equivalent to the absence of critical points of the potential, we can use the derivation formula [13,14]

$$\frac{d^k}{dv^k} \Omega(v, N) = \int_{\Sigma_v} \|\nabla V\| A^k \left(\frac{1}{\|\nabla V\|} \right) \frac{d\sigma}{\|\nabla V\|}, \quad (6)$$

where A^k stands for k iterations of the operator

$$A(\bullet) = \nabla \left(\frac{\nabla V}{\|\nabla V\|} \bullet \right) \frac{1}{\|\nabla V\|}.$$

The technical reason to work with S_N instead of $S_N^{(-)}$ is now evident: The derivatives of $\Omega(v, N)$ are transformed into the surface integrals of explicitly computable combinations and powers of a few basic ingredients, such as $\|\nabla V\|$, $\partial V/\partial q_i$, $\partial^2 V/\partial q_i \partial q_j$, $\partial^3 V/\partial q_i \partial q_j \partial q_k$, and so on. This is a technically crucial step to prove the Theorem.

The first uniform bound in Eq. (4), $|S_N(\bar{v})| < \infty$, is a simple consequence of the intensivity of $S_N(\bar{v})$.

To prove the boundedness of the first derivative of S_N , we first compute its expression by means of Eqs. (5) and (6), which reads

$$\frac{\partial S_N}{\partial \bar{v}} = \frac{1}{\Omega} \int_{\Sigma_{vN}} \left[\frac{\Delta V}{\|\nabla V\|^2} - 2 \frac{\sum_{i,j} \partial^i V \partial_{ij}^2 V \partial^j V}{\|\nabla V\|^4} \right] \frac{d\sigma}{\|\nabla V\|}, \quad (7)$$

with $\partial_i V = \partial V/\partial q^i$ and $i, j = 1, \dots, N$, whence (with an obvious meaning of $\langle \cdot \rangle_{\Sigma_v}$)

$$\left| \frac{\partial S_N}{\partial \bar{v}} \right| \leq \left\langle \frac{|\Delta V|}{\|\nabla V\|^2} \right\rangle_{\Sigma_v} + 2 \left\langle \frac{|\sum_{i,j} \partial^i V \partial_{ij}^2 V \partial^j V|}{\|\nabla V\|^4} \right\rangle_{\Sigma_v}. \quad (8)$$

The N dependences of the derivatives of S_N are estimated at constant potential energy density \bar{v} , for any given $\bar{v} \in$

$[\bar{v}_0, \bar{v}_1]$; thus, we can think of increasing N by glueing together an increasing number k of replicas of a given building block of N_0 particles at potential energy $v = \bar{v}N_0$. Now the *hypothesis of diffeomorphicity* of the Σ_v plays again a crucial role, in fact *in the absence of critical points*, for each building block we have $\min \|\nabla V_{N_0}\|^2 \geq \bar{C}^2 > 0$, with \bar{C} a constant and, as only short-range potentials are considered, the larger N_0 and $N (= kN_0)$ the less relevant are the boundary interactions among the building blocks. Thus, at large N , $\min \|\nabla V\|^2 \geq C^2 N$, where $C = \bar{C}/N_0$ is a constant; for an upper bound estimate of Eq. (8), we replace in its denominators the lower bound $C^2 N$ of $\min \|\nabla V\|^2$:

$$\left| \frac{\partial S_N}{\partial \bar{v}} \right| \leq \frac{\langle |\Delta V| \rangle_{\Sigma_v}}{C^2 N} + 2 \frac{\langle |\sum_{i,j} \partial^i V \partial_{ij}^2 V \partial^j V| \rangle_{\Sigma_v}}{C^4 N^2},$$

where now we have to estimate the N dependence of the numerators. To this purpose, as we have assumed that V is smooth and bounded below, we note that $\langle |\Delta V| \rangle_{\Sigma_v} = \langle |\sum_{i=1}^N \partial_{ii}^2 V| \rangle_{\Sigma_v} \leq N \max_i \langle |\partial_{ii}^2 V| \rangle_{\Sigma_v}$ and, as we have also assumed that V is a short-range potential, the number of nonvanishing matrix elements $\partial_{ij}^2 V$ is $N(d+1)$, where d is the number of neighboring particles in the interaction range of the potential, thus $\langle |\partial^i V \partial_{ij}^2 V \partial^j V| \rangle_{\Sigma_v} \leq N(d+1) \max_{i,j} \langle |\partial^i V \partial_{ij}^2 V \partial^j V| \rangle_{\Sigma_v}$. Finally, putting $m = \max_{i,j} \langle |\partial^i V \partial_{ij}^2 V \partial^j V| \rangle_{\Sigma_v}$,

$$\left| \frac{\partial S_N}{\partial \bar{v}} \right| \leq \frac{\max_i \langle |\partial_{ii}^2 V| \rangle_{\Sigma_v}}{C^2} + 2 \frac{m(d+1)}{C^4 N}, \quad (9)$$

which, in the limit $N \rightarrow \infty$, shows that the first derivative of the entropy is uniformly bounded by a finite constant. This first step proves that $S_\infty(\bar{v})$ is continuous.

The three further steps, concerning boundedness of the higher order derivatives, involve similar arguments to be applied to a number of terms which is rapidly increasing with the order of the derivative. Many of these terms can be grouped in the form of the variance or higher moments of certain quantities, thus allowing the use of a powerful technical trick to compute their N dependence. For example, using Eq. (6) in the expression for $\partial_{\bar{v}}^2 S_N$ just below Eq. (5), we get

$$\left| \frac{\partial^2 S_N}{\partial \bar{v}^2} \right| \leq N \langle \alpha^2 \rangle_{\Sigma_v} - \langle \alpha \rangle_{\Sigma_v}^2 + N \langle \underline{\psi}(V) \cdot \underline{\psi}(\alpha) \rangle_{\Sigma_v}, \quad (10)$$

where $\alpha = \|\nabla V\| A(1/\|\nabla V\|)$ and $\underline{\psi} = \nabla/\|\nabla V\|$. Now, it is possible to think of the scalar function α as if it were a random variable, so that the first term in the rhs of Eq. (10) would be its second moment. Such a possibility is related with the general validity of the Monte Carlo method to compute multiple integrals. In particular, since the Σ_v are smooth, closed (V is nonsingular), without critical points, and representable as the union of suitable subsets of \mathbb{R}^{N-1} , the standard Monte Carlo method [15] is applicable to the computation of the averages $\langle \cdot \rangle_{\Sigma_v}$ which become sums of standard integrals in \mathbb{R}^{N-1} . This means that a random

walk can be constructively defined on any Σ_v , which conveniently samples the desired measure on the surface. Along such a random walk, usually called Monte Carlo Markov chain (MCMC), α and its powers behave as random variables whose “time” averages along the MCMC converge to the surface averages $\langle \cdot \rangle_{\Sigma_v}$. Notice that the actual computation of these surface averages goes beyond our aim, in fact, we do not need the numerical values — but only the N dependences — of the upper bounds of the derivatives of the entropy. Therefore, all we need is just knowing that, in principle, a suitable MCMC exists on each Σ_v . Now, the function α is the integrand in square brackets in Eq. (7), where the second term vanishes at large N , as is clear from Eq. (9). Therefore, at increasingly large N , the approximate expression $\alpha = \sum_{i=1}^N \partial_{ii}^2 V / \|\nabla V\|^2$ tends to become exact. α is in the form of a sum function $\alpha = N^{-1} \sum_{i=1}^N a_i$ of terms $a_i = N \partial_{ii}^2 V / \|\nabla V\|^2$, of $\mathcal{O}(1)$ in N , which, along a MCMC, behave as independent random variables with probability densities $u_i(a_i)$ which we do not need to know explicitly. Then, after a classical ergodic theorem for sum functions, due to Khinchin [16], based on the central limit theorem of probability theory, α is a Gaussian-distributed random variable; as its variance decreases linearly with N , $\lim_{N \rightarrow \infty} N |\langle \alpha^2 \rangle_{\Sigma_v} - \langle \alpha \rangle_{\Sigma_v}^2| = \text{const} < \infty$.

Arguments similar to those above used for the first derivative of S_N lead to the result $\lim_{N \rightarrow \infty} N |\langle \psi(V) \cdot \psi(\alpha) \rangle_{\Sigma_v} - \langle \psi(V) \rangle_{\Sigma_v} \langle \psi(\alpha) \rangle_{\Sigma_v}| = \text{const} < \infty$, which, together with what has been just found for the variance of α , proves the uniform boundedness also of the second derivative of S_N under the hypothesis of diffeomorphicity of the Σ_v .

Similarly, but with an increasingly tedious work, we can treat the third and fourth derivatives of the entropy. In fact, despite the large number of terms contained in their expressions, they again belong only to two different categories: those terms which can be grouped in the form of higher moments of the function α , and whose N dependence is known after the above-mentioned theorem due to Khinchin, and those terms whose N dependence can be found by means of the same kind of estimates given above for $\partial_{\bar{v}} S_N$. Eventually, after a lengthy but rather mechanical work, also the third and fourth derivatives of S_N are shown to be uniformly bounded as prescribed by Eq. (4) — whence the proof of the Theorem.

A few comments are in order.

The converse of our Theorem is not true. There is not a one-to-one correspondence between phase transitions and topology changes; in fact, there are smooth, confining, and finite-range potentials, such as the one-dimensional XY model [9], with even a very large number of critical points, and thus many changes in the topology of the Σ_v , but with no phase transition. Therefore, an open problem is that of *sufficiency* conditions, that is to determine which kinds of topology changes can entail the appearance of a PT. Preliminary hints on this point are given by the

analytic study of particular models [9,17] for which topology and thermodynamics are exactly computed.

Finally, though at present our Theorem applies only to first and second order PTs and to those systems for which V is a good Morse function, it provides the grounding to an approach which can unify the mathematical description of very different kinds of PTs, such as those “exotic” ones occurring in glasses or in the folding of polymers and proteins, for which the so-called *energy landscape paradigm* [18] is currently studied overlooking the link with Morse theory and topology.

We thank H. van Beijeren, L. Casetti, E. Guadagnini, R. Lima, C. Liverani, A. Moro, P. Picco, M. Rasetti, and G. Vezzosi for discussions and comments.

*Electronic address: Roberto.Franzosi@df.unipi.it

†Electronic address: pettini@arceetri.astro.it

- [1] C. N. Yang and T. D. Lee, *Phys. Rev.* **87**, 404 (1952).
- [2] H. O. Georgii, *Gibbs Measures and Phase Transitions* (Walter de Gruyter, Berlin, 1988).
- [3] D. Ruelle, *Thermodynamic Formalism*, Encyclopaedia of Mathematics and Its Applications (Addison-Wesley, New York, 1978).
- [4] R. Franzosi, M. Pettini, and L. Spinelli, math-ph/0305032.
- [5] Two given manifolds Σ_v and $\Sigma_{v'}$ have the same topology if they can be continuously and differentiably deformed one into the other, that is, if they are diffeomorphic. Thus, by “topology change” we mean “loss of diffeomorphicity.”
- [6] L. Casetti, M. Pettini, and E. G. D. Cohen, *Phys. Rep.* **337**, 237 (2000).
- [7] M. W. Hirsch, *Differential Topology* (Springer, New York, 1976).
- [8] We use “contribute” because chaos stems also from a different mechanism as discussed in Ref. [6].
- [9] L. Casetti, M. Pettini, and E. G. D. Cohen, *J. Stat. Phys.* **111**, 1091 (2003).
- [10] These requirements for V are fulfilled by standard interatomic and intermolecular interaction potentials, as well as by classical spin potentials.
- [11] R. Bott and J. Mather, *Topics in Topology and Differential Geometry*, in *Battelle Rencontres*, edited by C. M. De Witt and J. A. Wheeler (Benjamin, New York, 1967), p. 460.
- [12] L. Schwartz, *Analyse. Topologie Générale et Analyse Fonctionnelle* (Hermann, Paris, 1970).
- [13] H. Federer, *Geometric Measure Theory* (Springer, New York, 1969), p. 249.
- [14] P. Laurence, *Z. Angew. Math. Phys.* **40**, 258 (1989).
- [15] P. Brémaud, *Markov Chains* (Springer, New York, 2001).
- [16] A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics* (Dover, New York, 1949).
- [17] L. Angelani, L. Casetti, M. Pettini, G. Ruocco, and F. Zamponi, *Europhys. Lett.* **62**, 775 (2003).
- [18] F. H. Stillinger, *Science* **267**, 1935 (1995); S. Sastry, P. G. Debenedetti, and F. H. Stillinger, *Nature (London)* **393**, 554 (1998).